Supporting Information

Cyclodipeptide-bridged Porphyrin Dimer SupramolecularAssemblies

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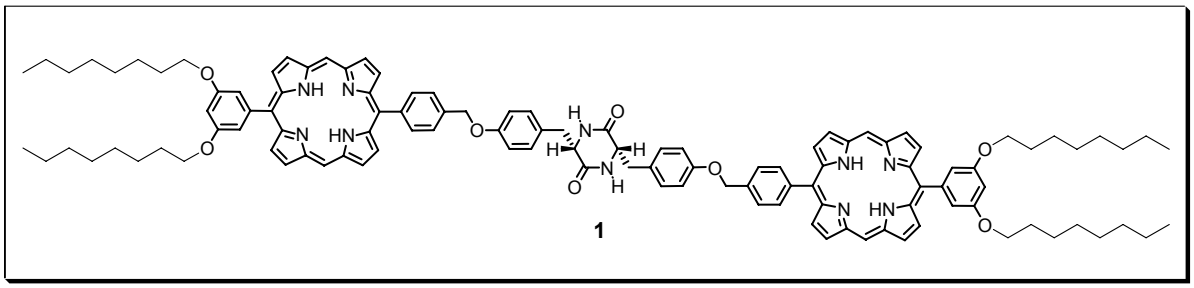
Experimental Details

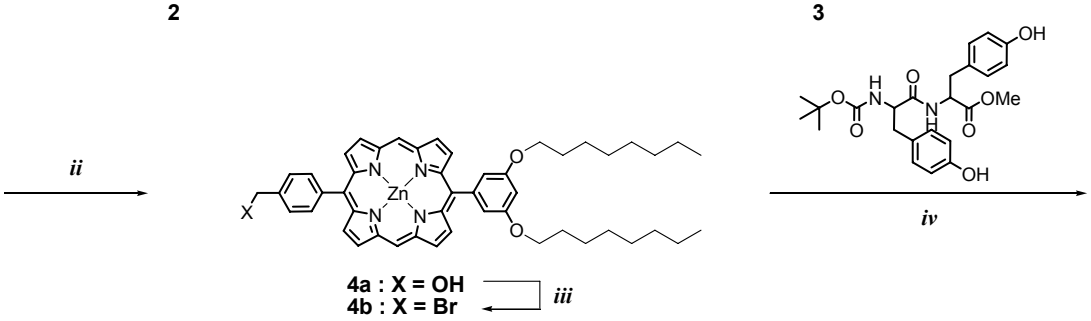
Materials. All reactions were performed under nitrogen unless stated otherwise.All commercially available reagents were reagent grade and used without furtherpurification. Dichloromethane, hexane, tetrahydrofuran (THF), and ethyl acetate were freshly distilled before each use.

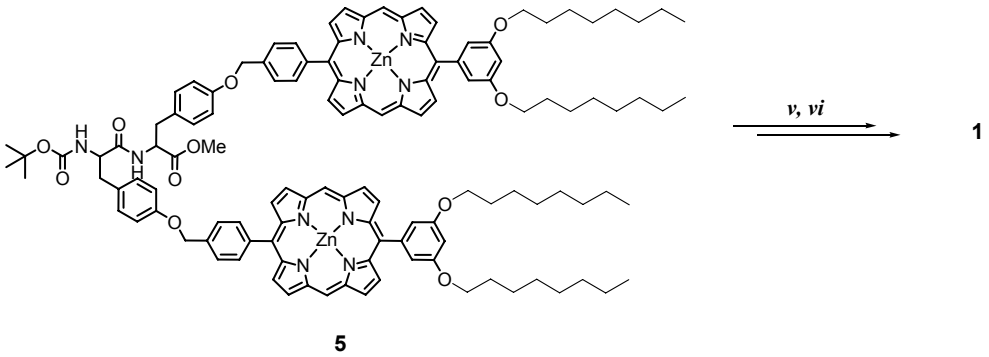
Measurements.UV-Vis, FT-IR absorption, fluorescence emission, and circular dichroism (CD) spectra were recorded using a JASCO model V-660, JASCO model FT-IR430 spectrometer,HitachiF–4500 fluorescence spectrophotometer, and JASCO J-810 spectropolarimeter, respectively. ^{1}HNMR spectra were recorded using a Bruker DPX 400 (400 MHz) spectrometer. MALDI-TOF-MSmeasurements were performed on a Perceptive Biosystems Voyager-DE STR using a-cyano-4-hydroxy-cinnamic acid as thematrix. Transmission electron microscopy (TEM) was performed at 100 and 200 kV using Hitachi-7600and JEOL-2100 instruments, respectively.The samples were prepared by drop-castingof a toluene solution of **1**onto carbon coated copper grids (200 mesh). TEM images were obtained after staining with RuO_4 vapor by placing the TEM grids above anaqueous RuO_4 solution for 15-30 min in a closed chamber, followed by drying thesample under vacuum for 24 hrs.For atomic force microscopy (AFM) observation, toluene solutions of **1**at various concentrationswere placed on freshly cleaved mica surface and spin-coatedat 2000 rpm for 1 min. Images were obtained usingSFM (Dimension 3100, Digital Instrument Co.), Agilent Technologies 5500 AFM, andPUCOStation STD™ (Bruker Nano-GmbH) instruments.

Time resolvedfluorescence. A picosecond time-correlated single photon counting (TCSPC) system was used for time-resolved fluorescence decay measurements. The system consisted of a cavity-dumped Kerr lens mode-locked Ti:sapphire laser pumped by a continuous wave Nd:YVO_4 laser (Spectra Physics, Millennia). The second-harmonic of the fundamental beam was generated in a 1-mm thick BBO crystal and served as the excitation source. The residual beam was used as a trigger source detected by a fast photodiode, and the excitation beam was focused onto a 10-mm thick cuvette containing the sample solution using a 5 cm focal length lens with s-polarization. Fluorescence from the sample was collected, focused to a monochromator (Acton Research) by a 2″ plano-convex lens pair, and detected using a microchannel plate photomultiplier tube (Hamamatsu). The full width at half-maximum (FWHM) of the instrument response function obtained by a dilute solution of coffee cream (diffuser) was typically 70 ps.

Synthesis







Scheme S1. Synthesis of a cyclodipeptide-bridged porphyrin dimer. Reagents and reaction conditions:*i*) $C_8H_{17}Br$, K_2CO_3, 18-C-6, THF, reflux, 24 h;*ii*) $LiAlH_4$,THF, 4°C, 1 hr;*iii*) CBr_4, PPh_3,THF, 4°C, 2 hrs;*iv*) ^{tert}Boc-(*L*)-Tyr-(*L*)-Ala-OMe, K_2CO_3, 18-C-6, THF, reflux, 24 hrs;*v*) TFA, CH_2Cl_2, r.t.,12 hrs;*vi*) 180°C, 24 hrs.

2:A CH_2Cl_2/MeOH (20:1) solution (800mL) mixture of 3,5-dihydroxybenzaldehyde (1.2g 7.24mmol), terephalaldehydic acid methyl ester (1.19g 7.24mmol), and dipyrromethane (2.11 g, 14.5mmol) was stirred in the presence of $BF_3{\cdot}OEt_2$ (2 mL, 15.92 mmol) under N_2 at room temperature for 12 hrs. After stirring,*p*-chloranil (5.18 g, 21.1mmol) was added, and the mixture was stirred for an additional 12 h at room temperature. The reaction mixture was concentrated to a volume of 200 mL and then separated by silica gel chromatography in 3% MeOH/CH_2Cl_2. Without further purification, the product was dissolved in 10% MeOH/CH_2Cl_2 containing $Zn(OAc)_2$ (6.51 g, 29.67 mmol) and then stirred for 12 h at 25°C. The reaction mixture was purified by column chromatography with 3% MeOH/CH_2Cl_2, and the second fraction was collected and evaporated to dryness. The residue was recrystallized from CH_2Cl_2/hexane to give **2** as a reddish purple powder (568 mg, 15%).^{1}H NMR (400 MHz, $CDCl_3$): δ 4.07(s, 3H; -OCH_3), 6.68 and 7.08(s, 3H; C_6H_3), 8.37-8.44(q, 4H; C_6H_4), 8.91-9.53(m, 8H; pyrrole-β-H), 10.37(s, 2H; meso-H in porphyrin). MALDI-TOF-MS m/z calcd for $C_{34}H_{22}N_4O_4Zn$ (M^+) 615.97, found 614.08.

3:A dry THF solution (30 mL) mixture of $C_8H_{17}Br$ (5 mL, 28.8 mmol), **2**(890 mg, 1.44 mmol), anhydrous K_2CO_3 (2 g, 14.4 mmol), and 18-crown-6 ether (760 mg, 0.288 mmol) was refluxed under N_2 for 24 hrs, and subsequently evaporated. A CH_2Cl_2 solution (100 mL) of the residue was washed with water (3 x 100 mL), dried over Na_2SO_4, and evaporated. The residue was chromatographed on silica gel using CH_2Cl_2 as the eluent, and the first fraction was collected and evaporated to dryness. The residue was freeze-dried from benzene, to give **3**as a bright red powder in 71% yield (840 mg). ^{1}H NMR (270 MHz, $CDCl_3$, 25°C): δ = 0.84-1.51 (m, 34H, -(CH_2)$_7$$CH_3$), 1.88 (m, 4H, -$OCH_2CH_2$-), 4.11 (s,3H; -$CO_2CH_3$), 4.16 (t, 4H; -$OCH_2$-), 6.90 (s, 1H; *p*-H in porphyrin-C_6H_3), 7.42 (d, 2H; *o*-H in porphyrin-C_6H_3), 8.20 (d, 2H; *m*-H in porphyrin-C_6H_4), 8.33 (d, 2H; *o*-H in prophyrin-C_6H_4), 8.91-9.34 (m, 8H; pyrrole-β-H), 10.10 (s, 2H; *meso*-H of porphyrin).MALDI-TOF-MS m/z calcd for $C_{50}H_{54}N_4O_4Zn$ (M^+) 840.40, found 840.69.

4a:A THF suspension (100 mL) of $LiAlH_4$ (57.6 mg, 1.52 mmol) was added to a dry THF solution (100 mL) of **3** (850 mg, 1.01 mmol) over a period of 1 hr with vigorous stirring at 4°C under N_2. The reaction mixture was then poured into ice water (100 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The combined extract was washed with water (3 x 100 mL), dried over Na_2SO_4, and evaporated to dryness. The residue was chromatographed on silica gel using CH_2Cl_2 as the eluent, and the second fraction was collected, evaporated to dryness, and freeze-dried from benzene to give **4a** as a bright red powder in 91% yield (812 mg). ^{1}H NMR (270 MHz, $CDCl_3$, 25°C): δ = 0.80-1.52 (m, 34H, -(CH_2)$_7$$CH_3$), 1.86 (m, 4H, -OC$H_2CH_2$-), 4.13 (t, 4H; -OC$H_2$-), 4.97 (d, 2H; -C$H_2$OH), 6.89 (s, 1H; *p*-H in porphyrin-C_6H_3), 7.41 (d, 2H; *o*-H in porphyrin-C_6H_3), 7.71 (d, 2H; *m*-H in porphyrin-C_6H_4), 8.23 (d, 2H; *o*-H in porphyrin-C_6H_4), 9.09-9.42 (m, 8H; pyrrole-β-H), 10.30 (s, 2H; meso-H of porphyrin).MALDI-TOF-MS m/z calcd for $C_{49}H_{54}N_4O_3Zn$ (M^+) 812.39, found 812.76.

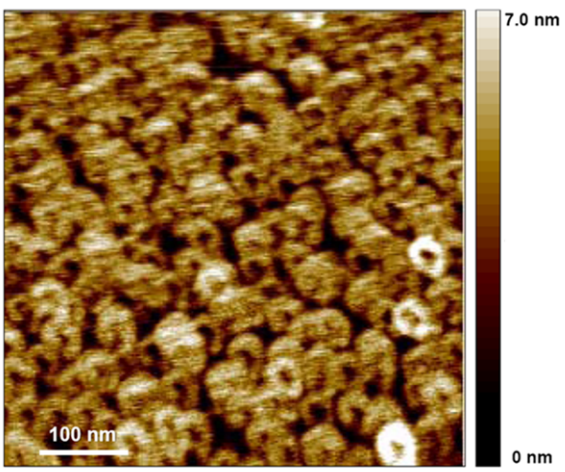
4b:PPh_3 (478 mg, 1.82mmol) was added to a dry THF solution (130 mL) mixture of **4a**(740 mg, 0.911mmol) and CBr_4 (604 mg, 182mmol)over a period of 1 hr with vigorous stirring at 4°Cunder N_2, with subsequentstirring for 2 hr at room temperature. The reactionmixture was poured into aqueous $NaHCO_3$ (50 mL) and extracted with CH_2Cl_2 (3 x50 mL). The combined extract was washed with water (3 x 100 ml), dried overNa_2SO_4, and evaporated to dryness. The residue was chromatographed on silica gelusing CH_2Cl_2 as the eluent, and the first fraction was collected, evaporated to dryness,and freeze-dried from benzene to give **4b**as a bright red powder in 48% yield (380mg). ^{1}H NMR(270 MHz, $CDCl_3$, 25°C): δ = 0.80-1.72 (m, 34H, -(CH_2)$_7$$CH_3$), 1.87 (m,4H, -OC$H_2CH_2$-), 4.13 (t, 4H; -OC$H_2$-), 4.87 (d, 2H; -C$H_2$OH), 6.89 (s, 1H; *p*-H in porphyrin-C_6H_3), 7.41 (d, 2H; *o*-H in porphyrin-C_6H_3), 7.71 (d, 2H; m-H in porphyrin-C_6H_4), 8.23 (d, 2H;*o*-H in porphyrin-C_6H_4), 9.09-9.40 (m, 8H; pyrrole-β-H), 10.29 (s, 2H; meso-H of porphyrin).MALDI-TOF-MS m/z calcd for $C_{49}H_{53}BrN_4O_2Zn$ (M^+) 875.28, found 874.1.

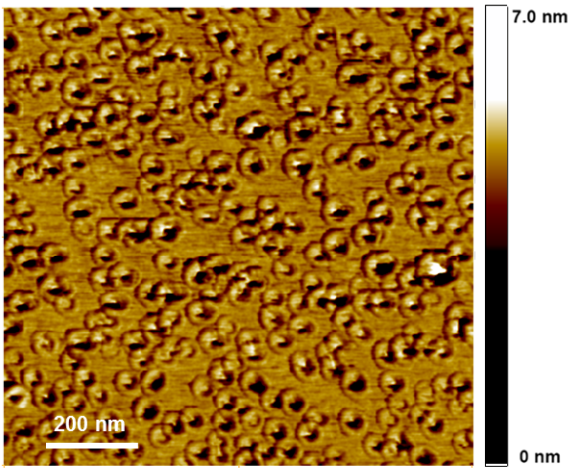
5:A dry THF solution (15 mL) mixed with^{tert}Boc-(*L*)-Tyr-(*L*)-Ala-OMe(25.6 mg, 0.0557mmol), **4b** (100 mg, 0.114 mmol),anhydrous K_2CO_3 (77 mg, 0.557mmol), and 18-crown-6 ether (2.95 mg, 0.011 mmol) was refluxed underN_2 for 24 hrs.The resulting reaction mixture was evaporated, and the residue was mixed with CH_2Cl_2 (15 mL) and washed with water (3 x 100 mL), dried over Na_2SO_4, and evaporated. The residue was chromatographed on silica gel using 3% MeOH/CH_2Cl_2 as the eluent, and the first fraction was collected and evaporated to dryness. The residue was freeze-dried from benzene, to give **5**as a reddish purple powder in 26% yield (61 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87(t, 12H; -$(CH_2)_7CH_3$), 1.26-1.45(m, 40H; -$(CH_2)_5CH_3$), 1.96(m, 8H; -OCH_2CH_2-), 2.90 and 3.12(m, 4H; -CH_2- in Tyr),3.88(s, 3H; -OCH_3), 4.29(m, 8H; -OCH_2-), 4.55 and 5.05(m, 2H; -CH- in Tyr), 5.53(d, 4H; -OCH_2-Ar), 7.16(m, 10H; *p*-H in C_6H_3 and C_6H_4 in Tyr), 7.64(s, 4 H; *o*-H in C_6H_3), 7.64-8.50(d, 8H; C_6H_4 in porphyrin), 9.09-9.57(m, 16H; pyrrole-β-H), 10.96(s, 4H; meso-CH in porphyrin). MALDI-TOF-MS m/z calcd for $C_{117}H_{126}N_{10}O_9Zn_2(M^+)$ 2047.21, found 2047.73.

1:Compound**5**(61 mg, 0.0298 mmol) was dissolved in CH_2Cl_2 (20 mL) with subsequent addition of CF_3CO_2H (TFA) (2 mL) for N-Boc deprotection. The reaction mixture was stirred for 12 hrs at room temperature. A CH_2Cl_2 solution (20 mL) of the residue was washed with water (3 x 100 mL), dried over Na_2SO_4, and evaporated. After solvent evaporation, the residue was heated at 180°C for 24 hrs. The residue was chromatographed on silica gel using 3% MeOH/CH_2Cl_2 as the eluent, and the first fraction was collected, evaporated to dryness, and freeze-dried from benzene to give **1** as a reddish purple powderwith 43% yield (23 mg).^{1}H NMR (400 MHz, $CDCl_3$): δ -3.17 (s, 4 H), 0.86(t, 12H; -$(CH_2)_7CH_3$), 1.25-1.45(m, 40H; -$(CH_2)_5CH_3$), 2.00(m, 8H; -OCH_2CH_2-), 2.50 and 3.20(m, 4H; -CH_2- in Tyr), 4.11(m, 8H; -OCH_2-), 4.22(m, 2H; -CH- in Tyr), 5.32(d, 4H; -OCH_2-Ar), 6.90(s, 2H; *p*-C_6H_3), 7.21(m, 8H; C_6H_4 in Tyr), 7.40(d, 4H; *o*-C_6H_3), 7.70 and 8.15(d, 8H; C_6H_4 in porphyrin), 8.99-9.32(m, 16H; pyrrole-β-H), 10.22(s, 4H; meso-CH in porphyrin).^{13}C NMR (400 MHz, $CDCl_3$): δ 14.10, 22.66, 26.13, 29.31, 29.42, 31.82, 39.50, 53.42, 56.43, 68.64, 69.78, 102.20, 106.01, 111.81, 114.71,

115.62, 116.60, 126.67, 127.79, 129.75, 130.02, 131.25, 137.11, 137.97, 139.54, 141.51, 143.77, 146.22, 146.48, 155.58, 155.95, 158.35, 159.26, 166.90. MALDI-TOF-MS m/z calcd for $C_{116}H_{126}N_{10}O_8$ (M^+) 1788.30, found 1789.2.

AFM images

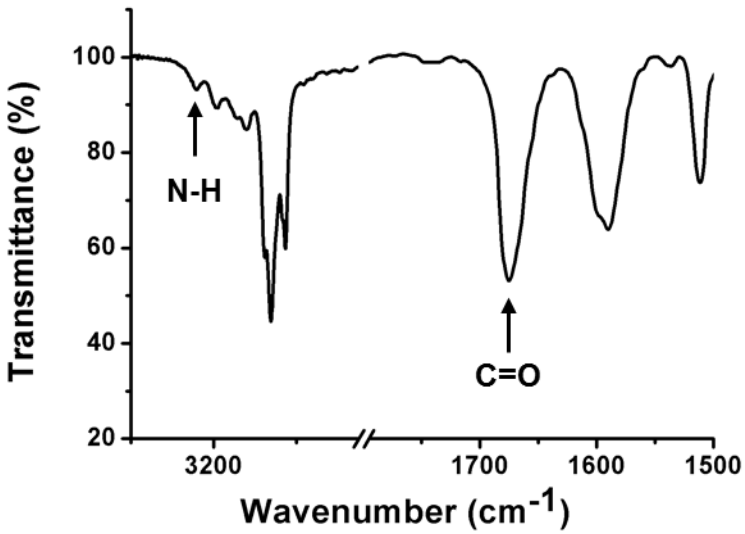




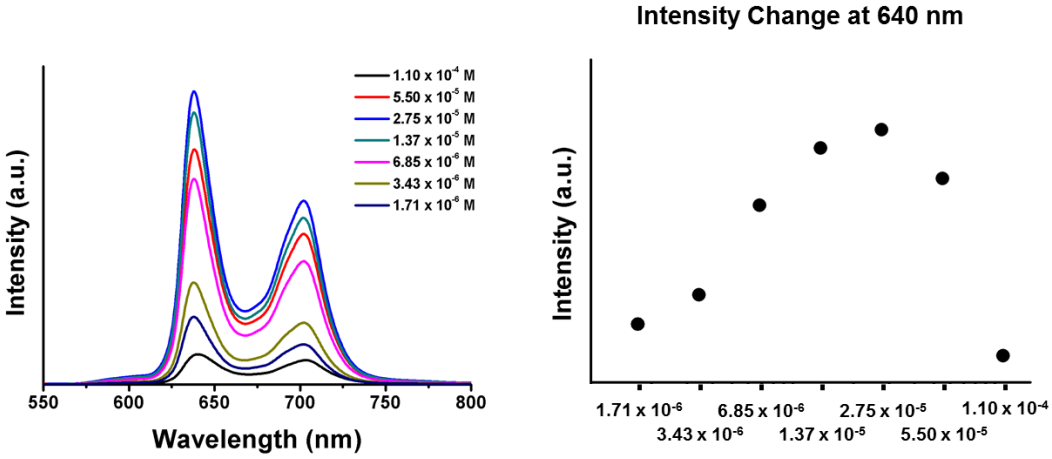
1.37×10^{-5} M
Agilent Technologies 5500 AFM,
MAC III controller, 90 um Scanner

6.87×10^{-6} M
Bruker Nano-GmbH PUCOStation STD ™

IR spectrum of 1



Concentration Dependent Fluorescence Change of 1



Time-resolved Fluorescence Measurements

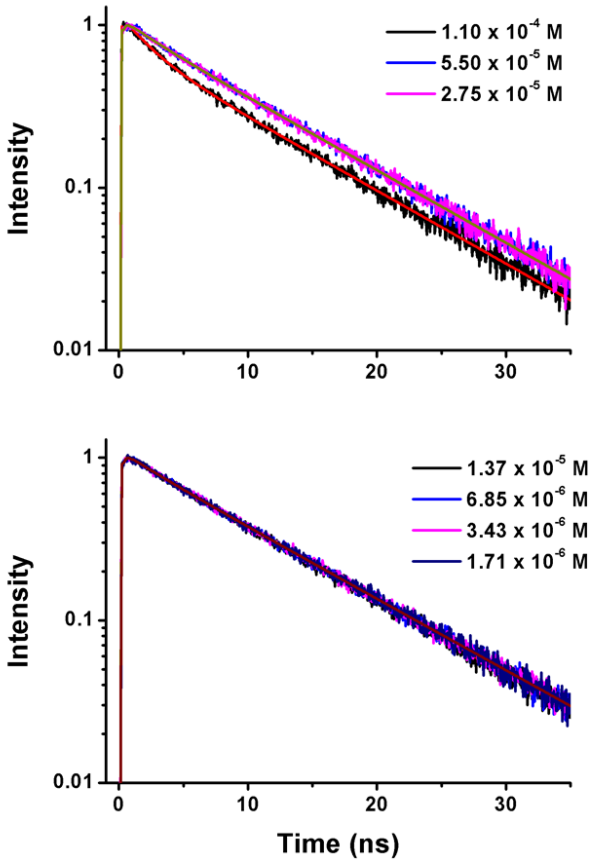


Fig.S1 Time-resolved fluorescence decay profiles of **1**.

Entry	Concentration (M)	τ_1 (ns) / A_1 (%)	τ_2 (ns) / A_2 (%)	χ^2
1	1.10×10^{-4}	9.7 / 66	2.2 / 34	1.09
2	5.49×10^{-5}	9.8 / 90	3.0 / 10	1.02
3	2.75×10^{-5}	9.7 / 90	2.8 / 10	1.09
4	1.37×10^{-5}	9.7 / 93	3.1 / 7	1.07
5	6.87×10^{-6}	9.9 / 92	3.9 / 8	1.06
6	3.43×10^{-6}	9.8 / 95	2.6 / 5	1.00
7	1.72×10^{-6}	9.9 / 92	3.5 / 8	1.00

Table S1 Fluorescencelifetime of **1** at various concentrations.

Plausible Structures of Self-Assemblies

From the TEM and AFM images, the self-assembled structure sizes were obtained, as shown in Fig.S2. From the literature,thecrystal structure of a cyclic phenylalanine dimer (Fig.S3a), which is a structural analog of cyclodipeptide core in**1**,was obtained.[*] The unit cell of the cyclic phenylalanine dimercrystal wasorthorhombic, $P22_12_1$, a = 0.6181, b = 1.0380, c = 2.3795 nm. The thickness of both the fibrous and toroidal structure was about 1 nm, which is consistent with the b axis length in the unit cell. Each cyclic phenylalanine dimer formeda cofacial dimeric array. Based on the crystallographic data, we calculated the molecular dimension of the cofacial dimeric array of **1** (Fig.S3b), which coincided well with the observed values (7 nm) in TEM measurement. Therefore, we concluded that **1**formeda cofacial dimeric array to avoid exposure of polar amide groups to the nonpolar environment.High-resolution TEM images also support the formation of a cofacial dimeric array, where each single elemental fibril is composed of a two-paralleled line with dark contrast (Fig. 3c). On the other hand, fragmentationof the long fibrous assembly could occur by solution dilution. In fact, when the 1.37 x 10^{-5} M solution of **1** was freshly prepared and then subjected to AFM measurement, short fragmented fibrils were observed (Fig. 1f). However, as mentioned before, homogenous toroidal structures were obtained after 1 week of incubation at 4 °C, indicating that the most thermodynamically stable structure is the toroidal assembly under this condition, as the short fragments would be unstable due to exposure of the polar terminals to the nonpolar environment. Therefore, the terminals can be closed to form a toroidal assembly.Considering the diameter of toroid, the number of porphyrin unit can be estimated to about 270 units. Although the diameter of toroid is 20 nm, we need to consider the thickness of fibrous assembly. Considering the thickness of fibrous assembly, exact diameter will be 13 nm. Therefore, the length needed to form toroidal structure will be about 41 nm.

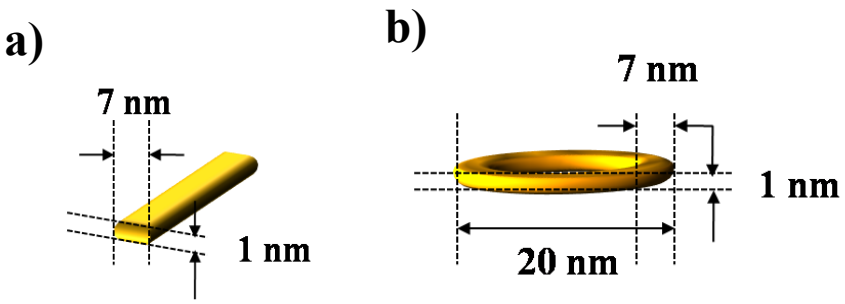


Fig.S2 Size of toroidal and fibrous self-assemblies.

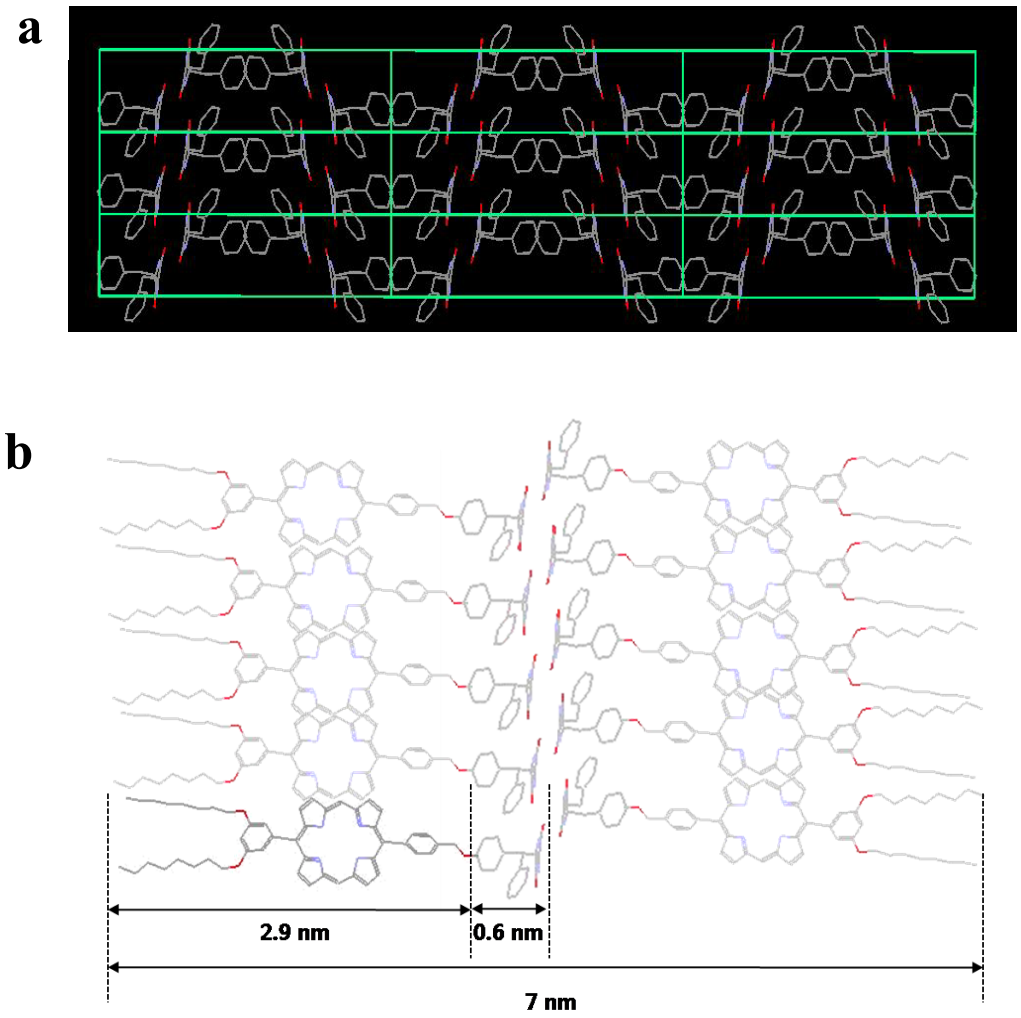


Fig.S3 Crystalstructure of cyc(Phe-Phe) (a) and proposed cofacial dimeric array of **1** (b).

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* Gdaniec, M.; Liberek, B. Acta Cryst. 1986, C42, 1343-1345.