Supplementary Information

Tubular Assembly of Amphiphilic Rigid Macrocycle with Flexible Dendrons

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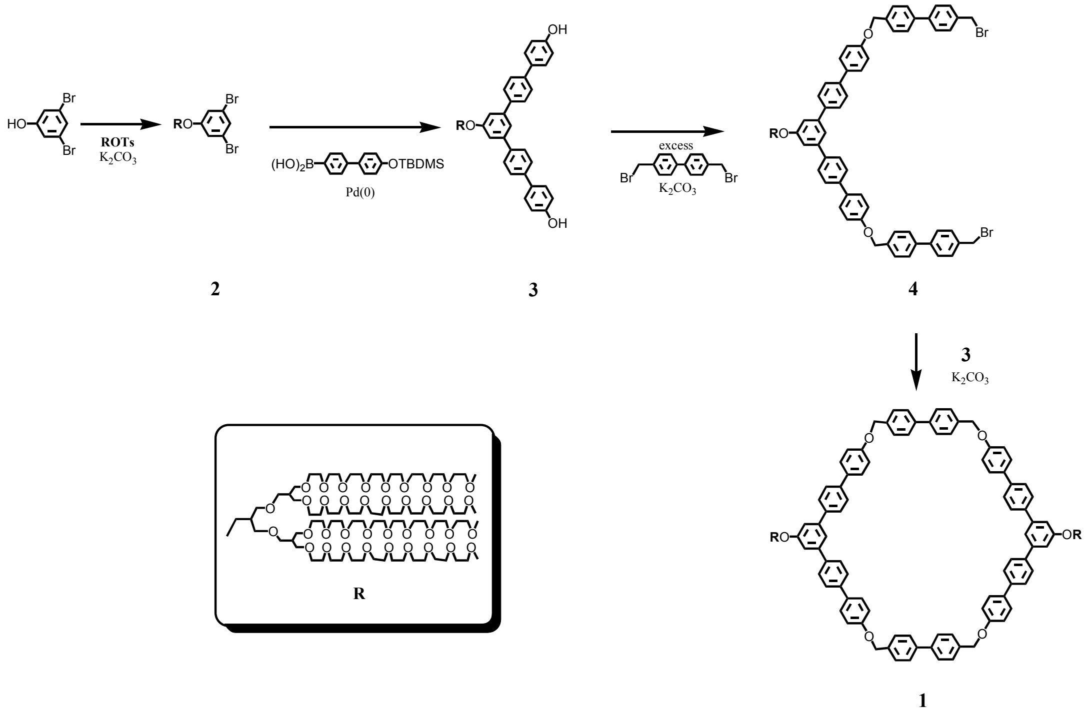
Experimental section

Materials. NaH (60%), *p*-toluenesulfonyl chloride (98%), 4-hydroxy-4'-bromobiphenyl (99%), tetrakis(triphenylphosphine) palladium (0) (99%), and 4,4'-bis(bromomethyl)biphenyl (99%), pentaerythritol (98%) from TCI and Tokyo Kasei were used as received. Poly(ethylene glycol) monomethyl ether (MW 350), *n*-butyllithium (1.6 M solution in *n*-hexane), borane-THF comeplx (1.0 M solution in THF), 18-crown-6 (99%), potassium iodide (99%), triisopropyl borate (98+%) from Aldrich were used as received. Unless otherwise indicated, all other starting materials were obtained from commercial suppliers (Aldrich, Lancaster, etc.) and were used without purification. Single walled carbon nanotubes (purified electric arc-grown SWNTs) were obtained from Iljin Nanotech Co., Ltd. Visualization was accomplished with UV light, iodine vapor. Flash chromatography was carried out with Silica Gel 60 (230-400 mesh) from EM Science. Dry THF was obtained by vacuum transfer from sodium and benzophenone. 4-(*tert*-Butyldimethylsilyloxy)biphenyl-boronic acid and dendritic oligoether coil (ROTs) were prepared according to procedures described previously.[4] Compounds were synthesized according to the procedure described scheme 1 and then purified by silica gel column chromatography and then prep-HPLC until transition temperature and polydispersity index remained constant.

Techniques. ^{1}H NMR and ^{13}C NMR spectra were recorded from $CDCl_3$ solutions on a Bruker AM 250 spectrometer. The purity of the products was checked by thin layer chromatography (TLC; Merck, silica gel 60). A Perkin Elmer DSC-7 differential scanning calorimeter equipped with 1020 thermal analysis controller was used to determine the thermal transitions, which are reported as the maxima and minima of their endothermic or exothermic peaks. In all cases, the heating and cooling rates were 10 ^{o}C min^{-1}. A Nikon optical polarized microscopy (magnification: 100 ×) equipped with a Mettler FP 82 hot-stage and a Mettler FP 90 central processor was used to observe the thermal transitions and to analyze anisotropic texture. Microanalyses were performed with a Perkin Elmer 240 elemental analyzer at the Organic Chemistry Research Center. X-ray scattering measurements were performed in transmission mode with synchrotron radiation at the 3C2 X-ray beam line at Pohang Accelerator Laboratory, Korea. In order to investigate structural changes on heating, the sample was held in an aluminum sample holder, which was sealed with the window of 7 μm thick Kapton films on both sides. The sample was heated with two cartridge heaters and the temperature of the samples was monitored by thermocouple placed close to the sample. Subtracting the scatterings from the Kapton made background scattering correction. Molecular weight distributions (M_n/M_w) were determined by gel permeation chromatography (GPC) with a Waters R401 instrument equipped with Stragel HR 3, 4 and 4E columns, M7725i manual injector, column heating chamber and 2010 Millennium data station. Measurements were made by using an UV detector, $CHCl_3$ as solvent (1.0 mL min^{-1}). Dynamic light scattering measurements were performed using an ALV / CGS-3 Compact Goniometer System. MALDI-TOF-MS was performed on Perseptive Biosystems Voyager-DE STR using a 2,5-dihydroxy benzoic acid matrix, with dissolving **1** in CH_2Cl_2. Optical absorption spectra were obtained from a Shimadzu 1601 UV spectrometer. The steady-state fluorescence spectra were obtained with a Hitachi F-4500 fluorescence spectrophotometer. The transmission electron microscopy (TEM) was performed at 120kV using JEOL 1020. After sample annealed in the liquid crystalline phase and quenched with liquid nitrogen, ultrathin sectioning (*ca.*

50~70 nm thick) of specimens was performed by cryoultramicrotom at -70□ using a RMC PowerTome-XL. Thin sections of specimen were transferred on a carbon-coated copper grid and stained with RuO_4 vapor.



Scheme 1. Synthesis of amphiphilic rigid macrocycle.

Synthesis of compound 2.

3,5-Dibromophenol (1.7 g, 6.8 mmol), **R**OTs (3.0 g, 1.7 mmol), and excess K_2CO_3 (2g, 14.5 mmol) were added to 250 mL of ethanol. The mixture was heated at reflux for 12 hours. The ethanol was removed in a rotary evaporator. The crude product was poured into water and extracted with methylene chloride. The methylene chloride solution was washed with water, dried over anhydrous magnesium sulfate, and then filtered. Solvent was removed in a rotary evaporator, and the crude product was then purified by column chromatography (silicagel, MeOH : ethyl acetate = 1 : 8) to yield 1.6 g (51%) of a colorless liquid. ^{1}H-NMR (250MHz, $CDCl_3$, δ, ppm) δ 7.17 (s, 1Ar-H), 7.00 (d, J = 8.5 Hz, 2Ar-H), 4.07 (d, J = 5.2 Hz, 2H, CH_2Ophenyl), 3.51-3.76 (m, 144H, OCH_2), 3.28 (m, 12H, OCH_3), 2.06-2.13 (m, 3H, $CH(OCH_2)_2$).

Synthesis of compound 3.

Compound **2** (1.6 g, 0.88 mmol) and 4-(*tert*-butyldimethylsilyloxy)biphenyl-boronic acid (0.87 g, 2.6 mmol) were dissolved in degassed THF (70 mL). Degassed 2M aqueous Na_2CO_3 (70 mL) was added to the solution and then tetrakis-(triphenylphosphine)palladium(0) (10 mg, 1 mol%) was added. The mixture was heated at reflux for 48 h with vigorous stirring under nitrogen. Cooled to room temperature, the layers were separated, and the aqueous layer was then extracted twice with methylene chloride. The combined organic layer was dried over anhydrous magnesium sulfate and filtered, and concentrated. The crude product was dissolved in dried THF (100 mL) and added 1M TBAF solution (1 mL). The mixture was stirred for 2 h at room temperature and the solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using ethyl acetate and methanol (4:1 v/v) to yield 1.3 g (68%) of a colorless liquid. ^{1}H-NMR (250MHz, $CDCl_3$, δ, ppm) : δ 7.70-7.41 (m, 13Ar-H), 7.11 (s, 2Ar-H; *o* to OCH_2), 6.91 (d, J=8.4 Hz, 4Ar-H; *o* to OH), 4.07 (d, J = 5.0 Hz, 2H, CH_2Ophenyl), 3.51-3.76 (m, 144H, OCH_2), 3.28 (m, 12H, OCH_3), 2.06-2.13 (m, 3H, $CH(OCH_2)_2$).

Synthesis of compound 4.

Compound **3** (290 mg, 0.13 mmol), 4,4'-bis(bromomethyl)biphenyl (99%) (442 mg, 1.3 mmol) and excess K_2CO_3 (1g, 7.2 mmol) were dissolved in 50 mL of acetone. The mixture was heated at reflux for 4 hours and then cooled to room temperature. The solvent was removed in a rotary evaporator, and the resulting mixture was poured into water and extracted with methylene chloride. The methylene chloride solution was washed with water, dried over anhydrous magnesium sulfate, and filtered. After the solvent was removed in a rotary evaporator, silica gel column chromatography (ethyl acetate: methanol = 1:1) yielded 310 mg (86%) of a waxy liquid. ^{1}H-NMR (250MHz, $CDCl_3$, *δ*, ppm) : *δ* 7.72-7.43 (m, 29Ar-H), 7.18 (s, 2Ar-H; *o* to OCH_2), 7.08 (d, *J*=8.7 Hz, 4Ar-H; *o* to OCH_2phenyl), 5.15 (s, 4H; O*CH₂*phenyl), 4.53 (s, 4H; phenyl*CH₂*Br), 4.07 (d, *J* = 5.3 Hz, 2H, C*H₂*Ophenyl), 3.51-3.76 (m, 144H, OC*H₂*), 3.28 (m, 12H, OC*H₃*), 2.06-2.13 (m, 3H, C*H*(OCH_2)$_2$).

Synthesis of compound 1.

Compound **4** (310 mg, 0.12 mmol), compound **3** (250 mg, 0.12 mmol) and excess K_2CO_3 (0.5 g, 3.1 mmol) were dissolved in 300 mL of acetone. The mixture was heated at reflux for 3 days and then cooled to room temperature. The solvent was removed in a rotary evaporator, and the resulting mixture was poured into water and extracted with methylene chloride. The methylene chloride solution was washed with water, dried over anhydrous magnesium sulfate, and filtered. After the solvent was removed in a rotary evaporator, silica gel column chromatography (ethyl acetate: methanol = 1:1) and then prep-HPLC yielded 110 mg (16%) of a white solid. ^{1}H-NMR (250 MHz, $CDCl_3$, ppm) : *δ* 7.69-7.44 (m, 40Ar-H), 7.38 (s. 2Ar-H), 7.13 (s, 4Ar-H; *o* to OCH_2), 7.00 (d, *J*=8.7 Hz, 8Ar-H; *o* to OCH_2phenyl), 5.25 (s, 8H, O*CH₂*phenyl), 4.16 (d, *J* = 5.1 Hz, 4H, C*H₂*Ophenyl), 3.51-3.76 (m, 288H, OC*H₂*), 3.28 (m, 24H, OC*H₃*), 2.06-2.13 (m, 6H, C*H*(OCH_2)$_2$). ^{13}C-NMR (250 MHz, $CDCl_3$, ppm) : *δ* 159.9, 157.9, 142.6, 140.2, 139.9, 139.3, 136.4, 133.3, 128.0, 127.54, 127.49, 127.3, 127.0, 115.6, 111.8, 71.9, 70.9, 70.5, 70.4, 69.6, 69.3, 59.0, 40.0. ; Mn/Mw = 1.04 (GPC); Anal. Calcd for :C98H142O31 : C, 63.68; H, 8.27. Found C, 63.68; H, 8.22 ; MALDI-TOF-MS m/z (M+Na$^+$) 4436.42, 4480.62, 4524.63, 4568.85, 4612.54, 4656.65, 4700.90, 4744.99, 4788.55, 4920.76, Calcd. 4697.59.

Typical preparation procedure for 1-SWNTs: 1 mg of SWNT was sonicated in 5mL of water for 30 min and 5mg of **1** were added. Most of the visible insoluble solid thereafter dissolved and formed a black colored solution by sonication for 1 hour with no precipitation for several days.

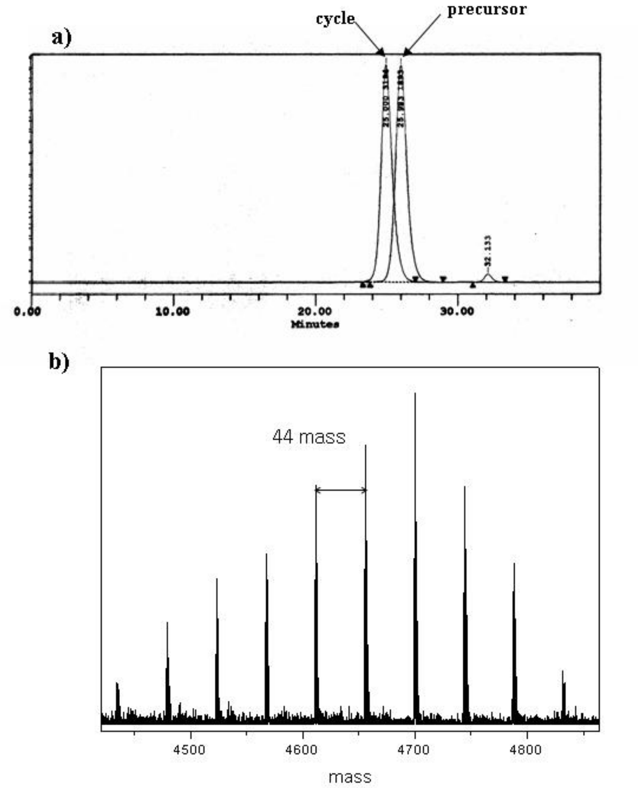


Figure S1. (a) GPC traces of **1** and precursor **4** and (b) MALDI-TOF mass spectroscopy showing same intervals(44 mass) from repeating unit of poly(ethylene oxide). (M + Na^+: 436.42, 4480.62, 4524.63, 4568.85, 4612.54, 4656.65, 4700.90, 4744.99, 4788.55, 4920.76, Calcd. 4697.59.)

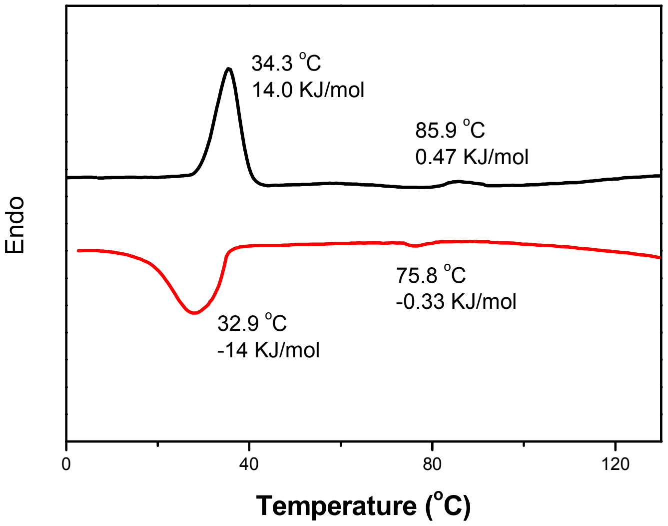


Figure S2. DSC traces recorded during the heating scan (a) and the cooling scan (b) of **1.**

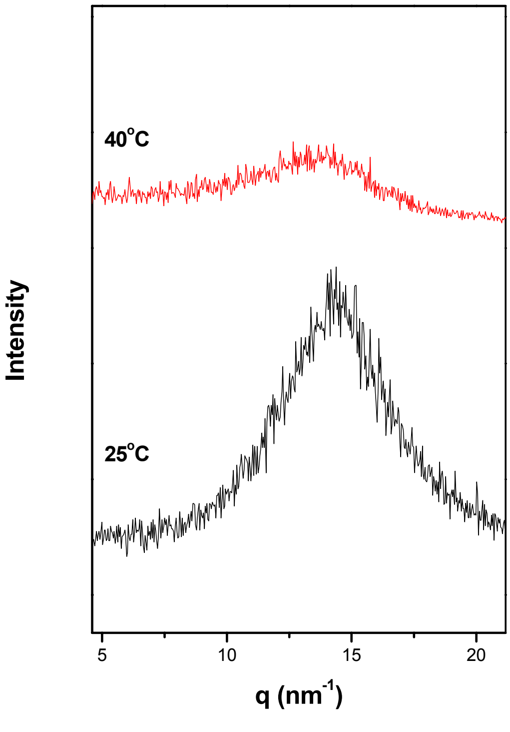


Figure S3. Wide angle X-ray scattering data of **1** in the crystalline (25 °C) and liquid crystalline phases (40 °C).

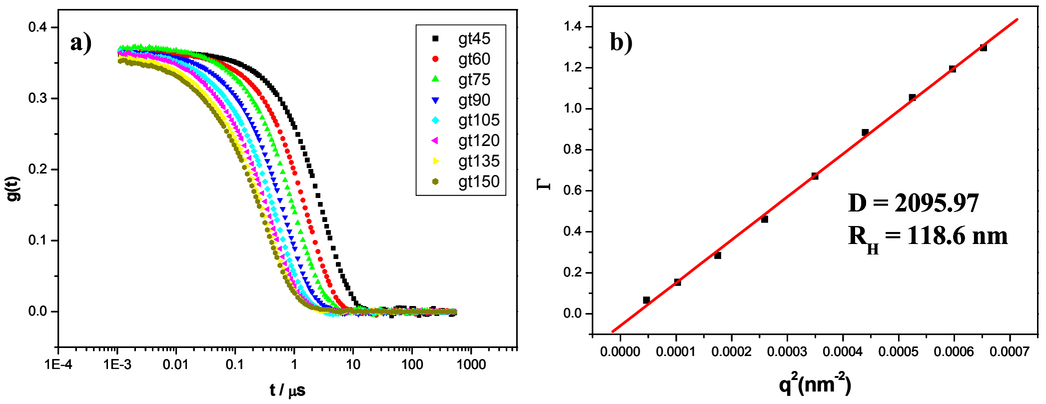


Figure S4. Dynamic laser light scattering of **1** (0.05 wt%) in H_2O (a) autocorrelation function (scattering angular range of 45^{o} to 150^{o}) and (b)a mono-exponential decay function.

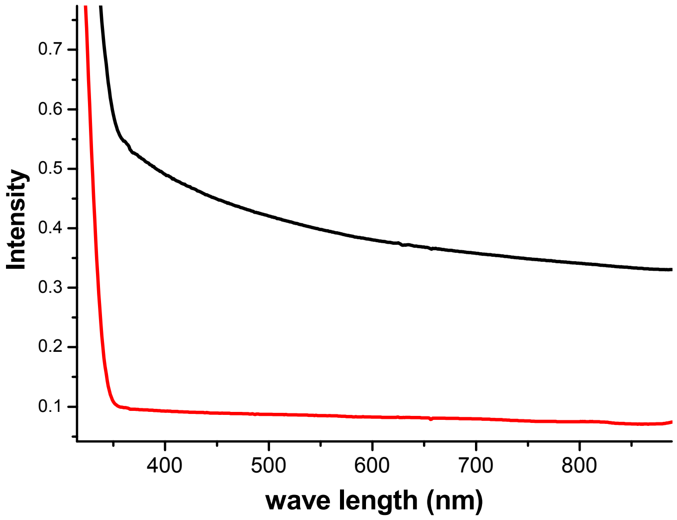


Figure S5. Absorption spectra of **1**(0.1 wt%) containing SWNT (Red line: in THF solution and black line: in aqueous solution). The solution was filtered through glass wool until no visible particles remain before UV-vis absorption experiment.

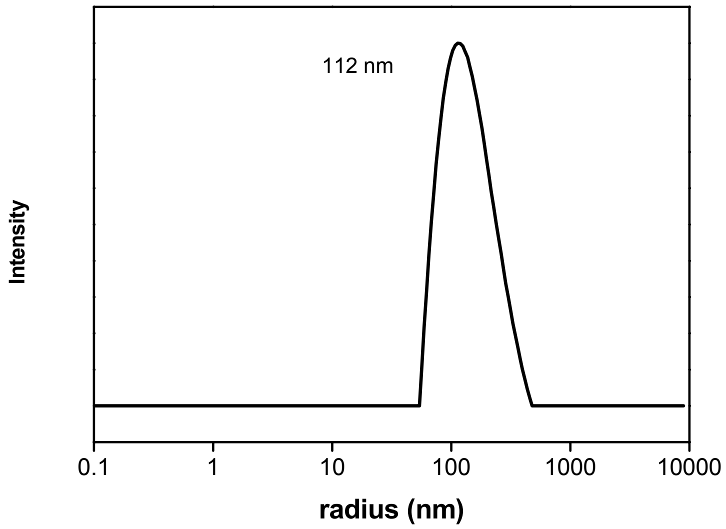


Figure S6. Dynamic laser light scattering of **1** (0.05 wt%) containing SWNTs in aqueous solution at scattering angle of 90° (from CONTIN analysis of the autocorrelation function). Macrocycle **1** and **1** containing SWNTs in aqueous solution show same distribution.