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Supporting Information

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Supramolecular Capsules with Gated Pores from Amphiphilic Rod Assembly

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Materials

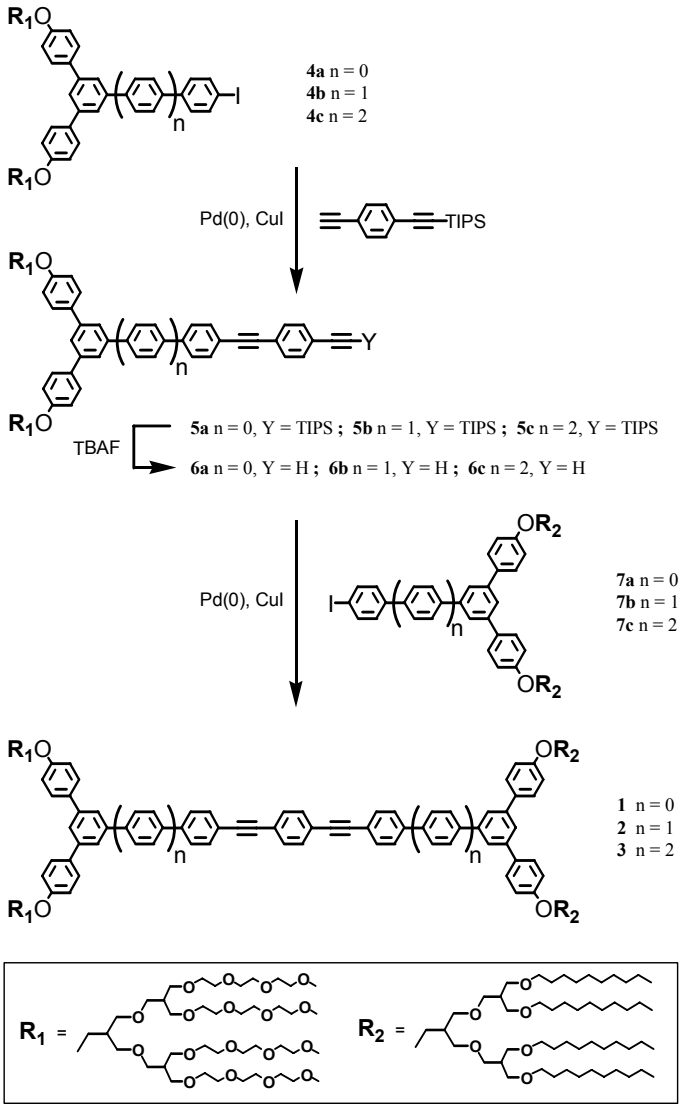
3−Chloro−2−chloromethyl−1−propene (96 %) from Acros, 4−toluenesulfonyl chloride (98 %) from Junsei and tetrakis(triphenylphosphine) palladium(0) (99 %) from TCI were used as received. Triethylene glycol monomethyl ether (95 %), decyl alcohol (98 %), 1,3,5−tribromobenzene (99 %), *n*−butyllithium (1.6 M solution in *n*–hexane), 4−bromoanisole (99 %), borane−THF complex (1.0 M solution in THF), triisopropyl borate (98 +%), 1–iodo–4−bromo benzene (98 %), (triisopropylsilyl)−acetylene (95 %), 2−methyl−3−butyn−2−ol (98 %), iodine monochloride (1.0 M solution in dichloromethane), tetrabutylammonium-fluoride (1.0 M solution in THF), 4−(trimethylsilyl)phenylboronic acid and calcein from Aldrich and the conventional reagents were used as received. All atmosphere sensitive reactions were done under nitrogen atmosphere. Dry triethylamine was prepared freshly by distillation over calcium hydride and dry THF was obtained by distillation over sodium and benzophenone. Flash chromatography was carried out using silica gel 60 (230−400 mesh) from EM Science. Visualization was accomplished by UV light irradiation and/or iodine vapor.

Methods

^{1}H−NMR, ^{13}C−NMR spectra were recorded from $CDCl_3$ solutions on a Bruker 250, 400 NMR spectrometers. The purity of the products was checked by thin layer chromatography (TLC; Merck, silica gel 60 F_{254}). Microanalyses were performed with a Perkin Elmer 240 elemental analyzer at Organic Chemistry Research Center. MALDI−TOF mass spectroscopy (MALDI–TOF–MS) was performed on a Perseptive Biosystems Voyager−DE STR using a 2,5−dihydroxy benzoic acid as matrix. Recycling preparative high performance liquid chromatography (HPLC) was performed at room temperature using a 20 mm × 600 mm polystyrene column on a Japan Analytical Industry Model LC−908 recycling preparative HPLC system, equipped with UV detector 310 and RI detector RI−5. Chloroform (HPLC

grade) was used as eluent. The optical transmittances were recorded at wavelength of 500 nm with a Shimadzu 1601 UV−vis spectrometer. The fluorescence microscopy image was obtained by Nikon Eclipse TE2000−U, inverted fluorescence microscope equipped with DXM1200C digital camera. The steady−state fluorescence spectra were measured in a Hitachi F−4500 fluorescence spectrophotometer. The transmission electron microscope (TEM) was performed at 120 kV using JEM−2010.

Synthesis of rod amphiphile



Scheme S1. Synthetic scheme for rod amphiphiles **1**, **2** and **3**.

1−ethynyl−4−(triisopropylsilylethynyl)benzene,[S1] 4−trimethylsilyl−biphenyl−4'−boronic acid[S2], second−generation dendritic triethylene glycol coils ($\mathbf{R_1}$)[S3] and second−

generation dendritic decyl coils (**R_2**)[S4] were prepared according to the similar procedures as described previously.

Synthesis of compound 4a, 4b and 4c.

The synthesis of compounds **4a−c** were performed according to the procedures as reported previously.[S5]

4a; ^{1}H–NMR (250 MHz, $CDCl_3$, ppm) : δ = 7.71–7.60 (m, 9Ar–*H*), δ = 7.34 (d, 2Ar–*H*, *o* to ArI, *J* = 8.4 Hz), 6.98 (d, 4Ar–*H*, *o* to ArO, *J* = 8.6 Hz), 4.04 (d, 4H, –C*H*$_2$OAr, *J* = 5.2 Hz), 3.62–3.42 (m, 128H, –OC*H*$_2$CH$_2$), 3.32 (s, 24H, –OC*H*$_3$), 2.39–2.15 (m, 6H, –C*H*(OCH$_2$)$_2$).

4b; ^{1}H–NMR (250 MHz, $CDCl_3$, ppm) : δ = 7.74–7.60 (m, 13Ar–*H*), δ = 7.34 (d, 2Ar–*H*, *o* to ArI, *J* = 8.4 Hz), 6.98 (d, 4Ar–*H*, *o* to ArO, *J* = 8.7 Hz), 4.05 (d, 4H, –C*H*$_2$OAr, *J* = 5.3 Hz), 3.63–3.42 (m, 128H, –OC*H*$_2$CH$_2$), 3.31 (s, 24H, –OC*H*$_3$), 2.38–2.16 (m, 6H, –C*H*(OCH$_2$)$_2$).

4c; ^{1}H–NMR (250 MHz, $CDCl_3$, ppm) : δ = 7.77–7.58 (m, 17Ar–*H*), δ = 7.34 (d, 2Ar–*H*, *o* to ArI, *J* = 8.5 Hz), 6.98 (d, 4Ar–*H*, *o* to ArO, *J* = 8.7 Hz), 4.06 (d, 4H, –C*H*$_2$OAr, *J* = 5.2 Hz), 3.64–3.43 (m, 128H, –OC*H*$_2$CH$_2$), 3.30 (s, 24H, –OC*H*$_3$), 2.38–2.17 (m, 6H, –C*H*(OCH$_2$)$_2$).

Synthesis of compound 5a, 5b and 5c.

These compounds were synthesized using the same procedure. A representative example is described for **5b**. 1–Ethynyl–4–(triisopropylsilylethynyl)benzene (130 mg, 0.46 mmol), compound **4b** (510 mg, 0.23 mmol) and copper(I) iodide (0.3 mg, 0.002 mmol) were added to a stirred suspension of tetrakis(triphenylphosphine) palladium(0) (6.2 mg, 0.004 mmol) in dry triethylamine. The mixture was degassed and then stirred at 60 ℃ under N_2 for 12 hrs. The solvent was removed in a rotary evaporator, and the crude product was then purified by column chromatography (silica gel) using methanol : ethyl acetate = 1 : 8 as eluent to yield 360 mg (65 %) of a slightly yellow waxy solid.

5a; ^{1}H–NMR (250 MHz, $CDCl_3$, ppm) : δ = 7.69–7.60 (m, 11Ar–*H*), 7.44 (s, 4Ar–*H*≡C), 7.00 (d, 4Ar–*H*, *o* to ArO, *J* = 8.6 Hz), 4.06 (d, 4H, –C*H*$_2$OAr, *J* = 5.1 Hz), 3.63–3.46 (m, 128H, –OC*H*$_2$CH$_2$), 3.36 (s, 24H, –OC*H*$_3$), 2.39–2.16 (m, 6H, –C*H*(OCH$_2$)$_2$), 1.13 (s, 21H, –SiC$_3$*H*$_7$).

5b; ^{1}H–NMR (250 MHz, $CDCl_3$, ppm) : δ = 7.72–7.60 (m, 15Ar–*H*), 7.45 (s, 4Ar–*H*≡C), 6.99 (d, 4Ar–*H*, *o* to ArO, *J* = 8.7 Hz), 4.05 (d, 4H, –C*H*$_2$OAr, *J* = 5.1 Hz), 3.62–3.45 (m, 128H, –OC*H*$_2$CH$_2$), 3.34 (s, 24H, –OC*H*$_3$), 2.39–2.15 (m, 6H, –C*H*(OCH$_2$)$_2$), 1.12 (s, 21H, –SiC$_3$*H*$_7$).

5c; ^{1}H–NMR (250 MHz, $CDCl_3$, ppm) : δ = 7.78–7.61 (m, 19Ar–*H*), 7.46 (s, 4Ar–*H*≡C), 7.01 (d, 4Ar–*H*, *o* to ArO, *J* = 8.7 Hz), 4.06 (d, 4H, –C*H*$_2$OAr, *J* = 5.2 Hz), 3.63–3.46 (m, 128H, –OC*H*$_2$CH$_2$), 3.35 (s, 24H, –OC*H*$_3$), 2.38–2.16 (m, 6H, –C*H*(OCH$_2$)$_2$), 1.12 (s, 21H, –SiC$_3$*H*$_7$).

Synthesis of compound 6a, 6b and 6c.

These compounds were synthesized using the same procedure. A representative example is described for **6b**. To a solution of compound **5b** (360 mg, 0.15mmol) in THF (100 mL), a solution of Bu_4NF (5.8 mL, 5.8 mmol) in THF (1.0 M) was added dropwise via syringe. After stirring 2 hrs at room temperature, reaction was quenched by NH_4Cl solution, resulting mixture was extracted with ethyl acetate and water. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was removed in a rotary evaporator, and the crude products were purified by column chromatography (silica gel) using ethyl acetate / methanol as eluent to yield 240 mg (71 %) of a slightly yellow waxy solid.

6a; ^{1}H–NMR (250 MHz, $CDCl_3$, ppm) : δ = 7.69–7.60 (m, 11Ar–*H*), 7.44 (s, 4Ar–*H*≡C), 7.00 (d, 4Ar–*H*, *o* to ArO, *J* = 8.6 Hz), 4.06 (d, 4H, –C*H*$_2$OAr, *J* = 5.1 Hz), 3.63–3.46 (m, 128H, –OC*H*$_2$CH$_2$), 3.36 (s, 24H, –OC*H*$_3$), 3.18 (s, 1H, ≡C*H*), 2.39–2.16 (m, 6H, –C*H*(OCH$_2$)$_2$.

6b; ^{1}H–NMR (250 MHz, $CDCl_3$, ppm) : δ = 7.72–7.60 (m, 15Ar–*H*), 7.47 (s, 4Ar–*H*≡C), 6.99 (d, 4Ar–*H*, *o* to ArO, *J* = 8.6 Hz), 4.05 (d, 4H, –C*H*$_2$OAr, *J* = 5.1 Hz), 3.62–3.46 (m, 128H, –OC*H*$_2$CH$_2$), 3.35 (s, 24H, –OC*H*$_3$), 3.18 (s, 1H, ≡C*H*), 2.39–2.15 (m, 6H, –C*H*(OCH$_2$)$_2$).

6c; ^{1}H–NMR (250 MHz, $CDCl_3$, ppm) : δ = 7.78–7.61 (m, 19Ar–*H*), 7.46 (s, 4Ar–*H*≡C), 7.01 (d, 4Ar–*H*, *o* to ArO, *J* = 8.7 Hz), 4.06 (d, 4H, –C*H*$_2$OAr, *J* = 5.2 Hz), 3.63–3.46 (m, 128H, –OC*H*$_2$CH$_2$), 3.35 (s, 24H, –OC*H*$_3$), 3.19 (s, 1H, ≡C*H*), 2.38–2.16 (m, 6H, –C*H*(OCH$_2$)$_2$).

Synthesis of compound 7a, 7b, and 7c.

The synthesis of a compound **7a−7c** was performed according to the procedures reported previously[S5] with second–generation dendritic decyl coils.[S4]

7a; ^{1}H–NMR (250 MHz, $CDCl_3$, ppm) : δ = 7.70–7.61 (m, 9Ar–*H*), δ = 7.41 (d, 2Ar–*H*, *o* to ArI, *J* = 8.6 Hz), 7.03 (d, 4Ar–*H o* to ArO, *J* = 8.6 Hz), 4.11 (d, 4Ar–*H*, –C*H*$_2$OAr, *J* = 5.5 Hz), 3.60–3.36 (m, 48H, –OC*H*$_2$CH$_2$), 2.46–2.16 (m, 6H, –C*H*(OCH$_2$)$_2$), 1.58–1.27 (m, 128H, –C*H*$_2$CH$_2$), 0.89 (t, 24H, –CH$_2$C*H*$_3$).

7b; ^{1}H–NMR (250 MHz, $CDCl_3$, ppm) : δ = 7.75–7.62 (m,13Ar–*H*), δ = 7.40 (d, 2Ar–*H*, *o* to ArI, *J* = 8.5 Hz), 7.03 (d, 4Ar–*H o* to ArO, *J* = 8.7 Hz), 4.11 (d, 4Ar–*H*, –C*H*$_2$OAr, *J* = 5.3 Hz), 3.60–3.36 (m, 48H, –OC*H*$_2$CH$_2$), 2.46–2.15 (m, 6H, –C*H*(OCH$_2$)$_2$), 1.58–1.27 (m, 128H, –C*H*$_2$CH$_2$), 0.89 (t, 24H, –CH$_2$C*H*$_3$).

7c; ^{1}H–NMR (250 MHz, $CDCl_3$, ppm) : δ = 7.78–7.62 (m, 17Ar–*H*), δ = 7.40 (d, 2Ar–*H*, *o* to ArI, *J* = 8.4 Hz), 7.03 (d, 4Ar–*H o* to ArO, *J* = 8.5 Hz), 4.10 (d, 4Ar–*H*, –C*H*$_2$OAr, *J* = 5.4 Hz), 3.59–3.35 (m, 48H, –OC*H*$_2$CH$_2$), 2.46–2.17 (m, 6H, –C*H*(OCH$_2$)$_2$), 1.56–1.26 (m, 128H, –C*H*$_2$CH$_2$), 0.89 (t, 24H, –CH$_2$C*H*$_3$).

Synthesis of rod amphiphile 1, 2 and 3.

These compounds were synthesized using the same procedure. A representative example is described for **2**. Compounds **6b** (240 mg, 0.11 mmol), **7b** (525 mg, 0.24 mmol) and copper(I) iodide (0.2 mg, 0.001 mmol) were added at 80 ℃ to a stirred suspension of tetrakis(triphenylphosphine) palladium(0) (2.3 mg, 0.002 mmol) in dry triethylamine. The mixture was degassed and then stirred at 80 ℃ under N_2 for 24 hrs. The solvent was removed in a rotary evaporator, and resulting mixture was poured into water and extracted with dichloromethane. The dichloromethane solution was washed with water, dried over anhydrous magnesium sulfate, and filtered. After the solvent was removed in a rotary evaporator, the crude product was then purified by column chromatography (silica gel) using methanol / ethyl acetate as eluent, and the product was further purified by recycling preparative HPLC to yield 260 mg (56 %) of a yellow waxy solid.

1; ^{1}H–NMR (250 MHz, $CDCl_3$, ppm) : δ = 7.69–7.56 (m, 26Ar–*H*), 7.03 (d, 8Ar–*H*, *o* to ArO, *J* = 8.5 Hz), 4.07 (m, 8H, –C*H*$_2$OAr), 3.63–3.26 (m, 200H, –C*H*$_2$O), 2.33–2.16 (m, 12H, –C*H*(OCH$_2$)$_2$), 1.55–1.25 (m, 128H, –C*H*$_2$CH$_2$), 0.86 (t, 24H, –CH$_2$C*H*$_3$); Anal. Calcd for: $C_{242}H_{406}O_{52}$: C, 70.08; H, 9.87. Found C, 70.10; H, 9.86; Calcd. MALDI–TOF–MS m/z ([M+Na]$^+$) 4169.78. Found 4169.65

2; ^{1}H–NMR (250 MHz, $CDCl_3$, ppm) : δ = 7.80–7.55 (m, 34Ar–*H*), 7.02 (d, 8Ar–*H*, *o* to ArO, *J* = 8.4 Hz), 4.07 (m, 8H, –C*H*$_2$OAr), 3.64–3.26 (m, 200H, –C*H*$_2$O), 2.33–2.17 (m, 12H, –C*H*(OCH$_2$)$_2$), 1.55–1.25 (m, 128H, –C*H*$_2$CH$_2$), 0.86 (t, 24H, –CH$_2$C*H*$_3$); ^{13}C–NMR (100 MHz, $CDCl_3$, ppm) : δ = 159.1, 142.1, 141.7, 140.8, 139.5, 133.6, 132.3, 131.7, 128.4, 128.3, 128.0, 127.5, 127.1, 124.1, 123.3, 122.2, 115.0, 91.4, 90.1, 71.5, 69.8, 69.6, 69.4, 69.3, 69.0, 66.5, 66.3, 59.1, 40.5, 40.3, 40.2, 40.1, 31.0, 29.8, 29.7, 29.6, 26.3, 22.8, 14.2 ; Anal. Calcd for: $C_{254}H_{414}O_{52}$: C, 70.95; H, 9.70. Found C, 70.89; H, 9.69; Calcd. MALDI–TOF–MS m/z ([M+Na]$^+$) 4321.97. Found 4322.42

3; ^{1}H–NMR (250 MHz, $CDCl_3$, ppm) : δ = 7.88–7.55 (m, 42Ar–*H*), 7.02 (d, 8Ar–*H*, *o* to ArO, *J* = 8.5 Hz), 4.08 (m, 8H, –C*H*$_2$OAr), 3.64–3.26 (m, 200H, –C*H*$_2$O), 2.33–2.15 (m, 12H, –C*H*$(OCH_2)_2$), 1.55–1.25 (m, 128H, –C*H*$_2$CH$_2$), 0.87 (t, 24H, –CH$_2$C*H*$_3$); Anal. Calcd for: $C_{266}H_{422}O_{52}$: C, 71.76; H, 9.55. Found C, 71.75; H, 9.60; Calcd. MALDI–TOF–MS m/z ($[M+Na]^+$) 4474.17. Found 4474.16

Solution Preparation

Aqueous solutions of compounds **1**, **2** and **3** were prepared by mixing molecules and deionized water in clean glass vials (25 mL). The samples were sealed with para film at room temperature. Before using in each experiment they were stirred 3 days and stabilized more than a week, except studies of controlling temperature in which case solutions were used after stabilizing less than 2 hrs.

Dynamic Laser Light Scattering Experiments

The dynamic light scattering (DLS) experiments were performed with the aqueous solutions of rod amphiphile **1**, **2** and **3** (0.01 wt%) at a scattering angle of 90 ° at 25 ℃, using a UNIPHASE He–Ne laser operating at 632.8 nm. The maximum operating power of the laser was 30 mW. The detector optics employed optical fibers coupled to an ALV/SOSIPD/DUAL detection unit, which employed an EMI PM–28B power supply and ALV/PM–PD preamplifier/discriminator. The Signal analyzer was an ALV5000/E/WIN multiple tau digital correlator with 288 exponentially spaced channels.

Fluorescence Microscopy Experiments

The fluorescence microscopic images were obtained with Nikon Eclipse TE2000–U, inverted fluorescence microscope equipped with DXM1200C digital camera, using a super high pressure mercury lamp (100 W) as a light source and a UV–2A filter. 5 μL of the dilute solutions (0.01 wt%) of **1**, **2** and **3** were deposited onto a glass slide and a cover glass was placed over the sample before observation.

Confocal Microscopy Experiments

The Laser scanning confocal microscopy was performed using a Zeiss 510 microscope equipped with a 100 × objective (numerical aperture (*N. A.*)) 1.40, Plan–Apochromat 100 × /

1.4 oil, Carl–Zeiss) or 40 × objectives (*N. A.*) 1.30, Plan– Apochromat 40 × / 1.3 oil, Carl–Zeiss) at room temperature (23 ℃). A diode with excitation line at 405 nm was used to induce fluorescence. A droplet of the hollow sphere solution of **2** was sandwiched between a glass slide and a coverglass.

Transmittances Experiments

The optical transmittances of aqueous solutions at various temperatures were recorded at wavelength of 500 nm with a Shimadzu 1601 UV–vis spectrometer. The sample quartz cell was thermostated with an external water bath of a Daehan Scientific precision digital refrigerated circulator. The rate of temperature increase was 0.3 ℃ / min. At each temperature, the solutions were equilibrated for 15 minutes.

NMR Experiments

^{1}H–NMR (400 MHz) spectra were recorded on a thermoregulated Bruker Avance 400 using a solution of molecule **2** in D_2O (99.9 D atom %) with a concentration of 0.08 wt%. At each temperature, the solution was equilibrated for 10 minutes before data acquisition. The dehydration of the hydrophilic coil segment of molecule **2** at different temperature was supported by variable temperature ^{1}H–NMR spectroscopy study. The position of 1,4–dioxane peak was used as the internal reference.

TEM Experiments

Transmission electron microscopy observation was carried out with a JEOL JEM–2010 operated at 120 kV. For study of structure of dumbbell–shaped molecule in aqueous solution, a drop of aqueous solution of dumbbell–shaped molecule (0.01–0.1 wt%) was placed on a carbon–coated copper grid and the solution was allowed to evaporate under ambient conditions. The samples were stained by depositing a drop of uranyl acetate aqueous solution (2 wt%) onto the surface of the sample–loaded grid.

The cryogenic transmission electron microscopy (cryo−TEM) experiments were performed with a thin film of aqueous solution of dumbbell–shaped molecule (5 μL) transferred to a lacey supported grid. The thin aqueous films were prepared under controlled temperature and humidity conditions (97–99 %) within a custom–built environmental chamber in order to prevent evaporation of water from sample solution. The excess liquid was blotted with filter paper for 2–3 seconds, and the thin aqueous films were rapidly vitrified by plunging them into liquid ethane (cooled by liquid nitrogen) at its freezing point. To investigate the

effect of temperature, solution were sealed with Teflon tape and elevated the desired temperature in Daehan Scientific precision digital refrigerated circulator having an accuracy ± 0.1 ℃. The system was maintained for 1 hr. And then solution was placed on the lacey supported grid, and thin aqueous films were quickly quenched in liquid ethane. The grid was transferred, on a Gatan 626 cryoholder, using a cryo−transfer device. After that they were transferred to a JEM–2010 TEM. Direct imaging was carried out at a temperature of approximately –175 ℃ and with a 120 kV accelerating voltage, using the images acquired with a Dual vision 300 W and SC 1000 CCD camera (Gatan, Inc.; Warrendale, PA)

Encapsulation of Calcein by LCST & Release of Entrapped Calcein

To the pre–equilibrated solution of **2** (0.5 mL, 0.1 wt%) was added 0.5 mL of 100 mM calcein stock solution. The resulting solution was sealed with para film, and then heated to 65 ℃ above LCST point. After stabilizing for 1 hr in room temperature, untrapped free calcein was removed by filtration over a Sephadex G–50 column. The early fraction containing the vesicles with calcien was collected and diluted to 10 mL stock solution, after confirming with DLS. At each time point, showed in manuscript, 1 mL of stock solution was ultrafiltrated with Amicon Ultra–4 (Millipore, USA) by centrifugation (4,000 × g) during 15 min, then only the solution of releasing free calcein from the capsule was pipetted into a quartz cuvette and the fluorescence intensity was measured with excitation at 490 nm and emission at 514 nm on Hitachi F–4500 fluorescence spectrophotometer.

Encapsulation and intracellular delivery experiment

The 5'–tetramethylrhodamine (TAMRA) labeled DNA (5'–TTGGCACCAGCAGCC-ACTT–3') was purchased from Integrated DNA technologies. For DNA encapsulation, 50 μL of the DNA solution (100 μM in water) was mixed with 50 μL of solution of **2** (0.1 wt% in water). Following overnight incubation, the pore in the capsules was closed as described above. The capsules were then separated from the free DNA by repeated centrifugation (16,110 × g) and wash cycles, and resuspended in 50 μL water. HeLa cells (2×10^4) were seeded on 8–well Lab–tek II chambered coverglass system (Nunc) in DMEM supplemented with 10 % FBS and cultured overnight. The cells were washed and then treated with the DNA–encapsulated capsules for 3 h in DMEM. The cells were washed three times with PBS before imaging. Live cell images were observed with Nikon Eclipse TE2000–U inverted fluorescence microscope using UV–2A or G–2A filter sets (Nikon).

For the encapsulation of fluorescently labeled protein (carboxyfluorescein immunoglobulin M; FAM–IgM), 50 μL of FAM–IgM solution (2 mg/mL) was mixed with 50 μL of **2** solution (0.1 wt%). The pore close and the separation from the free protein were done as described above. For the preparation of FAM–IgM, 5–carboxyfluorescein–succinimidyl ester (FAM–SE, Anaspec, Inc.) was reacted with IgM and the labeled IgM was purified by gel filtration over Superdex 200 column (GE Healthcare). The extent of labeling was about fifty FAM molecules per IgM molecule. Protein concentration was determined by Bradford assay. FAM concentration was calculated by using its extinction coefficient of 78,000 M^{-1} cm^{-1} at 494 nm.

Encapsulation experiments with a fluorescently labeled protein revealed that the capsules had enough capacity to encapsulate even huge protein molecules (carboxyfluorescein–immunoglobulin M; FAM–IgM, MW: ca. 760,000 daltons, Figure S12). Indeed, investigation after treating the capsules both with TAMRA–DNA and FAM–IgM revealed that the capsules can encapsulate the DNA and the protein simultaneously (Figure S13). The multifunctional properties of the capsules to encapsulate both DNA and protein simultaneously, to deliver the cargo into the inside of the cell, and to respond to the external stimuli are quite reminiscent of those functions that viruses have.

Supporting Figures

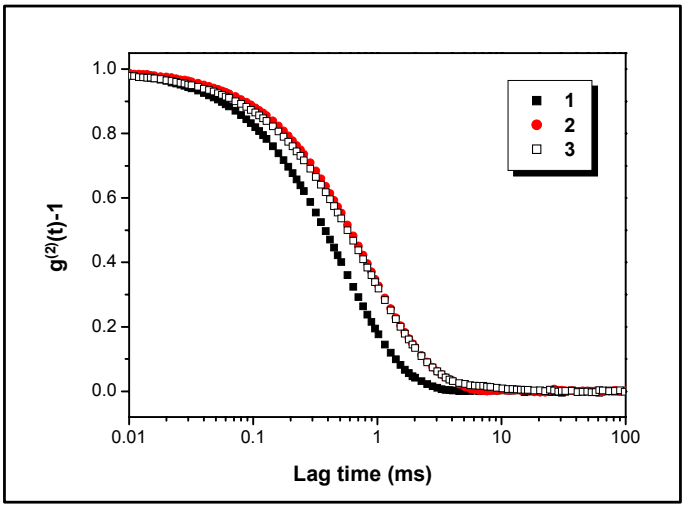


Figure S1. Field auto–correlation functions (Θ = 90 °) of rod amphiphile **1**, **2**, and **3** in 0.01 wt% aqueous solution.

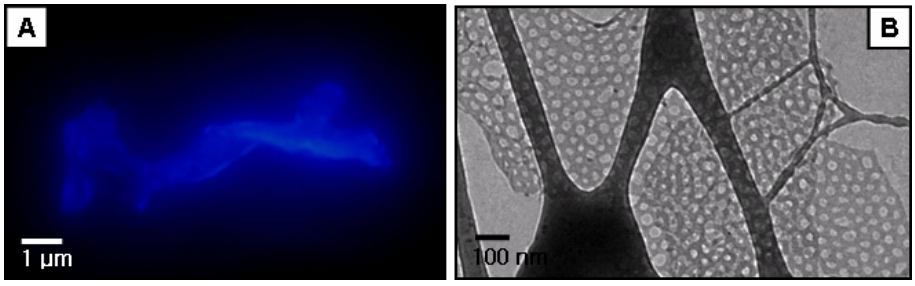


Figure S2. A, Fluorescence micrograph of 2D objects in aqueous solution (0.01 wt%) of **1**. B, Cryo−TEM image of **1** in aqueous solution (0.01 wt%).

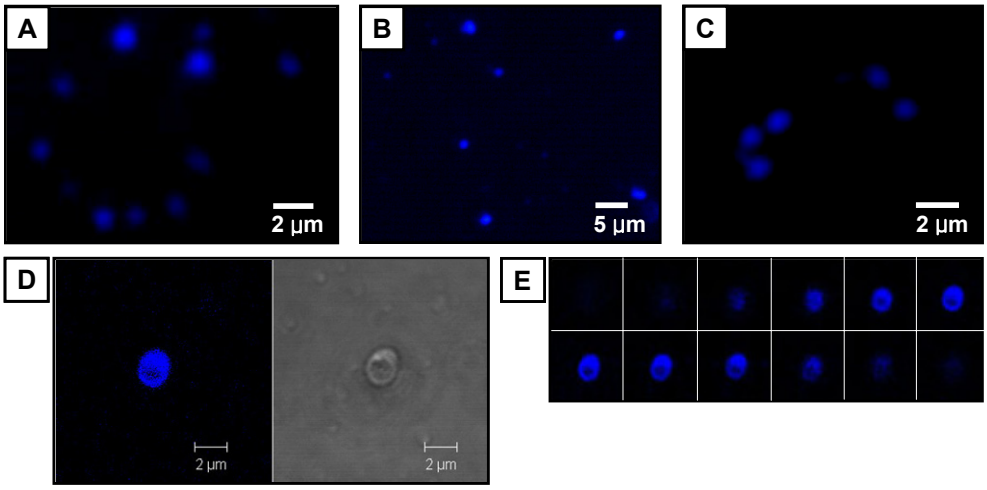


Figure S3. A-C, Fluorescence micrographs of spherical aggregates in aqueous solution (0.01 wt%) of **2**, which range from several hundred nanometers to a few micrometers in diameter. D, Laser Scanning confocal microscopy (LSCM) image and DIC image in aqueous solution of **2**. E, Laser scanning confocal images of a single hollow sphere in aqueous solution from **2**. The cross–sectional pictures are shown in series from the top of the sphere (top left image) to the bottom (bottom right image), clearly indicating the three–dimensional, hollow nature of the final structure.[S6] The imaged hollow sphere is about 2 µm in diameter.

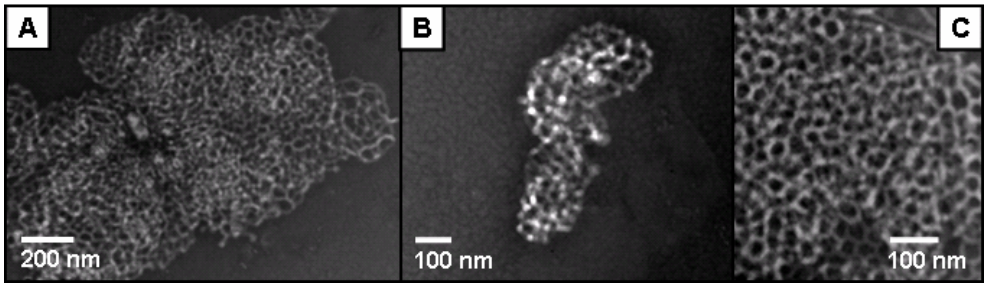


Figure S4. TEM images (negatively stained with uranyl acetate) of cast film of **2** in aqueous solution (0.01 wt%) at room temperature.

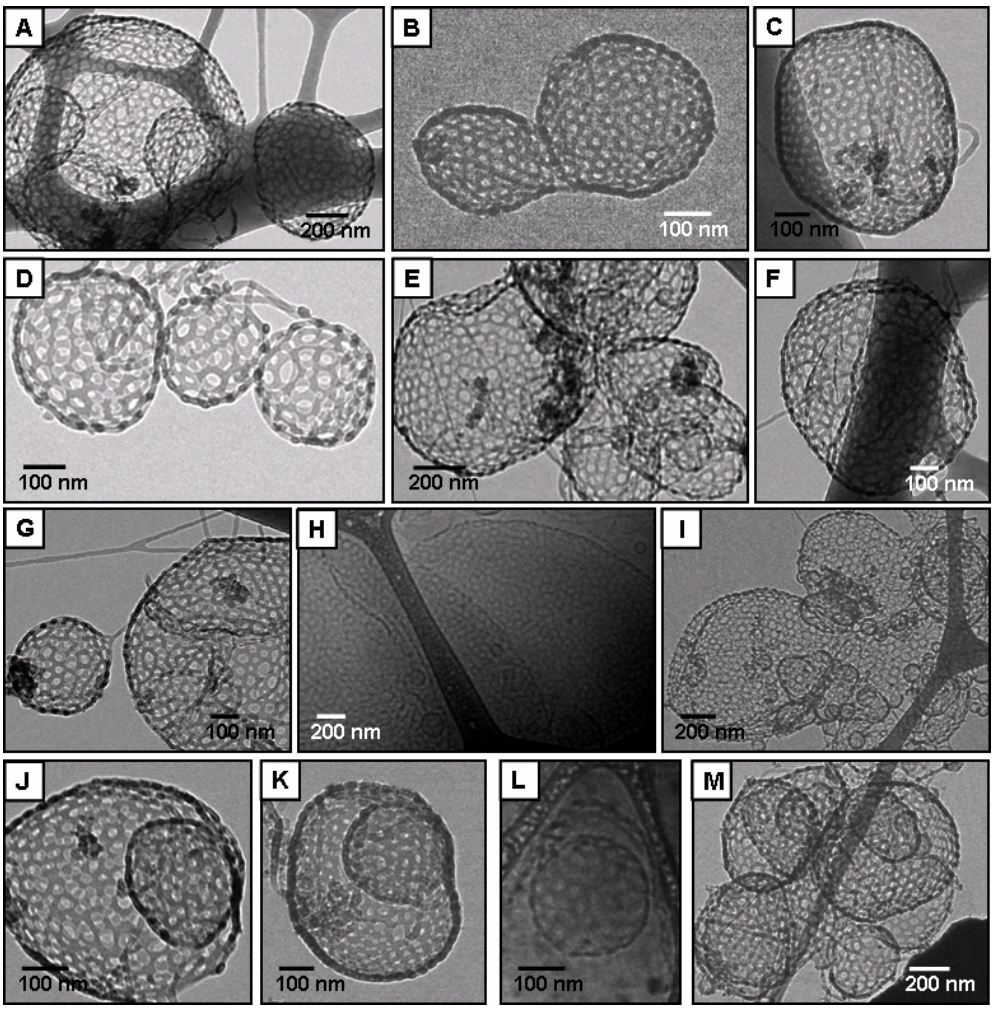


Figure S5. Cryo−TEM images of **2** in aqueous solution (0.01 wt%) at room temperature.

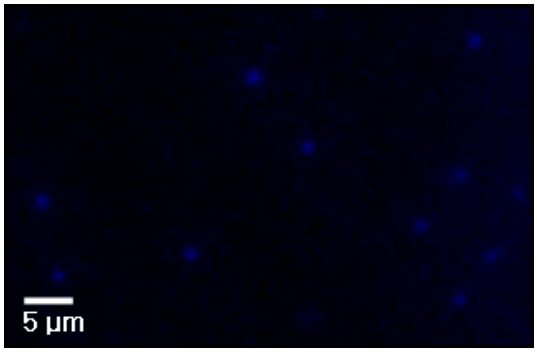


Figure S6. Fluorescence micrograph of spherical aggregates in aqueous solution (0.01 wt%) of **3**.

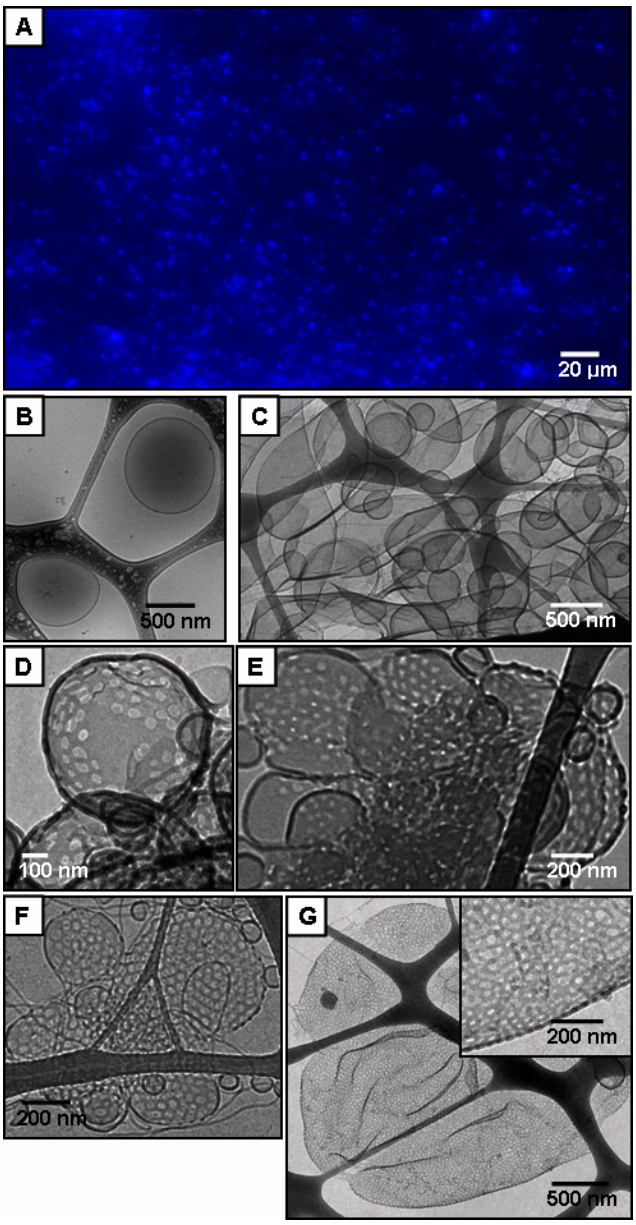


Figure S7. Reversible structural progression of self–assembled **2** by changing temperature. A, Fluorescence micrograph shows that the overall shapes of spherical aggregates are unchanged at 65 ℃. However, B,C, Cryo−TEM images indicates that the porous capsules transforms into closed capsules, on heating. D−G, After heating at 65 ℃ for 1 hr to close the pores in the capsules, the solution of **2** was slowly cooled down to room temperature. The closed capsules showed to be recovered into porous capsules. With increase of annealing time at room temperature, the number of the pores gradually increases and pore sizes become more uniform.

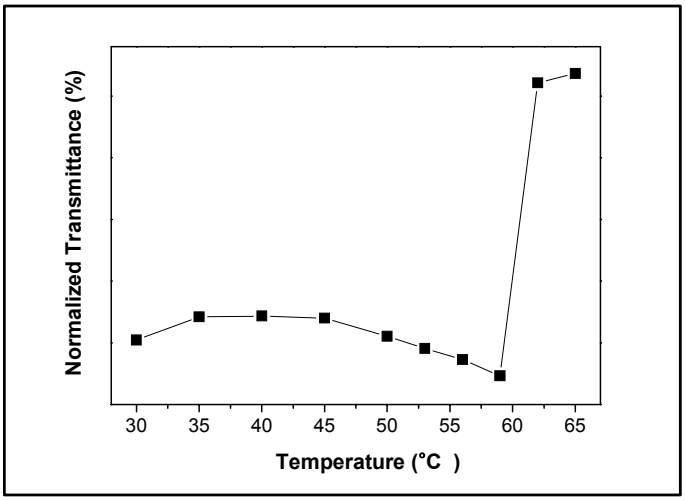


Figure S8. Change of optical transmittance of aqueous solution of **2** (1 wt%) upon heating at various temperatures.

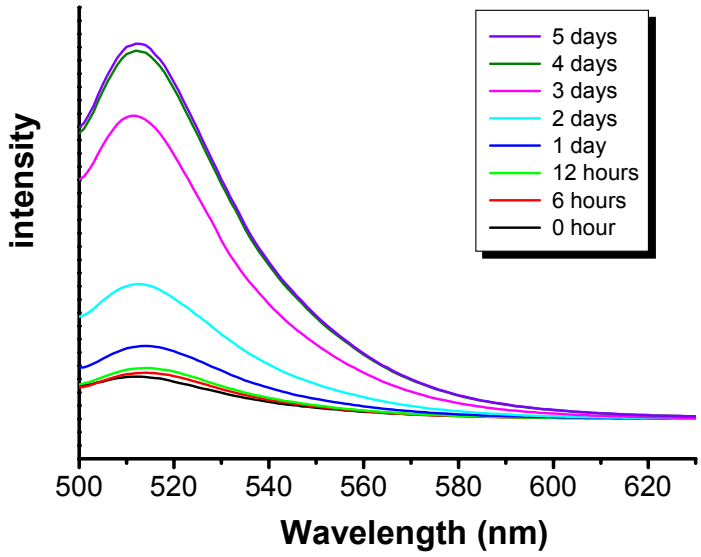


Figure S9. Variation in fluorescence emission spectrum with respect to time for calcein–loaded rod amphiphile **2** when heating above the LCST.

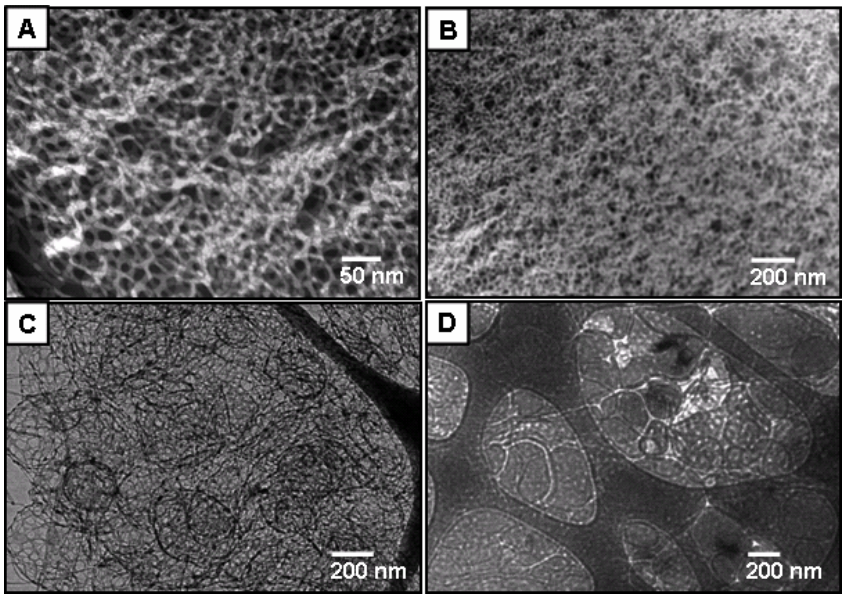


Figure S10. Influence of concentration on the aggregation structure of **2**. A,B, TEM images of sample cast from 0.1 wt% solution of **2**. C,D, Cryo–TEM images of 0.1 wt% aqueous solution of **2**. The images at this higher concentration (0.1 wt%) are almost identical to those obtained with 0.01 wt% solution. Therefore, their morphologies do not change within the range of concentration investigated (0.01–0.1 wt%).

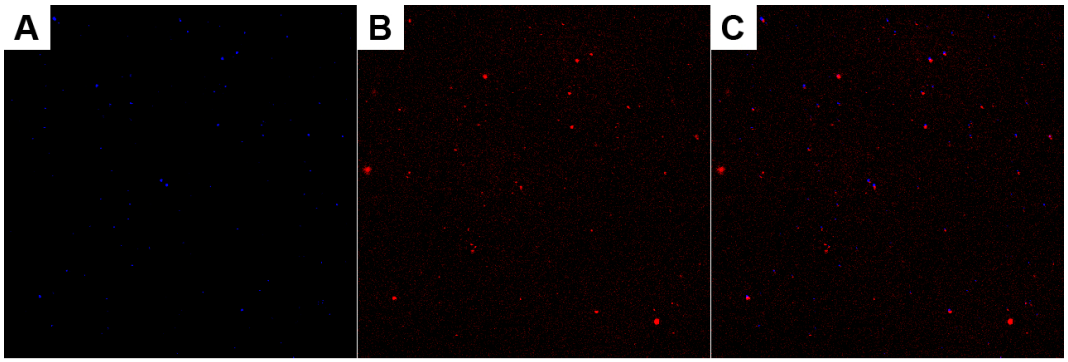


Figure S11. LSCM images of cross-sectional view of DNA-encapsulated capsules. A, Blue fluorescence from the capsules. B, Red fluorescence from the TAMRA-DNA. C, Overlay of A and B, showing the colocalization of the capsules and the DNA. The images were taken from the same field of microscope.

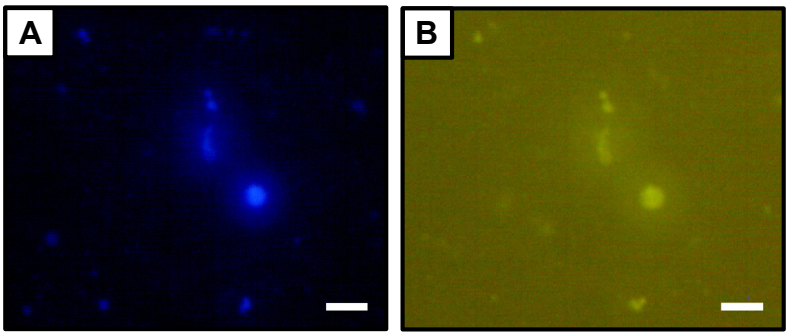


Figure S12. Encapsulation of huge proteins within the capsules. Fluorescence microscopy images of A, the capsules and B, FAM–IgM within the capsules. The images were taken from the same field of microscope. Some objects do not look like spheres due to their continuous Brownian motion, but they are in fact spherical in shape. Scale bar represents 20 μm.

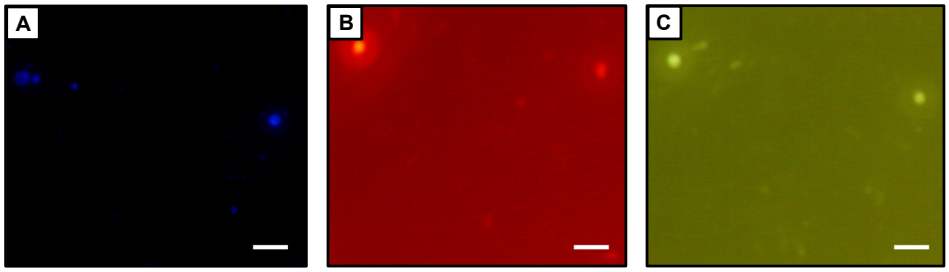


Figure S13. Simultaneous encapsulation of both DNA and protein within the capsules. Fluorescence microscopy images of A, the capsules, B, rhodamine–labeled DNA oligomer, and C, FAM–IgM. The images were taken from the same field of microscope. Scale bar represents 30 μm.

References for Supporting Information

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