Electronic Supplementary Information

Paraffinic metal-organic polyhedral cages: Solution-processable porous modules exhibiting three-dimensional molecular order

1. Abbreviations
2. Materials and methods
3. Preparation of paraffinic ligands H$_2$L
4. Metal complexation reactions of paraffinic ligands H$_2$L
5. X-ray diffraction analysis of organized structure of MOP
6. Thermal analysis and discussion
7. References

page S2
page S2
page S3
page S8
page S11
page S14
page S16
1. Abbreviations


2. Materials and methods

All solvents, organic and inorganic reagents are commercially available, and were used without further purification. 5-Bromo-1,2,3-tris(dodecyloxy)benzene (I\textsubscript{a}), 5-bromo-1,2,3-tris(hexadecyloxy)benzene (I\textsubscript{b}), and dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalate (2) were synthesized according to previously reported procedures.\textsuperscript{1} Single crystals of Cu\textsubscript{2+}Ip\textsubscript{Bu}\textsubscript{2} (Ip\textsubscript{Bu}\textsuperscript{2}: 5-tert-butylisophthalate) were prepared according to previously reported procedures.\textsuperscript{2} Silica-gel column chromatography was performed using Wakogel silica gel C-200 (64–210 µm). NMR spectroscopic measurements were performed using JEOL model ECS-400 (400 MHz for \textsuperscript{1}H, 100 MHz for \textsuperscript{13}C) spectrometer. NMR spectra were calibrated as below; \textit{d}<sub>o</sub>-DMSO: CH\textsubscript{3}D\textsubscript{2}CD\textsubscript{3}SO = 2.50 ppm for \textsuperscript{1}H, (CD\textsubscript{3})\textsubscript{2}SO = 39.52 ppm for \textsuperscript{13}C; CDCl\textsubscript{3}: (CH\textsubscript{3})\textsubscript{4}Si = 0.00 ppm for \textsuperscript{1}H, (CH\textsubscript{3})\textsubscript{4}Si = 0.00 ppm for \textsuperscript{13}C. APCI-TOF mass spectra were recorded on a Bruker model microOTOF II. MALDI-TOF mass spectra were recorded on a Bruker model Ultraflex III using DCTB as a matrix. Analytical SEC was performed at 313 K on a Shimadzu model HPLC Prominence system with two polystyrene gel columns in series (Shodex KF-804L) 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. XRD analyses were carried out using a Rigaku SmartLab diffractometer (CuK\textalpha) equipped with a temperature-controlled sample stage and Dectoris model PILATUS 200 K detector. Synchrotron radiation (SR) XRD data for the structural analysis of MOP-a\textsubscript{DNA} were collected using a synchrotron X-ray beam (\lambda = 0.92 Å) of BL8S3 beam line at AichiSR, Japan, equipped with a temperature controller (Linkam Scientific Instrument) and R-AXIS IV++ detector. Variable-temperature SR-XRD data were also collected using a synchrotron X-ray beam (\lambda = 1.0 Å) of BL45XU at SPring-8, Japan, equipped with a customized Linkam Scientific Instrument temperature controller and Dectoris model PILATUS 3X 2M detector. Thermogravimetric analyses (TGA) were carried out using Rigaku model Thermo plus EVO. Differential scanning calorimetry (DSC) was carried out using Hitachi High-Tech Science Corp. model DSC7020 at the scanning rate of 10 °C/min.
3. Preparation of paraffinic ligands H$_2$L

**Scheme S1.** Synthetic routes for paraffinic ligands H$_2$L.

Reagents and conditions: (a) Pd(dppf)Cl$_2$, Na$_2$CO$_3$aq., THF, 80 °C, 16 h, (86%); (b) (i) KOHaq., THF, reflux, 16 h, (ii) HClaq., 0 °C, (quant.); (c) Pd(PPh$_3$)$_4$, Na$_2$CO$_3$aq., THF, 80 °C, 16 h, (59%); (d) (i) KOHaq., THF, reflux, 16 h, (ii) HClaq., 0 °C, (95%).
Dimethyl-3',4',5'-tris(dodecyloxy)-[1,1'-biphenyl]-3,5-dicarboxylate (3a)

5-Bromo-1,2,3-tris(dodecyloxy)benzene (1a) (2.00 g, 2.82 mmol, 1.0 eq), dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalate (2) (1.17 g, 3.67 mmol, 1.3 eq), 2 M Na₂CO₃aq. (14.1 mL, 28.2 mmol, 10.0 eq), Pd(dppf)Cl₂ (103 mg, 0.14 mmol, 0.05 eq), and THF (28 mL) were placed in a flask. The inner gas was replaced with N₂, and the mixture was stirred at 80 °C for 16 h. After cooling down to room temperature, the reaction mixture was filtered through celite, and the filtrate was extracted with EtOAc. The organic phase was washed with brine, dried over Na₂SO₄, and evaporated under reduced pressure to obtain a black solid. The crude product was purified by column chromatography (SiO₂, EtOAc/n-hexane = 5/95) to afford 3a (2.00 g, 2.43 mmol, 86%) as a pale yellow solid.

¹H NMR (400 MHz, CDCl₃, 298 K, Fig. S1): δ (ppm) = 8.62 (t, J = 1.4 Hz, 1H, Ar-H), 8.39 (d, J = 1.4 Hz, 2H, Ar-H), 6.79 (s, 2H, Ar-H), 4.05 (t, 4H, J = 6.7 Hz, CH₂), 4.00 (t, J = 6.7 Hz, 2H, CH₂), 3.98 (s, 6H, CH₃), 1.71–1.89 (m, 6H, CH₂), 1.44–1.54 (m, 6H, CH₂), 1.20–1.40 (m, 48H, C₆H₂), 0.88 (t, J = 6.7 Hz, 9H, CH₃).

¹³C NMR (100 MHz, CDCl₃, 298 K, Fig. S2): δ (ppm) = 166.3, 153.6, 142.3, 138.7, 134.4, 132.2, 131.0, 129.0, 106.1, 73.6, 69.5, 52.5, 32.0, 30.4, 29.8–29.3, 26.2, 26.1, 22.7, 14.1. (The signals of alkyl side chains are overlapped.)

APCI-TOF mass (positive): calcd. for [C₅₂H₈₆O₇ + H]⁺, m/z = 823.64; found m/z = 823.66.

Figure S1.¹H NMR spectrum of 3a (400 MHz, CDCl₃, 298 K).

Figure S2.¹³C NMR spectrum of 3a (100 MHz, CDCl₃, 298 K).
3',4',5'-Tris(dodecyloxy)-[1,1'-biphenyl]-3,5-dicarboxylic acid ($\text{H}_2\text{La}$)

To the mixture of 3a (2.55 g, 3.10 mmol) and THF (26 mL) was added 2 M KOHaq. (15.5 mL, 31.0 mmol), which was then refluxed for 16 h. After cooling down to 0 °C, the reaction mixture was acidified with conc.HClaq.. The resulting precipitate was collected by filtration, washed with water, and dried under reduced pressure at 60 °C for 2 days to afford $\text{H}_2\text{La}$ (2.47 g, 3.10 mmol, quant.) as a colorless solid.

$^1$H NMR (400 MHz, $d_6$-DMSO, 373 K, Fig. S3): $\delta$ (ppm) = 13.3–12.4 (br, 2H, COOH), 8.44 (br, 1H, Ar-H), 8.30 (br, 2H, Ar-H), 6.89 (s, 2H, Ar-H), 4.07 (t, $J = 6.4$ Hz, 4H, $\text{CH}_2$), 3.94 (t, $J = 6.4$ Hz, 2H, $\text{CH}_2$), 1.79–1.64 (m, 6H, $\text{CH}_2$), 1.52–1.41 (m, 6H, $\text{CH}_2$), 1.39–1.20 (m, 48H, $\text{CH}_2$), 0.85 (t, $J = 6.4$ Hz, 9H, $\text{CH}_3$).

$^{13}$C NMR (100 MHz, $d_6$-DMSO, 373 K, Fig. S4): $\delta$ (ppm) = 166.0, 152.8, 140.9, 138.2, 133.5, 131.7, 130.6, 128.0, 106.0, 72.2, 30.7, 29.4, 28.6–28.0, 25.1, 21.4, 13.1. (The signals of alkyl side chains are overlapped.)

APCI-TOF mass (negative): calcd. for [C$_{50}$H$_{82}$O$_7$-H], $m/z = 795.61$; found $m/z = 795.64$.

**Figure S3.** $^1$H NMR spectrum of $\text{H}_2\text{La}$ (400 MHz, $d_6$-DMSO, 373 K).

**Figure S4.** $^{13}$C NMR spectrum of $\text{H}_2\text{La}$ (100 MHz, $d_6$-DMSO, 373 K).
Dimethyl-3′,4′,5′-tris(hexadecyloxy)-[1,1′-biphenyl]-3,5-dicarboxylate (3b)

5-Bromo-1,2,3-tris(hexadecyloxy)benzene (1b) (3.00 g, 3.42 mmol, 1.0 eq), dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalate (2) (976 mg, 4.10 mmol, 1.2 eq), 2 M Na₂CO₃aq. (17.1 mL, 34.2 mmol, 10.0 eq), Pd(PPh₃)₄ (198 mg, 0.17 mmol, 0.05 eq), and THF (40 mL) were placed in a flask. The inner gas was replaced with N₂, and the mixture was stirred at 80 °C for 16 h. After cooling down to room temperature, the reaction mixture was filtered through celite, and the filtrate was extracted with EtOAc. The organic phase was washed with brine, dried over Na₂SO₄, and evaporated under reduced pressure to obtain a black solid. The crude product was purified by column chromatography (SiO₂, EtOAc/n-hexane = 1/30) to afford 3b (2.00 g, 2.02 mmol, 59%) as a colorless solid.

¹H NMR (400 MHz, CDCl₃, 298 K, Fig. S5): δ (ppm) = 8.62 (t, J = 1.4 Hz, 1H, Ar-H), 8.39 (d, J = 1.4 Hz, 2H, Ar-H), 6.79 (s, 2H, Ar-H), 4.05 (t, J = 6.7 Hz, 4H, CH₂), 4.00 (t, J = 6.7 Hz, 2H, CH₂), 3.98 (s, 6H, CH₃), 1.71–1.89 (m, 6H, CH₂), 1.44–1.54 (m, 6H, CH₂), 1.20–1.40 (m, 72H, CH₂), 0.88 (t, J = 6.7 Hz, 9H, CH₃).

¹³C NMR (100 MHz, CDCl₃, 298 K, Fig. S6): δ (ppm) = 166.3, 153.6, 142.3, 138.7, 134.4, 132.2, 131.0, 129.0, 106.1, 73.6, 69.5, 52.5, 32.0, 30.4, 29.8–29.3, 26.2, 26.1, 22.7, 14.1. (The signals of alkyl side chains are overlapped.)

APCI-TOF mass (positive): calcd. for [C₆₄H₁₁₀O₇ + H]⁺, m/z = 991.83; found m/z = 991.84.

Figure S5. ¹H NMR spectrum of 3b (400 MHz, CDCl₃, 298 K).

Figure S6. ¹³C NMR spectrum of 3b (100 MHz, d₆-DMSO, 298 K).
3',4',5'-Tris(hexadecyloxy)-[1,1'-biphenyl]-3,5-dicarboxylic acid (H₂Lb)

To the mixture of 3b (1.89 g, 1.91 mmol) and THF (19 mL) was added 2 M KOHaq. (9.6 mL, 19.1 mmol), which was then refluxed for 16 h. After cooling down to 0 °C, the reaction mixture was acidified with conc.HClaq.. The resulting precipitate was collected by filtration, washed with water, and dried under reduced pressure at 60 °C for 2 days to afford H₂Lb (1.74 g, 1.82 mmol, 95%) as a white solid.

^1H NMR (400 MHz, d₆-DMSO, 373 K, Fig. S7): δ (ppm) = 13.5–12.4 (br, 2H, COOH), 8.42 (br, J = 1.6 Hz, 1H, Ar-H), 8.28 (br, J = 1.6 Hz, 2H, Ar-H), 6.86 (s, 2H, Ar-H), 4.04 (t, 4H, J = 6.4 Hz, CH₂), 3.91 (br, J = 6.4 Hz, 2H, CH₂), 1.78–1.63 (m, 6H, CH₂), 1.53–1.39 (m, 6H, CH₂), 1.39–1.17 (m, 72H, CH₃), 0.84 (br, t, J = 6.4 Hz, 9H, CH₃).

^13C NMR (100 MHz, d₆-DMSO, 373 K, Fig. S8): δ (ppm) = 166.0, 152.8, 140.9, 138.2, 133.5, 131.7, 130.6, 128.0, 106.0, 72.2, 30.7, 29.4, 28.6–28.0, 25.1, 21.4, 13.1. (The signals of alkyl side chains are overlapped.)

APCI-TOF mass (negative): calcd. for [C₆₂H₁₀₆O₇-H]⁻, m/z = 961.79; found m/z = 961.78.

**Figure S7.** ^1H NMR spectrum of H₂Lb (400 MHz, d₆-DMSO, 373 K).

**Figure S8.** ^13C NMR spectrum of H₂Lb (100 MHz, d₆-DMSO, 373 K).
4. Metal complexation reactions of paraffinic ligands H$_2$L

4-1. Complexation reaction of H$_2$La and Cu(OAc)$_2$·H$_2$O

To a THF solution of H$_2$La (65 mM, 2.0 mL, 130 µmol, 1.0 eq) was added another THF solution of Cu(OAc)$_2$·H$_2$O (33 mM, 5.0 mL, 170 µmol, 1.3 eq). A small aliquot of the resulting mixture was collected and diluted with THF, which was subjected to SEC analysis (Fig. S9b). In order to isolate the product, the reaction mixture was poured into MeOH (25 mL). The product thus precipitated out was purified through reprecipitation method using a mixture of THF (2 mL)/MeOH (20 mL) as a poor solvent for three times, then dried under vacuum at room temperature to afford MOP-a (107.2 mg, 5.2 µmol, 96%) as a blue viscous material. The SEC trace and MALDI-TOF mass spectrum, and XRD profile of isolated MOP-a are shown in Fig. S9c, Fig. 3 (main text), and Fig. S12a, respectively.

![SEC traces](image)

**Figure S9.** SEC traces of a) H$_2$La, b) a 1:1.3 mixture of H$_2$La and Cu(OAc)$_2$·H$_2$O in THF, and c) isolated MOP-a. SEC charts are recorded at 313 K with a UV detector using THF as the eluent.
4-2. Complexation reaction of H$_2$Lb and Cu(OAc)$_2$·H$_2$O

H$_2$Lb (408.0 mg, 423 µmol, 1.0 eq) and Cu(OAc)$_2$·H$_2$O (90.36 mg, 453 µmol, 1.1 eq) were dissolved in THF (17.5 mL), then the mixture was subjected to sonication at room temperature. A small aliquot of the resulting mixture was collected and diluted with THF, which was subjected to SEC analysis (Fig. S10b). In order to isolate the product, the reaction mixture was poured into MeOH (20 mL). The product thus precipitated out was purified through reprecipitation method using THF and MeOH as a poor solvent for three times, successively washed with MeOH, and then dried under vacuum at room temperature to afford MOP-b (397.7 mg, 16.1 µmol, 91%) as a blue viscos material. The SEC trace, MALDI-TOF mass spectrum, and XRD profile of isolated MOP-b are shown in Fig. S10c, Fig. S11, and Fig. S12b, respectively.

![Figure S10. SEC traces of a) H$_2$Lb, b) a 1:1.1 mixture of H$_2$Lb and Cu(OAc)$_2$·H$_2$O in THF, and c) isolated MOP-b. SEC charts are recorded at 313 K with a UV detector using THF as the eluent.](image1)

![Figure S11. MALDI TOF-mass spectrum (negative) of isolated MOP-b (matrix: DCTB).](image2)
The XRD profiles of the as-synthesized samples of MOP-a and MOP-b showed respective single broad peaks around $q = 1.70$ and $1.55$ nm$^{-1}$ at room temperature, corresponding to $d$-spacings of 3.7 and 4.1 nm, respectively (Fig. S12). The observed $d$-spacing could correspond to the interdistances of the MOP core and depend on the length of the alkyl side chains. The peak broadening observed herein indicates the random arrangement of MOP cores in the dried bulk condition.$^{2b}$
5. X-ray diffraction analysis of organized structure of MOP

5-1. Preparation of MOP-a\textsubscript{DMA}

MOP-a (5.35 mg, 0.26 \(\mu\)mol) was placed in a microtube, which was annealed at 80 °C for about 10 min in the presence of DMA (6.5 \(\mu\)L) to obtain MOP-a\textsubscript{DMA} as a blue viscous material. XRD profiles of MOP-a\textsubscript{DMA} are shown in Fig. S13. The content of DMA dopant was calculated to be ca. 60 wt.\%.

5-2. Preparation of MOP-b\textsubscript{DMA}

MOP-b (2.88 mg, 0.12 \(\mu\)mol) was placed in a microtube, which was annealed at 80 °C for about 10 min in the presence of DMA (3.0 \(\mu\)L) to obtain MOP-b\textsubscript{DMA} as a blue viscous material. XRD profiles of MOP-b\textsubscript{DMA} are shown in Fig. S13. The content of DMA dopant was calculated to be ca. 50 wt.\%.

Figure S13. XRD profiles of (i) MOP-a\textsubscript{DMA} and (ii) MOP-b\textsubscript{DMA}; a) whole profiles and b) magnified profiles, and c) their postulated body-centered cubic packing (r.t., CuK\(\alpha\), \(\lambda = 1.541\) Å).
5-3. Synchrotron radiation XRD measurement of MOP-a<sub>DMA</sub>

MOP-a (4.87 mg, 0.24 µmol) was placed in a borosilicate capillary (diameter: 1.5 mm), which was annealed at 80 °C for about 10 min in the presence of DMA (4 µL) to obtain MOP-a<sub>DMA</sub> as a blue viscous material. The content of DMA dopant was calculated to be ca. 50 wt.%.

Synchrotron radiation (SR) XRD profile of resulting MOP-a<sub>DMA</sub> is given in Fig. S14a that shows many sharp diffraction peaks indexed into a bcc structure (Fig. S13c). Notably, upon removal of DMA from MOP-a<sub>DMA</sub> by heating at 413 K for a few minutes, the structure reorganized into an uncharacterized crystalline structure (Fig. S14b).

Figure S14. SR-XRD profiles of a) MOP-a<sub>DMA</sub>, and b) MOP-a<sub>DMA</sub> after removing DMA by heating at 413 K measured using synchrotron X-ray beam (313 K, λ = 0.92 Å) of AichiSR facility, Japan.

Table S1. Summary of experimental and theoretical Millar index of MOP-a<sub>DMA</sub> and MOP-b<sub>DMA</sub>.

| q (nm<sup>-1</sup>) | Millar index | 2σ<sup>d</sup>
|------------------|-------------|-------|
| Experimental<sup>a</sup> | 110 | 200 | 211 | 220 | 310 | 322 | 321 | 400 | 2σ<sup>d</sup>
| 1.89 | 2.66 | 3.27 | 3.75 | 4.20 | 4.64 | 4.96 | 5.35 |
| Theoretical<sup>c</sup> | 1.89 | 2.67 | 3.27 | 3.78 | 4.23 | 4.63 | 5.00 | 5.35 |
| Experimental<sup>b</sup> | 1.97 | 2.80 | 3.42 | 3.95 | 4.41 | 4.85 | 5.22 | 5.93 |
| 1.97 | 2.79 | 3.41 | 3.94 | 4.41 | 4.83 | 5.21 | 5.57 |
| Theoretical<sup>c</sup> | 1.97 | 2.80 | 3.42 | 3.95 | 4.41 | 4.85 | 5.22 | 5.93 |

<sup>a</sup> Measured at room temperature using CuKα X-ray beam (λ = 1.541 Å, Fig. S13a-ii).
<sup>b</sup> Measured at 313 K using a synchrotron X-ray beam on the BL8S3 beam line at AichiSR (λ = 0.92 Å, Fig. S14a).
<sup>c</sup> Calculated based on lattice constant as follow. MOP-b<sub>DMA</sub>: a = 4.5 nm, MOP-b<sub>DMA</sub>: a = 4.7 nm (Figure S13c).

\[ \sigma = \left( \frac{1}{n} \sum (q_{\text{theoretical}} - q_{\text{experimental}})^2 \right)^{1/2} \]
5-4. Film preparation

MOP-b (10.5 mg) was dissolved in n-hexane (500 µL) to give a clear blue solution. The resulting solution was slowly layered on DMA. After slow evaporation of the n-hexane layer at room temperature for 4 h, a blue colored self-supporting film was obtained at the interface. The resulted film was robust enough to be collected by tweezers. XRD profiles of the resulting film (Fig. S15b-ii) showed identical diffraction patterns to the bulk MOP-bDMA (Fig. S15b-i), suggesting the formation of a bcc-type regular ordering structure of the MOP core even in the film form.

**Figure S15.** a) Preparation of liquid crystalline film of MOP-bDMA via a solution-based process, b) XRD profiles of (i) MOP-bDMA and (ii) MOP-bDMA film (r.t., CuKα, λ = 1.541 Å).
6. Thermal analysis and discussion

Thermogravimetric analyses (TGA) were performed for dried MOP-a and MOP-b. The TGA profiles are shown in Figure S16. Both MOPs were stable up to 300 °C and significant weight losses corresponding to material decomposition were observed above ~320 °C.

![Figure S16. TGA profile of MOP-a and MOP-b under a N₂ flow (Heating rate: 5 °C/min)](image)

The differential scanning calorimetry (DSC) profiles were measured for dried and DMA-impregnated MOPs, namely, MOP-a, MOP-b, MOP-a_{DMA}, and MOP-b_{DMA} at the heating rate of 10 °C/min under a N₂ flow. The DSC profiles are summarized in Figure S17.

![Figure S17. DSC profiles of a) MOP-a and MOP-a_{DMA}, and b) MOP-b and MOP-b_{DMA}.](image)

In the DSC profile, DMA-impregnated MOP, MOP-a_{DMA}, showed exo/endothermic peaks at 50 °C upon cooling and 90 °C upon heating, respectively, which can be ascribed to LC phase transitions. On the other hand, MOP-a without DMA did not show any significant peak of phase transitions in the range of ~50 to 150 °C (scan rate: 10 °C/min). The small broadened peaks around ~25 °C can be due to the alkyl chain
crystallization. In contrast to MOP-a, both MOP-b and MOP-b\textsubscript{DMA} showed peaks around 5-10 °C upon cooling and 15-20 °C upon heating, which may correspond to the alkyl chain crystallization.

Both MOP-a and MOP-b without DMA did not show melting behavior at high temperature until decomposition. Variable-temperature (SR) XRD profiles of as-synthesized MOP-a and MOP-b without DMA showed no difference in the random assembling structure and at given temperatures (Fig. S18) while the alkyl chain crystallization/solidification might take place at lower temperature below 5-10 °C in MOP-b (Fig. S17). It should be noted that the crystallization of MOP-a (Fig. S14) was observed only when MOP-a\textsubscript{DMA} was slowly desiccated to be dried. This suggests that DMA plays an important role for the structuring of MOP-a into the three-dimensionally ordered phase.

**Figure S18.** Variable-temperature (SR) XRD profiles of as-synthesized a) MOP-a and b) MOP-b without DMA. Those profiles of MOP-a and MOP-b were collected using synchrotron radiation X-ray beam of BL45XU ($\lambda = 1.0$ Å) at SPring-8, Japan and monochromatic X-ray (CuKα) of Rigaku SmartLab diffractometer, respectively.
7. References
