Implementing a tripodal relay station in a phthalocyanine–[60]fullerene conjugate†‡

Maurizio Quintiliani,[a] Axel Kahnt,[b] Purificación Vázquez,[a] Dirk M. Guldi*[b] and Tomás Torres*[a]

Received 23rd October 2007, Accepted 11th December 2007
First published as an Advance Article on the web 8th January 2008
DOI: 10.1039/b716322c

A tripodal architecture **1**—based on a tetraphenylmethane core bearing three phthalocyanine arms and a fullerene arm—has been realized *en route* towards a novel electron donor–acceptor conjugate that reveals long range electron transfer activity.

Introduction

Photoinduced electron transfer is an essential step in the conversion of solar energy into chemical energy in photosystems I and II, and is also frequently used by chemists to build complex molecules from simple precursors.[1] During this process, light absorption generates molecules in excited electronic states that are susceptible to accepting or donating charges.

One of the most important focuses of chemistry in recent decades has been the construction of molecular and supramolecular based artificial solar energy harvesting systems that have the ability to absorb light from the sun and convert it into useful and storable forms. The classical approach is based on the development of electron donor–acceptor conjugates using well defined molecular spacers. Long-lived radical ion pair states have been achieved, in some cases, by incorporating a third, a fourth or even a fifth component—donor and/or acceptor—to realize multicomponent arrays such as triads, tetrads, pentads, *etc*. This research is driven by the important incentives to govern factors such as the nature, electronic coupling or structural arrangement of the components. A better understanding of these factors will help to design molecular systems mimicking the high efficiency of solar energy conversion in natural photosynthesis, that is, efficient formation of radical ion pairs with superior properties.

In this context, a tetrahedral molecular building block may represent a valuable design strategy for achieving multifunctional donor–acceptor ensembles. Over the years, derivatives of tetraphenylmethane and tetraphenylsilane have played a significant role as molecular subunits. Such tetrahedral building blocks have been successfully incorporated into supramolecular networks,[2] nanoscale structures,[3] optoelectronic materials,[4] and liquid crystals,[5] and entered the market as scanning probe microscopy (SPM) tips.[6] Remarkably, Otsubo *et al.* have demonstrated the important role of a tripodal rigid anchor in preparing well-organized SAMs of [60]fullerene-linked oligothiophenes onto gold electrodes to construct highly efficient photovoltaic cells.[7]

Phthalocyanines[8] (Pcs), on one hand, emerged as a class of molecular building blocks that suggest their implementation as light harvesting antennae in light energy conversion systems. Particularly important are their very high extinction coefficients around 700 nm. The extraordinary electron acceptor properties of fullerenes, on the other hand, have led to noteworthy utilizations of such building blocks in areas of light induced electron

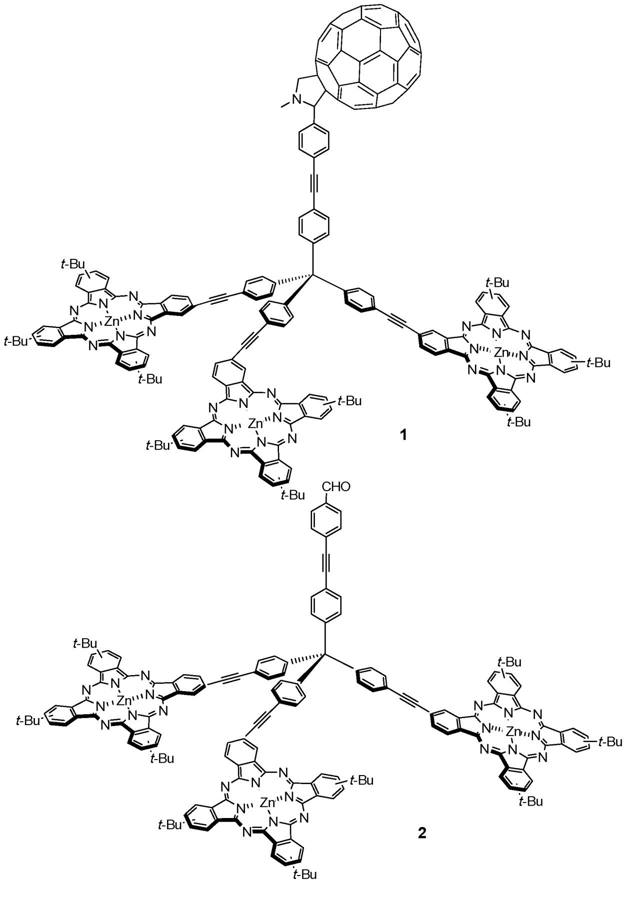


Fig. 1 Tripodal phthalocyanine systems **1** and **2**.

---

[a] *Departamento de Química Orgánica, Universidad Autónoma de Madrid, Cantoblanco, Madrid, 28049. E-mail: tomas.torres@uam.es; Fax: (+)34 914973966*
[b] *Department of Chemistry and Pharmacy & Interdisciplinary Center for Molecular Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, 91058, Germany. E-mail: dirk.guldi@chemie.uni-erlangen.de; Fax: (+)49 9131 8528307*

† This paper is part of a *Journal of Materials Chemistry* theme issue on carbon nanostructures.

‡ Electronic supplementary information (ESI) available: NMR, IR and mass spectra of **1**, **2** and **4**; fluorescence time profile of **1**, differential absorption spectra of **1**; singlet oxygen phosphorescence spectra of **1** and **2**. See DOI: 10.1039/b716322c

transfer chemistry and solar energy conversion.[9] To this end, several examples of phthalocyanine–fullerene ensembles have been synthesized for studying photoinduced electron transfer and applications in photovoltaic devices.[10] No doubt, some notable results have already been obtained—still more effort is needed, especially to achieve higher and better conversion efficiencies.

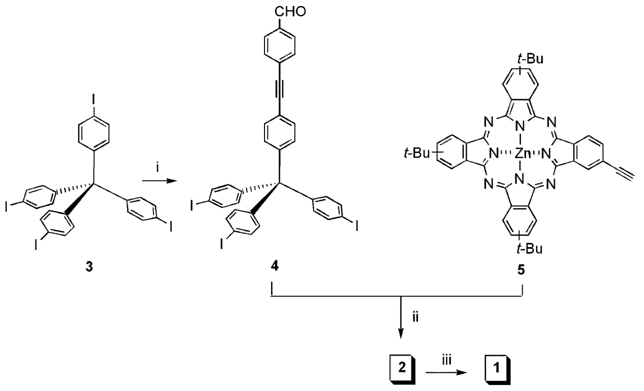
This motivated us to pursue a tetrahedral arrangement, which combines three phthalocyanines and one fullerene, as a unique molecular mimic for natural photosynthesis. In this article we describe the synthesis and photophysical properties of a tripodal architecture **1**—based on a tetraphenylmethane core bearing three phthalocyanine arms and a fullerene arm (Fig. 1)—and the corresponding reference system **2**.

Results and discussion

Synthesis

The synthetic strategy towards the tripodal system **1** consisted of the preparation of the precursor formyl-phthalocyanine **2**, followed by 1,3-dipolar cycloaddition reaction with C_{60} and sarcosine (Scheme 1).

Tetraphenylmethane derivative **4** was synthesized by means of Sonogashira cross-coupling reaction of 4-ethynylbenzaldehyde[11] over one of the iodophenyl moieties of **3**[12,6c] in the presence of Et_3N, THF and a catalytic amount of $[Pd(PPh_3)_2Cl_2]$ and CuI in 29% yield. Tri-*tert*-butyl-ethynylphthalocyaninatozinc(II) (**5**)[13] was then subjected to a threefold cross-coupling reaction over **4** to give precursor formyl tripod **2**. In order to minimize the formation of the bisphthalocyanine derivative from **5** *via* oxidative homocoupling, the reaction was carried out by using tris(dibenzylidenacetone)dipalladium(0) ($[Pd_2(dba)_3]$) as palladium catalyst and triphenylarsine as ligand. In spite of this, the Pc dimer butadynyl-bridged bisphthalocyaninato was formed at the very first steps to generate the active catalytic species [Pd(0)]. To avoid the formation of an undesired mixture of Pc adducts, a strong excess of phthalocyanine **5** (10 equivalents) was necessary, yielding 74% of **2** after column chromatography on silica gel (hexane–THF, 2 : 1) followed by an additional purification by gel permeation chromatography (Bio Beads SX-1)® in THF as eluent. Tripod **1** was finally obtained in 22% yield by 1,3-dipolar cycloaddition reaction of **2** with C_{60} in the presence of sarcosine and toluene as solvent.



Scheme 1 Synthesis of phthalocyanine–fullerene tripod **1**. (i) 4-ethynylbenzaldehyde, $[Pd(PPh_3)_2Cl_2]$, CuI, Et_3N, THF, rt, 24 h (29%); (ii) $Pd_2(dba)_3$, $AsPh_3$, Et_3N, THF, rt, 48 h (74%); (iii) C_{60}, sarcosine, toluene, reflux, 24 h (22%).

All the compounds were characterized by mass spectrometry, ^{1}H-NMR, UV-Vis and FT-IR spectroscopy. The ^{1}H-NMR spectra of tripods **1** and **2** show the typical broad multiplets in the aromatic region, between 9.0 and 7.0 ppm, characteristic of *tert*-butyl substituted phthalocyanines. The presence of a complex mixture of regioisomers renders the assignment of the peaks in this region of the spectra difficult. Additionally, the characteristic aldehyde signal appeared in the spectrum of formyl-Pc **2**, as well as signals corresponding to the pyrrolidine ring in the case of **1**. Concerning MS, molecular ion peaks were observed, while a peak corresponding to the $[M - C_{60}]^+$ fragment was present in the spectrum of **1**.

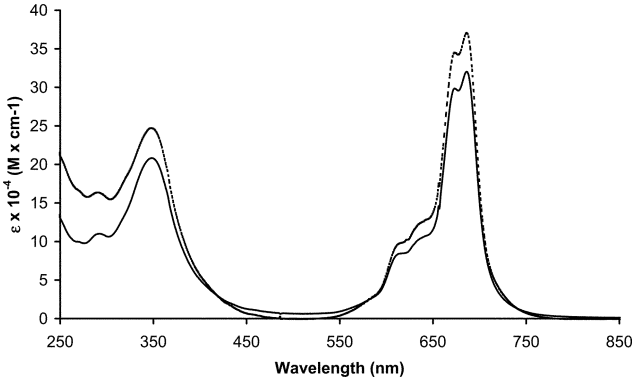


Fig. 2 Absorption spectra of **1** (dashed line) and **2** (solid line) in THF.

The UV-Vis spectra of tripods **1** and **2** in THF—see Fig. 2—reveal that both compounds exhibit in toluene, anisole, THF and benzonitrile a set of Q-bands. In particular, a strong maximum develops around 686 nm, which is flanked by a minor maximum around 673 nm and a shoulder around 620 nm. The Soret band, on the other hand, has a maximum at 348 nm. An additional band is seen at 330 nm in **1**, which reflects a fullerene centered transition.[14]

Photophysical studies

First insight into donor–acceptor interactions between ZnPc and C_{60} came from fluorescence assays. To ensure comparable excitation of the ZnPc chromophores, solutions of **1** and **2** were adjusted to exhibit absorbances of around 0.05 at the 610 nm excitation wavelength. Moreover, keeping the absorption low avoids inner filter effects, namely, artificial impact of the emission. In the monitored range between 600 and 850 nm **2**—as a reference system—emits strongly with a maximum at 698 nm. From the absorption and fluorescence features we derive an excited state energy of 1.8 eV. Surprisingly the fluorescence quantum yield is 0.056 in DMF, which is appreciably smaller than established, for example, for a ZnPc reference (0.3). Likewise, the fluorescence lifetime, which was determined in time-resolved measurements, is 1.19 ns, shorter than in a ZnPc reference (3.1 ns) (ESI‡ Fig. S11). When turning to **1**, the fluorescence quantum yield further drops to 0.029 (Fig. 3).

Transient absorption spectroscopy by means of femtosecond laser photolysis helped to provide evidence for a charge transfer

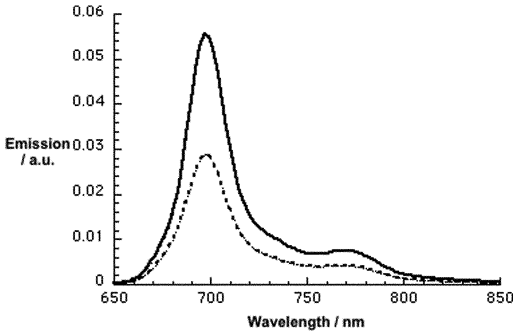


Fig. 3 Fluorescence spectra of the tripod reference **2** (solid line) and the donor–acceptor conjugate **1** (dotted line) in DMF upon 610 nm photoexcitation.

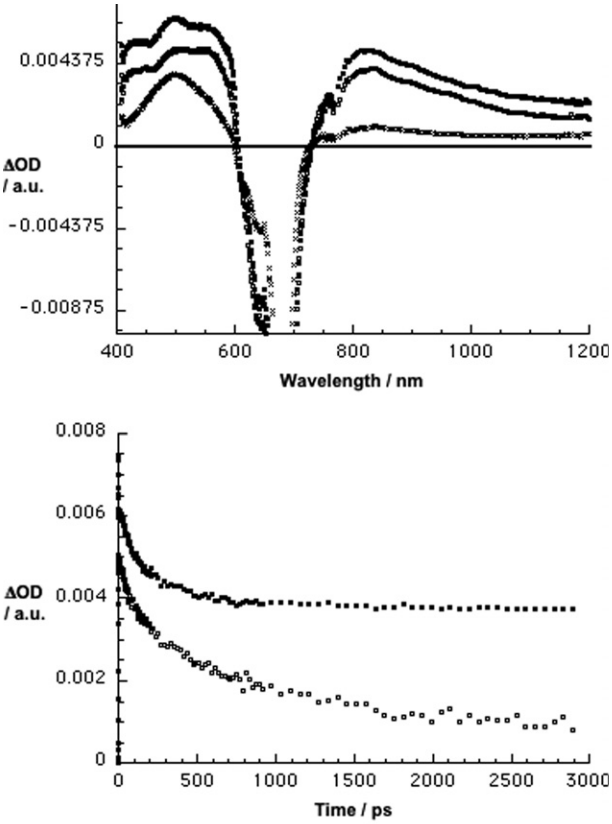


Fig. 4 Upper part: differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (387 nm) of **2** in argon saturated THF with several time delays (1 ps: closed squares; 100 ps: open squares; 2900 ps: crosses) at room temperature. Lower part: time–absorption profiles of the spectra shown above at 500 (closed squares) and 800 nm (open squares), monitoring the intersystem crossing.

mechanism between photoexcited ZnPc and C_{60}. Fig. 4 gathers the transient absorption changes that correlate with the ZnPc singlet excited state in **2**. An instantaneously formed broad transient maximum develops at 490 nm. Bleaching, on the other hand, is seen between 620 nm and 685 nm—a spectral range that is dominated by the ground state absorption of ZnPc. This transient decays rather slowly *via* intersystem crossing on the time scale of our instrumental detection (*i.e.*, up to 3000 ps). A multi-wavelength analysis gives rise a singlet excited state lifetime of about 680 ps. The product of this intersystem crossing is a triplet excited state, for which a broad transient with a notable maximum at 500 nm is registered. To determine the quantum yield of triplet excited state formation, we turned to singlet oxygen sensitization. In fact, for **2** a value of 0.44 was determined in DMF.

When probing donor–acceptor system **1** the ZnPc singlet excited state characteristics (*vide supra*)—despite the presence of the electron accepting C_{60}—were registered upon photoexcitation. The ZnPc singlet excited state features in **1** decay much faster than the slow intersystem crossing dynamics, which were noted for **2**. Singlet lifetimes of 96 ps and 50 ps were measured in benzonitrile and DMF, respectively, from fitting the 1200 nm time absorption profiles. Within this decay the formation of a new transient species evolves. Distinct maxima were noted at 520, 840 and 1000 nm. The earlier maxima, that is, at 520 and 840 nm, are attributes of the one-electron oxidized ZnPc radical cation. The latter maximum at 1000 nm matches the absorption of the one-electron reduced fullerene radical anion. In summary, transient absorption measurements testify to the formation of an intramolecularly formed radical ion pair state.§ The quantum yield of charge separation assumes values in benzonitrile that are typically around 0.28. Please note that in less polar anisole and THF (ESI‡ Fig. S12) neither kinetic nor spectroscopic evidence was gathered that would indicate charge separation.

Both features of the radical ion pair state—ZnPc (*i.e.*, 520 and 840 nm) and C_{60} (*i.e.*, 1000 nm)—decay on the time scale of our femtosecond experiments. The impact that the solvent polarity exerts on the decay of the radical ion pair state is reflected in the time profiles of the ZnPc radical cation absorption at 845 nm—see Fig. 5. The lifetime of the radical ion pair state is somewhat longer in less polar benzonitrile (1000 ps) than in more polar DMF (650 ps). Concomitantly with the decay of the transient radical ion pair state a new band with a maximum at 500 nm grows in. This transient absorption corresponds to the ZnPc triplet excited state.[15] We consider two pathways for the triplet formation: firstly, indirect formation through a deactivation of the radical ion state and, secondly, direct formation through a competition between intersystem crossing and charge separation. The triplet quantum yields were again estimated by following the singlet oxygen formation: 0.21 (THF), and 0.12 (DMF) (ESI‡ Fig. S13).

In summary, a tripodal architecture **1** based on a tetraphenylmethane core bearing three phthalocyanine arms and a fullerene arm has been prepared. The compound reveals long range electron transfer activity. Transient absorption spectroscopy by means of femtosecond laser photolysis provided spectroscopic evidence for a charge transfer mechanism between photoexcited ZnPc and C_{60}. When relating the radical ion pair state lifetime of 1000 ps (in benzonitrile) to previously assayed ZnPc–C_{60} donor–acceptor conjugates, we note in general a significant stabilization. As a leading example the *para*-cyclophane-vinylene bridged

---

§ Electrochemical measurements—by means of differential pulse voltammetry—revealed the first C_{60} reduction at -0.78 ± 0.1 V and the first ZnPc oxidation at $+0.68 \pm 0.1$ V *versus* Fc/Fc^{+}).

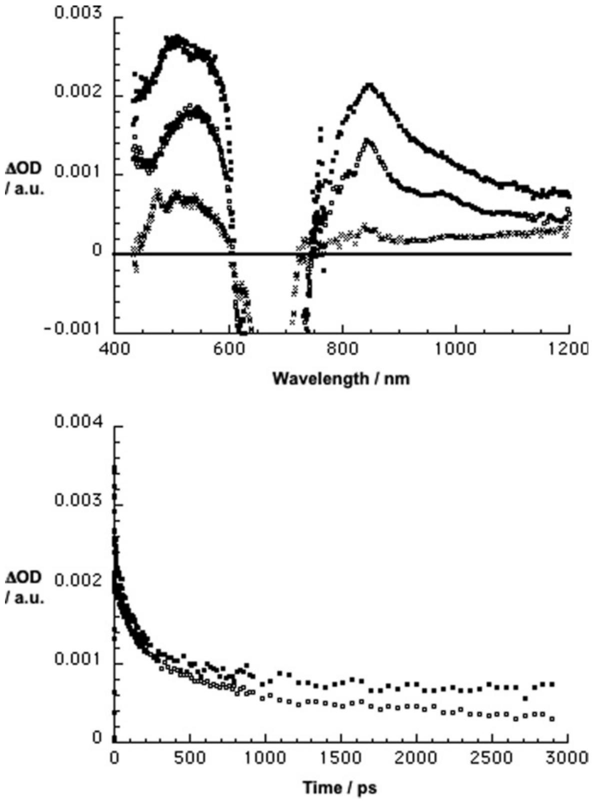


Fig. 5 Upper part: differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (670 nm) of **1** in argon saturated benzonitrile with several time delays (1 ps: closed squares; 102 ps: open squares; 2892 ps: crosses) at room temperature. Lower part: time–absorption profiles of the spectra shown above at 845 nm, monitoring the charge separation and charge recombination in DMF (open squares) and benzonitrile (closed squares).

analogue should be considered, for which a lifetime of 330 ps has been determined.[15] We are currently investigating related multinuclear Pc–fullerene-based systems in which both covalent and supramolecular motifs are involved *en route* towards novel electron donor–acceptor conjugates.

Experimental

Synthesis

4-{2-[4-Tris(4-iodophenyl)phenyl]ethynyl}benzaldehyde (4). A solution of tetrakis(4-iodophenyl)methane (**3**) (400 mg, 0.48 mmol), 4-ethynylbenzaldehyde[11] (60 mg, 0.46 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol), CuI (4 mg, 0.02 mmol), and triethylamine (0.5 mL) in dry THF (6 mL) was stirred at room temperature under argon for 24 h. After this period the solvent was removed under reduced pressure and the residue triturated with hexane. The precipitate was filtered off and purified by silica gel column chromatography (hexane–dioxane 4 : 1). Compound **4** (117 mg, 29%.) was obtained as a white solid; mp > 250 °C (Found: C, 49.05; H, 2.7. $C_{34}H_{21}I_3O$ requires C, 49.4; H, 2.6%); ν_{max}(KBr)/cm^{-1} 2222, 1705 (CO), 1597, 1479, 1398, 1308, 1207, 1167, 1011, 810, 756 and 716; δ_H(300 MHz; $CDCl_3$; Me_4Si) 10.02 (s, 1H; CHO), 7.86 (d, *J* 8.5, 2H), 7.66 (d, *J* 8.5, 2H), 7.59 (d, *J* 8.7, 6H), 7.44 (d, *J* 8.5, 2H), 7.16 (d, *J* 8.5, 2H) and 6.91 (d, *J* 8.7, 6H); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 191.4 (CHO), 145.6, 145.1, 137.1, 135.4, 132.8, 132.6, 132.1, 131.3, 130.7, 120.5, 92.4, 92.2 and 63.9 (central C); *m*/*z* (FAB; *m*-NBA) 826.9 [M]$^+$, 701.0 [M − I]$^+$ and 622.9 [M − C_6H_5I]$^+$.

Phthalocyanine tripod 2. A solution of tri-*tert*-butylethynylphthalocyaninatozinc(II) (**5**)[13] (54 mg, 0.07 mmol), **4** (6.1 mg, 0.007 mmol), $Pd_2(dba)_3$ (4 mg, 0.004 mmol), $AsPh_3$ (4 mg, 0.015 mmol) and triethylamine (0.5 mL) in dry THF (6 mL) was stirred at room temperature under argon during 2 days. The solvent was evaporated and the residual solid was extracted with $CHCl_3$, dried over Na_2SO_4 and purified first by silica gel column chromatography (hexane–THF 2 : 1) and then by Bio-Beads® size-exclusion column chromatography (THF). The green solid obtained was washed with MeOH and hexane, and dried under reduced pressure affording **2** (14 mg, 74%.) in the form of a mixture of regioisomers. Mp > 300 °C; λ_{max} (THF)/nm (log ϵ) 686 (5.5), 673 (5.5) and 348 (5.3); ν_{max}(KBr)/cm^{-1} 2966, 2926, 2872, 1705 (CO), 1610, 1489, 1462, 1394, 1367, 1327, 1286, 1259, 1192, 1151, 1097, 1057, 930, 835, 754 and 700; δ_H(500 MHz; THF-d_8; Me_4Si) 10.1 (s, 1H; CHO), 9.7–7.0 (br, 56H; arom H) and 1.9 (br m, 81H; CMe_3); *m*/*z* (MALDI; dithranol) 2753.0 [M]$^+$; *m*/*z* (HR-MALDI; dithranol) 2746.9263 ($C_{172}H_{138}N_{24}OZn_3$ requires 2746.9354).

Phthalocyanine–C_{60} tripod 1. A dry toluene solution (50 mL) of C_{60} (23.5 mg, 0.03 mmol), *N*-methylglycine (4.0 mg, 0.05 mmol) and **2** (30 mg, 0.01 mmol) was heated to reflux under argon atmosphere for 24 h. The solution was then cooled to room temperature and concentrated under vacuum until *ca.* 10 mL. The resulting mixture was poured onto a silica gel column and eluted with toluene–AcOEt 95 : 5, passing to toluene–AcOEt 8 : 1. The green solid obtained was washed with acetone, methanol and hexane, leading to **1** (8 mg, 22%.) in the form of a mixture of regioisomers. Mp > 250 °C; λ_{max} (THF)/nm (log ϵ) 686 (5.57), 673 (5.54) and 348 (5.39); ν_{max}(KBr)/cm^{-1} 2966, 1614, 1493, 1398, 1333, 1265, 1153, 1099, 1059, 922, 839, 750, 702 and 677; δ_H(500 MHz; THF-d_8; Me_4Si) 9.8–7.0 (br, 56H, arom H), 5.49, 5.45 and 4.83 (br, 3H; pyrrolidine H), 3.46 (s, 3H; N-Me) and 1.9 (br, 81H; CMe_3); *m*/*z*: (MALDI; dithranol) 3500.8 [M + H]$^+$, 2779.8 [M − C_{60}]$^+$; *m*/*z* (HR-MALDI; dithranol) 3494.9866 ($C_{234}H_{143}N_{25}Zn_3$ requires 3494.9860).

Photophysics

Optical absorptions were measured with a Cary 5000 UV-vis-NIR spectrometer (Varian). Such measurements, with the exception of the femtosecond photolysis experiments, were carried out by using quartz cells with a 1 cm optical path length. Steady-state fluorescence measurements were performed by using a Fluoromax 3 (Horiba Jobin Yvon). The time resolved fluorescence and steady state singlet oxygen phosphorescence measurements were performed using a Fluorolog TCSPC (Horiba Jobin Yvon). The solvents were always of spectroscopic grade. The femtosecond transient absorption measurements were carried out with a CPA-2001 femtosecond laser (Clark MXR). The excitation wavelength was generated with an NOPA (Clark MXR). The laser output energy was 240 nJ for **1** and 300 nJ for **2**.

Acknowledgements

This work has been supported by the Spanish MEC (CTQ-2005-08933-BQU and Consolider Ingenio 2010 CDS2007-00010 NANOCIENCIA MOLECULAR), the Comunidad de Madrid (S-0505/PPQ/000225), the European Union (STREP, 516982, HETEROMOLMAT), the ESF-MEC (project SOHYD), and by the Deutsche Forschungsgemeinschaft through SFB583, DFG (GU 517/4-1), FCI, and the Office of Basic Energy Sciences of the U.S. Department of Energy.

References

1 (*a*) *Photoinduced Electron Transfer*, ed. M. A. Fox and M. Chanon, Elsevier, Amsterdam, 1988; (*b*) V. Balzani and F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood, Chichester, 1991, pp. 161–196 and 355–394; (*c*) S. Speiser, *Chem. Rev.*, 1996, **96**, 1953–1976; (*d*) J. G. Calbert, *Photochemistry*, Wiley, New York, 1996; (*e*) D. Gust, *Nature*, 1997, **386**, 21–22; (*f*) *Electron Transfer in Chemistry*, ed. V. Balzani, Wiley-VCH, Weinheim, 2001 vol. I–V; M. N. Paddon-Row, in *Stimulating Concepts in Chemistry*, ed. F. Vögtle, J. F. Stoddart and M. Shibasaki, Wiley-VCH, Weinheim, 2000.

2 (*a*) M. Simard, D. Su and J. D. Wuest, *J. Am. Chem. Soc.*, 1991, **113**, 4696; (*b*) X. Li and B. C. Gibb, *Supramol. Chem.*, 2003, **15**, 495; (*c*) J.-H. Fournier, T. Maris, J. D. Wuest, W. Guo and E. Galoppini, *J. Am. Chem. Soc.*, 2003, **125**, 1002; (*d*) D. Laliberté, T. Maris and J. D. Wuest, *Can. J. Chem.*, 2004, **82**, 386.

3 (*a*) L. M. Wilson and A. C. Griffin, *J. Mater. Chem.*, 1993, **3**, 991; (*b*) O. Mongin and A. Gossauer, *Tetrahedron*, 1997, **53**, 6835; (*c*) U.-M. Wiesler and K. Müllen, *Chem. Commun.*, 1999, 2293; (*d*) S. Sengupta and S. K. Sadhukhan, *Tetrahedron Lett.*, 1999, **40**, 9157; (*e*) G. M. Hübner, G. Nachtsheim, Q. Y. Li, C. Seel and F. Vögtle, *Angew. Chem., Int. Ed.*, 2000, **39**, 1269; (*f*) E. C. Constable, O. Eich, C. E. Housecroft and D. C. Rees, *Inorg. Chim. Acta*, 2000, **300–302**, 158; (*g*) J. P. Novak and D. L. Feldheim, *J. Am. Chem. Soc.*, 2000, **122**, 3979; (*h*) E. C. Constable, O. Eich, D. Fenske, C. E. Houseeroft and L. A. Johnston, *Chem.–Eur. J.*, 2000, **6**, 4364.

4 (*a*) N. Armaroli, V. Balzani, J.-P. Collin, P. Gaviña, J.-P. Sauvage and B. Ventura, *J. Am. Chem. Soc.*, 1999, **121**, 4397; (*b*) S. Wang, W. J. Oldham, R. A. Hudack and G. C. Bazan, *J. Am. Chem. Soc.*, 2000, **122**, 5695; (*c*) T. J. Zimmermann, O. Freundel, R. Gompper and T. J. J. Müller, *Eur. J. Org. Chem.*, 2000, 3305; (*d*) H. Zhao, C. Tanjutco and S. Thayumanavan, *Tetrahedron Lett.*, 2001, **42**, 4421.

5 A. Pegenau, T. Hegmann, C. Tschierske and S. Diele, *Chem.–Eur. J.*, 1999, **5**, 1643.

6 (*a*) Y. Yao and J. M. Tour, *J. Org. Chem.*, 1999, **64**, 1968; (*b*) H. Jian and J. M. Tour, *J. Org. Chem.*, 2003, **68**, 5091; (*c*) Q. Li, A. V. Rukavishnikov, P. A. Petukhov, T. O. Zaikova and J. F. W. Keana, *Org. Lett.*, 2002, **4**, 3631.

7 D. Hirayama, K. Takimiya, Y. Aso, T. Otsubo, T. Hasobe, H. Yamada, H. Imahori, S. Fukuzumi and Y. Sakata, *J. Am. Chem. Soc.*, 2002, **124**, 532.

8 (*a*) G. de la Torre, C. G. Claessens and T. Torres, *Chem. Commun.*, 2007, 2000; (*b*) *Phthalocyanines: Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH, Weinheim, 1989, 1993, 1996, vol. 1–4; (*c*) *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, 2003, vol. 15–20.

9 (*a*) H. Imahori, K. Tamaki, D. M. Guldi, C. Luo, M. Fujitsuka, O. Ito, Y. Sakata and S. Fukuzumi, *J. Am. Chem. Soc.*, 2001, **123**, 2607; (*b*) H. Imahori, D. M. Guldi, K. Tamaki, Y. Yoshida, C. Luo, Y. Sakata and S. Fukuzumi, *J. Am. Chem. Soc.*, 2001, **123**, 6617; (*c*) H. Imahori, H. Yamada, D. M. Guldi, Y. Endo, A. Shimomura, S. Kundu, K. Yamada, T. Okada, Y. Sakata and S. Fukuzumi, *Angew. Chem., Int. Ed.*, 2002, **41**, 2344; (*d*) D. M. Guldi, H. Imahori, K. Tamaki, Y. Kashiwagi, H. Yamada, Y. Sakata and S. Fukuzumi, *J. Phys. Chem.*, 2004, **108**, 541; (*e*) N. Martín, *Chem. Commun.*, 2006, 2093; (*f*) A. Hirsch and M. Brettreich, *Fullerenes: Chemistry and Reactions*, Wiley-VCH, Weinheim, 2004; (*g*) D. M. Guldi and N. Martín, *Fullerenes: From Synthesis to Optoelectronic Properties, Series: Developments in Fullerene Science*, Kluwer Academic, Dordrecht, 2002; (*h*) *Fullerenes: Principles and Applications*, ed. F. Langa and J.-F. Nierengarten, Royal Society of Chemistry, Cambridge, 2007.

10 (*a*) A. Sastre, A. Gouloumis, P. Vázquez, T. Torres, V. Doan, B. J. Schwartz, F. Wudl, L. Echegoyen and J. Rivera, *Org. Lett.*, 1999, **1**, 1807; (*b*) D. M. Guldi, A. Gouloumis, P. Vázquez and T. Torres, *Chem. Commun.*, 2002, 2056; (*c*) M. A. Loi, H. Neugebauer, P. Denk, C. J. Brabec, N. S. Sariciftci, A. Gouloumis, P. Vázquez and T. Torres, *J. Mater. Chem.*, 2003, **13**, 700; (*d*) D. M. Guldi, J. Ramey, M. V. Martínez-Díaz, A. de la Escosura, T. Torres, T. Da Ros and M. Prato, *Chem. Commun.*, 2002, 2774; (*e*) M. V. Martínez-Díaz, N. S. Fender, M. S. Rodríguez-Morgade, M. Gómez-López, F. Diederich, L. Echegoyen, J. F. Stoddart and T. Torres, *J. Mater. Chem.*, 2002, **12**, 2095; (*f*) D. M. Guldi, I. Zilbermann, A. Gouloumis, P. Vázquez and T. Torres, *J. Phys. Chem. B*, 2004, **108**, 18485; (*g*) A. de la Escosura, M. V. Martínez-Díaz, D. M. Guldi and T. Torres, *J. Am. Chem. Soc.*, 2006, **128**, 4112; (*h*) M. E. El-Khouly, O. Ito, P. M. Smith and F. D'Souza, *J. Photochem. Photobiol., C*, 2004, **5**, 79; (*i*) D. M. Guldi, A. Gouloumis, P. Vázquez, T. Torres, V. Georgakilas and M. Prato, *J. Am. Chem. Soc.*, 2005, **127**, 5811; (*j*) J. L. Sessler, J. Jayawickramarajah, A. Gouloumis, T. Torres, D. M. Guldi, S. Maldonado and K. J. Stevenson, *Chem. Commun.*, 2005, 1892; (*k*) B. Ballesteros, G. de la Torre, T. Torres, G. L. Hug, G. M. A. Rahman and D. M. Guldi, *Tetrahedron*, 2006, **62**, 2097; (*l*) T. Torres, A. Gouloumis, D. Sanchez-García, J. Jayawickramarajah, W. Seitz, D. M. Guldi and J. L. Sessler, *Chem. Commun.*, 2007, 292; (*m*) B. Ballesteros, G. de la Torre, C. Ehli, G. M. A. Rahman, F. Agulló-Rueda, D. M. Guldi and T. Torres, *J. Am. Chem. Soc.*, 2007, **129**, 5061; (*n*) M. E. El-Khouly, O. Ito, P. M. Smith and F. D'Souza, *J. Photochem. Photobiol., C*, 2004, **5**, 79; (*o*) F. D'Souza and O. Ito, *Coord. Chem. Rev.*, 2005, **249**, 1410.

11 (*a*) W. B. Austin, N. Bilow, W. J. Kelleghan and K. S. Y. Lau, *J. Org. Chem.*, 1981, **46**, 2280; (*b*) M. Ravikanth, J. P. Strachan, F. Li and J. S. Lindsey, *Tetrahedron*, 1998, **54**, 7721.

12 D. Su and F. M. Menger, *Tetrahedron Lett.*, 1997, **38**, 1485.

13 E. M. Maya, P. Vázquez and T. Torres, *Chem.–Eur. J.*, 1999, **5**, 2004.

14 D. M. Guldi and M. Prato, *Acc. Chem. Res.*, 2000, **33**, 695.

15 A. Kahnt, D. M. Guldi, A. de la Escosura, M. V. Martınez-Díaz and T. Torres, *J. Mater. Chem.*, 2008, **18**, 77.