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Molecular Panels for Energy Transduction in C_{60}-Based Conjugates

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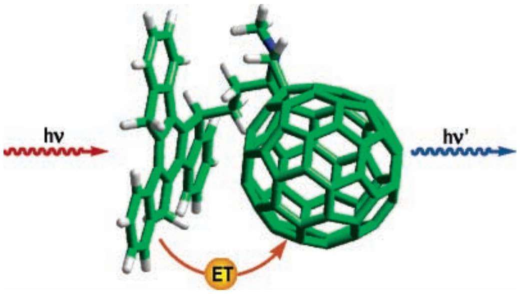
ABSTRACT



Light-harvesting C_{60}-based dyads endowed with a truxene fluorophore unit have been synthesized. Their photophysical studies in solution reveal a singlet–singlet energy transfer deactivation mechanism that confirms the actuation of the latter as an efficient molecular panel for light absorption and energy transduction. Those processes strongly depend on the nature of the linker connecting both chromophores, such as C_{60} and truxene, owing to the overlapping degree between their respective orbitals.

The conversion of sunlight into energy by natural or artificial devices—such as photosynthetic apparatus or organic solar cells—commences with light absorption and, upon a complex sequence of energy and electron-transfer processes, culminates with the generation of chemical or electrical power.[1,2] In nature, the absorption and transduction of incident light is performed by a broadly absorbing and efficient antennae system. A variety of chromophores have been utilized to construct simpler light-harvesting models capable of mimicking the key steps in photosynthesis.[3]

The outstanding photophysical and electrochemical features of [60]fullerene render it an ideal component for the integration into efficient electron and energy transduction systems.[4] An important thrust of current work is to gather fluorophores, with large absorption cross sections, to C_{60}.[5] This is meant to enhance the ground-state absorption of the final conjugates and, hence, to promote the light-harvesting

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effect.[6] In this context, polycyclic aromatics meet the criteria for efficient artificial photosynthetic antennas owing to their high-lying excited states and their strong fluorescing features.[7] In addition to these purely optical and electronic considerations, the facile modification of the $-CH_2-$ groups in truxenes and their ability to self-assemble through π-stacking interactions[8] has prompted the applicability of such polycyclic aromatics in molecular electronics.[9]

In this contribution, we present the synthesis of novel artificial antenna systems **8** and **9**, in which truxenes are connected to C_{60}. The spatial overlap between both building blocks is largely modulated by the aliphatic linkers. Two different geometrical scenarios affect the energy transduction processes between both photoactive moieties.

The synthesis of C_{60}−truxene conjugates started with the deprotonation of truxene (**1**) with butyllithium. The corresponding monoanion was reacted with 2-(2-bromoethyl)-1,3-dioxolane (**2**) to give the monosubstituted derivative **3** as a racemic mixture. Transacetalization from **3** with paraformaldehyde and *p*-toluenesulfonic acid yielded aldehyde **4**. Successive reduction of **4** followed by an esterification reaction with *p*-formylbenzoic acid (**5**) and DCC/DMAP, as activating reagents, led to aldehyde **7**. The final step toward **8** and **9** involved the 1,3-dipolar cycloaddition reaction between azomethine ylides, generated in situ from aldehydes **4** and **7**, and sarcosine, and a double bond of C_{60}. Both conjugates were isolated as stable brownish solids in moderate yields (>40%) (Scheme 1). The spectroscopic data—^{1}H and ^{13}C NMR, FTIR, MALDI-MS, and UV−vis (see Figure S1)—support the proposed structures of all new compounds (see Supporting Information).

Unlike pyrrolidino[3′,4′:1,2][60]fullerenes, in which the organic addends lack chirality, the presence of a stereogenic center in aldehydes **4** and **7** induces the formation of target compounds **8** and **9** as diastereomeric mixtures. Accordingly, ^{1}H NMR spectrum of **8** clearly shows two sets of resonances. These sets relate to the close proximity of both chiral centers. Nevertheless, no diastereoselectivity is observed due to the use of aldehydes **4** and **7** as a racemic mixture.[10]

To achieve a deeper understanding about the influence of the linker in the spatial orientation between both chromophores, quantum mechanical calculations at the semiempirical PM3 level were performed for all the diastereomeric forms of conjugate **8** (see Figure S2).[11] As expected, the four stereoisomers appeared to be practically isoenergetic. In correspondence with the rotational freedom in **8**, around the truxene$-CH_2-$ axis, two energy-minimized conformers were found, namely, **I** and **II**. In **I**, the truxene unit adopts a folded conformation, while for **II**, a stretched geometry dominates (see Figure 1). Theoretical calculations predict that conformer **II** is only 2.59 kcal mol^{-1} more stable than conformer **I**. Considering the geometric scenario, especially for conformer **I**, brings the C_{60} and truxene surfaces into close proximity (∼4 Å). Therefore, one might expect weak stacking aromatic interactions,[12] which would, in turn, accelerate the energy transduction between the two building blocks (vide infra). Calculations predict similar distances (ranging between 4 and 5 Å) and energies ($\Delta E \sim 0.6$ kcal mol^{-1}) for the diastereomers of dyad **8**.

In stark contrast, the optimized geometry for conjugate **9** shows a stretched configuration where a larger distance separates the two building blocks and prevents an optimal overlapping of their surfaces (Figure S3).

The redox behavior of **8** was investigated by cyclic voltammetry (CV) in an ODCB/MeCN (4/1) mixture at room temperature. Aldehyde **4**, truxene (**1**), and C_{60} have also been studied; see Table S1 in Supporting Information. The saturation of one of the C_{60}'s double bonds in **8** ($E^1_{\text{red}} = -0.98$ V, $E^2_{\text{red}} = -1.34$ V, $E^3_{\text{red}} = -1.87$ V) results in a cathodic shift of its reduction potentials in comparison with those of unsubstituted C_{60} ($E^1_{\text{red}} = -0.84$ V, $E^2_{\text{red}} = -1.24$ V, $E^2_{\text{red}} = -1.70$ V). In addition, a broad oxidation wave appears at 1.51 V, which we ascribe to the oxidation of truxene. Despite the redox amphoteric character in **8**, its high HOMO−LUMO gap (2.39 eV) prevents an electron-transfer process upon light irradiation (vide infra).

Steady-state and time-resolved studies were performed to elucidate the photophysical features of the new synthesized conjugates **8** and **9**. The characteristic fluorescence spectra (see Figure S4) that truxene **4** exhibits in a variety of solvents

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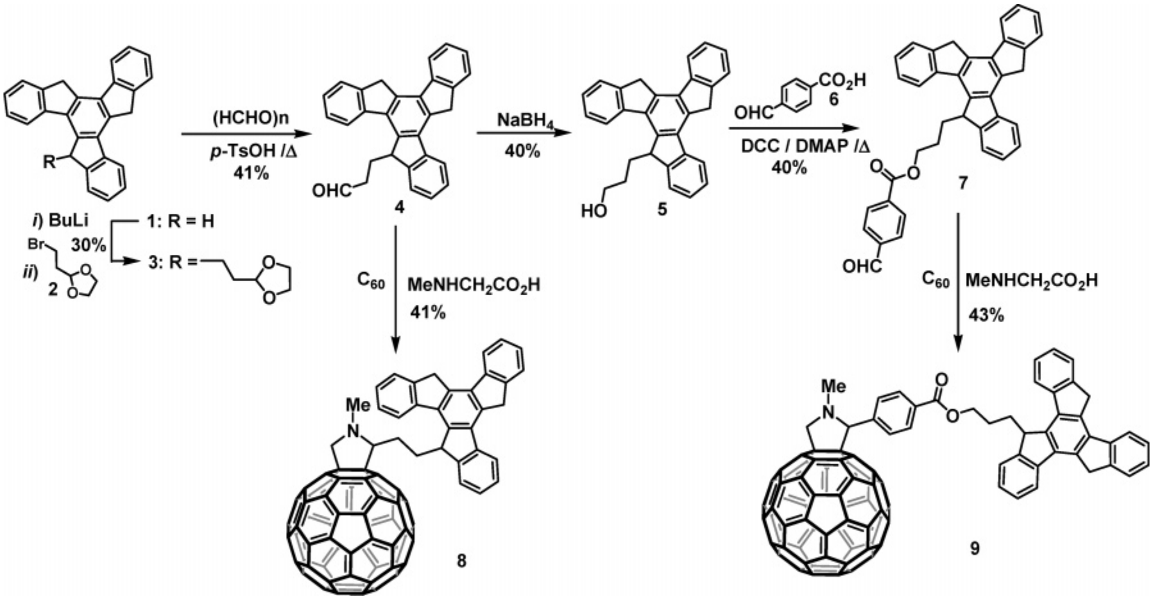
(10) The diastereomeric mixture was not observed in dyad **9** due, probably, to the larger separation between both stereogenic centers.

(11) *HyperChem*, release 7.51; HyperCube Inc.: Gainesville, FL, 2002.

(12) The small shifts observed for the aromatic signals in the ^{1}H NMR spectrum of dyad **8** in comparison to those of aldehyde **4** could be indicative of weak $\pi-\pi$ interactions (see Supporting Information and ref 8).

Scheme 1. Synthesis of C_{60}−Truxene Conjugates **8** and **9**



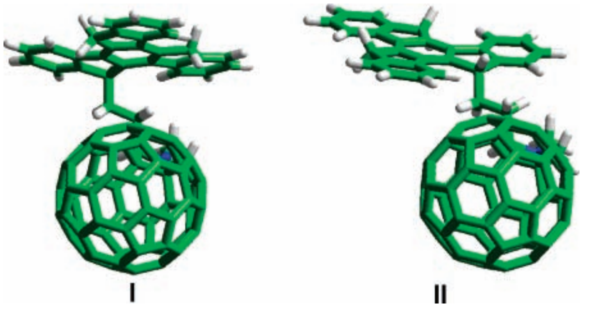


Figure 1. Lowest energy optimized (PM3) conformers for compound **8**. The depicted configuration for the pyrrolidine and truxene chiral carbons is *R* and *S*, respectively.

(i.e., toluene, THF, and dichloromethane) comprise a distinct maximum around 505 ± 5 nm. Such a value corresponds to a singlet excited state energy of around 2.45 eV. In parallel with the high fluorescence quantum yields (i.e., 0.18), we also see remarkably long-lived fluorescence lifetimes (toluene, 2.4 ± 0.1 ns; THF, 3.0 ± 0.1 ns, dichloromethane, 3.1 ± 0.1 ns).

In time-resolved transient absorption measurements performed with aldehyde **4**, following 150 fs photoexcitation at 387 nm, we see the nearly instantaneous formation of the truxene singlet excited-state features. Characteristics of the latter are transient maxima at 480, 625, and 750 nm (Figure S5). Analyzing the growth of the singlet helped in evaluating the formation rate as 6.9×10^{11} s^{-1}. It is very likely that such a fast rate reflects an internal conversion process evolving from a higher-lying excited state. In the femtosecond experiments, the singlet excited state decays only slowly within the 1.6 ns time scale to afford the corresponding triplet excited state. The triplet characteristics of **4** were tested in complementary nanosecond experiments, that is, 6 ns photoexcitation at 355 nm (Figure S6). In its transient triplet spectrum, a rather broad feature is discernible, for which a lifetime of 11 μs was determined in the absence of molecular oxygen.

In contrast to **4**, the corresponding C_{60}−truxene conjugates **8** and **9** give rise to a much lower truxene-centered fluorescence quantum yield in the visible range, namely, 450−650 nm (see Figure S4). The difference in fluorescence is as large as 2 orders of magnitude (i.e., a factor of nearly 450), but does not depend notably on the solvent polarity. On the other hand, the quenching seems to depend strongly on the chromophore distance. Hereby, conjugate **8**, in which the two chromophores adopt a spatially close geometry to each other, reveals an appreciable stronger quenching (i.e., toluene, 4×10^{-4} versus 1.2×10^{-3}), relative to dyad **9**, where the benzoate group prevents the approximation between the truxene and fullerene surfaces.

Insight into the nature of the photoproduct came from monitoring the fluorescence spectra in the range between 650 and 850 nm. In fact, a fluorescence pattern, which resembles that of a *N*-methylpyrrolidino[3′,4′:1,2][60]-fullerene (**Fp**), used as reference, supports an exothermic transduction of singlet excited-state energy from the truxene component (2.45 eV) to the fullerene component (1.76 eV). Figure 2 demonstrates that the transduction is quantitative, as confirmed by measurements, in which the fullerene fluorescence quantum yields were determined. The quantum yields in **Fp**, **8**, and **9** in toluene were close to constant: 6.0×10^{-4} (**Fp**), 5.9×10^{-4} (**8**), and 5.7×10^{-4} (**9**).[13]

Considering the quenching efficiency, it is hardly surprising that in time-resolved fluorescence measurements no particular detectable fluorescence was monitored within our instrumental time resolution of 0.1 ns.[14]

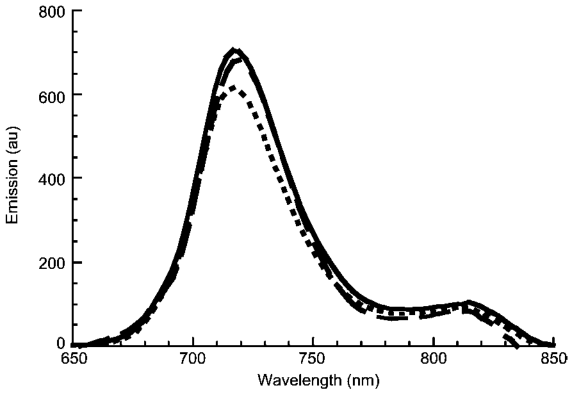


Figure 2. Room temperature fluorescence spectra of **Fp** (solid line), C_{60}−truxene (**8**, dashed line), and C_{60}−truxene (**9**, dotted line) in toluene photoexcited at 386 nm with matching absorption (i.e., 0.2) at the excitation wavelength.

With the objective to measure the intraconjugate energy transfer rates in **8** and **9** directly, we turned to femtosecond experiments (Figure S7). At early times, we see characteristics that are similar to those seen with **4**. This confirms, at least in part, the truxene photoexcitation. Instead of seeing, however, the slow intersystem crossing, which in **4** populates the triplet excited state, an ultrafast decay is noted in **8** (1.1×10^{12} s^{-1}) and **9** (6.6×10^{11} s^{-1}). The conclusion of the fast truxene decays is the C_{60} singlet excited state, which intersystem crosses at longer times (6.6×10^{-8} s^{-1}). Additional nanosecond experiments (Figure S8) corroborate the C_{60} triplet excited state as the quantitative photoproduct (i.e., 90−95%).

In short, two light-harvesting C_{60}−truxene conjugates have been synthesized. The different nature of the spacers—that connect the two chromophores—has been shown to vary the spatial overlap and, in turn, to exert a notable impact on the photophysical features. Moreover, steady-state and time-resolved investigations clearly exemplify that the truxene fragment acts as a molecular panel capable of harvesting light and transducing it efficiently through a singlet−singlet energy transfer mechanism.

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Supporting Information Available: Experimental details, spectroscopic characterization of all new compounds, Table S1, and Figures S1−S8. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Independent proof for the energy transfer assumption is based on excitation spectra, which mirror image the ground-state absorption of both chromophores, that is, truxene and fullerene

(14) Actually, the deactivation rates are assessed as ranging from 1.3×10^{12} to 4.6×10^{11} s^{-1}.