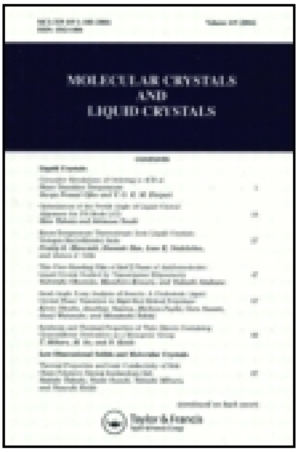

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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To cite this article: Olga Drozdova, Hideki Yamochi, Kyuya Yakushi, Mikio Uruichi & Gunzi Saito (2002): Charge Transfer Degree of BO Complexes, Molecular Crystals and Liquid Crystals, 376:1, 135-140

To link to this article: http://dx.doi.org/10.1080/10587250210800

Mol. Cryst. Liq. Cryst., Vol. 376, pp. 135-140

1058-725X/02 $12.00 + .00

Charge Transfer Degree of BO Complexes

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The accurate degree of charge transfer (CT) of BO complexes was obtained by Raman spectroscopy. A rich variety of states with partial CT in a wide range were available for BO materials, either due to stoichiometry or incomplete CT. Above certain acceptor strength, in the complex with BO there is a tendency for the acceptor to be ionized to the fully ionic state of -1 regardless the redox potential in general. The transport properties of BO complexes were discussed in terms of CT degree.

Keywords BEDO-TTF; Organic Metal; Charge Transfer Complex; Degree of Charge Transfer.

INTRODUCTION

BEDO-TTF (BO) is receiving continuous interest as organic donor molecule due to a large number of highly conducting complexes it has produced with both organic and inorganic components.[1-7] Origin of the metallic state was correlated with ability of BO to self-assemble into 2D conducting layer with small anisotropy by forming a number of short face-to-face (CH...O) and side-by-side (S...S) intermolecular contacts.[3] In charge transfer (CT) complexes, metallic conductivity can be achieved only when the charge on one or both of the components is partial, with only a few exceptions.[8] This can be confirmed by the presence of the CT band ("A-band") in the infrared region, and by the intramolecular absorption characteristic of both neutral and ionic species in the UV-VIS spectra. However, determination of the exact charge on the components of a CT complex is rather difficult. Besides, majority of DA-type complexes of BO are characterized by disorder in either the crystal structure or in the sample forms (powders). Often the charge residing on the molecule can be correlated with a particular bond length, or the frequency of some specific intramolecular vibration. Recently we have reported that linear dependence exists between the charge on BO and the frequencies of two C=C stretching modes (A_g) ν_2^D (ring C=C, superscript "D" stands for "donor") and ν_3^D (central C=C), in the range of ionicity of BO between 0 and +2.[9] Using this method, we were able to exactly determine the charge on BO in a large number of existing complexes.[9,10] This paper analyzes the correlation among the acceptor strength of the counter-component, charge on both components, and transport property of DA-type complexes of BO.

RESULTS AND DISCUSSION

Synthesis and properties of the complexes reviewed in this paper were reported in Refs [3-7] and Raman spectra were discussed in [9,10]. New data are included for complexes with TCNQ derivatives (see below). Table 1 summarizes the results. The complexes are classified into three large groups according to their transport properties and degree of ionization of the components: neutral insulators (both components are neutral), metallic and highly conducting ones with partially charged BO, and ionic insulators (both components are fully ionized). Within each group, the complexes are listed in the order of redox potential of the acceptor $E_{1/2}^1$ measured by CV in 0.1 M acetonitrile solutions of (TBA)(BF_4) *vs.* SCE at scan speeds of 10-20 mVs^{-1}.

Figure 1 shows how the charge on both components of the complexes changes with the redox potential of the acceptor. Generally, the stronger the acceptor, the more ionic complex it should form. Therefore, as the redox potential increases, one can anticipate gradual increase of the charge on the acceptor. However, on the contrary, the charge on the acceptor changes step-like from almost neutral to almost fully ionic (except for three cases of incomplete CT). Meanwhile, BO (which is also the component of the complex

TABLE 1. Redox potentials of the acceptor/anion (A), charge on the component molecules, and transport property of BO complexes.

$E_{1/2}{}^{1}(A)$, V	δ^A	δ^D	A	transport property
-0.98	-0.07	0.07	DNBP	I (insulating)
-0.95	-0.02	0.02	H_2TCNDQ	I
-0.56	-0.05	0.05	TNBP	I
-0.44	0.00	0.01	C_{60}	I
-0.38	-0.14	0.27	$Q(OH)_2$	I
-0.14	-0.08	0.08	TENF	I
0.01	-0.08	0.08	$(EtO)_2$TCNQ	I
-0.13	-1	0.5	$QCl_2(OH)_2$	M (metallic)
-0.12	-1	0.5	$QBr_2(OH)_2$	M
0.02	-0.9	0.45	DTNF	M
0.03	-0.79	0.45	BTDA-TCNQ	M
0.05	-0.84	0.42	$(MeO)_2$TCNQ	M
0.15	-0.96	0.48	Et_2TCNQ	M
0.16	-0.9	0.45	THBTCNQ	M
0.18	-1	0.5	DHBTCNQ	M
0.21	-1	0.4	C_{10}TCNQ	M
0.21	-0.9	0.45	DCNQ	M
0.22	-0.56	0.56	TCNQ	highly cond
0.29	-0.96	0.48	TCNE	M
0.32	-0.96	0.48	FTCNQ	M
0.40*	-2	0.33	HCDAH	highly cond
0.41	-0.96	0.48	F_2TCNQ	M
0.54	-0.99	0.63	DBDQ	M
0.64	-1	0.42	I_3	M
0.72	-0.94	0.47	HCBD	M
1.16*	-2	0.4	HCTMM	M
1.21*	-2	0.4	HCP	highly cond
1.32	-1	0.4	$C(CN)_3$	M
>1.34	-1	0.5	PIC	M
0.57	-1	1	$Ni(dto)_2$	I
0.6	-0.98	0.98	F_4TCNQ	I
0.64	-1	1	I_3	I
0.64	-1	2	I_3	I
0.9	-1	1	$Pt(dto)_2$	I
1.21	-1	1	$Pd(dto)_2$	I

* redox between 2- and 1- states.

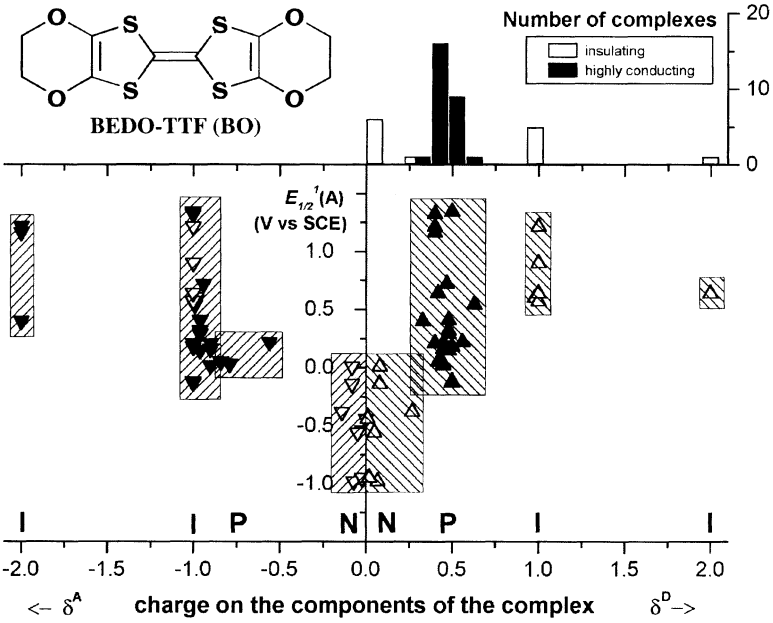

FIGURE 1. Charge on the components of DA type complexes of BO *vs.* $E_{1/2}^{1}$(A). N, neutral; I, fully ionic; P, partially charged state. Filled black and open triangles represent, respectively, highly conducting (including metallic) and insulating complexes. Top, number of complexes of BO as a function of the charge on BO.

responsible for the conducting properties) acquires partially charged states in a wide region of δ^D consistent with a diversity of conventional and non-conventional stoichiometries. Therefore, when the acceptor has certain strength, it is ionized in the complex to the fully ionic state of -1 regardless the redox potentials in general. Neutral insulators were formed when $E_{1/2}^{1}$(A) $\leq$ 0.01 V, ionic insulators when $E_{1/2}^{1}$(A) $\geq$ 0.57 V, while metallic and highly conducting complexes were found in a wide region of $E_{1/2}^{1}$(A) from -0.13 V to at least 1.34 V.

The top of the Figure 1 shows statistics of BO complexes as the number of complexes *vs.* the charge on BO. It is seen that: (1) the critical charge on BO is δ^D = +0.3, above which BO tends to provide metallic and highly conducting complexes; (2) there is a tendency to provide more complexes with high conductivity when $0.33 \leq \delta^D < 0.5$ than when $\delta^D \geq 0.5$. Both features characterize ability of BO to provide highly conducting complexes with δ^D lower than in other TTF-derived donors with similar size of π-electron system.

CONCLUSION

In the DA-type complexes, there was found a tendency of BO to disregard acceptor strength, reduce it to fully ionic state, while instead vary the charge on itself in accordance with the stoichiometry. A variety of the partially charged states of BO in the metallic and highly conducting complexes were observed. When BO is charged to $\delta^D \geq 0.3$, it shows the self-assembling nature and provides metallic complex in general, despite disordered feature in the crystal structure and in the sample form.

Raman spectra of complexes with TCNQ derivatives

Skeleton of TCNQ can be modified by chemical substitution, designing the derivative from the standpoint of the electron accepting ability, size, and symmetry. In the Raman spectra of the complexes, in addition to ν_2^D and ν_3^D of BO, two C=C stretching A_g modes of TCNQ appear in the same frequency region: ν_3^A (~ 64% of the external C=C) and ν_4^A (~ 50% of the ring C=C). Moreover, due to the resonance conditions (excitation wavelength λ=633 nm and λ=515 nm, absorption bands of $TCNQ^-$ at 420 nm, $TCNQ^0$ at 395 nm, and BO^+ at 1000 nm) the vibrational spectrum of TCNQ derivatives was strongly enhanced as compared to that of BO. In TCNQ ν_4^A as well as ν_2^A (C≡N stretch) were known to be charge sensitive (ionization shifts are $\Delta\nu_4$=63 cm^{-1} and $\Delta\nu_2$=23 cm^{-1}, respectively).[11] On the other hand, in F_4TCNQ no Raman-active mode is charge sensitive. Instead, four IR-active vibrations were found to have large ionization shifts, comprised of either ring C=C ($b_{2u}\nu_{33}^A$, 62 cm^{-1}), external C=C ($b_{1u}\nu_{19}^A$, 51 cm^{-1}), or C≡N stretch ($b_{2u}\nu_{32}^A$ and $b_{1u}\nu_{18}^A$, 42 and 34 cm^{-1}, respectively).[12] Therefore, we first examined Raman spectra of TCNQ derivatives in the region of C=C and C≡N stretching vibrations to check the ionization shifts, and then employed spectroscopic data for both donor and acceptor to analyze the charge transfer degree of the complexes. Stoichiometry of the complexes was established previously by other methods.[3]

Observed Raman frequencies for ring C=C, external C=C, and C≡N, respectively, were as follows (in cm^{-1}): $(EtO)_2$TCNQ, 1469, 1613, 2218; K·$(EtO)_2$TCNQ, 1418, 1606, 2201; $(MeO)_2$TCNQ, 1479, 1611, 2220; $(Et)_2$TCNQ, 1443, 1602, 2213; K·$(Et)_2$TCNQ, 1393, 1611, 2198; C_{10}TCNQ, 1446, 1604, 2221; K·C_{10}TCNQ, 1386, 1604, 2203; TCNQ, 1454, 1600, 2226; FTCNQ, 1460, 1619, 2221; Li·FTCNQ, 1412, 1619, 2212; F_2TCNQ, 1458, 1634, 2231; K·F_2TCNQ, 1424, 1634, 2214; CF_3TCNQ, 1456, 1612, 2222; K·CF_3TCNQ, 1396, 1613, 2210. Only ring C=C mode can be used as a measure of the charge, though the accuracy of such method falls as the absolute value of the ionization shift decreases and the crystal field effect becomes significant. In the complexes, the charge-sensitive modes ν_4^A, ν_3^D and ν_2^D were observed, respectively (in cm^{-1}): $(BO)((EtO)_2TCNQ)$, 1469, 1516, 1656; $(BO)_2((MeO)_2TCNQ)$, 1413, 1479, 1633; $(BO)((Et)_2TCNQ)$, 1403, 1473, 1632; $(BO)_{10}(C_{10}TCNQ)_4(H_2O)$, 1391, 1480, 1630; (BO)(TCNQ), 1419, 1464, 1613; $(BO)_4(FTCNQ)_2(AN)$, 1403, 1473, --; $(BO)_2(F_2TCNQ)$,1414, 1473, --; $(BO)(F_4TCNQ)$, 1448, 1423, 1585. Three complexes have 1:1 stoichiometry, among them two are insulators ($(BO)((EtO)_2TCNQ)$ is neutral and $(BO)_4(FTCNQ)_2(AN)$ is ionic), and (BO)(TCNQ) is a highly conductive one (on compressed pellet) with $|\delta^A|=\delta^D=0.56$, which is almost the same value as for organic metal (TTF)(TCNQ) ($|\delta^A|=\delta^D=0.55$).[13]

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