Synthesis and electrochemical investigations of molecular architectures involving C_{60} and tetraphenylporphyrin as building blocks

Elke Dietel,[a] Andreas Hirsch,*,[a] Jinkou Zhou[b] and Anton Rieker*,[b]

[a] *Institut für Organische Chemie, Universität Erlangen, Henkestr. 42, 91054 Erlangen, Germany*
[b] *Institut für Organische Chemie, Universität Tübingen, Auf der Morgenstelle 18,*
72076 Tübingen, Germany

A C_{60}–porphyrin diad 3a has been prepared by connecting a zinc porphyrin and C_{60} *via* nucleophilic cyclopropanation. The fullerene diad as well as the related precursor porphyrins 1a, 2a have been investigated by cyclic and differential pulse voltammetry in dichloromethane. Whereas no oxidation peaks were observed for C_{60}, all compounds 1a–3a exhibit two successive, quasi-reversible oxidation peaks in terms of an EE mechanism. The peak potentials of all three species almost coincide, due to an oxidation of the porphyrin ring system in all cases. In the cathodic process, on the other hand, the compounds are reduced in quasi-reversible four (C_{60}), two (1a,2a) and five (3a) one-electron transfers. The first two formal potentials of 3a (resulting from the C_{60} moiety) are shifted towards negative potentials by 40 mV, as compared to C_{60}, which is typical for methanofullerenes. Aside from coulombic effects, there is almost no electronic interaction between the C_{60} and porphyrin parts in 3a. Furthermore, a mixed hexaadduct 4 of C_{60} with an octahedral addition pattern incorporating a zinc tetraphenylporphyrin has been synthesized.

Introduction

The construction of molecular arrays consisting of fullerenes[1] and porphyrins is an appealing synthetic target. In C_{60}–porphyrin diads (type **a**, Fig. 1), where the porphyrin serves as a donor and the C_{60} moiety as an acceptor, which is able to undergo up to six reversible one-electron reductions,[2] the two chromophores are covalently linked *via* a bridging unit (**B**). Several examples of C_{60}–porphyrin diads have been synthesized[3–15] in order to develop model compounds for the investigation of light-induced electron-transfer processes reminiscent of photosynthesis events. A second attractive type of molecular architecture would comprise polyfunctionalized C_{60} cages incorporating porphyrin moieties together with additional addends like dendrons, long chain molecules or peptides (type **b**, Fig. 1). In such macromolecules, the role of the fullerene is to serve as the structure determining tecton. If, for example, the additional addends were dendrons of higher generation, the size and the shape of such model compounds would be comparable to the globular heme proteins. The redox properties of the porphyrin as well as the complexation behaviour of the central metal atom should be dependent on the surroundings and therefore be tunable by the nature of additional addends and the addition pattern itself. In order to study such phenomena a facile access to these types of model systems, allowing for a systematic variation of the bridges and the additional addends as well as of the addition pattern, would be desirable. One of the most versatile methods for the functionalization of fullerenes is their nucleophilic cyclopropanation using bromomalonates[16] or malonates.[17,18] These additions proceed in good yields, lead to stable products, allow for the introduction of almost any type of substituent -COOR on the methylene bridges and, most important for type **b** systems, the formation of multiple adducts like a symmetrical hexaadduct with an octahedral addition pattern is regioselective, especially if template mediated strategies are applied.[18,19] In this paper we show that this type of chemistry indeed works very well with tetraphenylporphyrin containing malonates. We report here on the synthesis and electrochemical characterization of type **a** diads involving a flexible bridging unit as well as on the first realization of a mixed hexaadduct of type **b**.

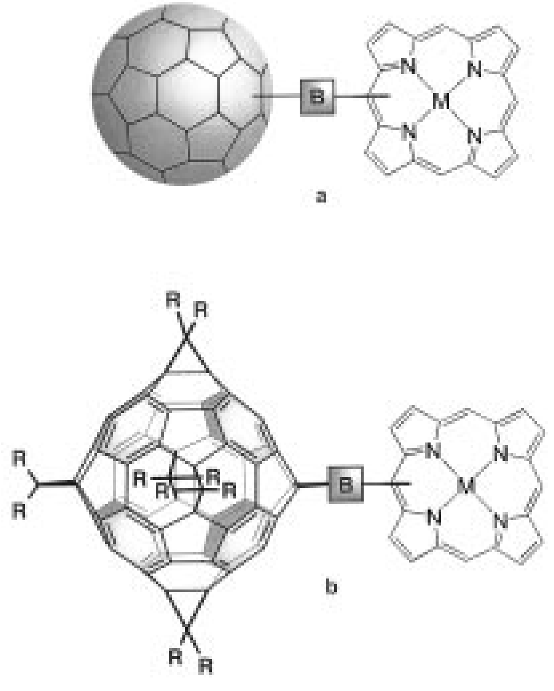
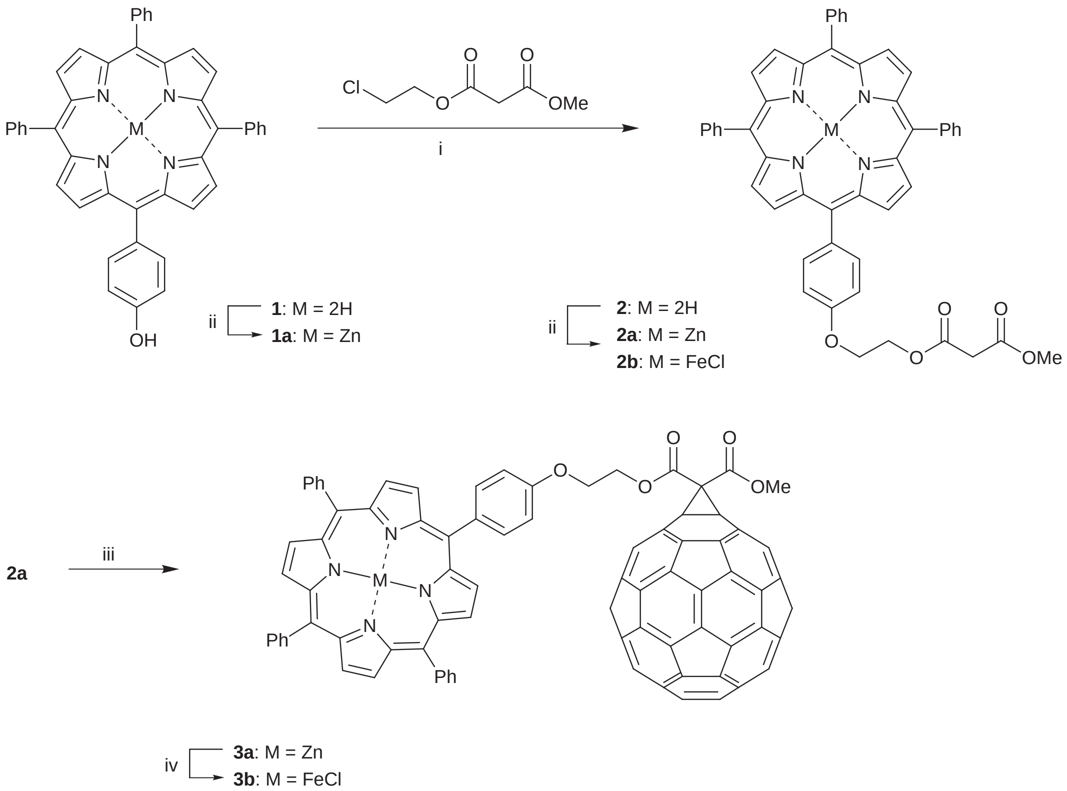


Fig. 1 Schematic representations of molecular architectures involving C_{60} and porphyrins as building blocks, (**a**) monoadduct (diad) and (**b**) mixed hexaadduct with an octahedral addition pattern

Results and discussion

Synthesis and characterization

The synthetic steps for the formation of the C_{60}–porphyrin diads **3** involving nucleophilic cyclopropanations of C_{60} are summarized in Scheme 1. This approach requires unsymmetrically substituted porphyrins, which can be coupled to



Scheme 1 Synthesis of the diads **3a**,**b**. *Reagents and conditions*: i, K_2CO_3; ii, MCl_2 (M = Zn, Fe), THF; iii, C_{60}, I_2, DBU; iv, 1) conc. HCl, CH_2Cl_2; 2) $FeCl_2$, THF.

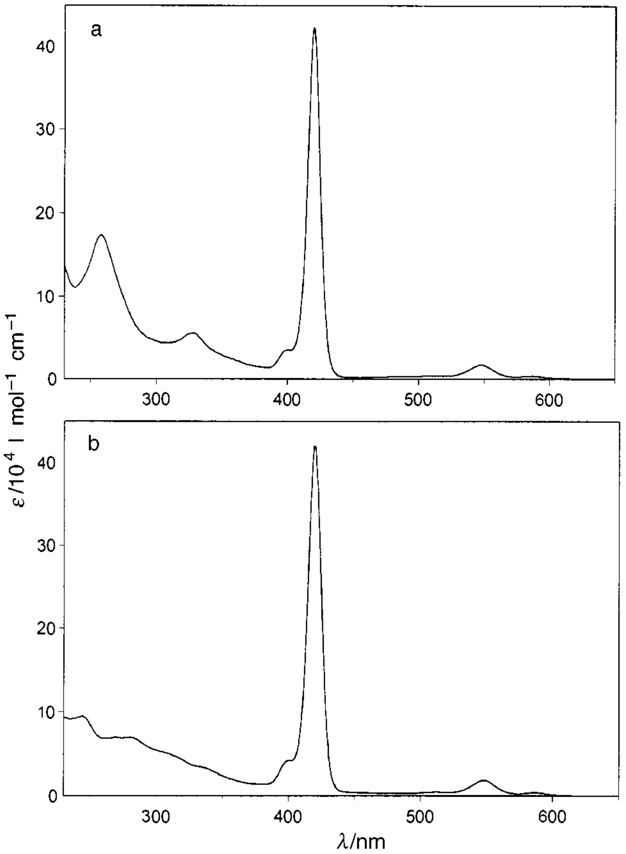


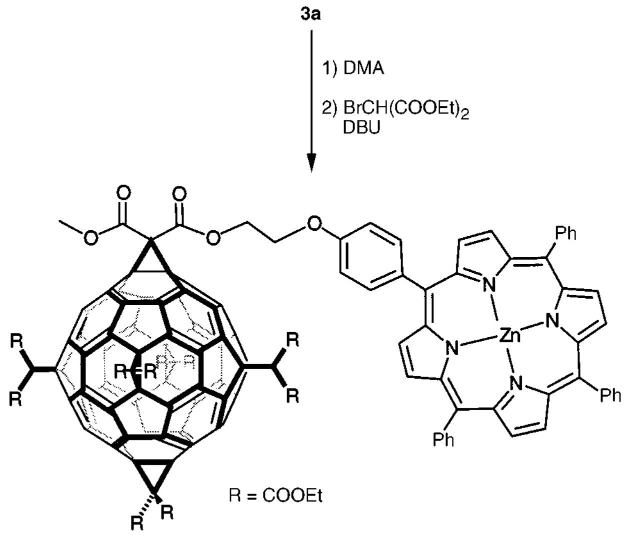
Fig. 2 Electronic absorption spectra (CH_2Cl_2) of (a) **3a** and (b) **4**

malonates. For this purpose, porphyrin **1** was synthesized by means of a mixed aldehyde approach[20] using pyrrole, benzaldehyde and 4-hydroxybenzaldehyde in a 4:3:1 ratio. Reaction with 2-chloroethyl methyl malonate, which was obtained by the reaction of 2-chloroethanol with methyl malonyl chloride in the presence of pyridine afforded the metal-free porphyrin **2**. The conversion into the metallated compound **2a** was achieved by treatment with $ZnCl_2$ in refluxing THF.[21] The subsequent cyclopropanation of C_{60} was carried out in the presence of iodine using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base. Under these conditions the malonate is halogenated *in situ* and can react with the fullerene. The diad **3a** was obtained in 43% isolated yield (76% based on recovered C_{60}). Separation of **3a** from C_{60} and bisadducts was accomplished by flash chromatography on silica gel using toluene as eluent. For comparison, the zinc porphyrin **1a** was synthesized in analogy to **2a**.[21]

All the new compounds were characterized by ^{1}H NMR, ^{13}C NMR, FTIR and UV–VIS spectroscopy as well as by mass spectrometry. The ^{13}C NMR spectrum of the diad **3a** shows resolved 24 of the 30 expected signals for the C_{60}-sp^2 C-atoms between $\delta = 139$ and 145. The signal for the two sp^3-C atoms of the fullerene cage appears at $\delta = 71.10$. In the UV–VIS spectrum (Fig. 2) no significant shift of the porphyrin absorption bands compared to those of **2a** is observed. The characteristic peak for C_{60} monoadducts[1] at 425 nm is covered by the intense Soret band of the porphyrin moiety. The fact that no bands in addition to those of a porphyrin like **2a** or a typical monocyclopropanated C_{60}[18] are observed in the spectrum of the diad **3a** indicates that there are no significant interactions between the two chromophores in the ground state.

Along with the zinc porphyrins **2a** and **3a**, the analogues **2b** and **3b** with iron as the central metal atom were also synthesized. The compound **2b** was obtained from **2** by reaction with anhydrous $FeCl_2$ in refluxing THF. For the synthesis of the C_{60}–porphyrin diad **3b**, the zinc chelate **3a** was demetallated with hydrochloric acid and then treated with anhydrous $FeCl_2$ as described above. Both complexes were characterized by UV–VIS and FTIR spectroscopy as well as by mass spectrometry.

We expected that the monoadduct **3a** could be a suitable precursor for the synthesis of higher addition products containing different addends (type **b** systems). For this purpose we intended to use our template mediation method[19] which provides a facile access to hexaadducts with an octahedral addition pattern. This procedure takes advantage of the fact that 9,10-dimethylanthracene (DMA) is able to undergo multiple and reversible [4 + 2]-cycloadditions with C_{60} or a monoadduct of C_{60}. These kinetically and thermodynamically controlled additions proceed preferably at octahedral sites. Since the remaining [6,6]-double bonds in these positions are the most reactive, templates are generated, which allow for very regioselective attacks of irreversibly binding addends into octahedral sites (successive *e* additions). The question arose, whether this method also works with monoadducts like **3a** where the first addend is sterically demanding. Using the same procedure that we developed previously for the synthesis of other mixed hexaadducts,[19] we were able to isolate **4** after repeated purification with flash chromatography in 40% yield (Scheme 2).This shows that the large tetraphenylporphyrin addend does not interfere with the hexaadduct formation.



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Scheme 2 Synthesis of the hexaadduct **4**

The ^{13}C NMR spectrum of **4** reveals a very interesting phenomenon. Although the depicted symmetry is C_s and therefore the expected number of signals in the sp^2 region is 24, only 2 signals at $\delta = 145.78$ and 141.18 are observed. Also, the sp^3-C atoms of the fullerene cage give rise to only one resonance at $\delta = 69.11$. This is reminiscent of the ^{13}C NMR spectrum of the T_h symmetrical hexaadduct $C_{66}(COOEt)_{12}$[22] which owing to its high symmetry contains only three types of magnetically different C-atoms within the fullerene cage. Therefore, the ^{13}C NMR spectrum of **4** pretends higher symmetry than the molecule actually has. The porphyrin substituent located in the periphery of one methylene bridge does not significantly influence the magnetic properties of the cage nuclei. In the ^1H NMR spectrum of **4** however, the signals for the ethyl groups appear as multiplets due to seven magnetically non-equivalent substituents.

Electrochemical investigations

Cyclovoltammetry (CV) and differential pulse voltammetry (DPV) were performed on C_{60} and **1a**, **2a**, **3a** in dichloromethane solutions containing 0.1 M Bu_4NPF_6 at room temperature under an argon atmosphere. Characteristic curves for anodic oxidation and cathodic reduction are shown in Figs. 3–5. The CV-peak potentials are typically influenced by the scan rate (not shown in the Figures). For oxidation, the oxidation peaks ($E_p{}^o$) move towards more positive potentials, whereas the re-reduction peaks ($E_p{}^r$) are shifted to more negative potentials, when the scan rate is increased. For reduction, the opposite behaviour is observed with increasing scan rate: the reduction peaks are shifted to more negative potentials, the re-oxidation peaks towards more positive potentials. In both cases, the resulting increase in the potential separations ΔE_p ($= E_p{}^o - E_p{}^r$) indicates that the electron-transfer processes are quasi-reversible.[23] Therefore, the formal potentials (E^o) can be obtained as the mean value of $E_p{}^r$ and $E_p{}^o$, or directly from the DPV curves; these values are listed in Table 1. The number *n* of electrons transferred per molecule in the electrochemical reduction or oxidation of C_{60} and **1a**–**3a** was confirmed by controlled-potential electrolysis (CPE) at appropriate potentials, chosen from the corresponding CV responses. For all transfer steps, aside from the fourth reduction peak of C_{60} (see below), *n* was close to 1.

Table 1 Formal potentials (E^o/mV)[a] for anodic oxidation and reduction

Comp.	$E_{ox}{}^{01}$	$E_{ox}{}^{02}$	$E_{red}{}^{01}$	$E_{red}{}^{02}$	$E_{red}{}^{03}$	$E_{red}{}^{04}$	$E_{red}{}^{05}$
C_{60}			−1015	−1380	−1850	−2310[b]	
1a	360	570	−1870	−2320[b]			
2a	365	575	−1880	−2330[b]			
3a	380	585	−1055	−1420	−1865	−2135	−2330[b]

[a] E^o, formal potentials, obtained as the mean value of $E_p{}^r$ and $E_p{}^o$, *vs.* Fc/Fc^+. [b] E^o obtained by DPV.

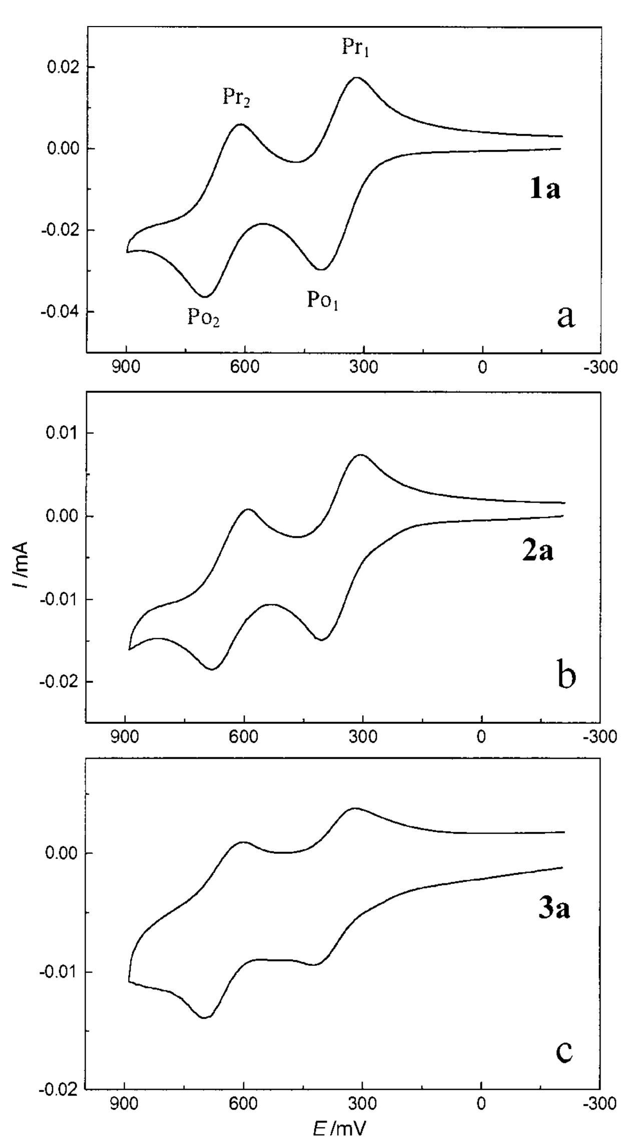


Fig. 3 CV curves of the anodic oxidation of **1a** (a), **2a** (b) and **3a** (c) in CH_2Cl_2 solution containing 0.1 M Bu_4NPF_6, scan rate 100 mV s^{-1}

The CV curves obtained on anodic oxidation at a scan rate of 100 mV s^{-1} (Fig. 3) reveal *no* peak for C_{60}, as reported[24] for the experimental conditions used. However, all three other com-

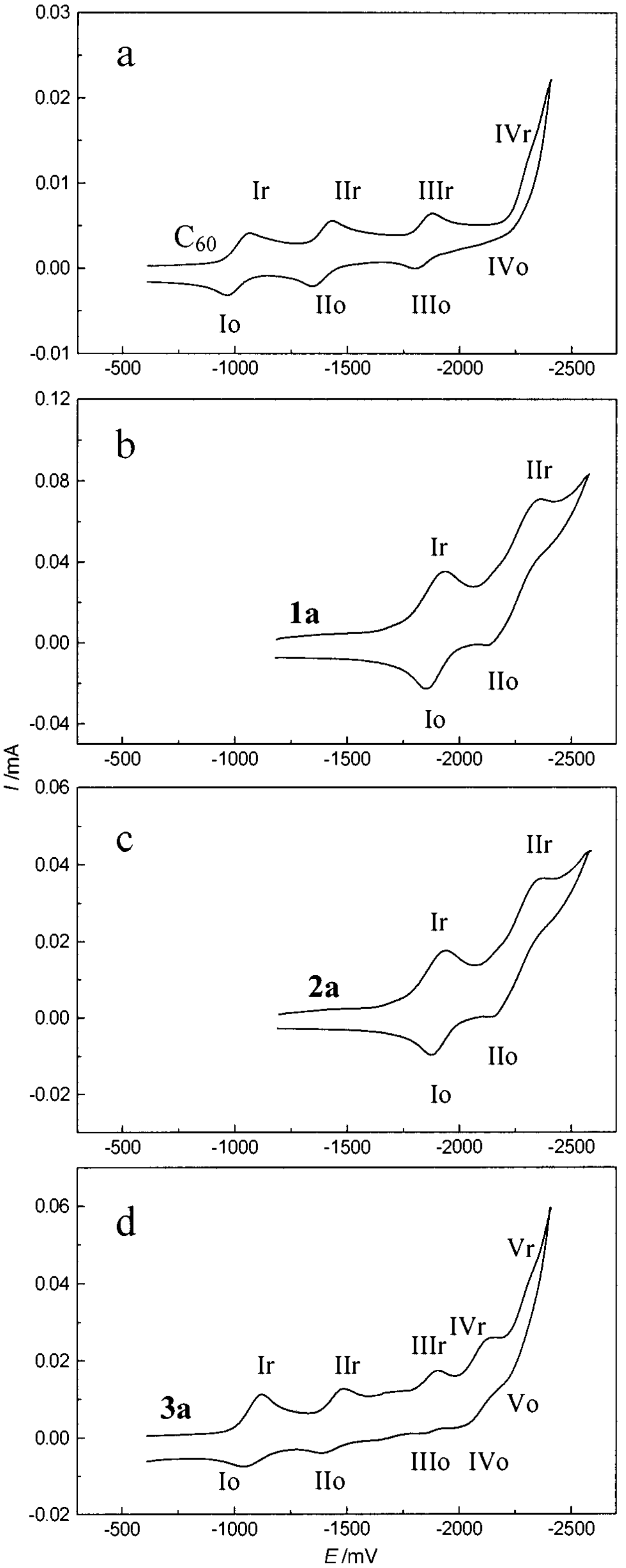


Fig. 4 CV curves of the cathodic reduction of C_{60} (a), **1a** (b), **2a** (c) and **3a** (d) in CH_2Cl_2 solution containing 0.1 M Bu_4NPF_6, scan rate 100 mV s^{-1}

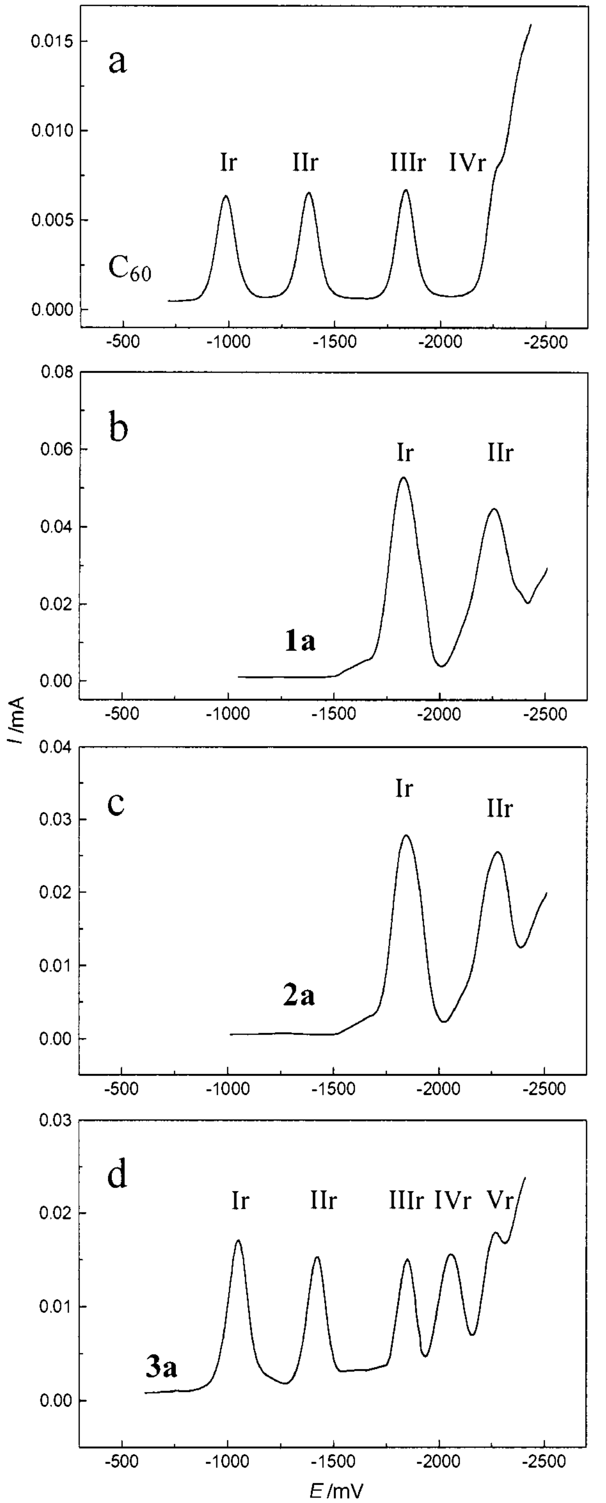


Fig. 5 DPV curves of the cathodic reduction of C_{60} (a), **1a** (b), **2a** (c) and **3a** (d) in CH_2Cl_2 solution, containing 0.1 M Bu_4NPF_6, scan rate 20 mV s^{-1}, pulse amplitude 50 mV, pulse width 50 ms, pulse period 200 ms

pounds **1a**–**3a** exhibit two well separated sequential oxidation peaks (Po^1, Po^2) and two re-reduction peaks (Pr^1, Pr^2). From the CV and CPE measurements it can therefore be derived that **1a**–**3a** are oxidizable in quasi-reversible EE processes in overall, stepwise two-electron transfers to form dications, which can be re-reduced to the corresponding neutral states. Similar results have been observed with other tetraarylporphyrins.[25,26] Since zinc is a redox-inactive metal in these porphyrins, the products of 1e oxidations are π-cation radicals, whose electronic structures have been studied comprehensively.[25–27] A comparison of the corresponding first and second formal potentials E_{ox}^{01} and E_{ox}^{02} (Table 1) of **1a** and tetraphenylporphyrin (TPP) (E_{ox}^{01} = 320 mV; E_{ox}^{02} = 680 mV, taken from ref. 25 and recalculated from the Ag/AgCl to the Fc/Fc^+ reference electrode) reveals no influence of the hydroxy group on E_{ox}^{01} within the error of the potential differences of the respective reference electrodes. On the other hand, the second oxidation step is facilitated by about 100 mV by the electron-donating power of OH. If we compare the E_{ox}^{0} values of **1a**–**3a**, each pair of potentials (E_{ox}^{01}, E_{ox}^{02}) is practically the same for all three compounds, thus indicating that the influence of the substituents at the ether-oxygen atom on the electron-donating ability of the species is very small. Especially, any charge interaction between the C_{60} and porphyrin moieties in **3a** on the oxidation process must be either extremely weak or completely missing. In addition, since C_{60} itself is not oxidized under these conditions, we have to assume that **3a** is oxidized in the porphyrin moiety (see above).

The CV and DPV curves of the cathodic reduction of C_{60} and **1a**–**3a** are shown in Figs. 4 and 5, respectively. In sharp contrast to its anodic processes, C_{60} exhibits three well separated reduction (Ir–IIIr) and three corresponding re-oxidation (Io–IIIo) peaks (Fig. 4a), representing sequential one-electron transfer processes as expected (see ref. 28 and literature quoted therein). As compared with the results obtained for C_{60} in 1,2-dichlorobenzene,[28] the redox potentials in dichloromethane are shifted to less negative values for about 150 mV. Therefore, one would expect the fourth reduction potential in dichloromethane at about −2.3 V. Indeed, there occurs a shoulder in the end rise of the supporting-electrolyte reduction current at this value (Fig. 4a). On the other hand, **1a** and **2a** exhibit only two peak couples of reduction (Ir, IIr) and re-oxidation (Io, IIo) (Fig. 4b,c), as expected for such porphyrins.[25] When compared to ZnTPP ($E_{\text{red}}{}^{01} = -1810$ mV; $E_{\text{red}}{}^{02} = -2140$ mV, taken from ref. 25 and recalculated from the Ag/AgCl to the Fc/Fc$^+$ reference electrode), **1a** and **2a** are more difficult to reduce, especially in the second reduction step. This again reflects the influence of the electron-donating OR group which is much stronger than in the case of oxidation. The second reduction step seems to be less reversible and of lower intensity (see Figs. 4b,c and 5b,c) than the first one. Similar observations have been made with extended quinones.[29] From the structures of C_{60} and **1a**, **2a**, and the experimental results of CV, DPV and CPE measurements, it can be derived that these species are reducible with overall four- and two-electron transfers to form a tetra-anion and dianions, respectively. Since all anion species can be re-oxidized up to their neutral states, the electrochemical behaviour of these three species can be formally denoted as quasi-reversible EEEE, EE and EE processes, respectively, where the higher reduction processes of **1a**, **2a** may be coupled to fast chemical reactions.

In the case of the diad **3a**, the poor solubility in dichloromethane only allows us to obtain electrochemical responses of modest quality. The CV reveals five peak couples of reduction (Ir–Vr) and re-oxidation (Io–Vo) (Fig. 4d), where the reduction peak Vr and the re-oxidation peaks IIo–Vo are not well expressed. The fifth reduction peak (Vr) can be more clearly observed in the DPV (Fig. 5d).

In order to draw conclusions on a possible interaction of the two subunits of the molecule, it is necessary to unequivocally assign all peaks. A comparison of the CVs and DPVs of Figs. 4 and 5 reveals that the first two peak couples of **3a** belong to the fullerene moiety. The corresponding formal potentials, $E_{\text{red}}{}^{01}$ and $E_{\text{red}}{}^{02}$, are shifted to negative positions by 40 mV as compared to C_{60}. This is no indication of an interaction between the porphyrin and fullerene moiety in **3a**, because the introduction into C_{60} of a cyclopropane ring alone generally causes a more negative reduction potential of about 50–150 mV for the first three waves[30] (see also ref. 31 and the literature quoted therein). Bearing this in mind, we should expect the third 'fullerene' reduction wave of **3a** at a potential of about −1890 mV. The third peak couple of **3a** shows indeed $E_{\text{red}}{}^{03} = -1865$ mV. However, we also should expect a peak couple at −1880 mV for the first reduction of the porphyrin moiety. If both reductions were completely independent of each other, a coincidence of the two mentioned peak couples should occur with an intensity twice that of the other peak couples. As the DPV curve convincingly shows, this is not the case. Therefore, both the peak couple at −1865 as well as that appearing at −2135 mV are candidates for the third reduction of the fullerene and for the first reduction of the porphyrin moiety in **3a**, *i.e.* one of these potentials is shifted by about 250 mV *versus* more negative potentials as compared to C_{60} or **1a**, **2a**.

Let us first consider the case that the third electron ($E_{\text{red}}{}^{03} = -1865$ mV) would enter into the fullerene moiety. The resulting trianion would then have to impede the transfer of the next electron to the porphyrin system ($E_{\text{red}}{}^{04} = -2135$ mV). This would surely not be due to a direct electronic interaction *via* the spacer or by through-space interactions with the porphyrin ring, because no feed-back effect on the fullerene-part potentials can be found. Moreover, in the case of other porphyrin and phthalocyanine diads no such effects have been observed.[15,31] Thus, only a coulombic repulsion effect of the highly negatively charged fullerene-trianion at the cathode would satisfactorily explain the shift of the first reduction potential of the porphyrin moiety, similar to the case of porphyrin–quinone diads.[32]

In the opposite case, *i.e.* first porphyrin reduction at $E_{\text{red}}{}^{03} = -1865$ mV, one would have to explain a 250 mV shift of the third reduction potential of the fullerene part ($E_{\text{red}}{}^{04} = -2135$ mV), which is incongruously high, even if one allows for coulombic effects, because here the negative charge of the anion being reduced is increased by only 1 as compared to the methanofullerene. Remember that in the consideration of the first case above, the charge of the trianion of **3a**, in which the first reduction of the porphyrin system should occur, was 3 as compared to 0 in the non-diadic porphyrins. Moreover, there is no indication of ring opening reactions to either a fulleroid or a carbanion,[33] which could explain the potential shift.

Although it is not possible to discriminate between the two above mentioned cases by electrochemical methods only, chemical evidence with several porphyrin diads as well as Ockham's razor[34] indicate that the first three electrons do enter the fullerene unit. Due to the coulombic repulsion, the first reduction potential of the porphyrin unit is shifted to −2135 mV ($E_{\text{red}}{}^{04}$). For similar reasons, the fifth reduction potential, $E_{\text{red}}{}^{05}$, although less well substantiated, does not correspond to a superposition of the fourth reduction of the fullerene moiety and the second reduction of the porphyrin system, as originally expected, but should be attributed to the fourth reduction of the fullerene part only; the second reduction of the porphyrin unit would then be shifted again to more negative potentials and therefore buried in the solvent reduction curve. Thus, the situation seems to be completely analogous to that with porphyrin–quinone diads,[35] in which first the quinone is reduced in two one-electron transfers at potentials corresponding to those of the free, non-diadic quinone; the third and fourth electrons then enter the porphyrin at potentials which are shifted to more negative values. Altogether, regardless, whether the first or the second explanation holds, no direct electronic interaction between the fullerene and porphyrin moiety of **3a** can be derived from the electrochemical experiments. This seems to be in contrast to fullerene–porphyrin diads in which the fullerene unit is bound *via* a shorter chain directly to the porphyrin ring,[8,12] although no detailed discussion of the CV curves is given for these species.

Conclusions

The synthesis of new C_{60}–porphyrin diads **3a**,**b** (type **a**) has been accomplished *via* facile nucleophilic cyclopropanations of [6,6]-double bonds with malonates containing a tetraphenylporphyrin moiety in the side chain. On the other hand, a mixed hexaadduct **4** in which the addends are located in octahedral sites of the C_{60} unit was made available in good yields. This first synthesis of a type **b** system shows that C_{60} can be used as a structure determining building block for the development of more complex architectures involving porphyrins as electrophores. The spectroscopic characterization of the diads **3a**,**b** demonstrates the absence of an electronic interaction in the ground state, since, for example, their UV–VIS

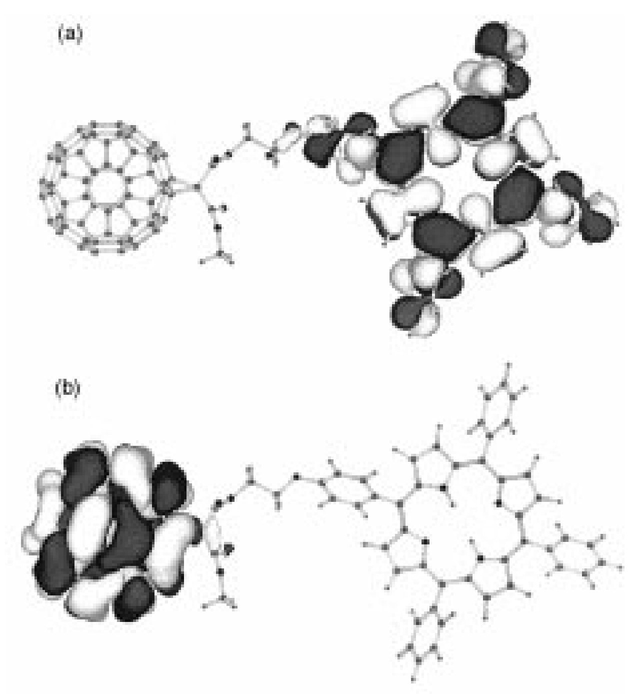
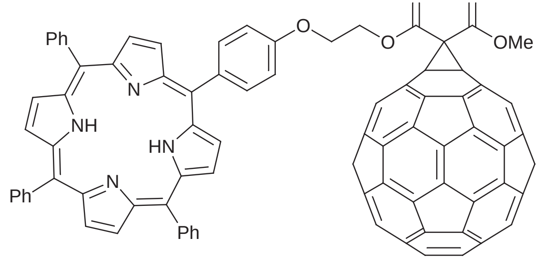


Fig. 6 PM3 calculated frontier orbitals of **5** and its monoanion, (a) HOMO ($E = -6.798$ eV), (b) SOMO ($E = -3.950$ eV)

and NMR spectra reflect the typical features of undisturbed fullerene or tetraphenylporphyrin building blocks. This is in line with other C_{60}–porphyrin diads described in the literature.[3–15] In order to predict the location of the first oxidation and reduction event in these diads, we carried out semiempirical calculations. The calculated structure of the metal-free compound **5** was obtained by PM3/RHF geometry optimization using the program package HyperChem 5.0.[36] The metal-free system is a good model for **3a** since at least for the potential range between the first reductions or oxidations of the tetraphenylporphyrin-zinc system the central metal is redox inactive. The HOMO of **5** is centred on the porphyrin macrocycle (Fig. 6a). Therefore, the first oxidation should take place on the addend. In order to predict the location of the first one-electron reduction, we carried out a PM3/UHF single point calculation on the monoanion $\mathbf{5}^-$ using the PM3/RHF geometry of **5**. This consideration of the SOMOs of the monoanion provides a more realistic estimation of reduction events than simply considering the LUMOs of the neutral species. The SOMO of $\mathbf{5}^-$ is fullerene based (Fig. 6b) and therefore the first reduction is predicted to take place on the C_{60} core. These predictions are confirmed by electroanalytical measurements (CV, DPV, CPE). Moreover, no appreciable electronic intramolecular interaction between the porphyrin and fullerene units was detected by these techniques. Potential shifts of about 250 mV of the first reduction of the porphyrin unit to more negative potentials seem to result from coulombic effects between the highly negatively charged trianions of **3a** and the cathode. The location of the third and fourth reduction in **3a** cannot be unambiguously assigned; calculations on the tri- and tetra-anions of **3** are difficult to perform, since, for example, convergence problems arise. Moreover, the role of the counterion is expected to become increasingly important. Investigations on the photophysical properties of **3a**,**b** and hexaadducts like **4** are currently underway.



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Experimental

^{1}H NMR and ^{13}C NMR: JEOL PMX and JEOL JNM GX 40 (J values are given in Hz throughout); MS: Micromass TofSpec (MALDI); FTIR: Bruker Vector 22; UV–VIS: Shimadzu UV 3102 PC; TLC: Merck, Silica gel 60 F_{254}. Solid reagents used were commercially available (reagent grade). Solvents and liquid reagents were distilled under reduced pressure. Chloroform was distilled without removing the stabilizing ethanol. Toluene was distilled from benzophenone ketyl. All air- or water-sensitive reactions were carried out under a positive pressure of nitrogen. Products were isolated by (flash) column chromatography (silica gel 60, particle size 0.04–0.063 nm, Merck). Electrochemical experiments were carried out on a Windows-driven BAS CV-50W electrochemical analyser (Bioanalytical Systems, Inc., West Lafayette, IN 47906, USA). For CV and DPV a 3 mm-diameter glassy carbon disk electrode was used as the working electrode. The auxiliary electrode consisted of a Pt wire. Ag/AgClO$_4$ (0.01 M in MeCN/0.1 M NBu$_4$PF$_6$) was used as the reference electrode and separated by two glass frits from the Haber-Luggin capillary. For controlled-potential electrolysis (CPE) cylindrical Pt (10% iridium) gauze working and auxiliary electrodes, separated by a porous glass frit, were used. All potentials are referenced to the ferrocene/ferrocenium couple (Fc/Fc$^+$) as the internal standard. All measurements were carried out with CH_2Cl_2 solutions containing 0.1 M Bu$_4$NPF$_6$ at room temperature under an argon atmosphere. CH_2Cl_2 was first boiled over P_2O_5 for 5–8 h, then distilled three times and filtered over Al_2O_3 under argon and finally kept over 3 Å molecular sieves. Tetrabutylammonium hexafluorophosphate (NBu$_4$PF$_6$) as supporting electrolyte was prepared from tetrabutylammonium bromide and ammonium hexafluorophosphate, crystallized four times from EtOH and dried *in vacuo* at 110 °C for 48 h.

10-{4-[2-(Methoxymalonyloxy)ethoxy]phenyl}-5,15,20-triphenylporphyrin (2)

A mixture of **1** (505 mg, 0.80 mmol), 2-chloroethyl methyl malonate (470 mg, 2.60 mmol), dry potassium carbonate (512 mg, 3.70 mmol) and a catalytic amount of potassium iodide was stirred in dry DMF (25 ml) for 14 h at 60 °C. The mixture was poured into 120 ml of a water–methanol solution (5:1). The precipitate formed was separated by centrifugation and purified by column chromatography (SiO$_2$, CHCl$_3$). The first fraction gave 316 mg of **2** (51% yield), the second contained unreacted **1**. δ_H(400 MHz, 31 °C, CDCl$_3$) 8.84 (s, 8 H, β-pyrrole), 8.21 (AA′BB′, 6 H, phenyl), 8.12 (AA′BB′, 2 H, phenyl), 7.76 (m, 9 H, phenyl), 7.27 (AA′BB′, 2 H, phenyl), 4.69 (t, J 4.7, 2 H, spacer), 4.46 (t, J 4.4, 2 H, spacer), 3.81 (s, 3 H, $\mathrm{OC}H_3$), 3.56 (s, 2 H, malonate $\mathrm{C}H_2$), −2.77 (s, 2 H, NH); δ_C(100 MHz, 31 °C, CDCl$_3$) 166.85, 166.60 (C=O), 158.21, 142.18, 135.61, 135.17, 134.54, 133–130, 127.68, 126.67, 120.09, 120.03, 119.73, 112.81 (porphyrin), 65.89, 63.95 (spacer), 52.65 (OCH$_3$), 41.27 (malonate CH$_2$); ν_{max}(KBr)/cm^{-1} 3316, 3053, 3024, 2962, 2921, 1737, 1596, 1557, 1506, 1471, 1439, 1400, 1348, 1261, 1245, 1175, 1151, 1105, 1071, 1030, 965, 876, 847, 800, 732, 701; λ_{max}(CH_2Cl_2)/nm 399 (sh), 418, 516, 551, 591, 647; m/z (MALDI) 774.2 (M$^+$).

10-{4-[2-(Methoxymalonyloxy)ethoxy]phenyl}-5,15,20-triphenylporphyrinatozinc(II) (2a)

A mixture of **2** (300 mg, 0.39 mmol) and ZnCl$_2$ (200 mg, 1.05 mmol) was heated in THF (40 ml) at reflux for 1 h. The solvent was evaporated under reduced pressure. Column chromatography (SiO_2, $CHCl_3$) gave 304 mg of **2a** (94% yield). δ_H(400 MHz, 31 °C, $CDCl_3$) 8.95 (s, 8 H, β-pyrrole), 8.23 (AA′BB′, 6 H, phenyl), 8.12 (AA′BB′, 2 H, phenyl), 7.76 (m, 9 H, phenyl), 7.24 (AA′BB′, 2 H, phenyl), 4.64 (t, *J* 4.7, 2 H, spacer), 4.41 (t, *J* 4.4, 2 H, spacer), 3.79 (s, 3 H, OCH_3), 3.50 (s, 2 H, malonate CH_2); δ_C(100 MHz, 31 °C, $CDCl_3$) 166.82, 166.56 (C=O), 158.19, 150.43, 150.24, 150.19, 142.81, 135.81, 135.43, 133–130, 127.48, 121.12, 121.07, 120.72, 112.68 (porphyrin), 65.86, 63.94 (spacer), 52.63 (OCH_3), 41.21 (malonate CH_2); ν_{max}(KBr)/cm^{-1} 3049, 3021, 2963, 1734, 1596, 1521, 1508, 1484, 1439, 1337, 1262, 1244, 1203, 1175, 1149, 1105, 1067, 1036, 992, 796, 751, 718, 700; λ_{max}(CH_2Cl_2)/nm 399 (sh), 420, 512, 549, 587; *m*/*z* (MALDI) 836.1 (M^+).

10-{4-[2-(Methoxymalonyloxy)ethoxy]phenyl}-5,15,20-triphenylporphyrinatoiron(III) chloride (2b)

A mixture of **2** (50 mg, 0.065 mmol) and anhydrous $FeCl_2$ (25 mg, 0.20 mmol) was heated in THF (25 ml) at reflux for 1 h. The solvent was evaporated under reduced pressure. The residue was dissolved in chloroform, washed with water and dried. Evaporation gave 51 mg of **2b** (94% yield). ν_{max}(KBr)/cm^{-1} 3048, 3017, 2956, 2925, 2860, 1735, 1602, 1576, 1509, 1489, 1440, 1337, 1260, 1176, 1072, 1027, 1003, 803, 754, 721, 703; λ_{max}(CH_2Cl_2)/nm 378 (sh), 419, 449 (sh), 512, 594, 651; *m*/*z* (MALDI) 863.2 (M^+), 828.3 ($M^+ - Cl$).

1′-Methoxycarbonyl-1′-{2-[4-(10-{5,15,20-triphenylporphyrinatozinc(II)})phenoxy]ethoxycarbonyl}-1,2-methano[60]fullerene (3a)

To a solution of **2a** (140 mg, 0.17 mmol) in toluene (75 ml) C_{60} (130 mg, 0.18 mmol), iodine (43 mg, 0.17 mmol) and DBU (71 mg, 0.47 mmol) were added. After stirring for 24 h at room temperature the solvent was evaporated and the crude mixture was separated by flash chromatography (SiO_2, toluene). The second fraction gave 113 mg of **4a** (43% yield). δ_H(400 MHz, 31 °C, $CDCl_3$) 8.92 (s, 4 H, β-pyrrole), 8.87 (s, 4 H, β-pyrrole), 8.19 (br, 6 H, phenyl), 8.03 (AA′BB′, 2 H, phenyl), 7.73 (m, 9 H, phenyl), 7.15 (AA′BB′, 2 H, phenyl), 4.91 (br, 2 H, spacer), 4.48 (br, 2 H, spacer), 4.08 (s, 3 H, OCH_3); δ_C(100 MHz, 31 °C, $CDCl_3$) 163.84, 163.60 (C=O), 157.88, 157.76, 150.38, 150.25, 150.17 (porphyrin), 145.06, 144.73, 144.62, 144.49, 144.36, 144.29, 144.04, 143.85, 143.67, 143.18, 143.09, 142.85, 142.46, 142.32, 142.26, 142.14, 142.08, 141.50, 141.46, 141.31, 140.42, 140.40, 139.10, 138.26 (C_{60}-sp^2 C), 135.90, 135.36, 134.44, 131.98, 130.52, 127.46, 126.71, 126.57, 121.18, 120.65, 117.21, 112.65 (porphyrin), 71.10 (C_{60}-sp^3 C), 65.75, 65.44 (spacer), 54.11 (OCH_3), 51.75 (methano bridge); ν_{max}(KBr)/cm^{-1} 3063, 3025, 2953, 2919, 2852, 1749, 1597, 1487, 1439, 1340, 1232, 1175, 1069, 1003, 797, 752, 701, 526; λ_{max}(CH_2Cl_2)/nm (ε/dm^3 mol^{-1} cm^{-1}) 257 (173 200), 326 (55 300), 400 (sh, 35 300), 418 (423 400), 513 (4000), 548 (17 300), 587 (4100); *m*/*z* (MALDI) 1558.7 ($M^+ + 2$), 1493 ($M^+ - Zn + 2$); **3b:** to a solution of **2a** (10 mg, 0.006 mmol) in CH_2Cl_2 two drops of conc. HCl were added and the mixture was vigorously stirred for 15 min. The organic layer was washed with water and dried. The solvent was evaporated under reduced pressure and the residue dissolved in THF. Anhydrous $FeCl_2$ (1.5 mg, 0.012 mmol) was added and the solution refluxed for 1 h. Work-up as described for **2b** gave 8 mg of **3b** (90% yield). ν_{max}(KBr)/cm^{-1} 2962, 2925, 2856, 1728, 1436, 1364, 1338, 1261, 1096, 1024, 868, 802, 754, 702, 527; λ_{max}(CH_2Cl_2)/nm 257, 327, 419, 508, 653; *m*/*z* (MALDI) 1583 (M^+), 1547 ($M^+ - Cl$).

1′-Methoxycarbonyl-1′-{2-[4-(10-{5,15,20-triphenylporphyrinatozinc(II)})phenoxy]ethoxycarbonyl}-1,2-methano-18,36:22,23:27,45:31,32:55,56-pentakis{[bis(ethoxycarbonyl)]methano}[60]fullerene (4)

A mixture of **3a** (82 mg, 0.053 mmol) and 9,10-dimethylanthracene (DMA) (82 mg, 0.402 mmol) was stirred at room temperature for 3 h. Then diethyl bromomalonate (88 mg, 0.37 mmol) and DBU (51 mg, 0.34 mmol) were added. After 120 h the solvent was evaporated and the crude mixture was separated by flash chromatography (SiO_2, toluene–ethyl acetate 20 : 1 gradually increasing to toluene–ethyl acetate 9 : 1) and purified by a second flash chromatography (SiO_2, toluene–ethyl acetate 9 : 1) to yield 50 mg of **5** (40% yield). δ_H(400 MHz, 31 °C, $CDCl_3$) 8.92 (br, 8 H, β-pyrrole), 8.20 (br, 6 H, phenyl), 8.11 (br, 2 H, phenyl), 7.74 (br, 9 H, phenyl), 7.26 (br, 2 H, phenyl), 4.80 (br, 2 H, spacer), 4.52 (br, 2 H, spacer), 4.38–4.26 (m, 20 H, ethyl CH_2), 3.92 (s, 1 H, OCH_3), 1.34–1.24 (m, 30 H, ethyl CH_3); δ_C(100 MHz, 31 °C, $CDCl_3$) 163.79 (C=O), 150.16 (porphyrin), 145.78, 141.18 (C_{60}-sp^2 C), 134.41, 131.98, 126.56 (porphyrin), 69.11 (C_{60}-sp^3 C), 63.16 (ethyl CH_2), 45.38 (methano bridges), 14.05 (ethyl CH_3), no signal for methoxy C; ν_{max}(KBr)/cm^{-1} 3057, 2979, 2935, 1747, 1637, 1600, 1508, 1465, 1442, 1391, 1368, 1340, 1221, 1176, 1075, 1005, 857, 801, 755, 714, 528; λ_{max}(CH_2Cl_2)/nm 244, 269, 280, 400 (sh), 419, 513, 548, 587; *m*/*z* (MALDI) 2348.4 ($M^+ + 2$), 2284.6 ($M^+ - Zn + 2$), 2189.4 [$M^+ - C(COOEt)_2$], 2126.6 [$M^+ - Zn - C(COOEt)_2 + 2$].

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