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# **Electronic Supporting Information**

# Dielectric Anomaly Observed for Doubly Reduced Mixedvalence Polyoxometalate

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# 1. Measurements

# 1-1. Single Crystal X-ray diffraction analysis

# Compound 1 and 2

Data were collected on an X-ray single crystal diffractometer equipped with a CCD detector (Bruker SMART APEX 2 Ultra) with Mo-K $\alpha$  radiation ( $\lambda = 0.71075$  Å), and a graphite monochromator by using the SMART software package. The structure was determined by direct methods and expanded using Fourier techniques.

# Compound 3 and 4

Single-Crystal XRD analysis was performed using Rigaku Mercury CCD area detector with graphitemonochromated Mo-K $\alpha$  radiation. The data was collected at 100 K (**3**) and 200 K (**4**) to a maximum  $2\theta$  value of 55.0. The structure was determined by direct methods and expanded using Fourier techniques.

### 1-2. Dielectric measurement

Dielectric measurements were performed by AC two probe measurement using single crystals for 1, 4 and pellets for 1, 2 and 3. Silver paste was utilized for electrodes and electrical contacts were made using gold wires. Temperature-dependent dielectric permittivity was measured using an Agilent E4980A Precision LCR meter between 20 and 300 K. The pellets were made from a powdered sample of 1, 2 and 3 for this measurement. The typical applied ac voltage was 1 V, and the frequency range was 1 kHz –1 MHz.

### 1-3. Other measurements

### UV-vis-NIR spectra and FTIR

UV-vis-NIR spectra were measured in solution (absorption spectra; 200–1800 nm) using a JASCO V-670 spectrophotometer. IR spectra ( $4000-450 \text{ cm}^{-1}$ ) measurements were carried out on KBr disks with a resolution of  $4 \text{ cm}^{-1}$ .

#### NMR

Solution <sup>31</sup>P-NMR spectra were recorded at room temperature on BRUKER SPECTROSPIN AVANCE 400S.  $H_3PO_4$  solution (85%) was used as a chemical shift reference.

# ΤG

The solvent number of CH<sub>3</sub>CN molecules was determined by TG-DTA measurement using a Rigaku Thermo Plus TG8120.

#### DSC

Measurements were performed using METTLER TOLEDO DSC 1 STAR system.

#### Powder XRD

Measurements were performed using Rigaku Mini Flex 600 at 2-20 degree of  $2\theta$ .

#### 2. Synthesis

### Compound 1: $(BI)_{5}[PMO^{V_{2}}MO^{VI}_{10}O_{40}] \cdot 4DMF \cdot nH_{2}O$ (1)

About 1.4 g of  $H_3[PMo^{VI}_{12}O_{40}] \cdot nH_2O$  was dissolved in 15 mL methanol, giving yellow solution. Then, triphenylphosphine PPh<sub>3</sub> (0.15 g, 0.57 mmol) in 15 mL of acetonitrile were added and the mixture was kept in refrigerator. After 1 day the yellow color of the solution had changed to blue, giving mixed-valence POM in the solution. The solution was treated with 10 mL of a mixed solution (DMF :  $H_2O = 1 : 1$ ) of 0.3 g (2.5 mmol) benzimidazole with 1 mL hydrochloric acid. This solution was kept for one week and black crystals of **1** were obtained that were suitable for X-ray structure analysis.

 $Elemental \ analysis \ (\%) \ calcd \ for \ C_{47}H_{65}N_{14}Mo_{12}O_{44}P: C \ 20.69, \ H \ 2.38, \ N, \ 7.18; \ found: \ C \ 20.57, \ H \ 2.55, \ N \ 6.98.$ 

FT-IR (KBr disc, cm<sup>-1</sup>): 1647, 1618, 1448, 1383, 1263, 1238, 1056, 951, 824, 789, 771, 748 (Figure S4).

Crystal data:  $C_{47}H_{65}N_{14}Mo_{12}O_{45}P$ ,  $M_w = 2726.36$ , T = 123 K, triclinic, space group P1, a = 11.9970(7), b = 12.9027(7), c = 14.6379(7) Å, a = 114.6658(7),  $\beta = 106.7857(7)$ ,  $\gamma = 95.9885(7)$ , V = 1904.30 (18) Å<sup>3</sup>, Z = 1,  $D_{calc} = 2.377$  g cm<sup>-3</sup>, 22708 reflections measured, 16942 unique which were used in all calculations, final  $R_1$ ,  $wR_2 = 0.0498$ , 0.1425. We investigated temperature dependence of single crystal structure at 123 K, 200 K and 270 K and these details are shown in ESI 3-3).

#### Compound **2**: (BI)<sub>5</sub> [BW<sup>VI</sup><sub>12</sub>O<sub>40</sub>]·4DMF·nH<sub>2</sub>O (**2**)

About 0.4 g of  $K_5[BW^{VI}_{12}O_{40}] \cdot nH_2O$  [S1] was dissolved in 5 mL hot water. The solution was treated with 5 mL of mixed solution (DMF :  $H_2O = 1 : 1$ ) of 0.3 g (2.5 mmol) benzimidazole. This solution was kept for 1 week and colorless crystal of **2** was obtained.

Elemental analysis (%) calcd for  $C_{47}H_{65}N_{14}W_{12}O_{45}B$  : C 14.99, H 1.73, N 5.21; found: C 15.04, H 2.00, N 5.10.

FT-IR (KBr disc, cm<sup>-1</sup>): 1649, 1618, 1448, 1383, 1265, 1236, 1001, 959, 903, 824, 748 (Figure S4).

Crystal data:  $C_{23}H_{36}N_{14}W_{12}O_{51}B$ ,  $M_w = 3817.90$ , T = 117 K, triclinic, space group P-1, a = 12.0275(4), b = 12.9977(4), c = 14.4568(5) Å,  $\alpha = 114.8192(3)$ ,  $\beta = 106.1529(3)$ ,  $\gamma = 95.9987(4)$ , V = 1905.78(11) Å<sup>3</sup>, Z = 1,  $D_{calc} = 3.327$  g cm<sup>-3</sup>, 22063 reflections measured, 8655 unique which were used in all calculations, final  $R_1$ ,  $wR_2 = 0.0537$ , 0.2378.

#### Compound **3**: $(PPh_4)_4H[PMo_{12}O_{40}] \cdot 4DMF$ (**3**)

About 1.4 g of  $H_3[PMo^{VI}_{12}O_{40}] \cdot nH_2O$  was dissolved in 15 mL methanol, giving yellow solution. Then, triphenylphosphine PPh<sub>3</sub> (0.15 g, 0.57 mmol) in 15 mL of acetonitrile were added and the mixture was kept in refrigerator. After 1day, the solution was treated with 10 mL of DMF solution of 0.94 g (2.5 mmol) tetraphenylphosphonium Chloride PPh<sub>4</sub>·Cl. The blue precipitate immediately appeared, which was filtered off and washed with water and methanol and dried in air. The compound was crystallized from DMF on keeping the solution open in air for 2 weeks. Black crystals of **3** were obtained for X-ray structure analysis.

Elemental analysis (%) calcd for  $C_{108}H_{109}N_4Mo_{12}O_{44}P_5$ : C 37.33, H 3.14, N, 1.61; found: C 37.13, H 3.41, N 1.61. FT-IR (KBr disc, cm<sup>-1</sup>): 1439, 1109, 1057, 947, 802, 723, 688, (Figure S4).

Crystal data:  $C_{54}H_{47}N_2Mo_6O_{24}P_{2.5}$ ,  $M_w = 1761.00$ , T = 100 K, monoclinic, space group  $P2_1/c$ , a = 13.660(6), b = 14.163(6), c = 32.542(14) Å,  $\beta = 96.619(2)$ , V = 6254(5) Å<sup>3</sup>, Z = 4,  $D_{calc} = 1.870$  g cm<sup>-3</sup>, 52013 reflections measured, 14007 unique which were used in all calculations, final  $R_1$ ,  $wR_2 = 0.0682$ , 0.2243.

#### Compound 4: $(PyHBI)_2H[PMO_2MO_{10}O_{40}] \cdot 6DMF$ (4)

About 1.4 g of  $H_3[PMo^{VI}_{12}O_{40}] \cdot nH_2O$  was dissolved in 15 mL methanol, giving yellow solution. Then, triphenylphosphine PPh<sub>3</sub> (0.15 g, 0.57 mmol) in 15 mL of acetonitrile were added and the mixture was kept in refrigerator. After 1day the yellow color of the solution had changed to blue, giving mixed-valence POM in the solution. The solution was treated with 6 mL of a mixed solution (DMF :  $H_2O = 5 : 1$ ) of 0.3 g (1.5 mmol) 2-(3-Pyridyl)-1H-benzimidazole with 1mL hydrochloric acid. This solution was kept open to air for 1 week, black crystals of **4** were obtained suitable for X-ray structure analysis.

Elemental analysis (%) calcd for  $C_{42}H_{65}N_{12}Mo_{12}O_{46}P$  : C 18.99, H 2.47, N, 6.33; found: C 19.00, H 2.60, N 6.34. FT-IR (KBr disc, cm<sup>-1</sup>): 1647, 1379, 1059, 951, 856, 793 (Figure S4).

Crystal data:  $C_{21}H_{32}N_6Mo_6O_{25}P_{0.5}$ ,  $M_w = 1359.65$ , T = 173 K, triclinic, space group P-1, a = 12.8074(2), b = 12.9424(2), c = 13.237(0) Å,  $\alpha = 62.519(3)$ ,  $\beta = 79.896(4)$ ,  $\gamma = 89.318(4)$ , V = 1910.45 (4) Å<sup>3</sup>, Z = 2,  $D_{calc} = 2.364$  g cm<sup>-3</sup>, 16652 reflections measured, 8216 unique which were used in all calculations, final  $R_1$ ,  $wR_2 = 0.0690$ , 0.2586.

#### 3. Crystallographic analysis

Single crystal X-ray crystallography was performed using a crystal of **1** at 123 K, 200 K and 270 K. Table S3-5 summarized P–P distance of the Keggin anion at each temperature. In addition, table S3-6 summarized P–N (N atoms of BI

<b>CCDC number</b>	sample code	Description
CCDC 1544373	1_123	SC-XRD data of compound 1 at 123 K
CCDC 1544374	1_200	SC-XRD data of compound 1 at 200 K
CCDC 1544375	1_270	SC-XRD data of compound 1 at 270 K
CCDC 1544376	2	SC-XRD data of compound 2 at 117 K
CCDC 1544377	3	SC-XRD data of compound <b>3</b> at 100 K
CCDC 1544378	4	SC-XRD data of compound 4 at 173 K

### 3-1. Crystal structure of 1 and 2

 Table S3-1. Crystal date, date collection, and reduction parameter of Crystal 1 and 2.

Compound	1	2		
Formula	$C_{47}H_{65}N_{14}Mo_{12}O_{45}P$	$C_{23}H_{36}N_{14}W_{12}O_{51}B$		
Crystal system	Tric	Triclinic		
Space group	<i>P</i> 1	<i>P</i> -1		
<i>a,</i> Å	11.9970(7)	12.0275(4)		
<i>b,</i> Å	12.9020(7)	12.9977(4)		
<i>c,</i> Å	14.6379(8)	14.4568(5)		
a, deg	114.6658(7)	114.8192(3)		
β, deg	106.7857(7)	106.1529(3)		
γ, deg	95.9885(7)	95.9987(4)		
V, Å <sup>3</sup>	1904.30(18)	1905.78(11)		
Z	1	1		
<i>Т</i> , К	123	117		
Reflections measured	22708	22063		
Independent reflections	16942	8655		
Reflections used	16942	8655		
$R_{_{ m int}}$	0.0285	0.0163		
R <sub>1</sub>	0.0498	0.0537		
wR <sub>2</sub>	0.1425	0.2378		



Figure S3-1. Comparison of structure of 1 and 2 (1: blue color, 2: red color).



Figure S3-2. Packing structure of 1 (left) and 2 (right). Unit cell viewed along the b-axis. Solvent molecules were omitted to clarify the figure.

	d <sub>P-P</sub> [a axis]	d <sub>P-P</sub> [b axis]	d <sub>P-P</sub> [c axis]
<b>1</b> (123 K) / Å	11.997	12.902	14.638
	d <sub>_B-B</sub> [a axis]	d <sub>B-B</sub> [b axis]	d <sub>_B-B</sub> [c axis]
<b>2</b> (117 K) / Å	12.028	12.998	14.457

Table S3-2. P–P or B–B distance of the Keggin anion in the1 and 2 along the *a*, *b* or *c*-axis.

Table S3-3. P–N or B–N distances (N atoms of BI cation) in the1 and 2.

	d <sub>P-N4</sub>	d <sub>P-N6</sub>	d <sub>P-N8</sub>	<b>d</b> Р-N10
<b>1</b> (123 K) / Å	6.705	5.567	5.612	6.131
	<b>d</b> <sub>В-N3</sub>	d <sub>B-N2</sub>	d <sub>B-N2</sub>	<b>d</b> B-N3
<b>2</b> (117 K) / Å	6.671	5.617	5.617	6.168



**Figure S3-3.** Hydrogen bonding manner between the nitrogen atom of BI and bridging oxygen atoms of  $[PMo_2^VMo_{10}^{VI}O_{40}]^{5-}$ .

#### 3-2 Crystal structure of 3

One electron reduced salt of  $Ph_4P^+$  was reported so far, [S2] while we isolated as two electrons reduced salt **3**. From XRD analysis, elemental analysis, composition was suggested as was  $(Ph_4P)_4H[PMoV_2MoV_{10}O_{40}] \cdot 4DMF$ . The cell parameter and molecular packing structure was identical to reported salt.



Figure S3-4. Ball/Stick view of the Ph<sub>4</sub>P<sup>+</sup> cations and keggin anion in the 3.



**Figure S3-5.** Packing structure of **3**. Unit cell viewed along the b-axis. The DMF molecules were omitted to clarify the figure.

### 3-3. Temperature dependence of single crystal Structure of 1

Single crystal X-ray crystallography was performed using a crystal of **1** at 123 K, 200 K and 270 K. Table S3-5 summarized P–P distance of the Keggin anion at each temperature. In addition, table S3-6 summarized P–N (N atoms of BI cation) in the**1** at each temperature. These results showed crystal structure of **1** at 123 K, 200 K and 270 K had no structure change.

	123 K	200 K	270 K
Formula	$C_{47}H_{65}N_{14}Mo_{12}O_{45}P$	$C_{47}H_{65}N_{14}Mo_{12}O_{45}P$	$C_{47}H_{65}N_{14}Mo_{12}O_{45}P$
Crystal system		Triclinic	
Space group		P1	
<i>a,</i> Å	11.9970(7)	12.0226(7)	12.0562(9)
b, Å	12.9020(7)	12.9527(8)	13.0160(10)
<i>c,</i> Å	14.6379(8)	14.7191(9)	14.7842(11)
α, deg	114.6658(7)	114.8324(7)	115.0352(9)
β, deg	106.7857(7)	107.0529(7)	107.2011(10)
γ, deg	95.9885(7)	95.6588(8)	95.3912(10)
V, Å <sup>3</sup>	1904.30(18)	1922.7(2)	1942.6(3)
Ζ		1	
<i>Т</i> , К	123	200	270
Flack parameter	0.07(4)	0.03(5)	0.09(7)
Reflections measured	22708	22940	22763
Independent reflections	16942	16942	17095
Reflections uced	16942	16942	17095
$R_{_{ m int}}$	0.0285	0.0298	0.0359
R <sub>1</sub>	0.0498	0.0505	0.0655
wR <sub>2</sub>	0.1425	0.1485	0.1877

Table S3-4. Crystal date, date collection, and reduction parameter of Crystal 1 at 123 K, 200 K and 270 K.



Figure S3-6. Ball/Stick view of the asymmetric unit of 1 at 123 K.



Figure S3-7. Ball/Stick view of the asymmetric unit of 1 at 200 K.



Figure S3-8. Ball/Stick view of the asymmetric unit of 1 at 270 K.

	d <sub>p-P</sub> [a axis]	d <sub>p-P</sub> [b axis]	d <sub>P-P</sub> [c axis]
123 K / Å	11.997	12.902	14.638
	d <sub>p-P</sub> [a axis]	d <sub>p-P</sub> [b axis]	d <sub>P-P</sub> [c axis]
200 K / Å	12.023	12.953	14.457
	d <sub>p-P</sub> [a axis]	d <sub>p-P</sub> [b axis]	d <sub>P-P</sub> [c axis]
270 K / Å	12.056	13.016	14.784

**Table S3-5.** P–P and B–B distance of the Keggin anion in the 1 along the a, b or c-axis at 123 K, 200 K and 270 K.

Table S3-6. This table summarized P–N (N atoms of BI cations) in the 1 at 123 K, 200 K and 270 K.

	<b>d</b> P-N1	d <sub>P-N4</sub>	<b>d</b> <sub>P-N6</sub>	d <sub>P-N8</sub>	<b>d</b> Р-N10
123 K / Å	6.539	6.705	5.567	5.612	6.131
	<b>d</b> P-N1	<b>d</b>	d <sub>P-N6</sub>	d <sub>P-N8</sub>	<b>d</b> Р-N10
200 K / Å	6.567	6.695	5.571	5.616	6.117
	<b>d</b> 1	<b>d</b>	d <sub>P-N6</sub>	<b>d</b> 8	<b>d</b> 10
270 K / Å	6.600	6.711	5.600	5.631	6.166

### 4. IR spectra

FTIR spectra (absorption) were characterized in the KBr discs and showed in figure S4 and summarized in table S4 with peak assignments. Bands derived from cations were denoted by an asterisk.



Figure S4. IR spectra of a) 1, b) 2 c) 3 d) 4 at 600-1700 cm<sup>-1</sup>.

	v_(M=O)	v_(X−O)	v_(M−O−M)
	M <sup>as</sup> Mo, W	X <sup>as</sup> = P, B	M = Mo, W
1	951	1056	824, 789, 771, 748
2	959	903	824,748
3	947	1057	802
4	951	1059	856, 793

Table S4. Summary and assignments of FTIE
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Figure S5-1. Solid state electronic spectra of salts 1, 3 and 4 in KBr pellets.

#### 5-2 NIR spectra

In the crystal of **2**, existence of water was not identified by single crystal XRD analysis. However, NIR absorption spectra showed absorption by O–H bonds of water at approximately 1450 nm and 1950 nm. [S3] These results indicated that water molecular is disordered in the single crystal. In addition, the absorption spectrum of Na<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>]·nH<sub>2</sub>O is shown on the figure S5-2 as reference.



**Figure S5-2.** NIR spectra of **2** and Na<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>]  $\cdot$  *n*H<sub>2</sub>O.



**Figure S6-1.** Temperature dependence of  $\varepsilon_1$  at various frequencies (up) and  $\varepsilon_2$  (down) at various frequencies (1 kHz-1 MHz) and frequency dependence at 70, 80, 90, 100, 110 and 120 K for pellet of 1.



**Figure S6-2.** Temperature dependence of  $\varepsilon_1$  at various frequencies (up) and  $\varepsilon_2$  (down) at various frequencies (1 kHz–1 MHz) for single crystal of **1**.



**Figure S6-3.** Temperature dependence of  $\varepsilon_2$  (down) at various frequencies for pellet of **3**. A real part of dielectric constant measured for the compound **3** was below measurement range ( $\varepsilon_1 < 1$ ).



**Figure S6-4.** Temperature dependence of (left)  $\varepsilon_1$  at various frequencies and (right)  $\varepsilon_2$  at various frequencies for pellet of **4**.

#### 7. BVS

For determination of the oxidation states of metal centers, bond valence sum (BVS) calculations were carried out using the method of I. D. Brown. [S4] Scheme S8-1 summarized BVS value of Mo for 1 at 123 K, 200 K and 270K. These values suggested that the Mo valence does not temperature dependence.



Scheme S7-1. BVS values of Mo at 123 K, 200 K and 270K for 1. Bond valence were estimated by to  $s = \exp[-(l_{ij}-l_o)/B]$  where  $l_{ij} = 1.89$  and B = 0.314.



Scheme S7-2. BVS values of Mo at 100 K for 3. Bond valence were estimated by to  $s = \exp[-(l_{ij}-l_o)/B]$  where  $l_{ij} = 1.89$  and B = 0.314.



Scheme S7-3. BVS values of Mo at 200 K for 4. Bond valence were estimated by to  $s = \exp[-(l_{ij}-l_o)/B]$  where  $l_{ij} = 1.89$  and B = 0.314.



*Valence of Mo* **Figure S7-1.** Histogram of BVS values of Mo for **1**, **2** and **3**.



Figure S8. Differential scanning calorimetry (DSC) of 1.

### 9. TG

The weight-loss of 10.80% in **1** was observed by increasing of the temperature up to 200°C, whose magnitude is consistent with the presence of four DMF molecules (calcd. 10.72%). Similarly, the weight-loss of 7.78% in **2** was observed by increasing of the temperature up to 200°C, whose magnitude is consistent with the presence of four DMF molecules (calcd. 7.76%).



Figure S9. TG diagrams of 1 and 2.

#### 10. NMR spectra

The two electron reduced mixed-valence  $[PMo^{V_2}Mo^{VI_{10}}O_{40}]^{5-}$  were confirmed by <sup>31</sup>P NMR chemical shift of salt **1** and **3**. The <sup>31</sup>P NMR chemical shift (Table S11) allowed the determination of the number of blue electrons within cluster. The <sup>31</sup>P NMR spectrum of complex 1 was recorded in DMSO-d<sub>6</sub>, referenced to <sup>31</sup>P in 85% H3PO4 for which  $\delta = 0$  ppm, and shows two peaks, one at 24.43 ppm assigned to PPh<sup>4+</sup> and the other at -5.9 and -5.8 ppm due to PO<sub>4</sub><sup>3-</sup> of {PMo<sub>12</sub>} cluster. In these results, we assigned {PMo<sub>12</sub>} clusters of **1**, **3** and **4** were two electrons reduced POM.

	δ (DMSO/[D6]DMSO) [ppm]	Reference
[PMo <sup>VI</sup> 12O40] <sup>3-</sup>	-2.9	[S5]
[PMo <sup>v</sup> Mo <sup>vI</sup> <sub>11</sub> O <sub>40</sub> ] <sup>4-</sup>	0.8	[S5]
[PMo <sup>V</sup> 2Mo <sup>VI</sup> 10O40] <sup>5-</sup>	-5.8	[S5]
1	-5.9	This work
3	-5.9	This work
4	-5.8	This work

Table S10. <sup>31</sup>P NMR chemical shift of some mixed-valence {PMo<sub>12</sub>} cluster, referenced to external 85% H<sub>3</sub>PO<sub>4</sub>.

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