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Two-Dimensional Flexible Ni(II)-based Porous Coordination Polymer Showing Single-Crystal to Single-Crystal Transformation, Selective Gas Adsorption and Catalytic Properties

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Abstract

Novel dimensional (2D)porous coordination А polymer two $\{[Ni_3(TBIB)_2(BTC)_2(H_2O)_6] \cdot 5C_2H_5OH \cdot 9H_2O\}_n$ (1) [TBIB = 1,3,5-tri(1H-benzo[d]imidazol-1yl)benzene, $H_3BTC = 1,3,5$ -benzenetricarboxylic acid) has been synthesized solvothermally. In 1 layers are stacked in ABAB... fashion by virtue of strong intermolecular hydrogen bonding interactions, to generate an overall 3D supramolecular framework, consisting of isolated pockets accommodated solvent molecules inside. These lattice-constituent solvent molecules are replaced by dichloromethane (DCM), after immersing complex 1 in DCM for seven days at room temperature, providing $\{[Ni_3(TBIB)_2(BTC)_2(H_2O)_6] \cdot 6CH_2Cl_2 \cdot 6H_2O\}_n$ (2). Arrangement of layers is slightly changed in compound 2 wherein, small pockets are completely absent. Characterization of these two compounds 1 and 2 has been performed employing, single crystal X-ray diffraction, IR spectroscopy, thermogravimetry and elemental analysis. Importantly, complex 1 shows selective sorption of CO_2 gas at low temperature and pressure, and

simultaneously displays high heterogeneous catalytic activity for Knoevenagel condensation at high temperature.

Keywords: Supramolecular Chemistry; Coordination Polymer; Gas Adsorption; Catalysis; Hydrothermal.

1. Introduction

Recently, the assembly of coordination polymers (CPs) with desired structures and functions has emerged as a very hot research topic for their intriguing structural features and potential applications in a wide range of research fields such as gas storage/separation [1], heterogeneous catalysis [2], sensor [3], and external stimuli (heat, pressure, light or guest) induced structural transformation [4]. Diverse range of dynamic behaviours e.g., breathing of three dimensional (3D) networks, sliding motion of constituent layers and, rotation or distortion of organic linkers coupled with changes in geometry around metal centres can be precisely manifested in guestinduced structural transformations [5]. For a dynamic coordination framework, various noncovalent interactions (e.g. π ... π stacking, hydrogen bonding etc.) are considered as the major responsible factors involved in guest-induced structural transformations [6]. Flexible host frameworks are anticipated to possess a superior selectivity for guest inclusion, to exhibit structural transformation on effective adsorption or desorption phenomenon of guest molecules, since these frameworks are based on coordination bonds as well as associated with supramolecular interactions [7]. Greater degree of flexibility has been exhibited by coordination polymers made up of two dimensional structures, because of the possible movement of the 2D layers in addition to the concomitant alteration in local bond lengths and angles, during the removal or accommodation of guest molecules.

Global climate change, caused mainly due to discharge of CO_2 into the atmosphere has surfaced as the focal point of scientific communities' prime concern [8]. The efficient separation of CO_2 from air under atmospheric pressure has become a pressing issue for academic researchers as well as from industrial standpoint [9]. Physisorption phenomena existent between certain adsorbent materials and CO_2 molecules is an expediently reversible process and it requires much lesser amount of energy, as compared to other conventional energy-intensive methods to remove CO_2 gas [10]. Adsorption properties of a particular material depend on its structural dimensionality (1D, 2D or 3D) in combination with porosity, pore size and surface area.

Porous coordination polymers (PCPs) can be used as heterogeneous catalysts, as these polymers have several advantages such as, easy crystallization in high yields, high thermal stability, insolubility in common organic solvents, fine tuning of the pores by appropriate ligand design and dynamic behaviour in response to guest species etc. To functionalize channel surface, two distinct strategies have been adopted: coordinatively unsaturated/open metal sites (OMS) [11], and introduction of functional organic sites (FOS) [12] by which basic catalyst is generated as a obvious strategic outcome [13]. Hence, PCPs having specific interaction sites in their channels have been envisioned for catalytic applications in organic syntheses, because of several advantages: 1) controlled reaction (stereo and regiocontrols); 2) fast reaction. However, use of these channels in PCPs with such remarkable effects has been very limited [14]. Herein we have reported a new layered coordination polymer $\{[Ni_3(TBIB)_2(BTC)_2(H_2O)_6] \cdot 5C_2H_5OH \cdot 9H_2O\}_n$ which **(1)**, upon immersing in DCM at room temperature provides $\{[Ni_3(TBIB)_2(BTC)_2(H_2O)_6] \cdot 6CH_2Cl_2 \cdot 6H_2O\}_n$ (2), wherein ethanol molecules present in cavities of 1 are replaced by DCM molecules in 2. Compound 1 proves to be an efficient heterogeneous catalyst at 60 °C for Knoevenagel condensation reaction and selective adsorbent material for

carbon dioxide (CO_2) over the other flue gas components at low temperature and ambient pressure.

2. Experimental Section

2.1. Materials and Physical measurements

Reagent grade 1,3,5-tifluorobenzene and metal salt Ni(NO₃)₂·6H₂O were acquired from Aldrich and used as received. All solvents, benzimidazole and K₂CO₃ were procured from S. D. Fine Chemicals, India. Solvents were purified prior to use, following standard procedures. Fourier Transform Infrared spectra (FTIR) were obtained (KBr disk, 400-4000 cm⁻¹) using a Perkin-Elmer model 1320 spectrometer. ¹H NMR and ¹³C NMR spectra were recorded using a JEOL-ECX 500 FT (500 MHz and 125 MHz, respectively) instrument in CDCl₃ with Me₄Si as the internal standard. ESI mass spectra were recorded using a WATERS Q-TOF premier mass spectrometer. Thermograms were recorded on a Mettler Toledo (heating rate of 10°C/min) TGA instrument. Microanalyses for the compounds were obtained using a CE-440 elemental analyzer (Exeter Analytical Inc.). Powder X-ray diffraction (PXRD) patterns were recorded using a Rigaku Rint 2000 X-ray diffractometer, with CuK_{α} radiation (λ = 1.5406 Å). Low pressure gas sorption measurements were performed using BelSorpmax (Bel Japan). All the gases used were of 99.999% purity. As-synthesized compound 1 was heated at 100 °C under vacuum for 10 h, to obtain the guest free compound. Prior to adsorption measurement, the guest-free sample was pretreated at 160 °C under vacuum for 4 h, using BelPrepvacII, and purged with He on cooling. For low temperature measurements, N₂ and H₂ adsorption isotherms were monitored at 77 K, while CO₂ gas adsorption isotherm was monitored at 195 K. Additionally, CO₂ adsorption isotherms were also monitored at 298 K and 273 K. Surface area and pore size distribution were calculated

using BelMaster analysis software package. Gas chromatography (GC) analyses have been recorded on a LingHua GC 9890E instrument, equipped with a flame ionization detector (FID).

2.2. Synthesis of 1,3,5-tri(1H-benzo[d]imidazol-1-yl)benzene (TBIB)

This ligand TBIB was synthesized as recently reported [15].

2.3. Synthesis of complex 1 { $[Ni_3(TBIB)_2(BTC)_2(H_2O)_6] \cdot 5C_2H_5OH \cdot 9H_2O$ }_n

A mixture of Ni(NO₃)₂·6H₂O (0.055 g, 0.19 mmol), TBIB (0.04 g, 0.094 mmol) and H₃BTC (0.02 g, 0.094 mmol) was taken in EtOH:H₂O (6 mL, 2:1 v/v), and heated to 180 °C under autogenous pressure in a Teflon-lined steel bomb for 3 days, followed by slow cooling (1 °C/min) to room temperature. The green colored needle-shaped crystals were collected, washed with ethanol. Yield: ~50%. Anal. calcd. for $C_{82}H_{102}N_{12}O_{32}Ni_3$: C, 50.63; H, 5.25; N, 8.64%. Found: C, 50.7; H, 5.28; N, 8.72%. IR (cm⁻¹, KBr pellet): 3633(m), 3596(m), 3387(m), 1607(s), 1556(s), 1502(s), 1475(s), 1433(s), 1370(s), 1232(s), 773(s), 752(s), 719(s) (Fig. S1).

2.4. Synthesis of complex 2 { $[Ni_3(TBIB)_2(BTC)_2(H_2O)_6]$ ·3CH₂Cl₂·12H₂O}_n

Crystals of **1** were immersed in DCM (dichloromethane) for 4 days at room temperature, whereupon compound **2** is obtained via SC-SC transformations. Anal. calcd. (%) for $C_{75}H_{52}N_{12}O_{30}Ni_{3}Cl_{6}$: C, 44.66; H, 2.6; N, 8.33%. Found: C, 44.8; H, 2.9; N, 8.35%. IR (cm⁻¹, KBr pellet): 3388(m), 1611(s), 1554(m), 1500(s), 1429(m), 1366(s), 1231(m), 770(m), 717(m) (Fig. S2).

2.5. X-ray crystallography

Single crystal X-ray data were collected at 100 K on a Bruker Smart APEX CCD diffractometer, using graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). Linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from

International Tables for X-ray Crystallography. Data integration and reduction were processed [16] with SAINT software. An empirical absorption correction factor was applied to the collected reflections with SADABS, [17] and the space group was determined using XPREP [18]. The structure was solved by direct method, using SHELXTL-97 [19] and refined on F^2 by full matrix least square technique using the SHELXTL-97 [20] package. Several DFIX and DANG commands were included for compound 1, to fix bond angles and bond distances in one distorted ethanol molecule and for compound 2, to fix the C-Cl bond in dichloromethane. All the non-hydrogen atoms were refined anisotropically, except O3W and O8W in 1 while for compound 2, most of the atoms have been refined isotropically including metal atoms. The hydrogen atoms attached to carbon atoms were positioned geometrically, and treated as riding atoms using SHELXL default parameters. Hydrogen atoms could not be located at all water molecules for both these compounds in the difference Fourier maps. Contribution of all hydrogen atoms from the solvent molecules has been incorporated in both the empirical formulae and formula weights in crystal and structure refinement data table. Because of the poor crystal quality of compound 2, the maximum residual electron density value has remained high. We tried the data collection with several crystals from different batches, but each of the crystals came up with similar data. Compound 2 did not diffract well at high angles, and as a result the data completeness was found to be 0.638. The crystal and structure refinement data are tabulated in Table S1, while selective bond lengths and bond angles are provided in Table S2.

2.6. General procedure for Knoevenagel condensation

The catalytic reactions are carried out in DCM medium. In a typical reaction, a solution (10 ml) containing an aromatic aldehyde and malononitrile (1:1 molar ratio) is stirred for 5 min, followed

by the addition of 5 wt% of **1**. The suspension is allowed to stir at 60 °C temperature, under nitrogen atmosphere for 2 h. The progress of the reaction is steadily monitored by TLC. On completion of reaction, the catalyst is removed by filtration, washed with DCM and recovered. The solid catalyst is in fact, reused for the same reaction later. The filtrate is evaporated to dryness under reduced pressure, and the residue is recrystallized from EtOAc:hexane mixture to obtain the pure products.

3. Results and discussion

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3.1. X-ray structural description of compound 1.

X-ray crystallographic analysis of **1** reveals that this complex crystallizes in the triclinic space group *P*-1 and its asymmetric unit contains three Ni(II) ion, two TBIB, two BTC^{3–} ligands, six coordinated water molecules besides five ethanol and nine water molecules in the lattice. Each Ni(II) ion has distorted octahedral NiN₂O₄ coordination [21], with ligation from two benzimidazole N atoms of two different TBIB ligands (Ni–N = 2.063(7)–2.113(6) Å), two carboxylates from two BTC^{3–} ions (Ni–O = 2.004(5)–2.084(5) Å) (both in monodentate fashion), and two coordinated water molecules (Ni–O = 2.004(5)–2.084(5) Å) (Fig. 1). Both Ni–N and Ni–O bond distances are within normal statistical range [22].



Fig. 1. A perspective view of the metal coordination environment in complex 1.

Two types of Ni(II) ions are present in complex **1**, one type (Ni1 and Ni3) is participating in macrocyclic ring formation, while the second type (Ni2) is extending the chain along *b* axis via extended bridging with BTC^{3-} ligand, as shown in the Fig. 2. Distance between Ni1 and Ni3 in the macrocyclic ring is 7.95 Å. These chains are further connected by benzimidazole N atoms of TBIB ligand to provide a typical layered structure along crystallographic *c* axis (Fig. 3).



Fig. 2. Metal running chain along crystallographic b axis (TBIB ligand has been omitted) in complex 1



Fig. 3. Showing, chains are connected through TBIB ligands forming layered structure in **1**. Hatoms are omitted for clarity

It is quite noteworthy, that the framework layers stack in an \cdots ABAB \cdots fashion and further reinforce to give rise an overall 3D supramolecular architecture, through intricate H-bonding interactions, involving metal coordinated water and benzene rings of benzimidazole (Fig. 4). These interactions between layers lead to formation of isolated pockets consisting four ethanol and six lattice water molecules and other small pockets containing one ethanol and one water molecule, while macrocyclic ring within the layer possesses two non-coordinated water molecules along *a* axis (Fig. 5). The solvent-accessible volume is ~36% of the unit cell volume, as calculated from the crystal structure using the PLATON analysis [23] (Fig. 6).



Fig. 4. H-bonding interactions between layers in coordination polymer **1** involving oxygen of coordinated water molecule and hydrogen atom of benzene ring of benzimidazole.





Fig. 5. Isolated pockets filled with solvent molecules in complex 1.

Fig. 6. Space-filled model of compound 1 showing isolated pockets, and connections between layers.

Topological analysis [24] of **1** shows that, it has a (3,3,4,4)-connected **3**,**3**,**4**,**4**L10 net by considering TBIB and BTC³⁻ as 3-connected, metal ions as 4-connected nodes in which Ni1, Ni3 take part in the formation of macrocyclic ring (Fig. 7). The point symbol for this net is $\{4.8^2\}_2\{4^2.6.8^3\}_2\{4^2.6\}_2\{4^2.8^3.10\}.$



Fig. 7. (a) 3-connected TBIB node, (b) 3-connected BTC^{3-} node, (c) 4-connected metal node and, (d) topological view of (3,3,4,4)-connected **3,3,4,4L10** net present in compound **1**.

3.2. Single crystal to single crystal transformation studies and structural description of complex

2

Upon immersion of complex 1 in DCM solvent at room temperature for seven days, compound 2 gets formed in single crystal to single crystal manner (Fig. S3), maintaining crystallinity. In IR spectra there is no OH- stretching for ethanol at 3635 and 3596 cm–1 which clearly indicates that exchange has been completed (Fig. S2). Complex 2 also crystallizes in triclinic space group *P*-1 and its asymmetric unit consists of one Ni(II) ion with full occupancy, alongside a second Ni(II) ion with half occupancy factor, one TBIB, one BTC^{3–}, three coordinated water molecules;

besides it three DCM molecules and three lattice water molecules. In this case, Ni(II) ion has similar distorted octahedron coordination environment as observed for **1**. But in this case, bond distances involving metal ions which are taking part in macrocycle formation are same for both the metal ions; on the contrary, for compound **1**, these bond distances are not similar for both the metal ions.



Fig. 8. Metal running chain along crystallographic *a* axis in coordination polymer 2. In case of compound 2, only two types of metal ions (Ni1 and Ni2) are involved in chain formation as shown in Figure 8, and form a layer similar to complex 1. Arrangement of layers is changed in compound 2, which is slightly shifted towards crystallographic *b* axis after admitting DCM molecules, as presented in Fig. 9. If we see guest removed space-filled model of structure 2, there are no small pockets consisting of solvent molecules (Fig. 10), as observed in the case of complex 1.



Fig. 9. Arrangement of layers in complex 2 along crystallographic b axis.



Fig. 10. (a) Guest free layered structure and, (b) space-filled model of complex 2.

The solvent-accessible volume is ~35% of the unit cell volume, almost same like complex 1. PXRD pattern resemble with the as-synthesized phase showing phase purity (Fig. S4).

3.3. Thermal stability

TGA experiments have been carried out to check the thermal stability of both the complexes **1** and **2**. Weight losses of ~19% (calculated 20.19%) and ~25% (calculated 27.9%) were observed for TGA curves of complexes **1** and **2** respectively, as shown in Figures S5 and S6. Guest molecules were released between the temperature range ~30 to 350 °C and both frameworks underwent collapse above 400 °C.

3.4. Gas adsorption studies

To examine porosity of the desolvated guest-free phase of layered compound **1**, sorption measurements have been performed at low pressure with CO₂, CH₄, Ar, N₂ and H₂ at 77 K (Ar, N₂ and H₂) and 195 K (CO₂ and CH₄). The CO₂ gas sorption isotherm at 195 K shows a typical type I behavior with a maximum value of 100 mL g^{-1} gas uptake at low pressure, suggesting the microporous nature of the framework (Fig. 11) [25]. The Brunauer-Emmett-Teller (BET) surface area, calculated from CO₂ sorption data recorded at 195 K, is 297.63 m² g⁻¹. The CO₂ sorption isotherms measured at 273 K and 298 K are showing moderate CO₂ uptake capabilities, 55 and 40 cm³ g⁻¹ respectively (Fig. 12). Strikingly, there is no adsorption uptake for N₂ and H₂ at 77 K, in spite of possessing adequate effective pore aperture for their entry. This may be due to the very strong interactions occurring between the adsorbate oxygen and nitrogen gas molecules at 77 K with the pore windows of the adsorbent surface, which is presumably blocking the next set of adsorptive molecules from passing into the pore, since the framework is devoid of any additional open channels [26]. Interestingly although, compound **1** shows large amount of CO₂ adsorption uptake, owing to the large quadrupole moment of CO₂ which induces electrostatic

interactions with the framework to enter inside the cavities. The blocking interactions prevalent in the cases of gaseous molecular species like N2, H2 etc. are sufficiently surpassed by the thermal energy operative for CO_2 . In fact, the host adsorbent framework with a combination of Ni(II), polar moieties and π -electron clouds from the constituent ligands inside the porous channels gives rise to an electrostatic field, which is indeed effectual behind carbon dioxide adsorption [26]. The dipole-induced-dipole interactions, where the quadrupole moment of carbon dioxide $(1.34 \times 10^{-39} \text{ Cm}^2)$ interacts with the electric field gradient of the adsorbent surface, facilitate the potential energy of CO₂ adsorption at low temperature (195K). Hence, the selective uptake of CO_2 by 1 can be attributed to the electrostatic interactions with free carboxylate oxygens of the BTC linker. There is no hysteresis trend observed during CO2 desorption-branch, suggesting that complex 1 is a potential candidate for industrial post-combustion carbon capture and storage (CCS) technology applications. The evident release of adsorbate CO2 molecules at reduced external pressures indicates anticipation of easy reusability/ bed regeneration attribute of this material toward CO2 storage. This kind of selective CO2 adsorption phenomena is vital in the domain of porous coordination polymers [27]. To check the phase purity of complex 1, variable temperature PXRD measurements were performed (Fig. S7). PXRD pattern for the assynthesized phase is shifting towards higher 20 value due to temperature effect but at very low temperature for simulated pattern it is expanding or shifting towards lower 20. It means complex is breathing at room temperature, because for the as-synthesized phase, intense hydrogen bonds are involved between layers, by virtue of which the entire porous structure gets constructed. At high temperature, just after the initiation of guest removal from the framework, characteristic peaks get somewhat shifted towards lower 20 value, referring to framework-expansion. Sometimes the whole pattern is different due to phase transitions between single crystal data

(probably measured at low temperatures) and powder data (often measured at room temperature).

Sometimes turbostratic disorder of a layered material may alter the pattern.



Fig. 11. Low temperature gas adsorption isotherms for complex 1; amount adsorbed (in mL g^{-1}) plotted against P/P₀ (Filled shapes = adsorption, hollow shapes = desorption).



Fig. 12. CO_2 sorption isotherms at 298 and 273 K for complex 1 (filled shapes = adsorption, hollow shapes = desorption).

3.5. Catalytic properties

Considering the demand for new-generation improved heterogeneous catalysts and the unparallel features of MOFs, the development of environment-friendly MOF catalyst for Knoevenagel condensation reaction is a topic of great interest in recent years [28]. Knoevenagel condensation reactions are well known organic reactions, largely employed in order to form C-C bonds for the synthesis of important derivatives targeted for various applications [29]. The present MOF compound with BTC³⁻ should also behave as a potential catalyst for Knoevenagel condensation reaction, due to the presence of guest interaction sites, specifically -C=O moieties decorating the channel wall. Recent years have witnessed, studies done with PCPs consisting of carbonyl oxygen atoms as catalytic interaction sites present on the channel wall [30]. Compound 1 was used as catalyst in its as-synthesized form, without any pre-activation. In each case, 5% by weight of compound 1 is used as catalyst. The heterogeneous catalytic properties of complex 1 for the reactions between benzaldehyde (4-methylbenzaldehyde, 4-fluorobenzaldehyde, 4nitrobenzaldehyde, 1-naphthaldehyde) and malononitrile in dry DCM, under nitrogen atmosphere at 60 °C, as shown in Table 1 were comprehensively verified. We have synthesized the targeted organic molecule, derived from benzylidene malononitrile (BMN) because of their reported inhibitory activity of the protein tyrosine kinase [31].

Aromatic aldehyde (10.4 mmol) is allowed to react with active methylene compound (10.4 mmol) at room temperature in DCM solvent under inert atmosphere. After 5 minutes, assynthesized complex 1 (5% by weight with respect to the amount of benzaldehyde) was used as a catalyst in the reaction and temperature was raised up to 60 °C, reaction progress was monitored

through TLC, which indicated completion in 2 h. Once the reaction gets over, the reaction mixture is filtered to recover the catalyst. Conversion was monitored by GCMS, which comes up with 100% product formation after two hours of reaction progress time (Fig. 13). To check the catalytic activity of **1**, blank experiments have been performed without using compound **1**, which led to only 15% conversion after 2 h under similar conditions.



Fig. 13. Evidence of heterogeneous nature of catalyst in the Knoevenagel condensation reaction of benzaldehyde with malononitrile (green curve showing catalysis reaction, and blue line presenting blank test for the reaction).

In presence of catalyst, the reaction was completed within 2 h. Consequently, it is evident that the reaction occurs within the channels functionalized with -C=0 groups of complex 1. Malononitrile interacts with carbonyl oxygen centres of the catalyst, as confirmed from the lower-wavenumber shift of the characteristic IR stretching band, and splitting of the same for nitrile group (Fig. S8) [32]. This suggests that reaction occurs in the pores of complex 1 not on the surface. The Knoevenagel reaction is not only a weak base-catalyzed reaction, but also it accompanies formation of a new C-C bond [33]. The guest-selective reaction suggests that the

reaction occurs in the channels, and not on the surface of the polymer. When substrate with steric environment is used the reaction does not proceed because this compound is not able to enter inside the pores. So we can say that this catalyst is showing guest selectivity. The base catalyst **1** shows good recyclability, when it is used five consecutive times for further catalysis. To probe its reusability, PXRD patterns have been recorded of the dried catalyst on completion of each catalytic cycle after using at least five times. The PXRD pattern after the adsorption experiment shows that some peaks are shifted toward the lower 20 values indicating expansion of the channels in response to entry of aldehydes and malononitrile (Fig. S9).

We have carried out the catalytic reactions with Ni(NO3)2.6H2O dissolved in DCM can poorly promote (yield ~20%) some Knoevenagel condensation reaction in 24 h.

Knoevenagel reaction catalyzed by compound 1					
R H H	2 ^C CN as-synthesized 7 CN 5 wt %	$\stackrel{H}{\rightarrow} \qquad \stackrel{R}{_{H}} \stackrel{CN}{_{CN}}$			
Run	R	Time (h)	Yield (%)		
1	Ph	2	100		
2	4-NO ₂ Ph	2	90		
3	4-MePh	2	100		
4	4-FPh	2	100		
5	1-Naphthyl	2	0		

Table 1

This selectivity depends upon the relationship between the size of the reactants and the pore window of the host.



Fig. 14. Time conversion plot for Knoevenagel condensation reactions of different aromatic aldehydes catalyzed by complex **1**.

4. Conclusion

This work describes the synthesis of a new layered multifunctional coordination polymer consisting of guest accessible Lewis basic sites, and large void volume inside the structure which is due to strong hydrogen bonding interactions between the adjacent layers. This complex acts as a good heterogeneous base catalyst for Knoevenagel condensation reaction. Reaction takes place at the functionalized channel surface of the host, providing good yield of the product. Desolvated phase of compound **1** acts as a selective adsorbent for green house CO_2 gas at low temperature and pressure. It shows single crystal to single crystal transformation on immersing in DCM for 7 days, at room temperature. This resultant DCM-exchanged coordination polymer is devoid of any small channels.

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Appendix A. Supplementary material

CCDC 1418347 and 1420299 contain the supplementary crystallographic data for 1 and 2 respectively. These of charge be obtained free via data can http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: MA deposit@ccdc.cam.ac.uk.

References

- 1) (a) M.P. Suh, H.J. Park, T.K. Prasad, D.-W. Lim, Chem. Rev. 112 (2012) 782-835;
 - (b) J.-R. Li, J. Sculley, H.-C. Zhou, Chem. Rev. 112 (2012) 869–932;
 - (c) 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. 112 (2012) 724–781;
 - (d) R.A. Agarwal, A. Aijaz, E.C. Sañudo, Q. Xu, P.K. Bharadwaj, Cryst. Growth Des. 13 (2013) 1238-1245;
- (e) A.K. Chaudhari, S. Mukherjee, S.S. Nagarkar, B. Joarder, S.K. Ghosh, CrystEngComm. 15 (2013) 9465-9471.
- 2) (a) A. Corma, H. Garcia, F.X. Llabres, Chem. Rev. 110 (2010) 4606-4655;
 - (b) A.M. Shultz, O.K. Farha, J.T. Hupp, S.T. Nguyen, J. Am. Chem. Soc. 131 (2009) 4204-4205;

- (c) J.S. Seo, D. Whang, H. Lee, S.I. Jun, J. Oh, Y.J. Jeon, K. Kim, Nature. 404 (2000) 982-986;
- (d) C.D. Wu, A. Hu, L. Zhang, W. Lin, J. Am. Chem. Soc. 127 (2005) 8940-8941;
- (e) T. Uemura, R. Kitaura, Y. Ohta, M. Nagaoka, S. Kitagawa, Angew. Chem. 118
 (2006) 4218-4222; Angew. Chem. Int. Ed. 45 (2006) 4112-4116;
- (f) K. Gedrich, M. Heitbaum, A. Notzon, I. Senkovska, R. Froehlich,; J. Getzschmann, U. Mueller, F. Glorius, S. Kaskel, Chem. Eur. J. 17 (2011) 2099-2106;
 (g) M.K. Sharma, P.P. Singh, P.K. Bharadwaj, J. Mol. Catal. A 342–343 (2011) 6-10;
- (h) M. Yoon, R. Srirambalaji, K. Kim, Chem. Rev. 112 (2012) 1196–1231.
- 3) (a) Y. Cui, Y. Yue, G. Qian, B. Chen, Chem. Rev. 112 (2012) 1126–1162;
 (b) N.B. Shustova, A.F. Cozzolino, S. Reineke, M. Baldo, M. Dincă, J. Am. Chem. Soc. 135 (2013) 13326–13329.
- (a) D. Bradshaw, J.B. Claridge, E.J. Cussen, T.J. Prior, M.J. Rosseinsky, Acc. Chem. Res. 38 (2005) 273-282;
 - (b) F. Salles, A. Ghoufi, G. Maurin, R.G. Bell, C. Mellot-Draznieks, G. Frey, Angew. Chem. 120 (2008) 8615-8619; Angew. Chem. Int. Ed. 47 (2008) 8487-8491;
 (c) G.J. Halder, C.J. Kepert, Aust. J. Chem. 59 (2006) 597-604;
 (d) M.P. Suh, Y.E. Cheon, Aust. J. Chem. 59 (2006) 605-612;
 (e) R.A. Agarwal, P.K. Bharadwaj, Cryst. Growth Des. 14 (2014) 6115-6121;
 - (f) R.A. Agarwal, S. Mukherjee, E.C. Sañudo, S.K. Ghosh, P.K. Bharadwaj, Cryst. Growth Des. 14 (2014) 5585-5592.
- 5) (a) J.-P. Zhang, Y.-Y. Lin, W.-X. Zhang, X.-M. Chen, J. Am. Chem. Soc. 127 (2005) 14162-14163;

(b) K.L. Gurunatha, T.K. Maji, Inorg. Chem. 48 (2009) 10886-10888.

- (a) M. Kawano, M. Fujita, Coord. Chem. Rev. 251 (2007) 2592-2605, and references therein;
 - (b) Y. Jiang, J. Huang, B. Kasumaj, G. Jeschke, M. Hunger, T. Mallat, A. Baiker, J. Am. Chem. Soc. 131 (2009) 2058-2059.
- (a) S. Kitagawa, R. Kitaura, S. Noro, Angew. Chem., Int. Ed., 43 (2004) 2334-2375;
 (b) X.-C. Huang, Y.-Y. Lin, J.-P. Zhang, X.-M. Chen, Angew. Chem., Int. Ed. 45 (2006) 1557-1559;
 - (c) M.-H. Zeng, X.-L. Feng, W.-X. Zhang, X.-M. Chen, Dalton Trans. (2006) 5294-5303;
 - (d) M.-H. Zeng, X.-L. Feng, X.-M. Chen, Dalton Trans. (2004) 2217-2223;
 - (e) R. Kitaura, K. Seki, G. Akiyama, S. Kitagawa, Angew. Chem., Int. Ed. 42 (2003) 428-431;
 - (f) S. Kitagawa, K. Uemura, Chem. Soc. ReV. 34 (2005) 109-119;
 - (g) K. Uemura, K. Saito, S. Kitagawa, H. Kita, J. Am. Chem. Soc. 128 (2006) 16122-16130;
 - (h) R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, T.C. Kobayashi, S. Horike, M. Takata, J. Am. Chem. Soc. 126 (2004) 14063-14070;
 - (i) S. Kitagawa, M. Kondo, Bull. Chem. Soc. Jpn. 71 (1998) 1739-1753;
 - (j) G.J. Halder, C.J. Kepert, Aust. J. Chem. 59 (2006) 597-604;
 - (k) M.P. Suh, J.W. Ko, H.J. Choi, J. Am. Chem. Soc. 124 (2002) 10976-10977;
 - (1) K. Biradha, Y. Hongo, M. Fujita, Angew. Chem., Int. Ed. 39 (2000) 3843-3845;
 - (m) K. Biradha, Y. Hongo, M. Fujita, Angew. Chem., Int. Ed. 41 (2002) 3395-3398;

(n) K. Takaoka, M. Kawano, T. Hozumi, S.-I. Ohkoshi, M. Fujita, Inorg. Chem. 45 (2006) 3976-3982;

(o) J.-P. Zhang, S. Horike, S. Kitagawa, Angew. Chem., Int. Ed. 46 (2007) 889-892.

- 8) H.Q. Yang, Z.H. Xu, M.H. Fan, R. Gupta, R.B. Slimane, A.E. Bland, I. Wright, J. Environ. Sci., 20 (2008) 14-27. 308
- 9) (a) W.S. Broecker, Science 315 (2007) 1371;
 - (b) E. Marris, Nature 442 (2006) 624-626;
 - (c) C. Song, Catal. Today 115 (2006) 2-32.
- 10) (a) A. Yamasaki, J. Chem. Eng. Jpn., 36 (2003) 361-375
 - (b) J.T. Yeh, K.P. Resnik, K. Rygle, H.W. Pennline, Fuel Process. Technol., 86 (2005) 1533-1546;
 - (c) X. Xu, C.S. Song, J.M. Andresen, B.G. Miller, A.W. Scaroni, Energy Fuels, 16 (2002) 1463-1469.
- 11) (a) S. Noro, S. Kitagawa, M. Yamashita, T. Wada, Chem. Commun. (2002) 222-223;
 - (b) R. Kitaura, G. Onoyama, H. Sakamoto, R. Matsuda, S. Noro, S. Kitagawa, Angew. Chem., Int. Ed. 43 (2004) 2684-2687;
 - (c) B. Chen, F.R. Fronczek, A.W. Maverick, Inorg. Chem. 43 (2004) 8209-8211;
 - (d) P.A. Maggard, B. Yan, J. Luo, Angew. Chem., Int. Ed. 44 (2005) 2-5;
 - (e) B. Chen, N.W. Ockwig, A.R. Millward, D.S. Contreras, O.M. Yaghi, Angew. Chem., Int. Ed. 44 (2005) 4745-4749;
 - (f) S.H. Cho, B. Ma, S.T. Nguyen, J.T. Hupp, T.E. Albrecht-Schmitt, Chem. Commun. (2006) 2563-2565.
- 12) Z. Zhang, Y. Zhao, Q. Gong, Z. Li, J. Li, Chem. Commun. 49 (2013) 653-661.

- (a) R. Kitaura, K. Fujimoto, S. Noro, M. Kondo, S. Kitagawa, Angew. Chem. Int. Ed. 41 (2002) 133-135;
 - (b) D.M. Shin, I.S. Lee, Y.K. Chung, Inorg. Chem. 42 (2003) 8838-8846;
 - (c) R. Custelcean, M.G. Gorbunova, J. Am. Chem. Soc. 127 (2005) 16362-16363.
- 14) (a) M. Fujita, Y.J. Kwon, S. Washizu, K. Ogura, J. Am. Chem. Soc. 116 (1994) 1151-1152;
 - (b) H.J. Choi, M.P. Suh, J. Am. Chem. Soc. 126 (2004) 15844-15851;
 - (c) L. Pan, H. Liu, X. Lei, X. Huang, D.V. Olson, N.J. Turro, J. Li, Angew. Chem. 115(2003) 560-564; Angew. Chem. Int. Ed. 42 (2003) 542-546.
- 15) R.A. Agarwal, Polyhedron 85 (2015) 740-747.
- 16) SAINT, version 6.02; Bruker AXS: Madison, WI, (1999).
- 17) G.M. Sheldrick, *SADABS*: Empirical Absorption Correction Program; University of Gottingen: Gottingen, Germany, (1997).
- 18) XPREP, version 5.1; Siemens Industrial Automation Inc.: Madison, WI, (1995).
- 19) Sheldrick, G.M. SHELXTL Reference Manual, version 5.1; Bruker AXS: Madison, WI, (1997).
- 20) G.M. Sheldrick, *SHELXL*-97: Program for the Refinement of Crystal Structures; University of Gottingen: Gottingen, Germany, (1997).
- 21) S. Banerjee, P.-G. Lassahn, C. Janiak, A. Ghosh, Polyhedron 24 (2005) 593-599.
- 22) (a) P. Lama, A. Aijaz, E. C. Sañudo, P. K. Bharadwaj, Cryst. Growth Des. 10 (2010) 283-290;
 - (b) E.W. Lee, Y.J. Kim, D.Y. Jung, Inorg. Chem. 41 (2002) 501-506.
- 23) A.L. Spek, *PLATON*; The University of Utrecht: Utrecht, The Netherlands, (1999).

- 24) (a) The network topology was evaluated by the program "TOPOS-4.0", see:http://www.topos.ssu.samara.ru; V.A. Blatov, IUCr Comp. Comm. Newsletter 7 (2006) 4-38;
 - (b) V.A. Blatov, A.P. Shevchenko, V.N. Serezhkin, J. Appl. Crystallogr. 33 (2000) 1193-1193;
 - (c) V.A. Blatov, M. O'Keeffe, D.M. Proserpio, CrystEngComm. 12 (2010) 44-48.
- 25) (a) S. Brunauer, L.S. Deming, W.E. Deming, E.J. Teller, Am. Chem. Soc. 62 (1940) 1723-1732.
 - (b) S.J. Gregg, K.S.W. Sing, Adsorption, Surface Area and Porosity. 2nd ed., Academic
 Press, London, (1982).
- 26) L. Ma, J.M. Falkowski, C. Abney, W. Lin, Nat. Chem. 2 (2010) 838-846.
- 27) (a) R. Vaidhyanathan, S.S. Iremonger, G.K.H. Shimizu, P.G. Boyd, S. Alavi, T.K. Woo, Science 330 (2010) 650-653;
 - (b) L. Pan, K.M. Adams, H.E. Hernandez, X. Wang, C. Zheng, Y. Hattori, K. Kaneko, J. Am. Chem. Soc. 125 (2003) 3062-3067;
 - (c) A. Comotti, S. Bracco, P. Sozzani, S. Horike, R. Matsuda, J. Chen, M. Takata, Y. Kubota, S. Kitagawa, J. Am. Chem. Soc., 130 (2008) 13664-13672.
- (a) S. Aguado, J. Canivet, D. Farrusseng, J. Mater. Chem., 21 (2011) 7582-7588;
 (b) S. Aguado, J. Canivet, Y. Schuurman, D. Farrusseng, J. Catal. 284 (2011) 207-214.
- 29) (a) L.F. Tietze, U. Beifuss, Comprehensive Organic Synthesis, Pergamon, New York, 2 (1991) 341-394;
 - (b) D. Michaud, F. Texier-Boullet, J. Hamelin, Tetrahedron Lett. 43 (1997) 7563-7564.

- 30) S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita, S. Kitagawa, J. Am. Chem. Soc. 129 (2007) 2607-2614.
- 31) A. Gazit, P. Yaish, C. Gilon, A. Levitzki, J. Med. Chem. 32 (1989) 2344-2352.
- 32) I.G. Binev, Y.I. Binev, B.A. Stamboliyska, I.N. Juchnovski, J. Mol. Struct. 435 (1997) 235-245.
- 33) (a) P.S. Rao, R.V. Venkataratnam, Tetrahedron Lett. 132 (1991) 5821-5822;
 - (b) T.I. Reddy, R.S. Varma, Tetrahedron Lett. 38 (1997) 1721-1724;
 - (c) I. Rodriguez, S. Iborra, A. Corma, F. Rey, J.L. Jorda', Chem. Commun. (1999) 593-594;
 - (d) J.R. Harjani, S.J. Nara, M.M. Salunkhe, Tetrahedron Lett. 43 (2002) 1127-1130;
 - (e) J.S. Yadav, B.V.S. Reddy, A.K. Basak, B. Visali, A.V. Narsaiah, K. Nagaiah, Eur. J. Org. Chem. (2004) 546-551;
 - (f) B. Tamami, A. Fadavi, Catal. Commun. 6 (2005) 747-751.

Two-Dimensional Flexible Ni(II)-based Porous Coordination Polymer Showing Single-Crystal to Single-Crystal Transformation, Selective Gas Adsorption and Catalytic Properties

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A two dimensional (2D) flexible coordination polymer of Ni(II) has been solvothermally synthesized, which upon immersing in DCM give rise to a daughter coordination polymer of Ni(II). Compound 1 behaves as a good selective adsorbent for CO_2 at low temperature and pressure as well as, an environment-friendly heterogeneous catalyst for Knoevenagel condensation reaction.

