

correlation, without producing even stronger 1.99Å (Fe-O) or 3.0Å (Fe-Fe vector from edge-sharing octahedra) correlations. The strong 3.44Å correlation is key since it suggests not only the presence of tetrahedrally coordinated Fe(III) but the presence of a Keggin cluster-like configuration with <sup>IV</sup>Fe(III) apex-sharing with the surrounding 12 <sup>VI</sup>Fe(III). Such a configuration maximize the intensity of the 3.44Å peak while keeping the edge-sharing Fe-Fe pair numbers, contributing to the peak at 3Å, low. Structural models containing phases with only Fe in 6-fold coordination, regardless of the number of phases added to the model, fit the XN data poorly.

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**Keywords:** ferrihydrite, nanomaterials, PDF

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### Modular assembly of porous organic materials

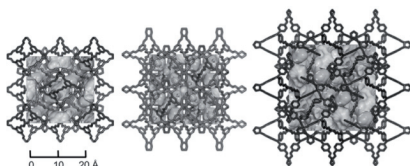
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The possibility of applications in areas such as catalysis, gas storage and separation has fuelled intensive research into the development of porous materials, in particular molecular and hybrid frameworks [1-3]. Much progress has been made with framework materials in terms of controlling properties such as pore size [2], but programmed placement of accessible functionality has proved more challenging [4], due in part to the ‘one pot’ synthetic methods employed.

An alternative strategy is the use of prefabricated porous components to assemble an array of specifically functionalised pores. Our work on organic cages has shown that these metal-free covalent molecules crystallise to form solids with permanent porosity. This results from the inherent cage voids and inefficiency in cage packing [5]. A wide synthetic diversity is available to tune both the internal pore size and the packing of the cage molecules by exploiting steric and non-covalent interactions of groups at the cage apices. These materials also exhibit solid state structural diversity, with a number of solvates and polymorphs being observed. For example, ‘on-off porosity’ switching [6] results from the capacity of these materials to undergo solid state transformations in response to the presence of chemical triggers.

Recent work has realised the potential to combine cages with different functionalities to achieve the modular assembly of porous materials from discrete cage components [7]. Simple mixing of the constituent prefabricated cages in solvent results in self-assembly of highly porous cocrystals, driven by chiral recognition. This highlights a promising new modular strategy for the design and synthesis of porous functional materials.

Crystal structures of porous organic crystals of (from left) quasiracemic cage cocrystal, (1-*S*, 3-*R*), racemic cage, (3-*S*, 3-*R*), and chiral cage, 5-*R*.



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**Keywords:** cage, microporous, organic

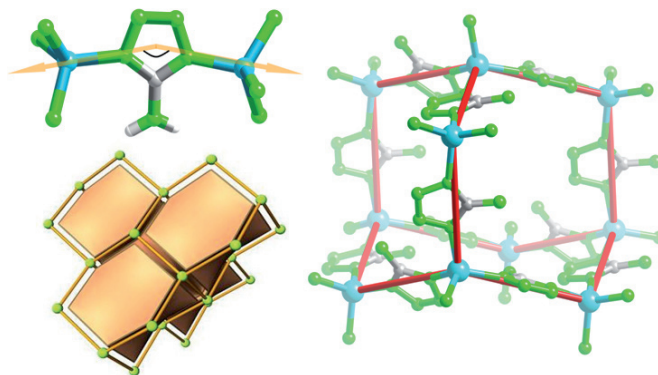
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### Zeolitic tetrazolate framework (ZTF) with high capacity storage of carbon dioxide

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Selective carbon dioxide capture from coal-fired power plant is critical issues as these plants produce post-combustion flue gases with ~15% CO<sub>2</sub> concentration [1]. At present, the separation of CO<sub>2</sub> from such a low pressure stream of gases is performed by amine sorbents through chemisorptions [2]. We describe herein, for the first time, the isolation of a three dimensional amino functionalized Zeolitic Tetrazolate Framework (ZTF-1) where N1 and N4 are coordinated to metal centers (M–TET–M angle is close to 145°, coincident with the Si–O–Si angle) and adopt a tetrahedral framework reminiscent of those found in zeolites. This is the first report of a –NH<sub>2</sub> functionalized MOF among different metal imidazoles/triazoles/tetrazoles where only N1 and N4 are coordinated to tetrahedral metal centers with M–L–M angle is close to 145°. The framework adopts a dia topology. ZTF-1 shows high CO<sub>2</sub> (273K) and H<sub>2</sub> (77K) uptake due to the presence of free –NH<sub>2</sub> group and uncoordinated tetrazolate nitrogen [3].



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