

Electronic Supplementary Information

Anisotropic Coordination Star Polymers Realized by Self-Sorting Core Modulation

Nobuhiko Hosono,* Kenichiro Omoto, and Susumu Kitagawa*

*To whom correspondence should be addressed.

E-mail: nhosono@icems.kyoto-u.ac.jp; kitagawa@icems.kyoto-u.ac.jp

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Materials and Methods

1. Materials.

5-*tert*-Butylisophthalic acid (**Ip**), azobenzene-3,3'-dicarboxylic acid (**Azo**), and *N,N*-diethylformamide (DEF) were purchased from Tokyo Chemical Industries (TCI). *tert*-Butylacrylate was purchased from TCI and passed through a short column of basic alumina to remove inhibitors prior to use. Dehydrated tetrahydrofuran (THF) was purchased from Kanto Chemical. Deuterated solvents for nuclear magnetic resonance (NMR) spectroscopy were purchased from Cambridge Isotope Laboratories. DCI (35% in D₂O) was purchased from Aldrich Chemicals. A reversible addition-fragmentation transfer (RAFT) agent, butyl 5-methylisophthalic acid trithiocarbonate **1** was synthesized in the literature procedure.^{S1} α,α' -Azobisisobutyronitrile (AIBN) was purchased from Nacalai Tesque and recrystallized from methanol. All other materials were purchased from TCI or Nacalai Tesque and used without any further purification.

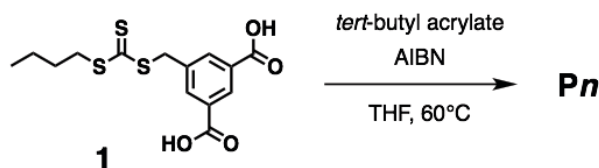
2. General.

Analytical size-exclusion chromatography (SEC) measurements were performed at 40 °C on a Shimadzu model, HPLC Prominence system with two polystyrene gel columns in series (Shodex KF-804L) and equipped with a refractive index detector (Shimadzu RID-10A) and an UV detector (Shimadzu SPD-20A). The mobile phase was THF at a flow rate of 1.0 mL/min. Molecular weights and molecular weight distribution ($\mathcal{D} = M_w/M_n$) were obtained relative to polystyrene standards (Shodex, Standard Polystyrene SM-105). ¹H and ¹³C NMR spectra were recorded at 25°C on a JEOL RESONANCE model ECS-400, operating at 400 and 100 MHz, respectively, where chemical shifts (δ in ppm) were determined with respect to tetramethylsilane (TMS) as an internal reference. Infrared (IR) spectra were recorded on a JASCO model FT/IR-4200 Fourier transform infrared spectrometer with an attenuated total reflection (ATR) equipment (ATR PR0450-S). Thermogravimetric analyses (TGA) were performed on a Rigaku model Thermo plus EVO with a heating rate of 5 °C/min under N₂. Atomic force microscopy (AFM) micrographs were obtained in non-contact tapping mode using Asylum Research model Cypher ES equipped with BlueDrive photothermal excitation. Gold-coated cantilevers (OMCL-AC160TSA-C3E, Olympus) with spring constants ranging from 21 to 28 pN/nm (resonant frequency of 300 kHz) were used and calibrated by the thermal fluctuation method. Igor Pro software (WaveMetrics) was used for all of the data acquisition and analysis. Powder X-ray diffraction data were collected by a Rigaku model SmartLab diffractometer equipped with CuK α radiation ($\lambda = 1.54056 \text{ \AA}$). Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on a Bruker Daltonics model Ultraflex III using DCTB as a matrix.

3. Synthesis.

AzoMOP(Ip₆). **Ip** (45 mg, 0.2 mmol) and **Azo** (54 mg, 0.2 mmol) were dissolved in DEF (8 mL), to which Cu(OAc)₂·H₂O (79.9 mg, 0.4 mmol) dissolved in DEF (8 mL) was added and stirred for 5 min. The solution color turned into green immediately. A small aliquot was taken from the reaction mixture and subjected to SEC analysis in order to check the formation of **AzoMOP(Ip₆)**. The mixture was left at 25 °C for 1 week, affording single prismatic crystals suitable for X-ray crystallography analysis. The crystals were collected from the mother liquor by filtration and powder X-ray diffraction (PXRD) analysis was performed. PXRD was only successful for the fresh sample because the collected crystals immediately became amorphous in air. The collected samples were washed with small amount of DEF and methanol, then dried under vacuum overnight. The final product has a formula of [Cu₁₂(**Ip**)₆(**Azo**)₆(H₂O)₁₂], which is determined based on crystallographic data (*vide infra*), elemental analysis, and TGA (Figure S8). Elemental analysis result (%calc/found): C 47.93/46.93; H 3.71/3.79; N 4.30/4.29. IR spectrum of the product is shown in Figure S9. The dried powdery product was slightly soluble in THF.

P10. 1 (1.00 g, 2.90 mmol) and *tert*-butyl acrylate (7.43 g, 58.0 mmol), and THF (25 mL) were placed in a round bottom flask (100 mL) capped with a three-way stopcock. To the mixture was added 0.1 M toluene solution of AIBN (14.5 mL, 1.45 mmol). The yellow solution was degassed by freeze-pump-thaw cycles (three times). The flask was placed in an oil bath thermostated at 60 °C. After 60 min, the reaction mixture was cooled down to room temperature and poured into 30 mL of methanol/water (8/2, v/v) mixture. The product thus precipitated out was collected by centrifugation (15000 rpm, 10 min) and dissolved into THF (3 mL). The product was precipitated again from 30 mL of methanol/water (8/2, v/v) mixture, collected by centrifugation (15000 rpm, 10 min), then dried at 70 °C under a reduced pressure for 16 h to give **P10** (3.0 g) as yellow glassy solid.



SEC analysis of **P10** (THF, polystyrene standards): $M_{n,AC} = 1800$ ($D = 1.17$). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.70 (s, 1H), 8.18 (m, 2H), 4.68 (m, 1H), 3.34 (m, 2H), 2.88–2.61 (m, 2H), 2.53–2.12 (9.1H), 2.09–1.11 (m), 0.92 (m, 3H). DP was calculated to be 10.1 with respect to the α-protons (4.68 and 2.53–2.12 ppm) of acrylate referring to the aromatic protons (8.13 ppm) on the isophthalic acid end of the polymer.

P30. 1 (1.0 g, 2.90 mmol) and *tert*-butyl acrylate (14.9 g, 116 mmol), and THF (25 mL) were placed in a round bottom flask (100 mL) capped with a three-way stopcock. To the mixture was added 0.1 M toluene solution of AIBN (14.5 mL, 1.45 mmol). The yellow solution was degassed by freeze-pump-thaw cycles (three times). The flask was placed in an oil bath thermostated at 60 °C. After 60 min, the reaction mixture was cooled down to room temperature and poured into 30 mL of methanol/water (8/2, v/v) mixture. The product thus precipitated out was collected by centrifugation (15000 rpm, 10 min) and dissolved into THF (3 mL). The product was precipitated again from 30 mL of methanol/water (8/2, v/v) mixture, collected by centrifugation (15000 rpm, 10 min), then dried at 70 °C under a reduced pressure for 16 h to give **P30** (7.0 g) as yellow glassy solid.

SEC analysis of **P30** (THF, polystyrene standards): $M_{n,AC} = 4200$ ($D = 1.12$). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.65 (s, 1H), 8.15 (m, 2H), 4.68 (m, 1H), 3.34 (m, 2H), 2.88–2.56 (m, 2H), 2.52–2.11 (29.0H), 2.08–1.10 (m), 0.93 (m, 3H). DP was calculated to be 30.0 with respect to the α -protons (4.68 and 2.52–2.11 ppm) of acrylate referring to the aromatic protons (8.13 ppm) on the isophthalic acid end of the polymer.

P54. The synthesis and characterization of this compound was described as **PtBA54** in a literature previously published.^{S1}

P148. The synthesis and characterization of this compound was described as **PtBA148** in a literature previously published.^{S1}

P272. The synthesis and characterization of this compound was described as **PtBA272** in a literature previously published.^{S1}

MOP(P10₂₄). A DEF solution (0.5 mL) of **P10** (30 mg, 16 μmol) was mixed with a DEF solution (0.5 mL) of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (3.2 mg, 16 μmol). The mixture was stirred at 25 °C for 30 min. A small aliquot of the reaction mixture was taken and diluted with THF to prepare the sample for SEC analysis.

MOP(P30₂₄). A DEF solution (0.5 mL) of **P30** (37 mg, 8 μmol) was mixed with a DEF solution (0.5 mL) of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (1.6 mg, 8 μmol). The mixture was stirred at 25 °C for 30 min. A small aliquot of the reaction mixture was taken and diluted with THF to prepare the sample for SEC analysis.

MOP(P54₂₄). A DEF solution (0.5 mL) of **P54** (32 mg, 4 μmol) was mixed with a DEF solution (0.5 mL) of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.8 mg, 4 μmol). The mixture was stirred at 25 °C for 30 min. A

small aliquot of the reaction mixture was taken and diluted with THF to prepare the sample for SEC analysis.

MOP(P148₂₄). A DEF solution (0.5 mL) of **P148** (48 mg, 2 μ mol) was mixed with a DEF solution (0.5 mL) of Cu(OAc)₂·H₂O (0.4 mg, 2 μ mol). The mixture was stirred at 25 °C for 30 min. A small aliquot of the reaction mixture was taken and diluted with THF to prepare the sample for SEC analysis.

MOP(P272₂₄). A DEF solution (0.5 mL) of **P272** (89 mg, 2 μ mol) was mixed with a DEF solution (0.5 mL) of Cu(OAc)₂·H₂O (0.4 mg, 2 μ mol). The mixture was stirred at 25 °C for 30 min. A small aliquot of the reaction mixture was taken and diluted with THF to prepare the sample for SEC analysis.

MOP(P10₆/Ip₁₈). A DEF solution (1.0 mL) of **P10** (30 mg, 16 μ mol) and **Ip** (10.6 mg, 48 μ mol) was mixed with a DEF solution (0.5 mL) of Cu(OAc)₂·H₂O (12.8 mg, 64 μ mol). The mixture was stirred at 25 °C for 30 min. A small aliquot of the reaction mixture was taken and diluted with THF to prepare the sample for SEC analysis.

MOP(P30₆/Ip₁₈). A DEF solution (1.0 mL) of **P30** (37 mg, 8 μ mol) and **Ip** (5.3 mg, 24 μ mol) was mixed with a DEF solution (0.5 mL) of Cu(OAc)₂·H₂O (6.4 mg, 32 μ mol). The mixture was stirred at 25 °C for 30 min. A small aliquot of the reaction mixture was taken and diluted with THF to prepare the sample for SEC analysis.

MOP(P54₆/Ip₁₈). A DEF solution (1.0 mL) of **P54** (32 mg, 4 μ mol) and **Ip** (2.6 mg, 12 μ mol) was mixed with a DEF solution (0.5 mL) of Cu(OAc)₂·H₂O (3.2 mg, 16 μ mol). The mixture was stirred at 25 °C for 30 min. A small aliquot of the reaction mixture was taken and diluted with THF to prepare the sample for SEC analysis.

MOP(P148₆/Ip₁₈). A DEF solution (1.0 mL) of **P148** (48 mg, 2 μ mol) and **Ip** (1.3 mg, 6 μ mol) was mixed with a DEF solution (0.5 mL) of Cu(OAc)₂·H₂O (1.6 mg, 8 μ mol). The mixture was stirred at 25 °C for 30 min. A small aliquot of the reaction mixture was taken and diluted with THF to prepare the sample for SEC analysis.

MOP(P272₆/Ip₁₈). A DEF solution (1.0 mL) of **P272** (89 mg, 2 μ mol) and **Ip** (1.3 mg, 6 μ mol) was mixed with a DEF solution (0.5 mL) of Cu(OAc)₂·H₂O (1.6 mg, 8 μ mol). The mixture was stirred at 25 °C for 30 min. A small aliquot of the reaction mixture was taken and diluted with THF to prepare the sample for SEC analysis.

AzoMOP(P10₆). A DEF solution (1.0 mL) of **P10** (30 mg, 16 μ mol) and **Azo** (4.3 mg, 16 μ mol) was mixed with a DEF solution (0.5 mL) of Cu(OAc)₂·H₂O (6.4 mg, 32 μ mol). The mixture was stirred at 25 °C for 30 min. A small aliquot of the reaction mixture was taken and diluted with THF to prepare the sample for SEC analysis. In order to isolate the CSP, the product was dissolved in THF and precipitated from MeOH twice, then dried in vacuum at 70°C for 16 h to give a glassy green-colored solid. IR spectrum was measured in terms of this dried sample (Figure S9).

AzoMOP(P30₆). A DEF solution (1.0 mL) of **P30** (37 mg, 8 μ mol) and **Azo** (2.2 mg, 8 μ mol) was mixed with a DEF solution (0.5 mL) of Cu(OAc)₂·H₂O (3.2 mg, 16 μ mol). The mixture was stirred at 25 °C for 30 min. A small aliquot of the reaction mixture was taken and diluted with THF to prepare the sample for SEC analysis.

AzoMOP(P54₆). A DEF solution (1.0 mL) of **P54** (32 mg, 4 μ mol) and **Azo** (1.1 mg, 4 μ mol) was mixed with a DEF solution (0.5 mL) of Cu(OAc)₂·H₂O (1.6 mg, 8 μ mol). The mixture was stirred at 25 °C for 30 min. A small aliquot of the reaction mixture was taken and diluted with THF to prepare the sample for SEC analysis.

AzoMOP(P148₆). A DEF solution (1.0 mL) of **P148** (96 mg, 4 μ mol) and **Azo** (1.1 mg, 4 μ mol) was mixed with a DEF solution (0.5 mL) of Cu(OAc)₂·H₂O (1.6 mg, 8 μ mol). The mixture was stirred at 25 °C for 30 min. A small aliquot of the reaction mixture was taken and diluted with THF to prepare the sample for SEC analysis.

AzoMOP(P272₆). A DEF solution (1.0 mL) of **P272** (179 mg, 4 μ mol) and **Azo** (1.1 mg, 4 μ mol) was mixed with a DEF solution (0.5 mL) of Cu(OAc)₂·H₂O (1.6 mg, 8 μ mol). The mixture was stirred at 25 °C for 30 min. A small aliquot of the reaction mixture was taken and diluted with THF to prepare the sample for SEC analysis.

4. X-ray Crystallography

AzoMOP(Ip₆). Single crystal X-ray structure determination of **AzoMOP(Ip₆)** was performed at 93 K on a Rigaku model XtaLAB P200 equipped with a Dectris model PILATUS detector, VariMax Mo optic with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$), and a confocal monochromator. The structure was solved by direct methods and refined by full-matrix least-square cycles on Olex² software^{S2} using SHELXL-2014/7. Hydrogen atoms were attached at geometrically calculated positions and refined with isotropic thermal parameters. Due to the severe disorder, the guest solvent molecules were removed using the SQUEEZE routine of PLATON, then the structures were refined again using the data generated. The SQUEEZE routine of PLATON treated total 944 electrons that correspond to ~ 24 DEF molecules in the unit cell ($\sim 26\%$ in the total weight). The oxygen atoms of DEF coordinated to the dicopper paddlewheel clusters were not removed by SQUEEZE and the adjacent disordering electrons still remain, thus causing an A alert in the CheckCIF file.

Crystal data for **AzoMOP(Ip₆)**: C₁₅₆H₁₂₀Cu₁₂O₆₀ (+ solvent), $M_r = 3885.25$, triclinic, space group $P \bar{1}$, $a = 20.1292(4)$, $b = 21.7528(4)$, $c = 22.5286(4) \text{ \AA}$, $\alpha = 107.9914(18)$, $\beta = 99.9315(16)$, $\gamma = 108.1284(18)$. $V = 8513.8(3) \text{ \AA}^3$, $Z = 1$, $D_x = 0.758 \text{ g/cm}^3$, $F_{000} = 1968.0$, rotating anode X-ray, $\lambda = 0.71073 \text{ \AA}$, $T = 93(2) \text{ K}$, $\theta_{\max} = 30.664^\circ$, 42007 reflections collected, 52716 unique. Final $Goof = 1.064$, $R_1 = 0.0801$, $wR_2 = 0.2730$. CCDC-1554167.

Supplementary Figures

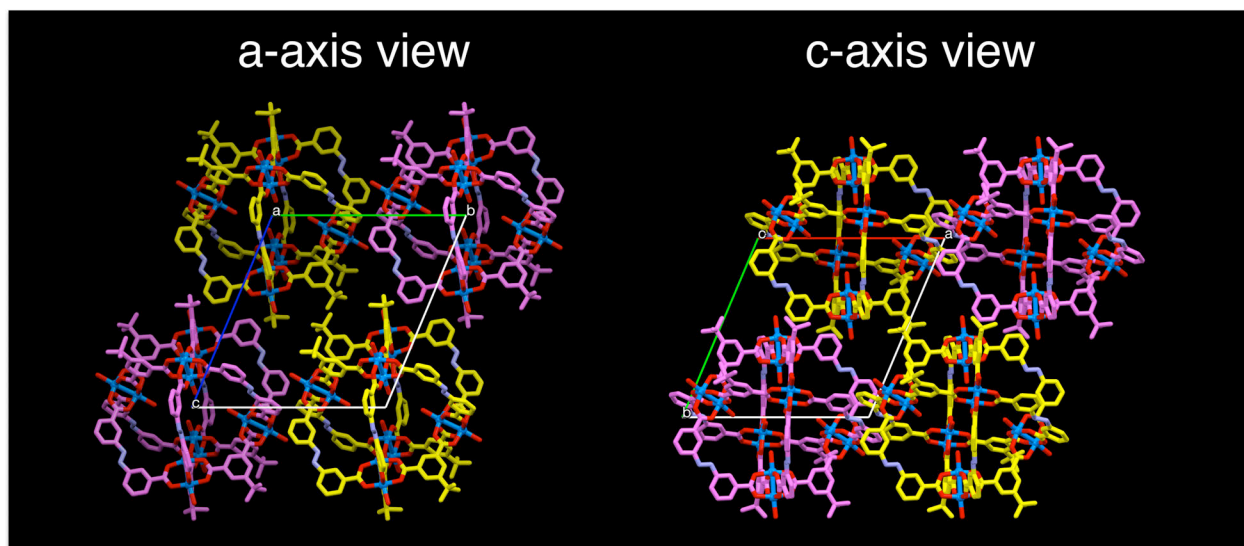


Figure S1. Single-crystal packing structure of AzoMOP(Ip₆).

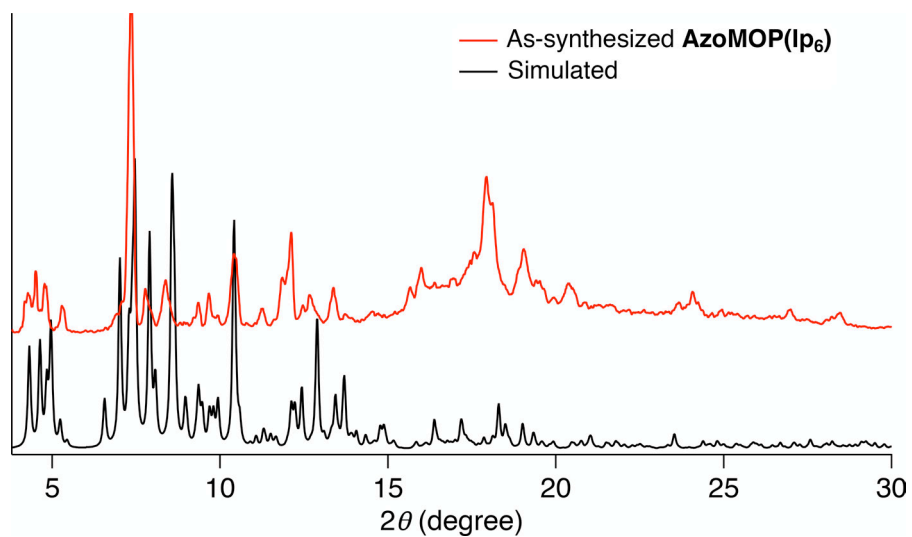


Figure S2. PXRD patterns of **AzoMOP(Ip₆)**: experimental pattern of as-synthesized powdery crystal (red) and the pattern simulated from single-crystal structure (black).

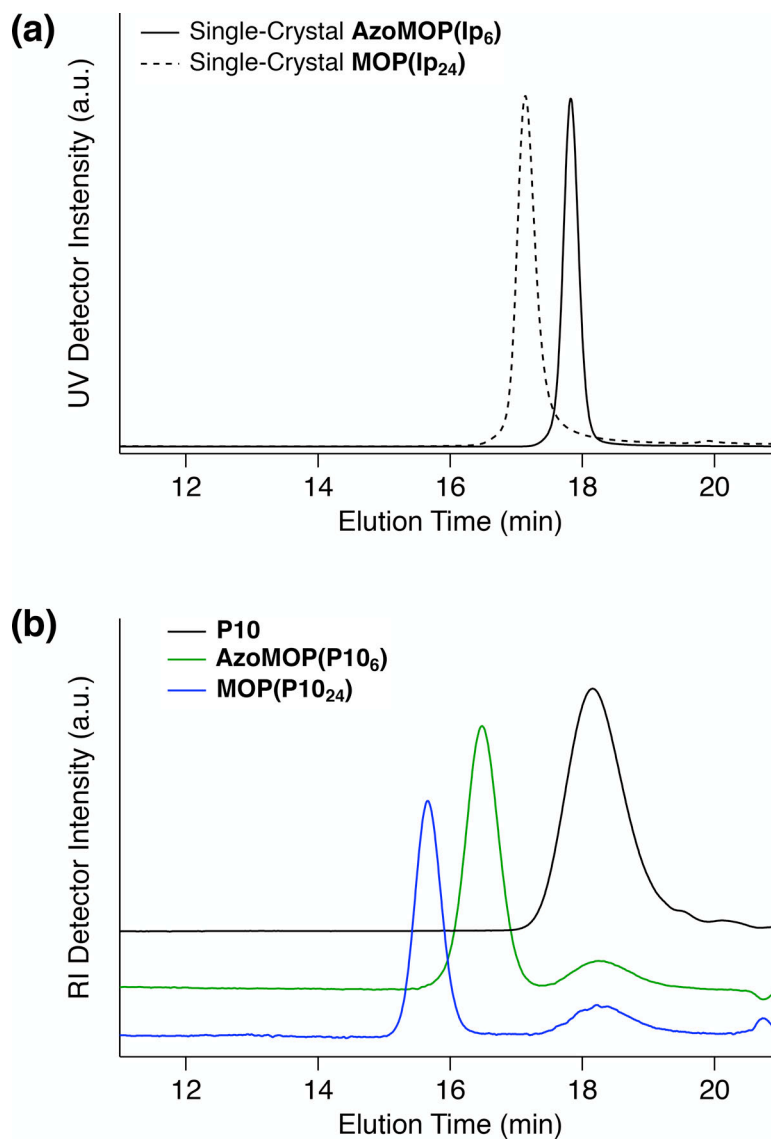


Figure S3. (a) SEC trace of **AzoMOP(Ip₆)**. A single crystal prepared through literature procedureS3 was picked up from the mother liquor, dissolved in THF, then measured by SEC. (b) SEC traces of **P10**, **AzoMOP(P10₆)**, and **MOP(P10₂₄)**.

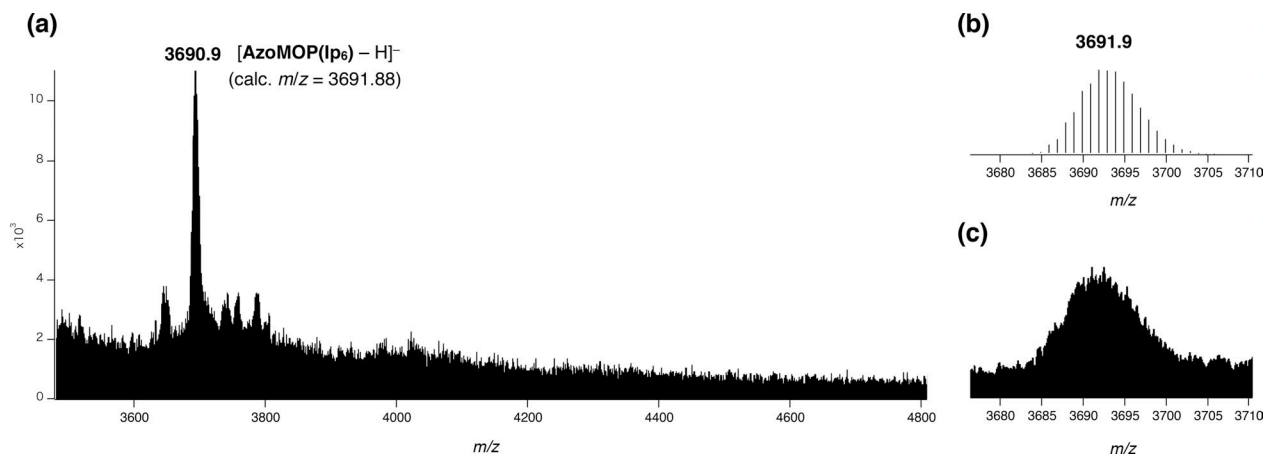


Figure S4. MALDI-TOF mass spectrum of **AzoMOP(Ip₆)** (negative mode, matrix: DCTB). (a) Wide band spectrum. (b) Simulated pattern. (c) Magnified spectrum of the major peak area.

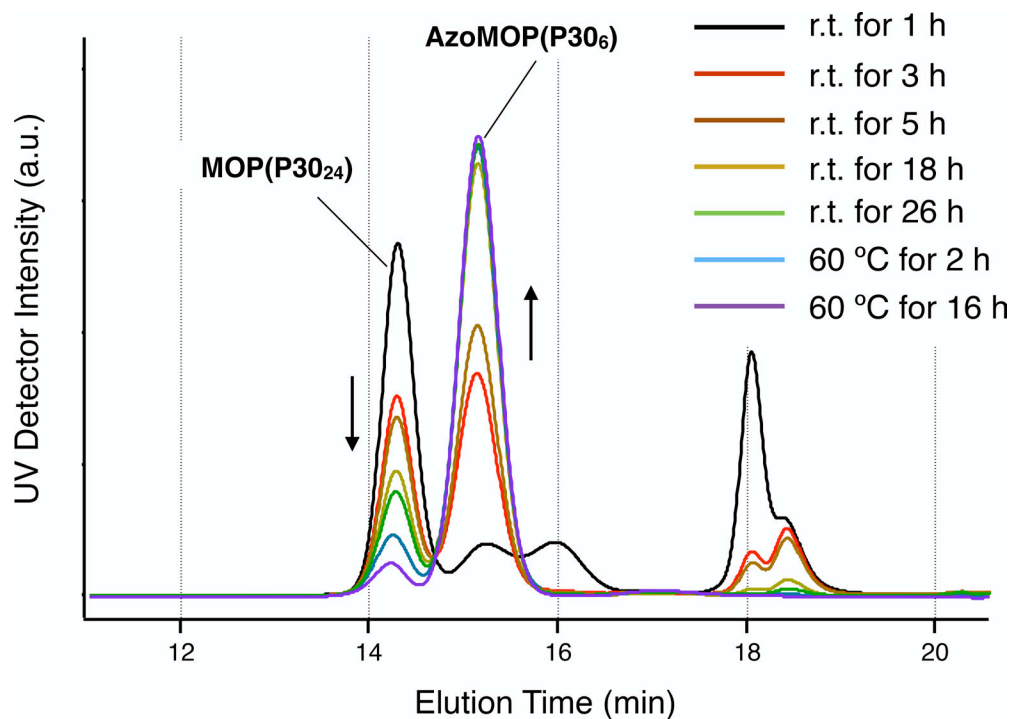


Figure S5. Time-course SEC traces of the self sorting process of **AzoMOP(P30₆)**. To the mixture of **P30** (5.3 mM) and Cu(OAc)₂·H₂O (10.7 mM) in DEF (1.48 mL) was added a solution of **Azo** (16.0 mM) in DEF (0.49 mL) to obtain clear green solution. After leaving at room temperature or at 60 °C for given hours, 20 μ L of the resulting mixture was collected and diluted with THF (1.0 mL), which was subsequently subjected to SEC analyses.

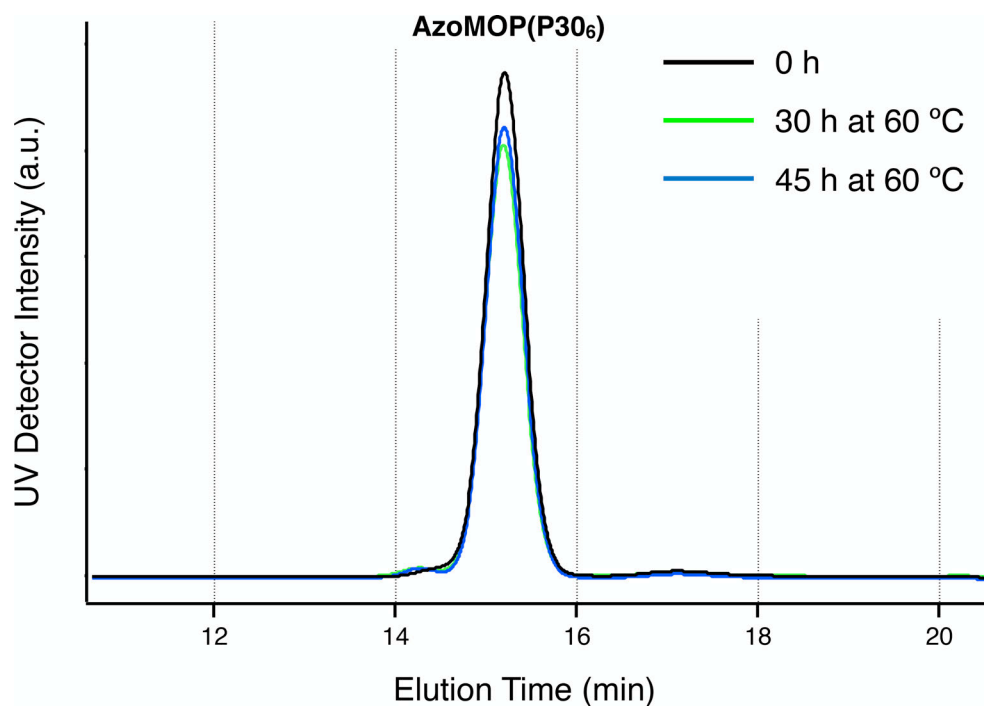


Figure S6. Time-course SEC traces of **AzoMOP(P30₆)**. To the mixture of **Azo** (8 mM) and **P30** (8 mM) in DEF (1.0 mL) was added a solution of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (16 mM) in DEF (1.0 mL) to obtain a clear green solution. After leaving at 60 °C for given hours, 20 μL of the resulting mixture was collected and diluted with THF (1.0 mL), which was subsequently subjected to SEC analyses.

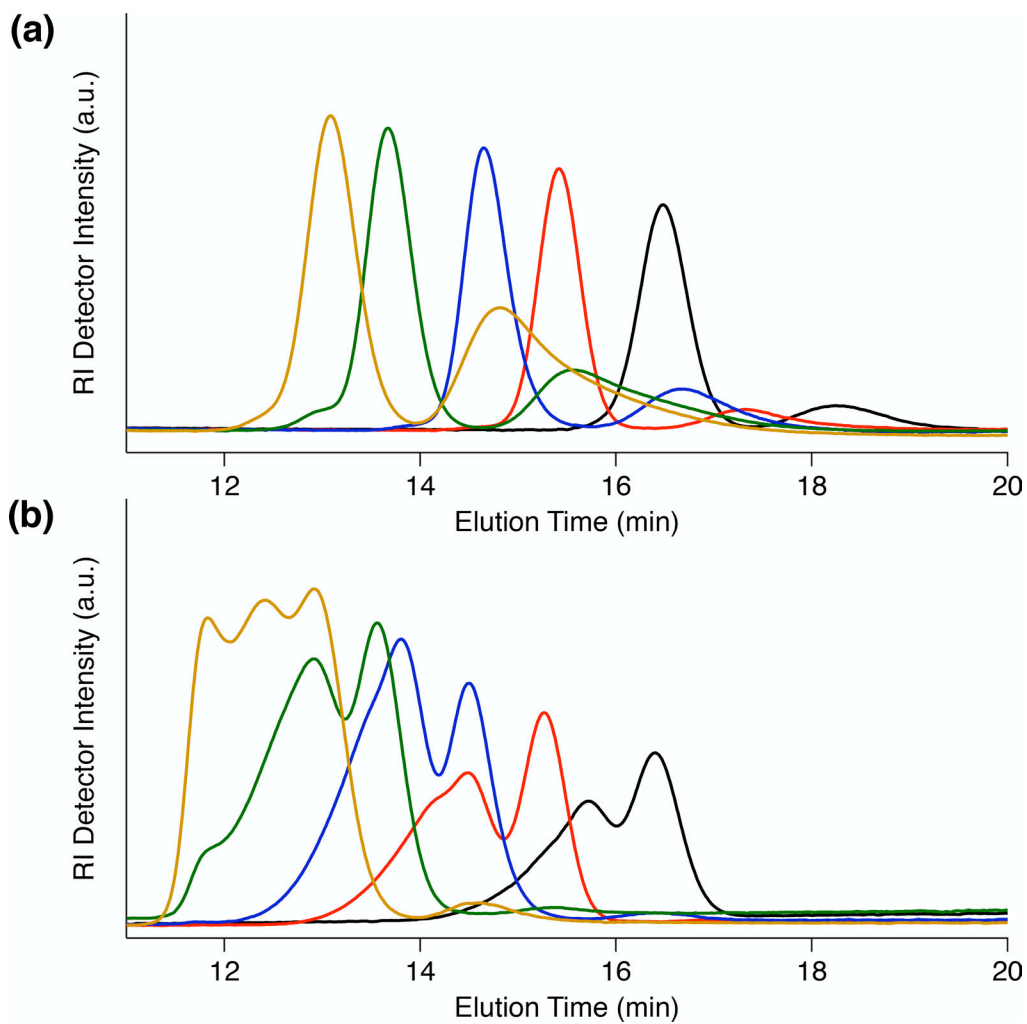


Figure S7. SEC traces of **AzoMOP(Pn_6)**, where $n = 10$ (black), 30 (red), 54 (blue), 148 (green), and 272 (yellow): (a) as-synthesized solution sample and (b) the sample after precipitation from methanol then dried in vacuum at 70 °C for 16 h.

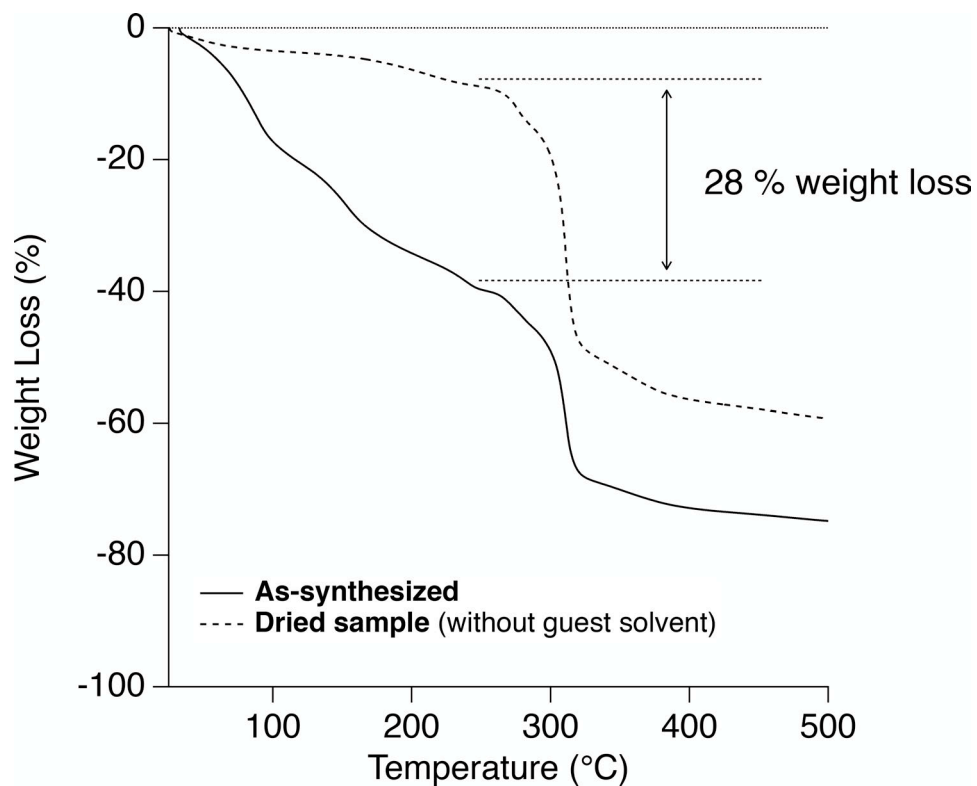


Figure S8. TGA curve of **AzoMOP(Ip₆)** (heating rate of 5 °C/min under N₂). TGA showed 28% weight loss of as-synthesized crystals at 250 °C, that corresponds to the release of the guest DEF solvent. The observed weight loss is consistent with the calculated value of 26wt% that is based on the SQUEEZE result on the single-crystal X-ray structure (See Section 4.).

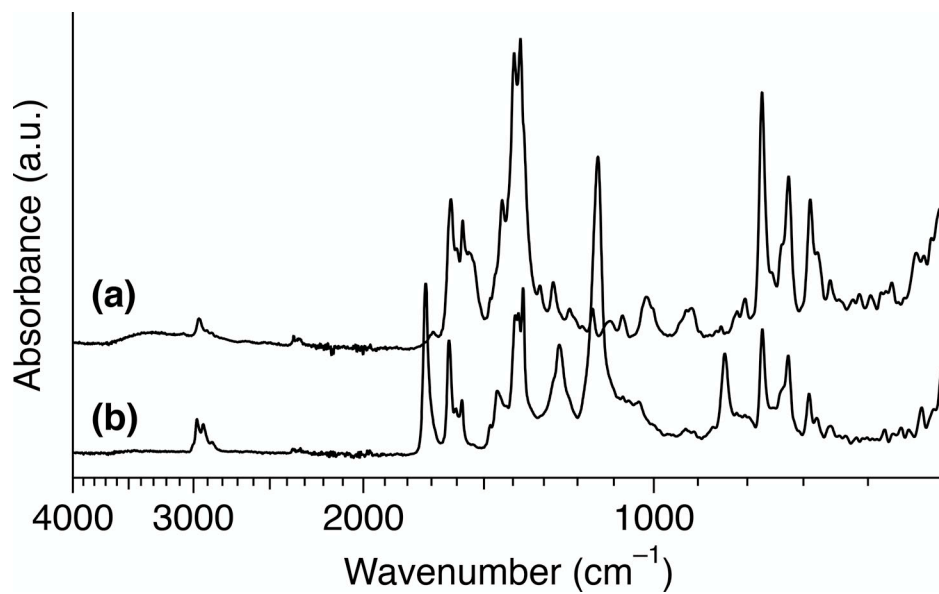


Figure S9. IR spectra of (a) **AzoMOP(Ip₆)** and (b) **AzoMOP(P10₆)**.

Supporting References

- (S1) N. Hosono, M. Gochomori, R. Matsuda, H. Sato and S. Kitagawa, *J. Am. Chem. Soc.*, 2016, **138**, 6525–6531.
- (S2) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339–341.