Supporting Information for:

Block Co-PolyMOCs by Stepwise Self-Assembly

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Materials.

Methyl methacrylate (MMA) and *n*-butyl acrylate (BA) were purchased from Sigma-Aldrich and were passed through basic alumina to remove inhibitor before use. Tris(2-(dimethylamino)ethyl)amine (Me$_6$Tren), copper(II) bromide (CuBr$_2$), and ethyl α-bromophenylacetate (EBPA) were purchased from Sigma-Aldrich and were used as received. 3,5-Dibromoanisole, 3-pyridylboronic acid pinacol ester, 4-pyridylboronic acid pinacol ester, and tetrakis(triphenylphosphine) palladium(0) (Pd(PPh$_3$)$_4$) were purchased from Ark Pharm, Inc. and were used as received. All other reagents and solvents were purchased from Sigma-Aldrich and used without further purification.

Synthetic Methods.

Ligand synthesis:

Ligands **L1** and **L3** were synthesized following literature procedures.[1-2] **L2** was synthesized using a similar protocol[1] as is described below.

Synthesis of **3,5-di(pyridin-3-yl)phenol (L2)**

1,3-Dibromo-5-methoxybenzene (2.66 g, 10.0 mmol), 4-pyridineboronic acid pinacol ester (5.0 g, 24.4 mmol), tetrakis(triphenylphosphine) palladium(0) (1.16 g, 1 mmol), and potassium carbonate (13.8 g, 0.1 mol) were added into a 100 mL single-neck round-bottom flask equipped with a magnetic stir bar and capped with a septum. Under nitrogen atmosphere, 60 mL of DMF along with 2 mL of H$_2$O were added and the resulting mixture was stirred for 60 h at 100 °C. After cooling to room temperature, the reaction residue was diluted with chloroform/methanol (10/1, v/v) and filtered through Celite. The filtrate was extracted with brine, dried over anhydrous

Na$_2$SO$_4$, and concentrated under vacuum. Using silica gel column chromatography, the crude product was purified to yield a light yellow solid. The solid was further dried under high vacuum, and was dissolved in 100 mL anhydrous dichloromethane (DCM) in a 250 mL round bottom flask equipped with a stir bar. The solution was cooled to -78 °C, and BBr$_3$ (50.0 mL, 1.0 M in CH$_2$Cl$_2$, 50 mmol) was added slowly to the flask over the course of 30 min. The reaction was stirred for another 10 min before it was gradually warmed to room temperature and stirred for 8 h. The reaction residue was poured into 400 mL of iced sodium bicarbonate saturated aqueous solution to quench. A light yellow precipitate formed and was collected by filtration. The solid was further purified by washing with deionized water, ethyl ether, and a large amount of CH$_2$Cl$_2$ to yield 1.1 g of **L2** as a white solid (65 %). ^{1}H NMR (DMSO-d$_6$): δ 8.92 (2H, d, J = 2.0 Hz), 8.57 (2H, dd, J = 4.8 Hz, J = 2.0 Hz), 8.10 (2H, dt, J = 8.0 Hz, J = 2.0 Hz), 7.47 (2H, dd, J = 8.0 Hz, J = 4.4 Hz), 7.41 (1H, t, J = 2.0 Hz), 7.10 (2H, d, J = 8.0 Hz). ^{13}C NMR (DMSO-d$_6$): δ 149.09, 148.25, 139.73, 136.09, 134.76, 124.29, 116.45, 114.16. HRMS (m/z): [M+H]$^+$ calculated for C$_{16}$H$_{12}$N$_2$O, 249.1022; found, 249.1016.

General procedures for block copolymer synthesis:

Synthesis of **PMMA**.

PMMA polymers were synthesized via atom transfer radical polymerization (ATRP) following a literature procedure.[3] Specifically, a long-neck Schlenk flask equipped with a magnetic stir bar was charged with 16.0 mL of MMA, 8.0 mL of 0.095 M EBPA in anisole, 1 mL of 0.076 M CuBr$_2$, and 0.149 M 4,4'-Dinonyl-2,2'-bipyridine (dNbpy) in DMF. The system was then degassed with three freeze-pump-thaw cycles.

After the last cycle, a copper wire (L = 3 cm, d = 1mm) cleaned by rinsing with aqueous HCl was added into the flask under nitrogen. The flask was then stopped and purged with three vacuum/nitrogen cycles. The system was allowed to thaw and the flask was heated at 35 °C in an oil bath. Reaction aliquots were withdrawn at timed intervals to calculate the conversion based on ^{1}H NMR analysis. The reaction was quenched after ~3.5 h (35-50 % conversion) by opening the flask to air and cooling to room temperature. Immediately after that, the reaction mixture was diluted in THF and passed through a column of neutral alumina. The polymer was then precipitated three times in hexanes, and was collected as a white solid by filtration and dried under vacuum.

Synthesis of **PMMA-PBA** block copolymer.

PMMA-PBA was synthesized via activator regenerated by electron transfer (ARGET) ATRP. A representative procedure is as follows. A long-neck Schlenk flask equipped with a magnetic stir bar was charged with 1.0 g of PMMA, 10 mL of n-butyl acrylate, 2 mL of 0.047 M Me_6Tren in anisole, and 300 µL of 0.076 M $CuBr_2$ in DMF. The resulting solution was degassed by bubbling nitrogen for 45 min. After that, 1.0 mL of tin(II) 2-ethylhexanoate in anisole (0.1 M, degassed) was added. The reaction mixture was then submerged in an oil bath that was maintained at 70 °C. Reaction aliquots were withdrawn at timed intervals to calculate the conversion based on ^{1}H NMR analysis. The reaction was quenched after 4 h by opening the flask to air and cooling to room temperature. Immediately after that, the reaction mixture was diluted in THF and passed through a column of neutral alumina to remove the copper catalyst. The resulting solution was then concentrated and dried under high vacuum at 50 °C.

Block copolymer end-functionalization (synthesis of **PMMA-PBA-L**)

A long-neck Schlenk flask equipped with a magnetic stir bar was charged with 1.0 g of PMMA-PBA block copolymer, 200 mg of Ligand **L1**, **L2**, or **L3**, 300 mg Cs_2CO_3, and a catalytic amount of KI. The Schlenk flask was then evacuated and back-filled with nitrogen for three cycles. Under nitrogen, 3.0 mL of DMF was added and the reaction mixture was heated to and maintained at 60 °C in an oil bath. After 8 h, the DMF was removed under high vacuum. The functionalized block copolymer was isolated via silica gel column chromatography (3 % methanol in DCM). Due to the polar pyridine group, the functionalized block copolymers have a higher polarity, making it straightforward to purify the polymer using silica gel chromatography. The ^{1}H NMR spectrum of **PMMA$_{4k}$-PBA$_{19k}$-L3** is shown in Figure S1.

Characterization Methods.

Atomic force microscopy (AFM). Tapping mode AFM experiments were conducted on an Asylum Research MFP-3D AFM system (Oxford Instruments). All experiments were done in air using silicon tips (AC160TS-R3, Asylum Research) with a spring constant of 26 N/m and a resonance frequency of 300 kHz. For block copolymer microphase-separation images, a filtered polymer solution in toluene (20 mg/mL) was drop-cast onto the surface of a silicon wafer (1 cm $\times$ 1 cm). Before polymer casting, the wafer was cleaned by rinsing with acetone, hexanes, and isopropanol and dried under nitrogen. For imaging of the star polymer containing the metal-organic cage (MOC) core, a dilute solution (0.1 mg/mL) of the star polymer was spin-coated on the surface of a cleaned silicon wafer.

Small angle X-ray scattering (SAXS). SAXS experiments were performed at the Sector 12 beamline of the Advanced Photon Source (APS) of Argonne National Laboratory. X-rays of wavelength 0.89 Å (14 keV) were used. The system was calibrated using silver behenate as the standard. For the bulk rubber samples, the exposure time was 0.5 s; for the gel samples, the exposure time was 1 s. For variable temperature (VT) experiments, the samples were mounted on a Linkam temperature control stage and were heated or cooled *in situ*. 2-dimensional scattering data were recorded and were converted to 1-dimensional plots via radial averaging of the 2D pattern. The background scattering (for example the Kapton tape) was subtracted.

Nuclear magnetic resonance spectroscopy (NMR). ^{1}H NMR and ^{13}C NMR were recorded using a Bruker AVANCE-400 NMR spectrometer. Chemical shifts are reported in parts per million (ppm), and are referenced to residual solvent peaks. Scalar coupling constants *J* are reported in Hertz (Hz).

Gel permeation chromatography (GPC). GPC analyses were carried out in tetrahydrofuran (THF) at a flow rate of 1.0 mL/min using an Agilent 1260 Infinity system with a variable-wavelength diode array (254, 450, and 530 nm) and a refractive index detector. The instrument was calibrated with low-dispersity poly(styrene) (PS) standards between 1.7 and 3150 kg/mol. The number-averaged molar mass, weight-averaged molar mass, and dispersity index were abbreviated as M_n, M_w, and $Đ$; $Đ = M_w/M_n$.

Rheometry. Rheology studies of the bulk rubber samples were measured on an Anton Paar MCR 301 rheometer. A disposable parallel-plate geometry (radius = 12 mm) and a disposable bottom plate were used together; the gap between the two plates was ~2 mm. Frequency sweep experiments were conducted from 0.1 to 100 rad/s at 1% strain, which is in the linear viscoelastic regime as confirmed using strain sweep experiments. The rubber samples were formed at 120 °C using a Teflon mold with a radius of 12 mm and a height of 2 mm. This process also anneals the polymers to induce phase separation. Rheology experiments of the gel samples were performed on a TA Discovery HR-2 rheometer. A parallel-plate with a radius of 20 mm was used and coupled with a bottom plate capable of varying temperature using a Peltier heating system. When loading the sample, a piece of gel (~30 mg) was transferred on the bottom plate and the plate temperature was raised to 50 °C to melt the gel. When the gel turned to a liquid, the top plate was lowered until the sample was fully sandwiched. The gap between the top and bottom plates was 0.5-1.0 mm. Temperature sweep experiments were performed where the moduli were measured as a function of temperature (5 to 70 °C). The strain and the angular frequency were kept at 1% and 10 rad/s, respectively. The temperature step was 1 °C per measurement.

Transmission electron microscopy (TEM). TEM images are obtained using a FEI Tecnai multipurpose scope (G2 Spirit TWIN). The samples were prepared by spin-coating a dilute acetonitrile solution (0.1 mg/mL) of the star polymers containing the MOC core onto a carbon coated copper grid. After drying under vacuum for 10 min, the sample-coated grids were placed in a small jar saturated with RuO_4 vapor prepared by

mixing 30 mg of RuCl$_3$ and 15 mL of sodium hypochlorite solution (10-15 %, Sigma). The polymer samples were allowed to stain for 45 min, and imaged at an electron accelerating voltage of 120 kV.

Dynamic Light Scattering (DLS). DLS experiments were performed on a Wyatt Dawn Heleo-II instrument at 20 °C. An acetonitrile solution of the linear or star polymers was filtered immediately before each measurement.

Supplementary Notes.

Estimation of the radius of gyration of the linear and star polymers.[4]

The radius of gyration of an ideal linear chain can be calculated by:

$$< R_g^2 > = \frac{b^2 N}{6}$$

where $< R_g^2 >$ is the mean-squared radius of gyration, b is the Kuhn length of the polymer, and N is the number of the Kuhn segments in the polymer chain. For a linear di-block copolymer:

$$< R_g^2 > = \frac{b_1^2 N_1}{6} + \frac{b_2^2 N_2}{6}$$

where b_1, N_1, b_2, and N_2, are specific values for each of the blocks in the copolymer-in our case, PMMA-PBA. (*For simplicity, we neglect interactions between PMMA and PBA.*)

The Kuhn length for PMMA is 1.7 nm and the molecular mass for a Kuhn segment is 655 g/mol. The Kuhn length for PBA is 1.96 nm and the molecular mass for the Kuhn segment is 960 g/mol. In the case of PMMA$_{4k}$-PBA$_{19k}$,

$$< R_g^2 > = \frac{b_1^2 N_1}{6} + \frac{b_2^2 N_2}{6} = \frac{1.7^2 \times 4000/655}{6} + \frac{1.96^2 \times 19000/960}{6} = 15.6 \, \text{nm}^2$$

so that $2R_g = 7.9$ nm. The experiment result based on DLS is 8.6 nm.

For the star polymers with n arms, the radius of gyration of an ideal linear chain is:

$$< R_g^2 > = \frac{b_1^2 N_{1total}/n}{6} \times (3 - \frac{2}{n}) + \frac{b_2^2 N_{2total}/n}{6} \times (3 - \frac{2}{n})$$

where N_{total} is the number of Kuhn segments from all arms. For the 4-arm PMMA$_{4k}$-PBA$_{19k}$ star polymer possessing a M$_2$L$_4$ paddlewheel MOC core, $n = 4$, and $2R_g$ is calculated to be 12.5 nm. The experiment result based on DLS is 12.2 nm. ***Note*: DLS measures the hydrodynamic diameter and not $2R_g$. Care must be taken in comparing these values.**

For the 24-arm star polymer possessing the M$_{12}$L$_{24}$ MOC core based on PMMA$_{4k}$-PBA$_{19k}$, $n = 24$. Considering that the polymer chains might be stretched due to the junction constraint[5], we assume that polymers are in a good solvent, instead of a θ solvent). In this case,

$$< R_g^2 > = \frac{b_1^2 N_{1total}^{1.2}/n}{6} \times (3 - \frac{2}{n}) + \frac{b_2^2 N_{2total}^{1.2}/n}{6} \times (3 - \frac{2}{n})$$

and therefore $2R_g = 17.8$ nm. Because the MOC core is about 3.5 nm in diameter, the size of the star polymer is 21.3 nm. The experiment result is 22.8 nm.

Calculation of spinodal curve.

We predict the thermal unstability limit of the disordered melt of a star-shape polymer with AB block copolymers –in our case PMMA-PBA– as arms, denoted as $(AB)_n$, where n is the number of arms. For a star-like architecture, all the AB arms are connected at each B block end. If the A and B blocks have a degree of polymerization (DP) of N_A and N_B, respectively, the total DP is $N = n(N_A + N_B)$. The average segment length is set to a for both A and B segments. The structure factor for the $(AB)_n$ star-shaped block copolymer is

$$\overline{S} = [S/W - 2\chi]^{-1}$$

where

$$S = S_{AA} + S_{BB} + 2S_{AB}$$

$$W = S_{AA} * S_{BB} - S_{AB}^{\ 2}$$

$$S_{AA} = nS_{AA}^{ii} + n(n-1)S_{AA}^{ij}$$

$$S_{BB} = nS_{BB}^{ii} + n(n-1)S_{BB}^{ij}$$

$$S_{AB} = nS_{AB}^{ii} + n(n-1)S_{AB}^{ij}$$

$$S_{AA}^{ii} = (nN_A + nN_B)^{-1} g(N_A)$$

$$S_{AA}^{ij} = \frac{1}{2}(nN_A + nN_B)^{-1}[g(2N_A + 2N_B) - 2g(N_A + 2N_B) + g(2N_B)]$$

$$S_{BB}^{ii} = (nN_A + nN_B)^{-1} g(N_B)$$

$$S_{BB}^{ij} = \frac{1}{2}(nN_A + nN_B)^{-1}[g(2N_B) - 2g(N_B)]$$

$$S_{AB}^{ii} = \frac{1}{2}(nN_A + nN_B)^{-1}[g(N_A + N_B) - g(N_A) - g(N_B)]$$

$$S_{AB}^{ij} = \frac{1}{2}(nN_A + nN_B)^{-1}[g(N_A + 2N_B) - g(N_A + N_B) - g(2N_B) + g(N_B)]$$

$$g(f, x) = \frac{2}{y^2}[fxy + \exp(-fxy) - 1]$$

$$y = \frac{q^2 a^2}{6}$$

The structure factor is divergent at spinodal point, which is equal to $\bar{S}^{-1}=0$. And based on the structure factor, a spinodal curve can be drawn to present the thermal unstability limit of the disordered melt.
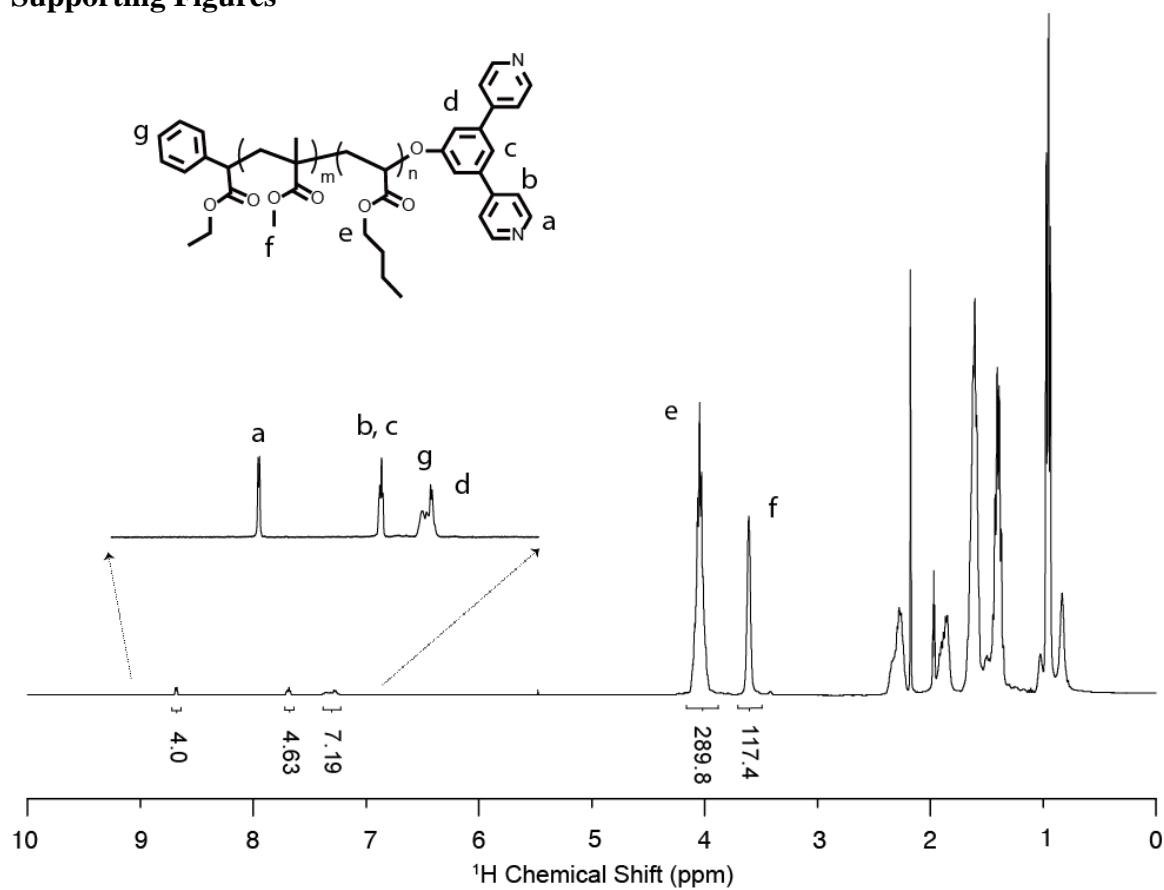
Supporting Figures

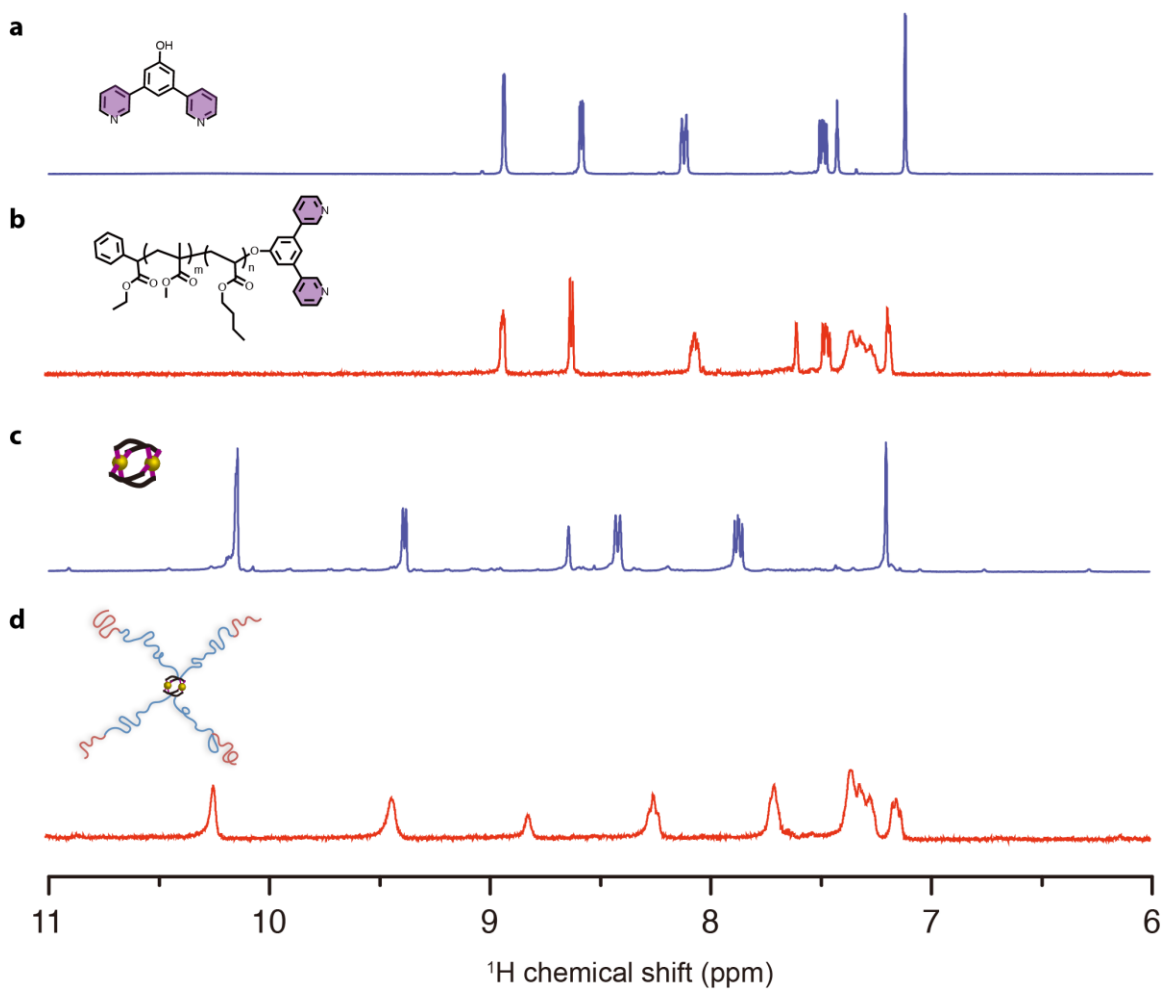**Figure S1**. ¹H NMR spectrum (400 MHz) of **PMMA₄ₖ-PBA₁₉ₖ-L3**. Solvent: acetonitrile-d₃.

Figure S2. ^{1}H NMR spectra comparing the formation of paddlewheel M_2L_4 MOC based on small molecules in DMSO-d_6 (blue) and block copolymers in acetonitrile-d_3 (red). Spectra before (a and b) and after (c and d) assembly are shown. Block copolymer **PMMA$_{4k}$-PBA$_{19k}$-L2** was used to obtain the spectra.
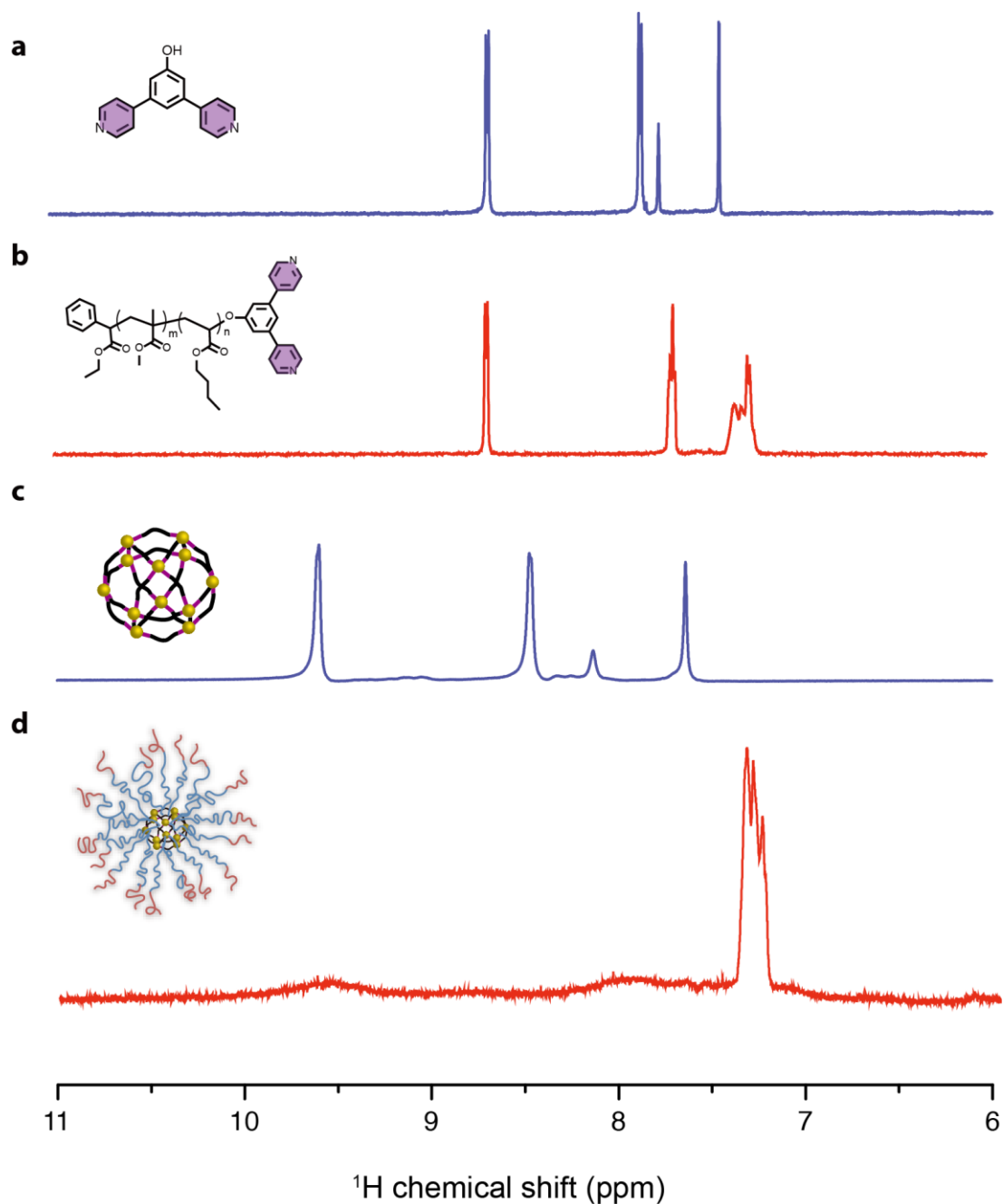
Figure S3. ^{1}H NMR spectra comparing the formation of Fujita sphere-like $M_{12}L_{24}$ MOC based on small molecules in DMSO-d_6 (blue) and block copolymers acetonitrile-d_3 (red). Spectra before (a and b) and after (c and d) assembly are shown. Block copolymer **PMMA$_{4k}$-PBA$_{19k}$-L3** was used to obtain the spectra. The molecular weight of the assembled star polymer (shown in d) is estimated to be 552,000 (23000×24), thus explaining the broadening of the MOC-associated resonances.
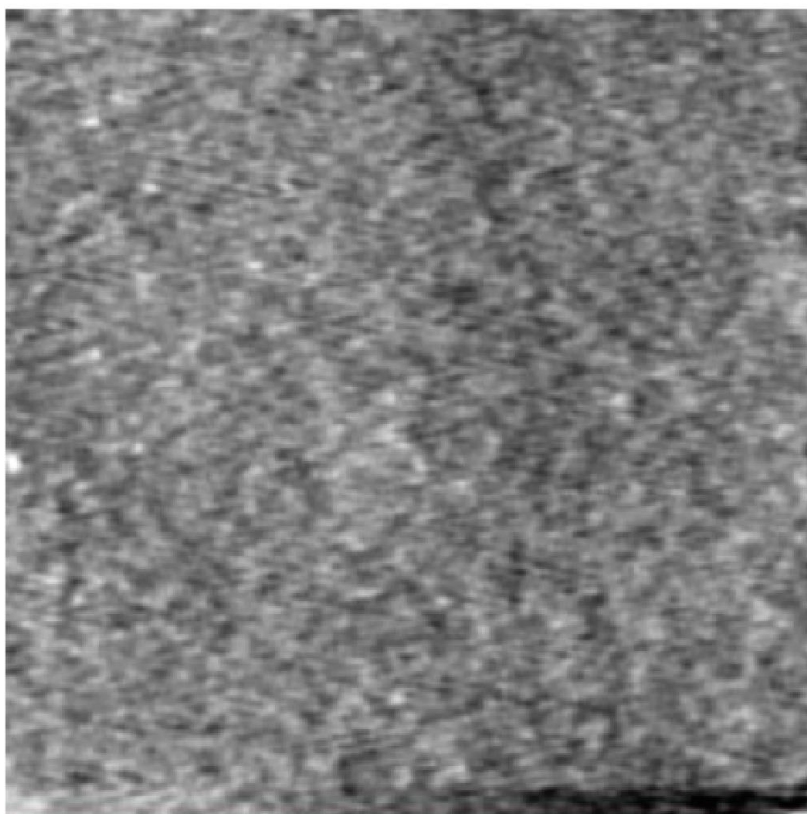
Figure S4. Atomic force microscopy (AFM) height image of linear block copolymer **PMMA$_{4k}$-PBA$_{19k}$** cast onto a silicon wafer, demonstrating that no nanoparticles were observed and ruling out the possibility of micelle formation.
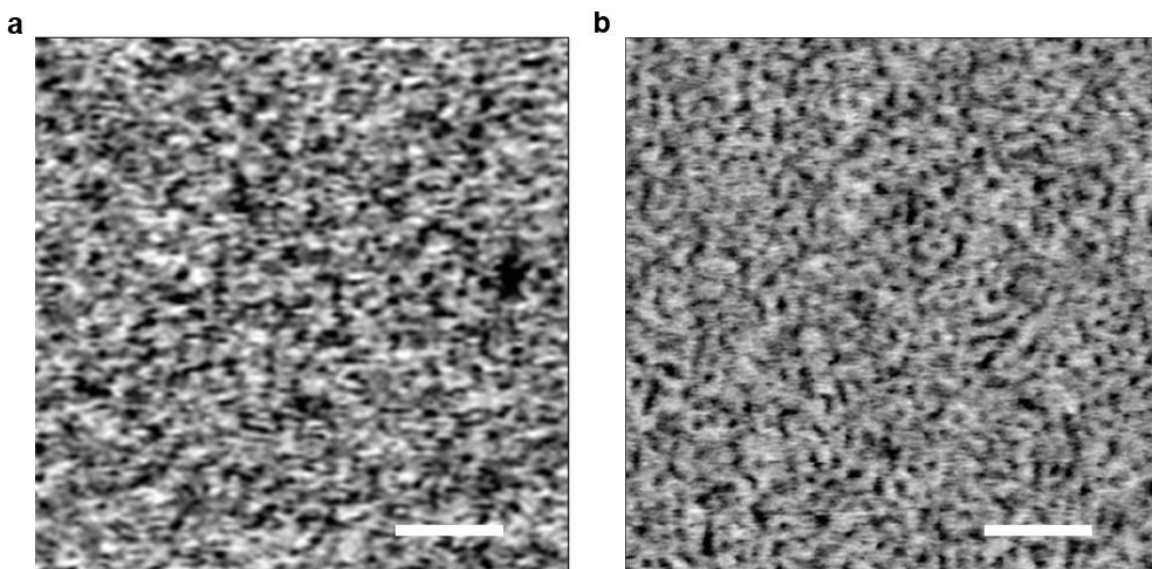
Figure S5. Atomic force microscopy (AFM) phase images of (a) the linear block copolymer **PMMA$_{4k}$-PBA$_{19k}$** and (b) the BCPMOC with M$_{12}$L$_{24}$ MOC core **PMMA$_{4k}$-PBA$_{19k}$-L3** (data in part b also shown in Figure 4a) showing the effect of MOC core on the phase separation behavior.
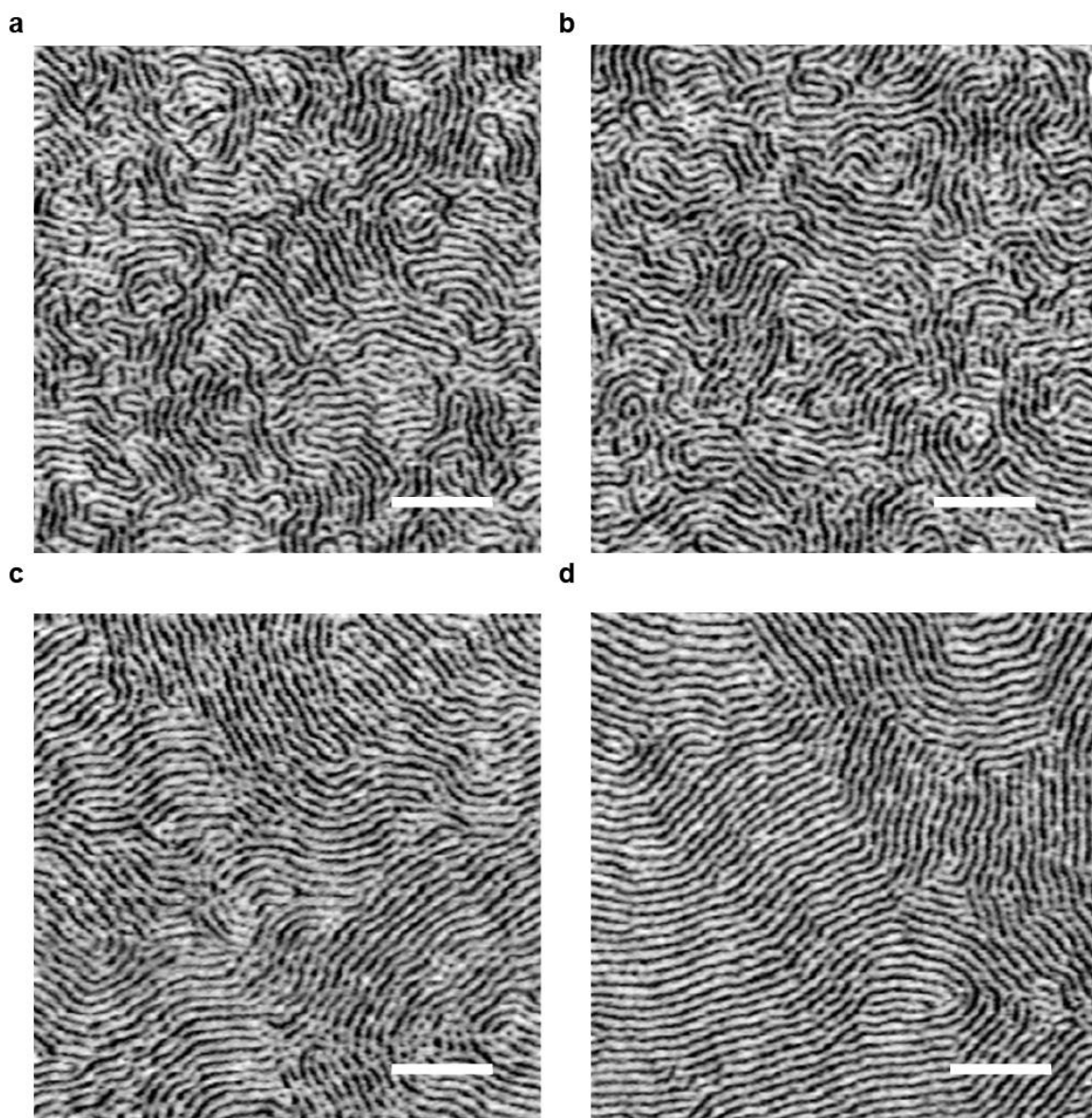
Figure S6. Atomic force microscopy (AFM) phase images of (a) the linear block copolymer **PMMA$_{8k}$-PBA$_{27k}$** and BCPMOCs derived from **PMMA$_{8k}$-PBA$_{27k}$-L1, -L2, and -L3** with M$_1$L$_4$, M$_2$L$_4$, and M$_{12}$L$_{24}$ MOCs showing the effect of the MOC core on the phase separation behavior. (data in part d also shown in Figure 4b)

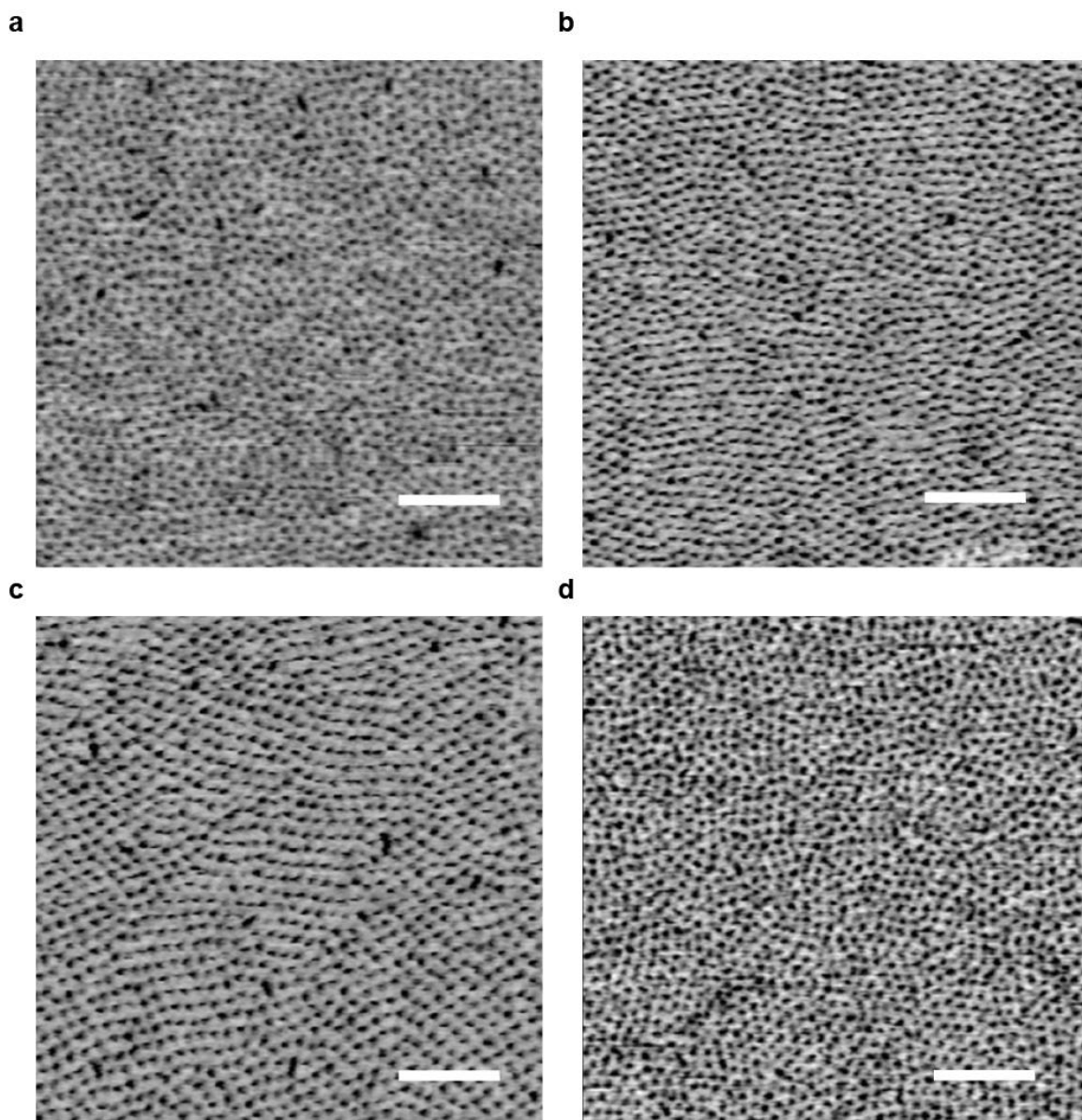**Figure S7.** Atomic force microscopy (AFM) phase images of (a) the linear block copolymer **PMMA$_{8k}$-PBA$_{48k}$** and the BCPMOCs **PMMA$_{8k}$-PBA$_{48k}$-L1**, **-L2**, and **-L3** with M_1L_4, M_2L_4, and $M_{12}L_{24}$ MOCs showing the effect of the MOC core on the phase separation behavior. (data in part d also shown in Figure 4c)
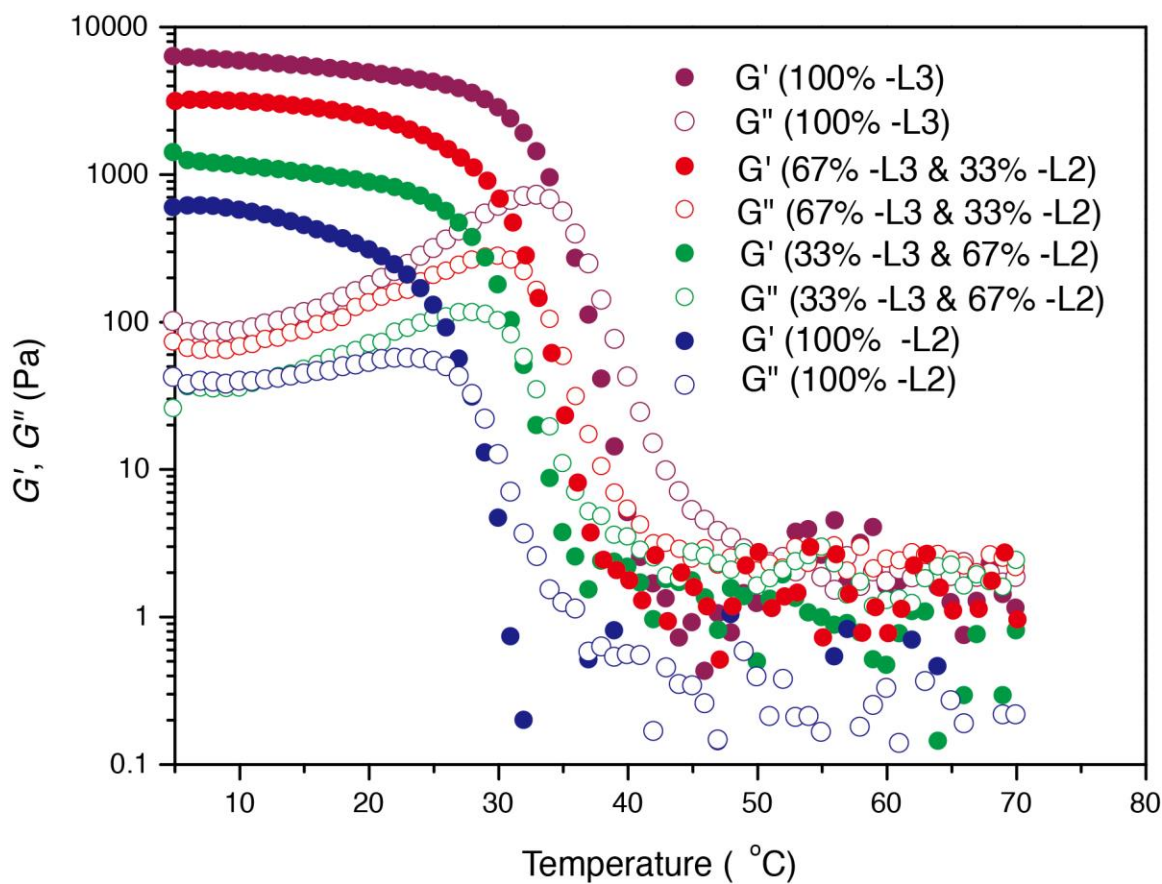
Figure S8. Temperature sweep experiments of BCPMOC organogels with various ratios of M_2L_4 and $M_{12}L_{24}$ MOC junctions shows the moduli and sol-gel transitions as a function of temperature.
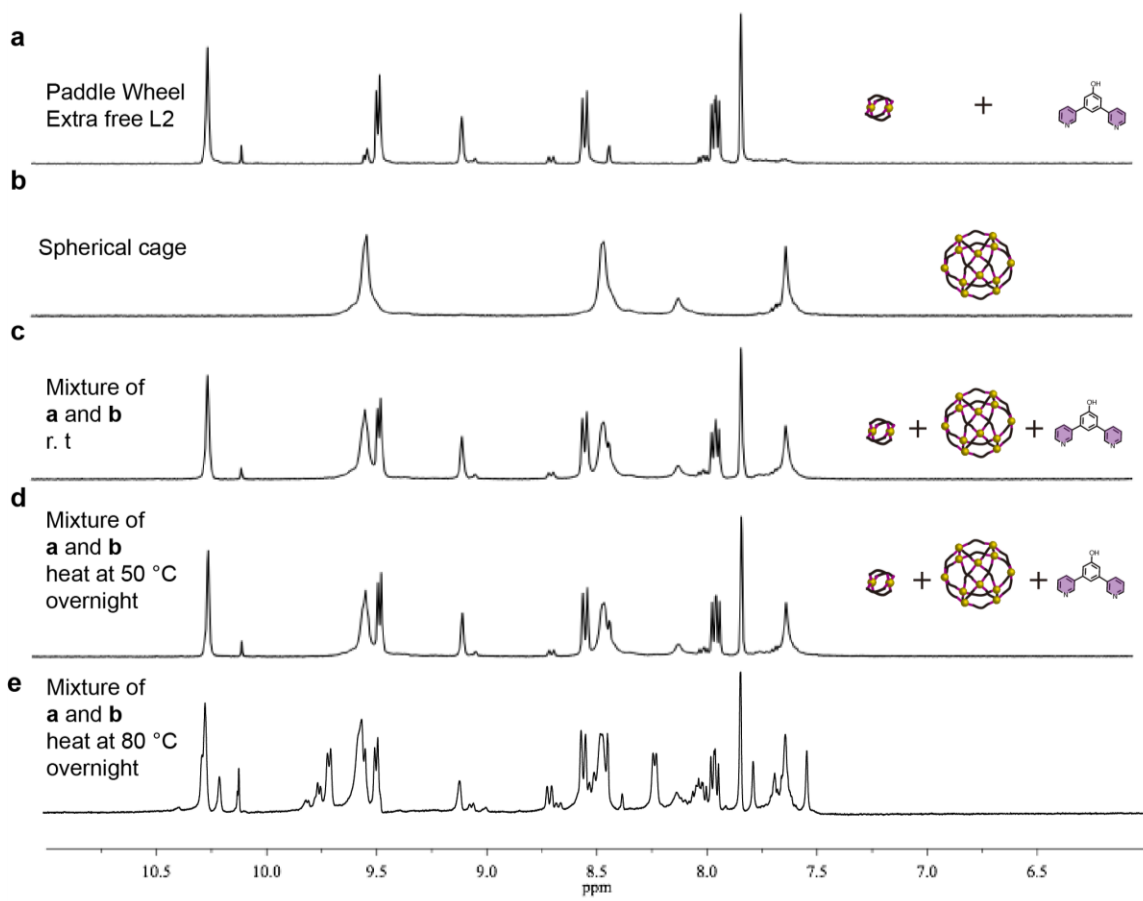
Figure S9. ^{1}H NMR spectra showing the M_2L_4 and $M_{12}L_{24}$ MOCs separately, as a mixture at room temperature, and after heating at 50 °C and 80 °C overnight. (a) Spectrum of paddlewheel MOC; small amount of extra free ligand is added to enhance ligand exchange (if any) purposely. (b) Spectrum of Fujita sphere MOC. (c) Spectrum of the mixture of **a** and **b**. (d) Spectrum shows no changes after the mixture was heated at 50 °C indicating that the cages are stable under these conditions. (e) New peaks developed after the mixture was heated at 80 °C overnight, suggesting ligand exchange or MOC degradation.
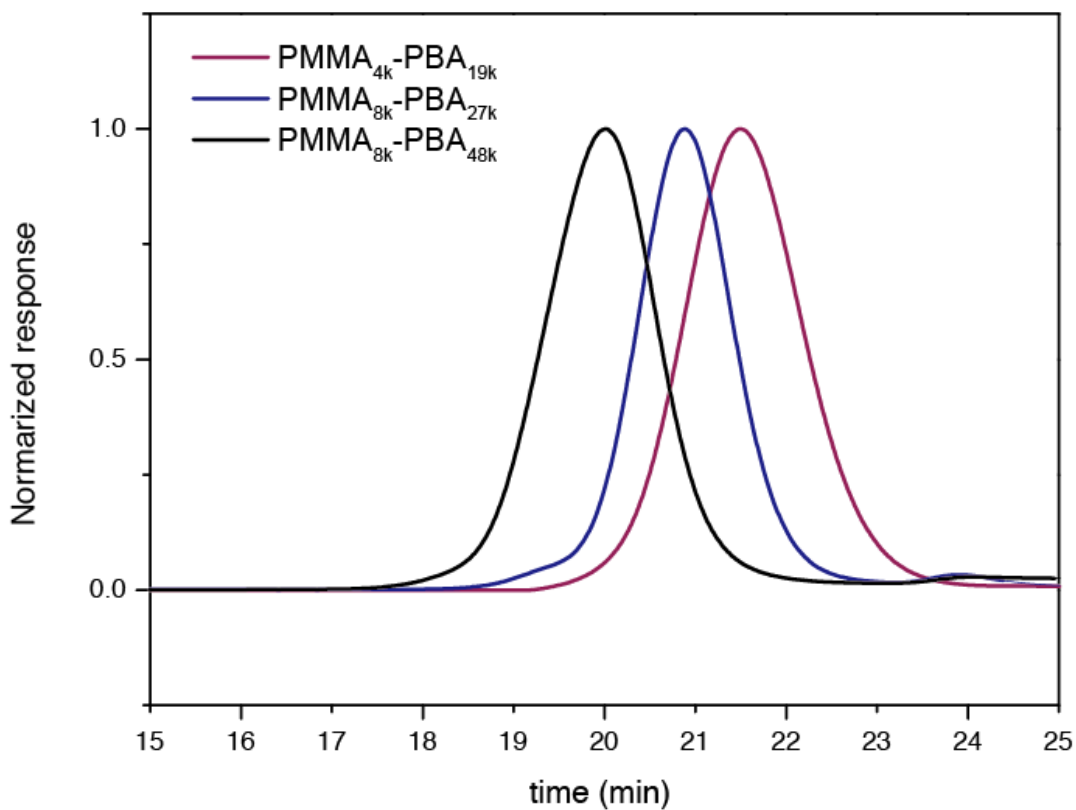
Additional Supporting Figures

Figure S10. Gel permeation chromatography (GPC) traces of the PMMA-PBA block copolymer synthesized.

References

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