

Porphyrin-C<sub>60</sub> Conjugates

### Exceptional Redox and Photophysical Properties of a Triply Fused Diporphyrin-C<sub>60</sub> Conjugate: Novel Scaffolds for Multicharge Storage in Molecular Scale Electronics\*\*

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

The expansion and functionalization of  $\pi$ -conjugated molecular architectures to enhance the optoelectronic properties of the resulting chromophores is a topic of broad current

interest.<sup>[1]</sup> 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.<sup>[2]</sup>

The past decade has seen the construction of a great variety of electron donor-acceptor dyads, frequently featuring C<sub>60</sub> as the electron-accepting component because of its three-dimensional structure and six easily accessible reduction states in solution.<sup>[3]</sup> 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.<sup>[4,5]</sup>

Since the chemical functionalization of the triply fused porphyrin sheets is largely unexplored<sup>[6]</sup> and the nature of their interactions with redox- and photoactive chromophores, such as fullerenes, unknown, we decided to prepare conjugate **1** with two C<sub>60</sub> 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<sup>[7]</sup> 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<sub>6</sub>, followed by silver-mediated iodination and subsequent Suzuki coupling with phenylboronic ester **4**,<sup>[8]</sup> afforded the biaryl-type dimer **5**. Dimer **5** was converted into **2** (11% yield over four steps) following the protocol by Tsuda and Osuka<sup>[2c]</sup> for oxidative ring closure (DDQ and Sc(OTf)<sub>3</sub>). 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<sub>4</sub>) to the corresponding bis(benzyl alcohol). Esterification with EtO<sub>2</sub>CCH<sub>2</sub>COCl yielded bismalonate **9**, and Bingel reaction with C<sub>60</sub> gave the target conjugate **1**.

The redox properties of **1**, **2**, **5**, and comparison compounds **10**,<sup>[9]</sup> **11**,<sup>[9]</sup> 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<sup>-</sup> 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<sub>2</sub>Cl<sub>2</sub> (Figure 1b). The first and second reduction couples correspond to two-step, 1-e<sup>-</sup> per porphyrin ring reductions. Likewise, the first and the

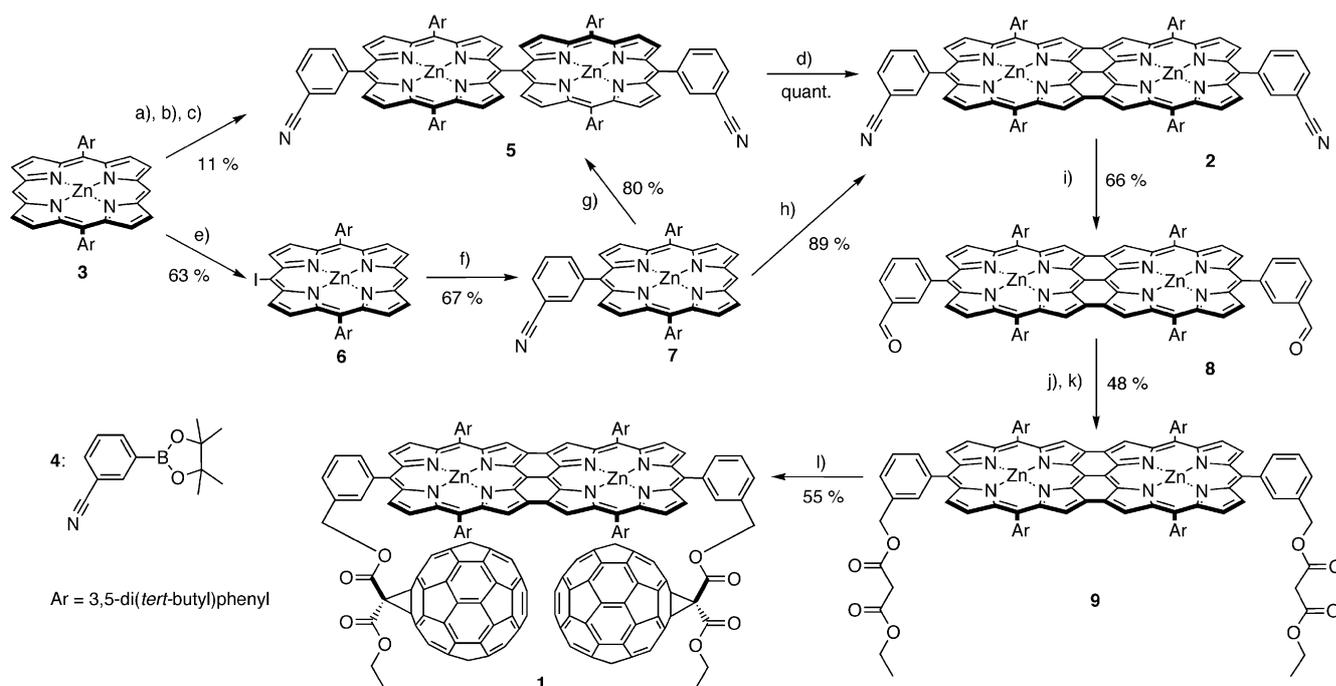
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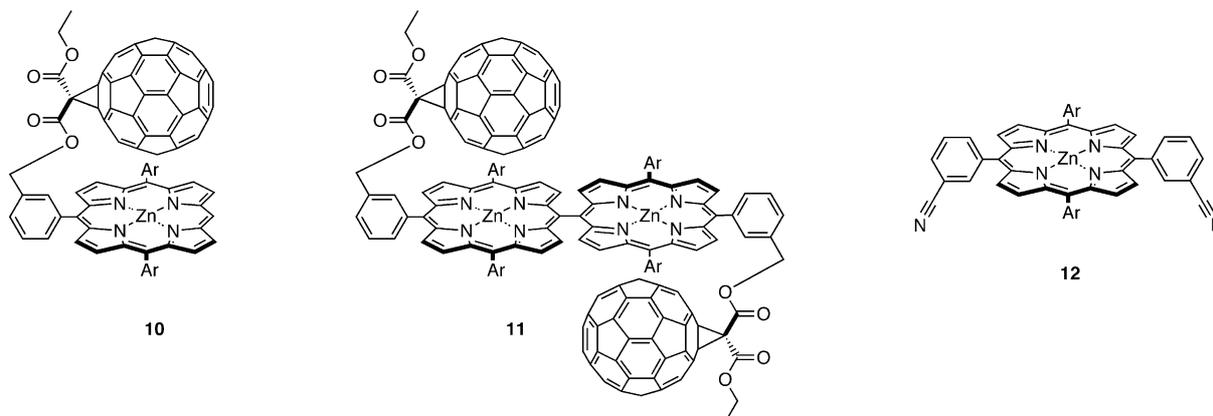
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Supporting information for this article (selected physical and spectral data of **1** and **2**, cyclic voltammograms of **1**, **2**, and **11**, luminescence spectra of **11** compared to reference compounds **5** and **13**, UV/Vis data of **1**,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



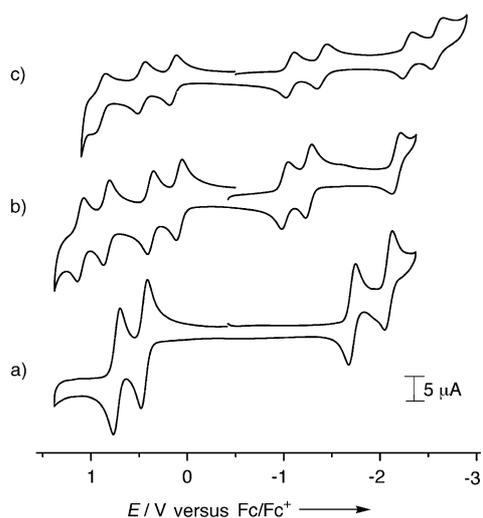
**Scheme 1.** Synthesis of conjugate 1. a)  $\text{AgPF}_6$ ,  $\text{CH}_3\text{CN}/\text{CHCl}_3$  1:6, RT, 15 h; b)  $\text{AgPF}_6$ ,  $\text{I}_2$ , pyridine/ $\text{CHCl}_3$  1:60, RT; c) **4**,  $\text{Cs}_2\text{CO}_3$ ,  $[\text{Pd}(\text{PPh}_3)_4]$ , toluene, reflux, 18 h; d) DDQ,  $\text{Sc}(\text{OTf})_3$ , toluene, reflux, 30 min; e)  $\text{AgPF}_6$ ,  $\text{I}_2$ , pyridine/ $\text{CHCl}_3$  1:60, RT; f) **4**,  $\text{Cs}_2\text{CO}_3$ ,  $[\text{Pd}(\text{PPh}_3)_4]$ , toluene, reflux, 18 h; g)  $\text{AgPF}_6$ ,  $\text{CH}_3\text{CN}/\text{CHCl}_3$  1:6, RT, 15 h; h) DDQ,  $\text{Sc}(\text{OTf})_3$ , toluene, reflux, 30 min; i) DIBAL-H,  $\text{CH}_2\text{Cl}_2$ ,  $-78^\circ\text{C} \rightarrow \text{RT}$ , 2.5 h; j)  $\text{NaBH}_4$ , THF/ $\text{EtOH}$  1:1,  $0^\circ\text{C} \rightarrow \text{RT}$ , 4 h; k)  $\text{EtO}_2\text{CCH}_2\text{COCl}$ ,  $\text{Et}_3\text{N}$ ,  $\text{CH}_2\text{Cl}_2$ , RT, 16 h; l)  $\text{C}_{60}$ ,  $\text{I}_2$ , 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.



**Table 1:** Cyclic voltammetry data in  $\text{CH}_2\text{Cl}_2$  (+0.1 M  $n\text{Bu}_4\text{NPF}_6$ ).<sup>[a]</sup>

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

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



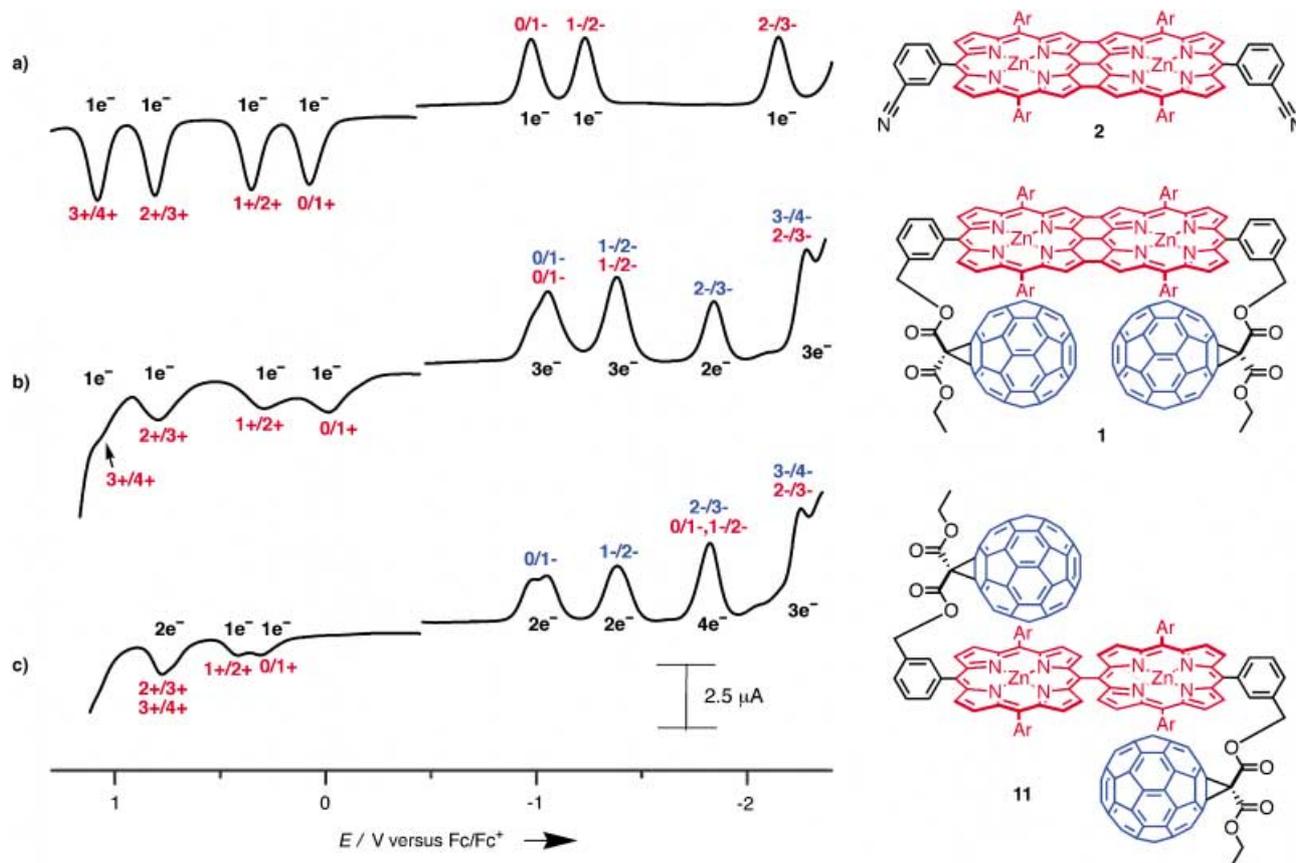
**Figure 1.** Cyclic voltammograms of a) **12** in  $\text{CH}_2\text{Cl}_2$ , b) **2** in  $\text{CH}_2\text{Cl}_2$ , and c) **2** in THF at  $20 \pm 2^\circ\text{C}$  ( $+0.1 \text{ M nBu}_4\text{NPF}_6$ ).

second oxidation peaks each correspond to a  $1\text{-e}^-$  process, one per porphyrin ring. Relative to **12**, the first  $1\text{-e}^-$  reduction potential of **2** is shifted positively by  $0.7 \text{ V}$  whereas the first  $1\text{-e}^-$  oxidation potential is shifted negatively by  $0.35 \text{ V}$ . The fourth reduction peak was not observed because of the limited potential window in  $\text{CH}_2\text{Cl}_2$ . However, CV and DPV

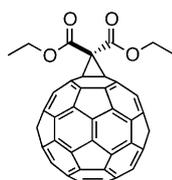
measurements in THF revealed the presence of the fourth reduction peak (Figure 1c). These results confirm that each redox couple for **12** splits into two couples for **2**.

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

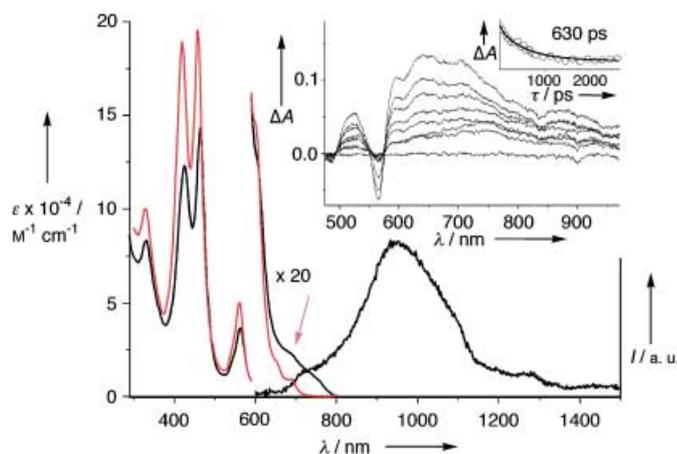


**Figure 2.** Differential pulse voltammograms of a) **2**, b) **1**, and c) **11** in  $\text{CH}_2\text{Cl}_2$  at  $20 \pm 2^\circ\text{C}$ .



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of conjugate **11** with the biaryl-type porphyrin dimer does not match the sum spectrum of its component units (**5** and  $2 \times$  **13**; Figure 3), particularly in the Soret-band region, which is split as a result of exciton coupling.<sup>[10]</sup> This result is attributed to strong face-to-face electronic interactions between the porphyrin and fullerene chromophores.<sup>[11]</sup> 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.<sup>[12]</sup> An emissive charge-transfer

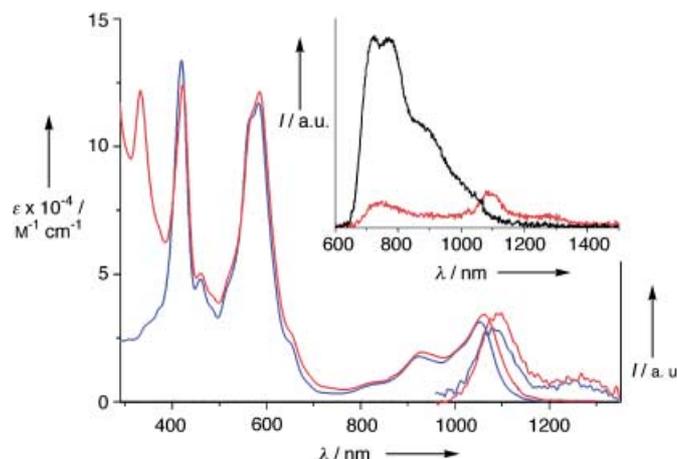


**Figure 3.** Red line: sum of the electronic absorption spectra of **5** and two fullerenes **13**. Black line: Absorption and (from 600 nm) emission spectra ( $\lambda_{\text{exc}} = 330$  nm) of **11**. Inset: Transient absorption spectrum of **11** at  $\lambda_{\text{exc}} = 532$  nm and spectral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

(CS) state is detected in the NIR region ( $\lambda_{\text{max}} = 950$  nm, Figure 3). The transient absorption spectrum of **11** in toluene ( $\lambda_{\text{exc}} = 532$  nm, Figure 3) exhibits the diagnostic broad band of the  $\text{Zn}^{\text{II}}$ -porphyrin radical cation with a maximum at 640 nm, thus indicating that photoinduced electron transfer from the porphyrin to the fullerene moieties occurs.<sup>[12]</sup> 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  $\lambda_{\text{max}} = 740$  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,  $\text{CH}_2\text{Cl}_2$ ) 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.<sup>[12b]</sup>

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).<sup>[13]</sup> The comparison of the absorption spectrum of **1** with the sum of its component units (**9** +  $2 \times$  **13**) shows two small but relevant differences: a) a 3-nm red shift and a very small decrease in



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

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  $\text{C}_{60}$  moieties,<sup>[12]</sup> thus suggesting weaker electronic interchromophoric interactions.

Dimer **9** exhibits an emission band in the NIR region ( $\lambda_{\text{max}} = 1080$  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 ( $\lambda_{\text{max}} = 1092$  nm) relative to that in **9**, and is in line with the trend seen in the absorption spectra. Preferential excitation of the  $\text{C}_{60}$  chromophores in **1** at 330 nm ( $\geq 80\%$ ) 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  $\text{CH}_2\text{Cl}_2$ , 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.<sup>[14]</sup> 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** ( $\Phi_F = 3.5 \times 10^{-4}$ ,  $\lambda_{exc} = 330$  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)<sup>[13]</sup> 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.

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

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