ChemComm

# Competition between photosensitization and charge transfer in soluble oligo(naphthylenevinylene)–fullerene dyads

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*Received (in Liverpool, UK) 5th January 2000, Accepted 14th February 2000*

**In a novel series of soluble $C_{60}$–oligo(naphthylenevinylene) dyads both singlet–singlet energy transfer and intramolecular electron transfer were found to take place and to compete with each other.**

Conjugated, polymeric semiconductors are effective and stable electron-donor materials. Upon illumination of the polymer, a valence band electron is excited across the band-gap into the conduction band and generates a highly reactive donor state. Charge separation evolving from the latter process is facilitated by a possible charge delocalization within the polymer or by structural relaxation. On the other hand, fullerenes also display strong electron-acceptor properties in their ground and excited states. In mixed composites of these two donor acceptor materials ultrafast photoinduced electron transfer can occur with high quantum efficiency.[1] This feature attracted interdisciplinary effort to utilize conjugated polymer/$C_{60}$ blends as novel materials for photovoltaic cells (*i.e.* the conversion of photon energy into electricity).[2]

The tendency of $C_{60}$ to phase-separate and crystallize limits its solubility in conjugated polymers. However, uniformity and high quality of conjugated polymer/$C_{60}$ thin films are essential requirements for opto-electronic device applications. Thus, soluble functionalized $C_{60}$ derivatives have been synthesized in an attempt to suppress the phase separation once these derivatives are blended with the conjugated polymers.[3]

A viable alternative for fabricating stable bicontinuous networks is the synthesis of molecular dyads[4] and triads[5] bearing conjugated oligomer moieties covalently linked to an electron acceptor, such as a fullerene.[6] Well structured oligomers allow the possibility for mimicking the basic structural and electronic properties of the related polymers and, therefore, have emerged as interesting materials for opto-electronic applications.[7,8]

Here, we report the preparation of a covalently linked [60]fullerene–oligo-2,6-naphthylenevinylene (ONV) derivative **4** as well as that of the [60]fullerene–monomer analogue **6**. Furthermore, a detailed investigation of intramolecular energy and electron transfer reactions in both dyads is presented.

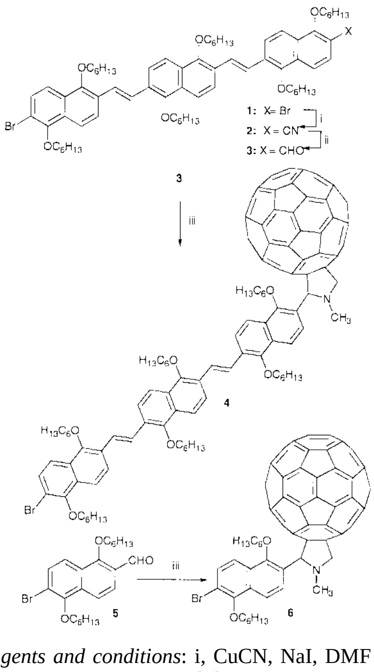
Among the suitable procedures for the functionalization of fullerenes, the 1,3-dipolar cycloaddition of azomethine ylides to $C_{60}$ emerged as an important methodology for the production of stable fullerene derivatives.[9] We have adapted this synthetic approach for the preparation of dyad **4** which was obtained in 63% yield (*i.e.* based on recovered $C_{60}$) by reacting sarcosine, $C_{60}$ and the formylsubstituted trimeric material **3** in refluxing toluene for 24 h. Oligomer **3** was obtained from the dibromoderivative **1**[10] by using a two step reaction pathway. Treatment of **1** with copper cyanide in dimethylformamide[11] under stoichiometric control led to a mixture of the monocyanoderivative **2** (49%) and dicyano derivative (21%) which were subsequently separated by column chromatography. Reduction with DIBAL-H at −78 °C of oligomer **2** yielded the aldehyde **3** in a 40% yield (Scheme 1).

Reaction of 2-bromo-6-formyl-1,5-dihexyloxynaphthalene[10] with [60]fullerene and sarcosine in refluxing toluene for 24 h yielded dyad **6** (Scheme 1). The good solubility afforded by the alkoxy chains allowed full spectroscopic and electrochemical characterization of both dyads (**4** and **6**).

The redox properties of the fullerene-linked oligomers were studied by cyclic voltammetry in toluene–acetonitrile (5 : 1 v/v) at room temperature. Dyads **4** and **6** both exhibit an amphoteric redox-active behaviour. In particular, they show an oxidation wave at $E_{1/2}$ *ca.* 1.4 V, (1.48 V for **3** *vs.* SCE) due to the oxidation of the oligomer, and three quasireversible waves at $E_{1/2} = -0.59$, $-1.04$ and $-1.66$ V corresponding to the fullerene reduction.

The absorption spectra of dyads **4** and **6** in dichloromethane solution disclose superimposed features of the $C_{60}$ and the trimeric or monomeric unit, respectively. Taking the electrochemical data and the absorption features into consideration, we reached the conclusion that no significant interactions arise between the two redox-active moieties in the ground state of the combined units.

Relative to the strong emission of the oligomer references [*i.e. ca.* 400 nm (**5**) and 430 nm (**3**)], the trimer and monomer emission in dyads **4** and **6** is nearly quantitatively quenched.[5] Instead, a familiar fullerene fluorescence spectrum was found with a strong $0 \rightarrow 0$ emission at 715 nm, despite exclusive excitation of the oligomer moiety (Table 1).[12] To unravel the mechanism of producing the emission, an excitation spectrum was measured. The excitation spectra of dyads **4** and **6** were exact matches of the ground state absorption of the oligomer (**3**) and monomer (**5**) moieties with maxima at 412 and 360 nm respectively. This implies that there is a rapid transfer of singlet excited state energy from the photoexcited oligomer to the covalently linked fullerene.



**Scheme 1** *Reagents and conditions*: i, CuCN, NaI, DMF ; ii, DIBAL-H, $Et_2O$ ; iii, $C_{60}$, $CH_3NHCH_2CO_2H$, Tol, heat.

DOI: 10.1039/b000289p

**Table 1** Photophysical data of oligo(naphthylenevinylene)–fullerene dyads

| | Fulleropyrrolidine | Dyad **4** | Dyad **6** |
|---|---|---|---|
| Fluorescence max/nm | 715,[a] 715[b] | 715,[a] 715[b] | 715,[a] 715[b] |
| $\Phi_{\mathrm{fluor.}}$ $C_{60}$ (Tol) | $6.0 \times 10^{-4}$ | $4.68 \times 10^{-4}$ | $4.98 \times 10^{-4}$ |
| $\Phi_{\mathrm{fluor}}$ $C_{60}$ (THF) | $6.0 \times 10^{-4}$ | $3.56 \times 10^{-4}$ | $4.59 \times 10^{-4}$ |
| $k_{\mathrm{energy}}$/s$^{-1}$ | —/— | $1.51 \times 10^{10}$[c]<br>$2.04 \times 10^{10}$[d] | $1.89 \times 10^{10}$[c]<br>$2.22 \times 10^{10}$[d] |
| ISC (Tol)/ns | 1.35 | 1.21 | 1.2 |
| Triplet max/nm | 700 | 700 | 700 |
| $\Phi_{\mathrm{triplet}}$(Tol) | 0.98 | 0.636 | 0.83 |
| $\Phi_{\mathrm{triplet}}$ (THF) | — | 0.595 | 0.748 |
| $\Phi_{\mathrm{triplet}}$(PhCN) | — | 0.570 | 0.72 |

[a] In toluene. [b] In THF. [c] Measured at 550 nm. [d] Measured at 880 nm.

In ps-resolved transient absorption measurements, oligomer **3** and monomer **5** gave rise to a broadly absorbing transient with a maximum at *ca.* 550 nm. On the ps timescale (*i.e.* up to 6000 ps), no significant decay of the excited state absorption was observed. $C_{60}$-oligomers **4** and **6**, on the other hand, displayed a drastically different behavior. The spectral features recorded immediately after the laser pulse (*i.e.* maximum at *ca.* 550 nm) clearly confirmed the excitation of the oligomer moieties. In contrast to reference compounds **3** and **5**, the excited state absorption was short-lived. In particular, lifetimes of 66 and 53 ps for dyads **4** and **6** (Table 1), respectively, corroborated the efficient emission quenching.

Once the rapid disappearance of the excited oligomer absorption comes to an end (*i.e. ca.* 200 ps after the laser pulse), only characteristics of the fullerene singlet excited state absorption remain. The noted maximum (880 nm) is reminiscent of that found for a reference fulleropyrrolidine.[13] In line with an energy transfer mechanism the singlet–singlet absorption revealed a two step grow-in dynamics. The faster process stems from the direct excitation of the fullerene core, while the slower component is ascribed to the actual transfer of excited state energy. The latter assignment is based on the nearly identical dynamics [49 ps (**4**) and 45 ps (**6**)] observed for the second components relative to those of the decays at 500 nm.

Another process follows the conclusion of the energy transfer reaction, the outcome of which on the timescale of a few thousand ps is the formation of a distinct, new maximum at 700 nm. This absorption is in excellent agreement with the triplet excited state absorption of a fulleropyrrolidine reference, which infers that the underlying reaction is an intersystem crossing (ISC) from the fullerene singlet to the energetically lower-lying triplet excited state.

In order to quantify the energy transfer, and to probe a possible contribution from an electron transfer channel, triplet quantum yields were measured in different solvents. The quantum yields deviate substantially from unity (Table 1) and are in the range of 57–63% for **4** and 72–83% for **6**. It is noteworthy that the values are particularly low in polar solvents.

Taking the redox potential of the electron accepting fullerene and those of the two oligomers into account (see above), the possibility of electron transfer is thermodynamically feasible, especially considering the high energies of the photoexcited trimer (**3**; $E_{\mathrm{singlet}}$ = 2.88 eV) and monomer (**5**; $E_{\mathrm{singlet}}$ = 3.09 eV). None of the photoexcited fullerene states (*i.e.* $E_{\mathrm{singlet}}$ = 1.76 eV; $E_{\mathrm{triplet}}$ = 1.50 eV) should, however, be powerful enough to initiate the intramolecular electron transfer and to yield the charge-separated radical pair ($E_{\mathrm{charge\text{-}separated}}$ *ca.* 2 eV).

In the context of confirming the electron transfer mechanism, the strong triplet–triplet absorptions ($\varepsilon_{700\ \mathrm{nm}}$ = 16 100 M$^{-1}$cm$^{-1}$) should be noted, which dominate in large the ps and ns spectra. Consequently, to obtain direct evidence in support of the weaker absorbing radical pair ($\varepsilon_{1000\ \mathrm{nm}}$ *ca.* 8000 M$^{-1}$ cm$^{-1}$) subtraction of the triplet absorption features from, for example, the ns spectrum became necessary. The resulting differential absorption changes reveal a near IR-maximum at 1000 nm and a visible-doublet at 660 and 800 nm, characteristics of the reduced fullerene moiety and the oxidized oligomer,[14] respectively. Another argument for an intramolecular electron transfer is the solvent dependence on the triplet quantum yields mentioned above. Lower $\Phi$-values in polar solvents correlate with larger free energy changes ($-\Delta G°$) for the associated electron transfer and, in turn, indicate a stronger competition to the energy transfer.

In summary, with a novel series of fullerene oligomer composites, we have demonstrated that an intramolecular electron transfer competes with the dominant singlet–singlet energy transfer. This observation is in good agreement with the thermodynamics of the investigated systems that predict a highly exergonic energy transfer ($-\Delta G°$ *ca.* 1.25 eV) and a less exergonic electron transfer reaction ($-\Delta G°$ *ca.* 1.0 eV). More important, lowering the energy of the charge-separated radical, by means of increasing the solvent polarity, enhances the efficiency of the electron transfer channel.

We are indebted to the DGICYT of Spain (Project PB98-0818) for financial support. Part of this work has been supported by the Office of Basic Energy Sciences of the US Department of Energy. This is document NDRL-4216 from the Notre Dame Radiation Laboratory. We are also indebted to Centro de Espectroscopia de la UCM.

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