A Mixed Metallic and Mixed Valent $Mo^V{}_4V^{IV}{}_2V^{III}{}_2$ Complex as Electron Transfer

Photo-Catalyst for Hydrogen Evolution Reaction

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Supporting Information

1. Experimental section

- 2. Spectroscopic studies
- 3. Photocatalytic hydrogen evolution reaction (HER) studies

1. EXPERIMENTAL SECTION

1.1 MATERIALS AND METHODS

Chemicals used for organic ligand synthesis, metal salts, and materials for photocatalytic studies were procured from commercial sources and used without purification. Millipore water was used for the synthesis of the compounds **1a** and **2a**, and for all other experiments.

Powder X-ray diffraction (P-XRD) data were collected at room temperature on Bruker D8ECO with Cu-K_{α} radiation source ($\lambda = 0.154$ nm) from an angular range of 5-50° 2 θ . Infrared spectra were recorded in transmittance mode on Thermofisher Scientific iS50 spectrometer in the mid-IR region (4000-400 cm⁻¹) at room temperature. Elemental analysis for C, H, N, and O was performed on Thermo Scientific Flash 2000 Organic Elemental Analyzer (CHNS/O Mode). Elemental analysis for Mo, V, Na and P was performed using a quadrupole inductively coupled plasma-mass spectrometer (ICP-MS, Thermo X Series II). XPS analysis were done on Omicron Nano tech instrument with MgK α (1253.6 eV) radiation. The X-band EPR spectra were recorded with JEOL JES-FA series at 9.45 GHz, and both complexes **1a** and **2a** were measured in solid and solution phase.

Magnetism data for **1a** and **2a** were collected on a Quantum Design MPMS–XL EverCool SQUID Magnetometer in temperature ranging 5–300 K, under an applied external dc field in the range of -5 to 5 T. Polycrystalline samples of **1a** and **2a** (16.45 and 14.52 mg, respectively), sealed inside polypropylene bag ($2.8 \times 0.75 \times 0.02$ cm), were subjected to measurement. M *vs* H data was recorded for both these compounds at 100 K to check for the presence of any ferromagnetic impurity, which was found to be absent. Magnetization as a function of temperature was measured under 1000 Oe external dc field. The isothermal magnetization was studied at 5, 8, and 10 K. The magnetic data was corrected for the sample holder and the diamagnetic contribution.

Single-Crystal X-ray Diffraction. Data on a single crystal of compound 1a and 2a were obtained on a BRUKER AXS (D8 Quest System) X-ray diffractometer equipped with PHOTON 100 CMOS detector using Mo K α radiation ($\lambda = 0.71073$ Å), at 293(2) K. Routine Lorentz and polarization corrections were applied, and an absorption correction was performed using the SADABS program. Direct methods were used to solve the structures and to locate the heavy atoms (SHELXS97), and the remaining atoms were found from successive difference maps (SHELXL-2018).² The hydrogens of all the C atoms were added in calculated positions and refined using a riding model. Crystallographic data are summarized in Table 1. CCDC 2369137 and 2442530 contains the supplementary crystallographic data for this paper. These be obtained free of charge data can via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

1.2 SYNTHESIS

Both diphosphonate ligands and molybdenum(V) precursor were prepared as per literature procedures.³



Scheme S1. Synthesis of diphosphonate functionalized mixed metallic vanado-molybdates, forming the mixed valent $Mo^{V_4}V^{IV_2}V^{III_2}$ (1) and homo-valent $Mo^{VI_4}V^{III}$ (2). Cations were omitted for clarity. Thes complexes are negatively charged. They act as electron transfer catalyst in photochemical hydrogen evolution reaction.

1.2.1 1-hydroxo-2-(2-pyridyl) ethylidene-1,1-bisphosphonic acid

To 2.0 g (11.5 mmol) of 2-pyridyl acetic acid hydrochloride, taken in a 100 mL two-necked flask equipped with a reflux condenser, was added 3.6 g (43.8 mmol) of phosphorus acid and 10 ml (86.3 mmol) of p-cresol. This mixture was heated to 90 °C for a period of approximately 2 h until all of the solids had melted and formed a homogenous mixture of a thick suspension. Then 7.0 g of phosphorus trichloride was added to this suspension, and the resulting mixture was kept at 90 °C for an additional period of 6 h, after which a yellow, gel-like material was formed. This mixture was allowed to cool to room temperature. 20 mL of water was then added dropwise, and the mixture was kept for refluxing for 12 h. Then the mixture was again allowed to cool to room temperature. 20 mL of methanol was then added, and the precipitated product was kept stirring at 0 - 5 °C for an additional period of 2 h.

The white amorphous product obtained was obtained by filtration and washed with methanol (yield 2.59 g, 78.96 %). ¹H NMR (500 MHz, D₂O/NH₃): δ (ppm) 3.567 (t, ³*J*_{H-P} = 12.5 Hz, 2H), 7.785 (t, ²*J*_{H-H} = 7 Hz, 1H), 7.897 (d, ²*J*_{H-H} = 8 Hz, 1H), 8.350 (t, ²*J*_{H-H} = 8 Hz, 1H), 8.522 (d, ²*J*_{H-H} = 5.5 Hz, 1H). ³¹P{¹H} NMR (500 MHz, D₂O/NH₃): δ (ppm) 15.84.

1.2.2 1-hydroxo-2-(4-pyridyl) ethylidene-1,1-bisphosphonic acid

To 2.0 g (11.5 mmol) of 4-pyridyl acetic acid hydrochloride, taken in a 100 mL two-necked flask equipped with a reflux condenser, was added 3.6 g (43.8 mmol) of phosphorus acid and 12 g (86.3 mmol) of p-nitrophenol. This mixture was heated to 90 °C for a period of approximately 2 h until all of the solids had melted to form a homogenous mixture and a thick suspension. Then 7.0 g of phosphorus trichloride was added to this suspension, and the resulting mixture was kept at 90 °C for an additional period of 6 h, after which a yellow, gel-like material was obtained. This mixture was allowed to cool to room temperature. 20 mL of water was then added dropwise, and the mixture was kept for refluxing for 12 h. Then the mixture was again allowed to cool to room temperature. 20 mL of methanol was then added, and the precipitated product was kept for stirring at 0 - 5 °C for an additional period of 2 h. The white, amorphous product obtained was obtained by filtration and washed with methanol (yield 2.271 g, 69.6 %). ¹H NMR (500 MHz, D₂O/ NH₃): δ (ppm) 3.156 (t, ³*J*_{H-P} = 12.5 Hz, 2H), 7.391 (d, ²*J*_{H-H} = 6 Hz, 2H), 8.259 (d, ²*J*_{H-H} = 6 Hz, 2H). ³¹P NMR (500 MHz, D₂O/NH₃): δ (ppm) 17.2.

1.2.3 [Mo^V₂O₄(H₂O)₆]²⁺

The synthesis of the dimeric unit of molybdenum $[Mo^V_2O_4(H_2O)_6]^{2+}$ was performed according to the literature procedure.⁴ To a suspension of Na₂MoO₄ (4 g, 3.2 mmol) in 4M hydrochloric acid solution (80 mL) was added N₂H₄•3H₂O (210 µL, 4.29 mmol). The color of solution changed slowly from

yellow to dark red during heating at 80 °C for 3 h. The solution was then allowed to cool to room temperature and used for further reactions.

$1.2.4 (NH_4)_4H_8[(MoV_2O_4)_2(V^{III}_2O_2)(V^{IV}O)_2\{O_3P-C(O)(CH_2-2-C_5NH_4)-PO_3\}_4] \bullet 40H_2O (1a)$

To 20 ml of $[Mo^{V_2}O_4(H_2O)_6]^{2+}$ solution (2 mmol) in 4M HCl, was added 0.1225 g of NaVO₃ (1 mmol), and the pH adjusted to 1.50 using concentrated ammonia solution. Following this 0.60 g of 1-hydroxo-2-(2-pyridyl) ethylidene-1,1-bisphosphonic acid (2 mmols) was added, and the final pH was increased and maintained at 7.80 by the further addition of concentrated ammonia solution. The solution mixture was kept for heating at 80 °C for one hour, and then the solution was allowed to cool to room temperature and filtered. The resulting solution was left for slow evaporation for a week, leading to yellow-coloured block-shaped crystals of **1a**. Yield: 0.34 g (20 % based on vanadium). Elemental analysis (%) calculated for **1a**: Mo: 16.04, V: 8.52, P: 10.36, C: 14.06, H: 3.54, N: 4.68, O: 42.80. Found: Mo: 16.41, V: 8.71, P: 10.60, C: 13.97, H: 3.39, N: 7.01, O: 38.20.

1.2.5 H₅[(Mo^{VI}₂O₅)₂(V^{III}O₂){O₃P-C(O)(CH₂-4-C₅NH₅)-PO₃}₂]•16H₂O (2a)

To 20 ml of $[Mo^{V}_{2}O_{4}(H_{2}O)_{6}]^{2+}$ solution (2 mmol) in 4M HCl, was added 0.1225 g of NaVO₃ (1 mmol) and the pH adjusted to 1.50 using concentrated ammonia solution. Following this 0.60 g of 1-hydroxo-2-(4-pyridyl) ethylidene-1,1-bisphosphonic acid (2 mmol) was added, and the final pH was increased and maintained at 7.80 by the further addition of concentrated ammonia solution. The solution mixture was kept for heating at 80 °C for one hour, and then the solution was allowed to cool to room temperature and filtered. The resulting solution was left for slow evaporation for two days, yielding dark brown colored block-shaped crystals of **1a**. Yield: 0.36 g (24 % based on vanadium). Elemental analysis (%) calculated for **2a**: Mo: 26.05, V: 3.46, P: 8.41, C: 11.41, H: 3.15, N: 1.90, O: 45.62. Found: Mo: 25.41, V: 3.51, P: 8.53, C: 11.50, H: 3.44, N: 7.12, O: 38.24.

Complex	1a	2a
Empirical formula	$Mo_4V_4P_8C_{28}N_8O_{64}H_{84}$	$Mo_4VP_4C_{14}N_2O_{42}H_{46}$
Molar mass	2392.31	1473.11
(g/mol)		
Crystal system	Monoclinic	Monoclinic
Space group	<i>C</i> 2/m	<i>P</i> 2 ₁
<i>a</i> (Å)	17.3825(4)	12.4325(4)
<i>b</i> (Å)	14.0926(3)	10.9812(4)
<i>c</i> (Å)	16.5564(4)	17.2749(6)
α (°)	90	90
β (°)	107.9860(10)	99.8790(10)
γ (°)	90	90
Volume (Å ³)	3857.54(15)	2323.46(14)
Z	2	2
Temp (K)	120(2)	120(2)
D_{calcd} (g cm ⁻³)	2.060	2.106
Abs coeff (μ /mm ⁻¹)	1.384	1.501
F(000)	2400	1462
Crystal size (mm)	0.305 x 0.188 x 0.13	0.383 x 0.311 x 0.289
Theta range for	2.072 - 29.13	2.207 - 28.699
data collection (°)		
Residual electron	2.405 / -1.736	1.164 / -1.298
density $(\Delta \rho)$		
max/min (eÅ ⁻³)		
R(int)	0.0288	0.0381
T _{min} /T _{max}	0.678 / 0.841	0.597 / 0.671
GoF	1.035	1.079
$R1 \ [I > 2\sigma(I)]$	0.0552	0.0400
wR2 ^a	0.1406	0.1010

Table S1: Crystal data and structure refinement parameters of the compounds 1a and 2a.

^a $R1 = \Sigma ||Fo| - |Fc|| / \Sigma ||Fo||$. $wR2 = \{\Sigma [w(Fo^2 - Fc^2)] / \Sigma [w(Fo^2)^2] \} s^{1/2}$.

 Table S2. Bond-valence sum calculations for polyanion 1.

Bond	Bond Length (Å)	Bond Valence	Bond Valence Sum
V1-O1V1	1.5905	1.687	$\sum(V1) = 3.930$
V1-O1C1	2.0154	0.535	
V1-O2C1	2.0154	0.535	
V1-O2P2	1.9815	0.586	
V1-O1P2	1.9815	0.586	

Bond	Bond Length (Å)	Bond Valence	Bond Valence Sum
V2-O2P1	2.0509	0.435	$\sum(V2) = 2.968$
V2-O2P2	2.0509	0.435	
V2-O3P1	1.9872	0.517	
V2-O3P2	1.9872	0.517	
V2-O3V4	1.9765	0.532	
V2-O3V4	1.9765	0.532	

Bond	Bond Length (Å)	Bond Valence	Bond Valence Sum
Mo1-O1P1	2.1062	0.584	\sum (Mo1) = 5.017
Mol-OlCl	2.1855	0.471	
Mol-Ol	1.9391	0.917	
Mo1-O2	1.9499	0.890	
Mo1-O5	1.6910	1.793	
Mo1-N1	2.2831	0.362	

Bond	Bond Length	Bond Valence	Bond Valence Sum
V1-O2P2	2.019	0.474	$\sum(V1) = 3.029$
V1-O2P1	2.012	0.472	
V1-01V1	1.952	0.568	
V1-O2P2	2.019	0.474	
V1-O2P1	2.012	0.472	
V1-01V1	1.952	0.568	

Bond	Bond Length (Å)	Bond Valence	Bond Valence Sum
Mo1-O1P1	2.3990	0.265	\sum (Mo1) = 6.078
Mo1-O12	1.9423	0.909	
Mo1-O1P2	2.3400	0.310	
Mo1-O1V1	1.8648	1.121	
Mo1-O1B	1.7015	1.747	
Mo1-O1A	1.7041	1.730	

Bond	Bond Length (Å)	Bond Valence	Bond Valence Sum
Mo2-O1P1	2.3048	0.341	\sum (Mo2) = 6.125
Mo2-O1P2	2.3332	0.316	
Mo2-O12	1.7891	1.375	
Mo2-O1C	2.0372	0.703	
Mo2-O2B	1.7117	1.695	
Mo2-O2A	1.7121	1.693	

1.3 Polyanionic structures – Assembly and Symmetric aspects

The asymmetric unit of polyanion **1** consists of 25 crystallographically independent atoms, one molybdenum, two vanadium, two phosphorous, twelve oxygen, one nitrogen, and seven carbon atoms, and constitutes one-fourth of the polyanion. The crystal symmetry includes a two-fold axis and a σ -plane, positioning several atoms in special positions with 50% occupancy, including all vanadium atoms.

The asymmetric unit of polyanion **2** consists of 24 crystallographically independent atoms, two molybdenum, one vanadium, two phosphorous, eleven oxygen, one nitrogen, and seven carbon atoms, with the solitary vanadium atom residing on a special position with 50% occupancy; and thus constitutes half of the polyanionic assembly.



Fig. S1. Ball and stick representation of polyanions $[(Mo^{VI}_2O_5)_2(V^{III}O_2)\{O_3P-C(O)(CH_2-4-C_5NH_5)-PO_3\}_2]^{5-}$ (2). Color code: Mo (V), dark red; Mo (VI), dark teal; V(IV), Turquoise; V(III), Teal; P, magenta; O, red; N, blue; and C, grey. Hydrogen atoms on carbon are omitted for clarity.

1.4 Weak Interactions and Crystal Packing

In both the compounds **1a** and **2a**, the three-dimensional arrangement as well as the orientation of the aromatic ring in the solid-state packing is observed to be directed by the dipolar, π ... π stacking as well as hydrogen-bonding interactions. For polyanions **1** and **2**, an inter-ring distance of approximately 3.5890 - 3.5967 Å and 3.6839 - 3.7205 Å, respectively, are observed. As mentioned earlier, in both the polyanions the vanadium atom(s) exist on the symmetry elements in special positions.

For compound **1a**, extrapolation of the assembly of the polyanion **1** within the 2 x 2 x 2 supercell reveals that a single polyanionic moiety is surrounded by four other such moieties along the four corners of the unit-cell, as viewed along the *a*-axis and *b*-axis [see Figure S2(a-b) in Supporting Information]. Single crystal X-ray diffraction studies reveal the existence of a localized metal-metal bond between both $\{MoV_2O_4\}$ units of 1, same as most of the oxido bridge containing Mo(V) complexes.⁶⁰ A few of the earlier synthesized complexes containing Mo-Mo bonds exhibit their distance ranging from 2.533 to 2.625 Å.⁶¹ In polyanion **1** it is found to be 2.5512(9) Å, indicating a mostly covalent and strong metal-metal bond [see Figure S2(a) in Supporting Information]. Zubeita et al. demonstrated the oxo-bridged ring-like octanuclear array of Mo atoms, showing the Mo-Mo bond distance of 2.5661(3) Å which differs from the non-bonding Mo....Mo short contacts with a longer distance of 3.4393(3).⁶² As a result of the strong Mo-Mo bonding interactions, the {Mo^V₂O₄} units are considered to be diamagnetic. In addition, the mono-oxo-bridged dimeric unit of metal ions generally exhibit antiferromagnetic exchange interactions.⁶³⁻⁶⁴ Furthermore, two types of strong hydrogenbonding interactions were noticed in 1, where one type of hydrogen bonding exists between O1M1 of hexacoordinated Mo(V) and H7 associated with the aromatic part of the ligand. The polyanion is also involved in an additional hydrogen bonding with O1V1 of the penta-coordinated V(IV) and H5 of coordinated ligand. In compound **1a**, the intermolecular hydrogen-bond distances between the donor and the acceptor atoms are in the range of 2.859 – 3.273 Å [see Table S3 in Supporting Information]. Such significant interactions lead to a supramolecular assembly that is held together by two different kinds of C-H···O hydrogen bonds [see **Figure S2(b)** in **Supporting Information**]. Such various types of C-H···O hydrogen bonds create the anionic assembly in the crystal lattice of **1**, similar to the previously reported oxo vanadium(IV) dimer by Animesh *et al.*⁶⁵

In compound **2a**, the three-dimensional assembly is orchestrated by intermolecular hydrogen bonding, arising because of the presence of donor atom(s) from the heteroaromatic ring, the sp² hybridized C–H bond, and the acceptor O–Mo group from the {Mo^{VI}₂O₅} unit, within the polyanions. In compound **2a**, the intermolecular hydrogen-bond distances between the donor and the acceptor atoms are in the range of 3.093 - 3.537 Å [see **Table S4** in **Supporting Information**]. Furthermore, π - π stacking interactions can also be considered to be significant in affecting the overall packing arrangement [see **Figure S3** in **Supporting Information**]. Along the *a*-axis, each polyanionic unit is thus assembled in a *zig-zag* manner. This results in the presence of cavities present within such an assembly, occupied by lattice water molecules and counter-cations.

 Table S4: Hydrogen-bonding parameters for compound 1a.

Donor - H ··· Acceptor	D - H(Å)	H … A (Å)	$D \cdots A(Å)$
$C5 - H5 - 01V1^{\#1}$	0.93	2.43	3.273
C6-H6O1W ^{#2}	0.93	2.46	3.381
C7 – H7…O1M1	0.93	2.38	2.859

Symmetry transformations used to generate equivalent atoms:

^{#1}: $\frac{1}{2}$ - x, $\frac{1}{2}$ + y, - z

#2: $\frac{1}{2} - x$, $-\frac{1}{2} + y$, -z

Table S5: Hydrogen-bonding parameters for compound 2a.

Donor - H ··· Acceptor	D – H (Å)	H … A (Å)	$D \cdots A(Å)$
C4 - H4 O2B ^{#1}	0.93	2.52	3.097
C4 - H4 O2A ^{#1}	0.93	2.40	3.179

Symmetry transformations used to generate equivalent atoms:

^{#1}: $\frac{1}{2} - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$



(a)



(b)

Figure S2. Packing of compound 1a in the solid state as viewed along the (a) *a*-axis, and (b) *b*-axis.



Figure S3. Packing of compound 2a in the solid state as viewed along the *a*-axis.



Figure S4. Simulated vs Experimental comparative PXRD of compound 1a



Figure S5. Simulated vs Experimental comparative PXRD of compound 2a

2. SPECTROSCOPIC STUDIES

2.1 Infrared spectroscopy

The infrared spectrum of compound **1a** shows characteristic vibrational peaks of functional groups present within the polyanions [see **Figure S6**]. For compound **1a**, the strong vibrational peaks at 1173, 1095, and 1076 cm⁻¹ are attributed to P-O and P=O bonds.⁵ The intense characteristic peak at 1030 and 991 cm⁻¹ corresponds to the Mo-O bond,⁶ the peaks at 960, 941, and 754 cm⁻¹ are characteristic of V=O and V-O bonds.⁷ For compound **2a**, characteristic peaks corresponding to P-O and P=O stretching are observed around 1040 and 1140 cm^{-1.8} The absorption band appearing around 920 – 870 cm⁻¹ corresponds to various Mo–O bond stretching vibrations.⁹ and also peaks between 750 – 680 cm⁻¹ can be attributed to O–Mo–O bending mode.¹⁰ Peaks observed at 788 and 818 cm⁻¹ correspond to V=O and V-O stretching, respectively,^{5.7}



Figure S6. IR spectra for compounds 1a and 2a, (a) Complete region, (b) Fingerprint region.

2.2 Optical (UV-visible) spectroscopy

Measurement of the optical spectra of the compounds, in solid-state and in solution, provided us with information on the band-gap, the electronic transitions in the metal orbitals, and the solution stability of the polyanions for extended periods of time.

Solution-phase UV-visible spectroscopy studies of the compounds **1a** and **2a** were performed in aqueous solution, within the range of 200 – 800 nm. Polyanion **1** exhibits a robust absorption peak at 261 nm, which is assigned to the ligand-to-metal charge transfer (LMCT) $p\pi$ -d π transition from the terminal oxygen atom to molybdenum(V). Additionally, a distinct absorption peak observed at 315 nm is attributed to the ligand to metal charge transfer (LMCT) $p\pi$ -d π transition from the bridging oxygen (O_b) atom to molybdenum(V) [**Figure S7(a**)]. Due to unpaired electrons present in all the metal atoms [Mo(V), V(IV) and V(III)], multiple d-d transition peaks are expected in the visible region. However due to low absorptivity associated with such transitions, a relatively weak peak at 676 nm was observed, which is associated with the ${}^{2}T_{2g} \rightarrow {}^{2}E_{g}$ d-d transition of vanadium(IV) atom [see **Figure S7(a)** inset].¹¹



Figure S7. Time-dependent solution-phase UV-Visible spectra of compounds (a) 1a, and (b) 2a. Inset shows the visible region.

For polyanion **2**, similar strong absorption peak(s) in the range of 210 - 220 nm are also attributed to $p\pi$ -d π ligand metal charge transfer (LMCT) from the terminal oxygen atom (O_t) to molybdenum, while peaks observed in the range of 230 - 250 nm are attributed to a $p\pi$ -d π charge transfer transition from bridging oxygen atoms (O_b) of molybdenum [see **Figure 6(b**)].¹² For polyanion **2** also, in the visible region relatively low intensity peaks (corresponding to d-d transitions) were observed, with the peak at 430 nm attributed to ${}^{3}T_{1g} \rightarrow {}^{3}T_{2g}$ transition [see **Figure S6(b) inset**].¹¹

The band gap energy of the compounds **1a** and **2a** were estimated experimentally using solidstate UV-DRS (Ultraviolet Diffused Reflectance Spectroscopy) studies. The precise evaluation of band gap energies by UV-DRS is crucial in revealing important information about the electronic characteristics of the photocatalytic hydrogen evolution process. The energy gap for compound **1a** and **2a** was observed as 1.55 and 1.78 eV, respectively [see **Figures S7a** and **S7b**].



Figure S8: UV-DRS spectrum for compounds (a) 1a, and (b) 2a.

The lowering of the band gap energy values for oxo-vanado-molybdate compounds **1a** and **2a**, with respect to purely oxo-vanadates, which show band-gaps in the range of 3 - 3.3 eV,¹³ can be explained due to the presence of two distinct metal sites (Mo and V) in their polyanionic structures. The high

nuclearity of the Mo-V centers, maybe the reason for the further lowering of band gap energy observed in compound **1a** with respect to compound **2a**. As such, minimization of the band gap energy increases the photocatalytic hydrogen production performance, by extending incident photon absorption into the visible region (*vide infra*).

2.3 X-ray Photoelectron spectroscopy

XPS studies were performed to corroborate the oxidation state values obtained from bond-valencesum calculations. Analysis performed on compounds **1a** and **2a** gave us a very good understanding on the electronic nature of the transitional metals present within these compounds, *viz*. vanadium and molybdenum, especially with respect to their formal oxidation state(s). Peaks in the spectra were calibrated with respect to carbon 1s signal having a binding energy 284.6 eV.

Molybdenum XPS spectra of **1a** shows the spectral region for the Mo 3d display two peaks at binding energies of 232.4 and 235.5 eV, attributed to $3d_{5/2}$ and $3d_{3/2}$, respectively [see **Figure S8(a**]. These binding energy values and data from the literature confirm the +5 oxidation state molybdenum.¹⁴ For compound **2a**, spectral data of Mo 3d [see **Figure S8(b**)] shows two deconvoluted peaks at binding energy values 235.3 and 232.7 eV, attributed to Mo $3d_{3/2}$ and Mo $3d_{5/2}$ also, which confirms the +6 oxidation state of Mo, as per literature data.¹⁵ Therefore, we can summarise that the values of binding energies in the Mo 3d region are in good accordance with the literature values, which are indicative of the +5 and +6 oxidation state of Mo in compounds **1a** and **2a**, respectively, and in good agreement with the bond-valence sum values.

For vanadium, determination of exact oxidation state(s) from XPS data is challenging due to overlapping peaks. Under these circumstances, the exact fitting of the deconvoluted data and the presence of shoulder peaks are indicative of the mixed-valent nature of vanadium present within the compound **1a**. Thus, the vanadium XPS spectra of **1a** shows four deconvoluted overlapping peaks at

binding energy values of 524.1, 523.4, 517, and 515.9 eV [see **Figure S8(c)**]. The two peaks at 523.4 and 515.9 eV binding energies are consistent with the literature values of 523.2 eV and 515.8 eV, corresponding to V $2p_{3/2}$ and V $2p_{1/2}$ respectively,¹⁶ assigned to the +4 oxidation state of vanadium. Another two peaks observed at 524.1 eV (V $2p_{3/2}$) and 517 eV (V $2p_{5/2}$) are compatible with literature data for vanadium in the +3 oxidation state.¹⁷ Hence, from the above results, we ascertain that the XPS values agree with BVS calculations for mixed-valent vanadium(III-IV) present in polyanion **1**. For compound **2a**, the V 2p peaks at 522.8 eV and 516.7 eV [see **Figure S8(d)**], corresponding to V $2p_{1/2}$ and V $2p_{3/2}$, respectively, affirm a +3-oxidation state for the vanadium atom.^{18, 19}



Figure S9. XPS Spectra of (a) $Mo^{+5} 3d_{3/2}$ and $3d_{5/2}$ of compound 1a , (b) $Mo^{+6} 3d_{3/2}$ and $3d_{5/2}$ of compound 2a, (c) V $2p_{1/2}$ and V $2p_{3/2}$ of compound 1a , and (d) V $2p_{1/2}$ and V $2p_{3/2}$ of compound 2a.



Figure S10. (a) Solid ESR spectrum of compound **1a** at room temperature under atmospheric conditions (microwave power: 1 mW, modulation amplitude: 2 mT). Magnified image of hyperfine resonances (Inset), (microwave power: 1 mW, modulation amplitude: 2 mT, v = 9.45 GHz). (b) Solid ESR spectrum of **2a** at liquid nitrogen temperature under atmospheric conditions (microwave power: 1 mW, modulation amplitude: 2 mT, v = 9.45 GHz). (b) Solid ESR spectrum of **2a** at liquid nitrogen temperature under atmospheric conditions (microwave power: 1 mW, modulation amplitude: 2 mT, v = 9.16 GHz).

3. PHOTOCATALYTIC HYDROGEN EVOLUTION REACTION (HER) STUDIES

Photocatalytic hydrogen evolution experiments were carried out in homogeneous phase at room temperature under visible light irradiation from 250 W Hg-lamp upon a mixed solvent system of CH₃CN/DMF/H₂O, and the eluent examined using gas chromatogram equipped with DID (discharge ionization detector), towards the detection and quantification of hydrogen gas produced. Studies were conducted using a three-component system, with the catalyst (either compound 1a or 2a in a range of μ M concentrations) and the sacrificial electron donor triethanolamine (0.25 M) present in aqueous solution; while the photosensitizer $[Ir(dtbbpy)(ppy)_2]^+$ (0.20 mM) present in CH₃CN/DMF solution. Controlled experiments performed initially, with either one or two of the components not present, showed negligible or no hydrogen production in the absence of the photosensitizer. With the photosensitizer present, hydrogen gas was detected, with amounts varied based upon the presence or absence of the sacrificial electron donor as well as the catalyst type. A substantially large amount of hydrogen produced for the three-component system, indicated the need for the presence of all three components in the reaction [see Figure S10(a) in Supporting Information]. The rate of hydrogen evolution was found to depend on the concentrations of the catalyst, photosensitizer $[Ir(dtbbpy)(ppy)_2]^+$, and sacrificial electron donor TEOA. Our preliminary investigations showed the activity of compound 1a towards HER to be substantially higher than compound 2a. Hence, all optimisation experiments were performed with 1a.

Extensive investigations were then carried out to understand the impact of varying concentrations of these components on catalytic H₂ evolution. Initially, catalyst concentration variation studies were performed under conditions obtained from literature, *i.e.* a concentration of 0.20 mM and 0.25 M for $[Ir(dtbbpy)(ppy)_2]^+$ and TEOA, respectively.^{20, 21} Figure S10(b) in Supporting Information illustrates the kinetics of hydrogen production under varying catalyst concentrations. A

concentration of 20 µM of the catalyst was observed to produce the maximum of hydrogen evolved, at a rate of 5816 µmol.g⁻¹. At catalyst concentration values slightly higher and lower than 20 µM, *i.e.* at 25 and 15 µM, respectively, identical yields were obtained. The increasing enhancement of HER activity upto a concentration of 20 µM, followed by a decrease, can be attributed to accelerated decomposition of the photosensitizer by the catalyst and potential catalysis side reactions.²² Subsequent experiments to improve HER performance by varying [Ir(dtbbpy)(ppy)₂]⁺ and TEOA concentrations were then performed at this optimised catalyst concentration of 20 µM. Further experiments were also carried out towards the optimization of the photosensitizer and sacrificial electron donor concentration values. Increasing the concentration of the photosensitizer from 0.15 to 0.20 mM led to an increase in catalytic H₂ evolution rate. However, further increasing the concentration to 0.25 mM resulted in decreased activity [see Figure S10(c) in Supporting Information]. This can be ostensibly attributed to the aggregation of the photosensitizer molecules or its free molecules blocking incident light.²² Similar observations were made in experiments of sacrificial electron donor (TEOA) concentration variation [see Figure S10(d) in Supporting Information]. As mentioned earlier, our extensive studies revealed that the presence of all three components to be necessary for highest H₂ evolution rate under visible light irradiation.



Figure S11. (a) Control experiments based on different components for catalyst (compound 1a or 2a), photosensitizer ([Ir(dtbbpy)(ppy)₂]PF₆), and sacrificial electron donor (**TEOA**). Catalysis optimization experiments: HER activity measured concerning varying concentrations of (b) compound 1a, (c) photosensitizer [Ir(dtbbpy)(ppy)₂]PF₆, and (c) sacrificial electron donor triethanolamine (TEOA). Conditions: Light source (250 W Hg Lamp), catalyst (20 μ M), [Ir(dtbbpy)(ppy)₂]PF₆ (0.20 mM), **TEOA** (0.25 M), H₂O (2 M), 6 ml of CH₃CN-DMF (v/v = 3/2), 5 h.

Calculations on the quantification of hydrogen evolved (in µmol/g):

The total volume of container used for photocatalytic experiment = 450 ml

The volume of the mixed solvent system = 6.514 ml

Therefore, the volume of the empty container = 443.486 ml

x ppm of $H_2 = x \frac{\mu mol}{mol}$ of H_2

H₂ evolution in µmol per gram of catalyst = $x \frac{\mu mol}{mol} \times \frac{Volume \text{ of empty container in ml}}{22400 \text{ ml at STP}} \times \frac{1000}{\text{Weight of catalyst in mg}}$

Turnover Number (TON) Calculation:

Let 'a' µmol of Hydrogen be produced by 'b' g of catalyst used.

Therefore, 1 g of catalyst produces $\frac{a \ \mu \text{mole}}{b \ g}$ Turnover number $= \frac{\text{No.of moles of Hydrogen evolved}}{\text{No.of moles of catalyst used}}$ $= \frac{a \ (\mu \text{mol})}{\frac{b \ (\text{mg})}{M.W. \ of \ catalyst \ (\text{g})}}$ $= \frac{a \ \mu \text{moles}}{\frac{b \ (\text{g})}{M.W. \ (\text{g})} \ x \ 10^6 \ \mu \text{moles}}$ $= \frac{a \times M.W}{b \times 10^6}$



Figure S12. Emission spectra of [Ir(dtbbpy)(ppy)2]+ (0.20 mM) in presence of increasing concentration of (**a**) catalyst (**1a**), and (**b**) TEOA. Stern-Volmer Plot of $[Ir(dtbbpy)(ppy)_2]^+ (0.20 \text{ mM})$ with increasing concentration of (**c**) catalyst (**1a**), and (**d**) TEOA. Lifetime Studies of $[Ir(dtbbpy)(ppy)_2]^+ (0.20 \text{ mM})$ with increasing concentration of (**e**) catalyst (**1a**), and (**f**) TEOA.

Table S6: Photoluminescence lifetime of photosensitizer [Ir(dtbbpy)(ppy)2] + (0.20 mM) in presenceof different quenchers: catalyst 1a (20 μ M), TEOA (0.25M) in CH₃CN/DMF (λ_{exc} = 430 nm)

	[Ir(dtbbpy)(ppy)2] ⁺	[Ir(dtbbpy)(ppy)2] ⁺ + 1a	[Ir(dtbbpy)(ppy)2] ⁺ + TEOA
Lifetime (ns)	86.02	82.21	61.40

EPR Studies and DFT calculation:



Fig. S13. X-band EPR spectra of the complexes (**a**) $Na(NH_4)_8H[(Mo^V_2O_4)_2(V^{III}_2O_2)(V^{IV}O)_2\{O_3P-C(O)(CH_2-2-C_5NH_4)-PO_3\}_4]\cdot 17H_2O$ (**1a**) and, (**b**) $Na_2(NH_4)_5[(Mo^{VI}_2O_5)_2(V^{III}O_2)\{O_3P-C(O)(CH_2-4-C_5NH_4)-PO_3\}_2]\cdot 10H_2O$ (**2a**) Red and blue lines represent the experimental and simulated spectra using EasySpin program.

Fitting paramters: Solid state EPR spectrum (red) of complex 1a at 77 K. Red and black lines represent the experimental and simulated spectra of complex 1a using EasySpin program. [V^{IV} ion, S =1/2; $g_x = 2.00986$, $g_y = 2.00998$, $g_z = 2.04998$, LWPP(1) = 0.506077 mT, LWPP(2) = 6.00054 mT, A_X = 80.0242 MHz, A_Y = 559.833 MHz, A_Z = 34.7481 MHz] (Fig. S13, left).

The EPR of V^{III}-complex (**2a**) has been previously²³ reported: K. S. Morla, D. Thakre, T. B. Deshmukh, S. Malo, S. Ahamed, R. K. Aparna, S. Sahoo, D. Sarma, K. C. Mondal, B. R. Sankapal and A. Banerjee, *J Mater Chem A*, 2024, **12**, 22013-22029.



Fig. S14. A) The Spin density plot of $[(Mo^V_2O_4)_2(V^{III}_2O_2)(V^{IV}O)_2\{O_3P-C(O)(CH_2-2-C_5NH_4)-PO_3\}_4]^{10-}$ (1) (S = 1) at B3LYP-D3(BJ)/Def2-SVP level of theory. B) The percentage (%) of α -spin density values are given in blue colour.



Fig. S15. A) The Spin density plot of $[(Mo^{VI}_2O_5)_2(V^{III}O_2)\{O_3P-C(O)(CH_2-4-C_5NH_4)-PO_3\}_2]^{7-}$ (2) (S = 1) at B3LYP-D3(BJ)/Def2-SVP level of theory. B) The percentage (%) of α -spin density values are given in blue colour. Spin density does not change on removing H⁺ from N-atoms keeping the charge balaned.





α-LUMO+1

α-SOMO



 α -SOMO-2



 α -SOMO-3



NBOs generated from the geometry obtained

Fig S16. NBOs generated from the geometry obtained from X-ray single structure determination of $[(Mo^V_2O_4)_2(V^{III}_2O_2)(V^{IV}O)_2\{O_3P-C(O)(CH_2-2-C_5NH_4)-PO_3\}_4]^{10-}$ (1) (S = 1) at B3LYP-D3(BJ)/Def2-SVP level of theory.

Sample ID	% Nitrogen	% Carbon	% Hydrogen	% Sulphur	% Oxygen
1a	7.01	13.97	3.39	Not detected	38.20
2a	7.12	11.50	3.44	Not detected	38.24

(a)

Sample	Elements	Instrumental	Volume of	Dilution	Weight of	Weight
		value (ppm)	solution (mL)	factor	sample (g)	percentage
1a	Mo	4.594	10	100	0.029	15.84
	V	2.433	10	100	0.029	8.39
	Р	2.935	10	100	0.029	10.12
	Na	0.264	10	100	0.029	0.91
2a	Mo	7.278	10	100	0.0288	25.27
	V	0.904	10	100	0.0288	3.14
	Р	2.292	10	100	0.0288	7.96
	Na	0.85	10	100	0.0288	2.95

(b)

Fig. S17. (a) CHNO analysis, and (b) ICP-MS analysis data for 1a and 2a.



(a)



(b)

Fig. S18. ORTEP representation of the assymetric unit structures of (**a**) **1a** and (**b**) **2a**, at 50% thermal ellipsoid probability, showing ADPs. Color code: vanadium, light blue; molybdenum, orange; nitrogen, purple; oxygen, red; carbon, blue; chlorine, yellow; sodium, green; hydrogen, white.

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