Supplementary Information

Synthesis, structures and luminescent properties of new Pb(II)/M(I) (M = K, Rb and Cs) frameworks based on dicarboxylic acids: a novel icosahedral Pb_6-M_6 SBU

Xian-Qiang Li,[ab] Hua-Bin Zhang,[ab] Shu-Ting Wu,[c] Jian-Di Lin,[a] Ping-Lin,[a] Zhi-Hua Li,[a] Shao-Wu Du*[a]

[a] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China*

[b] *Graduate University of Chinese Academy of Sciences, Beijing 100039, P. R. China*

[c] *College of Chemistry and chemical Engineering, Fuzhou University, Fuzhou, Fujian, 350002, P. R. China*

Table S1 Selected bond lengths (Å) and angles (°) for **1**–**5**

1			
Pb1—O1	2.347(5)	Pb1—O3	2.299(7)
Pb1—O2	2.925(5)	Pb1—O4	3.014(6)
Pb1—O2B	2.994(6)	K1—O2	2.780(5)
K1—O4B	2.810(5)	K1—O5	2.948(17)
O1—Pb1—O2	48.33(15)	O1—Pb1—O3	83.45(17)
O1—Pb1—O1A	74.9(2)	O1—Pb1—O2A	91.14(17)
O2—Pb1—O3	130.84(14)	O2—Pb1—O2C	148.96(12)
O2—Pb1—O4	144.42(12)	O2B—Pb1—O2C	128.58(19)
O2—K1—O2A	72.7(2)	O2—K1—O4B	69.78(17)
O5—K1—O4B	73.04(14)		

Symmetry codes: (A) *x*, *x* – *y*, *z*; (B) *y*, *x*, −*z* + 1; (C) *y*, −*x* + *y*, −*z* + 1

2			
Pb1—O1	2.348(7)	Pb1—O2	2.924(8)
Pb1—O3	2.293(10)	Pb1—O4	2.976(10)
Pb1—O2B	2.998(9)	Rb1—O2A	2.854(7)
Rb1—O4B	2.929(7)	Rb1—O5	2.998(18)
O1—Pb1—O1A	75.3(4)	O2—Pb1—O2B	70.6(3)

O1—Pb1—O3	82.8(3)	O2—Pb1—O2C	147.85(18)
O2—Pb1—O4	143.53(17)	O2B—Pb1—O2C	132.1(3)
O2—Rb1—O2A	72.6(3)	O2A—Rb1—O4F	68.6(2)
O5—Rb1—O4B	74.08(18)		

Symmetry codes: (A) *x*, *x* – *y*, *z*; (B) *x* – *y*, –*y*, –*z*; (C) *x* – *y*, *x*, –*z*; (F) *y*, *x*, –*z*.

3

Pb1—O1	2.357(9)	Pb1—O3	2.320(14)
Pb1—O2	2.939(12)	Pb1—O4	2.967(15)
Pb1—O2A	3.012(13)	Cs1—O2	3.023(15)
Cs1—O4B	3.045(12)	Cs1—O5	3.424(14)
O1—Pb1—O1C	75.7(5)	O2—Pb1—O4	142.6(3)
O1—Pb1—O3	82.8(4)	O2—Pb1—O2A	146.9(3)
O2B—Pb1—O4	67.8(2)	O2—Cs1—O2C	70.4(6)
O2—Cs1—O4B	66.7(4)	O4B—Cs1—O5	63.3(11)

Symmetry codes: (A) *y*, –*x* + *y*, –*z*; (B) *y*, *x*, −*z*; (C) *x*, *x* − *y*, *z*.

4

Pb1—O1	2.795(6)	Pb1—O2	2.833(6)
Pb1—O5D	2.471(11)	Pb2—O1	2.402(6)
Pb2—O2	3.194(6)	Pb2—O5	2.418(11)
K1—O2	2.679(6)	K1—O1D	2.770(6)
K1—O3F	2.878(8)	K1—O4G	2.736(7)
K1—O5D	2.879(2)		
O1—Pb1—O1B	113.5(2)	O1—Pb1—O1A	72.2(2)
O1—Pb1—O1C	72.8(3)	O2—Pb1—O2B	154.9(2)
O2—Pb1—O2A	77.4(3)	O2—Pb1—O5D	77.43(12)
O2—Pb1—O2C	97.1(3)	O2—Pb2—O2B	119.9(2)
O2—Pb2—O2C	83.3(2)	O2—Pb2—O2A	67.4(2)
O1—Pb2—O1B	153.6(3)	O1—Pb2—O1A	86.6(3)
O1—Pb2—O5	76.79(13)	O1—Pb2—O1C	87.4(3)
O1D—K1—O2	87.1(2)	O1D—K1—O1E	73.0(2)
O1D—K1—O2A	137.4(2)	O1D—K1—O3F	135.38(15)

O1D—K1—O4G	76.95(18)	O1D—K1—O5D	64.0(2)

Symmetry codes: (A) –0.5 – *x*, *y*, *z*; (B) –0.5 – *x*, 1.5 – *y*, *z*; (C) *x*, 1.5 – *y*, *z*; (D) *x*, *y*, 1 + *z*; (E) –0.5 – *x*, *y*, 1 + *z*; (F) –0.5 + *x*, 2 – *y*, 1 – *z*; (G) –0.5 + *x*, 2 – *y*, 2 – *z*.

5

Pb1—O1	2.422(10)	Pb1—O2	2.748(11)
Pb1—O4A	2.754(9)	Pb1—O7B	2.627(9)
Pb1—O8B	2.553(9)	Pb1—O9C	2.560(9)
Pb1—O10C	2.639(9)	Pb2—O13	2.460(8)
Pb2—O14	2.651(9)	Pb2—O2D	2.851(8)
Pb2—O3E	2.435(9)	Pb2—O4E	2.851(9)
Pb2—O7F	3.034(9)	Pb2—O15G	2.444(8)
Pb2—O16G	2.593(10)	Cs1—O2	3.066(9)
Cs1—O10C	3.452(10)	Cs1—O11	3.280(8)
Cs1—O12H	3.283(8)	Cs1—O16I	3.130(10)
Cs1—O17	3.276(7)	Cs1—O18F	3.287(8)
Cs1—O19	3.181(8)	Cs2—O3A	3.132(9)
Cs2—O6	3.385(18)	Cs2—O8K	3.119(9)
Cs2—O9	2.984(9)	Cs2—O13J	3.018(8)
Cs2—O15I	3.329(9)		
O4A—Pb1—O9C	137.1(3)	O4A—Pb1—O10C	100.1(3)
O1—Pb1—O2	50.6(3)	O1—Pb1—O7B	74.4(3)
O1—Pb1—O8B	71.4(3)	O7B—Pb1—O10C	147.9(4)
O13—Pb2—O2D	150.5(2)	O2D—Pb2—O4E	78.9(3)
O2D—Pb2—O7F	66.7(3)	O3E—Pb2—O13	80.2(3)
O3E—Pb2—O14	129.9(3)	O3E—Pb2—O15G	77.7(3)
O3E—Pb2—O16G	131.6(3)	O2—Cs1—O10C	59.8(2)
O2—Cs1—O11	148.2(2)	O2—Cs1—O12H	113.7(3)
O2—Cs1—O16I	62.8(3)	O2—Cs1—O17	86.2(2)
O2—Cs1—O19	101.1(2)	O3A—Cs2—O6J	131.0(4)

O3A—Cs2—O8K	164.6(3)	O3A—Cs2—O9	92.4(3)
O3A—Cs2—O13J	61.6(2)	O3A—Cs2—O15I	56.4(2)

Symmetry codes: (A) 2.5 − *x*, −0.5 + *y*, 0.5 − *z*; (B) 2.5 − *x*, 0.5 + *y*, 0.5 − *z*; (C) 1 + *x*, *y*, *z*; (C) 0.5 + *x*, 0.5 − *y*, − 0.5 + *z* (D) 0.5 + *x*, 0.5 − *y*, − 0.5 + *z*; (E) 3 − *x*, 1 − *y*, −*z*; (F) 3 − *x*, −*y*, −*z*; (G) −0.5 + *x*, 0.5 − *y*, −0.5 + *z*; (H) 2 − *x*, −*y*, −*z*; (I) −1 + *x*, *y*, *z*; (J) −0.5 + *x*, 0.5 − *y*, 0.5 + *z*; (K) 1.5 − *x*, 0.5 + *y*, 0.5 − *z*.

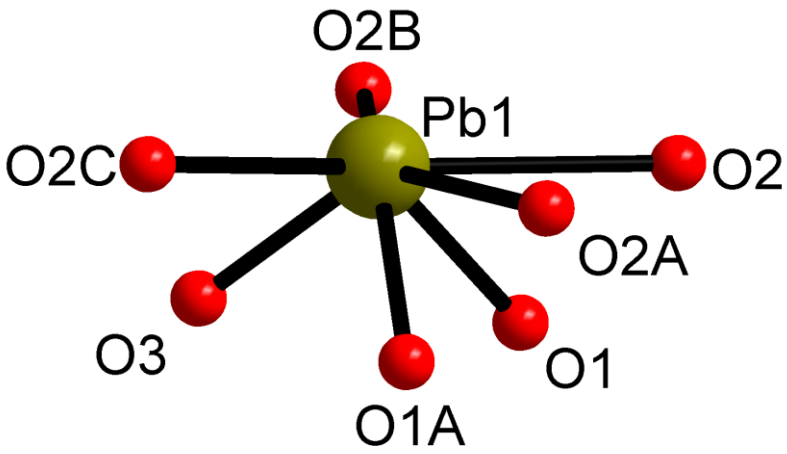


Fig. S1 The eight-coordinated geometry of Pb(II) in **1**, showing large gap occupied by the lone pair electrons.

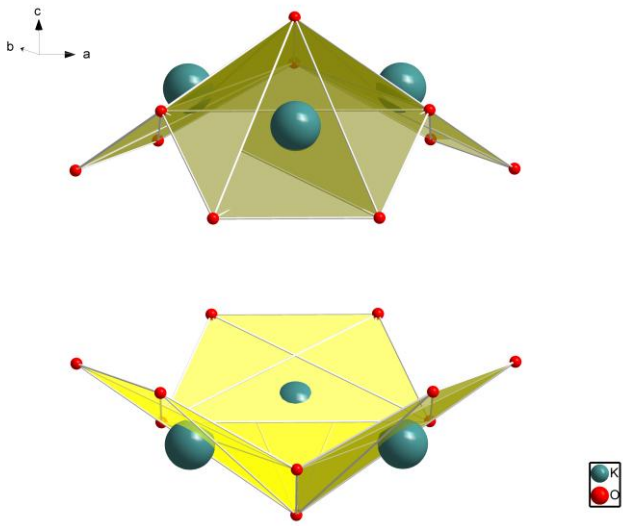


Fig. S2 The arrangement mode of K(I) ions in the Pb_6-K_6 cage of **1**.

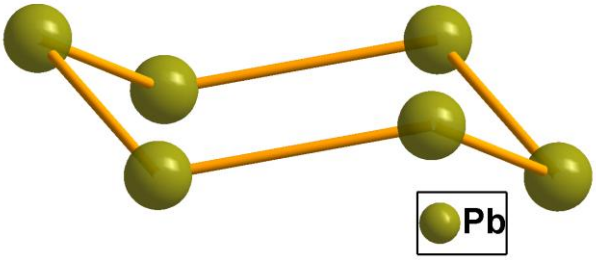


Fig. S3 The chair conformation of Pb(II) ions in the Pb_6-K_6 cage.

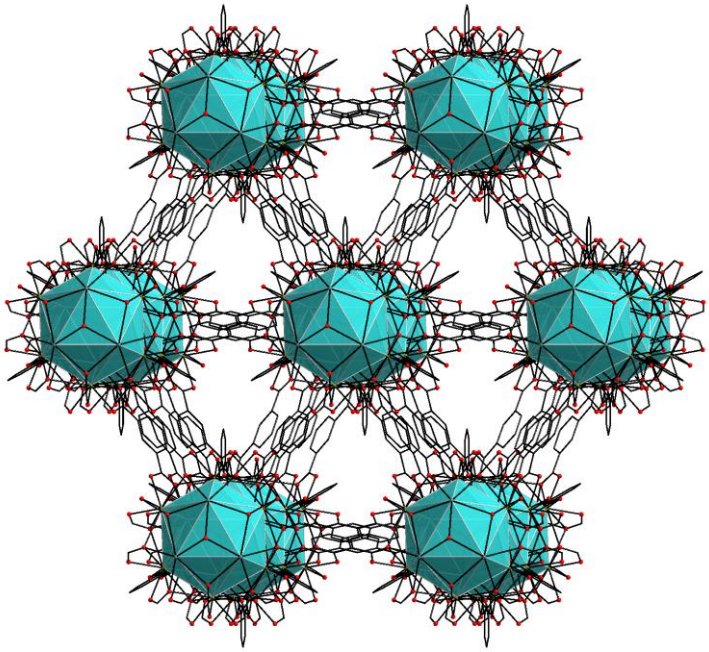
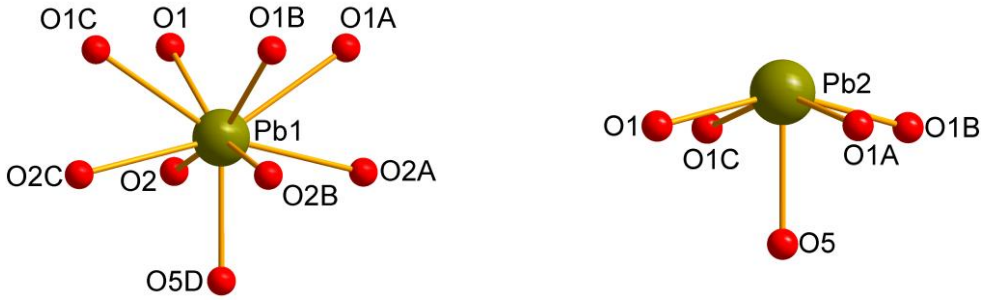


Fig. S4 View of the 3-D framework of **1**.



(a) (b)

Fig. S5 (a) The geometry of $Pb1O_9$ polyhedron in **4** and (b) the geometry of $Pb2O_5$ polyhedron in **4**.

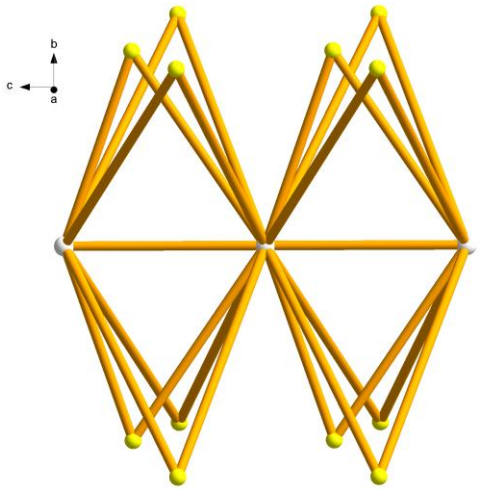


Fig. S6 The attended mode of the selected node in the topological network of **4**.

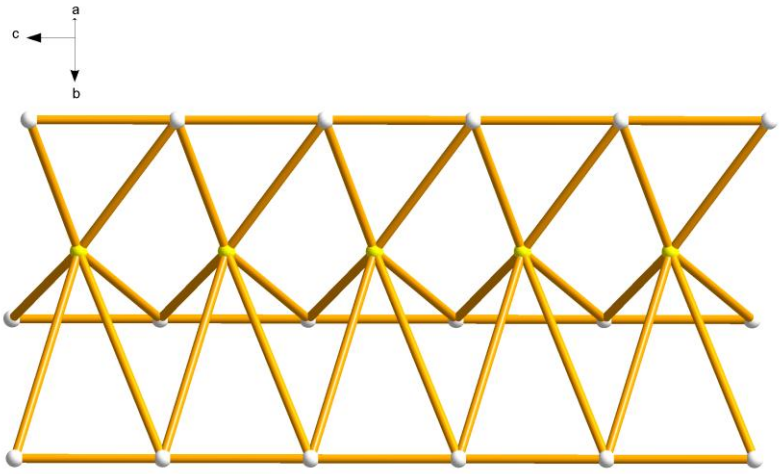
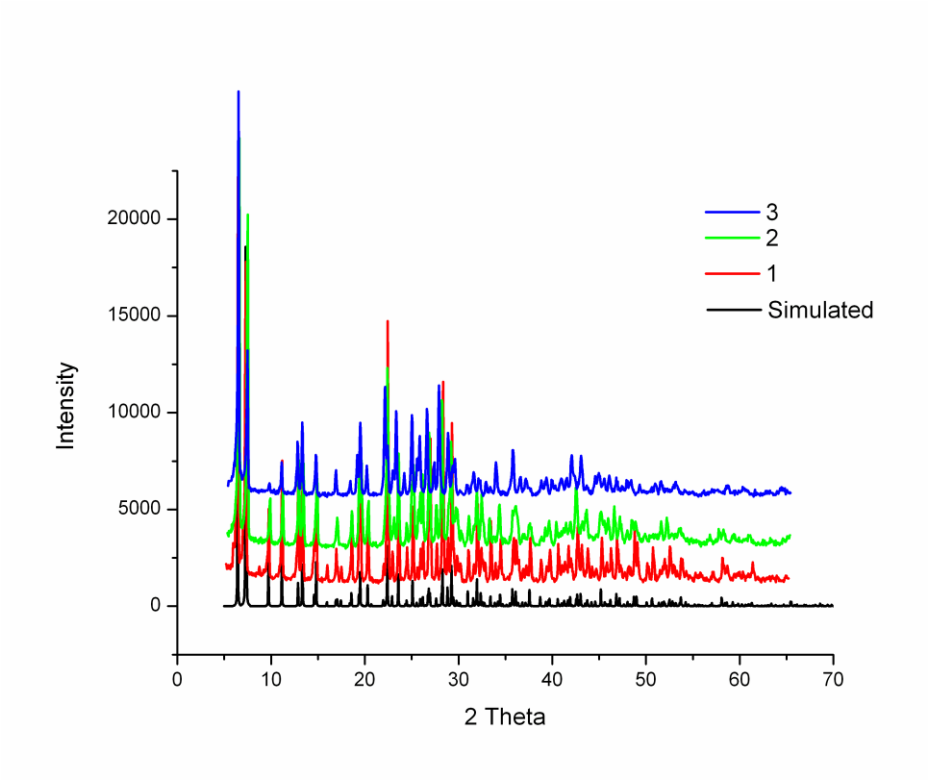
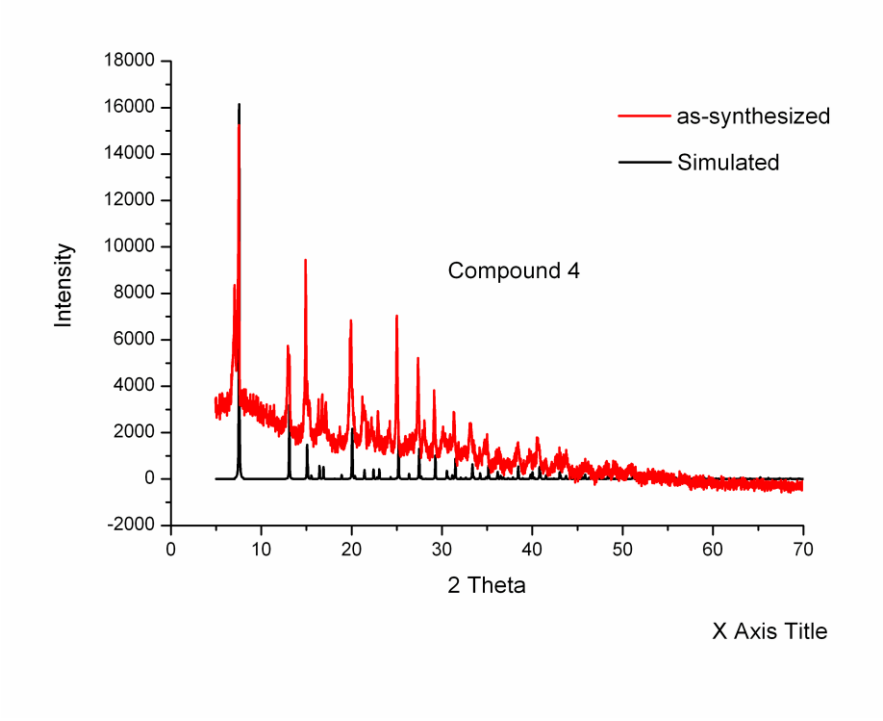


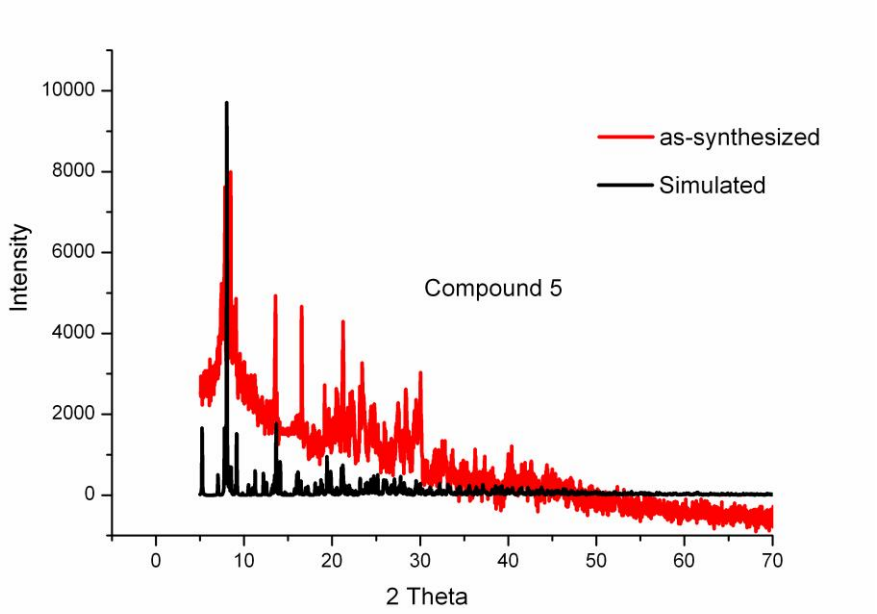
Fig. S7 The attended mode of the sulfur atom in the topological network of **4**.



(a)

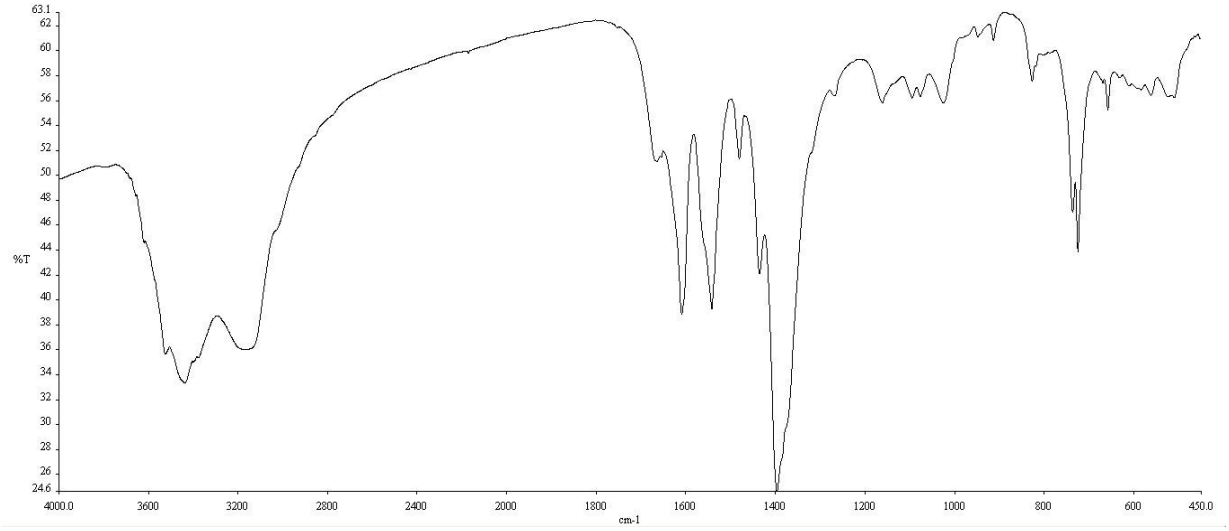


(b)

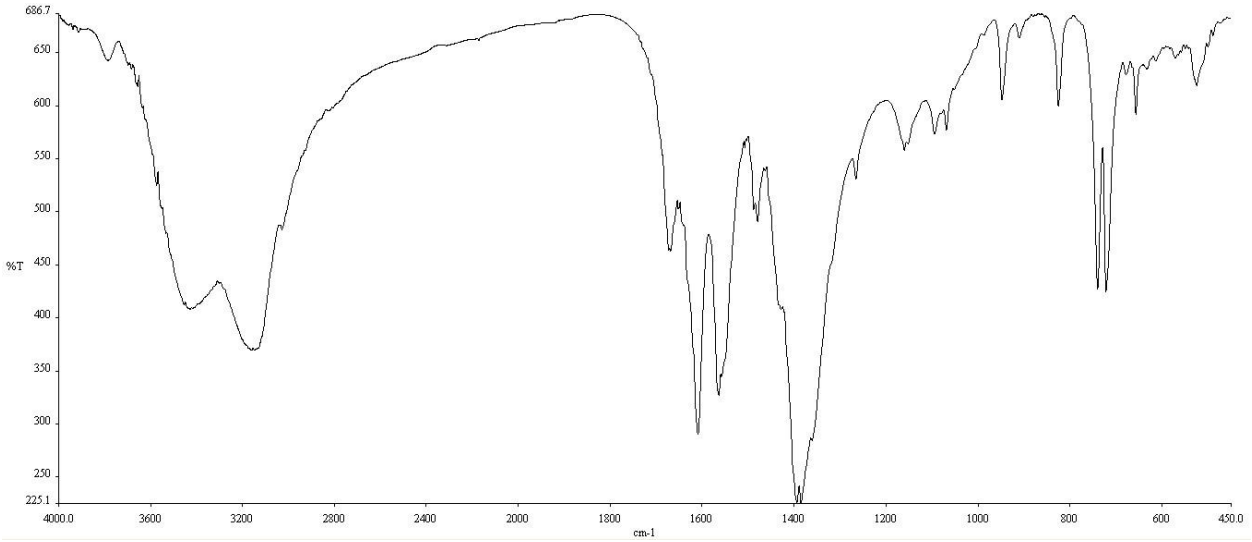


(c)

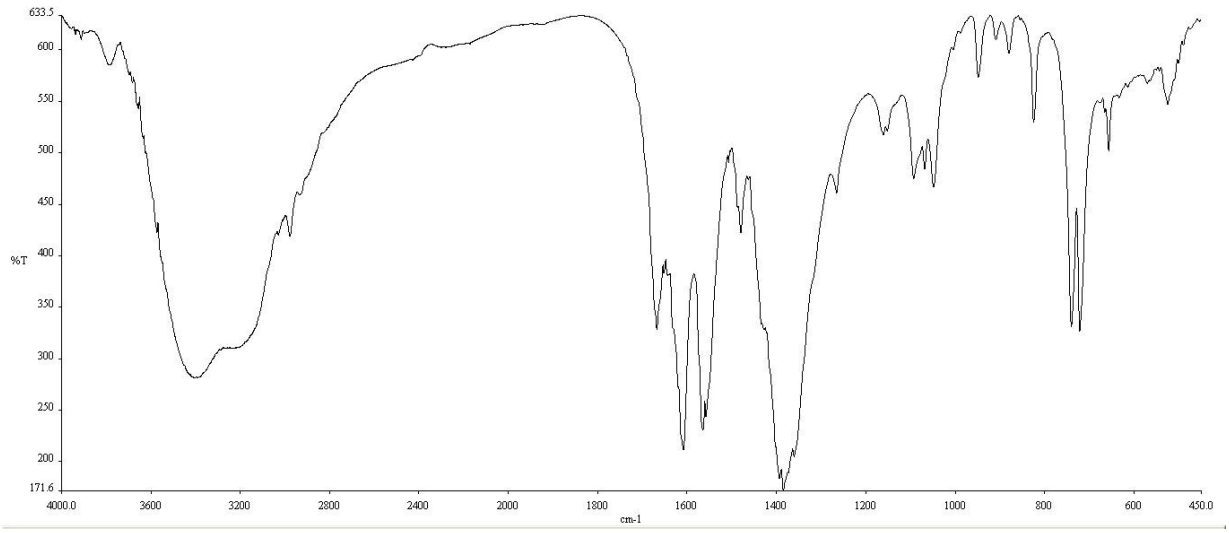
Fig. S8 The powder X-ray diffraction patterns for compounds **1**–**5**.



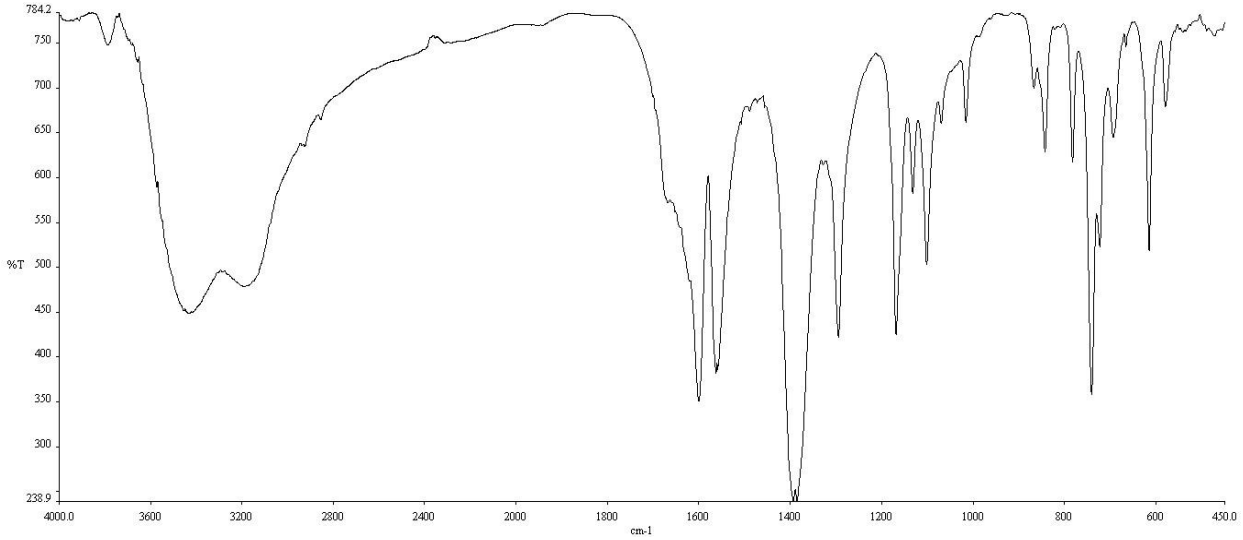
Compound **1**



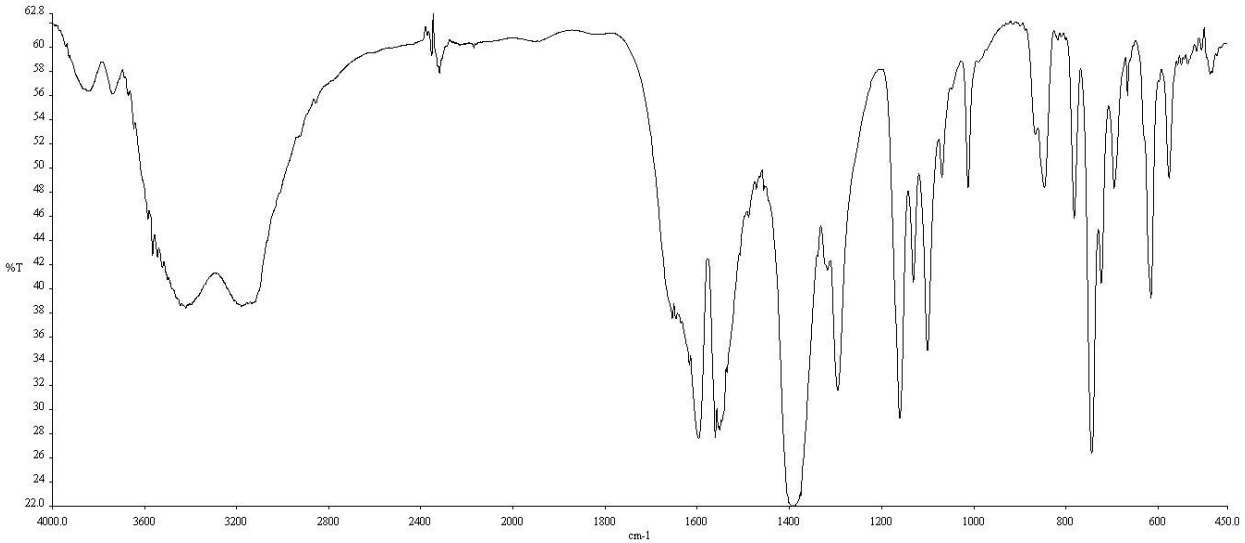
Compound **2**



Compound **3**

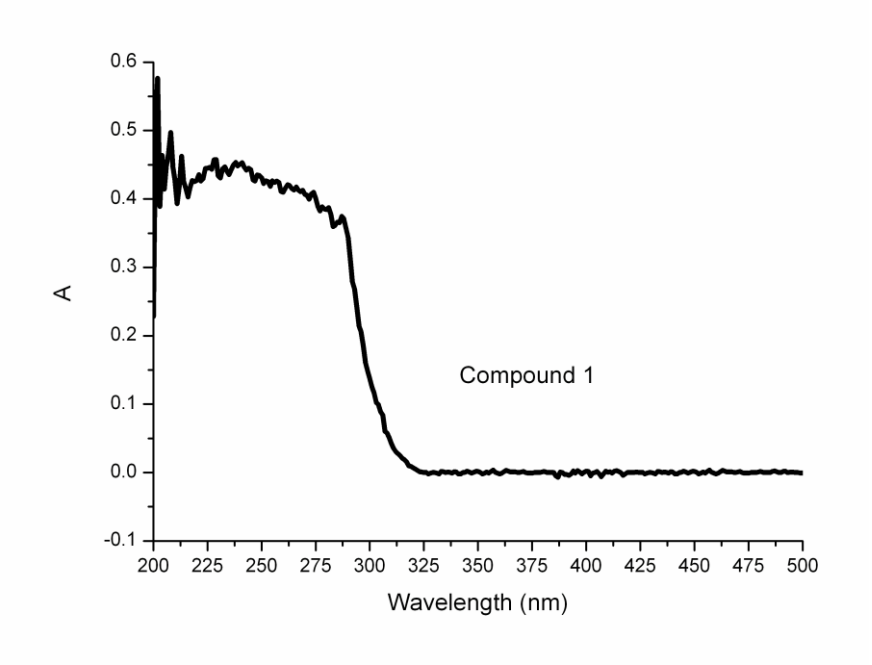


Compound **4**

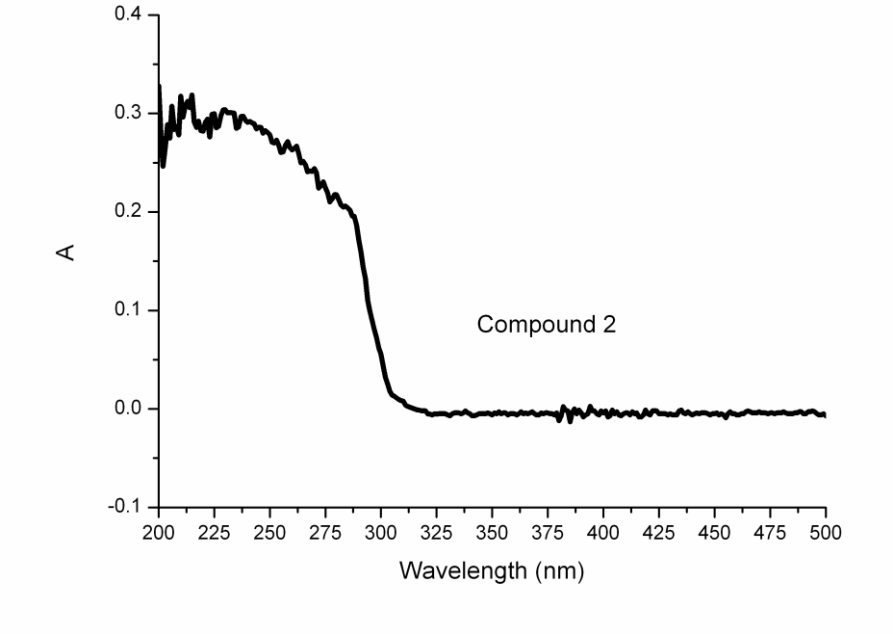


Compound **5**

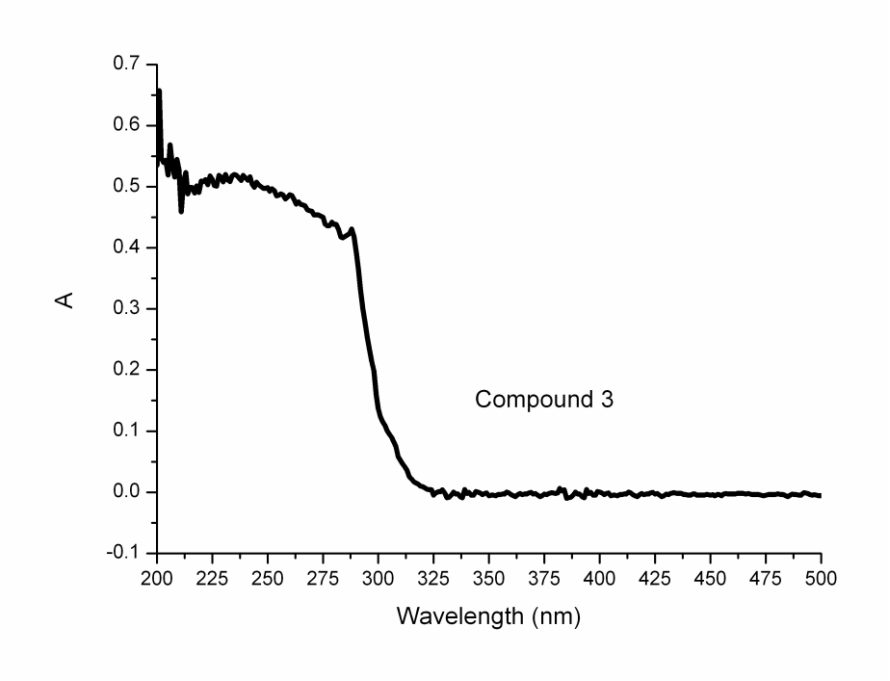
Fig. S9 IR spectra of compounds **1**–**5**.



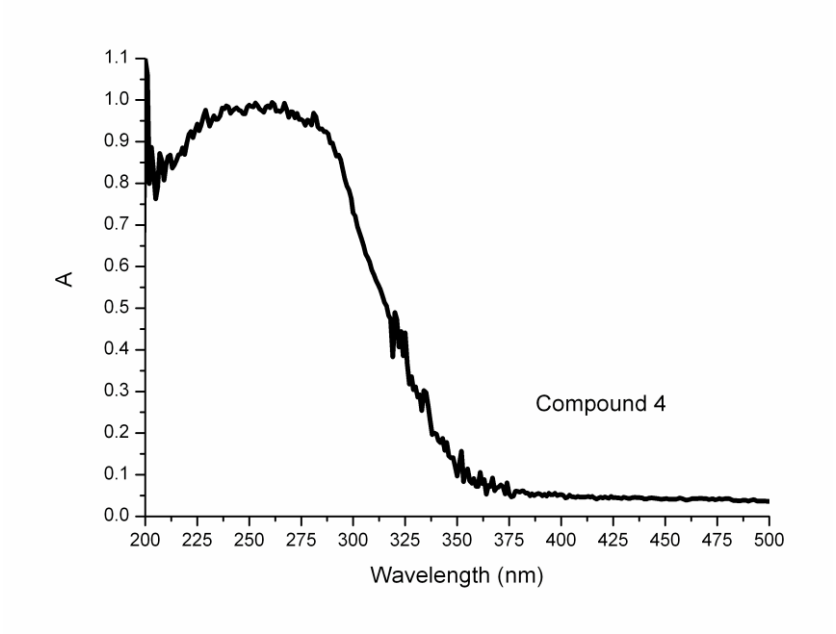
(a)



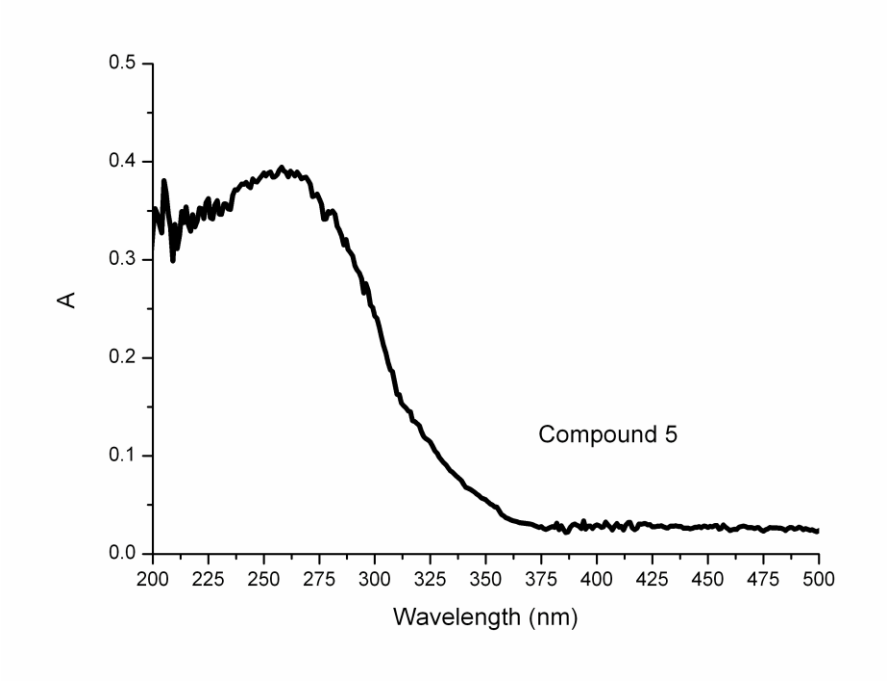
(b)



(c)

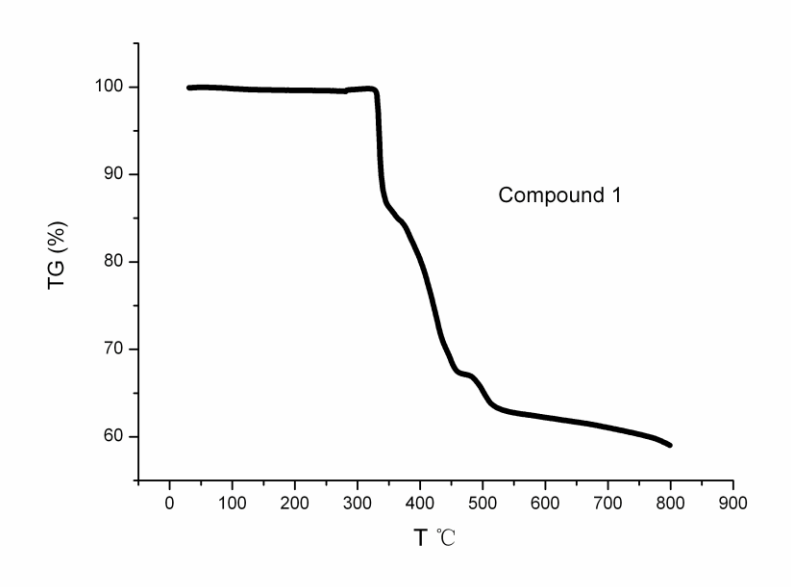


(d)

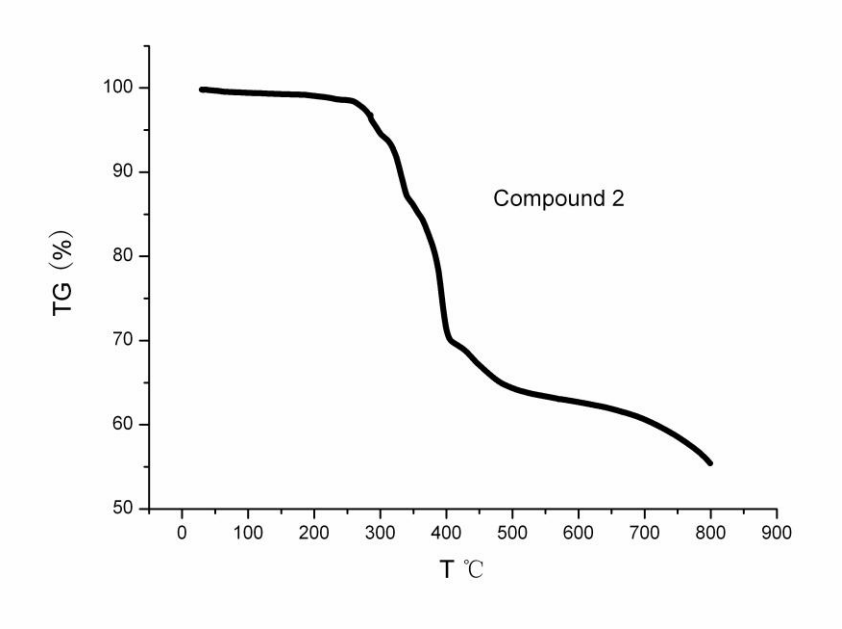


(e)

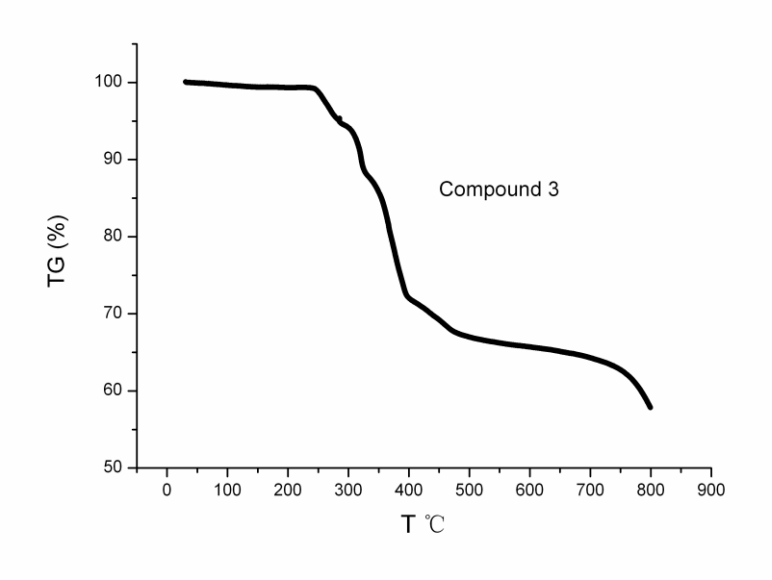
Fig. S10 The UV absorption spectra for compounds **1**–**5**.



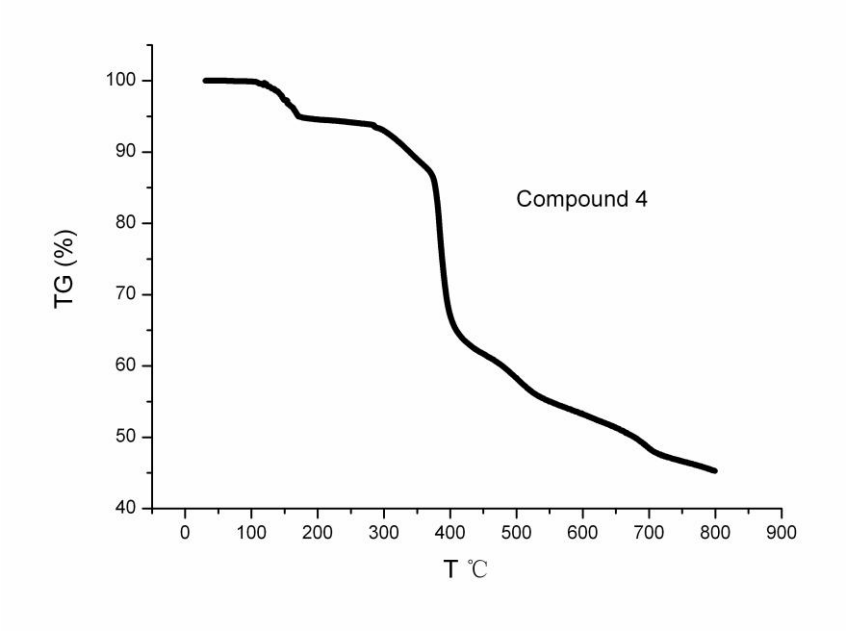
(a)



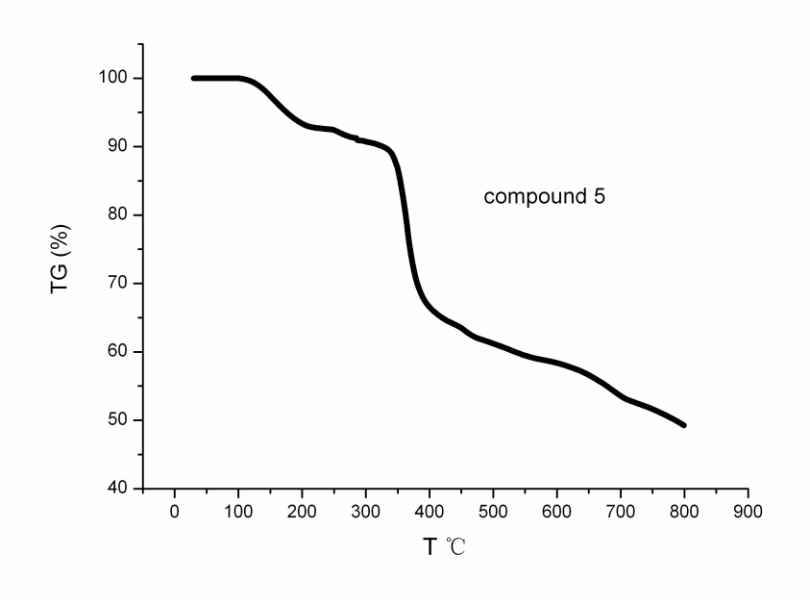
(b)



(c)



(d)



(e)

Fig. S11 TGA curves for compounds **1**–**5**.