







Organized by





(ISCOM2013)

Montréal, Québec, Canada July 14-19, 2013

10<sup>th</sup> International Symposium

# Welcome Message

Dear ISCOM-2013 participants,

On behalf of the organizing committee, we welcome you in Montreal to the 2013 International Symposium of Crystalline Organic Metals, Superconductors and Magnets (ISCOM2013), which is devoted to the most recent developments in the physics, chemistry, material science technology and modeling of molecular solids.

It is a great honour to host this 10<sup>th</sup> edition of the ISCOM symposium, an event first initiated in Mittelberg (1995), and followed by Sesimbra (1997), Oxford (1999), Rusutsu (2001), Port-Bourgenay (2003), Key West (2005), Peniscola (2007), Niseko (2009), and Poznan-Gniezno (2011).

In its 10<sup>th</sup> edition, ISCOM2013 returns to North America, at the heart of the city of Montréal in the Québec province of Canada. It will be the occasion for chemists and physicists of all over the world to present their latest contributions to the lively field of synthesis and physics of crystalline organic molecular solids.

We hope you will enjoy your stay in Montreal and take the advantage of the meeting to visit and discover the numerous cultural and historical attractions of the largest french speaking city outside Europe.

Claude Bourbonnais Chair ISCOM 2013

# Organization

#### **CHAIR**

Claude Bourbonnais | Université de Sherbrooke (Canada)

### **CO-CHAIRS**

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John Schlueter	Argonne National Laboratory (USA)
Stuart Brown	University of California Los Angeles (USA)

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# Acknowledgement

We want to thank the following sponsors for their contribution to the success of the symposium













10<sup>th</sup> International Symposium

Venue



**DELTA CENTRE-VILLE HOTEL** 777 rue Université, Montré al (Québec) Canada H3C 3Z7 Tel. 514-879-1370 | Fax: 514-879-1761

## **HOTEL AREA MAP**



July 14-19, 2013

10<sup>®</sup> International Symposium

# Floor Plan

The ISCOM2013 symposium will occupy the second floor below the lobby of the Delta Centre-Ville Hotel.



## Information

#### REGISTRATION

The registration desk is located on the second floor below the lobby.

Sunday, July 14	16:00 - 18:00	(Foyer Regence)
Monday, July 15	8:30 - 18:00	(Bonsecours room)
Tuesday, July 16	8:30 - 18:00	(Bonsecours room)
Wednesday, July 17	8:30 - 18:00	(Bonsecours room)
Thursday, July 18	8:30 - 18:00	(Bonsecours room)
Friday, July 19	8:30 - 12:00	(Bonsecours room)
Tuesday, July 16 Wednesday, July 17 Thursday, July 18 Friday, July 19	8:30 - 18:00 8:30 - 18:00 8:30 - 18:00 8:30 - 12:00	(Bonsecours room) (Bonsecours room) (Bonsecours room) (Bonsecours room)

Each ISCOM participant will receive a symposium kit upon registration. The registration fees comprise all the meals during the symposium, except the dinner on the Wednesday free period. Registration gives also free access to the welcome cocktail on Sunday evening and to Banquet reception on Thursday evening.

### MEALS

The breakfasts and lunches will be served in the Regence C room on the second floor below the lobby. Dinners on Monday and Tuesday will be served on the Rooftop restaurant of the Delta Centre-Ville Hotel.

### REFRESHMENTS

Refreshments are served in the Foyer Regence during the breaks scheduled between the oral sessions in the morning and afternoon.

### **INTERNET ACCESS**

Wireless is available throughout the second floor below the lobby, including the conference rooms. The access to internet is also complimentary in all the rooms of the hotel.

### **SECRETARIAT**

The secretariat office will be located in the Bonsecours room on the second floor below the lobby.

#### **PRACTICAL INFORMATION**

A convenience store is located on the lobby floor of the hotel.

# Instructions for Speakers

### TIME ALLOCATION FOR ORAL TALKS

Plenary: 50 min = 45 min + 5 min (discussion) Invited: 30 min = 25 min + 5 min (discussion) Contributed: 15 min = 12 min + 3 min (discussion)

Oral presentations can be done using your own PC or Mac computers. Mac owners must bring their display connector. You can also upload your (PowerPoint) presentation on the PC available in the session room. The uploading must be done during the break that precedes your session. Speakers are requested to seat in the first row of the session room close to the stage at least 20 minutes before their presentation.

### **INSTRUCTIONS FOR POSTER PRESENTATIONS**

The size of each poster on boards must not exceed 100 cm (width) x 120 cm (height). A poster number is assigned to each presentation. Pushpins will be provided by the ISCOM secretariat.

### SCHEDULE

#### **Poster Session I**

#### **Poster Session II**

**Monday, July 15** Afternoon: Poster Installation Session: 20:00-22:00 (Cartier Room)

**Tuesday, July 16** Morning: Poster Removal **Tuesday, July 16** Afternoon: Poster Installation Session: 20:00-22:00 (Cartier Room)

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Wednesday, July 17 Morning: Poster Removal

Agenda		
	Sunday, July 1	4 <sup>th</sup>
14:00-18:00	ISCOM Check-in (Foyer Régence)	
18:00-20:00	Welcome Reception (Mezzanine St-Jacques)	
<b>Monday, July 15<sup>th</sup></b> Oral Sessions • Location: Régence A-B		
8:30-8:40	Opening: Claude Bourbonnais	
Session 1 Cl	nair: John. A. Schlueter 🔹 (Ar	gonne National Laboratory, USA)
8:40-9:30	Patrick Batail (University of Angers, France)	Crystalline hybrids of molecular conductors and molecular rotor
9:30-10:00	Marc Fourmigué (University of Rennes, France)	The crucial role of weak CHX or strong OHO hydrogen bonds in metal/insulator transitions of organic conductors
10:00-10:15	Hiroshi Kitagawa (Kyoto University, Japan)	Conductive MOF Nanotube
10:15-10:30	Akira Ueda (Tokyo University, Japan)	Deuteration effect on a proton-electron- coupled kappa-type organic conductor based on catechol-fused TTF
10:30-11:00	Break	Foyer Régence
Session 2	• Chair: Sumit Mazumdar •	(University of Arizona, USA)
11:00-11:30	R. Torsten Clay (Missisipi State University, USA)	A minimal model for antiferromag- netism, charge-disproportionation, valence bond solid formation and su- perconductivity in the charge-transfer solids $\kappa$ -(ET) <sub>2</sub> X and Z-[Pd(dmit) <sub>2</sub> ] <sub>2</sub> ]
11:30-11:45	Sumio Ishihara (Tohoku University, Japan)	Dimer-type Organic Salt as Electronic Ferroelectric Material
11:45-12:00	Takashi Yamamoto (Ehime University, Japan)	Experimental study on the mechanism of the charge frustration in the mo- lecular superconductors
12:00-12:15	Yoshihiko Ihara (Hokkaido University, Japan)	Superconductivity and charge instability in $\beta$ "-(BEDT-TTF) <sub>4</sub> [(H <sub>3</sub> O) Ga(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ]· C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> studied by <sup>13</sup> C NMR
12:15-12:30	Kenichiro Hashimoto (Tohoku University, Japan)	Optical response of a charge glass state in $\theta$ -(BEDT-TTF) <sub>2</sub> CsZn(SCN) <sub>4</sub>
12:30-14:30	Lunch	Régence C

Monday, July 15 <sup>th</sup>			
Session 3 • Cha	air: Michael Lang 🔹 (Frankfurt	Institute of Physics, Germany)	
14 :30-15 :00	Hiroshi M. Yamamoto (RIKEN, Japan)	Electric field inducedsuperconduc- tivity in strongly correlated organic materials	
15:00-15:15	Sachio Horiuchi (AIST, Japan)	Ferroelectricity with proton tautomerization in organic molecular crystals	
15:15-15:30	Hiroshi Ito (Nagoya University, Japan)	Charge carrier injection into BEDT-TTF charge transfer salt single crystals using ion-gel-gated transistors	
15 :30-15 :45	Hirotake Itoh (Tohoku University, Japan)	Photoinduced Phase Transition in a Charge-Ordered Ferroelectric $\alpha$ '-(ET) <sub>2</sub> IBr <sub>2</sub>	
15:45-16:00	Tomoyuki Akutagawa (Tohoku University, Japan)	Designs of Molecular Rotators for Ferroelectric and Ionic Conducting Properties	
16:00-16:30	Break	Foyer Régence	
Session 4 • Chair: Sh	inya Uji 🔹 (National Institute f	or Materials Science, Ibaraki, Japan)	
16:30-17:00	Hitoshi Seo (Riken, Japan)	Modeling multi-orbital molecular conductors	
17:00-17:30	Enric Canadell (CSIC, Barcelona, Spain)	First Principles DFT study of charge and anion ordering in molecular conductors	
17:30-17:45	Hiroyuki Nishikawa (Ibaraki University, Japan)	Structural study on charge ordered state of DODHT salts	
17:45-18:00	Koichi Ichimura (Hokkaido University, Japan)	Charge Order Fluctuation in $\alpha$ -(BEDT-TTF) $_{_2I_3}$ Observed by STM	
18:00-20:00	Dinner	Rooftop Restaurant	
20 :00-22 :00	Poster Session I	Cartier Room	

<b>Tuesday, July 16<sup>th</sup></b> Oral Sessions • Location: Régence A-B		
Session 5 • Ch	air: Thierry Giamarchi 🔹 (Ui	niversity of Genève, Switzerland)
8:30-9:20	Reizo Kato (RIKEN, Japan)	Quantum spin liquid state of Pd(dmit) <sub>2</sub> salts
9:20-9:50	Patrick Lee (MIT, USA)	Theoretical aspects of the spin liquid state in frustrated layered organic materials
9:50-10:05	Michael Holt (University of Queensland, Australia)	Spin Liquid Induced By Ring Exchange in $\kappa$ -(BEDT-TTF) <sub>2</sub> X and Et <sub>n</sub> Me <sub>{4-n</sub> Pn Pd(dmit) <sub>2</sub> ] <sub>2</sub>
10:05-10:20	Janani Chander (University of Queensland, Australia)	Quantum spin liquid insulator at two thirds filling in the Hubbard model of $Mo_{3}S_{7}(dmit)_{3}$
10:20-10:35	Gunzi Saito (Meijo University, Japan)	Design and preparation of quantum spin liquid in κ-type ET salts
10:35-11:05	Break	Foyer Régence
Session 6	Chair: Martin Dressel 🔹 (Un	iversity of Stuttgart, Germany)
11:05-11:35	Richard T. Oakley (University of Waterloo, Canada)	Neutral Radicals: from Mott Insulators to Magnets and Metals
11:35-12:05	André-Marie Tremblay (University of Sher- brooke, Canada)	Superconductivity, antiferromagne- tism and Mott critical point in the BEDT family
12:05-12:20	Jens Müller (Goethe University, Frankfurt, Germany)	Influence of intrinsic disorder on the critical slowing down of the charge carrier dynamics at the Mott metal-insulator transition in κ-(BEDT-TTF) <sub>2</sub> X
12:20-12:35	Majed Abdel-Jawad (RIKEN, Japan)	Critical Exponents Of The Mott Transition In EtMe <sub>3</sub> P[Pd(dmit) <sub>2</sub> ] <sub>2</sub>
12:35-14:30	Lunch	Régence C

Tuesday, July 16 <sup>th</sup>		
Session 7 • Chair : Reizo	Kato (Condensed Mole	cular Materials Laboratory, RIKEN, Japan)
14:30-15:00	Michael Lang (Goethe University, Frankfurt, Germany)	Observation of multiferroicity in the Mott insulator $\kappa$ -(ET) <sub>2</sub> Cu[N(CN) <sub>2</sub> ]Cl
15:00-15:30	Silvia Tomic (Institute of Physics, Zagreb, Croatia)	Electrodynamics in Two-Dimensional BEDT-TTF Solids
15:30-15:45	Satoshi Iguchi (Tohoku University, Japan)	Relaxor-like dielectricity in dimer-Mott insulator $\beta'$ -(BEDT-TTF) <sub>2</sub> ICl <sub>2</sub>
15:45-16:00	Seiko Ohira-Kawamura (J-PARC Center, Japan)	Inelastic neutron scattering study on phonon spectra in dimer-Mott insulator β'-(BEDT-TTF) <sub>2</sub> ICl <sub>2</sub>
16:00-16:30	Break	Foyer Régence
Ses	sion 8 • Chair: Stuart Br	own (UCLA, USA)
16:30-17:00	Catherine Pépin (CEA-Saclay, France)	Quantum Critical Fluctuations in organic superconductors
17:00-17:15	Atsushi Kawamoto (Hokkaido Université, Japan)	Discommensurate magnetic structure of (TMTSF) <sub>2</sub> PF <sub>6</sub> below subphase transition probed by <sup>13</sup> C NMR
17:15-17:30	Francis Pratt (Rutherford Appleton Laboratory, UK)	Superconducting Properties of (TMTSF) <sub>2</sub> ClO <sub>4</sub> : Evidence for Odd-frequency Pairing at Low Fields
17:30-17:45	Toshihiro Takahashi (Gakushuin University, Japan)	Coupling between conduction $\pi$ -electrons and anion permanent electric dipoles in (TMTSF) <sub>2</sub> FSO <sub>3</sub> under Pressure
17:45-18:00	Manuel Almeida (Institute Superior Technic, Sacavem, Portugal)	Molecular Spin Ladders; Strong and Weak Disorder Effects
18:00-20:00	Dinner	Rooftop Restaurant
20:00-22:00	Poster Session II	Cartier Room

Wednesday, July 17 <sup>th</sup> Oral Sessions       Location: Régence A-B		
Session 9 •	Chair: Richard T. Oakley • (U	niversity of Waterloo, Canada)
8:30-9:20	Valentin Alek Dediu (Institute for Nanostruc- tured Materials, Bologna, Italy)	Multifunctional Organic Spintronic Devices
9:20-9:50	Clara Santato (Ecole Polytechnique of Montreal, Canada)	Electrolyte gating as a platform to control the conductivity of nanostructured thin films
9:50-10:20	Concepcio Rovira (Institut de Ciència de Materials de Barcelona, Spain)	Nanostructured objects by hierarchical self assembly of open shell molecules
10:20-10:35	Jaclyn Brusso (University of Ottawa, Canada)	Enhancing Intermolecular Interactions Through Expansion of the $\pi$ -Conjugated Framework
10:35-11:05	Break	Foyer Régence
Session	10 • Chair: Paul Goddard • (	(University of Oxford, UK)
11:05-11:35	(Paul Scherrer Institute, Switzerland)	Controlling Dimensionality, Frustration and Disorder in Model Quantum Magnets
11:05-11:35 11:35-12:05	Christian Ruegg (Paul Scherrer Institute, Switzerland) Thierry Giamarchi (University of Geneva, Switzerland)	Controlling Dimensionality, Frustration and Disorder in Model Quantum Magnets Magnetic insulators: from BEC to Luttinger liquids
11:05-11:35 11:35-12:05 12:05-12:20	Christian Ruegg (Paul Scherrer Institute, Switzerland) Thierry Giamarchi (University of Geneva, Switzerland) Andrea Daniele Bianchi (Université of Montreal, Canada)	Controlling Dimensionality, Frustration and Disorder in Model Quantum Magnets Magnetic insulators: from BEC to Luttinger liquids Magnetic phase diagram of the new quantum magnet NIT-2Py
11:05-11:35         11:35-12:05         12:05-12:20         12:20-12:35	<ul> <li>Christian Ruegg</li> <li>(Paul Scherrer Institute, Switzerland)</li> <li>Thierry Giamarchi (University of Geneva, Switzerland)</li> <li>Andrea Daniele Bianchi (Université of Montreal, Canada)</li> <li>Carlos J. Gómez-García (University of Valencia, Spain)</li> </ul>	Controlling Dimensionality, Frustration and Disorder in Model Quantum Magnets Magnetic insulators: from BEC to Luttinger liquids Magnetic phase diagram of the new quantum magnet NIT-2Py A new series of chiral porous molecular layered magnets with tunable Tc
11:05-11:35         11:35-12:05         12:05-12:20         12:20-12:35         12:35-12:50	<ul> <li>Christian Ruegg</li> <li>(Paul Scherrer Institute, Switzerland)</li> <li>Thierry Giamarchi (University of Geneva, Switzerland)</li> <li>Andrea Daniele Bianchi (Université of Montreal, Canada)</li> <li>Carlos J. Gómez-García (University of Valencia, Spain)</li> <li>Muralee Murugesu (University of Ottawa, Canada)</li> </ul>	Controlling Dimensionality, Frustration and Disorder in Model Quantum Magnets Magnetic insulators: from BEC to Luttinger liquids Magnetic phase diagram of the new quantum magnet NIT-2Py A new series of chiral porous molecular layered magnets with tunable Tc Fine Tuning Lanthanide Molecular Magnets to Increase Energy Barrier
11:05-11:35 11:35-12:05 12:05-12:20 12:20-12:35 12:35-12:50 13:00-14:30	<ul> <li>Christian Ruegg (Paul Scherrer Institute, Switzerland)</li> <li>Thierry Giamarchi (University of Geneva, Switzerland)</li> <li>Andrea Daniele Bianchi (Université of Montreal, Canada)</li> <li>Carlos J. Gómez-García (University of Valencia, Spain)</li> <li>Muralee Murugesu (University of Ottawa, Canada)</li> <li>Lunch</li> </ul>	Controlling Dimensionality, Frustration and Disorder in Model Quantum Magnets Magnetic insulators: from BEC to Luttinger liquids Magnetic phase diagram of the new quantum magnet NIT-2Py A new series of chiral porous molecular layered magnets with tunable Tc Fine Tuning Lanthanide Molecular Magnets to Increase Energy Barrier Régence C

Thursday, July 18 <sup>th</sup> Oral Sessions        Location: Régence A-B		
Session 11 🕠	Chair: Andrea Bianchi	(University of Montreal, Canada)
8 :30 – 9 :20	Jochen Wosnitza (Hochfeld-Magnetolabor, Dresden, Germany)	Recent developments in superconductivity in organic materials
9 :20 – 9 :50	Shinya Uji (National Institute for Materials Science, Ibaraki, Japan)	Is FFLO phase a Universal Feature in $\lambda$ -(BETS) <sub>2</sub> Fe <sub>x</sub> Ga <sub>(1-x)</sub> Cl <sub>4</sub> ?
9 :50 – 10:05	Charles C. Agosta (Clark University, USA)	Evidence For Inhomogeneous Superconductivity In Organic Superconductor
10:05 – 10 :20	Ben J. Powell (University of Queensland, Australia)	In-plane superfluid density and microwave conductivity of the organic superconductor κ-(BEDT- TTF) <sub>2</sub> Cu[N(CN) <sub>2</sub> ]Br: evidence for d-wave pairing and resilient quasiparticles
10 :20 – 10 :35	Tadashi Kawamoto (Tokyo Institute of Technology, Japan)	Electronic states of the dual-layered organic superconductor (BEDT-TTF) <sub>2</sub> Ag(CF <sub>3</sub> ) <sub>4</sub> (TCE)
10 <b>:</b> 35 – 11h05	Break	Foyer Régence
Session 12	• Chair: Torsten Clay • (	Missisipi State University, USA)
11:05 – 11 :35	Yoshihiro Kubozono (Okayama University, Japan)	Superconductivity in metal doped hydrocarbons: characterization, structure, transport properties and mechanism of superconductivity
11 :35 – 11 :50	Sumit Mazumdar (University of Arizona, USA)	What are so special about the phenacene structure and the triply negative charge on the molecular anions of the superconducting doped aromatics?
11 :50 – 12 :20	Takashi Shirahata (Ehime University, Japan)	Synthesis of New Organic Superconductor Based on Purely Organic Donor-Acceptor System
12 :20- 12 :35	Vladimir N. Zverev (Institute for Solid State Physics, Chernogolovka, Russia)	The first molecular superconductor based on BEDT-TTF radical cation salt with paramagnetic tris(oxalato) ruthenate anion
12 :35 - 14 :30	Lunch	Régence C

Thursday, July 18 <sup>th</sup>		
Sess	ion 13 • Chair: Hitoshi Sec	o (RIKEN, Japan)
14 :30 – 15 :00	Martin Dressel (University of Stuttgart, Germany)	Coupling of charge and spin order in organic charge transfer salts
15 :00 – 15 :15	Shinichiro Iwai (Tohoku University, Japan)	Capturing fluctuated charge/lattice dynamics in dimer Mott insulators by few-optical cycle infrared and terahertz pulses
15 :15 – 15 :30	Roman Swietlik (Institute of Molecular Physics, Poznan, Poland)	Optical investigations of organic semiconductors (tTTF) <sub>2</sub> X (X=Br, I)
15 :30 – 15 :45	Bin Zhang (Institute of Chemistry , Beijing, China)	Dual-functional molecular crystals from Cu-oxalato anion with the Jahn-Teller distortion
15 :45 – 16:00	Narcis Avarvari (University of Angers, France)	Helical chirality in TTF's and derived materials
16 :00 – 16 :30	Break	Foyer Régence
Session <sup>-</sup>	14 🔹 Chair: Jochen Wosnitz	a (Dresden Germany)
16 :30 – 17 :00	James S. Brooks (NHMFL, Tallahassee, USA)	Interaction of segregated spin and charge chains in Perylene <sub>2</sub> [Pt(mnt) <sub>2</sub> ] in high magnetic fields
17 :00 – 17 :15	Woun Kang (Ewha Womans University, Seoul, Korea)	Temperature, field and azimuthal dependence of the coherence peak in quasi-two-dimensional layered con- ductors
17 :15 – 17 :30	Wafa Kaddour (LPS, Orsay, France and Université of Tunis, Tunisia)	Competition between superconduc- tivity and charge density wave in the quasi-1D compound TTF[Ni(dmit) <sub>2</sub> ] <sub>2</sub>
17 :30 – 17 :45	Andrei G. Lebed (University of Arizona, USA)	Possible Triplet Superconductivity in the Quasi-One-Dimensional Layered Conductor Li <sub>0.9</sub> Mo <sub>6</sub> O <sub>17</sub>
17 :45 – 18 00	Keizo Murata (Osaka University, Japan)	Magnetic-Field-Induced Phases HMTSF-TCNQ studied at 1 GPa, up to 45 Tesla
18:00 - 18:15	Hidetoshi Fukuyama (Université of Tokyo, Japan)	Anomalous properties of Dirac electrons under weak magnetic field
19 :00 - 22:00	Banquet	Vieux-Port Steakhouse

Session 15Chair: Ben J. Powell • (University of Queensland, Australia)8 :15 - 9 :05Yoshikazu Suzumura (Nagoya University, Japan)Novel aspects of Dirac electron in organic conductors9 :05 - 9 :35Takako Konoike (ISSP, University of Tokyo, Japan)Thermal properties of organic Dirac fermion systems9 :05 - 9 :35Miguel Monteverde (LPS, Orsay, France)Evidence for the coexistence of Dirac and massive carriers in a (REDT-TTF)213 under hydrostatic pressure10 :05 - 10 :20Toshihito Osada (ISSP, University of Tokyo, Japan)Experimental Evidences for Quantum Hall Ferromagnetic Phase with Helical Edge Mode in the Organic Dirac Fermion System10 :20 - 10 :35Kasuya Miyagawa (University of Tokyo, Japan)"C NMR studies on the organic Massless Dirac Fermion materials10 :20 - 10 :35BreakFoyer RégenceSession 16Chair: James Brooks(NHMFL, Tallahassee, USA)11:05 - 11:35Paul Goddard (University of Oxford, UNIVERSITY, USA)Molecular quantum magnets under extreme conditions11:35 - 12:05Jamie L. Manson (Eastern Washington) University, USA)Strong hydrogen bonds as building blocks in magnetic coordination polymers12:05 - 12:20Tom Lancaster (Durham University (UK)Using muons to probe the exotic ground states and excitations in molecule-based ferromagnets using high-pressure electron paramagnetic usA)12:20 - 12:35CosingProbing magneti interactions in molecule-based ferromagnets using high-pressure electron paramagnetic usA)12:20 - 12:35CosingProbing magneti cordination polym	Friday, July 19 <sup>th</sup> Oral Sessions        Location: Régence A-B		
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10 : 35 - 11:05BreakFoyer RégenceSession 16- Chair: James Brooks(NHMFL, Tallahassee, USA)11:05 - 11 : 35Paul Goddard (University of Oxford, UK)Molecular quantum magnets under extreme conditions11 : 35 - 12:05Jamie L. Manson (Eastern Washington University, USA)Strong hydrogen bonds as building blocks in magnetic coordination polymers12:05 - 12 : 20Tom Lancaster (Durham University, USA)Using muons to probe the exotic ground states and excitations in onecular magnets12:20 - 12 : 35Komalavalli Thirunavukkuarasu (NHMFL, Tallahassee, USA)Probing magnetic interactions in molecule-based ferromagnets using high-pressure electron paramagnetic 	10 :20 – 10 :35	Kasuya Miyagawa (University of Tokyo, Japan)	<sup>13</sup> C NMR studies on the organic Massless Dirac Fermion materials
Session 16Chair: James Brooks(NHMFL, Tallahassee, USA)11:05 - 11:35Paul Goddard (University of Oxford, UK)Molecular quantum magnets under extreme conditions11:35 - 12:05Jamie L. Manson (Eastern Washington University, USA)Strong hydrogen bonds as building blocks in magnetic coordination polymers12:05 - 12:20Tom Lancaster (Durham University (UK))Using muons to probe the exotic ground states and excitations in 	10 :35 - 11:05	Break	Foyer Régence
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10 INTERNATIONAL SYMPOSIUM



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10<sup>®</sup> International Symposium

## S 1-1

## Crystalline hybrids of molecular conductors and molecular rotors

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Combining recent concepts from the fields of molecular conductivity and molecular machinery we discuss the design of crystalline molecular conductors that also possesses a molecular rotor. We discuss two likely channels by which the rotational motion of Brownian rotators, evaluated using variable-temperature (5300 K) proton spin-lattice relaxation experiments,  ${}^{1}H T_{1}^{-1}$ , might become slowed down in highly conducting solids. One is defined as a low-velocity viscous regime inherent to a non-covalent, physical coupling induced by the cooperativity between intermolecular interactions engaging the rotor in its environment. Another is quantum dissipation, a phenomenon addressing the difference of dynamics of the rotors in solids with different electrical properties, by which the large number of degrees of freedom of the low dimensional electron gas may serve as a bath for the dissipation of the energy of the rotors (local moments and induced dipoles) and the charges of the carriers.

# The crucial role of weak CH—X or strong OH—O hydrogen bonds in metal/insulator transitions of organic conductors

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The crucial role of subtle modifications of the organic lattice/anion interactions, on Spin-Peierls (SP) or Charge-Ordering (CO) transitions has been recently emphasized by Pouget and Canadell [1]. For example, in the non-dimerized, orthogonal chains of  $(o-Me_2TTF)_2X$ , X = Cl, Br, I, the halide anions are encaged into a tetrahedral cavity of C-H—X hydrogen bonds, involved themselves in the electronic localization [2]. We will report on novel o-Me<sub>2</sub>TTF salts with non-centrosymmetric anions (Y = SCN<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>), where the absence of such C-H—Y interactions allows now for anion disorder at room temperature, with a Spin-Peierls like Anion Ordering transition at 100 K (with NO<sub>3</sub><sup>-</sup>). Anothe example of the involvement of hydrogen bonds within the anion layer, will be found in the organic metal delta-(BEDT-TTF)<sub>4</sub>[anthracene-bis(sulfonate)](H<sub>2</sub>O)<sub>2</sub>, where subtle modifications of bifurcated O-H—O<sub>3</sub>S hydrogen bonds are associated to a Charge-Order transition, as demonstrated from IR-Raman experiments, and theoretical calculations.

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# S 1-3 Conductive MOF Nanotube

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Nanotubes are generally prepared from their constituent elements at high temperatures, and thus it is difficult to control their size, shape and electronic states. One useful approach for synthesizing well-defined nanostructures involves the use of building blocks such as metal ions and organic molecules. Here, we show the successful creation of an assembly of infinite square prism-shaped metal-organic nanotubes obtained from the simple polymerization of a square-shaped metal-organic frame. The constituent nanotube has a one-dimensional (1D) channel with a window size of 5.9x 5.92, and can adsorb water (H<sub>2</sub>O) and alcohol vapours, whereas N<sub>2</sub> and CO<sub>2</sub> do not adhere. It consists of four 1D covalent chains that constitute a unique electronic structure of "charge-density wave (CDW) quartets" on crystallization. Moreover, exchanging structural components and guest molecules into 1-D nanopore and obtain highly-conductive MOF nanotube. These findings demonstrate the possibility of bottom-up construction of new porous nanotubes, where their degrees of freedom in both pore space and framework can be used.

Ref.: H. Kitagawa et al., Nature Materials, 2011, 10, 291-295.

## S 1-4

# Deuteration effect on a proton-electron-coupled $\kappa$ -type organic conductor based on catechol-fused TTF

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Proton-electron coupled systems have attracted much attention not only in biology and chemistry but also in materials science and physics. Quinhydrone, which consists of hydroquinone and pbenzoquinone, is a representative proton-electron coupled molecular material. In this crystal, the intermolecular hydrogen bonds and the charge-transfer interaction coexist between the two components, playing an intrinsically important role for the construction of this unique proton-electron coupled system. We have recently prepared and characterized new proton-electron coupled purely organic conductors based on catechol-fused tetrathiafulvalene (Cat-TTF) donor molecules (Nat. Commun. 2013). Importantly, in these materials, the partially oxidized donor molecules are linked by a strong [OÖHÖO]- type intermolecular hydrogen-bond, to form a unique dimer unit. Each donor molecule in the unit further forms a pi-dimeric pair with another donor molecule in the adjacent hydrogen-bonded dimer unit, to construct a  $\kappa$ -type conducting layer connected by the hydrogen bonds. In order to gain insight into this new type of proton-electron coupled organic conductor, in this study, we have prepared single crystals of the deuterated analogue, where the protons in the hydrogen bonds are replaced with deuteriums. The deuteration effects were investigated in terms of the crystal structure, resistivity, and magnetism.

# A minimal model for antiferromagnetism, charge-disproportionation, valence bond solid formation and superconductivity in the charge-transfer solids $\kappa$ -(ET)<sub>2</sub>X and Z-[Pd(dmit)<sub>2</sub>]<sub>2</sub>

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The minimal model most commonly assumed for  $\kappa$ -(ET)<sub>2</sub>X and Z-[Pd(dmit)<sub>2</sub>]<sub>2</sub> is an effectively  $\frac{1}{2}$  filled band frustrated Hubbard model. In this talk I first review the properties of this model, which has antiferromagnetic (AFM), metallic, and quantum spin liquid phases. Mean-field calculations also find a superconducting (SC) phase. Correlated calculations however do not find long-range SC order or a valence-bond solid phase as occurs as in Z=EtMe<sub>3</sub>P.

These failures of the  $\frac{1}{2}$ -filled band effective model as well as recent experimental results which suggest that intra-dimer charge degrees of freedom are significant suggest that the minimal model for these systems must include individual molecules rather than their dimers as "sites" and hence be  $\frac{1}{4}$ -filled. I present computational results for a  $\frac{1}{4}$ -filled band Hubbard model on the full monomer lattice of  $\kappa$ -(ET)<sub>2</sub>X. For weak frustration our calculations find AFM order in agreement with the  $\frac{1}{2}$  filled band model. Importantly, no charge disproportionation is required within the  $\frac{1}{4}$ -filled band to realize AFM order. In the strongly frustrated region of the phase diagram singlet excited states occur below the lowest triplet. The presence of low-energy singlet states in this strongly frustrated system is reminiscent of the AFM Heisenberg model on the kagome lattice. I discuss the low temperature properties of  $\kappa$ -(ET)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> in view of the above developments.

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# S 2-2 Dimer-type Organic Salt as Electronic Ferroelectric Material

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In some low-dimensional organic compounds, two molecules form a dimer in a crystal lattice. Twodimensional molecular conductors, such as  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> are one of the examples, and are termed the dimer-Mott (DM) insulating system. Recently, dielectric anomalies are observed in this class of materials. It is believed that a charge imbalance inside of dimers is responsible for the observed dielectric anomalies. These are recognized as an electronic ferroelectricity [1]. We have examined theoretically electronic states, optical property, and superconductivity in organic salts with the molecular dimer degree of freedom. (1) The electronic structure in a DM system is examined. By analyzing the theoretical model, we clarify that the polar-charge ordered phase attributed to the charge imbalance inside of dimers competes to the non-polar insulating phase [2]. We further examine roles of randomness. (2) The collective charge excitation due to the dimer dipole is found to be realized [3]. The recently found peak structure in the THz spectroscopy is interpreted to be the collective mode [4]. (3) The superconductivity induced by the polar charge fluctuation is examined by the Hubbard-type model. Role of frustration and competition to the spin fluctuation are focused on [5].

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## S 2-3

# Experimental study on the mechanism of the charge frustration in the molecular superconductors

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Charge frustration has been attracting attention as a new pairing mechanism of the superconducting transition in the molecular conductors. A series of our experiments concerning the  $\beta''$ -ET salts (where ET is Bisethylenedithiotetrathiafulvalene) has demonstrated that the charge frustration in the superconductors is ascribed to the competition between several charge distributions. In this symposium, we present recent studies on the mechanism of charge frustration in the  $\beta$ -type and  $\kappa$ -type ET salts and X[Pd(dmit)<sub>2</sub>]<sub>2</sub> salts (where X = monovalent cation and dmit is 1,3-dithiole-2-thione-4,5dithiolate). Based on the vibrational spectra of the compounds above mentioned, the bond alternation and the inter-molecular Coulomb interactions are analyzed. Our experimental results will be compared with the theoretical studies conducted by S. Mazumdar, R. T.Clay, *et al.* 

S 2-4

# Superconductivity and charge instability in $\beta''$ -(BEDT-TTF)<sub>4</sub>[(H<sub>3</sub>O)Ga(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> studied by <sup>13</sup>C NMR

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Unconventional superconductivity has been found frequently in the vicinity of magnetic instability. Contrastingly in some organic conductors, superconductivity appears next to charge ordered phases. For such superconductor, the relationship between charge instability and superconductivity attracts interests.  $\beta''$ -(BEDT-TTF)<sub>4</sub>[(H<sub>3</sub>O)Ga(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> shows a charge instability at 100 K, which was observed by resistivity measurement and Raman spectroscopy [1]. As superconductivity emerges in the charge ordered state below  $T_c = 7.5$  K, the  $\beta''$ -Ga salt is suitable for the investigation of charge instability and superconductivity. We have carried out <sup>13</sup>C NMR measurement at low temperature and found the low-temperature charge instability at  $T_{CD}$ =12 K, slightly above the superconducting transition. At  $T_{CD}$ , we observed the NMR spectrum splitting and peak in the temperature dependence of nuclear spin-lattice relaxation rate divided by temperature  $1/T_1T$ . Analysis on these results leads us to invoke the relationship between charge fluctuations enhanced near  $T_{CI}$ and superconducting pairing mechanisms. In the superconducting state, we observed the reduction of Knight shift, which is indicative of the suppression of spin susceptibility due to spin-singlet pairing state. As the spin-singlet superconductivity is incompatible with extremely high  $H_{C2}$ , we suggest the FFLO state may be realized in high fields.

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## S 2-5

# **Optical response of a charge glass state in** *θ*-(**BEDT-TTF**)<sub>2</sub>**CsZn**(**SCN**)<sub>4</sub>

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The quasi-2D organic compounds with quarter-filled band  $\theta$ –(BEDT-TTF)<sub>2</sub>X have been extensively studied because of the occurrence of the charge-order (CO) metal-insulator transition. Whereas  $\theta$  – (BEDT-TTF)<sub>2</sub>RbZn(SCN)<sub>4</sub> ( $\theta$ -RbZn) is a well-known CO system with a horizontal-stripe structure, the Cs-analogue  $\theta$ –(BEDT-TTF)<sub>2</sub>CsZn(SCN)<sub>4</sub> ( $\theta$ –CsZn) located on the phase boundary exhibits no clear long-range CO, but rather a charge glass state with two competing short-range COs. Theoretically it has been pointed out that intersite Coulomb interaction or geometrical frustration can cause such a glassy CO state, but the origin still remains an open question. Here we report on optical conductivity measurements of  $\theta$ -CsZn. We found that the optical conductivity spectra in the charge glass state can be described by three characteristic Lorentzian terms, one of which, located at 200 cm<sup>-1</sup>, it strongly enhanced only for the polarization of  $E \parallel a$  as lowering the temperature. This is different from that of  $\theta$ -RbZn where the well-established charge gap is observed at low temperatures. To investigate the origin of the characteristic charge excitation in  $\theta$ -CsZn, we introduced disorder into the system by X-ray irradiation. Although the other two peaks attributed to the interband transitions arising from the onsite and intersite Coulomb interaction U and V remain unchanged, the peak below 200 cm<sup>-1</sup> is strongly suppressed by the disorder. We will discuss the possibility of a collective excitation derived from the metallic three-fold CO observed in X-ray diffraction measurements as the origin of the charge excitation sensitive to the disorder.

# Electric field induced superconductivity in strongly correlated organic materials

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 $\kappa$ –(BEDT-TTF)Cu[N(CN)<sub>2</sub>]Br ( $\kappa$ –Br) is an organic superconductor whose ground state can be guided into a Mott-insulating state by a tensile strain, when its thin crystal is laminated on top of a hard silicon substrate. We have chosen Nb-doped SrTiO<sub>3</sub> as a back-gate substrate because of its relatively larger thermal expansion coefficient (ca. 10 ppm/K) than Si in order to guide  $\kappa$ –Br in the vicinity of bandwidth-controlled Mott-transition, where phase-separation often occurs between superconducting and Mott-insulating states. The Mott-FET device thus prepared showed a weakly insulating behavior at low temperature. By applying a positive gate voltage, the resistivity of  $\kappa$ –Br goes down and weakly metallic behavior was observed at  $V_G > 2$  V. By further increasing the gate voltage up to 8 V, the device showed a sudden drop of resistivity around 5 K, which can be attributed to fieldinduced superconductivity. Taking account of bistable IV characteristics observed in the low resistance region, the above transition can be understood as a percolation transition of superconducting islands that is induced by the electrostatic doping of electrons. The transition temperature increases as the gate voltage rises and saturates around  $V_G = 11$  V. This device can be utilized for uncovering a phase diagram of organic Mott system in the band- filling controlled regime.

# Ferroelectricity with proton tautomerization in organic molecular crystals

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Organic ferroelectrics with advantages of light-weight, flexible, low-cost, and environmentally benign characteristics is in increasing demand, yet needs elaborate chemical designs of objective functions. Three years ago, the croconic acid has been found to exhibit high polarization through the cooperative proton tautomerism. However, this compound has problems to be solved: chemical stability in atmosphere and adaptability to solution process such as coating and printing. For this purpose, we explored new ferroelectric materials. We found above-room-temperature ferroelectricity (2 examples) and antiferroelectricity (3 examples) on benzimidazoles [1]. Imidazole is an important building block in biological systems such as vitamin B12, stable in air, and highly soluble in many common organic solvents. The linear hydrogen-bonded chains can be aligned in various three-dimensional architectures. The 2-methylbenzimidazole crystal with a pseudo-tetragonal symmetry exhibits orthogonal arrangement of two different hydrogen-bonded chains, and then allows polarity switching over two dimensions. On the other hand, 2-difluoromethylbenzimidazole crystal has a nonpolar crystal structure and exhibits double hysteresis loop characteristic of antiferroelectricity. These features are quite promising for finding new paradigms with various structure-property relationships.

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IO INTERNATIONAL SYMPOSIUM

# Charge carrier injection into BEDT-TTF charge transfer salt single crystals using ion-gel-gated transistors

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Ion-gel-gated transistors attract attention as a unique technique for charge carrier injection [1]. Large capacitance due to the electric double layer formation enables injection of large amount of carriers reaching 10<sup>15</sup> cm<sup>-2</sup> at the interface. This technique will be beneficial as a long-desired tool for the band filling control of organic charge transfer salts, however, applications to organic charge transfer salts are limited until now. We fabricated ion-gel-gated transistors of a charge-ordered insulator  $\alpha$ (BEDT-TTF)<sub>2</sub>IBr<sub>2</sub> and measured the characteristics at low temperature. Ionic liquid EMIM-TSFI was gelated by dissolving 15 wt% PMMA. Source and drain electrodes were attached to a single crystal with gold or carbon paste. The crystal surface was set in contact with the ion gel injected along a trench cut on a Teflon substrate. At the bottom of the trench, a gold wire was set as a gate electrode. Temperature dependence of the drain current was measured under gate voltages up to 5 V and drain voltages of 10-50 mV applied at 240 K. Below 200 K, we found a reversible n-type enhancement of the drain current. The field-effect gain, or on-off ratio, was 2 to 5 depending on samples. The activation energy of the drain current was reduced from 0.15 eV to 0.13 eV by the application of gate voltages, however, the semiconducting behavior remained. The n-type behavior agrees with the negative Seebeck coefficient observed below 200 K. Considering that charges up to 0.25 per BEDT-TTF molecule were injected by the ion-gel gating, this result indicates that the charge ordered state of  $\alpha$ -(BEDT-TTF)<sub>2</sub>IBr<sub>2</sub> is robust against the band filling control.

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# Photoinduced Phase Transition in a Charge-Ordered Ferroelectric $\alpha'$ -(ET)<sub>2</sub>IBr<sub>2</sub>

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Toward ultrafast and gigantic optical response, the ferroelectric charge ordering (FCO) formed by strong Coulomb repulsion is attracting much attention. The organic conductor  $\alpha$ –(ET)<sub>2</sub>I<sub>3</sub> for exam ple, the FCO has been revealed to host ultrafast photoinduced insulator-to-metal transition. Analogously, the FCO insulator  $\alpha'$ –(ET)<sub>2</sub>IBr<sub>2</sub> which undergoes successive transitions including charge-disorder/antiferroelectric (AFE) transition and AFE-ferroelectric (FE) transition, should be promising for photomanipulation among competing phases therein. In this presentation we discuss the results of i) optical pump(0.89 eV)-terahertz(THz) probe (20-250 cm<sup>-1</sup>) measurement and ii) optical pump/THz-wave-generation-probe measurement on  $\alpha'$ –(ET)<sub>2</sub>IBr<sub>2</sub>, implying photoinduced phase transitions in the FE phase. In the steady-state optical conductivity spectra, the peak was observed at 130 cm<sup>-1</sup>, and spectral weight of it was revealed to be sensitive to the charge fluctuation. Upon photoexcitation at 140 K in the FE phase, the spectral weight showed instantaneous (<1 ps) change indicating a decrease of charge fluctuation. This strongly suggests the photoinduced enhancement of the FCO. Actually, THz-wave-generation from the compound which works as a direct probe for the FE polarization instantaneously responded upon photoexcitation, revealing the photoinduced modulation of the FE polarization, or a phase transition.

# Designs of Molecular Rotators for Ferroelectric and Ionic Conducting Properties

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Coupling between the molecular rotation and ferroelectric property has been reported in (m-fluoroanilinum) (dibenzo [18] crown-6)[Ni(dmit)2] crystal [1]. We are now successively designed new type solid state molecular rotators coupled with ferroelectric properties and ionic conduction. The molecular rotation of dibromoiodomesitylene (DBIM) along the direction normal to the benzene plane resulted in the change of dipole moment. The reversible order-disorder phase transition at 350 K was associated with the molecular rotation and freezing, where the dielectric responses were reversibly observed. Phase transition behavior of liquid crystalline (Na+)(m-methoxybenzoate) were examined from the viewpoint of molecular rotations and dielectric responses. Phase transition temperature from the crystal to SmA was observed at 550 K, and huge dielectric response was observed in the temperatures below phase transition. VTXRD, DSC, and TG analyses showed the formation of layer structure of Na+ cations and m-methoxybenzoate ligands, which were also consistent with the formation of SmA phase. The Na+ ionic conduction within the two-dimensional cationic layer was achieved in both of the solid and liquid crystalline states. The designs of molecular rotators and physical properties will be discussed.

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## S 4-1 Modeling multi-orbital molecular conductors

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We theoretically study molecular conductors in which multiple molecular orbitals (MO) are involved. In metal complex molecules described as  $M(L)_2$ , where a metal atom M is bonded between two ligand units L, the energy gap between frontier MO becomes small, and then in the crystal, energy bands originated from different MO can overlap. We have proposed a scheme of constructing tight-binding models for such multi-MO systems,  $M(\text{tmdt})_2$  [1] and  $X[\text{Pd}(\text{dmit})_2]_2$  [2], based on first-principles band calculations; namely, to choose the basis functions as linear combinations of MO, which are more localized in space, called fragment-MO. This scheme enables us to systematically understand electronic structures of different materials, as well as to investigate effects of electron-electron Co! ulomb interaction in a natural way. Mean-field studies give a variety of phases including, in addition to conventional ordering seen in single-orbital systems, spin/charge ordering where the multiple MO degree of freedom is involved.

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S 4-2

# First-principles DFT study of charge and anion ordering transitions in molecular conductors

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Accurate first-principles density-functional theory (DFT) calculations have now become possible for systems with large and complex unit cells like many molecular conductors. Although simple tightbinding approaches based on the conducting sublattice have been and will continue to be extremely useful in understanding the basic aspects of the electronic structure of molecular conductors, some features require a more precise evaluation for a comparison with experimental results to be meaningful. A study combining the use of DFT and X-ray diffuse scattering for  $\alpha$ -(BEDT-TTF)<sub>2</sub>KHg(SCN). [1] suggested that the anion sublattice plays a very important role in understanding the charge density wave transition in this system. The modulation in this salt is considerably more involved than those following a standard Peierls mechanism and is triggered by the anion sublattice. Following these findings we have reexamined the nature of the charge and anion ordering transitions in some molecular metals like  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> and several Bechgaard salts. For  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> the cal culated charges of the room temperature structure are in good agreement with Raman studies but the variation as a result of the transition is smaller than suggested by the analysis of the X-ray structures. Our analysis [2] suggests again a strong involvement of the anion sublattice in the charge ordering transition coupled with a subtle polarization mechanism involving both the  $\sigma$  and  $\pi$  electrons of the donor as well as the hydrogen bonding at the donor-acceptor interface. The band structure calculated for the system under pressure clearly shows the emergence of a Dirac cone as well as carrier pockets very close to the Fermi level. The anion ordering transitions in several Bechgaard salts are revisited on the basis of these findings with special emphasis on the role of anions [3]. In particular we discuss the low-temperature Fermi surfaces for  $(TMTSF)_2X$  ( $X = ClO_4$ , NO<sub>3</sub> and PF<sub>6</sub>), the connection with the superconductivity gap for  $X = \text{ClO}_4$  and show that the transverse component of the SDW for  $X = \text{ClO}_4$  $PF_{6}$ ,  $ClO_{4}$  and  $NO_{3}$  salts are successfully accounted by the nesting vector of these surfaces.

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## Structural study on charge ordered state of DODHT salts

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We have been investigating molecular conductors based on a reduced  $\pi$  donor, DODHT [(1,4-dioxane) 2,3-divldithio)dihydrotetrathiafulvalene], and found pressure-induced superconductors,  $\beta$ -(DODH)  $(X = PF_6 \text{ and } AsF_6)$ . Both the salts showed superconductivity under pressure, but the physical properties such as transport and magnetic properties were apparently different; a clear insulator transition was observed for the  $PF_6$  salt but that of the  $AsF_6$  salt was not clear, and the magnetic susceptibility of the  $PF_6$  salt followed a 1-D alternating Heisenberg chain model but that of the AsF<sub>6</sub> salt did not and decreased abruptly to a non-magnetic state at 90 K. The insulating phase of the PF<sub>6</sub> salt at ambient pressure has already been revealed to be a charge ordered (CO) state with stripe-type CO pattern. In order to clarify the insulating state of the AsF<sub>6</sub> salt including the different physical behaviors, we carried out X-ray structural experiments using synchrotron radiation. From the oscillation photographs of the AsF<sub>6</sub> salt taken below 90 K and the precise structure analyses at 150 K and 250 K, which are just below and above the temperature where the b-axis was significantly increased, we conclude the insulating phase of the AsF<sub>6</sub> salt was also CO but the CO pattern was different from the PF<sub>6</sub> salt Furthermore, the electronic band structure changed from quasi 2-D to 1-D below 250 K. Although both the salts showed superconductivity under pressure, their insulating states at ambient pressure were completely different; in the AsF<sub>6</sub> salt, CO and spin Peierls transition occurred in stages at 235 K and 90 K, which is in contrast to the case of the PF<sub>6</sub> salt exhibiting only the CO insulator transition at 255 K.

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# S 4-4 Charge Order Fluctuation in $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> Observed by STM

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The electronic state of two dimensional organic conductor  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> was studied by scanning tunneling microscopy (STM). The conducting *a*-*b* plane of single crystals was imaged at room temperature. BEDT-TTF molecules were clearly observed as bright spots in STM current image. The obtained donor arrangement is characterized as  $\alpha$ -type arrangement. Each donor site is assigned by the shape of spots taking account of transfer integrals between the nearest donors. We found that the brightness of spots varies alternatively along the *a*-axis. The pattern is consistent with the charge stripe order formed below  $T_{\rm CO}$ =135 K. The result indicates that the charge stripe structure like the charge order is formed even above transition temperature.
### S 5-1 Quantum spin liquid state of Pd(dmit)<sub>2</sub> salts

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Quantum spin liquid proposed by P. W. Anderson in 1973 [1] exhibits the absence of magnetic or valence bond solid order among entangled quantum spins even at zero temperature. Although this third fundamental state for magnetism is a long-sought state of matter that has attracted much theoretical attention, the ground state and low-energy excitations of the S=1/2 antiferromagnetic triangular lattice are still far from full understanding and furthermore there are few candidates of real materials [2]. We found that an anion radical salt  $\beta'$ -EtMe<sub>3</sub>Sb[Pd(dmit)<sub>2</sub>]<sub>2</sub> (dmit=1,3-dithiol-2-thione 4,5-dithiolate) with a quasi triangular lattice of [Pd(dmit)<sub>2</sub>]<sub>2</sub> dimers is a promising candidate for the quantum spin liquid [3]. Measurements of various properties including magnetic suscept! ibility,  $\mu$ SR, magnetic torque, <sup>13</sup>C-NMR, specific heat, electrical/thermal transport, vibrational spectra, dielectric constant, and low-temperature crystal structure, have been performed. First-principles DFT calculations followed by tight-binding fitting were also carried out. The spin liquid in the  $\beta'$ -type Pd(dmit)<sub>2</sub> salts exists as a "phase" and is situated between an antiferromagnetic phase and a charge ordering phase. Ground states are classified by the anisotropy of the triangular lattice that can be finely tuned by mixed cations with a minimum of disorder effect on the magnetic layer.

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# S 5-2 Theoretical aspects of the spin liquid state in frustrated layered organic materials

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I shall discuss the theory background behind the spin liquid state that has been observed in certain classes of frustrated organic materials. The emphasis will be on the prediction of exotic excitations such as fermionic spinons which carry spin 1/2 and accompanying gauge fields. I shall discuss various experiments which have been proposed to probe these exotic behaviours.

#### S 5-3

# Spin Liquid Induced By Ring Exchange in $\kappa$ -(BEDT-TTF)<sub>2</sub>X and Et<sub>n</sub>Me<sub>4-n</sub>Pn[Pd(dmit)<sub>2</sub>]<sub>2</sub>

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We model the Mott insulating phases of quasi-two dimensional organic charge-transfer salts  $\kappa$  (BEDT-TTF)<sub>2</sub>X and Et<sub>n</sub>Me<sub>4-n</sub>Pn[Pd(dmit)<sub>2</sub>]<sub>2</sub> by a modified Heisenberg model on the anisotropic triangular lattice which include both Heisenberg exchange and ring exchange. Using the semi-classical spin wave approximation, we study the interplay of magnetic frustration and ring exchange on the ground state properties and excitation spectra. Surprisingly, we find that ring exchange strongly suppresses the long-range antiferromagnetic order and induces a large region of the phase diagram without long-range order due to strong quantum fluctuations. In addition, we find general conditions for the behaviour of the spin-excitation spectrum in the quantum critical regime. For the pure Heisenberg model, the spin-excitation spectrum softens and the spin-velocity vanishes. When ring-exchange is included in the model, an instability in the spin excitation-spectrum develops and results in the ordered phase undergoing a first order transition to a spin-liquid phase. Combined with recent electronic structure calculations [1] the results obained provide constraints on whether antiferromagnetic long-range order or a spin-liquid will be observed experimentally in these materials.

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#### S 5-4

## Quantum spin liquid insulator at two thirds filling in the Hubbard model of Mo<sub>3</sub>S<sub>7</sub>(dmit)<sub>3</sub>

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Spin liquids are one of the elusive ground states in nature. Several organic materials are believed to be spin liquids. We propose  $Mo_3S_7(dmit)_3$  is a correlated insulator described by the Hubbard model on a quasi one dimensional chain consisting of triangular clusters at two thirds filling. We show that the ground state of this insulator is a spin liquid born out of the interplay between ferromagnetic Kondo physics, Nagaoka ferromagnetism and the spin one Heisenberg chain (Haldane Chain). We make detailed comparison of our numerical and analytical findings to the properties of  $Mo_3S_7(dmit)_1^2$  and previous theoretical results for related models.

#### Design and preparation of quantum spin liquid in $\kappa$ -type ET salts

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Molecular and crystal designs of ET system for triangular spin lattice having spin liquid state next to metallic state were examined utilizing band parameters and anion structures. Many  $\kappa$ -(ET)<sub>2</sub>X include polymerized anions which exhibit periodic triangular patterns of anion opening, and an ET dimer (1 spin) fits to the anion opening resulting in the two-dimensional isosceles triangular spin lattice. The electron correlation in terms of U/W (U: on-site Coulomb repulsion, W: upper band width) and the shape of the triangular spin lattice in terms of t'/t (t, t': transfer interactions in triangular spin lattice) are the key parameters whether  $\kappa$ -(ET)<sub>2</sub>X exhibits metallic (and superconducting), antiferromagnetic, or spin liquid ground state. A dimer-type Mott insulator  $\kappa$ -(ET)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> has nearly equilateral triangular spin lattice (U/W = 0.93, t'/t = 1.06 - 1.09). As a consequence, the salt exhibited no long-range spin ordering and is the best candidate for quantum spin liquid. A superconducting state as well as a metallic state appears next to the quantum spin liquid state without passing through the antiferromagnetic state. A newly obtained dimer-type Mott insulator with discrete anion exhibits no long-range spin ordering down to 2 K with |J| = 160 - 180 K (U/W = 1.1)though it has a considerably large t'/t = 1.4. Another dimer-type Mott insulator with polymerized anion has the band parameters suitable for the spin liquid (U/W = 1.04, t'/t = 0.97. Preparation, crystal and band structures, and physical properties of them will be discussed.

#### S 6-1

# Neutral Radicals: from Mott Insulators to Magnets and Metals

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In principle, the unpaired electron in a molecular radical should be capable of serving as a charge carrier. Accordingly, a chain of interacting radicals R, each with one unpaired electron, would possess a half-filled  $(f = \frac{1}{2})$  electronic energy band, just like an array of atoms in an elemental metal such as sodium. The Achilles heel of the model lies in the fact that there is an intrinsically high onsite Coulombic barrier U to charge transfer for any  $f = \frac{1}{2}$  system. Overcoming the charge repulsion barrier requires that intermolecular charge transfer integrals t, and hence the electronic bandwidth W(=4t), be sufficiently large to offset U. When W > U, the Mott-Hubbard gap  $\Delta E$  vanishes, and a metallic state should prevail.

However, generating radicals in which W is large and U small is a major synthetic challenge. Our approach is to focus on heavy atom (sulfur and selenium) heterocyclic radicals. The presence of the heavy (soft) heteroatoms and a highly delocalized spin distribution lowers the value of U, while the enhanced intermolecular interactions afforded by the spatially extensive S/Se valence orbitals increases W. Magnetic exchange interactions and magnetic anisotropy is also increased. While physical pressure affords increased bandwidth and improved conductivity, the use of chemical pressure, sculpting radicals to allow a high density solid state packing, has led to some remarkable materials which approach the Mott insulator to metal phase transition

#### S 6-2

# Superconductivity, antiferromagnetism and Mott critical point in the BEDT family

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Layered organic superconductors of the BEDT family offer a unique opportunity to explore the interplay between superconductivity, antiferromagnetism and interaction-induced (Mott) metal-insulator transitions. Theoretical studies based on the Cluster version of Dynamical Mean-Field Theory for the Hubbard model lead to some insights on these problems. In this talk, I will introduce the model, the method and its predictions for the phase diagram of the BEDT organics. In particular, the connection to the phase diagram of the high-temperature superconductors will be discussed. Finally, after a general discussion of the Mott transition, I will focus on critical phenomena near the critical point of this transition. Given the quantum nature of the two phases involved in the transition, one may ask whether the observed unconventional exponents could arise as transient quantum behavior preceding the asymptotic critical behavior. Our results show instead that there are important subleading corrections to the mean-field critical behavior that must be taken into account.

# Influence of intrinsic disorder on the critical slowing down of the charge carrier dynamics at the Mott metal-insulator transition in $\kappa$ -(BEDT-TTF)<sub>2</sub>X

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The quasi-2D organic charge-transfer salts  $\kappa$ -(ET)<sub>2</sub>X are considered as model systems for studying the Mott metal-insulator transition (MIT) in reduced dimensions. Both the nature of the static and dynamic criticality of the Mott transition and the influence of disorder on the MIT recently have been in the focus of intense experimental and theoretical efforts. By means of fluctuation (noise) spectroscopy as a powerful new tool to study these materials, for the first time, we have observed a pronounced and sudden slowing down of the carrier dynamics near the finite-temperature critical endpoint  $(p_0/T_0)$  of the Mott transition, which may be a universal feature of MITs, irrespective of the dimensionality of the electronic system [1]. In these experiments, the low-frequency noise power spectral density of the resistance/conductance fluctuations of fully deuterated  $\kappa$ -(D<sub>8</sub>)  $ET_2Cu[N(CN)_2]Br$  exhibits a strong increase near  $T_0$  accompanied by a substantial shift of spectral weight to low frequencies. In this work, we present a comprehensive investigation of the glass-like structural kinetics of the ET molecules' ethylene endgroups, which is related to a controllable disorder potential influencing the electronic ground state properties strongest in the vicinity of the Mott transition. We utilize the possibility to reversibly tune the degree of disorder by employing different cooling rates in partially deuterated  $\kappa$ -[(H<sub>8</sub>-ET)-0.2(D<sub>8</sub>-ET)<sub>0.8</sub>]<sub>2</sub>Cu[N(CN)2]Br, which is located very close to  $p_0$ , i.e. in the critical region of the generalized phase diagram. We report on a striking near divergence of the low-frequency resistance fluctuations at  $T_0$  for a slow cooling rate and discuss our systematic studies of the influence of disorder on the low-frequency critical dynamics of the charge carriers.

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# S 6-4 Critical Exponents Of The Mott Transition In EtMe<sub>3</sub>P[Pd(dmit)<sub>2</sub>]<sub>2</sub>

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Isothermal pressure measurements of the conductivity in EtMe<sub>3</sub>P[Pd(dmit)<sub>2</sub>]<sub>2</sub> within a helium mediu and up to 4 kbar, are presented. EtMe<sub>3</sub>P[Pd(dmit)<sub>2</sub>]<sub>2</sub> is a dimer-Mott insulator with a triangular lattice of dimer sites. At ambient pressures, its ground state is a valence bond solid. We have extracted the critical exponents of the Mott transition within this compound from scaling functions of the conductivity within the metallic state. It is found that the values of the critical exponents deviates from the Ising universality and from those reported in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl. Discussion of the significance of the critical exponents and there relation to the universality class of the Mott transitions will be made.

#### S 7-1

# Observation of multiferroicity in the Mott insulator $\kappa$ -(ET)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl

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The organic charge-transfer salt  $\kappa$ -(ET)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl has a Mott-insulating ground state where localized spins, residing on a triangular lattice of ET dimers, give rise to antiferromagnetic (afm) order below  $T_N \approx 27$  K followed by a weak ferromagnetic canting around 23 K [1]. Very recently, by means of a comprehensive dielectric study, we have found that the system not only exhibits magnetic order but also undergoes a ferroelectric transition at  $T_{FE}$ , making this material the first multiferroic charge-transfer salt [2]. Our proof of ferroelectricity is based on (i) a peak in the dielectric constant  $\epsilon'(T)$ , reaching values of several hundred, (ii) the switching of the macroscopic polarization P(E) o the sample probed by measurements of the current response through so-called positive-up-negativedown (PUND) sweeps of the electric field E, and (iii) measurements of the polarization-electric field hysteresis curve. Most remarkably, the measurements reveal  $T_{FE} \approx T_N$ , suggesting a close interrelation between both types of ferroic order. From studies in a magnetic field of 9 T, which leaves the ferroelectric order can be ruled out. Here we summarize our results of dielectric measurements, including studies on four crystals with different geometries and contact materials, and discuss a possible charge-order driven mechanism to account for the observations.

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#### **Electrodynamics in Two-Dimensional BEDT-TTF Solids**

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A variety of organics with reduced dimensionality and competing interactions between charges, spins and lattice display a multiplicity of ordering phenomena and complex phase diagrams. Novel forms of the low-temperature phases, in particular those featuring ferroelectricity in the two-dimensional molecular solids, have been the focus of intense activity in recent years. Open issues concern the nature of collective charge excitations in the charge- and spin-ordered phases as well as their coupling to applied dc and ac fields. And while some of their features resemble the well-established electro-dynamics of conventional charge-density waves in 1D, others appear quite different and have not been encountered until now. In the charge-ordered phase with the formation of ferroelectric-like domains below t! he metal-to-insulator phase transition, the charge response seems to be reasonably well understood now. Conversely, rather intriguing is the dielectric response in dimer Mott insulator phases with either canted antiferromagnetism or spin liquid. The result that neither charge disproportionation nor charge fluctuations could be detected by infrared vibrational spectroscopy leaves the proposal of ferroelectricity fully open. In order to explain the prominent dielectric relaxation we rather suggest an alternative scenario invoking collective excitations associated to domain walls or charge defects formed in an either magnetically ordered or intrinsically disordered background.

#### S 7-3

# Relaxor-like dielectricity in dimer-Mott insulator $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub>

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Recently dielectric anomaly has been observed in the organic molecular dimer-Mott insulators, e.g. a spin liquid candidate  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> in which the dielectric constant shows relaxor-like strong frequency dependence [1]. More recently a ferroelectricity in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>[N(CN)<sub>2</sub>]C was discovered near the Neel temperature. Several theoretical studies suggested that the anomaly in dielectricity can be induced by the charge degrees of freedom in dimers in the Mott insulating phases. The charge degrees of freedom as well as its coupling with the spin ones are important for the deep understanding of the dimer Mott insulator. Here, we have investigated the dielectricity in the typical dimer-Mott insulator  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub> with the Neel temperature of 22 K. We observed an anomaly in the dielectric constant with strong frequency-dependence and the correspondent relaxor-like glassy ferroelectricity. The relaxor-like dielectric anomaly is estimated to freeze at around the Neel temperature and pyrocurrents start to appear at the temperature. Thus, the relaxor-like ferroelectricity is considered to be metastable state with the charge disproportionation in dimers, possibly coupled with the magnetism.

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#### S 7-4

### Inelastic neutron scattering study on phonon spectra in dimer-Mott insulator $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub>

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Recently, it has been reported that a molecular dimer-Mott insulator  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub> is a candidate for a new type of ferroelectric system which shows a relaxor-like dielectric response, following  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>. We have performed inelastic neutron scattering measurements on this system by using a chopper specrometer, and observed phonon spectra in a wide wave vector (Q)-energ (E) region for the first time. Clear optical modes with the energies up to ~36 meV were observed together with an acoustic phonon dispersion. The intensity of the optical mode with the lowest energy E = 4.2 meV increases at a zone boundary along the  $b^*$  axis, in which charge disproportionation is expected to occur, below  $T_{FE} = 62$  K, at which a glassy ferroelectricity appears. Furthermore, the intensity of this mode increases all over the measured Q range along the  $b^*$  axis below the long-range antiferromagnetic transition temperature  $T_N = 22$  K. The results suggest that the lattice dynamics characterized by this optical phonon mode is significantly coupled with strongly correlated charge and spin degrees of freedom.

### **Quantum Critical Fluctuations in organic superconductors\***

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We revisit the magnetic phase transition in organic superconductors,-Bechgaard salts. It is shown that quasi 1D effects are present in the phase diagram and can be described within the framework of a Quantum Critical Point (QCP) of itinerant electrons, where four points of the Fermi surface are subject to nesting. The paramagnon propagator has a very original form typical of quasi 1 D materials, where the logarithmic singularity is cut-off by the fluctuation in th perpendicular direction. We examine, within a hot-spot/cold-spot model, the resistivity in the compound (TMTSF)<sub>2</sub>PF<sub>6</sub>, and find good agreement with experiment.

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\* Work done in collaboration with H. Meier, P. Auban-Senzier and D. Jérome

# **Discommensurate magnetic structure of (TMTSF)**<sub>2</sub>**PF**<sub>6</sub> **below subphase transition probed by** <sup>13</sup>**C NMR**

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The Bechgaard salts (TMTCF)<sub>2</sub>X family demonstrates various ground states at low temperatures depending on counter anion X and/or physical pressures. Superconductivity was found in (TMTSF)<sub>2</sub>PI under pressure, while at ambient pressure this salt shows incommensurate spin-density-wave (IC-SDW) state. As the IC-SDW state locates very close to the commensurate magnetic structure, which is observed in (TMTSF)<sub>2</sub>Br, competition between commensurability and incommensurability induces complicated magnetic structure (subphase) at low temperatures [1]. In subphase, glass-like behavior in specific heat and electric permittivity were reported [2,3], but the detailed magnetic structure has not been clarified. We performed <sup>13</sup>C NMR experiment on single side 13C enriched (TMTSF)<sub>2</sub>PF<sub>6</sub> a ambient pressure down to 1.7 K [4], and found commensurate peaks emerging on the incommensurate u-shape NMR spectrum below 3 K. The hybrid commensurate-incommensurate spectrum was simulated using a discommensurate model, in which continuous phase evolution of IC-SDW structure is partially locked due to commensurability. The phase locking induces a gap in the collective excitations even in the IC-SDW state. The thermal activation type temperature dependence of 1/T observed in the subphase can also be explained by this model.

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# Superconducting Properties of (TMTSF)<sub>2</sub>ClO<sub>4</sub>: Evidence for Odd-frequency Pairing at Low Fields

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The low field phase of the organic superconductor  $(TMTSF)_2ClO_4$  is studied by muon spin rotation. The zero temperature limit of the magnetic penetration depth within the TMTSF layers is obtained to be  $\lambda_{ab}(0) = 0.86(2) \ \mu$ m. Temperature dependence of the muon spin relaxation shows no indication of gap nodes on the Fermi surface nor of any spontaneous fields due to time-reversal-symmetry breaking. The weight of evidence suggests that the symmetry of this low field phase is odd-frequency *p*-wave singlet; a novel example of odd-frequency pairing in a bulk superconductor.

# Coupling between conduction $\pi$ -electrons and anion permanent electric dipoles in (TMTSF)<sub>2</sub>FSO<sub>3</sub> under pressure

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The title compound is an exotic member of Bechgaard salt; a charge transfer complex with organic TMTSF and tetrahedral counter anion with permanent electric dipole. It has been discussed for a long time that this salt may exhibit new phenomena due to a possible coupling between conduction electrons and the anion electric dipoles. Temperature-pressure (T-P) phase diagram was determined by transport measurements [1]; a clear metal-insulator transition with an anion ordering occurs at 90 K at ambient pressure and there appear many subphases under pressure in contrast to the other members of the Bechgaard salt. We performed <sup>77</sup>Se NMR measurements on a single crystal sample under pressure of 6.5 and 10 kbar to clarify the properties of the conduction  $\pi$  electrons. We found a metallic state with an appreciable charge disproportionation below 90 K. We believe that this disproportionation is caused by a coupling with permanent electric dipoles on FSO<sub>3</sub> anions. To clarify this picture, we also performed <sup>19</sup>F NMR measurements which should detect the anion dynamics under pressure. A characteristic relaxation anomaly in <sup>19</sup>F NMR indicating a drastic change in anion dynamics at the subphase boundary was observed. On the basis of these experimental observations, we propose a model explaining a part of the T-P phase diagram of this compound, by taking into account a strong coupling between the conduction  $\pi$ -electrons and anion electric dipoles.

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#### Molecular Spin Ladders; Strong and Weak Disorder Effects

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In spite of the very large interest in spin-ladder systems the number of such molecular compounds remains rather small. The compounds derived from (DT-TTF)<sub>2</sub>[Au(mnt)<sub>2</sub>], the first organic based molecular spin ladder system reported by us are the only ones sharing a common structure thus providing a unique opportunity to establish important structure-properties correlations. The molecular changes, on both the donor and acceptor components, which can preserve the ladder structure of the donors and a spin-ladder behavior, were found to be rather limited. The anions have been restricted to mnt and i-mnt ligands and the donors DT-TTF and ETT-TTF. However the orientation disorder of the last asymmetric donor, completely destroys the magnetic spin-ladder behavior. The number of isotructural ladder systems of this series was recently enlarged by the synthesis of the related donor alpha-DT-TTF enabling the preparation of several salts and here we report in detail (a-DT- $TTF_{2}$  [Au(mnt)<sub>2</sub>] and (a-DT-TTF)<sub>2</sub> [Co(mnt)<sub>2</sub>]. These compounds share the same structure type of (DT-TTF)<sub>2</sub> [Au(mnt)<sub>2</sub>] with donors arranged in paired stacks. In spite of the cis-trans and orientation disorder of the donor the spin-ladder magnetic properties are preserved, and these compounds, not only enlarge this family of isostructural spin ladder systems but also provide interesting examples of weakly disordered spin-ladder systems at variance with the ETT-TTF analogue which behaves as a strongly disordered one.

### **Multifunctional Organic Spintronic Devices**

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Information and communication technology (ICT) is calling for solutions enabling lower power consumption, further miniaturization and multi-functionality requiring the development of new device concepts and new materials. A fertile approach to meet such demands is the introduction of the spin degree of freedom into electronics devices, an approach commonly known as spintronics. This already lead to a revolution in the information storage (GMR read heads) in the last decades. Nowadays, the challenge is to bring spintronics also into devices dedicated to logics, communications and storage within the same material technology [1]. In this context the electric control of the magnetoresistance represents one of the most promising issues enabling both further miniaturization and multifunctional operation of spintronic devices. We will discuss the multi-functionality as an intrinsic characteristics of organic based spintronic devices [2] leading to conceptually new device paradigms. We will further consider the example of the electrically controlled magnetoresistance that can be achieved combining magnetic bistability and electric bistability effects in one single device. The device is characterized by a fine tuning of the GMR amplitude within a multitude of nonvolatile states which can be achieved by applying different programming low voltage biases [3]. We will demonstrate that such device can be operated as a Magnetically Enhanced Memristor (MEM) able to act in both memory and logic gate applications. We will comment on this and other effects merging together spintronic and electronic lines towards new future device concepts [4].

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# Electrolyte gating as a platform to control the conductivity of nanostructured thin films

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Electrolyte gating relies on the use of electrolytes as gating media to modulate the conductivity of semiconducting thin films.

The principle of electrolyte gating is known since almost 60 years, having been used in the early works of Shockley, Bardeen and Brattain. Electrolyte-gated transistors consist of source and drain electrodes and a channel containing the semiconducting material in ionic contact with a gate electrode via an electrolyte solution, which replaces the gate dielectric used in more usual field-effect transistor structure.

In electrolyte-gated organic transistors the application of a gate voltage induces the formation of an electrical double layer (EDL) at the electrolyte/semiconductor interface. EDL capacitances per unit areas are in the order of 10 Fcm-2 and can be as high as 500 Fcm-2, whereas the typical capacitance of a 200 nm-thick SiO2 dielectric is of the order of tens of nFcm-2.

Electrolyte gating is used to fabricate transistors operating at low voltage (below 1 V) as an alternative to other approaches such the use of high-k, or ultrathin gate dielectrics.

Besides that, electrolyte-gating represents an exciting opportunity for investigating the properties of organic materials under high charge carrier and exciton density as well as high current density conditions, to unveil the interrelationships between charge carrier density, charge carrier mobility, and light emission in organic electroluminescent materials. Interestingly, high current density (1-100 A cm-2) has been observed in organic-light emitting transistors with no detrimental effect on the emission efficiency, in contrast to what is observed with organic light-emitting diodes.

Despite the tremendous progress in the field, the physics behind the electrolyte gating phenomenon, in particular the specific effect of a certain electrolyte on the conductivity modulation, is largely undiscovered.

Here we report on electrolyte-gated transistors based on organic semiconducting solution-processed thin films (making use of the light-emitting polymer poly[2-methoxy-5-(2-ethyl-hexyloxy)-1,4-pheny vinylene, MEH-PPV, and the n-type fullerene derivative phenyl-C61-butyric acid methyl ester, PCBM) and making use, as the electrolyte, of different imidazolium- and phosphonium-based ionic liquids (e.g. BMIM-PF6, BMIM-TFSI, EMIM-TFSI).

A tentative correlation between the effectiveness of the gating and the ionic conductivity, ionicity, and surface energy of the ionic liquids is proposed.

# Nanostructured objects by hierarchical self assembly of open shell molecules

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Currently great efforts are being devoted to control weak non covalent intermolecular interactions to direct the formation of self assembled systems with a high order of complexity which is not a straightforward task. We have developed different functional organizations both on surfaces and as free standing nanostructurated objects by using Polychlorotriphenylmethyl (PTM) organic free radicals with different substituents. When a tricarboxylic PTM derivative is deposited in Au(111) a racemic supramolecular organization can be imaged by STM [1]. PTM derivatives bearing three long alkyl chains, hierarchically self-assembles on HOPG forming head-to-head dimers that organize in rows following an interesting spin-containing two-leg molecular ladder topology, in which the alkyl chains determine the space between the radical units and act as diamagnetic barriers.[2] By using the hydrophobic-amphiphilic approach, these free radicals have been organized into complex and hierarchically organized microscale structures with unusual shapes. These multifunctional microscale materials exhibit magnetic properties, fluorescence and superhydrophobicity. [3]

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# Enhancing Intermolecular Interactions Through Expansion of the $\pi$ -Conjugated Framework

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The development of information and communications technologies such as laptop computers, cell phones and personal digital devices has transformed the way we live. Essential to the continuation of these technological advancements is the need for smaller, lighter, cheaper and more efficient electronic, optical and magnetic materials. Since the performance of electronic devices critically depends on the extent of molecular order (in addition to other factors), rational engineering of self-organizing molecular systems with multifunctional characteristics is one of the most attractive and active fields of current research. In pursuit of this goal, we develop molecular architectures in which conjugation is extended in multiple directions via a multidentate aromatic core. By utilizing the complementary and antagonistic interactions of rigid and flexible moieties, we aim to attain solid-state structures with elaborate networks of  $\pi - \pi$  interactions in order to achieve high charge carrier mobilities. This presentation will focus on the synthesis and characterization of the materials currently being pursued in our lab.

### S 10-1 Controlling Dimensionality, Frustration and Disorder in Model Quantum Magnets

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Studies of model low-dimensional quantum magnets reveal complex magnetic correlations, excitations and many-body effects that govern such systems. The discovery of exceptional model materials, recent progress in experimental techniques including neutron spectroscopy, and the development of powerful computational methods enable essentially complete experimental surveys of their properties and quantitative comparison with theory. As a recent example, studies of quantum spin ladders allow first quantitative tests of Luttinger-liquid theory. Chemical tuning of model metal-organic compounds or application of pressure and magnetic fields are exciting new directions geared towards controlling dimensionality, frustration, and quenched disorder in such systems. One-dimensional spin ladder materials are especially susceptible to the substitution of magnetic sites or of chemical bonds mediating magnetic exchange interactions. In the spin ladder materials  $(C_5H_{12}N)_2CuBr_4$  and  $BiCu_2PO_6$  we were able to control fluctuations and quenched disorder by chemical engineering, and studied the resulting ground states and excitations as a function of chemical composition and magnetic field by neutron scattering and measurements of magnetic and thermodynamic bulk properties. The results will be compared to predictions by theory and discussed in the context of experiments on alternative model systems like ultra-cold gases of atoms in optical lattices.

### S 10-2 Magnetic insulators: from BEC to Luttinger liquids

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Understanding the properties of itinerant electrons in solids is made extremely challenging due to the electronic interactions. To tackle this problem a certain number of simplified models, often with only purely local interactions, have been proposed and intensively studied. Unfortunately their solution is still so complicated that it is difficult to separate the real physical effects from the artifact of approximate solutions of these models.

Paradoxically a solution to this conundrum is provided by magnetic insulators, in particular dimer systems. They indeed provide a fantastic laboratory to realize exactly such models, and thus study directly their physics in a very controlled way. They can thus be used as "quantum simulators", in a similar way than cold atomic gases, to tackle with great success questions pertaining to itinerant electronic systems.

I will discuss the recent studies that were made using these systems, and show that we have good theoretical tools to understand both their static and dynamics, as well as remarkable experimental realizations. Such systems have provided excellent realizations of Bose-Einstein condensates, and more recently in a quasi-one dimensional geometry they allowed to obtain the first quantitative test of Tomonaga-Luttinger liquid physics, the paradigm of one dimensional interacting quantum systems. Disordering them also allows to probe the properties of dirty bosons such as the existence and properties of a Bose glass phase.

#### S 10-3

#### Magnetic phase diagram of the new quantum magnet NIT-2Py

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We present thermodynamic and magnetic properties of a new organic magnet which is built from molecules in the nitronyl nitroxide family of free radicals. NIT-2Py exhibits a complex magnetic phase diagram at low temperatures and high magnetic fields. Susceptibility measurements at high temperatures show the paramagnetism of a free spin 1/2 with antiferromagnetic interactions. We saw the onset of bulk magnetic order at 1.3 K, as determined from specific heat  $C_p$  measurements. This anomaly in  $C_p$  is suppressed by magnetic fields above 3 T. In this field range, the sharp peak in Cp is replaced by a Schottky anomaly pointing to collective switching of all magnetic moments between two distinct levels. At even higher fields of 5 T, we observed a second sharp anomaly indicating a second magnetic phase. Magnetisation curves measured below the ordering temperature show magnetization plateau at half of the saturation value of 1  $\mu_B$ /molecule. In combination with the specific heat results, this behaviour suggests a new quantum spin ground state in NIT-2Py. In order to get a better understanding of the magnetic interactions between the molecules, we carried out electronic structure calculations.

#### S 10-4

# A new series of chiral porous molecular layered magnets with tunable $T_c$

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Here we will present the synthesis of a novel series of chiral molecule-based ferrimagnets obtained with di-substituted anilato ligands  $[X_2C_6O_4]^{2-}$  (X = H, Cl, Br, I) and different cations, formulated as  $A[M^{III}M^{II}(X_2C_6O_4)_3] \cdot G$  (A<sup>+</sup> = NBu<sup>+</sup><sub>4</sub>,  $\Delta - [(Phez)_3(H_3O)]^+$ ; M<sup>III</sup> = Cr and Fe; M<sup>II</sup> = Mn, Fe, Co,...; X = H, Cl, Br and I; G = CH\_3COCH\_3, H\_2O). This family of porous magnets presents void hexagonal cavities with ca. 291 Å<sup>3</sup> for X = Cl (ca. 20 % of the unit cell volume) where the solvent (G) molecules are located. Besides chirality and porosity this series present long range ferrimagnetic orderings with ordering temperatures of 5.5 to 6.3, 8.2 and 11.0 K for X = Cl, Br, I and H, respectively. We will show the relationship between the electronegativity of the substituent group X and the ordering temperature, Tc. This series constitutes, thus, the first structurally and magnetically characterized series chiral porous molecule-based 2D magnets whose ordering temperatures can be easily tuned. Finally, we will present the great potentialities of these series of layered magnets for the preparation of multifunctional molecular materials by insertion of other cations with different functionalities as spin crossover

# S 10-5 Fine Tuning Lanthanide Molecular Magnets to Increase Energy Barrier

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Multimetallic rare-earth systems and especially DyIII-based materials have sparked much interest in the area of molecular magnetism due to the large intrinsic magnetic anisotropy of the lanthanide ions. When such a unique property is combined with a high-spin ground state (S) in a molecular complex, it causes slow relaxation of the magnetization as seen for Single-Molecule Magnets (SMMs). Lanthanide only SMMs are rare due to the difficulty in promoting the magnetic interactions via the overlapping bridging ligand orbitals with the contracted 4f orbital of the ions. Toward the goal of inducing significant magnetic interaction between lanthanide ions and subsequently isolating high-energy barrier SMMs, our research is currently focused on the use of phenoxide bridges as superexchange pathways between! spin carriers. In addition, organometallic lanthanide sandwich complexes provided an alternative approach for understanding intriguing quantum mechanical properties of SMMs.

#### S 11-1

#### **Recent developments in superconductivity in organic materials**

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More than 30 years after the discovery of the first organic superconductors, these materials remain a fascinating playground to study fundamental low-dimensional physics. With their simple electronic structure and the easily accessible complete superconducting phase diagram these chargetransfer salts serve as model systems for low-dimensional superconductors. Still, the understanding of the nature of the superconducting state remains a challenge. The experimental picture is controversial with evidence both for unconventional as well as for BCS-like superconductivity. Anyway, in these materials strong electronic correlations are clearly relevant, resulting in unique phase diagrams. For the quasi-two-dimensional charge-transfer salts based on BEDT-TTF (bisethylenedithiotetrathiafulvalene, or ET for short), the layered crystallographic structure leads to highly anisotropic electronic as well as superconducting properties. The corresponding very high orbital critical field for in-plane magnetic-field alignment allows for the occurrence of the FuldeFerrellLarkinOvchinnikov state as evidenced by thermodynamic measurements. In my talk, I will highlight some of the intriguing aspects of organic superconductivity.

### Is FFLO phase a Universal Feature in $\lambda$ -(BETS)<sub>2</sub>Fe<sub>x</sub>Ga<sub>1-x</sub>Cl<sub>4</sub>?

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A series of  $\lambda$ -(BETS)<sub>2</sub>Fe<sub>*x*</sub>Ga<sub>1-*x*</sub>Cl<sub>4</sub> have been extensively studied because of their intriguing magnetic and transport properties. In the field induced superconducting (S) phase for x=1, periodic dips in the interlayer resistance are observed, which are ascribed to the formation of an inhomogeneous superconducting state with spatially modulated order parameter (OP), so-called a Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state.[2] The diamagnetism perpendicular to the layers (M<sub>z</sub>) is suppressed at the FFLO transition in the FISC phase, which is consistent with the nodal plane formation of the OP.[3] For x=0, a reduction of M<sub>z</sub> is observed at 10 T in the S phase. For an alloy (x=0.37), the interlayer resistance show a dip and the field dependence of M<sub>z</sub> has a kink (reduction of M<sub>z</sub>) at about 23 T. All these results show that the FFLO phase is a universal feature in  $\lambda$ -(BETS)<sub>2</sub>Fe<sub>x</sub>Ga<sub>1-x</sub>Cl<sub>4</sub>.

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#### S 11-3

# **Evidence For Inhomogeneous Superconductivity In Organic Superconductor**

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Over 40 years ago it was predicted independently by Fulde and Ferrell and by Larkin and Ovchinnikov that if orbital limiting of the superconducting state in a magnetic field could be suppressed, superconductivity could persist beyond the Clogston-Chandrasekhar limit, which is the limit where the magnetic Zeeman energy dominates pair breaking of Cooper pairs. It was also predicted that above the Clogston-Chandrasekhar limit, the superconducting state could be inhomogeneous, such that the order parameter would become spatially modulated. Using a tunnel diode oscillator, we have measured the rf penetration depth in a number of quasi 2D organic superconductors as a function of temperature and magnetic field. By applying a magnetic field exactly parallel to the conducting layers, we have been able to suppress the orbital limiting of the superconducting state, and stabilize superconductivity above the Clogston - Chandrasekhar limit. By sweeping the magnetic field in a pulsed magnet at different temperatures, we have mapped out phase diagrams for a number of organic materials. In three different materials we have found phase diagrams that are consistent with inhomogeneous superconductivity, containing what we label an FFLO state, after the authors who predicted it. We will show additional evidence for the FFLO state by analyzing data taken with the magnetic field at angles near but not exactly parallel to the conducting layers.

# In-plane superfluid density and microwave conductivity of the organic superconductor κ-(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br: evidence for d-wave pairing and resilient quasiparticles

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We report the in-plane microwave surface impedance of a high quality single crystal of the title compound. In the superconducting state, we find three independent signatures of *d*-wave pairing: i) a strong, linear temperature dependence of superfluid density; ii) deep in the superconducting state the quasiparticle scattering rate  $\sim T^3$ ; and iii) no BCS coherence peak is observed in the quasiparticle conductivity. Above  $T_c$ , the Kadowaki-Woods ratio and the temperature dependence of the in-plane conductivity show that the normal state is a Fermi liquid below  $\simeq 23$  K, yet resilient quasiparticles dominate the transport up to  $\simeq 50$  K.

#### S 11-5

# Electronic states of the dual-layered organic superconductor (BEDT-TTF)<sub>2</sub>Ag(CF<sub>3</sub>)<sub>4</sub>(TCE)

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(BEDT-TTF)<sub>2</sub>Ag(CF<sub>3</sub>)<sub>4</sub>(TCE) has three polymorphs showing superconductivity, namely, the  $\kappa_{L}$ -,  $\kappa \alpha'_1$  and  $\kappa \alpha'_2$ -phases [1-3]. Although the first phase is a typical  $\kappa$ -type compound, the last two phases have recently been identified as dual-layered superconductors composed of the  $\kappa$ - and  $\alpha'$ -type dono: layers. In the  $\kappa \alpha'$ -phases, the bond lengths of the donors indicate that the  $\alpha'$ -layers are likely in charge ordered states. We investigate the superconducting properties and Fermi surface of the  $\kappa \alpha'_1$  phase. The temperature dependence of the resistance is similar to the typical  $\kappa$ -type BEDT-TTF salts, and the superconducting transition temperature (midpoint  $T_c$ ) is 9.5 K. The interlayer coherence length is sufficiently smaller than the thickness of the conducting layer, indicating a two-dimensional superconductor. The de Haas-van Alphen (dHvA) oscillation shows that the conducting layer is the  $\kappa$ -layer with a half-filled band; this is in agreement with the charge-ordered  $\alpha'$ -layer due to the quarter-filled band. The effective cyclotron mass observed in the dHvA oscillation is larger than the bare cyclotron mass calculated. The BEDT-TTF superconductors including a  $\kappa$ -layer show the following trend: the higher the  $T_c$  of the material, the larger the mass enhancement

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#### S 12-1

# Superconductivity in metal doped hydrocarbons: characterization, structure, transport properties and mechanism of superconductivity

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Our group discovered superconductivity in alkali-metal-doped picene samples (K<sub>x</sub>picene and Rb<sub>y</sub>) picene) for the first time [1]. In K<sub>x</sub>picene two superconducting transitions,  $T_c$  (= 7 and 18 K), were observed. Subsequently, the other group reported superconductivity in metal-doped phenanthrene samples, which exhibit  $T_c$ s as high as 4 – 7 K [2]. Furthermore, K doped dibenzopentacene samples exhibited superconductivity with the  $T_c$  of 33 K [3]. However, the superconducting fraction is still less than 10%. We have tried to make superconducting metal doped hydrocarbon samples with high superconducting volume fraction using various methods, such as annealing and liquid  $NH_3$  o  $CH_3NH_2$  techniques. In this presentation, we will fully show how to make the superconductin! g samples with high superconducting volume fraction. We have performed the characterization for the superconducting samples by magnetic susceptibility, Raman, X-ray diffraction and XPS, and the structure has been determined using powder X-ray diffraction. The location of K atoms is different between 7 K and 18 K phases of  $K_3$  picene. In the former phase, three K atoms are located in *ab* layer where picene molecules stack in herringbone form, while in the latter phase, two K atoms are located in *ab*-layer and one K atom is located in the space between *ab*-layers. Recently, we measured temperature dependence of resistivity for K<sub>3</sub>picene and observed zero-resistivity at low temperature, showing superconductivity in this sample.

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O INTERNATIONAL SYMPOSIUM

#### S 12-2

# What are so special about the phenacene structure and the triply negative charge on the molecular anions of the superconducting doped aromatics?

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The discovery of superconductivity (SC) in  $A_3$  picene,  $A_3$  phenanthrene,  $A_3$  dibenzopentacene,  $A_3$  coro nene (A=K, Rb), Sr<sub>1.5</sub>phenanthrene and La-phenanthrene is an exciting recent development. These observations have raised several perplexing questions, viz., (1) What is special about the phenacene structure - why is SC absent in the doped acenes? (2) Why is SC limited to compounds with triply negative phenacenes? (3) What is the relationship to SC in  $A_3C_{60}$ ? We report detailed theoretical and computational work based on a molecular exciton approach that retains all intramolecular manybody interactions, and grafts on intermolecular interactions that are far smaller. We give clean and understandable answers to all of the above questions. We show that crystals of mono and di-anions of the phenacenes are Mott-Hubbard semiconductors, but the trinegative ions give nearly 3/4-filled LUMO and LUMO+1-derived bands because of the proximity between these molecular levels in the phenacene structure. The tendency to 3/4-filling is a consequence of strong *intra*molecular electron electron (e-e) interactions, and is enhanced by cooperative electron-molecular vibration (e-mv) interactions. The much larger energy separation between the LUMO and LUMO+1 in the acenes precludes this effect there. Finally, limitation of SC to effective 3/4-filled LUMO and LUMO+1-derived bands with strong e-e and e-mv interactions suggests a common mechanism of SC in the aromatics and charge-transfer solids.

#### S 12-3

# Synthesis of New Organic Superconductor Based on Purely Organic Donor-Acceptor System

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In the course of our studies on  $\pi$ -extended electron donors, it was found that TTF derivatives condensed with 2-alkylidene-1,3-dithiole moiety afforded many stable molecular metals [1]. Exploration of new organic superconductors based on the  $\pi$ -extended electron donors requires the decrease in the intermolecular interaction. The introduction of the bulky alkyl groups toward the  $\pi$ -extendec electron donors is regarded as the promising strategy for exploring organic superconductors. Et-DTET bearing two ethyl groups was synthesized and its cation radical salts showed semiconducting behavior due to the steric hindrance of ethyl groups [2]. As a candidate for new organic superconductor, we have prepared (EtDTET)(TCNQ), and the transport, magnetic properties, and crystal structure are investigated. The EtDTET and TCNQ molecules form separate layers parallel to *ai* plane. The formal charges of EtDTET and TCNQ estimated from their bond lengths are +0.43(15) and -0.53(13), respectively. The diamagnetic transition was observed at around 5 K. This behavior attributes to superconducting transition. The superconductors based on purely organic components have been reported by two groups [3,4], (EtDTET)(TCNQ) is, however, the first purely organic superconductor at ambient pressure based on donor-acceptor type molecular conductors. We will discuss the features of purely organic superconductor (EtDTET)(TCNQ).

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# The first molecular superconductor based on BEDT-TTF radical cation salt with paramagnetic tris(oxalato)ruthenate anion

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The first molecular superconductor based on a BEDT-TTF radical cation salt with the paramagnetic tris(oxalato)ruthenate anion  $\beta''$ -(BEDT-TTF)<sub>4</sub>K<sub>x</sub>(H<sub>3</sub>O)<sub>1-x</sub>[Ru<sup>III</sup>(ox)<sub>3</sub>]C<sub>6</sub>H<sub>5</sub>Br is synthesized and its crystal and electronic structure, as well as transport and magnetotransport properties were studied. The single crystals have the monoclinic C2/c symmetry and  $\beta''$  packing of the conducting BEDT-TTF layer. The complex anion layer has a polymeric honeycomb-like structure: Ru<sup>3+</sup> and K<sub>x</sub>(H<sub>3</sub>O)<sub>1-x</sub><sup>+</sup> cations ( $x \sim 0.8$ ), linked by oxalate bridges alternate in vertices of the hexagonal network, the solvent molecules occupy hexagonal cavities. The samples were found to be superconductors with T<sub>c</sub>=6.3K. Well pronounced Shubnikov de-Haas oscillations of the out-of- plane magnetoresistance are observed at T=0.4K in the field range 7-17T. The Fourier spectrum of the oscillations mainly consists of two frequencies, which correspond to the Fermi surface cross sections 2.5 10<sup>18</sup>m<sup>-2</sup> and 3.4 10<sup>17</sup>m<sup>-2</sup>, i.e. 6.3% and 0.85% of the Brillouin zone (BZ) area respectively. The greater cross section value is in good agreement with the result of electronic structure calculation, according to which the Fermi surface contains two different pockets of the same area, about 7.5% of BZ. The origin of the smaller observed cross section is discussed.
### Coupling of charge and spin order in organic charge transfer salts

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There is a growing number of organic charge-transfer salts, such as TTF-CA, TMTTF, and BEDT-TTF salts, where electronic degrees of freedom and electronic interactions are directly responsible for electric polarization and ferroelectric transition. Recently, it was discovered that charge order in TMTTF salts not only produces electronic ferroelectricity but also breaks the symmetry of the magnetic degree of freedom in these organic quantum spin chains [1]. The interaction of charge order and spin order naturally involves also the underlying lattice. In two-dimensional BEDT-TTF salts, charge order is well known in  $\alpha$ - and  $\theta$ -phase systems, with a strong dielectric response due to domain-wall motion [2]. Fluctuating charge order was shown to drive superconductivity in  $\alpha$ and  $\beta$ "-salts [3]. Currently an intense debate takes place for the  $\kappa$ -phase compounds, where dimens form a triangular lattice. For  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl and  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>CN<sub>3</sub> vibrationa spectroscopy rules out any charge disproportionation required for electric dipoles on the dimers [4]; alternative explanations for the dielectric response have to be discussed. For the highly frustrated system  $\kappa$ -(BEDT-TTF)2 Hg(SCN)2Cl the on-site Coulomb repulsion is reduced making inter-site interaction more important and paving the way to quantum electric dipoles: in fact, the splitting of the vibrational modes proves that charge order drives the metal-insulator transition at 30 K [5]. We discuss th! e possible existence of fluctuating spin singlets.

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### Capturing fluctuated charge/lattice dynamics in dimer Mott insulators by few-optical cycle infrared and terahertz pulses.

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Recently, relaxor-like dielectric anomaly attracts much attention in dimer Mott (DM) insulators  $\kappa$ -(ET)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> ( $\kappa$ -CN) and  $\beta'$ -(ET)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> ( $\beta'$ -ICl). The origin of the dielectric responses has been attributable to the intra-dimer fluctuated charge imbalance, although such interpretation is now still controversial. i) The terahertz (THz) response in 10-150 cm<sup>-1</sup> was investigated in  $\kappa$ -CN. The 30 cm<sup>-1</sup> band in the optical conductivity was attributable to collective excitation of the fluctuating intra-dimer electric dipoles which are formed by an electron correlation [1]. Similar 30 cm<sup>-1</sup> response was also detected in  $\beta'$ -ICl. We succeeded in observing photoinduced enhancement of this 30 cm<sup>-</sup> band in  $\kappa$ -CN, reflecting the growth of the electric dipole cluster in the DM phase [1]. Such optical responses in  $\kappa$ -CN reflect instability near the boundary between the DM-ferroelectric charge ordered phases. ii) The primary dynamics of the photoinduced enhancement was investigated by pump-probe spectroscopy using 12 fs IR pulses [2]. The 700 cm<sup>-1</sup> oscillation in time axis was observed. The oscillating frequency corresponds to the peak of the optical conductivity that is related to the intra-dimer charge excitation. Such ultrafast dynamics are different from those observed in other DM insulator exhibiting photoinduced insulator- metal transition [3], i.e., the C=C stretching mode (1300 cm<sup>-1</sup>) oscillation is selectively induced in other kappa-type salt.

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### Optical investigations of organic semiconductors truecm $(tTTF)_2 X (X=Br, I)^*$

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The organic semiconductors  $(tTTF)_2 X$  (where: tTTF= trimethylene-tetrathiafulvalene and X = Br, I) are low-dimensional antiferromagnets with the highest Nel temperatures for charge-transfer salts based on TTF derivatives: about 35 K for Br salt and about 43 K for I salt [1]. The studied salts are isomorphous and within conducting layers, the donors are arranged in dimeric units  $(tTTF)_2$ . We studied the corresponding IR and Raman spectra of  $(tTTF)_2 X$  crystals over a temperature range of 5 - 300 K. Our spectroscopic data provide evidence of charge localization over this range. Within the region of C=C stretching (1400-1600 cm-1) and ring breathing modes (400 - 550 cm<sup>-1</sup>), Raman bands related to tTTF molecules with charge +1 were observed; i.e. the charge in dimers is not uniformly distributed. The bands assigned to the ring breathing mode show a specific splitting due to interactions between  $(tTTF)_2$  dimers. We suggest that these modes could be used for evaluation of the strength of interactions between dimers. The IR spectra also give clear evidence of non-uniform charge distribution as two charge transfer transitions (centred at about 4000 and 8000 cm<sup>-1</sup>) were observed. The spectroscopic data will be discussed in relation to formation of the antiferromagnetic states in  $(tTTF)_2 X$  salts.

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### Dual-functional Molecular Crystals from Cu-oxalato Anion with the Jahn-Teller Distortion

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The Jahn-Teller effect plays a key role to ceramic material from superconductivity to giant-magneticresistance. Organic-inorganic hybrids containing the 0D, 1D, 2D, and 3D Cu-oxalato anion with the Jahn-Teller distortion were obtained. They are dual-functional molecular crystal with magnetism from paramagnetic, antiferromagnetic, to ferromagnetic, conductivity from dielectric, protonic, to electronic. The dielectric property was influenced by the Jahn-Teller distortion of Cu-oxalato anion. The proton conductivity from hydrogen-bond between H<sub>2</sub>O and Cu-oxalato anion could be modulated by humidity of environment. The electronic conductivity could be modulated by changing the organic donor and configuration of Cu-oxalato anion. These materials are useful for research on molecular spintronics and protonics.

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### S 13-5 Helical chirality in TTF's and derived materials

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Introduction of chirality into conducting systems is a topic of much current interest as it allows the preparation of multifunctional materials in which the chirality might modulate the structural disorder or expresses its influence through the electrical magneto-chiral anisotropy effect. The access to various chiral electroactive precursors for molecular conductors is therefore of paramount importance [1]. We have recently developed two new families of TTFs in which the chiral information is expressed in different ways. A first series is based on a C3 symmetric core decorated with three TTF-amido-bipyridine fragments, which show self-assembling properties. One of the compounds provided for example an electroactive organogel and conducting nanowires [2]. Moreover, when substituted with chiral alkyl chains, these compounds show hierarchical chiral expressed through the formation of helical fibres of nano- or meso-scopic size following hierarchical self-assembly processes is a topic of great current interest in diverse scientific fields. A second family of chiral TTFs we will discuss present helical chirality provided by helicene units fused with the TTF moiety [5].

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### Interaction of segregated spin and charge chains in Perylene<sub>2</sub>[Pt(mnt)<sub>2</sub>] in high magnetic fields

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Recent inductive studies[1] of Per<sub>2</sub>[Pt(mnt)<sub>2</sub>] show evidence for a field- induced spin gap between 20 and 35 T. At 8 K this dual-chain organic conductor has concomitant charge density wave (insulating, CDW) and spin-Peierls (spin-singlet, SP) transitions, both suppressed above 18 T [2,3], indicating coupled CDW+SP order parameters . Above 20 T transport[2] shows a field-induced insulating phase (FICDW) which persists to nearly 40 T. The implication of the inductive results is that a FICDW [4] is a necessary condition for the re-entrant spin-gap behavior we observe between 20 and 35 T. These measurements also describe the magnetic susceptibility of a spin-chain coupled to a conducting chain in the absence of SP formation. Although theoretical work [5] has described the high field susceptibility of a non-interacting spin-chain (with some similarities to our results), there is now motivation for models to include the interaction of segregated chains with different order parameters.

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### Temperature, field and azimuthal dependence of the coherence peak in quasi-two-dimensional layered conductors

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Coherence peak, which appears when the magnetic field is aligned almost parallel to the conducting layers of quasi-two-dimensional conductors both organic and inorganic, has long been known as one of the criteria to determine the coherence in the electronic transport between layers. However, the origin of its appearance has never been settled. One possibility is the topological effect of the Fermi surface due to the small closed orbits formed on the side of the warped cylindrical Fermi surface when the magnetic field is perpendicular to it.[1] An alternative explanation strengthens the contribution from the effective electrons lying near the self-crossing orbit, which preserve the z-axis velocity to produce a local minimum in the angular dependence of the magnetoresistance.[2] In spite of the controversy, both scenarios predict the same value of critical angle based upon the warping nature of the Fermi surface. In this paper, we would like to present our temperature, magnetic field, and azimuthal dependence of critical angles and the peak amplitude which will shed light on the validity of each model. Experiments have been performed with pressurized  $\beta$ -(BEDT-TTF)<sub>2</sub> I<sub>3</sub>. Judging from quality of the quantum Shubnikov-de Haas oscillations and the semiclassical angular magnetic oscillations, we can tell that the Fermi surface is extremely well defined and that this compound is the most suitable for such a purpose. In fact, very interesting dependence on all the above mentioned three parameters is observed and analyzed.

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### Competition between superconductivity and charge density wave in the quasi-1D compound TTF[Ni(dmit)<sub>2</sub>]<sub>2</sub>

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We have revisited the pressure-temperature phase diagram of the quasi-1D organic salt TTF[Ni(dmit) which is a multi-band compound. At low temperature, a charge density wave (CDW) state was established through X-ray measurements at ambient pressure twenty years ago. However, the system exhibits a metallic behavior without any anomaly at the CDW transition temperature as seen in the resistivity measurements down to the lowest temperatures. This compound is also known to present superconductivity (SC) under an applied pressure of 0.7 GPa at 1.6K, which is a high value for an organic compound with a competition between SC and CDW. Thanks to measurements of longitudinal and transverse resistivities, thermopower and thermal conductivity under pressure up to 3 GPa in a wide range of temperature, we were able to establish a new phase diagram of  $TTF[Ni(dmit)_2]_2$ . First CDW transitions that exist at ambient pressure merge into only one transition at P=12 kbar preceding a commensurability peak of the transition temperature similar to the one observed in TTF-TCNQ. As far as superconductivity is concerned, it emerges at P = 0.2 GPa and the critical temperature,  $T_{c}$ , in creases rapidly up to 0.5 GPa then increases smoothly up to 3 GPa. However, a cusp of  $T_c$  is observed around P = 1.1 GPa. Thanks to DFT calculations, a new image of the band structure, so the Fermi surface, has been calculated at ambient pressure for different temperatures which allows estimating its evolution under pressure. In this presentation, we will try to explain the complex phase diagram of this compound and a tentative explanation of the merging of the CDW transitions and the cusp of  $T_c$  will be proposed. Few insights on the nature of superconductivity in TTF[Ni(dmit)\_2]\_2 will be also presented.

### Possible Triplet Superconductivity in the Quasi-One-Dimensional Layered Conductor Li<sub>0.9</sub>Mo<sub>6</sub>O<sub>17</sub>

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We solve a theoretical problem about the upper critical magnetic field, parallel to a conducting axis of a layered quasi-one-dimensional (Q1D) superconductor. In particular, we consider the case, where triplet superconducting order parameter is not sensitive to the Pauli destructive effects against superconductivity and has no zeros on two Q1D pieces of the Fermi surface. We demonstrate [1] that in this case the orbital destructive effects against superconductivity can destroy superconducting state at magnetic fields much higher than the so-called Clogston-Chandrasekhar paramagnetic limit. Comparison of our theoretical results with the recent experimental data [2] is in favor of a triplet superconducting pairing in the layered Q1D superconductor  $Li_{0.9}Mo_6O_{17}$ .

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### S 14-5 Magnetic-Field-Induced Phases HMTSF-TCNQ studied at 1 GPa, up to 45 Tesla

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Very new and refined results on the Magnetic-Field-Induced (FI) Phases, which is very likely the FICDW, in the ideal crystals of the HMTSF-TCNQ, examining up to 45 T down to 0.3 K tuning the pressure of 1 GPa, where CDW is suppressed, is to be reported. In this report, we show the precise AMRO (angular dependence of magnetoresistance oscillations) and its temperature dependence comparing with the FISDW in TMTSF2X salts. HMTSF-TCNQ, which is an analogue of TTF-TCNQ with a charge transfer of 0.74, has been known to undergo a CDW transition at 30 K at ambient pressure. Although the gross nature of the FI phases was obtained [1], further research has been limited because ideal single crystals were hard to obtain. Recently, one of us (R/K) succeeded to refine the crystal growth and we could unveil remarkably what is being realized in the FI phases, to a greater extent. The nature which became clear on the FI phases was: 1) the AMRO together with the magnetoresistance, which shows distinct entrance to the FI-phase as a first order transition with a consistent view for the first time, 2) the threshold field of the FI was unchanged at least between 0.3 and 4 K, irrespective of the positive or negative magnetoresistance below the FI threshold field, 3) New phase looks present above 30 T. The results are completely a new and help understanding not only of the new FI-phase, probably FICDW but also the FI-phase in general.

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### Anomalous properties of Dirac electrons under weak magnetic field

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In this talk, I will first touch upon how Dirac electrons emerge in solids in general and then report the results of theoretical studies regarding the inter-band effects of magnetic field on Dirac electrons leading to anomalous properties of orbital magnetism and Hall effect [1,2,3] to be compared with experiments.

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### S 15-1 Novel aspects of Dirac electron in organic conductors

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The discovery of Dirac electron in organic conductor, which successfully explained anomalous temperature dependence of Hall coefficient in  $\alpha$ –(BEDT-TTF)<sub>2</sub>I<sub>3</sub>, provides novel aspects compared with those of graphene. The Dirac point with the tilted cone is followed by an accidental degeneracy, and the location moves in the two-dimensional Brillouin zone under pressure with keeping the zero-gap state. In this talk I give an overview of such Dirac electron in organic conductor consisting of four molecular sites per unit cell, and present the mechanism originating from the transfer energy. The density of states vanishing linearly at the Fermi energy gives rise to the intimate correspondence between the experiment and theory in Hall effect, specific heat and NMR. The site selective susceptibility in NMR is understood from the combined effect of the tilting of the cone and the node of the wave function. The roles of the interaction and anion potential are suggested for the Dirac electron under the uniaxial and hydrostatic pressures. The evidence is also found in the magneto-resistance which displays a crossover from the quantum limit of zero Landau level to the Zeeman splitting regime with increasing the magnetic field. Such Dirac electron is analyzed in terms of a reduced model, Berry curvature, and the property of the Dirac point, which is relevant to the time reversal symmetry points.

### S 15-2 Thermal properties of organic Dirac fermion systems

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It has been shown that a massless Dirac fermion system with a tilted Dirac cone is realized in  $\alpha$  (BEDT-TTF)<sub>2</sub>I<sub>3</sub> under high pressure [1]. The anomalous behaviors in magnetoresistance are well understood in this scenario, while the thermodynamic and thermoelectric properties have not yet been studied well. In this study, we have measured the specific heat and thermopower of  $\alpha$ -(BEDT TTF)<sub>2</sub>I<sub>3</sub> under high pressure, to clarify the thermal properties of the massless Dirac fermion system. At high pressure, where the massless Dirac fermions are realized, the temperature dependence of the specific heat shows almost quadratic behavior at low temperature. It suggests the linear energy dispersion in this system. In a magnetic field, the specific heat first increases with magnetic field, and then turns to decrease in high field, and finally shows saturation. These behaviors can be understood by assuming the zero-mode Landau level (LL) characteristic of the Dirac fermion system and its spin splitting [2]. These results are quite consistent with the reported magnetoresistance. Recently, we observed a giant Nernst effect which is dominant rather than the longitudinal component. This unusual behaviors result from the intrinsic nature of the massless Dirac fermions. The possible origin of the giant signal rather than that of graphene is the sharp width of the LL and the Zeeman gap in  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>.

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### S 15-3

### Evidence for the coexistence of Dirac and massive carriers in $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> under hydrostatic pressure

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The layered organic material  $\alpha - (BEDT - TTF)_2 I_3$  (aI3), which has been studied since the 1980s, has recently attracted renewed interest because it reveals low-energy massless Dirac fermions under hydrostatic pressure (P ¿ 1.5 GPa). Compared to graphene, or electronic states at the surface of threedimensional topological insulators, aI3 is strikingly different in several respects. Apart from the tilt of the Dirac cones and the anisotropy in the Fermi surface, its average Fermi velocity is roughly one order of magnitude smaller than that in graphene. This, together with an experimentally identified low-temperature charge-ordered phase at ambient pressure, indicates the relevance of electronic correlations. Therefore, correlations are expected to be ten times larger in aI3 than in graphene, and ! aI3 thus opens the exciting prospective to study strongly-correlated Dirac fermions that are beyond the scope of graphene electrons. Here, we present magnetotransport measurements of aI3 crystals under hydrostatic pressure larger than 1.5 GPa where Dirac carriers are present. We show not only the existence of high-mobility Dirac carriers as already reported [1], but we also prove experimentally the presence of low-mobility massive carriers, in agreement with recent band-structure calculations [2]. The interplay between both carrier types at low energy is the main result of our studies [3]. Furthermore, we show that the measured mobilities for the two carrier types hint at scattering mechanisms due to strongly screened interaction potentials or other short-range scatterers.

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### S 15-4

### **Experimental Evidences for Quantum Hall Ferromagnetic Phase** with Helical Edge Mode in the Organic Dirac Fermion System

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A layered organic conductor  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> under pressures (P > 1.5GPa) is a Q2D massless Dirac fermion system with charge neutrality like undoped graphene. In the 2D massless Dirac fermion systems with charge neutrality, the  $\nu$ =0 QH state appears at the high-field quantum limit, resulting from the breaking of four-fold (spin and valley) degeneracy of the n=0 Landau level. Two kinds of the  $\nu=0$  QH states are possible; spin-unpolarized insulating phase (QH insulator) and the spinpolarized phase with metallic helical edge state. In graphene, it has been clarified that the high-field state is the QH insulator. In this paper, we report the experimental evidences that the high-field state of  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> is the QH ferromagnet in contrast to graphene. The QH ferromagnet can be confirmed by detecting the surface transport due to the helical edge state on the side surface of the crystal. The saturation of interlayer resistance must be caused by the surface residual conduction, and it must disappear under the finite in-plane magnetic field, which breaks the interlayer coupling. Based on this idea, we have performed the experiments on the interlayer resistance in  $\alpha$ -(BEDT TTF)<sub>2</sub>I<sub>3</sub>, and obtained the following results. The saturated value was not scaled by sample sectional area. This means that the saturation does not originate from bulk transport. The saturated value became minimum when the magnetic field was parallel to the stacking direction. as expected. These results are experimental evidences indicating the appearance of the QH ferromagnetic phase with the helical edge state.

#### S 15-5

### <sup>13</sup>C NMR studies on the organic Massless Dirac Fermion materials

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 $\alpha$ -(ET)<sub>2</sub>I<sub>3</sub> is a charge ordered insulator. It becomes a Massless-Dirac-Fermion (MDF) system with a conical dispersion under pressure. Different from graphene,  $\alpha$ -(ET)<sub>2</sub>I<sub>3</sub> has the following features; (a) the cone is largely tilted as a consequence of the low symmetry of crystal structure, (b) charge-ordered phase, which is induced by strong electron correlations resides nearby the Dirac phase, implying a highly correlated nature of MDFs, and (c) bulk system, which allows experimental accesses to Dirac phase by means of NMR. We performed <sup>13</sup>C-NMR measurements to explore the nature of Dirac phase in  $\alpha$ -(ET)<sub>2</sub>I<sub>3</sub> is a strongly correlated system with enhanced antiferromagnetic fluctuations; ii) Reshaping of the Dirac cone or an enhancement of Fermi velocity due to electron correlation is strongly *k*-dependent and so tremendous in a certain direction that the dispersion is nearly vertical; iii) Under perpendicular fields, the zero-mode Landau level inherent in MDFs, spin splitting and a signature of possible symmetry breaking were detected.  $\theta$ -(ET)<sub>2</sub>I<sub>3</sub> provides another route to MDFs, namely from a metallic state, as suggested by transport measurements, which points to a meta-to-MDF transition around 5 kbar. In this presentation, we also present the NMR indications of this transition.

### Molecular quantum magnets under extreme conditions

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Low-dimensional magnets can be constructed from transition-metal ions and molecular building blocks to create near ideal realizations of model quantum systems. The advantages to this approach include an enhanced capability for making adjustments to the crystal structure via chemical and applied pressure, as well as an ability to set the magnetic energy scales to levels that can be matched in the laboratory. In this way it is possible to tune interaction strengths, adjust anisotropy, cross phase boundaries and explore the predictions of quantum theory. Nevertheless, perturbing these "low-energy" systems still requires the deployment of specialist experimental techniques that allow magnetic measurements to take place in ultra-high magnetic fields and pressures in the gigapascal range.

Here I will describe these techniques and show how the combination of these extreme conditions and the versatility of coordination chemistry is used to manufacture, characterise and perturb a variety of S = 1/2 quasi-two-dimensional square-lattice Heisenberg antiferromagnets based on molecular-bridged networks of magnetic Cu<sup>2+</sup> ions. In particular, I will describe the importance of spin- and spatial-exchange anisotropy in such systems and show how both ligand substitution and pressure-induced switching of Jahn-Teller axes can be used to achieve crossovers in magnetic dimensionality.

### Strong hydrogen bonds as building blocks in magnetic coordination polymers

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Conventional hydrogen bonds are ubiquitous to many chemical and biological systems and are affluent in crystal engineering applications. By comparison, strong hydrogen bonds such as O-H•••l and F•••H•••F have largely been unexplored with regard to their functionality. Our materials discovery effort, which depends on an undergraduate workforce, aims to utilize and understand strong H-bond interactions and their ability to mediate magnetic exchange in coordination polymers of varying structural and spin dimensionality (i.e., 1- 2-, and 3D). Along these lines, we have synthesized several Cu(II) and Ni(II)-based compounds comprised of the desired H-bond components. The "soft" nature of these H-bonds also renders them sensitive to external stimuli such as high pressure. One such sy! stem undergoes successive Jahn-Teller switching followed by dimerization under modest pressures. This and other recent examples of our work, including polymorphism, isotope effects, etc., will be described.

### Using muons to probe the exotic ground states and excitations in low-dimensional, pyrazine-based molecular magnets

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Muons are subatomic particles that may be implanted in materials and used as sensitive magnetometers. In many cases, muons have been shown to be sensitive to magnetic transitions that are invisible to more conventional magnetometry. This is especially useful in low-dimensional and frustrated magnetism where strong thermal and quantum fluctuations often make transitions to states of long-range magnetic order difficult to observe.

Here we show how muon-spin relaxation has been used to identify magnetic transitions and excitations in several examples of low-dimensional molecular magnetic material. This includes the observation of long-range order in magnetic coordination polymers based on  $Cu^{2+}$  centres linked with pyrazine ligands. In such systems, exemplified by the series  $[Cu(HF_2)(pyz)_2]X$ , the interactions are constrained to act in reduced dimensions leading to low-dimensional magnetic behaviour. We discuss how muons may be used to probe the properties of the exotic magnetic ground states found in other pyz-based low-dimensional molecule-based magnets such as an unusual non-monotonic phase boundary that may have a topological origin in two dimensions; disordered states and spin diffusion in one-dimensional spin-chains; interacting dimers in zero dimensions; and the consequences of a pressure-induced switch of magnetic dimensionality from 2d to 1d in  $CuF_2(H_2O)_2(pyz)$ .

### Probing magnetic interactions in molecule-based ferromagnets using high-pressure electron paramagnetic resonance

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Multi-frequency electron paramagnetic resonance (EPR) spectroscopy is a powerful technique for investigating magnetic interactions in quantum matter. EPR spectroscopy when combined with techniques such as high-pressure will enable us to probe various quantum phase transitions that give rise to novel electronic and magnetic phases in correlated electron systems. However, this particular combination of experimental tools has remained uncommon for several decades. Recently, our group has successfully implemented high-pressure techniques together with EPR spectroscopy. Cavity-based single crystal high-frequency EPR measurements can now be performed in the frequency range from 40 GHz to 200 GHz at temperatures down to 1.6 K under quasi-hydrostatic pressures up to 30 kbar.

With the application of pressure, the inter-atomic/molecular correlations can be tuned continuously to reveal the nature of magnetic anisotropy and exchange interactions. In this contribution, the realization of high pressure EPR spectroscopy will be described using an organic ferromagnet as an example. This organic ferromagnet containing  $\pi$ -stacked arrays of bisdiselenazolyl radicals exhibits a record high transition temperature and coercivity. The large magnetic anisotropy of this material is attributable to spin-orbit mediated exchange processes between the adjacent radicals. Ferromagnetic resonance measurements under applied pressures that focus on unambiguously demonstrating the role of spin-orbit effects will be presented.

# Poster Session I

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**10**<sup>th</sup> International Symposium

### Coexistence of Superconductivity and Spin-density Wave in TMTSF<sub>2</sub>ClO<sub>4</sub> Tuned by Anion Ordering

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Coexistence of superconductor (SC) and spin-density wave (SDW) phases in (TMTSF)<sub>2</sub>PF<sub>6</sub> under pressure attracted considerable interest due to exotic SC properties. Yet the nature of SC on DW background is still unclear, one of the major complications being that all the band parameters are affected by pressure.

Using various transport and magnetotransport probes we investigate instead SC and SDW coexistence in  $(TMTSF)_2ClO_4$  at ambient pressure at various degrees of  $ClO_4$  anions ordering. When both SC and SDW are observed in transport, we find prehistory effects, enhancement of the SC critical field, and strong spatial anisotropy of the SC state. These features are inconsistent with the conventional model [1] of structural inhomogeneities produced by anion ordering. We reveal instead that SC and SDW regions overlap on the temperature – dimerization gap *V* phase diagram, where *V* is varied by anion ordering [2]. Using transport anisotropy measurements we study how the spatial texture of the SC phase on SDW background evolves with *V* [3]. Even though *V* affects only in-plane dispersion, SC emerges first in the interlayer direction and then inside the plane, similar to the behavior observed in (TMTSF)<sub>2</sub>PF<sub>6</sub> [4]. We discuss this result in the framework of the soliton phase scenario [5].

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### Studies of magnetism, κ-(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl by muSR methods

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The layered organics,  $\kappa$ -(BEDT-TTF)<sub>2</sub>X, have been attracting attention as a model systems of superconductor, anfiferromagnet, Mott transition and candidate of spin liquid. Among them,  $\kappa$ -(BEDT  $TTF)_2Cu[N(CN)_2]Cl$  (denoted as  $\kappa$ -Cl hereafter) is situated in an important position of these systems, because almost all electronic states mentioned above which are realized this salt under ambient or very low pressures. In these circumstances, the number of NMR studies and magnetization measurements have been investigated magnetic properties of  $\kappa$ -Cl. Through these studies, the nature of the magnetic transition of  $\kappa$ -Cl is elucidated to vary under magnetic fields by the effect of Dzyaloshinsky-Moriya interaction. However, zero-field magnetic properties have not been clarified yet except for measurement on spontaneous magnetism. Based on the principle, we aimed to reveal the genuine magnetism of this material by zero-field  $\mu$ SR measurement. We have synthesized single crystals of  $\kappa$ -Cl over 100mg and operated  $\mu$ SR in RAL in UK. Zero-field  $\mu$ SR spectrum was measured in the temperature range of 5.6K to 40 K. Below approximately 22 K, rotational signals were clearly observed at low temperatures. Internal field was determined as 57.3G at 5.6K by using the temperature dependence of this internal field. At low temperatures, rotational and exponential functions were used to analyze spectra, we discuss the value of zero-field  $T_N$ , and critical behaviour near  $T_N$ . We will also present possible locations of muon site with analyzing high temperature spectrum by using the value of  $\delta$  from Kubo-Toyabe function.

### <sup>13</sup>C-NMR study of superconducting fluctuations in κ-(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br

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Quasi-two-dimensional organic conductors  $\kappa$ -(BEDT-TTF)<sub>2</sub>X (X = Cu[N(CN)<sub>2</sub>]Cl, Cu[N(CN)<sub>2</sub>]Br Cu(NCS)<sub>2</sub>) are close to the boundary of antiferromagnetism and superconductivity. Among them, X = Cu[N(CN)<sub>2</sub>]Br salt is the closest superconductor ( $T_c$ =11.6 K) to the boundary and deuterated Cu[N(CN)<sub>2</sub>]Br salt comes even closer to the boundary. <sup>13</sup>C-NMR experiment has been performed on the fully deuterated d[4,4]-Cu[N(CN)<sub>2</sub>]Br salt to reveal the electronic state. The decrease in nuclear spin-lattice relaxation rate divided by temperature  $1/T_1T$  was observed above superconducting transition temperature  $T_c$  [1]. This result can be interpreted as pseudogap or superconducting fluctuations. Superconducting fluctuations were observed above  $T_c$  by the Nernst effect [2]. We performed <sup>13</sup>C-NMR study for single-site-enriched Cu[N(CN)<sub>2</sub>]Br salt and examined deuteration dependence and field dependence of  $1/T_1T$  to reveal whether the behavior of  $1/T_1T$  is affected by pseudogap or superconducting fluctuations. Deuteration dependence indicates that decrease in density of state is not due to pseudogap. Field dependence suggests that suppression of density of state above Tis due to superconducting fluctuations. In the presentation, we report the results for Cu(NCS)<sub>2</sub> salt and discuss the origin of superconducting fluctuations.

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### One-dimensional alternated extended Hubbard model and its application to the mechanism of anion ordering in (TM)<sub>2</sub>X

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The Fabre [TMTTF<sub>2</sub>X] and the Bechgaard [TMTSF<sub>2</sub>X] series of organic conductors, as well as the  $(TMTTF_xTMTSF_{2-x})X$  alloys are known to consist of weakly coupled chains of interacting electrons at quarter-filling. Electrons in these low dimensional structures are under the influence of alternate lattice potentials due to either small dimerization of the stacks or/and site potential alternation, the latter resulting from the different molecular species, especially in alloys. Electron correlations can also be responsible for anion "X" ordering at different wavevectors. In this work, we study the influence of both dimerization and local alternating potentials on the interacting parameters U and V of the one-dimensional extended Hubbard model. We then use the renormalization group method to determine the phase diagram of this generalized extended Hubbard model and the electronically driven different possibilities for anion ordering.

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## Charge disproportionation with lattice distortion of $\alpha$ -(BEDT-TTF)<sub>2</sub>MHg(SCN)<sub>4</sub> (M= Rb, and NH<sub>4</sub>) observed by <sup>13</sup>C-NMR

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The (BEDT–TTF)<sub>2</sub>X salts are organic conductors consisting of alternating conducting sheets of BEDT TTF and insulating sheets of anion. These materials have been classified as  $\alpha$ -,  $\beta$ -,  $\kappa$ -, and  $\theta$ -types depending on the arrangement of their BEDT–TTF molecules. The  $\alpha$ -type salts, which have been intensively investigated during the past two decades, were recently found to be candidates for a Dirac electron system. To resolve the difference between band picture and charge fluctuation of  $\alpha$  (BEDT–TTF)<sub>2</sub> *M*Hg(SCN)<sub>4</sub> (*M*=K, Rb, and NH<sub>4</sub>), we utilized <sup>13</sup>C-NMR to examine  $\alpha$ -(BEDT–TTF). *M*Hg(SCN)<sub>4</sub> (*M*= Rb, and NH<sub>4</sub>) under the conditions with a large hyperfine coupling constant at each site. We observed the temperature dependence of site susceptibility and spin-lattice relaxation rates,  $T_1^{-1}$ . We found that the linewidth of the A site only increased as temperature dependence, a change associated with the development of lattice modulation in both of the density-wave(DW) (*M*= Rb) salt, and superconducting (*M*= NH<sub>4</sub>) salt. These findings indicate that density-wave modulation occurs during charge disproportionation instability and suggest the connection between the the superconductivity and DW with the charge disproportionation.

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### Nodeless versus Nodal Scenarios of Triplet Superconductivity in the Quasi-One-Dimensional Layered Conductor Li<sub>0.9</sub>Mo<sub>6</sub>O<sub>17</sub>

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The problem of the orbital upper critical magnetic field, parallel to a conducting axis of a layered quasi-one-dimensional (Q1D) superconductor, is solved [1,2]. We consider two competing cases: where triplet superconducting order parameter (1) doesn't have [1] and (2) has zeros [2] on the Q1D Fermi surface. We demonstrate that in both cases the orbital effects against superconductivity destroy it in a magnetic field much higher than the so-called Clogston-Chandrasekhar paramagnetic limit. Comparison of our theoretical results [1,2] with the experimental data [3] is in favor of a nodeless triplet superconducting pairing in the layered quasi-one-dimensional superconductor  $Li_{0.9}Mo_6O_{17}$ , although we cannot completely exclude nodal triplet superconductivity.

(102)

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### Tunnel diode oscillator investigation of re-entrant magnetic field induced charge and spin gaps in the coupled dual-chain quasi-one dimensional organic conductor Perylene<sub>2</sub>[Pt(mnt)<sub>2</sub>]

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Recently, we have used a tunnel diode oscillator (TDO) as a resonant inductive method to follow the ac susceptibility of the coupled charge density wave (CDW) and spin-Peierls (SP) ground state as a function of field and temperature in the dual chain organic conductor Perylene<sub>2</sub>[Pt(mnt)<sub>2</sub>]. A TDO is essentially a self-resonating LC circuit driven by a tunnel diode. Changes in the magnetic susceptibility of samples placed in the inductor will be observed as a change in the resonant frequency. These measurements show, in addition to the CDW and SP ground state below 8 K and 20 K, the appearance of a second gapped phase between 20 and 35 T below 4 K. These findings are consistent with previous transport measurements that show a second, field induced insulating phase [1] in the same region of field and temperature, as well as with high field NMR studies [2,3]. The results support a strong coupling of the CDW and SP order parameters even at high fields, and provide motivation to extend the theoretical models to include the interaction of segregated chains with different order parameters.

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### Extended Infrared Study on the Zero Gap Semiconducting State in $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>

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The quasi two-dimensional organic molecular crystal  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> is a semimetal at high temperatures. At ambient pressure it undergoes a metal to insulator transition at T<sub>MI</sub> = 136 K to a charge-ordered state. The strong pressure dependence of this transition has been long known. For example resistivity measurements show the suppression of the transition temperature by approximately 10 K/kbar of applied hydrostatic pressure. Finally at 15 kbar the transition is completely suppressed and the resistivity becomes temperature independent. Eventually a solution for the mystery of the high-pressure state has been proposed in 2006, when theorists found a Zero Gap Semiconducting (ZGS) state in the band structure of  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> under uniaxial pressure. So far BEDT-TTF based crystals are the first and only bulk materials with possible massless Dirac fermions, but experimental confirmations for this state are still rare.

Infrared spectroscopy is an extremely powerful method to investigate the physics of organic crystals based on BEDT-TTF. It allows the simultaneous probing of the dynamics of free charge carriers, collective motions of carriers, interband transitions of localized electrons, lattice phonons, and molecular vibrations.

We will present an extended study on  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> under pressure (p < 15 kbar), at low temperatures (T > 10 K), and in the wide frequency range from 80-8000 cm<sup>-1</sup> (10-1000 meV). Experiments on powdered samples allow us to study the charge-ordered state in more detail, especially the evolution of the charge disproportionation with pressure. Additional experiments on single crystals follow the suppression of the charge-ordered state, the closure of the optical gap and finally investigate the emergence of the ZGS.

### Zero-Gap States of Organic Conductors Derived from a Honeycomb Lattice

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Zero-gap states in organic conductors in  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> have attracted a great deal attention due to the intriguing properties [1,2]. Here we show that such a zero-gap state is realized when non stripe charge order drops charge poor molecules to make hollows in the molecular network, to lead to a honeycomb lattice [3]. By using the method developed for topological insulators [4], the odd parity of the non-diagonal element of the Hamiltonian at the time-reversal invariant momenta (TRIM) guarantees the existence of a band contact point.  $\beta''$ -(BEDT-TTF)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub> is a prototype. The existence of molecules both on inversion centers and general positions, together with non stripe charge order, is the prerequisite of the topologically stable presence of such a zero-gap state

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### **Charge-carrier dynamics at the multiferroic transition in** *κ*-(ET)<sub>2</sub>-Cu[N(CN)<sub>2</sub>]Cl studied by fluctuation (noise) spectroscopy

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Recently we have reported on ferroelectric ordering coinciding with the antiferromagnetic transition in the quasi-two-dimensional triangular-lattice Mott insulator  $\kappa$ -(ET)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl ( $\kappa$ -Cl) makin§ this material the first multiferroic charge-transfer salt [1]. We proposed an electric-dipole driven mechanism for the magnetic order and, thus, a new coupling mechanism of magnetic and ferroelectric ordering.

In order to study the low-frequency charge carrier dynamics, recently we have established resistance fluctuation (noise) spectroscopy as new approach, which proved to be highly suitable for investigating the kinetic properties of the correlated  $\pi$ -carriers in the present materials [2].

Here, we present the first noise measurements within the Mott insulating state of  $\kappa$ -Cl. Superimposed on the 1/f background of the carrier fluctuations, we are able to resolve Lorentz-type spectra, i.e. signatures of single fluctuators, at characteristic temperatures  $T_{\rm INS} \approx 50$  K, coinciding with the localization of carriers on the ET dimers, and around  $T_{\rm FE} \approx 25$  K, the ferroelectric ordering temperature. Remarkably, the kinetics of these individual fluctuators are independent of the applied electrical field above  $T_{\rm FE}$ , whereas below  $T_{\rm FE}$  the characteristic energy shifts with the applied current through the sample. We discuss these results in terms of switching of ferroelectric domains and estimate the volume of latter.

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IO INTERNATIONAL SYMPOSIUM

### Synthesis, Structure, and Physical Properties of (DBrBTBT)<sub>3</sub>X<sub>2</sub>(PhCl)<sub>2</sub>

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[1]Benzothieno[3,2-*b*][1]benzothiophene (BTBT) derivatives have attracted considerable attention due to the high mobility in organic transistors. Recently, the charge-transfer (CT) salt,  $(BTBT)_2PF_6$ , has been found to show high electrical conductivity, though it is highly one dimensional. As an attempt to modify the crystal packing, we have prepared novel CT salts based on 2,7-di-bromo-BTBT (DBrBTBT). Rod-like black crystals of  $(DBrBTBT)_3X_2(PhCl)_2$  (X =  $ClO_4$ , BF<sub>4</sub>) were grown by electrochemical oxidation of DBrBTBT in chlorobenzene. The composition is 3:2, and the donor molecules form trimerized columns. The donor molecules are alternately oriented in the trimer in the  $ClO_4$  salt whereas the same orientation is kept in the BF<sub>4</sub> salt. There is no conduction path along the molecular short axis owing to the presence of the insulating layer composed of the tetrahedral anions and the solvent molecules. The donor molecules have large intracolumnar interactions and small intercolumnar interactions along the molecular long axis, so the electronic structure is quasi-one-dimensional.

### Field-Induced Phase of Quasi-One-Dimensional Conductor HMTSF-TCNQ

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HMTSF-TCNQ is a quasi-one-dimensional organic conductor. HMTSF-TCNQ, which is an analogue of TTF-TCNQ with a charge transfer of 0.74, has been known to undergo a CDW transition at 30 K at ambient pressure (p = 0). By the preceding studies of our group, this CDW at p = 0 is suppressed by the pressure of 1 GPa, where anomalous magnetoresistance kinks with hysteresis were observed but neither at p = 0 nor 2 GPa [1]. But due to the crystal twinning, etc., angular dependent magnetoresistance oscillations (AMRO) was not satisfactory, and accordingly the nature of the field-induce phase itself was not clear. This time, we were favoured with the single crystals which had much clear Bragg spots. We reexamined the magnetoresistance (MR) and AMRO of HMTSF-TCNQ with miniature pressure cells, which could rotate in high magnetic field. Pressure was fixed to 1 GPa. We plan to show the AMRO around three axes, and MR for various axes to discuss this field-induced phases. It turned out that the field-induced 1st order transition took place at 10 T in the field component parallel to the least conducting axis. The threshold field is unchanged at least between 0.3 - 4.2 K. The transition at very low field ~ 0.2 T, above which preliminary Hall voltage seemed to be stepwise, must be present [2].

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### Lattice effects in the 2D valence-bond-solid Mott insulator EtMe<sub>3</sub>P[Pd(dmit)<sub>2</sub>]<sub>2</sub>

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EtMe<sub>3</sub>P[Pd(dmit)<sub>2</sub>]<sub>2</sub> is a quasi-2D valence-bond-solid (VBS) Mott insulator where Pd(dmit)<sub>2</sub> molecule form dimers within the layers of highest conductivity. The dimers are arranged in an anisotropic triangular lattice with transfer integrals t and t' (t'/t = 0.87) and an average inter-dimer exchange coupling  $J/k_B \approx 250$  K. Despite this strong spin frustration the system reveals a low-temperature transition into a spin-gapped phase. Here we present results of the uniaxial expansion coefficients  $\alpha_i = l_i^{-1} dl_i / dT$  (*i* = *a*, *b*, *c*) on single crystals of EtMe<sub>3</sub>P[Pd(dmit)<sub>2</sub>]<sub>2</sub> for temperatures below 200 K and magnetic fields  $B \leq 8$  T. We find a sharp and well-pronounced, slightly broadened  $\lambda$ -type thermal expansion anomaly at 24 K indicating a second-order phase transition into the low-T VBS phase. Measurements in magnetic fields up to 8 T were found to have no effect on the VBS phase transition, *i.e.*, there are no indications of a field-induced melting of the VBS state at this field level. The data along the three crystallographic axes are strongly anisotropic for  $T \leq T_{VBS}$ , corresponding to a significant temperature-dependent lattice distortion upon cooling into the VBS state. On the other hand, an almost isotropic in-plane (ac) behavior is observed above  $T_{VBS}$ . While the in-plane a and c-axe show a large positive expansivity at  $T > T_{VBS}$ , as often found in soft organic materials, the out-ofplane *b*-axis reveals a large negative contribution of unknown origin which sets in rather abruptly around 40 K upon warming.

### Raman scattering spectra in spin-frustrated κ-type BEDT-TTF compounds

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We measured Raman scattering spectra in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> and  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]( over a wavenumber range, 120-1300 cm<sup>-1</sup>. In these compounds, the spins, which are on the triangular lattice of BEDT-TTF dimers, are frustrated. Particularly,  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> is an ideal candidate for the quantum spin-liquid state. On the other hand, in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl antiferromagnetic ordering is observed. Both compounds show not only vibrational Raman lines but also broad structures below 700 cm<sup>-1</sup>. In  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>, the intensity of the broad structure monotonically increases from 700 cm<sup>-1</sup> to 120 cm<sup>-1</sup>, while that in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]C has a maximum at 500 cm<sup>-1</sup>. The spectral weight of the broad structures in both compounds increases from 150 K to 4 K. From the above results, the broad structures are assigned to the magnetic excitation. The center position of the broad structure in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> is lower than in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl. The difference in spectral shape reflects the degree of spin frustration. Thus, we clarified the difference of the spin frustration between the two  $\kappa$ -type BEDT-TTI compounds in Raman scattering measurements.

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### A possible zero-gap-state in $\alpha$ -(BEDT-TSF)<sub>2</sub>I<sub>3</sub>, isostructural with $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>

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After the confirmation of a bulk zero-gap-state (ZGS) in  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> under pressure, exotic features of this system have been revealed and are attracting wide interests of researchers. One of the important questions is whether the bulk ZGS is observed in a system other than this salt. It is even desirable to find a bulk ZGS at ambient pressure. Possible candidates for another bulk-ZGS may include the title compound,  $\alpha$ -(BEDT-TSF)<sub>2</sub>I<sub>3</sub> and  $\alpha$ -(BEDT-STF)<sub>2</sub>I<sub>3</sub>, both of which are isostructural with the BEDT-TTF (ET) salt. Because of the larger size of Se ion than S, the electronic structure in these salts is believed to be similar to that of the ET salt under pressure. We reported the results of 77Se-NMR in these salts and claimed that some of the electronic properties are actually quite similar to those in the ET salt under pressure [1]. However, the local susceptibilities at all molecular sites were found to vanish more quickly than the *T*-linear behavior expected in the ZGS. In order to get more information at lower temperatures, we have synthesized <sup>13</sup>C-enriched single crystal sample of  $\alpha$ -(BEDT-TSF)<sub>2</sub>I<sub>3</sub> and carried out precise measurements of angular dependence of 13C-NMR as in the ET salt. We compare the low temperature behaviors of the local susceptibility at different molecular sites between the ET and BETS salts, and discuss the reason of the difference in the temperature dependence, considering the recent theoretical analysis by Nagoya University group [2].

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# Charge Transfer in Neutral-Ionic Transition: Detection of Neutral-Ionic Domain Walls and Scaling Analysis

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The quasi-one-dimensional mixed-stack charge-transfer complex TTF-CA exhibits the neutral-ionic (NI) transition, which is a strongly charge-spin-lattic-coupled phenomenon with large fluctuations due to the one-dimensionality. Among the materials exhibiting the NI transition, only TTF-CA has a neutral (N)-to-paraelectric-ionic ( $I_P$ ) crossover without dimerization, where the charge fluctuations are highly enhanced. In this region, NI domain walls (NIDWs) are expected to be intensively excited and play a role of charge carriers, as is theoretically predicted. To explore the NIDW excitation, we measured the four-terminal electric conductivity under hydrostatic pressure. As a result, we obtained the pressure dependence of the activation energy of conductivity, which turns out to have a minimum at the boundary between the N and  $I_p$  phases. The minimum value is about 0.055eV, less than a half of the CT energy, and is in line with the theoretical consequences of NIDW, supporting that the measured conductivity is mainly contributed by the NIDW motions. Likewise, we show that the electric conductivity in the NI crossover region free from the lattice dimerization is scaled into a single universal function. This implies that the so-called Widom line of the charge-transfer penetrates into ferro-electric ionic ( $I_f$ ) phase and the original charge-transfer NI transition without the symmetry breaking is behind the I<sub>f</sub> phase which is stabilized by the charge-spin-lattice-coupled energy gain.

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### **Density wave state in** $\alpha$ -(**BEDT-TTF**)<sub>2</sub>KHg(SCN)<sub>4</sub> probed by STM

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We studied electronic state in organic conductor  $\alpha$ -(BEDT-TTF)<sub>2</sub>KHg(SCN)<sub>4</sub> using Scanning Tunneling Microscopy (STM) in order to clarify the density wave state. In this material, broad peak as density wave transition was observed around 8 K by temperature dependence of resistivity. However, there are no direct evidence for CDW or SDW in the density wave state. In this study, we observed BEDT-TTF molecules alignment of  $\alpha$ -(BEDT-TTF)<sub>2</sub>KHg(SCN)<sub>4</sub> at room temperature by STM. The molecules arrangement in the obtained image was in agreement with the previous result by first principle calculation. In addition, the periodic structure corresponding charge disproportionation along c-axis were found. We consider that this periodic structure indicate the fluctuation like charge ordering, because in another  $\alpha$ -type BEDT-TTF compound,  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>, we observed same periodic structure. Therefore, we consider that inter-molecular electron-electron interaction should be taking into account in density wave state of  $\alpha$ -(BEDT-TTF)<sub>2</sub>KHg(SCN)<sub>4</sub>. In order to observe the density wave state directly, we are performing STM at low temperature.

# Mechanism of spin liquid phase transition in Mott-Hubbard insulator

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A new mechanism of the spin liquid phase transition is described that occurs in the magnetic subsystem of Mott-Hubbard insulator and in  $\kappa$ (BEDT-TTF)<sub>2</sub>[Cu<sub>2</sub>(CN)<sub>3</sub>. This mechanism is based on the effect of the dynamic expansion of the algebra generators. It is shown that it provides a transition between the levels of towers of the symmetry found in the Hubbard model by the author in [1-5]. The main distinguishing feature of this transition is a different number of generators, describing spontaneous symmetry on both sides of the phase transition. This method provides a qualitative explanation of the phase characteristics of the metal-insulator Mott-Hubbard type and spin liquid, which occurs in many materials with strong Coulomb repulsion between the electrons. It is shown that the transition to a spin liquid in an organic metal  $\kappa$ (BEDT-TTF)<sub>2</sub>[Cu<sub>2</sub>(CN)<sub>3</sub> is associated with spontaneous breaking of supersymmetry. Half of fermionic Hubbard generator gives the gap in electronic spectrum but other half which describe the magnetic degree do not have gap.

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# Crystal structure and magnetic properties of the second phase of a free organic radical molecule NIT2Py crystal

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We report the X-ray crystal structure and magnetic properties of the second phase of crystals formed from a free radical called 2-(2'-pyridyl)-4,4,5,5- tetramethyl-4,5-dihydro-1,H-imidazole-3-oxide-1-oxyl (NIT-2Py). The result of single crystal X-ray diffraction shows that the second phase of NIT-2Py crystallizes in a monoclinic crystal structure with the space group P21/c. By using susceptibility measurements, we have investigated the magnetic behavior of this organic magnet, which has a negative Curie-Weiss temperature of -4.4 K. The effective magnetic moment amounts to 1.68  $\mu_B$  indicating a delocalized unpaired electron, S=1/2, associated with each molecule. Having no transition down to 1.8 K implies the existence of competing magnetic interactions and a highly degenerate ground state in NIT-2Py. In addition, a paramagnetic behavior at 1.8 K in the applied DC magnetic field up to 7 T along with a saturation value of 1  $\mu_B$  per molecule was observed. We also measured the specific heat of single crystals of NIT-2Py magnetic fields down to 400 mK to explore the magnetic phase diagram.

# Crystal structures and magnetic ordered states of antiperovskite complexes: (TSF)<sub>3</sub>(Mo<sub>6</sub>X<sub>14</sub>)X] (X = Cl, Br)

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 $(TTF^{\bullet+})_3[(Mo_6X_{14}^{2-})(Y^-)]$  (X = Y = Cl; X = Br, Y = Cl, Br, I)[1] have the possibility of spin frustration, because they have the antiperovskite structure. However the six TTF<sup>•+</sup> (S = 1/2) surrounding a halogen anion (Y<sup>-</sup>) form a distorted octahedron. Reflecting this distortion, the antiferromagnetic phase transition occurred at 6.3 - 8.2 K (= T<sub>N</sub>). In this study, using a selenium-substituted TTF analog, TSF for enhancing the intermolecular interaction and modulating its anisotropy, we prepared the antiperovskite complexes:  $(TSF^{\bullet+})_3[(Mo_6X_{14}^{2-})X^-]$  (X = Cl, Br). The complexes are isostructural to the TTF complexes, and show no structural phase transition down to 24 K. They exhibit semiconductive behavior (ca.  $10^4\Omega$  cm at RT). The temperature dependence of magnetic susceptibility is very similar to those observed in the TTF complexes, which obeys the Curie-Weiss law ( $\Theta_{CW}$  are -1.6 K for X = Cl and -6.3 K for X = Br). The complexes exhibit the antiferromagnetic phase transition, and the magnetic field dependence suggests a spin-flop at ca. 3.5 T for X = Cl and ca. 1.6 T for X = Br. The observed T<sub>N</sub> (3.0 K for X = Cl and 5.5 K for X = Br) are lower than those observed in the TTF complexes, in contrast to the expectation from the calculated major overlap integrals (ca.  $3.5 \times 10^{-3}$  which are three times larger than those of the TTF complexes. We will make a presentation about the result of the NMR measurement on the session.

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# Structures and properties of pyridyl-substituted TTF and TSF derivatives and their charge-transfer complexe

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A correlation between a proton and an electron plays an important role not only for biological systems but also for functional molecular materials. For example, in a hydrogen-bonded (H-bonded) molecular complex composed of phenazine and chloranilic acid, it is reported that the proton displacement in the H-bond induces a ferroelectric transition. Such electronic effects of H-bond interactions have attracted researchers' attention in the field of molecular conductors. However, protonelectron coupled phenomena in H-bonded charge-transfer (CT) complexes have been little explored to date. We have recently prepared two kinds of proton-electron coupled H-bonded CT complexes based on 4-pyridyl-TTF (4Py-TTF) and 4-pyridyl-ethylenedithio-TTF (4Py-EDTTTF). Both of them form an N-HN type H-bonded dimer unit composed of the donors. The two TTF (or EDTTTF) skeletons in the unit are in a charge disproportionated state, and the H-bonded proton is located close to the donor with the charge-poor TTF (or EDTTTF) moiety to reduce an intradimer charge repulsion. Interestingly, the degree of the charge disproportionation in the unit of 4Py-EDTTTF is lower than that of 4Py-TTF, because the extension of the electronic system by the introduction of the EDT group suppresses the charge repulsion. For further understanding of the correlation between a proton and an electron in these H-bonded CT complexes, we have then designed 4-pyridyl-tetraselenafulvalene (4Py-TSF). It is of interest how stronger intermolecular interaction owing to the selenium atoms affects both the electronic structure and the proton distribution. In this presentation, the synthesis and characterization of 4Py-TSF and the preparation of the CT complexes will be reported.

# Development of Millimeter Wave ESR Using SQUID Magnetometer and Its Application to Molecular Magnets

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SQUID magnetometer is a well-known and widely used equipment to study magnetic properties of various materials including molecular magnets with very high sensitivity. Here we would like to show that this SQUID magnetometer can be also used to observe millimeter wave ESR of molecular magnets. As a change of magnetization occurs when the ESR resonance condition is satisfied under the irradiation of the electromagnetic wave, we can observe ESR by SQUID magnetometer. One big advantage of this method is that we can obtain the absolute value of ESR intensity, which is not possible for the conventional X-band ESR. Other advantages are that millimeter wave ESR can be made very easily as is demonstrated in this study, and the use of high magnetic field is the most reliable way to improve spectrum resolution. Moreover, not only the microscopic ESR measurement but also the macroscopic magnetization measurement can be done simultaneously. The setup is very simple. MPMS (Quantum Design Co. Ltd.) whose maximum magnetic field is 5 T is used as a magnetometer. The sample rod is replaced with a  $6\phi$  stainless light pipe and the electromagnetic wave is irradiated from the top of light pipe. Gunn oscillators are used as light sources. The minimum detectable spin number is evaluated to be  $2 \times 10^{13}$  spins/G and the frequency region is available from 70 to 315 GHz in our setup [1,2]. We have successfully improved the sensitivity and extended the frequency region as compared with the previous work by Cage et al. [3]. Some applications will be also shown.

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# Structural and Magnetic Properties of a Variety of Divalent Transitional Metal Incorporated DNA Double Helices

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Magnetic exchange interactions are studied theoretically for a variety of divalent transitional metal (M) ions (Mn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup>) incorporated into modified-DNA (M-DNA) helix. The DNA is modified with either hydroxypyridone (H) or bis(salicylaldehyde)ethylenediamine (S-en) metalated base pairs (MBPs) which were experimentally synthesized by Shionoyas group form University of Tokyo and Carells group form University of Munich. Formation of extended M-O network leads to the ferromagnetic interaction for the case of H-DNA. More ordered stacking arrangement was found for S-en-DNA. Ferromagnetic and antiferromagnetic interaction can be obtained by varying different transitional metal ions. The extent of the magnetic interaction depends on the number of transitional metal ions.

# Phase Transition and Dielectric Properties of Liquid Crystalline *m*-Substituted Benzoate Crystals with Alkali Metal Cations

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The molecular rotations in calamitic liquid crystalline state have been well known dynamic properties in the molecular assemblies. Liquid crystalline properties have been reported in alkali metal salts of *m*-halogeno and/or *m*-methoxy-benzoate derivatives, which showed the phase transition from crystal to smectic A (SmA) phase around 550~ 580 K. Since the molecular arrangements and motions in these molecular-assemblies were not sufficiently examined, we examined the phase transition behavior, molecular arrangements, and dielectric properties of (Na<sup>+</sup>)(*m*-methoxybenzoate from the viewpoint of molecular rotations both in the crystal and liquid crystalline states.  $(Na^+)(m)$ methoxybenzoate) was prepared by the equimolar mixing of *m*-methoxybenzoic acid and sodium hydroxide in H<sub>2</sub>O. The water molecule was included in the as-grown white powder, which were eliminated from the crystal by increasing in the temperatures up to 445 K. Phase transition temperature from the crystal to SmA was observed at 550 K, whereas that from SmA to isotropic liquid was observed at 570 K. Temperature- and frequency-dependent dielectric permittivity of  $(Na^+)(ma^+)$ methoxybenzoate) showed huge response after the elimination of water molecules, suggesting that the Na<sup>+</sup> conduction contributed to the dielectric responses. Since the VTXRD supported the headto-head layer structure of *m*-methoxybenzoates, the Na<sup>+</sup> conduction is expected within the twodimensional layer.

# Systematic studies of $\pi$ -d hybrid molecular conductors (DIETSe)<sub>2</sub>FeBr<sub>4x</sub>Cl<sub>4(1-x)</sub>

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We have studied the interplay between conductivity of quasi-one-dimensional (Q1D)  $\pi$ -electron and magnetism of local d-spin using isostructural (DIETSe)  $_2$ FeBr $_{4x}$ Cl $_{4(1-x)}$ . (DIETSe) $_2$ FeCl $_4$  undergoes a metal-SDW transition at about 12 K, followed by an AF transition of Fe<sup>3+</sup> spins below 2.5 K. Meanwhile, (DIETSe) <sub>2</sub>FeBr<sub>4</sub> shows both the metal-insulator and AF transitions at 7 K, indicating the AFinduced SDW transition. Thus, FeBr<sub>4</sub> salt is considered to have higher dimensionality of  $\pi$ -electror and larger  $\pi$ -d interaction than FeCl<sub>4</sub> salt. In order to systematically control their electronic states, we have synthesized a series of mixed crystals (DIETSe)<sub>2</sub>FeBr<sub>4x</sub>Cl<sub>4(1-x)</sub>. The crystal structures of mixed crystal are confirmed to be isostructural to mother materials by X-ray diffraction. We found the SDW transition temperature decreases with increasing Br content, while the Néel temperature tends to increase with increasing Br content. Therefore, we succeeded to systematically control their electronic states and  $\pi$ -d interaction by mixing anions. We also performed magnetoresistance (MR) and magnetic torque measurements up to 35 T for some mixed crystals. We found large anomalies in MR at the spin-flop and AF phase boundaries, indicating the significant  $\pi$ -d interaction. Interestingly, we observed hysteresis in both MR and magnetic torque, while the mother crystals did not show any hysteresis in the magnetic torque. The details of synthesis, crystal structures, and physical properties of the mixed crystals (DIETSe)<sub>2</sub>FeBr<sub>4x</sub>Cl<sub>4(1-x)</sub> will be discussed.

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#### **Anomalous Magnetotransport in DIETSe salts**

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We have studied the influence of local magnetic moments on the quasi-one-dimensional (Q1D)  $\pi$  electrons by magnetotransport and magnetic torque measurements on a series of DIETSe salts. The antiferromagnetic (AF) order of d-electron spins coexists with the incommensurate spin density wave (ICSDW) of  $\pi$ -electrons in (DIETSe)<sub>2</sub>FeCl<sub>4</sub>. It shows quite anomalous magnetoresistance (MR) at the spin-flop and the phase boundaries of AF order [1,2]. Notably, the spin-flop induces large positive MR and non-volatile memory [1]. The detailed study of angle dependent MR revealed the presence of hidden spin canting [2]. The ICSDW can be suppressed by applying hydrostatic pressure or substituting the FeCl<sub>4</sub> anion by FeBr<sub>4</sub> anion. We found the field-induced SDW (FISDW) transitions above the critical pressure of ICSDW in (DIETSe)<sub>2</sub>FeCl<sub>4</sub>. This is the first observation of FISDW in the  $\pi$ -d hybrid materials having the AF order of d-electron spins. Magnetic easy axis of 3d spins and magnetotransport behaviour of (DIETSe)<sub>2</sub>FeBr<sub>4</sub> salt are found to be different from those of (DIETSe)<sub>2</sub>FeCl<sub>4</sub> salt [3]. A large hysteresis appears in the MR of (DIETSe)<sub>2</sub>FeBr<sub>4</sub> below 24 T at 0.3 K. The magnetic torque measurement revealed that the critical field corresponds to the boundary of AF transition of d-electron spins. These results suggest strong correlation between the localized d-electron spins and mobile  $\pi$  electrons.

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#### Shear Stress and Photo Induced Chromism of Spiropyrans

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The shear stress effects on photochromic compounds have been studied by using the DAC -type sapphire anvil cell with rotating mechanism. In this paper, we present the shear stress effects on some kinds of spiropyrans, exhibiting the photochromic transformations between open and closed isomer. We have performed the in situ observations under a microscope with Raman spectroscopic measurements under shear stress or hydrostatic pressure. For nitrospiropyran (nitroSP), the color has been changed from yellow to green as applying shear stress. Subsequently, as releasing the shear stress, the green part changed to purple clearly. Raman spectrum at the purple state showed that shear stress induced the isomerization from SP to merocyanine(MC), as same as the photochromism in solution, while at the green part, the strong fluorescence was observed with an excitation light =780 nm. In addition, the shear stress effects on hydroxyspiropyran (hydroxySP), naphtospiropyran(naphtoSP) and methoxybenzospiropyran (methoxySP) have been studied. HydroxySP and methoxySP exhibited the similar green state under shear stress with strong fluorescence, while naphtoSP showed the blue state without fluorescence. These SPs are classified based on based on the chromic behaviors by shear stress, the threshold pressures occurring color change and fluorescence and the stabilities of MC.

# Effects of Coulomb interaction and hopping interaction in Dimer Mott insulators

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Dimer Mott insulators recently attract attention because of abundant properties such as superconductivity, spin liquid, and charge order. There are some dimer Mott insulator in organic Mott insulators such as  $\kappa$ -(BEDT-TTF)<sub>2</sub>[Cu<sub>2</sub>(CN)<sub>3</sub> and  $\beta$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub>, which show characteristic dietectric response and charge disproportionation within a dimer [1,2]. The dimer seems to affect that and the physical properties of those substances. Therefore, we thought that it is necessary to separately consider the molecules which make a dimer. We study charge order and dielectric response of dimer Mott insulator in two dimensional square lattice by quantum Monte Carlo method. We show the temperature dependence of charge order and dielectric constant for some Coulomb interaction and hopping interaction, which depend on the position of the charge in dimer. We find that whether charge order is formed or not and the transition temperature are determined by the details of the Coulomb interactions and intradimer hopping interaction. Coulomb interaction reinforces charge order and intradimer hopping interaction impedes that.

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# Defect-Induced Zero-Energy Localized State in Dirac Electron System α-(BEDT-TTF)<sub>2</sub>I<sub>3</sub>

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Recently, a quasi-two-dimensional organic molecular conductor  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> ( $\alpha$ -(ET)<sub>2</sub>I<sub>3</sub>) has attracted much attention because of its Dirac dispersion on the Fermi level [1]. In contrast to other Dirac electron systems such as graphene, bulk measurements such as specific heat, transport coefficients, and NMR are possible in  $\alpha$ -(ET)<sub>2</sub>I<sub>3</sub>. They have supported the nature of massless Dirac electrons. However, at low temperatures, resistivity does not become temperature independent, which is expected for massless Dirac electron systems. Instead, it has a log *T* dependence [2]. It is suggested that this behavior is due to the vacancies of ET molecules and randomness of I<sub>3</sub><sup>-</sup> anions. However, theoretical studies on the effects of such defects are limited so far [3]. We study the electronic states of  $\alpha$ -(ET)<sub>2</sub>I<sub>3</sub> with a single defect of ET molecule by solving a realistic tight-binding model in real space [4]. It is found that a localized state appears at the Dirac point depending on the defect site in the unit cell. This is understood from the construction of Dirac electrons in this material. Next, spin susceptibility of  $\alpha$ -(ET)<sub>2</sub>I<sub>3</sub> with defects on certain sites (*A* sites) is studied. It is shown that, owning to the modulation of density of states near the Fermi level, the spin susceptibility shows characteristic temperature dependence which deviates from the ideal linear *T* dependence of two-dimensional massless Dirac electron system

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#### Domain Wall in Two-Dimensional Multimode Peierls State

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The domain wall in the multimode Peierls state is studied using the two-dimensional Su-Schrieffer-Heeger model on the square lattice. We consider a half-filled system with a high-spin excitation in which the number of up spins is larger than that of down spins by L, where L is the linear dimension of the two-dimensional system. The additional unpaired spins are localized along the domain wall which is an one-dimensional discommensurate defect of the lattice distortion pattern of the multi-mode Peierls state. This domain wall is topologically stable and seems to be a two-dimensional analog of the spin soliton in polyacetylene. It is found that the electronic bound states localized around the domain wall form an almost flat band in the Peierls gap, converging to zero-energy states in the thermodynamic limit. We have analytically constructed the wave functions of the zero-energy states in the infinite system. The localization length of the edge states of graphene nanoribbons. The wave function is completely localized for  $k = \pi/2$ . The localization length increases as k devi ates from  $\pi/2$ . We will also discuss another type of the domain wall, which separates two distinct patterns of the multimode Peierls states.

# Three dimensional Mott insulator composed of axially substituted iron phthalocyanine

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Axially substituted metal phthalocyanines (M(Pc)L<sub>2</sub>) can enable us to construct various electronic systems due to their tendency to adopt the slipped stack structure. Up to now, we have reported 1-D, 2-D and 3-D Mott insulators based on Co(Pc)(CN)<sub>2</sub>, however, it was difficult to obtain them with Fe(Pc)(CN)<sub>2</sub>, which has magnetic moment of S = 1/2 in the central Fe ion. Recently, we have succeeded in preparing a 3-D Mott insulator based on Fe(Pc)(CN)<sub>2</sub> for the first time. We will report the preparation, crystal structure and electrical properties of it.

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# Thermoelectric transport coefficients for massless Dirac electrons in quantum limit

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Motivated by recent experiments in  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> organic conductor, we performed an analytic calculation of the thermoelectric transport coefficients for the massless Dirac electrons based on the generalized Motts relation. The main focus of our research is made on the quantum limit where the cyclotron energy is much greater than both impurity and thermal broadening of Landau levels (LLs). We report the chemical potential  $\mu$  and magnetic field dependence of the Seebeck and Nernst coefficients. Away from the Dirac point the  $\mu$ -dependence is similar to that found by Jonson and Girvin [Phys. Rev. B **29**, 1939 (1984)], while in the vicinity of Dirac point the absolute value of transport coefficients strongly depends on temperature and impurity scattering. In the quantizing magnetic field dependence of  $\mu$ . In the intermediate magnetic field region we found oscillations of the transport coefficients in the vicinity of the Dirac coefficients is defined by properties of the transport coefficients in the vicinity of the Dirac point. We also included the Zeeman splitting of the LLs in the final formulae and compare the theoretical results with experimental results of the magnetic field dependence of Seebeck and Nernst coefficients

# Dynamics of Spin Soliton in Bond-Charge-Density-Wave States in One-Dimensional Quarter-Filled Electron-Lattice Systems

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The dynamical behaviors of a spin soliton in bond-charge-density-wave (BCDW) backgrounds of nearly quarter-filled electron-lattice systems are studied by numerical technique using the one dimensional Peierls Hubbard model. In order to accelerate the spin soliton, a magnetic field gradient is introduced to the system through a spin-dependent vector potential. The numerical simulation has shown that the dynamics of the spin soliton depends on the applied field strength. For the lower critical filed strength lower than a critical value  $E_c$ , the soliton velocity is saturated to a maximum value even though the field is kept on. The saturation velocity is lower than the sound velocity and is independent of the field strength. In this range of the field strength, the soliton moves with acoustic phonons , which are condensed around the soliton. For the strength higher than the critical value  $E_c$ the soliton is separated from the condensed acoustic phonons and emits shock waves of the other modes of acoustic phonons just like a ultrasonic airplane. Eventually the soliton velocity increases beyond the sound velocity. The present results tell us that the dynamics of acoustic phonon is an important factor to determine the dynamics of the spin soliton just as in the previous work on the dynamics of the charged soliton.

# Thermopower measurements in $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> under hydrostatic pressure

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Understanding 2D conduction remains a wide and deep research topic since the 80's. Recently Dirac carriers physics in graphene have renewed and broadened this topic. But graphene is not the only system to present Dirac carriers, also can be found in the layered organic material  $\alpha$ –(BEDT-TTF)<sub>2</sub>I<sub>2</sub> (aI3) under hydrostatic pressure (P > 1.5 GPa). Here we report thermopower measurements on this material under hydrostatic pressure (P > 2GPa) and low temperatures (T > 4K). In particular a change of sign on the thermopower can be observed at low temperature suggesting the presence of two carrier types of different nature.

# **Pressure-induced Transitions in Single-Component** $\pi - d$ **systems** [M(tmdt)<sub>2</sub>] **Probed by NMR**

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Orbital degrees of freedom are among sources to give novel properties to strongly correlated electron systems. A family of single-component  $\pi - d$  systems,  $[M(tmdt)_2]$ , are multi-orbital correlated electron systems. The molecular orbitals near Fermi level consist of d-orbital in a metallic ion M and  $\pi$ -orbitals in tmdt ligands. The energy-level difference between the d and  $\pi$ -orbitals depends on M, leading to the diverse ground states; a one-dimensional antiferromagnetic Mott insulator ( $T_N = 13$ K) for M = Cu, an antiferromagnetic metal ( $T_N = 110$ K) for M = Au, paramagnetic metals for M = Ni. We performed <sup>1</sup>H- NMR study on M = Cu and Au salts under hydrostatic pressure. In both salts we found that the antiferromagnetic transitions disappeared above 0.4 GPa and the temperature profiles of NMR relaxation rates dramatically changed in the high pressure phase. These results imply sudden changes in electronic states, possibly first-order phase transitions. We argue the pressure-induced transitions in terms of electron correlation and orbital hybridization and propose the possibility of (orbital-selective) Mott transition in M = Cu and Au compounds.

#### First $\kappa$ -type ET salt formed with tetrahedral anion

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We obtained the first  $\kappa$ -type ET salt formed with a tetrahedral anion by an electrocrystallization method. The salt belongs to the orthorhombic system with space group Pnma, which is identical with 10 K-class superconductors,  $\kappa$ -(ET)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Y (Y = Cl and Br). The t'/t value, that gives a simple indication of spin frustration (t', t: transfer integrals between (ET)<sub>2</sub><sup>o+</sup> dimers), was estimated to be 1.42 at 298 K by the band calculation, and therefore, the (ET)<sub>2</sub><sup>o+</sup> dimers form a distorted triangular spin lattice. The salt shows semiconducting behavior with a room-temperature conductivity of 0.5 S cm<sup>-1</sup> and an activation energy of 0.14 eV. By applying hydrostatic pressure, the resistivity and activation energy gradually decreases, but remains semiconducting behavior up to 1.8 GPa. The magnetic susceptibility can be described by the S = 1/2 Heisenberg triangular antiferromagnetic lattice model with the J value in the range of 160 - 180 K, and no long-range magnetic ordering was observed down to the lowest temperature measured (2 K). This result indicates the presence of significant spin frustration, and we can therefore envisage the opening of opportunities for studying the electronic phases adjacent to spin liquid on the t'/t > 1 side.

# Reversible introduction of disorder by manipulating of the cooling/heating ramp rates and its influence on superconductivity of κ-(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> and κ-[D8-, and H8-](BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br

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Regulated ramp rate is a versatile way to introduce neatly controllable level of disorder in some organic superconductors. The prerequisite is a glass-like order-disorder transition connected with ordering of terminal ethylene groups of the organic donor BEDT-TTF (ET) at cooling. Compare with other methods of disorder introduction: X-Ray, neutron, proton irradiation, chemical impurities, etc. regulated ramp rate allow much lover level of scattering centers to be introduced but the advantage is a full reversibility of the process. We prepared several order states ranged from quenched to tempered (last one was prepared by keeping crystals at 70K for 6 hours). That gave rise to changing of  $T_c$  from 11.5K to 12K for [H8-]ET<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br while  $T_c$  of 10.4K for ET<sub>2</sub>Cu(NCS)<sub>2</sub> was mainly unaffected by ramp rate. Quenching of [D8-]ET<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br crystals led to shrinking of superconductive domains embedded into insulating matrix. We mapped disorder level of ethylene groups from 300K down to 90K by X-Ray single crystal crystallography. X-Ray is a relatively slow method, thus, we were able to measure only relaxed (tempered) states. The features found are continuous ordering of ethylene groups at cooling down to 110K in [H8-]ET<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br and then sharp disorder-order transition at 100K. The ordering process in  $ET_2Cu(NCS)_2$  is rather complicated. The continuous ordering is down to 200K, then, behavior of two crystallographically independent BEDT-TTF molecules A and B is separated. Molecule A is completely ordered at 150K whereas ordering in B happens only at 90K. Also, there is an elastic anomaly near 145K in ET<sub>2</sub>Cu(NCS)<sub>2</sub> crystals where lattice volume contraction experience a discontinuous jump.

# Temperature dependence of electronic and magnetic properties of (DOEO)<sub>4</sub>[HgBr<sub>4</sub>] TCE single crystals

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The organic charge-transfer salt  $(DOEO)_4$  [HgBr<sub>4</sub>] TCE was studied using a superconducting quantum interference device (SQUID) and hard X-ray photoelectron spectroscopy (HAXPES, at PETRA III (beamline P09)). The comparison of the resistivity [1], ESR [2] and SQUID measurements shows a similarity in the phase behavior with two critical temperatures T = 120 K and T = 70 K. Based on the experimental results we propose a phase model that consists of 3 phases a small gap semiconductor with energy gaps of  $\Delta_{\parallel}$  = 27.6 meV and  $\Delta_{\perp}$  = 48.6 meV for the in-plane and out-of-plane conductivity (in the temperature range 120 300 K), 2D metal (at T = 70 ... 120 K) and an antiferromagnetic insulator (at T < 70 K). We observe sudden changes in the HAXPES spectra when crossing the transition or crossover temperatures. This reflects changes in the electronic structure. The magnetic susceptibility of the uncompensated spin 1/2 in each DOEO dimer results in Langevin paramagnetism at temperatures > 300 K. At temperatures below the Neel temperature 260 K antiferromagnetic coupling suppresses the magnetic susceptibility. A second susceptibility maximum occurs below the phase transition at 70 K indicating a change of the antiferromagnetic coupling. Below 20 K the susceptibility sharply increases which is explained by uncoupled spins caused by defects. In the whole temperature range antiferromagnetic coupling exists in the system, however the coupling strength is weaker in the AFM insulator regime than in the metallic and semiconducting regime.

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### Surface Local Density of States of an Organic Superconductor

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Materials based on organic charge-transfer salts reveal interesting physical properties due to their electronic correlation effects. Especially the quasi-two dimensional (BEDT-TTF)<sub>2</sub>X salts are showing an interesting phase diagram [1]. We investigate the superconducting phase transition of  $\kappa$  [ET]<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br-crystals using scanning tunneling microscopy (STM) and spectroscopy (STS) from 5 K to T>T<sub>C</sub> under UHV conditions ( $p \leq 5 \cdot 10^{-11}$  mbar). The crystals are grown in a wet chemical process leading to a surface contamination. This is unsuitable for STM and STS measurements due to their sensitivity to the topmost layer of a sample. Therefore we developed a cleaving mechanism for in-situ preparation of clean surfaces. Investigations on these cleaved crystals show an atomically flat surface and an improved signal-to-noise ratio in the measured I(U) and the resultant dI/dU spectra. We report on temperature dependent measurements of the density of states of  $\kappa$ -[ET]<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br up to 15 K revealing a superconducting gap. As predicted by BCS theory [2] the spectra change with increasing temperature and the gap vanishes.

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# Poster Session II

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**10**<sup>th</sup> International Symposium

# Synthesis and structure of a new family of chiral porous molecular layered chiral magnets

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Here we report the synthesis and structures of a new family of chiral porous molecular layered magnets prepared with trivalent and divalent metals ions and di-substituted anilate-type ligands. We show haw the use of  $[M^{III}(L)_3]^{3-}$  precursors with divalent metal ions  $(M^{II})$   $(M^{III} = Cr \text{ and } Fe; L = dianion of the 2,5 dihydroxy-1,4-benzoquinone, <math>C_6O_4H_2^{2-} = dhbq^{2-}$  and its derivatives,  $C_6O_4X_2^{2-} = X_2An^{2-}$ , with X = Cl, Br, I, NO<sub>2</sub>,...;  $M^{II} = Mn$ , Fe, Co,...) allows the preparation of the family of compounds formulated as  $\Delta - [(H_3O)(phz)_3][MnCr(Cl_2An)_3(H_2O)]$  (1),  $[(H_3O)(phz)_3][MnCr(Br_2An)_3] \cdot H_2O \cdot G$  (2) and  $[(H_3O)(phz)_3][MnFe(Br_2An)_3] \cdot H_2O$  (3). In this communication we will present the synthesis and the structural analysis of these novel series whose structure consists in honeycomb hexagonal anionic layers  $[MnM^{III}(X_2An)_3]^-$  alternating with cationic chiral layers of  $\Delta - [(H_3O)(phz)_3]^+$  cations. We will analyse the differences and potentialities of this series of compounds and compare them with the closely related compound  $[NBu_4][MnCr(Cl_2An)_3]$  (4), that presents the same kind of honeycomb hexagonal anionic layer but contains  $[NBu_4]^+$  cations between the anionic layers. Finally, we will present a structural and thermal study that shows the capacity of these compounds to absorb and desorb guest molecules as water and acetone inside the hexagonal cavities (that represent ca. 20 % of the total volume).

# Se-NMR study on $\lambda$ -type BETS based Field Induced Superconductor

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 $\lambda$ -(BETS)<sub>2</sub>FeCl<sub>4</sub> is known as a field induced superconductor [1]. The field induced superconductivity was caused by the so-called "compensation" mechanism as experimentally confirmed by several experimental studies including our <sup>77</sup>Se NMR study [2]. On the other hand, the isostructual Ga salt exhibits a conventional superconductivity at zero magnetic field with similar transition temperature. Ga doping into the Fe site shifts the FISC phase towards the lower field side [3]; the compensation field depends on the Ga concentration. It is not obvious how the exchange field seen by the electrons is reduced with Ga doping. The exchange interaction between conduction spin on the BETS and localized d spin on the "dilute" Fe site was investigated by <sup>77</sup>Se NMR technique on the Fe-Ga alloy system. The angular dependence of the shift on Ga20% system can be well explained by J(lowT) ~ -25 T which shows a good agreement with the transport studies [3].

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### Magnetic field-dependent NMR relaxation in EtMe<sub>3</sub>Sb[Pd(dmit)<sub>2</sub>]<sub>2</sub>

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No onset of magnetic order has been observed to temperatures  $T \ll J$  in the Mott insulator EtMe<sub>3</sub>Sl [Pd(dmit)<sub>2</sub>]<sub>2</sub>, and consequently the ground state is proposed to be spin liquid. Since the observed thermal properties and magnetic susceptibility are what is expected for degenerate fermions, it is proposed that it be characterized by the existence of a spinon Fermi surface. However, the variation of the NMR spin lattice relaxation rate with temperature as  $T \rightarrow 0$  has been interpreted as evidence for a broken symmetry within the spin liquid state. Here, we report measurements of  ${}^{13}C 1/T_1$  ir fields B = 0.6-30T. In the limit of diminishing magnetic field, the features interpreted as a phase transition move systematically and monotonically to lower temperatures. We conclude that there is no evidence for a phase transition in zero field. In comparing the results with that expected for a spinon Fermi surface, we find that the relaxation is much faster. In this sense,  $1/T_1$  is dominated by an anomalous contribution that does not originate with the same excitations as in the thermal transport and specific heat measurements. We discuss further constraints, imposed by the results obtained up to 30T, on interpreting the NMR relaxation at low temperatures.

# Synthesis and structure of a new family of chiral porous molecular layered chiral magnets

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Here we report the synthesis and structures of a new family of chiral porous molecular layered magnets prepared with trivalent and divalent metals ions and di-substituted anilate-type ligands. We show haw the use of  $[M^{III}(L)_3]^{3-}$  precursors with divalent metal ions  $(M^{II})$   $(M^{III} = Cr and Fe; L = dianion of the 2,5 dihydroxy-1,4-benzoquinone, <math>C_6O_4H_2^{2-} = dhbq^{2-}$  and its derivatives,  $C_6O_4X_2^{2-} = X_2An^{2-}$ , with X = Cl, Br, I, NO<sub>2</sub>,...;  $M^{II} = Mn$ , Fe, Co,...) allows the preparation of the family of compounds formulated as  $\Delta - [(H_3O)(phz)_3][MnCr(Cl_2An)_3(H_2O)]$  (1),  $[(H_3O)(phz)_3][MnCr(Br_2An)_3]\cdot H_2O\cdot G$  (2) and  $[(H_3O)(phz)_3][MnFe(Br_2An)_3]\cdot H_2O$  (3). In this communication we will present the synthesis and the structural analysis of these novel series whose structure consists in honeycomb hexagonal anionic layers  $[MnM^{III}(X_2An)_3]^-$  alternating with cationic chiral layers of  $\Delta - [(H_3O)(phz)_3]^+$  cations. We will analyse the differences and potentialities of this series of compounds and compare them with the closely related compound  $[NBu_4][MnCr(Cl_2An)_3]$  (4), that presents the same kind of honeycomb hexagonal anionic layer but contains  $[NBu_4]^+$  cations betweer the anionic layers. Finally, we will present a structural and thermal study that shows the capacity of these compounds to absorb and desorb guest molecules as water and acetone inside the hexagonal cavities (that represent ca. 20 % of the total volume).

# On the coexistance of Spin Density Wave and Superconducting orders in (TMTSF)<sub>2</sub>PF<sub>6</sub>

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We study the organic conductor (TMTSF)<sub>2</sub>PF<sub>6</sub> at pressures where co-existence between Superconducting and Spin Density Wave orders occurs. In this region a peculiar anisotropic superconducting(SC) transition was reported. With increasing pressure SC arose first in domains along the least conducting C-axis. This was attributed to the formation of Soliton Walls perpendicular to the conducting chains. Firstly, We have been able to confirm the anisotropic domain structure with all three axes measured simultaneously in both Resistance and Thermopower measurements. Secondly by searching for and finding several unique signatures - Field Induced Spin Density Waves(FISDW) and Angular Magnetoresistance effects - of the high pressure metal phase in the coexistence regime, we have been able to identify the metallic domains as the high pressure metal and provide evidence for simple phase separation rather than soliton walls. Finally we find an unexpected evolution of the FISDW transitions in the coexistence regime. While for phase separation, the metallic domains should be identical to the high pressure metal, the FISDW transitions in coexistence metal domains have a surprisingly low frequency. We find that this frequency lowering occurs precisely as the sample undergoes the Spin Density Wave instability and phase separates into domains.

# Spin, charge and lattice effects in the low temperature phase of the spin liquid candidate $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>

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The microwave measurements of the in-plane dielectric function confirm that a spin-charge coupling dominate the low temperature electronic properties of the spin-liquid system  $\kappa$ -(ET)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>. Fron these measurements, the strange 6 K feature expresses a short-range AFE transition that is strongly affected by the spin-charge coupling. Although frustration prevents any long-range magnetic order, anomalies of the dielectric function within the QC<sub>M</sub> phase below 6 K are possibly due to short-range in-plane AFM ordering of the spins with a ferromagnetic component or to orbital moments along the perpendicular direction which originates from spontaneous orbital currents. The degree of frustration in these low temperature inhomogeneous phases can either be affected by a magnetic field and/or the amplitude of the microwave electric field. Magnetic fluctuations in the vicinity of 6 K are confirmed by the observation of a softening anomaly on the longitudinal ultrasonic velocity . These dielectric measurements confirm the pertinence of novel theoretical approaches where non-trivial charge degrees of freedom that survive in the dimer Mott insulator must be taken into account to characterize the spin-liquid state of this organic compound.

# Inter-layer transverse magnetoresistance measurement: A probe for the carrier dynamics in some organic conductors

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We demonstrate here the usefulness of the inter-layer transverse magnetoresistance (TMR) to probe the in-plane anisotropic transport properties in quasi two-dimensional layered conductors. With magnetic field applied within the plane, the TMR caused by the Lorentz force depends on in-plane conductivity or mobility along the direction perpendicular to the field. By rotating the field within the plane, the anisotropic conduction of carriers can be observed as anisotropic TMR. This measurement provides information equivalent to that by regulating current direction. According to the semi-classical transport theory, the inter-layer resistance  $R_{\perp}$  under low field of strength *B* and inplane angle  $\phi$  obeys the equation,  $R_{\perp}(B, \phi)^2/R_{\perp}(0)^2 = 1 + \mu_{\phi\pm\frac{\pi}{2}}^2 B^2$ , where  $\mu_{\phi}$  is the mobility for the field direction specified by  $\phi$ . This  $B^2$ -dependence is observed for  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> unde hydrostatic pressures above 1 GPa,  $\beta$ -(BEDT-TTF)<sub>2</sub>X (X = IBr<sub>2</sub>, I<sub>2</sub>Br), and  $\theta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>. The results were analyzed in terms of this relation to afford the  $\phi$ -dependence of  $\mu_{\phi}$ . The  $\kappa$ -salt has almost isotropic mobility. By contrast,  $\mu_{\phi}$  of the  $\beta$ - and  $\theta$ -salts exhibits strong anisotropy, which cannot be explained by the k-dependence of the Fermi velocity. The anisotropy is larger than that expected from the Fermi velocity. This means that the scattering rates of carriers have peculiar k-dependence on the Fermi surface in these systems. The origin of the anisotropic scattering will be discussed.

# **In-plane anisotropy of the flux-flow resistivity in the d-wave** organic superconductor λ-(**BETS**)<sub>2</sub>GaCl<sub>4</sub>

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Recently we observed a clear fourfold-symmetric anisotropy in flux-flow resistivity (FFR) for the *d*-wave organic superconductor  $\kappa$ -(ET)<sub>2</sub>Cu(NCS)<sub>2</sub>. Origin of the fourfold-symmetric anisotropy was discussed in terms of the interplay between the Josephson-vortex dynamics and the superconducting gap structure. Here, we report the in-plane anisotropy of FFR for another *d*-wave organic superconductor  $\lambda$ -(BETS)<sub>2</sub>GaCl<sub>4</sub>. In-plane angular dependence is mainly described by the twofold symmetry and dip structure appears when the magnetic field is applied parallel to the *c*-axis. This result is different from the case of  $\kappa$ -(ET)<sub>2</sub>Cu(NCS)<sub>2</sub> despite the Fermi surface topology of  $\lambda$ -(BETS)<sub>2</sub>GaCl<sub>4</sub> it very similar to that of  $\kappa$ -(ET)<sub>2</sub>Cu(NCS)<sub>2</sub>. The different anisotropic behavior is discussed in terms of the interlayer coupling strength.

# **THz and infrared conductivity of the quantum spin-liquid** compound κ-(**BEDT-TTF**)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>

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From our THz and infrared optical investigations of two  $\kappa$ -phase Mott-insulators with very similar triangular structure but different magnetic ground states, we conclude that only the magnetically ordered organic salt  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl exhibits a well-defined Mott gap at low temperatures. The quantum spin-liquid compound  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> reveals a strong in-gap absorption that becomes stronger as the temperature decreases. This excess conductivity exhibits a power-law behavior  $\sigma^{exc}(\omega) \propto \omega^n$  which extends from 20 cm<sup>-1</sup> all the way up to the mid-infrared [1]. Around 50 K the exponent reveals a change in the temperature dependence. With  $n \approx 0.8$  tr 1.5 the power-law exponent is significantly smaller than predicted by Ng and Lee [2] for spinon contributions to the optical conductivity. Thus we suggest that fluctuations become important in the spin-liquid state and couple to the electrodynamic properties differently compared to the anti-ferromagnetic Mott insulator $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl. Surprisingly the optical properties of the  $\kappa$ -phase salts are rather anisotropic. As the temperature is reduced, around 1 THz a very pronounced absorption feature develops in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> only for  $E \parallel c$  [3]. We discuss the possible origin due to collective excitations.

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# Theory of Mechanism of $\pi$ -d Interaction in Iron-Phthalocyanine

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Recently, it has been reported that one of Phthalocyanine compounds and transition metal, TPP [Fe(Pc)(CN)<sub>2</sub>]<sub>2</sub>, shows large negative magnetoresistance [1]. This compound has a one-dimensional conduction band of 3/4 filling constructed from a lowest unoccupied molecular orbital (LUMO) of Pc, and has local moments of S = 1/2 coming from the d orbitals of Fe. Assuming that the  $\pi$ -c interaction is antiferromagnetic, the origin of negative magnetoresistance was discussed [2]. On the other hand, recently it was claimed that the  $\pi$ -d interaction is ferromagnetic on the basis of quantum chemical calculation [3]. To clarify the sign of exchange interaction, we construct an effective model of this system and study the mechanism of exchange interaction *J* between *d* and  $\pi$  electrons basec on both second order perturbation of transfer integrals between *d* and  $\pi$  orbitals and numerical diagonalization. It is found that there is no hybridization between *d*-orbitals and LUMO of  $\pi$ -orbitals and then super-exchange interaction in the Anderson model does not exist. Instead, processes associated with Hund's rule both on *d* and  $\pi$  orbitals turn out to play important roles [4]. By analyzing an effective model with a magnetic anisotropy due to spin-orbit interactions on the basis of numerical renormalization group and comparing with the experimental result, it is indicated that the sign of .

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### **Dielectric and Optical properties in** $\kappa$ **-type BEDT-TTF salts**

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It is widely known that electric polarization in some kinds of materials is attributed to the charge order without inversion symmetry. This is seen in some transition metal oxides, e.g.  $LuFe_2O_4$ , and charge transfer salts. Quasi 2-dimesional organic salt  $\kappa$ -(ET)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> belongs to this kind of materials. Two ET molecules construct a dimer and are arranged on a triangular lattice. Recently, it is reported that a relaxor-like dielectric anomaly is experimentally observed around 30K. An origin of this anomaly is thought to be a "dimer dipole" generated by a localized hole in one side of the ET molecules in dimers. Motivated by this result, we study dielectric and optical properties in  $\kappa$ -type ET salts where the internal charge degree of freedom in a dimer exists. We adopt various models, extended Hubbard model, V-t model and these low-energy effective models for analysis without ambiguity. We analyze these models by utilizing mean-field approximation, Monte Carlo method, exact diagonalization method and spin wave approximation, and focus on the dielectric and optical responses due to the "dimer dipoles". In finite temperature, dimer-Mott (DM) and ferroelectric charge ordered (FCO) phases compete with each other. We investigate the temperature dependence of dielectric susceptibility, and find the anomaly with broad peak structure around the boundary of DM and FCO phases. Also, we find the low-energy intra-dimer charge excitations which show a strong light polarization dependence. The charge excitation mode which is observable by light being parallel to the electric polarization shows remarkable softening and frequency dispersion near the phase boundary, and is expected to be a collective charge excitation.
# Highly Conducting Organic Radical-Cation Salt (BTBT)<sub>2</sub>PF<sub>6</sub> Based on a Weak Electron Donor

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It has been believed for a long time that high-conducting and stable CT salts are realized by using strong electron donors such as tetrathiafulvalene (TTF) and 7,7,8,8-tetracyano-p-quinodimethane (TCNQ). Several CT salts show extremely high conductivity over 1000 S/cm at room temperature, and in particular, such CT salts are achieved by selenium- and tellurium-containing donors with enhanced intermolecular interaction. BTBT ([1]Benzothieno[3,2-*b*][1]benzothiophene) is a molecule which shows high performance in organic transistors. BTBT contains only two sulfur atoms, and the ionization potential is as large as 5.65 eV; BTBT is a considerably weaker donor than the conventional electron donors such as TTF derivatives. Nonetheless, the CT salt, (BTBT)  $_2PF_6$ , is stable enough and shows very high conductivity of 1500 S/cm even at room temperature. The crystal structure belongs to a highly symmetrical tetragonal group. The BTBT columns are arranged in a windmill manner, where the BTBT molecules are oriented alternately with a uniform transfer integral. This constructs a one-dimensional band with the bandwidth of 0.35 eV. This salt exhibits a resistivity jump around 150 K and an insulating state below 60 K. The ESR shows highly asymmetrical Dysonian at room temperature, and the spin susceptibility remains paramagnetic down to low temperatures.

#### **Mott-Anderson transition in the** $\kappa$ –(**BEDT-TTF**)<sub>2</sub>X system

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The Mott-Anderson transition has been known as a metal-insulator transition due to both strong electron-electron interactions and randomness for the electrons. We demonstrated recently the randomness effect of the strongly correlated electrons in the BEDT-TTF molecule based organic conductors [1]. X-ray irradiation on the crystals introduces molecular defects in the insulating anion layer, which cause random potential modulation to the correlated electrons in the conductive BEDT-TTF layer. Both of the antiferromagnetic Mott insulator  $\kappa$ –(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl and metal/superconductor  $\kappa$ –(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br become Anderson-type localization insulator by x-ray irradiation. We report further studies on the competition and/or cooperation of the Mott and Anderson transitions close to the Mott critical point for understanding the critical behavior of the electrons. Partial substitution by deuterated BEDT-TTF in  $\kappa$ –(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br can change the bandwidth and then the electron correlations from the metal/superconductor to Mott insulator. We demonstrate that the randomness effect becomes significant at the vicinity of the Mott transition as expected from the theoretical studies.

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# Electronic state of the spin liquid system EtMe<sub>3</sub>Sb[Pd(dmit)<sub>2</sub>]<sub>2</sub> under hydrostatic pressure

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Recently  $\beta'$ -[Pd(dmit)<sub>2</sub>]<sub>2</sub> systems have attracted great interest because of their various ground states which arise from the difference of the spin frustration ratio. Among them, a Mott insulator EtMe Sb[Pd(dmit)<sub>2</sub>]<sub>2</sub> is known as a spin liquid system and a metallic state is induced by high hydrostatic pressures. To investigate the metal-insulator transition and quantum criticality, we have performed the magnetoresistance measurements of EtMe<sub>3</sub>Sb[Pd(dmit)<sub>2</sub>]<sub>2</sub> under hydrostatic pressures down to 30 mK. At 1.0 GPa, we find that the temperature dependence of the interlayer resistivity shows S shape behavior, a broad hump and minimum at around 250 K and to 30 K, respectively. No sign of superconductivity is obtained down to 30 mK. The magnetoresistance is positive up to 18 T, which amounts to only 2 %. These results suggest non Fermi liquid behavior. We also discuss the pressure dependence of the non-Fermi liquid behavior and magnetoresistance.

# Crystal structure and physical properties of a supramolecular rotator in (m-fluoroanilinium+)(dicyclohexano[18]crown-6)[MnIICrIII(oxalate)3]-

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We already reported a ferroelectric salt, (m-fluoroanilinium+)(dibenzo[18] crown-6)[Ni(dmit)2-] with the transition temperature of 346 K, whose ferroelectricity arised from inversion of the dipole moments thorugh the flip-flop of the aryl moiety in the supramolecular rotator structure. In order to develop a new synthetic strategy for developing molecular multiferroics utilizing the molecular motions, we designed a crystal consisted of supramolecular cation of (m-fluoroanilinium+)(DCH[18] crown-6) (DCH[18] crown-6 = dicyclohexano[18]crown-6) sandwiched by ferromagnetic layers of [MnIICrIII (oxalate)3]-. The crystal, (m-fluoroanilinium+)(DCH[18] crown-6)[MnIICrIII(oxalate)3]- (1) had orthorhombic crystal system and the space group of P212121. In the crystal, each [MnIICrIII (oxalate)3]- layer formed two dimensional honeycomb structure, exhibiting a ferromagnetic transition at 5.5 K. Between the anionic layers, two kind of crystallographically independent supramolecular cations of (m-fluoroanilinium+)(DCH[18]crown-6) were located, each of which formed columner structures. The SHG (Second Harmonic Generation) measurement revealed that the crystal had at least three phases. At 285 K, the crystal became SHG active by increasing temperature, which may be related to change in dielectric properties. Details of the relationship between magnetic and dielectric properties in connection with molecular rotation will be discussed.

# Effect of long-range electronic correlation upon excitonic states in finite nondegerate one-dimensional organic $\pi$ -electron systems

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In this work, we have studied electron-hole pair excitation by doping both electron and hole into a finite one-dimensional organic  $\pi$ -electron system which has non degenerate ground state and effect of long-range electronic correlation upon the pairs in an applied electrical field by using the extended Hubbard model with long-rang electronic correlation Hamiltonian. We mainly discuss exciton situation and effect of the electronic correlation on them in different applied electron field and we find some interesting physical phenomena.

# Terahertz time domain spectroscopy of field-induced ferroelectricity in $\beta'$ -(ET)<sub>2</sub>ICl<sub>2</sub>

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Layered triangular organic dimer Mott insulator  $\beta'$ -(ET)<sub>2</sub>ICl<sub>2</sub> was shown to exhibit a relaxor-like dielectric anomaly below 100 K with strong dispersion relation, and pyroelectric current below 60 K, suggesting the intra-dimer fluctuated charge disproportionation[1]. We performed steady state and field induced terahertz (THz) time domain spectroscopy in  $\beta'$ -(ET)<sub>2</sub>ICl<sub>2</sub>. Spectral features of optical conductivity depending on temperature and polarization of THz light are analogous to those for  $\kappa$ (ET)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> [2], i.e. i) spectral weight of the 32 cm<sup>-1</sup> band markedly grows at the temperature lower than 100K exhibiting dielectric anomaly, ii) the 32 cm<sup>-1</sup> band is detected only for the polarization parallel to the electric polarization theoretically predicted [3]. Therefore, the broad peak around 32 cm<sup>-1</sup> is attributable to collective excitation of the intra-dimer fluctuated charges. Furthermore, external electric field(>3 kV/cm) induces the spectral change in THz region reflecting the reduction of the effective temperature of the charges, that demonstrates the field-induced ferroelectricity in  $\beta'$ -(ET)<sub>2</sub>ICl<sub>2</sub> [1].

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## Charge dynamics revealed by Raman scattering measurements under electric field in $\beta'$ -(B EDT-TTF)<sub>2</sub>ICl<sub>2</sub>

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A dimer Mott insulator,  $\beta' - (BEDT-TTF)_2ICl_2$ , shows relaxor-like dielectric behaviors and pyroelectric properties [1]. In order to clarify the charge dynamics under electric field for this compound, we performed Raman scattering measurements under electric field. At zero field, we observed no clear splitting of the Raman mode  $\nu_2$ , which is known to be a charge-sensitive mode, between 300 K and 15 K. This result is consistent with the fact that this compound is a dimer-Mott insulator. At 15 K, by applying DC electric field (5kV/cm) along the stacking axis, we observed two clear side peaks of the Raman mode  $\nu_2$ . One appears at the higher wavenumber side of the original peak, and the other appears at the lower wavenumber side. This strongly indicates that a part of charge transfers from one BEDT-TTF molecule to the other in a dimer. Thus, we achieved charge disproportionation in  $\beta' - (BEDT-TTF)_2ICl_2$  by the application of electric field.

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# Electronic structure calculations of the magnetic exchange in NIT-2Py: Organic radicals for a new quantum magnet

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We present electronic structure calculations for the new organic magnet which is part of the nitronyl nitroxide family of radicals. NIT-2Py exhibits a complex magnetic phase diagram at low temperatures and high magnetic fields. Susceptibility measurements at high temperatures show the paramagnetism of a free spin 1/2 with antiferromagnetic interactions. We saw the onset of bulk magnetic order at 1.3 K, as determined from specific heat Cp measurements. This anomaly in Cp is suppressed by magnetic fields above 3 T. In this field range, the sharp peak in Cp is replaced by a Schottky anomaly pointing to collective switching of all magnetic moments between two distinct levels. At even higher fields of 5 T, we observed a second sharp anomaly indicating a second magnetic phase. Magnetisation curves measured below the ordering temperature show magnetization plateau at half of the saturation value of 1  $\mu_B$ /molecule. In combination with the specific heat results, this behaviour suggests a new quantum spin ground state in NIT-2Py. As previously observed for other nitronyl nitroxide radicals, electronic structure calculations for an isolated NIT-2Py molecule show a spin polarization density located on the O-N branch of the molecule. We have extended these calculations to the NIT-2Py crystal in order to calculate the magnetic exchange, which will enable us formulate a model Hamiltonian for our system.

## Anisotropic exchange coupling of Cu-tetraazaporphyrin thin film to a magnetite surface

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The Heisenberg exchange coupling is one of the most popular models for the description of the magnetic coupling on a quantum-mechanical basis. This model plays an important role in the understanding of many effects which can be further applied to a number of different applications such as memory storage on the molecular level [1], quantum computers and in the field of spintronic devices. The research presented here is focused on the investigation of a  $Cu_4Dinit$  monolayer on Fe<sub>3</sub>O<sub>4</sub>(100) by X-ray magnetic circular dichroism (XMCD) at 20K and applied magnetic field of up to 4.5 T. The monolayer was prepared in ultrahigh vacuum and carefully transported to the measuring endstation at the ANKA in Karlsruhe, Germany. XMCD measurements under different angles of the field shows that the exchange coupling is ferromagnetic for magnetization direction perpendicular to the surface and antiferromagnetic for in-plane magnetization direction as sketched in Fig. 1. The anisotropy of the Heisenberg exchange coupling is attributed to an orbitally-dependent exchange Hamiltonian. A tentative model for the observed change of sign of the exchange coupling is that it results from the competition between ferromagnetic superexchange along Fe-N-Cu and antiferromagnetic superexchange along Fe-O-Cu with strength modified by strong spin-orbit coupling [2]. The observation is important for other organic materials with unsaturated spins in contact with a ferromagnetic surface.



Figure 1 Sketch of the anisotropic exchange coupling of the Cu spin in  $Cu_4Dinit$  molecule to the octahedral Fe spin in the  $Fe_3O_4(100)$  surface).

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### **The magnetic structure in antiferromagnetic state of frustrated spin** systems, β'-Et<sub>2</sub>Me<sub>2</sub>P[Pd(dmit)<sub>2</sub>]<sub>2</sub> and β'-Me<sub>4</sub>P[Pd(dmit)<sub>2</sub>]<sub>2</sub>

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 $\beta'$ -D[Pd(dmit)<sub>2</sub>]<sub>2</sub> (D = Me<sub>4</sub>P, Et<sub>2</sub>Me<sub>2</sub>P, etc. ) salts are known as two dimensional (2D) Mott insulators in which a 1/2-spin localizes on each Pd(dmit)<sub>2</sub> dimer. These salts are considered to be a frustrated spin system due to quasi-triangular dimer arrangement in the 2D layer. At ambient pressure, Me<sub>4</sub>] and Et<sub>2</sub>Me<sub>2</sub>P salts show antiferromagnetic (AF) ordering below 35K and 15K, respectively. The lager anisotropy of the triangle in the Me<sub>4</sub>P salt is considered to reduce the frustration leading to the higher ordering temperature than in the Et<sub>2</sub>Me<sub>2</sub>P salt. In order to clarify the magnetic structures of these salts and to figure out the effect of frustration systematically, we measured and analyzed the angular dependence of 13C-NMR spectra in the AF states. The external field of 7.0 8.3T, much larger than the spin-flop field of ~1.0T was rotated in the crystallographic *ac*- and *bc*\*-plane. The results were compared with the calculated angular dependence of peak positions. We found the results for Et<sub>2</sub>Me<sub>2</sub>P salt are very well explained with the localized moment of 0.08 B/dimer, assuming that the easy and the hard axes are *c*\* and *b*-axis, respectively. We believe that the extremely small value of the observed moment in the AF state should reflect the strong frustrations in this salt. The same measurements on the Me<sub>4</sub>P salt with less frustration are now going on. We will compare these two salts and reveal how the frustration may reduce the localized moment in the AF ordered state.

#### **Spin-Orbit Effects in Organic Radicals**

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In the investigation of magnetic properties of non-metal based organic materials, a common prejudice is to ignore spin-orbit (SO) effects entirely. While this practice is justified for molecules containing the lightest (2p) elements, it is unjustified for those containing heavier sulfur (3p) and selenium (4p) atoms. Recently, the synthesis of four isostructural radicals with different S/Se content has given us a direct handle for investigation these SO interactions. Two of these variants order ferromagnetically with high ordering temperatures (12.5K and 17K), and large magnetic anisotropy resulting in large coercive fields (290 Oe and 1250 Oe). The other two variants order as spin-canted antiferromagnets, likely as the result of Dzyaloshinskii-Moriya terms. In this presentation, I will discuss the results of electron magnetic resonance in the ordered phases of these materials. The data is interpreted in the context of strong anisotropic exchange interactions between radical sites, which explain correctly both the symmetry and magnitude of the observed effects. These results have implications for other organic materials, where interpretation of various results may be fundamentally altered by consideration of SO effects.

## Rotational Dynamics and Dielectric Responses of Dibromoiodomesitylene Crystal

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Rotational disorders of hexa-substituted benzene derivatives have been reported in crystalline state. When the molecular rotations in the solid sate are coupled with the changes in dipole moments, the ferroelectric and/or antiferroelectric properties can be observed. Herein, we noticed dibromoiodomesitylene (DBIM) and tribromomesitylene (TBM) crystals. The molecular rotation of DBIM along the direction normal to the benzene plane resulted in the change of dipole moment, whereas that of TBM did not change the dipole moment. The crystal structures, phase transition, and dielectric properties of these two crystals were examined from the viewpoint of dynamic behaviors within the crystals. The preparations of DBIM and TBM molecules were followed by the literatures, and the DBIM single crystals were obtained by vacuum sublimation technique. The DSC chart of DBIM crystals showed the irreversible phase transition at 380 K from the metastable to stable crystal form, accompanying the reversible order-disorder phase transition at 350 K. The X-ray crystal structural analysis of DBIM at 100 K revealed the  $\pi$ -stacking structure along the a-axis with the orientational disorder of bromo- and iodo-substituent. The measurement of temperature- and frequency-dependent dielectric constants with the pellet of DBIM showed the dielectric responses at the corresponding temperatures to that of DSC. Since the dielectric responses at low-frequency (f =1 kHz) was larger than those of high-frequency measurement (f = 1 MHz), slow molecular rotations were associated with the dielectric response

# Revisiting electronic structures of organic ferroelectrics TTF-CA and TTF-BA with maximally-localized Wannier orbitals

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Tetrathiafulvalenep-chloranil (TTFCA) and tetrathiafulvalenep-bromanil (TTFBA) are well known organic ferroelectrics. Their crystal structures consist of mixed stack columns of donors (TTF) and acceptors (CA/BA) [1,2]. Although there is a certain degree of similarity between two materials, the appearance of spontaneous polarization is quite different [3,4]. We performed first-principles electronic-structure calculations for these materials [5,6]. The electronic structures of TTF-CA and TTF-BA, which give reasonable spontaneous polarization values compared with the experimental results, are significantly different from each other. In the present study, we revisit the electronic structures of TTF-CA and TTF-BA by means of analyses using maximally-localized Wannier orbitals. The difference in the electronic structure between the paraelectric and ferroelectric phases for each material is straightforwardly represented. For example, dimerization is obvious from the shapes of Wannier orbitals.

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#### Carbon nanotubes on spider silk scaffold

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In the last few decades, extensive research has been done in the fields of carbon nanotubes (CNT) and spider silk (SS). CNTs have found their applications in energy harvesting, energy storage, sensor, field-effect, and other electronic devices. In another perspective, SS has been shown to be an excellent scaffold for adding functions due to its toughness, bio-compatibility, and bio-degradability. There are, however, very few attempts to link the developments in these two fields to generate novel functional materials. Here we report a strong affinity of amine functionalized multiwall carbon nanotubes (f-CNTs) for SS fibers coated by a water and shear assisted method. The coating is performed at room temperatures without using any f-CNT cross-linkers. The physical and chemical interactions at the frontier interface are studied by SEM, TEM, Raman, and Fast-Fourier Transform Infrared (FTIR) spectroscopy, revealing the uniformity of the annular f-CNT coating and formations of ionic and hydrogen bonding between the f-CNT amine and SS carboxylic acids. The f-CNT coated SS fibers are 400% tougher than that of a neat fiber, custom-shapeable, flexible, and electrically conducting. The conductivity is reversibly sensitive against strain and humidity, leading to proof-of-concept sensor and actuator demonstrations. The work is supported in part by NSF-DMR 1005293, and performed at the National High Magnetic Field Laboratory, supported by the NSF, DOE, and the State of Florida.

## Photoconduction Mechanism in Covalent Organic Framework (COF) Materials by using Time-Resolved ESR Spectroscopy

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Covalent organic framework (COF) materials are porus crystalline materials. They attracted much attention because of their functionalities. Recently, a variety of COF materials based on the Donor-Acceptor (D-A) system have been developed. Jiang and coworkers synthesized a variety of D-A type COFs such as NDI-ZnPc, PyDI-ZnPC and ZnPc-NDI-HHTP. While molecules are connected by tight covalent bonds within the two-dimensional layers, the molecules stack to form one-dimensional columns perpendicular to the planes. They show pronounced photo-conducting behavior. The possible photo-conduction origin is the electron transfer between donor and acceptor. However, the detail mechanism is an open question. We performed time-resolved photo-excited ESR spectroscopy for a series of D-A type COF materials to investigate the photo-conduction mechanism. After photo-excitation to D-A type COFs, an ESR signal originated from the charge-separated state was observed, which could not be observed in isolated molecules. As for ZnPc-NDI-COF, we can observe the charge-separated ESR signal even at R.T., indicating long lifetime of the photo-excited carriers. Actually, the lifetime of the photo-excited charge-separated states in ZnPc-NDI-COF are estimated as 865  $\mu$ s at 80K and 1.8  $\mu$ s at 280K. In this paper, we discuss the photoconduction mechanism of the D-A type COF materials.

# Photo-induced enhancement of superconductivity in κ-(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br laminated on a photochromic self-assembled monolayer

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Manipulating the electronic phase of condensed mater by external stimuli is a key topic in the field of modern electronics. Strongly-correlated materials are good candidates for phase transition devices. Recently, we have demonstrated a field-induced superconductivity in a thin-single crystal of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br ( $\kappa$ -Br). This is the first observation of field-induced superconductivity in an organic field-effect transistor. Optical stimuli are also of considerable importance because they present many possibilities for realizing future optical memory or switching devices. In this study, we fabricated novel devices by laminating a thin single crystal of  $\kappa$ -Br on SrTiO<sub>3</sub> substrates coated by self-assembled monolayer of spyropiran-derivatives (SP-SAM). Superconducting properties of the devices were monitored by four-probe resistivity and SQUID measurements. Because of the weak tensile strain effect from STO substrate, the initial resistances for the devices showed the partially superconducting phase. The superconducting fraction of the devices clearly increased after UV irradiation, and recovered to near the initial value by visible light irradiation. These photoinduced effects remained even after the irradiation was stopped. Spyropirans can switch between a neutral form and a open form triggered by light-irradiation with different wavelengths, resulting a significant change in the electric dipole moment. Reversible changes in dipole moment of SP-SAM triggered by lights produced two distinct electric fields between the  $\kappa$ -Br and the substrates. Finally, photo-induced-carrier doping effects like field-effects were induced and superconductivity could be switched by photo-irradiation.

# Electronic structure analysis of a single phthalocyanine molecule adsorbed on a gold surface

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Single-molecule devices have attracted much attention since they are expected to exhibit a variety of interesting electronic features. As a prime example, it has been argued that the Kondo effect can be controlled by using the STM technique in a single cobalt phthalocyanine molecule adsorbed on a Au(111) surface [Zhao et al., Science 309, 1542 (2005)]. For the theoretical description of the electronic states, the DFT-based ab initio calculations have been performed so far. However, such methodology has not succeeded in reproducing the Kondo effect due to the improper treatment of the correlation effects. In the present study, we develop a new theoretical approach by combining ab initio calculations and the numerical renormalization-group method. The local information of the single molecule, such as low-energy spectroscopy within the molecule is analyzed by using wavefunction-based ab initio calculations, while the coupling to the substrate is analyzed by the numerical renormalization-group method. Our theoretical scheme can successfully reproduce the Kondo effect in this single-molecule device by examining the local density of states.

# Revealing the mechanism of the photoinduced phase transition in a molecular solid, (EDO-TTF)<sub>2</sub>PF<sub>6</sub>, using a density-functional theory method

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A quasi-one-dimensional molecular solid, (EDO-TTF)<sub>2</sub>PF<sub>6</sub>, exhibits a photoinduced phase transition (PIPT), which is categorized as a transition from an insulating state with (0110) type charge ordering to a metallic state with the charge order being melted. In order to solve the difficulty in treating this type of phenomena based on a first-principles method and understand the mechanism of the PIPT, we propose a new theoretical framework using the combination of a density-functional method and a it self-consistent environment [1]. Only one or three tetramers of EDO-TTF molecules are calculated quantum mechanically, while other surrounding molecules are treated as a collection of point charges that affect the central ones via Coulombic interaction and/or van der Waals interaction. The point charges in the environment are determined iteratively so as to be self-consistent with the valencies of their corresponding atoms in the quantum region. Using this framework, we succeeded in preparing a stable molecular cluster that reproduces the following key aspects in the insulating state: (1) molecular valencies, (2) absorption spectrum, and (3) vibrational spectra [2].

After finishing such preparation, we proceeded to the investigation of photorelaxation and found a particular relaxational path starting from the second charge-transfer excitation (CT2) [2]. This path is basically characterized by an increase in the distance between the two central EDO-TTF molecules in the photoexcited tetramer, and is hence regarded as the very beginning of the observed PIPT

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# Doped polyacene derivatives: Theoretical prediction of intramolecular charge disproportionation.

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Oligoacenes and phenacenes are polycyclic aromatic hydrocarbons consisting of fused benzene rings juxtaposed in a linear or armchair arrangement, respectively. These long-known compounds have attracted renewed wide interest due to their recently discovered superconducting state, driven by alkali or alkaline earth-metals intercalation, reported by Kubozono group: doping in picene, phenanthrene and dibenzopentacene stabilizes a superconducting state with critical temperature up to 33 K. Here we present a detailed quantum chemical investigation of the phenacenes and dibenzoacenes series in their neutral and doped (-3 electrons) electronic configurations using unrestricted DFT methods. It turns out that, contrary to phenacenes, dibenzoacenes having  $C_{2h}$  symmetry develop an electronic instability in their doped electronic configurations: the ground state is likely to become the state with considerable intramolecular charge-disproportionation resulting from transfer of one electron-phonon coupling, which modulates the electronic charge transfer along the acenes molecular axis, as can be inferred by the huge infrared intensities of the most coupled antisymmetric molecular vibrations. The relevance of these findings for superconductivity and ferroelectric properties will be shortly discussed.

#### **Design and preparation of spin frustrated C**<sub>60</sub> salts

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A two-dimensional (2D) hexagonal packing of  $C_{60}^{\bullet-}$  was achieved in the charge-transfer crystal of (TPC)(MDABCO<sup>+</sup>)( $C_{60}^{\bullet-}$ ) according to the pattern of the polycationic supramolecular template of (TPC)(MDABCO<sup>+</sup>), where MDABCO<sup>+</sup> and TPC are N-methyldiazabicyclooctane cation and triptycene molecules, respectively, both having threefold symmetry. The compound had uniform closely packed hexagonal layers of two types (with ordered and disordered  $C_{60}^{\bullet-}$ ) coexist. The ordered  $C_{60}^{\bullet-}$  layers showed 2D metallic conductivity, whereas the antiferromagnetic interaction was observed in nonmetallic disordered  $C_{60}^{\bullet-}$  layers above 200 K. The disordered layers became metallic below 200 K through the ordering of  $C_{60}^{\bullet-}$ . (TPC)(MQ<sup>+</sup>)( $C_{60}^{\bullet-}$ ) also had a 2D hexagonal packing of  $C_{60}^{\bullet-}$  and showed a little longer interfullerene distances (10.12 - 10.18 Å) than that in (TPC)(MDABCO<sup>+</sup>)( $C_{60}^{\bullet-}$ ) (10.07 Å), where MQ<sup>+</sup> is N-methylquinoclidinium cation having threefold symmetry. Magnetic susceptibility of (TPC)(MQ<sup>+</sup>)( $C_{60}^{\bullet-}$ ) was described by the Curie-Weiss law in the 30 - 300 K range with negative Weiss temperature of -21.5 K and no magnetic ordering was observed down to 1.9 K owing to a strong topological spin frustration based on the triangular spin lattice. The molecular design of monomer-type Mott insulator with  $C_{60}^{\bullet-}$  hexagonal packing is discussed.

#### Possible Massless Dirac Electron in Molecular Two-Orbital Model

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Possible massless Dirac electron is found in a simple molecular two-orbital model for quasi-one or two dimensional molecular conductor. This model consists of two  $\pi$ -orbitals with opposite symmetry (bonding and anti-bonding) on a molecule in a unit cell. Using symmetry of  $\pi$ -orbitals, massless Dirac electron can be provided by crossing points of two lines where coefficients for  $\sigma_y$  or  $\sigma_z$  com ponents vanish in the momentum space. Small perturbation on  $\sigma_x$  component gives energy gap and the Berry curvature exhibits a peak structure at the Dirac point. Within a simplest model, varying anisotropy on the intra- and inter chain hoppings drives emergence of one or two pairs of Dirac electron, which can be called as accidental emergence is found, where two pairs of Dirac electrons emerge at incommensurate momentum.

# First-Principles Study of the Structural and Electronic Properties of $\kappa$ -H<sub>3</sub>(Cat-EDT-TTF)2 and $\kappa$ -H<sub>3</sub>(Cat-EDT-ST)<sub>2</sub>

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We theoretically study a new class of molecular conductors with hydrogen bonding that have been synthesized recently, by means of first-principles band calculations. The materials are based on catechol with ethylenedithiote-tetrathiafulvalene (H<sub>2</sub>Cat-EDT-TTF) and its diselena analogue (H<sub>2</sub>Cat EDT-TTF); in their crystal structures, two H<sub>2</sub>Cat-EDT-TTF molecules share a hydrogen atom per formula unit. The compounds do not have an insulating layer, which is different from conventional cation radical salts.  $\kappa$ -type H<sub>3</sub>(Cat-EDT-TTF)<sub>2</sub>( $\kappa$ -S) is a Mott insulator at ambient pressure and emerges as a candidate for a quantum spin liquid. Under applied pressure, it shows a structural phase transition where an enhancement of the electric resistivity is observed, and then turns to be metallic at 6 GPa. On the other hand, its diselena analogue,  $\kappa$ -H3(Cat-EDT-ST)2 ( $\kappa$ -Se) become metallic under applied pressure of 2.2 GPa. In this study, the structural properties and electronic structures are investigated by first-principles calculations based on the density functional theory (DFT). We discuss that an anisotropic triangular lattice describes the systems at ambient pressure; inter-dimer transfer integrals including non-negligible inter-layer values are obtained by performing tight-binding fitting to DFT band structures. By performing structural relaxation under pressure, the differences of the electronic structure between  $\kappa$ -S and  $\kappa$ -Se are discussed. We also report adiabatic potential energy surface for the shared H in the crystals.

# Intramolecular Orbital Excitations and Frequency Modulation of Molecular Vibrations during Photoinduced Charge-Order Melting

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Photoinduced phase transitions in the quasi-two-dimensional metal complex  $Et_2Me_2Sb[Pd(dmit)_2]_{.}$  is theoretically studied. It has a charge order below 70 K due to the presence of plural molecular orbitals near the Fermi level and strong electron-phonon interaction, meanwhile it shows a dimer-Mott phase above this temperature. T. Ishikawa *et al.* have found a phase transition triggered by intradimer photoexcitations in the charge-ordered phase and accompanied by charge-order melting. Photoinduced changes in the electronic state and the crystal structure are theoretically studied in a two-dimensional extended Peierls-Hubbard model. With the inclusion of intramolecular orbital excitations, we can calculate the alteration from moment to moment of intramolecular C=C (infrared or Raman active) vibration frequencies that are sensitive to molecular charge. Their time evolutions do not follow the adiabatic picture after strong photoexcitations. The comparison of numerical behaviors with experimentally observed behaviors will allow the analysis of energy transfer pathways in the future. We suggest the possibility of a novel electronic phase that is reached only after strong photoexcitation, which dynamically localizes electrons and partially pumps them up onto high-energy molecular orbitals.

# Properties of Quasi-One-Dimensional Organic Superconductors Close to their Anomalous Upper Critical Field

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The properties of the normal state of quasi-one-dimensional superconductors like Bechgaard salts (TMTSF)<sub>2</sub>X is reinvestigated in the vicinity of a spin density-wave (SDW) instability under an applied Zeeman magnetic field in the ab plane. We use weak coupling renormalization group (RG) method taking into account both normal and UmKlapp scattering processes. By increasing the magnetic field, we find a crossover from the d-wave superconducting to FFLO instability lines in the superconducting (SC) part of the  $T - t'_{\perp}$  (anti-nesting) phase diagram, as recently proposed for the anomalous pairing state for the organic Bechgaard salt series under magnetic field. The enhancement of SDW susceptibility precursor to the superconducting transition is also found to follow a Curie-Weiss law in temperature with the Curie-Weiss scale  $\Theta$  that increases with the  $t'_{\perp}$  or pressure Moreover, the H - T phase diagram for different  $t'_{\perp}$  determined by the singularity in SC susceptibilities confirms the low temperature anomalous enhancement of the upper critical field due to the d-wave FFLO fluctuations [1]. The temperature dependence of specific behaviour is also examined by considering the one-loop RG corrections to the free energy density. We explore the possibility of low T enhancement of the electronic specific heat due to the contribution from the interference of FFLO fluctuations with SDW correlations. The results are also compared with the experi- mental data [2, 3].

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#### Importance of subleading corrections for the Mott critical point

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The interaction-induced metal-insulator transition should be in the Ising universality class. Experiments on layered organic superconductors suggest instead that the observed critical endpoint of the first-order Mott transition in d = 2 does not belong to any of the known universality classes for thermal phase transitions. In particular, it is found that  $\delta = 2$ . Given the quantum nature of the two phases involved in the transition, we use dynamical mean-field theory and a cluster generalization to investigate whether the new exponents could arise as transient quantum behavior preceding the asymptotic critical behavior. In the cluster calculation, a canonical transformation that minimizes the sign problem in continuous-time quantum Monte Carlo calculations allows previously unattainable precision. Our results show that there are important subleading corrections in the mean-field regime that can lead to an *apparent* exponent  $\delta = 2$ . Experiments on optical lattices could verify our predictions for double occupancy.

# Crystal Structures and Solid State Optical Properties of 2,5-Di(1,3-dithiol-2-ylidene)-1,3-dithiolane-4-thione Derivatives

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Constructing of near-infrared (NIR) absorption system in the solid state is an attractive research issue because of their application in various fields such as NIR absorbing compounds in organic photovoltaic cells and NIR light emitting diodes. Common strategies to achieve red shift of the absorption maxima of organic compounds are the extension of  $\pi$ -conjugated system and the introduction of donor acceptor groups into the system. In some cases the chemical stability decreases with increasing extension of  $\pi$ -conjugation. Recently we found that solid state of a 2,5-di(1,3-dithiol-2-ylidene)-1,3-dithiolane-4-thione derivative exhibited a broad absorption spectrum which covered the whole visible and NIR regions, far beyond 1500 nm. In the crystal these derivatives are stacked one-dimensional to form columnar structure. In the column one molecule is rotated relative to the other by 40° about their longer molecular axis. 2,5-Di(1,3-dithiol-2-ylidene)-1,3-dithiolane-4-thione is a dark blue  $\pi$ -donor molecule. Most of the derivatives both in solution and in solid states exhibit absorption peaks at about 450 and 600 nm, and no absorption in NIR region. Hence the absorption of NIR region is accomplished by the intermolecular interaction in the solid state. Here we present the synthesis and solid state physical properties of the NIR absorbing derivative with others.

# A New Single-component Magnetic Molecular Conductor, [Fe<sub>2</sub>(dmdt)<sub>4</sub>] (dmdt = dimethyltetrathiafulvalenedithiolate)

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The magnetic single-component molecular conductors are expected to exhibit strong -d interactions. The twisted [Cu(dmdt)2] (dmdt = dimethyltetrathiafulvalenedithiolate) molecule with distorted D2 symmetry showed weakly metallic behavior around room temperature (110 S/cm) and a coupled electric and antiferromagnetic phase transition near 95 K. The three-dimensionally arranged spin 1/2 moments embedded in the sea of conduction electrons of [Cu(dmdt)2] cannot be realized in the D2X-type traditional molecular conductors. Recently, considerable interests have been attracted to the systems consisting of the iron arsenide superconductors, we succeed in the synthesis of a new single-component molecular iron complex, [Fe2(dmdt)4] with an dimeric structure. The electrical resistivity of [Fe2(dmdt)4] was measured on a compressed pellet sample with a four-probe technique in the temperature range 140-300 K. Neutral complex [Fe2(dmdt)4] showed a rather low room-temperature conductivity of 0.01 S/cm and a semiconducting behavior with the activation energy of 0.136 eV. Static magnetic susceptibilities of [Fe2(dmdt)4] were well fitted by S-T model with J = -260/cm all over the measured temperature range, which are consistent with the dimeric structure. The DFT calculation also suggested that the dimeric structure is more stable than the monomeric one.

# Search for Uniaxial Pressure Induced CDW Suppression and Superconductivity in TiSe<sub>2</sub>\*

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Through intercalation between the layers of the transition metal dichalcogenide TiSe<sub>2</sub>, it has previously been shown that the temperature at which the intrinsic charge density wave (CDW) transition occurs ( $T_{\rm CDW} \sim 165$  K) decreases with increased intercalation. To mimic the chemical pressure caused by intercalation, uniaxial physical pressure (both compression and expansion) is used along with the Poisson effect. In the control experiment with compressive pressure perpendicular to the layers ( $_{\rm CDW}$ ) resistivity data shows a shift in the peak (related to  $T_{\rm CDW}$ ) towards lower temperatures; expected for increasing dimensionality. For uniaxial pressure parallel to the layers, the Poisson effect should separate the layers, providing a separation of the layers similar to that of intercalation. Preliminary results show  $T_{\rm CDW}$  increases initially, and then decreases. A prototype to induce uniaxial tension perpendicular to the layers has recently been developed and preliminary results will be reported.

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# Metallic state induced by high pressure in single component molecular crystals [Ni(dmit)<sub>2</sub>] and [Ni(ddt)<sub>2</sub>]

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A molecular system has a soft lattice. Thus, application of high pressure is a very effective way to discover new single component molecular metals.[1,2] In this study, we prepared single component molecule crystals of [Ni(dimt)<sub>2</sub>] (Ni(S<sub>5</sub>C<sub>3</sub>)<sub>2</sub>: dmit=1,3-dithiole-2-thione-4,5-dithiolate) and [Ni(ddt)<sub>2</sub> (Ni(S<sub>4</sub>C<sub>4</sub>H<sub>2</sub>)<sub>2</sub>: ddt= 1,4-dithiin-2,3-dithiolate) and measured the high-pressure electrical resistivity up to 25.5 GPa by using a diamond anvil cell (DAC). We successfully observed metallic state in a wide temperature range above 15.9 GPa for [Ni(dimt)<sub>2</sub>], and 11GPa for [Ni(ddt)<sub>2</sub>], respectively. Two different band calculation methods, tight-binding calculation coupled with the interatomic repulsion model and ab initio density functional theory (DFT) calculations, indicated that small three-dimensional Fermi surfaces appear under high pressures in [Ni(dimt)<sub>2</sub>]. For the check of pressure quality, we also performed high pressure transport measurements for Mott insulators  $\beta'$ -ET<sub>2</sub>ICl<sub>2</sub> anc  $\beta'$ -ET<sub>2</sub>AuCl<sub>2</sub> up to 12 GPa. By comparing the results obtained by the cubic anvil cell measurements, we proved that our DAC method really provides hydrostatic pressure of high quality.

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# Disorder dependence of field induced coherent-incoherent crossover in interlayer transport in TMTSF<sub>2</sub>ClO<sub>4</sub>

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Coherent-incoherent crossover manifests most directly in non-monotonic temperature dependence of interlayer conductivity and non-Fermi-liquid behavior of magnetoresistance (MR) in metallic state of quasi one-dimensional systems [1]. The crossover to incoherent conductivity is seen as MR saturation [1,2] for magnetic field applied along the layers, even though non-saturating MR is expected for open orbits. Recently, it was suggested [3] that resonant tunneling through interlayer impurities can contribute in parallel with the conventional Boltzmann transport to interlayer conductivity and can be responsible for the field induced crossover [2]. We explore this possibility using the anion ordering transition in (TMTSF)<sub>2</sub>ClO<sub>4</sub> to introduce disorder in energies or positions of ClO<sub>4</sub> anion: located between the TMTSF layers. Here we present the results of high-field MR measurements for a wide range of disorders. We observe the gradual transition from non-saturating to saturating interlayer MR behavior with increasing disorder. Our results strongly support the proposed two-channel interlayer conductivity scenario [3] and show the key role of disorder in the competition between these channels.

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