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Novel Ti-O-Ti Bonding Species Constructed in a Metal-Oxide Cluster

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Fig. S1 Temperature-dependent ^{31}P NMR of **1** in D_2O: (a) at 23.7 ˚C, (b) at 39.7 ˚C, (c) at 58.9 ˚C, (d) at 79.7 ˚C, and (e) the solution of (d) remeasured at 24.7 ˚C.

Fig. S2 pH-Varied ^{31}P NMR of **1** in H_2O at room temperature. The pH values of the solutions were adjusted by using aqueous KOH solution: (a) the aqueous solution of 1.0 g of **1** dissolved in 20 mL water, which showed pH = 1.77, (b) the solution (a) was adjusted to pH 2.5 by adding the KOH solution, (c) the solution (b) was adjusted to pH 1.5, (c) the solution (b) was adjusted to pH 1.5, and (d) the solution (c) was adjusted to pH 0.5.

Table S1 All bond distances (Å) and angles (°) for POM **1a**

Table S2 Average bond distances (Å) and angles (°) [range] for the Keggin POM moiety in **1a**

Table S3 Bond valence sum (BVS) calcutions of W(1-11), Ti(1-2), P and O atoms

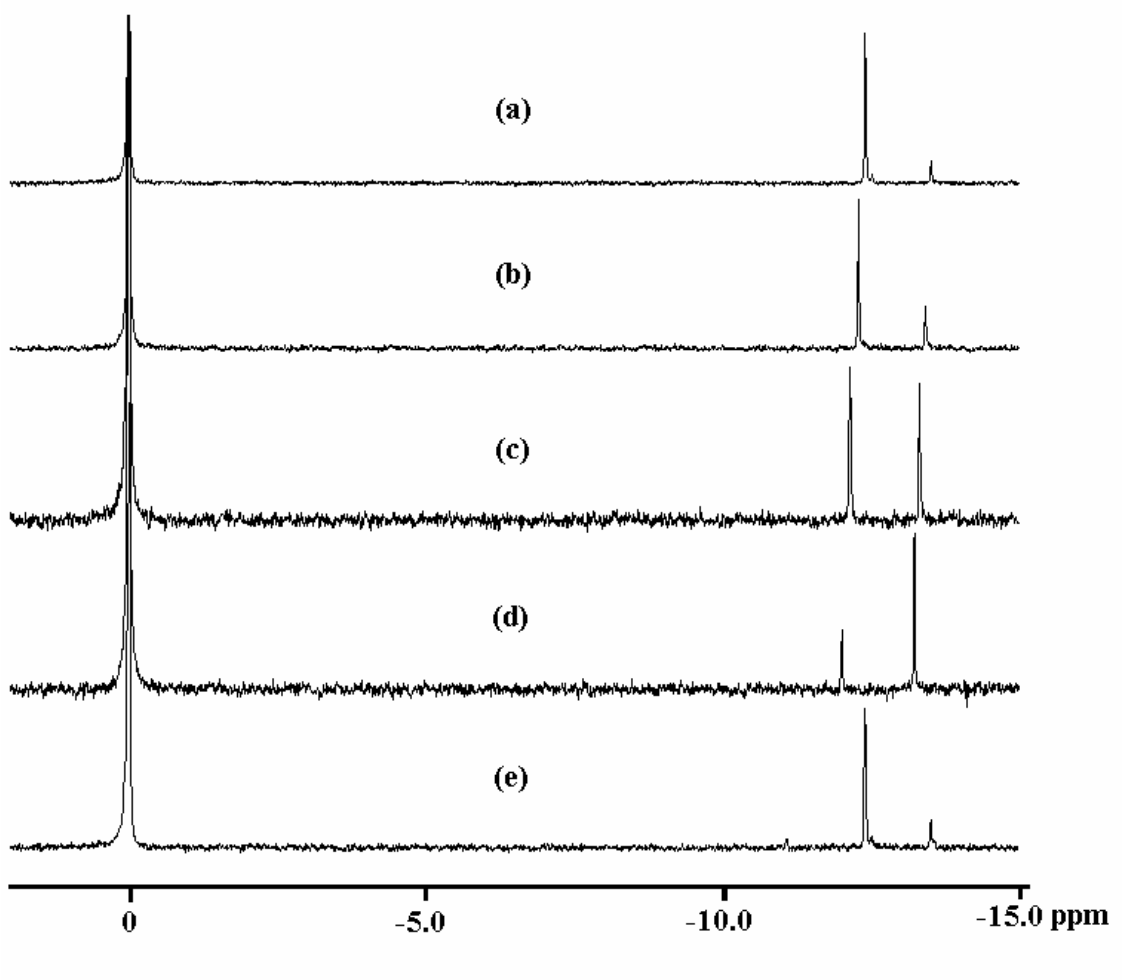

Fig. S1 Temperature-dependent ^{31}P NMR of **1** in D_2O: (a) at 23.7 ˚C, (b) at 39.7 ˚C, (c) at 58.9 ˚C, (d) at 79.7 ˚C, and (e) the solution of (d) remeasured at 24.7 ˚C.

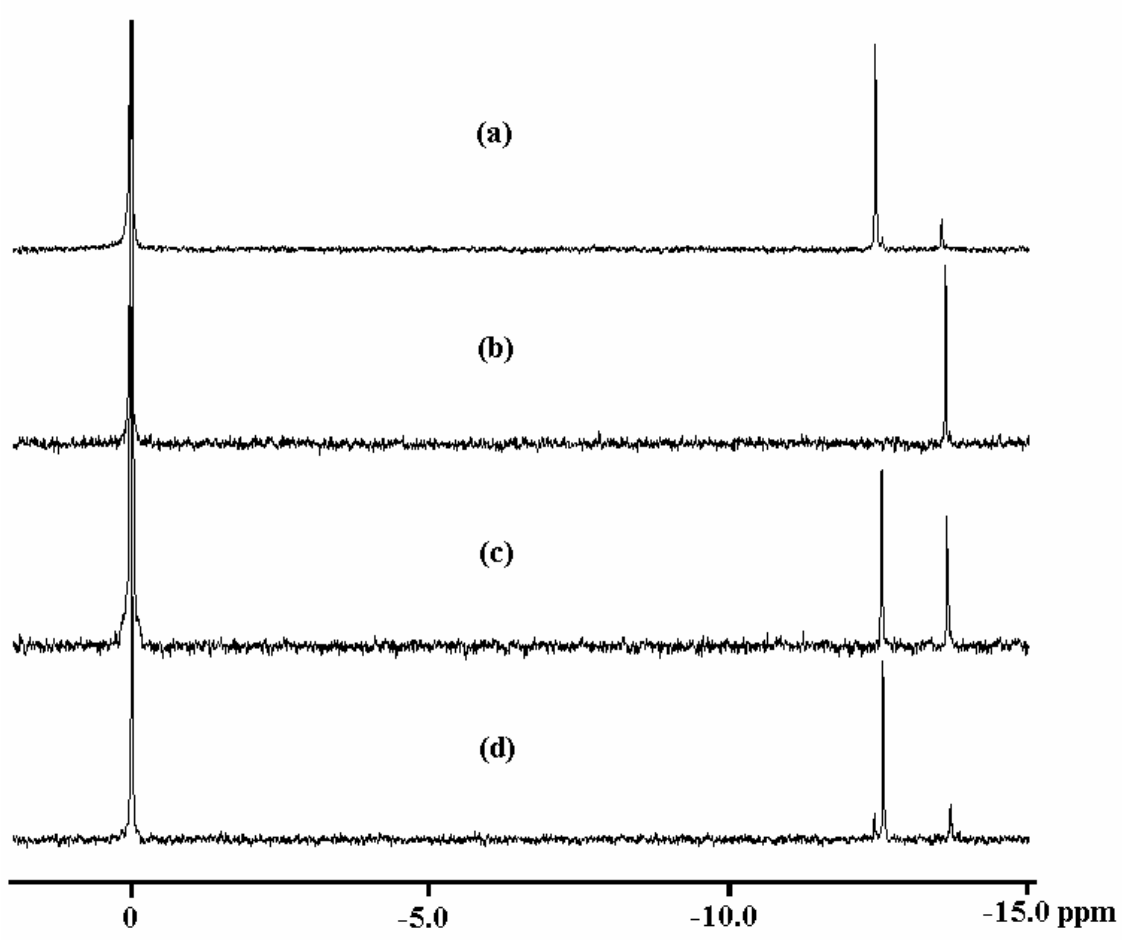

Fig. S2 pH-Varied ^{31}P NMR of **1** in H_2O at room temperature. The pH values of the solutions were adjusted by using aqueous KOH solution: (a) the aqueous solution of 1.0 g of **1** dissolved in 20 mL water, which showed pH = 1.77, (b) the solution (a) was adjusted to pH 2.5 by adding the KOH solution, (c) the solution (b) was adjusted to pH 1.5, (c) the solution (b) was adjusted to pH 1.5, and (d) the solution (c) was adjusted to pH 0.5.

Table S1 All bond distances (Å) and angles (°) for POM **1a**

Distance (Å)

atom	atom	distance	atom	atom	distance
C(1)	O(1C)	1.228(10)	C(1)	O(2C)	1.281(10)
C(1)	C(2)	1.555(12)	C(2)	O(3C)	1.229(10)
C(2)	O(4C)	1.294(10)	C(3)	O(5C)	1.209(10)
C(3)	O(6C)	1.291(10)	C(3)	C(4)	1.563(11)
C(4)	O(7C)	1.216(11)	C(4)	O(8C)	1.290(10)
O(1)	Ti(1)	2.137(6)	O(2)	W(1)	1.852(6)
O(2)	Ti(1)	1.861(6)	O(3)	W(1)	1.703(6)
O(4)	W(2)	1.884(5)	O(4)	W(1)	1.901(5)
O(5)	W(2)	1.702(6)	O(6)	W(2)	1.850(6)
O(6)	Ti(2)	1.861(6)	O(7)	Ti(2)	2.131(6)
O(8)	Ti(2)	1.813(6)	O(8)	Ti(1)	1.833(6)
O(9)	W(8)	1.859(5)	O(9)	Ti(1)	1.885(6)
O(10)	W(3)	1.910(5)	O(10)	W(1)	1.936(6)
O(11)	W(4)	1.870(6)	O(11)	W(1)	1.962(6)
O(12)	W(5)	1.906(6)	O(12)	W(2)	1.952(6)
O(13)	W(6)	1.896(5)	O(13)	W(2)	1.959(6)
O(14)	W(7)	1.867(6)	O(14)	Ti(2)	1.871(6)
O(15)	W(8)	1.701(6)	O(16)	W(3)	1.893(6)
O(16)	W(8)	1.913(6)	O(17)	W(3)	1.707(6)
O(18)	W(4)	1.921(6)	O(18)	W(3)	1.926(5)
O(19)	W(4)	1.708(6)	O(20)	W(4)	1.884(6)
O(20)	W(5)	1.924(6)	O(21)	W(5)	1.700(6)
O(22)	W(5)	1.884(6)	O(22)	W(6)	1.949(6)
O(23)	W(6)	1.710(6)	O(24)	W(6)	1.870(6)
O(24)	W(7)	1.942(6)	O(25)	W(7)	1.712(6)

atom	atom	distance	atom	atom	distance
O(26)	W(7)	1.912(5)	O(26)	W(8)	1.928(6)
O(27)	P(1)	1.537(6)	O(27)	W(3)	2.416(6)
O(27)	W(1)	2.429(5)	O(27)	W(4)	2.501(5)
O(28)	P(1)	1.540(6)	O(28)	W(2)	2.416(5)
O(28)	W(6)	2.430(5)	O(28)	W(5)	2.499(6)
O(29)	P(1)	1.520(6)	O(29)	W(7)	2.347(6)
O(29)	W(8)	2.373(6)	O(30)	W(9)	1.870(6)
O(30)	W(8)	1.971(6)	O(31)	W(3)	1.906(6)
O(31)	W(9)	1.914(6)	O(32)	W(10)	1.900(5)
O(32)	W(4)	1.929(6)	O(33)	W(10)	1.897(6)
O(33)	W(5)	1.897(5)	O(34)	W(11)	1.871(6)
O(34)	W(6)	1.930(6)	O(35)	W(11)	1.891(5)
O(35)	W(7)	1.938(5)	O(36)	P(1)	1.545(6)
O(36)	W(10)	2.417(5)	O(36)	W(11)	2.417(6)
O(36)	W(9)	2.427(6)	O(37)	W(9)	1.716(6)
O(38)	W(10)	1.918(6)	O(38)	W(9)	1.925(6)
O(39)	W(10)	1.702(6)	O(40)	W(11)	1.912(5)
O(40)	W(10)	1.916(6)	O(41)	W(11)	1.709(6)
O(42)	W(9)	1.907(6)	O(42)	W(11)	1.939(6)
O(2C)	Ti(1)	2.018(6)	O(4C)	Ti(1)	2.073(6)
O(6C)	Ti(2)	2.027(6)	O(8C)	Ti(2)	2.089(6)

Angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
O(1C)	C(1)	O(2C)	126.3(8)	O(1C)	C(1)	C(2)	120.5(8)
O(2C)	C(1)	C(2)	113.2(7)	O(3C)	C(2)	O(4C)	126.3(8)
O(3C)	C(2)	C(1)	121.0(7)	O(4C)	C(2)	C(1)	112.7(7)
O(5C)	C(3)	O(6C)	125.5(8)	O(5C)	C(3)	C(4)	121.0(8)
O(6C)	C(3)	C(4)	113.5(7)	O(7C)	C(4)	O(8C)	126.8(8)
O(7C)	C(4)	C(3)	120.7(7)	O(8C)	C(4)	C(3)	112.4(7)
W(1)	O(2)	Ti(1)	157.4(4)	W(2)	O(4)	W(1)	151.6(3)
W(2)	O(6)	Ti(2)	156.4(4)	Ti(2)	O(8)	Ti(1)	136.4(3)
W(8)	O(9)	Ti(1)	146.9(3)	W(3)	O(10)	W(1)	125.0(3)
W(4)	O(11)	W(1)	127.4(3)	W(5)	O(12)	W(2)	126.3(3)
W(6)	O(13)	W(2)	124.6(3)	W(7)	O(14)	Ti(2)	146.2(3)
W(3)	O(16)	W(8)	153.5(3)	W(4)	O(18)	W(3)	125.4(3)
W(4)	O(20)	W(5)	153.4(3)	W(5)	O(22)	W(6)	126.1(3)
W(6)	O(24)	W(7)	154.0(3)	W(7)	O(26)	W(8)	123.5(3)
P(1)	O(27)	W(3)	126.4(3)	P(1)	O(27)	W(1)	126.7(3)
W(3)	O(27)	W(1)	89.53(18)	P(1)	O(27)	W(4)	125.5(3)
W(3)	O(27)	W(4)	88.07(18)	W(1)	O(27)	W(4)	88.34(18)
P(1)	O(28)	W(2)	126.3(3)	P(1)	O(28)	W(6)	126.0(3)
W(2)	O(28)	W(6)	89.57(18)	P(1)	O(28)	W(5)	126.1(3)
W(2)	O(28)	W(5)	88.90(18)	W(6)	O(28)	W(5)	87.76(18)
P(1)	O(29)	W(7)	127.6(3)	P(1)	O(29)	W(8)	127.2(3)
W(7)	O(29)	W(8)	91.55(19)	W(9)	O(30)	W(8)	152.4(3)
W(3)	O(31)	W(9)	150.3(3)	W(10)	O(32)	W(4)	150.6(3)
W(10)	O(33)	W(5)	153.0(3)	W(11)	O(34)	W(6)	150.5(3)
W(11)	O(35)	W(7)	152.1(3)	P(1)	O(36)	W(10)	129.3(3)
P(1)	O(36)	W(11)	124.1(3)	W(10)	O(36)	W(11)	89.03(18)
P(1)	O(36)	W(9)	123.9(3)	W(10)	O(36)	W(9)	89.43(18)
W(11)	O(36)	W(9)	89.25(18)	W(10)	O(38)	W(9)	125.0(3)
W(11)	O(40)	W(10)	124.6(3)	W(9)	O(42)	W(11)	124.4(3)

atom	atom	atom	angle	atom	atom	atom	angle
C(1)	O(2C)	Ti(1)	118.1(5)	C(2)	O(4C)	Ti(1)	116.0(5)
C(3)	O(6C)	Ti(2)	117.1(5)	C(4)	O(8C)	Ti(2)	116.2(5)
O(29)	P(1)	O(27)	110.9(3)	O(29)	P(1)	O(28)	111.1(3)
O(27)	P(1)	O(28)	108.5(3)	O(29)	P(1)	O(36)	110.0(3)
O(27)	P(1)	O(36)	108.4(3)	O(28)	P(1)	O(36)	107.9(3)
O(8)	Ti(1)	O(2)	98.4(3)	O(8)	Ti(1)	O(9)	100.1(3)
O(2)	Ti(1)	O(9)	96.7(3)	O(8)	Ti(1)	O(2C)	92.5(2)
O(2)	Ti(1)	O(2C)	90.4(3)	O(9)	Ti(1)	O(2C)	164.5(3)
O(8)	Ti(1)	O(4C)	166.9(3)	O(2)	Ti(1)	O(4C)	90.1(2)
O(9)	Ti(1)	O(4C)	88.7(2)	O(2C)	Ti(1)	O(4C)	77.5(2)
O(8)	Ti(1)	O(1)	87.3(2)	O(2)	Ti(1)	O(1)	173.7(3)
O(9)	Ti(1)	O(1)	84.8(2)	O(2C)	Ti(1)	O(1)	86.7(2)
O(4C)	Ti(1)	O(1)	83.8(2)	O(8)	Ti(2)	O(6)	97.6(3)
O(8)	Ti(2)	O(14)	99.5(3)	O(6)	Ti(2)	O(14)	97.9(3)
O(8)	Ti(2)	O(6C)	93.6(2)	O(6)	Ti(2)	O(6C)	89.0(3)
O(14)	Ti(2)	O(6C)	164.2(3)	O(8)	Ti(2)	O(8C)	168.6(2)
O(6)	Ti(2)	O(8C)	89.1(2)	O(14)	Ti(2)	O(8C)	88.6(2)
O(6C)	Ti(2)	O(8C)	77.3(2)	O(8)	Ti(2)	O(7)	88.7(2)
O(6)	Ti(2)	O(7)	172.2(3)	O(14)	Ti(2)	O(7)	85.4(2)
O(6C)	Ti(2)	O(7)	86.1(2)	O(8C)	Ti(2)	O(7)	83.9(2)
O(3)	W(1)	O(2)	102.2(3)	O(3)	W(1)	O(4)	103.4(3)
O(2)	W(1)	O(4)	90.1(2)	O(3)	W(1)	O(10)	100.5(3)
O(2)	W(1)	O(10)	88.7(2)	O(4)	W(1)	O(10)	155.7(2)
O(3)	W(1)	O(11)	100.7(3)	O(2)	W(1)	O(11)	156.8(2)
O(4)	W(1)	O(11)	87.6(2)	O(10)	W(1)	O(11)	84.0(2)
O(3)	W(1)	O(27)	170.2(2)	O(2)	W(1)	O(27)	84.5(2)
O(4)	W(1)	O(27)	83.4(2)	O(10)	W(1)	O(27)	72.4(2)
O(11)	W(1)	O(27)	72.3(2)	(5)	W(2)	O(6)	103.3(3)
O(5)	W(2)	O(4)	103.8(3)	O(6)	W(2)	O(4)	90.8(2)
O(5)	W(2)	O(12)	99.7(3)	O(6)	W(2)	O(12)	156.2(2)

atom	atom	atom	angle	atom	atom	atom	angle
O(4)	W(2)	O(12)	89.4(2)	O(5)	W(2)	O(13)	99.1(2)
O(6)	W(2)	O(13)	86.7(2)	O(4)	W(2)	O(13)	157.0(2)
O(12)	W(2)	O(13)	83.9(2)	O(5)	W(2)	O(28)	169.2(2)
O(6)	W(2)	O(28)	83.4(2)	O(4)	W(2)	O(28)	84.4(2)
O(12)	W(2)	(28)	73.0(2)	O(13)	W(2)	(28)	72.6(2)
O(17)	W(3)	(16)	103.4(3)	O(17)	W(3)	(31)	103.0(3)
O(16)	W(3)	(31)	86.0(2)	O(17)	W(3)	(10)	100.1(3)
O(16)	W(3)	(10)	90.5(2)	O(31)	W(3)	(10)	156.8(2)
O(17)	W(3)	(18)	100.7(3)	O(16)	W(3)	(18)	155.9(2)
O(31)	W(3)	(18)	88.1(2)	O(10)	W(3)	(18)	85.8(2)
O(17)	W(3)	(27)	171.6(2)	O(16)	W(3)	(27)	81.9(2)
O(31)	W(3)	(27)	83.7(2)	O(10)	W(3)	(27)	73.1(2)
O(18)	W(3)	(27)	74.2(2)	O(19)	W(4)	(11)	103.2(3)
O(19)	W(4)	(20)	103.1(3)	O(11)	W(4)	(20)	90.6(3)
O(19)	W(4)	(18)	101.0(3)	O(11)	W(4)	(18)	87.5(2)
O(20)	W(4)	(18)	155.6(2)	O(19)	W(4)	(32)	101.9(3)
O(11)	W(4)	(32)	154.8(2)	O(20)	W(4)	(32)	85.2(2)
O(18)	W(4)	(32)	86.2(2)	O(19)	W(4)	(27)	171.6(2)
O(11)	W(4)	(27)	71.9(2)	O(20)	W(4)	(27)	84.1(2)
O(18)	W(4)	(27)	72.2(2)	O(32)	W(4)	(27)	82.9(2)
O(21)	W(5)	(22)	102.1(3)	O(21)	W(5)	(33)	103.9(3)
O(22)	W(5)	(33)	89.9(2)	O(21)	W(5)	(12)	101.0(3)
O(22)	W(5)	(12)	88.3(2)	O(33)	W(5)	(12)	154.9(2)
O(21)	W(5)	(20)	102.7(3)	O(22)	W(5)	(20)	155.2(2)
O(33)	W(5)	(20)	83.9(2)	O(12)	W(5)	(20)	87.4(2)
O(21)	W(5)	(28)	170.8(2)	O(22)	W(5)	(28)	72.7(2)
O(33)	W(5)	(28)	83.9(2)	O(12)	W(5)	(28)	71.7(2)
O(20)	W(5)	(28)	82.8(2)	O(23)	W(6)	(24)	102.7(3)
O(23)	W(6)	(13)	100.5(3)	O(24)	W(6)	(13)	93.1(2)
O(23)	W(6)	(34)	103.3(3)	O(24)	W(6)	(34)	85.6(2)

atom	atom	atom	angle	atom	atom	atom	angle
O(13)	W(6)	(34)	155.8(2)	O(23)	W(6)	(22)	102.3(3)
O(24)	W(6)	(22)	154.8(2)	O(13)	W(6)	(22)	85.2(2)
O(34)	W(6)	(22)	85.8(2)	O(23)	W(6)	(28)	172.5(2)
O(24)	W(6)	(28)	82.1(2)	O(13)	W(6)	(28)	73.2(2)
O(34)	W(6)	(28)	82.7(2)	O(22)	W(6)	(28)	73.4(2)
O(25)	W(7)	(14)	100.3(3)	O(25)	W(7)	(26)	100.4(3)
O(14)	W(7)	(26)	92.2(2)	O(25)	W(7)	(35)	96.1(3)
O(14)	W(7)	(35)	162.5(2)	O(26)	W(7)	(35)	90.6(2)
O(25)	W(7)	(24)	102.2(3)	O(14)	W(7)	(24)	87.1(2)
O(26)	W(7)	(24)	157.1(2)	O(35)	W(7)	O(24)	83.6(2)
O(25)	W(7)	O(29)	172.6(2)	O(14)	W(7)	O(29)	83.4(2)
O(26)	W(7)	O(29)	72.9(2)	O(35)	W(7)	O(29)	81.0(2)
O(24)	W(7)	O(29)	84.3(2)	O(15)	W(8)	O(9)	100.4(3)
O(15)	W(8)	O(16)	102.0(3)	O(9)	W(8)	O(16)	89.8(2)
O(15)	W(8)	O(26)	100.7(3)	O(9)	W(8)	O(26)	91.6(2)
O(16)	W(8)	O(26)	156.6(2)	O(15)	W(8)	O(30)	96.5(3)
O(9)	W(8)	O(30)	162.8(2)	O(16)	W(8)	O(30)	83.7(2)
O(26)	W(8)	O(30)	88.3(2)	O(15)	W(8)	O(29)	172.0(2)
O(9)	W(8)	O(29)	83.3(2)	O(16)	W(8)	O(29)	85.0(2)
O(26)	W(8)	O(29)	72.0(2)	O(30)	W(8)	O(29)	80.4(2)
O(37)	W(9)	O(30)	103.1(3)	O(37)	W(9)	O(42)	101.8(3)
O(30)	W(9)	O(42)	90.5(2)	O(37)	W(9)	O(31)	101.6(3)
O(30)	W(9)	O(31)	86.6(2)	O(42)	W(9)	O(31)	156.5(2)
O(37)	W(9)	O(38)	100.9(3)	O(30)	W(9)	O(38)	155.9(2)
O(42)	W(9)	O(38)	86.2(2)	O(31)	W(9)	O(38)	86.9(2)
O(37)	W(9)	O(36)	171.8(2)	O(30)	W(9)	O(36)	83.6(2)
O(42)	W(9)	O(36)	73.3(2)	O(31)	W(9)	O(36)	83.2(2)
O(38)	W(9)	O(36)	72.6(2)	O(39)	W(10)	O(33)	103.8(3)
O(39)	W(10)	O(32)	101.9(3)	O(33)	W(10)	O(32)	85.9(2)
O(39)	W(10)	O(40)	101.7(3)	O(33)	W(10)	O(40)	89.4(2)

atom	atom	atom	angle	atom	atom	atom	angle
O(32)	W(10)	O(40)	156.3(2)	O(39)	W(10)	O(38)	100.0(3)
O(33)	W(10)	O(38)	156.2(2)	O(32)	W(10)	O(38)	88.4(2)
O(40)	W(10)	O(38)	86.7(2)	O(39)	W(10)	O(36)	171.2(2)
O(33)	W(10)	O(36)	83.5(2)	O(32)	W(10)	O(36)	83.3(2)
O(40)	W(10)	O(36)	73.1(2)	O(38)	W(10)	O(36)	72.9(2)
O(41)	W(11)	O(34)	102.6(3)	O(41)	W(11)	O(35)	101.2(3)
O(34)	W(11)	O(35)	87.5(2)	O(41)	W(11)	O(40)	103.2(3)
O(34)	W(11)	O(40)	90.2(2)	O(35)	W(11)	O(40)	155.4(2)
O(41)	W(11)	O(42)	100.3(3)	O(34)	W(11)	O(42)	157.0(2)
O(35)	W(11)	O(42)	87.4(2)	O(40)	W(11)	O(42)	85.3(2)
O(41)	W(11)	O(36)	172.5(2)	O(34)	W(11)	O(36)	84.1(2)
O(35)	W(11)	O(36)	82.2(2)	O(40)	W(11)	O(36)	73.2(2)
O(42)	W(11)	O(36)	73.0(2)				

Table S2 Average bond distances (Å) and angles (°) [range] for the Keggin POM moiety in **1a**

W-Ot (Ot : terminal oxygen)	1.707 [1.700(6) – 1.716(6)]
W-Oc (Oc : corner sharing oxygen)	1.908 [1.870(6) – 1.971(6)]
W-Oe (Oe : edge-sharing oxygen)	1.922 [1.870(6) – 1.962(6)]
W-Oa (Oa : oxygen coordinated to P atom)	2.425 [2.347(6) – 2.501(5)]
W-Ob (Ob : oxygen coordinated to Ti atom)	1.857 [1.850(6) – 1.867(6)]
P-O distance	1.534 [1.520(6) - 1.545(6)]
O-P-O angles	109.5 [107.9(3) – 111.1(3)]

Table S3 Bond valence sum (BVS) calcutions of W(1-11), Ti(1-2), P and O atoms

W(1)	6.105		W(7)	6.092	
W(2)	6.143		W(8)	6.101	
W(3)	6.116		W(9)	6.123	
W(4)	6.150		W(10)	6.150	
W(5)	6.165		W(11)	6.174	
W(6)	6.075				
W(1-11) average = 6.127 [6.075-6.174]					
Ti(1)	4.159		Ti(2)	4.215	
Ti(1-2) average = 4.187 [4.159-4.215]					
P(1)	4.987				
O(1)	0.419	O(18)	1.965	O(35)	2.018
O(2)	2.075	O(19)	1.759	O(36)	1.985
O(3)	1.783	O(20)	2.074	O(37)	1.722
O(4)	2.137	O(21)	1.798	O(38)	1.976
O(5)	1.788	O(22)	2.010	O(39)	1.788
O(6)	2.082	O(23)	1.750	O(40)	2.017
O(7)	0.426	O(24)	2.070	O(41)	1.754
O(8)	1.958	O(25)	1.740	O(42)	1.969
O(9)	1.998	O(26)	1.985	O(1C)	
O(10)	1.969	O(27)	1.958	O(2C)	
O(11)	2.020	O(28)	1.948	O(3C)	
O(12)	1.940	O(29)	1.905	O(4C)	
O(13)	1.951	O(30)	1.999	O(5C)	
O(14)	2.005	O(31)	2.038	O(6C)	
O(15)	1.793	O(32)	2.015	O(7C)	
O(16)	2.078	O(33)	2.112	O(8C)	
O(17)	1.764	O(34)	2.097		