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Modulation of charge-transfer complexes assisted by complementary hydrogen bonds of nucleobases: TCNQ complexes of a uracil-substituted EDO-TTF[†]

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A hydrogen bond functionalized ethylenedioxytetrathiafulvalene (EDO-TTF) derivative having an *n*-butyluracil moiety was synthesized. In the crystal structure, the Watson–Crick-type complementary hydrogen bonds of the uracil moiety formed a pair of donor molecules, which further aggregated by S…S interactions and π -stacks of the TTF moiety to construct a two-dimensional sheet. In the charge-transfer complex formation with tetracyanoquinodimethane, the crystallization conditions modulated the subtle balance between Watson–Crick and reverse Watson–Crick types of complementary hydrogen-bonded pairs, controlling stoichiometry, ionicity and molecular packing of the complexes. A highly conducting mixed valence complex with the Watson–Crick-type hydrogen bonds was yielded by the quick evaporation of reaction solvent, and a low-conducting neutral complex forming reverse Watson–Crick-type hydrogen bonds was obtained by the slow vapor diffusion method.

Introduction

Organic charge-transfer (CT) complexes and salts based on tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) have provided various fascinating materials, such as organic conductors and superconductors.^{1,2} Chemical modifications of the TTF skeleton have been performed to control its selfassembling ability and intermolecular interactions to exhibit new functions and phenomena.³ The ethylenedioxy (EDO) substitution on the TTF skeleton yielded several intriguing molecular systems presenting new opportunities for functional CT complexes and salts: self-assembling ability by the face-to-face C– H…O H–bonds on the EDO groups giving stable metallic states in the BEDO-TTF complexes,⁴ and a peculiar phase transition system with the multi-instability⁵ showing an ultrafast and highly efficient photoresponse⁶ in the (EDO-TTF)₂XF₆ (X = P, As and Sb) salts.

The introduction of hydrogen bond (H bond) interactions into CT complexes and salts has served as an effective methodology to control the molecular packing of conductive components.^{7–9} Furthermore, our recent investigations on H-bonded CT complexes and salts have demonstrated that the molecular recognition ability and high polarizability of H bonds can modulate their electronic structures and physical properties.^{10,11}

We recently designed and synthesized TTF derivatives having nucleobase moieties as H-bonding units, and succeeded in the construction of various self-assembled structures based on the complementary H bonds of nucleobase moieties.^{12–15} In the crystal structures of uracil-substituted TTF derivatives (TTF-U), the subtle balance between Watson–Crick and reverse Watson–Crick complementary H bonds of the uracil moiety (Fig. 1)¹⁶ were modulated by the redox states of the TTF moiety^{12b} and the substituent groups on the uracil moiety^{12c} affecting the molecular arrangements.

Furthermore, a TTF-U derivative substituted with an ethylenedithio group (EDT-TTF-U) afforded a highly conductive CT complex with TCNQ in which the self-assembled onedimensional channel structure provided the conduction path.¹⁵ The crystal structure of the (EDT-TTF-U)₂TCNO complex indicates that the EDT substitution plays an important role in the construction of the one-dimensional channel by multiple S…S interactions in addition to Watson-Crick type complementary H bonds of the uracil moiety.¹⁵ The preceding work by Baudron et al. on F4TCNQ complexes of amido-functionalized TTF derivatives revealed that the EDT and EDO substitution on the TTF skeleton has significant effects on the D-A ratio, molecular packing and physical properties by modulating selfassembling abilities in addition to the redox abilities.⁹ In the present study, for the exploration of further self-assembling structures based on TTF nucleobases showing intriguing phenomena, we have designed an EDO-substituted TTF-U derivative (EDO-TTF-U). Here we describe the synthesis, physical properties and crystal structures of EDO-TTF-U and its TCNQ complexes. In the CT complex formation between

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Fig. 1 Watson-Crick and reverse Watson-Crick types of complementary H bonds of uracil.

EDO-TTF-U and TCNQ, two kinds of CT complexes exhibiting Watson–Crick or reverse Watson–Crick H bonds were obtained depending on the crystallization conditions, where the crystal and electronic structures and physical properties were affected by the complementary H bond types.

Results and discussions

Synthesis and electrochemical properties

Scheme 1 illustrates the synthetic procedure of EDO-TTF-U. Lithiation of EDO-TTF using *n*-BuLi followed by the treatment with Bu₃SnCl afforded tributylstannylated EDO-TTF. EDO-TTF-U was prepared by the Stille cross-coupling reaction of tributylstannylated EDO-TTF with benzoyl-protected 5-iodo-1-*n*-butyluracil in the presence of Pd(PPh₃)₄ and CuI catalysts followed by the removal of the benzoyl group using MeNH₂.

The cyclic voltammetry measurement of EDO-TTF-U shows two-stage reversible one-electron oxidation processes. The oxidation potentials of $E^{\text{ox1}} = -0.03$ V and $E^{\text{ox2}} = +0.15$ V vs. Fc/Fc⁺ are closely similar to those of pristine EDO-TTF ($E^{\text{ox1}} = -0.02$ V and $E^{\text{ox2}} = +0.18$ V). Such a small effect of



Scheme 1 Synthetic procedure of EDO-TTF-U.

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uracil substitution on the redox ability is similar to those observed in the TTF-U and EDT-TTF-U. 12,15

Crystal structure of EDO-TTF-U

The single crystals of EDO-TTF-U suitable for X-ray crystal structure analysis were obtained by the aerial evaporation from CH_2Cl_2 .[‡] The TTF skeleton is slightly distorted with bent angles of 4.9–6.2°. The uracil moiety is nearly parallel to the TTF skeleton with a dihedral angle of 9.6°.

The EDO-TTF-U molecules form a face-to-face dimer with a head-to-tail manner and an interplanar distance of 3.48 Å (Fig. 2a and 2b). The dimers are linked along the *c*-axis through complementary N–H···O=C H bonds (N···O distance, 2.82 Å) of the uracil moieties (Fig. 2c). The complementary H bonds in this crystal is the Watson–Crick type, which are also observed in the crystal structures of TTF-U and EDT-TTF-U.^{12a,15} The H-bonded pairs are further connected by S···S interactions on



Fig. 2 Crystal structure of EDO-TTF-U. (a) Molecular packing viewed along the *c*-axis. (b) Overlap mode in the π -stack dimer. (c) Two-dimensional donor sheet on the (0, 0.5, 0) layer viewed along the *b*-axis. *n*-Butyl groups were omitted for clarity in (a) and (c). Red and green dotted lines present N-H···O=C H bonds and S···S interactions, respectively. Ellipsoids are drawn at the 50% probability level.

‡ Crystallographic data for EDO-TTF-U: C₁₆H₁₆N₂O₄S₄, *M* = 428.55, monoclinic, space group *P*₂₁/*c* (no. 14), *a* = 11.06(3), *b* = 16.45(4), *c* = 10.99(4) Å, β = 111.4(2)°, *V* = 1863(10) Å³, *Z* = 4, *D_c* = 1.528 g cm⁻³, $\lambda = 0.71075$ Å, μ (Mo-Kα) = 5.35 cm⁻¹, *F*(000) = 888, *T* = 200 K, $2\theta_{max} = 54.96^{\circ}$, 4107 unique reflections of 14 973 collected (*R*_{int} = 0.1850), *R*₁ = 0.0994 and *R_w* = 0.2333 [*I* > 2.0σ(*I*)], *S*(GOF) = 0.928. Crystallographic data for complex **2**: C₄₄H₃₆N₈O₈S₈, *M* = 1061.29, triclinic, space group *P*Ī (no. 2), *a* = 7.249(1), *b* = 10.373(2), *c* = 16.028(3) Å, *α* = 89.459(9), $\beta = 77.009(7)$, $\gamma = 79.014(8)^{\circ}$, *V* = 1152.0(4) Å³, *Z* = 1, *D_c* = 1.530 g cm⁻³, $\lambda = 0.71070$ Å, μ (Mo-Kα) = 4.51 cm⁻¹, *F*(000) = 548, *T* = 93 K, $2\theta_{max} = 54.0^{\circ}$, 4802 unique reflections of 9021 collected (*R*_{int} = 0.0447), *R*₁ = 0.0447 and *R_w* = 0.1074 [*I* > 2.0σ(*I*)], *S*(GOF) = 0.984.

the TTF skeleton (3.57 Å) to build up a two-dimensional donor sheet (Fig. 2a and 2c).

Physical properties of TCNQ complexes

The CT complex formation between EDO-TTF-U and TCNQ was performed by the direct mixing method in CH_2Cl_2 . Two kinds of CT complexes were obtained depending on the crystallization process: quick evaporation of the reaction solvent (complex 1, dark green powder) and slow vapor diffusion of hexane into the reaction mixture (complex 2, black platelet crystals).[‡] Both complexes were afforded selectively, and the contamination of a complex with another one was not observed. The donor–acceptor ratio of 1 was estimated as 1 : 1 by the elemental analysis, and that of 2 was determined to be 2 : 1 in the crystal structure (*vide infra*).

Fig. 3 illustrates the electronic spectra using KBr pellets of 1 and 2. The spectra of 1 and 2 show similar patterns at wavenumber $>10\ 000\ \text{cm}^{-1}$ originating from the intramolecular transitions.¹⁷ The low-energy absorption bands assignable as the intermolecular CT transition¹⁷ are observed around 3500 cm⁻¹ for 1 and 5500 cm⁻¹ for 2. The lower energy intermolecular CT band of 1 indicates the mixed valence state with a segregated stack. In the IR spectra of 1, the C≡N stretching mode is observed at 2191 cm⁻¹ indicating the highly ionized state of the TCNQ moiety (Fig. S1[†]).¹⁸ The Raman spectrum of **1** shows two bands at 1420 and 1454 cm⁻¹ assignable to C=C stretching modes of the TCNQ and EDO-TTF skeletons, respectively (Fig. S2[†]). The ionicity (ρ) of TCNQ is estimated to be -0.59 from the band at 1420 cm⁻¹.¹⁹ The frequency of the band of EDO-TTF skeleton is slightly lower than that of (EDO-TTF)₂PF₆ (1472 cm^{-1}) in which EDO-TTF possesses +0.5 uniform charge.²⁰ This result indicates that the ρ value of EDO-TTF is slightly larger than +0.5 and coincides with the ρ value of the TCNQ moiety. In the electrical conductivity measurement for the compressed pellet, 1 exhibits a high conductivity of 6.4 \times 10^{-2} S cm⁻¹ at room temperature (activation energy = 82 meV). The ρ value of the TCNO moiety in **2** is estimated as -0.40 from the C=N stretching frequency in the IR spectra (2210 cm⁻¹, Fig. S1[†]).¹⁸ These optical measurements indicate the neutral ground state of 2. The room temperature conductivity and activation



Fig. 3 Electronic spectra of 1 and 2 in KBr pellets. Arrows indicate the intermolecular CT absorption bands.

energy of this complex are 2.3 $\times 10^{-4}$ S cm⁻¹ and 89 meV, respectively.

Crystal structure of (EDO-TTF-U)₂(TCNQ) (2)

In the crystal structure of 2, one EDO-TTF-U and half a TCNQ molecule are crystallographically independent, and the inversion center is located at the TCNQ molecule.[‡] The ρ value of the TCNO molecule is estimated as -0.33 from bond lengths (Table 1)²¹ and close to that obtained from the CN stretching frequency. The central C=C bond length of the TTF skeleton of 2 is 1.357(4) Å, whose value is in the middle between those of neutral EDO-TTF $(1.318(3) \text{ Å})^{22}$ and the cationic species in $(EDO-TTF)_2PF_6$ at the low-temperature phase (1.381(5) Å, $\rho = ca. +0.9$ ^{5a} and is slightly shorter than that of the mixed valence EDO-TTF in (EDO-TTF)₂PF₆ at the room-temperature phase (1.365(5) Å, $\rho = +0.5$).^{5a} These observations indicate the slightly oxidated state of the donor molecule. The EDO-TTF-U molecule is nearly planar with bent angles of 1.6-6.7° at the TTF skeleton and a twist angle of 2.0° between uracil and TTF moieties.

EDO-TTF-U and TCNQ molecules stack to form a onedimensional column in a D–A–D–D–A–D manner (Fig. 4a). The interplanar distance between donor and acceptor is 3.42 Å (Fig. 4b). The donor–donor stack has a head-to-tail manner, and the interplanar distance is 3.50 Å (Fig. 4c).

The donor molecules form a pair with the complementary H bonds of 2.83 Å (Fig. 4a and 4d). The H bond mode is the reverse Watson–Crick type and different from that observed in EDO-TTF-U itself (Fig. 2a). The H-bonded pairs are further linked through the S…S interactions (3.44 Å) and π -stacks of the TTF skeleton to form a two-dimensional donor sheet (Fig. 4d).

Complementary H-bonding modes in CT complexes

Fig. 5 compares the C=O stretching modes in the IR spectra of neutral EDO-TTF-U, CT complexes 1 and 2. EDO-TTF-U forming Watson–Crick type complementary H bonds (Fig. 2a) shows two bands at 1716 and 1667 cm⁻¹ assignable as those of C^2 =O and C^4 =O groups, respectively.²³ In the case of 2 in which reverse Watson–Crick type H bonds are observed (Fig. 4d), the C^2 =O stretching mode shows a significant red-shift and appeared at 1689 cm⁻¹ since the H bond formation softens the C=O bond. The C=O stretching modes of 1 are observed at 1715 and

Table 1 The C–C bond lengths (Å) of TCNQ molecules in 2 and related compounds

NCd	b/—	CN
		CN

	2	TCNQ ⁰ a	TCNQ [⊷] ^b
1	1.349(5)	1.346	1.373
5	1.434(5), 1.440(5)	1.448	1.426
	1.388(5)	1.374	1.420
d	1.433(5), 1.432(6)	1.441	1.416
c	0.484	0.476	0.500
o^d	-0.33	0	-1

^{*a*} Ref. 21a. ^{*b*} Ref. 21b. ^{*c*} r = c/(b + d). ^{*d*} $\rho = -(r - r^0)/(r^1 - r^0)$; r^0 and r^1 are the *r* values calculated for TCNQ⁰ and TCNQ⁻, respectively.



Fig. 4 Crystal structure of complex 2. (a) One-dimensional π -stacking column viewed along the *a*-axis. (b and c) Overlap modes of donor-acceptor and donor-donor stacks in the one-dimensional column, respectively. (d) Two-dimensional donor sheet formed by the complementary H-bonds, S...S interactions and π -stacks on the (0, 0, 0) plane viewed along the *b*-axis. *n*-Butyl groups were omitted for clarity in (d). Red and green dotted lines present the N-H···O=C H bonds and S···S interactions, respectively. Ellipsoids are drawn at the 50% probability level.

1671 cm⁻¹ and are close to those of EDO-TTF-U and (EDT-TTF-U)₂TCNQ complexes¹⁵ both of which exhibit Watson–Crick type complementary H bonds between donor molecules in the crystal structures. These results indicate that the uracil moiety in 1 forms the Watson–Crick type complementary H bonds. It is expected that the formation of additional H bonds causes a further low-frequency shift of the C=O stretching modes. Therefore, the similarity of these bands in EDO-TTF-U and 1 can eliminate the possibility of H bond formation between C=O groups and crystalline water molecules.

It has been known that the difference of stabilization energies of these two H-bonding motifs is small.²⁴ Actually, our previous investigations on TTF-U derivatives revealed that both types of complementary H bonds can be formed depending on the redox state of the TTF skeleton^{12b} and the substituent groups at the N¹ atom.^{12c} The stabilization energy calculated for the H-bonded pairs in the crystal structures are close to each other (-10.9 kcal mol⁻¹ for Watson–Crick type pair (EDO-TTF-U) and -10.2 kcal mol⁻¹ for reverse Watson–Crick type pair (**2**)). In the present case, the crystallization methods of the TCNQ



Fig. 5 C=O stretching modes in the IR spectra of EDO-TTF-U, 1 and 2 measured in KBr pellets.

complexes, quick evaporation (1) and slow vapor diffusion (2), probably affected the subtle balance of two H-bonding types, and caused the generation of two types of CT complexes. The differences in the H bond types modulate the molecular arrangements and electronic structures of CT complexes to achieve the highly conducting segregated stack of 1 and the lowconducting mixed stack of 2. Similar complex formation behaviors, "monotropic complex isomerism" where a donoracceptor pair affords multiple kinds of CT complexes having different crystal structures, ionicities and physical properties depending on the preparation conditions, have been also observed for several donor-acceptor type CT complexes.²⁵⁻²⁹ It has been known that such complex isomerisation is usually achieved for donor-acceptor systems locating at the vicinity of the redox boundary between neutral and mixed valence CT complexes (difference of the redox potentials between donor and acceptor (ΔE) = +0.34 V for conventional TTF-TCNQ systems).³⁰ Surprisingly, the ΔE value between EDO-TTF-U and TCNQ ($E^{\text{red}} = -0.11 \text{ V vs. Fc/Fc}^+$) is +0.08 V from the CV measurement, and much smaller than those of monotropic complex isomer systems. The complex formation of EDO-TTF-U with TCNQ implies that not only the redox valance between donor and acceptor molecules but also the structural modification by complementary H bond types are important factors in controlling the ionicity of a CT complex.

In the crystal structures of EDT-TTF-U and (EDT-TTF-U)₂(TCNQ) complex, the Watson–Crick type complementary H bonds on the uracil moiety and multiple S…S interactions on the EDT-TTF skeleton form one-dimensional chains.¹⁵ Further assembly of the chains builds up a one-dimensional channel in (EDT-TTF-U)₂(TCNQ) (Fig. 6). In the case of EDO-TTF-U, the self-assembling ability by S…S interactions is diminished due to the EDO substitution, and only a single S…S interaction is formed between adjacent TTF skeletons, resulting in the construction of diverse network structures. The difference of molecular packing of (EDT-TTF-U)₂(TCNQ) and **2**, one-dimensional channel structure and D–D–A mixed stack, respectively, would originate from the differences of self-assembling ability of the TTF skeleton in addition to the complementary H bonding types.



Fig. 6 One-dimensional chain of EDT-TTF-U formed by the Watson–Crick type complementary H bonds (red dotted lines) and multiple $S \cdots S$ interactions (green dotted lines).¹⁵

Conclusions

We have synthesized an EDO-TTF derivative having a uracil moiety as an H bonding unit and investigated the physical properties of TCNQ complexes. In the crystal structures, the selfassembling nature of EDO-TTF-U originating from the complementary H bonds inherent in nucleobases, S...S interactions and π -stacks of the TTF moieties constructed two-dimensional donor sheets. The EDO substitution modulated the selfassembling ability of the TTF skeletons and increased the variation of the supramolecular assemblies of the TTFnucleobase system. In the CT complex formation with TCNQ, the crystallization conditions produced the highly conducting complex with a segregated structure (1) and low-conducting complex with a mixed stacking column (2). The observation of Watson-Crick and reverse Watson-Crick type complementary H bonds in 1 and 2, respectively, indicates the importance of selfassembling ability of nucleobases in the control of electronic structures and physical properties of CT complexes. The crystal structure analysis of the highly conducting complex 1 is indispensable for the elucidation of the effect of complementary H bonds on the ionicity and molecular packing and is currently in progress.

Experimental

Materials and measurements

 N^3 -Benzoyl- N^1 -*n*-butyl-5-iodouracil was prepared according to our previous paper.¹⁵ EDO-TTF was synthesized by the previously reported procedure.³¹ The decarboxylation reaction of bis(methoxycarbonyl)EDO-TTF was modified in our laboratory, where the reaction solvent was changed to N,N-dimethylacetamide from harmful hexamethylphosphoramide (*vide infra*). All reactions requiring anhydrous conditions were performed under an argon atmosphere. Solvents were dried and distilled under an argon atmosphere prior to use.

The $R_{\rm f}$ value on TLC was recorded on E. Merck pre-coated (0.25 mm) silica gel 60 F₂₅₄ plates. The plate was sprayed with a solution of 10% phosphomolybdic acid in 95% ethanol and then heated until the spots became clearly visible. The melting point was measured with a hot-stage apparatus and uncorrected. ¹H NMR spectrum was obtained on a JEOL EX-270 with DMSO-d₆ using Me₄Si as an internal standard. The EI-Mass spectrum

was taken at 70 eV by using a Shimadzu QP-5000 mass spectrometer. The infrared spectra were recorded on a JASCO FT/IR-660 Plus spectrometer using KBr plates (resolution 2 cm⁻¹). The electronic spectra were measured by a Shimadzu UV-3100PC spectrometer using KBr plates. Measurement of Raman spectrum was carried out for the powder sample of 1 using a JASCO NR1800 (resolution 2 cm⁻¹) with the excitation wavelength of 632.8 nm (He–Ne line). Elemental analyses were performed at the Graduate School of Science, Osaka University. Temperature dependencies of electrical conductivity were measured for compressed pellets of 1 and 2 by four- and two-probe methods, respectively, in a temperature range of 100–300 K using a Fuso dc multi-channel conductivity device HECS 944C type.

Modified synthetic procedure of EDO-TTF

Bis(methoxycarbonyl)EDO-TTF³¹ (1.46 g, 3.86 mmol) and LiBr·H₂O (4.92 g, 48.3 mmol) was dissolved in *N*,*N*-dimethylacetamide (110 mL). The mixture was gradually warmed up to 150 °C, then stirred at the temperature for 20 min. After cooling to room temperature, water (200 mL) was poured to the reaction mixture, and extracted with CS₂ (80 mL × 3). The combined organic extracts were dried over Na₂SO₄, then filtered and concentrated under reduced pressure. The residual oil was subjected to a silica gel column chromatography with CS₂ as eluant, to give EDO-TTF (202 mg, 20%) and mono(methoxycarbonyl)EDO-TTF (822 mg, 66%). The same procedure was performed for mono(methoxycarbonyl)EDO-TTF (700 mg, 2.18 mmol) using LiBr·H₂O (1.37 g, 13.1 mmol) and *N*,*N*-dimethylacetamide (60 mL), to give EDO-TTF (232 mg, 57%) as a red powder.

Synthesis of EDO-TTF-U

EDO-TTF (193 mg, 0.74 mmol) was placed in a Schlenk tube and dissolved with THF (10 mL). To this mixture was added *n*-BuLi (1.6 M hexane solution, 0.55 mL, 0.88 mmol) at -78 °C and stirred at this temperature for 1 h. Bu₃SnCl (0.21 mL, 0.74 mmol) was added to this mixture, and the reaction mixture was gradually warmed up to room temperature over 0.5 h. To the resulting mixture was added a pH 7.0 phosphate buffer solution (0.1 M, 20 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (30 mL × 3). The combined organic extracts were dried over Na₂SO₄, then filtered and concentrated under reduced pressure. The residual oil was dried in vacuo at room temperature, to give Bu₃Snsubstituted TTF as a yellow oil.

The resulting oil, N^3 -benzoyl- N^1 -*n*-butyl-5-iodouracil (293 mg, 0.74 mmol), Pd(PPh₃)₄ (86 mg, 0.074 mmol) and CuI (42 mg, 0.22 mmol) were dissolved in THF (10 mL) in a Schlenk tube equipped with a reflux condenser, and the resulting mixture was refluxed for 4 h. After cooling to room temperature, the solvent was removed by evaporation, and then extracted with ethyl acetate (20 mL) and a saturated KF aqueous solution (20 mL). The organic extract was washed with a saturated KF aqueous solution (20 mL \times 2) and water (20 mL \times 2). The combined organic extracts were dried over Na₂SO₄, then filtered and concentrated under reduced pressure. The residual powder was purified by a silica gel column chromatography with 5 : 1

hexane–ethyl acetate and ethyl acetate, to give a mixture containing the benzovl-protected EDO-TTF derivative (165 mg).

The resulting mixture was placed in a Schlenk tube, then dispersed in 30% MeNH₂ MeOH solution (3 mL), and stirred at room temperature for 2.5 h. After being cooled to 0 °C, the solution was neutralized by acetic acid. The resulting precipitate was collected by filtration, then washed with MeOH to give EDO-TTF-U (84 mg) as a reddish orange powder in 27% yield in three steps from EDO-TTF: mp 203–204 °C (dec); TLC $R_{\rm f}$ 0.49 (1 : 1 hexane–ethyl acetate); ¹H NMR (DMSO-d₆) δ 0.89 (t, J = 7.3 Hz, 3H), 1.23–1.31 (m, 2H), 1.51–1.59 (m, 2H), 3.72 (t, J = 7.2 Hz, 2H), 4.30 (s, 2H), 7.35 (s, 1H), 7.85 (s, 1H); EI-MS, *mlz* 312 (M⁺–OCH₂CH₂O–C₄H₉, 100%), 428 (M⁺, 30%); IR (KBr) 3250–2700, 1716, 1667, 1456, 1164 cm⁻¹; UV (KBr) 428, 300 nm.

Preparation of (EDO-TTF-U)(TCNQ) (1)

To a solution of EDO-TTF-U (7.1 mg, 0.017 mmol) in CH₂Cl₂ (10 mL) in a 50 mL round-bottomed flask, TCNQ (7.3 mg, 0.036 mmol) was added at room temperature. The reaction mixture was concentrated under reduced pressure. The residual powder was suspended in a small amount of CH₂Cl₂, then collected by filtration to give the complex **1** (6.5 mg) as a dark green powder: mp 212–214 °C (dec); IR (KBr) 3100–2700, 2191(sh), 2180, 1715, 1671, 1559, 1507, 1165 cm⁻¹; UV (KBr) 316, 372, 766, 844, 2422 nm; Anal. Calcd for (C₁₆H₁₆N₂O₄S₄)(C₁₂H₄N₄)(H₂O)_{0.5}: C, 52.40; H, 3.30; N, 13.09%. Found: C, 52.54; H, 3.24; N, 12.71%. Since rapid precipitation from the reaction was required to afford **1**, single crystals suitable for X-ray crystal structure analysis and conductivity measurements could not be obtained. Structural information could not be achieved even by the X-ray diffraction study on the powder sample.

Preparation of (EDO-TTF-U)₂(TCNQ) (2)

To a solution of EDO-TTF-U (21.4 mg, 0.050 mmol) in CH_2Cl_2 (10 mL) in a 50 mL round-bottomed flask, TCNQ (5.1 mg, 0.025 mmol) was added at room temperature. This mixture was subjected to vapor diffusion using hexane. The resulting crystals were collected by filtration to give the complex **2** as dark green platelet crystals: IR (KBr) 3250–2700, 2210, 2179, 1689, 1670, 1559, 1539, 1506, 1164 cm⁻¹; UV (KBr) 312, 388, 670, 822, 1824 nm. As too small an amount of **2** was obtained from one batch, elemental analysis could not be performed.

Electrochemistry

Cyclic voltammetric measurement was performed with an ALS Electrochemical Analyzer model 630A. Cyclic voltammograms were recorded with 1.6 mm diameter gold plate and Pt wire counter electrodes in dry DMF containing 0.1 M Et_4NClO_4 as supporting electrolyte at room temperature. The experiment employed a Ag/AgNO₃ reference electrode, and the final result was calibrated with a ferrocene/ferrocenium couple (Fc/Fc⁺).

X-ray crystallography

X-ray crystallographic measurements were made on Rigaku Raxis-Rapid imaging plate and Rigaku Saturn 70 diffractometer with graphite monochromatic Mo-K α radiation. An empirical absorption correction was applied which resulted in transmission

factors ranging from 0.740 to 0.984 for EDO-TTF-U and from 0.577 to 0.914 for complex **2**. Structures were determined by a direct method using SIR-2004.³² Least-squares refinement was performed on F^2 with SHELXL-97.³³ 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 of the equivalent temperature factors of the bonding atoms were applied for hydrogen atoms.

Theoretical calculation

Density functional theory (DFT) calculations were performed at the RB3LYP/6-31G(d) level on Gaussian 98. The DFT calculations of H-bonded pairs were performed using the structures extracted from the crystal structures.

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