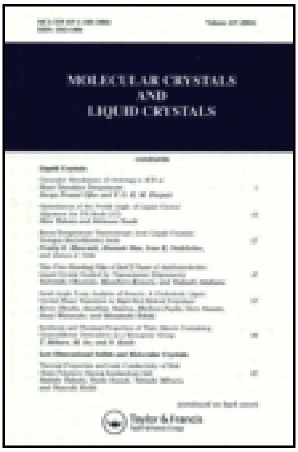

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Complex Formation of Strong Electron Donor: 1,3,6,8-Tetrakis(Dimethylamino)Pyrene

Kazukuni Nishimura [a], Seiji Hirate [a] & Gunzi Saito [a]
[a] Division of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto, 606-8502, Japan

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Complex Formation of Strong Electron Donor: 1,3,6,8-Tetrakis(Dimethylamino)Pyrene

KAZUKUNI NISHIMURA, SEIJI HIRATE and GUNZI SAITO

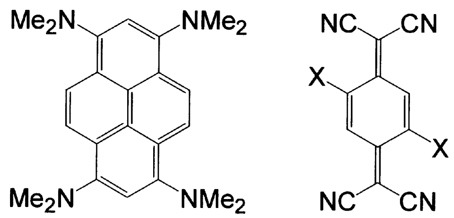
Division of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan

The strong electron donor 1,3,6,8-tetrakis(dimethylamino)pyrene (TDAP) provides three and two kinds of complexes with TCNQ and $(EtO)_2TCNQ$, respectively. Their structural, optical and magnetic properties are discussed.

Keywords : 1,3,6,8-Tetrakis(dimethylamino)pyrene (TDAP); Charge transfer (CT) complex; Crystal structure; UV-Vis-IR spectra; Polymorphism

INTRODUCTION

The strong electron donor 1,3,6,8-tetrakis(dimethylamino)pyrene (TDAP : Figure 1) was synthesized by Ueda, Sakata and Misumi, and they reported that the first redox potential (the averaged potential of oxidation and reduction peak potentials) of TDAP was -0.12 V *vs*. SCE in CH_3CN with two-electron transfer [1]. This value indicates that TDAP is a stronger electron donor than the conventional ones, namely any TTF derivatives and most of aromatic amines. We have prepared the TDAP complexes with a variety of TCNQs, *p*-benzoquinones and



TDAP **TCNQ** : X=H
$(EtO)_2$TCNQ : X=C_2H_5O

FIGURE 1 Chemical formulas in text

other acceptors, and discussed the criterion to afford partial charge transfer (CT) complexes of TDAP, however most of them were obtained with powder [2]. To improve further discussion about TDAP complexes, the studies on crystals of better quality are inevitable. Here, we present the single crystal study of TDAP complexes with TCNQ and $(EtO)_2$TCNQ.

EXPERIMANTAL

Three kinds of TCNQ complex (**1a**, **1b** and **1c** in Table 1) were obtained simultaneously by diffusion method with tetrahydrofuran. For **1a** and **1b**, only a few single crystals were found among many polycrystals. $(EtO)_2$TCNQ complex was obtained by direct mixing of a solution of TDAP and $(EtO)_2$TCNQ in chlorobenzene as black block single crystals (**2a**), however the yield was very low. Addition of hexane to the filtrate results in a precipitation of black powder, which exhibits the same UV-Vis-IR absorption spectra as those of **2a.** The stoichiometries were determined by elemental or crystal structure analysis. The diffraction intensity data were collected in four circle diffractometer or imaging plate with a monochromated Mo K_α radiation

TABLE 1 stoichiometry and appearance of TDAP complex

	acceptor	stoichiometry	appearance
1a	TCNQ	1:2	black plates
1b	TCNQ	~1:2	black needles
1c	TCNQ	~1:4	black block polycrystals
2a	$(EtO)_2TCNQ$	~1:2	black blocks

at room temperature. Optical measurements were carried out with a KBr disk. Static magnetic susceptibility measurements were done by the aid of SQUID.

RESULTS AND DISCUSSION

CRYSTAL STRUCTURE

Figure 2 shows the b^*-axis projection of **1a**. The DAA type alternating

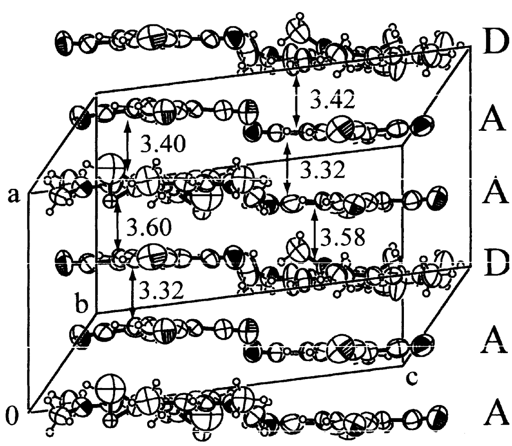


FIGURE 2 The b^*-axis projection of **1a**. The interplaner distances (Å) are also shown.

stacking column is formed along the *a*-axis, and each molecule is almost parallel to each other, of which dihedral angles are within 4°. Similar packing pattern is found in $[R(\eta^6\text{-}C_6Me_6)_2]^{2+}(TCNQ^-)_2$ (R=Fe,Ru) [3]. Two TDAP molecules and four TCNQ ones in the unit cell are crystallographically independent.

According to the molecular orbital calculation with the AM1 parameterization, the two 1,3-bis(dimethylamino)-allyl groups of $TDAP^{2+}$ twisted around the flat central naphthalene moiety, of which the dihedral angle is 22.8° [2]. However, the $TDAP^{2+}$ molecule is in fact planer in the crystal of **1a**, like as neutral TDAP molecule. In neutral crystal TDAP [2], the shifts of atom from the least square plane of pyrene moiety in TDAP molecule are within 0.1Å, while those of $TDAP^{2+}$ molecule in **1a** are 0.23-0.35Å at the outer side of naphthalene moiety.

For **1b** and **2a**, the structural analysis is in progress. The crystallographic data of **1a**, **1b** and **2a** are summarized in Table 2.

TABLE 2 The crystallographic data of TDAP complexes

compound	**1a**	**1b**	**2a**
chemical formula	$C_{48}H_{38}N_{12}$	$C_{48}H_{38}N_{12}$	$C_{56}H_{54}N_{12}O_4$
formula weight	782.91	782.91	959.12
$\boldsymbol{Z}$	2	4	4
space group	P1	(p monoclinic)	(c monoclinic)
a / Å	10.307(1)	22.57(2)	21.42(1)
b / Å	12.671(2)	25.05(3)	10.721(4)
c / Å	17.474(3)	7.132(8)	20.75(2)
α / °	72.899(8)	90	90
β / °	82.817(9)	97.76(9)	107.76(5)
γ / °	68.477(9)	90	90
d_{obs} / g·cm^{-3}	1.29	1.29	1.28
d_{cal} / g·cm^{-3}	1.282	1.302	1.284
V / Å^3	2028.7(6)	3995(7)	4963(4)
$\boldsymbol{R}$ ($\boldsymbol{F}$>4σ($\boldsymbol{F}$))	0.0814		

OPTICAL SPECTRA

Figure 3 shows the UV-Vis-NIR spectra of complexes **1a-1c** and **2a**. The C≡N stretch mode frequencies of TDAP complexes are summarized in Table 3. All peak positions of **1a** and **1c** are the same as those of the previously reported ones, namely fully ionic complex $(TDAP^{2+})(TCNQ^{-})_2$ and partially CT complex $(TDAP)(TCNQ)_4$, respectively [2]. The bands at around 11000-13000 cm^{-1} (band-C) in **1a-1c** can be assigned to absorption of $(TCNQ)_2^{2-}$ dimer [4], which is consistent with the DAA type structure of **1a**. The band at 3300 cm^{-1} in **1c** (band-A) is attributed to the electronic transition among the partially charged TCNQ molecules. The spectrum of **1b** resembles that of **1a**, while a band at 8000 cm^{-1} (band-B) is assigned to the electronic transition among the fully ionized molecules. This result strongly suggests the existence of the segregated columns of fully ionized $TCNQ^{-}$ in **1b**.

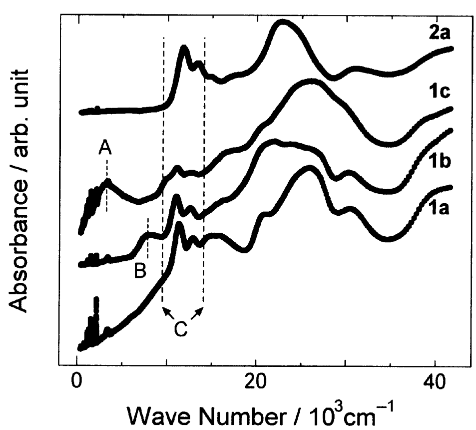


FIGURE 3 UV-Vis-NIR spectra in KBr of **1a-1c** and **2a**

TABLE 3 The C≡N stretching frequencies of TDAP complexes

	frequency ($\nu_{C\equiv N}$) / cm^{-1}				
$K^{+}\cdot TCNQ^{-}$			2196	2182	2167
1a				2179	2157
1b			2187	2174	2150
1c			2193	2178	2156
$K^{+}\cdot (EtO)_2TCNQ^{-}$				2185	2167
2a				2175	2153
$TCNQ^{0}$	2225	2222			
$(EtO)_2TCNQ^{0}$	2221				

Considering the absorption spectrum of **2a** together with the C≡N stretch mode frequencies, this complex is classified into a fully ionic complex $(TDAP^{2+})((EtO)_2TCNQ^{-})_2$ such as **1a.** That is different from the previously reported $(TDAP)((EtO)_2TCNQ)_3$ from benzene and acetonitrile, which is a partial CT complex [2].

MAGNETIC PROPERTIES

The magnetic susceptibility of **1b** obeys Curie-Weiss law (χ=C/(T-θ)) with C=0.273 and θ= -1.81K, though that of **1c** was well approximated by a 1D Heisenberg alternate chain model [5]. The Curie constant of **1b** corresponds to 73% of independent S=1/2 spins, suggesting the existence of antiferromagnetic interaction.

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