Supporting Information

Underlying Polar and Non-polar Modifications MOF-Based Factors that Influence Permanent Porosity in Porous Liquids

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S1: Chemicals

The materials were all used as received, with no further purification. p-xylene-2-sulfonate monosodium salt was provided from Eastman, and 2-aminoterephthalic acid (99 %) was obtained from Alfa Aesar. In addition, Zirconyl chloride octahydrate (ZrOCl₂·8H₂O), glacial acetic acid (CH₃COOH, 100 %), concentrated hydrochloric acid (HCl, 37 %), 1,3,5-triisopropylbenzene (TPB), 15-crown-5 (CE), phenylacetyl chloride, decanoyl chloride, valeroyl chloride, trimethylamine, triethylamine, zirconium tetrachloride, terephthalic acid, benzoic acid, 1,2,4,5-benzenetetracarboxylic acid, 4-tert-Butylcalix[6]arene, dimethylformamide (DMF), methanol (MeOH), chloroform (CHCl₃), toluene from Aldrich and Merck Chemistry and potassium permanganate (KMnO₄, 99 %) from Chem-Supply.
S2: Synthesis

\( \text{UiO-66, UiO-66-NH}_2, \text{UiO-66-SO}_3\text{H, and UiO-66-(COOH)}_2 \)

Terephthalic acid, 2-aminoterephthalic, 2-sulfoterephthalic acid monosodium salt, and 1,2,4,5-benzenetetracarboxylic acid (0.25 mmol) were dissolved DMF (0.5 mL) to synthesis UiO-66, UiO-66-NH\(_2\), UiO-66-SO\(_3\)H, and UiO-66-(COOH)\(_2\), respectively. In a separate vial, zirconyl chloride octahydrate (21 mg, 66 \(\mu\)mol) was dissolved in DMF (3 mL). The organic liker and metal solutions were mixed in a 10 mL scintillation vial, and acetic acid (0.5 mL) was added to the reaction mixture. The resulted solution was sonication for 15 min, and then it was heated at 90 °C in an oven for 6 h. The resulting product was collected by centrifugation, and then sequentially it was washed with DMF and MeOH, each at least 3 times before being dried under vacuum at 120 °C overnight.¹

2-sulfoterephthalic acid monosodium salt (\(\text{H}_2\text{BDC-SO}_3\text{Na}\)) was synthesised according to the literature.² A solution of \(\text{KmnO}_4\) (94.8 g, 600 mmol) was slowly added over 2 h to stirring water (250 mL). \(\text{p-xylene-2-sulfonate monosodium salt}\) (37.2 g, 200 mmol) was added slowly to the vigorously stirring mixture and stirred at room temperature for 3 d. The mixture was then filtered
and the supernatant acidified to pH = 2 with dropwise addition of HCl (37%). The resulting white precipitate was then separated under reduced pressure, washed with cold water and dried at 100 °C under reduced pressure to give H$_2$BDC-SO$_3$H.

![UiO-66, UiO-66-NH$_2$, UiO-66-SO$_3$H, and UiO-66-(COOH)$_2$ structures.](image)

**Figure S1.** The UiO-66, UiO-66-NH$_2$, UiO-66-SO$_3$H, and UiO-66-(COOH)$_2$ structures.

**4-tert-butylcalix[6]arene coated UiO-66 (UiO-66-Calix)**

Synthesized UiO-66 particles (0.2 g) were added to the toluene (20 mL) and mixed with 4-tert-butylcalix[6]arene (15 wt. %, mL) and sonicated for 1 h and left standing overnight. The solutions were filtered to get rid of parent solids. For porosity analysis, solutions were dried at 120 °C for 24 h under vacuum.$^3$
**Figure S2.** The UiO-66-Calix structure and synthesis procedure.

*Post-synthetic annealing UiO-66 ( UiO-66-PSE)*

Terephthalic acid (7.96 g, 47.9 mmol) with a large excess of benzoic acid (91.6 g, 749.7 mmol) were added to a mixture of DMF and water (1850:92 mL). Zirconium tetrachloride (11.1 g, 47.8 mmol) was dissolved in the resulting solution under stirring. Then it was heated at 120 °C in an oven overnight. In the next step, the resultant product was centrifuged and then washed sequentially with DMF and MeOH, and each time at least 3 times, before being dried under vacuum at 120 °C overnight. Synthesised UiO-66 particles (0.5 g) were added to DMF (10 mL), followed by stirring at room temperature for 5 days. The product was centrifuged (10 min, 20000
rpm) and washed first with DMF (3×) and then with MeOH (3×). The product was then dried in a 120 °C oven for 24 h under vacuum.\textsuperscript{4}

![UiO-66](image1)

**Figure S3.** The UiO-66-PSE structure and synthesis procedure.

**UiO-66-NH\textsubscript{2} Modifications**

**Modification of UiO-66-NH\textsubscript{2} with valeroyl acetyl group (UiO-66-NH-Val)**

UiO-66-NH\textsubscript{2} (2.0 g, 0.64 mmol) was placed in dry DMF (20 mL) with 3 Å molecular sieves (~5-10 sieve pellets dried for 2 days at 200 °C and then evacuated prior to use). While stirring, valeroyl chloride (2.0 g, 19.9 mmol) was added, and the mixture was heated at 60 °C for 16 h. The
yellow product was centrifuged (5 min, 20000 rpm), washed with DMF (3×), washed with CHCl₃ (3×), and then dried in a 130 °C oven (16 h). The product was stored in a capped vial.

**Modification of UiO-66-NH₂ with phenylacetyl group (UiO-66-NH-Phe)**

UiO-66-NH₂ (2.0 g, 0.64 mmol) was suspended in CHCl₃ (20 mL) in a 40 mL vial. While stirring, phenylacetyl chloride (1.5 mL, 11.4 mmol) and triethylamine (1.4 mL, 10 mmol) were added, and the resulting mixture was allowed to stir at room temperature for 16 h. The yellow product was centrifuged (5 min, 20000 rpm), washed with CHCl₃ (3×), and dried in a 130 °C oven for 16 h. The product was stored in a capped vial.

**Modification of UiO-66-NH₂ with decanoyl acetyl group (UiO-66-NH-Dec)**

UiO-66-NH₂ (2.0 g, 0.63 mmol) was suspended in CHCl₃ (20 mL) in a 40 mL vial. While stirring, decanoyl chloride (2.4 mL, 11.4 mmol) and triethylamine (1.4 mL, 10 mmol) were added, and the resulting mixture was allowed to stir at room temperature for 16 h. The yellow product was centrifuged (5 min, 20000 rpm), washed with CHCl₃ (3×), and dried in a 130 °C oven (16 h). The product was stored in a capped vial.
**Figure S4.** The UiO-66-NH-Val, UiO-66-NH-Phe, and UiO-66-NH-Dec structure and synthesis procedure.

**S3: Solvent**

Two solvents of CE, and TPB were chosen for porous liquid preparation. The concept behind selecting these solvents was based on their likelihood of being sterically excluded from the pores of the UiOs and possessing different hydrophobic/philic chemistry. The chosen solvents are shown in Table S1.
Table S1. Solvent properties including physiochemical properties and molecular shapes.

| Chemical Name          | Abbreviation | Type   | Shape    | Chemical formula | Van der Waals diameter (Å) |
|------------------------|--------------|--------|----------|------------------|----------------------------|
| 15-Crown-5             | CE           | Ether  | Cyclic   | C₂H₄O            | 8.76                       |
| 1,3,5-Triisopropylbenzene | TPB         | Hydrocarbon | Triangular | C₆H₃[CH(CH₂)₂]₃ | 9.06                       |
**S4: UiO-solvent combinations preparation**

The UiOs are introduced to each solvent individually and sonicated for 30 minutes to achieve initial dispersion or dissolution. UiOs were added to different solvents at different loadings of 1 wt.%, 2.5 wt.%, 5 wt.%, and 10 wt. %.
S5: Fourier-transform infrared spectroscopy (FTIR)

Fourier-transform infrared spectroscopy (FTIR) spectra were measured with a Thermo Scientific Nicolet 6700 FTIR over the wavenumber range of 400 to 2000 cm\(^{-1}\). The UiO-66 FTIR spectra indicated appropriate transmittance peaks associated with its consisting groups. The FTIR spectra of UiO-66 exhibited a peak at 552 cm\(^{-1}\) which is attributed to the asymmetric stretch of the Zr-(OC) group. The peaks at 665\% cm\(^{-1}\) and 744\% cm\(^{-1}\) correspond to the organic linker's C-H and O-H vibrations, respectively. Moreover, the symmetric stretch of COO group bonds can be characterised by a peak at 1391\%cm\(^{-1}\), whereas the peak at 1582\%cm\(^{-1}\) corresponds to the asymmetric stretching of the COO group. The peak at 1665 cm\(^{-1}\) is attributed to the stretching vibrations of the C=O group.\(^6\) Besides, the FTIR spectra of modified UiOs confirm the presence
of their respective functional groups and successful modifications. The UiO-66-PSE show a slight reduction in O-H vibrations of organic linker at 744 cm\(^{-1}\) and free C=O group at 1654 cm\(^{-1}\). Besides, there is an enhancement in the benzoate group at 717 cm\(^{-1}\). The addition of calix[6]arene to the surface of UiO-66 by grafting to the nodes is evident by greater O-H stretching at 747 cm\(^{-1}\).

FTIR spectra demonstrate the amine's presence by Ar-NH\(_2\) stretching at 1336 cm\(^{-1}\) in UiO-66-NH\(_2\). While, the intensity of the valeroyl, phenyl and decanoyl acetyl groups of UiO-66-NH-Val, UiO-66-NH-Phe, and UiO-66-NH-Dec, respectively, were not very intense and overlapped with the UiO-66-NH\(_2\) spectra as it is mostly surface modification only and FTIR can interact with a few microns of thickness from the device. In addition, the sulfonic acid by O=S=O symmetric and asymmetric stretching at 1253 cm\(^{-1}\) and 1170 cm\(^{-1}\) in UiO-66-SO\(_3\)H, and C=O stretching at 1726 cm\(^{-1}\) in UiO-66-(COOH)\(_2\) indicate the inclusion of these linkers into their respective MOF.
Figure S5. The structural groups of UiOs using FTIR spectra.
**Figure S6.** Effect of solvent exposure on the structural groups of UiO-66-Calix, and UiO-66-SO\(_3\)H using FTIR spectra.

**S6. Powder x-ray diffraction (PXRD)**

The powder X-ray Diffraction (PXRD) patterns were collected using a Bruker D8 Advance A25 XRD using Cu K\(\alpha\) radiation (40 kV, 40 mA) with the samples being scanned at 0.02° step size and 1.6 seconds count time per step over the 2\(\theta\) range 5° to 45°. During the data collection, samples were spun at a rate of 15 rpm. The UiO-66 XRD pattern agreed well with the standard pattern from literature single crystal data, with the two major peaks evidence in all samples, except the UiO-66-(COOH)\(_2\) sample which exhibits a lower level of crystallinity. Moreover, the PXRD patterns of modified UiOs were consistent with the original pattern, confirming that the crystallinity remained even after modifications.
Figure S7. The structure of UiOs using XRD patterns (UiO-66* standard pattern).
**Figure S8.** Effect of solvent exposure on the structure of UiO-66-Calix, and UiO-66-SO$_3$H using XRD patterns.

**S7. Thermogravimetric analysis (TGA)**

Thermogravimetric analysis (TGA) was conducted using a Mettler Toledo TGA/SDTA851 analyser to evaluate the thermal stability in a controlled atmosphere by measuring the change in
weight in relation to the temperature. The alumina crucibles were filled with samples and heated under a nitrogen atmosphere at a heating rate of 10 °C min$^{-1}$ from 25 °C to 900 °C. Please note that samples showed some initial mass change prior to the TGA run due to the delay in starting the analysis while queuing up on the autosampler. This could be possibly related to adsorbed moisture or some volatiles loss. The TGA results show remaining solvent removal around 200 °C, while a common and typical bimodal degradation of the framework occurred at 350 °C and 500 °C, respectively.

![Figure S9](image)

**Figure S9.** The thermal stability of UiOs using TGA.
Figure S10. Effect of solvent exposure on the thermal stability of UiO-66-Calix, and UiO-66-SO$_3$H using TGA.
S8. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Nexsa Surface Analysis System with a monochromatic Al Kα X-rays source (1486.6 eV), at a power of 144 W 72 W (6 mA × 12 kV). The core level binding energies were corrected with the C 1s binding energy of 284.8 eV. The spot size or area of analysis was 400 um² spot or 400 × 800 µm² area of analysis. Data processing was performed using Avantage software version 5. All elements were identified from the survey spectra, and atomic concentrations were calculated by combining integral peak intensities and the sensitivity factors provided by the manufacturer. The binding energies and atomic percentage of zirconium, carbon, oxygen, nitrogen agreed well with the energy levels from the literature, which confirm successful syntheses.\(^4\) Besides, since XPS
provides information about the surface composition, it is natural to see high amounts of carbon, nitrogen, and sulfur coming from calix[6]arene and amine, sulfur groups. Moreover, the presence of dicarboxylic, short and long aliphatic, and aromatic surface modifications regarding binding energies and atomic percentage comparisons are also confirmed.

![Figure S11. Binding energy levels of a) zirconium 3d, b) carbon 1s, c) oxygen 1s, and d) nitrogen 1s of UiOs using XPS.](image)

**Table S2.** Elemental composition of UiOs using XPS.
| MOFs          | Zr  | O    | C    | N    | S    |
|--------------|-----|------|------|------|------|
| UiO-66       | 5.18| 32.86| 61.34| 0.63 | ---  |
| UiO-66-NH₂   | 3.95| 29.38| 61.17| 5.5  | ---  |
| UiO-66-SO₃H | 5.36| 38.49| 49.35| 2.69 | 4.11 |
| UiO-66-(COOH)₂| 5.04| 37.81| 53.3 | 3.85 | ---  |
| UiO-66-NH-Val| 3.98| 28.08| 62.42| 5.52 | ---  |
| UiO-66-NH-Phe| 3.83| 28.25| 61.81| 6.12 | ---  |
| UiO-66-NH-Dec| 3.73| 27.91| 62.86| 5.49 | ---  |
| UiO-66-PSE   | 5.23| 31.12| 63.09| 0.56 | ---  |
| UiO-66-Calix | 2.95| 23.74| 73.23| 0.07 | ---  |
Figure S12. Binding energy levels of a) zirconium 3d, b) carbon 1s, c) oxygen 1s, d) nitrogen 1s, and e) sulfur 2p of UiO-66-Calix, and UiO-66-SO$_3$H using XPS.

Table S3. Elemental composition of UiO-66-Calix, and UiO-66-SO$_3$H using XPS.

| MOFs          | Atomic % |
|---------------|----------|
|               |          |
|                  | Zr  | O    | C    | N    | S    |
|------------------|-----|------|------|------|------|
| UiO-66-Calix     | 2.95| 23.74| 73.23| 0.07 | ---  |
| UiO-66-Calix_{EX-TPB} | 1.41| 18.18| 79.95| 0.47 | ---  |
| UiO-66-SO_{3}H   | 5.36| 38.49| 49.35| 2.69 | 4.11 |
| UiO-66-SO_{3}H_{EX-CE} | 4.8 | 36.69| 52.35| 2.52 | 3.63 |
S9. Proton nuclear magnetic resonance (\(^1\)H NMR)

Proton Nuclear Magnetic Resonance (\(^1\)H NMR) spectra were collected using a Bruker Av400X NMR, using a mixture of DMSO-d\(^6\) and D\(_2\)O/NaOD 0.8 % as solvents. The \(^1\)H NMR spectra of the digested MOFs also confirmed the surface modifications.

UiO-66: \(^1\)H NMR (500 MHz, DMSO-d\(^6\)/D\(_2\)O/NaOD 0.8 %) \(\delta\) 7.81 (s, 4H)

UiO-66-PSE: \(^1\)H NMR (500 MHz, DMSO-d\(^6\)/D\(_2\)O/NaOD 0.8 %) \(\delta\) 7.86 (s, 4H)

UiO-66-Calix: \(^1\)H NMR (500 MHz, DMSO-d\(^6\)/D\(_2\)O/NaOD 0.8 %) \(\delta\) 7.85 (s, 4H), 7.07 (s, 7H), 6.61 (s, 9H).
* The UiO-66 signal is superimposed with some other peaks, possibly from interaction with the calixarene causing a change in the chemical environment. Additional handling procedures shift the $^1$H of UiO-66 downfield.

UiO-66-NH$_2$: $^1$H NMR (500 MHz, DMSO-d$_6$/D$_2$O/NaOD 0.8 %) $\delta$ 7.65 (d, $J$ = 8.1 Hz, 1H), 7.17 (d, $J$ = 1.6 Hz, 1H), 7.09 (dd, $J$ = 8.1, 1.6 Hz, 1H).

UiO-66-NH-Val: $^1$H NMR (500 MHz, DMSO-d$_6$/D$_2$O/NaOD 0.8 %) $\delta$ 8.75 (s, 1H), 8.40 (d, $J$ = 6.5 1H), 7.92 (d, $J$ = 8.2 Hz, 1H), 7.68 (dd, $J$ = 8.1, 3.4 Hz, 1H), 7.56 (s, 1H), 7.19 (d, $J$ = 3.4 Hz, 1H), 7.11 (d, $J$ = 6.5 Hz, 1H), 2.50 – 2.43 (m, 2H), 1.36 – 1.18 (m, 6H), 0.98 – 0.95 (m, 3H)

* Some peak couplings are unresolved due to the similarity in chemical environments for $^1$H.

UiO-66-NH-Phe: $^1$H NMR (500 MHz, DMSO-d$_6$/D$_2$O/NaOD 0.8 %) $\delta$ 7.68 (d, $J$ = 8.1 Hz, 1H), 7.35 - 7.25 (m, 1H), 7.19 (s, 1H), 7.11 (dd, $J$ = 8.1, 0.7 Hz, 1H).

* Some peak couplings are unresolved due to the similarity in chemical environments for primary amine protons in the ligand UiO-66-NH$_2$ and the secondary amine protons modified UiO-66-NH-Phe. Methylene associated with UiO-66-NH$_2$-Phe not identified, potentially hidden behind a solvent peak, ca 4.2 simulated on MesTreNova for DMSO solvent.
UiO-66-NH-Dec: $^1$H NMR (500 MHz, DMSO-$d^6$/D$_2$O/NaOD 0.8 %) $\delta$ 7.89 (d, $J = 8.0$ Hz, 1H), 7.66 (d, $J = 8.1$ Hz, 1H), 7.54 (dd, $J = 8.1$, 1.4 Hz, 1H), 7.18 (d, $J = 1.4$ Hz, 1H), 7.09 (dd, $J = 8.1$, 1.7 Hz, 1H), 2.51 – 2.038 (m, $J = 15.0$, 11.6, 5.1 Hz, 7H), 2.11 – 2.05 (m, $J = 7.4$ Hz 1H), 1.71 – 1.59 (m, 2H), 1.35 (q, $J = 14.8$, 7.4 Hz, 2H), 0.95 (t, $J = 7.2$ Hz, 3H), 0.90 (t, $J = 7.4$ Hz, 3H), 0.84 (t, $J = 7.5$ Hz, 1H).

* Some peak couplings are unresolved in decanoyl-modified UiO-66-NH$_2$. $^1$H NMR prediction by MesTreNova software gave similar unresolvable multiplets.

UiO-66-SO$_3$H: $^1$H NMR (500 MHz, DMSO-$d^6$/D$_2$O/NaOD 0.8 %) $\delta$ 8.20 (d, $J = 1.6$ Hz, 1H), 7.88 (dd, $J = 7.8$, 1.6 Hz, 1H), 7.30 (d, $J = 7.8$ Hz, 1H).

UiO-66-(COOH)$_2$: $^1$H NMR (500 MHz, DMSO-$d^6$/D$_2$O/NaOD 0.8 %) $\delta$ 7.40 (s, 2H)

UiO-66-CaliX$_{EX}$-TPB: $^1$H NMR (500 MHz, DMSO-$d^6$/D$_2$O/NaOD 0.8 %) $\delta$ 7.84 (s, 10H), 7.07 (s, 9H), 6.61 (s, 12H).

* The UiO-66 signal is superimposed with some other peaks, possibly from interaction with the calixarene causing a change in the chemical environment. Additional handling procedures shift the $^1$H of UiO-66 downfield.
UiO-66-SO$_3$H$_{EX-C}$: $^1$H NMR (500 MHz, DMSO-$d^6$/D$_2$O/NaOD 0.8 %) δ 8.18 (d, $J$ = 1.6 Hz, 1H), 7.87 (dd, $J$ = 7.9, 1.7 Hz, 1H), 7.28 (d, $J$ = 7.9 Hz, 1H).

**Figure S13.** The chemical structure of UiOs using $^1$H NMR spectra.
Figure S14. Effect of solvent exposure on the chemical structure of UiO-66-Calix, and UiO-66-SO$_3$H using $^1$H NMR spectra.
S10. Low-pressure gas sorption

A Micromeritics ASAP 2420 was used to determine nitrogen adsorption isotherms at 77 K. From collected isotherms, Micromeritics software was used to calculate BET and Langmuir surface areas and also pore size distributions based on a non-local density-functional theory (NLDFT) model with a slit pore geometry. The samples have been activated overnight at 120 °C under vacuum. A significant amount of adsorption occurred in the low-pressure region, suggesting a considerable degree of microporosity, while the low hysteresis between adsorption and desorption isotherms mostly in the high-pressure regions suggested a minor degree of mesoporosity. Moreover, microporous regions exhibited multiple peaks of different pore sizes varying between 6 Å and 12 Å corresponding to the smaller tetrahedral and larger octahedral cavities.
Figure S15. The a) N₂ adsorption isotherm, and b) pore size distribution of UiOs using low-pressure gas sorption (adsorption is represented by filled markers and desorption by unfilled markers).

Table S4. The BET and Langmuir surface areas of UiOs using low-pressure gas sorption.

| Sample       | BET Surface Area (m² g⁻¹) | Langmuir Surface Area (m² g⁻¹) |
|--------------|---------------------------|--------------------------------|
| UiO-66       | 1070                      | 1420                           |
| UiO-66-PSE   | 760                       | 1000                           |
| UiO-66-Calix | 430                       | 560                            |
| UiO-66-NH₂   | 760                       | 1000                           |
| UiO-66-NH-Val| 580                       | 780                            |
Figure S16. Effect of solvent exposure on the a) N$_2$ adsorption isotherm, and b) pore size distribution of UiO-66-Calix, and UiO-66-SO$_3$H using low-pressure gas sorption (adsorption is represented by filled markers and desorption by unfilled markers).

Table S5. Effect of solvent exposure on the BET and Langmuir surface areas of UiO-66-Calix,
and UiO-66-SO$_3$H using low-pressure gas sorption.

| Sample          | BET Surface Area (m$^2$ g$^{-1}$) | Langmuir Surface Area (m$^2$ g$^{-1}$) |
|-----------------|-----------------------------------|----------------------------------------|
| UiO-66-Calix    | 430                               | 560                                    |
| UiO-66-Calix$_{\text{EX-TPB}}$ | 330                               | 450                                    |
| UiO-66-SO$_3$H  | 350                               | 460                                    |
| UiO-66-SO$_3$H$_{\text{EX-CE}}$ | 20                                | 30                                     |
S11. Scanning electron microscopy (SEM)

The scanning electron microscope (SEM) images of the UiOs and recovered samples were taken using an FEI Nova Nano scanning emission electron microscope with an accelerating voltage of 5 kV. SEM images clearly reveal UiOs with crystal structures are well-synthesised, confirming mesoscale order.
Figure S17. The morphology and size of UiOs using SEM images.
Figure S18. Effect of solvent exposure on the morphology and size UiO-66-Calix, and UiO-66-SO$_3$H using SEM images.
S12: UiO-solvent combinations stability using the natural settling and Tyndall effect of UiOs

In general, MOFs’ solubility or dispersion in solvents is limited; many of the previous failures have been attributed to the MOFs settling out of the solvent system.\textsuperscript{7-8} The gravimetric sedimentation method and visually observed observations were used to screen the stability of UiO-solvent combinations. Therefore, after ultrasonication and after standing for 24 hours, the samples were compared. Furthermore, the Tyndall effect was used to determine whether the UiO-solvent combinations were dispersion or dissolution when the samples with 1 weight percent were irradiated using laser light.\textsuperscript{9} Low concentration of porous host facilitates a quicker evaluation of dispersion/dissolution stability. As a matter of fact, high concentration increases the amount of time required for analysis due to the increase in viscosity.
Figure S19. Photographs of UiO-solvent combinations a) after ultrasonication, b) after 24 h standing, and c) irradiation with a laser (1 wt.% of UiO to solvent mass).

S13: Fluidity properties

Anton-Paar Rheometer MCR 302 was used to determine the viscosity of the samples at 298 K. This has been accomplished by running 20 measurements in sequence on each sample. Generally, a low standard deviation indicates good solvent and MOF pair compatibility, while a large standard deviation indicates an incompatibility. The viscosities of solvents and unmodified UiO PLs containing 10 wt. % of UiO to solvent mass were measured. Then, modified UiO PLs with the
same UiOs content viscosities. The viscosity results show that UiO-66-Calix$_{10\%}$ with TPB and 
UiO-66-SO$_3$H$_{10\%}$ with CE are compatible.

**Figure 20S.** Measured viscosities of UiOs PLs using unmodified and modified UiOs compared to 
solvents (10 wt.% of UiO to solvent mass).

**Table S6.** Average measured viscosities of UiOs PLs using unmodified and modified UiOs 
compared to solvents (10 wt.% of UiO to solvent mass).

| Sample                  | Viscosity (mPa s) | ±  | Difference between the solvent and PL (%) |
|-------------------------|-------------------|----|------------------------------------------|

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|          |          |          |          |
|----------|----------|----------|----------|
| TPB      | 0.1630   | 0.0042   | ---      |
| CE       | 1.2158   | 0.0047   | ---      |
| UiO-66\(_{10\%}\)\-TPB | 14.1565  | 16.7786  | 1315.6540 |
| UiO-66\(_{10\%}\)\-CE   | 6.8780   | 7.6282   | 587.7985  |
| UiO-66-Ca\(_{ix10\%}\)\-TPB | 7.5803   | 0.0525   | 658.0345  |
| UiO-66-SO\(_{3}\)\(_{10\%}\)\-CE | 1.4614   | 0.0046   | 46.1385   |
S14: Density

A Helium Pycnometer AccuPyc II 1340 was used to determine the skeletal or atomistic density of the sample based on the measured volume of known masses. Therefore, the UiOs and solvent density measurements were determined. Ideal densities of UiOs PLs containing 10 wt. % of UiO to solvent mass have been calculated using solvent and UiOs atomic density values as a perfect mixture. Finally, density measurements were conducted using UiO PLs with the same UiOs content.
**Figure S21.** Ideal and measured UiOs PLs densities (10 wt.% of UiO to solvent mass).

**Table S7.** Ideal and measured UiO PLs densities compared to measured UiOs and solvents densities (10 wt.% of UiO to solvent mass).

| Sample          | Experimental density (g cm\(^{-3}\)) | Calculation density (g cm\(^{-3}\)) | Difference (%) |
|-----------------|--------------------------------------|-------------------------------------|----------------|
| UiO-66          | 1.8189                               | ---                                 | ---            |
| UiO-66-PSE      | 1.8313                               | ---                                 | ---            |
| Material                  | Value | 10% TPB | 10% CE |
|--------------------------|-------|---------|--------|
| UiO-66-Calix             | 1.4759|         |        |
| UiO-66-NH₂               | 1.7047|         |        |
| UiO-66-NH-Val            | 1.6157|         |        |
| UiO-66-NH-Phe            | 1.7983|         |        |
| UiO-66-NH-Dec            | 1.6918|         |        |
| UiO-66-SO₃H              | 2.0349|         |        |
| UiO-66-(COOH)₂           | 2.0030|         |        |
| TPB                      | 0.8507|         |        |
| CE                       | 1.1021|         |        |
| UiO-66-Calix₁₀%·TPB      | 0.8824| 0.8883  | 0.5890 |
| UiO-66-SO₃H₁₀%·CE        | 1.1450| 1.1551  | 1.0070 |
S15: Positron annihilation lifetime spectroscopy (PALS)

Positron Annihilation Lifetime Spectroscopy (PALS) was used to investigate the average free volume sizes ($\tau_3$) and their associated intensity ($I_3$). The free volume sizes and associated relative intensity indicate the free pore sizes and the relative number of free pore elements.\textsuperscript{8, 10-11} The samples were prepared in advance of measurement and were kept at ambient temperature. The positrons are emitted from a $^{22}$NaCl point source (3.4 MBq) sealed in a mylar envelope. A half-cell (300 $\mu$l) was filled with the samples, and a positron source was placed on top using a 3 $\mu$m titanium foil in between to prevent the samples from interfering with the Mylar envelope. A coupon made of aluminium was placed on top. As a result of using a half cell, the intensities were doubled. Source correction (1.698 ns, 2.534%) was subtracted from the spectra to account for the Mylar/Ti casing (1.698 ns, 2.534 %). The spectra for each sample were analysed with LT-v9 using a minimum of five files consisting of 1 x $10^6$ integrated counts each. The Tao-Eldrup equation was used to calculate the average pore size.\textsuperscript{9, 12}

| Table S8. PALS analysis of porous liquids (10 wt.% of UiO to solvent mass). |
|---|---|---|---|---|
| Sample | Lifetimes $\tau_3$ (ns) | ± | Intensities $I_3$ (%) | ± | Pore sizes (nm) | ± |
| Material           | 3.2185 | 0.1874 | 8.3744 | 0.3810 | 0.7555 | 0.0241 |
|--------------------|--------|--------|--------|--------|--------|--------|
| Uio-66-Calix       | 4.9341 | 1.9061 | 0.3162 | 0.0557 | 0.9431 | 0.1863 |
| TPB                | 3.0015 | 0.0157 | 17.6676| 0.1278 | 0.7270 | 0.0021 |
| CE                 | 2.5954 | 0.0213 | 10.4720| 0.0875 | 0.6691 | 0.0032 |
| Uio-66-Calix_{2.5 \%}-TPB | 3.03906| 0.01242| 30.86762| 0.32741| 0.7326 | 0.0017 |
| Uio-66-Calix_{5 \%}-TPB | 3.00697| 0.0188 | 34.32793| 0.42078| 0.7283 | 0.0025 |
| Uio-66-Calix_{10 \%}-TPB | 3.03535| 0.01996| 35.1965 | 1.40844| 0.7294 | 0.0027 |
| Uio-66-SO_{3H}_{2.5 \%}-CE | 2.67415| 0.04158| 11.77986| 1.08073| 0.6184 | 0.0061 |
| Uio-66-SO_{3H}_{5 \%}-CE | 2.68121| 0.02833| 12.40977| 0.19206| 0.6825 | 0.0042 |
| Uio-66-SO_{3H}_{10 \%}-CE | 2.67117| 0.00818| 22.17735| 0.77751| 0.6810 | 0.0012 |

*Uio-66-SO_{3H} powders exhibited charging, which affects the measured intensity.*
Gravimetric sorption isotherms were measured using an Intelligent Gravimetric Analyser (IGA-001) supplied by HidenAnalytical (Ltd). A pressure transducer with a range of 0.1 – 20 Bar was used to measure the pressure, and a Grant refrigerator to maintain a constant temperature of 298
K with an accuracy of ±0.05 K. Automatic correction of buoyancy effects was carried out by the control software. Each UiO sample was in situ activated for 5 h at 120 °C and vacuum while the partial vacuum was used for all solvents and PLs before sorption measurements so that no guest molecules or vapours remained in the samples. High-pressure gas sorption measurements were carried out with UiO PLs containing 10 wt. % of UiO to solvent mass.

Figure S22. The CO₂ sorption capacity of the UiO-66-Calix, and UiO-66-SO₃H at 298 K.
### S17: Comparison of the current state-of-the-art Type II and III PLs with this study

**Table S9.** Comparison of the current state-of-the-art Type II and III PLs with this study.

| Composition | Porous host | Solvent                | Pore size (Å) | Specific surface area (m² g⁻¹) | Pore volume (cm³ g⁻¹) | Viscosity (mP.s) | Solubility /Dispersity | Stability | Sorption capacity | Ref |
|-------------|-------------|------------------------|---------------|-------------------------------|-----------------------|------------------|-----------------------|-----------|-------------------|-----|
| Two-component imine scrambled cage mixtures | 15-crown-5 (15-C-5) | 1,2,4-trichloroBenzene | 5             | 0.64 % increase               | 3.73 - 10.60 (porous host range of 2.5 -20 % w/v, 298 K) | Very high       | Stable                |           | 55 μmol g⁻¹ (Testing conditions: Scrambled cage CC3-R/PCP, porous host 20 % w/v, CO₂, 298 K, 10 bar) | 13  |
| Anionic porous organic cage | 15-crown-5 (15-C-5) | 4.022 | --- | --- | Viscous | --- | --- |           | 0.375 mmol g⁻¹ (Testing conditions: KACC/15-C-5, porous host 0.54 wt %, CO₂, 298 K, 10 bar) | 14  |
| Metal–organic polyhedra (MOP-18) | 15-crown-5 (15-C-5) | 3.8 (triangular windows) | 6.6 (square windows) | 11 % increase | 22.5 (porous host 5 wt %, 313 K) | Function of Temperature and porous host (PL-up to 30 wt % high solubility at 333 K while low solubility at 298 K. Besides, PL-5 | 0.157 mmol g⁻¹ (Testing conditions: porous host 5 wt %, CO₂) | 15 |
| Material                  | Composition     | wt % soluble at 313 K | wt % stable at 313 K | Homogeneity     | Stability       | Testing Conditions                                                                 |
|--------------------------|-----------------|-----------------------|----------------------|------------------|-----------------|-----------------------------------------------------------------------------------|
| ZIF-8                    | $[P_{6,6,6,14}]\text{NTf}_2^-$ | 3.4                   | 0.663                | ---              | Homogeneous     | Stable                                                            |
|                          |                 |                       |                      |                  |                 | 0.47 mmol g$^{-1}$ (CO$_2$) (porous host 5 wt %, 303 K, 5 bar) |
| UiO-66 nanocrystals      | $[P_{2070}]\text{IPA}$ | 5 – 9                 | ---                  | 11.2 Modulus/Pa (Viscous) | Homogeneous     | Extremely stable                                                         |
|                          |                 |                       |                      |                  |                 | 1.66 mmol g$^{-1}$ (Testing conditions: CO$_2$, 298 K, 10 bar) |
| ZIF-67                   | $[C_6\text{BIm}_2]\text{NTf}_2^-$ | 7.853                 | 1308.6               | 0.9595           | Homogeneous     | Stable                                                            |
|                          |                 |                       |                      |                  |                 | 1896.7 (porous host 10 wt %, 298 K)                                      |
|                          |                 |                       |                      |                  |                 | 9.542 mmol g$^{-1}$ (Testing conditions: CO$_2$, 298 K, 1 bar) |
| H-ZSM-5                  | $[P_{66614}]\text{Br}$ | 5.4 – 5.6             | 362.7                | 0.304            | Homogeneous     | Stable                                                            |
|                          | Aliquant$_{336}$|                       |                      |                  |                 | 9550 (298 K)                                   |
|                          | [Cl] $[P_{4442}]\text{Suc}$ |                       |                      |                  |                 | 810 (363 K)                                   |
|                          |                 |                       |                      |                  |                 | 2.83 wt % (H-ZSM-5/$[P66614]\text{Br}$)                                      |
|                          |                 |                       |                      |                  |                 | 3.31 wt % (H-ZSM-5/Aliquant$_{336}$/Cl)                                     |
|                          |                 |                       |                      |                  |                 | 1.75 wt % (H-ZSM-5/$[P4442]\text{Suc}$)                                     |
|                          |                 |                       |                      |                  |                 | (Testing conditions: CO$_2$, 298 K, 10 bar)                                  |
| All modified with PDMS  | Poly(dimethyl siloxane) (PDMS4k) | ---                  | ---                  | ---              | Homogeneous     | Stable                                                            |
|                          |                 |                       |                      |                  |                 | 6.85 (UiO-66(484)@xPDMS/PDMS4k, porous host 33.3 wt %)                        |
|                          |                 |                       |                      |                  |                 | 7.57 (UiO-66(185)@xPDMS/PDMS4k, porous host 33.3 wt %)                        |
|                          |                 |                       |                      |                  |                 | 20.84 (UiO-66(185)@xPDMS/PDMS4k, porous host 50 wt %)                         |
|                          |                 |                       |                      |                  |                 | ~293 K                                                      |
|                          |                 |                       |                      |                  |                 | 6.65 mmol g$^{-1}$ (UiO-66(185)@xPDMS/PDMS4k, porous host 50 wt %)            |
|                          |                 |                       |                      |                  |                 | 1.375 mmol g$^{-1}$ (UiO-66-NH$_2$@xPDMS/PDMS4k, porous host 50 wt %)        |
|                          |                 |                       |                      |                  |                 | 1.295 mmol g$^{-1}$ (UiO-66-Br$_2$@xPDMS/PDMS4k, porous host 50 wt %)        |
|                          |                 |                       |                      |                  |                 | 0.554 mmol g$^{-1}$ (UiO-66-NH$_2$@xPDMS/PDMS4k, porous host 50 wt %)          |
| Material                        | Type                              | Viscosity     | 
|--------------------------------|-----------------------------------|---------------|
| ZIF-8 modified with branched polyethyleneimine (BPEI) | Branched polyethyleneimine (BPEI) | 8.52          |
|                                |                                   | 1903.7        |
|                                |                                   | 0.716         |
|                                |                                   | 1700 (298 K)  |
|                                | Homogeneous                       | Stable        |
| ZIF-8                          | Glycol-2-methylimidazole-water    | ---           |
|                                |                                   | ---           |
|                                |                                   | ---           |
|                                | Low viscosity                     | Low           |
| UiO-66-Calix                   | 1,3,5-Triisopropylbenzene         | 430           |
|                                |                                   | 5-20          |
|                                |                                   | 7.5803        |
|                                | High                              | Stable        |
|                                | (porous host 10 wt %, 298 K)      |               |
| UiO-66-SO3H                    | 15-crown-5                        | 350           |
|                                |                                   | 5-20          |
|                                |                                   | 1.4614        |
|                                | Homogeneous                       | Stable        |
|                                | (porous host 10 wt %, 298 K)      |               |
| PDMS4k, porous host 50 wt%     |                                   |               |
|                                | (Testing conditions: CO₂, 273 K, 1 bar) |               |
|                                | 0.259 mmol g⁻¹ (ZIF-8-g-BPEI/BPEI, porous host 30 wt %) | 21 |
|                                | (Testing conditions: porous host 10 30 wt %, CO₂, 298 K, 10 bar) | |
|                                | 1.47 mol L⁻¹ (Testing conditions: ZIF-8 10 wt %/MIM 25 wt %+ water 40 wt %+glycol 35 wt %, CO₂, 303.15 K, 1 bar) 22 | |
|                                | 1.47 mol L⁻¹ (Testing conditions: ZIF-8 10 wt %/MIM 25 wt %+ water 40 wt %+glycol 35 wt %, CO₂, 303.15 K, 1 bar)  | |
|                                | This work                         |               |
|                                | 1.47 mol L⁻¹ (Testing conditions: ZIF-8 10 wt %/MIM 25 wt %+ water 40 wt %+glycol 35 wt %, CO₂, 303.15 K, 1 bar)  | |
|                                | This work                         |               |


**Author Contributions**

H.M. led the project administration, conceptual and experimental design, analysis, interpretation of results, and writing the draft. N.E. participated in UiO synthesis, modifications and characterisations’ interpretations. C.M.D. and D.A. lead the experimental design and data curation of PALS experiments presented. S.J.D.S., X.M. and M.R.H. contributed to the project administration, conceptual and experimental design, analysis, and interpretation of results.

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