Supplementary information

for

Ligand and solvent effects in the formation and self-assembly of a metallosupramolecular cage

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Figure S1. Conformational possibilities for ligand L1
Figure S2. Conformational possibilities for ligand L2
Figure S3: TGA of 1

Single crystal X-ray structure analysis of metallosupramolecular cage 1, revealed that the unit cell \([a = b = 17.3071(6), c = 28.5287(12), \alpha = \beta = \gamma = 90^\circ, \text{Tetragonal I4/m space group}]\) contains 8 molecules of \(\text{L1}\), 4 \(\text{CuSO}_4\), 4 molecules of coordinated \(\text{H}_2\text{O}\) and 4 molecules of coordinated DMSO. Moreover, the contents present inside and outside the pore of the cage 1 could not be assigned crystallographically and were therefore SQUEEZED\(^1\) out. SQUEEZE calculations showed the presence of 1031 electron per unit cell, meaning 515.5e per asymmetric unit, because the \(Z = 2\) for I4/m space group in this unit cell setting; this results indicates the presence of 8 molecules of DMSO, 7 molecules of MeOH and 5.35 molecules of \(\text{H}_2\text{O}\). A weight loss of 30.9\%, which may be due to the loss of 8 molecules of DMSO, 7 molecules of MeOH and 5.35 molecules of \(\text{H}_2\text{O}\) (Calc. weight loss = 35.4\%) in the temperature range of 26-159\(^\circ\)C from the crystal lattice in the thermogravimetric (TG) analyses. The difference between the calculated and observed weigh loss (35.4-30.9 = 4.5\%) could be due to the fast escape of solvents before loading the sample for TG experiments.
Table S1. Hydrogen Bonding Parameters of the metallocage 1

<table>
<thead>
<tr>
<th>D–H•••A</th>
<th>D–H (Å)</th>
<th>H•••A (Å)</th>
<th>D•••A (Å)</th>
<th>D–H•••A (°)</th>
<th>Symmetry operation for A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(7)–H(7)•••O(21)</td>
<td>0.86</td>
<td>2.07</td>
<td>2.893(5)</td>
<td>160.6</td>
<td>-1/2+x, -1/2+y, 1/2-z</td>
</tr>
<tr>
<td>N(10)–H(10)•••O(21)</td>
<td>0.86</td>
<td>2.14</td>
<td>2.954(5)</td>
<td>157.2</td>
<td>-1/2+x, -1/2+y, 1/2-z</td>
</tr>
</tbody>
</table>
Figure S4: SEM (a) and TEM (b) micrographs of xerogel of G1 obtained from MeOH diplaying the flakes and nanoparticles; corresponding EDX of nanoparticles (c) and flakes (d) are also shown.
**Figure S5.** Profile fitting of the powder diffraction pattern plot of xerogel catalyst G1 with the indexing results. Indexing was carried out using the program DICVOL06 (J. Appl. Cryst. 37, 2004, 724-731) and the profile fitting was executed with the “Lebail-Profile Fitting” module of the program FOX (J. Appl. Cryst. 35, 2002, 734-743).

Orthorhombic; 
a=29.71 (3), b= 18.89(2), c= 15.73(1)Å; 
Vol= 8825.63Å³. Space group: *Pbnb.*
Lebail-Profile fitting: Rwp= 5.63%

**Figure S6.** Rheological response of G1
Figure S7: FT-IR comparison plot of 1 and G1 under various conditions. From the comparison plot, it reveals that the chemical nature of the xerogel catalyst G1 isolated under various conditions are identical to that of 1. More interestingly, the FT-IR stretching and bending bands of the urea functionality present in the MSC 1 at 1703, 1664 cm$^{-1}$ (s, urea ν C=O) and 1604, 1561 cm$^{-1}$(s, urea δ N-H), respectively were also observed in the corresponding FT-IR spectra of G1 under all conditions. The characteristic stretching frequency band of SO$_4^{2-}$ was observed at 1116 cm$^{-1}$ for both 1 and G1 under various conditions. Moreover, the figure print region of 1 and G1 under various conditions were exactly identical, which confirms the chemical identity of 1 and G1 are same.

References