ORGANIC LETTERS

2005
Vol. 7, No. 5
807−810

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

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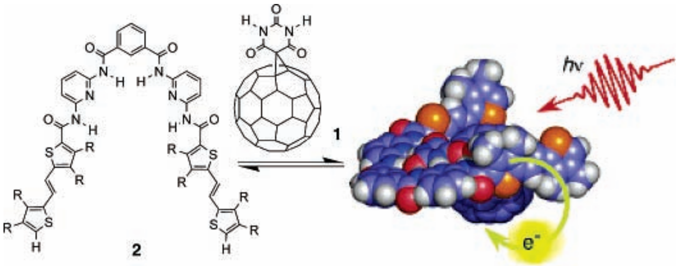
Received December 2, 2004

ABSTRACT



Complementary hydrogen-bonding interactions between a barbituric acid-substituted fullerene derivative (1) and corresponding receptor (2) bearing thienylenevinylene units are used to assemble a 1:1 supramolecular complex ($K = 5500\ M^{-1}$). 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 thienylenevinylene subunits to the fullerene is very fast ($k_{et} = 5.5 \times 10^{12}\ s^{-1}$), 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 M^{-1}.[4,5] Studies of covalent C_{60}-porphyrin assemblies

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10.1021/ol047527r CCC: $30.25

indicate that the distance and relative orientation of the partners are crucial in determining the strength of the observed CT band (log $\epsilon = 1$ to 3), and strong interactions are found for assemblies in which the porphyrin and fullerene moieties are forced into a face-to-face geometry.[3a−e] The recent availability of a C_{60}-barbituric acid derivative[6] 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.

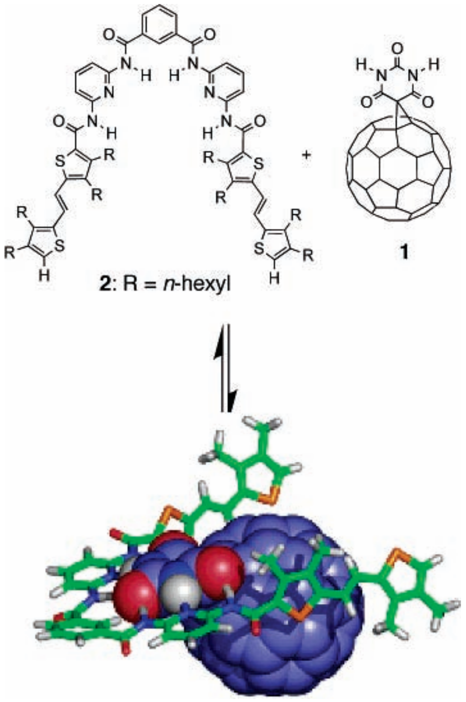
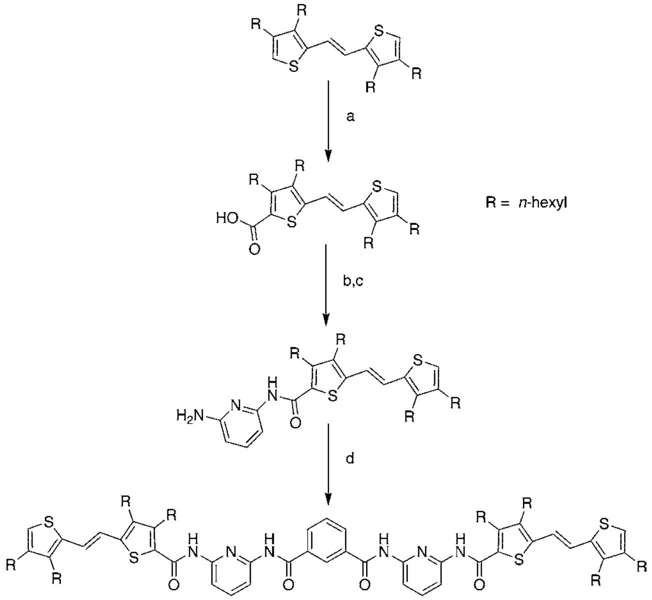


Figure 1. Compound **2** possesses a hydrogen-bonding receptor site connected to two bis(thienyenelvinylene) units. Bottom: Energy-minimized (semiempirical PM3 Hamiltonian, R = methyl) structure of complex **2·1** formed in the presence of the C_{60}-barbituric acid adduct **1**.

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.[7] The sidearms of the receptor unit are composed of oligo(thienylenevinylene)s (nTV, $n = 2$), which can be appended with solubilizing groups without affecting the planarity of the π-conjugated system.[2a] The synthesis of **2** is shown in Scheme 1, starting from 2TV.[8]

Scheme 1. Synthesis of **2**[a]



[a] Conditions: (a) LDA, CO_2, THF, −78 °C (40%); (b) oxalyl chloride, THF, DMF; (c) 2,6-diaminopyridine (4 equiv, 90%), THF; (d) isophthaloyl dichloride (0.5 equiv, 80%), THF.

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

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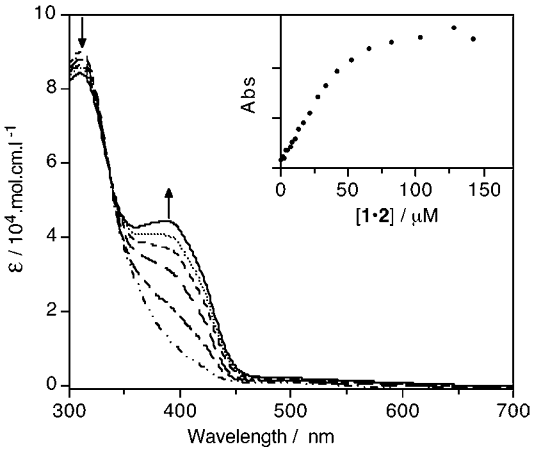

Figure 2. Left: Electronic absorption spectra (apparent molar extinction coefficient) of equimolar mixtures of **1** and **2** at different concentrations in *o*-dichlorobenzene. Concentrations used: 2.4 × 10^{-6} M (—••), 2.2 × 10^{-5} M (— - - —), 4.2 × 10^{-5} M (— — —), 6.6 × 10^{-5} M (- - -), 1.0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

transitions of the individual species, an additional band devoid of fine structure can be observed at 390 nm. This absorption feature, which gives direct evidence for complexation, is not observed in control experiments using **2** and pristine C_{60} or 5,5-diethylbarbituric acid or **1** and a barbituric acid receptor without the 2TV units. With the exception of the resonances of the N−H protons taking part in hydrogen bonding, which undergo a significant downfield shift, the ^{1}H NMR spectrum of **1·2** mixtures is similar to that of **2**, indicating that no covalent transformation of the components has taken place. The new absorption band is therefore attributed to ground-state EDA interaction between the electron-rich 2TV and electron-poor fullerene moieties, which has not been previously observed in analogous covalent assemblies. The strength of this interaction can be rationalized by the face-to-face approach between the 2TV and fullerene moieties, combined with favorable thermodynamic factors due to hydrogen-bonding. Increasing solvent polarity (toluene, oDCB, benzonitrile) enhances the strength of the CT band, though with only a minor effect on the energy of the band's absorption maximum.[9]

Monitoring the disappearance of the CT band upon dilution gives direct access to the binding constant for the formation of the **1·2** complex (log $K_a = 3.74 \pm 0.10$ M^{-1} in oDCB assuming 1:1 binding stoichiometry; see ESI for details), which is comparable to association constants observed for this host−guest binding motif.[7] The presence of an isosbestic point at 355 nm confirms the formation of a single species. The contribution of the CT transition to the electronic absorption spectra of **1·2** can be deduced by subtracting the spectra of the individual components **1** and **2**. The result is a strongly allowed transition typical of EDA complexes (λ_{max} = 390 nm; $\epsilon_{max} \approx$ 32 500 M^{-1} cm^{-1} in oDCB).

Like C_{60}, **1** is weakly fluorescent ($\Phi_F = 9 \times 10^{-4}$, τ = 1.2 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.[2,10] 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, λ_{ex} = 310 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 × 10^{-4} M in oDCB), an additional absorption band is seen at 560 nm (Figure 3). The latter is attributed to the absorption of the 2TV$^{\bullet+}$ formed by electron transfer to the nearby fullerene in **1·2** assemblies by comparison with the transient spectrum obtained from ns-laser flash-photolysis of solutions of **2** in the presence of another electron acceptor, tetracyanoethylene (Figure 3, curve C). This is further supported by the

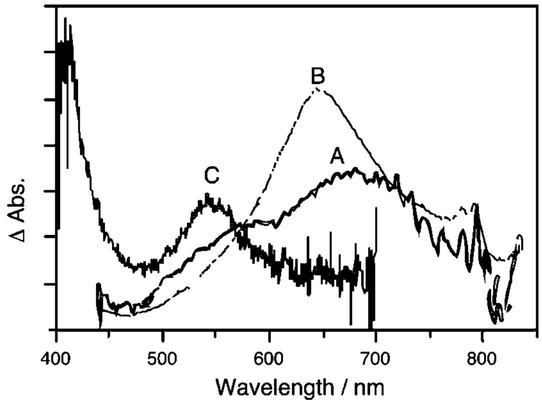

Figure 3. Transient absorption spectra of **1·2** and **2** (curves A and B, respectively, 3 ps after flash, in oDCB). The absorption of the free **2**$^{\bullet+}$ (curve C) was obtained by conventional ns-laser flash photolysis of **2** in the presence of tetracyanoethylene (1:1 CH_3CN/oDCB, λ_{ex} = 355 nm).

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(9) The high-energy position of the band (2.75 eV, as deduced from the onset of the absorption) suggests that it involves orbitals other than the LUMO of **1** and the HOMO of **2**.

(10) Photoinduced electron transfer in **1·2** is calculated to be strongly exothermic: $\Delta G_{ET} \approx -0.8$ eV, assuming $E_{ox}(\mathbf{2}) = 0.89$ V and $E_{red}(\mathbf{1}) = -0.7$ V vs SCE and $E_{00} = 2.75$ eV; see ref 2a.

observation of an absorption band in the NIR region at ca. 1050 nm, attributed to $\mathbf{1}^{\bullet-}$ bound to $\mathbf{2}^{\bullet+}$. Kinetic analysis at 570 nm provides a forward electron-transfer rate of 5.5×10^{12} s^{-1}. The recovery of the ground state (by back electron transfer) occurs with a rate constant $k_{bet} = 4.5 \times 10^9$ 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 *n*TV 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.

Acknowledgment. Financial support from the French Ministry of Research, the CNRS (AC Nanosciences), the DPI for M.Z., the NWO for the femtosecond equipment, and the Universiteit van Amsterdam is gratefully acknowledged.

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

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