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Synthesis and photophysical properties of [60]fullerene-oligo(thienylene–ethynylene) dyads[†]

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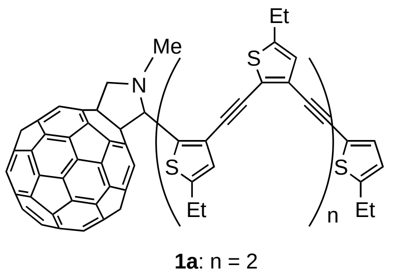
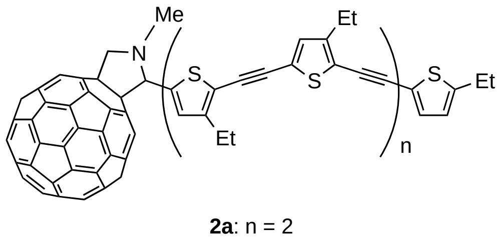
Abstract—Two series of [60]fullerene-linked oligo(2,3-thienylene–ethynylene)s and oligo(2,5-thienylene–ethynylene)s have been synthesized to elucidate their photophysical characteristics. Their fluorescence spectra in toluene reveals distinct photoinduced intramolecular interactions between the oligomers and C_{60}, which occur in a through-space fashion for the 2,3-thienylene–ethynylene system and in a through-bond fashion for the 2,5-thienylene–ethynylene system. © 2001 Elsevier Science Ltd. All rights reserved.

Since the discovery of photoinduced charge transfer from conjugated polymers to [60]fullerene,[1] such C_{60} composites have been of interest for a molecular approach to high-efficiency solar cells and high-sensitivity photodetectors.[2] In this context, considerable effort has been recently devoted to the synthesis of molecular dyads and triads covalently linking [60]fullerene with a rod type of conjugated oligomers, such as oligothiophenes,[3–5] oligo(phenylenevinylene)s,[6] oligo(thienylene-vinylene)s,[7] oligo(naphthylenevinylene)s,[8] and oligo-(phenylene–ethynylene)s,[9] because such well-structured oligomer systems have the possibility not only of mimicking the basic structural and electronic properties of the related polymer systems but also of emerging as advanced materials for optoelectronic applications. We recently discovered that a series of 2,3-thienylene–ethynylene oligomers[10] adopts favorable coil-shaped conformation, as deduced from analytical GPC and spectroscopic properties. This finding prompted us to develop a [60]fullerene-linked dyad system based on these oligomers. The coil-type oligomer–C_{60} dyad is expected to show unique photophysical properties compared with the above-mentioned rod-type oligomer–C_{60} dyads. Here, we report the synthesis and spectroscopic properties of [60]fullerene-linked oligo(2,3-thienylene–ethynylene)s **1** as well as oligo(2,5-thienylene–ethynylene)s **2** as a rod-type reference system.

The [60]fullerene-linked oligo(2,3-thienylene–ethynylene)s **1** and oligo(2,5-thienylene–ethynylene)s **2** were synthesized as shown in Scheme 1.[11] The 2,3-thienylene–ethynylene oligomers **3a**–**c**[10] were coupled with 2-ethyl-5-iodothiophene by the Sonogashira reaction to afford **4a** (78%), **4b** (50%), and **4c** (56%), which were then converted to the formyl derivatives **5a** (73%), **5b** (65%), and **5c** (45%), respectively, by consecutive



1a: n = 2
1b: n = 4
1c: n = 6



2a: n = 2
2b: n = 4

Keywords: alkynes; fullerenes; thiophenes; oligomers; photophysics; electron transfer.

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[†] This paper is dedicated to Emeritus Professor Masazumi Nakagawa on the occasion of his 85th birthday.

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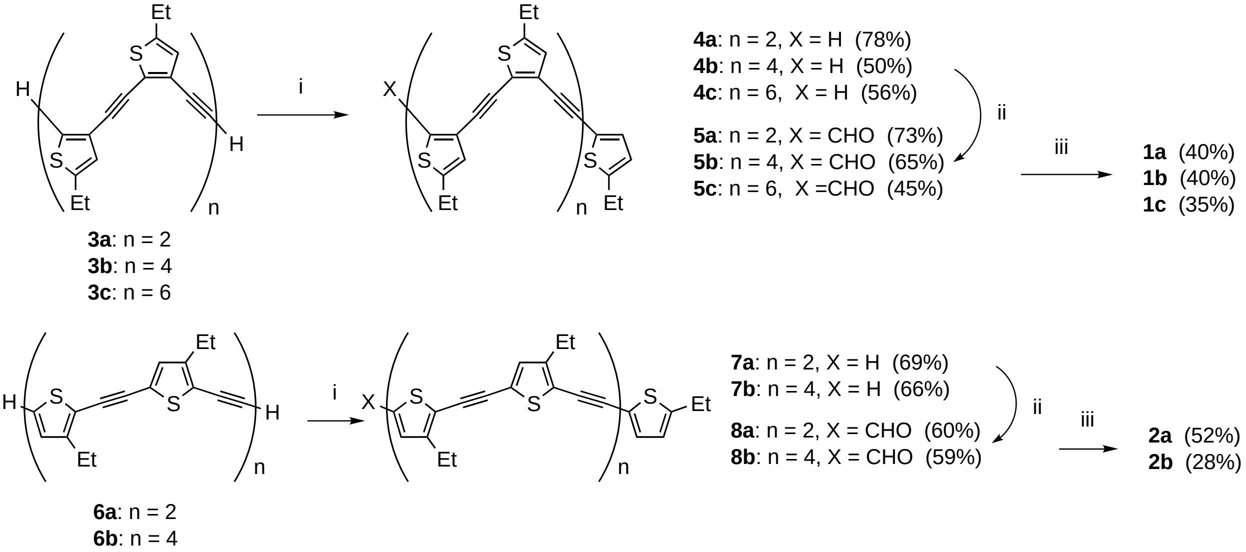


Scheme 1. *Reagents and conditions:* (i) 2-ethyl-5-iodothiophene, Pd(PPh$_3$)$_4$–CuI, Et$_3$N, 70°C; (ii) (1) LDA, ether, −78 to 0°C, 1 h; (2) DMF, −78°C, then rt, 12 h; (iii) C$_{60}$, *N*-methylglycine, toluene, reflux, 24 h.

treatment with LDA and *N*,*N*-dimethylformamide. The addition reactions of C$_{60}$ with the aldehydes **5** and *N*-methylglycine in toluene[12] afforded the desired fullerene-linked oligomers **1a** (40%), **1b** (40%), and **1c** (35%). The oligo(2,5-thienylene–ethynylene) derivatives **2** were similarly synthesized starting from the oligo(2,5-thienylene–ethynylene)s **6**.[13]

The ^{1}H NMR spectrum of **1a** exhibits six thiophene–proton resonances at different chemical shifts, in which the two signals (H1 and H3) due to the protons of the first and the third thiophenes from the C$_{60}$ side show downfield shifts by 0.49 and 0.15 ppm, respectively, relative to **4a** (Fig. 1), indicating that these protons are located in close proximity to the fullerene sphere.[14] Similar downfield shifts of the third thiophene protons are also observed in **1b** and **1c**. A computational geometrical optimization (PM3 level) of **1a** indicates that these fullerene-linked oligo(2,3-thienylene–ethynylene)s also adopt a coil-shaped conformation like the parent 2,3-thienylene–ethynylene oligomer system[10] as shown in Fig. 2. The distance between the third thiophene proton and the C$_{60}$ skeleton is very short (about 2.5 Å) in agreement with its downfield shift.

The electronic absorption and emission spectroscopic data of the fullerene-linked oligo(thienylene–ethynylene)s **1** and **2** are summarized together with those of the non-linked oligomers **4** and **7** and the simple C$_{60}$ adduct, *N*-methylfulleropyrrolidine **9**, in Table 1. The electronic absorption spectra of the fullerene-linked oligo(2,3-thienylene–ethynylene)s **1** are roughly interpreted as the superimposition of the electronic transitions of the two chromophores as represented by **1a** in Fig. 3. However, slight red shifts of the absorption bands due to the fullerene chromophore in the long-wavelength region of 600–750 nm are observed compared with the *N*-methylpyrrolidine–C$_{60}$ adduct **9**, which indicates the presence of a weak through-space electronic interaction between both components due to

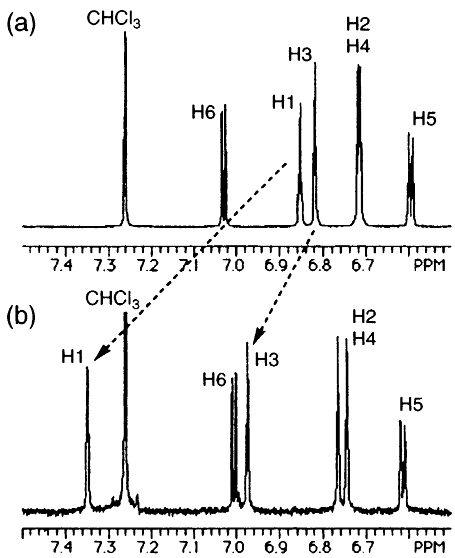


Figure 1. ^{1}H NMR spectra of **4a** (a) and **1a** (b) in CDCl$_3$.

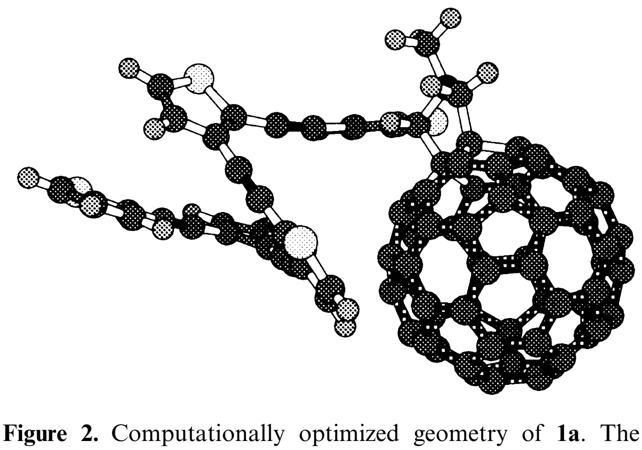


Figure 2. Computationally optimized geometry of **1a**. The ethyl groups were not included in the optimization.

Table 1. Spectroscopic data of the fullerene-linked oligo(thienylene–ethynylene)s and related compounds in toluene

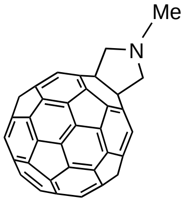
Comp.	Chromophore	Abs. max (nm) [$\varepsilon \times 10^{-3}$ (M^{-1} cm^{-1})]	Emis.[a] max (nm)	Φ/Φ (ref.)[b]
1a	Oligomer	334 sh [59.9], 416 sh [18.0], 443 sh [8.90]	467[c]	0.0044
	Fullerene	646 [0.31], 670 [0.18], 712 [0.15]	718, 757, 802	0.53
1b	Oligomer	328 sh [87.2], 443 sh [25.3], 461 sh [14.7]	480[c]	0.011
	Fullerene	645 [0.31], 677 [0.18], 712 [0.20]	716, 755, 804	0.61
1c	Oligomer	305 [168], 468 sh [23.0]	477, 506	0.095
	Fullerene	645 [0.45], 677 [0.27], 712 [0.22]	720, 751, 804	0.65
2a	Oligomer	330 [61.5], 410 [75.0]	469[c]	0.0012
	Fullerene	640 [0.49], 704 [0.42]	717, 798	1.0
2b	Oligomer	335 [81.8], 432 [14.7]	498, 535	0.011
	Fullerene	641 [0.43], 704 [0.37]	716, 798	1.0
4a	Oligomer	310 [45.4], 390 [20.4], 436 sh [6.0]	442, 470	–
4b	Oligomer	309 [84.0], 421 sh [34.0], 462 sh [10.8]	470, 504	–
4c	Oligomer	305 [139], 421 sh [62.0], 468 sh [20.0]	475, 506	–
7a	Oligomer	410 [66.3]	476, 508	–
7b	Oligomer	430 [13.7]	505, 541	–
9	Fullerene	330 [38.8], 434 [3.55], 640 [0.32], 705 [0.33]	717, 800	–

[a] Excited at 400 nm.

[b] Relative fluorescence quantum yield to the corresponding reference compound.

[c] Weak broad band.

the close contact. On the other hand, the spectra of the 2,5-thienylene–ethynylene series **2** entirely corresponds to the superimposition of the individual spectra of **7** and **9**.



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Unlike the absorption spectra, the emission spectra in both series are very interactive as shown in Fig. 4 for **1** and in Fig. 5 for **2**. The fluorescence emission spectra were measured in toluene solution at fixed optical density (0.10) at the excitation wavelength (400 nm). The fluorescences of the oligomer moieties of the dyads **1** and **2** are strongly quenched with respect to those of the corresponding nonlinked oligomers **4** and **7**; the quenching factors [$\Phi(\mathbf{1})/\Phi(\mathbf{4})$ or $\Phi(\mathbf{2})/\Phi(\mathbf{7})$] are estimated as shown in Table 1. These strong fluorescence quenchings by the fullerene chromophore show an efficient photoinduced intramolecular energy and/or electron transfer from the oligo(thienylene–ethynylene) moiety to the fullerene. The quenching factors increase with extension of the oligomer length in both series. However, the chain-length dependence of the quenching factor for the 2,3-thienylene–ethynylene system, especially in **1a** and **1b**, is small compared with that for the 2,5-thienylene–ethynylene system. This suggests that, in the 2,3-system, a through-space mechanism mainly contributes to the fluorescence quenching through the close contact between the third thiophene ring and the fullerene sphere in contrast with the through-bond contribution in the 2,5-system. Apart from the residual weak oligomer emission, the fluorescence spectra show a characteristic band with vibrational structures at 700–800 nm attributable to emission from the fullerene chromophore. The quenching of the oligomer fluorescence and the simultaneous appearance of the fullerene emission are clearly characteristic of intramolecular energy transfer from the oligomer to the fullerene. The

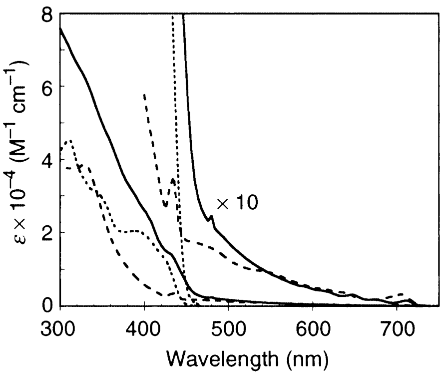

Figure 3. Electronic absorption spectra of **1a** (solid line), **4a** (dotted line), and **9** (dashed line).

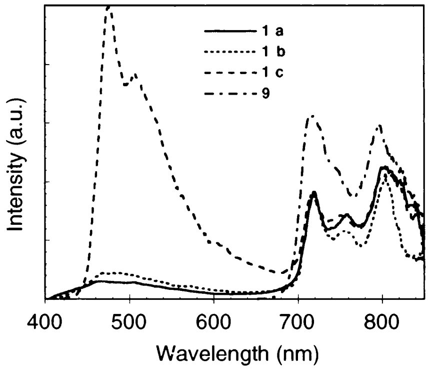

Figure 4. Fluorescence spectra of **1a**, **1b**, **1c**, and **9** measured in degassed toluene at 0.10 optical density at 400 nm excitation wavelength.

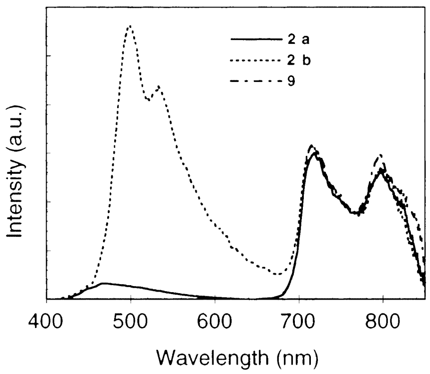

Figure 5. Fluorescence spectra of **2a**, **2b**, and **9** measured in degassed toluene at 0.10 optical density at 400 nm excitation wavelength.

relative fluorescence quantum yields of the fullerene moiety of 2,5-thienylene–ethynylene series **2** to the *N*-methylpyrrolidine–C_{60} adduct **9** are unity, indicating that complete energy transfer is induced by photoexitation as observed for other rod-type conjugated oligomer–fullerene dyads in nonpolar solutions.[4a,4b,5,6b,6c,8b] On the other hand, the fluorescence quantum yields of the fullerene moiety of 2,3-thienylene–ethynylene series **1** are considerably low compared with that of **9** by the factors [$\Phi(\mathbf{1})/\Phi(\mathbf{9})$] of 0.53 for **1a**, 0.61 for **1b**, and 0.65 for **1c**. This result strongly suggests that intramolecular electron transfer, in addition to energy transfer, contributes to the fluorescence quenching. Detailed photophysical studies by time-resolved fluorescence and transient absorption spectroscopy are currently under way.

The unique photophysical behaviors of the oligo(2,3-thienylene–ethynylene)–fullerene dyads are evidently attributable to the close arrangement of the two component chromophores due to the coil-shaped conformation of the oligomer moiety, leading not only to facilitation of through-space interaction but also to stabilization of a charge-separated state.

Acknowledgements

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11. All new compounds were fully cahracterized by spectroscopic analyses, and the selected data are as follows: compound **1a**: dark-brown powder; mp 170°C (decomp); ^{1}H NMR ($CDCl_3$): δ 1.25–1.35 (m, 15H), 2.54 (s, 3H), 2.27–2.91 (m, 10H), 3.86 (d, $J=9.5$ Hz, 1H), 4.39 (s, 1H), 4.62 (d, $J=9.5$ Hz, 1H), 6.61 (dt, $J=3.7$ and 1.1 Hz, 1H), 6.74 (t, $J=1.1$ Hz, 1H), 6.76 (t, $J=1.1$ Hz, 1H), 6.97 (t, $J=1.1$ Hz, 1H), 7.00 (d, $J=3.7$ Hz, 1H), 7.34 (t, $J=1.1$ Hz, 1H); MALDI-TOF *m*/*z* 1424.52 (M^+), calcd 1424.16. Compound **1b**: dark-brown powder; mp 165°C (decomp); ^{1}H NMR ($CDCl_3$): δ 1.21–1.35 (m, 27H), 2.52 (s, 3H), 2.65–2.91 (m, 18H), 3.85 (d, $J=9.5$ Hz, 1H), 4.39 (s, 1H), 4.63 (d, $J=9.5$ Hz, 1H), 6.60 (dt, $J=3.7$ and 1.0 Hz, 1H), 6.70 (m, 2H), 6.72 (m, 2H), 6.74 (m, 2H), 6.99 (t, $J=1.0$ Hz, 1H), 7.02 (d, $J=3.7$ Hz, 1H), 7.35 (t, $J=1.1$ Hz, 1H); MALDI-TOF *m*/*z* 1961.19 (M^+), calcd 1961.24. Compound **1c**: dark-brown powder; mp 150°C (decomp); ^{1}H NMR ($CDCl_3$): δ 1.21–1.35 (m, 39H), 2.52 (s, 3H), 2.65–2.90 (m, 26H), 3.84 (d, $J=9.5$ Hz, 1H), 4.36 (s, 1H), 4.61 (d, $J=9.5$ Hz, 1H), 6.60 (dt, $J=3.7$ and 1.1 Hz, 1H), 6.68–7.73 (m, 9H), 6.74 (t, $J=1.1$ Hz, 1H), 6.76 (t, $J=1.1$ Hz, 1H), 6.99 (t, $J=1.0$ Hz, 1H), 7.02 (d, $J=3.7$ Hz, 1H), 7.35 (t, $J=1.1$ Hz, 1H); MALDI-TOF *m*/*z* 2497.54 (M^+), calcd 2497.30. Compound **2a**: dark-brown powder; mp

143–145°C; ^{1}H NMR ($CDCl_3$): δ 1.19–1.27 (m, 12H), 1.31 (t, $J=7.7$ Hz, 3H), 2.67 (m, 8H), 2.84 (dq, $J=0.9$ and 7.7 Hz, 2H), 2.89 (s, 3H), 4.20 (d, $J=9.8$ Hz, 1H), 4.94 (d, $J=9.8$ Hz, 1H), 5.16 (s, 1H), 6.69 (dt, $J=3.7$ and 0.9 Hz, 1H), 7.03 (s, 1H), 7.05 (s, 1H), 7.06 (s, 1H), 7.10 (d, $J=3.7$ Hz, 1H), 7.21 (s, 1H); MALDI-TOF *m*/*z* 1425.01 (M^+), calcd 1424.16. Compound **2b**: dark-brown powder; mp 159–162°C; ^{1}H NMR ($CDCl_3$): δ 1.19–1.27 (m, 24H), 1.31 (t, $J=7.7$ Hz, 3H), 2.67–2.75 (m, 16H), 2.84 (dq, $J=0.9$ and 7.7 Hz, 2H), 2.90 (s, 3H), 4.20 (d, $J=9.8$ Hz, 1H), 4.94 (d, $J=9.8$ Hz, 1H), 5.16 (s, 1H), 6.69 (dt, $J=3.7$ and 0.9 Hz, 1H), 7.03 (s, 1H), 7.05 (s, 1H), 7.06–7.07 (m, 5H), 7.10 (d, $J=3.7$ Hz, 1H), 7.21 (s, 1H); MALDI-TOF *m*/*z* 1960.49 (M^+), calcd 1961.24.

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