Thieno[3,4-*d*]imidazolium-containing Molecular Wire: Switching Behavior of Photoinduced Intramolecular Electron Transfer

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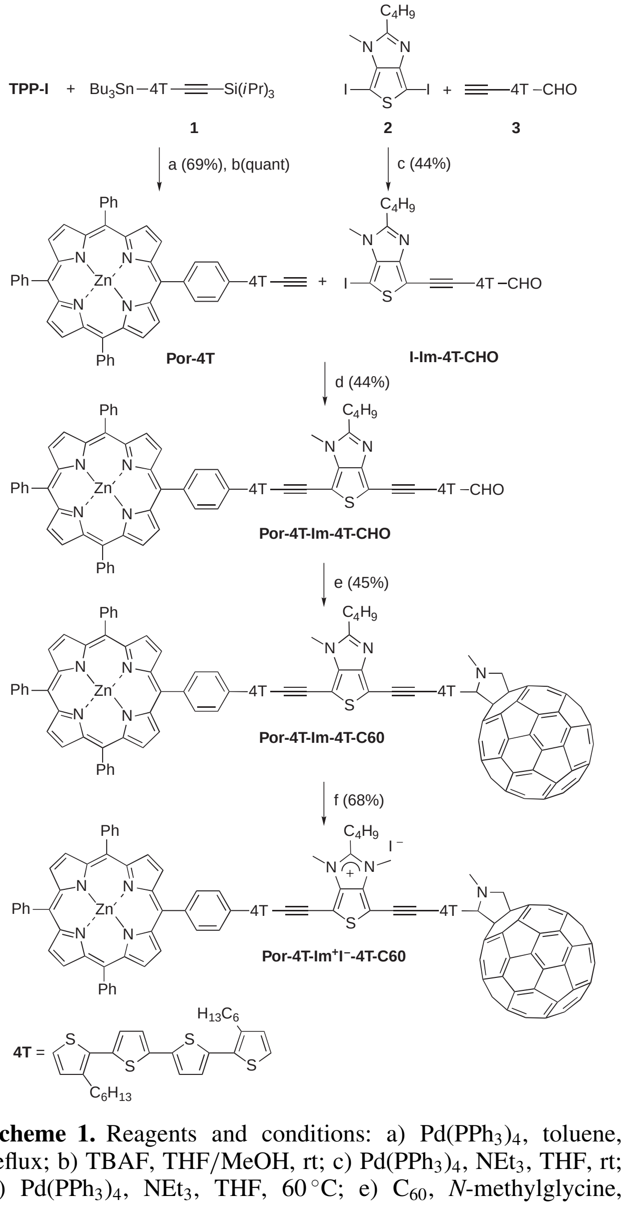
Zinc–porphyrin–oligothiophene–fullerene triad, where diethynylthieno[3,4-*d*]imidazolium is incorporated as a central unit of oligothiophene, has been synthesized. A dramatic enhancement of fluorescence from the zinc–porphyrin unit was observed on displacing counter anion from I^- to F^- in the imidazolium salt, indicating that photoinduced intramolecular electron transfer is controllable by the electronic perturbation to this unit.

Thiophene-based π-conjugated systems have attracted much attention as electron-transporting molecular wires for nanoscale molecular electronics.[1,2] One particularly important chemical aspect in molecular electronics is to control electron transfer through molecular wire by the installed switching unit that responds to an external stimulus and switches the electronic state of the conjugated system. The recent advances in the development of switching molecules are mostly based on the structural change of conjugated system leading to interconversion between two distinct electronic states.[3,4] We have previously reported on the porphyrin–oligothiophene–fullerene triad and its efficient photoinduced electron transfer from the porphyrin chromophore to the fullerene,[2] and recently reported that this electron transfer can be controlled by complexation/decomplexation of a sodium cation in the crown ether ring integrated with the oligothiophene part.[5] This switching function is also caused by a geometrical change of the oligothiophene conjugated system. In contrast, the switching without concomitant of structural change must be very useful but has received little attention,[6] in part due to the difficulty of choosing the appropriate external stimuli and controlling the electron transfer, except for the modulation with an electrical gate.[7] In this regard, we anticipated that an organic ionic unit incorporated into the molecular wire can induce different electronic perturbations to the conjugated system depending on the nature of counter ions without interrupting the conjugation. In this study, we have synthesized the porphyrin–oligothiophene–fullerene triad bearing a thieno[3,4-*d*]imidazolium salt in the oligothiophene part and elucidated the switching properties in photoinduced electron transfer.



Scheme 1. Reagents and conditions: a) $Pd(PPh_3)_4$, toluene, reflux; b) TBAF, THF/MeOH, rt; c) $Pd(PPh_3)_4$, NEt_3, THF, rt; d) $Pd(PPh_3)_4$, NEt_3, THF, 60 °C; e) C_{60}, *N*-methylglycine, C_6H_5Cl, reflux; f) MeI, 50 °C.

The synthesis of the triad **Por-4T-Im$^+$I$^-$-4T-C60** is schematically presented in Scheme 1. To avoid the steric influence of methyl substituents in the imidazolium salt upon the conjugation of the backbone, ethynyl spacers were introduced between quaterthiophene and 2-butyl-1,3-dimethylthieno[3,4-*d*]imidazolium iodide. The Stille coupling of zinc iodotetraphenylporphyrin (**TPP-I**)[8] with α-stannylquaterthiophene (**1**) followed by the treatment with TBAF gave **Por-4T** in 69% yield for two steps. The counter part **I-Im-4T-CHO** was synthesized by the Sonogashira coupling reaction between 1*H*-2-butyl-4,6-diiodo-1-methylthieno[3,4-*d*]imidazole (**2**) and α-ethynylquaterthiophene (**3**). Detailed synthetic procedures of **1**, **2**, and **3** are given in Supporting Information.[9] The palladium-catalyzed Sonogashira coupling of **Por-4T** with **I-Im-4T-CHO** furnished **Por-4T-Im-4T-CHO** in 44% yield. The azomethyne ylide generated in situ from **Por-4T-Im-4T-CHO** and *N*-methylglycine was allowed to react with [60]fullerene in refluxing chlorobenzene to give the fullerene adduct **Por-4T-Im-4T-C60** in a moderate yield.[10] In the final step, treatment of **Por-4T-Im-**

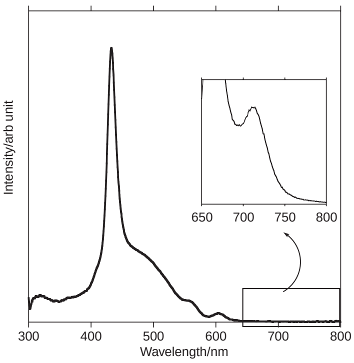


Figure 1. Electronic absorption spectrum of **Por-4T-Im^{+}I^{-}-4T-C60** in benzonitrile.

4T-C60 with methyl iodine gave the target triad **Por-4T-Im^{+}I^{-}-4T-C60**.[11]

The UV–vis spectrum of **Por-4T-Im^{+}I^{-}-4T-C60** in benzonitrile showed the porphyrin Soret band at 432 nm and Q-band absorption at 563 and 604 nm, accompanied with the π–π^* band of oligothiophene in the region of 450–550 nm as shown in Figure 1. The inset of Figure 1 shows the typical weak absorption of fulleropyrrolidine derivative at 710 nm. The essentially identical spectral features of the triad with the superposition of its component chromophores indicate that there is no electronic interaction among them in the ground state.

In contrast, the fluorescence from the porphyrin chromophore of **Por-4T-Im-4T-C60** in benzonitrile upon excitation at the Q band (563 nm) was quenched to 73% in comparison with the strong fluorescence of **Por-4T-Im-4T-CHO**,[9] caused by occurrence of a photoinduced intramolecular electron transfer from the porphyrin to the fullerene.[2] The fluorescence intensity of **Por-4T-Im^{+}I^{-}-4T-C60** was further reduced to 35%,[9,12] indicating a strong electronic perturbation of the imidazolium unit to accelerate the electron transfer. The controlling ability of counter anions for the photoinduced electron transfer was evaluated by intensity changes of the fluorescence upon addition of excess ammonium salts (TBA^{+}**F^{-}**, TBA^{+}**PF$_6$$^{-}$**, TBA^{+}**BF$_4$$^{-}$**, and TBA^{+}**ClO$_4$$^{-}$**) to a benzonitrile solution of **Por-4T-Im^{+}I^{-}-4T-C60**. A marked enhancement of the fluorescence intensity was observed on addition of TBA^{+}**F^{-}** as shown in Figure 2, while the other tested anions (**PF$_6$$^{-}$**, **BF$_4$$^{-}$**, and **ClO$_4$$^{-}$**) showed almost insignificant changes. This result suggests that the strong coordination of fluoride anion to the imidazolium cation takes place, so that the cationic charge of the imidazolium is effectively neutralized to suppress its acceleration effect on the photoinduced electron transfer.

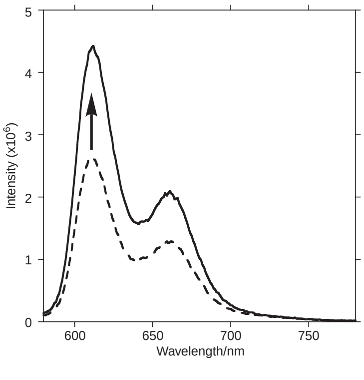


Figure 2. Fluorescence spectra of **Por-4T-Im^{+}I^{-}-4T-C60** (dashed line) and after addition of TBAF (solid line) in benzonitrile with excitation at 563 nm.

In conclution, we have successfully synthesized the **Por-4T-Im^{+}I^{-}-4T-C60** triad containing an imidazolium salt and demonstrated that the photoinduced intramolecular electron transfer is controllable by displacing the counter anion, realizing a new type of the chemical-gate system.[6]

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11 Synthesis of **Por-4T-Im^{+}I^{-}-4T-C60**: A solution of **Por-4T-Im-4T-C60** (25 mg, 0.009 mmol) in MeI (excess) was stirred at 60 °C for 4 h in a sealed tube. After removal of the volatile matter, the residue was purified by a reprecipitation method with $CHCl_3$/hexane. The resulting solid was filtered and washed with hexane to give **Por-4T-Im^{+}I^{-}-4T-C60** as a brown solid (17 mg, 68%); MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) m/z $[M–I]^+$, calcd for $C_{178}H_{114}N_7S_9Zn$, 2704.6; found, 2704.5; ^1H NMR ($CDCl_3$) δ 0.83–1.05 (m, 15H), 1.21–1.70 (m, 34H), 2.75–2.87 (m, 13H), 3.88 (d, 1H, $J = 9.6$ Hz), 4.12 (br s, 6H), 4.62 (d, 1H, $J = 9.9$ Hz), 4.93 (s, 1H), 7.06–7.15 (m, 11H), 7.42 (s, 1H), 7.74 (m, 9H), 7.95 (d, 2H, $J = 8.2$ Hz), 8.16–8.22 (m, 8H), 8.88–8.98 (m, 8H).

12 Upon conversion of **Por-4T-Im-4T-C60** to **Por-4T-Im^{+}I^{-}-4T-C60**, the absorption band of oligothiophene shifted to longer wavelength, while no change was observed in the absorption bands of the porphyrin and fullerene chromophores as shown in Figure S01.