

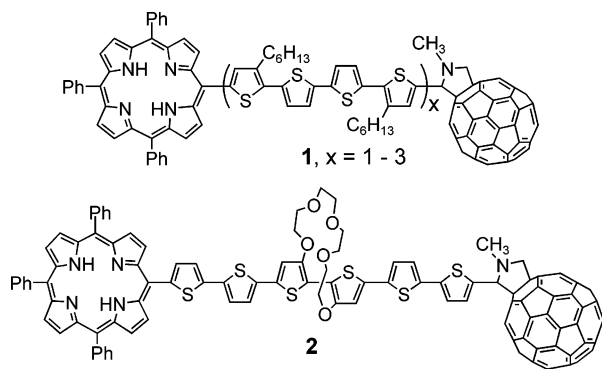
## Polyether-Bridged Sexithiophene as a Complexation-Gated Molecular Wire for Intramolecular Photoinduced Electron Transfer

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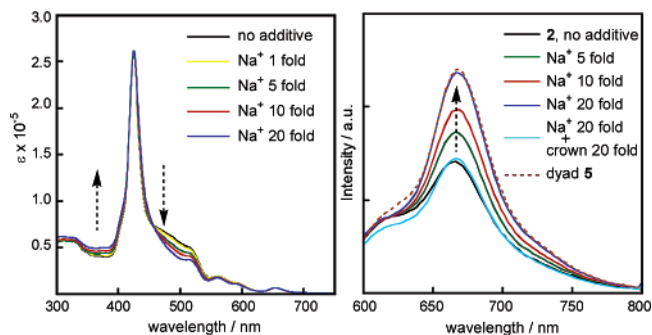
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Well-defined  $\alpha$ -oligothiophenes are particularly promising as molecular wires.<sup>1</sup> In the previous study of the porphyrin–oligothiophene–fullerene triad **1**, we actually found that the oligothiophene spacer can undergo efficient photoinduced electron transfer from the porphyrin chromophore to the fullerene.<sup>2</sup> It is essential in molecular electronics that the electron transfer properties of molecules can be controlled by an external stimulus (gate function).<sup>3</sup> Swager and co-workers reported that polythiophene systems modified with crown ethers display ionochromic responses.<sup>4</sup> This has prompted us to examine the possibility that crown ether-integrated oligothiophenes can behave as metal complexation-gated molecular wires. Inclusion of an alkaline–metal cation in the crown ether ring is expected to restrict the conformation of the oligothiophene backbone, resulting in a geometrical change crucial to electron transfer.<sup>5</sup> We now report the photophysical properties of the novel porphyrin–sexithiophene–fullerene triad **2** (abbreviated as Po–6T–C<sub>60</sub>), where the two central thiophene units of the sexithiophene spacer are bridged by a crown-ether-like polyether chain, where the reversible control of the photoinduced electron transfer is possible by metal complexation/decomplexation.



The synthesis of compound **2** was carried out via step-by-step couplings of the three components, porphyrin, sexithiophene, and fullerene, according to the protocol used for the synthesis of **1**.<sup>2a</sup> The synthetic details are described in the Supporting Information.

Figure 1 (left) displays the electronic absorption spectrum of the triad **2** in benzonitrile and is composed of  $\pi$ – $\pi^*$  transitions of the three chromophores. A marked peak at  $\lambda_{\text{max}}$  425 nm is assigned to the Soret band of the porphyrin chromophore. The  $\pi$ – $\pi^*$  transition of the sexithiophene chromophore appears as a shoulder on the low-energy side (450–520 nm) of the strong Soret band. Increasing



**Figure 1.** Electronic absorption spectra (left) and fluorescence spectra with 558 nm excitation (right) of **2** in benzonitrile with addition of increasing amounts of sodium perchlorate and 15-crown-5. The fluorescence spectrum of **5** is included for comparison.

addition of sodium perchlorate in the solution caused a decrease in the intensity of the shoulder peak and instead an increase of the small shoulder on the high-energy side (350–400 nm). This spectral change is ascribable to interruption of conjugation of the sexithiophene backbone induced by complexation with a sodium cation in the crown ether ring, as illustrated for **3**.

A more clearly defined spectral change caused by complexation was observed using the polyether-bridged sexithiophene **4**. Five-fold or more addition of sodium perchlorate to the benzonitrile solution of **4** caused a color change of orange to yellow, and concomitantly, the absorption maximum shows a large blue shift by 47 nm from  $\lambda_{\text{max}}$  460 to 413 nm (Supporting Information, Figure S1). This confirms marked interruption of the conjugation at the center of the sexithiophene backbone. Furthermore, the original spectrum of **4** can be restored by adding the same amount of 15-crown-5, which has a stronger affinity for sodium cation than the polyether chain in **4**.<sup>6</sup>

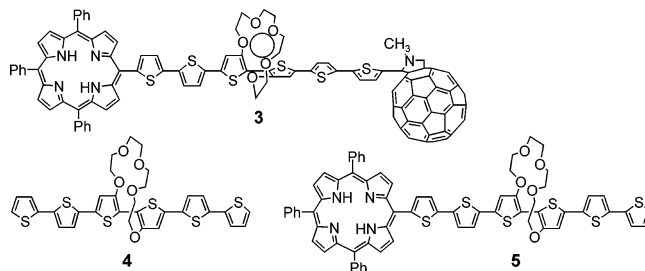
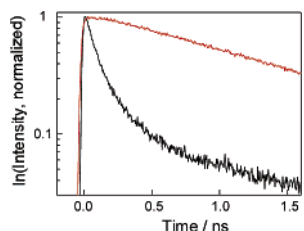
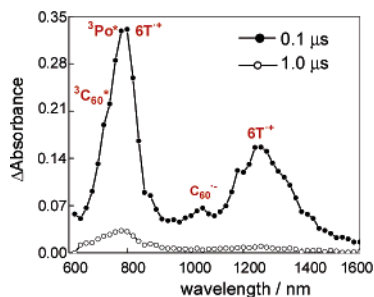


Figure 1 (right) compares the fluorescence of the triad **2** and the porphyrin–sexithiophene dyad **5** upon irradiation at the Q-band (558 nm) of the porphyrin. Obviously in **2**, the fluorescence is markedly reduced by the fullerene attached on the opposite site.

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**Figure 2.** Fluorescence decay spectra of **2** at 650 nm upon 410 nm excitation in benzonitrile with no additive (black line) and with 20-fold sodium perchlorate (red line).



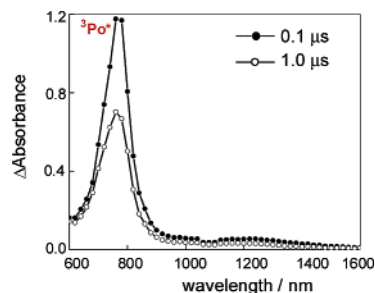
**Figure 3.** Transient absorption spectra of **2** in Ar-saturated benzonitrile under 532 nm laser photolysis.

This means that a fast electron transfer occurs from the singlet excited state of the porphyrin to the fullerene, through the oligothiophene.<sup>2</sup> However, the fluorescence of **2** is enhanced by addition of excess sodium perchlorate. Evidently, complexation with a sodium cation depresses the intramolecular electron transfer. Furthermore, addition of the same amount of 15-crown-5 restores the original fluorescence spectrum of **2**. These two-way fluorescence changes could be repeated at least several times.

Figure 2 shows the fluorescence time profiles of **2**. Simulation analysis of the black line observed for no additive indicated that the photophysical decay mechanism of the porphyrin consists of two paths with fluorescence lifetimes  $\tau_f = 105$  (89%) and 1080 ps (11%). The predominant fast decay path is assigned to intramolecular electron transfer from the porphyrin chromophore to the fullerene. In the presence of 20-fold sodium perchlorate, the time profile changed to the red line, with only a slow single decay path with  $\tau_f = 2580$  ps. Evidently, the fast intramolecular electron transfer is completely suppressed by complexation.

The nanosecond transient absorption spectra of **2** give definitive information on the decay mechanism. Figure 3 shows the absorption spectra of **2** at 0.1 and 1.0  $\mu$ s, after the porphyrin moiety was selectively excited by 532 nm laser photolysis. In the 0.1  $\mu$ s spectrum, a characteristic band due to  $C_{60}^{*-}$  is observed at around 1040 nm.<sup>7</sup> In addition, the two absorption bands are observed at around 1250 and 800 nm, assignable to  $6T^{*+}$ .<sup>8</sup> In contrast to the 1250 nm band, the 800 nm band remains after 1.0  $\mu$ s, so the 800 nm band must be overlapped by other bands presumably due to triplet porphyrin and fullerene species. This result is reasonably explained by the photophysical decay mechanism of **1** speculated in our previous paper:<sup>2b</sup>  $^1Po^* \rightarrow ^6T-C_{60}^{*-}$  first undergoes an intramolecular electron transfer to  $Po^{*+}-^6T-C_{60}^{*-}$ , which is followed by a fast hole shift to the energetically more stable charge separated state  $Po-^6T^{*+}-C_{60}^{*-}$ , and then deactivation occurs via charge recombination.

As shown in Figure 4, the transient absorption spectra of **2** in the presence of 20-fold sodium perchlorate are completely different from that obtained without sodium perchlorate. The specific bands due to both  $C_{60}^{*-}$  and  $6T^{*+}$  are no longer observed, and only a strong band due to the triplet porphyrin species is observed at 780 nm. The singlet excited porphyrin must take a simple decay path



**Figure 4.** Transient absorption spectra of **2** in Ar-saturated benzonitrile with 20-fold sodium perchlorate under 532 nm laser photolysis.

to the triplet porphyrin. Obviously, the transient absorption spectra support marked suppression of the intramolecular electron transfer of **2** by complexation.

In conclusion, we have demonstrated that in the porphyrin–sexithiophene–fullerene triad **2** photoinduced intramolecular electron transfer can be completely controlled by complexation/decomplexation of a sodium cation in the crown ether ring. Various types of on/off switchable molecular architectures have been actively studied,<sup>9</sup> and most of the molecular systems cleverly take advantage of photochemically controlled electron transfer.<sup>10</sup> The present triad **2** represents a novel switchable system responding to a metal ion. In this system, it is notable that the polyether-bridged sexithiophene can indeed function as a complexation-gated molecular wire.

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**Supporting Information Available:** Experimental procedures and characterization data of all new compounds and Figure S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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