SUPPORTING INFORMATION

Inorganic-Organic Hybrid High-dimensional Polyoxotantalates and

Their Structural Transformations Triggered by Water

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Section S1: Syntheses and Methods

1. Solvothermal Syntheses:

Synthesis of $H_2[Cu(en)_2(H_2O)_2]\{[Cu(en)_2]_4[Cu(en)(Ta_6O_{19})]_2\}\cdot 14H_2O$ (1): A mixture of $Na_8[Ta_6O_{19}]\cdot 24.5H_2O$ (Ta_6) (0.055 g), $CrCl_3\cdot 6H_2O$ (0.025 g) and CuSCN (0.053 g) was added into 4 mL of $C_4H_8O_2/H_2O$ (1:1) ($C_4H_8O_2 = 1,4$ -dioxane). Further, 0.10 mL en (en=ethylenediamine) was added to this solution and stirred for an hour, and then transferred into a Teflon-lined stainless steel autoclave (25 mL) and kept at 100 °C for 3 days, finally cooled to room-temperature. After washed by ethanol, violet bar crystals were obtained. Yield: 15 mg (25.8% based on Ta_6). Elemental analysis calcd (found %) for 1: C, 8.55 (6.80); H, 3.91 (3.09); N, 9.97 (7.93).

Synthesis of H₂[Cu(enMe)₂(H₂O)₂][Na₂(H₂O)₁₀]₂{[Cu(enMe)₂]₂[Cu(enMe)(Ta₆O₁₉)]₂·26H₂O (3): A mixture of Ta₆ (0.090 g), CrCl₃·6H₂O (0.037 g) and CuSCN (0.057 g) was added into 4 mL of C₄H₈O₂/H₂O (1:1). Further, 0.10 mL enMe (enMe= 1,2-Diaminopropane) was added to this solution and stirred for an hour, and then transferred into a Teflon-lined stainless steel autoclave (25 mL) and kept at 100 °C for 3 days, finally cooled to room-temperature. After washed by ethanol, violet slice crystals were obtained. Yield: 15 mg (15.3% based on Ta₆). Elemental analysis calcd (found %) for **3**: C, 6.22 (5.47); H, 3.83 (4.13); N, 4.83(6.38).

Synthesis of H₂[Cu(en)₂(H₂O)₂]{[Cu(en)₂]₂[Na₂(H₂O)₇]₂[Cu(en)(Ta₆O₁₉)]₂}·10H₂O (5): A mixture of Ta₆ (0.050 g), CrCl₃·6H₂O (0.035 g), Na₂MoO₄·2H₂O (0.040) and CuSCN (0.030 g) was added into 4 mL of C₄H₈O₂/H₂O (1:1). Further, 0.10 mL en was added to this solution and stirred for an hour, and then transferred into a Teflon-lined stainless steel autoclave (25 mL) and kept at 100 °C for 3 days, finally cooled to room-temperature. After washed by ethanol, violet bar crystals were obtained. Yield: 20 mg (41.1% based on Ta₆). Elemental analysis calcd (found %) for **5**: C, 4.64 (4.64); H, 2.88 (3.34); N, 5.41 (5.43).

Synthesis of $H_2[Na_2(H_2O)_{10}]_2[Cu(en)_2]_2\{[Cu(en)_2][Cu(en)(Ta_6O_{19})]_2\}\cdot 8H_2O$ (6): A mixture of Ta_6 (0.130 g), $CrCl_3\cdot 6H_2O$ (0.021 g), $NaBO_3\cdot 4H_2O$ (0.035) and CuSCN (0.050 g) was added into 4 mL of $NaCO_3/NaHCO_3$ (0.5M, PH=10.5) buffer solution. Further, 0.10 mL en was added to this solution and stirred for an hour, and then transferred into a Teflon-lined stainless steel autoclave (25 mL) and kept at 100 °C for 3 days, finally cooled to room-temperature. After washed by ethanol,

violet bar crystals were obtained. Yield: 40 mg (29.6% based on Ta_6). Elemental analysis calcd (found %) for **6**: C, 4.60 (5.83); H, 2.94 (3.74); N, 5.36 (6.75).

2. Structural transformations triggered by water

Synthesis of $H_2\{[Cu(en)_2]_3[Cu(en)(H_2O)_2Cu(en)(Ta_6O_{19})]_2\}$ ·30 H_2O (2): Violet bar of crystalline sample 1 was removed from the mother liquor and washed with ethanol. And then, the sample was dissolved in 2 ml water at room temperature. After more than one day, a spot of violet block crystals of 2 were obtained.

Synthesis of $H_4[Na_4(H_2O)_{18}]\{[Cu(enMe)_2]_2[Cu(enMe)(Ta_6O_{19})]_2\}\cdot 10H_2O$ (4): Violet slice of crystalline sample 3 was removed from the mother liquor and washed with ethanol. And then, the sample was dissolved in 2 ml water at room temperature. One week later, violet slice crystals of mixture 3 and 4 were obtained.

3. Synthetic Discussion

It has been known that the synthesis of novel polyoxotantalates (POTas) remains an enormous challenge in polyoxometalate chemistry. In this work, the successful syntheses of the series of novel transition-metal-bridged inorganic-organic hybrid POTas are attributed to the following considerations: 1) According to literature (J. Struct. Chem. 2011, 52, 1012–1017), a kind of soluble tantalate salt $Na_8[Ta_6O_{19}]\cdot 24.5H_2O$ was prepared as a precursor by using easily available but insoluble oxide Ta₂O₅ as raw material. 2) Owing to strong alkalinity of initial reaction solutions, we chose copper to react with $Na_8[Ta_6O_{19}] \cdot 24.5H_2O$. Different from most 3d transition-metal cations, Cu ion is an amphoteric cation which can dissolve in both acidic and basic solutions. Additionally, Cu-en/enMe complexes can not only act as bridges in linking polyoxotantalate clusters into extended structures, but also server as flexible charge compensation cations to meet the charge balance for growing bulk crystals. 3) The Cu^I salt is indispensable for the formation of these extended POTas. Parallel experiments showed that no crystals could be obtained if Cu¹ species were removed from the reactions system. Parallel experiments showed that if the Cu¹-containing reactant is replaced by Cu¹¹-containing reactant, nothing could be got but precipitates. 4) $CrCl_3$ is the other important additive for the formation these extended POTas, though it is not present in the final products. During our exploration, we also tried to replace Cr³⁺ with different metals (e.g., Cs⁺, Ca²⁺, Ba²⁺, Mn²⁺, Fe²⁺, Fe³⁺, Co²⁺, Ni²⁺,

Ln³⁺ Sc³⁺, Ti⁴⁺, Zr⁴⁺) for making heterometallic POTas, but we are fruitless. 5) With the aim of increasing solubility and reaction activity of reactants, we adopted a mixed solvents strategy and thus systematically explored the combination of different solvents with water, such as dichloromethane, acetonitrile, acetone, ethanol, benzene, methylbenzene, N,N-Dimethylformamide, and N,N-Dimethylacetamide, etc. Interestingly, only the combination of 1,4-dioxane (boiling point: 101 °C) with water (boiling point: 100 °C), which are similar in boiling point, is likely to greatly increase solubility and reaction activity of reactants.

4. Characterization Methods

Single-crystal structure analysis: Crystal data were collected on a Bruker APEX II diffractometer at 175 K equipped with a fine focus, 2.0 kW sealed tube X-ray source (MoK radiatioVBn, λ = 0.71073 Å) operating at 50 kV and 30 mA. Structures were solved by direct methods followed by successive difference Fourier methods. Computations were performed using SHELXTL 2013 and final full-matrix refinements were against F^2 . All non-hydrogen atoms were refined anisotropically. Due to porous structure and electron density of heavy atom, the guests within structure are highly disordered and thus couldn't be exactly determined, which are finally evaluated by the results of TGA analysis. The contribution of these disordered solvent molecules to the overall intensity data of all structures were treated using the SQUEEZE method in PLATON. Crystallographic data for compounds 1-6 are given in Table S1. CCDC: 1866075-1866080 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data request/cif</u>.

Proton Conduction measurement: The dependence of the proton conduction on the relative humidity and temperature of sample were performed on Zennium/IM6 impedance analyzer over the frequency ranging from 0.1Hz to 5MHz with an applied voltage of 10 mV. The relative humidity and temperature was controlled by a STIKCorp CIHI-150BS3 incubator. The test sample was pressed to form a cylindrical pellet of crystalline powder sample (~1mm thickness × 5mm diameter) coated with C-pressed electrodes, and both sides of sample pellet were attached to two silver electrodes. The self-made device containing cylindrical pellet was placed in constant

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temperature & humidity incubator before testing in a temperature range from 25 °C to 75 °C and relative humidity between 55% -98%.

Others: Powder XRD patterns were obtained using a Rigaku Ultima IV diffractometer with Cu $K\alpha$ radiation (λ = 1.54056 Å). Elemental analyses (C, H and N) were performed by using a Vario EL III elemental analyzer. IR spectra were recorded on Nicolet iS50 FT-IR spectrometer in the range of 4000-450 cm⁻¹. Thermal analyses were performed from 30 °C to 600 °C in a dynamic air atmosphere with a heating rate of 10 °C/min, using a NETZSCH STA 449C thermal analyzer.

Section S2 Additional Tables

Compounds	1	2	3	4	5	6
Empirical formula	$H_{130}C_{24}N_{24}O_{54}$ Cu_7Ta_{12}	$H_{150}C_{20}N_{20}O_{72}$ Cu_7Ta_{12}	$H_{176}C_{24}N_{16}O_{85}$ $Na_4Cu_5Ta_{12}$	$H_{120}C_{18}N_{12}O_{66}$ $Na_4Cu_4Ta_{12}$	$H_{118}C_{16}N_{16}O_{64}$ $Na_4Cu_5Ta_{12}$	$H_{122}C_{16}N_{16}O_{66}$ $Na_4Cu_5Ta_{12}$
formula weight	4235.61	4439.69	4630.77	4078.70	4140.24	4176.27
crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic
space group	P21/c	C2/m	<i>P</i> -1	<i>P</i> -1	C2/m	<i>P</i> -1
a (Å)	10.4000(12)	27.114(5)	13.8976(9)	12.9552(16)	15.6559(11)	13.1771(15)
b (Å)	14.4623(17)	27.532(5)	14.5477(9)	15.3682(19)	19.7079(14)	14.1882(15)
c (Å)	30.300(4)	18.723(4)	15.7824(10)	16.483(2)	14.9410(10)	15.5444(17)
α (°)	90	90	79.5988(15)	65.831(2)	90	92.667(2)
в (°)	97.551(2)	129.823(2)	66.3800(13)	84.959(2)	94.2070(10)	100.540(2)
γ (°)	90	90	67.5801(13)	66.770(2)	90	110.664(2)
volume (ų), Z	4517.8(9), 2	10735(3), 4	2701.1(3), 1	2740.7(6), 1	4597.5(6), 2	2653.8(5), 1
Temperature (K)	296	296	296	296	296	296
μ (mm ⁻¹)	16.168	13.602	13.168	12.772	15.453	13.397
θ range (°)	1.563 - 25.052	2.048 - 25.006	1.703 - 23.500	1.580 - 24.000	1.664 - 23.999	1.691 - 25.130
reflns collected / unique	15327 / 7928	23018 / 9596	14263 / 7691	15629 / 8423	12875 / 3674	18608 / 9320
restraints / parameters	66 / 547	54 / 508	366 / 571	377 / 487	145 / 273	49 / 550
completeness / %	98.9%	99.1%	96.1%	98.0%	98.3%	98.2%
GOF on F ²	0.999	0.998	1.091	1.008	1.078	1.078
R _{int}	0.0594	0.0509	0.393	0.0368	0.0341	0.0314
$R_1, wR_2 [I > 2\sigma(I)]$	$R_1 = 0.0520$	$R_1 = 0.0430$	$R_1 = 0.0490$	$R_1 = 0.0483$	$R_1 = 0.0301$	$R_1 = 0.0489$

Table S1 Crystallographic data of 1-6

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	$wR_2 = 0.0999$	$wR_2 = 0.0932$	$wR_2 = 0.1253$	$wR_2 = 0.1366$	$wR_2 = 0.0797$	$wR_2 = 0.1373$	
R ₁ , wR ₂ (all data)	$R_1 = 0.0995$ $wR_2 = 0.1171$	$R_1 = 0.0786$ $wR_2 = 0.1022$	$R_1 = 0.0717$ $wR_2 = 0.1366$	$R_1 = 0.0767$ $wR_2 = 0.1483$	$R_1 = 0.0349$ $wR_2 = 0.0817$	$R_1 = 0.0691$ $wR_2 = 0.01463$	
$R_1^a = \sum F_o - F_c \sum F_o . \ wR_2 = \sum w(F_o^2 - F_c^2)^2 \sum w(F_o^2)^2 ^{1/2}$							

Table S2 Comparison of the proton conductivity of some POM-based conducting materials.

Compounds	Conductivity [S cm ⁻¹]	Condition (Temp., RH)	Ref
$H_{14}[Na_6(H_2O)_{12}]_4[K_{42}Ge_8W_{72}O_{272}(H_2O)_{60}]$ ·solvent	$6.80 \times 10^{-2} \mathrm{S cm^{-1}}$	85 °C, 98% RH	S1
$K_8Na_3Li_5\{[Na(NO_3)(H_2O)]_4[AI_{16}(OH)_{24}(H_2O)_8(P_8W_{48}O_{184})]\}\cdot 66H_2O$	$4.50 \times 10^{-2} \mathrm{S cm^{-1}}$	85 °C, 70% RH	S2
$Na_{5}[H_{7}{N(CH_{2}PO_{3})_{3}}Mo_{6}O_{16}(OH)(H_{2}O)_{4}]_{4}$ ·18 $H_{2}O$	$2.55 \times 10^{-2} \mathrm{S cm^{-1}}$	100 °C, 98% RH	S3
$[P_2Mo_5O_{23}][C_7H_7N_2]_6$ ·H ₂ O	$1.91 \times 10^{-2} \text{ S cm}^{-1}$	50 °C, 98% RH	S4
$[La_3(H_2O)_{22}][P_2W_{15}Ta_3O_{62}]\cdot 16H_2O$	$1.26 \times 10^{-2} \mathrm{S} \mathrm{cm}^{-1}$	95 °C, 98% RH	S5
$[(CH_3)_4N]_{1.5}K_{5.5}Na_2[I_3 \subset (MoV_2O_2S_2)_8(Se^{IV}O_3)_8(OH)_8] \cdot 25H_2O$	$1.20 \times 10^{-2} \mathrm{S} \mathrm{cm}^{-1}$	55 °C, 97% RH	S6
$H_{2}[Cu(en)_{2}(H_{2}O)_{2}]{[Cu(en)_{2}]_{4}[Cu(en)(Ta_{6}O_{19})]_{2}\cdot14H_{2}O$	1.04× 10 ⁻² S cm ⁻¹	75 °C, 98% RH	This work
$\{Na_{7}[(nBu)_{4}N]_{17}\}[Zn(P_{3}Mo_{6}O_{29})_{2}]_{2}$	$1.04 \times 10^{-2} \mathrm{S} \mathrm{cm}^{-1}$	80 °C, 75% RH	S7
$Na_8K_4(H_2pip)_8H_{21}[\{Cu(pip)_2\}_2\{La_{29}Ge_{10}W_{106}O_{406}(OH)_4(H_2O)_{28}\}]\cdot 127H_2O$	$5.30 \times 10^{-3} \mathrm{S} \mathrm{cm}^{-1}$	85 °C, 98% RH	S5
$[Sm(H_2O)_5(CO_2CH_2NH_3)_2][Al(OH)_6MO_6O_{18}]\cdot 10H_2O$	$4.53 \times 10^{-3} \mathrm{S} \mathrm{cm}^{-1}$	80 °C, 95% RH	S8
[H ₃ (3-PyBim) ₂][PMo ₁₂ O ₄₀] [.] 3.5H ₂ O [.] CH ₃ CN [.] CH ₃ OH	$3.34 \times 10^{-3} \mathrm{S} \mathrm{cm}^{-1}$	100 °C, 98% RH	S9
$\begin{split} Na_{16}(NH_4)_{10}H_8\{[W_{14}Ce^{IV}_6O_{61}]([W_3Bi_6Ce^{III}_3(H_2O)_3O_{14}][BiW_9O_{33}]_3)_2\}\cdotca38H_2\\ O \end{split}$	$2.40 \times 10^{-3} \mathrm{S} \mathrm{cm}^{-1}$	25 °C, 98% RH	S10
[Co(bpz)(Hbpz)][Co(SO ₄) _{0.5} (H ₂ O) ₂ (bpz)] ₄ [PMo ^{VI} ₈ Mo ^V ₄ V ^{IV} ₄ O ₄₂]·13H ₂ O	$1.50 \times 10^{-3} \mathrm{S} \mathrm{cm}^{-1}$	75 °C, 98% RH	S11
[H ₃ (3-PyBim) ₂][PMo ₁₂ O ₄₀]·4H ₂ O·CH ₃ CN	$1.36 \times 10^{-3} \mathrm{S} \mathrm{cm}^{-1}$	100 °C, 98% RH	S9
${H[Ni(Hbpdc)(H_2O)_2]_2[PW_{12}O_{40}] \cdot 8H_2O}n$	$1.35 \times 10^{-3} \mathrm{S} \mathrm{cm}^{-1}$	100 °C, 98% RH	S12
[M(H ₂ O) ₈][H(H ₂ O) ₂₋₃](HINO) ₄ [PXO ₄₀] (M=Zn, Mn, Cu; X=W, Mo)	$1.30 \times 10^{-3} \mathrm{S \ cm^{-1}}$	100 °C, 98% RH	S13

Section S3 Additional Figures



Figure S1 View of 2D layer built by the dimers ${CuTa_6}_2$ and Cu3 complexes in compound 1



Figure S2 View of 1D chain built by the dimers ${CuTa_6}_2$ and Cu1 complexes in compound 1



Figure S3 View of the 1D channels of framework **1** filled with $[Cu(en)_2(H_2O)_2]^{2+}$ complexes and lattice water molecules.







Figure S5 Structures of the 1D chain of a) compound 5; b) compound 6



Section S4 Characterization Spectra of Compounds 1-6



PXRD patterns show that as-synthesized samples **1** to **3** and samples **5** to **6** are pure phases. While the pure phase of sample **4** cannot be obtained since only part of compound **3** could transform into compound **4**. As the obtained product contains mixed phases, the following characterization spectra (IR, TG) for compound **4** are not provided.



Figure S7 Thermodiffractograms of the as-synthesized sample 3.



Figure S8 IR spectra of as-synthesized samples

In the IR spectra, the CH₂ and NH₂ stretching bands are observed at \tilde{v} = 2900 to 3200, and their bending bands are observed at \tilde{v} = 1100 to 1600 cm⁻¹. These signals confirm the presence of organic amine species in the products. The peaks at \tilde{v} = 1060-450 cm⁻¹ are assigned to the $v(Ta-O_t)$ and $v(Ta-O_b-M)$ stretching vibrations. The peak at \tilde{v} = 3400 cm⁻¹ is assigned to the water molecules.





The guests in the formulas include water molecules. One of that is the water ligands linking to alkali metal ions or copper ions, which are determined by single-crystal X-ray diffraction, and the other ones are free water guests. It is hard to confirm the exact amount of isolated guests. So, TG analyses were performed to roughly calculate the amount of guests in compounds. As shown in Figure S9, The TG curves of compounds indicate that the first weight loss stage occurring from RT to 200 °C should be attributed to the loss of free water guests. Based on the first weight losses of ca. 7.8% for **1**, 15.2% for **2**, 10.1% for **3**, 5.6% for **5** and 3.7% for **6**, it can be found that there are about 10, 30, 26, 10 and 8 water guests, respectively.





The UV diffuse spectra of compounds show three absorption bands in the range 200 to 800 nm. The absorption peak around 270 nm attribute to oxide-to-metal ($O \rightarrow Ta$) charge transfer (OMCT) transitions.^{S14} There are two characteristic absorptions at in the range of 350 and 700 nm, which can be ascribed to the ligand-to-metal charge-transfer and the d–d transition of $[Cu(en)_2(H_2O)]^{2+}/[Cu(enMe)_2(H_2O)]^{2+}$ complexes.^{S15-S16}



Figure S11 Simulated and experimental PXRD patterns of **1** after proton conductivity test, showing that the framework of **1** is intact during the measurement process.

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