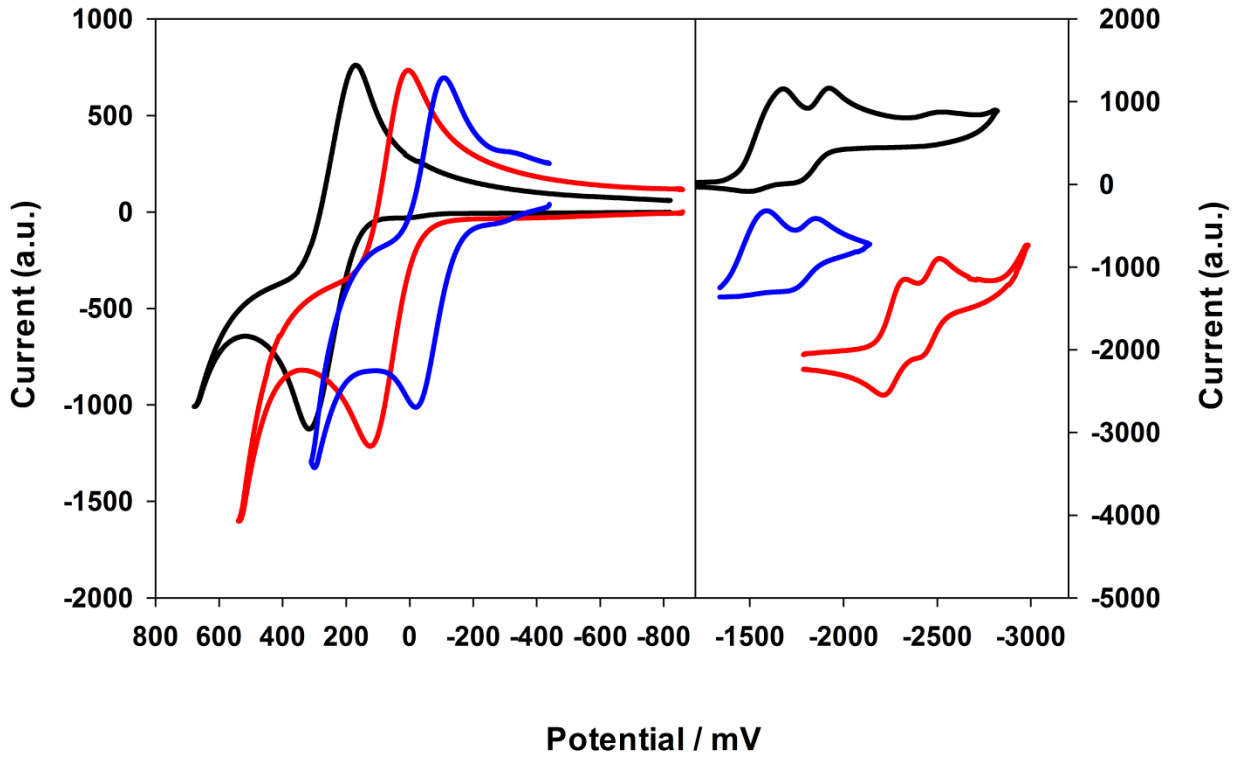
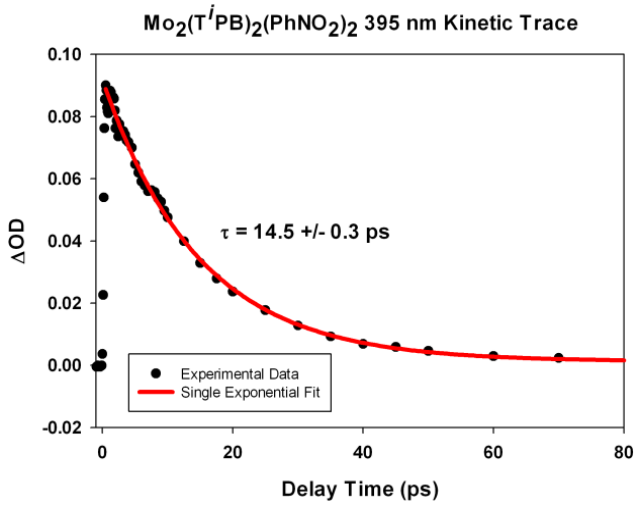
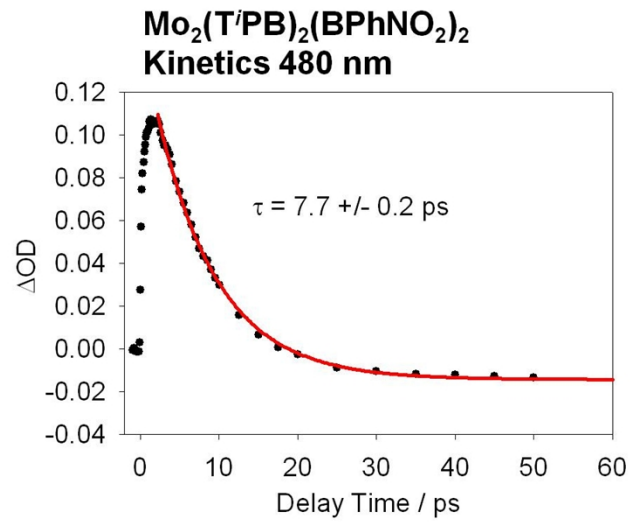
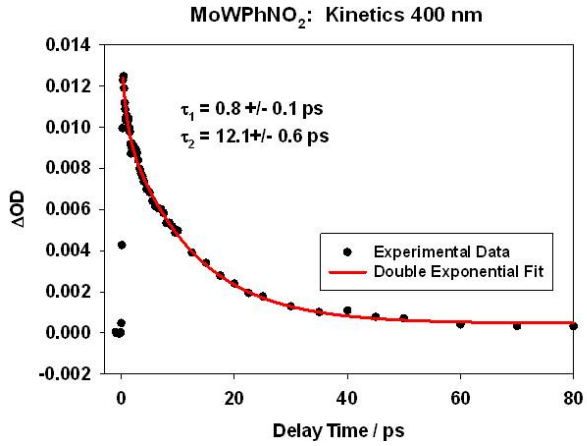
Electronic Supplementary Material (ESI) for Dalton Transactions.



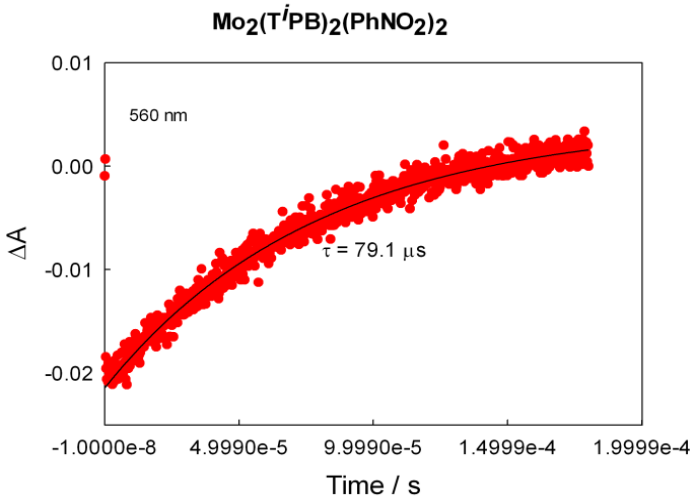
SI Figure 1. Cyclic voltammetry plot of **I** (black), **II** (red) and **III** (blue) in THF at room temperature referenced to Fc/Fc^{+}.



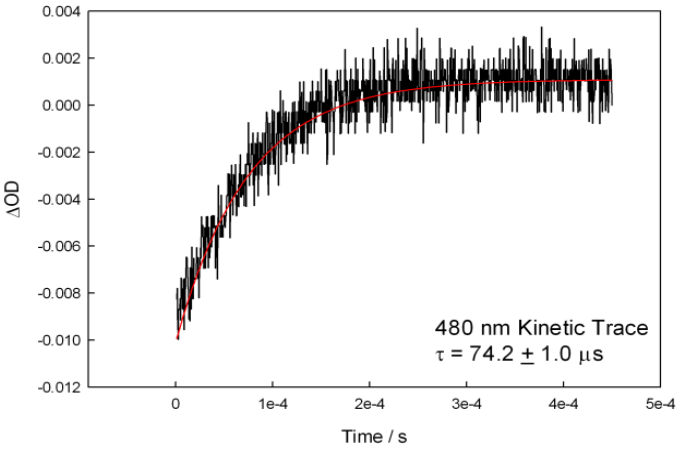




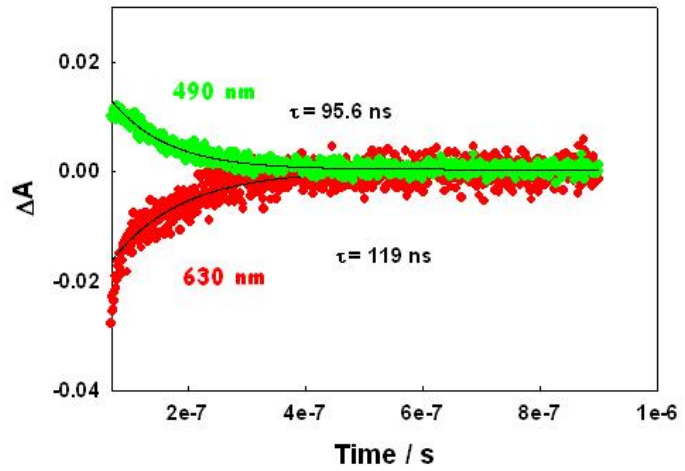
SI Figure 2. *fs*-transient absorption kinetic traces of compounds **I**-**III**.



SI Figure 3. Nanosecond transient absorption kinetic trace for **II** at 480 nm.



SI Figure 4. Nanosecond transient absorption kinetic trace for **II** at 480 nm.



SI Figure 5. Nanosecond transient absorption kinetic trace for **III** at 490 nm and 630 nm.

Compound	**I**
Chemical Formula	$C_{54}H_{70}Mo_2N_2O_{14}$
Formula Weight	1163
Temperature (K)	150(2)
Space Group	Monoclinic, $P2_1/n$
a (Å)	10.6152(1)
b (Å)	10.0959(1)
c (Å)	25.9337(2)
α (^{o})	
β (^{o})	94.003(1)
γ (^{o})	
V (Å^3)	2772.53(4)
Z	2
D_{calcd} (Mg/m^3)	1.393
Crystal Size (mm)	0.38 X 0.38 X 0.27
Theta range for data collection	2.04 to 27.48^o
μ,(Mo, Kα) (mm^{-1})	0.516
F(000)	1208
Reflections collected	58574
Unique reflections	6674 [R(int)= 0.043]
Completeness to theta max	99.5%
Data/restraints/parameters	6318 / 12 / 352
R1[a] (%) (all data)	2.9 (4.37)
wR2[b](%)(all data)	6.79 (7.23)
Goodness-of-fit on F^2	1.06
Largest diff. peak and hole (e Å^{-3})	0.963 and -0.452

[a]R1 = Σ | |F_o|-|F_c| | / Σ |F_o| x 100

[b]wR2 = [Σ w (F_o^2-F_c^2)^2 / Σ (w |F_o|^2)^2]$^{1/2}$ x 100

SI Table 1: Crystallographic Data Collection Parameters for **I**.

Crystals of compound **I** were a dark brown chunks with a triangular cross-section. Examination of the diffraction pattern on a Nonius Kappa CCD diffractometer indicated a monoclinic crystal system. All work was done at 150 K using an Oxford Cryosystems Cryostream Cooler. The data collection strategy was set up to measure a quadrant of reciprocal space with a redundancy factor of 4.5, which means that 90% of the reflections were measured at least 4.5 times. Phi and omega scans with a frame width of 1.0˚ were used. Data integration was done with Denzo[1], and scaling and merging of the data was done with Scalepack[1]. Merging the data and averaging the symmetry equivalent reflections resulted in an Rint value of 0.043.

The structure was solved by the Patterson method in SHELXS-97[2]for the position of the Mo atom, and standard Fourier methods were used to obtain the rest of the structure. Full-matrix least-squares refinements based on F^2 were performed in SHELXL-97[2], as incorporated in the WinGX package[3]. The Mo dimer contains a crystallographic inversion center and there is a THF molecule located on each end of the dimer.

One isopropyl group is disordered over two orientations, which are modeled with atoms C9, C10 for one orientation and C9A, C10A for the other. The occupancy factors for the two sets of atoms were restrained to sum to 1.0, and they refined to the following values of 0.66(1) for C9 and C10 and 0.34(1) for C9A and C10A. Similarity restraints were used for the refinement of this disordered group such that the distances between the following pairs of atoms were restrained to be equal within a standard uncertainty of 0.01 Å: C8 and C9, C8 and C10, C8 and C9A, and C8 and C10A (SADI restraint). Restraints were also applied to the displacement parameters of this disordered group. The components of the anisotropic displacement parameters along the bond between two atoms were restrained to be equal within a standard uncertainty of 0.01 $Å^2$ (DELU restraint) for atoms C8, C9, C10, C9A, and C10A.

For each methyl group, the hydrogen atoms were added at calculated positions using a riding model with U(H) = 1.5 * Ueq(bonded carbon atom). The torsion angle, which defines the orientation of the methyl group about the C-C bond, was refined. The rest of the hydrogen atoms were included in the model at calculated positions using a riding model with U(H) = 1.2 * Ueq(bonded atom).

The final refinement cycle was based on 6318 intensities, 12 restraints and 352 variables and resulted in agreement factors of R1(F) = 0.044 and wR2(F^2) = 0.072. For the subset of data with I > 2*sigma(I),the R1(F) value is 0.029 for 5074 reflections. The final difference electron density map contains maximum and minimum peak heights of 0.96 and -0.45 e/$Å^3$. Neutral atom scattering factors were used and include terms for anomalous dispersion[4].

CCDC 994112 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

References

1. Z. Otwinowski and W. Minor, *Methods in Enzymology, Vol. 276: Macromolecular Crystallography, Part A*, Academic Press, 1997.
2. G. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112–122.
3. L. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837–838.
4. A. J. C. Wilson and V. Geist, *International Tables for Crystallography, Volume C*, Kluwer Academic Publishers, Dordrecht, 1992.