

An unprecedented vanadoniobate cluster with 'trans-vanadium' bicapped Keggin-type $\{VNb_{12}O_{40}(VO)_2\}$

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Materials

All reagents except $K_7HNb_6O_{19} \cdot 13H_2O$ ¹ were purchased from commercial sources and used without further purification. IR spectra were recorded on a Nicolet 170SXFT/IR spectrometer using KBr pellets in the range of 4000-400 cm^{-1} . Powder X-ray Diffraction (PXRD) was performed on SHIMADZU XRD-6000 X-ray diffractometer equipped with graphite monochromatized Cu K α radiation ($\lambda = 0.154056$ nm). TGA was performed on a TGA Q50 instrument under nitrogen atmosphere with a heating rate of 10°C/min. X-ray photoelectron spectrum (XPS) analysis were performed on a VG Escalabmkll spectrometer (UK) with a Al K α ($h\nu = 1486.7$ eV) achromatic X-ray source. The UV spectra were obtained on a TU-1901 spectrophotometer in the range 190-400nm. The Visible spectrum of **1a** was carried out on UV-3600 spectrophotometer in the range of 400-1000nm.

Syntheses

After further investigation on the experimental conditions, it was found that the organic amine used in the reaction play a key role in the formation of **1a** and **1b**. We tried to replace en with 1,2-dap and 1,3-dap for **1a** and substitute en/2,2'-bipy with 1,2-dap/2,2'-bipy, 1,3-dap/2,2'-bipy, en/1,10-phen, 1,2-dap /1,10-phen and 1,3-dap/1,10-phen (dap=diaminopropane, 1,10-phen = 1,10-phenanthroline) for **1b** under the same conditions, but no isostructural compounds were obtained in both cases.

X-ray crystallography

Crystal data for compounds **1a-1b** were collected at 296(2)K on Bruker APEX-II CCD detector with graphite monochromatic Mo K α radiation ($\lambda=0.71073$ Å). Both structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL-97 program.²⁻³ Part of active hydrogen atoms in compound **1a** are not picked out in the refinement for the poor crystal quality, as are O46,O47,O48, O49, O53, O57, O60, O54, O55, O56, O59, O55',O59', O62, N18, N19, N19'. In compound **1b**, the H atoms attached to carbon and nitrogen atoms are placed in calculated positions and are refined with a riding model. Other active hydrogen atoms of water molecule are not incorporated in the refinement for the weak diffraction intensity. $\{Cu_6(en)_2\}^{2+}$ fragment in compound **1a** is in disorder. Cu6, N19, N19', C17, C18, N17 have the occupancy of 0.5. Cu6 and its symmetric generated atoms of Cu6A(symmetry code: A, -x,y,1/2-z) can't concurrence. When Cu6 is present, its two en molecules are N19-C19-C19A-N19'A and N17-C18-C17-N18, respectively; The other case is that Cu6A is present, its corresponding en molecules are N19A-C19A-C19-N19' and N17A-C18A-C17A-N18, respectively. The crystal data and structure refinement for two compounds were summarized in Table S2. Selected bond lengths (Å) and angles (°) were listed in Table S3.

Table S1. BVS results for compounds **1a-1b**.

| | V1 | V2 | V3 |
|--------------------|------|------|------|
| Compound 1a | 5.24 | 4.26 | 4.35 |
| Compound 1b | 5.64 | 5.22 | 5.08 |

Table S2. Crystallographic Data for Compounds **1a-1b**.

| Compounds | 1a | 1b |
|---|--|---|
| Formula | C ₂₂ H ₁₂₄ N ₂₂ Cu _{5.5} Nb ₁₂ V ₃ O ₆₀ | C ₃₄ H ₉₀ N ₁₈ Cu _{4.5} Nb ₁₂ V ₃ O ₅₁ |
| <i>M_r</i> | 3274.64 | 3120.91 |
| Crystal system | Monoclinic | Triclinic |
| Space group | <i>P2/c</i> | <i>P</i> -1 |
| Temperature | 296(2) K | 296(2) K |
| <i>a</i> (Å) | 25.6242(17) | 12.8610(11) |
| <i>b</i> (Å) | 14.3236(9) | 13.3752(11) |
| <i>c</i> (Å) | 25.0786(16) | 27.481(2) |
| <i>α</i> (deg) | 90 | 80.9320(10) |
| <i>β</i> (deg) | 103.0880(10) | 80.0650(10) |
| <i>γ</i> (deg) | 90 | 64.3310(10) |
| <i>V</i> (Å ³) | 8965.5(10) | 4178.5(6) |
| <i>Z</i> | 4 | 2 |
| <i>D</i> _{calc.} (g cm ⁻³) | 2.426 | 2.480 |
| <i>F</i> (000) | 6442 | 3039 |
| <i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] | 0.0394 | 0.0622 |
| <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] | 0.1036 | 0.2038 |
| <i>R</i> ₁ (all data) | 0.044 | 0.0882 |
| <i>wR</i> ₂ (all data) | 0.1079 | 0.2928 |
| GOOF | 1.096 | 1.139 |

Table S3. Selected bond distances (Å) and angles (°) of **1a-1b**.

| 1a | | | |
|-------------|-----------|-------------|----------|
| Nb(1)-O(1) | 1.780(4) | Nb(1)-O(14) | 2.095(4) |
| Nb(1)-O(17) | 2.089(4) | Nb(1)-O(23) | 1.899(4) |
| Nb(1)-O(33) | 1.914(4) | Nb(1)-O(37) | 2.443(4) |
| Nb(2)-O(2) | 1.766(4) | Nb(2)-O(21) | 1.947(4) |
| Nb(2)-O(22) | 1.971(4) | Nb(2)-O(24) | 2.018(4) |
| Nb(2)-O(30) | 1.995(4) | Nb(2)-O(39) | 2.428(4) |
| Nb(3)-O(3) | 1.771(4) | Nb(3)-O(13) | 2.116(4) |
| Nb(3)-O(17) | 2.081(4) | Nb(3)-O(18) | 1.902(4) |
| Nb(3)-O(32) | 1.911(45) | Nb(3)-O(38) | 2.438(4) |
| Nb(4)-O(4) | 1.743(4) | Nb(4)-O(18) | 2.009(4) |
| Nb(4)-O(23) | 1.969(4) | Nb(4)-O(31) | 2.018(4) |
| Nb(4)-O(36) | 1.988(4) | Nb(4)-O(40) | 2.470(4) |
| Nb(5)-O(5) | 1.745(4) | Nb(5)-O(19) | 1.968(4) |
| Nb(5)-O(27) | 2.002(4) | Nb(5)-O(33) | 2.037(4) |
| Nb(5)-O(35) | 1.974(4) | Nb(5)-O(37) | 2.458(4) |

| | | | |
|------------------|----------|------------------|------------|
| Nb(6)-O(6) | 1.773(4) | Nb(6)-O(19) | 1.915(4) |
| Nb(6)-O(20) | 2.082(4) | Nb(6)-O(34) | 2.085(4) |
| Nb(6)-O(36) | 1.914(4) | Nb(6)-O(40) | 2.469(4) |
| Nb(7)-O(7) | 1.767(4) | Nb(7)-O(15) | 2.095(4) |
| Nb(7)-O(25) | 1.906(4) | Nb(7)-O(29) | 2.072(4) |
| Nb(7)-O(30) | 1.928(4) | Nb(7)-O(39) | 2.457(4) |
| Nb(8)-O(8) | 1.764(4) | Nb(8)-O(14) | 2.086(4) |
| Nb(8)-O(16) | 2.070(4) | Nb(8)-O(22) | 1.908(4) |
| Nb(8)-O(27) | 1.921(4) | Nb(8)-O(37) | 2.465(4) |
| Nb(9)-O(9) | 1.771(4) | Nb(9)-O(13) | 2.071(4) |
| Nb(9)-O(16) | 2.075(4) | Nb(9)-O(21) | 1.912(4) |
| Nb(9)-O(28) | 1.934(4) | Nb(9)-O(38) | 2.435(4) |
| Nb(10)-O(10) | 1.761(4) | Nb(10)-O(20) | 2.087(4) |
| Nb(10)-O(26) | 1.911(4) | Nb(10)-O(29) | 2.080(4) |
| Nb(10)-O(31) | 1.934(4) | Nb(10)-O(40) | 2.425(4) |
| Nb(11)-O(11) | 1.761(4) | Nb(11)-O(15) | 2.085(4) |
| Nb(11)-O(24) | 1.931(4) | Nb(11)-O(34) | 2.095(4) |
| Nb(11)-O(35) | 1.901(4) | Nb(11)-O(39) | 2.424(4) |
| Nb(12)-O(12) | 1.762(5) | Nb(12)-O(25) | 1.990(4) |
| Nb(12)-O(26) | 1.973(4) | Nb(12)-O(28) | 2.004(4) |
| Nb(12)-O(32) | 1.997(5) | Nb(12)-O(38) | 2.453(4) |
| V(1)-O(37) | 1.701(4) | V(1)-O(38) | 1.701(4) |
| V(1)-O(39) | 1.713(4) | V(1)-O(40) | 1.696(4) |
| V(2)-O(15) | 2.004(4) | V(2)-O(20) | 2.000(4) |
| V(2)-O(29) | 1.915(4) | V(2)-O(34) | 1.917(4) |
| V(2)-O(41) | 1.622(5) | V(3)-O(13) | 1.993(4) |
| V(3)-O(14) | 1.988(4) | V(3)-O(16) | 1.911(4) |
| V(3)-O(17) | 1.896(4) | V(3)-O(42) | 1.622(4) |
| Cu(1)-O(1) | 2.350(5) | Cu(1)-N(1) | 2.008(7) |
| Cu(1)-N(2) | 2.000(7) | Cu(1)-N(3) | 2.007(7) |
| Cu(1)-N(4) | 1.993(8) | Cu(2)-N(5) | 2.000(7) |
| Cu(2)-N(6) | 2.012(9) | Cu(2)-N(7) | 2.003(8) |
| Cu(2)-N(8) | 2.003(7) | Cu(2)-O(45) | 2.356(8) |
| O(37)-V(1)-O(40) | 108.1(2) | O(37)-V(1)-O(38) | 110.6(2) |
| O(40)-V(1)-O(38) | 108.9(2) | O(37)-V(1)-O(39) | 108.91(19) |
| O(40)-V(1)-O(39) | 110.9(2) | O(38)-V(1)-O(39) | 109.4(2) |

1b

| | | | |
|-------------|----------|-------------|----------|
| Nb(1)-O(1) | 1.799(7) | Nb(1)-O(20) | 1.882(7) |
| Nb(1)-O(26) | 2.112(7) | Nb(1)-O(31) | 2.131(7) |
| Nb(1)-O(32) | 1.858(7) | Nb(1)-O(37) | 2.397(7) |
| Nb(2)-O(2) | 1.738(7) | Nb(2)-O(18) | 1.895(7) |
| Nb(2)-O(22) | 2.133(7) | Nb(2)-O(27) | 1.918(7) |
| Nb(2)-O(34) | 2.128(6) | Nb(2)-O(38) | 2.486(6) |
| Nb(3)-O(3) | 1.754(7) | Nb(3)-O(14) | 1.895(7) |

| | | | |
|------------------|-----------|------------------|-----------|
| Nb(3)-O(22) | 2.112(7) | Nb(3)-O(24) | 1.888(7) |
| Nb(3)-O(35) | 2.107(6) | Nb(3)-O(38) | 2.446(7) |
| Nb(4)-O(4) | 1.768(7) | Nb(4)-O(21) | 1.881(7) |
| Nb(4)-O(23) | 1.882(7) | Nb(4)-O(33) | 2.127(7) |
| Nb(4)-O(35) | 2.131(6) | Nb(4)-O(39) | 2.494(7) |
| Nb(5)-O(5) | 1.751(7) | Nb(5)-O(25) | 1.899(7) |
| Nb(5)-O(29) | 1.907(7) | Nb(5)-O(33) | 2.107(7) |
| Nb(5)-O(34) | 2.154(6) | Nb(5)-O(39) | 2.440(7) |
| Nb(6)-O(6) | 1.733(7) | Nb(6)-O(14) | 1.967(7) |
| Nb(6)-O(16) | 1.968(6) | Nb(6)-O(18) | 2.001(7) |
| Nb(6)-O(32) | 2.005(7) | Nb(6)-O(38) | 2.528(7) |
| Nb(7)-O(7) | 1.753(7) | Nb(7)-O(13) | 1.875(7) |
| Nb(7)-O(19) | 2.139(7) | Nb(7)-O(30) | 1.903(7) |
| Nb(7)-O(31) | 2.135(7) | Nb(7)-O(37) | 2.456(7) |
| Nb(8)-O(8) | 1.745(7) | Nb(8)-O(15) | 1.989(7) |
| Nb(8)-O(17) | 1.970(7) | Nb(8)-O(23) | 1.968(7) |
| Nb(8)-O(24) | 1.971(7) | Nb(8)-O(40) | 2.486(7) |
| Nb(9)-O(9) | 1.754(7) | Nb(9)-O(15) | 1.918(7) |
| Nb(9)-O(16) | 1.902(6) | Nb(9)-O(26) | 2.136(7) |
| Nb(9)-O(36) | 2.150(7) | Nb(9)-O(40) | 2.470(6) |
| Nb(10)-O(10) | 1.762(7) | Nb(10)-O(13) | 2.042(7) |
| Nb(10)-O(20) | 1.985(7) | Nb(10)-O(27) | 1.936(7) |
| Nb(10)-O(29) | 1.972(7) | Nb(10)-O(37) | 2.510(7) |
| Nb(11)-O(11) | 1.759(7) | Nb(11)-O(17) | 1.919(7) |
| Nb(11)-O(19) | 2.121(7) | Nb(11)-O(28) | 2.004(7) |
| Nb(11)-O(36) | 2.122(7) | Nb(11)-O(40) | 2.464(7) |
| Nb(12)-O(12) | 1.738(6) | Nb(12)-O(21) | 2.005(7) |
| Nb(12)-O(25) | 2.004(7) | Nb(12)-O(28) | 2.004(7) |
| Nb(12)-O(30) | 1.961(7) | Nb(12)-O(39) | 2.482(7) |
| V(1)-O(37) | 1.688(7) | V(1)-O(38) | 1.657(7) |
| V(1)-O(39) | 1.678(7) | V(1)-O(40) | 1.680(7) |
| V(2)-O(19) | 1.847(7) | V(2)-O(26) | 1.848(7) |
| V(2)-O(31) | 1.883(7) | V(2)-O(36) | 1.912(7) |
| V(2)-O(41) | 1.565(9) | V(3)-O(22) | 1.940(7) |
| V(3)-O(33) | 1.947(7) | V(3)-O(34) | 1.827(7) |
| V(3)-O(35) | 1.844(7) | V(3)-O(42) | 1.569(8) |
| Cu(1)-O(1) | 1.917(7) | Cu(1)-N(1) | 2.155(10) |
| Cu(1)-N(2) | 1.966(12) | Cu(1)-N(3) | 2.030(10) |
| Cu(1)-N(4) | 1.968(12) | Cu(2)-O(2) | 2.383(8) |
| Cu(2)-N(5) | 1.967(11) | Cu(2)-N(6) | 1.990(11) |
| Cu(2)-N(7) | 2.067(10) | Cu(2)-N(8) | 2.040(10) |
| O(38)-V(1)-O(40) | 109.6(3) | O(38)-V(1)-O(39) | 111.2(3) |
| O(40)-V(1)-O(39) | 108.5(3) | O(38)-V(1)-O(37) | 109.5(3) |
| O(40)-V(1)-O(37) | 110.5(3) | O(39)-V(1)-O(37) | 107.5(3) |

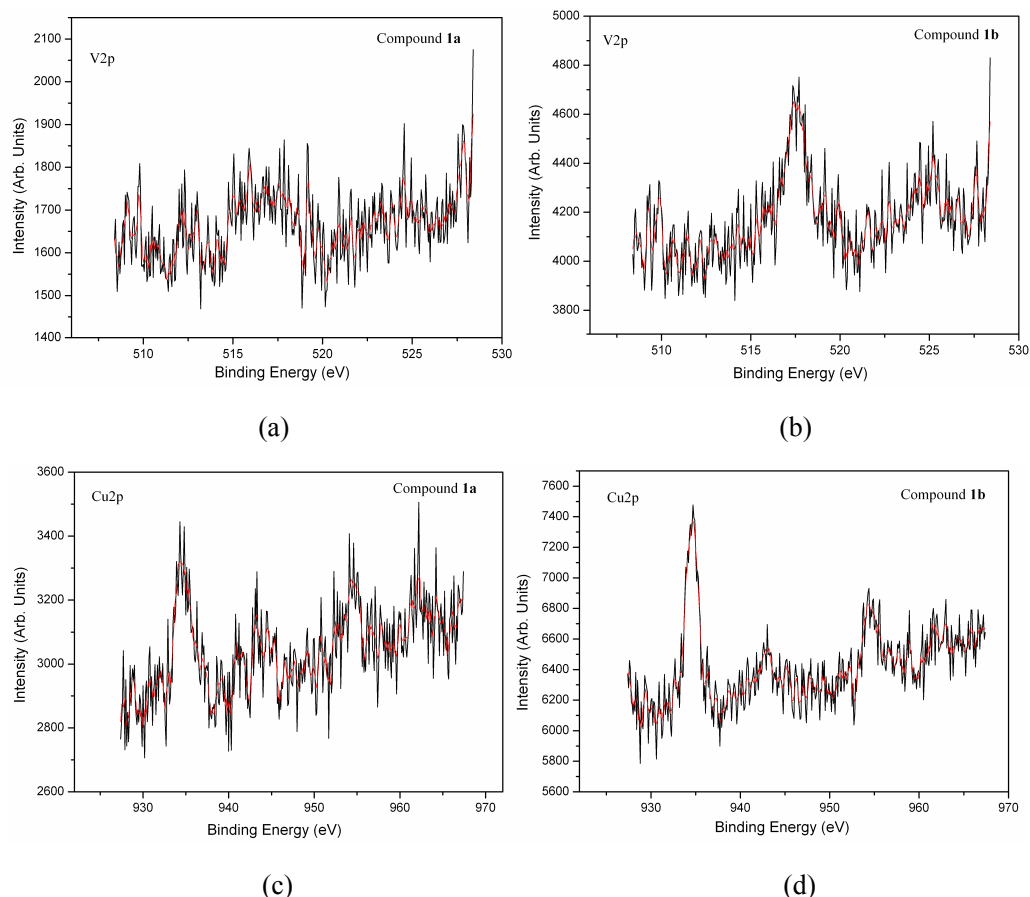


Fig. S1. (a) The XPS spectrum of **1a** gives two peaks at 517.8 and 515.9 eV, which should be attributed to $V^{5+}2p_{3/2}$ and $V^{4+}2p_{3/2}$,⁴⁻⁵ respectively; (b) The XPS spectrum of **1b** gives one peak at 517.4 eV, as can be ascribed to $V^{5+}2p_{3/2}$;⁵ (c)/(d) The XPS spectra of **1a–1b** present two peaks: 934.3 and 954.3 eV for **1a**, 934.6 and 954.2 eV for **1b**, as can be ascribed to $Cu2p_{3/2}$ and $Cu2p_{1/2}$,⁶⁻⁷ respectively.

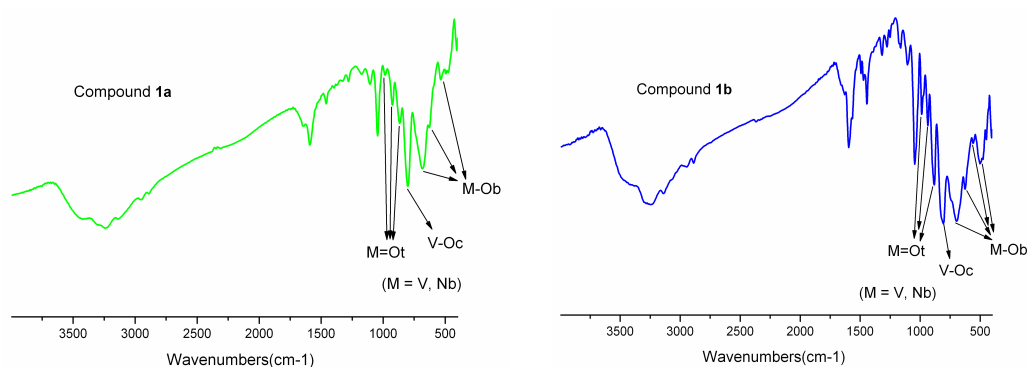


Fig. S2. The IR spectra of **1a** and **1b** display similar characteristic vibration patterns resulting from the bicapped Keggin structure in the region of $400\text{--}1000\text{cm}^{-1}$. There are three types of oxygen atoms: O_t (O_t = terminal oxygen atom, bonded to one V or Nb atom), O_b (O_b = bridging oxygen atom, bonded to two Nb atoms or bonded to one V atom and one Nb atom) and O_c (O_c = central oxygen atom, bonded to three Nb atoms and one V atom). The terminal $M = O_t$ ($M = V$,

Nb) vibrations appear at 987 , 925cm^{-1} and 869cm^{-1} for **1a**, and at 987 , 933 and 881cm^{-1} for **1b**, respectively.⁸⁻¹⁰ The characteristic peaks at 686 , 628 and 538cm^{-1} (**1a**) and at 696 , 624 , 557 and 501cm^{-1} (**1b**) are attributed to the bridging $\text{M-O}_b\text{-M}$ vibrations, respectively.^{9,10} Bands at 804cm^{-1} in **1a** and 806cm^{-1} in **1b** are assigned to V-O_c vibration, respectively.¹¹ The characteristic absorption bands of organic groups occur at $1045\text{--}1592\text{cm}^{-1}$ and $1045\text{--}1596\text{cm}^{-1}$ for **1a** and **1b**, respectively. The broad band at around 3245cm^{-1} (**1a**) and 3243cm^{-1} (**1b**) is ascribed to the O-H vibrations from the water molecules.

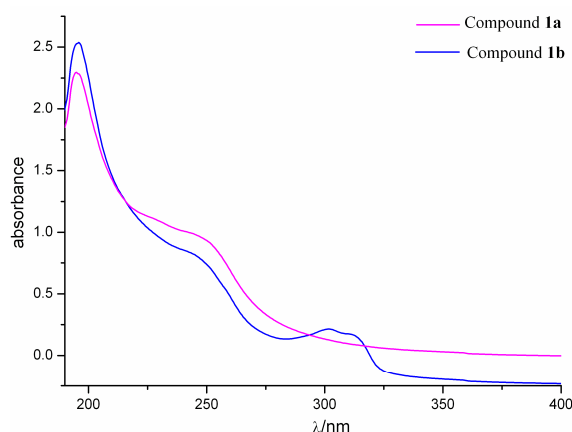


Fig. S3. The solubility of compounds **1a** and **1b** is usually very poor in water and organic solvents. Compounds **1a–1b** were placed in water heated at 60°C for 1 h, then slowly cooled to room temperature. The UV spectra of **1a–1b** were measured in aqueous solution. There are two characteristic absorption peaks appears at 195, 249nm in **1a**, which can be assigned to $\text{O}\rightarrow\text{M}$ ($\text{M} = \text{Nb}, \text{V}$) charge transfer transitions.^{12,13} There are four characteristic absorption bands occur at 196, 245, 302, 311nm in **1b**. The higher energy bands 196, 245nm in **1b** are associated with $\text{O}\rightarrow\text{M}$ ($\text{M} = \text{Nb}, \text{V}$) charge transfer transitions,^{12,13} whereas the lower energy band at 302 and 311nm in **1b** are ascribed to the ligand (2,2'-bipy)-to-metal (Cu^{II}) charge-transfer (LMCT) transitions.¹³

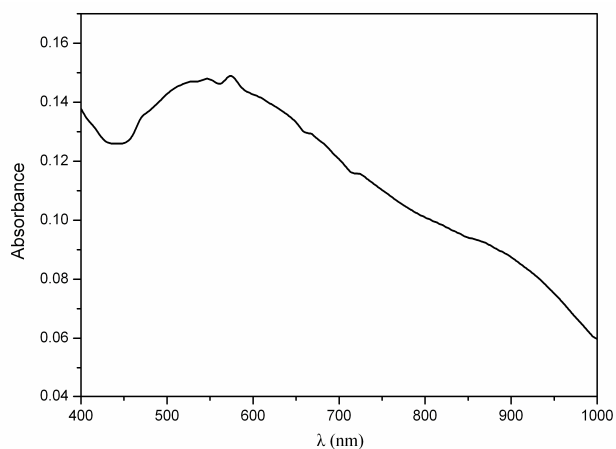


Fig. S4. Visible absorption spectrum of **1a** in solid form showing the broad bands from 460 to 1000nm, which should be attributed to the d-d transitions and intervalence charge transfer (IVCT, $\text{V}^{4+}\rightarrow\text{V}^{5+}$) transitions.¹⁴

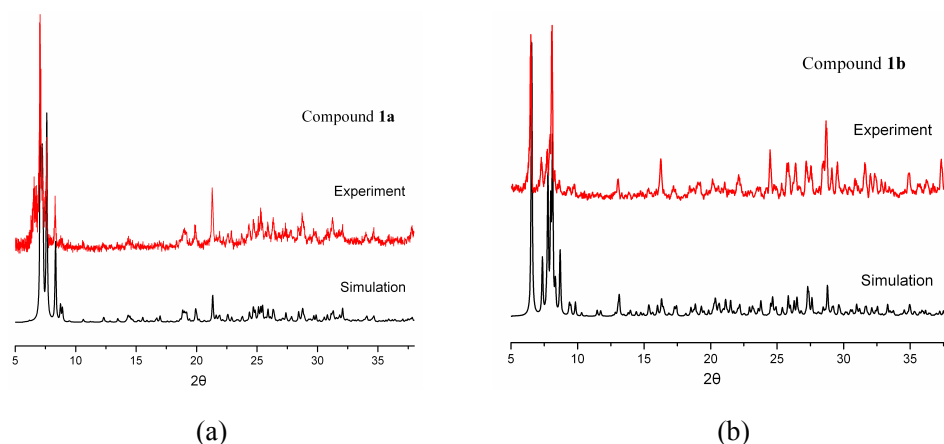


Fig. S5. (a)/(b) The experimental (red) and simulated (black) PXRD patterns for compounds **1a–1b**, respectively. The prominent diffraction peaks of experimental patterns match well with the simulated patterns from the single-crystal data in corresponding positions, indicating that the crystal phase purity of compounds **1a–1b**. In addition, the differences in reflection intensities may be due to the variation in preferred orientation of the powder samples.

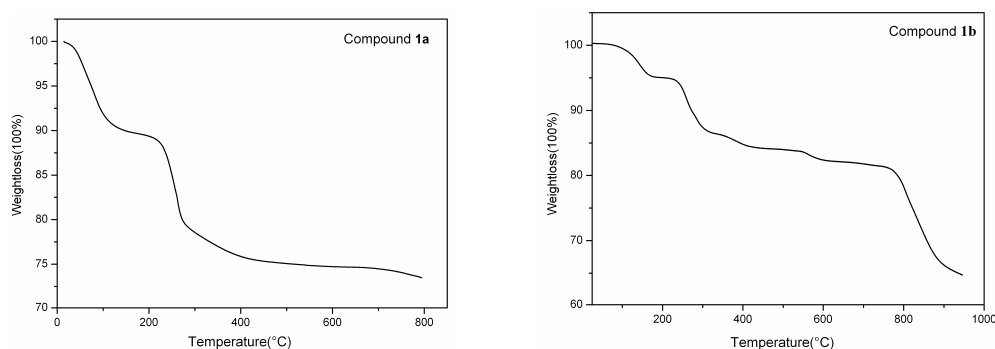


Fig. S6. Thermogravimetric analysis (TGA) studies of **1a–1b** were performed under N_2 at a $10^\circ C/min$ rate. Two continuous weight losses steps were observed on the TGA curve of **1a**. The first weight loss of 10.05% (calcd. 9.89%) in the range $25–150^\circ C$ is attributed to the removal of 17 lattice water molecules and one coordinated water molecule. And the second weight loss of 15.47% (calcd. 15.57%) from 150 to $700^\circ C$ comes from the release of 8.5 en ligands. The remaining 2.5 en ligands and the framework of compound **1a** begins to decompose when the temperature exceeds $700^\circ C$. Compound **1b** undergoes three weight loss stages. The first weight loss of 4.94% (calcd. 5.17 %) in the range $25–90^\circ C$ is ascribed to the removal of seven lattice water molecules and two coordinated water molecules. The second weight loss of 12.84% (calcd. 13.37%) from 190 to $620^\circ C$ results from the release of seven en ligands. Followed by a weight of 11.18% (calcd. 9.97%) in the temperature range $620–850^\circ C$ corresponds to the decomposition of two 2,2'-bipy. Then, the framework of compound **1b** starts to decompose at $850^\circ C$.

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