Selected Papers

Syntheses, Redox Properties, Self-Assembled Structures, and Charge-Transfer Complexes of Imidazole- and Benzimidazole-Annelated Tetrathiafulvalene Derivatives

Tsuyoshi Murata,¹ Yosuke Yamamoto,¹ Yumi Yakiyama,¹ Kazuhiro Nakasuji,¹ and Yasushi Morita^{*1,2}

¹Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043

²Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency, Chiyoda-ku, Tokyo 102-0075

Received February 15, 2013; E-mail: morita@chem.sci.osaka-u.ac.jp

New tetrathiafulvalene (TTF)-type electron-donor molecules annelated with imidazole or benzimidazole moiety were designed and synthesized by the phosphite-mediated coupling reactions of imidazole- or benzimidazole-annelated 1,3-dithiole-2-thiones. The effect of imidazole-annelation on the redox properties was evaluated by theoretical calculation and electrochemical measurement, and the imidazole-annelation slightly enhances the electron-donating abilities of parent TTF and benzo-TTF skeletons. The substitution of the imidazole ring with an electron-withdrawing cyano group caused a large high potential shift of the oxidation potentials in the cyclic voltammetry and an intense intramolecular charge-transfer absorption band in the electronic spectrum. The self-assembling ability was investigated by crystal structure analysis, where solvent or counter anion mediated one-dimensional hydrogen-bonded arrays of imidazole rings were linked through π -stacks and S.-S interactions to construct multidimensional networks. The donor molecules afforded weak charge-transfer complexes with tetracyanoquinodimethane (TCNQ) and fully ionic complexes with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) and 2,3,5,6-tetrafluoro-TCNQ. In the crystal structures of TCNQ complex and iodine salt of a benzimidazole-annelated derivative, π -stacking motifs, donor–acceptor alternating stack, and π -stacking dimer, respectively, were interacted through hydrogen-bonds.

Tetrathiafulvalene (TTF) is a strong π -donor molecule and has been widely utilized in the development of various molecule-based electronic materials.¹ The most attractive and noticeable properties of the TTF system is the electrical conduction in charge-transfer (CT) complexes and salts, and vigorous materials exploration based on the TTF system have produced intriguing phenomena and functions.² To achieve CT complexes and salts showing desired properties, the control of relative molecular orientation with the aid of intermolecular interactions is necessary.3,4 Hydrogen-bonding (H-bond) is a robust and highly directional intermolecular interaction and has been introduced into CT complexes and salts for the establishment of conduction paths and for the increase of electronic and structural dimensionalities.^{3,5,6} Furthermore, the cooperation of proton-transfer (PT) at the H-bonding sites with electrontransfer of the redox-active sites is expected to provide a new strategy for materials exploration.⁷

Imidazole is an aromatic ring having two nitrogen atoms as the H-bonding sites and constructs diverse supramolecular architectures.⁸ The self-assembling ability of imidazole has been also utilized in the development of electronic materials such as organic conductors⁹ and molecular magnets.¹⁰ Imidazole also behaves as a Brønsted acid and base and generates protonated cation and deprotonated anion species. We recently studied CT complexes of an imidazole-substituted TTF deriv-



Chart 1. Imidazole-functionalized TTF derivatives.

ative (TTF-Im, Chart 1).^{11a,11b} Our investigation revealed that the electronic effects of donor–acceptor H-bonds controlling donor–acceptor ratio and redox ability play key roles in the achievement of conducting CT complexes in addition to the structural regulation effects.¹¹

For the development of new H-bonded CT complexes based on the self-assembling ability and PT processes of imidazole

rings, we have designed imidazole-annelated TTF derivatives (Chart 1).¹² Annelation of the imidazole ring to TTF moiety enhances the electronic correlation between CT and PT processes and further strengthens the responses of redox and optical properties of TTF moiety to the PT process of imidazole ring. Decurtins et al. synthesized mono(benzimidazole)-annelated TTF derivatives having TCNAQ (tetracyanoanthraquinodimethane),¹³ pyridyl and quinolyl groups¹⁴ at the 2-position of the imidazole ring. Protonated states of the imidazole ring in these donors affected the redox and optical properties of the TTF skeleton, and furthermore, H-bonds on the imidazole ring contributed to the formation of self-assembled structures.^{13,14} In our previous study,¹² we synthesized a 2-methyl mono-(benzimidazole)-annelated TTF derivative 1 and elucidated its self-assembled structure, and redox and PT ability. In the present study, we have newly synthesized a mono(benzimidazole)annelated TTF derivative having an ethylenedithio (EDT) group at the TTF skeleton 2 to explore the self-assembling architecture formed by the S.S. interactions, and that having an electronwithdrawing cyano group at the 2-position of imidazole ring 3 was also prepared. Furthermore, bis(benzimidazole)-annelated TTF derivatives 4 and 5, and a TTF derivative directly annelated with imidazole ring 6 were synthesized for the first time. Here we report on the redox and optical properties of 1-6, and their CT complexes with several electron-acceptor molecules. The self-assembled structures constructed by the cooperation of π stacks, H-bonds, and S.-S interactions in the crystal structures of protonated salt, CT complex and simultaneous CT and PT salt are also discussed.

Results and Discussion

Synthesis. Scheme 1 shows the synthetic methods of benzimidazole-annelated TTF derivatives 1-5. The treatment of 5,6-diaminobenzene-1,3-dithiole-2-thione¹⁵ with corresponding carboxylic acids yielded 2-methyl- and 2-*n*-hexyl-benz-imidazole-annelated 1,3-dithiole-2-thione 7i and 7iv, respec-

tively. The reaction using 4,5-dichloro-1,2,3-dithiazolium chloride¹⁶ afforded a cyano derivative 7iii. The protection of the N–H group of 7 with SEM (2-(trimethylsilyl)ethoxymethyl) or tosyl group gave 8. The triethylphosphite-mediated crosscoupling reaction of **8i–8iii** with corresponding 1.3-dithiole-2ones followed by the deprotection reactions afforded mono-(benzimidazole)-annelated TTF 1-3. The imidazole ring formation of diaminobenzo-TTF by the treatment with acetic acid or 4.5-dichloro-1.2.3-dithiazolium chloride also yielded 1 and 3, respectively. The former method is advantageous for the chemical modification of TTF skeleton, and the latter one is useful for the introduction of various substituent groups at the 2-position of imidazole ring as demonstrated in Decurtins's work.^{13,14} Bis(benzimidazole)-annelated derivatives 4 and 5 were prepared by the homo-coupling reactions of 8i and 8iv, respectively, using trimethylphosphite followed by the deprotection of SEM group using tetrabutylammonium fluoride. Due to the poor solubility and instability under air, the dimethyl derivative 4 could not be isolated. The other donors 1-3 and 5 are stable under air and soluble in common organic solvents.

The synthetic procedure of the directly imidazole-annelated derivative **6** is illustrated in Scheme 2. The 4- and 5-positions of 2-*n*-propylimidazole were iodinated, and then the N–H group of **11** was protected by SEM group. The exchange of iodine atoms at the 4- and 5-positions of **12** with *N*,*N*-dimethylaminothiocarbonylthio groups was performed in two steps by lithiation using *n*-butyllithium followed by treatment with tetramethylthiuram disulfide. Bis(sulfide) **14** was reduced by LiAlH₄ and then acidified with AcOH to give an in situ generated 4,5-dithiol derivative, of which the cyclization using 1,1'-thiocarbonyldiimidazole afforded the imidazole-annelated 1,3-dithiole-2-thione **15**. The cross-coupling reaction of **15** with bis(*n*-propylthio)-1,3-dithiole-2-one using triethylphosphite gave **17**. The removal of the SEM group of **17** was performed by treatment with tetrabutylammonium fluoride



Scheme 1. Synthetic procedures for benzimidazole-annelated TTF 1–5. Reagents and conditions: (a) AcOH (7i) or 1-heptonic acid (7iv), reflux; (b) 4,5-dichloro-1,2,3-dithiazolium chloride, THF, reflux (7iii); (c) NaH, DMF, 40 °C; SEMCl, 40 °C (8i, 8iii, and 8iv); (d) TsCl, Et₃N, DMF–THF, reflux (8ii); (e) P(OEt)₃, toluene, 60 °C; (f) P(OMe)₃, benzene, 60 °C; (g) NaOH_{aq}, CH₂Cl₂–MeOH, rt (2); (h) Bu₄NF, THF, reflux (3–5). SEM: 2-(trimethylsilyl)ethoxymethyl, Ts: *p*-toluenesulfonyl.



Scheme 2. Synthetic procedure for imidazole-annelated TTF **6**. Reagents and conditions: (a) 3 equiv I₂, CHCl₃–2 M NaOH_{aq}; (b) NaH, DMF, rt; SEMCl, 40 °C; (c) *n*-BuLi, THF, –78 °C; tetramethylthiuram disulfide, –78 °C to rt; (d) 3 equiv LiAlH₄, THF, 0 °C; AcOH, –78 °C; 1,1'-thiocarbonyldiimidazole, rt; (e) 2 equiv Hg(OAc)₂, CHCl₃–MeOH–AcOH, rt; (f) P(OEt)₃, toluene, reflux; (g) Bu₄NF, THF, reflux.

to achieve **6** as a stable solid in air. It has been known that TTF derivatives having acidic N–H and O–H groups directly connected to the vinyl groups are unstable and have not been isolated excepting the dioxo- and aminooxo-pyrimidine-annelated TTF derivatives.¹⁷ The π -delocalization around the imidazole ring probably is essential to acquire the stability of **6**. The homo-coupling reaction of **15** and a ketone **16** did not yield the bis(imidazole)-annelated TTF derivative **18**.

Frontier Molecular Orbital Energies. To discuss the effect of benzimidazole- and imidazole-annelation on the redox ability, the frontier molecular orbital (MO) energies of 1-6 were calculated based on the density functional theory (DFT) at the B3LYP/6-31G(d) level. As shown in Figure 1, the highest occupied MO (HOMO) of 1, 3, 4, and 6 distribute around both TTF and imidazole moieties. The delocalization of HOMO to the imidazole ring in 1-6 is larger than that in TTF-Im (Figure 1e), suggesting that the imidazole-annelation causes a larger electronic correlation between TTF and imidazole skeletons than that of the imidazole-substitution. Table 1 lists the calculated HOMO energies of 1-6 and related compounds 19-21 (Chart 2). The imidazole annelation to benzo-TTF derivative 20 giving 1 raises the HOMO energy by 0.123 eV. In the cases of 4 and 5, since two imidazole rings are fused, the increment of HOMO energy from 21 (0.244 and 0.282 eV, respectively) is nearly twice of that between 1 and 20. The HOMO energy of **20** is lower by 0.125 eV than that of **19** due to the benzene ring annelation. In contrast, the HOMO energy of imidazole-annelated TTF 6 is higher than that of 19(-4.646 vs.)-4.725 eV, respectively). The enhancement of HOMO energies of TTF derivatives by the imidazole-annelation is contrastive to the imidazole-substitution (-4.518 eV for TTF and -4.537 eV for TTF-Im, Table 1) where the electron-withdrawing effect of C=N group causes a lowering of the HOMO energy. The electron-withdrawing feature of cyano group in 3 causes a



Figure 1. Calculated HOMO distributions of 1, 3, 4, 6, and TTF-Im.

lowering of HOMO energy by 0.352 eV in comparison with the methyl derivative **1**, suggesting that the substituent group at the 2-position of imidazole ring has a significant effect on the HOMO energy.

Donor	НОМО	Donor	HOMO
1	-4.727	19	-4.725
2	-4.697	20	-4.850
3	-5.079	21	-4.864
4	-4.620	TTF	-4.518
5	-4.582	TTF-Im	-4.537
6	-4.646		

Table 1. HOMO Energies (eV) of 1-6 and Related Compounds^{a)}

a) Calculated at the B3LYP/6-31G(d) level with optimized structures.



Chart 2. TTF derivatives in Table 1.

Table 2. Oxidation Potentials of 1–3, 5, 6, and Related Compounds (V vs. Fc/Fc^+)^{a)}

	E^{ox1}/V	$E^{\text{ox}2}/\text{V}$	$\Delta E/V$
1	+0.08	+0.28	0.20
2	+0.07	+0.28	0.21
3	+0.18	+0.36	0.18
5	+0.02	+0.32	0.30
6	+0.01	b)	b)
1b	+0.09	+0.29	0.20
20	+0.16	+0.33	0.17
21	+0.18	+0.39	0.21
22	+0.03	+0.20	0.21
TTF	-0.09	+0.15	0.24
TTF-Im ^{11a}	-0.06	+0.20	0.26

a) Conditions: concentration, 1 mM; solvent, DMF (0.1 M $Bu_4N^+ClO_4^-$); counter/working/reference electrodes, Pt wire/ Au disk/Ag/AgNO₃ (0.01 M in MeCN); room temperature. The results were calibrated with ferrocene/ferrocenium (Fc/Fc⁺) couple. b) Irreversible peak.

Electrochemical Properties. Cyclic voltammetry was measured to evaluate the effects of benzimidazole- and imidazoleannelation on the electron-donating abilities. The voltammograms of 1–3 and 5 show reversible two-stage one-electron oxidation waves (Figures S1 and S2). In the case of 6, the second oxidation wave is irreversible due to the instability of dication species under the measurement conditions. Table 2 lists the first and second oxidation potentials (E^{ox1} and E^{ox2} , respectively) and the difference between E^{ox1} and E^{ox2} (ΔE) which is an indicator of on-site Coulomb repulsion. The E^{ox1} value of 1 (+0.08 V) is lower than that of 20 (+0.16 V), indicating that the imidazole annelation of benzo-TTF skeleton strengthens the electron-donating ability. The *N*-methylated derivative 1b (Chart 3) shows similar oxidation potentials ($E^{\text{ox1}} = +0.09$ and $E^{\text{ox2}} = +0.29$ V) to those of 1, suggesting



Figure 2. Electronic spectra of 1–3 and 20 in THF (0.2–0.5 mM). Dotted lines show absorption bands of 20, and grayish lines indicate the peaks of 1–3.

that the protection of the N-H group of imidazole ring has a negligible effect on the redox ability. Oxidation potentials of the EDT substituted derivative 2 ($E^{ox1} = +0.07$ and $E^{ox2} =$ +0.28 V) are also close to those of 1. The cyano-substituted derivative 3 exhibits a ca. 0.10 V high potential shift of E^{ox1} due to the strong electron-withdrawing nature of the cyano group, demonstrating the lowering of HOMO energy in the theoretical calculation (Table 1). In the case of bis(benzimidazole)-annelated derivative 5, the low-potential shift of E^{ox1} from 21 (0.16 V) is twice that of 1 and 20 (0.08 V). Contrastively to the fact that the benzo annelation causes a high potential shift of E^{ox1} (+0.16 V for **20** and +0.03 V for **22**), the E^{ox1} value of 6 (+0.01 V) is slightly lower than that of 22. This result is also contrastive to the fact that the imidazole-substitution of TTF causes the high potentials shift of E^{ox1} (-0.09 V for TTF and -0.06 V for TTF-Im^{11a}). All these effects on the redox abilities of imidazole annelation to benzo-TTF and TTF skeletons show a good coincidence with those expected from the theoretical calculation (Table 1).

Electronic Spectra. Figures 2 and 3 illustrate the electronic spectra of 1–3, 5, and 6 in THF solution. Benzo-TTF derivative 20 shows peaks at 298 and 320 nm and a broad shoulder band around 360 nm. The former two bands of 1–3 exhibit slight long wavelength shifts due to the π -expansion. The strong electron-withdrawing effect of cyano group of 3 results in the appearance of an intramolecular CT absorption band at a lower energy region (393 nm). Such low energy absorption bands were also observed around 400 nm in the mono(benzimidazole)-annelated TTF derivatives with electron-

withdrawing pyridyl and quinolyl groups reported by Decurtins et al.¹⁴ Comparing **5** and **21**, and **6** and **22** (Figure 3), the imidazole annelation also causes slight red shifts of all bands.

Crystal Structure of (2)₂(MeOH). A crystal of 2 was obtained by the slow evaporation from a mixed solution of ethyl acetate and MeOH. The asymmetric unit of this crystal is composed of one molecule of 2 and MeOH solvent. The 2 molecule possesses a nearly planar molecular structure where the dihedral angles ϕ_1 and ϕ_2 are 2.0 and 2.5°, respectively (Table 3, ϕ_1 and ϕ_2 are the dihedral angles between the best planes defined by central C₂S₄ and terminal C₂S₂ moieties close to the imidazole ring and alkylthio groups, respectively). Two C–N–C bond angles of the imidazole ring (θ_1 and θ_2 , Table 3), which are sensitive to the protonation, are close to each other (106.3(8) and 106.7(8)°) suggesting the disordering of the N–H group into two sites. The N–H protons are placed at both N atoms with a site-occupancy factor of 0.5.

One side of the imidazole ring in **2** is connected by the direct N–H…N H-bonds (2.81 Å), and the other side is linked through the H-bonds with MeOH (N…O distance, 2.72 Å) forming a one-dimensional chain along the *a* axis (Figure 4a). The dihe-



Figure 3. Electronic spectra of 5, 21, 6, and 22 in THF (0.2–0.5 mM). Grayish lines indicate the peaks.

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dral angle of neighboring **2** molecules within the H-bonded chain is 64.3° . The **2** molecule stacks in a slip stack manner (Figure 4b) forming a one-dimensional uniform column along the *b* axis (Figure 4c). The face-to-face and slip distances within a column are 3.67 and 5.5 Å, respectively. Side-by-side S...S interactions of the EDT-TTF skeleton (3.60–3.63 Å, green lines in Figure 4a) which are close or slightly longer than the sum of van der Waals radii of S atoms (3.60 Å)¹⁸ construct a two-dimensional TTF layer, which is linked through the H-bonds of the imidazole ring.

Crystal Structure of (2·H⁺)(Cl⁻)(H₂O). The protonated salt of **2**, which was prepared by the treatment of **2** with HCl, crystallized as reddish yellow platelets by vapor diffusion using ethyl acetate and MeOH. One protonated **2·H⁺** molecule, Cl⁻ and crystalline water molecule disordering into two sites are crystallographically independent. C–N–C bond angles of the imidazole ring (θ_1 and θ_2 in Table 3) are 109.5(4) and 109.8(4)° and slightly larger than those of neutral **2** molecules indicating the protonation of both N atoms. The **2·H⁺** molecule in this crystal is planar with the ϕ_1 and ϕ_2 angles of 1.4 and 4.7°, respectively (Table 3).

The N-H-Cl-H-N H-bonds between 2·H⁺ and Cl⁻ (N-Cl distances, 3.09 and 3.02 Å) form a one-dimensional chain along the *a* axis, where the neighboring molecules in a chain are parallel to each other (Figure 5a). Furthermore, the $2 \cdot H^+$ molecule forms a one-dimensional π -stacking column along the [110] direction (Figures 5b and 5c). Two types of head-totail stackings are found in the column; TTF skeletons overlap to each other with a slipping of ca. 1.7 Å along the molecular short axis (stack-A, Figure 5d, face-to-face distance of 3.56 Å), and in stack-B, the TTF skeleton locates on the top of benzimidazole moiety of the next molecule (Figure 5e, face-toface distance of 3.53 Å). The side-by-side S...S interactions (3.69–3.71 Å) which are slightly longer than the sum of van der Waals radii of S atoms $(3.60 \text{ Å})^{18}$ are formed between the columns. It should be noted that the side-by-side S...S interaction in the $(2 \cdot H^+)(Cl^-)(H_2O)$ salt is weaker than that of the crystal structure of $(2)_2$ (MeOH) as shown in longer interatomic distances. This result would relate to the difference in the strength of π -stacks within the one-dimensional columns (faceto-face distance: 3.67 Å vs. 3.53–3.56 Å, Figures 4b and 5c, respectively). These intermolecular interactions form a two-

	s	_S ^{\$} _	$R \rightarrow R$	S S S	R'	
		ϕ_1/\deg	$\phi_2/{ m deg}$	$a/ m \AA$	θ_1/deg	θ_2/deg
(1)(CHCl ₃) ^{b) 12}	1-A	5.1	23.2	1.337(7)	106.7(4)	106.1(4)
	1-B	3.5	22.8	1.349(7)	105.9(4)	106.8(4)
$(2)_2$ (MeOH) ^{b)}	2	2.0	2.5	1.360(13)	105.9(4)	106.8(4)
$(2 \cdot H^+)(Cl^-)(H_2O)$	2 •H ⁺	1.4	4.7	1.383(7)	109.5(4)	109.8(4)
(1)(TCNQ)	1	14.7	21.3	1.384(16)	103.7(12)	107.2(12)
$(1^{+})(1^{+} \cdot H^{+})(I_{11}^{3-})(CH_2Cl_2)$	1-A	0.9	2.4	1.37(3)	110.3(15)	106.7(16)
	1-B	0.8	1.9	1.43(2)	107.5(15)	100.7(16)

Table 3. Folding Angles $(\phi_1 \text{ and } \phi_2)^{a}$ and C-N-C Bond Angles $(\theta_1 \text{ and } \theta_2)$ of **1** and **2** Molecules in the Crystal Structures

H_{θ1} NS a S SR

a) ϕ_1 and ϕ_2 are the dihedral angles between the best planes defined by central C_2S_4 and terminal C_2S_2 moieties close to the imidazole ring and alkylthio groups, respectively. b) N–H protons on the imidazole rings were disordered at the two N atoms.¹²



Figure 4. Crystal structure of (2)₂(MeOH). (a) Molecular packing viewed along the *c* axis showing N–H…N and N–H…O–H…N H-bonds (red lines) and S…S interactions (green lines). (b) Overlap pattern within the π -stacking column. (c) The *a* axis projection of molecular packing showing one-dimensional π -stacking columns. Deep and pale colored molecules in (c) locate around a = 0.2 and 0.7 planes, respectively.



Figure 5. Crystal structure of $(2 \cdot H^+)(Cl^-)(H_2O)$. (a) One-dimensional chain by the N-H…Cl…H-N H-bond bonded chain. (b) Molecular packing viewed along the $[1\bar{1}0]$ direction showing the two-dimensional donor sheet by the intercolumnar H-bonds (red lines), π -stacks and S…S interactions (green lines). (c) Crystal packing viewed along the *a* axis showing the π -stacking structure and arrangement of two-dimensional sheets. (d and e) Overlap patterns within the π -stacking column.

dimensional π -layer parallel to the *ab* plane. The water molecules locate between the π -layers (Figures 5b and 5c).

Charge-Transfer Complexes. CT complexes of 1–3, 5, and 6 were obtained by mixing the solutions of each donor and acceptor (2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 2,3,5,6-tetrafluorotetracyanoquinodimethane (F_4TCNQ), and

tetracyanoquinodimethane (TCNQ)) molecules. Table 4 summarizes the component ratio, the first CT absorption band $(h\nu_{\rm CT})$,¹⁹ characterization of the complexes (neutral, N; ionic, I), and room temperature conductivity measured for the compressed pellet ($\sigma_{\rm RT}$). TCNQ complexes of **3** and **6** and the DDQ complex of **6** could not be obtained. The donor–acceptor

Donor	Acceptor	D:A ratio ^{a)}	$\Delta E^{\rm DA}/{\rm V}^{\rm b)}$	$h\nu_{\rm CT}/{\rm cm}^{-1{\rm c}}$	Characterization ^{d)}	$\sigma_{ m RT}/ m Scm^{-1e)}$
1	DDQ	1:1	-0.01	9000	Ι	5.5×10^{-8}
1	F ₄ TCNQ	1:1	-0.11	6000	Ι	5.1×10^{-5}
1	TCNQ	1:1	+0.19	6700	Ν	$< 10^{-8}$
2	DDQ	1:1	-0.02	9100	Ι	2.9×10^{-3}
2	F4TCNQ	1:1	-0.12	5700	Ι	7.3×10^{-4}
2	TCNQ	1:1	+0.18	6500	М	$< 10^{-8}$
3	DDQ	1:1	+0.09	9100	Ι	2.5×10^{-5}
3	F ₄ TCNQ	1:1	-0.01	8000	Ι	6.3×10^{-5}
5	DDQ	1:1	-0.07	10000	Ι	9.1×10^{-5}
5	F ₄ TCNQ	1:1	-0.17	9700	Ι	$1.8 imes 10^{-6}$
5	TCNQ	2:1	+0.13	7000	М	$< 10^{-8}$
6	F ₄ TCNQ	1:1	-0.18	9000	Ι	$< 10^{-8}$

Table 4. Physical Properties of CT Complexes of 1-3, 5, and 6

a) Molar ratios were determined by elemental analyses. b) ΔE^{DA} is the difference of the first redox potentials of donor and acceptor. c) $h\nu_{\text{CT}}$ is the first CT absorption bands.¹⁹ d) N: neutral; M: mixed-valence; I: ionic CT states. e) Electrical conductivity was measured on a compressed pellet.



Figure 6. IR spectra (KBr pellet) of DDQ complexes of 1–3 and 5 and related compounds in the C=O stretching region.

component ratios of these complexes estimated by the elemental analysis are 1:1 except for the 2:1 ratio of 5-TCNQ complex.

DDQ Complexes. DDQ is a strong electron-acceptor with the reduction potential (E^{red}) of +0.09 V vs. Fc/Fc⁺. The differences between E^{ox1} of **1**, **2**, and **5** and E^{red} of DDQ (ΔE^{DA}) are in the range from -0.07 to -0.01 V, which locate around the vicinity of the border between the criteria for ionic and mixed-valence CT complexes in TTF-*p*-benzoquinone system ($\Delta E^{\text{DA}} = -0.04 \text{ V}$).²⁰ In the case of cyano derivative **3** possessing a weaker electron-donating ability, the ΔE^{DA} value with DDQ is +0.09 V, and the CT complex is expected to be a mixed-valence complex.

Figures 6 and 7 show IR spectra in the C=O stretching region and electronic spectra in KBr, respectively. The C=O stretching band of neutral DDQ appears at 1540 cm^{-1} , while the fully ionic DDQ⁻⁻ salt shows two bands at 1560 and 1528 cm⁻¹. The spectral feature of DDQ complexes of **1–3** and **5**



Figure 7. Electronic spectra of DDQ complexes of 1–3 and 5 in KBr pellet. Arrows indicate the hv_{CT} bands.

in this region is similar to that of DDQ^{•-} salt suggesting that these CT complexes include fully ionic DDQ^{•-} species. In the electronic spectra, low energy bands around 9000-10000 cm⁻¹ assignable as intermolecular CT bands between fully ionic species of electron-donor and -acceptor molecules are observed (Figure 7).¹⁹ Further lower energy CT bands characteristic to mixed-valence complexes are not found. DDQ can also accept a proton from the imidazole ring of 1-3 and 5, generating their anionic or neutral betainic radical species. The 1:1 D-A ratios and spectral features indicate that DDQ complexes of 1-3 and 5 are fully ionic CT complexes composed of radical cation of the donors and DDO radical anion species. The high ionicity of 3–DDQ complex unexpected from the ΔE^{DA} value might be caused by the redox activation effect of donor-acceptor H-bond^{6e} as speculated from the CT complexes of TTF-Im.^{11b} The $\sigma_{\rm RT}$ values of these complexes vary in the range of 10^{-3} to $10^{-7} \,\mathrm{S}\,\mathrm{cm}^{-1}$ probably due to the differences in the crystal packing.



Figure 8. IR spectra (KBr pellet) of F_4TCNQ complexes of 1–3, 5, and 6 and related compounds in the C \equiv N stretching region.

F₄TCNQ Complexes. The reduction potential of F₄TCNQ $(E^{\text{red}} = +0.19 \text{ V})$ is further higher than that of DDQ, and the ΔE^{DA} values with **1–3** and **5** (-0.17 to -0.01 V) are close or lower than the border between the criteria for ionic and mixed-valence CT complexes in TTF–TCNQ system ($\Delta E^{\text{DA}} = -0.02 \text{ V}$).²⁰

The C≡N stretching frequency of TCNQ derivatives is known to be sensitive to the ionicity and shifts to a lower frequency region with increment of the ionicity. Neutral F4TCNQ shows C=N stretching bands at 2227 and 2213 cm⁻¹, which shift to 2212 and 2192 cm⁻¹ in K⁺F₄TCNQ^{•-} salt (Figure 8). F₄TCNQ complexes of 1-3 and 5 show intense bands around 2195 cm^{-1} and one or two weak bands around 2170-2185 cm^{-1} . In the complexes of 2, 5, and 6, weak bands around 2210 cm^{-1} which is close to that of $K^+F_4TCNQ^{\bullet-}$ salt are also observed. Although the shapes and frequencies in $C \equiv N$ stretching modes are different from those of K⁺F₄TCNQ^{•-} probably due to the differences in stacking structures and intermolecular interactions with counter parts (e.g., H-bonds with donors), the low-frequency shift suggests the highly ionized state of F4TCNQ molecule in these complexes. Figure 9 shows electronic spectra of the F₄TCNQ complexes in KBr pellets. The hv_{CT} bands assignable as the intermolecular CT absorption between ionized species of electron-donor and -acceptor are observed at 5700–9700 cm⁻¹. These observations also suggest the fully ionic state of these complexes. The σ_{RT} value of F_4TCNO complexes of 1-3 are 10^{-3} to 10^{-4} S cm⁻¹.

TCNQ Complexes. The ΔE^{DA} values of pristine TCNQ $(E^{\text{red}} = -0.11 \text{ V})$ with **1**, **2**, and **5** are in the range of +0.13 to +0.19 V and locate within the criteria for mixed-valence CT complexes $(-0.02 < \Delta E^{\text{DA}} < +0.34 \text{ V}).^{20}$

Figure 10 shows IR spectra of the TCNQ complexes of 1, 2, and 5 in the C \equiv N stretching frequency region (2120–2270 cm⁻¹). The b_{1u} C \equiv N stretching modes show a slight lowfrequency shift from that of neutral TCNQ (2227 cm⁻¹) and appear at 2212–2215 cm⁻¹. According to the Chappell's equa-



Figure 9. Electronic spectra of F_4 TCNQ complexes of 1–3, 5, and 6 in KBr pellet. Arrows indicate the hv_{CT} bands.



Figure 10. IR spectra (KBr pellet) of TCNQ complexes of 1, 2, and 5 and related compounds in the C≡N stretching region.

tion,²¹ the ionicities of TCNQ moieties in **1**, **2**, and **5** complexes are estimated to be 0.27–0.34 suggesting the weakly ionized state. In the case of complexes of **2** and **5**, the lower frequency bands similar to those of K⁺TCNQ⁻⁻ salt are also observed. This suggests the coexistence of neutral and ionized species of TCNQ moiety. In the electronic spectra (Figure 11), the $h\nu_{\rm CT}$ bands assignable as that between electron-donor and -acceptor molecules in a mixed stack are observed at 6500–6700 cm⁻¹, and a lower-energy absorption band around 3000 cm⁻¹ characteristic of highly conductive mixed-valence salt with a segregated stack¹⁹ was not found. In conductivity measurements using compressed pellets, these complexes are insulators with $\sigma_{\rm RT} < 10^{-8} \, {\rm S \, cm^{-1}$.

Crystal Structure of (1)(TCNQ). Single crystals of (1)(TCNQ) complex were obtained by the slow evaporation of a 1:1 mixture of 1 and TCNQ in CH₂Cl₂. Similar to neutral 1,¹² the molecular structure of 1 in this complex has large bent angles ϕ_1 and ϕ_2 of 14.7 and 21.3°, respectively (Table 3). Since the quality of structural analysis is poor due to the disorder of propylthio groups (R = 0.12), the precise discussion on ionicities of 1 and TCNQ cannot be made. However, the central C–C bond length of TTF skeleton is somewhat longer than that of neutral 1 species¹² (Table 3) indicating the weakly ionized state of the donor molecule. The C–C bond length analysis of the TCNQ moiety (Table S1) also indicate the weakly ionized state of the acceptor molecule. These observations are not inconsistent with the neutral state of



Figure 11. Electronic spectra of TCNQ complexes of 1, 2, and 5 in KBr pellet. Arrows indicate the $h\nu_{CT}$ bands.

both **1** and TCNQ molecules as characterized by the optical measurements.

In the crystal structure, a one-dimensional column is formed by the alternating stack of 1 and TCNQ molecules along the *a* axis (Figure 12a). Two kinds of stacks are found in the column (stack-A and stack-B), where the benzimidazole moiety and one 1,3-dithiole ring mainly locate over the TCNQ molecule (Figures 12b and 12c, respectively). The face-to-face distances in stack-A and stack-B are 3.40 and 3.26 Å, respectively. The neighboring columns are linked by the N–H…N≡C H-bond (N…N distance, 3.02 Å), and the pair of columns is arranged along the *b* axis to form a π -layer (Figure 12d). The π -layers are separated with the propylthio groups along the *c* axis (Figure 12d).

Crystal Structure of (1'+)(1'+·H⁺)(I₁₁³⁻)(CH₂Cl₂). Single crystals of the iodine salt of **1** were prepared by the slow diffusion of **1** and I₂ in CH₂Cl₂. The asymmetric unit includes crystallographically two kinds of **1** molecules (**1-A** and **1-B**), three kinds of I₃⁻, two of which locate on the inversion center, one I₅⁻, and CH₂Cl₂ solvent molecules. Unlike neutral **1**, the molecular structures of both **1-A** and **1-B** are planar, and the ϕ_1 and ϕ_2 values are 0.9 and 2.4° for **1-A** and 0.8 and 1.9° for **1-B**, respectively (Table 3). In the electronic spectrum (Figure 13), the appearance of an intermolecular CT absorption band between TTF⁺⁺ species around 9000 cm⁻¹ and the absence of a lower energy band around 3000 cm^{-1} characteristic to the mixed-valence state indicate the fully oxidized state of the TTF skeleton. The composition ratio of $1:I_3^{--}:I_5^{--} = 2:2:1$ suggests the protonation of the imidazole ring of **1-A** or **1-B**.

Both 1-A and 1-B molecules individually form π -dimers, which are arranged along the *c* axis (Figure 14a). Two TTF skeletons within π -dimers eclipse each other (Figures 14b and 14c). The face-to-face distances of (1-A)₂ and (1-B)₂ dimers are 3.41 and 3.37 Å, respectively. The dimers of 1-A and 1-B are connected to each other by the N–H…N H-bond (N…N distance of 2.71 Å) to form a two-dimensional π -layer



Figure 12. Crystal structure of (1)(TCNQ). (a) Molecular packing viewed along the *c* axis (0 < c < 0.5) showing the onedimensional alternating columns. (b and c) Overlap patterns within the π -stacking column. (d) The *a* axis projection of the crystal structure showing the arrangement of π -sacking columns.

on the *bc*-plane (Figure 14a). The layers are separated by the propylthio groups and CH₂Cl₂ solvent molecules along the *a* axis (Figure 14d). The I₃⁻ and I₅⁻ units are linked in a $-(I_3^-)_3 - (I_5^-) - (I_3^-) - (I_5^-) -$ manner to form a meander-like polymeric chain along the [011] direction (Figure 14e). The (**1-A**)₂ and (**1-B**)₂ dimers are surrounded by the iodine chains along both face-to-face and side-by-side directions, and are isolated electronically.



Figure 13. Electronic spectrum of $(1^{+})(1^{+} \cdot H^{+})(I_{11}^{3-})$ -(CH₂Cl₂) salt in KBr pellet. Arrow indicates the $h\nu_{CT}$ band.

Conclusion

We have synthesized new TTF-type electron-donors annelated with benzimidazole (1-3), bis(benzimidazole) (4 and 5), and imidazole (6) skeletons. Theoretical calculations indicate that the annelation with benzimidazole and imidazole ring enhanced the HOMO energy of TTF moiety as experimentally confirmed by the low-potential shift of the oxidation waves in the electrochemical measurements. The substituent group on the imidazole ring affected the electronic structure of cyano derivative 3 as shown in the high potential shift of the oxidation potentials and the appearance of a low-energy intramolecular CT absorption band. Crystal structures elucidated the self-assembling abilities of 1 and 2 constructing multidimensional networks, where H-bonds of the imidazole ring linked the π -stacking motifs of TTF skeletons (onedimensional column, donor-acceptor alternating column and π -dimer). Further intriguing features of the present molecules is the PT ability of the imidazole ring.¹²⁻¹⁴ The correlation between CT on TTF and PT on imidazole will open a new opportunity for the development of multifunctional materials. Further investigations are currently in progress to elucidate the PT ability of **1–6** and to demonstrate the PET system.^{6a,7}



Figure 14. Crystal structure of $(1^{+})(1^{+} \cdot H^{+})(I_{11}^{3-})(CH_2CI_2)$. (a) Molecular packing viewed along the *a* axis around a = 0. The propyl groups are omitted for clarity. (b and c) Overlap patterns within the π -dimers. (d) The *b* axis projection of 1 molecules in the range of 0 < b < 0.5 showing the arrangement of π -layers. Deep and pale colored molecules locate around b = 0.1 and 0.4 planes, respectively. (e) One-dimensional of I_3^- and I_5^- units around b = 0. The gray bonds are the interactions between I_3^- and I_5^- units.

	(2) ₂ (MeOH)	$(2 \cdot H^+)(Cl^-)(H_2O)$	(1)(TCNQ)	$(1^{+})(1^{+} \cdot H^{+})(I_{11}^{3-})(CH_2Cl_2)$
Crystal formula	$C_{29}H_{24}N_4O_1S_{12}$	C ₁₄ H ₁₁ Cl ₁ N ₂ O ₁ S ₆	$C_{30}H_{24}N_6S_6$	C ₃₇ H ₄₃ Cl ₂ I ₁₁ N ₄ S ₁₂
Formula weight	829.24	451.06	660.91	2395.27
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	P2/c	$P\bar{1}$	$P\bar{1}$	C2/c
a/Å	12.335(1)	7.190(1)	6.9876(8)	31.615(1)
$b/ m \AA$	6.7603(7)	8.373(1)	7.791(1)	19.3517(8)
$c/\text{\AA}$	20.671(2)	15.649(2)	28.417(5)	22.960(1)
α /degree		85.36(2)	90.987(9)	
β /degree	95.548(7)	85.85(2)	90.104(7)	109.586(1)
γ /degree		76.75(2)	100.248(7)	
$V/Å^3$	1715.6(3)	912.6(2)	1522.1(4)	13234(1)
Ζ	2	2	2	8
$D_{\rm calcd}/{ m gcm^{-3}}$	1.605	1.641	1.442	2.404
$\mu/{ m mm^{-1}}$	7.375 ^{a)}	0.901 ^{b)}	4.411 ^{a)}	5.640 ^{b)}
Temperature/K	150	200	150	200
Unique reflns	3101	4113	5407	13481
Refln used $(I > 2\sigma(I))$	2616	2190	3265	5224
Parameters	231	217	378	566
$R_1 (I > 2.0\sigma(I))$	0.1042	0.0617	0.1209	0.0853
wR_2 (all data)	0.3077	0.2366	0.3358	0.2578
GOF	1.097	1.019	1.086	0.960

Table 5. Crystallographic Data of Mono(benzimidazole)-Annelated TTF 1 and 2

a) $Cu K\alpha$. b) $Mo K\alpha$.

Experimental

Materials and Methods. 5,6-Diaminobenzene-1,3-dithiole-2-thione.¹⁵ 4.5-dichloro-1.2.3-dithiazolium chloride.¹⁶ and 4,5-bis(propylthio)-1,3-dithiolo-2-one²² were synthesized by previously reported procedures. Preparation of 1, 7i, and 8ii were performed according to our previous papers.¹² TCNO. DDQ, and F4TCNQ were purchased and purified by sublimation in our laboratory. Solvents and reagents were dried (drying reagent in parenthesis) and distilled under an argon atmosphere prior to use: DMF, benzene, and toluene (CaH₂); THF (Nabenzophenone ketyl); P(OMe)₃ and P(OEt)₃ (Na). All reactions requiring anhydrous conditions were performed under an argon atmosphere. R_f values on TLC were recorded on E. Merck precoated (0.25 mm) silica gel 60 F_{254} plates. The plates were sprayed with a solution of 10% phosphomolybdic acid in 95% EtOH, and then heated until the spots became clearly visible. Silica gel 60 (100-200 mesh) was used for column chromatography. Recycle preparative gel permeation chromatography was performed by using two tandem polystyrene gel columns (JAIGEL 1H, Japan Analytical Industry) with CHCl₃ as eluant.

Measurements. ¹H NMR spectra were obtained on a JEOL-270 with CDCl₃ or DMSO- d_6 as solvent and tetramethylsilane or residual solvent as an internal standard. Infrared spectra were recorded using KBr plates on a JEOL JASCO FT/IR-660 Plus. Electronic spectra were measured using KBr plates or THF solutions on a Shimadzu UV–vis–NIR scanning spectrophotometer UV-3100 PC. EI-MS spectra were taken at 70 eV on using a Shimadzu QP-5000 mass spectrometer. FAB-MS spectra were recorded on a Shimadzu/KRATOS Concept 1S using 3-nitrobenzyl alcohol matrix. Melting points were measured with a hot-stage apparatus and were not corrected. Elemental analyses were performed at the Graduate School of Science and Osaka University. Cyclic voltammetry was demonstrated on an ALS Electrochemical Analyzer Model 612A. Measurements were made with 1.6 mm diameter gold plate and Pt wire counter electrodes in DMF containing 0.1 M $Bu_4N^+ClO_4^-$ as a supporting electrolyte at room temperature. The experiments employed a Ag/Ag^+ reference electrode, and the final results were calibrated with Fc/Fc⁺ couple. The resistivity of CT complexes was measured for compressed pellets by the conventional two-probe method.

X-ray Crystallography. X-ray crystallographic measurements were made on a Rigaku RAXIS-RAPID imaging plate with graphite monochromated Mo K α ($\lambda = 0.71070$ Å) or CuK α ($\lambda = 1.54187$ Å) radiation. The structures were determined by a direct method using SIR-2004.²³ Least-squares refinements were performed on F^2 with SHELXL-97.²⁴ All non-hydrogen atoms were refined anisotropically. Positional parameters of hydrogen atoms were calculated with sp² or sp³ configuration of the bonding carbon and nitrogen atoms, and hydrogen atoms were refined using the riding model. In the refinement procedures, isotropic temperature factors with magnitudes of 1.2 times the equivalent temperature factors of the bonding atoms were applied for hydrogen atoms. Selected crystal data and data collection parameters are given in Table 5. In $(2)_2$ (MeOH) and (1)(TCNQ), the analyses gave poor results due to the disorder of terminal ethylenedithio and propylthio groups, respectively. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-934538-934541. Copies of the data can be obtained free of charge via http//www.ccdc.cam.ac.uk/conts/ retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Theoretical Calculation. Density functional theory (DFT) calculations were performed with optimized structure at the B3LYP/6-31G(d) level on Gaussian $98.^{25}$

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Supporting Information

Synthetic procedures and properties for identification of **1–6** and their CT complexes, cyclic voltammograms of **1–3**, **5**, **6**, and related compounds, IR spectra of $(1^{++})(1^{++} \cdot H^+)(I_{11}^{3-})$ -(CH₂Cl₂) in the C=C and C=N stretching region, and a list of intramolecular C–C bond lengths of the TCNQ skeletons in (1)(TCNQ), and related compounds. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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