Electron Transfer

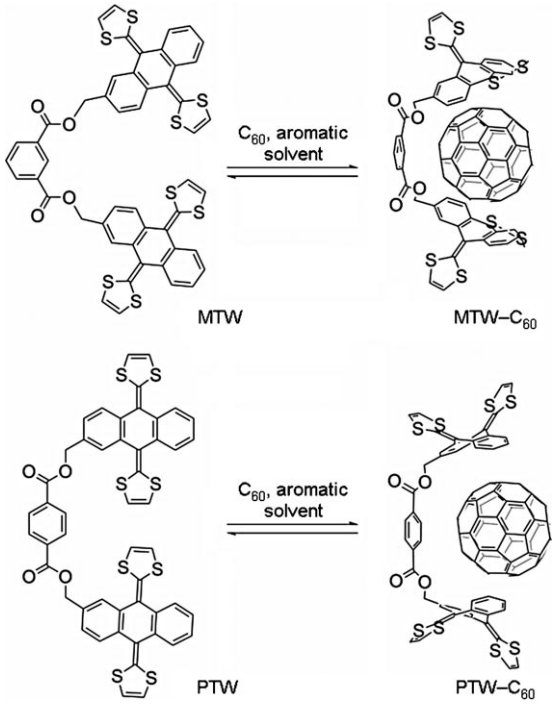
DOI: 10.1002/anie.200803984

Discrete Supramolecular Donor–Acceptor Complexes**

S. Shankara Gayathri, Mateusz Wielopolski, Emilio M. Pérez, Gustavo Fernández, Luis Sánchez, Rafael Viruela, Enrique Ortí, Dirk M. Guldi,* and Nazario Martín**

The renewed interest in noncovalently associating electroactive molecules[1,2] arises in part from the quest for new organic materials that convert solar energy into electrical/chemical equivalents.[3] In this context, the formation of charge-separated states is a key prerequisite. Charge-transfer events triggered by light have been studied in supramolecular donor–acceptor systems based on hydrogen bonds[1b,2a,b] and coordinative metal bonds.[2c,d] Although many of the most widely utilized electroactive fragments feature large π-conjugated surfaces, to date the use of π–π aromatic interactions[4] has mainly been limited to the construction of semi-infinite ensembles of chromophores either to achieve charge transport[5]—with the known example of charge transfer through DNA bases[6]—or to increase the efficiency of light absorption.[7] Detailed studies on charge-transfer interactions in discrete supramolecular systems held together by π–π aromatic interactions are surprisingly scarce.[8] Recently, we succeeded in the realization of donor–acceptor supramolecules based on the recognition of the convex exterior of C_{60} by the concave surface of π-extended tetrathiafulvalene derivatives.[9] Numerous incentives, especially in the context of constructing more efficient optoelectronic devices, are offered by these C_{60}/exTTF materials. Herein we describe the physicochemical characterization of the supramolecular donor–acceptor π complexes and provide a theoretical description of the underlying host–guest interactions.

The *meta* and *para* tweezers (MTW and PTW, respectively) share a straightforward design, in which two 2-[9-(1,3-dithiol-2-ylidene)anthracen-10(9*H*)-ylidene]-1,3-dithiole (exTTF) units are connected through isophthalic or terephthalic diester spacers, respectively (Scheme 1). MTW and PTW were synthesized in good yields by condensing the previously reported methyl alcohol derivative of exTTF and the corresponding commercially available acid chlorides. Since the characterization of MTW has already been reported,[9a] only selected spectroscopic data for PTW are provided in the Supporting Information.



Scheme 1. Structures of MTW and PTW as well as their complexes with C_{60}.

We previously demonstrated that MTW binds C_{60} effectively in a pincerlike manner in solution. In aromatic solvents, this receptor binds C_{60} to form a 1:1 complex, whereas in $CHCl_3/CS_2$ mixtures the binding isotherm is sigmoidal in

[*] Dr. R. Viruela, Prof. Dr. E. Ortí
Institut de Ciència Molecular
Universitat de València, 46980 Paterna (Spain)
Fax: (+34) 963-543-274
E-mail: enrique.orti@uv.es
Dr. S. S. Gayathri, M. Wielopolski, Prof. Dr. D. M. Guldi
Friedrich-Alexander-Universität Erlangen-Nürnberg
Department of Chemistry and Pharmacy
and
Interdisciplinary Center for Molecular Materials (ICMM)
Egerlandstrasse 3, 91058 Erlangen (Germany)
Fax: (+49) 9131-852-8307
E-mail: dirk.guldi@chemie.uni-erlangen.de
Dr. E. M. Pérez,[+] G. Fernández, Dr. L. Sánchez, Prof. Dr. N. Martín[+]
Departamento de Química Orgánica
Facultad de C. C. Químicas
Universidad Complutense de Madrid, 28040 Madrid (Spain)
Fax: (+34) 913-944-103
E-mail: nazmar@quim.ucm.es
[+] IMDEA-nanociencia, 28049 Madrid (Spain)

[**] Financial support by the MEC of Spain (projects CTQ2005-02609/BQU, CTQ2006-14987-C02-02/BQU, and Consolider-Ingenio CSD2007-00010), the Comunidad de Madrid (MADRISOLAR project P-PPQ-000225-0505), the Generalitat Valenciana (grant GVAINF/2007/051), and European FEDER funds (project CTQ2006-14987-C02-02/BQU) is acknowledged. E.M.P. thanks the MEC of Spain for a Juan de la Cierva contract, co-financed by the European Social Fund. Support from the Alexander von Humboldt Foundation is acknowledged by S.S.G.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200803984.

shape, which is generally regarded as an indication of positive cooperativity. The formation of a 2:2 sandwich-type complex in this solvent system has been evoked.[9a] To simplify the interpretation of the physicochemical results, we focus here only on aromatic solvents, in which MTW and PTW are expected to form 1:1 pincerlike complexes with C_{60} (Scheme 1).[10] Thus, absorption and fluorescence titrations—complemented by transient absorption measurements—were carried out in toluene, anisole, chlorobenzene, *o*-dichlorobenzene, and benzonitrile.

In the absorption assays, 7×10^{-6} M solutions of either tweezer were titrated against solutions of C_{60} of variable concentrations (2.5×10^{-7} to 8×10^{-5} M) at room temperature (Figure 1 and Figure S2 in the Supporting Information). The changes observed in the electronic absorption spectrum recorded in benzonitrile were in agreement with those seen for MTW in chlorobenzene.[9a] In particular, the evolution of a new broad transition at 488 nm appears in benzonitrile at the expense of the absorption maximum at 438 nm. Another notable feature is a low-energy isosbestic point around 450 nm, which reveals a considerable hypsochromic shift from 456 nm (polar benzonitrile) to 448 nm (nonpolar toluene). Similar hypsochromic shifts were noted for the absorption maximum, which was found, for example, in benzonitrile at 488 nm, while in toluene it occurs at 480 nm. We evoke charge-transfer transitions arising from the formation of $C_{60}^{\delta-}$exTTF$^{\delta+}$ to be responsible for these newly developed features. Importantly, the energies of the charge-transfer bands follow the trend seen in the electrochemically derived radical ion pair energies (see below). Such charge-transfer features are primarily a consequence of strong electronic coupling between the tweezers and the fullerene, with coupling constants of 168 cm^{-1} and 263 cm^{-1} for MTW and PTW, respectively, in benzonitrile.

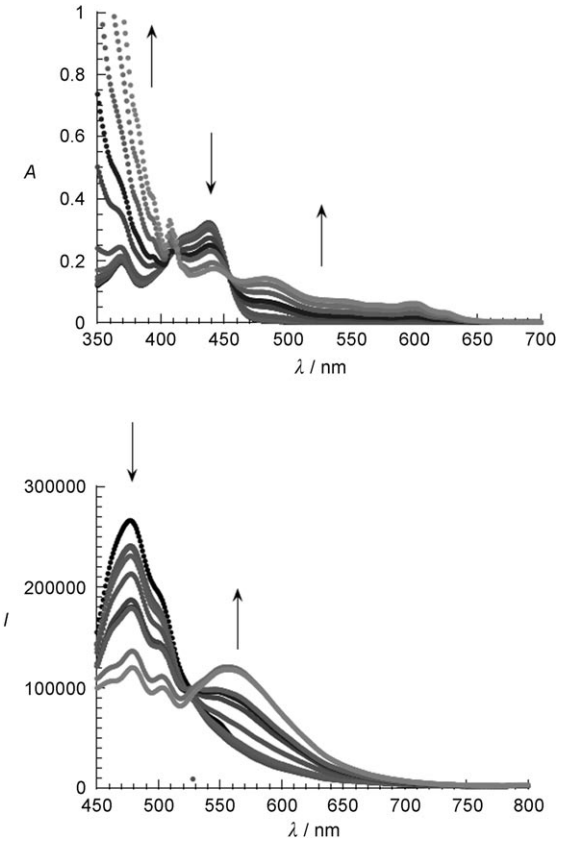


Figure 1. UV/Vis absorption spectra (top) and emission spectra (bottom) upon excitation at 435 nm of a dilute solution of MTW (7.0×10^{-6} M) in benzonitrile with variable concentrations of C_{60} (0, 2.5×10^{-7}, 7.5×10^{-7}, 1.25×10^{-6}, 2×10^{-6}, 5×10^{-6}, 1.5×10^{-5}, 2.5×10^{-5}, 4×10^{-5}, 6×10^{-5}, 8×10^{-5}). The arrows indicate the progression of the titration.

The fluorescence spectra of the tweezers recorded in the presence of C_{60} also confirm the mutual interactions with the electron-accepting C_{60}. More precisely, the excited state of the exTTF of MWT (2.6 eV) with an emission quantum yield of 10^{-3} and an emission lifetime of less than 100 ps,[11] which reaches a maximum at 470 nm, diminishes concomitantly with the rise of a new band centered around 557 nm (2.2 eV).[12] Again, we postulate the facile formation of a charge-transfer complex. These rather strong charge-transfer features are discernable in nonpolar as well as polar solvents, with emission quantum yields of about 10^{-3} and emission lifetimes shorter than our time-resolution of 100 ps. A large red-shift of the emission band by approximately 37 nm (from 520 nm in toluene to 557 nm in benzonitrile) reflects the different stabilization of the charge-transfer state by the solvent. By considering a 1:1 stoichiometry, we calculated the binding constants according to Equation (1).[13] Here, K is the binding

$$\frac{I_F}{I_0}=1-\frac{1}{2c_p}\left[\left(c_p+c_0+\frac{1}{K}\right)-\sqrt{\left(c_p+c_0+\frac{1}{K}\right)^2-4c_p c_0}\right] \quad (1)$$

constant, c_o is the concentration of the tweezer, and c_p is the concentration of the C_{60} added.[14] Overall, the binding constants were on the order of 10^4 M^{-1} (see Table S1 in the Supporting Information). The formation of the complex was also confirmed by mass spectrometric experiments.[10]

Molecular mechanics and semiempirical (AM1) calculations were employed to shed light on the $C_{60}^{\bullet-}$exTTF$^{\bullet+}$ complexes. These calculations provided indisputable evidence for the favorable interactions between the tweezers and C_{60}. Density functional theory (DFT) calculations (see the Supporting Information for computational details) helped to corroborate these findings. Figure 2 shows the energy-minimized structures (BH&H/6-31G**) of the MTW–C_{60} and PTW–C_{60} complexes. Both the MTW and PTW receptors display pincerlike conformations, in which the exTTF units adopt butterfly-shaped conformations consistent with previously reported structures.[15] The concave form adopted by the anthracene moieties is a perfect match to the convex surface of C_{60}. Specifically, the distances between the C9 (C10) atoms of the anthracene units are 12.56 Å (11.10 Å) in MTW and 12.85 Å (13.68 Å) in PTW. Thus, a molecular cavity is created that can adequately host C_{60} with a diameter of approximately 10.0 Å.[16] The complexation leads to the distances changing slightly to 12.98 (10.64) and 12.42 Å (13.76 Å), respectively. The average values of the angles formed by the two planes of the anthracene units increase slightly from 143.3° in MTW and PTW to 144.4° in MTW–C_{60} and 144.0° in PTW–C_{60}.

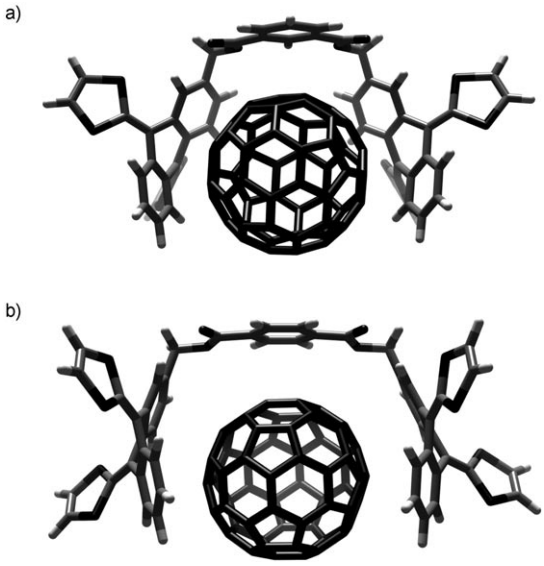


Figure 2. Energy-minimized structures of a) MTW–C_{60} and b) PTW–C_{60} calculated at the BH&H/6-31G** level.

The BH&H/6-31+G** calculations revealed binding energies of −13.40 and −15.75 kcal mol^{-1} for the MTW–C_{60} and PTW–C_{60} complexes, respectively.[17] The five aromatic rings of the receptor—two per exTTF unit plus the diester spacer—tend to interact more effectively with C_{60} in the PTW–C_{60} complex. The closest carbon–carbon distances in both complexes are in the range 3.1–3.4 Å. Such values are in excellent agreement with those observed for fullerene aggregates and fullerene host–guest complexes.[16,18] For example, the benzene ring of the terephthalic spacer in PTW–C_{60} is almost parallel with a benzene ring of C_{60} at an average distance of only 3.2 Å. This distance is considerably shorter than that reported for the benzene dimer in its parallel-displaced configuration (3.6 Å).[19]

To investigate the changes evident during the titration assays, the electronic excited states of MTW, PTW, MTW–C_{60}, and PTW–C_{60} were calculated by means of time-dependent DFT methods (TDDFT) at the B3LYP/6-31G** level. The calculations predict that the intense absorptions observed at 434 nm for MTW[9a] and 438 nm for PTW in chlorobenzene are due to electronic transitions with high oscillator strength values—calculated to be at 424 for MTW ($f=0.83$) and 425 nm for PTW (0.89). These transitions involve excitations from the nearly degenerate HOMO and HOMO−1 (HOMO = highest occupied molecular orbital) to the LUMO+1 and LUMO+2 (LUMO = lowest unoccupied molecular orbital), which are localized on the exTTF units, and correspond to the HOMO→LUMO excitation of exTTF.[20]

The same intense electronic transitions at 425 nm were calculated for the MTW–C_{60} and PTW–C_{60} complexes, but with an overall lower total intensity of $f=0.73$. As in the experiments, the addition of C_{60} lowers the intensity of these transitions, with the concomitant occurrence of two low-intensity transitions ($f=0.04$) at 479 nm that are calculated to be almost degenerate for both complexes. These transitions involve, however, excitations from the HOMO and HOMO−1, which are located on exTTF units, to the LUMO+4, which spreads over C_{60} (Figure 3). Moreover,

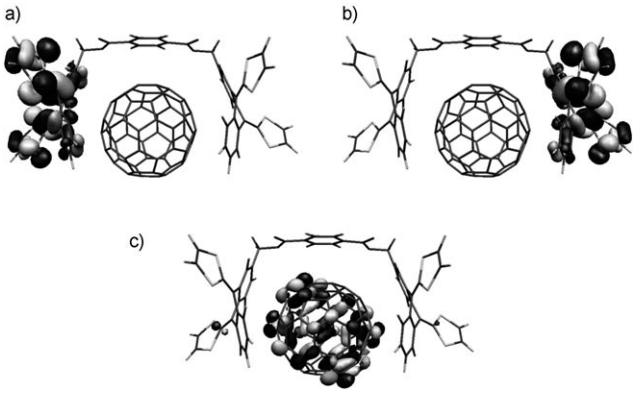


Figure 3. Electron density (0.03 e bohr^{-3}) calculated for the HOMO (a), HOMO−1 (b), and LUMO+4 (c) of PTW–C_{60}.

they are the origin of the absorption bands that emerge at 485 nm because of the formation of the supramolecular donor–acceptor π–π complexes. Thus, our calculations confirm the nature of these bands as charge transfer, evolving from the exTTF-type receptors to C_{60} and thereby affording $C_{60}^{\bullet-}$ exTTF$^{\bullet+}$.

The excited electronic states resulting from the HOMO,-HOMO−1,→LUMO+4 transitions accumulate a positive charge of $+1e$ on one exTTF unit and a negative charge of $-1e$ on C_{60}. Together with the charge transfer, the molecular dipole moment increases from 5.6 D (ground state of the complexes) to 40.0 D (excited state of the complexes; Figure 4. Notable, the six lowest energy excited states also

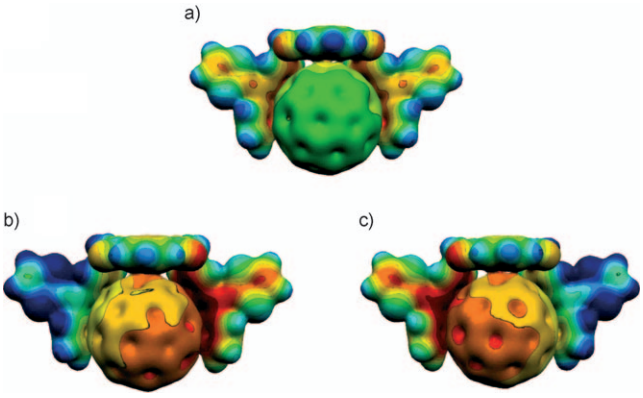


Figure 4. Electrostatic potential (B3LYP/6-31G**) calculated for MTW–C_{60} in a) the ground electronic state and b) the charge-separated HOMO→LUMO+4 and c) HOMO−1→LUMO+4 excited states. Blue: positive potential, red: negative potential (color scale for $\delta^+\rightarrow\delta^-$: blue→green→yellow→orange→red).

imply charge transfer from exTTF to C_{60}, but all of these excitations have very small intensities of $f=0.005$.[21]

Support for the formation of the charge-transfer state came from square-wave voltammetric measurements. Fig-

ure S4 in the Supporting Information illustrates the changes in the voltammetric behavior of C_{60} in the absence and presence of the tweezer. A substantial shift in the reduction peaks from −0.52 V to −0.65 V is observed, for example, for the first reduction wave.[22] This shift is due to the confinement of the π system of C_{60} by the exTTF receptor, which shifts the LUMOs of C_{60} to higher energies, thus making its reduction slightly less favorable.

Only one transient is observed for MTW and PTW by transient absorption measurements (both in the visible and near-infrared region), as shown in Figure S5 in the Supporting Information. This excited-state transient is centered on exTTF and appears simultaneously with the conclusion of the 387 nm laser pulse. This transient is characterized by absorptions around 609 nm in the visible region and 850 nm in the near-infrared region, and decays rapidly with a lifetime of only 1.2 ps. The short lifetime is rationalized by the presence of the sulfur atoms, with their strong second-order vibronic spin–orbit coupling.[11] Figure 5 shows the changes in the differential absorption obtained upon photoexciting a mixture of MTW and C_{60} (1:100) in benzonitrile to generate the charge-transfer features at 484 nm.[23] The spectroscopic features clearly reveal the instantaneous ($>10^{12}\ s^{-1}$) formation of a fully charge-separated $C_{60}^{\bullet-}$exTTF$^{\bullet+}$ state. In accordance with previous photolytic and radiolytic studies, we assign the transient centering at around 668 nm to the one-electron-oxidized radical cation of the tweezer.[1e] The one-electron-reduced radical anion of C_{60}, on the other hand, shows up as an absorption in the near-infrared region at 1100 nm. The instantaneous appearance of the charge-separated states further confirms the intimate interactions between MTW/PTW and C_{60}.[24] Excitation at 387 nm, however, results in the locally excited exTTF excited state being transformed into the same $C_{60}^{\bullet-}$exTTF$^{\bullet+}$ charge-separated state.

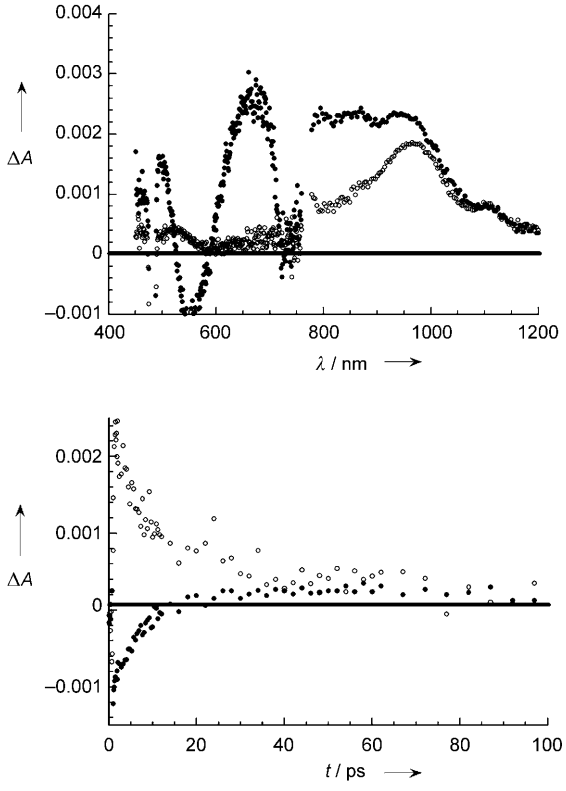


Figure 5. Top: Differential absorption spectra (visible and near-infrared regions) obtained upon femtosecond flash photolysis (484 nm) of a MTW/C_{60} mixture (MTW: 2.5×10^{-5} M; C_{60}: 2.5×10^{-3} M) in benzonitrile with time delays of 5 (●) and 100 ps (○) at room temperature. Bottom: Time/absorption profiles at 670 nm (○) and 580 nm (●), which reflect the charge-separation and charge-recombination dynamics.

The lifetime of the charge-separated states, as determined from the decay profiles at 668 and 1100 nm, were in general very short. Lifetimes of 12.7 ps for MTW and 9.6 ps for PTW in benzonitrile point to a stabilization by the solvent, since the lifetimes were notably shorter in *o*-dichlorobenzene (6.3 ps for PTW and 5.8 ps for MTW). The product of this charge recombination is the singlet ground state.

In summary, we have shown that both MTW and PTW form stable discrete, supramolecular donor–acceptor complexes with C_{60} in a variety of solvents that convert into a fully charge-separated $C_{60}^{\bullet-}$exTTF$^{\bullet+}$ state upon photoexcitation (Figure 6).[25,26] These results should pave the way for applying this recognition motif to construct photovoltaic devices.[9] Predictably, the lifetimes of the charge-separated states are short, in the range of picoseconds, since the formation of the complexes between MTW/PTW and C_{60} implies partial orbital overlap between the electroactive units, which facilitates both charge separation and charge recombination. As lifetimes in solution and in the solid state—where these systems would find application—often vary significantly, and other factors such as charge mobility frequently play a dominant role in the overall efficiency of the device, the short lifetimes in solution are far from being an unsurpassable hurdle.

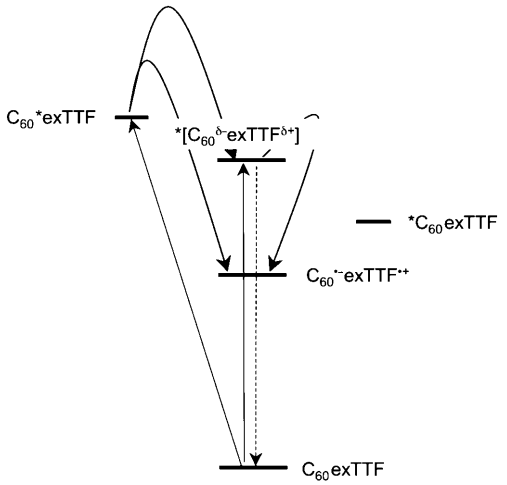


Figure 6. Energy diagram for MTW–C_{60}/PTW–C_{60} in benzonitrile.

Received: August 12, 2008

Keywords: charge transfer · density functional calculations · host–guest systems · photochemistry · pi interactions

[1] For reviews, see: a) M. R. Wasielewski, *Chem. Rev.* **1992**, *92*, 435 – 461; b) L. Sánchez, N. Martín, D. M. Guldi, *Angew. Chem.* **2005**, *117*, 5508 – 5516; *Angew. Chem. Int. Ed.* **2005**, *44*, 5374 – 5382; c) F. D'Souza, O. Ito, *Coord. Chem. Rev.* **2005**, *249*, 1410 – 1422; d) M. R. Wasielewski, *J. Org. Chem.* **2006**, *71*, 5051 – 5066; e) N. Martín, L. Sánchez, M. A. Herranz, B. Illescas, D. M. Guldi, *Acc. Chem. Res.* **2007**, *40*, 1015 – 1024.

[2] For recent examples, see: a) L. Sánchez, M. Sierra, N. Martín, A. J. Myles, T. J. Dale, J. Rebek, Jr., W. Seitz, D. M. Guldi, *Angew. Chem.* **2006**, *118*, 4753 – 4757; *Angew. Chem. Int. Ed.* **2006**, *45*, 4637 – 4641; b) F. Wessendorf, J.-F. Gnichwitz, G. H. Sarova, K. Hager, U. Hartnagel, D. M. Guldi, A. Hirsch, *J. Am. Chem. Soc.* **2007**, *129*, 16057 – 16071; c) F. D'Souza, R. Chitta, A. S. D. Sandanayaka, N. K. Subbaiyan, L. D'Souza, Y. Araki, O. Ito, *J. Am. Chem. Soc.* **2007**, *129*, 15865 – 15871; d) A. L. Schumacher, A. S. D. Sandanayaka, J. P. Hill, K. Ariga, P. A. Karr, Y. Araki, O. Ito, F. D'Souza, *Chem. Eur. J.* **2007**, *13*, 4628 – 4635.

[3] N. Armaroli, V. Balzani, *Angew. Chem.* **2007**, *119*, 52 – 67; *Angew. Chem. Int. Ed.* **2007**, *46*, 52 – 66.

[4] C. A. Hunter, K. R. Lawson, J. Perkins, C. J. Urch, *J. Chem. Soc. Perkin Trans. 2* **2001**, 651 – 669.

[5] a) Y. Yamamoto, T. Fukushima, Y. Suna, N. Ishii, A. Saeki, S. Seki, S. Tagawa, M. Taniguchi, T. Kawai, T. Aida, *Science* **2006**, *314*, 1761 – 1764; b) J. L. Mynar, T. Yamamoto, A. Kosaka, T. Fukushima, N. Ishii, T. Aida, *J. Am. Chem. Soc.* **2008**, *130*, 1530 – 1531.

[6] B. Giese, *Bioorg. Med. Chem.* **2006**, *14*, 6139 – 6143.

[7] a) C. Röger, Y. Miloslavina, D. Brunner, A. R. Holzwarth, F. Wuerthner, *J. Am. Chem. Soc.* **2008**, *130*, 5929 – 5939; b) P. G. A. Janssen, J. Vandenbergh, J. L. J. Van Dongen, E. W. Meijer, A. P. H. J. Schenning, *J. Am. Chem. Soc.* **2007**, *129*, 6078 – 6079.

[8] a) T. Kawase, H. Kurata, *Chem. Rev.* **2006**, *106*, 5250 – 5273; b) K. Tashiro, T. Aida, *Chem. Soc. Rev.* **2007**, *36*, 189 – 197; c) E. M. Pérez, N. Martín, *Chem. Soc. Rev.* **2008**, *37*, 1512 – 1519.

[9] a) E. M. Pérez, L. Sánchez, G. Fernández, N. Martín, *J. Am. Chem. Soc.* **2006**, *128*, 7172 – 7173; b) E. M. Pérez, M. Sierra, L. Sánchez, M. R. Torres, R. Viruela, P. M. Viruela, E. Ortí, N. Martín, *Angew. Chem.* **2007**, *119*, 1879 – 1883; *Angew. Chem. Int. Ed.* **2007**, *46*, 1847 – 1851; c) G. Fernández, E. M. Pérez, L. Sánchez, N. Martín, *Angew. Chem.* **2008**, *120*, 1110 – 1113; *Angew. Chem. Int. Ed.* **2008**, *47*, 1094 – 1097; d) G. Fernández, E. M. Pérez, L. Sánchez, N. Martín, *J. Am. Chem. Soc.* **2008**, *130*, 2410 – 2411; e) G. Fernández, L. Sánchez, E. M. Pérez, N. Martín, *J. Am. Chem. Soc.* **2008**, *130*, 10674 – 10683; f) E. M. Pérez, A. L. Capodilupo, G. Fernández, L. Sánchez, P. M. Viruela, R. Viruela, E. Ortí, M. Bietti, N. Martín, *Chem. Commun.* **2008**, 4567 – 4569.

[10] The formation of a 1:1 complex was also observed in the gas phase by mass spectrommetry. When a mixture of either MTW or PTW and C_{60} was analyzed by MALDI-TOF, a signal corresponding to the tweezer–C_{60} complex was clearly apparent (found: $m/z = 1669.961$, calcd for M/PTW–C_{60}: 1669.991); see Figure S1 in the Supporting Information.

[11] a) A. Maciejewski, R. P. Steer, *Chem. Rev.* **1993**, *93*, 67 – 98; H. Nishikawa, S. Kojima, T. Kodama, I. Ikemoto, S. Suzuki, K. Kikuchi, M. Fujitsuka, H. Luo, Y. Araki, O. Ito, *J. Phys. Chem. A* **2004**, *108*, 1881 – 1890.

[12] Rate constants of about $10^{12}\ s^{-1}$ for intracomplex deactivation were estimated by fluorescence quenching.

[13] a) H. J. Schneider in *Frontiers in Supramolecular Organic Chemistry and Photochemistry* (Ed.: H. Dürr), Wiley-VCH, Weinheim, **1991**; b) B. Valeur in *Molecular Fluorescence: Principles and Applications*, Wiley-VCH, Weinheim, **2002**.

[14] Figure S3 (Supporting Information) shows the fit for the binding constants, and affords values of about $10^4\ M^{-1}$.

[15] a) N. Martín, L. Sánchez, C. Seoane, E. Ortí, P. M. Viruela, R. Viruela, *J. Org. Chem.* **1998**, *63*, 1268 – 1279; b) M. C. Díaz, B. M. Illescas, N. Martín, I. F. Perepichka, M. R. Bryce, E. Levillain, R. Viruela, E. Ortí, *Chem. Eur. J.* **2006**, *12*, 2709 – 2721; c) M. C. Díaz, B. M. Illescas, N. Martín, R. Viruela, P. M. Viruela, E. Ortí, O. Brede, I. Zilbermann, D. M. Guldi, *Chem. Eur. J.* **2004**, *10*, 2067 – 2077.

[16] M. Makha, A. Purich, C. L. Raston, A. N. Sobolev, *Eur. J. Inorg. Chem.* **2006**, 507 – 517.

[17] Association binding energies are calculated as the difference between the total energy of the complex and the sum of the total energies of the receptor and C_{60}.

[18] A Sygula, F. R. Fronczek, R. Sygula, P. W. Rabideau, M. M. Olmstead, *J. Am. Chem. Soc.* **2007**, *129*, 3842 – 3843.

[19] a) T. Sato, T. Tsuneda, K. J. Hirao, *Chem. Phys.* **2005**, *123*, 104307; b) M. O. Sinnokrot, C. D. Sherrill, *J. Phys. Chem. A* **2004**, *108*, 10200 – 10207; c) M. O. Sinnokrot, E. F. Valeev, C. D. Sherrill, *J. Am. Chem. Soc.* **2002**, *124*, 10887 – 10893.

[20] Observed in chorobenzene at 429 nm, and calculated at 420 nm ($f = 0.49$). The LUMO for both MTW and PTW lies on the diester unit, and the lowest energy HOMO,HOMO−1→LUMO transitions have almost no intensity ($f < 0.01$).

[21] See the Supporting Information for a detailed description of the nature of the excited electronic states.

[22] The effects are not limited to the first reduction of C_{60}, since the peaks that correspond to the second, third, and fourth reductions undergo similar shifts.

[23] An additional band appears at 980 nm because of the singlet–singlet transition of free, uncomplexed C_{60}.

[24] L. Sánchez, I. Pérez, N. Martín, D. M. Guldi, *Chem. Eur. J.* **2003**, *9*, 2457 – 2468.

[25] See for example: T. J. Kesti, N. V. Tkachenko, V. Vehmanen, H. Yamada, H. Imahori, S. Fukuzumi, H. Lemmetyinen, *J. Am. Chem. Soc.* **2002**, *124*, 8067 – 8077.

[26] In toluene $C_{60}^{\bullet-}$ exTTF$^{\bullet+}$ has lifetimes of 3.9 ps for PTW and 3.5 ps for MTW.

