Supplementary Information

Syntheses, Topological Analyses, and NLO-Active Properties of New Cd(II)/M(II) (M = Ca, Sr) Metal-Organic Frameworks Based on R-Isophthalic Acids (R = H, OH, and *t*-Bu)

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Tables S1–S4 Selected bond distances (Å) and angles (°) for compounds **1**–**4**

Table S1 Selected bond distances (Å) and angles (°) for compound **1**

Cd1—O7^{i}	2.187 (3)	Ca1—O8^{i}	2.293 (3)
Cd1—O6^{ii}	2.285 (3)	Ca1—O9	2.302 (3)
Cd1—O1^{iii}	2.393 (3)	Ca1—O10	2.321 (3)
Cd1—O4	2.403 (3)	Ca1—O5	2.332 (3)
Cd1—O2^{iii}	2.440 (2)	Ca1—O4	2.333 (3)
Cd1—O5^{ii}	2.462 (3)	Ca1—O1^{iii}	2.348 (3)
Cd1—O3	2.491 (3)	O4—Cd1—O3	52.83 (12)
O7^{i}—Cd1—O6^{ii}	148.23 (12)	O2^{iii}—Cd1—O3	166.90 (10)
O7^{i}—Cd1—O1^{iii}	103.40 (11)	O5^{ii}—Cd1—O3	85.73 (12)
O6^{ii}—Cd1—O1^{iii}	101.23 (10)	O8^{i}—Ca1—O9	88.00 (13)
O7^{i}—Cd1—O4	95.46 (10)	O8^{i}—Ca1—O10	85.84 (12)
O6^{ii}—Cd1—O4	110.70 (10)	O9—Ca1—O10	109.54 (12)
O1^{iii}—Cd1—O4	73.33 (10)	O8^{i}—Ca1—O5	172.16 (11)
O7^{i}—Cd1—O2^{iii}	93.76 (10)	O9—Ca1—O5	96.59 (12)
O6^{ii}—Cd1—O2^{iii}	84.75 (11)	O10—Ca1—O5	98.54 (11)

O1^{iii}—Cd1—O2^{iii}	53.94 (11)	O8^{i}—Ca1—O4	81.86 (11)
O4—Cd1—O2^{iii}	127.17 (11)	O9—Ca1—O4	85.14 (11)
O7^{i}—Cd1—O5^{ii}	93.73 (10)	O10—Ca1—O4	160.53 (12)
O6^{ii}—Cd1—O5^{ii}	54.75 (9)	O5—Ca1—O4	92.16 (10)
O1^{iii}—Cd1—O5^{ii}	142.53 (9)	O8^{i}—Ca1—O1^{iii}	86.34 (11)
O4—Cd1—O5^{ii}	138.47 (9)	O9—Ca1—O1^{iii}	160.36 (12)
O2^{iii}—Cd1—O5^{ii}	92.38 (11)	O10—Ca1—O1^{iii}	88.79 (11)
O7^{i}—Cd1—O3	99.29 (11)	O5—Ca1—O1^{iii}	87.25 (10)
O6^{ii}—Cd1—O3	83.58 (11)	O4—Ca1—O1^{iii}	75.45 (11)
O1^{iii}—Cd1—O3	122.98 (13)		

Symmetry codes: (i) $-x+1/2, y+1/2, z-1/2$; (ii) $x, y, z-1$; (iii) $x-1/2, -y+1/2, z$; (iv) $x+1/2, -y+1/2, z$; (v) $x, y, z+1$; (vi) $-x+1/2, y-1/2, z+1/2$.

Table S2 Selected bond distances (Å) and angles (°) for compound **2**

Cd1—O3^{i}	2.305 (4)	Sr1—O2^{v}	2.640 (4)
Cd1—O1	2.355 (4)	Sr1—O3	2.679 (4)
Cd1—O2	2.359 (4)	Sr1—O9^{vi}	2.688 (5)
Cd1—O4^{i}	2.621 (4)	Sr1—O7	2.700 (5)
Sr1—O4^{iv}	2.515 (4)	Sr1—O8	2.709 (4)
Sr1—O6	2.550 (5)	Sr1—O8^{vi}	2.830 (4)
Sr1—O5	2.574 (5)	O6—Sr1—O3	76.32 (17)
O3^{i}—Cd1—O3^{ii}	107.1 (2)	O5—Sr1—O3	139.69 (14)
O3^{i}—Cd1—O1	132.14 (14)	O2^{v}—Sr1—O3	66.00 (12)
O3^{ii}—Cd1—O1	99.35 (16)	O4^{iv}—Sr1—O9^{vi}	131.48 (13)
O1—Cd1—O1^{iii}	90.9 (3)	O6—Sr1—O9^{vi}	78.0 (2)
O3^{i}—Cd1—O2	76.80 (13)	O5—Sr1—O9^{vi}	77.37 (17)
O3^{ii}—Cd1—O2	126.23 (14)	O2^{v}—Sr1—O9^{vi}	141.26 (14)
O1—Cd1—O2	55.44 (13)	O3—Sr1—O9^{vi}	140.58 (14)
O1—Cd1—O2^{iii}	97.99 (15)	O4^{iv}—Sr1—O7	148.16 (15)

O2—Cd1—O2^{iii}	144.46 (19)	O6—Sr1—O7	78.18 (19)
O3^{i}—Cd1—O4^{i}	52.60 (13)	O5—Sr1—O7	120.83 (14)
O1—Cd1—O4^{i}	175.21 (13)	O3—Sr1—O7	78.53 (14)
O2—Cd1—O4^{i}	129.33 (13)	O4^{iv}—Sr1—O8	153.43 (13)
O3^{i}—Cd1—O4^{ii}	77.45 (14)	O6—Sr1—O8	123.15 (18)
O1—Cd1—O4^{ii}	88.70 (17)	O5—Sr1—O8	77.12 (14)
O2—Cd1—O4^{ii}	77.88 (14)	O2^{v}—Sr1—O8	79.12 (12)
O4^{i}—Cd1—O4^{ii}	92.1 (2)	O3—Sr1—O8	101.42 (13)
O4^{iv}—Sr1—O6	81.51 (19)	O9^{vi}—Sr1—O8	69.11 (13)
O4^{iv}—Sr1—O5	90.49 (16)	O7—Sr1—O8	46.89 (13)
O6—Sr1—O5	138.52 (17)	O4^{iv}—Sr1—O8^{vi}	85.74 (13)
O4^{iv}—Sr1—O2^{v}	74.90 (13)	O6—Sr1—O8^{vi}	68.80 (16)
O6—Sr1—O2^{v}	139.86 (17)	O5—Sr1—O8^{vi}	70.07 (13)
O5—Sr1—O2^{v}	74.34 (14)	O2^{v}—Sr1—O8^{vi}	139.08 (12)
O4^{iv}—Sr1—O3	72.98 (13)	O3—Sr1—O8^{vi}	141.39 (13)
O7—Sr1—O8^{vi}	109.00 (14)	O9^{vi}—Sr1—O8^{vi}	45.85 (12)
O8—Sr1—O8^{vi}	111.12 (15)		

Symmetry codes: (i) $-x+1/2, y-1/2, -z-1/4$; (ii) $y-1/2, -x+1/2, z+1/4$; (iii) $y, x, -z$; (iv) $-y+1, -x+1, -z-1/2$; (v) $-x+1/2, y+1/2, -z-1/4$; (vi) $-y+3/2, x+1/2, z-1/4$; (vii) $-y+1/2, x+1/2, z-1/4$; (viii) $y-1/2, -x+3/2, z+1/4$.

Table S3 Selected bond distances (Å) and angles (°) for compound **3**

Cd1—O1	2.301 (3)	Ca1—O4	2.282 (3)
Cd1—O2	2.551 (3)	Ca1—O6W	2.321 (5)
Cd1—O3^{i}	2.261 (3)	Ca1—O1^{vi}	2.363 (3)
O1—Cd1—O1^{iii}	125.66 (13)	O4—Ca1—O4^{v}	92.88 (18)
O3^{i}—Cd1—O2	94.00 (11)	O4—Ca1—O6W	173.08 (17)
O3^{ii}—Cd1—O2	167.72 (12)	O4^{v}—Ca1—O6W	88.11 (18)
O1—Cd1—O2	53.30 (11)	O6W—Ca1—O6W^{v}	91.7 (3)

O3^{i}—Cd1—O2^{iii}	167.72 (12)	O4—Ca1—O1^{vi}	77.81 (10)
O3^{ii}—Cd1—O2^{iii}	94.00 (11)	O6W—Ca1—O1^{vi}	109.03 (16)
O1—Cd1—O2^{iii}	84.16 (11)	O4—Ca1—O1^{vii}	91.04 (11)
O1^{iii}—Cd1—O2^{iii}	53.30 (11)	O6W—Ca1—O1^{vii}	82.47 (17)
O2—Cd1—O2^{iii}	80.03 (14)	O1^{vi}—Ca1—O1^{vii}	163.90 (14)

Symmetry codes: (i) $-y, x+1, -z$; (ii) $x+1/2, -y+1/2, z$; (iii) $y-1/2, x+1/2, -z$; (iv) $y-1/2, -x-1/2, -z-1/2$; (v) $y-1, x+1, -z-1/2$; (vi) $x-1/2, -y+1/2, z$; (vii) $-y-1/2, x+1/2, -z-1/2$; (viii) $y-1, -x, -z$.

Table S4 Selected bond distances (Å) and angles (°) for compound **4**

Cd1—O3	2.312 (6)	O3—Cd1—O5	89.78 (16)
Cd1—O2^{i}	2.331 (6)	O2^{i}—Cd1—O5	114.05 (16)
Cd1—O4	2.404 (6)	O4—Cd1—O5	131.85 (14)
Cd1—O6	2.412 (5)	O6^{ii}—Cd1—O5	122.54 (14)
Cd1—O5	2.509 (5)	O6—Cd1—O5	52.84 (15)
Cd1—O1^{i}	2.584 (6)	O5^{ii}—Cd1—O5	69.70 (19)
Ca1—O1^{i}	2.274 (6)	O3—Cd1—O1^{i}	157.15 (19)
Ca1—O5	2.307 (4)	O2^{i}—Cd1—O1^{i}	52.4 (2)
O3—Cd1—O2^{i}	150.5 (2)	O4—Cd1—O1^{i}	148.2 (2)
O3—Cd1—O4	54.7 (2)	O6—Cd1—O1^{i}	88.65 (11)
O2^{i}—Cd1—O4	95.8 (2)	O5—Cd1—O1^{i}	71.63 (14)
O3—Cd1—O6	90.49 (11)	O1^{iii}—Ca1—O1^{i}	180.0
O2^{i}—Cd1—O6	90.71 (11)	O1^{iii}—Ca1—O5	98.81 (17)
O4—Cd1—O6	92.17 (11)	O1^{i}—Ca1—O5	81.19 (17)
O6^{ii}—Cd1—O6	175.3 (2)	O5^{iv}—Ca1—O5	180.0
O4—Cd1—O5^{ii}	131.85 (14)	O5—Ca1—O5^{v}	103.2 (2)
O6—Cd1—O5^{ii}	122.54 (14)	O5—Ca1—O5^{ii}	76.8 (2)

Symmetry codes: (i) $y, -x, -z$; (ii) $x, y, -z$; (iii) $-y, x-1, z$; (iv) $-x, -y-1, -z$; (v) $-x, -y-1, z$; (vi) $-y, x, z$; (vii) $x, y, -z+1$.

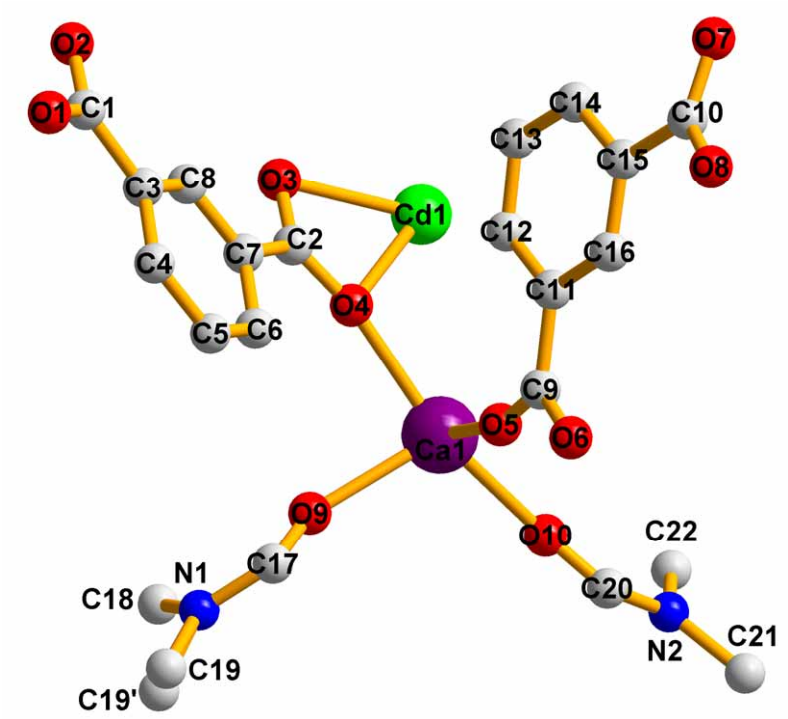


Fig. S1 View of the asymmetric unit of **1**. One methyl C atom (C19 and C19') in one DMF molecule is positional disordered. Hydrogen atoms are omitted for clarity.

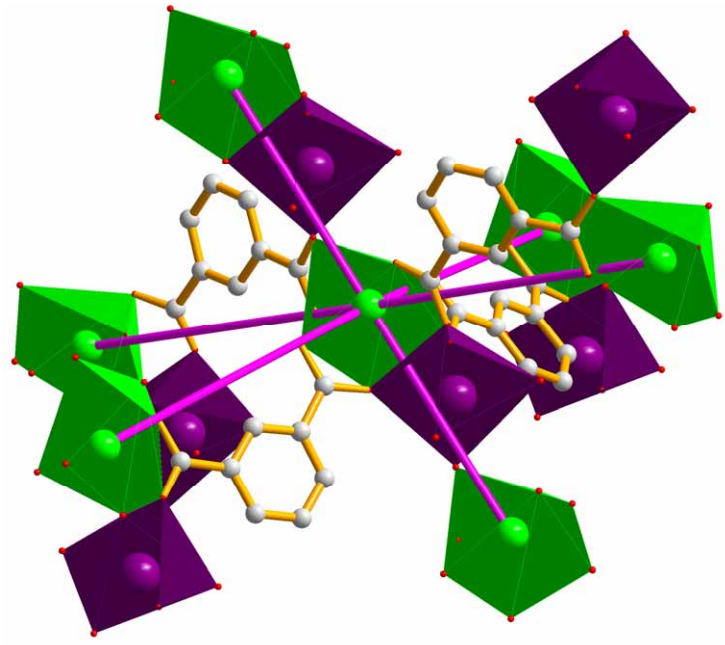


Fig. S2 View of the topological simplification mode of compound **1**.

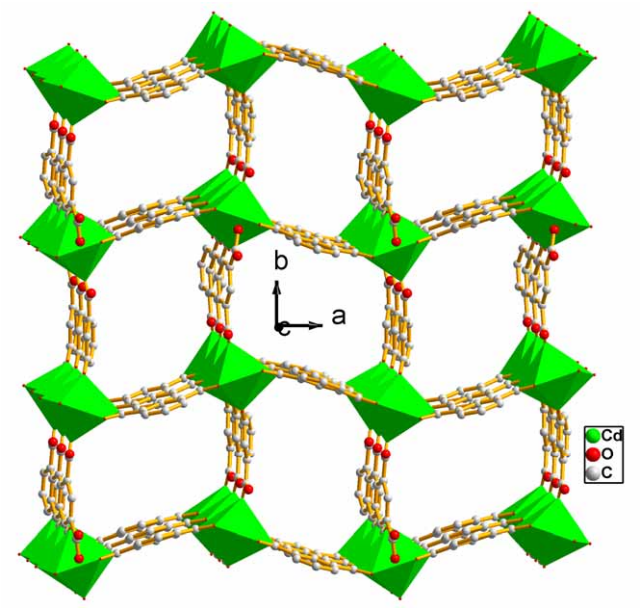


Fig. S3 Polyhedral view of the 3D anionic microporous framework with Ca(II) ions and DMF molecules omitted for **1**. Hydrogen atoms are omitted for clarity.

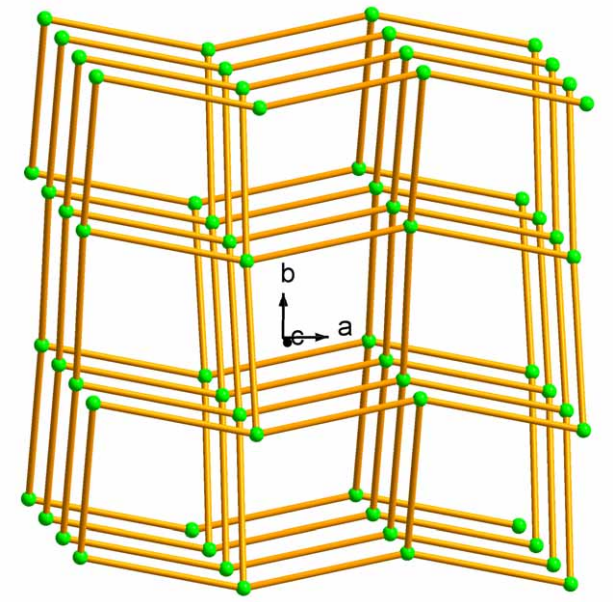


Fig. S4 The **cds** topological net of the Ca(II)-omitted anionic network in **1**.

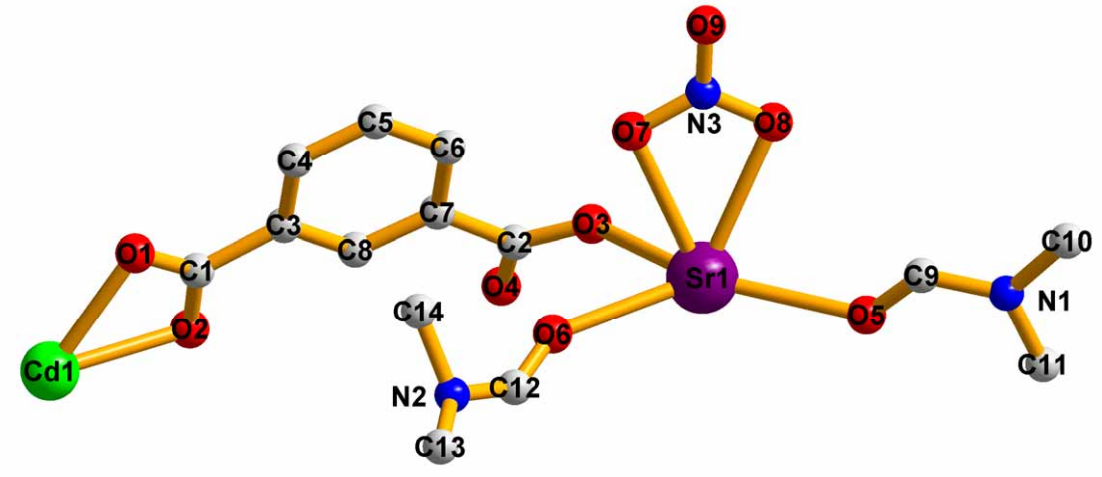


Fig. S5 View of the asymmetric unit of **2**. Hydrogen atoms are omitted for clarity.

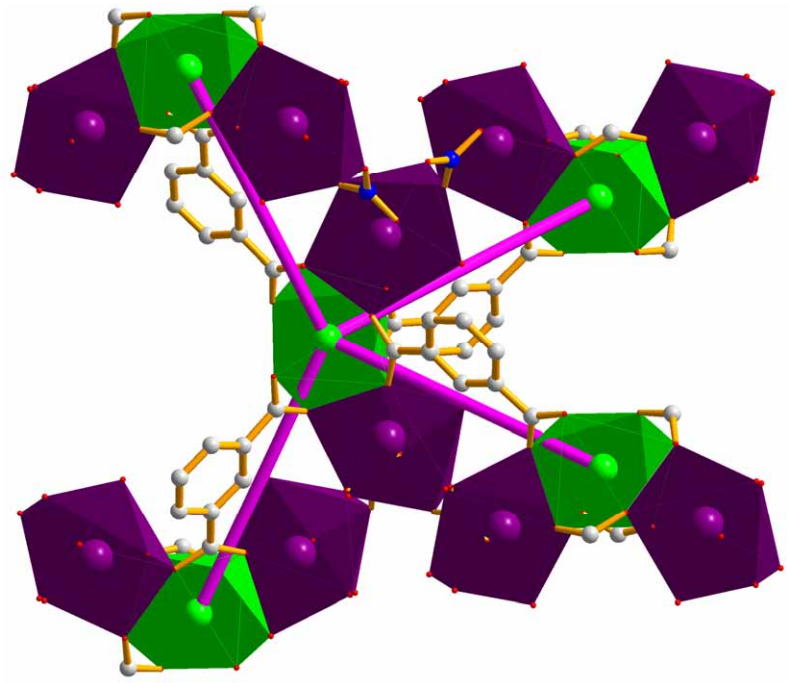


Fig. S6 View of the topological simplification mode of compound **2**.

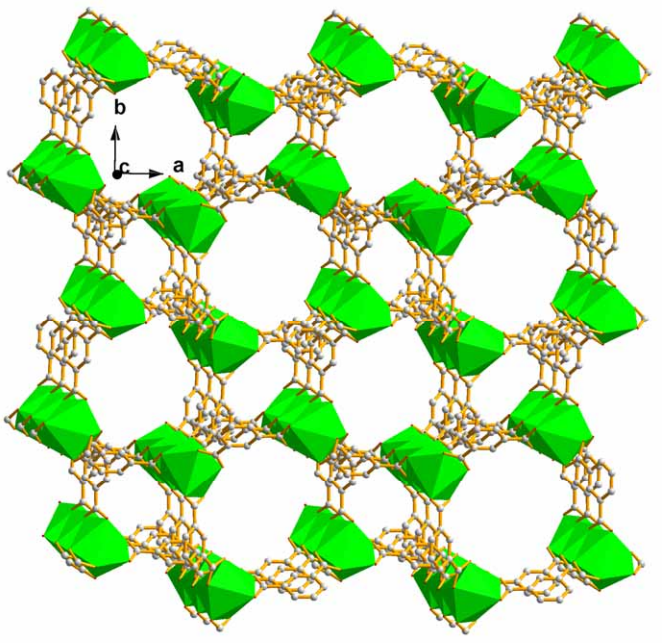


Fig. S7 Polyhedral view of the 3D anionic microporous framework with Sr(II) ions and DMF molecules omitted for **2**. Hydrogen atoms are omitted for clarity.

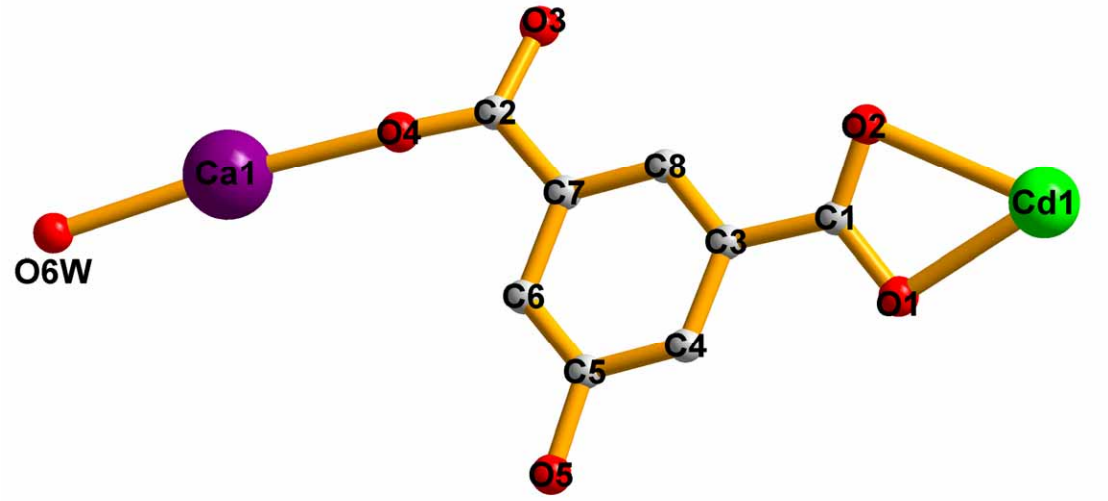


Fig. S8 View of the asymmetric unit of **3**. Hydrogen atoms are omitted for clarity.

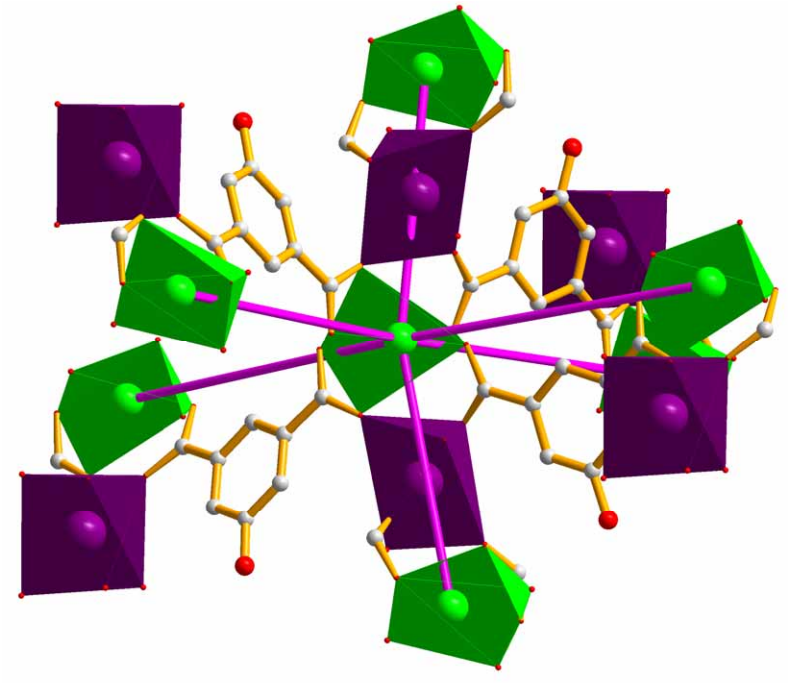


Fig. S9 View of the topological simplification mode of compound **3**.

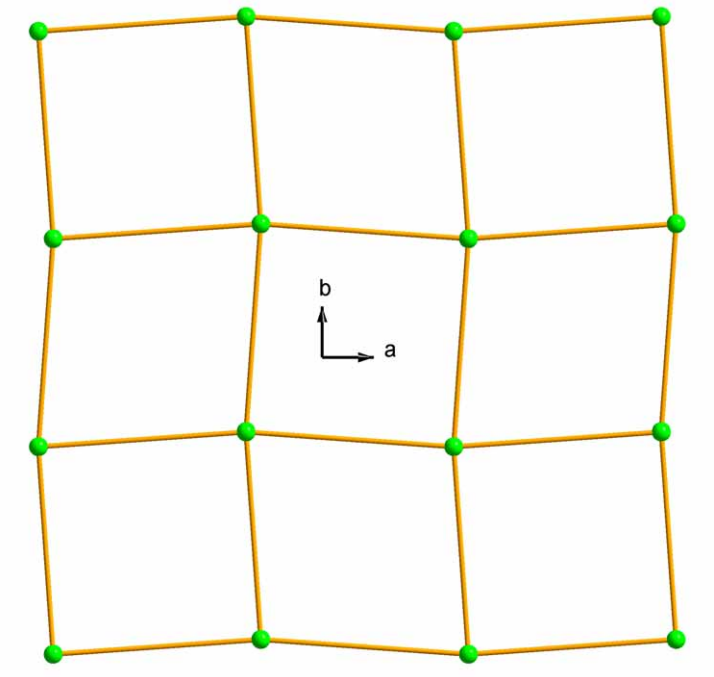


Fig. S10 The (4, 4) topological network of the Ca(II)-omitted 2D anionic layer structure in **3**.

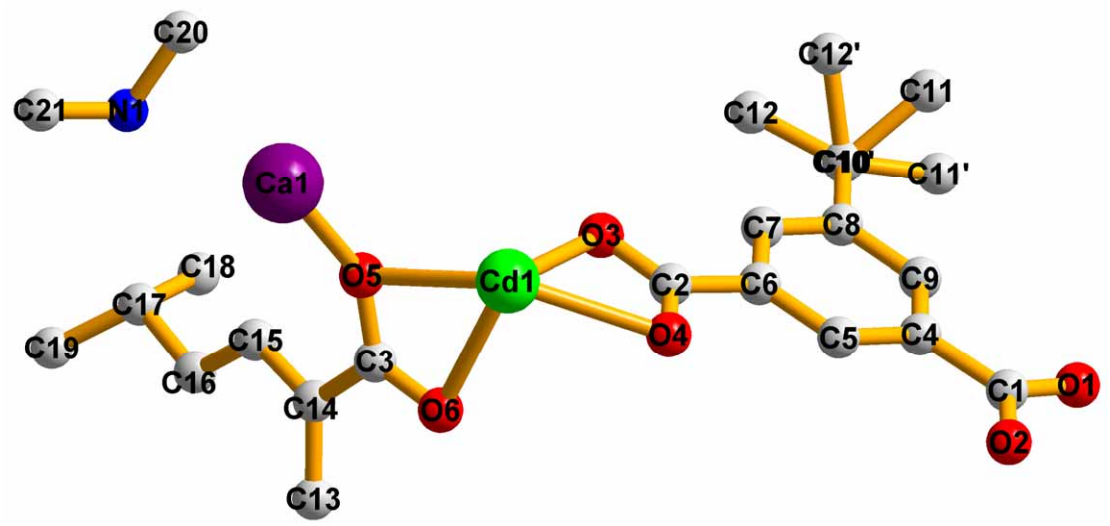


Fig. S11 View of the asymmetric unit of **4**. One $-Bu^t$ group containing C10 and $(Me_2NH_2)^+$ cation are positional disordered. The hydrogen atoms are omitted for clarity.

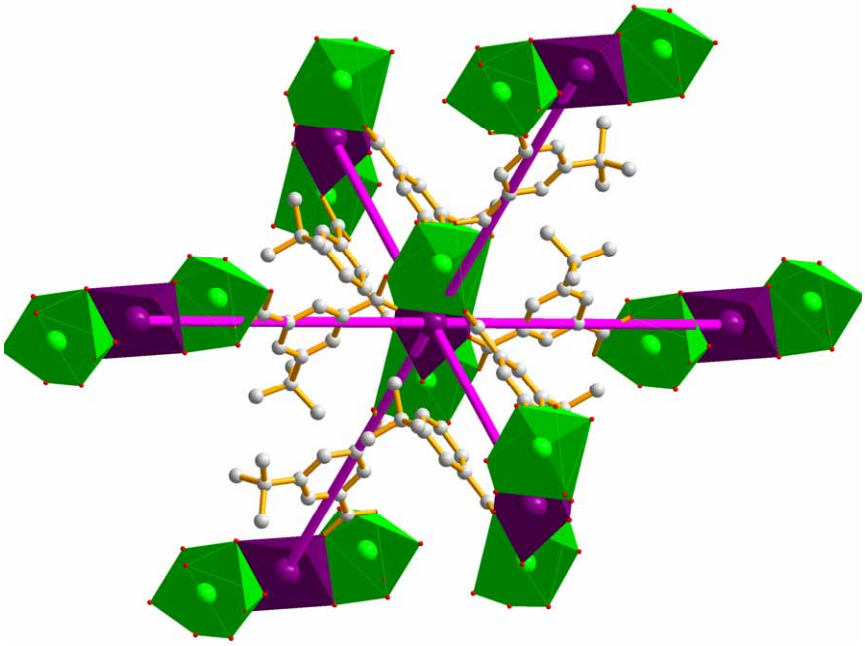
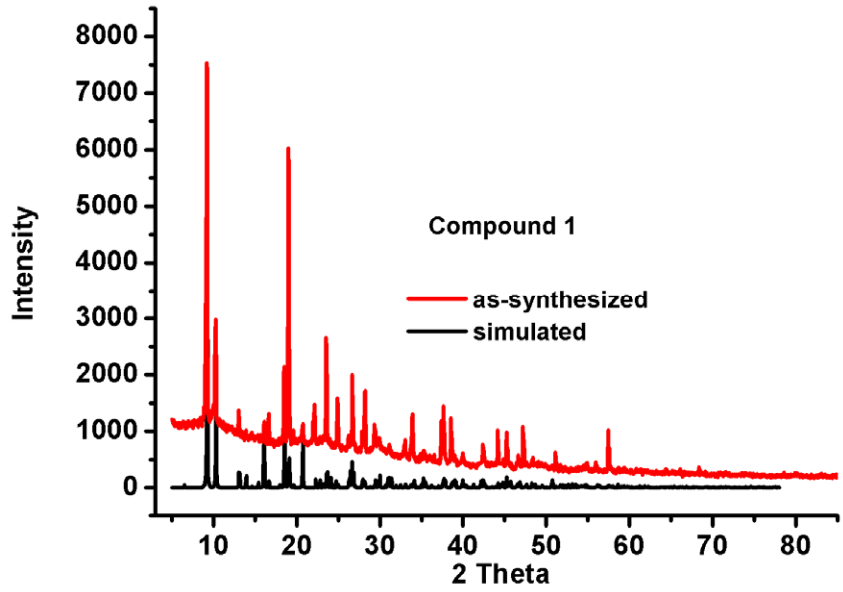
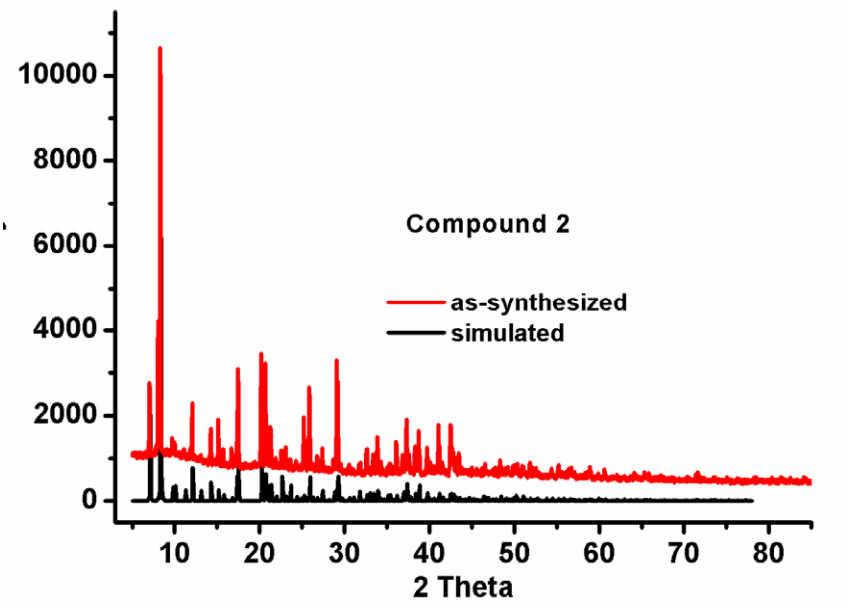


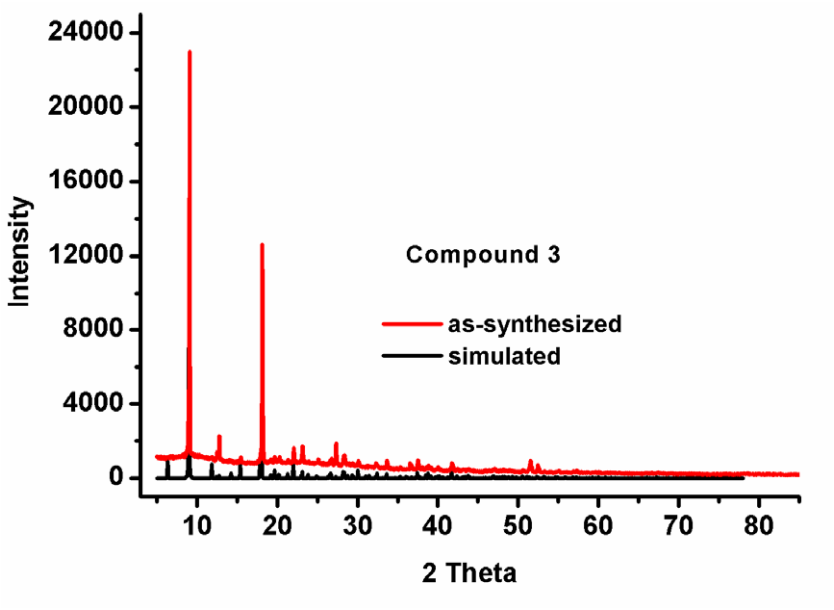
Fig. S12 View of the topological simplification mode of compound **4**.


Intensity
8000
7000
6000
5000
4000
3000
2000
1000
0
Compound 1
as-synthesized
simulated
10
20
30
40
50
60
70
80
2 Theta

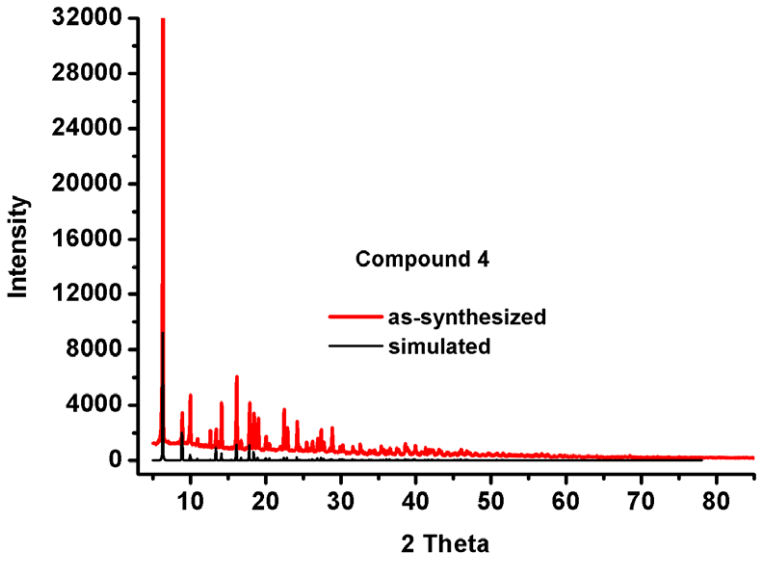
(a)


10000
8000
6000
4000
2000
0
Compound 2
as-synthesized
simulated
10
20
30
40
50
60
70
80
2 Theta

(b)

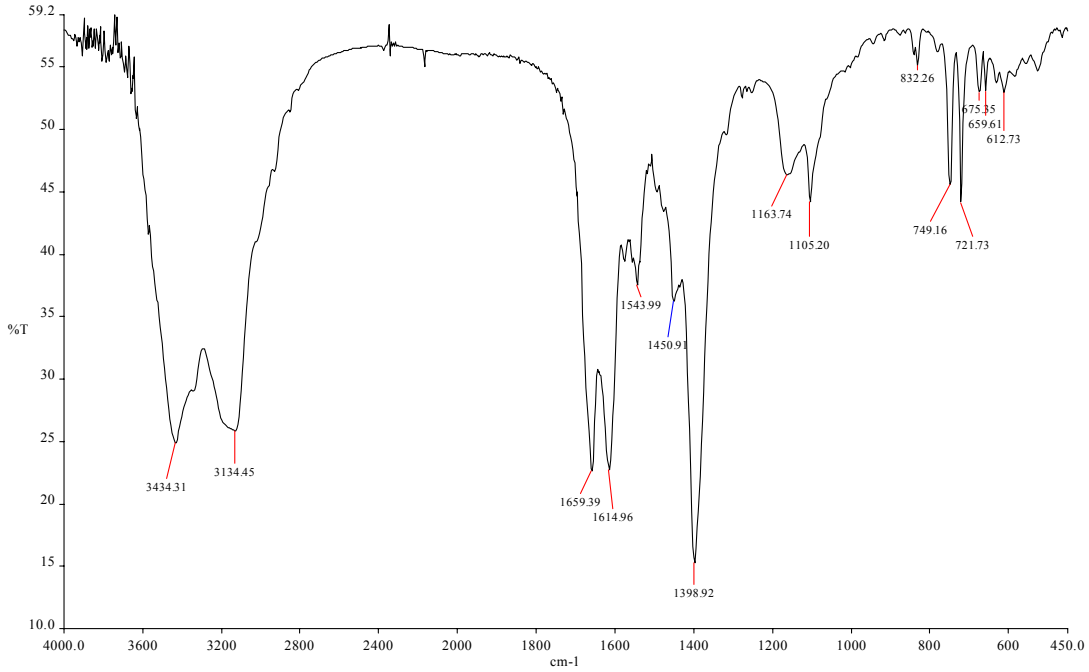


(c)

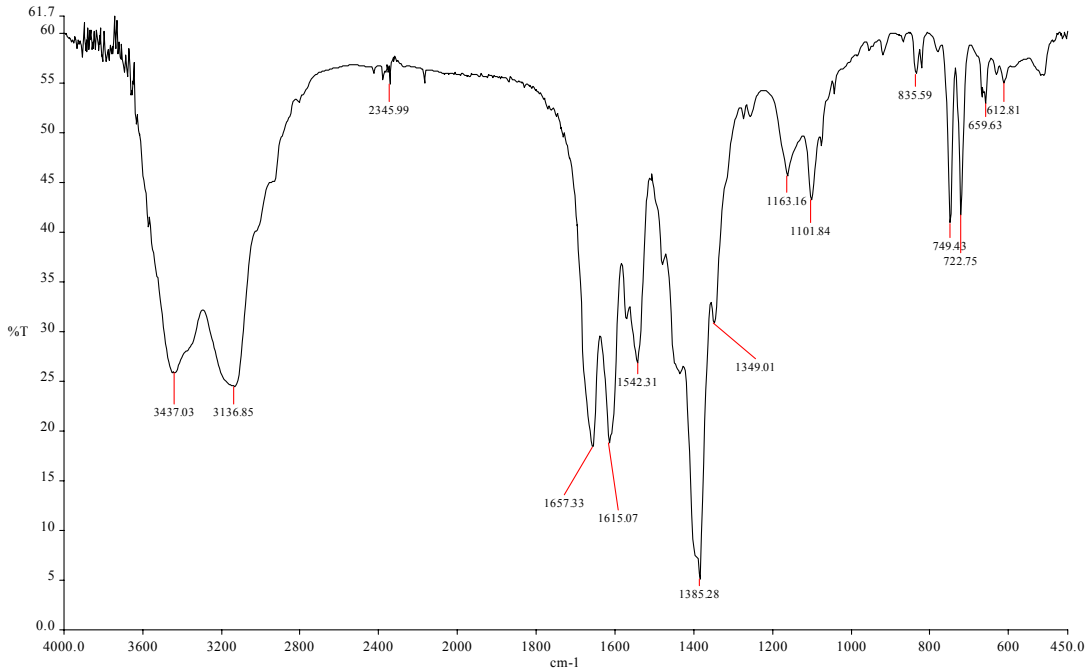


(d)

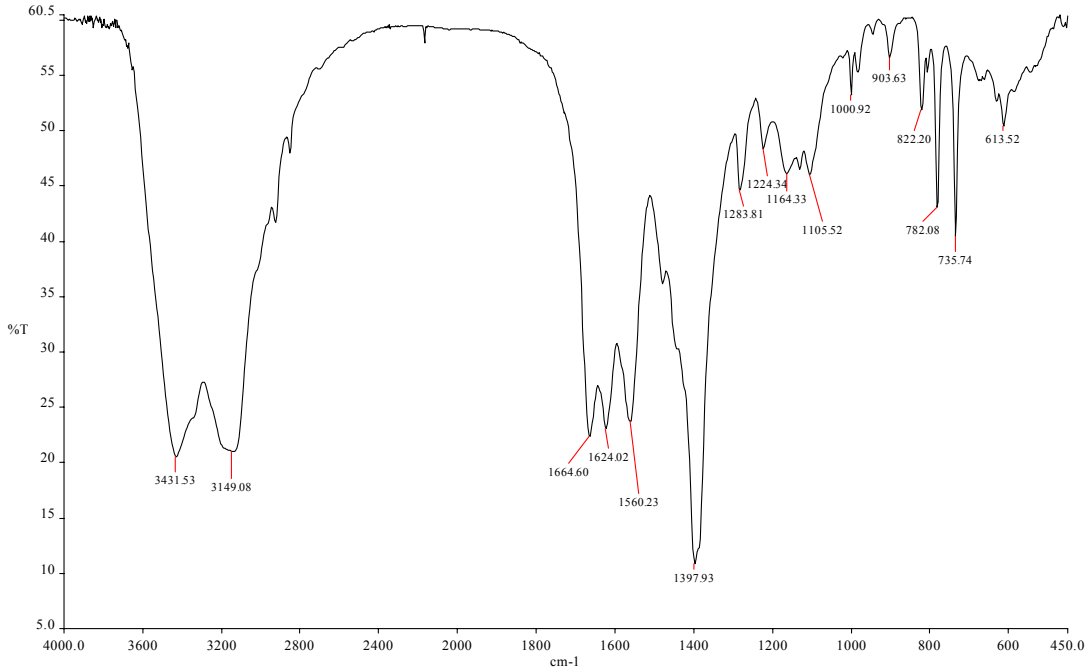
Fig. S13 The power X-ray diffraction patterns for compounds **1–4 (a-d)**



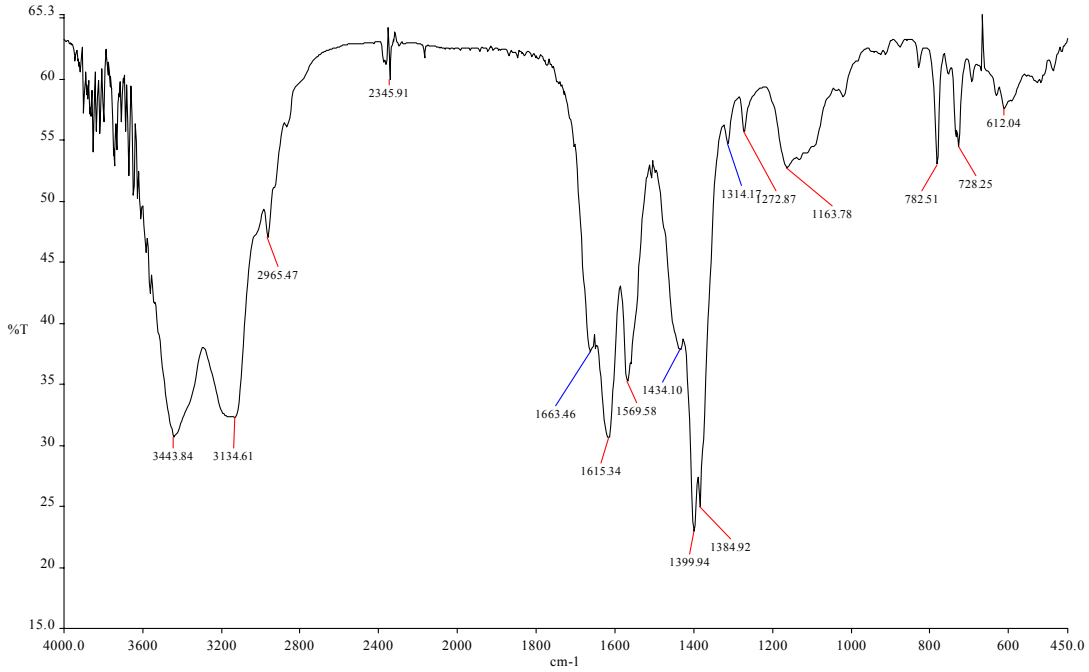
Compound **1**



Compound **2**



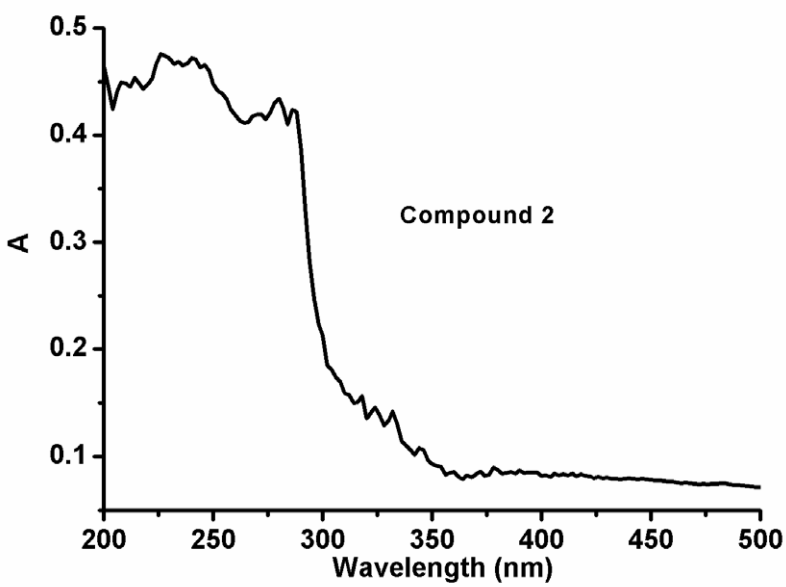
Compound **3**



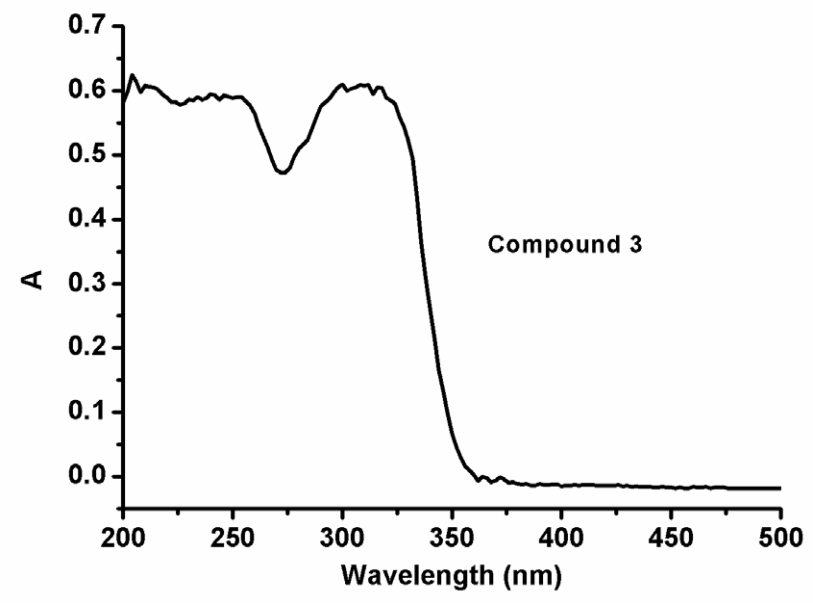
Compound **4**

Fig. S14 IR spectra of compounds **1**–**4**

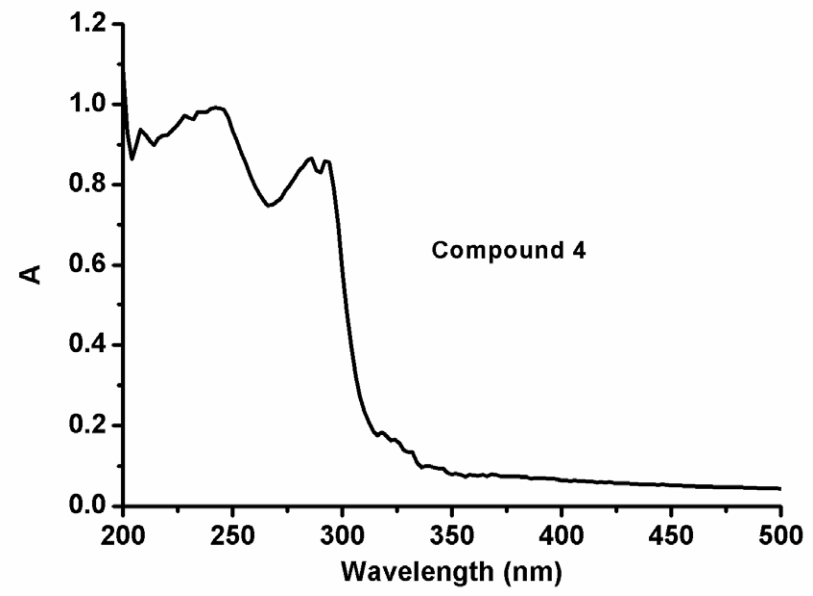
(a)


0.5
0.4
0.3
0.2
0.1
A
Compound 2
200
250
300
350
400
450
500
Wavelength (nm)

(b)

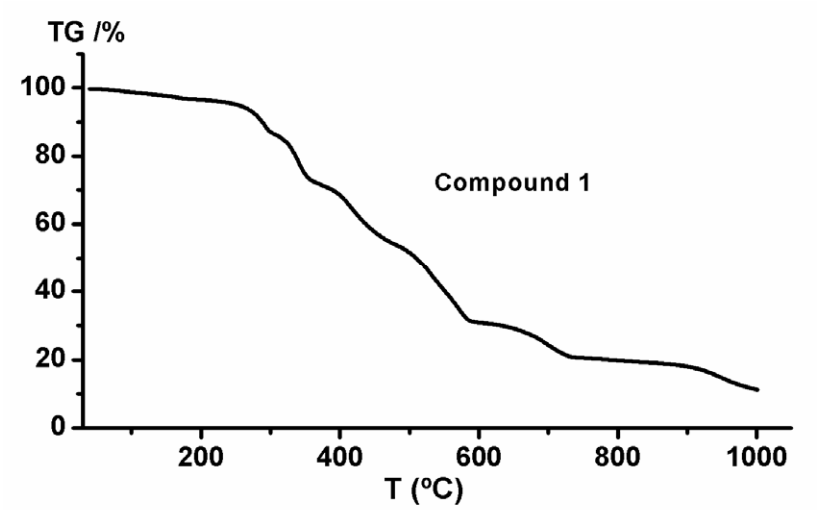


(c)

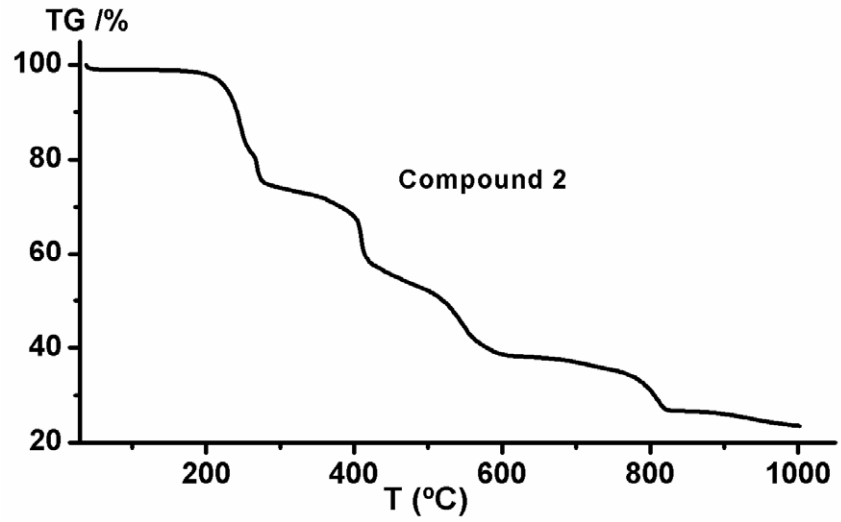


(d)

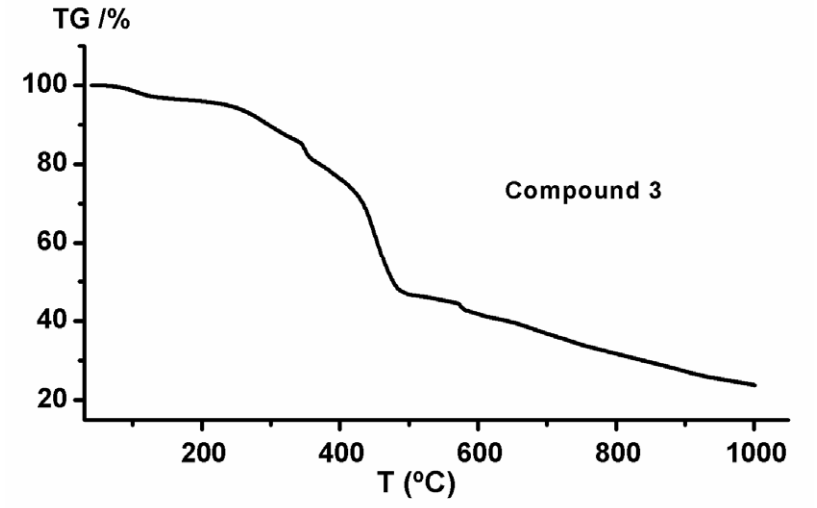
Fig. S15 The UV absorption spectra for compounds **1**–**4** (a–d) in the solid state at room temperature.


TG /%
100
80
60
40
20
0
200
400
600
800
1000
T (ºC)
Compound 1

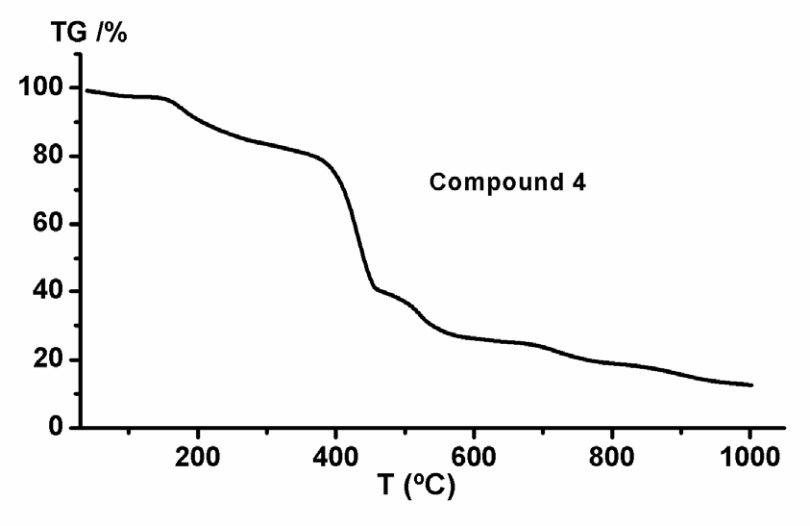
(a)


TG /%
100
80
60
40
20
200
400
600
800
1000
T (ºC)
Compound 2

(b)


TG /%
100
80
60
40
20
200
400
600
800
1000
T (ºC)
Compound 3

(c)



(d)

Fig. S16 TGA curves for compounds **1**–**4**

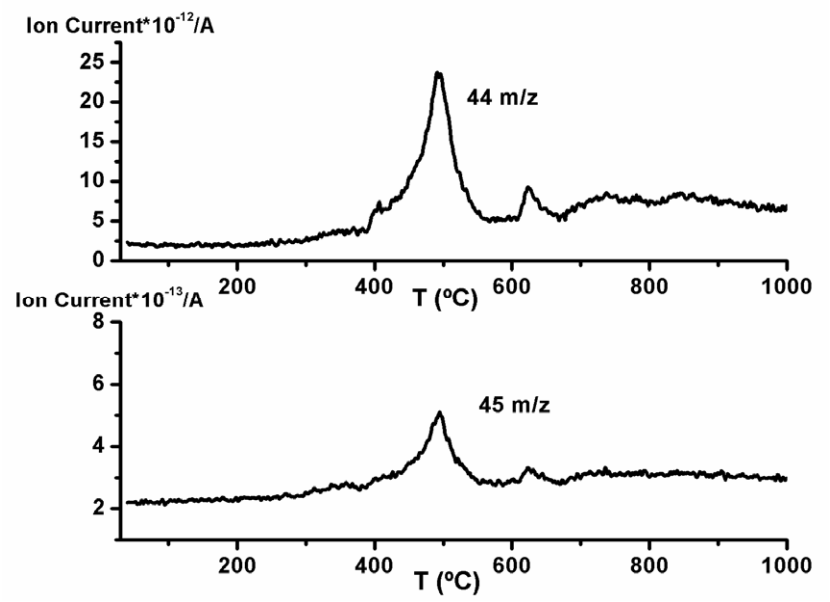


Fig. S17 MS analysis of **3** with ion current signals for m/z = 44 and 45.

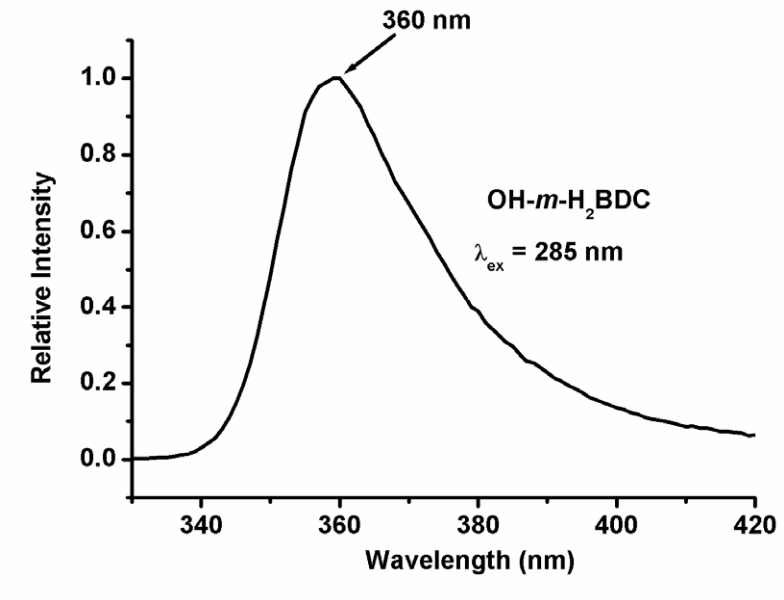


Fig. S18 Emission spectrum for the free OH-*m*-H_2BDC ligand in the solid state at room temperature.