Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Retention of Single Crystals of Two Co(II) Complexes During Chemical Reactions and Rearrangement

Shaikh M. Mobin* **and Akbar Mohammad**

Discipline of Chemistry, School of Basic Sciences, Indian Institute of Technology Indore, Khandwa Road, Indore 452017, India. Tel: +91 731 2438 762; E-mail: xray@iiti.ac.in

Table S1. Selected Bond Lengths (Å) and Bond Angles (°) for all complexes

Selected Bond Distance (Å) for [1]SO_4	
Co(1)-O(1)	2.063(3)
Co(1)-O(5)	2.074(2)
Co(1)-O(4)	2.106(3)
Co(1)-O(3)	2.113(3)
Co(1)-N(1)	2.123(2)
Co(1)-O(2)	2.131(3)
Selected Bond Angles (°) for [1]SO_4	
O(1)-Co(1)-O(5)	90.29(12)
O(1)-Co(1)-O(4)	91.52(12)
O(5)-Co(1)-O(4)	87.78(11)
O(1)-Co(1)-O(3)	176.89(13)
O(5)-Co(1)-O(3)	91.33(11)
O(4)-Co(1)-O(3)	91.19(9)
O(1)-Co(1)-N(1)	87.84(12)
O(5)-Co(1)-N(1)	177.17(15)
O(4)-Co(1)-N(1)	90.15(12)
O(3)-Co(1)-N(1)	90.64(11)
O(1)-Co(1)-O(2)	92.16(11)
O(5)-Co(1)-O(2)	87.16(11)
O(4)-Co(1)-O(2)	173.76(11)
O(3)-Co(1)-O(2)	85.28(11)
N(1)-Co(1)-O(2)	95.03(12)
Selected Bond Distance (Å) for 3	
Co(1)-O(6)#1	2.080(5)

Co(1)-O(2)	2.106(6)
Co(1)-O(4)	2.108(6)
Co(1)-O(3)	2.111(5)
Co(1)-O(1)	2.113(5)
Co(1)-N(1)	2.132(6)
Selected Bond Angles (°) for 3	
O(6)#1-Co(1)-O(2)	83.8(2)
O(6)#1-Co(1)-O(4)	90.6(2)
O(2)-Co(1)-O(4)	174.2(2)
O(6)#1-Co(1)-O(3)	93.11(19)
O(2)-Co(1)-O(3)	87.7(2)
O(4)-Co(1)-O(3)	91.2(2)
O(6)#1-Co(1)-O(1)	175.0(2)
O(2)-Co(1)-O(1)	93.3(2)
O(4)-Co(1)-O(1)	92.2(2)
O(3)-Co(1)-O(1)	82.70(19)
O(6)#1-Co(1)-N(1)	94.1(2)
O(2)-Co(1)-N(1)	87.9(2)
O(4)-Co(1)-N(1)	94.0(2)
O(3)-Co(1)-N(1)	171.0(2)
O(1)-Co(1)-N(1)	89.8(2)
Symmetry transformations used to generate equivalent atoms:#1 -x+1,-y,-z+2	
Selected Bond Distance (Å) for [5]SO_4	
Co(2)-O(10)#1	2.052(3)
Co(2)-O(10)	2.052(3)

Co(2)-O(8)	2.095(3)
Co(2)-O(8)#1	2.095(3)
Co(2)-O(9)	2.100(3)
Co(2)-O(9)#1	2.100(3)
Co(1)-O(2)#2	2.069(3)
Co(1)-O(2)	2.069(3)
Co(1)-O(1)	2.074(3)
Co(1)-O(1)#2	2.074(3)
Co(1)-O(3)	2.110(3)
Co(1)-O(3)#2	2.110(3)
Selected Bond Angles (°) for [5]SO_4	
O(10) -Co(2)-O(10)#1	180.0(12)
O(10)#1-Co(2)-O(8)	88.19(13)
O(10)-Co(2)-O(8)	91.81(13)
O(10)#1-Co(2)-O(8)#1	91.81(13)
O(10)-Co(2)-O(8)#1	88.19(13)
O(8)-Co(2)-O(8)#1	180.0(19)
O(10)#1-Co(2)-O(9)	87.84(15)
O(10)-Co(2)-O(9)	92.16(15)
O(8)-Co(2)-O(9)	85.20(12)
O(8)#1-Co(2)-O(9)	94.80(12)
O(10)#1-Co(2)-O(9)#1	92.16(15)
O(10)-Co(2)-O(9)#1	87.84(15)
O(8)-Co(2)-O(9)#1	94.80(12)
O(8)#1-Co(2)-O(9)#1	85.20(12)
O(9)-Co(2)-O(9)#1	180.00(18)

O(2)#2-Co(1)-O(2)	179.21(17)
O(2)#2-Co(1)-O(1)	92.70(12)
O(2)-Co(1)-O(1)	87.85(12)
O(2)#2-Co(1)-O(1)#2	87.85(12)
O(2)-Co(1)-O(1)#2	92.70(12)
O(1)-Co(1)-O(1)#2	90.46(18)
O(2)#2-Co(1)-O(3)	92.87(12)
O(2)-Co(1)-O(3)	86.57(13)
O(1)-Co(1)-O(3)	89.93(12)
O(1)#2-Co(1)-O(3)	179.17(12)
O(2)#2-Co(1)-O(3)#2	86.57(12)
O(2)-Co(1)-O(3)#2	92.87(12)
O(1)-Co(1)-O(3)#2	179.17(12)
O(1)#2-Co(1)-O(3)#2	89.93(12)
O(3)-Co(1)-O(3)#2	89.70(16)
Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z #2 -x+1,y,-z+1/2	
Selected Bond Distance (Å) for [2]$(NO_3)_2$	
Co(1)-O(1)	2.0897(12)
Co(1)-O(2)	2.1081(12)
Co(1)-N(1)	2.1489(14)
Selected Bond Angles (°) for [2]$(NO_3)_2$	
O(1)#1-Co(1)-O(1)	180.0
O(1)-Co(1)-O(2)	89.25(5)
O(1)#1-Co(1)-O(2)#1	89.25(5)
O(1)-Co(1)-O(2)#1	90.75(5)

O(1)#1-Co(1)-O(2)	90.75(5)
O(2)#1-Co(1)-O(2)	180.000(1)
O(1)#1-Co(1)-N(1)	92.41(5)
O(1)-Co(1)-N(1)	87.59(5)
O(2)-Co(1)-N(1)	89.83(5)
Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z+2	
Selected Bond Distance (Å) for [4]NO_3	
N(1)-Co(1)	2.076(6)
N(2)-Co(1)	2.101(5)
O(1)-Co(1)	2.035(5)
O(2)-Co(1)	2.021(5)
O(3)-Co(1)	2.139(5)
O(4)-Co(1)	2.208(5)
Selected Bond Angles (°) for [4]NO_3	
N(1)-Co(1)-N(2)	175.8(3)
O(1)-Co(1)-N(1)	89.0(2)
N(3)-O(3)-Co(1)	92.9(5)
N(3)-O(4)-Co(1)	90.2(5)
O(2)-Co(1)-O(3)	95.2(2)
O(3)-Co(1)-O(4)	59.70(19)
O(1)-Co(1)-O(4)	108.1(2)
O(2)-Co(1)-O(1)	97.1(2)
O(1)-Co(1)-O(3)	167.5(2)
N(1)-Co(1)-O(4)	87.0(2)
N(1)-Co(1)-O(3)	92.5(2)

N(2)-Co(1)-O(3)	90.2(2)
O(1)-Co(1)-N(2)	87.7(2)
N(1)-Co(1)-O(4)	87.0(2)
N(2)-Co(1)-O(4)	91.5(2)
O(2)-Co(1)-N(1)	92.3(2)

Table S2. Hydrogen Bonding [Å and (°)].

	D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
			[1]SO_4		
1	O3-H333...O6# (0)	0.857(.026)	1.899(.029)	2.674(.004)	149.47(2.38)
2	O2-H111...O9 #(1)	0.883(.037)	1.892(.038)	2.730(.004)	157.97(3.34)
3	O2-H222...O8# (2)	0.882(.048)	1.841(.047)	2.709(.004)	167.70(4.47)
Equivalent positions: (0) x,y,z (1) -x,+y-1/2,-z+1 (2) -x,+y+1/2,-z+1					
			3		
1	O1 -H101...O5#(0)	0.893(.084)	1.873(.075)	2.749(.008)	166.23(6.94)
2	O2-H444...O7#(0)	0.895(.122)	1.824(.126)	2.718(.010)	176.98(8.82)
Equivalent positions: (0) -x+1,-y,-z+1					

[2]$(NO_3)_2$

1	O2-H103...O3#(0)	0.797(.020)	1.984(.020)	2.779(.002)	174.97(2.68)
2	O2-H102...O4 #(1)	0.851(36)	1.909(35)	2.757(3)	173.7(312)
3	O1-H101…O5#(2)	0.796(30)	1.910(31)	2.703(8)	173.69(260)

Equivalent positions:

(0) x,y,z

(1) 3-x, -y, 2-z

(2) 3-x, 1-y, 2-z

[4]NO_3

1	O1-H101...O6 #(0)	0.750(.058)	1.949(.058)	2.698(.008)	176.46(6.04)
2	O2-H102...O8#(1)	0.877(.070)	1.874(.069)	2.700(.008)	156.43(6.52)
3	C7-H7A...O7#(2)	0.990(.008)	2.559(.005)	3.393(.009)	141.86(0.46)
4	C3-H3...O7#(3)	0.950(.010)	2.588(.005)	3.526(.011)	169.27(0.61)

Equivalent positions:

(0) x,y,z

(1) -x-1/2,+y+1/2,+z

(2) -x,+y,-z+1/2

(3) -x,+y+1,-z+1/2

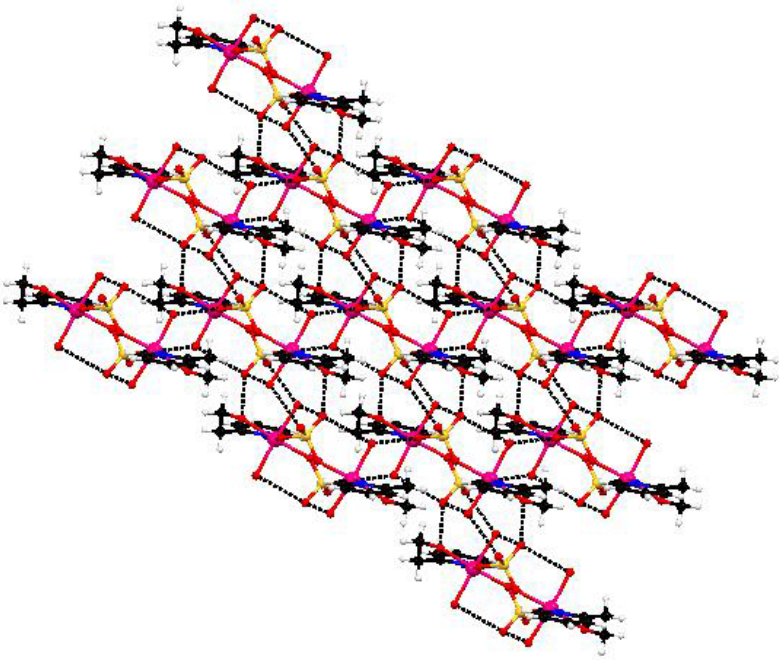
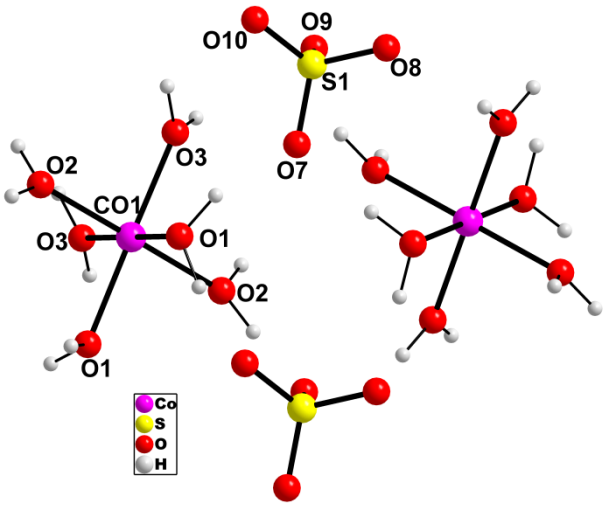


Fig. S1 Hydrogen bonded 2D-network in **3** along the *c*-axis.

(a)



(b)

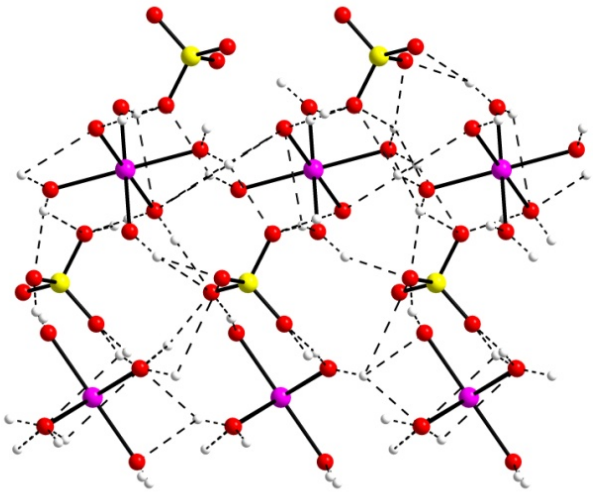


Fig. S2 (a) Perspective view of **[5]**SO_4 in asymmetric unit **(b)[5]**SO_4showing H-bonded network along *b*-axis.

[5]SO_4 crystallizes monoclinic *C 2/c* space group with crystallographically imposed inversion centre. Co^{II} ion in **[5]**SO_4 consists of successive layers of hexa-aqua coordinated octahedral geometry as cation and independent tetrahedra sulfate ions as anion. Although the crystal structure of **[5]**SO_4 is reported but we could able to generate it by SCSC transformation of **3**. All the bond distances and angles in **[5]**SO_4 are similar to reported (Fig. S2a and S2b).

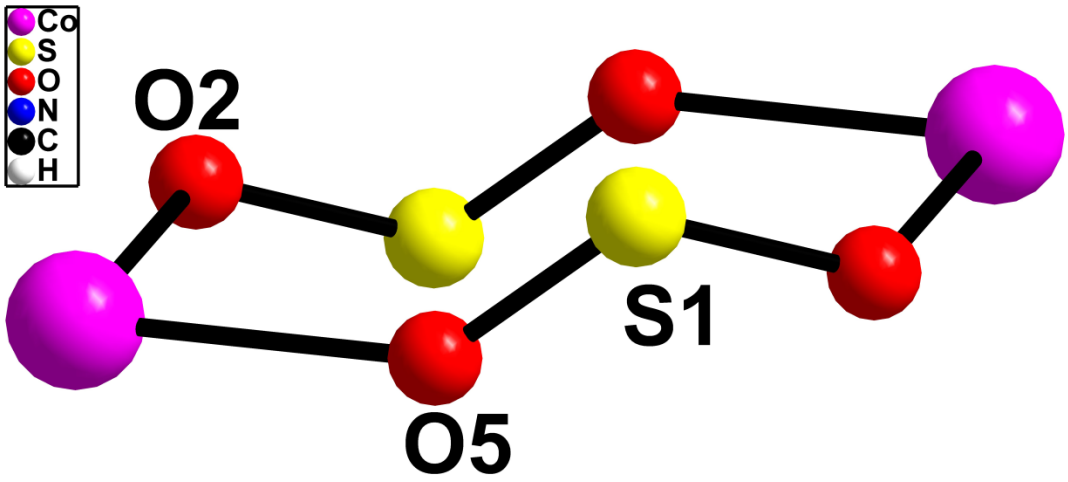


Fig. S3 8-membered metallacyclic ring in **3**.

IR spectra

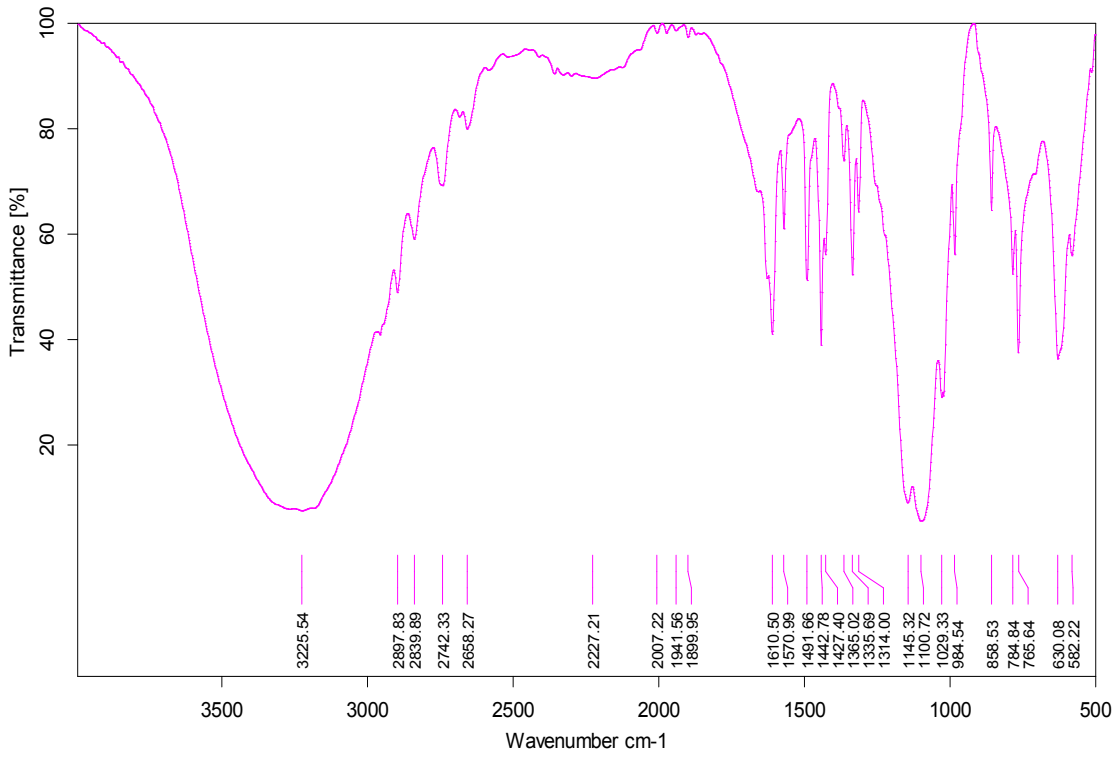


Fig. S4 IR spectra of **[1]**SO_4 (Orange crystals) in KBr disk.

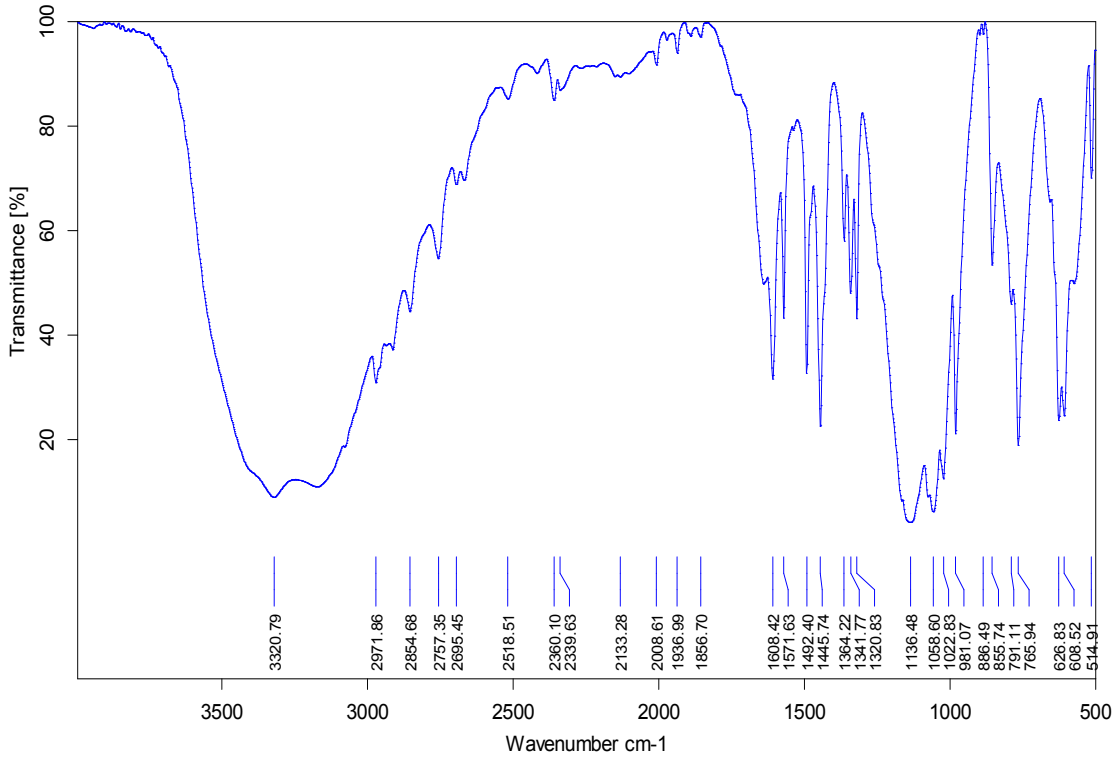


Fig. S5 IR spectra of **3**(Pink crystals) in KBr disk.

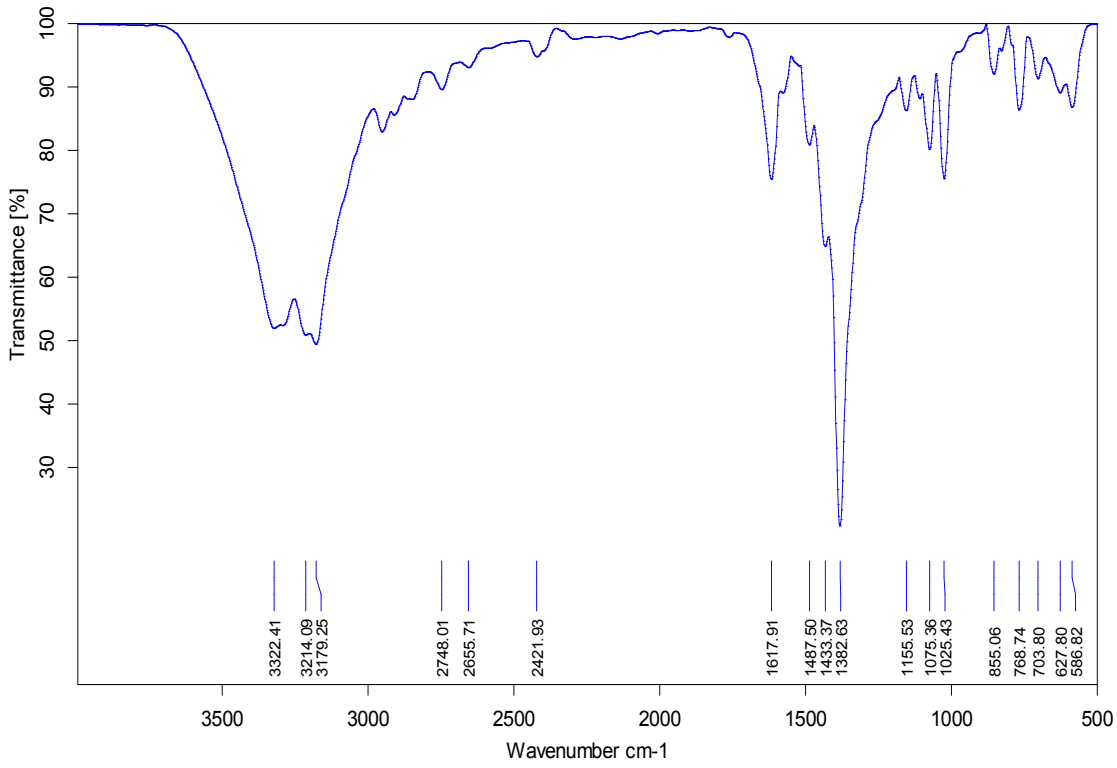


Fig. S6 IR spectra of **[2]**$(NO_3)_2$ (Orange crystals) in KBr disk.

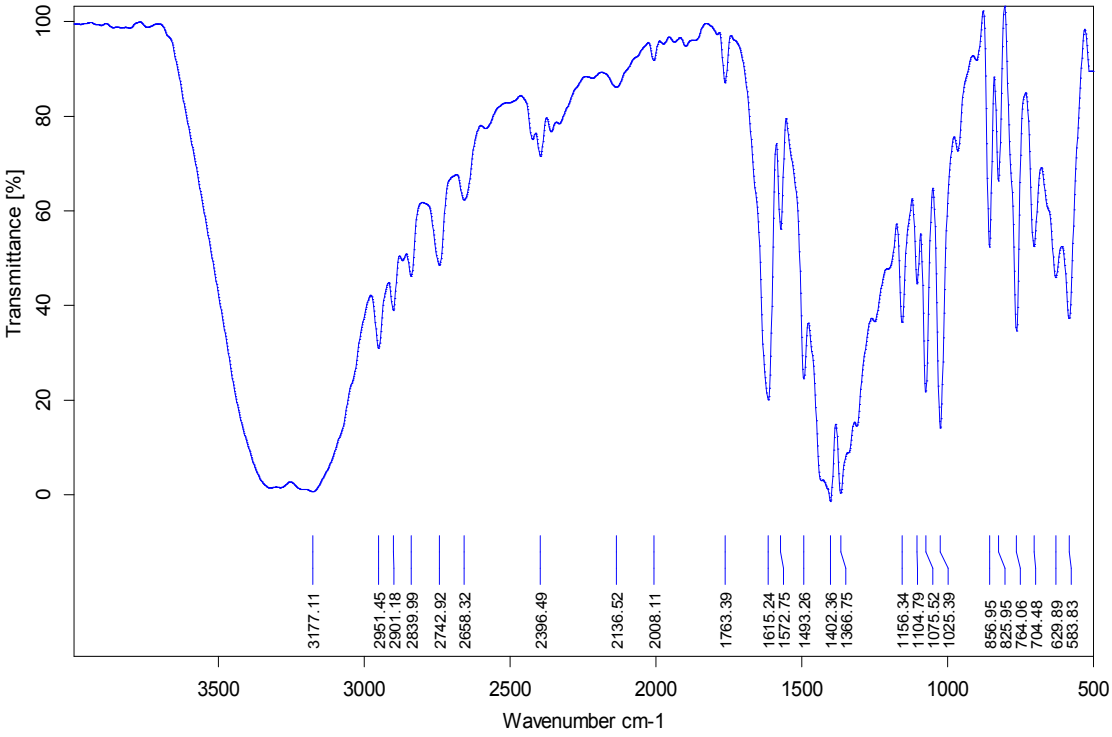


Fig. S7 IR spectra of **[4]**NO_3(Orange crystals) in KBr disk.

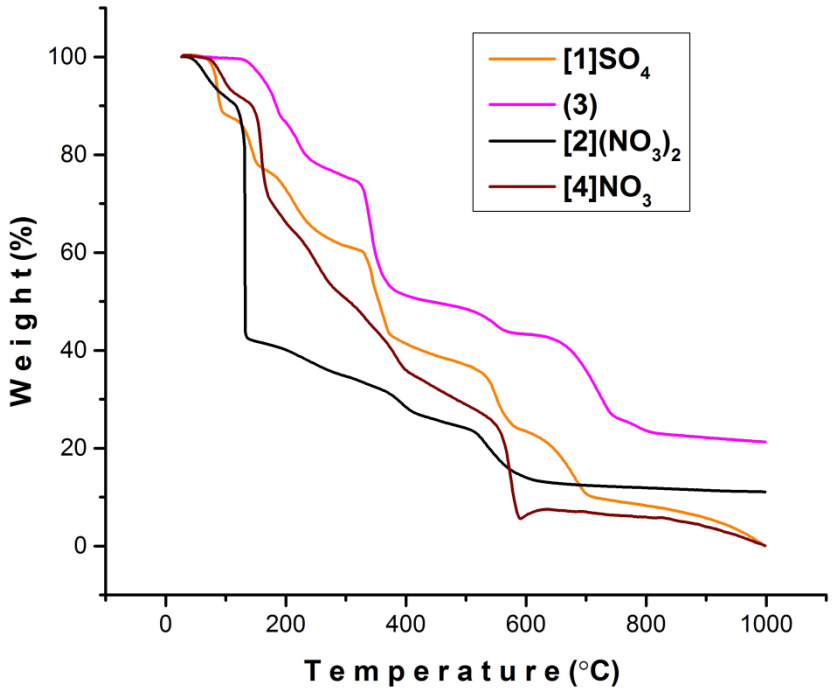


Fig. S8 TGA analysis of **[1]**SO_4/**(3)** /**[2]**$(NO_3)_2$/**[4]**NO_3).

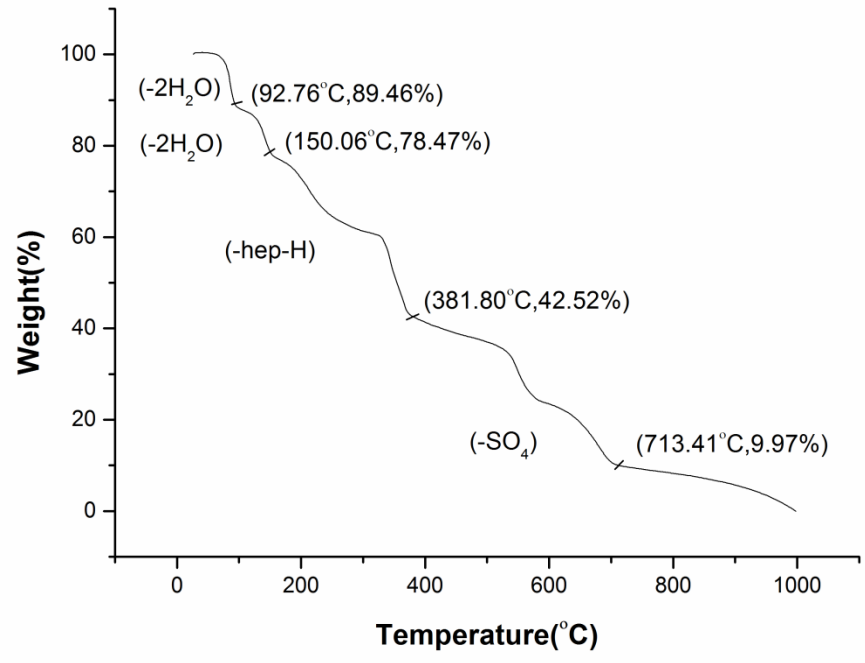


Fig. S9 TGA of **[1]**SO_4(Orange crystals).

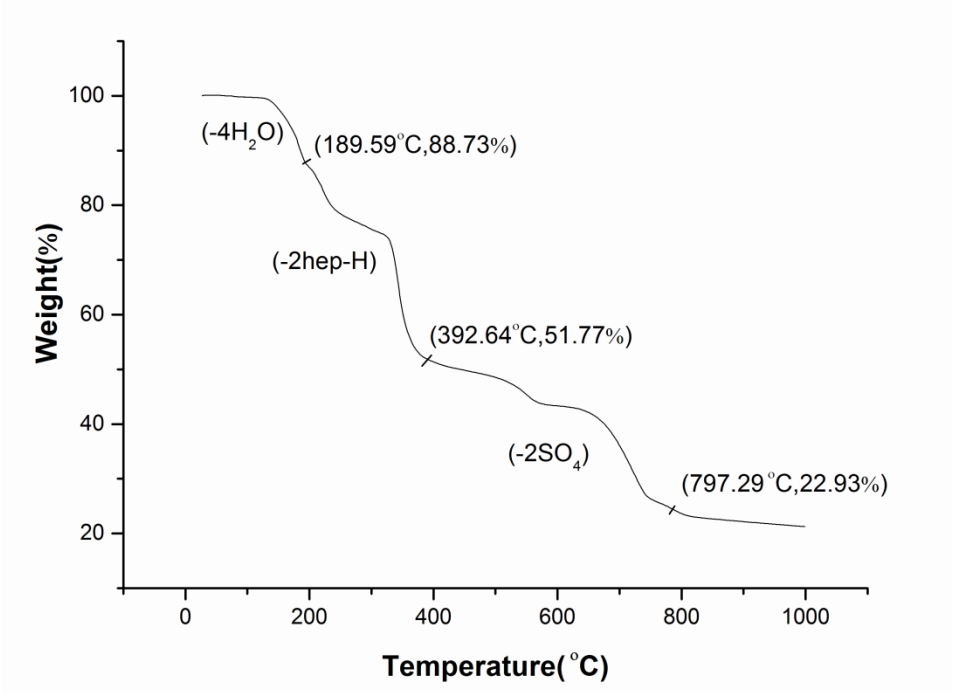


Fig. S10 TGA of **3**(Pink crystals).

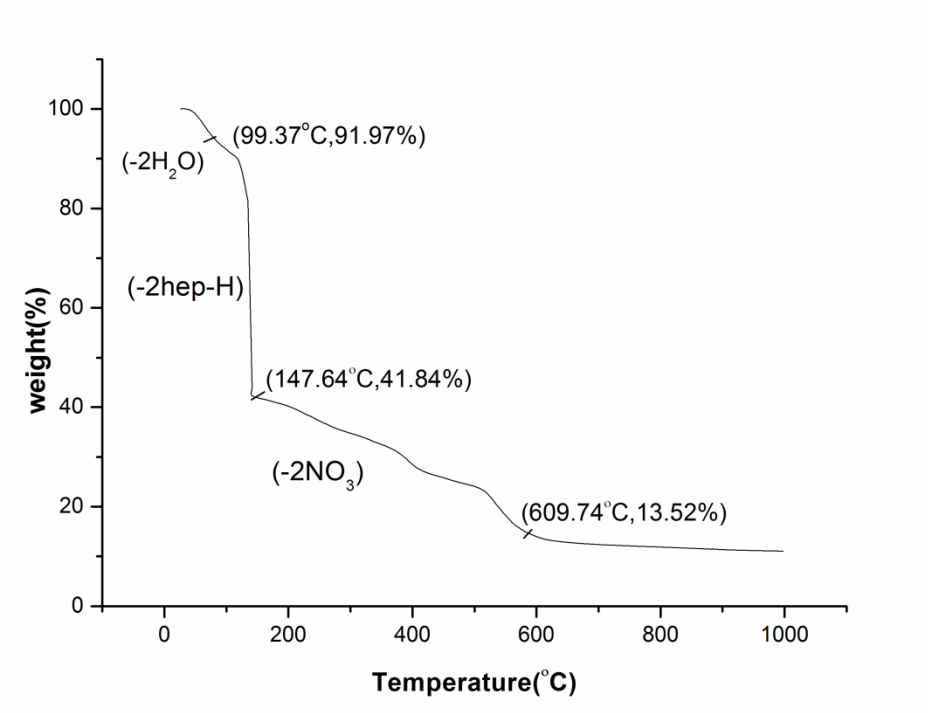


Fig. S11 TGA of **[2]**$(NO_3)_2$(Orange crystals).

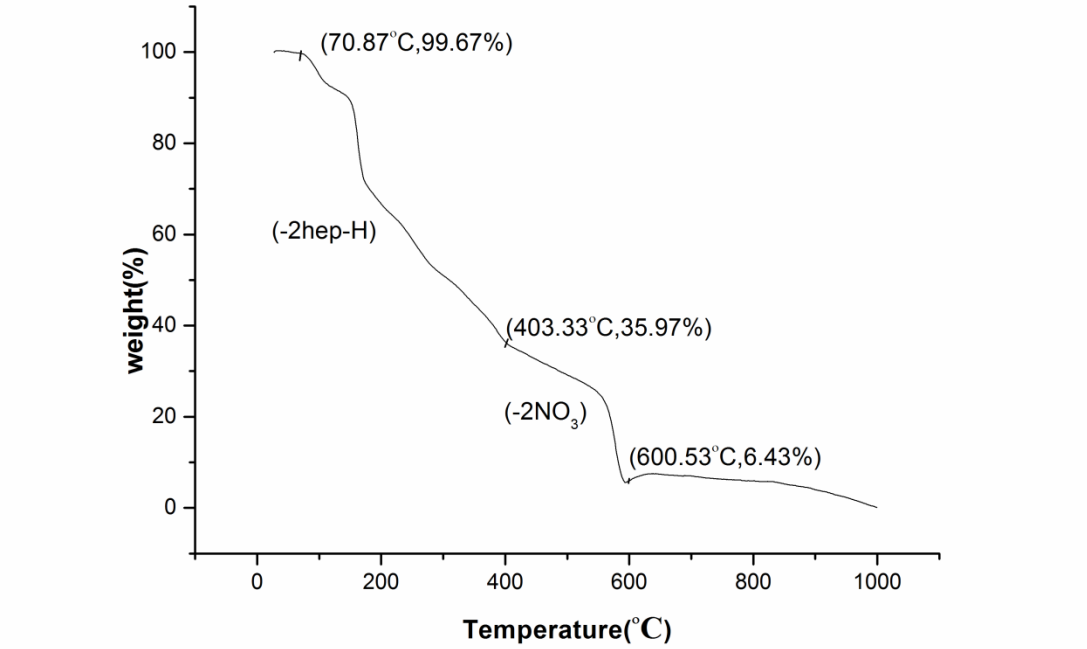
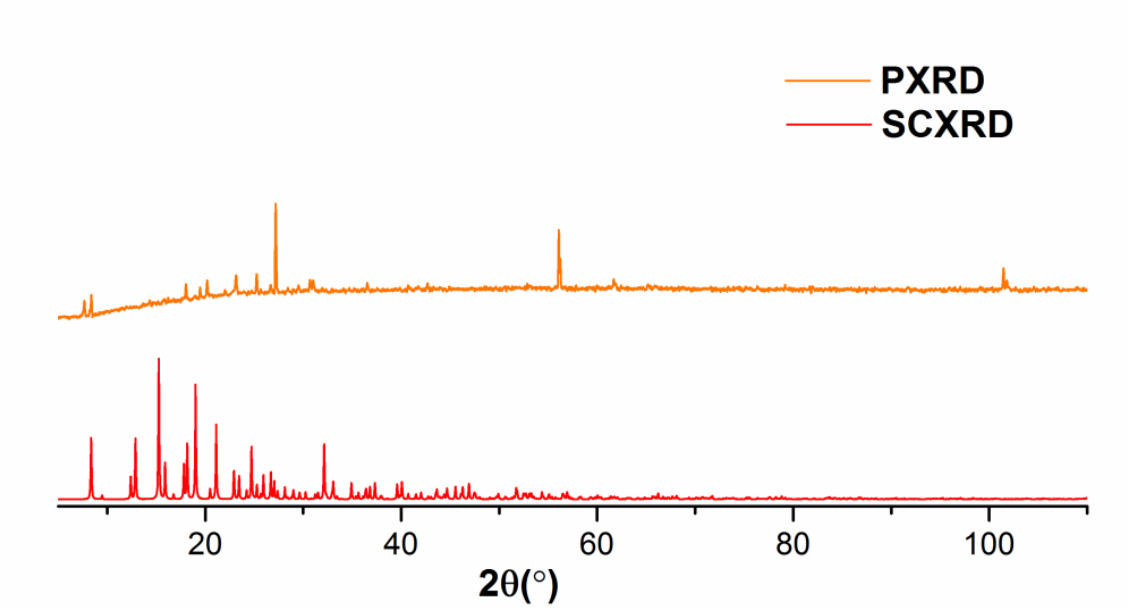


Fig. S12 TGA of **[4]**NO_3(Orange crystals).

(a)



(b)

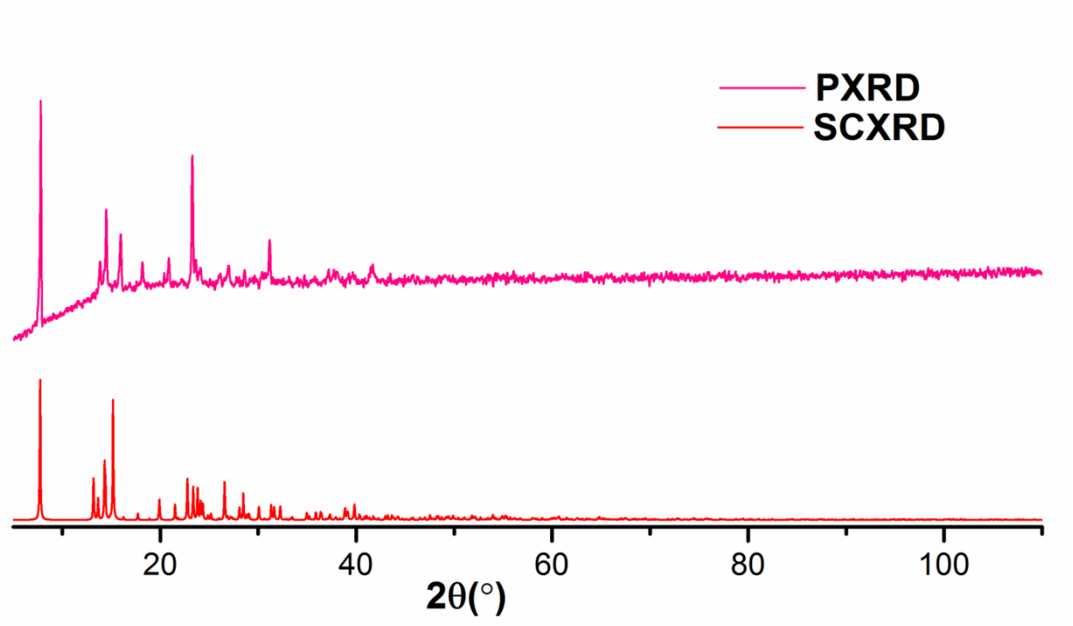
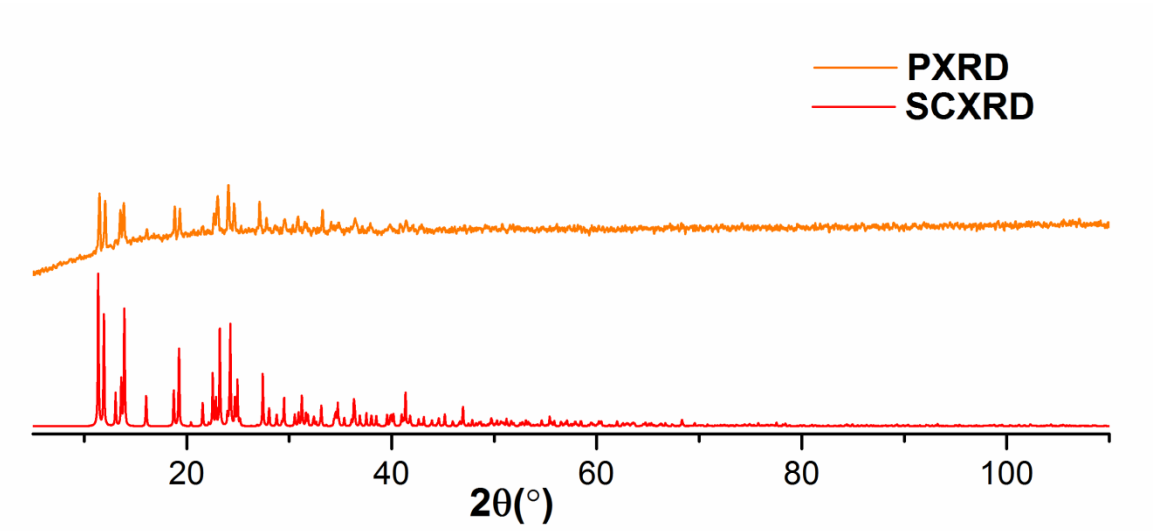


Fig. S13 (a) PXRD pattern of **[1]**SO_4(Orange crystals)(Orange colour) and simulated SCXRD pattern of **[1]**SO_4(Orange crystal)(Red colour).

(b)PXRD pattern of **3**(Pink crystals) (Pink colour)and simulated SCXRD pattern of **3** (Pink crystal)(Red colour).

(a)



(b)

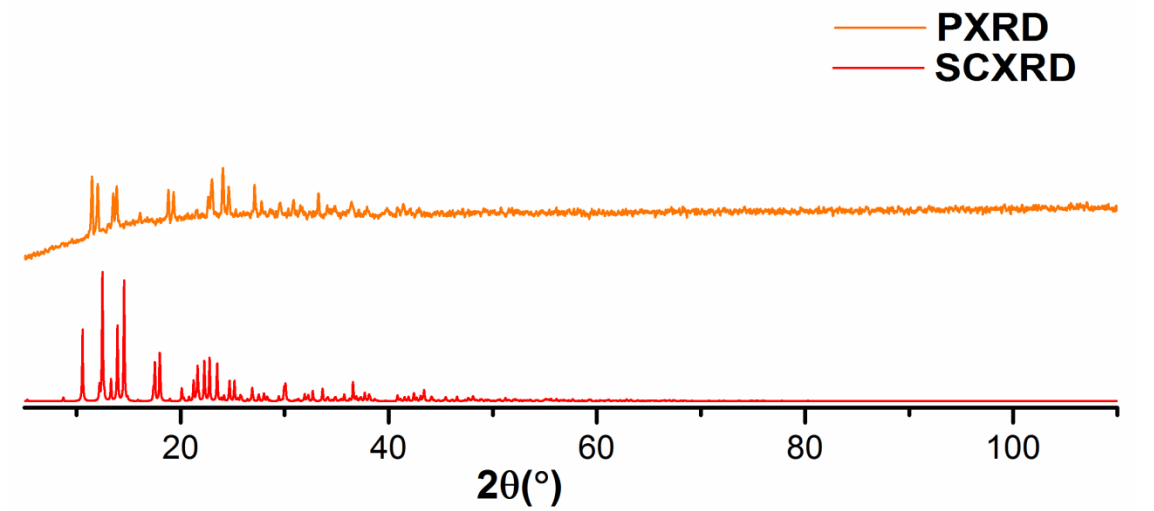


Fig. 14 (a) PXRD pattern of **[2]**$(NO_3)_2$ (Orange crystals)(Orange colour)and simulated SCXRD pattern of **[2]**$(NO_3)_2$ (Orange crystal)(Red colour).

(b) PXRD pattern of **[4]**NO_3(Orange crystals)(Orange colour) and simulated SCXRD pattern of **[4]**NO_3(Orange crystal)(Red colour).

Note

The PXRD for [**1**]SO_4/**3**/**[2]**$(NO_3)_2$/**[4]**NO_3 were performed on bulk single crystals as we could not able to generate polycrystalline or powder samples for the same, thus some shifts are observed in PXRD patterns.

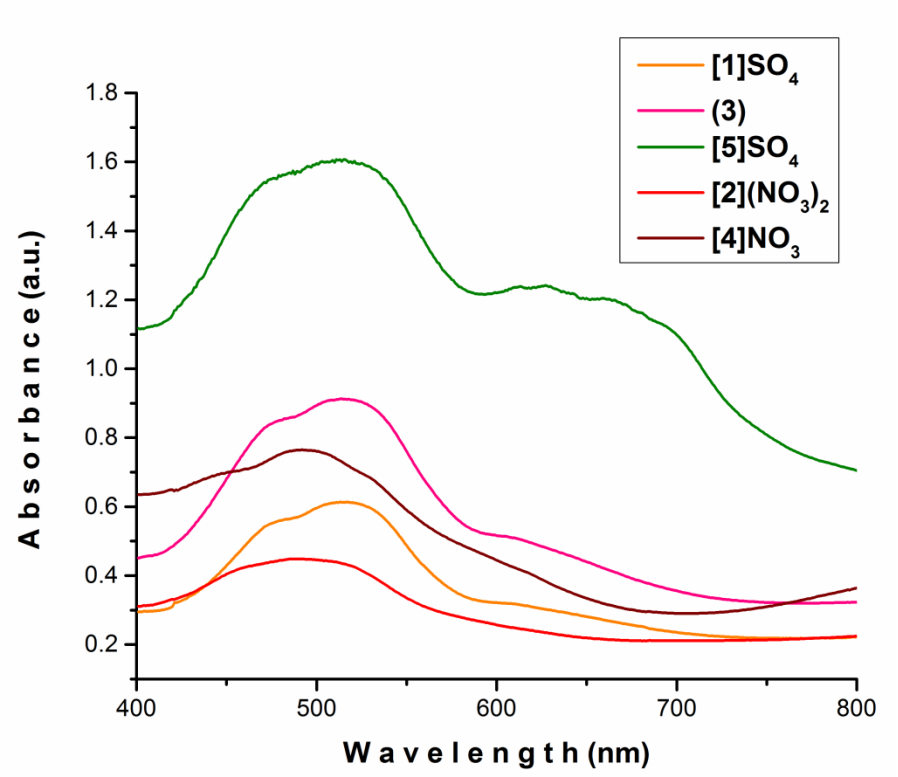


Fig. S15 Solid state UV-vis pattern of **[1]**SO_4/**3**/**[5]**SO_4/**[2]**$(NO_3)_2$/**[4]**NO_3.

The UV-Vis analysis shows the optical band gap of **[1]**SO_4/**3**/**[5]**SO_4/**[2]**$(NO_3)_2$/**[4]**NO_3, was found to be 1.79, 1.56, 1.44, 1.94 and 1.76 eV respectively.