Supporting Information

Synthesis of 3D cadmium(II)-carboxylate framework having potential for co-catalyst free CO_2 fixation to cyclic carbonates

Zafar A. K. Khattak [1,2], Nazir Ahmad [3,*], Hussein A. Younus [4,5], Habib Ullah [6], Baoyi Yu [7], Khurram S. Munawar [8], Muhammad Ashfaq [9], Sher Ali [10], Hossain M. Shahadat [11] and Francis Verpoort [1,12,*]

1 State Key Laboratory of Advanced Technology for Materials Synthesis and Processing,Wuhan University of Technology, Wuhan 430070, China
2 Institute of Chemistry, Baghdad-ul-Jadeed Campus, The Islamia University of Bahawalpur, Bahawalpur 63100, Pakistan
3 Chemistry Department, Government College University Lahore, Lahore 54000, Pakistan
4 Chemistry Department, Faculty of Science, Fayoum University, Fayoum 63514, Egypt
5 Department of Chemical and Petroleum Engineering, College of Engineering, Sultan Qaboos University, Al Khould, P.O Box 33, Muscat PC 123, Oman
6 Department of Material Science and Engineering, Chungnam National University, Daejeon 34134, Korea
7 Key Laboratory of Urban Agriculture (North China), Ministry of Agriculture, College of Biological Sciences Engineering, Beijing University of Agriculture, Beijing 102206, China
8 Department of Chemistry, University of Mianwali, Mianwali 42200, Pakistan
9 Department of Physics, University of Sargodha, Sargodha 40100, Pakistan
10 Department of Chemistry, Khushal Khan Khattak University Karak, Karak 27200, Pakistan
11 Department of Chemistry, Faculty of Science, Comilla University, Comilla 3506, Bangladesh
12 Research School of Chemical and Biomedical Technologies, National Research Tomsk Polytechnic University, Lenin Avenue 30, 634050 Tomsk, Russia
* Correspondence: dr.nazirahmad@gcu.edu.pk (N.A.); francis@whut.edu.cn (F.V.)

Contents

1. NMR Spectra of Ligand

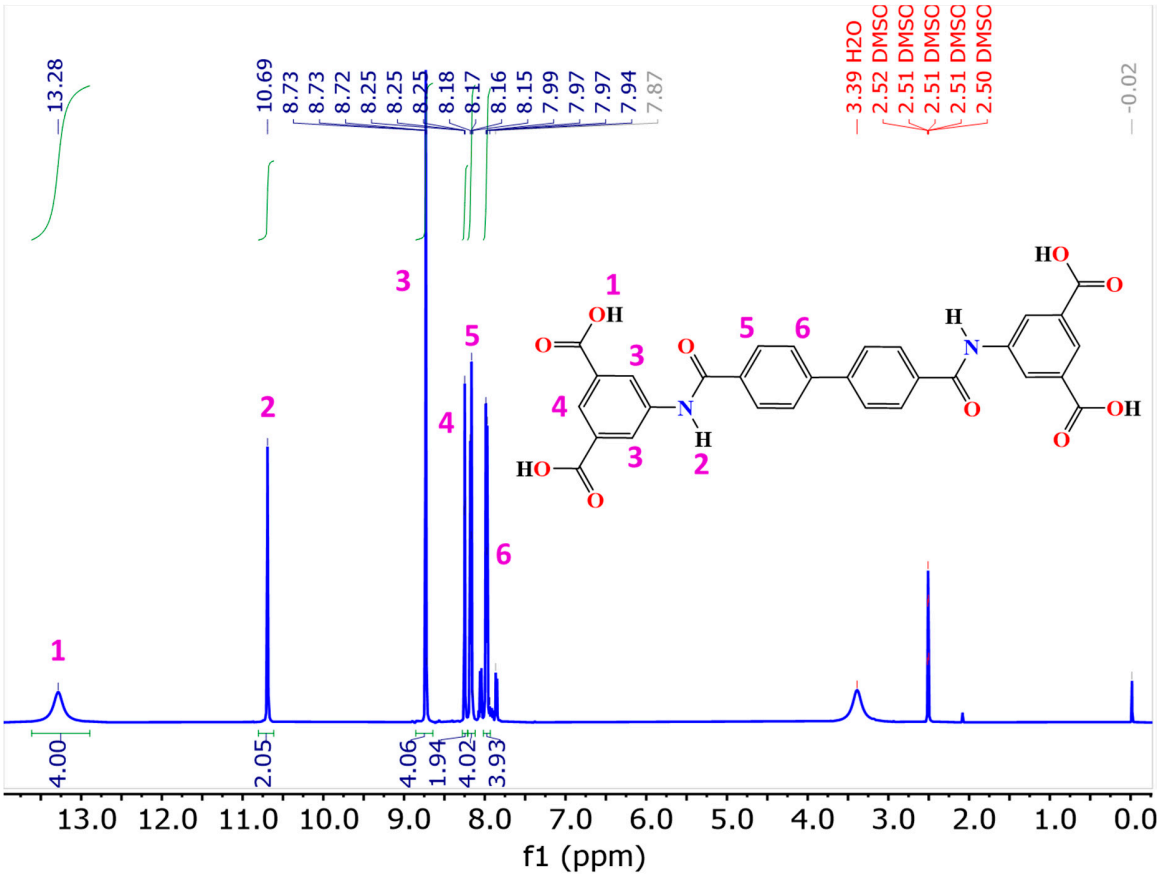

Figure S1. ^{1}H-NMR spectra of ligand acid (H_4L)

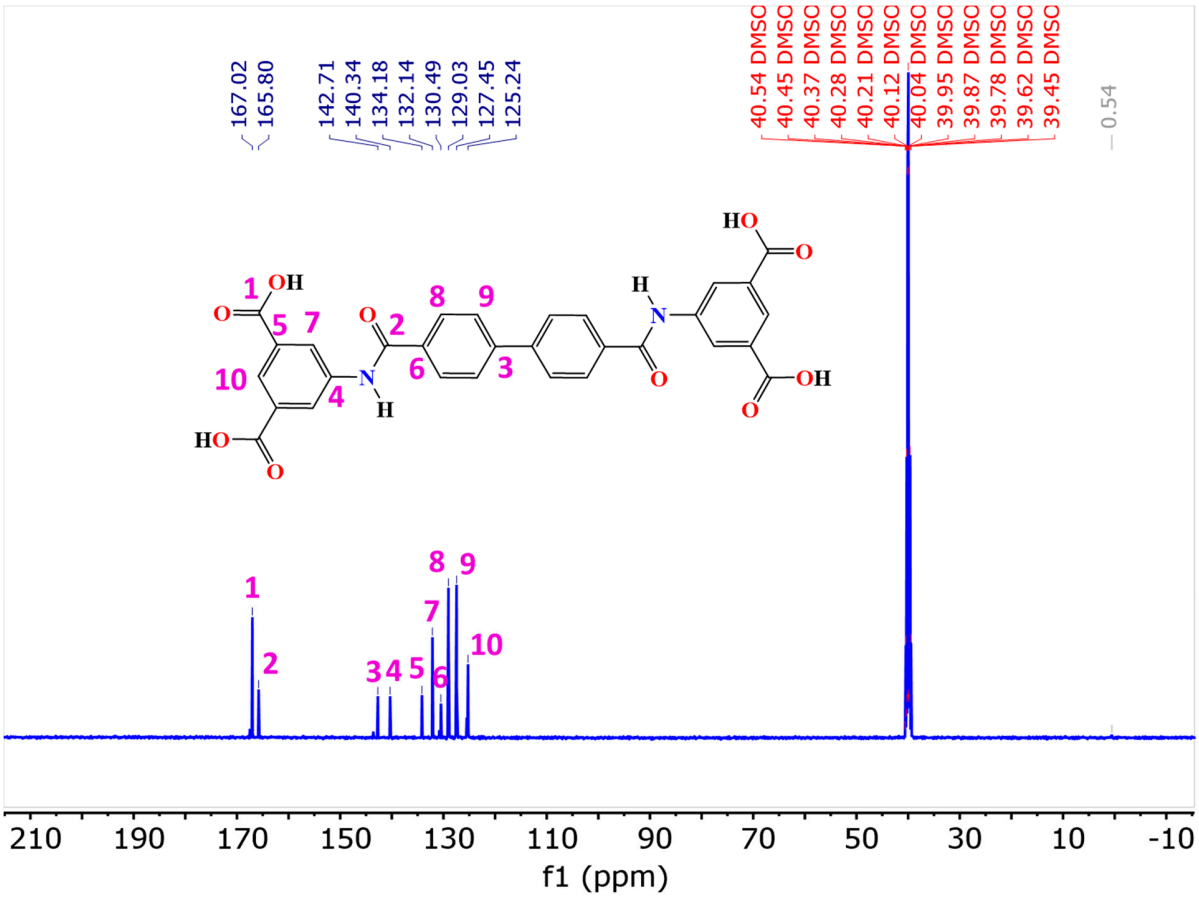

Figure S2. ^{13}C-NMR spectra of ligand acid (H_4L)

2. Single Crystal Data

Table S1. Single crystal XRD experimental description of **3D-CdMOF.**

Crystal data	CdMOF
CCDC	2097250
Chemical formula	$C_{33}H_{27}Cd_2N_3O_{13}$
M_r	898.37
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	296
a, b, *c* (Å)	14.184(3), 14.503(3), 21.814(5)
α, β, γ (°)	90, 99.035 (5), 90
V (Å^3)	4431.7(17)
Z	4
Density (calculated)g/cm^{-3}	1.347
F(000)	1784
Radiation type	Mo *Kα*
Wavelength (λ)	0.71073
μ (mm^{-1})	1.014

Crystal size (mm)	0.25 × 0.24 × 0.18
Data Collection	
Diffractometer	Bruker APEX-II CCD
Absorption correction	multi-scan
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7511, 7511, 5462
Theta range for data collection (°)	2.531 to 26.987
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.595
Data Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.086, 0.282, 1.11
No. of reflections	7511
No. of parameters	480
No. of restraints	603
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.59, −1.25

Note: While creating the CCDC cif entry, we performed the refinement by using SEQUEEZE software and there were only a few residual peaks (non-ordered density of electrons) which we excluded [a]. The main reason for this was that the orientations or the positions of such specific electronic density peaks were very strange because these were quite randomly oriented and were not corresponding to any of the complete solvent molecule (neither DMF nor water) as guest(s). The difference between the crystallographic formula (the bulk formula) with CHN analysis might be due to removing those few strangely observed electron densities from the refinement model. As the unbound (guest) solvent is missing in the crystallographic representation so the bulk formula has a small difference from the CHN data.

[a] The following peaks were removed during the refinement

Q1	1	0.3811	0.8963	-0.4713	11.00000	0.05	6.99
Q2	1	0.7002	0.5377	-0.0468	11.00000	0.05	5.94
Q3	1	0.1539	0.6733	-0.8731	11.00000	0.05	4.04
Q4	1	0.3455	0.5224	-0.8546	11.00000	0.05	3.69
Q5	1	0.3254	0.5336	-0.7959	11.00000	0.05	3.30
Q6	1	0.7156	0.5184	-0.0971	11.00000	0.05	3.16
Q7	1	0.0992	0.8137	-0.9518	11.00000	0.05	2.75
Q8	1	0.5928	0.7592	-0.5502	11.00000	0.05	2.59
Q9	1	0.4331	0.5474	-0.8594	11.00000	0.05	2.31

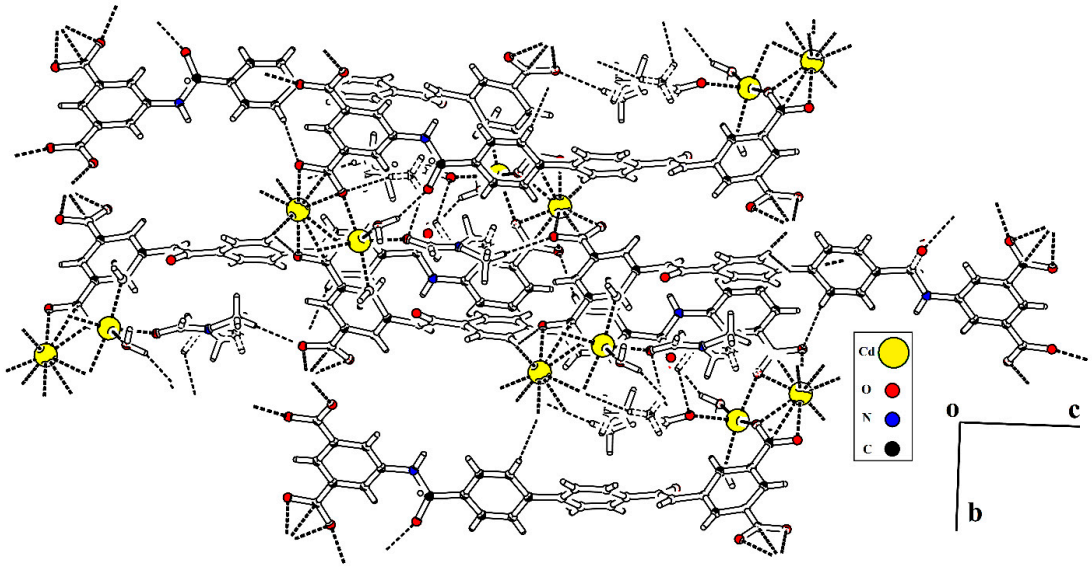

Figure S3. Packing diagram of **CdMOF**. Selected H-atoms are shown for clarity.

Table S2. Selected bond lengths (Å) and angles (°) in **CdMOF**.

Bonds	**Bond Lengths (Å)**	**Bonds**	**Bond Lengths (Å)**
Cd1-O11	2.266(8)	Cd2-O9^{i}	2.226(7)
Cd1-O12	2.259(9)	Cd2-O2	2.485(6)
Cd1-O00C	2.259(8)	Cd2-O4^{ii}	2.365(7)
Cd1-O10^{i}	2.217(9)	Cd2-O3^{ii}	2.331(6)
Cd1-O7^{iii}	2.321(7)	Cd2-O8^{iii}	2.487(7)
Cd1-O1	2.291(7)	Cd2-O7^{iii}	2.403(7)
Cd2-O1	2.374(7)		
Bonds	**Bond Angles (°)**	**Bonds**	**Bond Angles (°)**
O7^{iii}-Cd1-O1	73.6(2)	O1-Cd2-O3^{ii}	98.5(2)
O7^{iii}-Cd1-O10^{i}	88.1(3)	O1-Cd2-O8^{iii}	124.3(2)
O7^{iii}-Cd1-O11	171.0(3)	O1-Cd2-O7^{iii}	70.7(2)
O7^{iii}-Cd1-O12	92.2(3)	O9^{i}-Cd2-O2	87.5(3)
O7^{iii}-Cd1-O00C	100.5(3)	O9^{i}-Cd2-O4^{ii}	97.5(3)
O1-Cd1-O10^{i}	88.7(3)	O9^{i}-Cd2-O3^{ii}	153.8(3)
O1-Cd1-O11	99.7(3)	O9^{i}-Cd2-O8^{iii}	90.2(3)
O1-Cd1-O12	165.4(3)	O9^{i}-Cd2-O7^{iii}	103.8(3)
O1-Cd1-O00C	89.0(3)	O2-Cd2-O4^{iii}	90.0(2)
O10^{i}-Cd1-O11	85.8(3)	O2-Cd2-O3^{ii}	89.4(2)
O10^{i}-Cd1-O12	94.5(4)	O2-Cd2-O8^{v}	176.3(2)
O10^{i}-Cd1-O00C	170.1(4)	O2-Cd2-O7^{iii}	124.1(2)
O11-Cd1-O12	94.8(4)	O4^{ii}-Cd2-O3^{ii}	56.4(2)
O11-Cd1-O00C	85.1(3)	O4^{ii}-Cd2-O8^{iii}	93.1(2)
O12-Cd1-O00C	90.2(3)	O4^{ii}-Cd2-O7^{iii}	139.8(2)
O1-Cd2-O9^{i}	100.5(3)	O3^{ii}-Cd2-O8^{iii}	93.9(2)
O1-Cd2-O2	53.5(2)	O3^{ii}-Cd2-O7^{iii}	99.4(2)
O1-Cd2-O4^{ii}	137.9(2)	O8^{iii}-Cd2-O7^{iii}	53.7(2)

Table S3. Hydrogen-bond geometry (Å, º) for **CdMOF**.

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	**<(*D*—H···*A*)º**
O12—H12*B*···O6^{i}	0.88	2.29	3.08(4)	150
O12—H21*B*···O6*A*^{i}	0.88	1.90	2.73(2)	157
C28—H28···O6	0.93	2.08	2.67(4)	120
C28—H28···O6*A*	0.93	2.32	2.81(2)	112
C32*A*—H32*D*···O00C^{ii}	0.96	2.37	3.07(7)	129
C32*A*—H32*D*···N3^{ii}	0.96	2.69	3.65(9)	173
C32*A*—H32*E*···O7^{iii}	0.96	2.53	3.47(3)	168
C33—H33*A*···O3^{iv}	0.96	2.42	3.36(3)	166
C33*A*—H33*F*···O7^{iii}	0.96	2.50	3.44(5)	168
***C*—H···π**	***C*—H**	**H··· π**	***C*··· π**	**<(*C*—H··· π)º**
C33—H33C···Cg2	0.96	2.99	3.68 (4)	130

Symmetry codes: (i) −*x*+1/2, *y*+1/2, −*z*−3/2; (ii) −*x*+1, −*y*+2, −*z*−2; (iii) *x*+1/2, −*y*+3/2, *z*−1/2; (iv) *x*−1/2, −*y*+3/2, *z*−3/2. Cg2 is the centroid of phenyl ring (C10-C15) in **CdMOF**.

3. NMR Spectra of Carbon Dioxide Fixation Reactions

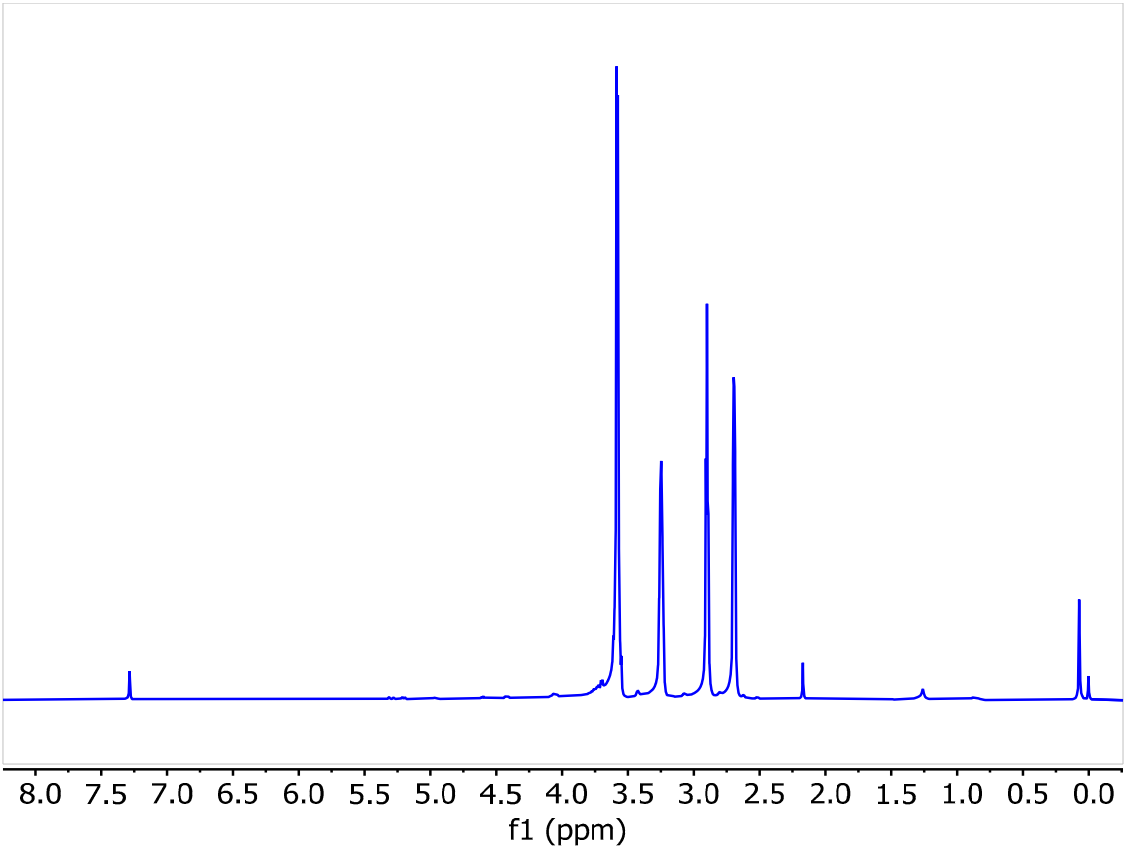

Figure S4: ^{1}H-NMR spectrum in $CDCl_3$ of the reaction mixture obtained from the conversion of epichlorohydrin after 12 h in absence of catalyst

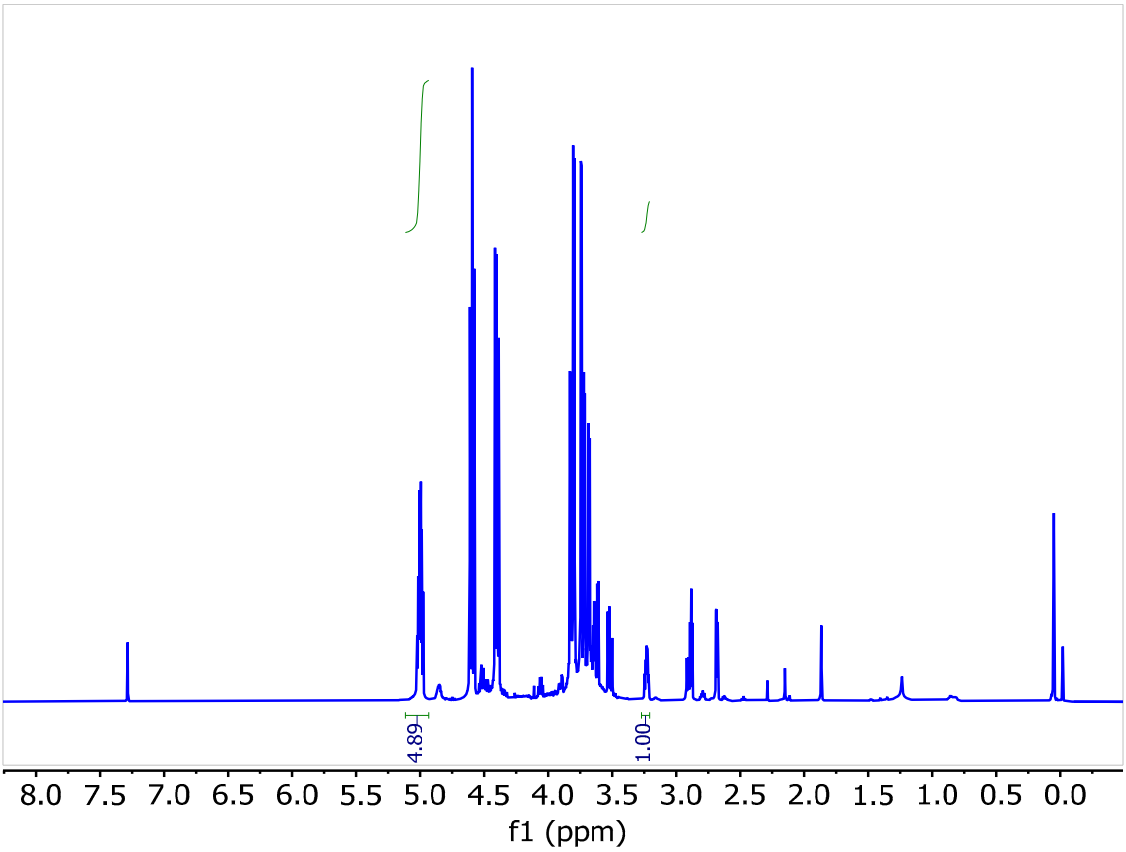

Figure S5: ^{1}H-NMR spectrum in $CDCl_3$ of the reaction mixture obtained from the conversion of epichlorohydrin after 12 h using CdMOF as a catalyst.