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A New Photoactive and Highly Soluble C_{60}–TTF–C_{60} Dimer: Charge Separation and Recombination

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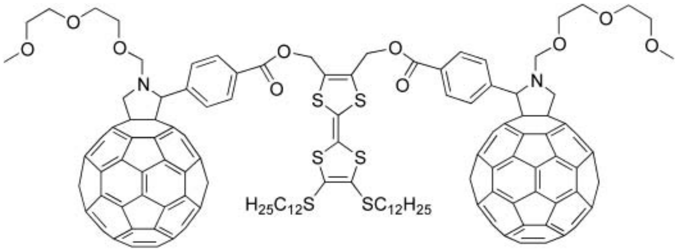
ABSTRACT



The covalent linkage of two [60]fullerene cores to a tetrathiafulvalene (TTF) donor affords a soluble and photoactive C_{60}–TTF–C_{60} triad. Spectroscopic and photophysical characterization of the C_{60}–TTF–C_{60} triad are given. Although the cyclic voltammetry measurements reveal no notable interaction between the chromophores in the ground state, photophysical data show that in the excited state an intramolecular electron transfer, evolving from the TTF donor to the singlet state of C_{60}, prevails, yielding a long-lived charge separated radical pair.

The implementation of the unique 3-dimensional electron acceptor C_{60} into molecular donor−acceptor ensembles, in conjunction with appropriate photosensitizers and/or electron donors, is a viable concept to design novel materials for artificial photosynthesis, photovoltaics, and molecular electronics.[1] An intriguing, but far less examined, approach involves fullerene dimers in which, for instance, two fullerene cores are connected to the two opposite ends of a molecular, electroactive bridge.[2] The broad and interdisciplinary interest in connecting fullerene cages was initiated by the early observation that fullerenes coalesce in thin films upon laser irradiation.[3] Consequently, different synthetic methodologies have been developed to control the formation, composition, and orientation of fullerene dimers.[2] The most promising procedures encompass (i) dimerization of [60]fullerene or a functionalized fullerene precursor, (ii) bifunctional cycloaddition to [60]fullerene, (iii) covalent attachment of two fullerene spheres through a molecular bridge, or (iv) noncovalent dimers.

In the present Letter, we wish to report on a novel synthetic strategy toward fullerene dimers in which an electroactive tetrathiafulvalene (TTF) moiety is incorporated as an electroactive spacer. Furthermore, we present for the first time photophysical studies carried out with this new molecular C_{60}−TTF−C_{60} triad.

A major shortcoming, commonly encountered in the study of fullerene dimers, is their inherently weak solubility. This, in turn, prevents their meaningful spectroscopic or electrochemical characterization. To circumvent this intrinsic

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(2) Segura, J. L.; Martín, N. *Chem. Soc. Rev.* **2000**, *29*, 13.

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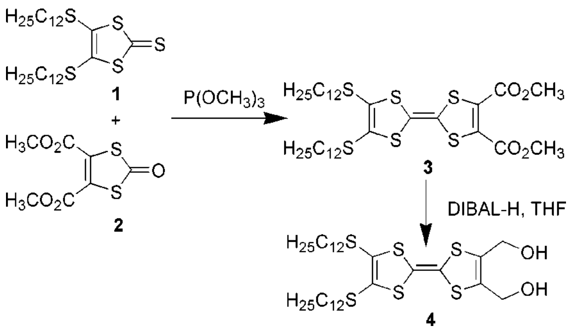
problem, both the TTF and the fullerene moiety were functionalized with solubilizing dodecyl and oligoether chains, respectively. In particular, TTF derivative **4** was synthesized by following the synthetic route summarized in Scheme 1. The latter was adapted from a procedure developed earlier by Bryce and co-workers regarding the synthesis of bis(hexylthio)analogues.[4] Under standard phosphite-induced cross-coupling conditions, the reaction of 4,5-bis(dodecylthio)-1,3-dithiole-2-thione (**1**) with 4,5-bis-(methoxycarbonyl)-1,3-dithiol-2-one (**2**) afforded TTF derivative **3** as the main product. Subsequent reduction of diester **3** with diisobutylaluminum hydride led to bis(hydroxymethil)derivative **4** in 70% yield.

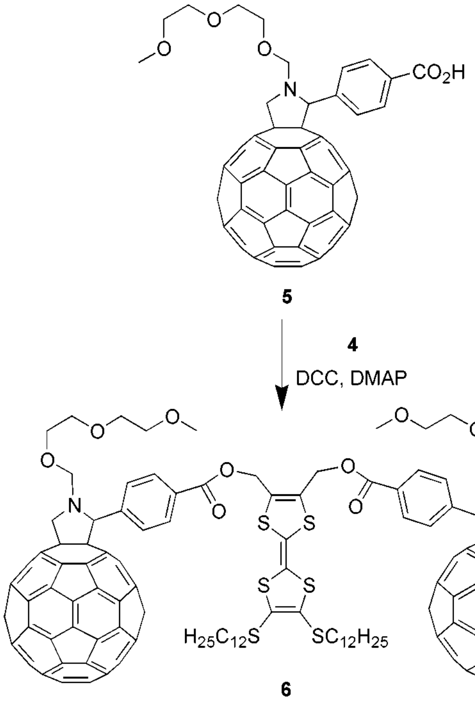
Scheme 1



Compound **4** served as starting material for the preparation of the C_{60}−TTF−C_{60} triad as is depicted in Scheme 2.

Thus, bis(hydroxymethyl)TTF derivative **4** was reacted with a fullerene derivative (**5**)[5] in chloroform in the presence of dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP) to yield C_{60}−TTF−C_{60} triad **6** (43%).

Scheme 2



Because of the presence of the long alkyl and oligoether chains, triad **6** is quite soluble in different organic solvents, thus allowing a full spectroscopic and electrochemical characterization.[6]

Cyclic voltammetry measurements, performed in dichloromethane,[7] reveal in the anodic scan the presence of two quasireversible oxidation waves at $E^1_{ox} = 0.51$ V and $E^2_{ox} = 0.92$ V. They correspond to the formation of the TTF π-radical cation and dication, respectively. In the cathodic scan, the three quasireversible waves at $E^1_{red} = -0.75$ V, $E^2_{red} = -1.15$ V, and $E^3_{red} = -1.67$ V were assigned to the first three reduction steps of the fulleropyrrolidine. Closer inspection of the redox features reveals a good correspondence between the redox potential of the triad (**6**) and those of the two references (**5** and **4**).

Importantly, the absorption spectrum of triad **6**, for example, in dichloromethane solution shows superimposed features of fulleropyrrolidine **5** and bis(dodecylthio)tetrathiafulvalene **4**. These data indicate that both electroactive units (i.e., TTF and C_{60}) preserve their identity in the corresponding triad **6** with no significant electronic interaction in the ground state. This is in excellent agreement with previous reports regarding C_{60}-based dyads containing either TTF[8] or π-extended TTF[9] donors.

In an effort to characterize the photophysics of triad **6**, a series of time-resolved and steady-state experiments were conducted in different solvents, ranging from toluene ($\epsilon = 2.38$) to dimethylformamide ($\epsilon = 36.7$). Taking the fullerene's susceptibility toward electrons and the strong donor properties of TTF in concert, charge separation is expected to dominate the deactivation of the fullerene singlet excited state. Calculations regarding the free energy changes ($-\Delta G°_{ET}$), associated with an intramolecular electron transfer from TTF to the photoexcited fullerene, further support this view, that is, a strongly exothermic electron transfer in polar solvents (see Table 1).

The steady-state fluorescence spectra of triad **6** in toluene, *o*-dichlorobenzene, benzonitrile, and dimethylformamide were probed, relative to that of a reference fulleropyrrolidine,

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(6) Triad **6** gave satisfactory analytical and spectroscopic data. Selected spectroscopic data for **6**. ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.89 (2 × d, $J = 8.2$ Hz, 4H, C_6H_4), 7.58 (2 × d, $J = 8.2$ Hz, 4H, C_6H_4), 5.30 (2 × s, 2H, 2 NC*H*), 5.22 (2 × s, 4H, N−C*H*$_2$−O), 4.33 (d, $J = 9.8$ Hz, 2H, NC*H*H), 4.2−3.6 (m, 28H, O−CH_2, O−CH_3, NCH*H*), 2.9 (2 × t, 4H, S−C*H*$_2$), 2.2−0.8 (m, 46H, CH_2, CH_3). FT-IR (KBr, cm^{-1}): 2922, 2850, 1701, 1643, 1521, 1448, 1342, 1108, 33. UV−vis (CH_2Cl_2) λ (nm): 234, 260, 318.

(7) Reference electrode, SCE; working electrode, glassy carbon; supporting electrolyte, 0.1 M $Bu_4N^+ClO_4^-$, at 200 mV/s.

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Table 1. Photophysical Data of Triad **6** in Different Solvents

compound	solvent	dielectric constant (ϵ)	quantum yield fluorescence (Φ)	lifetime singlet state (τ)	lifetime radical pair (τ)	$-\Delta G°_{ET}$[a]	quantum yield triplet (Φ)
reference	toluene	2.38	6.0×10^{-4}	1.6 ns	"-"	"-"	1.0
triad **6**	toluene	2.38	4.0×10^{-4}	0.97 ns		0.06 eV	0.93
	o-dcb	9.8	3.5×10^{-4}	0.71 ns	54 ns	0.70 eV	0.83
	bzcn	24.8	2.7×10^{-4}	0.47 ns	88 ns	0.85 eV	0.63
	dmf	36.7	1.8×10^{-4}	0.32 ns	121 ns	0.88 eV	0.62

[a] Calculated from the following expressions: $-\Delta G_{ET} = \Delta E_{0-0} - (\Delta G_{BET})$; $\Delta G_{ET} = E_{OX} - E_{RED} + \Delta G_S$; $\Delta G_S = e^2/(4\pi\epsilon_0))\ [(1/(2R_+) + 1/(2R_-) - 1/R_{D-A})\ 1/\epsilon_S - (1/(2R_+) + 1/(2R_-))\ 1/\epsilon_R]$; $E_{OX} = E_{1/2}(D^{\bullet+}/D)$; $E_{RED} = E_{1/2}(A/A^{\bullet-})$; R_+ = radius donor (3.37 Å); R_- = radius acceptor (4.4 Å); R_{D-A} = center to center distance (9.16 Å). ϵ_S = dielectric constant of solvent used for photophysical studies. ϵ_R = dielectric constant of solvent used for measuring the redox potentials (9.08). $^\bullet E_{0-0}$ = excited-state energy of chromophore (1.76 eV).

as a first, crude measure to indicate excited-state interactions. In the reference itself, only a weak solvent dependence was noted. Specifically, the *0−0 transition shifts progressively from 713 nm (toluene) to 719 nm (dimethylformamide), while the emission intensity remains unaffected. Triad **6**, on the other hand, gives rise, besides the same solvent-dependent red- hifts, to substantially lower fluorescence intensities (see Table 1 and Figure 1). Most importantly, a clear correlation can be drawn between the fluorescence quantum yields (Φ) and the solvent polarity: (Φ_{toluene}) > ($\Phi_{o-\text{dichlorobenzene}}$) > ($\Phi_{\text{benzonitrile}}$) > ($\Phi_{\text{dmf}}$).

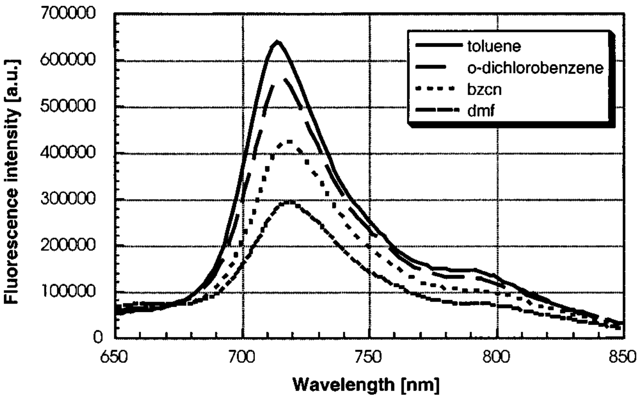

Figure 1. Emission spectra of triad **6** in different solvents (excitation wavelength 337 nm).

Time-resolved pico- and nanosecond transient absorption spectroscopy was conducted to probe the fate of the photoexcited fullerene in **6** and to inspect the identity of the resulting products. In particular, the instantaneously formed fullerene singlet−singlet absorption, with a characteristic maximum around 880 nm,[10] decays rapidly, following the completion of the short laser pulse in **6** (18 ps; 355 nm). This is in sharp contrast to the singlet excited-state dynamics of the reference fulleropyrrolidine, which is governed by a much slower (τ = 1.6 ns) and nearly quantitative ($\Phi \sim 1.0$) intersystem crossing to the triplet excited state. Furthermore, the fast deactivation dynamics in triad **6** are coupled to a synchronously occurring grow-in of a new and broad transient absorption in the monitored wavelength region between 440 and 960 nm.

To complement the picosecond measurements, triad **6** was probed under identical conditions in a set of nanosecond experiments. In all solvents, except toluene, a set of VIS and NIR maxima at 430 and 1000 nm, respectively, were recorded. These attributes agree unmistakably with the spectral fingerprints known for the one-electron oxidized $TTF^{\bullet+}$ [8b] and the one-electron reduced $C_{60}^{\bullet-}$,[9] respectively. From this spectral resemblance we conclude that the resulting $C_{60}^{\bullet-}-TTF^{\bullet+}$ radical pair is formed via a photoinduced electron-transfer evolving from the TTF donor to the electron-accepting singlet excited state of the fullerene.

On a time scale of a few hundred nanoseconds the $C_{60}^{\bullet-}-TTF^{\bullet+}$ radical pair exhibits monoexponential decay dynamics, converting the distinct features of the radical ions into a new transient. Interestingly, the product of back electron transfer was confirmed to be the fullerene triplet excited state, as distinguished by maxima at 360 and 700 nm (Figure 2).[9] This pathway can be best rationalized on the basis of the

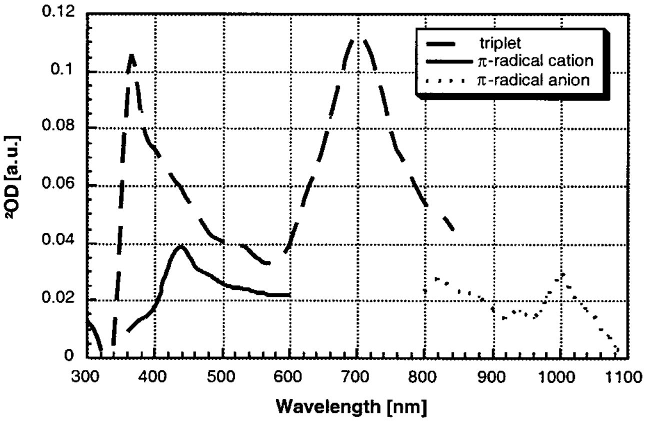

Figure 2. Differential absorption spectra obtained upon flash photolysis of triad **6**, revealing the characteristics of the π-radical cation and π-radical anion (immediately after the laser pulse) and those of the fullerene triplet excited state (300 ns after the laser pulse).

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strong second-order vibronic spin–orbit coupling induced by the sulfur nucleus.[11] The latter results in a rapid spin-state transformation of the TTF π-radical cation. In turn, the singlet character of the $C_{60}^{\bullet-}$–$TTF^{\bullet+}$ radical pair changes to the corresponding triplet features and, therefore, facilitates the fullerene triplet production. Probing a solution of the fulleropyrrolidine reference with matching absorption at the 337 nm excitation wavelength allowed the determination of the quantum yield of the fullerene triplet in triad **6** via relative actinometry. High triplet yields, ranging typically between 62 and 93%, are a clear token of the overall efficiency.

To further test the triplet formation via the back electron transfer route, the triplet quantum yields of triad **6** were measured in an oxygenated and deoxygenated system, 50 ns after the laser pulse, and compared to that of a fulleropyrrolidine reference. It should be noted that $C_{60}^{\bullet-}$ itself reacts quite slowly with oxygen, for instance, in benzonitrile at $\sim 10^2$ M^{-1} s^{-1}.[12] Thus, not surprisingly the quantum yields in triad **6** were identical for the two scenarios. In contrast, the reference showed a marked decreased (i.e., 12%) which is due to the nearly diffusion-controlled reaction between fullerene triplets and molecular oxygen.

In summary, we reported the synthesis, electrochemistry, and photophysical properties of a new, highly soluble C_{60}–TTF–C_{60} triad. Although no significant electronic interactions were found between the electroactive species in the ground state, an efficient intramolecular electron transfer occurs in the excited state resulting in the formation of a long-lived charge-separated state. These data reveal that electroactive C_{60} dimers are appealing ensembles and potentially useful in photovoltaic devices.

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