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Supramolecular Control of Oligothienylenevinylene− Fullerene Interactions: Evidence for a Ground-State EDA Complex

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ABSTRACT

Complementary hydrogen-bonding interactions between a barbituric acid-substituted fullerene derivative (1) and corresponding receptor (2) bearing thiénylenevinylene units are used to assemble a 1:1 supramolecular complex ($K = 5500 \text{ M}^{-1}$). Due to the close proximity of the redox-active moieties within the assembly, strong ground-state electron−donor−acceptor interactions are observed. Photoinduced electron transfer from electron-rich thiénylenevinylene subunits to the fullerene is very fast ($k_{et} = 5.5 \times 10^{12} \text{ s}^{-1}$), as determined by fs-time-resolved transient absorption spectroscopy.

The incorporation of fullerenes into conjugated polymer systems affords composite all-organic devices possessing improved photovoltaic properties.1 To investigate the ground- and excited-state interactions between $C_{60}$ and conjugated polymers, numerous covalent and supramolecular model systems have been studied in great detail.2 Although $C_{60}$ is well-known to participate in the formation of electron donor−acceptor (EDA) complexes with electron donors, including porphyrins,3 aromatic hydrocarbons,4 and aromatic amines,5 no clear evidence for such interactions has been observed in covalent oligothiophene systems reported to date. Intermolecular ground-state EDA complexes involving $C_{60}$ are generally weak, with association constants in the range $10^1$−$10^2 \text{ M}^{-1}$.4,5 Studies of covalent $C_{60}$-porphyrin assemblies


The energy-minimized structure (PM3 Hamiltonian, see Figure 1) of the anticipated complex formed with six hydrogen bonds between 2 and the fullerene-based electron acceptor species 1 shows the intimate contact that is possible between the electron donor and the electron acceptor units. Other conformations in which the 2TV units are not proximal to the fullerene are less stable, requiring either rotation of the amide N=CO bonds or perturbation of the binding site.

Mixing equimolar quantities of building blocks 1 and 2 in aprotic solvents such as toluene or o-dichlorobenzene (oDCB) results in the solubilization of the otherwise poorly soluble fullerene component. The electronic absorption spectra of 1-2 mixtures ([1]/[2] = 1) at various concentrations in oDCB are shown in Figure 2. In addition to the electronic absorption bands of the porphyrin and fullerene, the energy transfers from the porphyrin to the fullerene are observed. The porphyrin-based electron donor exhibits a typical Soret band at around 400 nm, while the fullerene-based acceptor shows a broad absorption band at around 700 nm. The emergence of a new band around 500 nm in the spectrum of the solution indicates the presence of a charge-transfer (CT) state. The CT band intensity increases with increasing concentration of the solution, suggesting the formation of a CT complex 1:1 between the porphyrin and fullerene.

The following text continues with the details of the synthesis and properties of the CT complexes formed with methanofullerene derivatives 1 by association with the matched donor–acceptor hydrogen bonding sites present in the designed receptor introduced by Hamilton. The sidearms of the receptor unit are composed of oligo(thiophylenevinylene)s (nTV, n = 2), which can be appended with solubilizing groups without affecting the planarity of the π-conjugated system. The synthesis of 2 is shown in Scheme 1, starting from 2TV.

### Scheme 1. Synthesis of 2

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\begin{align*}
\text{Scheme 1. Synthesis of 2}^a \\
\text{(a) LDA, CO$_2$, THF, \(-78\, ^\circ\text{C} (40\%)); (b) oxalyl chloride, THF, DMF; (c) 2,6-diaminopyridine (4 equiv, 90\%), THF; (d) isophthaloyl dichloride (0.5 equiv, 80\%), THF.}
\end{align*}
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The recent availability of a C$_{60}$-barbituric acid derivative greatly facilitates the construction of similar C$_{60}$-conjugated oligomer dyads using supramolecular interactions. In this approach, the hydrogen-bonding molecular recognition motif in 1 (Figure 1) is used to bind this fullerene-bearing moiety within the cavity of a barbituric acid receptor bearing complementary hydrogen-bond donor/acceptor sites. This arrangement allows alignment of electron donor and fullerene acceptor units in a geometry suitable for promoting EDA interactions.

Compound 2 is thus expected to form discrete 1:1 complexes with methanofullerene derivative 1 by association with the matched donor–acceptor hydrogen bonding sites present in the designed receptor introduced by Hamilton. The sidearms of the receptor unit are composed of oligo(thiophylenevinylene)s (nTV, n = 2), which can be appended with solubilizing groups without affecting the planarity of the π-conjugated system. The synthesis of 2 is shown in Scheme 1, starting from 2TV.
The contribution of the CT transition to the electronic absorption spectra of the individual components 1 and 2. The result is a strongly allowed transition typical of EDA complexes ($\lambda_{\text{max}} = 390 \text{ nm}; \epsilon_{\text{max}} \approx 32 \, 500 \text{ M}^{-1} \text{ cm}^{-1}$ in oDCB).

Like $C_{60}$, 1 is weakly fluorescent ($\Phi_F = 9 \times 10^{-4}$, $\tau = 1.2 \text{ ns}$ in oDCB). Steady-state fluorescence emission spectra show that the emission of 1 or 2 in 1·2 mixtures is strongly quenched (no emission from the CT state was detected). This decrease in luminescence and lack of sensitized $C_{60}$ fluorescence upon excitation of the 2TV units in 2 is in agreement with fast photoinduced electron transfer (PET) from 2TV to the excited $C_{60}$ unit in 1·2, as previously observed in covalent dyad and triad systems containing $C_{60}$ as an electron acceptor.$^{5,10}$ Addition of methanol (30% v/v) to solutions of 1·2 proved to be effective in restoring the fluorescence of 1, presumably by disrupting the hydrogen-bond network in 1·2. The quenching of the fluorescence of 1 must be accompanied by a reduction of the excited state lifetime. However, time-resolved emission studies indicate that the quenching process is significantly faster than the resolution of our instrument (20 ps fwhm).

Preliminary experiments using ultrafast transient absorption spectroscopy (180 fs fwhm pulse, $\lambda_{\text{ex}} = 310 \text{ nm}$) confirmed the occurrence of fast PET in the supramolecular assembly. Whereas the transient absorption spectra of 2 in oDCB are characterized by a single band centered at 650 nm, in mixtures of 1 and 2 ($[1] = [2] = 4 \times 10^{-4} \text{ M}$ in oDCB), an additional absorption band is seen at 560 nm (Figure 3). The latter is attributed to the absorption of the

Figure 2. Left: Electronic absorption spectra (apparent molar extinction coefficient) of equimolar mixtures of 1 and 2 at different concentrations in o-dichlorobenzene. Concentrations used: $2.4 \times 10^{-6} \text{ M}$ (---), $2.2 \times 10^{-5} \text{ M}$ (----), $4.2 \times 10^{-5} \text{ M}$ (-----), $6.6 \times 10^{-5} \text{ M}$ (--), $1.0 \times 10^{-4} \text{ M}$ (-----), $1.4 \times 10^{-4} \text{ M}$ (---). Arrows indicate spectral changes upon increasing concentration. Inset shows the change in absorption at 390 nm with increase of concentration.

Figure 3. Transient absorption spectra of 1·2 and 2 (curves A and B, respectively, 3 ps after flash, in oDCB). The absorption of the free $2^+$ (curve C) was obtained by conventional ns-laser flash photolysis of 2 in the presence of tetracyanoethylene (1:1 CH$_3$CN/oDCB, $\lambda_{\text{ex}} = 355 \text{ nm}$).
observation of an absorption band in the NIR region at ca. 1050 nm, attributed to $^{1}¥-$ bound to $^{2}¥+$. Kinetic analysis at 570 nm provides a forward electron-transfer rate of $5.5 \times 10^{12}$ s$^{-1}$. The recovery of the ground state (by back electron transfer) occurs with a rate constant $k_{\text{bet}} = 4.5 \times 10^{9}$ s$^{-1}$. No evidence for energy transfer to the lower-lying $S_1$ or $T_1$ states of 1 could be detected.

In conclusion, supramolecular 1:1 hydrogen-bonded assemblies were constructed using a fullerene–barbituric acid component and a suitable receptor dyad possessing nTV arms. The structure, whose engineered orientation between the oligothienylenevinylene electron donor and fullerene electron acceptor is characterized by a large binding constant and the observation of an intense EDA absorption feature between the 2TV and C$_{60}$ moieties, demonstrates the utility of supramolecular systems in understanding the molecular-scale interactions between redox-active components.

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Supporting Information Available: Data for 2 (1H NMR, 13C NMR, HRMS, IR), binding measurements, and fs-TRA experiments. This material is available free of charge via the Internet at http://pubs.acs.org.