

Zwitterionic π -radical involving EDT-TTF-imidazole and F₄TCNQ: redox properties and self-assembled structure by hydrogen-bonds and multiple S \cdots S interactions†

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The reaction between an imidazole-functionalized EDT-TTF and F₄TCNQ produced a zwitterionic π -radical, which formed a self-assembled structure by the cooperation of hydrogen-bonds and multiple S \cdots S interactions and exhibited three-step oxidation processes and a high electrical conductivity as a single-component organic molecule.

Unimolecular donor (D)–acceptor (A) systems have recently been intensively studied for the development of functional molecule-based materials such as nonlinear optics¹ and rectifiers.² In such research fields, the combination of tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) is recognized as an attractive strategy of molecular design,³ and several unimolecular TTF–TCNQ systems have been synthesized.^{2b,4} Furthermore, the redox active zwitterionic π -radicals based on TTF or TCNQ skeletons have been investigated as single-component organic conductors.^{5–7} For example, zwitterionic π -radicals of pyrimido-fused TTF⁵ and pyridinium-TCNQ⁶ derivatives gave semiconductors (room-temperature conductivity, $\sigma_{\text{rt}} = \sim 10^{-1}$ and $\sim 10^{-5}$ S cm⁻¹, respectively). Among such zwitterionic TTF or TCNQ systems, only Me₃TTF⁺–phosphonate⁻, which is an insulator, was structurally well elucidated.⁷ Besides them, spirobis(phenalenyl)-borons demonstrated metallic conductor behavior ($\sigma_{\text{rt}} = 0.3$ S cm⁻¹).⁸

A TTF derivative having an imidazole moiety has been designed and synthesized by our group as a hydrogen-bond (H-bond) functionalized electron-donor, demonstrating electronic and structural modulation effects in organic conductors.⁹ In a reaction of the ethylenedithio derivative (EDT-TTF-Im)¹⁰ with tetrafluoro-TCNQ (F₄TCNQ), the imidazole moiety reacted with the acceptor, producing a D–A zwitterionic π -radical, EDT-TTF-Im^{•+}–F₄TCNQ⁻ (**1**, Chart 1), which forms a self-assembled structure by H-bonds and S \cdots S interactions and exhibits oxidation processes on both D and A moieties. Here we report on the

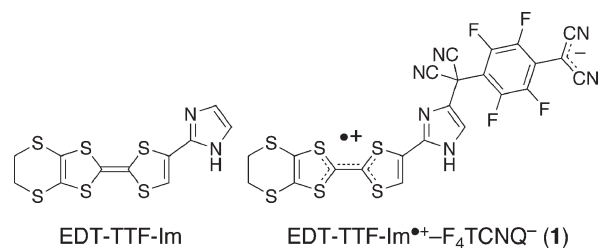


Chart 1

structural, redox, and transport properties of **1**. The reaction mechanism is also discussed.

Single crystals of **1** suitable for X-ray analysis were prepared by the slow diffusion of EDT-TTF-Im and F₄TCNQ in a 5 : 1 mixture of MeCN–THF and obtained as deep green crystals which included THF and MeCN as crystalline solvents.† The direct mixing of EDT-TTF-Im and F₄TCNQ also gave **1** as a dark green powder. **1** is stable under air in both solid and solution states at room temperature.

Crystal structure analysis revealed the molecular structure of **1**, where the vinyl carbon of imidazole-ring and C(CN)₂ group of F₄TCNQ were connected (Fig. 1). The C2–C12 bond length (1.513(5) Å) is consistent with a normal C–C σ -bond length (Fig. S4, ESI†). The planar structure of the terminal C(CN)₂ group and the C–C bond lengths (1.382(5)–1.439(5) Å) around the C21 atom indicate that the minus charge is located at this group (Fig. S4, ESI†). The EDT-TTF skeleton is planar, and the central C6–C7 bond length (1.405(5) Å) is longer than that of neutral EDT-TTF-Im (1.347(3) Å) (Fig. S4 and Table S1, ESI†). These structural features show that the EDT-TTF-Im skeleton exists as a radical cation species. This assignment was confirmed by the solution and solid-state ESR measurement of **1**.

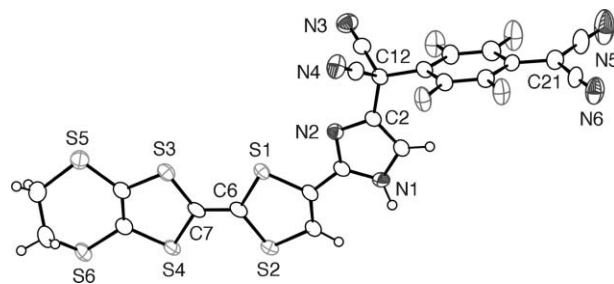


Fig. 1 ORTEP drawing of molecular structure (50% probability thermal ellipsoids) and selected atomic numberings of **1**.

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† Electronic supplementary information (ESI) available: Synthetic procedure of EDT-TTF-Im and **1**, IR and ESR spectra, temperature dependence of magnetic susceptibility, and selected intramolecular bond lengths. See DOI: 10.1039/b707113b

The ESR spectrum recorded in a DME solution consists of two lines ($g = 2.0077$) separated by 0.105 mT, as depicted in Fig. S2, ESI,† which corresponds to the hyperfine constant for hydrogen nuclei $I = 1/2$ in the EDT-TTF moiety.¹¹ The solid-state ESR spectrum showed a broad signal with a g -value of 2.0064. Thus, the electronic structure of **1** is presented as a zwitterionic neutral π -radical, EDT-TTF-Im^{•+}-F₄TCNQ⁻. The EDT-TTF skeleton is nearly parallel to the imidazole-ring (8.0°) and nearly perpendicular to the F₄TCNQ⁻ moiety (97.4°).

In the crystal structure, the N-H \cdots N=C H-bond (2.758(4) Å) between the imidazole moiety and the terminal C(CN)₂ group formed a zigzag one-dimensional chain (Fig. 2(a)). The sulfur atoms on the EDT-TTF skeleton formed S \cdots S contacts (S4 \cdots S6# 3.528(2) Å), connecting the H-bonded chains. These interactions constructed a two-dimensional structure (Fig. 2(a)). Furthermore, EDT-TTF skeletons stacked and formed a face-to-face dimer with an interplanar distance of 3.35 Å. These stacks and S \cdots S interactions formed a one-dimensional structure along the a -axis (Fig. 2(b)).

In the IR spectrum, **1** showed two intense C=N stretching absorptions at 2144 and 2185 cm⁻¹ (Fig. 3(a)). These modes are quite different from those of neutral F₄TCNQ (2228 cm⁻¹) and F₄TCNQ⁻ (2212 and 2193 cm⁻¹) and indicate the structural change of the F₄TCNQ moiety. The electronic spectrum of **1** in THF solution showed a broad band at 700–1000 nm which is assignable to the EDT-TTF-Im^{•+} species (Fig. 3(b)). In the solid state, a broad absorption appeared at >1000 nm, originating from the intermolecular charge-transfer transition within the dimer of EDT-TTF^{•+} moieties which is shown in Fig. 2(b). The magnetic

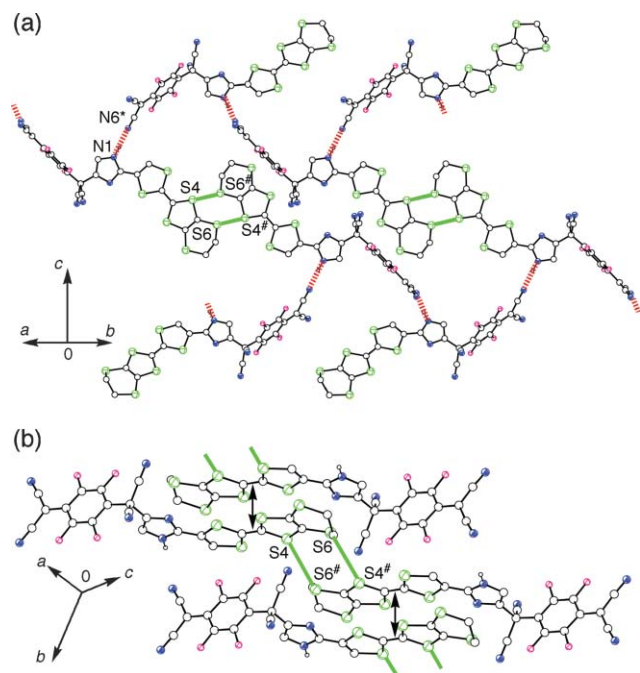


Fig. 2 Crystal packing of **1**. (a) Two-dimensional structure by H-bonding and S \cdots S interactions. (b) Assembled structure by face-to-face dimerization and S \cdots S interactions. Solvent molecules are omitted. The red dotted lines and green solid lines indicate H-bonds and S \cdots S interactions, respectively, and double head arrows show face-to-face stacks. The symbols * and # indicate atoms at equivalent positions ($1/2 + x, 1/2 - y, -1/2 + z$) and ($2 - x, -y, -z$), respectively.

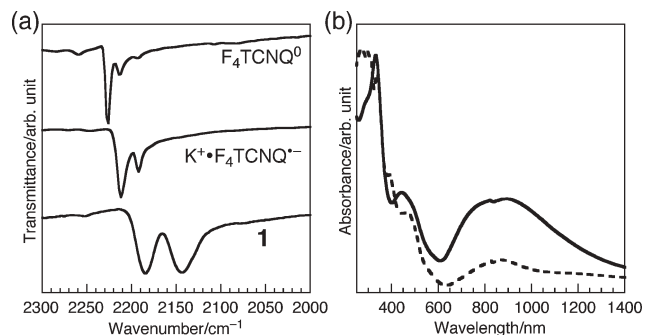


Fig. 3 (a) IR spectra of **1** (crystal sample) in the C=N stretching region together with related compounds measured by KBr pellets. (b) Electronic spectra of **1** (crystal sample) in a THF solution (2×10^{-4} M, dotted line) and KBr pellet (solid line).

susceptibility measurement for the powder sample showed a strong antiferromagnetic interaction ($2J/k_B > 1000$ K), supporting the dimerization of EDT-TTF^{•+} moieties (Fig. S3, ESI†).

In cyclic voltammetry, **1** showed three-step redox processes (Fig. 4). The first two steps ($E_{1/2} = +0.08$ and $+0.26$ V) were reversible and corresponded with those of the EDT-TTF-Im moiety ($+0.05$ and $+0.24$ V). Only the third step ($E_p = +0.44$ V), which is the oxidation peak of F₄TCNQ⁻ moiety, was irreversible probably due to the instability of neutral radical species of the F₄TCNQ moiety.

One of the intriguing features of redox active zwitterionic π -radicals is their electrical conductivity.^{5–8} **1** exhibited a semiconducting behaviour with σ_{rt} of 7.0×10^{-6} S cm⁻¹ and an activation energy of 419 meV (compressed pellet). The conductivity is lower than those of several zwitterionic π -radicals ($\sigma_{rt} = \sim 10^{-1}$ S cm⁻¹)^{5,8} and dithiazolyl radicals ($\sigma_{rt} = \sim 10^{-3}$ S cm⁻¹),¹² but substantially high compared to those of single-component organic molecules including zwitterionic π -radicals ($\sigma_{rt} = \sim 10^{-5}$ S cm⁻¹)^{6,7} and phenalenyl-based neutral π -radicals ($\sigma_{rt} < 10^{-6}$ S cm⁻¹).¹³

A plausible mechanism of the reaction is illustrated in Scheme 1. The key step is nucleophilic attack of the imidazole-ring to the electron-deficient C(CN)₂ group, forming an anionic adduct.

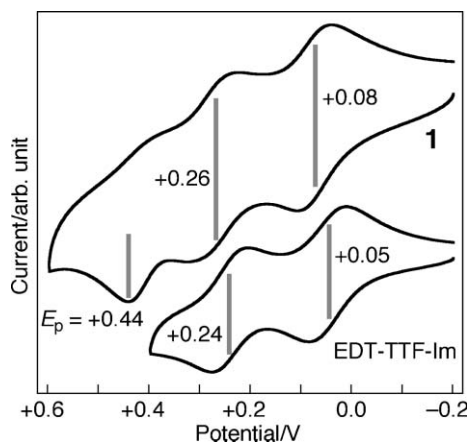
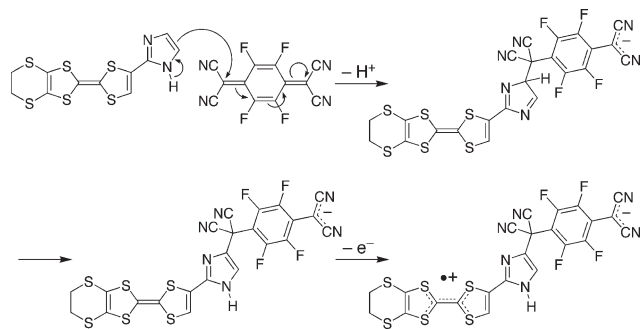


Fig. 4 Cyclic voltammograms of **1** and EDT-TTF-Im in DMF. The results were calibrated with the Fc/Fc⁺ couple. Lines indicate oxidation peaks.



Scheme 1

Oxidation of the EDT-TTF-Im skeleton by F_4TCNQ or air produces the zwitterionic π -radical structure. The strong electron-withdrawing ability of fluorine atoms would increase the electrophilic reactivity of the F_4TCNQ molecule, and aromatization of the benzene-ring would stabilize the product.

In summary, this study demonstrated a new way to prepare an air-stable D–A zwitterionic π -radical based on the EDT-TTF-Im system. The molecular structure of **1** and its two-dimensional structure constructed by the cooperation of H-bonds and multiple S...S interactions were well determined in terms of X-ray crystallographic analysis. The three-step redox activity and electrical conductivity show the high potential of **1** as a unimolecular electronic material. The solvato-/thermochromic behaviour induced by intramolecular charge-transfer interaction is a representative example of functions of unimolecular D–A systems.^{11b} Further experiments are currently being carried out in our laboratory to extend the potential of this system.

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Notes and references

† Crystallographic data for **1**: $C_{31}H_{21}F_4N_8O_1S_6$, $M = 789.91$, monoclinic, space group $P2_1/n$ (no. 14), $a = 11.050(7)$, $b = 25.24(2)$, $c = 12.334(8)$ Å, $\beta = 104.751(2)^\circ$, $V = 3326(3)$ Å³, $Z = 4$, $D_c = 1.577$ g cm⁻³, $\lambda = 0.71070$ Å, $\mu(\text{Mo-K}\alpha) = 4.76$ cm⁻¹, $F(000) = 1612$, $T = 150$ K, $2\theta_{\text{max}} = 55.0^\circ$, 7402 unique reflections of 23718 collected (Rigaku Mercury CCD), ($R_{\text{int}} = 0.037$), $R_1 = 0.074$ and $R_w = 0.202$, S (GOF) = 1.52. Structure solution with direct methods (SIR-92) and refinement with full-matrix least squares on $|F|^2$ for 7402 reflections (all data) and 413 parameters. CCDC 646929. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b707113b

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