Porphyrin–C60 Conjugates

Exceptional Redox and Photophysical Properties of a Triply Fused Diporphyrin–C_{60} Conjugate: Novel Scaffolds for Multicharge Storage in Molecular Scale Electronics**

Davide Bonifazi, Markus Scholl, Fayi Song,
Luis Echegoyen, Gianluca Accorsi, Nicola Armaroli,**
*and François Diederich**

Dedicated to Professor Manfred T. Reetz
on the occasion of his 60th birthday

The expansion and functionalization of π-conjugated molecular architectures to enhance the optoelectronic properties of the resulting chromophores is a topic of broad current interest.[1] Fascinating examples are the molecular tapes consisting of triply fused porphyrins, reported by Osuka and co-workers, which exhibit exceptionally low-energy electronic states and hold great potential as molecular wires in nanoscale electronics devices.[2]

The past decade has seen the construction of a great variety of electron donor–acceptor dyads, frequently featuring C_{60} as the electron-accepting component because of its three-dimensional structure and six easily accessible reduction states in solution.[3] In a biomimetic fashion, many of these dyads feature porphyrin donors which lose their characteristic luminescence properties as a result of light-induced energy and/or electron transfer to the fullerene acceptor.[4,5]

Since the chemical functionalization of the triply fused porphyrin sheets is largely unexplored[6] and the nature of their interactions with redox- and photoactive chromophores, such as fullerenes, unknown, we decided to prepare conjugate **1** with two C_{60} spheres covalently attached to a triply fused porphyrin dimer (Scheme 1). Here, we describe the synthesis and the exceptional physical properties of **1**. The first full electrochemical study on triply fused porphyrin sheets shows that **1** is capable of undergoing as many as fifteen reversible electron-transfer processes. Moreover, photophysical investigations demonstrate that **1** does not exhibit at all the classical[7] behavior documented for numerous porphyrin–fullerene dyads. Rather, photoexcitation of the fullerene units results in quantitative sensitization of the weakly emitting lowest singlet level of the porphyrin sheet while the fullerene emission is quenched.

The functionalized triply fused porphyrin dimer **2** on the way to **1** was obtained following two routes (Scheme 1). Dimerization of diarylporphyrin **3** with $AgPF_6$, followed by silver-mediated iodination and subsequent Suzuki coupling with phenylboronic ester **4**,[8] afforded the biaryl-type dimer **5**. Dimer **5** was converted into **2** (11% yield over four steps) following the protocol by Tsuda and Osuka[2c] for oxidative ring closure (DDQ and $Sc(OTf)_3$). As a better alternative, monoiodination of **3** afforded **6** and Suzuki coupling with **4** gave **7**. Oxidative ring closure of **7** directly led to **2** (39% yield over three steps). Reduction of **2** (DIBAL-H) provided dialdehyde **8** which was reduced ($NaBH_4$) to the corresponding bis(benzyl alcohol). Esterification with EtO_2CCH_2COCl yielded bismalonate **9**, and Bingel reaction with C_{60} gave the target conjugate **1**.

The redox properties of **1, 2, 5**, and comparison compounds **10**,[9] **11**,[9] and **12** were examined by cyclic (CV) and differential pulse (DPV) voltammetry (Table 1, Figures 1 and 2).

The cyclic voltammogram of **5** (Table 1) features two partially overlapped reduction couples at −1.75 and −1.86 V (difference of 0.11 V). The first 1-e^- oxidation of the two porphyrin moieties appears as separated couples at 0.38 and 0.51 V whereas the second oxidation of both rings also gives two couples at 0.78 and 1.10 V. Seven reversible redox couples with identical current for each peak were observed for the triply fused porphyrin dimer **2** in CH_2Cl_2 (Figure 1b). The first and second reduction couples correspond to two-step, 1-e^- per porphyrin ring reductions. Likewise, the first and the

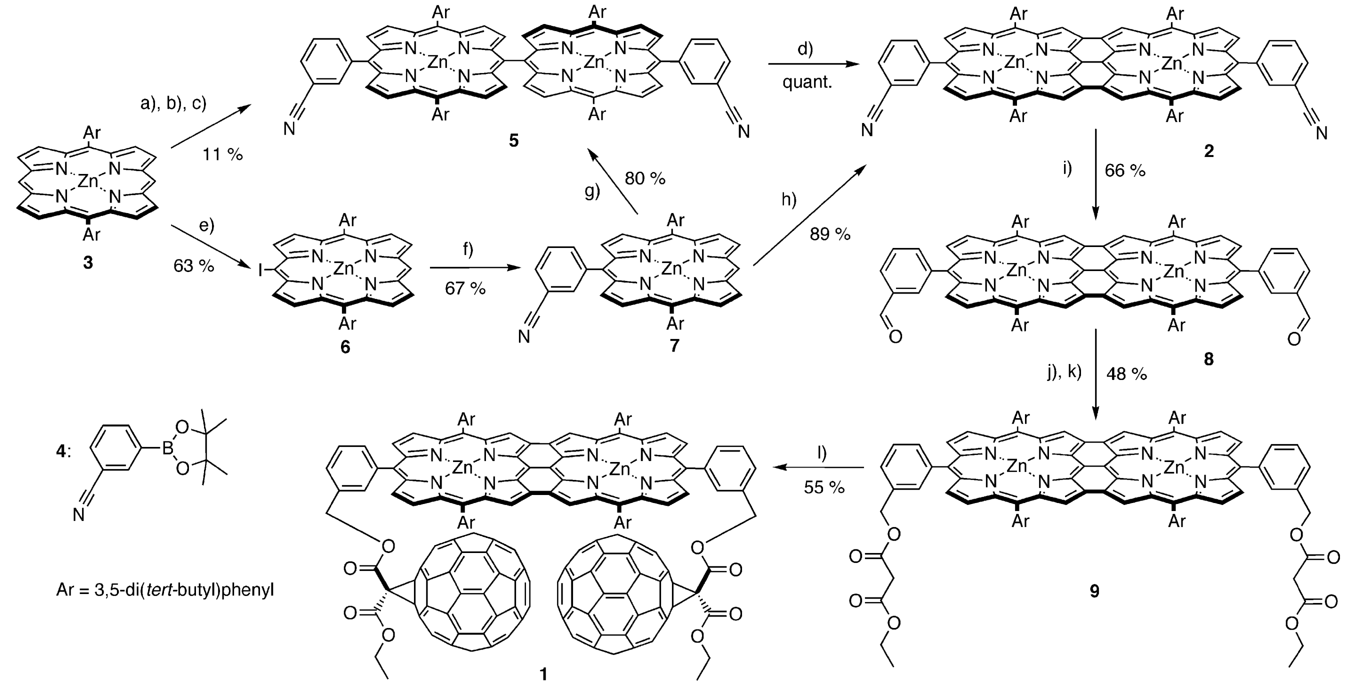
---

[*] Prof. Dr. L. Echegoyen, Dr. F. Song
Department of Chemistry
Clemson University
219 Hunter Laboratories, Clemson SC 29634 (USA)
Fax: (+1) 864-656-6613
E-mail: luis@clemson.edu
Dr. N. Armaroli, Dr. G. Accorsi
Istituto per la Sintesi Organica e la Fotoreattività
40129 Bologna (Italy)
Fax: (+39) 051-6399844
E-mail: armaroli@isof.cnr.it
Prof. Dr. F. Diederich, D. Bonifazi, M. Scholl
Laboratorium für Organische Chemie
ETH-Hönggerberg, HCI
8093 Zürich (Switzerland)
Fax: (+41) 1-632-1109
E-mail: diederich@org.chem.ethz.ch

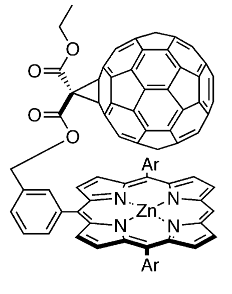
[**] We thank Rolf Häfliger for the mass spectrometric measurements. This research was supported by the Swiss National Science Foundation and the NCCR "Nanoscale Science", the Spinner Agency (Regione Emilia-Romagna, Italy), and the US National Science Foundation (CHE-0135786).

Supporting information for this article (selected physical and spectral data of **1** and **2**, cyclic voltammograms of **1, 2**, and **11**, luminescence spectra of **11** compared to reference compounds **5** and **13**, UV/Vis data of **1, 2, 9**, and **13**) is available on the WWW under http://www.angewandte.org or from the author.

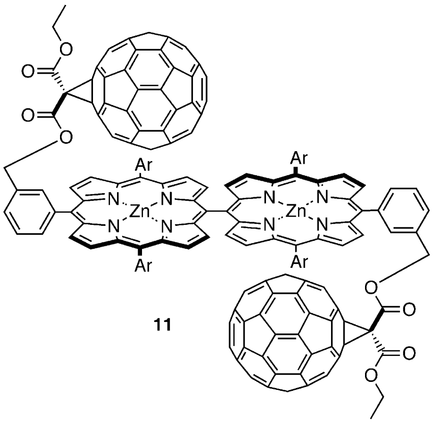
DOI: 10.1002/ange.200352265



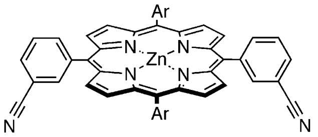
Scheme 1. Synthesis of conjugate **1**. a) $AgPF_6$, $CH_3CN/CHCl_3$ 1:6, RT, 15 h; b) $AgPF_6$, I_2, pyridine/$CHCl_3$ 1:60, RT; c) **4**, Cs_2CO_3, $[Pd(PPh_3)_4]$, toluene, reflux, 18 h; d) DDQ, $Sc(OTf)_3$, toluene, reflux, 30 min; e) $AgPF_6$, I_2, pyridine/$CHCl_3$ 1:60, RT; f) **4**, Cs_2CO_3, $[Pd(PPh_3)_4]$, toluene, reflux, 18 h; g) $AgPF_6$, $CH_3CN/CHCl_3$ 1:6, RT, 15 h; h) DDQ, $Sc(OTf)_3$, toluene, reflux, 30 min; i) DIBAL-H, CH_2Cl_2, −78 °C→RT, 2.5 h; j) $NaBH_4$, THF/EtOH 1:1, 0 °C→RT, 4 h; k) EtO_2CCH_2COCl, Et_3N, CH_2Cl_2, RT, 16 h; l) C_{60}, I_2, DBU, toluene, RT, 1.5 h. DDQ = 2,3-dichloro-5,6-dicyano-*p*-benzoquinone; DIBAL-H = di(*iso*-butyl)aluminum hydride; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; Tf = trifluoromethanesulfonyl.



10



11



12

Table 1: Cyclic voltammetry data in CH_2Cl_2 (+0.1 M nBu_4NPF_6).[a]

	$E^{1/2}_{\mathrm{red},1}$	$E^{1/2}_{\mathrm{red},2}$	$E^{1/2}_{\mathrm{red},3}$	$E^{1/2}_{\mathrm{red},4}$	$E^{1/2}_{\mathrm{ox},1}$	$E^{1/2}_{\mathrm{ox},2}$	$E^{1/2}_{\mathrm{ox},3}$	$E^{1/2}_{\mathrm{ox},4}$
12	−1.71(1 e^-)	−2.09(1 e^-)	–	–	0.44(1 e^-)	0.74(1 e^-)	–	–
5	−1.75(1 e^-)	−1.86(1 e^-)	−2.20(1 e^-)	–	0.38(1 e^-)	0.51(1 e^-)	0.78(1 e^-)	1.10(1 e^-)
2[b]	−1.06(1 e^-)	−1.40(1 e^-)	−2.29(1 e^-)	−2.59(1 e^-)	0.15(1 e^-)	0.47(1 e^-)	0.92(1 e^-)	–
2	−1.01(1 e^-)	−1.26(1 e^-)	−2.18(1 e^-)	–	0.09(1 e^-)	0.37(1 e^-)	0.83(1 e^-)	1.10(1 e^-)
10	−1.06(1e^-)	−1.41(1 e^-)	−1.84(2 e^-)	–	0.36(1 e^-)	0.74(1 e^-)	–	–
11	−0.98 −1.06(2 e^-)	−1.41(2 e^-)	−1.84(4 e^-)	–	0.37(1 e^-)	0.50(1 e^-)	0.73(1 e^-)	0.84(1 e^-)
1	−0.99 −1.09(3 e^-)	−1.40(3 e^-)	−1.87(2 e^-)	−2.29(3 e^-)	0.03(1 e^-)	0.34(1 e^-)	0.82(1 e^-)	1.09(1 e^-)

[a] Potentials versus Fc/Fc^+. Working electrode: glassy carbon electrode; counter electrode: Pt; reference electrode: Ag/AgCl. Scan rate: 0.1 Vs^{-1}. $E^{1/2} = (E_{pa} + E_{pc})/2$, where E_{pc} and E_{pa} = cathodic and anodic peak potentials, respectively. [b] Solvent: THF.

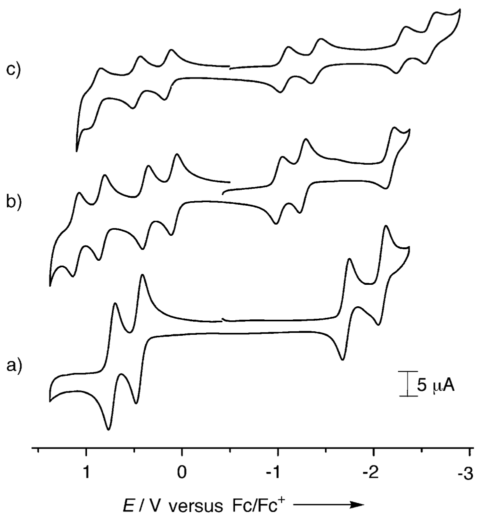


Figure 1. Cyclic voltammograms of a) **12** in CH_2Cl_2, b) **2** in CH_2Cl_2, and c) **2** in THF at 20 ± 2 °C (+0.1 M nBu_4NPF_6).

second oxidation peaks each correspond to a 1-e^- process, one per porphyrin ring. Relative to **12**, the first 1-e^- reduction potential of **2** is shifted positively by 0.7 V whereas the first 1-e^- oxidation potential is shifted negatively by 0.35 V. The fourth reduction peak was not observed because of the limited potential window in CH_2Cl_2. However, CV and DPV measurements in THF revealed the presence of the fourth reduction peak (Figure 1 c). These results confirm that each redox couple for **12** splits into two couples for **2**.

Conjugation of two C_{60} moieties to the triply bridged porphyrin dimer in **1** results in nine reversible redox processes involving a total of fifteen electrons (Figure 2 b). The four oxidation peaks correspond to the four 1-e^- oxidation steps centered at the porphyrin units, and the first oxidation peak is cathodically shifted relative to **2** (Figure 2 a) by 60 mV. The two partially overlapped peaks at −1.0 V correspond to the first reduction of the two C_{60} units and a 1-e^- process for the porphyrin system (a 3-e^- net process). The peak at −1.38 V corresponds, likewise, to the second reduction of the two C_{60} units and a second reduction of the porphyrin sheet (again, a net 3-e^- process). The smaller peak at −1.85 V is attributed to the third 1-e^- reduction of each of the two C_{60} moieties (a 2-e^- process). The peak at −2.28 V corresponds to the fourth 1-e^- reduction of the fullerene moieties and the third 1-e^- reduction of the porphyrin (a 3-e^- net process). The cyclic voltammogram of biaryl-type dimer **11** features the first porphyrin-based oxidation peak potential anodically shifted by 300 mV relative to **1** (Figure 2 c). Furthermore, the first two porphyrin-centered reduction steps in **11** are shifted cathodically by 850 mV relative to the corresponding first reduction couple in **1**.

The photophysical properties of the two conjugates **1** and **11** also differ dramatically. The absorption spectrum (toluene)

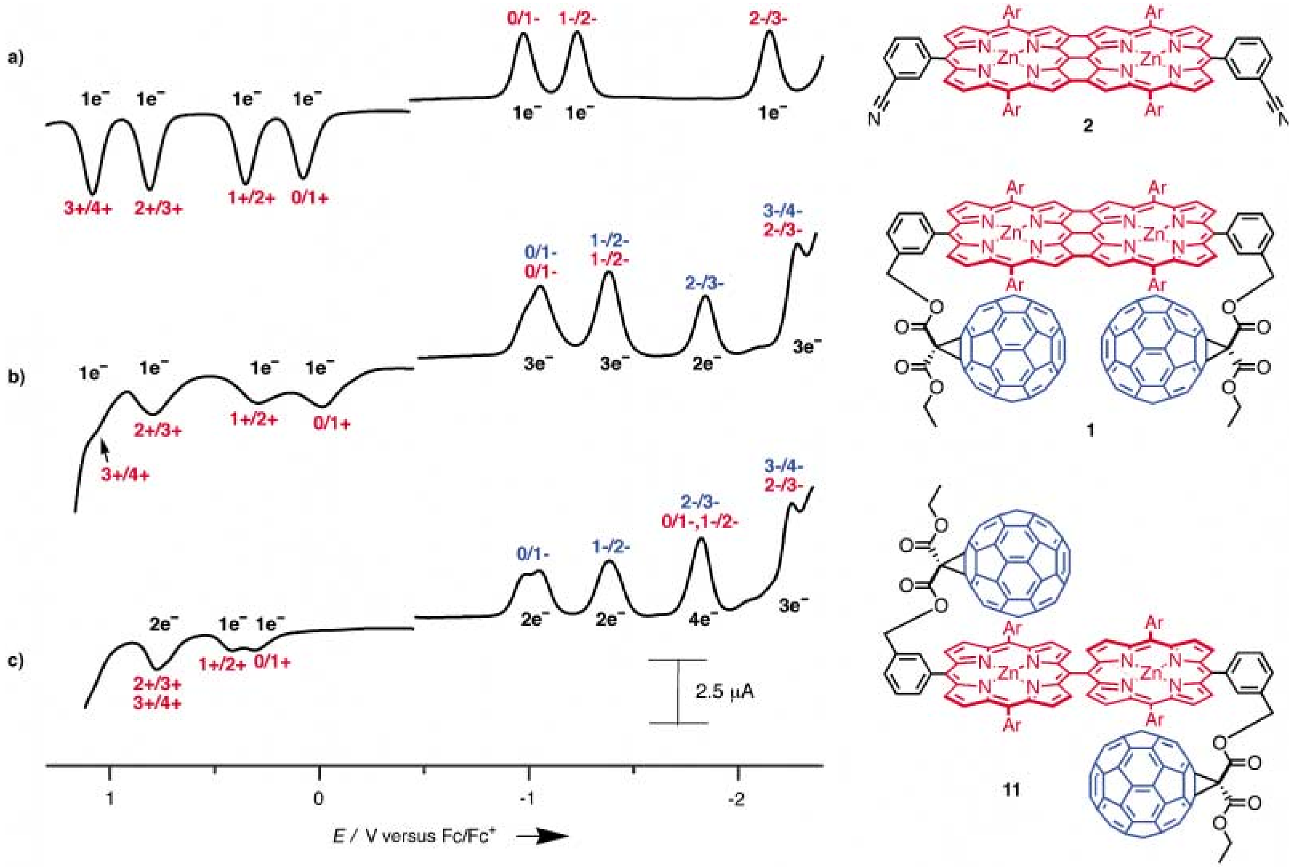
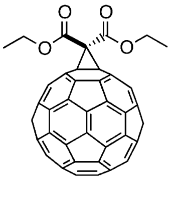


Figure 2. Differential pulse voltammograms of a) **2**, b) **1**, and c) **11** in CH_2Cl_2 at 20 ± 2 °C.



13

of conjugate **11** with the biaryl-type porphyrin dimer does not match the sum spectrum of its component units (**5** and 2 × **13**; Figure 3), particularly in the Soret-band region, which is split as a result of exciton coupling.[10] This result is attributed to strong face-to-face electronic interactions between the porphyrin and fullerene chromophores.[11] Only the 630–800-nm region of the spectrum of **11** is more intense than its calculated counterpart, which suggests the occurrence of sizeable interchromophoric charge transfer interactions.[12] An emissive charge-transfer (CS) state is detected in the NIR region ($\lambda_{max} = 950$ nm, Figure 3). The transient absorption spectrum of **11** in toluene ($\lambda_{exc} = 532$ nm, Figure 3) exhibits the diagnostic broad band of the Zn^{II}–porphyrin radical cation with a maximum at 640 nm, thus indicating that photoinduced electron transfer from the porphyrin to the fullerene moieties occurs.[12] The lifetime of the CS state is 630 ps. Porphyrin singlet and triplet excited states are dramatically quenched as shown from fluorescence and phosphorescence spectra at 298 and 77 K, respectively. In contrast, some residual excited-state features of the fullerene are detected (that is, a tail of fullerene fluorescence above 700 nm and a very weak fullerene triplet absorption trace at $\lambda_{max} = 740$ nm), which are accompanied by a very minor amount of singlet oxygen luminescence (Figure 3). All the above results indicate that the local excited states of **11** centered on the porphyrin and fullerene moieties are deactivated to a lower lying luminescent charge-separated state that is localized at about 1.4 eV, as derived from electrochemical (Table 1, CH_2Cl_2) and luminescence data (Figure 3, toluene). The residual localized excited states of the fullerene are attributed to a minority (< 10 %) of loose molecules where strong donor–acceptor porphyrin–fullerene attractions are not established.[12b]

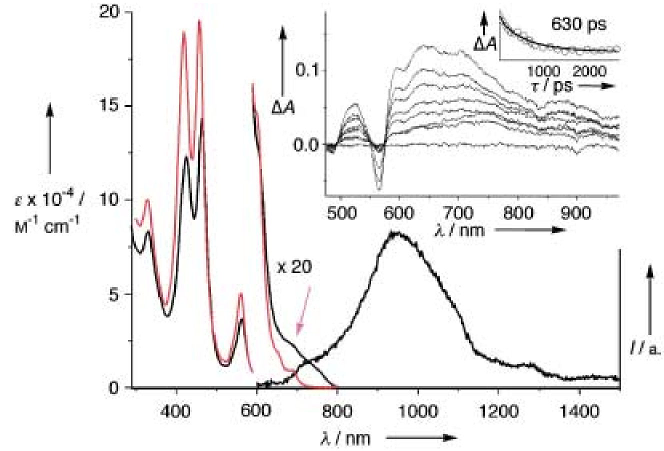


Figure 3. Red line: sum of the electronic absorption spectra of **5** and two fullerenes **13**. Black line: Absorption and (from 600 nm) emission spectra ($\lambda_{exc} = 330$ nm) of **11**. Inset: Transient absorption spectrum of **11** at $\lambda_{exc} = 532$ nm and spectral time decay at 660 nm. All spectra were recorded in toluene at 298 K.

The steady-state absorption spectrum of **9** is characterized by splitting of the Soret band as a result of exciton coupling between the two fused porphyrin units and a shift of the Q-band envelope into the NIR region (Figure 4).[13] The comparison of the absorption spectrum of **1** with the sum of its component units (**9** + 2 × **13**) shows two small but relevant differences: a) a 3-nm red shift and a very small decrease in the intensity of the highest energy Soret band and b) a 10-nm shift to lower energy of the most intense Q-band in the NIR domain. These spectral changes are smaller than those observed for **11** or other conjugates with face-to-face alignment of porphyrin and C_{60} moieties,[12] thus suggesting weaker electronic interchromophoric interactions.

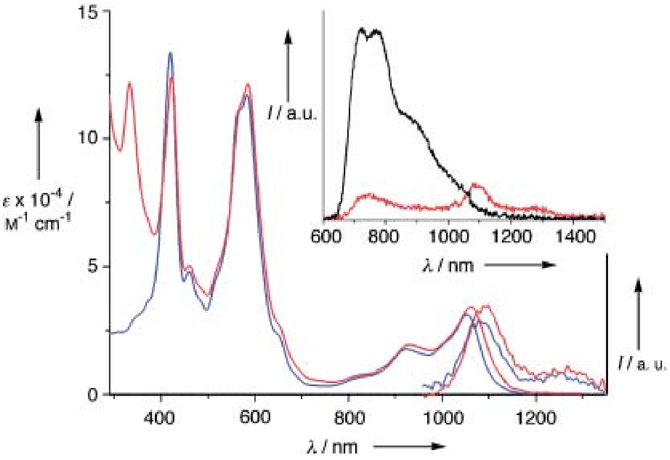


Figure 4. Absorption and (from 960 nm) fluorescence spectra ($\lambda_{exc} = 420$ nm, $A = 0.20$) of **9** (blue) and **1** (red). Inset: fluorescence spectra of **13** (black) and **1** (red), $\lambda_{exc} = 330$ nm, $A = 0.30$. All fluorescence spectra were recorded from air-purged samples.

Dimer **9** exhibits an emission band in the NIR region ($\lambda_{max} = 1080$ nm) at all excitation wavelengths. This is a mirror image of the profile of the Q bands (Figure 4), and is unambiguously assigned to fluorescence from the lowest singlet excited state. The NIR emission band is observed also for **1** upon selective excitation of the porphyrin chromophore (420 or 585 nm). This band is shifted by 12 nm ($\lambda_{max} = 1092$ nm) relative to that in **9**, and is in line with the trend seen in the absorption spectra. Preferential excitation of the C_{60} chromophores in **1** at 330 nm (≥ 80 %) shows a dramatic quenching of the fullerene fluorescence relative to **13**, whereas a pure porphyrin fluorescence band is detected in the NIR region (Figure 4, inset). According to the electrochemical data in CH_2Cl_2, the charge-separated state, which corresponds to the reduction of a fullerene unit and oxidation of the porphyrin moiety, is located at about 1.0 eV.[14] This energy value is comparable to the singlet level of the porphyrin, as estimated from the wavelength of the fluorescence band (Figure 4). Thus, in principle, both energy and electron transfer may be responsible for the observed quenching of the fullerene luminescence. Two experimental results helped to unravel the quenching mechanism: 1) the picosecond transient absorption of **1** with a time resolution of 35 ps shows only (at early times) the spectral features of the fused porphyrin dimer, and 2) the porphyrin fluorescence quantum yield is identical, within experimental uncertainty, for **1** and **9** ($\Phi_F = 3.5\times10^{-4}$, $\lambda_{exc} = 330$ nm). We conclude that excitation of the fullerene chromophore results in quantitative sensitization of the lowest singlet state of the porphyrin, and that the role of the nearly isoenergetic charge-separated state in toluene solution, if any, is not relevant.

In summary, despite the fact that triply fused porphyrin dimers are much better electron donors than simple porphyrins, their low-lying and very short lived (4.5 ps)[13] singlet level offers an extremely competitive deactivation pathway and acts as a sink for the higher energy electronic levels. Hence, the photoinduced process in **1** ($C_{60}\rightarrow$porphyrin energy transfer) is completely different from that in the biaryl-type bisporphyrin conjugate **11** (porphyrin$\rightarrow C_{60}$ electron transfer) while, notably, both molecules are NIR emitters.

Received: June 30, 2003 [Z52265]

Keywords: electrochemistry · electron transfer · fullerenes · luminescence · porphyrinoids

---

[1] a) J. M. Tour, *Acc. Chem. Res.* **2000**, *33*, 791–804; b) R. E. Martin, F. Diederich, *Angew. Chem.* **1999**, *111*, 1440–1469; *Angew. Chem. Int. Ed.* **1999**, *38*, 1351.

[2] a) A. Tsuda, H. Furuta, A. Osuka, *Angew. Chem.* **2000**, *112*, 2649–2652; *Angew. Chem. Int. Ed.* **2000**, *39*, 2549–2552; b) A. Tsuda, H. Furuta, A. Osuka, *J. Am. Chem. Soc.* **2001**, *123*, 10304–10321; c) A. Tsuda, A. Osuka, *Science* **2001**, *293*, 79–82.

[3] L. Echegoyen, F. Diederich, L. E. Echegoyen, *Fullerenes: Chemistry and Physics & Technology* (Eds.: K. M. Kadish, R. S. Ruoff), Wiley, New York, **2000**, pp. 1–51.

[4] Recent reviews: a) H. Imahori, Y. Mori, Y. Matano, *J. Photochem. Photobiol. C* **2003**, *3*, 55–83; b) N. Armaroli, *Photochem. Photobiol. Sci.* **2003**, *2*, 73–87; c) D. Gust, T. A. Moore, A. L. Moore, *Acc. Chem. Res.* **2001**, *34*, 40–48; d) D. A. K. Burrell, D. L. Officer, P. G. Pflieger, D. C. W. Reid, *Chem. Rev.* **2001**, *101*, 2751–2796; e) D. M. Guldi, *Chem. Commun.* **2000**, 321–327; f) D. M. Guldi, M. Prato, *Acc. Chem. Res.* **2000**, *33*, 695–703.

[5] Some selected publications: a) H. Imahori, N. V. Tkachenko, V. Vehmanen, K. Tamaki, H. Lemmetyinen, Y. Sakata, S. Fukuzumi, *J. Phys. Chem. A* **2001**, *105*, 1750–1756; b) D. Sun, F. S. Tham, C. A. Reed, P. D. W. Boyd, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 5088–5092.

[6] I. M. Blake, A. Krivokapic, M. Katterle, H. L. Anderson, *Chem. Commun.* **2002**, 1662–1663.

[7] D. M. Guldi, *Chem. Soc. Rev.* **2002**, *31*, 22–36.

[8] L. Sebo, V. Gramlich, F. Diederich, *Helv. Chim. Acta* **2000**, *83*, 93–113.

[9] D. Bonifazi, F. Diederich, *Chem. Commun.* **2002**, 2178–2179.

[10] N. Aratani, A. Osuka, H. S. Cho, D. Kim, *J. Photochem. Photobiol. C* **2002**, *3*, 25–52.

[11] The interchromophoric ground-state interaction in **10** and **11** was quantified as about 12 kJ mol^{-1} (toluene, 298 K), see ref. [9]. In contrast, interchromophoric interactions in **1** are weaker (see text). Thus, the conformation of **1** depicted in Scheme 1 is only one of many possible; conformers with the carbon spheres nesting on opposite faces of the porphyrin dimer or turned away from the heterocycle are of equal probability.

[12] a) N. Armaroli, G. Marconi, L. Echegoyen, J.-P. Bourgeois, F. Diederich, *Chem. Eur. J.* **2000**, *6*, 1629–1645; b) N. Armaroli in *Fullerenes: From Synthesis to Optoelectronic Properties* (Eds.: D. M. Guldi, N. Martin), Kluwer, Dordrecht, **2002**, pp. 137–162.

[13] H. S. Cho, D. H. Jeong, S. Cho, D. Kim, Y. Matsuzaki, K. Tanaka, A. Tsuda, A. Osuka, *J. Am. Chem. Soc.* **2002**, *124*, 14642–14654.

[14] The use of the electrochemical data in CH_2Cl_2 to estimate the energy of the CS state of **1** in toluene is a reasonable approximation in light of the good accord found between the energy of the CS state calculated by luminescence data (toluene) and electrochemistry (CH_2Cl_2) for the similar system **11**.