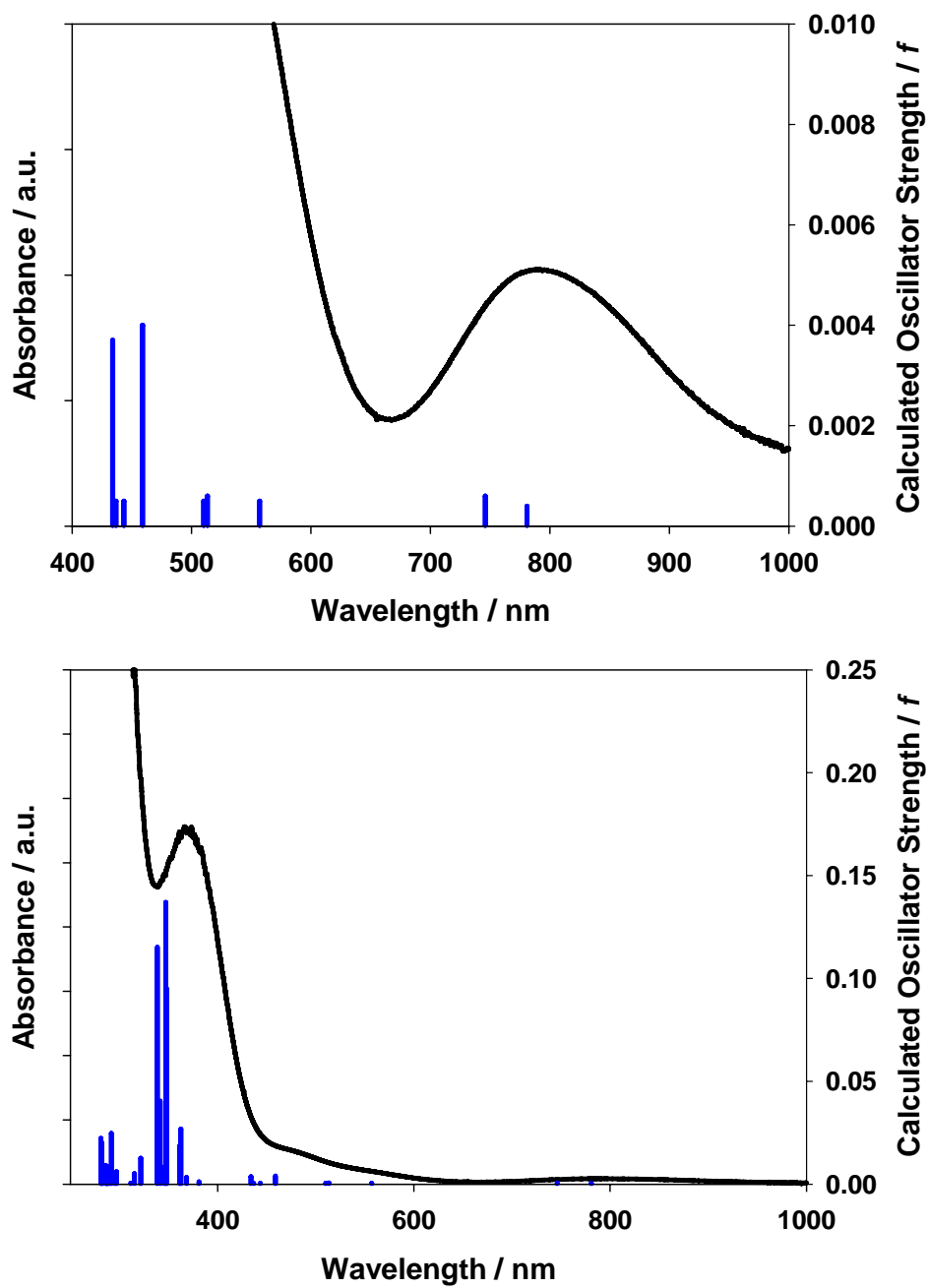


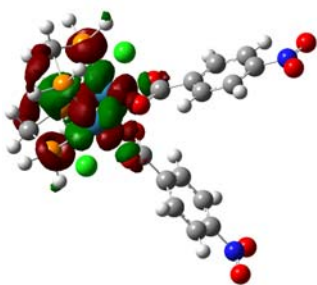
Supporting Information



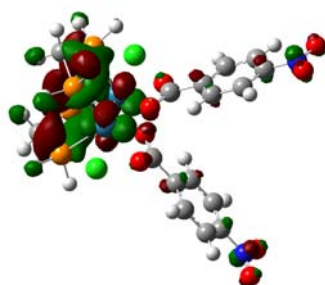
S1: Absorption spectra of $\text{Re}_2(\text{dppm})_2(\text{O}_2\text{CC}_6\text{H}_4\text{NO}_2)_2\text{Cl}_2$ in CH_2Cl_2 and calculated electronic transitions of singlet ground state.

S2: Orbital contributions of electronic transitions of $\text{Re}_2(\text{dppm})_2(\text{O}_2\text{CC}_6\text{H}_4\text{NO}_2)_2\text{Cl}_2$ singlet ground state. *Orbitals involved in transitions that are not shown in Figure 4.

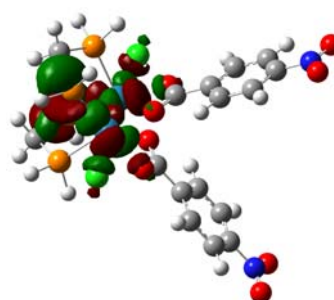
$\lambda_{\text{calc}} / \text{nm}$	major transitions (contribution)
780.81	$\text{H} \rightarrow \text{L}$ (0.506), $\text{H} \rightarrow \text{L}+2$ (0.434)
745.92	$\text{H} \rightarrow \text{L}+1$ (0.357), $\text{H} \rightarrow \text{L}+3$ (0.565)
348.19	$\text{H}-4 \rightarrow \text{L}$ (0.481), $\text{H}-4 \rightarrow \text{L}+2$ (-0.472), $\text{H}-2 \rightarrow \text{L}+3$ (-0.117)
347.16	$\text{H}-4 \rightarrow \text{L}+1$ (0.576), $\text{H}-4 \rightarrow \text{L}+3$ (-0.359)
338.56	$\text{H}-4 \rightarrow \text{L}+2$ (-0.220), $\text{H}-3 \rightarrow \text{L}$ (0.142), $\text{H}-3 \rightarrow \text{L}+2$ (0.255), $\text{H}-2 \rightarrow \text{L}+1$ (0.108), $\text{H}-2 \rightarrow \text{L}+3$ (0.325), $\text{H}-1 \rightarrow \text{L}+15$ (-0.143), $\text{H} \rightarrow \text{L}+10$ (0.262), $\text{H} \rightarrow \text{L}+13$ (0.148)



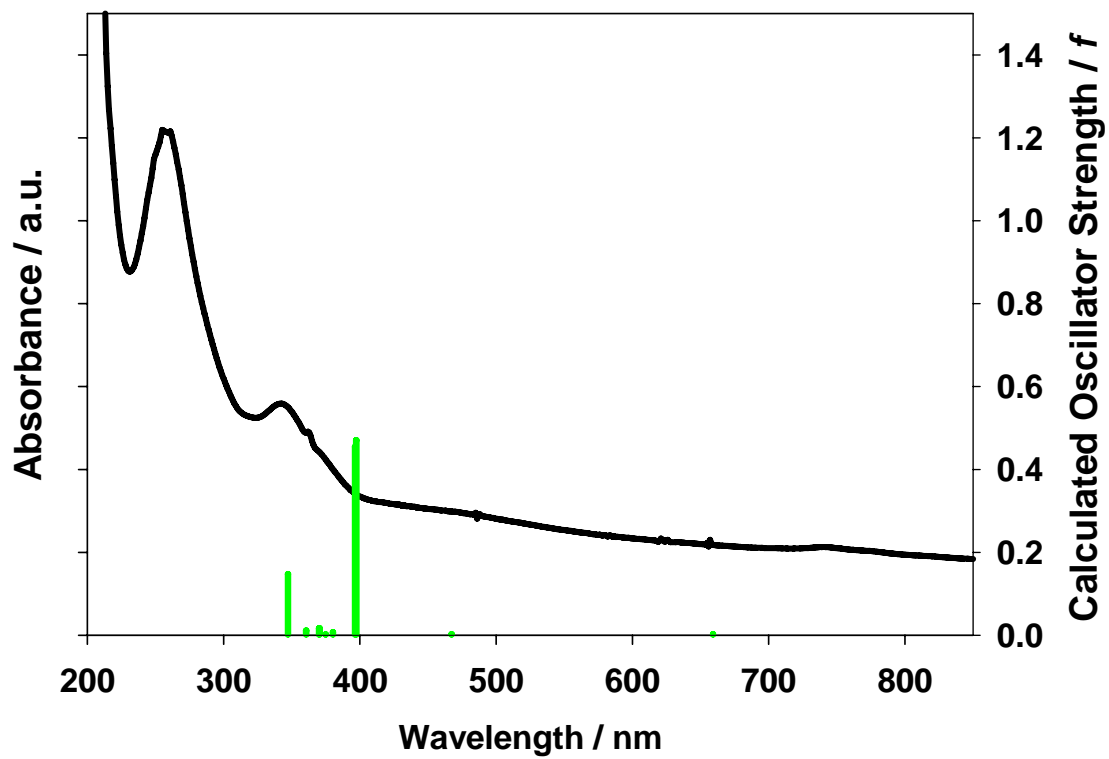
*L+10



L+13



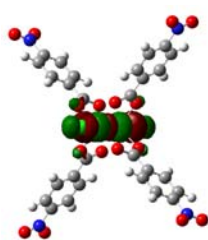
L+15



S3: Absorption spectra of $\text{Re}_2(\text{O}_2\text{CC}_6\text{H}_4\text{NO}_2)_4\text{Cl}_2$ in THF and calculated electronic transitions of singlet ground state.

S4: Orbital contributions of electronic transitions of $\text{Re}_2(\text{O}_2\text{CC}_6\text{H}_4\text{NO}_2)_4\text{Cl}_2$ singlet ground state. H = HOMO, L = LUMO. *Orbitals involved in transitions that are not shown in Figure 6.

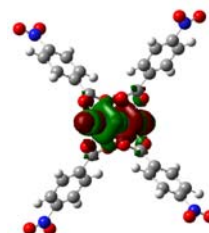
$\lambda_{\text{calc}} / \text{nm}$	major transitions (contribution)
972.48	H \rightarrow L (0.683)
659.24	H-22 \rightarrow L+1 (-0.121), H-3 \rightarrow L+1(-0.173), H-2 \rightarrow L+4 (-0.145), H-1 \rightarrow L (0.631)
397.38	H-1 \rightarrow L+2 (0.471)
396.51	H-1 \rightarrow L+3 (0.455)
347.29	H-27 \rightarrow L (-0.283), H-17 \rightarrow L+4 (-0.131), H-3 \rightarrow L+1 (0.312), H-2 \rightarrow L+4 (0.370), H-2 \rightarrow L+6 (0.133), H-1 \rightarrow L (0.119), H \rightarrow L+18 (0.229)



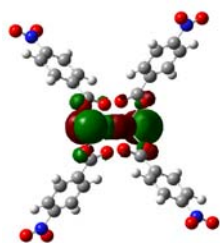
* L+4



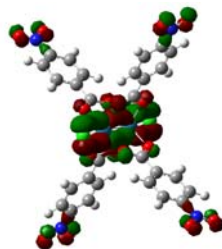
L+6



L+18



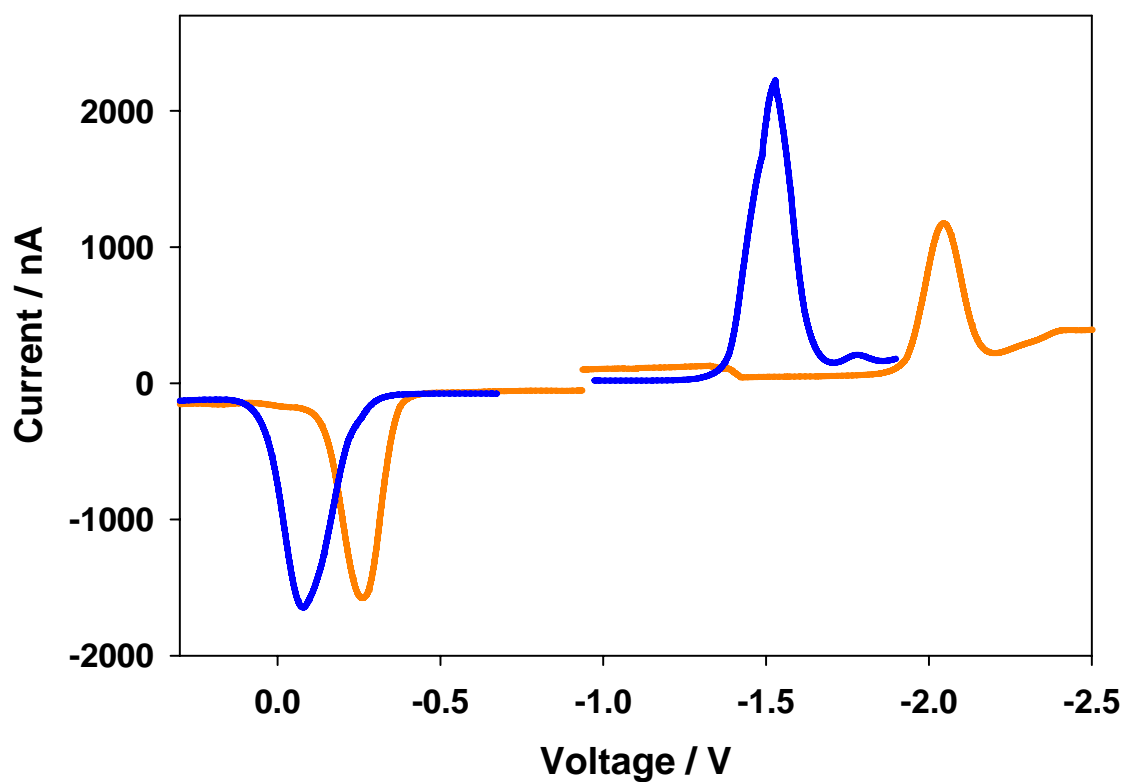
* H-17



H-22



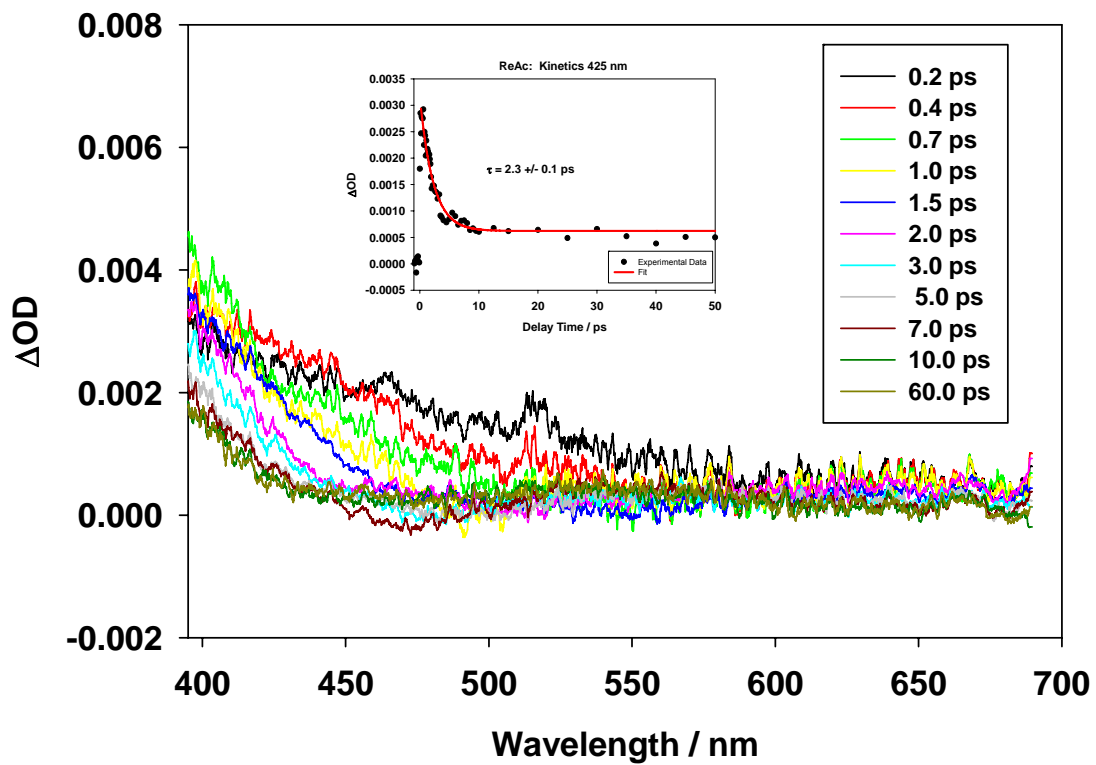
H-27



S5: Differential pulse voltammograms of $\text{Re}_2(\text{dppm})_2(\text{O}_2\text{CR})_2\text{Cl}_2$ in THF where $\text{R} = \text{CH}_3$ (orange) and $\text{R} = \text{C}_6\text{H}_4\text{NO}_2$ (blue). Potentials are reported versus the $\text{Cp}_2\text{Fe}^{0/+}$ couple.

S6: Electrochemical oxidation and reduction potentials of compounds in THF versus $\text{Cp}_2\text{Fe}^{0/+}$ couple.

Complex	$E_{1/2}^{\text{OX}} / \text{V}$	$E_{1/2}^{\text{RED}} / \text{V}$
$\text{Re}_2(\text{dppm})_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_2$	-0.260	-2.046
$\text{Re}_2(\text{dppm})_2(\text{O}_2\text{CC}_6\text{H}_4\text{NO}_2)_2\text{Cl}_2$	-0.079	-1.529



S7: fs-TA broadband spectrum of $\text{Re}_2(\text{dppm})_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_2$ in THF ($\lambda_{\text{exc}} = 365$ nm). Kinetic trace at 4125 nm shows $\tau = 2.3 \pm 0.1$ ps.