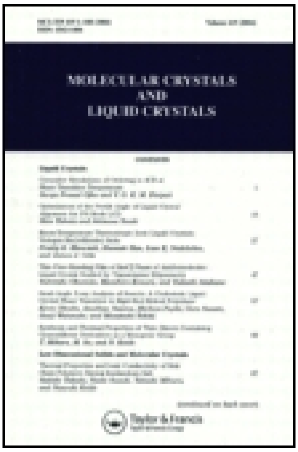

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Hydrogen-Bond Character of 2,2′-Bi-1H-Imidazole Systems

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HYDROGEN-BOND CHARACTER OF 2,2'-BI-1H-IMIDAZOLE SYSTEMS

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Abstract The characters of hydrogen-bond of 2,2'-bi-1H-imidazole (H2BIM) system were examined from a viewpoint of the proton-transfer (PT) and electron-transfer (CT) interactions. To make the effects of the dibenzo substitution of H2BIM molecule clear, we prepared the charge-transfer complexes of dibenzo-2,2'-bi-1H-imidazole (H2BBIM) and H2BIM systems with 7,7,8,8-tetracyanoquinodimethane (TCNQ). The one-dimensional column of TCNQ was confirmed by the crystal structural analysis, however, the packing forms of the H2BIM and H2BBIM systems were entirely different to each other. The H2BBIM system in the TCNQ complex formed the one-dimensional column which is parallel to the TCNQ stack, while the H2BIM system was constructed by the hydrogen-bonded dimer unit along the perpendicular direction to the TCNQ column.

INTRODUCTION

It has been known that some solid molecular complexes can take place the phase transitions concerning with the proton-transfer by the thermal or pressure applications.[1, 2] In these complexes, each component molecules are connected by the hydrogen-bonds forming the proton donor and proton acceptor sites. The addition of adequate electron-donating and -accepting abilities to these PT complexes will cause a large deformation of the electronic state of charge-transfer (CT) complexes.[3, 4]

The H2BIM system with 6π-6π electronic structure can exist as five kinds of protonated species responsible for the four-step PT processes (Fig. 1). The cation species, 2-(2-1H-imidazolyl)-1H-imidazolium ($H3BIM^+$) and 2,2'-bi-1H-imidazolium ($H4BIM^{2+}$), have unsatisfactory electron-accepting abilities relating to their low reduction potentials.[5] Thus, the stable existence of cation species prevents the generation of radical species. On the contrary, the proton-donating abilities of $H4BIM^{2+}$

($pK_a = 0.24$) and $H3BIM^+$ ($pK_a = 4.60$) are higher than that of 2,3-dichloro-5,6-dicyanohydroquinone ($pK_a = 5.14$) in dimethylformamide-water (7:3) media.[5] We have been studying on the 2,2'-bi-1H-imidazole (H2BIM) system from the point of its high PT character. The structural properties of 7,7,8,8-tetracyanoquinodimethane (TCNQ) complexes with H2BIM and dibenzo-2,2'-bi-1H-imidazole (H2BBIM) systems were examined in addition to the electrical conductivities of these. The enlargement of molecular size and the existence of the benzene-rings will influence the characters of hydrogen-bond and crystal packing of H2BBIM system in the CT-complexes.

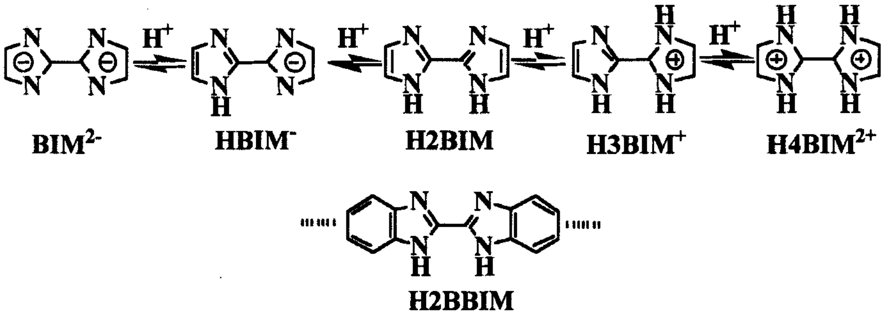


FIGURE 1 Four-step proton-transfer (PT) processes of H2BIM system with 6π-6π electronic structure. Same PT processes exist for H2BBIM system.

EXPERIMENTAL

The $[H3BIM^+][I^-]$ and $[H3BBIM^+][I^-]$ were prepared by one molar reaction of hydroiodic acid to H2BIM and H2BBIM, respectively.[5] The CT-complex $[H3BIM^+]_2[TCNQ]_3$ was obtained by the method of metathesis reaction between $[H3BIM^+][I^-]$ and $[Li^+][TCNQ^{-\bullet}]$, and the $(H3BBIM)(TCNQ)(Cl)_{0.5}(H_2O)$ was prepared by the electrocrystallization method using the supporting electrolyte of $[H3BBIM^+][I^-]$ in acetonitrile - buffer solution (pH = 1.2, KCl - HCl). Here, the parenthesis and bracket indicate the tentative and real chemical formula, respectively. The crystal data were collected by the Rigaku AFC-5 diffractometer with CuK_α radiation. Crystal structures were solved by the direct method (SHELXS 86) and block-diagonal least-squares technique were employed for the structure refinements. The measurements of electrical conductivities were done by the four-prove method for $(H3BBIM)(TCNQ)(Cl)_{0.5}(H_2O)$ and two-prove one for $[H3BIM^+]_2[TCNQ]_3$ with gold contacts.

RESULTS AND DISCUSSION

The crystal structures of the TCNQ complexes of H3BIM$^+$ and H3BBIM$^+$ were described together with those of neutral components and examined the characters of hydrogen-bonds and the packing motif of H3BIM$^+$ and H3BBIM$^+$ in the TCNQ complexes. The electrical conducting behaviour of these TCNQ salts was elucidated in relation with the structural properties. Finally, we discuss the CT and PT states of TCNQ and biimidazole system in the complexes based on the vibration and electronic spectra.

CRYSTAL STRUCTURE OF H2BBIM

The crystal data of H2BBIM and H2BIM[6] were summarized in Table 1.

TABLE 1. Crystal data of H2BBIM and H2BIM.

	H2BBIM	H2BIM
Crystal system and	Orthorhombic	Monoclinic
Space Group	$Pca2_1$	$P2_1/c$
Lattice constants	a=10.165(8), b=11.380(9), c=9.902(7)Å	a=5.067(2), b=10.786(3), c=11.490(3)Å, β=102.58(3)°
Unit cell volume	1145.17Å^3	612.88Å^3
Z	4	4
Density (calc.)	1.356g/cm^3	1.453g/cm^3
R-value	0.037	0.054

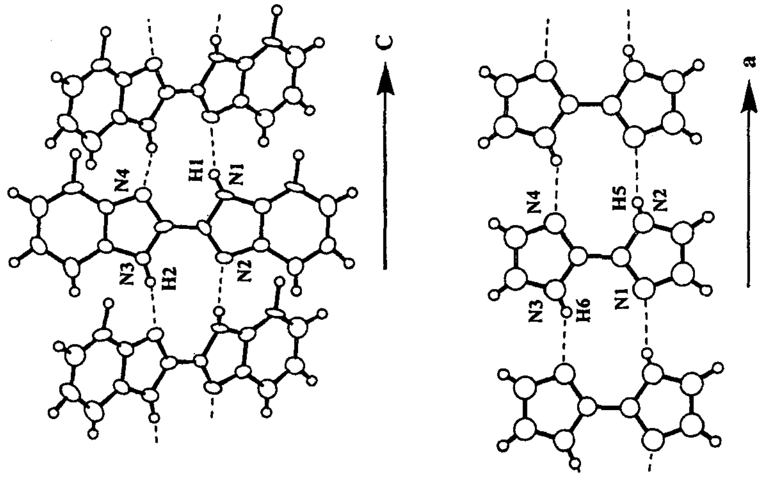


FIGURE 2. Hydrogen-bonded structures of H2BBIM and H2BIM. The hydrogen-bonds are depicted by the dashed lines.

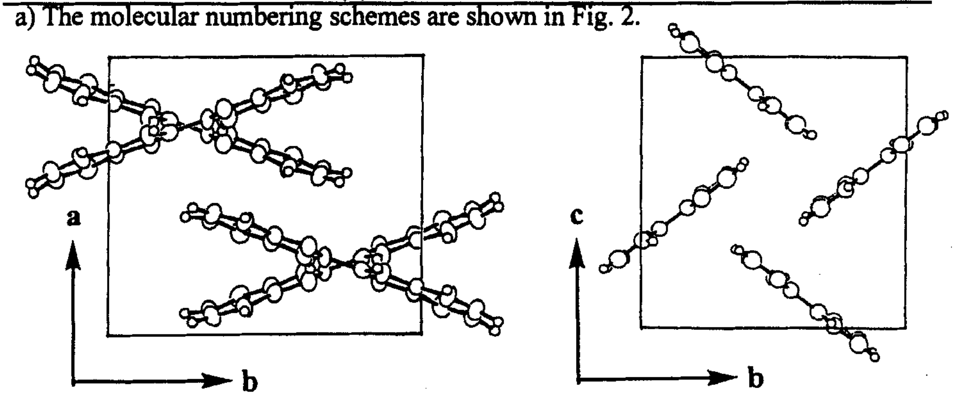
In both crystals, one H2BBIM and H2BIM molecule is the crystallographically independent. The crystal systems of H2BBIM and H2BIM are the orthorhombic and monoclinic, respectively. Both have the primitive unit cell and 2_1-axis. The calculated density of H2BBIM is lower than that of H2BIM, which implies the loose packing of H2BBIM compared with H2BIM.

Figure 2 shows the forms of hydrogen-bond for H2BBIM and H2BIM. Each biimidazole molecule is connected by four N-H•••N hydrogen-bonds at the side-by-side direction to the molecular plane. The infinite N-H•••N hydrogen-bonds for H2BBIM and H2BIM are elongated along the c- and a-axis, respectively. For the H2BIM, the planar sheet structure is formed by the hydrogen-bond. On the contrary, the H2BBIM molecule is inclined by about 45° from the next H2BBIM one to avoid the steric repulsion between the benzene-rings. Table 2 summarizes the hydrogen-bond distances and angles of H2BBIM and H2BIM.

TABLE 2. Hydrogen-bond distances (Å) and angles (deg) of H2BBIM and H2BIM.

H2BBIM[a)]	H2BIM[a)]
N1•••N2 = 2.916(8)	N1•••N2 = 2.865(8)
N3•••N4 = 2.811(8)	N3•••N4 = 2.879(8)
N1-H1 = 0.887(8)	N2-H5 = 0.89(7)
N2•••H1 = 2.099(8)	N1•••H5 = 2.10(8)
N3-H2 = 0.909(8)	N3-H6 = 0.70(5)
N4•••H2 = 2.008(9)	N4•••H6 = 2.19(5)
N1-H1•••N2 = 152.8(7)	N2-H5•••N1 = 143(7)
N3-H2•••N4 = 160.8(7)	N3-H6•••N4 = 165(5)

a) The molecular numbering schemes are shown in Fig. 2.



H2BBIM **H2BIM**

FIGURE 3. Overall crystal packing of H2BBIM and H2BIM viewed along the c- and a-axis, respectively.

For the H2BBIM, the hydrogen-bond distances between two nitrogens are 2.916(8) and 2.811(8)Å. Those of H2BIM are 2.865(8) and 2.879(8)Å, and the N-H•••N angles of these two systems are also little differences. These results indicate the same order of the strength of hydrogen-bonds between H2BBIM and H2BIM crystals. In the case of H2BBIM, the formation of 45°-inclined hydrogen-bond structure by the steric repulsion of benzene rings maintains the same order of hydrogen-bonds in contrast to H2BIM one.

The overall crystal packing of H2BBIM and H2BIM is shown in Fig. 3. There are no intermolecular contacts shorter than the sum of the van der Waals radius except for the formation of the strong hydrogen-bonds. In the ab-plane, the H2BBIM molecules are arranged as 45°-inclined positions and the H2BIM ones form the herringbone packing in the bc-plane. For the H2BBIM crystal, the 45°-inclined hydrogen-bond structure make the packing of crystal loose resulted in a slight reduce of density in contrast to H2BIM.

CRYSTAL STRUCTURES OF TCNQ COMPLEXES

The crystal data of $[H3BIM^+]_2[TCNQ]_3$ and $(H3BBIM)(TCNQ)(Cl)_{0.5}(H_2O)$ were summarized in Table 3.

TABLE 3. Crystal data of $[H3BIM^+]_2[TCNQ]_3$ and $(H3BBIM)(TCNQ)(Cl)_{0.5}(H_2O)$.

	$[H3BIM^+]_2[TCNQ]_3$	$(H3BBIM)(TCNQ)(Cl)_{0.5}(H_2O)$
Crystal system and Space Group	Triclinic $P\bar{1}$	Triclinic P1
Lattice constants	a=10.411(9), b=13.998(8), c=7.822(7)Å, α=75.15(9), β=68.62(3), γ=83.37(2)°	a=7.664(7), b=19.09(4), c=3.883(5)Å, α=88.7(1), β=102.58(3), γ=88.3(1)°
Unit cell volume	1041.43Å^3	565.71Å^3
Z	2	1
Density (calc.)	1.408g/cm^3	1.492g/cm^3
R-value	0.084	0.066

The crystal systems of $[H3BIM^+]_2[TCNQ]_3$ and $(H3BBIM)(TCNQ)(Cl)_{0.5}(H_2O)$ were the triclinic, and we adopted the non symmetrical P1 for $(H3BBIM)(TCNQ)(Cl)_{0.5}(H_2O)$. In the $[H3BIM^+]_2[TCNQ]_3$, two kinds of TCNQ, one of them is located on the symmetrical point, and one $H3BIM^+$ molecules are crystallographically independent. The $(H3BBIM)(TCNQ)(Cl)_{0.5}(H_2O)$ is composed of one crystallographically independent $H3BBIM^+$ and TCNQ molecules in addition to the one-half of chlorine and a water.

The $[H3BIM^+]_2[TCNQ]_3$ crystal was made of the segregated TCNQ column and the $H3BIM^+$ dimer which is connected by two N-H•••N hydrogen-bonds (Fig. 4). The dimer unit of $H3BIM^+$ is located between the TCNQ columns perpendicularly and connects to the nitrile groups of TCNQ molecules by the N-H•••NC hydrogen-bonds with N•••N distance of 2.903Å (Fig. 4b). In the $H3BIM^+$ dimer, the N•••N distance of N-H•••N hydrogen-bond is 2.795(7)Å which is contracted by about 0.1Å than that of H2BIM. The non-uniform stack in TCNQ column is composed of trimer unit of TCNQ and the mean interplanar distance of the trimer unit is 3.27Å and that of inter-trimer is 3.28Å (Fig. 4c). The overlap mode of TCNQ in the trimer unit is the ring-over-bond and that of intertrimer is ring-over-ring.

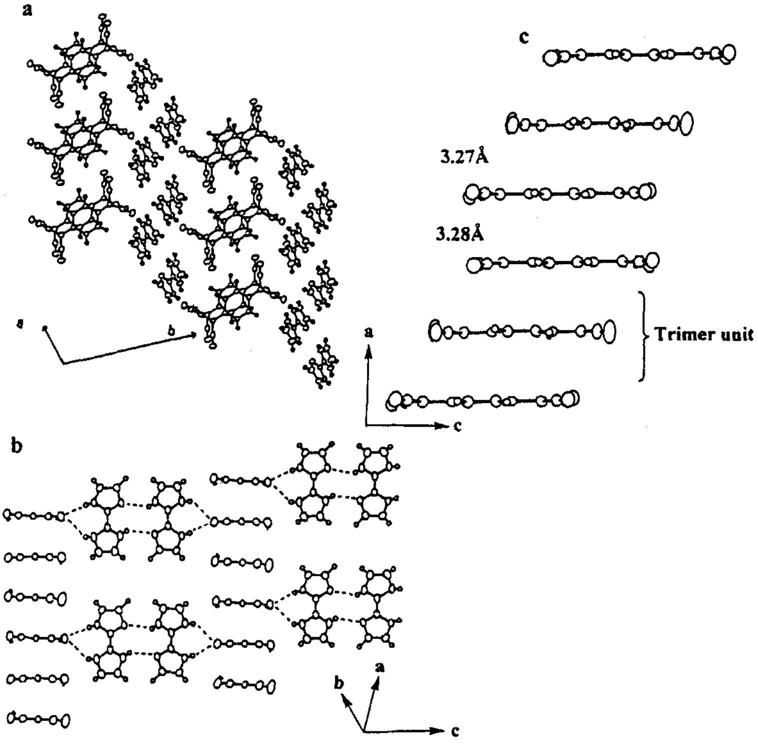


FIGURE 4. The crystal structure of $[H3BIM^+]_2[TCNQ]_3$. a) Overall packing pattern viewed along the perpendicular direction to the TCNQ plane. b) $H3BIM^+$ dimer and the N-H•••NC and N-H•••N hydrogen-bonds (dashed lines) viewed along the long axis of TCNQ. c) Stacking pattern of TCNQ column viewed along the short axis of TCNQ.

The (H3BBIM)(TCNQ)$(Cl)_{0.5}(H_2O)$ has the uniform stacking of TCNQ and H3BBIM along the c-axis (Fig. 5). The mean interplanar distances of TCNQ and $H3BBIM^+$ are determined as 3.25 and 3.33Å, respectively. The overlap mode of TCNQ is the type of ring-over-ring. The $H3BBIM^+$ molecules are arranged along the a-axis and connected by the hydrogen-bonds through Cl and H_2O. The Cl and H_2O are located at the space between two $H3BBIM^+$ molecules and have the positional disorder. In this crystal, there are no hydrogen-bonds between the TCNQ and $H3BBIM^+$, however, the N-H groups of $H3BBIM^+$ are connected to chlorine and water by N-H•••Cl and N-H•••H_2O hydrogen-bonds. At the same time, the disordered Cl and H_2O were also connected by the H_2O•••Cl hydrogen-bonds along the c-axis (Fig. 5b). Thus, two types of hydrogen-bond networks spread to the a- and c-directions.

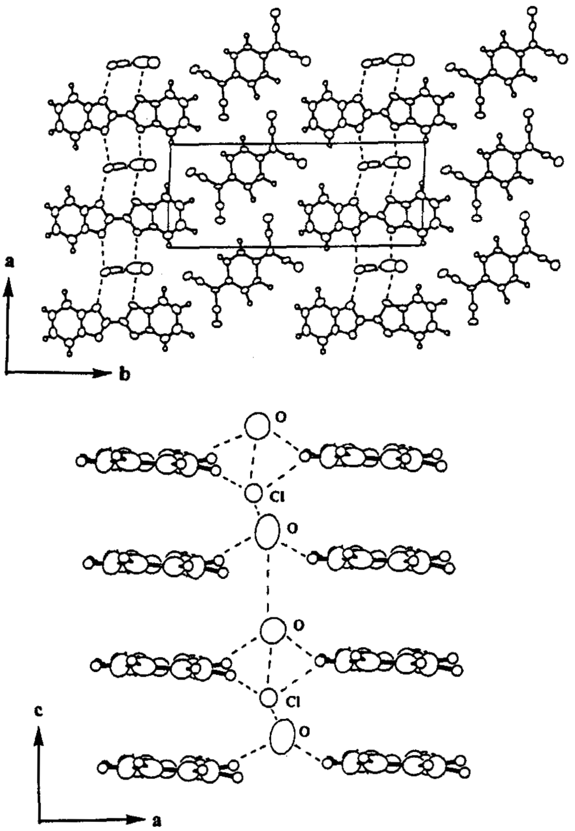


FIGURE 5. The crystal structure of (H3BBIM)(TCNQ)$(Cl)_{0.5}(H_2O)$. a) Overall crystal packing viewed along c-axis. b) $H3BBIM^+$, Cl, and H_2O viewed along the b-axis. The Cl and H_2O were drawn one of the disordered position.

ELECTRICAL CONDUCTING BEHAVIOUR OF TCNQ COMPLEXES

The electrical conducting behaviour of $[H3BIM^{+}]_2[TCNQ]_3$ is the semiconductive which is consistent with the non-uniform stack of TCNQ. The room temperature conductivity (σ_{RT}) is 7.3×10^{-7}Scm^{-1} and the activation energy is 0.33eV. On the contrary, the $(H3BBIM)(TCNQ)(Cl)_{0.5}(H_2O)$ has the σ_{RT} value of 5.2Scm^{-1}. Reflecting the uniform stacks of TCNQ, the high conductivity was attained in contrast to that of $[H3BIM^{+}]_2[TCNQ]_3$. Fig. 6 shows the temperature dependence of conductivity and the inserted figure is the logarithmic plots of resistivity (ρ). Above 280K, the σ value increased slightly by the lowering of temperature. In the temperature region from 100 to 250K, the activation energy is 0.04eV and one order of abrupt decreasing of conductivity was observed at 100K.

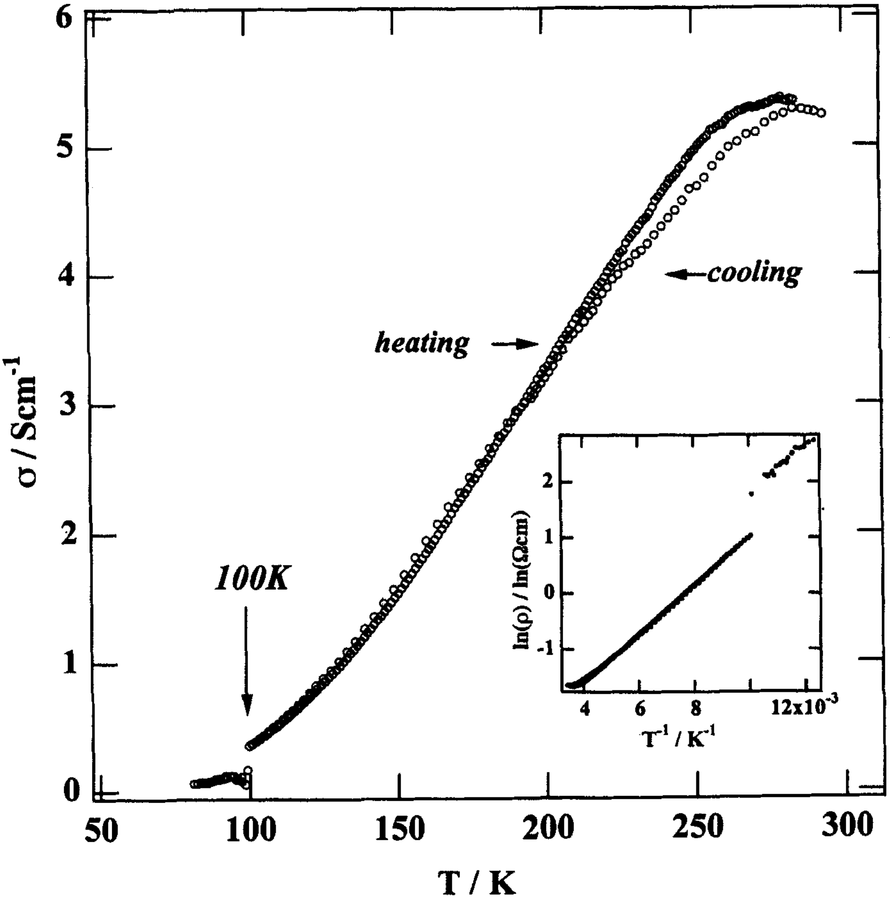


FIGURE 6. Temperature dependence of conductivity (σ) of $(H3BBIM)(TCNQ)(Cl)_{0.5}(H_2O)$. Inserted figure is the logarithmic plots of resistivity (ρ).

CHARGE-TRANSFER AND PROTON-TRANSFER STATES OF TCNQ COMPLEXES

The electronic absorptions (A-band) ascribable to the charge-transfer band ($h\nu_{CT}$) of $[H3BIM^+]_2[TCNQ]_3$ and $(H3BBIM)(TCNQ)(Cl)_{0.5}(H_2O)$ are 4.90 and 2.80×10^3cm^{-1}, respectively (Fig. 7). The noise like features below 5×10^3cm^{-1} are due to the vibrational absorptions. For the complete ionic TCNQ salt $[K^+][TCNQ^{-\bullet}]$, the value of $h\nu_{CT}$ is 8.19×10^3cm^{-1} (B-band in Fig 7) which is higher in energy than that of partial charge-transfer TCNQ salts.[7] The low $h\nu_{CT}$ of our TCNQ complexes imply the partial charge-transfer states of TCNQ in the complexes and resembles to the high conducting TCNQ complexes.[8] The C- and D-bands in Fig. 7 are related to the $TCNQ^{-\bullet}$ species, and F- and F'-bands are attributed to the biimidazole species.

The vibration spectrum of $[H3BIM^+]_2[TCNQ]_3$ was the superposition of those of neutral TCNQ, $TCNQ^{-\bullet}$, and $H3BIM^+$ indicating the charge separated state of TCNQ. Thus, the precise representation of electronic states is deduced as $[H3BIM^+]_2[TCNQ^{\bullet-}]_2[TCNQ^0]$. The vibration spectrum of $(H3BBIM)(TCNQ)(Cl)_{0.5}(H_2O)$ indicates the existence of two kinds of protonated species, $H3BBIM^+$ and $H4BBIM^{2+}$, in the crystal. This complex contains the different protonated species of H2BBIM system, thus the mixed protonated and charged states were attained in the crystalline state. Assuming the chlorine as chloride ion, the real chemical formula of $(H3BBIM)(TCNQ)(Cl)_{0.5}(H_2O)$ is $[H3BBIM^+]_x[H4BBIM^{2+}]_{1-x}[TCNQ^{-(1.5-x)}][Cl^-]_{0.5}[H_2O]$, $1 > x > 0.5$.

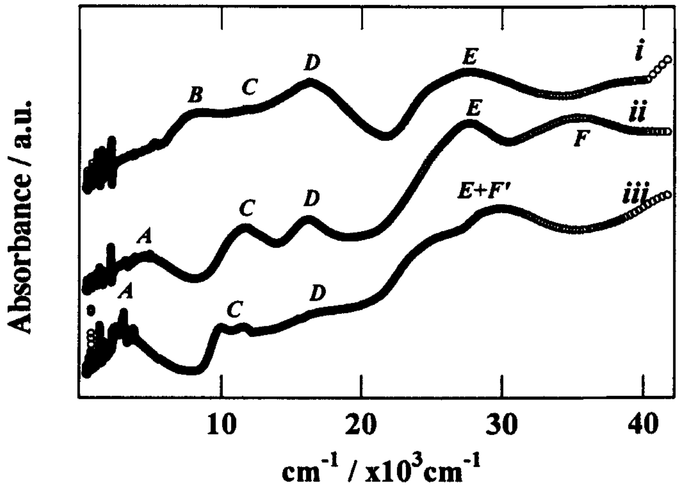


FIGURE 7. The absorption spectra of i) $[K^+][TCNQ^{-\bullet}]$, ii) $[H3BIM^+]_2[TCNQ]_3$, and iii) $(H3BBIM)(TCNQ)(Cl)_{0.5}(H_2O)$ in KBr pellet.

CONCLUSION

The character of hydrogen-bond for H2BBIM was compared with that of H2BIM. The infinite N-H•••N hydrogen-bonds were elongated along the side-by-side direction of the molecules plane, however, each H2BBIM molecule is inclined about 45° due to the steric repulsion between the neighbouring benzene rings. The same order of hydrogen-bonds strength for H2BIM and H2BBIM were confirmed by the N•••N distances and N-H•••N angles. In the TCNQ complexes, the $H3BIM^+$ existed as the planar dimer structure connected by two N-H•••N hydrogen-bonds. For $H3BBIM^+$ complex, the hydrogen-bonds were formed through the Cl and H_2O instead of the direct N-H•••N one. In the CT-complex, the direct hydrogen-bonds between $H3BBIM^+$ is not preferable due to the 45° twisting of the $H3BBIM^+$ molecules.

Reflecting the stacking manner of TCNQ, the electrical conducting behaviour of these two TCNQ complexes were quite different. The $[H3BIM^+]_2[TCNQ]_3$ and $(H3BBIM)(TCNQ)(Cl)_{0.5}(H_2O)$ have non-uniform and uniform stacking of TCNQ molecules, respectively. In both complexes, the electronic states of TCNQ were the partial CT states, however, the TCNQ in $[H3BIM^+]_2[TCNQ]_3$ existed as the charge-separated state according to the vibration spectrum. On the other hand, $(H3BBIM)(TCNQ)(Cl)_{0.5}(H_2O)$ indicated the high conductivity (σ_{RT} = 5.2Scm^{-1}) and the real chemical formula was represented as $[H3BBIM^+]_x[H4BBIM^{2+}]_{1-x}[TCNQ^{-(1.5-x)}][Cl^-]_{0.5}[H_2O]$, $1 > x > 0.5$, with mixed proton-transfer state of H2BBIM system. The high electrical conductivity of this complex is ascribable to both the partial charge-transfer state and the uniform stacking of TCNQ.

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