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New multi-stage redox systems and new organic molecular metals

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Abstract - Exploration of new multi-stage redox systems and realization of new organic molecular metals are reviewed. New multi-stage redox systems, "peri-condensed Weitz type donors", have been designed. As basic skeletons, 3,9-, 1,7-, and 1,10-dithiaperylene (DTPR) and 1,6-dithiapyrene (DTPY) were synthesized. As chemical modifications for multi-dimensionality, alkylthio groups were introduced on the DTPY skeleton. Thus, 2,7-, and 3,8-methylthio derivatives (MTDTPY) and an ethylenedithio derivative (ETDTPY) were synthesized. All these donors showed reversible two-stage redox behavior with potentials comparable to that of TTF. Among charge transfer complexes prepared, 2,7-MTDTPY has produced new organic molecular metals which contain neither a TTF nor a TCNQ type framework.

INTRODUCTION

Pursuit of aromaticity, an important concept in organic chemistry, has created a variety of molecules with either expected or peculiar molecular properties, by integrating concepts of organic, physical, and theoretical chemistry (ref. 1). Aromaticity also participates in the recent remarkable scientific development of organic molecular conductors, by controlling the redox properties of the component molecules. The developments have been achieved by the advent of charge transfer (CT) complexes composed of tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) type molecules (ref. 2), which possess multi-stage redox nature as an essential molecular property (ref. 3). The redox nature depends greatly on the contribution of aromaticity of their ionic states.

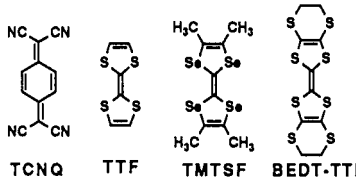

Fig. 1. TCNQ-and TTF-type conjugated molecules.

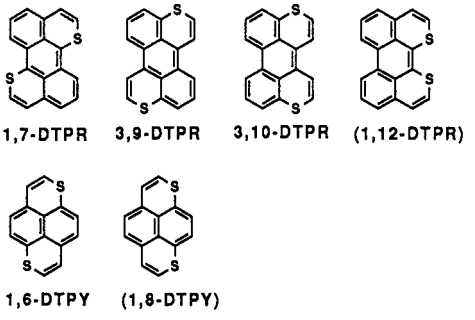

Fig. 2. Peri-condensed Weitz type donors with two chalcogens, DTPR's and DTPY's.

Even organic superconductors derived from TTF type donors have been explored , such as TMTSF and BEDT-TTF (Fig. 1). The chemical modifications of the TTF type donors play a central role in the development of this chemistry and physics. In this stage of progress, exploration of new classes of donors which do not contain TTF type skeletons is also important to extend the component molecules for CT complexes, to explore new materials and to enrich the basis of this science. Recently, we have designed and synthesized "*peri-condensed Weitz type donors*", 3,9-, 1,7-, and 3,10-dithiaperylene (DTPR) and 1,6-dithiapyrene (DTPY), as new multi-stage redox systems (Fig. 2) (ref. 4). Furthermore, non-TTF and non-TCNQ type organic molecular metals have been realized (ref. 5). We now describe the present stage of our investigations.

CORRELATION BETWEEN MOLECULAR PROPERTIES AND SOLID STATE PROPERTIES

Exploration of new organic molecular solids related to electrical, magnetic and optical properties has grown into an interdisciplinary area among organic chemistry, physical chemistry, and solid state physics. It is important, for this purpose, to correlate between the molecular properties and the solid state properties. In particular, the electronic structures in band theory have to be related to the molecular electronic structure.
The four schematic stacking models for the electronic structures of molecular solids are convenient to understand the electrical conduction process from a chemical viewpoint (Fig. 3): (1) stacking of closed-shell molecules, (2) stacking of radical ions, (3) uniform stacking of partial-ionic radical ions, and (4) distorted lower symmetry stacking. The HOMO-LUMO energy gap in (1) and the intramolecular Coulombic repulsion in (2) prevent smooth movement of electrons. In model (3), there exist no such unfavorable energies, that is, electron configurations before and after electron movement are isoelectronic. Peierls transition in one-dimensional electronic systems, which corresponds to pseudo Jahn-Teller distortion in a molecule, distorts uniform stacking into a lower symmetry one with more favorable energy (4). This is a typical schematic model for organic molecular conductors.

In sum, electronic conduction processes correspond to intermolecular redox phenomena or intermolecular CT phenomena. In molecular level considerations, multi-stage redox type molecules are essential to reduce the intramolecular Coulombic repulsion. A multi-dimensional electronic structure is useful to suppress the Peierls transition and to construct a metallic state. From such molecular level consideration, we can draw the essential molecular design strategies to realize new molecular metals: 1) construction of new multistage redox systems and 2) chemical modifications to introduce interstack interactions.

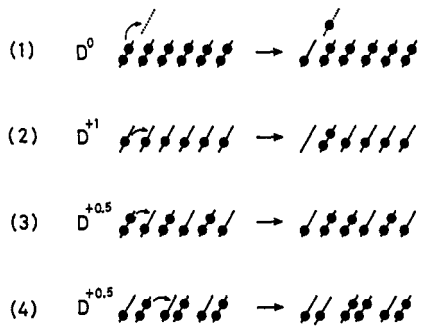

Fig. 3. Schematic models of electronic structures for organic molecular conductors.

MOLECULAR DESIGN AND SYNTHESIS OF NEW MULTI-STAGE REDOX TYPE DONORS, "PERI-CONDENSED WEITZ TYPE DONORS"

Polycyclic arenes, such as perylene, for example, opened the investigation for organic molecular semiconductors (ref. 6). Furthermore, perylene radical cation salts show metallic conductivity (ref. 7). Since the donor ability of polycyclic arenes is relatively weak, they usually formed neutral CT complexes with organic acceptors. We aimed at enhancement of donor ability for condensed polycyclic systems. Our molecular design strategy for new organic donors is the replacement of two of the sp^2 carbon atoms in a polycyclic arene by two chalcogens. This might produce a heterocycle with an increased donor ability, since the two electron oxidation state, the dication, of the resulting molecule is isoelectronic with the original arene (Fig. 4). Thus, dithiaperylene (DTPR) and dithiapyrene (DTPY) are designed based on the peri-condensed arenes, perylene and pyrene.

There are four reasonably stable isomers of DTPR and two isomers of DTPY. Among the isomers, 3,9-DTPR (ref. 8), 1,7-DTPR (ref. 9), and 3,10-DTPR , and 1,6-DTPY and their derivatives (ref. 4) have been prepared (Fig. 5, 6). The key steps in each synthetic schemes are the intramolecular dicarbonyl coupling in (1), the hydro-alkoxy-elimination in (2), the photochemical cyclization in (3), and the Friedel-Crafts type condensation in (4) for DTPY. In order to introduce multi-dimensionality, alkylthio groups are substituted on DTPY skeleton. Thus, by methylthio (MT-type) and ethylenedithio ET-type) modifications, 2,7-MTDTPY and ETDTPY were synthesized (ref. 5). Methylseleno derivative, 2,7-MSDTPY, and 3,8-MTDTPY were also synthesized (ref. 11). The key step for ETDTPY is the ring expansion in (5). All these donors are stable in the solid state, though 3,9- and 1,7-DTPR decomposed slowly in solution. Their electrochemistry measured by cyclic voltammetry shows that these heterocycles are actually two-stage redox systems and the oxidation potentials are much lower than those of perylene (1.06 V) and pyrene (1.16 V), and comparable to that of TTF (0.34 V) (Table 1, 2). Reflecting such electrochemical characteristics, these donors were oxidized to stable dications merely by dissolution in concentrated sulfuric acid. These new multi-stage redox systems are termed "*peri-condensed Weitz type donors* ".

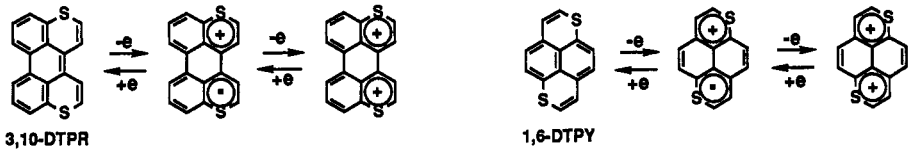

Fig. 4. Multi-stage redox nature of DTPR and DTPY.

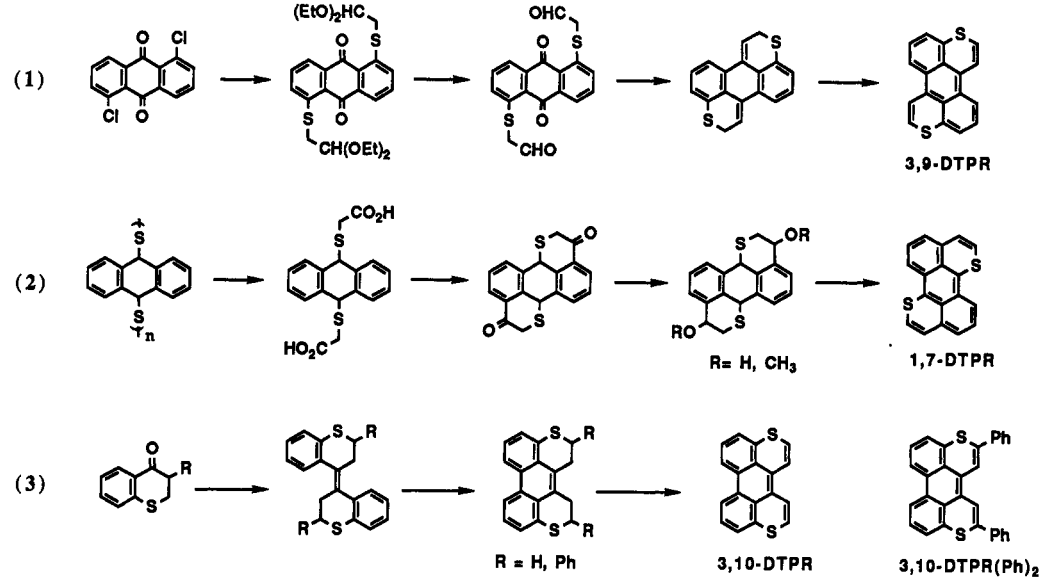

Fig. 5. Synthetic schemes for DTPR's.

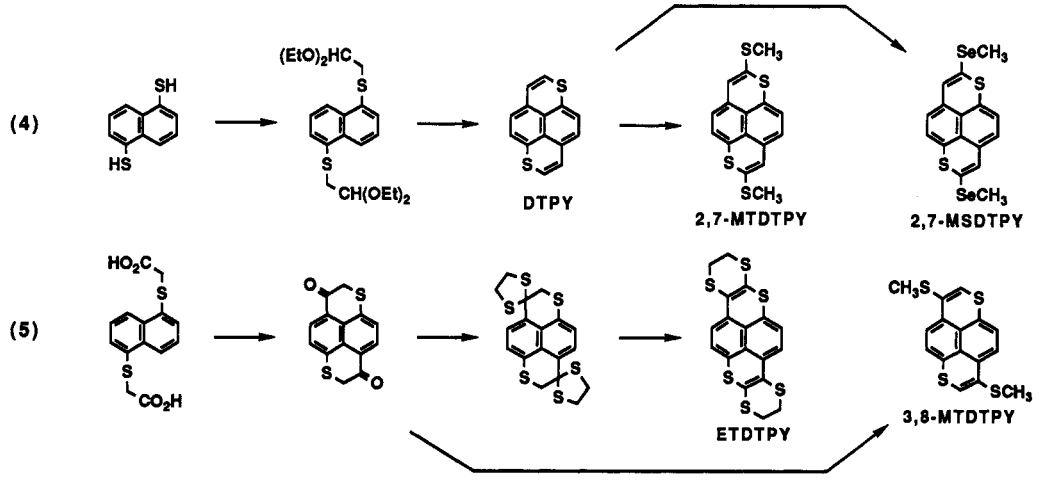

Fig. 6. Synthetic schemes for DTPY's.

Comparison of the physical properties of the three isomers of DTPR's clarifies their electronic characteristics. Three donors, 3,9-, 1,7-, and 3,10-DTPR, in this order, show increasing oxidation potentials which indicate that the energies of the HOMO's for the three donors are lowering in that order. This behavior coincides with the structural consideration that the anthracene moiety in 3,9- and 1,7-DTPR contributes to raise their HOMO's to a larger extent than the phenanthrene moiety in 3,10-DTPR. The MNDO calculations support such a qualitative consideration. In addition, the differences in the chemical shifts of ^{1}H-NMR data between neutral and dication species for each isomer also illustrate their electronic characteristics. Thus, as can be expected from one of the canonical formulae for dicationic species (for example, see Fig 4), the chemical shift differences of H-1, 2 and 3 which lie on the thiopyrane moieties are larger than those of the rest of protons. In sum, the physical properties of DTPR's are easily understandable from the structural formulae.

TABLE 1. Oxidation potentials of DTPR's.

Donor	3,9-DTPR	1,7-DTPR	3,10-DTPR
E_1^{ox}	0.30	0.39	0.49
E_2^{ox}	0.66	0.82	0.87
ΔE^{ox}	0.36	0.43	0.38
Solvent	PhCN	PhCN	PhCN

TABLE 2. Oxidation potentials of DTPY's.

Donor	DTPY	2,7-MT-DTPY	2,7-MS-DTPY	3,8-MT-DTPY
E_1^{ox}	0.36	0.34	0.37	0.40
E_2^{ox}	0.75	0.64	0.64	0.82
ΔE^{ox}	0.39	0.30	0.27	0.42
Solvent	CH_3CN	CH_3CN	CH_3CN	PhCN

CHARGE TRANSFER COMPLEXES AND V-SHAPE CORRELATION

Charge transfer complexes of these donors with organic acceptors and charge transfer salts with inorganic counter anions were prepared. The following five preparation methods were applied: (1) mixing, (2) concentration, (3) diffusion, (4) recrystallization, and (5) electrocrystallization. Methods (2) and (3) were used for most of the CT complexes and the method (5) for most of the CT salts. We obtained more than 100 CT complexes containing low-conducting semiconductors, high-conducting semiconductors, and molecular metals.

We can conveniently classify the CT complexes prepared into three groups, I, II and III, based on the so-called V-shape correlation (ref. 10). An important relationship known as the V-shape correlation between $h\nu_{CT}$ and $\Delta E^{o,r}$ is convenient to select the potentially highly conducting complexes and to predict the stacking mode, the ionicity or the energy of $h\nu_{CT}$ for complexes (ref. 11, 12, 13). Here, $h\nu_{CT}$ and $\Delta E^{o,r}$ denote the CT transition energy and the difference between the oxidation potential of the donor and the reduction potential of the acceptor, respectively. The plots of the experimental values of $h\nu_{CT}$ against the $\Delta E^{o,r}$ for our CT complexes are shown in Fig. 7. In order to make allowance for the experimental errors, the dotted lines are drawn on the upper and lower side from the V-shape in a range of 0.12 eV (1000 cm^{-1}). By using this plot, groups I, II, and III are characterized as neutral, ionic and non-V-shape complexes.

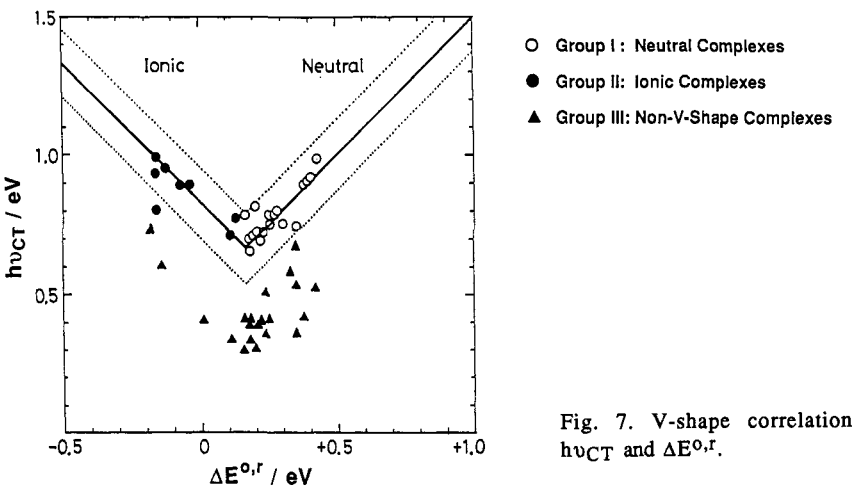

Fig. 7. V-shape correlation between $h\upsilon_{CT}$ and $\Delta E^{o,r}$.

The energies of CT transitions for the complexes of groups I and II can be conveniently evaluated from the following equations (1) and (2), respectively: (1) $h\nu_{CT,N} = \Delta E^{o,r} + 0.5$ (eV), (2) $h\nu_{CT,I} = 0.83 - \Delta E^{o,r}$ (eV). There are relatively good correlations between the calculated and the experimental values. The CT transition energies for group III complexes deviate from the correlation on the lower energy side. It is highly provable that the complexes possess no face to face overlap between the donor and acceptor components. In addition, the $\Delta E^{o,r}$ values of this group are in the range of -0.2 - +0.4 eV which correspond to the values to produce partial charge transfer between the donor and the acceptor. Therefore, the deviating, non-V-shape group might contain the potentially highly conducting complexes, and even metallic complexes.

Within group III, complexes of 2,7-MTDTPY with TCNQ, chloranil (CHL), and bromanil (BRL) and of 2,7-MSDTPY with TCNQ are found to show metallic conducting behavior (Table 3). *The two p-benzoquinone complexes, 2,7-MTDTPY-CHL and 2,7-MTDTPY-BRL are the first pure organic molecular metals within the limits of component molecules having non-TTF- and non-TCNQ-type conjugated electronic systems.*

In sharp contrast to the CT complexes with organic acceptors, the CT salts of peri-condensed Weitz type donors have hardly produced organic metals with unambiguous metallic solid state properties so far. However, a large number of highly conducting CT salts with conductivities larger than 10 Scm^{-1} are obtained (Table 4). Among them, 2,7-MTDTPY-$(PF_6)_n$ and 2,7-MSDTPY-$(AsF_6)_n$ show metallic conducting behavior around room temperature (ref. 14). In addition, preliminary result of crystal structure analysis for 2,7-MTDTPY-$(PF_6)_n$ indicates columnar stacking of the donor components (ref. 15). The V-shape correlation cannot be applied for the CT salts with inorganic counterions. However, the CT transition energies can be utilized to select highly conducting complexes, since the CT salts with the columnar stacking of the partially oxidized donor components might have lower energies than those of stoichiometric 1:1 CT salts with semiconducting behavior. As shown in Table 4, most of the electronic absorption spectra of the CT salts having high conductivities show low energies of transition, less than 0.5 eV, which is lower than the apex of the V-shape (0.67 eV).

TABLE 3. Selected prperties of organic molecular metals based on 2.7-MTDTPY

A	σ /Scm^{-1}	T_{MI} /eV	CT Transition obs. /eV	CT Transition calcd. /eV	$\Delta E^{o,r}$ /eV
TCNQ	110	110	0.41	0.66	0.16
CHL	140	240	0.58	0.83	0.33
BRL	230	125	0.35	0.84	0.34

TABLE 4. Selected Properties of highly conducting CT salts (> 10 Scm^{-1})

Donor	Anion	σ /Scm^{-1}	Ea /eV	CT /eV
2,7-MTDTPY	$I_{2.2}$	13	0.15	0.41
2,7-MTDTPY	BrI_2	11	0.11	0.42
2,7-MTDTPY	PF_6	43	metal	
2,7-MSDTPY	$I_{2.1}$	14	0.11	0.35
2,7-MSDTPY	BrI_2	11	0.11	0.42
2,7-MSDTPY	AsF_6	37	metal	0.42
2,7-MSDTPY	$CuBr_2$	160		0.36
ETDTPY	$I_{2.3}$	42	0.04	0.43
1,7-DTPR	NO_3	14	0.07	0.37

CRYSTAL STRUCTURES AND SELECTED PHYSICAL PROPERTIES FOR NEW ORGANIC MOLECULAR METALS

The crystal structures of 2,7-MTDTPY-TCNQ and 2,7-MTDTPY-CHL show the segregated, uniform stacking of the component molecules (Fig. 8). There are no short intrastack S...S distances. In sharp contrast, shorter interstack S...S distances which are less than the sum of van der Waals radii are found between sulfur atoms in the DTPY skeleton. The ionicity (the degree of CT) of the TCNQ complexes is evaluated to be 0.6-0.7 from the CN stretching frequency and the bond length ratio in TCNQ moiety. The ionicity of the CHL complex was assumed to be 0.6 from the bond length ratio in the chloranil moiety. Such segregated stacking structures and their partial ionicity are consistent with the metallic conductivity of the complexes (Table 3). A thermoelectric power measurement for the TCNQ complexes shows that the predominant electron carriers exist on the acceptor columns at higher temperatures and on the donor columns below 150 K. The electrical conduction of the CHL complexes is dominated by carriers on the donor. The sharp ESR linewidth suggests one-dimensionality. Thus the origin of the metal-insulator transition (T_{MI}) can be attributed to a Peierls instability (ref.16).

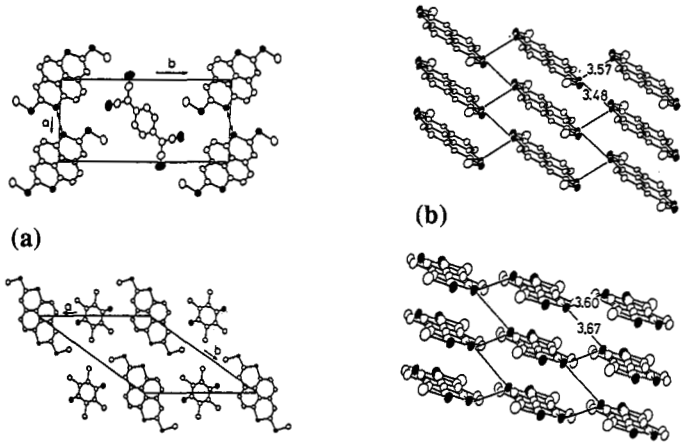

Fig. 8. Crystal structures of 2,7-MTDTPY-TCNQ (upper) and 2,7-MTDTPY-CHL (lower): (a) view along c axis and (b) view of sheet-like network of the donors.

Extended HMO calculations of overlap integrals for both complexes indicate a one-dimensional electronic structure with large anisotropy of the transfer integral between the stacking axis direction ($t_{//}$) and the perpendicular direction ($t_{\perp}$). The ratios, $t_{//}/t_{\perp}$, are 10-20 for the MTDTPY columns. Although the electronic structures show one-dimensional nature, the slightly short S...S contacts found in the crystal structures might contribute to realize the segregated stacking modes of crystal structures.

Apparently, our next step is the enhancement of the dimensionality in the electronic structures through stronger interstack interactions. This might be produced by selecting the other organic acceptors or inorganic counter-ions. Furthermore, in addition to enhance the dimensionality, introduction of a third force, for example hydrogen bonding, might also be important to explore new organic materials.

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