Supporting Information

REVERSIBLE *TRANS* ⇌ *CIS* PHOTOISOMERIZATIONS OF $[Re(CO)_3(ph_2phen)(stpyCN)]^+$ TOWARDS MOLECULAR MACHINES

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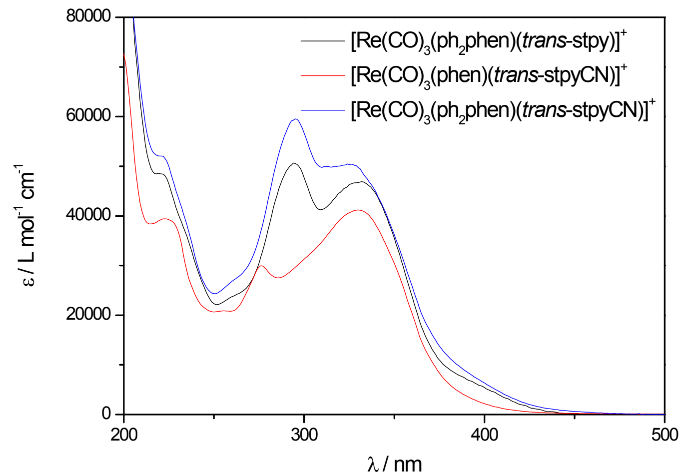

Figure S1. A comparison between the absorption spectra in acetonitrile (298 K) for $[Re(CO)_3(ph_2phen)(\textit{trans}\text{-stpyCN})]^+$ and similar complexes.

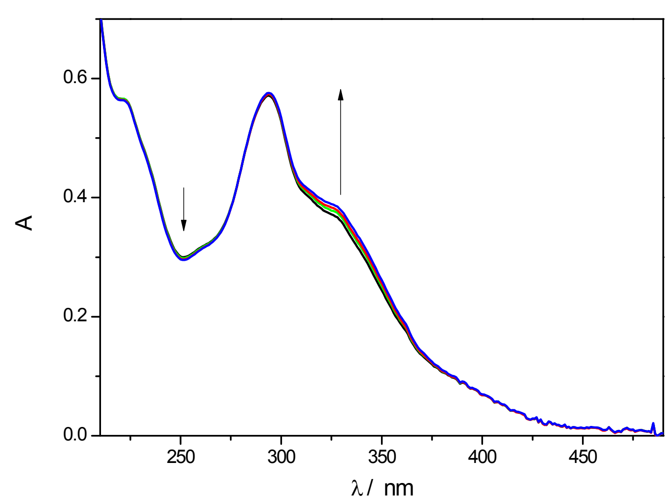

Figure S2. Spectral changes of a photostationary solution of the fac-$[Re(CO)_3(ph_2phen)(stpyCN)]^+$ system as a function of photolyses time (λ_{exc} = 255 nm, Δt = 25 s), ascribed to the *cis*-to-*trans* photoisomerization.

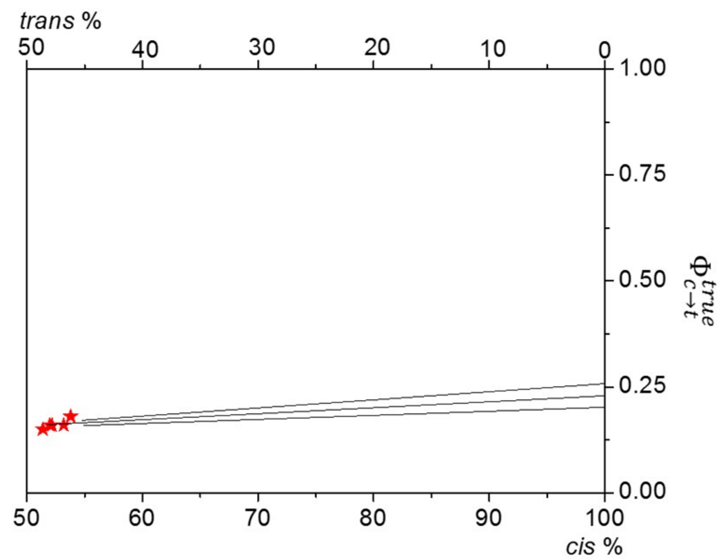

Figure S3. Extrapolation of the $\Phi_{c\to t}^{true}$ magnitude for a pure (100%) cis-solution.

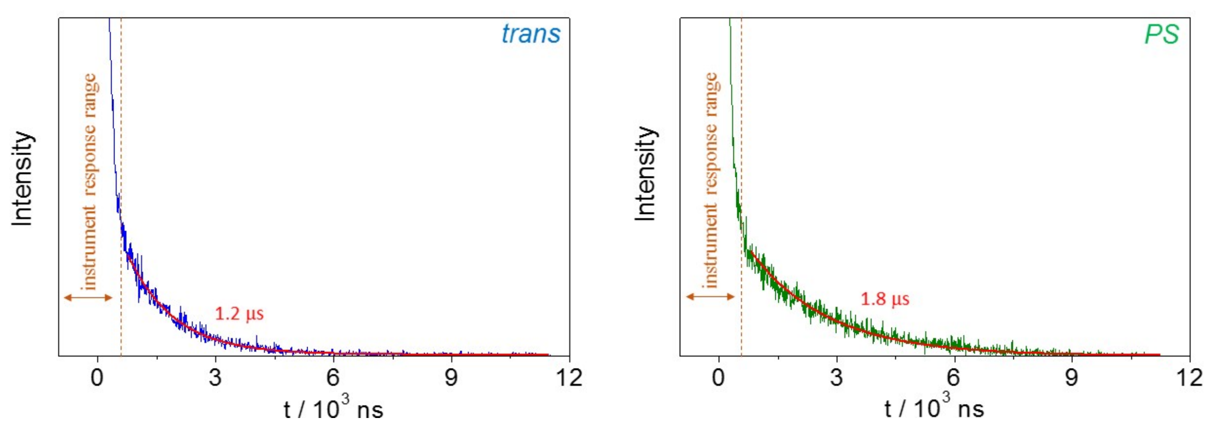

Figure S4. Nanosecond emission decays of *fac*-[Re(CO)$_3$(ph$_2$phen)(*trans*-stpyCN)]$^+$ (blue, left side) and PS (green, right side) solutions in degassed acetonitrile monitored at 540 nm (λ_{exc} = 378 nm; room temeprature).

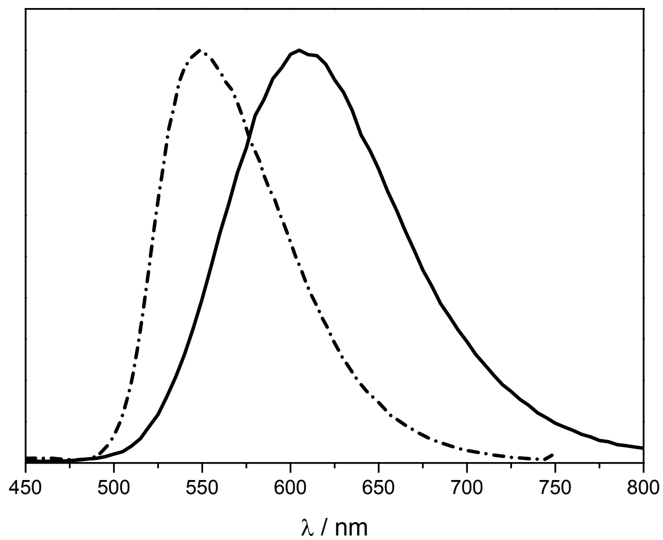

Figure S5. Emission spectra of *fac*-[Re(CO)$_3$(ph$_2$phen)(Cl)] in acetonitrile at 298 K (——) or in EPA at 77 K (—••—••).

Table S1. True quantum yields obtained for irradiations at 313 nm. (I_0 = 2.12x10^{16} quanta s^{-1})

λ_{irr} / nm	Following wavelength / nm	Sample	Concentration / 10^{-4} mol L^{-1}	Percentage of photolyses	Irradiation time / s	$\Phi_{t\rightarrow c}$	$\Phi_{t\rightarrow c}$ Average for each following wavelength	$\Phi_{t\rightarrow c}$ Average at the λ_{irr}
313	320	A	1.97	10.1	5	0.34	0.40 ± 0.10	0.38 ± 0.08
				15.4	10	0.26		
				23.8	15	0.29		
		B	2.13	12.7	4	0.58		
				18.7	8	0.42		
				26.3	12	0.40		
		C	2.18	10.0	4	0.47		
				19.8	8	0.46		
				28.2	12	0.44		
	330	A	1.97	9.7	5	0.32	0.36 ± 0.08	
				14.8	10	0.24		
				23.0	15	0.25		
		B	2.13	12.2	4	0.32		
				18.2	8	0.41		
				25,4	12	0.38		
		C	2.18	10.3	4	0.48		
				19.1	8	0.44		
				27.1	12	0.42		
	340	A	1.97	9.2	5	0.30	0.36 ± 0.09	
				13.6	10	0.22		
				21.6	15	0.23		
		B	2.13	11.3	4	0.51		
				17.1	8	0.38		
				23.6	12	0.35		
		C	2.18	9.7	4	0.45		
				18.0	8	0.41		
				25.2	12	0.38		

Table S2. True quantum yields obtained for irradiations at 334 nm. (I_0 = 6.99x10^{15} quanta s^{-1})

λ_{irr} / nm	Following wavelength / nm	Sample	Concentration / 10^{-4} mol L^{-1}	Percentage of photolyses	Irradiation time	$\Phi_{t\rightarrow c}$	$\Phi_{t\rightarrow c}$ Average for each following wavelength	$\Phi_{t\rightarrow c}$ Average at the λ_{irr}
334	320	A	2.44	4.9	6	0.51	0.38 ± 0.09	0.37 ± 0.08
				9.3	12	0.49		
				11.8	18	0.41		
		B	2.43	2.4	6	0.25		
				7.2	12	0.38		
				9.3	18	0.32		
		C	2.44	2.4	6	0.25		
				6.6	12	0.35		
				12.0	18	0.42		
	330	A	2.44	4.9	6	0.51	0.37 ± 0.11	
				9.5	12	0.50		
				12.3	18	0.43		
		B	2.43	2.7	6	0.28		
				7.5	12	0.39		
				9.3	18	0.32		
		C	2.44	1.7	6	0.18		
				5.8	12	0.31		
				11.6	18	0.40		
	340	A	2.44	4.9	6	0.50	0.38 ± 0.08	
				9.4	12	0.48		
				11.8	18	0.40		
		B	2.43	2.4	6	0.25		
				7.3	12	0.37		
				9.2	18	0.31		
		C	2.44	2.9	6	0.30		
				7.1	12	0.36		
				12.1	18	0.41		

Table S3. True quantum yields obtained for irradiations at 365 nm. ($I_0 = 2.99\text{x}10^{16}$ quanta s^{-1})

λ_{irr} / nm	Following wavelength / nm	Sample	Concentration / 10^{-4} mol L^{-1}	Percentage of photolyses	Irradiation time / s	$\Phi_{t\rightarrow c}$	$\Phi_{t\rightarrow c}$ Average for each following wavelength	$\Phi_{t\rightarrow c}$ Average for the λ_{irr}
365	320	A	2.17	6.1	3	0.39	0.38 ± 0.04	0.38 ± 0,03
				11.7	6	0.37		
				26.5	13	0.39		
		B	2.16	7.0	3	0.44		
				10.5	6	0.33		
				26.5	13	0.42		
		C	2.10	8.0	3	0.30		
				15.9	6	0.37		
				24.0	13	0.40		
	330	A	2.17	6.1	3	0.38	0.38 ± 0.05	
				10.9	6	0.35		
				26.7	13	0.39		
		B	2.16	7.6	3	0.48		
				11.1	6	0.35		
				21.1	13	0.33		
		C	2.10	8.0	3	0.29		
				16.2	6	0.37		
				23.9	13	0.40		
	340	A	2.17	6.6	3	0.41	0.39 ± 0.04	
				11.8	6	0.37		
				27.7	13	0.40		
		B	2.16	7.4	3	0.46		
				10.9	6	0.34		
				27.3	13	0.43		
		C	2.10	9.0	3	0.33		
				17.3	6	0.40		
				25.3	13	0.42		

Table S4. True quantum yields obtained for irradiations at 404 nm. (I_0 = 1.17x10^{16} quanta s^{-1})

λ_{irr} / nm	Following wavelength / nm	Sample	Concentration / 10^{-4} mol L^{-1}	Percentage of photolyses	Irradiation time / s	$\Phi_{t\to c}$	$\Phi_{t\to c}$ Average for each following wavelength	$\Phi_{t\to c}$ Average at the λ_{irr}
404	320	A	1.36	5.1	3	0.39	0.36 ± 0.03	0.37 ± 0.02
				9.5	6	0.36		
				14.0	9	0,35		
		B	1.35	3.7	3	0.28		
				9.1	6	0.35		
				13.7	9	0.35		
		C	1.36	4.9	3	0.38		
				9.4	6	0.36		
				15.0	9	0.38		
	330	A	1.36	5.4	3	0.41	0.37 ± 0.03	
				9.6	6	0.37		
				14.5	9	0.37		
		B	1.35	4.2	3	0.32		
				9.5	6	0.36		
				14.5	9	0.37		
		C	1.36	5.4	3	0.41		
				9.9	6	0.38		
				15.1	9	0.38		
	340	A	1.36	5.4	3	0.40	0.37 ± 0.02	
				10.1	6	0.38		
				14.8	9	0.37		
		B	1.35	4.3	3	0.32		
				10.0	6	0.37		
				15.1	9	0.38		
		C	1.36	5.3	3	0.39		
				10.2	6	0.38		
				15.5	9	0.38		

Table S5. True quantum yields obtained for irradiations at 255 nm (*cis*-to-*trans* photoisomerization). (I_0 = 1.20x10^{15} quanta s^{-1})

λ_{irr} / nm	Following wavelength / nm	Sample	Concentration / 10^{-4} mol L^{-1}	Percentage of photolyses	Irradiation time / s	$\Phi_{c\to t}$	$\Phi_{c\to t}$ Average for each following wavelength	$\Phi_{c\to t}$ Average at the λ_{irr}
255	320	A	0.96	1.1	30	0.17	0.15 ± 0.02	0.16 ± 0.01
				2.7	80	0.15		
				3.3	105	0.14		
		B	0.96	0.7	25	0.12		
				1.5	50	0.14		
				2.4	75	0.14		
		C	0.97	1.0	25	0.19		
				1.6	50	0.15		
				2.6	75	0.16		
	330	A	0.96	1.2	30	0.17	0.16 ± 0.01	
				3.1	80	0.16		
				3.7	105	0.15		
		B	0.96	0.9	25	0.15		
				1.8	50	0.15		
				2.8	75	0.16		
		C	0.97	1.2	25	0.19		
				1.8	50	0.15		
				2.8	75	0.17		
	340	A	0.96	1.2	30	0.19	0.17 ± 0.02	
				3.1	80	0.18		
				3.7	105	0.16		
		B	0.96	0.9	25	0.16		
				1.8	50	0.16		
				2.7	75	0.16		
		C	0.97	1.2	25	0.22		
				1.8	50	0.16		
				2.9	75	0.17		