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Electronic Supporting Information

Covalent hybrids based on Re(I) tricarbonyl complexes and polypyridine-functionalized polyoxometalate: synthesis, characterization and electronic properties

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Materials and Instrumentation

Solvents and reagents were obtained from commercial sources (VWR, Fisher Scientific or Sigma Aldrich) and used as received, unless stated otherwise. $Re_2(CO)_{10}$ was purchased from Pressure Chemical Corporation. Nuclear magnetic resonance (NMR) spectra were recorded in deuterated solvents at room temperature (RT) on a Bruker AV spectrometer at 400MHz for ^1H NMR and 162MHz for ^{31}P NMR. Chemical shifts (δ) are reported in part per million (ppm) relative to residual proton resonance of the solvent (for example, 1.94 ppm for acetonitrile-D_3) and relative to pure phosphoric acid (0.0 ppm) for phosphorous resonance. IR spectra were recorded using an ATR sampler on a Bruker Alpha FT-IR spectrometer, ranging from 375 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. The high-resolution mass spectrometry (HR-MS) experiments were performed on a Bruker Daltonics MicroOTOF II in negative (or positive) electrospray mode, using HPLC grade solvents for the injected solutions. Appropriate $[M]^z$ species were used for empirical formula determination; exact masses were calculated and images were produced using mMass.[1] Electrochemical measurements were carried out in dry and nitrogen-purged solvents (freshly CaH_2 distilled acetonitrile or commercial anhydrous N,N-dimethylformamide stored in a glovebox) at RT with a BioLogic-SP50 potentiostat-galvanostat interfaced to a PC on which was installed the EC-lab software. The working electrode was a glassy carbon electrode (3mm diameter) which was polished with 0.05µm alumina paste before each sample. The counter electrode was a Pt wire and the pseudo-reference electrode was a silver wire placed in a vycor frit filled with a 0.1M solution of supporting electrolyte to keep it separated from the analyte. The reference was set using either ferrocenium/ferrocene (450mV vs. SCE in DMF[2]) or acetylferrocenium/ acetylferrocene (710 mV vs. SCE in acetonitrile[3]). The analyte concentration was about 1 mM and tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was used as supporting electrolyte at 0.10 M. Cyclic voltammograms were obtained at scan rates between 50 and 500 mV/s. For irreversible processes, we used the cathodic potential determined by square-wave measurements. Adsorption phenomena of POMs on glassy carbon electrode are known to enlarge signals and a desorption peak was sometimes observed and is identified on the cyclovoltammogram when observed. UV-visible absorption spectra at RT were acquired on a Cary 5000i UV-vis-NIR spectrophotometer while luminescence spectra were obtained on a Perkin-Elmer LS55 fluorescence spectrometer. For the luminescence lifetimes, an Edinburgh OB 900 single-photon-counting spectrometer was used, employing a Hamamatsu PLP2 laser diode as pulse (wavelength output, 408 nm; pulse width, 59 ps). Spectroscopic grade solvents were used to prepare the solution for the luminescence measurements which were nitrogen purged. The microanalyses were performed at the Elemental Analysis Service of the Université de Montréal.

Synthesis and characterization

As a general procedure, POMs were only manipulated with glass or plastic spatula and kept away from light to minimize the formation of partially reduced species.

Polypyridines with triol function

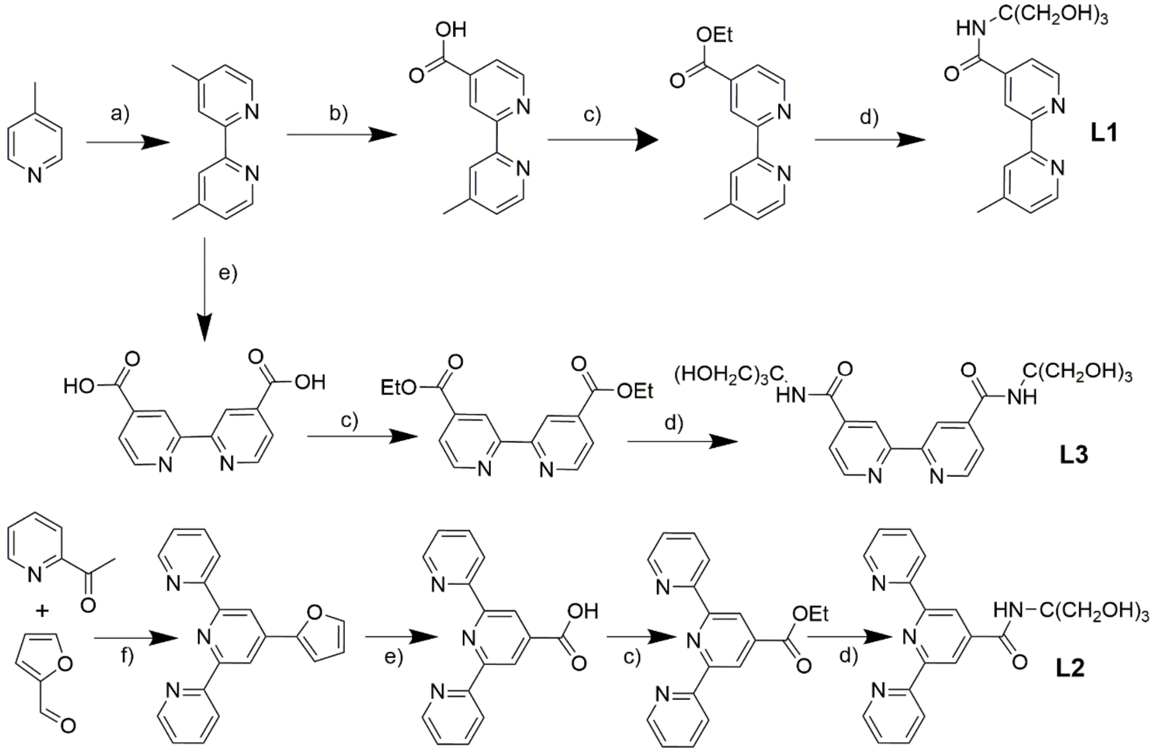


Figure S1 Synthetic pathways for L1, L2 and L3.
***a)** Pd/C, MnO_2, neat, 140°C 7d [4] **b)** 2 steps : SeO_2 in 1,4-dioxane at reflux 24h – $AgNO_3$, NaOH in EtOH/H_2O at RT overnight[5] **c)** anhyd. EtOH, conc. H_2SO_4 (cat.) at reflux for 3d[6] **d)** TRIS and K_2CO_3 in DMSO at RT for 2d[7] **e)** $KMnO_4$ and NaOH in H_2O (pH = 11) for 12h at reflux[8] and **f)** KOH and conc. NH_3(aq) in EtOH at RT 24h[9]*

L1 N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)-4'-methyl-[2,2'-bipyridine]-4-carboxamide

Prepared from the corresponding ethyl ester following a published protocol.[7c] 1.2eq of the solid ester were dissolved in dry DMSO, then K_2CO_3 (1.1eq) and TRIS (1eq) were added and the quasi colorless suspension was stirred under N_2 for 2 days. The suspension turned progressively to a limpid yellow solution. A few drops of EtOH were added to ensure that all the salts had precipitated before filtration. The solvents were then removed under vacuum on a rotary evaporator (a strong vacuum with a bath at 80°C max. was used in order to avoid the formation of oxazoline). The residual orange oily material is then dissolved in a minimum of anhydrous EtOH and a few drops of Et_2O were added till a precipitate started to appear. The solution was then poured in excess water and a white suspension was obtained. If precipitation wasn't immediate, partial evaporation on a rotary evaporator was performed to induce the apparition of a solid. The suspension was left for 24h at 4°C to maximize precipitation. The fine white solid was then filtered on a fine glass frit or on a 0.45µm Nylon membrane (centrifugation can be performed before filtration to facilitate it), washed with H_2O then Et_2O and dried under vacuum overnight. If needed, recrystallization using $CHCl_3$ was performed. Yield : 160mg (50% on a 1mmol scale)

^1H NMR (D_6-DMSO, 400 MHz, 298 K) : δ 8.78 (dd, 1H), 8.68 (dd, 1H), 8.59 (m, 1H), 8.27 (m, 1H), 7.74 (dd,, 1H), 7.65 (s, 1H, NH), 7.34 (m, 1H), 4.70 (t, 3H), 3.73 (d, 6H), 2.43 (s, 3H). ESI-MS (MeOH): $[M+Na]^+$ calc. for $C_{16}H_{19}N_3O_4Na$ 340.1268; found 340.1267 and $[2M+Na]^+$ calc. 657.2644 for $C_{32}H_{38}N_6O_8Na$; found 657.2699. IR (ATR, cm^{-1}) : 3397 (m), 3272 (s, br), 3078 (m), 1644 (s), 1610 (sh), 1563 (s), 1597 (s), 1545 (s), 1463 (s), 1364 (s), 1335 (m), 1270 (m), 1246 (s), 1149 (w), 1068 (s), 1040 (vs), 992 (m), 923(w), 844 (s), 774 (s), 691 (s), 666 (s), 623 (s), 606 (s), 560 (m), 510 (s), 488 (s) and 408 (s).

L2 N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)-[2,2':6',2''-terpyridine]-4'-carboxamide

Prepared like **L1** from the corresponding ethyl ester as stated in our previous report.[7b] Yield : 250mg (66% on a 1mmol scale)

^1H NMR (D_6-DMSO, 400 MHz, 298 K) : δ 8.77 (ddd, 2H), 8.74 (s, 2H), 8.66 (dt, 2H), 8.04 (td, , 2H), 7.81 (s, 1H,NH), 7.54 (ddd, , 2H), 4.73 (t, 3H), 3.76 (d, 6H). ESI-MS (MeOH): $[M+Na]^+$ calc. for $C_{20}H_{20}N_4O_4Na$ 403.1377; found 403.1345 and $[2M+Na]^+$ calc. 783.2861 for $C_{40}H_{40}N_8O_8Na$; found 783.2842. IR (ATR, cm^{-1}) : 3404 (sh), 3292 (s, br), 3059 (m), 1658 (s), 1585 (m), 1539 (vs), 1468 (s), 1395 (s), 1367 (m), 1357 (sh), 1271 (sh), 1265 (s), 1118 (w), 1054 (s), 1041 (s), 1017 (vs), 991 (sh), 888(m), 792 (s), 767 (m), 731 (s), 674 (m), 655 (w), 625 (s), 617(s), 606 (s), 530 (m), 510 (s), 464 (s) and 405 (s).

L3 $N^4,N^{4'}$-bis(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)-[2,2'-bipyridine]-4,4'-dicarboxamide

Prepared from the corresponding ethyl ester via the same protocol than **L1**, except that the ratios were 1.2:2.2:2 – ester:K_2CO_3:TRIS to account for the presence of two ester group on the precursor. Yield : 245mg (64% on a 0.85mmol scale)

^1H NMR (D_6-DMSO, 400 MHz, 298 K) : δ 8.85 (dd, 1H), 8.72 (m, 1H), 7.79 (dd, 1H), 7.69 (s, 1H, NH), 4.70 (t, 6H), 3.73 (d, 12H). ESI-MS (MeOH): $[M+Na]^+$ calc. for $C_{20}H_{26}N_4O_8Na$ 473.1643; found 473.1632 and $[2M+Na]^+$ calc. 923.3393 for $C_{40}H_{52}N_8O_{16}Na$; found 923.3347. IR (ATR, cm^{-1}) : 3404 (sh), 3364 (w), 3231 (s, br), 3092 (m), 1644 (s), 1600 (w), 1541 (s), 1538 (s), 1459 (m), 1405 (w), 1364 (m), 1310 (m), 1242 (m), 1155 (w), 1110 (s), 1040 (vs), 979 (w), 874 (m), 753 (m),714 (sh), 700(m), 631 (m), 574 (m), 560 (sh), 487 (s) and 398 (br).

Covalently modified POMs

7 ($TBA_5H_4[P_2V_3W_{15}O_{62}]$) was prepared following the rigorous work from Finke *et al.*.[10]

^1H NMR (CD_3CN, 400 MHz, 298 K) : δ 3.14 (m, 40H), 1.64 (m, 40H), 1.40 (m, 40H), 0.99 (t, 60H). (hereafter referred as the TBA resonances). ^{31}P NMR (162 MHz, CD_3CN) δ -7.16 (s), -12.64 (s). IR (ATR, cm^{-1}) : 2959(m), 2931(m), 2871 (m), 1482 (m), 1461 (m), 1379 (m), 1085 (s), 1062 (m), 950(s), 904 (s), 777 (vs), 731 (vs), 599 (m), 561 (w), 526 (s), 467 (w). Elemental analysis calc (%) for $C_{80}H_{184}N_5O_{62}P_2V_3W_{15}$: C 18.55, H 3.58, N 1.35; found: C 19.14, H 3.59, N 1.23.

8 ($TBA_5H[P_2V_3W_{15}O_{62}C_4H_8N]$) was prepared by adapting the reported procedure: a 1:1 mixture of **7** and TRIS in DMAc was heated at 80°C in the dark for 24h. Dropwise addition to excess Et_2O, filtration, redissolution in the minimum of MeCN followed by re-precipitation dropwise in Et_2O yielded the desired compound in 73% yield.

^1H NMR (CD_3CN, 400 MHz, 298 K) : δ 5.56 (s, 6H), in addition to the TBA resonances. ^{31}P NMR (162 MHz, CD_3CN) δ -6.70 (s), -12.74 (s). IR (ATR, cm^{-1}) : 2959(m), 2931(m), 2871 (m), 1482 (m), 1461 (m), 1379 (m), 1085 (s), 1062 (m), 950(s), 904 (s), 777 (vs), 731 (vs), 599 (m), 561 (w), 526 (s), 467 (w). Elemental analysis calc (%) for $C_{84}H_{189}N_6O_{62}P_2V_3W_{15}$: C 19.23, H 3.63, N 1.60; found: C 19.63, H 3.72, N 1.68.

1 ($TBA_5H[P_2V_3W_{15}O_{63}C_{16}H_{16}N_3]$)[7c] was prepared by combining in a 1:1 molar ratio **7** and **L1** in DMAc (3mL for 520mg/0.1mmol of **7**) under N_2 and heating them in the dark for 8 days at 80°C. After cooling, the desired compound was then obtained through precipitation by dropwise addition to excess Et_2O. The yellow solid was re-dissolved in a minimum of MeCN and re-precipitated twice in Et_2O before being dried at 50°C. Yield : 490mg (90%)

^1H NMR (CD_3CN, 400 MHz, 298 K) : δ 8.89 (d,1H), 8.80 (s, 1H), 8.73 (d, 1H), 8.56 (s, 2H), 7.87 (s, 1H), 7.73 (s, 1H), 7.16 (s, 1H), 5.81 (s, 6H), 2.67 (s, 3H) in addition to the TBA resonances. ^{31}P NMR (162 MHz, CD_3CN) δ -6.75 (s), -12.77 (s). IR (ATR, cm^{-1}) : 2960(m), 2931(m), 2871 (m), 1671 (w), 1545 (w), 1482 (m), 1461 (m), 1379 (m), 1328 (w), 1084 (s), 1062 (m), 948 (s), 905 (s), 796 (vs), 722 (vs), 597 (m), 561 (w), 526 (s), 478 (w). Elemental analysis calc (%) for $C_{96}H_{197}N_8O_{63}P_2V_3W_{15}$: C 21.18, H 3.65, N 2.06; found: C 21.56, H 3.77, N 2.20.

2 ($TBA_5H[P_2V_3W_{15}O_{63}C_{20}H_{17}N_4]$) was prepared as **1** using **L2**. Yield : 510mg (93%)

^1H NMR (CD_3CN, 400 MHz, 298 K) : δ 8.83 (br s, 2H), 8.75 (s, 2H), 8,71(d, 2H), 8.12 (s, 2H), 7.58 (br s, 2H), 7.10 (s, 2H, NH), 5.86 (s, 6H) in addition to the TBA resonances. ^{31}P NMR (162 MHz, CD_3CN) δ -6.73 (s), -12.78 (s). IR (ATR, cm^{-1}) : 2960(m), 2931(m), 2871 (m), 1678 (w), 1584 (w), 1482 (m), 1466 (m), 1379 (m), 1310 (w), 1083 (s), 1062 (m), 947 (s), 904 (s), 797 (vs), 719 (vs), 597 (m), 561 (w), 524 (s), 477 (w). Elemental analysis calc (%) for $C_{100}H_{198}N_9O_{63}P_2V_3W_{15}$: C 22.78, H 3.62, N 2.26; found: C 22.48, H 3.66, N 2.28.

3 ($TBA_{10}H_2[(P_2V_3W_{15}O_{59})_2C_{20}H_{20}N_4O_8]$) was previously reported by Cronin *et al.*[11]. It was prepared in the same fashion than **1**, except that the ratio was 2:1 **7**:**L3** to account for the bifunctionality of the ligand. Yield : 920mg (86%)

^1H NMR (CD_3CN, 400 MHz, 298 K) : δ 8.81 (br s, 2H), 8,73 (br s, 2H), 7.75 (br s, 2H), 6.96 (s, 2H, NH), 5.86 (s, 12H), in addition to the TBA resonances. ^{31}P NMR (162 MHz, CD_3CN) δ -6.73 (s), -12.76 (s). IR (ATR, cm^{-1}) : 2960(m), 2931(m), 2871 (m), 1703 (w), 1666 (w), 1584 (w), 1482 (m), 1465 (m), 1379 (m), 1318 (w), 1084 (s), 1061 (m), 947 (s), 905 (s), 797 (vs), 721 (vs), 597 (m), 525 (s), 477 (w). Elemental analysis calc (%) for $C_{180}H_{382}N_{14}O_{126}P_4V_6W_{30}$: C 20.19, H 3.62, N 1.83; found: C 20.49, H 3.64, N 2.00.

Re^{I} complexes based on covalently modified POMs

General procedure : In a dried Schlenk cooled under N_2, $Re(CO)_5Br$ and the desired hybrid were combined in stoichiometric amount (typical scale: 20µmol) and dissolved in DMAc (2.5mL). The yellow solution was then heated overnight at 80°C in the dark. Once cooled back to RT, the now orange solution was added dropwise to excess Et_2O, resulting in a really fine yellow solid. The suspension was left in the fridge for 1h to ensure total precipitation. The fine yellow solid was then filtered on a 0.45µm PTFE membrane and washed with THF (5mL), DCM (5mL) and Et_2O (10mL). The solid was re-precipitated by retaking it in MeCN (3mL) before dropwise addition to excess Et_2O followed by filtration, yielding a fine solid that was air dried for 2h.

4 ($TBA_5H[P_2V_3W_{15}O_{66}C_{19}H_{16}N_3ReBr]$) yellow-orange powder Yield : 101mg (87%, 20µmol scale) ^1H NMR (400 MHz, CD_3CN) δ 9.11 (t, 1H), 8.87 (t, 1H), 8.74 (s, 1H), 8.50 (s, 1H), 7.93 (m, 2H), 7.50 (m, 1H), 7.16 (s, 1H, NH), 5.97 (s, 6H), 2.60 (s, 3H) in addition to the TBA resonances. ^{31}P NMR (162 MHz, CD_3CN) δ -6.97 (s), -12.43 (s). IR (ATR, cm^{-1}) : 2960(m), 2931(m), 2871 (m), 2019 (s), 1916 (s), 1891 (s), 1672 (w), 1621 (w), 1542 (w), 1482 (m), 1462 (m), 1379 (m), 1318 (w), 1084 (s), 1062 (m), 951 (s), 905 (s), 804 (sh), 794 (vs), 719 (vs), 598 (m), 526 (s), 478 (w).Elemental analysis calc (%) for $C_{99}H_{197}N_8O_{66}P_2V_3W_{15}ReBr$: C 20.52, H 3.43, N 1.93; found: C 20.54, H 3.40, N 1.98.

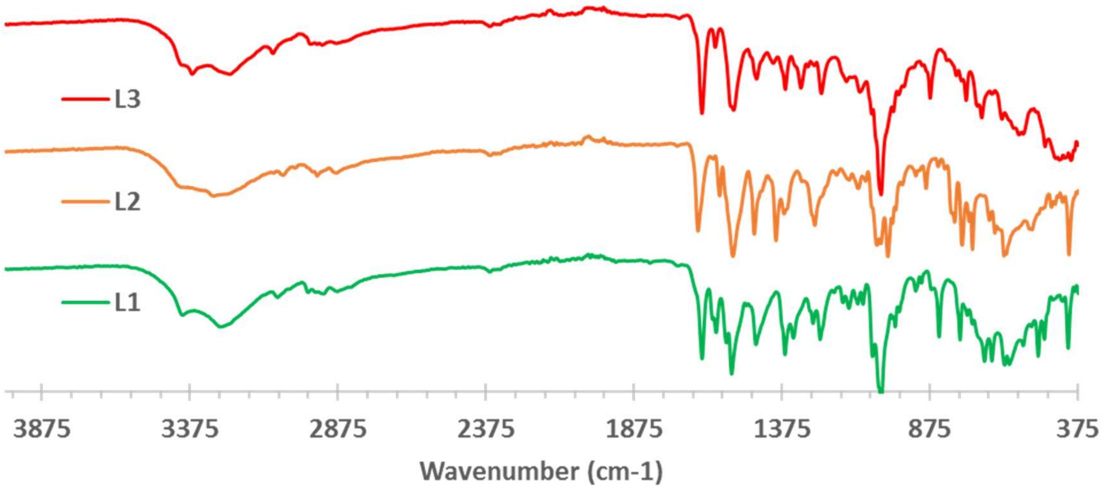
5 ($TBA_5H[P_2V_3W_{15}O_{66}C_{23}H_{17}N_4ReBr]$) greenish-yellow powder Yield : 110mg (94%, 20µmol scale) ^1H NMR (400 MHz, CD_3CN) δ 9.06 (d, 1H), 8.80 (m, 2H), 8.70 (d, 1H), 8.27 (t, 1H), 8.08 (d, 1H), 8.00 (td, 1H), 7.82 (d, 1H), 7.65 (t, 1H), 7.57 (t, 1H), 7.20 (s, 1H, NH), 5.90 (s, 6H), in addition to the TBA resonances. ^{31}P NMR (162 MHz, CD_3CN) δ -6.88 (s), -12.60 (s). IR (ATR, cm^{-1}) : 2960(m), 2931(m), 2871 (m), 2020 (s), 1916 (s), 1894 (s), 1674 (w), 1542 (w), 1482 (m), 1462 (m), 1415 (w), 1379 (m), 1315 (w), 1084 (s), 1065 (m), 949 (s), 904 (s), 800 (vs br), 722 (vs), 598 (m), 526 (s), 478 (w).Elemental analysis calc (%) for $C_{103}H_{198}N_9O_{66}P_2V_3W_{15}ReBr$: C 21.12, H 3.41, N 2.15; found: C 21.21, H 3.38, N 2.19.

6 ($TBA_{10}H_2[(P_2V_3W_{15}O_{59})_2C_{23}H_{20}N_4O_{11}ReBr]$) yellow-orange powder Yield : 90mg (82%, 10µmol scale) ^1H NMR (400 MHz, CD_3CN) δ 9.11 (m, 2H), 8.84 (br s, 2H), 8.01 (m, 2H), 7.12 (s, 2H, NH), 5.92 (s, 12H), in addition the TBA resonances. ^{31}P NMR (162 MHz, CD_3CN) δ -6.70 (s), -12.66 (s). IR (ATR, cm^{-1}) : 2960(m), 2931(m), 2872 (m), 2023 (s), 1925 (s), 1899 (s), 1672 (w), 1542 (w), 1482 (m), 1462 (m), 1415 (w), 1379 (m), 1330 (w), 1264 (w), 1084 (s), 1063 (m), 949 (s), 906 (s), 805 (vs br), 723 (vs), 598 (m), 526 (s), 478 (w). Elemental analysis calc (%) for $C_{183}H_{382}N_{14}O_{129}P_4V_6W_{30}ReBr$: C 19.88, H 3.48, N 1.77; found: C 19.98, H 3.49, N 1.91.

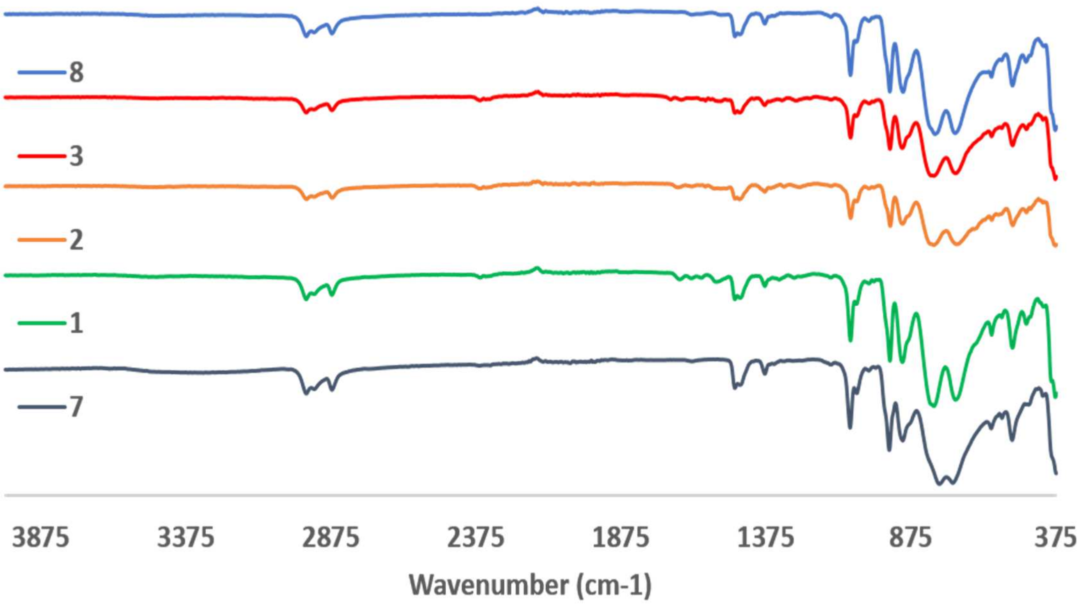
9 [$Re(CO)_3Br(dmb)$] was prepared following literature procedure. Briefly, dmb (4,4'-dimethyl,2,2'-bipyridine) and $Re(CO)_5Br$ were refluxed in cyclohexane for 3h, a yellow precipitate progressively appearing. The solid was filtered and washed with Et_2O. Yield 230mg (86%, 50 µmol scale)

^1H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, 2H), 7.98 (s, 2H), 7.32 (dd, 2H), 2.58 (s, 6H). ESI-MS (MeOH): $[M-Br]^+$ calc. for $C_{15}H_{12}N_2O_3Re$ 455.0405; found 455.0408 and $[2M-Br]^+$ calc. 988.9994 for $C_{30}H_{24}N_4O_6Re_2Br$; found 998.9973. IR (ATR, cm^{-1}) : 3030 (w), 2012 (vs), 1882 (vs), 1865 (vs), 1620 (s), 1555 (w), 1484 (m), 1444 (m), 1379 (w), 1300 (m), 1243 (m), 1183 (w), 1077 (w), 1031 (m), 892 (m), 839 (s), 742 (m), 647 (s), 630 (s), 567 (m), 537 (s), 506 (s), 484 (s), 417(s). Elemental analysis calc (%) for $C_{15}H_{12}BrN_2O_3Re$: C 33.71, H 2.26, N 5.24; found: C 33.81, H 2.17, N 5.18.

FT-IR and UV-visible spectra



*<u>Figure S2</u> FTIR spectra of the three triol decorated polypyridyl ligands **L1-L3**.*



*<u>Figure S3</u> Comparison of the FTIR spectra for the starting POM **7** and functionalized POMs **1,2,3** and **8**.*

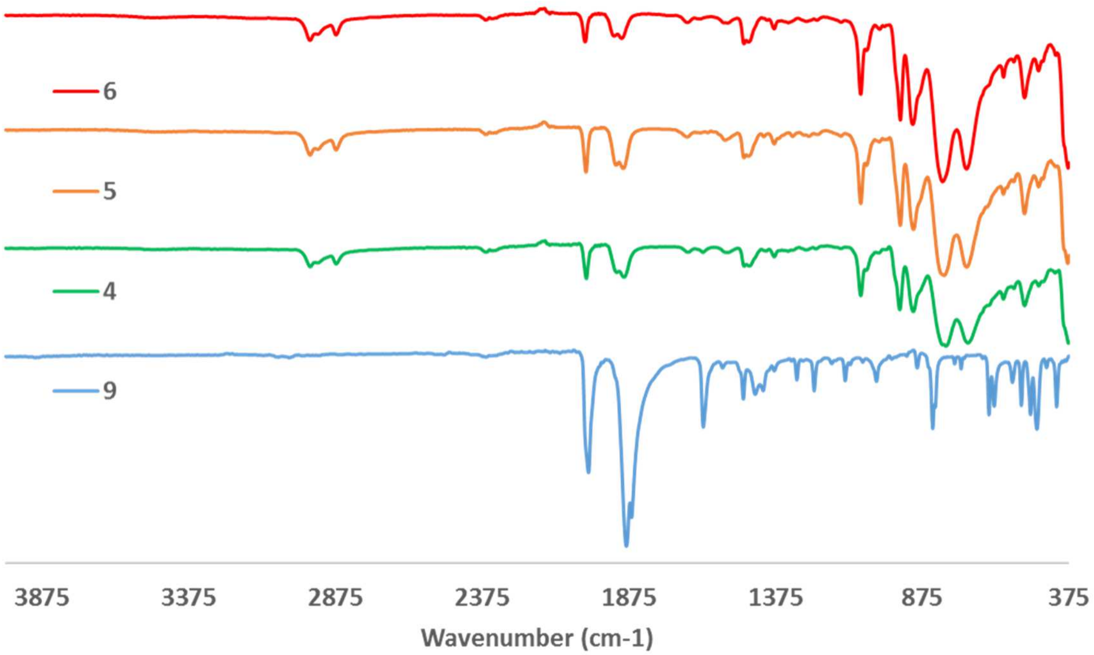


Figure S4 *Comparison of the FTIR spectra of the Re(I) complexes* ***4****,* ***5****,* ***6*** *and* ***9*** *(as reference).*

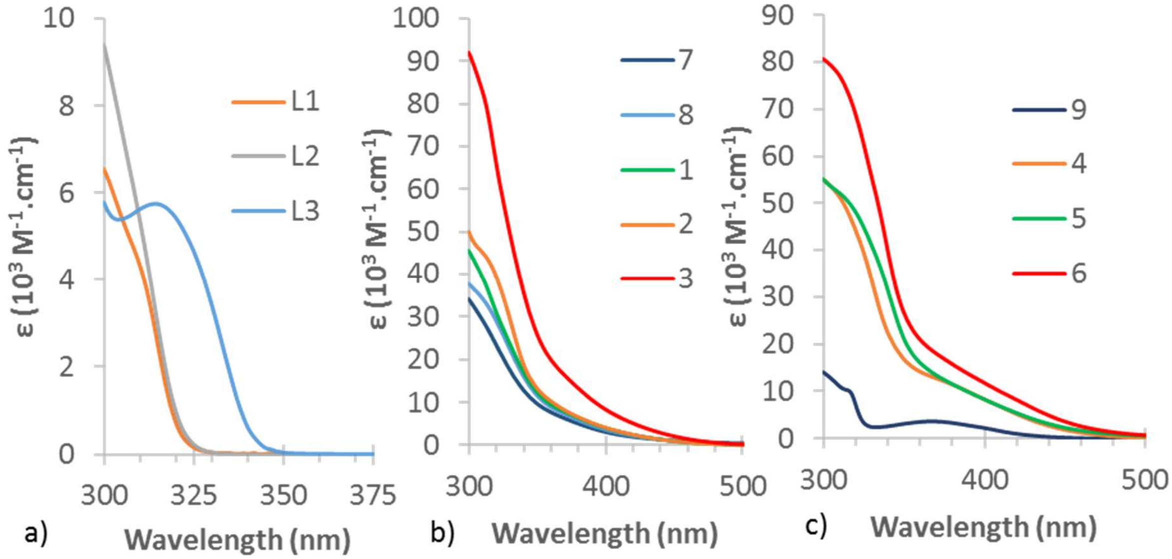


Figure S5 *Absorption spectra in DMF for a) ligands* ***L1****-* ***L3*** *b) POMs* ***1****-****3****,****7 and 8*** *c) complexes* ***4****-****6*** *and* ***9****.*

ESI-MS analysis

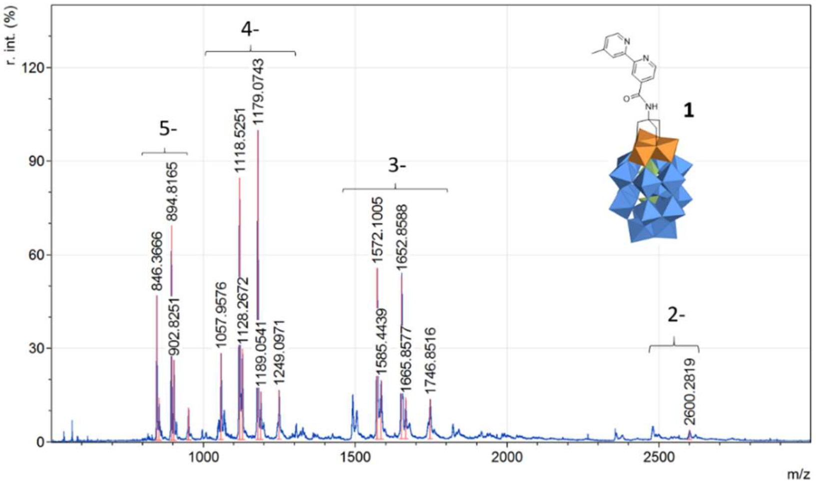


Figure S6 *ESI-MS full spectrum for 1 (negative mode).*

Composition	Formula	Calc.	Observed
[M+H]5-	$C_{16}H_{17}N_3O_{63}P_2V_3W_{15}{}^{5-}$	846.1740	846.1631
[M+TBA]5-	$C_{32}H_{52}N_4O_{63}P_2V_3W_{15}{}^{5-}$	894.6298	894.6262
[M+2TBA]4-	$C_{48}H_{88}N_5O_{63}P_2V_3W_{15}{}^{4-}$	1178.8584	1178.8341
[M+3TBA]3-	$C_{64}H_{124}N_6O_{63}P_2V_3W_{15}{}^{3-}$	1652.5727	1652.4896
[M+4TBA]2-	$C_{80}H_{160}N_7O_{63}P_2V_3W_{15}{}^{2-}$	2600.0013	2599.9900

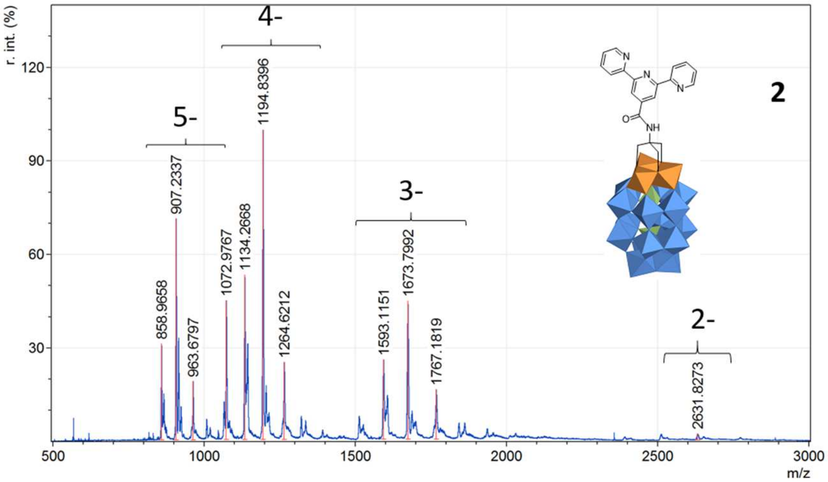


Figure S7 *ESI-MS full spectrum for 2 (negative mode).*

Composition	Formula	Calc.	Observed
[M+TBA]5-	$C_{36}H_{53}N_5O_{63}P_2V_3W_{15}{}^{5-}$	907.2320	907.2337
[M+2TBA]4-	$C_{52}H_{89}N_6O_{63}P_2V_3W_{15}{}^{4-}$	1194.6111	1194.5538
[M+3TBA]3-	$C_{68}H_{125}N_7O_{63}P_2V_3W_{15}{}^{3-}$	1673.5763	1673.4871
[M+4TBA]2-	$C_{84}H_{161}N_8O_{63}P_2V_3W_{15}{}^{2-}$	2632.0075	2631.8273

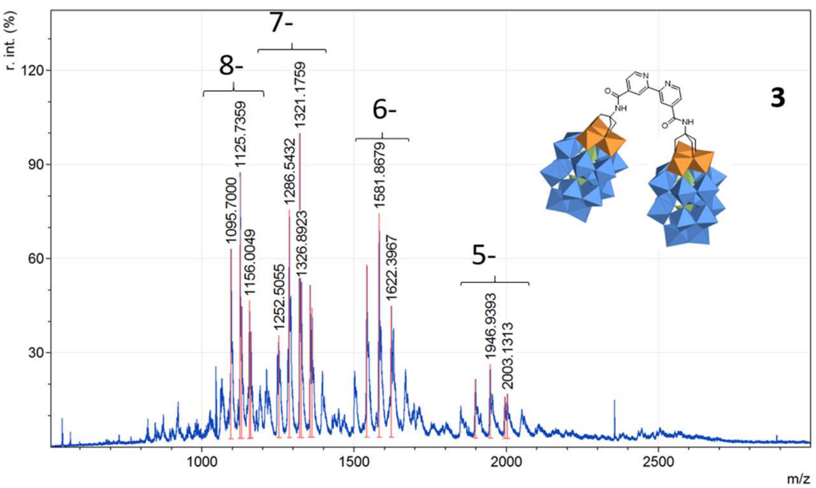


Figure S8 ESI-MS full spectrum for 3 (negative mode).

Composition	Formula	Calc.	Observed
[M+4TBA]8-	$C_{84}H_{164}N_8O_{126}P_4V_6W_{30}{}^{8-}$	1155.8458	1155.7887
[M+5TBA]7-	$C_{100}H_{200}N_9O_{126}P_4V_6W_{30}{}^{7-}$	1355.5787	1355.6362
[M+6TBA]6-	$C_{116}H_{236}N_{10}O_{126}P_4V_6W_{30}{}^{8-}$	1621.8893	1621.9612
[M+7TBA]5-	$C_{132}H_{272}N_{11}O_{126}P_4V_6W_{30}{}^{8-}$	1994.9244	1995.0549

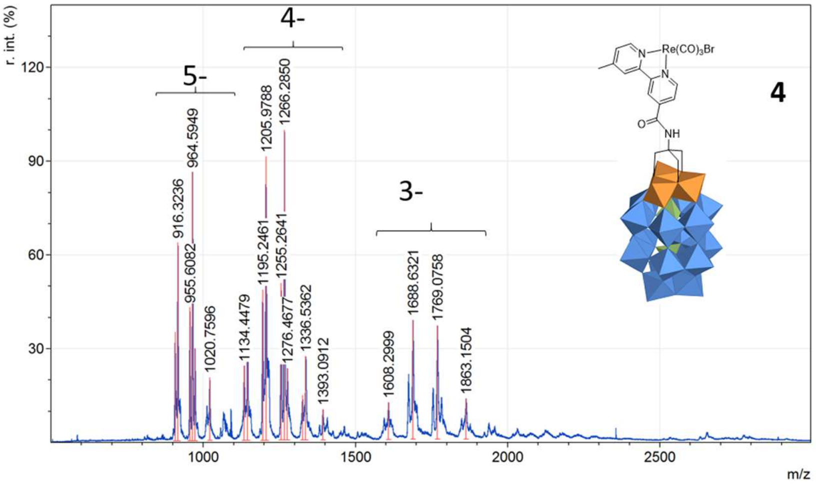


Figure S9 ESI-MS full spectrum for 4 (negative mode).

Composition	Formula	Calc.	Observed
[M+TBA]5-	$C_{35}H_{52}N_4O_{66}P_2V_3W_{15}ReBr^{5-}$	964.6011	964.5949
[M+2TBA]4-	$C_{51}H_{88}N_5O_{66}P_2V_3W_{15}ReBr^{4-}$	1266.3225	1266.2825
[M+3TBA]3-	$C_{67}H_{124}N_6O_{66}P_2V_3W_{15}ReBr^{3-}$	1769.5253	1769.4236

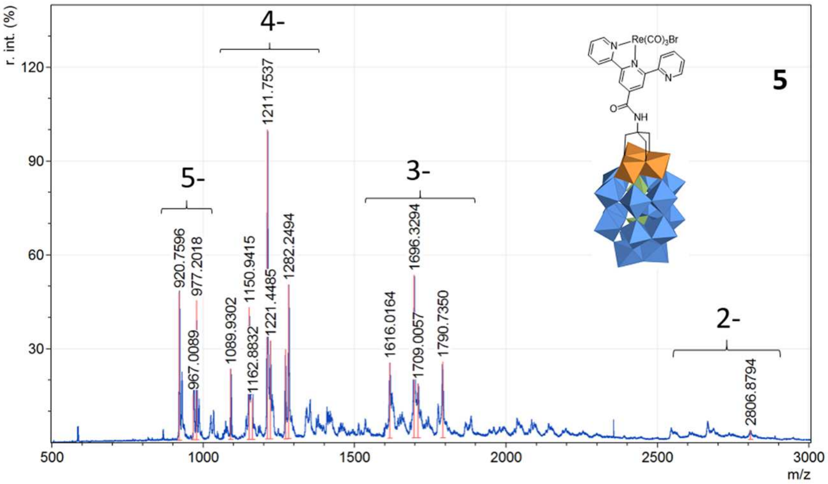


Figure S10 *ESI-MS full spectrum for 5 (negative mode).*

Composition	Formula	Calc.	Observed
[M+TBA]5-	$C_{39}H_{53}N_5O_{66}P_2V_3W_{15}ReBr^{5-}$	977.2033	977.2018
[M+2TBA]4-	$C_{55}H_{89}N_6O_{66}P_2V_3W_{15}ReBr^{4-}$	1282.0752	1282.0217
[M+3TBA]3-	$C_{71}H_{125}N_7O_{66}P_2V_3W_{15}ReBr^{3-}$	1790.5290	1790.4121
[M+4TBA]2-	$C_{87}H_{161}N_8O_{66}P_2V_3W_{15}ReBr^{2-}$	2806.9346	2806.8794

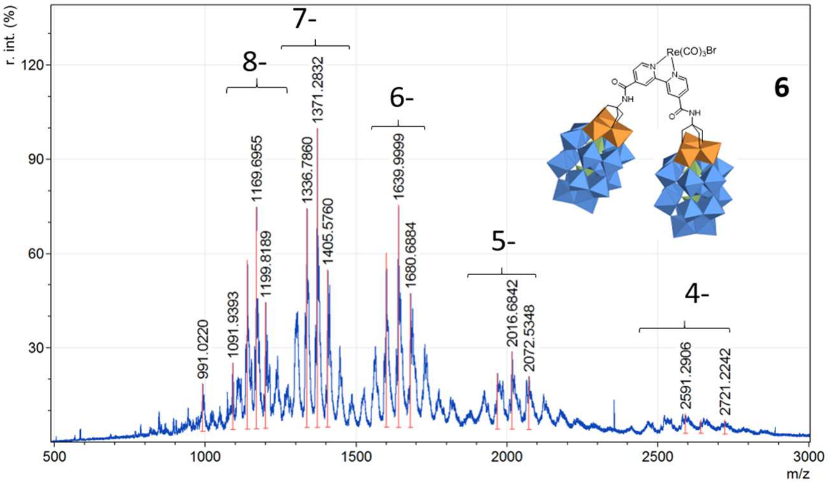


Figure S11 *ESI-MS full spectrum for 6 (negative mode).*

Composition	Formula	Calc.	Observed
[M+4TBA]8-	$C_{87}H_{164}N_8O_{129}P_4V_6W_{30}ReBr^{8-}$	1199.5779	1199.5986
[M+5TBA]7-	$C_{103}H_{200}N_9O_{129}P_4V_6W_{30}ReBr^{7-}$	1405.5582	1405.5760
[M+6TBA]6-	$C_{119}H_{236}N_{10}O_{129}P_4V_6W_{30}ReBr^{6-}$	1680.3656	1680.3234
[M+7TBA]5-	$C_{135}H_{272}N_{11}O_{129}P_4V_6W_{30}ReBr^{5-}$	2064.8957	2064.7819
[M+8TBA]4-	$C_{151}H_{308}N_{12}O_{129}P_4V_6W_{30}ReBr^{4-}$	2641.6894	2641.7580

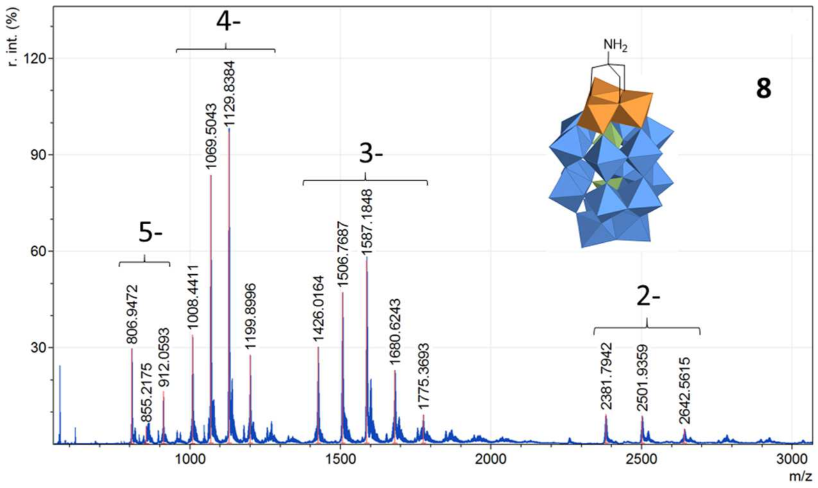


*Figure S12 ESI-MS full spectrum for **8** (negative mode)*

Composition	Formula	Calc.	Observed
[M+TBA]5-	$C_{20}H_{44}N_2O_{62}P_2V_3W_{15}^{5-}$	855.2167	855.2175
[M+2TBA]4-	$C_{36}H_{80}N_3O_{62}P_2V_3W_{15}^{4-}$	1129.8424	1129.8384
[M+3TBA]3-	$C_{52}H_{116}N_4O_{62}P_2V_3W_{15}^{3-}$	1587.2180	1587.1848
[M+4TBA]2-	$C_{68}H_{152}N_5O_{62}P_2V_3W_{15}^{2-}$	2501.9693	2501.9359

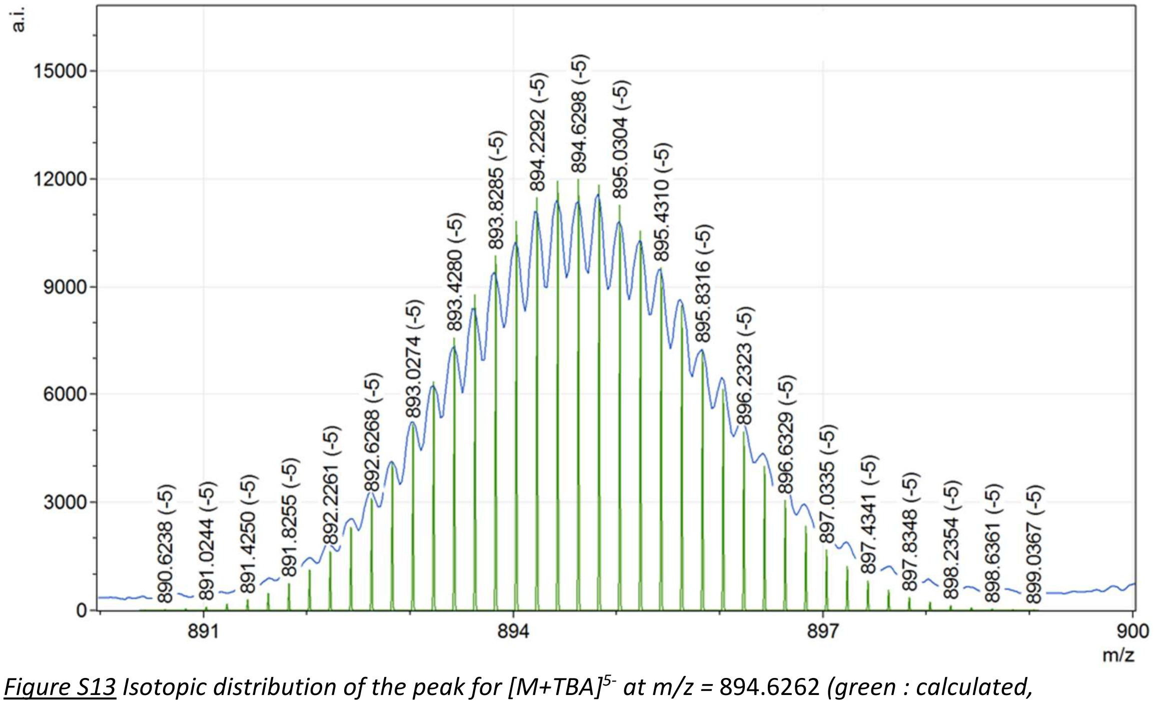
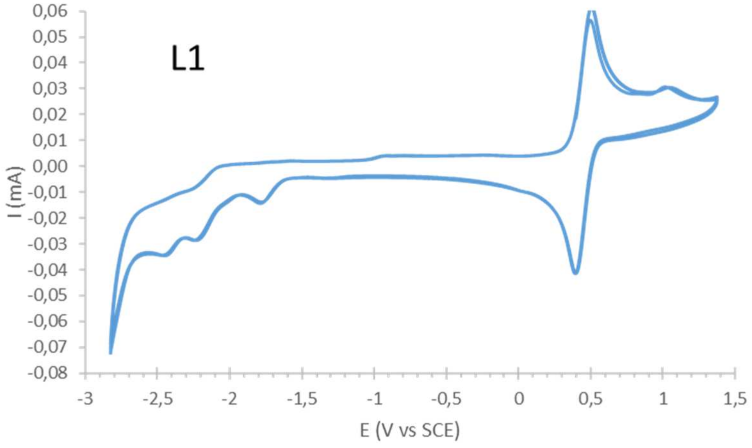
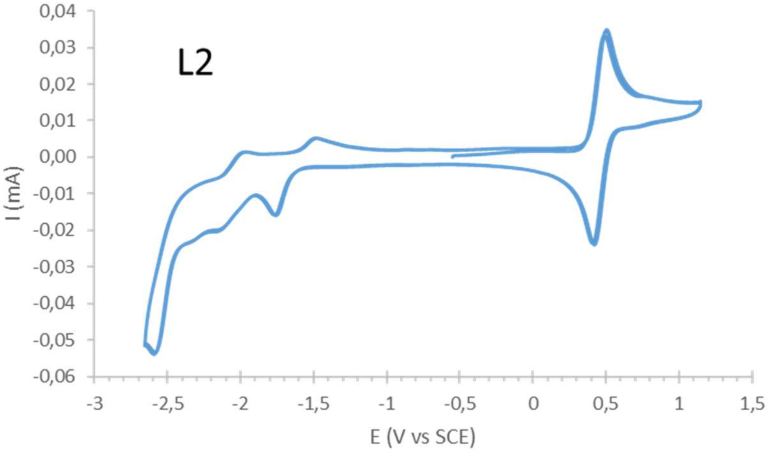


Figure S13 Isotopic distribution of the peak for [M+TBA]$^{5-}$ at m/z = 894.6262 *(green : calculated, blue : observed) for **1**. Values are for the calculated peaks.*

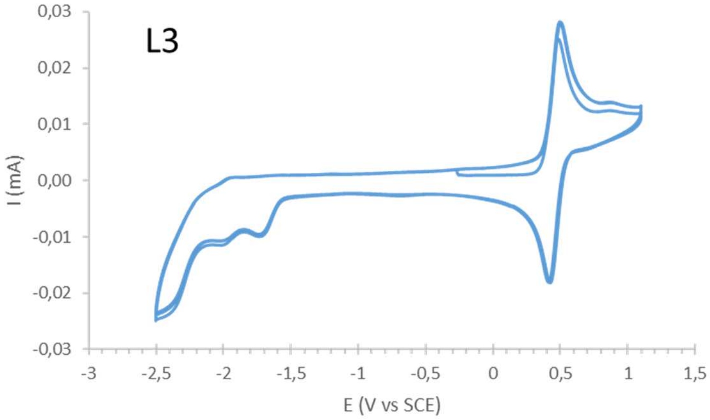
Electrochemistry



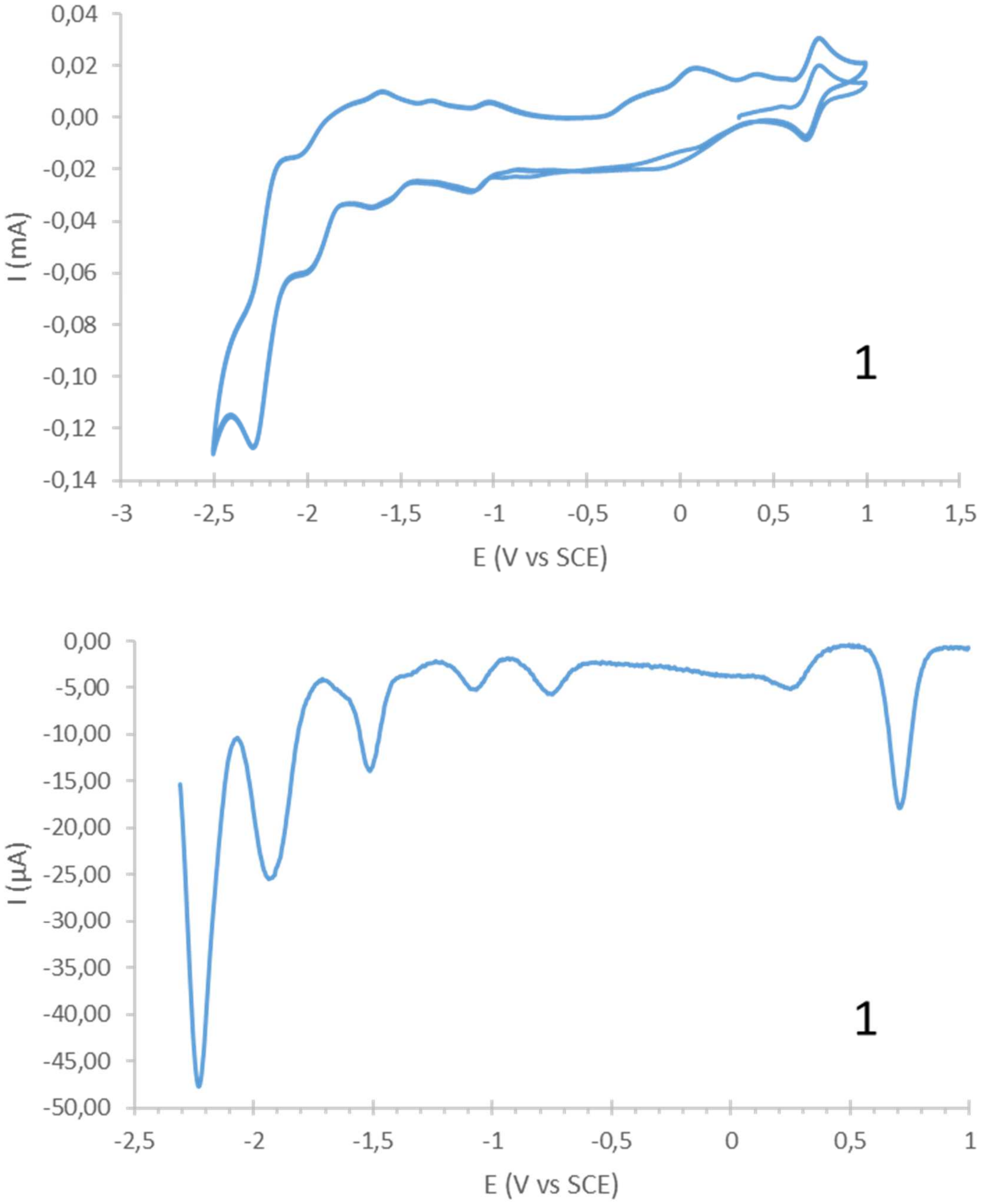
*<u>Figure S14 :</u> Cyclovoltamogram for **L1** in DMF, with Fc as internal ref. (200mV.s^{-1})*



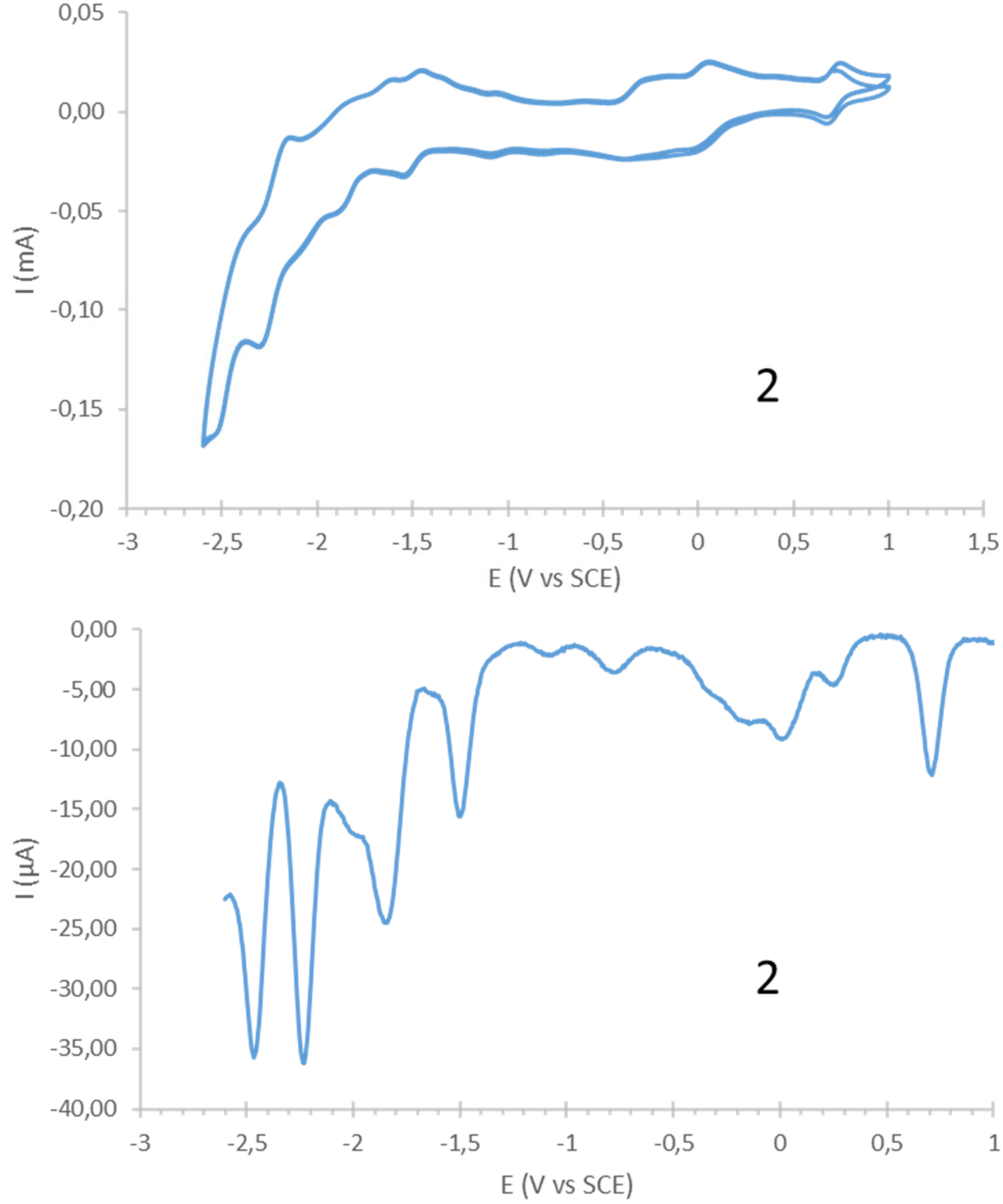
*<u>Figure S15 :</u> Cyclovoltamogram for **L2** in DMF, with Fc as internal ref. (200mV.s^{-1})*



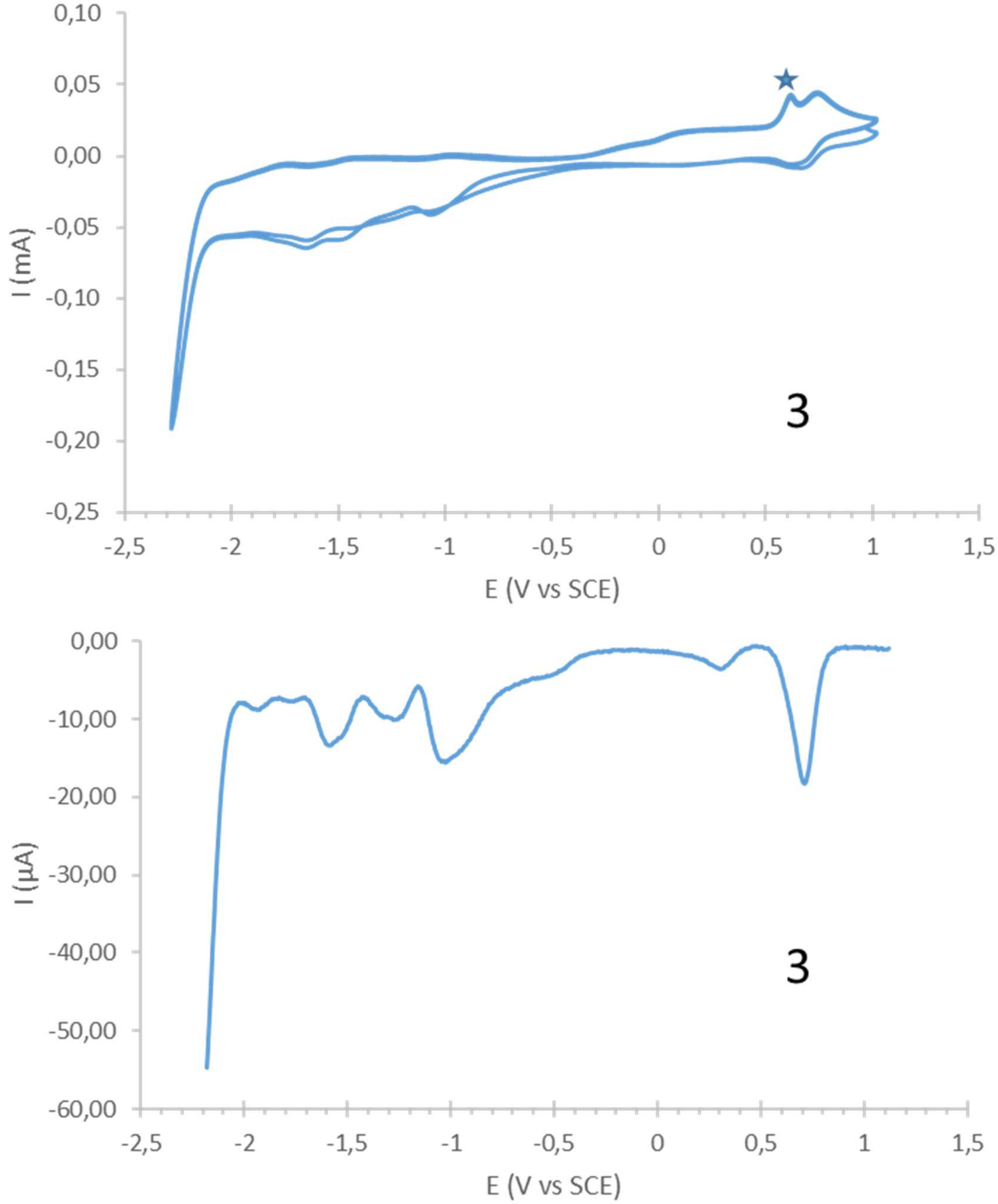
*<u>Figure S16 :</u> Cyclovoltamogram for **L3** in DMF, with Fc as internal ref. (200mV.s^{-1})*



<u>Figure S17 :</u> *Top/ Cyclovoltamogram (200mV.s^{-1}) Bottom/ SW voltammogram of **1** in MeCN (AcFc as reference)*



*<u>Figure S18 :</u> Top/ Cyclovoltamogram (200mV.s^{-1}) Bottom/ SW voltammogram of **2** in MeCN (AcFc as reference)*



*<u>Figure S19 :</u> Top/ Cyclovoltamogram (200mV.s^{-1}) Bottom/ SW voltammogram of **3** in MeCN (AcFc as reference) The measurements were highly affected by the adsorption on the electrode as shown by the desorption peak marked with a star on the CV.*

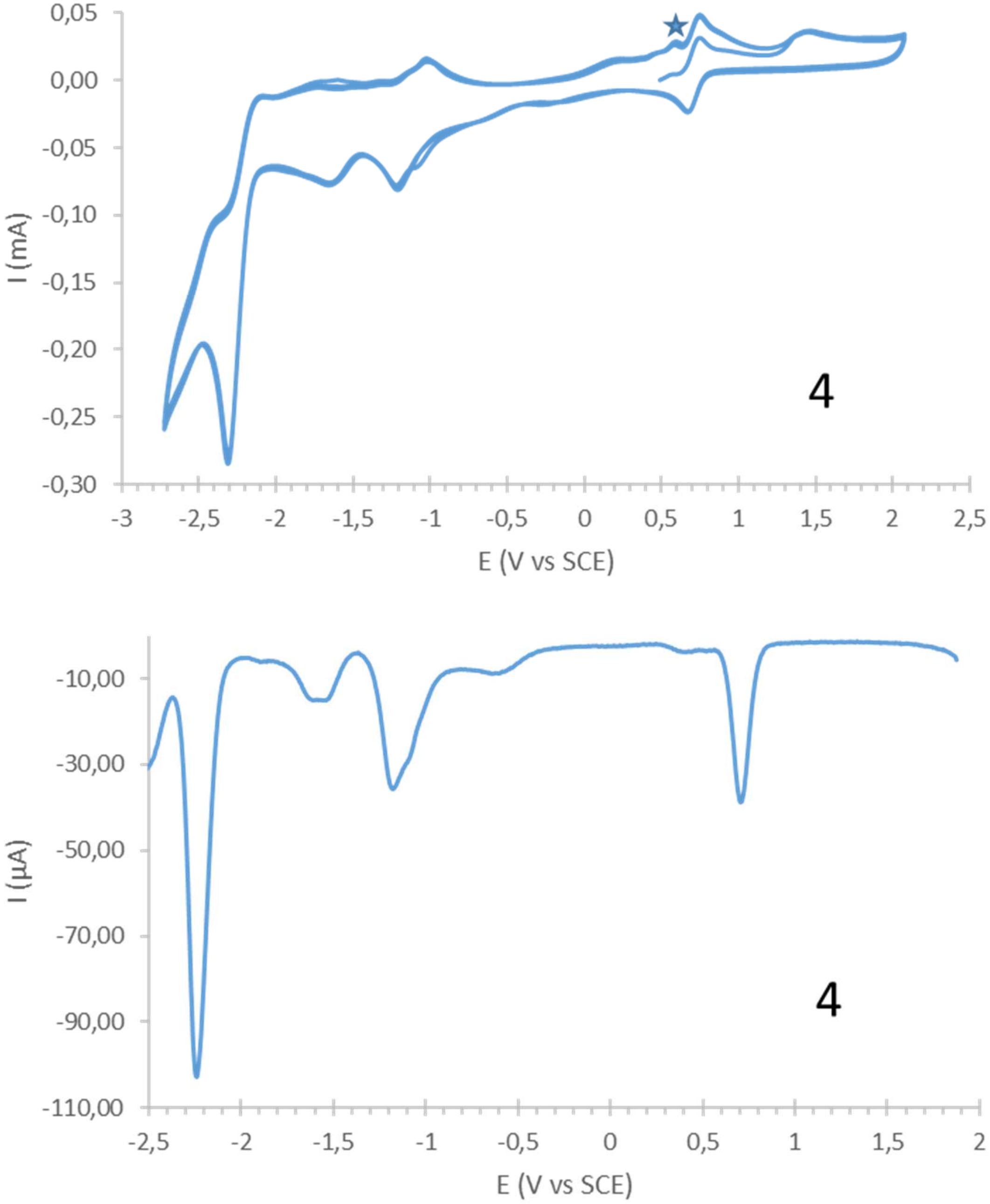
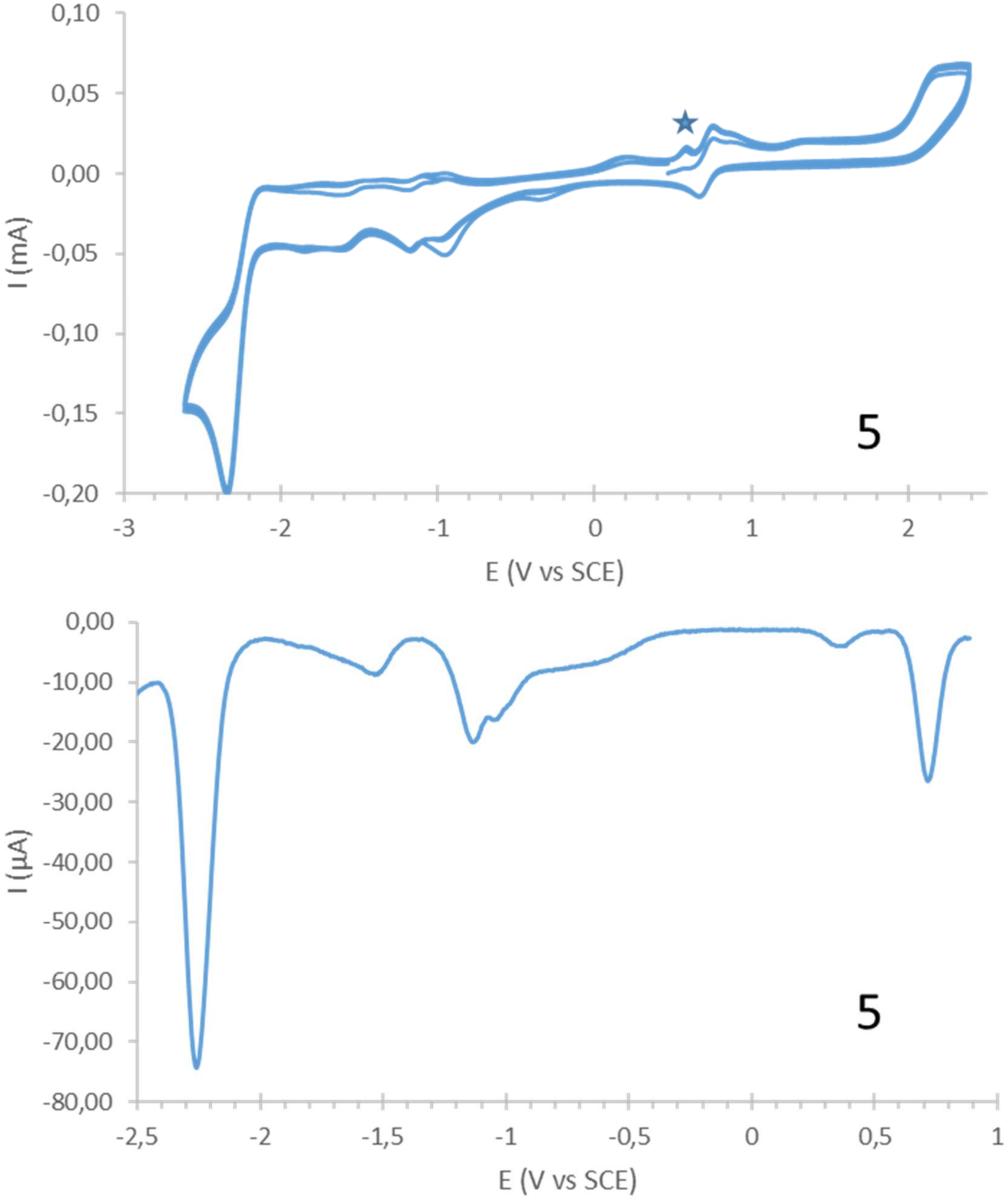


Figure S20 : *Top/ Cyclovoltamogram (200mV.s^{-1}) Bottom/ SW voltammogram of* ***4*** *in MeCN (AcFc as reference) The measurements were highly affected by the adsorption on the electrode as shown by the desorption peak marked with a star on the CV.*



<u>Figure S21 :</u> *Top/ Cyclovoltamogram (200mV.s^{-1}) Bottom/ SW voltammogram of **5** in MeCN (AcFc as reference) The measurements were highly affected by the adsorption on the electrode as shown by the desorption peak marked with a star on the CV.*

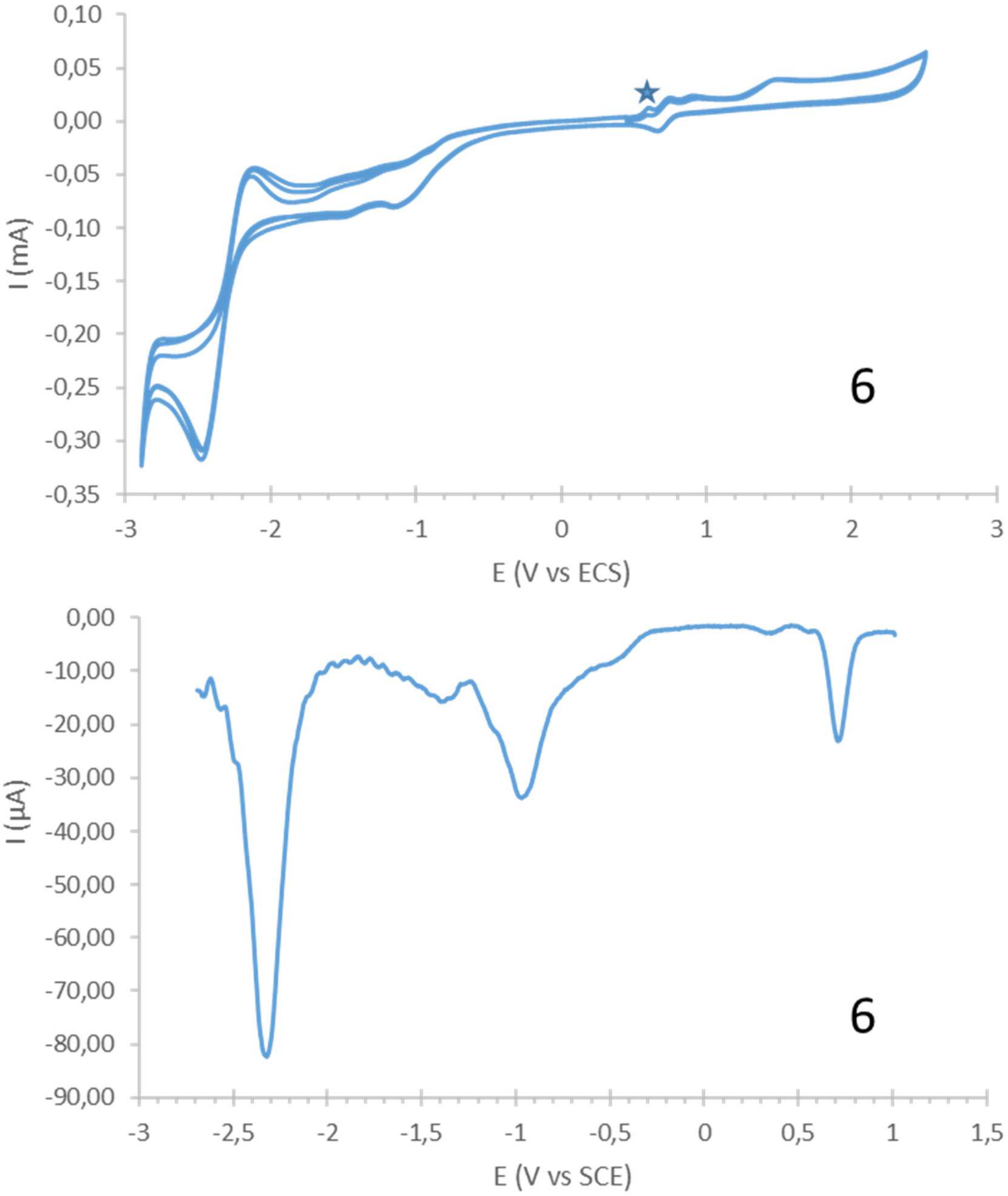
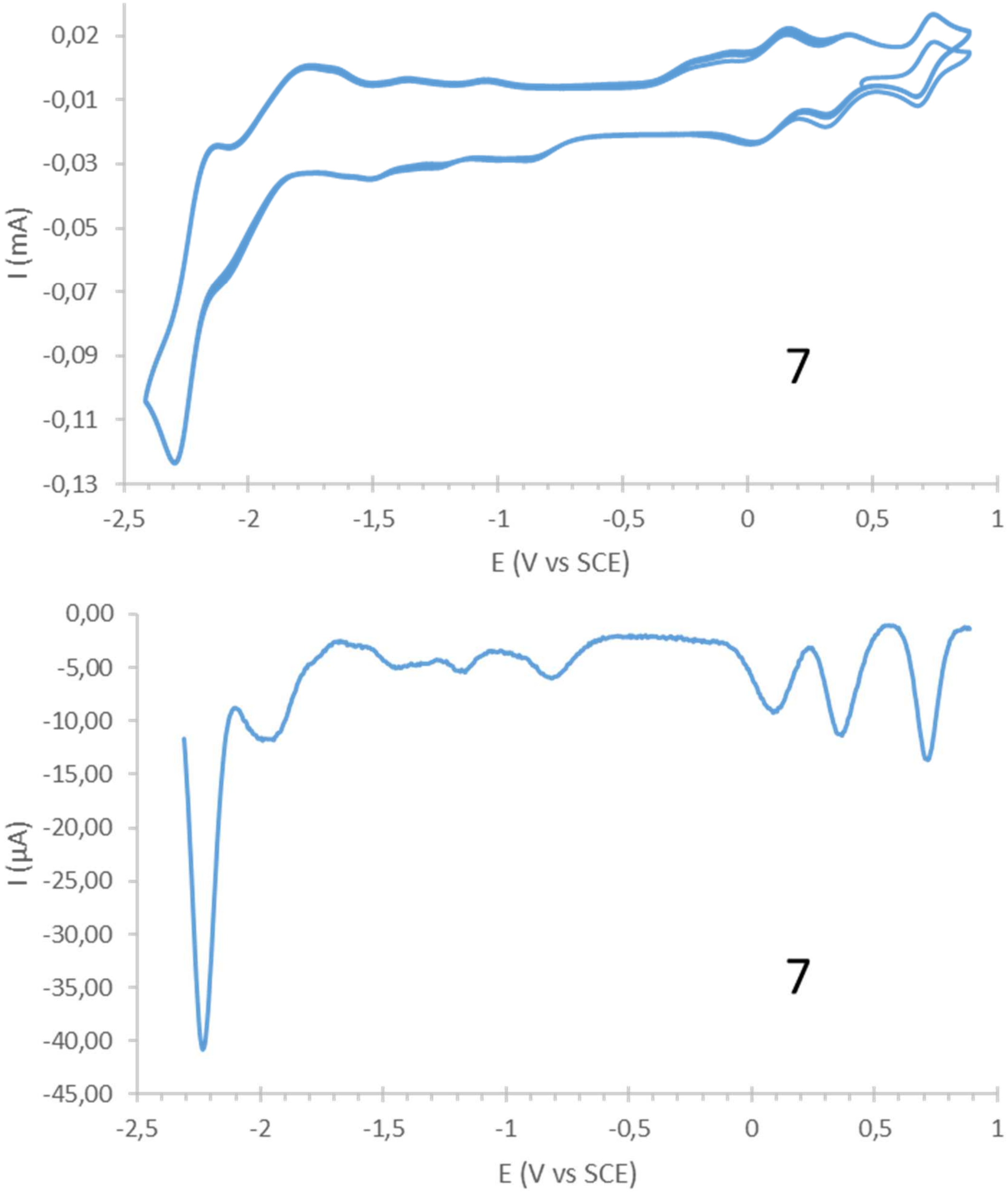


Figure S22 : *Top/ Cyclovoltamogram (200mV.s^{-1}) Bottom/ SW voltammogram of **6** in MeCN (AcFc as reference) The measurements were highly affected by the adsorption on the electrode as shown by the desorption peak marked with a star on the CV.*



*<u>Figure S23 :</u> Top/ Cyclovoltamogram (200mV.s^{-1}) Bottom/ SW voltammogram of **7** in MeCN (AcFc as reference).*

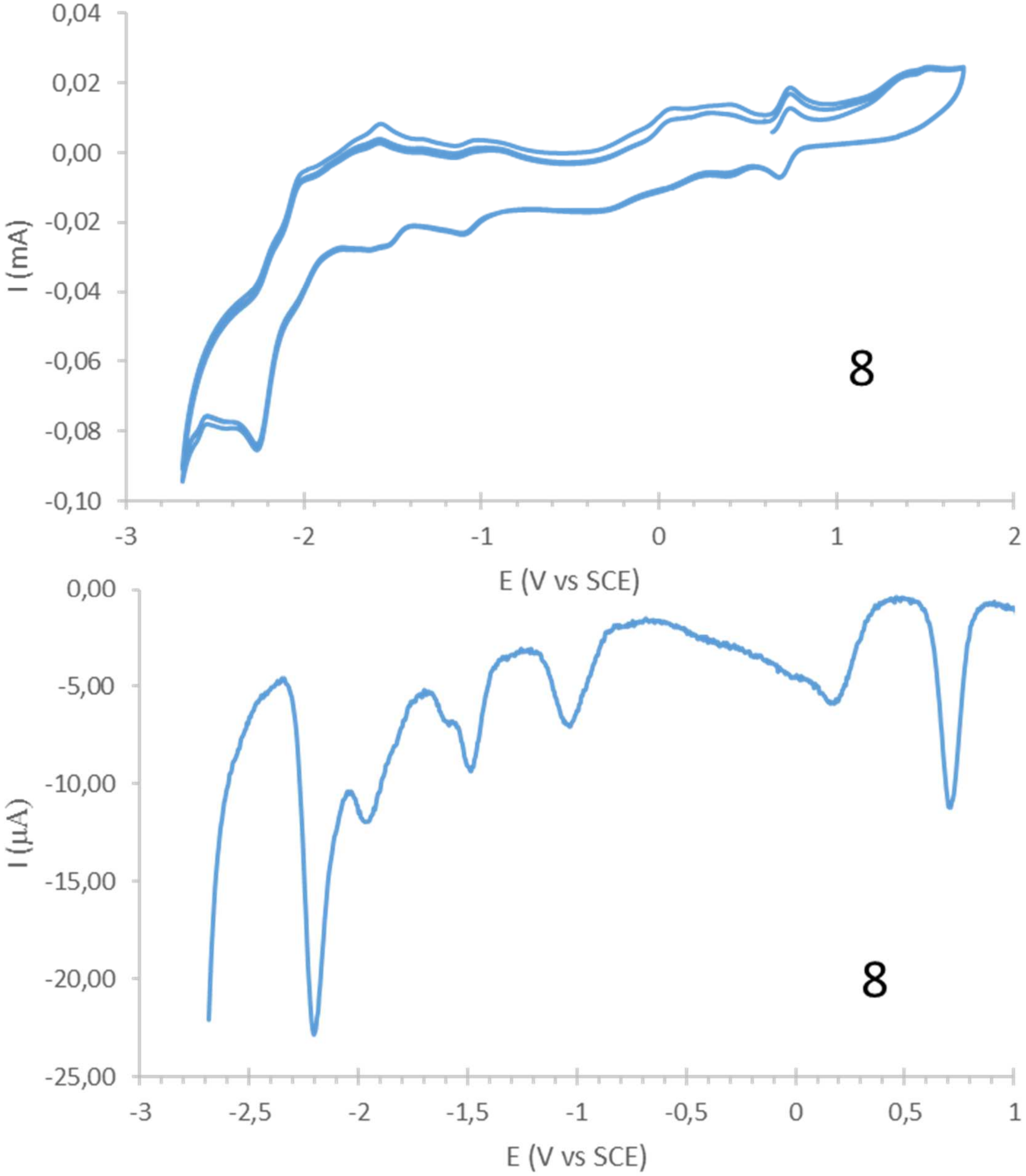


Figure S24 : *Top/ Cyclovoltamogram (200mV.s^{-1}) Bottom/ SW voltammogram of* ***8*** *in MeCN (AcFc as reference).*

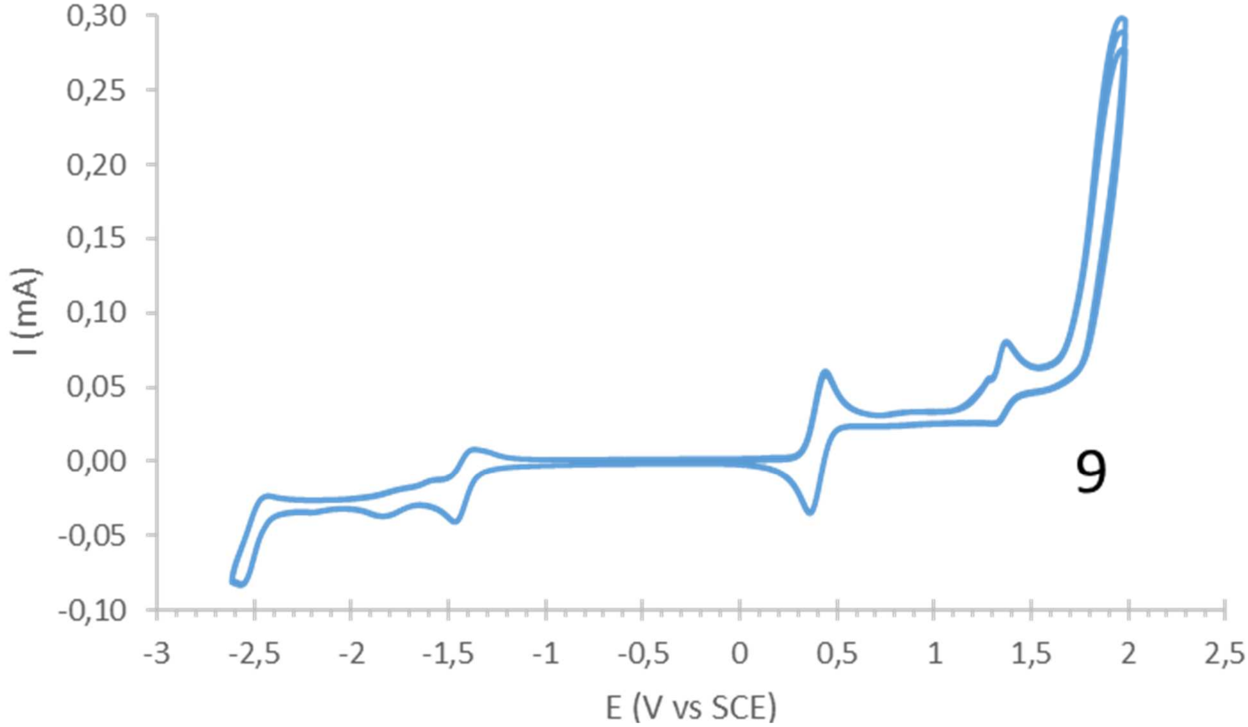


Figure S25 : Cyclovoltamogram for ***9*** *in MeCN, with Fc as internal ref. (200mV.s*$^{-1}$*)*

Quenching study

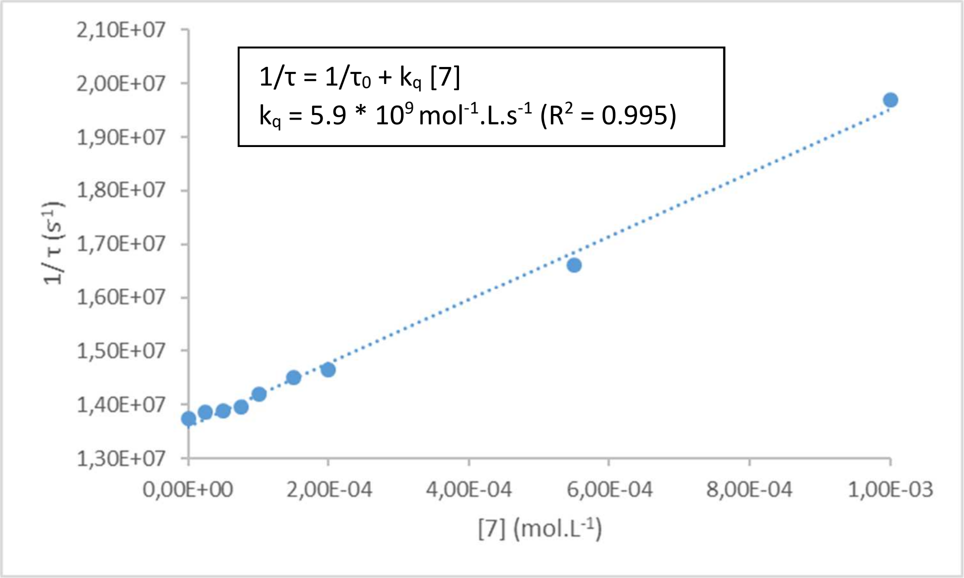
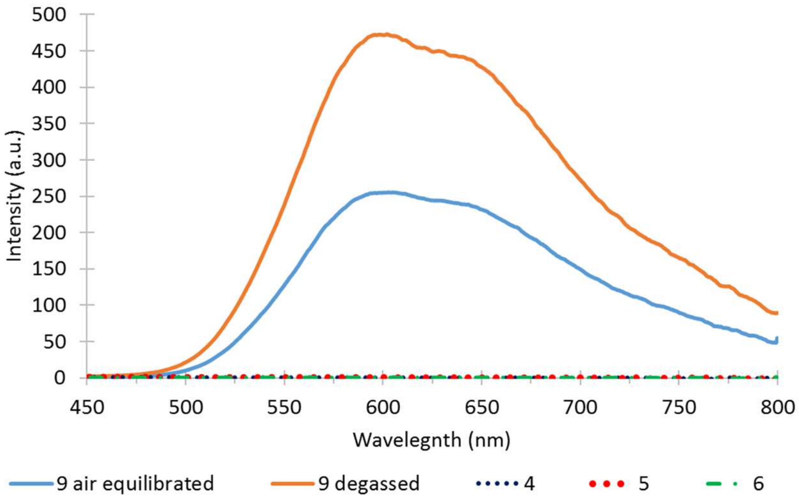


Figure S26 : Stern-Volmer plot for quenching by ***7*** *TBA*$_5$*H*$_4$*[P*$_2$*V*$_3$*W*$_{15}$*O*$_{62}$*] of* ***9*** *fac-[ReBr(CO)*$_3$*(dmb)] at 0.1mM in a degassed solution of 0.1 M TBAPF*$_6$ *in CH*$_3$*CN at 298 K. Excitation wavelength for the emission is 405 nm.*



*<u>Figure S27 :</u> Emission spectra in N_2 purged CH_3CN for the hybrid Re complexes **4-6**, and in both air equilibrated or degassed CH3CN for the reference **9**. Excitation wavelength : 385nm.*

Computational details

DFT calculations were performed using Gaussian 09 rev E01.[12] The B3LYP method[13] was used to carry the DFT[14] and TD-DFT[15] calculations. The 6-31G** basis set was used for the light atoms (H, C, N, O, P and V)[16] while the LanL2DZ basis set was used for heavier atoms (Br, W, Re)[17]. Geometry optimizations were conducted without symmetry constraints. Frequency calculations after optimization confirmed that energy minima had been reached in all cases. Energy, oscillator strength, and related MO contributions for the 100 lowest singlet–singlet and 10 lowest singlet–triplet excitations were obtained from the TD-DFT/singlets and the TD-DFT/triplets output files, respectively, for the S_0-optimized geometry. GaussView5.0.9[18], GaussSum 3.0[19] and Chemissian 4.44[20] were used for data analysis, visualization and surface plots. All calculations were performed in CH_3CN solution by use of the polarized continuum (PCM) solvation model as implemented in Gaussian 09.[21]

Compound **9** was modeled using the same method to confirm the reliability of the model obtained.

<u>*Table S1 :*</u> Predicted and experimental CO stretching vibrations (σ / cm^{-1}) for compounds **4** and reference **9**

Experimental (4)	Predicted (4)	Experimental (9)	Predicted (9)
2019	2088	2012	2012
1916	1981	1882	1897
1891	1967	1865	1891

<u>*Table S2 :*</u> Predicted luminescence wavelength for reference **9**

Compound	λ_{TDDFT}	$\lambda_{0,0}$	λ_{AE}	λ_{298}	Error
9	436	472	561	584^{ref}	4%

λTDDFT = wavelength of $S_0 \rightarrow T_1$ transition obtained by TDDFT at the S_0 optimized geometry. $\lambda_{0,0} = 1240/[E(T_1) - E(S_0)]$ at their respective optimized geometries obtained by DFT. $\lambda_{AE} = 1240/[E(T_1) - E(S_0)]$ at the T_1 optimized geometry (adiabatic electronic emission) obtained by DFT. Error = $|[\lambda_{em}(298\ K) - \lambda_{AE}]/\lambda_{298}|/100$ in %.

Table S3 : Extended frontiers orbitals of compound **4**

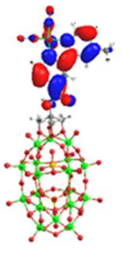
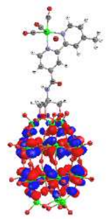
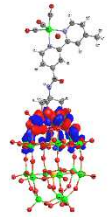
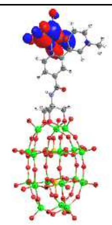
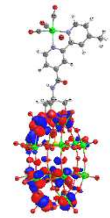
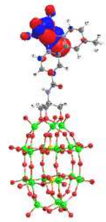
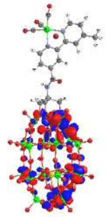
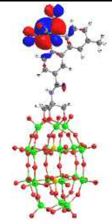
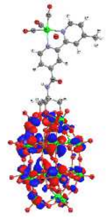
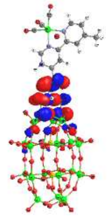
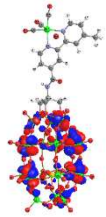
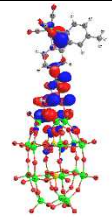
Orbitals (energy)	*Contributions*	*Orbitals (energy)*	*Contributions*
 LUMO+6	Re(CO)$_3$Br : 8% POM : 1% Triol : 0% bpyCONH : 91%	 LUMO -3.5eV	Re(CO)$_3$Br : 0% POM : 99% Triol : 1% bpyCONH : 0%
 LUMO+5 -2.58eV	Re(CO)$_3$Br : 0% POM : 97% Triol : 6% bpyCONH : 0%	 HOMO -6.05eV	Re(CO)$_3$Br : 97% POM : 0% Triol : 0% bpyCONH : 3%
 LUMO+4 -2.85eV	Re(CO)$_3$Br :0 % POM : 97% Triol : 3% bpyCONH : 0%	 HOMO-1 -6.11eV	Re(CO)$_3$Br : 96% POM : 0% Triol : 0% bpyCONH : 4%
 LUMO+3 -2.85eV	Re(CO)$_3$Br : 0% POM : 97% Triol : 3% bpyCONH : 0%	 HOMO-2 -6.62eV	Re(CO)$_3$Br : 98% POM : 0% Triol :0 % bpyCONH : 2%
 LUMO+2 -3.23eV	Re(CO)$_3$Br : 0% POM : 99% Triol : 1% bpyCONH : 0%	 HOMO-3 -6.73eV	Re(CO)$_3$Br : 0% POM : 12% Triol : 62% bpyCONH : 26%
 LUMO+1 -3.24eV	Re(CO)$_3$Br : 0% POM : 99% Triol : 1% bpyCONH : 0%	 HOMO-4 -6.93eV	Re(CO)$_3$Br : 14% POM : 14% Triol : 54% bpyCONH : 18%

Figure S28 Experimental and calculated transitions for **4** in CH_3CN

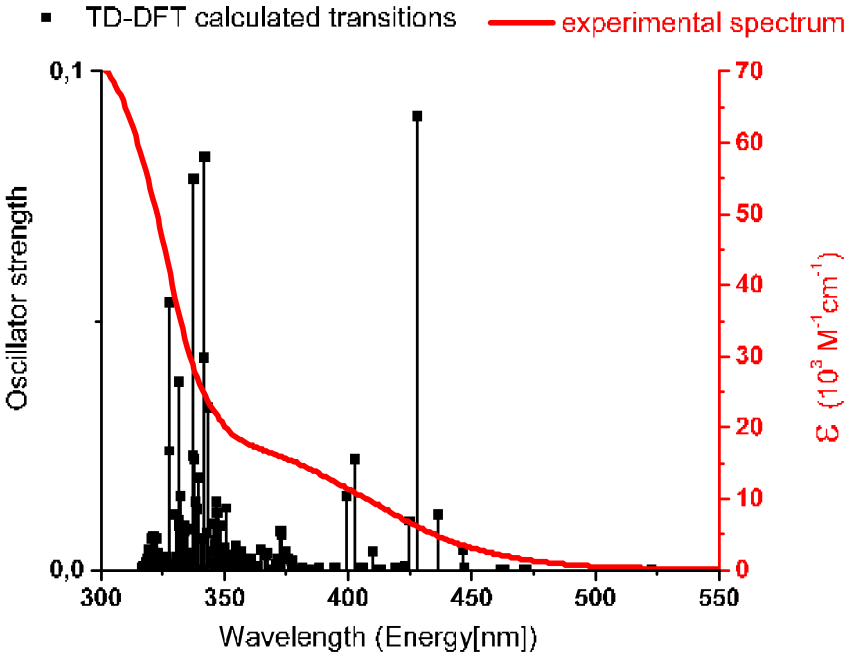


Figure S29 Experimental and calculated transitions for **9** in CH_3CN

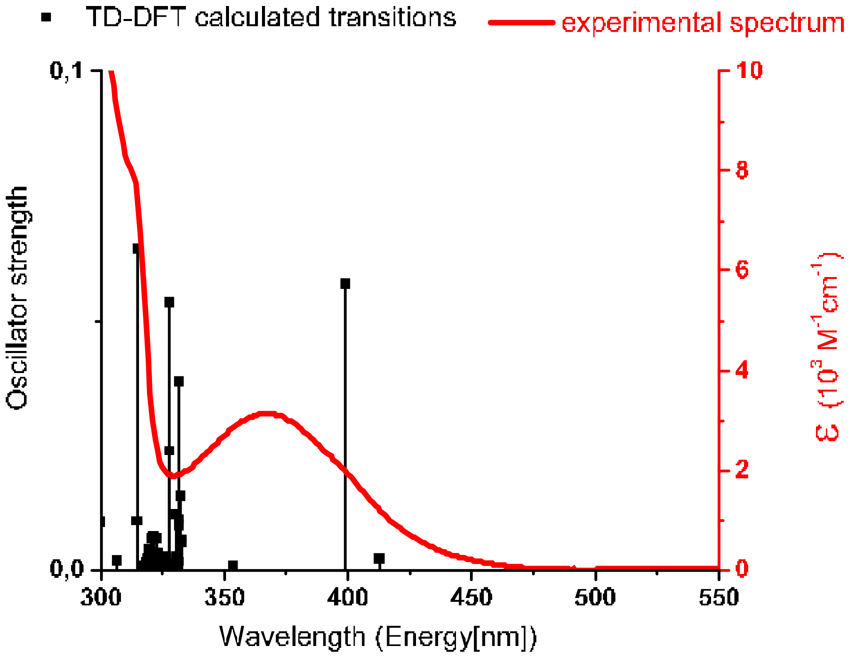


Table S4 : The 150 lowest singlet–singlet and 10 lowest singlet–triplet transitions obtained from the TD-DFT/singlets and the TD-DFT/triplets output files for **4** at the S_0-optimized geometry.

S_0 to Sx	λ (nm)	Osc. Strength	Major contributions (above 5%)	triol	POM	ReCO$_3$Br	Bpy-amide
1	522,74	0.0	HOMO->LUMO (100%)	0-->1 (1)	0-->99 (99)	97-->0 (-97)	3-->0 (-3)
2	511,42	0.0	H-1->LUMO (100%)	0-->1 (1)	0-->99 (99)	96-->0 (-96)	4-->0 (-4)
3	472,41	0.0	HOMO->L+1 (98%)	0-->1 (1)	0-->99 (99)	97-->0 (-97)	3-->0 (-3)
4	471,05	0.0001	HOMO->L+2 (98%)	0-->1 (1)	0-->99 (99)	97-->0 (-97)	3-->0 (-3)
5	463,32	0.0001	H-1->L+1 (97%)	0-->1 (1)	0-->99 (99)	95-->0 (-95)	4-->0 (-4)
6	461,90	0.0002	H-1->L+2 (97%)	0-->1 (1)	0-->99 (99)	96-->0 (-96)	4-->0 (-4)
7	446,85	0.0003	H-3->LUMO (95%)	60-->1 (-59)	13-->99 (86)	1-->0 (-1)	26-->0 (-26)
8	446,55	0.0041	HOMO->L+6 (97%)	0-->0 (0)	0-->3 (3)	97-->8 (-89)	3-->89 (86)
9	436,35	0.0111	H-3->L+1 (65%), H-3->L+3 (22%)	59-->2 (-57)	13-->98 (85)	3-->0 (-3)	25-->0 (-25)
10	427,92	0.091	H-1->L+6 (94%)	2-->1 (-1)	0-->6 (6)	93-->7 (-86)	5-->86 (81)
11	424,81	0.0098	H-3->L+2 (60%), H-3->L+4 (14%)	54-->1 (-53)	13-->96 (83)	10-->0 (-10)	23-->2 (-21)
12	423,08	0.0009	H-4->LUMO (23%), H-2->LUMO (61%)	19-->1 (-18)	5-->99 (94)	67-->0 (-67)	9-->0 (-9)
13	419,39	0.0003	H-4->LUMO (51%), H-2->LUMO (35%)	30-->1 (-29)	10-->99 (89)	48-->0 (-48)	12-->0 (-12)
14	413,18	0.0001	HOMO->L+3 (97%)	0-->2 (2)	0-->97 (97)	97-->0 (-97)	3-->0 (-3)
15	412,15	0.0001	HOMO->L+4 (95%)	1-->3 (2)	0-->96 (96)	96-->0 (-96)	3-->1 (-2)
16	410,14	0.0037	H-4->L+2 (49%), H-4->L+4 (17%)	43-->2 (-41)	16-->98 (82)	23-->0 (-23)	18-->0 (-18)
17	406,20	0.0003	H-1->L+3 (96%)	1-->2 (1)	0-->97 (97)	95-->0 (-95)	4-->0 (-4)
18	405,06	0.0003	H-1->L+4 (95%)	0-->3 (3)	0-->96 (96)	95-->0 (-95)	4-->2 (-2)
19	402,59	0.0221	H-4->L+1 (48%), H-4->L+3 (12%)	39-->2 (-37)	25-->98 (73)	21-->0 (-21)	16-->0 (-16)
20	399,47	0.0147	H-10->LUMO (62%)	9-->1 (-8)	84-->99 (15)	4-->0 (-4)	3-->0 (-3)
21	394,92	0.0003	H-9->LUMO (47%), H-8->LUMO (28%)	2-->1 (-1)	96-->99 (3)	1-->0 (-1)	2-->0 (-2)
22	394,64	0.0005	H-9->LUMO (29%), H-8->LUMO (46%)	2-->1 (-1)	96-->99 (3)	0-->0 (0)	2-->0 (-2)
23	388,04	0.0004	H-2->L+1 (97%)	1-->1 (0)	0-->99 (99)	96-->0 (-96)	2-->0 (-2)
24	387,29	0.0	H-2->L+2 (98%)	1-->1 (0)	0-->99 (99)	97-->0 (-97)	2-->0 (-2)
25	383,45	0.0002	H-12->LUMO (39%), H-11->LUMO (28%)	2-->2 (0)	79-->98 (19)	8-->0 (-8)	11-->0 (-11)
26	383,15	0.0	HOMO->L+5 (92%)	0-->6 (6)	6-->94 (88)	90-->0 (-90)	4-->0 (-4)
27	381,51	0.0005	H-13->LUMO (14%), H-12->LUMO (25%), H-11->LUMO (27%)	5-->1 (-4)	78-->99 (21)	4-->0 (-4)	14-->0 (-14)
28	378,30	0.0	H-5->LUMO (87%)	10-->1 (-9)	5-->99 (94)	69-->0 (-69)	15-->0 (-15)
29	377,56	0.0001	H-1->L+5 (90%)	5-->6 (1)	1-->93 (92)	88-->0 (-88)	6-->0 (-6)
30	377,22	0.0018	H-2->L+6 (97%)	0-->0 (0)	0-->3 (3)	98-->8 (-90)	2-->89 (87)
31	375,63	0.0021	H-3->L+1 (13%), H-3->L+3 (32%)	37-->2 (-35)	40-->98 (58)	4-->0 (-4)	19-->0 (-19)
32	374,43	0.0039	H-3->L+3 (24%)	26-->2 (-24)	57-->98 (41)	2-->0 (-2)	15-->0 (-15)
33	373,21	0.0071	H-15->LUMO (15%), H-6->LUMO (22%), H-3->L+4 (23%)	26-->2 (-24)	39-->98 (59)	21-->0 (-21)	14-->0 (-14)
34	372,75	0.0078	H-6->LUMO (40%), H-3->L+4 (30%)	31-->2 (-29)	16-->98 (82)	35-->0 (-35)	18-->0 (-18)
35	372,37	0.0005	H-16->LUMO (38%)	7-->2 (-5)	77-->98 (21)	5-->0 (-5)	10-->0 (-10)
36	371,48	0.0021	H-15->LUMO (45%), H-6->LUMO (12%)	11-->2 (-9)	71-->98 (27)	10-->0 (-10)	7-->0 (-7)
37	371,19	0.001	H-16->LUMO (13%), H-6->LUMO (13%), H-3->L+5 (42%)	32-->4 (-28)	35-->96 (61)	15-->0 (-15)	17-->0 (-17)
38	368,97	0.0002	H-14->L+1 (15%)	5-->2 (-3)	86-->98 (12)	3-->0 (-3)	7-->0 (-7)
39	367,63	0.0033	H-14->LUMO (45%)	7-->2 (-5)	85-->98 (13)	1-->0 (-1)	6-->0 (-6)
40	366,51	0.0028	H-3->L+5 (13%)	12-->2 (-10)	78-->98 (20)	2-->0 (-2)	8-->0 (-8)

41	364,56	0.0041	H-21->LUMO (46%)	2-->1 (-1)	95-->99 (4)	1-->0 (-1)	3-->0 (-3)
42	363,22	0.0009	H-22->LUMO (17%), H-9->L+2 (14%), H-8->L+1 (15%)	2-->1 (-1)	92-->99 (7)	1-->0 (-1)	5-->0 (-5)
43	362,81	0.0004	H-23->LUMO (14%), H-9->L+1 (15%), H-8->L+2 (14%)	3-->1 (-2)	90-->99 (9)	2-->0 (-2)	5-->0 (-5)
44	360,44	0.0021		8-->1 (-7)	70-->99 (29)	6-->0 (-6)	16-->0 (-16)
45	359,57	0.002	H-24->LUMO (20%), H-7->LUMO (14%)	4-->1 (-3)	74-->99 (25)	4-->0 (-4)	18-->0 (-18)
46	358,81	0.0022	H-17->LUMO (23%), H-10->L+2 (16%)	6-->1 (-5)	85-->99 (14)	3-->0 (-3)	6-->0 (-6)
47	358,11	0.0003	H-10->L+1 (11%), H-7->LUMO (51%)	2-->1 (-1)	43-->99 (56)	5-->0 (-5)	50-->0 (-50)
48	357,27	0.0006	H-4->L+2 (13%), H-4->L+4 (31%)	30-->2 (-28)	40-->98 (58)	15-->0 (-15)	16-->0 (-16)
49	356,52	0.0037	H-4->L+3 (24%)	23-->2 (-21)	54-->98 (44)	11-->0 (-11)	12-->0 (-12)
50	355,03	0.0015	H-10->LUMO (14%), H-9->L+1 (19%), H-8->L+2 (19%)	2-->1 (-1)	95-->99 (4)	1-->0 (-1)	2-->0 (-2)
51	354,82	0.0021	H-4->L+5 (46%)	32-->4 (-28)	37-->95 (58)	17-->0 (-17)	14-->0 (-14)
52	354,41	0.0048	H-22->LUMO (16%), H-7->LUMO (10%)	8-->1 (-7)	65-->99 (34)	10-->0 (-10)	17-->0 (-17)
53	354,18	0.0004	HOMO->L+7 (88%)	1-->1 (0)	3-->97 (94)	93-->0 (-93)	3-->1 (-2)
54	353,82	0.003	H-4->L+5 (12%), HOMO->L+8 (43%)	13-->2 (-11)	29-->98 (69)	51-->0 (-51)	8-->0 (-8)
55	353,68	0.0023	HOMO->L+8 (51%)	10-->2 (-8)	23-->98 (75)	60-->0 (-60)	7-->0 (-7)
56	351,65	0.0016	H-5->L+1 (67%)	10-->1 (-9)	16-->99 (83)	58-->0 (-58)	15-->0 (-15)
57	350,93	0.0029	H-5->L+2 (49%)	10-->1 (-9)	32-->99 (67)	45-->0 (-45)	13-->0 (-13)
58	350,60	0.0124	H-5->L+1 (13%)	5-->2 (-3)	70-->98 (28)	16-->0 (-16)	9-->0 (-9)
59	349,88	0.0044	H-5->L+2 (23%)	4-->1 (-3)	62-->99 (37)	23-->0 (-23)	10-->0 (-10)
60	349,55	0.0039		3-->1 (-2)	84-->99 (15)	8-->0 (-8)	6-->0 (-6)
61	349,25	0.0035	H-10->L+2 (10%)	3-->1 (-2)	90-->99 (9)	3-->0 (-3)	5-->0 (-5)
62	349,01	0.0003	H-1->L+7 (92%)	0-->1 (1)	0-->97 (97)	95-->0 (-95)	4-->1 (-3)
63	348,55	0.0001	H-1->L+8 (92%)	0-->1 (1)	0-->99 (99)	95-->0 (-95)	4-->0 (-4)
64	348,28	0.0089	H-17->LUMO (13%), H-10->L+1 (17%)	4-->1 (-3)	80-->99 (19)	10-->0 (-10)	6-->0 (-6)
65	348,09	0.0021	H-14->L+1 (10%), H-12->L+2 (16%)	5-->1 (-4)	74-->99 (25)	13-->0 (-13)	8-->0 (-8)
66	347,27	0.0007	H-6->L+1 (16%), H-2->L+3 (55%)	3-->2 (-1)	21-->98 (77)	71-->0 (-71)	5-->0 (-5)
67	346,96	0.0115	H-26->LUMO (10%), H-6->L+1 (15%), H-2->L+3 (28%)	3-->2 (-1)	44-->98 (54)	46-->0 (-46)	7-->0 (-7)
68	346,88	0.0058	H-26->LUMO (12%), H-11->L+2 (10%), H-2->L+4 (21%)	3-->2 (-1)	52-->98 (46)	38-->0 (-38)	7-->0 (-7)
69	346,63	0.0136	H-26->LUMO (28%), H-2->L+4 (31%)	2-->2 (0)	56-->98 (42)	39-->0 (-39)	3-->0 (-3)
70	346,38	0.0051	H-2->L+4 (34%)	3-->2 (-1)	53-->98 (45)	39-->0 (-39)	6-->0 (-6)
71	346,06	0.0047		5-->2 (-3)	71-->98 (27)	17-->0 (-17)	6-->0 (-6)
72	345,85	0.0092	H-8->L+1 (10%)	4-->1 (-3)	83-->98 (15)	8-->0 (-8)	5-->0 (-5)
73	345,27	0.0015	H-6->L+1 (12%), H-6->L+2 (46%)	6-->1 (-5)	34-->99 (65)	49-->0 (-49)	10-->0 (-10)
74	344,62	0.0036	H-12->L+1 (12%), H-6->L+1 (14%), H-6->L+2 (14%)	5-->1 (-4)	60-->99 (39)	25-->0 (-25)	10-->0 (-10)
75	343,38	0.0325		3-->1 (-2)	89-->99 (10)	3-->0 (-3)	4-->0 (-4)
76	342,84	0.0073		3-->1 (-2)	89-->99 (10)	2-->0 (-2)	6-->0 (-6)
77	341,86	0.0829	H-26->LUMO (10%), H-20->LUMO (10%)	3-->1 (-2)	88-->99 (11)	4-->0 (-4)	5-->0 (-5)
78	341,53	0.0426	H-19->LUMO (14%)	4-->1 (-3)	87-->99 (12)	4-->0 (-4)	5-->0 (-5)
79	340,88	0.0002	HOMO->L+9 (94%)	2-->2 (0)	1-->97 (96)	94-->0 (-94)	4-->1 (-3)
80	340,46	0.0063	H-25->LUMO (13%), H-10->L+1 (12%)	4-->1 (-3)	88-->99 (11)	2-->0 (-2)	5-->0 (-5)
81	339,62	0.0186	H-32->LUMO (15%), H-27->LUMO (10%)	10-->1 (-9)	78-->99 (21)	6-->0 (-6)	7-->0 (-7)
82	338,73	0.0121	H-3->L+11 (17%)	29-->1 (-28)	42-->98 (56)	13-->0 (-13)	16-->1 (-15)
83	338,31	0.0136		7-->1 (-6)	81-->98 (17)	4-->0 (-4)	7-->0 (-7)

84	337,85	0.0221	H-30->LUMO (12%)	3-->1 (-2)	94-->98 (4)	1-->0 (-1)	3-->0 (-3)
85	337,83	0.0083	H-29->LUMO (10%)	3-->2 (-1)	91-->98 (7)	2-->0 (-2)	4-->0 (-4)
86	337,47	0.0022	HOMO->L+10 (60%)	4-->1 (-3)	29-->98 (69)	63-->0 (-63)	5-->0 (-5)
87	337,45	0.0784	H-39->LUMO (10%), H-28->LUMO (18%)	4-->1 (-3)	84-->98 (14)	9-->0 (-9)	3-->1 (-2)
88	337,22	0.023	HOMO->L+10 (17%), HOMO->L+11 (13%)	8-->1 (-7)	50-->98 (48)	35-->0 (-35)	7-->1 (-6)
89	336,86	0.0035	H-1->L+9 (13%), HOMO->L+11 (30%)	6-->2 (-4)	36-->96 (60)	53-->0 (-53)	6-->2 (-4)
90	336,77	0.0011	HOMO->L+11 (25%)	3-->1 (-2)	57-->96 (39)	35-->0 (-35)	5-->2 (-3)
91	336,63	0.0029		3-->1 (-2)	87-->99 (12)	4-->0 (-4)	6-->0 (-6)
92	336,16	0.0013	H-1->L+9 (61%)	10-->2 (-8)	8-->94 (86)	73-->0 (-73)	8-->3 (-5)
93	335,40	0.0034	H-3->L+10 (12%), HOMO->L+20 (14%), HOMO->L+23 (20%)	20-->1 (-19)	10-->67 (57)	58-->1 (-57)	13-->30 (17)
94	335,25	0.0025		10-->1 (-9)	48-->84 (36)	32-->1 (-31)	11-->14 (3)
95	335,17	0.0083	H-34->LUMO (15%)	6-->1 (-5)	67-->93 (26)	14-->0 (-14)	13-->5 (-8)
96	335,07	0.0032	H-33->LUMO (11%), H-7->L+1 (13%)	18-->1 (-17)	38-->94 (56)	16-->0 (-16)	28-->4 (-24)
97	334,31	0.0028	H-7->L+1 (42%), H-7->L+2 (19%)	3-->1 (-2)	32-->98 (66)	4-->0 (-4)	60-->0 (-60)
98	333,70	0.0091	H-7->L+2 (22%)	7-->1 (-6)	52-->96 (44)	6-->0 (-6)	34-->3 (-31)
99	333,50	0.0079	H-33->LUMO (10%)	2-->1 (-1)	87-->99 (12)	1-->0 (-1)	9-->0 (-9)
100	333,00	0.0011	H-3->L+6 (45%), H-3->L+9 (20%)	45-->1 (-44)	18-->51 (33)	13-->4 (-9)	24-->45 (21)
101	332,50	0.0057	H-1->L+10 (38%)	3-->1 (-2)	45-->98 (53)	41-->0 (-41)	11-->0 (-11)
102	332,42	0.0061	H-1->L+10 (36%), H-1->L+11 (12%)	6-->1 (-5)	32-->93 (61)	51-->0 (-51)	11-->6 (-5)
103	332,28	0.0149	H-7->L+2 (10%)	5-->1 (-4)	76-->95 (19)	6-->0 (-6)	13-->4 (-9)
104	331,78	0.0102	H-1->L+11 (41%)	13-->1 (-12)	22-->88 (66)	55-->1 (-54)	11-->10 (-1)
105	331,68	0.0088	H-5->L+6 (16%), H-3->L+9 (16%)	25-->1 (-24)	14-->60 (46)	46-->3 (-43)	15-->37 (22)
106	331,46	0.0377	H-5->L+6 (43%), H-1->L+11 (12%)	10-->1 (-9)	13-->38 (25)	64-->4 (-60)	13-->57 (44)
107	331,25	0.0017		11-->1 (-10)	76-->92 (16)	5-->0 (-5)	7-->6 (-1)
108	331,07	0.0017		9-->1 (-8)	78-->92 (14)	5-->1 (-4)	8-->7 (-1)
109	330,61	0.0025	H-38->LUMO (19%)	6-->1 (-5)	84-->98 (14)	3-->0 (-3)	8-->1 (-7)
110	330,29	0.0112	H-6->L+6 (16%), H-4->L+6 (11%), H-1->L+20 (19%), H-1->L+23 (29%)	9-->1 (-8)	3-->42 (39)	76-->3 (-73)	11-->55 (44)
111	329,68	0.0003	H-41->LUMO (16%)	3-->1 (-2)	92-->99 (7)	2-->0 (-2)	4-->0 (-4)
112	329,50	0.0011	H-40->LUMO (11%), H-16->L+2 (10%)	3-->1 (-2)	89-->99 (10)	2-->0 (-2)	5-->0 (-5)
113	329,32	0.0001	H-16->L+2 (14%), H-15->L+1 (15%), H-15->L+2 (13%)	2-->1 (-1)	92-->99 (7)	2-->0 (-2)	4-->0 (-4)
114	327,81	0.0239	H-39->LUMO (22%)	8-->1 (-7)	74-->81 (7)	13-->1 (-12)	6-->17 (11)
115	327,70	0.0537	H-6->L+6 (10%), H-4->L+6 (28%), H-1->L+23 (11%)	20-->1 (-19)	30-->43 (13)	40-->4 (-36)	10-->53 (43)
116	327,38	0.0009	H-40->LUMO (18%)	5-->1 (-4)	87-->98 (11)	3-->0 (-3)	5-->0 (-5)
117	327,01	0.0011	H-42->LUMO (10%), H-21->L+1 (12%)	3-->1 (-2)	92-->98 (6)	3-->0 (-3)	3-->1 (-2)
118	326,67	0.0026	H-3->L+12 (11%), HOMO->L+12 (52%)	13-->2 (-11)	22-->96 (74)	57-->0 (-57)	8-->2 (-6)
119	326,51	0.0022	HOMO->L+12 (12%)	4-->2 (-2)	78-->98 (20)	14-->0 (-14)	4-->1 (-3)
120	326,01	0.0001	HOMO->L+13 (57%)	2-->2 (0)	35-->98 (63)	59-->0 (-59)	4-->0 (-4)
121	325,99	0.001	HOMO->L+13 (39%)	2-->2 (0)	51-->98 (47)	43-->0 (-43)	4-->0 (-4)
122	325,67	0.0014	H-2->L+5 (63%), HOMO->L+12 (11%)	11-->5 (-6)	5-->94 (89)	78-->0 (-78)	6-->1 (-5)
123	325,61	0.0022	H-3->L+12 (15%), H-2->L+5 (34%), HOMO->L+12 (19%)	21-->4 (-17)	9-->95 (86)	60-->0 (-60)	10-->1 (-9)
124	324,87	0.0013	H-43->LUMO (27%)	3-->1 (-2)	93-->98 (5)	2-->0 (-2)	2-->0 (-2)
125	324,45	0.0012		3-->1 (-2)	93-->98 (5)	1-->0 (-1)	3-->0 (-3)
126	324,34	0.0011	H-36->LUMO (10%)	3-->1 (-2)	94-->99 (5)	1-->0 (-1)	2-->0 (-2)

127	323,62	0.0002	H-23->L+2 (10%)	3-->2 (-1)	89-->98 (9)	2-->0 (-2)	7-->0 (-7)
128	323,01	0.0033	H-25->L+2 (11%)	6-->2 (-4)	84-->98 (14)	4-->0 (-4)	6-->0 (-6)
129	322,39	0.0062	H-6->L+6 (12%), H-1->L+12 (23%), H-1->L+13 (13%)	20-->2 (-18)	14-->76 (62)	54-->2 (-52)	13-->21 (8)
130	322,23	0.0034	H-3->L+13 (10%), H-1->L+12 (16%), H-1->L+13 (37%)	17-->2 (-15)	14-->95 (81)	58-->0 (-58)	10-->3 (-7)
131	321,69	0.003	H-25->L+1 (10%), H-21->L+1 (10%)	3-->2 (-1)	92-->98 (6)	2-->0 (-2)	4-->0 (-4)
132	321,59	0.0068	H-6->L+6 (14%), H-1->L+12 (37%), H-1->L+13 (11%)	11-->2 (-9)	12-->67 (55)	66-->2 (-64)	11-->29 (18)
133	321,27	0.0032	H-1->L+13 (13%)	7-->2 (-5)	64-->87 (23)	20-->1 (-19)	9-->10 (1)
134	321,19	0.0025	H-23->L+1 (12%)	5-->2 (-3)	83-->96 (13)	6-->0 (-6)	6-->2 (-4)
135	320,93	0.0066		4-->2 (-2)	89-->96 (7)	3-->0 (-3)	4-->2 (-2)
136	320,69	0.0031	H-4->L+10 (12%), H-1->L+13 (11%)	26-->2 (-24)	39-->92 (53)	22-->0 (-22)	13-->6 (-7)
137	320,53	0.0064	H-4->L+9 (11%), H-3->L+12 (11%), H-1->L+12 (10%)	27-->2 (-25)	34-->88 (54)	25-->1 (-24)	14-->9 (-5)
138	320,03	0.0021		10-->2 (-8)	75-->94 (19)	8-->0 (-8)	8-->4 (-4)
139	319,80	0.0002	HOMO->L+14 (84%)	4-->2 (-2)	4-->97 (93)	88-->0 (-88)	4-->0 (-4)
140	319,65	0.0016	H-24->L+1 (11%)	4-->2 (-2)	85-->98 (13)	7-->0 (-7)	4-->0 (-4)
141	319,29	0.0041	H-20->L+1 (12%)	7-->2 (-5)	70-->97 (27)	11-->0 (-11)	12-->1 (-11)
142	318,93	0.0021	H-4->L+11 (17%), H-3->L+13 (14%)	38-->2 (-36)	24-->97 (73)	21-->0 (-21)	17-->1 (-16)
143	318,12	0.0015	H-12->L+3 (11%)	5-->2 (-3)	82-->98 (16)	7-->0 (-7)	6-->0 (-6)
144	318,06	0.0001	H-18->LUMO (43%)	3-->1 (-2)	54-->99 (45)	38-->0 (-38)	5-->0 (-5)
145	318,00	0.0004	H-18->LUMO (28%)	4-->1 (-3)	63-->98 (35)	28-->0 (-28)	6-->0 (-6)
146	317,53	0.0005	H-5->L+3 (56%)	9-->2 (-7)	29-->98 (69)	51-->0 (-51)	12-->0 (-12)
147	317,36	0.0006	H-45->LUMO (11%), H-21->L+2 (10%)	5-->2 (-3)	80-->98 (18)	10-->0 (-10)	5-->0 (-5)
148	317,12	0.0006	H-5->L+3 (11%), H-5->L+4 (16%)	9-->2 (-7)	56-->97 (41)	26-->0 (-26)	10-->1 (-9)
149	316,99	0.0009		4-->2 (-2)	83-->98 (15)	7-->0 (-7)	6-->0 (-6)
150	316,61	0.0006	H-5->L+4 (42%)	6-->2 (-4)	47-->97 (50)	36-->0 (-36)	11-->1 (-10)

S_0 to Sx	λ (nm)	Osc. Strength	Major contributions (above 5%)	triol	POM	$ReCO_3Br$	Bpy-amide
1	522,77	0	HOMO->LUMO (100%)	0-->1 (1)	0-->99 (99)	97-->0 (-97)	3-->0 (-3)
2	511,44	0	H-1->LUMO (100%)	0-->1 (1)	0-->99 (99)	96-->0 (-96)	4-->0 (-4)
3	472,48	0	HOMO->L+1 (98%)	0-->1 (1)	0-->98 (98)	97-->0 (-97)	3-->0 (-3)
4	471,15	0	HOMO->L+2 (98%)	0-->1 (1)	0-->98 (98)	97-->0 (-97)	3-->0 (-3)
5	465,34	0	HOMO->L+6 (80%)	0-->0 (0)	0-->5 (5)	91-->8 (-83)	8-->87 (79)
6	463,93	0	H-1->L+1 (82%)	9-->1 (-8)	2-->98 (96)	82-->0 (-82)	7-->1 (-6)
7	462,46	0	H-1->L+2 (87%)	4-->1 (-3)	1-->98 (97)	89-->0 (-89)	6-->0 (-6)
8	458,79	0	H-3->L+1 (32%), H-3->L+3 (12%), H-1->L+1 (12%)	45-->2 (-43)	13-->98 (85)	22-->0 (-22)	20-->0 (-20)
9	454,35	0	H-3->LUMO (60%), H-3->L+2 (13%)	56-->2 (-54)	14-->98 (84)	6-->0 (-6)	24-->0 (-24)
10	453,66	0	H-1->L+6 (88%)	0-->0 (0)	0-->3 (3)	95-->8 (-87)	5-->88 (83)

Crystallography

The data collection was carried out on a Bruker Venture Metaljet diffractometer equipped with an Oxford Cryosystem liquid N_2 device set at 150K, using Ga-Kα radiation (λ = 1.34139 Å). The cell parameters were determined from reflections taken from three sets of omega scans (104 frames, 1° per frame) using APEX3 software package[22]. Data reduction was performed with SAINT[23], adsorption correction with SADABS[24]. The structure was solved by dual-space refinement via SHELXT[25] in OLEX2[26]. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2, the H-atoms were included in calculated positions and treated as riding atoms (SHELXL97[27]).

The absorption correction optimization appeared to be difficult for this dataset containing several highly absorbing heavy atoms of tungsten. Besides, a complex mix of disordered solvent and counter-cations surrounding the functionalized cluster was affecting the model. Some of the counter cations could however be identified and were modeled using the appropriate restraints (DFIX, DANG, RIGU, SIMU and BUMP). The first two TBAs yielded a reasonable model, while the third one required the use of tighter restraints. Albeit the two remaining cations (5 TBA expected according to other analytical results) could be partially identified, we were unable to obtain a reasonable model for them. We thus used the solvent-mask protocol in OLEX2 to remove the remaining densities (void of 6432 Å^3 i.e. 40% containing 644 electrons while 2 TBA$^+$ would correspond to 278 electrons). During the solvent mask procedure, the flack-x parameter value (refined using TWIN/BASF) increased from 0.010(4) to 0.255(19) while the hooft-y remained around 0.02. Similar observations were made using the PLATON/SQUEEZE routine. This systematic observation was treated as an artefact from the solvent-mask procedure. CCDC 1548013 contains the complete crystallographic data for this structure.

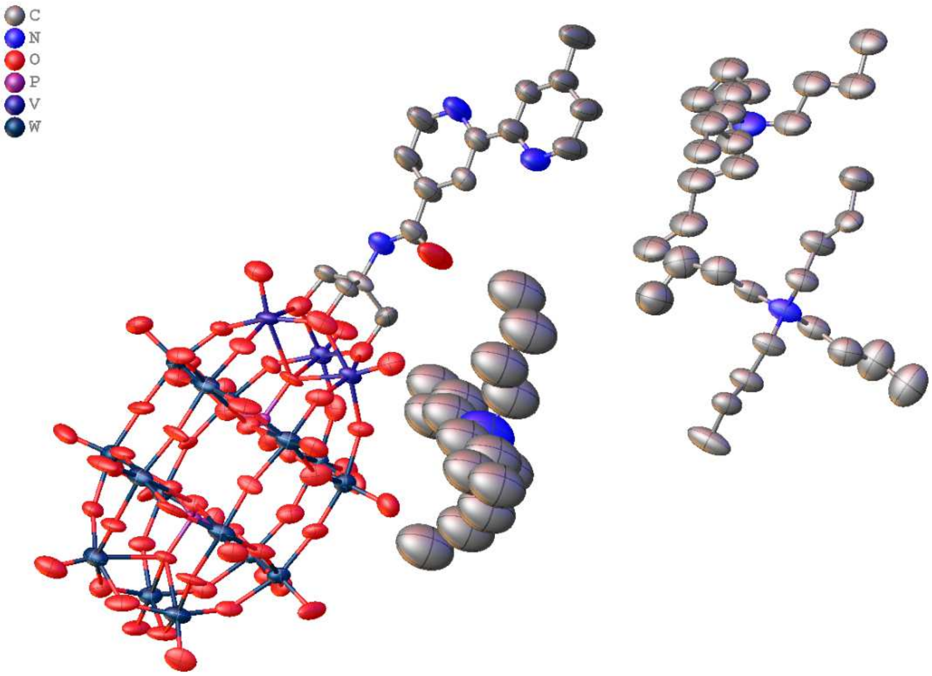


Figure S30 X-ray structure of compound **1** (Ellipsoids are at 50% probability, hydrogens are omitted for clarity)

Identification code	auvr28
Empirical formula	$C_{64}H_{124}N_6O_{63}P_2V_3W_{15}$
Formula weight	4958.19
Temperature/K	150.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	28.0308(10)
b/Å	36.9998(13)
c/Å	15.5102(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	16086.2(10)
Z	4
ρ_{calc}g/cm^3	2.047
μ/mm^{-1}	15.072
F(000)	9052.0
Crystal size/mm^3	0.19 × 0.19 × 0.04
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	3.44 to 108.51
Index ranges	$-33 \leq h \leq 33$, $-44 \leq k \leq 44$, $-18 \leq l \leq 18$
Reflections collected	413250
Independent reflections	29712 [R_{int} = 0.1004, R_{sigma} = 0.0386]
Data/restraints/parameters	29712/674/1380
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0652, wR_2 = 0.1782
Final R indexes [all data]	R_1 = 0.0726, wR_2 = 0.1867
Largest diff. peak/hole / e Å^{-3}	3.52/-1.28
Flack parameter	0.255(19)

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