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Acid–base directed supramolecular isomers of isophthalate based MOFs for CO₂ adsorption and transformation†

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The ubiquitous [Cu(O₂CR)₄] paddlewheel molecular building block (MBB) is renowned for producing highly porous metal–organic frameworks (MOFs), yet some carboxylate based ligands can result in supramolecular isomers. We show that it is possible to manipulate the synthesis conditions to favor one isomer over another yielding MOFs with either an *lvt* or *nbo* topology. These isomers exist because the 4-connected paddlewheel MBB and isophthalate based ligand can form either a square grid or a Kagomé lattice, where layers can join to give their respective framework topologies. Topology differences and accessible Cu(II) centers in isomers of [Cu₂L]_n were evaluated for their porous properties towards CO₂ and their abilities to transform CO₂ into value added chemicals under ambient conditions.

Continual efforts have been made to develop porous materials for useful applications in the disciplines of separation,^{1,2} sensing,^{3–5} catalysis,^{6,7} and gas storage.^{8–12} Metal–organic frameworks (MOFs) are positioned to address these topics due to their modular nature.^{13–19} Yet the combination of metal ions/clusters and organic/organometallic molecules to facilitate the bottom-up design of MOFs is influenced by many factors during their syntheses. For example, the [Cu₂(O₂CR)₄] paddlewheel molecular building block, MBB, and the ligand 1,3-benzenedicarboxyate, 1,3-BDC, is notorious for forming supramolecular isomers in the form of discrete structures known as metal–organic polyhedra,^{20,21} two-dimensional structures with topologies of a square grid (*sql*) and Kagomé lattice (*kgm*),^{22,23} and a three-dimensional *usf* topology.²⁴ In these instances, differences in the reaction conditions favour certain products; however, sometimes mixtures occur and this is when separation based on their physical properties, such as density, has been used to separate multiple products.²⁵

MOFs can be designed to avoid supramolecular isomers by targeting specific network topologies, such as *rht*,^{26–28} but some MOFs are inherently prone to form isomers or even to interpenetrate. One case in-point is the joining of two 1,3-BDC molecules yielding a tetracarboxylate ligand (Scheme 1) that has been used in an isostructural series of NOTT and related materials.^{29–36} These materials have shown an abundance in *nbo* or pillared Kagomé lattice structures; whereby their utility has been in gas sorption of H₂ and CO₂. It would be interesting to develop their counterpart *lvt* or pillared square grid isomers of this series for comparison.

The concentration of CO₂ in the atmosphere is annually increasing and this valuable commodity should be utilized rather than stored in MOFs or sequestered underground. Therefore, research conducted on copper paddlewheel based MOFs have shown useful results in converting CO₂ into value added chemicals.^{37–40} It has further been shown that by increasing the density of copper paddlewheel MBBs, the reaction yields can be improved.⁴¹ Therefore, supramolecular isomers that display different arrangements of the copper paddlewheel may similarly show differences in chemical reactivity.

Solvothermal synthesis of *nbo* and *lvt* supramolecular isomers (Fig. 1) was controlled by varying the amount of trifluoroacetic acid (TFA) or pyridine added to a DMF solution containing copper nitrate hydrate and the protonated ligand (details in the ESI†).⁴² The isomers were identified by comparing the powder X-ray diffraction (PXRD) profiles with the calculated structures deposited in the CCDC (CCDC ref #



Scheme 1 Connected isophthalic acid molecules.

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† Electronic supplementary information (ESI) available: TGA, FTIR, and catalysis NMR information is available for the *lvt* and *nbo* MOFs. See DOI: 10.1039/c7ce00405b

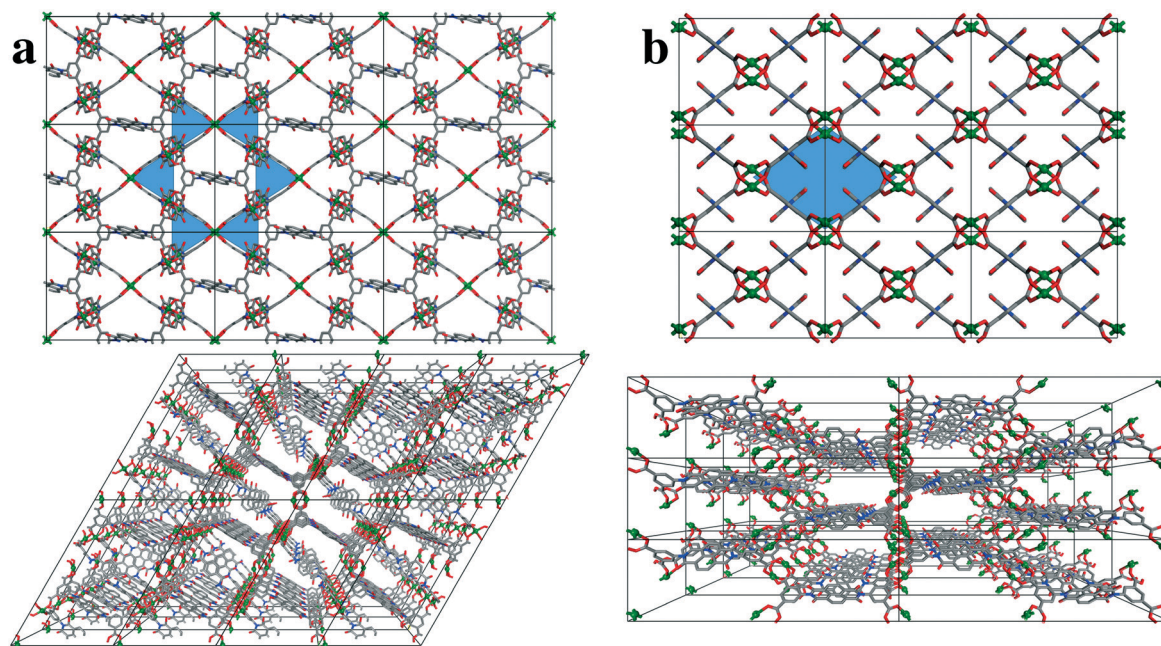


Fig. 1 a) View of **nbo** along the *c*-axis shown as triangles and *b*-axis perspective, b) view of **lvt** along its *b*-axis shown as parallelograms and *a*-axis perspective.

789422-789424) as shown in Fig. 2. Major differences between the two isomers are identified from their initial diffraction peaks at 2θ values of 4.8° and 5.2° respectively for **lvt** and **nbo** topologies of $[\text{Cu}_2\text{L}\cdot\text{X}_2]_n$ (X = solvent or water). The diffractograms show that increasing the TFA amount from $5\ \mu\text{L}$ to $40\ \mu\text{L}$ per reaction alters the relative isomer abundance of **nbo** and **lvt**. At $30\ \mu\text{L}$, **nbo** was prevalent, which is then followed by a mixed state at $40\ \mu\text{L}$ addition of TFA.

The influence of TFA as a templating chemical agent is hard to envision, yet varying its amount had profound influence on the outcome of the crystalline material. With more TFA added to the reaction, the time to grow crystals steadily increased from 24 to 48 hours. Meanwhile, 3,5-lutidine or

other pyridine bases showed predominance of the **lvt** supramolecular isomer. The ligand's flexibility around the imide bond also differs than previous molecules used to synthesize similar **nbo** MOFs. Meanwhile, the previously reported MOF with an **lvt** topology (NOTT-109) is similar in structure with a naphthalene moiety in between the two isophthalates.

The infrared spectra showed no perceivable difference between the structures as coordination is similar between the two isomers (Fig. S1†). The samples were washed with DMF to remove unreacted ligands and their thermogravimetric analysis (TGA, Fig. S2†) profiles showed continual weight loss believed to be due to solvent loss and framework decomposition. We tried, with difficulty, to activate these samples for gas sorption, by first exchanging the mother liquor with DMF followed by either CHCl_3 or methanol. The methanol exchanged samples were additionally treated for supercritical drying by exchanging methanol for liquid CO_2 , followed by heating the sample above the CO_2 critical temperature of $31.1\ ^\circ\text{C}$ using a critical point dryer instrument. CO_2 isotherms were collected at 273 K and 298 K to evaluate the MOFs' adsorption capabilities (Fig. S3†). Adsorption maxima of 37 (25) and 27 (18) $\text{cm}^3\ \text{g}^{-1}$ for **nbo** and **lvt** were obtained at 273 K (298 K), but the surface area determined from the N_2 isotherms (Fig. S4†) collected at 77 K only showed surface areas as high as 1041 and $670\ \text{m}^2\ \text{g}^{-1}$, respectively.

Because $\text{Cu}(\text{II})$ ions show a high affinity towards CO_2 and can participate as a Lewis-acid metal, their incorporation into a MOF can afford it as a heterogeneous catalyst for CO_2 chemical fixation reactions. We therefore used chloroform exchanged samples of $[\text{Cu}_2\text{L}]_n$ to perform cycloaddition reactions between epoxides and CO_2 . The **lvt** and **nbo** MOF catalysts displayed high catalytic efficiency for CO_2 and propylene

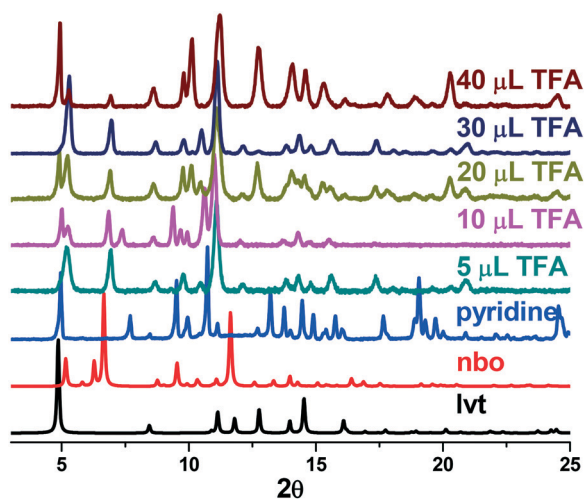

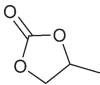

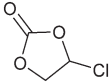

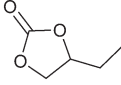
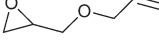
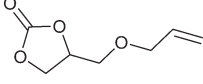
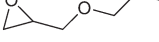
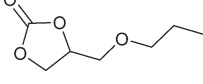


Fig. 2 PXRD diffractograms of calculated **lvt** (black), **nbo** (red) and experimental results.

Table 1 Cycloaddition reaction yields using the supramolecular isomers, different substituted epoxides, and CO₂ for their best yield^a

Epoxides	Products	lvt yield (%)	nbo yield (%)
		89 ± 5	94 ± 2
		64 ± 5	81 ± 6
		35 ± 6	44 ± 3
		22 ± 1	26 ± 2
		13 ± 1	18 ± 1

^a Reaction conditions: epoxide (10.0 mmol), *n*-Bu₄NBr (290.0 mg, 0.9 mmol) and MOF (35 mg, 0.25 mol% based on Cu(II)), under 1 atm of CO₂ and stirred at room temperature for 48 h. The yield was monitored by ¹H NMR.

oxide transformation into propylene carbonate under ambient conditions with yields averaging 89% and 94% (Table 1), respectively and maintained their crystallinity (Fig. S5†). The yields for **nbo** remained higher for larger epoxide reactants than for reactions carried out using the **lvt** MOF, which we attribute to the larger pores in **nbo** allowing for better diffusion of the reacts to the catalytic copper paddlewheel sites.

Conclusions

To summarize this project, we have successfully synthesized two structural isomers of [Cu₂L]_{*n*} that exhibited either an **lvt** or **nbo** topology, where the synthetic conditions – using an organic acid or base – favoured the isomer outcome. Both isomers could adsorb CO₂, which allowed these MOFs to act as catalysts as they participated in the chemical transformation of CO₂ and epoxides into cyclic carbonates. The difference in pore structure also led to the enhanced catalysis efficiency of the larger substrate within **nbo** over **lvt**. This technique of controlling supramolecular isomers will be further developed to test additional tetracarboxylic ligands using a similar design.

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