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# A New Type of Dendritic [60]Fullerene–Metallo-tetraphenylporphyrin Diads (M = Zn, Co)

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**Keywords:** Fullerenes / Porphyrins / Dendrimers / Metal complexes / Diads

The synthesis of unsymmetrical malonates **19**–**23** terminated by a metallo-tetraphenylporphyrin (M = $Zn^{II}$, $Co^{II}$, $Co^{III}$) and by Newkome-type amide dendrons of generation two and three is reported. Cyclopropanation of $C_{60}$ with the second-generation dendrons **20** and **21** leads to the formation of fullerene monoadducts **24** and **25**, representing a new type of dendritic diads. The establishment of Co in the oxidation sates of +II and +III was achieved by the treatment with $Na_2S_2O_4$ or with $O_2$ in the presence of $CN^-$ and $SCN^-$, respectively, leading to the paramagnetic complex **26** and the diamagnetic axially coordinated complexes **27**. Deprotection of the *tert*-butyl groups terminating the dendritic branch of the diads **24** and **25** generates the corresponding water-soluble systems **28** and **29**. Due to their amphiphilic character micellar aggregates are formed in water. DOSY NMR measurements showed that the aggregates consisting of **28** have an average diameter of approximately 7 nm in a buffered $D_2O$ solution (pH = 7.2).


**Abbreviations**

DBU: diazabicyclo[5.4.0]undec-7-ene; DCC: dicyclohexylcarbodiimide; DDQ: 2,3-dichloro-5,6-dicyanobenzoquinone; DMAP: 4-(dimethylamino)pyridine; DOSY: diffusion-ordered spectroscopy; FC: flash column chromatography; HETCOR: heteronuclear correlation spectroscopy, HOBt: hydroxybenzotriazole; TBAC: *n*-tetrabutylammonium cyanide; TBAR: *n*-tetrabutylammonium rhodanide; TFA: trifluoroacetic acid; THF: tetrahydrofuran; TLC: thin layer chromatography.

## Introduction

Abiotic model systems for heme proteins involving dendritic building blocks offer the opportunity to systematically investigate the influence of the microenvironment on the redox, coordination and photophysical properties of (porphyrinato)metal complexes serving as mimics for the heme group. Examples of such model compounds are the dendritic (porphyrinato)iron and -cobalt complexes investigated by the groups of Diederich[1] and Aida.[2] It has been demonstrated, for example, that the polarity of the dendritic surrounding causes changes of the redox potential of the $Fe^{III}/Fe^{II}$ couple, measured in water, of up to 420 mV.[3] Also the tuneable size of the dendrons attached to the porphyrin has significant influences on the stereochemistry of simple organic reactions.[2] In own studies[4] we developed a series of fullerene–tetraphenylporphyrin hybrids such as **1** and **2** (Figure 1) involving Frechet-type[5] dendrons attached to the remaining octahedral sites of the fullerene core by regioselective *template-mediated* cyclopropanation reactions. It turned out that the spectroscopic and electrochemical properties of the tetraphenylporphyrin chromophore surrounded by the dendritic coverage is not only governed by the dendritic type but also by the generation number.[6] With respect to the addition pattern of the fullerene core, compounds such as **1** and **2** represent hexakisadducts with an octahedral [5:1]addition pattern.[7] Compared to the parent $C_{60}$ or lower [6,6]adducts the characteristic electronic properties of the fullerene chromophore are almost lost in this prototype of dendritic porphyrin architectures and the fullerene just serves as a structure-determin-

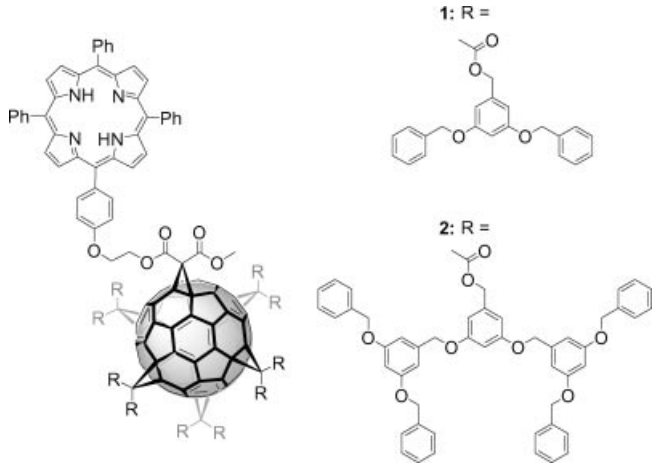


Figure 1.Porphyrin–fullerene diads **1**–**2** with benzyl ether dendrons involving an octahedral addition pattern.[6]

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ing platform.[8] On the other hand electronic communication between $C_{60}$ and a tetraphenylporphyrin addend is very pronounced if monoadducts and bisadducts such as **3**–**5** (Figure 2) are investigated.

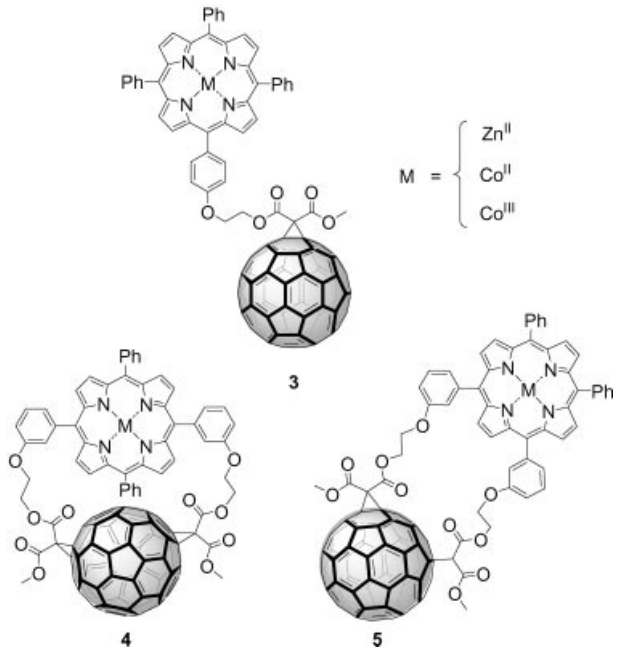



Figure 2. Singly and doubly linked porphyrin–fullerene diads **3**–**5**.[4,14–15]

We and other groups have recently synthesized a broad variety of such diads and systematically investigated their electronic and photophysical properties.[4,8–13] These diads are able to undergo photoinduced electron transfer with the porphyrin serving as donor and the fullerene as acceptor.

Significantly, the electron-transfer properties strongly depend on the spatial arrangements of the two chromophores and the rigidity of the whole architecture. Also, the redox properties of the central metal coordinated by the porphyrin moiety depends considerably on the precise arrangement within these diads.[4] For example, in contrast to diads **3** and **5** the very close metal–fullerene contact (2.71 Å) in the rigid diad **4** disfavours the oxidation of $Co^{II}$ to $Co^{III}$.[14–15]

We now wish to present the development of a new type of porphyrin–fullerene–dendrimer hybrids of the general formula **6** (Figure 3), where one addend only, namely a malonate involving a tetraphenylporphyrin and a dendritic terminus, is attached to $C_{60}$. In monoadducts of $C_{60}$ the characteristic fullerene properties are largely retained. Therefore, the $C_{60}$ moiety could be used as an additional sensor for the modification of the electronic properties of the porphyrin caused by the variation of the dendritic surrounding. As dendritic building blocks we chose the Newkome-type dendrons of second and third generation **17**–**18**[16] for which we developed a convergent synthesis.[17] These amide-like dendrons can easily be deprotected to give the corresponding water-soluble representatives of **6**. As a consequence, the nature of dendritic environment can easily be altered and even amphiphilic architectures can be obtained. Possible aggregation to micelles in water can have an additional influence on the electronic properties. Introduction of cobalt as central metal of the porphyrin allows further redox chemistry and the coordination of versatile ligands. In this paper we focus on the synthesis and spectroscopic characterization of this new type of molecular architectures whereas the electrochemical and photochemical properties of these hybrids will be reported in a forthcoming contribution.

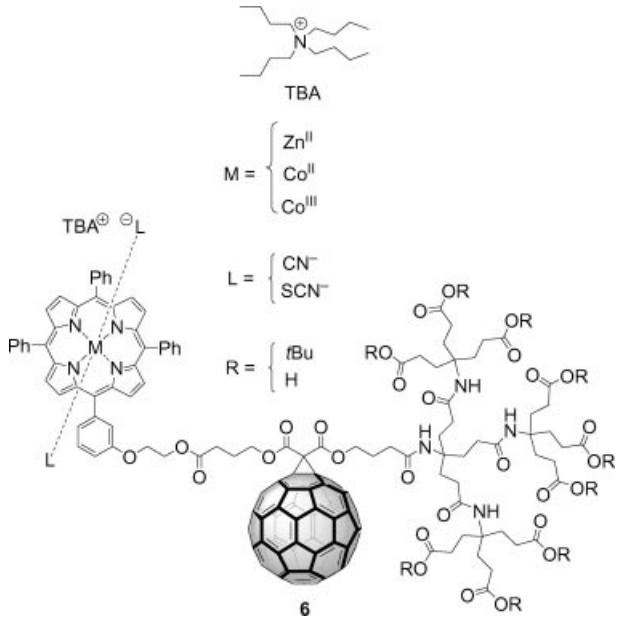


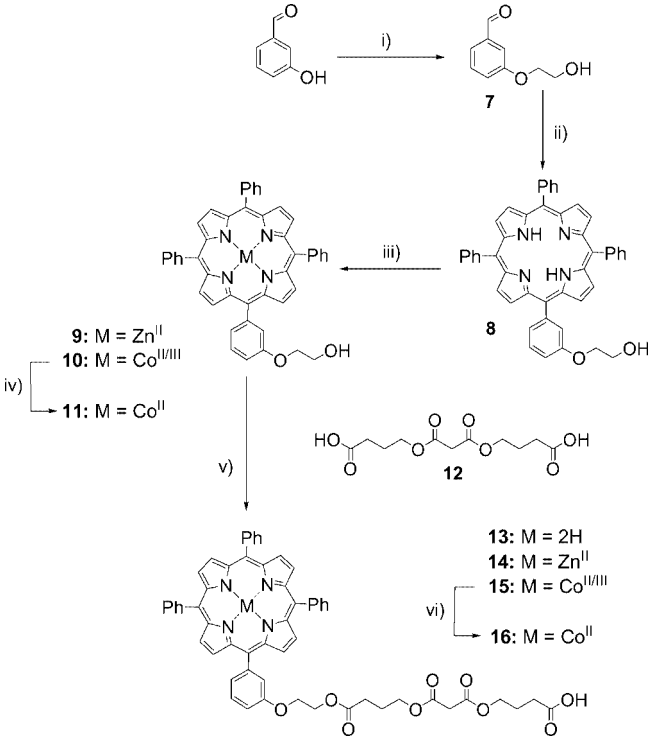

Figure 3. General representation of dendritic [60]fullerene–metallo-tetraphenylporphyrin diads (M = Zn, Co). The axial ligands ($CN^-$ and $SCN^-$) and the counterion ($TBA^+$) are involved in the corresponding $Co^{III}$ complexes.

## Results and Discussion

The free-base porphyrin **8** was chosen as suitable building block for terminating one malonate side chain. It was synthesized by the statistical condensation of 2 equiv. of pyrrole, 1 equiv. of benzaldehyde and 1 equiv. of 3-(2-hydroxyethoxy)benzaldehyde (**7**)[18] under high-dilution conditions followed by oxidation with excess DDQ as described by Lindsey[19] and co-workers (Scheme 1). It turned out that by using both aldehyds in equimolar quantities the yield of the desired A3B porphyrin **8** is significantly higher than using a 3:1 ratio. Purification of the product was accomplished by FC (silica; dichloromethane/ethyl acetate, 20:1) and precipitation in dry *n*-pentane. This method is well suited for the synthesis of unsymmetrically substituted porphyrins. As expected for a statistical reaction, lower and higher substituted derivatives (A4, A2B2 *trans*/*cis*, AB3, and B4) were obtained as well but only the monosubstituted free-base porphyrin **8** was used for the further synthesis. This intermediate represents also a useful precursor for the insertion of various metal atoms. Porphyrin **8** was metalated using an excess of zinc acetate or cobalt acetate in refluxing THF. In both cases the yields were almost quanti-

tative (Scheme 1). In the case of the metalation of **8** with cobalt acetate, a mixture of (porphyrinato)Co complexes **10** with Co in the oxidation states of +II and +III was obtained. This is a typical phenomenon which is commonly observed during the formation of (porphyrinato)Co complexes.[15] In order to obtain a clean sample of **11** with $Co^{II}$ exclusively, the mixture of **10** was allowed to react with a saturated aqueous solution of $Na_2S_2O_4$. Compounds **8**, **9** and **11** were completely characterized by $^1H$ NMR (Figure 4), $^{13}C$ NMR, UV/Vis, IR spectroscopy, mass spectrometry, and elemental analysis. After metalation of the free-base porphyrin **8** with cobalt or zinc, the resonance of the pyrrolic protons 21-H and 23-H in the $^1H$ NMR spectrum vanishes completely. Due to the paramagnetism of the $d^7$ cobalt(II) metal atom, the characterisation by NMR spectroscopy was, however, complicated. Compared to **8** the signals in the $^1H$ NMR spectra are downfield-shifted and broadened, most markedly those peaks corresponding to proton resonances nearest to the metal center. Nevertheless, with the help of HETCOR spectroscopy each resonance could be unambiguously assigned.




Scheme 1. Synthesis of the unsymmetrical malonates **13**–**16**. i: NaOH, chloroethanol, $H_2O$, 56%; ii: pyrrole, benzaldehyde, TFA, $Et_3N$, DDQ, $CH_2Cl_2$, 12%; iii: $Zn(OAc)_2{\cdot}2H_2O/Co(OAc)_2{\cdot}4H_2O$, THF, 90–99%; iv: $Na_2S_2O_4$, 99%; v: DMAP, DCC, $CH_2Cl_2$, 36–43%; vi: $Na_2S_2O_4$, 99%.

For the attachment to a malonate building block, we used the carboxy-terminated precursor molecule **12**, whose synthesis and crystallographic properties we described recently.[20] One of the most difficult steps was the synthesis and purification of the unsymmetrical malonates **13**–**16**. All three malonates were generated by a statistical DCC/DMAP coupling with compound **12** in dry dichloromethane under nitrogen (Scheme 1) and purified by FC using a short silica column. The by-products and the DCU eluted as the first fractions with dichloromethane/ethyl acetate as eluent in a ratio of 1:1. The remaining polar products **13**–**15** were then eluted with methanol and precipitated in dry *n*-pentane in order to remove the remaining contamination with by-products. Here again, instead of a clean initial formation of **16**, a mixture containing the Co centers in both oxidation states +II and +III was obtained. Subsequent treatment of **15** with $Na_2S_2O_4$ led to the quantitative conversion into the cobalt(II) derivative **16**. The purple-red products **13**, **14** and **16** were finally obtained in acceptable yields of 36–43% and were fully characterized by $^1H$ NMR, $^{13}C$ NMR, UV/Vis, IR spectroscopy, mass spectrometry, and elemental analysis.

In the next step, the second- and third-generation Newkome-type dendrons **17** and **18** were coupled with **8**–**10** under DCC/HOBt conditions in THF (Scheme 2). Contrary to the procedure outlined in Scheme 1, this coupling reaction was achieved with HOBt as an additive. For this purpose, the dendrons **17** and **18** were dissolved in dry THF together with **13**–**15**. After cooling, HOBt and DCC were added subsequently. In order to remove by-products, the metalloporphyrin–dendrimer adducts **19**–**21** were purified by FC (silica; dichloromethane/ethyl acetate, 1:1) and precipitated in dry *n*-pentane. The products **19**–**22** were obtained in yields of 24–26%, whereas the product **23** was furnished with 8% only. Scheme 2 shows the entire reaction sequence for the second- and third-generation metalloporphyrin–dendrimer adducts **19**–**23**. In the case of the Co complexes, subsequent treatment with TBAC was required to obtain a clean sample of the $Co^{III}$ complex **22**.

Taking into account that the amino function of the bulky third-generation dendrimer is sterically hindered, the 8% yield of **23** is quite satisfactory. Using an excess of **17** and **18** is not recommended, because in this case the $^1H$ NMR spectra show resonances of the dendrons **17** and **18** which are coordinated to the metal atom of the porphyrin through their amino termini. This effect is especially pronounced when the second-generation dendrimer **17** is used. The synthesis of the $C_{60}$ monoadducts **24**–**27** was performed by applying a modified Bingel[21] reaction (Scheme 3). It was not possible to obtain a $C_{60}$ monoadduct of compound **23**, because of the bulkiness of the third-generation dendron **18**. In order to optimize the yields of the corresponding second-generation systems **24**–**27**, an excess of $C_{60}$ was allowed to react with the malonates. Unreacted $C_{60}$ can easily be recovered by FC on silica with toluene. For this purpose, $C_{60}$, iodine and the compounds **20**–**21** were dissolved in dry toluene. DBU was diluted in toluene and added dropwise. The resulting $C_{60}$ monoadducts **24** and **25** were then purified by FC (silica; dichloromethane/ethyl acetate, 1:1), and in this case again by subsequent precipitation with *n*-pentane. Both monoadducts were fully characterized by $^1H$ NMR, $^{13}C$ NMR, UV/Vis, IR spectroscopy, mass spectrometry, and elemental analysis. The electronic absorption spectra clearly show the presence of the fullerene core with the characteristic bands at 257 and 329 nm due to $^1T_{1u}$–$^1A_g$

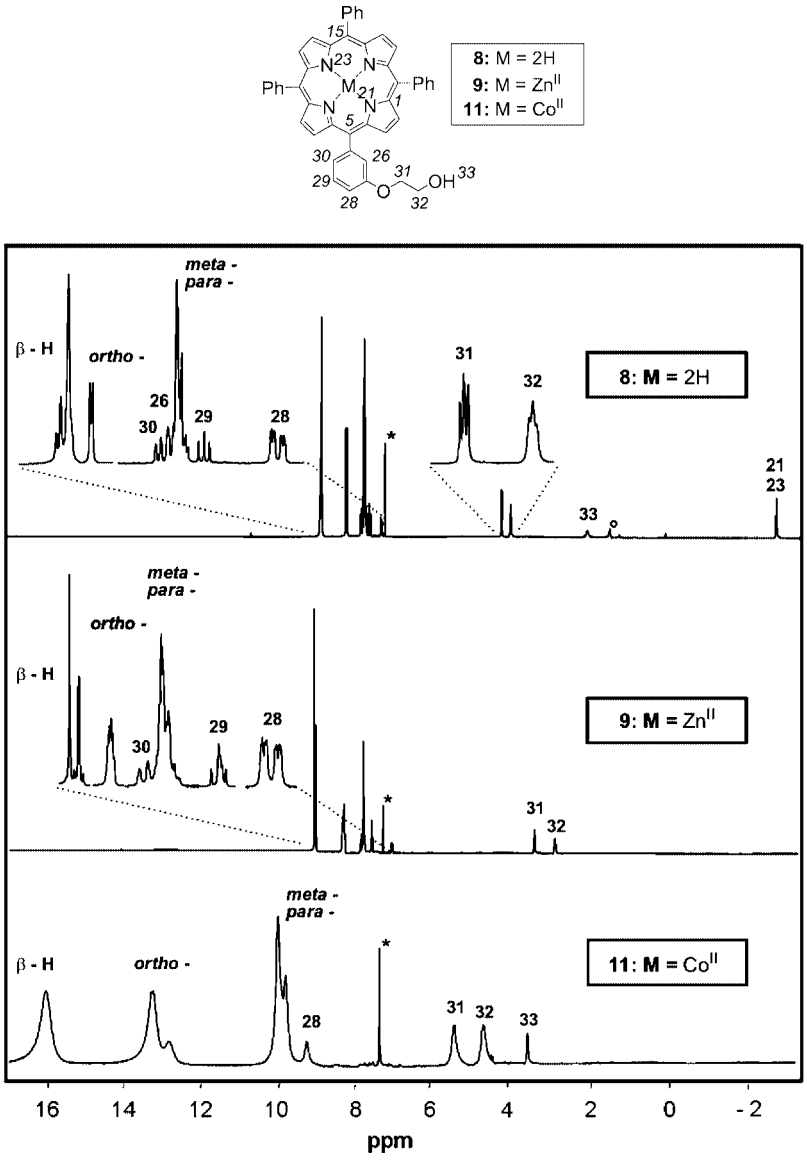
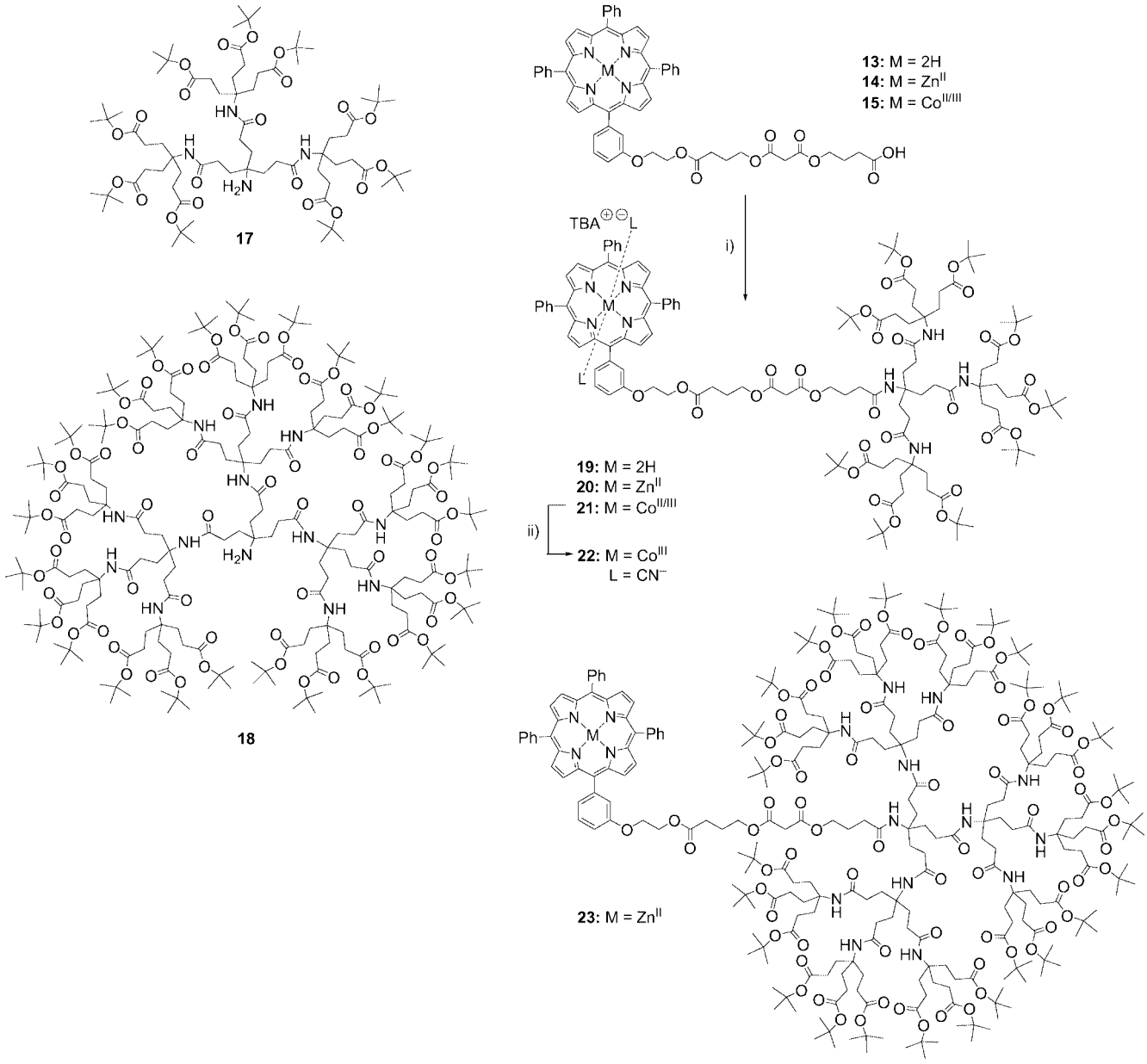



Figure 4. $^1$H NMR spectra (300 MHz, room temp., $CDCl_3$) of the porphyrins **8**, **9**, and **11** (* and ° denote $CHCl_3$ and $H_2O$, respectively, phenyl protons marked as *ortho*, *meta*, and *para*).

transitions (Figure 5). The close proximity of the [60]fullerene and porphyrin π-systems leads to a red shift of the Soret and Q-band transitions of the porphyrin. As already pointed out during the description of the (porphyrinato)Co precursors, the Co-containing diad **25** was formed as a $Co^{II/III}$ mixture. This can be seen, for example, in the UV/Vis spectrum which shows an asymmetrical Soret band with low extinction coefficients, compared to the Zn complex **24** (Figure 5).[15] The $^{13}$C NMR spectra of compounds **24**, **26**, and **27a**–**b** show the characteristic resonances of the [60]-fullerene $sp^2$- and $sp^3$-carbon atoms and the typical resonances of the carbon atoms of the porphyrin moiety. The adducts have a local $C_{2v}$ symmetry of the fullerene core which causes the appearance of 16 resonances only for the [60]fullerene $sp^2$-carbon atoms in the range between $\delta$ = 140 and 145 ppm. The lack of the malonate proton signal in the $^1$H NMR spectrum is an evidence for the successful Bingel[21] reaction as well. The electronic influence of the [60]fullerene core in the UV spectra is also very evident (Figure 5). It is obvious that the absorbance of the $Co^{II/III}$ mixture **25** is much weaker than that of the zinc derivative. This behaviour is in agreement with that of related compounds reported in the literature.[15]

However, using the mixture **25** as starting material allows for the clean formation of either pure $Co^{II}$ or $Co^{III}$ complexes (Scheme 3). The reduction of **25** with a saturated aqueous $Na_2S_2O_4$ solution leads to the paramagnetic cobalt(II) diad **26**. On the other hand, the oxidation of **25** with $O_2$ (air) in the presence of strongly coordinating axial ligands leads to the diamagnetic cobalt(III) diad **27**. As strongly coordinating ligands facilitating the clean oxidation reaction leading to **27a**–**b** we used cyanide and rhodanide. The binding of $CN^-$ and $SCN^-$ is reflected, for example, by the resonance of the cyanide ligand at $\delta$ = 118 ppm

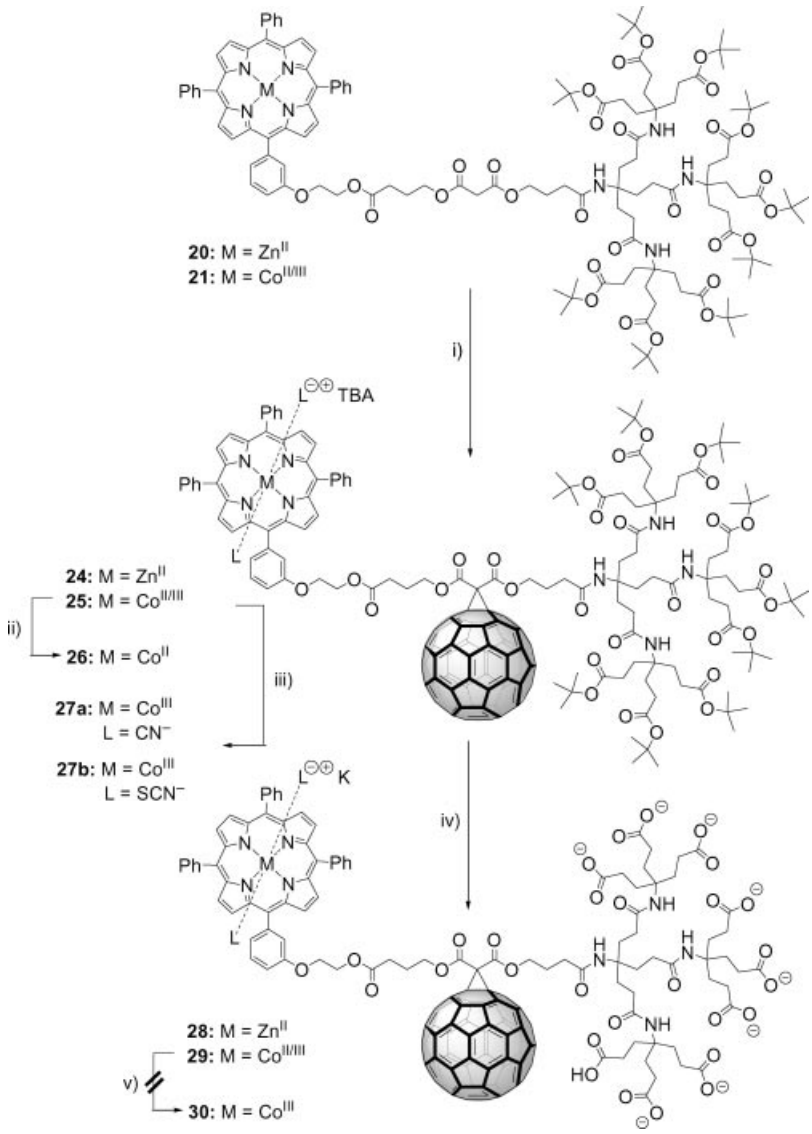



Scheme 2. Synthesis of the unsymmetrical malonates **19**–**23**. i: DCC, HOBt, $CH_2Cl_2$, **17** or **18**, 8–28%; ii: $O_2$, TBAC.

and by the $CN^-$ and $SCN^-$ valence frequencies in the IR spectra at 2167 $cm^{-1}$ and 2057 $cm^{-1}$, respectively. The influence of the two ligands on the electronical behavior of the porphyrin moiety is very pronounced and causes a significant red shift of more than 8 nm (Figure 5). The transformation of **25** into **27** can be monitored by UV/Vis spectroscopy as shown in Figure 5 where the corresponding absorption spectra are synoptically depicted. It can be observed that the Soret bands of the cobalt(III) diads **27a** and **27b** become much sharper after oxidation, whereas the Soret band of the reduced diad **26** is shifted hypsochromically. These results are well known and in strong agreement with already reported model systems.[4,15]

As already mentioned, the dendrons **24** and **25** can be easily deprotected by acid treatment leading to the formation of the highly water-soluble diads **28** and **29** which carry 8 negative charges in a physiological solution at pH = 7 as determined by a titration study. In order to obtain such water-soluble systems, **24** and **25** were stirred with an excess of formic acid over a period of 2 d (Scheme 3). The formic acid was then evaporated and the red-brown solid was dissolved in pure $H_2O$ with the help of $K_2CO_3$ added in traces. The whole mixture was then heated overnight at 40 °C. After evaporation of the $H_2O$ and drying in vacuo, the $^1H$ NMR spectrum recorded in buffered $D_2O$ showed that the *tert*-butyl proton resonances of the protected dendritic branch had disappeared. Due to the aggregation, the signals in the NMR spectra of the deprotected diads **28** and **29** are broadened. This line broadening of $^1H$ NMR signals was also observed in a number of dendritic amphiphiles that we studied previously.[22–25] Some of them led to first examples of shape-persistent micelles. Their structure could be deter-




Scheme 3. Synthesis of the dendritic [60]fullerene–porphyrin diads **24**–**29**. i: iodine, DBU, $C_{60}$, toluene, 35–28%; ii: $Na_2S_2O_4$, 99%; iii: $O_2$, TBAC/TBAR; iv: HCOOH, 99%; v: $O_2$, KCN.

mined with molecular accuracy by a systematic analysis of cryo-TEM images.[23–24] The overall 8 negative charges in the case of the second-generation and 27 negative charges in the case of the third-generation deprotected dendrimer give rise to strong repulsions of the individual branches. This fact was confirmed with semiempirical and molecular-dynamic calculations.[25] DOSY NMR measurements show that diad **28** forms micellar aggregates with an average diameter of approximately 7 nm in a buffered $D_2O$ solution (pH = 7.2).

## Conclusions

The development of unsymmetrical malonates which are terminated by a metallo-tetraphenylporphyrin (M = Zn, Co) and by a Newkome-type amide dendron was accomplished in order to synthesize a new type of porphyrin–fulleren–dendrimer hybrid of the general formula **6**. These architectures represent molecular donor–acceptor diads whose properties can be modified by the nature of the dendritic attachment and by the choice of the central metal of the porphyrin moiety including its oxidation state. Oxidation of the central Co atom from the oxidation state of +II to +III with oxygen from air is facilitated by the simultaneous axial coordination of $CN^–$ and $SCN^–$ leading to the complexes **27**. Whereas diads **24**–**27** with *tert*-butyl-protected dendritic termini are very soluble in organic solvents, the corresponding free nonaacids **28** and **29** are very soluble in neutral water. Under these conditions, micelles with a diameter of approximately 7 nm are formed as demonstrated by DOSY-NMR spectroscopy. The determination of the electronic and photophysical properties of such diads and the corresponding dependence on the nature of the dendron, the aggregation properties and the solvent is currently underway and will be reported in due course.

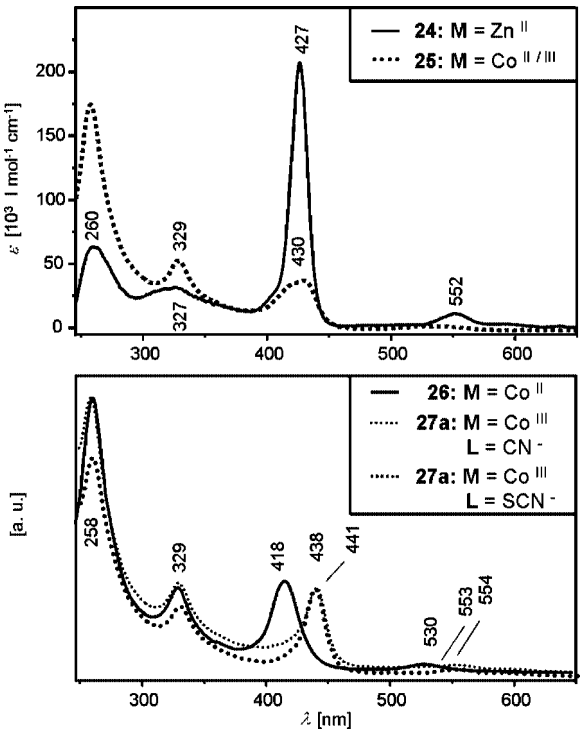



Figure 5. UV/Vis ($CH_2Cl_2$) spectra of the oxidized and stabilized cobalt(III) diads **27a**–**b** (counterion: $TBA^+$) and the reduced cobalt(II) diad **26** compared with the precursor diad **25** and the zinc(II) diad **24**.

## Experimental Section

**General Remarks:** Chemicals: $C_{60}$ was obtained from Hoechst AG/Aventis and separated from higher fullerenes by a plug filtration.[26] All analytical reagent-grade solvents were purified by distillation. Dry solvents were prepared using customary literature procedures.[27] Thin layer chromatography (TLC): Riedel–de Haën silica gel $F_{254}$ and Merck silica gel 60 $F_{254}$. Detection: UV lamp and iodine chamber. Preparative thin layer chromatography (PTLC): Merck PLC plates 20×20 cm; silica gel 60 $F_{254}$, 2 mm. Flash chromatography (FC): Merck silica gel 60 (230–400 mesh, 0.04–0.063 nm). Analytical high performance liquid chromatography (HPLC): Shimadzu Liquid Chromatograph LC-10 with Bus modul CBM-10A, auto injector SIL-10A, two pumps LC-10AT, diode array detector. The HPLC-grade solvents were purchased from SDS or Acros Organics; analytical column Nucleosil 5 μm, 200×4 mm, Macherey–Nagel, Düren. Preparative high performance liquid chromatography (HPLC): Shimadzu Class LC 10 with Bus module CBM-10A, auto injector SIL-10A, two pumps LC-8A, UV detector SPD-10A, fraction collector FRC-10A. Solvents were purified by distillation prior to use. IR spectroscopy: Bruker FT-IR Vector 22, KBr pellets, $\tilde{\nu}$ values in $cm^{-1}$. UV/Vis spectroscopy: Shimadzu UV-3102 PC UV/Vis/NIR scanning spectrophotometer; absorption maxima $\lambda_{max}$ are given in nm. Mass spectrometry: Micromass Zabspec, FAB (LSIMS) mode, matrix 3-nitrobenzyl alcohol. NMR spectroscopy: JEOL JNM EX 400 and JEOL JNM GX 400 and Bruker Avance 300. The chemical shifts are given in ppm relative to TMS. The resonance multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet), non-resolved and broad resonances as br. Elemental analysis (C, H, N): Succeeded by combustion and gas chromatographical analysis with an EA 1110 CHNS analyser (CE Instruments). 3-(2-Hydroxyethoxy)-benzaldehyde (**7**),[18] compounds **8**, **9** and **10**,[19] and spacer **12**[20] were synthesized according to literature procedures.

**{5-[3-(2-Hydroxyethoxy)phenyl]-10,15,20-triphenylporphyrinato}-cobalt(II) (11):** The synthesis was performed according to a literature procedure.[19] The obtained crude product was afterwards washed with a saturated aqueous $Na_2S_2O_4$ solution, the concentrated organic phases were concentrated and dried in vacuo to obtain the $Co^{II}$ complex exclusively in quantitative yield. $^1H$ NMR (400 MHz, room temp., $CDCl_3$): $\delta$ = 3.36 (br., 1 H), 4.20–4.80 (br., 2 H), 5.00–5.70 (br., 2 H), 8.70 –9.40 (br., 1 H), 9.43–10.30 (br., 11 H), 12.20–13.80 (br., 8 H), 15.10–16.70 (br., 8 H) ppm. $^{13}C$ NMR (100.4 MHz, room temp., $CDCl_3$): $\delta$ = 62, 71 (2 C), 98 (1 C), 117 (4 C), 129–131 (8 C), 138–145 (7 C), 156 (1 C) ppm. IR (film/KBr): $\tilde{\nu}$ = 1598, 1579, 1540, 1490, 1444, 1351, 1309, 1285, 1254, 1193, 1073, 1004, 953, 884, 795, 748, 699, 671 $cm^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log $\varepsilon$) = 266 (4.32), 410 (5.38), 528 (4.12) nm. MS (FAB, NBA): *m*/*z* = 731 $[M]^+$. $C_{46}H_{32}CoN_4O_2$ (731.01): calcd. C 75.51, H 4.41, N 7.66; found C 75.31 H 4.45 N 7.61.

**5-(3-{2-[(4-{[3-(3-Carboxypropoxy)-3-oxopropanoyl]oxy}butanoyl)-oxy]ethoxy}phenyl)-10,15,20-triphenylporphyrin (13):** The coupling of the ester bonds was achieved by activation of the carboxy group with DCC and DMAP. Compounds **8** (810 mg, 1.2 mmol) and **12** (995 mg, 3.6 mmol) were dissolved in dry degassed dichloromethane (300 mL) under nitrogen. After cooling to 0 °C, DMAP (159 mg, 1.3 mmol) was added. Afterwards, a solution of DCC (268 mg, 1.3 mmol) in dried dichloromethane (300 mL) was added dropwise. The solution was then stirred at room temp. for 24 h. TLC control showed a conversion of the starting material. The precipitating DCU by-product was filtered off. After evaporation of the solvent, FC (silica; dichloromethane/ethyl acetate/triethylamine, 10:1:0.5), precipitation in dry *n*-pentane and drying in vacuo, the desired porphyrin–malonate **13** (404 mg) was obtained as a red solid in 46% yield. $^1H$ NMR (400 MHz, room temp., $CDCl_3$): $\delta$ = –2.80 (br., 2 H), 1.89–2.01 (m, 4 H), 2.33–2.50 (m, 4 H), 3.31 (s, 2 H), 4.11–4.24 (m, 4 H), 4.37 (t, $^3J$ = 4.2 Hz, 2 H), 4.52 (t, $^3J$ = 4.2 Hz, 2 H), 7.33–7.87 (m, 13 H), 8.22 (m, 6 H), 8.21–8.23 (m, 8 H) ppm. $^{13}C$ NMR (100.4 MHz, room temp., $CDCl_3$): $\delta$ = 23.94, 25.01, 25.68 (3 C), 33.88 (1 C), 41.51 (1 C), 63.20, 64.58, 66.26 (3 C), 126.85 (7 C), 127.78, 127.89 (4 C), 131.04–133.05 (8 C), 134.70 (8 C), 143.76 (4 C), 166.50 (1 C), 172.95 (2 C) ppm. IR (film/KBr): $\tilde{\nu}$ = 2160, 2025, 1729, 1701, 1594, 1482, 1438, 1409, 1336, 1279, 1249, 1154, 1061, 992, 764, 757, 721, 662 $cm^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log $\varepsilon$) = 400 (sh, 4.44), 418 (5.57), 515 (4.10), 549, 589, 645 nm. MS (FAB, NBA): *m*/*z* = 957 $[M+Na]^+$, 933 $[M]^+$, 871, 847, 656, 629. $C_{57}H_{48}N_4O_9 \cdot NEt_3 \cdot CH_2Cl_2$ (933.01): calcd. C 68.69, H 5.85, N 6.26; found C 69.51 H 5.73 N 6.15.

**[5-(3-{2-[(4-{[3-(3-Carboxypropoxy)-3-oxopropanoyl]oxy}butanoyl)-oxy]ethoxy}phenyl)-10,15,20-triphenylporphyrinato]zinc(II) (14):** Compounds **9** (650 mg, 0.88 mmol) and **12** (730 mg, 2.64 mmol) were dissolved in dry degassed dichloromethane (200 mL) under nitrogen. After cooling to 0 °C, DMAP (129 mg, 1.06 mmol) was added. Afterwards, a solution of DCC (218 mg, 1.06 mmol) in dry dichloromethane (200 mL) was added dropwise. The solution was then stirred at room temp. for 24 h. TLC control showed a conversion of the starting material. The precipitating DCU by-product was filtered off. After concentration, FC (silica; dichloromethane/ethyl acetate, 9:1) and precipitation in dry *n*-pentane, the desired porphyrin–malonate **14** (278 mg) was obtained as a purple red solid in 43% yield. $^1H$ NMR (400 MHz, room temp., $CDCl_3$): $\delta$ = 1.43–1.78 (m, 4 H), 2.97 (m, 4 H), 3.24 (s, 2 H), 3.93 (m, 4 H), 4.20 (t, $^3J$ = 4.2 Hz, 2 H), 4.29 (t, $^3J$ = 4.2 Hz, 2 H), 6.75–6.93 (m, 11 H), 8.10 (m, 6 H), 8.33–8.52 (m, 8 H) ppm. $^{13}C$ NMR (100.4 MHz,

room temp., $CDCl_3$): $\delta$ = 24.04, 25.17, 25.86 (3 C), 33.91 (1 C), 41.47 (1 C), 63.98, 64.67 (3 C), 126.83 (7 C), 127.75 (4 C), 132.11, 132.28 (8 C), 134.85 (8 C), 143.44 (4 C), 150.51 (8 C), 166.70 (1 C), 173.83 (2 C) ppm. IR (film/KBr): $\tilde{\nu}$ = 2162, 2023, 1733, 1706, 1594, 1575, 1482, 1440, 1409, 1336, 1274, 1251, 1154, 1069, 996, 957, 765, 753, 718, 660 $cm^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\log\varepsilon$) = 400 (sh, 4.53), 419 (5.63), 547 (4.23) nm. MS (FAB, NBA): *m*/*z* = 994 $[M]^+$. $C_{57}H_{46}N_4O_9Zn$·EtOAc (994.26): calcd. C 67.56 H 5.02 N 5.17; found C 67.69 H 5.09 N 5.08.

**[5-(3-{2-[(4-{[3-(3-Carboxypropoxy)-3-oxopropanoyl]oxy}butanoyl)-oxy]ethoxy}phenyl)-10,15,20-triphenylporphyrinato]cobalt(II) (16):** Compounds **10** (650 mg, 0.88 mmol) and **12** (738 mg, 2.67 mmol) were dissolved in dry degassed dichloromethane (200 mL) under nitrogen. After cooling to 0 °C, DMAP (129 mg, 1.06 mmol) was added. Afterwards, a solution of DCC (218 mg, 1.06 mmol) in dried dichloromethane (200 mL) was added dropwise. The solution was then stirred at room temp. for 24 h. TLC control showed a conversion of the starting material. The precipitating DCU by-product was filtered off. The FC purification was carried out with silica and dichloromethane/ethyl acetate, 1:1. The organic phases were washed with a saturated aqueous $Na_2S_2O_4$ solution to obtain the desired cobalt(II) complex **16**. After concentration of the organic phases, the product (313 mg) was obtained as a red solid in 36% yield. $^1$H NMR (400 MHz, room temp., $CDCl_3$): $\delta$ = 0.14 (br.), 0.91 (br.), 1.29 (br., 2 H), 1.48 (br., 2 H), 1.63 (br., 2 H), 2.26 (br., 2 H), 3.63 (br., 4 H), 4.66 (br., 2 H), 5.44 (br., 2 H), 8.55–10.41 (br., 11 H), 11.90–13.64 (br., 8 H), 14.83–16.75 (br., 8 H) ppm. $^{13}$C NMR (100.4 MHz, room temp., $CDCl_3$): $\delta$ = 24.87, 25.63, 26.66, 34.45, 67.67, 98.40, 130.36, 130.78, 141.33, 156.64, 158.04, 207.90 ppm. IR (KBr): $\tilde{\nu}$ = 2382, 2222, 1725, 1695, 1613, 1227, 1065, 1065, 1007, 950, 795, 765, 752, 637 $cm^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\log\varepsilon$) = 268 (4.45), 411 (4.51), 529 (4.01) nm. MS (FAB, NBA): *m*/*z* = 1012 $[M + Na]^+$, 989 $[M]^+$. $C_{57}H_{46}N_4O_9Co$·EtOAc·$CH_2Cl_2$ (989.93): calcd. C 64.03 H 4.85 N 4.82; found C 64.23 H 5.11 N 5.01.

**General Procedure for the Formation of Porphyrin–Dendrimer Adducts by DCC/HOBt Coupling (GP1):** Contrary to the synthesis of compound **14**–**16**, the coupling of the amide bond was achieved by activation of the carboxy group with DCC and HOBt as additive. The dendrons **17** and **18** (1.2 equiv.) were dissolved with **13**–**15** (1 equiv.) under nitrogen in dry THF. The mixture was then cooled by an ice bath. HOBt (1.2 equiv.) and DCC (1.2 equiv.) were added subsequently. The solution was then stirred at room temp. for 48 h. The complete reaction was monitored by TLC. DCU was precipitated in cooled ethyl acetate and was afterwards filtered off. After evaporation of the solvent, the product was purified by FC (silica; dichloromethane/ethyl acetate, 1:1). In order to remove by-products, the metalloporphyrin–dendrimer adducts **19**–**21** were precipitated in dry *n*-pentane.

**Porphyrin–Dendrimer Adduct 19:** Compounds **13** (322 mg, 0.35 mmol) and **17** (325 mg, 0.23 mmol), DCC (52 mg, 0.25 mmol) and HOBt (34 mg, 0.25 mmol) were added to dry THF (150 mL). According to GP1, the reaction mixture was then purified. The product (152 mg) was obtained as purple red solid in 28% yield. $^1$H NMR (400 MHz, room temp., $CDCl_3$): $\delta$ = –2.84 (br., 2 H), 1.43 (s, 81 H), 1.86–2.27 (m, 56 H), 3.48 (s, 2 H), 4.23 (m, 4 H), 4.39 (t, $^3J$ = 4.2 Hz, 2 H), 4.55 (t, $^3J$ = 4.2 Hz, 2 H), 6.07 (br., 3 H), 7.35–8.24 (m, 19 H), 8.58–8.90 (m, 8 H) ppm. $^{13}$C NMR (100.4 MHz, room temp., $CDCl_3$): $\delta$ = 21.40, 24.16, 24.70 (3 C), 28.20, 28.40, 28.59, 28.69, 30.07, 30.82 (27 C), 31.84, 31.90, 32.99 (24 C), 57.71 (1 C), 66.39 (3 C), 80.65, 80.85 (9 C), 126.81 (6 C), 127.96, 128.06, 128.46 (3 C), 131.40 (8 C), 134.87 (8 C), 143.91 (4 C), 167.13, 167.24 (2 C), 171.50, 172.04 (12 C), 173.03, 173.11 (2 C) ppm. IR (film/KBr): $\tilde{\nu}$ = 3270, 2060, 1727, 1680, 1515, 1365, 1333, 1290, 1146, 1093, 994, 952, 847, 795, 756, 751, 691, 636 $cm^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\log\varepsilon$) = 400 (sh, 3.90), 417 (5.40), 514 (3.61), 546 (3.30), 589 (3.11), 645 (2.95). MS (FAB, NBA): *m*/*z* = 2354 $[M]^+$. $C_{133}H_{180}N_8O_{29}$·EtOAc (2354.89): calcd. C 67.35 H 7.76 N 4.59; found C 66.93 H 7.69 N 4.41.

**Zinc(II)-porphyrin–Dendrimer Adduct 20:** Compounds **14** (330 mg, 0.33 mmol) and **17** (575 mg, 0.40 mmol), DCC (75 mg, 0.37 mmol) and HOBt (49 mg, 0.37 mmol) were added to dry THF (150 mL). According to GP1, the reaction mixture was then purified. The product (207 mg) was furnished as a purple red solid in 26% yield. $^1$H NMR (400 MHz, room temp., $CDCl_3$): $\delta$ = 1.31 (s, 81 H), 1.43–2.19 (m, 56 H), 3.24 (s, 2 H), 3.84–4.48 (m, 8 H), 6.09 (s, 4 H), 7.49–8.21 (m, 19 H), 8.68–8.97 (m, 8 H) ppm. $^{13}$C NMR (100.4 MHz, room temp., $CDCl_3$): $\delta$ = 22.77, 22.83, 23.83 (3 C), 27.04, 27.07, 28.07, 28.44, 28.63, 28.77 (27 C), 32.69 (24 C), 56.30 (1 C), 66.55 (3 C), 79.62 (9 C), 126.74 (6 C), 127.42 (3 C), 131.08 (8 C), 134.35 (8 C), 140.24 (4 C), 171.58 (2 C), 171.69, 171.78 (12 C), 172.91 (2 C) ppm. IR (film/KBr): $\tilde{\nu}$ = 3277, 3239, 1725, 1648, 1509, 1366, 1316, 1251, 1146, 1096, 992, 845, 795, 752, 698, 636, 591 $cm^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\log\varepsilon$) = 400 (sh, 3.95), 425 (5.47), 554 (3.30), 598 (3.11) nm. MS (FAB, NBA): *m*/*z* = 2417 $[M]^+$. $C_{133}H_{178}N_8O_{29}Zn$ (2418.26): calcd. C 66.06 H 7.42 N 4.63; found C 65.89 H 7.65 N 4.45.

**Cobalt(III)-porphyrin–Dendrimer Adduct 22:** Compounds **15** (450 mg, 0.46 mmol) and **17** (680 mg, 0.50 mmol), DCC (103 mg, 0.50 mmol), and HOBt (67 mg, 0.50 mmol) were added to dry THF (200 mL). The reaction mixture was then further treated and purified according to GP1. To obtain the cobalt(III) derivative, the purified compound was oxidized with $O_2$ (air) and stabilized with TBAC (see GP3). The yield could not be calculated and elemental analysis data could not be obtained because of the excess of the stabilizing reactant (TBAC), which could not be separated. The product was obtained as a red solid. $^1$H NMR (400 MHz, room temp., $CDCl_3$): $\delta$ = 0.87 (t, $^3J$ = 7.01 Hz, 4 H, TBAC), 1.23 (m, 8 H, TBAC), 1.39 (s, 81 H), 1.43–2.24 (m, 56 H), 3.36 (s, 2 H), 4.12–4.59 (m, 8 H), 6.08 (s, 4 H), 7.25–8.20 (m, 11 H), 8.66–9.07 (m, 8 H) ppm. $^{13}$C NMR (100.4 MHz, room temp., $CDCl_3$): $\delta$ = 24.89, 25.57 (3 C), 28.07, 28.11, 29.71 (27 C), 31.56, 33.85 (24 C), 57.42 (1 C), 80.55 (9 C), 126.23, 127.12 (9 C), 131.80–132.20 (8 C), 134.12–134.62 (8 C), 171.69, 172.66 (14 C) ppm. IR (film/KBr): $\tilde{\nu}$ = 2980, 2162, 1729, 1683, 1656, 1529, 1455, 1393, 1366, 1297, 1251, 1154, 1100, 1069, 996, 957, 849, 795, 752, 756, 702, 683, 660 $cm^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\log\varepsilon$) = 260 (4.91), 326 (4.66), 402 (sh, 4.60), 427 (5.34), 551 (4.40) nm. MS (FAB, NBA): *m*/*z* = 2424 $[M+Na]^+$, 2411 $[M]^+$, 2355 $[M-t\text{Bu}]^+$, 2325, 2281, 2194.

**Zinc(II)-porphyrin–Dendrimer Adduct 23:** Compounds **14** (49.7 mg, 50 μmol) and **18** (226 mg, 50.1 μmol), DCC (1.25 mg, 6.1 μmol), and HOBt (0.8 mg, 6.1 μmol) were added to dry THF (20 mL). According to GP1, the reaction mixture was then treated and purified. The product (22 mg) was obtained as a purple red solid in 8% yield. $^1$H NMR (500 MHz, room temp., $CDCl_3$): $\delta$ = 1.33 (s, 243 H), 1.72–2.19 (m, 148 H), 3.38 (s, 2 H), 3.85–4.58 (m, 8 H), 6.23 (br., 9 H), 6.62 (br., 4 H), 7.29–7.83 (m, 11 H), 8.18–8.24 (m, 8 H), 8.79–8.93 (m, 8 H) ppm. $^{13}$C NMR (100.4 MHz, room temp., $CDCl_3$): $\delta$ = 23.85, 24.39, 24.89, 25.57 (4 C), 27.34, 27.87, 28.99, 28.05 (27 C), 30.29, 30.45, 31.00, 31.39, 33.85 (24 C), 57.30, 57.98 (13 C), 63.06, 64.62, 66.06 (3 C), 80.34 (27 C), 126.35, 127.23 (11 C), 131.69 (8 C), 134.50 (8 C), 143.28 (4 C), 167.19 (1 C) 171.87, 172.66, 172.69 (41 C), 172.84, 173.06 (2 C) ppm. IR (film/KBr): $\tilde{\nu}$ = 2150, 1733, 1649, 1520, 1397, 1393, 1301, 1288, 1249, 1134, 1100,

1065, 994, 952, 847, 792, 750, 701, 660 $cm^{-1}$. UV/Vis($CH_2Cl_2$): $\lambda_{max}$ ($\log\varepsilon$) = 400 (sh, 3.30), 424 (5.23), 556 (2.21) nm. MS (FAB, NBA): *m/z* = 5514 $[M+Na]^+$, 5491 $[M^+]$, 5458, 5432, 5403, 5333, 5311. $C_{295}H_{457}N_{17}O_{74}Zn{\cdot}CH_2Cl_2$ (5491.24): calcd. C 63.76 H 8.30 N 4.27; found C 62.33 H 8.45 N 4.45.

**General Procedure for the Formation of $C_{60}$ Monoadducts (GP2):** The synthesis of monoadducts of $C_{60}$ was performed with a modified Bingel[21] reaction. In order to obtain higher yields of the desired monoadduct, an excess of $C_{60}$ was applied. The unreacted $C_{60}$ can be easily recovered by FC on silica with pure toluene. $C_{60}$ (1.9 up to 2.0 equiv.) was dissolved in dry toluene (ca. 0.5 mL of toluene per mg of $C_{60}$) resulting in a dark purple solution. Compounds **20**–**21** (1.0 equiv.) and iodine (1.1 equiv.) were added. DBU (1.1 equiv.) was diluted in toluene and added dropwise to the stirred solution at room temp. over a period of 1 up to 3 h. After 4 h of stirring, TLC control showed the remaining $C_{60}$, the monoadduct and traces of bis- and trisadducts. The resulting $C_{60}$ monoadduct was then purified by FC (silica; dichloromethane/ethyl acetate, 1:1) and precipitated in dry *n*-pentane.

**Zinc(II)-porphyrin–Dendrimer–[60]Fullerene Diad 24:** Compound **20** (750 mg, 0.31 mmol), $C_{60}$ (309 mg, 0.050 mmol), iodine (150 mg, 0.60 mmol), and DBU (95 μL, 0.60 mmol) were added under nitrogene to dry toluene (50 mL). The whole reaction procedure was carried out as previously noted in GP2. The hazelnut-brown product (370 mg) was furnished in 38% yield. $^1$H NMR (400 MHz, room temp., $CDCl_3$): $\delta$ = 1.34 (s, 81 H), 1.52–2.16 (m, 56 H), 4.22–4.48 (m, 8 H), 5.98 (s, 4 H), 7.25–8.33 (m, 19 H), 8.75–8.95 (m, 8 H) ppm. $^{13}$C NMR (100.4 MHz, room temp., $CDCl_3$): $\delta$ = 24.89, 25.57 (3 C), 28.07, 28.11, 29.71 (27 C), 31.56, 33.85 (24 C), 57.42 (1 C), 80.55 (9 C), 126.23, 127.12 (9 C), 131.80–132.20 (8 C), 134.12–134.62 (8 C), 140–145 (58 C, $C_{60}$ $sp^2$), 171.69, 172.66 (14 C) ppm. IR (film/KBr): $\tilde{\nu}$ = 2980, 2162, 1729, 1683, 1656, 1529, 1455, 1393, 1366, 1297, 1251, 1154, 1100, 1069, 996, 957, 849, 795, 752, 756, 702, 683, 660 $cm^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\log\varepsilon$) = 260 (4.91), 326 (4.66), 402 (sh, 4.60), 427 (5.34), 551 (4.40) nm. MS (FAB, NBA): *m/z* = 3135 $[M]^+$. $C_{193}H_{176}N_8O_{29}Zn$ (3133.86): calcd. C 73.90 H 5.66 N 3.57; found C 71.85 H 5.61 N 3.55.

**Cobalt(II)-porphyrin–Dendrimer–[60]Fullerene Diad 26:** Compound **21** (434 mg, 0.18 mmol), $C_{60}$ (86 mg, 0.34 mmol), and iodine (168 mg, 0.23 mmol) were added under nitrogen to dry toluene (50 mL). DBU (51 μL, 0.34 mmol) was diluted in dry toluene (10 mL) and added dropwise under nitrogen to the solution. The whole reaction procedure was carried out as in GP2 already noted. The product was then diluted in dichloromethane and washed with a saturated aqueous $Na_2S_2O_3$ solution to obtain the cobalt(II) compound only. The dark brown product (197 mg) was obtained in 35% yield. $^1$H NMR (400 MHz, room temp., $CDCl_3$): $\delta$ = 1.34 (s, 81 H), 1.37–2.39 (m, 56 H), 3.88–4.45 (m, 4 H), 4.50–4.78 (m, 4 H), 6.32 (br., 4 H), 6.57 (br., 4 H), 8.71–10.32 (br., 11 H), 11.34–12.88 (br., 8 H), 14.15–15.55 (br., 8 H) ppm. $^{13}$C NMR (100.4 MHz, room temp., $CDCl_3$): $\delta$ = 24.89, 24.58 (2 C), 28.02, 28.06, 29.77 (27 C), 31.51, 33.98 (24 C), 57.28 (1 C), 57.40 (3 C), 72.11 (2 C, $C_{60}$ $sp^3$), 80.54, 80.62 (9 C), 127.33, 129.01 (11 C), 130.05, 131.11 (8 C), 134.12–135.23 (8 C), 140–152 (58 C, $C_{60}$ $sp^2$), 154.03 (1 C), 156.78 (14 C), 172.77, 173.12 (2 C) ppm. IR (KBr): $\tilde{\nu}$ = 3312, 2976, 1729, 1679, 1660, 1536, 1455, 1428, 1390, 1366, 1309, 1243, 1150, 1100, 1007, 957, 919, 845, 799, 757, 703, 668, 637 $cm^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\log\varepsilon$) = 259 (5.21), 329 (4.74), 418 (4.96), 530 (3.99) nm. MS (FAB, NBA): *m/z* = 3129 $[M]^+$, 3073, 2978. $C_{193}H_{176}N_8O_{29}Co{\cdot}CH_2Cl_2{\cdot}H_2O$ (3233.28): calcd. C 72.06 H 5.61 N 3.47; found C 71.55 H 5.79 N 3.40.

**General Procedure for the Oxidation of 21 and 25 (GP3):** The (porphyrinato)cobalt(II/III) compounds **21** and **25** were oxidized with $O_2$ (air) and stabilized on the one hand with *n*-tetrabutylammonium cyanide (TBAC) and on the other hand with *n*-tetrabutylammonium rhodanide (TBAR). The (porphyrinato)$Co^{II/III}$ derivatives (1.0 equiv.) and either a surplus of *n*-tetrabutylammonium cyanide (1.5 equiv.) or *n*-tetrabutylammonium rhodanide (3.1 equiv.) were stirred in dry dichloromethane (50 mL) under an inert gas for 20 h. The solvent was then evaporated and the product was precipitated with dry *n*-pentane. The yields could not be calculated and elemental analysis data could not be obtained because of the excess of the stabilizing reactant, which could not be separated.

**Cobalt(III)-porphyrin–Dendrimer–[60]Fullerene Diad 27a:** Diad **25** (50 mg, 0.02 mmol) and TBAC (8.6 mg, 0.03 mmol) were added to dry dichloromethane (50 mL). The reaction mixture was then stirred overnight. According to GP3, the product was obtained as brown solid. $^1$H NMR (400 MHz, room temp., $CDCl_3$): $\delta$ = 0.88 (t, $^3J$ = 7.01 Hz, 4 H, TBAC), 1.25 (m, 8 H, TBAC), 1.39 (s, 81 H), 1.52–2.33 (m, 56 H), 4.19–4.62 (m, 8 H), 6.12 (s, 4 H), 7.31–8.46 (m, 19 H), 8.80–9.33 (m, 8 H) ppm. $^{13}$C NMR (100.4 MHz, room temp., $CDCl_3$): $\delta$ = 13.67 (4 C, TBAC), 19.68 (4 C, TBAC), 24.14, 25.89, 26.44 (3 C), 28.12, 28.19, 29.01 (27 C), 30.49, 31.32, 31.47 (24 C), 57.47 (1 C), 70.03, 70.13 (3 C), 71.36 (2 C, $C_{60}$ $sp^3$), 80.57 (9 C), 119.02 (2 C, $C_{CN}$), 127.39 (11 C), 133.25 (8 C), 140–147 (58 C, $C_{60}$ $sp^2$), 157.34 (1 C), 173.66 (14 C) ppm. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\log\varepsilon$) = 257 (5.20), 329 (4.78), 441 (4.65), 544 (4.02), 591(3.51) nm. IR (film/KBr): $\tilde{\nu}$ = 2966, 2946, 2933, 2167, 1590, 147, 1389, 1349, 1038, 1009, 864, 760, 668 $cm^{-1}$.

**Cobalt(III)-porphyrin–Dendrimer–[60]Fullerene Diad 27b:** Diad **25** (20 mg, 6.39 μmol) and TBAR (5.0 mg, 0.02 mmol) were added to dry dichloromethane (50 mL). The reaction mixture was then stirred overnight. According to GP4, the product was furnished as brown solid. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\log\varepsilon$) = 258 (4.88), 329 (4.39), 438 (4.49), 553 (3.48) nm. IR (film/KBr): $\tilde{\nu}$ = 3327, 2962, 2933, 2875, 2057, 1727, 1665, 1627, 1576, 1542, 1465, 1382, 1366, 1312, 1245, 1152, 1108, 1067, 1030, 1011, 928, 879, 849, 793, 735, 704 $cm^{-1}$.

**Water-Soluble Zinc(II)-porphyrin–Dendrimer–[60]Fullerene Diad 28:** Diad **24** (63 mg, 0.02 mmol) was dissolved in 99% formic acid and was stirred at room temp. for 20 h. The formic acid was then evaporated. Afterwards, the residue was dissolved in degassed water and treated with traces of potassium carbonate. The water was then evaporated. The product (50 mg) was obtained as purple-red solid in quantitative yield. $^1$H NMR (400 MHz, room temp., $D_2O$): $\delta$ = 1.52–2.53 (m, 56 H) ppm. MS (FAB, NBA): *m/z* = 2630 $[M]^+$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 426, 556 nm.

**Water-Soluble Cobalt(II/III)-porphyrin–Dendrimer–[60]fullerene Diad 29:** Diad **25** (30 mg, 9.58 μmol) was dissolved in 99% formic acid and was stirred at room temp. for 20 h. The acid was then evaporated. Afterwards, the residue was treated with traces of potassium carbonate in order to dissolve it in degassed water. A slight excess of potassium cyanide was added to oxidize and stabilize the cobalt(III) oxidation state. The water was then evaporated. The solid was obtained as brown-red solid in quantitative yield. $^1$H NMR (400 MHz, room temp., $CDCl_3$): $\delta$ = 1.53–2.61 (m, 56 H) ppm. UV/Vis($CH_2Cl_2$): $\lambda_{max}$ ($\log\varepsilon$) = 262 (5.17), 434 (4.94) nm.

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