SUPPLEMENTARY MATERIAL ACCOMPANYING:

Bulky substituent and solvent-induced alternative nodes for layered Cd-isophthalate/acylhydrazone frameworks

Kornel Roztocki,[a] Magdalena Lupa,[a] Maciej Hodorowicz,[a] Irena Senkovska,[b] Stefan Kaskel[b] and Dariusz Matoga*[a]

[a]*Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Poland*
[b]*Department of Inorganic Chemistry, Technische Universität Dresden, Bergstrasse 66, 01062 Dresden, Germany*

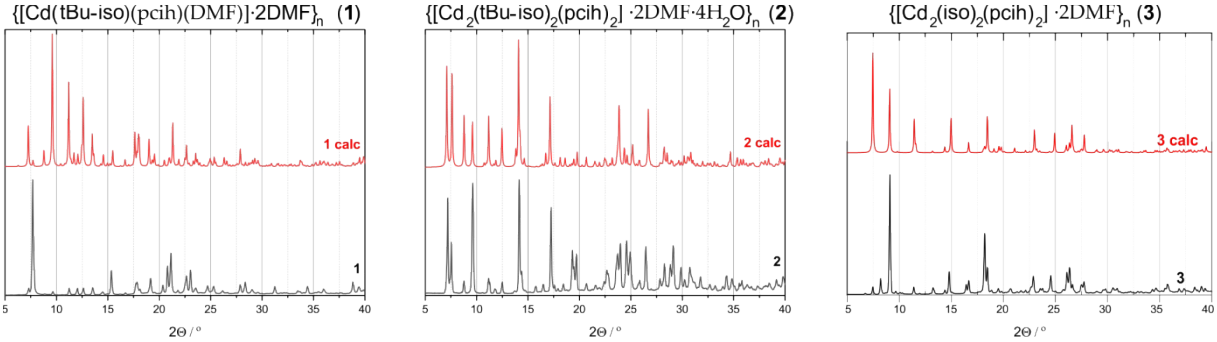

Figure S1 Experimental powder XRD patterns for as-synthesized **1** (left), **2** (middle) and **3** (right) compared with the patterns calculated from single-crystal structures (calc).

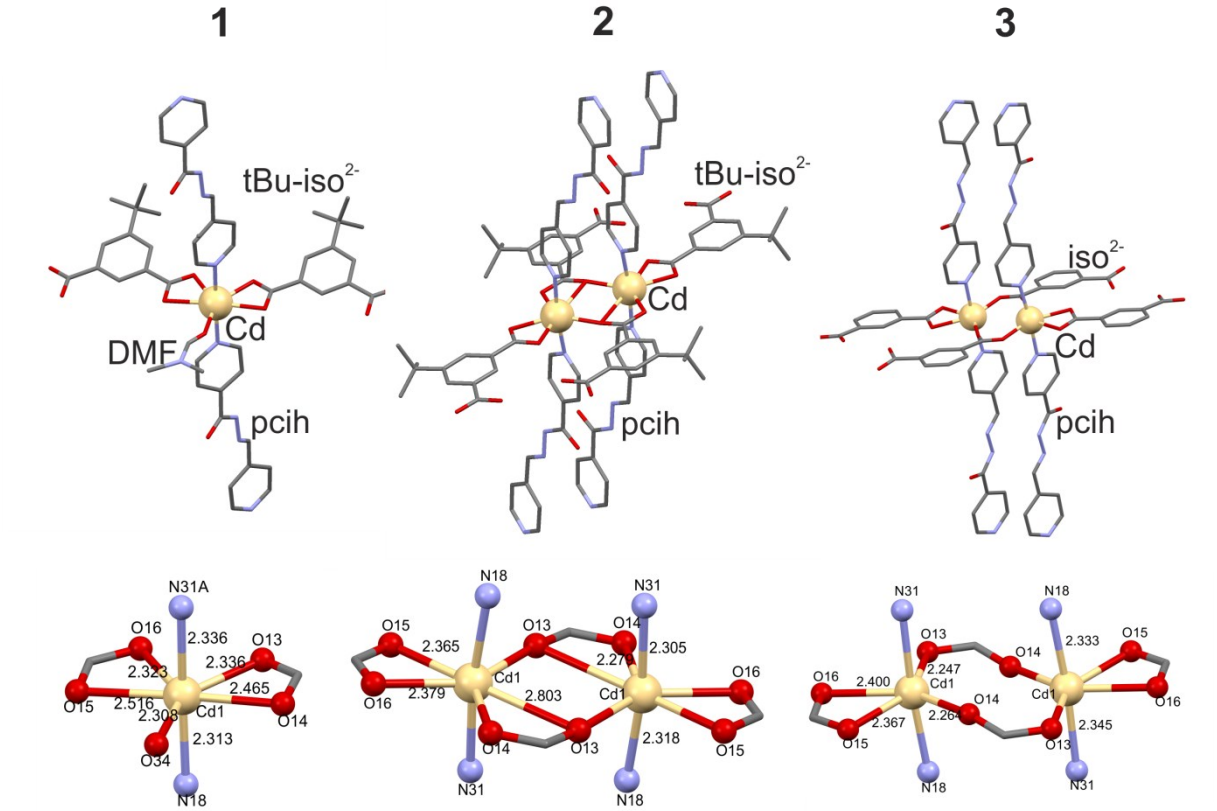

Figure S2 X-ray crystal structures of **1** (left), **2** (middle) and **3** (right): [Cd(tBu-iso)(pcih)(DMF)], $[Cd_2(tBu\text{-}iso)_2(pcih)_2]$ and $[Cd_2(iso)_2(pcih)_2]$ units, respectively.

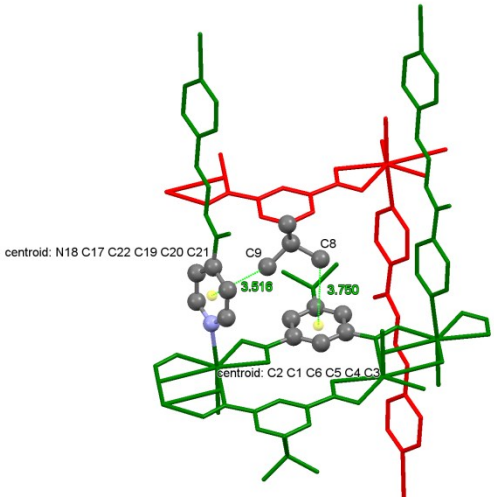

Figure S3 Supramolecular interactions ($CH_3\cdots\pi$) involving adjacent layers in $\{[Cd_2(tBu\text{-}iso)_2(pcih)_2]\cdot 2DMF\cdot 4H_2O\}_n$ (**2**).

	H..Cg	X-H..Cg	X..Cg
C(8)-H(**8**B)…Cg(1) [1-X,-1-Y,2-Z]	2.93	142	3.7491(1)
C(43)-H(43C)…Cg(1) [1-X,-Y,1-Z]	2.95	123	3.5807(1)
C(9)-H(9A)…Cg(2) [1-X,1-Y, -Z]	3.05	110.1	3.5190(1)

Cg(1): C(1)-C(2)-C(3)-C(4)-C(5)-C(6)
Cg(2): N(18)-C(17)-C(22)-C(21)-C(20)-C(19)

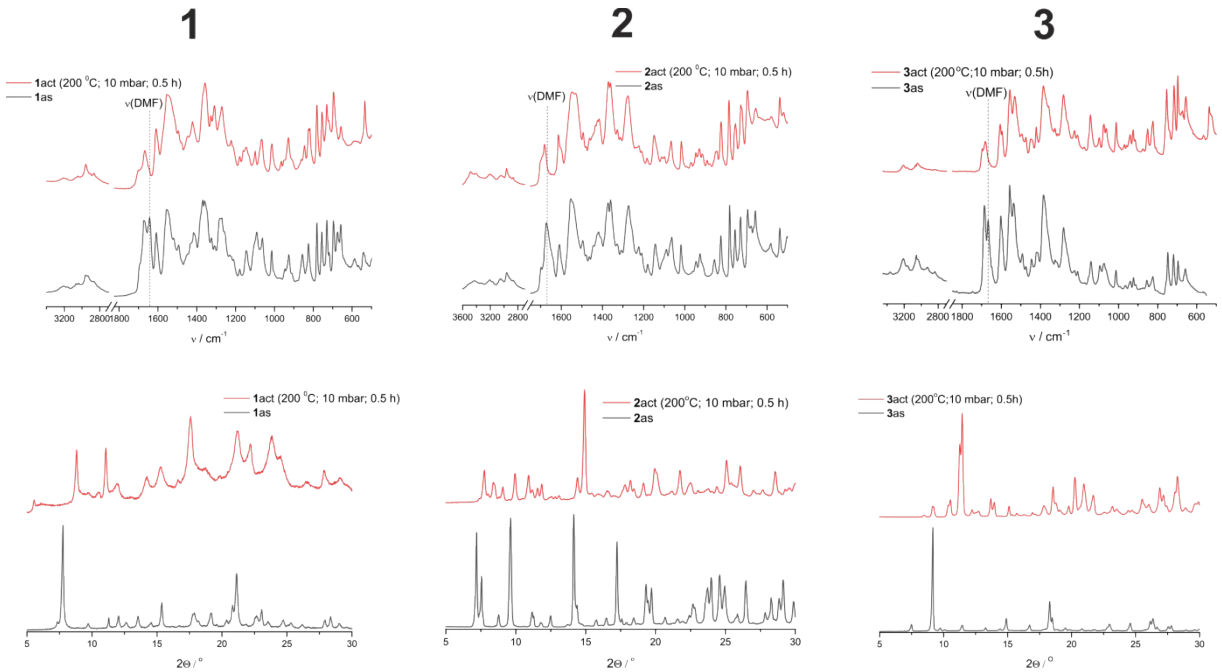

Figure S4 *Ex Situ* IR spectra (top) and PXRD patterns (bottom) for **1-3** conditioned for 30 minutes at 200 °C and 10 mbar (act), followed by cooling in air to room temperature; compared with the as-synthesized samples (as).

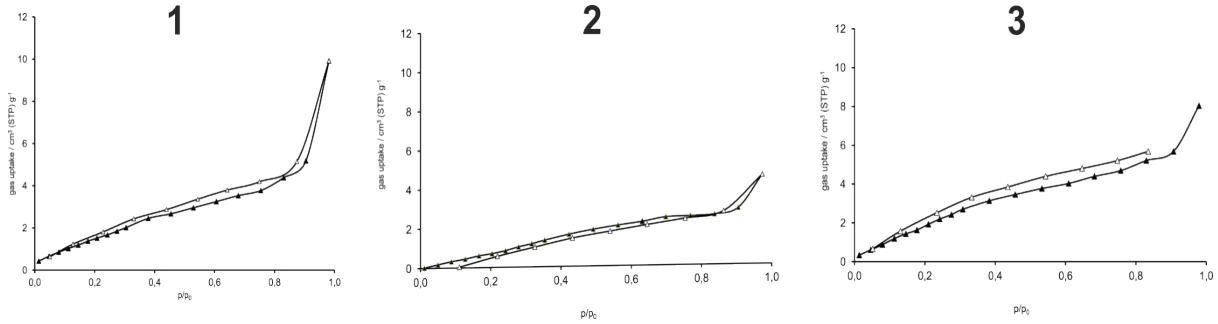

Figure S5 Adsorption isotherms of N_2 at 77 K for **1-3**. Solid and open symbols represent adsorption and desorption branches, respectively.

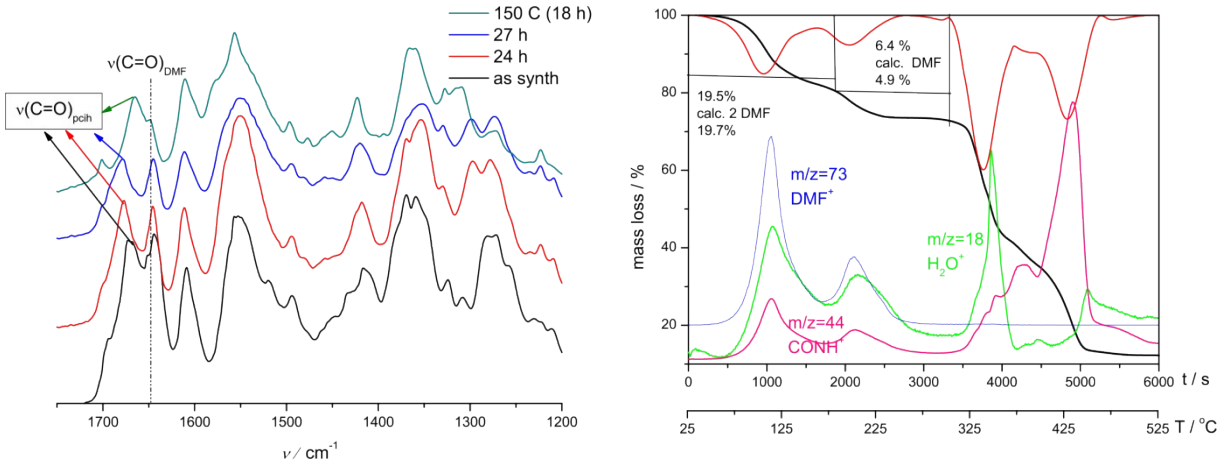

Figure S6 IR spectra of **1**: (Left) as-synthesized (as synth), conditioned in DCM for 24 hours and dried at RT (24 h), immersed again in DCM for 3 hours and dried at RT (27 h) as well as activated for 18 hours at 150 °C after soaking in DCM for 27 hours in total (150 C). (Right) TG-MS analysis of the material **1**.

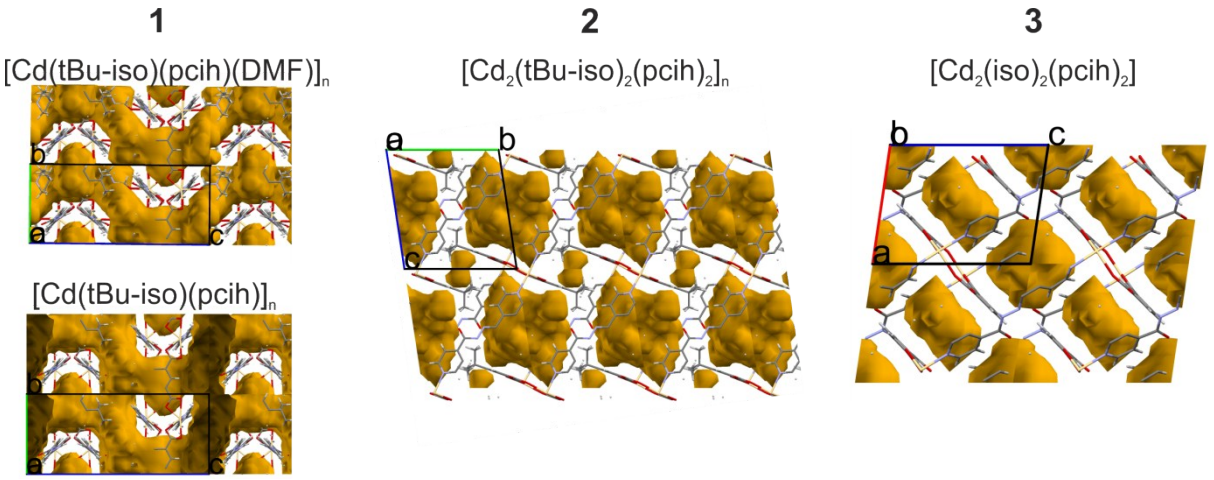

Figure S7 X-ray crystal structures of **1-3**: solvent accessible voids calculated with Mercury software by using a probe molecule with a radius of 1.2 Å.

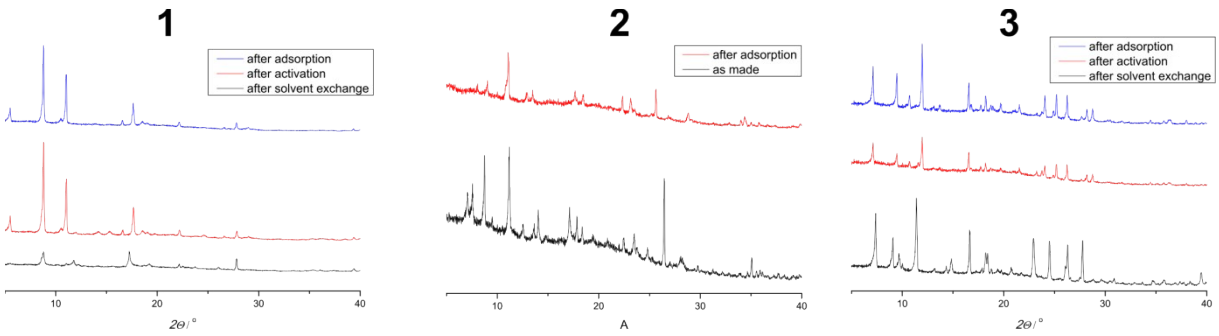

Figure S8 PXRD patterns for **1-3** recorded prior to and after adsorption experiments.

Table S1 Crystal data and structure refinement parameters for $\{[Cd(tBu\text{-}iso)(pcih)(DMF)]\cdot 2DMF\}_n$ (**1**), $\{[Cd_2(tBu\text{-}iso)_2(pcih)_2]\cdot 2DMF\cdot 4H_2O\}_n$ (**2**) and $\{[Cd_2(iso)_2(pcih)_2]\cdot 2DMF\}_n$ (**3**).

Compound	**1**	**2**	**3**
Empirical formula	$C_{30}\ H_{36}\ Cd\ N_6\ O_7$	$C_{27}\ H_{33}\ Cd\ N_5\ O_9$	$C_{46}\ H_{28}\ Cd_2\ N_9\ O_{12}$
Formula weight	705.05	683.98	1123.57
Crystal size (mm)	0.200 x 0.100 x 0.100	0.300 x 0.300 x 0.100	0.200 x 0.200 x 0.200
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	P 2/n	P -1	P-1
Unit cell dimensions			
a (Å)	15.9888(3)	10.2150(2)	9.3264(2)
b (Å)	10.0556(2)	11.9013(2)	10.3880(2)
c (Å)	23.1510(6)	12.6419(2)	12.3659(2)
α	90	80.6080(10)	104.506(2)
γ(°)	90	80.6600(10)	102.756(2)
β (°)	98.775(2)	84.6970(10)	94.778(2)
Volume (Å^3)	3678.58(14)	1492.76(5)	1118.97(4)
Temperature (K)	129.6(8)	100(2)	130.05(10)
Z	4	2	1
Density (calculated) (g/cm^3)	1.273	1.522	1.667
Absorption coefficient (mm^{-1})	0.641	0.791	1.025
F(000)	1448	700	559
Theta range for data collection (°)	2.901 to 28.572	3.368 to 27.600	4.062 to 28.667
Index ranges	-21<=h<=21, -13<=k<=13, -30<=l<=29	-12<=h<=13, -15<=k<=15, -16<=l<=16	-12<=h<=12, -13<=k<=14, -16<=l<=16
Reflections measured	51218	12574	47522
Reflections unique	8860 [R(int) = 0.0484]	6818 [R(int) = 0.0194]	5451 [R(int) = 0.0565]
Completeness to theta = 25.242°	99.7 %	99.3 %	99.1 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F2
Data / restraints / parameters	8860 / 63 / 472	6818 / 6 / 404	5451 / 6 / 292
Goodness-of-fit on F^2	1.089	1.075	1.094
Final *R* indices [I>2sigma(I)]	R1 = 0.0590, wR2 = 0.1426	R1 = 0.0264, wR2 = 0.0695	R1 = 0.0346, wR2 = 0.0840

R indices (all data)	R1 = 0.0734, wR2 = 0.1520	R1 = 0.0270, wR2 = 0.0699	R1 = 0.0425, wR2 = 0.0894
Largest diff. peak and hole [e.Å^{-3}]	1.427 and -1.103	1.782 and -0.614	1.702 and -0.998