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Article

Co(II)-based Metal-Organic Frameworks and Their Application in Gas Sorption and Solvatochromism

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ABSTRACT. We report the synthesis and structural characterization of a unique Co-MOF-1 with the formula $[Co_2(dpmndi)(bdc)_2)]$ ·DMF; (dpmndi = N,N'-bis(4pyridylmethyl)-1,4,5,8-naphthalenediimide and bdc²⁻ = benzene-1,4-dicarboxylate) along

> formula with isonicotinate based Co-MOF-2 having of the an $[Co_3(ina)_4(OH)(H_2O)_3]$ ·H₂O·NO₃. A single crystal X-ray analysis reveals that Co-MOFs 1 and 2 exhibits (5)-connected and (8)-connected 3D framework architecture having the tts and hex topology, respectively. Importantly, Co-MOF-1 possess micro-sized cage with an internal cavity of 8.6 Å. The gas sorption analysis was also performed on both Co-MOFs 1 and 2 and results show high uptake for N_2 and CO_2 compare to H_2 and CH_4 . Moreover, both Co-MOFs 1 and 2 display high value of isosteric heat of adsorption (Q_{st}) for CO₂ gas. In addition, Co-MOF-1 also exhibits the promising solvatochromic behaviour.

INTRODUCTION

Over the past few years the design and development of metal-organic frameworks (MOFs) have attracted tremendous attention of the wider scientific community, not only because of their molecular connectivity and topologies¹⁻³ but also due to their wide range of societally and industrially relevant potential applications such as

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heterogeneous catalysis,^{4–6} drug delivery,^{7–9} molecular recognition,^{10,11} sensing,¹² optics,¹³ luminescence,^{12,14} ion exchange,¹⁵ ionic/electronic conductivity,^{16,17} magnetism and gas sorption.¹⁸⁻²⁰ In addition, similar to naturally occuring zeolites, MOFs also contains large cavities in their structures,^{21,22} however, the versatility and adaptively in the coordination mode of the linkers together with the geometrical preference of the constitutive metal ions provide an advantage to tune the porosity and topology of the resultant architecture and thus, provide advantage over the zeolites and mesoporous silica.^{23,24} The MOFs can be synthesized by using an organic linker and a suitable metal ion. However, there are several reaction factors such as temperature, pH, metal-toligand ratios, solvent systems and so on, influences the topology of the resultant architecture. Therefore, the synthesis of multifunctional MOFs with the desired structural topology and applications is still a challenging task for the researcher. To date, tremendous efforts and strategies have been used by the researchers to construct the multifunctional MOFs for diverse range of applications.^{25–28} The mixed-ligand strategy is one of them and widely examined in recent years as this is the very straightforward procedure and also retain the structural integrity of the resultant structure.^{29–31} In this

approach different linkers with different donor atoms are mixed before synthesis. Though, this protocol is well explored, yet, only few literature examples are available wherein, the naphthalenediimide (NDI) based linker along with the co-ligand has been used for the solvothermal preparation of a three-dimensional multifunctional MOF.^{32–34}

Herein, we report the design and synthesis of an unique Co-MOF-1 with the $[Co_2(dpmndi)(bdc)_2] \cdot DMF;$ (dpmndi = formula N,N'-bis(4-pyridylmethyl)-1,4,5,8naphthalenediimide and bdc = benzene-1,4-dicarboxylate) along with an isonicotinate based Co-MOF-2, $[Co_3(ina)_4(OH)(H_2O)_3] \cdot H_2O \cdot NO_3$ (ina = isonicotinic acid). The Co-MOF-2 is similar to the previously reported isonicotinate based Co-MOF $[Co_3(ina)_4(OH)(C_2H_5OH)_3]$ ·NO₃·C₂H₅OH ·3H₂O by Chen and co-workers.¹⁹ A single crystal analysis reveals that Co-MOFs 1 and 2 exhibit (5)-connected and (8)-connected 3D framework architecture having the **tts** and **hex** topology, respectively. The gas sorption properties were also investigated for both Co-MOFs 1 and 2 and results are very promissing for the host-guest chemistry. Besides this Co-MOF-1 also shows promissing solvatochromism behaviour.

EXPERIMENTAL SECTION

Materials and methods. The starting materials 1.4.5.8-Naphthalenetetracarboxylic dianhydride (NDA), 4-(aminomethyl)pyridine, 1, 4-benzene dicarboxylic acid (bdc) and anhydrous DMF were purchased either from the Sigma-Aldrich, LobaChemie or TCI chemicals. Solvents 1,2-dichlorobenzene and metal salts Co(NO₃)₂·6H₂O and NaOH were purchased from the FINAR, AVRA and CDH chemicals, respectively and used as received. The micro analytical data were obtained with a FLASH EA 1112 Series CHNS Analyzer. The NMR spectroscopic measurements were carried out with a Bruker Avance 400 spectrometer. The FTIR spectra were recorded with a Perkin–Elmer FTIR 2000 spectrometer. The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurement were carried out on an SDT Q600 (V20.9 Build 20) instrument (Artisan Technology Group, Champaign, IL) under N₂ atmosphere with a heating rate of 10 °C per min. The powder X-ray diffraction (XRD) data were recorded on a PANalytical X'PertPRO X-ray diffractometer with Cu K α radiation (λ = 1.54059 Å).

The samples were ground and subjected to the range of theta = $5 - 50^{\circ}$ with a scan rate of 1° per minute at room temperature.

Synthesis of ligand N,N'-bis(4-pyridylmethyl)-1,4,5,8-naphthalenediimide (dpmndi). The ligand dpmndi has been synthesized by using the literature protocol (Scheme S1) with slight modification.³⁵ Wherein, a mixture of NDA (1 g, 3.73 mmol) and 4-(aminomethyl)pyridine (0.807 g, 7.46 mmol) were stirred at 80-90 °C under N₂ atmosphere in anhydrous DMF (20 mL) for 12 h, afforded an orange-brown suspension. The solid was filtered off and washed with acetonitrile and acetone and finally dried under vacuum. Yield: 1.50 g (90% based on NDA). FT-IR (KBr disc, selected peaks, cm⁻ ¹): 3076 (C-H), 2958 (CH₂), 1702 (C=O; imide), 1651 (-N-C=O; imide), 1601, 1581, 1491 (for pyridyl group). ¹H NMR (400 MHz, DMSO- d_6), δ = 8.74 (s, 4H), 8.50 (d, J = 6.0 Hz, 4H), 7.40 (*d*, J = 5.8 Hz, 4H), 5.31 (s, 4H). Anal. Calcd for C₂₆H₁₆N₄O₄: C, 69.64; H,

Synthesis of $[Co_2(dpmndi)(bdc)_2] \cdot DMF$ (Co-MOF-1). A mixture of ligands dpmndi (10 mg, 0.022 mmol) and H₂bdc (7 mg, 0.044 mmol), Co(NO₃)₂·6H₂O (12 mg, 0.044 mmol), and solvents DMF:1,2-dichorobenzene (4:1, v/v, 2.5 mL) followed by the addition of few

3.60; N, 12.49; Found: C, 69.59; H, 3.65; N, 12.53%.

drops of 2M NaOH, were placed in 5 mL glass vial with screw caps and sonicated for 15 min and then placed in programmable oven at 80 °C for 72 h and finally cooled to room temperature. The needle shaped dark green color crystals suitable for single crystal Xray analysis were collected. Yield, 12.6 mg (58.6%; based on dpmndi). Anal. Calcd. For C₄₂H₂₄Co₂N₄O₁₂·DMF: C, 55.86; H, 3.23; N, 7.24; Found: C, 55.76%; H, 3.26%; N, 7.15%. FT-IR spectrum (selected peaks): 1708 (C=O), 1673, 1613 (COO) cm⁻¹. Synthesis of $[Co_3(ina)_4(OH)(H_2O)_3] \cdot H_2O \cdot NO_3$ (Co-MOF-2). The Co-MOF-2 was also synthesized using the solvothermal protocol. In a 5 mL glass vial with screw cap a mixture of ligand dpmndi (10 mg, 0.022 mmol), Hina (5.4 mg, 0.044 mmol) and Co(NO₃)₂·6H₂O (12 mg, 0.044 mmol) in DMF (3 mL) was initially sonicated for 10–15 min and then placed in programmable oven at 90 °C for 48 h, which was then slowly cooled to room temperature. The block shaped light red color crystals suitable for single crystal X-ray analysis were isolated. Yield: 35 mg (52.79% based Hina); Anal. Calcd. For C₂₄H₂₃Co₃N₄O₁₂·H₂O·NO₃: C, 35.31; H, 3.09; N, 8.58; Found: C, 36.21%; H, 2.95%; N, 8.81%. FT-IR spectrum (selected peaks): 3350 (OH), 1648, 1587 (COO) cm⁻¹. The

formulation of Co-MOF-2 is based on the elemental and TGA analysis along with the single crystal analysis.

Single crystal X-ray diffraction analysis. Suitable, apparently single crystals for Co-MOFs 1 and 2 were selected and data were collected on one of these single crystals at 298(2) K on a Rigaku Super Nova HyPix3000 diffractometer with monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å). Diffraction data were processed by the CrysalisProv39.31.³⁶ followed by absorption correction with the included Scale3 ABSPACK program.³⁶ The structures were solved by intrinsic phasing with the SHELXS structure solution program and refinement were carried out with SHELXL, using the Olex2 GUI.^{37,38} The hydrogen atoms were fixed at the calculated positions with isotropic thermal parameters. In the crystal structures of Co-MOF-1, positional disorder was observed for the guest DMF molecule, and the contribution of DMF molecule is added in the empirical formula (see Table 1 for detail). In case of Co-MOF-1 the solvent accessible void (SAVs) volume is calculated without removing lattice DMF molecule as obtained by using grid points/probe radius of 1.2 Å from the nearest van der Waals surface with the PLATON.³⁹ Details of the crystallographic data collection and structural solution

parameter and selected bond lengths are given in Tables 1 and 2 (see Table S1 for hydrogen bonding details). CCDC numbers 1577550 and 1578157 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via www. ccdc.cam.ac.uk/data request/cif [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk].

Sorption measurements. The N₂, H₂, CH₄ and CO₂ sorption experiments were carried out on an Autosorb-IQ2 gas adsorption analyzer (Quantachrome Instruments) at variable temperatures. The samples were activated prior to the measurements by soking the crystals of Co-MOFs **1** and **2** in CH₃OH for three days (fresh CH₃OH replaced every 12 h), and then pumped under the dynamic vacuum at 60 °C.

RESULTS AND DISCUSSION

Synthesis and characterization. The ligand dpmndi has been prepared using the literature protocol with slight modification and details are provided with the experimental section ³⁵ Whereas, the solvothermal reaction of dpmndi with Co(NO₃)₂·6H₂O in

presence of H₂bdc as co-ligand afforded [Co₂(dpmndi)(bdc)₂)]·DMF (Co-MOF-1) (see Scheme 1). On the other hand reaction of Co(NO₃)₂·6H₂O and isonicotinic acid gave [Co₃(ina)₄(OH)(H₂O)₃]·H₂O·NO₃ (Co-MOF-**2**) which is very similar to{Co₃(OH)} based cluster reported by Chen and co-workers.¹⁹ The ligand dpmndi and Co-MOFs **1** and **2** are well characterized by various analytical and spectroscopic techniques (Figures S1– S3, Supporting Information). The FT-IR spectra of Co-MOFs **1** and **2** (Figure S3) show strong bands between 1605–1577 cm⁻¹ due to the ν_{COO} stretches. In addition, broad features between 3400–3430 cm⁻¹ were indicative of the presence of coordinated as well as lattice water molecules in Co-MOF-**2**. The microanalysis results and single crystal analysis also support this observation.

Crystal structure description of $[Co_2(dpmndi)(bdc)_2] \cdot DMF$ (*Co-MOF-1*). A single crystal X-ray analysis of Co-MOF-1 reveals that it crystallizes in the tetragonal unit cell with the space group of l_4 /mcm. The asymmetric unit of Co-MOF-1 consists of a half of dpmndi ligand, a half of bdc²⁻ ligand, a half of cobalt ion, as mirror plane bisects them all and a quarter of lattice occluded DMF molecule (disordered) as it lies on a four-fold screw axis passing through it. The framework is neutral as positive charge contributed by half of

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cobalt ion is balanced by half of the bdc²⁻ ligand in the asymmetric unit. As shown in Figure 1a, the Co(II) ion of Co-MOF-1 displayed distorted square pyramidal geometry, wherein, the four equatorial sites are occupied by the four $O_{carboxylate}$ atoms coming from four different bdc²⁻ ligands while the apical site is occupied by $N_{pyridyl}$ atom stemming from dpmndi ligand. The coordination mode for bdc²⁻ ligands is $\mu_2(\eta_1,\eta_1)$ resulting in a binuclear paddle-wheel secondary building unit [Co₂(COO)₄(N)₂] (Figure 1d) with a Co-Co distance equal to 2.731(4) Å, which is in the close range of cobalt-cobalt binuclear clusters Co₂(RCOO)₄ complexes.⁴⁰ The Co-O and Co-N bonds falls in the range 2.02–2.07 Å (Table S1). Since the two pyridyl arms can rotate freely about the methylene groups, both *anti-* and *syn-*conformations are possible for dpmndi.⁴¹

In the crystal structure of Co-MOF-1, both 4-pyridyl arms are located on the same sides of the central NDI core in *syn*-conformation, thus generating a micro-sized metallacyclic cage with Co---Co distance of 13.096 Å and 17.090 Å (Figure 1e) encapsulating the lattice DMF. Moreover, the micro-sized cage shows an internal cavity of 8.6 Å diameters (Figure 1c).



Scheme 1. Synthetic route for Co-MOFs 1 and 2.

The two dpmndi ligands bridges two paddle-wheel secondary building unit to form a metallacycle $Co_4(dpmndi)_2$ which further extends into two dimensional network through bdc^{2-} ligands. Interestingly, these adjacent two dimensional sheets further interlace via the π ··· π interactions between the NDI cores of each cage in parallel fashion resulting a polycatenated 3D architecture as shown in 1g & 1h. The crystal packing reveals the formation of porous channels running along the crystallographic *c*-axis as shown in Figures 1d, 1e & S4. The structure of Co-MOF-1 possesses two types of channels running along the crystallographic σ axis and having the dimensions of 15.46 × 15.46 Å²

and 15.91 × 16.87 Å² (containing DMF molecule) respectively. Notably, the structure of Co-MOF-1 exhibits solvent accessible voids (SAVs) of 30.9% per unit cell volume (3273/10587 Å³) (Figure S4) as suggested by PLATON³⁹ analysis without removal of guest molecules. Importantly, the topological analysis of Co-MOF-1 shows an interesting (5)-connected uninodal network with **tts** topology⁴² and point symbol of $\{3^3.4^3.5^4\}$ (Figure 1g). The detailed crystallographic information for Co-MOF-1 is given in Table 1.



Figure 1. (a) ORTEP depiction of the crystal structure of Co-MOF-1 (50% probability level). Hydrogen atoms are omitted for clarity. Color code: gray, C; cyan, N; red, O; Co, brown. (b) Construction of a binuclear Co-paddle-wheel by the linkage of the Co(II) ion with dpmndi and bdc²⁻. (c) Packing view of the Co-MOF-1 along the *a*-axis displaying three different kinds of 1D channel. (d) Packing view of the Co-MOF-1 along *c*-axis showing cage-to-cage connection and

porous nature of the structure. (e) The cage built from four $[Co_2(COO)_4(N)_2]$, two dpmndi and two bdc²⁻ ligands and exhibiting porous nature as shown by orange and magenta ball. (g) Orthogonal interlocking of metallocyclic rings and π ··· π stacking between the NDI cores. (h) (5)-connected framework structure of Co-MOF-1 having **tts** topology and point symbol {3³.4³.5⁴}.



Figure 2. (a) ORTEP depiction of the crystal structure of Co-MOF-2 (50% probability level). Hydrogen atoms are omitted for clarity. Color code: gray, C; blue, N; red, $O_{carboxylate}$; violet, O_{water} ; Co, yellow. (b) Construction of a tri-nuclear Co-cluster linkage by the μ_3 -OH group. (c) Packing view of the Co-MOF-2 along the *a*-axis displaying 1D channel. (d) Hexagonal packing view of the Co-MOF-2 along *c*-axis showing pores and channels. (e) Space-fill model of 3D porous

framework of Co-MOF-**2**, wherein the coordinated water molecules are penetrated towards the channels. (h) (8)-connected 3D framework architecture having the **hex** topology with point symbol {3⁶.4¹⁸.5³.6}.

Crystal structure description of $[Co_3(ina)_4(OH)(H_2O)_3] \cdot H_2O \cdot NO_3$ (Co-MOF-2). The solvothermal reaction of dpmndi, isonicotinic acid and nitrate salt of cobalt afforded 3D porous framework of Co-MOF-2 (as shown in Figure 2) which is very similar with the previously reported Co-MOF [Co₃(ina)₄(OH)(C₂H₅OH)₃][NO₃]·C₂H₅OH·3H₂O.¹⁹ The structure of Co-MOF-2 reveals that all the cobalt ions show octahedral geometry containing aqua ligand coordinated to each of the cobalt ion in contrary to the alcoholic solvent as observed in previous report.¹⁹The structure of Co-MOF-2 possesses a triangle windows running along the crystallographic a-axis and having the dimensions of 9.04 × 9.08 × 9.14 Å. Notably, the structure of Co-MOF-2 contains the 45% SAVs per unit cell volume (2080/4625.47 Å³) as shown in Figure S5 which is more than doubled to that of 19.8% reported for Co-MOF $[Co_3(ina)_4(OH)(C_2H_5OH)_3]\cdot NO_3\cdot C_2H_5OH\cdot 3H_2O$. The detail crystallographic information for Co-MOF-2 is given in Table 1.



Figure 3. XRD powder pattern of Co-MOF-1 (left) and Co-MOF-2 (right). The blue, red, black and wine color traces represents the simulated, as-synthesized, activated and after gas sorption sample, respectively.

Thermal analyses and PXRD. As thermal stability of any compound is one of the important feature to use that as functional material, thus thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) was employed for the Co-MOFs 1 and 2. TGA of Co-MOF-1 shows weight loss of 8.18% (observed) which fitted closely with the calculated weight loss of 7.58% in the temperature range of 50 and 250 °C, corresponding to the liberation of one lattice occluded DMF molecule (Figure S6). Co-MOF-2 exhibits its first weight loss of 18.18% (observed) which

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 Table 1. Crystal data and structure refinement for Co-MOFs 1 and 2.

Identification code	Co-MOF-1	Co-MOF- 2	
CCDC No.	1577550	1578157	
Empirical formula	$C_{42}H_{24}Co_2N_4O_{12}\cdot C_3H_7NO$	$C_{24}H_{23}Co_3N_4O_{12}\cdot H_2O\cdot NO_3$	
Formula weight	967.06	815.93	
Temperature/K	298 (2)	298(2)	
Crystal system	tetragonal	Orthorhombic	
Space group	/4/mcm	<i>P</i> nma	
<i>a</i> lÅ	21.7617(3)	19.3544(4)	
b/Å	21.7617(3)	19.8314(5)	
dÅ	22.3556(6)	12.0510(2)	
al°	90	90	
βl°	90	90	
М°	90	90	
Volume/Å ³	10587.0(4)	4625.47(17)	
Ζ	8	4	
$ ho_{ m calc} g/ m cm^3$	1.210	1.057	
µ/mm⁻¹	0.687	1.106	
<i>F</i> (000)	3912	1488	
Crystal size/mm ³	0.2 × 0.15 × 0.13	0.200 × 0.150 × 0.050	
Radiation	ΜοΚα (λ = 0.71073)	ΜοΚα (λ = 0.71073)	
2θ range for da collection/°	ta 6.886 to 51.996	3.393 to 26.000	
Index ranges	-26≤ <i>h</i> ≤26, -26≤ <i>k</i> ≤26, 19≤ <i>l</i> ≤27	- -23≤ <i>h</i> ≤16, -24≤ <i>k</i> ≤22, -14≤ <i>l</i> ≤13	

Reflections collected	41664	21303	
Independent reflections	2766 [<i>R</i> _{int} = 0.1504]	4668 [<i>R</i> _{int} = 0.0525]	
Data/restraints/parameters	2766/159/169	4668 / 13 / 228	
Goodness-of-fit on <i>F</i> ²	1.080	1.094	
Final <i>R</i> indexes [<i>I</i> ≥2σ (<i>I</i>)]	$R_1 = 0.0709$, w $R_2 = 0.2196$	<i>R</i> ₁ = 0.0815, w <i>R</i> ₂ = 0.2577	
Final <i>R</i> indexes [all data]	$R_1 = 0.0859, wR_2 = 0.2340$	<i>R</i> ₁ = 0.0877, w <i>R</i> ₂ = 0.2619	
Largest diff. peak/hole / e			
Å-3	1.14/-0.74	1.342/-0.749	

corresponds to the liberation of three coordinated water molecules, one hydroxide ion, one lattice occluded water molecule and one lattice nitrate anion (*ca.* 18.51%) in the temperature range of 50° to 200°C (Figure S6). DSC analyses also supported the TGA findings for Co-MOFs 1 and 2, as it show the respective weight loss in its first transition in the exothermic region (Figure S7). To analyse the phase purity of the bulk samples powder X-ray diffraction measurement has been carried out for the both samples and noticed that the simulated diffraction pattern generated from the single crystal X-ray diffraction are nicely fitted with the as-synthesized one and thus advocating the purity of the bulk compounds (Figure 3).

Gas adsorption studies. To probe the porous nature of the Co-MOFs 1 and 2, the adsorption-desorption isotherms for N₂, H₂, CH₄ and CO₂ were measured for the activated samples and their respective isotherms are depicted in Figure 4. The N₂ and H₂ gas sorption isotherms of Co-MOFs 1 and 2 were recorded at 77 K, whereas for CH₄ its 295 K. For both Co-MOFs 1 and 2 the CO₂ adsorption isotherms were recorded at 273 and 298 K, respectively. The N₂ and H₂ gas isotherms of Co-MOF-1 show uptakes of 126.87 and 62.15 cm³ g⁻¹, respectively. Whereas, CH₄ exhibits only the surface sorption (2.26 cm³ g⁻¹). As shown in Figure 4a, CO₂ uptake capacities of Co-MOF-1 at 273 and 298 K are 76.48 and 33.03 cm³ g⁻¹, respectively, which are better/comparable to several micro-porous materials reported in literature (see Table S3 in the Supporting Information for a comprehensive list of MOFs and their sorption behavior).^{43–47} The N₂ sorption exhibits an adsorption-desorption type-II isotherm. However, H₂ and CO₂ adsorption by Co-MOF-1 shows the reversible type-I isotherm. The high uptake of N₂, H₂ and CO₂ compare to CH₄ predominantly ascribed to their diverse electrostatic interactions with the surface of the porous channels/voids and their large quadrupole moment (CO₂ = $4.30 \times 10^{-26} \text{ esu}^{-1} \text{ cm}^{-1}$, N₂ = $1.52 \times 10^{-26} \text{ esu}^{-1} \text{ cm}^{-1}$, H₂ = 0.66×10^{-26}

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esu⁻¹ cm⁻¹ and 0 esu⁻¹ cm⁻¹ for CH₄).⁴⁸ The Brunauer–Emmett–Teller (BET) surface area and pore volume of Co-MOF-**1** was found to be 69.4 m²g⁻¹ and 0.09 cm³ g⁻¹, respectively, which are estimated from the N₂ sorption data.



Figure 4. (a) Gas sorption isotherms of Co-MOF-1 for N₂, H₂ (77K), CH₄ (295 K), and CO₂ at 273, 298 K, respectively. (b) Gas sorption isotherms of Co-MOF-2 for N₂, H₂ (77K), CH₄ (295 K) and CO₂ at 273, 298 K, respectively. (c) Q_{st} of Co-MOFs 1 and 2 for CO₂.

Under similar conditions, N₂ sorption isotherm of Co-MOF-2 shows 52.38 cm³ a⁻¹ uptake capacity. However, H₂ and CH₄ isotherms exhibit low uptakes of 15.96 and 2.43 cm³ g⁻¹, respectively. In addition, CO₂ isotherms of Co-MOF-2 display uptakes of 37.91 cm³ g⁻¹ and 31.28 cm³ g⁻¹ at 273 and 298 K, respectively. The high uptake capacity shown by N₂ and CO₂ gases compare to H₂ and CH₄ might be due to their more affinity towards the micro-pores of Co-MOF-2. The BET surface area and pore volume of Co-MOF-2 was found to be 22.4 m² g⁻¹ and 0.048 cm³ g⁻¹, respectively. Importantly, TGA profile of the activated sample of Co-MOFs 1 and 2 clearly indicates that their framework integrity are remain intact even after the loss of guest solvent molecules (See Figure S9 of supporting information). In addition, XRD pattern of activated and after the gas adsorption analysis sample of Co-MOFs 1 and 2 also advocated that both these materials intact their crystallinity and framework integrity (see Figure 3).

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Moreover, to probe the affinity of Co-MOF-1 for CO₂, the isosteric heat of adsorption (Q_{st}) was calculated in accordance with the Clausius–Clapeyron equation by fitting sorption isotherms at 298 K. The Q_{st} isotherm of Co-MOF-1 shows heat of adsorption of 32.41 kJ mol⁻¹ (see Figure 4c), which is higher than the enthalpy of liquefaction of CO_2 (17 kJ mol⁻¹) and comparable to Q_{st} values of recently reported MOFs.^{49–52} The Q_{st} value (32.41 kJ mol⁻¹) and SAVs (30.9%) for Co-MOF-1 are higher than those of several reported Co-MOFs.^{53,54} Co-MOF-2 also exhibits quite similar surface coverage with Q_{st} value of 30.26 kJ mol⁻¹. Notably, the Q_{st} values for Co-MOF-1 at the low surface coverage region steadily decreases and increases at the high surface coverage region (see Figure 4c). This result indicates that the pre-adsorbed CO₂ molecules in the channels of Co-MOF-1 interact strongly with other incoming CO₂ molecules resulted in a high Q_{st} value. On the other hand, the Q_{st} values for Co-MOF-2 initially increases upon the increase of CO_2 uptake and decreases at higher coverage region (see Figure 4c). These observations also clearly supports the idea that the absorption of a particular gas not only depend on the BET surface area and pore volume of a porous material but also

depend on other factors such as affinity of that particular gas towards the framework, open metal sites, arrangement of the pores and so on.^{55,56}

Solvatochromism. In literature, reports are available wherein, porous MOFs have been used for the inclusion of various analytes and their color change was explored, however, their numbers are rationally scarce.⁵⁷⁻⁶¹ Still this is a challenging task for the researcher working in the domain of MOFs and their applications, to develop both the stable pores and solvatochromism in a single material. So based on aforementioned fact, we have also investigated the solvatochromic behavior of Co-MOFs 1 and 2 by immersing their crystals in a number of solvents such as CH₃OH, CHCl₃, CH₂Cl₂, diethyl ether, hexane, THF, CH₃CN, DMF, DMA and DMSO. Notably, we observed a color change from colorless to green (in DMA) and red (in DMSO) for Co-MOF-1 at room temperature. This color change might be due to the exchange of guest DMF molecule (molecular dimension, 5.84 × 6.74 $Å^{2}$)⁶² by the DMA (molecular dimension, 6.31 × 7.25 Å²)⁶² or DMSO (molecular dimension, 5.99 × 6.26 Å²)⁶² molecules, which are very comparative to the guest DMF molecule in terms of their molecular dimension (See Table S4). The presence of channels with dimensions of 15.46 × 15.46 Å² and 15.91 ×

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16.87 Å² in Co-MOF-1 also facilitate the diffusion of these analyts in to the pores and thus exchange process. The tendency to form strong C-H \cdots O and C-H \cdots m interaction between the host and guest molecules might be another reason for this exchange. However, under similar circumstances we did not observed any color change for Co-MOF-2 (see Figure S8). The lack of electron-rich framework architecture might be the cause for the absence of solvatochromic behavior in Co-MOF-2. The photographs of these experiments are shown in Figure S8 of the supporting information. The solvatochromic effect was further analyzed by FT-IR, TGA, UV-vis and XRD Powder analysis (see Figures S9 – S15). As expected the impregnated sample of Co-MOF-1 in DMA (Co-MOF-1 \square DMA) exhibits v_{CO} stretching band at 1671 cm ⁻¹ (Figure S10). However, under identical conditions the impregnated sample of Co-MOF-1 in DMSO (Co-MOF-1 DMSO) shows a red shift of 20 cm⁻¹, which clearly indicates that DMF in the channels of Co-MOF-1 is exchanged by DMSO (Figure S11).63 Whereas, new broad peak appear at 3423 cm⁻¹ ascribed to the presence of water molecules along with DMSO in the cavity of Co-MOF-1. The TGA analysis of Co-MOF-1 DMA displays the first weight loss of 16.31% (observed 16.32%), which corresponds to the loss of two

lattice occluded DMA molecules in the region of 25 - 200 °C (see Figure S12). In a similar fashion, Co-MOF-1 DMSO exhibits an initial weight loss of 22.02% (observed 22.52%), which is nicely fitted with the loss of three DMSO and one water molecules in the region of 25 – 200 °C (see Figure S13), thereby strongly advocating the inclusion of DMA/DMSO molecules inside the channels of Co-MOF-1, resulting in visible color change. The UV-vis spectra and photographs of these inclusion compounds are shown in Figure S14. Due to the comparable polarity of the analysts {Polarity Index (P'): DMF, 6.4; DMA, 6.5, and DMSO, 7.2; DMSO have slightly higher than DMF and DMA},⁶⁴ we did not observed any significance shift in the UV-vis absorption bands after the solventexchange.⁶⁵ The XRD pattern of the Co-MOF-1 DMA and Co-MOF-1 DMSO show that the crystallinity of the Co-MOF-1 retained even after the solvent exchange (Figure S15).

SUMMARY AND CONCLUSION

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In summary, we have successfully demonstrated the synthesis and characterization of a unique Co-MOF-1; [Co₂(dpmndi)(bdc)₂] DMF along with an isonicotinate based Co-MOF-2; $[Co_3(ina)_4(OH)(H_2O)_3] \cdot H_2O \cdot NO_3$. The structural analysis reveals that Co-MOFs 1 and 2, exhibit 3D porous framework architecture and displaying (4)-connected tts and (8)-connected hex topology with the point symbol $\{3^3, 4^3, 5^4\}$ and $\{3^6, 4^{18}, 5^3, 6\}$, respectively. Interestingly, Co-MOF-1 possesses two types of channels having dimensions of 15.46 × 15.46 Å² and 15.91 × 16.87 Å². Whereas, Co-MOF-2 contain channel having the dimension of $9.04 \times 9.08 \times 9.14$ Å. Notably, in both cases the channels are occupied by the occluded solvent molecules and thus opens the door for host-guest chemistry in these molecules. In this perspective, gas sorption analysis was performed and results show that Co-MOFs 1 and 2 show high uptake for N₂ and CO₂ compare to H₂ and CH₄. In addition, Co-MOFs **1** and **2** also display high isosteric heat of adsorption for the CO₂ gas. Notably, Co-MOF-1 also exhibits promising solvatochromism behaviour.

ASSOCIATED CONTENT

Supporting Information. FT-IR spectra, ¹H NMR, TGA and DSC plots, additional structural figures, photographs of solvatochromism, bond angles and hydrogen bond tables for both Co-MOFs **1** and **2**. This material is available free of charge via the Internet at <u>http://pubs.acs.org</u>.

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Notes

The authors declare no competing financial interest.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given

approval to the final version of the manuscript.

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Manuscript title: "Co(II)-based Metal-Organic Frameworks and Their Application in Gas

Sorption and Solvatochromism"

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Synopsis

Co-MOF-1 based on N,N'-bis(4-pyridylmethyl)-1,4,5,8-naphthalenediimide (dpmndi) and benzene-1,4-dicarboxylate, and an isonicotinate based Co-MOF-2 were reported. The Co-MOFs 1-2 exhibits (5)-connected and (8)-connected 3D framework architecture with **tts** and **hex** topology, respectively. The gas sorption analysis for Co-MOFs 1 and 2 show high uptake capacities and isosteric heat of adsorption (Q_{st}) for CO₂ gas. Notably, Co-MOF-1 also shows promising solvatochromic behaviour.