

Supporting Information

The photochemistry of $fac\text{-}[\text{Re}(\text{CO})_3(\text{dcbH}_2)(\text{trans}\text{-stpy})]^+$: new insights on the isomerization mechanism of coordinated stilbene-like ligands

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Figure S1. Electronic spectra of $fac\text{-}[\text{Re}(\text{CO})_3(\text{dcbH}_2)(\text{cis-stpy})]^+$ in acetonitrile

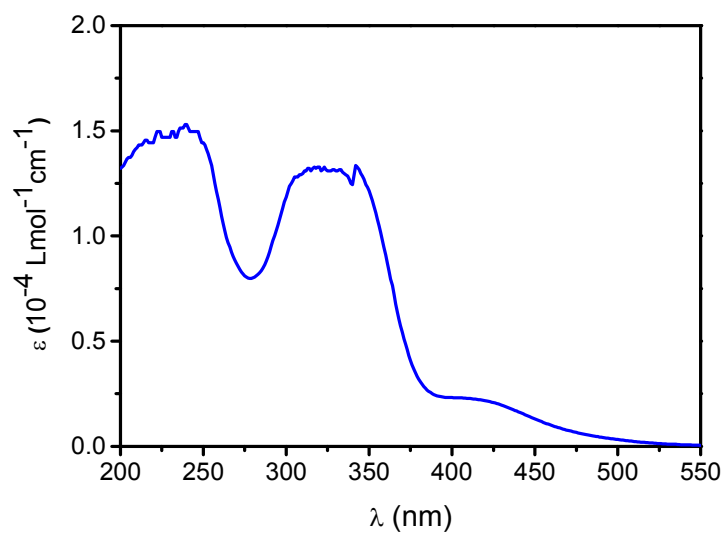


Figure S2. H-H COSY spectrum (400 MHz) of $fac\text{-}[\text{Re}(\text{CO})_3(\text{dcbH}_2)(\text{trans-stpy})]^+$ in CD_3CN .

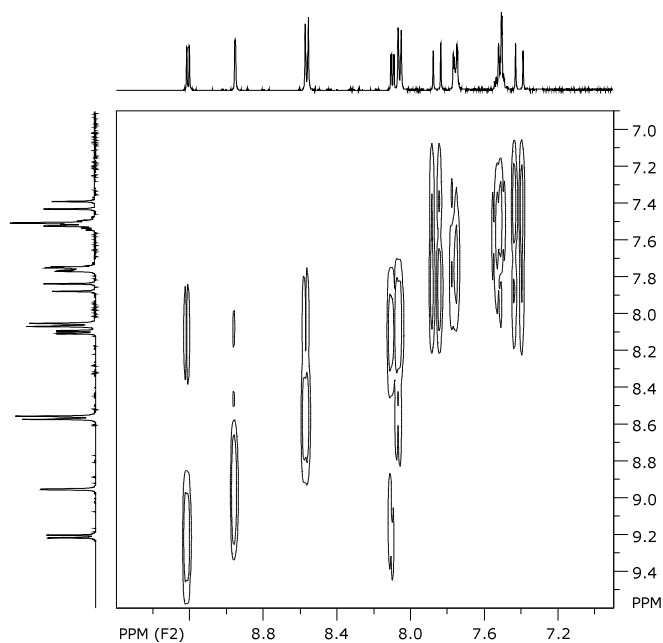


Figure S3. ^1H NMR (400 MHz) spectral changes of $\text{fac-}[\text{Re}(\text{CO})_3(\text{dcbH}_2)(\text{trans-stpy})]^+$ in CD_3CN under 405 nm irradiation

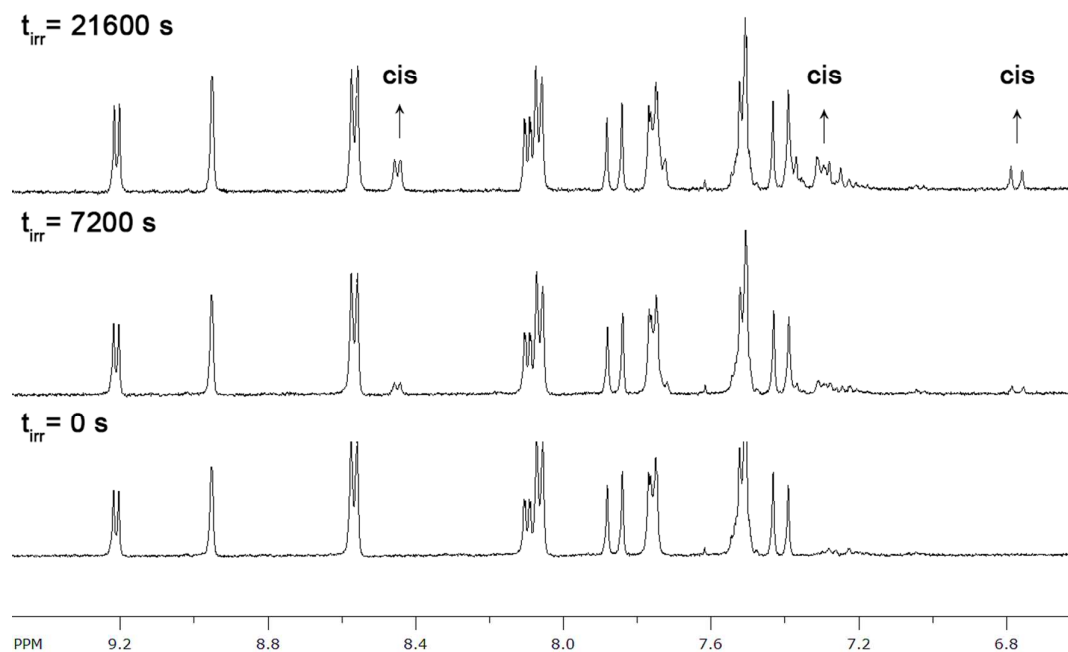


Figure S4. Emission spectra of $\text{fac-}[\text{Re}(\text{CO})_3(\text{dcbH}_2)(\text{trans-stpy})]^+$ in acetonitrile at 298 K (—) and in 4:1 ethanol/methanol at 77 K (—); $\lambda_{\text{exc}} = 405 \text{ nm}$.

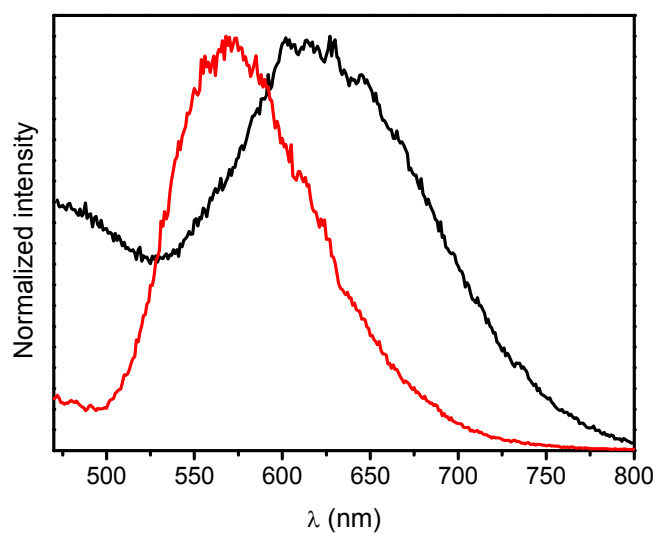


Figure S5. TD-DFT theoretical diagram for the first singlet and triplet excited states in $fac-[Re(CO)_3(dcbH_2)(trans-stpy)]^+$ and $fac-[Re(CO)_3(dcbH_2)(cis-stpy)]^+$

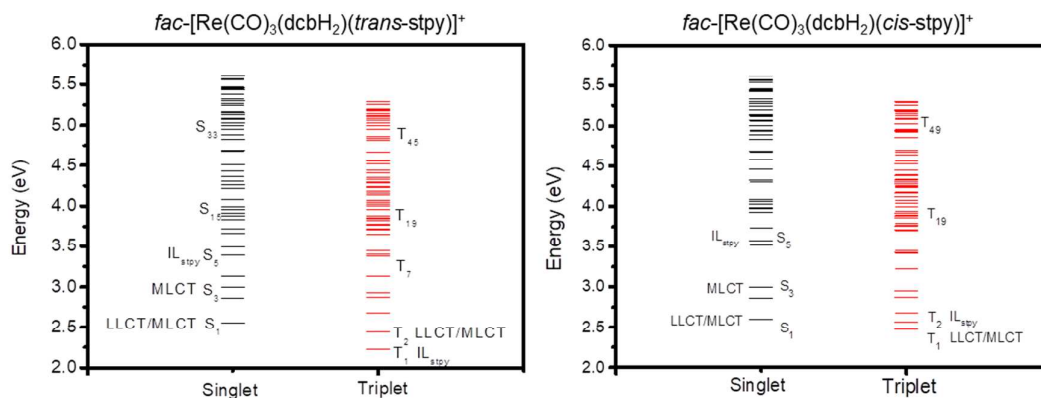


Figure S6. Natural Transition Orbitals (NTOs) obtained for the lowest lying triplet states in $fac-[Re(CO)_3(dcbH_2)(trans-stpy)]^+$ and $fac-[Re(CO)_3(dcbH_2)(cis-stpy)]^+$

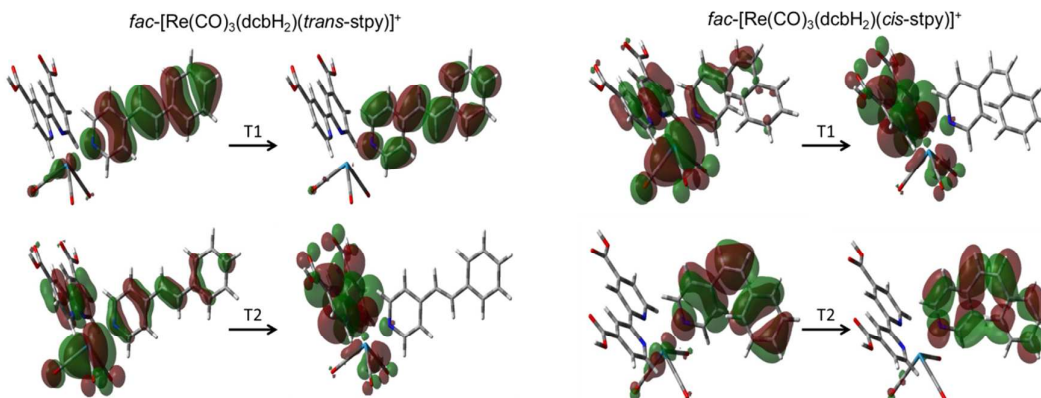


Figure S7. ATR-FTIR spectra of a TiO_2 film sensitized by *fac*- $[\text{Re}(\text{CO})_3(\text{dcbH}_2)(\text{trans-stpy})]^+$ (a) and of the complex in powder form (b)

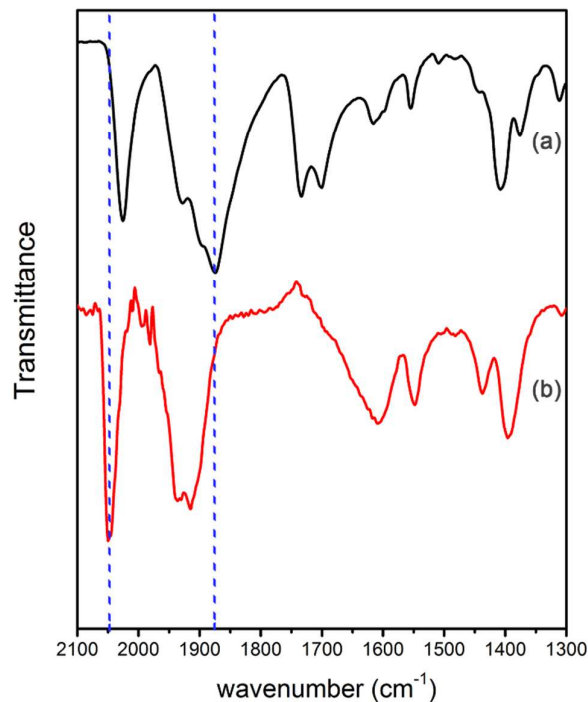


Table S1. Solvent corrected (acetonitrile) major transition energies to the excited states of *fac*- $[\text{Re}(\text{CO})_3(\text{dcbH}_2)(\text{trans-stpy})]^+$ with their contributing excitations (%), oscillator strengths (f) and associated wavelengths (λ)

Transition ^a	f	Energy (eV)	λ (nm)	Character
H – L	0.0148	2.38	520	$\text{LLCT}_{\pi\text{stpy} \rightarrow \pi^*\text{dcbH}_2}$
H-2 – L (40%) H-3 – L (60%)	0.0266	2.70	458	$\text{LLCT}_{\pi\text{stpy} \rightarrow \pi^*\text{dcbH}_2}$ $\text{MLCT}_{\text{d(Re)} \rightarrow \pi^*\text{dcbH}_2}$
H-2 – L (37%) H-1 – L (13%) H-3 – L (50%)	0.1406	2.83	437	$\text{LLCT}_{\pi\text{stpy} \rightarrow \pi^*\text{dcbH}_2}$ $\text{MLCT}_{\text{d(Re)} \rightarrow \pi^*\text{dcbH}_2}$
H-6 – L+1 (80%) H – L+1 (20%)	0.1297	3.21	385	$\text{LMCT}_{\text{O}(2p) \rightarrow \text{d(Ti)}}$ $\text{LMCT}_{\pi\text{stpy} \rightarrow \text{d(Ti)}}$
H – L+4	1.1161	3.41	363	$\text{IL}_{\pi\text{stpy} \rightarrow \pi^*\text{stpy}}$

^a H = HOMO, L = LUMO

Figure S8. Electronic spectra of $fac-[Re(CO)_3(dcbH_2)(trans-stpy)]^+$ (—) adsorbed on TiO_2 films along with the calculated electronic transitions (vertical lines) for the complex covalently linked to an anatase cluster (refer to the main text for details).

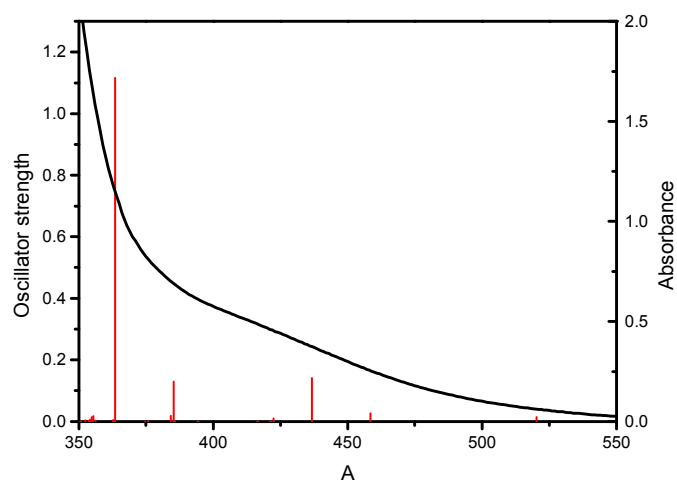


Figure S9. Natural Transition Orbitals (NTOs) obtained for $fac-[Re(CO)_3(dcbH_2)(trans-stpy)]^+$ adsorbed on an anatase cluster.

