Supplementary Information

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

Marie-Pierre Santoni, a,b Amlan K. Pal, a Garry S. Hanan,* a Marie-Christine Tang, a Alexandra Furtos, a Bernold Hasenknopf* b

Electronic Supporting Information

Materials and Instrumentation ................................................................................................2

Synthesis and characterization ..............................................................................................3

Bpy-amide-triol ligand, 1 ........................................................................................................3
Dawson POM-Bpy TBA$_5$H$_{C_{16}H_{16}N_3O_{63}P_2V_3W_{15}}$, 2 .................................................................4
Fig. 1. ESI-MS full spectrum for 2 ..........................................................................................5
Fig. 2. Isotopic distribution for [2+3TBA]$^{3-}$ .......................................................................6
Hybrid Re-POM TBA$_5$H$_2$[(2)(Re(CO)$_3$Br], 3 .........................................................................6
Fig. 3. ESI-MS full spectrum for 3 ..........................................................................................7
Fig. 4. Isotopic distribution for [3+3TBA]$^{3-}$ .......................................................................8
Fig. 5. $^1$H NMR spectrum for 3 ............................................................................................8
Fig. 6. $^{31}$P NMR spectrum for 3 ............................................................................................9
Fig. 7. Cyclovoltamogram and SW voltamogram for 1 in DMF ..............................................10
Fig. 8. Cyclovoltamogram and SW voltamogram for 2 in CH$_3$CN .........................................11
Fig. 9. Cyclovoltamogram and SW voltamogram for 3 in CH$_3$CN .........................................12
Fig. 10. Electronic absorption spectra in the UV-visible for 2-3 ..............................................13
Fig. 11. IR spectra for 2-3 ........................................................................................................14
Fig. 12. Redox diagram and scheme for electron transfer between Re$^I$ complex and POM ....15

References ................................................................................................................................16
Materials and Instrumentation

All available chemicals were purchased from commercial sources and used as received: 2-amino-2-hydroxymethyl-propane-1,3-diol, thionyl chloride, triethylamine, potassium carbonate, 4,4’-dimethyl-2,2’-dipyridyl. Dry solvents and amines were kept in Schlenk flasks, under nitrogen, on activated molecular sieves. Precursors were synthesized following published procedures: TBA$_5$[H$_4$P$_2$V$_3$W$_{15}$O$_{62}$], Re(CO)$_5$Br. Precursor ligand ((4-COOEt)(4’-Me)bpy) was prepared following previous reports starting from 4,4’-dimethyl-2,2’-dipyridyl oxidized to the corresponding acid ((4-COOH)(4’-Me)bpy) and then esterified (neat thionyl chloride at reflux and subsequent treatment in absolute ethanol).

Nuclear magnetic resonance (NMR) spectra were recorded in deuterated solvents at room temperature (r.t.) on Bruker AV spectrometers at 300, 400, 500 or 700 MHz for $^1$H NMR and at 75, 100, 125 or 175 MHz for $^{13}$C NMR (as stated in each case). Chemical shifts are reported in part per million (ppm) relative to residual solvent protons (for example, 1.94 ppm for acetonitrile-$d_3$) and the carbon resonance of the solvent. IR spectra were recorded using KBr pellets (unless otherwise stated) on a Perkin-Elmer Spectrum One FT-IR spectrometer, ranging from 500 to 4000 cm$^{-1}$. Relative intensities are given after the wavenumber as vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad. Accurate mass measurements were performed on a 6210 TOF mass spectrometer from Agilent technologies, coupled to a 1100 series LC system in negative (or positive) electrospray mode. Appropriate [M]$^{n-}$ species were used for empirical formula determination, exact masses were calculated and images were produced using mMass Software. Electrochemical measurements were carried out in the dry and argon-purged stated solvent (acetonitrile or N,N’-dimethylformamide), at r.t. with a BAS CV50W multipurpose equipment interfaced to a PC. The working electrode was a glassy carbon electrode. The counter electrode was a Pt wire, and the pseudo-reference electrode was a silver wire. The reference was set using the redox couple ferrocene/ferrocinium at 395 mV vs. SCE in acetonitrile, and at 432 mV vs. SCE in DMF (internal reference). The concentration in analyte was about 1 mM, unless otherwise stated. Tetrabutylammonium hexafluorophosphate (TBAPF$_6$) was used as supporting electrolyte and its concentration was 0.10 M. Cyclic voltammograms were obtained at scan rates between 50 and 500 mV/s and were stated in each case. For irreversible processes, we used the cathodic potential determined by OSWV. The criteria for
reversibility were the separation of 60 mV between cathodic and anodic peaks, the close to unity ratio of the intensities of the cathodic and anodic currents, and the constancy of the peak potential on changing scan rate. The number of exchanged electrons was established using OSWV. Adsorption phenomena of POMs on glassy C electrode are known to enlarge signals. Absorption spectra, in acetonitrile solution at r.t. have been obtained with a Cary 500iUV-vis-NIR spectrophotometer. Experimental uncertainties are as follows: UV-visible absorption maxima, ±2 nm; UV-visible molar absorption coefficient, 10%; redox potentials, ±10 mV; IR absorption maxima, ±4 cm⁻¹.

**Synthesis and characterization**

**Bpy-amide-triol ligand, 1**
Following published procedure, the solid ester (762 mg, 3.15 mmol) was dissolved in dry DMSO (10 mL) before H₂N-C(CH₂OH)₃ (318 mg, 2.62 mmol) and K₂CO₃ (394 mg, 2.83 mmol) were added. The mixture was stirred under N₂ for 68h at r.t. Insoluble K₂CO₃ was filtered off and the filtrate was concentrated to maximum (a few milliliters) under vacuum at 80-90°C. The resulting oil was triturated in Et₂O, dissolved in EtOH and precipitated in water. The solid was filtered and dried to give 1 (416 mg, 50 %). ¹H NMR (d₆-DMSO, 400 MHz, 298 K)*: δ 8.86 (d, J = 5 Hz, 1H), 8.76 (s, 1H, H₃'), 8.66 (d, J = 5 Hz, 1H), 8.50 (br, 1H, Hₐ), 7.87 (d, 1H), 7.50 (d, J = 4 Hz, 1H), 3.69 (d, J = 4 Hz, 6H, H₃), 2.54 (s, H₄). ¹³C NMR (d₆-DMSO, 100 MHz, 298 K): δ 165.8; 164.8; 164.2; 150.8; 150.1; 144.5; 140.1; 138.2; 127.0; 124.2; 123.9; 120.1; 59.9; 21.5. ESI-MS: [M+H]⁺ calcd for C₁₆H₂₀N₅O₄ 318.1448; found 318.1448.
*¹H NMR chemical shifts for 1 in DMSO were found to be concentration dependant (variations of 0.1-0.3 ppm), probably due to intermolecular H-bonding in solution.
Dawson POM TBA₅H[C₁₆H₁₆N₅O₆₃P₂V₃W₁₅], 2

TBA₅[H₄P₂V₃W₁₅O₆₃] (494 mg, 0.095 mmol), 1 (30 mg, 0.094 mmol) were suspended in dry DMAc (2 mL). The mixture was heated in the dark at 80°C for 16 days. The obtained brown solution was left to cool down and then added to Et₂O to precipitate the product. The yellow fine solid was centrifugated, solubilized in minimum acetone (a few drops of EtOH were added) and reprecipitated with Et₂O to give 2 (0.450 g, 87%). ¹H NMR (CD₃CN, 400 MHz, 298 K): δ 8.86 (br, 1+1H), 8.70 (br, 1H), 8.52 (br, 1H), 8.15 (s, 1H), 7.92 (br, 1H), 7.65 (br, 1H), 5.88 (s, 6H, H₄), 3.16 (m, 40H, -NCH₂-), 2.51 (s, 3H, H₄), 1.66 (m, 40H, -NCH₂CH₂-), 1.42 (q, J = 10 Hz, 40H, -NCH₂CH₂CH₂CH₂-), 1.01 (t, J = 8 Hz, 60H, -NCH₂CH₂CH₂CH₂). ³¹P NMR (CD₃CN, 162 MHz, 298 K): -7.06, -13.12. IR (KBr pellet, cm⁻¹): 2969 (ν C-H, s), 2933 (ν C-H, s), 2869 (ν C-H, s), 1720 (w), 1667 (ν C=O, w), 1640 (w), 1553 (w), 1490 (δ C-H, m), 1463 (w), 1386 (δ C-H, w), 1296 (w), 1151 (w), 1087 (ν C-O, s), 1074 (ν C-O, w), 1033 (w), 952 (ν V=O, vs), 914 (ν W=O, vs), 820 (ν M-O-M, vs), 737 (ν M-O-M, vs). ESI-MS: [M+4TBA]²⁻ calcd for C₈₀H₁₆₀N₇O₆₃P₂V₃W₁₅ 2600.4988; found 2600.4932. Anal. Caled for (C₈₀H₁₆₀N₇O₆₃P₂V₃W₁₅): C, 21.18; H, 3.65; N, 2.06. Found: C, 20.58; H, 3.75; N, 2.08.
ESI-MS:

<table>
<thead>
<tr>
<th>Composition</th>
<th>Formula</th>
<th>Simulated</th>
<th>Observed</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>[M+H]$^+$</td>
<td>C$<em>{16}$H$</em>{18}$N$_5$O$_6$S$<em>3$W$</em>{15}$</td>
<td>846.7746</td>
<td>846.7766</td>
<td>1.7 x 10$^4$</td>
</tr>
<tr>
<td>[M+TBA]$^+$</td>
<td>C$<em>{32}$H$</em>{53}$N$_4$O$_6$S$<em>3$W$</em>{15}$</td>
<td>894.8301</td>
<td>894.8150</td>
<td>8.5 x 10$^4$</td>
</tr>
<tr>
<td>[M+2H]$^+$</td>
<td>C$<em>{16}$H$</em>{19}$N$_5$O$_6$S$<em>3$W$</em>{15}$</td>
<td>1058.2163</td>
<td>1058.2183</td>
<td>2.2 x 10$^4$</td>
</tr>
<tr>
<td>[M+TBA+H]$^{4+}$</td>
<td>C$<em>{32}$H$</em>{54}$N$_4$O$_6$S$<em>3$W$</em>{15}$</td>
<td>1118.7595</td>
<td>1118.7879</td>
<td>3.0 x 10$^4$</td>
</tr>
<tr>
<td>[M+TBA+H+CH$_3$CN]$^{4+}$</td>
<td>C$<em>{34}$H$</em>{56}$N$_4$O$_6$S$<em>3$W$</em>{15}$</td>
<td>1129.2961</td>
<td>1129.3356</td>
<td>7.0 x 10$^4$</td>
</tr>
<tr>
<td>[M+2TBA]$^{4+}$</td>
<td>C$<em>{48}$H$</em>{89}$N$_5$O$_6$S$<em>3$W$</em>{15}$</td>
<td>1179.3587</td>
<td>1179.3570</td>
<td>2.0 x 10$^3$</td>
</tr>
<tr>
<td>[M+3H+CH$_3$CN]$^{3-}$</td>
<td>C$<em>{19}$H$</em>{23}$N$_4$O$_6$S$<em>3$W$</em>{15}$</td>
<td>1425.6384</td>
<td>1425.6384</td>
<td>1.6 x 10$^4$</td>
</tr>
<tr>
<td>[M+2TBA+H]$^{3-}$</td>
<td>C$<em>{48}$H$</em>{90}$N$_5$O$_6$S$<em>3$W$</em>{15}$</td>
<td>1572.8142</td>
<td>1572.8114</td>
<td>4.0 x 10$^4$</td>
</tr>
<tr>
<td>[M+3TBA]$^{3-}$</td>
<td>C$<em>{64}$H$</em>{125}$N$_6$O$_6$S$<em>3$W$</em>{15}$</td>
<td>1653.2399</td>
<td>1653.2346</td>
<td>1.2 x 10$^5$</td>
</tr>
<tr>
<td>[M+4TBA]$^{2-}$</td>
<td>C$<em>{80}$H$</em>{160}$N$_7$O$_6$S$<em>3$W$</em>{15}$</td>
<td>2600.4988</td>
<td>2600.4932</td>
<td>2.5 x 10$^4$</td>
</tr>
</tbody>
</table>

Figure 1. ESI-MS full spectrum for 2 (negative mode).
Figure 2. Isotopic distribution of the peak for \([M+3TBA]^{-3}\) at m/z = 1653.2346 (red: experimental; blue: calculated) for bpy-functionalized POM 2.

Dawson POM TBA$_5$H[C$_{19}$H$_{16}$N$_3$BrO$_6$P$_2$Re$_3$W$_{15}$], 3

Following usual complexation conditions for bipyridyl ligands on Re(I) carbonyl precursors. 2 (152 mg, 0.0279 mmol) and Re(CO)$_5$Br (0.011 g, 0.0279 mmol) were refluxed in dry CH$_3$CN overnight in the dark. After cooling down to r.t., the resulting clear yellow solution was evaporated to dryness. The product was extracted from this residue by trituration in DCM. The yellow filtrate was evaporated and its residue triturated in THF. The yellow solid was collected, washed with THF and dried under vacuum, affording 3 (27 mg, 17%). $^1$H NMR (CD$_3$CN, 400 MHz, 298 K): $\delta$ 9.10 (t, $J = 6$ Hz, 1H, $H_5$), 8.87 (t, $J = 6$ Hz, 1H, $H_5'$), 8.75 (s, 1H,
$H_3$, 8.51 (s, 1H, $H_3$), 7.92 (d, $J = 4$ Hz, 1H, $H_6$), 7.49 (d, $J = 4$ Hz, 1H, $H_6$), 7.11 (s, 1H, $H_2$), 5.91 (s, 6H, $H_2$), 3.16 (m, 32H, -NCH$_2$-), 2.60 (s, 3H, $H_4$), 1.66 (m, 32H, -NCH$_2$CH$_2$-), 1.42 (q, $J = 10$ Hz, 32H, -NCH$_2$CH$_2$-), 1.01 (t, $J = 8$ Hz, 48H, -NCH$_2$CH$_2$CH$_2$-).

$^{31}$P NMR (CD$_3$CN, 162 MHz, 298 K): -7.36, -12.73. IR (KBr pellet, cm$^{-1}$): 2963 (v C-H, s), 2926 (v C-H, s), 2869 (v C-H, s), 2019 (v C=O(Re), s), 1913 (v C=O(Re), s), 1980 (v C=O(Re), s), 1658 (v C-O, s), 1617 (sh), 1483 ($\delta$ C-H, m), 1461 (m), 1383 ($\delta$ C-H, m), 1270 (w), 1150 (w), 1086 (v C-O, s), 1060 (v C-O, w), 1024 (w), 951 (v V=O, vs), 912 (v W=O, vs), 883 (w), 816 (v M-O-M, vs), 730 (v M-O-M, vs), 598 (w), 595 (w), 530 (w). ESI-MS: [M+TBA]$^{5-}$ calcd for C$_{35}$H$_{52}$BrN$_4$O$_{66}$P$_2$ReV$_3$W$_{15}$ 964.8008; found 964.7990. Anal. Calcd for (C$_{16}$H$_{36}$N)$_4$H$_2$ [P$_2$W$_{15}$V$_3$O$_{66}$C$_{16}$H$_{16}$N$_3$Re(CO)$_3$Br]: C, 17.95; H, 2.94; N, 1.77. Found: C, 18.03; H, 2.94; N, 1.92.

ESI-MS:

<table>
<thead>
<tr>
<th>Composition</th>
<th>Formula</th>
<th>Simulated</th>
<th>Observed</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>[M+TBA]$^{5-}$</td>
<td>C$<em>{35}$H$</em>{52}$BrN$<em>4$O$</em>{66}$P$_2$ReV$<em>3$W$</em>{15}$</td>
<td>964.8008</td>
<td>964.9891</td>
<td>7.8 x 10$^4$</td>
</tr>
<tr>
<td>[M+2TBA]$^{4-}$</td>
<td>C$<em>{51}$H$</em>{88}$BrN$<em>5$O$</em>{66}$P$_2$ReV$<em>3$W$</em>{15}$</td>
<td>1266.5714</td>
<td>1266.5546</td>
<td>8.8 x 10$^4$</td>
</tr>
<tr>
<td>[M+3TBA]$^{3-}$</td>
<td>C$<em>{67}$H$</em>{124}$BrN$<em>6$O$</em>{66}$P$_2$ReV$<em>3$W$</em>{15}$</td>
<td>1769.5235</td>
<td>1769.4952</td>
<td>5.0 x 10$^3$</td>
</tr>
</tbody>
</table>

Figure 3. ESI-MS full spectrum for 3 (negative mode).
Figure 4. Isotopic distribution of the peak for \([\text{M}+3\text{TBA}]^{3-}\) at m/z = 1769.4952 (red: experimental; blue: calculated) for hybrid 3.

Figure 5. \(^1\text{H} \) NMR spectrum for 3.
Figure 6. $^{31}$P NMR spectrum for 3.
Electrochemistry

During CV measurements, several parameters were investigated (scan rate, potential range). Also, reproducibility of measurements was verified by: (i) repeated separate scans on freshly polished electrode; (ii) doing several loops/cycles. Significant adsorption of analyte was observed with increasing number of cycles. For clarity, we only show the first cycle of the CV measurements.
Figure 7. Cyclovoltamogram (top, scan-rate: 100 mV/s) and Square-Wave voltamogram (bottom) for 1 in DMF.

Figure 8. Cyclovoltamogram (top, scan-rate: 100 mV/s) and Square-Wave voltamogram (bottom) for 2 in CH$_3$CN.
Figure 9. Cyclovoltamogram (top - scan-rate: 100 mV/s) and Square-Wave voltamogram (bottom) of 3 in CH$_3$CN.
UV spectroscopy

Figure 10. Absorption spectra of 2 and 3 recorded in CH$_2$CN. The absorption of hybrid 3 is improved in the visible due to the chromophore and correspond to the addition of its sub-units (POM and coordination complex of Re(I)) confirming the electronic decoupling between them in the ground state.
IR spectroscopy

Figure 11. IR spectra for 2 and 3 (KBr pellet).
Luminescence measurements were performed in order to investigate the intramolecular interaction between POM and Re units in the ground/excited states. With similar interests, Lindsey et al. reported a supramolecular system composed of two photoactive units covalently linked via amide bond: a [Re(α-diimine)(CO)3Br] complex and a Zn-tetraphenylporphyrin. ReI(L)(CO)3Br complexes (L = derivatized bipyridine) typically emit in the 500-600 nm range due to radiative relaxation of the 3MLCT excited state. Model compound [(Me2bpy)Re(CO)3Br] absorbs at 368 nm and emits at 584 nm in DMF solution. In Lindsey’s dyad, no emission from the 3MLCT excited state of the Re moiety could be detected in the expected region under their experimental conditions (for comparison, the emission of model Re(CO)3Br(bpy) 6 was detected between 580 and 670 nm with a lifetime of 63 ns). The authors attributed the quenching of luminescence of the Re complex in the dyad either to the ZnTPP or to a significant decrease in the lifetime of the emission due to the presence of the ZnTPP (lifetime shorter than the instrumental limits).

In hybrid 3, the \{ReI(L)(CO)3Br\} moiety was found to have a maximum absorbance at 371 nm. Here the well-known electron acceptor character of the POM and the suitable redox potential of both partners are in favor of luminescence quenching by electron transfer for the *Re to the POM. Preliminary time-resolved measurements for absorption and emission indicated that the processes were fast, below the ns regime (limit of our instrumentation).
References


