Intramolecular Energy Transfer of [60]Fullerene-linked Oligothiophenes

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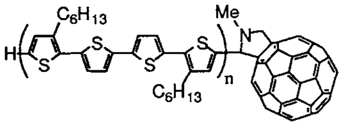
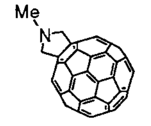
[60]Fullerene-linked quarter-, octi-, and duodeci-thiophenes have been synthesized, and their emission spectra demonstrate efficient intramolecular energy transfer from the thiophene moiety to the fullerene, whose rate constant largely depends on the chain length of the oligothiophene moiety.

Recently, oligothiophenes have attracted much attention not only as useful alternatives to conducting polymer systems but also as potential advanced materials, such as nonlinear optics, electroluminesence materials, and field effect diodes.[1] Thus various chemical modifications, such as chain extension and functionalization, of the oligomeric structures have been intensively conducted. As parts of our efforts directing to the design of molecular electronic devices based on oligothiophenes, we have been interested in an electroactive fullerene-linked oligothiophene system. Such electron donor/C_{60} dyad systems are the topic of current investigations on photoinduced intramolecular energy transfer and electron transfer, since fullerene can behave as an effective acceptor.[2] We here would like to report the synthesis and properties of fullerene-linked oligothiophenes **4T-C_{60}**, **8T-C_{60}**, and **12T-C_{60}**, in which the [60]fullerene **1** is covalently connected to a series of long oligothiophenes. These compounds are expected to provide useful information on efficient intramolecular energy transfer depending on the chain lengths of the oligothiophene moieties.[3]



4T-C_{60} n = 1
8T-C_{60} n = 2
12T-C_{60} n = 3



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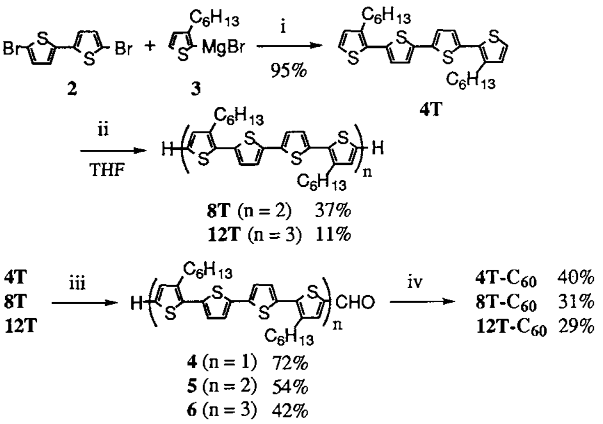
The fullerene-linked oligothiophenes were synthesized according to Scheme 1. First, 3,3'''-dihexyl-2,2':5',2'':5'',2'''-quaterthiophene (**4T**) was prepared in 95% yield by a nickel-catalyzed coupling reaction between 5,5'-dibromo-2,2'-bithiophene (**2**) and 2 equiv. 3-hexyl-2-thienylmagnesium bromide (**3**) in ether/benzene. Then, **4T** was lithiated with 1.2 equiv. lithium diisopropylamide in tetrahydrofuran, and a mixture of the resulting monolithiated and dilithiated species was subjected to oxidative coupling with copper(II) chloride at room temperature to give a mixture of tetrahexyloctithiophene (**8T**) (37% yield) and hexahexylduodecithiophene (**12T**) (11% yield), which were smoothly separated by column chromatography. These oligothiophenes were converted to the formyl derivatives **4** (72%), **5** (54%), and **6** (42%) by the Vilsmeier reaction, and then treated with fullerene and *N*-methylglycine in toluene[4] to give the corresponding fullerene-linked oligothiophenes **4T-C_{60}** (40%), **8T-C_{60}** (31%), and **12T-C_{60}** (29%).[5]



Scheme 1. Reagents and conditions: i) Ni(dppp)Cl_2, ether/benzene, reflux, 5 h; ii) 1.2 eq. LDA, THF, -30 °C, 1 h then $CuCl_2$, rt, 10 h; iii) DMF, $POCl_3$, dichloroethane, 50 °C, 10 h; iv) C_{60}, *N*-methylglycine, toluene, reflux, 15 h.

The fullerene-linked oligothiophenes are amphoteric redox-active compounds: thus their cyclic voltammograms demonstrate an oxidation peak due to the oligothiophene moiety and a reduction peak due to the fullerene moiety: **4T-C_{60}**, +1.04 and -0.63 V; **8T-C_{60}**, +0.76 and -0.63 V; **12T-C_{60}**, +0.67 and -0.63 V vs. Ag/AgCl in benzonitrile. The oxidation potentials tend to lower with extension of the oligothiophene segment. These values are in roughly harmony with those of the non-linked oligothiophenes, **4T**, +1.07 V; **8T**, +0.78 V; **12T**, +0.63 V. On the other hand, the reduction potentials are unchanged in the series and the same as that (-0.63 V) of the simple C_{60} adduct (**1**).[4] These observations indicate that both redox active moieties are not interactive.

The spectroscopic data of the fullerene-linked oligothiophenes are summarized together with those of the non-linked oligothiophenes and the simple C_{60} adduct **1** in Table 1. The electronic spectra of the fullerene-linked oligothiophenes are understood to consist of superimposition of the electronic transitions of the two chromophores; the oligothiophenes **4T**, **8T**, and **12T** show a strong absorption in the ultraviolet/visible region of 350-470 nm, whose wavelength is red-shifted and intensity is enhanced with the extension. On the other hand, the spectrum of **1** has a strong absorption peak at 328 nm accompanied with weak peaks at 434 nm and 704 nm tailing to the near-infrared region.

Unlike the non-interactive absorption spectra, the emission spectra are interactive, as shown in Figure 1. Although oligothiophenes exhibit strong fluorescent emission with extension,[6] the emission spectrum of **4T-C_{60}** demonstrates only fluorescence with vibrational structures at around 700 nm assigned to an emission from the fullerene moiety, even if the thiophene chromophore is excited. This means that the efficient

Table 1. Spectroscopic data of the fullerene-linked oligothiophenes and related compounds

Comp.	Chromophor	Abs. max./nm (log ε)[a]	Emis. max./nm[a,b]	Φ_f[f]	τ / ns
4T-C$_{60}$	oligothiophene	378 sh (4.59)	not observed[c]	≈0	unmeasured
	fullerene	333 (4.63), 707 (2.48)	712, 790	1×10^{-3}	1.26
8T-C$_{60}$	oligothiophene	448 (4.83)	554	4×10^{-4}	unmeasured
	fullerene	332 (4.75), 704 (3.00)	712, 790	1×10^{-3}	1.26
12T-C$_{60}$	oligothiophene	456 (4.97)	567, 601	4×10^{-3}	unmeasured
	fullerene	335 (4.73), 704 (2.90)	712, 790	1×10^{-3}	1.26
4T	oligothiophene	379 (4.64)	460, 484[d]	0.16	0.45
8T	oligothiophene	439 (4.77)	544, 586[e]	0.44	0.74
12T	oligothiophene	457 (4.91)	567, 610	0.52	0.71
Adduct (**1**)	fullerene	328 (4.85), 434 (3.79), 704 (2.84)	712, 790	1×10^{-3}	1.26

[a] Measured in toluene. [b] Excited at 480 nm unless otherwise stated. [c] Excited at 425 nm. [d] Excited at 400 nm. [e] Excited at 450 nm.
[f] Determined using 5,10,15,20-tetraphenylporphyrin (Φ_f=0.11) as the standard.

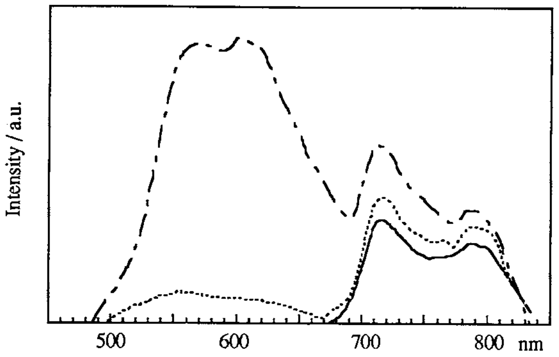


Figure 1. Fluorescence spectra of **4T-C$_{60}$** (————), **8T-C$_{60}$** (--------), and **12T-C$_{60}$** (— - — -) in toluene.

fluorescence quenching of the oligothiophene by the fullerene chromophore takes place. On the other hand, **8T-C$_{60}$** and **12T-C$_{60}$** show dual fluorescence not only from the fullerene moiety, but also from the oligothiophene moiety. However, the quantum yields (Φ_f) of the oligothiophene fluorescence drastically decrease by a factor of 10^2-10^3 as compared to those of the non-linked oligothiophenes **8T** and **12T**, whereas the quantum yields of the fullerene fluorescence are the same as the value of **1**, indicating that there is also rapid intramolecular energy transfer from the thiophene moiety to the fullerene (see also Table 1). The fluorescence quantum yields and singlet state life times (τ) of **4T**, **8T**, and **12T** can give an estimate of the rate constants of their fluorescence and nonradiation decay processes: **4T**, k_f 3.6 x 10^8 s^{-1} and k_{nr}1.9 x 10^9 s^{-1}; **8T**, 5.9 x 10^8 s^{-1} and 7.6 x 10^8 s^{-1}; **12T**, 7.3 x 10^8 s^{-1} and 6.8 x 10^8 s^{-1}, respectively. Assuming that these values are approximately comparative to those of the oligothiophene moiety of the fullerene-linked oligothiophenes, we are able to estimate by using an equation $\Phi_f = k_f / (k_f + k_{nr} + k_{et})$ that the rate constants of the intramolecular energy transfer processes are as follows: **4T-C$_{60}$**, $k_{et} > 10^{12}$ s^{-1}; **8T-C$_{60}$**, 10^{12} s^{-1}; **12T-C$_{60}$**, 2 x 10^{11} s^{-1}. This result obviously indicates that the intramolecular singlet-singlet energy transfer occurs in the picosecond time scale and markedly depends on the chain length of the oligothiophene moiety, in other words, the distance between the two chromophores.[7] Further investigation on the energy transfer mechanism of the present system is under way.[8]

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