Electronic Supplementary Information

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

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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 Bruker AV-400 spectrometer. $^{13}$C spectrum was measured on a Bruker 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°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$_3$I (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$_3$I 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$_2$O) 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$_2$O) 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, 110.37, 67.44, 61.79, 48.27, 26.93, 24.71. HRMS (ESI) (m/z): [M-Br-I]$^+$ calcd for [C$_{24}$H$_{24}$N$_2$O$_3$]$^+$, 388.1787; found, 388.1785. Elem Anal. calcd for C$_{24}$H$_{24}$N$_2$O$_3$BrI: 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$_2$O, the concentrations are (a) 0.1 mM, (b) 0.5 mM, (c) 1mM, (d) 5 mM, (e) 10 mM, 25 °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&BS4 complex, [3]/[BS4]=1/0.5, (c) 3&BS4&γ-CD complex, [3]/[BS4]/[γ-CD]=1/0.5/0.5, D$_2$O, 25 °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 BS4 to sample (a) forms the amorphous worm-like network (N-state); and (c) continue adding BS4 up to 0.5 eq and 0.5 eq of γ-CD to sample (b) forms the linear polymer (L-state).

3. References

4. Additional spectra.

$^1$H NMR of compound 3, D$_2$O, 25 °C

$^{13}$C NMR of compound 3, D$_2$O, 25 °C
ESI-MS of compound 3