Supporting Information for

Metal-Organic Cycle-Based Multistage Assemblies

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Additional $^1$H NMR spectra, $^{31}$P{$^1$H} NMR, electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) data, optical microscopy, DOSY NMR, ROESY, VT-NMR, and crystals data are provided in the Supporting Information.
1. Materials and Methods

All reagents were commercially available and used as supplied without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). NMR experiments were recorded on a spectrometer at room temperature. $^1$H NMR spectra were recorded in the designated solvents on a Varian Inova 400 MHz and a Bruker Neo 500 MHz spectrometers. $^{31}$P{${^1}$H} NMR spectra were recorded on a Varian Unity 300 MHz and a Bruker Neo 500 MHz spectrometers, and $^{31}$P{${^1}$H} NMR chemical shifts were referenced to an external unlocked sample of 85% H$_3$PO$_4$ ($\delta$ 0.0 ppm). Mass spectra were recorded on Waters TQD Acquity UPLC w/ Acquity H Class UPLC mass spectrometer.

**Synthesis of MOC 1.** A solution of tetra(4-pyridylphenyl)ethylene 4 (1.60 mg, 2.50 μmol) in 3 mL acetone was mixed with a solution of carboxylate ligand 5 (1.10 mg, 5.0 μmol) in 2 mL H$_2$O, the resulting mixture was heated and stirred at 50 °C for 5 min, the solution will be clear, then, the acetone solution of cis-Pt(PEt$_3$)$_2$(OTf)$_2$ 8 (7.30 mg, 10.0 μmol) was added into the mixture. Afterwards, the reaction mixture was allowed to slowly cool to room temperature, after stirring for 1 h, the solvent was removed by a N$_2$ flow. The resultant residue was dissolved in 1 mL acetone, and then filtered to remove insoluble materials. The filtrate was concentrated using N$_2$ flow to afford MOC 1, light yellow powder, yield: 92%. The $^1$H NMR spectrum of 1 is shown in Figure S1. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, room temperature) δ (ppm) 8.72 – 8.58 (m, 8H), 8.03 (s, 2H), 7.89 (d, $J$ = 7.8 Hz, 4H), 7.70 (d, $J$ = 5.8 Hz, 8H), 7.48 (d, $J$ = 8.6 Hz, 8H), 7.31 – 7.24 (m, 2H), 7.17 (d, $J$ = 7.9 Hz, 8H), 1.96 – 1.87 (m, 24H), 1.82 – 1.73 (m, 24H), 1.35 – 1.27 (m, 36H), 1.25 – 1.16 (m, 36H). The $^{31}$P {${^1}$H} NMR spectrum of 1 is shown in Figure S4. $^{31}$P{${^1}$H} NMR (121 MHz, CD$_2$Cl$_2$, room temperature) δ (ppm) -0.95, -6.73. The stoichiometry of discrete bicycles is further supported by the electrospray ionization time of flight mass spectrometry (ESI-TOF-MS) results (Figure S7). ESI-TOF-MS (m/z): calcd for [M–3OTf]$^{2+}$, (C$_{111}$H$_{150}$F$_2$N$_{11}$O$_{11}$P$_3$Pt$_4$S$^{2-}$, 947.6080 (100%); found, 947.6107.

MOC 2 was prepared from tetra(4-pyridylphenyl)ethylene compound 4 (1.60 mg, 2.50 μmol), carboxylate ligand 6 (1.10 mg, 5.0 μmol), and cis-Pt(PEt$_3$)$_2$(OTf)$_2$ 8 (7.60 mg, 10.0 μmol), analogously to MOC 1, light yellow powder (yield: 92%). The $^1$H NMR spectrum of 2 is shown in Figure S2. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, room temperature) δ 8.69 – 8.63 (m, 8H), 7.70 (d, $J$ = 5.9
Hz, 8H), 7.64 (s, 8H), 7.47 (d, J = 8.0 Hz, 8H), 7.17 (d, J = 8.0 Hz, 8H), 1.96 – 1.87 (m, 24H), 1.80 – 1.71 (m, 24H), 1.34 – 1.26 (m, 36H), 1.26 – 1.18 (m, 36H). The $^{31}$P $^1$H NMR spectrum of MOC 2 is shown in Figure S5. $^{31}$P $^1$H NMR (121 MHz, CD$_2$Cl$_2$, room temperature) δ (ppm) -1.40, -6.64. The stoichiometry of discrete bicycles is further supported by the electrospray ionization time of flight mass spectrometry (ESI-TOF-MS) results (Figure S8). ESI-TOF-MS (m/z): calcd for [M–3OTf]$^3+$, (C$_{111}$H$_{160}$F$_3$N$_4$O$_{11}$P$_8$Pt$_4$) $^3+$, 947.6080 (100%); found, 947.6107.

MOC 3 was prepared from tetra(4-pyridylphenyl)ethylene compound 4 (1.60 mg, 5.00 μmol), carboxylate ligand 6 (3.05 mg, 5.00 μmol), and cis-Pt(PEt$_3$)$_2$(OTf)$_2$ (7.30 mg, 10.0 μmol), analogously to MOC 1, light yellow powder, yield: 90%. The $^1$H NMR spectrum of 3 is shown in Figure S3. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, room temperature) δ (ppm) 8.79 – 8.61 (m, 8H), 7.76 – 7.64 (m, 12H), 7.55 (s, 4H), 7.47 (d, J = 8.1 Hz, 8H), 7.15 (d, J = 8.0 Hz, 8H), 4.51 (s, 4H), 3.72 – 3.61 (m, 50H), 3.57 – 3.53 (m, 6H), 3.36 (m, 6H), 1.97 – 1.86 (m, 24H), 1.79 – 1.71 (m, 24H), 1.35 – 1.26 (m, 36H), 1.26 – 1.17 (m, 36H). The $^{31}$P $^1$H NMR spectrum of MOC 3 is shown in Figure S6. $^{31}$P $^1$H NMR (121 MHz, CD$_2$Cl$_2$, room temperature) δ (ppm) -1.04, -6.78. The stoichiometry of discrete bicycles is further supported by the electrospray ionization time of flight mass spectrometry (ESI-TOF-MS) results (Figure S9). ESI-TOF-MS (m/z): calcd for [M–4OTf]$^4+$, (C$_{144}$H$_{226}$N$_6$O$_{26}$P$_8$Pt$_4$) $^4+$, 871.3236 (100%); found, 871.3246.

**Self-assembly of MOC 1-3 in DCM and dioxane/toluene/cyclohexane.** In a typical experiment, 100 μL MOC 1 solution (100 μM) in DCM and 400 μL DCM were mixed in a vial. Then, 500 μL dioxane/toluene/cyclohexane was added into the above solution. The solvent ratio can be adjust by changing the amount of DCM and dioxane/toluene/cyclohexane. For other MOCs (MOC 2 and MOC 3), a similar procedure was applied to prepare the assemblies.

**NMR experiments.** NMR spectra were recorded on a spectrometer at room temperature and were used to get insight into the interactions between MOCs in CD$_2$Cl$_2$/toluene-d$_8$ or CD$_2$Cl$_2$/cyclohexane-d$_{12}$ mixtures. Because of the signal of the assemblies (final concentration: 100 μM) could not be detected due to the insolubility with toluene-d$_8$ (or cyclohexane-d$_{12}$) contents greater than 40%. Thus, the signal could only be measured when the toluene-d$_8$ below 40%, and these samples were measured to provide information about the interactions among assemblies. For DOSY, ROESY, $^1$H-NMR, and $^{31}$P-NMR spectra were recorded on a spectrometer at room
temperature. In a typical experiment to prepare NMR samples in CD$_2$Cl$_2$/toluene-d$_8$, 100 μL MOC 1 solution (1mM) in CD$_2$Cl$_2$ and 700 μL CD$_2$Cl$_2$ were mixed in a vial. Then, 200 μL toluene-d$_8$ was slowly added into the above solution to afford the solution of MOC 1 with 20% toluene-d$_8$. For the solution of MOC 1 with toluene-d$_8$ content beyond 20% toluene-d$_8$, sediment appears rapidly, which is not suitable for the NMR characterization. In a typical experiment to prepare NMR samples in CD$_2$Cl$_2$/cyclohexane-d$_{12}$, 100 μL MOC 1 (1mM) in CD$_2$Cl$_2$ and 700 μL CD$_2$Cl$_2$ were mixed in a vial, then, 400 μL cyclohexane-d$_{12}$ was slowly added into the above solution to afford the solution of MOC 1 with 20% cyclohexane-d$_{12}$. For the solution of MOC 1 with cyclohexane-d$_{12}$ content beyond 20% cyclohexane-d$_{12}$, sediment appears rapidly, which is not suitable for the NMR characterization.

**EM experiments.** Transmission electron microscopy investigations were performed on a JEM-2100EX instrument. For TEM, dispersions of the assemblies were dried on carbon-coated copper support grids. HRTEM images were obtained using a Tecnai G2 F30 S-TWIN instrument. A Zeiss Supra55 field-emission scanning electron microscope was used to investigate the assemblies. For SEM, dispersions of the assemblies were dried on silicon wafers. The number of samples used in those histograms is around 150-200.

**Optical microscopy (OM) experiments.** OM images were obtained using a Leica Microsystems DM LM/P instrument. For OM, dispersions of aggregates were dried onto glass slides for observation.

**Crystal Structure Determination.** Single-crystal X-ray diffraction data were collected using a Nonius Kappa CCD diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å) and a BRUKER APEXII CCD. The APEX3$^3$ software suite was used to manage data collection, integration, absorption correction via the multiscan method (SADABS$^3$), structure determination via direct methods (SHELXT$^3$) and model refinement (SHELXL$^4$). The crystals were cooled to 103(2) K throughout the data collection process. All nonhydrogen atoms were refined anisotropically with all hydrogen atoms ideally constrained to their carriers. The positional disorder found in triethylphosphine groups and triflate anions was modeled using the PART command as two-part disorder with appropriate distance and angle restraints as well as restraints on atomic displacement parameters. Platon Squeeze$^5$ was used to account for the electron density in solvent channels that were heavily disordered and could not be modeled. The largest peak in
the final electron density calculation was 3.805 e/Å³, and the largest hole was -3.085 e/Å³, which are both near the Pt atoms, have been examined carefully and cannot be explained by further modeling. The crystal structure was deposited with the Cambridge Crystallographic Data Centre (CCDC 2113310, 2113311-2113312).

1. APEX3. Ver. 2017.3-0. Bruker AXS Inc., Madison, Wisconsin, USA, 2017.
2. L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, J. Appl. Cryst. 2015, 48, 3-10.
3. G. Sheldrick, Acta Cryst. A 2015, 71, 3-8.
4. G. Sheldrick, Acta Cryst. C 2015, 71, 3-8.
5. A. Spek, Acta Cryst. C 2015, 71, 36, 7-13.
2. Characterization

2.1 $^1$H NMR spectrum of MOC 1

Figure S1. $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$) recorded for MOC 1.

2.2 $^1$H NMR spectrum of MOC 2

Figure S2. $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$) recorded for MOC 2.
2.3 ^1^H NMR spectrum of MOC 3

![Image of MOC 3's NMR spectrum]

**Figure S3.** ^1^H NMR spectrum (400 MHz, CD$_2$Cl$_2$) recorded for MOC 3.

2.4 ^3^1^P{^1^H} NMR spectrum of MOC 1

![Image of MOC 1's NMR spectrum]

**Figure S4.** ^3^1^P{^1^H}NMR spectrum (121.4 MHz, CD$_2$Cl$_2$) recorded for MOC 1.
2.5 $^{31}$P{$^1$H} NMR spectrum of MOC 2

![Diagram](image1)

**Figure S5.** $^{31}$P{$^1$H} NMR spectrum (121.4 MHz, CD$_2$Cl$_2$) recorded for MOC 2.

2.6 $^{31}$P{$^1$H} NMR spectrum of MOC 3

![Diagram](image2)

**Figure S6.** $^{31}$P{$^1$H} NMR spectrum (121.4 MHz, CD$_2$Cl$_2$) recorded for MOC 3.
2.7 ESI-TOF-MS spectrum of MOC 1

![ESI-TOF-MS spectrum of MOC 1](image)

Figure S7. ESI-TOF-MS spectrum of MOC 1.

2.8 ESI-TOF-MS spectrum of MOC 2

![ESI-TOF-MS spectrum of MOC 2](image)

Figure S8. ESI-TOF-MS spectrum of MOC 2.
2.9 ESI-TOF-MS spectrum of MOC 3

Figure S9. ESI-TOF-MS spectrum of MOC 3.
Table S1 Crystallographic Data for MOCs 1-3 (M1-3).

| Compound | M1 | M2 | M3 |
|----------|----|----|----|
| Empirical formula | $C_{16}H_{10}F_2N_2O_2P_2P_0S_2$ | $C_{16}H_{10}F_2N_2O_2P_2P_0S_2$ | $C_{16}H_{10}F_2N_2O_2P_2P_0S_2$ |
| Formula weight | 3290.81 | 3147.74 | 2080.14 |
| Temperature/K | 100.13 | 100(2) | 100(2) |
| Wavelength | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | triclinic | triclinic | triclinic |
| Space group | P-1 | C2/c | P-1 |
| Unit cell dimensions | a=15.562(5) Å, b=18.2238(5) Å, c=26.330(3) Å | a=18.667(3) Å, b=18.4582(18) Å, c=113.347(3) Å | a=18.043(2) Å, b=18.536(2) Å, c=108.144(2) Å |
| Volume | 7750.9(4) Å$^3$ | 14894(3) Å$^3$ | 5537.0(11) Å$^3$ |
| Z | 2 | 4 | 1 |
| Density(calculated) | 1.41 | 1.401 | 0.953 |
| Absorption coefficient | 3.803 | 3.936 | 2.665 |
| F(000) | 3272 | 6212 | 1182 |
| Crystal size | 0.32 × 0.15 × 0.1 | 0.11 × 0.07 × 0.045 | 0.28 × 0.2 × 0.17 |
| Theta range for data collection | 2.906 to 57.746 | 3.342 to 41.844 | 2.362 to 58.103 |
| Index ranges | -20 ≤ h ≤ 20, -32 ≤ k ≤ 22, -32 ≤ l ≤ 32 | -27 ≤ h ≤ 27, -18 ≤ k ≤ 18, -31 ≤ l ≤ 30 | -25 ≤ h ≤ 25, -25 ≤ k ≤ 25, -25 ≤ l ≤ 25 |
| Reflections collected | 97230 | 41705 | 178706 |
| Independent reflections | 35146 [R(int) = 0.0447, R(int) = 0.0193] | 7805 [R(int) = 0.1278, R(int) = 0.0993] | 50954 [R(int) = 0.6446, R(int) = 0.0465] |
| Completeness to theta | 0.9524° [69.8%] | 0.9524° [69.5%] | 0.7524° [60.6%] |
| Absorption correction | multi-scan | multi-scan | none |
| Refinement method | Full-matrix least-squares on F$^2$ | Full-matrix least-squares on F$^2$ | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters | 31586/6/1510 | 7805/511/771 | 30954/318/770 |
| Goodness-of-fit on F$^2$ | 0.945 | 1.033 | 1.745 |
| Final R indexes [I>2sigma(I)] | R$_p$ = 0.0410, wR$_p$ = 0.1003 | R$_p$ = 0.0541, wR$_p$ = 0.1256 | R$_p$ = 0.1161, wR$_p$ = 0.3673 |
| R indexes (all data) | R$_p$ = 0.0697, wR$_p$ = 0.1130 | R$_p$ = 0.1037, wR$_p$ = 0.1459 | R$_p$ = 0.1506, wR$_p$ = 0.4204 |
| Largest diff. peak and hole | 3.06/1.51 | 1.77/-0.79 | 10.45/-2.89 |
2.10 Images of MOC 1 based linear aggregates obtained at TOL content of 50%

Figure S10. (left) Optical microscopic and (right) SEM images of MOC 1 based linear aggregates obtained at TOL content of 50% (10 μM).

2.11 Images of MOC 2 based obtained at TOL content of 50%

Figure S11. SEM images of MOC 2 based aggregates obtained at TOL content of 50%(well-defined polygons/polyhedron were labeled as red color) (10 μM).

2.12 Images of MOC 1 based linear aggregates obtained at TOL content of 60%

Figure S12. (left) Optical microscopic and (right) SEM images of MOC 1 based linear aggregates obtained at TOL content of 60% (10 μM).
2.13 Images of MOC 1 based linear aggregates obtained at TOL content of 80%

![Images of MOC 1 based linear aggregates obtained at TOL content of 80%](image1)

**Figure S13.** (left) Optical microscopic and (right) SEM images of MOC 1 based linear aggregates obtained at TOL content of 80% (10 μM).

2.14 Images of MOC 2 based aggregates obtained at TOL content of 60%

![Images of MOC 2 based aggregates obtained at TOL content of 60%](image2)

**Figure S14.** SEM images of MOC 2 based aggregates obtained at TOL content of 60% (well-defined polygons were labeled as red color) (10 μM).

2.15 Images of MOC 2 based aggregates obtained at TOL content of 80%

![Images of MOC 2 based aggregates obtained at TOL content of 80%](image3)

**Figure S15.** SEM images of MOC 2 based aggregates obtained at TOL content of 80% (well-defined polygons were labeled as red color) (10 μM).
2.16 X-ray single-crystal structure of the atomic distances and dihedral angles in MOCs 1-3.

Figure S16. X-ray single-crystal structure of the distances between benzene rings, pyridine rings, platinum, and phosphorous atoms in (a) MOC 1, (b) MOC 3 (OEG moieties are omitted because of the disorder in crystal structures), and (c) MOC 2; dihedral angles between benzene rings and pyridine rings in (d) MOC 1, (e) MOC 3, (f) MOC 2.

The substituent effects on the NBBs are influenced by the bimetallacycle structure difference based on the atomic distance and the dihedral angle. Figure S16 displays the symmetry difference of three bimetallacycles dependent on the atomic distances, along the diagonal line, in MOC1 (Figure S16a, pink) and MOC3 (Figure S16b, green); the same color in the background shows the same distances between atoms on both sides. These similarities indicate that the OEG modified ligand (7) does not change the symmetry feature of MOC1 in terms of atomic distances. However, the symmetry of MOC2 (along the diagonal line) changes after using p-dicarboxylate (instead of m-dicarboxylate) as the ligand, and the four background colors in Figure S16c display the asymmetry of the atomic distances in MOC2. Specifically, MOC1 exhibits a symmetrical structure in the atom distances; above the diagonal line in Figure S16a. The C-C distances between the benzene rings of the TPPE moiety are 7.556 Å (length) and 5.409 Å (width). The N-N distances between the pyridines are 15.193 Å (length) and 9.258 Å (width). The Pt-Pt distances between the corners are 19.048 Å (length) and 11.912 Å (width). For MOC3, the atomic distance symmetry along the diagonal remains the same but changes the C-C, N-N, Pt-Pt, and P-P distances. The length between the benzenes rings in TPPE decreases to 7.498 Å, whereas the width increases to 5.493 Å. The N-N length increases to 15.234 Å, and the width decreases to 9.079 Å. In MOC2, none of the C-C, N-N, Pt-Pt, or P-P distances remained the same. For example, the C-C distances are 7.217 Å and 7.292 Å; the N-N distances are 14.819 Å and 14.887 Å; the Pt-Pt distances are 18.766 Å and 18.758 Å; and the P-P distances are 17.631 Å and 17.461 Å. In addition to the atomic distance symmetry difference caused by the substituent effects, the dihedral angles between the benzene rings and pyridine rings show similarities in MOC1 and MOC3. The dihedral angles \( \angle B1-Py1= \angle B4-Py4= 22.96^\circ \) and \( \angle B2-Py2= \angle B3-Py3= 21.62^\circ \) in MOC1 and the dihedral angles \( \angle B1-Py1= \angle B4-Py4= 35.28^\circ \)(Part A) or \( 32.05^\circ \)(Part B) (Figure S16d) and \( \angle B2-Py2= \angle B3-Py3= 26.55^\circ \)(Part A) or \( 32.78^\circ \)(Part B) in MOC3 are shown in the Figure S16e. However, for structure MOC2, the four dihedral angles between the benzene rings and pyridine rings are \( 42.67^\circ \) (\( \angle B1-Py1 \)), \( 21.44^\circ \) (\( \angle B2-Py2 \)), \( 37.60^\circ \) (\( \angle B3-Py3 \)), and \( 25.16^\circ \) (\( \angle B4-Py4 \)) respectively. As shown in Figure S16f, the asymmetrical conformation of TPPE can be observed (left: small portion; right: big portion).
2.17 Images of MOC1 based linear aggregates obtained at cyclohexane content of 50%

![Image of MOC1 based linear aggregates obtained at cyclohexane content of 50%](image1.png)

**Figure S17.** (left) Optical microscopic and (right) SEM images of MOC1 based linear aggregates obtained at cyclohexane content of 50% (10 µM).

2.18 Images of MOC1 based linear aggregates obtained at cyclohexane content of 60%

![Image of MOC1 based linear aggregates obtained at cyclohexane content of 60%](image2.png)

**Figure S18.** (left) Optical microscopic and (right) SEM images of MOC1 based linear aggregates obtained at cyclohexane content of 60% (10 µM).

2.19 Images of MOC1 based linear aggregates obtained at cyclohexane content of 80%

![Image of MOC1 based linear aggregates obtained at cyclohexane content of 80%](image3.png)

**Figure S19.** (left) Optical microscopic and (right) SEM images of MOC1 based linear aggregates obtained at cyclohexane content of 80% (10 µM).
2.20 Images of MOC2 based linear aggregates obtained at cyclohexane content of 50%

![Optical microscopic and SEM images of MOC2 based linear aggregates obtained at cyclohexane content of 50%](image1)

**Figure S20.** (left) Optical microscopic and (right) SEM images of MOC2 based linear aggregates obtained at cyclohexane content of 50% (10 μM).

2.21 Images of MOC2 based linear aggregates obtained at cyclohexane content of 60%

![Optical microscopic and SEM images of MOC2 based linear aggregates obtained at cyclohexane content of 60%](image2)

**Figure S21.** (left) Optical microscopic and (right) SEM images of MOC2 based linear aggregates obtained at cyclohexane content of 60% (10 μM).

2.22 Images of MOC2 based linear aggregates obtained at cyclohexane content of 80%

![Optical microscopic and SEM images of MOC2 based linear aggregates obtained at cyclohexane content of 80%](image3)

**Figure S22.** (left) Optical microscopic and (right) SEM images of MOC2 based linear aggregates obtained at cyclohexane content of 80% (10 μM).
2.23 Images of MOC 1 based linear aggregates obtained at dioxane content of 50% 

Figure S23. (left) Optical microscopic and (right) SEM images of MOC 1 based linear aggregates obtained at dioxane content of 50% (10 µM).

2.24 Images of MOC 1 based linear aggregates obtained at dioxane content of 60% 

Figure S24. (left) Optical microscopic and (right) SEM images of MOC 1 based linear aggregates obtained at dioxane content of 60% (10 µM).

2.25 Images of MOC 1 based linear aggregates obtained at dioxane content of 80% 

Figure S25. (left) Optical microscopic and (right) SEM images of MOC 1 based linear aggregates obtained at dioxane content of 80% (10 µM).
2.26 SEM images of MOC 1 based linear aggregates and MOC 2 based non-linear aggregates

![SEM images](image)

**Figure S26.** Optical microscopic images of (a) MOC 1 based linear aggregates and (b) MOC 2 based non-linear aggregates in DCM/EA (1: 4) (10 μM).

2.27 Enlarged $^1$H-NMR of MOC 1 in CD$_2$Cl$_2$/cyclohexane-d$_{12}$ at the temperature from 15-30 °C

![Enlarged $^1$H-NMR](image)

**Figure S27.** Enlarged $^1$H-NMR of MOC 1 in CD$_2$Cl$_2$/cyclohexane-d$_{12}$ at the temperature (a-c) from 15-30 °C (CD$_2$Cl$_2$/cyclohexane-d$_{12}$ =8 : 2, 100 μM) and (d) restored to 15 °C.
2.28 Enlarged $^1$H-NMR of MOC 1 in CD$_2$Cl$_2$/toluene-d$_8$ at the temperature from 15-30 °C

![NMR Spectra](image)

Figure S28. Enlarged $^1$H-NMR of MOC 1 in CD$_2$Cl$_2$/toluene-d$_8$ at the temperature (a-c) from 15-30 °C (CD$_2$Cl$_2$/toluene-d$_8$ = 8 : 2, 100 μM) and (d) restored to 15 °C.

2.29 Enlarged $^1$H-NMR of MOC 2 in CD$_2$Cl$_2$/cyclohexane-d$_{12}$ at the temperature from 15-30 °C

![NMR Spectra](image)

Figure S29. Enlarged $^1$H-NMR of MOC 2 in CD$_2$Cl$_2$/cyclohexane-d$_{12}$ at the temperature (a-c) from 15-30 °C (CD$_2$Cl$_2$/cyclohexane-d$_{12}$ = 8 : 2, 100 μM).
2.30 Enlarged $^1$H-NMR of MOC 2 in CD$_2$Cl$_2$/toluene-d$_8$ at the temperature from 16-30 °C

Figure S30. Enlarged $^1$H-NMR of MOC 2 in CD$_2$Cl$_2$/toluene-d$_8$ at the temperature from (a-c) 16-30 °C (CD$_2$Cl$_2$/toluene-d$_8$ = 8 : 2, 100 µM) and (d) restored to 15 °C.
2. X-ray single-crystal structure of hydrogen bond distribution of MOCs 1 and 2

As shown in Figure S30 (Table S2-4), several hydrogen bonds (labelled as different colours), such as PEt₃-OTf (blue), PEt₃-COO⁻ (pink), and OTf-Py (light purple), can be found in MOC 1 (Figure S30a). However, for MOC 2, in addition to the same interactions as in MOC 1, three more hydrogen bonds between Py-COO⁻ (yellow), Py-PEt₃ (green), and benzene ring and OTf (light green) are observed (Figure 30b-d). These observations are consistent with the VT-NMR results, in which MOC 2 shows a lower shift than MOC 1 when changing the temperature. By comparing the weak interaction distributions in MOCs 1-2, it was shown that COO⁻-PEt₃, OTf-PEt₃, and OTf-Py existed in both MOC 1 and MOC 2. In MOC 2, these three interactions still acted as the main influence, whereas more interactions, such as pyridine rings and COO⁻, PEt₃ and benzene rings, and OTf and pyridine rings, were found. These results further indicate that bimetalacycle MOC 2 is more hindered in the assembly process than MOC 1. In addition, more H-bonds in MOC 2 than MOC 1 were observed at the intramolecular level as well, and more hindrances for MOC 2 were also found at the intermolecular level (Figure S30e-f). Figure S30e displays three hydrogen bonds between carboxylate oxygen (O2B) and pyridine (H25), carboxylate oxygen (O2B/O3B) and CH₃(PEt₃) (H24B and H37B), including O2B-H25 (green), O2B-H24, O3B-H37B (purple) between layers of MOC 1, which promotes the formation of layered arrangements in parallel structures. Whereas the six hydrogen bonds formed by carboxylate oxygen and pyridine/benzene rings, in particular, (H12-O2, H12'-O2', H13-O2, H22-O3, H22'-O3') involve bonds to pyridine rings participate (dark green), and only H31'-O3' is based on the pyridine and benzene rings (light green). The association of these interlayer bonds strengthens the suprastructure, leading to the formation of a more stable staggered stacking system.
Table S2 Selected hydrogen bond parameters (Å) for MOC 1

| D–H···A   | D–H (Å) | H···A (Å) | D···A (Å) | ∠D–H···A(°) |
|-----------|---------|-----------|-----------|-------------|
| C12–H12···O5 | 0.95    | 2.39      | 3.16(3)   | 138         |
| C13–H13···O6 | 0.95    | 2.42      | 3.28(3)   | 151         |
| C22–H22···O9 | 0.95    | 2.5       | 3.05(6)   | 117         |
| C24–H24···O2B | 0.95   | 2.32      | 2.98(7)   | 126         |
| C24–H24···O2A | 0.95   | 2.39      | 3.05(7)   | 126         |
| C25–H25···O2B | 0.95   | 2.59      | 3.12(10)  | 115         |
| C37–H37B···O3B | 0.98   | 2.48      | 3.15(10)  | 125         |
| C37–H37B···O3A | 0.98   | 2.59      | 3.25(12)  | 125         |
| C44–H44A···O7 | 0.99    | 2.54      | 3.34(3)   | 138         |
| C44–H44B···O1 | 0.99    | 2.45      | 2.93(3)   | 110         |
| C47B–H47E···F1 | 0.98    | 2.24      | 3.22(4)   | 174         |
| C47B–H47F···O3B | 0.98    | 2.42      | 3.36(13)  | 161         |
| C48B–H48D···O4 | 0.99    | 2.50      | 2.94(3)   | 106         |
| C50B–H50C···O10 | 0.99    | 2.23      | 3.15(5)   | 153         |
| C50B–H50C···F6 | 0.99    | 2.35      | 3.16(5)   | 138         |
Table S3  Selected hydrogen bond parameters (Å) for MOC 2

| D-H···A  | D-H (Å) | H···A (Å) | D···A (Å) | ∠D-H···A (°) |
|---------|---------|----------|----------|-------------|
| C9-H9'···O13 | 0.95    | 2.41     | 3.274 (6) | 151         |
| C9'-H9···O16  | 0.95    | 2.29     | 3.235 (7) | 171         |
| C10-H10···O12 | 0.95    | 2.55     | 3.399 (7) | 149         |
| C12-H12···O2  | 0.95    | 2.32     | 3.054 (6) | 134         |
| C12'-H12···O2' | 0.95    | 2.27     | 3.210 (6) | 172         |
| C13-H13···O2  | 0.95    | 2.51     | 3.044 (7) | 116         |
| C13'-H13'···O2' | 0.95   | 2.59     | 3.138 (6) | 117         |
| C21-H21···O3  | 0.95    | 2.59     | 3.128 (6) | 121         |
| C21'-H21'···O3' | 0.95    | 2.59     | 3.104 (6) | 115         |
| C22-H22···O3  | 0.95    | 2.26     | 3.122 (6) | 153         |
| C22'-H22'···O3' | 0.95   | 2.29     | 3.222 (6) | 168         |
| C25-H25···O10 | 0.95    | 2.37     | 3.273 (6) | 158         |
| C28-H28···O5  | 0.95    | 2.48     | 3.019 (7) | 116         |
| C31'-H31···O3' | 0.95    | 2.58     | 3.326 (7) | 136         |
| C32'-H32C···N1' | 0.99    | 2.6      | 3.019 (6) | 106         |
| C33'-H33B···N6 | 0.98    | 2.44     | 3.367 (6) | 158         |
| C38'-H38C···O1' | 0.99   | 2.48     | 3.976 (6) | 111         |
| C40-H40A···O1  | 0.99    | 2.46     | 3.024 (6) | 117         |
| C41-H41B···O2' | 0.98    | 2.45     | 3.372 (7) | 156         |
| C42-H42B···O17 | 0.99    | 2.46     | 3.411 (7) | 160         |
| C42'-H42C···O14 | 0.99    | 2.56     | 3.549 (7) | 174         |
| C44-H44C···O4  | 0.99    | 2.46     | 3.055 (6) | 118         |
| C45-H45B···O3  | 0.98    | 2.49     | 3.328 (7) | 147         |
| C46-H46B···O14 | 0.99    | 2.57     | 3.506 (7) | 157         |
| C46'-H46C···O4' | 0.99   | 2.49     | 2.928 (6) | 106         |
| C47'-H47B···O17 | 0.98    | 2.57     | 3.454 (7) | 156         |
| C48'-H48C···O17 | 0.99    | 2.57     | 3.551 (7) | 173         |
| C50'-H50C···N2' | 0.99   | 2.61     | 3.012 (6) | 104         |
| D–H···A   | D–H (Å) | H···A (Å) | D···A (Å) | \(\angle D–H···A(°)\) |
|-----------|---------|----------|-----------|---------------------|
| C13–H13···02 | 0.95    | 2.43     | 3.131 (9) | 130                 |
| C33–H33C···03 | 0.98    | 2.59     | 3.327 (13)| 132                 |
| C34–H34B···03 | 0.99    | 2.50     | 3.432 (10)| 156                 |
| C42–H42A···01 | 0.99    | 2.48     | 2.989 (11)| 112                 |
2.32 X-ray single-crystal structure of 3D structure of MOC 1 along the a-axis (top), b-axis (middle), and c-axis (bottom)

Figure S32. X-ray single-crystal structure of 3D structure of MOC 1 along the a-axis (top), b-axis (middle), and c-axis (bottom).
2.33 X-ray single-crystal structure of 3D structure of MOC 2 along the a-axis (top), b-axis (middle), and c-axis (bottom)

**Figure S33.** X-ray single-crystal structure of 3D structure of MOC 1 along the a-axis (top), b-axis (middle), and c-axis (bottom).
2.34 2D DOSY spectrum of MOC 1

![Figure S34. 2D DOSY spectrum of MOC 1 (CD$_2$Cl$_2$, room temperature, concentration 100 µM), diffusion coefficient $D = 4.64 \times 10^{-10}$ m$^2$/s).]

2.35 2D DOSY spectrum of MOC 2

![Figure S35. 2D DOSY spectrum of MOC 2 (CD$_2$Cl$_2$, room temperature, 100 µM), diffusion coefficient $D = 6.90 \times 10^{-10}$ m$^2$/s).]
2.36 2D DOSY spectrum of MOC 2 in DCM/cyclohexane

Figure S36. DOSY of MOC 2 (CD$_2$Cl$_2$/cyclohexane-d$_{12}$=8 : 2, room temperature, 100 μM), diffusion coefficient D = 3.81 × 10$^{-10}$ m$^2$/s.

2.37 2D DOSY spectrum of MOC 2 in DCM/toluene

Figure S37. DOSY of MOC 2 (CD$_2$Cl$_2$/toluene-d$_8$=8 : 2, room temperature, 100 μM), diffusion coefficient D = 3.80 × 10$^{-10}$ m$^2$/s.
2.38 $^1$H-$^1$H ROESY NMR spectra of MOC 1, 2

![Diagram](image1)

Figure S38. $^1$H-$^1$H ROESY NMR spectra (500 MHz) of MOC 1 in (a, c) CD$_2$Cl$_2$/CY-d$_{12}$ = 8:2 and (b, d) CD$_2$Cl$_2$/TOL-d$_{8}$ = 8:2. MOC 2 in (e, f) CD$_2$Cl$_2$/TOL-d$_{8}$ = 8:2.

2.39 $^1$H-$^1$H ROESY NMR spectra of MOC 2 in (a) CD$_2$Cl$_2$/CY-d$_{12}$

![Diagram](image2)

Figure S39. $^1$H-$^1$H ROESY NMR spectra (500 MHz) of MOC 2 in (a) CD$_2$Cl$_2$/CY-d$_{12}$ = 8:2 and (b) scheme illustrates the proton that involved in long-range interactions.
Figure S40. The histograms show the chemical shift in the (a) proton and (c) phosphor spectra of MOC 1 after the addition of CY (CD_{2}Cl_{2}/cyclohexane-d_{12} = 8 : 2, room temperature, 100 µM) and TOL (CD_{2}Cl_{2}/toluene-d_{8} = 8 : 2, room temperature, 100 µM). The histograms show the chemical shift in (b) proton and (d) phosphor spectra of MOC 2 after the addition of CY and TOL. Chemical shifts based colour span shows the influence of solvents on P-spectra are similar in (e) MOC 1 and (f) MOC 2.

Figure S40a (left, histogram top, dark red) shows the impact of the addition of CY and TOL on the chemical shifts of MOC 1. Specifically, all the signals in the 'H-NMR spectra show a slight downfield shift after the addition of CY (ΔδH=0.05, ΔδH=0.04, ΔδH=0.04, ΔδH=0.03, ΔδH=0.05, ΔδH=0.03, ΔδH=0.02, ΔδHCH=0.05 ppm, ΔδHCH=0.04 ppm) (Figure S41). A similar but more dramatic downfield shift occurs after the addition of toluene, as shown in Figure S40a (bottom, light pink), ΔδH=0.16, ΔδH=0.12, ΔδH=0.15, ΔδH=0.19, ΔδH=0.29, ΔδH=0.23, ΔδH=0.20, ΔδHCH=0.12 ppm, ΔδHCH=0.15 ppm (Figure S42). The corresponding chemical shift distributions across MOC 1 were shown in the middle and right images in Figure S40a. By comparing these images (colour span), it was found that toluene (Figure S40a, right) causes more delicate and multi-level change than cyclohexane (Figure S40a, middle). For MOC 2, the addition of toluene (Figure S40b, yellow), ΔδH=0.21, ΔδH=0.16, ΔδH=0.03, ΔδH=0.05, ΔδH=0.04, ΔδH=0.03, ΔδH=0.03, ΔδHCH=0.05 ppm, ΔδHCH=0.04 ppm, Figure S43) to the solvent system causes a greater chemical shift than the addition of cyclohexane (Figure S40b, left, orange, ΔδH=0.05, ΔδH=0.05, ΔδH=0.04, ΔδH=0.03, ΔδH=0.03, ΔδHCH=0.05 ppm, ΔδHCH=0.04 ppm, Figure S44). The influence of solvent on tuning the intermolecular interactions of MOC 2 is provided in Figure S40b (colour span), toluene (right) causes more multi-level change than cyclohexane (middle). The corresponding chemical shifts of P-Py (Δδ=7.82 ppm, light purple) in the 31P-NMR spectra (DCM/CY) show a similar shift with P-COO (Δδ=7.76 ppm, light pink) (Figures S40c and S45) in MOC 1. For MOC 1, after the addition of toluene, the change in P-Py (Δδ=5.83 ppm) in the 31P-NMR spectrum was almost the same as that in P-COO (Δδ=5.82 ppm) (Figures S40d and S46). Figures S40d and S47-48 show that the change of the solvent system for MOC 2 has a similar influence on P-COO (Δδ=7.60 ppm in DCM/CY; Δδ=7.81 ppm in DCM/TOL) and Py (Δδ=7.74 ppm in DCM/CY; Δδ=7.94 ppm in DCM/TOL). Figure S40e-f shows that either pyridine or carboxylate parts have similar interaction with PEt3 (similar colour of four corners in MOC 1/MOC 2).
2.41 Partial $^1$H-NMR of MOC 1 before and after the addition of cyclohexane-d$_{12}$

(a) CD$_2$Cl$_2$

(b) CD$_2$Cl$_2$/cyclohexane-d$_{12}$ = 8:2

Figure S41. Partial $^1$H-NMR of MOC 1 (a) before (CD$_2$Cl$_2$, room temperature, concentration 100 μM) and (b) after the addition of cyclohexane-d$_{12}$ (CD$_2$Cl$_2$/cyclohexane-d$_{12}$ = 8 : 2, room temperature, 100 μM).

2.42 Partial $^1$H-NMR of MOC 1 before and after the addition of toluene-d$_8$

(a) CD$_2$Cl$_2$

(b) CD$_2$Cl$_2$/toluene-d$_8$ = 8:2

Figure S42. Partial $^1$H-NMR of MOC 1 (a) before (CD$_2$Cl$_2$, room temperature, concentration 100 μM) and (b) after the addition of toluene-d$_8$ (CD$_2$Cl$_2$/toluene-d$_8$ = 8 : 2, room temperature, 100 μM).
2.43 Partial $^1$H-NMR of MOC 2 before and after the addition of cyclohexane-$d_{12}$

![NMR spectrum of MOC 2 in CD$_2$Cl$_2$ and CD$_2$Cl$_2$/cyclohexane-$d_{12}$ (8:2).](image)

Figure S43. Partial $^1$H-NMR of MOC 2 (a) before (CD$_2$Cl$_2$, room temperature, concentration 100 µM) and (b) after the addition of cyclohexane-$d_{12}$ (CD$_2$Cl$_2$/cyclohexane-$d_{12}$ = 8:2, room temperature, 100 µM).

2.44 Partial $^1$H-NMR of MOC 2 before and after the addition of toluene-$d_8$

![NMR spectrum of MOC 2 in CD$_2$Cl$_2$ and CD$_2$Cl$_2$/toluene-$d_8$ (8:2).](image)

Figure S44. Partial $^1$H-NMR of MOC 2 (a) before (CD$_2$Cl$_2$, room temperature, concentration 100 µM) and (b) after the addition of toluene-$d_8$ (CD$_2$Cl$_2$/toluene-$d_8$ = 8:2, room temperature, 100 µM).
2.45 $^{31}$P-NMR of MOC 1 before and after the addition of cyclohexane-d$_{12}$

(a) CD$_2$Cl$_2$

(b) CD$_2$Cl$_2$/cyclohexane-d$_{12}$ = 8:2

Figure S45. $^{31}$P-NMR of MOC 1 (a) before (CD$_2$Cl$_2$, room temperature, concentration 100 µM) and (b) after the addition of cyclohexane-d$_{12}$ (CD$_2$Cl$_2$/cyclohexane-d$_{12}$ = 8 : 2, room temperature, 100 µM).

2.46 $^{31}$P-NMR of MOC 1 before and after the addition of toluene-d$_8$

(a) CD$_2$Cl$_2$

(b) CD$_2$Cl$_2$/toluene-d$_8$ = 8:2

Figure S46. $^{31}$P-NMR of MOC1 (a) before (CD$_2$Cl$_2$, room temperature, concentration 100 µM) and (b) after the addition of toluene-d$_8$ (CD$_2$Cl$_2$/toluene-d$_8$ = 8 : 2, room temperature, 100 µM).
2.47 $^{31}$P-NMR of MOC 2 before and after the addition of cyclohexane-$d_{12}$

(a) CD$_2$Cl$_2$

(b) CD$_2$Cl$_2$/cyclohexane-$d_{12}$ = 8:2

Figure S47. $^{31}$P-NMR of MOC 2 (a) before (CD$_2$Cl$_2$, room temperature, concentration 100 μM) and (b) after the addition of cyclohexane-$d_{12}$ (CD$_2$Cl$_2$/cyclohexane-$d_{12}$ = 8 : 2, room temperature, 100 μM).

2.48 $^{31}$P-NMR of MOC 2 before and after the addition of toluene-$d_8$

(a) CD$_2$Cl$_2$

(b) CD$_2$Cl$_2$/toluene-$d_8$ = 8:2

Figure S48. $^{31}$P-NMR of MOC 2 (a) before (CD$_2$Cl$_2$, room temperature, concentration 100 μM) and (b) after the addition of toluene-$d_8$ (CD$_2$Cl$_2$/toluene-$d_8$ = 8 : 2, room temperature, 100 μM).