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Determination of the Charge on BEDO-TTF in Its Complexes by Raman Spectroscopy

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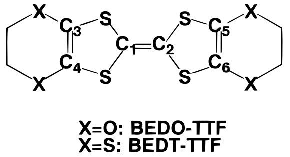
Abstract: Raman spectroscopy was employed as a fast and exact general method to determine the charge on BEDO-TTF (BO) in its complexes in any sample form such as single crystals, powders, and dispersed polymer films. Linear dependencies between the frequencies of two totally symmetric C═C stretching modes and the charge on BO were found and used to evaluate the charge transfer (CT) degree. The border between neutral (insulating) and partially CT (conducting) complexes based on BO was estimated as 0.3.

Introduction

The crystal structure and the degree of charge transfer (CT) between the components of a solid organic CT complex are the key parameters governing its physical properties. As a feature of organic π-systems, the total charge on a molecule (ρ) can be changed not only to integer but also to noninteger values owing to stoichiometry and/or incomplete (partial) CT. ρ is one of the important clues in determining the nature of the phase transition. In the case of a Peierls distortion, the periodicity of the modulated structure corresponds to ρ. For example, the first organic metal (TTF)(TCNQ),[1] in which $\rho = 0.59$, shows X-ray diffuse scattering at $(+1 - 0.59)b^*$ and at $(-1 + 0.59)b^*$ as evidence of structural fluctuation.[2a] The uniform partially charged state of a component molecule packed into uniform segregated columns or two-dimensional (2D) layers is required for metallic conductivity. However, in some cases special noninteger values of ρ cause nonmetallic states even for CT complexes having 2D conducting layers of uniformly charged components. The Mott insulators α′-(BEDT-TTF)$_2$X (X = AuBr$_2$, CuCl$_2$, Ag(CN)$_2$)[3a] and κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$[3b] are examples in which the conducting component molecule BEDT-TTF (ET, Chart 1) is charged to $\rho = 0.5$. Furthermore, for CT complexes consisting of alternating stacks of donor and acceptor molecules, a phase transition related to ρ was found. Namely, (TTF)(QCl$_4$) shows a neutral−ionic transition in which ρ changes between 0.34 and 0.64.[4]

Chart 1. BEDO-TTF and BEDT-TTF



Among conducting component molecules, BEDO-TTF (BO, Chart 1) is known to be an excellent donor in providing organic metals.[5] In the partially ionized state, a strong self-aggregation of BO leads to an apparently easy formation of the structurally and electronically 2D conducting layer. This feature, combined with the low ionization potential, allowed BO to afford metallic[5] and superconducting[6] complexes with a wide variety of organic acceptor molecules and organic and inorganic anions. Moreover, the metallic nature is stabilized down to low temperatures even

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(1) Abbreviation of the chemicals in the text: TTF, tetrathiafulvalene; TCNQ, 7,7,8,8-tetracyano-*p*-quinodimethane; BEDO-TTF or BO, bis(ethylenedioxy)tetrathiafulvalene; BEDT-TTF or ET, bis(ethylenedithio)-tetrathiafulvalene; TMTTF, tetramethyltetrathiafulvalene; TMTSF, tetramethyltetraselenafulvalene; HMTTF, hexamethylenetetrathiafulvalene; HMTSF, hexamethylenetetraselenafulvalene; QCl$_4$, *p*-chloranil; dto^{2-}, 1,2-dithiooxalate; HCDAH^{2-}, 1,1,2,5,6,6-hexacyano-3,4-diazahexadienediide; HCP^{2-}, hexacyanotrimethylenecyclopropanediide; HCTMM^{2-}, hexacyanotrimethylenemethanediide; SQA^{2-}, squarate; DNBP, 4,4′-dinitrobiphenyl; TNBP, 3,3′,5,5′-tetranitrobiphenyl-4,4′-diol; TENF, 2,4,5,7-tetranitrofluoren-9-one; Q(OH)$_2$, 2,5-dihydroxy-*p*-benzoquinone; BTDA-TCNQ, bis-1,2,5-thiadiazolo-7,7,8,8-tetracyano-*p*-quinodimethane; PIC$^-$, picrate; DTNF, 9-(dicyanomethylene)-2,4,7-trinitrofluorene; DCNQ, 2,3,-dicyano-1,4-naphthoquinone; DHBTCNQ, dihydrobarreleno-7,7,8,8-tetracyano-*p*-quinodimethane; THBTCNQ, tetrahydrobarreleno-7,7,8,8-tetracyano-*p*-quinodimethane; QBr$_2$(OH)$_2$, 2,5-dibromo-3,6-dihydroxy-*p*-benzoquinone; QCl$_2$(OH)$_2$, 2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone; Et$_2$TCNQ, 2,5-diethyl-7,7,8,8-tetracyano-*p*-quinodimethane; DBDQ, 2,3-dibromo-5,6-dicyano-*p*-benzoquinone; PhCN, benzonitrile; DCE, 1,2-dichloroethane; TCE, 1,1,2-trichloroethane.

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in severely disordered systems, such as single crystals with structural disorder of the counter component,[5c] polycrystalline samples, Langmuir−Blodgett films,[7,8] and composite polymer films.[9]

Unlike organic metals based on other TTF-related donors, such as ET or TMTSF, highly conducting BO complexes often have peculiar stoichiometries in a wide range, apart from the simple 2:1, 1:1, and 3:2,[5c] yet within only a few types of molecular packing. In the ordinary 1:1 $D^{+\rho}A^{-\rho}$ (D = donor, A = acceptor) type CT complexes, organic metals have usually been obtained as the CT degree is $0.5 \leq \rho < 1$, from the combination of D and A with $-0.02 \leq \Delta E \leq 0.34$ V (where ΔE is the difference in redox potentials between the first oxidation of D and the first reduction of A).[10] On the other hand, the ΔE region for metallic BO complexes is expanded far outside the upper boundary.[5c] Accordingly, one can expect that the metal/insulator border may be modified in the ρ value as well. Therefore, the exact estimation of the CT degree in BO complexes is inevitable. Unfortunately, however, an adequate general technique for BO complexes has not been reported. Among common methods, the IR absorption spectra (the frequency shift of skeletal vibrations)[11] and the single-crystal structure analysis (the change in the bond lengths)[12] were used to roughly estimate ρ. However, the former turned out to be inadequate because of poor accuracy,[5c] while the latter is limited to single crystals of good quality, which are not common for BO complexes.

On the other hand, Raman spectroscopy has been established as a powerful tool for the study of the oxidation state of the components of solid organic CT complexes.[2,13−17] An intramolecular vibrational mode appropriate for the analysis must satisfy the following criteria: (i) the character of the mode should not change on removing an electron from the HOMO or adding to the LUMO (i.e. the same spectral assignments can be used in the neutral and ionic species); (ii) the frequency should be sensitive to the degree of electron transfer and the ionization shift should be much larger than the environmental (crystal field) effects; and (iii) the linearity of the ν vs ρ dependence should be checked on samples with a priori known partial ρ. In the infrared spectra, vibrational modes are often superimposed on the low-energy electronic absorption typical of highly conducting materials, and overlapped with vibronic features whose frequencies and intensities are strongly dependent on the efficiency of the electron-molecular vibration (e-mv) coupling.[2b,13,14] Therefore, the more explicit Raman spectra are usually preferred. For TTF- and TCNQ-based molecules, the stretching mode of the carbon−carbon double bond commonly serves as an indication of the degree of CT.[2b,13−17] Alternatively, in TCNQ-type acceptors, the C≡N stretching mode can be used even though its ionization shift is smaller and the C≡N wings of TCNQ are known to be sensitive to the intermolecular interactions.[2b]

Our recent research has proved that Raman spectroscopy is the most suitable method for estimating ρ in BO complexes. This paper describes the relationship between ρ and the Raman shift of two charge-sensitive C═C stretching modes of the BO molecule in the compounds where the degrees of CT are well defined by the stoichiometry. Furthermore, the ρ values are determined for samples that have no adequate estimations from other methods.

Experimental Section

BO complexes examined were prepared according to the published method. Single crystals were used when available; otherwise, compressed powder pellets were employed. Raman spectra were measured at ambient conditions using a Renishaw Raman grating microscope spectrometer equipped with a He−Ne laser (λ = 632.6 nm) in 180° reflective geometry. To avoid damage, the laser power was attenuated down to as low a level as 0.20, 0.07, or 0.02 mW and focused in a 5 μm spot onto the sample surface. Spectra were collected by the static mode in the 1200−1700 cm^{-1} range for 300 s with 2 cm^{-1} resolution. An Ar laser (λ = 514.5 nm) was used for $(BO)_3(C_{60})(solvent)_x$ complexes and bromide reticulate doped polymer (RDP) films, in which the laser power and the accumulation time were 0.20 mW/100 s and 7 mW/10 s, respectively.

Results

Raman spectra of the neutral, monocation, and dication BO in the 1250−1700 cm^{-1} range are shown in Figure 1. Two peaks are assigned to the totally symmetric (A_g) stretching vibrations of the central (C_1═C_2, Chart 1) and ring (C_3═C_4 and C_5═C_6) bonds, ν_3 and ν_2, respectively, according to the normal coordinate analysis.[18,19] The ionization shifts are approximately 110 and 70 cm^{-1} per unit charge for ν_3 and ν_2, respectively, and are large enough to correlate each of them with ρ.

Standard materials of the degree of CT are listed in Table 1 along with observed Raman shifts. Neutral BO and cation radical salts with closed-shell anions were selected whose compositions were unambiguously established by such methods as X-ray crystal structure analysis, elemental analysis, and crystal density measurement. Then the ρ values were simply calculated from

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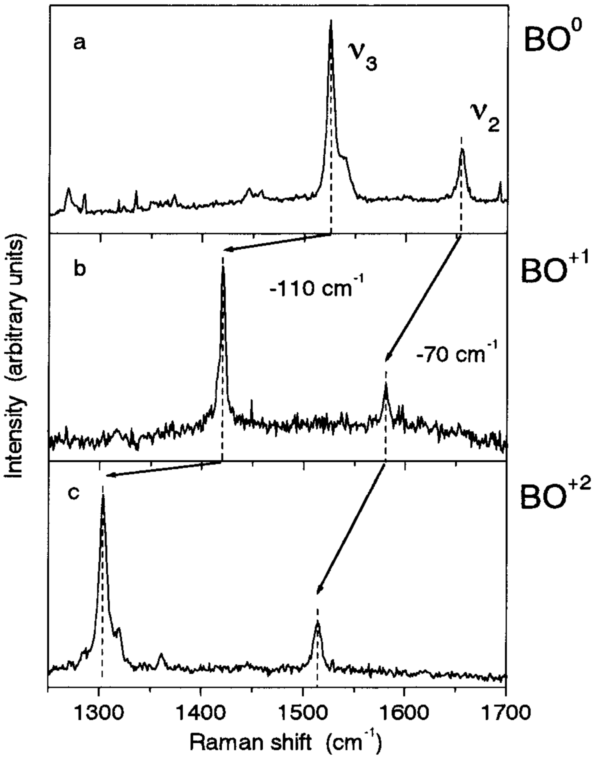

Figure 1. Raman spectra of the (a) neutral BO, (b) monocation in $(BO)_2[Ni(dto)_2]$, and (c) dication in $(BO)(I_3)_2$ in the region of C=C stretching vibrations.

Table 1. Standard Materials of the Degree of CT

compd	ρ	ν_3 (cm^{-1})	ν_2 (cm^{-1})	notes
neutral BO	0	1526	1655	*a, e*
$(BO)_6(HCDAH)$	1/3	1489.5	1639	*a, b, f*
$(BO)_5(HCP)(Ph\text{-}CN)_{0.2}$	0.4	1481	1632	*a, b, g*
$(BO)_5(HCTMM)(Ph\text{-}CN)_2$	0.4	1480	1632	*a, b, g*
$(BO)_{10}[C(CN)_3]_4(H_2O)_3$	0.4	1475	1630	*a, g*
$(BO)_{2.4}I_3$	0.42	1476	1630	*a, b*
$(BO)_9(NiBr_4)_2(DCE)_4$	4/9	1475	1630	*b, c, h*
$(BO)_4(SQA)(H_2O)_6$	0.5	1475.5	1629.6	*a, b, g*
$(BO)_2Cl(H_2O)_3$	0.5	1472	1625.5	*d*
$(BO)_2Br[MnBr_2(H_2O)_4](H_2O)$	0.5	1470	1625	*a, b, i*
$(BO)I_3$	1.0	1414	1588	*a, b, j*
$(BO)_2[Ni(dto)_2]$	1.0	1421	1581	*b, c, k*
$(BO)_2[Pd(dto)_2]$	1.0	1420	1581	*b, k*
$(BO)(I_3)_2$	2.0	1304	1514.5	*b, j*

[a] The elemental analysis confirmed the composition. [b] The composition was determined by the X-ray crystal structure analysis. [c] The crystal density was measured to support the structural analysis. [d] Although different compositions were reported for this complex, the degree of CT on the BO molecule was concluded to be 0.5 (see ref 20). Conducting properties were first reported in ref 20a. [e] For sample preparation, see refs 5a and 21. [f] For sample preparation and conductivity, see ref 22. [g] For sample preparation and conductivity, see ref 5c. [h] For sample preparation and conductivity, see ref 23. [i] For sample preparation and conductivity, see ref 24. [j] For sample preparation and conductivity, see ref 12. [k] For sample preparation and conductivity, see ref 25.

the charge on the counter component and the stoichiometry. For inorganic anions, the charge usually can be regarded as an integer value. However, an exceptional case was reported for I_3. For this anion, the noninteger charge was estimated in $[\text{tetrakis(thiomethyl)TTF}](I_3)_{0.823}$, based on the ESR spectra to which the donor molecule and I_3 contributed individual signals.[26] In the case of $(BO)_{2.4}(I_3)$, only a signal from the BO radical cation was observed, and hence, it was concluded that I_3 is a monoanion in this complex. The charge of this anion in 1:1 and 1:2 complexes was also estimated as −1 because of their nonmagnetic property.[12] Also, it should be mentioned that $[MnBr_2(H_2O)_4]$ was found to be a neutral species based on the magnetic properties of $(BO)_2Br[MnBr_2(H_2O)_4](H_2O)$.[24] For $(BO)_2[Ni(dto)_2]$ which consisted of alternating stacks of BO dimers and the counterion, the temperature dependence of the magnetic susceptibility was well explained by the singlet−triplet model of the dimerized spins in the BO monocation dimers.[27] The Pd derivative shows higher oxidation potential for the redox process between dianion and monoanion states;[25] therefore, it is safe to conclude that BO has the unit positive charge in $(BO)_2[Pd(dto)_2]$. Organic anions could have a noninteger charge in the complexes. However, for HCP, HCTMM, $C(CN)_3$, and SQA, the integer values of negative charges were estimated based on the spectroscopic or redox data in ref 5c. For the HCDAH complex, the ESR spectra consisted of only one Lorentzian whose angle dependence was interpreted as a signal from the BO cation radical.[28] This result assigned HCDAH in this complex as a closed-shell dianion.

Among the standard materials, all complexes with partial CT were conducting. No difference was observed between frequencies measured on powder and a single crystal of a given material. On single crystals, the ν_3 mode was observed as a narrow Lorentzian with line width (full width at a half-maximum) $\Gamma \leq 12$ cm^{-1}.

Data for standard materials are plotted in Figure 2a. The dependencies of ν_2 and ν_3 vs charge were almost linear up to $\rho = 2$. Linear fitting of the standard points gave the following formulas for determining the charge on BO:

$$\rho = (1524.9 - \nu_{3,\text{obs}}\,(\text{cm}^{-1}))/109.0 \qquad (1)$$

$$\rho = (1660.8 - \nu_{2,\text{obs}}\,(\text{cm}^{-1}))/74.1 \qquad (2)$$

from observed values of $\nu_{3,\text{obs}}$ and $\nu_{2,\text{obs}}$.

The error of the determination of the charge value, $\Delta\rho$, was ±0.05 and ±0.1 from ν_3 and ν_2, respectively, given $\Delta\rho$ was deduced from the scatter of the standard points with the same charge. Since the spectral resolution in our experiments gave only a minor contribution of ±0.01 charge unit, the error $\Delta\rho$ was entirely determined by the crystal field effects.

Representative Raman spectra of $(BO)_2Cl(H_2O)_3$ ($\rho = 0.5$), $(BO)_5(HCTMM)(Ph\text{-}CN)_2$ ($\rho = 0.4$), and $(BO)_6(HCDAH)$ ($\rho = 0.33$) with different ρ values are shown in Figure 3.

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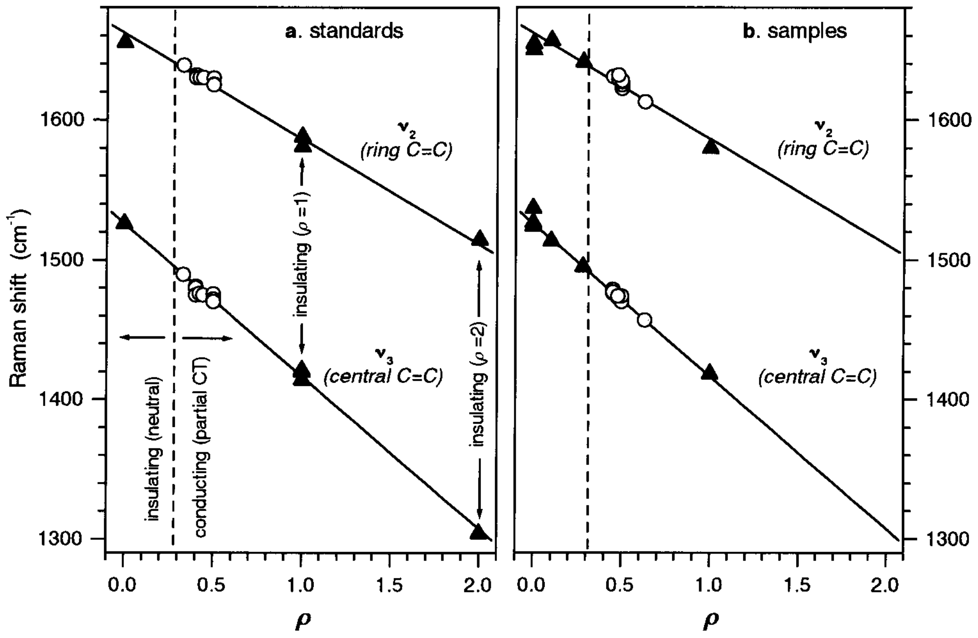

Figure 2. Dependence of the Raman frequencies ν_2 and ν_3 vs the charge on BO. (a) Standard materials from Table 1. Solid lines: linear fits on standard materials. (b) Sample materials from Table 2. Solid lines are reproduced from part (a) for estimation of the ρ values of the samples by measured frequencies ν_2 and ν_3. Triangles: insulating. Circles: metallic and highly conducting materials.

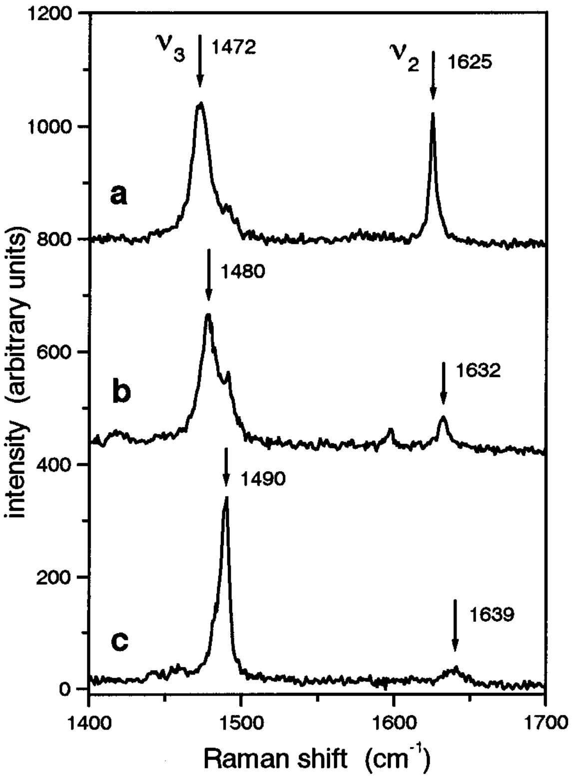

Figure 3. Raman spectra of (a) $(BO)_2Cl(H_2O)_3$, (b) $(BO)_5(HCTMM)(Ph\text{-}CN)_2$, and (c) $(BO)_6(HCDAH)$ with ρ = 0.5, 0.4, and 0.33, respectively (from top to bottom).

Table 2. Raman Shift and Estimated Charge on BO in Sample Materials[g]

	compd	ν_3 (cm^{-1})	ν_2 (cm^{-1})	ρ	notes[a]
I	$(BO)(DNBP)$	1537	1663	0	*b*
II	$(BO)(TNBP)$	1526.5	1654.5	0	*b*
III	$(BO)_3(C_{60})(C_6H_6)_x$	1524	1650	0	*b*, *c*
IV	$(BO)_3(C_{60})(CS_2)_x$	1524	1650	0	*b*, *c*
V	$(BO)(TENF)$	1513.5	1656.5	0.1	*b*
VI	$(BO)(Q(OH)_2)_2$	1495	1641	0.28	*b*
VII	$(BO)_2Br(H_2O)_3$	1474	1628	0.50	*d*
VIII	$(BO)_7(BTDA\text{-}TCNQ)_4$	1476.5	1631	0.45	
IX	$(BO)_6(PIC)_3(TCE)$	1471	1628	0.50	
X	$(BO)_2(DTNF)(CH_3CN)$	1479	1631	0.45	
XI	$(BO)_2(DCNQ)$	1477	1631	0.45	
XII	$(BO)_2(TCNE)$	1473	1629	0.48	
XIII	$(BO)_2(DHBTCNQ)$	1471.5	1622.5	0.50	
XIV	$(BO)_2(THBTCNQ)$	1477	*h*	0.45	
XV	$(BO)_2(QBr_2(OH)_2)$	1470	1625	0.50	
XVI	$(BO)_2(QCl_2(OH)_2)$	1470	1627	0.50	*e*
XVII	$(BO)_2(Et_2TCNQ)$	1474	1632	0.48	
XVIII	$(BO)_{11}(DBDQ)_7(CH_3CN)$	1457	1613	0.63	
XIX	$(BO)_x[Pt(dto)_2]_y$	1418.5	1580	1.00	*f*

a: For sample preparation and conductivity data, except for the complexes (III), (IV), (VII) and (XIX), see ref 5c. *b*: The infrared absorption spectrum was represented as a superposition of the neutral component molecules, and hence the complexes were supposed to be neutral. *c*: The composition was estimated by the elemental analysis, where x ≤ 2. *d*: For sample preparation and conductivity, see refs 9c, 12. *e*: See also ref 24. *f*: For sample preparation, see ref 25. [g] The spaces separate insulating (neutral, top and ionic, bottom) and conducting (middle) complexes. [h] Overlapped with the 1592 cm^{-1} peak of THBTCNQ.

Table 2 lists observed Raman shifts and estimated ρ values on several complexes where the CT degree is unknown from other methods. The data are plotted in Figure 2b using the correlation lines taken from Figure 2a.

It should be noted that although ν_3 is more easily detectable and gives ρ values that are more accurate than those from ν_2, it is important to use both peaks to check the oxidation state of BO. The advantage of having two criteria in determining ρ is invaluable when multiple peaks are observed in the region of interest — that is, when organic acceptor/anion has C=C, C=O, or N=O bonds complicating the spectrum. To distinguish between donor and acceptor/anion peaks, we considered the spectral regions where ν_2 and ν_3 could appear, respectively. Then, using (1) and (2) we calculated ρ for all features in those regions and looked for the correspondence between estimations from ν_2 and ν_3, which agreed within experimental error ($\Delta\rho$). To illustrate the method, below we give an example of the determination of ρ in **XIII**. Since the ΔE value for the donor−acceptor pair is calculated as 0.25 V, the D/A ratio is greater than unity, and furthermore the complex is metallic, therefore we expect $0 < \rho \leq 0.5$ (at most 1), and the frequency regions of interest are from 1415 to 1540 cm^{-1} (ν_3) and from 1585 to 1665 cm^{-1} (ν_2). The following peaks were observed: 1453 (within the region of ν_3), 1471.5 (ν_3), 1590 (ν_2), and 1622.5 cm^{-1} (ν_2). Assigning all of them formally to BO, we calculated ρ as +0.66, +0.49, +0.96, and +0.52, respectively, using (1) or (2) where appropriate. Two of them coincided within experimental error: +0.49 and +0.52. Therefore, we finally identified these as ν_3 (1471.5 cm^{-1}) and ν_2 (1622.5 cm^{-1}) of BO and concluded ρ as 0.50 ± 0.05, while remaining at 1453 and 1590 cm^{-1} as Raman-active modes including C═C bonds of DHBTCNQ.

The final results are presented in Table 2 and the spectra are contained in the Supporting Information.

Discussion

Correlation of ν vs ρ. Among TTF-class donors (TTF, TMTXF, HMTXF, ET), the largest ionization shifts of 140 cm^{-1} per unit charge were reported for heavier-atom substituted moieties TMTSF ($a_g\nu_2$)[15] and HMTSF ($a_g\nu_3$).[16] The ionization shift found in BO (ν_3, 110 cm^{-1}) was similar to those of TTF (ν_3, 100 cm^{-1}),[2b,13,14] TMTTF (ν_2, 120 cm^{-1}),[2b,13,15] and HMTTF (ν_3, 120 cm^{-1}).[16] All the modes mentioned above, except ν_3 of TTF, involve the central C═C bonds of the corresponding donor. As to ν_3 of TTF, there is some degree of mixing of both kinds of C═C bonds, though it does not affect the applicability of the Raman spectroscopy to the estimation of ρ.[13]

It is worthwhile to note the distinctive differences over the correlation of the corresponding modes with ρ for BO and its sulfur analogue, ET. For ET, the corresponding shift of ν_2[29] and ν_3 was reported as ca. 80 cm^{-1}, for both modes.[17] At the same time, the frequency separation between them was very small, for example $\delta\nu = \nu_2 - \nu_3 \approx 30$ cm^{-1} when $\rho = 0.5$ (2:1 complex). Moreover, frequency regions in which these modes were observed for different stoichiometries significantly overlapped, and the scattering of the points with the same charge $\Delta\nu$ was large (see Table 1 in ref 17): ν_3 appeared at 1457−1471 cm^{-1} ($\Delta\nu = 14$ cm^{-1}) for 2:1 complexes and at 1460−1468 cm^{-1} ($\Delta\nu = 8$ cm^{-1}) for 3:2 complexes, while ν_2 was observed in the same 1448−1465 cm^{-1} region ($\Delta\nu = 17$ cm^{-1}) for both 3:2 and 1:1 complexes. Thus, even the correct assignment of the vibrational modes in the spectrum of a new complex can be not obvious.

We found almost the opposite situation for BO. ν_3 and ν_2 for different ρ values never overlapped when ρ was between 0 and 1. The frequency separation $\delta\nu = \nu_2 - \nu_3$ for a given ρ increased with ρ, being $\delta\nu \approx 130$ cm^{-1} for $\rho = 0$ and $\delta\nu \approx 170$ cm^{-1} for $\rho = 1$. The scattering of the points with the same charge was within $\Delta\nu = 5$ ($\rho = 0.5$) to 7 cm^{-1} ($\rho = 1.0$).

The origin of the above-mentioned differences between BO and ET is supposed to be due to the nature of the corresponding modes. As mentioned above, the contributions of two kinds of C═C bonds in BO^0 are completely separated, with ν_2 being entirely the vibration of the ring C═C bonds while ν_3 is only the vibration of the central C═C bonds.[18] In contrast, in ET^0 both modes ν_2 and ν_3 are combinations, in an approximately equal ratio, of both kinds of C═C bonds, one in-phase and one out-of-phase.[30a] However, ^{13}C isotope shifts showed that in one of the 2:1 salts, κ-(ET)$_2$Cu[N(CN)$_2$]Br, these modes have completely separated contributions, with ν_3 being only the central C═C stretch and ν_2 being the stretch of only the inner-ring carbon pair.[30b] Close energies as well as changing the character of the modes upon oxidation of ET may cause deviation of the whole ν vs ρ dependence from linear and enhance scattering of the points, and therefore undermine their use for exact estimation of the CT degree in ET salts.

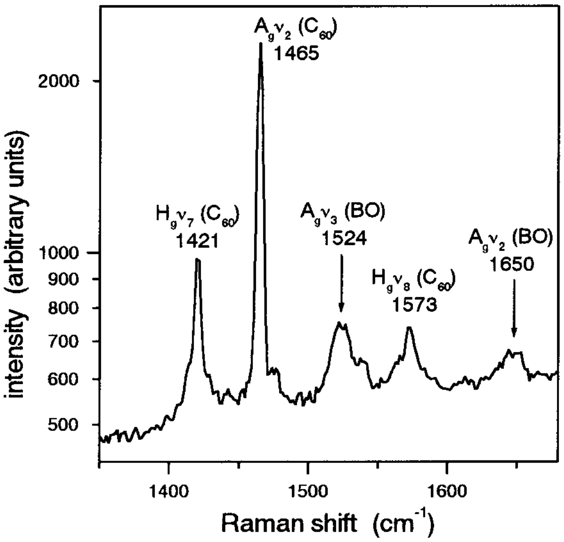

Figure 4. Raman spectrum of the $(BO)_3(C_{60})(C_6H_6)_x$ single crystal.

Sample Materials. Among the neutral complexes, **I**−**V** revealed the highest frequencies of ν_2 and ν_3 and nil charge density on BO.

III and **IV** are newly prepared single crystals. Figure 4 shows the Raman data of the complex grown from benzene while similar spectra were recorded for IV. The A$_g$ ν_2 mode of C$_{60}$ dominates the spectrum. Its position at 1465 cm^{-1} corresponds to the neutral species.[31] Other observed peaks are two H$_g$ modes of C$_{60}$ (ν_7 at 1421 cm^{-1} and ν_8 at 1573 cm^{-1}) and two A$_g$ modes of BO (ν_3 at 1524 cm^{-1} and ν_2 at 1650 cm^{-1}). The latter confirm the neutrality of the donor molecules as well.

For the complex **VI**, the peaks characteristic of BO^0 were absent while two features at some lower frequencies were identified as ν_2 and ν_3, corresponding formally to $\rho = 0.28$.

VII−**XVIII** are metallic with estimated ρ values ranging from 0.45 to 0.63.

We excluded the complex **VII** from the standard materials of the degree of CT, since recently obtained reflectance spectra of the same single crystals in the 3000−3500 cm^{-1} frequency range had shown a possible small contribution by the hydroxonium ions in addition to the H$_2$O signal.[32] Our Raman data confirmed the charge on BO as 0.5. Therefore either the contamination of H$_3$O$^+$ was small (less than 3% of total H$_2$O is replaced) or it was compensated by the modified amount of Br$^-$.

The oxidation state of BO in **VIII** was lower than that expected from its 7:4 stoichiometry and therefore CT was incomplete. For the 6:3 complex **IX**, 2:1 complexes **X**−**XVII**, and 11:7 complex **XVIII**, the values of ρ (±0.05) coincided

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(29) For simplicity of comparison, we employ the same numbering of C═C stretching modes for ET and BO, as ν_2 and ν_3, which is correct in D_{2h} molecular symmetry. The same numbering has been used in ref 30, though it differs from that used in ref 17. The mode ν_3 in ref 17 corresponds to ν_2, while ν_4 in ref 17 corresponds to ν_3.

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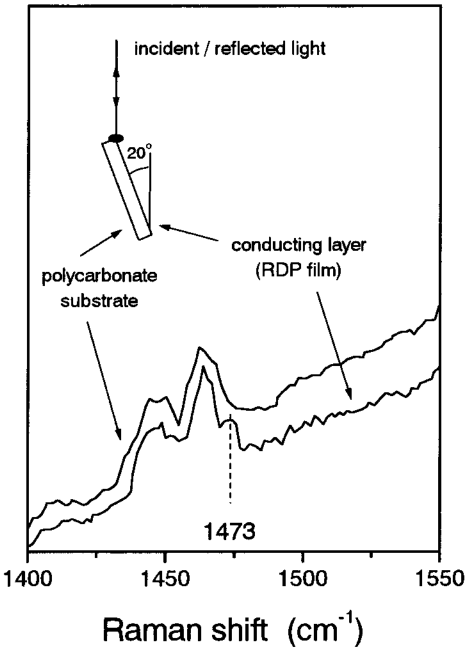

Figure 5. Geometry of the sample and the Raman spectra of the RDP film of the BO−Br complex.

with those deduced from their D/A ratios. The $\rho = 0.5$ in complex **XV** corresponded to the deprotonation from the weak acceptor molecule to form a stable chloranilate anion, as supposed in ref 24.

For complex **XIX**, neither structural nor composition data are ready. Obtained results revealed the ionic state of BO, similar to that of $(BO)_2[Ni(dto)_2]$ and $(BO)_2[Pd(dto)_2]$ (see Table 1). Therefore, 2:1 stoichiometry is most probable for **XIX**.

To expand the range of materials beyond the usual solid charge-transfer complexes, we attempted to apply the method to the RDP films. The sample examined here was transparent, colorless, *and* metallic down to low temperatures. To make the surface conductive, the polycarbonate film dispersed with 1 wt % of BO was exposed to CH_2Cl_2 vapor containing Br_2.[9] In the targeted frequency region, the polycarbonate substrate gave very strong and obstructing peaks. To avoid their effect, the geometry of the sample was modified, as shown in Figure 5. The incident light was irradiated at the edge of the conducting surface of the film, which was inclined by ca. 20° from the direction of the film surface. To obtain maximum strength of the Raman scattering without sample damaging, strong laser power and short accumulation time were applied. As a result, we were able to detect an additional, reproducible signal coming from the CT complex on one side of the film (Figure 5), either as a very weak peak or a shoulder at 1470−1475 cm^{-1}, which is similar to ν_3 of BO in **VII** (1474 cm^{-1}). The absence of the peaks from neutral BO (which remained in the film after Br-doping) was a result of the combined effect of sample geometry in the experiment and its dispersed location in the whole film, while the CT complex was concentrated in a thin surface layer.

Border between a Neutral/Insulating and a Partially CT/Conducting Complex. Among the neutral complexes, **VI** has $\rho = 0.28$, while the room-temperature conductivity of a single crystal of **VI** was reported as $\sigma_{RT} = 10^{-7}$ S cm^{-1}, similar to that of a single crystal of **II** ($\sigma_{RT} = 3.5 \times 10^{-8}$ S cm^{-1}).[5c] From the viewpoint of the border between the neutral and partially charge-transferred complex, **VI** is a highly charged, but insulating one. While $(BO)_6(HCDAH)$ (see Table 1) is the highly conducting complex examined in this report, it has the lowest CT degree 1/3, which is the same value as reported for the superconductor $(BO)_3Cu_2(NCS)_3$.[6a]

Thus, our analysis shows that organic metals are afforded when the charge on BO exceeds ca. 0.3. Clearly, the critical value of ρ is determined by the extension of the intramolecular π-system, dimensionality of the crystal structure, and molecular arrangement of the conducting components within the segregated layer or column. Among typical components of organic metals, the size of the intramolecular π-system increases in the following way: TTF < ET, BO < phthalocyanine (Pc), tetrathiapentalene (TTP). It is well-known that in TTF-TCNQ and its analogues, the alternating stack and therefore insulating state is favored when $\rho < 0.5$. A metallic state with small ρ is more common for materials having a much more extended π-system such as Pc and TTP derivatives, where the lowest oxidation states of the conducting component molecules have been observed to be 0.33[33] and 0.12−0.20,[34] respectively. BO and ET have the same intermediate size of the π-system. However, BO tends to provide metals with smaller ρ than ET. Therefore, effect of sulfur−oxygen substitution and specific molecular arrangement of BO in its complexes should be taken into account. The former leads to a strong self-aggregation of the donor through two kinds of short intermolecular contacts (CH···O atomic contacts along the face-to-face stacking direction and $S_{in}\cdots S_{in}$ atomic contacts along the oblique direction to the stacking axis, where S_{in} is a sulfur atom of TTF), resulting in 2D electronic bands with wide bandwidths. The specific molecular arrangement of BO within the conducting layer, namely, absence of the strong dimerization (that often occurs in ET complexes), prevents splitting of the conduction band, which in turn prevents effective reducing of the bandwidth.

Conclusions

In conclusion, the present study revealed that Raman spectroscopy is a fast, nondestructive, and highly accurate method for determining the charge on BO in its complexes, which applies to any available material (microcrystals, powders, and films). Linear correlations between the frequencies of two totally symmetric C═C stretching modes, ν_2 and ν_3, and the charge on BO were found and should be used to evaluate the CT degree (ρ) in complexes. The border in the CT degree between neutral (insulating) and partially CT (conducting) complex based on BO was estimated as 0.3.

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Supporting Information Available: Figure S1 shows Raman spectra of the sample materials **I**, **II**, **V**−**XV**, and **XVII**−**XIX** in the 1400−1700 cm^{-1} region where peaks assigned to BO are marked (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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