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An electron rich porous extended framework as a heterogeneous catalyst for Diels–Alder reactions†

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An electron rich porous metal–organic framework (MOF) has been synthesized, which acts as an effective heterogeneous catalyst for Diels–Alder reactions through encapsulation of the reactants in confined nano-channels of the framework.

Metal–Organic Frameworks (MOFs) with high surface area, high thermal stability and large pore volume have attracted much attention recently due to their versatile applications in storage, separation, drug delivery, sensing and catalysis.[1] Their poor solubility in common solvents and tuneable and uniform pore size are the emerging prospects for heterogeneous catalysis in chemical reactions.[2] In particular, selective encapsulation of reactants into the pores leads to size- and shape-selectivity of the catalytic reactions.[3] Moreover, the minimization of entropy loss and reduction of transition state energy due to the organization of the reactants in suitable positions may facilitate the reaction like enzyme catalysis.[4] Compared to homogeneous catalysis, heterogeneous catalysis is widely used for industrial applications because of easy separation and reusability of the catalyst.[5] Although MOFs have emerged as one of the promising candidates for heterogeneous catalysis, many organic reactions are less explored and their catalytic mechanisms need further exploration.

The [4 + 2] cycloaddition reaction between dienes and dienophiles, widely known as the Diels–Alder reaction, is the most fascinating one-step transformation with complete atom economy and has been widely used in many organic transformations.[6] Diels–Alder reactions are thermally allowed and need elevated temperature, and high boiling solvents in many cases. However, this difficulty can be overcome by designing suitable catalysts that can encapsulate the reactants and reorganise them in the confined space of the catalyst. This ultimately results in a low temperature, high-yield reaction with a facile reaction rate. Yet, achieving such catalysts is a challenging task for synthetic chemists. MOFs can be promising candidates in this aspect. Fujita and co-workers for the first time reported Diels–Alder reactions inside a crystalline polymeric framework.[7] To the best of our knowledge, there has been no report on catalytic Diels–Alder reactions using MOFs. In this regard we have prepared an electron rich anthracene based rigid tetra-carboxylic acid (H_4ADBTD) employing a Suzuki–Miyaura coupling reaction. The corresponding Cu-MOF (**MOF-1**) of this acid, with high surface area, has been synthesized. **MOF-1** exhibits effective catalytic activity for Diels–Alder reactions of aromatic reactants. The advantages of using a MOF as a catalyst over the traditional homogeneous catalysts are the heterogeneity and the reusability of the catalyst.

Solvothermal reaction of H_4ADBTD and $Cu(NO_3)_2{\cdot}3H_2O$ in *N*,*N*-dimethylformamide (DMF) at 90 °C in the presence of HBF_4 for 24 h afforded **MOF-1** as green crystals with the empirical formula $Cu_2(H_2O)_2$(ADBTD)$\cdot x$S (S stands for non-coordinated solvent molecules). A single-crystal X-ray diffraction study revealed that **MOF-1** crystallizes in an orthorhombic system with an *Ima*2 space group. In **MOF-1**, the ADBTD^{4-} anion connects the $Cu_2(COO)_4(H_2O)_2$ secondary building units to form a three-dimensional (3D) network (Fig. 1). The PLATON calculation suggests that **MOF-1** contains 79.6% void space, which is accessible by the solvent molecules. The huge porosity is generated by the porous nano-channels present along each crystallographic direction, *a*, *b* and *c* of dimensions $\sim 14.93 \times 17.39$ Å^2, $\sim 21.34 \times 13.79$ Å^2 and 11.71×11.53 Å^2, respectively (Fig. 2, Connolly surfaces).

Thermogravimetric analysis (TGA) showed a weight loss of 47% in the temperature range 30–150 °C, which corresponds to the loss of DMF and water molecules. The framework decomposes beyond 320 °C (ESI†). The activated sample (**MOF-1a**) was stable after desolvation of **MOF-1**, as indicated by TGA. The phase purity and stability of the **MOF-1** were confirmed by comparing PXRD patterns of the bulk material and **MOF-1a** with the simulated pattern (ESI†).

High porosity and thermal stability make **MOF-1a** a potential material for gas storage. The permanent porosity was measured by the N_2 adsorption study at 77 K, which showed typical type-**II** adsorption behaviour (Fig. 3). The estimated BET surface area of **MOF-1a** is 1058 $m^2\ g^{-1}$ and the obtained pore volume from the

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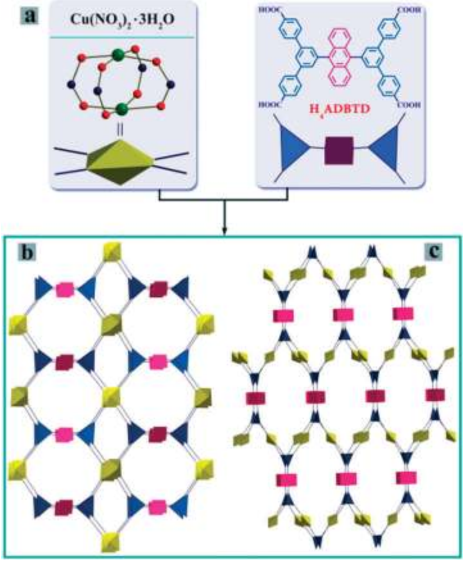


Fig. 1 (a) Schematic representation of the formation of 3D **MOF-1** and the hexagonal nano-channels in the structure along (b) the *b*-axis and (c) *c*-axis (bottom). Colour codes: Cu green, O red, C blue.

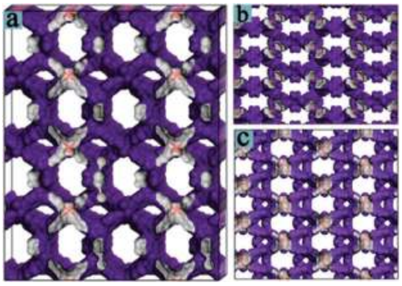


Fig. 2 (a) Connolly surface of **MOF-1** showing large three-dimensional cross-linking channels along (a) the *b*-axis (b) *c*-axis and (c) *a*-axis (inner surfaces: purple; outer surfaces: gray).

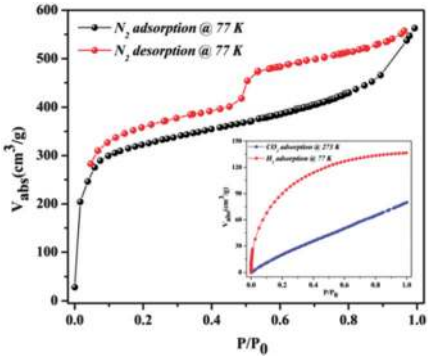


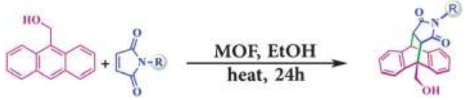
Fig. 3 N_2 adsorption isotherm of **MOF-1a** at 77 K (0–1 bar). The black and red spheres represent adsorption and desorption, respectively. Inset: H_2 and CO_2 adsorption isotherms.

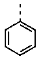
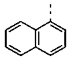
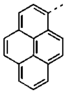
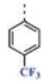
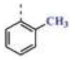
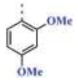
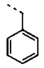
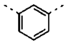
isotherm is 0.793 cc g^{-1}. The pore size distributions derived from N_2 adsorption revealed the presence of three different pore diameters of ∼7.1 Å, 8.5 Å and 20.7 Å, which are as expected from the crystal structure. The H_2 and CO_2 adsorption isotherms show moderate uptake at 77 and 273 K, respectively. It adsorbed up to 12.2 mg g^{-1} of H_2 (136.6 cc g^{-1} at STP) at 77 K and 1 bar, and 80 cc g^{-1} of CO_2 at 273 K and 1 bar (Fig. 3, inset).

Structure analysis revealed that the pore walls are made of the electron rich conjugated anthracene backbone of the ligand, which could encapsulate aromatic reactants through π–π interaction. This expectation encouraged us to attempt catalysis involving aromatic compounds. However, the catalytic activity of porous materials requires encapsulation of reactants into channels to facilitate heterogeneous catalysis. A reactant uptake measurement was carried out with 9-hydroxymethylanthracene (**1a**) to further establish the intrinsic porosity of **MOF-1a** and its affinity for aromatic moieties. When **MOF-1a** was added to an ethanol solution of **1a** at room temperature, the initial absorption intensity gradually decreased during regular time intervals, confirming encapsulation of **1a** into **MOF-1a** (ESI†). PXRD of the **1a** adsorbed **MOF-1a** showed that the framework structure remained intact, which suggests the suitability of the present system for heterogeneous catalysis (ESI†). **1a** generally acts as a diene and forms the Diels–Alder adduct in the presence of dienophiles by bridging the central ring of the anthracene moiety (9, 10 positions).

When **1a** and *N*-phenylmaleimide were added to ethanol in the presence of **MOF-1a** (11%) at 40 °C and stirred for 24 h, we found the yield of adduct formation to be 86% (based on NMR analysis), whereas in the absence of **MOF-1a** only 22% product was isolated under the same reaction conditions. To explore this catalytic activity further, we have used a variety of other N-substituted maleimide derivatives (Table 1, entries 2–11) as dienophiles, while **1a** was used as a diene in all the cases. Poly-aromatic *N*-maleimides like *N*-(1-naphthalene)maleimide and *N*-(1-pyrenyl)maleimide are generally less reactive, but in the presence of **MOF-1a** high yields were obtained even at 50 °C using a low boiling solvent. The strong π–π interactions of the highly electron delocalized poly-aromatic reactants with the aromatic walls of **MOF-1a** facilitate encapsulation, which results in higher catalytic efficiency. In contrast, *N*-cyclohexylmaleimide under almost similar conditions showed a relatively lower reactivity (60%) compared to phenyl analogues. This phenomenon indicates weaker encapsulation of it owing to the presence of the aliphatic cyclohexyl group, which is not suitable for the π–π interaction with the backbone of the MOF. A similar observation was made with *N*-(2,4-dimethoxyphenyl)maleimide (75%), where the π–π interaction with the walls of the MOF is restricted by the methoxy groups. Different electronic effects could also be a reason for such a difference in the reactivity of the aliphatic and aromatic substituted maleimides. Asymmetric maleimides, such as *N*-(*o*-tolyl)-maleimide and *N*-(2,4-dimethoxyphenyl)maleimide, give two different isomeric products (as indicated by NMR spectroscopy) because of their relative orientation with respect to the hydroxymethyl group of **1a** (ESI†). Interestingly, for *N*,*N*-(1,3-phenylene)dimaleimide, we were able to isolate exclusively a product formed by the [2 + 4] cycloaddition of both the maleimides in the presence and absence of **MOF-1a**. Formation of adducts on both the maleimide groups of such reactants was not known earlier. However, the rate of the reaction in the presence of **MOF-1a** is much higher than the non-catalytic one. Diels–Alder reactions are known to be catalysed by a Lewis acid like Cu(II). To check whether the Cu(II) present in the MOF played a key role in the catalysis, a few similar reactions were carried out in the presence of $Cu(OAc)_2·2H_2O$ (which has the paddle-wheel backbone like **MOF-1a**). Surprisingly, we have not seen any significant change in the yields compared to reactions without

Table 1 Diels–Alder reactions of 9-hydroxyanthracene and N-substituted maleimides



Entry	R	Temp (°C)	Yield (%)	
			With MOF	Without
1		40	86	22
2		50	77	10
3		50	65	8
4		40	80	15
5		40	82	17
6		40	85	15
7		40	75	10
8		40	80	17
9		45	70	10
10		45	60	13
11		50	65	7

catalyst. This clearly reflects the potential of **MOF-1a** as a heterogeneous catalyst for the Diels–Alder reactions (ESI†). All the products were purified using column chromatography and characterized using NMR spectroscopy and ESI-HRMS (ESI†). The catalyst was separated by filtration and washed several times with ethanol. It is noteworthy that the recovered catalyst was activated every time prior to further use. The catalytic activity of **MOF-1a** remains almost the same even after three different cycles and PXRD of the recovered catalyst (ESI†) showed it to be quite stable under the reaction conditions and can be used for further catalytic cycles.

The above-mentioned catalytic reactions presumably involve a three-step mechanism: encapsulation of the reactants, reorganization and adduct formation. After adduct formation, the product is released from **MOF-1a** as the initial planar **1a** becomes bent (after product formation) and thereby weakens the π–π interaction with the walls of the MOF, which makes it difficult for the product to stay in the confined space of the MOF. The enhanced catalytic activity using **MOF-1a** could be attributed to the reduction of entropy loss (Δ*S*) and activation energy of such addition reactions due to encapsulation and reorganization of the reactants, respectively, prior to product formation. Such pre-organization in confined space decreases the activation energy of the reaction by stabilizing the transition state through π–π interaction (Fig. 4).

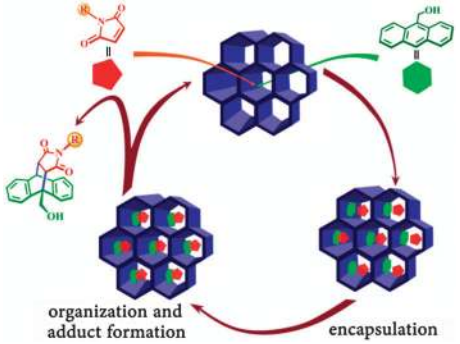


Fig. 4 Proposed mechanism for the catalytic Diels–Alder reaction.

In conclusion, a highly porous electron rich **MOF-1** has been synthesized using a π-electron rich tetracarboxylic acid. The high surface area and electron rich nature of the pore ensured high affinity towards aromatic reactants through π–π interaction. In particular, it shows effective catalytic Diels–Alder reactions under mild reaction conditions within porous nano-channels. Moreover, less reactive poly-aromatic maleimides undergo excellent conversion in the presence of **MOF-1a** even using low boiling solvents. Aliphatic reactants have been shown to have lower reactivity than aromatic reactants due to their weaker interaction with the MOF. Finally, the heterogeneous nature and high thermal stability under the reaction conditions were successfully utilized for many catalytic cycles.

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