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Porphyrin–Oligothiophene–Fullerene Triads as an Efficient Intramolecular Electron-Transfer System

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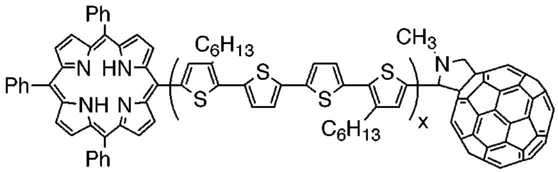
ABSTRACT



Por-nT-C60 (x = 1–3)

A series of porphyrin–oligothiophene–fullerene triads containing quaterthiophene, octithiophene, and dodecithiophene spacers has been synthesized. The fluorescence of the porphyrin chromophore in benzonitrile is efficiently quenched by electron transfer to the fullerene moiety. This process shows a weak distance dependence of the oligothiophene spacer with an attenuation factor $\beta = 0.11$ Å^{-1}.

Conjugated nanoscale oligomers have received current attention as molecular wires in the fields of molecular electronics[1] and light-harvesting molecular antenna-type architecture.[2] The rates of electron and energy transfer through oligomeric molecules exponentially decrease with their increasing lengths, and the preexponential coefficients (attenuation factor) are closely related to their chemical bonding.[3] Well-defined oligothiophenes are of special interest in terms of their ready accessibility, structural modifications, high π-conjugation, low oxidation potentials, and environmental stability,[4] but how efficiently oligothiophenes can function as a molecular wire is a still unclear key issue. In this regard, Effenberger and co-workers recently reported that in anthryloligothienylporphyrins[5] and anthryloligothienylfullerenes[6] photoinduced electron or energy transfer smoothly occurred from the excited anthracene as a donor to the porphyrin or fullerene as an acceptor via the oligothiophene spacer. However, the spacer is limited to only short oligomers up to the 5-mer, so that the distance dependence of oligothiophenes remains unsolved. Extending our study of an intriguing charge separation dyad system ***n*T-C60**,[7,8]

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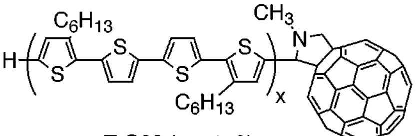
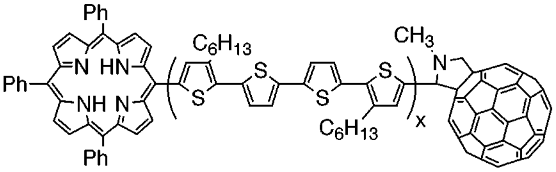
we have prepared the novel triad system **Por-*n*T-C60**, which comprises three components of porphyrin, oligothiophene, and fullerene. The involvement of a series of long oligothiophene spacers, such as quarterthiophene, octithiophene, and dodecithiophene, in the system has allowed us to study a long-range electron transfer and to evaluate its distance dependence. Here we would like to report the synthesis and photophysical properties of **Por-*n*T-C60**.



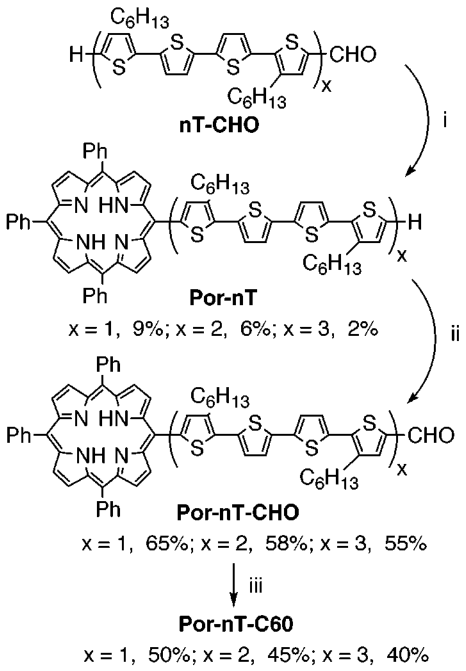
nT-C60 (x = 1–3)



Por-nT-C60 (x = 1–3)

The porphyrin–oligothiophene–fullerene triads were synthesized as shown in Scheme 1. The formyl oligothiophenes, readily accessible by the Vilsmeier reaction of oligothiophenes,[7a] were subjected together with 3 molar equiv of benzaldehyde to hybrid condensation with 4 molar equiv of pyrrole in the presence of 4 molar equiv of trifluoroacetic acid according to the Lindsey method.[9] Subsequent oxidation with *p*-chloranil formed hybrid porphyrins containing both oligothienyl and phenyl substituents together with tetraphenylporphyrin, which were separated from one another by a column chromatographic technique (silica gel/hexane–dichloromethane). Although the yield is low (2–9%), this access to **Por-*n*T** is straightforward. Subsequently, **Por-*n*T** were converted to **Por-*n*T-CHO** by the Vilsmeier reaction (55–65% yield) and finally treated with fullerene and *N*-methylglycine in toluene according to the Prato method[10] to give the target **Por-*n*T-C60** (40–50% yield).[11]

Scheme 1[a]



[a] Reagents and conditions: (i) 4 equiv of pyrole, 3 equiv of benzaldehyde, 4 equiv of trifluoroacetic acid, dichloromethane, rt, 2 h, then 3 equiv of chloranil, reflux, 1 h, finally potassium carbonate, rt, 2 h; (ii) 10 equiv of DMF, 10 equiv of POCl$_3$, 1,2-dichloroethane, 40 °C, 12 h; (iii) C$_{60}$, 5 equiv of *N*-methylglycine, toluene, reflux, 48 h.

The electronic absorption spectra of **Por-*n*T-C60** in benzonitrile, as shown in Figure 1, are understood in terms of simple superimposition of the electronic transitions of the three constituent chromophores: the porphyrin component shows a very strong absorption at 426 nm (Soret band) and

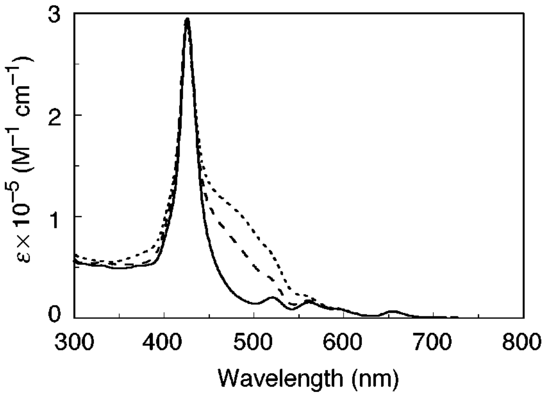


Figure 1. Electronic absorption spectra of **Por-4T-C60** (solid line), **Por-8T-C60** (dashed line), and **Por-12T-C60** (dotted line) in benzonitrile.

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(11) All new compounds **Por-*n*T-C60** were characterized by spectroscopic and elemental analyses. **Por-4T-C60**: brown powder; mp 255 °C (dec); MS (MALDI-TOF) *m/z* 1810 (M$^+$); ^{1}H NMR (CDCl$_3$) δ −2.71 (s, 2H), 0.88 (t, $J = 6.8$ Hz, 6H), 1.27 (m, 12H), 1.84–1.92 (m, 2H), 1.96 (quin, $J = 7.7$ Hz, 2H), 2.80 (t, $J = 7.7$ Hz, 2H), 2.92 (s, 3H), 3.12 (t, $J = 7.7$ Hz, 2H), 4.11 (d, $J = 9.4$ Hz, 1H), 4.87 (d, $J = 9.4$ Hz, 1H), 5.08 (s, 1H), 7.07 (d, $J = 3.9$ Hz, 1H), 7.18 (d, $J = 3.9$ Hz, 1H), 7.21 (s, 1H), 7.22 (d, $J = 3.9$ Hz, 1H), 7.28 (d, $J = 3.9$ Hz, 1H), 7.76 (s, 1H), 7.74–7.78 (m, 9H), 8.19–8.22 (m, 6H), 8.82 (s, 4H), 8.87 (d, $J = 4.6$ Hz, 2H), 9.22 (d, $J = 4.6$ Hz, 2H). Anal. Calcd for $C_{129}H_{63}N_5S_4$: C, 85.55; H, 3.51; N, 3.89. Found: C, 85.23; H, 3.58; N, 3.80. **Por-8T-C60**: brown powder; mp 181 °C (dec); MS (MALDI-TOF) *m/z* 2309 (M$^+$); ^{1}H NMR (CDCl$_3$) δ −2.71 (s, 2H), 0.81–0.95 (m, 12H), 1.22–1.43 (m, 24H), 1.59–1.69 (m, 6H), 1.94–1.99 (m, 2H), 2.72–2.90 (m, 6H), 2.89 (s, 3H), 3.13 (t, $J = 7.8$ Hz, 2H), 4.07 (d, $J = 9.5$ Hz, 1H), 4.84 (d, $J = 9.5$ Hz, 1H), 5.03 (s, 1H), 7.000 (s, 1H), 7.001 (s, 1H), 7.02 (d, $J = 3.9$ Hz, 2H), 7.07 (d, $J = 3.9$ Hz, 1H), 7.095 (d, $J = 3.9$ Hz, 1H), 7.101 (d, $J = 3.9$ Hz, 1H), 7.18 (s, 1H),

four weak absorptions at 521, 562, 591, and 655 nm (Q-band), the oligothiophene shows a $\pi-\pi^*$ band in the region of 350−470 nm, whose wavelength is red-shifted and intensity is enhanced with the chain extension, and the fullerene shows a strong $\pi-\pi^*$ band at 328 nm accompanied with weak long-wavelength bands tailing to 704 nm. Evidently there is no electronic interaction among the three chromophores in the ground state. On the other hand, the emission spectra are interactive, as demonstrated for **Por-4T-C60** in Figure 2. When the porphyrin chromophore is excited in benzonitrile, 95% of the porphyrin fluorescence from **Por-4T-C60** as compared to **Por-4T** is quenched by the additionally attached fullerene. Considering no appreciable emitting from the fullerene, this result indicates that a substantial amount of electron transfer occurs from the porphyrin moiety to the fullerene. Similar quenching is also observed for the extended homologues, but reduced with the extended chain length; 46% from **Por-8T-C60** and 21% from **Por-12T-C60** in benzonitrile are quenched as compared to the respective porphyrin-linked oligothiophenes **Por-*n*T**. On the basis of the quenching and the fluorescence lifetimes of **Por-*n*T** ($n = 4$, τ 3.3 × 10^{-9} s; $n = 8$, 1.4 × 10^{-9} s; $n = 12$, 1.3 × 10^{-9} s), we can estimate from the relation $k_{\rm ET} = [\Phi(\textbf{Por-}n\textbf{T})/\Phi(\textbf{Por-}n\textbf{T-C60}) - 1]/\tau(\textbf{Por-}n\textbf{T})$ that the rate constants for electron transfer reaction ($k_{\rm ET}$) are the following: **Por-4T-C60**, 5.7 × 10^9 $\rm s^{-1}$; **Por-8T-C60**, 6.2 × 10^8 $\rm s^{-1}$; **Por-12T-C60**, 2.0 × 10^8 $\rm s^{-1}$. Molecular modeling shows that the donor−acceptor distances (R) are 1.4 nm for **Por-4T-C60**, 3.0 nm for **Por-8T-C60**, and 4.6 nm for **Por-12T-C60**. A plot of ln $k_{\rm ET}$ vs R gives a good straight line according to equation $k_{\rm ET} = A \exp(-\beta R)$. From the slope of the line, an attenuation factor $\beta = 0.11$ Å^{-1} is obtained. This value for electron transfer is much smaller than 0.6−1.2 Å^{-1} for saturated hydrocarbon bridges[12] and 0.32−0.66 Å^{-1} for conjugated phenylenes,[13] and comparable to 0.04−0.2 Å^{-1} for polyenes[3,14] and 0.04−0.17 Å^{-1} for polyynes.[14b,15] Evidently, the efficient electronic coupling between the donor and the acceptor of **Por-*n*T-C60** occurs through the oligothiophene spacer. Taking accessibility to extraordinarily long oligothiophenes into account,[16] oligothiophenes are most promising for long-distance molecular wires.

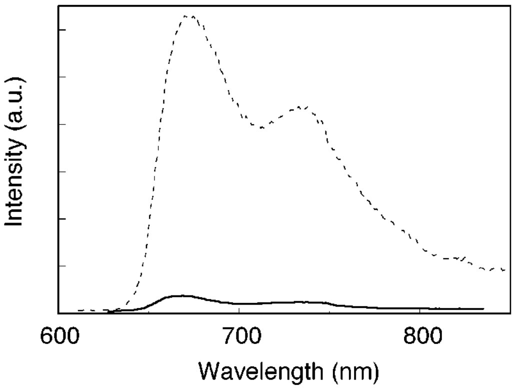

Figure 2. Fluorescence spectra of **Por-4T** (dashed line) and **Por-4T-C60** (solid line) in benzonitrile with excitation at 558 nm.

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Supporting Information Available: Detailed experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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7.20 (d, J = 3.9 Hz, 1H), 7.24 (d, J = 3.6 Hz, 1H), 7.31 (d, J = 3.6 Hz, 1H), 7.76 (s, 1H), 7.74−7.80 (m, 9H), 8.20−8.22 (m, 6H), 8.82 (s, 4H), 8.87 (d, J = 5.0 Hz, 2H), 9.23 (d, J = 5.0 Hz, 2H). Anal. Calcd for $C_{157}H_{95}N_5S_8$: C, 81.32; H, 4.24; N, 3.10. Found: C, 81.06; H, 4.04; N, 2.94. **Por-12T-C60**: brown powder; mp 119 °C (dec); MS (MALDI-TOF) *m/z* 2804 (M^+); ^{1}H NMR ($CDCl_3$) δ −2.71 (s, 2H), 0.89−0.95 (m, 18H), 1.23−1.45 (m, 36H), 1.67−1.71 (m, 10H), 1.97 (quin, J = 7.8 Hz, 2H), 2.72−2.90 (m, 10H), 2.93 (s, 3H), 3.14 (t, J = 7.8 Hz, 2H), 4.12 (d, J = 9.6 Hz, 1H), 4.88 (d, J = 9.6 Hz, 1H), 5.07 (s, 1H), 7.00 (s, 2H), 7.02 (s, 2H), 7.01−7.05 (m, 4H), 7.08 (d, J = 3.9 Hz, 1H), 7.104 (d, J = 3.7 Hz, 1H), 7.108 (d, J = 3.7 Hz, 1H), 7.13 (d, J = 3.7 Hz, 3H), 7.215 (s, 1H), 7.21 (d, J = 3.9 Hz, 1H), 7.24 (d, J = 3.9 Hz, 1H), 7.30 (d, J = 3.9 Hz, 1H), 7.76 (s, 1H), 7.74−7.80 (m, 9H), 8.20−8.22 (m, 6H), 8.82 (s, 4H), 8.87 (d, J = 5.0 Hz, 2H), 9.23 (d, J = 5.0 Hz, 2H). Anal. Calcd for $C_{185}H_{127}N_5S_{12}$: C, 79.22; H, 4.56; N, 2.50. Found C, 79.12; H, 4.42; N, 2.46.

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