

Photoinduced δ Electron Transfer in Phenylene Bridged Mo₂ Dimers

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1. Preparation of Compounds.

The four neutral Mo₂ dimers were synthesized by following the published procedures (Xiao, X.; Liu, C. Y.; He, Q.; Han, M. J.; Meng, M.; Lei, H.; Lu, X. *Inorg. Chem.* **2013**, *52*, 12624–12633). The compounds were characterized by ¹H NMR spectra. The corresponding mixed-valence complexes were prepared by chemical oxidation using one equiv of ferrocenium hexafluorophosphate.

2. Physical Measurements.

2.1 Electronic Spectroscopies for the Neutral and the Mixed-valence Complexes

Cyclic voltammograms (CVs) were performed using a CH Instruments model-CHI660D electrochemical analyzer in 0.10 M ⁿBu₄NPF₆ solution in CH₂Cl₂ with Pt working and auxiliary electrodes, Ag/AgCl reference electrode, and a scan rate of 100 mV/s. UV-vis spectra were measured on a Shimadzu UV-3600 UV-vis-NIR spectrophotometer in CH₂Cl₂ solutions using IR quartz cells with light path length of 2 mm.

2.2 Femtosecond Transient Spectral Spectroscopies

The femtosecond transient spectral studies were performed on the time-resolved absorbance difference spectrometer equipped with a regenerative Ti/sapphire amplifier with 500 Hz repetition (Legend Elite USP HE+, Coherent, 35 fs, 800 nm). The output laser was split into two beams. One beam with a power of 6 μJ per pulse was focused onto pure water to generate a white light continuum as a probe beam. The other beam went into an optical parametric amplifier (OPerA Solo) to generate the pump beam centered at 355 nm and then passed to the translation stage. A mechanical chopper was employed to modulate the pump repetition frequency. The pump and probe pulses were focused to a diameter of 500 and 200 μm, respectively, at a cell interface using two plano-concave mirrors. The samples were stirring in the cell to avoid photo damage. The probe pulse was recorded on a fiber spectrometer (Avantes, AvaSpec_ULS2048L-USB2) in external trigger mode. The polarization of the pump beam was set to the magic angle (54.7°) with respect to the probe beam. The optical path in samples was 5 mm and the pump energy was 2 μJ per pulse.

Table S1. Spectroscopic and electrochemical data for estimation of δ electron energies in the excited states.

compound	$E_{1/2}(1)$ (mV)	$E(\delta \rightarrow \delta^*)$ (nm/eV)	$E(\text{MLCT})$ (nm/eV)	$E(\text{LMCT})$ (nm/eV)
[O ₂ -ph-O ₂]	335	425/2.92	491/2.52	560
[OS-ph-OS]	468	460/2.69	650/1.91	750
[S ₂ -ph-S ₂]	502	500/2.48	722/1.72	807
[O ₂ -ph-S ₂]	292	450/2.75	627/1.98	780

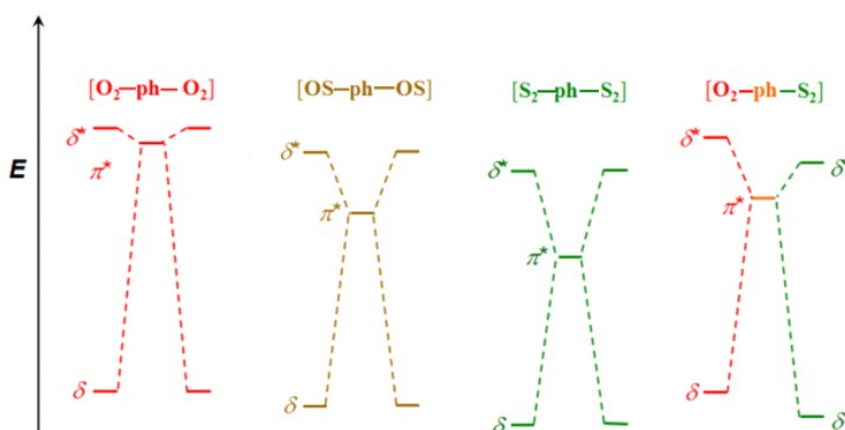


Figure S1. Energy diagrams for electronic states for the studied Mo₂ dimeric systems, plotted based on electrochemical and spectroscopic data.

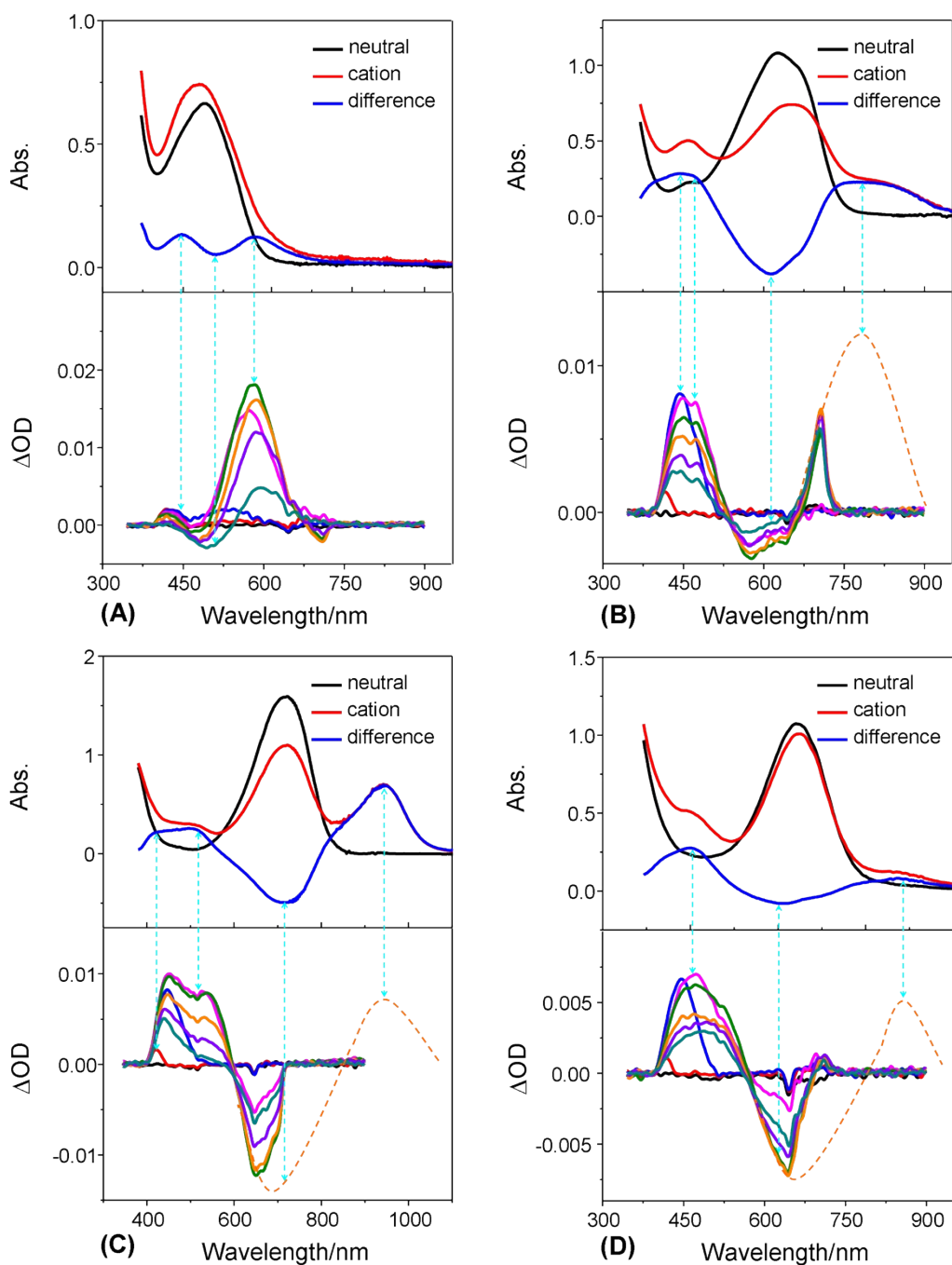


Figure S2. Stead-state electronic spectra of the neutral and MV states and the resultant difference spectra for complexes [O₂-ph-O₂](A), [OS-ph-OS](B), [S₂-ph-S₂](C) and [O₂-ph-S₂](D), in comparison with the femtosecond transient absorptions for the corresponding photochemical system. The dashed lines indicate the absorptions trucked by the instrumental limits.

3. Kinetic traces and data fitting for the excited states

3.1 For systems $[Mo_2]-ph-[Mo_2]$

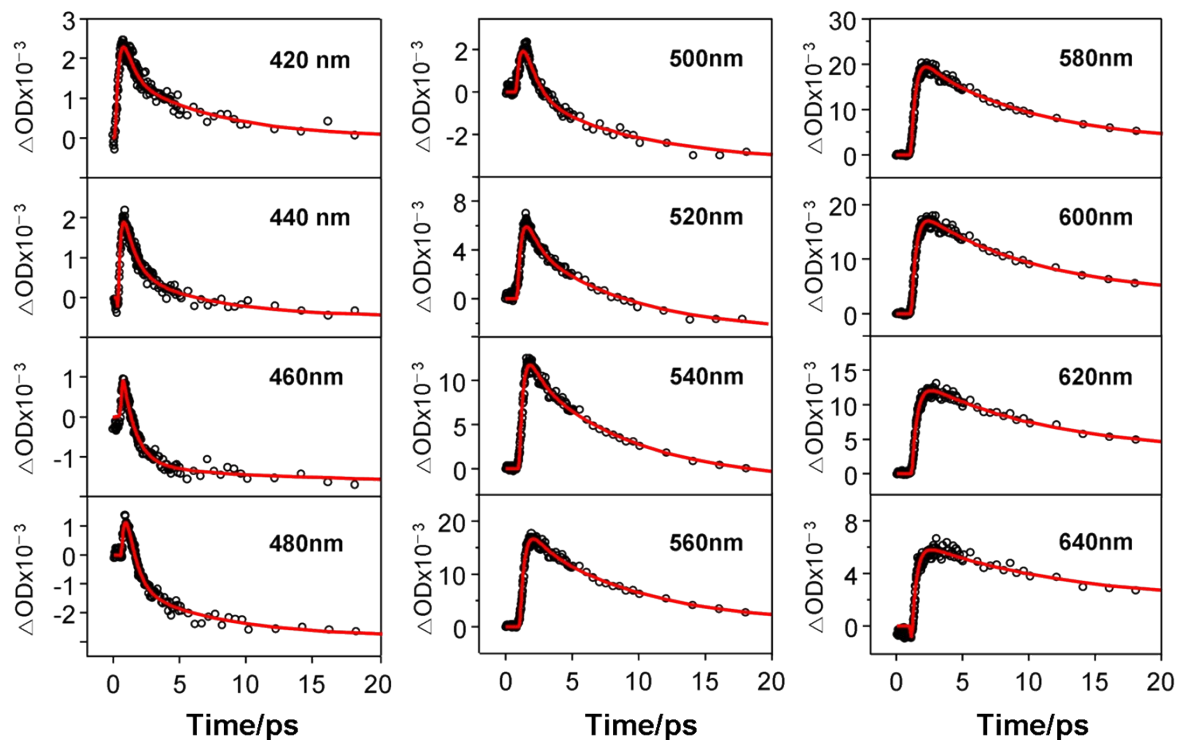


Figure S3: Transient absorption traces for $[O_2-ph-O_2]$ at various wavelengths.

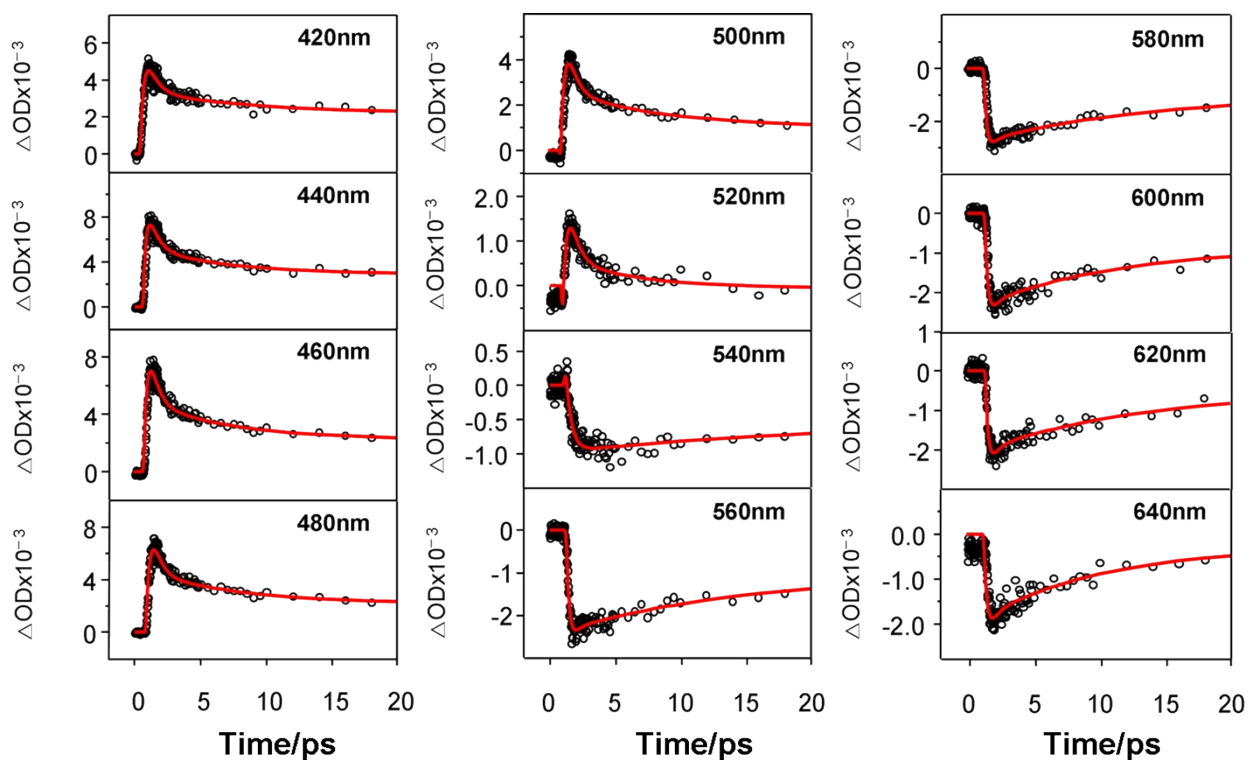


Figure S4: Transient absorption traces for $[OS-ph-OS]$ at various wavelengths.

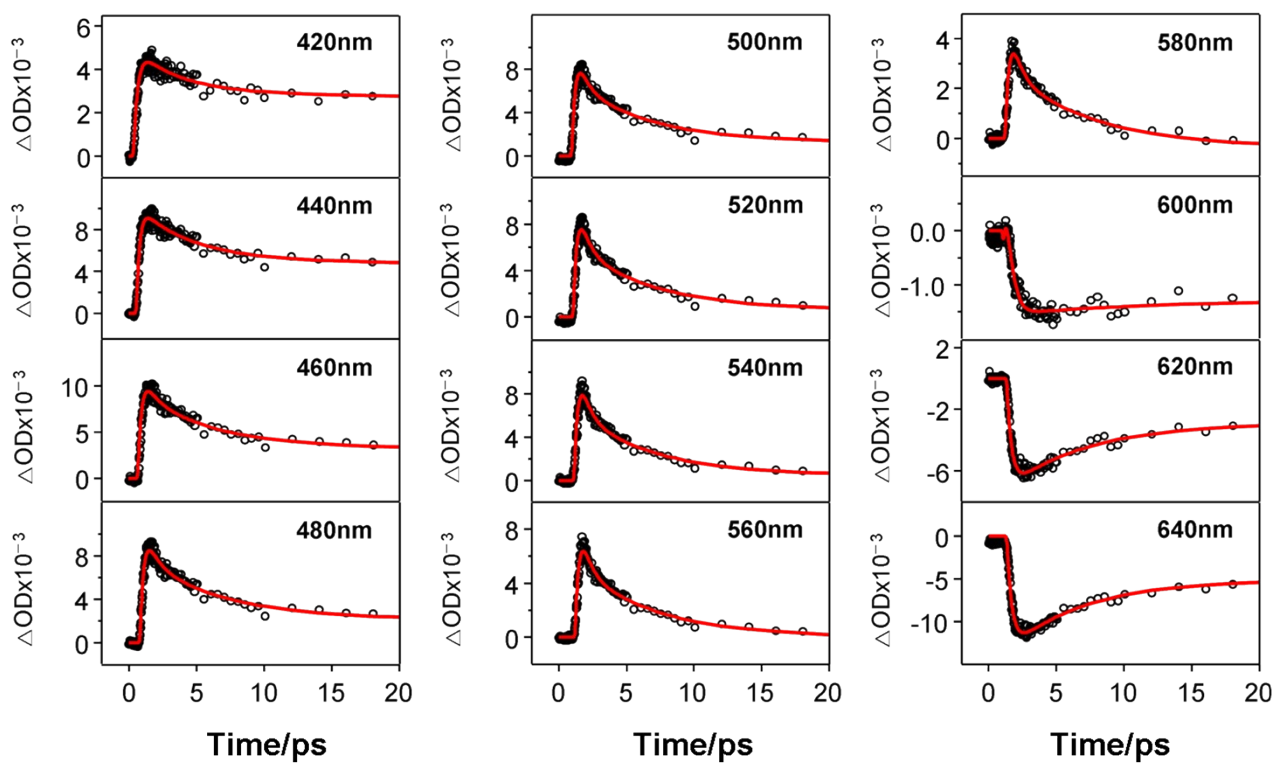


Figure S5: Transient absorption traces for $[S_2\text{-ph-S}_2]$ at various wavelengths.

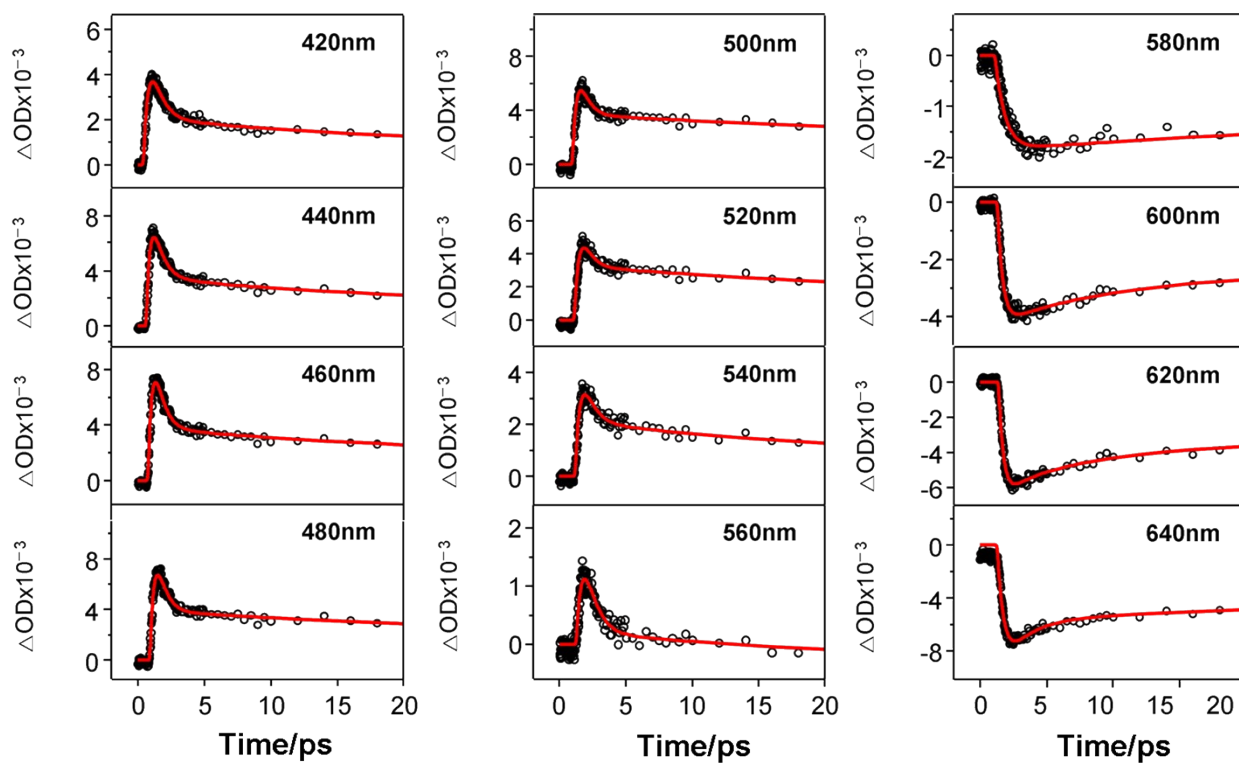


Figure S6: Transient absorption traces for $[O_2\text{-ph-S}_2]$ at various wavelengths.

Table S2. Formation time (τ_{CS}) and lifetimes (τ_{CR-1} and τ_{CR-2}) for the excited states in system [O₂-ph-O₂].

τ (ps)	420 nm	440 nm	460 nm	480 nm	500 nm	520 nm
τ_{CS}	0.36	0.19	0.26	0.26	0.36	0.35
τ_{CR-1}	0.56 (81%)	0.82 (70%)	0.58 (88%)	0.69 (77%)	0.92 (65%)	0.76 (53%)
τ_{CR-2}	6.85 (19%)	5.98 (30%)	4.97 (12%)	6.63 (23%)	8.52 (35%)	7.86 (47%)
τ (ps)	540 nm	560 nm	580 nm	600 nm	620 nm	640 nm
τ_{CS}	0.33	0.34	0.38	0.34	0.34	0.37
τ_{CR-1}	0.51 (75%)	0.47 (80%)	0.46 (88%)	0.29 (94%)	/	/
τ_{CR-2}	5.44 (23%)	5.53 (19%)	6.36 (12%)	8.60 (1%)	5.79 (59%)	5.58 (67%)
τ_{CR-3}					312 (41%)	276 (33%)

Table S3. Formation time (τ_{CS}) and lifetimes (τ_{CR-1} and τ_{CR-2}) for the excited states in system [OS-ph-OS].

τ (ps)	420 nm	440 nm	460 nm	480 nm	500 nm	520 nm
τ_{CS}	0.27	0.22	0.29	0.35	0.39	0.41
τ_{CR-1}	0.70 (21%)	0.68 (25%)	0.51 (15%)	0.47 (8%)	0.45 (4%)	0.45 (2%)
τ_{CR-2}	8.32 (79%)	6.62 (75%)	6.25 (85%)	7.25 (92%)	7.10 (96%)	5.40 (98%)
τ (ps)	540 nm	560 nm	580 nm	600 nm	620 nm	640 nm
τ_{CS}	0.43	0.27±0.24	0.26±0.19	0.29	0.32	0.31
τ_{CR-1}	0.47 (49%)	0.30 (11%)	0.32 (20%)	0.32 (8%)	0.35 (7%)	0.34 (8%)
τ_{CR-2}	24.7 (51%)	14.0 (89%)	12.7 (80%)	10.7 (92%)	12.3 (93%)	9.53 (92%)

Table S4. Formation time (τ_{CS}) and lifetimes (τ_{CR-1} and τ_{CR-2}) for the excited states in system [S₂-ph-S₂].

τ (ps)	420 nm	440 nm	460 nm	480 nm	500 nm	520 nm
τ_{CS}	0.36	0.26	0.29	0.29	0.30	0.29
τ_{CR-1}	0.39 (14%)	0.47 (46%)	0.58 (38%)	0.62 (38%)	0.51 (30%)	0.57 (32%)
τ_{CR-2}	3.48 (17%)	4.16 (39%)	5.14 (19%)	5.55 (13%)	5.34 (7%)	5.49 (4%)
τ_{CR-3}	306 (69%)	381 (15%)	403 (43%)	344 (49%)	307 (63%)	157 (64%)
τ (ps)	540 nm	560 nm	580 nm	600 nm	620 nm	640 nm
τ_{CS}	0.33	0.34	0.38	0.34	0.34	0.37
τ_{CR-1}	0.51 (75%)	0.47 (80%)	0.46 (88%)	0.29 (94%)	/	/
τ_{CR-2}	5.44 (23%)	5.53 (19%)	6.36 (12%)	8.60 (1%)	5.79 (59%)	5.58 (67%)
τ_{CR-3}	48.4 (2%)	9.6 (1%)	/	440 (5%)	312 (41%)	276 (33%)

Table S5. Formation time (τ_{CS}) and lifetimes (τ_{CR-1} and τ_{CR-2}) for the excited states in system [O₂-ph-S₂].

τ (ps)	420 nm	440 nm	460 nm	480 nm	500 nm	520 nm
τ_{CS}	0.41	0.31	0.33	0.38	0.40	0.44
τ_{CR-1}	0.65 (87%)	0.65 (79%)	0.56 (86%)	0.51 (90%)	0.47 (92%)	0.48 (94%)
τ_{CR-2}	17.2 (7%)	14.7 (10%)	17.9 (6%)	25.5 (4%)	29.3 (4%)	76.8 (3%)
τ_{CR-3}	152 (6%)	170 (11%)	163 (8%)	167 (6%)	208 (4%)	178 (3%)
τ (ps)	540 nm	560 nm	580 nm	600 nm	620 nm	640 nm
τ_{CS}	0.49	0.60	0.58	0.47	0.48	0.63
τ_{CR-1}	0.53 (96%)	0.57 (99%)	0.58(97%)	0.48 (94%)	0.50 (91%)	0.69 (88%)
τ_{CR-2}	16.3 (2%)	19.9 (1%)	49.1 (2%)	7.71 (2%)	5.74 (3%)	2.21 (5%)
τ_{CR-3}	148 (2%)		486 (1%)	131 (4%)	105 (6%)	85 (7%)