A light-harvesting polyoxometalate-polypyridine hybrid induces electron transfer as its Re(I) complex

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A light-harvesting polyoxometalate-polypyridine hybrid induces electron transfer as its Re(I) complex

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A derivative of the Dawson polyoxometalate $[P_2V_3W_{15}O_{62}]^{9-}$ functionalized with one remote bipyridine coordination site (2) has been synthesized and combined with neutral $\{Re(CO)_3Br\}$ moiety. The new Re^I-hybrid (3) was characterized by various analytical techniques. Hybrid 3 exhibits several redox processes on a wide range of potentials with reductions centered on V(V), W(VI) and the organic ligand in order of decreasing potentials. Both units, polyoxometalate and transition metal complex, retain their intrinsic properties in the hybrid 3, which displays photosensitization in the UV region with tailing into high-energy visible region.

Polyoxometalates (POMs) are a large class of anionic oxo-clusters of early-transition metals that demonstrate useful applications in material science and catalysis,[1] including proton reduction to dihydrogen.[2] We recently reported the preparation of mono- and bis-functionalized POM platforms with mono-[3] and tri-dentate[4] ligands. These remote binding sites allow the self-assembly of POM-based redox-active units using metal coordination[5] yielding new hybrid materials that can take advantage of synergestic effects between the sub-units for potential applications as photo-/redox-active materials.[6] However, the development of molecular assemblies for photoinduced multi-electron transfer is still a highly relevant challenge.[7,8]

$[Re(L)(CO)_3(\alpha\text{-diimine})]$ complexes are relatively stable and present rich photochemistry.[9,10] In particular, the photochemistry of $[Re^I(R\text{-bpy})(CO)_3Br]^{1+/0}$ (R-bpy = substituted 2,2'-bipyridine) complexes involves mostly electron transfer and is based on the high reactivity of the reduced species:[9b] for example, $[Re^I(4,4'\text{-}R_2\text{-bpy})(CO)_3Br]$ complexes have demonstrated catalytic activity in CO_2 reduction.[10b,11] On the other hand, excited states of such coordination species being both strong reductants and oxidants (see redox diagram in ESI),[12] they found versatile use in photocatalysis: for example, they have been advantageously combined with Co catalysts for light-driven H_2 evolution by proton reduction.[13] In such artificial models for photosystem PSI, the photoexcited $*Re^I$ sensitizer is reductively quenched by a sacrificial electron donor and the reduced species transfer an electron, with rates close to diffusion control, to the catalyst.

Here, we report the incorporation of a triol-functionalized bipyridine **1** into a Dawson vanado-tungstate $[P_2V_3W_{15}O_{62}]^{9-}$, **2** and its subsequent complexation with Re(I) in order to yield a *covalent* hybrid POM-derivative **3** (Figure 1) absorbing in the more energetic part of the visible range of the electromagnetic spectrum. The covalent link between photosensitizer and POM, as compared to mere mixing of the components, ensures a better control of stoichiometry and relative orientation of the sub-units. Complex **3** was characterized and preliminary photophysical studies suggest a photo-induced intramolecular electron transfer from the Re-to-bpy ^{3}MLCT to the POM.

Ligand **1** was synthesized adapting previous reports.[3,5b,14] Commercially available 4,4'-dimethyl-2,2'-bipyridine (Me_2bpy) was oxidized to the mono carboxylic acid[15] and then was esterified with ethanol via the acyl chloride. The reaction of this ester with tris(hydroxymethyl)aminomethane gave **1** in 50% yield.

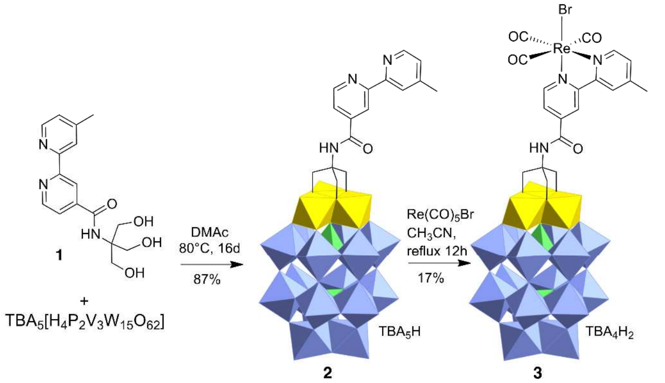

Figure **1**. Functionalisation of the Dawson phosphovanadotungstate with a bipyridine ligand, and post-functionalization with a rhenium complex.

Following previously reported triol-functionalization of $[P_2V_3W_{15}O_{62}]^{9-}$,[4,8b,14b,16,17] the grafting of the bipyridine-triol to the POM was performed in N,N'-dimethylacetamide (DMAc) at 80°C for 16 days to give the functionalized POM **2** in high yield (87%). The long reaction time is necessary to convert the compound where the amide oxygen atom is inserted into the POM framework.[18] The

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reaction of the bipyridine ligand in **2** with [Re^I(CO)$_5$Br] was achieved in refluxing CH$_3$CN to give the hybrid complex **3** after loss of two CO ligands. POM **3** was isolated with four TBA$^+$ and two H$^+$ counterions. Spectroscopic analyses confirmed the complexation: (i) the IR spectra displayed both the characteristic bands of the Dawson phospho-vanado-tungstate structure (between 700 and 1100 cm^{-1})[16a,19] and the three $\nu_{C=O}$ bands (at 2019, 1913 and 1890 cm^{-1}) typical of *fac*-Re(CO)$_3$X(bipyridine) complexes (see ESI);[20] (ii) the ^{1}H NMR spectrum displayed the typical shifts in the bipyridine resonances due to coordination of the Re^I(CO)$_3$Br moiety (Figure 2),[21] and the ^{31}P spectrum showed two singlets at δ = –7.36 and -12.73 ppm which were slightly shifted from the parent Dawson POM **2**, δ = –7.06 and –13.12 ppm (see ESI). The identity of **3** was further ascertained by ESI-TOF high-resolution MS (Figure 3) while its purity was confirmed by elemental analysis (see ESI). The compound is stable as a solid and in CH$_3$CN under ambient conditions for an extended period of time.

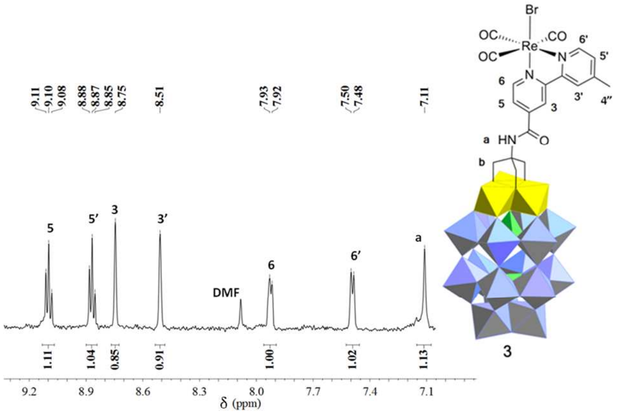

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Figure **2**. ^{1}H NMR spectrum of **3** (400 MHz, CD$_3$CN). Chemical shifts observed are typical of [(R-bpy(Me))Re(CO)$_3$Br] complexes.

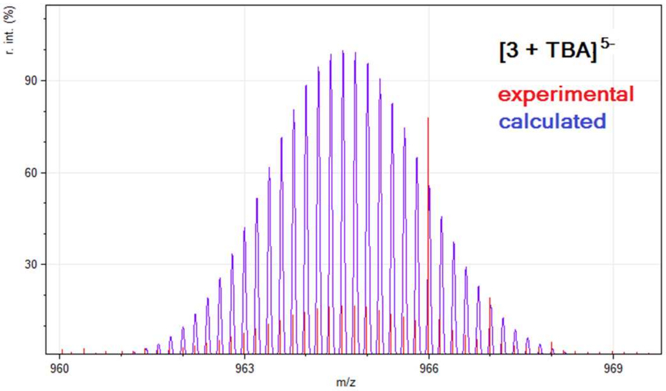

Figure **3**. Isotopic distribution of the peak for [M+TBA]$^{5-}$ at m/z = 964.9891 (red: experimental; blue: calculated) for hybrid **3**, confirming its identity. Intense peak at m/z=965.9908 is the internal reference used for calibration.

The electrochemical data for the ligand **1** and complexes **2**-**3** are gathered in Table **1** (voltamograms in ESI). Ligand **1** displayed two irreversible reductions (-0.91 and -1.59 V *vs.* SCE) associated with the amino-triol function as well as the reduction of the bipyridine moiety at a more negative potential (-2.03 V). Dawson derivative **2** displayed several reversible processes on a wide range of potentials (–0.08 V, –0.63 V, –0.84 V, –1.17 V and –1.95 V; Table **1**). These reductions were assigned to three successive V(V/IV) reductions followed by the reduction of W(VI/V) centres and the bipyridine moiety, in agreement with observations made for similar compounds.[8] The enlargement of the observed signals is not due to irreversibility of the processes, but due to adsorption of the analyte on the surface of the glassy carbon electrode (see ESI). The first three reductions of the V ions of the POM affect the successive processes by electrostatic repulsion of charges on the highly charged cluster leading to ill-defined cyclic voltamograms. The comparison of the redox behaviours of compounds **2**-**3** and ligand **1** showed that the sub-units are electronically isolated in the ground-state, in agreement with observations from NMR and electronic absorption spectra: the effect of the organic ligand and of the Re complex on the redox processes of the POM is negligible. The POM sub-unit maintained its functionality as an electron reservoir despite the grafting of the organic moiety. Thus, compound **3** is a suitable candidate as a photoinduced redox-catalyst as it has several redox processes in an accessible range.

Table **1**. Redox Potentials of ligand **1** and grafted POMs **2**-**3**.[a]

Compound	Oxidation	Reductions
1	0.96	-0.91 (irr); -1.59 (irr); -2.03 (105)
2[*b*]	-	0.08; -0.63; -0.84; -1.05; -1.17; -1.95
3[*b*]	1.8	0.08; -0.69; -0.84; -1.05; -1.23; -1.62
[(Me$_2$bpy)Re(CO)$_3$Br][22]	1.63 (irr) 1.33 (irr)	-1.47 (irr)

[a] Redox potentials were measured (V *vs.* SCE) at r.t. in degassed solutions with 1 mM of compound and 0.1 M TBAPF$_6$ as supporting electrolyte (DMF for **1** and CH$_3$CN for **2**-**3**). Glassy carbon electrode and ferrocene as internal standard (E = +0.39 V *vs.* SCE in CH$_3$CN and E = +0.43 V *vs.* SCE in DMF) were used. For irreversible processes, the potential is given for the cathodic wave; for reversible processes, the half-wave potential is given. [b] Measurement performed in degassed CH$_3$CN by Square-Wave voltammetry, due to the increased problems of adsorption of multi-charged species in DMF which resulted in ill-defined waves in CV.

UV-Visible absorption data are reported in Error! Reference source not found. (for spectra see ESI). In general, the [P$_2$V$_3$W$_{15}$O$_{62}$]$^{9-}$, derivatives are yellow, due to the tailing end of the LMCT O → M absorption in the lower energy UV region.[8b,14b] Ligand **1** presents four bands between 240 and 300 nm due to π → π* transitions. By comparing the spectra of **2** and **3** with that of **1**, all of the transitions distinguished between 245 and 310 nm are due to LMCT O → M transitions (M = W[23] and V[24]), which are superimposed with absorption maxima of the ligand (the ε values indicate the strong contribution from the POM). In **3**, the ^{1}MLCT (Re-π*) transition is observed superimposed on the absorption of the POM **2** in the 350-450 nm range, thus improving photosensitization in the high-energy visible region (at 450 nm, **3** absorbs 60% more than **2**). Within the POMs **2**-**3**, the π → π* transitions remain unchanged compared to ligand **1**. Thus, the UV-visible absorption data confirm the electronic isolation between the sub-units, POM and organic ligand, in agreement with the observations made by ^{1}H NMR spectroscopy and electrochemistry.

[Re^I(L)(CO)$_3$Br] complexes (L = derivatized bipyridine) typically emit in the 500-600 nm range due to radiative relaxation of the ^{3}MLCT excited state.[21] In the case of covalent hybrid **3** (Figure 4), the luminescence is quenched by rapid photoinduced electron transfer from the Re^I ^{3}MLCT state to the POM. As the ^{3}MLCT state has an energy E$_{0\text{-}0}$ of approximately 2.4 eV and the oxidation of Re^I in **3** occurs at E(Re^{2+}/Re^{1+}) = +1.8 V, the excited state oxidation potential of Re^I in **3** is estimated E(Re^{2+}/*Re^{1+}) ~ -0.6 V (see ESI), sufficient to reduce the POM moiety in **3** (with a first reduction for

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V(V/IV) at 0.08 V). The large driving force (0.7 eV) for the photoinduced reduction of the POM in **3** is a starting point for the photocatalytic production of H_2 based on POM-organic hybrids.

Table **2**. Absorption and emission data for compounds **1**-**3** and for reference complex $(Me_2bpy)Re(CO)_3Br$. All measurements were done in CH_3CN at r.t. (except for the reference compound **4** done in DMF).

Compound	Absorption, λ / nm (ε / 10^3 $M^{-1}\cdot cm^{-1}$)	Emission, λ / nm
1	240 (3.8); 250 (sh); 287 (3.1); 297 (2.3)	------
2	247 (65.8); 306 (38.1)	------
3	246 (83.2); 300 (49.3); 371 (10.6)	quenched
4 $[(Me_2bpy)Re(CO)_3Br]^{21}$	368 (3.6)	584

Model compound **4** from reference [21]: $[(4\text{-}(4'\text{-methyl-}2,2'\text{-bipyridyl}))Re(CO)_3Br]$.

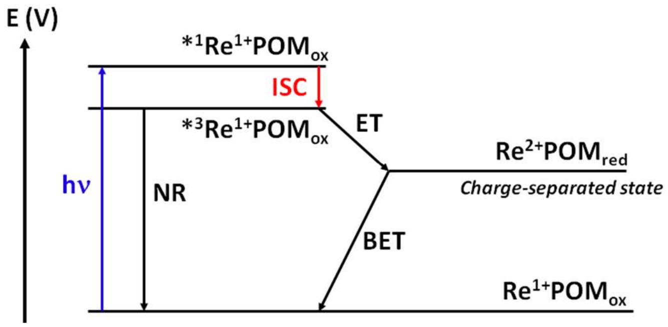

Figure **4.** Energy level diagram assumed for covalent hybrid **3**: photon absorption generates the singlet excited–state $(^{*1}Re^{1+}POM_{ox})$ which interconverts to the triplet state $(^{*3}Re^{1+}POM_{ox})$ by Inter-System Crossing (ISC). In general, radiative decay of the triplet state to the ground state is in competition with two other processes: non-radiative decay (NR) and electron transfer (ET) to the charge separated state with subsequent back electron transfer (BET). Here the observed luminescence quenching of the Re is attributed to ET from the *Re to the POM.

Conclusions

In conclusion, we have synthesized the first Re^I complex grafted to a POM by way of an organic spacer which displays the independent properties of the Re^I(α-diimine) moiety and the POM moiety. Photoinduced electron tranfer from the Re^I-bipyridine MLCT quenches the inherent luminescence of the rhenium complex. This modular synthetic approach allows fine tuning of both the redox and photo-active units. We are currently working on the monoelectronic photochemistry of charge transfer hybrid **3** for light-driven H_2 evolution in solution.

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Notes and references

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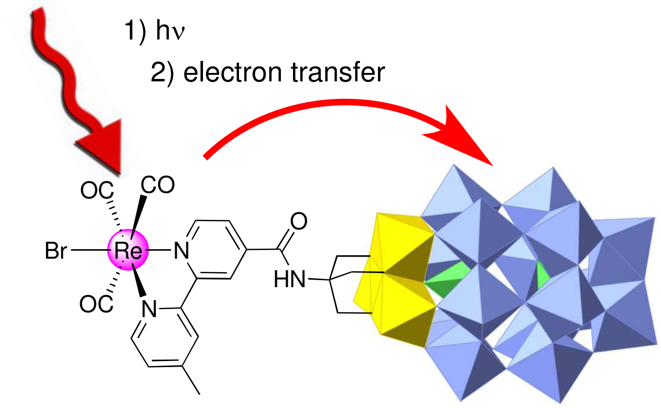

A polyoxometalate functionalized with bipyridine was successfully combined with a {Re(CO)$_3$Br} moiety and the hybrid exhibits the intrinsic properties of both subunits.

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