Supporting Information

MM Quadruple Bonds Supported by Cyanoacrylate Ligands. Extending Photon Harvesting into the Near Infrared and Studies of the MLCT States

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Table S1. Select crystallographic information from **MoL′** and **MoL**

Compound	**MoL′**	**MoL**
Chemical Formula	$C_{92}H_{96}Mo_2N_4O_{10}S_2$	$C_{176}H_{200}Mo_4N_4O_{22}$
Formula Weight	1673.73	3163.20
Temperature (K)	150(2)	150(2)
Space Group	Triclinic, P-1	Triclinic,P-1
a (Å)	12.6203(2)	12.843(3)
b (Å)	13.1151(2)	16.816(3)
c (Å)	13.4075(2)	21.696(4)
α (^{o})	81.395(1)	74.31(3)
β (^{o})	89.382(1)	76.48(3)
γ (^{o})	84.039(1)	72.72(3)
V (Å^3)	2182.29(6)	4247.0(15)
Z	1	1
D_{calcd} (Mg/m^3)	1.274	1.237
Crystal Size (mm)	0.23 X 0.19 X 0.15	0.27 X 0.23 X 0.12
Theta range for data collection	1.54 to 25.02^o	2.57 to 24.71^o
μ,(Mo, Kα) (mm^{-1})	0.393	0.354
Reflections collected	51400	83352
Unique reflections	7685 [R(int)= 0.042]	14986[R(int)= 0.060]
Completeness to theta	(25.02^o) 99.9%	(24.71^o) 99.9%
Data/restraints/parameters	7685 / 3 / 515	14467 / 0 / 946
R1[a] (%) (all data)	3.47 (4.67)	5.90 (9.98)
wR2[b](%)(all data)	8.50 (9.24)	15.44 (16.82)
Goodness-of-fit on F^2	1.079	1.080
Largest diff. peak and hole (e Å^{-3})	0.568 and -0.412	0.929 and -0.508

[a]R1 = $\Sigma \mid |F_o|-|F_c| \mid / \Sigma |F_o|$ X 100

[b]wR2 = $\{ \Sigma [w(F_o^2-F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$ X 100

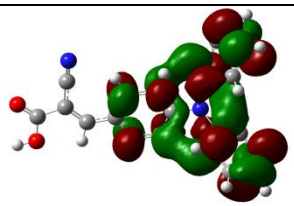
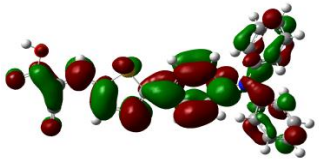
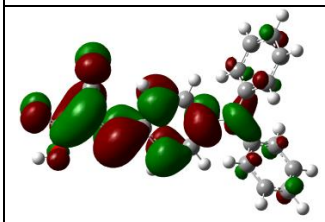
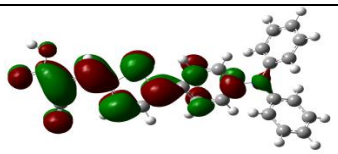
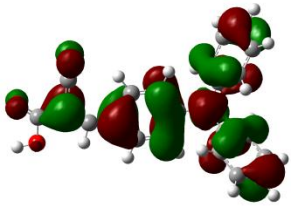
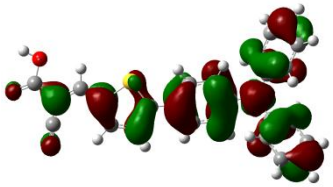
LH	E/eV	L′H	E/eV	MO
	-0.79		-0.99	L+1
	-2.28		-2.60	L
	-5.47		-5.27	H

Figure S1. Frontier molecular orbitals and calculated energies for **LH** and **L′H**.

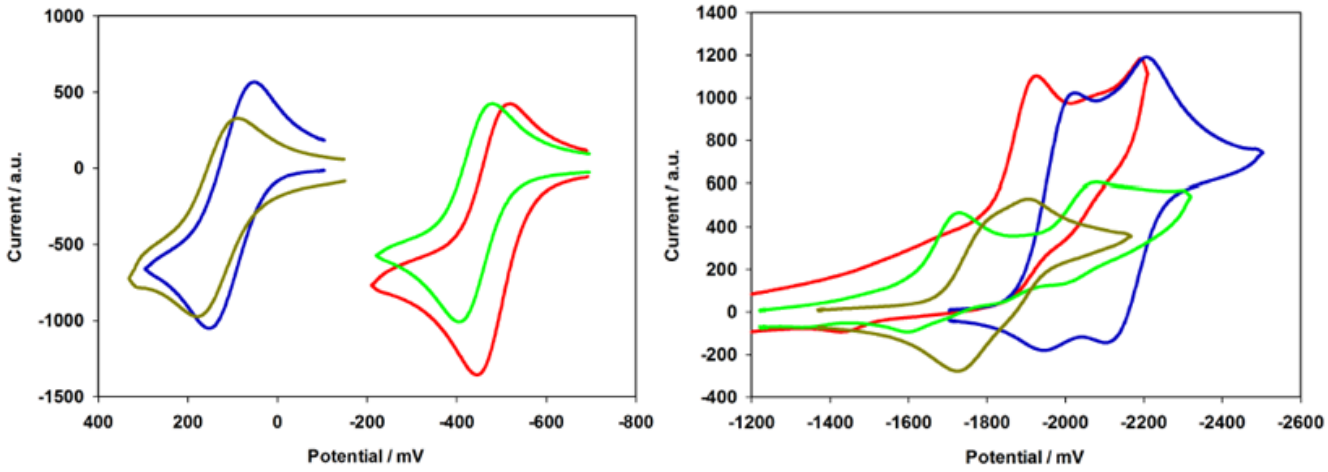


Figure S2.Cyclic voltammograms of **MoL** (blue), **WL** (red), **MoL′** (dark green) and **WL′** (yellow-green). The redox potentials are referenced to the $Cp_2Fe^{+/0}$ couple.

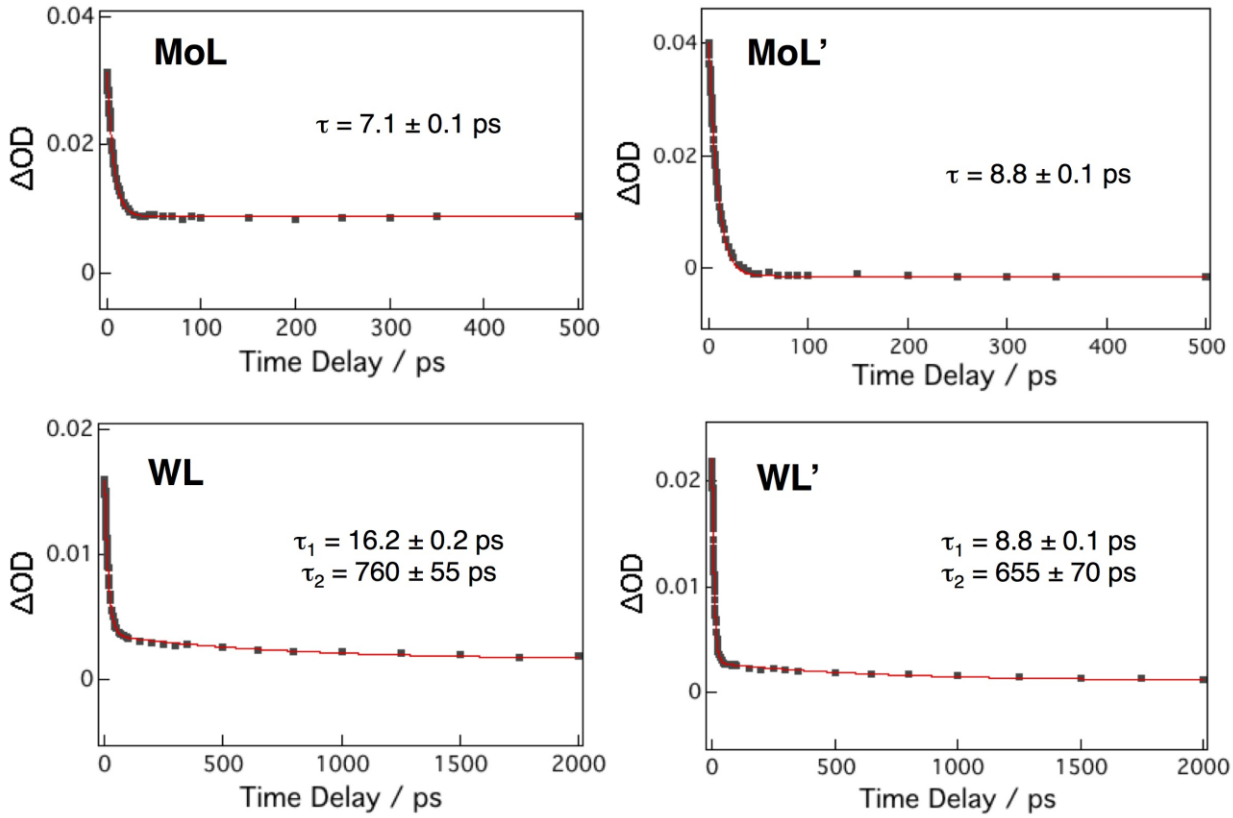


Figure S3. Kinetic traces from fsTA spectra of **MoL** monitored at 470 nm; **MoL′** monitored at 565 nm; **WL** monitored at 477 nm; and **WL'** monitored at 551 nm.

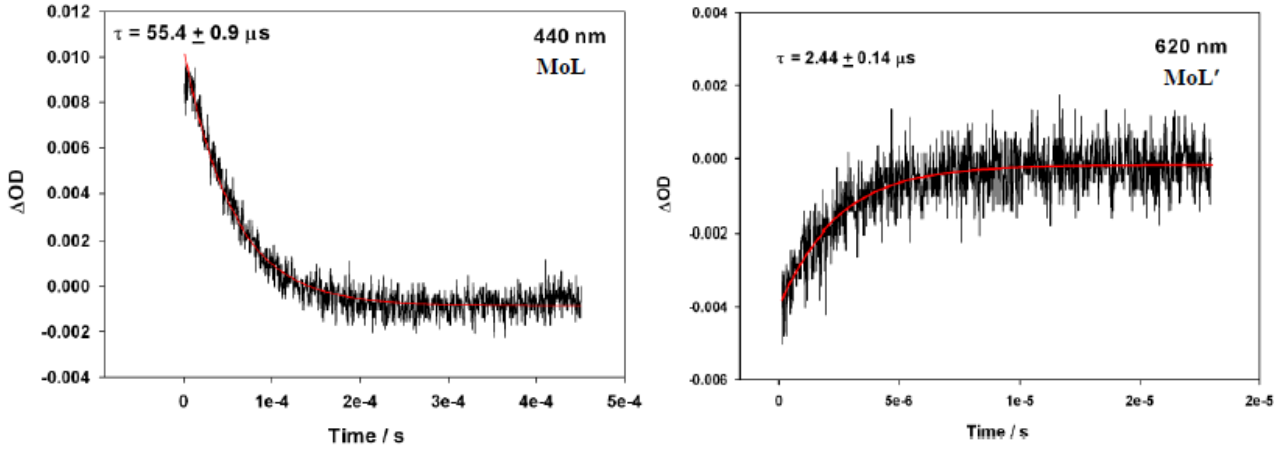


Figure S4. Kinetic traces from nsTA spectra of **MoL** (left) monitored at 440 nm and **MoL′** monitored at 620 nm

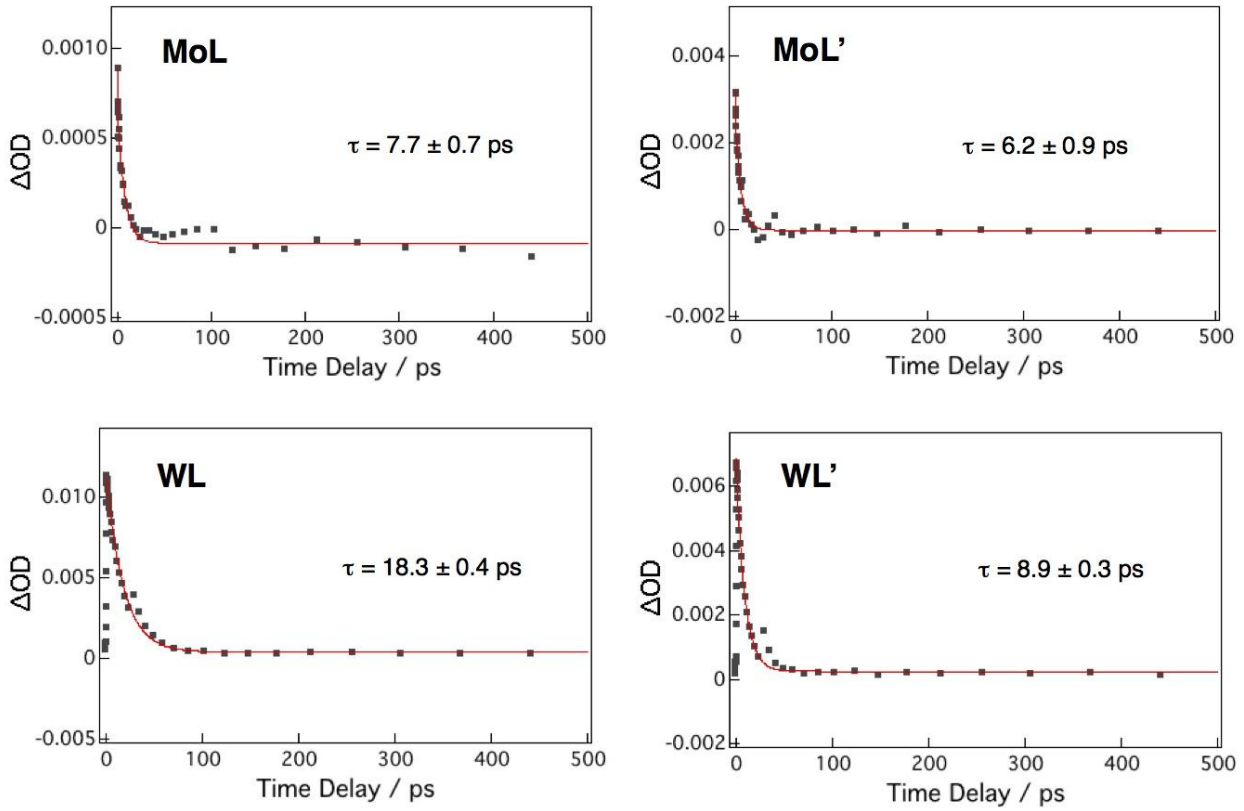


Figure S5. Kinetic traces from fs-TRIR spectra of **MoL** monitored at 2164 cm^{-1}; **MoL′** monitored at 2171 cm^{-1}; **WL** monitored at 2166 cm^{-1}; and **WL′** monitored at 2172 cm^{-1}.

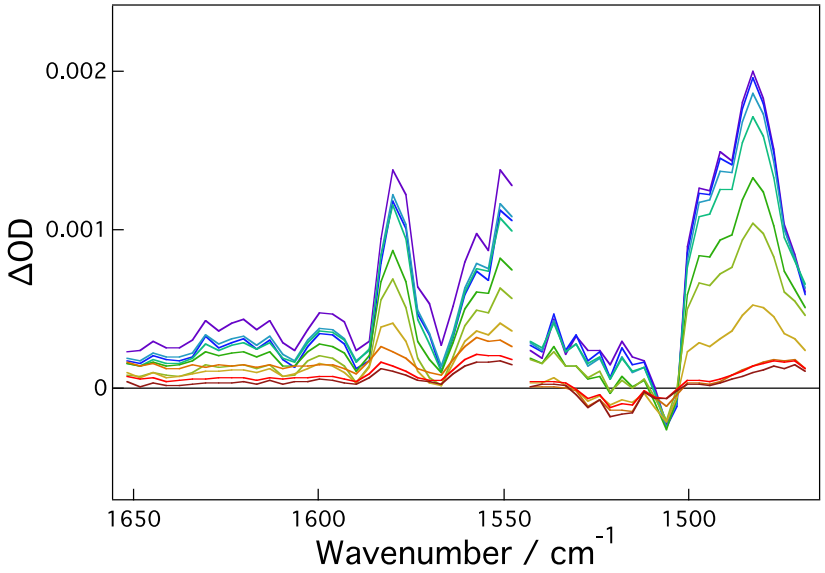


Figure S6. fs-TRIR spectra of **WL**, λ_{ex} = 800 nm; recorded in THF at RT.