Supporting Information

Modular Type III Porous Liquids based on Porous Organic Cage Microparticles

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1. General synthetic and analytical methods

**Materials:** 1,3,5-triformylbenzene (TFB) was purchased from Manchester Organics, UK. Other chemicals were purchased from Sigma-Aldrich. These chemicals were used as received. Oils and ionic liquids were purchased either from TCI UK or Sigma-Aldrich, listed below:

**Table S1:** List of liquids screened.

| Chemical                                      | Supplier       |
|-----------------------------------------------|----------------|
| Silicone oil (5 cSt)                          | Sigma Aldrich  |
|                                               | 317667         |
| Silicone oil AR 20                            | Sigma Aldrich  |
|                                               | 10836          |
| Olive oil                                     | Sigma Aldrich  |
|                                               | 01514          |
| Sunflower oil                                 | Sigma Aldrich  |
|                                               | 88921          |
| Paraffin Oil                                  | Sigma Aldrich  |
|                                               | 18512          |
| Halocarbon oil 27®                            | Sigma Aldrich  |
|                                               | H8773          |
| Fomblin Y®                                    | Sigma Aldrich  |
|                                               | 317926         |
| Genosorb 1753®                                | Sigma Aldrich  |
|                                               | 445878         |
| 15-crown-5                                    | Sigma Aldrich  |
|                                               | 188832         |
| 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][NTf₂]) | Sigma Aldrich  |
|                                               | 711713         |
| 1-butylpyridinium bis(trifluoromethylsulfonyl)imide ([BPy][NTf₂]) | TCI UK         |
|                                               | B5571          |
| Trihexyltetradecylphosphonium bis(trifluoromethanesulfonyl)imide ([P₆₆₆₁₄][NTf₂]) | Sigma Aldrich  |
|                                               | 50971          |
| benzyl(ethyl)dimethyl ammonium bis(trifluoro- methanesulfonyl)imide ([BEMA][NTf₂]) | TCI UK         |
|                                               | B5427          |
**Nuclear Magnetic Resonance (NMR):** \(^1\)H NMR spectra were recorded in deuterated dichloromethane or deuterated chloroform at 400 MHz using a Bruker Avance 400 NMR spectrometer. Chemical shifts are reported in ppm (δ) with reference to internal residual protonated species of the deuterated solvent.

**Powder X-ray diffraction (PXRD):** PXRD patterns were collected in transmission mode on samples loaded in borosilicate glass capillaries on a Panalytical Empyrean diffractometer, equipped with a capillary spinner, X-ray focusing mirror, and PIXcel detector, using Cu-Kα (λ = 1.541 Å) radiation. Unless stated, PXRD patterns were recorded at room temperature. Diffraction patterns were measured over the 2θ range 2–50°, in 0.013° steps, for 30-60 minutes.

**Scanning electron microscope (SEM):** SEM characterizations were performed on a Hitachi S4800 scanning electron microscope. Samples were prepared by depositing nanocrystals onto an adhesive high-purity carbon tab on 15mm Hitachi aluminium stubs, and coated in chromium before imaging.

**Dynamic light scattering (DLS):** DLS measurements were performed on a Zetasizer instrument. Samples were prepared by dispersing and sonicating a small amount of nanocrystals (0.5 mg) in 20 mL dichloromethane (DCM).

**Static Light Scattering (SLS):** SLS measurements were carried out using a Malvern Instruments Mastersizer 3000. Samples were dispersed in ethanol before dropping into sample chamber with constant stirring to ensure scattering intensity was within range.

**Gas sorption analysis:** Gas uptakes of the Type III porous liquids were measured on a Quantachrome Nova 4200e (Figure S1). The adsorption program, corresponding setup and measuring conditions were studied and benchmarked to known literature uptakes of [BMIM][NTf₂] and 15-crown-5 (Table S2).\(^{[1,2]}\) Method - 0.5 mL sample was injected into a 9 mm sample cell with large bulb (P/N: 74064) and a glass-coated stirrer bar was added. The sample was degassed under vacuum with stirring overnight at room temperature and backfilled with helium before being removed from the degassing station. A filler rod (P/N: 74105-L) was used with the sample cell during sorption measurements at room temperature and the adsorption settings were as follows: 20 pressure points from 0.05 to 1.0 bar in 0.05 increments; pressure tolerance = 0.05 mmHg; equilibration time = 1800 seconds; equilibration timeout = 5400 seconds. Dispersions were kept stirring during all measurements. If a higher temperature was needed during adsorption, a heating block was used.
**Figure S1:** Quantachrome Nova 4200e and configuration used to measure gas uptake in liquid samples.

**Table S2:** Comparisons of CO₂ uptakes from literature to those measured with the Quantachrome Nova 4200e

| Sample       | Literature HCO₂ (bar)       | Calculated Literature CO₂ Uptake (μmol/g L) | Average Measured Experimental Uptake (μmol/g L) |
|--------------|-----------------------------|-------------------------------------------|-----------------------------------------------|
| [BMIM][NTf₂] | 33.0±0.3 (298 K, 1 bar)     | 71-73                                     | 75.1 ± 6.8                                    |
| 15-crown-5   | 45.8 (308 K, 1 bar)         | 85-113                                    | 78.5 ± 3.1                                    |

Gas uptake of the solid microparticles were measured using a Micromeritics (RTM) ASAP 2020 volumetric adsorption analyser. The uptakes from two measurements at 1 bar were used to calculate an expected uptake for the solid present in the dispersions. Powder samples were degassed offline at 90 °C for 15 h under dynamic vacuum (10⁻⁵ bar) before analysis, followed by degassing on the analysis port under vacuum, also at 90 °C.

**Viscosity measurements:** Viscosity measurements were carried out with a calibrated RheoSense μVISC viscometer (10-2000 cp) at room temperature. Measurements were performed three times and the average viscosity was reported.

**Thermal gravimetric analysis (TGA):** TGA was performed on a Q5000IR with an automated vertical overhead thermobalance. Samples were heated in an aluminium pan at a ramp rate of 10 °C/min up to 600 °C under a dry nitrogen flow.

**Lumisizer:** Stability of dispersions study was performed on a LUMiSizer® dispersion analyser, using transparent sample cells (2 mm, rectangular synthetic cell 110-131 mm). Measurement conditions were at 25 °C with a wavelength of 865 nm, with speed and scan settings as 2000 revolutions per minute (RPM) and 700 x 30 (or 1000 x 21) second intervals for a total run time of 350 min.
2. Synthesis and characterization of porous organic cage microparticles

2.1 Formation of CC3-R/CC3-S microparticles

**Synthesis of CC3-R and CC3-S:** CC3-R and CC3-S were synthesized according to a previously reported procedure.\[^3\] 1,3,5-Triformylbenzene (TFB, 2.5 g, 15.418 mmol, 4 eq.) was added to a round bottom flask, and DCM (50 mL) was then slowly added to avoid disturbance of the TFB. (1R, 2R)-Cyclohexane-1,2-diamine (R,R-CHDA, 2.64 g, 23.19 mmol, 6 eq.) or (1S, 2S)-cyclohexane-1,2-diamine (S,S-CHDA, 2.64 g, 23.19 mmol, 6 eq.) was dissolved in DCM (50 mL) and the solution was slowly added to the flask with a pipette to form a layer. Trifluoroacetic acid (50 μL) was added and the mixture was left covered for five days. The crystals that formed were collected by filtration and washed with a mixture solvent (95% ethanol + 5% DCM) to afford CC3-R or CC3-S as off-white crystals (3.5 g, 81%). \[^1\] H NMR (400MHz, CDCl\(_3\)) δ 8.13 (12H, s, CH=N), 7.85 (12H, s, ArH), 3.34 (12H, m, CHN), 1.9-1.4 (48H, m, CH and CH\(_2\) groups). The NMR data was in accordance with the literature values.\[^3\]

**CC3-R/CC3-S microparticles:** CC3-R/CC3-S microparticles from Table entries 1 to 5 were all synthesized using the same procedure as follows: A solution (1.5 mg/mL) of CC3-R (1.35 g) in DCM (900 mL) was poured directly into a solution (1.5 mg/mL) of CC3-S (1.35 g) in DCM (900 mL) with overhead mechanical stirring. The mixture was stirred for a further 10 minutes to afford a white suspension. Fine, colourless particles were then collected by filtering the suspension through a nylon membrane with 0.45 μm pore diameter, and dried in a vacuum oven at 90 °C overnight (2.32 g, 86%). Table 1 entry 6 CC3-R/CC3-S microparticles with an octahedral morphology were synthesized in a similar manner, except that the CC3-R solution was added into the CC3-S solution at a controlled rate of 0.66 mL/min. CC3-R/CC3-S microparticles were characterised by PXRD, SEM and DLS.

![Figure S2](image-url): DLS of CC3-R/CC3-S microparticles in DCM (Table 1, entries 1-6).
Figure S3: PXRDs of CC3-R, CC3-S, and CC3-R/CC3-S microparticles (Table 1, entries 1-6).
Figure S4: SEM images of CC3-R/CC3-S microparticles (Table 1, Entries 1-6)
Figure S5: Representative CO₂ and CH₄ adsorption (filled) and desorption (empty) isotherms in solid CC3-R/CC3-S microparticles.
1,1',1''-(Benzene-1,3,5-triyl)tris(N-cyclohexylmethanimine): The control molecule 1,1',1''-(benzene-1,3,5-triyl)tris(N-cyclohexylmethanimine) was synthesized according to a previously reported method.[4] Cyclohexylamine (1.09 mL, 9.25 mmol, 3 eq.) was added to a solution of TFB (0.5 g, 3.08 mmol, 1 eq.) in DCM (50 mL), and the resulting solution was stirred at room temperature overnight before being concentrated in vacuo. The resulting solid was dried in a vacuum oven at 90 °C to afford the desired product as a colourless powder (1.15 g, 92%). \[\text{H NMR (400 MHz, CDCl}_3\] \(\delta\) H 8.36 (3H, s, N=CH), 8.10 (3H, s, ArH), 3.19 (3H, tt, \(J = 4.0 \text{ Hz}, \text{NCH}\)), 1.82 (6H, dt, \(J = 3.0 \text{ Hz}, \text{cHex}\)), 1.75 - 1.66 (9H, m, cHex), 1.57 (6H, qd, \(J = 3.5 \text{ Hz}, \text{cHex}\)), 1.36 (6H, qt, \(J = 3.0 \text{ Hz}, \text{cHex}\)), 1.30 - 2.20 (3H, m, cHex). The NMR data was in accordance with the literature values.[4]

2.2 Synthesis of CC3-R/CC19-S and CC3-R/CC15-S microparticles

Synthesis of CC15-S: CC15-S was synthesized according to a previously reported method.[6] A solution of S,S-CHDA (3.06 g, 26.8 mmol, 6 eq.) in DCM (35 mL) and molecular sieves (0.7 g, 3 Å) were added to 1,3,5-triacetylbenzene (TAB, 3.65 g, 17.9 mmol, 4 eq.) in a round bottom flask. The flask was equipped with reverse Dean-Stark apparatus, which was charged with DCM, and the solution was heated to 45 °C and kept stirring for 24 h before being allowed to cool to room temperature. The molecular sieves were removed by filtration and the resulting pale yellow solution was evaporated to obtain crude CC15-S. The crude product was washed with diethyl ether (3 x 50 mL) before dissolving in the minimum volume of 1:1 DCM/hexane possible, and the DCM was carefully removed under reduced pressure to precipitate CC15-S. The resulting pale cream solid was collected by filtration and dried in a vacuum oven to yield pure product (3.28 g, 82%). \[\text{H NMR (400 MHz, CDCl}_3\] \(\delta\) H 8.05 (12H, s, ArH), 3.82 (12H, m, N-CH), 2.1 (36H, s, CH$_3$), 1.84 (12H, m, CH$_\text{Hex}$), 1.69 (12H, m, CH$_\text{Hex}$), 1.65 (12H, m, CH$_\text{Hex}$), 1.49 (12H, m, CH$_\text{Hex}$). Data in accordance with literature values.[6]

CC3-R/CC15-S microparticles: CC3-R/CC15-S microparticles were prepared in a slightly modified way to CC3-R/CC3-S, with the solvent changed to DCM and methanol in 1:1 ratio.

Synthesis of CC19-S: 2-Hydroxy-1,3,5-benzenetricarbaldehyde (3.19 g, 17.9 mmol, 4 eq.) and S,S-CHDA (3.06 g, 26.8 mmol, 6 eq.) were dissolved in methanol (500 mL) and stirred at room temperature for 3–5 days. Once the reaction had reached completion, CC19-S was obtained by filtration and washed with ethyl acetate (3 x 50 mL) before redissolving in DCM. The solvent was then removed under reduced pressure to afford pure CC19-S as a yellow solid (3.42 g, 65%). \[\text{H NMR (400 MHz, CDCl}_3\] \(\delta\) H 8.58 (4H, m, N=CH), 8.26 (4H, m, N=CH), 8.06 (4H, m, N=CH), 7.87 (8H, m, ArH), 3.30 (12H, m, N-CH), 1.75 (48H, m, CH$_\text{Hex}$), 1.45 (s(b), OH). Data in accordance with literature values.[5]

CC3-R/CC19-S microparticles: CC3-R/CC19-S microparticles were prepared using the same method as for CC3-R/CC3-S.
Figure S6: SLS of CC3-R/CC15-S microparticles in EtOH (top) and DLS of CC3-R/CC19-S microparticles in DCM (bottom).
Figure S7: PXRDs of CC3, CC3-R/CC3-S microparticles, CC15-S, CC3-R/CC15-S microparticles (Table 1, entry 7), CC19-S, and CC3-R/CC19-S microparticles (Table 1, entry 8).
**Figure S8**: SEM images of CC3-R/CC15-S microparticles (left) and CC3-R/CC19-S microparticles (right) (Table 1, entries 7-8).
3. Screening of Type III CC3-R/CC3-S microparticle porous liquids and gas sorption studies

Representative preparations of the dispersions are as follows:

**Oil-based systems:** The cages or microparticles were desolvated at 90 °C overnight in a vacuum oven before the direct addition of the as bought liquids, and the resulting suspension was sonicated for 10 minutes until a homogenous dispersion was formed.

**Ionic liquid systems:** CC3-R/CC3-S microparticles were desolvated as above, and [BPy][NTf₂] was dried at 80 °C in a separate vacuum oven for at least 24 hours before mixing with CC3-R/CC3-S microparticles. Then the weighed CC3-R/CC3-S and [BPy][NTf₂] were put into a glass vial with cap and sonicated for at least 10 minutes until a homogenous dispersion was formed.

For a 5 wt. % dispersion: 150 mg microparticles dispersed in 2.85 g liquid; for a 12.5 wt. % dispersion: 200 mg microparticles dispersed in 1.4 g liquid; for a 20 wt. % dispersion: 100 mg microparticles dispersed in 0.4 g liquid.

The dispersions were then transferred to sorption tubes using wide-bore needles fitted to a syringe for gas uptake measurements.
Table S3: Summary of gas uptakes of liquids and corresponding dispersions. The number in parentheses indicates which batch of microparticles from Table 1 was used for the measurement. The average uptake is based on a minimum of 2, typically 3, measurements with the standard deviation also shown.

| Disp. No. | Solid      | Liquid  | Loading (wt. %) | Gas | Average Uptake, 298-303 K, 1 bar (μmol/gₐ unless otherwise stated) | Average increase in uptake over base liquid(μmol/gₐ) |
|-----------|------------|---------|-----------------|-----|---------------------------------------------------------------|--------------------------------------------------------------|
| 1         | CC3-R/S    | -       | -               | CO₂ | 1792 ± 72 μmol/gₐ                                            | -                                                            |
| 2         | -          | Silicone oil | -               | CO₂ | 84.8 ± 2.4                                                   | -                                                            |
| 3         | CC3-R/S (2) | Silicone oil | 12.5            | CO₂ | 199.5 ± 1.9                                                  | 114                                                          |
| 4         | CC3-R/S (3) | Silicone oil | 12.5            | CO₂ | 198.0 ± 3.8                                                  | 113                                                          |
| 5         | CC3-R/S (2) | Silicone oil | 20              | CO₂ | 279.7                                                        | 195                                                          |
| 6         | CC3-R/S (6) | Silicone oil | 12.5            | CO₂ | 199.8 ± 6.4                                                  | 115                                                          |
| 7         | Control molecule | Silicone oil | 12.5          | CO₂ | 83.7 ± 8.7                                                   | 0                                                            |
| 8         | CC3-R/S    | -       | -               | CH₄ | 1064 ± 77 μmol/gₐ                                            | -                                                            |
| 9         | -          | Silicone oil | -               | CH₄ | 17.1 ± 1.4                                                   | -                                                            |
| 10        | CC3-R/S    | Silicone oil | 12.5            | CH₄ | 105.2 ± 16.5                                                 | 88                                                           |
| 11        | CC3-R/S    | Silicone oil | 20              | CH₄ | 121.7                                                        | 104                                                          |
| 12        | CC3-R      | Silicone oil | 12.5            | CO₂ | 185.2 ± 13.0                                                 | 100                                                          |
| 13        | -          | Silicone oil AR 20 | -           | CO₂ | 61.0 ± 1.1                                                   | -                                                            |
| 14        | CC3-R/S (3) | Silicone oil AR 20 | 12.5          | CO₂ | 181.8 ± 3.8                                                  | 120                                                          |
| 15        | -          | Olive Oil | -               | CO₂ | 61.1 ± 1.8                                                   | -                                                            |
| 16        | CC3-R/S (3) | Olive Oil | 12.5            | CO₂ | 77.2 ± 4.5                                                   | 16                                                           |
| 17        | -          | Sunflower Oil | -              | CO₂ | 74.0 ± 6.3                                                   | -                                                            |
|    |       |                |     |   |    |   |
|----|-------|----------------|-----|---|----|---|
| 18 | CC3-R/S (3) | Sunflower Oil | 12.5 | CO₂ | 133.2 ± 1.4 | 59 |
| 19 | -     | Paraffin Oil  | -   | CO₂ | 41.9 ± 0.1  | -  |
| 20 | CC3-R/S (3) | Paraffin Oil  | 12.5 | CO₂ | 65.0 ± 5.3  | 23 |
| 21 | -     | Halocarbon 27 | -   | CO₂ | 37.0 ± 3.1  | -  |
| 22 | CC3-R/S (3) | Halocarbon 27 | 5   | CO₂ | 74.8 ± 8.1  | 37 |
| 23 | -     | Fomblin Y    | -   | CO₂ | 28.5 ± 1.5  | -  |
| 24 | CC3-R/S (3) | Fomblin Y    | 5   | CO₂ | 67.0 ± 0.9  | 38 |
| 25 | -     | Genosorb 1753| -   | CO₂ | 104.0 ± 4.4 | -  |
| 26 | CC3-R/S (3) | Genosorb 1753| 12.5 | CO₂ | 85.0 ± 16.0 | 0  |
| 27 | -     | 15-crown-5   | -   | CO₂ | 78.5 ± 3.1  | -  |
| 28 | CC3-R/S (3) | 15-crown-5   | 12.5 | CO₂ | 94.0 ± 7.7  | 15 |
| 29 | -     | [BMIM][NTf₂] | -   | CO₂ | 75.1 ± 6.8  | -  |
| 30 | CC3-R/S (3) | [BMIM][NTf₂] | 12.5 | CO₂ | 80.0 ± 1.2  | 5  |
| 31 | -     | [BPy][NTf₂]  | -   | CO₂ | 78.3 ± 4.5  | -  |
| 32 | CC3-R/S (4) | [BPy][NTf₂]  | 5   | CO₂ | 111.4 ± 6.4 | 36 |
| 30 | CC3-R/S (4) | [BPy][NTf₂]  | 12.5 | CO₂ | 170.1 ± 7.7 | 92 |
| 31 | CC3-R/S (5) | [BPy][NTf₂]  | 12.5 | CO₂ | 172.1 ± 3.6 | 94 |
| 32 | CC3-R/S (5) | [BPy][NTf₂]  | 20  | CO₂ | 209.8 ± 6.7 | 131|
| 33 | Control molecule | [BPy][NTf₂] | 5   | CO₂ | 74.58   | 0  |
| 34 | -     | [BPy][NTf₂]  | -   | CH₄ | 7.94 ± 0.12 | -  |
| 35 | CC3-R/S (4) | [BPy][NTf₂]  | 5   | CH₄ | 36.02 ± 0.32 | 28 |
| 36 | CC3-R/S (4) | [BPy][NTf₂]  | 12.5 | CH₄ | 71.31 ± 3.94 | 63 |
|   | System                        | Compound 1 | Compound 2 | CO₂ (μmol)  | Pressure (bar) |
|---|-------------------------------|------------|------------|-------------|---------------|
| 37| CC3-R/S (S)                   | [BPy][NTf₂]| CH₄        | 103.78 ± 0.71 | 95            |
| 38| CC3-S                         | [BPy][NTf₂]| CO₂        | 164.8 ± 3.67  | 86            |
| 39| -                             | [P₆₆₆₁₄][NTf₂]| CO₂     | 77.6         | -             |
| 40| CC3-S                         | [P₆₆₆₁₄][NTf₂]| CO₂     | 155.7 ± 3.67  | 78            |
| 41| -                             | [BEMA][NTf₂]| CO₂     | 86.5 ± 3.67   | -             |
| 42| CC3-S                         | [BEMA][NTf₂]| CO₂     | 144.9 ± 3.67  | 58            |
| 43| CC3-R/CC15-S                  | Silicone oil| CO₂     | 68.5 ± 1.3    | -16           |
| 44| CC3-R/CC15-S                  | Silicone oil| CH₄     | 30.2 ± 0.3    | 13            |
| 45| CC3-R/CC19-S                  | Silicone oil| CO₂     | 210.3 ± 3.3   | 125           |
| 46| CC3-R/CC19-S                  | Silicone oil| CH₄     | 117.4 ± 21.4  | 100           |
Figure S9a: CO$_2$ adsorption isotherms of silicone oil and the corresponding 12.5 wt. % dispersions of CC3-R/CC3-S microparticles, homochiral CC3-R, and the non-porous control molecule. The numbers in parentheses indicate the batch of microparticles used from Table 1.

Figure S9b: CO$_2$ adsorption isotherms of silicone oil AR 20 and the corresponding 12.5 wt. % dispersions of CC3-R/CC3-S microparticles. The numbers in parentheses indicate the batch of microparticles used from Table 1.
Figure S9c: CO₂ adsorption isotherms of olive oil and the corresponding 12.5 wt. % dispersions of CC3-R/CC3-S microparticles. The numbers in parentheses indicate the batch of microparticles used from Table 1.

Figure S9d: CO₂ adsorption isotherms of sunflower oil and the corresponding 12.5 wt. % dispersions of CC3-R/CC3-S microparticles. The numbers in parentheses indicate the batch of microparticles used from Table 1.
Figure S9e: CO₂ adsorption isotherms of paraffin oil and the corresponding 12.5 wt. % dispersions of CC3-R/CC3-S microparticles. The numbers in parentheses indicate the batch of microparticles used from Table 1.

Figure S9f: CO₂ adsorption isotherms of halocarbon 27 and the corresponding 5 wt. % dispersions of CC3-R/CC3-S microparticles. The numbers in parentheses indicate the batch of microparticles used from Table 1.
Figure S9g: CO₂ adsorption isotherms of Fomblin Y and the corresponding 5 wt. % dispersions of CC3-R/CC3-S microparticles. The numbers in parentheses indicate the batch of microparticles used from Table 1.

Figure S9h: CO₂ adsorption isotherms of Genosorb 1753 and the corresponding 12.5 wt. % dispersions of CC3-R/CC3-S microparticles. The numbers in parentheses indicate the batch of microparticles used from Table 1.
Figure S9i: \( \text{CO}_2 \) adsorption isotherms of 15-crown-5 and the corresponding 12.5 wt. % dispersions of CC3-R/CC3-S microparticles. The numbers in parentheses indicate the batch of microparticles used from Table 1.

Figure S9j: \( \text{CO}_2 \) adsorption isotherms of [BMIM][NTf_2] and the corresponding 12.5 wt. % dispersions of CC3-R/CC3-S microparticles. The numbers in parentheses indicate the batch of microparticles used from Table 1.
**Figure S9k**: CO$_2$ adsorption isotherms of [BPy][NTf$_2$] and the corresponding 12.5 wt. % dispersions of CC3-R/CC3-S microparticles. The numbers in parentheses indicate the batch of microparticles used from Table 1.

**Figure S9l**: CO$_2$ adsorption isotherms of [P$_{66614}$][NTf$_2$] and the corresponding 12.5 wt. % dispersion of CC3-S.
Figure S9m: CO₂ adsorption isotherms of [BEMA][NTf₂] and the corresponding dispersion of CC3-S.
The theoretical maximum CO₂ uptake for the dispersion was calculated based on the ratio of CC₃-R/CC₃-S microparticles (average 1792 μmol/gₜ) and liquid present in that dispersion.

**Table S4:** Comparisons between the average experimental CO₂ uptakes and the theoretical maximum uptakes of the dispersions. The numbers in parentheses indicate the batch of microparticles used from Table 1.

| Solid | Liquid           | Loading (wt. %) | Average Liquid Uptake (μmol/gₖ) | Average Dispersion Uptake (μmol/gₖ) | Calculated uptake for dispersion (μmol/g) | Percentage Porosity Obtained (%) (Measured vs Calculated) |
|-------|------------------|----------------|---------------------------------|-----------------------------------|------------------------------------------|----------------------------------------------------------|
| CC₃-R/S (3) | Silicone oil    | 12.5           | 85                             | 198                               | 298                                      | 66                                                       |
| CC₃-R/S (2) | Silicone oil    | 20             | 85                             | 280                               | 426                                      | 66                                                       |
| CC₃-R/S (3) | Silicone oil AR 20 | 12.5        | 61                             | 182                               | 277                                      | 66                                                       |
| CC₃-R/S (3) | Olive oil       | 12.5           | 61                             | 77                                | 277                                      | 28                                                       |
| CC₃-R/S (3) | Sunflower oil   | 12.5           | 74                             | 133                               | 289                                      | 46                                                       |
| CC₃-R/S (3) | Paraffin oil    | 12.5           | 42                             | 65                                | 261                                      | 25                                                       |
| CC₃-R/S (3) | Halocarbon      | 5              | 37                             | 75                                | 125                                      | 60                                                       |
| CC₃-R/S (3) | Fomblin Y       | 5              | 29                             | 67                                | 117                                      | 57                                                       |
| CC₃-R/S (3) | Genosorb 1753   | 12.5           | 104                            | 85                                | 315                                      | 27                                                       |
| CC₃-R/S (3) | 15-crown-5      | 12.5           | 79                             | 94                                | 293                                      | 32                                                       |
| CC₃-R/S (3) | [BMIM][NTf₂]    | 12.5           | 75                             | 80                                | 290                                      | 28                                                       |
| CC₃-R/S (4) | [BPy][NTf₂]     | 5              | 78                             | 111                               | 164                                      | 68                                                       |
| CC₃-R/S (5) | [BPy][NTf₂]     | 12.5           | 78                             | 172                               | 292                                      | 59                                                       |
| CC₃-R/S (5) | [BPy][NTf₂]     | 20             | 78                             | 210                               | 421                                      | 50                                                       |
4. Characterization and Properties of Type III CC3-R/CC3-S microparticle based porous liquids

4.1 Gas uptake vs. CC3-R/CC3-S concentration

Table S5: Parameters of linear fit for gas uptakes at different CC3-R/CC3-S concentrations.

| Equation       | CC3-R/CC3-S in silicone oil - CO₂ | CC3-R/CC3-S in [BPy][NTf₂] - CO₂ | CC3-R/CC3-S in silicone oil - CH₄ | CC3-R/CC3-S in [BPy][NTf₂] - CH₄ |
|----------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| Plot           | y = a + b*x                        |                                   |                                   |                                   |
| Intercept      | 88.90 ± 4.480                     | 82.50 ± 1.799                     | 19.50 ± 4.459                     | 9.710 ± 1.795                    |
| Slope          | 9.459 ± 0.3717                    | 6.944 ± 0.1492                    | 5.228 ± 0.3275                    | 4.6759 ± 0.1489                  |
| Residual Sum of Squares | 63.45                              | 10.23                             | 21.90                             | 10.19                             |
| Pearson's r    | 0.9985                            | 0.9995                            | 0.9980                            | 0.9990                            |
| R-Square (COD) | 0.9969                            | 0.9991                            | 0.9961                            | 0.9980                            |
| Adj. R-Square  | 0.9954                            | 0.9986                            | 0.9921                            | 0.9970                            |
Figure S10: CO$_2$ adsorption isotherms of [BPy][NTf$_2$] and the corresponding 5 wt. %, 12.5 wt. % and 20 wt. % dispersions of CC3-R/CC3-S microparticles. The numbers in parentheses indicate the batch of microparticles used from Table 1.

Figure S11: CH$_4$ adsorption isotherms of [BPy][NTf$_2$] and the corresponding 5 wt. %, 12.5 wt. % and 20 wt. % dispersions of CC3-R/CC3-S microparticles. The numbers in parentheses indicate the batch of microparticles used from Table 1.
Figure S12: CO$_2$ adsorption isotherms of silicone oil and the corresponding 5 wt. %, 12.5 wt. % and 20 wt. % dispersions of CC3-R/CC3-S microparticles.

Figure S13: CH$_4$ adsorption isotherms of silicone oil and the corresponding 12.5 wt. % and 20 wt. % dispersions of CC3-R/CC3-S microparticles. The numbers in parentheses indicate the batch of microparticles used from Table 1.
Table S6: Summary of CO$_2$ uptakes of CC3-R/CC3-S dispersions in silicone oil at different concentrations

| Loading (wt. %) | CO$_2$ Uptake, 298-303 K, 1 bar (μmol/g$_L$) |
|----------------|---------------------------------------------|
| 0              | 86.5                                        |
| 5              | 141.8                                       |
| 12.5           | 202.3                                       |
| 15             | 221.7                                       |
| 17.5           | 255.9                                       |
| 20             | 279.7                                       |
| 25             | 360.6                                       |
| 30             | 398.8                                       |
| 50             | 635.5                                       |
| 100            | 1792                                        |

Figure S14: Linear fit of CO$_2$ uptakes at 1 bar in silicone oil and the corresponding 5 wt. %, 12.5 wt. %, 15 wt. %, 17.5 wt. %, 20 wt. %, 30 wt. % and 50 wt. % dispersions of CC3-R/CC3-S microparticles.
4.2 Thermal stability study of dispersions of CC3-R/CC3-S microparticles

Figure S15: TGA of silicone oil and 5 wt. %, 12.5 wt. % and 20 wt. % CC3-R/CC3-S dispersions in silicone oil – here you can see the percentage of cage remaining after the silicone oil has been removed prior to thermal decomposition at ~ 400 °C.
4.3 Recyclability study of dispersions of CC3-R/CC3-S microparticles

![Graph showing CO₂ uptake vs. pressure for CC3-R/CC3-S dispersions.](image)

**Figure S16**: Recyclability study of CO₂ uptake in a 12.5 wt. % CC3-R/CC3-S dispersion in [BPy][Ntf₂]. The number in parentheses indicate the batch of microparticles used from Table 1.

![Graph showing CO₂ uptake vs. pressure for CC3-R/CC3-S dispersions in silicone oil.](image)

**Figure S17**: Recyclability study of CO₂ uptake with 12.5 wt. % CC3-R/CC3-S dispersions in silicone oil. The numbers in parentheses indicate the batch of microparticles used from Table 1.
4.4 PXRD patterns for dispersions of CC3-R/CC3-S microparticles

**Figure S18:** Capillary PXRD patterns of CC3-R/CC3-S microparticles and corresponding 5 wt. %, 12.5 wt. % and 20 wt. % dispersions in [BPy][NTf₂]. The numbers in parentheses indicate the batch of microparticles used from Table 1.

**Figure S19:** Capillary PXRD patterns of CC3-R/CC3-S microparticles and the corresponding 12.5 wt. % dispersion in silicone oil. The numbers in parentheses indicate the batch of microparticles used from Table 1.
Figure S20: PXRD patterns of CC3-R/CC3-S microparticles before and after CO$_2$ adsorption when dispersed in [Bpy][NTf$_2$]. CC3-R/CC3-S microparticles in [Bpy][NTf$_2$] were collected by filtration and washed after CO$_2$ adsorption to remove [Bpy][NTf$_2$].
4.5 Stability study of CC3-R/CC3-S microparticle dispersions

Stability studies of CC3-R/CC3-S microparticle dispersions were performed on a LUMiSizer® dispersion analyser, which is based on centrifugal technology and STEP (space and time resolved extinction profiles) technology. It detects changes in light transmission which characterizes processes such as sedimentation, creaming, and consolidation. CC3-R/CC3-S microparticle dispersions were pipetted into transparent sample cells (2 mm, rectangular synthetic cell 110-131 mm) and measured at 25 °C with a wavelength of 865 nm. Speed and time settings were 2000 revolutions per minute (RPM) with 700 scans at 30 second intervals (or 1000 x 21) for a total run time of 350 min. Relative centrifugal force (RCF) can be calculated from RPM and the centrifugal radius (r) in mm by the formula below:

\[
RCF = \left( \frac{RPM \times 1000}{1000} \right)^2 \times r \times 1.118
\]

The sedimentation velocity at a certain RCF can be converted into sedimentation velocity at gravity, which allows us to determine the phase stability of dispersions. The results are summarized in Table S6 below.

Table S7: Summary of dispersion stability results from LUMiSizer® - the numbers in parentheses indicate the batch of microparticles used from Table 1.

| Dispersions                  | RPM | Stability | Miniscus (mm) | Bottom (mm) | RCF at midpoint | Average V at RCF(um/s) | Average V at gravity (um/s) | Average V at gravity (mm/day) |
|------------------------------|-----|-----------|---------------|-------------|-----------------|------------------------|----------------------------|------------------------------|
| 12.5 wt. % CC3-R/CC3-S (3) in silicone oil | 2000 | Creaming | 107 | 130 | 530 | 1.454 | 2.744×10⁻³ | 0.24 |
| 5 wt. % CC3-R/CC3-S (5) in [BPy][NTf₂] | 2000 | Creaming | 108 | 130 | 532 | 0.8305 | 1.560×10⁻³ | 0.12 |
| 12.5 wt. % CC3-R/CC3-S (5) in [BPy][NTf₂] | 2000 | Creaming | 108 | 130 | 532 | 0.2554 | 4.799×10⁻⁴ | 0.04 |
Figure S21: 12.5 wt. % CC3-R/CC3-S dispersion in silicone oil (propagation from right to left indicates creaming).

Figure S22: 5 wt. % CC3-R/CC3-S dispersion in [Bpy][NTf₂] (propagation from right to left indicates creaming).
Figure S23: 12.5 wt. % CC3-R/CC3-S dispersion in [BPy][NTf₂] (propagation from right to left indicates creaming).
4.6 Temperature swing study

**Table S8**: Summary of CO$_2$ uptakes of [BPy][NTf$_2$] and 12.5 wt. % CC3-R/CC3-S dispersion in [BPy][NTf$_2$] at RT, 40, 60, 80, 100 °C

| T (°C) | CO$_2$ Uptake of [BPy][NTf$_2$] at 1 bar (μmol/g$_L$) | CO$_2$ Uptake of 12.5 wt. % CC3-R/CC3-S in [BPy][NTf$_2$] at 1 bar (μmol/g$_L$) |
|--------|--------------------------------------------------|---------------------------------------------------------------------------------|
| RT     | 84.8                                             | 175.2                                                                          |
| 40     | 83.0                                             | 162.3                                                                          |
| 60     | 59.2                                             | 130.8                                                                          |
| 80     | 54.8                                             | 77.7                                                                           |
| 100    | 47.5                                             | 70.9                                                                           |
**Figure S24:** CO₂ adsorption isotherms of [BPy][NTf₂] at RT, 40, 60, 80, and 100 °C.

**Figure S25:** CO₂ adsorption isotherms of a 12.5 wt. % CC3-R/CC3-S dispersion in [BPy][NTf₂] at RT, 40, 60, 80, and 100 °C. The numbers in parentheses indicate the batch of microparticles used from Table 1.
5. Gas sorption study of Type III CC3-R/CC15-S and CC3-R/CC19-S microparticle porous liquids

**Figure S26**: Summary of the gas uptakes in silicone oil and 12.5 wt.% CC3-R/CC3-S, CC3-R/CC15-S, and CC3-R/CC19-S dispersions in silicone oil.

**Figure S27**: CO₂ isotherms of silicone oil and 12.5 wt.% CC3-R/CC3-S, CC3-R/CC15-S, and CC3-R/CC19-S dispersions in silicone oil.
Figure S28: CH₄ isotherms of silicone oil and 12.5 wt.% CC3-R/CC3-S, CC3-R/CC15-S, and CC3-R/CC19-S dispersions in silicone oil.
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