Electronic Supporting Information
For

Photoinduced Electron Transfer from Oxo-Mo^{IV}Selenolato Complex to Oxygen

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1. Table S1: Crystallographic parameters for 1 and 2

Compound	**1**	**2**
Empirical Formula	C_{37} H_{51} Cl_2 Mo N_5 O S_2 Se	C_{39} H_{51} Cl_2 Mo N_5 O S_2 Se
Formula Weight	891.77	915.79
Crystal System	Triclinic	Triclinic
Space Group	P-1	P-1
Temperature (K)	100(2)	100(2)
Z	4	2
a(Å)	9.562(5)	9.288(5)
b(Å)	19.281(5)	11.771(5)
c(Å)	23.109(5)	19.492(6)
α(°)	79.293(5)	83.300(5)
β(°)	83.660(5)	84.385(5)
γ(°)	77.619(5)	83.738(5)
V(Å^3)	4078(3)	2096.0(15)
D calc (g cc^{-1})	1.452	1.451
F (000)	1832	940
Absorption (mm^{-1})	1.483	1.445
Theta Range (°)	2.19 – 27.00	2.11 – 26.00
GOF (F^2)	1.021	1.117
R_1[a] (%)	7.13	6.85
wR_2[b](%)	29.00	22.38

[a] $R_1 = \Sigma||F_0| - |F_c||/ \Sigma|F_0|$ [b] $wR_2 = \{ \Sigma[w(F_0^2 - F_c^2)^2]/ \Sigma w(F_0^2)^2]\}^{1/2}$

3. Table S2: Relevant bond lengths and angles for 1 and 2.

Complexes		**1**	**2**
Bond Length (Å)	Mo-O	1.693(4)	1.691(4)
	Mo-Se	2.558(1)	2.566(1)
	Mo-Savg	2.412	2.417
	Mo-Navg	2.270	2.273
Angles (°)	O-Mo-Se	101.62(15)	102.66(14)
	S-Mo-S	84.37(6)	84.25(5)
	N-Mo-N	70.00(18)	70.55(18)

4. Effect of solvent on the absorbance spectra of 1 and 2.

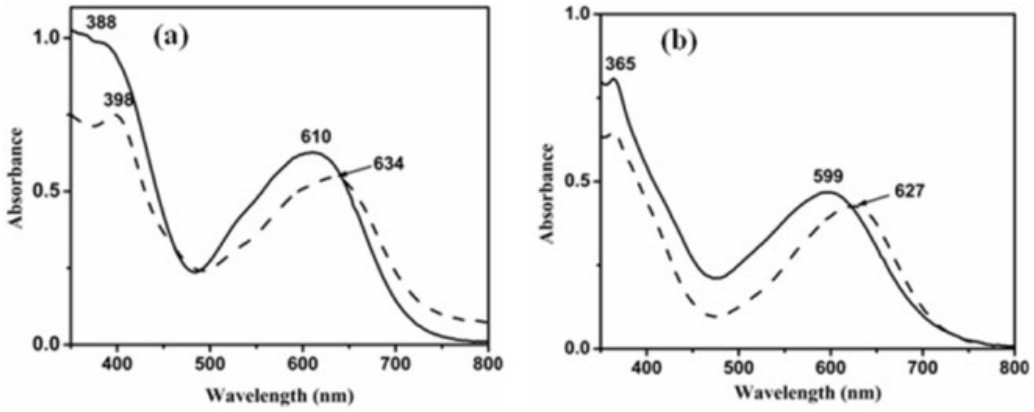

Figure S1: Electronic spectra of 10^{-4}M solutions of **1** and **2** in DCM (solid line) and acetone (dashed line) are depicted as (a) and (b) respectively.

5. TDDFT Data for 1 and 2 in DCM using B3LYP and BP86 functional

Table S3: Details of relevant transitions from TDDFT calculations of **1** in DCM

B3LYP in DCM				BP86 in DCM			
Wavelength (nm)	**Oscillator Strength**	**Transition**	**Assignment**	**Wavelength (nm)**	**Oscillator Strength**	**Transition**	**Assignment**
547.95	0.0313	125→126 125→127 125→128	MLCT	726.76	0.0081	125→126 125→127	MLCT
496.71	0.0546	125→126 125→127 125→128	MLCT	655.58	0.0662	125→126 125→127	MLCT
471.79	0.0169	124→126	ILCT	594.82	0.0118	125→126	MLCT
437.99	0.0313	124→127	ILCT	547.15	0.0183	123→127 124→127	ILCT
416.04	0.0386	123→126	ILCT	469.64	0.0401	123→127 124→128	ILCT
383.55	0.0233	122→126 123→127 124→128	ILCT	451.08	0.0367	122→126	ILCT
380.12	0.0304	122→126	ILCT	439.87	0.0218	122→127	ILCT
362.47	0.0255	122→127	ILCT	406.23	0.0476	123→128	ILCT
355.86	0.0329	125→131	MLCT	371.89	0.0277	123→129 123→130	ILCT

Table S4: Details of relevant transitions from TDDFT calculations of **2** in DCM

B3LYP in DCM				BP86 in DCM			
Wavelength (nm)	**Oscillator Strength**	**Transition**	**Assignment**	**Wavelength (nm)**	**Oscillator Strength**	**Transition**	**Assignment**
595.57	0.0086	131→132 131→134	MLCT	737.84	0.0136	131→132 131→133	MLCT
558.04	0.0192	121→132 131→134 131→135	MLCT	615.41	0.0785	131→133	MLCT
489.44	0.0790	131→133	MLCT	599.11	0.028	130→132	ILCT
485.10	0.0367	131→132 131→135	MLCT	574.02	0.150	130→132	ILCT
425.73	0.0271	129→132 129→134	ILCT	459.15	0.0193	128→132 128→133	ILCT
410.86	0.0425	129→132	ILCT	459.15	0.0193	128→132 128→133	ILCT
384.21	0.0338	128→132	ILCT	435.71	0.0282	128→133 130→135	ILCT
375.25	0.0219	128→132 129→134 130→135	ILCT	430.35	0.0412	128→133 128→134 131→137	ILCT
356.70	0.0195	128→134	ILCT	391.13	0.0483	129→135 130→137	ILCT

Table S5: Emission wavelengths calculated from TDDFT calculations of **1** and **2** in DCM using B3LYP and BP86 functionals:

Complexes:	**1**		**2**	
Emission Wavelengths (nm)	**B3LYP**	**BP86**	**B3LYP**	**BP86**
	722.57	649.94	740.91	652.84
	594.98	579.86	612.16	636.70
	478.17	533.38	544.33	561.27
		481.65	490.03	484.75
		472.21	470.17	477.97
			434.43	467.88

6. Major orbitals contributing to the electronic transitions(Red-Green for B3LYP functional and orange-cyan for BP86 functional respectively)

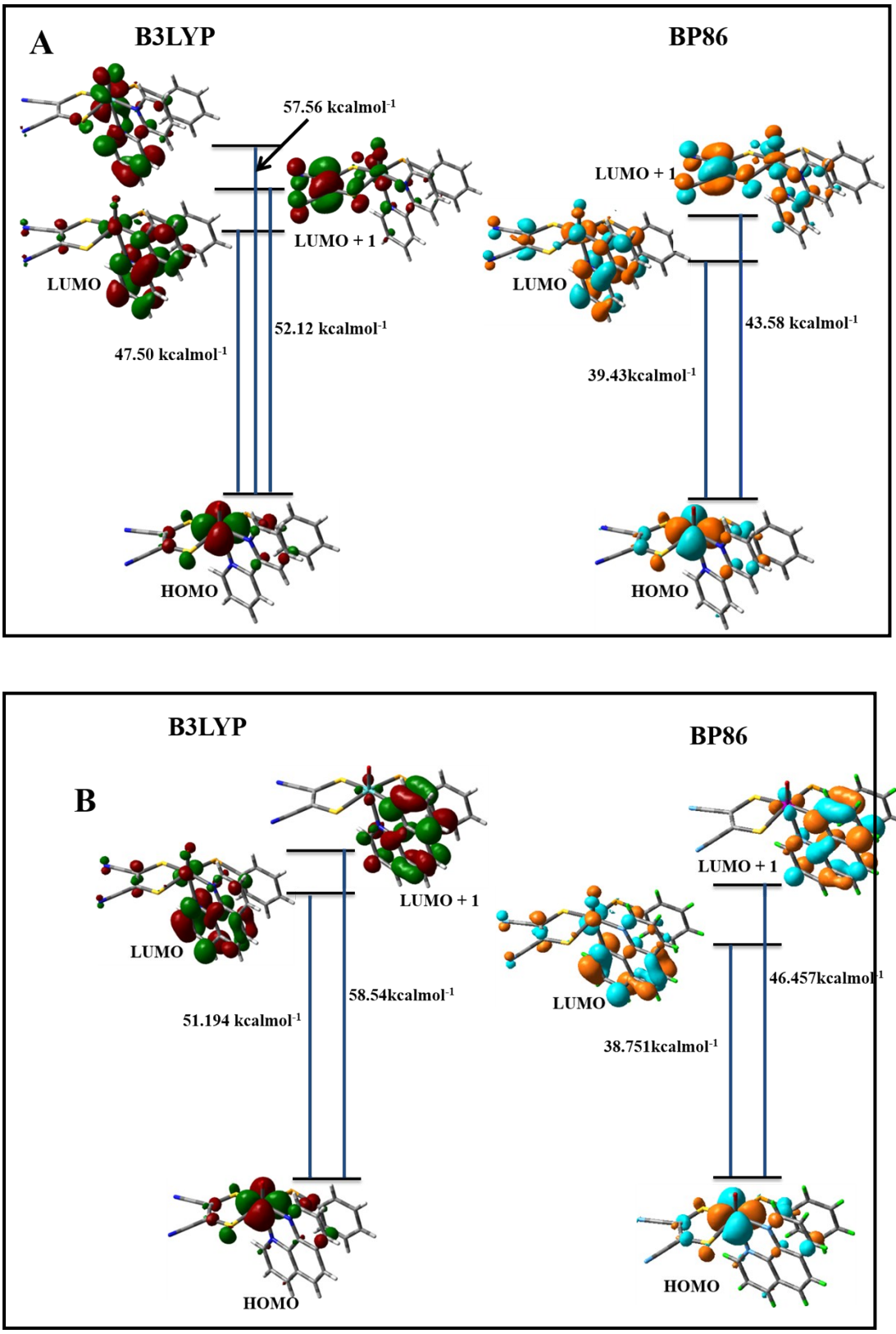

Figure S2: Major Orbital Contribution to MLCT (A) in **1** and (B)**2**.

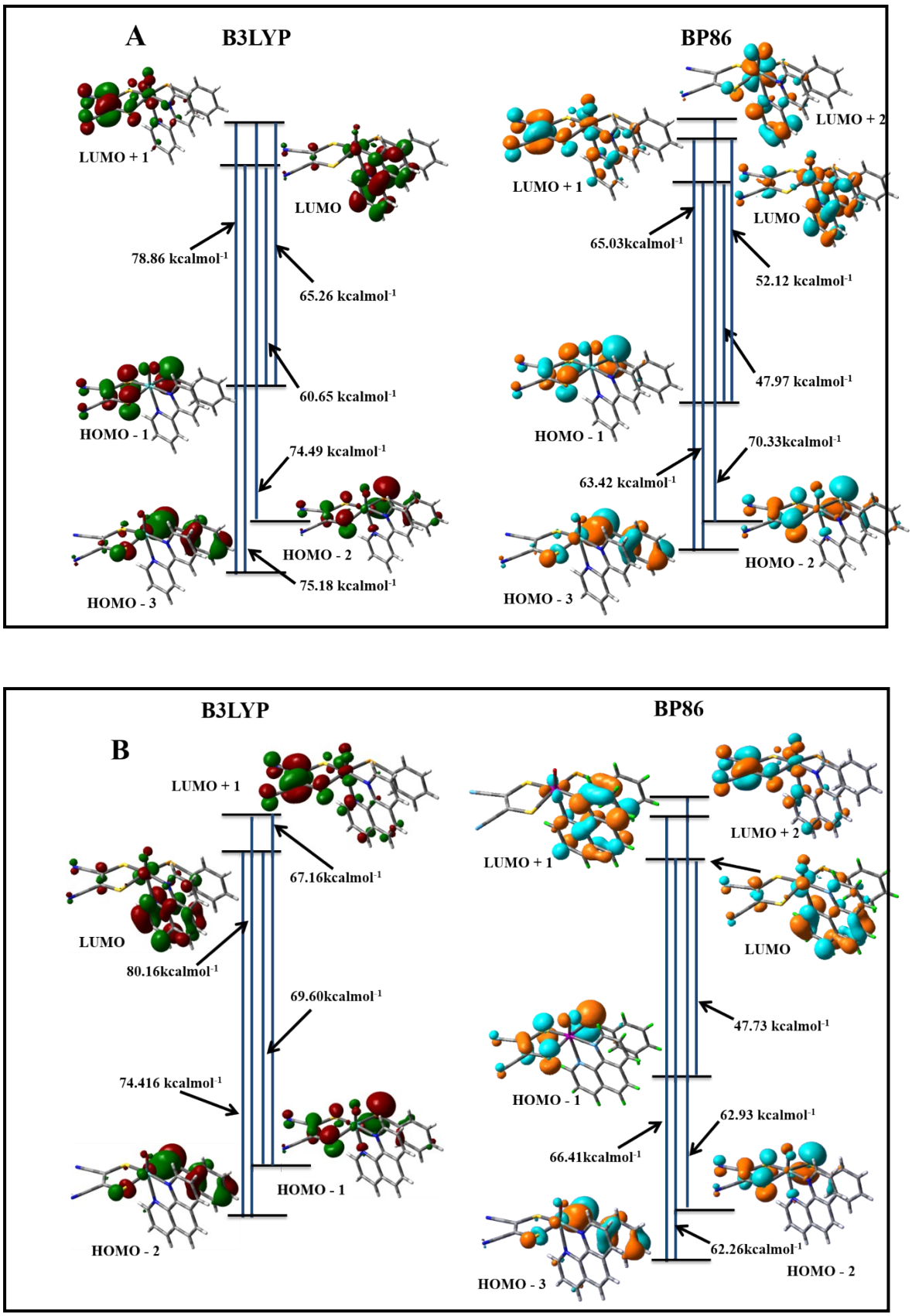

Figure S3: Major Orbital Contribution to ILCT in (A)**1** and (B)**2.**

7. Table S6:Comparison of the energies (kcal mol^{-1}) of the frontier orbitals of 1 and 2 obtained from calculations in gas phase and with DCM solvent with B3LYP and BP86 functional

Complexes		B3LYP		BP86	
		Gas Phase	DCM	Gas Phase	DCM
1	HOMO	-48.427	-109.998	-33.899	-90.858
	LUMO	-7.610	-39.895	-4.843	-54.192
HOMO – LUMO Gap		40.817	70.103	29.056	36.666
2	HOMO	-48.658	-107.231	-32.746	-89.508
	LUMO	5.534	-37.589	-7.379	-53.500
HOMO – LUMO Gap		54.192	69.642	25.367	36.008

8. Electrochemistry

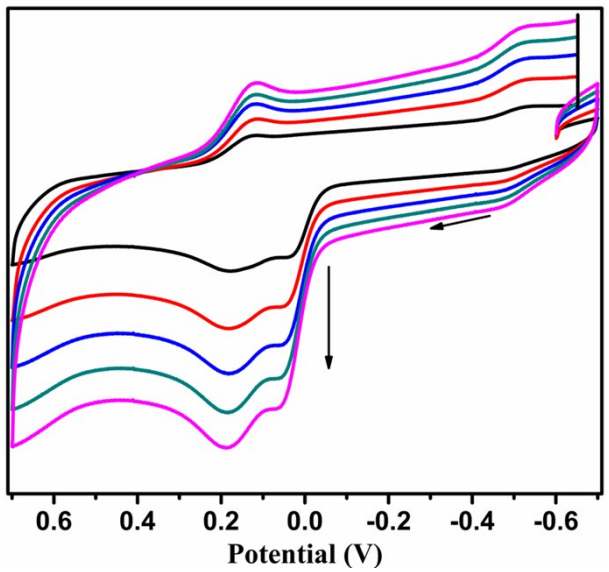

Figure S4: Cyclic voltammograms of **1** in DCM using $TBAPF_6$ as supporting electrolyte and glassy carbon as working electrode. Scan rate has been progressively increased from 100mV/s to 500mV/s.

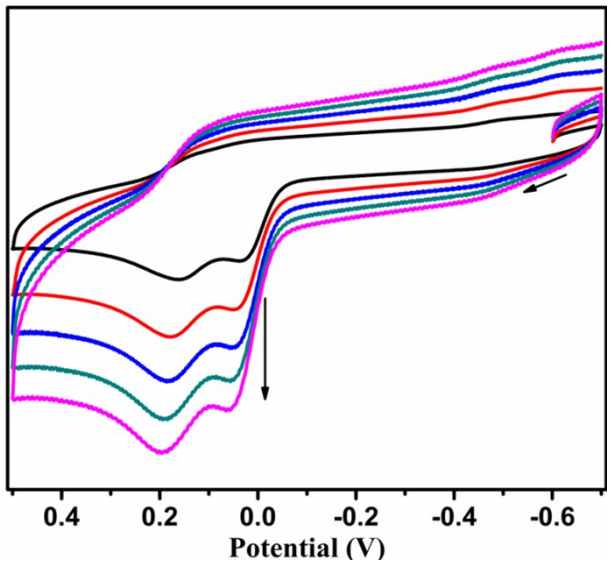

Figure S5: Cyclic voltammograms of **2** in DCM using $TBAPF_6$ as supporting electrolyte and glassy carbon as working electrode. Scan rate has been progressively increased from 100mV/s to 500mV/s.

9. Electron transfer from 1 to dichlorophenol indophenol (DCPIP)

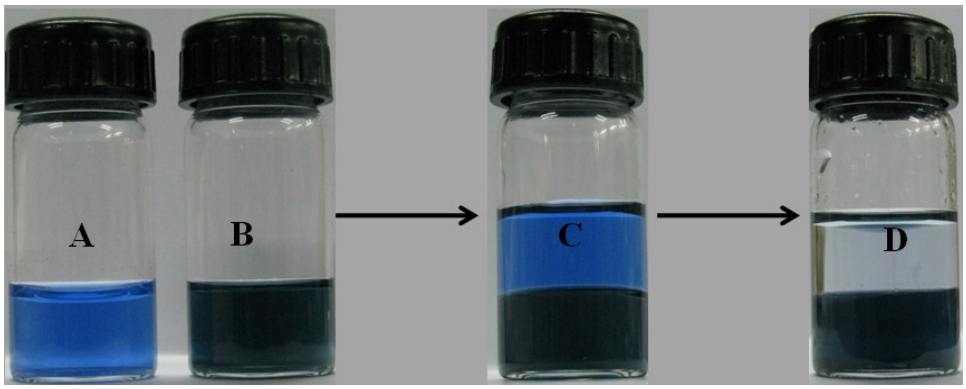

Figure S6: Facile electron transfer of 1 to DCPIP dye.