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Introduction of Amino Groups into the Dibenzo-TTF π-System: Enhanced Electron-Donating Ability and Intermolecular Hydrogen Bonding

Yasushi Morita,[*,1,2] **Eigo Miyazaki,**[1] **Kozo Fukui,**[2] **Suguru Maki,**[1] **and Kazuhiro Nakasuji**[*,1]

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

[2]PRESTO, Japan Science and Technology Agency, Hon-cho, Kawaguchi, Saitama 332-0012

Received March 25, 2005; E-mail: morita@chem.sci.osaka-u.ac.jp

A new dibenzo-TTF (DBTTF) derivative directly connected with amino groups has been designed and synthesized as a stable molecule in air with enhanced electron-donating ability compared with that of DBTTF. A crystal structure analysis of its TCNQ complex has shown that intermolecular hydrogen bondings are formed between the two amino groups and CH_3CN molecules contained as a crystal solvent. Despite the alternated stacking structure, the TCNQ complex exhibited relatively high electrical conductivity ($\sigma_{\rm rt} = 0.12$ S cm^{-1}) and low activation energy ($E_{\rm a} = 106$ meV).

The hydrogen-bonding (H-bonding) interaction is one of the effective tools to associate molecules and to control molecular arrangements.[1] In recent years, a variety of tetrathiafulvalene (TTF) derivatives connected with OH and NHR functional groups by spacers, such as methylene or carbonyl groups, have been widely investigated in view of crystal engineering to construct multi-dimensional and highly ordered networks in the field of organic conductors.[2] As a result of efforts based on this strategy, H-bonded charge-transfer (CT) complexes and salts with high conductivity with semiconductive or metallic behavior were prepared by Akutagawa and Batail.[3,4] In addition to such a well-known role of H-bonding, we recently focused on an electronic effect of H-bonding interaction in the solid state, and studied the H-bonded CT and metal complexes.[5] Notably, our recent results on the CT complex of TTF-imidazole with chloranil demonstrated for the first time the marked electronic modulation role of H-bonding interactions in the CT complex: control of the ionicity of redox-active molecules and of the electron-donor/-acceptor ratio.[6] This new role in the CT complex resulted in the first purely organic molecular metal based on a H-bonded network.[6]

The physical properties of organic π-molecular systems are controllable by the introduction of various electron-donating and electron-withdrawing substituents. Despite studies on a variety of TTF derivatives having H-bonded functionalities, to our knowledge, TTF derivatives *directly* connected with OH and NHR functional groups are not known so far, likely because of their instability in air. The direct introduction of these electron- and proton-donating substituents into the TTF π-system is expected to modulate its π-electronic structure, which may increase the electron-donating ability of the molecule and cause a redistribution of the coefficients in the highest occupied molecular orbital (HOMO). Furthermore, intermolecular H-bondings through these substituents open a new possibility of additional π-electronic modulation on the redox-active systems in the multi-dimensional networks in CT complexes and salts.[7] In the present work, we took advantage of a dibenzo-TTF (DBTTF) π-molecular system as a suitable molecular framework for H-bonded functionalization, and designed a diamino derivative of DBTTF, DADBTTF (Chart 1). Here, we report on the synthesis and isolation of DADBTTF as a stable solid in air, and also on the crystal structure of its TCNQ complex. Emphasis is laid on the doubly enhanced electron-donating ability of DADBTTF by the substituents *and* intermolecular H-bondings, revealing a new electronic modulation by H-bonded functional groups in CT complexes.

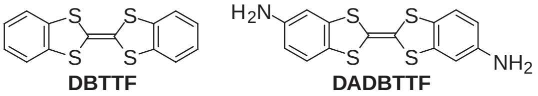


Chart 1.

Results and Discussion

Molecular Design. Molecular-orbital calculations of redox-active molecules help us to understand their π-electronic structures and redox properties. The calculated HOMO coefficients of DBTTF, based on its crystal structure, are reported to be widely spread over not only the central TTF moiety, but also the peripheral fused-benzene rings.[8] DBTTF, however, possesses a poor electron-donating ability compared with that of TTF, hampering systematic studies on a variety of CT complexes of DBTTF with organic electron-acceptors. One of the effective methods to increase in electron-donating ability in redox-active molecules is the introduction of electron-donating substituents. In fact, DBTTF derivatives with ethylenedioxy or methoxy groups exhibited higher electron-donating ability than that of DBTTF.[9] Our density functional theory (DFT) calculations based on the crystal structures of DADBTTF[10] have shown a sizeable increase in the HOMO energy compared with that of DBTTF by 0.3162 eV, and the extended HOMO coefficients onto the nitrogen atoms (Fig. 1). These calculated results are indicative of a strong electron-donating ability of DADBTTF.

Synthesis. DADBTTF was prepared by the reduction of a DBTTF derivative with nitro groups **1**[11] with $SnCl_2 \cdot 2H_2O$ under acidic conditions, and was obtained as a stable solid in air (Scheme 1).[10,12] A TCNQ complex of DADBTTF was prepared by the evaporation of a solvent after mixing the THF solutions of each compound. Single crystals of the TCNQ complex of DADBTTF suitable for X-ray analysis were obtained by slow evaporation of its CH_3CN solution.

***π*-Electronic Structure of DADBTTF.** To evaluate the electron-donating ability of DADBTTF, we measured the cyclic voltammetry (CV) in DMF (Fig. 2A). As expected, the half-wave potential of the first oxidation state of DADBTTF is negatively shifted by 0.24 V compared with that of DBTTF due to the introduced two amino groups, and is comparable to that of TTF (Table 1).

It is interesting to investigate the π-electronic structure of DADBTTF in a solution state. Neilands and co-workers reported on positive shifts of oxidation potentials of a uracil-fused TTF derivative on CV in a CH_2Cl_2 solution by the addition of diaminopyridine derivatives.[13] They pointed out an electron-donating effect from the uracil moiety to diaminopyridine derivatives in the triple H-bondings in the solution, leading to a positive shift of the oxidation potential of the uracil-fused TTF derivative.[13] To evaluate the influence of the H-bonding interaction on the electron-donating ability of DADBTTF, including an effect of the dielectric constant of the solvent, we measured CV in THF and a mixture of THF–MeOH (Fig. 2B). The first half-wave oxidation potential of DADBTTF in a THF solution shifted negatively compared with that in a DMF solution, which is probably caused by the typical solvent effect (Table 1).[14] Upon the addition of MeOH into the THF solution, no appreciable changes were observed for the first half-wave and second peak oxidation potentials. Although the formation of H-bonding on the amino groups with solvents is ambiguous, these observations indicate a small and negligible influence of the solvent polarity on the π-electronic structure of DADBTTF. The same observations were also seen in the electronic spectra measured in THF, MeOH, and DMSO solutions of DADBTTF at room temperature (Fig. 3). The shoulder absorptions around 22000 cm^{-1} due to the HOMO–LUMO transition show no significant shifts of the absorption peaks in these solutions.

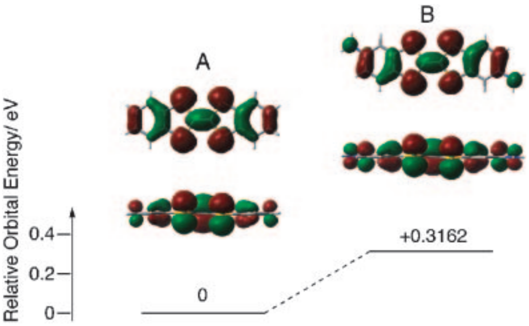
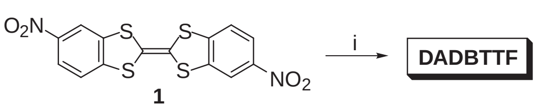


Fig. 1. Comparison of HOMO energies for DBTTF (**A**) and DADBTTF (**B**). HOMO energies were calculated at the RB3LYP/6-31G(d) level, and the structures were taken from the X-ray crystal structures.[8,10]



Scheme 1. Reagents and conditions: (i) $SnCl_2 \cdot 2H_2O$, CH_3CO_2H–HCl aq, 60 °C, 92%.

Crystal and *π*-Electronic Structure of DADBTTF–TCNQ Complex. In sharp contrast to the solution state, we have observed a remarkable effect of H-bondings on electronic modulation in the TCNQ complex in the solid state (vide infra). The crystal is composed of DADBTTF, TCNQ, and two CH_3CN molecules, formulated as DADBTTF–TCNQ$\cdot$2CH_3CN. Intermolecular H-bondings were formed between the two amino groups of DADBTTF and the cyano groups of CH_3CN (N$\cdots$N, 3.09 Å, Fig. 4).[15] DADBTTF and TCNQ were alternately stacked with an interplanar distance of 3.4 Å along the [$2\bar{2}0$] direction (Fig. 5). There are

Table 1. Half-Wave Oxidation Potentials in DMF and THF Solutions[a)]

	Solvent	$E_{1/2}{}^{ox1}$	$E_{1/2}{}^{ox2}$	ΔE
DADBTTF	DMF	−0.04	+0.21[b)]	—
	THF	−0.14	+0.23[b)]	—
DBTTF	DMF	+0.20	+0.41	0.21
	THF	+0.19[b)]	+0.51[b)]	—
TTF	DMF	−0.08	+0.15	0.23
	THF	−0.13	+0.11	0.24

a) Conditions, see: experimental. b) Peak potential and irreversible behavior.

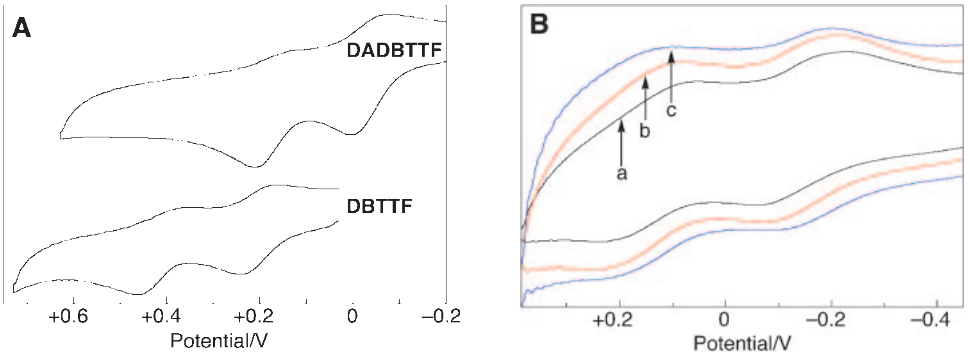


Fig. 2. Cyclic voltammograms of DADBTTF and DBTTF in DMF (**A**), and DADBTTF (**B**) in THF (black, a), 10:1 THF–MeOH (red, b), and 2:1 THF–MeOH (blue, c). Fc/Fc$^+$ = 0 V, conditions, see: experimental section.

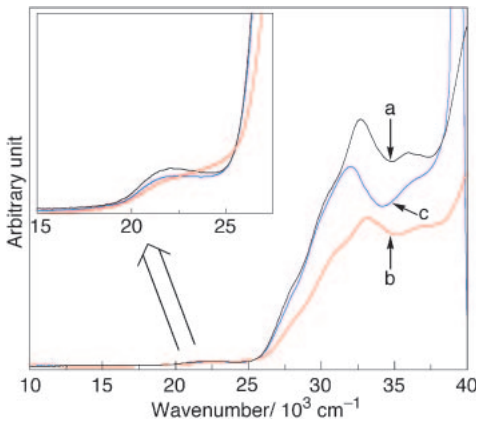


Fig. 3. Electronic spectra of DADBTTF in THF (black, a), MeOH (red, b), and DMSO (blue, c). Conditions, see: experimental section.

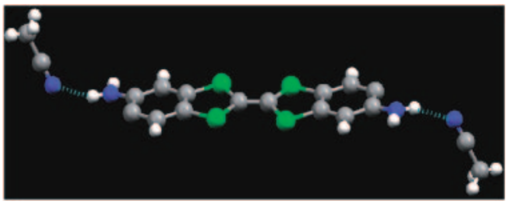


Fig. 4. Formation of H-bondings between the two amino groups of DADBTTF and CH_3CN in the TCNQ complex. Intermolecular N···N distance is 3.09 Å.[15]

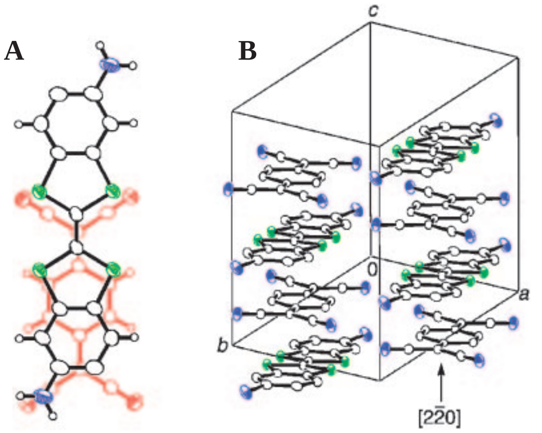


Fig. 5. Overlap mode of the DADBTTF and TCNQ molecules with interplanar distance of 3.4 Å (**A**), and alternated stacking structure along the [2$\bar{2}$0] direction (**B**).[15] CH_3CN molecules and hydrogen atoms are omitted for clarity.

double intermolecular short S···N contacts (3.30 Å) between DADBTTF and TCNQ within the sum of the van der Waals radii (3.35 Å),[16] resulting in the formation of an infinite chain structure along the side-by-side direction (Fig. 6). The ionicity of TCNQ was estimated to be 0.4–0.5 based on the bond lengths[17] and nitrile stretching frequency[18] characteristic of the TCNQ molecule (see Supporting Information). Interestingly, this partial CT state of TCNQ moieties with alternated stacking modes gives a rare event of CT complexes composed of a 1:1 ratio of electron-donor and -acceptor molecules.[19]

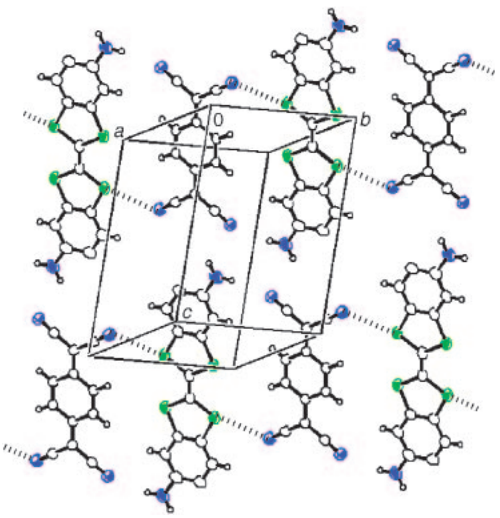


Fig. 6. Infinite chain structure formed by double intermolecular short S···N contacts (3.30 Å) between DADBTTF and TCNQ.[15] CH_3CN molecules are omitted for clarity.

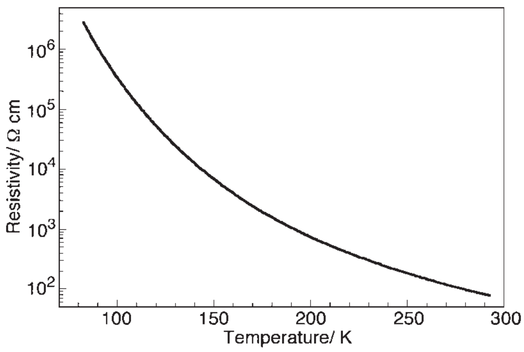


Fig. 7. Temperature dependence of resistivity of DADBTTF–TCNQ•$2CH_3CN$ CT complex measured by four-probe method of the compressed pellet.

As expected from the crystal structure, a CT transition was observed at around 6600 cm^{-1} in the electronic spectra in a KBr pellet (see Supporting Information).

The electrical conductivity of the compressed pellet of DADBTTF–TCNQ•$2CH_3CN$ was measured in the temperature range of 80–290 K. In general, a CT complex with alternated stacking modes of electron-donor and -acceptor molecules is known to be an insulator or a semiconductor with poor electrical conductivity.[20,21] Contrary to the prevailing notion, the room-temperature conductivity (σ_{rt}) and activation energy (E_a) of this CT complex were 0.12 $S\,cm^{-1}$ ($\rho_{rt} = 7.8$ $\Omega\,cm$) and 106 meV, respectively with a semiconductive behavior (Fig. 7). This relatively high electrical conductivity and low E_a with an alternating stacking structure of the TCNQ complex display the importance of H-bondings and S···N interactions.

The formation of H-bondings between the two amino groups of DADBTTF and CH_3CN may cause an additional perturbation on the electronic structure of the donor molecule. To evaluate this electrostatic effect induced by noncovalent interactions, we carried out DFT calculations of DADBTTF using the crystal structure of the TCNQ complex at the RB3LYP/6-31G(d) level in order to estimate any energy difference in the HOMO energy of the donor molecule with CH_3CN attached and that with CH_3CN removed, respectively (see Supporting Information). The difference is 0.3306 eV, which is additionally brought about by noncovalent H-bonding interactions, aside from the contribution by NH_2-functionalization. The resulting electron-donating ability of DADBTTF in the *crystal* may facilitate a charge-transfer interaction between the two redox-active molecules favorably to the extent that a relatively high electrical conductivity is achieved.[22]

Conclusion

We synthesized and isolated a new amino derivative of DBTTF, DADBTTF, as a stable molecule, and revealed its low oxidation potential from both experimental and theoretical sides. The amino groups in the DADBTTF π-system act as not only a tool for crystal engineering, but also functional groups for effective electronic modulation, which brought about an enhanced effect of the electron-donating ability. These findings do not entail a new mechanism of the electron-conduction pathway and the preparation of an organic metal. However, this function of H-bonding in modulating electronic structures of the parent molecule has never been documented to date, and thus suggests a new direction of the design concept of molecule-based conductors.[5,6] We are currently extending and applying the chemistry described in this paper into acetylamino and formylamino derivatives of DBTTF, and investigating the roles of H-bondings in their CT complexes and salts.

Experimental

General. ^{1}H NMR spectra were recorded at 270 MHz with DMSO-d_6 as a solvent and Me_4Si as an internal standard. Infrared spectra were recorded using KBr plates on Perkin Elmer 1600 series FT-IR. Electronic spectra were measured in the solution and KBr plates on a Shimadzu UV–vis–NIR scanning spectrophotometer UV-3100 PC. EI-MS spectra were recorded at 70 eV on a Shimadzu mass spectrometer QP-5000. The melting points were measured with a hot-stage apparatus, and were uncorrected. Elemental analyses were performed at the Graduate School of Science of Osaka University. The R_f values on TLC were recorded on E. Merck precoated (0.25 mm) silica gel 60 F254 plates. The plates were sprayed with a solution of 10% phosphomolybdic acid in 95% ethanol, and then heated until the spots became clearly visible. The solvents were dried (drying reagent in parenthesis) and distilled under an argon atmosphere prior to use: DMF (CaH_2). An alternating-current electrical-conductivity measurement for a compressed pellet was performed between 290 and 80 K by a conventional four-probe method using gold paint and Au wire (25 µm ϕ).

***(E)*-5-Amino-2-(5-amino-1,3-benzodithiole-2-ylidene)-1,3-benzodithiole (DADBTTF).** The DBTTF derivative **1**[11] (39 mg, 0.1 mmol) was placed in a 100-mL round-bottomed flask, dissolved with acetic acid (0.6 mL). To this solution were added 6 M HCl aq (0.4 mL) and tin(II) chloride bishydrate (0.26 g, 1.15 mmol), and the mixture was stirred at 60 °C for 1 h. After being cooled down to room temperature, the mixture was stirred for 2 h. The solids were then precipitated by standing at 0 °C. The residue was collected and washed with ether (50 mL), to give DADBTTF (30.8 mg, 93%) as a peach-pink powder. mp >300 °C. TLC R_f 0.42 (1:3 hexane/ethyl acetate). ^{1}H NMR (270 MHz, DMSO-d_6): δ 5.28 (brs, 4H), 6.45 (dd, $J = 8.4$ and 2.0 Hz, 2H), 6.65 (d, $J = 2.0$ Hz, 2H), 7.09 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR (270 MHz, DMSO-d_6): δ 107.4, 109.8, 112.8, 119.9, 122.7, 136.3, 147.9. IR (KBr) 3585, 3369 cm^{-1}. EI-MS, m/z 334 (M^+, 100%). Anal. Calcd for $C_{14}H_{10}N_2S_4$: C, 50.27; H, 3.01; N, 8.37%. Found: C, 50.03; H, 2.98; N, 8.12%.

DADBTTF–TCNQ•2CH_3CN. Both solutions of DADBTTF (19.5 mg, 0.058 mmol) in THF (80 mL) and of TCNQ (11.9 mg, 0.058 mmol) in THF (5 mL) were combined and stirred at 80 °C. After being cooled at room temperature, the precipitates were filtered. The filtrate was evaporated under reduced pressure, and dissolved in acetonitrile (80 mL) at 80 °C. After being filtered, the solution was concentrated under reduced pressure until the total volume was ~10 mL, to give DADBTTF–TCNQ•2CH_3CN (19.0 mg) as dark greenish-blue microcrystals. mp >300 °C. IR (KBr) 3380, 2251, 2206, 2191 cm^{-1}. UV (KBr) 1524, 612, 364 nm. Anal. Calcd for $(C_{14}H_{10}N_2S_4)(C_{12}H_4N_4)(CH_3CN)_{0.2}$: C, 57.98; H, 2.69; N, 15.88%. Found: C, 57.96; H, 2.55; N, 15.96%. Due to the efflorescence of CH_3CN molecules in air, an elemental analysis was carried out after the sample was dried in vacuo at room temperature for 6 h. We confirmed the existence of CH_3CN molecules in the CT complex by the nitrile stretching frequency of 2251 cm^{-1} in the IR spectrum.

Cyclic Voltammetry. Cyclic voltammetric measurements were made with an ALS Electrochemical Analyzer Model 612A. Cyclic voltammograms were recorded by the following conditions: 1 mM in DMF with 0.1 M $Et_4N^+ClO_4^-$ as the supporting electrolyte at room temperature, a 1.6 mm diameter gold working electrode and a Pt counter electrode in 0.1 V/s; 0.1 mM in THF for DADBTTF, DBTTF, and TTF and in the mixture of THF–MeOH for DADBTTF with 0.1 M $Bu_4N^+ClO_4^-$ as the supporting electrolyte, and a 1.6 mm diameter glassy carbon working electrode. The experiments employed an Ag/Ag$^+$ reference electrode, and the final results were calibrated with a ferrocene/ferrocenium couple.

Electronic Spectra. THF and DMSO solutions of DADBTTF were prepared for 0.02 mM, and a MeOH solution of DADBTTF was prepared for a saturated solution below 0.02 mM because of its poor solubility. All of the spectra were measured in a quartz cell (1 × 1 cm^2).

X-ray Crystallography. The diffraction data of DADBTTF–TCNQ•2CH_3CN were collected with graphite-monochromated Mo Kα ($\lambda = 0.71075$ Å) radiation on a Rigaku RAXIS-RAPID Imaging Plate at −73 °C. The structure of DADBTTF–TCNQ•2CH_3CN was determined by a direct method using SHELXS-86. The non-hydrogen atoms were refined anisotropically. Amino groups of DADBTTF were disordered, and the extent of disorder was determined by refining their site occupancies: 0.80 for the N1 atom and 0.20 for the N2 atom. All hydrogen atoms were placed by a geometric method, and fixed. The site occupancies of hydrogen atoms in N1 and N2 atoms were the same as that of the nitrogen atoms.

Crystal data for DADBTTF–TCNQ•2CH_3CN: $C_{30}H_{20}N_8S_4$, MW = 620.78; triclinic, space group $P\bar{1}$, $a = 7.614(6)$, $b = 8.271(5)$, $c = 12.667(9)$ Å, $\alpha = 99.53(5)$, $\beta = 86.41(6)$, $\gamma = 112.14(6)$°, $V = 728.7(10)$ Å^3, $Z = 1$, $T = 200$ K, μ(Mo Kα) = 0.362 mm^{-1}, $D_{\rm calcd} = 1.414$ g cm^{-3}, 6703 reflections were measured of which 3209 independent ($R_{\rm int} = 0.016$), $R_1 = 0.033$ [2069 data with $I > 3\sigma(I)$], $R_{\rm w} = 0.075$.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-247711. 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, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information

Estimation of ionicity for the TCNQ molecule in DADBTTF–TCNQ•$2CH_3CN$, the electronic spectra of the TCNQ complex in a KBr pellet, and the detailed crystal structure and crystallographic coordinates of this CT complex in the PDF format. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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19 DBTTF–F_2TCNQ CT complex gives an exceptional example, see: Ref. 8.

20 For a few exceptional cases, hexamethylenetetratellurafulvalene CT complex with diethyl-TCNQ, (HMTTeF)–Et_2TCNQ, was reported, see: G. Saito, S. S. Pac, and O. O. Drozdova, *Synth. Met.*, **120**, 667 (2001).

21 A few exceptional cases are also known in H-bonded CT complex of 1,6-diaminopyrene. For example, 1,6-diaminopyrene CT complex with chloranil exhibited high electric conductivity despite alternated stacking structure, see: H. Goto, T. Fujinawa, H. Asahi, T. Inabe, H. Ogata, S. Miyajima, and Y. Maruya, *Bull. Chem. Soc. Jpn.*, **69**, 85 (1996).

22 CV measurement of DADBTTF in a CH_3CN solution was difficult because of its poor solubility. However, we measured electronic spectrum of DADBTTF in a saturated CH_3CN solution below 0.02 mM. The shoulder absorption around 22000 cm^{-1} showed no shift compared with those in other solutions such as DMF and THF, which indicates no appreciable solvent effect of CH_3CN in *solution*.