ORGANIC LETTERS

2003
Vol. 5, No. 4
557–560

Addition Reaction of Azido-exTTFs to C_{60}: Synthesis of Fullerotriazoline and Azafulleroid Electroactive Dyads

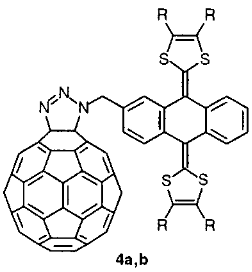
Susana González,[†] Nazario Martín,[†,*] Angela Swartz,[‡] and Dirk M. Guldi[‡,*]

*Departamento de Química Orgánica, Facultad de Ciencias Químicas,
Universidad Complutense, E 28040 Madrid, Spain, and Radiation Laboratory,
University of Notre Dame, Notre Dame, Indiana 46556*

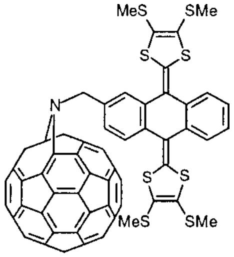
nazmar@quim.ucm.es

Received December 16, 2002

ABSTRACT



4a,b



5b

The addition reaction of azido-exTTFs to C_{60} affords electroactive fullerotriazoline and azafulleroid dyads, which behave as amphoteric redox systems. Fluorescence experiments and transient absorption spectroscopy reveal that excitation of the fullerene moiety leads to radical pair lifetimes that are 2 orders of magnitude higher than those previously reported for related fullerotriazolines.

The synthesis of donor–acceptor (D–A) ensembles has received an unabated interest due to the ability of these synthetic model systems to mimic key processes in photosynthesis as well as their use in the preparation of molecular electronic devices.[1]

Among the different electron acceptors, fullerenes and particularly [60]fullerene come to the fore in the design of novel D–A donors as a consequence of their unique electrochemical (undergoing up to six reversible one-electron reductions)[2] and electron transfer (low reorganization energy, λ)[3] features.

Recently, we have reported on the synthesis and photophysical studies of C_{60}-based ensembles bearing a tetrathiafulvalene (TTF)[4] or π-extended TTF (exTTF)[5] electron donor, which upon oxidation transform into aromatic and planar structures. These important electronic and structural modifications have a great impact on photoinduced charge-separation and charge-recombination processes. Interestingly, the choice of exTTF as a sacrificial electron donor increased the charge-separation lifetimes by around 2 orders of magnitude (C_{60}-TTF, $\tau \approx 2$ ns; C_{60}-exTTF, $\tau \approx 200$ ns).[4,5] On the acceptor side, it is well-known that the linkage of an organic addend to the C_{60} core results in a decrease of the acceptor ability. This stems primarily from the saturation of a double bond on the C_{60} surface, which raises the LUMO energy.[6]

Despite the "azidophobia" existing within the organic-synthetic community, azides are currently safely used, and

---

[†] Universidad Complutense.

[‡] University of Notre Dame.

(1) For a recent review, see: Prato, M., Martín, N., Eds.; Functionalized Fullerene Materials; *J. Mater. Chem.* **2002**, *12*, 1931–2159.

(2) Xie, Q.; Pérez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978–3980.

(3) Guldi, D. M. *Chem. Commun.* **2000**, 321–322.

(4) (a) Martín, N.; Sánchez, L.; Seoane, C.; Andreu, R.; Garín, J.; Orduna, J. *Tetrahedron Lett.* **1996**, *37*, 5979–5982. (b) Martín, N.; Sánchez, L.; Herranz, M. A.; Guldi, D. M. *J. Phys. Chem. A* **2000**, *104*, 4648–4657.

(5) (a) Martín, N.; Pérez, I.; Sánchez, L.; Seoane, C. *J. Org. Chem.* **1997**, *62*, 5690–5695. (b) Herranz, M. A.; Martín, N. *Org. Lett.* **1999**, *1*, 2005–2007. (c) Martín, N.; Sánchez, L.; Guldi, D. M. *Chem Commun.* **2000**, 113–114.

(6) Echegoyen, L.; Echegoyen, L. E. *Acc. Chem. Res.* **1998**, *31*, 593–601.

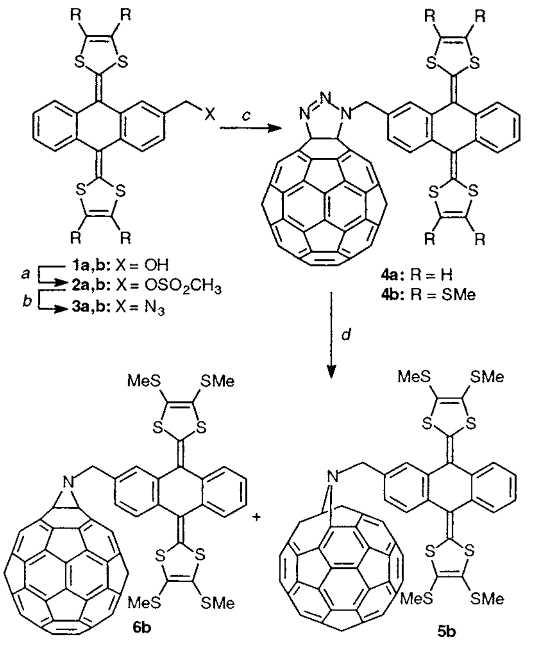
10.1021/ol027473q CCC: $25.00

contrary to the general feeling, they exhibit an extraordinary stability toward water, oxygen, and most organic conditions.[7] Because of these properties and their synthetic versatility, azides emerge as one of the most crucial functional group for "click chemistry" endeavors.[8] Despite the renewed interest in azides, their use in fullerene chemistry is rather sporadic.[9] Nevertheless, triazolinofullerenes, resulting from the 1,3-dipolar cycloaddition of azides to fullerenes, are key intermediates for further chemical transformations. Leading examples include extrusion of nitrogen molecules, affording azafulleroids and/or aziridinofullerenes,[10] or the preparation of nitrogen-containing heterofullerenes.[11]

In this Letter we describe the synthesis and redox properties of the first triazolino[4′,5′:1,2] [60]fullerenes, endowed with exTTF electron donors, and subsequent transformation into the respective azafulleroids, as a new type of donor−acceptor dyads. Although fullerotriazolines are less known fullerene derivatives, they exhibit electron acceptor properties slightly better than those of the parent unsubstituted [60]fullerene.[12] Preliminary photophysical results will complement this work.

Preparation of the novel dyads (**4a,b**) was carried out within the frame of a multistep synthetic procedure, starting from the previously reported hydroxymethyl-exTTFs (**1a,b**), which were in turn prepared in a seven-step synthesis.[13] First we attempted the preparation of azides (**3a,b**) in a one-step synthesis from alcohols (**1a,b**) by treatment with $BF_3 \cdot Et_2O$ and sodium azide in refluxing dioxane. However, under these conditions,[14] no formation of azides **3** was observed. Therefore, we revised our strategy and pursued the synthetic route shown in Scheme 1. In particular, treating alcohols **1a,b** with mesyl chloride in dry methylene dichloride and anhydrous trimethylamine as base led to mesyl derivatives (**2a,b**). These relatively unstable compounds were submitted to flash chromatography to avoid decomposition and immediately used for further reaction with activated sodium azide in dry acetonitrile. After heating under an argon atmosphere at 60 °C (to avoid thermal decomposition) for 24 h, azides **3a,b** were purified by flash chromatography (silica gel) using hexane/methylene dichloride (1:1) as eluent. The resulting solids were obtained in 90% and 40% yields, respectively, as crystals with high melting points (**3a**, 203−205 °C; **3b**, 171−173 °C).

Scheme 1[a]



[a] Reagents and conditions: (a) MsCl/dry CH_2Cl_2; (b) activated NaN_3/dry MeCN/60 °C; (c) C_{60}/ODCB/60 °C; (d) ODCB/120 °C.

Dyads (**4a,b**) were obtained by 1,3-dipolar cycloaddition of azides (**3a,b**) to C_{60} in *o*-dichlorobenzene (ODCB). During the 24 h of stirring the temperature should never surpass 60 °C to avoid thermal nitrogen extrusion. Compounds **4a,b** were purified by column chromatography (silica gel, toluene/cyclohexane, 1:1), and the greenish solids were further purified by washing and centrifugation in hexane, methanol, and diethyl ether. The novel dyads were obtained in low yield [**4a**, 8% (14% based on recovered C_{60}); **4b**, 12% (55% based on recovered C_{60})] as stable solids at room temperature.[15]

---

(7) Rostoutsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596−2599 and references therein.

(8) For a review on "click chemistry", see: Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004−2021.

(9) (a) Prato, M.; Chan Li, Q.; Wudl, F.; Lucchini, V. *J. Am. Chem. Soc.* **1993**, *115*, 1148−1150. (b) Shen, C. K.-F.; Yu, H.; Juo, C.-G.; Chien, K.-M.; Her, G.-R.; Luh, T.-Y. *Chem. Eur. J.* **1997**, *3*, 744−748. (c) Lamparth, I.; Nuber, B.; Schick, G.; Skiebe, A.; Grösser, T.; Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2257−2260. (d) Schick, G.; Hirsch, A.; Hauser, H.; Clark, T. *Chem.−Eur. J.* **1996**, *2*, 935−943. (e) Dong, G.-X.; Li, J.-S.; Chan, T.-H. *J. Chem. Soc., Chem. Commun.* **1995**, 1725−1726. (f) Bellavia-Lund, C.; Wudl, F. *J. Am. Chem. Soc.* **1997**, *119*, 943−946. (g) Grösser, T.; Prato, M.; Lucchini, V.; Hirsch, A.; Wudl, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1343−1345. (h) Kanakamma, P. P.; Huang, S.-L.; Juo, C.-G.; Her, G.-R.; Luh, T.-Y. *Chem.−Eur. J.* **1998**, *4*, 2037−2042. (i) Hummelen, J. C.; Prato, M.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 7003−7004. (j) Shen, C. K.-F.; Chien, K.-M.; Juo, C.-G.; Her, G.-R.; Luh, T.-Y. *J. Org. Chem.* **1996**, *61*, 9242−9244. (k) Nuber, B.; Hirsch, A. *Chem. Commun.* **1996**, 1421−1422. (l) Hummelen, J. C.; Knight, B.; Pavlovich, J.; González, R.; Wudl, F. *Science* **1995**, *269*, 1554−1556. (m) Keshavarz-K., M.; González, R.; Hicks, R.; Srdanov, G.; Srdanov, V.; Collins, T.; Hummelen, J.; Bellavia-Lund, C.; Pavlovich, J.; Wudl, F. *Nature* **1996**, *383*, 147−150.

(10) Cases, M.; Duran, M.; Mestres, J.; Martín, N.; Solá, M. *J. Org. Chem.* **2001**, *66*, 433−442 and references therein.

(11) For a recent review, see: Hummelen, J. C.; Bellavia-Lund, C.; Wudl, F. *Top. Curr. Chem.* **1999**, *199*, 93−134.

(12) Guldi, D. M.; González S.; Martín, N.; Antón, A.; Garín, J.; Orduna, J. *J. Org. Chem.* **2000**, *65*, 1978−1983.

(13) González, S.; Martín, N.; Guldi, D. M. *J. Org. Chem.*, in press.

(14) Kumar, H. M. S.; Reddy, B. V. S.; Anjanegulu, S.; Yadav, J. S. *Tetrahedron Lett.* **1998**, *39*, 7385−7388.

(15) Selected spectroscopic data for **4b**: 12% yield (55% based on unreacted C_{60}); IR−FT (KBr) 2963, 2915, 1648, 1528, 1492, 1452, 1419, 1308, 1261, 1093, 1022, 964, 868, 803, 751, 525 (C60) cm^{-1}; ^{1}H NMR ($CDCl_3/CS_2$ 1/1, 300 MHz) δ 7.90−7.14 (7H, m, ArH), 5.88 (1H, AB, J = 15.6 Hz, CH_2N), 5.59 (1H, AB, J = 15.6 Hz, CH_2N), 2.42−2.31 (12H, m, 4 SCH_3); ^{13}C NMR ($CDCl_3/CS_2$ 1/1, 75 MHz) δ 147.34, 147.16, 146.02, 145.97, 145.95, 145.90, 145.86, 145.80, 145.79, 145.72, 145.69, 145.67, 145.66, 145.60, 145.57, 145.48, 145.22, 144.96, 144.92, 144.89, 144.80, 144.42, 144.32, 144.21, 144.16, 144.13, 144.09, 143.73, 143.68, 143.66, 142.90, 142.63, 142.59, 142.53, 142.49, 142.46, 142.34, 142.28, 142.21, 142.05, 141.92, 141.86, 141.85, 141.76, 141.56, 140.69, 140.53, 140.50, 139.88, 139.70, 139.17, 139.07, 137.51, 136.40, 136.17, 136.17, 136.01, 135.85, 135.34, 134.60, 134.28, 134.15, 133.49, 132.97, 132.09, 128.87, 128.09, 127.42, 126.32, 125.73, 125.50, 125.25, 125.19, 125.17, 123.15, 122.57, 80.54 (Csp^{3}C$_{60}$), 77.20 (Csp^{3}C$_{60}$), 52.39 (CH_2N), 19.41 (SCH_3), 19.17 (SCH_3), 19.06 (SCH_3), 18.98 (SCH_3); MS m/z (%) 1311 ($M^+ - N_2$, 100); UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 438 (4.30), 420 (shoulder, 4.26), 368 (shoulder, 4.32), 316 (4.53), 254 (4.99) nm.

The high resolution ^{1}H NMR spectra of **4a,b** show the methylene hydrogens, adjacent to the nitrogen atom, as an AB system of anisocronous protons at around 5.6−5.8 ppm ($J \approx 16$ Hz). The unsymmetric ^{13}C NMR spectra reveal the presence of the two C sp^3 atoms of the fullerene cage at δ 88.40 and 77.20 (**4a**) and δ 80.54 and 77.20 (**4b**), as well as the CH$_2$-N carbon atom at δ 52.55 and 52.39, respectively.

Evidence for the low thermal stability of **4a,b** was found in their mass spectra, which showed molecular ion signals that correspond to the loss of N$_2$ at m/z 1127 and 1311, respectively.

To ascertain the chemical structure of dyads **4a,b**, as well as to study their thermal behavior, we heated compound **4b** in ODCB at 120 °C under argon atmosphere for 4 h. Then, the reaction mixture was submitted to column chromatography (silica gel, toluene/cyclohexane 1:1) and centrifugation (see above). This led to azafulleroid **5b** in 20% yield, together with unreacted **4b** and a more polar compound **6b** (aziridinofullerene). Since the latter product was obtained only in trace amounts, it could not be isolated nor chemically characterized.[16]

In an attempt to isolate aziridinofullerene **6b**, we carried out the reaction of azide **3b** and C$_{60}$ in ODCB at 120 °C for 6 h. The reaction behavior was quite similar, that is, after column chromatography unreacted [60]fullerene (51%), azafulleroid **5b** (17%), and trace amounts of **6b** were obtained. These results are in agreement with previous thermal treatment of triazolines affording open [5,6]azafulleroids as the only isolable compound after extrusion of molecular nitrogen.[10]

The electrochemical properties of triazolines (**4a,b**) were studied by cyclic voltammetry at room temperature. Quasireversible two-electron oxidation waves, involving the formation of the dicationic exTTF^{2+}, were observed at 0.48 V (**4a**) and 0.61 V (**4b**). This is in agreement with the observation for the parent, unsubstituted exTTF (0.45 V), revealing an anodic shift of the oxidation potential of the exTTF unit upon placing methylthio (SMe) groups at the 1,3-dithiole rings.[17]

On the reduction side, three quasireversible one-electron reduction waves were observed for **4a** (−0.57, −0.98, −1.55 V) and **4b** (−0.59, −1.01, −1.53 V) corresponding to the first three reduction processes of C$_{60}$. The less negative reduction potential values of **4a,b** relative to parent C$_{60}$ (−0.60, −1.00, −1.52 V) are worth mentioning. In other words, the reduction potential peak of **4a,b** is anodically shifted by 10−30 mV relative to C$_{60}$ and around 100 mV relative to the well studied fulleropyrrolidines or methanofullerenes.[18] A likely rationale for this electrochemical behavior infers the presence of the two electronegative nitrogen atoms.

To determine the existence of electronic communication between exTTF and C$_{60}$, we studied the CV behavior of reference *N*-phenylthiomethyltriazolinofullerene, **7**, in which the electroactive exTTF unit was replaced by a phenylthio group. The reduction waves for **7** (−0.57, −1.02, −1.56 V) are essentially similar to those found for dyads **4a,b**, indicating the lack of significant donor−acceptor interactions in the ground state.

Steady-state fluorescence experiments with triazolinofullerene **7** gave quantum yields (Φ) of 6×10^{-4}. Matching the absorption of donor−acceptor systems **4a** and **4b** at the 337 nm maximum, where exTTFs lack appreciable absorption, allowed us to probe the impact of the electron donors on the photoexcited fullerene. In fact, in toluene and benzonitrile the fullerene fluorescence quantum yields in **4a,b** are strongly reduced with values ranging between 0.2×10^{-4} and 0.68×10^{-4} (Figure 1).

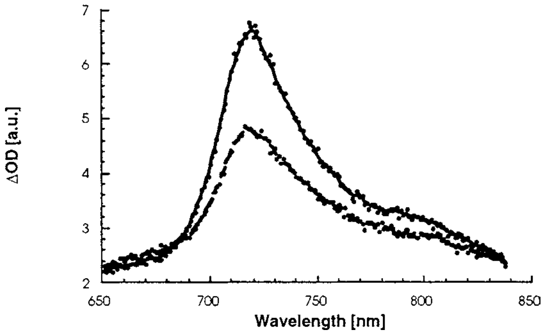


Figure 1. Emission spectra of dyads **4a** in toluene (solid line) and **4b** in toluene (dashed line) with matching absorption at the 337 nm excitation wavelength; OD$_{337}$ nm = 0.5.

Despite their overall low quantum yields, fluorescence lifetimes were determined for **7** and **4a,b**. In particular, a value of 1.74 ns was derived for **7** from fitting the radiative decay around 720 nm to a monoexponential fitting option. On the other hand, **4a,b** give rise to lifetimes of 0.25 ns and 0.16 ns in toluene, respectively, which corresponds to a high electron-transfer quenching efficiency.

From the difference between the long-wavelength absorption and the short-wavelength emission, we estimate a singlet excited-state energy for **7** of 1.76 eV. This is sufficiently energetic to power in **4** a thermodynamically driven electron transfer to yield C$_{60}$$^{\bullet-}$-exTTF$^{\bullet+}$ (vide infra).

Transient absorption measurements shed light onto the electron-transfer mechanism. Picosecond time-resolved absorption spectra (i.e., laser pulses at 355 nm), recorded for a deoxygenated toluene solution of **7** (1.0×10^{-5} M), are characterized by broad absorptions in the 900 nm region. These features are attributes of the fullerene singlet excited

---

(16) Azafulleroid **5b** could not be characterized by UV−vis spectroscopy because of the absorption of the exTTF moiety in the visible region. However, a broad singlet was observed in the ^{1}H NMR spectrum at δ 5.01 corresponding to the methylene −CH$_2$−N group, which indicates a strong shift to higher field in going from **4b** to **5b**. The confirmation of the azafulleroid structure came from the ^{13}C NMR spectrum which showed the absence of Csp^3 signals for the fullerene core and the disappearance of the Csp^3 signals at 80.54 and 77.20 ppm corresponding to **4b**. Interestingly, compound **5b** showed a mass spectrum with a well-defined molecular ion at 1311 (M$^+$, 98), thus confirming the loss of nitrogen from **4b**.

(17) For a recent review on TTF, see: Segura, J. L.; Martín, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 1372−1409.

(18) Martín, N.; Sánchez, L.; Illescas, B. M.; Pérez, I. *Chem. Rev.* **1998**, *98*, 2527−2548.

state (1.76 eV). At longer times, $^{1*}\mathrm{C}_{60}$ deactivates via a monoexponential rate law and a rate of $5.2 \times 10^{8}\ \mathrm{s}^{-1}$, which corresponds to a singlet lifetime of 1.9 ns, to produce the energetically lower-lying triplet excited state (1.50 eV). Spectral $^{3*}\mathrm{C}_{60}$ characteristics are broad absorptions at wavelengths greater than 500 nm, including a maximum at 740 nm.

The picture associated with the picosecond absorption spectroscopy of **4a,b** (ca. 10^{-5} M) is different. Despite the unequivocal excitation of the fullerene moieties at 355 nm the fullerene's singlet−singlet absorption was found only at short delay times (i.e., 50 ps) following the 18 ps laser pulse in oxygen-free solvents. At longer delays (i.e., 200 ps), instead of the slow intersystem crossing dynamics, the $^{1*}\mathrm{C}_{60}$ transients were found to be short-lived. Formation of a new transient develops as a result of the rapid decay; see Table 1. A key feature of the new products is a maximum around 680 nm, which resembles the well-known one-electron oxidized exTTF radical cation, exTTF$^{\bullet+}$.[5]

Figure 2 compares the differential absorption changes recorded upon photoexciting solutions of **7** with those of **4a** (2.0×10^{-5} M). In the case of **7**, the features correspond to the long-lived ($\tau = 25\ \mu$s) and oxygen-sensitive ($k_q \approx 1.0 \times 10^{9}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$) triplet excited state. A particularly broad triplet−triplet transition is noted with a maximum at 740 nm. Quite different are the spectra seen for **4a,b**, which bear no similarity with the triplet excited state of triazolinofullerene **7**. Around 680 nm a maximum was recorded that resembles the characteristic fingerprint of the one-electron oxidized exTTF$^{\bullet+}$. The near-IR transition was ascribed to the one-electron reduced fullerene species, $\mathrm{C}_{60}^{\bullet-}$. This confirms that the product of the intramolecular singlet excited-state deactivation is $\mathrm{C}_{60}^{\bullet-}$-exTTF$^{\bullet+}$.

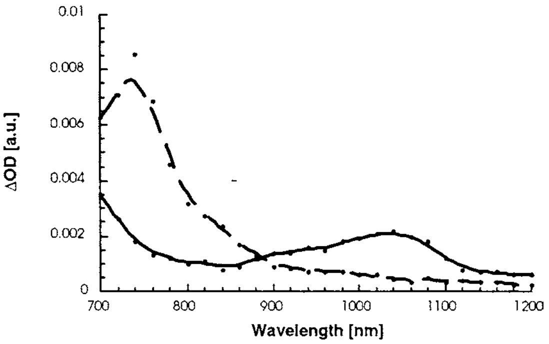


Figure 2. Differential absorption spectrum obtained 50 ns upon flash photolysis of **7** (dashed line) and **4a** (solid line) in deoxygenated benzonitrile. The absorbance of the solutions was adjusted to 0.5 at the excitation wavelength, 337 nm.

The charge-separated state is metastable and decays quantitatively to the singlet ground state. A monoexponential rate law fits best the decay of both fingerprint absorptions, that is, $\mathrm{C}_{60}^{\bullet-}$ and exTTF$^{\bullet+}$. From the corresponding fits we derived a radical pair lifetime of 137 ns (**4a**) and 94 ns (**4b**) in deoxygenated benzonitrile.

In summary, we describe the synthesis of a scarcely studied class of fullerene derivatives, such as triazolino[4′,5′:1,2][60]fullerenes (**4a,b**), which are stable solids at ambient conditions. The electrochemical study reveals that the presence of the nitrogen atoms results in a better acceptor ability than the parent [60]fullerene and that no significant electronic interaction occurs between the donor and acceptor moieties in the ground state. Steady-state fluorescence experiments and transient absorption spectroscopy disclose that excitation of the fullerene moiety results in the formation of a radical pair, showing the characteristic fingerprint of $\mathrm{C}_{60}^{\bullet-}$ and exTTF$^{\bullet+}$, with lifetimes in the range of hundred of nanoseconds, nearly 2 orders of magnitude larger than those reported for TTF-containing triazolino[4′,5′:1,2][60]fullerenes.[12]

This work paves the way for the preparation of novel azafulleroid-based electroactive dyads, which exhibit the original fullerene π-system, that is, 30 double bonds and, to the best of our knowledge, have not been studied yet.

Acknowledgment. This work has been supported by DGSIC of Spain (Project PB98-0818). Part of this work was supporrted by the Office of Basic Energy Sciences of U.S. Department of Energy (Contribution NDRL-4435 from the Notre Dame Radiation Laboratory). The authors thank Prof. L. Sánchez for his help in the preparation of the manuscript.

Supporting Information Available: Spectroscopical data of compounds **4a** and **5b** and a table containing the photophysical properties of compounds **4a**, **4b**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL027473Q