Electronic Supplementary Information

Multistate self-assembled micro-morphology transitions controlled by host-guest interactions†

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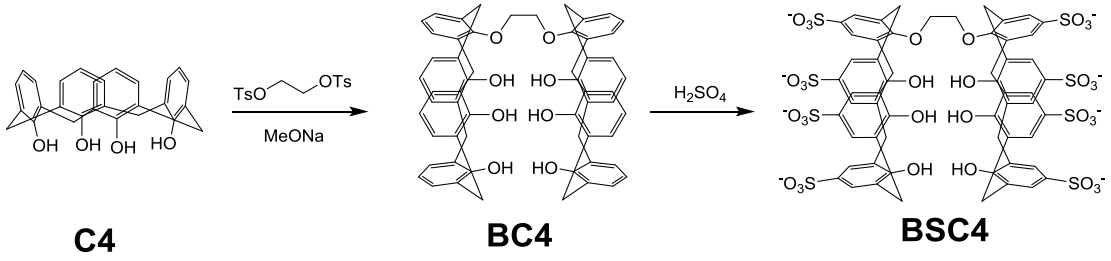
Contents

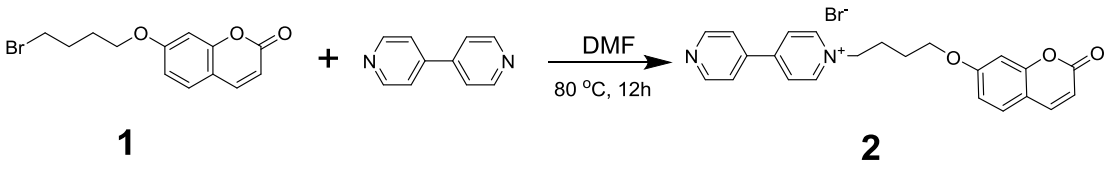
1. Materials, general procedures and syntheses

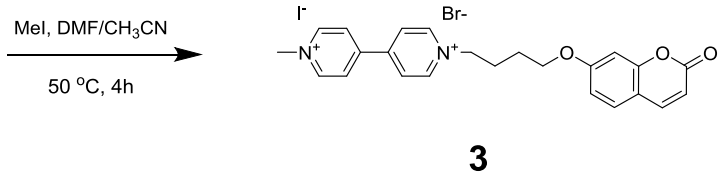
1.1. Materials. Unless stated otherwise, all reagents were purchased from Sigma-Aldrich or TCI Chemicals and used without further purification. Solvents were purified according to standard laboratory methods.

1.2. General. ^{1}H NMR spectra were measured on a Brüker AV-400 spectrometer. ^{13}C spectrum was measured on a Brüker AV-500 spectrometer. The electronic spray ionization (ESI) high resolution mass spectra were tested on a HP 5958 mass spectrometer. Fluorescence spectra were obtained on a HORIBA FluoroMax 4. DLS results were measured on MALV RN, ZETA SIZER, Model ZEN3600, 25^{o}C. Elemental analysis was measured on a VARIO EL III. TEM images were recorded on a JEOL JEM-1400 apparatus. The samples (1×10^{-3} M) were dropped on a perforated copper grid (200 mesh) covered with a carbon film and then negative-stained by phosphotungstic acid.

1.3. Syntheses







Bis-sulfonatocalix[4]arene (BSC4). This compound was synthesized according to literature procedure.[1]

7-(4-bromobutoxy)-2H-chromen-2-one (1). This compound was synthesized conveniently in one step from commercial materials 7-hydroxyl coumarin and 1,4-dibromobutane according to literature procedure.[2]

1-(4-((2-oxo-2H-chromen-7-yl)oxy)butyl)-[4,4'-bipyridin]-1-ium bromide (2). This compound was synthesized conveniently according to literature procedure.[3]

1-methyl-1'-(4-((2-oxo-2H-chromen-7-yl)oxy)butyl)-[4,4'-bipyridine]-1,1'-diium bromide iodide (3). Compound **2** (200 mg, 0.44 mmol, 1 eq) and CH_3I (627 mg 4.42

mmol, 10eq) were dissolved in 20 mL acetonitrile and 20 mL DMF. The solution was stirred at 50 °C under argon for 4 hours and then the CH_3I and acetonitrile were removed under reduced pressure. The remaining solution was poured into large amount of ethyl acetate, and orange-red solid was precipitated which was then filtrated and washed with a small amount of acetonitrile. The solid was dried in vacuo to provide compound **3** (250 mg, 95% yield), m.p. 223.3-224.7 °C. ^{1}H NMR (400 MHz, D_2O) δ 9.06 (d, J = 6.9 Hz, 2H), 8.94 (d, J = 6.8 Hz, 2H), 8.40 (d, J = 6.8 Hz, 2H), 8.37 (d, J = 6.8 Hz, 2H), 7.77 (d, J = 9.5 Hz, 1H), 7.41 (d, J = 8.7 Hz, 1H), 6.82 (dd, J = 8.7, 2.4 Hz, 1H), 6.70 (d, J = 2.3 Hz, 1H), 6.15 (d, J = 9.4 Hz, 1H), 4.75 – 4.71 (m, 2H), 4.40 (s, 3H), 4.03 (t, J = 5.9 Hz, 2H), 2.31 – 2.12 (m, 2H), 1.95 – 1.76 (m, 2H). ^{13}C NMR (125 MHz, D_2O) δ 164.44, 161.36, 154.78, 149.56, 149.23, 146.24, 145.86, 145.44, 129.58, 126.69, 126.38, 113.35, 112.89, 111.53, 101.37, 67.44, 61.79, 48.27, 26.93, 24.71. HRMS (ESI) (m/z): $[M\text{-}Br\text{-}I]^+$ calcd for $[C_{24}H_{24}N_2O_3]^+$, 388.1787; found, 388.1785. Elem Anal. calcd for $C_{24}H_{24}O_3N_2BrI$: C 48.43, H 4.06, N 4.71. Found: C 48.58, H 4.16, N 4.85.

2. Spectra on the morphology transition process.

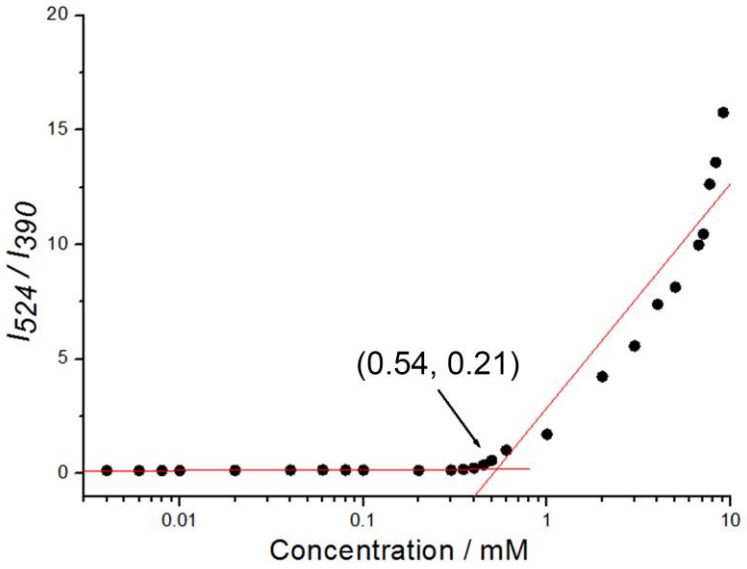


Fig. S1 Plot of the ratio of the fluorescence emission intensity of **3** excimer/monomer (I_E/I_M) to concentration, 25 °C.

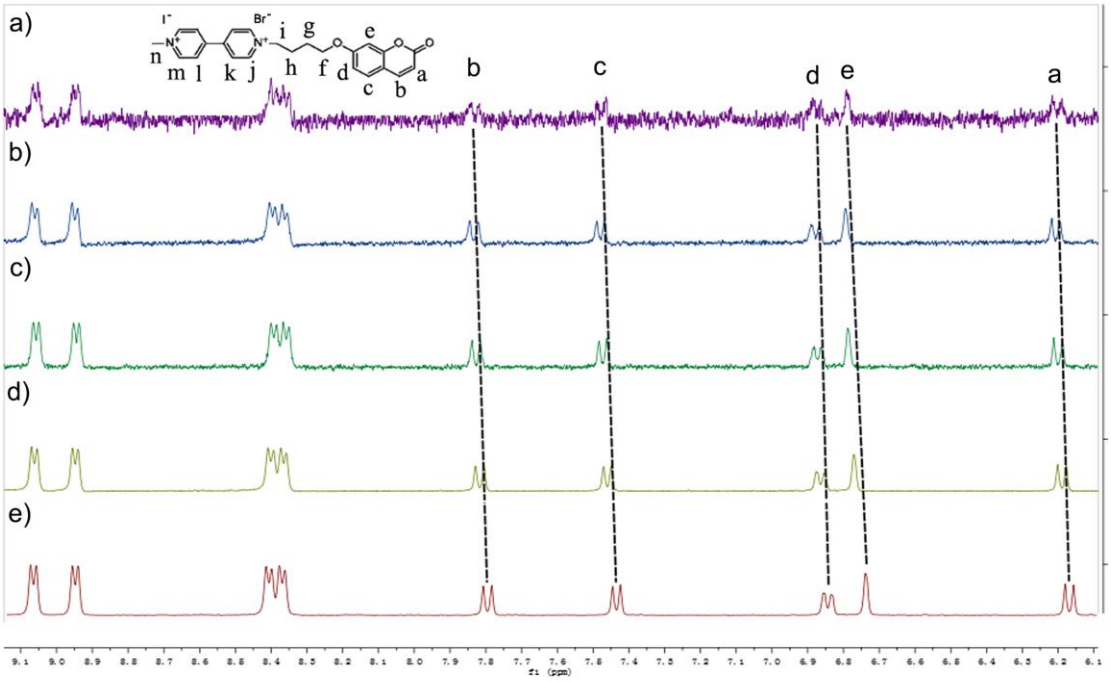


Fig. S2 Partial ^{1}H NMR spectra of compound **3** in D_2O, the concentrations are (a) 0.1 mM, (b) 0.5 mM, (c) 1mM, (d) 5 mM, (e) 10 mM, 25 ^{o}C.

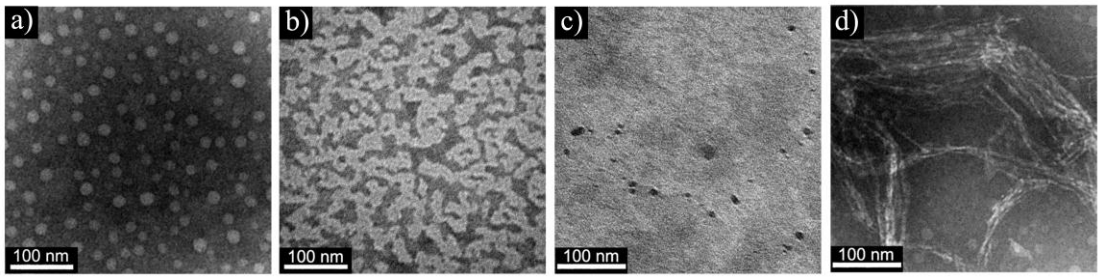


Fig. S3 Negative-staining TEM images of (a) **3** spherical micelles (**S**-state), prepared in aqueous solution, [**3**] = 1 mM; (b) amorphous worm-like network (**N**-state) formed by adding 0.1 eq **BSC4** to **3** micelle solution; (c) **3**&**BSC4** complex solution obtained by adding 0.5 eq **BSC4** to **3** micelle solution, [**3**] = 1 mM; and (d) the linear supramolecular polymer (**L**-state) formed by **3**, **BSC4** and γ-CD ternary complex..

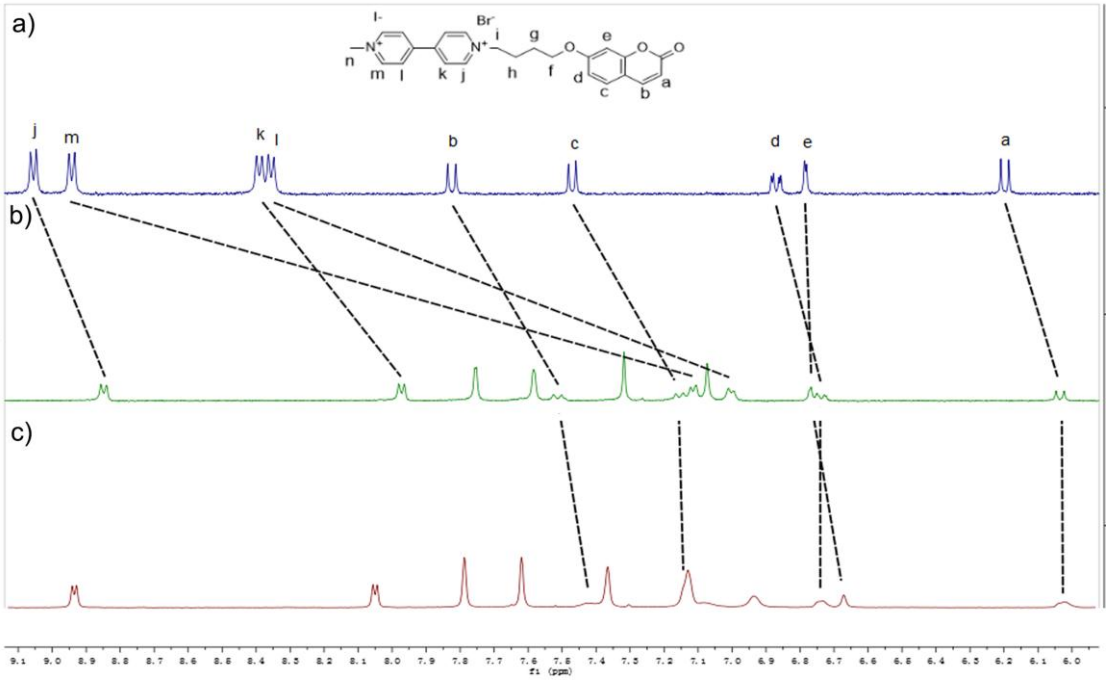


Fig. S4 Partial ^{1}H NMR spectra of (a) **3** solution, [**3**]=1 mM, (b) **3**&**BSC4** complex, [**3**]/[**BSC4**]=1/0.5, (c) **3**&**BSC4**&γ-CD complex, [**3**]/[**BSC4**]/[γ-CD]=1/0.5/0.5, D_2O, 25 ^{o}C.

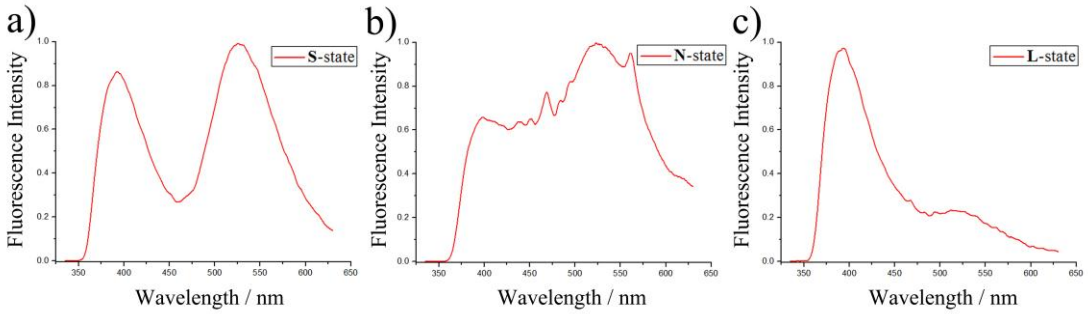
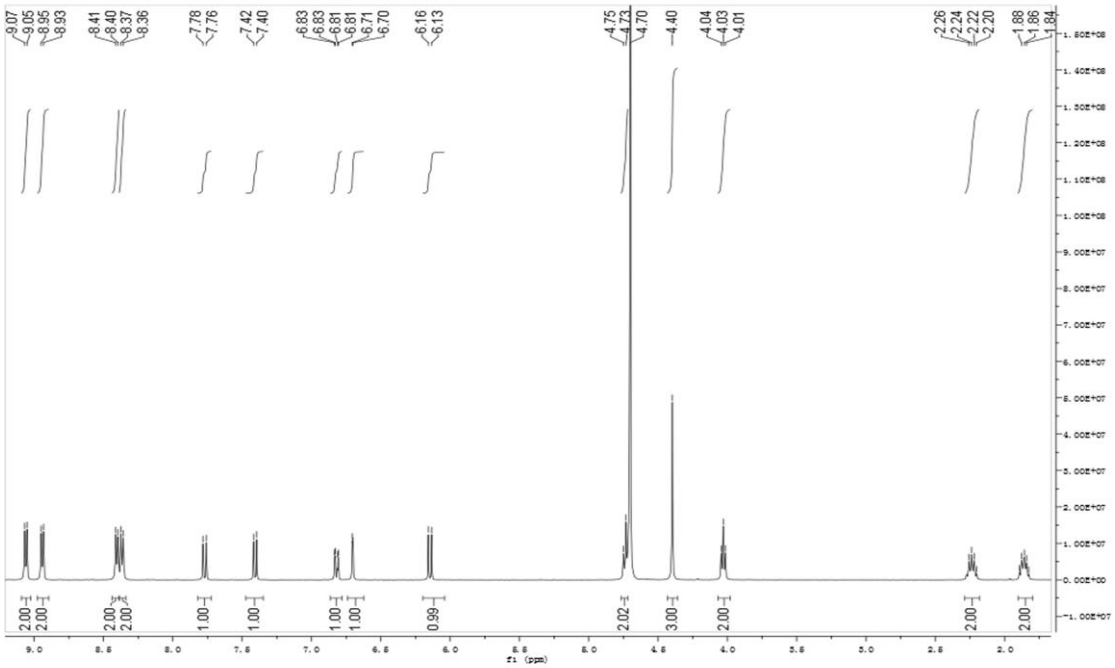


Fig. S5 Normalized fluorescent emission spectra of (a) 1 mM of **3** aqueous solution forms the spherical micelles (**S**-state); (b) adding 0.1 eq **BSC4** to sample (a) forms the amorphous worm-like network (**N**-state); and (c) continue adding **BSC4** up to 0.5 eq and 0.5 eq of γ-CD to sample (b) forms the linear polymer (**L**-state).

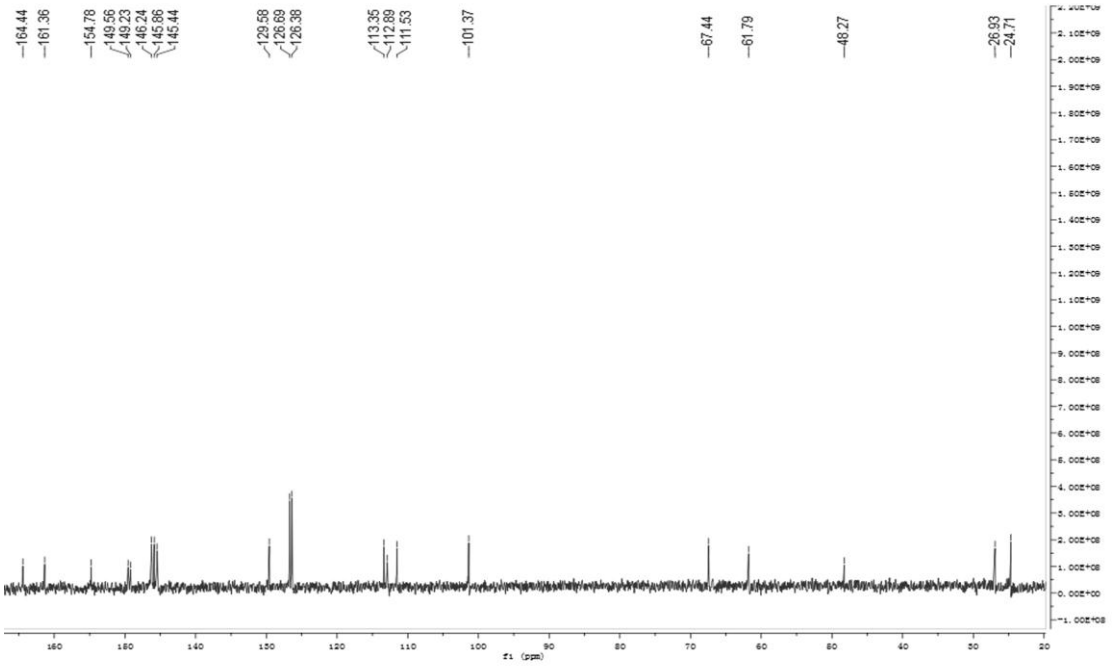
3. References

1. D.-S. Guo, S. Chen, H. Qian, H.-Q. Zhang and Y. Liu, *Chem. Commun.*, 2010, **46**, 2620.
2. Q. Zhang, D.-H. Qu, J. Wu, X. Ma, Q. Wang and H. Tian, *Langmuir*, 2013, **29**, 5345.
3. Q. Zhang, D.-H. Qu, X. Ma and H. Tian, *Chem. Commun.*, 2013, **49**, 9800.

4. Additional spectra.



^{1}H NMR of compound **3**, D_2O, 25 ^{o}C



^{13}C NMR of compound **3**, D_2O, 25 ^{o}C

Elemental Composition Report

Single Mass Analysis
Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Odd and Even Electron Ions
7 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-24 H: 0-30 N: 0-2 O: 0-3

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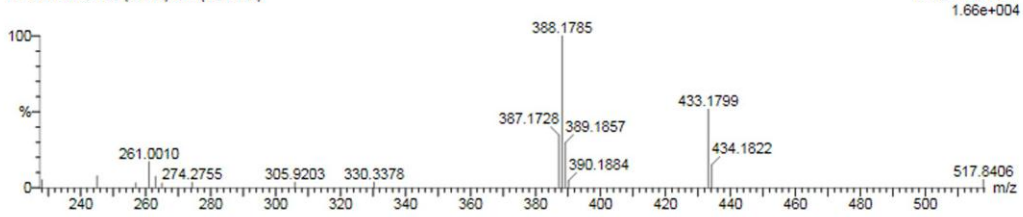
TH-QW-MVC 123 (0.846) Cm (123:125) 1: TOF MS ES+ 1.66e+004



Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
388.1785	388.1787	-0.2	-0.5	14.0	14.3	0.0	C24 H24 N2 O3

ESI-MS of compound **3**