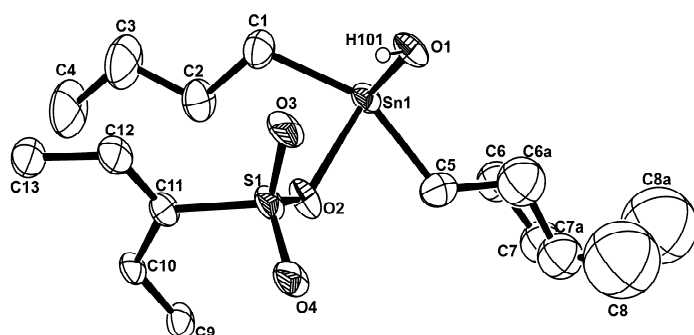


## Supporting Information

# In Situ Generated Hydrated Diorganotin Cations as Synthons for Hydrogen-Bonded and Coordination- Driven 1D-, 2D- and 3D-Assemblies

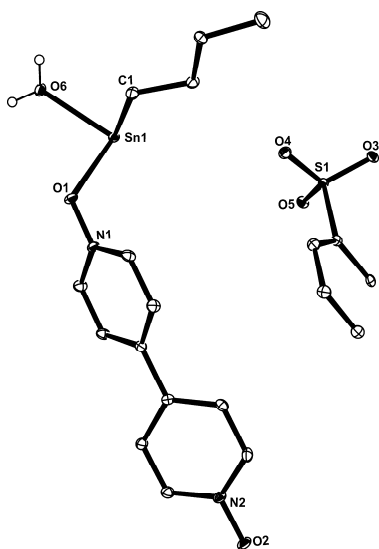
*Vadapalli Chandrasekhar,\* and Puja Singh*

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



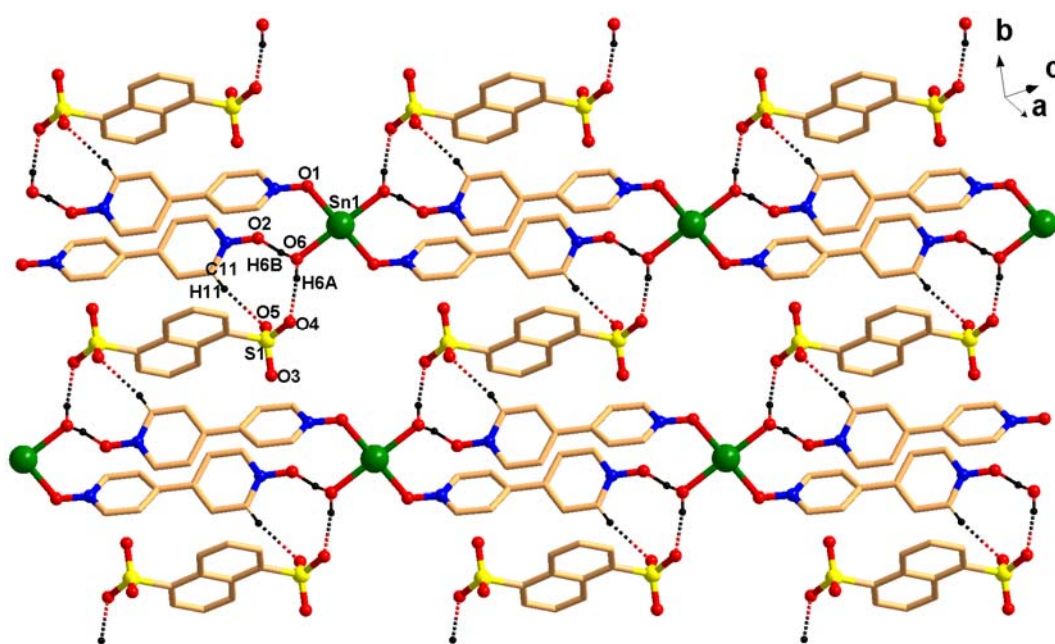
**Figure S1.** ORTEP representation of the asymmetric unit of **1**, shown at 30 % ellipsoids.

Hydrogen atoms (except the one belonging to hydroxide group) are omitted. The asymmetric unit of **1** shows one tin atom, one hydroxide, two *n*-butyl groups and half of 1,5-naphthalenedisulfonate unit.

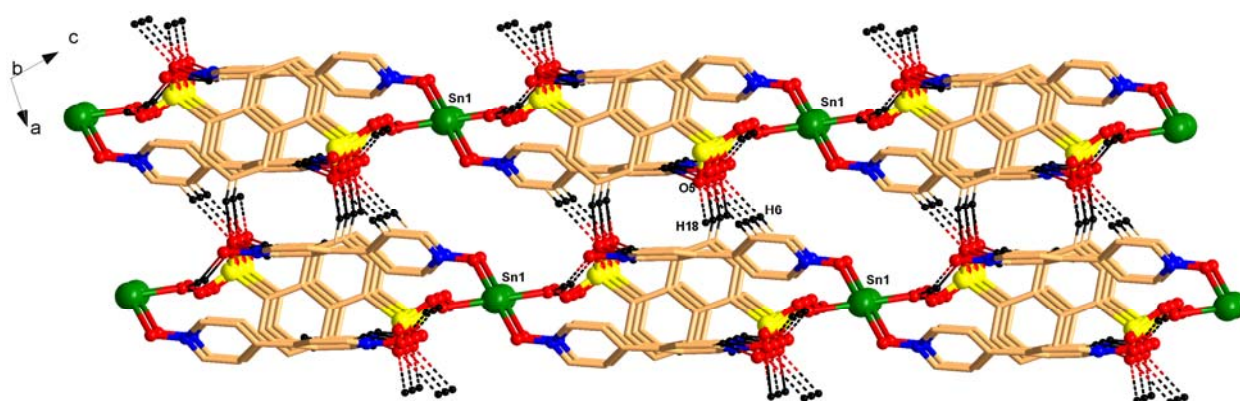


**Figure S2.** ORTEP representation of the asymmetric unit of **2**, shown at 50 % ellipsoids.

Hydrogen atoms are not shown. The asymmetric unit of **2** contains one tin atom with 0.5 occupancy, one *n*-butyl group, one BPDO-II ligand, half of the 1,5-naphthalenedisulfonate group and one bound water molecule.

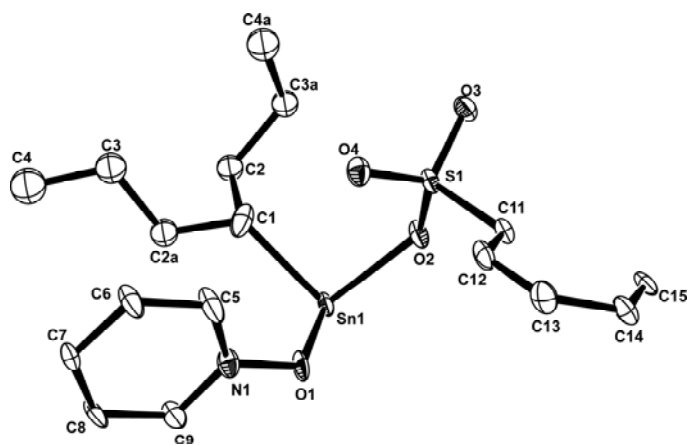


(a)



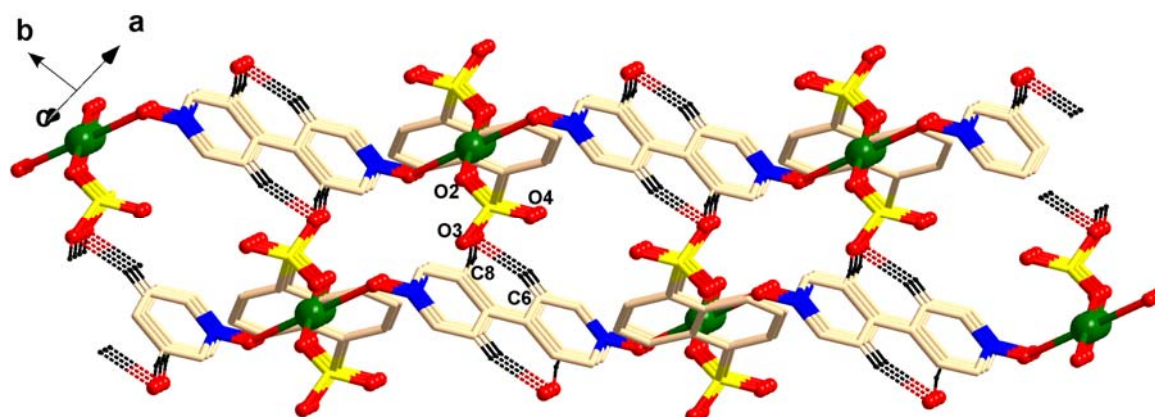
(b)

**Figure S3.** (a) 2-D hydrogen bonded layer of **2**. (b) 3D-view of **2**. “*n*-Butyl” groups and hydrogen atoms (except those involved in O–H···O or C–H···O interactions) have been omitted for clarity. The 2D-H-bonded sheets of **2** (Figure S3(a)) are associated with each other through strong C–H···O interactions that occur between one of the oxygen atoms (O5) of disulfonate of one layer and two hydrogen atoms, one each from BPDO-II (H6), and naphthyl moiety (H18) of disulfonate, belonging to the adjoining layer (Figure S3b). (See Table S5 for the metric parameters of H-bonds)

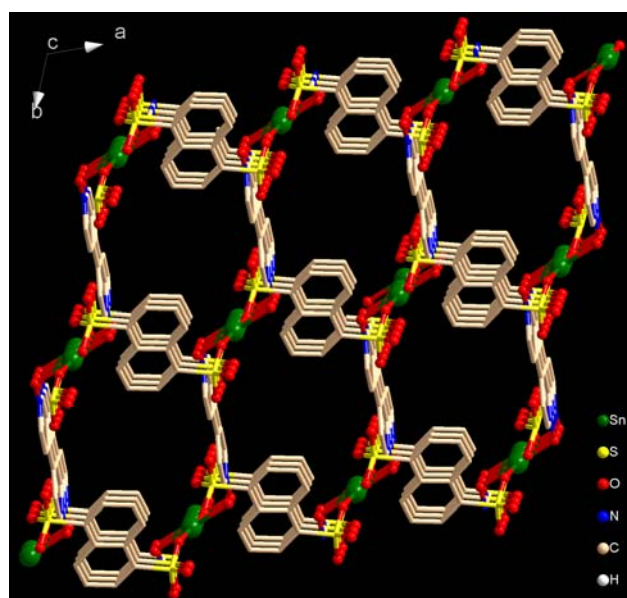


**Figure S4.** ORTEP representation of the asymmetric unit of **3** showing 50 % ellipsoids.

Hydrogen atoms are not shown. The asymmetric unit of **3** is composed of one tin atom with an occupancy factor of 0.5, half of the molecule of BPDO-II and half of the molecule of 1,5-naphthalenedisulfonate.



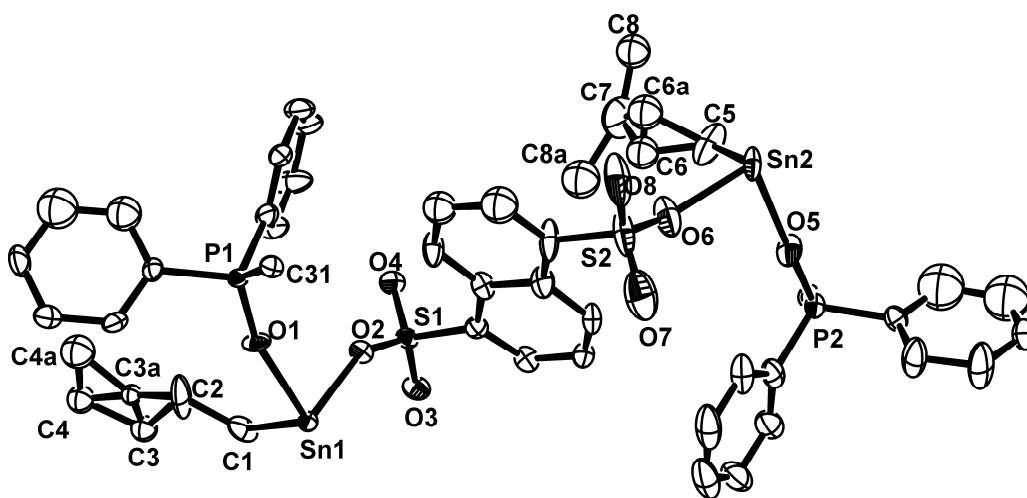
(a)



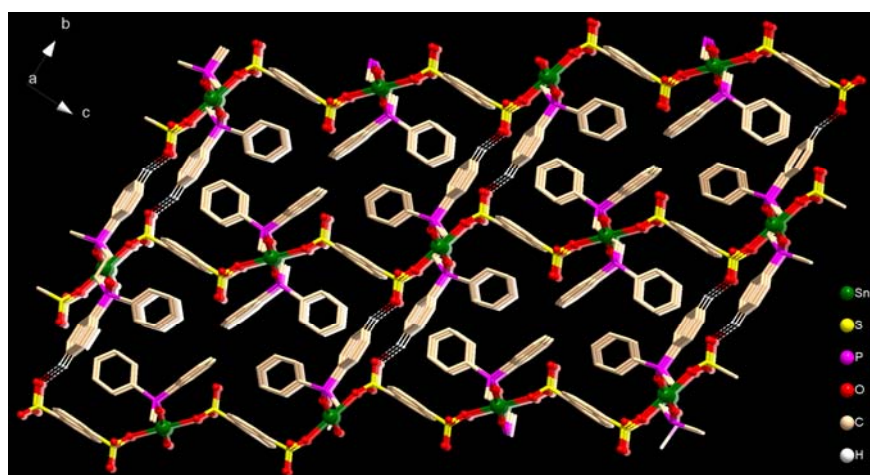
(b)

**Figure S5.** (a) C–H...O interactions present between adjacent 2D-sheets of **3**, assist in the formation of a 3D-assembly. ‘*n*-Butyl’ groups and all the hydrogen atoms (except H6 & H8) have been omitted for clarity (b) View of the three-dimensional assembly formed by **3** across the *ab* plane. C–H...O hydrogen bonding interactions occur between hydrogen atoms (H6, H8) of BPDO-II of one sheet and one of the free oxygen atom (O3) of 1,5-naphthalenedisulfonate ligand of the adjacent layer. For metric parameters see Table S6. The cavity present parallel to

the crystallographic  $c$  axis (Figure S5b) is occupied by  $n$ -butyl groups coordinated to the tin centre.



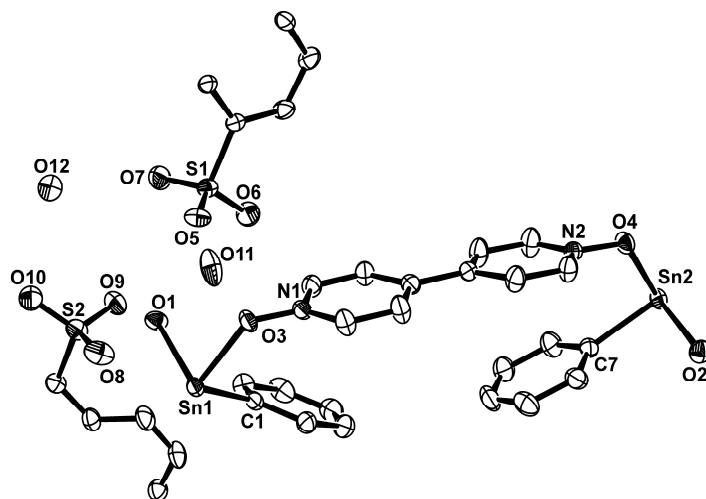
**Figure S6.** ORTEP representation of the asymmetric unit of **4** shown at 50 % probability displacement ellipsoids. Hydrogen atoms are not shown. The asymmetric unit of **4** contains two crystallographically unique tin atoms (Sn1 and Sn2) with an occupancy factor of 0.5 each, two *n*-butyl groups, one DPPOE, and one 1,5-naphthalenedisulfonate ligand.



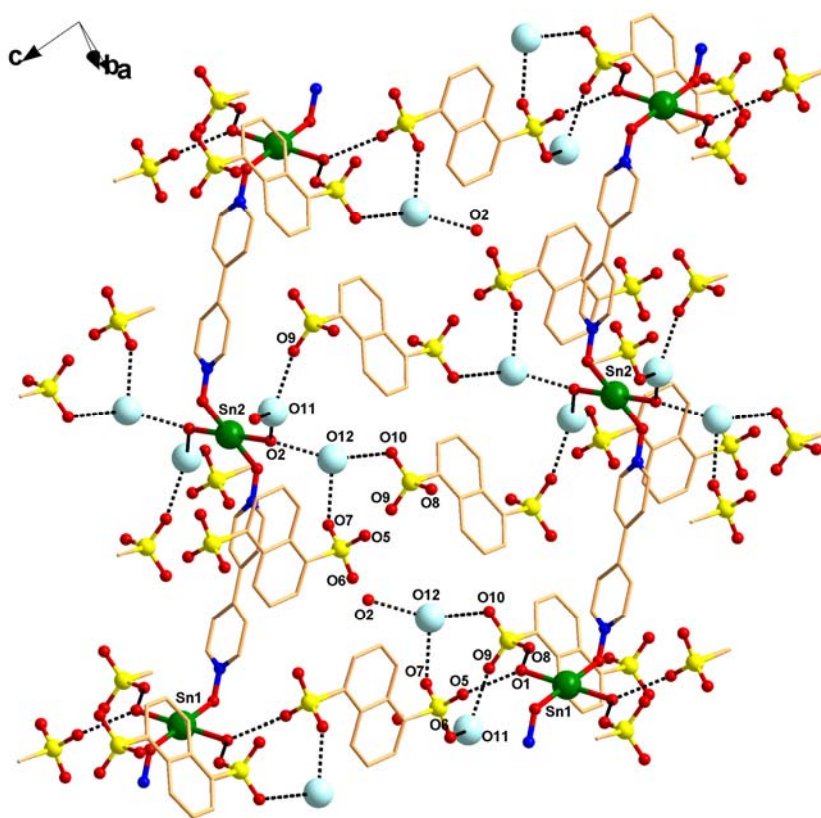
**Figure S7.** Stacking of 2D-sheets of **4**, down the crystallographic *a* axis through weak C–H...O hydrogen bond, and interlayer hydrophobic interaction due to *phenyl* groups emerging from DPPOE. The weak C–H...O contacts exist between the phenyl substituent (H28) of DPPOE ligand of one layer and the free oxygen atom (O4) of one of the sulfonate groups of a 1,5-naphthalenedisulfonate present in the adjacent layer (C28–H28...O4 2.519(5) Å 129.31(50)°).



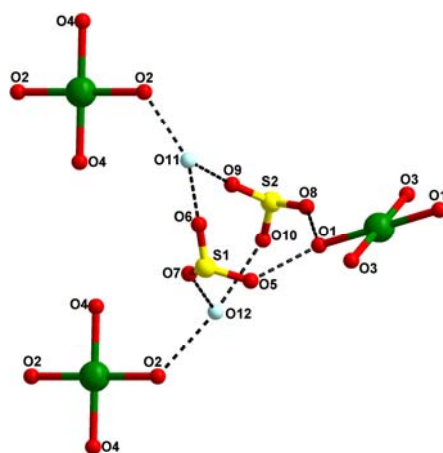
Tin bound '*n*-butyl' groups and all the hydrogen atoms (except H28) are omitted for the sake of clarity.



**Figure S8.** ORTEP representation of the asymmetric unit of **5**·2H<sub>2</sub>O showing 50 % probability displacement ellipsoids. Hydrogen atoms are not shown. The asymmetric unit of **5**·2H<sub>2</sub>O shows two crystallographically independent tin atoms with 0.5 occupancy each (Sn1 & Sn2), two phenyl groups, two coordinated water molecules (one on each tin atom), one BPDO-II ligand, and two crystallographically different halves of 1,5-naphthalenedisulfonate anion.

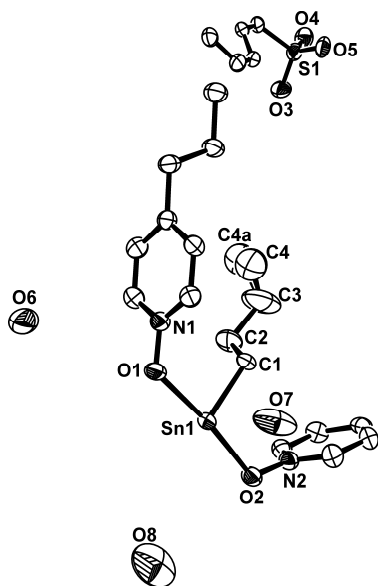


(a)

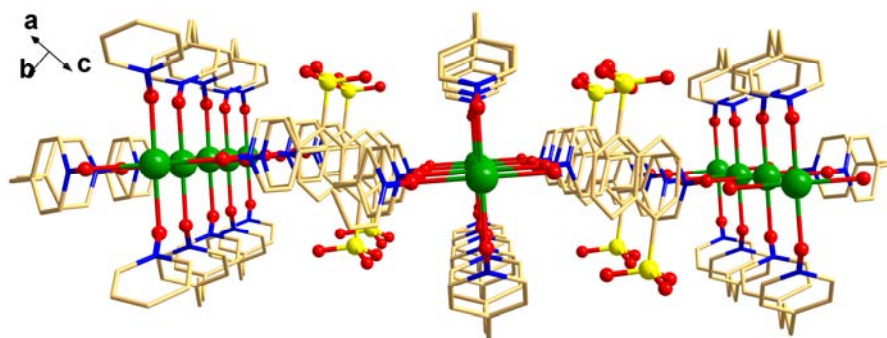


(b)

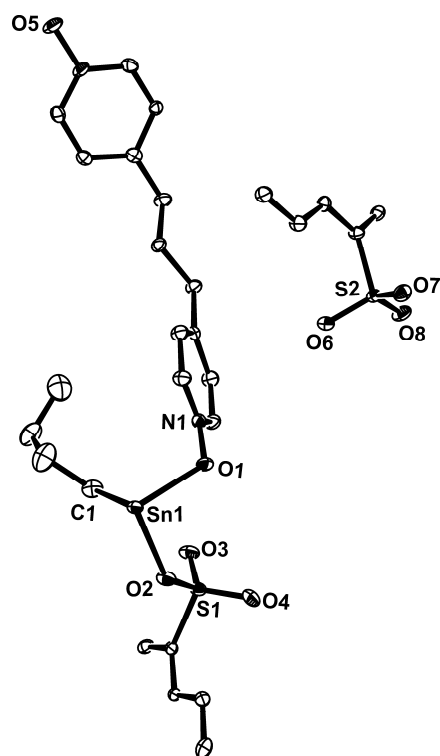
**Figure S9.** (a) Formation of 2D-layer (along the *ab* plane), assisted by hydrogen bonding interactions (Table S7) between the water molecules of cationic 1D-chains, 1,5-naphthalenedisulfonate anions, and lattice water molecules. (b) Basic hydrogen bonding motif responsible for the formation of 3D-assembly in **5**·2H<sub>2</sub>O. Three tin atoms shown in *green* belong to three different 1D-chains. Tin bound *phenyls* and all the hydrogen atoms are omitted for the sake of clarity.



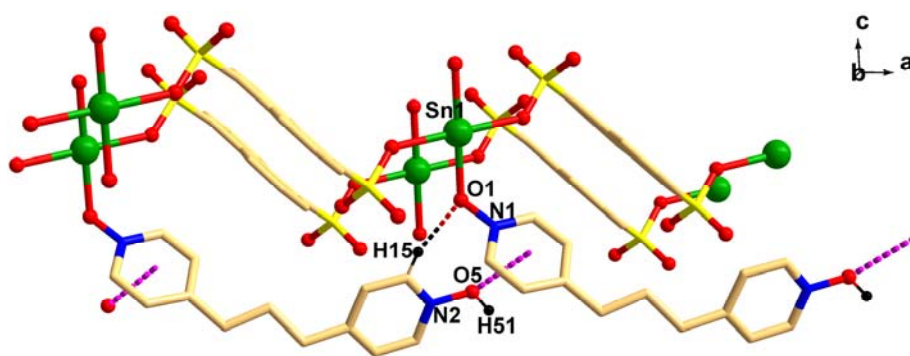
**Figure S10.** ORTEP representation of the asymmetric unit of **6**·5H<sub>2</sub>O shown at 30 % probability displacement ellipsoids. Hydrogen atoms are omitted. The asymmetric unit of **6**·5H<sub>2</sub>O contains one tin atom (Sn1) with a structure occupancy factor of 0.5, one *n*-butyl group, one BPDO-III, one-half of the 1,5-naphthalenedisulfonate ligand and two and a half of lattice water molecules.



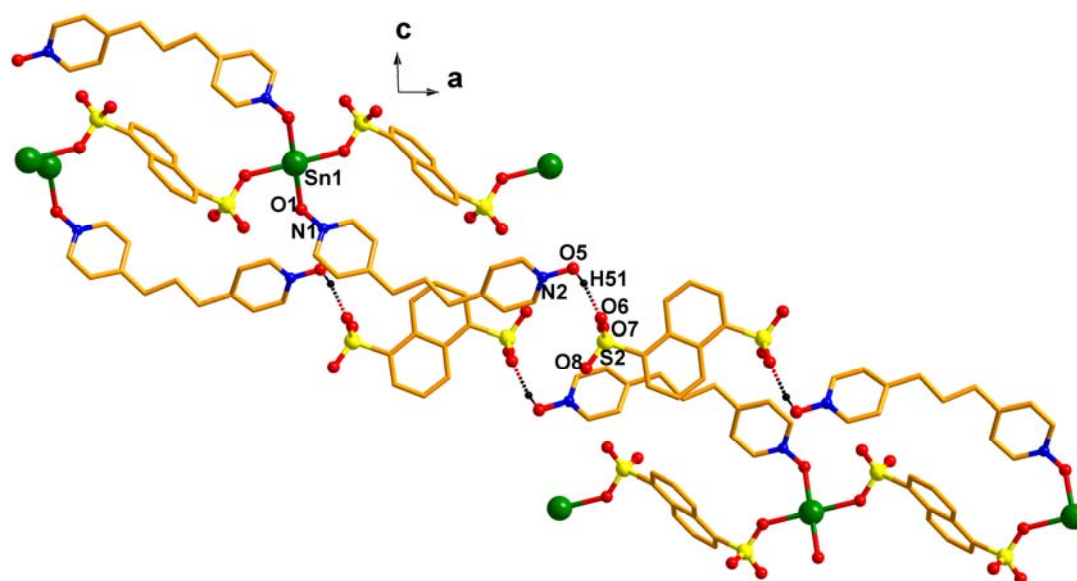
**Figure S11.** Another view of the 2D-assembly of **6**.



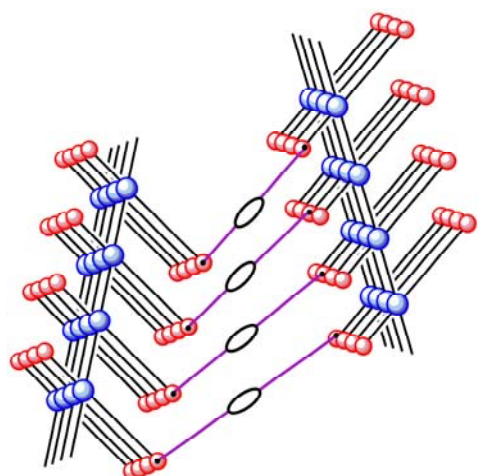
**Figure S12.** ORTEP representation of the asymmetric unit of **7** shown at 50 % probability displacement ellipsoids. Hydrogen atoms are not shown. The asymmetric unit of **7** reveals one tin atom with 0.5 occupancy, one *n*-butyl group, one monoprotonated BPDO-III and two independent halves of 1,5-naphthalenedisulfonate (one is bound to tin and the other is anionic).



(a)



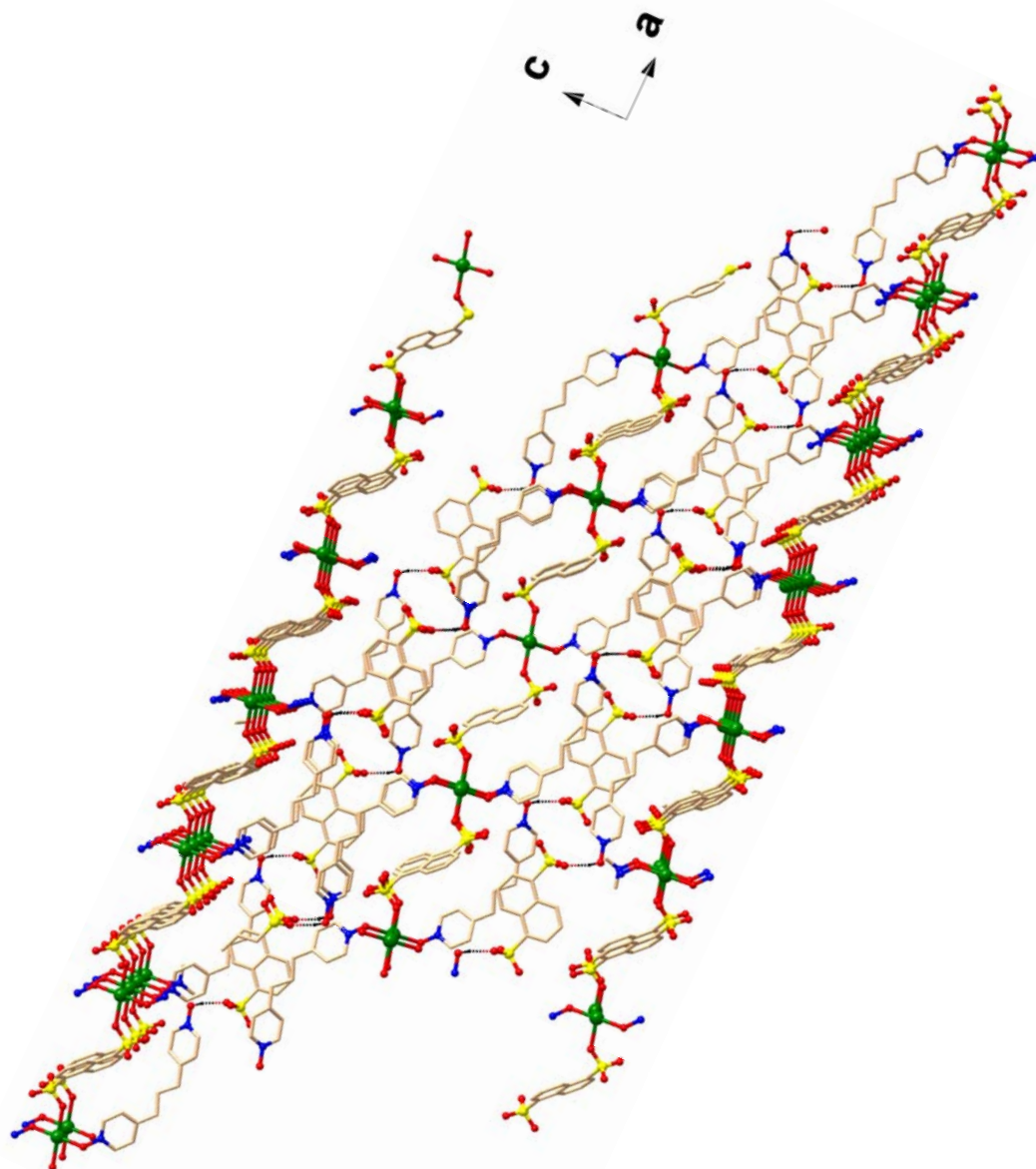
(b)



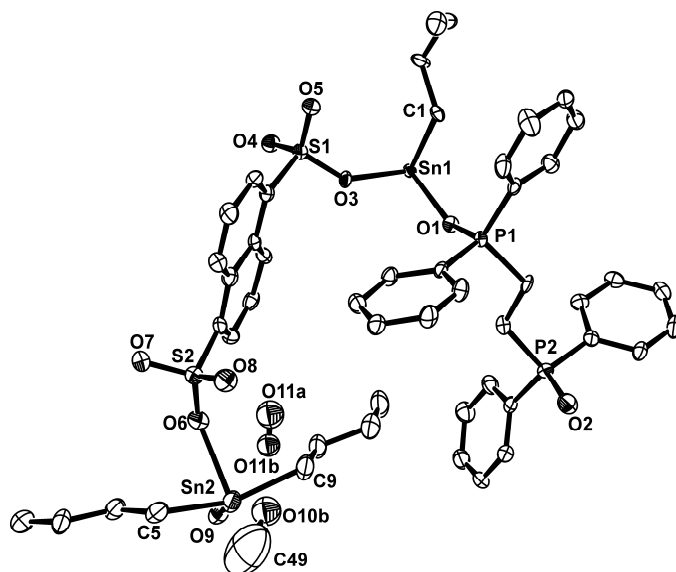
- $n\text{Bu}_2\text{Sn}$
- Terminal and protonated N-oxide
- Naphthalene-1,5-disulfonate anion
- links through coordinate or covalent bond
- links through hydrogen bond

(c)

**Figure S13.** (a)  $O\cdots\pi$  and  $C\cdots H-O$  contacts assists in stacking of 1D-chains in **7**. Metric parameters for these interactions are provided in Table S9. (b)  $O\cdots H-O$  contacts between disulfonate anion and adjoining 1D-chains of **7**. (c) Cartoon diagram representing the pattern of hydrogen bonding existing between adjacent stacks of 1D-chains of **7**. '*n*-butyl' groups and all the hydrogen atoms (except H15 and H51 in Figure S13(a)), are omitted for the sake of clarity.

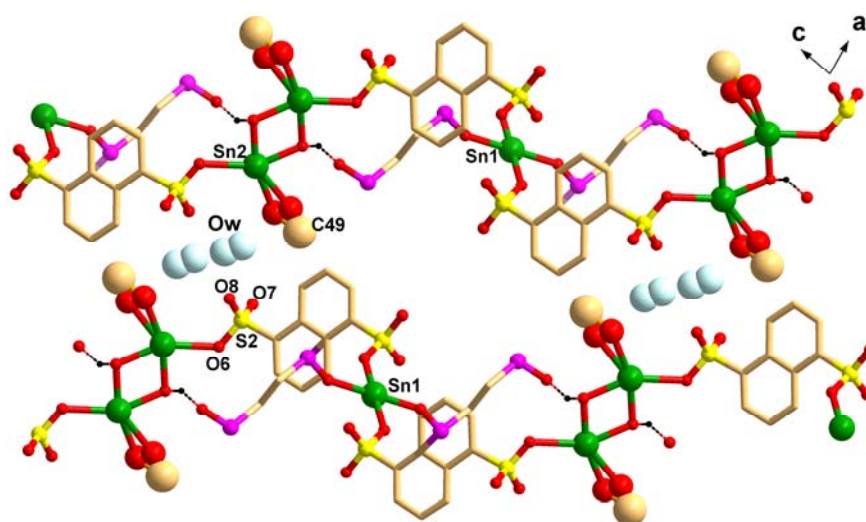


**Figure S14.** View of **7** down the crystallographic *b* axis, showing entangled 1D-chains. ‘*n*-butyl’ groups and all the hydrogen atoms are omitted for the sake of clarity.



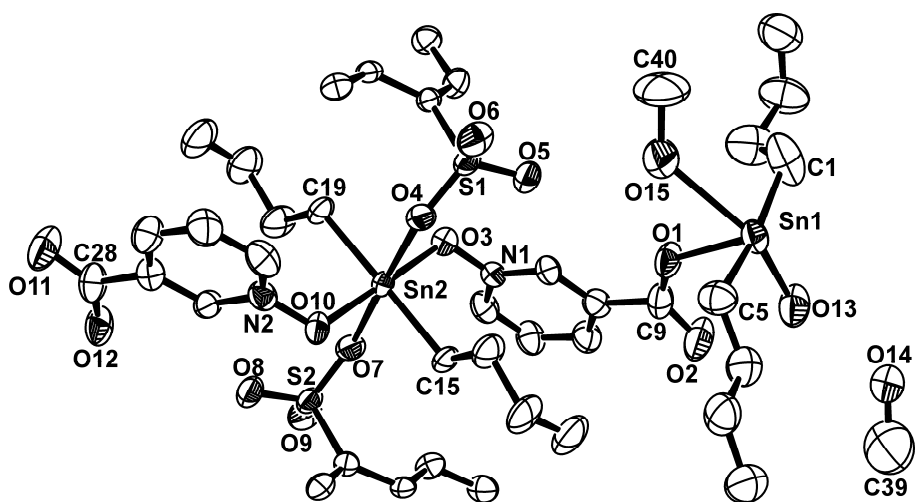
**Figure S15.** ORTEP representation of the asymmetric unit of **8·2H<sub>2</sub>O** shown at 50 % probability displacement ellipsoids Hydrogen atoms are omitted for clarity. The asymmetric unit of **8·2H<sub>2</sub>O** contains two different types of tin centers, among which one (Sn1) has an occupancy of 0.5, while the other (Sn2) shows full occupancy. Other components present in the asymmetric unit are three *n*-butyl groups (one is present on Sn1 and two are bound to Sn2), one monodentate DPPOE ligand bound to Sn1, one bridging 1,5-naphthalene disulfonate ligands, one hydroxide and one methanol bound to Sn2 and one lattice water molecule.



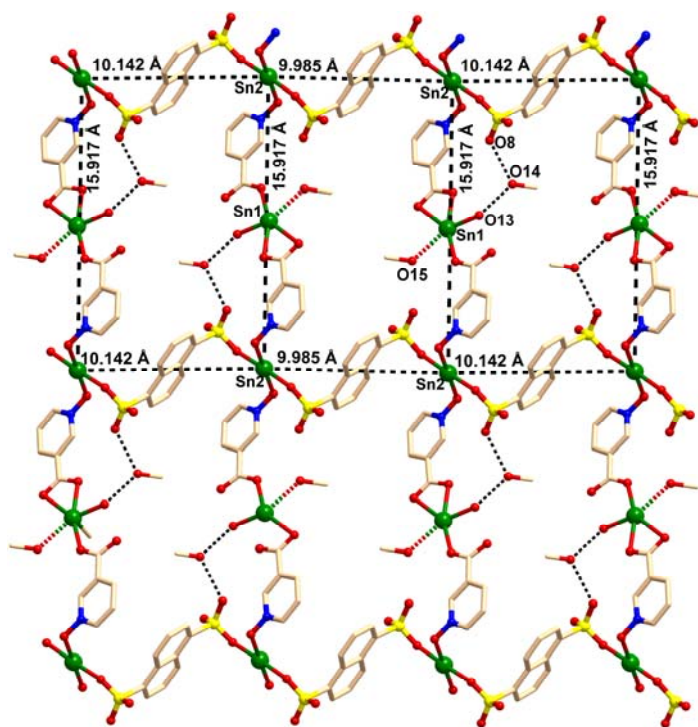


**Figure S16.** Guest water molecules ( $O_w$  (disordered), shown as ‘*light blue*’ balls) occupying the interlayer region of  $8 \cdot 2H_2O$ . *n*-Butyl’ groups, ‘phenyl’ groups of DPPOE ligand, and all the hydrogen atoms (except that of hydroxide bridge), have been omitted for clarity.

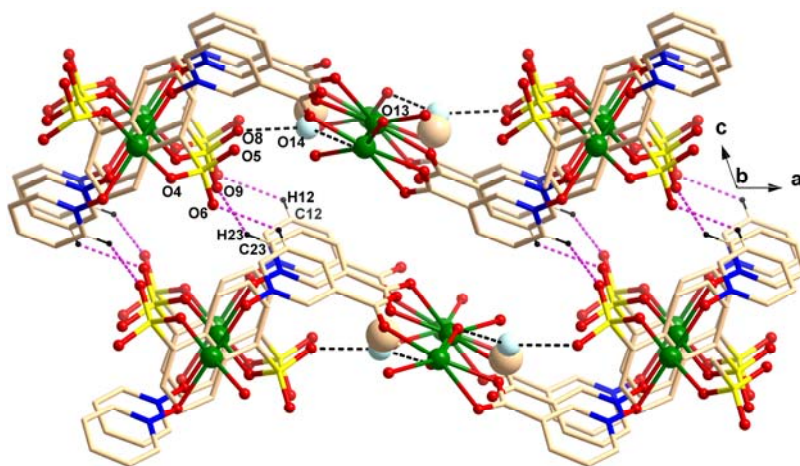
Figure S16 depicts the layered structure of  $8 \cdot 2H_2O$ . The asymmetric unit of  $8 \cdot 2H_2O$  contains one lattice water molecule ( $O_w$ ), which is disordered over two positions ( $O11a$  and  $O11b$ ). These guest water molecules are held in position with the help of hydrogen bonding interactions with coordinated methanol molecules belonging to one chain, as well with one of the non-bonding oxygen atom ( $O8$ ) of sulfonate moiety coordinated to  $Sn2$ , latter being located on the adjacent chain. The  $O \cdots O$  distance involved in these contacts range from 2.03 Å - 3.47 Å. The interlayer separation in this region ( $Sn \cdots Sn$ ) is 15.22 Å.



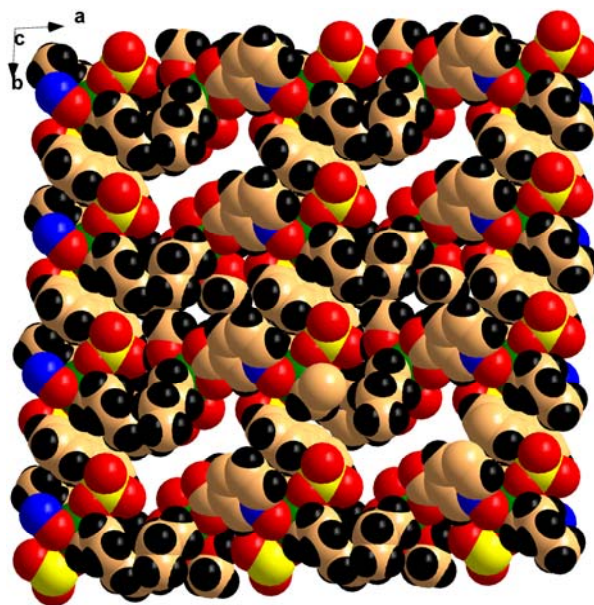
**Figure S17.** ORTEP representation of the asymmetric unit of **9-CH<sub>3</sub>OH** showing 50 % probability displacement ellipsoids. Hydrogen atoms are not shown. The asymmetric unit of **9-CH<sub>3</sub>OH** consists of two tin atoms (Sn1 and Sn2), four *n*-butyl groups, two NO-IV ligands, half of each of the two crystallographically different 1,5-naphthalenedisulfonate moieties [(S1, O4, O5, O6) and (S2, O7, O8, O9)], one bound water molecule (at Sn1) and two methanol molecules.



(a)

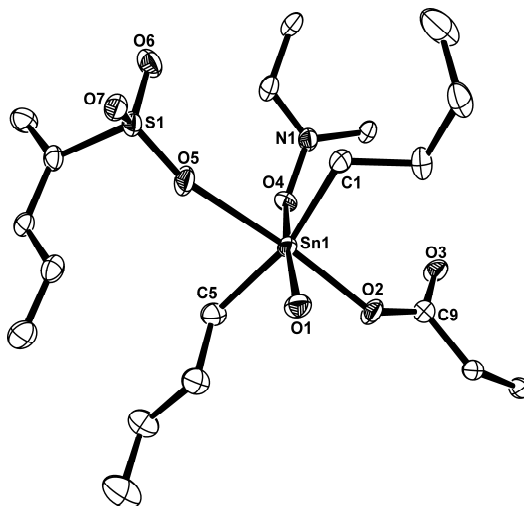


(b)

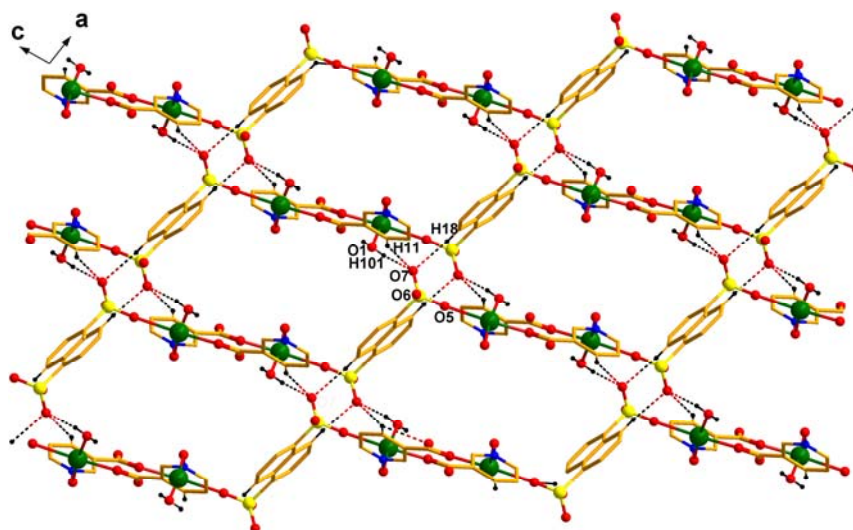


(c)

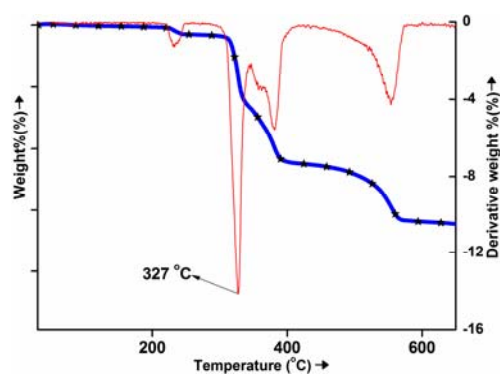
**Figure S18.** (a) Two types of rectangular grids (slightly varying width) of **9-CH<sub>3</sub>OH**. (b) Association between 2D-layers of **9-CH<sub>3</sub>OH** through weak C–H...O contacts existing between aromatic hydrogen atoms (H23 and H12) of NO-IV belonging to one layer, and non-bonding oxygen atoms (O6 and O9) of the disulfonate ligand present in the adjacent layer (See Table S9 for metric parameters). *n*-Butyl groups, and the hydrogen atoms (except those involved in C–H...O interactions) have been omitted for clarity. (c) A *space-filling* diagram of **9-CH<sub>3</sub>OH**, after omitting the completely free methanol (C39, O14) molecules



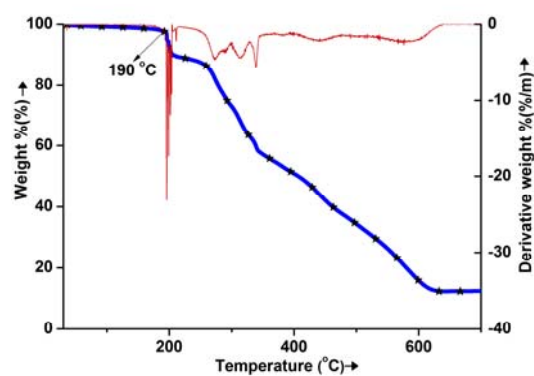
**Figure S19.** ORTEP representation the asymmetric unit of **10** shown at 50 % probability displacement ellipsoids. Hydrogens have been omitted for clarity.



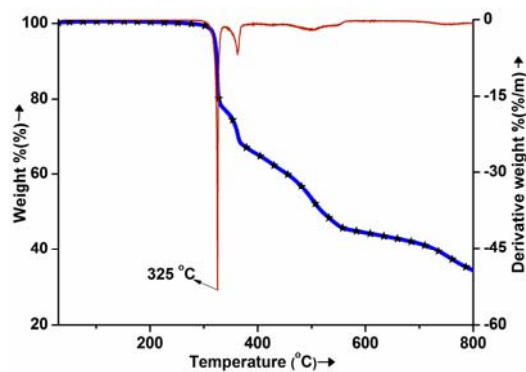
**Figure S20.** 3D- packing of **10** down the *b* axis. The 2D-layers of **10** are piled up along the *a* axis with the help of interlayer O–H...O and C–H...O contacts between one of the non-bonding oxygen atom (O7) of disulfonate of one layer and three different hydrogen atoms (H101, H11, and H18) belonging to the adjoining layer. Among these, H101 belongs to bound water molecule, H11 is from NO-IV, and H18 is owned by 1,5-naphthalenedisulfonate. The metric parameters involved in these interactions are given in Table S9.



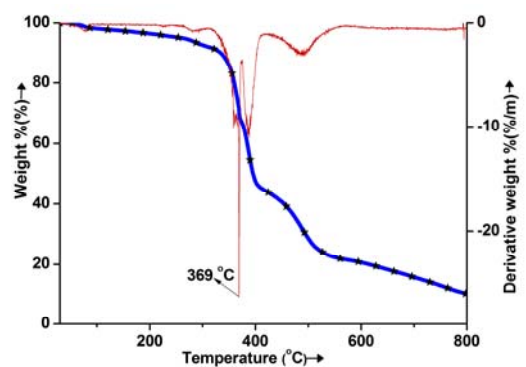
**Figure S21.** Thermogravimetric curve for **1**



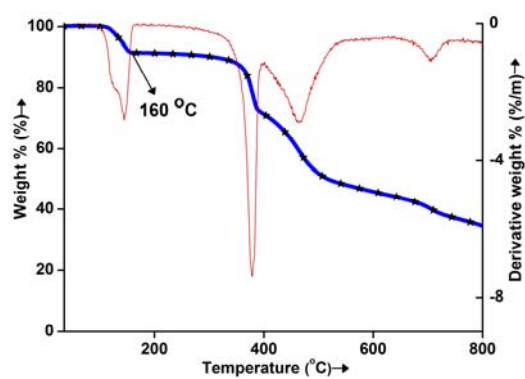
**Figure S22.** Thermogravimetric curve for **2**



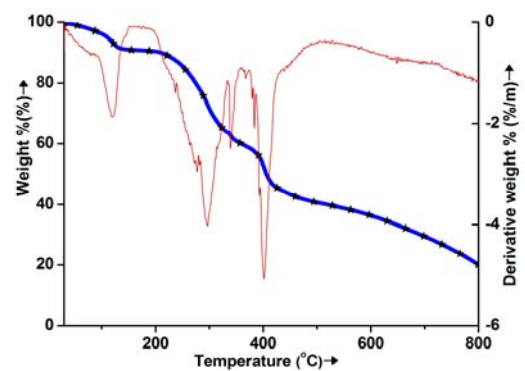
**Figure S23.** Thermogravimetric curve of **3**



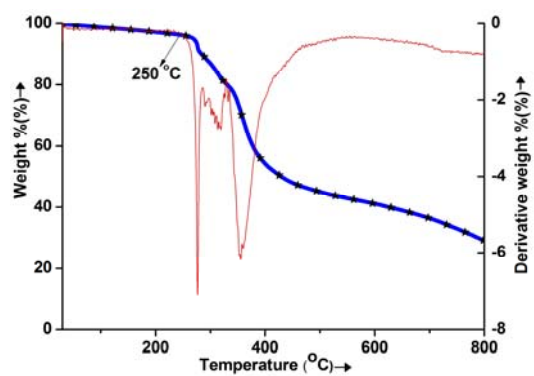
**Figure S24.** Thermogravimetric curve of **4**



**Figure S25.** Thermogravimetric curve of 5·2H<sub>2</sub>O



**Figure S26.** Thermogravimetric curve of 6·5H<sub>2</sub>O.



**Figure S27.** Thermogravimetric curve of 7



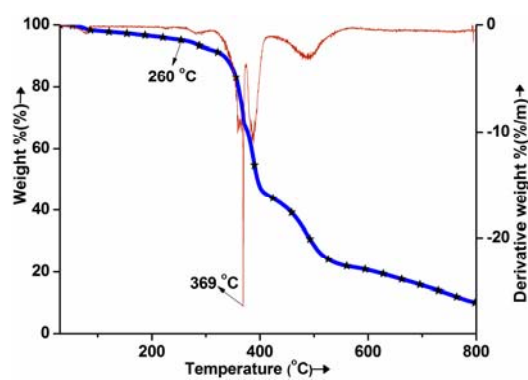


Figure S28. Thermogravimetric curve of 8·2H<sub>2</sub>O

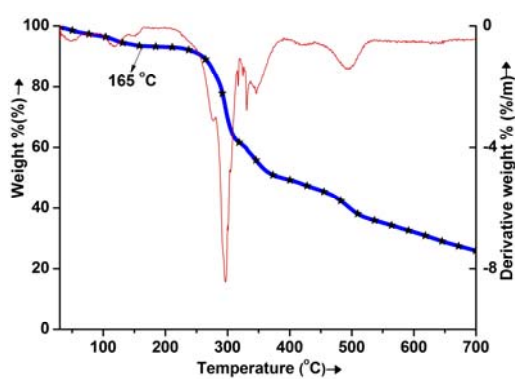


Figure S29. Thermogravimetric curve of 9·CH<sub>3</sub>OH

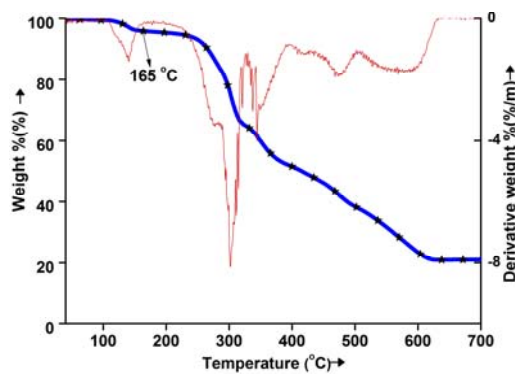


Figure S30. Thermogravimetric curve of 10



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

Compound	<b>1</b>
Empirical formula	<b>C<sub>26</sub>H<sub>44</sub>O<sub>8</sub>S<sub>2</sub>Sn<sub>2</sub></b>
Formula weight (g)	<b>786.11</b>
Temperature (K)	273(2)
Crystal system, Space group	Monoclinic, I2/a
Unit cell dimensions	a = 12.482(4) b = 11.464(4) c = 23.561(8) $\alpha$ = 90.00 $\beta$ = 93.501(6) $\gamma$ = 90.00
Volume (Å <sup>3</sup> )	3365(2)
Z, Density (Calculated)	<b>4</b> 1.552 mg/m <sup>3</sup>
F(000)	1584
Crystal size (mm <sup>3</sup> )	0.10 x 0.06 x 0.05
$\theta$ range for data collection (°)	2.41 to 26.00
Limiting indices	-15 $\leq$ h $\leq$ 15, -13 $\leq$ k $\leq$ 14, -29 $\leq$ l $\leq$ 23
Reflections collected / unique	9089 / 3288 [R(int)= 0.0407]
Completeness to $\theta$ (%)	99.4 % ( $\theta$ = 26.00 °)
Data / Restraints / Parameters	3288 / 1 / 175
Goodness-of-fit on F <sup>2</sup>	1.143
Final R indices [I > 2 $\sigma$ (I)]	R1 = 0.0712,
R indices (all data)	R1 = 0.0883,
Largest diff. Peak and hole (e.Å <sup>-3</sup> )	2.700 and -0.733

**Table S2.** Crystal data collection and refinement parameters for **2, 3** and **4**.

Compound	<b>2</b>	<b>3</b>	<b>4</b>
Empirical formula	<b>C<sub>28</sub>H<sub>44</sub>N<sub>4</sub>O<sub>12</sub>S<sub>2</sub>Sn</b>	<b>C<sub>28</sub>H<sub>32</sub>N<sub>2</sub>O<sub>8</sub>S<sub>2</sub>Sn</b>	C <sub>44</sub> H <sub>48</sub> O <sub>8</sub> P <sub>2</sub> S <sub>2</sub> Sn
Formula weight (g)	<b>931.58</b>	<b>707.37</b>	949.57
Temperature (K)	100(2)	293(2)	100(2)
Crystal system, Space group	Triclinic, P-1	Triclinic, P-1	Triclinic, P-1

Unit cell dimensions	a = 7.586(5) b = 9.937(5) c = 13.658(5) $\alpha$ = 91.602(5) $\beta$ = 99.890(5) $\gamma$ = 107.579(5)	a = 7.9839(9) Å b = 9.9867(12) Å c = 10.9059(13) Å $\alpha$ = 106.101(2) ° $\beta$ = 106.472(2) ° $\gamma$ = 106.237(2) °	a = 9.201(5) Å b = 13.445(5) Å c = 17.380(5) Å $\alpha$ = 90.066(5) ° $\beta$ = 93.106(5) ° $\gamma$ = 105.472(5) °
Volume (Å <sup>3</sup> )	963.4(9)	738.12 (15)	2068.8(15)
Z, Density (Calculated)	1, 1.606 mg/m <sup>3</sup>	1, 1.591 mg/m <sup>3</sup>	2, 1.524 mg/m <sup>3</sup>
F(000)	478	360	976
Crystal size (mm <sup>3</sup> )	0.2 x 0.2 x 0.2	0.08 x 0.06 x 0.05	0.2 x 0.2 x 0.2
$\theta$ range for data collection (°)	2.16 to 25.99	2.30 to 25.00 °	1.98 to 25.00 °
Limiting indices	-9 ≤ h ≤ 9, -12 ≤ k ≤ 7, -16 ≤ l ≤ 16	-5 ≤ h ≤ 9, -11 ≤ k ≤ 11, -12 ≤ l ≤ 12	-10 ≤ h ≤ 10, -15 ≤ k ≤ 8, -20 ≤ l ≤ 20
Reflections collected / unique	5427 / 3700 [R(int)= 0.0214]	3737 / 2500 [R(int)= 0.0192]	10630/7134 [R(int)= 0.0318]
Completeness to $\theta$ (%)	97.7 % ( $\theta$ = 25.99 °)	97.8 % ( $\theta$ = 25.00 °)	98.3 % ( $\theta$ = 25.00 °)
Data / Restraints / Parameters	3700 / 1 / 268	2530 / 0 / 187	7134 / 0 / 489
Goodness-of-fit on F <sup>2</sup>	1.149	1.158	1.058
Final R indices [I > 2 $\sigma$ (I)]	R1 = 0.0342, wR2 = 0.0896	R1 = 0.0433, wR2 = 0.1227	R1 = 0.0652, wR2 = 0.1678
R indices (all data)	R1 = 0.0377, wR2 = 0.1057	R1 = 0.0469, wR2 = 0.1380	R1 = 0.0897, wR2 = 0.1937
Largest diff. Peak and hole (e.Å <sup>-3</sup> )	0.668 and -0.518	1.418 and -1.205	1.733 and -1.021

**Table S3.** Crystal data collection and refinement parameters for 5·2H<sub>2</sub>O, 6·5H<sub>2</sub>O and 7.

Compound	5·2H <sub>2</sub> O	6·5H <sub>2</sub> O	7
Empirical formula	C <sub>32</sub> H <sub>32</sub> N <sub>2</sub> O <sub>12</sub> S <sub>2</sub> Sn	C <sub>44</sub> H <sub>62</sub> N <sub>4</sub> O <sub>15</sub> S <sub>2</sub> Sn	C <sub>54</sub> H <sub>60</sub> N <sub>4</sub> O <sub>16</sub> S <sub>4</sub> Sn
Formula weight (g)	819.41	1069.79	1267.99
Temperature (K)	273(2)	293(2)	100(2)
Crystal system, Space group	Triclinic, P-1	Monoclinic, C2/c	Monoclinic, C2/c

Unit cell dimensions	a = 9.0055(17) b = 13.531(3) c = 14.507(3) $\alpha$ = 88.756(3) $\beta$ = 81.254(3) $\gamma$ = 75.653(3)	a = 22.765(5) Å b = 13.306(5) Å c = 17.780(5) Å $\alpha$ = 90.000(5) ° $\beta$ = 111.187(5) ° $\gamma$ = 90.000(5) °	a = 22.376(2) Å b = 7.6045(8) Å c = 30.762(3) Å $\alpha$ = 90.0 ° $\beta$ = 91.763(2) ° $\gamma$ = 90.0 °
Volume (Å <sup>3</sup> )	1692.5(6)	5022(3)	5231.9(10)
Z, Density (Calculated)	2, 1.608 mg/m <sup>3</sup>	4, 1.408 mg/m <sup>3</sup>	4, 1.610 mg/m <sup>3</sup>
F(000)	832	2204	2616
Crystal size (mm <sup>3</sup> )	0.14 x 0.07 x 0.04	0.2 x 0.2 x 0.2	0.2 x 0.2 x 0.2
$\theta$ range for data collection (°)	2.09 to 25.00	2.37 to 28.36 °	2.22 to 25.99 °
Limiting indices	-7 ≤ h ≤ 10, -16 ≤ k ≤ 15, -16 ≤ l ≤ 17	-19 ≤ h ≤ 30, -16 ≤ k ≤ 17, -23 ≤ l ≤ 23	-15 ≤ h ≤ 27, -8 ≤ k ≤ 9, -37 ≤ l ≤ 35
Reflections collected / unique	8781 / 5868 [R(int) = 0.0260]	16250 / 6179 [R(int) = 0.0553]	14102 / 5121 [R(int) = 0.0422]
Completeness to $\theta$ (%)	98.4 % ( $\theta$ = 25.00 °)	98.2 % ( $\theta$ = 28.36 °)	
Data / Restraints / Parameters	5868 / 6 / 469	6179 / 0 / 301	5121 / 0 / 360
Goodness-of-fit on F <sup>2</sup>	1.036	1.054	1.070
Final R indices [I > 2 $\sigma$ (I)]	R1 = 0.0468, wR2 = 0.1167	R1 = 0.0532, wR2 = 0.1239	R1 = 0.0441, wR2 = 0.1112
R indices (all data)	R1 = 0.0663, wR2 = 0.1341	R1 = 0.0932, wR2 = 0.1623	R1 = 0.0589, wR2 = 0.1229
Largest diff. Peak and hole (e.Å <sup>-3</sup> )	1.085 and -0.348	0.624 and -0.711	0.950 and -0.555

**Table S4.** Crystal data collection and refinement parameters for **8·2H<sub>2</sub>O**, **9·2CH<sub>3</sub>OH** and **10**.

Compound	<b>8·2H<sub>2</sub>O</b>	<b>9·2CH<sub>3</sub>OH</b>	<b>10</b>
Empirical formula	<b>C<sub>98</sub>H<sub>128</sub>O<sub>22</sub>P<sub>4</sub>S<sub>4</sub>Sn<sub>3</sub></b>	C <sub>40</sub> H <sub>60</sub> N <sub>2</sub> O <sub>15</sub> S <sub>2</sub> Sn <sub>2</sub>	C <sub>19</sub> H <sub>27</sub> NO <sub>7</sub> SSn
Formula weight (g)	2266.19	1110.40	532.17
Temperature (K)	293(2)	100(2)	153(2)
Crystal system, Space group	Triclinic, P-1	Monoclinic, P21/c	Monoclinic, P21/c
Unit cell dimensions	a = 11.751(5) b = 11.816(5) c = 18.039(5) α = 88.629(5) β = 78.684(5) γ = 89.348(5)	a = 15.917(19) Å b = 20.121(2) Å c = 15.568(18) Å α = 90.000 ° β = 109.276(2) ° γ = 90.000 °	a = 8.277(5) Å b = 11.073(5) Å c = 24.350(5) Å α = 90.0 ° β = 99.485(5) ° γ = 90.0 °
Volume (Å <sup>3</sup> )	2455.3(16)	4706.5(10)	2201.2(17)
Z, Density (Calculated)	1, 1.533 mg/m <sup>3</sup>	4, 1.567 mg/m <sup>3</sup>	4, 1.606 mg/m <sup>3</sup>
F(000)	1166	2264	1080
Crystal size (mm <sup>3</sup> )	0.09 x 0.06 x 0.05	0.1 x 0.06 x 0.05	0.09 x 0.07 x 0.04
θ range for data collection (°)	2.30 to 26.00	2.44 to 26.99 °	2.03 to 26.00 °
Limiting indices	-14 ≤ h ≤ 14, -14 ≤ k ≤ 12, -22 ≤ l ≤ 21	-20 ≤ h ≤ 19, 0 ≤ k ≤ 25, 0 ≤ l ≤ 19	-10 ≤ h ≤ 9, -7 ≤ k ≤ 13, -30 ≤ l ≤ 26
Reflections collected / unique	13679 / 9421 [R(int) = 0.0370]	10173 / 10173 [R(int) = 0.0000]	11922 / 4310 [R(int) = 0.0300]
Completeness to θ (%)	97.6 % (θ = 26.00 °)	99.1 % (θ = 26.99 °)	99.7 % (θ = 26.00 °)
Data / Restraints / Parameters	9421 / 1 / 599	10173 / 1 / 558	4310 / 2 / 272
Goodness-of-fit on F <sup>2</sup>	1.073	1.055	1.058
Final R indices [I > 2σ(I)]	R1 = 0.0696, wR2 = 0.1868	R1 = 0.0732, wR2 = 0.1827	R1 = 0.0316, wR2 = 0.0728
R indices (all data)	R1 = 0.0975, wR2 = 0.2213	R1 = 0.1066, wR2 = 0.2350	R1 = 0.0379, wR2 = 0.0769
Largest diff. Peak and hole (e.Å <sup>-3</sup> )	5.810 and -1.034	6.045 and -1.522	1.166 and -0.564

**Table S5.** Hydrogen bonding parameters for **2**

<b>D–H...A</b>	<b>D–H</b>	<b>H...A</b>	<b>D...A</b>	<b>D–H...A</b>	<b>symmetry</b>
	(Å)	(Å)	(Å)	(°)	
O6–H6B...O2	0.808(5)	1.927(5)	2.681(4)	154.93(45)	-1+x, y, -1+z
O6–H6A...O4	0.824(5)	1.889(5)	2.706(4)	171.12(47)	2-x, 2-y, 2-z
C11–H11...O5	0.930(6)	2.291(2)	3.177(5)	159.12(22)	1-x, 2-y, 1-z
C6–H6...O5	0.930(3)	2.441(2)	3.33(4)	160.36(20)	1+x, y, z
C18–H18...O3	0.930(4)	2.437(3)	3.30(5)	153.89(24)	1+x, y, z
O2... $\pi_{\text{centroid}}$ (N1,C5-C7,C13-C14)				3.62(4) Å	

**Table S6.** Hydrogen bonding parameters for the compound **3**

<b>D–H...A</b>	<b>D–H</b>	<b>H...A</b>	<b>D...A</b>	<b>D–H...A</b>	<b>symmetry</b>
	(Å)	(Å)	(Å)	(°)	
C6–H6...O3	0.931(6)	2.337(4)	3.223(8)	159.14(39)	-x, 1-y, 2-z
C8–H8...O3	0.929(6)	2.310(4)	3.197(7)	159.48(33)	x, y, 1+z

**Table S7.** Hydrogen bonding parameters for **5·2H<sub>2</sub>O**

<b>D–H...A</b>	<b>D–H</b>	<b>H...A</b>	<b>D...A</b>	<b>D–H...A</b>	<b>symmetry</b>
	(Å)	(Å)	(Å)	(°)	
O1–H51...O5	0.806(6)	1.895(6)	2.683(5)	165.53(61)	x, y, z
O1–H52...O8	0.797(3)	1.835(3)	2.618(5)	166.96(28)	x, y, z
O2–H53...O12	0.775(5)	1.947(5)	2.690(7)	160.43(50)	1+x, 1+y, z
O2–H54...O11	0.785(4)	1.818(6)	2.590(8)	167.78(66)	x, 1+y, z
O11–H55...O6	0.785(4)	2.066(4)	2.850(6)	176.48(42)	x, y, z
O11–H56...O9	0.814(5)	1.870(6)	2.675(8)	169.63(49)	x, y, z
O12...O7				2.746(8)	x, y, z
O12...O10				3.016(6)	x, y, z

**Table S8.** O...O distances for hydrogen bonding interactions in **6**·5H<sub>2</sub>O

<b>D...A</b>	<b>D...A</b> (Å)	<b>symmetry</b>
O3...O6	2.728(6)	1+x, y, z
O6...O8	3.026(1)	x, 1-y, 0.5+z
O8...O7	2.973(1)	0.5-x, 0.5-y, 1-z
O4...O7	2.901(1)	1.5-x, 0.5+y, 1.5-z
O7...O4*	2.979(1)	1+x, 1-y, 0.5+z

**Table S9.** Hydrogen bonding parameters for the compounds **7-10**

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)	symmetry
7					
O5–H51...O6	0.840(3)	1.750(3)	2.578(4)	167.97(19)	-0.5+x, 0.5+y, z
C15...H15–O1	0.949(4)	2.237(2)	3.164(4)	165.0(22)	0.5+x, -0.5+y, z
O... $\pi$			3.343(5) Å		
8·2H <sub>2</sub> O					
O9–H101...O2	0.817(9)	1.955(9)	2.664(8)	144.76(88)	x, -1+y, z
9·CH <sub>3</sub> OH					
C12–H12...O6	0.931(8)	2.456(5)	3.097(9)	126.14(45)	x, 1.5-y, -0.5+-z
C23–H23...O9	0.931(8)	2.480(5)	3.183(9)	132.42(45)	x, 1.5-y, -0.5+z
O5...O15			2.821(9)	x, y, z	
O8...O14			2.713(9)	-1+x, y, z	
O13...O14			2.553(1)	x, y, z	
10					
O1–H101...O7	0.792(2)	1.891(3)	2.676(3)	170.92(23)	1-x, -y, 1-z
C11–H11...O7	0.930(3)	2.500(2)	3.326(4)	148.20(20)	x, 0.5-y, -0.5+z
C18–H18...O7	0.930(3)	2.441(2)	3.247(4)	145.01(21)	1-x, -y, 1-z

## Experimental Section

**General Methods:** Solvents were distilled and dried prior to use according to standard procedures.  $[n\text{-Bu}_2\text{SnO}]_n$ ,  $[\text{Ph}_2\text{SnO}]_n$ , 1,5-naphthalenedisulfonic acid tetrahydrate, 4,4'-bipyridine, 1,3-bis(4-pyridyl)propane, nicotinic acid, 1,2-bis(diphenylphosphino)ethane (all from Aldrich), glacial acetic acid (sd fine, India), 30 % hydrogen peroxide (Rankem, India) were purchased and used without any further purification. A 0.1N  $\text{H}_2\text{SO}_4$  (pH = 1.33) solution was made in double distilled water to be used for the maintenance of acidic pH during crystallization. Melting points were measured using a JSGW melting point apparatus and are uncorrected. Elemental analyses were carried out using a Thermoquest CE instruments model EA/110 CHNS-O elemental analyzer. Infrared spectra were recorded as KBr pellets on a FT-IR Bruker-Vector Model.  $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{119}\text{Sn}$  NMR spectra were obtained on a JEOL-DELTA2 500 model spectrometer using  $(\text{CD}_3)_2\text{SO}$  as solvent. Chemical shifts were referenced with respect to tetramethylsilane (for  $^1\text{H}$  NMR), 80 %  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ) and tetramethyltin (for  $^{119}\text{Sn}$  NMR) respectively.  $^{119}\text{Sn}$  NMR spectra were recorded under broad-band decoupled conditions. Thermogravimetric Analysis was carried out on a Perkin Elmer Pyris 6 Thermogravimetric analyzer.

**X-ray Crystallographic Study:** The crystal data for compounds **1-10** were collected on a Bruker SMART APEX CCD Diffractometer. SMART software package (version 5.628) was used for collecting data frames, SAINT software package (version 6.45) for integration of the intensity and scaling and SADABS was used for absorption correction. The details pertaining to the data collection and refinement for crystals are provided in Tables S1-S4 of Supporting information. The structures were solved and refined by full-matrix least squares on  $F^2$  using SHELXTL software package.<sup>1</sup> Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions, and a riding model was used. In case of **1** (Figure S1), three carbons of tin bound '*n*-butyl' group are doubly disordered and labeled as C6 & C6A; C7 & C7A; C8 & C8A. The highest residual electron density of 2.70 is located near tin atom. For **3** (Figure S4), three carbon atoms of the *n*-butyl group were found to have orientational disorder and were refined isotropically. These are labeled as C2 & C2A; C3 & C3A; C4 & C4A & CB. The highest residual electron density of 1.42 is located near Sn1. In the asymmetric unit of **4** (Figure S6), four carbon atoms, two from each of the two *n*-butyl groups present, are doubly disordered (C3 & C3A; C4 & C4A (for Sn1) and C6 & C6A; C8 & C8A (for Sn2)) and were refined isotropically. Because of the large anisotropic displacement parameters, some of the carbon atoms (C20, C21, C40) of phosphorus bound *phenyls* were refined isotropically. The highest residual electron density of 1.73, situated near C39, may be attributed to the unresolved disorder associated with this atom, which in turn was refined isotropically. The asymmetric unit of **5**·2H<sub>2</sub>O (Figure S8) contains two lattice water molecules (O11 & O12). In the asymmetric unit of **6**·5H<sub>2</sub>O (Figure S10), due to diffused electron density, hydrogens were not added to the oxygen atom of the lattice water molecules and these have been refined isotropically. The terminal carbon atom of the *n*-butyl group is doubly disordered (C4 & C4A) and was refined isotropically. In the case of **8**·2H<sub>2</sub>O (Figure S15), the oxygen atom of methanol molecule bound to Sn2, is disordered over two positions, labeled as O10 A & O10 B. Similarly, oxygen atom of the lattice water molecule is having orientational disorder (O11 A & O11 B). The positions of these oxygens have been refined isotropically. Hydrogens have not been added to these oxygen atoms. In the asymmetric unit of **9**·CH<sub>3</sub>OH (Figure S17), it was difficult to locate the hydrogens around the oxygen atom (O13) of bound water, and oxygen atom (O14) of one of the methanol molecule, because of diffused electron density around these atoms. The highest residual electron density in this case is 6.04 and is situated near one of the tin atom (Sn1). Figures (1-11) of main text and their bonding parameters were obtained from DIAMOND 3.1f software package.<sup>2</sup>

### References:

- 1) G. M. Sheldrick, *SHELXTL* version 6.14, Bruker AXS Inc., Madison, WI, **2003**.
- 2) *DIAMOND* version 3.1f, Crystal Impact GbR, Bonn, Germany, **2004**.