Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Role of Solvent on Framework Dimensionality and Its Effect towards Band Gap Energy

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Theoretical Methods

First principles electronic structure studies within a gradient-corrected density functional framework were carried out to understand the experimental findings on the band gaps. Two kinds of theoretical studies were performed. Electronic structure calculations with the PBE exchange-correlation functional[1] were performed on periodic solids using the experimentally determined crystal structures to understand the origins of changes in the band gap energy. These calculations were performed using the Vienna Ab-Initio Simulation Package (VASP).[2] The projector augmented wave (PAW) pseudopotentials were used to describe the electron-ion interaction. The kinetic energy cut-off of 400 eV was found to give converged results and was used for the plane wave basis. The geometries in these studies used the experimentally determined crystal structures. Secondly, gradient-corrected calculations using the PBE functional[1] were performed on free clusters to understand the nature of bonding, using the Amsterdam Density Functional Package (ADF).[3] Relativistic effects were taken in account using the Zeroth Order Regular Approximation, and the TZ2P basis set was used.[4]

References

1. Perdew, J. P.; Burke, K.; Enzerhof, M. *Phys. Rev. Lett.* 1996, **77**, 3865.

2. Kresse, G.; Furthmuller, *J. Phys. Rev. B* 1996, **54**, 11169.

3. Te Velde, G.; Bichelhaupt, F. M.; van Gisbergen, S. J. A.; Fonseca, G. C.; Baerends, E .J.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* 2001, **22**, 931.

4. van Lenthe, E.; Baerends, E.J.; Snijders, J. G. *J. Comput. Chem.* 1993, **99**, 4597.

Table S1. Crystallographic parameters for compounds **1** and **2**, respectively.[a]

Parameters	**Compound 1**	**Compound 2**
Empirical formula	$C_{15}H_{18}Cd_{1.5}N_2O_{10}$	$C_{14}H_{14}Cd_{1.5}NO_{11}$
Formula weight	554.91	540.87
Crystal System	Monoclinic	Triclinic
Space Group	$P2_1/n$ (no. 14)	$P(-1)$ (no. 2)
a(Å)	10.013	9.4327
b(Å)	18.617	10.1954
c(Å)	21.2365	11.2452
α(°)	90	63.983
β(°)	91.84	73.212
γ(°)	90	83.22
Volume(Å^3)	3956.7	930.4
Z	4	2
Calculated density (g/cm^3)	1.848	1.931
θ range (°)	2.477 to 28.418	3.152 to 28.379
Absorption coefficient (mm^{-1})	1.681	1.78
Reflections collected	35944	16146
Unique reflections	9731	4517
Goodness-of-fit	1.080	1.050
Number of parameters	482	255
Final R indices [I>2sigma(I)]	$R_1 = 0.0670$, $wR_2 = 0.1740$	$R_1 = 0.0635$, $wR_2 = 0.1395$
R indices (all data)	$R_1 = 0.0865$, $wR_2 = 0.1869$	$R_1 = 0.0639$, $wR_2 = 0.1396$

[a] $R_1 = \Sigma||F_0| - |F_c||/ \Sigma|F_0|$; $wR_2 = \{[w(F_0^2 - F_c^2)^2]/ [w(F_0^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_0)^2 + (aP)^2 + bP]$; $P = [\max(F_0^2,0) + 2(F_c)^2]/3$, where $a = 0.0762$ and $b = 41.3041$ for compound **1** and $a = 0.0090$ and $b = 20.4366$ for compound **2**, respectively.

Table S2. Selected bond length for compound **1**.

Moiety	**Bond lengths (Å)**
Cd(1)-O(5)	2.214(6)
Cd(1)-O(3)	2.262(5)
Cd(1)-O(1)	2.273(6)
Cd(1)-O(4)	2.378(8)
Cd(1)-O(2)	2.378(8)
Cd(1)-O(6)	2.378(12)
Cd(2)-O(12)	2.284(5)
Cd(2)-O(11)	2.305(6)
Cd(2)-O(9)	2.316(7)
Cd(2)-O(10)	2.325(6)
Cd(2)-O(8)	2.402(6)
Cd(2)-O(7)	2.425(6)
Cd(2)-O(1)#1	2.500(5)
Cd(3)-O(17)	2.215(6)
Cd(3)-O(16)	2.315(6)
Cd(3)-O(12)	2.381(5)
Cd(3)-O(14)	2.385(5)
Cd(3)-O(13)	2.386(6)
Cd(3)-O(15)	2.397(6)
Cd(3)-O(3)#1	2.575(5)

Symmetry transformations used to generate equivalent atoms: #1 x-1, y,z

Table S3. Important observed hydrogen bond interactions in compound **1**.

D – H … A	**D – H (Å)**	**H … A (Å)**	**D … A (Å)**	**D – H … A (º)**
O(5) --H(5A) ..O(7)	0.85	1.92	2.694(1)	150
O(5) --H(5B) ..O(14)	0.85	1.80	2.638(1)	169
C(3) --H(3) ..O(15)	0.93	2.36	3.172(1)	145
C(4) --H(4) ..O(16)	0.93	2.58	3.450(1)	156
C(14) --H(14) ..O(10)	0.93	2.55	3.347(1)	144
C(15) --H(15) ..O(8)	0.93	2.50	3.315(1)	147
C(21) --H(21) ..O(14)	0.93	2.57	3.408(1)	150
C(23) --H(23B) ..O(6)	0.96	2.57	3.39(2)	143
C(27) --H(27C) ..O(13)	0.96	2.51	3.40(2)	155

Table S4. Selected bond length for compound **2**.

Moiety	**Bond lengths (Å)**
Cd(1)- O(2)#1	2.221(4)
Cd(1)- O(2)	2.221(4)
Cd(1)- O(3)#1	2.320(4)
Cd(1)- O(3)	2.320(4)
Cd(1)- O(1)	2.324(4)
Cd(1)- O(1)#1	2.324(4)
Cd(2)- O(4)	2.185(4)
Cd(2)- O(5)	2.217(4)
Cd(2)- O(6)	2.281(4)
Cd(2)- O(3)	2.377(4)
Cd(2)- O(7)#2	2.516(4)
Cd(2)- O(7)	2.519(4)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z+1; #2 -x,-y+1,-z

Table S5. Characteristic IR bands of compounds **1** and **2**, respectively.

IR BANDS	**Compound 1**	**Compound 2**
ν_S (H_2O)	3460 cm^{-1}	3458 cm^{-1}
ν_S (N – H)	3084 cm^{-1}	3109 cm^{-1}
ν_S (C – H)	2742	2782 cm^{-1}
ν_S (C=O)	1601 cm^{-1}	1593 cm^{-1}
ν_b (C – N)	1370 cm^{-1}	1370 cm^{-1}
ν_b (C-O)	1210-1163 cm^{-1}	1245 cm^{-1}

TOPOS analysis of compound **1**

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1:C15 H12.50 Cd N0 O5

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Topology for Cd1

Atom Cd1 links by bridge ligands and has

Common vertex with					R(A-A)	
Cd 3	0.3140	0.3268	0.1464	(0 0 0)	6.361A	1
Cd 2	0.3049	0.3740	0.3281	(0 0 0)	6.578A	1
Common edge with					R(A-A)	
Cd 2	1.3049	0.3740	0.3281	(1 0 0)	4.387A	2
Cd 3	1.3140	0.3268	0.1464	(1 0 0)	4.554A	2

Topology for Cd2

Atom Cd2 links by bridge ligands and has

Common vertex with					R(A-A)	
Cd 1	0.9178	0.3954	0.2271	(0 0 0)	6.578A	1
Cd 3	0.1860	0.8268	0.3536	(0 0 0)	8.534A	1
Cd 2	0.1951	0.8740	0.1719	(0 0 0)	9.930A	1
Cd 2	0.1951	-0.1260	0.1719	(0-1 0)	9.930A	1
Cd 2	1.3049	0.3740	0.3281	(1 0 0)	10.013A	1
Cd 2	-0.6951	0.3740	0.3281	(-1 0 0)	10.013A	1
Cd 3	0.1860	-0.1732	0.3536	(0-1 0)	10.272A	1
Common edge with					R(A-A)	
Cd 1	-0.0822	0.3954	0.2271	(-1 0 0)	4.387A	2
Common face with					R(A-A)	
Cd 3	0.3140	0.3268	0.1464	(0 0 0)	3.960A	3

Topology for Cd3

Atom Cd3 links by bridge ligands and has

Common vertex with					R(A-A)	
Cd 1	0.9178	0.3954	0.2271	(0 0 0)	6.361A	1
Cd 2	0.1951	-0.1260	0.1719	(0-1 0)	8.534A	1
Cd 3	-0.6860	0.3268	0.1464	(-1 0 0)	10.013A	1
Cd 3	1.3140	0.3268	0.1464	(1 0 0)	10.013A	1
Cd 2	0.1951	0.8740	0.1719	(0 0 0)	10.272A	1
Cd 3	0.1860	0.8268	0.3536	(0 0 0)	10.393A	1
Cd 3	0.1860	-0.1732	0.3536	(0-1 0)	10.393A	1
Common edge with					R(A-A)	
Cd 1	-0.0822	0.3954	0.2271	(-1 0 0)	4.554A	2
Common face with					R(A-A)	
Cd 2	0.3049	0.3740	0.3281	(0 0 0)	3.960A	3

Structural group analysis

Structural group No 1

Structure consists of layers (0 0 1) with Cd3O3C

Coordination sequences

Cd1:	1	2	3	4	5	6	7	8	9	10
Num	4	14	28	40	52	64	76	88	100	112
Cum	5	19	47	87	139	203	279	367	467	579

Cd2: 1 2 3 4 5 6 7 8 9 10

Num 9 22 34 46 58 70 82 94 106 118

Cum 10 32 66 112 170 240 322 416 522 640

Cd3: 1 2 3 4 5 6 7 8 9 10

Num 9 22 34 46 58 70 82 94 106 118

Cum 10 32 66 112 170 240 322 416 522 640

TD10=619

Vertex symbols for selected sub lattice

Cd1 Point symbol:{$3^4.4^2$}

Extended point symbol:[3.3.3.3.4(2).4(2)]

Cd2 Point symbol:{$3^{10}.4^{23}.5^2.6$}

Extended point symbol:[3.3.3.3.3.3.3.3.3.3.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4(2).4(2).5(2).5(2).6(8)]

Cd3 Point symbol:{$3^{10}.4^{23}.5^2.6$}

Extended point symbol:[3.3.3.3.3.3.3.3.3.3.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4(2).4(2).5(2).5(2).6(8)]

Point symbol for net: {$3^{10}.4^{23}.5^2.6$}2{$3^4.4^2$}

4,9-c net with stoichiometry (4-c)(9-c)2; 2-nodal net

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TOPOS analysis of compound **2**

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1:C20 H15 Cd N0 O6

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Topology for Cd1

Atom Cd1 links by bridge ligands and has

Common vertex with					R(A-A)	
Cd 2	0.0142	-0.6588	0.1868	(0-1 0)	8.821A	1
Cd 2	-0.0142	0.6588	0.8132	(0 1 1)	8.821A	1
Cd 2	-1.0142	-0.3412	0.8132	(-1 0 1)	9.678A	1
Cd 2	1.0142	0.3412	0.1868	(1 0 0)	9.678A	1
Cd 2	-0.0142	-0.3412	-0.1868	(0 0 0)	9.800A	1
Cd 2	0.0142	0.3412	1.1868	(0 0 1)	9.800A	1
Cd 2	0.9858	-0.3412	0.8132	(1 0 1)	10.560A	1
Cd 2	-0.9858	0.3412	0.1868	(-1 0 0)	10.560A	1
Common edge with					R(A-A)	
Cd 1	1.0000	0.0000	0.5000	(1 0 0)	9.433A	2
Cd 1	-1.0000	0.0000	0.5000	(-1 0 0)	9.433A	2
Common face with					R(A-A)	
Cd 2	-0.0142	-0.3412	0.8132	(0 0 1)	3.689A	4
Cd 2	0.0142	0.3412	0.1868	(0 0 0)	3.689A	4

Topology for Cd2

Atom Cd2 links by bridge ligands and has

Common vertex with					R(A-A)	
Cd 1	0.0000	1.0000	0.5000	(0 1 0)	8.821A	1
Cd 2	1.0142	0.3412	0.1868	(1 0 0)	9.433A	1

Cd 2 -0.9858 0.3412 0.1868 (-1 0 0) 9.433A 1

Cd 1 -1.0000 0.0000 0.5000 (-1 0 0) 9.678A 1

Cd 1 0.0000 0.0000 -0.5000 (0 0-1) 9.800A 1

Cd 2 0.0142 1.3412 0.1868 (0 1 0) 10.195A 1

Cd 2 0.0142 -0.6588 0.1868 (0-1 0) 10.195A 1

Cd 1 1.0000 0.0000 0.5000 (1 0 0) 10.560A 1

Common edge with R(A-A)

Cd 2 -0.0142 0.6588 -0.1868 (0 1 0) 4.089A 2

Cd 2 -0.0142 -0.3412 -0.1868 (0 0 0) 9.636A 2

Common face with R(A-A)

Cd 1 0.0000 0.0000 0.5000 (0 0 0) 3.689A 4

Structural group analysis

Structural group No 1

Structure consists of 3D framework with Cd3O2

Coordination sequences

Cd1: 1 2 3 4 5 6 7 8 9 10

Num 12 44 102 170 278 380 542 674 894 1052

Cum 13 57 159 329 607 987 1529 2203 3097 4149

Cd2: 1 2 3 4 5 6 7 8 9 10

Num 11 46 95 178 263 398 515 706 851 1102

Cum 12 58 153 331 594 992 1507 2213 3064 4166

TD10=4160

Vertex symbols for selected sub lattice

Cd1 Point symbol: $\{3^{18}.4^{36}.5^{11}.6\}$

Extended point symbol:[3.3.3.3.3.3.3.3.3.3.3.3.3.3.3.3.3.3.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4(2).4(2).4(2).4(2).4(2).4(2).4(2).4(2).4(2).4(2).4(2).4(2).4(2).4(2).4(2).4(2).4(3).4(3).4(3).4(3).5(2).5(2).5(2).5(2).5(2).5(3).5(3).5(3).5(3).5(6).5(6).6(16)]

Cd2 Point symbol:{3^15.4^33.5^7}

Extended point symbol:[3.3.3.3.3.3.3.3.3.3.3.3.3.3.3.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4(2).4(2).4(2).4(2).4(2).4(2).4(2).4(2).4(2).4(2).4(2).4(2).4(2).4(3).4(3).5.5(2).5(4).5(4).5(6).5(6).5(8)]

Point symbol for net: $\{3^{15}.4^{33}.5^{7}\}2\{3^{18}.4^{36}.5^{11}.6\}$

11,12-c net with stoichiometry (11-c)2(12-c); 2-nodal net

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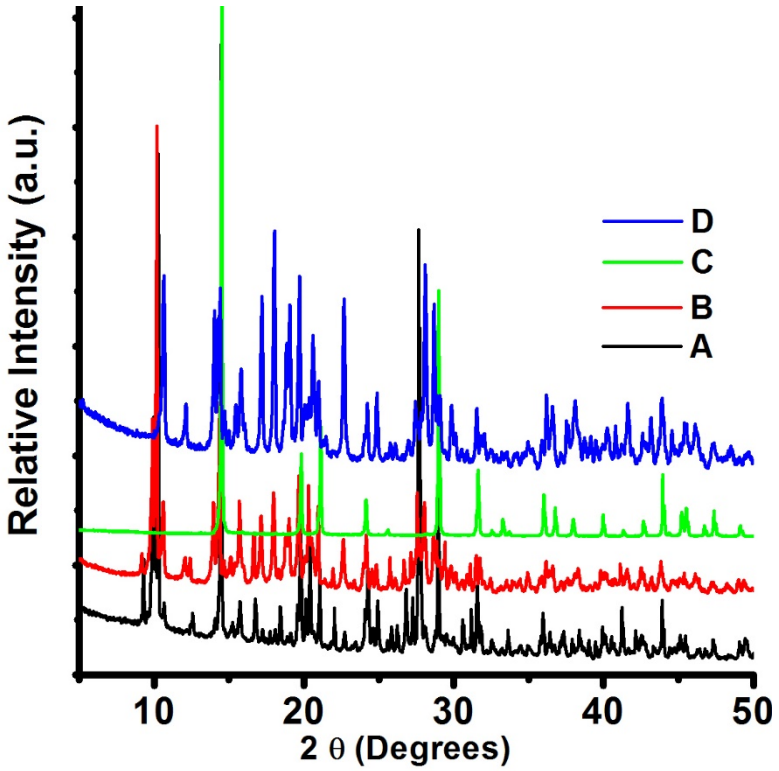
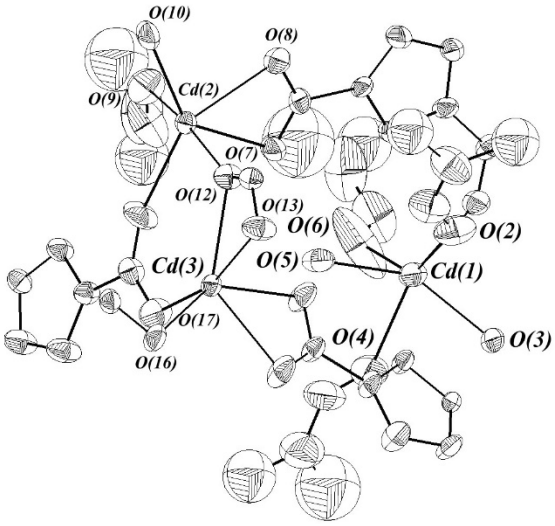


Fig. S1 PXRD pattern of different crystalline materials synthesized with different volume ratios of water in DMF-water mixed solvents: (A) few drops, (B) 25 vol %, (C) 50 vol %, (D) 75 vol %.

(a)



(b)

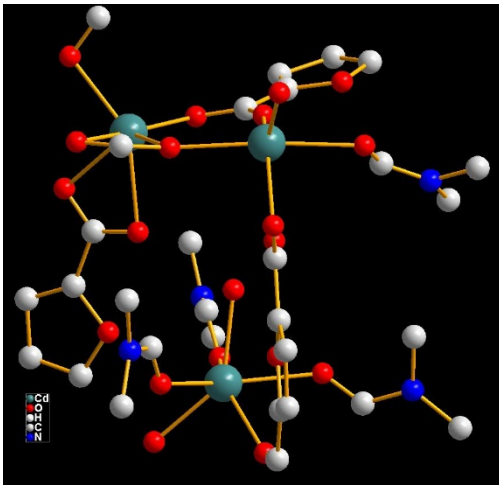


Fig. S2 (a) ORTEP diagram of **1** at 50% probability. For clarity we have shown only metal coordination. (b) Ball-stick model of the asymmetric unit of compound **1**.

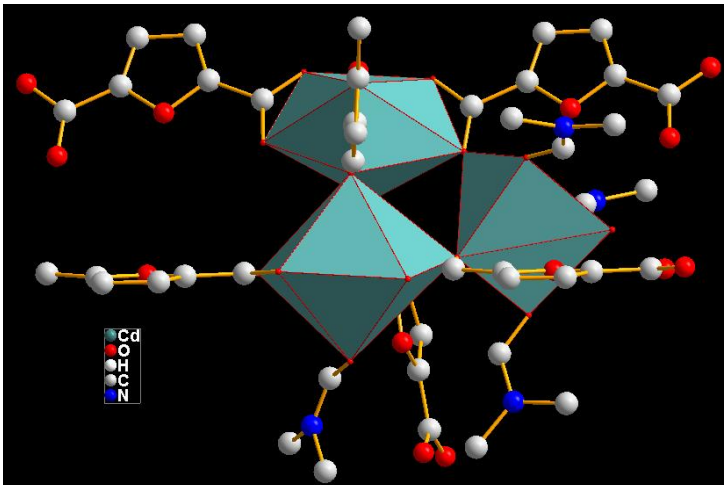


Fig. S3 Six connected $Cd_3(RCOO)_6$ node of compound **1**.

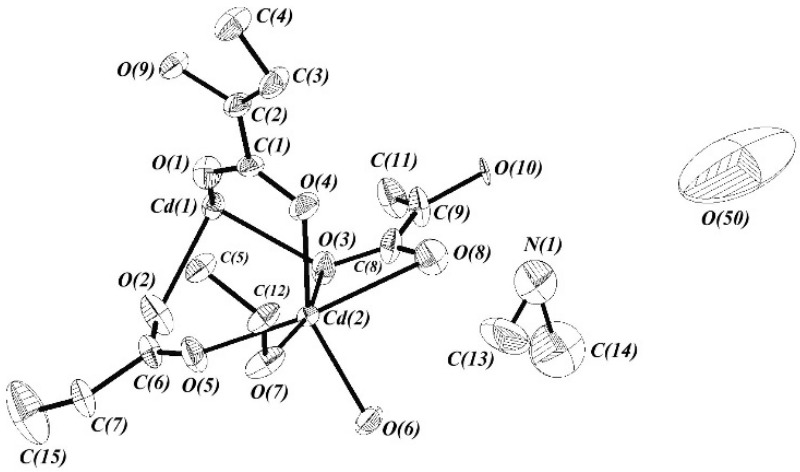


Fig. S4 ORTEP diagram of **2** at 50% probability.

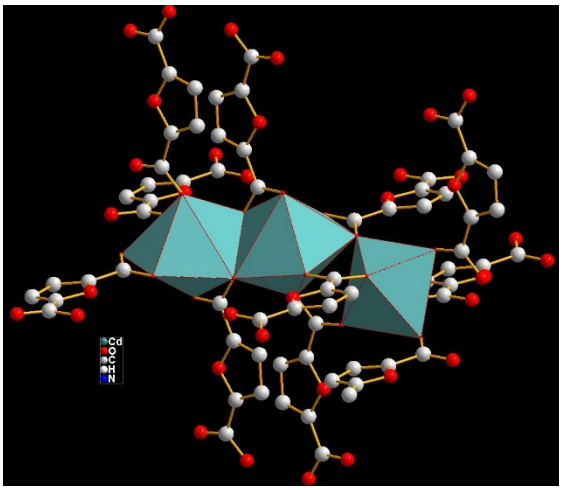


Fig. S5 Eleven connected $Cd_3(RCOO)_{11}$ node of compound **2**.

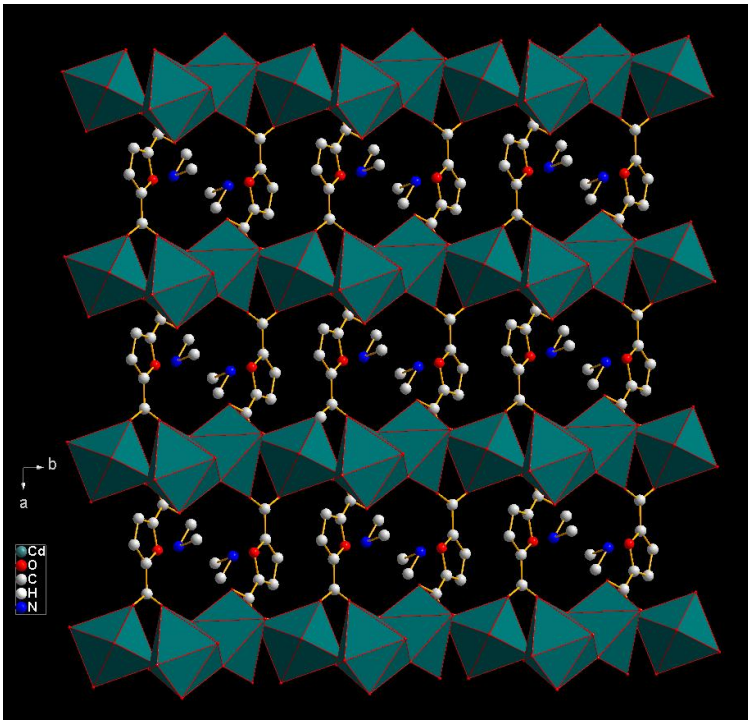


Fig. S6 Three-dimensional structure of **2** along ab plane, which shown that hydrophilic channels contain dimethylammonium cation.

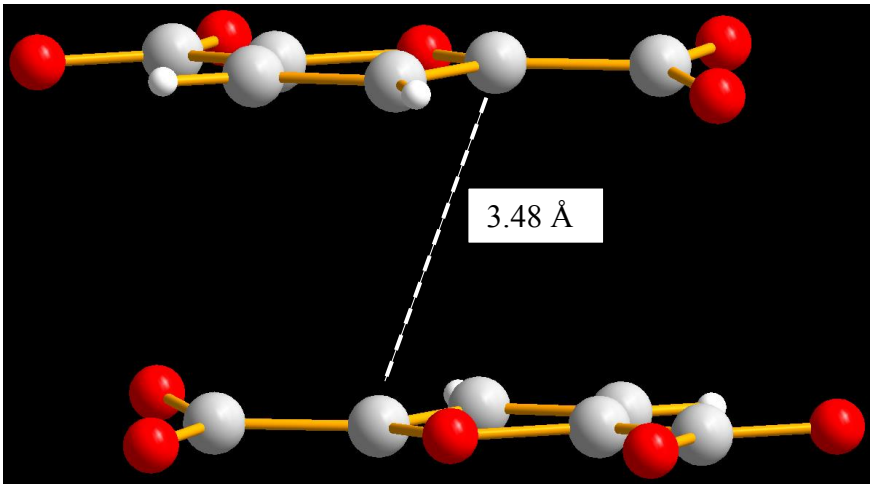
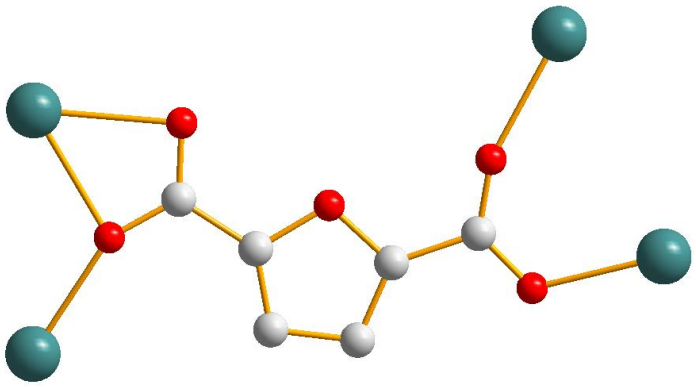
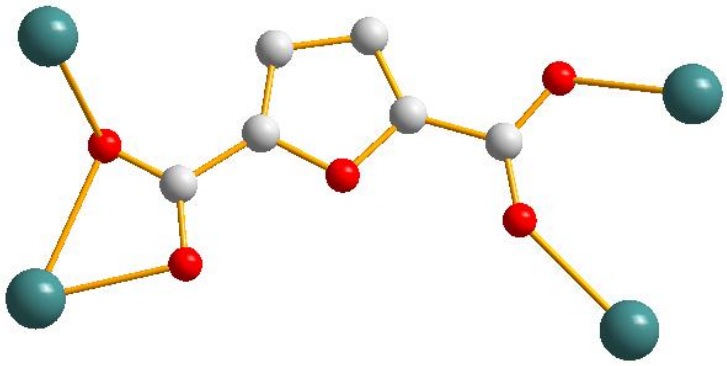


Fig. S7 Possible π-π stacking arrangement of furan rings in compound **2**.

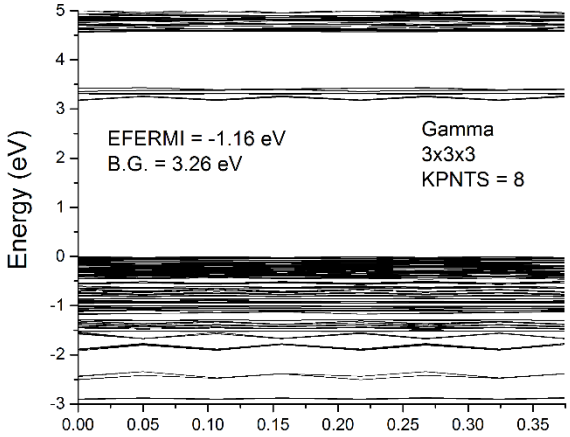


(a)

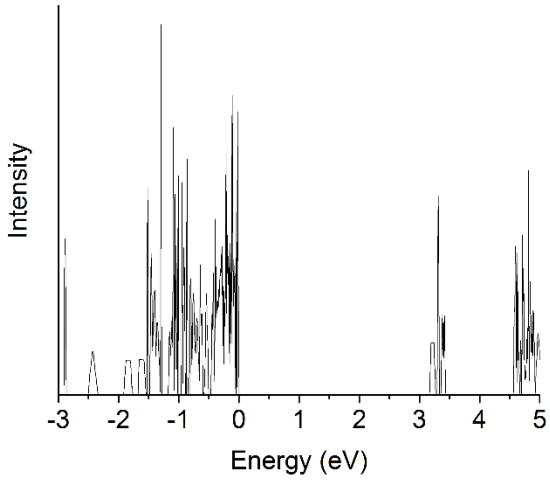


(b)

Fig. S8 Binding mode of FDC ligand in (a) **1** and (b) **2**, respectively.

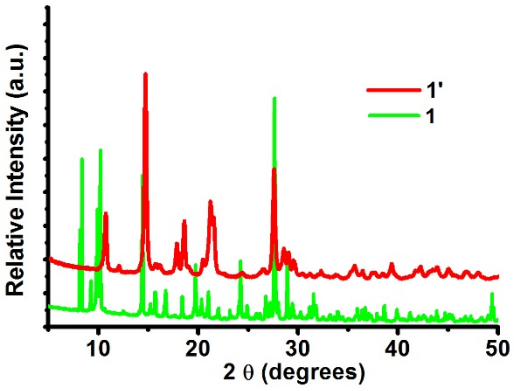


(a)

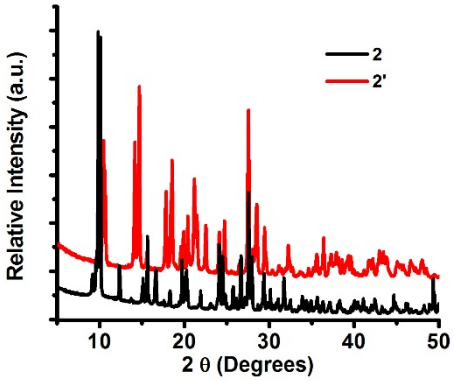


(b)

Fig. S9 (a) band structure of **1** (b) density of states of **1**.

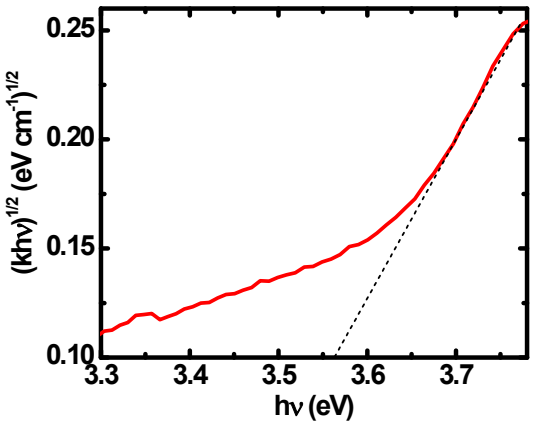


(a)

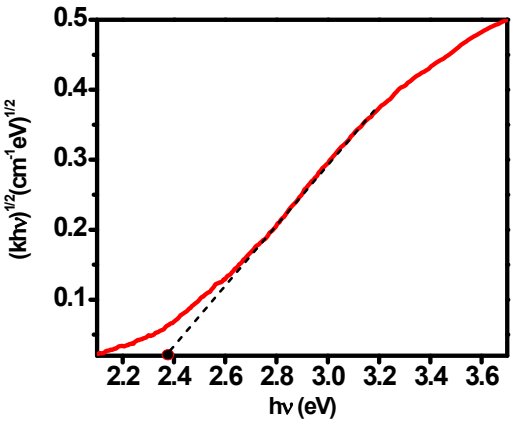


(b)

Fig. S10 PXRD patterns of (a) **1** and **1'**, and (b) **2** and **2'**.

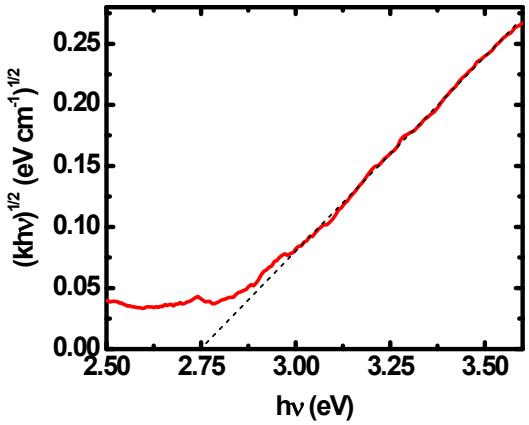


(a)

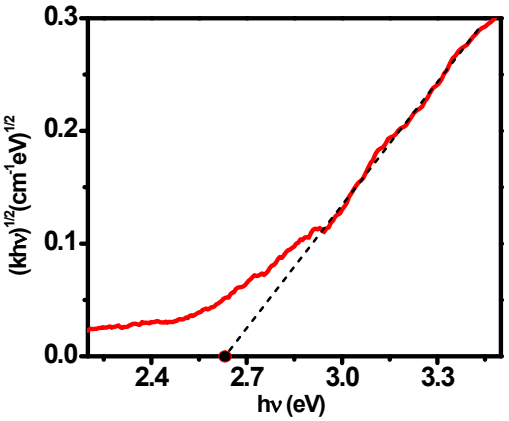


(b)

Fig. S11 Tauc plots showing the band gap energies determined from the optical absorption spectra (see text) of compounds (a) **1** and (b) **1'**, respectively.

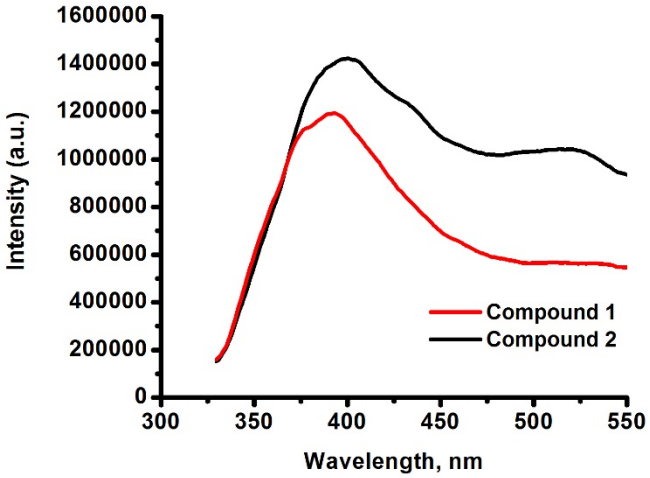


(a)

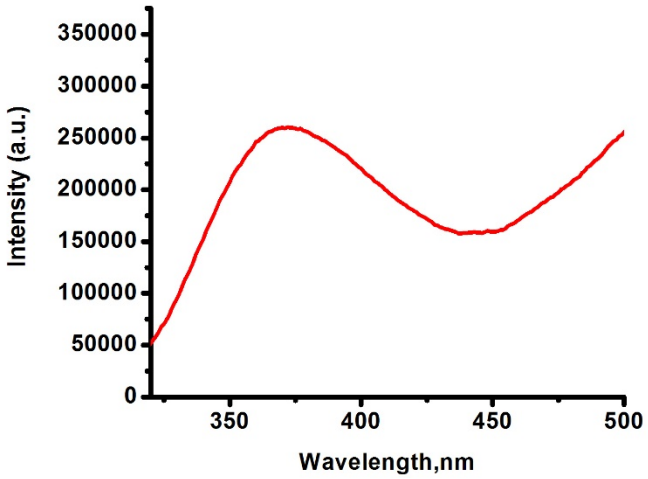


(b)

Fig. S12 Tauc plots showing the band gap energies determined from the optical absorption spectra (see text) of compounds (a) **2** and (b) **2'**, respectively.

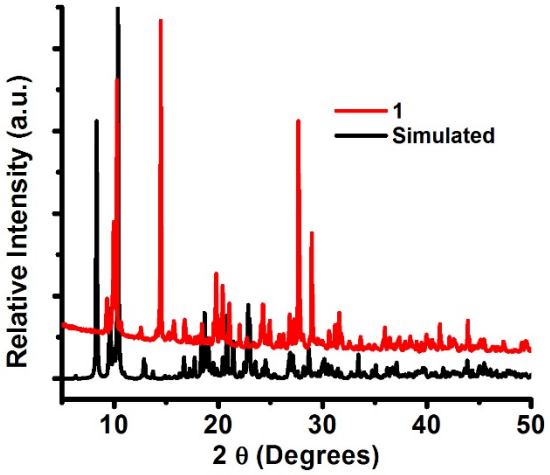


(a)

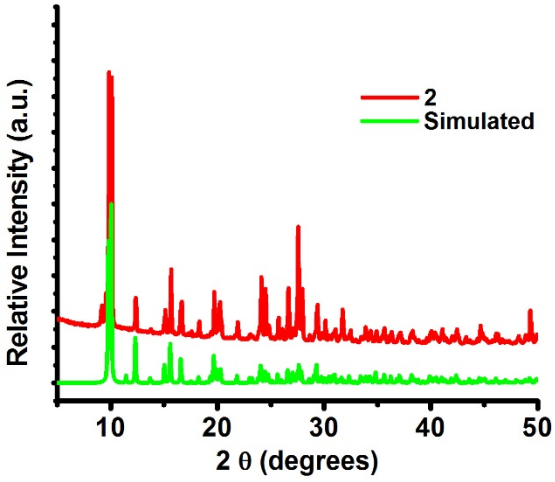


(b)

Fig. S13 The emission spectra for (a) compounds **1** and **2**, respectively, (b) free FDC ligand.



(a)



(b)

Fig. S14 PXRD patterns of experimental and simulated (a) **1** and (b) **2**. Compound **1** losses solvent at room temperature and changes structure as found in PXRD.

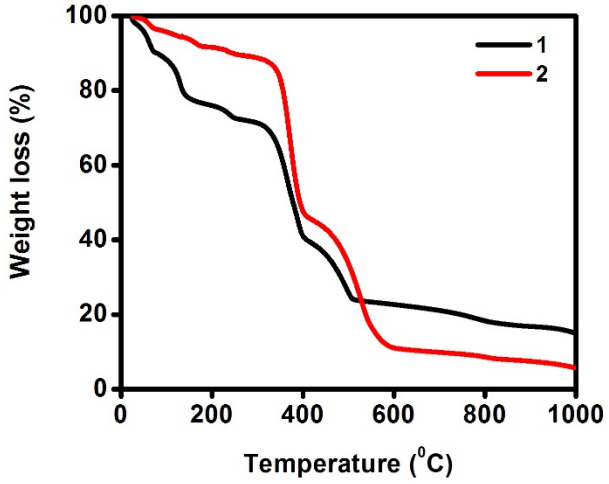
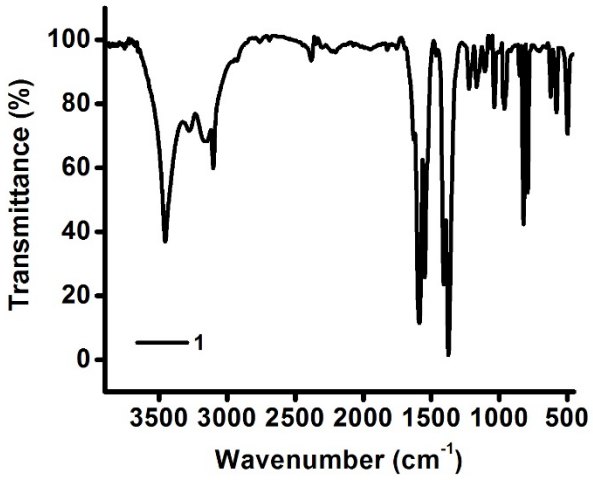
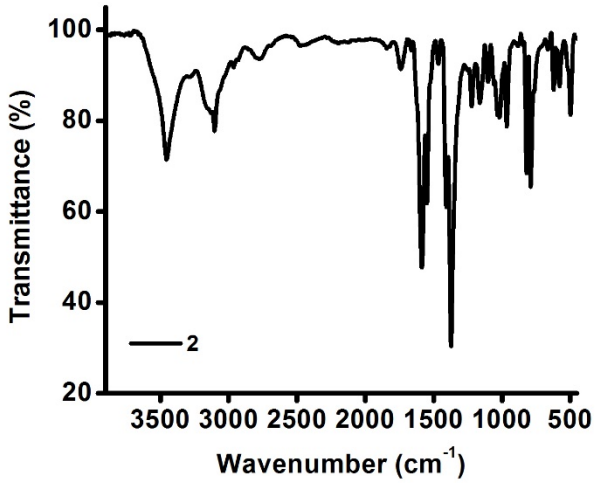


Fig. S15 Thermogravimetric analysis plot of compounds **1** and **2**, respectively.

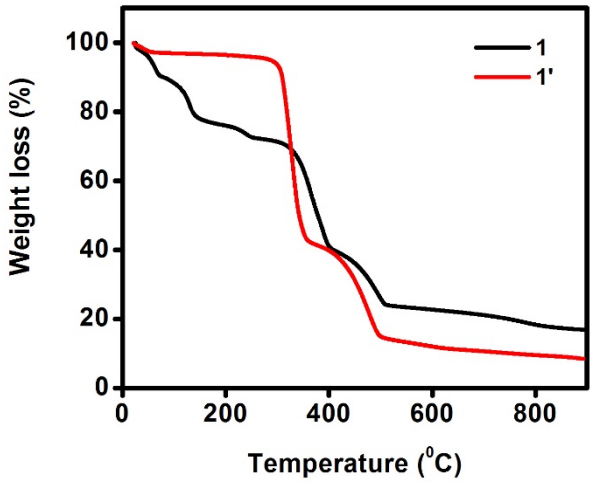


(a)

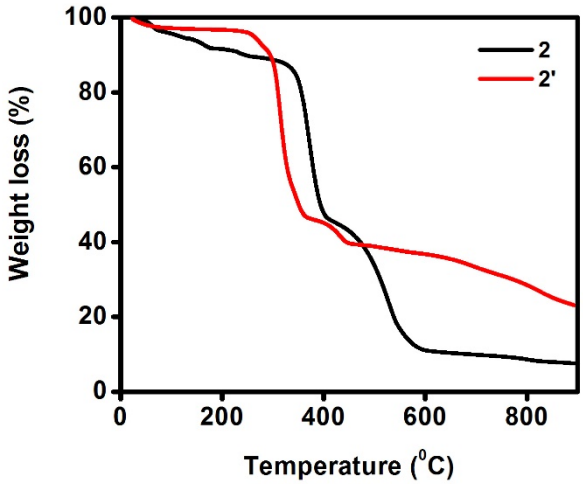


(b)

Fig. S16 The characteristics IR peaks of compounds (a) **1** and (b) **2**, respectively.



(a)



(b)

Fig. S17 TGA plots for (a) **1** and **1'**, and (b) **2** and **2'**.