

Electronic supplementary information

Versatile Self-Assembly of Supramolecular Block Copolymers with Ionic Cluster Junctions

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1. Materials.

2, 2'-Azobis (2-methylpropionitrile) (AIBN, 99%, Aladdin) was recrystallized from methanol. Styrene (99%, Aladdin) washed with 10% NaOH and distilled water for three times separately, dried with anhydrous MgSO₄, and then distilled under reduced pressure. DMF was stirred with CaH₂ for 7 days at the room temperature and distilled under reduced pressure. Carbon disulfide (CS₂, 99.9% from Aladdin), 1-butanethiol (99%, J&K), bromoethanol (97%, Aladdin), trimethylamine (33% w/w in ethanol, Alfa Aesar), 1, 3-dicyclohexylcarbodiimide (DCC, Sigma-Aldrich) and 4-(dimethylamino) pyridine (DMAP, Alfa Aesar) were used as received. All of the used solvents were analytical grade.

2. Measurements.

¹H NMR spectra (with tetramethylsilane as reference) were recorded on a Bruker UltraShield 500 MHz spectrometer. Organic elemental analysis was carried out on a Flash EA1112 from Thermo-Quest Italia S.P.A. FTIR spectra (KBr pellets) were collected on a Bruker Vertex 80v spectrometer equipped with a deuterated triglycine sulfate detector (32 scans) at a resolution of 4 cm⁻¹. MALDI-TOF spectra were measured on a Bruker autoFlex™ MALDI-TOF mass spectrometer. The molecular weights of CBCs were measured by gel permeation chromatography (GPC), equipped with a wat044225 column, a LC-20AD pump and a RI detector. THF was used as eluent at 40 °C at 1.0 mL min⁻¹. In the GPC measurement, the PS chains were cleaved from CBCs by hydrolysis with LiOH. Small angle X-ray scattering (SAXS) data were collected on a Bruker NANOSTAR instrument. An X-ray wavelength of 1.542 Å was

used and the sample-to-detector distance was 107.4 cm. Dynamic light scattering (DLS) measurements were performed by using a Malvern Zetasizer NanoZS instrument at room temperature. Angular dependent DLS measurements were performed using an ALV/CGS-3 Compact Goniometer System with a He-Ne laser ($\lambda = 632.8$ nm). TEM images were obtained with a JEM-2100F electron microscope operating at 200 kV.

3. Synthesis of Cationic RAFT Agent. The agent was synthesized by using a modified method as reported in our group previous works.^[1] The whole synthetic route is shown in **Fig. S1**, which includes three steps as follows.

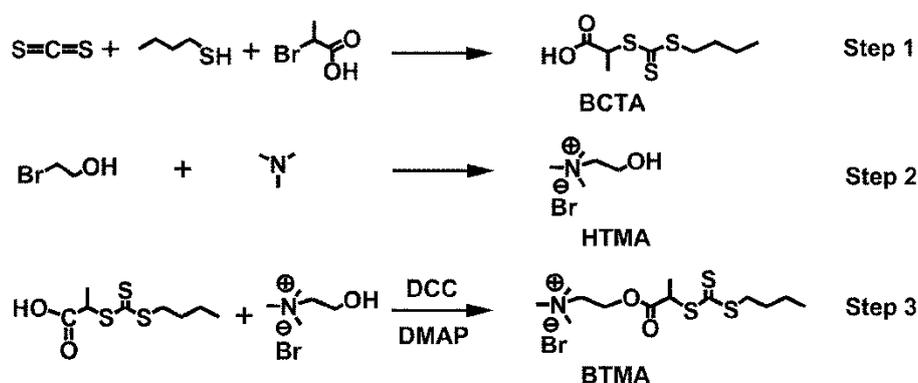


Fig. S1. Synthetic route of cationic RAFT agent.

3.1. Synthesis of 1,2-(Butylthiocarbonothioylthio)propanoic Acid (abbreviated as BCTA). 1-Butanethiol (5 mL) and trimethylamine (7.2 mL) were added to 50 mL of dichloromethane. The mixture solution was cooled to 0 °C by ice bath and stirred at this temperature for 30 min, protected with nitrogen. And then, the carbon disulfide (3.1 mL) in dichloromethane (50 mL) was added. The ice bath was removed after another 30 min, followed by dropwise adding the 2-bromopropanoic acid (7.7 g) in dichloromethane (25 mL). After a 2 hour reaction, the solvent was removed by rotary evaporation. The raw product was dissolved in the n-pentane, washed with 10% HCl, and dialyzed water for 3 times separately, and then the solvent was removed by rotary evaporation. The pure product was obtained by silica gel column chromatography (petroleum ether:ethyl acetate = 20:1; yield: 81%). ¹H NMR (500M, CDCl₃, 25 °C, TMS, as shown in **Fig. S2**): δ (ppm) = 4.87 (q, 1H, -SCH-, $J_1 = 7.5$ Hz, $J_2 = 15$ Hz),

3.39 (t, 2H, $-\text{CH}_2\text{S}-$, $J = 7.5$), 1.72 (m, 2H, $-\text{CH}_2\text{CH}_2\text{S}-$), 1.66 (d, 3H, $-\text{SCHCH}_3$, $J = 7.5$ Hz), 1.50 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 0.98 (t, 3H, $-\text{CH}_2\text{CH}_3$, $J = 7.5$ Hz).

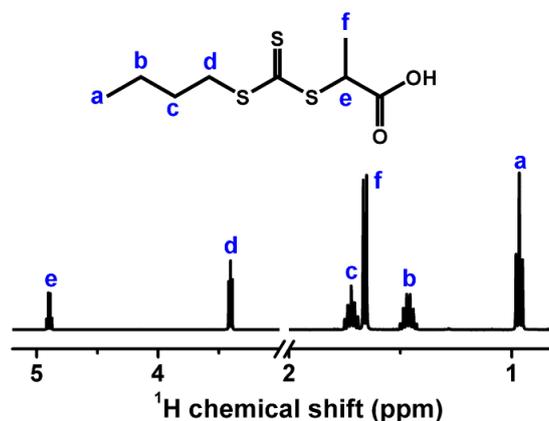


Fig. S2. ^1H NMR spectrum of BCTA in CDCl_3 .

3.2. Synthesis of 2-hydroxy-*N,N,N*-trimethylethanaminium bromide (abbreviated as HTMA). Bromoethanol (5g) and trimethylamine (21g, 33% w/w in ethanol) were added to round-bottom flask and stirred at room temperature, protected with nitrogen. After a 24 hour reaction, the reaction solution was concentrated and added dropwise to diethyl ether to obtain a precipitate which is the raw product. The precipitate was dissolved in ethanol and washed with diethyl ether for three times. After removing the solvent, the pure product was obtained with a yield of 95%. ^1H NMR (500M, d-DMSO, 25 $^\circ\text{C}$, TMS, as shown in Fig. S3): δ (ppm) = 5.29 (t, 1H, $-\text{CH}_2\text{OH}$, $J = 5$ Hz), 3.83 (m, 2H, $-\text{CH}_2\text{CH}_2\text{OH}$), 3.39 (t, 2H, $-\text{CH}_2\text{CH}_2\text{OH}$, $J = 5$ Hz), 3.11 (s, 9H, $-\text{CH}_2\text{N}(\text{CH}_3)_3$).

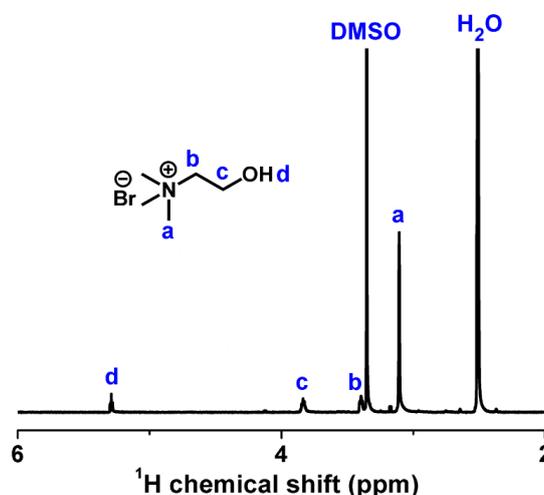


Fig. S3. ^1H NMR spectrum of HTMA in d-DMSO.

3.3. Synthesis of 2-((2-(((butylthio)carbonothioyl)thio)propanoyl)oxy)-N,N,N-trimethylethanaminium bromide (abbreviated as BTMA). The BCTA (1g) and the HTMA (0.77g) were dissolved in 80 mL of acetonitrile and stirred for 30 min under ice bath. Then, DCC (1.20 g) in acetonitrile was added into the solution. After stirring for 10 min, the DMAP (0.066g) in 5 mL of acetonitrile was added. After 30 min, the ice bath was removed. The solution gradually turned from red to yellow. After 12 hours, the reaction was stopped and the solution was filtrated. A raw product was obtained by dropping the filtrate into diethyl ether, which resulted in a yellow precipitate. The pure product was obtained by washing with diethyl ether for three times with a yield of 88%. ^1H NMR (500M, d-DMSO, 25 °C, TMS, as shown in **Fig. S4**): δ (ppm) = 4.86 (t, 1H, $-\text{SCH}(\text{CH}_3)-$, $J_1 = 7.5$ Hz, $J_2 = 15$ Hz), 4.53 (m, 2H, $-\text{CH}_2\text{N}(\text{CH}_3)_3$), 3.69 (m, 2H, $-\text{CH}_2\text{CH}_2\text{O}-$), 3.57 (m, 2H, $-\text{CH}_2\text{N}(\text{CH}_3)_3$), 3.13 (s, 9H, $-\text{CH}_2\text{N}(\text{CH}_3)_3$), 1.64 (m, 2H, $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.56 (d, 3H, $-\text{SCHCH}_3$, $J = 7.5$ Hz), 1.37 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 0.90 (t, 3H, $-\text{CH}_2\text{CH}_3$, $J = 7.5$ Hz). The MALDI-TOF spectrum of BTMA shows a dominant peak at m/z of 324.4, well consistent with the cationic part of BTMA ($\text{C}_{13}\text{H}_{26}\text{NO}_2\text{S}_3^+$) whose molecular weight is 324.5, thus confirming the expected composition of BTMA, as shown in **Fig. S5**.

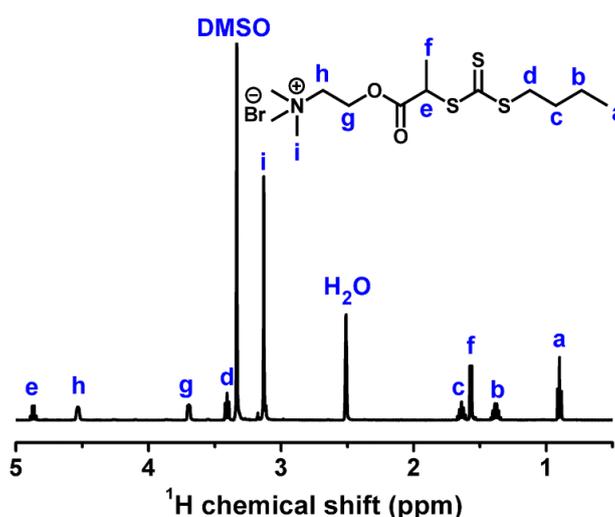


Fig. S4. ^1H NMR spectrum of BTMA in d-DMSO.

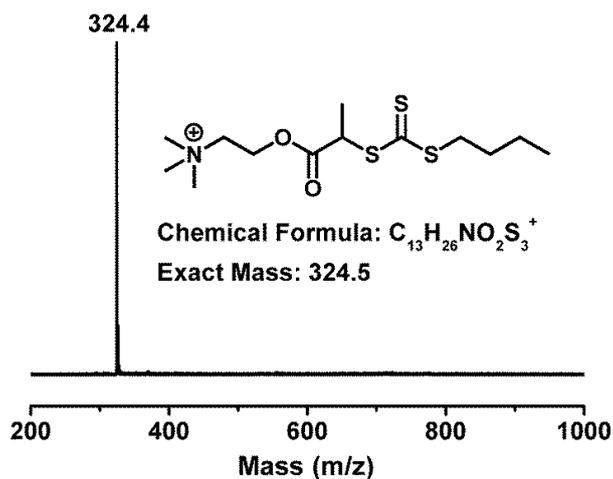


Fig. S5. MALDI-TOF spectrum of BTMA.

4. Synthesis of BTMA–W₆ ionic complex. The complex was obtained by two steps. Firstly, the [W₆O₁₉]²⁻ clusters with tetrabutylammonium (TBA) as counter cations were synthesized, named as TBA–W₆; and then, BTMA was used to replace the TBA cations of (TBA)₂W₆O₁₉, yielding the final BTMA–W₆ complex.

4.1. Synthesis of TBA–W₆ complex. This compound was synthesized according to the literature.^[2] ¹H NMR (500 MHz, d-DMSO, 25 °C, TMS, as shown in Fig. S6): δ (ppm) = 0.936 (t, 12H, -CH₂CH₃, J=7.5 Hz), 1.282–1.343 (m, 8H, -CH₂CH₃), 1.569 (m, 8H, -NCH₂CH₂-), 3.163 (m, 8H, -NCH₂-); elemental analysis calcd (%) for TBA–W₆ complex (C₃₂H₇₂N₂W₆O₁₉, 1892.0): C 20.31, H 3.84, N 1.48; found: C 20.28, H 3.56, N 1.39, corresponding to the chemical formula (C₈H₁₈N)₂W₆O₁₉, that is (TBA)₂W₆O₁₉; IR (KBr, cm⁻¹, as shown in Fig. S7): 1468 (s), 1378 (m), 978 (vs), 888 (vw), 873 (vw), 813 (vs), 752 (vw), 716 (vw), 664 (vw), 588 (m), 448 (vs).

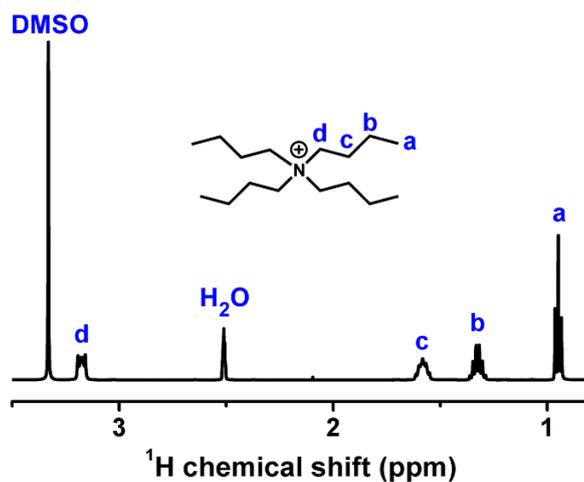


Fig. S6. ¹H NMR spectrum of TBA–W₆ in d-DMSO.

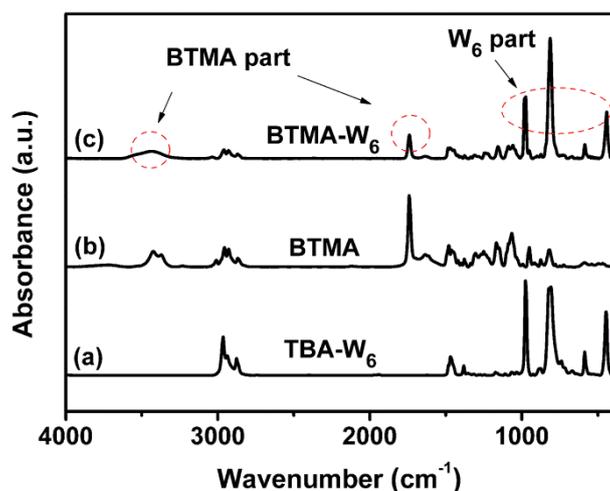


Fig. S7. FTIR spectra of TBA- W_6 (a), BTMA (b) and BTMA- W_6 complex (c).

4.2. Synthesis of BTMA- W_6 Complex. BTMA (1.2 g) and TBA- W_6 complex (0.3 g) were dissolved in 10 mL of acetonitrile and stirred at room temperature for 24 hours. And then, methanol was added dropwise into the solution under stirring. A yellow precipitation formed slowly. The resulting precipitate was collected by filtration, washed with methanol for three times, and dried under vacuum overnight to give 0.26 g of product. The BTMA- W_6 complex is insoluble in water, but readily soluble in organic solvents such as DMF and DMSO. ^1H NMR (500 MHz, d-DMSO, 25°C, TMS, as shown in **Fig. S8**): δ (ppm) = 4.86 (t, 1H, -SCH(CH₃)-, $J_1 = 7.5$ Hz, $J_2 = 15$ Hz), 4.53 (m, 2H, -CH₂N(CH₃)₃), 3.69 (m, 2H, -CH₂CH₂O-), 3.57 (m, 2H, -CH₂N(CH₃)₃), 3.13 (s, 9H, -CH₂N(CH₃)₃), 1.64 (m, 2H, -SCH₂CH₂CH₂CH₃), 1.56 (d, 3H, -SCHCH₃), 1.37 (m, 2H, -CH₂CH₂CH₃), 0.90 (t, 3H, -CH₂CH₃, $J = 7.5$ Hz). The proton signals of TBA are disappeared in the ^1H NMR spectrum, replaced by the signals of BTMA, which demonstrates a complete ion exchange between TBA and BTMA. Elemental analysis calcd (%) for BTMA- W_6 (C₂₆H₅₂N₂S₆W₆O₂₃, 2056.1): C 15.19, H 2.55, N 1.36; found: C 15.22, H 2.33, N 1.27, corresponding to the chemical formula (C₁₃H₂₆NO₂S₃)₂W₆O₁₉, that is (BTMA)₂W₆O₁₉. IR (KBr, cm⁻¹, **Fig. S7**): 1741 (C=O), 1062 (C=S), 978 (W-O_d), 813, 588, and 448 (W-O_c-W).

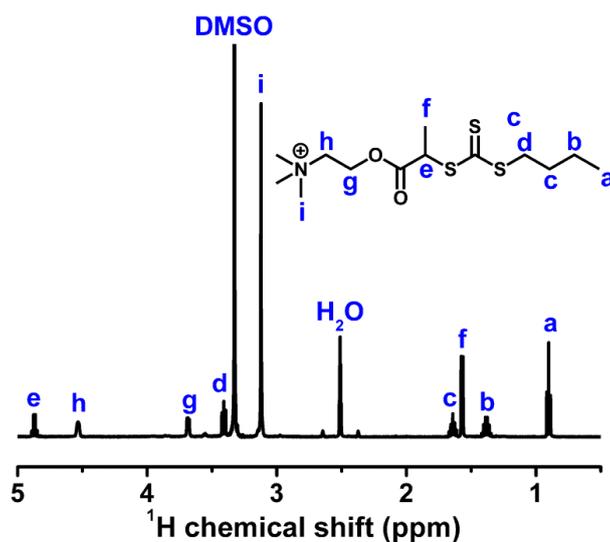


Fig. S8. ¹H NMR spectrum of BTMA–W₆ complex in d-DMSO.

5. Synthesis of CBCs through RAFT polymerization.

BTMA–W₆ complex (0.2 g, 0.025 mmol) was dissolved in 2 ml DMF. And then, styrene and AIBN were added. The amounts of styrene were adjusted of 1.5 and 2.7 mL respectively to control the length of grafted PS chains. The amount of AIBN is controlled at 0.2% of the weight of styrene. The mixture solution was placed into an ampoule, degassed by the freeze–pump–thaw cycle 3 times, backfilled with nitrogen and then reacted at 70 °C in an oil bath for 12 hours. The pure polymers were obtained by participating from diethyl ether three times, which finally led to CBC-1 and CBC-2, respectively. ¹H NMR (500 MHz, d-DMSO, 25°C, TMS) spectra of CBCs show the signals of both PS segments and BTMA part (**Fig. S9**). Elemental analysis (%) calcd for CBC-1 (C₃₇₂H₃₄₆N₂S₆W₆O₂₃, 6222.1): C 66.79, H 6.03, N 0.45; found: C 66.73, H 5.78, N 0.27, corresponding to the chemical formula [C₁₃H₂₆NO₂S₃(C₈H₈)₂₀]₂W₆O₁₉; for CBC-2 (C₁₀₄₄H₁₀₁₈N₂S₆W₆O₂₃, 14970.6): C 81.67, H 7.03, N 0.19; found: C 81.62, H 7.03, N 0.29, corresponding to the chemical formula (C₁₃H₂₆NO₂S₃(C₈H₈)₆₂)₂–W₆O₁₉.

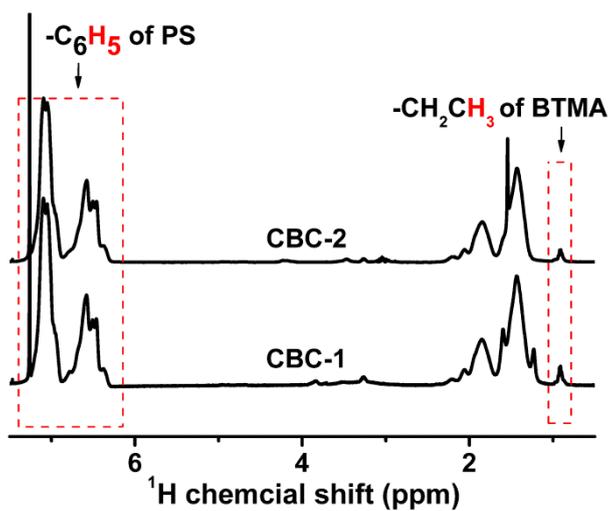


Fig. S9. ^1H NMR spectra of CBC-1 and CBC-2 in CDCl_3 .

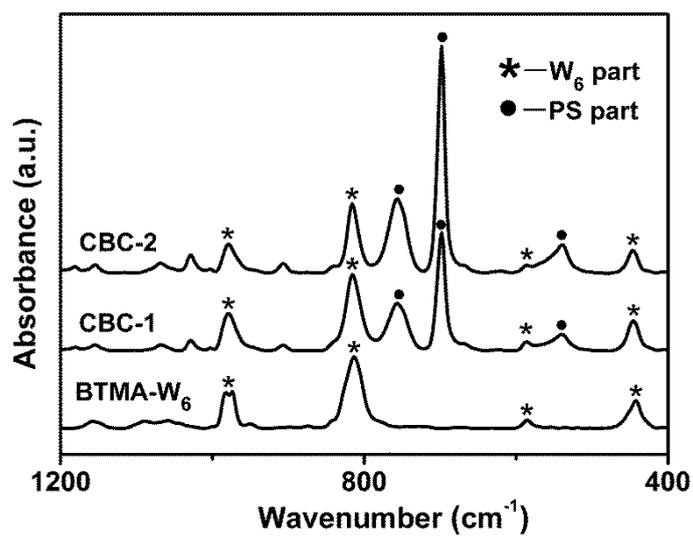


Fig. S10. FTIR spectra of BTMA- W_6 complex, CBC-1 and CBC-2.

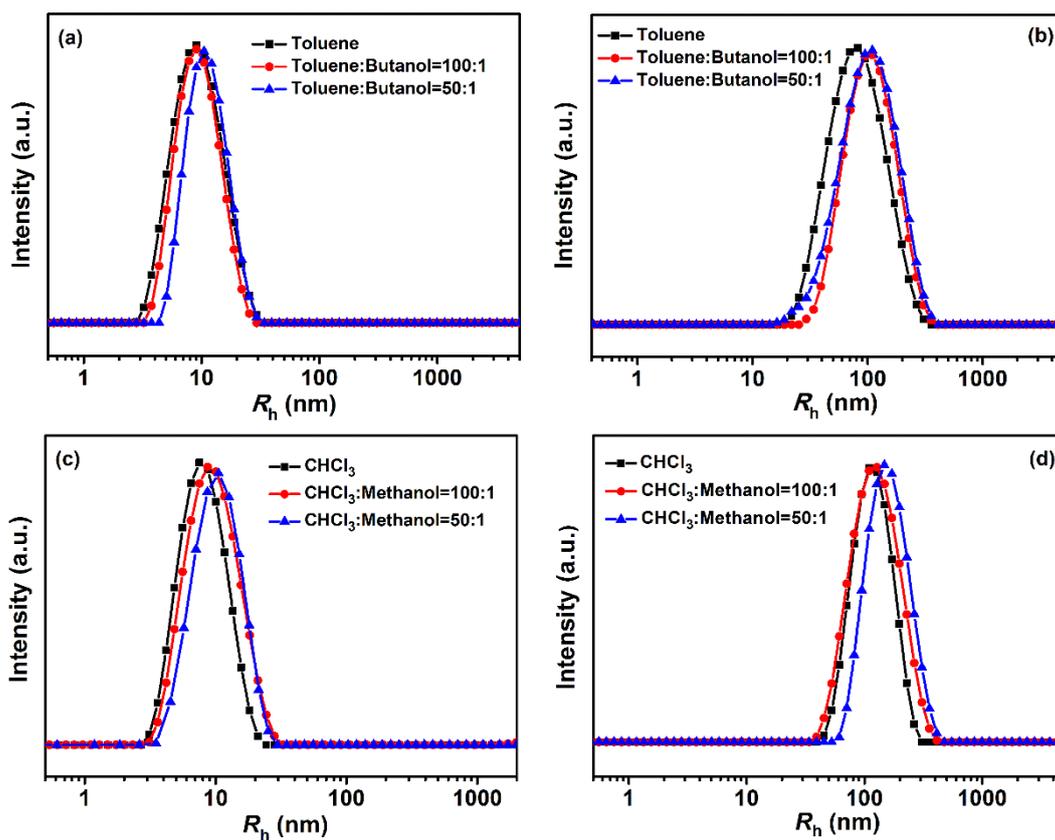


Fig. S11. DLS results of CBC-1 (a, b) and CBC-2 (c, d) in different solvents at the concentration of 1 mg mL^{-1} .

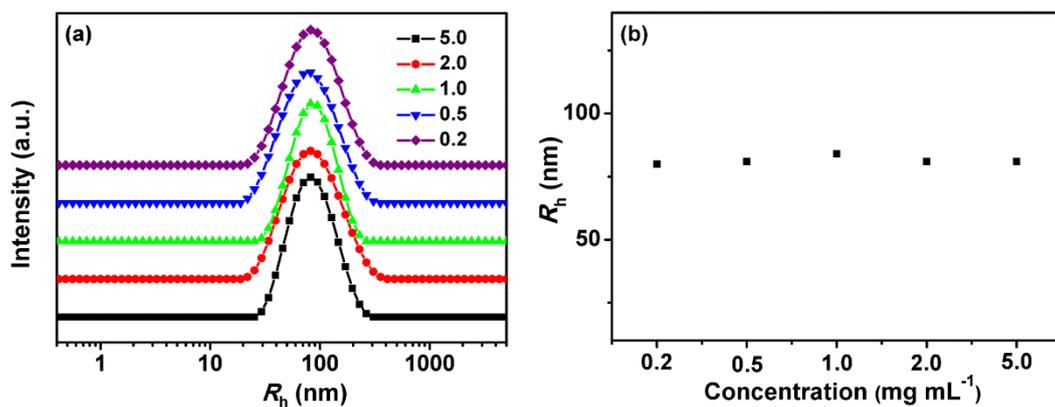


Fig. S12. Concentration-dependent DLS results of CBC-1 in toluene from 0.2 to 5 mg mL^{-1} (a) and the plotting of R_h versus concentrations (b).

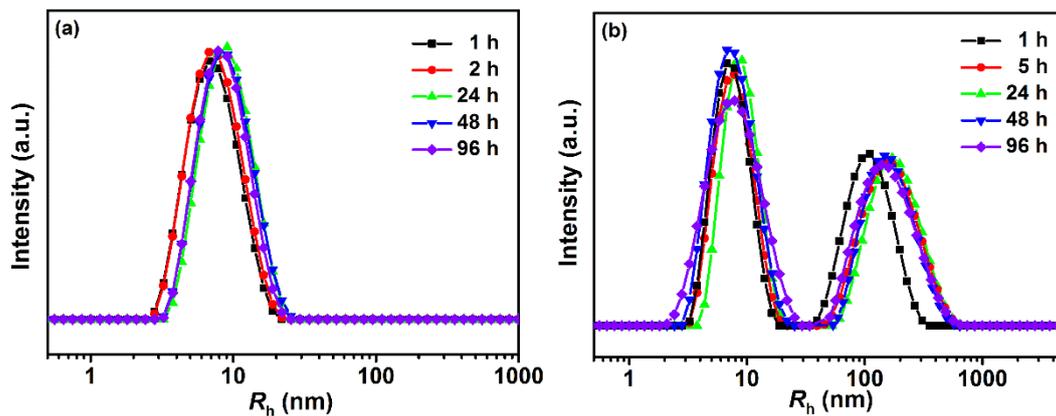


Fig. S13. Time-dependent DLS results of CBC-2 in toluene with the concentration of 1 mg mL⁻¹ (a) and 0.5 mg mL⁻¹ (b).

References:

- [1] P. G. Alvin, *Inorg. Synth.*, **1990**, 27, 80.
- [2] D. Li, H. Li and L. Wu, *Polym. Chem.*, 2014, 5, 1930.