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Efficient Charge Separation in C_{60}-Based Dyads: Triazolino[4′,5′:1,2][60]fullerenes

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Triazoline[4,5][60]fullerenes are strong electron acceptors that form with tetrathiafulvalene (TTF), a novel type of donor−acceptor dyad exhibiting efficient improved electron-transfer dynamics. In particular, a rapid photoinduced intramolecular electron transfer, forming a charge-separated state, is followed by a slow charge recombination to generate the fullerene triplet excited state in moderate quantum yields.

Introduction

The design of photoactive composites bearing strong electron-donor moieties attached to electron acceptors, such as C_{60}, is an intriguing approach for the design of materials suitable for artificial photosynthesis or molecular electronic devices.[1] Therefore, during the past few years, a variety of C_{60}-donor arrays have been synthesized in search of systems with improved charge separation properties.[2]

Recently, we reported that the small HOMO−LUMO gap (−5.35 eV) in a C_{60}-based tetrathiafulvalene (TTF)-containing system, even in nonpolar solvents, enables intramolecular electron-transfer processes, yielding a short-lived charge-separated radical pair, $C_{60}^{\bullet -}$−$TTF^{\bullet +}$. Intramolecular charge recombination results in a fullerene triplet excited state.[3] In this context, it also noted that TTF forms an aromatic 1,3-dithiolium dication[4] via two different one-electron oxidation steps on separate time scales. In light of electron-transfer processes, this gain of aromaticity upon oxidation is an important requisite, assisting in the stabilization of the charge-separated radical pairs.[3,5]

Despite the general interest to employ improved electron-acceptor moieties, fullerotriazolines have not yet been utilized as building blocks for donor−acceptor dyads. In this paper, we report the synthesis, electrochemistry, and photophysical properties of the first fullerotriazoline dyad (**5**) bearing a substituted TTF functionality as an electron-donor unit. Recently, C_{60}−TTF donor−spacer−acceptor dyads have been prepared by Diels−Alder cycloaddition[5] as well as by 1,3-dipolar cycloadditions of azomethyne ylides to C_{60}.[6] However, no information was given on the implication of the fullerene singlet state in intramolecular electron-transfer processes. In this work, we have studied the effect of increasing the electron accepting properties of the C_{60} moiety on the photophysics of these dyads from the initially formed fullerene singlet state.

Fullerotriazolines form a rare class of fullerene derivatives that are thermally labile intermediates in the reaction of C_{60} with azides.[7] As intermediates, they are of interest as precursors by thermal nitrogen extrusion of azafulleroids (opened 5,6-adducts) and fulleroaziridines (closed 6,6-adducts).[8] Furthermore, bis-azafulleroids have been efficiently converted into nitrogen heterofullerenes $(C_{59}N)_2$ and $C_{59}NH$.[9] Only two examples have been previously isolated and characterized, one of which could be fully characterized by X-ray analysis.[10] The synthetic procedure for the preparation of dyad **5** is summarized in Scheme 1. The *hitherto-described* TTF-containing alkyl azides were used as intermediates for the preparation of the corresponding amines. Here, we describe the first

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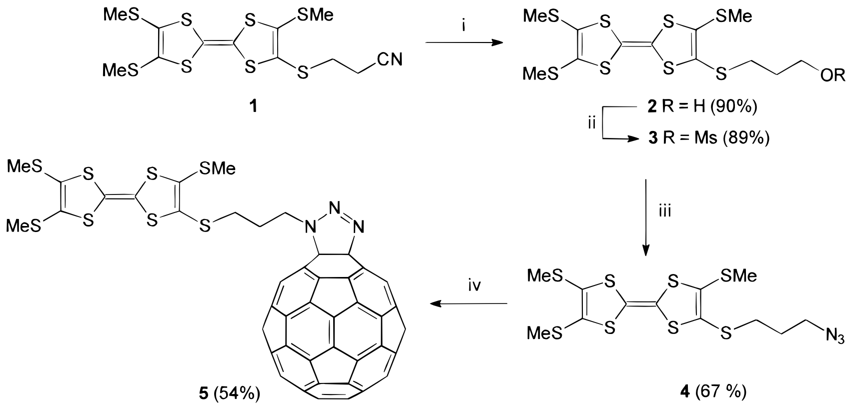
10.1021/jo991248d CCC: $19.00

Scheme 1[a]



[a] Reagents and conditions: (i) *t*-BuOK, DMF, then $Br(CH_2)_3OH$, rt; (ii) MsCl, Et_3N, CH_2Cl_2, rt; (iii) NaN_3, MeCN, reflux; (iv) C_{60}, ODCB, 60 ×bcC.

example of a 1,3-dipolar cycloaddition reaction of such an azide precursor to fullerene C_{60}.

Compound **4** was prepared from the previously reported compound **1**[11] in three steps. In particular, deprotection of compound **1** with *t*-BuOK in DMF afforded the thiolate, which was then reacted in situ with 3-bromopropanol, forming compound **2** (90% yield). Mesylation of **2** gave **3** in 89% yield, which, after treatment with activated NaN_3 in refluxing acetonitrile, furnished the azido derivative **4** in 67% yield (see the Experimental Section).

Finally, reaction of C_{60} with azide **4** in *o*-dichlorobenzene at 60 °C overnight led to dyad **5** in 24% yield (54% based on reacted C_{60}) as a perfectly stable solid at room temperature. Preparation of **5** requires inert atmosphere and a careful control of the temperature, which should never surpass 60 °C during the experimental workup in order to avoid formation of azafulleroids and fulleroaziridines. Dyad **5** was purified by column chromatography (silica gel, toluene/hexane 1:1) followed by centrifugation in hexane, methanol, and ether.

Compound **5** has a weak absorption band at 428 nm, and the ^{13}C NMR spectrum exhibits 32 signals for the fullerene core. This indicates a C_s symmetry for dyad **5** with a mirror plane between the two carbon atoms of the 6−6 junction and the three nitrogens of the triazoline ring. The sp^3-hybridized carbon atoms of the C_{60} core that are bound to two nitrogens appear at 77.21 and 81.17 ppm.

The electrochemical properties of **5** were studied by cyclic voltammetry at room temperature in toluene/acetonitrile (4:1) using tetrabutylammonium perchlorate as the supporting electrolyte and glassy carbon as the working electrode. The voltammogram shows the presence of two reversible one-electron oxidation waves at $E_{ox}^1 = 0.57$ V (vs SCE) and $E_{ox}^2 = 0.70$ V (vs SCE), yielding the radical cation and dication of the TTF moiety, respectively.

On the reduction side, the CV presents four quasireversible one-electron steps corresponding to the fullerene reductions at −0.57, −0.97, −1.52, and −2.00 V (vs SCE). It is remarkable that the value of the first and second reduction potential is anodically shifted (∼100 mV) relative to other 1,2-dihydrofullerenes such as pyrrolidino [3,4:1,2][60]fullerenes as well as the parent C_{60} (−0.60 V vs SCE). We attribute this shift to the electronegative character of the two nitrogen atoms covalently linked to the C_{60} core. Functionalized fullerene derivatives that give rise to easier reduction processes than C_{60} are still rare,[2] since saturation of a C=C double bond of the C_{60} core raises the LUMO energy and, in turn, shifts the reduction potentials to more negative values.[12] For this reason, no C_{60}-based D/A dyads in which the C_{60} derivative moiety presents better electron-accepting properties than the parent C_{60} have been previously studied.[2,13]

The structure of dyad **5** was optimized by semiempirical PM3 calculations. A perfect agreement with the previously reported X-ray structure of 1′-(2-methoxyethoxymethyl)triazolinyl[4′,5′:1,2]-1,2-dihydro[60]fullerene was noted.[10] Accordingly, the C-1 and C-2 bond length, bearing the organic addend, is slightly elongated (PM3, 1.585 Å; X-ray, 1.574 Å). Interestingly, the distortion of the fullerene cage reflected by the bond length deviations of the C=C double bonds from the mean average value (1.385 Å) correlates quite well with the experimental data. Bond lengths for the cis-1-bond (1.370 Å), *e*′-bond (1.383 Å), and *e*″-bond (1.382 Å) are similar to the experimental findings of 1.362 Å (*cis*-1) and 1.383 Å (*e*′ and *e*″).[10]

The HOMO of dyad **5** is situated at −8.09 eV and is localized on the TTF moiety. The atomic orbital composition of this orbital is similar to that of TTF (−8.00 eV) and explains the low oxidation potential measured for **5**. In agreement with the determined reduction potentials, the LUMO of **5** spreads on the C_{60} core and is lower in energy (−2.97 eV) than the related *N*-methylfulleropyrrolidines (−2.81 eV).[14]

A particularly sensitive set of parameters for studying the electronic properties of fullerenes and functionalized fullerene derivatives are optical absorption and emission spectroscopy. The emission of the fullerene singlet excited state in dyad **5** discloses a strong quenching, with fluorescence quantum yields (Φ) ranging from 1.8×10^{-4}

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[13] Recently, Prato et al have reported fulleropyrrolidinium salts, which are stronger acceptors than C_{60}, linked to a ferrocene as an electron-donor moiety. However, no photophysical data were reported: Ros, T. D.; Prato, M.; Carano, M.; Ceroni, P.; Paolucci, F.; Roffia, S. *J. Am. Chem. Soc.* **1998**, *120*, 11645−11648.

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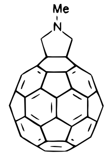
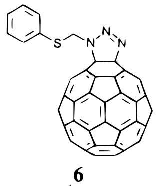
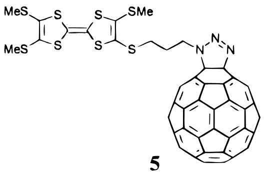
Table 1. Photophysical Parameters of Fullerene Reference 6 and Fullerene–TTF Dyad 5

Compound	Toluene	CH_2Cl_2	Benzonitrile
	Φ: 6.0×10^{-4} $\tau_{SINGLET}$: 1740 ps		
 **6**	Φ_{FLUOR} : 5.3×10^{-4} τ_{FLUOR}: 1325 ps $\tau_{SINGLET}$: 1900 ps $^{1*}E_{0-0}$: 1.76 eV $^{3*}E_{0-0}$: 1.50 eV		Φ_{FLUOR} : 4.9×10^{-4} $\tau_{SINGLET}$: 1900 ps
 **5**	Φ_{FLUOR} : 1.8×10^{-4} τ_{FLUOR} : 402 ps $\tau_{SINGLET}$: 334 ps k_{ET} : 2.9×10^{9} s^{-1} ΔG_S : 0.537 eV^a $-\Delta G_{CS}$: 0.09 eV^a $-\Delta G_{CR}$: 1.67 eV^a k_{BET} : 5.9×10^{8} s^{-1} $\Phi_{TRIPLET}$: 0.44	Φ_{FLUOR} : 1.0×10^{-4} τ_{FLUOR} : 215 ps $\tau_{SINGLET}$: 170 ps k_{ET} : 5.8×10^{9} s^{-1} ΔG_S : -0.146 eV^a $-\Delta G_{CS}$: 0.77 eV^a $-\Delta G_{CR}$: 0.99 eV^a k_{BET} : 4.7×10^{8} s^{-1} $\Phi_{TRIPLET}$: 0.39	Φ_{FLUOR} : 0.44×10^{-4} τ_{FLUOR} : 110 ps $\tau_{SINGLET}$: 86 ps k_{ET} : 1.2×10^{10} s^{-1} ΔG_S : -0.299 eV^a $-\Delta G_{CS}$: 0.92 eV^a $-\Delta G_{CR}$: 0.84 eV^a k_{BET} : 3.8×10^{8} s^{-1} $\Phi_{TRIPLET}$: 0.24

[a] This determination was performed following the continuum model. $\Delta G_{CR} = E_{OX} + E_{RED} + \Delta G_S$ $\Delta G_{CS} = \Delta E_{0-0} - \Delta G_{CR}$ $\Delta G_S = e^2/(4\Delta\epsilon_0))\,[(1/(2R_+) + 1/(2R_-) - 1/R_{D-A})\,1/\epsilon_S - (1/(2R_+) + 1/(2R_-)\,1/\epsilon_R]$ $E_{OX} = (TTF/TTF^{\bullet+})$ $E_{RED} = (C_{60}/C_{60}^{\bullet-})$ R_+ = radius TTF (4.4 Å) R_- = radius fullerene core (3.7 Å) ϵ_S = dielectric constant of solvent used for photophysical studies ϵ_R = dielectric constant of solvent used for measuring the redox potentials; toluene/acetonitrile 4:1 v/v ($\epsilon_R = 9.24$) ΔE_{0-0} = singlet excited-state energy of the fullerene core (1.76 eV).

to 0.44×10^{-4} in nonpolar toluene and polar benzonitrile, respectively. Under identical experimental conditions, monofunctionalized fullerene derivatives show a solvent-independent and, more importantly, a much higher fluorescence intensity on the order of $\Phi = 6 \times 10^{-4}$.[15] Moreover, the fluorescence quantum yield of the triazoline reference (**6**) is 5.3×10^{-4} (toluene) and 4.9×10^{-4} (benzonitrile).

A similar solvent-dependence was noted in complementary time-resolved fluorescence lifetime measurements. While the fluorescence lifetime of the triazoline reference (**6**) in toluene is about 1.325 ns (e.g., similar to a *N*-methylfulleropyrrolidine), a lifetime of only 0.402 ns was measured for the fullerene emission in dyad **5**. Increasing the solvent polarity to dichloromethane ($\epsilon = 9.08$) and benzonitrile ($\epsilon = 24.8$) led expectedly to a further decrease of the fluorescence lifetime with values of 0.215 ns and ~0.110 ns, respectively. The corresponding values are summarized, together with some other basic photophysical properties of dyad **5** and reference **6**, in Table 1.

It should be noted that the signature of the fullerene emission, despite its overall low yield, is still sustained.[16] In particular, a maximum at 704 nm, which corresponds to a singlet excited-state energy of 1.76 eV, is noted in the emission spectra of dyad **5** and reference **6**. In light of the flexible spacer (i.e., $-(CH_2)_n-$ chain), this observation is quite important, since, in principle, dyad **5** is prone to conformational changes in solution. Thus, the geometry of the flexibly linked system is not well defined, and the rapid deactivation of the fullerene singlet excited state may be ascribed to formation of an "*intra*molecular exciplex" that would be lower in energy than the parent fullerene singlet excited state.

In summary, time-resolved and steady-state fluorescence experiments suggest the rapid and, more importantly, the solvent-dependent deactivation of the fullerene singlet excited state in dyad **5**. A rationalization for the noted solvent dependence involves an electron-transfer mechanism. In the current dyad, it is expected that this evolves from a reaction between the singlet excited state (1.76 eV) of the electron-accepting fullerene moiety and the TTF donor.

This hypothesis was further corroborated by probing the photoexcited-state behavior of dyad **5** via time-resolved optical transient spectroscopy. Similar to a *N*-methylfulleropyrrolidine reference and a triazoline reference (**6**) used, 355 nm illumination of dyad **5** leads to the instantaneous formation of the fullerene singlet excited-state absorption. This transient exhibits a maximum around 880 nm, whose lifetime (see Table 1) is impacted by the presence of the TTF electron donor. The short singlet lifetimes fall in line with the above trend of the fluorescence lifetimes, and therefore, we ascribe

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[15] Sun, Y.-P. In *Molecular and Supramolecular Photochemistry*; Ramamurthy, V., Schanze, K., Eds.; Marcel Dekker: New York, 1997; Vol. 1, 325–390.

[16] Guldi, D. M.; Asmus, K.-D. *J. Phys. Chem. A* **1997**, *101*, 1472–1481.

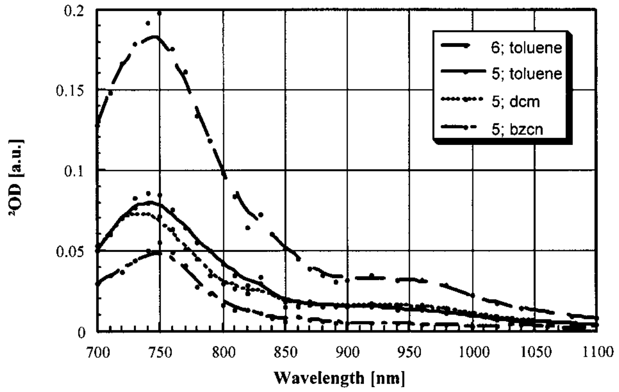

Figure 1. Differential absorption spectrum obtained 200 ns upon flash photolysis (~50 ns laser pulses) of dyad **5** in deoxygenated toluene, dichloromethane (dcm), and benzonitrile (bzcn) solutions and reference triazoline **6** in deoxygenated toluene solutions. The absorbance of the solutions was adjusted to 0.5 at the excitation wavelength, 337 nm.

this reaction to a rapid intramolecular electron transfer, yielding the charge-separated radical pair, $(C_{60}^{\bullet-})-(TTF^{\bullet+})$. Further support for this assumption stems from calculations (i.e., within the frame of the dielectric continuum model)[17] on the thermodynamic driving force ($-\Delta G_{ET}$) yielding values typically between 0.1 eV (toluene) and 0.92 eV (benzonitrile). It should be noted that the free energy changes were calculated for a stretched configuration and, thus, do not account for the structural flexibility of the spacer.

The moderate coupling within the $-(CH_2)_n-$ spacer, combined with the charge delocalization, e.g., within the carbon network and between the overlapping d-orbitals of the sulfur atoms, decreases the rate of back electron transfer (see Table 1).

To shed further light onto the product of charge-recombination, dyad **5** was studied in nanosecond-resolved photolysis following 50 ns laser pulses. Surprisingly, the same transient absorption spectrum was recorded regardless of the solvent used (see Figure 1). In particular, the new transient exhibits a maximum at 740 nm, which was further accompanied by a shoulder around 825 nm. It is interesting to note that the 740 nm maximum is similar to that described for the triplet excited state of pristine C_{60} ($\lambda_{max} = 750$ nm).[18] At the same time, the 740 nm is, however, strongly red-shifted compared to that of a monofunctionalized *N*-methylfulleropyrrolidine ($\lambda_{max} \approx 690$ nm).[19] This necessitated probing the excited-state spectrum of the triazoline reference (**6**) and comparing it to that of dyad **5**. In fact, **5** gave rise to exactly the same triplet–triplet absorption, which, in turn, suggests that in all solvents the product of intramolecular charge recombination is the fullerene triplet excited state. The triplet quantum yields differ quite substantially, ranging from 0.44 in toluene to 0.28 in benzonitrile.

In toluene, the moderate redox potentials of the TTF and fullerene moieties lead to an energy of the charge-separated state (1.67 eV), which is actually higher than the fullerene triplet excited state (1.50 eV). Thus, the combination of the spin-state with a simple energetic consideration (i.e., exergonic process) suggests population of the triplet excited state with a high quantum yield, rather than recovery of the singlet ground state.

The situation is quite different in benzonitrile: On the basis of the more polar environment, the energy of the intramolecular charge-separated state (0.84 eV) is lowered relative to the toluene case (1.67 eV). The latter state falls drops even below that of the fullerene triplet excited state (1.50 eV). Despite these energetic considerations, the measurements still reveal a fullerene triplet quantum yield (Φ) of 0.24.[20] A likely reason for this surprising observation could be an electron-transfer process in the singlet excited state that proceeds with an efficiency less than unity. This argument may be further supported by the flexibility of the spacer, which leads in solution to a degree of freedom for configurational rearrangements.

The triplet excited state is subject to yet another, though intermolecular, quenching process as can be deduced from an observed concentration dependence. In particular, we probed dyad concentrations ranging between 2.0×10^{-6} and 5.0×10^{-5} M. The decay of the fullerene triplet absorption was found to increase linearly with increasing dyad concentration. The intermolecular quenching rates derived are listed in Table 1. In solvents of low polarity, such as toluene ($k_q = 3.9 \times 10^9$ M^{-1} s^{-1}) and dichloromethane ($k_q = 2.6 \times 10^9$ M^{-1} s^{-1}), the quenching of the fullerene triplet excited state did not lead to any stable product. Instead, the singlet ground state was recovered quantitatively. This may speak for an intermolecular electron transfer, but a simple collisional deactivation route cannot be ruled out on the basis of the current data.

The weak solvent polarity can be regarded to be an insufficient means to separate the initially formed contact pair and, consequently, to stabilize the separate radical ions (i.e., the fullerene π-radical anion and the TTF π-radical cation). With the scope to obtain unambiguous evidence for an electron-transfer pathway, the more polar benzonitrile was employed. This should promote the stabilization of the radical pair via an exergonic gain of solvation energy, solvating the two separate radical ions. In fact, in benzonitrile efficient charge separation takes place, which can be conveniently confirmed through formation of the characteristic fullerene π-radical anion absorption around 1080 nm (see Figure 2). It should be added that full characterization of the intermolecularly generated radical pair was accomplished by also detecting the characteristics of the oxidized TTF entity around 430 nm. Experiments in benzonitrile give rise to a bimolecular rate constant for the forward electron transfer of 2.1×10^9 M^{-1} s^{-1} (i.e., close to diffusion-controlled; $k_{diff} = 5.0 \times 10^9$ M^{-1} s^{-1}). This value was independently confirmed by analyzing the triplet decay and the simultaneous fullerene π-radical anion and the TTF radical cation formation at 1080 and 430 nm, respectively.

A similar intermolecular electron transfer between a fullerene triplet excited state and a TTF donor was previously reported by Ito and co-workers.[21] In the

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(17) Weller, A. Z. *Physik. Chem.* **1982**, *132*, 93.

(18) Foote, C. *Top. Curr. Chem.* **1994**, *169*, 347.

(19) Guldi, D. M.; Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1997**, *119*, 974.

(20) An alternative mechanism implies a disproportionation reaction between two $(C_{60}^{\bullet-})-(TTF^{\bullet+})$ molecules, to yield the fullerene triplet excited state $((^3C_{60})-TTF)$ and a ground-state molecule ($C_{60}-TTF$). To probe this bimolecular reaction, the triplet quantum yield of dyad **5** and reference **6** was determined as a function of laser intensity (5.9%, 15.7%, 80%, and 100%), but no significant deviation in the triplet quantum yields were noticed, which rules out this mechanism.

(21) Alam, M. M.; Watanabe, A.; Ito, O. *Photochem Photobiol.* **1997**, *104*, 59–64.

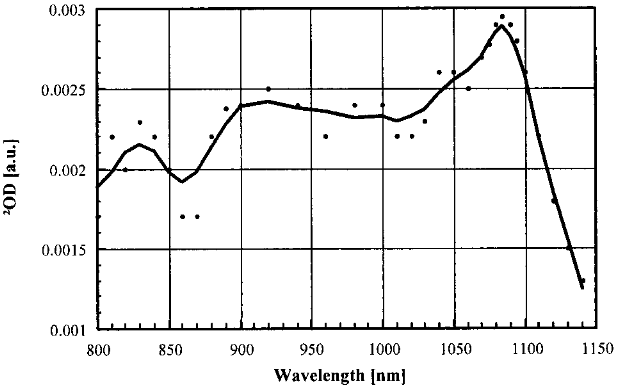

Figure 2. Differential absorption spectrum obtained 20 μs upon flash photolysis (~50 ns laser pulses) of dyad **5** in deoxygenated benzonitrile solutions (dyad concentration: 7.5×10^{-5} M).

context of stabilizing an intermolecular radical pair in reference to an intramolecular pair, the solvation energy of both species should be considered. In general, the free ions are better solvated than the intramolecular radical pair. We are currently intensifying our work to calculate the solvation energies of the ($C_{60}^{\bullet-}$)−($TTF^{\bullet+}$) and ($C_{60}^{\bullet-}$)/($TTF^{\bullet+}$) pairs more precisely.

The time profile of the fullerene π-radical anion and the TTF radical cation absorption indicates that the charge-separated species decays over a few hundred microseconds. Since the fullerene π-radical anion (i.e., $C_{60}^{\bullet-}$) has been shown to be stable when produced in γ- or pulse-irradiated solutions,[22] or by electrochemical reduction in polar and nonpolar solvents,[12] this decay is attributable to the highly exergonic back electron transfer. A concentration dependence (i.e., probing different radical concentrations) provided further evidence for the intermolecular decay kinetics. In particular, increasing the laser intensity leads consequently to a higher radical concentration, which, in turn, accelerates the back-electron-transfer process. Thus, it is safe to conclude that second-order kinetics govern the back electron reaction. This reaction, for which we derived a bimolecular rate constant of $k_{BET} \approx 1.5 \times 10^{10}$ M^{-1} s^{-1} (in benzonitrile), results in the singlet ground state.

On the other hand, by admitting oxygen to the dyad solutions, a nearly diffusion controlled ($k \geq 10^9$ M^{-1} s^{-1}) intermolecular reaction of the triplet state with molecular oxygen emerges, generating singlet oxygen ($^1O_2$) and correspondingly suppressing the electron-transfer event.

It is interesting to note that the rate of charge separation to charge recombination in dyad **5** is around 32 (in benzonitrile), which is slightly higher than that observed for analogous fulleropyrrolidines.[3] However, this rate value is remarkably smaller than that reported by Paddon-Row (~10^4) for the optimum design of a molecular photovoltaic device[23] or other high rate values (~4000) reported in the literature for other C_{60}-based chromophoric ball-and-chain systems.[24]

In conclusion, fullerotriazoline-TTF dyad gives rise to a reduced HOMO−LUMO energy gap (−5.12 eV) relative to previously reported fulleropyrrolidine−TTF dyads (−5.35 eV).[14] This has a large effect on the electron-transfer rates, which are similar to those observed in systems where the spatial separations between the donor and acceptor are markedly decreased.[3] Thus, increasing the electron accepting behavior of the C_{60} moiety in C_{60}-based dyads such as fullerotriazoline **5** can be used as a useful tool to improve (i) the dynamics of the forward electron transfer and (ii) the lifetime of the CS state. This is a valuable aid regarding concepts such as increasing the interchromophore separation[25] or the use of polychromophoric systems,[23] as well as the gain of aromaticity on the donor moiety.[3] Work is in progress for the design of such appealing systems.

Experimental Section

Instrumentation. Transient Absorption Measurements. Picosecond laser flash photolysis experiments were carried out with 355-nm laser pulses from a mode-locked, Q-switched Quantel YG-501 DP Nd:YAG laser system (pulse width 18 ps, 2−3 mJ/pulse). Passing the fundamental output through a D_2O/H_2O solution generated the white continuum picosecond probe pulse. The excitation and the probe were fed to a spectrograph (HR-320, ISDA Instruments, Inc.) with fiberoptic cables and were analyzed with a dual diode array detector (Princeton Instruments, Inc.) interfaced with an IBM-AT computer. Nanosecond laser flash photolysis experiments were performed with laser pulses from a Molectron UV-400 nitrogen laser system (337.1 nm, 8 ns pulse width, 1 mJ/pulse) in a front-face excitation geometry. The photomultiplier output was digitized with a Tektronix 7912 AD programmable digitizer. A typical experiment consisted of 5−10 replicate pulses per measurement. The averaged signal was processed with a LSI-11 microprocessor interfaced with a VAX-370 computer. The details of the experimental setups and their operation have been described elsewhere.[26]

Emission Measurements. Steady-state emission spectra were recorded on a SLM 8100 spectrofluorimeter. Fluorescence spectra were measured in different solvents at room temperature. A 570 nm long-pass filter in the emission path was used in order to eliminate the interference from the solvent and stray light. Long integration times (20 s) and low increments (0.1 nm) were applied. The slits were 2 and 8 nm. Each spectrum was an average of at least five individual scans. Fluorescence lifetimes were measured with a Laser Strope fluorescence lifetime spectrometer (Photon Technology International) with 460 nm laser pulses from a nitrogen/dye laser fiber-coupled to a lens-based T-formal sample compartment equipped with a stroboscopic detector.

Synthesis of Fullerene Derivatives. (3-Hydroxypropylthio)tris(methylthio)tetrathiafulvalene (2). To a solution of 427 mg (1 mmol, 1 equiv) of (2-cyanoethylthio)tris(methylthio)tetrathiafulvalene (**1**) in 20 mL of dry DMF was added 141 mg (1.25 mmol, 1.25 equiv) of potassium tercbutoxide under nitrogen atmosphere. The resulting dark solution was stirred for 10−15 min, and then 3-bromo-1-propanol (0.09 mL, 1 equiv) was added. After the mixture was stirred for 30 min at room temperature, the DMF was evaporated to yield a brown oil. CH_2Cl_2 was added, and the solution was washed three times with plenty of water. The organic phase was dried over magnesium sulfate. After evaporation the solvent, the crude material was purified by column chromatography (silica gel) using CH_2Cl_2 as eluent. Compound **2** was obtained in 90% yield: IR (Nujol/NaCl) 3299 (OH), 1043 (CO) cm^{-1}; ^1H NMR

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($CDCl_3$) δ 3.77 (t, J = 5.7 Hz, 2H), 2.92 (t, J = 7 Hz, 2H), 2.41 (s, 3H), 1.95−1.82 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.15, 19.27, 32.71, 60.89, 110.75, 110.83, 124.83, 127.33, 127.46, 130.38; MS (EI$^+$) *m/z* 432 (M$^+$, 100), 373 (20), 238 (30), 118 (20); HRMS (EI$^+$) *m/z* 431.8963 (M$^+$), calcd for $C_{12}H_{16}OS_8$ 431.8967.

(3-Methanesulfenyloxypropylthio)tris(methylthio)tetrathiafulvalene (3). To a solution of alcohol **2** (1 mmol) and 0.1 mL of $MeSO_2Cl$ (1.3 mmol, 1.3 equiv) in 30 mL of dry CH_2Cl_2 at room temperature and under nitrogen atmosphere was added 0.14 mL of triethylamine (1 mmol, 1 equiv), and the solution was stirred for 2 h. Water (100 mL) was added, and the solution was extracted with CH_2Cl_2 and washed three times with water. The organic phase was dried over anhydrous magnesium sulfate, and the solvents were evaporated. Further purification of the crude was accomplished by column chromatography (silica gel) using CH_2Cl_2 as the eluent. Compound **3** was obtained in 89% yield: IR (Nujol/NaCl) 1353, 1172 (S═O) cm^{-1}; ^{1}H NMR ($CDCl_3/Al_2O_3$) δ 4.36 (t, J = 6.0 Hz, 2H), 3.02 (s, 3H), 2.89 (t, J = 6.8 Hz, 2H), 2.42 (s, 3H), 2.40 (s, 3H), 2.08−2.00 (tt, 2H); ^{13}C NMR ($CDCl_3/Al_2O_3$) δ 19.18, 28.84, 37.37, 38.10, 67.54, 122.90, 127.42,127.54, 132.28; MS (EI$^+$) *m/z* 510 (M$^+$, 100), 495 (10), 373 (35), 360 (15), 238 (40), 223 (25), 118 (25), 103 (30), 91 (40); HRMS (EI$^+$) *m/z* 509.8741 (M$^+$), calcd for $C_{13}H_{18}O_3S_9$ 509.8742.

(3-Azidopropylthio)tris(methylthio)tetrathiafulvalene (4). To a solution of mesilate **3** (1 mmol) in 20 mL of acetonitrile was added 1.95 g of activated NaN_3 (30 equiv). The reaction mixture was refluxed (60 °C) with stirring under nitrogen atmosphere for 24 h. After the mixture was cooled to room temperature, water (100 mL) was added, and the mixture was extracted with CH_2Cl_2 and washed three times with water. The organic phase was dried over anhydrous magnesium sulfate, and then the solvent was evaporated. Further purification was accomplished by column chromatography (silica gel) using CH_2Cl_2 as the eluent. Compound **4** was obtained in 67% yield: IR (Nujol/NaCl) 2096, 1245 ($-N{=}N^+{=}N^-$) v/cm^{-1}; ^{1}H NMR ($CDCl_3/Al_2O_3$) δ 3.45 (t, J_2 = 6.6 Hz, 2H), 2.85 (t, J_2 = 6.9 Hz, 2H), 2.41 (s, 3H), 2.40 (s, 6H), 1.87 (tt, J_2 = 6.9, 6.6 Hz, 2H); ^{13}C NMR ($CDCl_3/Al_2O_3$) δ 19.21, 28.74, 33.06, 49.61, 110.52, 111.22, 123.61, 127.38, 127.55, 131.58; MS (EI$^+$) *m/z* 457 (M$^+$, 100), 373 (25), 238 (95), 118 (70), 91 (95), HRMS (EI$^+$) *m/z*) 456.9033 (M$^+$), calcd for $C_{12}H_{15}N_3S_8$ 456.9032.

3-[3-Tris(methylthio)tetrathiafulvalenylthiopropyl]triazolino[4,5:1,2][60]-fullerene (5). To a hot solution (60 °C) of [60]fullerene (72 mg, 0.1 mmol) in 6 mL of dry *o*-DCB under argon atmosphere was added a solution of **4** (46 mg, 0.1 mmol) in dry *o*-DCB (1 mL) dropwise. The resulting solution was stirred at 60 °C overnight. Hexane (100 mL) was added, and a solid precipitated and was then centrifugated. Further purification was accomplished by column chromatography (silica gel) using cyclohexane/toluene (1:1) as the eluent. After three centrifugations using hexane, methanol, and ether as solvents, compound **5** was obtained in 24% yield (54% based on reacted C_{60}): FT-IR (KBr) v/cm^{-1} 1462, 1425, 580 (C_{60}), 528 (C_{60}); ^{1}H NMR ($CDCl_3/CS_2$ 1:1) δ 4.60 (t, J_2 = 6.9 Hz, 2H), 3.20 (t, J_2 = 6.9 Hz, 2H), 2.59 (q, J_2 = 6.9 Hz, 2H), 2.80 (s, 3H), 2.40 (s, 3H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3/CS_2$ 1:1) δ 18.90, 18.99, 19.12, 29.82, 33.23, 47.05, 77.21, 81.17, 110.12, 110.66, 123.59, 127.06, 127.25, 131.40, 135.97, 136.41, 140.10, 140.37, 140.58, 141.74, 141.95, 141.98, 142.08, 142.36, 142.40, 142.53, 142.71, 142.75, 142.97, 143.81, 142.22 (2C), 144.30, 145.00, 145.08, 145.28, 145.55, 145.82 (2C), 145.89, 146.02, 146.09, 147.33, 147.48; UV−vis λ_{max}/nm ($\log \epsilon$) (CH_2Cl_2) 252 (2.15), 312 (1.71), 422 (0.66), 428 (0.59).

3-[Phenylthiomethyl]triazolino[4,5:1,2][60]fullerene (6). To a hot solution (60 °C) of [60]fullerene (216 mg, 0.3 mmol) in 6 mL of dry *o*-DCB under argon atmosphere was added a solution of azidomethyl phenyl sulfide (50 mg, 0.3 mmol) in dry *o*-DCB (1 mL) dropwise. The resulting solution was stirred at 60 °C overnight. Hexane (100 mL) was added, and a solid precipitated that was then centrifugated. Further purification was accomplished by column chromatography (silica gel) using cyclohexane/toluene (1:1) as the eluent. After three centrifugations using hexane, methanol, and ether as solvents, compound **6** was obtained in 22% yield (57% based on reacted C_{60}): FT-IR (KBr) v/cm^{-1} 2919, 2849, 1637, 1468, 1427, 1247, 1181, 1143, 1049, 796, 738, 687, 526; ^{1}H NMR ($CDCl_3/CS_2$ 1:1) δ 7.68 (d, J = 9.36 MHz, 2H); 7.41 (m, 3H); ^{13}C NMR ($CDCl_3/CS_2$ 1:1) δ 53.95, 77.21, 98.48, 112.16, 117.45, 119.55, 119.97, 120.39, 125.24, 128.15, 128.29, 128.95, 129.16, 129.38, 131.73, 132.79, 133.32, 136.22, 136.23, 140.04, 140.62, 140.88, 141.81, 141.90, 141.92, 142.05, 142.15, 142.36, 142.49, 142.656, 142.77, 142.90, 143.01, 143.89, 144.26, 144.41, 145.08, 145.32, 145.72, 145.85, 145.87, 145.99, 146.15; UV−vis λ_{max}/nm ($\log \epsilon$) (CH_2Cl_2) 254 (2.99), 274 (2.68), 318 (1.96), 428 (1.27).

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