Supplementary Information

A series of novel Pb(II) or Pb(II)/M(II) (M = Ca and Sr) hybrid inorganic-organic frameworks based on polycarboxylic acids with diverse Pb–O–M (M = Pb, Ca and Sr) inorganic connectivities

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Tables S1–S6 Selected bond distances (Å) and angles (°) for compounds **1**–**6**

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

Pb1—O1	2.495 (3)	Pb1—O2	2.614 (3)
Pb1—O3	2.523 (3)	Pb1—O4	2.635 (3)
Pb1—O5	2.596 (3)	Pb1—O1^{i}	2.754 (3)
Pb1—O3^{i}	2.704 (3)	O1—Pb1—O3^{i}	91.19 (10)
O1—Pb1—O3	76.38 (11)	O3—Pb1—O3^{i}	150.67 (8)
O1—Pb1—O5	72.75 (10)	O5—Pb1—O3^{i}	80.04 (12)
O3—Pb1—O5	70.96 (12)	O2—Pb1—O3^{i}	103.73 (12)
O1—Pb1—O2	51.18 (10)	O4—Pb1—O3^{i}	152.64 (11)

O3—Pb1—O2	89.16 (13)	O1—Pb1—O1^{i}	153.09 (2)
O5—Pb1—O2	123.65 (11)	O3—Pb1—O1^{i}	111.55 (11)
O1—Pb1—O4	115.84 (12)	O5—Pb1—O1^{i}	85.37 (10)
O3—Pb1—O4	49.80 (11)	O2—Pb1—O1^{i}	149.43 (10)
O5—Pb1—O4	110.75 (12)	O4—Pb1—O1^{i}	86.16 (12)
O2—Pb1—O4	91.19 (13)	O3^{i}—Pb1—O1^{i}	69.28 (10)

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

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

Pb1—O3^{i}	2.554 (5)	Ca1—O9	2.252 (5)
Pb1—O6^{ii}	2.593 (4)	Ca1—O5^{iv}	2.300 (4)
Pb1—O4^{i}	2.670 (4)	Ca1—O4^{i}	2.304 (4)
Pb1—O2	2.696 (4)	Ca1—O2	2.317 (4)
Pb1—O1	2.707 (5)	Ca1—O8^{ii}	2.320 (4)
Pb1—O5	2.727 (4)	Ca1—O7^{v}	2.333 (5)
O3^{i}—Pb1—O4^{i}	49.86 (14)	O9—Ca1—O4^{i}	92.9 (2)
O6^{ii}—Pb1—O4^{i}	77.43 (14)	O5^{iv}—Ca1—O4^{i}	171.12 (16)
O3^{i}—Pb1—O2	117.42 (14)	O9—Ca1—O2	168.1 (2)
O6^{ii}—Pb1—O2	89.04 (13)	O5^{iv}—Ca1—O2	95.40 (16)
O4^{i}—Pb1—O2	68.08 (12)	O4^{i}—Ca1—O2	81.10 (14)
O3^{i}—Pb1—O1	165.04 (19)	O9—Ca1—O8^{ii}	103.5 (2)
O6^{ii}—Pb1—O1	91.8 (2)	O5^{iv}—Ca1—O8^{ii}	79.26 (15)
O4^{i}—Pb1—O1	115.19 (15)	O4^{i}—Ca1—O8^{ii}	92.36 (15)
O2—Pb1—O1	47.75 (15)	O2—Ca1—O8^{ii}	87.03 (16)

$O3^{i}$—Pb1—O5	85.44 (16)	O9—Ca1—$O7^{v}$	90.9 (2)
$O6^{ii}$—Pb1—O5	118.14 (12)	$O5^{iv}$—Ca1—$O7^{v}$	109.07 (17)
$O4^{i}$—Pb1—O5	132.90 (13)	$O4^{i}$—Ca1—$O7^{v}$	78.30 (17)
O2—Pb1—O5	146.80 (13)	O2—Ca1—$O7^{v}$	77.84 (17)
O1—Pb1—O5	108.72 (18)	$O8^{ii}$—Ca1—$O7^{v}$	163.22 (17)
$O3^{i}$—Pb1—$O4^{i}$	49.86 (14)		

Symmetry codes: (i) $x+1, y, z$; (ii) $-x, -y+2, -z$; (iii) $-x, y+1/2, -z+1/2$; (iv) $-x, y-1/2, -z+1/2$; (v) $x, -y+5/2, z+1/2$; (vi) $x-1, y, z$; (vii) $x, -y+5/2, z-1/2$.

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

Pb1—O2	2.326 (4)	Ca1—O1	2.323 (4)
Pb1—$O4^{ii}$	2.668 (4)	Ca1—O6	2.352 (7)
Pb1—$O3^{ii}$	2.859(4)	Ca1—$O3^{ii}$	2.304 (4)
O2—Pb1—$O2^{i}$	73.992(37)	$O3^{v}$—Ca1—$O3^{iii}$	171.53 (6)
O2—Pb1—$O4^{ii}$	74.641(37)	$O3^{v}$—Ca1—$O1^{vi}$	83.91 (4)
$O2^{i}$—Pb1—$O4^{ii}$	81.779 (37)	$O3^{v}$—Ca1—O1	89.70 (4)
$O4^{ii}$—Pb1—$O4^{iii}$	150.413 (33)	$O1^{vi}$—Ca1—O1	82.21 (6)
O2—Pb1—$O3^{iii}$	76.416(38)	O1—Ca1—$O6^{vi}$	90.54 (6)
O2—Pb1—$O3^{ii}$	116.982(37)	$O3^{v}$—Ca1—O6	91.61 (5)
$O3^{iii}$—Pb1—$O3^{ii}$	164.251(36)	$O3^{iii}$—Ca1—O6	94.02 (5)
$O3^{iii}$—Pb1—$O4^{ii}$	138.989(33)	O1—Ca1—O6	172.46 (6)
$O3^{ii}$—Pb1—$O4^{ii}$	46.794(33)	$O6^{vi}$—Ca1—O6	96.78 (10)

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

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

Pb1—O9^{i}	2.278 (5)	Sr1—O2	2.434 (6)
Pb1—O1	2.483 (6)	Sr1—O3^{iv}	2.476 (6)
Pb1—O4^{ii}	2.582 (5)	Sr1—O8^{v}	2.500 (5)
Pb1—O3^{ii}	2.678 (6)	Sr1—O7^{vi}	2.597 (6)
Pb1—O6^{iii}	2.711 (5)	Sr1—O6^{iii}	2.604 (5)
Pb1—O5^{iii}	2.813(7)	Sr1—O5	2.622 (5)
O9^{i}—Pb1—O1	92.4 (2)	Sr1—O8^{vi}	2.736 (6)
O9^{i}—Pb1—O4^{ii}	78.4 (2)	O3^{iv}—Sr1—O7^{vi}	91.9 (2)
O1—Pb1—O4^{ii}	85.10 (19)	O8^{v}—Sr1—O7^{vi}	112.7 (2)
O9^{i}—Pb1—O3^{ii}	84.4 (2)	O2—Sr1—O6^{iii}	76.7 (2)
O1—Pb1—O3^{ii}	134.3 (2)	O3^{iv}—Sr1—O6^{iii}	94.52 (19)
O4^{ii}—Pb1—O3^{ii}	49.56 (17)	O8^{v}—Sr1—O6^{iii}	165.61 (18)
O9^{i}—Pb1—O6^{iii}	81.63 (18)	O7^{vi}—Sr1—O6^{iii}	81.1 (2)
O1—Pb1—O6^{iii}	106.1 (2)	O2—Sr1—O5	82.0 (2)
O4^{ii}—Pb1—O6^{iii}	157.52 (18)	O3^{iv}—Sr1—O5	77.84 (19)
O3^{ii}—Pb1—O6^{iii}	118.33 (17)	O8^{v}—Sr1—O5	93.68 (17)

O5^{iii}—Pb1—O3^{ii}	71.36(19)	O7^{vi}—Sr1—O5	151.69 (18)
O5^{iii}—Pb1—O4^{ii}	118.46(18)	O6^{iii}—Sr1—O5	73.62 (17)
O5^{iii}—Pb1—O9^{i}	80.53(19)	O2—Sr1—O8^{vi}	88.1 (2)
O5^{iii}—Pb1—O1	152.91(21)	O3^{iv}—Sr1—O8^{vi}	111.96 (19)
O5^{iii}—Pb1—O6^{iii}	47.16(18)	O8^{v}—Sr1—O8^{vi}	69.3 (2)
O2—Sr1—O3^{iv}	159.6 (2)	O7^{vi}—Sr1—O8^{vi}	48.48 (17)
O2—Sr1—O8^{v}	95.2 (2)	O6^{iii}—Sr1—O8^{vi}	121.50 (17)
O3^{iv}—Sr1—O8^{v}	89.2 (2)	O5—Sr1—O8^{vi}	159.55 (16)
O2—Sr1—O7^{vi}	104.6 (3)		

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

Table S5 Selected bond distances (Å) and angles (°) for compound **5**

Pb1—O1	2.448 (3)	Pb1—O1^{v}	2.8681(37)
Pb1—O2^{i}	2.424 (3)	Pb1—O1^{vii}	2.8902(42)
O2^{i}—Pb1—O1	118.04 (13)	O1—Pb1—O4^{vii}	140.840(83)
O2^{ii}—Pb1—O1	72.73 (12)	O1^{v}—Pb1—O4^{vii}	73.121(71)
O2^{i}—Pb1—O2^{ii}	79.65 (18)	O2^{i}—Pb1—O4^{vii}	94.886(80)

O1^{iii}—Pb1—O1	73.57 (17)		

Symmetry codes: (i) *x*+1/2, −*y*+1/2, −*z*+3/2; (ii) *x*+1/2, *y*, −*z*+3/2; (iii) *x*, −*y*+1/2, *z*; (iv) *x*, −*y*−1/2, *z*; (v) *x*−1/2, *y*, −*z*+3/2; (vi) *x*−1/2, −*y*+1/2, −*z*+3/2; (vii) −*x*+7/2, −*y*, *z*−1/2.

Table S6 Selected bond distances (Å) and angles (°) for compound **6**

Pb1—O1	2.515 (4)	Ca1—O2	2.308 (3)
Pb1—O2	2.863(4)	Ca1—O4	2.368 (4)
O1^{i}—Pb1—O1	87.6 (2)	O2—Pb1—O1^{i}	94.07(14)
O1^{ii}—Pb1—O1	92.4 (2)	O2—Pb1—O1^{iii}	131.91(13)
O1—Pb1—O1^{iii}	180	O2—Ca1—O2^{i}	82.97(13)
O2—Pb1—O1	48.10(13)	O2—Ca1—O2^{iv}	180
O2—Pb1—O1^{ii}	85.93(14)	O2—Ca1—O2^{v}	97.03 (13)
O2—Pb1—O2^{iii}	180	O2—Ca1—O4	92.67 (9)
O2—Pb1—O2^{i}	64.52(9)	O2—Ca1—O4^{vi}	87.33 (9)
O2—Pb1—O2^{ii}	115.48(9)	O4—Ca1—O4^{vi}	180

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

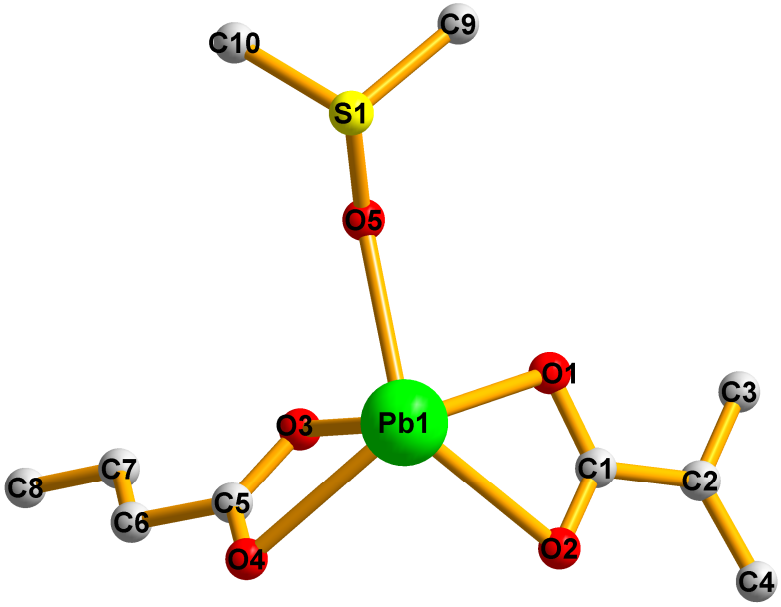


Fig. S1 View of the asymmetric unit of **1**. Hydrogen atoms are omitted for clarity.

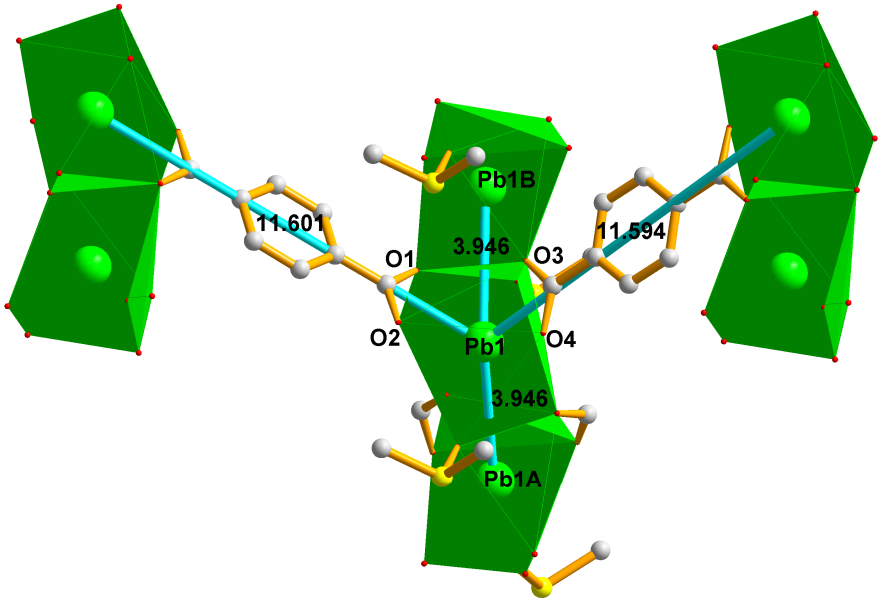


Fig. S2 View of the topological simplification mode of compound **1**.

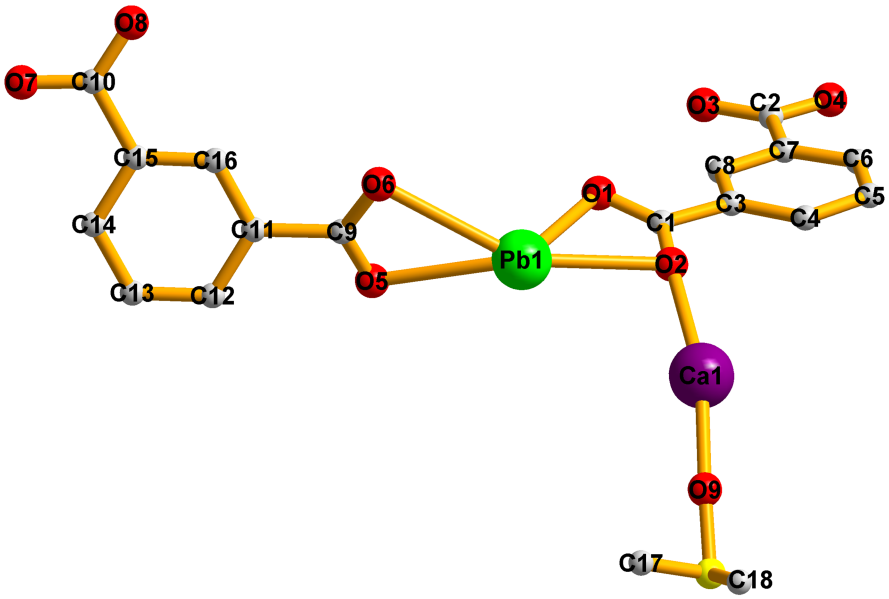


Fig. S3 View of the asymmetric unit of **2**. Hydrogen atoms are omitted for clarity.

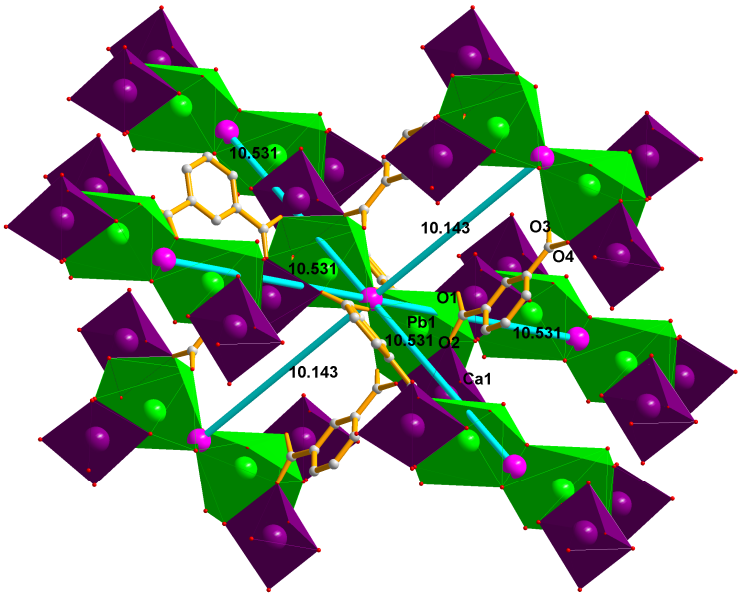


Fig. S4 View of the topological simplification mode of compound **2**.

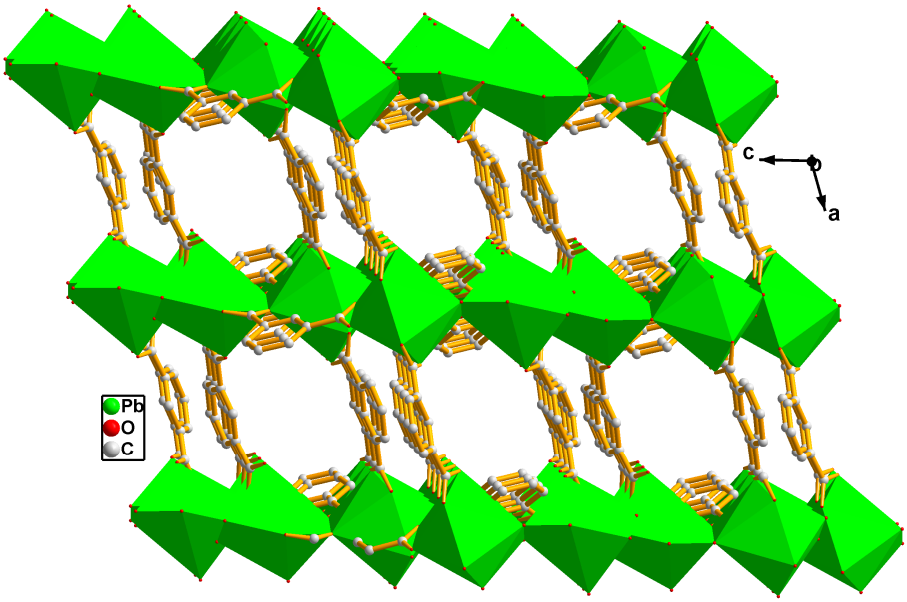


Fig. S5 Polyhedral view of the 3D anionic microporous framework with Ca(II) ions and DMSO molecules omitted for **2**. Hydrogen atoms are omitted for clarity.

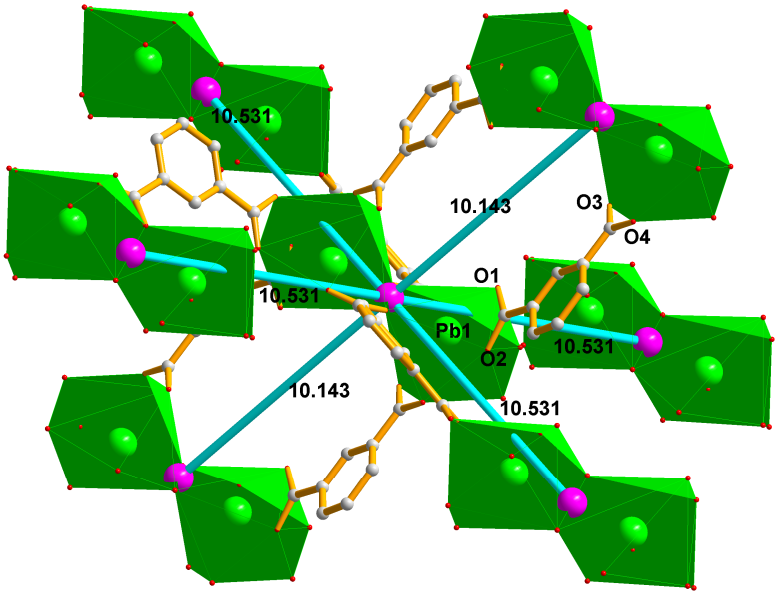


Fig. S6 View of the topological simplification mode of the Ca(II)-omitted anionic network in compound **2**.

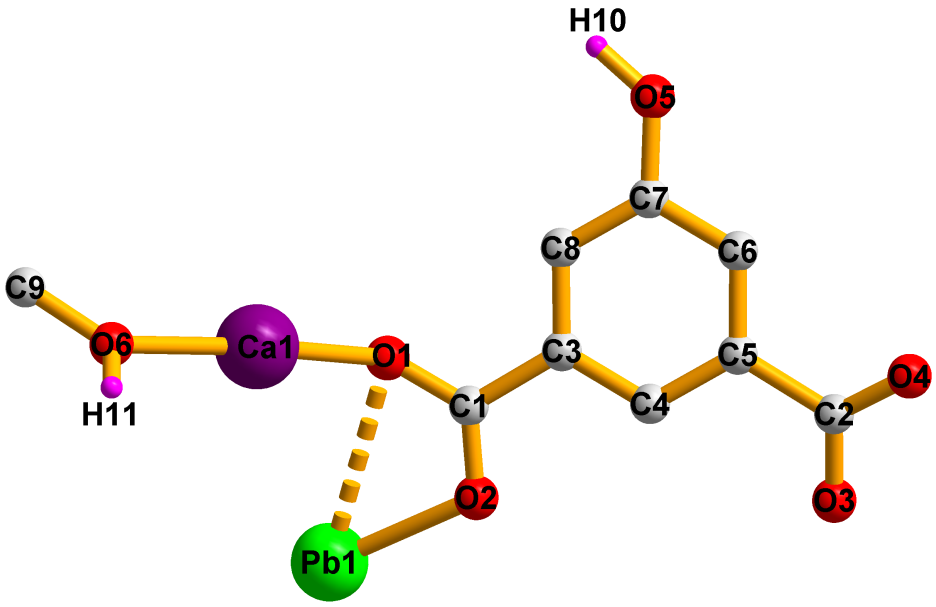


Fig. S7 View of the asymmetric unit of **3**. Hydrogen atoms belonged to C atoms are omitted for clarity.

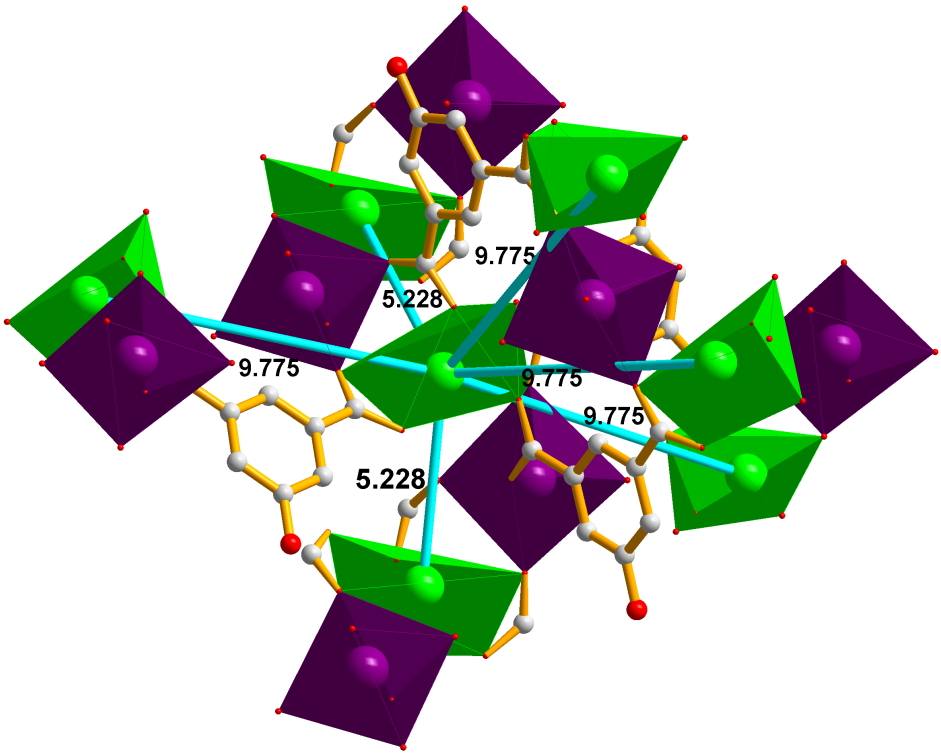


Fig. S8 View of the topological simplification mode of compound **3**.

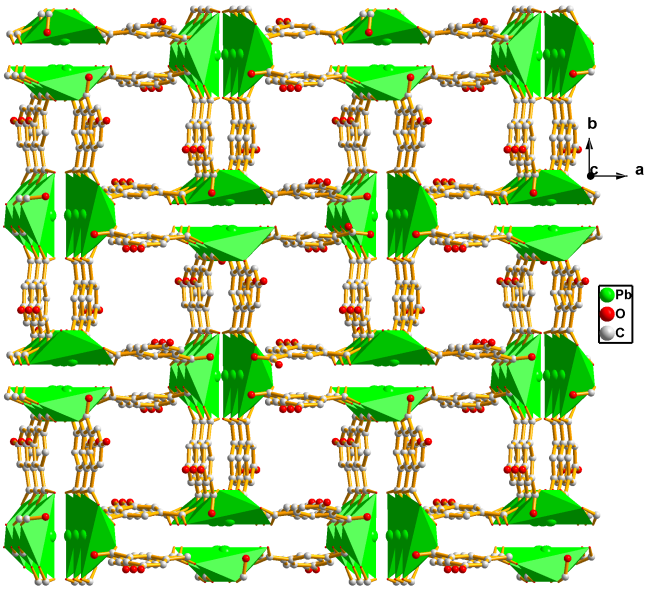


Fig. S9 Polyhedral view of the 3D anionic microporous framework with Ca(II) ions and CH_3OH molecules omitted for **3**. Hydrogen atoms are omitted for clarity.

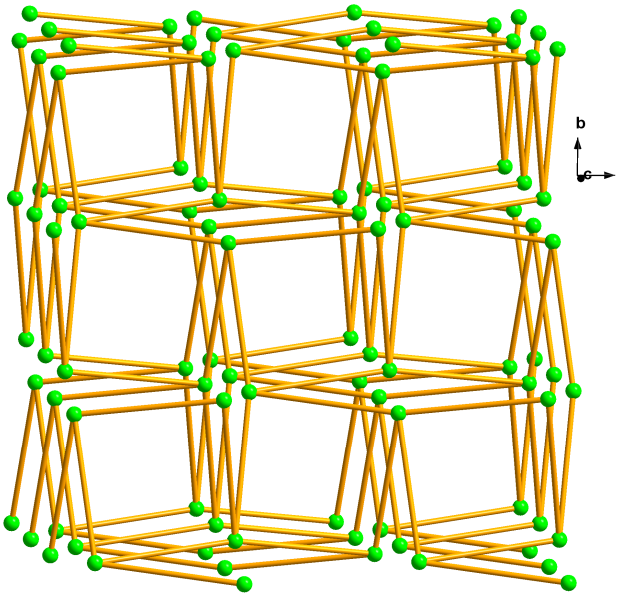


Fig. S10 The **lvt** topological net of the Ca(II)-omitted anionic network in **3**.

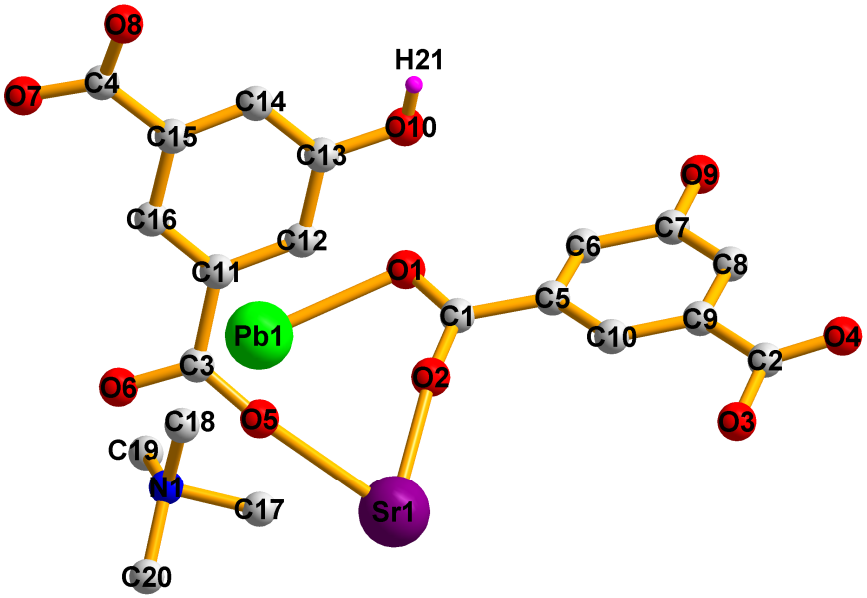


Fig. S11 View of the asymmetric unit of **4**. Hydrogen atoms belonged to C atoms are omitted for clarity.

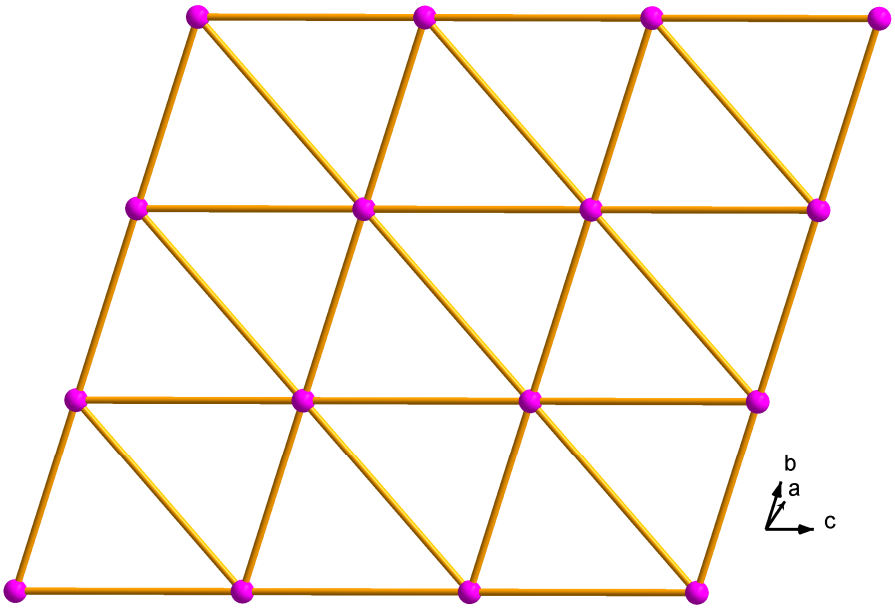


Fig. S12 View of the (6, 3)-topology network for the the 2D layer substructure in **4** constructed from the tetrametallic $Pb_2Sr_2O_{20}$ cluster (SBU) and μ_5-O-*m*-BDC^{3-} anion.

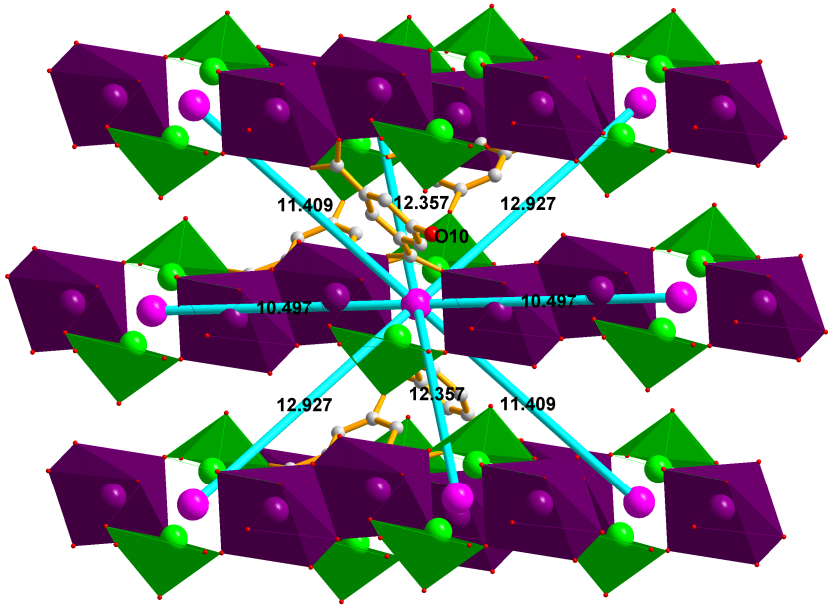


Fig. S13 View of the topological simplification mode of compound **4**.

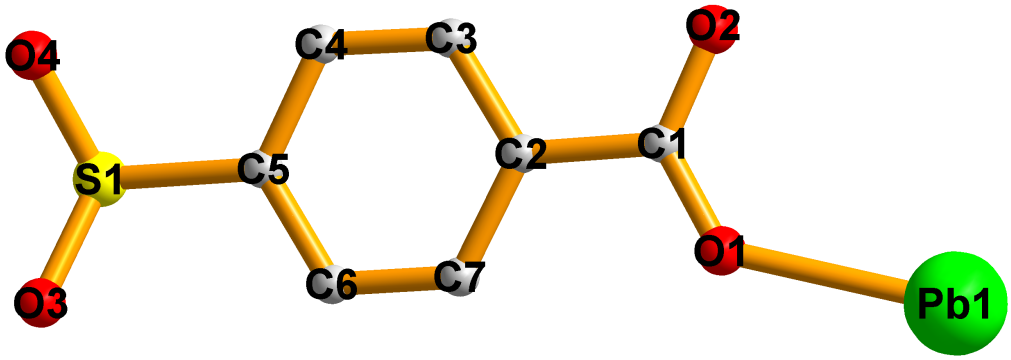


Fig. S14 View of the asymmetric unit of **5**. Hydrogen atoms are omitted for clarity.

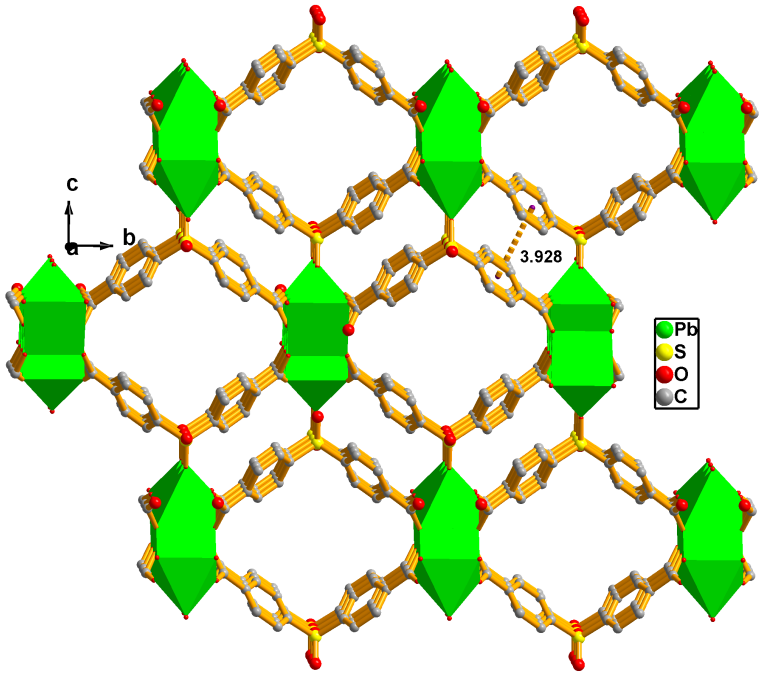


Fig. S15 View of the weak offset $\pi\cdots\pi$ intramolecular interactions in the 3D framework of **5**.

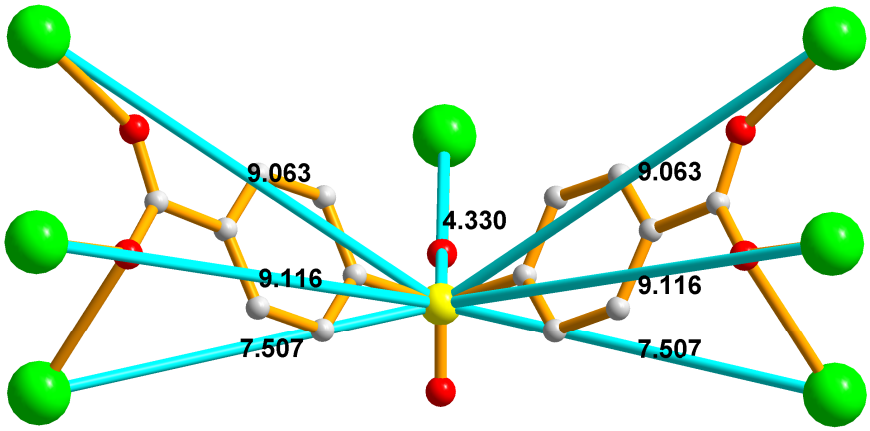


Fig. S16 View of the topological simplification mode of compound **5**.

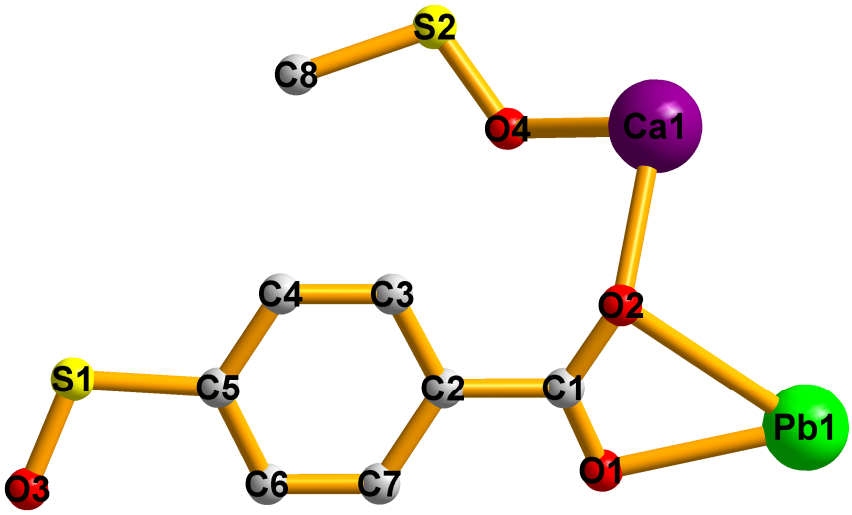


Fig. S17 View of the asymmetric unit of **6**. Hydrogen atoms are omitted for clarity.

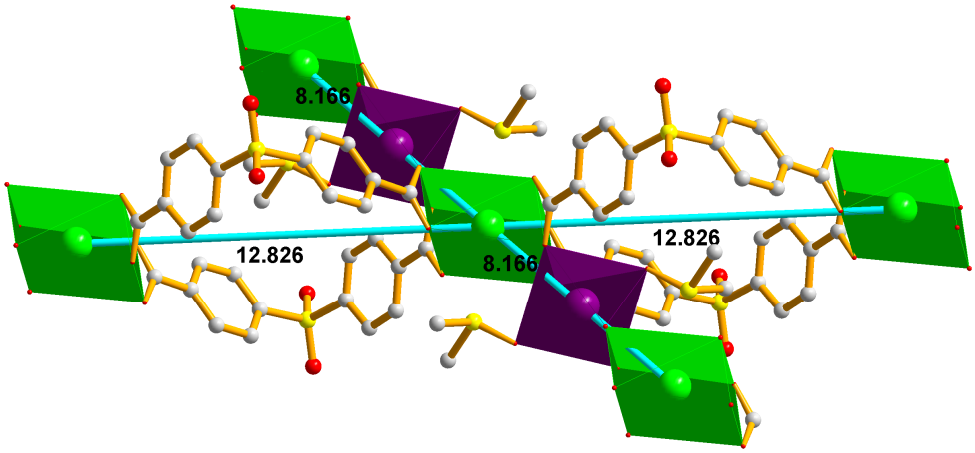
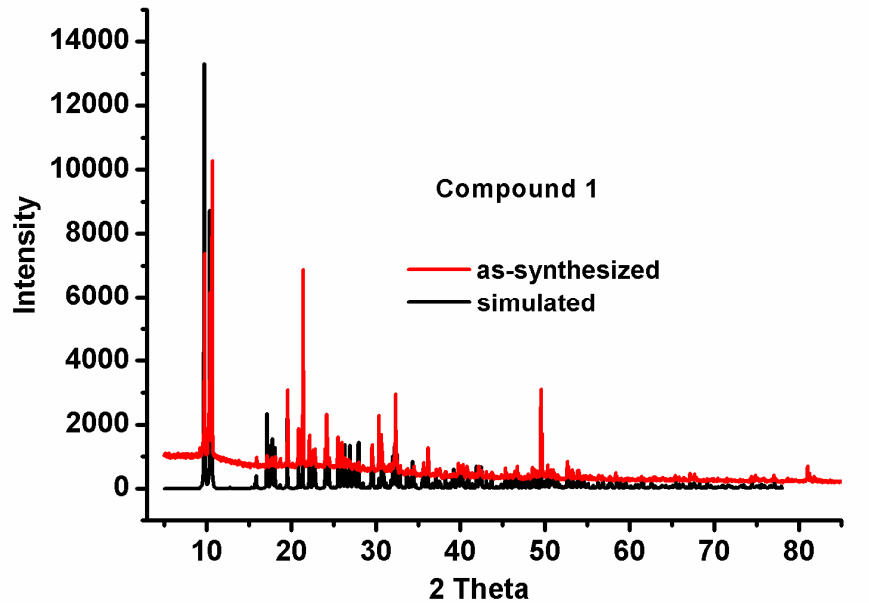


Fig. S18 View of the topological simplification mode of compound **6**.



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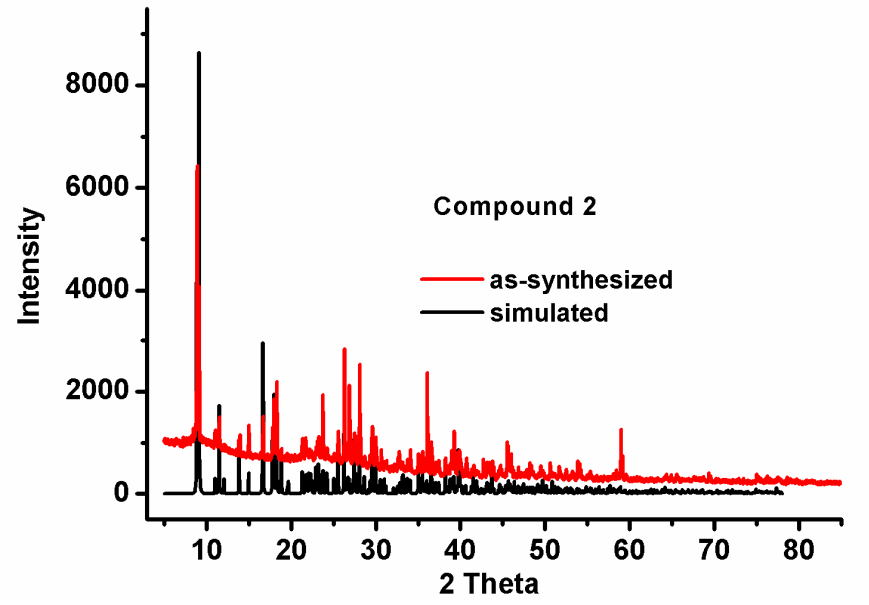

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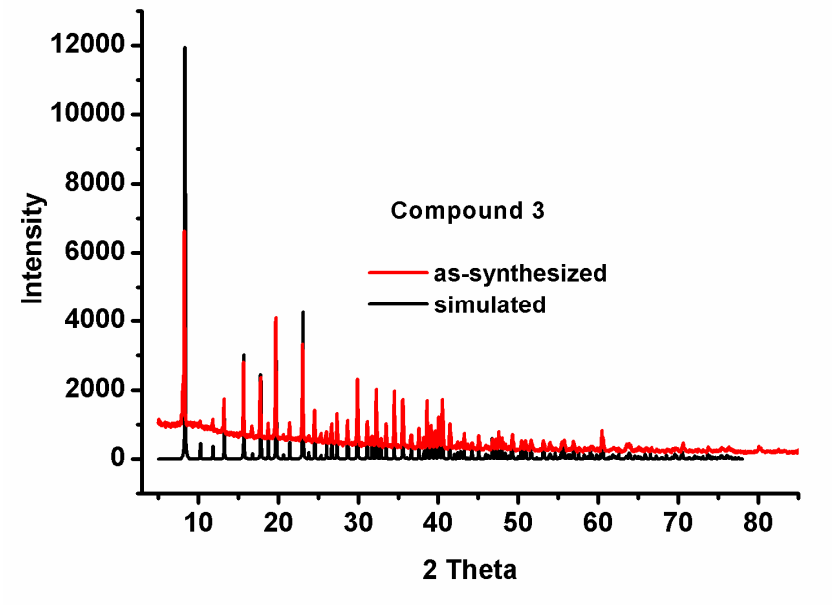

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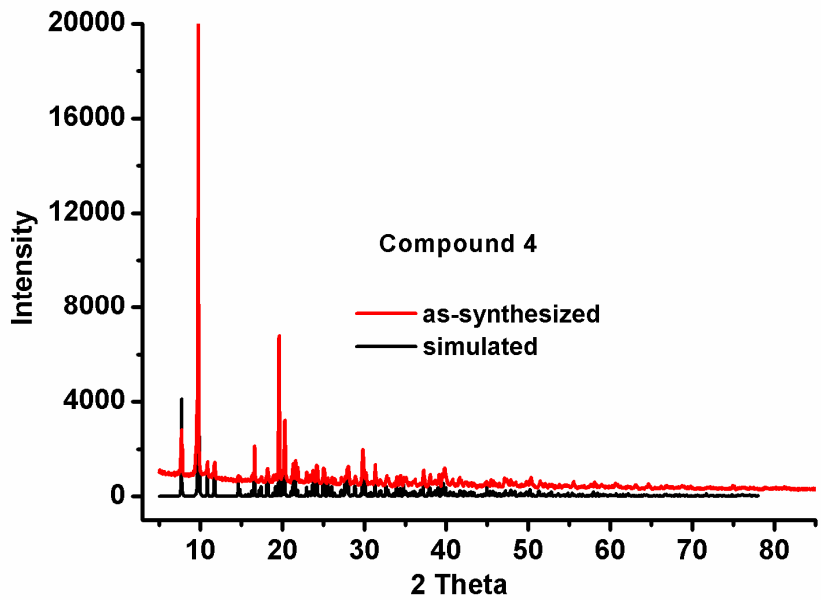

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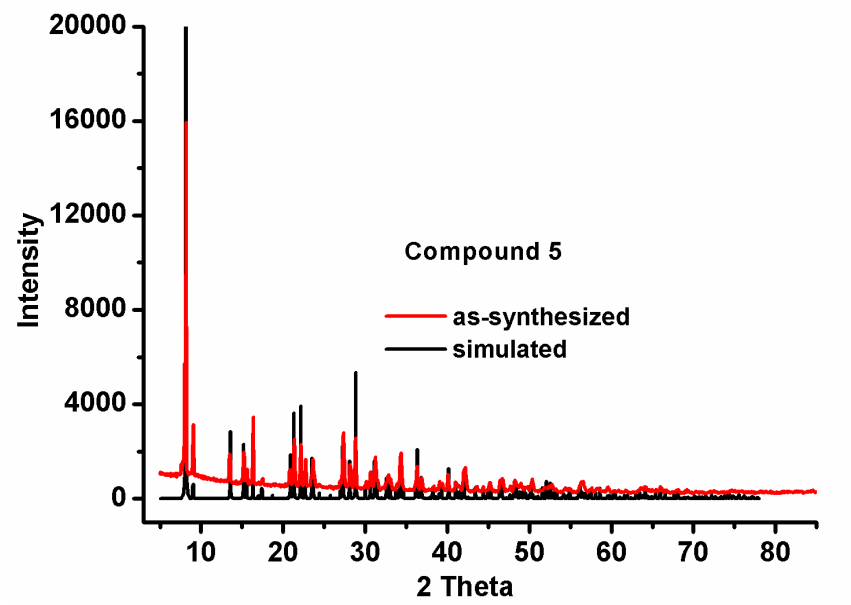
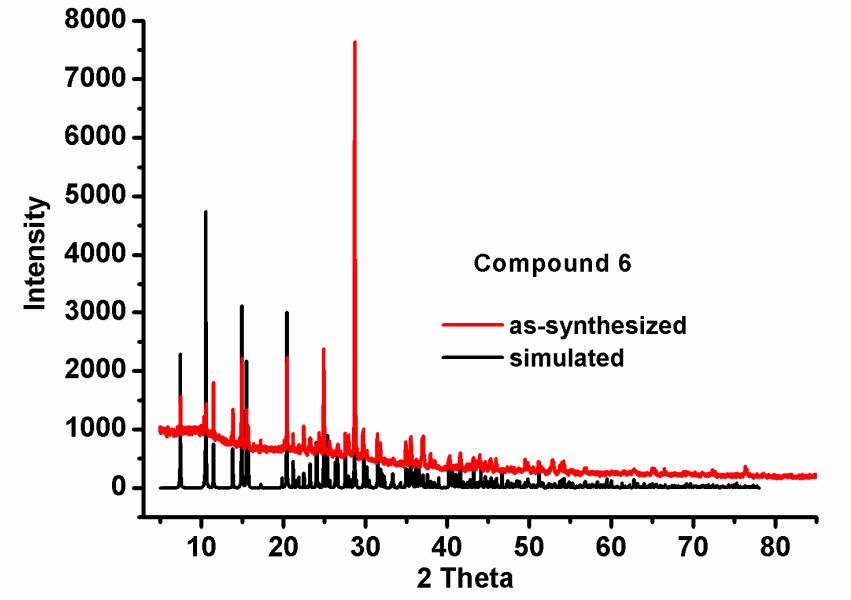
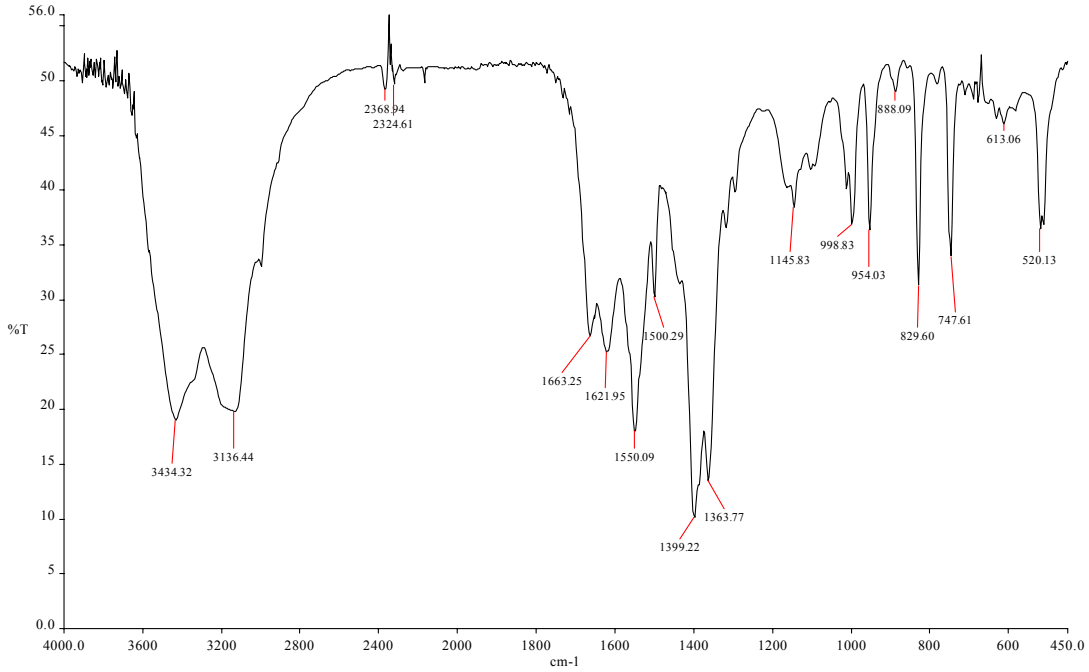


(e)

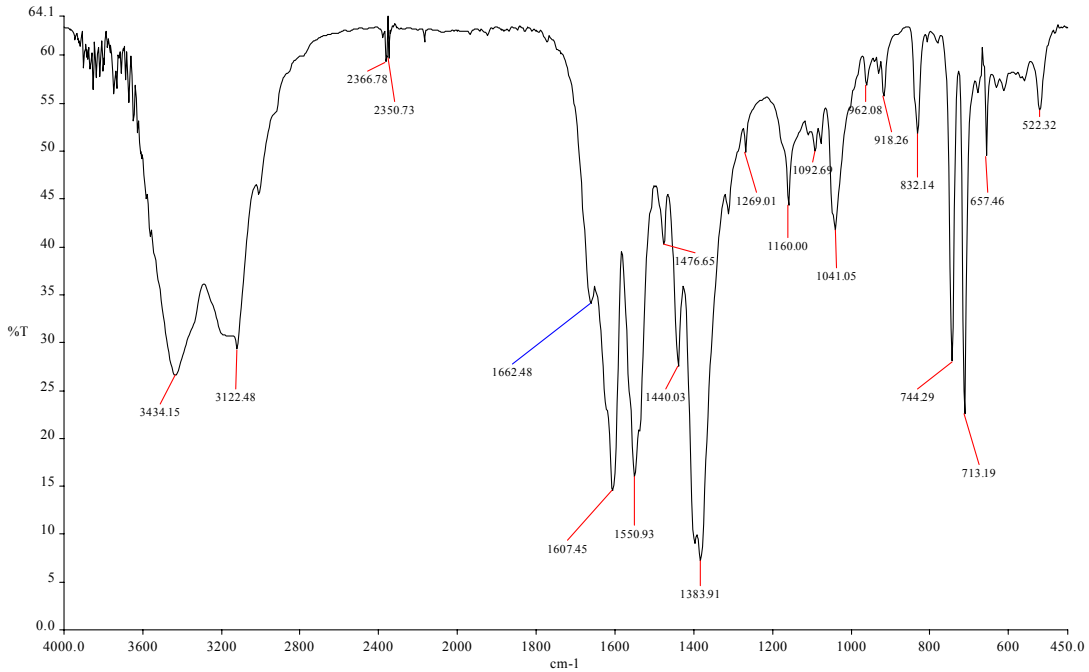


(f)

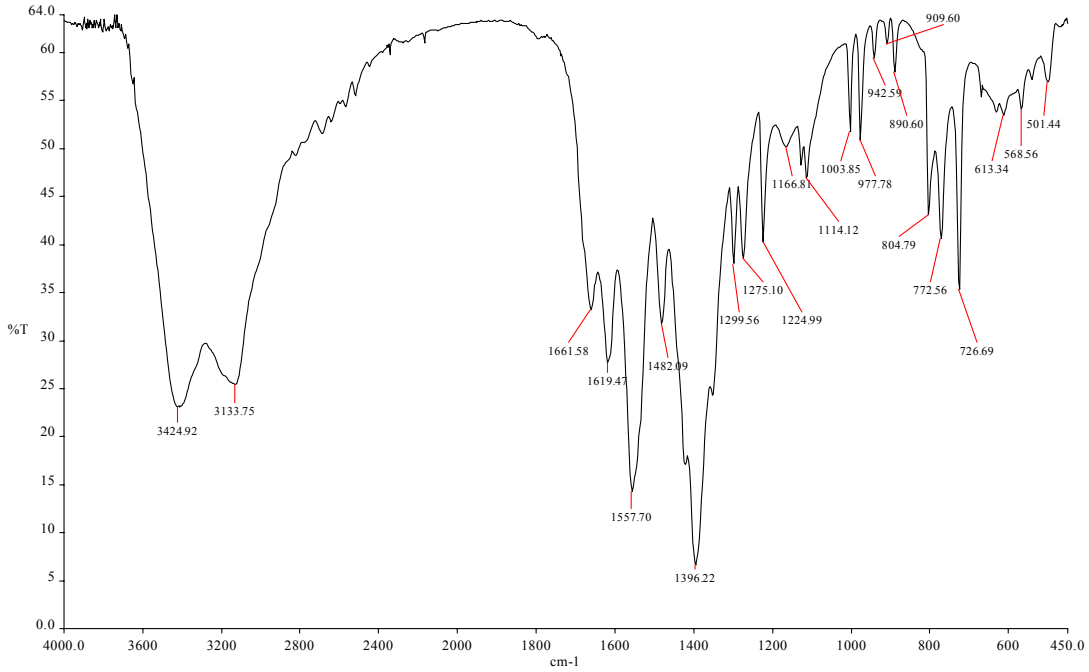
Fig. S19 The power X-ray diffraction patterns for compounds **1–6**



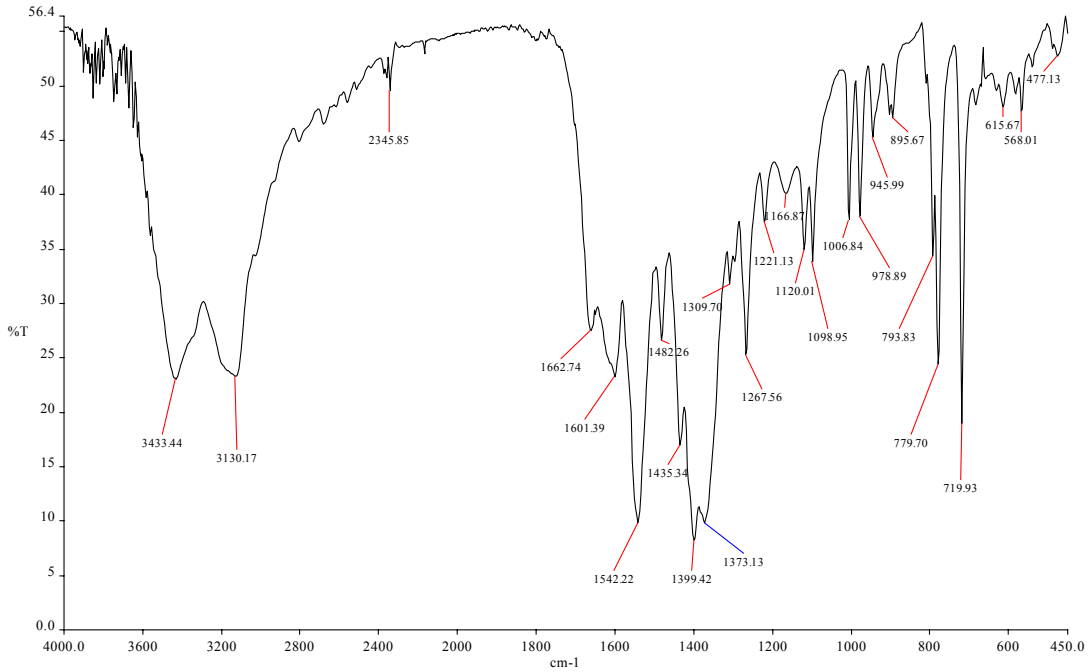
Compound **1**



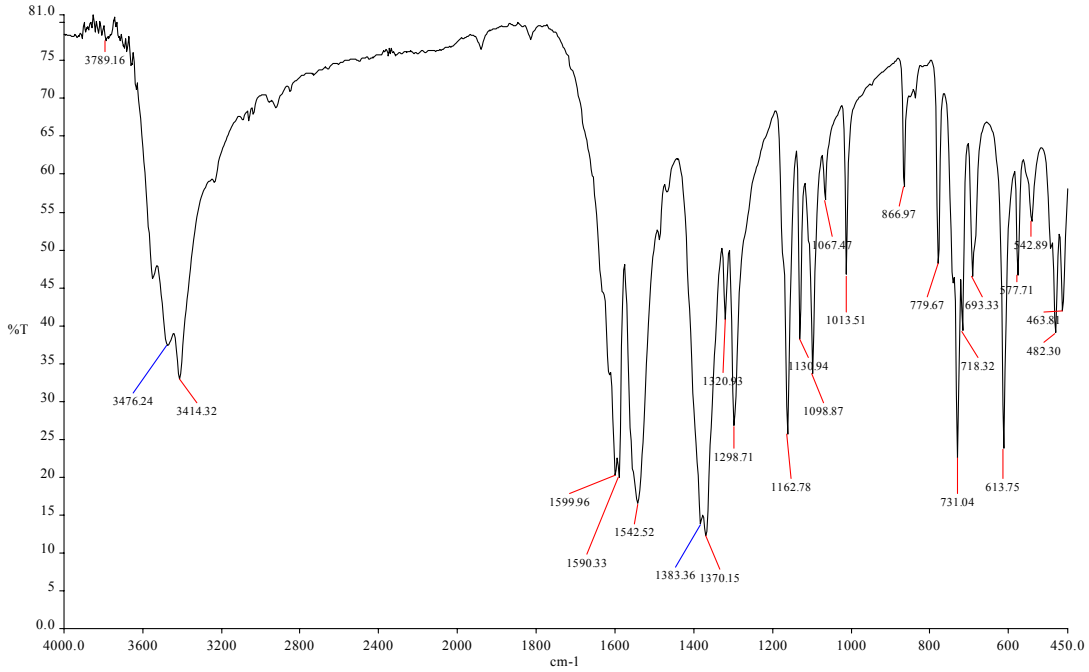
Compound **2**



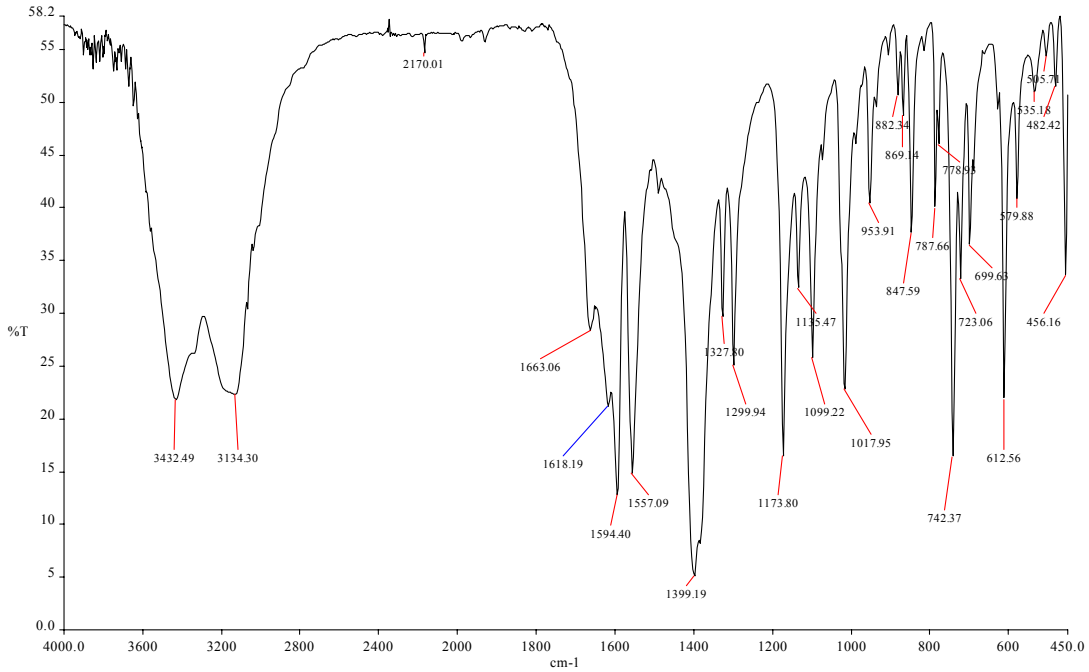
Compound **3**



Compound **4**

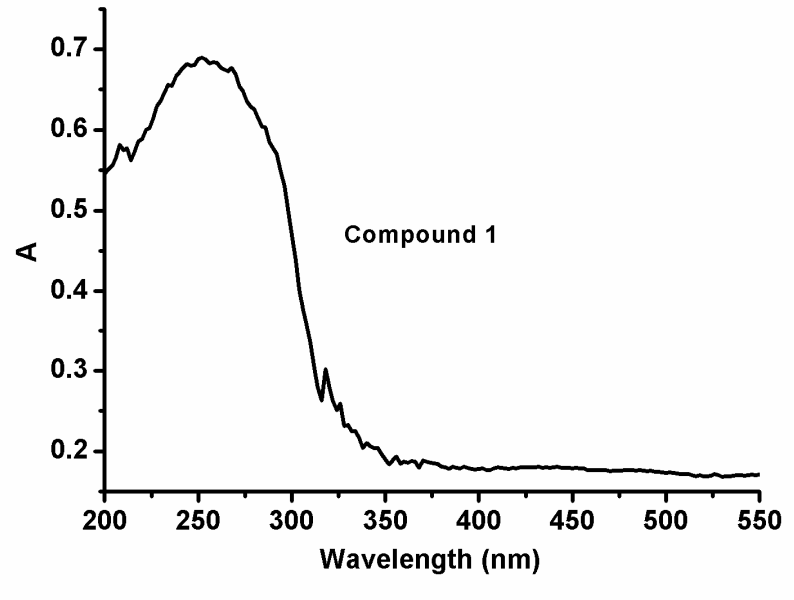


Compound **5**

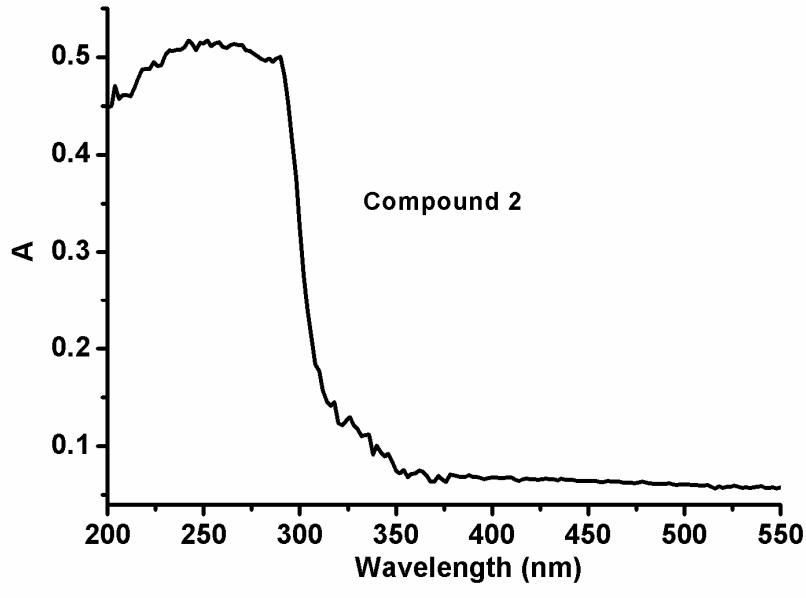


Compound **6**

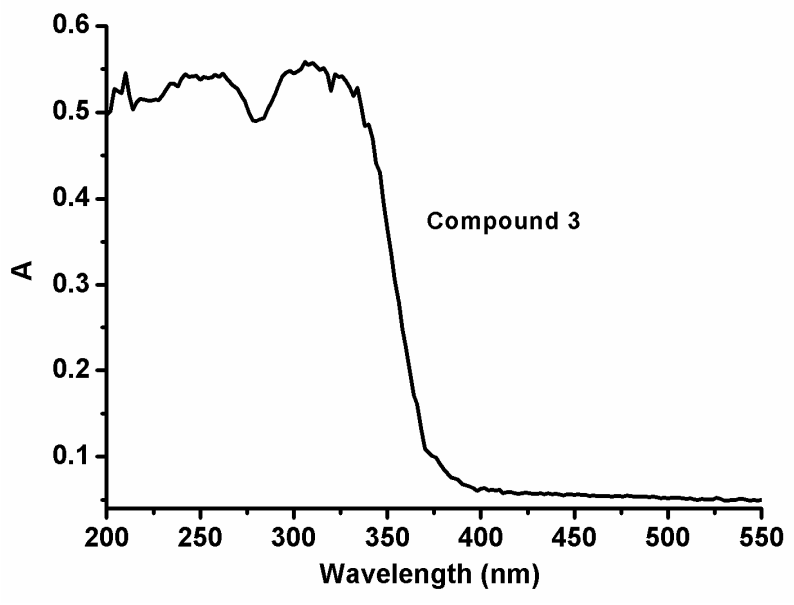
Fig. S20 IR spectra of compounds **1**–**6**


Compound 1
A
Wavelength (nm)
0.7
0.6
0.5
0.4
0.3
0.2
200
250
300
350
400
450
500
550

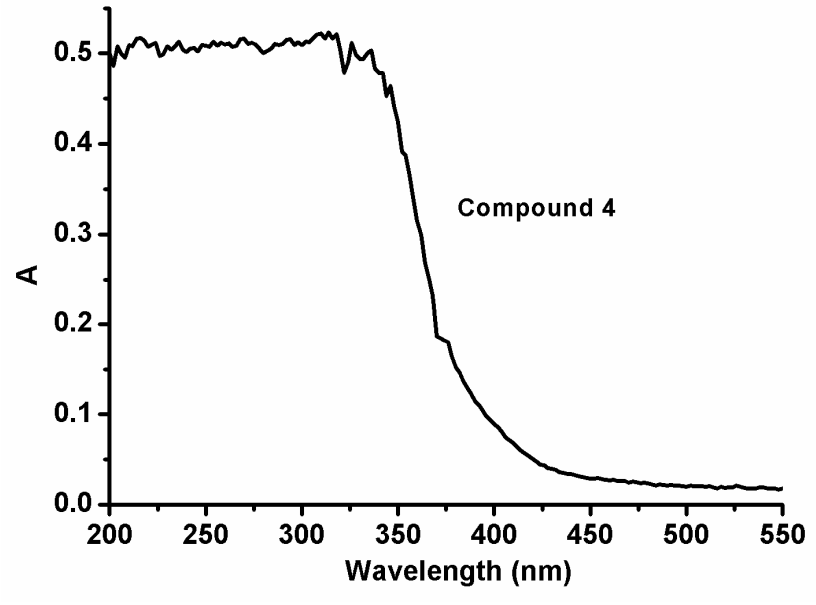
(a)


Compound 2
A
Wavelength (nm)
0.5
0.4
0.3
0.2
0.1
200
250
300
350
400
450
500
550

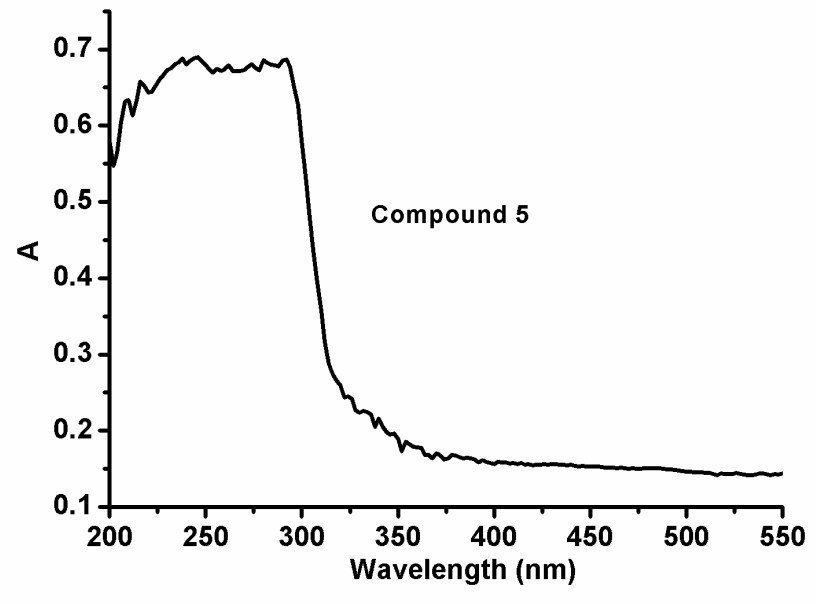
(b)


0.6
0.5
0.4
0.3
0.2
0.1
A
Compound 3
200
250
300
350
400
450
500
550
Wavelength (nm)

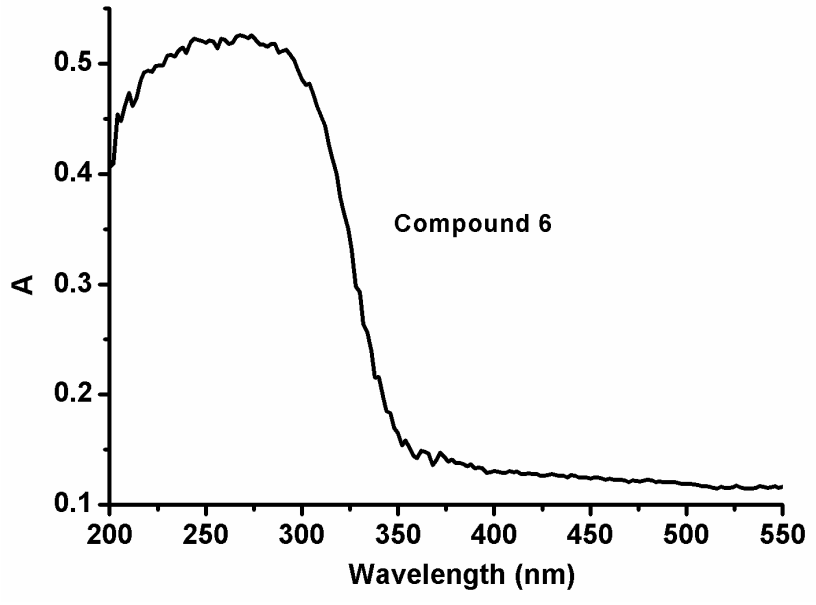
(c)


0.5
0.4
0.3
0.2
0.1
0.0
A
Compound 4
200
250
300
350
400
450
500
550
Wavelength (nm)

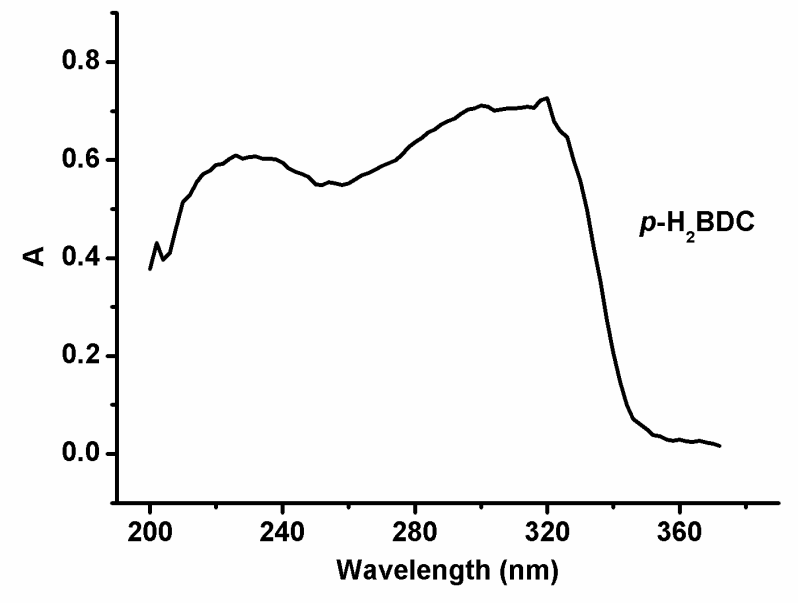
(d)


Compound 5
A
Wavelength (nm)
0.1
0.2
0.3
0.4
0.5
0.6
0.7
200
250
300
350
400
450
500
550

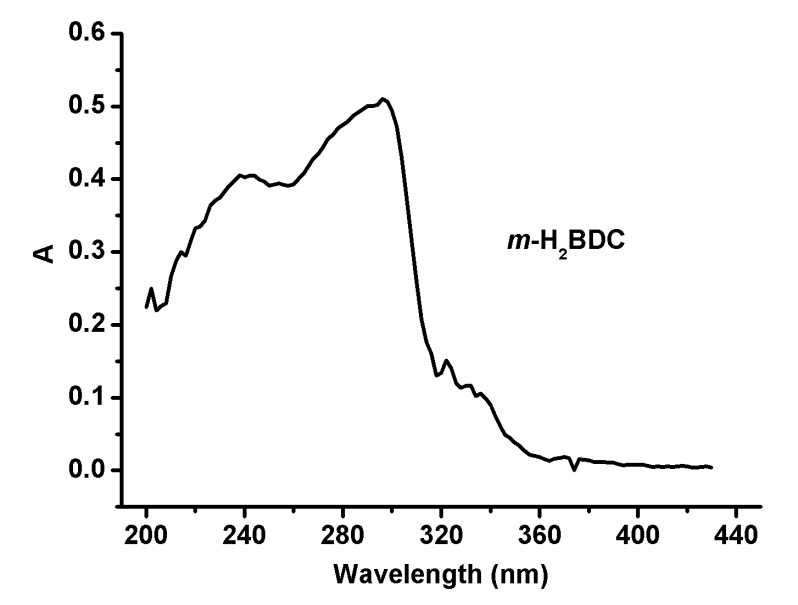
(e)


Compound 6
A
Wavelength (nm)
0.1
0.2
0.3
0.4
0.5
200
250
300
350
400
450
500
550

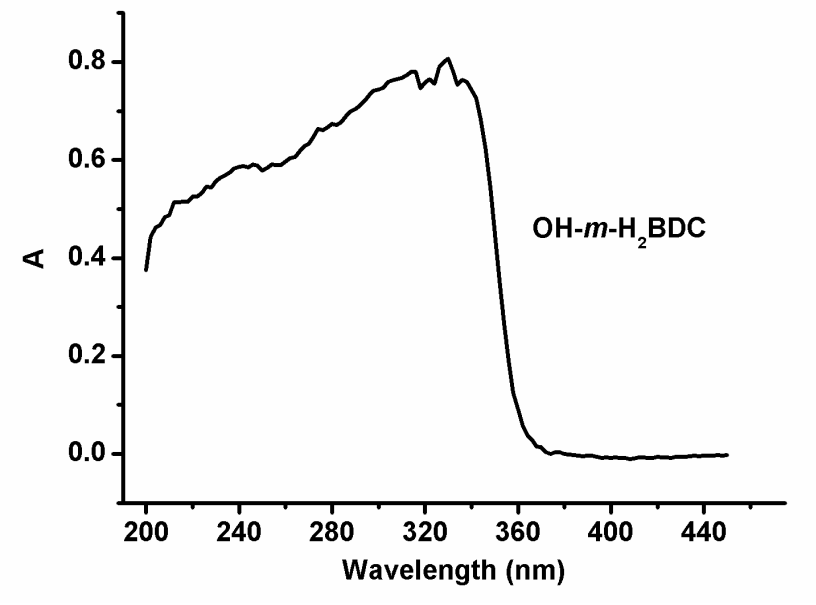
(f)


0.8
0.6
0.4
0.2
0.0
A
200
240
280
320
360
Wavelength (nm)
p-H2BDC

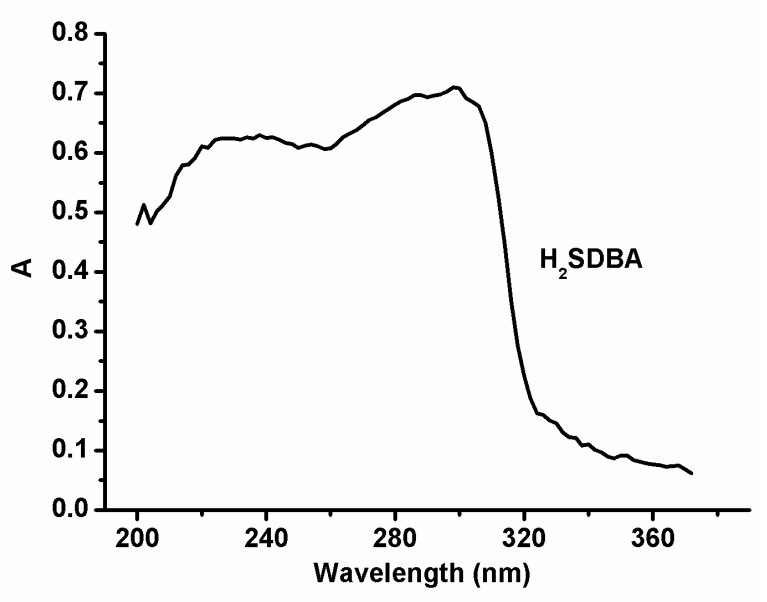
(g)


0.6
0.5
0.4
0.3
0.2
0.1
0.0
A
200
240
280
320
360
400
440
Wavelength (nm)
m-H2BDC

(h)

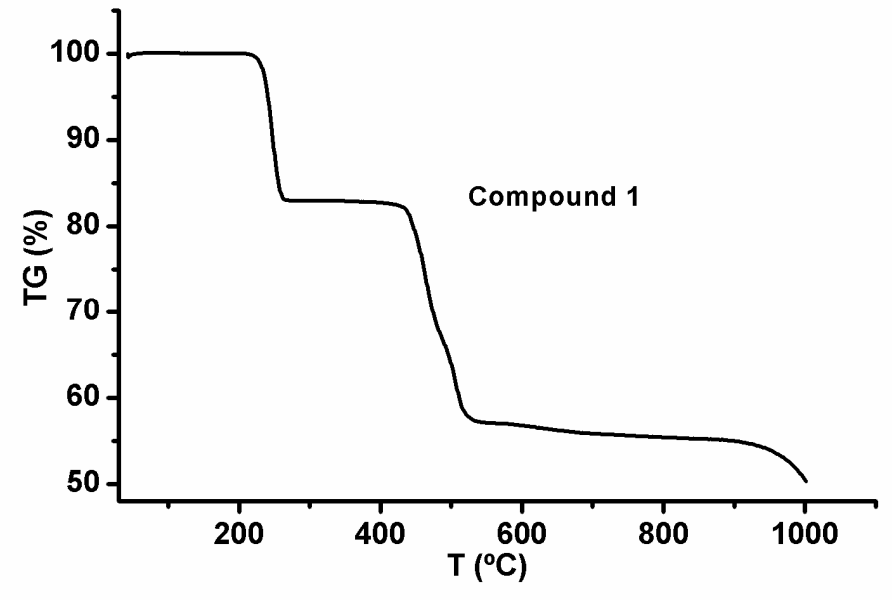


(i)

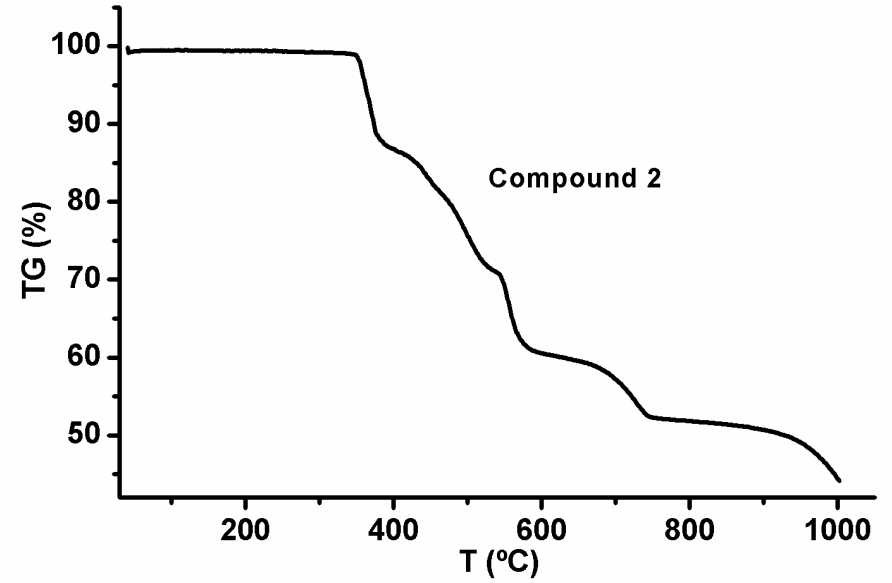


(j)

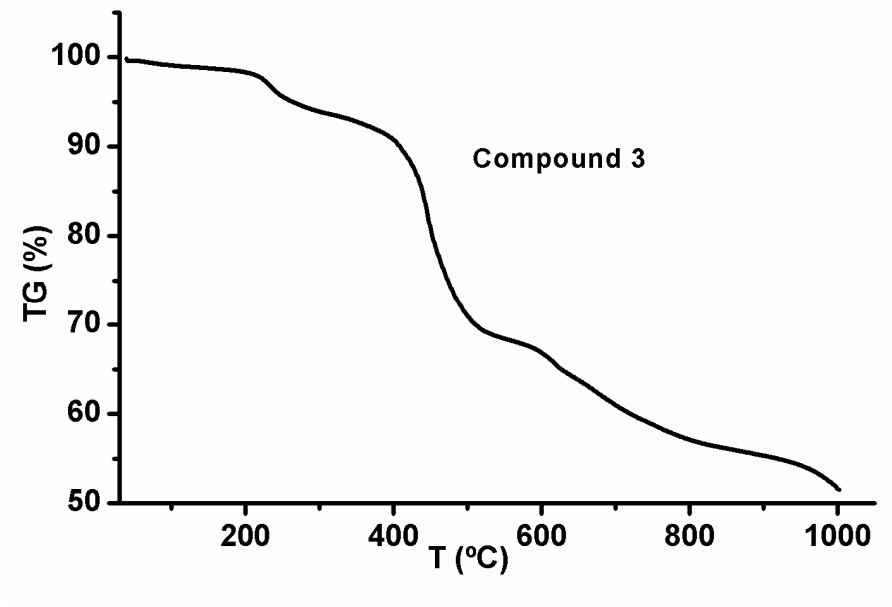
Fig. S21 The UV absorption spectra for compounds **1**–**6** (a–f) and the four free polycarboxylate ligands (g–j) in the solid state at room temperature.


Compound 1
TG (%)
T (ºC)
100
90
80
70
60
50
200
400
600
800
1000

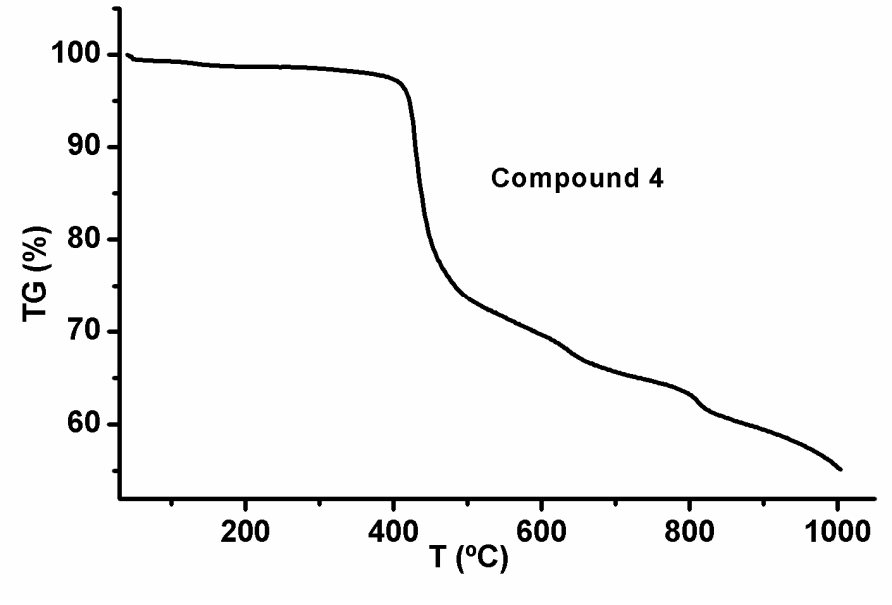
(a)


Compound 2
TG (%)
T (ºC)
100
90
80
70
60
50
200
400
600
800
1000

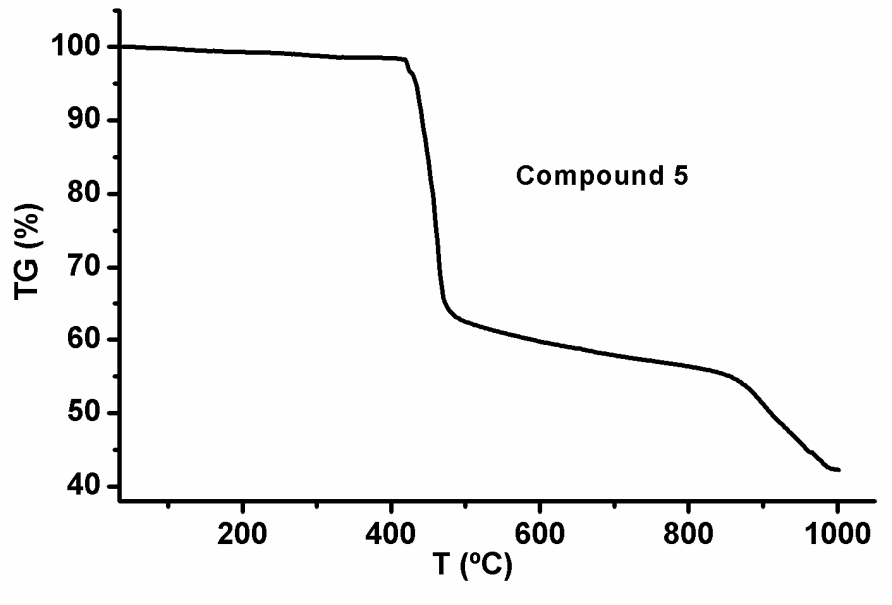
(b)


Compound 3
TG (%)
T (ºC)
100
90
80
70
60
50
200
400
600
800
1000

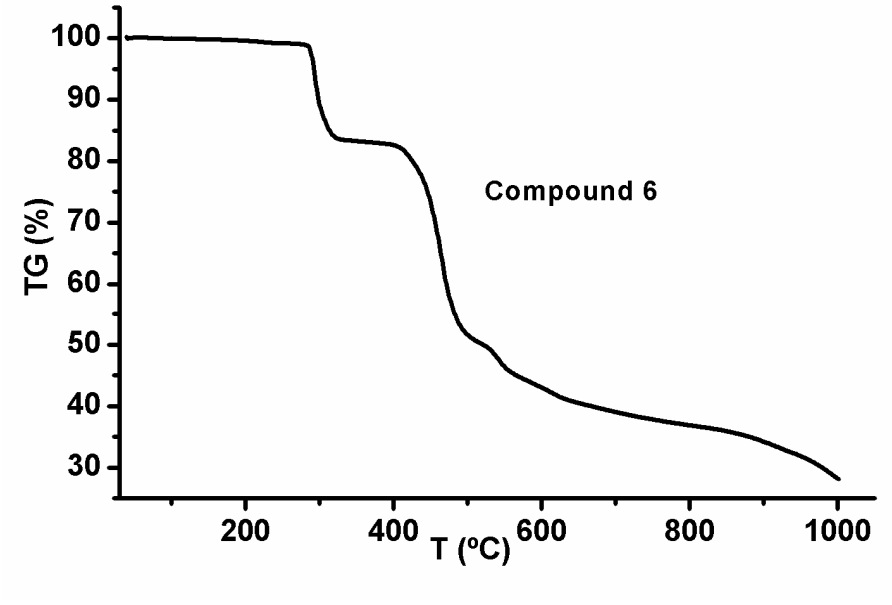
(c)


Compound 4
TG (%)
T (ºC)
100
90
80
70
60
200
400
600
800
1000

(d)



(e)



(f)

Fig. S22 TGA curves for compounds **1**–**6**

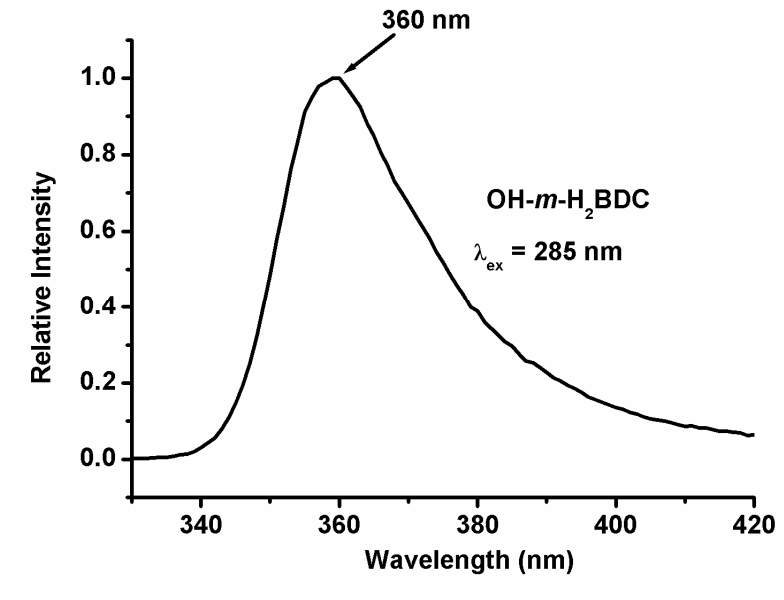


Fig. S23 Emission spectrum for the free OH-*m*-H_2BDC ligand in the solid state at room temperature.