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Synthesis and Photophysical Properties of Two Dual Oligothiophene-Fullerene Linkage Molecules as Photoinduced Long-Distance Charge Separation Systems

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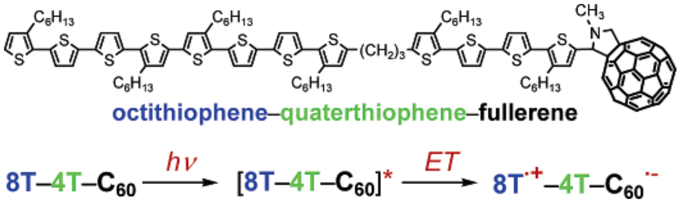

To further extend photoinduced charge separation previously observed for oligothiophene-fullerene dyads (**nT-C$_{60}$**), we have studied two novel dual oligothiophene-fullerene triads, **8T-4T-C$_{60}$** and **4T-8T-C$_{60}$**, where quaterthiophene (**4T**) and octithiophene (**8T**) are linked by a trimethylene chain and either one is attached to a fullerene (**C$_{60}$**). The cyclic voltammograms and electronic absorption spectra of these triad compounds indicated no electronic interactions among the three components. On the other hand, the emission spectra were markedly perturbed by electron transfer and/or energy transfer from the oligothiophene to fullerene. Detailed comparisons between the emission spectra of the triads (**8T-4T-C$_{60}$** and **4T-8T-C$_{60}$**) and the dyads (**4T-C$_{60}$** and **8T-C$_{60}$**) suggest that the additionally attached octithiophene or quaterthiophene in the triads is involved in the photophysical decay mechanism, and the **8T-4T-C$_{60}$** triad undergoes photoinduced electron transfer leading to long-distance charge separation. This was actually corroborated by observation of the specific bands due to **8T$^{\bullet+}$-4T-C$_{60}{}^{\bullet-}$** species in the transient absorption spectra after photoexcitation of the octithiophene. The sandwich device based on the **8T-4T-C$_{60}$** triad produced a more effective photovoltaic response to visible light owing to the contribution of the additional octithiophene chromophore compared to that using the dyad **4T-C$_{60}$**. On the other hand, the **4T-8T-C$_{60}$**-based device demonstrated a rather poorer photovoltaic performance when compared to the **8T-C$_{60}$** device.

Introduction

Charge separation originated from photoinduced electron transfer is a key function for the construction of optoelectronic devices or artificial photosynthetic systems.[1,2] Directed toward the embodiment of this function, molecular systems covalently bonded between an electron donor and an electron acceptor have been actively investigated, where intramolecular through-bond charge separation readily takes place via the excited singlet state of either the electron-donor or electron-acceptor chromophore.[3] We previously studied the photophysical properties of [60]-fullerene-linked oligothiophene dyads **1a−c** ($x = 1-3$, abbreviated as **nT-C$_{60}$**) and revealed that this dyad system underwent

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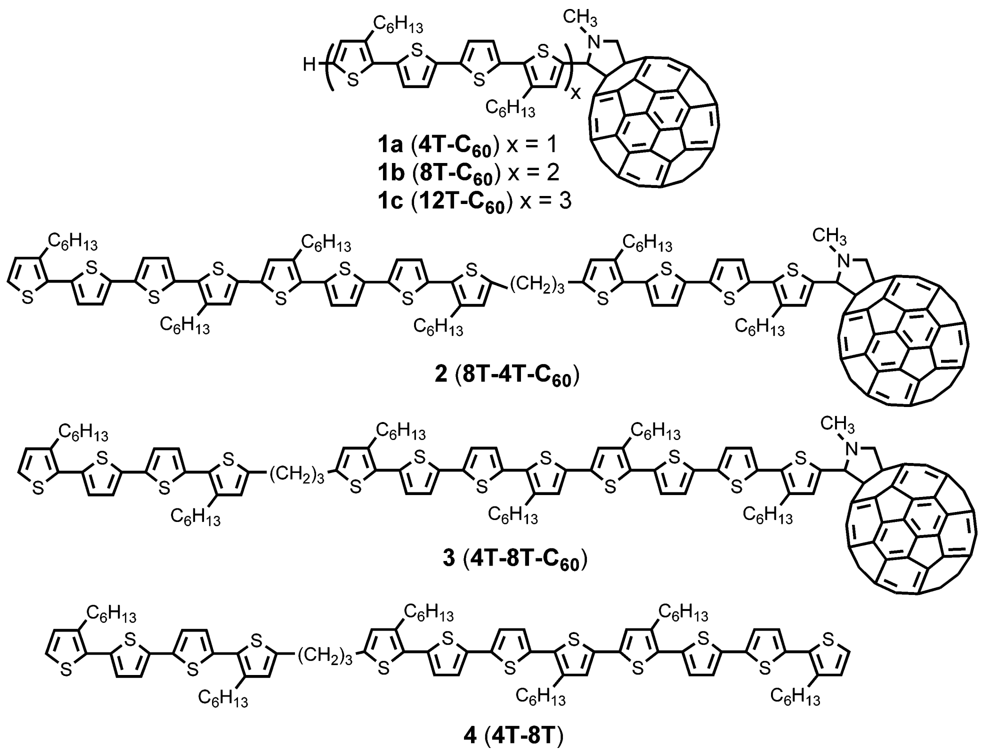
CHART 1



1a (**4T-C$_{60}$**) x = 1
1b (**8T-C$_{60}$**) x = 2
1c (**12T-C$_{60}$**) x = 3

2 (**8T-4T-C$_{60}$**)

3 (**4T-8T-C$_{60}$**)

4 (**4T-8T**)

energy transfer from the sensitizing oligothiophene chromophore to the fullerene in nonpolar toluene[4] and efficient photoinduced electron transfer in polar benzonitrile[5] and in solid state.[6] In addition, these dyads found application as active photovoltaic materials.[7] As the ensuing step of our efforts in the development of oligothiophene-based optoelectronic materials, we have focused on novel dual oligothiophene-fullerene triads, octithiophene-quaterthiophene-fullerene **2** (abbreviated as **8T-4T-C$_{60}$**) and quaterthiophene-octithiophene-fullerene **3** (abbreviated as **4T-8T-C$_{60}$**), where the two oligothiophenes are connected by a trimethylene spacer. Although the additional attached octithiophene in **2** and quaterthiophene in **3** are not directly conjugated with **4T-C$_{60}$** and **8T-C$_{60}$**, respectively, we have expected that they can participate in the excited mechanism owing to their close proximity to the remaining dyads; the photophysical properties must be thus different from those of **4T-C$_{60}$** and **8T-C$_{60}$** as well as the trimethylene-inserted quaterthiophene-octithiophene dyad **4** (abbreviated as **4T-8T**). Here we would like to report the synthesis, photophysical properties, and photovoltaic performances of these novel compounds (Chart 1).

Results and Discussion

Synthesis. Compound **2** was obtained according to the route shown in Scheme 1. First, 3,3‴-dihexyl-2,2′:5′,2″:5″,2‴-quaterthiophene **5** (**4T**)[8] was lithiated with 1 equiv of butyllithium in THF, and the resulting lithiated species was reacted with 1,3-dibromopropane to give the trimethylene-inserted bisquaterthiophene **6** in 20% yield. The Vilsmeier reaction of **6** with DMF and phosphorus oxychloride gave the formyl derivative **7** (44% yield), which was then brominated with NBS to produce the bromo-formyl derivative **8** (82% yield). Also, **5** was converted via lithiation to the tributylstannyl derivative **9** in 52% yield. A Stille coupling reaction between **8** and **9** in the presence of catalytic tetrakis(triphenylphosphine)palladium gave the formyl derivative of trimethylene-inserted quaterthiophene-octithiophene **10** in 79% yield. Finally, treatment of **10** with fullerene and *N*-methylglycine (Prato method)[9] in refluxing chlorobenzene afforded the octithiophene-quaterthiophene-fullerene triad **2** in 63% yield.

The synthesis of the other triad **3** is shown in Scheme 2. First, the trimethylene-inserted bis-quaterthiophene **6** was converted via lithiation into the tributylstannyl derivative **11** (15% yield), which was subjected to a Stille coupling reaction with bromoquaterthiophenecarbaldehyde **12**[8] to produce another type of the formyl derivative of trimethylene-inserted quaterthiophene-octithiophene **13** in 60% yield. Finally, a Prato coupling of **13** with fullerene smoothly afforded the quaterthiophene-octithiophene-fullerene triad **3** in 60% yield.

As shown in Scheme 3, the quaterthiophene-octithiophene dyad **4** was obtained in 31% overall yield by bromination of the bis-quaterthiophene **6** with 1 equiv of NBS, followed by a Stille coupling of the resulting monobromo derivative **14** with tributylstannylquaterthiophene **9**.

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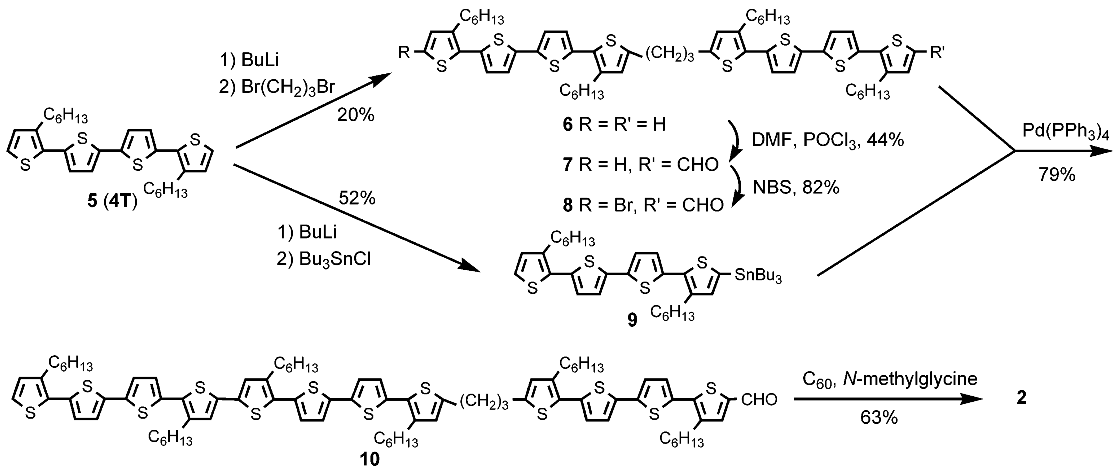
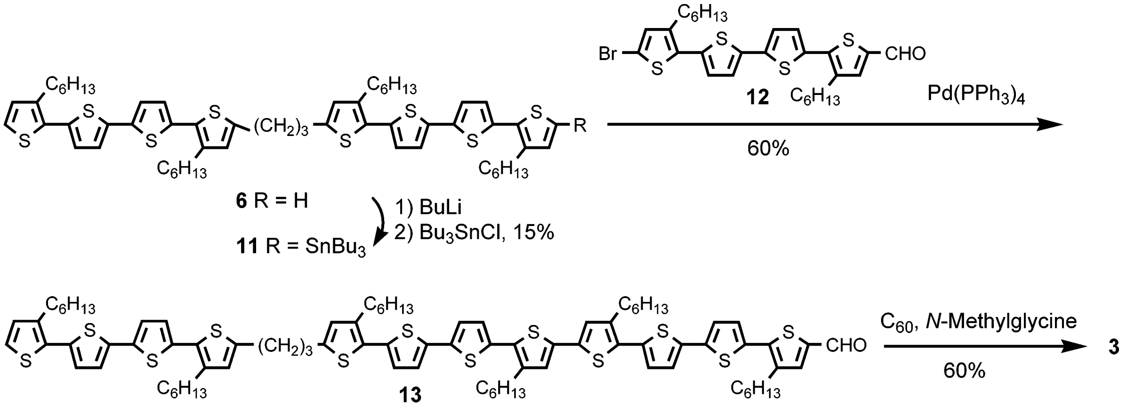
SCHEME 1. Synthesis of Triad 8T-4T-C$_{60}$ (2)



SCHEME 2. Synthesis of Triad 4T-8T-C$_{60}$ (3)



SCHEME 3. Synthesis of Dyad 4T-8T (4)

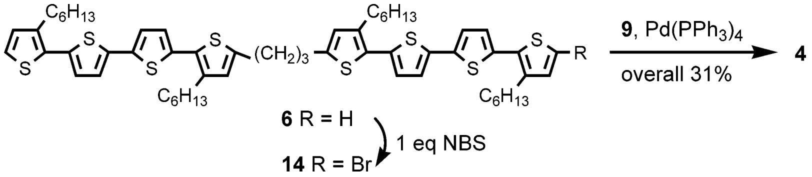


TABLE 1. Oxidation and Reduction Potentials of the Dual Oligothiophene-Fullerene Triads and Related Compounds [a]

compound	E_{pa} (V)	E_{pc} (V)
4T−C$_{60}$ (1a)	+0.98, +1.22	−0.65, −1.02
8T−C$_{60}$ (1b)	+0.78, +1.00, +1.25	−0.60, −1.03
8T-4T-C$_{60}$ (2)	+0.74, +0.97, +1.25	−0.63, −1.02
4T-8T-C$_{60}$ (3)	+0.74, +0.95, +1.17, +1.35	−0.62, −1.03
4T-8T (4)	+0.78, +0.90, +1.15, +1.30	

[a] Measurement conditions: solvent, benzonitrile; supporting electrolyte, 0.1 M n-Bu$_4$NPF$_6$; working electrode, Pt wire; counter electrode, Pt wire; reference electrode, Ag/AgCl; scan rate, 100 mV/s.

Cyclic Voltammograms. Figure 1 demonstrates the cyclic voltammograms of **8T-4T-C$_{60}$** (**2**) and **4T-8T-C$_{60}$** (**3**), which are composed of overlapping oxidation waves due to the two different oligothiophene components in the positive potential region and reduction waves due to the fullerene component in the negative potential region. The oxidation and reduction peak potentials are summarized together with those of the dyads **4T-C$_{60}$** (**1a**), **8T-C$_{60}$** (**1b**), and **4T-8T** (**4**) in Table 1. Since octithiophene is oxidized more easily than quaterthiophene, the first oxidation waves of **2**−**4** are assigned to be due to the octithiophene component. Roughly speaking, these oxidation potentials are almost the same as those of **1b**. In addition, the first reduction potentials due to the fullerene component of **2** and **3** are almost identical to those of the dyads **1a** and **1b**. These results suggest no electronic interaction among the three components in the ground state.

Electronic Absorption Spectra. Figure 2 demonstrates the electronic absorption spectra of dyads and triads **1**−**4**, together with quaterthiophene **5**, and octithiophene **15** in benzonitrile. The spectra of these compounds in toluene are essentially the same (Figure S1, Supporting Information). Table 2 compares the electronic absorption data measured in both solvents, together with their emission data. Quaterthiophene **5** and octithiophene **15** show a strong $\pi-\pi^*$ absorption band in the ultraviolet/visible region: **4T** (**5**), λ_{max} 379 nm (log ϵ 4.64); **8T** (**15**), 439 nm (log ϵ 4.77). N-Methyl-3,4-fulleropyrolidine (**16**) shows a strong absorption band at 330 nm (log ϵ 4.59) accompanied with weak peaks at 434 nm (log ϵ 4.55), 640 nm (log ϵ 2.51), and 704 nm (log ϵ 2.52) tailing to the near-infrared region.[8,9] The absorption spectra observed for the triads **2** and **3** are explained in terms of superposition of the electronic

TABLE 2. Spectroscopic Data of the Dual Oligothiophene-Fullerene Triads and Related Compounds

compound	solvent	absorbance$_{max}$, nm (log ϵ) nT	absorbance$_{max}$, nm (log ϵ) C_{60}	emission$_{max}$, nm nT*	emission$_{max}$, nm C_{60}*
4T-C_{60} (1a)	toluene	379 (4.64)	335 (4.69), 708 (2.59)	447[a]	714[a,c,d]
	benzonitrile	384 (4.59)	327 (4.61), 703 (2.47)	ca. 450[a,d]	
8T-C_{60} (1b)	toluene	436 (4.83)	335 (4.75), 708 (2.54)	546[b]	715[b–d]
	benzonitrile	450 (4.81)	330 (4.81), 702 (2.56)	ca. 550[b,d]	
8T-4T-C_{60} (2)	toluene	408 (4.93)	340 (4.81), 704 (2.64)	543[a,b]	707[a–d]
	benzonitrile	418 (4.90)	333 (4.75), 704 (2.57)	551[a,b]	
4T-8T-C_{60} (3)	toluene	408 (4.89)	348 (4.83), 705 (2.62)	ca. 550[a,b]	710[a–d]
	benzonitrile	415 (4.90)	336 (4.78), 704 (2.69)	ca. 470[a,d], ca. 530[b,d]	
4T-8T (4)	toluene	413 (4.82)		544[a,b]	
	benzonitrile	423 (4.80)		553[a,b]	

[a] Observed with excitation at 379 nm. [b] Observed with excitation at 440 nm. [c] Observed with excitation at 650 nm. [d] Very weak emission.

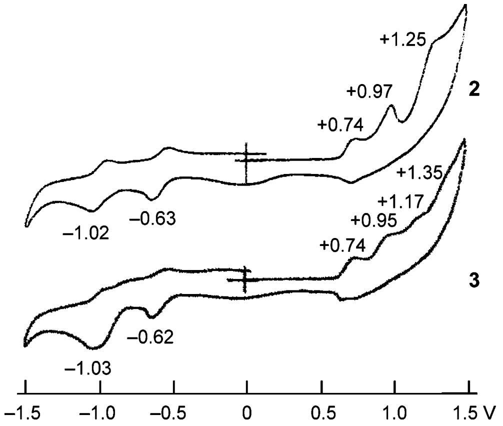


FIGURE 1. Cyclic voltammograms of the triads **2** and **3** in benzonitrile.

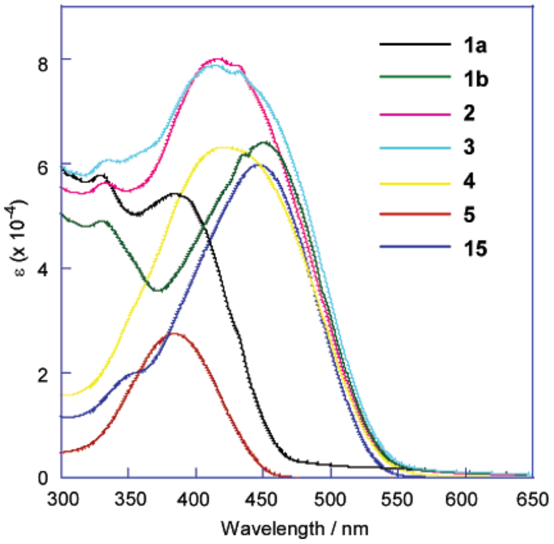


FIGURE 2. Electronic absorption spectra of **4T-C_{60}** (**1a**), **8T-C_{60}** (**1b**), **8T-4T-C_{60}** (**2**), **4T-8T-C_{60}** (**3**), **4T-8T** (**4**), **4T** (**5**), and **8T** (**15**) in benzonitrile.

transitions of the three component chromophores. This evidently corroborates no electronic interactions among the components in the ground state, as above estimated on the basis of the voltammetric results.

Emission Spectra. We previously reported that the **nT-C_{60}** dyads efficiently underwent a photoinduced intramolecular energy and/or electron transfer from the oligothiophene component to the fullerene.[4,5] The quenching process of the excited states of **nT-C_{60}** is markedly solvent-dependent: an energy transfer occurs in nonpolar toluene, whereas an electron transfer is predominant in polar benzonitrile. It is thus understood that high solvation in the polar solvent stabilizes the charge-separation state of **nT-C_{60}** much more, and as a result, an electron transfer takes precedence over an energy transfer. Figure 3 shows the emission spectra of **4T-C_{60}** (**1a**), **8T-4T-C_{60}** (**2**), and **4T-8T-C_{60}** (**3**) measured upon photoexcitation at 379 nm in benzonitrile. It should be noticed that the irradiation of **2** and **3** with 379 nm light mainly excites both quaterthiophene and octithiophene chromophores. For comparison, the emission spectra of **4T-8T** (**4**) and **4T** (**5**) are also included. Because the

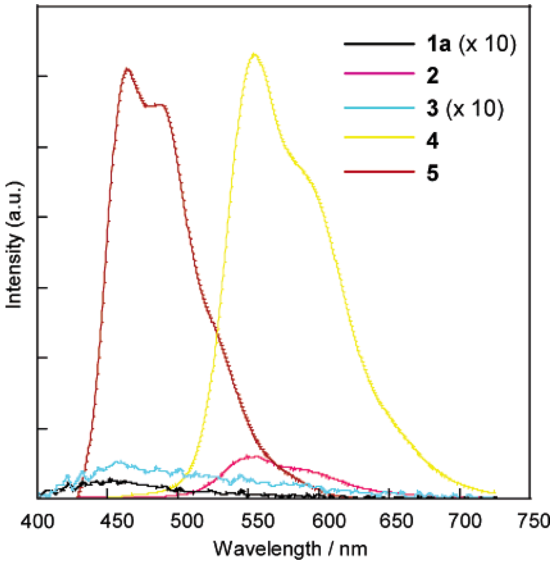
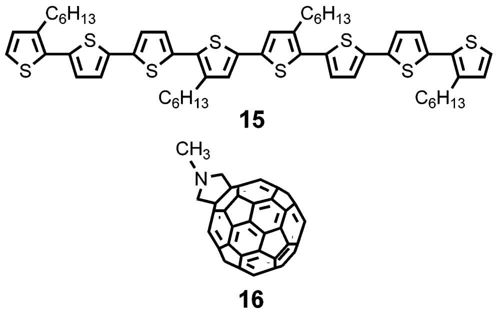


FIGURE 3. Emission spectra of **4T-C_{60}** (**1a**), **8T-4T-C_{60}** (**2**), **4T-8T-C_{60}** (**3**), **4T-8T** (**4**), and **4T** (**5**) with excitation at 379 nm in benzonitrile, where the absorbances of all samples were kept constant.

CHART 2



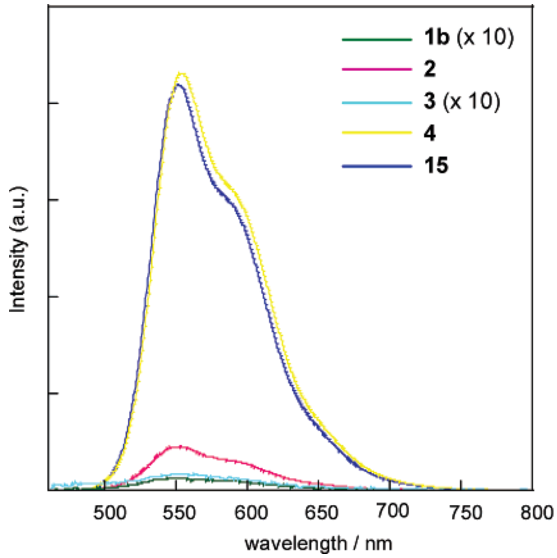


FIGURE 4. Emission spectra of **8T-C$_{60}$** (**1b**), **8T-4T-C$_{60}$** (**2**), **4T-8T-C$_{60}$** (**3**), **4T-8T** (**4**), and **8T** (**15**) upon excitation at 440 nm in benzonitrile, where the absorbances of all samples were kept constant.

observed emissions of **1a** and **3** are very week, their spectra are depicted on a high scale of 1 order of magnitude. In contrast to strong emission of **4T**, only little emission for dyad **4T-C$_{60}$** (**1a**) at around 450 nm indicates an efficient intramolecular electron transfer from **^{1}4T*** to **C$_{60}$**.[5] On the other hand, the emission spectrum of **8T-4T-C$_{60}$** (**2**) with excitation at 379 nm demonstrates no emission from the **4T** component but only a weak emission due to the **8T** component. This can be interpreted mainly in terms of an intramolecular electron transfer from **^{1}4T*** to **C$_{60}$**, but an intramolecular energy transfer from **^{1}4T*** to **8T** must be also considered, because dyad **4T-8T** (**4**) shows a similar spectrum with only an emission due to the **8T** component. From the result that the emission intensity of **8T-4T-C$_{60}$** is about 1/10 of that of **4T-8T**, it is speculated that in this quenching process, an intramolecular electron transfer from **^{1}4T*** to **C$_{60}$** takes precedence over an energy transfer from **^{1}4T*** to **8T**. The emission spectrum of **8T-4T-C$_{60}$** measured in toluene is almost the same as in benzonitrile, suggesting similar competitive quenching processes (Figure S2). However, the emission spectrum of **4T-C$_{60}$** shows an additional weak emission at around 700 nm assignable to the fullerene chromophore, meaning that the involvement of an energy transfer from **^{1}4T*** to **C$_{60}$** must be considered in the quenching process.[4,5] Presumably, the photophysical decay process of **8T-4T-C$_{60}$** involves a similar energy transfer, but the emission tail of the octithiophene in the long wavelength region does not allow the detection of such weak emission from **^{1}C$_{60}$***. The spectrum of **4T-8T-C$_{60}$** (**3**) in benzonitrile shows a very little emission from **^{1}4T*** and nearly no emission from **^{1}8T***. This can be understood in terms of an intramolecular energy transfer from **^{1}4T*** to **8T** followed by an electron transfer from **^{1}8T*** to **C$_{60}$**. In toluene, an additional weak emission is observed around 700 nm, being assignable to that from the fullerene chromophore (Figure S3). It is also the case for **8T-C$_{60}$**. Obviously, an energy transfer from **^{1}8T*** to **C$_{60}$** contributes to the quenching process.[4,5]

Figure 4 shows the emission spectra of **8T-C$_{60}$** (**1b**), **8T-4T-C$_{60}$** (**2**), and **4T-8T-C$_{60}$** (**3**) measured with irradiation at 440 nm in benzonitrile. The 440 nm light mainly excites the octithiophene chromophore. The **8T-C$_{60}$** dyad emits almost no fluorescence from **^{1}8T***, indicating a nearly complete intramolecular electron transfer from **^{1}8T*** to **C$_{60}$**. In contrast, the **8T-4T-C$_{60}$** triad shows an inherent emission from the excited octithiophene, but its intensity is about 1/10 as compared to those of **4T-8T** (**4**) and **8T** (**15**). This result clearly indicates that an intramolecular electron transfer from **^{1}8T*** to **C$_{60}$** contributes considerably to the quenching process. In this quenching process, two electron-transfer paths are speculated: tunneling electron transfer through the intermediary **4T** as a molecular wire and through-space electron transfer from **8T*** to **C$_{60}$** caused by the conformational flexibility of the trimethylene chain. In the case of **4T-8T-C$_{60}$**, a direct intramolecular electron transfer from **^{1}8T*** to **C$_{60}$** is more advantageous thanks to close proximity of both chromophores, leading to a smaller emission from **^{1}8T***. The emission spectra of **8T-C$_{60}$** (**1b**), **8T-4T-C$_{60}$** (**2**), and **4T-8T-C$_{60}$** (**3**) measured with irradiation at 440 nm in toluene are almost the same as those observed in benzonitrile (Figure S3). The observation of an additional weak emission from the fullerene around 700 nm for **1b** and **3** again means the involvement of an energy transfer from **8T*** to **C$_{60}$**.

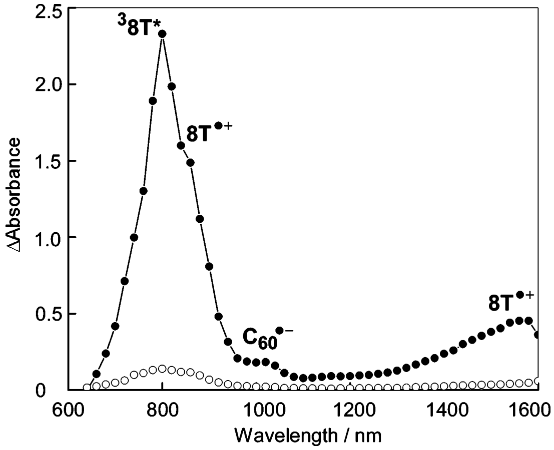


FIGURE 5. Transient absorption spectra of **8T-4T-C$_{60}$** (**2**) in Ar-saturated benzonitrile obtained by 532 nm laser photolysis: (●) at 100 ns and (○) at 1000 ns.

When the fullerene is selectively excited by light of 650 nm, both triads **8T-4T-C$_{60}$** and **4T-8T-C$_{60}$** exhibit a weak emission of **^{1}C$_{60}$*** in toluene (Figure S4) but no emission in benzonitrile. This result is reminiscent of the cases of **4T-C$_{60}$** and **8T-C$_{60}$**. Evidently, an intramolecular electron transfer from **4T** or **8T** to **^{1}C$_{60}$*** entirely dominates the quenching process in the polar solvent as a result of the stabilization of the charge separation state.

Transient Absorption Spectra. To elucidate the photophysical decay mechanism in more detail, we measured the nanosecond transient absorption spectra of **8T-4T-C$_{60}$** (**2**) with 532 nm laser photolysis in benzonitrile. The 532 nm light excites both octithiophene and fullerene chromophores. The absorption spectra shown in Figure 5 shows a strong absorption band at 800 nm, which is assignable to the triplet octithiophene species. In addition, the characteristic absorption bands of **8T$^{\bullet+}$** were observed at around 1550 and 820 nm; the latter appears as a shoulder owing to overlapping with the strong band of **^{3}8T***.[5b] In addition, a weak band due to **C$_{60}$$^{\bullet-}$** is observed at around 1020 nm.[5b] This result obviously provides a definitive evidence that an intramolecular electron transfer from **^{1}8T*** to **C$_{60}$** occurs after photoexcitation, and the long-distance charge separation species **8T$^{\bullet+}$-4T-C$_{60}$$^{\bullet-}$** exists.

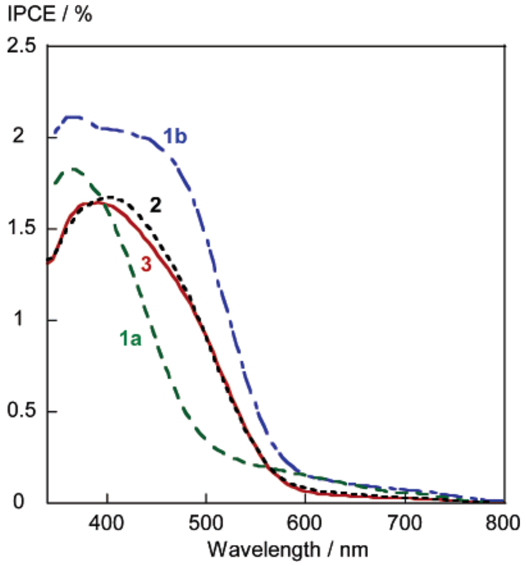


FIGURE 6. Photovoltaic performances of **4T-C$_{60}$** (**1a**), **8T-C$_{60}$** (**1b**), **8T-4T-C$_{60}$** (**2**), and **4T-8T-C$_{60}$** (**3**).

Photovoltaic Performances. To examine the potential of the triads **2** and **3** as photovoltaic materials, their sandwich devices with a configuration structure Al/organic film/Au were fabricated in the following manner: a semitransparent Al film (100 Å) was first vacuum deposited on a glass substrate, an organic thin film (2500−3000 Å) of the triad was spin-coated from a chloroform solution, and finally, a Au-film covered electrode (100 Å) was vacuum deposited. Under illumination from the Al side with a 24 mW/cm^2 tungsten−halogen lamp attached to a monochromator, the photocurrents generated were measured and converted into the incident photon to current conversion efficiencies (IPCE). The action spectra of the **8T-4T-C$_{60}$** and **4T-8T-C$_{60}$** devices together with those with **4T-C$_{60}$** (**1a**) and **8T-C$_{60}$** (**1b**)[7] are given in Figure 6. The wavelength-dependent IPCE spectra of the **4T-C$_{60}$** and **8T-C$_{60}$** devices are in rough accordance with the electronic absorption spectra of the respective oligothiophene chromophores. Surprisingly, the present devices using the **8T-4T-C$_{60}$** and **4T-8T-C$_{60}$** triads show action spectra quite similar to each other, which are related with the electronic absorption bands of both component oligothiophenes. When compared to the **4T-C$_{60}$** device, the **8T-4T-C$_{60}$** device produces a more effective photovoltaic response to visible light owing to the contribution of the additional octithiophene chromophore. It is thus evident that the attached octithiophene in the triad serves as an additional light harvester, and the subsequent long-distance charge separation contributes to the generation of photocurrent. However, when compared to the **8T-C$_{60}$** device, the **4T-8T-C$_{60}$** device demonstrated a rather poorer photovoltaic performance in the whole wavelength region. Considering that the **4T-8T-C$_{60}$** triad like the **8T-C$_{60}$** dyad undergoes effective photoinduced charge separation to **4T-8T$^{•+}$-C$_{60}$$^{•-}$**, one may speculate that the attached quaterthiophene in the triad rather interferes intermolecular charge transport from **4T-8T$^{•+}$-C$_{60}$$^{•-}$** to generate photocurrent.

Conclusions

To develop photoinduced long distance charge-separated systems, we have developed two types of the dual oligothiophene-fullerene triads, **8T-4T-C$_{60}$** and **4T-8T-C$_{60}$**. Although the three components are not interactive due to nonconjugation in the ground state, the photophysical properties of the triads in the excited state are markedly perturbed by intramolecular electron transfer and/or energy transfer among the components. In particular, it has been revealed that the **8T-4T-C$_{60}$** triad promotes a photoinduced electron transfer leading to the long-distance charge separation state **8T$^{•+}$-4T-C$_{60}$$^{•-}$**. Thanks to this effective charge separation as well as the additional light-harvesting and charge-transporting abilities of the attached octithiophene, the **8T-4T-C$_{60}$** device demonstrates much improved photovoltaic performance as compared to that of the **4T-C$_{60}$** device. On the other hand, the **4T-8T-C$_{60}$** triad does not lead to such long-distance charge separation by photoinduced electron transfer, this presumably being responsible for its poor photovoltaic performance.

Experimental Section

General. All reactions were carried out under nitrogen atmosphere. All chemicals are of reagent grade. Reaction solvents, THF, dichloromethane, and DMF, were dried over appropriate drying agents and used after fresh distillation. ^{1}H NMR spectra (400 MHz) and ^{13}C NMR spectra (90 MHz) were measured in deuteriochloroform using tetramethylsilane as internal standard. MS spectra were recorded on a MALDI-TOF spectrometer using a dithranol matrix.

Quaterthiophene-trimethylene-quaterthiophene (6). Into a solution of dihexylquaterthiophene **5** (1.1 g, 2.2 mmol) in dry THF (35 mL) cooled at −78 °C was slowly added a 1.58 N hexane solution of butyllithium (1.26 mL, 2.0 mmol) under nitrogen atmosphere, and the mixture was stirred at −30 °C for 30 min. After 1,3-dibromopropane (0.1 mL, 1.0 mmol) was added at −78 °C, the mixture was stirred at room temperature for 12 h, then treated with water (50 mL), and finally extracted with dichloromethane. The extract was washed with water and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by column chromatography (silica gel, 9:1 hexane−dichloromethane, R_f 0.24) to give an orange oil of **6** (207 mg, 20% yield): ^{1}H NMR δ 0.87−0.90 (m, 12H), 1.25−1.40 (m, 24H), 1.60−1.70 (m, 8H), 2.063 (quin, J = 7.6 Hz, 2H), 2.720 (t, J = 7.8 Hz, 4H), 2.777 (t, J = 7.6 Hz, 4H), 2.853 (t, J = 7.9 Hz, 4H), 6.652 (s, 2H), 6.935 (d, J = 5.1 Hz, 2H), 6.968 (d, J = 3.8 Hz, 2H), 7.012 (d, J = 3.7 Hz, 2H), 7.106 (d, J = 3.8 Hz, 2H), 7.110 (d, J = 3.7 Hz, 2H), 7.170 (d, J = 5.1 Hz, 2H); ^{13}C NMR δ 14.1, 22.6, 29.2, 29.3, 29.4, 30.6, 30.6, 31.7, 32.8, 123.6, 123.7, 125.9, 126.4, 127.7, 128.0, 130.0, 130.3, 135.1, 135.7, 136.2, 136.9, 139.6, 139.7, 143.0; MALDI-TOF MS *m/z* 1035.86 (M$^+$, calcd 1036.34). Anal. Calcd for $C_{59}H_{72}S_8$: C, 68.29; H, 6.99. Found: C, 68.22; H, 6.96.

Quaterthiophene-trimethylene-quaterthiophenecarbaldehyde (7). Into an ice-cooled solution of **6** (571 mg, 0.55 mmol) in 1,2-dichloroethane (20 mL) were successively added phosphorus oxychloride (0.5 mL, 5.36 mmol) and DMF (0.043 mL, 0.55 mmol) under nitrogen atmosphere, and the mixture was refluxed for 14 h. Then, 1 N aqueous sodium hydroxide solution (50 mL) was carefully added with ice-cooling, and the mixture was extracted with dichloromethane. The extract solution was washed with water and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by column chromatography (silica gel, dichloromethane, R_f 0.76) to give a red oil of **7** (257 mg, 44% yield): ^{1}H NMR δ 0.87−0.92 (m, 12H), 1.30−1.40 (m, 24H), 1.60−1.72 (m, 8H), 2.064 (quin, J = 7.8 Hz, 2H), 2.720 (t, J = 7.8 Hz, 4H), 2.775 (t, J = 8.0 Hz, 2H), 2.819 (t, J = 8.0 Hz, 2H), 2.853 (t, J = 8.0 Hz, 4H), 6.651 (s, 1H), 6.660 (s, 1H), 6.934 (d, J = 5.2 Hz, 1H), 6.966 (d, J = 4.0 Hz, 1H), 6.986 (d, J = 4.0 Hz, 1H), 7.010 (d, J = 4.0 Hz, 1H), 7.105 (d, J = 3.6 Hz, 1H), 7.108 (d, J = 4.0 Hz, 1H), 7.146 (d, J = 3.6 Hz, 1H), 7.154 (d, J = 3.6 Hz, 1H), 7.169 (d, J = 5.2 Hz, 1H), 7.198 (d, J = 4.0 Hz, 1H), 7.585 (s, 1H), 9.820 (s, 1H); ^{13}C NMR δ 14.1, 22.6, 22.6, 29.1, 29.2, 29.3, 29.4, 29.5, 30.2, 30.6, 30.6, 30.6, 31.6, 31.7, 32.9, 123.7, 123.8, 123.9, 124.5, 125.9, 126.0, 126.5, 127.8, 127.9, 128.0, 128.3, 130.1, 133.5, 135.2, 135.4, 136.3, 136.7, 136.9, 139.0, 139.3, 139.6, 139.8, 139.9, 140.2, 140.4, 141.0, 143.0, 143.4, 182.5; MALDI-TOF MS *m/z* 1064.08 (M$^+$, calcd 1064.33); IR (neat) 1676.3 cm^{-1} (C═O). Anal. Calcd for $C_{60}H_{72}OS_8$: C, 67.62; H, 6.81. Found: C, 67.61; H, 6.82.

Bromoquaterthiophene-trimethylene-quaterthiophenecarbaldehyde (8). Into an ice-cooled solution of **7** (251 mg, 0.236 mmol) in DMF (20 mL) was slowly added NBS (62 mg, 0.30 mmol), and the mixture was stirred at room temperature for 11 h. After saturated aqueous sodium hydrogen carbonate (30 mL) was added with ice-cooling, the mixture was filtered through a Celite pad and extracted with dichloromethane. The extract layer was washed with water and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by column chromatography (silica gel, dichloromethane) to give a red oil of **8** (220 mg, 82% yield): ^{1}H NMR δ 0.87−0.92 (m, 12H), 1.25−1.40 (m, 24H), 1.60−1.70 (m, 8H), 2.065 (quin, J = 7.6 Hz, 2H), 2.67−2.74 (m, 4H), 2.826 (t, J = 7.4 Hz, 4H), 2.858 (t, J = 7.8 Hz, 4H), 6.656 (s, 1H), 6.663 (s, 1H), 6.894 (s, 1H), 6.957 (d, J = 4.0 Hz, 1H), 6.969 (d, J = 4.0 Hz, 1H), 6.991 (d, J = 3.6 Hz, 1H), 7.095 (d, J = 3.6 Hz, 1H), 7.109 (d, J = 3.6 Hz, 1H), 7.154 (d, J = 3.8 Hz, 1H), 7.162 (d, J = 3.6 Hz, 1H), 7.207 (d, J = 3.8 Hz, 1H), 7.596 (s, 1H), 9.829 (s, 1H); ^{13}C NMR δ 14.07, 14.10, 22.57, 22.61, 29.08, 29.12, 29.2, 29.3, 29.4, 30.2, 30.5, 30.6, 31.6, 31.7, 32.8, 123.6, 123.9, 124.0, 124.5, 125.89, 125.94, 126.9, 127.78, 127.83, 127.9, 128.2, 131.8, 132.7, 133.4, 133.6, 135.4, 135.9, 136.0, 136.7, 137.4, 139.0, 139.2, 139.7, 139.9, 140.1, 140.3, 140.4, 141.0, 143.1, 143.3, 182.5; IR (neat) 1674.4 cm^{-1} (C═O); MALDI-TOF MS *m/z* 1144.01 (M$^+$, calcd 1142.25). Anal. Calcd for $C_{60}H_{71}BrOS_8$: C, 62.96; H, 6.25. Found: C, 62.94, H, 6.08.

Tributylstannyldihexylquaterthiophene (9). Into a solution of dihexylquaterthiophene **5** (1.98 g, 3.97 mmol) in THF (40 mL) cooled at −78 °C was slowly added a hexane solution of butyllithium (1.58 N, 2.5 mL, 4.0 mmol) under nitrogen atmosphere, and the mixture was stirred at −30 °C. After tributylstannyl chloride (1.2 mL, 4.4 mmol) was added, the mixture was stirred at room temperature for 12 h, quenched with water (20 mL), and extracted with hexane. The extract layer was washed with water and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by column chromatography (silica gel, dichloromethane) followed by preparative gel-permeation liquid chromatography (JAIGEL 1H/2H, chloroform) to give a yellow oil of **9** (1.64 g, 52% yield): ^{1}H NMR δ 0.888 (t, J = 6.1 Hz, 9H), 0.912 (t, J = 7.3 Hz, 12H), 1.11 (t, J = 8.3 Hz, 8H), 1.31−1.40 (m, 18H), 1.56−1.70 (m, 10H), 2.780 (t, J = 8.1 Hz, 2H), 2.800 (t, J = 8.1 Hz, 2H), 6.938 (d, J = 5.4 Hz, 1H), 6.960 (s, 1H), 7.017 (d, J = 3.9 Hz, 2H), 7.117 (d, J = 3.7 Hz, 1H), 7.121 (d, J = 3.6 Hz, 1H), 7.174 (d, J = 5.4 Hz, 1H); MALDI-TOF MS *m/z* 788.15 (M$^+$, calcd 787.88). Anal. Calcd for $C_{40}H_{60}S_4Sn$: C, 60.98; H, 7.68. Found: C, 60.98; H, 7.64.

Octithiophene-trimethylene-quaterthiophenecarbaldehyde (10). A mixture of **8** (213 mg, 0.186 mmol), tributylstannylquaterthiophene **9** (220 mg, 0.279 mmol), and tetrakis(triphenylphosphine)palladium (8 mg) in toluene (10 mL) was refluxed for 20 h under dark in a nitrogen atmosphere. The mixture was filtered through a Celite pad and concentrated in vacuo. The residue was purified by column chromatography (silica gel, dichloromethane) followed by preparative gel-permeation liquid chromatography (JAIGEL 1H/2H, chloroform) to give a red oil (231 mg, 79% yield): ^{1}H NMR δ 0.87−0.92 (m, 18H), 1.25−1.45 (m, 36H), 1.60−1.70 (m, 12H), 2.056 (quin, J = 7.5 Hz, 2H), 2.70−2.86 (m, 16H), 6.651 (s, 2H), 6.933 (d, J = 5.1 Hz, 1H), 6.964 (d, J = 4.3 Hz, 1H), 6.975 (d, J = 4.3 Hz, 1H), 6.988 (s, 2H), 7.00−7.03 (m, 3H), 7.09−7.13 (m, 4H), 7.134 (s, 1H), 7.139 (d, J = 3.9 Hz, 1H), 7.167 (d, J = 5.2 Hz, 1H), 7.186 (d, J = 3.9 Hz, 1H), 7.568 (s, 1H), 9.805 (s, 1H); ^{13}C NMR δ 14.1, 22.56, 22.60, 29.11, 29.19, 29.23, 29.4, 29.5, 29.6, 29.7, 30.2, 30.4, 30.52, 30.55, 30.59, 31.58, 31.64, 32.8, 123.7, 123.82, 123.84, 124.5, 125.88, 125.90, 126.2, 126.46, 126.53, 127.76, 127.81, 128.0, 128.2, 129.45, 129.50, 130.1, 130.3, 133.4, 134.77, 134.79, 134.81, 134.9, 135.4, 135.8, 136.1, 136.63, 136.66, 136.74, 136.9, 138.9, 139.2, 139.6, 139.8, 140.1, 140.3, 140.45, 140.48, 141.0, 143.0, 143.3, 182.4; MALDI-TOF MS *m/z* 1563.68 (M$^+$, calcd 1561.80); IR (neat) 1674.4 cm^{-1} (C═O). Anal. Calcd for $C_{88}H_{104}OS_{12}$: C, 67.64; H, 6.71. Found: C, 67.34; H, 6.78.

Octithiophene-trimethylene-quaterthiophene-fullerene (2). A mixture of **10** (154 mg, 0.099 mmol), fullerene (108 mg, 0.150 mmol), and *N*-methylglycine (26.7 mg, 0.300 mmol) in chlorobenzene (20 mL) was refluxed for 24 h under nitrogen atmosphere. After evaporation of the solvent, the residue was purified by column chromatography (silica gel) to elute first the fraction including unreacted fullerene with carbon disulfide and then the fraction including the desired product with chloroform. Preparative gel-permeation liquid chromatography of the latter fraction gave a brown oil of **2** (143 mg, 63% yield): ^{1}H NMR δ 0.822 (t, J = 6.8 Hz, 3H), 0.80−0.92 (m, 15H), 1.10−1.40 (m, 36H), 1.60−1.70 (m, 12H), 2.052 (quin, J = 7.2 Hz, 2H), 2.68−2.80 (m, 12H), 2.841 (t, J = 7.2 Hz, 4H), 2.925 (s, 3H), 4.202 (d, J = 10.0 Hz, 1H), 4.944 (d, J = 10.0 Hz, 1H), 5.138 (s, 1H), 6.640 (s, 2H), 6.939 (d, J = 5.1 Hz, 1H), 6.948 (d, J = 3.9 Hz, 1H), 6.966 (d, J = 3.6 Hz, 1H), 6.997 (s, 2H), 7.017 (d, J = 3.9 Hz, 1H), 7.023 (d, J = 3.9 Hz, 1H), 7.031 (d, J = 3.9 Hz, 1H), 7.034 (d, J = 3.9 Hz, 1H), 7.081 (d, J = 3.9 Hz, 1H), 7.083 (d, J = 3.9 Hz, 1H), 7.108 (d, J = 3.9 Hz, 1H), 7.112 (d, J = 3.6 Hz, 1H), 7.129 (d, J = 3.9 Hz, 2H), 7.174 (d, J = 5.6 Hz, 1H), 7.215 (s, 1H); MALDI-TOF MS *m/z* 2309.73 (M$^+$, calcd 2309.52). Anal. Calcd for $C_{150}H_{109}NS_{12}$: C, 77.98; H, 4.76; N, 0.61. Found: C, 78.16; H, 4.64; N, 0.62.

Tributylstannylquaterthiophene-trimethylene-quaterthiophene (11). Compound **11** was prepared in 15% yield from **6** in a similar manner as described for the synthesis of tributylstannyldihexylquaterthiophene **9**: orange oil, ^{1}H NMR δ 0.892 (t, J = 7.6 Hz, 12H), 0.911 (t, J = 7.6 Hz, 16H), 1.11 (t, J = 7.6 Hz, 12H), 1.31−1.40 (m, 36H), 1.54−1.70 (m, 12H), 2.06 (quin, J = 7.5 Hz, 2H), 2.719 (t, J = 7.8 Hz, 4H), 2.778 (t, J = 7.6 Hz, 2H), 2.797 (t, J = 7.8 Hz, 2H), 2.853 (t, J = 7.4 Hz, 4H), 6.653 (s, 2H), 6.937 (d, J = 5.4 Hz, 1H), 6.958 (s, 1H), 6.963 (d, J = 4.1 Hz, 1H), 6.969 (J = 3.9 Hz, 1H), 7.011 (d, J = 3.9 Hz, 1H), 7.013 (d, J = 3.6 Hz, 1H), 7.099 (d, J = 3.7 Hz, 1H), 7.108 (d, J = 3.6 Hz, 2H), 7.112 (d, J = 3.7 Hz, 1H), 7.173 (d, J = 5.4 Hz, 1H); MALDI-TOF MS *m/z* 1326.26 (M$^+$, calcd 1326.45). Anal. Calcd for $C_{71}H_{98}NS_8Sn$: C, 64.27; H, 7.44. Found: C, 64.37; H, 7.47.

Quaterthiophene-trimethylene-octithiophenecarbaldehyde (13). Compound **13** was prepared by the Negishi coupling between **11** and bromoquaterthiophenecarbaldehyde **12** as described above for the synthesis of **10**: yield 60%; deep red oil; ^{1}H NMR δ 0.88−0.92 (m, 18H), 1.30−1.40 (m, 36H), 1.60−1.75 (m, 12H), 2.065 (quin, J = 7.5 Hz, 2H), 2.70−2.87 (m, 16H), 6.657 (s, 2H), 6.936 (d, J = 5.2 Hz, 1H), 6.969 (d, J = 3.7 Hz, 1H), 6.976 (d, J = 3.9 Hz, 1H), 7.006 (s, 2H), 7.012 (d, J = 4.0 Hz, 1H), 7.039 (d, J = 3.9 Hz, 1H), 7.059 (d, J = 3.9 Hz, 1H), 7.108 (d, J = 4.0 Hz, 1H), 7.112 (d, J = 4.0 Hz, 1H), 7.117 (d, J = 4.0 Hz, 1H), 7.120 (d, J = 4.0 Hz, 1H), 7.170(d, J = 4.0 Hz, 1H), 7.172 (d, J = 5.4 Hz, 1H), 7.180 (d, J = 4.0 Hz, 1H), 7.213 (d, J = 3.6 Hz, 1H), 7.595 (s, 1H), 9.829 (s, 1H); ^{13}C NMR δ 14.1, 22.58, 22.60, 29.1, 29.20, 29.23, 29.3, 29.4, 29.5, 29.6, 30.2, 30.38, 30.41, 30.58, 30.62, 31.59, 31.65, 31.67, 32.9, 123.65, 123.74, 123.78, 123.9, 124.1, 124.6, 125.9, 126.3, 126.5, 126.6, 126.7, 127.8, 128.0, 128.3, 129.2, 129.7, 130.1, 133.7, 134.7, 135.1, 135.7, 135.9, 135.9, 136.1, 136.2, 137.0, 139.0, 139.6, 139.7, 139.8, 140.2, 140.4, 140.5, 140.8, 140.9, 143.1, 143.1, 182.5; MALDI-TOF MS *m/z* 1563.68 (M$^+$, calcd 1561.80); IR (neat) 1674.4 cm^{-1}. Anal. Calcd for $C_{88}H_{104}OS_{12}$: C, 67.64; H, 6.71. Found: C, 67.50; H, 6.68.

Quaterthiophene-trimethylene-octithiophene-fullerene (3). Compound **3** was prepared from **13** according to the Prato protocol as described above for the synthesis of **2**: yield 60%; brown oil; ^{1}H NMR δ 0.829 (t, J = 6.7 Hz, 3H), 0.87−0.91 (m, 15H), 1.23−1.43 (m, 36H), 1.60−1.70 (m, 12H), 2.063 (quin, J = 7.5 Hz, 2H), 2.70−2.80 (m, 12H), 2.853 (t, J = 7.5, 4H), 2.944 (s, 3H), 4.226 (d, J = 9.8 Hz, 1H), 4.968 (d, J = 9.8 Hz, 1H), 5.159 (s, 1H), 6.653 (s, 2H), 6.935 (d, J = 5.6 Hz, 1H), 6.968 (d, J = 3.9 Hz, 1H), 6.972 (d, J = 3.9 Hz, 1H), 6.992 (s, 2H), 7.012 (d, J = 3.9 Hz, 1H), 7.025 (d, J = 3.9 Hz, 1H), 7.031 (d, J = 3.9 Hz, 1H), 7.106 (d, J = 3.9 Hz, 3H), 7.111 (d, J = 3.9 Hz, 3H), 7.172 (d, J = 5.4 Hz, 1H), 7.232 (s, 1H); MALDI-TOF MS m/z 2307.94 (M^+, calcd 2309.52). Anal. Calcd for $C_{150}H_{109}NS_{12}$: C, 77.98; H, 4.76; N, 0.61. Found: C, 77.77; H, 4.75; N, 0.75.

Quaterthiophene-trimethylene-octithiophene (4). Into an ice-cooled solution of **6** (307 mg, 0.296 mmol) in DMF (30 mL) was slowly added a solution of NBS (53.4 mg, 0.300 mmol) in DMF (20 mL), and the mixture was stirred at room temperature for 12 h. Aqueous saturated sodium hydrogen carbonate solution (30 mL) was slowly added with ice-cooling. The mixture was filtered through a Celite pad and then extracted with chloroform. The chloroform solution was washed with water and dried ($MgSO_4$). After evaporation of the solvent, the residue was chromatographed through silica gel with dichloromethane to give an orange oil (323 mg), which was mainly composed of a mixture of monobromoquaterthiophene-trimethylene-quaterthiophene **14**, the dibromo derivative, and the starting material **6**. This mixture was then refluxed with **9** (394 mg, 0.500 mmol) and tetrakis(triphenylphosphine)palladium (35 mg) in toluene (10 mL) under dark in an argon atmosphere. The mixture was filtered through a Celite pad and concentrated in vacuo. The residue was purified by column chromatography (silica gel, dichloromethane) and then preparative gel-permeation liquid chromatography (JAIGEL-1H/2H, chloroform) to give a brown oil of **4** (148 mg, 31% two-step yield): ^{1}H NMR δ 0.86−0.93 (m, 18H), 1.25−1.45 (m, 36H), 1.60−1.72 (m, 12H), 2.064 (quin, J = 7.4 Hz, 2H), 2.70−2.80 (m, 12H), 2.853 (t, J = 7.3 Hz, 4H), 6.655 (s, 2H), 6.936 (d, J = 5.4 Hz, 1H), 6.942 (d, J = 5.4 Hz, 1H), 6.965 (d, J = 4.0 Hz, 1H), 6.971 (d, J = 4.0 Hz, 1H), 6.997 (s, 2H), 7.009 (d, J = 4.0 Hz, 1H), 7.021 (d, J = 4.0 Hz, 1H), 7.032 (d, J = 4.0 Hz, 1H), 7.037 (d, J = 4.0 Hz, 1H), 7.103 (d, J = 4.0 Hz, 1H), 7.107 (d, J = 4.0 Hz, 1H), 7.109 (d, J = 4.0 Hz, 1H), 7.115 (d, J = 4.0 Hz, 1H), 7.126 (d, J = 4.0 Hz, 2), 7.165 (d, J = 5.4 Hz, 1H), 7.174 (d, J = 5.4 Hz, 1H); ^{13}C NMR δ 14.10, 22.6, 29.21, 29.24, 29.27, 29.45, 29.53, 29.65, 29.67, 30.4, 30.59, 30.63, 31.66, 32.9, 123.66, 123.75, 123.79, 123.9, 125.9, 126.3, 126.5, 126.5, 126.6, 127.8, 127.96, 127.99, 129.45, 129.53, 130.02, 130.06, 130.08, 130.28, 130.34, 134.79, 134.86, 134.94, 135.1, 135.4, 135.7, 135.9, 136.1, 136.2, 136.7, 136.8, 136.90, 136.94, 139.6, 139.7, 139.8, 139.9, 140.50, 140.54, 143.07, 143.12; MALDI-TOF MS m/z 1535.43 (M^+, calcd 1534.48). Anal. Calcd for $C_{87}H_{104}S_{12}$: C, 68.09; H, 6.83. Found: C, 68.06; H, 6.87.

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Supporting Information Available: Emission spectra of **2**−**5** and **15** measured in toluene. This material is available free of charge via the Internet at http://pubs.acs.org.

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