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Supplementary information

Supramolecular vesicle: triggered by formation of pseudorotaxane between cucurbit[6]uril and surfactant †

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Content

Materials. All reagents and solvents for syntheses were purchased from commercial sources and used without further purification.

General Characterization and Physical Measurements. ^{1}H NMR spectra were recorded on a Varian Mercury VX-300 spectrometer. The IR spectra (in KBr pellets) are recorded on a Shimadzu FT-IR 157 spectrophotometer; Thermogravimetric study was carried out with a NETZSCH STA 449C at a heating rate of 10 K/min under nitrogen; HRTEM was performed with a JEM-2010FEF field emission electron microscope operating at 200 kV, equipped with an EDAX Phoenix EDS analyzer. ESI-MS measurement was performed on Thermo Finnigan LCQ advantage at room temperature in H_2O. Dynamic light scattering (DLS) was carried out at 25℃ by using Malvern instrumentation. Single crystal X-ray diffraction data was collected on a Bruker SMART 1000 CCD area detector system using Mo Kα radiation. Cryo-TEM was performed with Tecnial 20 at room temperature. UV titration was carried out at 25°C by using TU-1901. The conductivity of HBPB-8 and HBPB-8@CB[6] were performed on DDSJ-308A at 25°C. The encapulation of fluorescence dye was performed on RF-5301 at room temperature.

Experimental data:

Cucurbit[6]uril (CB[6]) and HBPB-8: CB[6] and HBPB-8 were synthesized and purified by procedures reported earlier. [1-2]

CB[6]: **^{1}H NMR** (300 MHz, 2 mol/L D_2O/NaCl): δ 4.13 (H_b, d, J = 15.6, 12H), 5.37 (H_c, s, 12H), 5.52 (H_a, d, J = 15.6, 12H).

HBPB-8: **^{1}H NMR** (300 MHz, D_2O): δ 8.78 (H_a, d, J = 5.8, 4H), 8.06 (H_b, d, J = 5.9, 4H), 4.43 (H_4, t, J = 7.2, 4H), 3.21 (H_c, t, J = 6.7, 4H), 1.80 (H_3, s, 4H), 1.43 (H_d, s, 4H), 1.20 (H_e, d, J = 32.4, 4H), δ 1.09 (H_2, m, 20H), 0.59 (H_1, d, J = 6.1, 6H). IR (KBr)υ/ cm^{-1}: 3491 (N-H), 3226 (Py-H), 2920 and 2857 (CH_2), 1662 (amide, C=O), 1549, 1509 and 1466 (skeleton stretching frequency of pyridine), 1400 (C-N); ESI-MS: m/z = 633 ([M-Br]$^+$); Anal. $C_{34}H_{56}N_4O_2Br_2$ calcd: C, 57.22; H, 7.84; N, 7.85. Found: C, 57.13; H, 7.87; N, 7.85.

HBPB-8@CB[6]: A mixture of CB[6] (1.20 g, 1.20 mmol) and HBPB-8 (0.712 g, 1.0mmol) in water (30 mL) was heated at 70 °C for 8 h. After the sample was stirred at room temperature overnight, the residue of CB[6] was filtered off. The filtrate was heated at 100 °C for 24 h in a sealed container, then cooled down to room temperature. Colorless single crystal of pseudorotaxane was formed after several weeks. **^{1}H NMR** (300 MHz, D_2O): δ 8.75 (H_a, d, J = 6.6, 4H), 8.45 ($H_{b'}$, d, J = 6.6, 4H), 4.44 (H_4, t, J = 7.3, 4H), 3.07 ($H_{c'}$, t, 4H), 1.80 (H_3, s, 4H), 1.09 (H_2, m, 20H), 0.59 (H_1 & $H_{d'}$, m, 6H+4H), 0.25 ($H_{e'}$, m, 4H). **IR** (KBr) υ/cm^{-1}: 3447 (the O-H stretching frequency of water), 1749 (C=O of CB[6]), 3020 and 2988 (C-H stretching frequencies

of CB[6]); 1651 (C=O stretching frequency of pyridicarboxamide), 1500 (skeleton stretching frequency of pyridine). 3134 and 1532 (N-H stretching and bending vibration frequencies of amide), 1310 (C-N stretching frequency of pyridicarboxamide), 1460 and 1380 (CH_2 or a C-H bending vibration frequencies of alkyl chain). ESI-MS: m/z = 774.8 $[M\text{-}2Br]^{2+}$.

Crystal data for HBPB-8@CB[6] *($C_{140}H_{184}N_{56}O_{26}Br_4 \cdot 12H_2O$)*: M = 3635.26, Triclinic, Space group P-1, 0.30 × 0.26 × 0.20 mm^3, a = 15.2922 (18)Å, b = 22.693 (3) Å, c = 26.547 (3)Å, α = 70.259 (2)°, β = 77.455 (2)°, γ = 80.448 (2)°, U = 8421.0 (18) $Å^3$, Z = 2, D_c = 1.434 $mg.m^{-3}$, T = 298 (2) K, Bruker SMART 1000 CCD diffractometer, Mo-K_α radiation (λ = 0.71073 Å), μ = 1.048 mm^{-1}, F(000) = 3800. Refinement method: Full-matrix least-squares on F2. Data/ restraints/parameters: 29406/12/2237. Independent reflections 29406 (Rint = 0.0000). Theta range for data collection: 1.91 to 25.01°. Index ranges: -17 <= h <= 18, -25 <= k <= 26, 0 <= l <= 31. *R1* (I>2σ (I)) = 0.1227, *wR2* (all data) = 0.3671, and GOF=0.950. CCDC: 772384.

Specimens of suitable quality and size of HBPB-8@CB[6] crystal was mounted on the ends of quartz fibers and used for intensity data collection on a Bruker SMART 1000 CCD area detector system using Mo Kα radiation. Cell parameters were obtained using SMART software.[3] Data reduction and integration were performed using the software package SAINT PLUS,[4] which also corrects for Lorentz and polarization effects, while absorption corrections were applied using the program SADABS.[5] In the structure, all the non-hydrogen atomic positions were found via direct methods using the SHELXTL software.[6] Subsequent cycles of least-squares refinement, followed by difference Fourier syntheses, revealed the positions of the remaining non-hydrogen atoms. All nonhydrogen atoms were refined anisotropically and hydrogen atoms were placed at idealized calculated positions. Due to some potential disorders, solvent molecules were also badly disordered. The crystallographic asymmetric unit contains two HBPB-8@CB[6] complexes and about 12 water molecules. The larger residual peak density indicates some other solvent water molecules. However, attempts made to model them failed. Then the contributions of the unassigned disordered solvent molecules were removed from the diffraction data using the SQUEEZE routine of PLATON software (c.a. 179e/c.u.). The relatively large thermal parameters for some carbon atoms are probably due to librational motion and were not treated as a disorder.

Surface Tension Measurements: The surface tension of surfactant in 0.1 M NaCl aqueous solution was measured with a Krűss K100 tensiometer (Germany) by the Wilhelmy plate technique. The temperature of the measurement cell was controlled by a water thermostat at 25.0 ±0.1 □. Sets of measurements were taken until the change in surface tension was less than 0.05 mN/m every 10 min. All surface tension values were mean quantities of at least three measurements.

Dynamic light scattering: The solutions (concentration = 0.1 g/L) were filtered through 0.45um filters prior to light-scattering measurements.

High-resolution transmission electron microscopy (HRTEM): Samples for HRTEM were prepared on 400 mesh carbon-coated grids. A drop of solution (concentration = 0.1 g/L) was left on the grid. The samples were negatively stained with phosphotungstic acid (0.2 wt % in water) for 30s and blotted again.

UV/Vis titration: UV/Vis spectra were recorded on TU-1901 double-beam spectrophotometer using 1 cm path length cells. A series of spectra were obtained by the addition of a stock solution containing CB[6] to a cell containing HBPB-8 at 25 °C. The maximum absorptions peak at 290 nm increase gradualy with the additon of CB[6] at room temperature. The 1:1 host-guest stability constant ($K = 2.51\times10^{3}$) was gained from nonlinear least squares fitting curve from the results of UV titration (Figure S2).

Although the surfactant guest has two inclusion active site, hydrophobic "tails" and intermediate connection part, CB[6] inclines to interact with only the intermediate part. The polarity of carbonyl group of the guest may be responsible for the interaction, because hydrophobic chain "tails" is too short to fit the axial size of the cavity of CB[6], and only the pyridine nitrogen binds with carbonyl group of CB[6] through ion-dipole interaction. The hydrophobic interaction, ion-dipole interaction, and the inclusion of this polar group will give an energetically unfavorable state, leading the inclusion of the hydrophobic chain "tails" into the cavity of CB[6] unstable and easy to breakup. But for the intermediate part, the orientation of pyridine nitrogen makes it suitable to bind with carbonyl group of CB[6] through ion-dipole interaction. The cooperation of hydrophobic interaction and ion-dipole interaction makes the inclusion complex with intermediate part of the surfactant in the cavity of CB[6] stable.

The conductivity of HBPB-8 and HBPB-8@CB[6]: The Critical Aggregation Concentration (CAC) determined by conductivity apparatus of HBPB-8 and HBPB-8@CB[6] are 1.063×10^{-5} mol/L and 4.937×10^{-7} mol/L (Figure S11), which are consistent with the CAC determined by Surface tension determine instrument.

***Encapsulation of carboxyfluorescein (CF)*:** The complex HBPB-8@CB[6] (2.1mg) was dissolved in 2ml Tris buffer solution containing 10 mM carboxyfluorescein (CF). [7] Untrapped free CF was removed by passing the complex solution through Sephadex G-50. The early fraction was collected and used directly in the release study. The fluorescence spectrum was recorded at emission wavelenght of 515nm. Release percent of carboxyfluorescein from the supramolecular vesicles of HBPB-8@CB[6] as a function of time is show in Figure S12.

***Cryo-TEM experiment*:** For the Cryo-TEM experiment, the specimen was prepared by Vitrobot Mark IV(FEI company). A 3.5 μL drop of solution was placed on a TEM copper grid covered with a perforated carbon film and blotted with filter paper (4 s) to form a thin liquid film of the sample at 20 °C and 100% relative humidity. The thin film sample was plunged into liquid ethane at its freezing temperature (–183 °C) to get vitrified and then transferred to liquid nitrogen (–196 °C) for storage. The vitrified specimens were examined in an FEI Tecnai 20 TEM operating at an accelerating voltage of 200 kV with low dose mode. A Gatan 626 cryoholder that maintained the specimens below –175 °C during sample transfer and observation was used. A Gatan Ultrascan 894 2K*2K CCD was used to acquire the image. (Figure S10)

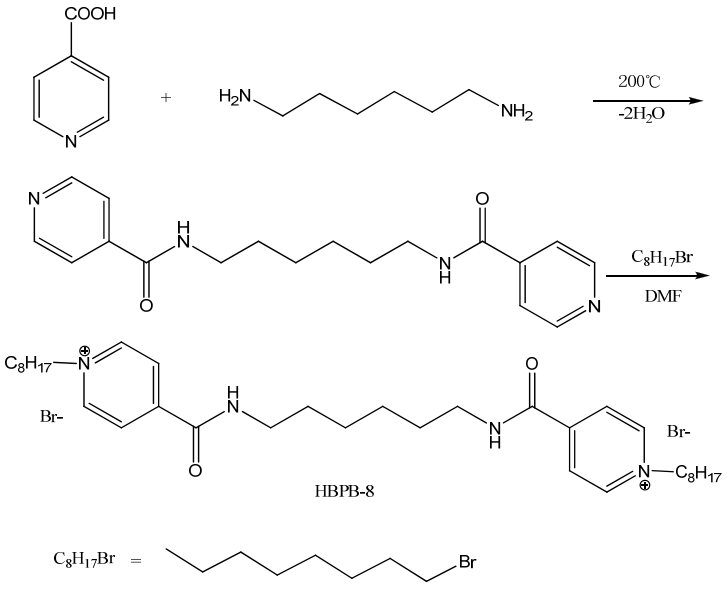

Figure S1. The synthesis process of HBPB-8

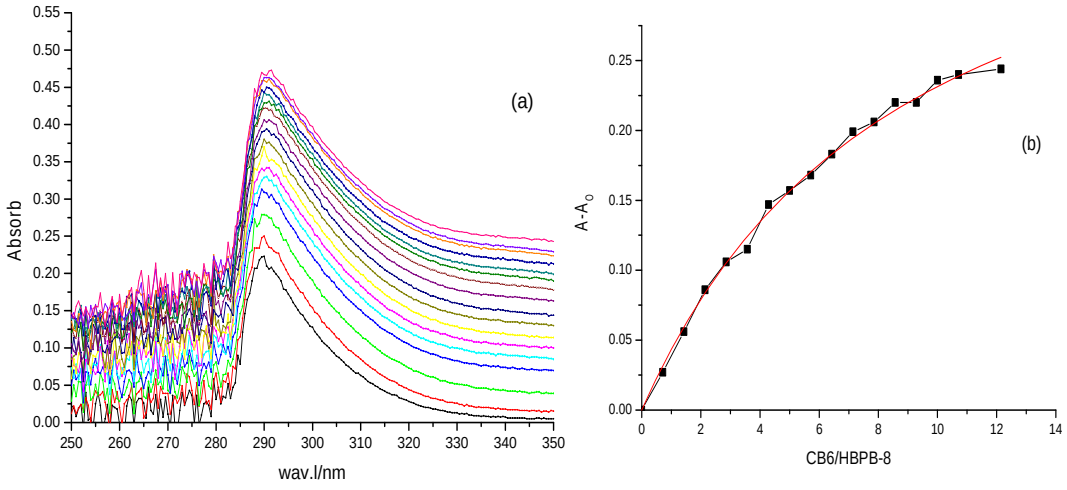

Figure S2. (a) UV titration of HBPB-8 with CB[6] in water. (b) Nonlinear least squares fitting curve from the results of (a).

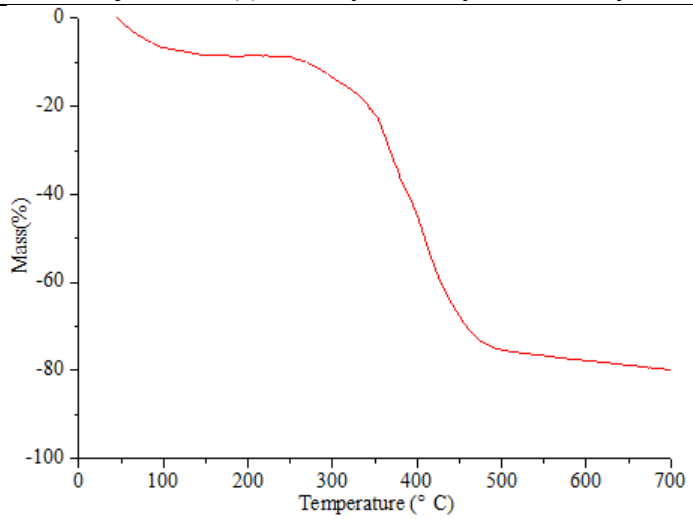

Figure S3. The TGA curve of pseudorotaxane in N_2 atmosphere.

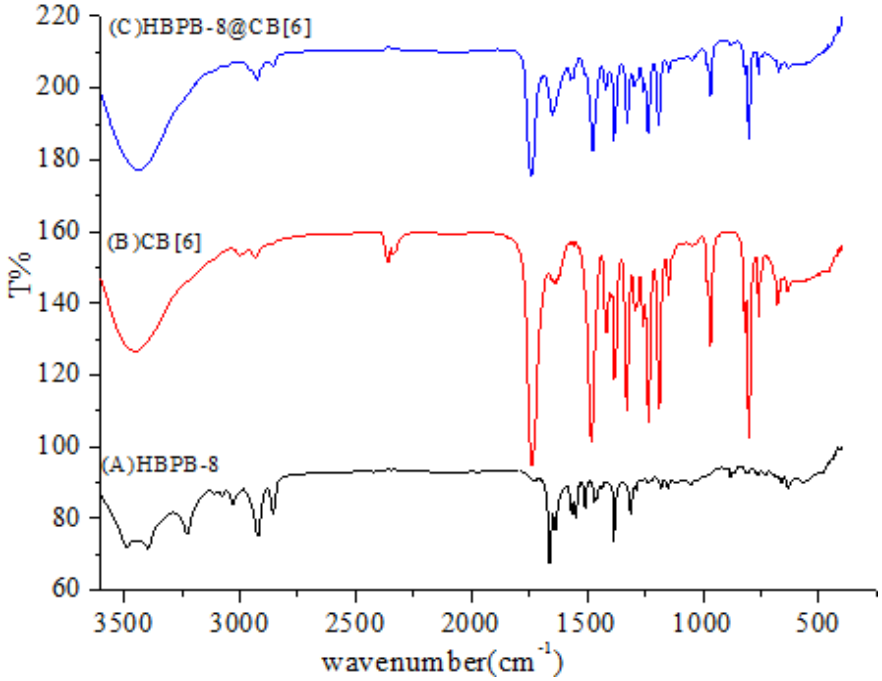

Figure S4. IR of (a) The guest molecule HBPB-8 (b) the host molecule CB[6] (c) the pseudorotaxane H8@CB[6]

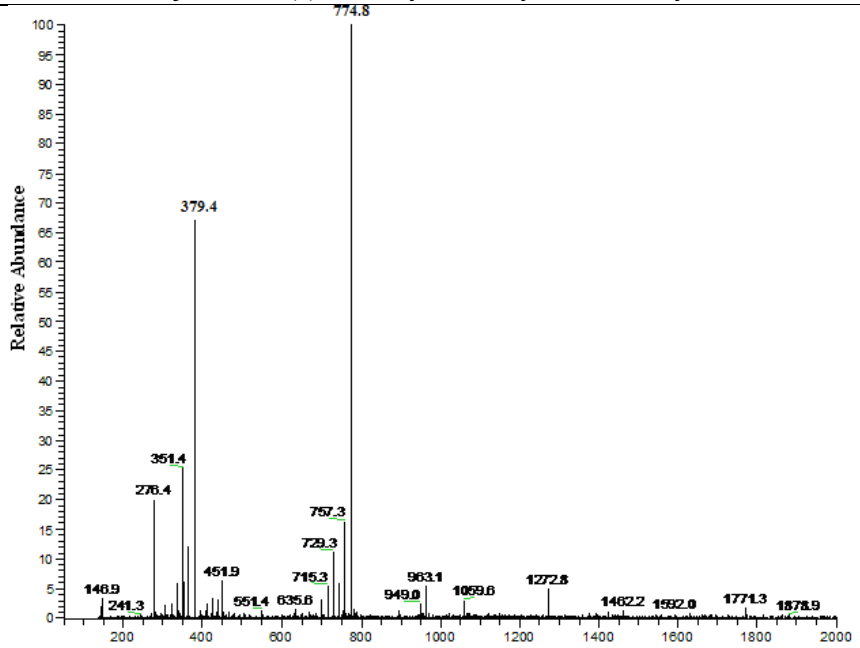

Figure S5. ESI-MS of pseudorotaxane. The main peak at m/z 774.8 corresponds to the whole pseudorotaxane with two positive charges.

			Mean (nm)	% by Intensity	% by Volume
Z-Average (d.nm):	106.7				
PdI:	0.197	Peak 1:	129.2	100.0	100.0
Intercept:	0.873	Peak 2:	0.000	0.0	0.0
CPF:	137	Peak 3:	0.000	0.0	0.0
Result quality :	Good				

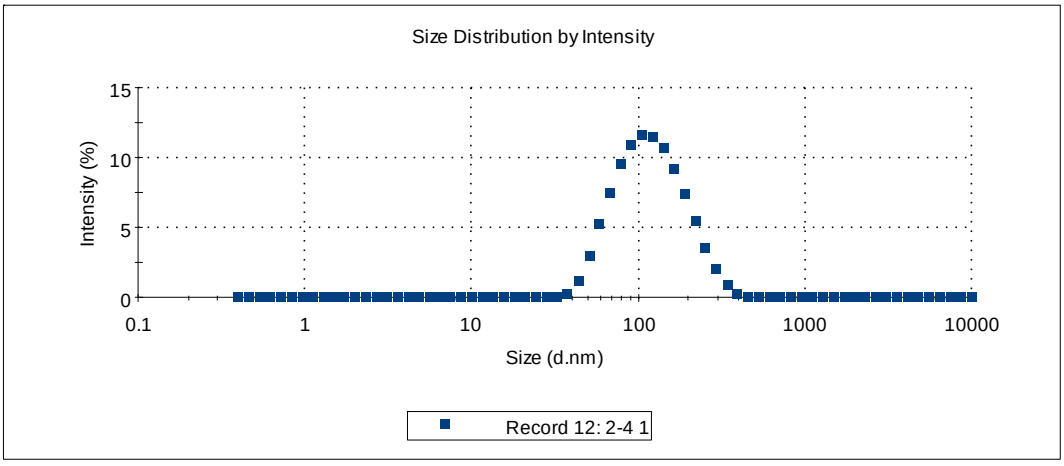

Figure S6. Particle size distribution of pseudorotaxane (HBPB-8@CB[6]), according to DLS. It is necessary to mention that the guest HBPB-8 does not spontaneously form detectable aggregates in aqueous solution.

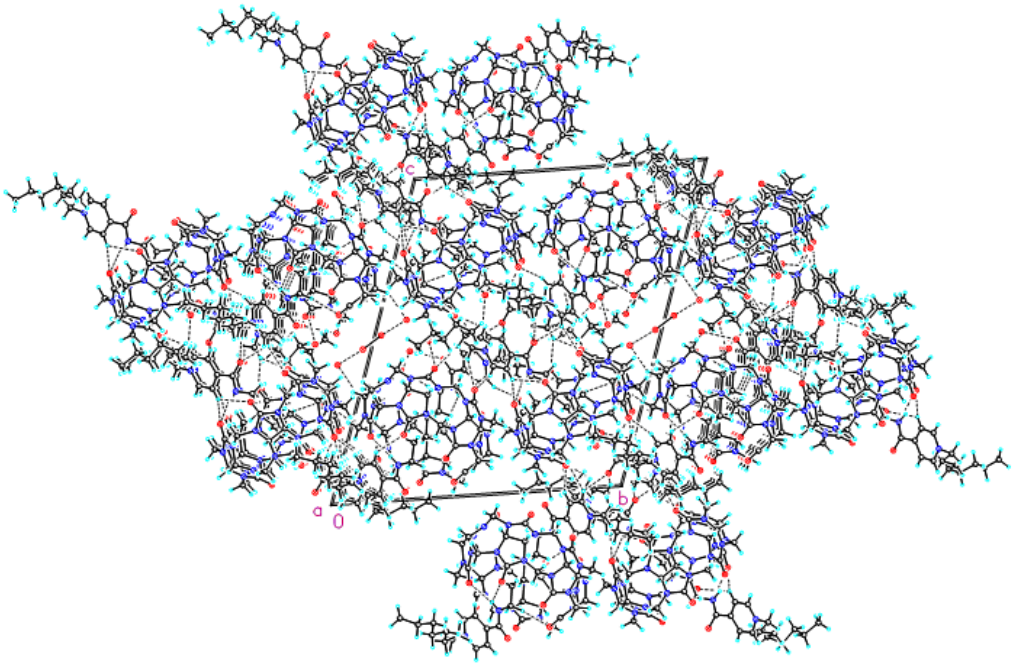

Figure S7. The crystal packing of pseudorotaxane (HBPB-8@CB[6])

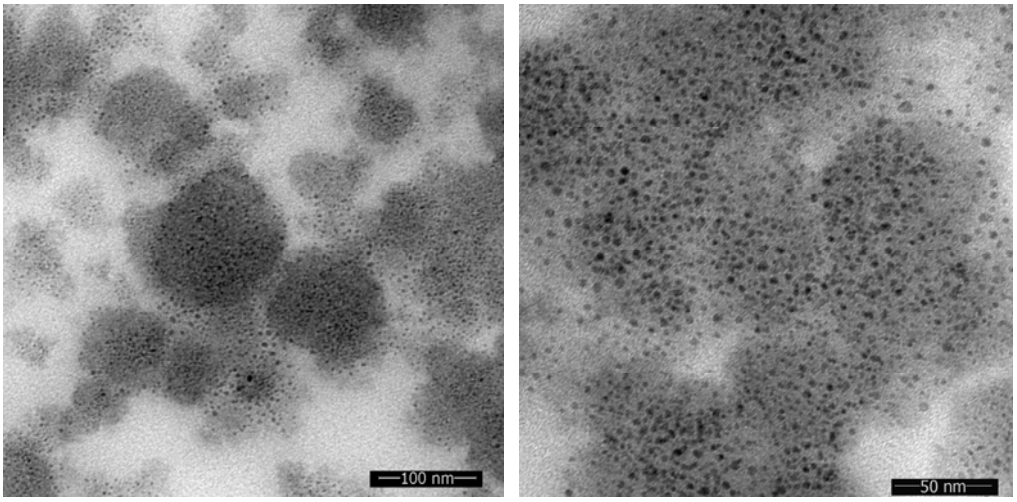

Figure S8. TEM of the guest HBPB-8

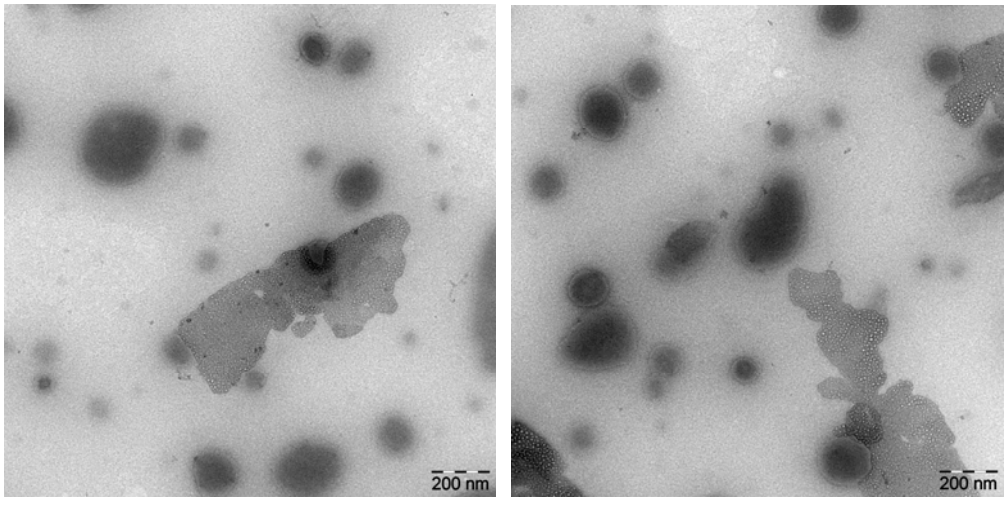

Figure S9. TEM of supramolecular vesicle (HBPB-8@CB[6])

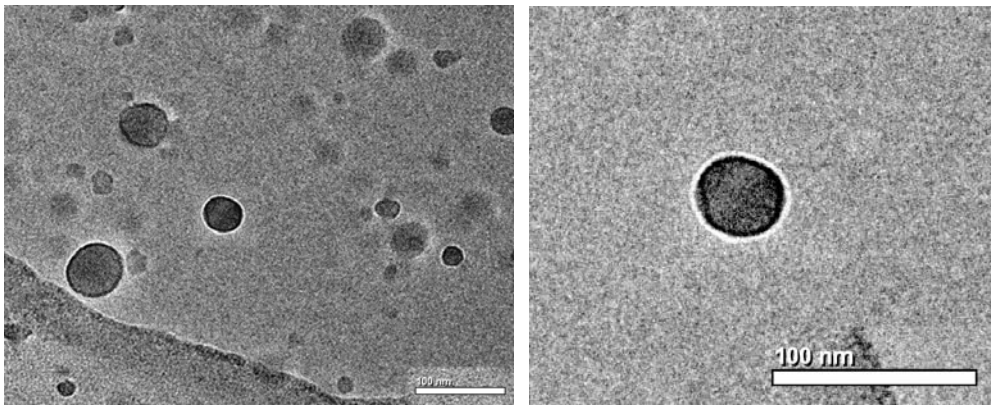

Figure S10. Cryo-TEM of supramolecular vesicle (HBPB-8@CB[6])

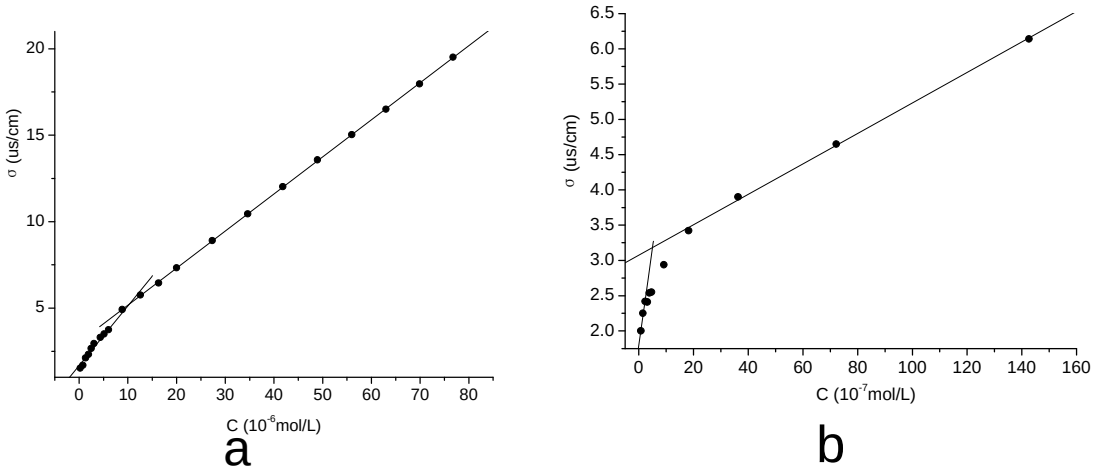

Figure S11. The conductivity of HBPB-8 (a) and HBPB-8@CB[6] (b).

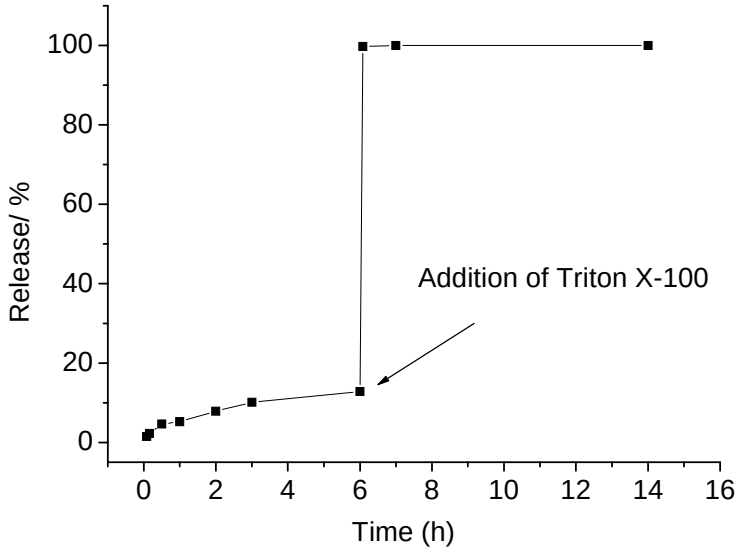

Figure S12. Release percent of carboxyfluorescein from the supramolecular vesicles of HBPB-8@CB[6] as a function of time.

Referenes

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