Research Center for Molecular Materials

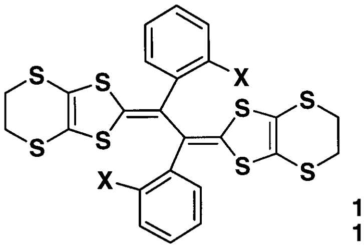
VIII-E Development of Novel Heterocyclic Compounds and their Molecular Assemblies for Advanced Materials

Heterocycles containing sulfur and/or nitrogen atoms are useful as components of functional materials since heteroatoms in their rings are helpful to stabilize ions or ion-radical species, and extended π-conjugation decreases Coulombic repulsion. In addition intermolecular interactions caused by heteroatom contacts can be expected to form novel molecular assemblies. In this project new electron acceptors, donors, and donor-acceptor compounds based on heterocycles such as 1,2,5-thiadiazole and 1,3-dithiole were synthesized and their properties including those of the charge-transfer complexes or ion-radical salts were investigated. Unique crystal structures were constructed by using weak intermolecular interactions such as hydrogen bonding or heteroatom contacts. Thiophene oligomers with rigid structures were also synthesized for molecular wires.

VIII-E-1 Cation Radical Salts of TTF Vinylogues with Au(CN)$_2$ Anion

YAMASHITA, Yoshiro; TOMURA, Masaaki; IMAEDA, Kenichi

TTF vinylogues bearing substituents have been easily obtained and the TTF skeletons can be planar when the aryl substituents are twisted from the π-conjugated framework. We have now found that TTF vinylogues **1a-c** containing one halogen atom at the ortho position afford cation radical salts [**1**·Au(CN)$_2$] as single crystals when they are electrochemically oxidized in dichloromethane in the presence of Bu$_4$N·Au(CN)$_2$. The X-ray crystal structure analyses of **1b,c**·Au(CN)$_2$ salts were carried out to reveal the unique crystal structures. The molecular and crystal structure of **1b**·Au(CN)$_2$ is shown in Figure 1. The TTF vinylogue skeleton is planar and the phenyl groups are orthogonal from the π-framework. The donor molecules do not take a stacking structure and the 1,3-dithiole parts sandwich the counter anion. The crystal structure of **1c**·Au(CN)$_2$ is very similar to that of **1b**·Au(CN)$_2$. These cation radical salts showed semiconducting behaviour since these have a 1:1 stoichiometry [**1b**·Au(CN)$_2$; $\sigma = 1 \times 10^{-2}$ Scm^{-1}, $E_a = 0.11$ eV, **1c**·Au(CN)$_2$; $\sigma = 5 \times 10^{-3}$ Scm^{-1}, $E_a = 0.11$ eV].



1a; X = F
1b; X = Cl
1c; X = Br

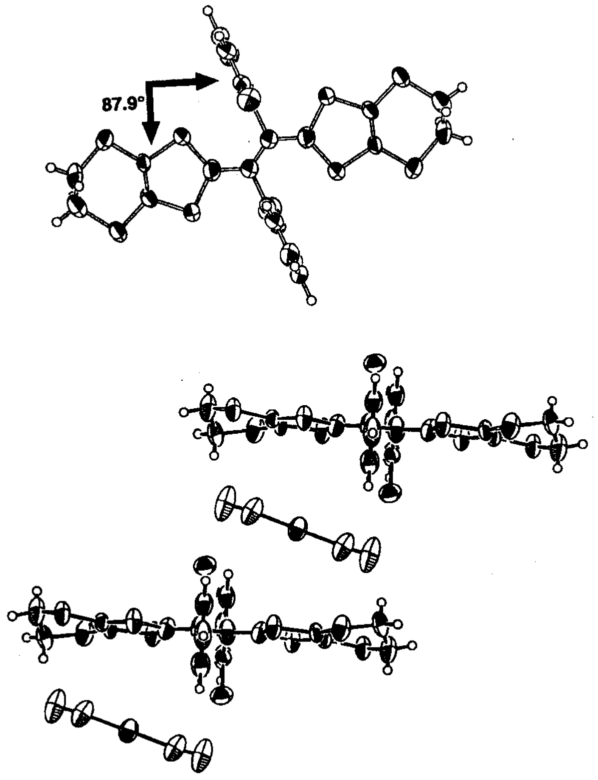


Figure 1. Molecular and crystal structure of **1b**·Au(CN)$_2$.

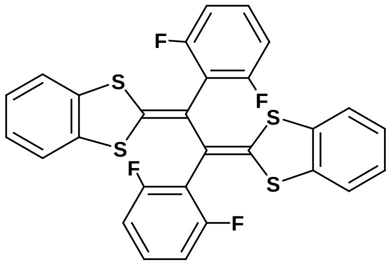
VIII-E-2 Control of Packing Mode in Crystals of Cation Radical Salts of TTF Vinylogues

TOMURA, Masaaki; YAMASHITA, Yoshiro

Molecular and crystal structures of cation radical salts of novel tetrathiafulvalene (TTF) vinylogues with extended π-conjugation and aryl groups in their vinyl part have been studied by X-ray crystallographic analysis. We reported that the unique conformation with a planar TTF vinylogue framework in **1**-PF$_6$ salt causes an interesting two-dimensional stacking mode where one donor molecule bridges two molecules like a brick wall in the crystal.$^{1)}$ We have succeeded in controlling the packing mode in the two-dimensional stack by changing the counter anion. In the case of **1**-FeCl$_4$ salt, we observed a partial two-dimensional stacking in the crystal. On the other hand, the zigzag two-dimensional stacking with an angle of nearly 90° exists in the crystal of **1**-ReO_4 salt, as shown in Figure 1.

Reference

1) Y. Yamashita, M. Tomura, M. B. Zaman and K. Imaeda, *Chem. Commun.* 1657 (1998).



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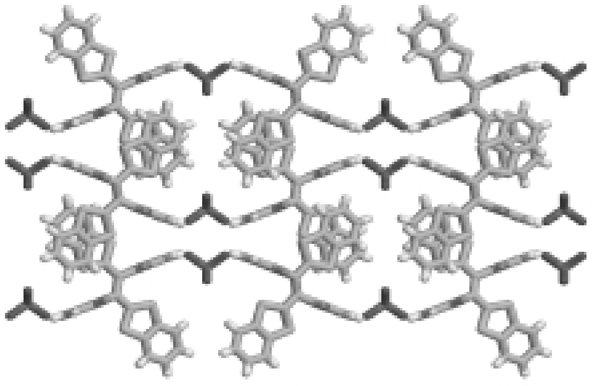
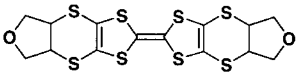


Figure 1. Crystal structure of **1**-ReO_4 salt.

VIII-E-3 Non-Planar BEDT-TTF Derivatives Fused with Tetrahydrofuran Rings Affording Cation Radical Salts with Unusual Structures

YAMASHITA, Yoshiro; TOMURA, Masaaki

Unusual crystal structures are expected from non-planar molecules to avoid steric interactions. Three-component conductors might be prepared from non-planar molecules by inclusion of solvent molecules. We have now designed new electron donors **1** and **2** where tetrahydrofuran (THF) rings are fused to BEDT-TTF. The new donors were prepared using the addition reaction of oligo(1,3-dithiole-2,4,5-trithione) with 2,5-dihydrofuran. The donor **2** gave two cation radical salts [**2**·$Au(CN)_2$ and **2**·PF_6·$(PhCl)_{0.5}$] as single crystals when electrochemically oxidized in chlorobenzene. The salts exhibit semiconducting behavior [**2**·$Au(CN)_2$; $\sigma = 3 \times 10^{-3}$ Scm^{-1}, $E_a = 0.20$, **2**·PF_6·$(PhCl)_{0.5}$; $\sigma = 5 \times 10^{-5}$ Scm^{-1}, $E_a = 0.24$ eV]. The X-ray crystal analyses of these salts revealed their unusual crystal structures. The donor molecule is non-planar and the cis-fused THF ring is like a hook. In **2**·$Au(CN)_2$ one $Au(CN)_2$ anion is sandwithched between the donor molecules. This sandwiched structure is stacked to give a column. In **2**·PF_6·$(PhCl)_{0.5}$, instead of a stacking structure, a complicated molecular network is observed, where one neighboring molecule is highly leaned (77°) and the molecules are combined by short S···S contacts as shown in Figure 1.



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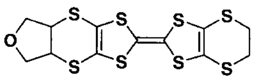

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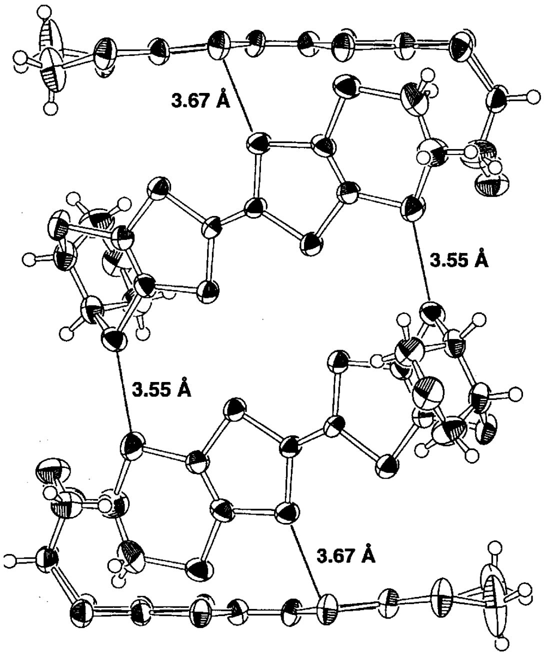
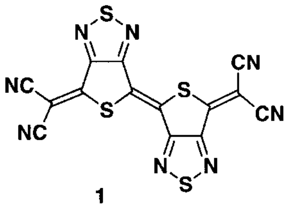


Figure 1. Crystal structure of **2**·PF_6·$(PhCl)_{0.5}$.

VIII-E-4 Bithiophene-TCNQ Analogue with Fused 1,2,5-Thiadiazole Rings

SUZUKI, Kazuharu; TOMURA, Masaaki; YAMASHITA, Yoshiro

Sulfur containing TCNQ analogues are highly polarized and are expected to have strong intermolecular interactions by heteroatom contacts. We have now prepared π-extended electron acceptor **1** containing fused thiadiazole rings and carried out the X-ray structure analysis to reveal the intermolecular interactions. The acceptor **1** was obtained by the reaction of dibromide **2** with tetracyanoethylene oxide (TCNEO) in 3% yield. However, thiophen-TCNQ analogue **3** could not be isolated in this reaction. The mechanism for the formation of **1** is still ambiguous. In the reaction to give **1**, a small amount of new compound **4** was isolated whose structure was determined by X-ray structure analysis. The dibromide **4** gave **1** upon heating, suggesting that **4** is an intermediate to give **1**. The absorption maximum of **1** is observed at 461 nm in dichloromethane. The reduction potential (–0.31 V *vs.* SCE) is lower than that of TCNQ, indicating that the interaction between the dicyanomethylene parts is weak in **1**. The X-ray analysis revealed that **1** forms a molecular assemble by heteroatom interactions. The crystal structure is shown in Figure 1. The planar molecules are combined by short S···N contacts to give a three-dimensional network. The distance of S···N contact (3.18 Å) is shorter than the sum of the van der Waals distances (3.35 Å).



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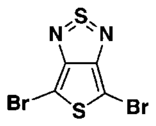

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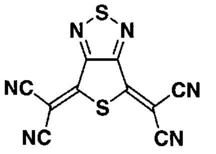

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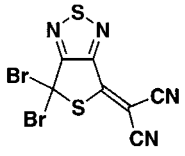

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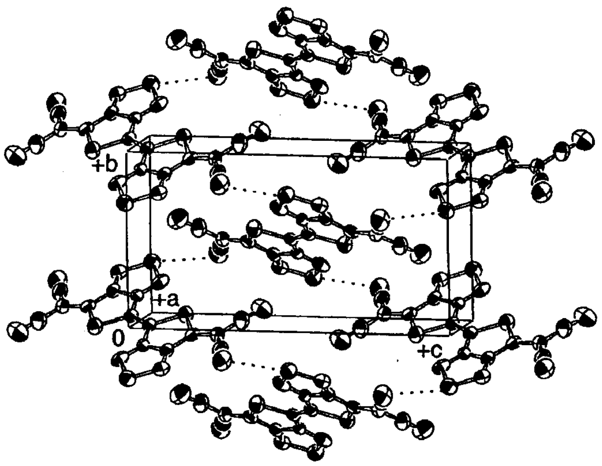


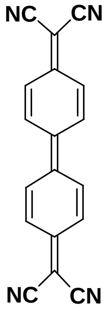
Figure 1. Crystal structure of **1**.

VIII-E-5 First Stable Tetracyanodiphenoquinodimethane with a Completely Planar Geometry: Preparation, X-Ray Structure, and Highly Conductive Complexes of Bis[1,2,5]thiadiazolo-TCNDQ

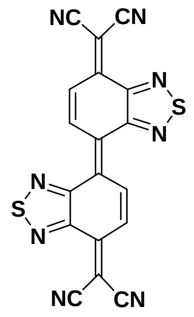
FUKUSHIMA, Takanori[1]; OKAZERI, Nobuharu[1]; MIYASHI, Tsutomu[1]; SUZUKI, Kazuharu; YAMASHITA, Yoshiro; SUZUKI, Takanori[2]
([1]Tohoku Univ.; [2]Hokkaido Univ.)

[*Tetrahdron Lett.* **40**, 1175 (1999)]

The title tetracyanodiphenoquinodimethane (TCNDQ) derivative **1** was newly designed and prepared as a novel component for highly conductive organic materials. This is the first stable TCNDQ derivative which is a π-extended electron acceptor. The synthesis was achieved by using Pd(0)-catalyzed reaction of the corresponding diiodo compound with $NaCH(CN)_2$ followed by oxidation. Introduction of thiadiazole rings into the TCNDQ skeleton leads to large stabilization in the neutral state. X-ray analysis has revealed the unique structure, where interatomic interactions (CH$\cdots$N, S$\cdots$N) play an important role in determining the molecular and crystal structure. The novel electron acceptor shows strong electron affinity (E_{red} = +0.33, +0.12 V *vs.* SCE in CH_2Cl_2) comparable with that of TCNQ, and gave highly conductive charge transfer complexes and anion radical salts.



TCNDQ



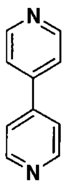
1

VIII-E-6 Novel Supramolecular Synthon in Crystal Engineering: Ionic Complexes of 4,4'-Bipyridine and 1,2-Bis(2-pyridyl)ethylene with 2,5-Dichloro-3,6-dihydroxy-1,4-benzoquinone

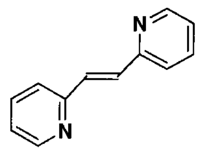
ZAMAN, Md. Badruz; TOMURA, Masaaki; YAMASHITA, Yoshiro

[*Chem. Commun.* 999 (1999)]

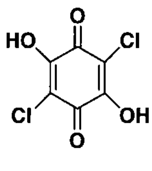
In order to develop a new type of hydrogen-bonding system, we have selected bipyridine (BPY) and 1,2-bis(2-pyridylethylene) (2-PDE) as proton acceptor, and chloranilic acid (2H-CLA) as proton donor. The complexes were prepared by reacting BPY and 2-PDE with an equal amount of 2H-CLA in acetone and/or a mixture of acetone-MeOH. The crystal structure analysis revealed that molecular complexes $[BPY\text{-}2H]^{2+}[CLA]^{2-}$ **1** and $[2\text{-}PDE\text{-}2H]^{2+}[CLA]^{2-}$ **2** are formed where proton transfer occurs. The component molecules are combined via three-center hydrogen bonded interactions to build a linear molecular chain for **1** and a zigzag molecular tape for **2**. The structure of **1** is shown in Figure 1. In both **1** and **2**, bifurcated interionic [N^+-H$\cdots O^-$ and N^+-H$\cdots$O] hydrogen bonds between the nitrogen atoms of the cations and the two oxygen atoms from the anions are observed. This is a new supramolecular synthon motif. In complex **1** alternating DA-type pairs of the cation and anion molecules are observed in the stacking, while complex **2** has a segregated stacking assembly as DD- and AA-type pairs.



BPY



2-PDE



2H-CLA

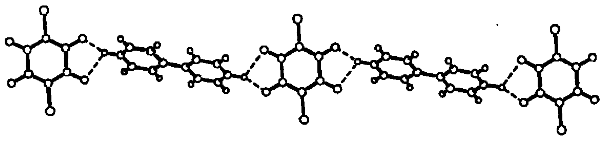


Figure 1. Hydrogen bonding in **1**.

VIII-E-7 Design and Synthesis of Soluble Linear Macromolecules with Highly Extended π-Conjugated Backbone

TANAKA, Shoji; YAMASHITA, Yoshiro

The development of soluble linear macromolecules with highly extended π-conjugated system is of crucial importance to establish the structure-conductance relationship in ballistic-type molecular electric wires. Although the introduction of alkyl substituents into the main chain is an effective method to improve the solubility, this modification often results in conjugation defects in the main chain due to the enhanced inter-unit steric repulsion. Here we report on a tactics in molecular design to do well both in solubility and π-conjugation of linear oligomers. We have synthesized a series of mixed oligomers **1-5**. All of the alkyl-substituted oligomers are more soluble in CH_2Cl_2, $CHCl_3$, and THF compared with the unsubstituted ones. As shown in Figure 1, the hexyl substitution on **1a** induces only a small blue shift of the absorption maximum, indicating a tiny loss of conjugation in spite of the long alkyl-chain substitution. These results suggest that **1b** unit can be used as a building block for soluble and effectively π-conjugated macromolecules. Along this line, we have obtained soluble highly oligomers **1c-d**. The red shift values induced by the chain extension (**1b** → **1c** → **1d**) are significantly higher than the shift value of the related oligomers (**3c** → **3d**). This supports the highly extended π-conjugation in the main chain of **1c-d**.

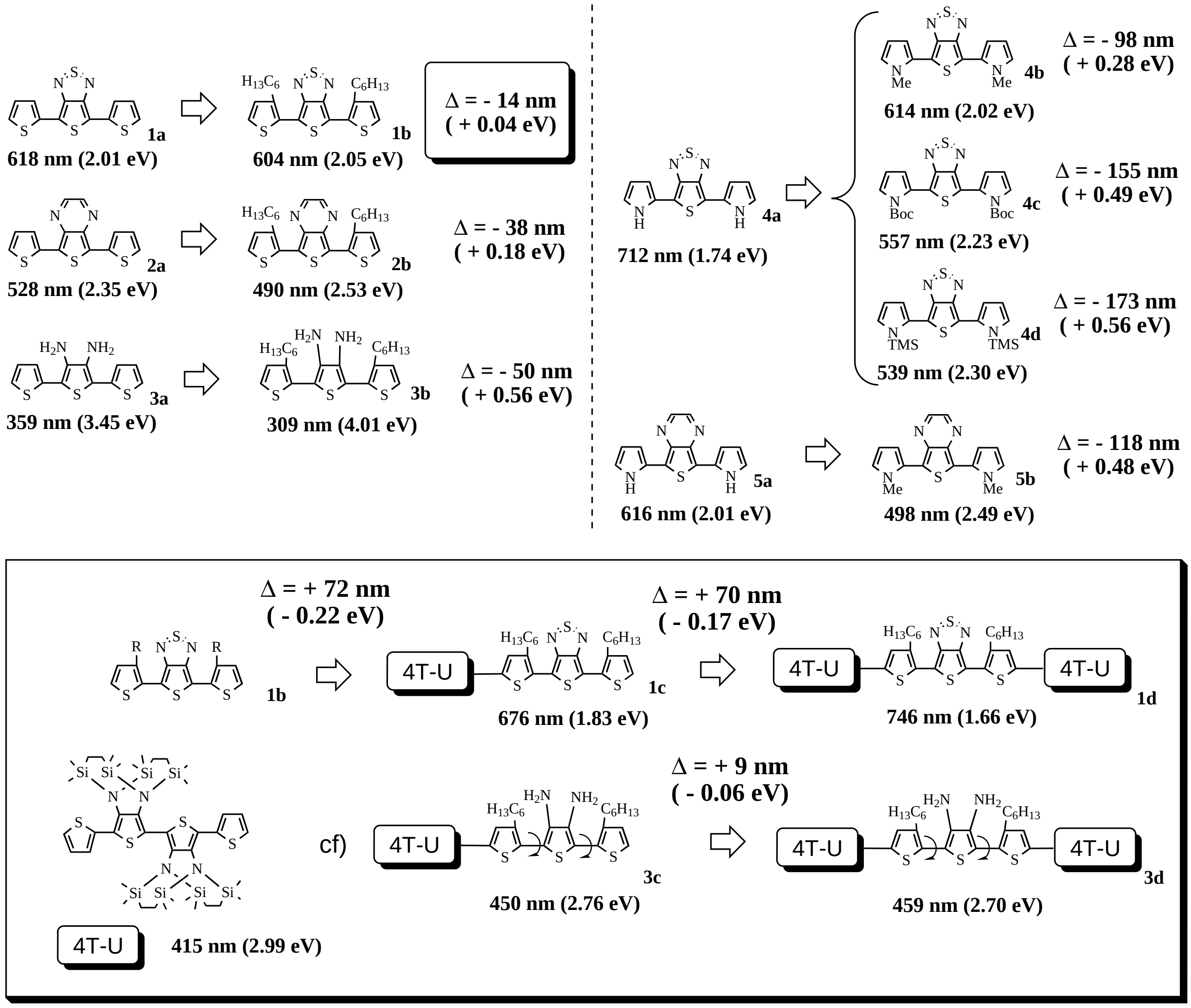


Figure 1. Substituent effects on the absorption maximum of the obtained mixed oligomers.

VIII-F Elecrtonic Structures and Rectivities of Active Sites of Metalloproteins

Metalloproteins are a class of biologically important macromolecules which have various functions such as oxygen transport, electron transfer, oxidation, and oxygenation. These diverse functions of metalloproteins have been thought to depend on the ligands from amino acid, coordination structures, and protein structures in immediate vicinity of metal ions. In this project, we are studying the relationship between the structures of the metal active sites and functions of metalloproteins.

VIII-F-1 High-Spin (*meso*-Tetraalkylporphyrinato)iron(III) Complexes As Studied by X-ray Crystallography, EPR, and Dynamic NMR Spectroscopies

IKEUE, Takahisa[1]; OHGO, Yoshiki[1]; UCHIDA, Akira[1]; NAKAMURA, Mikio[1]; FUJII, Hiroshi; YOKOYAMA, Masataka[2]
([1]Toho Univ.; [2]Chiba Univ.)

[*Inorg. Chem.* **38**, 1276 (1999)]

^{1}H-NMR spectra of a series of high-spin (*meso*-tetraalkylporphyrinato)iron(III) chlorides, [Fe(TRP)Cl] where R = Me, Et, Pr, or iPr, have been measured at various temperatures in CD_2Cl_2 solution. In the case of the Et, Pr, and iPr complexes, either the methyl or the methylene signal split into two signals with equal integral intensities at low temperature. In contrast, the Me complex did not show any splitting even at –100 °C. The results have been ascribed to the hindered rotation of the meso-alkyl groups about Cmeso-C bonds. The activation free energies for rotation have been determined as 8.0 (–72 °C), 8.5 (–60 °C), and 8.9 (–62 °C) kcal·mol^{-1} for the Et, Pr, and iPr complexes, respectively, at coalescence temperatures given in parentheses. The small activation free energy for rotation of the isopropyl groups observed in the present system is explained in terms of the nonplanarity of the porphyrin ring, which has been verified both by the X-ray crystallographic analysis and by the EPR spectrum taken in a frozen CH_2Cl_2-toluene solution. The success in observing the hindered rotation of less bulky primary alkyl groups such as ethyl and propyl groups at an easily accessible temperature range is attributed to the large difference in chemical shifts of the mutually exchanging protons, *ca.* 3500 Hz in the case of the Et complex, caused by the paramagnetism of the five-coordinated ferric porphyrin complexes.

VIII-F-2 Insensitivity of Vanadyl-Oxygen Bond Strengths to Radical Type ($^2A_{1u}$ *vs.* $^2A_{2u}$) in Vanadyl Porphyrin Cation Radicals

CZARNECKI, Kazimierz[1]; PRONIEWICZ, Leonard M.[1]; FUJII, Hiroshi; JI, David[2]; CZERNUSZEWICZ, Roman S.[2]; KINCAID, James R.[1]
([1]Marquette Univ.; [2]Univ. Houston)

[*Inorg. Chem.* **38**, 1543 (1999)]

Resonance Raman (RR) spectra are reported for vanadyl octaethylporphyrin, O=V(OEP), tetramesityltetramethylporphyrin, O=V(TMTMP), and tetramesitylporphyrin, O=V(TMP), and their corresponding π-cation radicals obtained by chemical and electrochemical oxidation. The behavior of the ν_2 RR porphyrin "marker band," which moves to higher frequency upon oxidation of the O=V(OEP) and O=V(TMTMP) and to lower frequency for O=V(TMP), shows that the resultant cation radicals have predominantly $^2A_{1u}$ and $^2A_{2u}$ ground states, respectively. In contrast to earlier work (K. A. Macor, R. S. Czernuszewicz and T. G. Spiro, *Inorg. Chem.* **29**, 1990 (1996)), it is demonstrated here that the shift of the ν(V=O) is insensitive to radical type, behavior which is in agreement with similar studies of the ferryl analogues (K. Czarnecki *et al.*, *J. Am. Chem. Soc.* **116**, 2929 and 4680 (1996)). It is suggested that the observed downshifts of the ν(V=O) previously reported for RR spectra of vanadyl porphyrin π-cation radicals, relative to their neutral parents, are most reasonably ascribed to trans oxo ligand coordination (most probably a water molecule) during low-temperature electrochemical oxidation of the neutral species.

VIII-F-3 Electron Configuration of Ferric Ions in Low-Spin (Dicyano)(meso-tetraarylporphyrinato)iron(III) Complexes

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([1]Toho Univ.)

[*Inorg. Chem.* **38**, 3857 (1999)]

The electron configuration of a series of low-spin (dicyano){meso-tetrakis(2,4,6-trialkylphenyl)porphyrinato}iron(III) complexes, $[Fe(R\text{-}TPP)(CN)_2]^-$ where R = Me, Et, or iPr, together with the parent $[Fe(TPP)(CN)_2]^-$, has been examined in dichloromethane-methanol solution by ^{1}H-NMR, ^{13}C-NMR, and EPR spectroscopies. While the ferric ion of $[Fe(TPP)(CN)_2]^-$ has shown a common $(d_{xy})^2(d_{xz},d_{yz})^3$ configuration, the ferric ions of the alkyl-substituted complexes $[Fe(R\text{-}TPP)(CN)_2]^-$ have exhibited the preference of a less common $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration. Spectroscopic characteristics of the complexes in which ferric ions take the $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration are (i) axial type EPR spectra, (ii) downfield shifted pyrrole and meta signals in ^{1}H-NMR spectra, and (iii) downfield shifted meso-carbon signals in ^{13}C-NMR spectra. Occurrence of the less common $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration in $[Fe(R\text{-}TPP)(CN)_2]^-$ has been ascribed to the electronic interaction between iron(d) and cyanide(p*) orbitals. The interaction stabilizes the d orbitals and induces $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration. Since the electron configuration of (dicyano){meso-tetrakis(2,6-dichlorophenyl)porphyrinato}iron(III), $[Fe(Cl\text{-}TPP)(CN)_2]^-$, which carries bulky electronegative chlorine atoms at the ortho positions, is presented as a common $(d_{xy})^2(d_{xz},d_{yz})^3$, the less common $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration in $[Fe(R\text{-}TPP)(CN)_2]^-$ can be ascribed, at least partially, to the electron-donating ability of the meso-aryl groups.

VIII-F-4 Resonance Raman Spectra of Legitimate Models for the Ubiquitous Compound I Intermediates of Oxidative heme Enzymes

CZARNECKI, Kazimierz[1]; KINCAID, James R.[1]; FUJII, Hiroshi
([1]Marquette Univ.)

[*J. Am. Chem. Soc.* in press]

Resonance Raman (RR) spectra are reported for two models of the compound I intermediates of oxidative heme proteins; namely, the imidazole (Im) and 2-methyl-imidazole (2-MeIm) complexes of the ferryl π-cation radical derivative of iron-(5,10,15,20-tetra-mesitylporphyrin), $[O{=}Fe(TMP^{+\bullet})(Im)]^+$ and $[O{=}Fe(TMP^{+\bullet})(2\text{-}MeIm)]^+$, which are stablized in dichloromethane solution at –80 °C. The present study yields high quality RR spectra of these complexes and provides the forst opportunity to compare the ν(Fe=O) stretching modes and the structure-sensitive core maker modes for a ferrylporphyrin π-cation radical with the corresponding modes of the neutral parent bearing the same trans-axial ligand. While the observed shifts in the frequencies of the core modes are in agreement with those expected upon formation of the π-cation radical, the results suggest that the isolated effect of macrocycle oxidation on the Fe=O stretching frequency is rather small; the observed shift being only about 4 cm^{-1} to lower frequency.

VIII-F-5 Newly Designed Iron-Schiff Base Complexes as Models of Mononuclear Non-Heme Iron Active Sites

FUNAHASHI, Yasuhiro; FUJII, Hiroshi

High valent iron-oxo species have been suggested as the active intermediates for catalytic oxygenation reactions by iron-containing oxygenases. In the reaction mechanisms of heme and binuclear non-heme iron enzymes, an $Fe^{IV}{=}O$ porphyrin radical species (Compound I) and a $Fe^{IV}_2(\mu\text{-}O)_2$ species (Intermediate Q) have been found to be responsible oxidant for alkane hydroxylation and alkene epoxidation. Such the high valent iron-oxo species are inferred to involve in hydroxylation of aromatic compounds by mononuclear non-heme iron oxygenases, the reaction processes of which, however, still remains to be established. In order to gain insight into the active intermediates, we try to synthesize iron complexes with bulky schiff-base ligands as biomimetic models of mononuclear non-heme iron active sites. The active oxygen adduct of these complexes, which would be kinetically stabilized by their steric hindrance, might provide a basis for understanding the oxygenation by mononuclear iron sites.

VIII-F-6 ^{17}O-NMR Study of Oxygen Molecules Bound to Copper Ions of Mononucler and Dineucler Copper Complexes

MIZUTANI, Mamoru; FUJII, Hiroshi

The activation of molecular oxygen by transition metals has fascinated chemists for decades. In particular copper-dioxygen complexes are suggested as key reaction intermediates in many enzymatic reactions. The differentiation in the function of these copper enzymes is attributed primarily to the coordination structure of the copper-dioxygen intermediate formed in the protein matrices, depending on the ligand donors, the geometry, and the coordination mode of the dioxygen. However, the correlation between these structural factors and the function/catalysis of the enzymes remains to be elucidated. To this end, there have been reported the structural and/or functional model complexes of copper-dioxygen adducts, such as μ-peroxo complex and μ-η_2,η_2 complex. The copper-bound dioxygen is not activated when it is end-on structure but activated via O-O bond cleavage when it is side-on structure. In order to investigate the relationships between electronic structure and reactivity of copper-dioxygen complex, we have examined ^{17}O-NMR spectroscopies of several copper-dioxygen complexes.

VIII-G Molecular Mechanism of Heme Degradation and Oxygen Activation by Heme Oxygenase

Heme oxygenase (HO), an amphipathic microsomal proteins, catalyzes the regiospecific oxidative degradation of iron protoporphyrin IX (heme) to biliverdinIXα, carbon monoxide, and iron in the presence of NADPH-cytochrome P-450 reductase, which functions as an electron donor. Heme oxygenase reaction is the biosynthesis processes of bile pigments and CO which is a possible physiological messenger. Recent development in the bacterial expression of a soluble form of heme oxygenase has made it possible to prepare in the large quantities for structural studies. In this project, we are studying the molecular mechanism of heme degradation and the oxygen activation by heme oxygenase using various spectroscopic methods.

VIII-G-1 Molecular Oxygen Oxidizes the Porphyrin Ring of the Ferric α-Hydroxyheme in Heme Oxygenase in the Absence of Reducing Equivalent

MIGITA, Catharina T.[1]; FUJII, Hiroshi; MATERA, Kathryn M.[1]; TAKAHASHI, Satoshi[2]; ZHOU, Hong[3]; YOSHIDA, Tadashi[3]; IKEDA-SAITO, Masao[1]
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[*Biochim. Biophys. Acta* **1432**, 203 (1999)]

Heme oxygenase catalyzes the regiospecific oxidative degradation of iron protoporphyrin IX (heme) to biliverdin, CO and Fe, utilizing molecular oxygen and electrons donated from the NADPH-cytochrome P450 reductase. The catalytic conversion of heme proceeds through two known heme derivatives, α-hydroxyheme and verdoheme. In order to assess the requirement of reduction equivalents, we have prepared the α-hydroxyheme complex with rat heme oxygenase isoform-1 and examined its reactivity with molecular oxygen in the absence of added electrons. Upon reaction with oxygen, a minor portion of the α-hydroxyheme in heme oxygenase is converted to verdoheme with the majority altered to a species which exhibits an optical absorption spectrum with a broad Soret band. The major species, which is EPR-silent, can be converted to the original α-hydroxyheme by addition of sodium dithionite. We have also found that oxidation of the α-hydroxyheme-heme oxygenase complex by ferricyanide or iridium chloride yields a species which exhibits an optical absorption spectrum and reactivity similar to those of the main product of the oxygen reaction. We infer that the oxygen reaction with the ferric α-hydroxyheme-heme oxygenase complex forms a ferric-porphyrin cation radical. We conclude, inconsistent to a previous report (Y. Liu, P. Moenne-Loccoz, T. M. Loehr and P. R. Ortiz de Montellano, *J. Biol. Chem.* **272**, 6909 (1997)), that in the absence of reducing agents, the oxygen molecule functions mainly as an oxidant for the porphyrin ring and has no role in the oxygenation of α-hydroxyheme. This result corroborates our previous conclusion that the catalytic conversion of α-hydroxyheme to verdoheme by heme oxygenase requires one reducing equivalent along with molecular oxygen.

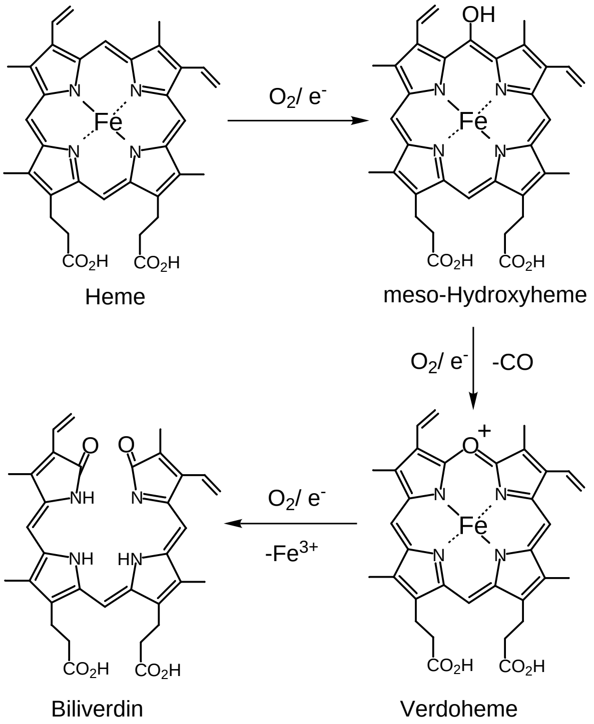

Figure 1. Reaction intermediates in the heme oxygenase catalyzed oxidation of heme to biliverdinIXα.

VIII-H Designing Artificial Photosynthesis at Molecular Dimensions

Photosynthesis is one of the finest piece of molecular machinery that Nature has ever created. Its ultrafast electron transfer and following well-organized sequence of chemical transformation have been, and will continue to be, challenging goals for molecular scientists. We are trying to mimic the function of photosynthesis by assembling molecular units that perform individual physical/chemical action. The molecular units include porphyrins, redox active organic molecules, and transition metal complexes.

Our present efforts focus on chemistry of manganese complexes (which are known to play a key role in oxygenic photosynthesis), and photochemistry of porphyrin/transition metal complex dyads. Our ultimate goal is to design artificial molecular systems that effect multiple chemical reactions triggered by light, on the basis of molecular rationale.

VIII-H-1 Synthesis and Characterization of Manganese Complexes

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([1]Kyoto Univ.)

In search for rationally designed dimanganese complexes that catalyze four-electron oxidation of water to dioxygen, we developed two xanthene-based dinucleating ligands, XT-btpa and XT-bterpy (Figure 1).

The XT-btpa (xanthene-bis(tris(2-pyridylmethyl)-amine) ligand has two metal-binding sites that are located in a well-defined geometry determined by the rigid xanthene spacer. The manganese complex was found to have an $[Mn_2(\mu\text{-}O)_2]$ core.

The XT-bterpy ligand also has two metal-binding sites with a well-defined geometry, and has two terpyridine units which provide more rigid and less decomposition-prone organic environment. Three manganese complexes, $[(XT\text{-}bterpy)Mn_2Cl_4]$, $[(XT\text{-}bterpy)Mn_2(tropolonato)_2](ClO_4)_2$, and $[(XT\text{-}bterpy)\text{-}Mn_2(2\text{-}picolinato)_2](ClO_4)_2$, were prepared; the X-ray structure of $[(XT\text{-}bterpy)Mn_2Cl_4]$ is shown in Figure 2. Either of these three complexes catalyzed disproportionation of H_2O_2 to water and dioxygen, with much higher activity than the related mononuclear complex $[(terpyridine)MnCl_2]$.

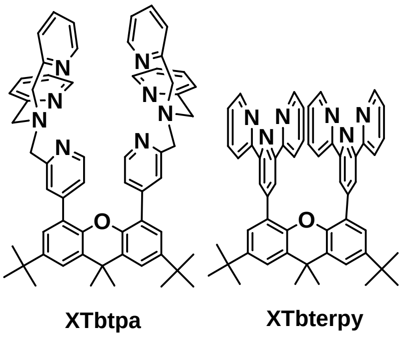


Figure 1. Two xanthene-based binucleating ligands.

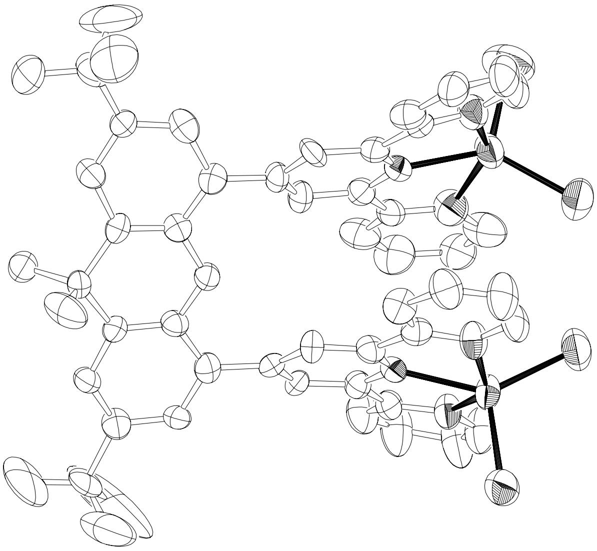


Figure 2. X-ray structure of $[(XT\text{-}bterpy)Mn_2Cl_4]$.

VIII-H-2 Synthesis and Photochemical Reaction of Porphyrin/Cobalt-complex Dyad Molecules

KIKUZAWA, Yoshihiro[1]; NAGATA, Toshi; OSUKA, Atsuhiro[1]
([1]Kyoto Univ.)

One of the essential features in natural photosynthetic reaction centers is ejection of the quinone acceptor from the protein to the “quinone pool,” which takes place after photoinduced electron transfer. To mimic this function, we prepared a porphyrin/Co(III)-complex dyad molecule (Figure 1), where the Co(III) moiety is expected to depart from the porphyrin moiety after photoreduction, due to the relative instability of six-coordinate Co(II) complex. The steady-state fluorescence spectrum of this dyad molecule revealed that the excited singlet state of the porphyrin in effectively quenched by the presence of the Co(III) moiety. Electrochemical estimation of the reduction/oxidation potentials suggested photoinduced electron transfer from the excited porphyrin to Co(III) can take place. Irradiation of this dyad molecule in CD_3COCD_3/CD_3CN solution led to formation of the $Co(III)\text{-}CD_3CN$ complex (80% yield by ^1H NMR) together with the imidazolyl porphyrin without the cobalt moiety. Since this ligand-exchange reaction proceeds only slowly in the absence of light, it is likely that the reaction is catalyzed by intramolecular photoinduced electron transfer.

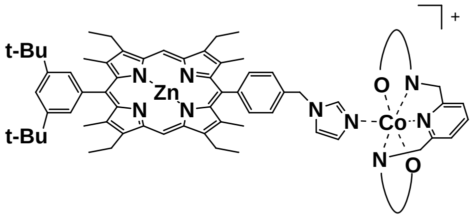


Figure 1. The porphyrin/cobalt(III)-complex dyad molecule.

VIII-I Development of New Metal Complexes as Redox Catalysts

Redox catalysis is an important field of chemistry which translates a flow of electron into chemical transformation. It is also one of the requisites for artificial photosynthesis. This project of ours aims at developing new metal complexes that perform redox catalysis at low overpotential. So far we have succeeded in preparing a series of terpyridine-catechol linked ligands; application of these ligands for development of new redox catalysts is currently in progress.

VIII-I-1 Synthesis of Terpyridine-catechol Linked Ligands and Their Cobalt(III) Complexes

NAGATA, Toshi; TANAKA, Koji

Transition metal catechol complexes are gaining interest because of unique electronic properties of the catechol ligand, specifically the two-electron redox transformation between catechol and quinone forms. Combination with the terpyridine ligand should provide metal complexes with interesting redox properties and well-defined geometry. The chemistry of terpyridine/catechol/metal ternary complexes, however, is often complicated by ligand disproportionation to give stable bis(terpyridine) complexes.

We prepared three terpyridine-catechol linked ligands (Figure 1) and their cobalt(III) complexes. The X-ray structure of two Co(III) complexes are shown in Figure 2. The two complexes have a different number of CH_2 units in the linker between terpyridine and catechol. It was revealed that the C_4 linked complex (part a) has a symmetric structure with the $(CH_2)_4$ linker running along an approximate mirror plane that contains the catechol ring and bisects the terpyridine ligand, whereas the C_5 linked complex (part b) has no such approximate symmetry. Since the local structures around the Co(III) center are very similar for the two complexes, the structural difference is solely due to the different lengths of the polymethylene linkers; the C_4 linker presents the “just fit” length while the C_5 linker has to go the winding way to accommodate the extra CH_2 unit.

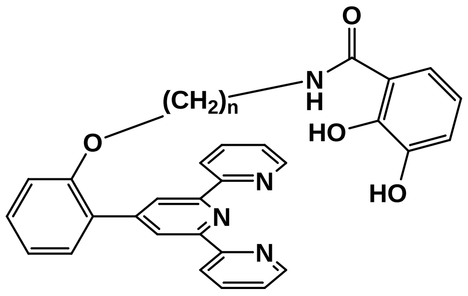
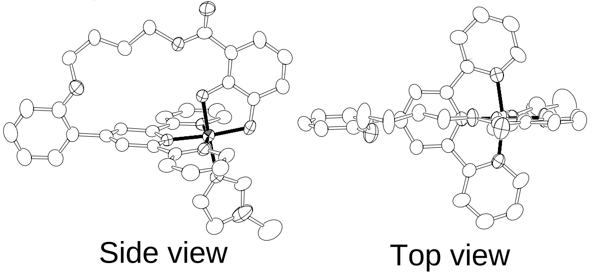


Figure 1. The terpyridine-catechol linked ligands.

(a) C_4-linkage



(b) C_5-linkage

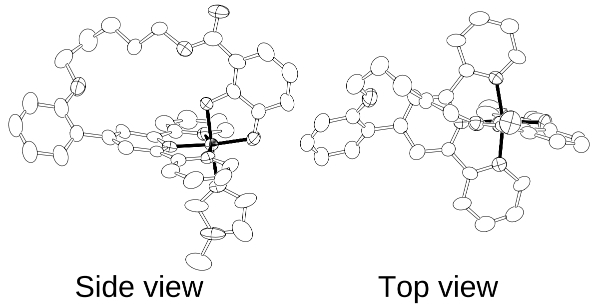


Figure 2. The X-ray structures of cobalt(III) complexes of the C_4- and C_5- linked ligands.

VIII-J Organic Molecular Materials with Novel Electronic Properties

Some aromatic and heterocyclic compounds show intriguing physical properties, such as superconductivity, ferromagnetism, and electroluminescence, in the solid state. The aim of our research is to design and synthesize such molecules. We have been working on three research projects: synthesis of organic conductors, fullerene chemistry, and organic electroluminescent (EL) materials.

VIII-J-1 Synthesis and Electron-Transporting Properties of Perfluorinated Decaphenylenes

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([1]Toyota Central R&D Labs.)

Recently, π-conjugated oligomers such as oligophenylenes and oligothiophenes have gained considerable attentions as organic electronic materials. Unlike polymers, these oligomers are monodisperse and can form clean thin films by vacuum deposition. If an electron-deficient oligomer forms a stable amorphous film and transports electrons with high mobility, it will be a good candidate for an electron-transporting material, which is an important component of highly efficient organic electroluminescent (EL) devices. Perfluorinated benzene rings are positively charged due to electronegative fluorine atoms and show intriguing interactions with electron-donating molecules due to quadrupole moments. We have developed the repetitive synthesis method of perfluorinated phenylenes **1-3** containing 10 phenyl rings. All $C_{60}F_{42}$s are colorless solid and soluble in CH_3Cl, THF, and aromatic solvents such as toluene. The differential scanning calorimetry (DSC) curves indicated that decaphenylenes **1-3** have the glass transitions at T_g = 123, 128, and 131 °C, respectively. The reduction potential peaks of the cyclic voltammograms (CV) shift more negative in the order **3** (–2.17 V), **2** (–2.24 V), and **1** (–2.49 V vs Fc/Fc^+) in THF. We fabricated organic EL devices with these perfluorinated compounds **1-3** to examine their electron-transporting properties. The luminance-voltage curves (Figure 1) indicated that **3** has the best electron-transporting ability in the three compounds.

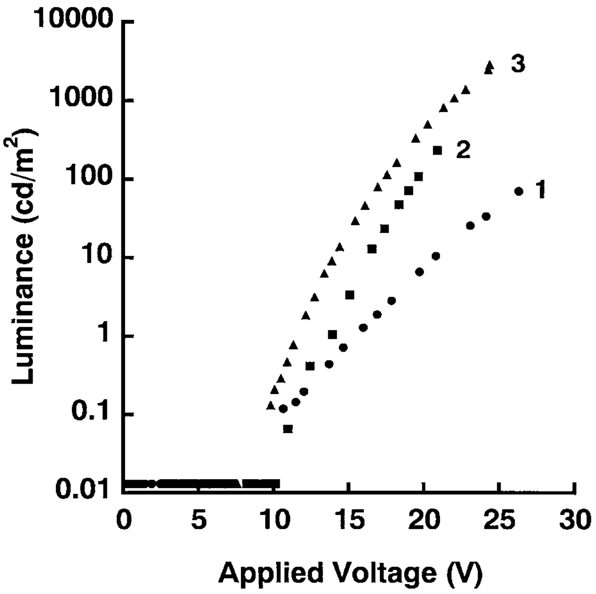
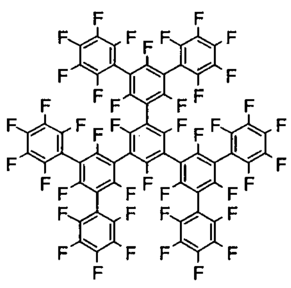


Figure 1. Luminance-voltage characteristics for the EL devices with **1-3** as electron-transporting layers: ITO/TPTE (60 nm)/Alq_3 (40 nm)/**1-3** (20 nm)/LiF (0.5 nm)/Al (160 nm).



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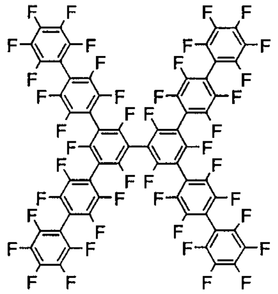

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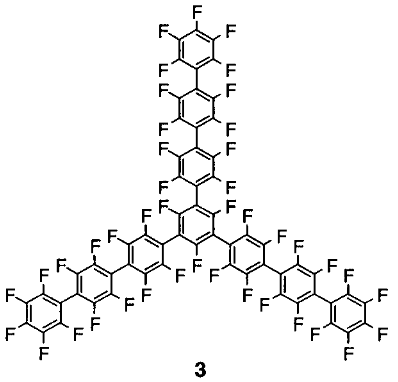

3

VIII-K The Effects of the 2D Spin-Echo NMR Pulse Sequence on Homonuclear Spin Systems

Dipolar interactions for homonuclear spin systems are averaged out by magic-angle sample spinning (MAS). The 2D spin-echo NMR pulse sequence can reintroduce the influence of the homonuclear dipolar interactions into MAS powder signals.

VIII-K-1 Novel Satellites in a Two-Dimensional Spin-Echo NMR Spectrum for a Homonuclear Spin-1/2 Pair in Rotating Solids

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([1]Tokyo Univ. Agric. Tech.; [2]Kyoto Univ.)

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We found additional resonance lines on both sides of the center line along the F1 axis, when the 2D spin-echo pulse sequence was applied to a solid-state ^{13}C-^{13}C spin system undergoing MAS. The lines are not attributed to well-known *J*-resolved doublets. To our surprise, the positions of the lines are determined by a quantity κ, which is a function of the sample spinning frequency and the difference of the isotropic chemical shifts. These lines were discovered for the first time as far as we know. The analysis based on a former publication was useful, but could not describe the general experimental scheme which employs an arbitrary value of t_1 increment. An arbitrarily chosen t_1 increment was applied for the experiments in the present study. The analytical representation for the 2D experiment is inevitable to explain the origin of the additional lines. We are now preparing such representation and the optimized simulation spectra.