Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary material

Reversible Hydrocarbon/Perfluorocarbon Phase-Switching of $[Ru(bipy)_3]^{2+}$ Driven by Supramolecular Heteromeric Fluorous Carboxylate-Carboxylic Acid H-Bond Interactions

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General remarks: All reagents and solvents were obtained from commercial sources (highest available purity) and used as received except for dichloromethane which was distilled over CaH_2 prior to use. The fluorous acid R*f*CO_2H was purchased from ABCR. NMR analysis were carried out on a spectrometer Bruker avanceII-300. The ESI-TOF mass spectra were recorded at the CESAMO analytical center (Institut des Sciences Moléculaires, Université Bordeaux 1) on a QSTAR Elite spectrometer from Applied Biosystem. Elemental analysis was performed by the Service Central d'Analyses, Vernaison, France. Results are expressed in weight percent. The infrared spectra of R*f*CO_2H and complex **1.**(R*f*$CO_2H)_2$ were recorded with a ThermoNicolet Nexus 670 FTIR spectrometer at a resolution of 4 cm^{-1}, by coadding 50 scans. Samples were held in a fixed path length (50 μm) cell with BaF_2 windows. Spectra of the two compounds were measured in perfluorodecalin solvent at a concentration of about 50 mM. All infrared spectra were shown with solvent absorption subtracted out. Electronic absorption spectra were recorded with a Varian Cary 5000 spectrophotometer. Steady-state emission spectra were recorded with a Horiba Jobin-Yvon Fluorolog-3 fluorimeter fitted with Hamamatsu R928P, R2658P and H10330-45 detectors and exciting with a 450W Xe-lamp across a double monochromator, and were corrected for instrumental function. Luminescence decays were recorded in single-photon counting mode on the Fluorolog-3, with high frequency pulsed IBH nanoLEDs (λ_{exc} = 460nm, FWHM = ca. 1.2 ns) as the excitation source. The luminescence quantum yield (Φ_f) was calculated by using the equation $\Phi_f = \Phi_r(I/I_r)(A_r/A)(\eta^2/\eta_r^2)$ in which r refers to the quantum yield reference, I is the integrated emission intensity, A is the absorbance at the excitation wavelength and η is the refractive index of the solvent. An optically dilute solution of $Ru(bipy)_3Cl_2$ in air-equilibrated water (Φ_f = 0.028).[A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, Coord. Chem. Rev., 1998, 84, 85.] was used as the reference. Concerning kinetics: k_r was estimated using equation 1 ($\Phi_f = \Phi_{Isc}.k_r.\tau_{av}$), where the average decay time τ_{av} is defined as $\Sigma B_i\tau_i/\Sigma B_i$ = 375 ns for the cited air-equilibrated solution. The proportions 1.3:1 correspond to B_1:B_2, with τ_1 = 166 ns and τ_2 = 788 ns resulting from a 3-exponential fitting (τ_3 = 16 ns). Similarly, on N_2 bubbling, decay times of τ_1 = 325 ns, τ_2 = 949 ns (B_1:B_2 = 0.3:1), τ_3 = 12 ns and τ_{av} = 642 ns were measured. The ratio of τ_{av} (N_2) / τ_{av} (air) = 1.71 is in agreement with the ratio of quantum yields Φ_f (N_2) / Φ_f (air) = 1.87.

$$\Phi_f = \Phi_{isc} k_r \tau_{av} \qquad \text{eq. 1}$$

$$\frac{1}{\tau} = k_r + k_{nr} \qquad \text{eq. 2}$$

Synthesis of $[Ru(bipy)_3](CF_3CF_2CF_2O[(CF_3)CFCF_2O]_3(CF_3)CFCO_2)_2$, 1:

Ag_2CO_3 (0.129 g, 0.470 mmol) was added to a solution of $C_{14}F_{29}O_4CO_2H$ (0.500 g, 0.603 mmol) in EtOH (5 mL) to give a greenish suspension which was stirred for 16h. The reaction mixture was filtered and the solvent evaporated to give $C_{14}F_{29}O_4CO_2Ag$ as a clear viscous oil (0.524 mg).

A round-bottomed flask was charged with a solution of $C_{14}F_{19}O_4CO_2Ag$ (0.500 g, 0.53 mmol) in EtOH (4.0 mL). $Ru(Bipy)_3Cl_2$ (0.100 g, 0.134 mmol) was added in small portions under stirring to give an off-white precipitate. The mixture was further stirred for 30 minutes and the off-white precipitate was removed by filtration. The filtrate was transferred into a round-bottomed flask, protected from light and heated at 50 °C overnight. The orange mixture was filtered through a pad of celite and the solvent was removed to give an orange residue, which was washed abundantly with diethyl ether to give the product as a bright orange solid (0.2876 g, 97%).

FTIR (cm^{-1}): 3440, 3080, 1698 (C=O), 1604, 1466, 1448, 1425, 1400-1050 (CF), 1033, 983, 807, 768, 746, 733, 659, 534; Anal. Calcd for $C_{60}H_{24}F_{58}N_6O_{12}Ru$: C, 32.41; H, 1.09; N, 3.78; Ru, 4.54 Found: C, 31.70; H, 1.21; N, 3.94; Ru, 4.04; Cl < 200 ppm; ESI^+-MS *m/z* (%): 1396.7 (100) $[M - R_fCO_2]^+$; UV-visible (MeOH) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 449 (14500). ^1H NMR (300 MHz, CD_2Cl_2) δ ppm: 8.75 (d, *J* = 8.29 Hz, 6H), 7.99 (td, *J* = 7.82 Hz, 6H), 7.62 (dd, *J* = 5.65, 0.75 Hz, 6H), 7.30 – 7.38 (m, 6H). ^{13}C NMR (101 MHz, MeOD) δ ppm: 102.24, 102.52, 102.92, 104.86, 105.21, 105.62, 105.97, 114.50, 117.38, 117.65, 119.28, 119.58, 119.90, 120.23, 120.47, 122.43, 125.81, 129.08, 139.40, 152.76, 158.71, 162.02 (C=O).

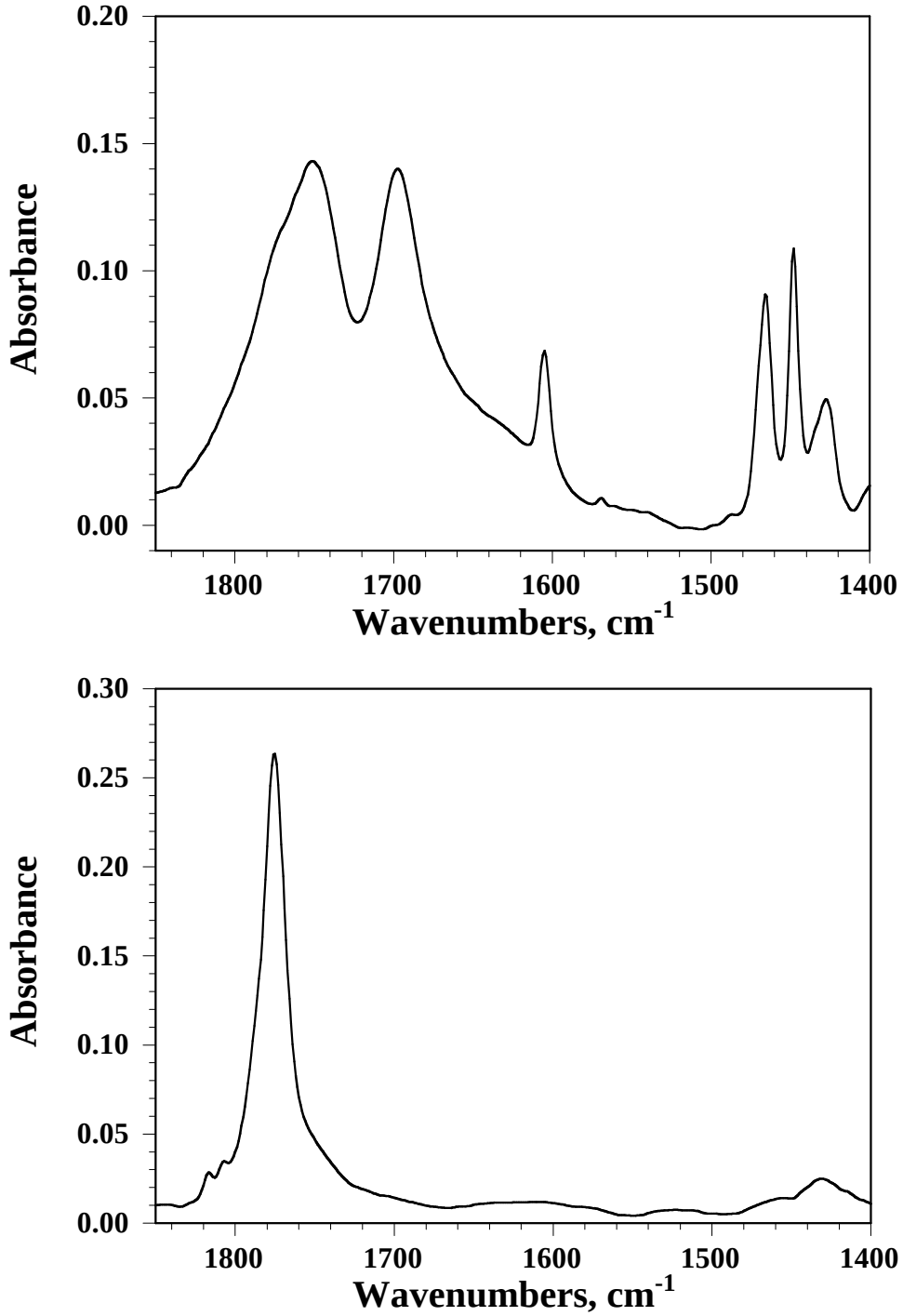

Figure S1 IR spectrum of the perfluorodecalin solution (upper spectrum) resulting from a phase-switching experiment conducted with a DCM solution (0.250 mL) containing **1** (17.8 mg, 8 μmol) and a perfluorodecalin solution (0.150 mL) containing R_fCO_2H (14.0 mg, 16.9 μmol). The lower spectrum corresponds to the perfluorodecalin solution of R_fCO_2H before extraction.

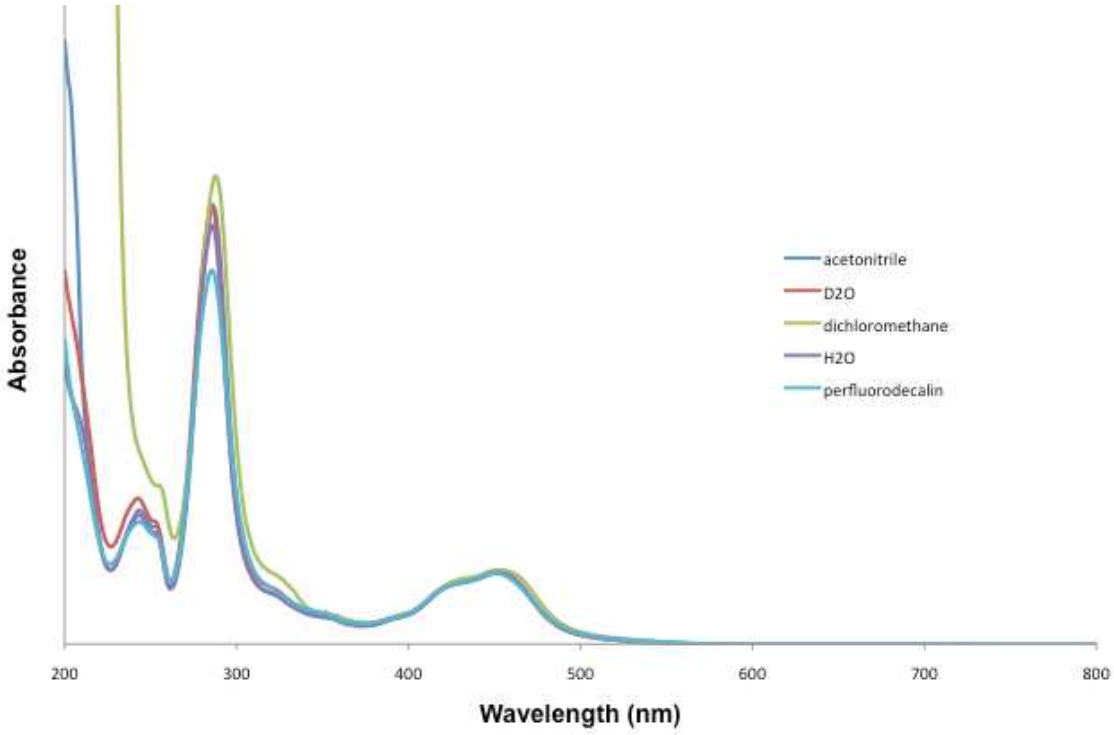

Figure S2 Electronic absorption spectra of **1**.$(RfCOOH)_2$ in PFD and **1** in DCM, ACN, D_2O and H_2O, normalised at 450nm.

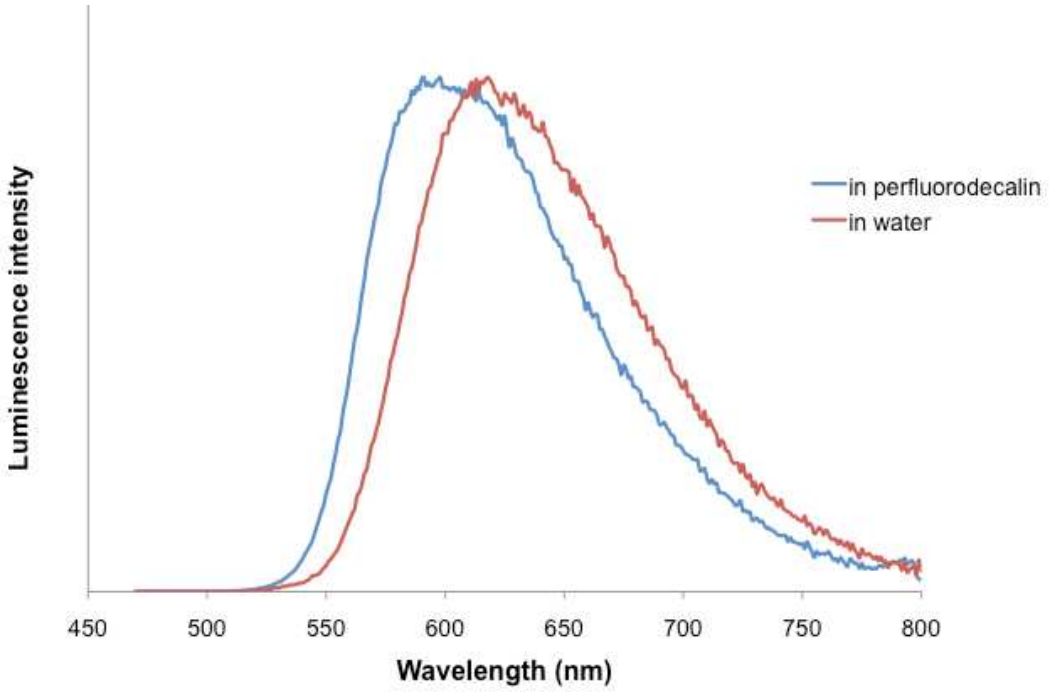

Figure S3 Normalised emission spectra of $Ru(bipy)_3Cl_2$ in H_2O and **1**.$(RfCOOH)_2$ in perfluorodecalin. λ_{exc} = 450nm.

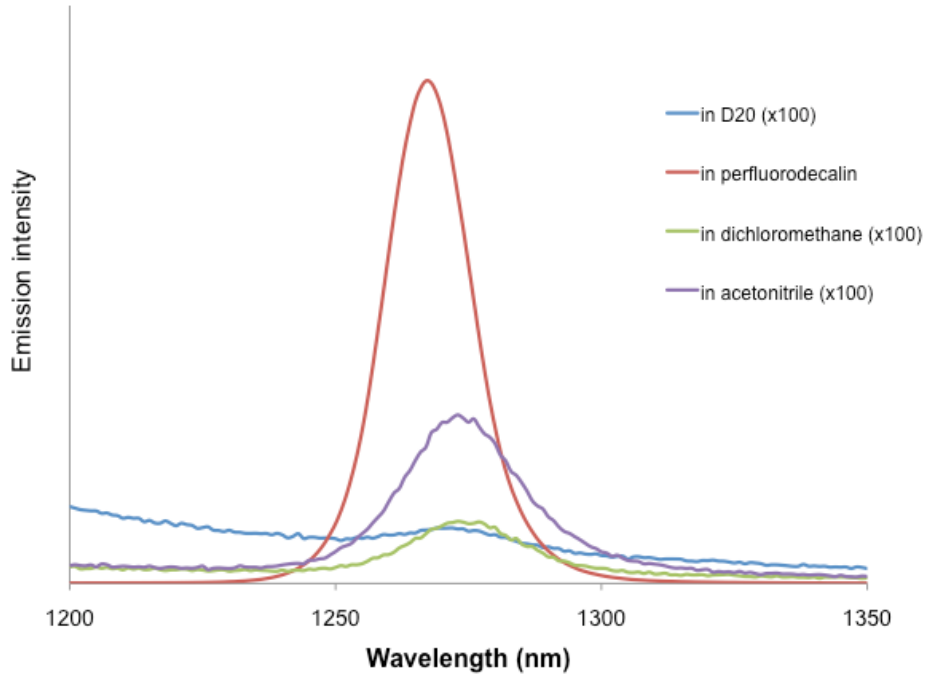

Figure S4 $^1O_2$ emission obtained using $Ru(bipy)_3Cl_2$ as photosensitizer in D_2O , **1** in DCM and acetonitrile and **1**.$(RfCOOH)_2$ in perfluorodecalin, corrected for absorption. λ_{exc} = 450nm.

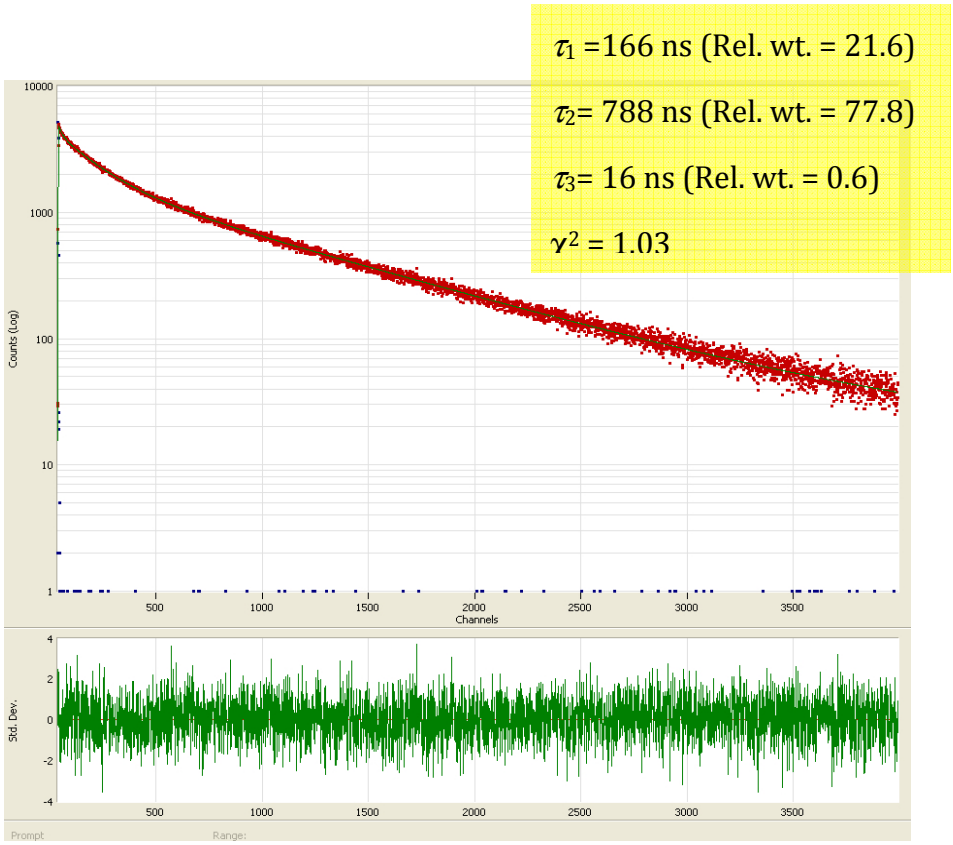

Figure S5 Luminescence decay of **1**.$(RfCOOH)_2$ at 600 nm. λ_{exc} = 460nm, concentration = 1 x 10^{-5} M. Fitted to biexponential decay (a) and a triexponential decay (b).