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Supporting Information

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Self-Assembling Molecular Dumbbell: From Nanohelices to Nanocapsules Triggered by Guest Intercalation

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Experimental Section

Materials. 4-Bromo-4'-hydroxybiphenyl (99%), 4,4’-dibromobiphenyl (98%), tetrakis(triphenylphosphine)palladium(0) (99%), toluene-*p*-sulfonyl chloride (98%) and 4-hydroxy-4’-methoxybiphenyl (99%) from Tokyo Kasei were used as received. Poly(propylene glycol)s ({DP} = 21), Chlorotrimethylsilane (98%), *n*-butyllithium (1.6 M solution in *n*-hexane)and borane-THF comeplx (1.0 M solution in THF) from Aldrich and the other conventional reagents were used as received. Hexane, dichloromethane, and ethyl acetate were distilled before use. Dry THF was obtained by vacuum transfer from sodium and benzophenone. Visualization was accomplished with UV light, iodine vapor. Compounds were synthesized according to the procedure described scheme 1 and 4-4’-(trimethylsilyl)biphenyl-boronic acid and dendritic oligoether coil were prepared according to the same procedures described previously.[1],[2] and then purified by silica gel column chromatography by using ethyl acetate as an eluent until polydispersity value remains constant.

Techniques. ^{1}H-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). Microanalyses were performed with a Perkin Elmer 240 elemental analyzer at Organic Chemistry Research Center. MALDI-TOF-MS was performed on Perseptive Biosystems Voyager-DE STR using a 2,5-dihydroxy benzoic acid matrix. Dynamic light scattering (DLS) measurements were performed using an ALV / CGS-3 Compact Goniometer System. UV/vis absorption spectra were obtained from a Shimadzu 1601 UV spectrometer. The fluorescence spectra were obtained from a Hitachi F-4500 fluorescence spectrometer. Circular dichroism (CD) spectra were obtained using JASCO J-810 spectropolarimeter. Transmission electron microscope (TEM) was performed at 120 kV using JEOL-JEM 2010. Atomic Force Microscope (AFM) measurements were performed using a Nanoscope IIIa microscope (Veeco Instruments, Santa Babara, CA) with silicon probes (Nanosensordimensions: T = 3.5-4.5 μm, W = 30-40 μm, L = 115-135 μm) in tapping mode. Compounds were synthesized according to the procedure described scheme 1 and then purified by silica gel column chromatography and prep. HPLC (Japan Analytical Instrument).

Synthesis. The synthetic procedures used in the preparation of rod-coil molecules are described in Scheme 1.

Synthesis of tris-(4-benzlyoxy-biphenyl-4-yl)-methanol(2).

4'-Bromo-biphenyl-4-ol (2.5 g, 10.35 mmol), excess benzyl bromide and excess K_2CO_3 were dissolved in 250mL of acetone. The mixture was heated at reflux for 6 h and then cooled to room temperature. The solvent and excess benzyl bromide were removed using aspirator vacuum 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. To a solution of the resulting products (3.2 g, 9.44 mmol) in THF at -75℃ was dropped 1.6M solution of *n*-BuLi in hexane (6.4 mL) for 90 min. The mixture was stirred for 1h, after which diethyl carbonate (0.32 g, 2.71 mmol) in THF (5 mL) was added slowly. The mixture was allowed to warm to 0℃ (ice bath) and was stirred for 3h. The mixture was quenched with methanol (10 mL) and the solvent was removed under vacuum. The residue was extract with ethyl acetate, and the extract was washed with water, dried ($MgSO_4$), and concentrated. The solid was subjected to recrystallization two times in CH_2Cl_2 to afford 1.8 g (82%) of white powder. ^{1}H-NMR (250 MHz, DMSO, δ, ppm) 7.61-7.31 (m, 33Ar-H), 7.08 (d, 6Ar-H, *o* to OCH_2phenyl, *J* = 8.7 Hz), 6.51(s, C(phenyl)$_3$*OH*), 5.13(s, 6H, O*C*H_2phenyl); ^{13}C-NMR (250 MHz, DMSO, δ, ppm) 69.69, 80.59, 115.69, 125.87, 128.13, 128.16, 128.29, 128.76, 128.90, 132.85, 137.51, 138.55, 146.68, 158.40.

Synthesis of 4-[Tris-(4'-benzyloxy-biphenyl-4-yl)-methyl]-phenol(3a).

To a solution of compound **2** (1.5 g, 1.86 mmol) in toluene(50 mL) excess phenol (10 g, 106.26 mmol) and HCl (35%, 0.1 mL) as a catalyst was added. A reddish-blue color was observed immediately. The mixture was heated at reflux 8 hours, and then cooled to

room temperature. The product was extracted with toluene (3 x 50 mL) and the combineorganic phase was washed with aqueous NaOH solution (3 x 100 mL) and with water (3 x 100 mL) and dried with $MgSO_4$. The crude products were purified by column chromatography (silica gel, methylene chloride) to yield 1.1 g (67%) of a white powder. ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm) 7.71-7.42 (m, 33Ar-H), 7.28 (d, 2Ar-H, *o* to $C(phenyl)_3$, *m* to OH, *J* = 8.3 Hz), 7.12 (d, 6Ar-H, *o* to OCH_2phenyl, *J* = 8.2 Hz), 6.82(d, 2Ar-H, *o* to OH, *m* to $C(phenyl)_3$), 5.14 (s, 6H, OCH_2phenyl); ^{13}C-NMR (250 MHz, $CDCl_3$, δ, ppm) 70.08, 77.24, 114.36, 115.15, 125.64, 127.51, 127.98, 128.61, 131.44, 132.39, 133.39, 136.97, 138.05, 139.23, 145.51, 153.54, 158.30.

Synthesis of 4-[Tris-(4'-benzyloxy-biphenyl-4-yl)-methyl]-phenol(3b, 3c).

To solution of compound **3a** (0.52 g 0.57 mmol) in CH_2Cl_2 (30 mL) and 3,4-dihydro-2H-pyran (0.1 g, 0.85 mmol) were slowly added pyridium-*p*-toulene sulfate (30 mg, 0.1 mmol) at 0 ^{o}C, and stirring was continued at 25 ^{o}C untile the starting material was disappeared. The resulting solution 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. To a solution of the resulting products (0.56 g, 0.58 mmol) in MeOH/THF (30 mL 1/1 v/v) was added 5% Pd/C (50 mg) and stirred at room temperature overnight under H_2 (1 atm). The catalyst was then removed by filtration and, after evaporation to dryness, the crude product was purified by flash column chromatography (silica gel, ethyl acetate) to yield 0.39 g (98%) of a waxy solid. ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm) 7.53-7.46 (m, 12Ar-H), 7.22 (d, 6Ar-H, *o* to OH, *J* = 7.5 Hz), 7.16 (d, 2Ar-H, *m* to OTHP, *J* = 8.4 Hz), 6.96 (d, 2Ar-H, *o* to OTHP, *J* = 8.0 Hz), 6.82(d, 6Ar-H, *o* to OTHP, *J* = 7.8 Hz), 5.41 (m, 1H, $OCH(CH_2)$Ophenyl of THP group), 4.0-3.6 (m, 2H, OCH_2 of THP group), 1.85-1.4 (m, 6H, $OCH_2(CH_2)_3$CH of the

THP group).

Synthesis of Compound 4a and 4b.

Compound **3c** (0.19 g, 0.27 mmol), ROTs (1.2 g, 1.1 mmol) and excess K_2CO_3 were dissolved in 30 mL of anhydrous acetonitrile. The mixture was refluxed for 24 h. The resulting solution was poured into water and extracted with Et_2O. The Et_2O solution was washed with water, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed in a rotary evaporator, and the crude product was dissolved in 30 ml of MeOH. After cooling of the solution in ice for 15 min, TsOH•H_2O (1 g, 5 mmol) was added and stirred for 4 h at room temperature to remove the THP group. $NaHCO_3$ was then added to the reaction mixture. H_2O/Et_2O extraction, drying of the collected Et_2O layers with $MgSO_4$, and then evaporation of the solvent yielded a mixture. Purification of the residue by flash column chromatography on silica gel in a ethyl acetate yielded 0.71 g (78.2 %) of colorless liquid. ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm) 7.54-7.44 (m, 12Ar-H), 7.32 (d, 6Ar-H, *m* to OCH_2, *J* = 6.2 Hz), 7.13 (d, 2Ar-H, *m* to OH, *J* = 8.4 Hz), 6.96 (d, 6Ar-H, *o* to OCH_2, *J* = 8.4 Hz), 6.76 (d, 2Ar-H, *o* to OH, *J* = 8.2 Hz), 4.05 (d, 6H, CH_2Ophenyl, *J* = 4.8 Hz), 3.51-3.76 (m, 180H, OCH_2), 3.28 (m, 36H, OCH_3), 2.39-2.35 (m, 3H, phenyl$OCH_2CH(CH_2O)_2$), 2.17- 2.06 (m, 6H, $CH(CH_2O)_2$), 1.15-1.10 (m, 36H, $CHCH_3$).

Synthesis of Compound 5.

Compound **4b** (0.71 g, 0.21 mmol), 4-bromobenzyl bromide (0.33 g, 1.3 mmol) and excess K_2CO_3 were dissolved in 30 mL of acetone. The mixture was heated at reflux for 6 h 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, excess 4-bromobenzyl bromide in the mixture was removed by column chromatography (silica gel) from methylene chloride and ethyl acetate/ methanol (1/8 v/v) eluents to yield 0.71 g (95.2%)of colorless liquid. ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm) 7.54-7.44 (m, 14Ar-H), 7.33-7.30 (m, 8Ar-H, *m* to OCH_2 and *m* to Br, *J* = 6.2 Hz), 7.24 (d, 2Ar-H, *m* to OCH_2phenyl, *J* = 8.7 Hz), 6.96 (d, 6Ar-H, *o* to OCH_2, *J* = 8.4 Hz), 6.89 (d, 2Ar-H, *o* to OCH_2phenyl, *J* = 8.8 Hz), 5.00 (s, 2H, OCH_2phenyl), 4.05 (d, 6H, CH_2Ophenyl, *J* = 4.8 Hz), 3.51-3.76 (m, 180H, OCH_2), 3.28 (m, 36H, OCH_3), 2.39-2.35 (m, 3H, phenyl$OCH_2CH(CH_2O)_2$), 2.17- 2.06 (m, 6H, $CH(CH_2O)_2$), 1.15-1.10 (m, 36H, $CHCH_3$).

Synthesis of Compound 6a and 6b.

Compound **5** (0.71 g, 0.20 mmol) and 4-4'-(trimethylsilyl)biphenyl-boronic (83 mg, 0.30 mmol) were dissolved in degassed THF (40 mL). Degassed 2M aqueous Na_2CO_3 (20 mL) was added to the solution and then tetrakis(triphenylphosphine) palladium (0) (10 mg, 0.009 mmol) 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 washed twice with methylene chloride. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using methlylene chloride: methanol (8:1 v/v) as eluent to yield 0.7 g (94.5 %) of colorless liquid (**6a**). Then **6a** (0.7 g, 0.19 mmol) was dissolved in CH_2Cl_2 (300 ml) at -78 ^{o}C and 1.0 M solution of ICl in CH_2Cl_2 (1.5 ml, 1.5 mmol) was dropped. The reaction mixture was stirred over 30 min under nitrogen. 1M aqueous $Na_2S_2O_5$ (15 ml) solution was added and stirred over 4 h. The layers were separated,

and the aqueous layer was then washed twice with CH_2Cl_2. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using methlylene chloride: methanol (8:1 v/v) as eluent to yield 0.7 g (98.6 %) of colorless liquid (**6b**).

6a: ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm) 7.69-7.27 (m, 32Ar-H), 6.96 (d, 8Ar-H, *o* to OCH_2, *J* = 8.4 Hz), 5.11 (s, 2H, OCH_2phenyl), 4.05 (d, 6H, CH_2Ophenyl, *J* = 4.8 Hz), 3.51-3.76 (m, 180H, OCH_2), 3.28 (m, 36H, OCH_3), 2.39-2.35 (m, 3H, phenyl$OCH_2CH(CH_2O)_2$), 2.17- 2.06 (m, 6H, $CH(CH_2O)_2$), 1.15-1.10 (m, 36H, $CHCH_3$). 0.31 (s, 9H, phenyl$Si(CH_3)_3$).

6b: ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm) 7.77 (d, 2Ar-H, *o* to I), 7.68-7.31 (m, 28Ar-H), 7.25 (d, 2Ar-H, *m* to I), 6.96 (d, 8Ar-H, *o* to OCH_2, *J* = 8.4 Hz), 5.11 (s, 2H, OCH_2phenyl), 4.05 (d, 6H, CH_2Ophenyl, *J* = 4.8 Hz), 3.51-3.76 (m, 180H, OCH_2), 3.28 (m, 36H, OCH_3), 2.39-2.35 (m, 3H, phenyl$OCH_2CH(CH_2O)_2$), 2.17- 2.06 (m, 6H, $CH(CH_2O)_2$), 1.15-1.10 (m, 36H, $CHCH_3$).

Synthesis of Compound 1.

A mixture of compound **6b** (0.7 g, 0.19 mmol), TDAE (75 mg, 0.38 mmol), and $PdCl_2(PhCN)_2$ (7 mg, 0.02 mmol) in DMF (10 mL) was heated at 50 ^{o}C for 4 h. Cooled to room temperature, the layers were separated, and the aqueous layer was then washed twice with methylene chloride. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using methylene chloride: methanol (8:1 v/v) as eluent to yield 0.3 g (44.4%) of waxy liquid. ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm) 7.75-7.24 (m, 64Ar-H), 6.96 (d, 8Ar-H, *o* to OCH_2, *J* = 8.4

Hz), 5.11 (s, 4H, OCH_2phenyl), 4.05 (d, 12H, CH_2Ophenyl, J = 4.8 Hz), 3.51-3.76 (m, 360H, OCH_2), 3.28 (m, 72H, OCH_3), 2.39-2.35 (m, 6H, phenylOCH_2CH($CH_2O)_2$), 2.17- 2.06 (m, 12H, CH($CH_2O)_2$), 1.15-1.10 (m, 72H, CHCH_3); ^{13}C-NMR (250 MHz, $CDCl_3$, δ, ppm) 17.06, 39.99, 40.74, 59.01, 67.45, 69.27, 69.51, 70.48, 70.56, 70.68, 71.89, 74.73, 74.76, 74.96, 114.71, 125.57, 127.21, 127.51, 127.85, 128.13, 131.41, 132.92, 138.08, 145.42, 158.62); Anal. Calcd for $C_{388}H_{618}O_{116}$: C, 65.28; H, 8.73. Found C, 65.45; H, 8.53; MALDI-TOF-MS *m/z* ($M+Na^+$) 7157.25, Calcd 7157.

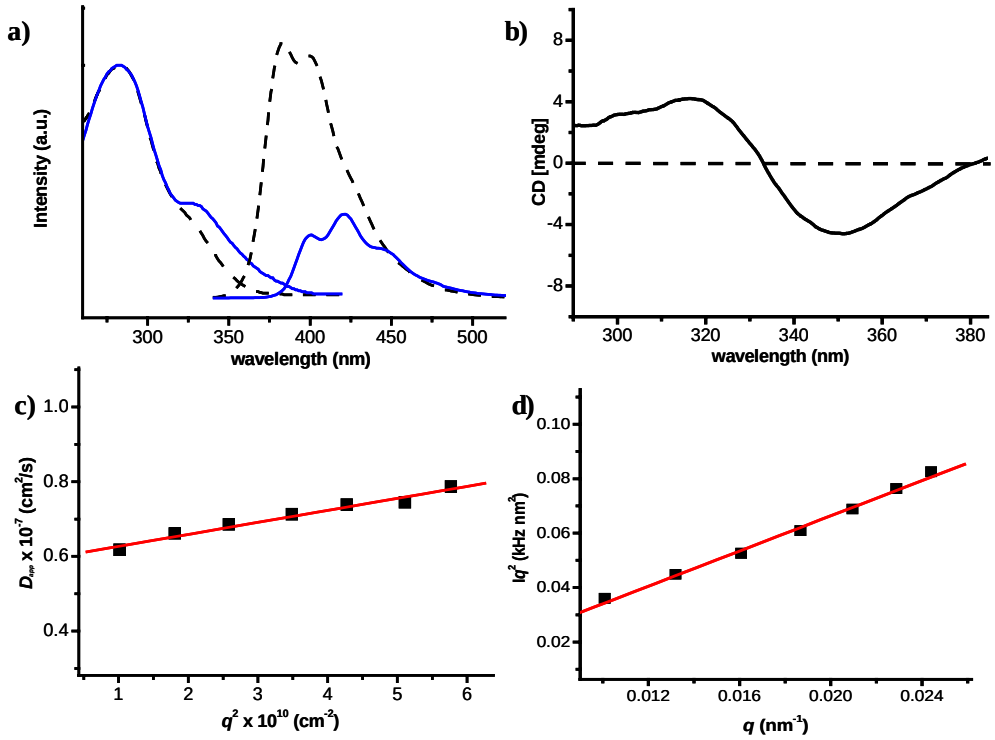

Figure S1. (a) Absorption (left) and emission (right) spectra of the aqueous solution (0.01 wt%, solid line) and chloroform solution (0.01 wt%, dashed line) of **1**, (b) CD spectrum of **1** aqueous solution (0.01 wt %), (c) Angular dependence (q is the scattering vector) of the apparent diffusion coefficient, D_{app}, for the cylindrical micelle in aqueous solution (C = 0.1 gL^{-1}). (d) Kratky plot (■) and linear fit was confirmed the cylindrical micelle in aqueous solution (C = 0.1 gL^{-1}).

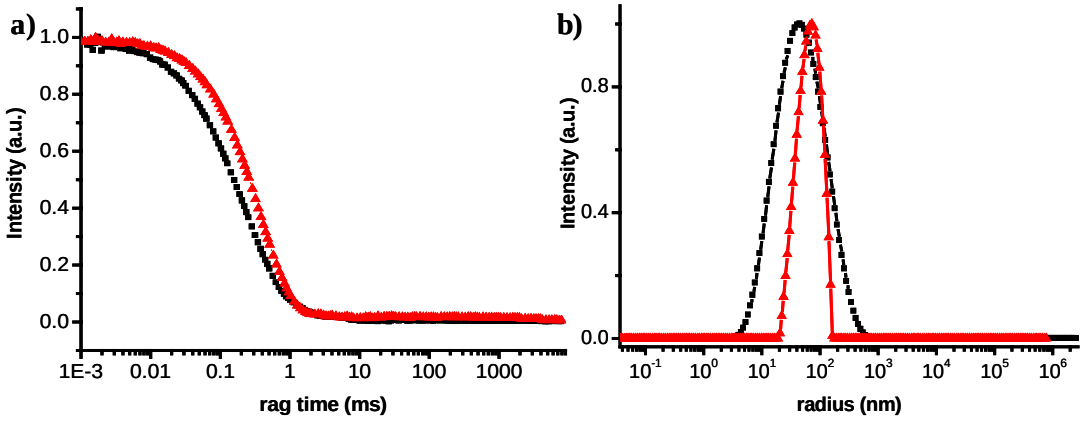

Figure S2. Laser light scattering of aqueous solution of **1** (■, 0.01 wt%) and mixture solution of **1** containing 3 equivalents of 4-bromonitrobenzene (▲, 0.01 wt%). (a) Autocorrelation functions and (b) size distribution graph at scattering angle of 90^{o} (from CONTIN analysis of the autocorrelation function).

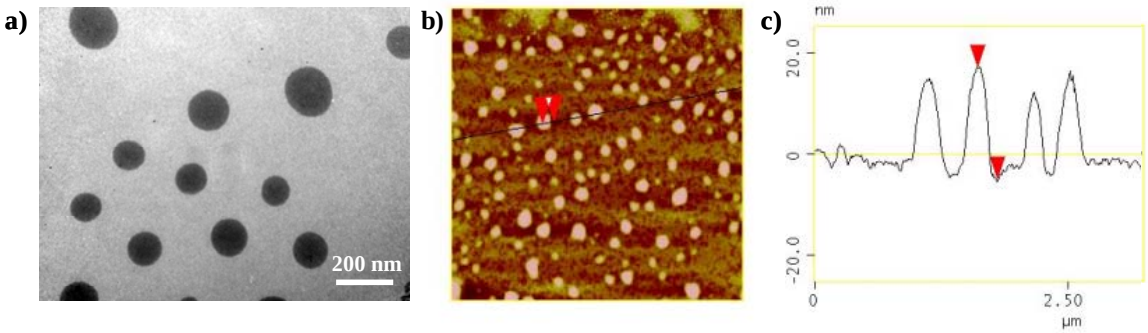

Figure S3. (a) TEM image for the spherical capsules. (b) Height image (5 µm x 5 µm) of atomic force micrograph (AFM) with the surface profile curve of vesicles of **1** containing 3 equivalents of 4-bromonitrobenzene adsorbed on a silicon wafer. AFM measurements indicated that the vesicle particles had a flattened shape, and (c) the average vertical cross-sectional thickness was about 20 nm, which was consistent with

about twice thickness of the molecular length of **1**.[3]

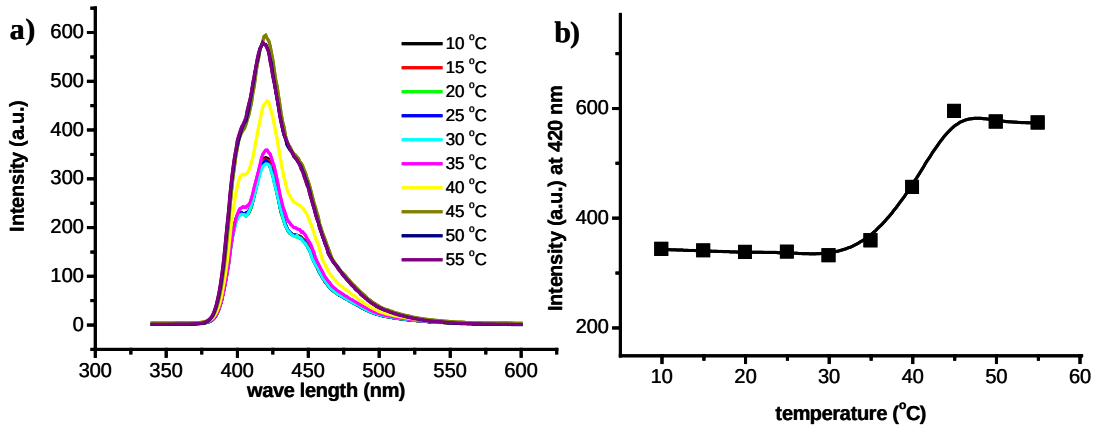

Figure S4. (a) Temperature-dependent fluorescence spectra of the aqueous solution of **1**(0.01 wt%). (b) Intensity at 420 nm at different temperatures. This showed a transition from the aggregated phase to molecularly dissolved species when the temperature was increased.

Reversible transformation from helical fibers to spherical capsules: CD spectra of the aqueous solution of **1** (0.01 wt%) show the bisignate Cotton effect, indicating the formation of a helical fiber. These fibers showed to transform into spherical objects on addition of small aromatic guests (3 equivalent 4bromonitrobenzene), therefore the CD signal strongly decreases. After extraction this mixture solution with hexane that is selective solvent for bromonitrobenzene (Dumbbell molecules is not soluble in hexane.), the CD signal showed to be fully recovered again. These results indicate that this structural transformation is reversible.

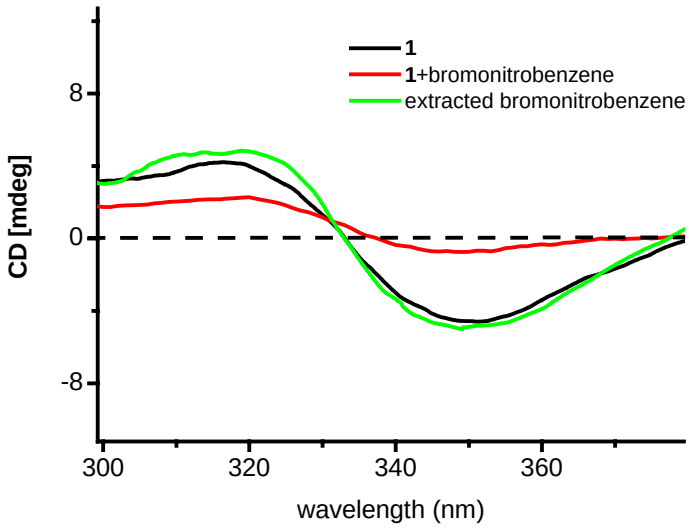

Figure S5. CD spectra of **1** by adddition and removal of bromonitrobenzene. Upon removal of the guest molecules by extraction with n-hexane, the CD spectrum showed to be fully recovered, indicating that this structural transformation is reversible.

Fluorescence titration experiments: Aqueous solution of **1** (0.01 wt%) was first prepared. Then 4-bromonitrobenzene was added to the solution and sonicated for 10 minutes. The solution was pipetted into a quartz cuvette and the fluorescence spectrum was recorded at excitation wavelength of 332 nm. Also, each of fluorescence spectra were recorded as the same methods, as increasing the molar ratio from 0 to 10. One equivalent is enough to destroy supramolecular chirality. Aromatic guest molecules would be intercalated between the rod segments, and this intercalation of the guest molecules would drive twisted packing arrangement of the rod segments to parallel arrangement which allows more space for guest molecules. Considering the molecular length and the space between molecular dumbbells by CPK, a stochiometry of 3 guest molecules per dumbbell molecule seems to be reasonable.

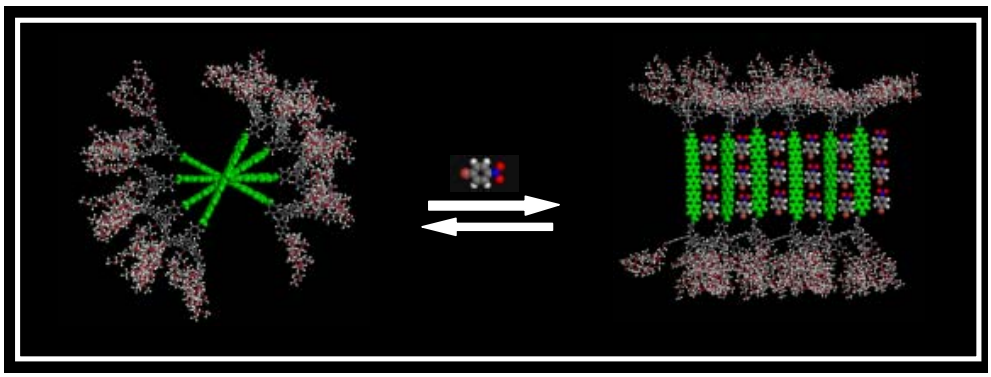

Figure S6. CPK model of **1** by adddition and removal of bromonitrobenzene.

Intercalation of guest molecules: We used other guest molecules such as nitrobenzene, anisole, aniline, and benzeonitrile. As shown following figure, addition of aromatic guest molecules give rise to decrease the CD signal like that of 4-bromonitrobenzene, and diffusion coefficient are also independent to angle. These results mean that the helical fibers of **1** were transformed into spherical capsules by intercalation of aromatic guest molecules between the rod bundles.

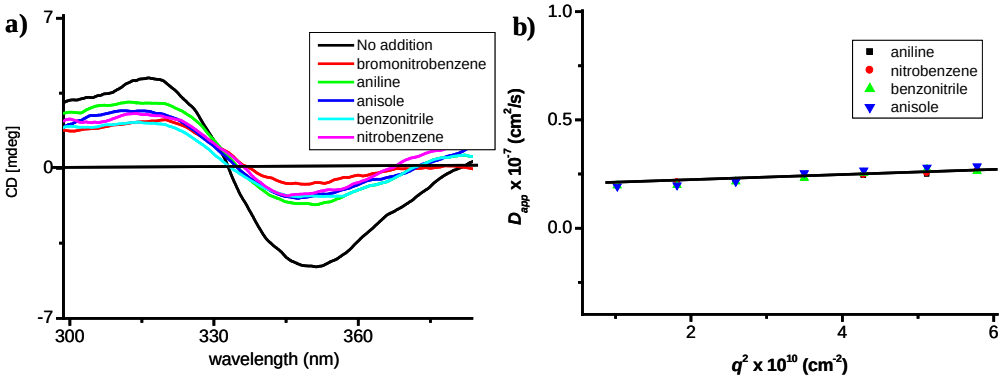

Figure S7. (a) CD spectra of **1** by addition of guest molecules. (b) Angular dependence (*q* is the scattering vector) of the apparent diffusion coefficient (0.01 wt% aqueous solution added 3 equivalent guest molecules).

References

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[2] H.-J. Kim, W.-C. Zin, M. Lee, *J. Am. Chem. Soc.* **2004**, *126*, 7009.

[3] Y. Tanaka, M, Miyachi, Y. Kobuke, *Angew. Chem.* **1999**, *111*, 565-567; *Angew. Chem. Int. Ed.* **1999**, *38*, 504.