Dendritic Metallophthalocyanines—Synthesis, Electrochemical Properties, and Catalytic Activities

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Abstract: A new class of sterically hindered dendritic phthalocyanines was synthesized to evaluate the effects of the dendritic structure on the electrochemical properties and catalytic activities. This dendritic phthalocyanine possesses a well-defined structure which has a nanosized, three-dimensional shape. The dendritic structure around the cobalt phthalocyanine prevented the molecular aggregation among phthalocyanine moieties in polar solvents and thin films. Electrochemical studies indicated that the electron-transfer process was hindered in the dendritic cobalt phthalocyanine. This is the result of a shielding effect by the dendrimer branch on the cobalt phthalocyanine core. Thiol oxidation catalyzed by the dendritic cobalt phthalocyanine was carried out in the presence of dioxygen. A high stability of the catalytic site was observed for the dendritic cobalt phthalocyanine.

Keywords: catalysis · cyclic voltammetry · dendrimers · metallodendrimers · phthalocyanines

Introduction

Dendrimers are well-defined, three-dimensional, and nanosized macromolecules constructed from an interior core with a regular array of branch units.[1] There has been considerable interest in the incorporation of functional units in the interior core or on the surface of the dendrimers as a method of generating new functional dendrimers. An attractive feature of dendrimers is the spatial control of functionalities, such as catalytic, photophysical, and electrochemical properties.[2] The construction of a dendrimer around a catalytic core may result in the steric protection of the catalytic site and a means to finely tune the catalytic activity and selectivity. Moore, Suslick, and their co-workers have reported shape-selective catalytic activity in porphyrin-based dendrimers.[3] Shortly afterwards, Mak and Chow reported dendritic effects on the reactivity and selectivity in the catalytic activity on a Diels–Alder reaction.[4] More recently, Crooks et al. have investigated the reaction control of dendrimer-encapsulated Pd and Pt nanoparticles; they indicated the importance of the size of the dendrimer on the reactivity and the stability of the catalyst.[5]

Phthalocyanines and their metal complexes display interesting catalytic, electronic, and optical properties.[6] We have studied the catalytic activities of metallophthalocyanines and polymer-supported catalysts for several reactions.[7] The catalytic activities of metallophthalocyanines were influenced by the aggregation among phthalocyanines which results from strong intermolecular cohesion. Therefore, the steric isolation of the phthalocyanine rings could enhance the catalytic activities of metallophthalocyanines. Recently, we have reported the first synthesis of a series of dendritic phthalocyanines and demonstrated the control of molecular aggregation among phthalocyanine moieties in aqueous media by the encapsulation with the dendritic structure.[8] McKeown et al. also synthesized dendritic phthalocyanines for optical applications.[9] Herein, we report the synthesis of dendritic phthalocyanines and their cobalt complexes, and dendritic effects on the electrochemical properties and catalytic behavior.

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Results and Discussion

Synthesis and characterization: A new dendritic phthalocyanine was synthesized by means of the methodology developed by Newkome et al. (Scheme 1, see page 3497).[10] The phthalocyanine precursor **1** was obtained from 2-methoxyphenol and methyl 4-bromobutanoate according to a reported procedure.[11] Metal-free phthalocyanine **2** was obtained from the

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reaction of the phthalonitrile **1** in hexan-1-ol at 140 °C in the presence of a strong organic base (1,8-diazabicyclo[5,4,0]undec-7-ene) (DBU). During the reaction, transesterification occurred and the hexyl ester derivative was formed. After hydrolysis, the reaction of the resulting tetraacid with Behera's amine produced the phthalocyanine core **4**. This phthalocyanine core was readily hydrolyzed with formic acid to give the hygroscopic compound **5**, which was treated with the branching unit **7**. The one-step preparation of the $(n+1)$th generation from the $(n-1)$th generation acid was developed by Kaifer et al. with the second-generation analogue of Behera's amine **7**.[12] The direct coupling reaction of **5** with **7** gave the second-generation dendrimer **6**, which was purified by column chromatography. The formation of dendrimer **6** was verified by ^{1}H NMR, UV/Vis, FT-IR, and matrix-assisted laser-desorption ionization time-of-flight (MALDI-TOF) mass spectrometry. The MALDI-TOF mass spectrum of **6** shows the molecular ion peak as a base peak at m/z 19016 (calcd 19010) and peaks corresponding to fragment ions that result from the successive loss of $NHC(CH_2CH_2COOC(CH_3)_3)_3$ moieties. The GPC chromatogram of **6** shows a single sharp peak ($M_w/M_n = 1.02$). These results show that the dendrimer **6** which contains the phthalocyanine core is monodispersed. Cobalt complexes **8** and **9** were synthesized from the core **4** and the dendritic phthalocyanine **6**, respectively. The successful introduction of the metal ion was confirmed by the characteristic UV/Vis spectrum for cobalt(II) phthalocyanines and the expected mass spectral data. Compounds **8** and **9** were highly soluble in a wide range of nonpolar to polar organic solvents, such as CH_2Cl_2, toluene, acetone, and methanol.

An examination of the second-generation dendrimer **6** with transmission electron microscopy (TEM) provided the dimensional information. Tomalia et al. have reported that the coordination of the terminal groups at the periphery of the dendrimer surface with Na^+ allowed the direct observation without the need for metal shadowing.[13] Na^+ disposition on the dendrimer surface was accomplished by the hydrolysis of the terminal *tert*-butyl ester with **6** by formic acid; the coordination of the carboxy groups with Na^+ was accomplished by the addition of a stoichiometric amount of sodium hydroxide. Figure 1 is a micrograph of an isolated dendrimer

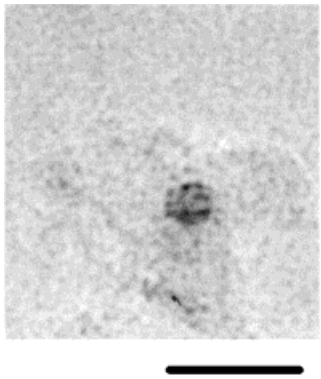

Figure 1. Transmission electron micrograph of hydrolyzed second-generation dendrimer **6**. Scale bar = 20 nm.

functionalized with a sodium carboxylate surface. The high density of Na^+ on the surface of the dendrimer produced a good contrast and we observed a single spherical dendrimer molecule. The diameters of the TEM image (7.0 ± 0.5 nm) agreed well with the collapsed and extended dendrimer dimensions predicted according to the CPK model (4.0 nm and 8.0 nm, respectively). The agreement between the observed dimensions from the TEM image and the predicted CPK model dimensions strongly supports the proposed dendritic structure.

The UV/Vis spectra of **8** and **9** showed a sharp peak at $\lambda =$ 670 nm as the Q band in methanol, which can be attributed to a nonaggregated cobalt(II) phthalocyanine species.[14] The spectrum of the dendritic cobalt phthalocyanine **9** in the visible region is almost the same as that of the core complex **8**. It is well known that UV/Vis spectra are strongly influenced by the intermolecular interaction between phthalocyanine moieties.[15] The spectra of **8** and **9** did not change within the concentration range of 5.0×10^{-7} to 2.0×10^{-4} mol L^{-1}. The introduction of dendritic branches prevents molecular aggregation among phthalocyanine moieties in methanol. Figure 2 shows the UV/Vis spectra of spin-coated films of **8** and **9** on

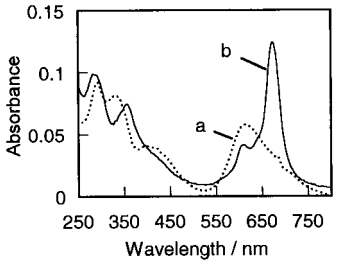

Figure 2. UV/Vis spectra of spin-cast films of **8** (curve a) and **9** (curve b).

Abstract in Japanese:

コバルトフタロシアニン錯体を包含したメタロデンドリマーを合成し、デンドリマー鎖による機能変化について検討を行った。フタロシアニン錯体からデンドリマー鎖を成長させることによりナノメートルスケールの球状形態となった。コバルトフタロシアニン錯体周辺へのデンドリマー鎖の導入によって、種々の溶媒中および薄膜内での錯体の会合を抑制することができ、電気化学的測定から電極とデンドリマー内の錯体間での電子授受がデンドリマー鎖の包含によって困難になることが明らかとなった。チオールの酸化触媒活性について検討を行ったところ、デンドリマー鎖によって多少の活性の減少はみられたが、チオールの酸化触媒として機能した。さらに、触媒反応後の可視吸収スペクトルを比較したところ、コア錯体では錯体の分解が観察されたのに対しメタロデンドリマーでは錯体の分解はみられなかった。このことから、デンドリマー鎖で触媒部を覆うことにより触媒の安定性を向上させることができた。

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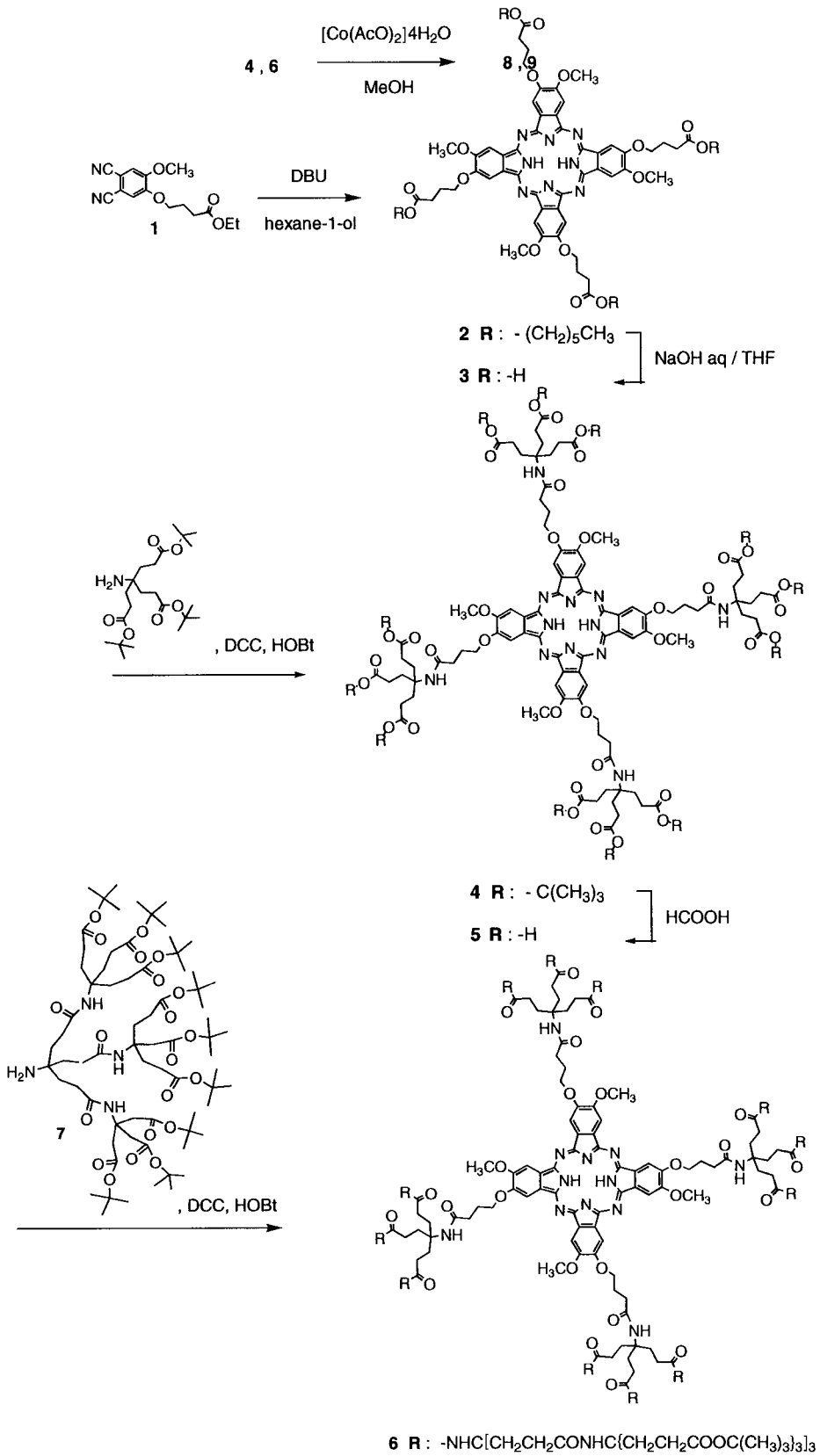

Scheme 1. Synthesis of cobalt complexes **8** and **9**. DCC: dicyclohexylcarbodiimide; HOBt: 1-hydroxy-1*H*-benzotriazole hydrate.

quartz plates obtained from methanol. The Q bands of the spin-coated film of **8** are broad and shifted to a shorter wavelength, which indicates that the phthalocyanine moieties are in an aggregated form and in a cofacial arrangement. In contrast, the UV/Vis spectrum of the spin-coated film of **9** is a spectrum typical of nonaggregated phthalocyanines and thus indicates that **9** is free from molecular aggregation in the thin film. Cobalt phthalocyanine in the second-generation dendrimer is sterically shielded by the highly branched dendritic structure which results from the aggregation of phthalocyanine moieties.

Electrochemistry: The encapsulation of electroactive subunits into the dendritic branches can influence the microenvironment around the electroactive core and sterically inhibit electron transfer from the electrodes. Electrochemical studies of **8** and **9** were performed in solutions in methanol containing $TBAPF_6$ (0.1 mol L^{-1}) as the supporting electrolyte. The phthalocyanine core **8** exhibits one reversible one-electron oxidation process from Co^{II} to Co^{III} at +0.32 V vs. SCE, which is a typical value for cobalt phthalocyanine (Figure 3a).[16] On the other hand, second-generation dendrimer **9** containing cobalt phthalocyanine exhibits no defined oxidative wave (Figure 3b). This electrochemical behavior of **9** suggests that the electron transfer from the electroactive core to the electrode becomes difficult as a result of the encapsulation in the dendritic structure. This observation agrees with the results previously reported by several groups on dendrimers which contain electroactive core subunits.[17] The remoteness of the cobalt phthalocyanine from the electrode surface hinders the electron-transfer

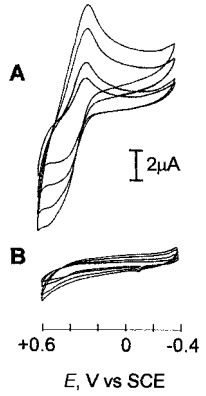

Figure 3. Cyclic voltammogrammes of the phthalocyanine core **8** (A) and second-generation dendrimer **9** (B) in MeOH which contained $TBAPF_6$ (0.1 mol L^{-1}) at varying scan rates (50, 100, 200, 300 mV s^{-1}). [**8**, **9**] = 1.0×10^{-3} mol L^{-1}.

process as a result of the encapsulation. This electrochemical study also shows that the cobalt phthalocyanine in **9** is sterically shielded by the dendritic structure.

Catalytic oxidation of 2-mercaptoethanol: Cobalt(II) phthalocyanines have been employed as effective catalysts for the thiol oxidation.[18] This oxidation obeys the following equation, in which the consumption of four molecules of thiol is accompanied by that of one molecule of dioxygen.

$$4\,RSH + O_2 \xrightarrow{\text{catalyst}} 2\,RS{-}SR + 2\,H_2O$$

The consumption rate of the thiol was determined by measuring the dioxygen concentration in the solution. The dioxygen consumption agreed with the stoichiometry of this equation. The investigation of the catalytic activity in the thiol oxidation reaction was carried out with 2-mercaptoethanol (RSH, R = $HOCH_2CH_2$-) in the presence of triethylamine on account of the dissociation of RSH. The mole ratio between the catalyst and the substrate was ≈11 000. Figure 4 shows the rate curves for the dioxygen consumption in the RSH

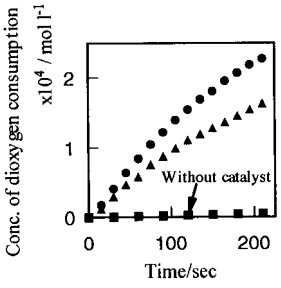

Figure 4. Oxidation of 2-mercaptoethanol catalyzed by **8** (●) and **9** (▲) in MeOH in the presence of triethylamine at 25 °C. [Catalyst] = 8.8×10^{-7} mol L^{-1}, [RSH] = 1.0×10^{-2} mol L^{-1}, [O_2] = 2.2×10^{-4} mol L^{-1}, [triethylamine] = 1.0×10^{-2} mol L^{-1}.

oxidation catalyzed by **8** and **9** in methanol at 25 °C. Thus, both the phthalocyanine core **8** and the dendrimer **9** successfully catalyzed the RSH oxidation. The catalytic activity of **9** is 20% less than that of **8** (initial rate: 339 turnovers per cobalt phthalocyanine per minute). The similarity in the reactivity suggests that the penetration of the reacting molecules (RSH and dioxygen) is not significantly restricted by the dendritic structure around the catalytic site. After the RSH oxidation had run with a continuous dioxygen supply for up to one hour, the spectrum of **8** changed dramatically (Figure 5). In sharp contrast, the spectrum of the second-generation dendrimer **9** remained virtually intact after the catalytic reaction. This result indicates that the dendrimer-encapsulated catalyst is stable compared with the nondendritic catalyst.

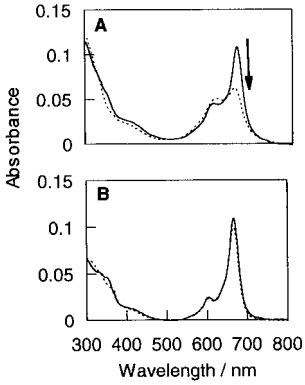

Figure 5. UV/Vis spectra of **8** (A) and **9** (B) after the catalytic reaction in MeOH. [**8**, **9**] = 8.9×10^{-7} mol L^{-1}, [RSH] = 1.0×10^{-2} mol L^{-1}, [triethylamine] = 1.0×10^{-2} mol L^{-1}.

Conclusions

We have reported the details of the preparation and characterization of a new dendritic cobalt phthalocyanine. The second-generation dendrimer **9** is of well-defined nanoscopic dimension; the dendritic structure around the cobalt phthalocyanine prevented the molecular aggregation among phthalocyanine moieties in polar solvents and thin films. The electron-transfer reaction was hindered by the steric shielding of the dendrimer structure. The dendritic cobalt phthalocyanine **9** catalyzed the oxidation of 2-mercaptoethanol in the presence of dioxygen, and its catalytic activity is similar to the core **8**. The catalytic stability was enhanced by the encapsulation in the dendritic structure. The construction of a dendrimer around a catalytic site provides a means to control the catalytic stability by the incorporation of a catalytic site at a precise depth inside the macromolecule. The catalytic dendrimers may be endowed with substrate selectivity for a catalytic reaction by the introduction of recognition units for substrates with the correct disposition around the catalytic site. Attempts are now under way to accomplish this.

Experimental Section

Materials and methods: All chemicals were purchased from commercial suppliers and used without purification. The dinitrile **1**, the monomeric branching unit (Behera's amine), and the dendron unit **7** were prepared according to published procedures.[10–12] Dimethylformamide (DMF) was distilled from CaH_2 under reduced pressure. Column chromatography was performed with Wakogel C-200, gel permeation chromatography (GPC) with Biorad Biobeads SX-1, and analytical thin-layer chromatography with commercial Merck plates coated with silica gel $60F_{254}$. ^1H NMR spectra

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were recorded in $CDCl_3$ solutions on a JEM LA400 FT-NMR spectrometer operating at 399.65 MHz. Chemical shifts were relative to internal TMS. IR spectra were recorded on a JASCO FS-420 spectrometer as KBr pellets. UV/Vis spectra were measured on a JASCO V-570. Elemental analyses were performed with a Perkin Elmer series II CHNS/O analyzer 2400. MALDI-TOF mass spectra were obtained on a PerSeptive Biosystems Voyager-DE-Pro spectrometer with 2-(4-hydroxyphenylazo)benzoic acid and dithranol as matrices. GPC analyses were carried out with a JASCO HPLC system (pump: 1580; UV detector: 1575; refractive-index detector: 930) with Showa Denko GPC KF-804L column (8.0 × 300 mm, polystyrene standards, $M = 900 - 400000\ g\,mol^{-1}$) in THF as the eluent at 35 °C (1.0 mL min^{-1}). Melting points were recorded on a Shibata MEL-270 melting point apparatus and are corrected. Electron micrographs were taken on a JEOL JEM-2010 electron microscope. The hydrolyzed second-generation dendrimer was dissolved in NaOH aqueous solution (6.0×10^{-3} mol L^{-1}, 1 mL) with a concentration of 1 mg mL^{-1}, and a droplet of the solution was put on a carbon-coated copper grid (400 mesh). The solvent was evaporated spontaneously at room temperature over a period of 1 h.

The electrochemical behavior of the dendrimers was studied with a Bio-Analytical Systems (BAS) CV-27 potentiostat. The voltammetric experiments were performed in a 1.0 mL cell equipped with a Pt electrode (0.0177 cm^{-2}), a Pt counterelectrode, and a Ag/AgCl reference electrode. The dendrimers were dissolved in degassed methanol which contained *n*-tetrabutylammonium hexafluorophosphate ($TBAPF_6$, Aldrich) as the supporting electrolyte (0.1 mol L^{-1}). Prior to its use, $TBAPF_6$ was purified by recrystallization three times from ethyl acetate and dried under vacuum for 48 h. Dry nitrogen was bubbled through solutions for 5 min before the start of the cyclic voltammetry experiments. The catalytic activities for the oxidation of 2-mercaptoethanol by catalysts were measured according to the following procedure: A methanolic solution of the catalyst (0.8 mL) was placed in a thermostated reaction vessel fitted with a dioxygen microelectrode and stirred at 25 °C. A solution of 2-mercaptoethanol which contained triethylamine (0.2 mL) was added into the vessel by means of a syringe. The consumption of dioxygen was monitored. During the measurements at 25 °C the reaction solution was stirred with a magnetic bar (500 rpm). The initial rate of dioxygen consumption was determined from the slope of the consumption curve vs. time. The exact concentration of 2-mercaptoethanol in the stock solution was determined by the reaction with I_2, followed by a titration of the excess I_2 with a NaS_2O_3 solution. The concentrations of all the reagents are given in the figure captions. The nomenclature used to indicate the dendrimers is that suggested by Newkome et al.

2: A mixture of dinitrile **1** (2.0 g, 6.94×10^{-3} mol) and DBU (1.06 g, 6.94×10^{-3} mol) in hexan-1-ol (5 mL) was heated at 140 °C with stirring for 24 h. After evaporation of the solvent, the residue was purified by column chromatography (SiO_2, CH_2Cl_2/methanol 9:1). Recrystallization from CH_2Cl_2/methanol gave green crystals of **2**. Yield: 0.64 g (24 %); m.p. > 300 °C; FT-IR (KBr): $\tilde{\nu} = 1734$ cm^{-1} (C=O); ^{1}H NMR (399.65 MHz, $CDCl_3$, 25 °C): $\delta = -3.35$ (br., 2H, NH), 0.88 (t, CH_3, 12H), 1.32 (s, -CH_2-, 32H), 2.57 (s, 8H, -CH_2-), 2.91 (m, 8H, -CH_2-), 4.11 (m, 8H, -CH_2-), 4.24 (m, 12H, OCH_3), 4.60 (br., 8H, -OCH_2-), 8.22 (br., 8H, Pc); MALDI-TOF MS (2-(4-hydroxyphenylazo)benzoic acid): *m*/*z* (%): 1379 ([*M*+H]$^+$, 100); calcd for $C_{76}H_{98}N_8O_{16}$: 1378; anal. calcd C 66.16, H 7.15, N 8.12; found C 65.91, H 7.09, N 8.03.

3: An aqueous solution of NaOH (1.0 M, 1 mL) was added to a solution of **2** (0.6 g, 2.28×10^{-4} mol) in THF (5 mL). The mixture was stirred at 60 °C for 48 h. The solvent was removed in vacuo and the residue was dissolved in water (10 mL). The resulting green solution was filtered and neutralized with acetic acid. The precipitate was collected by filtration and dried in vacuo. Yield: 0.40 g (90 %); FT-IR (KBr): $\tilde{\nu} = 1716$ cm^{-1} (C=O); MALDI-TOF MS (2-(4-hydroxyphenylazo)benzoic acid): *m*/*z* (%): 1043 ([*M*+H]$^+$, 100); calcd for $C_{52}H_{50}N_8O_{16}$: 1042.

12-Cascade 4: **3** (0.30 g, 2.88×10^{-4} mol) and 1-hydroxy-1*H*-benzotriazole hydrate (HOBT) (0.20 g, 1.50×10^{-3} mol) were dissolved in dry DMF (20 mL). This solution was cooled to −5 °C and Behera's amine (0.48 g, 1.15×10^{-3} mol) was added. A solution of dicyclohexylcarbodiimide (DCC, 0.31 g, 1.50×10^{-3} mol) in dry DMF (5 mL) was added to the solution. This reaction mixture was stirred for 72 h at room temperature. The precipitate was filtered off, and the solvent removed in vacuum. The green residue was dissolved in $CHCl_3$ and extracted with NaOH (0.2 M), 10 % HCl, and brine. The organic layer was dried (Na_2SO_4) and the solvent removed in vacuum. Purification was accomplished by column chromatography (SiO_2, CH_2Cl_2/methanol 9:1). Recrystallization from CH_2Cl_2/hexane gave **4** as a green solid. Yield: 0.40 g (51 %); FT-IR (KBr): $\tilde{\nu} = 1729$, 1660 cm^{-1} (C=O); ^{1}H NMR (399.65 MHz, $CDCl_3$, 25 °C): $\delta = 1.39$(s, $C(CH_3)_3$, 108H), 1.98(br., -CH_2-, 24H), 2.23(br., -CH_2-, 24H), 2.54 (br., -CH_2-, 8H), 2.71 (br., -CH_2-, 8H), 4.49 (d, -OCH_3, 12H), 6.28 (br., NH, 4H), 8.55 (s, Pc, 8H); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 698 (53900), 660 (57700), 344 (55800); MALDI-TOF MS (2-(4-hydroxyphenylazo)benzoic acid): *m*/*z* (%): 2632 ([*M*+H]$^+$, 100) calcd. for $C_{140}H_{206}N_{36}O_{36}$: 2631.

12-Cascade 5: A solution of **4** (0.3 g, 1.14×10^{-4} mol) in formic acid was stirred at room temperature for 48 h. The solvent was removed in vacuo and the residue was dissolved in methanol. The compound **5** was obtained as a green solid, which was used for further reactions without purification. Yield: 0.20 g (90 %); FT-IR (KBr): $\tilde{\nu} = 1716$, 1650 cm^{-1} (C=O); MALDI-TOF MS (2-(4-hydroxyphenylazo)benzoic acid): *m*/*z* (%): 1959 ([*M*+H]$^+$, 100); calcd for $C_{52}H_{50}N_8O_{16}$: 1958.

108-Cascade 6: **5** (0.052 g, 2.63×10^{-5} mol) and HOBT (0.047 g, 3.47×10^{-4} mol) were dissolved in dry DMF (10 mL). This solution was cooled to −5 °C and **7** (0.5 g, 3.34×10^{-4} mol) was added. A solution of DCC (0.072 g, 3.34×10^{-4} mol) in dry DMF (5 mL) was added to the solution. This reaction mixture was stirred for 96 h at room temperature. The precipitate was filtered off, and the solvent removed in vacuum. The green residue was dissolved in $CHCl_3$ and extracted with NaOH (0.2 M), 10 % HCl, and brine. The organic layer was dried (Na_2SO_4) and the solvent removed in vacuum. The residue was purified by gel permeation chromatography (Biorad Biobeads SX-1, CH_2Cl_2) followed by chromatography (SiO_2, CH_2Cl_2/methanol 9:1) to give **5** as a green foam. Yield: 0.23 g (46 %); FT-IR (KBr): $\tilde{\nu} = 1730$, 1655 cm^{-1} (C=O); ^{1}H NMR (399.65 MHz, $CDCl_3$, 25 °C): $\delta = 1.44$ (s, $C(CH_3)_3$, 972H), 1.97 (m, -CH_2-, 320H), 2.23 (m, -CH_2-, 216H), 3.10 (br., -CH_2-, 104H), 4.48 (br., -OCH_3, 12H) 4.67 (br., -OCH_2-, 8H), 6.05–6.78 (m, N*H*, 52H), 8.94 (s, Pc, 8H); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 698 (52000), 660 (53300), 344 (52200); MALDI-TOF MS (Dithanol): *m*/*z*: 19016 (broad, [*M*$^+$]); calcd for $C_{1004}H_{1694}N_{60}O_{276}$: 19010.

Cobalt(II) complex with 4 (8): Cobalt(II) acetate tetrahydrate (0.1 g, 4.0×10^{-4} M) and **4** (0.1 g, 3.80×10^{-5} M) were dissolved in methanol (10 mL) and the reaction mixture was refluxed, during which time the peak height of the product in the UV/Vis spectrum gradually changed. The mixture was refluxed until the change of the Q band at $\lambda = 670$ nm was not observed. Cobalt complex **8** was purified by chromatography (SiO_2, CH_2Cl_2/methanol 9:1). Yield: 0.08 g (78 %); (UV/VIS (methanol): λ_{max} (ε) = 670 (101000), 606 (29000), 351 (49200); MALDI-TOF MS (2-(4-hydroxyphenylazo)benzoic acid): *m*/*z* (%): 2689 ([*M*+H]$^+$, 100) calcd for $C_{140}H_{204}N_{36}O_{36}Co$: 2688.

Cobalt(II) complex with 6 (9): Cobalt(II) acetate tetrahydrate (0.1 g, 4.0×10^{-4} M) and **6** (0.3 g, 1.58×10^{-5} M) were dissolved in methanol (10 mL) and the reaction mixture was refluxed for 96 h. Cobalt complex **8** was purified by chromatography (SiO_2, CH_2Cl_2/methanol 9:1). Yield: 0.18 g (60 %); UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon) = 670$ (98400); MALDI-TOF MS (dithranol): *m*/*z*: 19072 (broad, [*M*$^+$]); calcd for $C_{1004}H_{1692}N_{60}O_{276}Co$: 19067.

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