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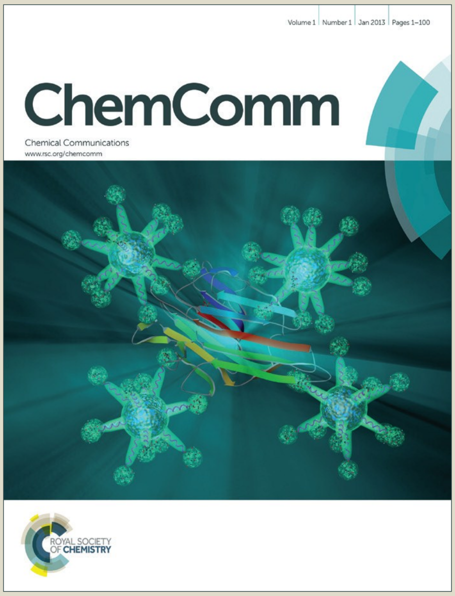

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COMMUNICATION

An Azine-Linked Hexaphenylbenzene Based Covalent Organic Framework

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In this communication, we report an azine linked covalent organic framework based on a six-fold symmetric hexphenylbenzene (HEX) monomer functionalized with aldehyde groups. HEX-COF 1 has an average pore size of 1 nm, a surface area in excess of 1200 m^2/g and shows excellent sorption capability for carbon dioxide (20 wt%) and methane (2.3 wt%) at 273 K and 1 atm.

Covalent organic frameworks[1-4] (COFs) are a class of porous polymers whose structures are formed under dynamic control in either two or three dimensions. The structure and properties of two-dimensional COFs in particular are controlled by the dynamic interplay between noncovalent aromatic interactions (*i.e.*, π-stacking) and covalent bond formation under thermodynamic control. COFs have become a rapidly growing part of micro and mesoporous materials discovery for gas storage,[1, 5-10] catalysis,[11-14] and especially as components for electronic and conductive materials[2, 15-22] The wide range of these potential applications is made possible by the modular design of COFs, enabling one to not only predict with high certainty, but also to tune, the pore size, shape, and symmetry of the resulting 2D COF sheets through careful design of the starting materials. Two and three fold symmetric monomers are commonly used to form materials with lattices that fit into hexagonal space groups. Porous polymers containing HEX units have been previously reported by our group[23, 24] and others.[25-29] Recently, the first COFs containing six-fold symmetric HEX-based components were reported resulting in materials with triangular shaped micropores and electrically conductive properties.[17]

HEX-based COFs with this type of structure are interesting due to their high π-density and extremely small pore size. To date, much of the gas storage behaviour (specifically CO_2 and CH_4) for HEX-based COFs has yet to be reported.

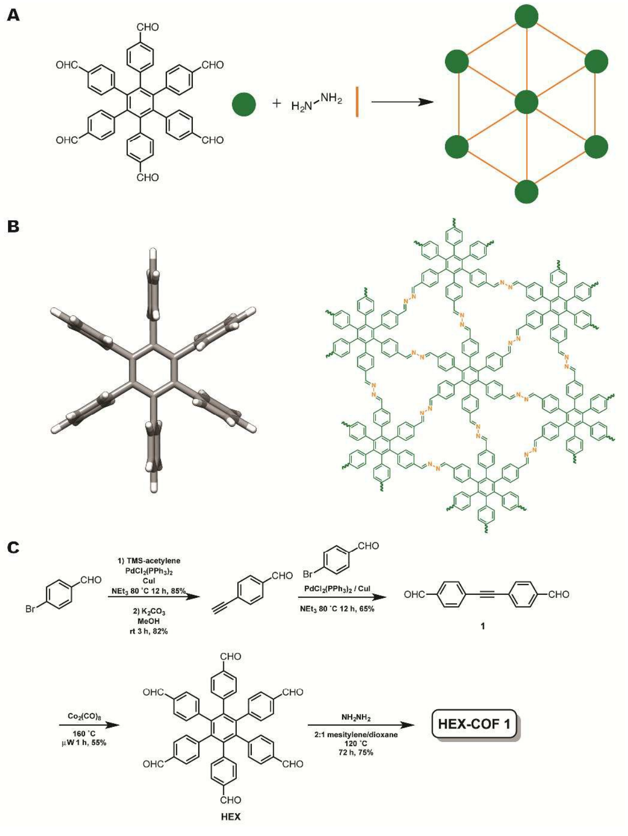

Figure 1. (A) Synthesis of a COF using a six fold symmetric HEX monomer containing aldehyde groups and hydrazine. (B) HEX-based monomers are non-planar as a result of the steric hindrance between the phenyl rings. Resultant COFs have topologically planar 2D structures despite the lack of planarity in the monomers. (C) Synthesis of HEX and HEX-COF 1.

To accomplish this we have synthesized an aldehyde functionalized HEX monomer (Figure 1a-b) with six-fold symmetry. Polymerization with a two-fold symmetric co-monomer, such as hydrazine, will result in a COF containing triangular pores. Since azine linkages[7, 8, 30-33] are among the smallest linkers available for COF synthesis, these pores should

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be approximately 1 nm, making them interesting for a variety of sorption applications including gas separation *via* sieving.

The synthesis of HEX is carried out using a cobalt-catalyzed cyclotrimerization as shown in Figure 1c. The precursor 4,4’-diformyltolan (**1**) is made through a Sonogashira coupling as previously reported in the literature.[34] The polymerization of HEX-COF 1 was performed using a solvent system of 2:1 mesitylene:dioxane with 0.1 mL of 6M aqueous AcOH catalyst for 72 h at 120 °C. FT-IR spectra (Figure S3-4) showed the conversion of aldehyde peaks from HEX into azines as demonstrated in previous work.[30] The surface area and pore size distributions were analysed by nitrogen adsorption measurements at 77 K (Figure 2a). Using the Brunauer-Emmett-Teller (BET) model the surface area was calclulated to be 1214 m^2/g. The pore size distribution (Figure 2b) was determined using a non-local density functional theory carbon slit pore model showing that the major population of NLDFT pore width resides at ~11 Å.

The narrow pore size distribution and high surface area indicate that this is an ordered material. However, powder X-ray diffraction (PXRD) measurements of HEX-COF 1 have low peak intensity (~10^2 counts) regardless of the solvent conditions or reaction time used (Figure 3b). The poor long-range order may be related to the inherent propeller shape of the HEX monomer. It was recently shown that increasing van der Waals interactions between 2D COF sheets drastically impacts their rate of formation and resulting stability.[35] The canonical “face to face” π-stacking found in most COF monomers is lacking in our system, which must instead rely on edge-to-edge interactions for interlayer adhesion.

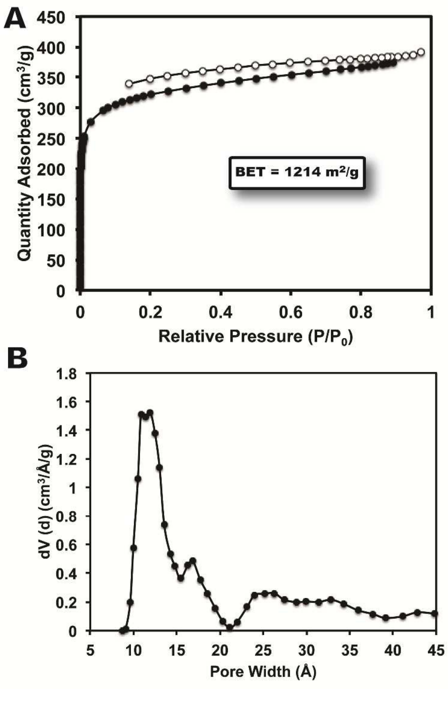

Figure 2. (A) N_2 isotherm at 77 K. The BET surface area of HEX-COF 1 was measured to be 1214 m^2/g. (B) NLDFT pore size distribution obtained from the N_2 isotherm.

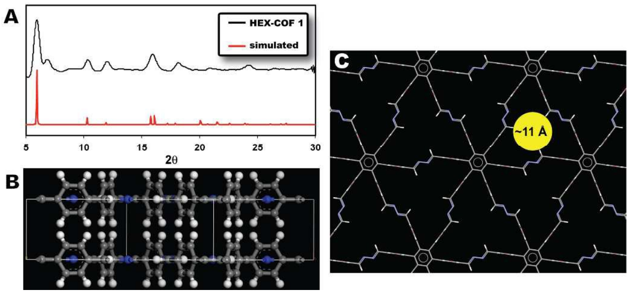

Figure 3. (A) The powder X-ray diffraction pattern of HEX-COF 1 (black line) and the simulated diffraction pattern from the model (red line). (B) A view of the interlayer spacing of the model showing the lack of face-to-face π stacking interactions. (C) Molecular model of HEX-COF 1 showing the pores measuring 11 Å in diameter.

Weak, or improperly aligned interlayer interactions could result in poor adhesion and reduced long-range crystallinity – something that has also been observed with other COFs that utilize aromatic systems that have non-planar structures.[11, 32] Simulated PXRD patterns generated from a molecular model of HEX-COF 1 in a hexagonal *P*6/*m* space group (Figure 3a,c) give unit cell parameters of 17.8 Å x 17.8 Å x 5.5 Å. Given the low intensity of the peaks, additional Pawley refinement of the raw data was not possible. The model in Figure 3b-c depicts a perfectly eclipsed structure while the real structure is likely slightly offset, these small differences cannot be resolved by PXRD measurements. The modelled pore diameter is in good agreement with the data in Figure 2b.

Other gas adsorption properties with HEX-COF 1 were also evaluated. CO_2 adsorption studies were performed at both 273 and 298 K (Figure 4a) up to 1 atm. These measurements indicate a strong affinity between the HEX-COF 1 and CO_2 gas molecules with nearly 20 wt% adsorbed at 273 K and an enthalpy of adsorption that is 42 kJ/mol (Figure 4c). This is an excellent value that ranks among the highest observed in COF-based materials.[6-8, 36, 37]

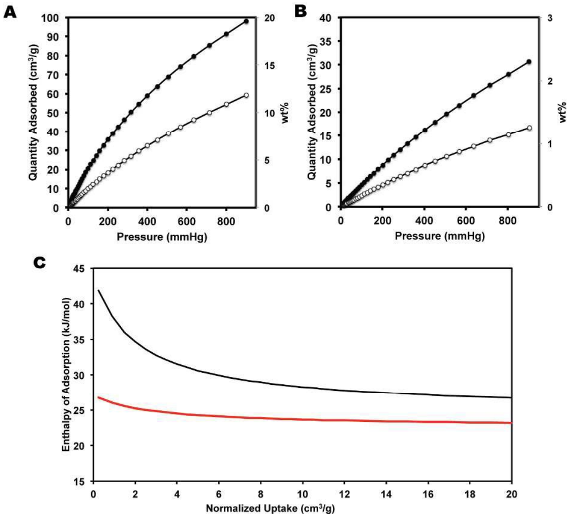

Figure 4. (A) CO_2 isotherms at 273 K (filled circles) and 298 K (open circles). (B) CH_4 isotherms at 273 K (filled circles) and 298 K (open circles). (C) Enthalpy of adsorption measurements for CO_2 (black line) and CH_4 (red line).

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In addition to the polar azine functional groups, which no doubt contribute to the strong adsorption, the small pore sizes (~11 Å in diameter) within HEX-based materials could also be a factor. CH_4 adsorption measurements (Figure 4b) were also carried out showing that HEX-COF 1 can store up to 2.3 wt% of CH_4 at 273 K with maximum enthalpies of adsorption around 27 kJ/mol (Figure 4c, red line).

In conclusion, we have synthesized a novel azine linked COF based on a six-fold symmetrical aldehyde functionalized hexaphenylbenezene monomer. Interestingly, these COFs display the adsorptions properties of an ordered microporous material with a type I isotherm and a narrow pore size distribution, but with a relatively weak PXRD pattern indicating a low level of long range order, likely owing to the poor interlayer interactions between the propeller-shaped HEX units. Despite the low level of long-range order, HEX-COF 1 exhibits outstanding surface area, CO_2 and CH_4 adsorption capability. We believe the unique triangular shape and very small pore sizes accessible through HEX-based monomers make them an interesting family of COFs to study for insight on how to design new materials for gas storage and sieving. Designing HEX systems with improved interlayer stacking will further improve our understanding of the structure and design rules required to reliably stitch together complex monomers into ordered COFs with designed properties.

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