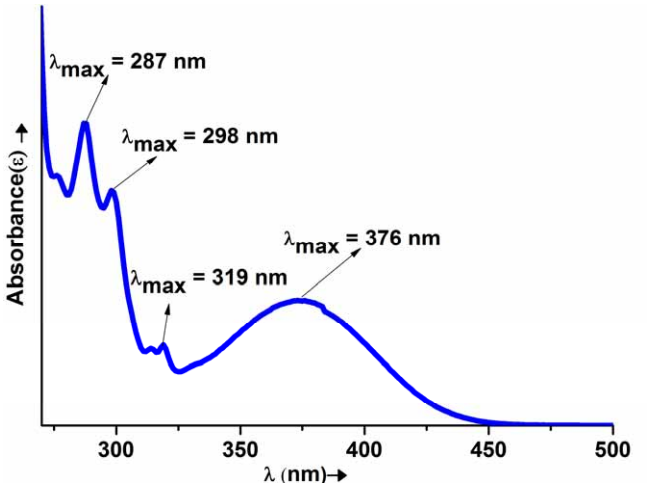
Supporting Information

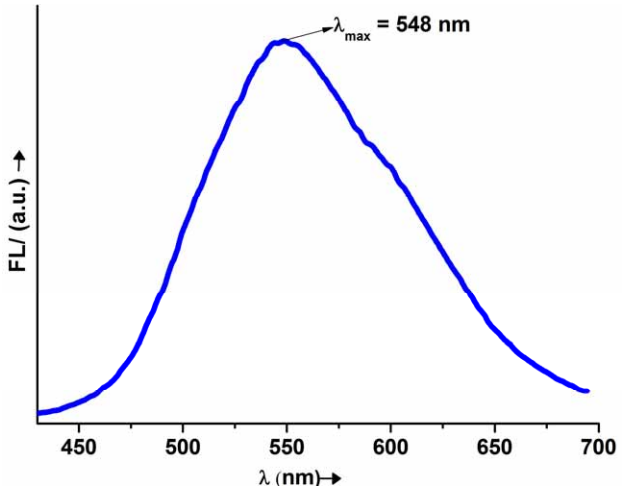
Reactions of in situ Generated Hydrated Organotin Cations with Chelating *O*,*O*- or *O*, *N*- Ligands: A Possible Structure-directing Influence of the Organic Substituent on Tin

Vadapalli Chandrasekhar, and Puja Singh*

Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur – 208016, India.



(a)



(b)

Figure S1(a). UV-visble absorption spectrum of methanol solution of **6** (10^{-6} M). **(b)** Fluorescence emission spectra of **6** in methanol (10^{-6} M)

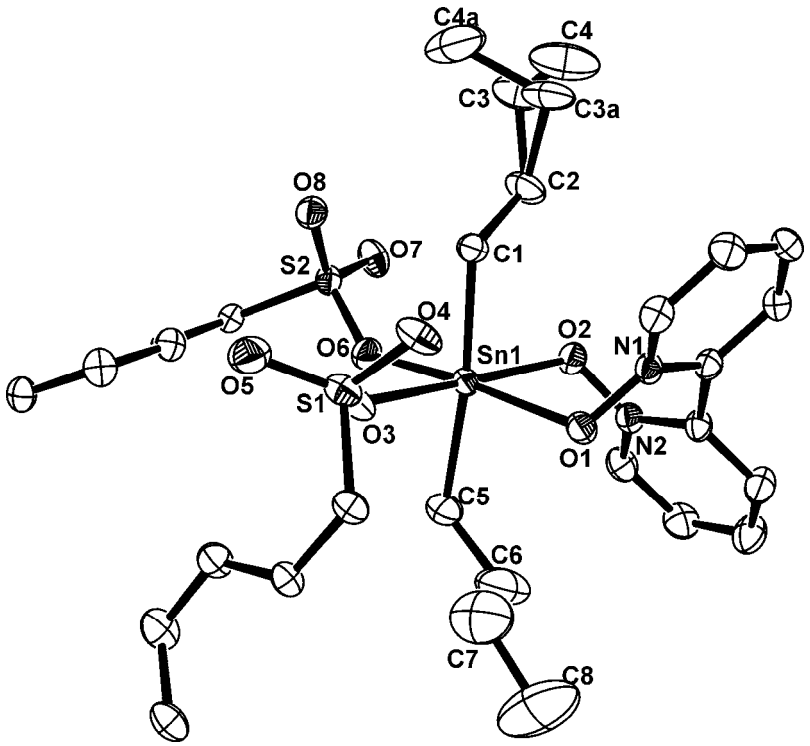
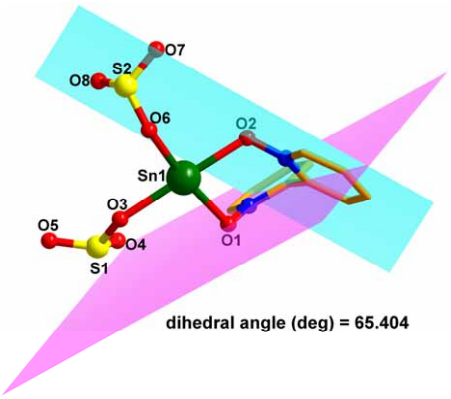
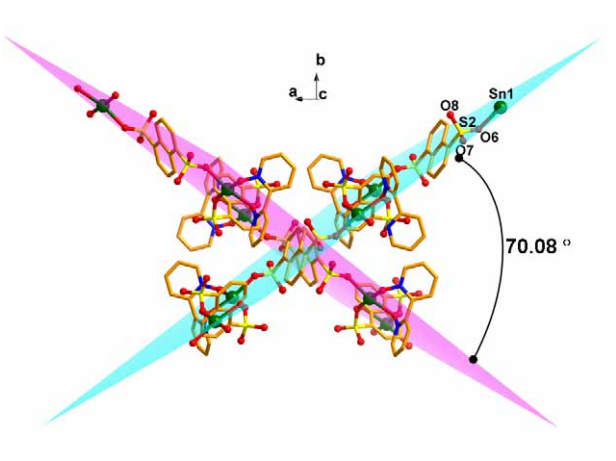


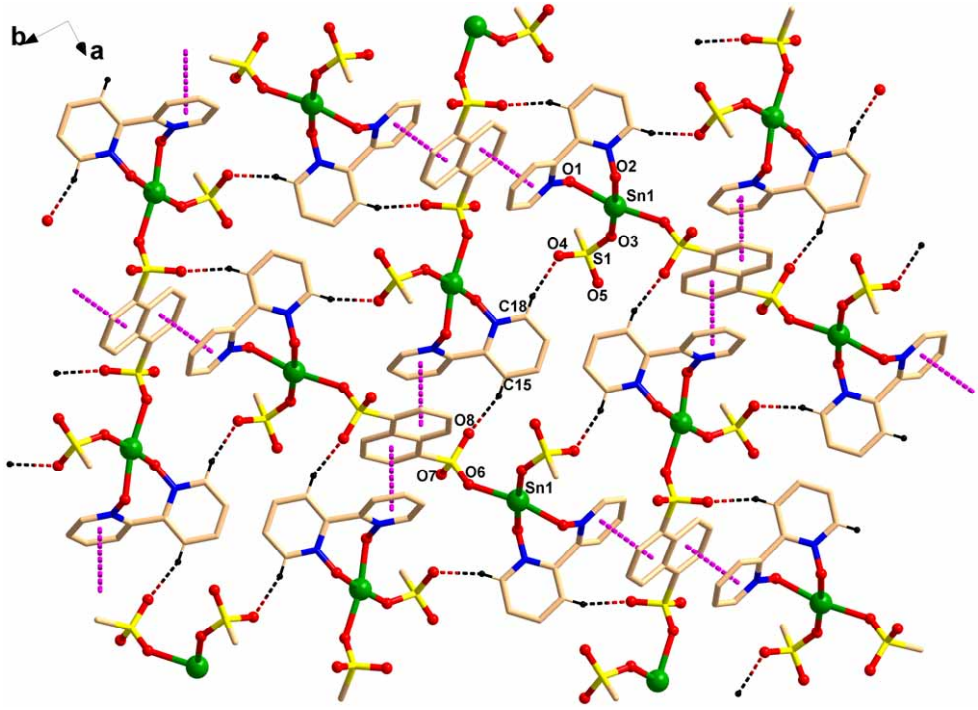
Figure S2. ORTEP representation of the asymmetric unit of **1**, shown at 50 % probability displacement ellipsoids. Hydrogens atoms are not shown.


O7
S2
O8
O6
O2
Sn1
O3
O5
O4
O1
S1
dihedral angle (deg) = 65.404

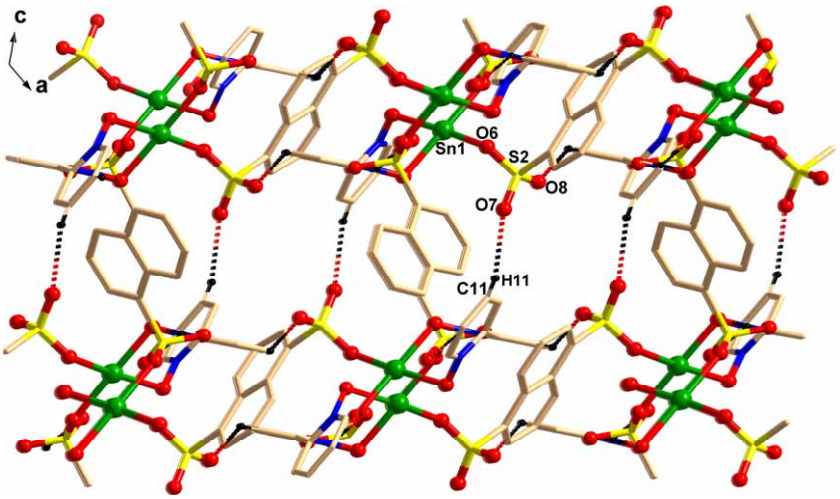
(a)


b
a
c
Sn1
O8
S2
O6
O7
70.08 °

(b)


b
a
O1
O2
Sn1
O4
O3
S1
O5
C18
C15
O8
O7
O6
Sn1

(c)



(d)

Figure S3. (a) Twisting of the two aromatic rings of BPDO-I in **1** (at an angle of 65.40 °). **(b)** Two 1D-chains of **1** cross each other and are oriented at an angle of 70.07(6) ° with respect to each other **(c)** Cross-section of **1** across the *ab* plane, 1D- chains cross each other and glued together through strong C–H···O and π···π interactions. The H···A ('A' = acceptor) distances involved in these C–H···O contacts are: C15−H15···O8 2.484(3) Å and C18−H18···O4 2.433(3) Å. **(d)** View across the *ac* plane, showing another set of C–H···O interaction, assisting the formation of three dimensional assembly of **1** (C11–H11···O7 2.460(5) Å, 144.99(31)°).

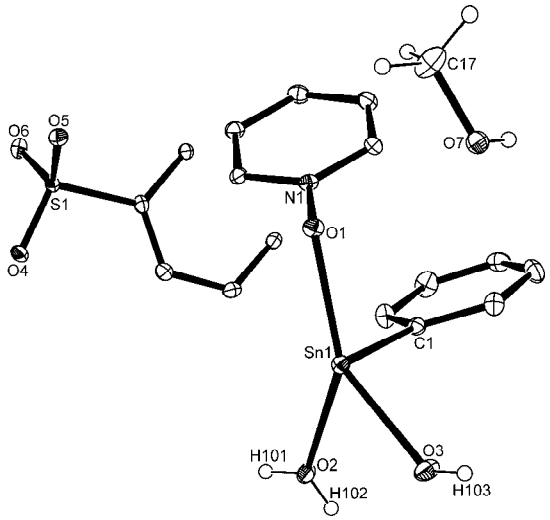


Figure S4: ORTEP representation of the asymmetric unit of **2**, shown at 50 % probability displacement ellipsoids. Only hydrogens of methanol and water molecules are shown.

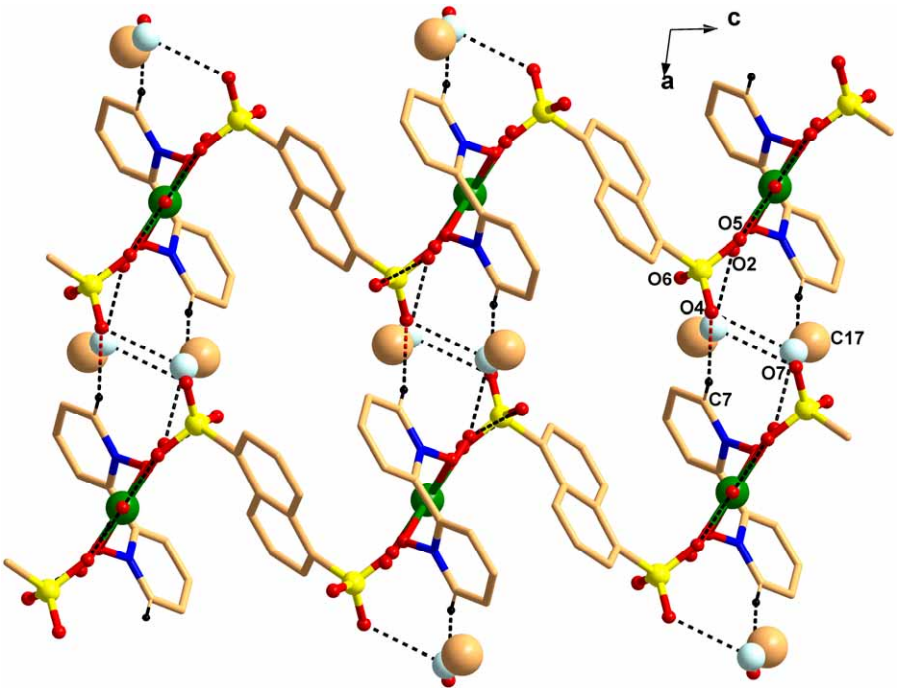


Figure S5: This figure reveals the presence of guest (methanol, C17 O7) molecules (shown in *space-filling* model) in between H-bonded layers of **2**·2CH_3OH. They are involved in forming strong O–H···O and C–H···O contacts with BPDO-I and 1,5-naphthalenedisulfonate moieties of adjacent layers. For metric parameters see Table S5B.

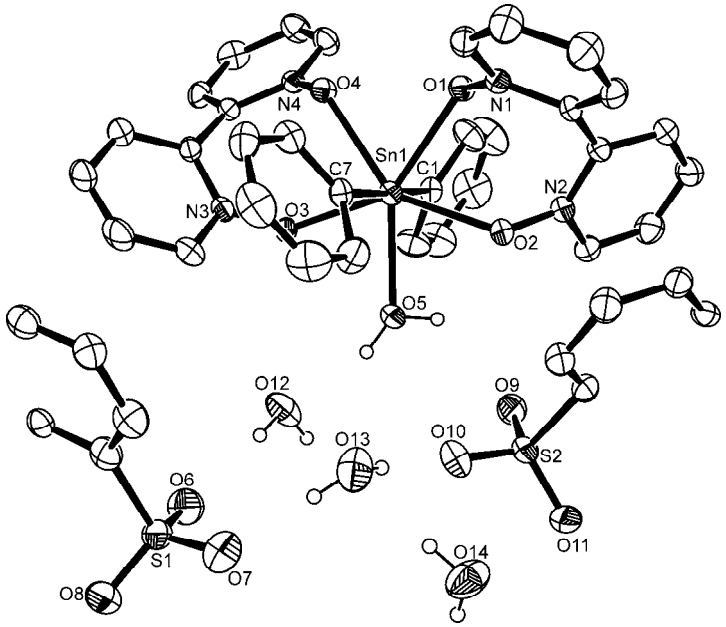


Figure S6: ORTEP representation of the asymmetric unit of **3**·3H_2O, shown at 50 % probability displacement ellipsoids. Hydrogen atoms of only water molecules are shown.

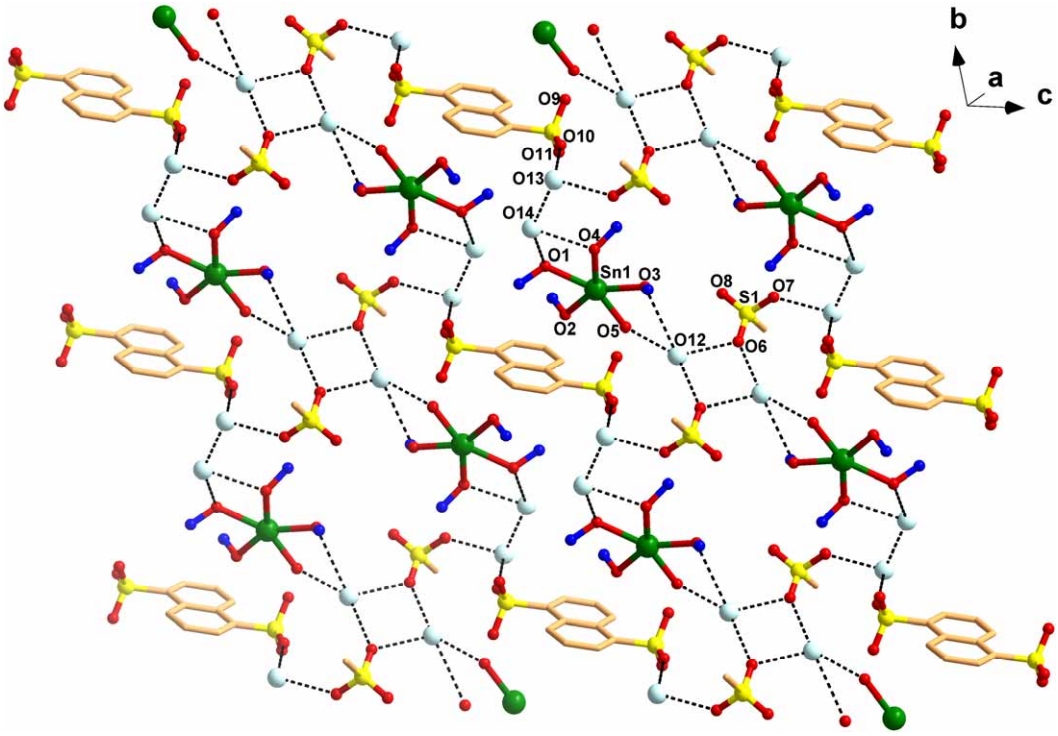


Figure S7: 2D-H-bonded sheet of **3**·3H_2O mediated by O–H···O interactions. Guest water molecules are shown as *light blue* spheres. *Phenyl* groups of tin and aromatic rings of BPDO-I ligand and all the hydrogen atoms have been omitted for clarity.

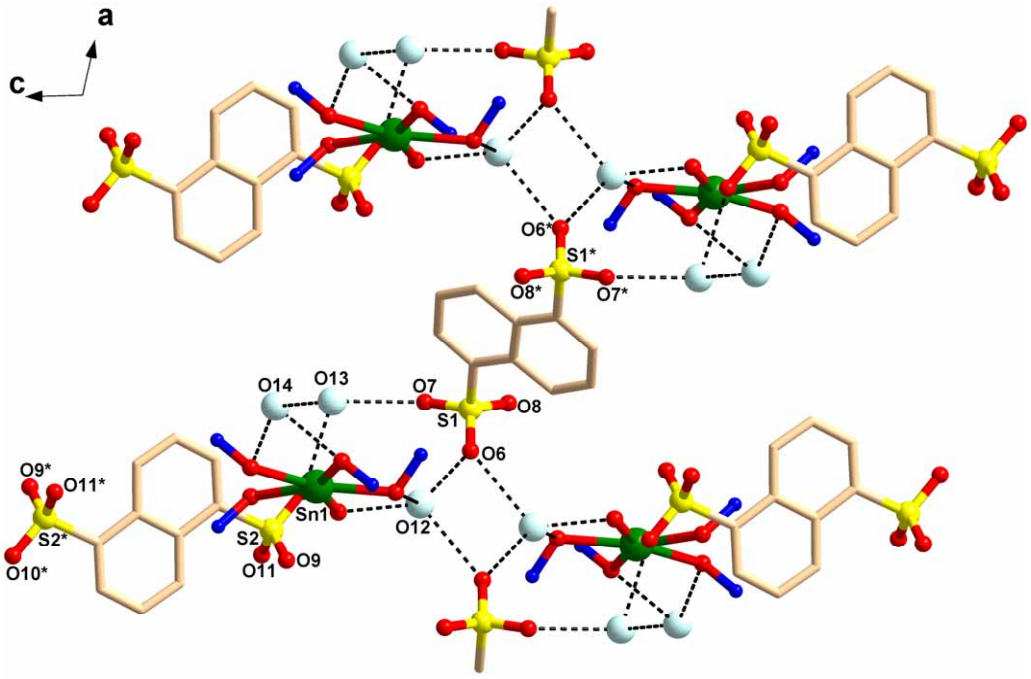


Figure S8: Formation of 3D-assembly in **3**·3H_2O assisted by H-bonding interactions between lattice water molecules and second set of 1,5-naphthalene-disulfonate anions (S1, O6 O7 O8).

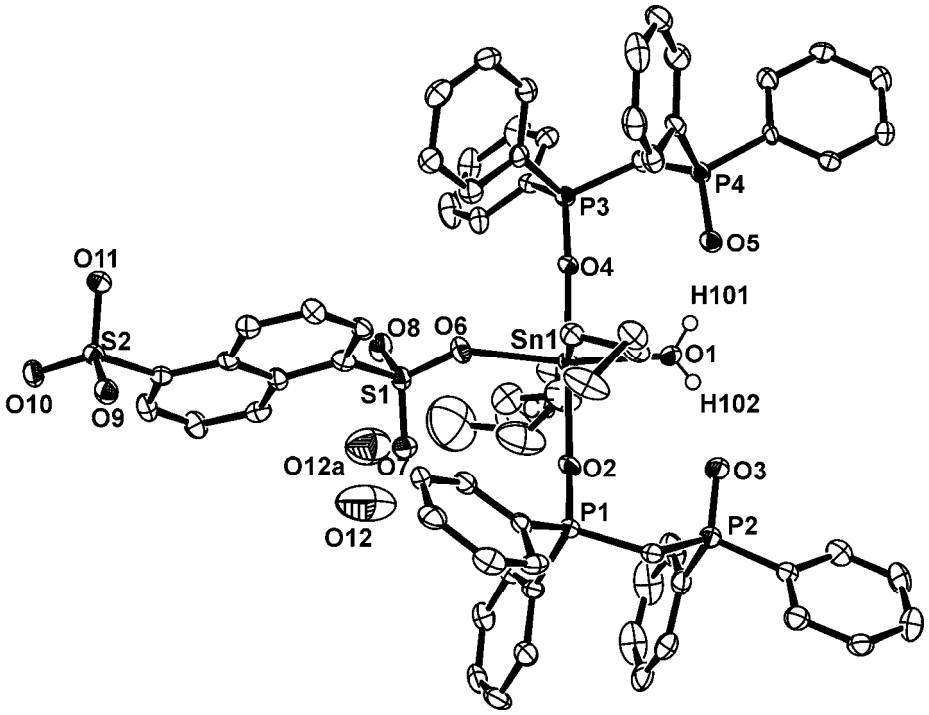
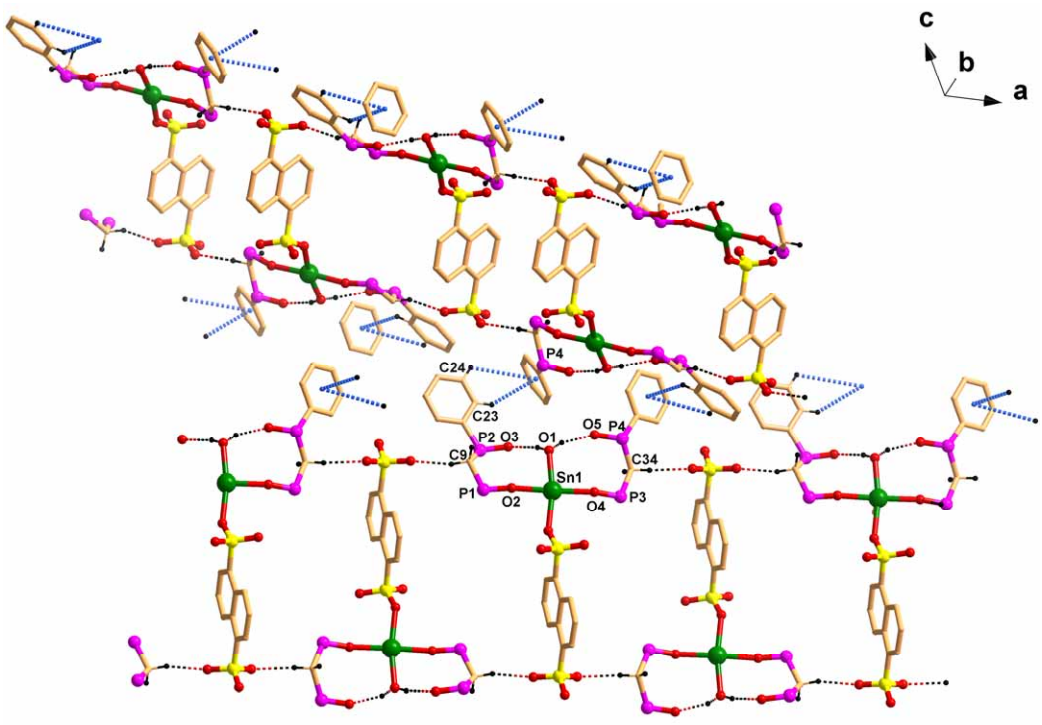
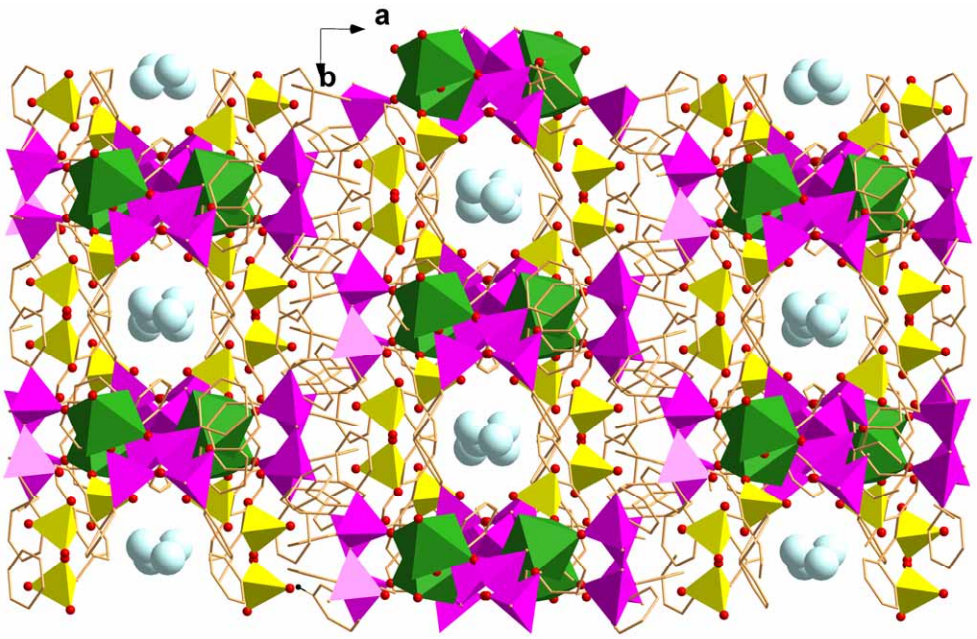


Figure S9: ORTEP representation of the asymmetric unit of **4**·H_2O, shown at 30 % probability displacement ellipsoids. Two of the carbons of one of the two *n*-butyl groups are triply disordered ((C6, C6a & C6b) and (C7, C7a & C7b). Hydrogen atoms (except those of tin bound water molecule) are excluded for clarity.



(a)



(b)

Figure S10: (a) C–H···O interactions extends the H-bonded dimers of **4**·H_2O in to 1D-tapes. Two such tapes crossing each other, are glued at points through C–H···π contacts. (b) **)** A 3D-supramolecular net formed by **4** due to crosslinking of its 1D-H-bonded tapes (Figure S10(a)) 'Green', 'violet' and

'yellow' colored polyhedra represents Sn, P and S atoms respectively). Disordered solvent (water) molecules, depicted as *light blue* spheres, are occupying the channels present parallel to the *c* axis.

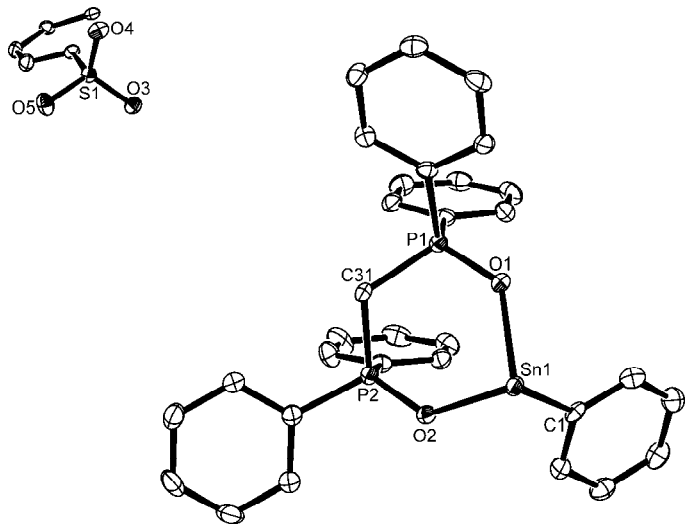
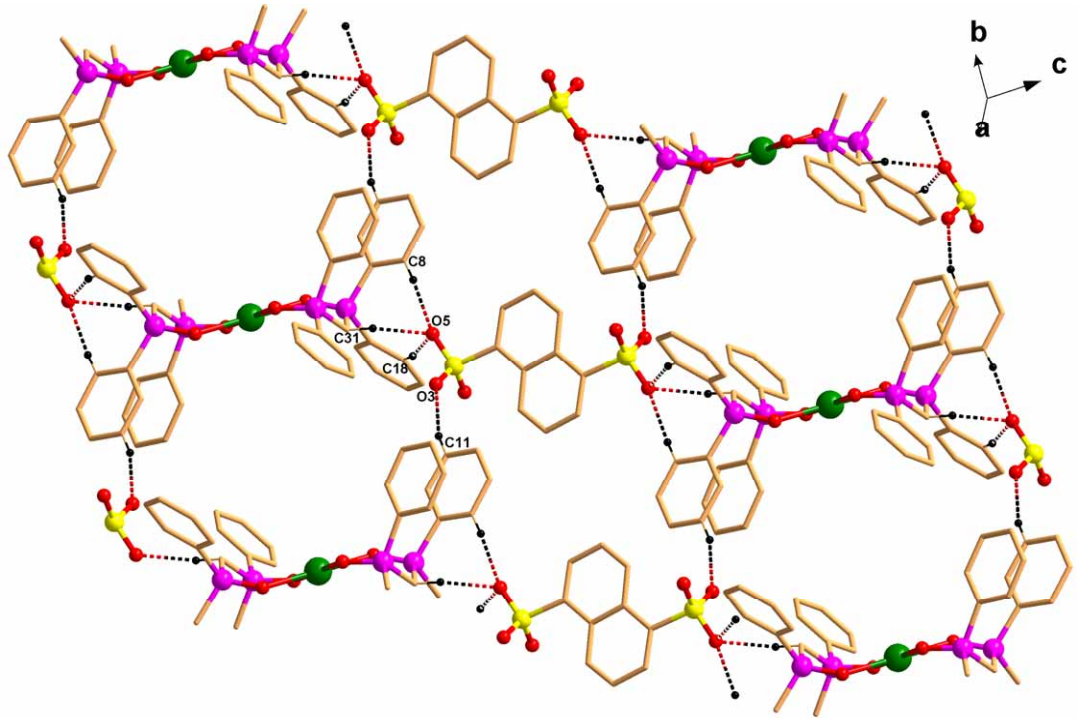
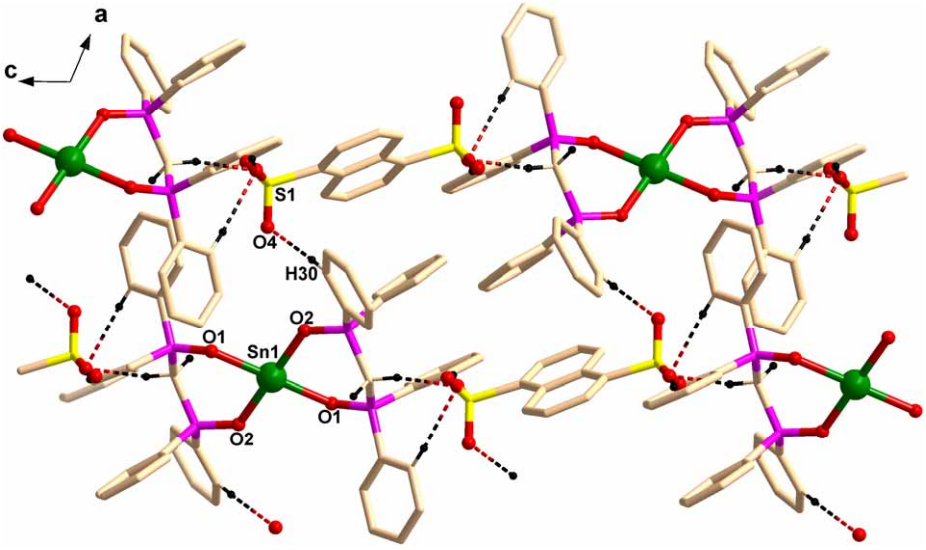


Figure S11: ORTEP representation of the asymmetric unit of **5** shown at 50 % probability displacement ellipsoids. Hydrogen atoms are not shown.



(a)



(b)

Figure S12. (a) 2D-supramolecular sheet of **5**, built by C–H···O hydrogen bonds (C11−H11···O3 2.424(3) Å, 164.51(23)°). For parameters involved see Table S8B. **(b)** View of 3D-packing of **5** in the crystal lattice, down the crystallographic *b* axis, reveal C–H···O contacts (C30–H30···O4) between aromatic C*H*s of DPPOM and oxygen atoms of the disulfonate anion adhering 2D-layers of **5** [shown in Figure S12(a)] (C30–H30···O42.377(2), 170.78(22))

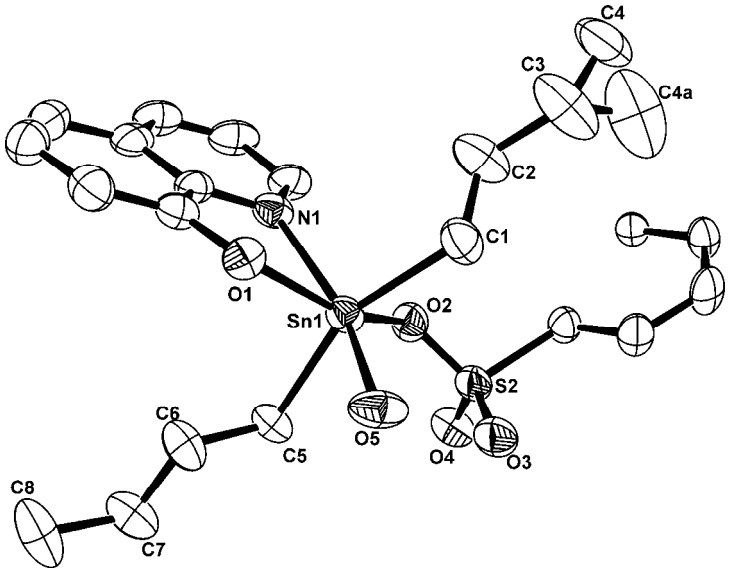


Figure S13: ORTEP representation of the asymmetric content of **6** shown at 30 % probability displacement ellipsoids. Hydrogen atoms are not shown.

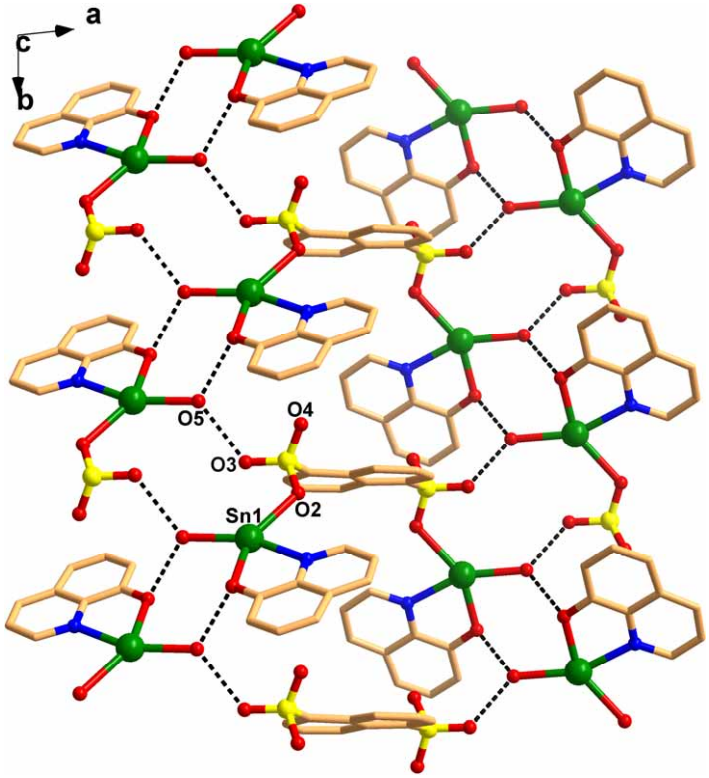


Figure S14: Formation of two dimensional assembly by **6** parallel to the *ab* plane

Table S1. Crystal data collection and refinement parameters for **1**.

	1
Empirical formula	$C_{28}H_{32}N_2O_8S_2Sn$
Formula Weight	707.37
Temperature(K)	293(2)
Wavelength($Mo_{k\alpha}$)	0.71069 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 25.099(5) Å b = 15.666(5) Å c = 19.433(5) Å α = 90 ° Å = 129.327(5) ° γ = 90 °
Volume	5911(3) $Å^3$
Z, Density (Calculated)	8, 1.590 mg/m^3
Absorption coefficient	1.058 mm^{-1}
F (000)	2880
Crystal size(mm)	0.11 x 0.08 x 0.04 mm
θ range for data collection	2.54 to 26.00 °
Limiting indices	-30<=h<=15, -19<=k<=19, -23<=l<=23
Reflections collected/ unique	16015/5781 [R(int)= 0.0401]
Completeness to θ	99.4 (θ = 26.00 °)
Data/ restraints/ parameters	5781 / 83 / 390
Goodness - of - fit on F^2	1.083
Final R indices [I>2σ (I)]	R1 = 0.0452, wR2 = 0.1254
R indices (all data)	R1 = 0.0543, wR2 = 0.1375
Largest diff. peak and hole ($e.Å^{-3}$)	1.765 and -0.820 $e.Å^{-3}$
Refinement method	Full-matrix least-squares on F^2

Table S2. Crystal data collection and refinement parameters for **2-4**

	2·2CH_3OH	**3**·3H_2O	**4**·H_2O
Empirical formula	$C_{34}H_{38}N_2O_{13}S_2Sn$	$C_{42}H_{40}N_4O_{14}S_2Sn$	$C_{68}H_{72}O_{12}P_4S_2Sn$
Formula Weight	865.47	1007.59	1387.95
Temperature(K)	153(2)	293(2)	100(2)
Wavelength($Mo_{k\alpha}$)	0.71073 Å	0.71069 Å	0.71069 Å
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	C2/c	P-1	C2/c
Unit cell dimensions	a = 18.2329(13) Å b = 11.0763(8)Å c = 18.0241(13)Å α = 90 ° β = 99.3740(10) ° γ = 90 °	a = 10.526(5) Å b = 11.739(5)Å c = 18.285(5)Å α = 92.530(5) ° β = 103.242 (5) ° γ = 100.479(5) °	a = 33.071(5) Å b = 11.224(5)Å c = 37.192(5)Å α = 90 ° β = 114.090(5) ° γ = 90 °
Volume	3591.4(4) $Å^3$	2153.9(15) $Å^3$	12603(6) $Å^3$
Z, Density (Calculated)	4, 1.601 mg/m^3	2, 1.554 mg/m^3	8, 1.463 mg/m^3
Absorption coefficient	0.897 mm^{-1}	0.763 mm^{-1}	0.637 mm^{-1}
F (000)	1768	1028	5744
Crystal size(mm)	0.12 x 0.08 x 0.04 mm	0.10 x 0.08 x 0.06 mm	0.10 x 0.06 x 0.04 mm
θ range for data collection	2.16 to 26.00 °	2.02 to 25.00 °	2.11 to 25.00 °
Limiting indices	-22<=h<=22, -13<=k<=11, -21<=l<=22	-12<=h<=10, -8<=k<=13, -21<=l<=18	-37<=h<=39, -11<=k<=13, -44<=l<=44
Reflections collected/ unique	9742 / 3518 [R(int)= 0.0237]	10866 / 7408 [R(int)= 0.0269]	31925 / 11069 [R(int)= 0.0877]
Completeness to θ	99.7 % (θ = 26.00 °)	97.6 % (θ = 25.00 °)	99.7 % (θ = 25.00 °)
Data/ restraints/ parameters	3518 / 5 / 249	7408 / 30 / 592	11069 / 358 / 848
Goodness - of - fit on F^2	1.075	1.026	1.029
Final R indices [I>2σ (I)]	R1 = 0.0271, wR2 = 0.0654	R1 = 0.0474, wR2 = 0.1248	R1 = 0.0592, wR2 = 0.1454
R indices (all data)	R1 = 0.0289, wR2 = 0.0665	R1 = 0.0577, wR2 = 0.1361	R1 = 0.0913, wR2 = 0.1659
Largest diff. peak and hole	0.813 and -0.374 e.$Å^{-3}$	1.304 and -0.436 e.$Å^{-3}$	1.698 and -1.023 e.$Å^{-3}$
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2

Table S3. Crystal data collection and refinement parameters for **5** and **6**

	5	**6**
Empirical formula	$C_{72}H_{60}O_{10}P_4S_2Sn$	$C_{44}H_{58}N_2O_{10}S_2Sn_2$
Formula Weight	1391.89	1076.42
Temperature(K)	100(2)	293(2)
Wavelength($Mo_{k\alpha}$)	0.71069 Å	0.71069 Å
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/n	C2/c
Unit cell dimensions	a = 15.154(5) Å b = 11.657(5)Å c = 19.051(5)Å α = 90 ° β = 112.254(5) ° γ = 90 °	a = 25.783(5) Å b = 8.597(5)Å c = 24.133(5)Å α = 90 ° β = 116.270 (5) ° γ = 90 °
Volume	3114.7(19) $Å^3$	4796.8(3) $Å^3$
Z, Density (Calculated)	2, 1.484 mg/m^3	4, 1.491 mg/m^3
Absorption coefficient	0.642 mm^{-1}	1.183 mm^{-1}
F (000)	1428	2192
Crystal size(mm)	0.09 x 0.05 x 0.03 mm	0.09 x 0.07 x 0.06 mm
θ range for data collection	2.09 to 25.00 °	2.53 to 28.27 °
Limiting indices	-18<=h<=12, -11<=k<=13, -19<=l<=22	-33<=h<=34, -11<=k<=8, -31<=l<=31
Reflections collected/ unique	15603 / 5471 [R(int)= 0.0542]	14974 / 5837 [R(int)= 0.0514]
Completeness to θ	99.9 % (θ = 25.00 °)	98.1 % (θ = 28.27 °)
Data/ restraints/ parameters	5471 / 0 / 403	5837 / 46 / 281
Goodness - of - fit on F^2	1.094	1.020
Final R indices [I>2σ (I)]	R1 = 0.0440, wR2 = 0.1087	R1 = 0.0593, wR2 = 0.1599
R indices (all data)	R1 = 0.0550, wR2 = 0.1229	R1 = 0.1011, wR2 = 0.2125
Largest diff. peak and hole	1.612 and -0.585 $e.Å^{-3}$	1.102 and -1.093 $e.Å^{-3}$
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2

Table S4A. Selected bond distances and bond angles for **1**

Bond distances (Å)	**Bond angles (°)**	
Sn1−C1 2.128(4)	C1−Sn1−C5 173.69(19)	C5−Sn1−O6 82.01(16)
Sn1−C5 2.125(4)	O1−Sn1−O6 169.50(10)	C1−Sn1−O6 92.87(14)
Sn1−O1 2.234(3)	O2−Sn1−O3 175.90(10)	O2−Sn1−O6 92.88(10)
Sn1−O2 2.220(3)	C5−Sn1−O2 94.12(18)	O3−Sn1−O6 90.44(11)
Sn1−O3 2.257(3)	C1−Sn1−O2 89.80(14)	
Sn1−O6 2.267(3)	C5−Sn1−O1 90.57(16)	
S1−O3 1.479(3)	C1−Sn1−O1 94.97(14)	
S1−O4 1.447(3)	O2−Sn1−O1 80.20(18)	
S1−O5 1.438(3)	C5−Sn1−O3 88.71(19)	
N1−O1 1.341(4)	C1−Sn1−O3 87.64(14)	
N2−O2 1.333(4)	O1−Sn1−O3 96.83(11)	

Table S4B. Hydrogen bonding parameters of **1**.

D–H···A	**D–H** (Å)	**H···A** (Å)	**D···A** (Å)	**D–H···A** (°)	**symmetry**
C18−H18···O4	0.930(4)	2.433(3)	3.243(5)	145.58(30)	1.5-x,-0.5+y,0.5-z
C15−H15···O8	0.930(4)	2.484(3)	3.267(5)	142.01(30)	0.5+x, 0.5-y, 0.5+z
C11−H11···O7	0.930(6)	2.460(5)	3.265(8)	144.99(31)	1.5-x,0.5-y, -z
$\pi_{cent}\cdots\pi_{cent}$ (N1 C9-C13; C19-C23) = 3.669(6) Å					

Table S5A. Selected bond parameters of **2**·2CH_3OH

Bond distances (Å)	Bond angles (°)
Sn1-C1 2.119(2)	C1-Sn1-C1* 175.46(12)
Sn1-O1 2.297(2)	O1-Sn1-O1* 74.99(7)
Sn1-O1* 2.297(2)	O1-Sn1-O2 69.46(6)
Sn1-O2 2.336(2)	O3-Sn1-O2 73.10(4)
Sn1-O2* 2.336(2)	O3-Sn1-O2* 73.10(4)
Sn1-O3 2.240(2)	O2*-Sn1-O1* 69.46(6)
S1-O4 1.456(2)	O1- Sn1-O2* 144.30(6)
S1-O5 1.462(2)	O1- Sn1-O3 142.50(4)
S1-O6 1.452(2)	O2-Sn1-O2* 146.21(8)
N1-O1 1.336(2)	O2- Sn1- O1* 144.30(6)
	O3-Sn1- O1* 142.51(4)
Symmetry transformations used to generate equivalent atoms: C1*, O1*, O2* -x+1, y, -z+1.5	

Table S5B. Hydrogen bonding parameters of **2**·2CH_3OH

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A (°)	symmetry
O2−H102···O6	0.795(2)	2.029(3)	2.816(2)	170.41(24)	x, -1+y, z
O3−H103···O5	0.804(3)	1.859(2)	2.654(2)	170.01(24)	1-x, -1+y, 1.5-z
O7−H104···O4	0.783(2)	1.933(2)	2.710(2)	171.63(19)	0.5+x, -0.5+y, z
O2−H101···O7	0.797(3)	1.950(3)	2.725(2)	163.65(25)	1-x, y, 1.5-z
C10−H10···O5	0.930(2)	2.441(2)	3.323(3)	158.40(14)	x, y, z
C7−H7···O4	0.930(2)	2.484(2)	3.375(3)	160.47(14)	0.5+x, -0.5+y, z

Table S6A. Selected bond parameters of **3**·3H_2O

Bond distances (Å)	Bond angles (°)
Sn1-C1 2.116(4)	C1-Sn1-C7 176.22(15)
Sn1-C7 2.122(4)	O1-Sn1-O2 71.23(10)
Sn1-O1 2.370(3)	O2-Sn1-O5 71.98(11)
Sn1-O2 2.286(3)	O5-Sn1-O3 72.87(10)
Sn1-O3 2.270(3)	O3-Sn1-O4 72.95(10)
Sn1-O4 2.333(3)	O4-Sn1-O1 71.02(10)
Sn1-O5 2.249(3)	O5-Sn1-O1 143.20(11)
S1-O6 1.425(4)	O3-Sn1-O2 144.85(10)
S1-O7 1.482(4)	O3-Sn1-O1 143.90(10)
S1-O8 1.418(4)	O2-Sn1-O4 142.19(10)
S2-O9 1.464(4)	O5-Sn1-O4 145.77(10)
S2-O10 1.447(4)	
S2-O11 1.449(4)	
N1-O1 1.330(4)	
N2-O2 1.336(4)	
N3-O3 1.340(4)	
N4-O4 1.332(4)	

Table S6B. D···A bond distances for hydrogen bonds in **3**·3H_2O

D···A	**D···A (Å)**	**symmetry**
O5···O9	2.769(6)	x, y, z
O5···O12	2.656(5)	x, y, z
O12···O6	2.845(6)	1-x, 1-y, 1-z
O12···O6*	2.789(6)	x, y, z
O13···O10	2.779(6)	x, y, z
O14···O13	2.796(8)	x, y, z
O14···O4	2.953(3)	x, -1+y, z

Table S7A. Selected bond parameters of **4**·H_2O

Bond distances (Å)	Bond angles (°)
Sn1-C1 2.119(5)	C1-Sn1-C5 175.5(3)
Sn1-C5 2.148(8)	O1-Sn1-O6 169.70(14)
Sn1-O1 2.200(4)	O2-Sn1-O4 177.73(14)
Sn1-O2 2.181(4)	O1-Sn1-O4 94.82(14)
Sn1-O4 2.227(4)	O4-Sn1-O6 95.38(14)
Sn1-O6 2.267(4)	O6-Sn1-O2 86.12(14)
P1-O2 1.497(4)	O2-Sn1-O1 83.73(14)
P2-O3 1.494(4)	
P3-O4 1.499(4)	
P4-O5 1.480(4)	
S1-O6 1.483(4)	
S1-O7 1.439(4)	
S1-O8 1.438(4)	
S2-O9 1.454(4)	
S2-O10 1.443(4)	
S2-O11 1.445(4)	

Table S7B. Hydrogen bonding parameters of **4**·H_2O

D−H···A	**D−H (Å)**	**H···A (Å)**	**D···A (Å)**	**D−H···A (°)**	**symmetry**
O1−H101···O5	0.830(6)	1.795(6)	2.591(6)	160.09(66)	x, y, z
O1−H102···O3	0.838(6)	1.859(6)	2.682(6)	166.97(59)	x, y, z
C34−H34B··O11	0.968(6)	2.295(4)	3.260(7)	175.25(34)	2-x, 2-y, 1-z
C52−H52···O11	0.929(6)	2.609(4)	3.507(7)	162.68(35)	2-x, 2-y, 1-z
C58−H58···O11	0.930(6)	2.552(4)	3.331(8)	141.46(35)	2-x, 2-y, 1-z
C9−H9B···O9	0.969(5)	2.224(4)	3.145(7)	158.41(34)	1.5-x, 1.5-y, 1-z
C-H---π distances					
C38−H38···π				3.157(4) Å	
C39−H39···π				3.107(5) Å	
C40−H40···π				3.177(5) Å	
C23−H23···π				2.744(4) Å	

Table S8A. Selected bond parameters of **5**

Bond distances (Å)	**Bond angles (°)**
Sn1-C1 2.122(3)	C1-Sn1-C1* 180.0(0)
Sn1-O1 2.212(2)	O1-Sn1-O1* 180.0(0)
Sn1-O2 2.184(2)	O2-Sn1-O2* 180.0(1)
P1-O1 1.517(2)	O1-Sn1-O2 87.60(8)
P2-O2 1.521(2)	O1-Sn1-O2* 92.40(8)
S1-O3 1.457(2)	O2*-Sn1-O1* 87.59(8)
S1-O4 1.448(2)	O1*-Sn1-O2 92.40(8)
S1-O5 1.460(3)	
Symmetry transformations used to generate equivalent atoms: C1*, O1*, O2* -x+2, -y+2, -z	

Table S8B. Hydrogen bonding parameters of **5**.

D−H···A	**D−H (Å)**	**H···A (Å)**	**D···A (Å)**	**D−H···A (°)**	**symmetry**
C31−H31···O5	0.969(4)	2.173(3)	3.129(5)	168.38(21)	-0.5+x, 1.5-y, 0.5+z
C18−H18···O5	0.930(4)	2.500(3)	3.418(5)	169.64(22)	-0.5+x, 1.5-y, 0.5+z
C8−H8···O5	0.930(4)	2.295(3)	3.219(4)	172.77(23)	-0.5+x, 1.5-y, 0.5+z
C11−H11···O3	0.931(4)	2.424(3)	3.330(4)	164.51(23)	-0.5+x, 2.5-y, 0.5+z
C30−H30···O4	0.930(3)	2.377(2)	3.298(4)	170.78(22)	x, y, 1+z
π(C19-C24)··· π(7-C12) 3.60(8) Å					

Table S9. Selected bond parameters of **6**

Bond distances (Å)	Bond angles (°)
Sn1-C1 2.103(8)	C1-Sn1-C5 156.4(4)
Sn1-C5 2.127(6)	O1-Sn1-O2 151.22(16)
Sn1-O1 2.125(4)	N1-Sn1-O5 156.1(2)
Sn1-N1 2.294(5)	O1-Sn1-N1 74.28(18)
Sn1-O5 2.309(5)	N1-Sn1-O2 77.01(18)
Sn1-O2 2.424(5)	O2-Sn1-O5 126.71(18)
S2-O2 1.456(5)	O5-Sn1-O1 81.90(19)
S2-O3 1.463(5)	
S2-O4 1.420(6)	

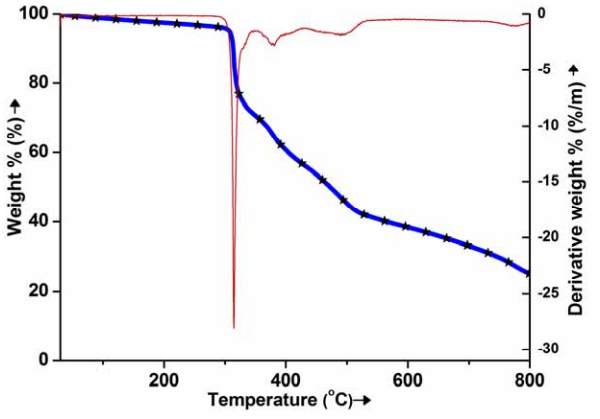


Figure S15. Thermogravimetric curve of **1**

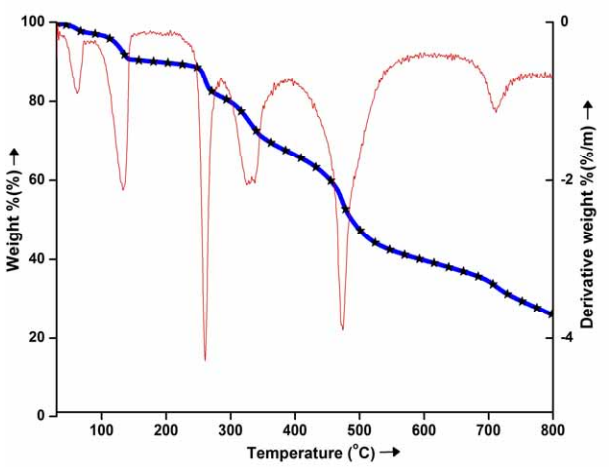


Figure S16. Thermogravimetric curve for **2**·2CH_3OH

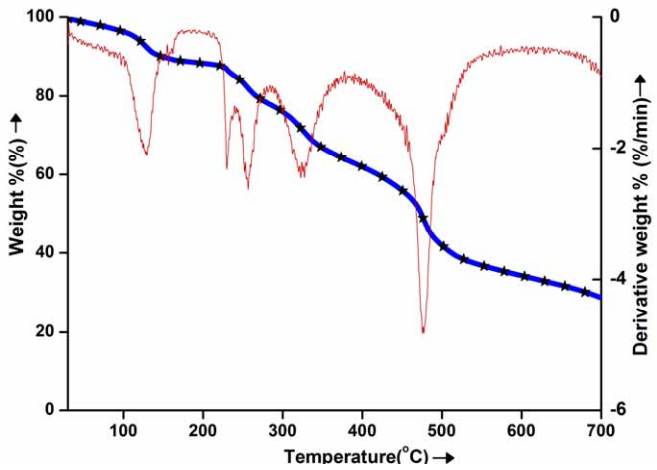


Figure S17. Thermogravimetric curve for **3**·3H_2O

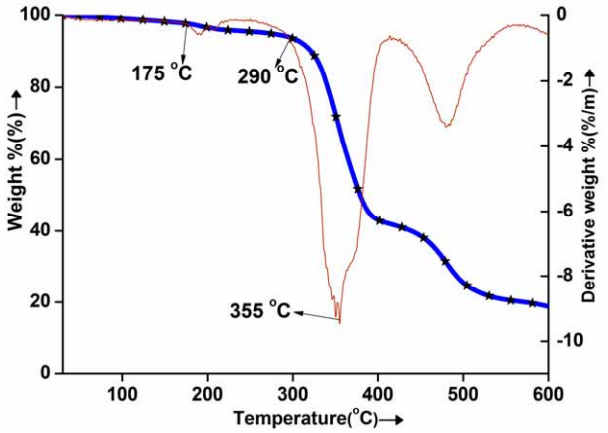


Figure S18. Thermogravimetric curve of **4**·H_2O

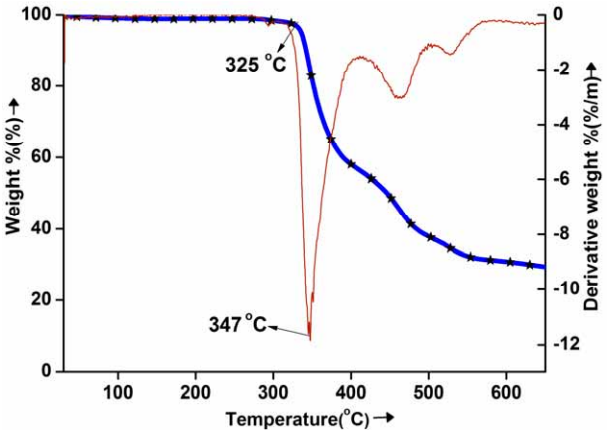


Figure S19. Thermogravimetric curve of **5**

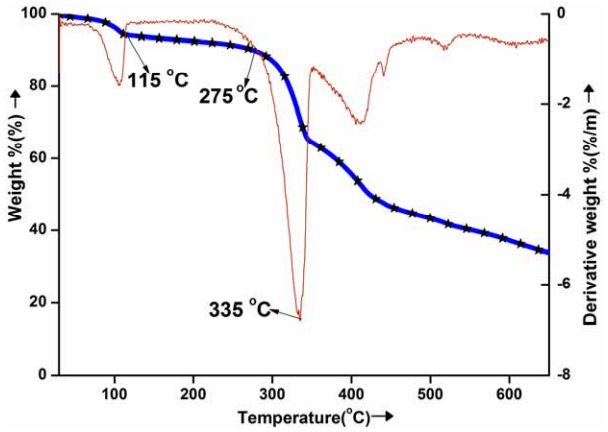


Figure S20. Thermogravimetric curve of **6**