Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

for

Easily reduced bis-pincer (NS_2)$_2$Molybdenum(IV) to (NHS_2)$_2$Mo(II) by alcohols vs redox-inert (NS_2)(NHS_2)Iron(III) complexes

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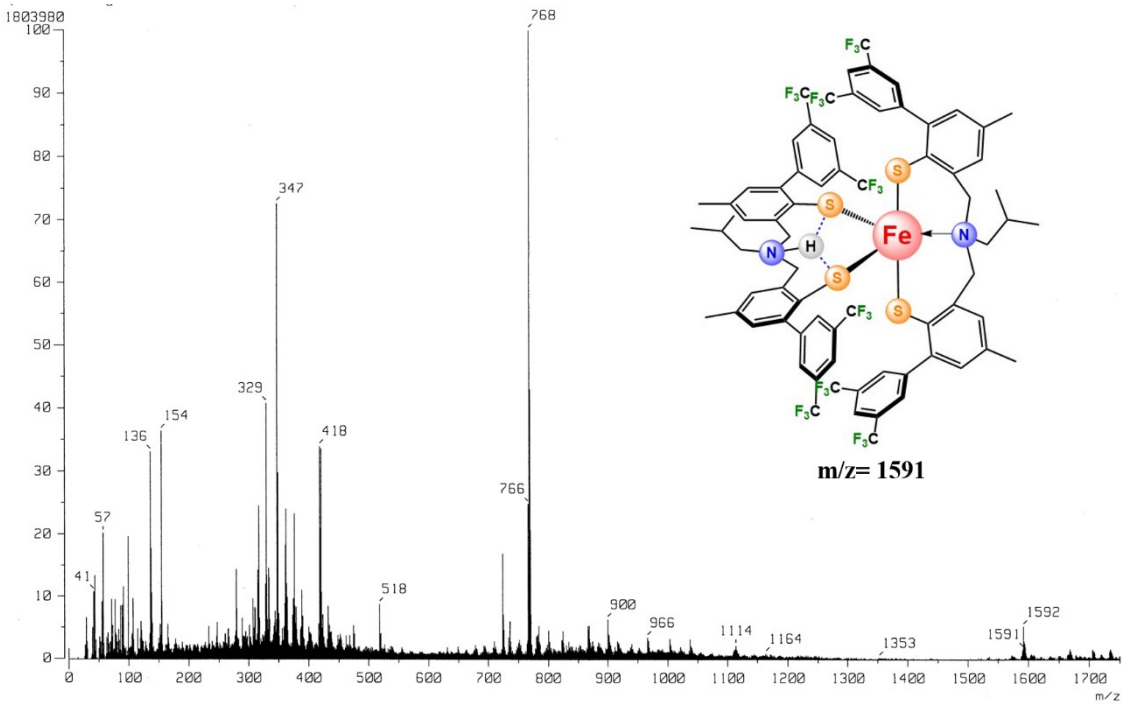

Figure S1. FAB⁺ MS spectrum of complex **1**.

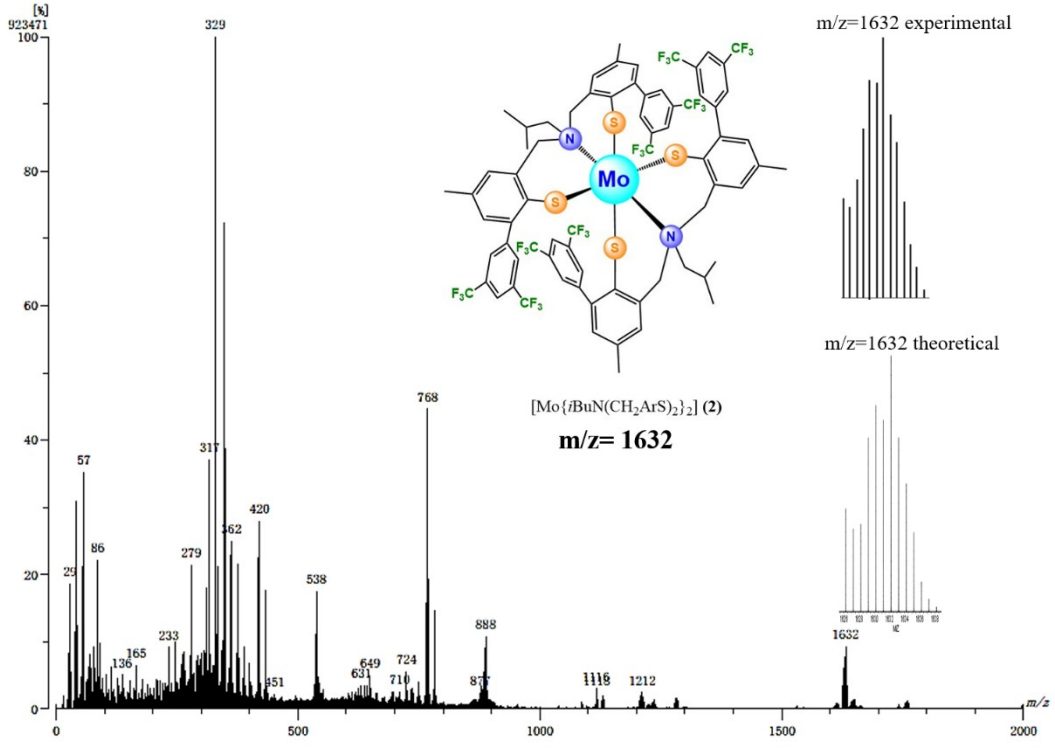

Figure S2. FAB⁺ MS spectrum of complex **2**.

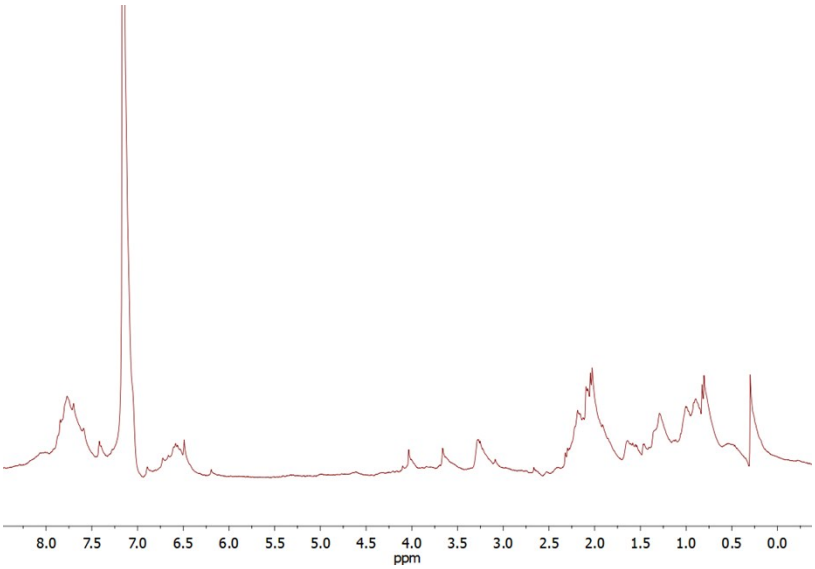

Figure S3. ^{1}H NMR spectrum of complex **2** in benzene-d_6 at 295 K.

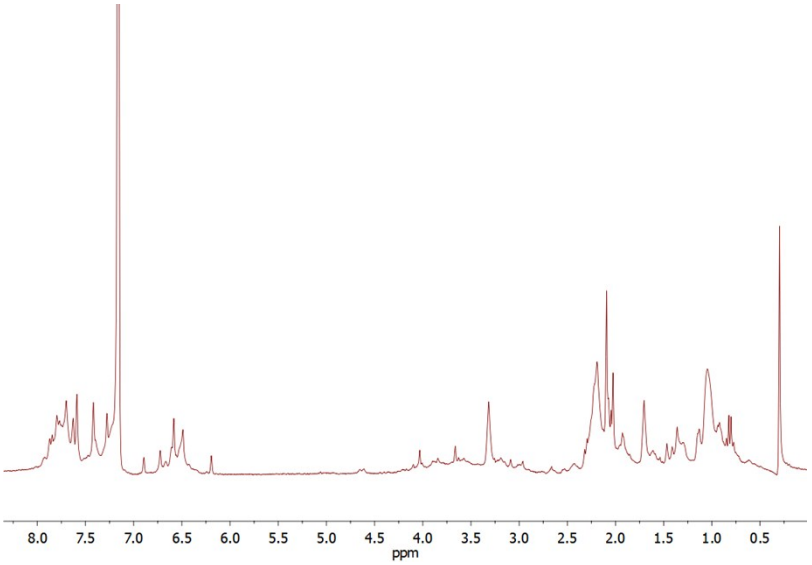

Figure S4. ^{1}H NMR spectrum of complex **3** in benzene-d_6 at 295 K.

CHROMOTROPIC ACID TEST FOR FORMALDEHYDE:

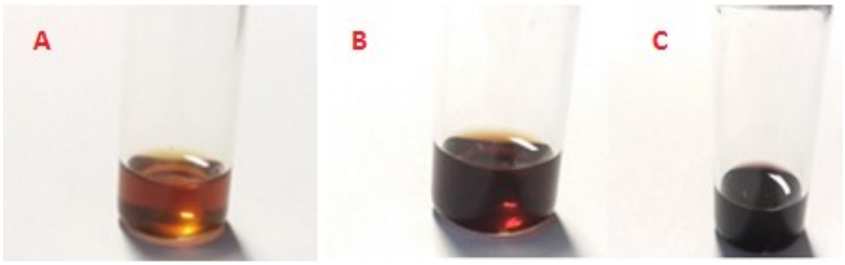

Figure S5. A-C: Chromotropic acid test for the detection of formaldehyde in the reaction mixture of **2** with MeOH.

A solution of 1,8-dihydroxynaphthalene-3,6-disulphonic acid (green solid, 3 mg) in 3 mL of concentrated sulfuric acid, from which 0.5 mL were taken and then mixed with 0.5 mL of the reaction mixture to be analysed. A colour change was not observed immediately upon mixing the two solutions (Fig. S3A), whereby the mixture was heated to 75°C for a period of 20 minutes, with a change in colour from dark yellow to light violet (Fig. S3B). The solution was subsequently heated further for 25 minutes to afford a dark violet solution (Fig. S3C), confirming the presence of formaldehyde.

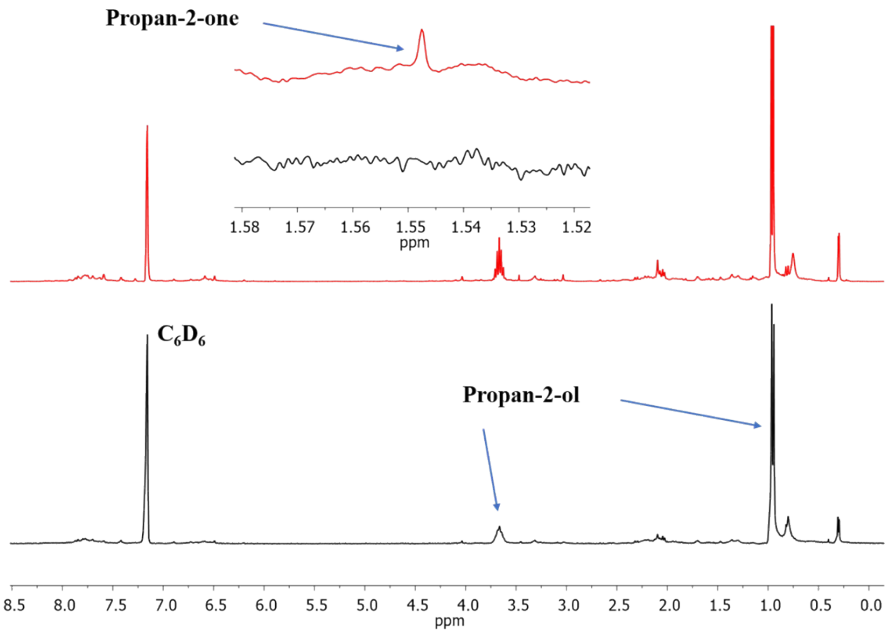

Figure S6. Monitoring of the formation of propan-2-one from propan-2-ol catalysed by **2** by ^{1}H NMR spectroscopy after one (black trace), and 30 days (red trace).

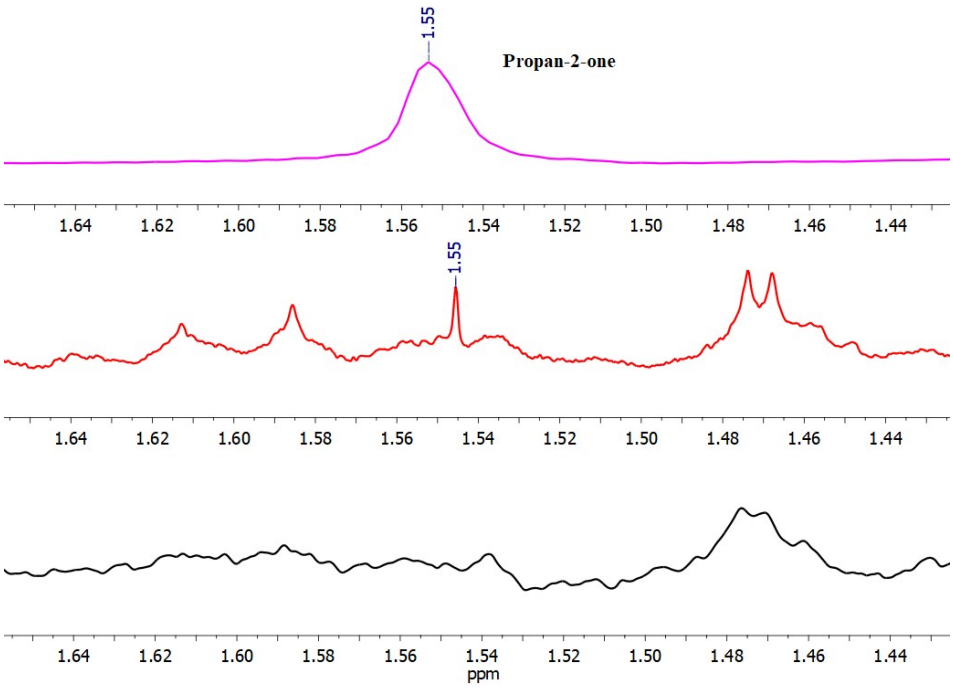

Figure S7. Conversion of **2** (bottom, black trace) to **3** with concomitant formation of propan-2-one (middle, red race) by ^{1}H NMR spectroscopy; addition of authentic sample of anhydrous propan-2-one (1 μL, top, magenta trace) observed at 1.55 ppm.

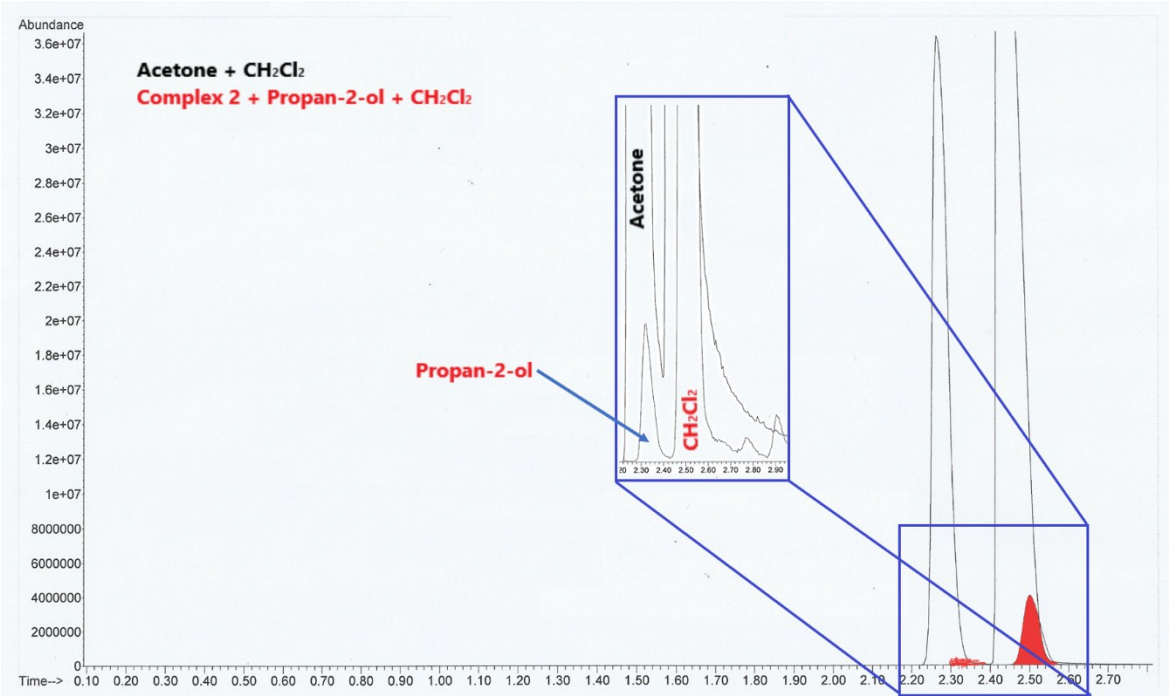

Figure S8. Comparison of chromatograms of **2** in propan-2-ol (red) and authentic acetone sample (black) in dichloromethane as carrier solvent.

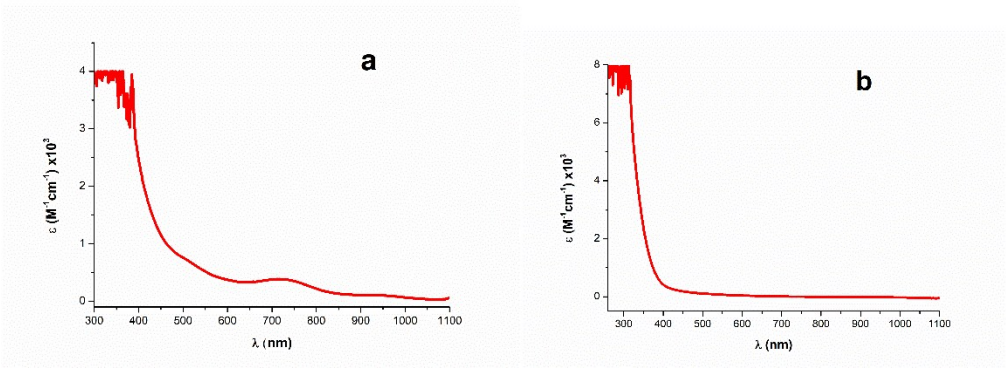

Figure S9. a) UV-vis spectra of **2** in 1 mM THF solution, and b) **3** in 5 mM THF solution.

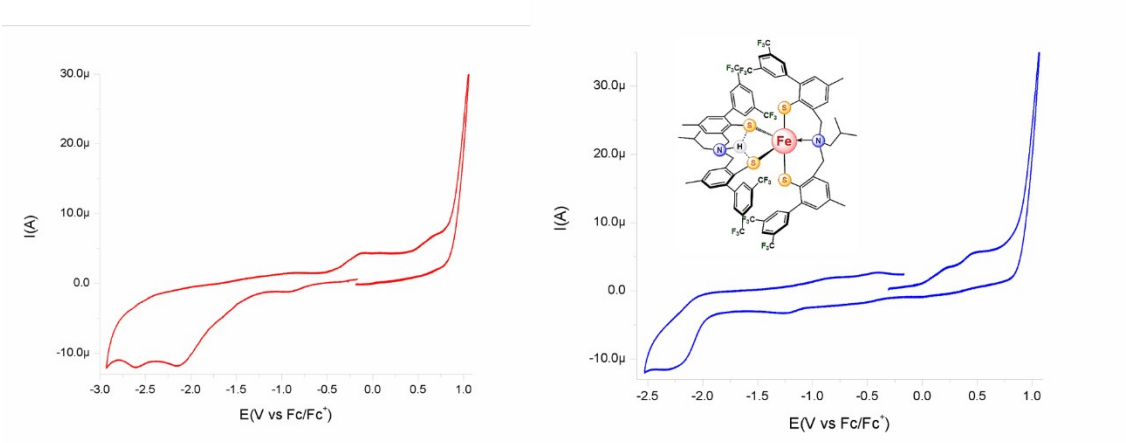

Figure S10. Cathodic (red trace) and anodic (blue trace) cyclic voltammograms of **1** at 1 mM concentration in 0.1 M NBu_4PF_6-THF at 100 mV s^{-1} scan rate, glassy carbon electrode.

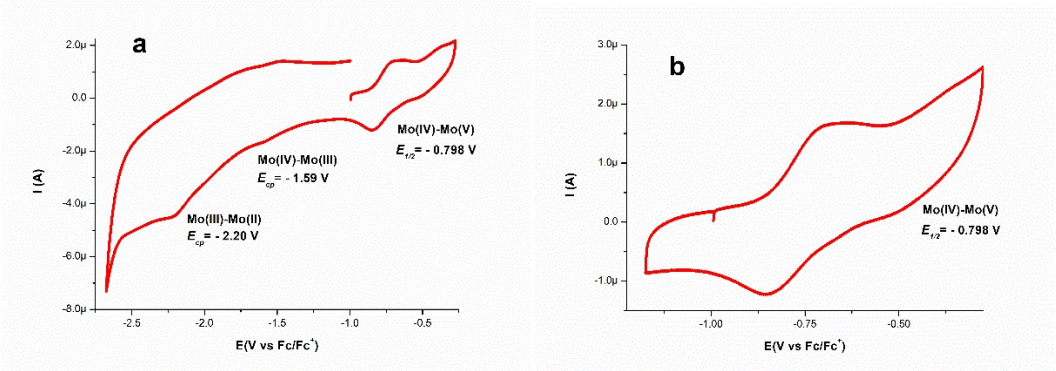

Figure S11. a) Anodic cyclic voltammogram a 1 mM solution of **2** in 0.1 M NBu_4PF_6–THF, scan rate 100 mV s^{-1}; b) reversible process of complex **2** at -0.80 V.

Table S1. Mulliken charges of **2** - **4**.

Mulliken charge	2	3	4
Mo	0.36	-0.10	0.11
S1	-0.22	-0.34	-0.29
S2	-0.24	-0.34	-0.28
S3	-0.24	-0.34	-0.28
S4	-0.22	-0.34	-0.32
N_1	-0.34	-0.16	-0.40
N_2	-0.34	-0.16	-0.16
H_{N1}	---	0.23	---
H_{N2}	---	0.23	0.20
Ar	0.16, 0.23	0.13	0.08, 0.21 0.21, 0.25
$^{i}PrCH_2$	0.28	0.54	0.43, 0.48

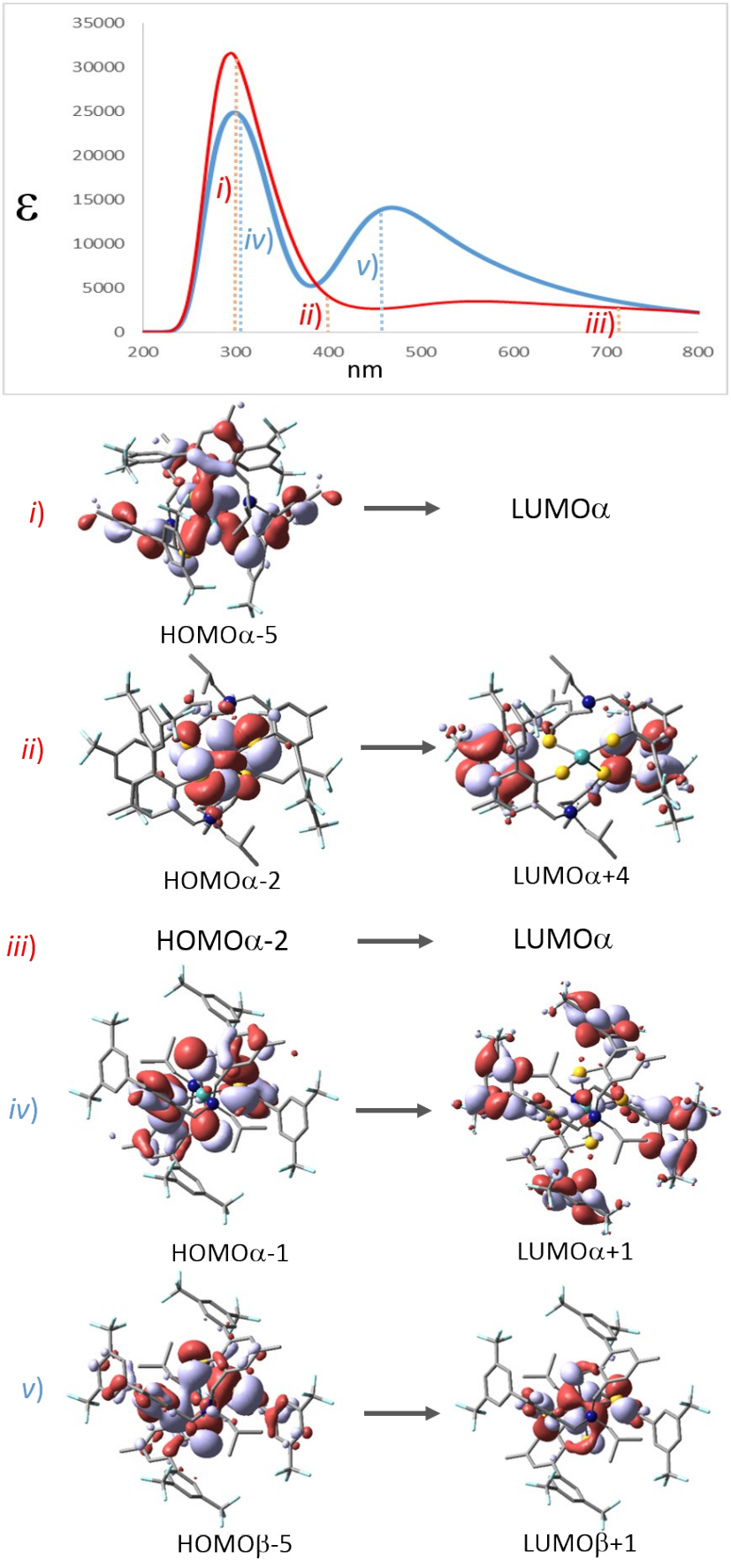

Figure S12. Calculated UV-vis spectra for **2** (blue trace), and **3** (red trace) in THF, and their orbital assignments.