

## Supporting Information

### Amphiphile-like Self-assembly of Metal Organic Polyhedra with Polar and Non-polar Groups

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#### Experimental Section:

##### S1: Materials

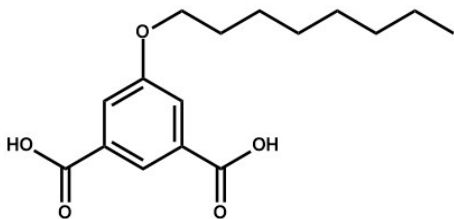
Cu (NO<sub>3</sub>)<sub>2</sub> · 2.5 H<sub>2</sub>O was purchased from Anachemia, a VWR company. 5-hydroxy isophthalic acid and 1-Bromo-octane were purchased from Sigma Aldrich. 2,6-lutidine was obtained from Alfa Aesar. Solvents such as methanol, hexane, acetone, dichloromethane were obtained from Sigma Aldrich. Deuterated solvents used for nuclear magnetic resonance (NMR) spectroscopy or any other chemical used were also purchased from Sigma Aldrich chemicals. All materials were used without any further purification.

##### S2: Methods

UV spectroscopy (solution state) was performed using quartz cuvettes on Cary 300 UV-Vis Spectrophotometer. Fourier transform infrared spectra (FT-IR) were taken using Thermo-Nicolet Nexus 470 on KBr plate. <sup>1</sup>H-NMR spectra were collected on Bruker Advanced II 400 MHz NMR spectrometer. Elemental analysis was performed on Perkin Elmer 2400 Series II. Tecnai F20 which is a 200 kV Transmission Electron Microscope (TEM) was used for imaging. The sample was drop-casted from respective solvents over holey carbon grids and well dried before imaging. FEI XL30 which is 30 kV Scanning Electron Microscope (SEM) with inbuilt Energy Dispersive X-ray spectroscopy (EDX) was used for elemental mapping. For this, the sample was drop-casted over a double-sided carbon tape and well-dried before use. Powder X-ray Diffraction patterns were obtained using Rigaku Miniflex II bench top PXRD equipped with Cu Kα x-ray source. Single crystal X-ray diffraction (SC-XRD) data for compounds **1** was collected using the Canadian Macromolecular Crystallography Facility CMCF-BM beamline at the Canadian Light Source (CLS) [1]. CMCF-BM is a bending magnet beamline equipped with a Si (111) double crystal monochromator, Rayonix MX300HE CCD detector and MD2 microdiffractometer equipped with Mini Kappa Goniometer Head.

### S3: Preparations

#### 1) 5-(octyloxy) isophthalic acid (L2)



*Step1:* 1-Bromooctane (4 mL, 23 mmol) was added into a mixture of 5-hydroxy isophthalate (4.5 g, 21.42 mmol) and anhydrous potassium carbonate  $K_2CO_3$  (8.872 g, 64.2 mmol) in dry DMF (60 mL). The reaction mixture was heated to  $110^\circ C$  and stirred under  $N_2$  atmosphere for 24 hours. After being cooled to room temperature, the solid was filtered off and the filtrate was concentrated under reduced pressure. The residue was dissolved in DCM (100 mL) and liquid-liquid extraction was performed using brine and 2N HCl (20 mL). The organic phase was dried using magnesium sulphate and concentrated under reduced pressure to give a white solid. This was further recrystallized using hot methanol to give dimethyl 5-(octyloxy) isophthalate (6.656 g).

*Step 2:* To a suspension of dimethyl 5-(octyloxy) isophthalate (6.656 g, 20.65 mmol) in 60 mL methanol was added a solution of sodium hydroxide NaOH (3.305 g, 82.63 mmol) in 30 mL water. The mixture was refluxed for 24 hours and became clear gradually. After completion of the reaction, the organic phase was evaporated under reduced pressure. The basic aqueous phase was treated with catalytic amount of HCl to give white solid. The crude product was vacuum dried and recrystallized from hot methanol to give pure product 5-octyloxy isophthalic acid (6 g, 98%).  $^1H$ -NMR in  $DMSO-d_6$ ,  $\delta$ : 13.24 (br, 2H, COOH), 8.05 (t, 1H, Ar-H), 7.62 (d, 2H, Ar-H), 4.05 (t, 2H,  $-OCH_2$ ), 1.73 (m, 2H,  $-CH_2$ ), 1.46-1.26 (m, 10H,  $-CH_2$ ), 0.86 (t, 3H,  $-CH_3$ )

#### 2) Synthesis of Mixed linker 1:1 L1: L2 MOP:

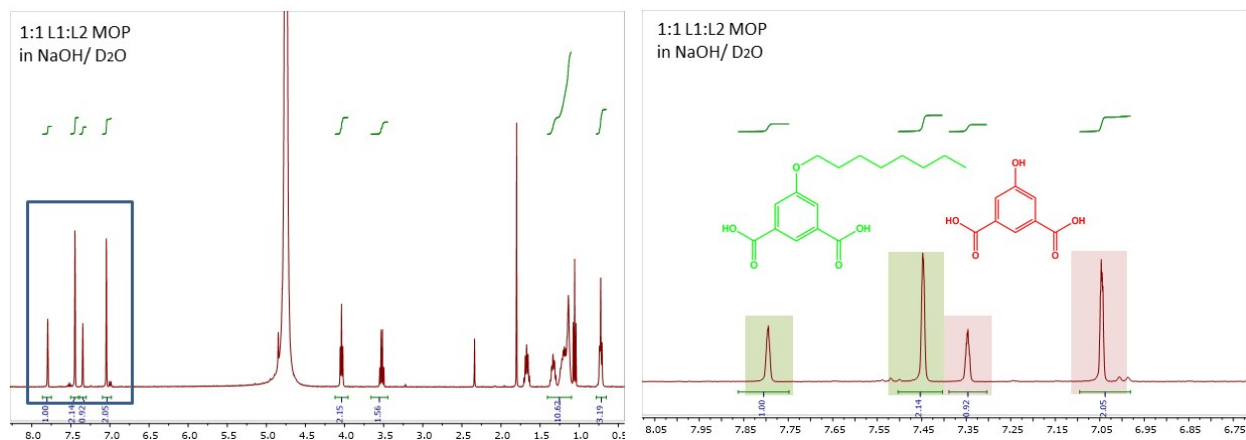
Mixed linkers, 5-hydroxy isophthalic acid (182.13 mg, 0.5 mmol) and 5-octyloxy isophthalic acid (294.34 mg, 0.5 mmol) were dissolved in 7 mL methanol. This solution was then added to  $Cu(NO_3) \cdot 2.5 H_2O$  (232.59 mg, 1 mmol) solution in 13 mL methanol. 2, 6- Lutidine (0.233 mL, 2 mmol) was then slowly added to the metal-linker solution to give blue precipitates containing MOPs. The blue precipitates were then filtered and washed thoroughly with methanol and acetonitrile to get rid of excessive linkers and lutidinium salt. MOPs were separated from the precipitates by dissolving it in acetone and filtering out the insoluble polymeric residue. The filtrand is then

concentrated to give 1:1 MOP powder. EA analysis: (expected) C -47.71, H-4.63; (found) C- 46.36, H- 4.95

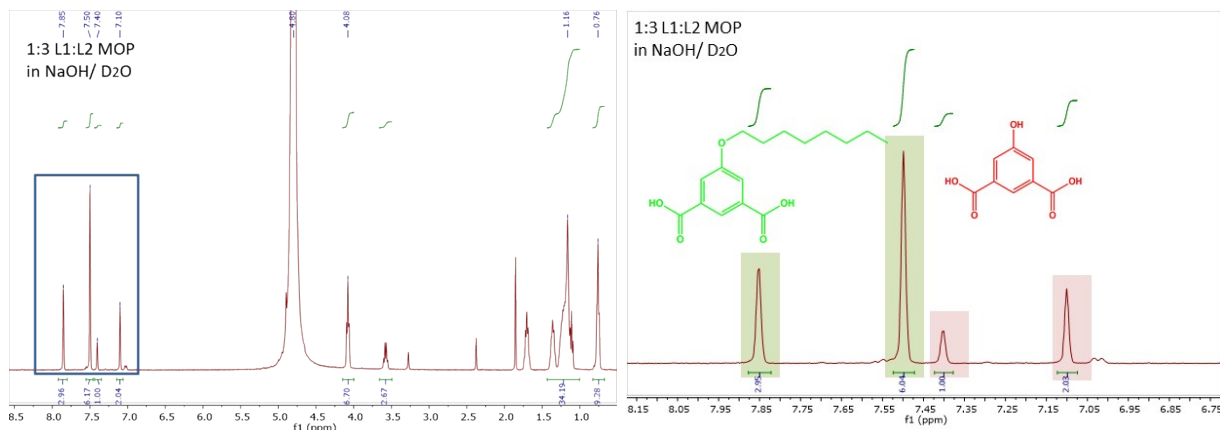
The amount of each linker in the bulk MOP was verified by  $^1\text{H-NMR}$  by disintegrating the MOPs in 1M NaOH/  $\text{D}_2\text{O}$  solution.

Similarly, 1: 3 L1: L2 MOPs were synthesized by changing the amount of each linker and verified via  $^1\text{H-NMR}$ .

#### S4: NMR Spectroscopy of MOPs



**Fig. S1:** (left)  $^1\text{H-NMR}$  of 1:1 MOP (right) zoomed aromatic region which confirms presence of 1:1 L1: L2.



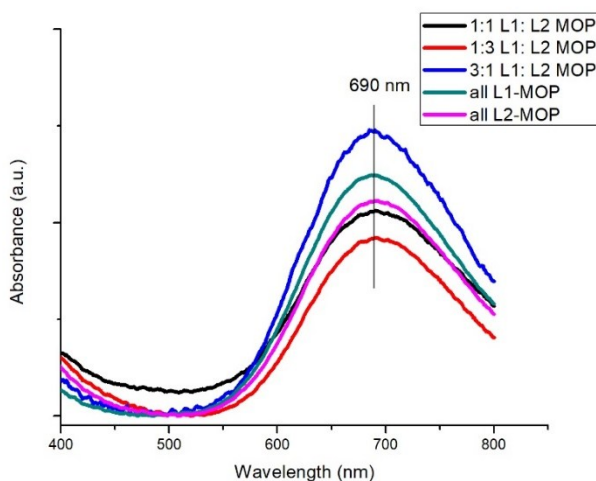
**Fig. S2:** (left)  $^1\text{H-NMR}$  of 1:3 MOP (right) zoomed aromatic region which confirms presence of 1:3 L1: L2.

## S5: Solubility of the MOPs

| Solvents              | All L1 | 3:1<br>L1: L2 | 1:1<br>L1: L2 | 1:3<br>L1: L2 | All L2 |
|-----------------------|--------|---------------|---------------|---------------|--------|
|                       | Hexane | x             | x             | x             | x      |
| Diethyl ether         | x      | x             | x             | x             | ✓      |
| Dichloromethane       | x      | x             | x             | ✓             | ✓      |
| Chloroform            | x      | x             | x             | ✓             | ✓      |
| Ethyl Acetate         | x      | x             | ✓             | ✓             | ✓      |
| Methanol              | ✓      | ✓             | x             | x             | x      |
| Acetone               | x      | ✓             | ✓             | ✓             | x      |
| Acetonitrile          | x      | x             | x             | x             | x      |
| Dimethyl<br>formamide | x      | x             | ✓             | ✓             | ✓      |
| Dimethyl<br>sulfoxide | x      | x             | x             | x             | x      |
| Water                 | x      | x             | x             | x             | x      |

**Table S1:** Table showing solubility of the given MOPs in different solvents. The “check” denotes a clear solution but MOPs can be dispersed in solvents for TEM sample preparation.

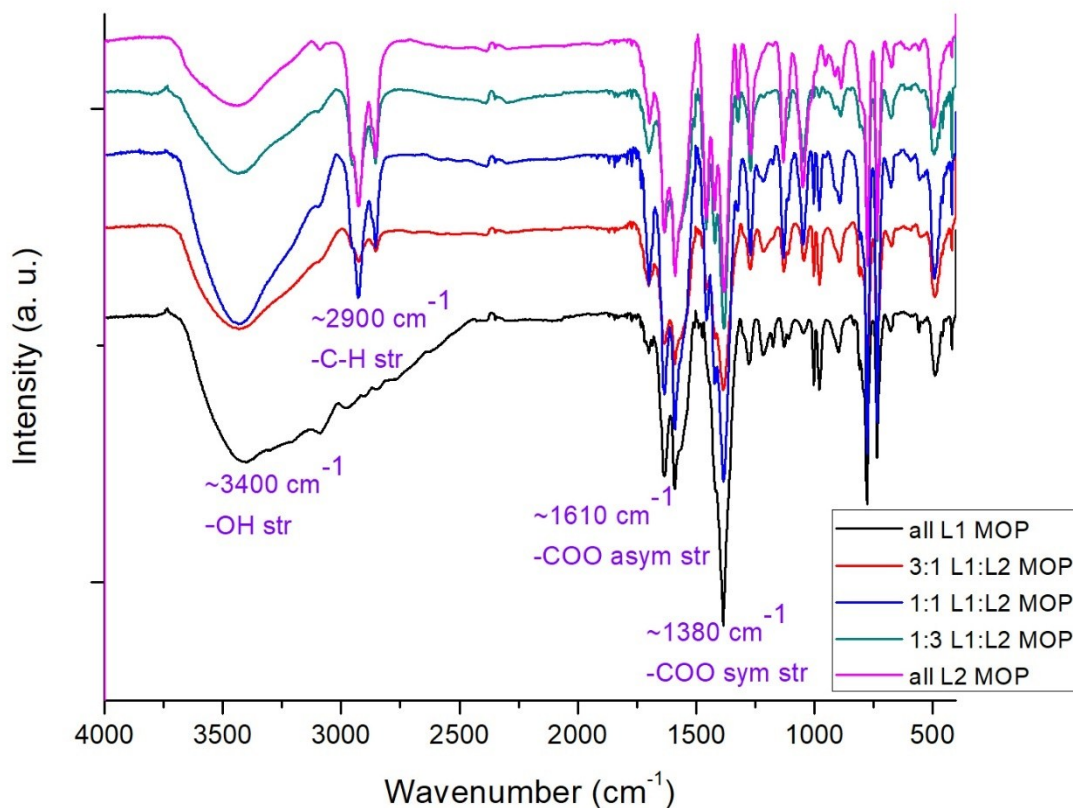
## S6: UV Spectroscopy



**Fig. S3:** UV-Vis spectra of the mixed linker MOPs in acetone showing characteristic  $\sim 690$  nm peak for presence of copper paddlewheel unit.

## S7: IR Spectroscopy

FT-IR spectra of the MOPs with different ratios of L1: L2 show similar fingerprint region as can be seen from Fig. S4. Absence of the free carboxylic acid peak at  $\sim 1700$   $\text{cm}^{-1}$  confirms that all the linkers have coordinated to form the MOP and no free acid group is present. The difference between asymmetric and symmetric carboxylate ( $-\text{COO}$ ) peak tells us about the coordination behavior i.e. monodentate, bridging or chelate; as studied by M. Iqbal et al.<sup>9</sup> The difference for asym and sym peaks here is  $(1610-1380)$   $230$   $\text{cm}^{-1}$  which is indicative of bridging behavior of carboxylate. The presence of  $\sim 2900$   $\text{cm}^{-1}$  peak can be seen which confirms the presence of alkyl moiety for mixed linker MOPs. The  $-\text{OH}$  stretch at  $\sim 3400$   $\text{cm}^{-1}$  indicates the presence of free hydroxyl group of L1 and can also be due to atmospheric water molecules adsorbed as seen in all L2 MOP.



**Fig. S4:** FT-IR spectra of the MOPs.

## S8: Crystal Structure Determination

Data for compound **1** was collected at 18.000 keV (0.68881 Å, CMCF-BM) using a single crystal. All data was collected at low temperature (100 K).

Cell refinement and data reduction were performed using Mosflm [2]. An empirical absorption correction, based on spherical harmonics was performed using Aimless [3]. The space group was confirmed by XPREP [4] routine.

The initial model and difference Fourier map for the compound **1** was obtained with SHELXL-2014. The crystal structure of **1** was solved by combination of direct-methods and real space refinement. The real space refinement was performed using COOT [5]. Direct methods refinement was performed with SHELXL-2014 [6] using conjugate-gradient refinement (CGLS) in the initial stages and then by full-matrix least-squares and difference Fourier techniques at the final stages. Initial structure solution was attempted in Pa-3 space group, but due to a poor and sometimes absent electron density map (Fobs-Fcalc) for alkyl chains, the structure could not be fully refined in this space group. Due to the nature of the crystalline material, high resolution data could not be obtained for this compound. The crystal used for data collection was only diffracted to 1.0 Å (1/Sigma=2).

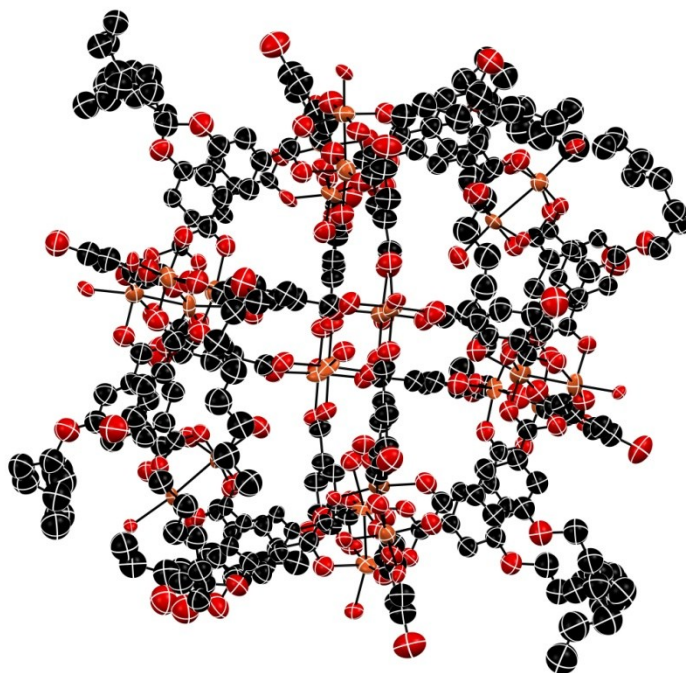
All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were set in calculated positions and refined as riding atoms with a common thermal parameter. Disorders of water molecules were refined as two-component disorders using PART instructions and atom occupancies were refined using free variables. The alkyl groups (C9-C16) in the residues 3, 5, 8, 13 were refined as a sum of occupancies equal to 2.

All publication materials (CIF files validation, listings of bonds and angles, and ORTEP drawings) were prepared using LinXTL [7] and Mercury [8]. Routine checkCIF and structure factor analyses were performed by Platon [Error! Bookmark not defined.].

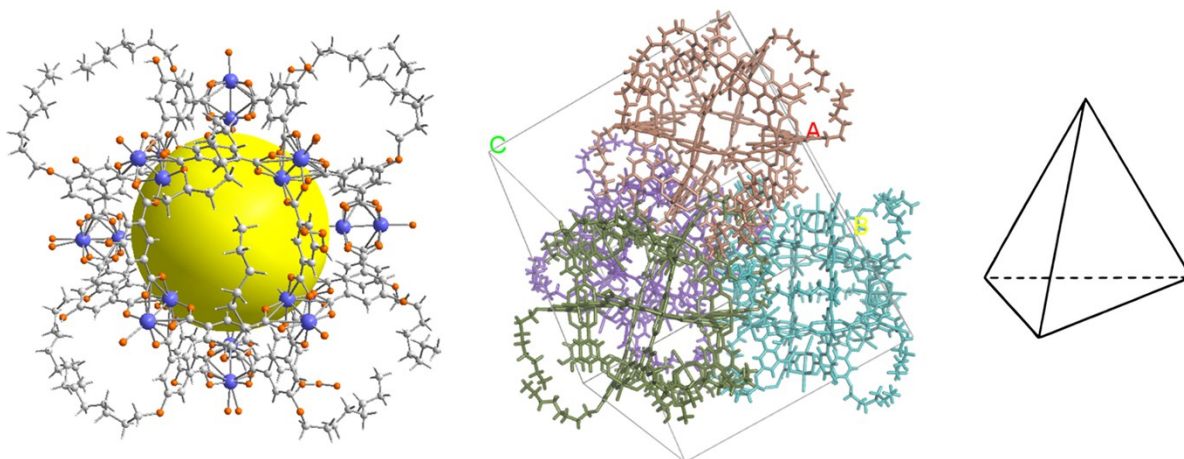
**Table S2. Crystal Data Collection and Refinement Parameters for Complex 1.**

|  | <b>1</b>  |
|--|---|
| <b>chemical formula</b>                    | C <sub>77</sub> H <sub>56</sub> Cu <sub>8</sub> O <sub>49</sub> |
| <b>crystal colour</b>                      | Blue  |
| <b><i>F</i><sub>w</sub>; <i>F</i>(000)</b> | 2272.58; 13696  |
| <b><i>T</i> (K)</b>                        | 100   |
| <b>wavelength (Å)</b>                      | 0.68881   |

|  |                       |
|--|-----------------------|
| space group  | P2 <sub>1</sub> 3     |
| <i>a</i> (Å)   | 34.773(4)             |
| <i>b</i> (Å)   | 34.773(4)             |
| <i>c</i> (Å)   | 34.773(4)             |
| $\alpha$ (deg)   | 90                    |
| $\beta$ (deg)  | 90                    |
| $\gamma$ (deg)   | 90                    |
| <i>Z</i>   | 12                    |
| <i>V</i> (Å <sup>3</sup> )   | 42046(15)             |
| $\rho_{\text{calcd}}$ (g·cm <sup>-3</sup> )  | 1.077                 |
| $\mu$ (mm <sup>-1</sup> )  | 1.108                 |
| $\theta$ range (deg); completeness   | 1.269 – 24.987; 0.997 |
| collected reflections; <i>R</i> <sub>c</sub>   | 27081; 0.1219         |
| unique reflections   | 27081                 |
| <i>R</i> 1 <sup>a</sup> ; <i>wR</i> 2 <sup>b</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] | 0.1030; 0.2345        |
| <i>R</i> 1; <i>wR</i> 2 [all data]   | 0.1622; 0.2599        |
| GOF  | 1.156                 |
| largest diff peak and hole   | 10.797 and -0.507     |



**Fig. S5:** ORTEP diagram for compound **1**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

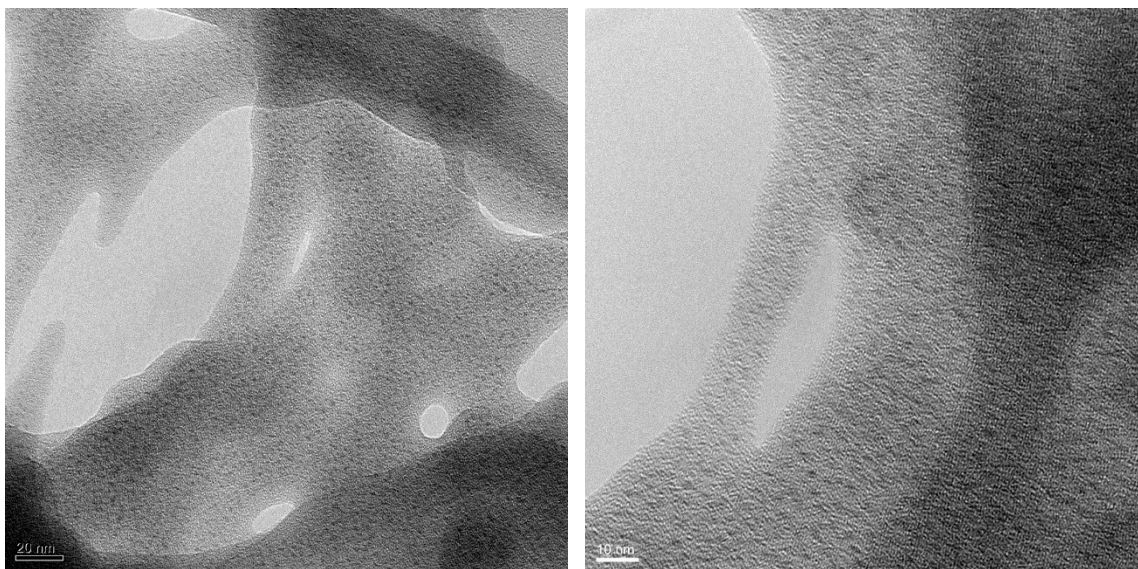


**Fig. S6:** (left) SC-XRD of **1**, showing even and symmetric distribution of linkers; (right) MOP **1** packs as a tetrahedron in the cubic unit cell of space group  $P2_13$ .

### S9: Transmission Electron Microscopy (TEM)

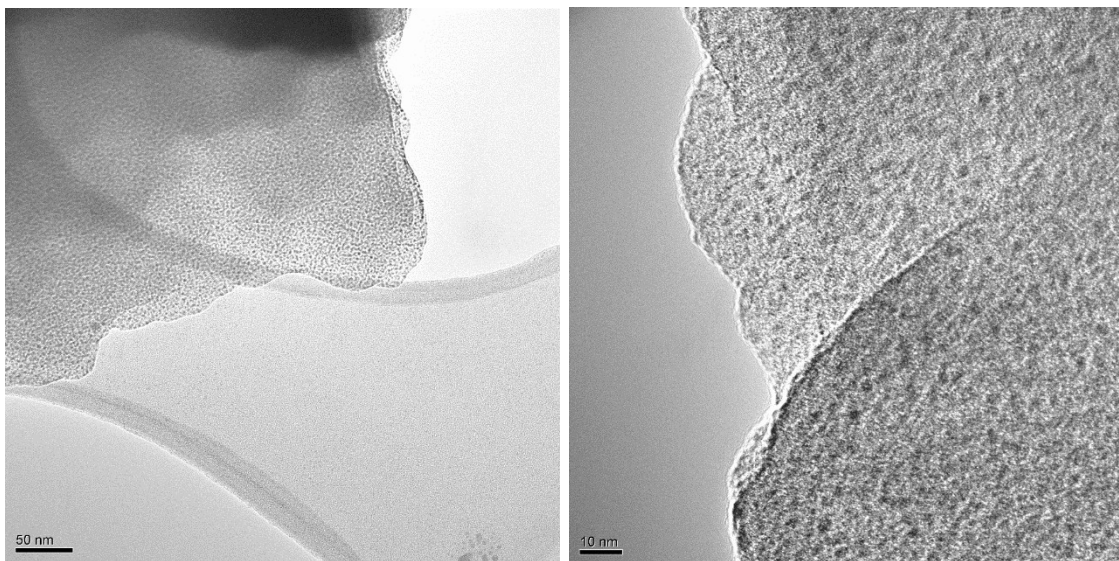
The MOPs were subjected to solvents -hexane, DCM, acetone and methanol for 4 days in a vial and then imaged using TEM.

#### a) 1:1 L1: L2 MOP **1**

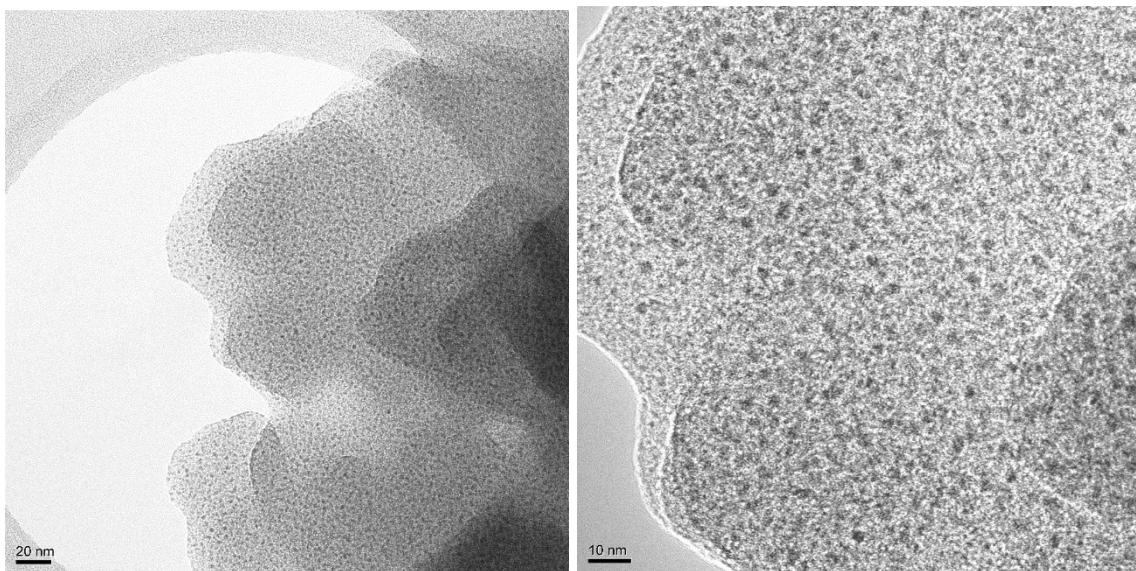


**Fig. S7:** TEM images of the symmetric MOP **1** in hexane.

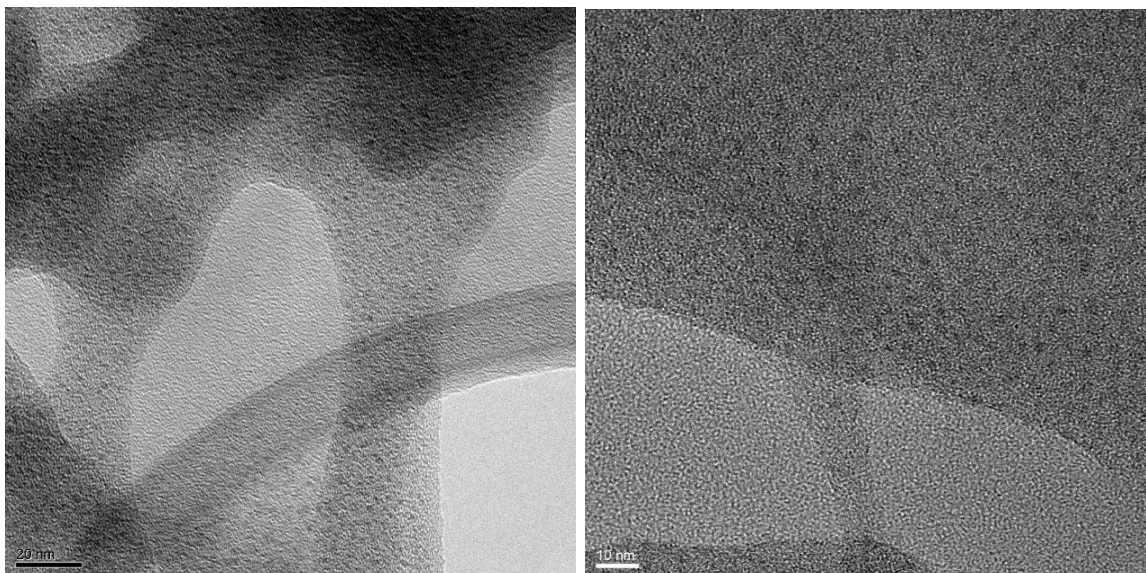




**Fig. S8:** TEM images of the symmetric MOP 1 in dichloromethane.



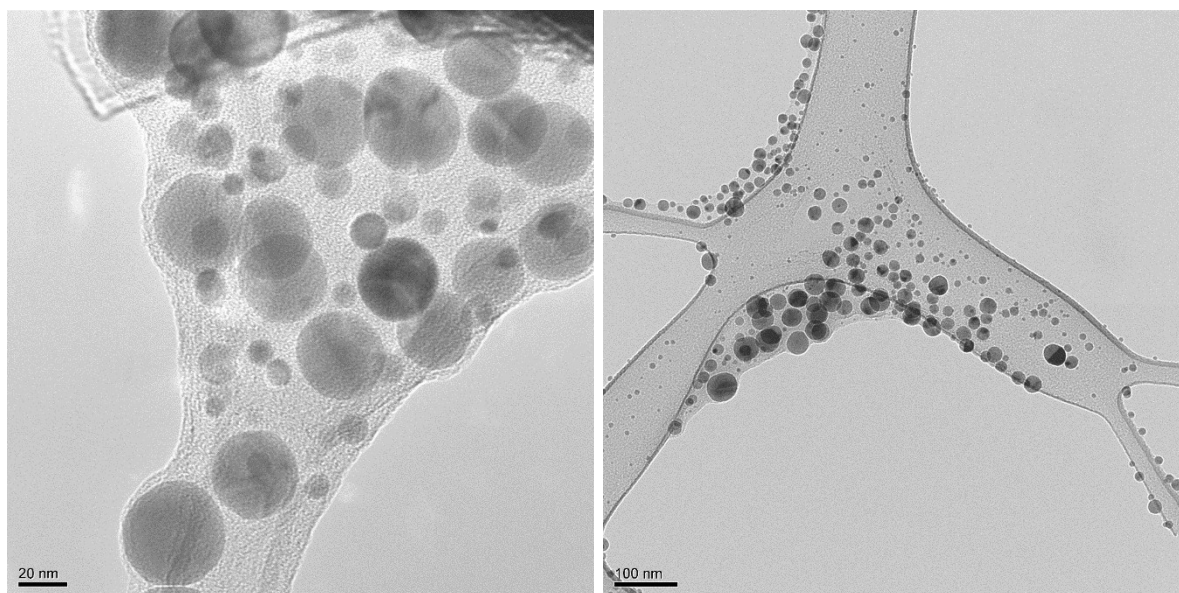
**Fig. S9:** TEM images of the symmetric MOP 1 in acetone.



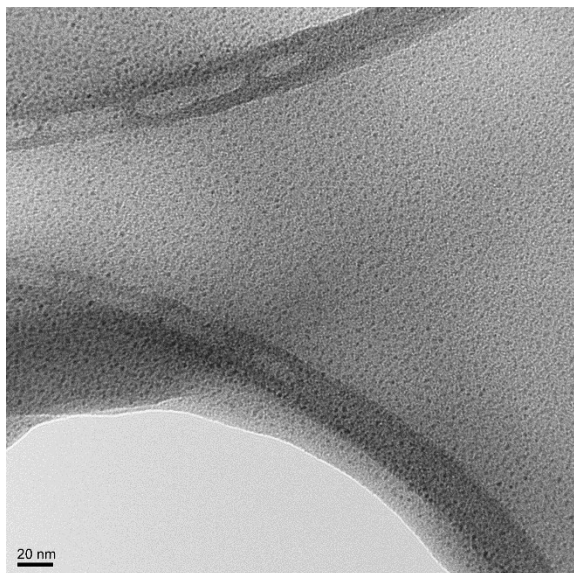
**Fig. S10:** TEM images of the symmetric MOP **1** in methanol.

Here we see the images of the symmetric MOP of  $\sim 2$  nm dimension which doesn't show self assembly in any of these solvents.

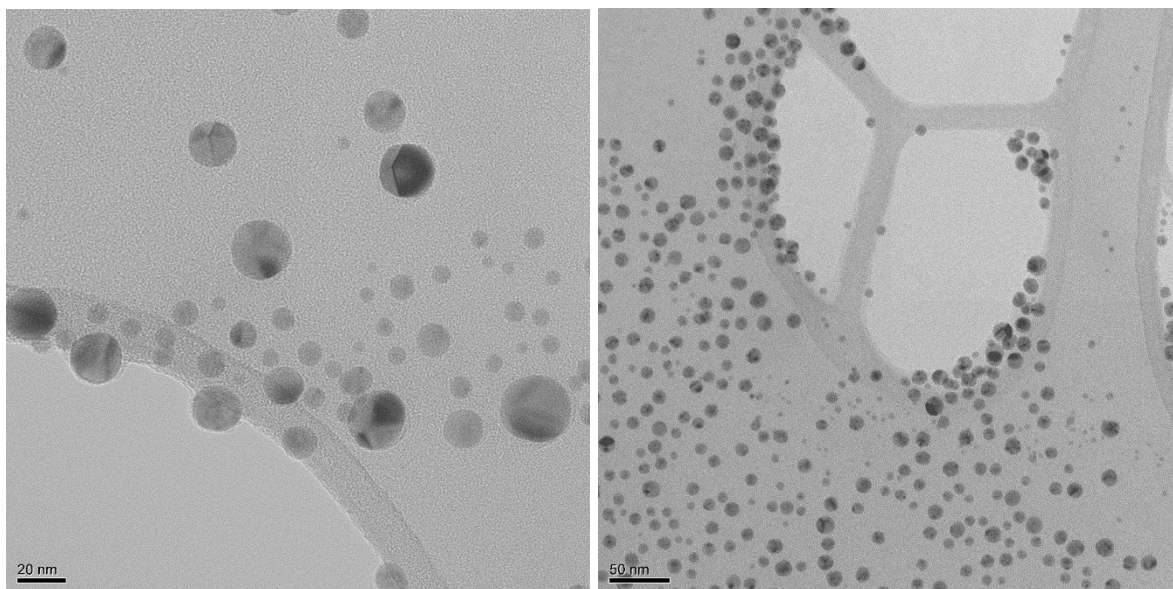
b) 1:1 L1: L2 MOP **2**



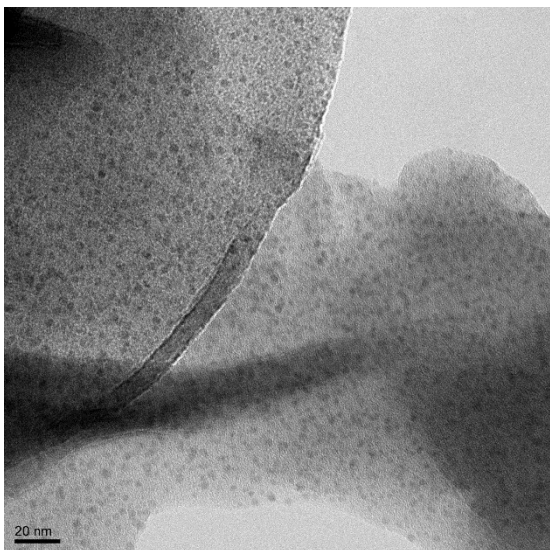
**Fig. S11:** TEM images of Janus MOP **2** in hexane.



**Fig. S12:** TEM image of Janus MOP 2 in DCM.



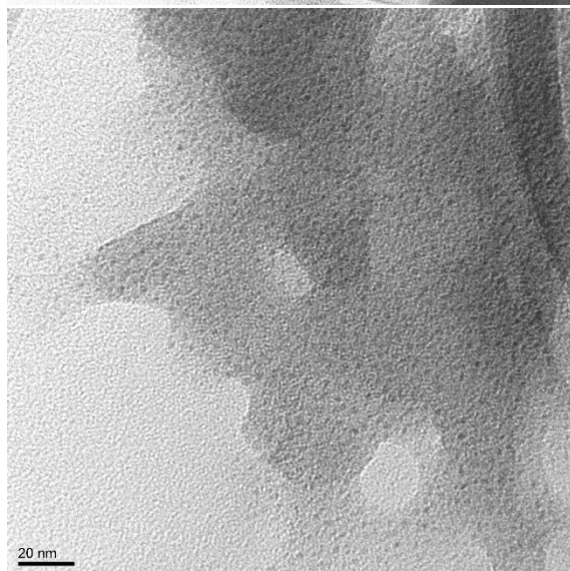
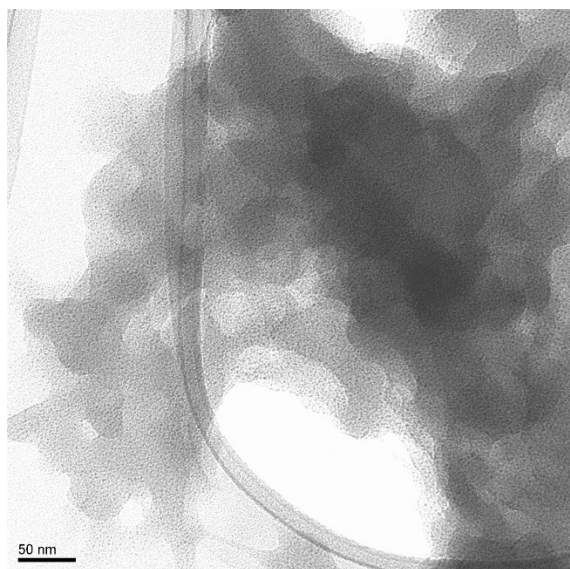
**Fig. S13:** TEM images of Janus MOP 2 in acetone.



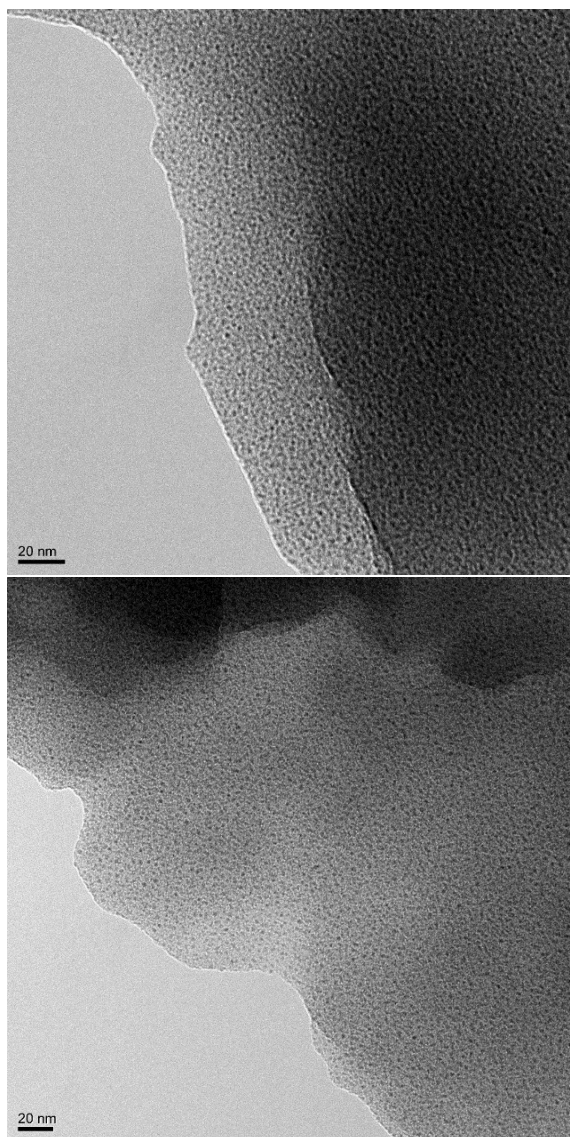
**Fig. S14:** TEM image of Janus MOP **2** in methanol.

The janus MOP **2** forms assemblies as big as 40 nm in hexane while in methanol it forms 3-4 nm clusters. The self-assembly is driven by interaction among the functional groups on the MOP surface as well as the solvent molecules.

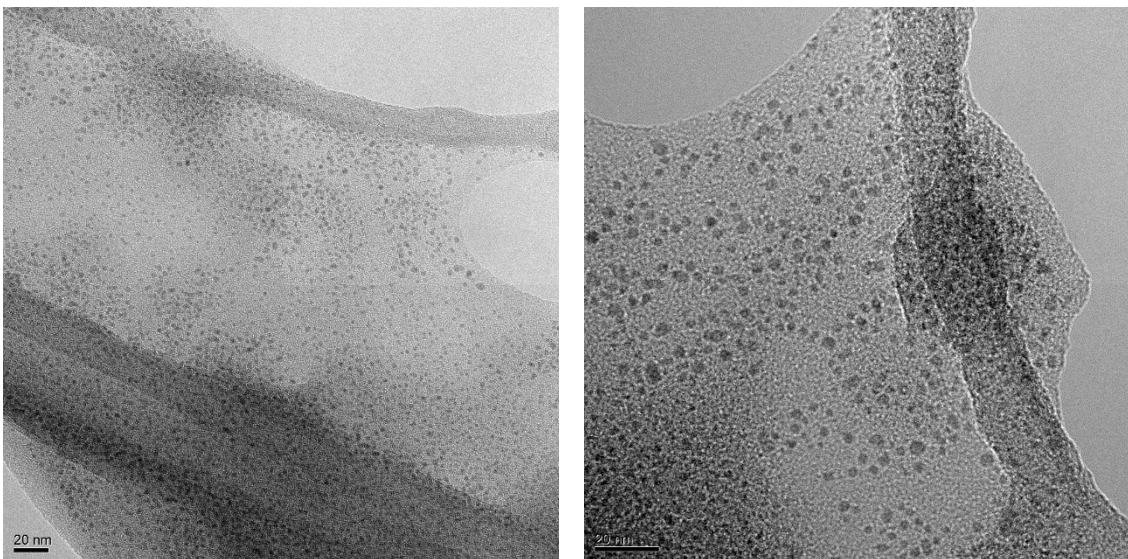
c) 1:3 L1: L2 MOP **3**



**Fig. S15:** TEM images of **3** in hexane.



**Fig. S16:** TEM images of **3** in (left) DCM, (right) acetone.

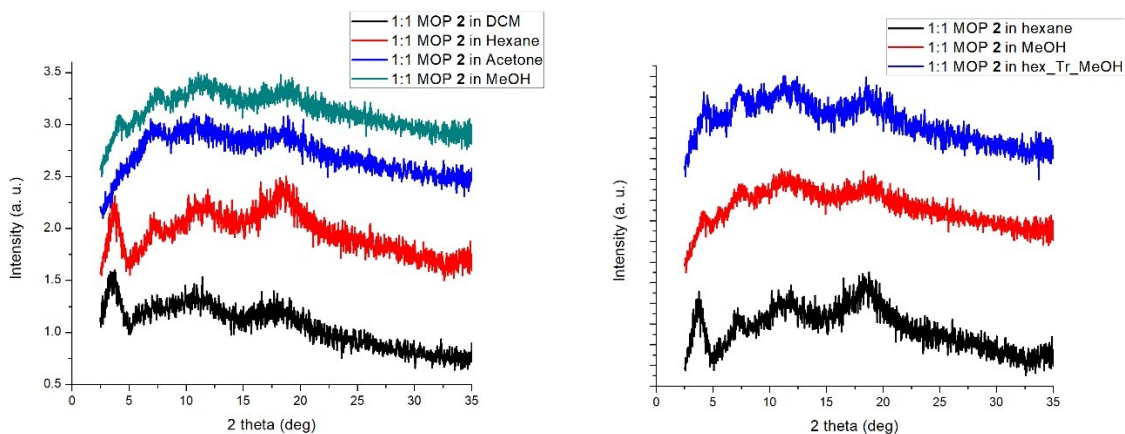


**Fig. S17:** TEM images of **3** in methanol.

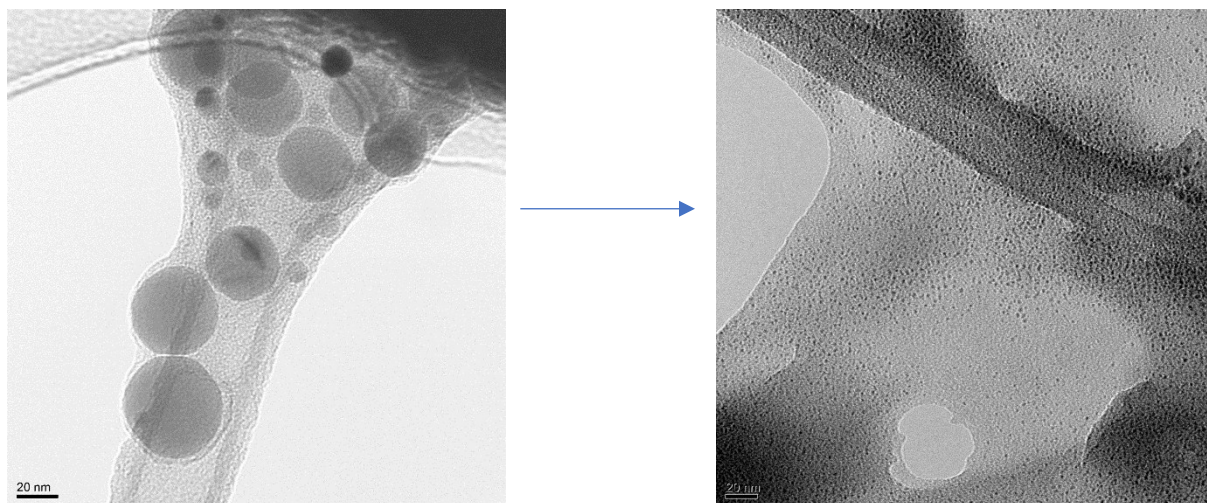
MOP **3** doesn't show self-assembly in any of the solvents and discrete  $\sim 2$  nm sized nanoparticles can be seen. However, it does form 3-4 nm clusters in methanol.

### **S10: Reversibility of aggregates**

The PXRD of the mixed linker MOPs varies, when subjected to different polarity of solvents which might be due to different arrangement of functional groups. When MOP **2** subjected to hexane is dried and then put in methanol, its PXRD changes like the one put directly in methanol. Similar was observed for various pair of solvents. Thus, indicating the flexible arrangement of MOPs back and forth between different solvents.



**Fig. S18:** PXRD pattern of MOP 2 (left) in the given 4 solvents, (right) showing reversibility of the arrangement between hexane and methanol.



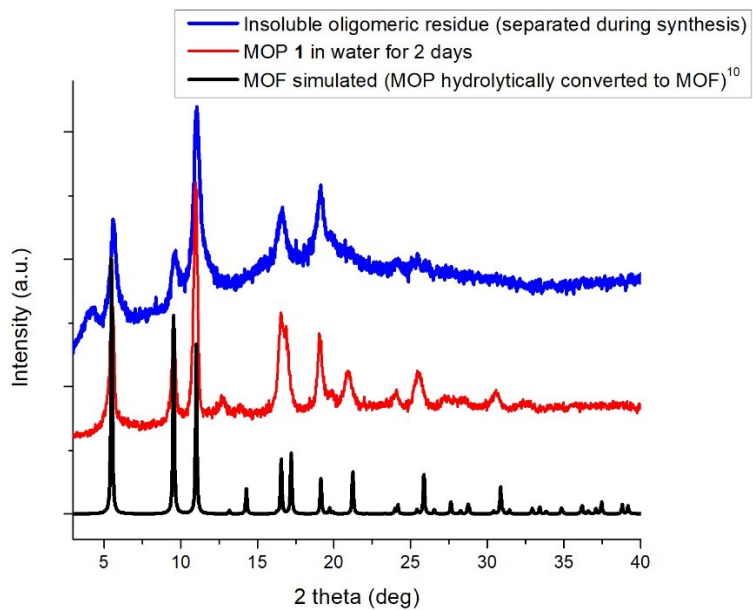
**Fig. S19:** TEM image of MOP 2 in hexane (left) having assemblies change to discrete MOPs when subjected to methanol (right).

### S11: Degradation of the MOPs

MOPs when exposed to moisture gets degraded into insoluble polymorph. There is a report by Mallick et al.<sup>10</sup> where the Cu<sub>24</sub>MOP gets converted into a MOF when exposed to water. Similar behavior was observed when MOP 1 was exposed to water (Fig. S20). It can be seen that the PXRDs for the MOF reported by Mallick et al. and degraded 1 on exposure to water match. This

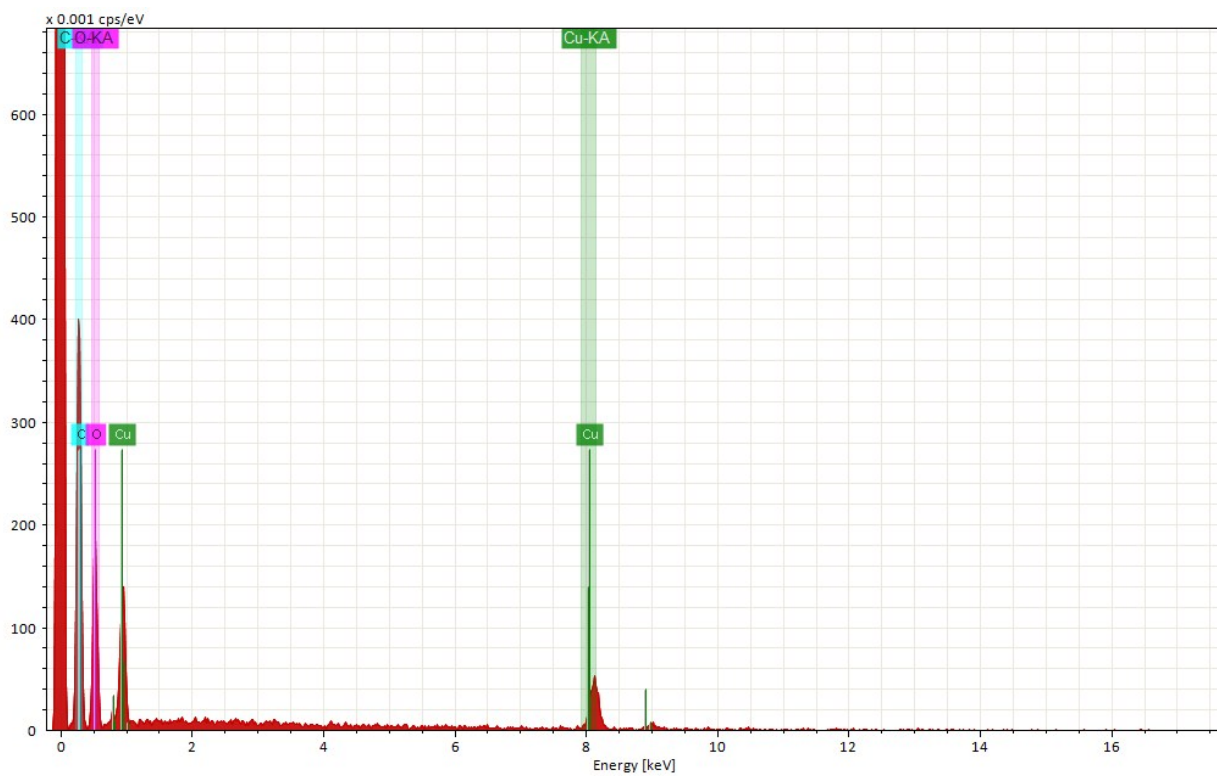


PXRD pattern is also similar to the insoluble species obtained during the MOP synthesis which was removed as a residue (see procedure S3-2).



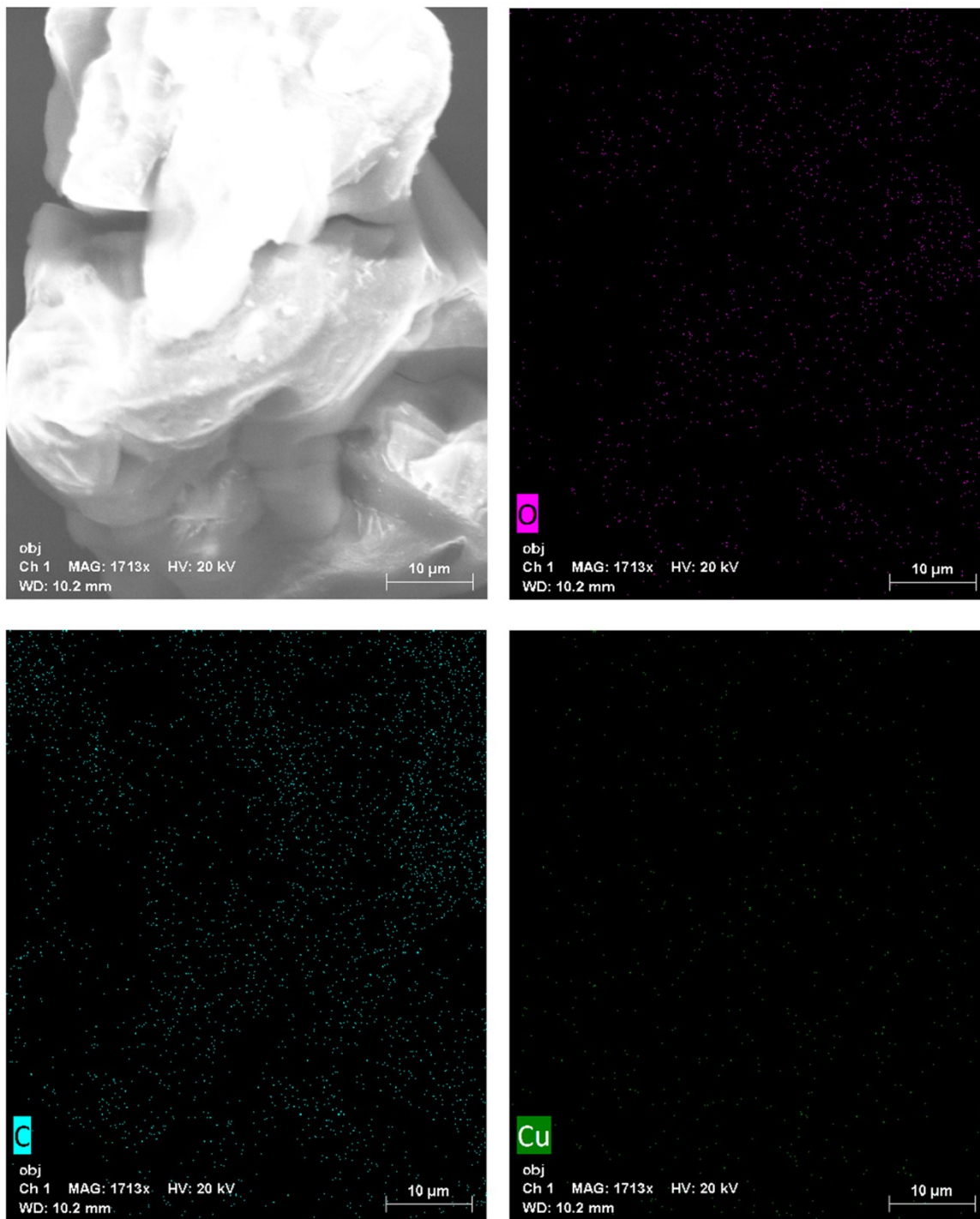
**Fig. S20:** PXRD pattern showing degradation of MOP to insoluble polymorph.

## S12: Energy dispersive X-ray spectroscopy



**Fig. S21.** EDX spectra of the bulk 1: 1 L1: L2 MOP confirming the presence of Cu.

### S13: Elemental mapping



**Fig. S22:** (top right) SEM image of bulk 1:1 MOP particle; elemental map showing presence of (top left) oxygen, (bottom right) carbon and (bottom left) copper in the MOPs.

**References:**

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