Synthesis, and Optical and Electrochemical Properties of Cyclophane-Type Molecular Dyads Containing a Porphyrin in Close, Tangential Orientation Relative to the Surface of *trans-1* Functionalized C_{60}

Preliminary Communication

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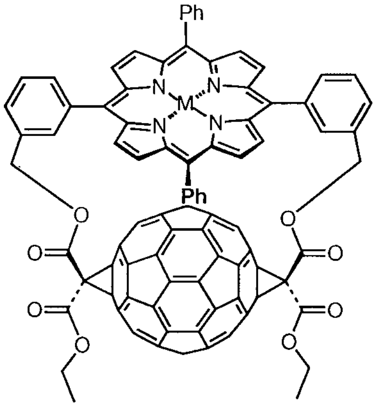
The synthesis of the cyclophane-type molecular dyads **1** and **1·Zn** was accomplished by *Bingel* macrocyclization of porphyrin-tethered bis-malonates **5** or **5·Zn**, respectively, with C_{60} (*Scheme*). In these macrocycles, the doubly bridged porphyrin adopts a close, tangential orientation relative to the surface of the C-sphere. The porphyrin derivatives **6** and **6·Zn** with two appended, singly-linked C_{60} moieties were also formed as side products in the *Bingel* macrocyclizations. The *trans-1* addition pattern of the fullerene moiety in **1** and **1·Zn** was unambiguously established by ^{1}H- and ^{13}C-NMR spectroscopy. Due to the close spatial relationship between the fullerene and porphyrin components in **1** and **6** and the corresponding Zn^{II} complexes, the porphyrin fluorescence is efficiently quenched as compared to the luminescence emitted by **5** and **5·Zn**, respectively (*Fig. 2*). Cyclic-voltammetry studies show that the mutual electronic effects exerted by the fullerene on the porphyrin and *vice versa* in **1** and **1·Zn** are relatively small despite the close proximity between the porphyrin donor and the fullerene acceptor (*Fig. 3*).

We have reported the efficient regio- and stereoselective preparation of bis(cyclopropanated) [60]fullerene derivatives by macrocyclization of the C-sphere *via* double *Bingel* addition [1]. This reaction provides a highly effective method for precisely positioning organic chromophores in close proximity to the fullerene surface, thus offering the potential for inducing profound changes in the properties of the C-allotrope. Thus, we recently observed a significant perturbation of the electronic structure of C_{60} in *trans-1*, *trans-2*, and *trans-3* bis-adducts in which a dibenzo[18]crown-6 moiety is attached by double *Bingel* addition, and adopts a close, tangential orientation relative to the surface of the C-sphere [2]. Upon complexation with K^+, the first reduction step of the fullerene becomes greatly facilitated as evidenced by anodic shifts in the cyclic voltammogram (CV). The largest anodic shift (+ 90 mV) was observed for the *trans-1* derivative in which the distance between the crown ether bound cation and C_{60} is smallest. In all previous crown ether conjugates [1b] (for recent examples of fullerene-crown ether conjugates, see [3]), the ionophore part was located at a much greater distance from the surface of the fullerene, and, correspondingly, significant cation-mediated electrochemical effects were not detected.

Molecular dyads composed of an electron donor capable of energy transfer or photoinduced electron transfer to a covalently linked electron-acceptor component have been widely studied as mimics of the natural photosynthetic reaction centers [4]. With its relatively strong electron-accepting capability, C_{60} is an interesting candidate for incorporation into molecular dyads [5a] (for a first report on a fullerene-containing dyad, see [5b]). Correspondingly, a variety of systems containing a porphyrin as electron donor and C_{60} as electron acceptor have been constructed [6]. In these compounds, the porphyrin usually is attached to the fullerene by a single linker and, consequently, the distance and orientation between the two components are often not well-defined. To control these essential geometrical parameters, we applied our tether-directed remote-functionalization strategy and attached the porphyrin to two points of the C_{60} surface, leading to the formation of a cyclophane structure. Here, we report the synthesis of the *trans-1* bis-adducts **1** and **1·Zn** by regioselective *Bingel* macrocyclization as well as preliminary investigations of their electrochemical and photophysical properties¹). Previously, *Staab* and co-workers had demonstrated that the incorporation of porphyrins and quinones (as electron acceptors) into cyclophane-type dyads and triads provides enhanced control of the interchromophoric spatial relationship [7].



1 M = 2H
1·Zn M = Zn

In the synthesis of **1**, aldehyde **2** [8] was converted into malonate **3** (87%) which was reacted with dipyrromethane **4** [9] in the presence of CF_3COOH to yield porphyrinogen which, after oxidation with chloranil, provided bis-malonate appended porphyrin **5** in 5% yield (*Scheme*)²). The low yield of **5** is due to the reversibility of porphyrinogen formation [9c] which leads to a mixture of porphyrins containing four,

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¹) Using the same methodology, a macrocyclic [60]fullerene-porphyrin dyad, in which the porphyrin is attached by different malonate bridges presumably to the *trans-2* position of the C-sphere, was prepared (E. Dietel, A. Hirsch, E. Eichhorn, A. Rieker, S. Hackbarth, B. Röder, *Chem. Commun.*, in press). We thank Prof. *A. Hirsch* for making this information available to us.

²) All new porphyrin derivatives were fully characterized (UV/VIS, fluorescence, IR, ^1H- and ^{13}C-NMR, FAB or MALDI-TOF-MS). Accurate high resolution FAB mass spectra were obtained for **1**, **1·Zn**, **5**, and **5·Zn**.

three, two (two isomers), one, and zero malonate-appended *meso*-phenyl rings, respectively, from which the desired compound was isolated by flash chromatography (SiO_2 – *H*, CH_2Cl_2/AcOEt 98:2). A modified *Bingel* reaction³) [10] of **5** with 1 equiv. of C_{60} in the presence of I_2 and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in PhMe provided regioselectively the *trans-1* bis-adduct **1** in 17% yield besides a small amount (< 2%) of the non-macrocyclic bis-fullerene derivative **6**. Compound **6** can also be obtained as the major product when an excess of C_{60} is used in the *Bingel* reaction: with 5 equiv. of C_{60} at 0°, **6** was obtained in 50% yield. It serves as a useful control to evaluate the specific properties of **1** that arise as a consequence of the macrocyclic bridging. The regioselectivity in the macrocyclization reaction is high; other regioisomers were only produced in minor amounts and were not isolated in pure form. The *trans-1* regioselectivity had been predicted during the design of the tethered bis-malonate **5** by computer modeling⁴).

For the preparation of metallated derivatives, bis-malonate **5** was quantitatively converted into **5 · Zn** by reaction with $Zn(OAc)_2$ in $CHCl_3$/MeOH 1:1. By applying the double *Bingel* addition procedure described above to **5 · Zn**, the two metallated derivatives **1 · Zn** and **6 · Zn** were obtained. The yield and regioselectivity of the macrocyclization were not changed by the zinc complexation.

The relative position of the two cyclopropane rings on the C_{60} surface in the macrocyclic fullerene-porphyrin dyads **1** and **1 · Zn** was unambiguously established by ^{1}H- and ^{13}C-NMR spectroscopy⁵), which clearly demonstrated the C_{2v}-symmetry of the two cyclophanes (*cf. Exper. Part*). In the ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of both compounds, the PhC*H*₂O protons appeared as a sharp *singlet*. The ^{13}C-NMR spectrum (125.8 MHz, $CDCl_3$) of **1** displayed a single resonance for the four sp^3-C-atoms of the C-sphere as well as 31 of the 34 resonances expected for the sp^2-C-atoms of the fullerene moiety, the *meso*-tetraphenylporphyrin, and the malonate C=O groups in a C_{2v}-symmetrical dyad. In the ^{13}C-NMR spectrum of **1 · Zn**, all 34 expected sp^2-C-atom resonances appeared clearly separated. Among all possible regioisomeric macrocyclic dyads, the symmetry as high as C_{2v} can only be present if the addition pattern on the fullerene moiety is *trans-1*.

The number and multiplicity of the resonances in the ^{1}H- and ^{13}C-NMR spectra of **6** and **6 · Zn** at 300 K do not reflect a time-averaged C_{2v}-symmetry of these compounds. Rather, there seem to exist two conformers which are in slow equilibrium on the NMR time; this dynamic process is being further investigated.

The macrocyclic dyads **1** and **1 · Zn** are high-melting black solids with good solubility in solvents such as $CHCl_3$ or CH_2Cl_2. Their electronic absorption spectra (CH_2Cl_2) are dominated by the fullerene transitions below 350 nm and, above that wavelength, by the porphyrin bands. A comparison of the porphyrin absorptions shows

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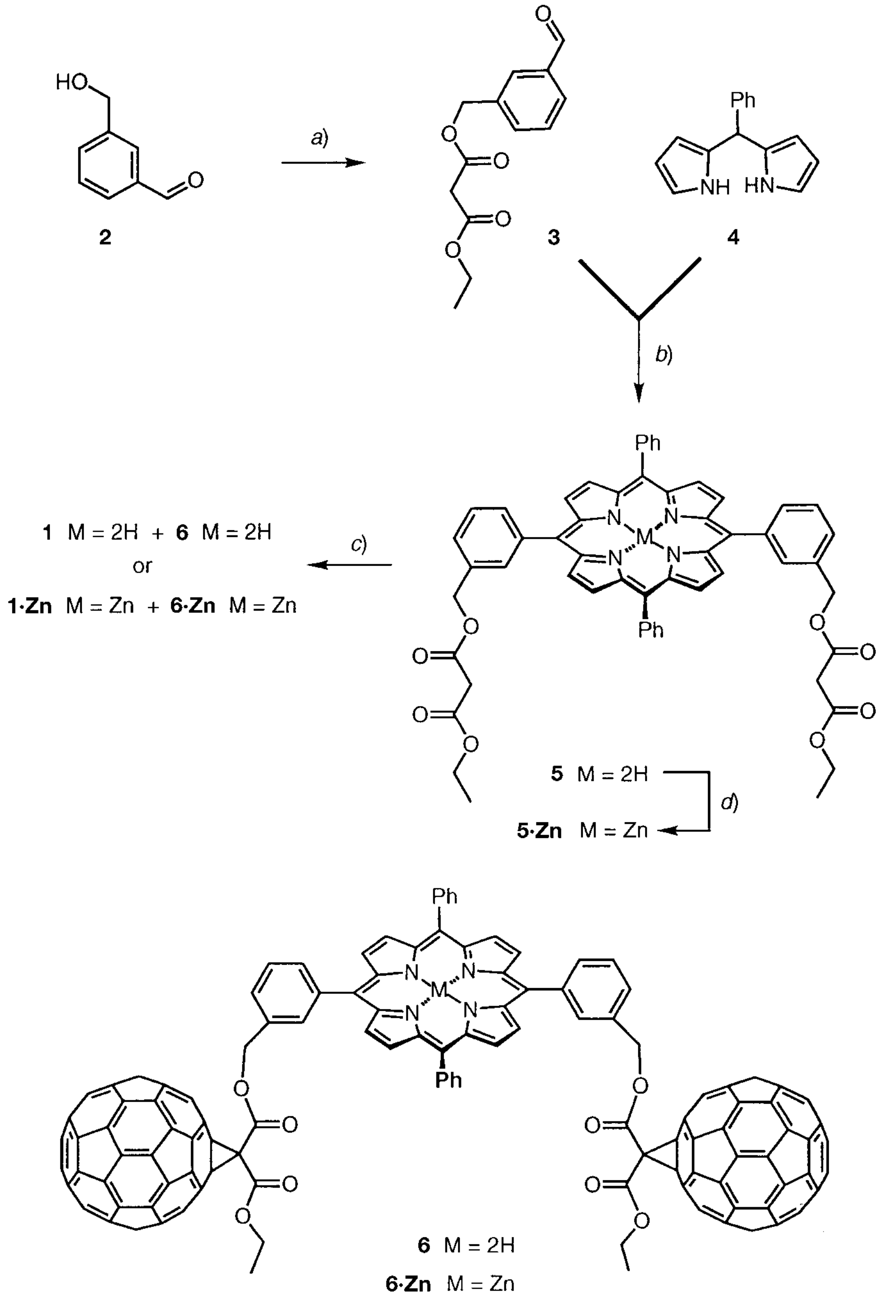
³) The modification of the *Bingel* reaction used consistently in our tether-directed remote functionalization was first presented by *C. Bingel* at the conference *New Perspectives in Fullerene Chemistry and Physics* in Rome (Italy) in 1994. For the first published experimental protocol, see [1a].

⁴) Force-field simulations using the CVFF force field in the program Insight II 95.0 of Discover 2.9.7, *Biosym Technologies*, San Diego, 1997.

⁵) A regioisomeric assignment based on the UV/VIS spectra was not possible due to the overlap of the strong *Soret* band of the porphyrin with characteristic absorption bands of the fullerene in the discriminating region of the spectrum (see [11]).

Scheme. *Synthesis of the Macrocyclic Fullerene-Porphyrin Dyads* **1** *and* **1·Zn**



a) Ethyl malonyl chloride, Et_3N, CH_2Cl_2, 0°, 1 h, 87%. *b*) CF_3COOH, CH_2Cl_2, 20°, 24 h, then chloranil, Δ, 1 h, 5%. *c*) C_{60}, I_2, DBU, PhMe, 20°, 1 h, 17% (**1** or **1·Zn**); <2% (**6** or **6·Zn**). *d*) $Zn(OAc)_2$, $CHCl_3$/MeOH 1 : 1, 20°, 1 h, quant. yield.

that both the *Soret* band and the $\pi\pi^*$ transitions of the fullerene-appended porphyrin derivatives **1** and **6** are slightly hypsochromically shifted as compared to the positions of these bands in the spectrum of **5**, which lacks a fullerene moiety. The same observations hold for the series of metallated derivatives (*Fig. 1*).

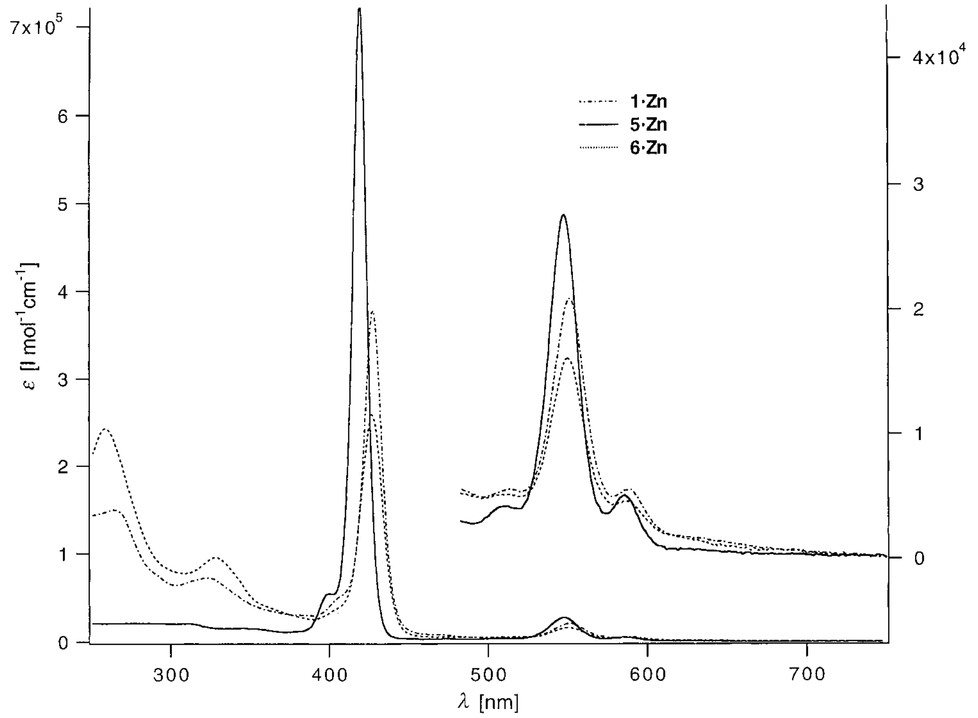


Fig. 1. *Electronic absorption spectra of* **1·Zn**, **5·Zn**, *and* **6·Zn** *recorded in* CH_2Cl_2

The close spatial proximity of the fullerene to the porphyrin in the macrocyclic dyads **1** and **1·Zn** causes a strong decrease in the porphyrin fluorescence in CH_2Cl_2[6]). The emission intensity of **1** is reduced by a factor of 1500 as compared to fullerene-free **5**, whereas that of **1·Zn** is reduced by a factor of 4500 as compared to **5·Zn** (*Fig. 2*). Interestingly, the porphyrin emission in **6** and **6·Zn** is also reduced by a factor of *ca.* 1500. We tentatively explain this strong reduction in the luminescence intensity of **6** and **6·Zn** by preferred conformations of these derivatives, in which one of the two fullerenes adopts a position in close proximity to the porphyrin moiety, establishing a geometrical relationship between donor and acceptor similar to that in the cyclophane-

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[6]) In these experiments, the maximum of the *Soret* band in each case was chosen as the excitation wavelength. To compare the emissions of different compounds, each solution was prepared with an optical density of 1.0 at this wavelength. The concentration was *ca.* 2×10^{-6}M. In the spectra of **5** and **5·Zn**, an additional weak band was observed at 839 nm which was shifted to *ca.* 850 nm in the spectra of **1**, **6**, and their metallated derivatives. Since the position of this band is strongly dependent on the excitation wavelength, we assign it as a *Raman* band.

type dyads. It remains to be clarified in time-dependent measurements whether the efficient quenching of the porphyrin luminescence results from energy transfer and/or photoinduced electron transfer.

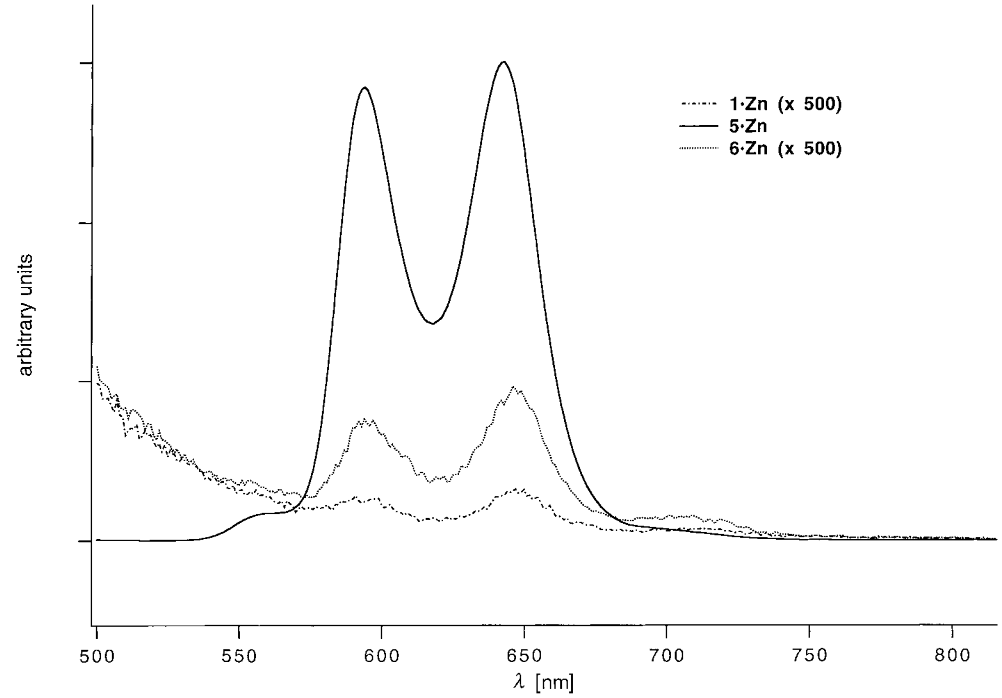


Fig. 2. *Luminescence spectra of* **1·Zn**, **5·Zn**, *and* **6·Zn** *recorded in* CH_2Cl_2

In the electrochemical studies, the *trans-1* bis-adduct **7** was used as a reference to assess the electronic effects, if any, of the porphyrin on the measured reduction potentials (cathodic processes) of the C-spheres in conjugates **1** and **6**, and their metallated derivatives **1·Zn** and **6·Zn**, respectively. Compounds **5** and **5·Zn** provided appropriate controls to evaluate the effects of the fullerene moieties on the porphyrin oxidation potentials (anodic processes) in the conjugates. The results of the cyclic voltammetric studies are summarized in the *Table*. In general, while some differences were observed, it can be stated that the changes in potential of one component in the dyads, due to the presence of the second one, were typically small. For example, comparing the first reduction potential of **1** with that of **7** shows only a 20-mV cathodic shift, while the effect on the second reduction is somewhat larger, at 70 mV. These reductions are all fullerene-based, as confirmed by the results obtained for **6** and **6·Zn**, which clearly show that these peaks are twice as large as those corresponding to the oxidation of the porphyrin moiety (*Fig. 3*). Interestingly, the first reduction process for **5** (– 1.67 V) occurs at a potential that is very close to the second reduction step for **1** (– 1.54 V).

Anodic scans revealed even smaller effects of the fullerene moiety on the oxidation potentials of the porphyrin chromophores. For example, bis-malonate appended

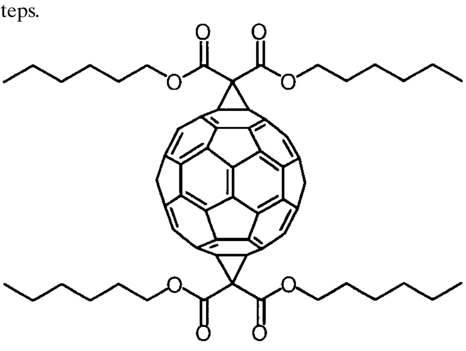
Table. *Redox Potentials in Ar-Degassed CH_2Cl_2 Containing 0.1M Bu_4NPF_6 as Supporting Electrolyte*[a])

Compound	Reduction			Oxidation	
	$E_1^{1/2}$	$E_2^{1/2}$	$E_3^{1/2}$	$E_1^{1/2}$	$E_2^{1/2}$
1	– 1.11 (70)[b])	– 1.54 (80)		0.57 (60)	0.94 (70)
5	– 1.67 (82)	– 1.97 (120)		0.55 (75)	0.87 (80)
6	– 1.05 (84)[c])	– 1.39 (91)[c])	– 1.62 (66)	0.58 (60)	–
7	– 1.09 (76)	– 1.47 (79)		–	–
1·Zn	– 1.13 (71)	– 1.54 (90)		0.38 (74)	0.71 (75)
5·Zn	– 1.83 (73)	–		0.37 (72)	0.67 (78)
6·Zn	– 1.09 (71)[c])	– 1.45 (103)[c])	0.37 (62)	0.72 (54)	

[a]) A 3-mm diameter glassy C electrode was used as the working electrode, while a Pt wire served as the counter electrode. An aqueous Ag/AgCl electrode, separated by a *Vycor* tip, was used as the reference. In every run, ferrocene (Fc) was also added as an internal potential reference, and all the values reported here are relative to the Fc/Fc^+ couple. Typical scan rates were 100 mV s^{-1}, and the potentiostat used was an *EG&G PAR* model *263A*.

[b]) Values in parenthesis are the ΔE_{pp} in mV.

[c]) Two-electron reduction steps.



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porphyrin **5** has a first oxidation potential of 0.55 V, while the corresponding process for **1** occurs at 0.57 V. An electronic effect of the fullerene is more pronounced for the second porphyrin-centered oxidation process, which occurs at 0.87 V for **5** but at 0.94 V for **1**, corresponding to a 70-mV shift.

While the presence of the Zn^{II} ion caused pronounced potential shifts, (between 160 and 200 mV cathodic shifts of both oxidation and reduction processes when changing from **5** to **5·Zn**), it had almost no effect on the fullerene-based reductions in the cyclophane dyad. Thus, **1·Zn** has a fullerene-based first reduction potential of – 1.13 V, which is very close to the corresponding value measured for **1**, and the second, fullerene-based reduction process occurs exactly at the same potential (– 1.54 V) in both compounds.

Therefore, in general, it can be stated that the mutual electronic effects exerted by the fullerene on the porphyrin and *vice versa* in dyads **1** and **1·Zn** are relatively small, and, thus, the ground-state donor-acceptor interactions are hardly measurable by electrochemistry.

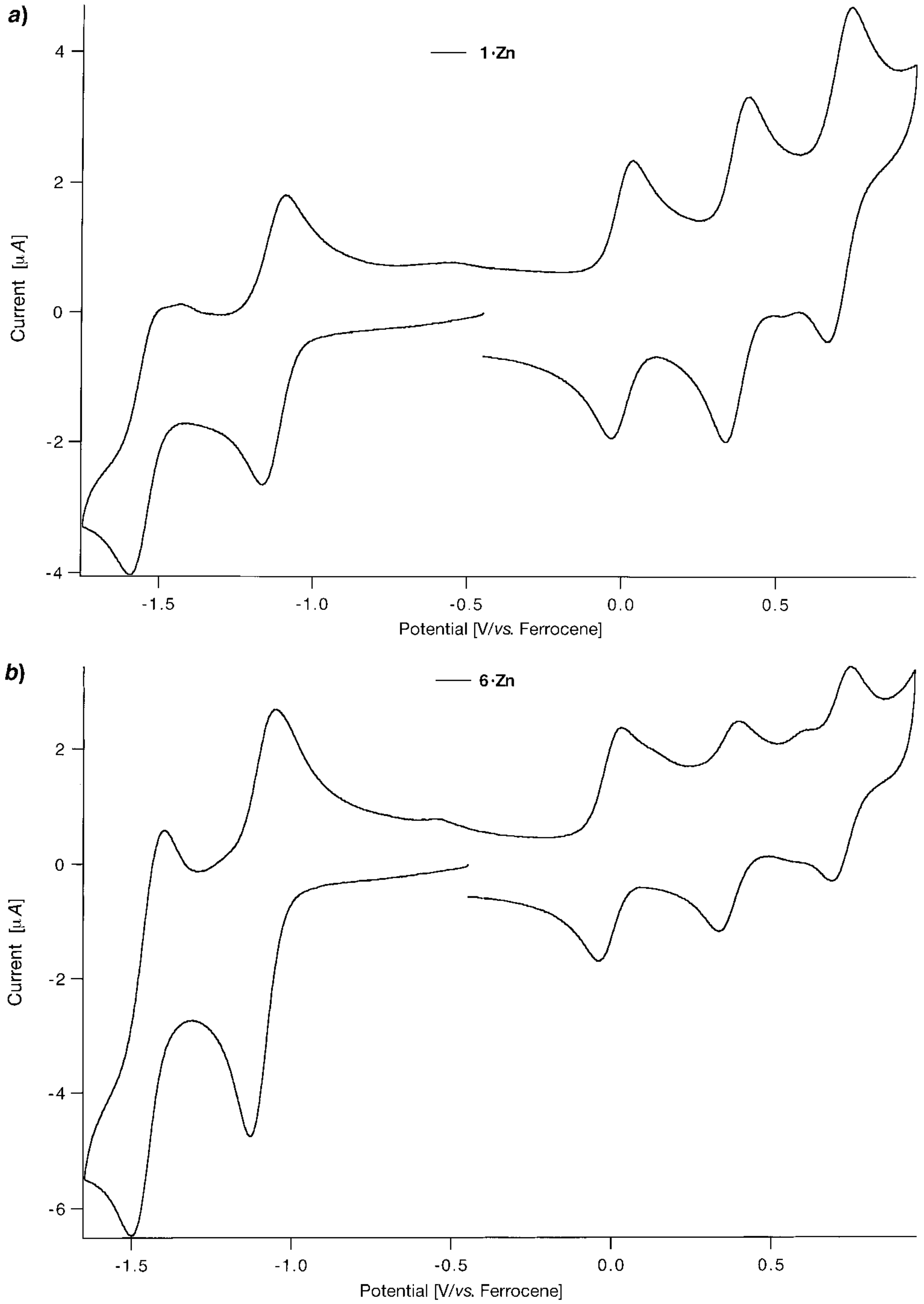

Fig. 3. *Cyclic voltammograms of a)* **1·Zn** *and b) of* **6·Zn** *in* CH_2Cl_2 *(+ 0.1* M Bu_4NPF_6*)*

We are now continuing the investigation of the interesting photophysical properties of the macrocyclic fullerene-porphyrin dyads reported in this communication.

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Experimental Part

Selected Physical and Spectral Data of the Fullerene-Porphyrin Conjugates **1**, **1·Zn**, **6**, *and* **6·Zn**. **1**: M.p. > 400° (CH_2Cl_2/hexane). UV/VIS (CH_2Cl_2): λ_{max} [nm] (ε[1 mol^{-1} cm^{-1})]: 650 (3400), 595 (5900), 553 (8500), 518 (16300), 426 (235800), 325 (58800), 261 (139000). Fluorescence (λ_{exc} = 426 nm): λ_{max} [nm] 713, 650, 595. IR (KBr): 3432*m*, 2956*m*, 2911*m*, 2856*m*, 1749*s*, 1467*w*, 1439*w*, 1367*w*, 1344*w*, 1243*s*, 1206*s*, 1167*m*, 1090*w*, 1072*m*, 1016*w*, 972*m*, 922*w*, 867*w*, 799*s*, 728*m*, 700*m*, 667*w*, 633*w*, 578*w*, 550*w*, 522*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): −2.88 (*s*, 2 H); 1.50 (*t*, *J* = 7.1, 6 H); 4.55 (*q*, *J* = 7.1, 4 H); 5.98 (*s*, 4 H); 7.61–8.15 (*m*, 14 H); 7.91 (*t*, *J* = 7.6, 2 H); 8.64 (*d*, *J* = 7.6, 2 H); 8.69 (*s*, 8 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 14.30; 45.65; 63.54; 67.84; 69.33; 119.13; 120.35; 125.69; 126.54; 126.88; 127.65; 129.03; 132.19; 133.84; 134.26; 134.32; 135.75; 138.85; 139.66; 139.99; 140.12; 141.13; 141.43; 141.79; 141.87; 141.98; 142.29; 142.39; 142.74; 142.81; 142.99; 144.25; 144.37; 144.77; 163.74; 163.80. FAB-MS (*m/z* (% relative intensity)): 1619.6 (100, *M*H$^+$). HR-FAB-MS: 1618.3006 (M^+; calc. for $C_{116}H_{42}N_4O_8^+$: 1618.3002).

1·Zn: M.p. > 400° (CH_2Cl_2/hexane). UV/VIS (CH_2Cl_2): λ_{max} [nm] (ε[1 mol^{-1} cm^{-1}]): 586 (5500), 548 (20900), 512 (5600), 467 (sh, 8100), 427 (377900), 411 (sh, 57500), 323 (72700), 264 (149600). Fluorescence (λ_{exc} = 427 nm): λ_{max} [nm] 647, 595. IR (KBr): 2956*m*, 2921*m*, 2856*m*, 1764*s*, 1628*m*, 1589*m*, 1561*w*, 1456*w*, 1440*w*, 1378*w*, 1333*w*, 1244*s*, 1206*s*, 1167*m*, 1100*m*, 1067*s*, 794*m*, 750*w*, 733*w*, 700*w*, 527*w*, 467*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.50 (*t*, *J* = 7.1, 6 H); 4.56 (*q*, *J* = 7.1, 4 H); 5.99 (*s*, 4 H); 7.67–8.15 (*m*, 16 H); 8.64–8.88 (*m*, 10 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 14.21; 45.71; 63.50; 67.90; 69.28; 119.94; 121.17; 125.42; 126.30; 126.70; 127.33; 128.14; 128.95; 131.74; 131.92; 132.24; 133.45; 134.02; 134.15; 135.53; 138.71; 139.63; 140.14; 140.79; 141.70; 141.79; 142.78; 142.53; 142.60; 142.76; 143.10; 143.39; 144.17; 144.32; 144.81; 149.74; 149.99; 163.64; 163.66. HR-FAB-MS: 1680.2143 (M^+; calc. for $C_{116}H_{40}N_4O_8Zn^+$: 1680.2137).

6: M.p. > 400° (CH_2Cl_2/hexane). UV/VIS (CH_2Cl_2): λ_{max} [nm] (ε [1 mol^{-1} cm^{-1}]): 648 (3400), 593 (5800), 551 (7500), 517 (14000), 425 (226100), 327 (84500), 259 (254700). Fluorescence (λ_{exc} = 425 nm): λ_{max} [nm] 713, 650. IR (KBr): 3322*m*, 2956*m*, 2922*m*, 2856*w*, 1748*s*, 1628*w*, 1600*w*, 1478*w*, 1457*w*, 1439*w*, 1428*w*, 1367*w*, 1350*w*, 1267*m*, 1232*s*, 1200*m*, 1183*m*, 1106*w*, 1094*m*, 1056*m*, 1017*w*, 972*w*, 800*m*, 728*m*, 700*m*, 578*w*, 550*w*, 526*s*, 461*w*, 417*w*. ^{1}H-NMR (500 MHz, $CS_2/CDCl_3$ 5 : 1): −2.85 (*s*, 2 H); 1.32 (*t*, *J* = 7.1, 3 H); 1.36 (*t*, *J* = 7.1, 3 H); 4.40 (*q*, *J* = 7.1, 2 H); 4.43 (*q*, *J* = 7.1, 2 H); 5.81 (*s*, 2 H); 5.82 (*s*, 2 H); 7.68–8.36 (*m*, 18 H); 8.75 (*s*, 8 H). ^{13}C-NMR (125.8 MHz, $CS_2/CDCl_3$ 5 : 1): 14.07; 14.15; 51.64; 62.97; 68.07; 68.16; 70.89; 70.96; 118.93; 120.04; 126.53; 126.60; 126.77; 126.89; 127.14; 127.48; 128.03; 128.78; 130.85 (br.); 133.18; 133.21; 133.92; 134.23; 134.62; 137.82; 138.00; 138.81; 138.82; 139.80; 139.96; 140.13; 140.23; 140.38; 140.61; 141.14; 141.16; 141.23; 141.27; 141.44; 141.51; 141.71; 141.94; 142.03; 142.07; 142.09; 142.14; 142.21; 142.32; 142.45; 142.50; 142.64; 143.08; 143.17; 143.26; 143.30; 143.33; 143.39; 143.70; 143.78; 143.82; 143.91; 144.00; 144.03; 144.07; 144.15; 144.24; 144.35; 144.38; 144.41; 144.47; 144.50; 144.54; 144.58; 144.61; 144.67; 162.40; 162.43; 162.58. FAB-MS (*m/z* (% relative intensity)): 2341.1 (100, *M*H$^+$; calc. for $^{13}C_2{}^{12}C_{174}H_{43}N_4O_8^+$: 2341.3). MALDI-TOF-MS (HABA (= 2-(4-hydroxyphenylazo)benzoic acid): 2340.1 (M^+; calc. for $^{13}C_2{}^{12}C_{174}H_{42}N_4O_8^+$: 2340.3).

6·Zn: M.p. > 400° (CH_2Cl_2/hexane). UV/VIS (CH_2Cl_2): λ_{max} [nm] (ε [1 mol^{-1} cm^{-1}]): 581 (sh, 4600), 550 (16100), 510 (5100), 427 (257200), 329 (95800), 259 (247900). Fluorescence (λ_{exc} = 427 nm): λ_{max} [nm] 647, 594. IR (KBr): 2956*m*, 2922*m*, 2844*m*, 1744*s*, 1728*s*, 1594*w*, 1561*w*, 1472*w*, 1367*w*, 1328*m*, 1261*m*, 1144*s*, 1027*m*, 1000*w*, 967*m*, 911*w*, 794*s*, 778*m*, 733*m*, 700*m*, 661*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.33–1.48 (*m*, 6 H); 4.42–4.57 (*m*, 4 H); 5.87–5.88 (*m*, 4 H); 7.68–8.43 (*m*, 18 H); 8.77 (*s*, 8 H). ^{13}C-NMR (125.8 MHz, $CS_2/CDCl_3$ 5 : 1): 13.84; 51.30; 62.60; 67.82; 67.89; 70.53; 70.60; 119.50; 120.61; 124.79; 126.02; 126.10; 126.24; 126.40; 126.59; 126.92; 127.67; 128.40; 131.29; 131.72; 132.63; 133.47; 133.74; 134.13; 136.80; 137.47; 137.64; 138.42; 138.45; 139.37; 139.53; 139.80; 139.89; 140.06; 140.26; 140.79; 140.84; 140.89; 140.91; 141.00; 141.13; 141.20; 141.25; 141.51; 141.64; 141.67; 141.75; 141.81; 141.85; 141.90; 141.93; 142.00; 142.02; 142.13; 142.23; 142.67; 142.74; 142.89; 142.92; 142.97; 143.33; 143.45; 143.65; 143.69; 143.71; 143.74; 143.76; 143.80; 143.90; 143.94; 144.07; 144.15; 144.17; 144.21; 144.24; 144.29; 144.34; 149.17; 149.22; 149.44; 149.47; 161.87; 162.06. FAB-MS: 2403.8 (*M*H$^+$; calc. for $^{13}C_2{}^{12}C_{174}H_{41}N_4O_8Zn^+$: 2402.2). MALDI-TOF-MS (HABA): 2403.4 (M^+; calc. for $^{13}C_2{}^{12}C_{174}H_{40}N_4O_8Zn^+$: 2402.2).

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