Supporting Information for

Assembly-Disassembly Switching of Self-Sorted Nanotubules forming Dynamic 2-D Porous Heterostructure

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1. General Methods.

All reactions were performed in oven-dried glassware under dry argon atmosphere. Toluene and tetrahydrofuran (THF) were dried by distillation from sodium-benzophenone immediately prior to use. Dichloromethane (DCM) was dried by distillation from CaH_2. Distilled water was polished by ion exchange and filtration. Other solvents and organic reagents were purchased from commercial vendors and used without further purification unless otherwise mentioned. The reactions were monitored by thin-layer chromatography (TLC; Merck, silica gel 60 F254 0.25 mm) with visualization under UV light (254 and 365 nm) or treating iodine, phosphomolybdic acid. The products were purified by flash column chromatography on silica gel (230-400 mesh). Recycling preparative high-pressure chromatography (HPLC) was performed for further purification of the final desired molecules by using Prominence LC-20AP (SHIMADZU) and YMC C4 and C8 reverse phase column (250 x 4.6 mm I.D., S-5 um, 12 nm). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker AVANCE III 500 and Varian NMR System 300 MHz. All compounds were subjected to ^{1}H NMR analysis to confirm ≥98% sample purity. Chemical shifts were reported in ppm relative to the residual solvent peak ($CDCl_3$:^{1}H, 7.26; ^{13}C, 77.23) or tetramethylsilane (TMS) peak. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), td (triplet of doublets), br s (broad singlet). Coupling constants are reported in Hz. Matrix-Assisted Laser Desorption/ Ionization Time of Flight Mass Spectrometry (MALDI-TOF-MS) was performed on a Bruker Microflex LRF20 using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-2-propenylidene]malononitrile (DCTB) as a matrix. UV/Vis spectra were obtained from a Hitachi U-2900 Spectrophotometer. Fluorescence spectra were obtained from a SHIMADZU FL-5301PC Fluorescence Spectrophotometer.

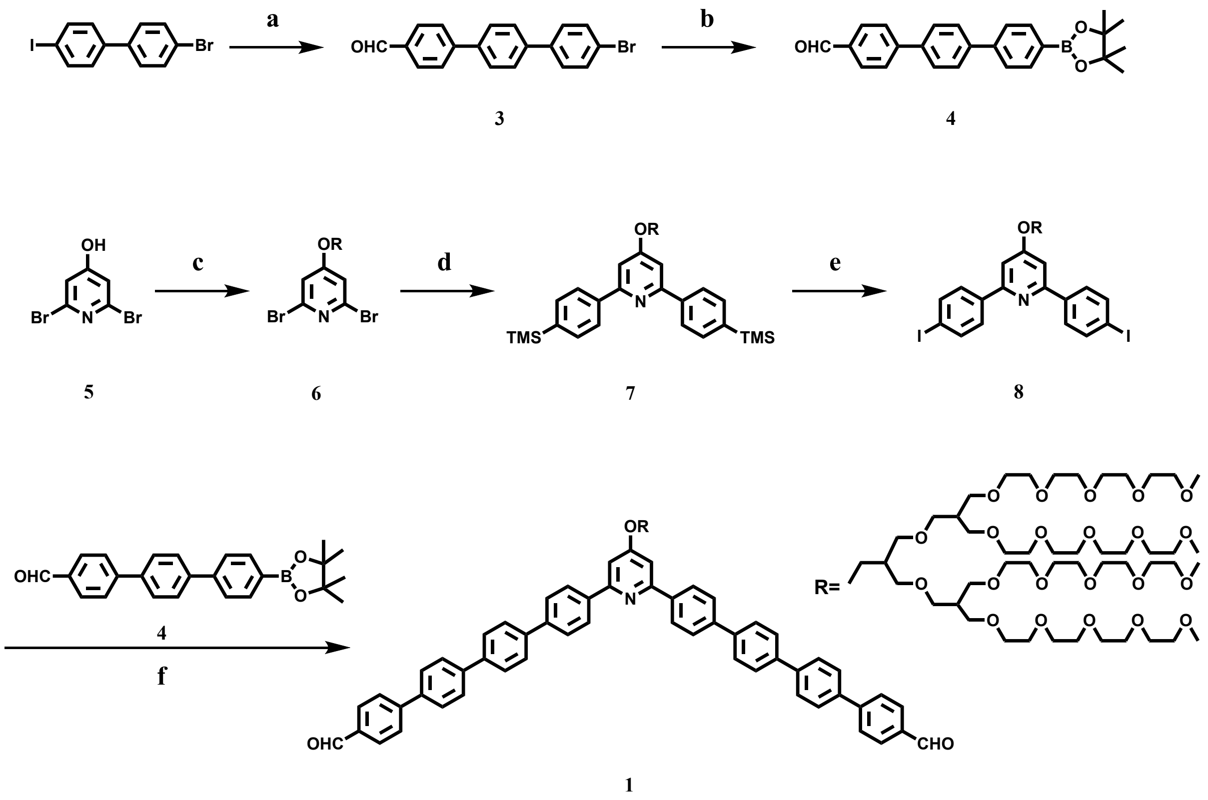
TEM Experiments. To investigate the self-assembled structures in aqueous solution, a drop of each sample solution was placed on a carbon-coated copper grid (Carbon Type B (15-25 nm) on 200 mesh, with Formvar; Ted Pella, Inc.) and the solution was allowed to evaporate under ambient conditions. These samples were stained by depositing a drop of uranyl acetate aqueous solution (0.2-0.4 wt %) onto the surface of the sample-loaded grid. The dried specimen was observed by a JEOL-JEM HR2100 operated at 120 kV. The cryogenic transmission electron microscopy (cryo-TEM) experiments were performed with a thin film of aqueous solution of amphiphiles (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. The grid was transferred, on a Gatan 626 cryo holder, using a cryo-transfer device and transferred to the JEOL-JEM HR2100 TEM. Direct imaging was carried out at a temperature of approximately -175 °C 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). The data were analyzed using Digital Micrograph software.

AFM experiments. The sample films on mica surface were prepared from evaporation of sample solutions. The measurements were conducted on a MultiMode 8 AFM with NanoScope V controller, NanoScope software and NanoScope Analysis software (Bruker AXS Corporation, Santa Barbara, CA, USA) in air at ambient temperature (ca. 25 °C) in the tapping mode and scanasyst in air mode.

Solution Preparation. Hierarchical co-assembled samples were prepared by dissolving amphiphilic molecules **1** and **2** in deionized water, separately. For different equivalents of molecule **1** in mixture solution, prepared 120 μM amphiphiles **1** and 120 μM **2** in aqueous solution, separately, then fixed total volume of solution to 300 uL, add 150 uL of **2** aqueous solution in each vial, and 0.1 eq (15 μL), 0.2 eq (30 μL), 0.3 eq (45 μL), 0.4 eq (60 μL), 0.5 eq (75 μL), 0.6 eq (90 μL), 0.7 eq (105 μL), 0.8 eq (120 μL), 0.9 eq (135 μL), 1.0 eq (150 μL) added to vial, separately. The residual part was added deionized water to get total volume 300 uL. The samples were sonicated for 30 min in the ice water and incubated for overnight before using in the experiment.

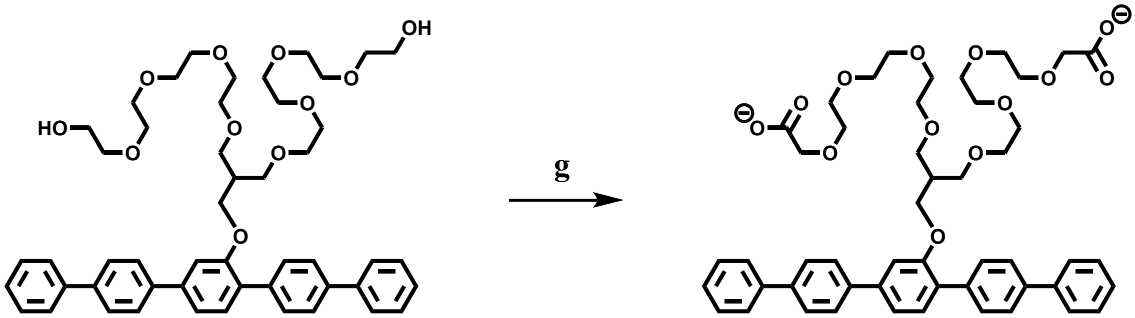
Encapsulation of Guests. Prepared 120 μM amphiphiles **1** and 120 μM **2** in aqueous solution, separately. Then added 2.0 mL of **2** and 1.0 mL of **1** in a vial, added 1.0 mL deionized water to get mixture solution ([**1**]/[**2**]=0.5). The C_{60} was dissolved in toluene followed by evaporation of toluene and add 10 μL of THF. After addition of 500 μL mixture solution, THF was slowly removed at ambient condition. The samples were sonicated for 5 min in ice water before using in the experiment. The sampling of encapsulation of coronene was used the same method.

2. Synthetic method.



Scheme 1: Synthetic method of amphiphile **1**

Reagents and conditions: (a) 4-formylphenylboronic acid, Pd(PPh$_3$)$_4$, 2 M Na$_2$CO$_3$ (*aq*), THF, reflux, 12 h, yield, 72 %; (b) Bis(pinacolato)diboron, Pd(dppf), KOAc, DMF, 100°C, 12 h, yield, 57 %; (c) K$_2$CO$_3$, CH$_3$CN, reflux, 12 h, yield, 80 %; (d) 4-(trimethylsilyl)phenyl- boronic acid, Pd(PPh$_3$)$_4$, 2 M Na$_2$CO$_3$ (*aq*), THF, reflux, 12 h, yield, 69 %; (e) ICl, dichloromethane, -78°C, 1 h, yield, 98 %; (f) Pd(PPh$_3$)$_4$, 2 M Na$_2$CO$_3$ (*aq*), ethanol, toluene, reflux, 12 h, yield, 50 %.



9 **2**

Scheme 2: Synthetic method of amphiphile **2**

Reagents and conditions: (g) CrO_3, H_2SO_4, H_2O, 0°C, 2 h, 19 %.

Compound 3. 4-Bromo-4'-iodobiphenyl (1.436 g 4 mmol) and 4-formylphenylboronic acid (500 mg, 3.34 mmol) were dissolved in degassed toluene (33.4 mL), EtOH (16.7 mL) and 2 M aqueous Na_2CO_3 (8.5 mL), then $Pd(PPh_3)_4$ (193 mg, 0.167 mmol) was added to mixture. The mixture was refluxed for 12 h under argon. After completion of the reaction as monitored by TLC, the reaction mixture was cooled to room temperature and was extracted with ethyl acetate many times. The combined organic layers were dried over anhydrous $MgSO_4$. After the filtrate was condensed under the reduced pressure, the crude product was purified by silica gel flash column chromatography using ethyl acetate: hexane (1:10, v/v) as an eluent to yield 72 % (810 mg) of white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 10.08 (s, 1H), 7.98 (d, J = 8.3 Hz, 2H), 7.80 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H).

Compound 4. Compound **3** (337 mg, 1 mmol) and bis(pinacolato)diboron (304.7 mg, 1.2 mmol) were dissolved in degassed DMF (10 mL), then Pd(dppf) (49 mg, 0.06 mmol) and KOAc (588.8 mg, 6 mmol) were added carefully. The mixture was refluxed overnight. After completion of the reaction as monitored by TLC, the reaction mixture was cooled to room temperature and was extracted with ethyl acetate many times. The combined organic layers were dried over anhydrous $MgSO_4$. After the filtrate was condensed under the reduced pressure, the crude product was purified by silica gel flash column chromatography using dichloromethane: hexane (1:2, v/v) as an eluent to yield 57 % (217 mg) of pale yellow solid. ^1H NMR (300 MHz, $CDCl_3$) δ 10.06 (s, 1H), 7.97 (d, J = 8.5 Hz, 2H), 7.91 (d, J = 8.3 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H), 7.73 (s, 4H), 7.66 (d, J = 8.2 Hz, 2H), 1.36 (s, 12H).

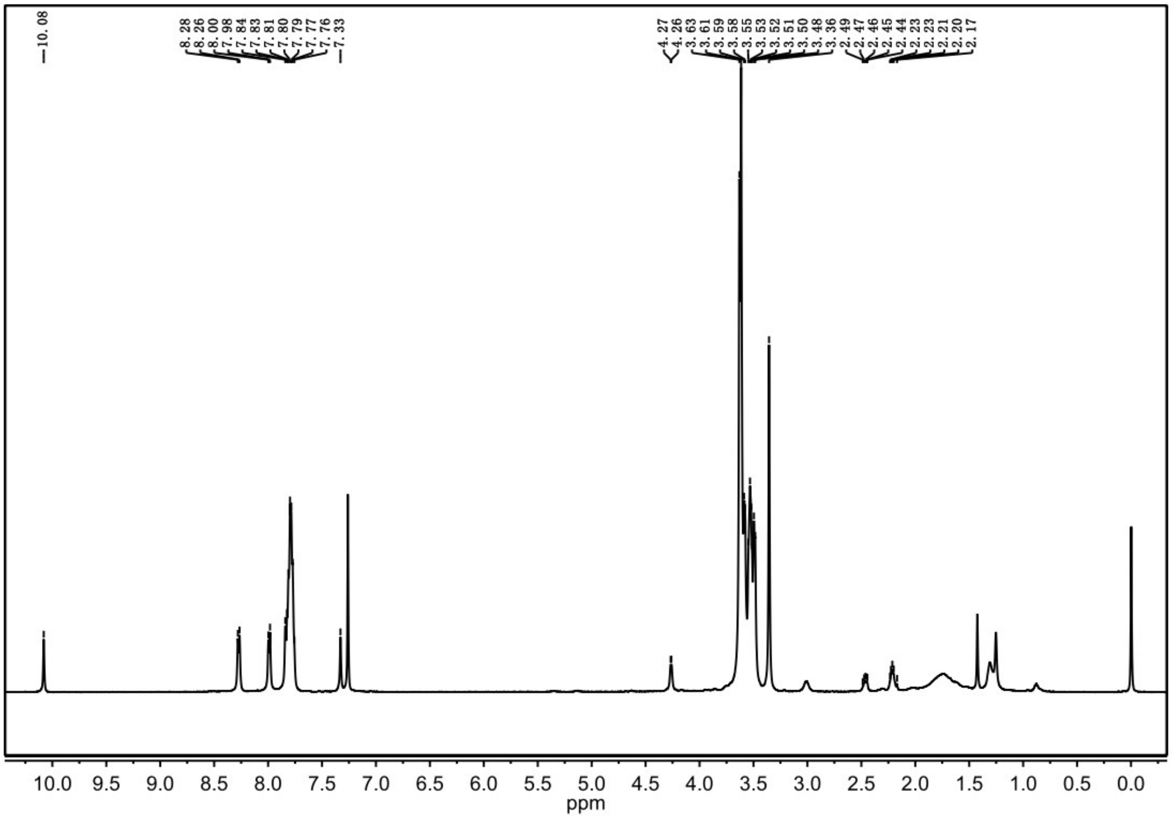
Compound 6. Compound **5** (0.25 g, 1 mmol), ROTs[1] (1.197 g, 1 mmol) and K_2CO_3 (1.1 g, 7.0 mmol) were dissolved in 20 mL of anhydrous acetonitrile. The mixture was refluxed overnight and then cooled to room temperature. The solvent was removed in a rotary evaporator, and the resulting mixture was poured into water and extracted with ethyl acetate. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. After removed the solvent in a rotary evaporator, the crude product was purified by silica gel flash column chromatography using methanol: ethyl acetate (1:20, v/v) as an eluent to yield 80 % (1.02 g) of colorless liquid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.03 (s, 2H), 4.08 (d, *J* = 5.6 Hz, 2H), 3.68 – 3.40 (m, 80H), 3.38 (s, 12H), 2.32 (s, 1H), 2.08 – 2.03 (m, 2H). MALDI-TOF mass: *m/z* calcd. for $C_{53}H_{99}Br_2NO_{23}$ $[M+Na]^+$, 1298.49; found: $[M+Na]^+$, 1298.55.

Compound 7. Compound **6** (226.8 mg, 0.177 mmol) and 4-(Trimethylsilyl)phenylboronic acid were dissolved in degassed THF (1.77 mL) and 2M aqueous Na_2CO_3 (1.416 mL), then $Pd(PPh_3)_4$ (10.3 mg, 0.0086 mmol) was added to mixture. The mixture was refluxed overnight under argon. After completion of the reaction as monitored by TLC, the reaction mixture was cooled to room temperature and was extracted with ethyl acetate many times. The combined organic layers were dried over anhydrous $MgSO_4$. After the filtrate was condensed under the reduced pressure, the crude product was purified by silica gel flash column chromatography using methanol: ethyl acetate (1:15, v/v) as an eluent to yield 69 % (173 mg) of colorless liquid. ^1H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.3 Hz, 4H), 7.62 (d, *J* = 8.2 Hz, 4H), 7.22 (s, 2H), 4.18 (d, *J* = 6.0 Hz, 2H), 3.63 – 3.44 (m, 80H), 3.35 (s, 12H), 2.44 – 2.41 (m, 1H), 2.08 – 2.01 (m, 2H), 0.29 (s, 18H). MALDI-TOF mass: *m/z* calcd. for $C_{71}H_{125}NO_{23}Si_2$ $[M+Na]^+$, 1438.81; found: $[M+Na]^+$, 1438.95.

Compound 8. Compound **7** (173 mg, 0.122 mmol) was dissolved in anhydrous dichloromethane (DCM) (2 mL). ICl (1.0 M in DCM solution) (0.671 mL, 0.671 mmol) was added dropwise at -78°C. The reaction mixture was stirred for 1h under nitrogen before 1M aqueous $Na_2S_2O_3$ (0.7 mL) solution was added and the solution was stirred for 2h. The layer was separated, and the aqueous layer was then washed with DCM. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. After removed the solvent in a rotary evaporator, the crude product was purified by silica gel flash column chromatography using methanol: ethyl acetate (1:15, v/v) as an eluent to yield 98% (120 mg) of colorless liquid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.6 Hz, 4H), 7.81 (d, *J* = 8.5 Hz, 4H), 7.22 (s, 2H), 4.20 (d, *J* = 5.5 Hz, 2H), 3.64 – 3.44 (m, 80H), 3.37 (s, 12H), 2.43 – 2.40 (m, 1H), 2.18-2.10 (m, 2H). MALDI-TOF mass: *m/z* calcd. for $C_{65}H_{107}I_2NO_{23}$ $[M+Na]^+$, 1546.52; found: $[M+Na]^+$, 1546.44.

Compound 1. Compound **8** (35 mg, 0.023 mmol) and compound **4** (36 mg, 0.093 mmol) were dissolved in degassed toluene (0.2 mL), EtOH (0.1 mL) and 2M aqueous Na_2CO_3 (0.05 mL), then $Pd(PPh_3)_4$ (1.33 mg, 0.0013 mmol) was added to mixture. The mixture was refluxed overnight under argon. After completion of the reaction as monitored by TLC, the reaction mixture was cooled to room temperature and was extracted with ethyl acetate many times. The combined organic layers were dried over anhydrous $MgSO_4$. After the filtrate was condensed under the reduced pressure, the crude product was purified by silica gel flash column chromatography using methanol: ethyl acetate (1:15, v/v) as an eluent and the further purified by prep-HPLC (C8 column, acetonitrile: H_2O=80: 20) to yield 50 % (20 mg) of white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 10.08 (s, 2H), 8.27 (d, *J* = 7.7 Hz, 4H), 7.99 (d, *J* = 7.4 Hz, 4H), 7.80 (m, 24H), 7.33 (s, 2H), 4.31 – 4.23 (m, 2H), 3.64 – 3.48 (m, 80H), 3.36 (s, 12H), 2.50 – 2.43 (m, 1H), 2.24 – 2.18 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.89, 158.06, 146.64, 141.07, 140.80, 139.99, 139.41, 138.69, 138.65, 135.26, 130.36, 127.84, 127.61, 127.58, 127.54, 127.50, 127.22, 105.37, 71.91, 70.58, 70.55, 70.49, 70.45, 69.69, 69.62, 69.13, 59.02, 46.11, 40.17, 39.88, 29.70, 11.18. MALDI-TOF mass: *m/z* calcd. for $C_{103}H_{133}NO_{25}$ $[M+H]^+$, 1784.92, $[M+Na]^+$, 1806.91; $[M+K]^+$ 1822.88 found: $[M+H]^+$, 1785.44. $[M+Na]^+$, 1807.14, $[M+K]^+$, 1823.76.

Compound 2. Compound **9**[2] (100 mg, 0.119 mmol) was dissolved in degassed acetone (2 mL), then Jones reagent (0.75 mL) was added dropwise. The mixture was stirred 2 hours under argon at 0°C. After completion of the reaction as monitored by TLC, the reaction was quenched by isopropanol. The solvent was removed in a rotary evaporator. The resulting mixture was poured into water and was extracted with ethyl acetate many times. The combined organic layer was dried over anhydrous $MgSO_4$. The filtrate was condensed under reduced pressure and purified by HPLC (C4 column, acetonitrile: H_2O=60: 40) to yield 19 % (20 mg) of white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.64 (m, 12H), 7.47 (td, *J* = 7.7, 2.9 Hz, 5H), 7.40 – 7.28 (m, 4H), 4.19 (d, *J* = 4.8 Hz, 2H), 4.11 (s, 4H), 3.68 (d, *J* = 4.6 Hz, 4H), 3.65– 3.47 (m, 24H), 2.43– 2.37 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.33, 156.30, 141.36, 140.85, 140.63, 140.33, 139.77, 139.54, 137.29, 130.97, 130.91, 129.99, 129.48, 128.85, 128.82, 127.52, 127.49, 127.41, 127.27, 127.03, 126.52, 119.61, 111.33, 71.22, 70.59, 70.31, 68.94, 66.53, 65.58, 39.69, 30.58, 19.19, 13.74. MALDI-TOF mass: *m/z* calcd. for $C_{50}H_{58}O_{13}$ $[M+Na]^+$, 889.38; found: $[M+Na]^+$, 889.07.



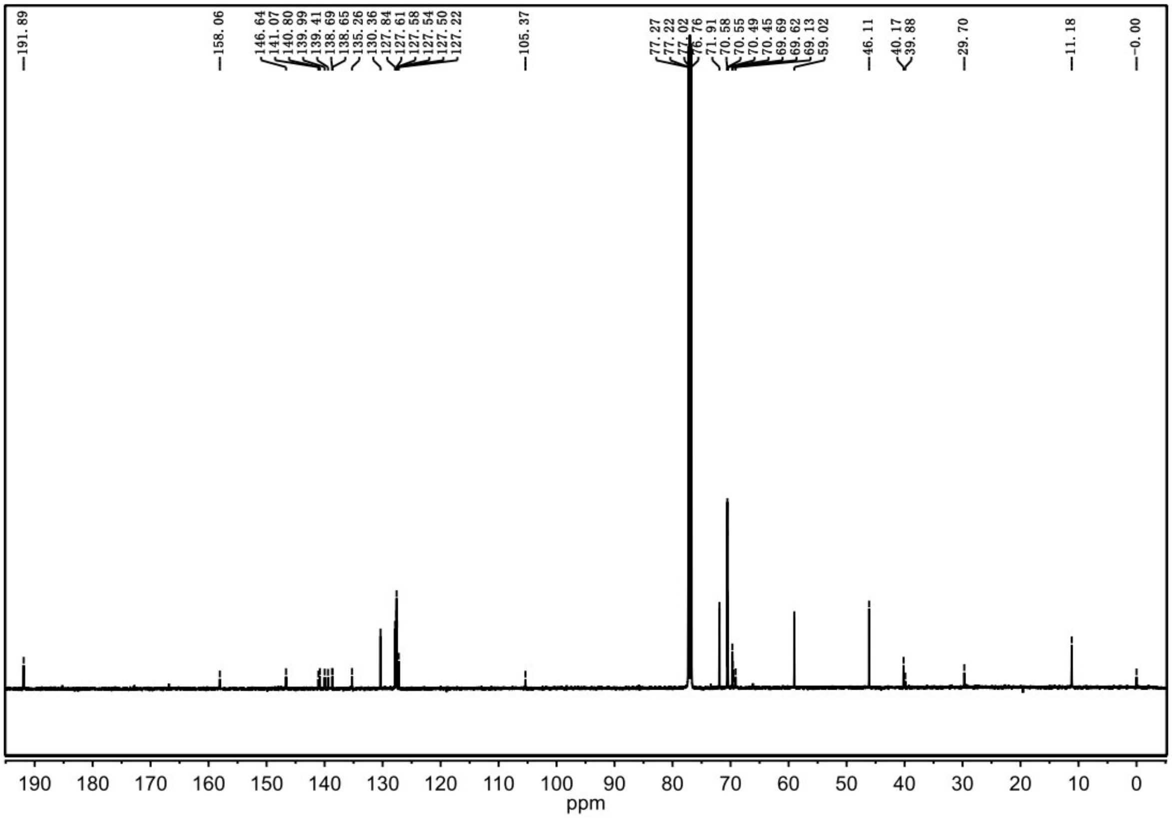


Figure S1. ^{1}H and ^{13}C- NMR spectra of **1** in $CDCl_3$

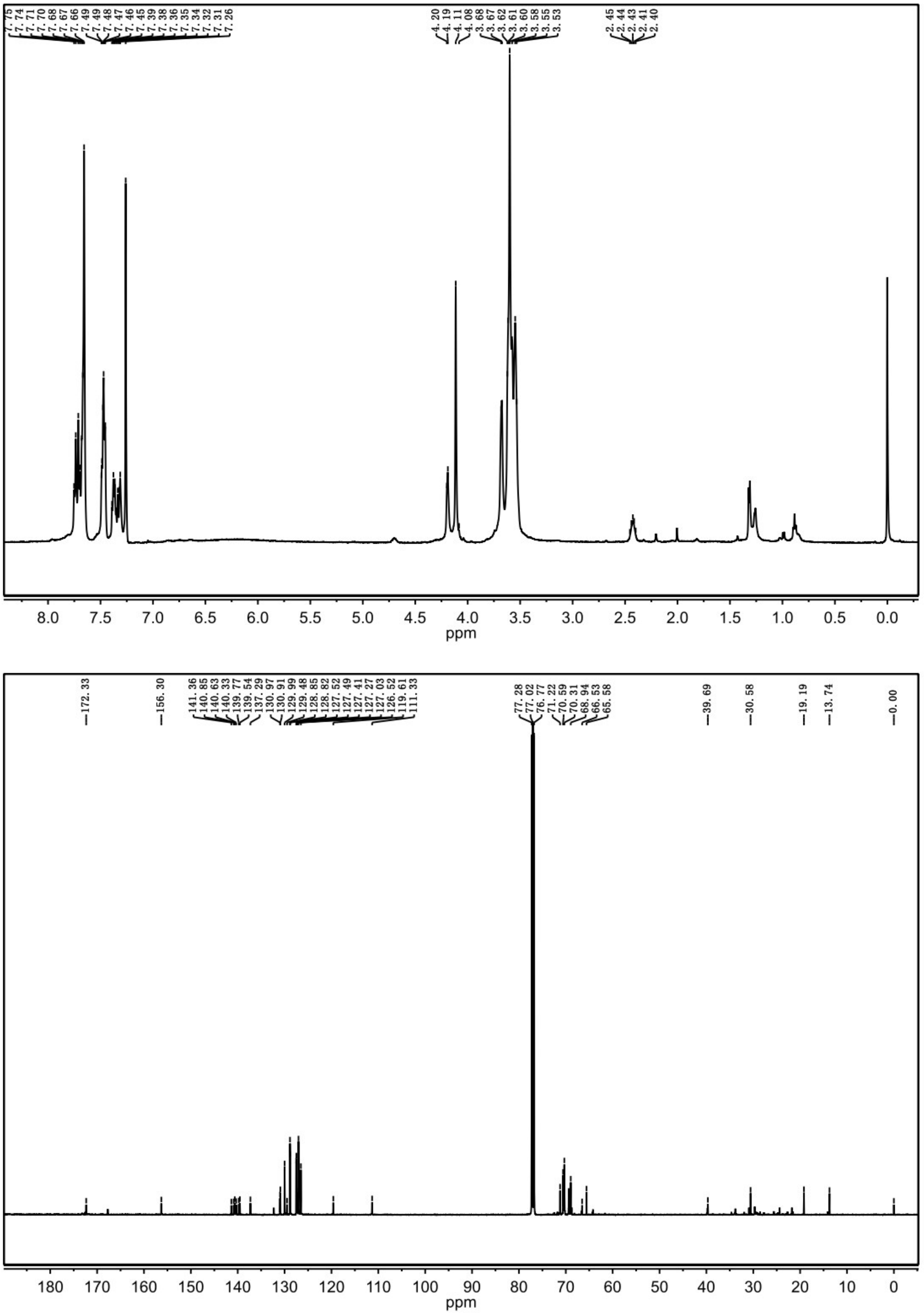


Figure S2. ^{1}H and ^{13}C- NMR spectra of **2** in $CDCl_3$

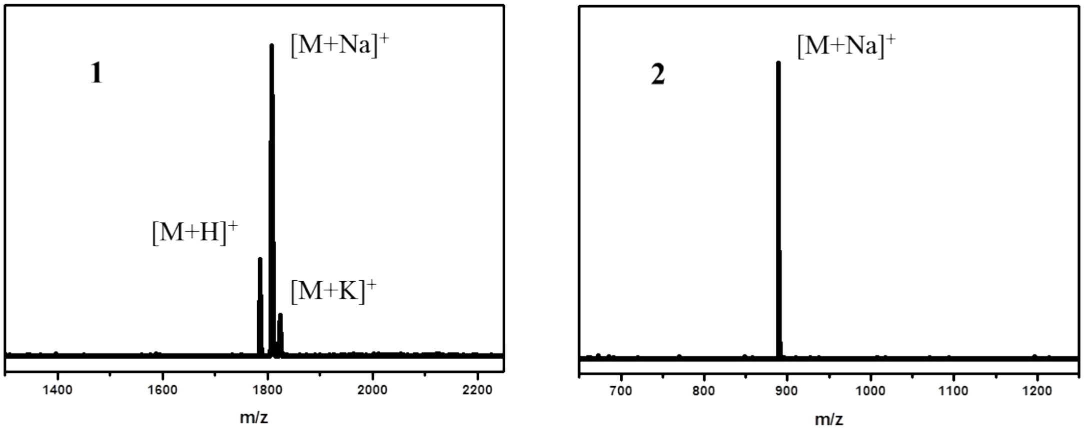


Figure S3. MALDI-TOF mass spectra of **1** and **2**.

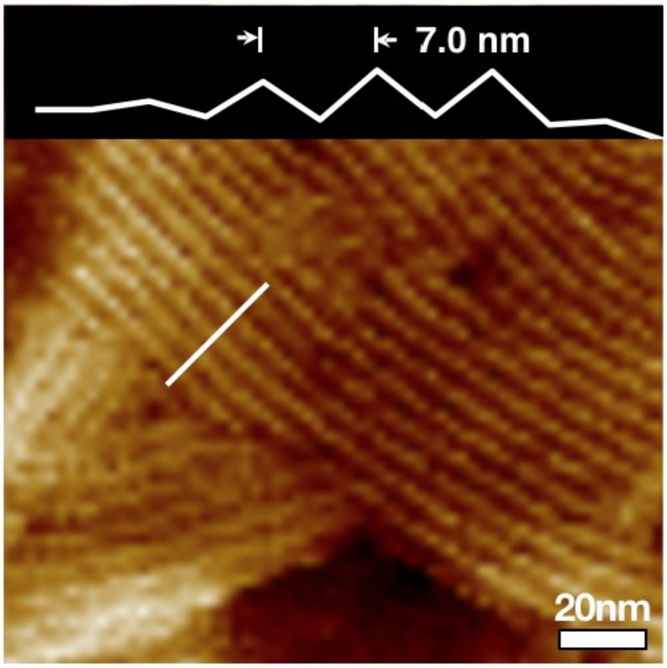


Figure S4. AFM height image of tubules on mica surface from evaporated film of **1** (30 μM) at neutral pH 7.4 buffer. The cross-sectional profile (top) is along the white line.

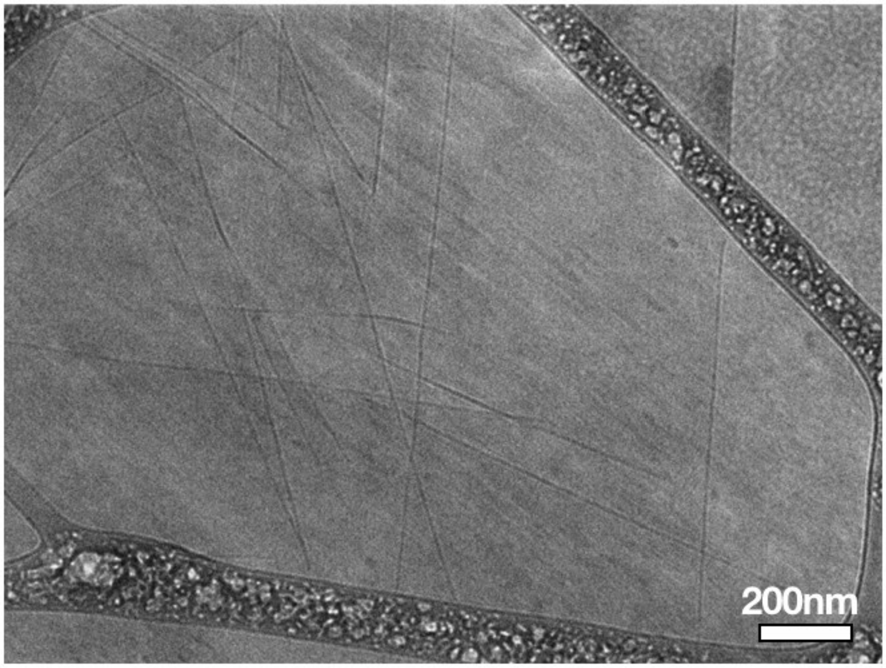
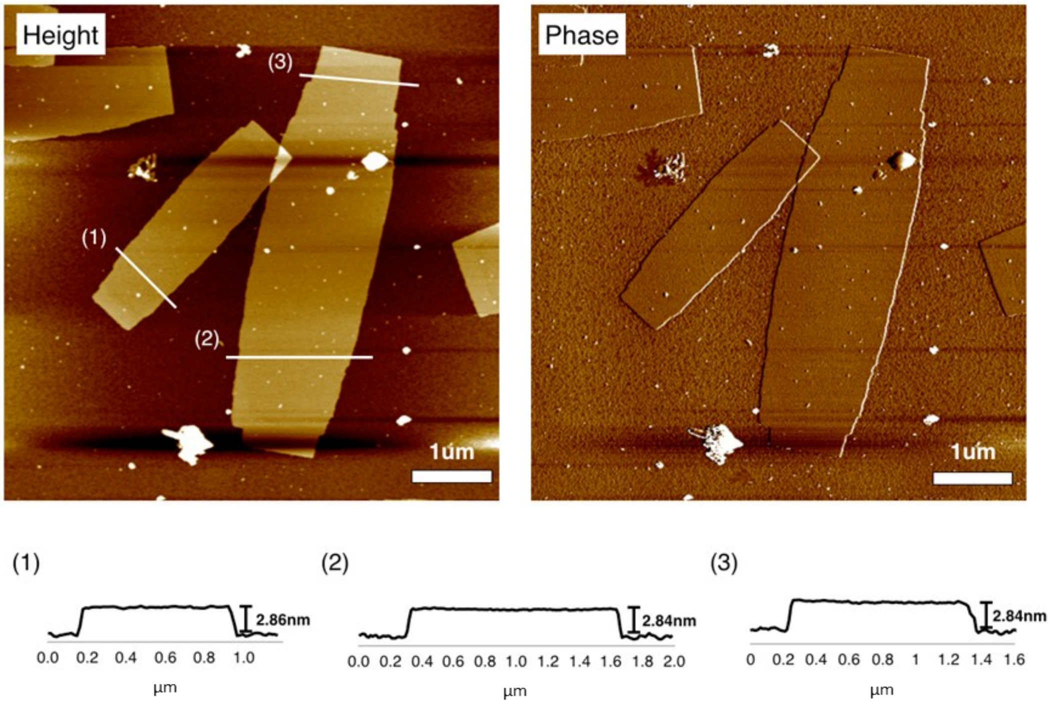


Figure S5. Cryo-TEM image of **2** (60 μM) in aqueous solution.



Fiugre S6. AFM height and phase images of **2** (60 μM aqueous solution). (1), (2) and (3) are height profiles along the white lines in height image.

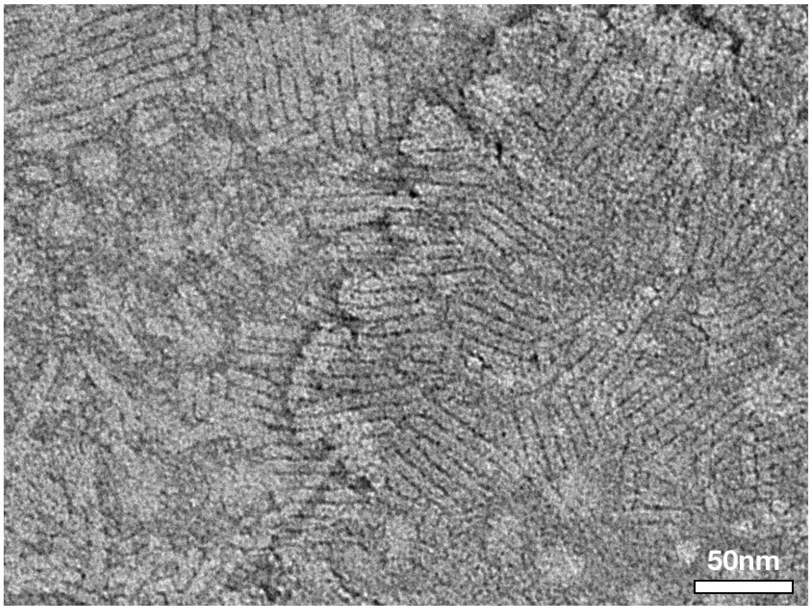


Figure S7. Negatively-stained TEM image of a mixture solution ([1]/[2]=1.0) at neutral pH 7.4 buffer solution.

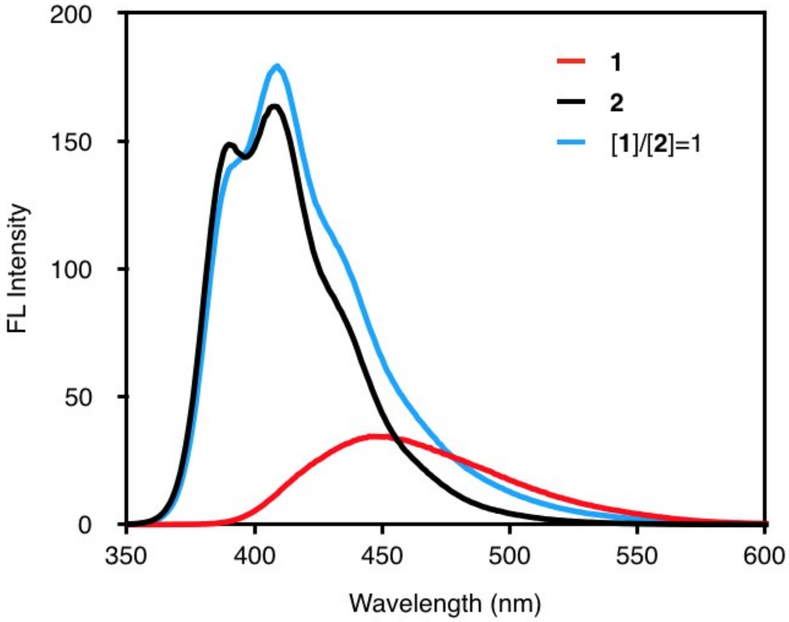


Figure S8. Fluorescence spectra of **1**, **2** and mixture solution ([**1**]/[**2**]=1.0) at neutral pH 7.4 buffer solution. Excitation wavelength: 330 nm.

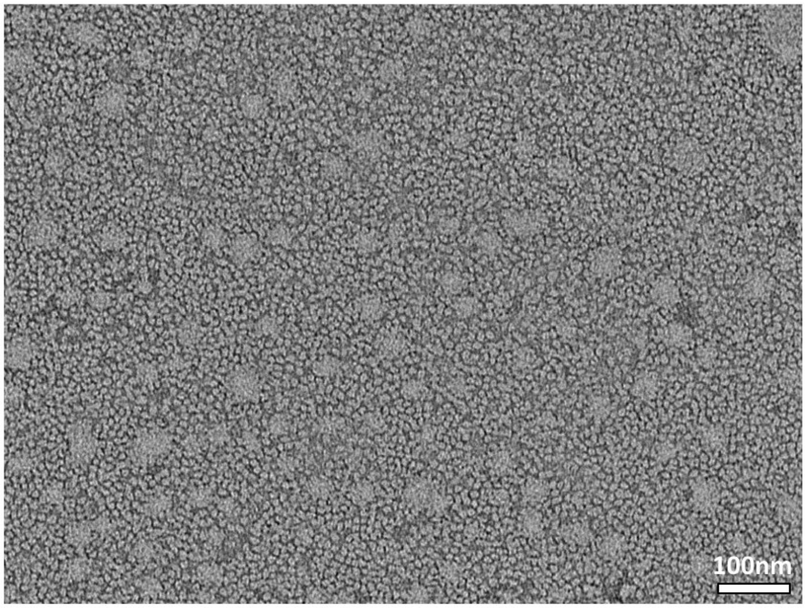


Figure S9. Negatively-stained TEM image of pure **1** at pH 5.5.

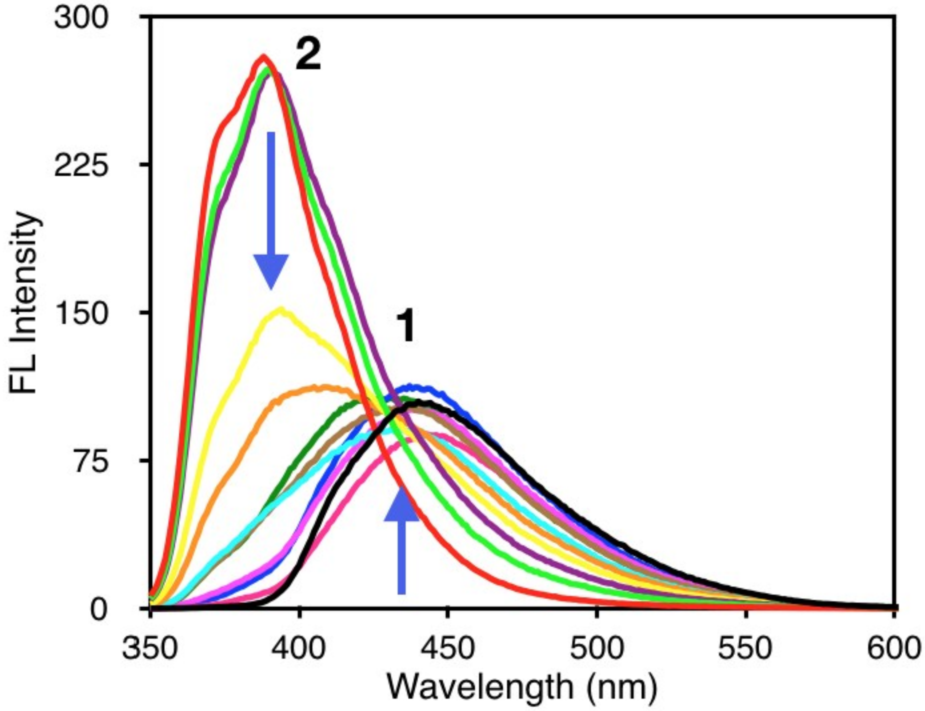


Figure S10. Emission spectra of a series of [**1**]/[**2**] ratio based on 60 μM **2** at pH 5.5. Excitation wavelength: 330 nm.

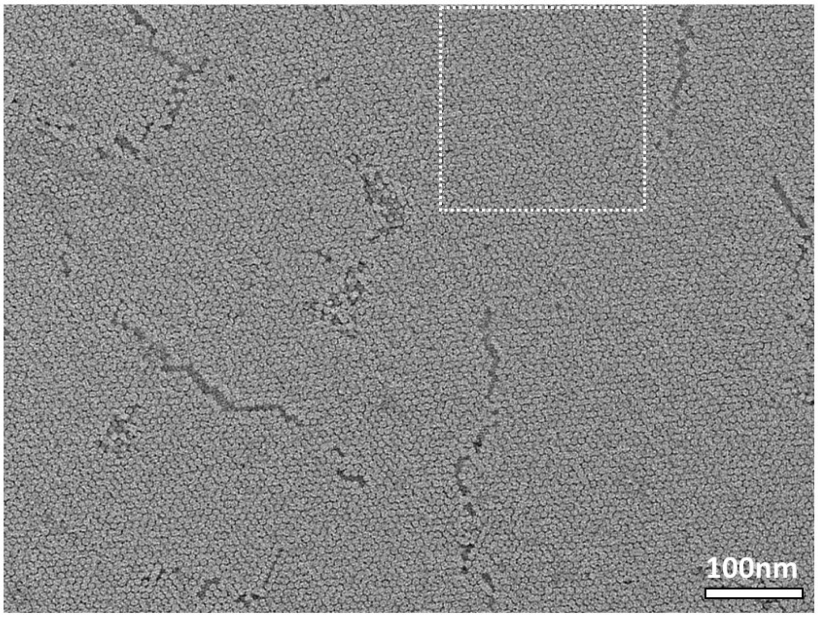


Figure S11. Large area TEM image of a mixture solution ([**1**]/[**2**]=0.5) at pH 5.5.

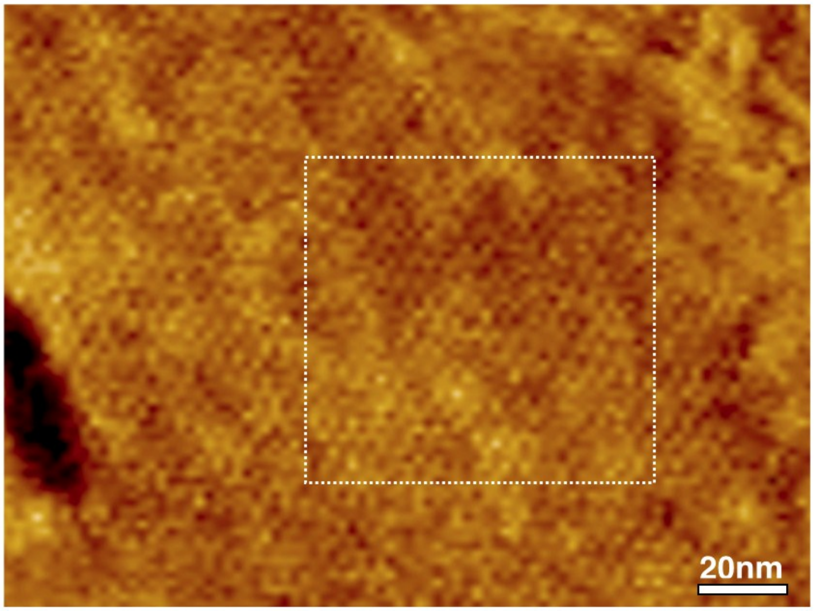


Figure S12. Large area AFM image of a mixture solution ([**1**]/[**2**]=0.5) at pH 5.5.

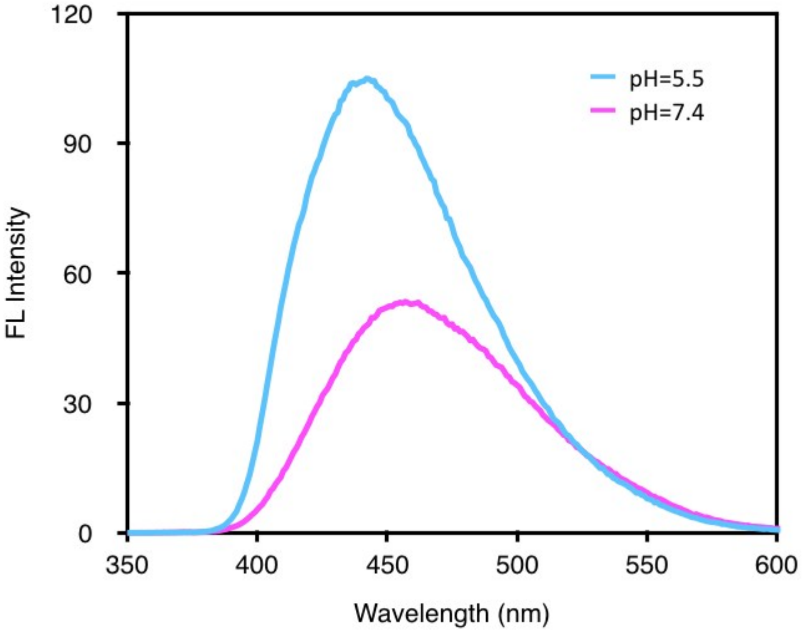


Figure S13. Fluorescence spectra of 30 μM **1** at different pH buffer solutions. Excitation wavelength: 330 nm.

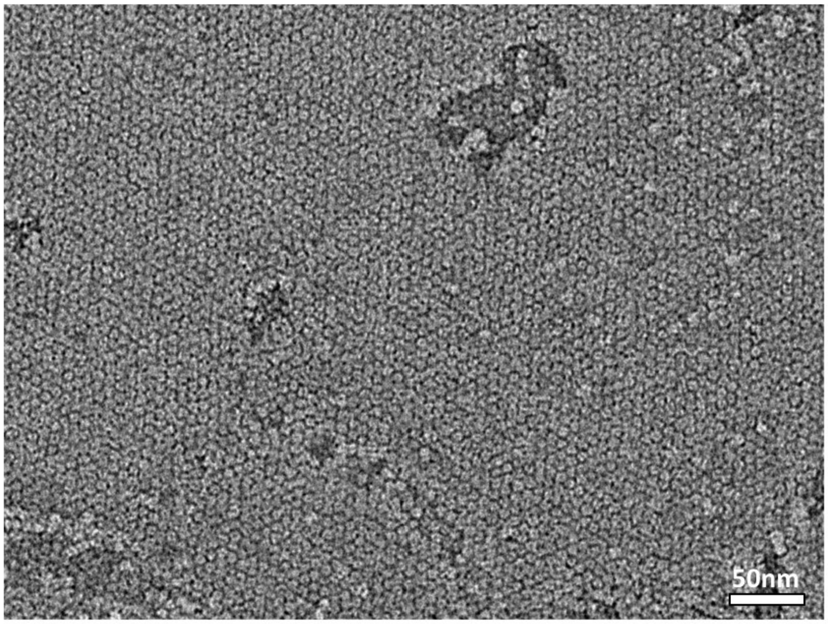


Figure S14. Negatively-stained TEM image after encapsulation of C_{60} using 2D porous heterstructure at pH 5.5.

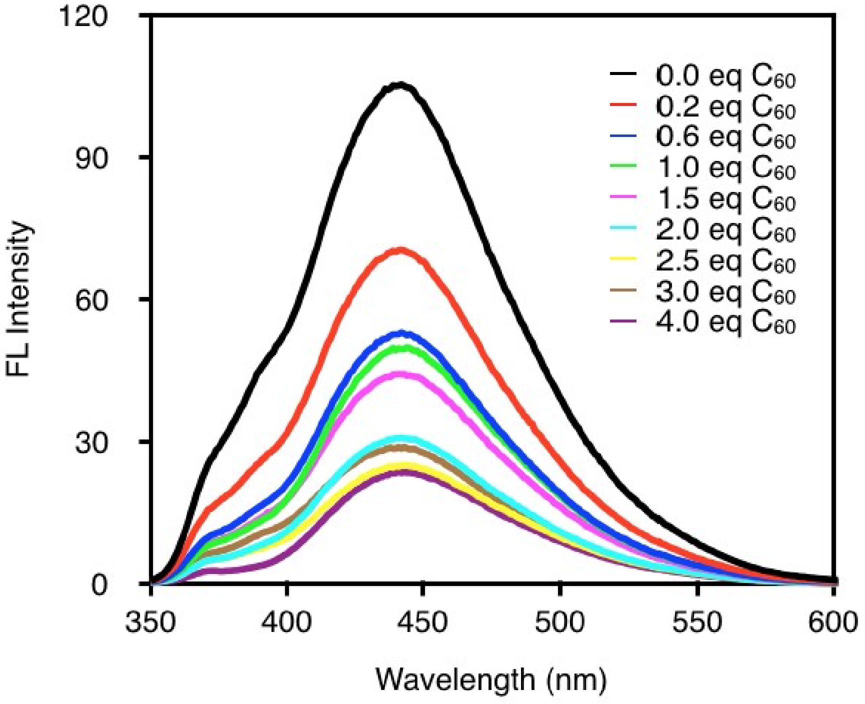


Figure S15. Emission spectra of different equivalents of C_{60} per cavity based on 30 μM **1** at pH 5.5. Excitation wavelength: 330 nm.

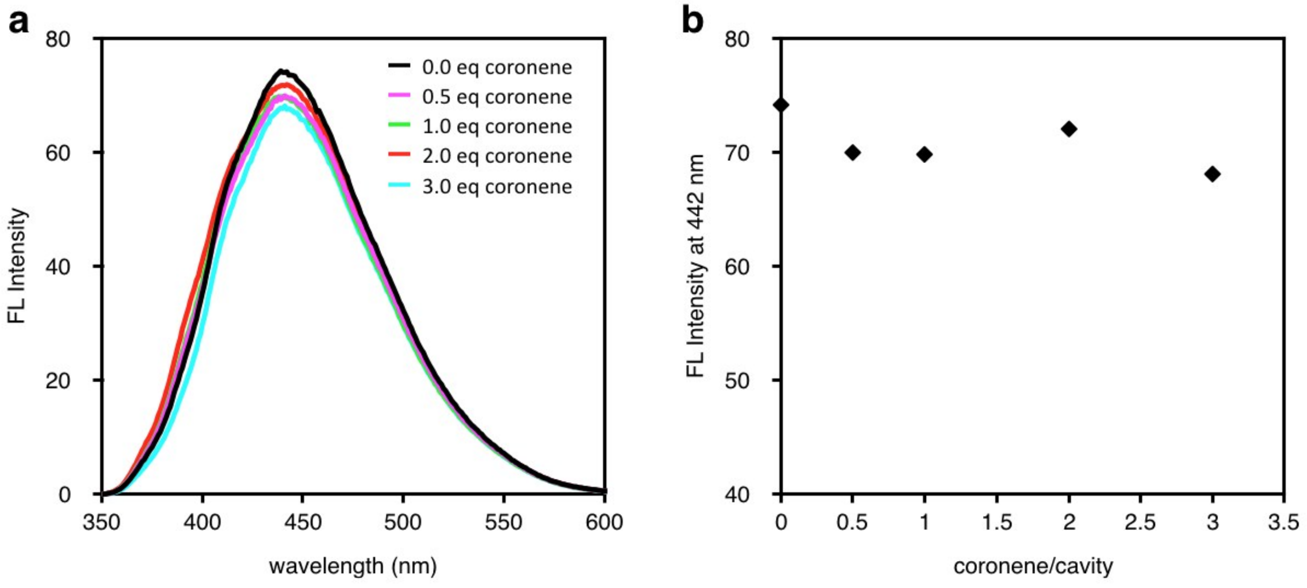


Figure S16. (a) Emission spectra of different equivalents of coronene per cavity based on 30 μM **1** at pH 5.5. Excitation wavelength: 330 nm. (b) Fluorescence intensity variety at 442 nm with different amount of coronene per cavity.

3. Reference

(1) Lee, E.; Huang, Z.; Ryu, J-H.; Lee, M. *Chem. Eur. J.* **2008**, *14*, 3883-3888.

(2) Lee, D.-W.; Kim, T.; Park, I.-S.; Huang, Z.; Lee, M. *J. Am. Chem. Soc.* **2012**, *134*,14722-14725.