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Cadmium Imidazolate Frameworks with Polymorphism, High Thermal Stability, and a Large Surface Area

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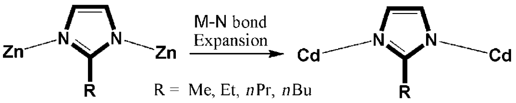
Since the initial inspiration for realizing metal–organic frameworks (MOFs) with zeolitic structures,[1] considerable effort has been made towards novel approaches to construct zeolitic metal–organic frameworks (ZMOFs) by using tetrahedral metal imidazolates.[2–6] To date, numerous ZMOFs have been synthesized with the motifs of which only those with desired porosity and thermal stability are potentially applicable for gas storage, separation, catalysts, encapsulation of target molecules, etc. For rational synthesis of porous and thermostable ZMOFs with the imidazole ligands, the introduction of smaller substituent groups onto imidazole ring has been found to be a vital strategy,[3,4] because the groups play not only the role of structure-directing agent (template), but also the sites for functionalizing.[4d] Moreover, as an inseparable supporting template, the substituent group can stabilize the imidazolate ZMOFs, however, it also presents an encumbrance that inevitably blocks pores—leading to a reduction of the pore size and surface area.

Furthermore, any 2-substituent at the imidazole ring may restrict the flexibility of the M—N bond rotation and render the imidazolates either barely to be generated or lacking in framework diversity. For example, the MOFs of metal 2-substituent imidazolates $[\{M(R\text{-im})_2\}]_\infty$ ($M=Zn^{II}$ and Co^{II}, R-im = 2-substituent imidazolates)[3,4a] have been only prepared for those with R-group to be methyl, ethyl, nitro and carboxaldehyde and each of them has been observed with no more than one MOF structure that exhibits the M—N bond ≈2.05 Å (and M···M distance ≈6.0 Å). On the supposition that the M—N bond (and M···M distance) could be expanded (Scheme 1), the lack of framework diversity from a 2-substituent imidazolate might be improved because the elongated M—N bond (and M···M distance) can weaken the self-template effect of the 2-substituent group and then, the M—N bond is rewarded with a modified flexibility of rotation. Apparently, the synthesis of cadmium 2-substituent imidazolates (CdIFs) of $[\{Cd(R\text{-im})_2\}]_\infty$ (R = methyl, ethyl, *n*-propyl, *n*-butyl, phenyl and nitro) shall display the role of a R-group and the effect of M—N bond elongation since the already reported cadmium imidazolate framework[7] was observed with a elongated M—N bond ≈2.20 Å (and M···M distance ≈6.40 Å). In this paper, we report the synthesis, structure and gas adsorption properties of the polymorphous CdIFs.



Scheme 1. A representation of the strategy for the M—N bond elongation.

CdIFs of 2-substituent imidazolates were synthesized by solvothermal (or room-temperature) reaction of $[Cd(CH_3COO)_2]\cdot 2H_2O$ and 2-substituent imidazoles [R-im-H, R = methyl (mimH), ethyl (eimH), *n*-propyl (pimH), *n*-butyl (buimH), phenyl (phimH) and nitro (nimH)] in alkyl-alcohols (or *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA) and 1-methyl-2-pyrollidone (NMP)). Four MOF structures were produced from $[\{Cd(mim)_2\}]_\infty$, CdIF-**1**, -**2**, -**3**, and -**5**; two MOF structures were formed from $[\{Cd(eim)_2\}]_\infty$, CdIF-**4** and -**6**; three MOF structures were formed from $[\{Cd(nim)_2\}]_\infty$, CdIF-**7**, -**8**, -**9**; and one MOF structure each for the remaining other cadmium 2-alkylimi-

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Table 1. The ZCIFs of $[\{Cd(R\text{-}im)_2\}]_\infty$ and their structural characteristics.

CdIF-*n*	Composition	Net	Zeolite	T/V[a] [nm^{-3}]	ρ_{FM}[b] [g cm^{-3}]	D_a[c] [Å]	D_p[d] [Å]	*PSA*[e] [%]
CdIF-**1**	$Cd(mim)_2$	*sod*	SOD	2.02	0.923	6.2	14.2	55.5
CdIF-**2**	$Cd(mim)_2$	*mer*	MER	1.85	0.842	12.1	15.2	53.7
CdIF-**3**[f]	$Cd(mim)_2$	*yqt1*	–	3.87	1.766	–	–	10.2
CdIF-**4**	$Cd(eim)_2$	*rho*	RHO	1.63	0.819	6.8; 9.6	21.6	? (54.1)
CdIF-**5**	$Cd(mim)_2$	*ict*	–	3.34	1.53	5.5	7.0	18.9
CdIF-**6**	$Cd(eim)_2$	*ana*	ANA	2.19	1.099	4.8	6.0	43.1
CdIF-**7**α	$Cd(nim)_2$	*dia*	–	3.51	1.961	–	3.0	13.3
CdIF-**7**β	$Cd(nim)_2$	*dia*	–	3.44	1.930	–	2.8	2.0
CdIF-**8**[f]	$Cd(nim)_2$	*sod*	SOD	2.03	1.135	6.0	15.2	59.8
CdIF-**9**	$Cd(nim)_2$	*rho*	RHO	1.69	0.948	9.0; 9.6	23.0	63.2
CdIF-**10**	$Cd(pim)_2$	*ana*	ANA	2.18	1.199	4.0	5.2	?
CdIF-**11**	$Cd(buim)_2$	*ana*	ANA	2.17	1.294	2.0	3.2	?
CdIF-**12**	$Cd(phim)_2$	*dia*	–	2.42	1.602	2.8	2.8	3.6

[a] The number of metal atoms per unit volume. [b] Framework density. [c] Diameter of pore. [d] Diameter of the sphere that fit the cage. [e] Potential solvent area calculated by PLATON (for which "?" indicates that a calculation for the guest-free MOF has failed; the value for CdIF-**4** in bracket was obtained when the crystal water was retained). [f] the CdIFs with metastability.

dazolates, CdIF-**10** for $[\{Cd(pim)_2\}]_\infty$, CdIF-**11** for $[\{Cd(bim)_2\}]_\infty$, and CdIF-**12** for $[\{Cd(phim)_2\}]_\infty$ (Table 1 and Supporting Information Table S1).

X-ray single-crystal analyses reveal that CdIF-**1**–**12**[8] are all three-dimensional (3D) frameworks (Figure 1), in which each Cd^{II} ion is tetrahedrally coordinated by four imidazolate nitrogen atoms and each imidazolate bridges two Cd^{II} ions (Cd–N 2.15 to 2.40 Å, N-Cd-N 109.5 to 120.6° and Cd···Cd distance ≈6.4 Å) that are all similar to those of zinc (or cobalt) imidazolate frameworks except the M–N bonds (and M···M) being about ≈0.2 Å (and M···M about 0.4 Å) elongated. It is just this small elongation of the M–N bond that has led to the cadmium 2-methyl-, 2-ethyl- and 2-nitro-imidazolates being polymorphous:

CdIF-**1** to -**3** and -**5** exhibit the net topology of *sod*, *mer*, *yqt1*[9] and *ict*;[10] CdIF-**4** and -**6** display the net topology of *rho* and *ana* while CdIF-**7**, -**8** and -**9** show that of *dia*, *sod* and *rho*, respectively. However, for the other cadmium imidazolates with the relative large R-substituent groups, the increased size of R-group again dismisses the flexibility of M–N bond rotation resulted from M–N bond elongation, leading to the cadmium imidazolates again with no more than one MOF: both of CdIF-**10** and CdIF-**11** demonstrate the net topology of *ana*, while CdIF-**12** shows the topology of *dia*.

Besides the polymorphous phenomenon, the elongated M–N bonds (and M···M distance) also make increased pore

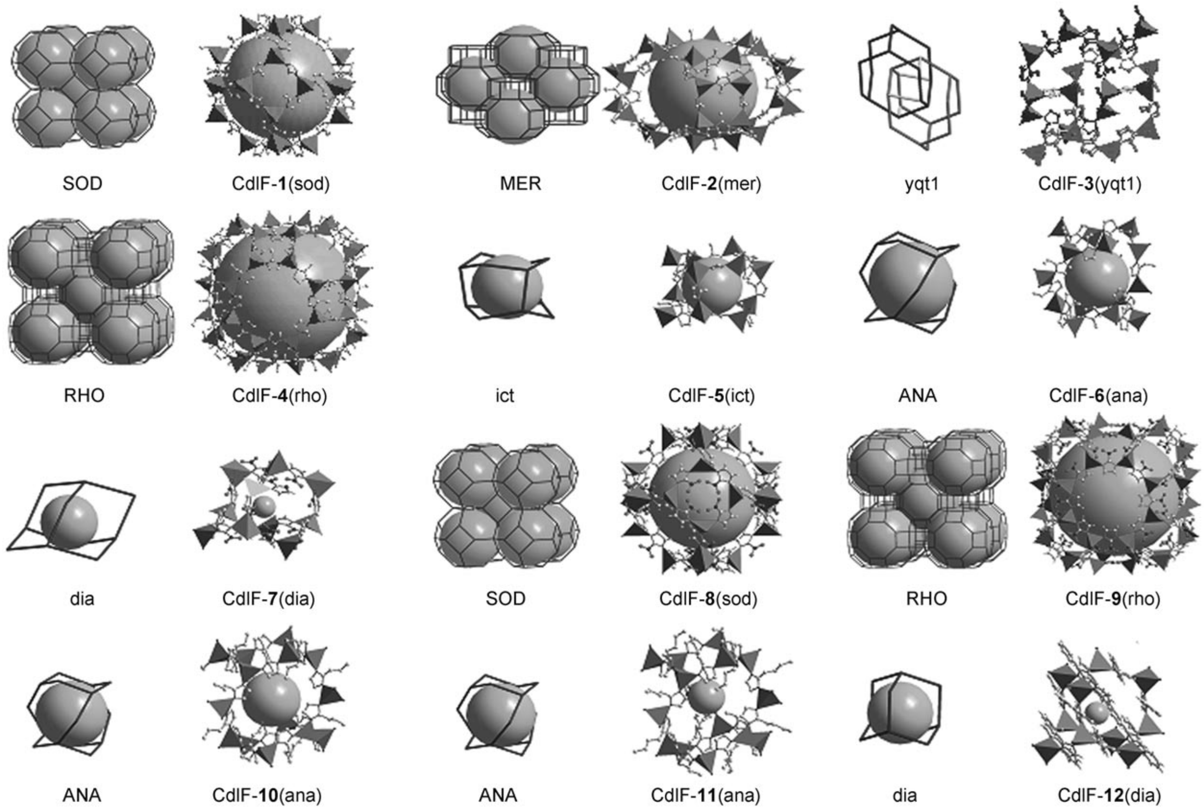

Figure 1. The crystal structures of CdIFs, in which the stick diagrams show their nets and the polyhedral diagrams exhibit their largest cages (H atoms are omitted for clarity).

opening for the CdIFs. To evaluate their porosity, we have also ranked their relevant structural characteristics in Table 1. With T/V in the range of 1.63 to 3.87 nm^{-3}, CdIFs are generally regarded as more open than those of their zinc (and cobalt) imidazolate counterparts (T/V in the range of 2.0 to 4.6 nm^{-3}).[4a] However, in respect that the inclusion of heavier metal Cd ions reduces any gain in gravimetric capacity, it should be more amenable to evaluate their porosity with apparent surface area.

Gas adsorption studies were carried out for CdIF-**1** (SOD), CdIF-**4** (RHO), CdIF-**9** (RHO) and CdIF-**10** (ANA) as the prototypes because not only they are thermostable up to 400 °C (TGA analyses and XRD studies for the CdIFs, see the Supporting Information), but also they with pure phases can be readily prepared on a gram-scale and they have the zinc counterparts for the surface area comparison. Nitrogen adsorption isotherms show type I curves, which reveal the microporous nature (Figure 2a).The Langmuir surface areas of CdIF-**1**, -**4**, -**9**, -**10** are 2420, 2420, 3010 and 1060 m^{2}g^{-1}, respectively, and are based on data collected from the adsorption branch in the range of P/P_0=0.01–0.10. Whereas the micropore volumes are calculated based on a single data point at P/P_0=0.10 and are 0.860, 0.764, 0.994 and 0.372 cm^{3}g^{-1}for CdIF-**1**, -**4**, -**9** and -**10**, respectively. As compared with ZIF-**8** (SOD) (Langmuir surface area of 1810 m^{2}g^{-1}),[4c] BIF-**9**-Li (RHO) (Langmuir surface area of 1820 m^{2}g^{-1})[5d] and [Zn(pim)$_2$]$_\infty$ (ANA)[11] (Langmuir surface area of 579 m^{2}g^{-1}, see Figure S16 in the Supporting Information), the four prototypical CdIFs prepared here by the approach of elongating M−N bond do not appear to have reduced surface areas, as a result of the inclusion of heavier metal Cd atoms, actually it seems that an increase in surface area resulted from the M−N bond expansion. Their porosities characterized with N$_2$ adsorptions are agreeable to that of the total potential solvent accessible volume calculated by PLATON program.

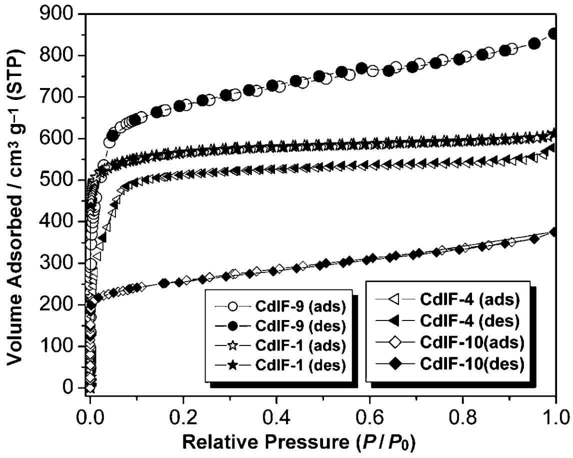

Figure 2. Nitrogen gas sorption isotherm for CdIF-**1**, -**4**, -**9** and -**10** at 77 K.

Three cycles of H$_2$ sorption-desorption for CdIF-**1** and -**4** at 77 K were performed under applied pressure up to 10 bar, which showed reversible and stable hydrogen adsorption behavior. The H$_2$-uptakes at 10 bar are 2.68 wt% (or 297 cm^{3}g^{-1}) and 1.91 wt% (or 212 cm^{3}g^{-1}) for CdIF-**1** and CdIF-**4**, respectively (Figure 3). In the comparison to ZIF-**8** with 1.29 wt% uptake of H$_2$ at 1 bar,[4c] a lower 0.93 wt% H$_2$-uptake for CdIF-**1** at 1 bar is resulted from the pore expansion[12] and the replacement of Zn with heavier Cd in the CdIFs.

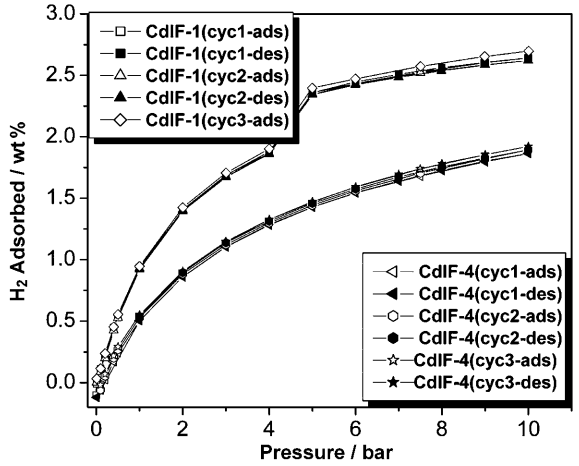

Figure 3. H$_2$ sorption isotherm of CdIF-**1** and -**4** at 77 K.

CO$_2$ adsorption isotherms at 273 K and 1 bar for CdIF-**1**, -**4**, and -**9** samples (Figure 4) show the volumetric uptakes of 48 cm^{3}g^{-1}(2.2 mmol g^{-1}), 30 cm^{3}g^{-1}(1.34 mmol g^{-1}) and 21 cm^{3}g^{-1}(0.94 mmol g^{-1}), respectively. The high CO$_2$ adsorption amount for CdIF-**9** is not just a result of its relative large surface area, but also to the -NO$_2$ groups that can interact with CO$_2$ molecules.[13]

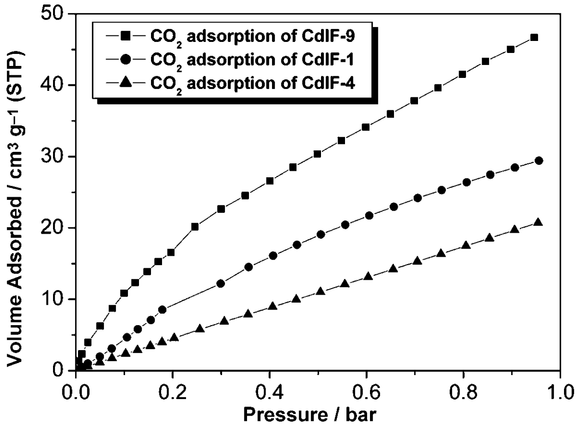

Figure 4. CO$_2$ sorption isotherm for CdIF-**1**, -**4**, -**9** at 273 K.

In summary, we have successfully synthesized a family of cadmium 2-substituent imidazolates (CdIF-**1** to -**12**) with highly thermostable and polymorphous MOFs by the approach of elongating the M–N bond. So far, we have obtained more than twelve CdIFs that exhibit not only the expected polymorphism, high thermal stability (up to 400 °C), but also surprisingly large porosity: CdIF-**9** (rho) has a surface area of 3010 $m^3 g^{-1}$, representing the highest value among the so far discovered metal imidazolate frameworks; CdIF-**1** and -**4** exhibit to be the most applicable porous MOFs because of their low costs of precursors and the massive producible synthesis, as well as their relatively high surface area of 2420 $m^3 g^{-1}$and thermal stability up to 400 °C.

Experimental Section

Typical synthesis for CdIFs:

The solvothermal method: Cadmium acetate dihydrate (0.267 g, 1.0 mmol) and 2-alkylimidazole (5.0 mmol) dissolved in 15 mL of alkylalcohols were placed in a 20 mL Teflon-lined autoclave. The reactant mixture was heated at 100–140 °C for 24–72 h and then cooled to room temperature. The obtained products were filtered and washed with ethanol (3×10 mL), colorless (or pale yellow) crystals were collected, yield 40–70 %;

The organic-base diffusion method: A mixture of cadmium nitrate tetrahydrate (0.1543 g, 0.5 mmol) and 2-alkylimidazole (1.0 mmol) in a selected solvent (5 mL) was placed in a 10 mL vial that was stirred until all stating materials dissolved. This vial was inserted in a larger vial containing another 10 mL vial filled with triethylamine (0.2 mL) and the selected solvent (5 mL). The larger vial was sealed and left undisturbed for about two weeks to crystallize. The colorless crystals were selected for single crystal analysis.

Crystal structure analysis for CdIFs: The single-crystal data for CdIF-**1**–**12** were collected by using a Bruker SMART-APEX-II CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-square techniques on F_2 using the SHELXL program package. All non-hydrogen atoms except those disordered ones were refined anisotropically and the hydrogen atoms were generated and included in the structure calculations with assigned isotropic thermal parameters but not refined. Powder X-ray diffraction patterns were determined by using a Bruker D8 Advance diffractometer at room temperature with $Cu_{K\alpha}$ radiation. CCDC-736757 (CdIF-**3**), 743551 (CdIF-**1**), 743552 (CdIF-**2**), 743553 (CdIF-**4**), 743554 (CdIF-**5**), 743555 (CdIF-**6**), 743556 (CdIF-**7a**), 743557 (CdIF-**7b**), 743558 (CdIF-**8**), 743559 (CdIF-**9**), 743560 (CdIF-**10**), 743561 (CdIF-**11**), 743562 (CdIF-**12**), and 743563 ($[Zn(pim)_2]_n$(ANA)) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The sorption isotherm for N_2 was measured at 77 K by using an automatic volumetric adsorption apparatus (AUTOSORB-1MP); The sorption isotherms of H_2 and CO_2 were measured by using an automatic gravimetric adsorption apparatus (IGA-003 series, Hiden Isochema Ltd).

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Keywords: cadmium imidazolates · gas adsorption · metal–organic frameworks · microporous materials · zeolites

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[8] Crystal data for CdIF-**1** (sod)($C_8H_{11}N_4CdO_{0.5}$) at 293 K: cubic, space group $I\bar{4}3m$, $a = 18.1206(6)$ Å, $Z = 12$, $V = 5950.0(3)$ Å^3, $\rho_{calcd} = 0.950$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 1.084$ mm^{-1}, $F(000) = 1668$, Gof = 1.019, $R1 = 0.0395$, $Rw2 = 0.1164$; CdIF-**2** (mer)($C_{16}H_{21}N_8Cd_2O_{0.5}$) at 293 K: tetragonal, space group $I4m$, $a = 29.220(2)$, $c = 20.287(3)$ Å, $Z = 16$, $V = 17321(3)$ Å^3, $\rho_{calcd} = 0.856$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 0.991$ mm^{-1}, $F(000) = 4368$, Gof = 1.059, $R1 = 0.0697$, $Rw2 = 0.1980$; CdIF-**3** (yqt1)($C_{24}H_{30}N_{12}Cd_3$) at 293 K: monoclinic, space group $C2/c$, $a = 14.7024(10)$, $b = 17.0783(12)$, $c = 13.9048(15)$ Å, $\beta = 117.4720(10)°$, $Z = 4$, $V = 3097.7(5)$ Å^3, $\rho_{calcd} = 1.766$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 2.075$ mm^{-1}, $F(000) = 1608$, Gof = 1.043, $R1 = 0.0289$, $Rw2 = 0.0766$; CdIF-**4** (rho)($C_{10}H_{14.33}N_4CdO_{0.17}$) at 293 K: cubic, space group $Im\bar{3}m$, $a = 30.8871(7)$ Å, $Z = 48$, $V = 29466.7(12)$ Å^3, $\rho_{calcd} = 0.827$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 0.878$ mm^{-1}, $F(000) = 7280$, Gof = 1.606, $R1 = 0.0730$, $Rw2 = 0.3813$; CdIF-**5** (ict)($C_{48}H_{60}N_{24}Cd_6$) at 293 K: monoclinic, space group $P2_1/c$, $a = 16.9693(17)$, $b = 29.411(3)$, $c = 14.6756(15)$ Å, $\beta = 103.622(2)°$, $Z = 4$, $V = 7118.4(12)$ Å^3, $\rho_{calcd} = 1.537$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 1.806$ mm^{-1}, $F(000) = 3216$, Gof = 0.984, $R1 = 0.0541$, $Rw2 = 0.1319$; CdIF-**6** (ana)($C_{10}H_{14}N_4Cd$) at 293 K: cubic, space group $Ia\bar{3}d$, $a = 27.9997(8)$ Å, $Z = 48$, $V = 21951.3(11)$ Å^3, $\rho_{calcd} = 1.099$ Mg m^3, $\mu(Mo_{K\alpha}) = 1.177$ mm^{-1}, $F(000) = 7200$, Gof = 1.064, $R1 = 0.0493$, $Rw2 = 0.1725$; CdIF-**7a** (dia)($C_{12}H_8N_{12}O_8Cd$) at 293 K: orthorhombic, space group $Pbcn$, $a = 9.4370(10)$, $b = 33.637(4)$, $c = 14.6329(15)$ Å, $Z = 8$, $V = 4645.0(8)$ Å^3, $\rho_{calcd} = 1.961$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 1.930$ mm^{-1}, $F(000) = 2592$, Gof = 0.988, $R1 = 0.0366$, $Rw2 = 0.0900$; CdIF-**7b** (dia)($C_{12.75}H_{9.75}N_{12.25}O_{8.25}Cd_2$) at 293 K: orthorhombic, space group $Pbca$, $a = 15.8508(18)$, $b = 11.9363(14)$, $c = 24.097(3)$ Å, $Z = 8$, $V = 4559.1(9)$ Å^3, $\rho_{calcd} = 1.977$ Mg m^3, $\mu(Mo_{K\alpha}) = 1.898$ mm^{-1}, $F(000) = 2672$, Gof = 0.993, $R1 = 0.0387$, $Rw2 = 0.0967$; CdIF-**8** (sod)($C_6H_4N_6CdO_4$) at 293 K: Cubic, space group $I\bar{4}3m$, $a = 18.0772(6)$ Å, $Z = 12$, $V = 5907.4(3)$ Å^3, $\rho_{calcd} = 1.135$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 1.117$ mm^{-1}, $F(000) = 1944$, Gof = 0.1010, $R1 = 0.0420$, $Rw2 = 0.1041$; CdIF-**9** (rho)($C_6H_{4.08}N_6CdO_{4.04}$) at 293 K: cubic, space

group $Im\bar{3}m$, $a=30.4997(11)$ Å, $Z=48$, $V=28\,371.8(18)$ Å^3, $\rho_{calcd}=0.948$ Mg m^{-3}, $\mu(Mo_{K\alpha})=0.931$ mm^{-1}, $F(000)=7796$, Gof = 1.319, $R1=0.0663$, $Rw2=0.2532$; CdIF-**10** (ana)($C_{12}H_{18}N_4Cd$) at 293 K: cubic, space group $Ia\bar{3}d$, $a=28.0174(7)$ Å, $Z=48$, $V=21\,993.0(10)$ Å^3, $\rho_{calcd}=1.199$ Mg m^{-3}, $\mu(Mo_{K\alpha})=1.180$ mm^{-1}, $F(000)=7968$, Gof = 1.013, $R1=0.0337$, $Rw2=0.1369$; CdIF-**11** (ana)($C_{14}H_{22}N_4Cd$) at 293 K: cubic, space group $Ia\bar{3}d$, $a=28.0630(12)$ Å, $Z=48$, $V=22\,100.5(16)$ Å^3, $\rho_{calcd}=1.294$ Mg m^{-3}, $\mu(Mo_{K\alpha})=1.180$ mm^{-1}, $F(000)=8736$, Gof = 1.014, $R1=0.0365$, $Rw2=0.1161$; CdIF-**12** (dia)($C_{18}H_{14}N_4Cd$) at 293 K: tetragonal, space group $I\bar{4}2d$, $a=10.500$, $c=14.999$ Å, $Z=4$, $V=1653.6$ Å^3, $\rho_{calcd}=1.602$ Mg m^{-3}, $\mu(Mo_{K\alpha})=1.324$ mm^{-1}, $F(000)=792$, Gof = 0.979, $R1=0.0196$, $Rw2=0.0397$.

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