

# 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 how 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,  $C_6O_4H_2^{2-} = dhbq^{2-}$  and its derivatives,  $C_6O_4X_2^{2-} = X_2An^{2-}$ , with  $X = Cl, Br, I, NO_2, \dots$ ;  $M^{II} = Mn, Fe, Co, \dots$ ) 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 isostructural 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 $\text{EtMe}_3\text{Sb}[\text{Pd}(\text{dmit})_2]_2$

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No onset of magnetic order has been observed to temperatures  $T \ll J$  in the Mott insulator  $\text{EtMe}_3\text{Sb}[\text{Pd}(\text{dmit})_2]_2$ , 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  $^{13}\text{C}$   $1/T_1$  in fields  $B = 0.6\text{-}30\text{T}$ . 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.

# Studies of Metal-Insulator Transition in One-Dimensional Organic Metal (DMEDO-TTF)<sub>2</sub>ClO<sub>4</sub>

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Structural and physical properties of quasi-one-dimensional charge transfer salts composed of the unsymmetrical donor DMEDO-TTF (DMEDO-TTF : dimethyl(ethylenedioxy)tetrathiafulvalene) and octahedral anions XF<sub>6</sub> (X = P, As, Sb) are sensitive to the anion volume [1]. They have three phases, the high-temperature metallic, low-temperature metallic, and nonmagnetic insulating phases. The metal-metal transition temperature increases with increasing the anion size, whereas the metal-insulator transition temperature is independent of the anion size. In order to clarify the anion shape effect on the crystal structure and electronic state, we investigate the structural and physical properties of (DMEDO-TTF)<sub>2</sub>ClO<sub>4</sub>. The ClO<sub>4</sub> salt has a uniform donor stack like (*o*-DMTTF)<sub>2</sub>Y (Y = Cl, Br, I), and the anion is in the disordered state [2]. The electrical resistivity and spin susceptibility show a metal- nonmagnetic insulator transition at  $T_{MI} = 190$  K in the cooling process, and have hysteresis indicating the first order phase transition. The superlattice reflections are observed in the x-ray oscillation photograph at 185 K, which indicates that the anion ordering is the origin of the MI transition.

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# On the coexistence of Spin Density Wave and Superconducting orders in $(\text{TMTSF})_2\text{PF}_6$

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We study the organic conductor  $(\text{TMTSF})_2\text{PF}_6$  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 dominates the low temperature electronic properties of the spin-liquid system  $\kappa$ -(ET)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>. From 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 in-plane 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> under hydrostatic pressures above 1 GPa,  $\beta$ -(BEDT-TTF)<sub>2</sub>X ( $X = \text{IBr}_2, \text{I}_2\text{Br}$ ), 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  $\mathbf{k}$ -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  $\mathbf{k}$ -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 $\lambda$ -(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> is 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 $\kappa$ -(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  $n \approx 0.8$  to 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 antiferromagnetic 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  $\pi$ -d 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 based 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  $J$  is antiferromagnetic.

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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.  $\text{LuFe}_2\text{O}_4$ , and charge transfer salts. Quasi 2-dimensional organic salt  $\kappa\text{-(ET)}_2\text{Cu}_2(\text{CN})_3$  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)<sub>2</sub>PF<sub>6</sub>, 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 $\text{EtMe}_3\text{Sb}[\text{Pd}(\text{dmit})_2]_2$ under hydrostatic pressure

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Recently  $\beta'$ - $[\text{Pd}(\text{dmit})_2]_2$  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  $\text{EtMe}_3\text{Sb}[\text{Pd}(\text{dmit})_2]_2$  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  $\text{EtMe}_3\text{Sb}[\text{Pd}(\text{dmit})_2]_2$  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 thourgh 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 columnner 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 nondegenerate 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 $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub>

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A dimer Mott insulator,  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub>, 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)<sub>2</sub>ICl<sub>2</sub> by the application of electric field.

[1] S. Iguchi et al., Phys. Rev. B **87**, 075107 (2013).

# 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  $C_p$  measurements. This anomaly in  $C_p$  is suppressed by magnetic fields above 3 T. In this field range, the sharp peak in  $C_p$  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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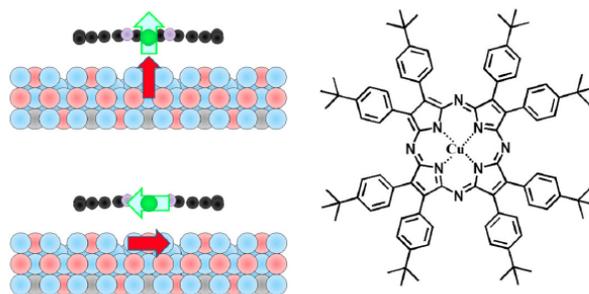
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The Heisenberg exchange coupling is one of the most popular models for the description of the magnetic coupling on a quantum-mechanical basis. This model plays an important role in the understanding of many effects which can be further applied to a 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<sub>4</sub>Dinit 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<sub>4</sub>Dinit molecule to the octahedral Fe spin in the Fe<sub>3</sub>O<sub>4</sub>(100) surface).

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# The magnetic structure in antiferromagnetic state of frustrated spin systems, $\beta'$ -Et<sub>2</sub>Me<sub>2</sub>P[Pd(dmit)<sub>2</sub>]<sub>2</sub> and $\beta'$ -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>P and Et<sub>2</sub>Me<sub>2</sub>P salts show antiferromagnetic (AF) ordering below 35K and 15K, respectively. The larger 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 <sup>13</sup>C-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 Dibromiodomesitylene 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 state are coupled with the changes in dipole moments, the ferroelectric and/or antiferroelectric properties can be observed. Herein, we noticed dibromiodomesitylene (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 porous 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  $\mu\text{s}$  at 80K and 1.8  $\mu\text{s}$  at 280K. In this paper, we discuss the photoconduction mechanism of the D-A type COF materials.

# Photo-induced enhancement of superconductivity in $\kappa$ -(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 matter 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 photo-induced effects remained even after the irradiation was stopped. Spyropirans can switch between a neutral form and an open form triggered by light-irradiation with different wavelengths, resulting in a significant change in the electric dipole moment. Reversible changes in dipole moment of SP-SAM triggered by light 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, $(\text{EDO-TTF})_2\text{PF}_6$ , using a density-functional theory method

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A quasi-one-dimensional molecular solid,  $(\text{EDO-TTF})_2\text{PF}_6$ , 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 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 from one side of the molecule to the other. The instability is driven by strong *antisymmetric* 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<sub>60</sub><sup>•-</sup> was achieved in the charge-transfer crystal of (TPC)(MDABCO<sup>+</sup>)(C<sub>60</sub><sup>•-</sup>) 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<sub>60</sub><sup>•-</sup>) coexist. The ordered C<sub>60</sub><sup>•-</sup> layers showed 2D metallic conductivity, whereas the antiferromagnetic interaction was observed in nonmetallic disordered C<sub>60</sub><sup>•-</sup> layers above 200 K. The disordered layers became metallic below 200 K through the ordering of C<sub>60</sub><sup>•-</sup>. (TPC)(MQ<sup>+</sup>)(C<sub>60</sub><sup>•-</sup>) also had a 2D hexagonal packing of C<sub>60</sub><sup>•-</sup> and showed a little longer interfullerene distances (10.12 - 10.18 Å) than that in (TPC)(MDABCO<sup>+</sup>)(C<sub>60</sub><sup>•-</sup>) (10.07 Å), where MQ<sup>+</sup> is N-methylquinoclidinium cation having threefold symmetry. Magnetic susceptibility of (TPC)(MQ<sup>+</sup>)(C<sub>60</sub><sup>•-</sup>) 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<sub>60</sub><sup>•-</sup> 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  $\sigma_z$  components 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 electrons at the time reversal symmetry point. In addition, a new type of emergence 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)<sub>2</sub> 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 ethylenedithio-tetrathiafulvalene (H<sub>2</sub>Cat-EDT-TTF) and its diseleno 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 diseleno analogue,  $\kappa$ -H<sub>3</sub>(Cat-EDT-ST)<sub>2</sub> ( $\kappa$ -Se) becomes 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  $\text{Et}_2\text{Me}_2\text{Sb}[\text{Pd}(\text{dmit})_2]_2$  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  $(\text{TMTSF})_2\text{X}$  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 experimental 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  $40^\circ$  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  $d-d$  interactions. The twisted [Cu(dmdt)<sub>2</sub>] (dmdt = dimethyltetrathiafulvalenedithiolate) molecule with distorted D<sub>2</sub> 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)<sub>2</sub>] cannot be realized in the D<sub>2</sub>X-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, [Fe<sub>2</sub>(dmdt)<sub>4</sub>] with a dimeric structure. The electrical resistivity of [Fe<sub>2</sub>(dmdt)<sub>4</sub>] was measured on a compressed pellet sample with a four-probe technique in the temperature range 140-300 K. Neutral complex [Fe<sub>2</sub>(dmdt)<sub>4</sub>] 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 susceptibility measurement of [Fe<sub>2</sub>(dmdt)<sub>4</sub>] was performed in the temperature range of 1.9-300 K. The susceptibilities of [Fe<sub>2</sub>(dmdt)<sub>4</sub>] were well fitted by S-T model with  $J = -260$  K 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 $\text{TiSe}_2$ \*

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Through intercalation between the layers of the transition metal dichalcogenide  $\text{TiSe}_2$ , it has previously been shown that the temperature at which the intrinsic charge density wave (CDW) transition occurs ( $T_{\text{CDW}} \sim 165 \text{ K}$ ) 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 ( $c$  axis), resistivity data shows a shift in the peak (related to  $T_{\text{CDW}}$ ) 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  $T_{\text{CDW}}$  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.

\*Author thanks NSF DMR 1005293 and NSF AGEP-GRS for support.

# 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(dmit)<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(dmit)<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(dmit)<sub>2</sub>]. For the check of pressure quality, we also performed high pressure transport measurements for Mott insulators β'-ET<sub>2</sub>ICl<sub>2</sub> and β'-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 $\text{TMTSF}_2\text{ClO}_4$

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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  $(\text{TMTSF})_2\text{ClO}_4$  to introduce disorder in energies or positions of  $\text{ClO}_4$  anions 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.

Part of this work has been supported by EuroMagNET II under the EU contract number 228043.

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