Supporting Information

Polynuclear Bismuth Oxido Sulfonato Clusters, Polymers and Ion-Pairs from Bi_2O_3 under Mild Conditions

Dimuthu C. Senevirathna,[a] Victoria L. Blair, [a] Melissa V. Werrett [a] and Philip C. Andrews [a*]

[a] School of Chemistry, Monash University, Clayton, Melbourne, VIC 3800, Australia.

Contains:

^{1}H NMR spectra of complexes **1** - **8**.

Table S1 Characteristic symmetric and asymmetric vibrations (cm^{-1}) of SO_3^- observed in **1** - **8**.

Summary of Crystallographic Data for **1, 2, 4, 6 – 8.**

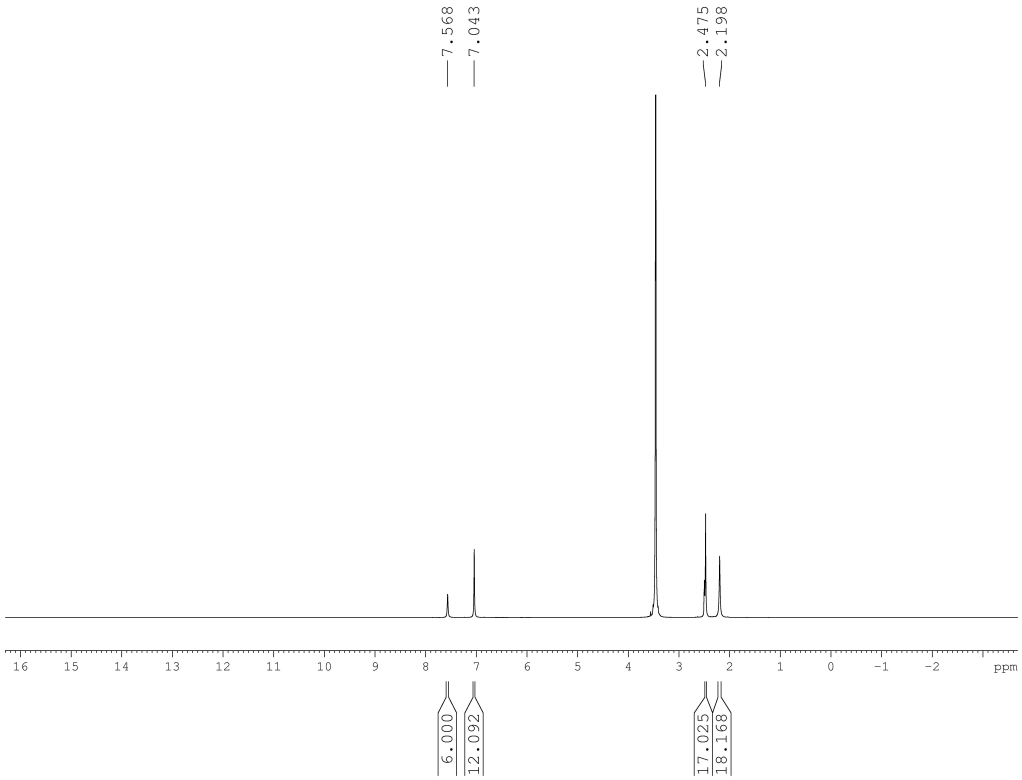

Figure S1. ^{1}H NMR spectrum of $[Bi_6O_4(OH)_4(2,5\text{-DMS})_6(H_2O)_6]\cdot 10H_2O$ (**1**·$10H_2O$) in D_6-DMSO.

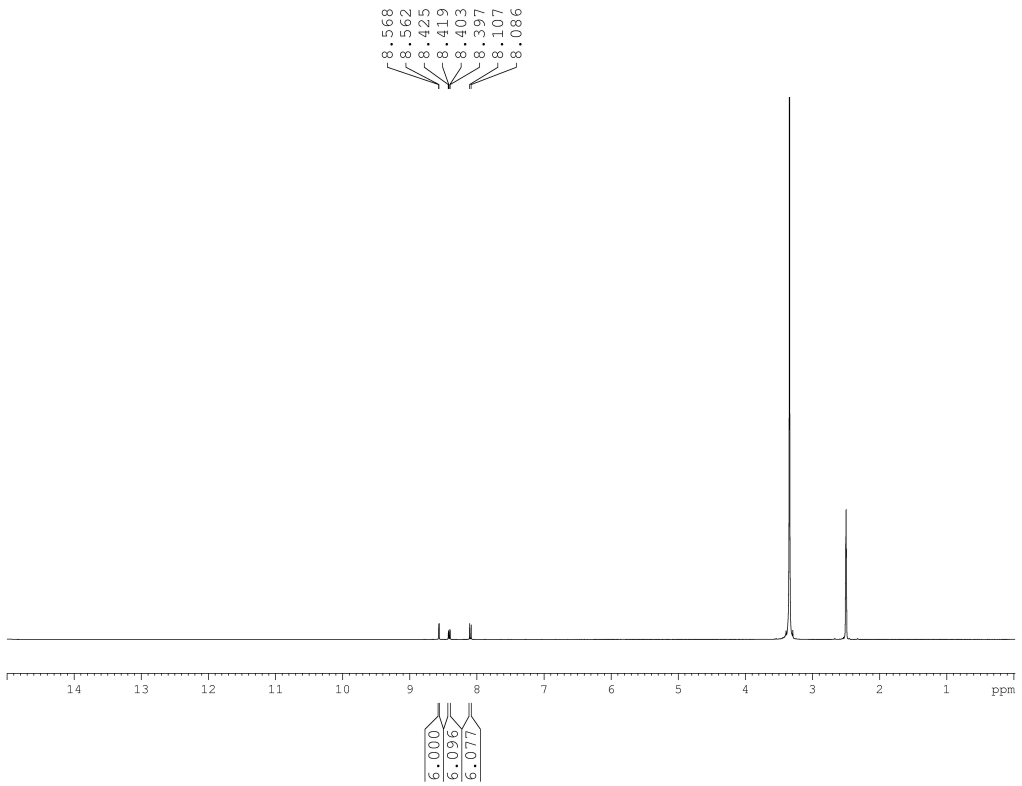

Figure S2. ^{1}H NMR spectrum of $[Bi_6O_4(OH)_4(2,4\text{-DNS})_6(H_2O)_6]\cdot 6H_2O$ (**2**·$6H_2O$) in D_6-DMSO.

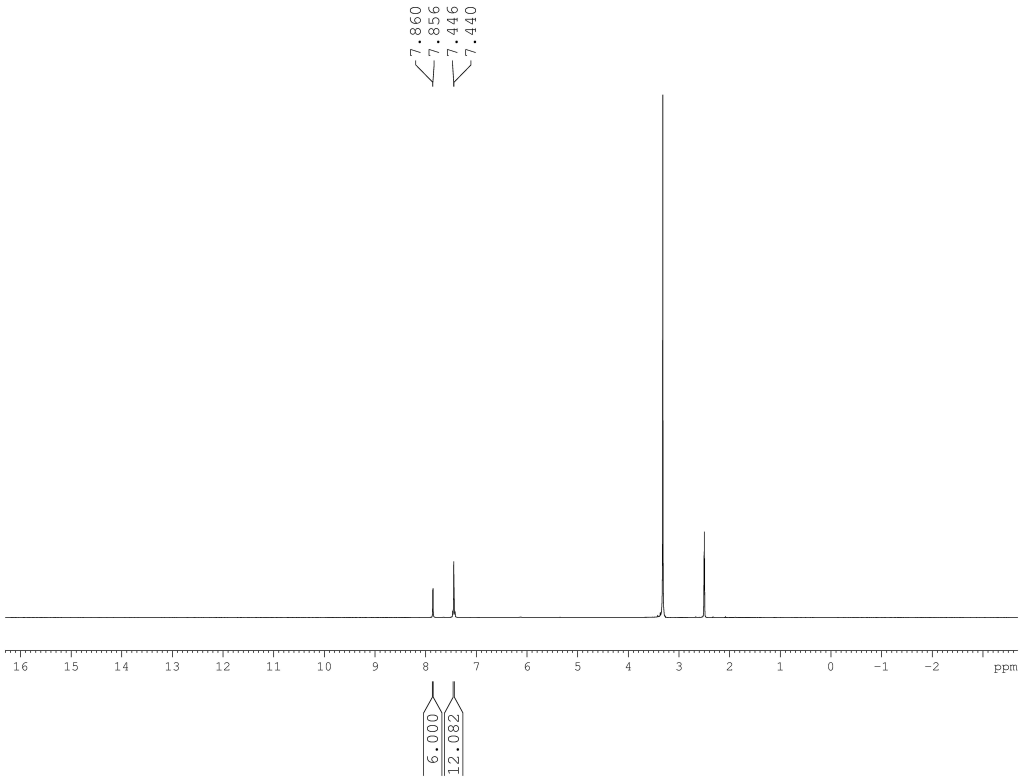

Figure S3. ^{1}H NMR spectrum of $[Bi_6O_4(OH)_4(2,5\text{-DCS})_6(H_2O)_6]$ (**3**) in D_6-DMSO.

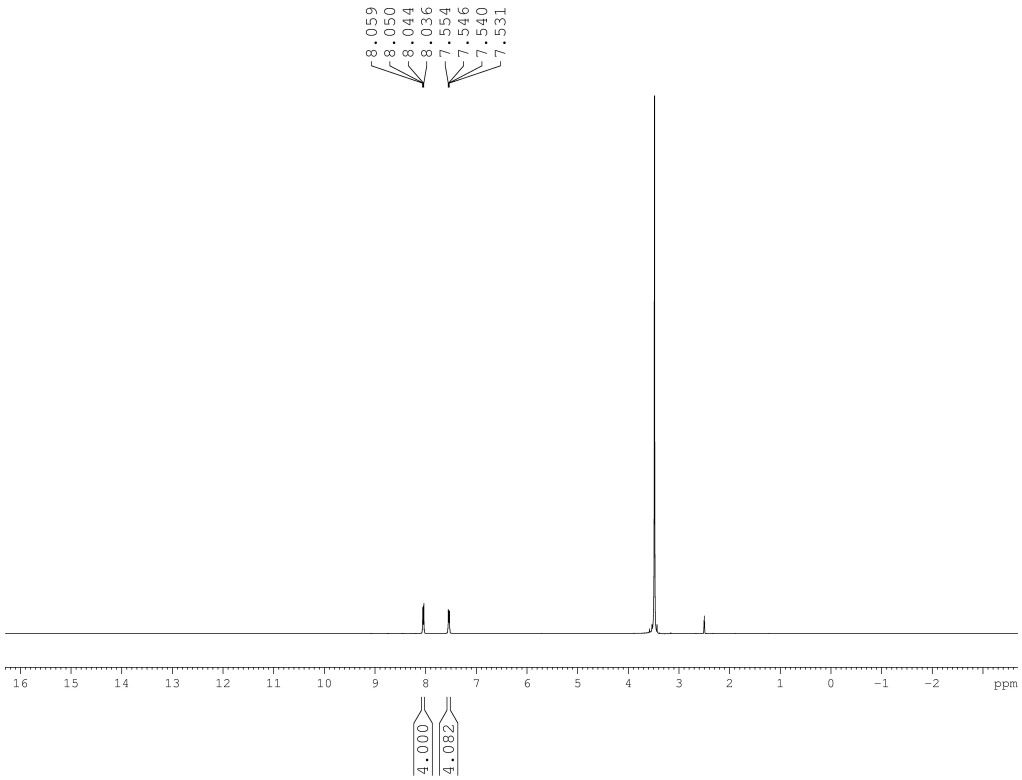

Figure S4. ^{1}H NMR spectrum of $[Bi(1,2\text{-BDS})(OH)(H_2O)_2]_\infty$ (**4**) in D_6-DMSO.

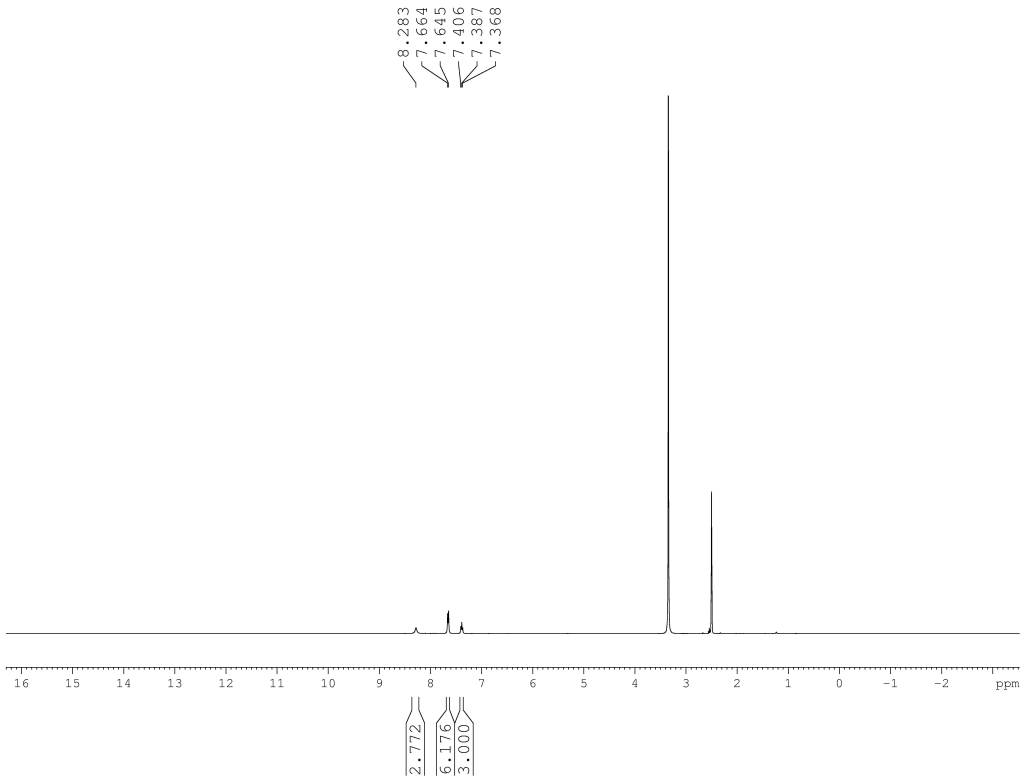

Figure S5. ^{1}H NMR spectrum of $[Bi_6O_4(OH)_4(1,3\text{-}BDS)_3]\cdot 8H_2O$ (**5**$\cdot 8H_2O$) in D_6-DMSO.

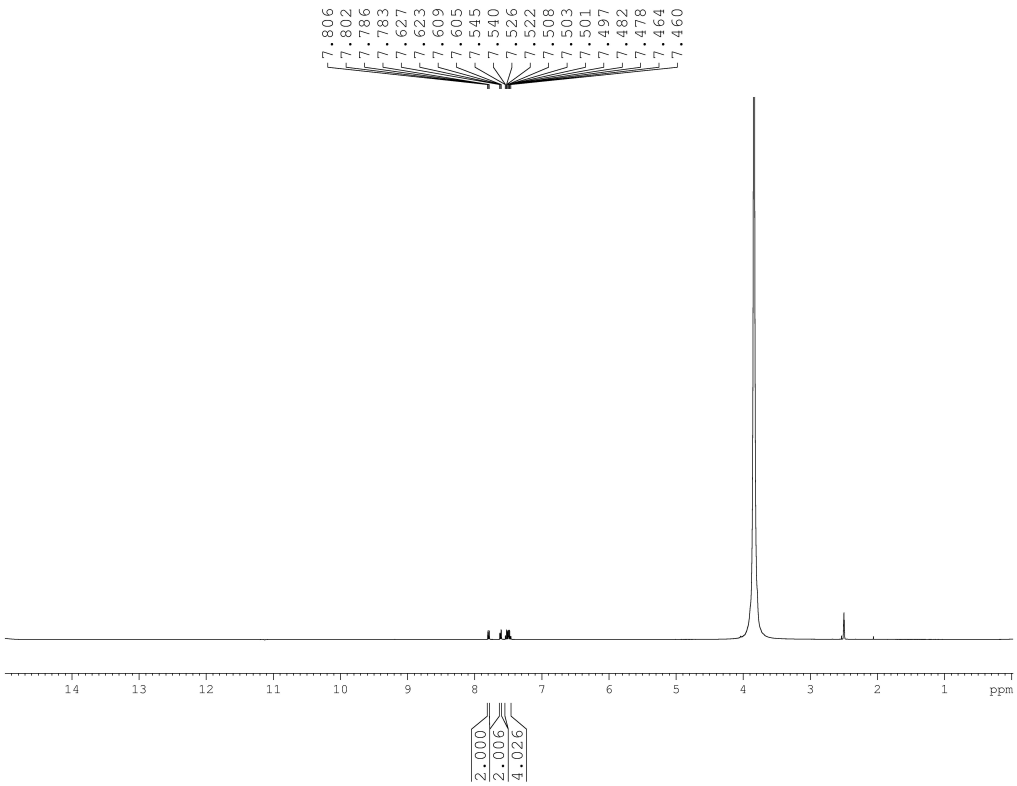

Figure S6. ^{1}H NMR spectrum of [Bi(2-SB)(2-SB*H*)H_2O]$_\infty$·2H_2O (**6**·2H_2O) in D_6-DMSO.

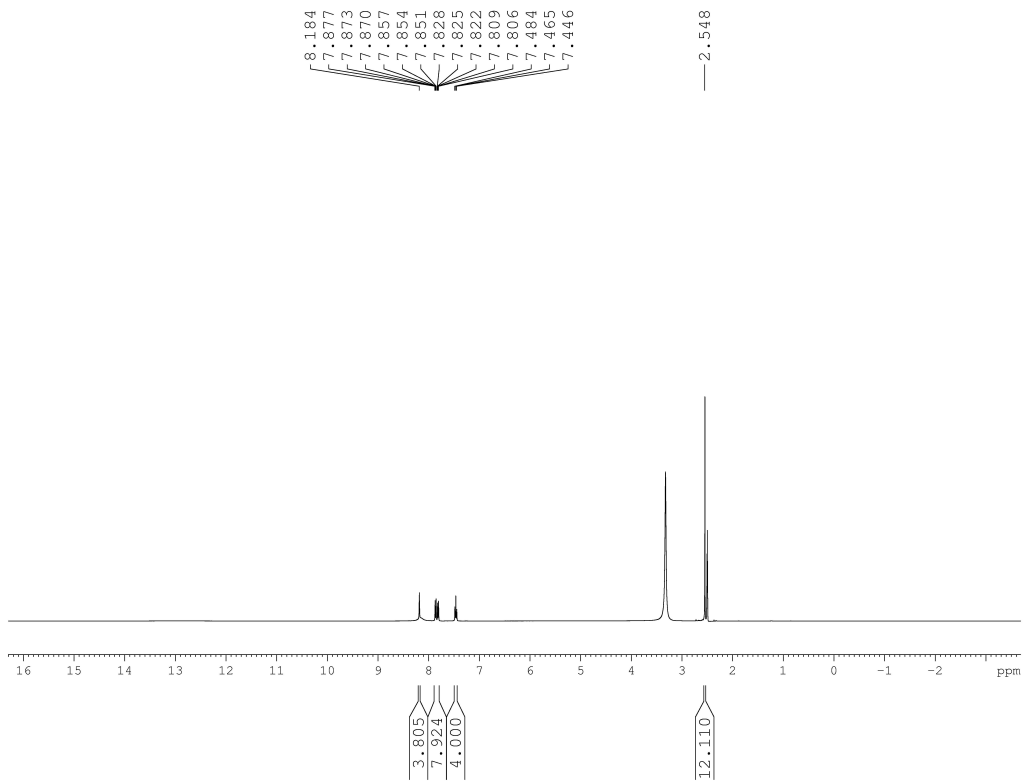

Figure S7. ^{1}H NMR spectrum of $[NH_2(Me)_2]_2[Bi_2(3\text{-}SB)_4]$ (**7**) in D_6-DMSO.

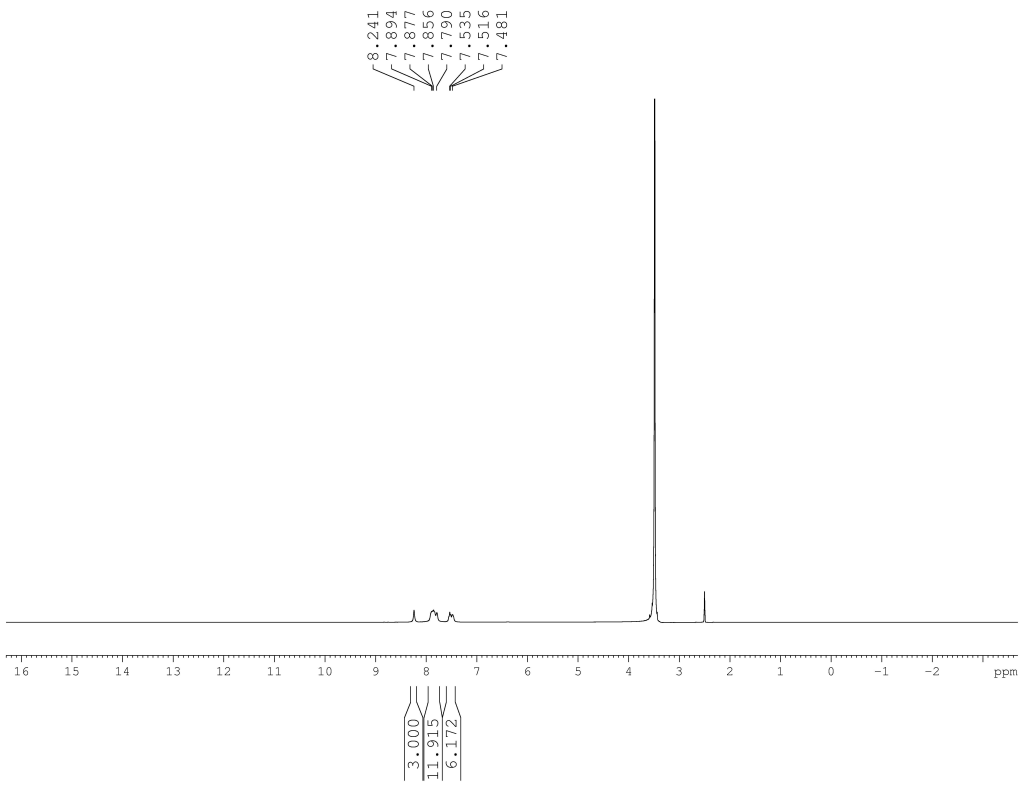

Figure S8. ^{1}H NMR spectrum of $[Bi(NPS)_2(H_2O)_6][NapS]\cdot 3H_2O$ (**8**$\cdot 3H_2O$) in D_6-DMSO.

Table S1. Characteristic symmetric and asymmetric vibrations (cm^{-1}) of SO_3^- observed in **1-8**.

Bismuth Compound	**ν_{as} (SO_3^-)/cm^{-1}**	**ν_s (SO_3^-)/cm^{-1}**
1	1199, 1138, 1113	1079, 1005
2	1187, 1114, 1136	1063, 1018
3	1177, 1146, 1120	1096, 1065, 1011
4	1201, 1152, 1122	1079, 1046, 1025
5	1159	1088, 1020
6	1224, 1138	1081, 1013
7	1220, 1190, 1137	1097, 1081, 1029
8	1151, 1134	1089, 1028

Crystallography Details

Crystallographic data for compounds **1**, **2**, **4**, **6**, **7** and **8** were obtained on a Bruker X8 APEXII CCD diffractometer equipped with an OXFORD Cryosystems 700 and cooled to 123(1) K. Data was collected with monochromatic (graphite) Mo Kα radiation (λ = 0.71073 Å) and processed using the Bruker Apex2 v2012.2.0 software[1]; Lorentz, polarization and absorption corrections (multi-scan – SADABS)[2] were applied. Compounds **1, 2, 4, 7** and **8** were solved and refined with SHELX-97.[3] All non-hydrogen atoms were refined with anisotropic thermal parameters unless otherwise indicated and hydrogen atoms were placed in calculated positions using a riding model with C-H = 0.95-0.98 Å and U_{iso}(H)=xU_{iso}(C), x = 1.2 or 1.5.

Table S2. Crystallographic data and structure refinement for compounds **1**·10H_2O, **2**·6H_2O, and **4**.

	1·10H_2O	**2**·6H_2O	**4**
Formula	C_{48} H_4 Bi_6O_{42} S_6	$C_{36}H_{22}Bi_6N_{12}O_{62}S_6$	$C_6H_5BiO_9S_2$
M_r	2698.75	3060.90	494.20
Crystal size [mm]	0.36 × 0.05 × 0.04	0.42 X 0.26 X 0.23	0.10 x 0.07 x 0.06
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P-1*	*P2(1)/n*	*P2(1)/c*
a [Å]	12.5097(4)	11.8859(4)	10.8699(4)
b [Å]	16.9984(7)	32.8361(12)	14.5978(5)
c [Å]	18.3985(7)	19.1944(8)	7.4365(3)
α [°]	81.864(3)	90	90
β [°]	89.629(3)	91.744(4)	101.677(2)
γ [°]	77.331(3)	90	90
V [Å^3]	3777.5(2)	7487.8(5)	1155.58(7)
Z	2	4	4
T [K]	173(2)	173(2)	173(2)
$\rho_{calcd.}$ [mg cm^{-1}]	2.373	2.715	2.841
μ [mm^{-1}]	14.185	14.352	15.656
Reflections collected/unique	33054/16473	48498/23897	21099
R_{int}	0.0400	0.0545	0.0797
$R1$ [$I>2\sigma(I)$]	0.0475	0.0588	0.0582
$wR2$ (all data)	0.1099	0.1033	0.1847
GoF	1.092	1.027	1.076

Table S2. Crystallographic data and structure refinement for compounds **6**·2H_2O, **7** and **8**·3H_2O.

	6·2H_2O	**7**	**8**·3H_2O
Formula	$C_{56}H_{32}Bi_4O_{52}S_8$	$C_{16}H_{16}BiNO_{10}S_2$	$C_{30}H_{21}BiO_{18}S_3$
M_r	2629.22	655.40	974.63
Crystal size [mm]	0.43 x 0.12 x 0.12	0.41 x 0.32 x 0.24	0.36 x 0.05 x 0.04
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P2(1)/c*	*C2/c*	*P 1 2(1)/n 1*
a [Å]	20.5422(12)	18.2952(11)	16.9759(17)
b [Å]	11.3347(7)	12.5655(7)	7.5200(7)
c [Å]	8.3209(5)	10.1319(6)	28.236(3)
α [°]	90	90	90
β [°]	93.223(2)	117.9820(10)	98.536(9)
γ [°]	90	90	90
V [Å^3]	1934.4(2)	2056.9(2)	3564.7(6)
Z	1	4	4
T [K]	173(2)	173(2)	173(2)
ρcalcd. [mg cm^{-1}]	2.257	2.116	1.816
μ [mm^{-1}]	9.399	8.829	5.200
Reflections collected/unique	30138/5471	15735/3023	16678/7823
R_{int}	0.0535	0.0288	0.0669
$R1$ [$I>2\sigma(I)$]	0.0268	0.0149	0.0602
$wR2$ (all data)	0.0610	0.0317	0.1676
GoF	1.040	1.064	1.079

References

1. *Bruker Apex2 v2012.2.0,* Bruker AXS, Madison, US, 2006.
2. Sheldrick, G. M. *SADABS v2.30,* University of Göttingen, 2002.
3. Sheldrick, G. M. *Acta. Cryst. Sect. A: Fundam. Crystallogr.,* **2008**, *64*, 112.