IV-H Molecular Crystals toward Nano-Devices by Use of d-π Interaction, Crystal Designing and Optical Doping

After some 30 years' intensive research on molecular charge transfer (CT) salts as potential functional materials, the research field has now gotten ready to examine how to make them into actual devices. Such efforts are concentrated on the developments of organic thin films for field effect transistors and light-emitting devices, both of which are carried out in a number of laboratories and groups with worldwide competitions. In order to examine the potential applicability of molecular materials from a different point of view, we are carrying out basic studies on development and physical properties of molecular CT single crystals. Major part of our study can be classified into three categories; the physical properties of the CT salts including localized spins, crystal designing using poly-carboxylate anions, and device formation by optical doping method.

IV-H-1 Light-Induced Transformation of Molecular Materials into Devices

NAITO, Toshio; INABE, Tamotsu[1]; NIIMI, Hironobu[1]; ASAKURA, Kiyotaka[1]
([1]Hokkaido Univ.)

[*Adv. Mater.* **16**, 1786–1790 (2004)]

Many kinds of molecular solids are now attracting a worldwide interest as promising candidates for advanced materials such as electronic/magnetic/optical devices and energy converters. In particular, semiconductor diodes based on photovoltaic effect appear one of the most effective ways to utilize molecular materials, if there is an appropriate doping method available. This work concerns a finding of a novel method of (persistent) carrier doping to molecular materials. The method is simple and versatile; just illuminating the desired part of material as long as it contains a photosensitive chemical species in addition to an electroactive one. Although various kinds of photoexcited states reported thus far have typical lifetimes of some hundreds of micro-seconds at longest in general, the doped state survived even several months after the illumination was finished. The experimental results demonstrate that one can control the conducting properties of an arbitrary part of a molecular material using appropriately focussed illumination. In other words, this method opens a new way for making devices and conducting nano-architectures from a wide variety of molecular solids, which have awaited for a space-resolved doping method under a mild condition.

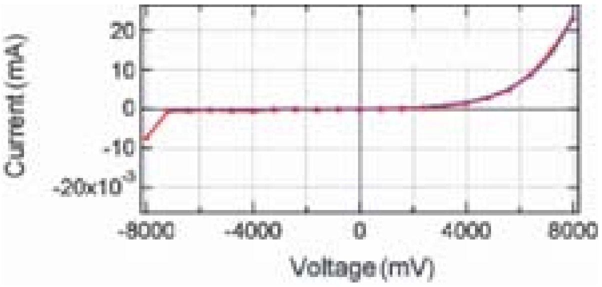

Figure 1. Current-Voltage property curve of the single crystal of $Ag(DM)_2$ after UV-VIS illumination upon only half of it for ~21 days.

IV-H-2 Molecular Conductors Containing Photoreactive Species

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[*J. Phys. IV France* **114**, 553–555 (2004)]

In order to examine the possibility of (persistent) carrier doping to molecular crystals by light exposure, some different types of molecular crystals containing photoreactive species are synthesized and characterized. The $[Ru(bpy)_3]^{2+}$ cation (bpy = 2,2'-bipyridyl) yielded two different new complexes with $[Ni(dmit)_2]^-$ radical species, both of which were structurally characterized and turned out to be band insulators. Methy viologen (MV) has been found to yield a new phase of the complex with $[Ni(dmit)_2]^-$, $MV[Ni(dmit)_2]_2$. The temperature dependences of electrical resistivity (decreasing with lowering temperature down to 1.0 K) and magnetic susceptibility (Pauli paramagnetism from 300 K to 1.8 K with a hysteresis below ~100 K) clearly indicate that this phase is metallic. The thermoelectric power exhibited ~0 μVK^{-1} from 300 K–4.2 K. This phase turned out to be metastable, and the crystals gradually turned into insulating ones. The effects of UV-VIS light exposure to the conducting and magnetic properties of $Ag(DMe\text{-}DCNQI)_2$ have been studied, and clear differences between the exposed and the pristine crystals were observed. The ESR signal at 3.7 K suggested that the exposed sample should include the Ag(0) species.

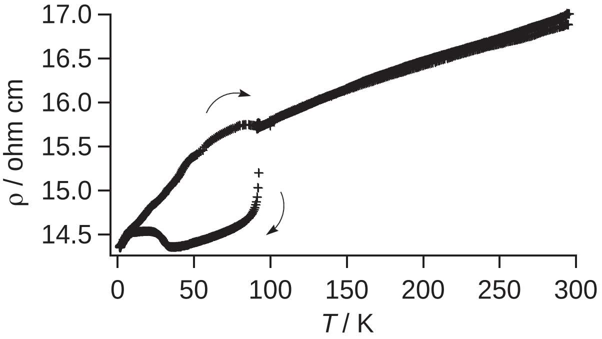

Figure 1. Temperature-dependent electrical resistivity of $MV[Ni(dmit)_2]_2$.

IV-H-3 A New Optical Doping Method toward Molecular Electronics

NAITO, Toshio; INABE, Tamotsu[1]; NIIMI, Hironobu[1]; ASAKURA, Kiyotaka[1]
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[*Synth. Met.* **152**, 289–292 (2005)]

This work concerns a finding of a novel method of (persistent) carrier doping to molecular materials. The method is simple and versatile; just illuminating the material as long as it contains a photosensitive chemical species in addition to an electroactive one. Although various kinds of photo-excited states reported thus far have typical lifetimes of some hundreds of microseconds at longest in general, the doped state survived even a week after the illumination was finished. The experimental results demonstrate that one can control the conducting properties of an arbitrary part of a molecular material using appropriately focussed illumination. In other words, this method opens a new way for making devices and conducting nano-architectures from a wide variety of molecular solids, which have awaited for a space-resolved doping method.

IV-H-4 Photochemical Method of Device Fabrication Starting from Molecular Crystals

NAITO, Toshio; SUGAWARA, Hideyuki[1]; INABE, Tamotsu[1]; MIYAMOTO, Takeshi[1]; NIIMI, Hironobu[1]; ASAKURA, Kiyotaka[1]
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[*Mol. Cryst. Liq. Cryst.* submitted]

The conductivity of a silver salt of *N,N*'-dicyanoquinonediimine irreversibly varied in approximate proportion to an illumination of a wide range of wavelengths. Depending on the illumination conditions, four different states (β, γ, δ, and ε) were obtained with different structures. The β structure is in particular important, where the formal charge of the *N,N*'-dicyanoquinonediimine molecules continuously decreased to –0.4– –0.35 with retaining the crystal structure, when we kept the temperature < 155 ºC during the illumination. The non-illuminated area of the sample retained its original electrical property with a well-defined interface, which enabled a fabrication of a junction-structure in the single crystal.

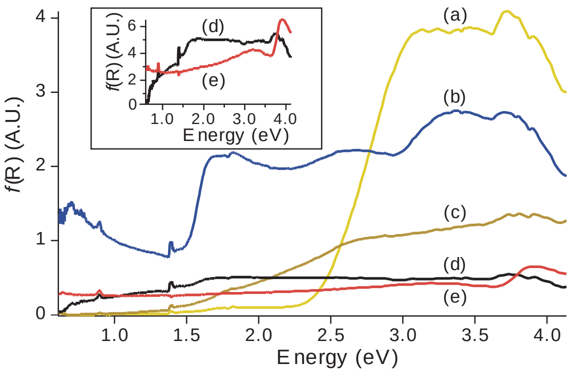

Figure 1. Diffuse scattering spectra of (a) isolated neutral DM species, (b) α-, (c) γ-, (d) δ-, and (e) ε-Ag(DM)$_2$, respectively. The inset shows (d) and (e) spectra with *f*(*R*) enlarged by 10 times.

IV-H-5 Photochemical Control of Dark Conductivity—A New Approach to Devices Based on Molecular Crystals

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([1]Hokkaido Univ.; [2]KEK)

[*J. Low Temp. Phys.* submitted]

Thermal analysis of Ag(DM)$_2$, where DM = 2,5-dimethyl-*N,N*'-dicyanoquinonediimine, clarified that the salt had an insulating amorphous phase (≥ 155 °C). Characterization of this and related solid states of Ag(DM)$_2$ indicated that a photo-induced process should be essential in controlling the number of carriers and thus conduction behavior of the salt by illumination. In fact, while heating could do nothing but make the salt insulating when the sample temperature exceeded 155 °C, ultraviolet-visible light illumination (< 155 °C) could gradually change the properties to be semiconducting with retaining the crystal lattice (average structure).

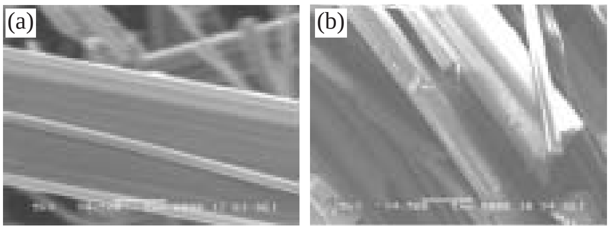

Figure 1. Scanning Electron Microprobe (SEM) photographs of different states after UV-Vis illumination on single crystals of Ag(DM)$_2$; (a) β-, and (b) γ-states, respectively. The SEM photographs of the pristine (α-) samples (not shown here) much resemble those of the β-state.

IV-H-6 Molecular Unit Based on Metal Phthalocyanine; Designed for Molecular Electronics

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([1]Univ. Tokyo; [2]Hokkaido Univ.)

[*J. Phys. IV France* **114**, 541–543 (2004)]

We obtained three conducting crystals based on a [Fe^{III}(Pc)(CN)$_2$] molecular unit. All crystals showed a large anisotropic negative magnetoresistance arising from the π-d interaction self-contained in the [Fe^{III}(Pc)(CN)$_2$] unit. The anisotropy is attributable to the anisotropic *g*-tensor in the [Fe^{III}(Pc)(CN)$_2$] unit. We also obtained a thin film containing [Fe^{II}(Pc)(CN)$_2$]. The film exhibits photocurrent response for the UV irradiation. These features suggest [M(Pc)(CN)$_2$] molecular unit is a well-designed one for a building block of molecular devices.

IV-H-7 Anisotropic Giant Magnetoresistance Originating from the π-d Interaction in a Molecule

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([1]Univ. Tokyo; [2]Hokkaido Univ.)

[*J. Phys. Chem. Solids* **65**, 749–752 (2004)]

We synthesized TPP[Fe^{III}(Pc)$(CN)_2$]$_2$, PTMA$_x$[Fe^{III}(Pc)$(CN)_2$]·*y*(MeCN), and PXX[Fe^{III}(Pc)$(CN)_2$], a new series of charge-transfer salts containing the axially-substituted phthalocyanine (Pc), [Fe^{III}(Pc)$(CN)_2$]$^-$. In this molecular unit, the π conduction electron derived from the Pc-ring coexists with the d electron which is a potential source of a local magnetic moment. Therefore various phenomena associated with the interplay between local magnetic moments and conduction electrons are expected. We observed the giant negative magnetoresistance (GNMR) in all the three salts. The GNMR is highly anisotropic for the magnetic-field direction, and reflects the *g*-tensor anisotropy of the local magnetic moment in the [Fe^{III} (Pc)$(CN)_2$]$^-$ unit. This indicates that the GNMR in these salts originates from the strong π-d interaction in the [Fe^{III}(Pc)$(CN)_2$]$^-$ unit.

IV-H-8 Phthalocyanine-Pphthalocyanine Salt Crystal: A Unique Assembly Design

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([1]Hokkaido Univ.)

[*J. Porphyrins Phthalocyanines* **9**, 68–71 (2005)]

A unique salt composed of cationic and anionic phthalocyanine complexes has been prepared and structurally characterized. The cationic component is di(pyridine)(phthalocyaninato)cobalt(III) and the anionic one is dicyano(phthalocyaninato)cobalt(III). They arrange alternately in the crystal, forming a two-dimensional sheet with partial π-π overlaps.

IV-H-9 Physical Properties of Electrically Conducting and Stable Molecular Neutral Radical Solid [Co(2,3-Nc)$(CN)_2$]CH_3CN (2,3-Nc = 2,3-Naphthalocyanine)

NAITO, Toshio; MATSUMURA, Naoko[1]; INABE, Tamotsu[1]; MATSUDA, Masaki[2]; TAJIMA, Hiroyuki[2]
([1]Hokkaido Univ.; [2]Univ. Tokyo)

[*J. Porphyrins Phthalocyanines* **8**, 1258–1268 (2004)]

Solid state properties of dicyano(2,3-naphthalocyaninato)cobalt(III) neutral radical crystal, [Co(2,3-Nc)$(CN)_2$]CH_3CN, were characterized by the measurements of the resistivity under high pressure and under uniaxial strain, thermoelectric power, magnetic susceptibility, ESR and polarized reflectance spectra. The title compound exhibited thermally activated-type electrical conductivity along the *c*-axis. The room temperature (RT) resistivity ρ_{RT} along the *c*-axis and activation energy E_a rapidly decreased with increasing pressure. The temperature-dependent thermoelectric power *S* was that of a typical one-dimensional (1D) semiconductor. However the high absolute value of *S* suggested that this electronic system should be strongly correlated. Although the electrical resistivity exhibited monotonical temeperature-dependence, the magnetic susceptibility clearly indicated a Peierls-type transition and marked fluctuation from RT. Both of Peierls-type transitions and fluctuations are characteristic phenomena to 1D conductors. Furthermore ESR spectra manifested that the Peierls-type transition occurred at 100 K. The inconsistency between the electrical behaviour (without a phase-transition) and magnetic behaviour (with a phase-transition) indicates the separation of the degrees of freedom in spin and charge (spin-charge separation) of this material. Spin-charge separation is a theoretically predicted phenomenon peculiar to the 1D conductors with strong correlation. The reflectance spectra were quantitatively explained by a 1D Hubbard model, and manifested the existence of a structural fluctuation of this material from RT. Based on these observed physical properties it is concluded that [Co(2,3-Nc)$(CN)_2$]-CH_3CN is a strongly correlated 1D semiconductor with a Mott-Hubbard type energy gap and characterised with a fluctuation and spin-charge separation.

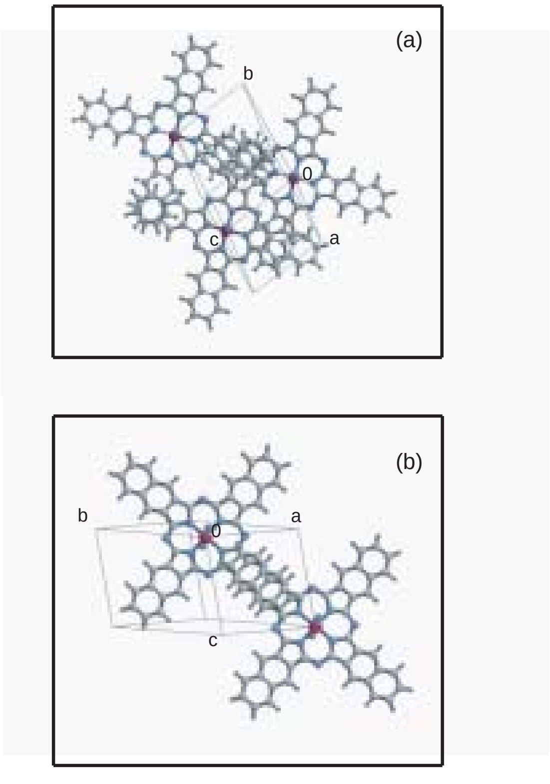

Figure 1. Crystal structure. For simplicity, (a) only three radical species at origin, [011] and [001], and (b) two radical species at origin and [101] are shown. The CH_3CN molecules are omitted for clarity.

IV-H-10 Charge Disproportionation and Anomalous Giant Magnetoresistance in a One-dimensional Conductor, TPP[Co(Pc)(CN)$_2$]$_2$

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([1]Univ. Tokyo; [2]Hokkaido Univ.; [3]NICT)

[*Synth. Met.* in press]

Magnetoresistance study on the charge transfer salts of [Fe(Pc)(CN)$_2$] revealed various interesting phenomena, such as anisotropic giant negative magnetoresistance, weak ferromagnetism, and anisotropic Curie-Weiss magnetic susceptivility.1) These interesting phenomena originate from the orbital magnetic moment remaining in the [Fe(Pc)(CN)$_2$] unit, and the d-π interaction inherently existing in this unit. Contrary to the [Fe(Pc)(CN)$_2$] salts, physical properties of the [Co(Pc)(CN)$_2$] salts have not been investigated in detail. In this paper, we report the magnetotransport and NQR studies on TPP[Co(Pc)(CN)$_2$]$_2$ salts. This salt is a one-dimensional conductor, where the partially oxidized [Co(Pc)(CN)$_2$] units stack uniformly along the *c*-axis. The salt exhibits Pauli-paramagnetic susceptibility. The electrical resistivity is semiconducting with a very small activation energy less than 0.01 eV. Interestingly, this salt exhibits very large positive magnetoresistance at low-temperature ($\Delta R(8\ \mathrm{T})/R(0\ \mathrm{T}) \sim 6$). Moreover, the field orientation dependence is quite small below 10 T. These facts indicate that the magnetoresistance in this salt is not an ordinary orbital effect. In order to examine the mechanism of the anomalous magnetoresistance, we have measured ^{59}Co NQR spectra. We found a sign of charge disproportionation at 1.8 K. On the basis of magnetotransport ($B < 38$ T), NQR and NMR ($B < 16$ T) measurements, we will discuss the anomalous electronic state of this salt.

Reference

1) For example see, N. Hanasaki *et al., Phys. Rev. B* **62**, 5839–5842 (2000).

IV-H-11 Structural, Electrical and Magnetic Properties of α-(ET)$_7$[MnCl$_4$]$_2$·(1,1,2-C$_2$H$_3$Cl$_3$)$_2$ (ET = bis(ethylenedithio)tetrathiafulvalene)

NAITO, Toshio; INABE, Tamotsu[1]
([1]Hokkaido Univ.)

[*Bull. Chem. Soc. Jpn.* **77**, 1987–1995 (2004)]

A new charge-transfer salt of ET with a chloromanganate(II) complex anion has been synthesized and characterized by X-ray structural analysis, resistivity measurements, magnetic susceptibility, electron spin resonance (ESR) and extended Hückel tight biding band calculation. The crystal has a sheet structure comprised of α-type two-dimensional (2D) donor arrangement in the *bc*-plane and insulating sheets of discrete [MnCl$_4$]$^{2-}$ anions and 1,1,2-C$_2$H$_3$Cl$_3$ (TCE) molecules. Its conducting property exhibits considerable anisotropy, which is of effectively metallic along the *b*-axis down to 1.2 K under 2.9 kbar and higher pressure. The magnetic susceptibility is approximately reproduced by the Curie-Weiss law with the Weiss temperature θ = –(1.35±0.07) K from 2–300 K. ESR measurements revealed that the π-electron system in this salt exhibits Pauli paramagnetism at least at 3.6– ~50 K. The band calculation suggests that the HOMO (the highest occupied molecular orbital) band has extremely small dispersion almost solely along the *b**-axis with a simple one-dimensional (1D) Fermi surface. Considering all the data above, it is concluded that this salt has unusually stable and narrow 1D metallic band structure, which is a rare example even in a great number of molecular conducting salts reported to date.

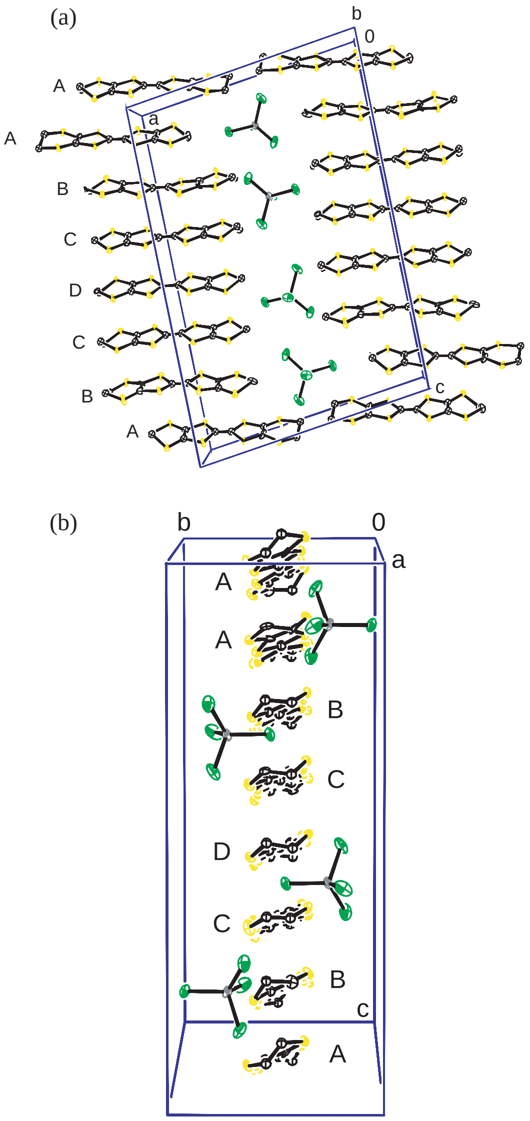

Figure 1. Unit cell; front view of (a) *ac*-, and (b) *bc*-planes. Hydrogen atoms are omitted for clarity.

IV-H-12 New Binuclear Copper Complexes [(9S3)Cu(CN)Cu(9S3)]X$_n$ (X = BF$_4$, n = 1; X = TCNQ, n = 2) (9S3 = 1,4,7-trithiacyclononane): Syntheses, Crystal Structures and Magnetic Properties

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([1]Hokkaido Univ.)

[*Z. Anorg. Allg. Chem.* **630**, 2725–2730 (2004)]

The binuclear Cu complexes of 1,4,7-trithiacyclononane (9S3) with an inorganic anion (BF_4^-) and with an organic radical anion $TCNQ^-$ (7,7',8,8'-tetracyanoquinodimethanide) were synthesized and their molecular and crystal structures were examined in connection with each magnetic property. A new complex cation [Cu(9S3)CN(9S3)Cu] varied its charges and magnetic properties depending on the counter anions; [Cu(9S3)-CN(9S3)Cu](BF_4) (**1**) was obtained as diamagnetic colorless crystals, while [Cu(9S3)CN(9S3)Cu]$(TCNQ)_2$ (**2**) was obtained as dark blue crystals with antiferromagnetic property. Complex **1** crystallized in the monoclinic space group *C*2/c with a = 26.863(2), b = 7.0878(5), c = 13.4864(8) Å, β = 116.318(2)°. Complex **2** crystallized in the triclinic space group $P\bar{1}$ with a = 12.521(1), b = 20.2698(8), c = 8.0205(4) Å, α= 100.688(4), β = 93.846(5), γ = 94.953(4)°. Both complexes were comprised of cyano-bridged two Cu(9S3) ions with tetrahedral coordination geometry. The X-ray structural study revealed that **1** had two crystallographically equivalent Cu(I) centers, while **2** had two crystallographically independent Cu(I/II) sites. The two Cu(I/II) sites could not be distinguished from the X-ray structural study. As for **2** the IR spectra showed that both crystallographically independent TCNQ species were monoanions and were strongly dimerized due to pstacking, which well explained their diamagnetic contribution to the magnetic susceptibility and the highly insulating property of this salt. The temperature-dependent magnetic susceptibility of **2** showed a deviation from the Curie-Weiss behavior around 60 K, which indicated a strong antiferromagnetic intermolecular interaction between the copper complexes and that such intermolecular interaction should partly occur *via* the TCNQ radical anion dimer.

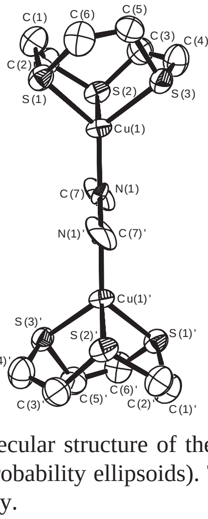

Figure 1. The molecular structure of the [Cu(9S3)CN(9S3)-Cu]$^+$ cation (50% probability ellipsoids). The hydrogen atoms are omitted for clarity.

IV-H-13 Crystal Design of Cation-Radical Salts Based on the Supramolecular Self-Organizing Arrangement of Mellitate Anions

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([1]Hokkaido Univ.)

[*J. Phys. IV France* **114**, 449–453 (2004)]

Mellitate anions form hydrogen-bonding infinite networks in the salts with pyridinium cations. The network pattern depends on the number of deprotonation (n) from the mellitic acid; for n = 3, triangular hydrogen-bond units form a two-dimensional sheet, while for n = 2, dual hydrogen-bond units induce one-dimensional belts or two-dimensional grids. These self-organizing properties have been utilized for the crystal design of the TTF-type radical cation salts. Crystallization with TMTTF gave two kinds of crystals. One of the radical cation salt crystals consists of channel network of the anions and one-dimensional columns of TMTTF in the channels. In the other TMTTF salt, the anions with n = 1 form a two-dimensional sheet with methanol molecules. The TMTTF radicals are packed between the sheets with their molecular planes parallel to the anion planes.

IV-H-14 A Helical π-Radical Cation Column in the Double Helix of Mellitate Anions

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([1]Hokkaido Univ.)

[*Adv. Mater.* **16**, 1803–1806 (2004)]

Recent investigations of supramolecular network formation of mellitate anions in pyridinium salts have revealed that strong hydrogen bonds between the carboxy and carboxylate groups (the pair can be considered as dual hydrogen bond) predominantly form between neighboring anions, and its infinite sequence results in a chain, grid, or channel network. This self-organizing property is useful for aligning the cationic counterions. Herein, these anion structures have been utilized for the crystallization of π-radical cations. Electrochemical oxidation of TTF in the presence of mellitic acid and pyridine gave hexagonal platelets of $[TTF]_2[C_6(COO)_6H_4{}^{2-}]$. A TTF π-radical cation salt with a unique helical columnar structure has been successfully constructed within the supramolecular double helix of mellitate anions. The TTF radical tends to dimerize in a one-dimensional column; however, the twisting distortion induces a kink defect, which appears as orientational disorder. The absence of three-dimensionally correlated dimerization phase locking may arise from shielding of the one-dimensional column by the mellitate anions. This investigation indicates that combining charged functional molecules with a supramolecular network formed by their counterions is a promising approach to the crystal design of novel functional molecular materials. Indeed, it has recently been revealed that unique π-radical arrangements occurred in mellitate salts formed with other TTF-type molecules, in which mellitate anions formed a channel or sheet network by self-organization.

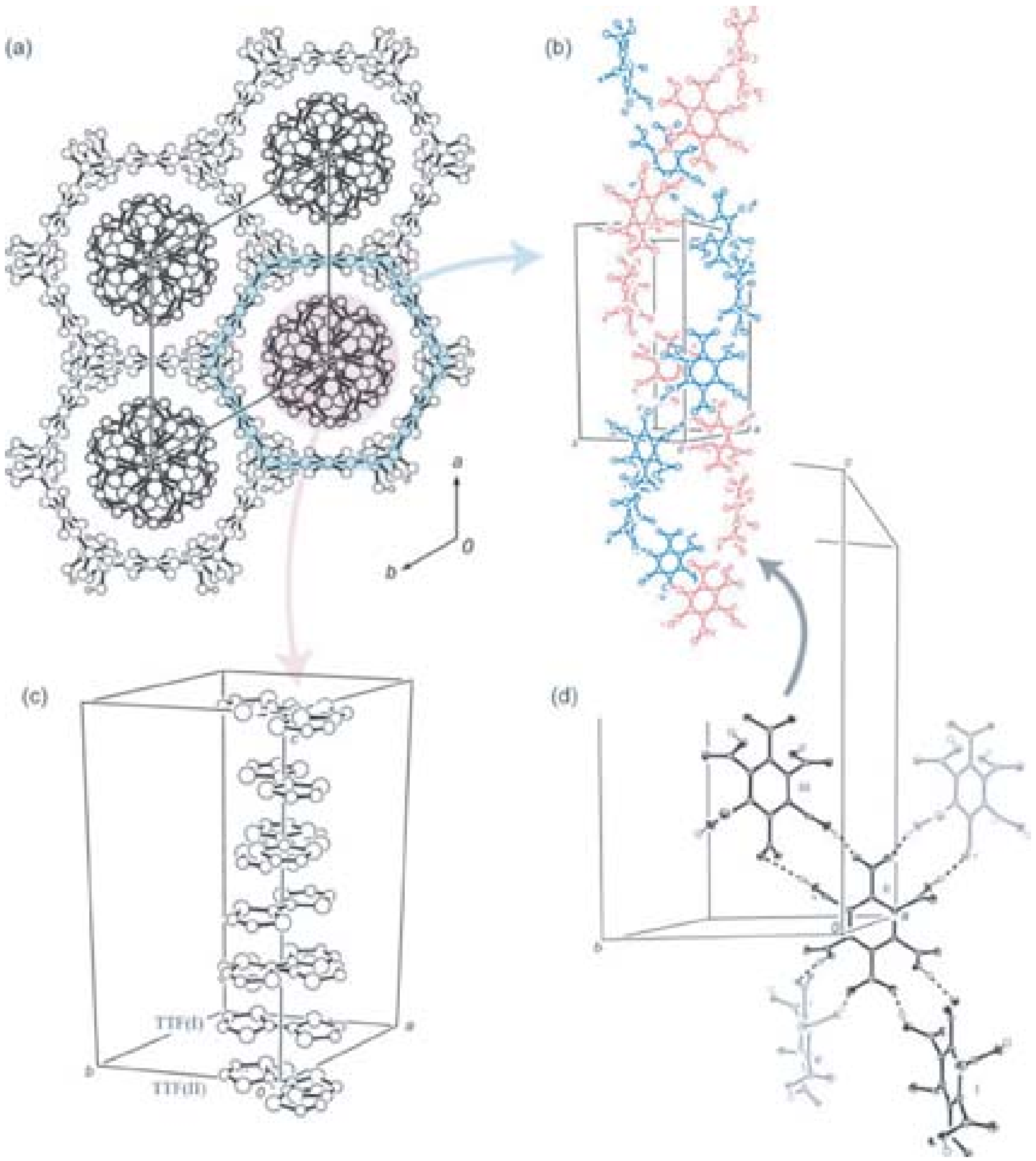

Figure 1. Molecular arrangement in $[TTF^+]_2[C_6(COO)_6H_4{}^{2-}]$. a) Hexagonal channel structure of mellitate anions and the TTF columns viewed along the *c*-axis. b) Mellitate-anion double helix. c) Helical TTF column. d) Hydrogen bond in the mellitate network; anions **I**, **II**, and **III** are related by the 6_2 screw axis at (0,0,*z*).

IV-H-15 Network Formation of Mellitate Anions ($[C_6(COO)_6H_{6-n}]^{n-}$) in the Salts with Piperidinium Derivatives and *o*-Phenylenediammonium

KOBAYASHI, Norihito[1]**; INABE, Tamotsu**[1]**; NAITO, Toshio**
([1]Hokkaido Univ.)

[*CrystEngComm* **6**, 189–196 (2004)]

Single crystals of mellitate anion ($[C_6(COO)_6H_{6-n}]^{n-}$) with piperidinium $[C_5H_{10}NH_2{}^+]_3[C_6(COO)_6H_3{}^{3-}]$ (**1**) and $[C_5H_{10}NH_2{}^+]_2[C_6(COO)_6H_4{}^{2-}]\cdot CH_3OH\cdot 3H_2O$ (**2**), with 1-methylpiperidinium $[C_5H_{10}NHCH_3{}^+]_2[C_6(COO)_6H_4{}^{2-}]\cdot 2H_2O$ (**3**), and with *o*-phenylenediammonium $[C_6H_4(NH_3)_2{}^{2+}]_2[C_6(COO)_6H_2{}^{4+}]\cdot 2CH_3OH$ (**4**) have been prepared and structurally characterized. In all of the salts, two-dimensional (2D) networks of mellitate anions were formed due to the strong self-organization of the anion. In **1**, a 2D hexagon-type network of hydrogen-bond has been observed to form among the anions. This is characteristic of the mellitate anions with $n = 3$ (*n*: deprotonation number from the acid). In other salts, a 2D anion network containing either water molecules or $–NH_3$ groups commonly formed. Since the network pattern occurs with different cation species, this hydrogen-bonding unit was determined to be dominant in the $n = 2$ anion with water and the $n = 4$ anion with $–NH_3$ species.