CHEMISTRY LETTERS, pp. 2061-2064, 1990.

Tetraaminoanthraquinones. New Donor for CT Complexes with Electric Conductivity

Masaru MATSUOKA, Hidetaka OKA, and Teijiro KITAO
Department of Applied Chemistry, University of Osaka Prefecture, Sakai, Osaka 591

Tetraaminoanthraquinones are found to be a novel electron donor to form intermolecular charge-transfer (CT) complexes with various acceptors. They show electric conductivity of 10^{-3} - 20 S cm^{-1} and are semiconductors.

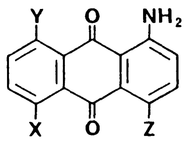
Dyes are recently very interested as functional materials for electronic, opto-electronic and photonic devices.[1)]

TTF, TMTSF or BEDT-TTF have been synthesized as a donor molecule and their CT complexes have been synthesized as synthetic metals,[2)] organic superconductors[3)] and the third order nonlinear optical materials.[4)] Their properties are correlated with the chemical structures for molecular design of these materials.

Dye molecules have coplanar π-conjugated structures and will become a valuable candidate as a donor for CT complex, but few of them have been reported. Recently we found that 1,4,5,8-tetraaminoanthraquinone **1a** is a good candidate for a donor component for CT complexes, and their electric conductivity and spectroscopic properties were determined.[5)]

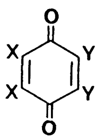
Aminoanthraquinones **1** have large and planar π-electron system which may stabilize the cation radical formed by intermolecular CT interaction with an acceptor, and have chromophoric system of intramolecular CT character. It has a partial charge separation even in the ground state and also has an ability to form intramolecular and intermolecular hydrogen bonding. Then it looks very interesting how this molecule interact with an acceptor in the formation of the CT complexes. Their packing mode in crystals are also interested from a view of their electrical properties.

Aminoanthraquinones **1a** - **1d** were synthesized as a donor. Among these, **1a** and **1d** gave the CT complexes with acceptors such as TCNQ or I_2 in methylene chloride. When **1b** or **1c** were mixed with TCNQ in solution, the interactions occurred and absorption peaks, indicating the formation of the anion radicals of TCNQ,[6] at 750 and 850 nm were observed but no precipitates formed. The hydroxy groups in **1b** and **1c** are not effective for the formation of the CT complexes (Table 1). The conductivity of the CT complexes was measured on a pressed power pellet.[7] Complexes were prepared by mixing each solution of a donor and an acceptor. Donors 1 have very low solubility in organic solvents. Various methods were employed to prepare the CT complexes. The details will be reported elsewhere.



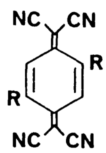
	X	Y	Z
a,	NH_2	NH_2	NH_2
b,	OH	NH_2	OH
c,	NH_2	OH	OH
d,	NH_2	NH_2	NHC_6H_4Ac-p

1



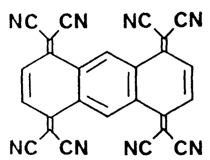
a, X=Y=F
b, X=Y=Cl
c, X=Y=Br
d, X=Cl, Y=CN

2

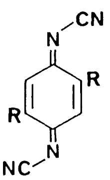


a, X=H
b, X=Me
c, X=Et

3

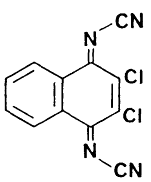


3d

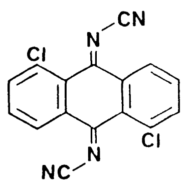


a, R=H
b, R=Me

4



4c



4d

Table 1. Conductivity and activation energy of CT complexes

Donor	Acceptor	σ/S cm^{-1} ($\times 10^3$)	Eg/eV ($\times 10^2$)
1a	**2a**	2.8	13
1a	**2b**	100	15
1a	**2c**	6.3	7.9
1a	**2d** (DDQ)	9.0	8.3
1a	**3a** (TCNQ)	19000	4.4
1a	**3b**	a)	
1a	**3c**	a)	
1a	**3d**	52	9.2
1a	**4a**	7.0	17
1a	**4b**	a)	
1a	**4c**	4.2	b)
1a	**4d**	c)	
1a	TCNE	a)	
1a	I_2	500	b)
1a	ClO_4	39	9.3
1a	ClO_4 d)	330	
1a	PF_6	250	7.1
1b	TCNQ	a)	
1c	TCNQ	a)	
1d	I_2	13	b)

a) Insulator. Test samples were obtained by evaporation of solvent.
b) Temperature dependence of the conductivity could not be attained and σ was measured at 304 K.
c) Complex did not be precipitated.
d) On a single crystals.

The conductivity of the CT complexes obtained from **1a** or **1b** - **1d** with various acceptors were measured and the results are summarized in Table 1. Benzoquinones **2**, TCNQ analogues **3**, dicyanoquinoneimines **4**,[9] TCNE and iodine were used as acceptors. Perchlorate and hexafluorophosphate of **1a** were also synthesized by the electrolysis method. The CT complexes generally consist of equimolar amounts of a donor and an acceptor. The conductivity of **1a** series are quite high and the highest value of 19 S cm^{-1} is obtained in **1a**-TCNQ complex, but it is drastically decreased to give insulator when methyl (**3b**) or ethyl (**3c**) groups are substituted in TCNQ molecule. The same tendencies are also observed in the complexes of **1a** - **4** series. Unsubstituted **4a** gave the conductivity of 7×10^{-3} S cm^{-1} but gives insulator in methyl analogue (**4b**). Naphthoquinone analogue **4c** gives conducting complex but non-planar anthraquinone analogue **4d** no longer forms the CT complex. Coplanar geometry of an acceptor is required for the formation of the conducting CT complexes. TCNE gives insulator but iodine gives high conductivity for **1a** and moderate one for **1d**.

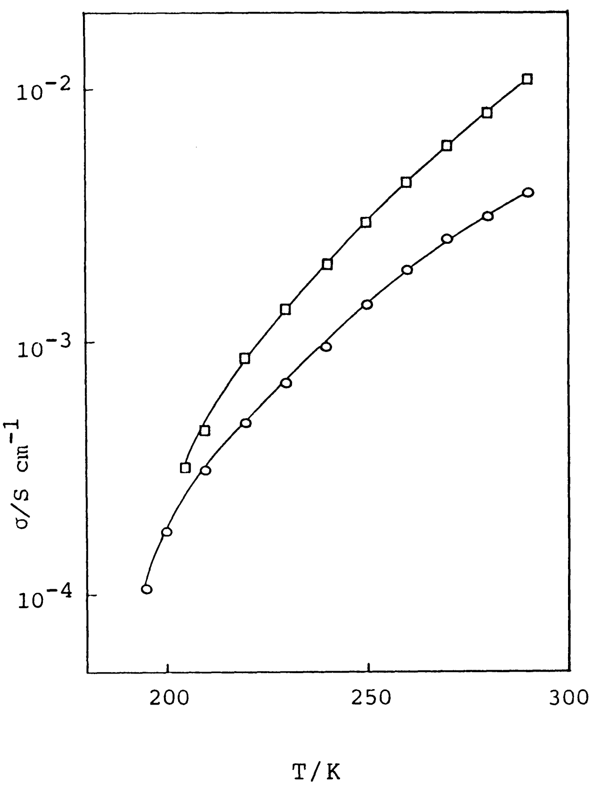


Fig. 1. Temperature dependence of σ value, ○; **1a-2d**, □; **1a-4a**.

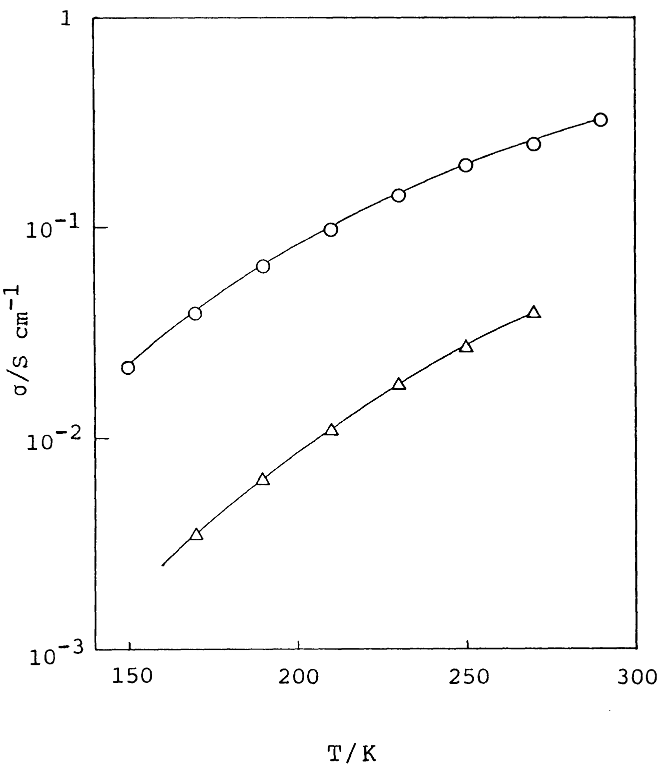


Fig. 2. Temperature dependence of σ value, ○; **1a**-PF_6, Δ; **1a**-ClO_4.

The **1a**-ClO_4 and **1a**-PF_6 complexes show quite high conductivities. In the case of **1a**-ClO_4, a small single crystals was obtained which shows higher conductivity in one order than that of the powdered sample. The TCNQ-**1b** and -**1c** complexes are insulator.

The temperature dependences of the conductivity were measured on the powder pellet samples. The results on **1a-2d** and **1a-4d** are shown in Fig. 1. Another plots for **1a**-PF_6 and **1a**-ClO_4 complexes are shown in Fig. 2. The conductivity decreases with the decrease of temperature in all cases. The Arrhenius' plots of these results show straight line, which mean these complexes are semiconductors. The activation energy (Eg) of each complexes are calculated and are summarized in Table 1. All samples exhibit similar temperature dependences of the conductivity and are semiconductors.

References

1) M. Matsuoka, J. Soc. Dyers Colourists, **105**, 167 (1989).

2) J. P. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, J. Am. Chem. Soc., **95**, 948 (1973).

3) D. Jerome, A. Mazaud, M. Ribault, and K. Bechgaard, J. Phys. (Paris), **41**, L95 (1980) ; S. S. P. Parkin, E. M. Engler, R. R. Schumaker, R. Lagier, V. Y. Lee, J. C. Scott, and R. L. Greene, Phys. Rev. Lett., **50**, 270 (1983).

4) P. G. Huggard, W. Blau, and D. Schweitzer, Appl. Phys. Lett., **51**, 2183 (1987).

5) M. Matsuoka, L. Han, H. Oka, and T. Kitao, Chem. Express, **3**, 491 (1988).

6) R. Foster and T. J. Tomson, Trans. Faraday Soc., **58**, 860 (1962).

7) Powder samples (100 mg) were pressed at 500 kg/cm^2 for 5 min. in a steel mold to get the pressed pellet. Gold was vacuum deposited at four points and four gold lead wires were attached by silver paste, respectively. The conductivity was measured by the four prove method.

8) J. R. Andersen and O. JØrgensen, J. Chem. Soc., Perkin Trans. 1, **1979**, 3095.

9) A. Aumüller and S. Hünig, Liebigs Ann. Chem., **1986** 142.

(Received August 16, 1990)