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Synthesis and Photophysical Properties of Ferrocene−Oligothiophene−Fullerene Triads

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Received May 22, 2004

To promote photoinduced charge separation previously observed for the oligothiophene−fullerene dyads (**nT-C60**), we have designed an additional attachment with a strongly electron-donating ferrocene at the unsubstituted terminal site of the oligothiophene and synthesized two types of the ferrocene−oligothiophene−fullerene triads, **Fc-nT-C60** directly linking the ferrocene to the oligothiophene and **Fc-tm-nT-C60** inserting a trimethylene spacer between the ferrocene and the oligothiophene. For the central oligothiophene of the triads, a homologous series of quaterthiophene (**4T**), octithiophene (**8T**), and duodecithiophene (**12T**) are systematically examined. The cyclic voltammograms and electronic absorption spectra of **Fc-nT-C60** indicate conjugation between the ferrocene and oligothiophene components. The emission spectra of **Fc-nT-C60** measured in toluene demonstrate that the fluorescence of the oligothiophene is markedly quenched, as compared to that observed for the dyads **nT-C60**. This quenching is explained in terms of the involvement of intramolecular electron transfer in the photophysical decay process. The additionally conjugated ferrocene evidently contributes to the stabilization of charge separation states, thus promoting intramolecular electron transfer. This is corroborated by the observation that the emission spectra of the nonconjugated triads **Fc-tm-nT-C60** are essentially similar to the corresponding dyads **nT-C60**.

Introduction

Charge separation originating from photoinduced electron-transfer is a key function for the construction of optoelectronic devices or artificial photosynthetic systems.[1,2] In this context, molecular systems covalently bonded between electron donors and electron acceptors have been actively investigated, where intramolecular through-bond charge separation readily takes place via the excited singlet states of either the sensitizing electron-donor chromophores or electron-acceptor chromophores.[3] In general, however, such charge separation is followed by fast intramolecular charge recombination, so it is difficult to keep the generated electron or hole for enough time to participate in redox reaction systems.[4] Fullerenes are electron acceptors of choice to solve this problem, because they have small reorganization energies in electron-transfer reactions and, therefore, force the charge separation systems into the inverted region of the Marcus

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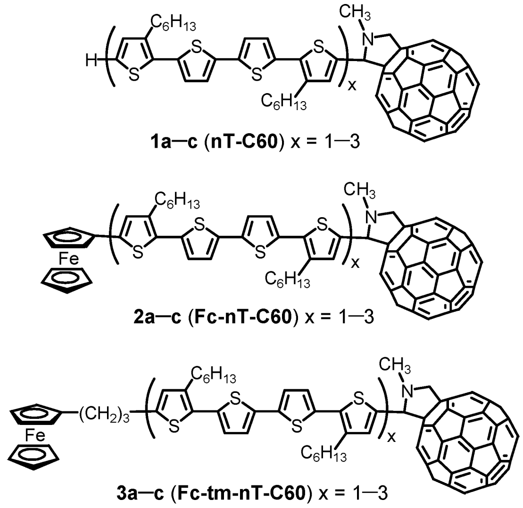
10.1021/jo049137o CCC: $27.50

parabola,[5] thus leading to slow charge recombination.[6] A variety of donors have been thus attached to fullerenes.[7] Among them, we studied the [60]fullerene-oligothiophene dyads **1a**−**c** (x = 1−3, abbreviated as **nT-C60**) (Chart 1), in which the fullerene is covalently bonded to a terminal position of oligothiophenes.[8] The photophysical study of the dyads **1a**−**c** revealed that, although energy transfer from the excited oligothiophene chromophore to the fullerene occurred in nonpolar toluene,[8] highly efficient photoinduced electron transfer preferably occurred in polar solvents[9] and in the solid state.[10] As the ensuing step of our efforts directed toward the development of oligothiophene-based optoelectronic materials, we have focused on the ferrocene−oligothiophene−fullerene triads **2** (abbreviated as **Fc-nT-C60**). Direct attachment of a strongly electron-donating ferrocene at the unsubstituted terminal site of the oligothiophene might promote photoinduced electron-transfer due to the stabilization of the resulting charge-separated states. For comparison, we have also studied another type of triads **3** (abbreviated as **Fc-tm-nT-C60**) inserting a trimethylene spacer between the ferrocene and the oligothiophene moiety, which interferes with direct conjugation between the two chromophores. Here we would like to report the synthesis and photophysical properties of these two types of triads **2a**−**c** and **3a**−**c**.

Results and Discussion

Synthesis. For the basic skeletons of the **Fc-nT-C60** and the **Fc-tm-nT-C60** triads, three oligothiophenes, quaterthiophene (**6a**, abbreviated as **4T**), octithiophene (**6b**, **8T**), and duodecithiophene (**6c**, **12T**), were examined. According to the route shown in Scheme 1,[8,11] 3,3‴-dihexyl-2,2′:5′,2″:5″,2‴-quaterthiophene (**4T**) was prepared in 95% yield by a nickel-catalyzed coupling reaction between 5,5′-dibromo-2,2′-bithiophene (**4**)[12] and 2 equiv of Grignard reagent (**5b**) in-situ derived from 3-hexyl-2-thienyl bromide (**5a**)[13] in ether−benzene under reflux. Then, **4T** was lithiated with 1 equiv of butyllithium in THF, and the resulting lithiated species was subjected to oxidative coupling with copper(II) chloride at room temperature to give a mixture of tetrahexyloctithiophene (**6b**, **8T**) (40% yield) and hexahexylduodecithiophene (**6c**, **12T**) (10% yield), which were smoothly separated by column chromatography.

CHART 1



1a—**c** (**nT-C60**) x = 1—3

2a—**c** (**Fc-nT-C60**) x = 1—3

3a—**c** (**Fc-tm-nT-C60**) x = 1—3

Oligothiophenes **6a**−**c** were subjected to Vilsmeier reactions at one of the terminal positions with DMF and phosphorus oxychloride in 1,2-dichloroethane at 40 °C to give the corresponding formyl derivatives **7a**−**c** in 40−53% yields, and subsequent bromination at the other terminal position with NBS in CS_2−DMF at room temperature led to the formation of the bromo-oligothiophene-carbaldehydes **8a**−**c** in 80−90% yields (Scheme 2). The Negishi coupling of **8a**−**c** with ferrocenylzinc chloride (**9**) in the presence of catalytic tetrakis(triphenylphosphine)palladium in THF[14] provided the ferrocenyl-oligothiophene-carbaldehydes **10a**−**c** in 40−60% yields. Finally, treatment of **10a**−**c** with fullerene and *N*-methylglycine (Prato method)[15] in refluxing toluene afforded the ferrocene-oligothiophene-fullerene triads **2a**−**c** in 40−50% yields.

The syntheses of another type of triads **3a**−**c** (**Fc-tm-nT-C60**) are not so straightforward. The key to their syntheses is how to approach the ferrocenylpropyl-oligothiophene-carbaldehydes **15a**−**c**. The initially attempted approach shown in Scheme 3 was successful only for the synthesis of the quaterthiophene derivative **15a**. Thus, ferrocene (**11**) was lithiated with *t*-butyllithium in 1:1 hexane−THF at 0 °C and then reacted with 1-bromo-3-chloropropane at room temperature to give 3-chloro-

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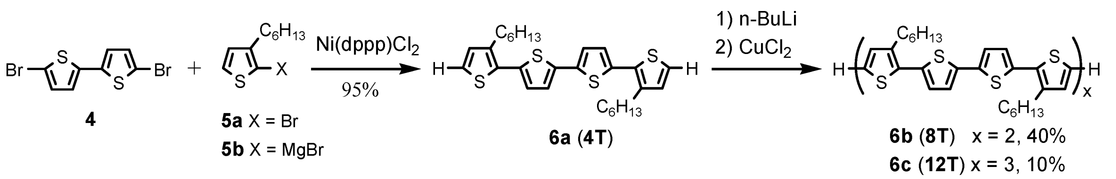
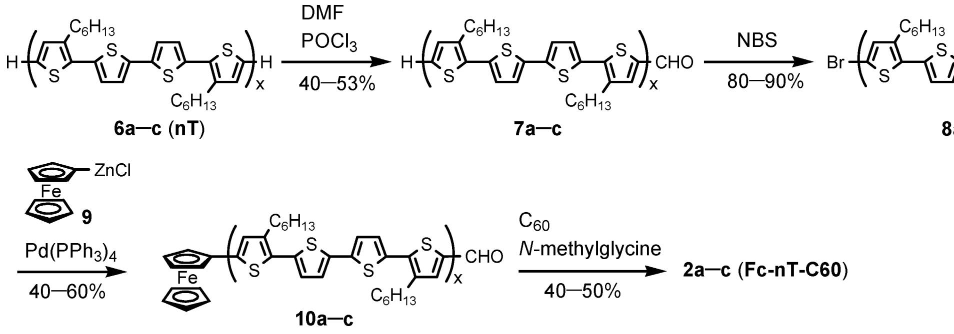
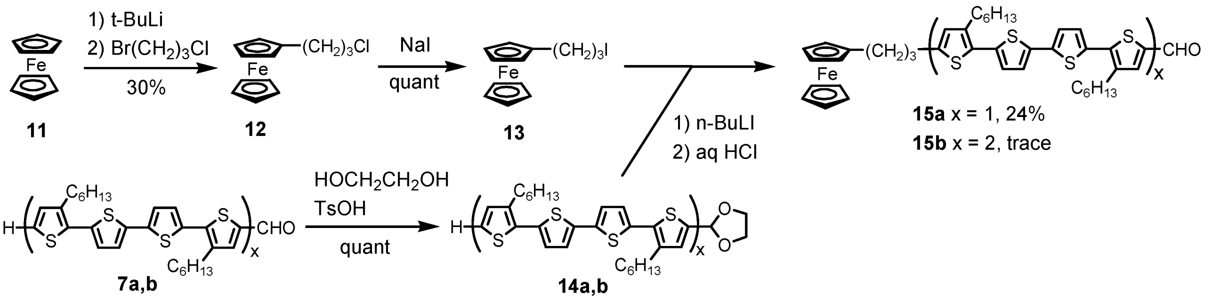
SCHEME 1. Synthesis of Oligothiophenes nT



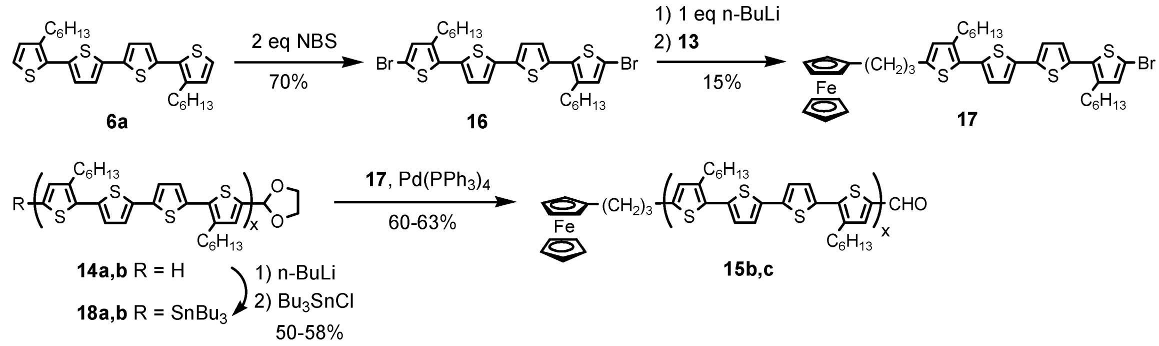
SCHEME 2. Synthesis of Triads Fc-nT-C60



SCHEME 3. Synthesis of Ferrocenylpropyl−Oligothiophene−Carbaldehydes 15a,b



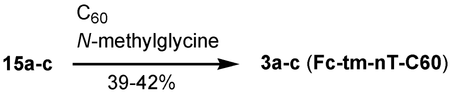
SCHEME 4. Synthesis of Ferrocenylpropyl−Oligothiophene−Carbaldehydes 15b,c



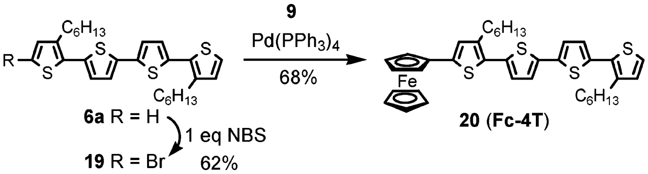
propylferrocene (**12**) in 30% yield. Haloexchange of **12** with sodium iodide in refluxing butanone afforded 3-iodopropylferrocene (**13**) quantitatively. After the quaterthiophene-carbaldehyde **7a** was quantitatively protected to the acetal **14a** by treatment with ethylene glycol and *p*-toluenesulfonic acid in refluxing benzene, the unsubstituted terminal of **14a** was lithiated with butyllithium in THF at 0 °C followed by treatment with **13** at room temperature to produce the desired **15a** in 24% yield. It was, however, found that this approach could not be applied to the higher oligothiophenes: a similar coupling using the octithiophene **14b** gave only a trace of **15b**.

An alternative approach to **15b** and **15c** was devised as shown in Scheme 4. First, quaterthiophene **6a** (**4T**) was brominated with 2 equiv of NBS in CS_2−DMF at room temperature to the dibromo derivative **16** (70% yield), which was subjected to a metal−halogen exchange with 1 equiv of butyllithium in THF at −70 °C, followed by treatment with 3-iodopropylferrocene (**13**) at room temperature, to give the bromo-ferrocenylpropyl-quaterthiophene **17** in 15% yield. The acetals **14a** and **14b** were converted to the respective tributyltin derivatives **18a** and **18b** (50−58% yield) by treatment with tributyltin chloride in THF at room temperature after lithiation with butyllithium. The Stille coupling between **17** and **18a**,**b** in the presence of catalytic tetrakis(triphenylphosphine)-palladium in refluxing toluene gave the desired ferrocenylpropyl-oligothiophene-carbaldehydes **15b** and **15c** in 60−63% yield. Finally, the Prato reactions of **15a**−**c** afforded the triads **3a**−**c** (**Fc-tm-nT-C60**) in 39−42% yields (Scheme 5).

SCHEME 5. Synthesis of Triads Fc-tm-nT-C60



SCHEME 6. Synthesis of Dyad Fc-4T



To examine the physical properties of the present triads **2a**−**c** and **3a**−**c**, the oligothiophene-fullerene dyads **1a**−**c** (**nT-C60**), the ferrocene-quaterthiophene dyad **20** (**Fc-4T**), and the ferrocenylpropyl-oligothiophene dyads **21a**−**c** (**Fc-tm-nT**) were used as reference compounds. The dyads **1a**−**c** were prepared in 46−60% yield by utilizing the Prato reactions of the oligothiophenecarbaldehydes **7a**−**c**.[8] **Fc-4T** was synthesized in 68% yield by coupling the ferrocenylzinc chloride (**9**) with the bromo-quaterthiophene **19** prepared by monobromination of **4T** (Scheme 6).

The synthesis of **Fc-tm-nT** was attempted by lithiation of oligothiophenes with butyllithium, followed by coupling with 3-iodopropylferrocene (**13**) (Scheme 7). This was successful with quaterthiophene and octithiophene, but the yields tended to decrease with long oligothiophenes: 30% for **Fc-tm-4T** and 10% for **Fc-tm-8T**. Instead, the synthesis of the duodecithiophene derivative **21c** was accomplished in 80% yield by the Stille coupling between the bromo-ferrocenylpropyl-quaterthiophene **17** and tributylstannyl-octithiophene **22**, derived from octithiophene **6b**.

Cyclic Voltammograms. The **Fc-nT-C60** and **Fc-tm-nT-C60** triads are characterized by amphoteric properties due to the presence of both donor and acceptor components. As demonstrated in Figure 1, the cyclic voltammograms of the **Fc-nT-C60** triads include multioxidation waves due to the ferrocene and oligothiophene components in the positive potential region and one reduction wave due to the fullerene component in the negative potential. The half-wave redox potentials of **Fc-nT-C60** are summarized in Table 1, together with those of **Fc-tm-nT-C60** and the reference compounds. Considering the half-wave oxidation potential (+0.45 V vs Ag/AgCl) of ferrocene (**11**) itself, the lowest oxidation wave (+0.48−0.50 V) of the **Fc-nT-C60** triads can be assigned to be due to the ferrocene component. The following oxidation waves are attributable to the oligothiophene component. For **Fc-4T-C60**, only the first one-electron oxidation wave due to the quaterthiophene is observed at +0.97 V. For the higher homologues **Fc-8T-C60** and **Fc-12T-C60**, the multioxidation waves of the long oligothiophenes are observed as a result of stabilization of the cationic states due to the extended π-conjugation.

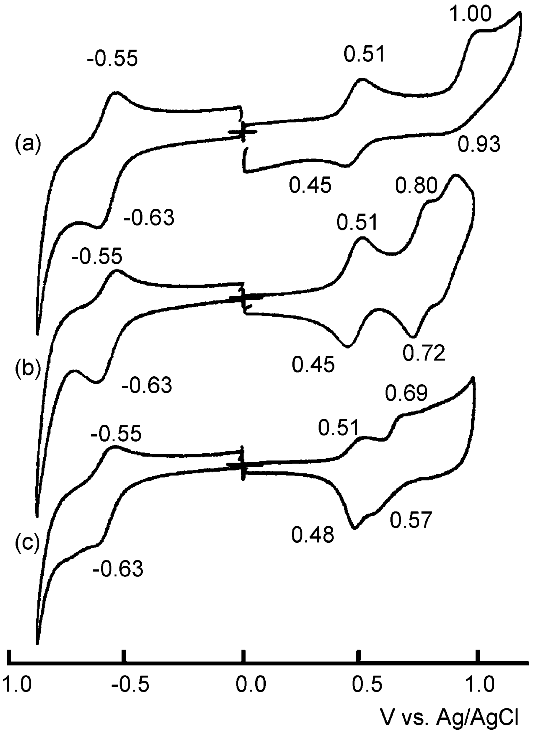


FIGURE 1. Cyclic voltammograms of (a) **Fc-4T-C60**, (b) **Fc-8T-C60**, and (c) **Fc-12T-C60** in benzonitrile.

In these triads, it is evident that the attached ferrocene component has a lower oxidation potential than the oligothiophene component. From this result, it is expected that an electron transfer from the ferrocene component to the photoexcited oligothiophene may occur. On the other hand, the half-wave reduction potentials due to the fullerene component of **Fc-nT-C60** are quite identical to those of the dyads **nT-C60** and *N*-methyl-3,4-fulleropyrrolidine (**23**) (Chart 2). This reflects nonconjugated linkage between the oligothiophene and fullerene components, and the remote attachment of the ferrocene has no influence on the reduction of the fullerene.

Apparently, the **Fc-tm-nT-C60** triads exhibit similar cyclic voltammograms. However, on careful comparison, there are some differences in half-wave oxidation potentials between **Fc-tm-nT-C60** and **Fc-nT-C60**, although

SCHEME 7. Synthesis of Dyads Fc-tm-nT

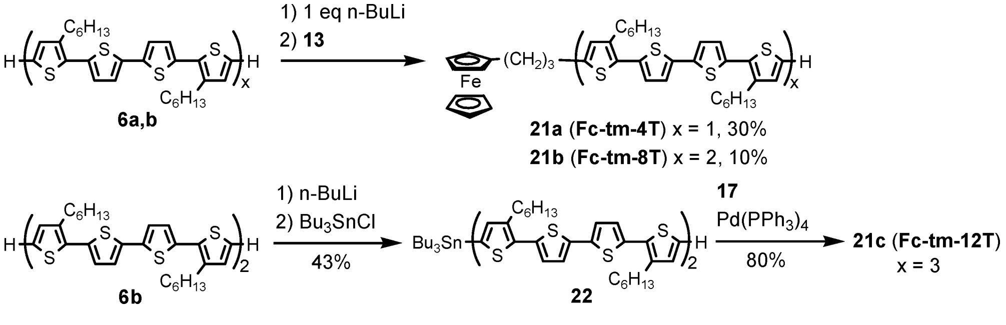
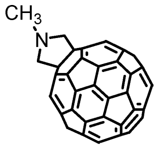


TABLE 1. Half-Wave Redox Potentials of the Ferrocene−Oligothiophene−Fullerene Triads and Related Compounds[a]

compd	Fc	nT	C60
Fc-4T-C60	+0.48	+0.97	−0.59
Fc-8T-C60	+0.48	+0.76	−0.59
Fc-12T-C60	+0.50	+0.63	−0.59
Fc-tm-4T-C60	+0.40	+0.87	−0.59
Fc-tm-8T-C60	+0.40	+0.76	−0.59
Fc-tm-12T-C60	+0.40	+0.64	−0.59
4T-C60		+0.92	−0.59
8T-C60		+0.69	−0.59
12T-C60		+0.59	−0.59
Fc-4T	+0.48	+0.97	
Fc-tm-4T	+0.40	+0.86	
Fc-tm-8T	+0.40	+0.76	
Fc-tm-12T	+0.40	+0.64	
ferrocene (**11**)	+0.45		
13	+0.42		
23			−0.59

[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.

CHART 2



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the half-wave reduction potentials of the fullerene are the same (−0.59 V). The oxidation potentials due to the ferrocene component of the **Fc-tm-nT-C60** triads are all identical (+0.40) in the series and appreciably lower than the potentials (+0.48−0.50 V) of the **Fc-nT-C60** series. In addition, the oxidation potentials due to the quaterthiophene between **Fc-tm-4T-C60** and **Fc-4T-C60** are different, although this is not the case with the higher oligothiophene systems. One should notice that the oxidation potentials due to the ferrocene of the **Fc-tm-nT-C60** triads are identical to those of the **Fc-tm-nT** dyads (**21a**−**c**) and nearly the same as that (+0.42 V) of 3-iodopropylferrocene (**13**). From these results, it is reasonable to consider that the oxidation potentials of the directly linked **Fc-nT-C60** triads are rather affected by a definitive electronic interaction between the ferrocene and oligothiophene moieties. This leads to different photophysical behaviors for these two types of triads, as described later.

Electronic Absorption Spectra. Figure 2 demonstrates the electronic absorption spectra of the **Fc-nT-C60** triads measured in toluene. Roughly speaking, these spectra consist of superposition of the electronic transitions of three component chromophores. Oligothiophenes (**6**) show a strong $\pi-\pi^*$ absorption band in the ultraviolet/visible region, which is red-shifted and intensified with chain extension: **4T**, λ_{max} 379 nm (log ϵ 4.64); **8T**, 439 (4.77); **12T**, 457 (4.91). Ferrocene (**11**) has an electronic transition at 444 nm, but its intensity (log ϵ 1.97) is very weak as compared to those of oligothiophenes. N-Methyl-3,4-fulleropyrrolidine (**23**) has 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.[16] Thus, it follows that the absorption peaks observed for **Fc-nT-C60** mainly originate from the transition of the oligothiophene chromophore and the two transitions of the fullerene chromophore, and the absorption band due to the ferrocene and the second absorption band of the fullerene are concealed by the strong absorption band of the oligothiophene. Table 2 summarizes the electronic absorption and fluorescence data of the two types of triads and the reference compounds. The structural modification from **nT-C60** to **Fc-nT-C60** results in red-shifts for the absorption bands of oligothiophenes; in particular, it is eminent for the quaterthiophene series. On the other hand, the **Fc-tm-nT-C60** triads show no such shifts. This evidently corroborates the presence of an electronic interaction, presumably conjugation between the ferrocene and the oligothiophene, as estimated above on the basis of the voltammetric study.

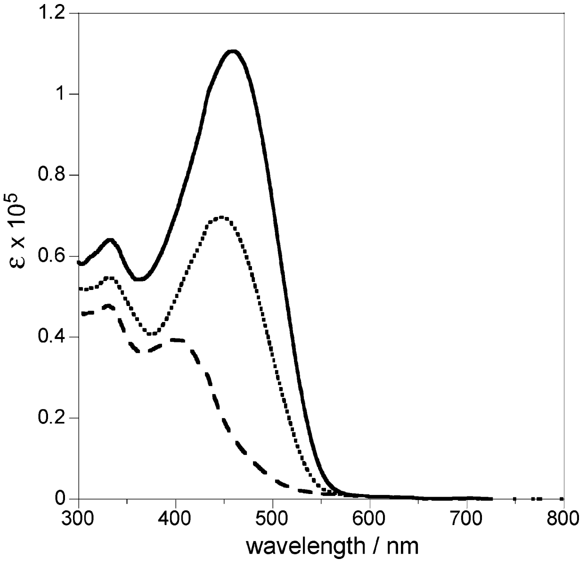

FIGURE 2. Electronic absorption spectra of **Fc-4T-C60** (dashed line), **Fc-8T-C60** (dotted line), and **Fc-12T-C60** (solid line) in toluene.

Emission Spectra. We previously discovered that the **nT-C60** dyads efficiently undergo photoinduced intramolecular energy or electron transfer from the oligothiophene component to the fullerene.[8,9] The decay process of **nT-C60** is markedly solvent-dependent: energy transfer occurs in nonpolar toluene, whereas electron transfer is predominant in polar benzonitrile or THF. It is considered that high solvation by polar solvents stabilizes charge separation states much more, and as a result, electron transfer takes precedence over energy transfer. Figure 3 shows the emission spectra of **Fc-4T-C60**, **4T-C60**, and **Fc-4T** measured with excitation in the region of the quaterthiophene chromophore in toluene. For ready comparison, the emission spectrum of **4T** is also included on a low scale of 2 orders of magnitude. In contrast to strong emission of **4T**, these linkage compounds **4T-C60** and **Fc-4T-C60** demonstrate little or no emission from the oligothiophene moiety. In **4T-C60**, an alternative emission is observed around 700

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[16] Obara, Y.; Takimiya, K.; Aso, Y.; Otsubo, T. *Tetrahedron Lett.* **2001**, *42*, 6877−6881.

TABLE 2. Spectroscopic Data of the Ferrocene−Oligothiophene−Fullerene Triads and Related Compounds

		abs max/nm (log ϵ)		emission max/nm[a]	
compd	solvent	**nT**	**C60**	**nT***	**C60***
Fc-4T-C60	toluene	402 (4.59)	335 (4.68), 703 (2.41)	nd	nd
	benzonitrile	408 (4.62)	327 (4.69), 705 (2.43)		
Fc-8T-C60	toluene	449 (4.84)	331 (4.74), 706 (2.48)	549, 715	718
	benzonitrile	454 (4.84)	327 (4.89), 704 (2.56)		
Fc-12T-C60	toluene	459 (5.04)	331 (4.81), 702 (2.55)	566, 713	714
	benzonitrile	465 (5.02)	329 (4.78), 702 (2.53)		
Fc-tm-4T-C60	toluene	379 (4.67)	335 (4.63), 708 (2.53)	460, 705	716
	benzonitrile	395 (4.61)	327 (4.63), 701 (2.53)		
Fc-tm-8T-C60	toluene	436 (4.83)	335 (4.75), 706 (2.54)	544, 714	715
	benzonitrile	452 (4.89)	327 (4.70), 708 (2.50)		
Fc-tm-12T-C60	toluene	459 (5.03)	334 (4.81), 705 (2.46)	566, 715	714
	benzonitrile	463 (4.99)	327 (4.75), 708 (2.56)		
4T-C60	toluene	379 (4.64)	335 (4.69), 708 (2.59)	447, 698	714
	benzonitrile	384 (4.59)	327 (4.61), 703 (2.47)		
8T-C60	toluene	436 (4.83)	335 (4.75), 708 (2.54)	546, 547 sh, 713	715
	benzonitrile	450 (4.81)	330 (4.81), 702 (2.56)		
12T-C60	toluene	456 (5.03)	334 (4.81), 706 (2.57)	567, 712	714
	benzonitrile	463 (4.98)	332 (4.74), 703 (2.43)		
Fc-tm-4T	toluene	378 (4.49)		462, 490, 524 sh	
	benzonitrile	391 (4.47)			
Fc-tm-8T	toluene	442 (4.78)		546, 588, 640 sh	
	benzonitrile	448 (4.78)			
Fc-tm-12T	toluene	459 (5.03)		567, 615, 655 sh	
	benzonitrile	462 (4.96)			

[a] Excited at 379 nm for **4T***, 437 nm for **8T***, 457 nm for **12T***, and 650 nm for **C60***.

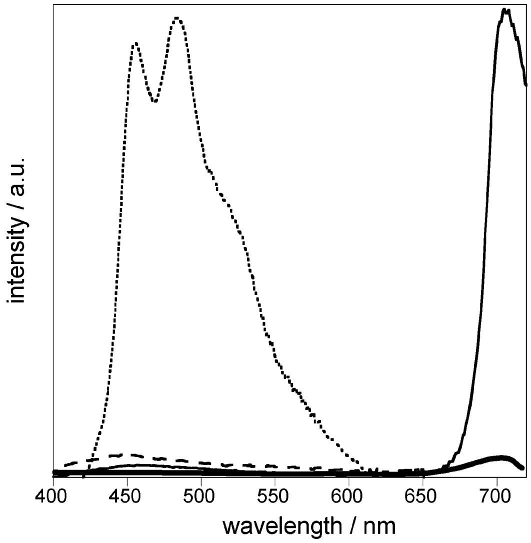

FIGURE 3. Emission spectra of **4T** (× 0.1, dotted line), **4T-C60** (solid line), **Fc-4T-C60** (bold solid line), and **Fc-4T** (dashed line) with excitation at 379 nm in toluene, where the absorbances of all samples were kept constant.

nm, being assignable to that from the fullerene chromophore. This evidently indicates the involvement of intramolecular energy transfer in the quenching process. However, the spectrum of **Fc-4T-C60** gives little emission not only from the quaterthiophene but also from the fullerene. This quenching is interpreted in terms of the precedence of intramolecular electron transfer even in nonpolar toluene.

The intramolecular electron transfer of **Fc-4T-C60** has two possibilities. One is that the HOMO electron of the ferrocene moiety transfers to the half-filled HOMO orbital of the excited quaterthiophene. This is evidenced by the observation that the dyad **Fc-4T** also shows a weak emission from the quaterthiophene moiety as compared to quaterthiophene **4T** itself. The other is that the excited electron of the quaterthiophene transfers to the LUMO orbital of the fullerene. Such electron transfer from the quaterthiophene to the fullerene was also observed by the experiment that, when the fullerene chromophore is excited, the emission from the fullerene of **Fc-4T-C60** is markedly depressed, as compared to that of **4T-C60** (Figure 4). Presumably, the interaction between the ferrocene and the quaterthiophene of the **Fc-4T-C60** triad contributes to the stabilization of the charge

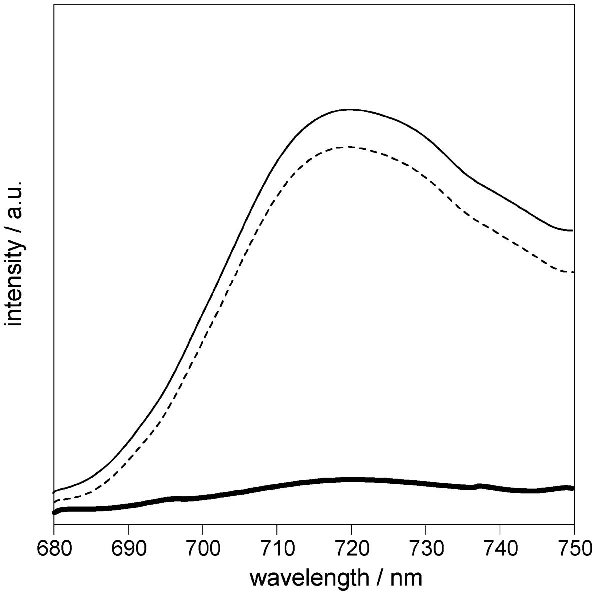

FIGURE 4. Emission spectra of **4T-C60** (dashed line), **Fc-4T-C60** (bold solid line), and *N*-methyl-3,4-fulleropyrrolidine (solid line) with excitation at 650 nm in toluene, where the absorbances of all samples were kept constant.

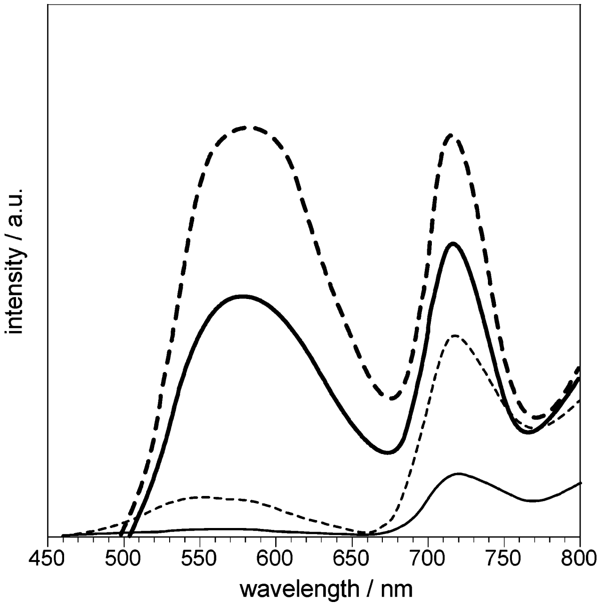

FIGURE 5. Emission spectra of **8T-C60** (dashed line), **Fc-8T-C60** (solid line), **12T-C60** (bold dashed line), and **Fc-12T-C60** (bold solid line) with excitation at 437 nm for the octithiophene chromophore and at 457 nm for the duodecithiophene chromophore in toluene, where the absorbances of all samples were kept constant.

separation state, and as a result, electron transfer takes precedence over energy transfer.

The spectra of the dyads **8T-C60** and **12T-C60** are characterized by dual fluorescence not only from the fullerene chromophore but also from the oligothiophene chromophore (Figure 5). The π-centers of these long oligothiophenes become more distant from the fullerene, so that energy transfer is retarded and competes with direct fluorescence. The emission spectra of the triads **Fc-8T-C60** and **Fc-12T-C60** also show dual fluorescence, but the intensities of both bands are smaller than those of the corresponding dyads. It is reasonable to consider that intramolecular electron transfer also participates in the decay process of these long oligothiophene-containing triads.

The photophysical decay process of the **Fc-tm-nT-C60** system is quite different from those of the **Fc-nT-C60** system. Their fluorescence spectra measured in toluene, with excitation of either the oligothiophene or the fullerene chromophore, are essentially similar to the corresponding dyads **nT-C60**. It seems that the nonconjugated ferrocene component has apparently no influence on the quenching process. However, it is worth noting that the reference dyad **Fc-tm-4T** shows very weak emission with an intensity of 1/36 compared to quaterthiophene **4T**. This means that, even though the two chromophores are separated by the trimethylene chain, electron transfer from the ferrocene to the excited oligothiophene can occur. In the **Fc-tm-nT-C60** system, such electron transfer is presumably not large enough to overwhelm the dominant energy transfer in the decay process.

Both triads **Fc-nT-C60** and **Fc-tm-nT-C60** exhibited inappreciable emission either from the oligothiophene or from the fullerene, when measured in benzonitrile. Evidently, intramolecular electron transfer almost entirely dominates the decay process as a result of the stabilization of the charge separation states in the polar solvent. Since even the dyads **nT-C60** also favor intramolecular electron transfer in benzonitrile, the effect of the additional ferrocene of these triads on the photophysical properties cannot be elucidated only by the emission study.

Conclusion

To promote photoinduced electron transfer previously observed for the oligothiophene−fullerene dyads (**nT-C60**), we have developed two types of the ferrocene−oligothiophene−fullerene triads, **Fc-nT-C60** and **Fc-tm-nT-C60**, designed by additional attachment of a strongly electron-donating ferrocene to the dyads. The two types of triads demonstrate different photophysical properties. The directly linked **Fc-nT-C60** triads are characterized by conjugation between the ferrocene and oligothiophene components, as evidenced by an examination of their cyclic voltammograms and electronic absorption spectra. This conjugated interaction serves to promote electron transfer either from the excited oligothiophene to the fullerene or from the oligothiophene to the excited fullerene. In particular, in the emission spectrum of **Fc-4T-C60** in toluene, the quenching process is governed by electron transfer, in contrast to energy transfer for **4T-C60**. On the other hand, the photophysical properties of the trimethylene-inserted **Fc-tm-nT-C60** triads are not so largely perturbed by the attached ferrocene as those of **Fc-nT-C60**. When measured in toluene, their emission spectra, like those of **nT-C60**, are still dominated by photoinduced energy transfer in the decay process. However, the effect of the additional ferrocene of the two types of triads on the stabilization and lifetimes of charge separation states still remain unclear. Further investigation on these subjects by measuring transient absorption spectra is under way and will be reported elsewhere.

Acknowledgment. This research was partly supported by Grants-in-Aid of Scientific Research (Category A, No. 1330405, and Priority Areas of Molecular Conductors, No. 15073218) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: All experimental details for the syntheses of the triads **Fc-nT-C60** and **Fc-tm-nT-C60**, as well as reference compounds, and the electronic absorption and emission spectra of the triads **Fc-tm-nT-C60** and **Fc-tm-4T**. This material is available free of charge via the Internet at http://pubs.acs.org.

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