Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Lipophilic Bismuth Phosphates: A Molecular Tetradecanuclear Cage and a 1D-Coordination Polymer. Synthesis, Structure and Conversion to $BiPO_4$

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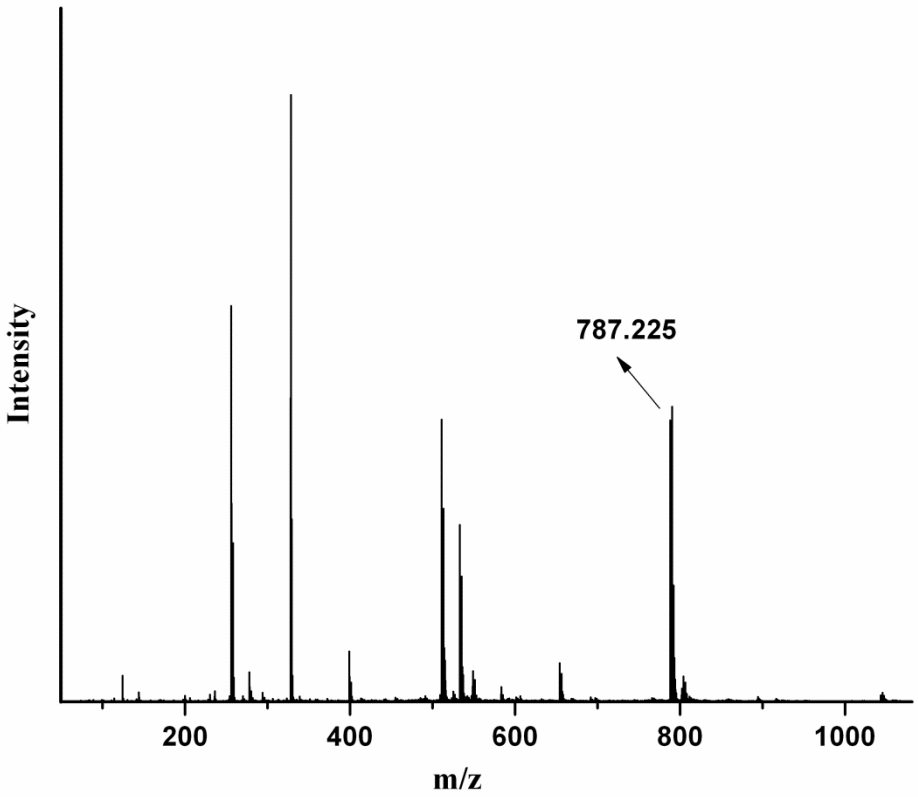
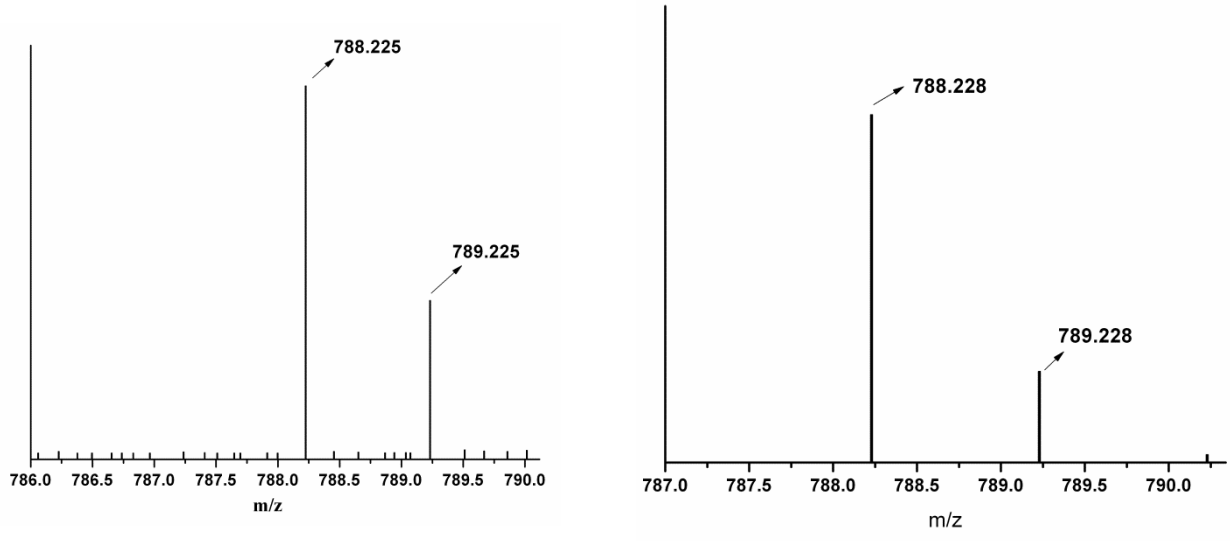


Figure S1 ESI-MS of **1**

$[(Bi(L1H)_2(CH_3OH)_2]^+$



a) Experimental **b) Simulated**

Figure S2 ESI-MS isotopic pattern of fragment in **1.**

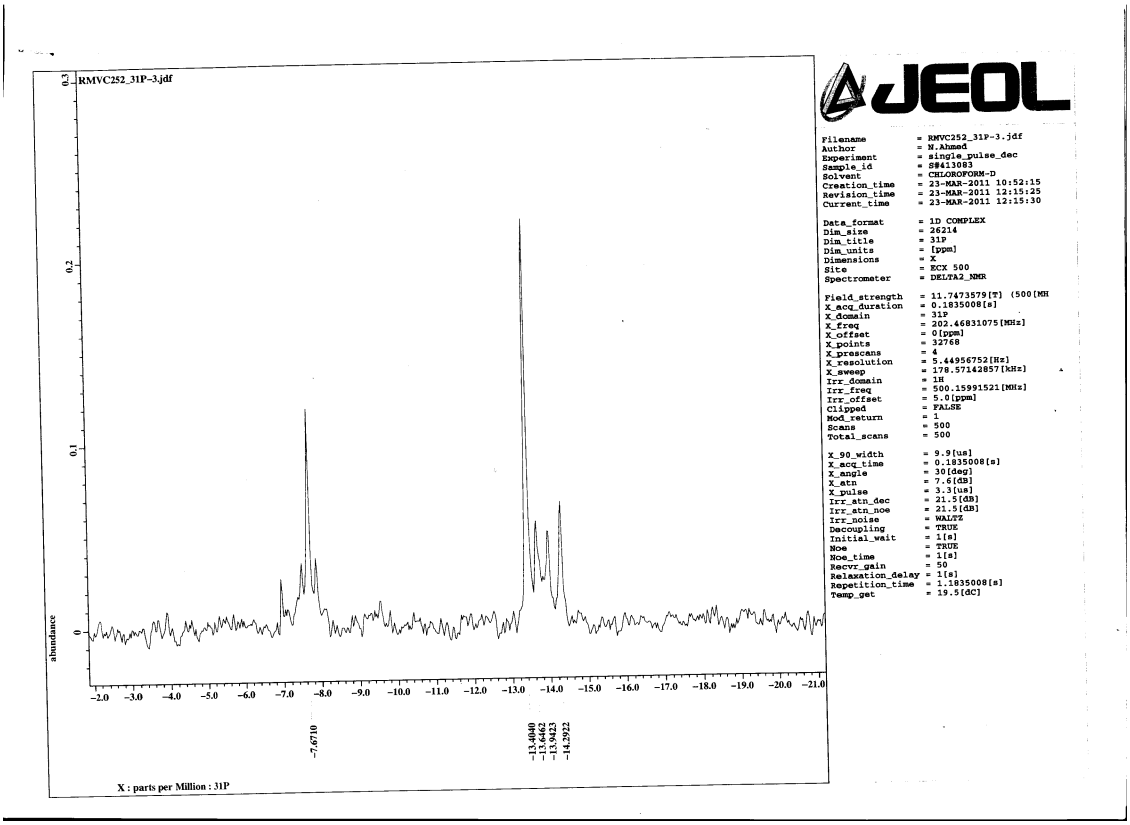


Figure S3 ^{31}P NMR spectra of **1**

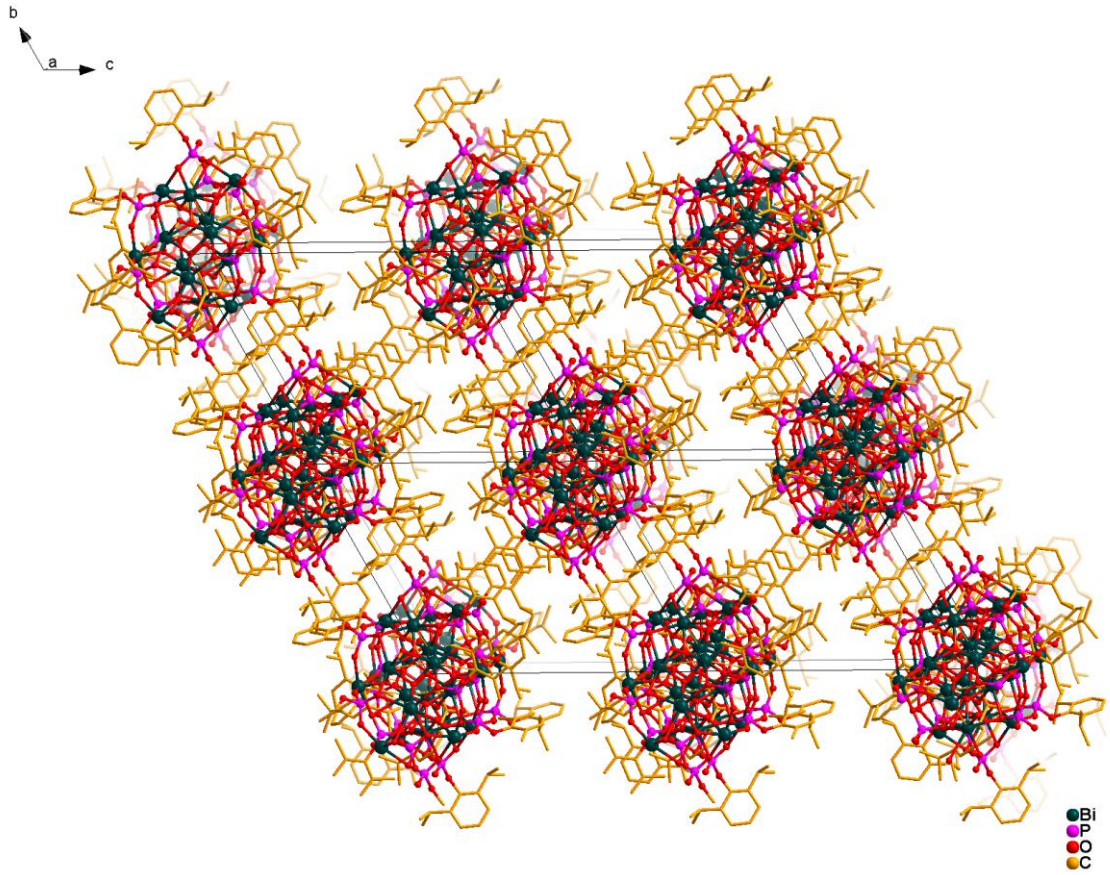


Figure S4. View showing the 3D arrangement in **1.** hydrogen atoms have been omitted for the sake of clarity.

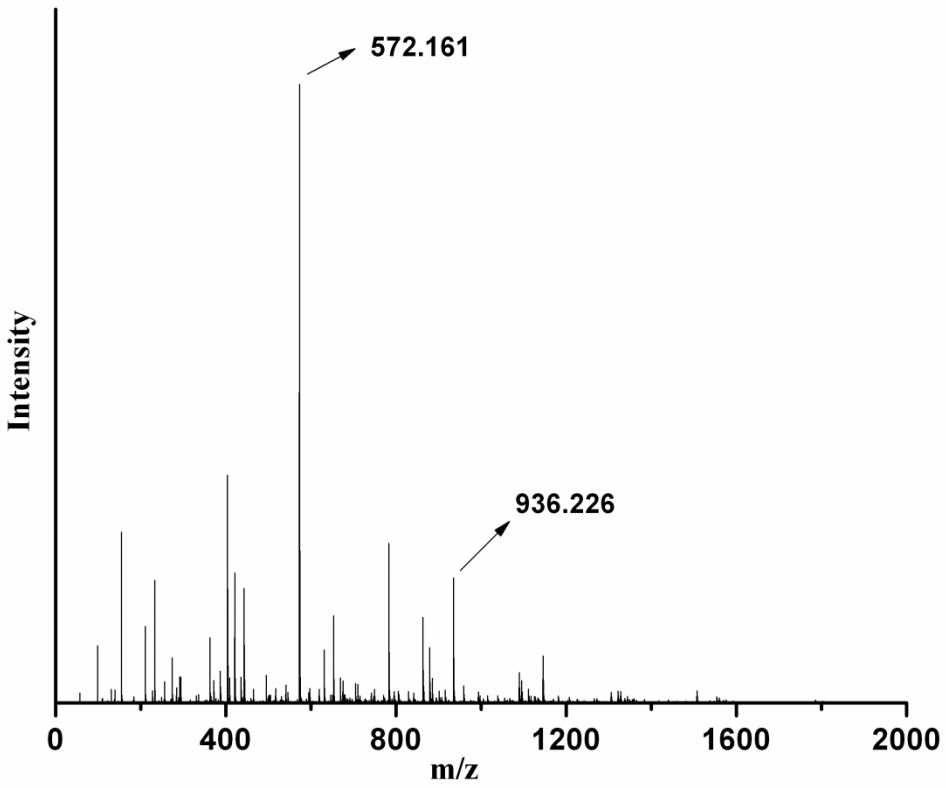
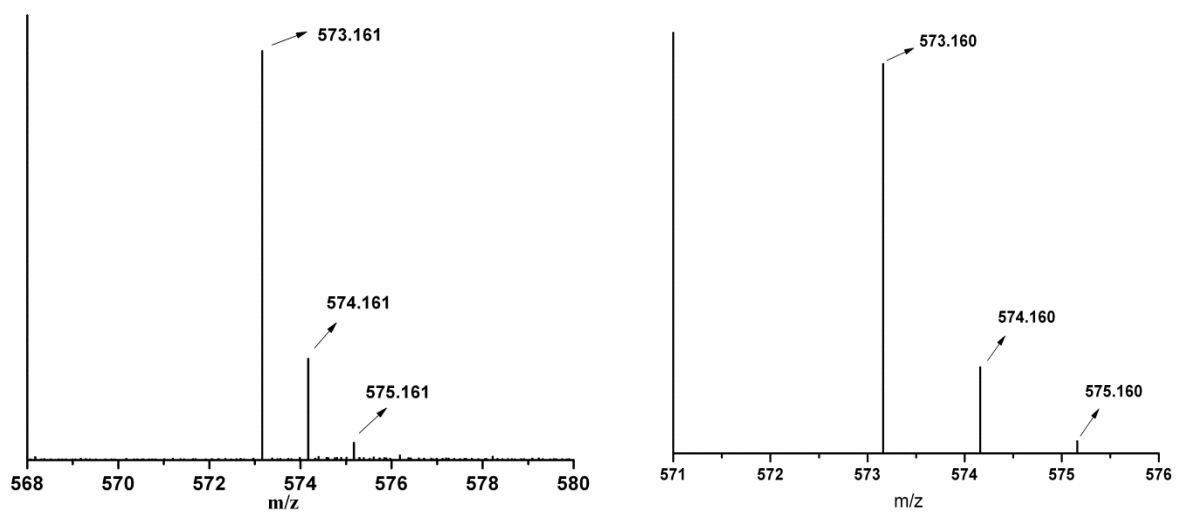


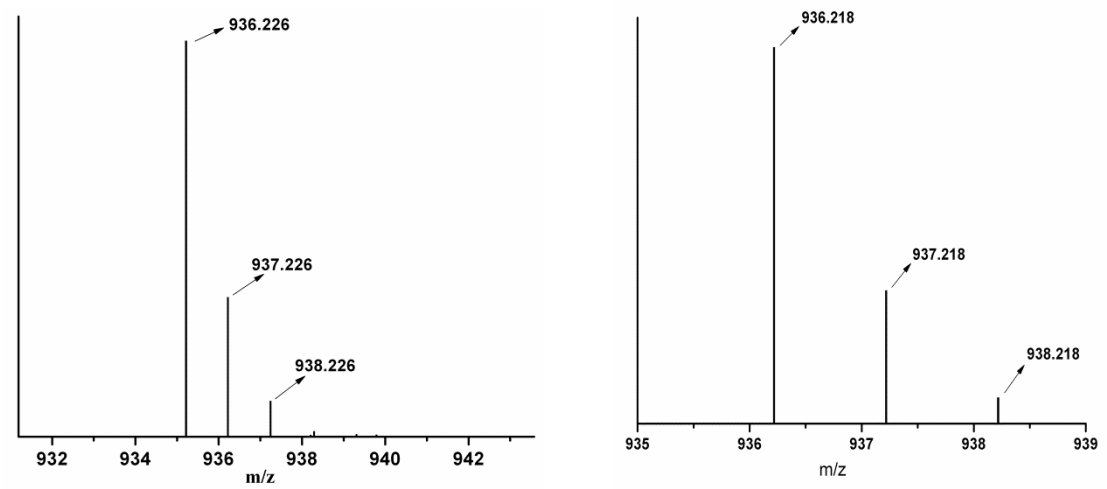
Figure S5 ESI-MS of **2**

$[(Ph_2BiL2]^+$



Experimental Simulated

$[(Ph_2Bi)_2L2]^+$



Experimental Simulated

Figure S6 ESI-MS isotopic pattern for the fragments in **2.**

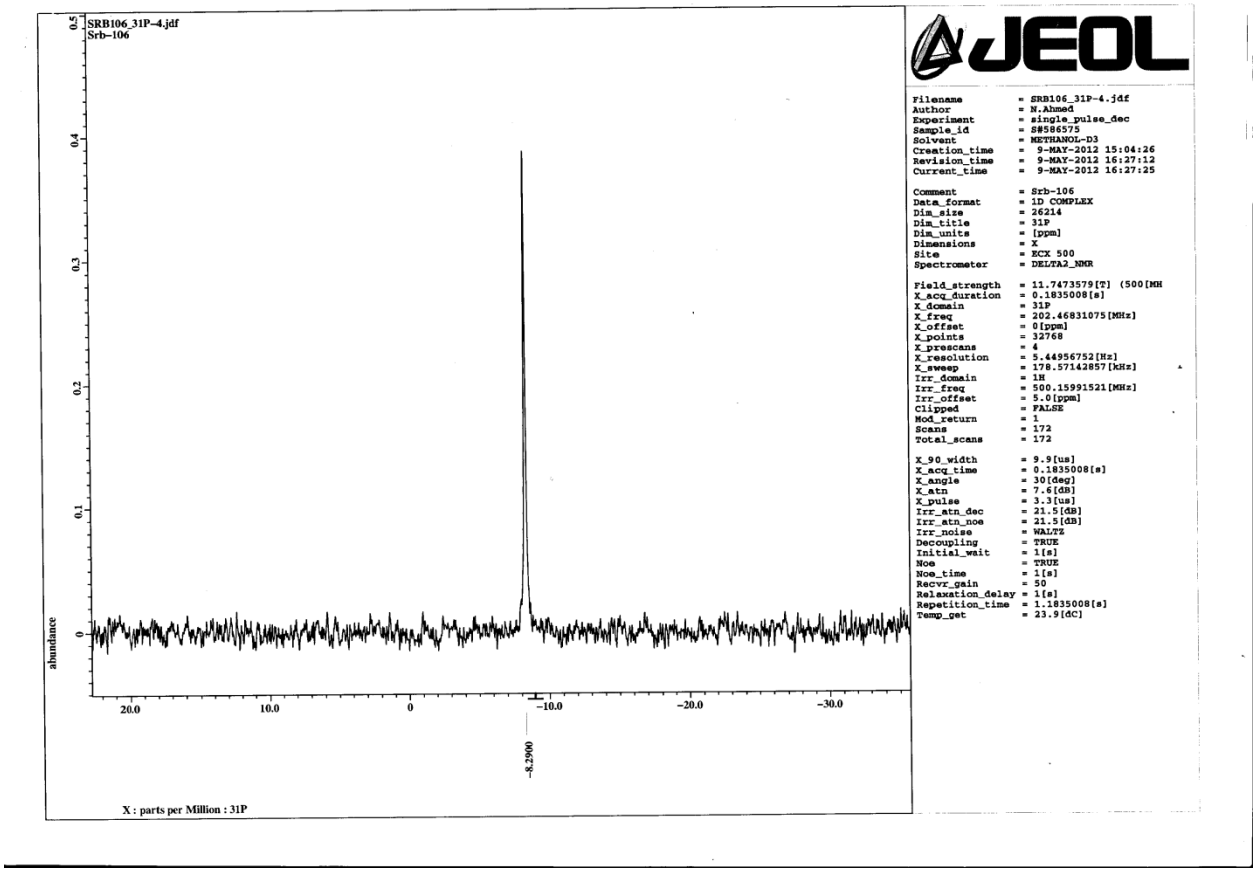


Figure S7 ^{31}P NMR spectra of **2**

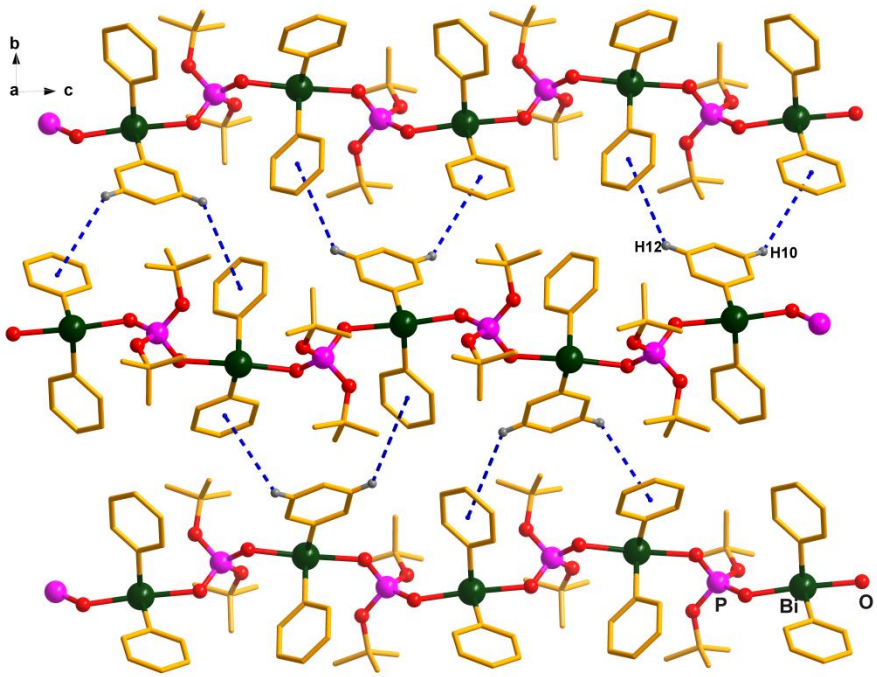


Figure S8. View showing the 2D arrangement of the 1D polymeric chain in **2** resulting due to C-H…pi interactions. The metric parameters involved are: C(10)-H(10), 0.930 (8)Å C10-H10…π, 3.698 (8) Å, C10-H10…π, 130.68 (4)° ; C(12)-H(12), 0.930 (7)Å , C12-H12…π, 4.271 (1) Å, C12-H12…π, 133.65 (4)° Hydrogen atoms have been omitted for the sake of clarity.

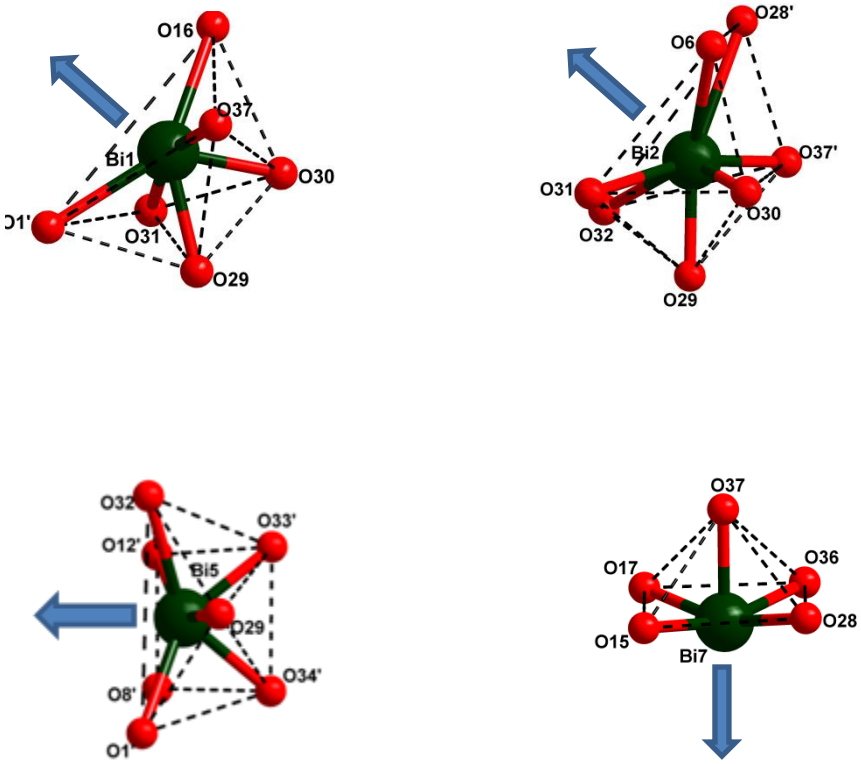
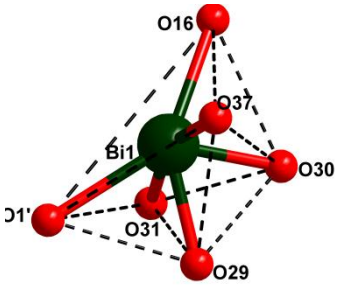
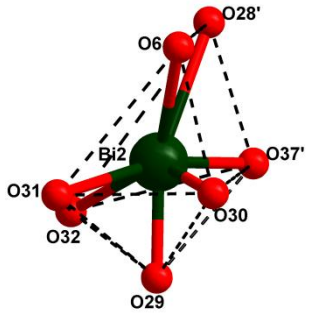
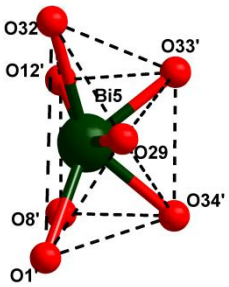


Chart S1: Presence of Stereochemically active lone pair of bismuth atoms in **1** (green color) and **2** (blue color), the arrows show the approximate location of lone pair electrons.

Table S1. Individual coordination environment of bismuth in **1** and Selected bond lengths (Å) and bond angles (°) parameters.

individual bismuth	bond distances		bond angles	
	Bi(1)-O(37)	2.228(11)	O(37)-Bi(1)-O(29)	92.1(6)
	Bi(1)-O(29)	2.199(10)	O(37)-Bi(1)-O(30)	91.7(5)
	Bi(1)-O(30)	2.187(11)	O(29)-Bi(1)-O(30)	71.2(6)
	Bi(1)-O(16)	2.628(13)	O(37)-Bi(1)-O(16)	96.4(5)
	Bi(1)-O(1)′	2.637(13)	O(37)-Bi(1)-O(1)′	99.0(6)
	Bi(1)-O(31)	2.735(13)	O(29)-Bi(1)-O(1)′	70.3(6)
	Bi(2)-O(30)	2.173(10)	O(30)-Bi(2)-O(37)′	94.8(6)
	Bi(2)-O(37)′	2.169(12)	O(30)-Bi(2)-O(29)	71.6(5)
	Bi(2)-O(29)	2.159(11)	O(37)′-Bi(2)-O(29)	92.1(5)
	Bi(2)-O(32)	2.589(11)	O(37)′-Bi(2)-O(32)	98.2(5)
	Bi(2)-O(31)	2.746(13	O(29)-Bi(2)-O(32)	71.2(6)
	Bi(2)-O(6)	2.614(13)	O(30)-Bi(2)-O(31)	72.9(5)
	Bi(2)-O(28)′	2.879(19)	O(29)-Bi(2)-O(31)	74.7(6)
			O(32)-Bi(2)-O(31)	86.0(6)
			O(30)-Bi(2)-O(6)	69.3(6)
			O(31)-Bi(2)-O(6)	82.8(5)
	Bi(5)-O(29)	2.164(11)	O(29)-Bi(5)-O(34)′	89.2(5)
	Bi(5)-O(34)′	2.203(9)	O(29)-Bi(5)-O(33)′	87.9(5)
	Bi(5)-O(33)′	2.229(10	O(34)-Bi(5)-O(33)′	74.7(4)
	Bi(5)-O(1)′	2.564(13)	O(29)-Bi(5)-O(1)′	72.8(6)
	Bi(5)-O(32)	2.591(12)	O(34)-Bi(5)-O(1)′	79.1(5)

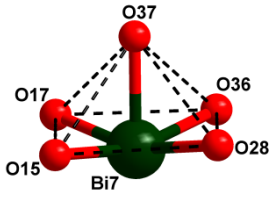
	Bi(5)-O(12)′ 2.717(13) Bi(5)-O(8)′ 2.416(13)	O(33)-Bi(5)-O(32) 76.3(5) O(34)-Bi(5)-O(12)′ 101.7(6) O(33)-Bi(5)-O(12)′ 69.6(5) O(32)-Bi(5)-O(12)′ 85.2(6)
	Bi(7)-O(37) 2.121(11) Bi(7)-O(17) 2.264(13) Bi(7)-O(36) 2.283(11) Bi(7)-O(15) 2.299(13) Bi(7)-O(28) 2.326(11)	O(37)-Bi(7)-O(17) 84.6(5) O(37)-Bi(7)-O(36) 82.7(6) O(17)-Bi(7)-O(36) 81.2(7) O(37)-Bi(7)-O(15) 81.9(5) O(37)-Bi(7)-O(28) 76.9(6) O(15)-Bi(7)-O(28) 81.7(6)

Table S2. bond distance (Å) and bond angle (°) data for **1**

Bi1	O1[1]	2.637(13)	O32	P1[1]	1.532(12)
Bi1	O16	2.628(13)	O36	P6[1]	1.526(11)
Bi1	O29	2.199(10)	O37	Bi2[1]	2.169(12)
Bi1	O30	2.187(11)	C1	C2	1.34(4)
Bi1	O31	2.735(13)	C1	C43	1.46(4)
Bi1	O37	2.228(11)	C2	C3	1.541(18)
Bi2	Bi7[1]	3.5718(12)	C2	C45	1.43(4)
Bi2	O6	2.719(13)	C3	C4	1.535(18)
Bi2	O29	2.159(11)	C3	C51	1.543(18)
Bi2	O30	2.173(10)	C5	C6	1.40(3)
Bi2	O31	2.746(13)	C5	C8	1.40(3)
Bi2	O32	2.589(11)	C6	C7	1.43(3)
Bi2	O37[1]	2.169(12)	C6	C42	1.523(18)
Bi3	O6	2.614(13)	C7	C41	1.38(3)
Bi3	O10	2.750(13)	C8	C9	1.553(18)
Bi3	O16	2.596(13)	C8	C10	1.40(3)
Bi3	O30	2.169(10)	C9	C67	1.546(18)
Bi3	O33	2.226(10)	C9	C70	1.530(18)
Bi3	O34	2.209(10)	C10	C41	1.40(3)
Bi4	O2	2.241(13)	C11	C12	1.42(4)
Bi4	O7	2.175(13)	C11	C16	1.40(4)
Bi4	O8	2.416(13)	C12	C13	1.513(18)
Bi4	O9	2.446(13)	C12	C46	1.43(4)
Bi4	O34	2.155(9)	C13	C14	1.545(18)
Bi5	O1	2.564(13)	C13	C15	1.544(13)
Bi5	O12	2.717(13)	C16	C38	1.498(18)
Bi5	O29[1]	2.164(11)	C16	C77	1.53(4)
Bi5	O32[1]	2.591(12)	C18	C19	1.41(3)
Bi5	O33	2.229(10)	C18	C21	1.39(3)
Bi5	O34	2.203(9)	C19	C20	1.527(18)
Bi6	O10	2.446(13)	C19	C48	1.34(3)
Bi6	O12	2.338(13)	C20	C55	1.542(17)
Bi6	O14	2.207(13)	C20	C66	1.521(17)
Bi6	O18	2.249(13)	C21	C22	1.539(17)
Bi6	O33	2.134(10)	C21	C24	1.43(3)
Bi7	Bi2[1]	3.5718(12)	C22	C23	1.546(17)
Bi7	O15	2.299(13)	C22	C47	1.534(17)
Bi7	O17	2.264(13)	C24	C25	1.27(3)
Bi7	O28	2.326(11)	C25	C48	1.36(3)

Bi7	O36	2.283(11)	C27	C28	1.44(3)
Bi7	O37	2.121(11)	C27	C34	1.27(3)
P1	O14	1.527(13)	C28	C29	1.522(17)
P1	O15	1.519(14)	C28	C31	1.38(3)
P1	O22	1.614(14)	C29	C30	1.544(17)
P1	O32[1]	1.532(12)	C29	C59	1.561(17)
P2	O16	1.495(13)	C31	C32	1.35(3)
P2	O17	1.552(13)	C32	C33	1.33(3)
P2	O18	1.526(14)	C33	C34	1.46(3)
P2	O19	1.575(13)	C34	C35	1.507(17)
P3	O6	1.504(13)	C35	C36	1.495(17)
P3	O7	1.537(14)	C35	C37	1.556(17)
P3	O21	1.581(14)	C38	C62	1.501(17)
P3	O28[1]	1.530(12)	C38	C73	1.540(18)
P4	O9	1.503(14)	C42	C60	1.528(18)
P4	O10	1.484(13)	C42	C61	1.537(18)
P4	O11	1.527(14)	C43	C44	1.519(18)
P4	O20	1.590(14)	C43	C53	1.36(4)
P5	O8	1.521(14)	C44	C71	1.507(18)
P5	O12	1.541(14)	C44	C72	1.524(18)
P5	O23	1.623(14)	C45	C52	1.40(4)
P5	O24	1.524(13)	C46	C54	1.23(3)
P6	O1	1.520(13)	C52	C53	1.32(4)
P6	O2	1.495(13)	C54	C77	1.29(4)
P6	O25	1.619(14)	C63	C74	1.535(19)
P6	O36[1]	1.526(11)	C63	C78	1.536(18)
O1	Bi1[1]	2.637(13)	C63	C56	1.540(18)
O19	C18	1.39(3)	C64	C65	1.532(19)
O20	C27	1.47(3)	C64	C80	1.552(19)
O21	C26	1.32(2)	C64	C40	1.547(18)
O22	C1	1.43(3)	C146	C56	1.3900
O23	C5	1.37(2)	C146	C147	1.3900
O25	C11	1.41(3)	C56	C26	1.3900
O28	P3[1]	1.530(12)	C26	C40	1.3900
O29	Bi5[1]	2.164(10)	C40	C145	1.3900
O31	C81	1.465(17)	C145	C147	1.3900
O32	Bi5[1]	2.591(11)			

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z+2 #2 -x+2,-y+2,-z+1

Table S3. Bond lengths [Å] and angles [°] for **2**

Bi(1)-C(1)	2.242(8)
Bi(1)-C(7)	2.250(7)
Bi(1)-O(4)	2.356(6)
Bi(1)-O(1)	2.368(6)
P(1)-O(1)	1.499(6)
P(1)-O(4)#1	1.505(6)
P(1)-O(3)	1.577(5)
P(1)-O(2)	1.590(6)
O(2)-C(13)	1.479(10)
O(3)-C(17)	1.479(9)
O(4)-P(1)#2	1.505(6)
C(1)-C(2)	1.367(11)
C(1)-C(6)	1.398(10)
C(2)-C(3)	1.382(11)
C(3)-C(4)	1.382(11)
C(4)-C(5)	1.394(12)
C(5)-C(6)	1.392(11)
C(7)-C(8)	1.384(10)
C(7)-C(11)	1.401(11)
C(8)-C(12)	1.388(11)
C(9)-C(10)	1.374(12)
C(9)-C(12)	1.389(13)
C(10)-C(11)	1.391(11)

C(13)-C(15)	1.509(11)
C(13)-C(16)	1.529(12)
C(13)-C(14)	1.539(13)
C(17)-C(18)	1.514(11)
C(17)-C(20)	1.521(11)
C(17)-C(19)	1.543(11)

C(1)-Bi(1)-C(7)	91.3(3)
C(1)-Bi(1)-O(4)	88.9(2)
C(7)-Bi(1)-O(4)	86.9(2)
C(1)-Bi(1)-O(1)	89.4(2)
C(7)-Bi(1)-O(1)	85.1(2)
O(4)-Bi(1)-O(1)	171.81(18)
O(1)-P(1)-O(4)#1	116.3(3)
O(1)-P(1)-O(3)	105.3(3)
O(4)#1-P(1)-O(3)	112.0(3)
O(1)-P(1)-O(2)	111.5(3)
O(4)#1-P(1)-O(2)	103.6(3)
O(3)-P(1)-O(2)	108.1(3)
P(1)-O(1)-Bi(1)	129.2(3)
C(13)-O(2)-P(1)	128.8(5)
C(17)-O(3)-P(1)	129.6(5)
P(1)#2-O(4)-Bi(1)	123.7(3)
C(2)-C(1)-C(6)	119.2(7)
C(2)-C(1)-Bi(1)	121.5(6)
C(6)-C(1)-Bi(1)	119.2(5)

C(1)-C(2)-C(3)	121.1(7)
C(2)-C(3)-C(4)	120.5(8)
C(3)-C(4)-C(5)	119.0(8)
C(6)-C(5)-C(4)	120.2(8)
C(5)-C(6)-C(1)	119.9(7)
C(8)-C(7)-C(11)	119.5(7)
C(8)-C(7)-Bi(1)	120.6(6)
C(11)-C(7)-Bi(1)	119.9(5)
C(7)-C(8)-C(12)	120.3(7)
C(10)-C(9)-C(12)	119.4(8)
C(9)-C(10)-C(11)	121.2(8)
C(10)-C(11)-C(7)	119.3(7)
C(8)-C(12)-C(9)	120.2(8)
O(2)-C(13)-C(15)	108.1(7)
O(2)-C(13)-C(16)	111.3(7)
C(15)-C(13)-C(16)	111.4(7)
O(2)-C(13)-C(14)	103.4(7)
C(15)-C(13)-C(14)	112.4(8)
C(16)-C(13)-C(14)	110.0(8)
O(3)-C(17)-C(18)	110.1(6)
O(3)-C(17)-C(20)	102.8(6)
C(18)-C(17)-C(20)	112.4(7)
O(3)-C(17)-C(19)	109.4(6)
C(18)-C(17)-C(19)	111.3(7)
C(20)-C(17)-C(19)	110.5(7)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z-1/2 #2 x,-y+1/2,z+1/2