Molecular Engineered Rhenium(I) Carbonyl Complexes to Promote Photoisomerization of Coordinated Stilbene-like Ligands in the Visible Region

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Electronic Supplementary Information (ESI)

1. Experimental Section

1.1. Molar absorptivity of *fac*-[Re(CO)$_3$(*cis*-stpyR)]$^+$ complexes

The $\varepsilon_{cis}(\lambda)$ were obtained using the ratio between the integrals of *trans* and *cis* ^{1}H NMR signals in irradiated solutions, Equation S1, as previously described.[4]

$$\varepsilon_{cis}(\lambda) = \varepsilon_{trans}(\lambda) \times \frac{\left(A_{irr}(\lambda) - A_{trans}(\lambda).\,\%_{trans}^{1\text{H NMR}}\right)}{A_{trans}(\lambda).\,\%_{cis}^{1\text{H NMR}}}, \qquad \text{(S1)}$$

in which $\varepsilon_{trans}(\lambda)$ = molar absorptivity for the *trans*-isomer (L mol^{-1} cm^{-1}); $\%_{trans}^{1\text{H NMR}}$ and $\%_{cis}^{1\text{H NMR}}$ = percentages of trans- and cis-isomers in the irradiated solution obtained by the distinct integrals in the ^{1}H NMR spectrum; $A_{trans}(\lambda)$ = absorbance of the *trans*-isomer solution before irradiation; $A_{irr}(\lambda)$ = absorbance of the irradiated solution.

1.2. Apparent *trans*-to-*cis* photoisomerization quantum yields

Apparent *trans*-to-*cis* photoisomerization quantum yields ($\Phi_{trans\to cis}^{app}$) were obtained following absorbance changes by Equation S2 (Table S2-S11 in the ESI); they are apparent, since both *trans*- and *cis*-isomers absorb in the same region.[1,2,4–9]

$$\Phi_{trans\to cis}^{app} = \frac{1}{I_0 \, . \, t_{irr}} \times \frac{(A_{trans} - A_{irr}). N_A. V_{irr}}{\varepsilon_{trans}. b}, \qquad (S2)$$

where t_{irr} = irradiation time (s); I_0 = light intensity (quanta s^{-1}); b = optical path length of the irradiated cuvete (cm); V_{irr} = volume of the irradiated solution; N_A = Avogadro number.

1.3. True *trans*-to-*cis* photoisomerization quantum yields

True quantum yields ($\Phi_{trans\to cis}^{true}$) were obtained by correcting $\Phi_{trans\to cis}^{app}$ to the molar absorptivities of the *cis*-isomer ($\varepsilon_{cis}(\lambda)$ / L mol^{-1} cm^{-1}) using Equation S3 (Table S2-S11 in the ESI) and just named as $\Phi_{trans\to cis}$ in this paper.[2,4,6,10]

$$\Phi_{trans\to cis}^{true} = \frac{1}{I_0 \, . \, t_{irr}} \times \frac{(A_{irr} - A_{trans}). N_A. V_{irr}}{(\varepsilon_{cis} - \varepsilon_{trans}). b} \qquad (S3)$$

1.4. Reverse *cis*-to-*trans* photoisomerization quantum yields

Quantum yields for the reverse *cis*-to-*trans* photoreaction ($\Phi_{cis\to trans}$) were obtained at 255 nm irradiation of the photostationary solution by using Equation S4 (Table S12-S13 in the ESI).[10–13]

$$\Phi_{cis\to trans} = \frac{1}{I_0 \, . \, t_{irr}} \times \frac{(A_{PS} - A_{irr}). N_A. V_{irr}}{(\varepsilon_{cis} - \varepsilon_{trans}). b}, \qquad (S4)$$

in which A_{PS} = initial absorption of the photostationary solution.

2. NMR, IR and electronic spectra

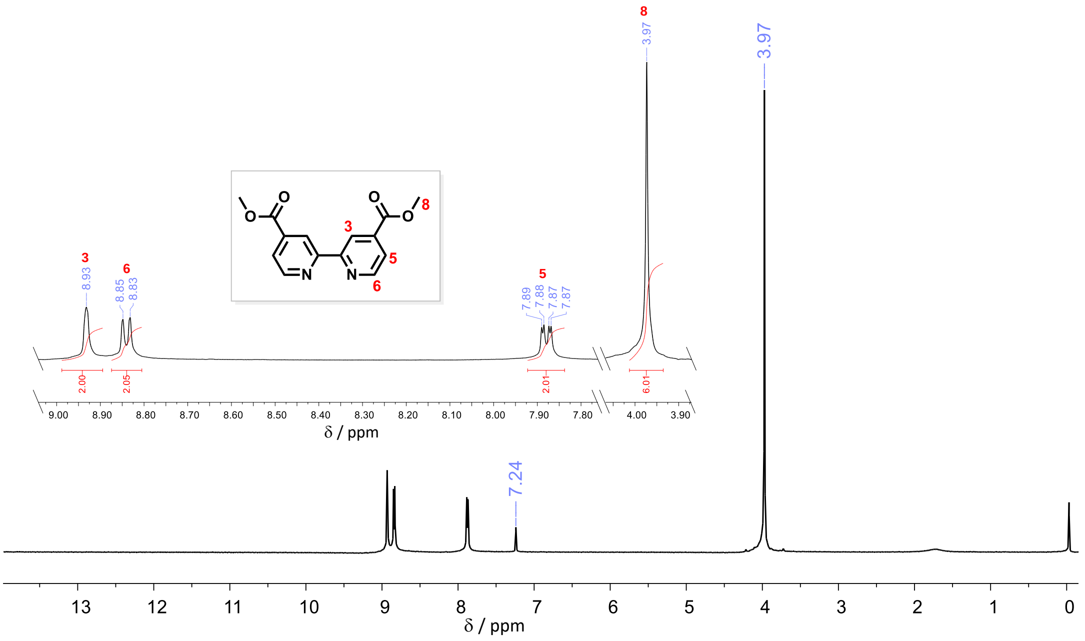


Figure S1. ^{1}H NMR spectrum (300 MHz) for dmcb in CD_3Cl (T = 298 K).

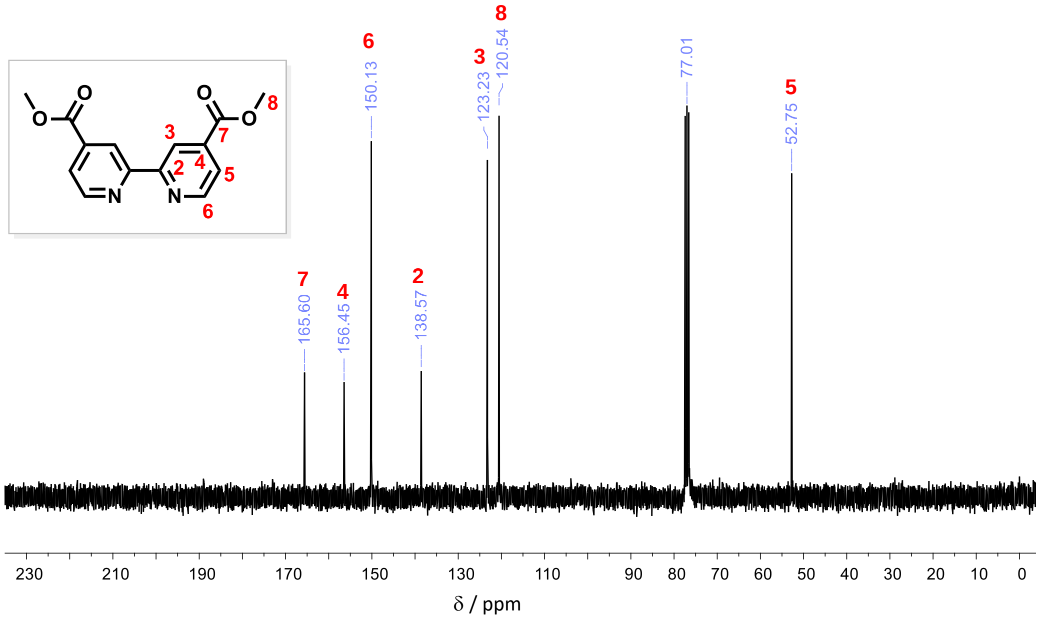


Figure S2. ^{13}C NMR spectrum (75 MHz) for dmcb in CD_3Cl (T = 298 K).

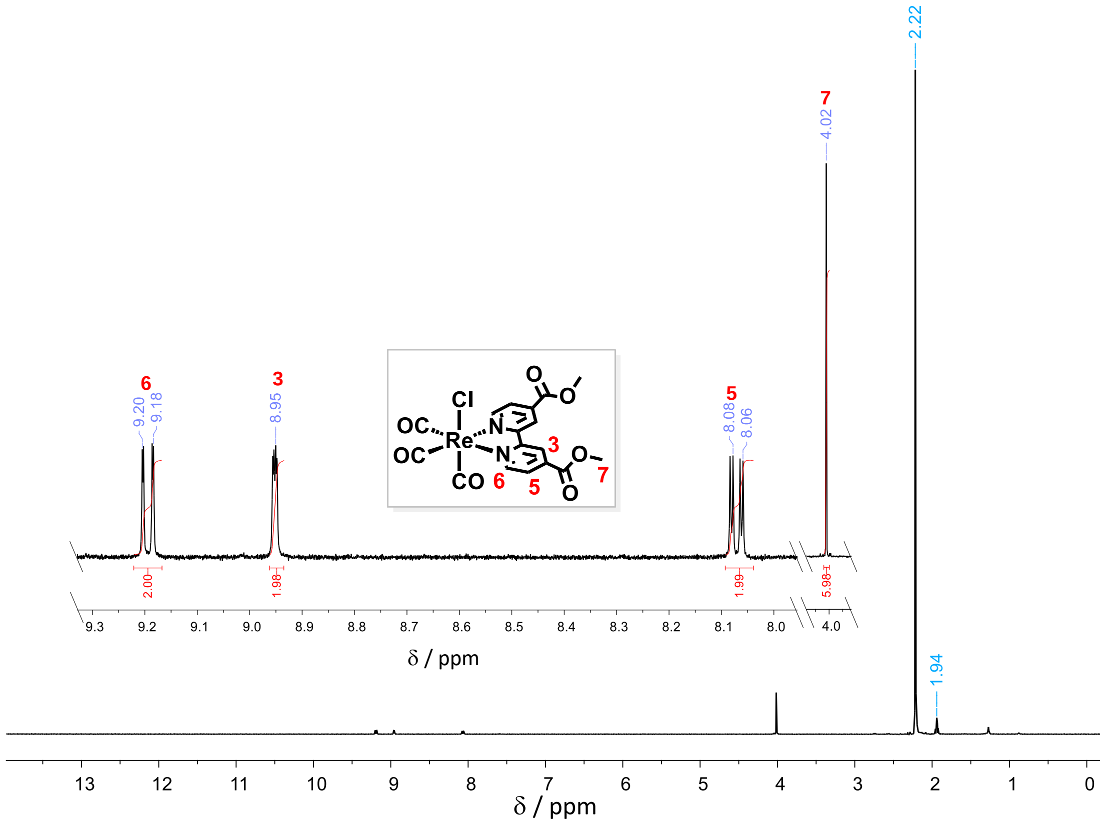


Figure S3. [1]H NMR spectrum (300 MHz) for *fac*-[Re(CO)$_3$(dmcb)Cl] in CD_3CN (T = 298 K).

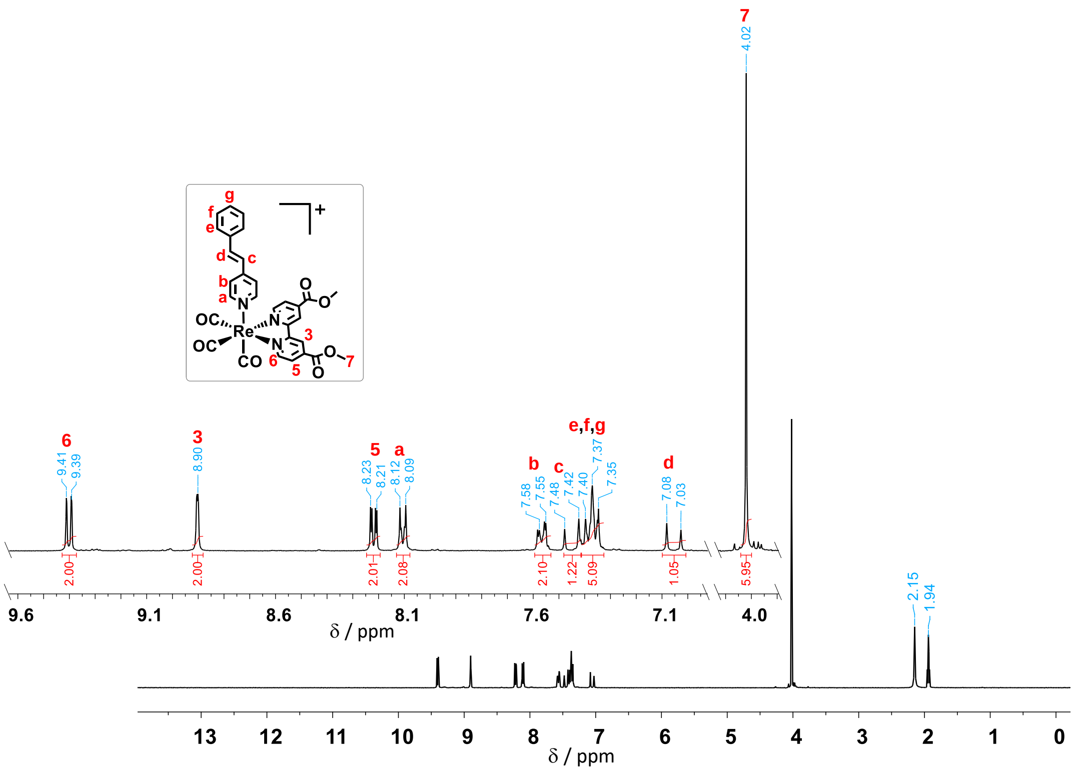


Figure S4. [1]H NMR spectrum (300 MHz) for *fac*-[Re(CO)$_3$(dmcb)(*trans*-stpy)]PF_6 in CD_3CN (T = 298 K).

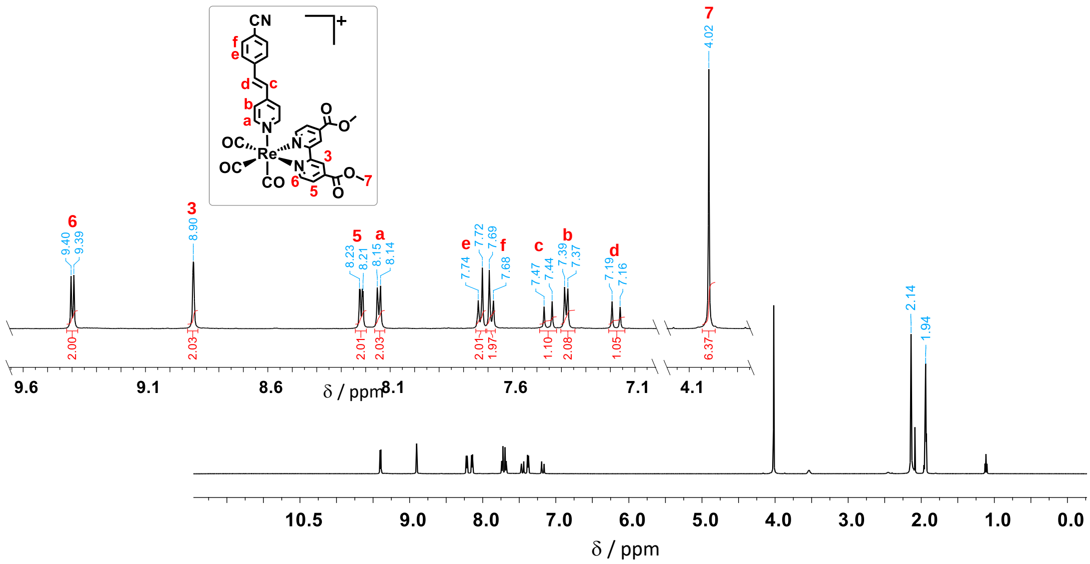


Figure S5. [1]H NMR spectrum (500 MHz) for *fac*-[Re(CO)$_3$(dmcb)(*trans*-stpyCN)]PF_6 in CD_3CN (T = 298 K).

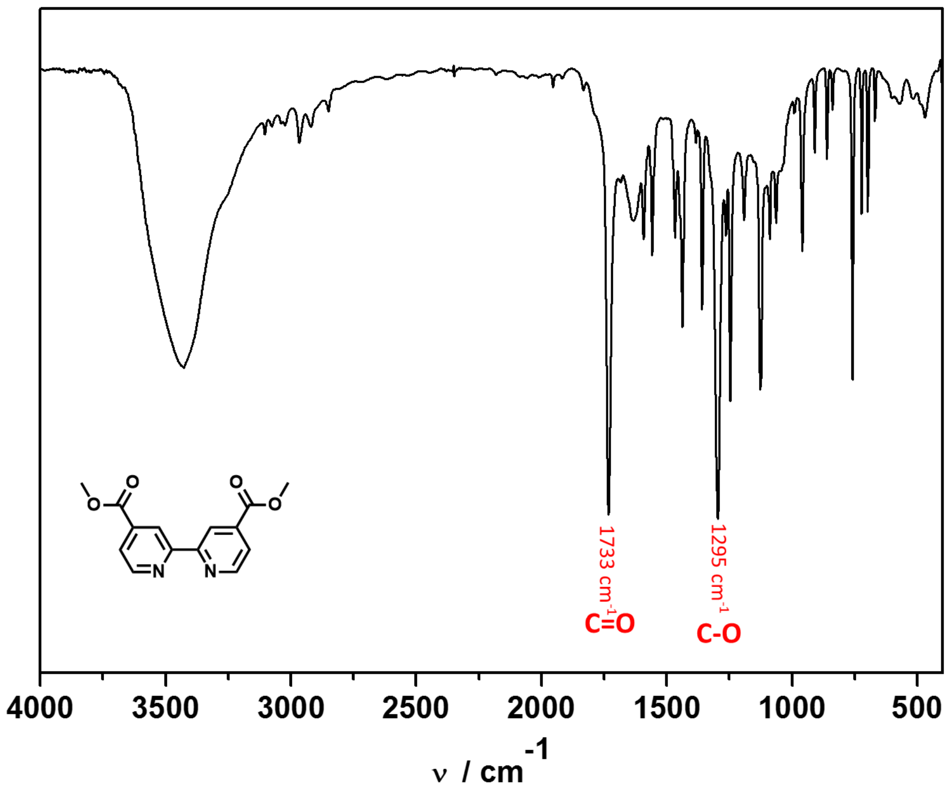


Figure S6. IR spectrum for dmcb in KBr.

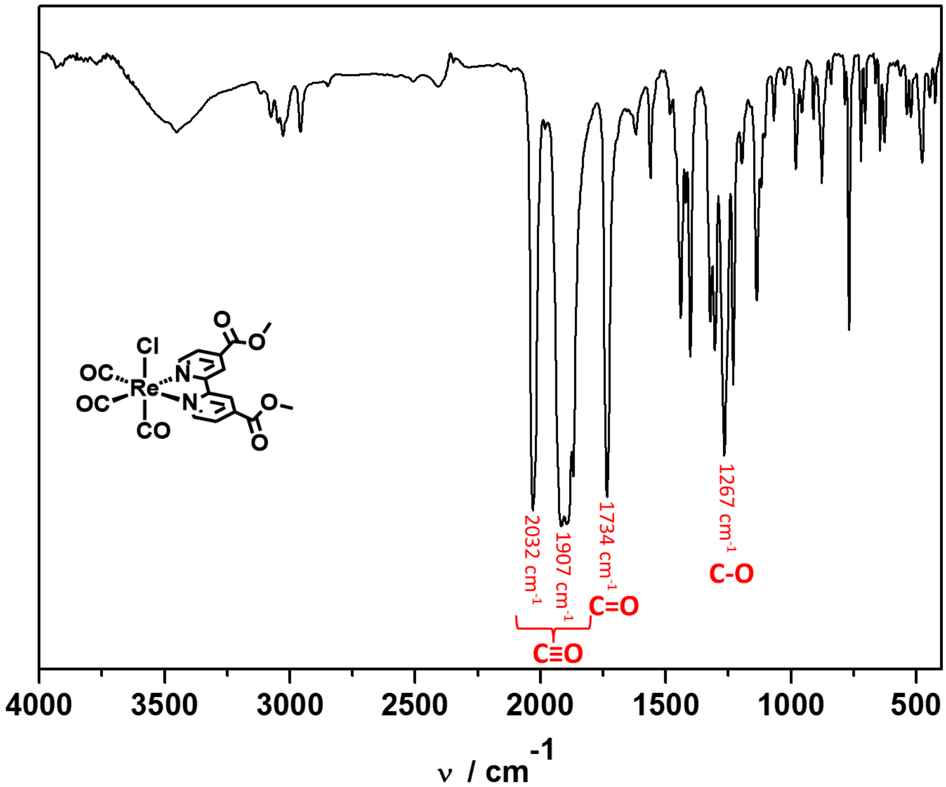


Figure S7. IR spectrum for *fac*-[Re(CO)$_3$(dmcb)Cl] in KBr.

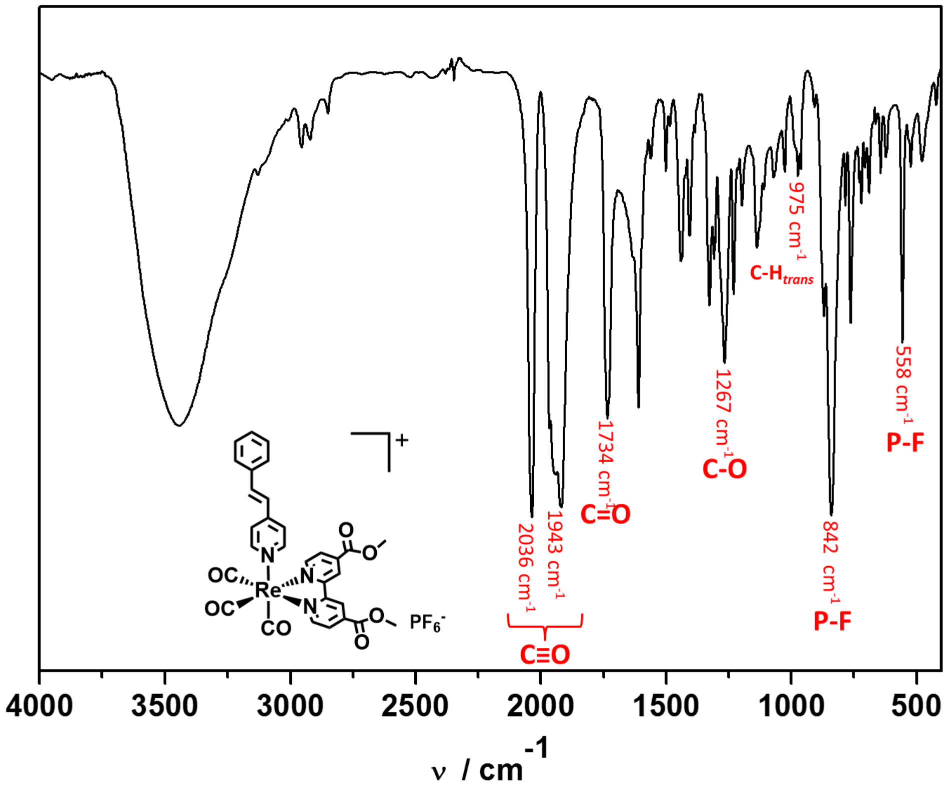


Figure S8. IR spectrum for *fac*-[Re(CO)$_3$(dmcb)(*trans*-stpy)] in KBr.

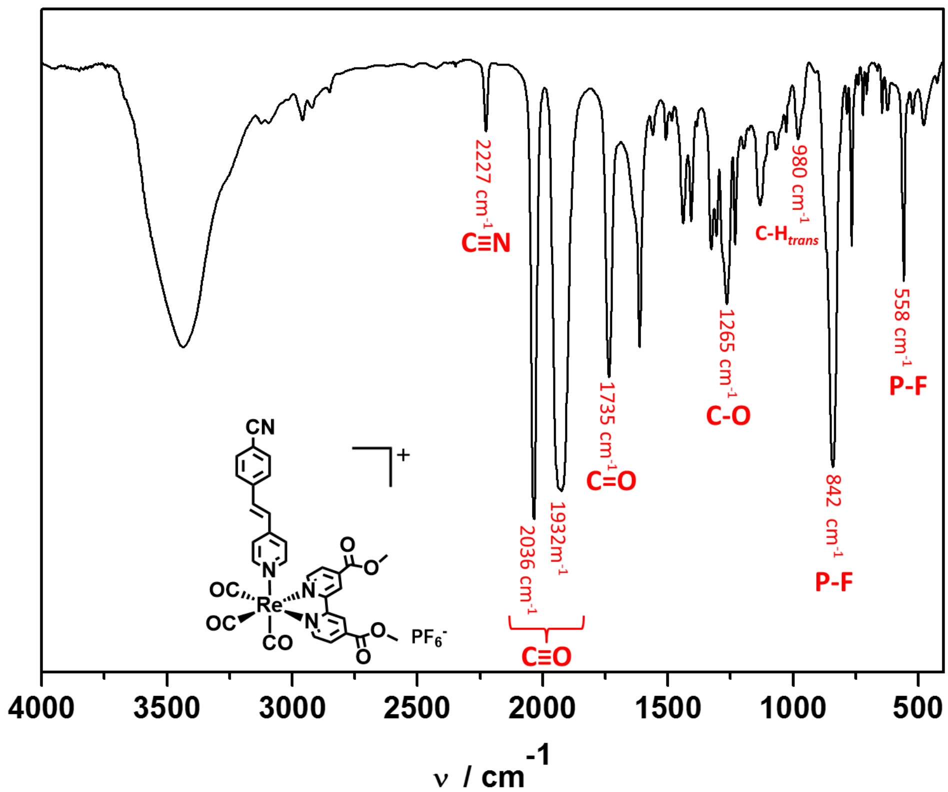


Figure S9. IR spectrum for *fac*-[Re(CO)$_3$(dmcb)(*trans*-stpyCN)] in KBr.

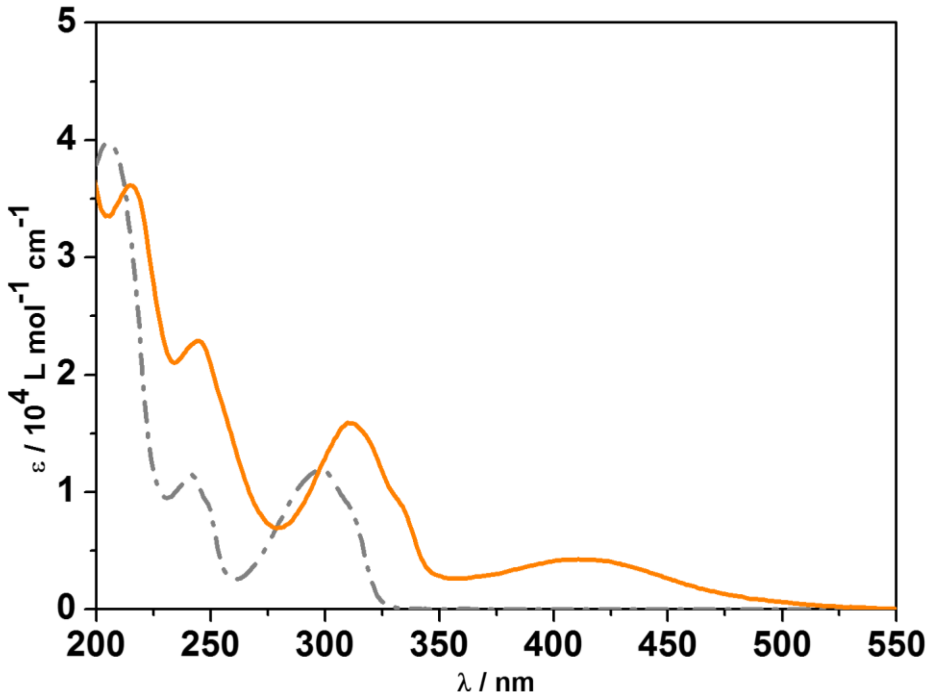
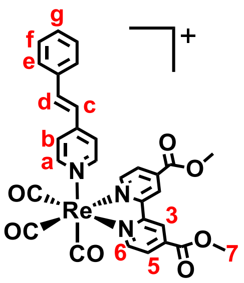
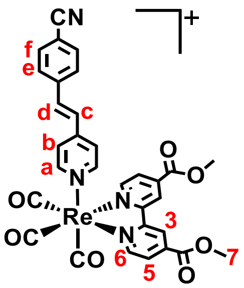
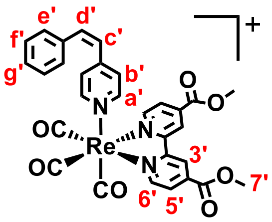
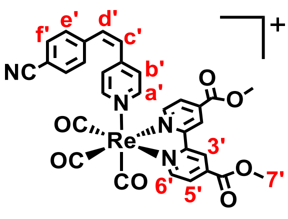


Figure S10. Electronic spectra for *fac*-[Re(CO)$_3$(dmcb)Cl] (orange ——) and dmcb (gray —··—··—) in CH_3CN at 298 K.

Table S1. ^{1}H NMR spectral data (300 MHz or 500 MHz) for *fac*-[Re(CO)$_3$(dmcb)(*trans*-stpy)]$^+$, *fac*-[Re(CO)$_3$(dmcb)(*trans*-stpyCN)]$^+$, *fac*-[Re(CO)$_3$(dmcb)(*cis*-stpy)]$^+$ and *fac*-[Re(CO)$_3$(dmcb)(*cis*-stpyCN)]$^+$ in CD_3CN at 298K.

Complex	Hydrogen	δ / ppm	J / Hz
fac-[Re(CO)$_3$(dmcb)(*trans*-stpy)]$^+$	3	8.90 (dd, 2H)	J^4 = 1.6 Hz, J^5 = 0.7 Hz
	5	8.22 (dd, 2H)	J^3 = 5.7 Hz, J^4 = 1.7 Hz
	6	9.40 (dd, 2H)	J^3 = 5.7 Hz, J^5 = 0.7 Hz
	7	4.02 (s, 6H)	
	a	8.10 (dd, 2H)	J^3 = 6.8 Hz, J^3 = 1.4 Hz
	b	7.56 (dd, 2H)	J^3 = 7.4 Hz, J^3 = 1.9 Hz
	c	**7.45 (d, 1H)**	**J^3 = 16.4 Hz**
	d	**7.05 (d, 1H)**	**J^3 = 16.4 Hz**
	e,f,g	7.37 (m, 5H)	
fac-[Re(CO)$_3$(dcmb)(*trans*-stpyCN)]$^+$	3	8.91 (s, 2H)	
	5	8.22 (dd, 2H)	J^3 = 5.7 Hz, J^4 = 1.5 Hz
	6	9.40 (d, 2H)	J^3 = 5.7 Hz
	7	4.02 (s, 6H)	
	a	8.15 (d, 2H)	J^3 = 6.7 Hz
	b	7.38 (d, 2H)	J^3 = 6.7 Hz
	c	**7.45 (d, 1H)**	**J^3 = 16.5 Hz**
	d	**7.18 (d, 1H)**	**J^3 = 16.5 Hz**
	e	7.73 (d, 2H)	J^3 = 8.5 Hz
	f	7.69 (d, 2H)	J^3 = 8.5 Hz
fac-[Re(CO)$_3$(dcmb)(*cis*-stpy)]$^+$	3’	8.90 (dd, 2H)	J^4 = 1.6 Hz, J^5 = 0.7 Hz
	5’	8.18 (dd, 2H)	J^3 = 5.7 Hz, J^4 = 1.7 Hz
	6’	9.34 (dd, 2H)	J^3 = 5.7 Hz, J^5 =0.7 Hz
	7’	4.03 (s, 6H)	
	a’	7.96 (dd, 2H)	J^3 = 5.2 Hz, J^3 = 1.5 Hz
	b’e’	7.05 (m, 2H)	
	c’	**6.93 (d, 1H)**	**J^3 = 12.2 Hz**
	d'	**6.93 (d, 1H)**	**J^3 = 12.2 Hz**
	f’,g’	7.22 (m, 3H)	
fac-[Re(CO)$_3$(dcmb)(*cis*-stpyCN)]$^+$	3’	8.90 (s, 2H)	
	5’	6.62 (dd, 2H)	J^3 = 5.5 Hz, J^4 = 1.2 Hz
	6’	9.34 (d, 2H)	J^3 = 5.7 Hz
	7’	4.02 (s, 6H)	
	a’	7.97 (d, 2H)	J^3 = 6.5 Hz
	b’	6.96 (d, 2H)	J^3 = 6.5 Hz
	c’	**6.93 (d, 1H)**	**J^3 = 12.4 Hz**
	d'	**6.57 (d, 1H)**	**J^3 = 12.2 Hz**
	e’	7.20 (d, 2H)	J^3 = 7.5 Hz
	f’	7.53 (d, 2H)	J^3 = 8.2 Hz

2. True and apparent quantum yields for *fac*-[Re(CO)$_3$(dmcb)(stpy)]$^+$ and *fac*-[Re(CO)$_3$(dmcb)(stpyCN)]$^+$ complexes.

Table S2. *trans*-to-*cis* photoisomerization quantum yields at 313 nm irradiation for *fac*-[Re(CO)$_3$(dmcb)(*trans*-stpy)]$^+$ in CH_3CN (I_0 = 6.00x10^{14} quanta s^{-1}, Δt = 30 s).

$\lambda_{monitoring}$ / nm	concentration/ 10^{-4} mol L^{-1}	% photolysis apparent	$\Phi^{aapparent}_{trans\rightarrow cis}$	% photolysis true	$\Phi^{true}_{trans\rightarrow cis}$	$\Phi^{apparent\ average}_{trans\rightarrow cis}$	$\Phi^{true\ average}_{trans\rightarrow cis}$
	9.1	3.0	0.27	5.9	0.54		
		5.7	0.26	11.5	0.52		
		8.6	0.26	17.2	0.53		
	9.1	3.2	0.29	6.4	0.58		
330		6.0	0.27	11.9	0.55	0.27 ± 0.02	0.54 ± 0.03
		8.5	0.26	17.1	0.52		
	9.1	3.3	0.30	6.6	0.60		
		5.6	0.26	11.2	0.51		
		8.1	0.25	6.2	0.49		
	9.1	3.2	0.30	6.2	0.57		
		6.1	0.28	11.7	0.54		
		9.0	0.28	17.3	0.53		
	9.1	3.4	0.31	6.5	0.60		
335		6.3	0.29	12.1	0.55	0.29 ± 0.02	0.55 ± 0.04
		8.9	0.27	17.0	0.52		
	9.1	3.6	0.33	7.0	0.63		
		5.9	0.27	11.3	0.51		
		8.6	0.26	16.4	0.50		
	9.1	3.1	0.29	5.5	0.50		
		6.4	0.30	11.2	0.51		
		9.6	0.29	16.7	0.51		
	9.1	3.6	0.33	6.3	0.58		
340		6.8	0.31	11.8	0.54	0.30 ± 0.02	0.52 ± 0.04
		9.6	0.29	16.8	0.51		
	9.1	3.6	0.33	6.3	0.58		
		6.0	0.28	10.5	0.48		
		8.9	0.27	15.6	0.47		
					Average	**0.29 ± 0.02**	**0.54 ± 0.04**

Table S3. *trans*-to-*cis* photoisomerization quantum yields at 334 nm irradiation for *fac*-$[Re(CO)_3(dmcb)(\textit{trans}\text{-stpy})]^+$ in CH_3CN ($I_0 = 1.43 \times 10^{15}$ quanta s^{-1}, $\Delta t = 10$ s).

$\lambda_{monitoring}$ / nm	concentration/ 10^{-4} mol L^{-1}	% photolysis apparent	$\Phi_{trans\to cis}^{aapparent}$	% photolysis true	$\Phi_{trans\to cis}^{true}$	$\Phi_{trans\to cis}^{apparent\ average}$	$\Phi_{trans\to cis}^{true\ average}$
	7.9	2.4	0.24	5.2	0.52		
		5.1	0.26	10.9	0.54		
		7.6	0.25	16.1	0.53		
	7.9	2.9	0.28	6.1	0.60		
330		5.4	0.27	11.6	0.57	0.27 ± 0.02	0.57 ± 0.03
		8.0	0.26	17.0	0.56		
	7.9	2.9	0.29	6.2	0.62		
		5.6	0.28	12.0	0.60		
		8.2	0.27	17.5	0.58		
	7.9	2.6	0.25	4.9	0.49		
		5.8	0.29	11.0	0.55		
		8.2	0.27	15.6	0.52		
	7.9	2.9	0.28	5.5	0.54		
335		5.8	0.29	11.0	0.55	0.28 ± 0.01	0.53 ± 0.02
		8.4	0.28	16.0	0.52		
	7.9	2.9	0.29	5.6	0.55		
		5.6	0.28	10.7	0.53		
		8.5	0.28	16.1	0.53		
	7.9	2.9	0.29	5.2	0.51		
		6.5	0.32	11.6	0.58		
		9.3	0.31	16.6	0.55		
	7.9	3.1	0.31	5.5	0.55		
340		6.4	0.32	11.3	0.56	0.31 ± 0.01	0.55 ± 0.02
		9.1	0.30	16.1	0.53		
	7.9	3.2	0.32	5.7	0.57		
		6.3	0.31	11.2	0.56		
		9.2	0.31	16.4	0.54		
					Average	**0.29 ± 0.02**	**0.55 ± 0.03**

Table S4. *trans*-to-*cis* photoisomerization quantum yields at 365 nm irradiation for *fac*-$[Re(CO)_3(dmcb)(trans\text{-}stpy)]^+$ in CH_3CN (I_0 = 6.93x10^{15} quanta s^{-1}, Δt = 8 s).

$\lambda_{monitoring}$ / nm	concentration/ 10^{-4} mol L^{-1}	% photolysis apparent	$\Phi^{aapparent}_{trans\rightarrow cis}$	% photolysis true	$\Phi^{true}_{trans\rightarrow cis}$	$\Phi^{apparent\ average}_{trans\rightarrow cis}$	$\Phi^{true\ average}_{trans\rightarrow cis}$
	2.9	2.9	0.28	5.9	0.55		
		5.8	0.27	11.6	0.54		
		8.5	0.26	16.9	0.53		
	2.9	2.8	0.26	5.5	0.52		
330		5.8	0.27	11.7	0.55	0.26 ± 0.01	0.53 ± 0.01
		8.3	0.26	16.5	0.52		
	2.9	2.7	0.25	5.4	0.51		
		5.6	0.26	11.1	0.52		
		8.3	0.26	16.6	0.52		
	2.9	3.2	0.30	6.2	0.58		
		6.0	0.28	11.4	0.53		
		8.8	0.27	16.8	0.52		
	2.9	3.0	0.28	5.8	0.54		
335		5.6	0.26	10.8	0.50	0.28 ± 0.01	0.53 ± 0.02
		8.6	0.27	16.5	0.51		
	2.9	3.1	0.29	5.9	0.55		
		5.9	0.28	11.3	0.53		
		8.8	0.27	16.8	0.53		
	2.9	3.5	0.32	6.0	0.57		
		6.7	0.31	11.7	0.55		
		9.7	0.30	17.0	0.53		
	2.9	3.2	0.30	5.6	0.53		
340		6.3	0.30	11.0	0.52	0.30 ± 0.01	0.53 ± 0.02
		9.3	0.29	16.2	0.51		
	2.9	3.2	0.30	5.5	0.52		
		6.4	0.30	11.1	0.52		
		9.2	0.29	16.1	0.50		
					Average	**0.28 ± 0.02**	**0.53 ± 0.02**

Table S5. *trans*-to-*cis* photoisomerization quantum yields at 404 nm irradiation for *fac*-$[Re(CO)_3(dmcb)(\textit{trans}\text{-stpy})]^+$ in CH_3CN (I_0 = 2.2x10^{15} quanta s^{-1}, Δt = 40 s).

$\lambda_{monitoring}$ / nm	concentration/ 10^{-4} mol L^{-1}	% photolysis apparent	$\Phi^{aapparent}_{trans\rightarrow cis}$	% photolysis true	$\Phi^{true}_{trans\rightarrow cis}$	$\Phi^{apparent\ average}_{trans\rightarrow cis}$	$\Phi^{true\ average}_{trans\rightarrow cis}$
	3.4	3.4	0.25	6.9	0.50		
		6.4	0.23	12.8	0.46		
		9.0	0.22	17.9	0.43		
	3.4	3.1	0.22	6.1	0.44		
330		6.0	0.22	12.0	0.43	0.21 ± 0.02	0.43 ± 0.04
		8.2	0.20	16.4	0.40		
	3.4	2.7	0.20	5.4	0.39		
		5.4	0.20	10.8	0.39		
		8.2	0.20	16.3	0.39		
	3.4	3.0	0.22	5.8	0.42		
		6.5	0.23	12.4	0.45		
		9.1	0.22	17.3	0.42		
	3.4	3.1	0.22	5.9	0.42		
335		6.0	0.22	11.5	0.42	0.22 ± 0.01	0.42 ± 0.01
		8.6	0.21	16.5	0.40		
	3.4	3.0	0.22	5.8	0.42		
		5.8	0.21	11.1	0.40		
		8.9	0.21	17.0	0.41		
	3.4	3.7	0.27	6.4	0.46		
		6.8	0.25	11.9	0.43		
		9.8	0.24	17.1	0.41		
	3.4	3.4	0.25	5.9	0.43		
340		6.8	0.25	11.9	0.43	0.24 ± 0.01	0.43.± 0.02
		9.7	0.23	16.9	0.41		
	3.4	3.5	0.26	6.2	0.45		
		6.5	0.24	11.4	0.41		
		9.5	0.23	16.5	0.40		
					Average	**0.23 ± 0.02**	**0.43 ± 0.03**

Table S6. *trans*-to-*cis* photoisomerization quantum yields at 436 nm irradiation for *fac*-$[Re(CO)_3(dmcb)(trans\text{-}stpy)]^+$ in CH_3CN (I_0 = 3.6x10^{15} quanta s^{-1}, Δt = 40 s).

$\lambda_{monitoring}$ / nm	concentration/ 10^{-4} mol L^{-1}	% photolysis apparent	$\Phi^{aapparent}_{trans\to cis}$	% photolysis true	$\Phi^{true}_{trans\to cis}$	$\Phi^{apparent\ average}_{trans\to cis}$	$\Phi^{true\ average}_{trans\to cis}$
	3.4	4.4	0.23	9.3	0.51		
		7.6	0.20	16.2	0.44		
		10.6	0.18	22.6	0.41		
	3.4	3.6	0.21	7.6	0.48		
330		6.7	0.20	14.2	0.44	0.21 ± 0.02	0.47 ± 0.05
		9.6	0.19	20.5	0.43		
	3.5	3.7	0.26	7.9	0.59		
		5.7	0.20	12.1	0.45		
		8.8	0.21	18.6	0.47		
	3.4	4.0	0.21	7.7	0.42		
		7.6	0.20	14.5	0.40		
		11.1	0.19	21.1	0.39		
	3.4	3.6	0.21	6.8	0.42		
335		6.8	0.20	13.0	0.41	0.21 ± 0.02	0.42 ± 0.05
		10.1	0.20	19.2	0.40		
	3.5	3.8	0.27	7.3	0.54		
		6.0	0.21	11.5	0.43		
		9.0	0.21	17.1	0.43		
	3.4	4.3	0.23	7.7	0.42		
		8.5	0.22	15.1	0.41		
		11.8	0.21	21.1	0.39		
	3.4	4.2	0.25	7.4	0.46		
340		7.9	0.23	14.1	0.44	0.23 ± 0.02	0.43 ± 0.03
		11.2	0.22	19.9	0.41		
	3.5	3.7	0.26	6.7	0.49		
		6.7	0.24	12.0	0.45		
		9.3	0.22	16.6	0.41		
					Average	**0.22 ± 0.02**	**0.44 ± 0.05**

Table S7. *trans*-to-*cis* photosiomerization quantum yields at 313 nm irradiation for *fac*-[Re(CO)$_3$(dmcb)(*trans*-stpyCN)]$^+$ in CH_3CN (I_0 = 1.50x10^{15} quanta s^{-1}, $^a\Delta t$ = 10 s, $^b\Delta t$ = 20 s).

$\lambda_{monitoring}$ / nm	concentration/ 10^{-4} mol L^{-1}	% photolysis apparent	$\Phi^{aapparent}_{trans\rightarrow cis}$	% photolysis true	$\Phi^{true}_{trans\rightarrow cis}$	$\Phi^{apparent\ average}_{trans\rightarrow cis}$	$\Phi^{true\ average}_{trans\rightarrow cis}$
	9.0^a	2.9	0.32	6.5	0.70		
		7.8	0.28	17.3	0.63		
		9.4	0.26	20.9	0.57		
	9.2^b	2.7	0.32	6.4	0.71		
330		7.9	0.29	17.6	0.65	0.30 ± 0.02	0.66 ± 0.05
		10.4	0.29	23.0	0.64		
	9.2^a	3.0	0.33	6.6	0.73		
		6.8	0.30	15.2	0.67		
		9.1	0.29	20.2	0.64		
	9.0^a	3.0	0.33	6.1	0.66		
		8.0	0.29	16.1	0.58		
		10.6	0.29	21.2	0.58		
	9.2^b	3.1	0.34	6.1	0.68		
335		8.3	0.31	16.6	0.61	0.31 ± 0.02	0.63 ± 0.04
		10.8	0.30	21.7	0.60		
	9.2^a	3.2	0.35	6.3	0.70		
		7.2	0.32	14.4	0.64		
		9.5	0.30	19.1	0.60		
	9.0^a	3.2	0.35	6.1	0.66		
		8.7	0.32	16.4	0.60		
		11.4	0.31	21.6	0.59		
	9.2^b	3.6	0.40	6.7	0.49		
340		8.9	0.33	16.9	0.47	0.34 ± 0.03	0.65 ± 0.05
		11.7	0.33	22.2	0.48		
	9.2^a	3.4	0.38	6.4	0.52		
		7.6	0.34	14.5	0.40		
		10.2	0.33	19.4	0.48		
					Average	**0.32 ± 0.03**	**0.65 ± 0.05**

Table S8. *trans*-to-*cis* photosiomerization quantum yields at 334 nm irradiation for *fac*-$[Re(CO)_3(dmcb)($*trans*-stpyCN$)]^+$ in CH_3CN (I_0 = 2.61x10^{15} quanta s^{-1}, Δt = 8 s).

$\lambda_{monitoring}$ / nm	concentration/ 10^{-4} mol L^{-1}	% photolysis apparent	$\Phi^{aapparen}_{trans\to cis}$	% photolysis true	$\Phi^{true}_{trans\to cis}$	$\Phi^{apparent\ average}_{trans\to cis}$	$\Phi^{true\ average}_{trans\to cis}$
	9.5	3.8	0.31	8.4	0.69		
		7.1	0.30	15.9	0.66		
		10.5	0.29	23.4	0.64		
	9.6	3.7	0.31	8.3	0.69		
330		7.2	0.30	16.0	0.66	0.29 ± 0.03	0.64 ± 0.06
		10.5	0.29	23.3	0.65		
	9.5	2.8	0.23	6.2	0.51		
		6.4	0.26	14.2	0.58		
		10.5	0.29	23.4	0.64		
	9.5	4.0	0.33	8.0	0.66		
		7.6	0.31	15.2	0.63		
		11.1	0.31	22.3	0.61		
	9.6	4.0	0.33	7.9	0.66		
335		7.5	0.31	15.1	0.63	0.32 ± 0.01	0.64 ± 0.02
		11.1	0.31	22.2	0.61		
	9.5	3.9	0.32	7.8	0.64		
		7.7	0.32	15.3	0.63		
		11.8	0.33	23.7	0.65		
	9.5	4.3	0.36	8.2	0.68		
		8.3	0.34	16.0	0.65		
		12.1	0.33	23.0	0.63		
	9.6	4.2	0.35	8.0	0.67		
340		8.1	0.34	15.4	0.64	0.34 ± 0.01	0.65 ± 0.02
		12.0	0.33	22.7	0.63		
	9.5	4.2	0.35	8.0	0.66		
		8.1	0.34	15.4	0.64		
		12.7	0.35	24.0	0.66		
					Average	**0.32 ± 0.03**	**0.64 ± 0.04**

Table S9. *trans*-to-*cis* photosiomerization quantum yields at 365 nm irradiation for *fac*-$[Re(CO)_3(dmcb)(trans\text{-stpyCN})]^+$ in CH_3CN (I_0 = 2.61x10^{15} quanta s^{-1}, $^a\Delta t$ = 20 s, $^b\Delta t$ = 40 s).

$\lambda_{monitoring}$ / nm	concentration/ 10^{-4} mol L^{-1}	% photolysis apparent	$\Phi^{aapparent}_{trans\rightarrow cis}$	% photolysis true	$\Phi^{true}_{trans\rightarrow cis}$	$\Phi^{apparent\ average}_{trans\rightarrow cis}$	$\Phi^{true\ average}_{trans\rightarrow cis}$
	3.2[a]	2.7	0.30	6.1	0.68		
		5.0	0.28	11.0	0.62		
		8.8	0.25	19.6	0.55		
	3.4[a]	2.5	0.30	5.7	0.67		
330		5.0	0.29	11.1	0.65	0.28 ± 0.03	0.62 ± 0.06
		8.7	0.26	19.5	0.57		
	3.4[b]	2.6	0.30	5.7	0.68		
		4.8	0.28	10.7	0.63		
		7.9	0.24	17.7	0.52		
	3.2[a]	3.0	0.34	6.1	0.68		
		5.5	0.31	11.0	0.61		
		10.0	0.28	20.1	0.56		
	3.4[a]	2.9	0.34	5.8	0.68		
335		5.1	0.30	10.3	0.61	0.31 ± 0.03	0.62 ± 0.06
		9.2	0.27	18.5	0.55		
	3.4[b]	2.9	0.34	5.8	0.68		
		5.5	0.32	10.9	0.65		
		9.4	0.28	18.8	0.55		
	3.2[a]	3.2	0.36	6.1	0.69		
		6.1	0.34	11.5	0.64		
		10.6	0.29	20.0	0.56		
	3.4[a]	3.1	0.37	5.9	0.70		
340		5.8	0.34	10.9	0.65	0.33 ± 0.03	0.63 ± 0.05
		10.1	0.30	19.1	0.57		
	3.4[b]	3.0	0.36	5.7	0.67		
		5.6	0.33	10.6	0.63		
		10.3	0.30	19.4	0.58		
					Average	**0.31 ± 0.03**	**0.62 ± 0.05**

Table S10. *trans*-to-*cis* photoisomerization quantum yields at 404 nm irradiation for *fac*-$[Re(CO)_3(dmcb)(\textit{trans}\text{-stpyCN})]^+$ in CH_3CN ($I_0 = 5.3x10^{15}$ quanta s^{-1}, $\Delta t = 20$ s).

$\lambda_{monitoring}$ / nm	concentration/ 10^{-4} mol L^{-1}	% photolysis apparent	$\Phi^{aapparent}_{trans\rightarrow cis}$	% photolysis true	$\Phi^{true}_{trans\rightarrow cis}$	$\Phi^{apparent\ average}_{trans\rightarrow cis}$	$\Phi^{true\ average}_{trans\rightarrow cis}$
	8.1	3.9	0.29	8.7	0.66		
		7.5	0.28	16.7	0.63		
		10.3	0.26	23.0	0.58		
	8.2	3.4	0.26	7.5	0.57		
330		6.7	0.25	14.8	0.56	0.26 ± 0.02	0.58 ± 0.04
		9.8	0.25	21.9	0.56		
	8.2	3.4	0.26	7.5	0.57		
		6.6	0.25	14.7	0.56		
		9.3	0.24	20.7	0.53		
	8.1	3.9	0.29	7.7	0.58		
		7.6	0.28	15.1	0.57		
		10.4	0.26	20.9	0.53		
	8.2	3.8	0.29	7.6	0.58		
335		7.5	0.29	15.1	0.57	0.27 ± 0.02	0.53 ± 0.05
		10.0	0.25	20.0	0.51		
	8.2	3.3	0.25	6.7	0.51		
		6.3	0.24	12.7	0.48		
		9.1	0.23	18.3	0.46		
	8.1	4.2	0.32	8.0	0.60		
		7.6	0.29	14.56	0.55		
		10.9	0.27	20.6	0.52		
	8.2	4.0	0.30	7.5	0.57		
340		7.7	0.29	14.5	0.55	0.28 ± 0.03	0.52 ± 0.05
		10.5	0.27	19.9	0.50		
	8.2	3.5	0.26	6.6	0.50		
		6.2	0.23	11.7	0.45		
		9.6	0.24	18.2	0.46		
					Average	**0.27 ± 0.02**	**0.55 ± 0.05**

Table S11. *trans*-to-*cis* photoisomerization quantum yields at 436 nm irradiation for *fac*-$[Re(CO)_3(dmcb)(trans\text{-}stpyCN)]^+$ in CH_3CN (I_0 = 2.71x10^{16} quanta s^{-1}, $^a\Delta t$ = 4 s, $^b\Delta t$ = 3 s).

$\lambda_{monitoring}$ / nm	concentration/ 10^{-4} mol L^{-1}	% photolysis apparent	$\Phi^{aapparent}_{trans\to cis}$	% photolysis true	$\Phi^{true}_{trans\to cis}$	$\Phi^{apparent\ average}_{trans\to cis}$	$\Phi^{true\ average}_{trans\to cis}$
	3.5[a]	3.9	0.27	8.7	0.61		
		7.5	0.26	16.7	0.58		
		9.9	0.25	22.0	0.56		
	3.5[a]	3.6	0.25	8.1	0.56		
330		7.0	0.24	15.5	0.54	0.26 ± 0.02	0.58 ± 0.05
		9.4	0.24	21.0	0.53		
	3.5[b]	4.5	0.31	9.9	0.70		
		7.7	0.27	17.1	0.60		
		10.0	0.26	22.2	0.57		
	3.5[a]	4.4	0.30	8.8	0.61		
		8.1	0.28	16.3	0.57		
		10.6	0.27	21.3	0.54		
	3.5[a]	3.9	0.27	7.9	0.55		
335		7.4	0.26	14.8	0.51	0.28 ± 0.02	0.56 ± 0.04
		10.5	0.27	21.1	0.53		
	3.5[b]	4.4	0.31	8.9	0.62		
		8.0	0.28	15.9	0.56		
		10.3	0.26	20.7	0.53		
	3.5[a]	4.2	0.29	8.0	0.56		
		8.5	0.30	16.2	0.57		
		11.1	0.28	21.0	0.53		
	3.5[a]	4.2	0.29	7.9	0.55		
340		7.8	0.27	14.9	0.52	0.29 ± 0.01	0.54 ± 0.02
		10.4	0.27	19.7	0.50		
	3.5[b]	4.3	0.30	8.2	0.58		
		8.1	0.28	15.4	0.54		
		10.8	0.28	20.4	0.52		
					Average	**0.28 ± 0.01**	**0.56 ± 0.04**

Table S12. *cis*-to-*trans* photoisomerization quantum yields at 255 nm irradiation for *fac*-$[Re(CO)_3(dmcb)(cis\text{-stpy})]^+$ in CH_3CN (I_0 = 1.86x10^{15} quanta s^{-1}, Δt = 20 s).

$\lambda_{monitoring}$ / nm	concentration/ 10^{-4} mol L^{-1}	% photolysis true	$\Phi^{true}_{trans\rightarrow cis}$	$\Phi^{true\ average}_{trans\rightarrow cis}$
	2.2	4.9	0.18	
		11.5	0.21	
		16.8	0.21	
	2.2	4.3	0.14	
330		9.7	0.16	0.18 ± 0.03
		14.7	0.16	
	2.2	6.3	0.19	
		12.4	0.19	
		18.1	0.18	
	2.2	4.8	0.18	
		9.9	0.19	
		15.0	0.19	
	2.2	4.4	0.15	
335		9.1	0.15	0.17 ± 0.02
		14.2	0.16	
	2.2	4.9	0.15	
		12.1	0.19	
		18.1	0.19	
	2.2	3.2	0.19	
		6.8	0.20	
		9.9	0.19	
	2.2	3.1	0.17	
340		5.8	0.16	0.18 ± 0.02
		8.6	0.15	
	2.2	3.5	0.18	
		7.1	0.19	
		11.0	0.19	
			Average	**0.18 ± 0.02**

Table S13. *cis*-to-*trans* photoisomerization quantum yields at 255 nm irradiation for *fac*-[Re(CO)$_3$(dmcb)(*cis*-stpyCN)]$^+$ in CH_3CN (I_0 = 1.86x10^{15} quanta s^{-1}, Δt = 10 s).

$\lambda_{monitoring}$ / nm	concentration/ 10^{-4} mol L^{-1}	% photolysis true	$\Phi^{true}_{trans\rightarrow cis}$	$\Phi^{true\ average}_{trans\rightarrow cis}$
	1.2	1.1	0.23	
		2.5	0.27	
		3.8	0.28	
	1.2	1.1	0.24	
330		2.6	0.28	0.27 ± 0.02
		3.8	0.28	
	1.2	1.2	0.26	
		2.9	0.31	
		3.9	0.28	
	1.2	1.0	0.20	
		2.3	0.24	
		3.6	0.25	
	1.2	1.3	0.25	
335		2.5	0.26	0.25 ± 0.03
		3.7	0.25	
	1.2	1.3	0.27	
		2.8	0.28	
		4.1	0.28	
	1.2	0.9	0.22	
		2.0	0.25	
		3.1	0.25	
	1.2	1.0	0.26	
340		2.1	0.25	0.26 ± 0.02
		3.2	0.26	
	1.2	1.1	0.28	
		2.3	0.29	
		3.4	0.28	
			Average	**0.26 0.02**

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