Supporting information

A Chromium-Substituted Polyoxoniobate with High Ionic Conductivity

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Section 1 Synthesis and Methods

All chemicals were commercially purchased and directly used without further purification except K$_7$HNb$_6$O$_{19}$·13H$_2$O precursor was prepared as described in the literature$^1$.

**Synthesis of 1:** K$_7$HNb$_6$O$_{19}$·13H$_2$O (0.5 g, 0.34 mmol) was added to 10 ml 0.02 M Na$_2$CO$_3$/NaHCO$_3$ buffer solution (pH = 9) followed by CrCl$_3$·6H$_2$O (0.03 g, 0.11 mmol) and Na$_2$CO$_3$ (0.1 g, 0.94 mmol). The mixture was vigorously stirred for about 1h, then transferred to a 25 ml Teflon-lined stainless steel autoclave and heated at 140 ºC for 72 h. The pH values before and after the reaction were 11.5 and 9.6, respectively. After cooling to room temperature, filtrate was kept at room temperature for two weeks and light green crystals suitable for X-ray crystallography were obtained. Yield: 3.9% (based on Nb). IR (KBr pellet): 3202s, 1646w, 1459w, 1360w, 849s, 632s, 500s. We had tried a series of parallel experiments with different amount of CrCl$_3$ to check if the amount of CrCl$_3$ could affect the stoichiometric amount of Cr in the final product. The experimental results reveal that crystal I could only be obtained by controlling the amount of CrCl$_3$ in the range of 0.1 - 0.2 mmol, but the amount of CrCl$_3$ had no effect on the stoichiometric amount of Cr in the final product. Additionally, the Cr$^{3+}$ ions play a key role for the formation of 1 because it couldn’t be obtained without adding Cr$^{3+}$ or by switching Cr$^{3+}$ to other transition metal ions.

**Single-crystal X-ray diffraction:** Crystal 1 was collected on a Bruker APEX II CCD area diffractometer equipped with a fine focus, 2.0 kW sealed tube X-ray source (MoKα radiation, $\lambda$ = 0.71073 Å) operating at 293(2) K. The empirical absorption correction was based on equivalent reflections. The structure was solved by direct methods followed by successive difference Fourier methods. Computations were performed using SHELXTL and final full-matrix refinements were against F$^2$. The contribution of disordered solvent molecules to the overall intensity data of structure was treated using the SQUEEZE method in PLATON. Crystal data for 1: $M_r$ = 10451.08, triclinic, P-1, $a$ = 18.001(3) Å, $b$ = 20.849(4) Å, $c$ = 21.063(4) Å, $\alpha$ = 81.145(3)$^\circ$, $\beta$ = 88.830(3)$^\circ$, $\gamma$ = 80.775(3)$^\circ$, $V$ = 7710(2) Å$^3$, $Z$ = 1, $\rho$ = 1.991 g cm$^{-3}$, GOF = 1.053. A total of 45254 reflections were collected, 25436 of which were unique ($R_{int}$ = 0.0350). $R_1$(w$R_2$) = 0.0859(0.2417) for 1318 parameters and 15393 reflections ($I > 2\sigma(I)$). CCDC-1885821 contains the crystallographic data.

**Instruments:** Powder XRD patterns were obtained using a Rigaku Ultima IV diffractometer, X’PertPRO, MiniFlex II with Cu-Kα radiation ($\lambda$ = 1.54056 Å). IR spectra (KBr pellets) were recorded on a Nicolet iS50 FT-IR spectrometer. Thermogravimetric analysis (TGA) was performed on a TGA/DSC 3+ thermal analyzer instrument in flowing air atmosphere with a heating rate of 10ºC min$^{-1}$. The optical diffuse reflectance spectrum was measured at room temperature using a Perkin-Elmer Lambda 900 UV-Vis spectrophotometer equipped with an integrating sphere attachment and BaSO$_4$ as reference. ICP analysis was conducted on an Ultima2 spectrometer.

**Ionic conductivity experiments:** Ac impedance measurements were carried out with a zennium/IM6 impedance analyzer over the frequency range from 0.1 Hz to 5 MHz with an applied voltage of 50mV. The relative humidity was controlled by a STIK Corp. CIHI-150B incubator.
The sample was pressed to form a cylindrical pellet of crystalline powder sample (~1.6 mm thickness \( \times 5 \) mm \( \phi \)) coated with Cpressed electrodes. Two silver electrodes were attached to both sides of pellet to form four end S3 terminals (quasi-four-probe method). The bulk conductivity was estimated by semicircle fittings of Nyquist plots.
Section 2 Additional Tables

Table S1. ICP analyses of 1. (The total amount of Nb and Cr is normalized to 100 %.)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Calculated (%)</th>
<th>Found (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>5.25</td>
<td>4.92</td>
</tr>
<tr>
<td>Nb</td>
<td>94.75</td>
<td>95.08</td>
</tr>
</tbody>
</table>

Table S2. A comparison of the conductivity of 1 with that of some representative POM-based conducting materials. σ represents conductivity; RH stands for relative humidity.

<table>
<thead>
<tr>
<th>compounds</th>
<th>$\sigma_{\text{max}}$ (S cm$^{-1}$)</th>
<th>condition</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$[H$_7${N(CH$_2$PO$_3$)$_3$}$_2$]Mo$<em>6$O$</em>{10}$(OH)(H$_2$O)$_4$]·18H$_2$O</td>
<td>$6.4 \times 10^{-2}$</td>
<td>70 °C, 98% RH</td>
<td>This work</td>
</tr>
<tr>
<td>[Cu$_2$(μ$_2$-OH)(H$_2$O)$_3$]$<em>3$[P$<em>3$W$</em>{18}$O$</em>{71}$]·14H$_2$O</td>
<td>$2.55 \times 10^{-2}$</td>
<td>100 °C, 98% RH</td>
<td>2</td>
</tr>
<tr>
<td>[Co(bpz)(Hbpz)][Co(SO$<em>4$)$</em>{1.5}$]$<em>{4.5}$[PMo$^{V}<em>3$Mo$^{V}</em>{4}$V$^{IV}</em>{4}$O$_{42}$]·13H$_2$O</td>
<td>$4.4 \times 10^{-6}$</td>
<td>25 °C, 97% RH</td>
<td>3</td>
</tr>
<tr>
<td>[Ni$_2$(bpz)(Hbpz)]$<em>2$[H$<em>2$SiW$</em>{12}$O$</em>{40}$]·8H$_2$O</td>
<td>$1.7 \times 10^{-4}$</td>
<td>75 °C, 98% RH</td>
<td>4</td>
</tr>
<tr>
<td>[Ce$^{III}$H$_2$O$_6$]{<a href="OH">Ce$^{IV}<em>{7}$Ce$^{III}</em>{3}$O$_6$</a>$_6$(CO$<em>3$)(H$<em>2$O)$</em>{11}$}$</em>{16}$</td>
<td>$2.65 \times 10^{-4}$</td>
<td>100 °C, 75% RH</td>
<td>5</td>
</tr>
<tr>
<td>Cu$<em>6$ (Trz)$</em>{10}$(H$_2$O)$<em>4$[H$<em>2$SiW$</em>{12}$O$</em>{40}$]·8H$_2$O</td>
<td>$1.84 \times 10^{-6}$</td>
<td>95 °C, 95% RH</td>
<td>6</td>
</tr>
<tr>
<td>K$_{1.3}$H</td>
<td>$1.7 \times 10^{-3}$</td>
<td>65 °C, 75% RH</td>
<td>7</td>
</tr>
<tr>
<td>[Na(H$<em>2$O)P$<em>3$W$</em>{30}$O$</em>{116}$]·0.03PAA5000·20H$_2$O</td>
<td>$1.04 \times 10^{-2}$</td>
<td>80 °C, 75% RH</td>
<td>8</td>
</tr>
<tr>
<td>[Na$_3$[(nBu)$<em>4$N]$</em>{17}$[Zn(P$_3$Mo$<em>3$O$</em>{11}$)$_2$]·xG (G = guest solvent molecules)]</td>
<td>$4.5 \times 10^{-2}$</td>
<td>85 °C, 70% RH</td>
<td>9</td>
</tr>
<tr>
<td>{[Na(NO$_3$)(H$_2$O)]$_4$<a href="H$_2$O">Al$<em>{16}$(OH)$</em>{24}$</a>$<em>8$(P$<em>8$W$</em>{48}$O$</em>{184}$)]$^{16-}$</td>
<td>$2.4 \times 10^{-3}$</td>
<td>25 °C, 90% RH</td>
<td>10</td>
</tr>
<tr>
<td>{<a href="%5BW$_3$Bi$_6$Ce$%5E%7BIII%7D_%7B3%7D$$(H_2O)_3O_%7B13%7D$%5D%5BB-a-Bi$_%7B3%7D$W$_%7B5%7D$O$_%7B13%7D$%5D">W$<em>{14}$Ce$^{IV}</em>{6}$O$_{60}$</a>$^{34-}$</td>
<td>$2.4 \times 10^{-3}$</td>
<td>25 °C, 90% RH</td>
<td>10</td>
</tr>
</tbody>
</table>

Hatz = 3-amino-1, 2, 4-triazololate; G = guest solvent molecules; bpz = 3, 3', 5, 5'-tetramethyl-4, 4'-bipyrazole; Trz = 3, 4-triazole; PAA5000 = polyallylamine (molecular weight $m = 5000$).
Section 3 Additional Structural Figures and Characterizations

Figure S1. The PXRD patterns of simulated 1 and as-synthesized sample of 1.

Figure S2. View of the dimeric \{\text{CrNb}_{11}\text{O}_{37}\}.
**Figure S3.** XPS spectra of (a) compound 1 and (b) Cr(2p).

As shown in Figure S3b, the doublet peak signals at 577.8 and 587.3 eV were resolved for Cr(2p3/2) and Cr(2p1/2), respectively. The spin-orbit splitting value was calculated to be 9.8 eV, confirming that the oxidation states of all Cr ions in 1 are +3.\textsuperscript{11}

**Figure S4.** View of cube-like ionic cluster 1b.

**Figure S5.** View of protonated oxygen atoms in 1a.
Figure S6. The PXRD patterns of simulated 1 and sample of 1 collected after ionic conduction tests.

Figure S7. The IR spectrum of compound 1.

The broad band in 3210 cm⁻¹ can be attributed to O-H stretching. The strong bands at 849 cm⁻¹ can be assigned to the stretching vibrations of Nb=Oₖ bonds. A series of bands in the 500-650 cm⁻¹ region are characteristic of ν (M-O-M) (M = Nb or Cr).

Figure S8. The Solid-state UV-Vis spectrum of compound 1.
Figure S9. The TGA curve of compound 1.

References
