Hydrogen-Bonded Assemblies of Two-Electron Reduced Mixed-Valence \([\text{XMo}_{12}\text{O}_{40}]\) (X = P and Si) with \(p\)-Phenylenediamines

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Supporting Information

ABSTRACT: Hydrogen-bonded assemblies of the two-electron reduced mixed-valence Keggin clusters \([\text{PMo}_{12}\text{O}_{40}]^{5-}\) and \([\text{SiMo}_{12}\text{O}_{40}]^{6-}\) were obtained by the one-pot electron-transfer reactions between \(p\)-phenylenediamine (PPD) or 2,3,5,6-tetramethyl-PPD (TMPPD) (donors) and \(\text{H}^+\) or \(\text{H}^+\) of \([\text{PMo}_{12}\text{O}_{40}]^{3-}\) or \([\text{SiMo}_{12}\text{O}_{40}]^{4-}\) (acceptors) in CH3CN. The redox states of the \([\text{PMo}_{12}\text{O}_{40}]^{5-}\) and \([\text{SiMo}_{12}\text{O}_{40}]^{6-}\) clusters were confirmed by the redox titrations and electronic absorption measurements. In \((\text{HPPD}^{+})_3(\text{H})_2\)\([\text{PMo}_{12}\text{O}_{40}]^{5-}\)(CH3CN)$_6$ (1), the \(\text{N}–\text{H} \sim \text{O}\) hydrogen-bonded interactions between the monoprotonated HPPD$^+$ (or diprotonated H2PPD$^{2+}$) and the \([\text{PMo}_{12}\text{O}_{40}]^{5-}\) resulted in a windmill-like assembly and hydrophilic one-dimensional channels are formed with a cross-sectional area of 0.065 nm$^2$, and these are filled by the CH3CN molecules. Also, the CH3CN molecules in salt 1 were removed by immersing the single crystals of 1 in H$_2$O, CH$_3$OH, and CH$_2$H$_2$OH solvents. In the compound, \((\text{HTMPPD}^{+})_6[\text{PMo}_{12}\text{O}_{40}]^{6-}\)(CH3CN)$_6$ (2), the \(\text{N}–\text{H} \sim \text{O}\) hydrogen-bonded interactions between the monoprotonated HTMPPD$^+$ molecules and the \([\text{SiMo}_{12}\text{O}_{40}]^{6-}\) formed a “Saturn-ring”-like assembly. Each Saturn-ring was arranged into an hexagonally packed array via hydrogen-bonded and \(\pi\)-stacking interactions of HTMPPD$^+$, while the CH$_3$CN solvent present in salt 2 are only found in the zero-dimensional isolated cavities.

INTRODUCTION

Hydrogen-bonded interactions can play a vital role in defining supramolecular assemblies both in solution and the solid state. Although the precise, predetermined, structural control of assemblies constructed using hydrogen-bonded interactions is still far from reach in global sense, the local molecular orientations determined by the intermolecular hydrogen-bonding interactions are often predictable and are controlled by utilizing functional groups of –OH, –NH$_2$, –COOH and so on. On the other hand, the arrangement of charged molecules in solid state crystalline arrays are mainly dominated by the electrostatic interaction between the cationic and the anionic species, so that the gain of the lattice/Madelung energy can be maximized by the system. In this category, polyoxometalate (POM) clusters show a rich range of complex and interesting structures with a bewildering variety of molecular-assemblies and motifs due to the size and shape and possibility to adopt one of many possible charge states. The charged states of the POM-based polyanions can widely vary from \([\text{Mo}_6\text{O}_{19}]^{2-}\), \([\text{Mo}_5\text{O}_{24}]^{6-}\), \([\text{Mo}_5\text{O}_{26}]^{3-}\), \([\text{Mo}_3\text{O}_{8}]^{7-}\), and \([\text{PMo}_{12}\text{O}_{40}]^{5-}\), and \([\text{PMo}_{12}\text{O}_{40}]^{3-}\), to \([\text{PMo}_{12}\text{O}_{40}]^{5-}\), which strongly affects the packing structures of POMs in the crystals depending on the size and valence of counter-cations. Keggin-type molybdenum clusters of \([\text{XMo}_{12}\text{O}_{40}]\) (X = S, P, Si, As, etc.) have a spherical molecular structure with a diameter of ~1 nm (Scheme 1), which are one of the appropriate candidates to examine the POM assembly structures in solids. In the \([\text{XMo}_{12}\text{O}_{40}]\), two kinds of oxygen atoms (24 metal-bridging Mo–O$\sim$Mo and 12 terminal Mo=O$_b$) can contribute to the intermolecular hydrogen-bonds, which can contribute to form a variety of molecular-assembly structures in solids. Several

Scheme 1. Molecular Structures of PPD, TMPPD, and \([\text{XMo}_{12}\text{O}_{40}]\) (X = P and Si)$^a$

\[\text{H}_3\text{N}–\text{NH}_2\] PPD
\[\text{H}_3\text{C}–\text{CH}_3\] TMPPD
\[\text{H}_3\text{C}–\text{CH}_3\] \([\text{XMo}_{12}\text{O}_{40}]\)

$^a$ The metal bridging Mo–O$\sim$Mo and terminal Mo = O$_b$ oxygen sites are shown in \([\text{XMo}_{12}\text{O}_{40}]\).

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ammonium-phosphotungstic acid (APWA) or ammonium-phosphomolybdic acid (APMA), which not only modified the surface properties, but also acted as a cation exchanger for the metal ions. The chemical composition of the resulting mixture was analyzed by infrared spectroscopy and X-ray diffractometry. The X-ray patterns showed that the mixture contained a single phase with a crystalline structure, as evidenced by the sharp peaks in the diffraction pattern. The infrared spectra exhibited strong absorption bands at frequencies characteristic of the tungsten and molybdenum oxo groups, indicating the presence of the corresponding metal oxo clusters.

In conclusion, the present study demonstrates the potential of using APWA or APMA as modifiers for the preparation of metal oxo clusters with tunable electronic and structural properties. Further experiments are needed to explore the applications of these clusters in catalysis, sensing, and other advanced materials.

References:

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Table 1. Crystal Data, Data Collection, and Reduction Parameters of Crystals 1 and 2 at 100 K

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R = Σ|F_{o}|-|F_{c}|/Σ|F_{o}| and Rω = {Σω(F_{o}² - F_{c}²)²/Σω(F_{c}²)²}^{1/2}.

hydrogen atoms, and these were refined using the riding model with a fixed C–H distance of 0.95 Å.

**Solvent Removal.** Single crystals of salt 1 were immersed into H₂O, CH₃OH, C₂H₅OH, hexane, CH₂Cl₂ (∼10 mL) for 2 min at 296 K. The single crystals were collected by filtration, then the IR spectra on KBr pellets was measured. The nitrile stretching vibrational mode (C≡N) was monitored before and after immersing of the corresponding solvents.

**RESULTS AND DISCUSSION**

**Crystal Growth and Redox Properties.** The p-phenylene-diamine (PPD) derivatives have strong electron-donating and proton accepting associated with the two amino (–NH₂) groups, which are good candidates to form the hydrogen-bonded assemblies with the reduced [PMo₁₂O₄₀]⁴⁻ and [SiMo₁₂O₄₀]⁵⁻ clusters. We already reported the crystal structures and magnetic properties of (PPD)₂([12]crown-4)₄[PMo₁₂O₄₀]⁴⁻, (PPD)₄([18]-crown-6)₄[PMo₁₂O₄₀]⁴⁻, and (PPD)₃([18]crown-6)₄[PMo₁₂O₄₀]⁴⁻ hybrids, in which the hydrogen-bonding interactions between the protonated PPD and crown ethers were preferentially observed. On the other hand, in the (Cs⁺)₃([18]-crown-6)₄[H⁺]₂[PMo₁₂O₄₀]⁵⁻ hybrid, the Cs⁺([18]crown-6)³⁺ assembly formed through the Cs⁺ – O interactions. Since the oxygen atoms of crown ethers preferentially form supramolecular assemblies with the cationic species and defines the hydrogen-bonded interactions between the cation and the POM, the direct reaction between PPD derivatives (PPD and tetramethyl-PPD) and [PMo₁₂O₄₀]⁵⁻ or [SiMo₁₂O₄₀]⁵⁻ was carried out. During the reaction the color of the solvent changed from yellow to blue-purple as the slow diffusion between (H⁺)^⁶⁻ [XM₀₁₂O₄₀]⁶⁻ (n = 3 for X = P and n = 4 for X = Si) and PPD (or TMPPD) in CH₂CN over 2–3 days proceeded, which then finally resulted in the growth of black-colored single crystals of salts (HPPD)^⁺)[PMo₁₂O₄₀]⁶⁻ (CH₂CN)₃·₆ (1) and (HTMPPD)^⁺)[SiMo₁₂O₄₀]⁶⁻ (CH₂CN)₆ (2), which were obtained as the two-electron reduced mixed-valence [XMo₁₂O₄₀]ⁿ⁻(n+2)− salts. It should be noted that the two possible protonated states of HPPD⁺ and H₂PPD²⁺ were assumed in the formula of salt 1.

The redox potentials for the [PMo₁₂O₄₀]³⁻ (or [SiMo₁₂O₄₀]⁴⁻) and PPD (or TMPPD) were measured by cyclic voltammetry in CH₂CN at 296 K. Reversible two-step one-electron reduction of [PMo₁₂O₄₀]³⁻ was observed at the half-wave reduction potentials of E₁/₂(1) = +0.186 V and E₁/₂(2) = -0.251 V, respectively, while those of [SiMo₁₂O₄₀]⁴⁻ were observed at E₁/₂(1) = -0.314 V and E₁/₂(2) = -0.723 V vs SCE, n-Bu₄NF, Pt in CH₂CN. The electron accepting ability of [PMo₁₂O₄₀]³⁻ was about 0.5 V higher than that of [SiMo₁₂O₄₀]⁴⁻ in CH₂CN, which was consistent with the previous results. Since the E₁/₂(1) values of typical electron-acceptors of 7,7,8,8-tetrayano-p-quinodimethane (TCNQ) was observed at E₁/₂(1) = +0.223 V, the electron accepting strengths of [PMo₁₂O₄₀]³⁻ was almost similar to that of TCNQ. Also, the half-wave first oxidation potentials [E₁/₂(1)] of PPD and TMPPD were observed at +0.299 V and +0.146 V, respectively, under the same measurement conditions. The electron-donating ability of TMPPD was about 0.15 V higher than that of PPD because of the existence of electron-donating methyl groups.

The abilities of electron-transfer from PPD (or TMPPD) to [PMo₁₂O₄₀]³⁻ (or [SiMo₁₂O₄₀]⁴⁻) during the crystallization were estimated from the difference of redox potentials between E₁/₂(1) of PPD (or TMPPD) and E₁/₂(1) of [PMo₁₂O₄₀]³⁻ (or [SiMo₁₂O₄₀]⁴⁻). The ΔE values of salts 1 and 2 were 0.113 and 0.460 V, respectively. From the theoretical V-shaped diagram by Torrance et al.,²²a the electronic ground states of donor–acceptor type charge transfer (CT) complexes have been predicted as ionic or neutral from the ΔE values. When the ΔE was larger than about 0.3 V, the neutral electronic ground state was preferable in the CT complex, while the condition of ΔE < 0.3 V yielded the ionic electronic ground state through the full charge transfer from the electron donor to the electron acceptor. The ionic and neutral electronic ground states of salts 1 and 2 were expected from the ΔE values of 0.113 and 0.460 V, respectively. However, it has been reported that the reduction potentials of [SiMo₁₂O₄₀]⁴⁻ were sensitive to the concentration of the cationic species in CH₂CN.²³ The one-electron reduction wave of E₁/₂(1) changed to the two-electron reduction one by adding the cationic species such as H⁺, Li⁺, Na⁺, and so forth, with about 0.25 V anodic shift of the reduction potential,²³ although such potential shift was not detected in [PMo₁₂O₄₀]³⁻ species in CH₂CN. The anodic shift of E₁/₂(1) of [SiMo₁₂O₄₀]⁴⁻ resulted in the ionic electronic ground states of [SiMo₁₂O₄₀]⁶⁻ during the crystallizations of salt 2 as in case of [PMo₁₂O₄₀]⁵⁻ in salt 1, which have been confirmed by the redox titrations and electronic spectra.

**Two-Electron Reduced [PMo₁₂O₄₀]⁷⁻ and [SiMo₁₂O₄₀]⁶⁻ Compounds.** The two-electron reduced mixed-valence [PMo₁₂O₄₀]⁶⁻ and [SiMo₁₂O₄₀]⁶⁻ were confirmed by the redox titrations of salts 1 and 2 at 296 K. The redox titrations (Figure 1a) allowed the determination of the number of MoV ions within the cluster. However, the potential jumps that occurred during the redox titration of salts 1 and 2 corresponded to 8 and 14 electrons, respectively (Figure 1a). In these salts, the electron donors PPD and TMPPD in acidic solution also contribute to the redox titration as a consequence of PPD → PPD⁺ + e⁻ → PPD²⁺ + e⁻ (or TMPPD → TMPPD⁺ + e⁻ → TMPPD²⁺ + e⁻). However, the stoichiometries of (PPD)₆[PMo₁₂O₄₀]⁶⁻ and (TMPPD)₆[SiMo₁₂O₄₀]⁶⁻ are consistent.
with the 8 and 14 electrons respectively, that is, the oxidation process of 3PPD + 2MoV (8 electrons) and 6TMPD + 2MoV (14 electrons), respectively.

The mixed-valence electronic states of [PMo12O40]5− and [SiMo12O40]6− in salts 1 and 2 were confirmed by UV–vis–NIR–IR spectra of the solid (Figure 1b), and the yellow-colored (H+)2[PMo12O40]5− did not show the d–d transition (blue line in Figure 1b) because of the (4d)0 electronic state of the MoVI ions. Also, the electronic absorptions at 32 and 46 × 103 cm−1 can be assigned to metal-ligand charge transfer electronic excitations from the doubly occupied oxo-orbitals to unoccupied d-orbitals of MoVI.24 On the other hand, the electronic spectra of salts 1 and 2 show a broad absorption in the vis–NIR–IR energy region, and the octahedral coordination of the six oxygen atoms to a MoIII ion split in an octahedral field, that is, the d-orbitals are divided into τ2g and eg-orbitals, whose energy separation is usually larger than 10 × 103 cm−1. Therefore, the low energy electronic absorption in salts 1 and 2 at ~8 × 103 cm−1 was assigned to the inter-valence transition from the MoIII to MoVI ions through the Mo–O–Mo bond within the cluster,24 and the bands at ~12 and ~18 × 103 cm−1 were observed in the typical energy region of the d–d transitions of MoVI ion.

### Vibrational Spectra of Salts 1 and 2

From the elemental analysis and X-ray crystal structural analysis, the stoichiometries of salts 1 and 2 were determined to be (HPPD)2,(H+)2,[PMo12O40]5−,[SiMo12O40]6−,(CH3CN)3−6 (1) and (HTMPPD)3,(SiMo12O40)6−,(CH3CN)6 (2), respectively. To compensate the total charge within the crystals, the PPD and TMPD must be protonated, and the vibrational spectra of salts 1 and 2 were useful to confirm the protonated states of PPD and TMPD molecules; thus we evaluated the N–H stretching vibrational modes (νN–H) and the N–H deformation modes (δN–H) of -NH2 and -NH3+ in salts 1 and 2 (see Supporting Information, Figure S2). The νN–H modes of -NH2 and -NH3+ have been typically observed at 3500–3300 cm−1 and 3130–3030 cm−1, respectively, while the δN–H modes of -NH2 and -NH3+ were observed at around 1650–1560 cm−1 and 1600 cm−1, respectively.25 The νN–H modes of -NH2 group in salts 1 and 2 were observed as broad band around 3400 cm−1, while the νN–H modes of -NH3+ group of salts 1 and 2 were confirmed as a broad band with absorption maxima at 3052 and 2050 cm−1, respectively. In the δN–H energy region, two δN–H bands in both of the salts 1 and 2 were observed around 1630 and 1600 cm−1, corresponding to the -NH2 and -NH3+ groups, respectively.

### Thermal Stabilities of Salts 1 and 2

Thermal Stabilities of Salts 1 and 2. Temperature dependent thermogravimetry (TG) diagrams (Figure 2) revealed the thermal stabilities of salts 1 and 2. Since the hydrogen-bonding ionic structures between the PPD derivatives and [XMo12O40]3−(n+2)− should be relatively stable, the weight-loss during the TG analyses is dominated by the acetone solvent. The weight-loss of 7.8% in salt 2 was observed by increasing of the temperature up to 450 K, whose magnitude is consistent with the presence of six CH3CN molecules (calcd. 8.1%). The weight-loss of salt 2 started around 350 K, indicating that the salt 2 was thermally stable up to about 350 K. On the contrary, rapid weight-loss of salt 1 occurred around room temperature, which reached at about 6% around 450 K, and the weight-loss of ~6% was much smaller than that for six CH3CN molecules (10.2%), indicating that two or three CH3CN molecules were already removed from the salt 1 before the start of TG measurement, that is, (HPPD)3,(H+)2,[PMo12O40]5−,(CH3CN)3−6, the magnitude of weight-loss for three CH3CN molecules (5.3%) was well consistent with the experimental result. The difference of thermal stabilities between the salts 1 and 2 can be explained by the dimensionality of nanospaces in the crystal occupied by solvent molecules (see Packing Structures). From the redox titration, optical measurements, TG analysis, and X-ray crystal structural analysis, the stoichiometries of salts 1 and 2 were assumed to be (HPPD)3,(H+)2,[PMo12O40]5−,(CH3CN)3−6 (1) and (HTMPPD)3,(SiMo12O40)6−,(CH3CN)6 (2), respectively.

### Packing Structure

In salts 1 and 2, the formation of α-Keggin structures was observed which crystallized in the space group of R3 and R3c for salts 1 and 2, respectively. The [PMo12O40]5− clusters are arranged hexagonally within the ab-plane (Figure 3a) connected through hydrogen-bonded interactions to each other, where the [PMo12O40]5− clusters exists alternately above and below in the ab-plane (Figure 3b). The infinite N–H–O hydrogen-bonding interactions between the [PMo12O40]5− and HPPD+ (or H2PPD)+ effectively constructed the three-dimensional assembly structure of mixed-valence [PMo12O40]5−. The intercluster interaction between the [PMo12O40]5− in the ab-plane was negligible because of the long P–P distances (dp−p) of 13.80 Å, while relatively short dp−p of 10.12 Å was
observed along the c-axis (Figure 3c). Along the c-axis, each \([\text{PMo}_{12}\text{O}_{40}]^{5-}\) directly interacted through the interatomic \(\text{O}_a - \text{O}_b\) distance of 3.009(9) Å.

The space filling representation of the (HPPD\(^+\))\(_2\)(H\(^+\))\(_2\)\([\text{PMo}_{12}\text{O}_{40}]^{5-}\) assembly shown in Figure 3b shows one-dimensional triangular spaces which are elongated along the c-axis, where the CH\(_3\)CN solvent molecules are occupied. The cross-sectional area of the nanospace was about 0.065 nm\(^2\), and its sectional triangular spaces which are elongated along the c-axis. The CH\(_3\)CN molecules were omitted to clarify the CH\(_3\)CN molecules are easily released from the crystal, even at room temperature. The CH\(_3\)CN molecules present in the one-dimensional channels are easily removed by immersing the single crystals into H\(_2\)O, CH\(_3\)OH, and C\(_2\)H\(_5\)OH (see the section on Solvent Removal), suggesting that hydrophilic molecular recognition environments are present in the crystal.

Figure 4 shows the packing structure of salt 2. The hydrogen-bonding (HTMPPD\(^-\))\(_6\)[SiMo\(_{12}\text{O}_{40}]^{6-}\) assembly further formed the \(\pi\)-stacking interaction between the TMPPD molecules. In the ab-plane, the hexagonal [SiMo\(_{12}\text{O}_{40}]^{6-}\) arrangement was observed through the N\(_2\) – H \(\sim\) O hydrogen-bonded interactions, that is, the hydrogen-bonding Saturn-ring-like assemblies of (TMPPD)\(_6\)[SiMo\(_{12}\text{O}_{40}]^{6-}\) were further connected infinitely within the ab-plane. The nearest-neighbor intercluster Si–Si distance \((d_{\text{Si–Si}})\) of 16.89 Å in the ab-plane indicated the independent cluster arrangement, while the effective intercluster interaction of \(d_{\text{Si–Si}}\) of 10.25 Å was observed along the c-axis. Along the c-axis, the shortest \(\text{O}_a - \text{O}_b\) distance of 3.060(8) Å was observed between the [SiMo\(_{12}\text{O}_{40}]^{6-}\) (see Supporting Information, Figure S8), which distance was similar to that in salt 1 \((d_{\text{O}_a - \text{O}_b} = 3.009\) Å). The HTMPPD\(^-\) molecules formed the \(\pi\)-stacking dimer with a mean interplanar distance of 3.3 Å (Figure 4c). Between the \(\pi\)-dimer stacks (Figure 4c), two CH\(_3\)CN molecules arranged in the antiparallel manner to cancel the dipole moments. The CH\(_3\)CN molecules surrounding by

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**Figure 3.** Packing structure of salt 1. (a) Unit cell viewed along the c-axis. (b) Space filling representation of the assembly, where the one-dimensional channels elongated along the c-axis. The CH\(_3\)CN molecules were omitted to clarify the figure. (c) One-dimensional [PMo\(_{12}\text{O}_{40}]^{5-}\) arrangement along the c-axis, where the shortest \(\text{O}_a - \text{O}_b\) distance of 3.009(9) Å was observed.

**Figure 4.** Packing structure of salt 2. (a) Unit cell viewed along the c-axis. The CH\(_3\)CN molecules are omitted to clarify the figure. (b) Space filling representation of (TMPPD)\(_6\)[SiMo\(_{12}\text{O}_{40}]^{6-}\) assembly viewed along the c-axis. (c) One-dimensional [SiMo\(_{12}\text{O}_{40}]^{6-}\) arrangement along the c-axis were connected by the N\(_2\) – H \(\sim\) O hydrogen-bonding and the \(\pi\) – \(\pi\) stacking interactions. Between the \(\pi\)-dimer of TMPPD molecules, two CH\(_3\)CN molecules existed in the antiparallel arrangement.

**Figure 5.** Hydrogen-bonding PPD – [PMo\(_{12}\text{O}_{40}]^{5-}\) assembly in salt 1. (a, b) Windmill-like (PPD)\(_6\)[PMo\(_{12}\text{O}_{40}]^{5-}\) assembly. (c, d) Hydrogen-bonding sites between the nitrogen atom of PPD and the bridging \(\text{O}_a\) and terminal \(\text{O}_b\) oxygen atoms of [PMo\(_{12}\text{O}_{40}]^{5-}\). Blue, red, brown, and gray spheres are nitrogen, oxygen, molybdonum, and carbon atoms, respectively.

TMPPD molecules could not be easily released from the crystals, which was consistent with higher thermal stability of salt 2 than that of salt 1.

**Hydrogen-Bonding Assemblies in Salts 1 and 2.** The hydrogen-bonding assemblies in salts 1 and 2 were characterized by the X-ray crystal structural analyses. In the Keggin cluster, two kinds of oxygen atoms (24 metal-bridging Mo – \(\text{O}_b\) and 12 terminal Mo = \(\text{O}_a\) in Scheme 1) can contribute to the intermolecular hydrogen-bonds. It has been reported that the acidic protons in (H\(^+\))\(_3\)[PMo\(_{12}\text{O}_{40}]^{3-}\) cluster were located at the bridging Mo – \(\text{O}_b\) – Mo oxygen atomic sites from the Electron Nuclear Double Resonance (ENDOR)-NMR and density functional theory (DFT) calculations,\(^{26}\) suggesting that the \(\text{O}_a\) oxygen atoms have higher hydrogen-bonding ability than that of \(\text{O}_b\) ones.
Figures 5a and 5b show the hydrogen-bonded (PPD)₆⁻-[PMo₁₂O₄₀]⁵⁻ assembly in salt 1. The [PMo₁₂O₄₀]⁵⁻ cluster was surrounded by the six protonated PPD molecules (HPPP⁺ or H₂PPP⁺₂⁻), forming a windmill-like assembly and six PPD molecules arranged alternately at the upper and lower position of [PMo₁₂O₄₀]⁵⁻ through the N–H~O hydrogen-bonding interactions (Figure 5a and Figure 5b). The dihedral angle of the nearest-neighboring mean π-planes of PPD was 60 degrees, and the interacting nitrogen atom of PPD exists at a central position of four bridging Mo–O–Mo oxygen atoms (Figure 5c), where the N–Oₐ distances of 2.894(8), 2.905(6), 3.073(6), and 3.078(9) Å were about 1 Å shorter than the N₂/Ob distance of 3.163 Å. The dihedral angle at Ob site is of negligible magnitude.

On the other hand, since the N₂/Ob distance of 4.049(10) Å (the hydrogen-bonding interactions) between the oxygen atoms of [SiMo₁₂O₄₀]⁶⁻ was surrounded by the six protonated PPD molecules (HPPP⁺)₂(H₂PPP⁺₂⁻)([PMo₁₂O₄₀]⁵⁻), in which the average structure of N–H~O and N–H~O hydrogen bonding interactions was observed in the X-ray crystal structural analysis.

The molecular-assembly of (HTMPD⁺)[₆SiMo₁₂O₄₀]⁶⁻ in salt 2 was constructed from six N–H~O hydrogen bonding interactions between the oxygen atoms of [SiMo₁₂O₄₀]⁶⁻ and nitrogen atoms of TMPD (Figure 6a and Figure 6b). The π-planes of HTMPD⁺ were parallel to each other, forming a Saturn-ring-like molecular-assembly. In salt 2, one HTMPD⁺ molecule was the crystallographically independent unit, where two nitrogen atoms (N₁ and N₂) had a different hydrogen-bonding environment (site-I and site-II). The hydrogen-bonds at the site-I and site-II corresponded to the N₁–H~O and the N₂–H~O interactions, respectively, and the site-I was observed around the [SiMo₁₂O₄₀]⁶⁻ cluster. The hydrogen-bonding at site-II corresponded each Saturn-ring infinitely within the ab-plane (see Figure 4a). In the site-I, the N₁–Oₐ distance of 3.084 Å was slightly shorter than the N₁–Oₐ distance of 3.163 Å. On the other hand, since the N₂–Oₐ distances of 2.783(12), 2.835(12), 2.993(9), and 3.06(1) Å in site-II were much shorter than the N₂–Oₐ distance of 4.049(10) Å (the hydrogen-bonding at Ob site is of negligible magnitude).

From the crystal stoichiometry and vibrational spectra, the protonated state of HTMPPD⁺ should be reasonable ones in (HTMPPD⁺)[₆SiMo₁₂O₄₀]⁶⁻[(CH₃CN)₆]⁻. We evaluated the N–C bond distances of TMPD to distinguish the type of C-NH₂ and C-NH₃⁺ bonds. It has been reported that the C–NH₃⁺ bond length for the ammonium site is longer than the C–NH₂ one for the amino site. Since the N₁–Cl₁ = 1.39(5) Å of TMPPD (site-I) was about 0.5 Å longer than the N₂–Cl₁ = 1.44(3) Å (site-II), the NH₃⁺ ~ O and NH₂ ~ O hydrogen-bonding sites could be safely assigned to the site-I and site-II, respectively. Therefore, six ionic N–H~O hydrogen-bonding interactions around the [SiMo₁₂O₄₀]⁶⁻ formed the Saturn-ring-like assembly to reduce the electrostatic interactions.

**Solvent Remove from Salt 1.** The one-dimensional channels of salt 1 were occupied by CH₃CN molecules, whose removal in CH₂O, CH₃OH, C₂H₅OH, CH₂Cl₂, and hexane was evaluated at 296 K. The solvent removal was monitored by vibrational spectra. Although the overall spectral features were the same before and after immersion of the single crystals into (ii) CH₃OH, (iii) H₂O, (iv) C₂H₅OH, (v) CH₂Cl₂, and (vi) hexane.

Figure 6. Hydrogen-bonding TMDP – [SiMo₁₂O₄₀]⁶⁻ assembly in salt 2. (a, b) Hydrogen-bonding Saturn-ring-like (TMPPD)₆[SiMo₁₂O₄₀]⁶⁻ assembly, where the hydrogen atoms were omitted in figure. Two kinds of hydrogen-bonding interactions of N₁ ~ O₁ and N₂ ~ O₂ were defined as site-I (c and d) and site-II (e and f), respectively. Blue, red, brown, and gray spheres are nitrogen, oxygen, molybdenum, and carbon atom, respectively.

Figure 7. Vibrational spectra of salt 1 in the frequency range from 2300–2200 cm⁻¹ in KBr pellets. The spectra of (i) initial state of salt 1 and after immersion of the single crystals into (ii) CH₃OH, (iii) H₂O, (iv) C₂H₅OH, (v) CH₂Cl₂, and (vi) hexane.
removal reaction. Since the one-dimensional channel surrounded by PPD molecules and terminal Mo=O oxygen atoms formed the hydrophilic channel, small size polar molecules such as H$_2$O and CH$_3$OH were responsible for the solvent remove reaction. Such phenomena were not detected in salt 2, and is consistent with high thermal stability of salt 2 in the TG analysis.

## CONCLUSIONS

The electron-transfer and proton-transfer reactions between the electron-donor (proton-acceptor) of PPD derivatives and the electron-acceptor (proton-donor) of (H$^+$)$_n$M$^{4+}$O$_{2n+6}$O$_{40}$ resulted in the formation of two-electron reduced [PMo$_{12}$O$_{40}$]$^{5-}$ and [SiMo$_{12}$O$_{40}$]$^{6-}$ (1) and (HTMPD)$^{5-}$ [SiMo$_{12}$O$_{40}$]$^{6-}$ (2). The electrostatic and hydrogen-bonding interactions between the PPD (or TMPPD) and the electron-donor (proton-acceptor) of PPD derivatives and the electron-acceptor (proton-donor) of (H$^+$)$_n$M$^{4+}$O$_{2n+6}$O$_{40}$ resulted in the formation of two-electron reduced [PMo$_{12}$O$_{40}$]$^{5-}$ and [SiMo$_{12}$O$_{40}$]$^{6-}$.

## ASSOCIATED CONTENT

### Supporting Information

Atomic numbering scheme of structural analysis of salts 1 and 2 (CIF), IR and Raman spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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