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THREE DIMENSIONALLY MODIFIED TCNQ. A CASE STUDY OF INTRAMOLECULAR CHARGE TRANSFER PHENOMENA

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Abstract Eight different 1:1 charge-transfer complexes prepared from the three-dimensionally modified TCNQ's with TTF, TMTTF, and OMTTF can be classified into three groups, I-III, on the basis of the magnitude of both the degree of CT and the electrical resistivity. These groups are characterized by small band gap semiconductivity with moderate CT, low conductivity with weak CT, and low conductivity with complete CT, respectively. The stacking mode of the complexes are also discussed.

INTRODUCTION

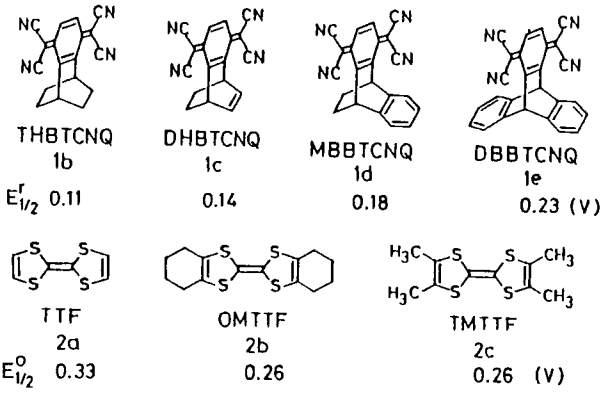
The paper presented at the Symposium on Celebration of 30 Years of Mulliken's Charge-transfer Theory falls into two parts. In the first part there is a brief review of our study on the intramolecular CT phenomena, and interesting but rarely documented notion "charge-transfer transition for symmetry-forbidden charge-transfer interaction", observed in the three-dimensionally modified tetracyanoquinodimethane (TCNQ).[1]

Since the main body of the first part has already been published, some solid state properties of the intermolecular CT-complexes between the three-dimensionally modified TCNQ's and tetrathiafulvalene (TTF) family, which form the second part of the paper, will be described in the present report.

The highly conducting organic CT complexes usually have the following structural and electronic properties in the solid state:[2] (a) segregated stacking of donors and acceptors, and (b) incomplete CT between the components. Several synthetic design criteria have been proposed for obtaining high conductivity. Generally, two-chain organic conductors composed of donor and acceptor moieties have been designed mainly with planar π-systems. We started the first systematic study on the effect of certain bulky group on the solid state properties of CT complexes composed of three dimensionally modified molecules of the TCNQ and TTF family, and would like to stress that (i) small band gap semiconductor can be prepared even from TCNQ having bulky groups, and that both (ii) the stacking mode, and (iii) the degree of CT (Z) can be affected by the bulky groups.

RESULTS AND DISCUSSION

In this study, we aimed at gaining rigid and bulky modifications with small electronic perturbations on TCNQ. To this end, four acceptors, tetrahydrobarreleno-TCNQ (THBTCNQ, 1b), dihydrobarreleno-TCNQ (DHBTCNQ, 1c), monobenzobarreleno-TCNQ (MBBTCNQ, 1d), and dibenzobarreleno-TCNQ (DBBTCNQ, 1e) in which a TCNQ moiety is incorporated into the rigid barrelene skeleton, were used to explore new intermolecular CT complexes. The first reduction potentials ($E^{r}_{1/2}$) of 1b-1e show that the acceptor strength increases gently and gradually with increasing unsaturation in the barrelene moieties. However, the difference of $E^{r}_{1/2}$ between TCNQ (1a) and both extremes, 1b and 1e, is only +0.07 V and -0.05 V, respectively: thus the electronic perturbation to the TCNQ caused by the introduction of bridged segments is fairly small.



Eight different 1:1 CT complexes were prepared using 1b -1e as acceptors and TTF (2a), octamethylene-TTF (OMTTF, 2b) and tetramethyl-TTF (TMTTF, 2c) as donors. Some of their physical properties are summarized in Table I. The difference between oxidation potential ($E^o_{1/2}$) of the donor and reduction potential ($E^r_{1/2}$) of the acceptor, i.e., $\Delta E^{o,r} = E^o_{1/2} - E^r_{1/2}$, can be used to predict the degree of CT for a complex. The $\Delta E^{o,r}$ values for the eight complexes of Table I are in the range of $+0.03 \sim +0.22$ V, which meet the requirement for incomplete CT.[2b,3] Interestingly, the complexes can be classified into three distinct groups, I-III, on the basis of the magnitude of both the degree of CT, Z,[4] and the electrical resistivity, ρ, of compacted powders (see Table I).

First, the group-I complexes are characterized by small band gap semiconductivity and incomplete CT. The two requisites (a) and (b) for the organic highly conducting complexes, TTF-TCNQ for example, can be substantiated by the detection of a very low energy band at near 3000 cm^{-1}, which has been determined to be an intrastack CT transition in a segregated stack with an incomplete CT.[5] Figure 1(a) shows the solid state electronic spectra of TTF-THBTCNQ and TTF-DHBTCNQ as

TABLE II Selected physical properties of eight 1:1 CT complexes.

Group	Group-I SBG Semiconducting complexes		Group-II Non-ionic complexes			Group-III Ionic complexes		
CT complex	2a-1b TTF-THBTCNQ	2a-1c TTF-DHBTCNQ	2b-1b OMTTF-THBTCNQ	2b-1c OMTTF-DHBTCNQ	2c-1c TMTTF-DHBTCNQ	2b-1d OMTTF-MBBTCNQ	2b-1e OMTTF-DBBTCNQ	2c-1e TMTTF-DBBTCNQ
$\Delta E^{o,r}$, V	+0.22	+0.19	+0.15	+0.12	+0.12	+0.08	+0.03	+0.03
Z, (IR)	0.76	0.84	0.11	0.13	0.24	0.92	1.00	0.97
Z, (Raman)	0.74	0.75	0.22	0.28	0.31	0.98	0.93	0.92
ρ, Ωcm (297K)	2.8	13	6.8×10^{5}	5.5×10^{7}	4.2×10^{6}	2.1×10^{6}	2.2×10^{7}	2.8×10^{3}
E_a, eV	0.095	0.14	0.39	0.44	0.36	0.34	0.64	0.30

well as that of TTF-TCNQ. In addition to the similarity of the spectra between TTF-TCNQ and the group-I complexes in the bands B, C, and D, the presence of band A at near 3000 cm^{-1} suggests that the group-I complexes possess a segregated stacking mode. In addition, the electrical resistivity for a single crystal of TTF-THBTCNQ (2.5×10^{-2} Ω cm) is fairly low and about two orders of magnitude smaller than that for the compacted powder sample. Such small resistivity and activation energy (0.045 eV) also support the prediction of a segregated stacking mode for the group-I complexes, although more data are needed to conclude the argument.

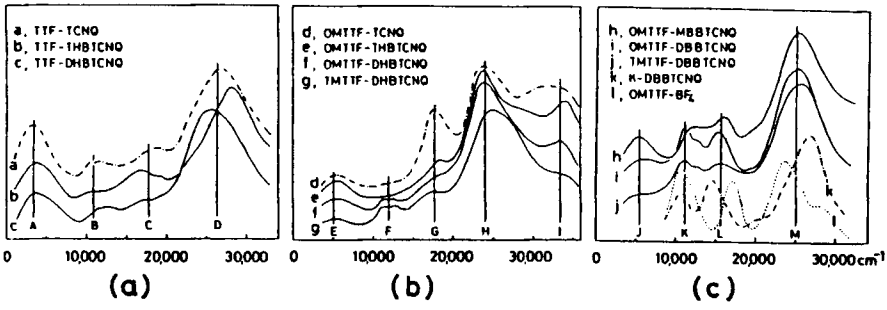


FIGURE 1 Absorption spectra of three distinct groups of CT complexes as powders dispersed in KBr.

The group-II complexes are characterized by low conductivity and small CT, i.e., neutral or non-ionic complexes. Such properties closely resemble those of OMTTF-TCNQ. The stacking mode of the complexes has been shown to be a mixed stacking of donor and acceptor components.[6] As shown in Figure 1(b), we found a weak CT transition for OMTTF-TCNQ (curve-d) at 5300 cm^{-1} which is in good agreement with an estimated value based on $\Delta E^{o,r} = +0.08$ V.[7] The strong absorption band H and I are nearly identical with the intramo-

lecular absorption of neutral TCNQ and OMTTF, respectively: this is consistent with a small degree of CT of the complex. These spectral features are recognized exactly in the group-II complexes (Figure 1(b)). Hence, we expect that the group-II complexes possess a mixed stacking mode.

The group-III complexes are characterized by low conductivity and almost complete CT, i.e., ionic complexes. In agreement with the complete CT, the absorption bands K, L, and M of the group-III complexes were also found in the ionic salts of the corresponding components, K-MBBTCNQ, K-DBBTCNQ, and OMTTF-BF_4 (Figure 1(c)). Furthermore, an additional band at 5000 cm^{-1} (band J) was observed in each of the group-III complexes, which can be assigned to a back CT transition between donor and acceptor.[7] These results strongly suggest a mixed stacking mode of this group.

Crystal structure analysis of OMTTF-DBBTCNQ shows indeed a mixed stacking donor and acceptor. This complex contains solvent molecule, benzene: the molecular ratio of the components, OMTTF : DBBTCNQ : benzene, was found to be 1:1:1. As shown in Figure 2, the donor and the acceptor form mixed stacking columns along c-axis with alternating the two components. The acceptors arrange in a columnar array so as to release the unfavorable steric repulsion between the bulky dibenzobarreleno moiety on TCNQ. The mean separation between the π-electron frameworks of the donor and the acceptor is 3.46 Å. The overlapping mode of the two components and the view of interstack interaction are depicted in Figure 3. The components are shifted from the direct overlap mode as found in OMTTF-TCNQ, in which the symmetry planes perpendicular to the long axis coincide nearly with each other.[6] Interestingly, there exist no short interstack interactions of S···S and S···N types.

The shortest S···N contact distance is 4.69 Å, which is fairly longer than the sum of the appropriate van der Waals radii. Thus the mixed columns in OMTTF-DBBTCNQ are strongly isolated with each other.

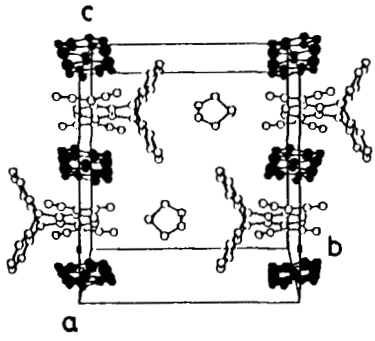


FIGURE 2

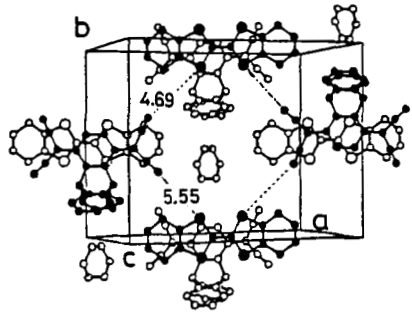


FIGURE 3

We calculated the degree of CT using the bond length ratio procedure by Kistenmacher et al.[8] For OMTTF-DBBTCNQ, the calculated Z is 1.08, which indicates complete transfer of charge. This value is well consistent with Z determined by IR and Raman procedures (Table I).

CONCLUSION

Recently, Soos et al. presented experimental and theoretical aspects on ionicity and paramagnetism of strong organic CT complexes. One of their important findings is that M_2P-$TCNQF_4$ and TMPD-$TCNQF_4$ are the first highly ionic ($Z \geq 0.9$) and paramagnetic organic CT complexes.[9] Although OMTTF-DBBTCNQ is found to be the third example of such highly ionic complexes with regular mixed stacking mode, the complex is, to best of our knowledge, the first example within the limits of the TTF-TCNQ type complexes. Interestingly, although the

acceptor strength of MBBTCNQ and DBBTCNQ are close to that of TCNQ and much weaker than that of $TCNQF_4$,[10] the group-III complexes are complete CT.

Finally, we prepared relatively highly conducting, non-ionic, and ionic CT complexes having bulky groups on acceptor, which are probably suited to theoretical study on the crystal cohesion in organic CT complexes. These results may open an unexplored area for chemical modifications to design molecular conductors, since many variations of the barrelene skeleton are possible.[11]

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