Synthesis, structure and physical properties of a new TTF derivative containing a PPD part

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Abstract. To develop new photo-conducting multi-functional materials, a new tetrathiafulvalene (TTF) derivative containing a 2,5-diphenyl-1,3,4-oxadiazole (PPD) moiety, in which the PPD part is connected directly to the TTF part with a single bond, was synthesized by the Pd(PPh₃)₄-catalyzed Stille coupling reaction. X-Ray crystal structure analysis of the t-Butyl derivative (I) indicated the high planarity of the molecular skeleton and possible conduction pathways along the side-by-side direction of the TTF parts. Fluorescence from the PPD part of I was almost quenched by the intramolecular electron transfer from the electron-donating TTF part to the PPD part even when the PPD was irradiated by the excitation light of 315 nm. The single crystalline sample of the TCNQ complex of I (I-TCNQ) was prepared by a mixing method in CH₃CN. The X-ray crystal structure analysis of I-TCNQ revealed that there is PPD - TCNQ - TTF - type mixed stacking structure along the stacking direction, resulting in insulating behaviour of this complex.

1. Introduction
In the field of organic conductors, development of new materials that possess multi-functionalities has been intensively studied.[1,2] Among them, interactions between conducting properties and photonics are also investigated in photo-conducting materials and solar cells. The photoinduced interactions between the donor and acceptor parts such as intramolecular charge-transfer interactions and the resultant formation of charge-separated state have played an important role for the development of optoelectronic devices.[3,4] We focused on the development of photo-induced conducting materials based on the organic conductors in which their conductivities can be switched by external lights. 2,5-Diphenyl-1,3,4-oxadiazole (PPD) and its derivatives are known to show strong fluorescence and are used as electron-transport materials in electroluminescence devices.[5,6] TTF derivatives bearing a PPD part through an ethynyl-spacer were already reported to be potential candidates for electrochromic materials.[7] To realize novel photo-switchable conducting materials, we designed a new TTF derivative containing a PPD part (I), in which the PPD part is connected directly to the TTF part with a single bond to strengthen the intramolecular interaction between the TTF and PPD parts, and investigated the synthesis, structure and physical properties of I and its TCNQ complex (I-TCNQ).

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2. Synthesis, structure and properties of 1

A new TTF derivative containing a PPD part 1 was synthesized as described in scheme 1. Thus, tributylstannyl-substituted TTF (2) was prepared from TTF by the reported method. [8,9] Then, Pd(PPh3)4-catalized Stille coupling reaction of 2 and bromo-substituted PPD derivative (3)[10,11] was performed under toluene reflux for 24 hours. After purification by column-chromatography on silica gel with CHCl3 as an eluent, compound 1 was obtained as red microcrystals in the yield of 53%.[12] The electrochemical property of 1 was investigated by cyclic voltammetry technique in benzonitrile at 25 °C. 1 showed two pairs of one-electron reversible redox waves at \( E_1 = +0.44 \) V and \( E_2 = +0.84 \) V vs. Ag/AgCl as summarized in table 1. Because these redox potentials are almost similar to those of TTF, compound 1 has a good electron-donating ability despite of the substitution of the electron-withdrawing 1,3,4-oxadiazole ring.

![Scheme 1. Synthesis of 1.](image)

**Table 1. Redox potentials of 1 and TTF**.

| Compound | \( E_1 \) (V) | \( E_2 \) (V) | \( E_2 - E_1 \) (V) |
|----------|---------------|---------------|-------------------|
| 1        | +0.44         | +0.84         | 0.40              |
| TTF      | +0.41         | +0.80         | 0.39              |

*V vs. Ag/AgCl, 0.1 mol L⁻¹ n-Bu₄NClO₄ in benzonitrile at 25 °C, Pt electrodes, scan rate of 50 mV s⁻¹.

Crystal structure of 1 was cleared by an X-ray diffraction analysis of a red plate-like crystal of 1 that was recrystallized from CS₂ / heptane.[13] There are two crystallographically independent molecules A and B in the unit cell. Both of them adopt only one of two possible planar conformers as shown in figure 1. The molecular structures of molecules A and B are almost planar except for the terminal benzene rings. Each of molecules A and B constructs an independent stacking array along the \( b \)-axis as shown in figure 2. In both of these two kinds of stackings, donor molecules form head-to-tail dimers with overlapping their PPD parts over the TTF parts with an interplanar distance of 3.38 Å, and these dimers also construct head-to-tail stackings along the \( b \)-axis. On the other hand, along the \( a \)-axis donor molecules form side-by-side arrays in a head-to-head manner with several short S-S contacts (< 3.9 Å) between the TTF parts as shown in figure 3. Although the intermolecular interaction along the mixed-stacking direction of the TTF and PPD parts is apparently strongest in this crystal, such short side-by-side contacts between the TTF parts can be considered as possible conduction pathways to realize photo-induced conductivity using the single crystalline sample.

In the UV-Vis absorption spectra measured in \( 10^{-4} \) M CHCl3 solution at room temperature, 1 showed a strong absorption maximum at 315 nm (log\( \varepsilon \) = 4.59) and a weak maximum at 451 nm (log\( \varepsilon \) = 3.65), whereas absorption maxima were observed at 312 and 369 nm in the case of TTF, as shown in
PPD also showed a strong maximum at 282 nm (logε = 4.43). Molecular orbital (MO) calculation of 1 was performed by the density functional theory, B3LYP/6-31G** method using Gaussian 93. The atomic coefficients of HOMO and LUMO orbitals of 1 are mainly localized on the TTF and PPD moieties, respectively. The energy of HOMO-LUMO gap is estimated to be 2.82 eV, which corresponds to the wavelength of 440 nm (= 1240/2.82), from the energy levels of HOMO (−4.71 eV) and LUMO (−1.89 eV) and is almost equal to the weak absorption maximum at 451 nm of 1, suggesting that this absorption band corresponds to the charge transfer absorption from the TTF part to the PPD part.

Emission spectra of 1, PPD and TTF were measured in 10⁻⁴ M CHCl₃ solutions at room temperature. When the solution of PPD was irradiated by the excitation light of 281 nm that corresponds to the absorption maximum of PPD, already-known quite strong fluorescence was observed around 350 nm. On the other hand, the CHCl₃ solution of 1 gave only a subtle fluorescence around 375 nm that may correspond to the fluorescence of the TTF part when the PPD part was irradiated by the excitation light of 315 nm. This result suggests that the fluorescence from the excited PPD (PPD*) part is almost quenched by the intramolecular electron transfer process from the electron-donating TTF part to the PPD* part because the PPD* part possesses electron-accepting ability upon excitation.[14–16]

![Figure 1](image1.png)

**Figure 1.** Molecular structure of 1. (a) Side view and (b) top view of molecule A. (c) Side view and (d) top view of molecule B.

![Figure 2](image2.png)

**Figure 2.** Crystal structure of 1 projected along the a-axis.
3. Preparation, structure and properties of TCNQ complex of 1 (1-TCNQ)

Donor molecule 1 gave its charge-transfer complex with TCNQ as brown plate-like crystals by mixing their CH$_3$CN solutions. The X-ray crystal structure analysis of the TCNQ complex revealed that the ratio of 1:TCNQ is 1:1. Figure 5 showed the crystal structure of the TCNQ complex of 1 (1-TCNQ). In the unit cell, there are crystallographically independent one donor molecule 1 and one TCNQ. Two donor molecules form a dimer with a head-to-tail manner (the intradimer interplanar distance: 3.64 Å).
Two TCNQ molecules locate in almost parallel to each other along the molecular long axis and are sandwiched by the donor dimers. Therefore, PPD - TCNQ - TTF -type mixed stacking structure is constructed along the stacking direction ( // b-axis). The degree of charge transfer (Z) of 1-TCNQ was estimated to be ca. 0.2 by the infrared C≡N stretching frequency (2216 cm⁻¹). The single crystalline sample of 1-TCNQ showed insulating behavior with a very low room temperature electrical conductivity (10⁻⁵ S cm⁻¹) probably due to the PPD / TCNQ / TTF mixed stacking structure along the stacking direction of the complex.

4. Conclusion
We have synthesized a new TTF derivative 1 in which the PPD part connects directly to the TTF part with a single bond. The studies on fluorescence spectrum of 1 suggest the photo-induced intramolecular electron transfer between the TTF and PPD parts. X-Ray crystal structure analysis revealed that short side-by-side contacts between the TTF parts can be considered as possible conduction pathways to realize photo-induced conductivity.

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[12] 1: mp 230–232 °C (dec.); 1H NMR (300 MHz; CDCl₃) δ 8.14–8.05 (m, 4H), 7.57–7.54 (m, 4H), 6.71 (s, 1H), 6.36 (s, 2H), 1.38 (s, 9H); Calcd for C₂₄H₂₀N₂O₅S₄: C, 59.97; H, 4.19; N, 5.83. Found: C, 59.82; H, 4.04; N, 5.82; m/z 480 [M⁺, 100%], 481 [M++1, 47%], 482 [M++2, 29%].
[13] Crystal data for 1: C₃₆H₂₄N₄O₂S₄, M = 961.34, triclinic, P-1, a = 6.4307(4), b = 10.9806(8), c = 34.498(2) Å, α = 88.3986(16), β = 87.6038(15), γ = 69.5979(15)°, V = 2281.0(3) Å³, Z = 2, T = 295 K, Dcalcd = 1.400 g cm⁻³, µ(Mo Kα) = 4.36 cm⁻¹, Mo Kα radiation (λ = 0.7107 Å), R₁ = 0.049, wR₂ = 0.061.
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