

Accepted Article

Title: Controlling gas selectivity in molecular porous liquids by tuning the cage window size

Authors: Benjamin Egleston, Konstantin Luzyanin, Michael Brand, Rob Clowes, Michael Briggs, Rebecca L Greenaway, and Andrew Cooper

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201914037
Angew. Chem. 10.1002/ange.201914037

Link to VoR: <http://dx.doi.org/10.1002/anie.201914037>
<http://dx.doi.org/10.1002/ange.201914037>

COMMUNICATION

Controlling gas selectivity in molecular porous liquids by tuning the cage window size

Benjamin D. Egleston,^[a] Konstantin V. Luzyanin,^[b] Michael C. Brand,^[a] Rob Clowes,^[a] Michael E. Briggs,^[a] Rebecca L. Greenaway*^[b] and Andrew I. Cooper*^[a]

Abstract: Control of pore window size is the standard approach for tuning gas selectivity in porous solids. Here, we present the first example where this is translated into a molecular porous liquid formed from organic cage molecules. Reduction of the cage window size by chemical synthesis switches the selectivity from Xe-selective to CH₄-selective, which is understood using ¹²⁹Xe, ¹H, and pulsed-field gradient NMR spectroscopy.

Porous liquids (PLs) are a new class of porous material.^[1–3] They differ from conventional liquids because they have permanent, intrinsic micropores, in contrast to the transient, sub-molecular extrinsic voids found in all liquids (Figure 1). PLs can be categorized by their composition: Type 1 PLs are neat molecular liquids containing internal cavities; Type 2 PLs (Figure 1b) are solutions of porous molecules in a solvent that is size-excluded from the pores; and Type 3 PLs are dispersions of porous particles suspended in a cavity excluded liquid.^[4] Examples of all three types of PL have been described recently,^[5–12] and molecular simulations have led to a better understanding of their microstructure.^[13–16]

Porous organic cages (POCs) are a relatively new class of microporous solids that, unlike extended frameworks, are constructed from discrete organic molecules.^[17–19] POCs are shape-persistent molecules containing an internal cavity, which allows them to be dissolved in solvents while retaining their pore structure, setting them apart from many other types of insoluble porous materials, such as zeolites, metal organic frameworks and covalent organic frameworks.^[20] The discrete nature of POCs has led to attempts to produce Type 1 PLs,^[13,21] and to the successful production of Type 2 PLs.^[1,22] The latter PLs were obtained by dissolving POCs at high concentration in a solvent that was too bulky to pass through the windows of the cage. Recently, we investigated the uptake, gas selectivity and diffusion of different gases in a PL consisting of a scrambled [4+6] imine POC mixture dissolved in a bulky chlorinated solvent, hexachloropropene (HCP).^[22] Dynamic covalent scrambling was used to produce highly soluble vertex-disordered POC mixtures.^[23] The POC used in our first scrambled cage PL, **CC3³:13³-R** (Scheme 1), was based on the scrambling of the discrete POCs **CC3** and **CC13**. The gas uptake capacity of this PL correlated with the heats of adsorption of the respective solid, crystalline POC, **CC3**. This showed that the thermodynamic gas selectivity of the PL was governed by the structure and interactions of the constituent POC, suggesting to us a scheme for tuning selectivity in PLs.

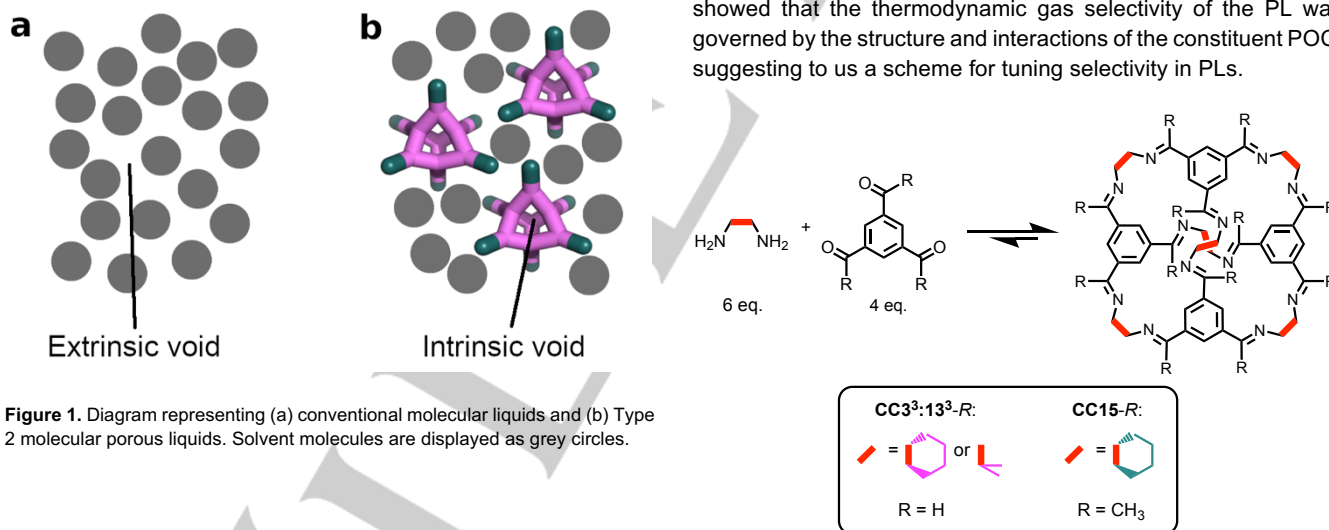


Figure 1. Diagram representing (a) conventional molecular liquids and (b) Type 2 molecular porous liquids. Solvent molecules are displayed as grey circles.

- [a] B. D. Egleston, M. C. Brand, R. Clowes, Dr. M. E. Briggs, Prof. A. I. Cooper
Department of Chemistry and Materials Innovation Factory
University of Liverpool
Oxford Street, Liverpool, L7 3NY, U.K.
E-mail: aicooper@liverpool.ac.uk
- [b] Dr. K. V. Luzyanin, Dr. R. L. Greenaway
Department of Chemistry
University of Liverpool
Crown Street, Liverpool, L69 7ZD, U.K.
E-mail: rebecca.greenaway@liverpool.ac.uk

Supporting information for this article is given via a link at the end of the document.

Scheme 1. Synthesis of POCs for PLs. Conditions: (**CC3³:13³-R**) dichloromethane, room temperature, 72 h; (**CC15-R**) dichloromethane, 3Å molecular sieves, 50 °C, reverse Dean Stark, 24 h.

Here, we exploited the synthetic modularity of POC molecules to produce PLs with different gas selectivities. This is the first example of tuning gas selectivity in a Type 2 PL by using chemistry. The imine POC, **CC15-R** (Scheme 1), is a close analogue of **CC3-R** that has smaller pore windows (1.7 Å vs 4.0 Å respectively), which are partially occluded by methyl groups (Figure 2a).^[24] The inclusion of methyl groups in the windows also leads to a reduction in cavity size (OPT pore sizes calculated

COMMUNICATION

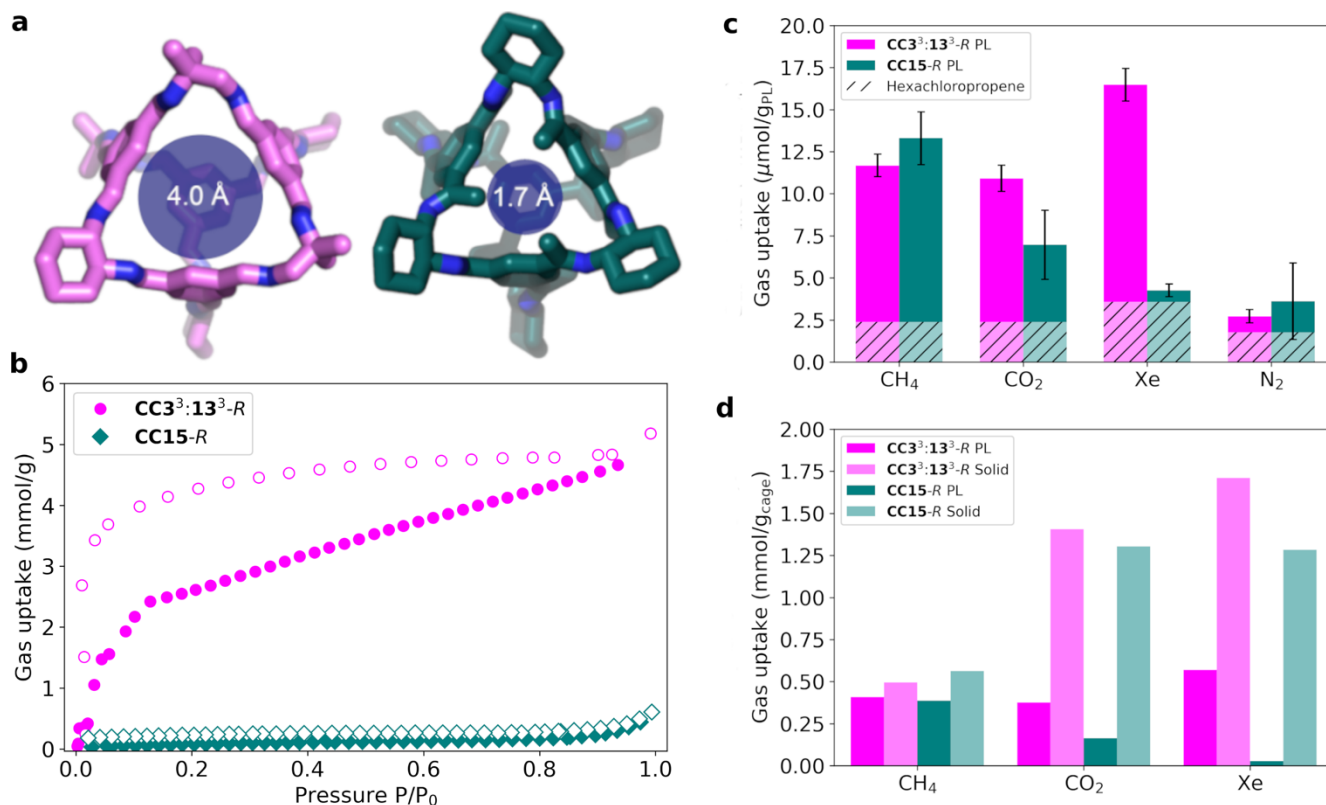


Figure 2. (a) Structures of the *trans*-3³13³ component of the scrambled cage mixture **CC3³:13³-R** (magenta, left) and **CC15-R** (teal, right) with the average window diameters calculated using the pywindow package;^[25] (b) N₂ adsorption (filled) and desorption (empty) isotherms for **CC3³:13³-R** and **CC15-R**; (c) Uptake by volumetric gas evolution for CH₄, CO₂, Xe, and N₂ for **CC3³:13³-R** (magenta) and **CC15-R** (teal) PLs, compared with uptake in hexachloropropene (HCP, dashed lines, overlaid). **CC3³:13³-R** PL at 4% w/v and **CC15-R** PL at 5% w/v; (d) Comparison of gas uptake in the liquid and solid state for each POC. Uptake for PLs is adjusted by subtracting the native gas capacity of HCP to show the POC uptake only, and normalized to the mass of cage present.

using pywindow^[25]: **CC3³:13³-R** 5.85 Å, **CC15-R** 4.61 Å). As a result, **CC15-R** adsorbs very little N₂ in the solid state, quite unlike **CC3-R** (Figure 2b). **CC15-R** still adsorbs smaller gas molecules, such as H₂; this is because the window size, and the smaller cavity size, modulates the gas selectivity in the solid, crystalline state.

Here we sought to translate this principle for the first time into PLs. **CC15-R** was found to be soluble in HCP at a concentration (50 mg_{cage} in 1 mL_{HCP}, 5% w/v) that was high enough to investigate gas uptake properties, albeit at a significantly lower concentration than our previous **CC3³:13³-R** scrambled cage in this solvent (200 mg_{cage} in mL_{HCP}, 20% w/v).^[22] Even though the solubility of **CC15-R** appears low when benchmarked against a scrambled cage mixture, it should be noted that this solubility is still much higher than for the structurally related **CC3-R** in HCP (<15.6 mg_{cage} in 1 mL_{HCP}). We also tried to increase the solubility by forming a scrambled analogue of **CC15-R**, but HPLC analysis indicated that only **CC15-R** was formed; no scrambling occurred, possibly because the three methyl groups in 1,3,5-triacetylbenzene clash sterically with the methyl groups in 1,2-diamino-2-methylpropane, preventing scrambling.

To compare these PL systems directly, equimolar solutions (39 μmol_{cage} in 1 mL_{HCP}) were prepared in HCP of **CC3³:13³-R** (40

mg_{cage} in 1 mL_{HCP}, 4% w/v) and **CC15-R** (5% w/v), thus ensuring the same volumetric density of pore cavities in each case. Gas uptakes were determined for both PLs for CH₄, CO₂, Xe, and N₂, using a guest displacement method that we described previously.^[22] With the exception of Xe in **CC15-R** PL, the gas uptake was enhanced in the PLs in all cases compared to the neat solvent (Figure 2c). Because of the significantly lower cage concentration in these two PLs, gas uptakes were reduced for all gases with respect to our previous 20% w/v scrambled PL; for example, the CH₄ uptake in the **CC3³:13³-R** scrambled PL was 45.8 μmol/g_{PL} at 20% w/v^[22] compared to 11.7 μmol/g_{PL} at 4% w/v here. In the case of N₂, the improvement in uptake with respect to the neat solvent was low for both PLs compared to neat HCP (Figure 2c), reflecting our previous observations at higher cage concentrations.^[22] For other gases, despite the lower pore concentration, the gas solubility improvements were more marked with up to a ~5.5 fold increase over the neat solvent, and there were large differences between the two PLs. The Xe uptake in **CC3³:13³-R** PL (16.6 μmol/g_{PL}) was almost four times that measured for **CC15-R** PL (4.3 μmol/g_{PL}) at the same pore concentration. The reduction in Xe uptake can be attributed to the methyl groups in **CC15-R**, which encroach on the cage windows and available pore volume that is accessible to Xe in **CC3³:13³-R**. The **CC3³:13³-R** PL absorbs more Xe than the other gases tested, reflecting the thermodynamic preference for Xe observed

COMMUNICATION

previously in these imine POCs,^[26] but this is totally lost in the PL derived from the methylated analogue, **CC15-R**. We carried out a much longer gas saturation experiment (Table S2) to rule out this being a kinetic limitation due to the saturation time, and found no increase in uptake. Furthermore, the **CC15-R** PL absorbs CH₄ most preferentially, and more effectively than **CC3³:13³-R**; that is, the **CC3³:13³-R** PL shows preferential uptake for Xe, while the **CC15-R** PL is CH₄ shows preferential uptake for CH₄.

The gas uptake in these two PLs can be compared directly to the gas uptake in the corresponding POC solids by subtracting the baseline solubility in HCP and normalizing to the mass of cage present (Figure 2d). Nitrogen was not included in these comparisons since the solid-state sorption measurements were carried out at 77 K, not at 298 K. Direct comparison of the gas uptakes in the two solid POCs shows similar trends (**CC3³:13³-R** Xe > CO₂ > CH₄, **CC15-R** CO₂ ≈ Xe > CH₄). The gas uptake in **CC3³:13³-R** directly mirrors the isosteric heats of adsorption that were calculated previously for **CC3-R** (Xe 31.31 kJ.mol⁻¹, CO₂ 27.73 kJ.mol⁻¹, CH₄ 22.05 kJ.mol⁻¹).^[22] **CC15-R**, however, shows a weaker correlation: the CO₂ and Xe uptakes are similar, and both are reduced compared to **CC3³:13³-R**. Previously, for **CC3-R**, it was found that CO₂ has a preference to occupy the space in the crystal structure that corresponds to the cage portals, as well as having favorable electrostatic interactions with the imine bonds in the POC.^[27] Therefore, the CO₂ uptake in **CC15-R** is reduced compared to **CC3³:13³-R** since the addition of the window-occluding methyl groups inhibits both of these effects. Xe has a high affinity for the pore cavity in **CC3-R** due to its excellent fit.^[26] The methyl groups in **CC15-R** reduce the ability for Xe to occupy this cavity, resulting in a lower gas uptake in the solid. However, the porosity is not completely lost for these gases in the solid state because the methyl groups in **CC15-R** only affect the intrinsic pores, leaving the extrinsic pores intact.

When comparing between the solid and liquid state for CH₄, the mass-normalized gas uptake in the cages in the PLs (0.409 mmol/g_{cage} for **CC3³:13³-R** PL, 0.386 mmol/g_{cage} for **CC15-R** PL) is broadly comparable to the uptake observed in the solid state (0.495 mmol/g_{cage} for **CC3³:13³-R** solid, 0.562 mmol/g_{cage} **CC15-R** solid). This suggests that, like Xe and CO₂, CH₄ does not have a preference for the extrinsic cavities in the solid state. However the kinetic diameter (3.8 Å)^[28] is smaller than the cavities in the cages (**CC3³:13³-R** 5.85 Å, **CC15-R** 4.61 Å), and hence CH₄ is able to occupy the cage cavities both in the solid and liquid state. However, this does not hold for Xe and CO₂. The solid state CO₂ uptakes for the cages (1.407 mmol/g_{cage} for **CC3³:13³-R** solid, 1.304 mmol/g_{cage} for **CC15-R** solid) are around one order of magnitude higher than the mass-normalized uptakes for the PLs (0.375 mmol/g_{cage} for **CC3³:13³-R** PL, 0.164 mmol/g_{cage} for **CC15-R** PL). This difference can be attributed, at least in part, to the interconnected solid-state porosity that comprises both intrinsic pores (inside cages) and extrinsic pores (between cages), whereas these PLs only have intrinsic pores. Furthermore, while CO₂ has a tendency to occupy the portal sites in solid POCs, the cages in these PLs are solvated, meaning that these portal sites do not exist. Hence, uptake enhancement is due solely to the intrinsic pore.^[29] This also explains the reduction in CO₂ capacity in the **CC15-R** PL compared to the **CC3³:13³-R** PL, as the methyl

groups further inhibit occupancy of CO₂ in the portal site, as well as limiting the electrostatic interaction.

For Xe, there is a much larger disparity in gas uptakes in these PLs (0.568 mmol/g_{cage} for **CC3³:13³-R** PL, 0.027 mmol/g_{cage} for **CC15-R** PL); this does not reflect the solid state trend for these POCs, where both of the cage materials adsorb significant amounts of Xe (1.710 mmol/g_{cage} for **CC3³:13³-R** solid, 1.283 mmol/g_{cage} for **CC15-R** solid). While the uptake of Xe is reduced in the **CC3³:13³-R** PL compared to the solid state, it still mirrors the calculated isosteric heats for **CC3-R** due to its near-ideal cavity size. In the **CC15-R** PL,^[26] the methyl groups reduce the ability for Xe to occupy this cavity. Effectively, the Xe uptake has been 'shut off' in **CC15-R** compared to **CC3³:13³-R** when translated into the PL state due to the window occlusion and reduced pore size. This suggests that the Xe uptake in solid **CC15-R** may be due mostly to extrinsic intermolecular pores.^[24]

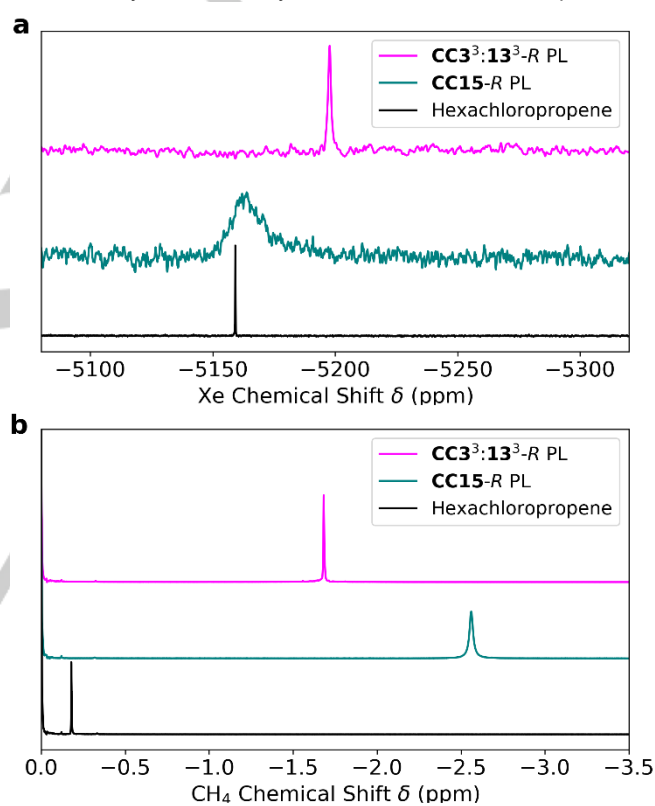


Figure 3. (a) ¹²⁹Xe and (b) ¹H NMR spectra for Xe and CH₄ gas in **CC3³:13³-R** and **CC15-R** PLs compared to in neat HCP. **CC3³:13³-R** PL at 4% w/v and **CC15-R** PL at 5% w/v.

To investigate these differences, ¹H and ¹²⁹Xe NMR spectroscopy were used to characterize the chemical environment of the gases in both the PLs and in the neat solvent, HCP (Figure 3). This allowed us to probe the extent of gas binding in each PL, since the ¹H and ¹²⁹Xe nuclei are highly sensitive to their chemical environment, leading to upfield shifts when the cage cavities are occupied. In the ¹²⁹Xe spectra, the **CC3³:13³-R** PL exhibits a large upfield shift relative to HCP ($\Delta\delta = -38.6$ ppm), whereas this shift is relatively small for the **CC15-R** PL ($\Delta\delta = -4.7$ ppm), where the

COMMUNICATION

Xe signal is also weak. This shows that the Xe gas cannot easily occupy the pores in the **CC15-R** PL, whereas in **CC3³:13³-R** PL, the much larger downfield shift is due to the Xe gas readily occupying the cage cavities. This confirms that Xe uptake in the **CC15-R** PL is switched off by reducing the cage window size.

This relationship between gas uptake and downfield chemical shift also holds for CH₄. In both PLs, there is a significant upfield shift compared to HCP ($\Delta\delta = -1.50$ ppm in **CC3³:13³-R** PL, $\Delta\delta = -2.38$ ppm in **CC15-R** PL). The larger shift observed in the **CC15-R** PL shows that CH₄ is experiencing a larger shielding effect. ¹H NMR spectroscopy can be used to quantify the saturation concentrations of CH₄ by using a sealed, calibrated d₂-DCM/TMS capillary. The gas uptakes measured by NMR (17.5 $\mu\text{mol/g}_{\text{PL}}$ in **CC3³:13³-R** PL, 21.5 $\mu\text{mol/g}_{\text{PL}}$ in **CC15-R** PL) are higher than for the gas displacement measurements (11.6 $\mu\text{mol/g}_{\text{PL}}$ in **CC3³:13³-R** PL, 13.3 $\mu\text{mol/g}_{\text{PL}}$ in **CC15-R** PL), reflecting trends in a previous study.^[22] This is because gas evolution experiments cannot release all of the gas dissolved in a PL because of the baseline gas solubility in both HCP and in the displacement solvent.

Next, pulsed-field gradient (PFG) NMR experiments were carried out to measure diffusion of CH₄ in the two PL systems. The results of these experiments are related to the binding of CH₄ in the PLs. The measured diffusion co-efficients for each POC (6.14×10^{-11} m²/s for **CC3³:13³-R**, 6.33×10^{-11} m²/s for **CC15-R**) and sample viscosities (Table S6) were used to calculate solvodynamic radii using the Stokes-Einstein equation for the two POCs in the PLs (8.2 Å for **CC3³:13³-R**, 8.3 Å for **CC15-R**); these values agree with the expected size of a [4+6] imine cage.^[30] The diffusion co-efficients for CH₄ in the two PLs (5.43×10^{-10} m²/s in **CC3³:13³-R** PL, 4.58×10^{-10} m²/s in **CC15-R** PL) are significantly lower than in neat HCP (1.34×10^{-9} m²/s), indicating that association of the gas with the cage is occurring and that this is observable by PFG NMR. Since the CH₄ has not adopted the same diffusion co-efficient as the POCs, this indicates that the gas is in dynamic equilibrium on the NMR timescale between the POC cavity and the HCP solvent. Therefore, this information can be used to calculate the fraction of gas molecules occupying the cage cavities (X_{occ}), as well as the association constant (K_a) for each system.^[31] In the **CC3³:13³-R** PL, $X_{\text{occ}} = 0.49$, while for the **CC15-R** PL $X_{\text{occ}} = 0.60$. The corresponding association constants for CH₄ in each PL can be calculated from the diffusion co-efficients measured for CH₄ in each PL ($K_a = 2.71 \times 10^4$ mol⁻¹ dm³ for CH₄ in **CC3³:13³-R** PL, $K_a = 4.36 \times 10^4$ mol⁻¹ dm³ for CH₄ in **CC15-R** PL). These measurements confirm that CH₄ more preferentially occupies the cavity in the **CC15-R** PL than in the **CC3³:13³-R** PL, in keeping with the gas uptake measurements, where the **CC15-R** PL absorbs more CH₄ (Figure 2c).

Retention of CH₄ in these PLs was also examined by measuring the kinetics of gas loss using ¹H NMR spectroscopy. The CH₄ concentration at a series of time intervals was recorded and the rate of loss of CH₄ while open to air was compared after normalizing the curves to the saturation concentration for each porous liquid (Figure S13). After 1 day, the **CC15-R** PL retained 23% more of the initial CH₄ concentration when compared with **CC3³:13³-R** PL, and over a period of ca. 2 days, the CH₄ was lost more slowly from the **CC15-R** PL than from the **CC3³:13³-R** PL.

This shows that narrowing the pore diameter in the molecular cage component in a PL can also improve the retention of gases over time.

In summary, modification of the window and pore size in POCs can modulate the gas selectivity in PLs, demonstrating that a key structure-function design principle in porous solids can be translated into these new materials: for example, we can shut off Xe absorption by narrowing the cage window, which also reduces the pore size, in the **CC15-R** PL (Figure 2d). There are also some differences between these two types of porous materials: for example, for CO₂ (Figure 2d), the amount of gas per cage is significantly lower in the PLs, probably because the PLs, unlike the corresponding porous solids, lack intermolecular pores between cages that allow multilayer adsorption and pore filling as saturation is approached.

In the longer term, this offers the potential of flowable, gas-selective liquids for separation processes; for example, where a gas-selective PL is cycled between a cold absorption zone and a hot desorption zone. The relatively modest viscosities of these PLs (up to 11.7 cP at 20% w/v)^[22] should allow such processes. The selectivity might be increased further by designing analogous cage materials with higher solubilities; likewise, eliminating the solvent altogether could enhance selectivity since the carrier solvent in these Type 2 PLs is relatively unselective, although in that case, liquid viscosity might be a major challenge.

Acknowledgements

We thank the Engineering and Physical Sciences Research Council (EPSRC) under the Grants EP/N004884/1 and EP/R005710/1, and the European Research Council under FP7, RobOT, ERC Grant Agreement No. 321156, for financial support. R.L.G. thanks the Royal Society for a University Research Fellowship. We acknowledge the MicroBioRefinery for assistance with QTOF-MS measurements. We thank Dr. Tom Hasell (University of Liverpool) and Prof. Stuart James (Queen's University Belfast) for helpful discussions.

Keywords: adsorption selectivity • porous organic cages • porous liquids

- [1] N. Giri, M. G. Del Pópolo, G. Melaugh, R. L. Greenaway, K. Rätzke, T. Koschine, L. Pison, M. F. C. Gomes, A. I. Cooper, S. L. James, *Nature* **2015**, *527*, 216–220.
- [2] S. L. James, *Adv. Mater.* **2016**, *28*, 5712–5716.
- [3] A. I. Cooper, *ACS Cent. Sci.* **2017**, *3*, 544–553.
- [4] N. O'Reilly, N. Giri, S. L. James, *Chem. - A Eur. J.* **2007**, *13*, 3020–3025.
- [5] J. Zhang, S. H. Chai, Z. A. Qiao, S. M. Mahurin, J. Chen, Y. Fang, S. Wan, K. Nelson, P. Zhang, S. Dai, *Angew. Chemie - Int. Ed.* **2015**, *54*, 932–936.
- [6] P. Li, J. A. Schott, J. Zhang, S. M. Mahurin, Y. Sheng, X. Hu, G. Cui, D. Yao, S. Brown, Y. Zheng, et al., *Angew. Chemie Int. Ed.* **2017**, *56*, 14958.
- [7] S. Liu, J. Liu, X. Hou, T. Xu, J. Tong, J. Zhang, B. Ye, B. Liu, *Langmuir* **2018**, *34*, 3654–3660.
- [8] X. Li, Y. Ding, L. Guo, Q. Liao, X. Zhu, *Energy* **2019**, *171*, 109–119.
- [9] P. Li, H. Chen, J. A. Schott, B. Li, Y. Zheng, **2019**, 1515–1519.

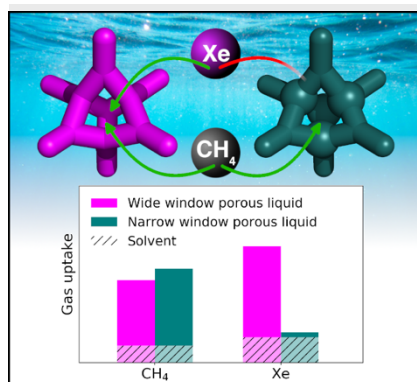
COMMUNICATION

- [10] W. Shan, P. F. Fulvio, L. Kong, J. A. Schott, C. L. Do-Thanh, T. Tian, X. Hu, S. M. Mahurin, H. Xing, S. Dai, *ACS Appl. Mater. Interfaces* **2018**, *10*, 32–36.
- [11] T. Shi, Y. Zheng, T. Wang, P. Li, Y. Wang, D. Yao, *ChemPhysChem* **2018**, *19*, 130–137.
- [12] X. Wang, D. Shang, S. Zeng, Y. Wang, X. Zhang, X. Zhang, J. Liu, *J. Chem. Thermodyn.* **2019**, *128*, 415–423.
- [13] G. Melaugh, N. Giri, C. E. Davidson, S. L. James, M. G. Del Pópolo, *Phys. Chem. Chem. Phys.* **2014**, *16*, 9422–31.
- [14] F. Zhang, F. Yang, J. Huang, B. G. Sumpter, R. Qiao, *J. Phys. Chem. B* **2016**, *120*, 7195–7200.
- [15] F. Zhang, Y. He, J. Huang, B. G. Sumpter, R. Qiao, *J. Phys. Chem. C* **2017**, *121*, 12426.
- [16] M. Costa Gomes, L. Pison, C. Červinka, A. Padua, *Angew. Chemie Int. Ed.* **2018**, *54*, 932–936.
- [17] F. Beuerle, B. Gole, *Angew. Chemie - Int. Ed.* **2018**, 2–31.
- [18] P. S. Mukherjee, K. Acharyya, *Angew. Chemie Int. Ed.* **2019**, DOI 10.1002/anie.201900163.
- [19] M. Mastalerz, *Acc. Chem. Res.* **2018**, *51*, 2411–2422.
- [20] T. Hasell, A. I. Cooper, *Nat. Rev. Mater.* **2016**, *1*, 16053.
- [21] N. Giri, C. E. Davidson, G. Melaugh, M. G. Del Pópolo, J. T. a. Jones, T. Hasell, A. I. Cooper, P. N. Horton, M. B. Hursthouse, S. L. James, *Chem. Sci.* **2012**, *3*, 2153.
- [22] R. L. Greenaway, D. Holden, E. G. B. Eden, A. Stephenson, C. W. Yong, M. J. Bennison, T. Hasell, M. E. Briggs, S. L. James, A. I. Cooper, *Chem. Sci.* **2017**, *8*, 2640–2651.
- [23] S. Jiang, J. T. a. Jones, T. Hasell, C. E. Blythe, D. J. Adams, A. Trewin, A. I. Cooper, *Nat. Commun.* **2011**, *2*, 207.
- [24] A. G. Slater, P. S. Reiss, A. Pulido, M. A. Little, D. L. Holden, L. Chen, S. Y. Chong, B. M. Alston, R. Clowes, M. Haranczyk, et al., *ACS Cent. Sci.* **2017**, *3*, 734–742.
- [25] M. Miklitz, K. E. Jelfs, *J. Chem. Inf. Model.* **2018**, *58*, 2387–2391.
- [26] L. Chen, P. S. Reiss, S. Y. Chong, D. Holden, K. E. Jelfs, T. Hasell, M. A. Little, A. Kewley, M. E. Briggs, A. Stephenson, et al., *Nat Mater* **2014**, *13*, 954–960.
- [27] T. Hasell, J. A. Armstrong, K. E. Jelfs, F. H. Tay, K. M. Thomas, S. G. Kazarian, A. I. Cooper, *Chem. Commun.*, **2013**, *49*, 9410–9412.
- [28] Robeson L. M., *J. Membrane. Sci.*, **1991**, *62*, 165–185.
- [29] S. Jiang, K. E. Jelfs, D. Holden, T. Hasell, S. Y. Chong, M. Haranczyk, A. Trewin, A. I. Cooper, *J. Am. Chem. Soc.*, **2013**, *135*, 17818–17830.
- [30] R. L. Greenaway, V. Santolini, M. J. Bennison, B. M. Alston, C. J. Pugh, M. A. Little, M. Miklitz, E. G. B. Eden-Rump, R. Clowes, A. Shakil, et al., *Nat. Commun.* **2018**, *9*, 2849.
- [31] K. S. Cameron, L. Fielding, *J. Org. Chem.* **2001**, *66*, 6891–6895.

COMMUNICATION

COMMUNICATION

Narrowing the windows of the organic cage used to form molecular porous liquids leads to tuning of the gas selectivity.



Benjamin D. Egleston, Konstantin V. Luzyanin, Michael C Brand, Rob Clowes, Michael E. Briggs, Rebecca L. Greenaway and Andrew I. Cooper

Page No. – Page No.

Controlling gas selectivity in molecular porous liquids by tuning the cage window size

Accepted Manuscript