

Porous Materials

Significant Gas Adsorption and Catalytic Performance by a Robust Cu^{II}–MOF Derived through Single-Crystal to Single-Crystal Transmetalation of a Thermally Less-Stable Zn^{II}–MOF

Tapan K. Pal,^[a] Dinesh De,^[a] Subhadip Neogi,^[b] Pradip Pachfule,^[c] S. Senthilkumar,^[b] Qiang Xu,^{*[c]} and Parimal K. Bharadwaj^{*[a]}

Abstract: By using a bent tetracarboxylic acid ligand that incorporates a pendent $-NH_2$ functional group, a 3D Zn^{II}-framework (1) based on Zn₂(CO₂)₄ secondary building units and Zn₁₂(CO₂)₂₄ supramolecular building blocks has been synthesized. Framework 1 is thermally less stable, which precludes its application as a porous framework for gas adsorption or catalytic studies. This framework undergoes single-crystal to single-crystal transmetalation to give isostructural

 $\mathbf{1}_{cu}.$ Unlike 1, the Cu^{II} analogue is very stable and can be activated by removing metal-bound lattice solvent molecules by heating to afford $\mathbf{1}_{cu'}$. The activated $\mathbf{1}_{cu'}$ exhibits excellent H₂ storage (2.29 wt%) at 77 K and a high 32.1 wt% CO₂ uptake at 273 K. Additionally, it displays significant selectivity for CO₂ adsorption over N₂ and H₂ and can catalyse size-selective Knoevenagel condensation reactions.

Introduction

Metal-organic frameworks (MOFs) are crystalline porous materials, for which most of the studies are focused towards systematic variation of porosity through 1) creation of unsaturated metal centres (UMCs) and 2) channel (pore) functionalization with organic groups to augment their potential applications.^[1] Formation of a thermally robust framework that contains metal-bound solvent molecules is an essential prerequisite for the creation of UMCs, whereas the position of functional groups in the linker is crucial in the sense that it should remain free.^[2] Frequently, however, difficulties arise due to thermal/chemical instability of the as-synthesized frameworks because they may collapse upon solvent removal by heating. Accordingly, much effort has been devoted to structural aspects of MOFs with a view to gaining superior stability.^[3] Post-synthetic modification (PSM), involving single-crystal to single-crystal (SC-SC) transformation,^[4] is a fascinating technique. The presence of secondary building units (SBUs) and supramolecular building blocks (SBBs), based on metal clusters,

- [b] Dr. S. Neogi, S. Senthilkumar Inorganic Materials and Catalysis Division, CSIR-CSMCRI Bhavnagar, G. B. Marg, Gujarat 364002 (India)
- [C] P. Pachfule, Prof. Q. Xu
 National Institute of Advanced Industrial Science and Technology Ikeda, Osaka, 563-8577 (Japan)
 E-mail: q.xu@aist.go.jp
- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201503163.

is a helpful approach to maintaining framework integrity after a metal-exchange reaction.^[5] By using this technique, multifunctional MOFs can be obtained that may or may not be accessible by the de novo method. Moreover, transmetalation can be used to fabricate the interior and exterior of MOFs with improved properties.^[6] With the aforesaid annotations in mind, and evoking our experiences on bent carboxylates,^[7] a new angular 2'-amino-[1,1':3',1''-terphenyl]-3,3'',5,5''-tetracarboxylic acid ligand (H_4L ; Figure 1a) has been designed. In this ligand, the -NH₂ group is placed to sterically preclude binding a metal that is coordinated to the carboxylates.



Figure 1. a) Ligand H_4L ; b) view of 3D architecture of framework; c) secondary building unit (SBU); and d) supramolecular building block (SBB).

Chem. Eur. J. 2015, 21, 19064-19070

Wiley Online Library

© 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

[[]a] T. K. Pal, D. De, Prof. P. K. Bharadwaj Department of Chemistry, Indian Institute of Technology Kanpur Uttar Pradesh, Kanpur 208016 (India) E-mail: pkb@iitk.ac.in



Results and Discussion

Under solvothermal conditions, H₄L reacts with Zn(NO₃)₂·6H₂O (1:2 molar ratio) to form a non-interpenetrated 3D MOF, $\{[Zn_2(L)(H_2O)_2] \cdot (5DMF) \cdot (4H_2O)\}$ (1; $L = L^{4-}$). It crystallizes in the hexagonal space group P63/mmc (Table S1 in the Supporting Information), in which the asymmetric unit contains one fourth of the ligand, one Zn^{II} ion and a water molecule (half occupancy). The structure contains paddlewheel Zn₂(COO)₄ clusters as SBUs (Figure 1c), in which every Zn²⁺ ion adopts distorted square-pyramidal coordination. Four equatorial positions of Zn²⁺ are occupied by carboxylate oxygen atoms from four different L units and the apical position is coordinated to one water molecule. The bulk phase purity is confirmed by comparing the experimental and simulated powder X-ray diffraction (PXRD) patterns (Figure S7 in the Supporting Information). As illustrated in Figure 1b, three isophthalate moieties of ligand L link three SBUs to form a triangular window. Two such windows are further linked by three L units to produce a Zn₁₂(CO₂)₂₄ polyhedra (Figure 1d) with six vertices, five faces and nine edges. The core cavity is accessible through two triangular and three square faces (Figure 1d). The internal spherical cavity of this polyhedron has a diameter of approximately 5.680(1) Å (distance refers to atom-to-atom connection throughout), ignoring coordinated solvents, whereas the size of the triangular aperture is approximately 5.08 Å. As expected, the -NH₂ groups remain free and are pointed towards the cavity of $Zn_{12}(CO_2)_{24}$ polyhedron. These polyhedral $Zn_{12}(CO_2)_{24}$ units can be regarded as SBBs. A close look at the packing diagram of 1 reveals that six SBBs are interconnected along the crystallographic c axis to afford the overall 3D framework (Figure 1b).

The solvent molecules present in the cavity are highly disordered and cannot be located unambiguously. However, the exact solvent composition was established from a combination of thermogravimetric weight loss and elemental analysis, which are in good agreement with the solvent-accessible volume calculated by using PLATON (4648 Å³, 65.13%).^[8] The PXRD patterns reveal that the framework turns amorphous at 50°C (Figure S8 in the Supporting Information). Even solvent exchanges by using different solvents like MeOH, EtOH, Me₂CO or CH₂Cl₂, followed by mild activation, lead to complete breakdown of the framework. This behaviour leads us to postulate that Zn^{2+} ions with d^{10} electron configuration provide no ligand-field stabilization energy and presumably the vulnerability of framework 1 originates from the removal of the axial aqua ligand.^[9] The unstable nature of **1** upon de-solvation prevents us from obtaining a porous framework for gas-storage applications.

The presence of paddlewheel SBUs and the accessibility of polyhedral SBBs from the large channels provide an opportunity to explore metal-ion exchange reactions through a post-synthetic exchange (PSE) approach. When dipped in a solution of $Cu(NO_3)_2$ ·3H₂O (0.05 M) in DMF at room temperature, the colourless crystals of **1** gradually turns greenish blue in 6 d. Optical microscopic observation shows that the crystals maintain their original shapes and sizes throughout the PSE process

(Figure S9 in the Supporting Information). The metal replacement was initially verified by the EPR spectrum (Figure S10 in the Supporting Information) of the greenish-blue crystals. The X-ray fluorescence spectroscopy (XFS) demonstrates that no significant amount of Zn²⁺ ion is left in the metal-exchanged framework. Also, the PXRD pattern of the metal-exchanged product does not reveal the formation of any new phase (Figure S11 in the Supporting Information). These observations clearly indicate a metal-ion exchange in a SC-SC manner. Fortunately, framework 1 maintains single crystallinity, which allows single-crystal X-ray data collection. The X-ray structural investigation (Table S1 in the Supporting Information) indicates that the transmetalated product has a similar structure (Figure S12 in the Supporting Information) to that of 1, with the formula { $[Cu_2(L)(H_2O)_2]$ ·(5 DMF)·(H_2O)} (1_{cu}). However, the M···M distance in the paddlewheel SBU decreases in 1_{cu} (Table S2 in the Supporting Information). Although ligand H₄L bears close resemblance to the previously reported diisophthalate ligand,^[10] the structure of 1 is novel due to inward positioning of the $-NH_2$ group in H_4L , and exhibits 4,4-c net with different ssa network topology (Figure S13 in the Supporting Information). MOF 1_{cu} could be synthesized solvothermally by treating $Cu(NO_3)_2 \cdot 3H_2O$ with H_4L , although in poor yields (<10%).

The kinetics of the Zn²⁺-to-Cu²⁺ ion exchange, monitored by energy-dispersive X-ray spectroscopy (EDX), indicate a 50% replacement of Zn²⁺ ions by Cu²⁺ within 2 d, whereas a 95% exchange took place in 4 d. Complete exchange is achieved in 6 d (Figure S14 in the Supporting Information). However, the reverse transmetalation does not occur even in a concentrated solution of Zn(NO₃)₂-6H₂O (0.5 m) in DMF with a long exposure time, even under warm conditions, which points to the greater thermodynamic stability of 1_{cu}. Also, Zn^{II} ions of 1 could not be replaced by other transition-metal ions, such as Co²⁺ and Ni²⁺. The variable-temperature PXRD experiment of 1_{cu} shows that, in contrast to 1, it is highly stable and maintains framework integrity up to at least 200 °C (Figure S12 in the Supporting Information).

The presence of porous channels and the high thermal stability of 1_{cu} led us to probe its gas sorption measurements. Activation of the sample was accomplished by dipping crystals of 1_{cu} in EtOH for 7 d, followed by heating at 150 °C under high vacuum to produce the guest-free framework (1_{cu} '). During activation, the colour of the crystals changed from greenish blue to deep blue. However, the crystallinity of 1_{cu} ' was not sufficient for single-crystal X-ray data collection. The activated framework was first subjected to N₂ gas sorption measurements at 77 K up to a relative pressure (*P*/*P*₀) of 1.0. It shows a type I reversible isotherm (Figure 2a), which indicates the microporous nature of the framework. The calculated Brunauer–Emmett–Teller (BET) surface area was 1410 m²g⁻¹, with a pore volume of 0.97 cm³g⁻¹ and a pore size in the range of 3.01 to 7.2 Å (Figure S15 in the Supporting Information).

Further interesting results were obtained from the H_2 and CH_4 adsorption studies. Importantly, both these gases represent a potential replacement for depleted energy sources, for which the main goal is to develop on-board gas-storage systems.^[11] The H_2 sorption isotherm of 1_{cu} at 77 K showed type I





Figure 2. a) N_2 adsorption isotherm of $\mathbf{1}_{cu}$ at 77 K and b) H_2 adsorption isotherm of $\mathbf{1}_{cu}$ at 77 K.

behaviour (Figure 2b) with a storage capacity of 261 cm³g⁻¹ (2.29 wt%) at 1 bar (Figure 2b and Figure S16 in the Supporting Information). The adsorption and desorption isotherm curves completely overlap with each other without any hysteresis. Noticeably, the hydrogen uptake shown by 1_{cu} ' is comparable and even better than many reported MOFs (Table S3 in the Supporting Information). At 13 bar pressure, the H₂ uptake capacity of 1_{cu} ' reached a maximum of 364 cm³g⁻¹ (3.26 wt%; Figure S17 in the Supporting Information). Such good storage performance may be attributed to high electrostatic interactions between H₂ molecules and exposed Cu^{II} sites in the structure.

The room-temperature CH₄ uptake study of $1_{cu}'$ under both low- (Figure S18 in the Supporting Information) and high-pressure conditions also displayed type I adsorption behaviour without any hysteresis. The framework adsorbs a substantially high 10.30 wt% of methane (144.25 cm⁻³g⁻¹) at 44 bar (Figure 3a). This uptake value is higher or comparable to some known MOFs, such as MIL-53(AI) and MIL-53(Cr) (8.8 wt%), HKUST-1 (10.2 wt%), UMCM-1 (11.4 wt%), Ni-MOF-74 (11.9 wt%), CPO-27-Mg (13.7 wt%), PCN-11 (14.0 wt%) measured at different high pressures.^[12]

Given the importance of developing protocols to reduce the massive emission of CO₂, we next explored the CO₂ gas storage^[13] potential of $\mathbf{1}_{cu'}$ at different temperatures and pressures



CHEMISTRY

A European Journal Full Paper

Figure 3. a) CH₄ adsorption isotherm of 1_{cu} 'up to 50 bar, b) CO₂ adsorption isotherm, c) Q_{st} of CO₂ and d) CO₂, CH₄, H₂ and N₂ adsorption isotherms of 1_{cu} at 273 K.

of up to 1 bar (Figure 3b). The isotherms at 273 and 298 K displayed type I adsorption behaviour without hysteresis, in which the maximum CO_2 uptake at 273 K was found to be

Chem. Eur. J.	2015,	21,	19064 -	19070
---------------	-------	-----	---------	-------

www.chemeurj.org



164.65 cm³g⁻¹ (32.1 wt%), whereas the value at 298 K approximated to 104.39 cm³g⁻¹ (20.5 wt%; Figure S19 in the Supporting Information). Though numerous MOFs with significant CO₂ uptake have been reported, only limited examples of porous MOFs that exhibit over 30.0 wt% CO₂ uptake at 273 K and 1 atm (Table S4 in the Supporting Information) are known.

The isosteric heat of CO_2 adsorption (Q_{st}), evaluated by using the Clausius-Clapeyron equation^[14] from the isotherms at 273 and 298 K, gives a value of 37.51 kJ mol⁻¹ (Figure 3c) at zero coverage, which indicates a strong adsorbate-adsorbant interaction. This value is lower than known MOFs with -NH₂ groups, such as bio-MOF-11 (45 kJ mol⁻¹), CAU-1 (48 kJ mol⁻¹), NH₂-MIL-53(AI) and USO-1-AI-A (50 kJ mol⁻¹), but significantly higher than that of CuTATB-60, PCN-6 (35 kJ mol⁻¹), HKUST-1 (35 kJ mol^{-1}) , IRMOF-1, MOF-5 (34 kJ mol^{-1}) , MIL-53(Cr) $(32 \text{ kJ mol}^{-1}),$ NOTT-140 (25 kJ mol^{-1}) and UMCM-1 (12 kJmol^{-1}) .^[15] We also evaluated the CO₂ adsorption selectivity of $\mathbf{1}_{cu'}$ over CH_4 , H_2 or N_2 with the ideal adsorbed solution theory (IAST) based on single-component isotherms^[16] at 273 K (Figure 3d). As shown in Figure 3d, N₂ and H₂ gases do not diffuse into the pores of $\mathbf{1}_{\mathsf{Cu}'}$, whereas CH_4 gas enters only slightly. We presume that the high quadrupole moment and polarizability of CO₂ $(13.4 \times 10^{-40} \text{ Cm}^2 \text{ and } 26.3 \times 10^{-25} \text{ cm}^3, \text{ respective-}$ ly) induce better interaction with the channels and interior wall of the framework, composed of NH₂ functionalities. The CO_2 selectivities over N_2 , H_2 and CH_4 were found to be 280, 288 and 6.95, respectively. Clearly, $1_{cu'}$ exhibits better CO_2/N_2 selectivity compared with other reported MOFs,^[13a] which suggests that it may have potential applications for selective CO₂ capture from flue gas.

The open Cu²⁺ coordination sites and presence of -NH₂ groups in 1_{cu}' subsequently prompted us to explore its catalytic ability for Knoevenagel condensation reactions. In spite of its simplicity, the challenges of Knoevenagel condensation involve 1) base- or acid-catalysed condensation, 2) association of high temperature or microwave irradiation, and 3) self-condensation-/oligomerization-mediated byproducts. As a demonstration, aromatic aldehydes were chosen as substrates due to their possible enclathration inside the cavity of the MOF. The formation of the desired product in each case was confirmed by using ¹H and ¹³C NMR spectroscopy (Figures S20–27 in the Supporting Information), and progress of the reaction was monitored by using TLC. Table 1 summarizes the results with diverse substrates. The absence of any leaching of metal ions

Table 1. Knoevenagel reactions catalysed by $1_{Cu'}$					
	$R H + \langle CN - CN \rangle$	1 _{cu} (10 wt%) CH ₂ Cl ₂ ►	R CN CN		
Entry	R	<i>t</i> [h]	Yield [%]		
1	Ph	2	90		
1 2	Ph 4-FPh	2 2	90 95		
1 2 3	Ph 4-FPh 4-MePh	2 2 3	90 95 90		
1 2 3 4	Ph 4-FPh 4-MePh 4-OMePh	2 2 3 2	90 95 90 95		
1 2 3 4 5	Ph 4-FPh 4-MePh 4-OMePh 1-naphthyl	2 2 3 2 5	90 95 90 95 6		

from the active sites was checked in a control experiment, in which removal of the catalyst after 25 min resulted in complete shutdown of the reaction as monitored by using GC-MS (Figure S28 in the Supporting Information).

The recovered catalyst can be used at least five times without any loss of activity. The PXRD pattern of the recovered catalyst after five cycles was found to be unchanged (Figure S29 in the Supporting Information), which demonstrates the framework integrity. In presence of the catalyst, the IR spectrum of benzaldehyde experiences a 20 cm⁻¹ redshift in the C=O stretching frequency (Figure S30 in the Supporting Information), presumably due to the interaction of carbonyl group with the metal centre.^[17] When a bulky aldehyde was chosen as the substrate, the reaction did not proceed (Table 1), which indicates that sterically encumbered aldehydes are not able to fit inside the cavity of the framework. Finally, we found the -NH₂ groups remain inert towards any post-synthetic covalent modification. A close look at the structure of 1_{cu} reveals that the pendent -NH₂ groups are positioned inward to sterically preclude any post-synthetic covalent modification (Figure S31 in the Supporting information).^[18]

Conclusion

By using angular tetracarboxylic acid H₄L, which incorporates pendent -NH₂ groups, 3D Zn^{II}-framework **1** has been synthesized. The framework is thermally less stable and easily decomposes upon de-solvation. Post-synthetic transmetalation of the Zn^{II} ions by Cu^{II} ions, through a SC–SC transformation generates iso-structural framework $\mathbf{1}_{cu}.$ Framework $\mathbf{1}_{cu}$ shows high thermal stability in the absence of lattice and metal-bound water molecules. The activated framework, $1_{cu'}$, exhibits a large BET surface area with appreciable uptake of H₂, CO₂ and CH₄ gases under both low- and high-pressure conditions. Moreover, framework $\mathbf{1}_{\mathsf{Cu}'}$ selectively adsorbs an appreciable amount of CO₂ gas from a mixture of H₂, N₂ and CH₄ at 273 K, which provides some benefits towards the significant challenge of gas separation under ambient conditions. Additionally, the presence of vacant coordination sites at the Cu^{II} centres allows $\mathbf{1}_{cu'}$ to act as a heterogeneous catalyst for size-selective Knoevenagel condensation reactions.

Experimental Section

Materials and method

Reagent-grade 2,6-dibromoaniline, 1-bromo-3,5-dimethylbenzene, trimethyl borate, $Zn(NO_3)_2$ ·6H₂O and $Cu(NO_3)_2$ ·3H₂O were purchased from Sigma–Aldrich and used as received. All solvents, such as *N*,*N*'-dimethylformamide (DMF), hexane and ethyl acetate were procured from S. D. Fine Chemicals, India, and their purification and drying was accomplished according to standard protocols.

Physical measurements

Infrared (IR) spectra were performed (KBr disk, 400–4000 cm⁻¹) by using a Perkin–Elmer model 1320 spectrometer. Thermogravimetric analyses (TGA) were acquired by using a Mettler Toledo Star

Chem. Eur. J. 2015, 21, 19064-19070

www.chemeurj.org



system (heating rate 5°Cmin⁻¹). Powder X-ray diffraction spectra (Cu_{ka} radiation, scan rate 3° min⁻¹, 293 K) were obtained by using a Bruker D8 Advance Series 2 powder X-ray diffractometer. Microanalyses of all the compounds were carried out by using a Perkin-Elmer Series II elemental analyser model 2400. ¹H and ¹³C NMR spectra (500, 400 and 125 MHz) were recorded in CDCl₃ or [D₆]DMSO by using a JEOL ECX 500 FT instrument with Me₄Si as the internal standard. The following abbreviations are used to describe peak patterns: s=singlet, d=doublet, t=triplet, dd=doublet of doublets, br = broad and m = multiplet. The percentage of metal ions after transmetalation reactions was measured by using X-ray fluorescence (XRF) spectroscopy by using a Rigaku WD-XRF (X-ray generation 4 kW, 60 kV, 150 mA) system and energy-dispersive X-ray spectroscopic data (EDX) were recorded by using a JSM-6010A JEOL Tungsten-Electron Microscope (W-SEM). ESI mass spectra were recorded by using a WATERS Q-TOF Premier mass spectrometer. Melting points were recorded by using an electrical melting point apparatus from PERFIT India and are uncorrected. Low-pressure gas adsorption measurements were performed by using an automatic volumetric BELSORP-MINI-II adsorption equipment and a static volumetric system (Micromeritics ASAP 2020). The high-pressure gas adsorption measurements were carried out by using an automated high-pressure gas adsorption system BELSORP-HP, (BEL, Japan). Prior to BET adsorption measurements, as-synthesized compounds were immersed in ethanol for 5 d at RT to replace lattice guest molecules. The solvent-exchanged frameworks were then heated to $150\,^\circ\text{C}$ for 8 h under vacuum to produce guest-free compounds. The PXRD pattern of the activated samples matched that of the parent compound.

X-ray structural studies

Single-crystal X-ray data of all the complexes were collected at 100 K by using a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo_{$\kappa\alpha$} radiation ($\lambda = 0.71073$ Å). The linear absorption coefficients, scattering factors for the atoms and the anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography.^[19] The data integration and reduction were carried out by using SAINT^[20] software. For each set of data, empirical absorption correction was applied to the collected reflections with SADABS^[21] and the space group was determined by using XPREP^[22] The structure was solved by using direct methods in SHELXTL-97^[23] and refined on F^2 by using full-matrix least-squares in the SHELXL-97^[24] program package. The unit cell contains a large number of disordered solvent molecules that could not be modelled as discrete atomic sites. Therefore, we employed PLATON/SQUEEZE^[8] to calculate the diffraction contribution of the solvent molecules and thus produce a set of solvent-free diffraction intensities. In all compounds, the non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to carbon atoms were positioned geometrically and treated as riding atoms by using the SHELXL default parameters. The hydrogen atoms of the coordinated water molecule in both the structures could not be located in the difference Fourier maps. CCDC 1414679 (1) and 1414680 (1_{cu}) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre. Lattice parameters of the compounds, data collection and refinement parameters are summarized in Table S1 (Supporting Information) and selected bond lengths and bond angles are given in Table S5 (Supporting Information).

Synthesis and characterization of ligand H₄L

Synthesis of tetra-acid ligand H_4L was achieved in the following steps, as shown in Scheme 1. Compound B was prepared according to a reported procedure. $^{[25]}$



Scheme 1.

0.016 mol) and palladium acetate (10 mg) in water (10 mL). The mixture was heated at 80 °C overnight. After cooling to RT, the reaction mixture was extracted with ethyl acetate three times and washed with water. The combine organic phase was dried over anhydrous Na₂SO₄. Evaporation of the solvent afforded the crude product as a pale yellow solid. This was purified by column chromatography (silica gel; ethyl acetate/hexane 1:9) to obtain **C** as a pale yellow solid (700 mg, 33% yield). M.p.: $150 \,^{\circ}$ C; ¹H NMR (500 MHz, CDCl₃, 25 °C, Si(CH₃)₄): $\delta = 1.42$ (t, 12 H), 3.70 (s, 2H) 4.42 (q, 8H), 6.92 (s, 1 H), 7.15 (d, 2H), 8.36 (d, 4H), 8.68 ppm (d, 2H); ¹³C NMR (125 MHz, CDCl₃, 25 °C, Si(CH₃)₄): $\delta = 14.43$, 29.78, 61.61, 118.67, 126.28, 129.73, 130.62, 131.81, 134.59, 140.21, 165.75 ppm; elemental analysis calcd (%) for C₃₀H₃₁NO₈: C 67.53, H 5.86, N 2.63; found: C 67.35, H 5.75, N 2.50.

2'-Amino-[1,1':3',1"-terphenyl]-3,3",5,5"-tetracarboxylic acid (H₄L): The ester, tetraethyl 2'-amino-[1,1':3',1"-terphenyl]-3,3",5,5"tetracarboxylate (C; 1 g), was hydrolysed by refluxing with KOH (5 N, 50 mL) for 72 h. The solution was filtered, the filtrate cooled in an ice-bath and then acidified carefully with concentrated HCl to obtain a pale yellow precipitate. After standing overnight in the freezer, the solid was collected by filtration, washed many times with water and finally dried at 80 °C to obtain H₄L as a yellow powder (yield: 700 mg, 88%). M.p. > 300 °C; ¹H NMR (500 MHz, CDCl₃, 25 °C, Si(CH₃)₄): δ =6.80 (t, 1 H), 7.08 (d, 2 H), 8.17 (d, 4 H), 8.42 ppm (d, 2 H); ¹³C NMR (125 MHz, CDCl₃, 25 °C, Si(CH₃)₄): δ = 122.88, 130.85, 133.99, 135.61, 137.24, 139.26, 145.52, 147.11, 171.89 ppm; elemental analysis calcd (%) for C₂₂H₁₅NO₈: C 62.71, H 3.59, N 3.32; found: C 62.50, H 3.68, N 3.20.

Synthesis of $\{[Zn_2(L)(H_2O)_2] \cdot (5DMF) \cdot (4H_2O)\}$ (1)

A mixture of H_4L (20 mg, 0.05 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (28 mg, 0.1 mmol) in DMF (2 mL) and ethanol (1 mL) were heated at 90 °C under autogenous pressure in a Teflon-lined stainless steel autoclave for 72 h, followed by cooling to RT at a rate of 10 °C h⁻¹. Colourless block-shaped crystals of 1 were isolated (yield: 50%). FT-IR

Chem. Eur. J. 2015, 21, 19064 - 19070

www.chemeurj.org

19068



(KBr pellets): $\tilde{\nu}$ = 3447 (b), 3094 (s), 2929 (s), 1657 (s), 1525 (s), 1438 (m, 1107 (s), 623 cm^{-1} (s); elemental analysis calcd (%) for $C_{37}H_{58}N_6O_{19}Zn_2$: C 43.50, H 5.72, N 8.22; found: C 43.20, H 5.53, N 8.10.

Synthesis of {[$Cu_2(L)(H_2O)_2$]·(5 DMF)·(1 H₂O)} (1_{cu}) by post-transmetalation: As-synthesized single crystals of 1 were dipped in DMF for 2 d to dissolve any remaining reactants and side products that may have been adhered to the crystals. During this process, the solvent was refreshed four times. After this treatment, the single crystals were dipped in Cu(NO₃)₂ (0.05 M) in DMF for 6 d at RT to afford 1_{cu} without any loss of crystallinity. FT-IR (KBr pellets): $\tilde{\nu} = 3435$ (br), 3380 (br), 2940 (s), 1674 (s), 1630 (s), 1372 (s), 1091 (s), 728 cm⁻¹ (s); elemental analysis calcd (%) for C₃₇H₅₂N₆O₁₆Cu₂: C 46.11, H 5.44, N 8.72; found: C 45.90, H 5.20, N 8.50%.

Direct solvothermal synthesis of 1_{cu}: Complex 1_{cu} could also be synthesised by direct solvothermal synthesis in poor yields after several attempts. A mixture of Cu(NO₃)₂·3 H₂O (35 mg, 0.15 mmol) and H₄L (20 mg, 0.05 mmol) in a mixed solvent of DMF (2 mL), H₂O (1 mL), and conc. HCl (0.1 mL) was placed in a Teflon-lined stainless steel autoclave and heated under autogenous pressure to 90 °C for 48 h and then allowed to cool to RT at a rate of 10 °Ch⁻¹) to give crystals of 1_{cu} (yield < 10%).

General procedure for the Knoevenagel condensation reactions

Activated sample $1_{cu'}$ (10 wt%), an aldehyde (1.0 mmol) and malononitrile (1.0 mmol) in CH_2Cl_2 (3 mL) were placed in a roundbottom flask and stirred at RT. The progress of the reaction was monitored by TLC, and the reaction was complete within 2 h. Next, the reaction mixture was filtered and washed several times with CH_2Cl_2 to recover the catalyst. The filtrate was dried over Na_2SO_4 and the solvent was removed in a rotary evaporator. The crude product was purified by using silica gel column chromatography (eluent: 10% ethyl acetate in hexane). The recovered catalyst could be reused without loss of activity after heating at 150 °C under vacuum for 6 h. The PXRD pattern of the catalysts taken after each cycle was found to be identical to that of $1_{cu'}$.

Acknowledgements

We gratefully acknowledge financial support from the Department of Science and Technology, New Delhi, India (J.C. Bose National Fellowship to P.K.B.). T.K.P and D.D. thank the CSIR for a SRF fellowship. P.P. and Q.X. are thankful to AIST for financial support.

Keywords: carbon dioxide · hydrogen · metal–organic frameworks · porous materials · transmetalation

 a) L. Sun, H. C. Hendon, M. A. Minier, A. Walsh, M. Dincă, J. Am. Chem. Soc. 2015, 137, 6164–6167; b) Y. Cui, Y. Yue, G. Qian, B. Chen, Chem. Rev. 2012, 112, 1126–1162; c) J. A. Mason, T. M. McDonald, T.-H. Bae, J. E. Bachman, K. Sumida, J. J. Dutton, S. S. Kaye, J. R. Long, J. Am. Chem. Soc. 2015, 137, 4787–4803; d) K. Manna, T. Zhang, M. Carboni, C. W. Abney, W. Lin, J. Am. Chem. Soc. 2014, 136, 13182–13185; e) R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi, T. K. Woo, Science 2010, 330, 650–653; f) Y.-P. Chen, Y. Liu, D. Liu, M. Bosch, H.-C. Zhou, J. Am. Chem. Soc. 2015, 137, 2919–2930; g) K. M. Choi, K. Na, G. A. Somorjai, O. M. Yaghi, J. Am. Chem. Soc. 2015, 137, 7810–7816; h) P. Müller, F. M. Wisser, V. Bon, R. Grünker, I. Senkovska, S. Kaskel, Chem. Mater. 2015, 27, 2460–2467; i) H. Aggarwal, P. M. Bhatt, C. X. Bezuidenhout, L. J. Barbour, J. Am. Chem. Soc. **2014**, *136*, 3776–3779; j) J. Taylor, S. Dekura, R. Ikeda, H. Kitagawa, Chem. Mater. **2015**, *27*, 2286–2289; k) M. K. Sharma, I. Senkovska, S. Kaskel, P. K. Bharadwaj, Inorg. Chem. **2011**, *50*, 539–544.

- [2] a) Z. Xiang, S. Leng, D. Cao, J. Phys. Chem. C 2012, 116, 10573–10579;
 b) P. V. Dau, K. K. Tanabe, S. M. Cohen, Chem. Commun. 2012, 48, 9370–9372; c) C. D. Wu, A. Hu, L. Zhang, W. Lin, J. Am. Chem. Soc. 2005, 127, 8940–8941; d) Y.-B. Zhang, H. Furukawa, N. Ko, W. Nie, H. J. Park, S. Oka-jima, K. E. Cordova, H. Deng, J. Kim, O. M. Yaghi, J. Am. Chem. Soc. 2015, 137, 2641–2650; e) A. Karmakar, A. V. Desai, B. Manna, B. Joarder, S. K. Ghosh, Chem. Eur. J. 2015, 21, 7071–7076.
- [3] X.-J. Wang, P. Z. Li, L. Liu, Q. Zhang, P. Borah, J. D. Wong, X. X. Chan, G. Rakesh, Y. Li, Y. Zhao, Chem. Commun. 2012, 48, 10286–10288.
- [4] a) C. K. Brozek, M. Dincă, Chem. Soc. Rev. 2014, 43, 5456–5467; b) S. Das, H. Kim, K. Kim, J. Am. Chem. Soc. 2009, 131, 3814–3815; c) J. Tian, L. V. Saraf, B. Schwenzer, S. M. Taylor, E. K. Brechin, J. Liu, S. J. Dalgarno, P. K. Thallapally, J. Am. Chem. Soc. 2012, 134, 9581–9584; d) T.-F. Liu, L. Zou, D. Feng, Y.-P. Chen, S. Fordham, X. Wang, Y. Liu, H.-C. Zhou, J. Am. Chem. Soc. 2014, 136, 7813–7816.
- [5] S. Sen, S. Neogi, K. Rissanen, P. K. Bharadwaj, Chem. Commun. 2015, 51, 3173-3176.
- [6] a) D. Denysenko, T. Werner, M. Grzywa, A. Puls, V. Hagen, G. Eickerling, J. Jelic, K. Reuter, D. Volkmer, *Chem. Commun.* **2012**, *48*, 1236–1238; b) X. Song, T. K. Kim, H. Kim, D. Kim, S. Jeong, H. R. Moon, M. S. Lah, *Chem. Mater.* **2012**, *24*, 3065–3073.
- [7] a) J. K. Schnobrich, O. Lebel, K. A. Cychosz, A. Dailly, A. G. W. -Foy, A. J. Matzger, J. Am. Chem. Soc. 2010, 132, 13941–13948; b) Z. Chen, S. Xiang, T. Liao, Y. Yang, Y. S. Chen, Y. Zhou, D. Zhao, B. Chen, Cryst. Growth Des. 2010, 10, 2775–2779; c) D. Wang, T. Zhao, Y. Cao, S. Yao, G. Li, Q. Huo, Y. Liu, Chem. Commun. 2014, 50, 8648–8650; d) J. Park, D. Feng, H.-C. Zhou, J. Am. Chem. Soc. 2015, 137, 1663–1672.
- [8] A. L. Spek, J. Appl. Crystallogr. 2003, 36, 7-13.
- [9] M. Bosch, M. Zhang, H. C. Zhou, Adv. Chem. 2014, 2014, 1-8.
- [10] Y. Liu, J. R. Li, W. M. Verdegaal, T. F. Liu, H. C. Zhou, Chem. Eur. J. 2013, 19, 5637–5643.
- [11] a) M. P. Suh, H. J. Park, T. K. Prasad, D. W. Lim, *Chem. Rev.* 2012, *112*, 782–835; b) L. J. Murray, M. Dincă, J. R. Long, *Chem. Soc. Rev.* 2009, *38*, 1294–1314; c) T. A. Makal, J. R. Li, W. Lua, H. C. Zhou, *Chem. Soc. Rev.* 2012, *41*, 7761–7779.
- [12] a) S. Bourrelly, P. L. Llewellyn, C. Serre, F. Millange, T. Loiseau, G. Férrey, J. Am. Chem. Soc. 2005, 127, 13519–13521; b) I. Senkovska, S. Kaskel, Microporous Mesoporous Mater. 2008, 112, 108–115; c) H. Wu, W. Zhou, T. Yildirim, J. Am. Chem. Soc. 2009, 131, 4995–5000; d) P. D. C. Dietzel, V. Besikiotis, R. Blom, J. Mater. Chem. 2009, 19, 7362–7370; e) B. Mu, P. M. Schoenecker, K. S. Walton, J. Phys. Chem. C 2010, 114, 6464–6471; f) X.-S. Wang, S. Ma, K. Rauch, J. M. Simmons, D. Yuan, X. Wang, T. Yildirim, W. C. Cole, J. J. López, A. D. Meijere, H.-C. Zhou, Chem. Mater. 2008, 20, 3145–3152.
- [13] a) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae, J. R. Long, *Chem. Rev.* 2012, *112*, 724–781; b) T. M. McDonald, J. A. Mason, X. Kong, E. D. Bloch, D. Gygi, A. Dani, V. Crocella, F. Giordanino, S. O. Odoh, W. Drisdell, B. Vlaisavljevich, A. L. Dzubak, R. Poloni, S. K. Schnell, N. Planas, K. Lee, T. Pascal, L. F. Wan, D. Prendergast, J. B. Neaton, B. Smit, J. B. Kortright, L. Gagliardi, S. Bordiga, J. A. Reimer, J. R. Long, *Nature* 2015, *519*, 303–308.
- [14] S. S. Kaye, J. R. Long, J. Am. Chem. Soc. 2005, 127, 6506-6507.
- [15] Supporting Information (reference [45]).
- [16] T. M. McDonald, D. M. D'Alessandro, R. Krishna, J. R. Long, Chem. Sci. 2011, 2, 2022–2028.
- [17] a) S. Horike, M. Dincă, K. Tamaki, J. R. Long, J. Am. Chem. Soc. 2008, 130, 5854–5855; b) R. K. Das, A. Aijaz, M. K. Sharma, P. Lama, P. K. Bharadwaj, Chem. Eur. J. 2012, 18, 6866–6872.
- [18] a) C. Volkringer, S. M. Cohen, Angew. Chem. Int. Ed. 2010, 49, 4644–4648; Angew. Chem. 2010, 122, 4748–4752; b) K. Hirai, S. Furukawa, M. Kondo, M. Meilikhov, Y. Sakata, O. Sakata, S. Kitagawa, Chem. Commun. 2012, 48, 6472–6474; c) A. Modrow, D. Zargarani, R. Herges, N. Stock, Dalton Trans. 2012, 41, 8690–8696; d) D. Jiang, L. L. Keenan, A. D. Burrows, K. J. Edler, Chem. Commun. 2012, 48, 12053–12055; e) J. Canivet, S. Aguado, G. Bergeret, D. Farrusseng, Chem. Commun. 2011, 47, 11650–11652.

Chem. Eur. J. 2015, 21, 19064-19070

www.chemeurj.org



- [19] International Tables for X-ray Crystallography, Vol. III, Kynoch, Birmingham, 1952.
- [20] SAINT+, version 6.02, Bruker AXS: Madison, WI, 1999.
- [21] G. M. Sheldrick, SADABS, Empirical Absorption Correction Program, University of Göttingen, Göttingen, Germany, 1997.
- [22] XPREP, 5.1 ed., Siemens Industrial Automation, Madison, WI, 1995.
- [23] G. M. Sheldrick, SHELXTL Reference Manual, version 5.1, Bruker AXS, Madison, WI, 1997.
- [24] G. M. Sheldrick, SHELXL-2014, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 2014.
- [25] T. Li, M. T. Kozlowski, E. A. Doud, M. N. Blakely, N. L. Rosi, J. Am. Chem. Soc. 2013, 135, 11688 – 11691.

Received: August 11, 2015 Published online on November 20, 2015