Supplementary Information

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

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Electronic Supporting Information

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 synthezised following published procedures: $TBA_5[H_4P_2V_3W_{15}O_{62}]$,[i] $Re(CO)_5Br$.[ii] Precursor ligand ((4-COOEt)(4'-Me)bpy) was prepared following previous reports[iii] 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 temperatutre (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.[iv] 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}.

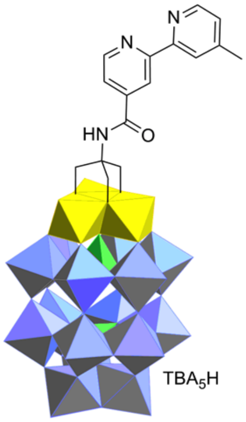
Synthesis and characterization

Bpy-amide-triol ligand, 1

Following published procedure,[v] the solid ester (762 mg, 3.15 mmol) was dissolved in dry DMSO (10 mL) before $H_2N\text{-}C(CH_2OH)_3$ (318 mg, 2.62 mmol) and K_2CO_3 (394 mg, 2.83 mmol) were added. The mixture was stirred under N_2 for 68h at r.t. Insoluble K_2CO_3 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 Et_2O, dissolved in EtOH and precipitated in water. The solid was filtered and dried to give **1** (416 mg, 50 %). ^1H NMR (d_6-DMSO, 400 MHz, 298 K)*: δ 8.86 (d, $J = 5$ Hz, 1H), 8.76 (s, 1H, $H_{3'}$), 8.66 (d, $J = 5$ Hz, 1H), 8.50 (br, 1H, H_a), 7.87 (d, 1H), 7.50 (d, $J = 4$ Hz, 1H), 3.69 (d, $J = 4$ Hz, 6H, H_b), 2.54 (s, $H_{4''}$). ^{13}C NMR (d_6-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 $C_{16}H_{20}N_3O_4$ 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 $TBA_5H[C_{16}H_{16}N_3O_{63}P_2V_3W_{15}]$, 2



2

$TBA_5[H_4P_2V_3W_{15}O_{62}]$ (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 Et_2O to precipitate the product. The yellow fine solid was centrifugated, solubilized in minimum acetone (a few drops of EtOH were added) and reprecipitated with Et_2O to give **2** (0.450 g, 87%). ^{1}H NMR (CD_3CN, 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, H_b), 3.16 (m, 40H, -NCH_2-), 2.51 (s, 3H, $H_{4''}$), 1.66 (m, 40H, -$NCH_2$$CH_2$-), 1.42 (q, J = 10 Hz, 40H, -$NCH_2CH_2$$CH_2$-), 1.01 (t, J = 8 Hz, 60H, -$NCH_2CH_2CH_2$$CH_3$). ^{31}P NMR ($CD_3CN$, 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 $C_{80}H_{160}N_7O_{63}P_2V_3W_{15}$ 2600.4988; found 2600.4932. Anal. Calcd for $(C_{16}H_{36}N)_5H[C_{16}H_{16}N_3O_{63}P_2V_3W_{15}]$: C, 21.18; H, 3.65; N, 2.06. Found: C, 20.58; H, 3.75; N, 2.08.

ESI-MS:

Composition	**Formula**	**Simulated**	**Observed**	**Intensity**
$[M+H]^{5-}$	$C_{16}H_{18}N_3O_{63}P_2V_3W_{15}$	846.7746	846.7766	1.7 x 10^4
$[M+TBA]^{5-}$	$C_{32}H_{53}N_4O_{63}P_2V_3W_{15}$	894.8301	894.8150	8.5 x 10^4
$[M+2H]^{4-}$	$C_{16}H_{19}N_3O_{63}P_2V_3W_{15}$	1058.2163	1058.2183	2.2 x 104
$[M+TBA+H]^{4-}$	$C_{32}H_{54}N_4O_{63}P_2V_3W_{15}$	1118.7595	1118.7879	3.0 x 10^4
$[M+TBA+H+CH_3CN]^{4-}$	$C_{34}H_{56}N_5O_{63}P_2V_3W_{15}$	1129.2961	1129.3356	7.0 x 10^4
$[M+2TBA]^{4-}$	$C_{48}H_{89}N_5O_{63}P_2V_3W_{15}$	1179.3587	1179.3570	2.0 x 10^5
$[M+3H+CH_3CN]^{3-}$	$C_{18}H_{23}N_4O_{63}P_2V_3W_{15}$	1425.6384	1425.6384	1.6 x 10^4
$[M+2TBA+H]^{3-}$	$C_{48}H_{90}N_5O_{63}P_2V_3W_{15}$	1572.8142	1572.8114	4.0 x 10^4
$[M+2TBA+H+CH_3CN]^{3-}$	$C_{50}H_{93}N_6O_{63}P_2V_3W_{15}$	1586.4897	1586.5382	5.0 x 10^4
$[M+3TBA]^{3-}$	$C_{64}H_{125}N_6O_{63}P_2V_3W_{15}$	1653.2399	1653.2346	1.2 x 10^5
$[M+4TBA]^{2-}$	$C_{80}H_{160}N_7O_{63}P_2V_3W_{15}$	2600.4988	2600.4932	2.5 x 10^4

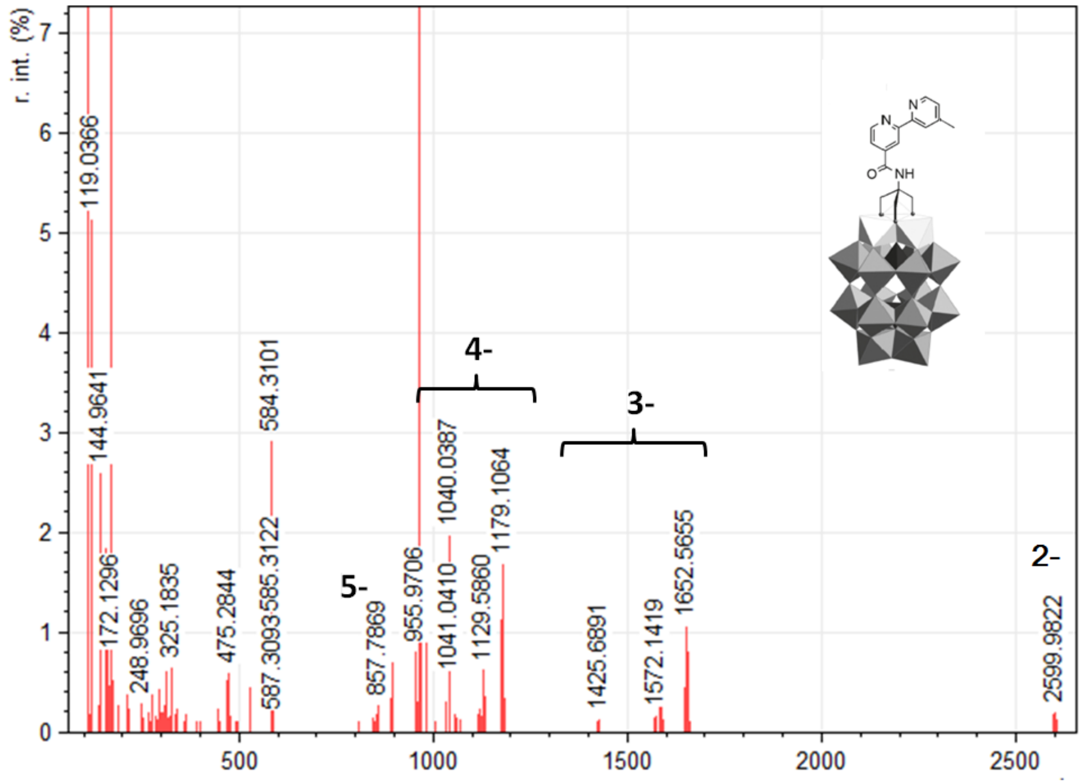


Figure 1. ESI-MS full spectrum for 2 (negative mode).

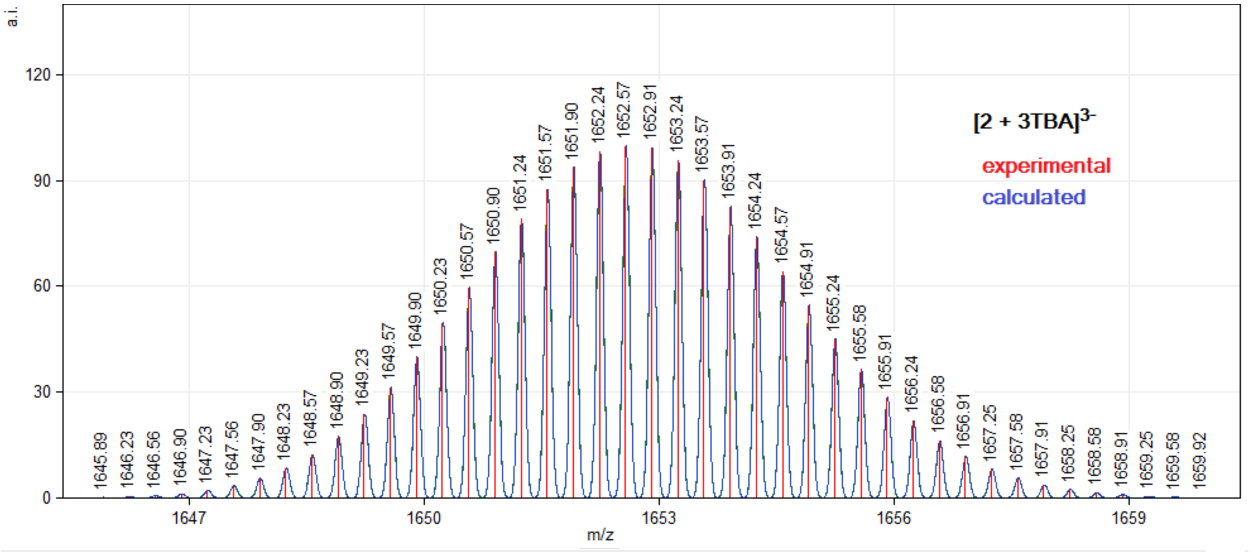
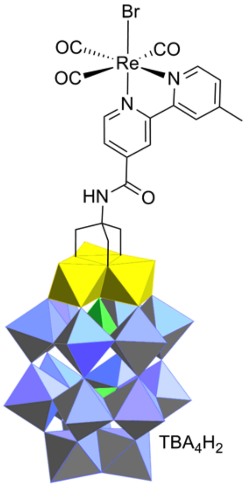


Figure 2. Isotopic distribution of the peak for $[M+3TBA]^{3-}$ at m/z = 1653.2346 (red: experimental; blue: calculated) for bpy-functionalized POM 2.

Dawson POM $TBA_5H[C_{19}H_{16}N_3BrO_{66}P_2ReV_3W_{15}]$, 3



3

Following usual complexation conditions for bipyridyl ligands on Re(I) carbonyl precursors. **2** (152 mg, 0.0279 mmol) and $Re(CO)_5Br$ (0.011 g, 0.0279 mmol) were refluxed in dry CH_3CN 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%). ^1H NMR (CD_3CN, 400 MHz, 298 K): δ 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$_a$*), 5.91 (s, 6H, *H$_b$*), 3.16 (m, 32H, -N*CH$_2$*-), 2.60 (s, 3H, *H$_{4''}$*), 1.66 (m, 32H, -NCH$_2$*CH$_2$*-), 1.42 (q, *J* = 10 Hz, 32H, -NCH$_2$CH$_2$*CH$_2$*-), 1.01 (t, *J* = 8 Hz, 48H, -NCH$_2$CH$_2$CH$_2$*CH$_3$*). ^{31}P NMR (CD_3CN, 162 MHz, 298 K): -7.36, -12.73. IR (KBr pellet, cm^{-1}): 2963 (ν C-H, s), 2926 (ν C-H, s), 2869 (ν C-H, s), 2019 (ν C=O(Re), s), 1913 (ν C=O(Re), s), 1890 (ν C=O(Re), s), 1658 (ν C=O, s), 1617 (sh), 1483 (δ C-H, m), 1461 (m), 1383 (δ C-H, m), 1270 (w), 1150 (w), 1086 (ν C-O, s), 1060 (ν C-O, w), 1024 (w), 951 (ν V=O, vs), 912 (ν W=O, vs), 883 (w), 816 (ν M-O-M, vs), 730 (ν M-O-M, vs), 598 (w), 595 (w), 530 (w). ESI-MS: [M+TBA]$^{5-}$ calcd for $C_{35}H_{52}BrN_4O_{66}P_2ReV_3W_{15}$ 964.8008; found 964.7990. Anal. Calcd for $(C_{16}H_{36}N)_4H_2[P_2W_{15}V_3O_{63}C_{16}H_{16}N_3Re(CO)_3Br]$: C, 17.95; H, 2.94; N, 1.77. Found: C, 18.03; H, 2.94; N, 1.92.

ESI-MS:

Composition	**Formula**	**Simulated**	**Observed**	**Intensity**
[M+TBA]$^{5-}$	$C_{35}H_{52}BrN_4O_{66}P_2ReV_3W_{15}$	964.8008	964.9891	7.8 x 10^4
[M+2TBA]$^{4-}$	$C_{51}H_{88}BrN_5O_{66}P_2ReV_3W_{15}$	1266.5714	1266.5546	8.8 x 10^4
[M+3TBA]$^{3-}$	$C_{67}H_{124}BrN_6O_{66}P_2ReV_3W_{15}$	1769.5235	1769.4952	5.0 x 10^3

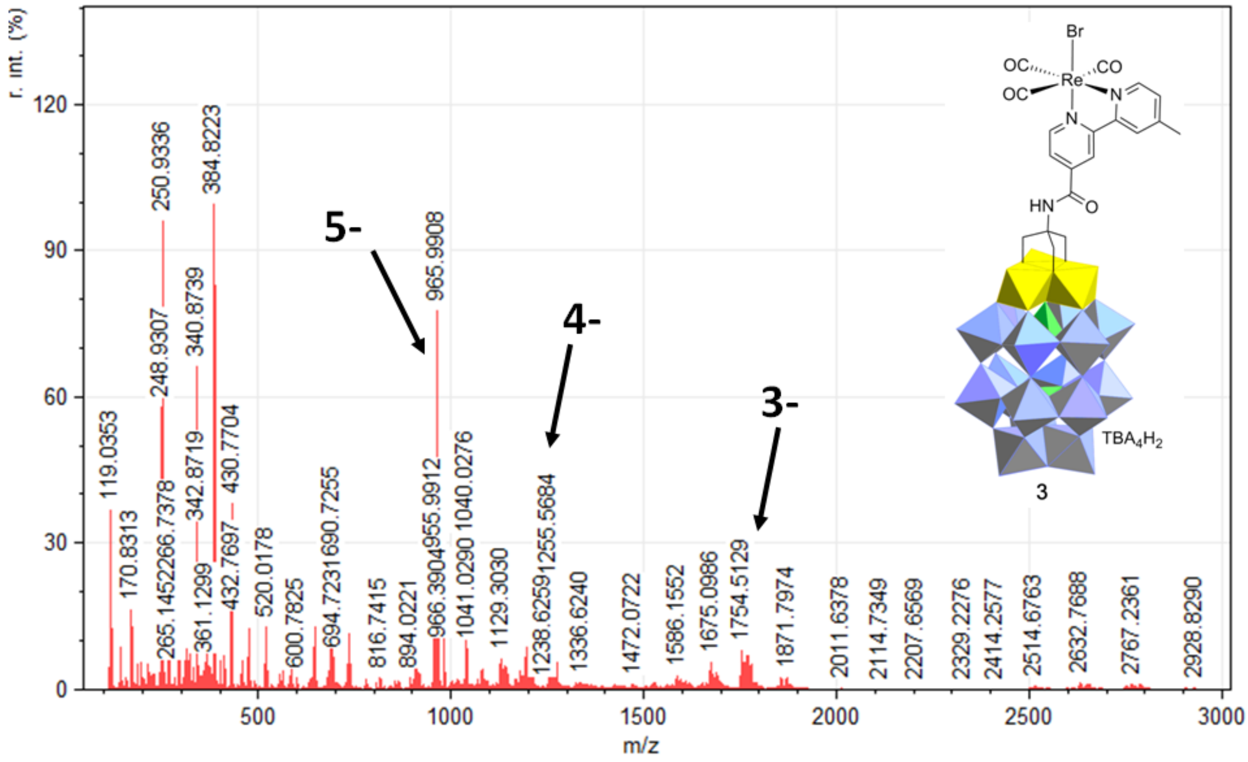


Figure 3. ESI-MS full spectrum for 3 (negative mode).

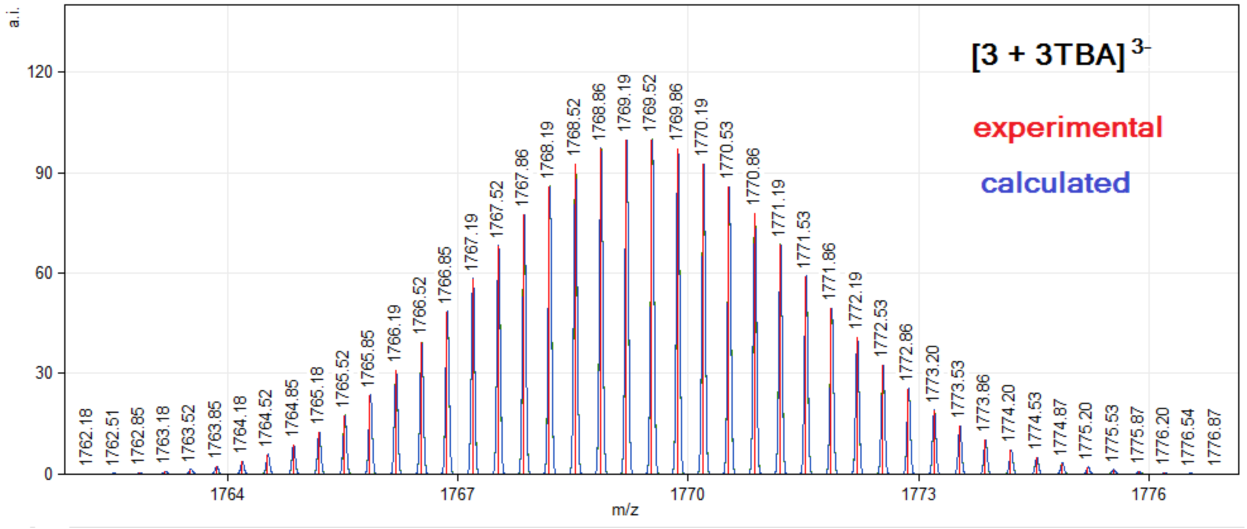


Figure 4. Isotopic distribution of the peak for [M+3TBA]$^{3-}$ at m/z = 1769.4952 (red: experimental; blue: calculated) for hybrid 3.

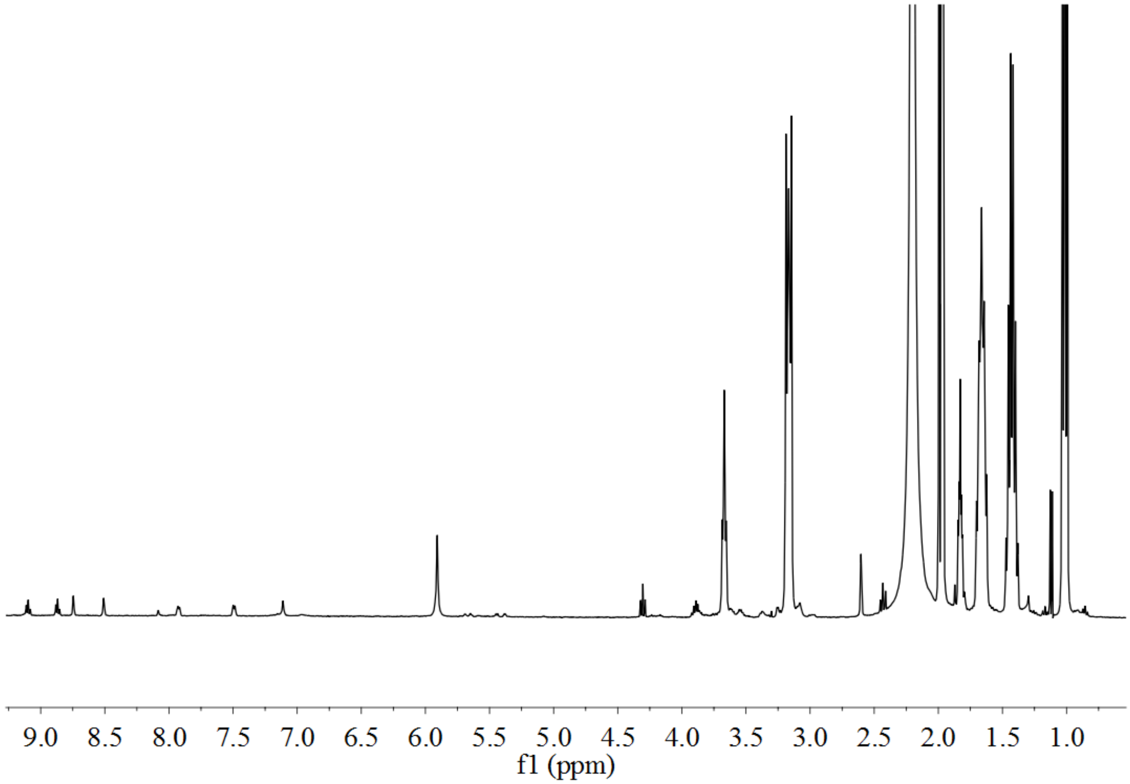


Figure 5. ^{1}H NMR spectrum for 3.

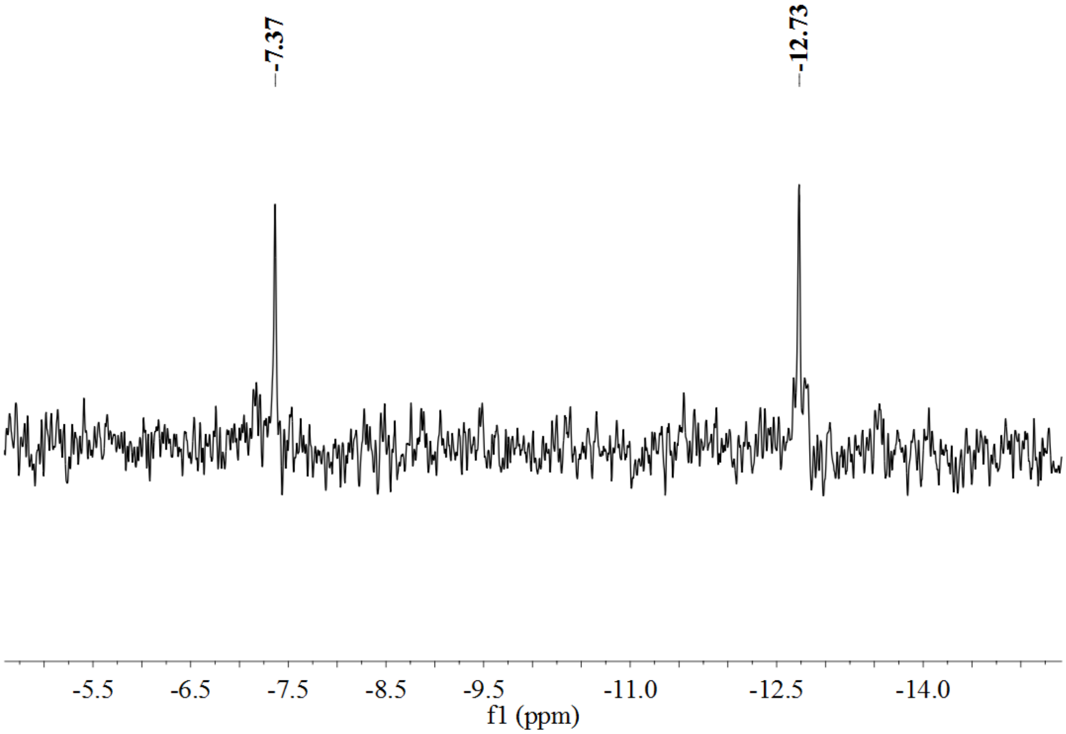
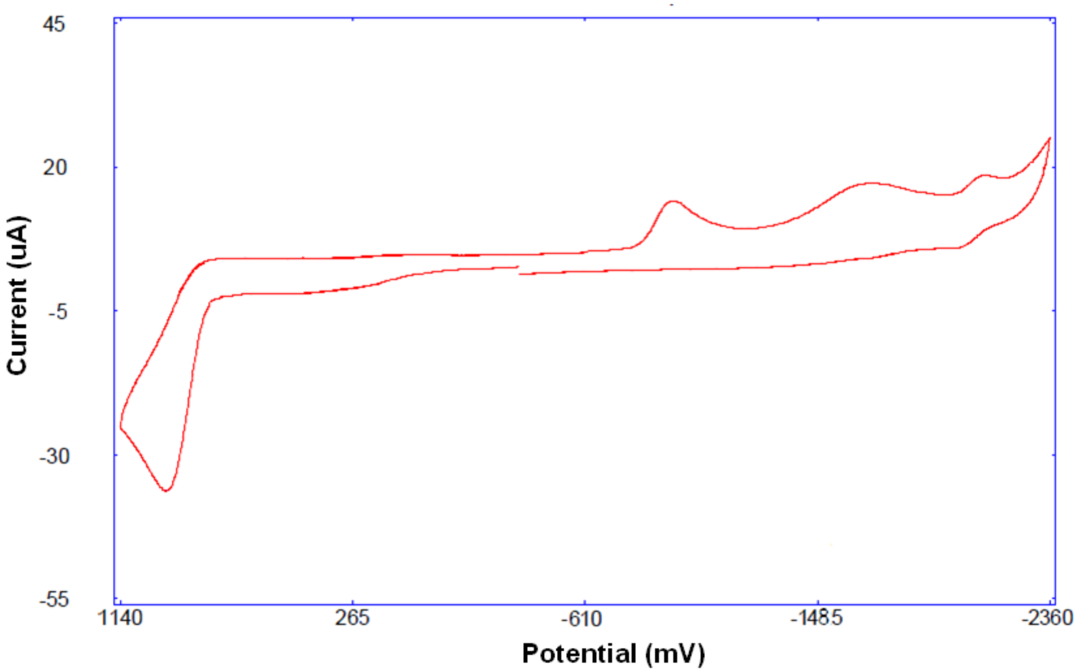


Figure 6. ^{31}P NMR spectrum for 3.

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.



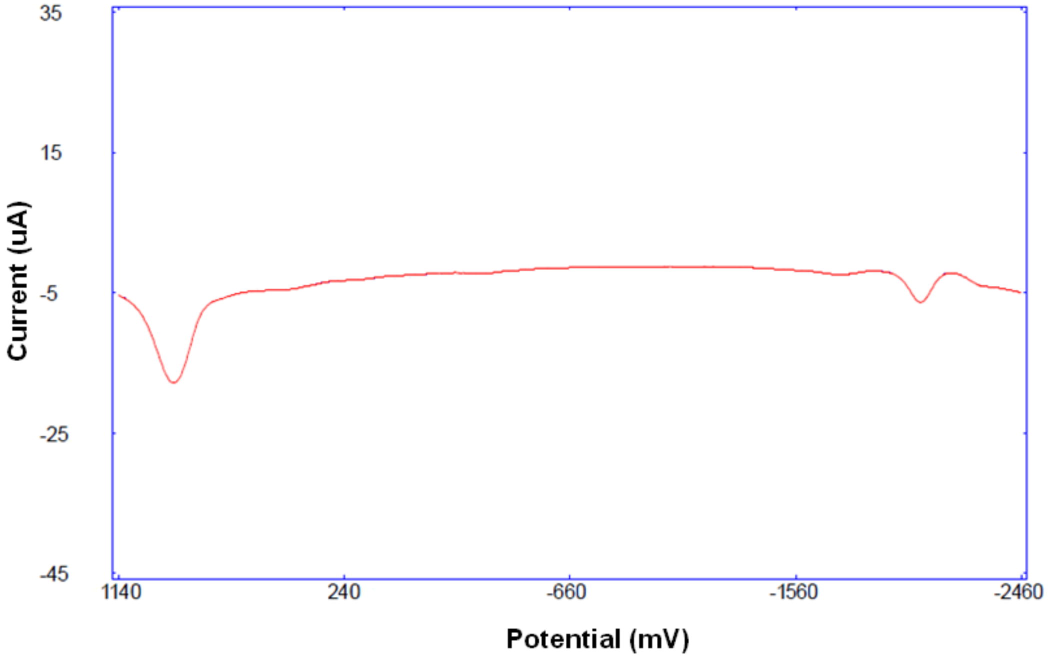


Figure 7. **Cyclovoltamogram (top, scan-rate: 100 mV/s) and Square-Wave voltamogram (bottom) for 1 in DMF.**

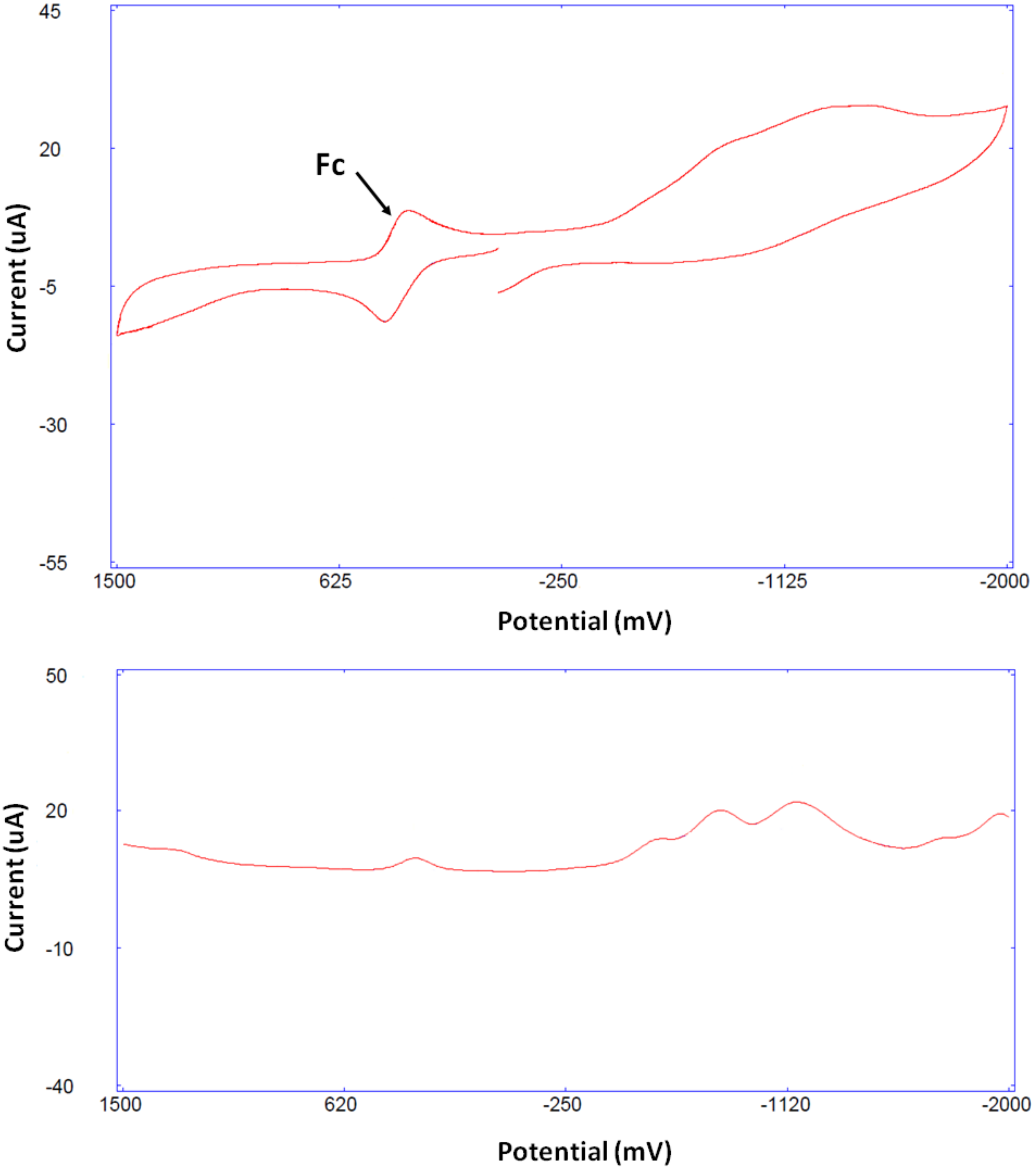


Figure 8. **Cyclovoltamogram (top, scan-rate: 100 mV/s) and Square-Wave voltamogram (bottom) for 2 in CH_3CN.**

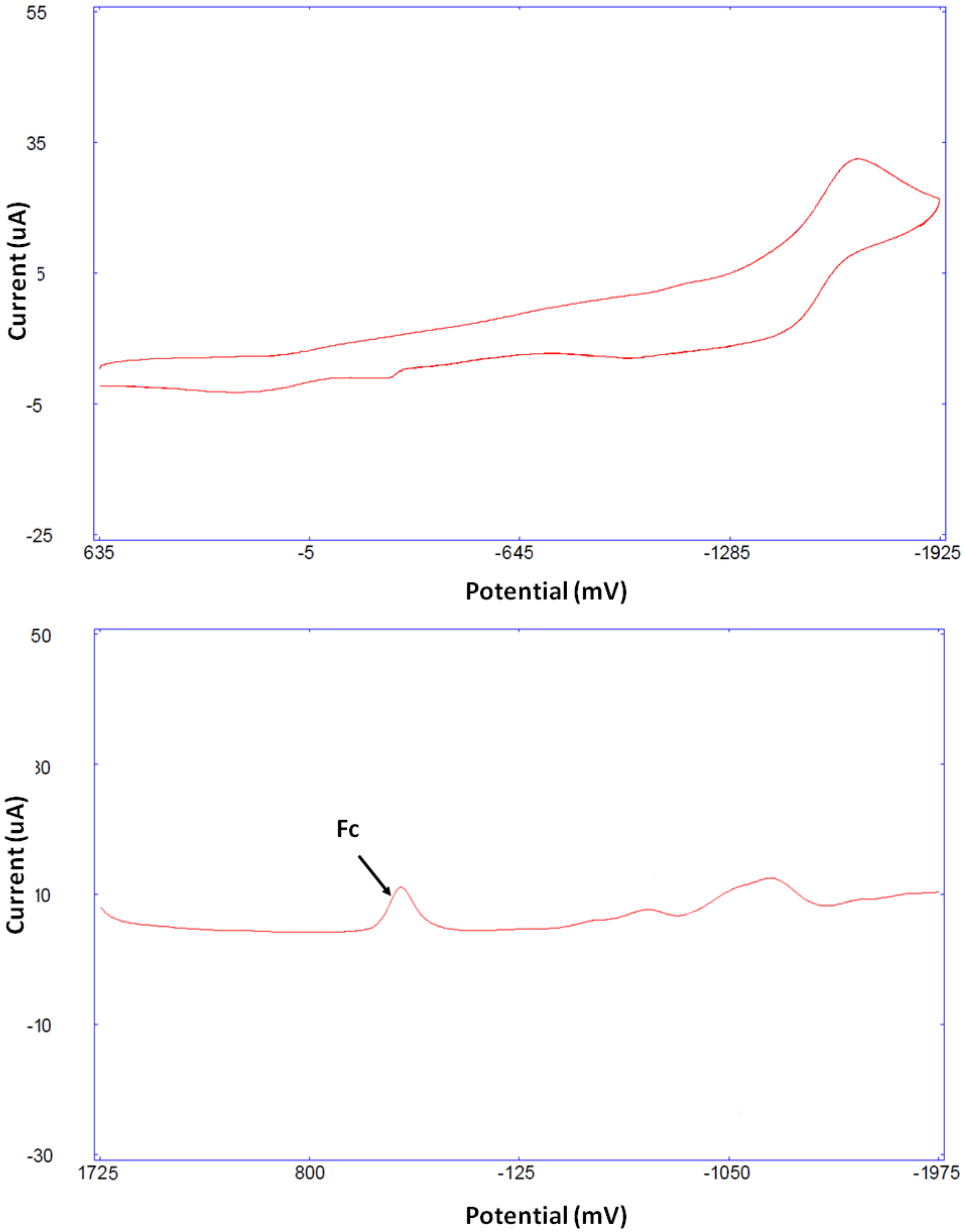


Figure 9. **Cyclovoltamogram (top - scan-rate: 100 mV/s) and Square-Wave voltamogram (bottom) of 3 in CH_3CN.**

UV spectroscopy

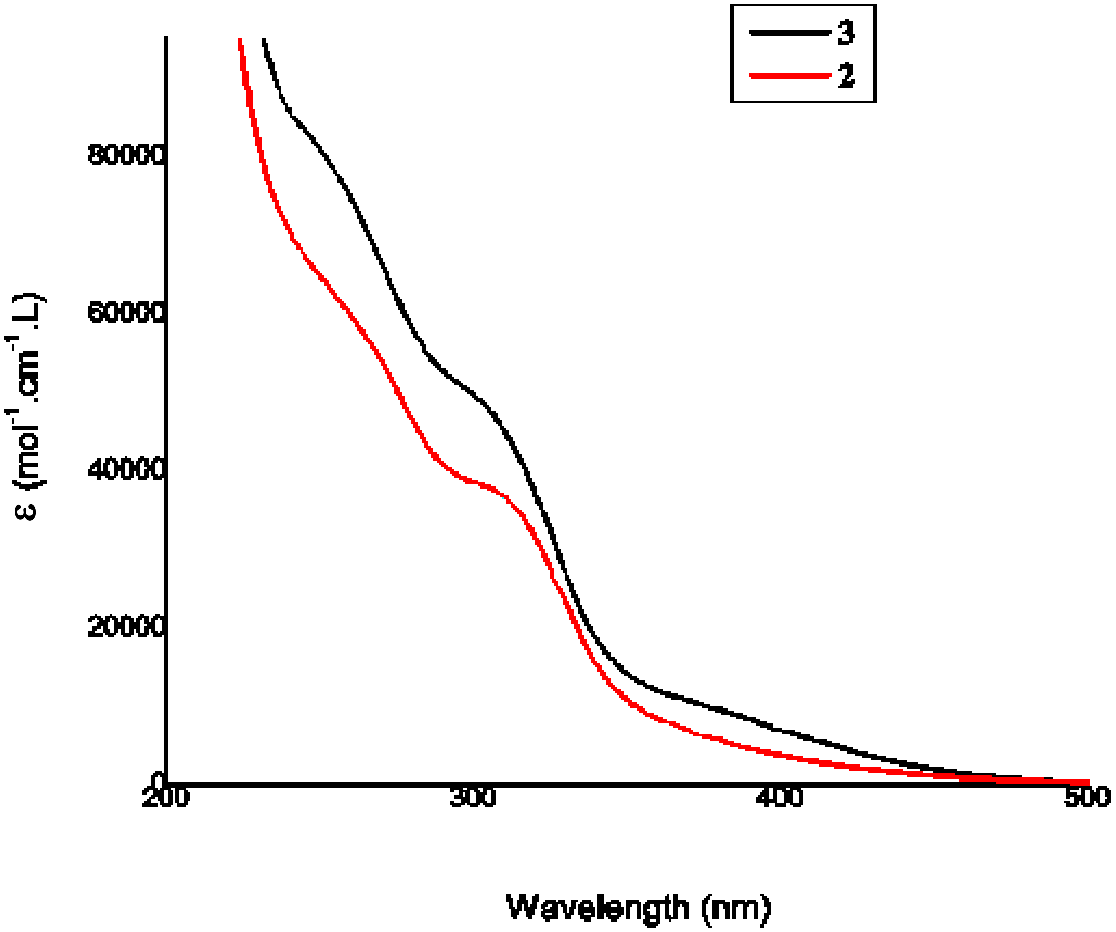


Figure 10. Absorption spectra of 2 and 3 recorded in CH_3CN. The absorption of hybrid 3 is improved in the visible due to the chromophore and correspond to the addition of its sub-units (POM and coordination complex of Re(I)) confirming the electronic decoupling between them in the ground state.

IR spectroscopy

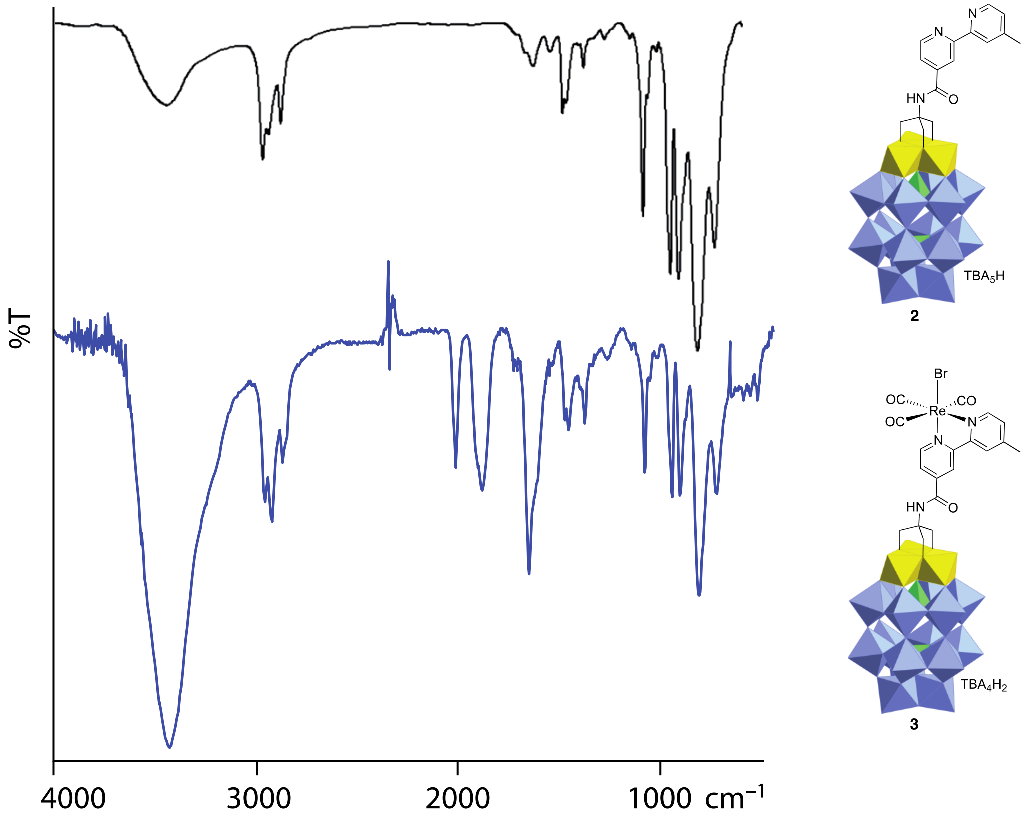


Figure 11. IR spectra for 2 and 3 (KBr pellet).

Photochemistry

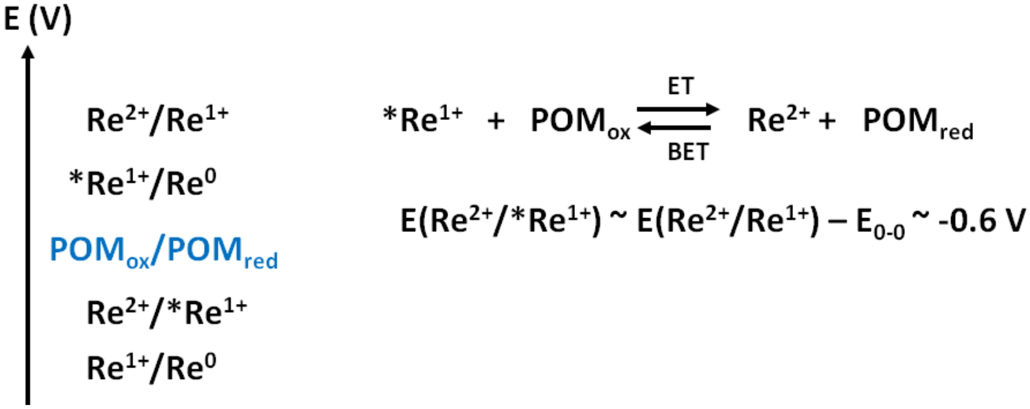


Figure 12. Redox diagram and scheme for electron transfer between Re^I complex and POM.

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)$_3$Br] complex and a Zn-tetraphenylporphyrin.[vi]
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. Model compound [(Me$_2$bpy)Re(CO)$_3$Br] absorbs at 368 nm and emits at 584 nm in DMF solution. In Lindsey's dyad, no emission from the ^{3}MLCT 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)$_3$Br(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 {Re^I(L)(CO)$_3$Br} 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

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