Unprecedented coupling reaction between two anionic species of Closodecahydrodecaborate cluster and Anderson-type polyoxometalates.

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Part 1: Experimental section

1°) General methods

Fourier Transform Infrared (FT-IR) spectra were recorded on a 6700 FT-IR Nicolet spectrophotometer, using diamond ATR technique. The spectra were recorded on non-diluted compounds and ATR correction was applied.

Elemental analyses of C, H, and N were carried out by the analytical service of the CNRS at Gif sur Yvette, France. Quantitative analyses of metals were carried out by ICP analysis performed in CREALINS laboratory in Vernaison, France.

Energy-dispersive X-ray spectroscopy_(EDX) measurements were performed using a SEM-FEG (Scanning Electron Microscope enhanced by a Field Emission Gun) equipment (JSM 7001-F, Jeol). The measures were acquired with a SDD XMax 50 mm² detector and the Aztec (Oxford) system working at 15 kV and 10 mm working distance. The quantification is realized with the standard library provided by the constructor using L α lines.

Water contents were determined by thermal gravimetric analysis (TGA) with a Mettler Toledo TGA/DSC 1, STAR^e System apparatus under oxygen or nitrogen flow (50 mL min⁻¹) at a heating rate of 5 °C min⁻¹ up to 700 °C.

UV-Vis spectra were recorded on a Perkin-Elmer UV-Vis-NIR Lambda-750 spectrometer using calibrated 0.1 cm Quartz-cell.

Nuclear magnetic resonance (NMR) solution spectra were recorded at 25 °C. ¹H, ¹¹B, and ¹³C, NMR were measured with a Bruker Avance 400 MHz spectrometer equipped with a 5 mm BBI probe head and operated at a magnetic field strength of 9.4 T. Quartz NMR tubes are used to avoid background signals from the standard glass tubes in case of ¹¹B. CD₃CN was used as solvent. Typically, ¹H spectra were recorded with one pulse sequence at 30° flip angle (pulse duration 2.4 μ s), using 1 s recycle delay, 1.6 s acquisition time, and 80 number of scans. In case of samples containing boron, Waltz16 ¹¹B decoupling was applied during the acquisition of ¹H spectra. The ¹¹B spectra were recorded with Hahn echo sequence (echo delay 117 μ s) under proton decoupling condition, using 0.1 s recycle delay, 21 ms acquisition time, and 1024 number of scans. The ¹³C spectra were obtained with either standard powergated decoupling or Dept145 pulse sequences, using typically 4.5 s recycle delay, 1.3 s acquisition time, and ca. 8000 number of scans. Chemical shifts are reported relative to 1 % Me₄Si in CDCl₃ (¹H and ¹³C), and 15 % BF₃.Et₂O in CDCl₃ (¹¹B) according to conventional standards.^[1]

Electrospray Ionization Mass Spectrometry (ESI-MS) spectra were collected using a Q-TOF instrument supplied by WATERS. Samples were solubilized in water at a concentration of 10⁻⁴ M and were introduced into the spectrometer via an ACQUITY UPLC WATERS system whilst a Leucine Enkephalin solution was co-injected via a micro pump as internal standard

Electrochemistry. For electrochemical experiments, we used a glassy carbon that is polished with cloth of different sizes (1 µm, 3 µm and 6 µm) composed of 100 % wool and provided by Struers. We used for polishing three-pastes with high performance diamond product containing exclusively polycrystalline diamonds with also the same sizes (1 µm, 3 µm and 6 μ m). The electrochemical set-up was a PZG402 Potentiostat with the voltmaster 4 software. Potential is measured against a saturated calomel reference electrode (SCE) in a compartment separated from the test solution by a fine prosity glass frit.. The counter electrode was platinum of large surface area in a separated comportment with a medium prosity glass frit. Freshly distilled acetonitrile (ACN) was used throughout. The solutions were deaerated thoroughly for at least 45 minutes with pure argon and kept under a positive pressure of this gas during the experiments. The supporting electrolyte was 0.1 M TBACIO₄ in ACN. The electrochemical experiment was performed in a compartment cell with a four places for 3 electrodes and purge of argon gaz. The working electrode was a glassy carbon with a 0.07 cm² as surface and had been polished before the electrochemical measure. Experiments were performed at the laboratory temperature. The stability of the products was assessed by electrochemistry method. The initial cyclic voltammogram of each product was recorded at the end of the electrolysis after argon desoxygenation. Provisionally perfect reproducibility of the voltammogram for a selected potential scan rate was taken as a complementary stability criterion.

2°) Syntheses and characterizations

All reagents were purchased from commercial sources and used without further purification. All synthetic reactions were performed under argon atmosphere using vacuum line and Schlenk-techniques. All solvents were dried and distilled unless stated otherwise, because of the sensitivity of the boron precursor used. $(NH_4)_2[B_{10}H_{10}]$ was provided by Boron Biological in USA and $(TBA)_2[B_{10}H_{10}]$ was precipitated from an aqueous solution of $(NH_4)_2[B_{10}H_{10}]$ using a saturated solution of TBABr. $[N(C_4H_9)_4]_4[\alpha-Mo_8O_{26}]^{[2]}$ was prepared according to literature and checked by routine analysis prior using.

Synthesis of the Boron precursor TBA[$B_{10}H_9CO$]. TBA[$B_{10}H_9CO$] was prepared according to literature.^[3] A mixture of (TBA)₂[$B_{10}H_{10}$] (4 g, 6.6 mmol) in 150 mL of dry CH₂Cl₂ was chilled in an ice bath with stirring under argon. A solution of COCl₂ (2 mL, 22.9 mmol) was added with a syringe, and the mixture was stirred at 0 °C for 30 min. The solution was allowed to warm to room temperature and stirred an additional 30 min. The volume of the solution was reduced by 2/3 under reduced pressure and the resulting solution was passed through a column of silica gel, eluting with CH₂Cl₂. After evaporation in vacuum, 2.4 g of a yellow product corresponding to TBA[$B_{10}H_9CO$] were obtained (yield 93 %). The product was analyzed by FT-IR, ¹¹B NMR and ESI-MS in CH₃CN and all were consistent with that of the literature. FT-IR spectrum: in addition to the vibration bands of TBA cations, the spectrum displays the characteristic bands that are at 2515 cm⁻¹ and 2095 cm⁻¹ assigned to B-H and C=O groups respectively. ¹¹B NMR (δ ppm, 400 MHz, CD₃CN): 6.2 (d, 1 B), 5.4 (d, 1 B), -18.3 (d, 1 B), -26.5 (d, 2 B), -28.9 (d, 2 B), -29.4 (d, 2 B), -44.4 (s, 1 B). ¹H NMR (δ ppm, 400 MHz, CD₃CN): 3.39 to 4.81 (crown like structure, 2 H apical), 3.15 (t, TBA), 1.63 (m, TBA), 1.38 (m, TBA), 0.99 (t, TBA)

-0.27 to 0.64 (crown like structure, 7 H equatorial). ${}^{1}H{}^{11}B{}$ NMR (δ ppm, 400 MHz, CD₃CN): 4.06 (s, 1 H), 3.83 (s, 1 H), (s, 1 H), 0.69 (d, 3 H), 0.65 (d, 3 H), 0.38 (d, 1 H) in addition to TBA⁺ peaks listed above. ESI-MS (Negative mode, CH₃CN): [B₁₀H₉CO]⁻, *m/z* calculated (found): 145.19 (145.16).

Synthesis of (N(C₄H₉)₄)₃[MnMo₆O₁₈{(OCH₂)₃CNH₂}₂].2H₂O denoted hereafter MnMo₆(TRIS)₂ $MnMo_{6}$ -(TRIS)₂ was prepared according to literature.^[4] A mixture of $[N(C_{4}H_{9})_{4}]_{4}[\alpha-Mo_{8}O_{26}]$ (8.00 g, 3.7 mmol), Mn(CH₃COO)₃·2H₂O (1.49 g, 5.6 mmol) and (HOCH₂)₃CNH₂ (1.56 g, 12.8 mmol) in 150 mL of acetonitrile was refluxed for 16 h. The orange solution was cooled to room temperature and filtered to remove a very fine black solid. The filtrate was exposed to ether vapor. After 2 h, a white precipitate was filtered off. The orange filtrate was again exposed to ether vapor for several days. Large orange crystals were obtained, isolated by filtration, washed with a small amount of acetonitrile and ether, and dried under vacuum to give 7 g of $(C_{16}H_{36}N)_3(MnMo_6O_{18})(O_6C_8H_{16}N_2)(H_2O)_2$ (74 %). The product was analyzed by FT-IR, ¹ H NMR and ESI-MS in CH₃CN. FT-IR (v/cm⁻¹): 3391 (w, br), 2962 (s), 2936 (s), 2874 (s), 1609 (w), 1480 (s), 1382 (m), 1128 (w), 1043 (s), 939 (s), 920 (s), 903 (s), 797 (w), 664 (vs), 563 (m). Elemental analysis for $(C_6H_{36}N)_3[MnMo_6O_{18}{(OCH_2)_3CNH_2}_2].2H_2O$ $(C_{56}H_{128}MnMo_6N_5O_{26}, FW = 1918.23 \text{ g.mol}^{-1})$ Calc. (found): H 6.73 (6.55); C 35.06 (34.95); N 3.65 (3.69). TGA showed a weight loss of 1.9 % in the 20-150 °C temperature range corresponding to the hydration water (calculated 1.8 %). EDX, ratio, calc. (found): Mn/Mo, 0.17 (0.16). ¹H NMR (δ ppm, 400.13 MHz, CD₃CN): 3.16 (t, TBA⁺), 1.65 (m, TBA⁺), 1.40 (m, TBA⁺), 0.99 (t, TBA⁺), 60.72 ((-OCH₂)₃-CNH₂).

Synthesis of (C₁₆H₃₆N)_{3.5}(C₈H₁₉N)_{3.5}[MnMo₆O₁₈)(O₃C₄H₇NB₁₀H₉CO)₂] denoted here after MnMo₆(TRIS-B₁₀)₂. MnMo₆-(TRIS)₂ (0.3 g, 0.156 mmol) was dissolved in 5 mL of dry acetonitrile, and TBAB₁₀H₉CO (0.157 g, 0.407 mmol, 2.6 equivalents) was then added. A precipitate was formed upon this addition which disappeared by the dropwise addition of diisopropylethylamine, DIPEA, (109 µL, 0.624 mmol). The reaction was kept stirring overnight at room temperature under nitrogen. The product was isolated by precipitation with excess of diethyl ether, filtrated, washed, and dried to give 0.32 g of orange powder of **MnMo₆(TRIS-B₁₀)**₂ (yield 72 %). The product was analyzed by FT-IR, ¹H, ¹¹B NMR and ESI-MS in CH₃CN. FT-IR (v/cm⁻¹): 3504 (m, br.), 2964 (s), 2936 (m), 2875 (m), 2472 (s), 1588 (w), 1480 (m), 1382 (w), 1017 (w), 939 (s), 920 (s), 901 (sh), 667 (s). Elemental analysis for $(C_{16}H_{36}N)_{3.5}(C_8H_{19}N)_{3.5}[MnMo_6O_{18}(O_3C_4H_7NB_{10}H_9CO)_2]$ (B₂₀C₉₄H_{224.5}MnMo₆N₉O₂₆, FW = 2744.16 g.mol⁻¹) Calc. (found): H 8.25 (8.15); C 41.14 (41.08); N 4.59 (4.09); B 7.88 (7.92); Mo 20.98 (21.14). EDX, ratio, calc (found): Mn/Mo, 0.166 (0.133). ¹H NMR (δ ppm, 400.13 MHz, CD_3CN): -0.5-0.78 (crown, B-H), 60-64.8 (m, $(-OCH_2)_3$ -CNHCOB₁₀), 8.6 ([(CH₃)₂CH]₂NH⁺CH₂CH₃), 6.28 ((-OCH₂)₃-CNHCOB₁₀), 3.70 (m, [(CH₃)₂CH]₂NH⁺CH₂CH₃), 3.14 (t, -N⁺CH₂CH₂CH₂CH₃), 3.26 (m, [(CH₃)₂CH]₂NH⁺CH₂CH₃), 1.65 (m, -N⁺CH₂CH₂CH₂CH₂CH₃), 1.39 (m, overlapping [(CH₃)₂CH]₂NH⁺CH₂CH₃ and -N⁺CH₂CH₂CH₂CH₃), 1.00 (t,- N⁺CH₂CH₂CH₂CH₃). ¹¹B NMR (δ ppm, 128.38 MHz, CD₃CN): -0.2 (d, 1 B), -0.6 (d, 1 B), -25.6 (s, 1 B), -28.0 (m, broad, 7 B).

Part 2: Characterizations by FT-IR spectra

FT-IR spectum of $MnMo_6(TRIS-B_{10})_2$ is given in Figure S1, in comparison with the FT-IR spectra of the precursors.



Figure S1: Infrared spectra comparing **MnMo₆(TRIS)**₂, TBAB₁₀H₉CO, and **MnMo₆(TRIS-B₁₀)**₂, the dashed line represents a guide for the eye to notice the shift in B-H band.

The main vibration bands of our compounds are gathered in Table S1. Comparison of the FT-IR spectra of MnMo₆(TRIS-B₁₀)₂ with MnMo₆(TRIS)₂ shows that the vibrations band assigned to the POM part at around 940, 920 and 901 cm⁻¹ corresponding to terminal Mo=O groups, and at around 660 cm⁻¹ for bridging Mo–O–Mo^[5] are unaffected after grafting the [B₁₀H₉CO]⁻ group which indicates that the inorganic platform integrity is maintained during the reaction. The disappearance of CO band at 2098 cm⁻¹ typical of the carbonyl function in the [B₁₀H₉CO]⁻ cluster is observed for the product MnMo₆(TRIS-B₁₀)₂. Concomitantly, a new band assigned to the formation of an amide function –C(O)-NH-^[6] is observed at 1588 cm⁻¹. These results constitute a first evidence of the reaction success for the covalent grafting of the [B₁₀H₉CO]⁻ cluster to POM-TRIS compounds. Finally, a broad band centered at 2473 cm⁻¹ typical of B-H vibration bands of the decaborate and shifted from the B-H band found at 2517 cm⁻¹ in the precursor [B₁₀H₉CO]⁻ cluster is found. It confirms the presence of B₁₀ clusters in the analyzed powders and the shift towards the lower frequencies is in agreement with the formation of dihydrogen contacts between hydrides of B₁₀H₁₀ cluster with H-O (water) or H-N groups (the amide) in their vicinity.^[7] In summary, FT-IR experiments are in agreement with the reaction of [B₁₀H₉CO]⁻ cluster on the POM-TRIS platform through the formation of an amide function.

MnMo₀(TRIS)₂		MnMo ₆ (TRIS-B ₁₀) ₂		Assignments
2962	3000	2964	3044	CH ₂ asym. Str
2936	2998	2936	3022	CH ₂ asym. Str
2874	2992	2875	2986	CH ₂ asym. Str
_	_	2472	2489	B-H str
_	_	_	_	δ (Al)-OH
_	_	1588	1573	Amide
1480	_	1480	_	N+-CH ₂ -scissoring
1382	_	1382	_	CH ₃ scissoring
939	920	939	920	Mo=O sym
920	904	920	909	Mo=O sym
903	879	901	879	Mo=O asym
664	699	667	700	Mo-O-Mo

Table S1: Main vibrational modes v (cm⁻¹) and assignments for the compound $MnMo_6(TRIS-B_{10})_2$ and for its parent precursors. Values in black: experimental. Values in blue: calculated by DFT.

Part 3: ESI-MS spectroscopy

Characterization of MnMo₆(TRIS-B₁₀)₂.

The ESI-MS spectrum depicted in the Figure S2 below for the di-adduct $MnMo_6(TRIS-B_{10})_2$ indicates the presence of starting precursors at m/z 146.2 ({ $B_{10}H_9CO$ }⁻) and m/z 578.7 ({ $MnMo_6(TRIS)_2$ }²⁻) and some degradation products at m/z 1157.4 ({ $MnMo_6O_{18}(TRIS)(OH).HCOOH.CH_3CN.H_2O$ }⁻) or at m/z 1399.6 ({ $HMnMo_6O_{18}(TRIS-B_{10}).HCOOH.2CH_3CN.5H_2O$ }⁻). Finally, a minor peak assigned to the expected species {[$H_5MnMo_6O_{18}(TRIS-B_{10})_2$].CH₃CN.2H₂O}²⁻ is evidenced at m/z 763.4 (calculated value is m/z763.6).



Figure S2: ESI-MS spectrum of $MnMo_6(TRIS-B_{10})_2$ in CH₃CN in negative mode (10⁻⁴ M, HCOOH 0.1%).

In summary, ESI-MS experiments evidenced the formation of the expected di-adduct compound $MnMo_6(TRIS-B_{10})_2$ in CH₃CN. These experiments also showed that in contrast to many hybrid derivatives of Anderson-Evans POMs, this hybrid product seem to be highly fragile and can easily decompose into the starting components.

Part 4: NMR studies in solution

The main part of the NMR spectra of $MnMo_6(TRIS)_2$ are given in the main text of this study. Additional comments, spectra and discussion are found in this Supporting Information part.

Due to the paramagnetism of the Mn(III) center in the middle of the Anderson structure, it was not possible to perform satisfyingly 13 C NMR nor specific experiment such as DOSY 1 H NMR.

The ¹H and the ¹H{¹¹B} NMR spectra of **MnMo₆(TRIS-B₁₀)**₂, **MnMo₆(TRIS)**₂ and TBA[B₁₀H₉CO] are given in Figures S3 and Figure 3 in the main text. In addition to the peaks of TBA⁺ and solvents, the ¹H and the ¹H{¹¹B} NMR spectra of **MnMo₆(TRIS-B₁₀)**₂ display additional peaks assigned to DIPEAH⁺ found as secondary countercations in the isolated product and a small new broad peak at 6.2 ppm attributed to an amide function,^[6] accordingly to the expected grafting of boron cluster on the Anderson POM. The singlet signal attributed to the three methylene groups of the TRIS ligands are shifted to 60.7 ppm in the starting compound MnMo₆(TRIS)₂ due to the coordination of the TRIS ligand to the paramagnetic Mn(III) center.^[5b, 8] In the adduct compound MnMo₆(TRIS-B₁₀)₂, the Figure 3 evidences that the singlet was shifted a little bit to a broad peak centered at 61 ppm upon grafting $[B_{10}H_9CO]^{-1}$ group and split into at least four components in the range 61-64 ppm. This result originates from the formation of the amide blocked in a configuration in which the methylene groups of the TRIS ligands are not equivalent. ¹H variable temperature measurements were performed on this system in order to access to the energy barrier of free rotation of the amide. Upon heating, the signals begin to merge into one unique signal. Unfortunately, the compound revealed to be unstable in these conditions and it was therefore difficult to exploit these data. Finally, the equatorial B-H groups of the boron cluster are well seen in the ¹H^{{11}B} NMR spectrum of **MnMo₆(TRIS-B₁₀)**₂ at 0.2 and 0.4 ppm and appears significantly shifted from those observed in the precursor TBA(B₁₀H₉CO) (0.7 and 0.4 ppm respectively). A shoulder at ca. 3.2 ppm in the ¹H{¹¹B} NMR spectrum of **MnMo₆(TRIS-B₁₀)**₂, which disappears in the ¹H NMR should be attributed to the two apical B-H protons.



Figure S3: ¹H NMR spectra of TBA[$B_{10}H_9CO$], $MnMo_6(TRIS)_2$ and $MnMo_6(TRIS-B_{10})_2$ compounds in CD_3CN .

Part 5: Electronic and electrochemical properties in solution

1°) UV-Visible spectra MnMo₆(TRIS-B₁₀)₂.

The electronic spectra of $MnMo_6(TRIS-B_{10})_2$ were recorded in CH_3CN containing 0.1 M TBACIO₄ (conditions used for electrochemical studies) at room temperature and at concentrations around 2 10⁻⁴ mol.L⁻¹. The spectra are depicted in Figure S4 in comparison with the electronic spectra of the precursors $MnMo_6(TRIS)_2$ and $[B_{10}H_9CO]^-$ synthetized as TBA⁺ salts.

Due to the presence of the Mn(III) center, the Mn-containing POMs are orange colored and the electronic spectrum contains d-d absorption bands in the 300-400 nm range. Nevertheless in all cases, the spectra remain dominated by strong absorption bands in ultraviolet region (200-350 nm) corresponding to the LMCT transition between p-orbitals of the oxo ligands and d-type orbitals centered on molybdenum,^[9] while the cluster [B₁₀H₉CO]⁻ exhibits weak absorption band between 300 and 200 nm notably assigned to π - π * transitions.^[10]

Interestingly, the electronic spectrum of the adduct $MnMo_6(TRIS-B_{10})_2$ differ significantly from the spectra of its parent precursors, especially in terms of intensities of the absorption bands, while the positions of their maxima appears very similar. Moreover, the spectrum of the compound $MnMo_6(TRIS-B_{10})_2$ also differ from the mathematical addition of the spectra of its Anderson and boron precursors depicted in Figures S4 as dashed lines. These observations argue in favour of the formation of the expected adduct compounds and suggest that the boron clusters induce electronic change within the Anderson part in $MnMo_6(TRIS-B_{10})_2$ compound through the "TRIS" ligands. These features could be at the origin of the apparent limited stability of these adducts.



Figure S4: Electronic spectra of $MnMo_6(TRIS-B_{10})_2$ (red line) in CH_3CN containing 0.1 M TBACIO₄ at 20 °C and C = 2 10⁻⁴ mol.L⁻¹ in comparison with the spectra of the precursors $MnMo_6(TRIS)_2$ (blue line) and $[B_{10}H_9CO]^-$ (green line). The sum of spectra of $MnMo_6(TRIS)_2 + 2 [B_{10}H_9CO]^-$ is given in dashed violet line.

Finally, these studies allowed assessing the stability of these compounds in CH_3CN containing 0.1 M TBACIO₄, a medium in which the electrochemical studies have been performed (see next section). As far as absorbance, peak locations and intensities, the obtained spectra remained unchanged for several days, a feature suggesting that $MnMo_6(TRIS-B_{10})_2$ is stable in such conditions.

2°) Electrochemical studies performed on MnMo₆(TRIS-B₁₀)₂.

Electrochemistry allows evidencing electronic modification induced by the grafting of the reducing boron clusters on the POM moieties. Concerning Anderson-type compounds, relatively few studies are known in the literature^[5b, 8, 11] mainly due to the fact that the irreversible reduction of d⁰ Mo centers to the d¹ state within Anderson-type anions leads to their decomposition.^[12] We focused only on the Mn-based compounds which are expected to be the most interesting from electrochemical point of view, due to the presence of the redox active Mn center.

The cyclic voltamograms (CVs) recorded for $MnMo_6(TRIS)_2$ at room temperature on 0.2 mM solution of POMs in $CH_3CN + 0.1$ M TBAClO₄ are given in Figure S5. On the oxidation side, $MnMo_6(TRIS)_2$ displays a one-electron reversible wave. The oxidation peak potential for Mn couple is located at E_p = +410 mV vs. Fc⁺/Fc with the anodic to cathodic peak potential

difference $\Delta Ep = 145 \text{ mV}$ at $v = 0.1 \text{ V.s}^{-1}$, and this process is assigned to the oxidation of the Mn^{III} center of the Anderson POM into Mn^{IV}.^[5b, 11a, b] This wave displays an excellent linearity for the peak current with the square root of the scan rate, thus indicating diffusion controlled behavior. On the reduction side, another reversible process is observed at $E_{pc} = -1250 \text{ mV}$ vs. Fc⁺/Fc with reoxidation peak at $E_{pa} = -930 \text{ mV}$ vs. Fc⁺/Fc. This process, separated by $\Delta E = 320 \text{ mV}$, is also mono-electronic and corresponds to the reduction of Mn^{III} into Mn^{III} as demonstrated in literature.^[11a] The reduction of Mo^{VI} centers is usually observed at lower potential but this process is usually irreversible.^[12]



Figure S5: Cyclic voltammograms (CVs) of 0.2 mM of $MnMo_6(TRIS)_2$ at different scan rates (from 10 to 100 mV s⁻¹) (a) and with different windows of potentials (b). The electrolyte was ACN + 0.1 M TBACIO₄.



Figure S6: Cyclic voltammograms (CVs) of 0.2 mM of $MnMo_6(TRIS-B_{10})_2$ at different scan rates (from 10 to 100 mV s⁻¹) (a) and with different windows of potentials (b).

The CVs recorded in similar conditions for $MnMo_6(TRIS-B_{10})_2$ are given in Figure S6. On the oxidation side, the grafting of the B₁₀ clusters on $MnMo_6(TRIS)_2$ provokes a shift of the Mn^{IV}/Mn^{III} wave in the negative direction as evidenced in Figure S7. From E_p = +410 mV vs. Fc⁺/Fc in $MnMo_6(TRIS)_2$, the oxidation peak is shifted at E_p = +320 mV vs. Fc⁺/Fc after grafting. Moreover, the reversibility of the process is lost in $MnMo_6(TRIS-B_{10})_2$. An opposite

effect was observed by Oms at al. by grafting Spiropyran molecules on MnMo₆(TRIS)₂, who concluded that spiropyran probably exhibits an electron-withdrawing ability from the Mn^{III} center.^[5b] Our results thus would feature an electron-donating ability of the boron clusters B₁₀H₉ on the Mn^{III} center, accordingly to literature data.^[13] Furthermore, a small oxidation peak is also observed at E = -26 mV vs. Fc⁺/Fc. The origin of this oxidative process is not clear. Moreover, CVs recorded in a smaller potential range (see Figure S6b) allow removing it. It seems to be related to the reduction processes observed for this compound at E_{pc} = -1314 mV vs. Fc⁺/Fc and it could correspond to the oxidation of the amino group into nitro groups, the amino groups coming from a partial degradation of the compound. It could also correspond to the oxidation of B₁₀H₉ moiety which irreversibly occurs in this region (see Figure S8). On the reduction side, two reduction processes are observed at E_{pc} = -1314 mV vs. Fc⁺/Fc and E_{pc} = -1712 mV vs. Fc⁺/Fc. Interestingly, the former disappears when reduced window of potential is used (see pink CV on Figure S16b) and as mentioned above is related to the oxidation process occurring at E = -26 mV vs. Fc^+/Fc . Since the reduction of Mo^{VI} centers in Mn-Anderson POMs is expected at potential lower than -2.0 V vs Fc⁺/Fc,^[5b, 11a] the reduction process at -1712 mV is thus assigned to the reduction of Mn^{III} into Mn^{II} of the Mn-Anderson moiety. It is significantly shifted by around 450 mV towards the more negative values of potential compared to its precursor MnMo₆(TRIS)₂. This is in agreement with the increase of the negative charge from 3- in MnMo₆(TRIS)₂ to 7- in MnMo₆(TRIS-B₁₀)₂ and also in agreement with the grafting of two electron-donating boron clusters, which increases the electronic density at the Mn^{III} center of the POM and hence should destabilizes the reduced state of the POMs. The reoxidation process occurs at E_{pa} = -1118 mV vs Fc⁺/Fc, thus giving a very large difference of potential.



Figure S7: Comparison of Cyclic voltamograms (CVs) of $MnMo_6(TRIS)_2$ and $MnMo_6(TRIS-B_{10})_2$ at a scan rate of 30 mV.s⁻¹. The concentrations of compounds are around 2 10^{-4} M; the electrolyte was $ACN + 0.1 M TBACIO_4$. Dashed lines are only guides for eyes.

In summary, these studies evidence the effect of the grafting of boron cluster on the Mn-Anderson moiety and especially the significant effect induces on the electronic properties of the Mn^{III} center, in agreement with UV-Visible spectra which showed electronic effects on the electronic spectra.



Figure S8. Cyclic voltammograms (CVs) of TBA[$B_{10}H_9CO$] cluster at 2 10⁻⁴ M. The electrolyte was $CH_3CN + 0.1 M TBACIO_4$.

Part 6: DFT Calculations

1- Computational Details

All results presented herein correspond to full geometry optimizations carried out by means of the Amsterdam Density Functional package ADF.^[14] The GGA plus Grimme's empirical dispersion BP86-D functional^[15] was used together with a Slater triple-ζ plus polarization basis set in all atoms. Relativistic corrections were introduced by the scalar-relativistic zero-order regular approximation (ZORA).^[16] Solvent effects were included by using the continuum model COSMO.^[17] For constructing the solvent cavity, the atomic radii values chosen were those Van der Waals radii from Klamt.^[18] The UV-Vis spectra were computed using the SAOP functional on the BP86-D optimized geometry.^[19]

A data set collection of computational results is available in the ioChem-BD repository^[20] and can be accessed via <u>https://doi.org/10.19061/iochem-bd-1-136</u>

2- Analysis of HOMO, LUMO and LUMO+1 DFT orbitals of $MnMo_6(TRIS)$, $MnMo_6(TRIS-B_{10})$ and $MnMo_6(TRIS-B_{10})_2$

We analysed the molecular orbitals to evaluate the electronic properties of $MnMo_6(TRIS)$, $MnMo_6(TRIS-B_{10})$, and $MnMo_6(TRIS-B_{10})_2$. The orbital analysis shows that the addition of the boron cluster to the polyoxometalate destabilizes both the HOMO and LUMO orbitals by 0.1 eV, which are both mainly Manganese centered, as it is illustrated in Figure S9.



Figure S9. HOMO, LUMO and LUMO+1 orbitals and energy levels for $MnMo_6(TRIS)_2$, $MnMo_6(TRIS-B_{10})$ and $MnMo_6(TRIS-B_{10})_2$.

3- Molecular models (geometry optimized) and variation of the free energy upon reaction

Figure S10 shows the free energy profile for the formation of $MnMo_6(TRIS-B_{10})$ and of $MnMo_6(TRIS-B_{10})_2$. $MnMo_6(TRIS)_2 + [B_{10}H_9CO]^-$ is exothermic for the intermediate and the final product. The stability of $MnMo_6(TRIS-B_{10})$ and $MnMo_6(TRIS-B_{10})_2$ explains why we obtain a mixture of the intermediate and the product by using stoichiometric mixture of reactants.



Figure S10: Molecular models obtained by geometrical optimization for $MnMo_6(TRIS)_2$, $MnMo_6(TRIS-B_{10})$, $MnMo_6(TRIS-B_{10})_2$ and $[B_{10}H_9CO]^-$ and variation of the free energy upon reaction of $MnMo_6(TRIS)_2$ with one and two clusters $[B_{10}H_9CO]^-$.

As seek of comparison, Figure S11 depicts the free energy profile for the formation of $AIMo_6(TRIS-B_{10})$ from $AIMo_6(TRIS)$ and $[B_{10}H_9CO]^-$. This reaction is isoergonic indeed, and this explains why similar coupling does not work with such Al-based andersion compound.



Figure S11. Structural models obtained by geometrical optimization of $AIMo_6(TRIS)$ and $AIMo_6(TRIS-B_{10})$ and variation of the free energy upon reaction of $AIMo_6(TRIS)$ with cluster $(B_{10}H_9CO)^{-1}$

References

[1] E. D. B. Robin K. Harris, Sonia M. Cabral De Menezes, Robin Goodfellow, Pierre Granger, *Pure and Applied Chemistry* **2001**, *73*, 1795–1818.

[2] Wiley-Interscience publication **1990**, 27.

[3] C. B. K. Kenneth Shelly, and M. Frederick Hawthorne, *Inorganic Chemistry* **1992**, *31*, 2889-2892.
[4] P. R. Marcoux, B. Hasenknopf, J. Vaissermann and P. Gouzerh, *European Journal of Inorganic Chemistry* **2003**, 2406-2412.

[5] a) H. Ai, Y. Wang, B. Li and L. Wu, *European Journal of Inorganic Chemistry* 2014, 2014, 2766-2772; b) O. Oms, K. Hakouk, R. Dessapt, P. Deniard, S. Jobic, A. Dolbecq, T. Palacin, L. Nadjo, B. Keita, J. Marrot and P. Mialane, *Chemical Communications* 2012, *48*, 12103-12105; c) J. S. Xiuli Wang, Hongyan Lin, Zhihan Chang, Guocheng Liu and Xiang Wang, *CrystEngComm* 2017, *19*, 3167; d) G.-C. L. Xiu-Li Wang, Dan-Na Liu, Xing Rong, Hong-Yan Lin, *Journal of Cluster Science* 2016, *27*, 169-181.
[6] F. Abi-Ghaida, Z. Laila, G. Ibrahim, D. Naoufal and A. Mehdi, *Dalton Trans* 2014, *43*, 13087-13095.
[7] E. S. Shubina, E. V. Bakhmutova, A. M. Filin, I. B. Sivaev, L. N. Teplitskaya, A. L. Chistyakov, I. V. Stankevich, V. I. Bakhmutov, V. I. Bregadze and L. M. Epstein, *Journal of Organometallic Chemistry* 2002, *657*, 155-162.

[8] Y. Yan, B. Li, Q. Y. He, Z. F. He, H. Ai, H. B. Wang, Z. D. Yin and L. X. Wu, *Soft Matter* **2012**, *8*, 1593-1600.

[9] K. Hakouk, O. Oms, A. Dolbecq, J. Marrot, A. Saad, P. Mialane, H. El Bekkachi, S. Jobic, P. Deniard and R. Dessapt, *Journal of Materials Chemistry C* **2014**, *2*, 1628-1641.

[10] L. P. P and R. D.S, *larjset* **2015**, *2*, 92-95.

[11] a) S. Schoenweiz, M. Heiland, M. Anjass, T. Jacob, S. Rau and C. Streb, *Chemistry-a European Journal* 2017, *23*, 15370-15376; b) S. Schonweiz, S. A. Rommel, J. Kubel, M. Micheel, B. Dietzek, S. Rau and C. Streb, *Chemistry-a European Journal* 2016, *22*, 12002-12005; c) X. L. Wang, J. J. Sun, H. Y. Lin, Z. H. Chang, G. C. Liu and X. Wang, *Crystengcomm* 2017, *19*, 3167-3177; d) X. L. Wang, D. N. Liu, H. Y. Lin, G. C. Liu and X. Rong, *Journal of Cluster Science* 2016, *27*, 169-181.

[12] M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, Berlin, **1983**, p.
[13] I. B. Sivaev, A. V. Prikaznov and S. A. Anufriev, *Journal of Organometallic Chemistry* **2013**, 747, 254-256.

[14] a) G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. F. Guerra, S. J. A. Van Gisbergen, J. G. Snijders and T. Ziegler, *Journal of Computational Chemistry* 2001, *22*, 931-967; b) C. F. Guerra, J. G. Snijders, G. te Velde and E. J. Baerends, *Theor. Chem. Acc.* 1998, *99*, 391-403; c) E. Vanlenthe, E. J. Baerends

and J. G. Snijders, Journal of Chemical Physics 1994, 101, 9783-9792.

[15] a) A. D. Becke, *Journal of Chemical Physics* **1993**, *98*, 5648-5652; b) J. P. Perdew, *Physical Review B* **1986**, *33*, 8822-8824.

[16] a) E. van Lenthe, A. Ehlers and E. J. Baerends, *Journal of Chemical Physics* 1999, *110*, 8943-8953;
b) E. Vanlenthe, E. J. Baerends and J. G. Snijders, *Journal of Chemical Physics* 1993, *99*, 4597-4610.

[17] a) C. C. Pye and T. Ziegler, *Theor. Chem. Acc.* **1999**, *101*, 396-408; b) A. Klamt and G.

Schuurmann, Journal of the Chemical Society-Perkin Transactions 2 **1993**, 799-805.

[18] A. Klamt, V. Jonas, T. Burger and J. C. W. Lohrenz, *Journal of Physical Chemistry A* **1998**, *102*, 5074-5085.

[19] a) O. V. Gritsenko, P. R. T. Schipper and E. J. Baerends, *Chemical Physics Letters* **1999**, *302*, 199-207; b) P. R. T. Schipper, O. V. Gritsenko, S. J. A. van Gisbergen and E. J. Baerends, *Journal of Chemical Physics* **2000**, *112*, 1344-1352.

[20] M. Alvarez-Moreno, C. de Graaf, N. Lopez, F. Maseras, J. M. Poblet and C. Bo, *Journal of Chemical Information and Modeling* **2015**, *55*, 95-103.