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Fullerene–fluorescein–anthracene hybrids: a model for artificial photosynthesis and solar energy conversion

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Abstract—Two novel C_{60}–fluorescein–anthracene hybrids have been synthesized. Fluorescence quenching in the hybrids indicates an energy transfer from the excited state of anthracene to fluorescein and photoinduced intramolecular electron transfer from the excited state of fluorescein to the C_{60} moiety.

The chemistry of fullerenes has attracted a lot of attention and is currently under very active investigation. The unusual properties of fullerene derivatives suggest potential applications in many areas. A most promising one is the artificial mimicking of photosynthesis and related solar energy conversion. Fullerenes as novel electron acceptors, particularly the readily available C_{60}, present a wide range of chemical and physical properties that make them potential chromophores in photoinduced redox processes.[1–3] Also a remarkable property of C_{60} related to electron transfer phenomena is that it can efficiently induce a rapid charge separation accompanied by a slow charge recombination. The potential availability of a wide variety of dyads and triads containing covalently bonded C_{60} and donors/acceptors units offer a useful opportunity to investigate and correlate this intrigue photoinduced electron transfer behavior. In these dyads and triads, porphyrins,[3–9] oligothiophene,[10,11] pyrene,[12] carbazole,[13] ferrocene,[14] polypyridine ruthenium(II) complexes,[15] *N*,*N*-dialkylaniline,[16] TTFs,[17,18] carotenoid,[19] are usually the donors, while relatively fewer number of acceptors such as pyromellitimide,[20] nitroaromatic,[21,22] benzoquinone derivatives,[23] have been used to form electron acceptor–fullerene or donor–fullerene–acceptor dyads and triads. Among these, the systems consisting of porphyrins and C_{60} are the most prominent and have been extensively studied. It is well known that fluorescein (FL) is a very important xanthene dye, which has a high fluorescence quantum yield, excellent redox properties as well as relatively large extinction coefficients at the visible region. Thus, FL has acquired many technical applications and has been frequently used as electron donor/acceptor and sensitizer in artificial photosynthetic models.[24] Our previous study[25] on FL–C_{60} dyad shows that intramolecular photoinduced electron transfer (IPET) from the singlet excited state of FL (^{*1}FL) to C_{60} takes place efficiently. Therefore FL–C_{60} provides a good model to mimic artificial photosynthesis. Considering the rather low absorptions of both C_{60} and FL in the range of 320–400 nm, and by contrast, high absorption for anthracene (AN) in the same region, as well as the fact that AN is known to be a good electron and energy donor, which can efficiently transfer its singlet excited energy to FL (almost 100%) both intramolecularly and intermolecularly,[26–28] introduction of AN to the FL–C_{60} dyad to form AN–FL–C_{60} triad should allow favorable light harvesting as well as charge separation. Therefore we prepared two hybrids **1** and **2**, composing of a FL, AN, and fullerene, covalently linked to each other, as well as the fullerene model compound **3**.

The synthetic approach[25] to compounds **1–3** (Scheme 1) relies upon the 1,3 dipolar cycloaddition of azomethine ylides to C_{60}. Thus a mixture of related aldehydes (**4**, **5**, or *p*-anisaldehyde) (0.1 mmol), *N*-methylglycine (0.36 mmol), and C_{60} (0.1 mmol) in toluene (100 mL) was refluxed for 8–12 h under Ar, giving the corresponding fulleropyrolidines **1–3**. Purification was accomplished by column chromatography (silica gel, toluene/methanol, 50:1). The aldehydes **4**, **5** were prepared by sequential

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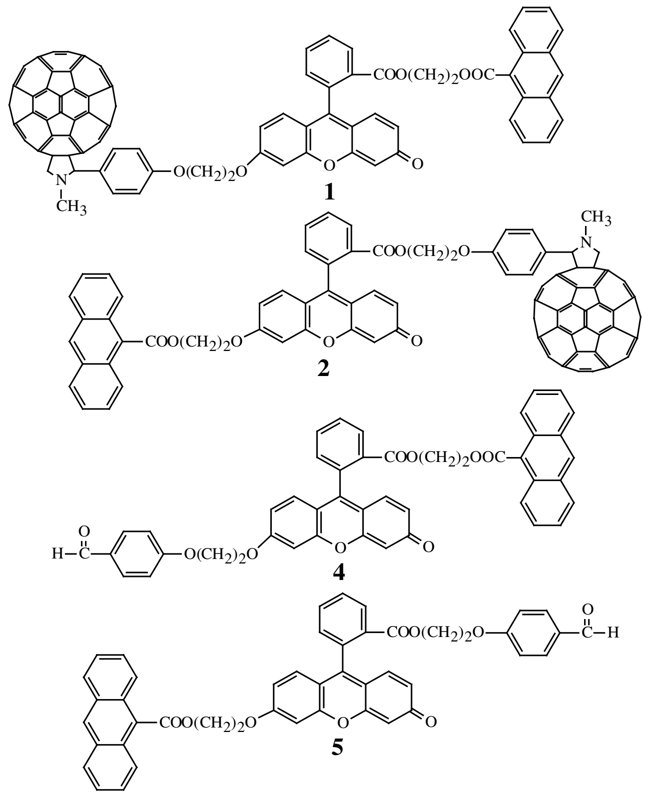
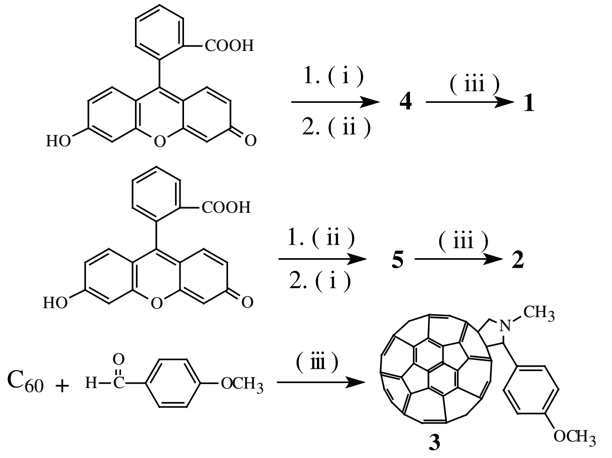
alkylation of FL as depicted in Scheme 1 using the corresponding alkylbromides in DMF at 90 °C for 2–3 h with anhydrous potassium carbonate as base. The structures of all these compounds were verified by spectroscopic analyses.[†]

The UV–vis spectra of hybrids **1** and **2** (Fig. 1) in chloroform/methanol (1:1) are composed of the individual chromophoric subunits: C_{60}, FL, and AN, indicating the absence of significant interaction among FL, C_{60}, and AN in the ground state. As of the steady-state fluorescence spectra of precursor dyads (FL–AN) **4** and **5** in chloroform/methanol (1:1), when excited at 460 nm at which the absorption of FL is dominant, no obvious change of FL's fluorescence intensity occurs compared to 6-ethoxyl fluorescein ethylester (FLdiEt), which means that there is no energy/electron transfer between ^{*1}FL and AN. The electron transfer from AN to ^{*1}FL was not observed as expected, though this process is thermodynamically allowed ($\Delta G = -0.33\,\mathrm{eV} < 0$).[29] The same result had previously been obtained by Shen's group[28] and this was attributed to the conformation mismatch of the chromophoric planes. By contrast, when AN was excited at 364 nm, the emission from the singlet excited state of AN (^{*1}AN) was completely quenched, while the fluorescence from ^{*1}FL was observed. These results indicate that intramolecular singlet energy transfer occurs from ^{*1}AN moiety to FL moiety. It is known that singlet excited-state energies of 9-anthracene carboxylic acid ethyl ester ($ANCO_2Et$) and FLdiEt are 3.21 and 2.43 eV, respectively.[26] Moreover, the fluorescence spectrum of AN overlaps well with the absorption spectrum of FLdiEt. Hence the energy transfer from $^{*1}ANCO_2Et$ to the FLdiEt is feasible. Though the electron transfer from ^{*1}AN to FL is also thermodynamically allowed ($\Delta G = -1.09\,\mathrm{eV} < 0$), no electron transfer from ^{*1}AN to FL was observed in this case as reported by others.[26,28] This is probably because the energy transfer of 'emission–absorption' is a more



The Structures of Hybrids **1**, **2** and Precursors **4**, **5**



Scheme 1. Reactions and conditions: (i) (2-bromoethyl) anthracene-9-carboxylate ibid; (ii) 4-(2-bromoethoxyl) benzaldehyde, anhydrous K_2CO_3, DMF, 90 °C for 2–3 h; (iii) *N*-methylglycine, Ar, toluene, reflux for 8–12 h.

[†] All new compounds gave satisfactory spectroscopic and analytical data consistent with the assigned structures. All ^{1}H NMR spectra were recorded on a Bruker 300 MHz instrument; chemical shifts are reported in ppm and are referenced to residual solvent. All UV spectra were recorded using a U-3010 spectrophotometer (HITACHI). Emission spectra were recorded on a Hitachi F-450 fluorescence spectrometer. Solvents used for UV and fluorescence measurements were redistilled and the related samples were prepared in aerated methanol/chloroform (1:1, v/v) and the concentration is about 2×10^{-5} M. IR spectra were recorded on KBr pellets with a Perkin Elmer System 2000FTIR. Mass spectra were obtained on MALDI-TOF MS, Bruker BIFLEX III, or AEI-MS 50 mass spectrometers.

Hybrid **1**: ^{1}H NMR ($CDCl_3$, δ, ppm): 2.97 (s, 3H), 3.44–3.58 (m, 2H), 4.21–4.45 (m, 5H), 4.95–5.05 (m, 4H), 6.00–6.50 (m, 2H), 6.61–6.65 (m, 3H), 6.75–7.10 (m, 3H), 7.25–7.40 (m, 1H), 7.54 (d, 4H), 7.70–7.90 (m, 4H), 8.04–8.15 (m, 4H), 8.37 (d, 1H), 8.59 (d, 1H); ^{13}C NMR ($CDCl_3$, δ, ppm): 39.9, 63.0, 63.1, 65.1, 66.7, 68.8, 77.2, 77.3, 82.7, 82.8, 100.9, 105.7, 115.4, 117.9, 125.0, 125.6, 127.2, 128.7, 128.8, 129.1, 129.8, 130.0, 130.3, 130.4, 131.0, 131.9, 133.0, 140.1, 141.7, 142.0, 142.1, 142.2, 142.5, 144.4, 145.2, 145.3, 145.5, 145.9, 146.1, 146.3, 147.3, 153.1, 153.7, 154.1, 158.0, 158.6, 165.3, 168.9, 169.1, 169.2; FT-IR: 1725, 1643, 1597, 1512, 1447, 1377, 1286, 1246, 1203, 1105, 853, 527; MALDI-TOF, *m/z*: 720.24, 756.36, 868.17, 1474.36 (M−1).

Hybrid **2**: ^{1}H NMR ($CDCl_3$, δ, ppm): 2.80 (s, 3H), 4.22–4.32 (m, 5H), 4.52 (s, 2H), 4.58–4.75 (m, 2H), 4.91 (s, 1H), 4.98 (d, 1H), 6.35–6.58 (m, 3H), 6.66 (s, 1H), 6.77–6.83 (q, 2H), 7.00 (d, 2H), 7.26 (d, 1H), 4.40–7.51 (hexa, 4H), 7.66–7.78 (hexa, 4H), 7.94–7.97 (d, 2H), 8.03–8.06 (d, 2H), 8.34 (d, 1H), 8.58 (s, 1H); ^{13}C NMR ($CDCl_3$, δ, ppm): 39.9, 62.8, 63.3, 65.8, 67.3, 68.8, 77.2, 82.9, 96.1, 100.7, 105.4, 114.1, 114.2, 114.5, 114.7, 115.0, 117.6, 124.8, 125.5, 127.0, 128.4, 128.7, 128.9, 129.7, 129.8, 130.2, 130.5, 130.9, 131.3, 133.0, 134.5, 139.8, 141.6, 141.9, 142.0, 142.1, 142.2, 142.5, 142.6, 145.1, 145.4, 145.5, 145.8, 146.0, 146.1, 146.2, 147.2, 153.3, 153.9, 154.4, 156.1, 158.3, 158.8, 163.3, 164.7, 169.0; FT-IR: 1727, 1642, 1597, 1510, 1206, 1106, 853, 527; MALDI-TOF, *m/z*: 1474.36 (M−1).

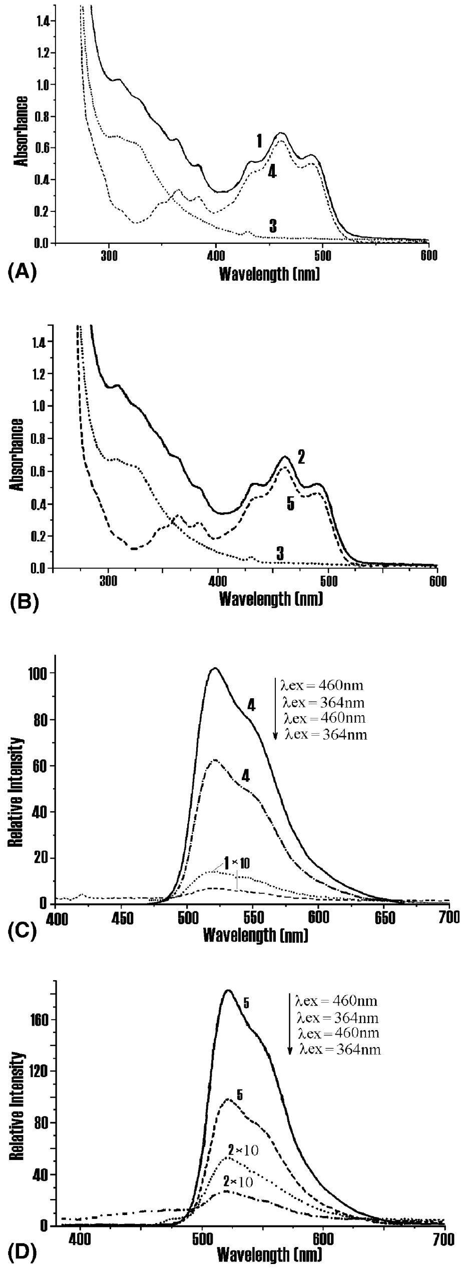


Figure 1. Electronic absorption (A, B) and fluorescence (C, D) spectra of **1**, **2** and their model compounds **3**, **4**, and **5**. (A) is for **1**, **3**, **4** and (B) is for **2**, **3**, and **5**. (C, D) are the fluorescence spectra of the related hybrids and their model compounds with different excitation wavelength (364 or 460 nm). Both electronic and fluorescence spectra were measured in $CH_3OH/CHCl_3$ (1:1) (2×10^{-5} M).

favorable pathway than electron transfer. Whereas dyads AN–FL **4**, **5** have strong fluorescence with either 364 or 460 nm as excitation wavelength, emissions from hybrids **1** and **2** are very weak. Also, the emissions of **1** and **2** (480–650 nm) were observed only from the FL, without detectable emission from the AN (380–480 nm) and C_{60} (680–750 nm) moieties. Furthermore, the weak emission from C_{60} in model **3** was observed (680–750 nm). Thus there is no evidence for the existence of singlet–singlet energy transfer from ^{*1}FL to the C_{60}, and these results indicate that intramolecular energy transfer from ^{*1}AN to FL is responsible for a lack of AN's fluorescence, while IPET from the ^{*1}FL to C_{60} ($\Delta G = -0.97\,\mathrm{eV}^{29}$) is a main pathway for the emission quenching in chloroform/methanol (1:1, v/v).

In summary, two hybrids consisting of AN, fullerene and FL were prepared in which AN, as an energy antenna collects light in the range of 320–400 nm, transfers its energy to reaction center FL. FL itself can absorb the light in the visible region (400–600 nm), and transfers an electron to C_{60}, generating a charge separated state. This model (AN–FL–C_{60}) may find applications in the areas such as artificial photosynthesis and solar energy conversion. Detailed photophysical properties of the two hybrids are under investigation.

Acknowledgments

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29. According to the Rehm–Weller equation: $\Delta G = E_{\mathrm{ox}}(D) - E_{\mathrm{red}}(A) - E^{0-0} - C$, ΔG is the free energy change of the electron transfer process, $E_{\mathrm{ox}}(D)$ is the ground oxidation potential of donor, $E_{\mathrm{red}}(A)$ is reduction potential of acceptor, E^{0-0} is the zero–zero excitation energy (equal to singlet energy E^{S} or triplet energy E^{T}) and C is ca. 0.06 in polar solvent. So $\Delta G(\mathrm{AN\ to\ }^{*1}\mathrm{FL}) = E_{\mathrm{ox}}(\mathrm{AN}) - E_{\mathrm{red}}(\mathrm{FL}) - E^{\mathrm{S}}(\mathrm{FL}) - 0.06 = 0.95 - (-1.2) - 2.42 - 0.06 = -0.33$ eV; $\Delta G(^{*1}\mathrm{AN\ to\ FL}) = E_{\mathrm{ox}}(\mathrm{AN}) - E_{\mathrm{red}}(\mathrm{FL}) - E^{\mathrm{S}}(\mathrm{AN}) - 0.06 = 0.95 - (-1.2) - 3.18 - 0.06 = -1.09$ eV; $\Delta G(^{*1}\mathrm{FL\ to\ C_{60}}) = E_{\mathrm{ox}}(\mathrm{FL}) - E_{\mathrm{red}}(\mathrm{C_{60}}) - E^{\mathrm{S}}(\mathrm{FL}) - 0.06 = 0.90 - (-0.61) - 2.42 - 0.06 = -0.97$ eV. The photophysical and electrochemical data about FL, ANCO$_2$Et, and C$_{60}$ are summarized in the following table:

	E_{ox} (eV)	E_{red} (eV)	E^{S} (eV)	E^{T} (eV)
FL[a]	0.90	−1.20	2.42	1.94
ANCO$_2$Et[a]	0.95	—	3.18	1.85
C$_{60}$[b]	—	−0.61, −1.00, −1.46, −1.74	1.74	1.45

[a] Cited from Refs. 26 and 28.

[b] Cited from Ref. 1.