

Supporting Information for

Influence of Ligand Variation on the Deactivation Process of
Metal-to-Ligand Charge Transfer Excited States in Quadruply
Bonded Dimolybdenum Complexes

Yuqing Shi,^a Juanjuan Li,^a Can Cui,^a Guanzhi Wu*,^b Tao Cheng*^a

^a School of Chemistry and Chemical Engineering, Qilu University of Technology (Shandong

Academy of Sciences), Jinan, 250353, P.R. China

^b Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, UK

1. Experimental methods

Compounds preparation. The synthesis of **[Mo₂]-ph** has been previously published.¹ **[Mo₂]-naph** and **[Mo₂]-anth** were prepared using a similar method, and the synthesis procedures are depicted in Scheme S1. HDAniF,² Mo₂(O₂CCH₃)₄,³ and Mo₂(DAniF)₃(O₂CCH₃)₄⁴ were used as starting materials, following established protocols. Synthetic manipulations requiring an inert atmosphere were conducted under N₂ gas, using standard Schlenk line techniques. To maintain anhydrous conditions, we used dry solvents such as tetrahydrofuran (THF), CH₂Cl₂, and ethanol. These solvents were purified by distillation over Na, CaH₂, and Mg respectively, under an N₂ atmosphere over 4 Å molecular sieves. NMR spectra were recorded on Bruker Ascend 300 MHz spectrometers, and chemical shifts were reported relative to the residual solvent signal (CHCl₃, ¹H δ, 7.26 ppm).

Steady-state spectroscopies. All measurements were performed at room temperature. UV-Vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer equipped with a 2 mm quartz cuvette. Fluorescence measurements were performed using a Shimadzu RF-6000 spectrophotometer.

Femtosecond Transient Absorption (TA) Experiment. The TA experiments were conducted using a spectrometer equipped with a Ti/sapphire regenerative amplifier, which provided 800 nm pulses with a full width at half maximum (FWHM) of 40 fs. The laser output was divided into two beams. One of the beams served as the probe beam, generating a white light continuum. The other beam was directed into an optical parametric amplifier to generate the pump beam centered at 355 nm, which was then directed to the translation stage. A mechanical chopper was used to modulate the pump repetition frequency. The polarization of the pump beam was set to the magic angle (54.7°) with respect to the probe beam. The optical path through the samples was set to 2 mm.

2. Synthesis

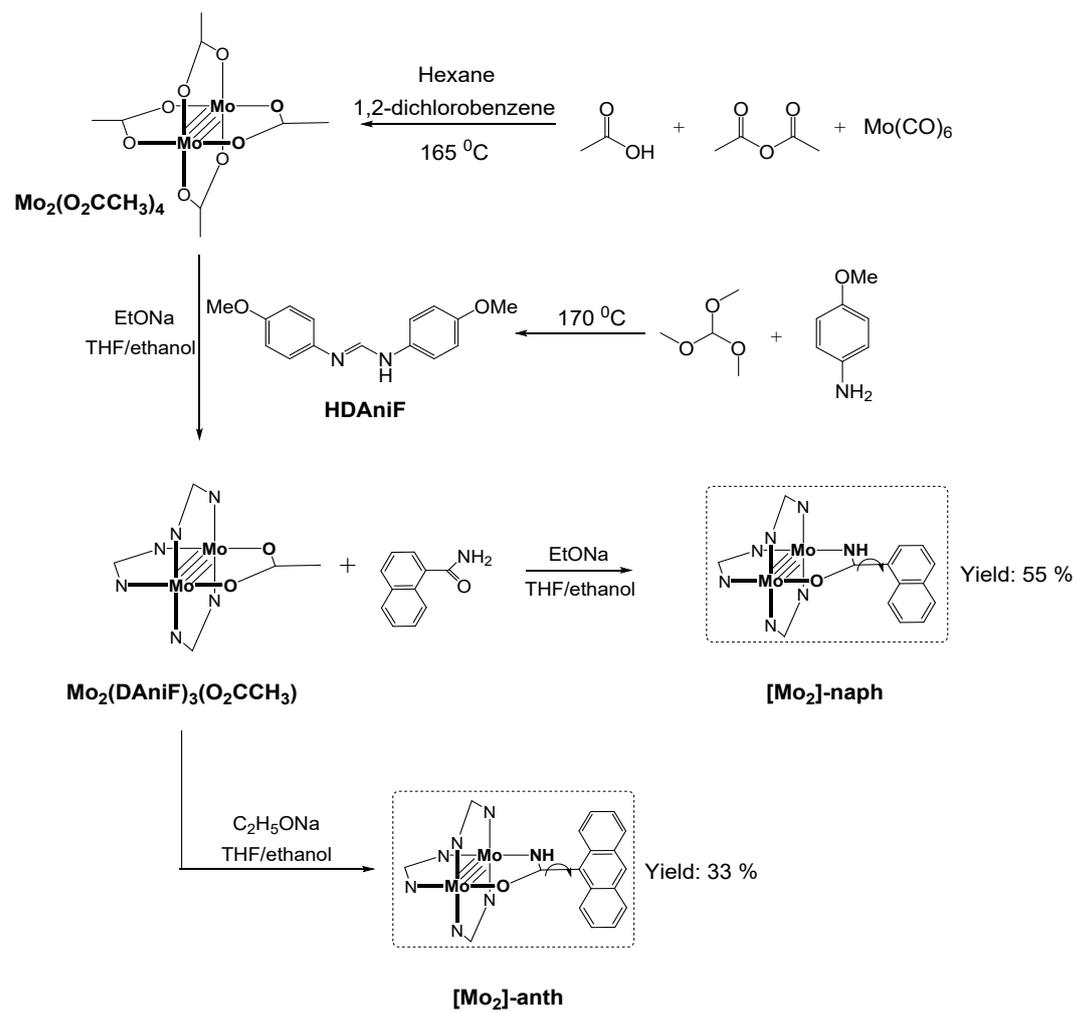
General method for the synthesis of [Mo₂]-naph and [Mo₂]-anth

A solution of sodium ethoxide (0.20 mmol) in 10 mL of ethanol was added to a solution of Mo₂(DAniF)₃(O₂CCH₃) (0.20 mmol) in 20 mL of THF. The resulting mixture was stirred at room temperature for 2 hours, and then the solvent was removed under vacuum. The residue was dissolved in 25 mL of CH₂Cl₂ and filtered through a Celite-packed funnel. The filtrate was then mixed with amide ligands (0.15 mmol) and stirred for an additional 3 hours, leading to the formation of the products. The products were collected by filtration and washed with ethanol three times, each with 20 mL of ethanol.

[Mo₂]-naph: ¹H NMR (300 MHz, CDCl₃) δ 8.81 (s, 1H), 8.58 – 8.40 (m, 3H), 8.38 (d, *J* = 4.1 Hz, 1H), 7.84 (dd, *J* = 13.3, 6.9 Hz, 3H), 7.48 (dd, *J* = 15.9, 8.4 Hz, 2H), 7.30 (dd, *J* = 14.9, 7.5 Hz, 1H), 6.71 – 6.57 (m, 11H), 6.50 (dt, *J* = 11.3, 5.7 Hz, 3H), 6.42 (dd, *J* = 8.6, 6.3 Hz, 6H), 6.34 – 6.20 (m, 4H), 3.69 (dd, *J* = 10.5, 7.4 Hz, 18H).

[Mo₂]-anth: ¹H NMR (400 MHz, CDCl₃) δ 8.89 (s, 1H), 8.64 (s, 2H), 8.58 – 8.42 (m, 4H), 8.00 (d, *J* = 7.7 Hz, 2H), 7.41 (dt, *J* = 14.3, 6.4 Hz, 4H), 6.73 – 6.54 (m, 12H), 6.48 (dt, *J* = 12.4, 9.5 Hz, 8H), 6.38 – 6.20 (m, 4H), 3.75 – 3.63 (m, 18H).

Scheme S1. Synthetic routes for **[Mo₂]-naph** and **[Mo₂]-anth**.



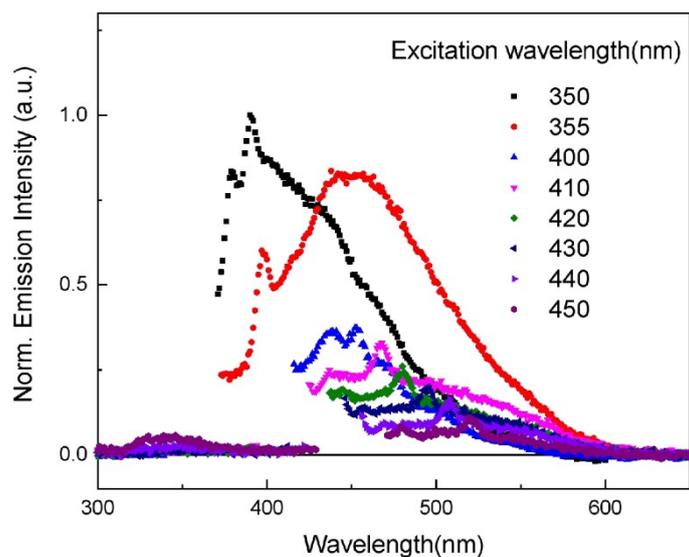


Figure S3. Emission spectra of $[\text{Mo}_2]\text{-naph}$ in CH_2Cl_2 with excitation at various wavelengths.

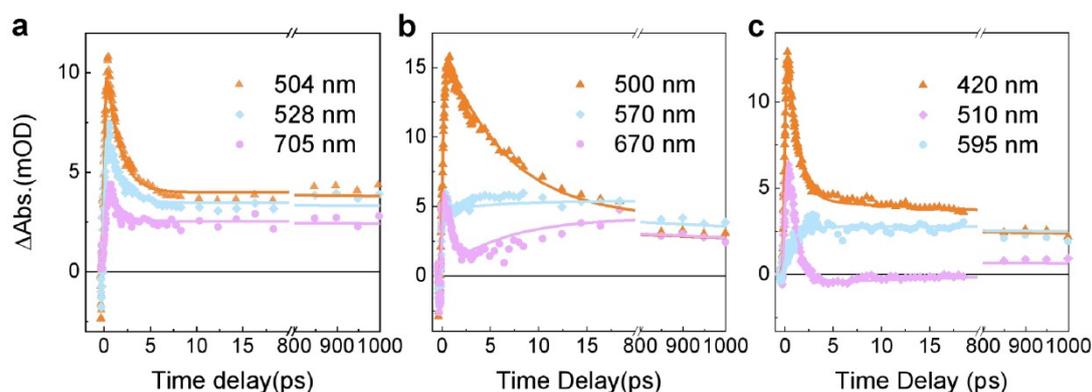


Figure S4. Kinetic traces (dots) and fitting traces (line) at selected wavelengths obtained by global fitting on the TA spectra of $[\text{Mo}_2]\text{-ph}$ (a), $[\text{Mo}_2]\text{-naph}$ (b) and $[\text{Mo}_2]\text{-anth}$ (c).

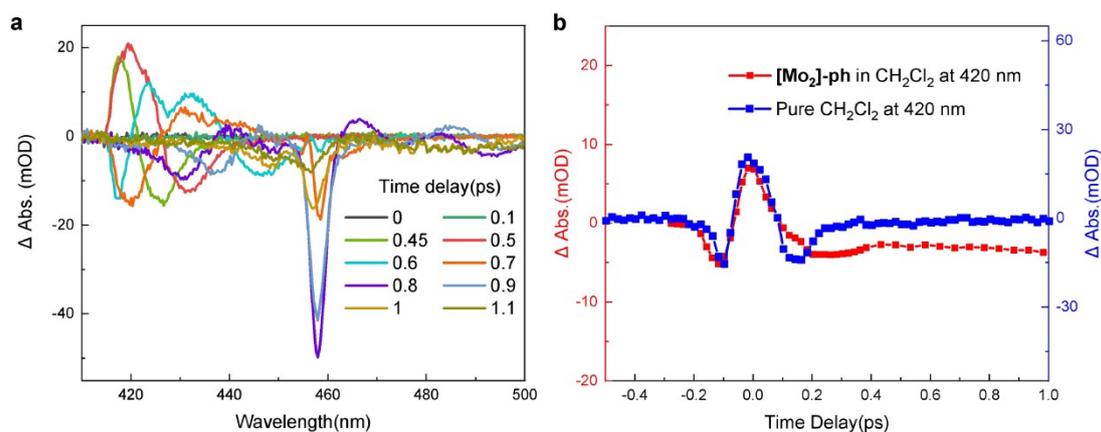


Figure S5. Transient absorption spectra of pure CH_2Cl_2 (a) and a comparison of the kinetic trace obtained from 355 nm excitation and probed at 420 nm for $[\text{Mo}_2]\text{-ph}$ (red) and CH_2Cl_2 (blue).

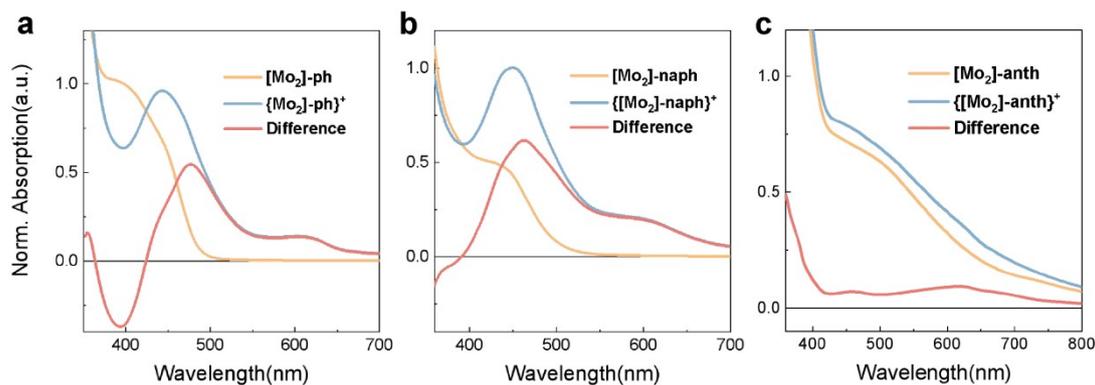


Figure S6. Steady-state difference spectra for $[\text{Mo}_2]\text{-ph}$ (a), $[\text{Mo}_2]\text{-naph}$, (b) and $[\text{Mo}_2]\text{-anth}$ (c), resulting from subtraction of the absorption for the neutral from those of the cationic species generated by chemical oxidation using one equiv of ferrocenium hexafluorophosphate

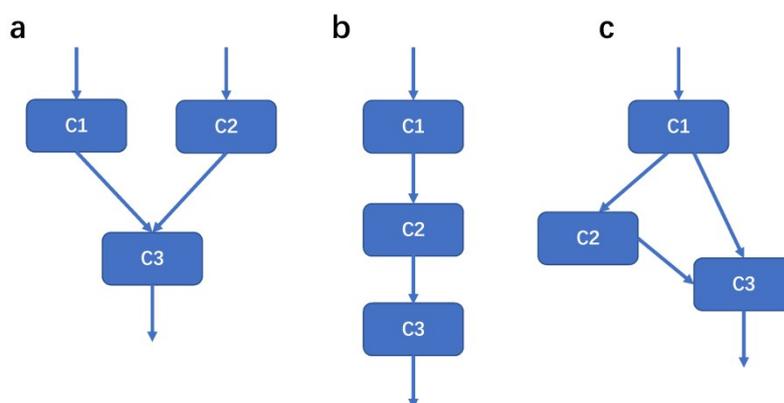


Figure S7. Global analysis model used in global analysis on TA spectra of $[\text{Mo}_2]\text{-ph}$ (a), $[\text{Mo}_2]\text{-naph}$ (b) and $[\text{Mo}_2]\text{-anth}$ (c).

Reference

- 1 W. Y. Yu, M. Meng, H. Lei, X. D. He and C. Y. Liu, *J. Phys. Chem. C.*, 2016, **120**, 12411-12422.
- 2 C. Lin, J. D. Protasiewicz, E. T. Smith and T. Ren, *Inorg. chem.*, 1996, **35**, 6422-6428.
- 3 A. B. C. Brignole, F. A. Cotton, *Inorg. Synth.*, 1972, **13**, 81-89.
- 4 F. A. Cotton, C. Y. Liu, C. A. Murillo, D. Villagrán and X. Wang, *J. Am. Chem. Soc.*, 2003, **125**, 13564-13575.