

Metal–organic frameworks as stationary phases
for mixed-mode separation applications†Cite this: *Chem. Commun.*, 2014,
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Polymorphic metal–organic framework (MOF) materials offer a platform for small-scale separation of complex mixtures of polycyclic aromatic hydrocarbons (PAHs) and polar compounds. Retention factors show dependence on both analyte dimensions and polarity, suggesting mixed-mode separation, allowing complete resolution of some analytes from multi-component mixtures.

Metal–organic frameworks (MOFs) are nanoporous materials consisting of metal ions or clusters coordinated by organic bridging ligands,¹ with widely reported applications, particularly in gas storage and related areas.² MOFs also possess desirable qualities for separations; they contain uniform molecular-scale cavities, display high surface areas and are insoluble and highly stable in common solvents. By virtue of their modular design, porous coordination polymers (often referred to as MOFs) have customisable surfaces with the ability to modify polarity, pore size and include functional groups. These benefits have led to investigations of MOFs as sampling, extraction and separation materials, largely focused on the uptake of small molecules from simple mixtures.³ The diversity in structures and pore sizes permit specific interactions augmented by in-pore functionalities, including metal sites.⁴ Surface modification⁵ and the use of MOFs as supporting materials⁶ are also possible. Several MOFs have demonstrated feasibility as GC stationary phases,⁷ or shown good performance in HPLC, often separating analytes on the basis of polarity.⁸ The tightly-bound and coordinatively saturated nature of the metal ions within most MOFs seemingly prevents the peak

tailing which would be expected from the presence of metal ions within HPLC stationary phases.

Progress has also been made for size selective separation⁹ or extraction¹⁰ of a limited range of analytes, *e.g.*, size discrimination in separation from a binary mixture using two polymorphic MOFs.¹¹ To date, most reports have employed only simple analyte mixtures, often with the analytes of interest varying greatly in both polarity and size. Furthermore, most studies have used structurally rigid MOFs with monodisperse pore dimensions which, although suitable for specifically targeted analytes, often fall short in the separation of more complex mixtures containing analytes of subtly varying dimensions. Despite the advances in the field of separation science using MOFs, a full proof-of-principle demonstration of mixed-mode separation on a large range of analytes has yet to be reported. Such studies are needed to provide clearer insight into the possible mechanisms of micropore-based separations in the solution phase, and to provide information regarding the possible analyte scope of MOF stationary phases.

Recently, Gao *et al.* reported the synthesis of a new cadmium MOF *poly*–[Cd(L1)] **1A**, based on benzoate-substituted cyclen-derived ligand 1,4,7,10-tetrakis(4-carboxybenzyl)-1,4,7,10-tetraazacyclododecane **L1** (Fig. 1).¹² During our own studies of **L1**,¹³ a second phase of *poly*–[Cd(L1)], **1B**, was isolated. Both **1A** and **1B** are porous, doubly interpenetrated 3-dimensional networks, related to the **ins** and **kdd** nets, respectively. Cadmium ions occupy both macrocycle- and carboxylate-bound positions in each case, and the differing topologies are achieved by only a change in the positions of the benzoate arms (ESI†). Gas sorption isotherms of **1B**, after soaking in methanol and supercritical CO₂ activation, confirmed the presence of porosity (ESI†), as was reported for compound **1A**.

Due to the presence of several pore openings of different size and shape, a direct comparison of channel dimensions of **1A** and **1B** is best limited to the size of the largest square channels, which, based on the determined structures, possess diagonal atom-to-atom distances of *ca.* 14 Å (**1A**) and 11 Å (**1B**). It must be noted that, due to the presence of flexible interpenetration in both MOFs, these values are likely to show some degree of fluidity. Nonetheless, by all metrics (pore volume, pore dimensions and

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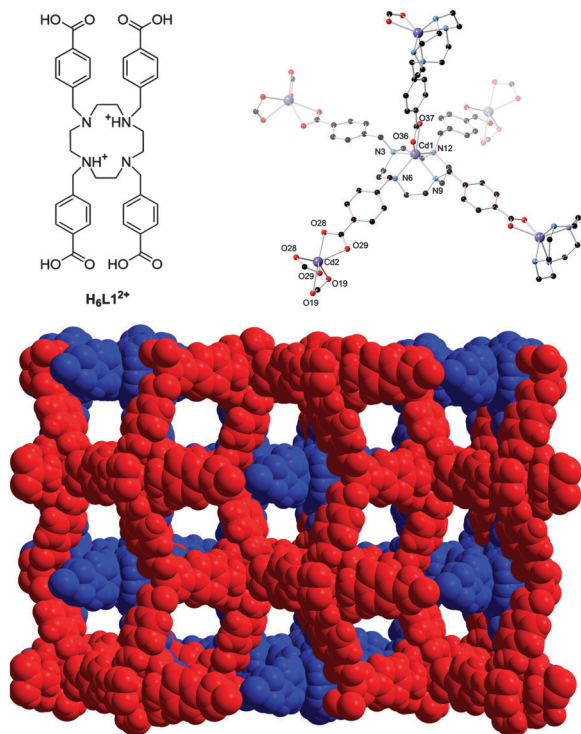


Fig. 1 (top) Structure of H_6L1^{2+} (left) and coordination environment of $L1$ in $poly-[Cd(L1)]$ **1B** (right). Hydrogen atoms and framework disorder (ESI[†]) omitted for clarity. (bottom) Space-filling diagram of the extended structure of **1B** with independent interpenetrated networks coloured separately.

surface area), MOF **1A** contains larger pores, and given the similarity in the internal structures and interpenetration modes, any framework flexibility would likely impact both materials in a similar fashion. Both MOFs showed rapid solvent exchange upon immersion in a range of solvents (ESI[†]), indicating good pore accessibility. This property is expected to be more crucial for separation applications than stability on full desolvation; indeed, many MOFs are unstable to evacuation,¹⁴ but may retain pore accessibility under milder conditions.

MOFs **1A** and **1B**, with very similar surface polarities but differing channel diameters and void volumes, are ideal to test for size-selective separation capability. Small-scale separation experiments were carried out by packing pipette tips with *ca.* 60 mg of the MOF (ESI[†]), and studying the elution of compounds from the micro-pipette tips.¹⁵ A commercially available mixture of 16 PAH compounds was selected as the probe analytes for size selectivity and 9 compounds with differing polarity were selected to test polar and coordination interactions (ESI[†], Table S1). Separation of all 16 PAH and polar compounds was quantified with GC-FID using a mid-polarity column, with peak areas plotted as functions of elution volume from the tips. To provide baseline information and to test for any surface hydrogen-bonding effects, the elution experiments were repeated using the confirmed non-porous dihydrochloride salt of the ligand **L1**, $H_6L1 \cdot 2Cl \cdot 2H_2O$ as the stationary phase.¹³ $CdCO_3$ was also tested to investigate any possible coordinative interactions.

As expected, $H_6L1 \cdot 2Cl \cdot 2H_2O$ displayed no interaction with the PAH mixture, with all analytes exhibiting elution peak apices within the first 30 μL fraction (Table S1, ESI[†]). $CdCO_3$ gave

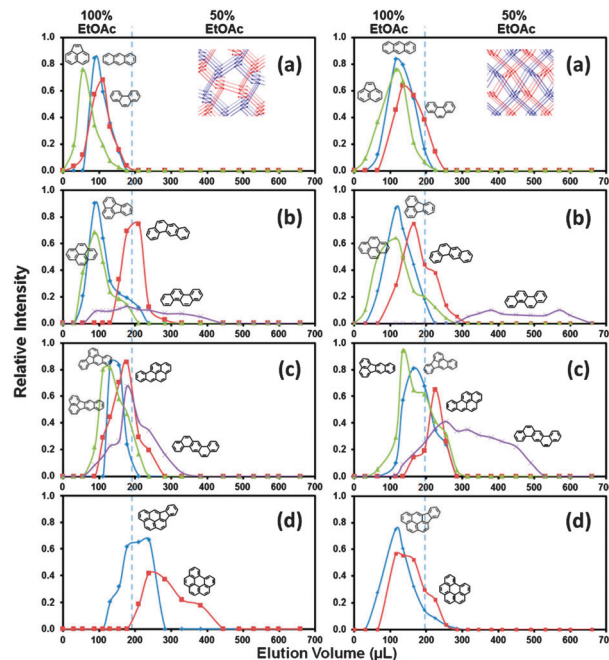


Fig. 2 Elution profiles of PAHs with 3–6 aromatic rings using stationary phases **1A** (left) and **1B** (right). Inset: topological representations of MOFs **1A** and **1B**. Listed compounds are in the order of elution for each set. From left to right: (a) acenaphthylene, anthracene, phenanthrene; (b) pyrene, fluoranthene, benzo[a]anthracene, chrysene; (c) benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene; (d) indeno[1,2,3-*cd*]-pyrene, benzo[ghi]perylene. The corresponding retention factors are shown in Table S1 (ESI[†]).

similar results, except for slight retention of indeno[1,2,3-*cd*]-pyrene. For MOF materials **1A** and **1B**, retention behaviours of PAHs were markedly different. Retention values for **1A** were highest for the larger analytes, especially those containing 6 aromatic rings (Fig. 2d). Benzo[ghi]perylene showed the strongest retention with **1A** (Table S1, ESI[†]). MOF **1B** showed improved separation of analytes with 4 and 5 aromatic rings (Fig. 2b and c), compared to those with 3 and 6 rings (Fig. 2a and d), with the strongest retention being for chrysene.

The interaction mechanics of the PAH analytes with the MOF stationary phases was expected to consist of a combination of surface-based effects and (partial) entry of the analytes into the MOF pores. Reference experiments with non-porous substrates show that any analyte-surface interactions would be minor, and are not expected to lead to discrimination by analyte size. Entry of the analytes into the surface openings is therefore postulated as a possible mechanism of the observed separation. In this case, residence time within the MOF pores can be ascribed as the combination of ease of analyte entry (smaller analyte cross-section) and difficulty of removal (contributions of molecular friction from length, flat surface area and non-linear features). A trend is observed in both MOFs of increasing retention with length for analytes of the same width. For example, fluoranthene, benzo[*k*]-fluoranthene and dibenz[*a,h*]-anthracene have similar widths (6.6–6.8 Å), but exhibit increasing retention values with increasing length, from 8.7 Å to 13.6 Å. Small variations in this trend are likely due to the smaller secondary pore openings in both materials. Retention factors can be plotted against functions of

analyte size and shape, and not only support the assignment of separation based on aspect ratio, but also indicate differences in separation characteristics between the two MOF materials containing different pore sizes (ESI[†], Fig. S2 and S3).

For separation of polar compounds, both hydrogen-bonding and coordination interactions would be expected for analytes containing alcohol or amide groups, which also contribute to the greater polarity of those analytes. Polar interactions can be predicted to some extent from the analyte dipole moment, shown in Table S1 (ESI[†]) and plotted in Fig. S1 (ESI[†]).

Both MOFs display a trend of increasing retention with analyte dipole moment, with several analytes containing strong hydrogen-bonding functionality displaying greatly increased retention above the trendline for the non-hydrogen bonding analytes. Separations using CdCO₃ and H₆L1·2Cl·2H₂O were examined as comparisons to investigate the possibility of hydrogen bonding and coordinative interactions. Unsurprisingly, strong retentions (above 0.6) were observed for analytes containing functional groups capable of such interactions (Table S1, ESI[†]). However, only 4,4'-biphenol, bisphenol A and benzamide with the CdCO₃ stationary phase showed extra retention above the polar interaction trend as plotted in Fig. S1 (ESI[†]). The interactions of these three analytes most likely involve a combination of coordination interactions and hydrogen bonding.

In contrast to the PAH separations, the H₆L1·2Cl·2H₂O stationary phase displayed strong affinity for caffeine, 4,4'-biphenol and bisphenol A (Table S1, ESI[†]), suggestive of analyte-surface interactions, due in part to the surface polarity and hydrogen bonding groups of the ligand. Acid-base reactivity may also play a role, especially in the case of caffeine. For most analytes, both MOFs provided additional retention in comparison to that of the ligand, most likely due to the combination of increased surface area (the presence of pores), surface charge arising from the zwitterionic combination of coordination spheres, and the number of free hydrogen bond acceptors within the MOF structures. For each MOF, correlation between analyte retention and their dipole moment revealed that those retentions were likely primarily related to polar interactions (Fig. S1, ESI[†]), with additional retention of 4,4'-biphenol and bisphenol A due to hydrogen bonding interactions. Notably, **1A** displayed higher retentions than **1B**, possibly as a result of the larger pore size allowing more favourable alignment of the polar analytes.

In summary, we have demonstrated the use of MOFs for the separation of both PAH and polar analyte mixtures. Combined size- and polarity-based discrimination was observed and delineated from surface polarity effects by comparison with non-porous materials of similar composition, showing a clear suggestion of interactions between analytes and MOF pores. These results provide crucial evidence of the usefulness of porous framework materials in real-world chromatographic applications, where

new stationary phases are required for the separation of complex, multi-component mixtures.

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