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Control of the Aggregation Properties of Tris(maltohexaose)-Linked Porphyrins with an Alkyl Chain

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A series of porphyrins with three maltohexaose units and one alkyl chain (ethyl, butyl, hexyl, decyl, and hexadecyl) has been synthesized. Aggregation properties were investigated by absorbance and circular dichroism (CD) spectra. These trismaltohexaosylated tetraphenylporphyrins exhibited high water solubility. Although these porphyrins exhibited sharp Soret bands in DMSO solution, the Soret band broadened in a concentration-dependent manner in aqueous solution. This is the result of the aggregation of porphyrin molecules in aqueous solution. Interestingly, trismaltohexaosylated porphyrins with long alkyl chains of a certain length exhibited a broad Soret band in water without concentration dependency due to the stability of such aggregates. The CD spectra were silent in DMSO solution in all porphyrin derivatives, indicating that the maltohexaose moiety does not interact with the porphyrin chromophore in the monomeric state. However, in water, a splitting Cotton effect was observed at the Soret band. Intensity of this CD signal decreased as the length of the alkyl chain was extended. These observations show the formation of a chiral, face-to-face aggregate, in which the porphyrin rings are in close proximity to each other for short alkyl chain derivatives. The porphyrin derivatives with long alkyl chains exhibit edge-to-edge aggregation, where hydrophobic interaction of the alkyl chains separates the porphyrin chromophores.

Introduction

Porphyrin derivatives play important roles in biological systems. In recent years, photodynamic therapy (PDT) using porphyrin derivatives as a photosensitizing biological chromophore is considered as a clean, effective cancer therapy.[1–3] For clinical use, it is important to make porphyrin derivatives soluble in aqueous solution. From the viewpoint of biological applications, non-ionic, cell-permeable carbohydrates that exist abundantly in nature are considered to be attractive materials for hydrophilic functionalities. Carbohydrates play many important roles such as energy sources for living systems, construction materials, and adhesion between cells.[4,5] Thus, hybrid materials of carbohydrates and porphyrins may become a photofunctional molecule with biological similarity.[6–16] On the other hand, amphiphilic porphyrins tend to aggregate in solution.[9,12,17–21] Thus, introduction of a wide variety of alkyl chains to the porphyrin derivatives enables us to control the aggregation state by hydrophobic forces.[22–25] It is also of significant interest to organize porphyrins in nanoscale order.[26–29] The present research is established on the basis of the above consideration, creating a hybrid material with biological similarity to regulate aggregation properties by cooperative effects between the carbohydrates and the alkyl chains.

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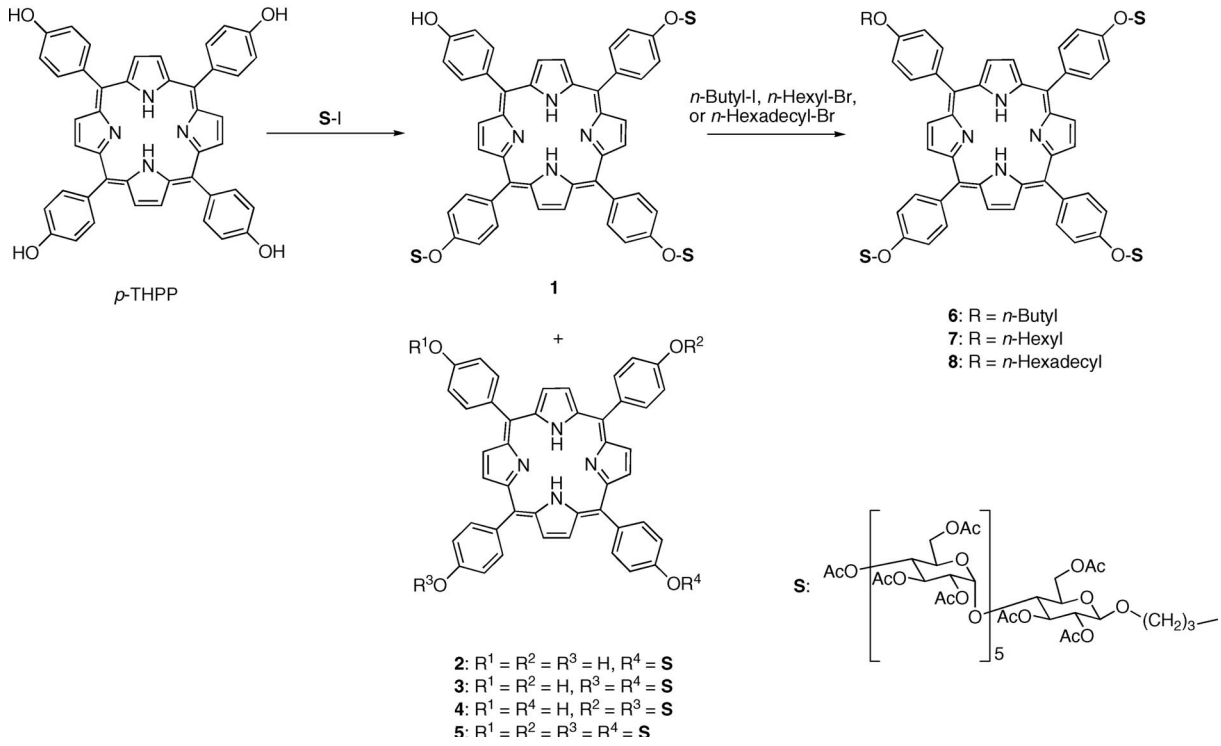
Results

Synthesis

A series of porphyrins with three maltohexaose units and one alkyl chain (3MalTPP, 1E3MalTPP, 1B3MalTPP, 1H3MalTPP, 1D3MalTPP, and 1HD3MalTPP) was synthesized from 3-iodopropyl nonadeca-*O*-acetyl-β-D-maltohexaoside (**S-I**)[30–32] and 5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin (*p*-THPP)[33,34] according to Schemes 1, 2, and 3. For the synthesis of acetyl-protected derivatives of 3MalTPP, 1B3MalTPP, 1H3MalTPP, and 1HD3MalTPP, *p*-THPP was treated with **S-I**, and thus obtained trismaltohexaosylated porphyrin **1** (3MalTPP) was subjected to further alkylation (Scheme 1). As shown in Scheme 2, an alkyl chain was in advance introduced to *p*-THPP to obtain **9** and **14**, and then, these monoalkylated porphyrins were



Scheme 1.

treated with **S-I** for the synthesis of 1E3MalTPP and 1D3MalTPP. The acetyl groups of maltohexaose-conjugated porphyrins **1**, **6**–**8**, **19**, and **20** were removed by sodium methoxide in $CHCl_3$/MeOH to give the desired amphiphilic porphyrins (Scheme 3).

Absorbance Spectra

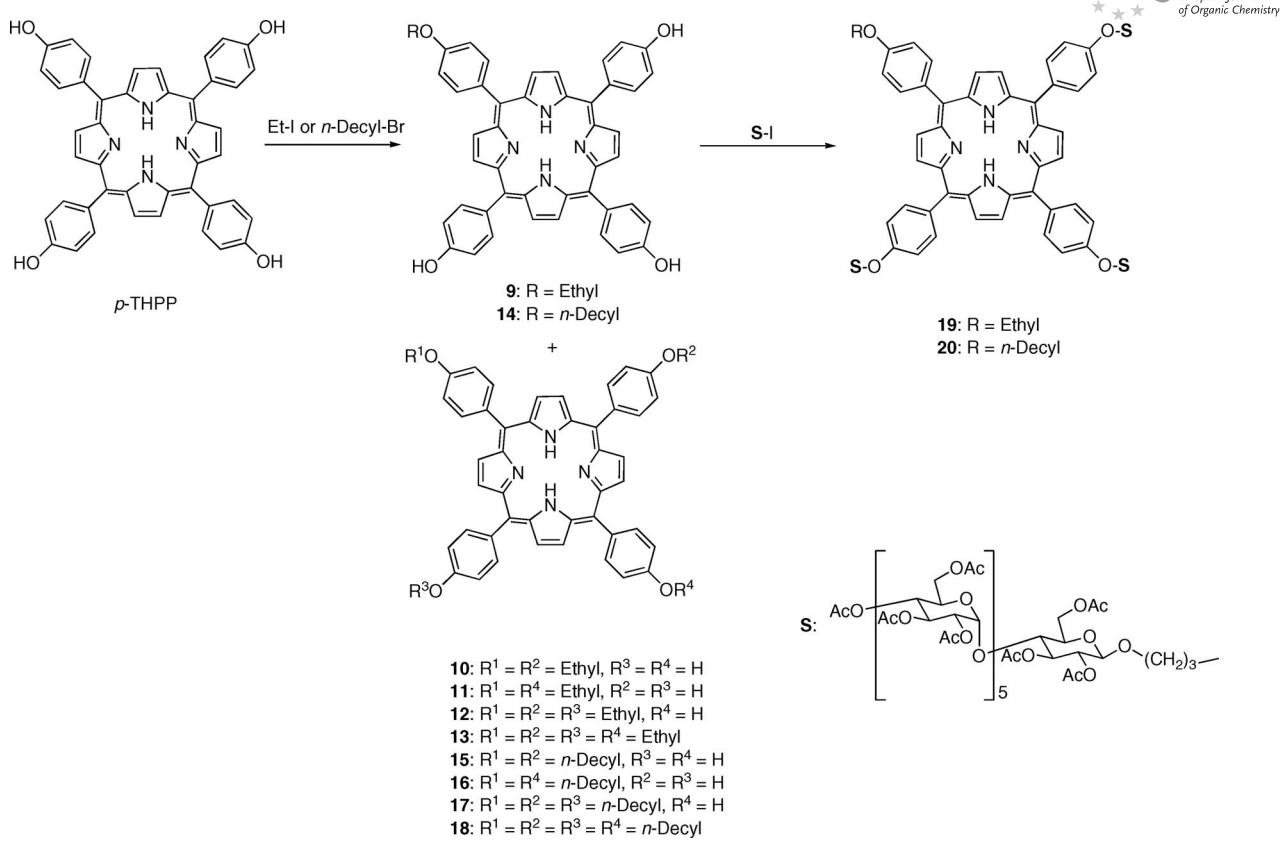
The absorbance spectra of all maltohexaosylated porphyrin derivatives exhibit a Soret band and four Q bands around 425 nm and 500–680 nm, respectively (Figure 1). The Soret band is very sharp in DMSO solution, indicating that these porphyrins exist as a monomer in this solution. In contrast, in aqueous solution, the absorbance spectra become broad, and the half-height width widened when the concentration was increased from 10^{-7} to 10^{-5} M (Figure 1). This observation suggests the formation of porphyrin aggregates in water solution with a variety of absorption energy levels. It should be noted that, for porphyrin derivatives with long alkyl chains, the shape of the Soret band was unchanged in the concentration range from 10^{-7} to 10^{-5} M. This indicates that the porphyrins form stable aggregates without a concentration dependency. Table 1 summarizes the Soret band absorption properties of the porphyrin derivatives in DMSO and water at a concentration of 1.0×10^{-5} M.

CD Spectra

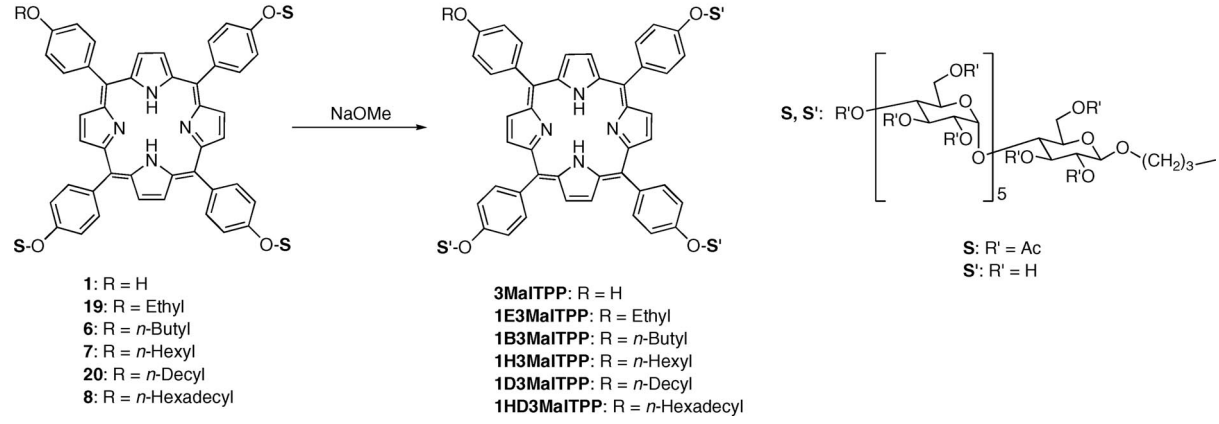
In DMSO solution, no active Cotton effect was observed at the Soret band (Figure 2, broken lines), indicating that these porphyrins exist as a monomer in this solution. In aqueous solution, however, strong exciton coupling signals in the region from 380 to 460 nm[35–37] were observed (Figure 2, solid lines). Thus, the trismaltohexaosylated porphyrins with an alkyl chain form aggregates with chirality around the porphyrin chromophore in aqueous solution. The intensity of this CD signal decreased as the length of the alkyl chain was extended. For porphyrins with longer alkyl chains, in contrast to the smooth and sharp negative Cotton effect at the long-wavelength region, a broad positive Cotton effect at the short-wavelength region exhibits broad, structureless features. The examination of concentration dependency in the CD spectra resulted in very complicated characteristics and further study was avoided at the present stage. Figure 3 summarizes the differences in the CD and absorption spectra at the Soret band of all porphyrin derivatives in aqueous solution at a concentration of 1.0×10^{-5} M.

Discussion

A series of porphyrins with three acetyl-protected maltohexaose units and one alkyl chain has been synthesized by two synthetic routes shown in Schemes 1 and 2. The ratio of alkylating agent and hydroxyporphyrin were optimized from several trials considering the product yield and separation efficiency. For the series of compounds studied in this work, Scheme 1 would be a better synthetic route because laborious separation by column chromatography is common for all compounds. In this case, however, a considerable amount of **S-I** is necessary. In addition, the syn-



Scheme 2.



Scheme 3.

thesis of 1E3MalTPP according to Scheme 1 was problematic because of the difficulty in separating compounds **19** and **1** (starting material of the second step) due to their small differences in polarity or molecular size. As evidenced by the synthesis of 1D3MalTPP, the present paper demonstrates that both syntheses can be used to prepare the tris-maltohexaosylated porphyrins with a long alkyl chain.

The peak-top wavelength in the absorbance spectra are almost unchanged for all porphyrin derivatives; however, the half-height width ($W_{1/2}$) in aqueous solution was found to increase in proportion to the alkyl chain length, and it became constant for longer alkyl chains than 1B3MalTPP and decreased for 1HD3MalTPP (Table 1). The increase in half-height width for other compounds is due to the shoulder around 410 nm. Considering that this shoulder as a splitting peak, the edge-to-edge type aggregate (Figure 4a) seems to be predominant for 1B3MalTPP, 1H3MalTPP, and 1D3MalTPP, as alkyl chains interact with each other by hydrophobic interactions in aqueous solution. The 1HD3MalTPP derivative, which has an extremely long alkyl

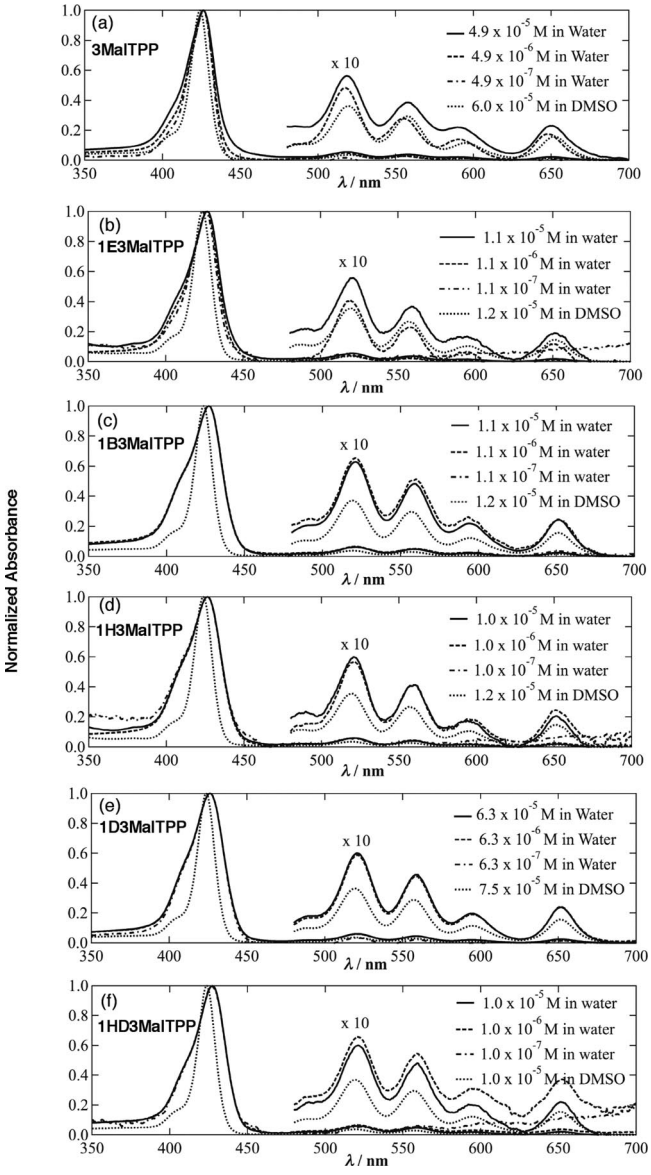


Figure 1. UV/Vis spectra of 3MalTPP, 1E3MalTPP, 1B3MalTPP, 1H3MalTPP, 1D3MalTPP, and 1HD3MalTPP in DMSO and water with normalized intensity.

chain, exists also as an edge-to-edge aggregate with a decreased half-height width, because the porphyrin rings are separated from each other.

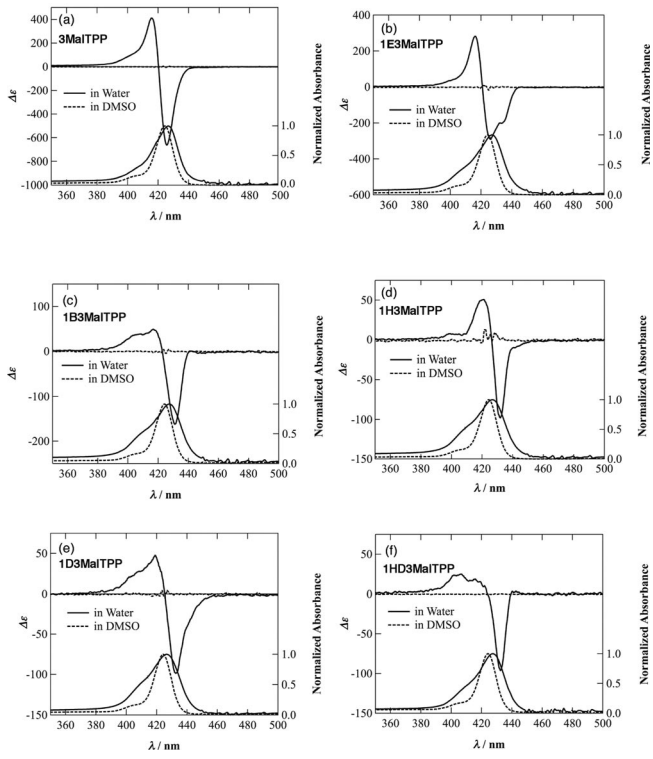


Figure 2. CD spectra of 3MalTPP, 1E3MalTPP, 1B3MalTPP, 1H3MalTPP, 1D3MalTPP, and 1HD3MalTPP in DMSO and water (1.0×10^{-5} M concentration).

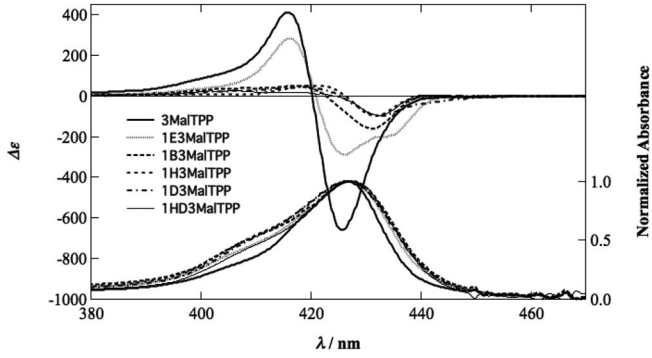


Figure 3. Overlay plot of CD and absorption spectra of trismaltohexaosylated porphyrins in water (1.0×10^{-5} M concentration).

Table 1. Soret band absorbance spectral data for 3MalTPP, 1E3MalTPP, 1B3MalTPP, 1H3MalTPP, 1D3MalTPP, and 1HD3MalTPP in DMSO and water.[a]

Compound	in DMSO		in Water	
	Soret band / nm	$W_{1/2}$ / nm (ε / $M^{-1}cm^{-1}$)	Soret band / nm	$W_{1/2}$ / nm (ε / $M^{-1}cm^{-1}$)
3MalTPP	424	13.5 (383000)	426	22.5 (219000)
1E3MalTPP	424	14 (447000)	427	25.5 (227000)
1B3MalTPP	424	13.5 (485000)	427	29 (216000)
1H3MalTPP	424	14 (433000)	427	29.5 (206000)
1D3MalTPP	424	13.5 (422000)	426	28 (221000)
1HD3MalTPP	424	13.5 (546000)	428	25.5 (240000)

[a] Concentration: 1.0×10^{-5} M.

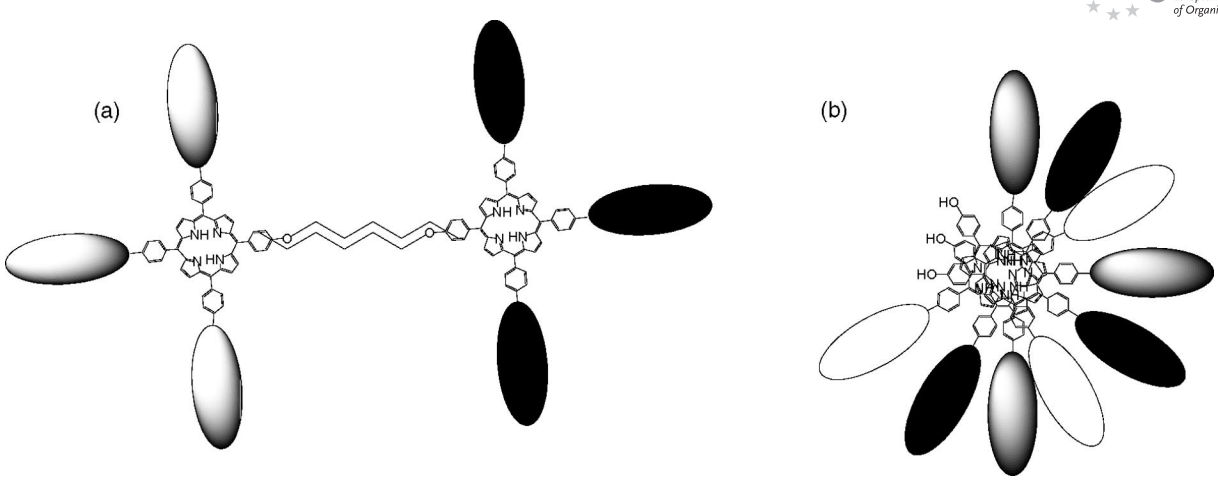


Figure 4. Schematic diagram representing the aggregation properties with (a) edge-to-edge association and (b) face-to-face association.

From the CD spectra, 3MalTPP exhibits a large Cotton effect with a splitting pattern, suggesting that this compound mainly exists as a face-to-face aggregate with negative helicity (Figure 4b), where the porphyrin rings are in close proximity to each other. 1E3MalTPP, which has an ethyl group, has a decreased CD intensity compared to that of 3MalTPP, exhibiting a new, negative Cotton effect in the long-wavelength region (around 436 nm). These observations are considered as a mixture of two Cotton effects, indicating the formation of edge-to-edge aggregates in addition to face-to-face aggregates by the ethyl-substituent effect. The porphyrin derivatives with alkyl chains longer than butyl exhibit a decreased CD intensity and a redshifted peak-top. These observations suggest that 1B3MalTPP, 1H3MalTPP, and 1D3MalTPP exist mainly as an edge-to-edge aggregate. The porphyrin ring itself tends to form an aggregate, however, repulsive forces from electrostatic interactions in charged water-soluble porphyrins such as TPPS [5,10,15,20-tetrakis(4-sulfonylphenyl)porphyrin] separates them. In contrast, the present porphyrin derivatives with oligosaccharide and alkyl chain are non-ionic, forming the stable aggregates with negative helicity by attached maltohexaose group. Moreover, introduction of alkyl chains of certain length into these porphyrins affords a stable edge-to-edge association without concentration-dependency. Preliminary estimation of aggregation number for 1D3MalTPP by SLS measurement suggests that the aggregation number is >2,000 in low and high concentrations and the rotational square radius is small, indicating the formation of stable, micelle-like, high-density aggregate.

Conclusion

A hydrophobic porphyrin chromophore was solubilized in water by attaching three maltohexaose units. All of the porphyrins exhibit sharp Soret bands and an inactive CD in DMSO solution. In contrast, in water solution, the Soret band was broadened and active CD Cotton effects were observed. These observations indicate that these porphyrins exist as a monomer in DMSO solution but as an aggregate in water. The alkyl chain length is the important factor that governs the aggregation mode, namely, long alkyl chain increases the half-height width for the Soret band and decreases the intensity in the CD spectrum. Both parameters, however, were unaffected by derivatives that have alkyl chains longer than a hexyl group. This indicates that a face-to-face aggregate was formed for short alkyl chain derivatives where the porphyrin rings are twisted, whereas an edge-to-edge aggregate was formed for long alkyl chain derivatives. Especially, the UV spectrum of the derivative with decyl and maltohexaose substituents was unchanged in water at all concentrations tested (10^{-5}–10^{-7} M). This is probably because the edge-to-edge aggregate was formed by hydrophobic interaction of the decyl chains. The present information could help us to create novel photofunctional nanomaterials.

Experimental Section

Reagents: DMF was dried with 4 Å molecular sieves. THF was distilled from $LiAlH_4$. Water was obtained from a Milli-Q system (Millipore). Other dry solvents, spectrometry grade solvents were used as received. Potassium carbonate was dried at 100 °C under reduced pressure. Other reagents were used as received. Column chromatography was performed by using Cica Silica Gel 10N 40–50 μm. Recycle column chromatography was performed by JAI LC-908 using a JAIGEL-3H column and THF as the eluent. Dialysis was performed using SPECTRAM Spectra/Por 7 Membrane MW1000.

5,10,15-Tris[4-(3-nonadeca-*O*-acetyl-β-D-maltohexaosyloxy)propyloxy]phenyl-20-(4-hydroxyphenyl)porphyrin (1): 5,10,15,20-Tetrakis(4-hydroxyphenyl)porphyrin (*p*-THPP)[33,34] (100 mg, 147 μmol) was treated with 1-iodopropyl nonadeca-*O*-acetyl-β-D-maltohexaoside (**S-I**) (577 mg, 295 μmol) in the presence of K_2CO_3 (202 mg, 1.47 mmol) in DMF (30 mL) at room temperature for 2 d and at 60 °C for 2 h. After filtration, the material was extracted with ethyl acetate, washed with water and brine, and dried with sodium sulfate. The solvent was removed under reduced pressure, and the porphyrin derivatives having one to four maltohexaose units were separated by column chromatography. Yield: 112.8 mg (12%). R_f = 0.15

(toluene/acetone, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.85 (d, 8 H, pyr), 8.09 (m, 8 H, 2,6-H aryl), 7.26 (m, 8 H, 3,5-H aryl), 5.42–3.92 (m, 3×42 H, maltohexaose), 4.07 (t, 3×4 H, 1,3-H propyl), 2.24–1.99 (m, 3×57 H, acetyl), –2.77 (br. s, 2 H, NH) ppm. $C_{275}H_{342}N_4O_{154}$ (6167.66): calcd. C 53.55, H 5.59, N 0.91; found C 53.09, H 5.67, N 0.90.

5,10,15-Tris(4-hydroxyphenyl)-20-{4-[3-(nonadeca-*O*-acetyl-β-D-maltohexaosyl)propoxy]phenyl}porphyrin (2): Compound **2** was obtained as a byproduct in the synthesis of **1**. Yield: 132.9 mg (36%). R_f = 0.30 (toluene/acetone, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.84 (s, 4 H, pyr), 8.79 (d, J = 4.8 Hz, 2 H, pyr), 8.73 (d, J = 4.8 Hz, 2 H, pyr), 7.99 (m, 6 H, 2,6-H aryl), 7.90 (d, J = 8.5 Hz, 2 H, 2,6-H aryl), 7.08 (m, 6 H, 3,5-H aryl), 7.01 (d, J = 8.5 Hz, 2 H, 3,5-H aryl) 5.45–3.77 (m, 42 H, maltohexaose), 4.07 (t, 4 H, 1,3-H propyl), 2.23–1.99 (m, 57 H, acetyl), –2.77 (br. s, 2 H, NH) ppm. $C_{121}H_{134}N_4O_{54}$ (2508.38): calcd. C 57.94, H 5.38, N 2.23; found C 57.83, H 5.45, N 2.11.

5,10-Bis(4-hydroxyphenyl)-15,20-bis{4-[3-(nonadeca-*O*-acetyl-β-D-maltohexaosyl)propoxy]phenyl}porphyrin (3): Compound **3** was obtained as a byproduct in the synthesis of **1**. Yield: 94.9 mg (15%). R_f = 0.21 (toluene/acetone, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.82 (m, 8 H, pyr), 8.06 (d, J = 8.1 Hz, 8 H, 2,6-H aryl), 7.21 (m, 8 H, 3,5-H aryl), 5.47–3.80 (m, 2×42 H, maltohexaose), 4.06 (t, 2×4 H, 1,3-H propyl), 2.24–1.99 (m, 2×57 H, acetyl), –2.78 (br. s, 2 H, NH) ppm. $C_{198}H_{238}N_4O_{104}$ (4338.02): calcd. C 54.82, H 5.53, N 1.29; found C 54.68, H 5.67, N 1.30.

5,15-Bis(4-hydroxyphenyl)-10,20-bis{4-[3-(nonadeca-*O*-acetyl-β-D-maltohexaosyl)propoxy]phenyl}porphyrin (4): Compound **4** was obtained as a byproduct in the synthesis of **1**. Yield: 40.9 mg (6%). R_f = 0.36 (toluene/acetone, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.85 (dd, J = 4.8, 7.5 Hz, 8 H, pyr), 8.07 (m, 8 H, 2,6-H aryl), 7.22 (m, 8 H, 3,5-H aryl), 5.47–3.80 (m, 2×42 H, maltohexaose), 4.07 (t, 2×4 H, 1,3-H propyl), 2.24–1.99 (m, 2×57 H, acetyl), –2.78 (br. s, 2 H, NH) ppm. $C_{198}H_{238}N_4O_{104}$ (4338.02): calcd. C 54.82, H 5.53, N 1.29; found C 54.92, H 5.68, N 1.23.

5,10,15,20-Tetrakis{4-[3-(nonadeca-*O*-acetyl-β-D-maltohexaosyl)-propoxy]phenyl}porphyrin (5): Compound **5** was obtained as a byproduct in the synthesis of **1**. Yield: 41.2 mg (4%). R_f = 0.09 (toluene/acetone, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.84 (s, 8 H, pyr), 8.11 (d, J = 7.5 Hz, 8 H, 2,6-H aryl), 7.27 (d, J = 7.5 Hz, 8 H, 3,5-H aryl), 5.47–3.93 (m, 4×42 H, maltohexaose), 4.07 (t, 4×4 H, 1,3-H propyl), 2.25–1.99 (m, 4×57 H, acetyl), –2.77 (br. s, 2 H, NH) ppm. $C_{352}H_{446}N_4O_{204}$ (7997.30): calcd. C 52.87, H 5.62, N 0.70; found C 52.77, H 5.74, N 0.67.

5-(4-Butoxyphenyl)-10,15,20-tris{4-[3-(nonadeca-*O*-acetyl-β-D-maltohexaosyl)propoxy]phenyl}porphyrin (6): A mixture of **1** (148.7 mg, 24.1 μmol), 1-iodobutane (41.0 μmol), and K_2CO_3 (33.3 mg, 0.24 mmol) in DMF (10 mL) was stirred for 5 d at room temperature. After filtration, the material was extracted with ethyl acetate, washed with water and brine, and dried with sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography. Yield: 129.1 mg (86%). R_f = 0.19 (toluene/acetone, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.84 (m, 8 H, pyr), 8.11 (d, J = 8.3 Hz, 8 H, 2,6-H aryl), 7.23 (d, J = 8.3 Hz, 8 H, 3,5-H aryl), 5.47–3.76 (m, 3×42 H, maltohexaose), 4.06 (m, 14 H, 1,3-H propyl, 1-H hexyl), 2.24–1.98 (m, 3×57 H, acetyl), 1.63 (m, 4 H, 2,3-H hexyl), 1.11 (t, 3 H, 4-H hexyl), –2.76 (br. s, 2 H, NH) ppm. $C_{279}H_{350}N_4O_{154}$ (6223.77): calcd. C 53.84, H 5.67, N 0.90; found C 53.37, H 5.58, N 0.87.

5-(4-Hexanoxyphenyl)-10,15,20-tris{4-[3-(nonadeca-*O*-acetyl-β-D-maltohexaosyl)propoxy]phenyl}porphyrin (7): A mixture of **1** (200 mg, 32.4 μmol), 1-bromohexane (24.2 mM in DMF, 2.0 mL, 48.6 μmol), and K_2CO_3 (45.0 mg, 0.32 mmol) in DMF (10 mL) was stirred for 5 d at room temperature. After filtration, the material was extracted with ethyl acetate, washed with water and brine, and dried with sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography. Yield: 168.6 mg (83%). R_f = 0.21 (toluene/acetone, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.84 (m, 8 H, pyr), 8.11 (m, 8 H, 2,6-H aryl), 7.27 (m, 8 H, 3,5-H aryl), 5.47–3.78 (m, 3×42 H, maltohexaose), 4.06 (m, 14 H, 1,3-H propyl, 1-H hexyl), 2.24–1.98 (m, 3×57 H, acetyl), 1.59 (m, 6 H, 2-H propyl), 1.47 (m, 4 H, 3,4-H hexyl), 1.26 (m, 2 H, 5-H hexyl), 0.99 (t, 3 H, 6-H hexyl), –2.76 (br. s, 2 H, NH) ppm. $C_{281}H_{354}N_4O_{154}$ (6251.82): calcd. C 53.98, H 5.71, N 0.90; found C 54.09, H 5.91, N 0.91.

5-(4-Hexadecanoxyphenyl)-10,15,20-tris{4-[3-(nonadeca-*O*-acetyl-β-D-maltohexaosyl)propoxy]phenyl}porphyrin (8): A mixture of **1** (153.5 mg, 24.9 μmol), 1-bromohexadecane (18.7 mM in acetone, 2.0 mL, 37.3 μmol), and K_2CO_3 (34.4 mg, 0.25 mmol) in acetone (30 mL) was stirred for 5 d at room temperature. After filtration, the material was extracted with ethyl acetate, washed with water and brine, and dried with sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography. Yield: 80.9 mg (51%). R_f = 0.29 (toluene/acetone, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.84 (m, 8 H, pyr), 8.11 (d, J = 7.7 Hz, 8 H, 2,6-H aryl), 7.27 (d, J = 7.7 Hz, 8 H, 3,5-H aryl), 5.47–3.78 (m, 3×42 H, maltohexaose), 4.07 (m, 14 H, 1,3-H propyl, 1-H hexadecyl), 2.25–1.99 (m, 3×57 H, acetyl), 1.78 (m, 3×2 H, 2-H propyl), 1.61 (m, 2 H, 3-H hexadecyl), 1.46–1.25 (m, 24 H, 4,5,6,7,8,9,10,11,12,13,14,15-H, hexadecyl), 0.88 (t, 3 H, 16-H hexadecyl), –2.77 (br. s, 2 H, NH) ppm. $C_{291}H_{374}N_4O_{154}$ (6392.09): calcd. C 54.68, H 5.90, N 0.88; found C 54.55, H 5.92, N 0.81.

5-(4-Ethoxyphenyl)-10,15,20-tris(4-hydroxyphenyl)porphyrin (9): *p*-THPP[33,34] (300 mg, 0.44 mmol) was treated with ethyl iodide (0.88 mmol) in the presence of K_2CO_3 (608 mg, 4.4 mmol) in DMF (30 mL) at room temperature for 2 d. After filtration, the material was extracted with chloroform, washed with water and brine, and dried with sodium sulfate. The solvent was removed under reduced pressure, and porphyrin derivatives having one to four ethyl groups were separated by column chromatography. Yield: 66.3 mg (21%). R_f = 0.13 (chloroform/methanol, 20:1). ^{1}H NMR (300 MHz, [D_6]-DMSO): δ = 8.87 (m, 8 H, pyr), 8.10 (d, J = 8.5 Hz, 2 H, 2,6-H aryl), 8.05 (d, J = 8.3 Hz, 6 H, 2,6-H aryl), 7.26 (d, J = 8.5 Hz, 2 H, 3,5-H aryl), 7.21 (d, J = 8.3 Hz, 6 H, 3,5-H aryl), 4.32 (t, 2 H, 1-H ethyl), 1.59 (t, 3 H, 2-H ethyl), –2.76 (br. s, 2 H, NH) ppm.

5,10-Bis(4-ethoxyphenyl)-15,20-bis(4-hydroxyphenyl)porphyrin (10): Compound **10** was obtained as a byproduct in the synthesis of **9**. Yield: 74.9 mg (23%). R_f = 0.27 (chloroform/methanol, 20:1). The synthesis of **10** was described previously.[38]

5,15-Bis(4-ethoxyphenyl)-10,20-bis(4-hydroxyphenyl)porphyrin (11): Compound **11** was obtained as a byproduct in the synthesis of **9**. Yield: 25.7 mg (8%). R_f = 0.33 (chloroform/methanol, 20:1). The synthesis of **11** was described previously.[38]

5,15,20-Tris(4-ethoxyphenyl)-20-(4-hydroxyphenyl)porphyrin (12): Compound **12** was obtained as a byproduct in the synthesis of **9**. Yield: 77.9 mg (23%). R_f = 0.50 (chloroform/methanol, 20:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.84 (d, 8 H, pyr), 8.06 (m, 6 H, 2,6-H aryl), 7.98 (d, J = 8.5 Hz, 2 H, 2,6-H aryl), 7.19 (m, 6 H, 3,5-H aryl), 7.01 (d, J = 8.5 Hz, 2 H, 3,5-H aryl), 4.23 (m, 3×2 H, 1-H ethyl), 1.56 (t, 3×3 H, 2-H ethyl), –2.73 (br. s, 2 H, NH) ppm.

5,10,15,20-Tetrakis(4-ethoxyphenyl)porphyrin (13): Compound **13** was obtained as a byproduct in the synthesis of **9**. Yield: 29.5 mg (9%). The synthesis of **13** was described previously.[39]

5-(4-*n*-Decanoxyphenyl)-10,15,20-tris(4-hydroxyphenyl)porphyrin (14): *p*-THPP[33,34] (300 mg, 0.44 mmol) was treated with 1-bromodecane (0.4 M in DMF, 2.2 mL, 0.88 mmol) in the presence of K_2CO_3 (608 mg, 4.40 mmol) in DMF (30 mL) at room temperature for 1 d and at 70 °C for 2 h. After filtration, the material was extracted with chloroform, washed with water and brine, and dried with sodium sulfate. The solvent was removed under reduced pressure, and the porphyrin derivatives having one to four decyl groups were separated by column chromatography. Yield: 118.3 mg (33%). R_f = 0.22 (chloroform/methanol, 20:1). ^{1}H NMR (300 MHz, [D$_6$]-DMSO): δ = 8.89 (m, 8 H, pyr), 8.06 (d, J = 8.4 Hz, 2 H, 2,6-H aryl), 7.98 (d, J = 8.3 Hz, 6 H, 2,6-H aryl), 7.27 (d, J = 8.4 Hz, 2 H, 3,5-H aryl), 7.21 (d, J = 8.3 Hz, 6 H, 3,5-H aryl), 4.20 (t, 2 H, 1-H decyl), 1.91 (m, 2 H, 2-H decyl), 1.58–1.19 (m, 14 H, 3,4,5,6,7,8,9-H decyl), 0.90 (t, 3 H, 10-H decyl), –2.85 (br. s, 2 H, NH) ppm.

5,10-Bis(4-decanoxyphenyl)-15,20-bis(4-hydroxyphenyl)porphyrin (15): Compound **15** was obtained as a byproduct in the synthesis of **14**. Yield: 82.9 mg (20%). R_f = 0.31 (chloroform/methanol, 20:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.84 (m, 8 H, pyr), 8.08 (d, J = 8.3 Hz, 4 H, 2,6-H aryl), 7.99 (d, J = 8.1 Hz, 4 H, 2,6-H aryl), 7.23 (d, J = 8.3 Hz, 4 H, 3,5-H aryl), 7.03 (d, J = 8.1 Hz, 4 H, 3,5-H aryl), 4.19 (t, 2×2 H, 1-H decyl), 1.95 (m, 2×2 H, 2-H decyl), 1.60–1.25 (m, 2×14 H, 3,4,5,6,7,8,9-H decyl), 0.91 (t, 2×3 H, 10-H decyl), –2.77 (br. s, 2 H, NH) ppm.

5,15-Bis(4-decanoxyphenyl)-10,20-bis(4-hydroxyphenyl)porphyrin (16): Compound **16** was obtained as a byproduct in the synthesis of **14**. Yield: 45.4 mg (11%). R_f = 0.38 (chloroform/methanol, 20:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.79 (d, J = 4.9 Hz, 4 H, pyr), 8.77 (d, J = 4.9 Hz, 4 H, pyr), 8.01 (d, J = 8.6 Hz, 4 H, 2,6-H aryl), 7.97 (d, J = 8.4 Hz, 4 H, 2,6-H aryl), 7.17 (d, J = 8.6 Hz, 4 H, 3,5-H aryl), 7.07 (d, J = 8.4 Hz, 4 H, 3,5-H aryl), 4.14 (t, 2×2 H, 1-H decyl), 1.90 (m, 2×2 H, 2-H decyl), 1.51–1.18 (m, 2×14 H, 3,4,5,6,7,8,9-H decyl), 0.85 (t, 2×3 H, 10-H decyl), –2.86 (br. s, 2 H, NH) ppm.

5,15,20-Tris(4-decanoxyphenyl)-20-(4-hydroxyphenyl)porphyrin (17): Compound **17** was obtained as a byproduct in the synthesis of **14**. Yield: 85.3 mg (18%). R_f = 0.58 (chloroform/methanol, 20:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.86 (m, 8 H, pyr), 8.09 (d, J = 8.5 Hz, 6 H, 2,6-H aryl), 8.05 (d, J = 8.4 Hz, 2 H, 2,6-H aryl), 7.25 (d, J = 8.5 Hz, 6 H, 3,5-H aryl), 7.15 (d, J = 8.4 Hz, 2 H, 3,5-H aryl), 4.23 (t, 3×2 H, 1-H decyl), 1.98 (m, 3×2 H, 2-H decyl), 1.64–1.25 (m, 3×14 H, 3,4,5,6,7,8,9-H decyl), 0.91 (t, 3×3 H, 10-H decyl), –2.75 (br. s, 2 H, NH) ppm.

5,10,15,20-Tetakis(4-decanoxyphenyl)porphyrin (18): Compound **18** was obtained as a byproduct in the synthesis of **14**. Yield: 28.9 mg (5%). R_f = 0.19 (hexane/chloroform, 1:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.87 (m, 8 H, pyr), 8.08 (d, J = 8.5 Hz, 8 H, 2,6-H aryl), 7.23 (d, J = 8.5 Hz, 8 H, 3,5-H aryl), 4.20 (t, 4×2 H, 1-H decyl), 1.95 (m, 4×2 H, 2-H decyl), 1.50–1.25 (m, 4×14 H, 3,4,5,6,7,8,9-H decyl), 0.91 (t, 5×3 H, 10-H decyl), –2.74 (br. s, 2 H, NH) ppm.

5-(4-Ethoxyphenyl)-10,15,20-tris{4-[3-(nonadeca-*O*-acetyl-β-D-maltohexaosyl)propoxy]phenyl}porphyrin (19): A mixture of **9** (64.0 mg, 90.6 μmol), **S**-I (531.8 mg, 271.8 μmol), and K_2CO_3 (125.0 mg, 0.91 mmol) in DMF (20 mL) was stirred for 7 d at room temperature. After filtration, the material was extracted with ethyl acetate, washed with water and brine, and dried with sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography. Yield: 215.5 mg (38%). R_f = 0.16 (toluene/acetone, 2:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.84 (m, 8 H, pyr), 8.11 (m, 8 H, 2,6-H aryl), 7.26 (m, 8 H, 3,5-H aryl), 5.47–3.76 (m, 3×42 H, maltohexaose), 4.06 (m, 14 H, 1,3-H propyl, 1-H ethyl), 2.24–1.98 (m, 3×57 H, acetyl), 1.62 (t, 3 H, 2-H ethyl), –2.77 (br. s, 2 H, NH) ppm. $C_{277}H_{346}N_4O_{154}$ (6195.71): calcd. C 53.70, H 5.63, N 0.90; found C 53.88, H 5.70, N 0.97.

5-(4-Decanoxyphenyl)-10,15,20-tris{4-[3-(nonadeca-*O*-acetyl-β-D-maltohexaosyl)propoxy]phenyl}porphyrin (20): A mixture of **14** (89.6 mg, 109.4 μmol), **S**-I (642.5 mg, 0.33 mmol), and K_2CO_3 (150.6 mg, 1.09 mmol) in DMF (10 mL) was stirred for 5 d at room temperature. After filtration, the material was extracted with ethyl acetate, washed with water and brine, and dried with sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography. Yield: 246.8 mg (36%). R_f = 0.23 (toluene/acetone, 2:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.84 (m, 8 H, pyr), 8.11 (d, J = 8.5 Hz, 8 H, 2,6-H aryl), 7.27 (d, J = 8.5 Hz, 8 H, 3,5-H aryl), 5.47–3.76 (m, 3×42 H, maltohexaose), 4.06 (m, 14 H, 1,3-H propyl, 1-H decyl), 2.24–1.98 (m, 3×57 H, acetyl), 1.60 (m, 3×2 H, 2-H propyl), 1.32–1.21 (m, 14 H, 3,4,5,6,7,8,9-H decyl), 0.91 (t, 3 H, 10-H decyl), –2.77 (br. s, 2 H, NH) ppm. $C_{285}H_{362}N_4O_{154}$ (6307.93): calcd. C 54.27, H 5.78, N 0.89; found C 54.15, H 5.88, N 0.90.

5-(4-Hydroxyphenyl)-10,15,20-tris{4-[3-(β-D-maltohexaosyl)-propoxy]phenyl}porphyrin (3MalTPP): Sodium methoxide in dry methanol (2.0 mL, 2 wt.-%) was added to a solution of **1** (241.2 mg, 39.1 μmol) in dry THF (10.0 mL). After desalting by dialysis, 3MalTPP was purified by freeze drying (126.5 mg, 86%). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.97 (br. s, 1 H, -OH phenol), 8.81 (s, 8 H, pyr), 8.05 (d, J = 8.1 Hz, 6 H, 2,6-H aryl), 7.94 (d, J = 8.3 Hz, 2 H, 2,6-H aryl), 7.33 (d, J = 8.1 Hz, 6 H, 3,5-H aryl), 7.15 (d, J = 8.3 Hz, 2 H, 3,5-H aryl), 5.80–2.96 (m, 3×42 H, maltohexaose), 4.33 (m, 3×4 H, 1,3-H propyl), 2.14 (m, 3×2 H, 2-H propyl), –2.96 (br. s, 2 H, NH) ppm. MS (ESI): m/z = 3771.41. UV/Vis (DMSO): λ (ε / M^{-1} cm^{-1}) = 424 (383000), 520 (13900), 558 (11300), 595 (4500), 652 (6100) nm. UV/Vis (H$_2$O): λ (ε / M^{-1} cm^{-1}) = 426 (219000), 519 (12300), 558 (8500), 590 (4800), 649 (5100) nm.

5-(4-Ethoxyphenyl)-10,15,20-tris{4-[3-(β-D-maltohexaosyl)-propoxy]phenyl}porphyrin (1E3MalTPP): Sodium methoxide in dry methanol (2.0 mL, 2 wt.-%) was added to a solution of **19** (163.6 mg, 26.4 μmol) in dry THF (10.0 mL). After desalting by dialysis, 1E3MalTPP was purified by freeze drying (91.2 mg, 91%). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.87 (s, 8 H, pyr), 8.12 (d, J = 8.1 Hz, 8 H, 2,6-H aryl), 7.38 (d, J = 8.1 Hz, 8 H, 2,6-H aryl), 5.61–3.03 (m, 3×42 H, maltohexaose), 4.39–4.31 (m, 14 H, 1,3-H propyl, 1-H ethyl), 2.20 (br. m, 3×2 H, 2-H propyl), 1.54 (t, 3 H, 2-H ethyl), –2.89 (br. s, 2 H, NH) ppm. MS (ESI): m/z = 3800.35. UV/Vis (DMSO): λ (ε / M^{-1} cm^{-1}) = 424 (447000), 520 (16200), 557 (12100), 596 (4900), 651 (6400) nm. UV/Vis (H$_2$O): λ (ε / M^{-1} cm^{-1}) = 427 (227000), 521 (13600), 559 (9300), 595 (4800), 651 (5300) nm.

5-(4-Butoxyphenyl)-10,15,20-tris{4-[3-(β-D-maltohexaosyl)-propoxy]phenyl}porphyrin (1B3MalTPP): Sodium methoxide in dry methanol (2.0 mL, 2 wt.-%) was added to a solution of **6** (109.4 mg, 17.6 μmol) in dry THF (8.0 mL). After desalting by dialysis, 1B3MalTPP was purified by freeze drying (67.1 mg, 99%). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.87 (s, 8 H, pyr), 8.10 (m, 8 H, 2,6-H aryl), 7.38 (m, 8 H, 2,6-H aryl), 5.57–3.06 (m, 3×42 H, maltohexaose), 4.39–4.31 (m, 14 H, 1,3-H propyl, 1-H butyl), 2.20 (br. m, 3×2 H, 2-H propyl), 1.91 (m, 2 H, 2-H butyl), 1.60 (m, 2 H, 3-H butyl), 1.07 (t, 3 H, 4-H butyl), –2.90 (br. s, 2 H, NH) ppm. MS (ESI): m/z = 3828.31. UV/Vis (DMSO): λ (ε / M^{-1} cm^{-1}) = 424 (485000), 519 (18000) 557 (14400), 595 (5900), 652 (7600) nm. UV/Vis (H$_2$O): λ (ε / M^{-1} cm^{-1}) = 427 (216000), 521 (14100), 560 (11100), 594 (5600), 652 (5300) nm.

5-(4-Hexanoxyphenyl)-10,15,20-tris{4-[3-(β-D-maltohexaosyl)-propoxy]phenyl}porphyrin (1H3MalTPP): Sodium methoxide in dry methanol (2.0 mL, 2 wt.-%) was added to a solution of **7** (145.6 mg, 23.3 μmol) in dry THF (10.0 mL). After desalting by dialysis, 1H3MalTPP was purified by freeze drying (89.6 mg, 100%). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.80 (s, 8 H, pyr), 8.05 (m, 8 H, 2,6-H aryl), 7.32 (m, 8 H, 3,5-H aryl), 5.55–2.96 (m, 3×42 H, maltohexaose), 4.33 (m, 3×4 H, 1,3-H propyl) 4.20 (m, 2 H, 1-H hexyl), 2.13 (br. m, 6 H, 2-H propyl), 1.84 (m, 2 H, 2-H hexyl), 1.52 (m, 2 H, 3-H hexyl), 1.36 (m, 4 H, 4,5-H hexyl), 0.90 (t, 3 H, 6-H hexyl), –2.96 (br. s, 2 H, NH) ppm. MS (ESI): *m*/*z* = 3855.66. UV/Vis (DMSO): λ (ε / M^{-1}cm^{-1}) = 424 (433000), 519 (15500), 557 (11700), 596 (4600), 651 (6500) nm. UV/Vis (H$_2$O): λ (ε / M^{-1}cm^{-1}) = 427 (206000), 521 (13300), 561 (9500), 594 (4600), 652 (5300) nm.

5-(4-Decanoxyphenyl)-10,15,20-tris{4-[3-(β-D-maltohexaosyl)-propoxy]phenyl}porphyrin (1D3MalTPP): Sodium methoxide in dry methanol (5.0 mL, 2 wt.-%) was added to a solution of **20** (797.8 mg, 126.5 μmol) in dry THF (30.0 mL). After desalting by dialysis, 1D3MalTPP was purified by freeze drying (487.1 mg, 98%). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.81 (s, 8 H, pyr), 8.06 (m, 8 H, 2,6-H aryl), 7.32 (m, 8 H, 3,5-H aryl), 5.80–2.96 (m, 3×42 H, maltohexaose), 4.32 (m, 3×4 H, 1,3-H propyl) 4.20 (m, 2 H, 1-H decyl), 2.13 (m, 3×2 H, 2-H propyl), 1.84 (m, 2 H, 2-H decyl), 1.51 (m, 2 H, 3-H decyl), 1.24 (m, 12 H, 4,5,6,7,8,9-H decyl), 0.82 (t, 3 H, 10-H decyl), –2.96 (br. s, 2 H, NH) ppm. MS (ESI): *m*/*z* = 3911.28. UV/Vis (DMSO): λ (ε / M^{-1}cm^{-1}) = 424 (422000), 519 (15400), 557 (12200), 594 (4800), 651 (6600) nm. UV/Vis (H$_2$O): λ (ε / M^{-1}cm^{-1}) = 426 (211000), 521 (12700), 559 (9700), 595 (4100), 652 (5000) nm.

5-(4-Hexadecanoxyphenyl)-10,15,20-tris{4-[3-(β-D-maltohexaosyl)-propoxy]phenyl}porphyrin (1HD3MalTPP): Sodium methoxide in dry methanol (1.0 mL, 2 wt.-%) was added to a solution of **8** (47.3 mg, 7.4 μmol) in dry THF (5.0 mL). After desalting by dialysis, 3HD1MalTPP was purified by freeze drying (21.4 mg, 72%). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.87 (s, 8 H, pyr), 8.12 (m, 8 H, 2,6-H aryl), 7.38 (m, 8 H, 3,5-H aryl), 5.60–3.07 (m, 3×42 H, maltohexaose), 4.39 (m, 3×4 H, 1,3-H propyl) 4.27 (m, 2 H, 1-H hexadecyl), 2.20 (m, 3×2 H, 2-H propyl), 1.88 (m, 2 H, 2-H hexadecyl), 1.58 (m, 2 H, 3-H hexadecyl), 1.21–1.09 (m, 24 H, 4,5,6,7,8,9,10,11,12,13,14,15-H hexadecyl), 0.82 (t, 3 H, 16-H hexadecyl), –2.89 (br. s, 2 H, NH) ppm. UV/Vis (DMSO): λ (ε / M^{-1}cm^{-1}) = 424 (546000), 519 (20200), 557 (16100), 595 (6700), 651 (8400) nm. UV/Vis (H$_2$O): λ (ε / M^{-1}cm^{-1}) = 428 (240000), 522 (14400), 560 (11500), 592 (4900), 651 (5300) nm.

Measurements: NMR was measured with a Bruker ASX 300. Absorbance spectra were measured with a JASCO Ubest-50, fluorescent spectra were measured with a Hitachi F-4500, CD spectra were measured with a JASCO J-720. SLS measurement was performed at Ohtsuka denshi, using DLS-7000. Aggregation properties of these porphyrins were investigated by absorbance and CD spectra. A 1-mm cell was used for a measurement for 10^{-4} to 10^{-5} M order of concentration, and a 1-cm cell was used for 10^{-6} to 10^{-7} M concentration. Measurement was performed within 15 min after the solution was prepared.

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