Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting information

CuAAC-based assembly and characterization of a ruthenium-copper dyad containing a diimine dioxime ligand framework

Nicolas Queyriaux,[a] Eugen S. Andreiadis,[a] Stéphane Torelli,[a] Jacques Pecaut,[b,c] Brad S. Veldkamp,[d,e] Eric A. Margulies,[d,e] Michael R. Wasielewski,[d,e] Murielle Chavarot-Kerlidou,[a,]* Vincent Artero[a,]*

[a]Laboratoire de Chimie et Biologie des Métaux, Univ. Grenoble Alpes, CNRS UMR 5249, CEA, 17 rue des martyrs, F-38054, Grenoble Cedex 9, France

[b]Univ. Grenoble Alpes, INAC-SyMMES, F-38000 Grenoble, France.

[c]CEA, INAC-SyMMES, Chimie Interface Biologie pour la Santé l'Environnement et la Toxicologie, F-38000 Grenoble, France.

[d]Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113, United States

[e]Argonne-Northwestern Solar Energy Research (ANSER) Center, Northwestern University, Evanston, Illinois 60208-3113, United States.

Email: murielle.chavarot-kerlidou@cea.fr; vincent.artero@cea.fr

General characterization methods and equipment. ^{1}H and ^{13}C NMR spectra were recorded at 298 K in 5 mm o.d. tubes on a Bruker AC 300 spectrometer equipped with a QNP probehead operating at 300.0 MHz for ^{1}H and 75.5 MHz for ^{13}C. Chemical shifts reported in ppm are given relative to TMS and were internally referenced to the residual solvent resonance. UV-visible spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Emission spectra were recorded on a Perkin Elmer LS50B spectrofluorimeter. Accurate mass measurements (HRMS) were performed on a Bruker maXis mass spectrometer by the "Fédération de Recherche" ICOA/CBM (FR2708) platform and elemental analysis on a Thermofisher Scientific "Flash 2000" by the "Plateforme d'analyse pour la chimie" (GDS 3648, Strasbourg).

X-band EPR spectra were recorded on a Bruker EMX spectrometer equipped with an Oxford ESR 910 cryostat for low temperature studies. The microwave frequency was calibrated with a frequency counter and the magnetic field with an NMR gaussmeter. The samples were irradiated with a 300W ozone-free Xenon lamp (Newport) operated at 280W, coupled to a water-filled Spectra-Physics 6123NS Liquid filter for elimination of IR radiation and a Spectra-Physics 59472 UV cut-off filter ($\lambda > 400$ nm). Irradiance at the samples was adjusted to 60 mW.cm^{-2} (ca. 1 sun) thanks to a Newport PM1918-R optical power meter.

Electrochemical measurements. Electrochemical analysis was performed using a BioLogic SP300 potentiostat fitted with a high current/high voltage board (1 A/48 V) controlled via the EC-Lab® V10 software. The voltammetry experiments were carried out in a three-electrode electrochemical cell using glassy carbon (GC) or platinum (Pt) as the working electrodes, a platinum wire as auxiliary electrode and a commercial reference electrode based on the Ag/AgCl/KCl 3M couple (Ag/AgCl). This electrode was calibrated after each experiment with the internal reference system Fc^+/Fc, usually found at 0.450 V vs Ag/AgCl in CH_3CN. Solution concentrations were ca. 2 mM for the complex and 0.1 M for the supporting electrolyte ($TBAClO_4$ or $TBAPF_6$) in acetonitrile. Spectroelectrochemical experiments were carried out in a spectroelectrochemical quartz cell from CH Instruments (0.1 cm optical path length) fitted with a Pt gauze working electrode, a Ag/AgCl reference electrode and a Pt wire counter electrode. The evolution of the UV/vis absorbance was recorded with a Cary 50 Probe UV-vis spectrophotometer, upon electrolysis at -0.7 V vs Ag/AgCl of a 1 mM acetonitrile solution of the complex (containing 0.1 M $TBAClO_4$ or $TBAPF_6$ as supporting electrolyte).

X-ray crystallography. Diffraction data were collected using an Oxford Diffraction XCalibur S Kappa area detector four-circle diffractometer (Mo-Kα radiation $\lambda = 0.71073$ Å, graphite monochromator), controlled by the Oxford Diffraction CrysAlis CCD software.[1] Unique intensities with I > 10σ (I) detected on all frames using the Oxford Diffraction RED were used to refine the values of the cell parameters. The substantial redundancy in data allows analytical absorption corrections to be applied using crystal shape determination. The space group was determined from systematic absences, and it was confirmed by the successful resolution of the structure. The structure was solved by charge flipping method using SUPERFLIP software[2] in Olex1.2 environment[3] and all the atoms were found by difference Fourier syntheses. All non-hydrogen atoms were anisotropically refined on F^2 using ShelXL program.[4] Hydrogen atoms were fixed in ideal positions. X-ray suitable crystals of **2** were grown by slowly evaporating a methanolic solution. The asymmetric unit contains C_{11} $H_{17.91}$ Cu N_7 O_2, ClO_4.

Experimental details for X-ray data collection: formula C11 H17.91 Cl Cu N7 O6; FW = 443.22 g·mol^{-1}; T = 150(2)K; crystal system orthorhombic; space group P 2_1 2_1 2_1; unit cell dimensions a = 6.9919(3) Å, b = 11.5174(4) Å, c = 20.7014(7) Å, $\alpha = \beta = \gamma = 90$ deg.; V = 1667.06(11) Å^3; Z = 4; ρ = 1.766 g·cm^3; μ = 1.518 mm^{-1}; θ range 3.075 to 30.508°; reflns. collected 20092; indep. reflns. 5083 (R_{int} = 0.0704); parameters 301; GOF on F^2 1.073; final R indices [R1 = 0.0571, wR2 = 0.1136]; Flack parameter 0.028(11). CCDC 1476499.

Femtosecond transient absorption measurements. Femtosecond pulses were derived from a Ti:sapphire oscillator as previously described[5] and passed through a commercial amplifier (Spectra-Physics Spitfire) to produce 1 mJ pulses centred at 827 nm at a 1 kHz repetition rate. A 50% beam splitter divided the output to provide 500 μJ/pulse of the fundamental to drive the experiment.

Second-harmonic generation in a lithium-triborate crystal ($\theta = 90°$, $\varphi = 31.7°$) produced excitation pulses of up to 150 μJ/pulse. As previously described,[5] the continuum probe pulses were generated by focusing the infrared fundamental into a 1 mm sapphire disk and detected by a CCD spectrograph. By modulating the pump beam at 1/50th the repetition rate, spectra were recorded with 4 seconds of averaging at each time delay. As measured by the optical Kerr-gating cross correlation between the pump and continuum probe pulses, the overall temporal resolution of the system was ~ 90 – 150 fs across the 450 – 800 nm spectral range.

Samples were excited with 1.0 μJ/pulse of 414 nm light focused to a ~200 μm spot. Each sample was dissolved in dry acetonitrile in a 2 mm glass cuvette at an optical density between 0.5 and 0.6 at the excitation wavelength. Samples were subjected to four freeze-pump-thaw cycles before data collection.

Fits of each single wavelength kinetic were obtained by a non-linear least squares fit to a constant convoluted with a Gaussian instrument response function.

Nanosecond transient absorption measurements. The chromophore systems were dissolved in still-dried acetonitrile, forming solutions of approximately 0.7 OD at 416 nm. The samples were then subjected to four freeze-pump-thaw cycles in a 1 cm quartz cuvette. Nanosecond transient absorption experiments were performed by exciting the sample with 7 ns, 1.5 mJ, 416 nm pulses using the frequency-tripled output of a Continuum Precision II 8000 Nd-YAG laser pumping a Continuum Panther OPO. The probe pulse, generated using a xenon flashlamp (EG&G Electro-Optics FX-200), and pump pulse are overlapped on the sample with the pump being focused to a spot size slightly larger than the probe. Samples were illuminated at a 90 degree configuration with the pump excitation beam coming from the side of the sample. An aperture was introduced at the focal point of the probe beam between the sample and detector in order to minimize the detected fluorescence. Kinetic traces are observed from 425-800 nm every 5 nm using a 416 nm long-pass filter, a monochromator, and photomultiplier tube (Hamamatsu R928) with high voltage applied to only 4 dynodes. Kinetic traces are recorded with a LeCroy Wavesurfer 42Xs oscilloscope interfaced to a customized Labview program (Labview v. 8.6.1). Spectra are built from the single wavelength kinetic traces taken every 5 nm. Each kinetic trace is representative of an average of 150 shots over a five microsecond time window. To increase the signal to noise ratio of the spectral profiles, 5-10 ns segments of data are averaged together and the median time reported as the time of the spectral slice.

Synthesis. Solvents, starting materials and reagents such as benzyl azide were purchased from Sigma-Aldrich and used without further purification, unless otherwise stated. $Ru(bpy)_2Cl_2.2H_2O$ was purchased from STREM Chemicals. All reactions in solution were routinely performed under an inert atmosphere of argon using conventional vacuum-line and glasswork techniques. The metal complexes were however handled in air in the solid state.
$[Cu(DO)(DOH)pn(OH_2)](ClO_4)$[6] and the azide-substituted diimine dioxime ligand N^2,N^{2}'-2-azidepropanediylbis(2,3-butadione-2-imine-3-oxime[7, 8] have been prepared according to previously-reported procedures.

2-(4-ethynylphenyl)-1H-imidazo[4,5-f][1,10]phenanthroline. The alkyne ligand was prepared according to a reported procedure,[9] using 4-ethynylbenzaldehyde instead of 4–(trimethylsilylethynyl)–benzaldehyde. Yield: 86 %.
^{1}H NMR 300 MHz (DMSO d6): δ (ppm) 9.05 (d, 2H, $H^{2,9\text{-}phen}$), 8.92 (d, 2H, $H^{4,7\text{-}phen}$), 8.31 (d, 2H, $H^{phenylene}$), 7.86 (m, 2H, $H^{3,8\text{-}phen}$), 7.74 (d, 2H, $H^{phenylene}$), 4.40 (s, 1H, CH^{alkyne}), 1.91 (s, 1H, NH).

1.[9] A degassed suspension of Ru(bipy)$_2$Cl$_2$·2H$_2$O (146 mg, 0.28 mmol, 0.9 eq.) and alkyne ligand (100 mg, 0.31 mmol, 1 eq.) in a 1:1 ethanol–water mixture (50 mL) was refluxed for 6 hours at 80°C under argon in the dark. After evaporation of the ethanol solvent under reduced pressure, a saturated aqueous KPF$_6$ solution was added dropwise resulting in the precipitation of an orange powder. The crude complex was purified by chromatography on silica gel using a gradient of CH$_3$CN/aqueous KNO$_3$ solution (saturated solution diluted at 10% in water). After evaporation of the acetonitrile, the purified compound was precipitated by addition of a saturated aqueous KPF$_6$ solution. Filtration, washing with water and drying under vacuum afforded the desired complex as an orange powder (173 mg; 60 % yield).

^{1}H NMR (300 MHz, CD$_3$CN) δ (ppm) 9.05 (d, *J* = 8.2 Hz, 2H, H$^{4,7\text{-phen}}$), 8.54 (d, *J* = 8.2 Hz, 2H, H$^{3,3'\text{-bpy}}$), 8.51 (d, *J* = 8.2 Hz, 2H, H$^{3,3'\text{-bpy}}$), 8.31 (d, *J* = 8.2 Hz, 2H, H$^{\text{phenylene}}$), 8.10 (dd, *J* = 8.0 Hz, 2H, H$^{4,4'\text{-bpy}}$), 8.06-7.94 (m, 4H, H$^{2,9\text{-phen}}$ + H$^{4,4'\text{-bpy}}$), 7.85 (d, *J* = 5.5 Hz, 2H, H$^{6,6'\text{-bpy}}$), 7.78 (dd, *J* = 8.2, 5.3 Hz, 2H, H$^{3+8\text{-phen}}$), 7.72 (d, *J* = 8.2 Hz, 2H, H$^{\text{phenylene}}$), 7.59 (d, *J* = 5.5 Hz, 2H, H$^{6,6'\text{-bpy}}$), 7.45 (dd, *J* = 7.8 Hz, 2H, H$^{5/5'\text{-bpy}}$), 7.22 (dd, *J* = 7.9 Hz, 2H, H$^{5/5'\text{-bpy}}$), 3.58 (s, 1H, H$^{\text{alkyne}}$).

^{13}C NMR (75 MHz, CD$_3$CN) δ (ppm) C$_q$: 166.9, 150.3, 144.2, 144.0, 135.5, 129.1, 128.7, 127.2, 123.8, 83.0; C$_H$: 149.1, 148.5, 138.6, 132.5, 132.2, 131.2, 130.2, 129.7, 127.1, 126.7, 125.0, 123.3, 122.3, 119.9.

MS (ESI$^+$): *m/z* 733.4 [M – 2 PF$_6^-$ – (H$^+$)]$^+$, 367.3 [M – 2 PF$_6$]$^{2+}$.

2. To a hot diimine-dioxime ligand solution (147 mg, 0.523 mmol, 1.7 eq.) in acetone (1 mL) was added dropwise upon stirring a concentrated solution of Cu(ClO$_4$)$_2$·6H$_2$O (114 mg, 0.308 mmol, 1 eq.) in acetone (0.5 mL). The resulting dark red-brown solution was left standing overnight at room temperature. Crystals started appearing within minutes. The supernatant was removed and the crystals washed three times with little amounts of acetone, then dried under vacuum to give 102 mg (82 % yield) of pure red-brown crystals.

3. In a round bottom flask, complex **1** (30 mg, 0,029 mmol, 1 eq.) and commercially available benzyl azide (90 µL of a 0.5M solution in dichloromethane, 0.044 mmol, 1.5 eq.) were dissolved in a homogeneous solvent mixture of methanol, dichloromethane and water (3:3:1; 5 mL). The solution was degassed with argon before the addition of sodium ascorbate (3.2 mg, 0.026 mmol, 0.9 eq.) and CuSO$_4$·5H$_2$O (2.2 mg, 0.009 mmol, 0.3 eq.).The reaction mixture was stirred at room temperature under argon in the dark. After 24 hours, 0.9 eq of sodium ascorbate and 0.3 eq of copper sulfate were added and the reaction mixture was stirred for another 24 hours. The solvents were evaporated to dryness and the residue solubilized in a minimum amount of acetone. The desired compound was precipitated by dropwise addition of a saturated KPF$_6$ aqueous solution. The precipitate was filtered, washed with water and dried under vacuum to give 22 mg (65 % yield) of the expected complex as an orange powder. For the photophysical studies, the complex was further passed through a Sephadex LH20 size-exclusion column using a methanol-dichloromethane (1:1) eluent.

^{1}H NMR (400 MHz, CD_3CN) δ (ppm) 8.99 (d, *J* = 8.0 Hz, 2H, $H^{4,7\text{-phen}}$), 8.54 (d, *J* = 8.2 Hz, 2H, $H^{3,3'\text{-bpy}}$), 8.50 (d, *J* = 8.1 Hz, 2H, $H^{3,3'\text{-bpy}}$), 8.32 (d, *J* = 8.4 Hz, 2H, $H^{\text{phenylene}}$), 8.24 (s, 1H, H^{triazole}), 8.10 (td, *J* = 8.0, 1.4 Hz, 2H, $H^{4,4'\text{-bpy}}$), 8.06 (d, *J* = 8.4 Hz, 2H, $H^{\text{phenylene}}$), 8.03 – 7.95 (m, 4H, $H^{2,9\text{-phen}}$ + $H^{4,4'\text{-bpy}}$), 7.86 (d, *J* = 5.0 Hz, 2H, $H^{6,6'\text{-bpy}}$), 7.76 (dd, *J* = 8.3, 5.3 Hz, 2H, $H^{3,8\text{-phen}}$), 7.60 (d, *J* = 5.1 Hz, 2H, $H^{6,6'\text{-bpy}}$), 7.50 – 7.37 (m, 7H, H^{Ph} + $H^{5,5'\text{-bpy}}$), 7.22 (ddd, *J* = 7.3, 5.7, 1.2 Hz, 2H, $H^{5,5'\text{-bpy}}$), 5.63 (s, 2H, CH_2Ph).

MS (ESI^+) m/z 1011 $[M - PF_6]^+$, m/z 433 $[M - 2PF_6]^{2+}$.

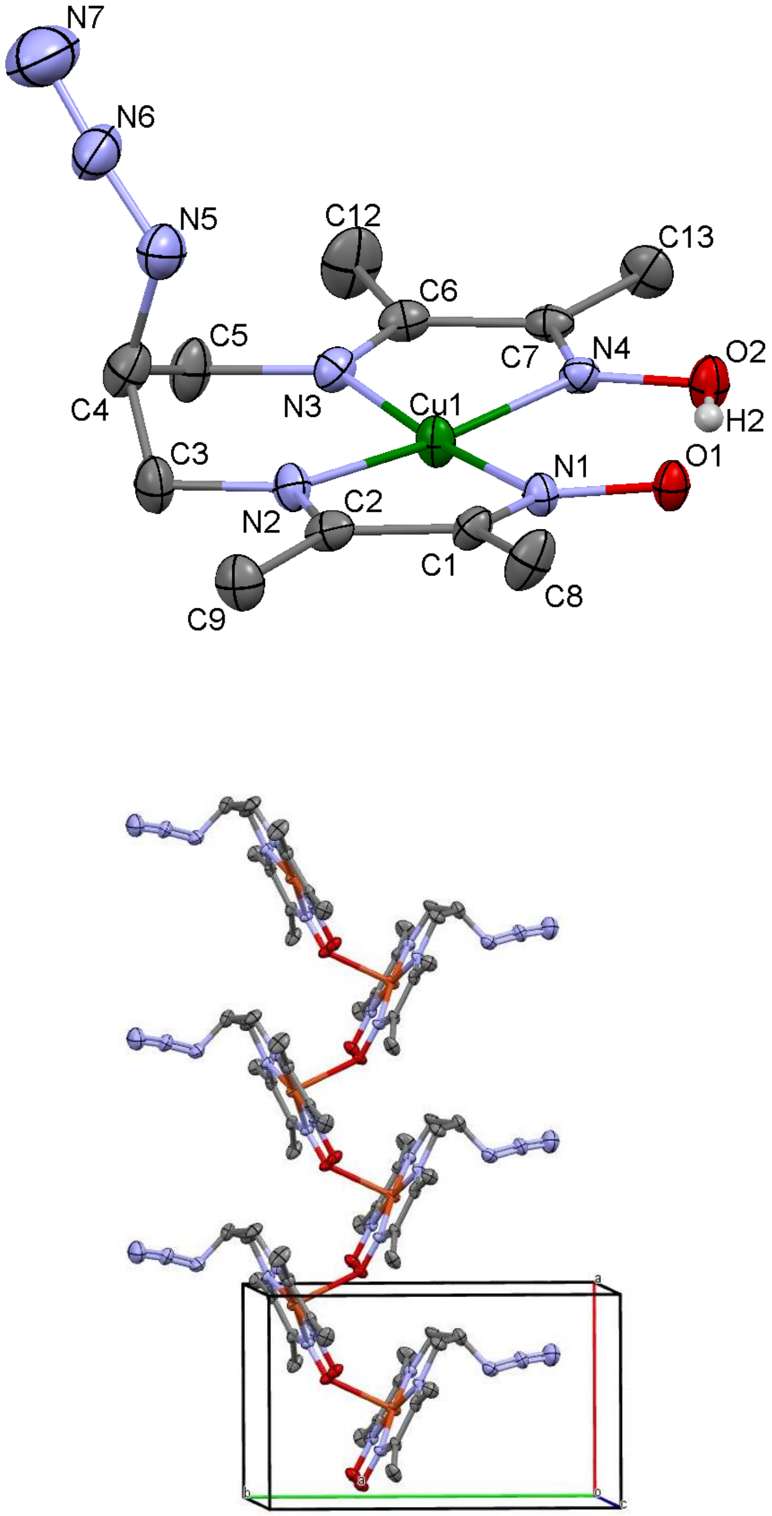


Figure S1. ORTEP view (with thermal ellipsoids at the 50 % probability level) of complex **2** (top) and of the crystal lattice (bottom). Hydrogen atoms and counter-anion have been omitted for clarity (Selected bond lengths and angles in Table 1).

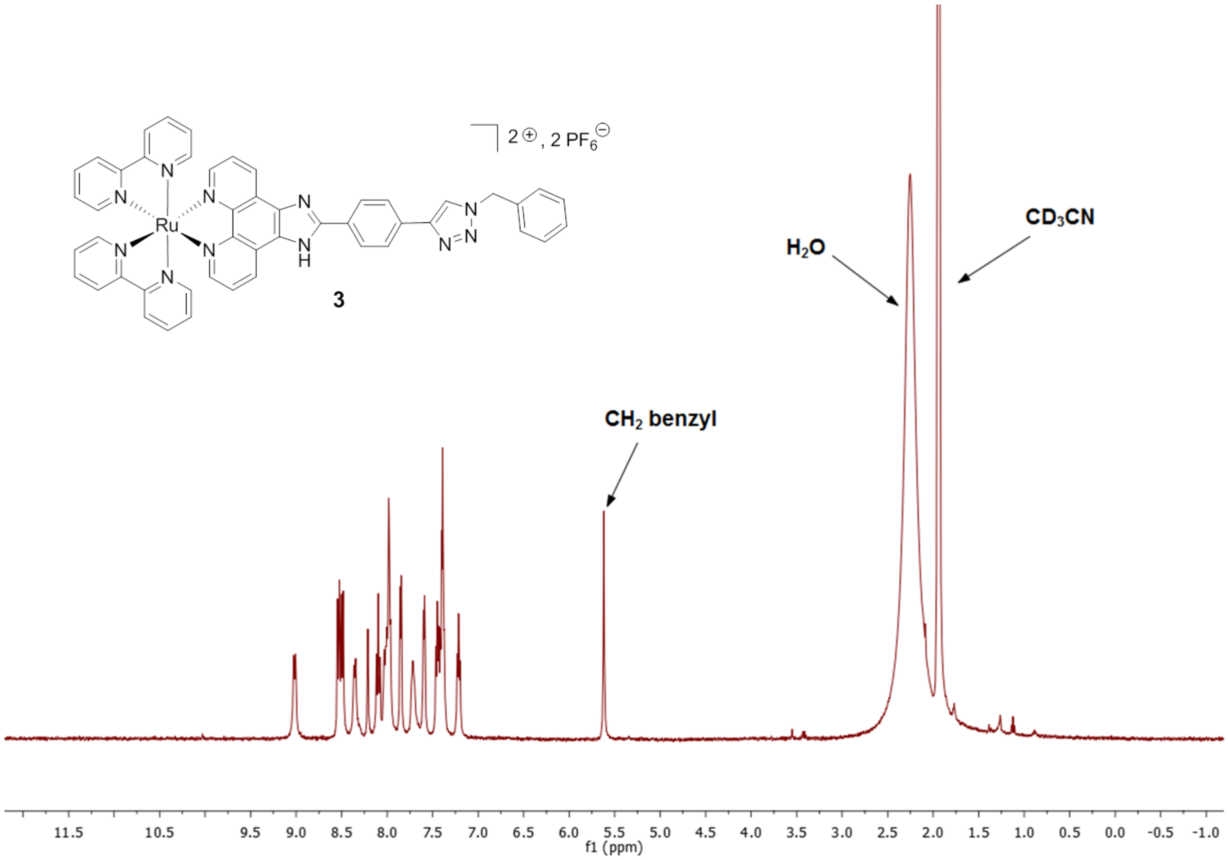


Figure S2. Full ^{1}H NMR spectrum of compound **3**, recorded in CD_3CN.

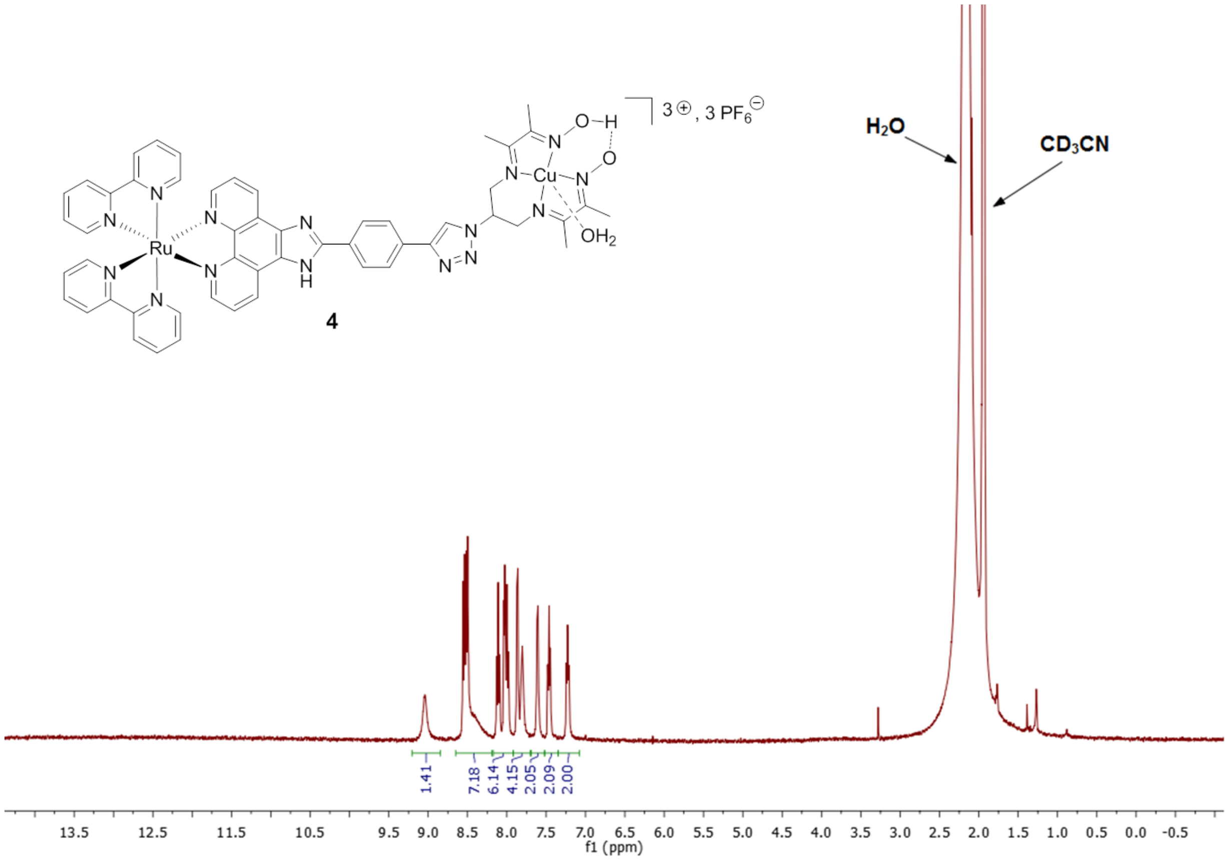


Figure S3. Full ^{1}H NMR spectrum of compound **4**, recorded in CD_3CN.

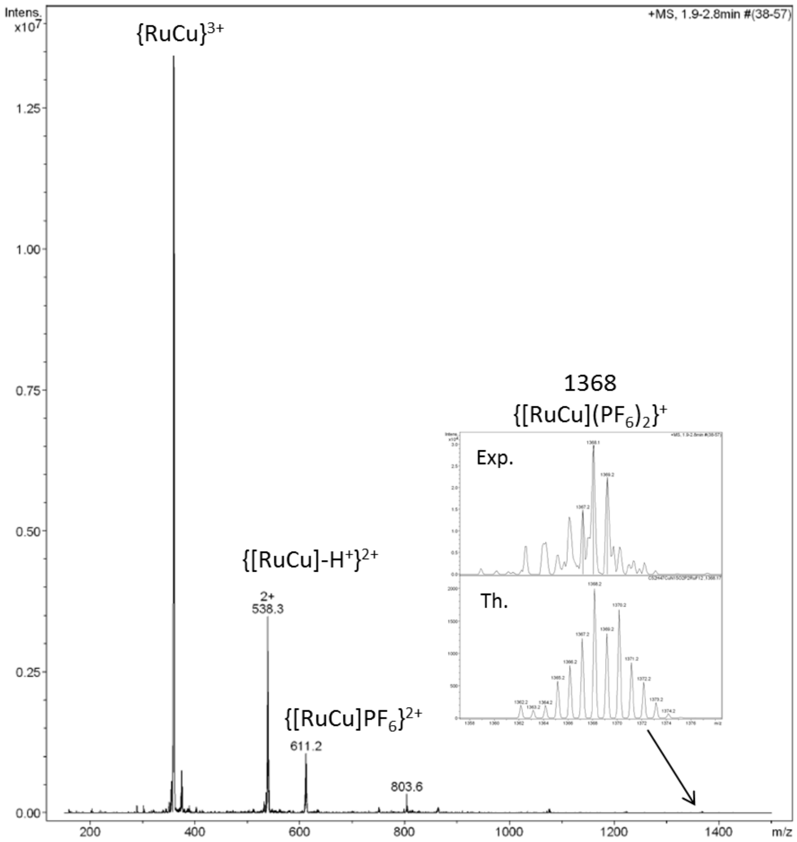


Figure S4. ESI mass spectrum of **4**. Inset: Zoom at m/z 1368 and theoretical mass spectrum for the monocation $[M – PF_6]^+$.

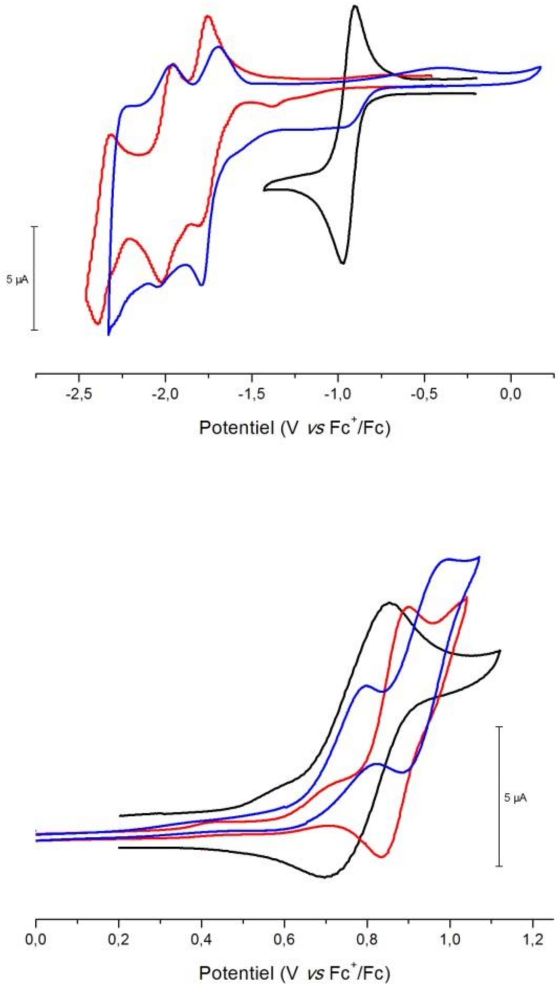
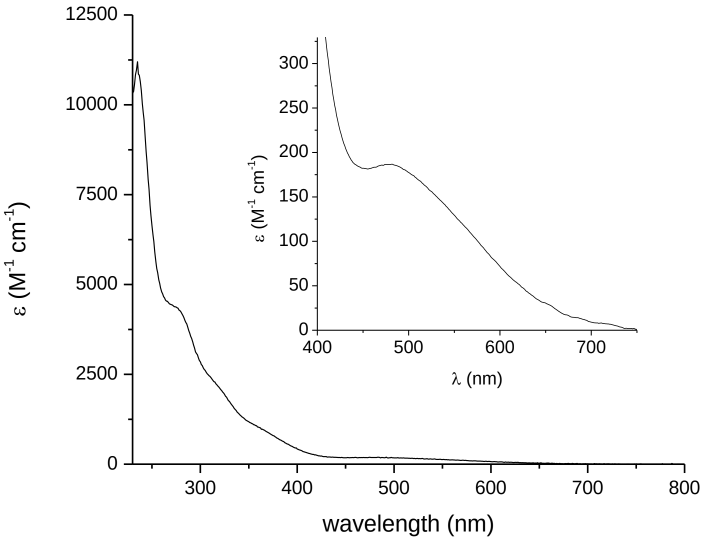


Figure S5. Cyclic voltammograms of complexes **1** (red), **2** (black) and **4** (blue) recorded at 1 mM in a CH_3CN solution of *n*-Bu_4NPF_6 (0.1 mol.L^{-1}), at a scan rate of 100 mV.s^{-1}, with glassy carbon (top) or platinum (bottom) working electrodes.



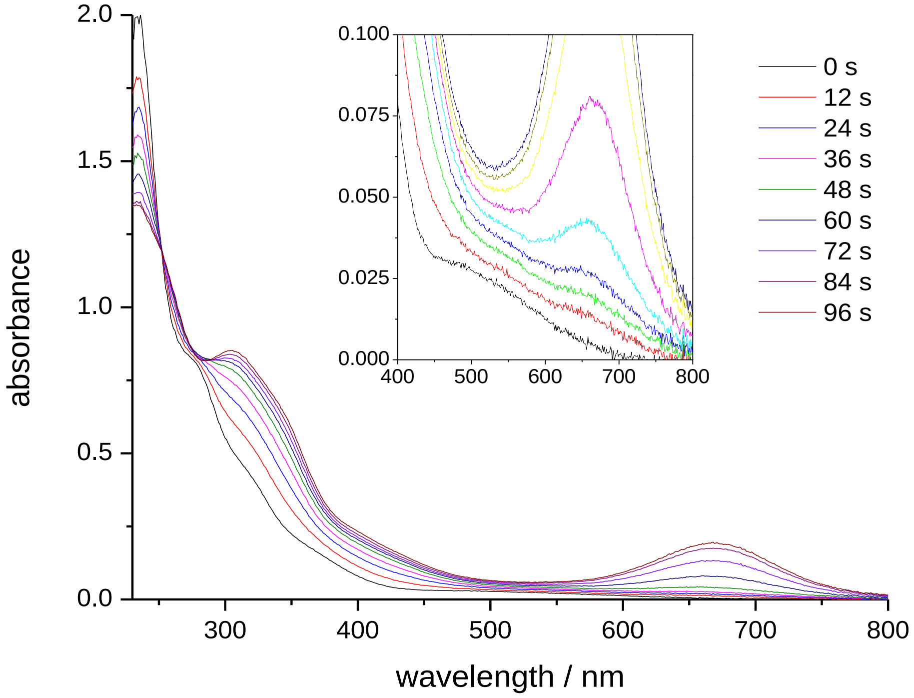


Figure S6. *Top*: UV-vis absorption spectrum of reference complex [Cu(DO)(DOH)pn(OH$_2$)](ClO$_4$) displaying an absorption band at 480 nm (inset) corresponding to a spin-forbidden d–d transition. *Bottom*: Spectroelectrochemical reduction (– 0.7 V *vs*. Ag/AgCl) of a 1 mM solution of [Cu(DO)(DOH)pn(OH$_2$)](ClO$_4$) in a CH$_3$CN solution of *n*-Bu$_4$NPF$_6$. A new absorption band centred at 665 nm grows during the course of the electrolysis.

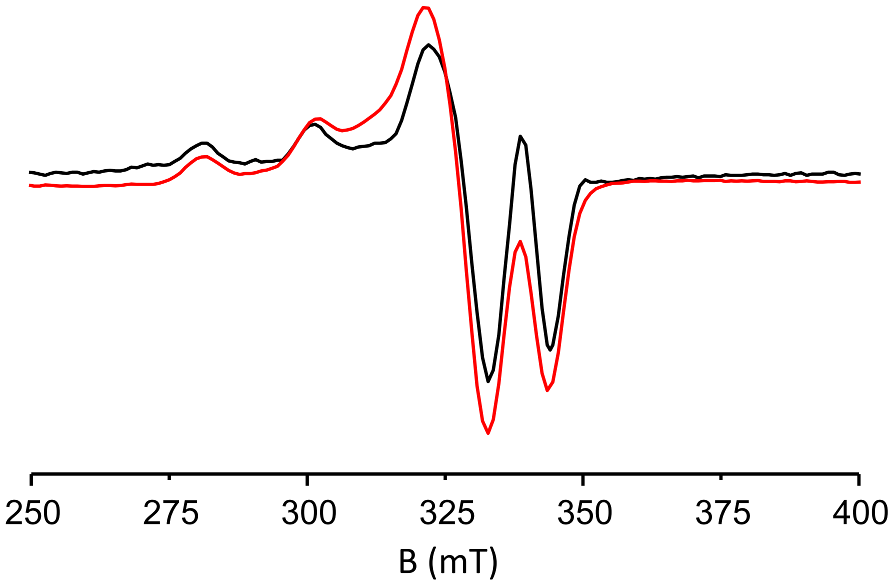


Figure S7. X-band EPR spectra of **2** (black) and **4** (red) recorded in CH_3CN at 42 K.

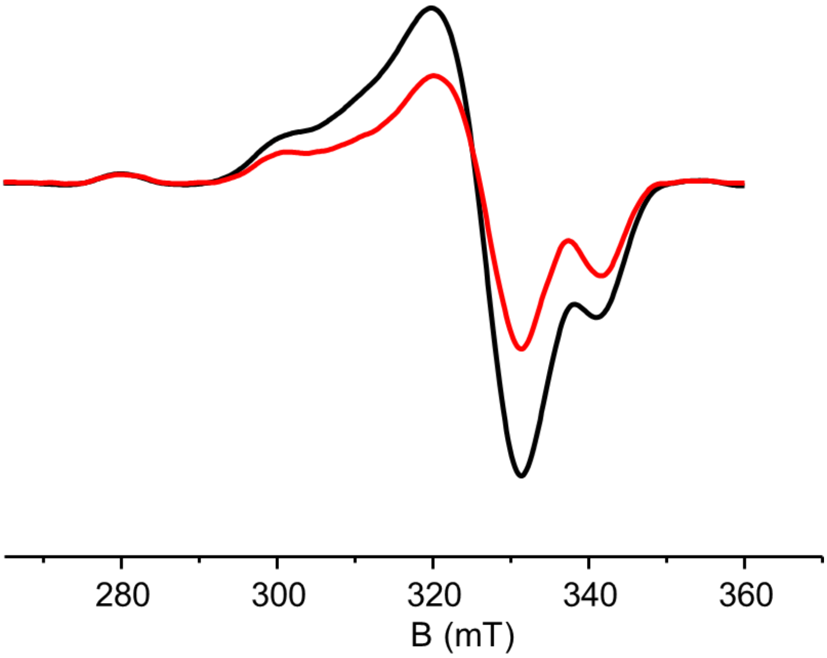


Figure S8. Evolution of the X-band EPR spectrum of **4** in CH_3CN in absence of TEA before (black) and after (red) 1 hour of irradiation.

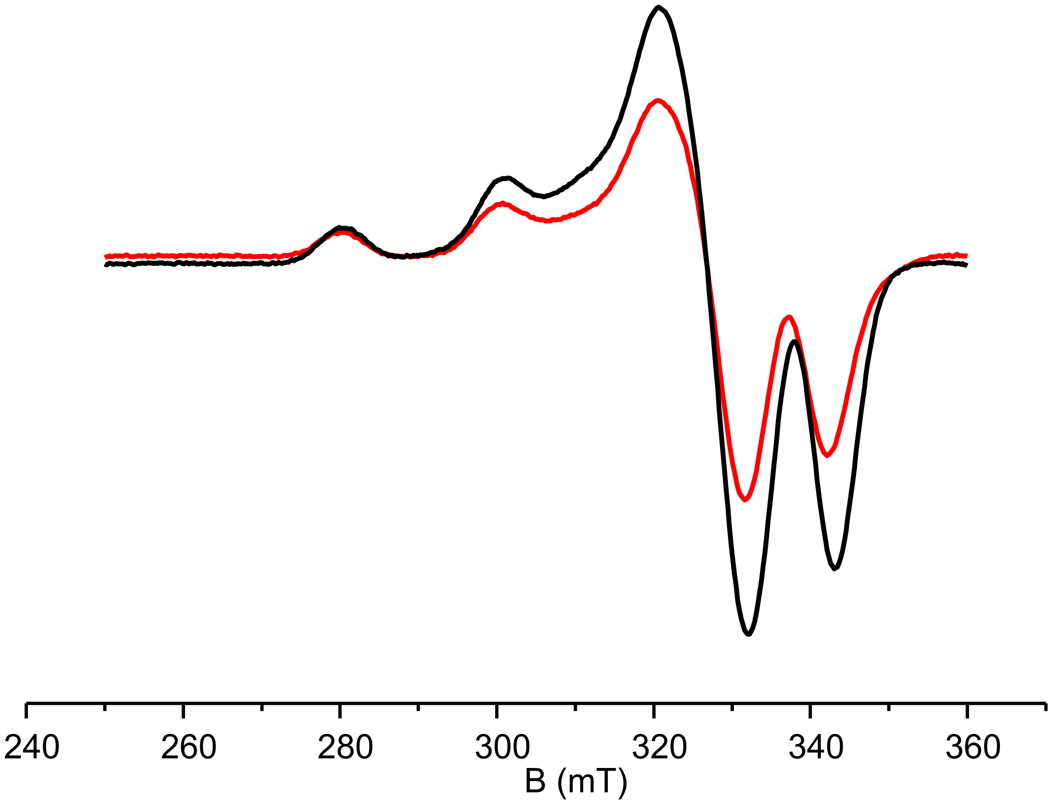


Figure S9. X band EPR spectrum of **4** in CH_3CN in presence of TEA (200 eq) before (black) and after (red) 1 hour in the dark. The loss of about 15 % of the initial signal could be primary attributed to the formation of EPR silent Cu(II) dimers (antiferromagnetically coupled) issued form residual water deprotonation.

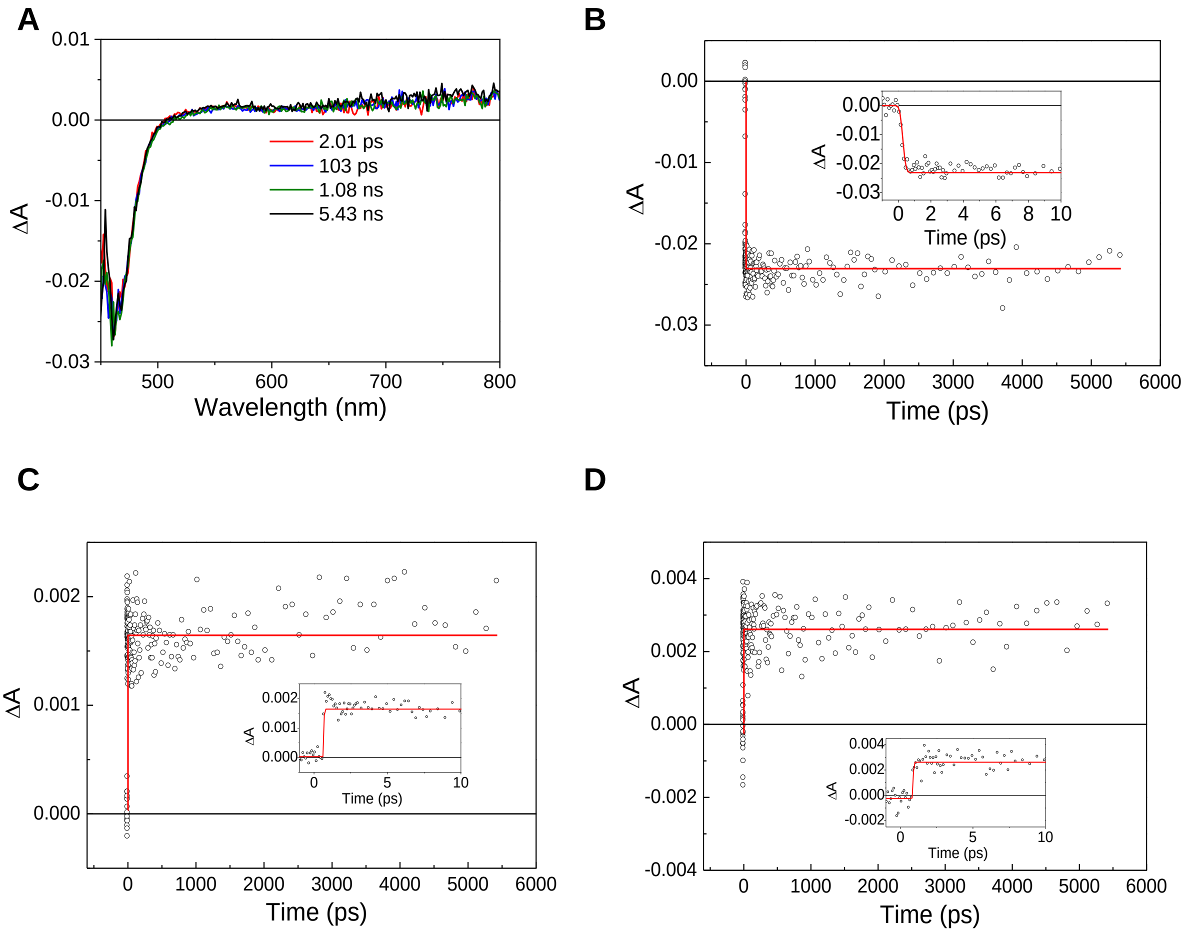


Figure S10. Femtosecond transient absorption spectra of **1** recorded in acetonitrile after excitation with a 414 nm laser pulse (A). Transient kinetics at 465 nm (B), 565 nm (C) and 775 nm (D). Insets: short pump to probe delay times. The initial sub-2-ps process seen when monitoring the excited state absorption is vibrational relaxation and was not captured in the fit.

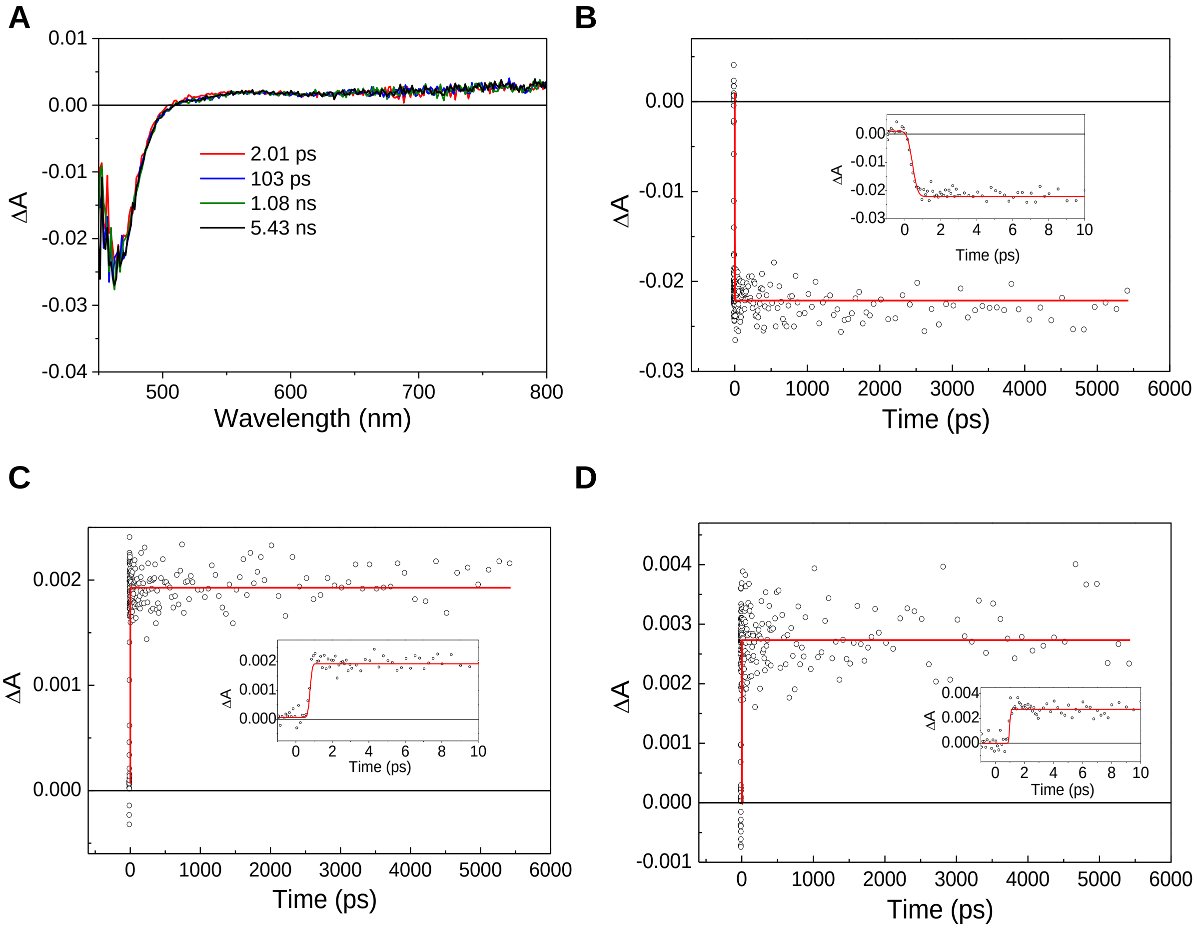


Figure S11. Femtosecond transient absorption spectra of **3** recorded in acetonitrile after excitation with a 414 nm laser pulse (A). Transient kinetics at 465 nm (B), 565 nm (C) and 775 nm (D), respectively. Insets: short pump to probe delay times. The initial sub-2-ps process seen when monitoring the excited state absorption is vibrational relaxation and was not captured in the fit.

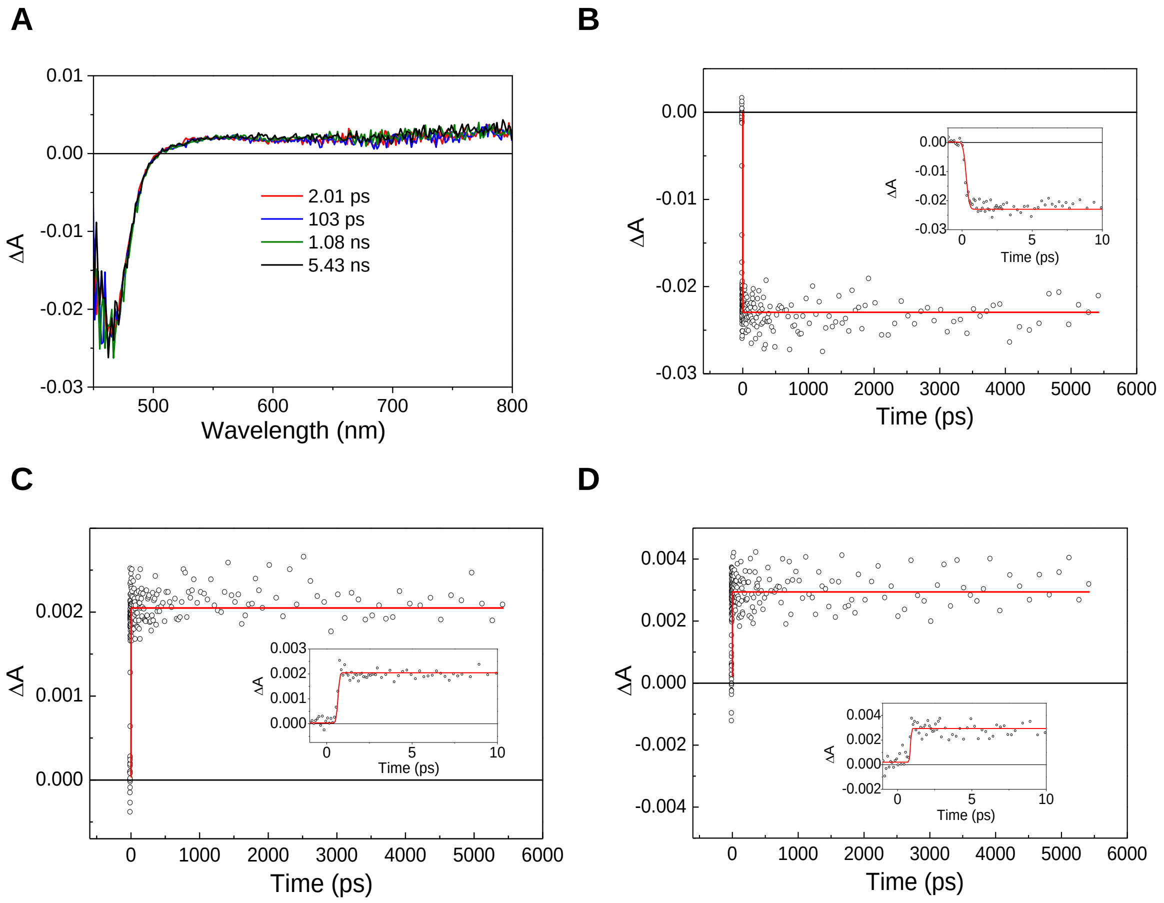


Figure S12. Femtosecond transient absorption spectra of **4** recorded in acetonitrile after excitation with a 414 nm laser pulse (A). Transient kinetics at 465 nm (B), 565 nm (C) and 775 nm (D), respectively. Insets: short pump to probe delay times. The initial sub-2-ps process seen when monitoring the excited state absorption is vibrational relaxation and was not captured in the fit.

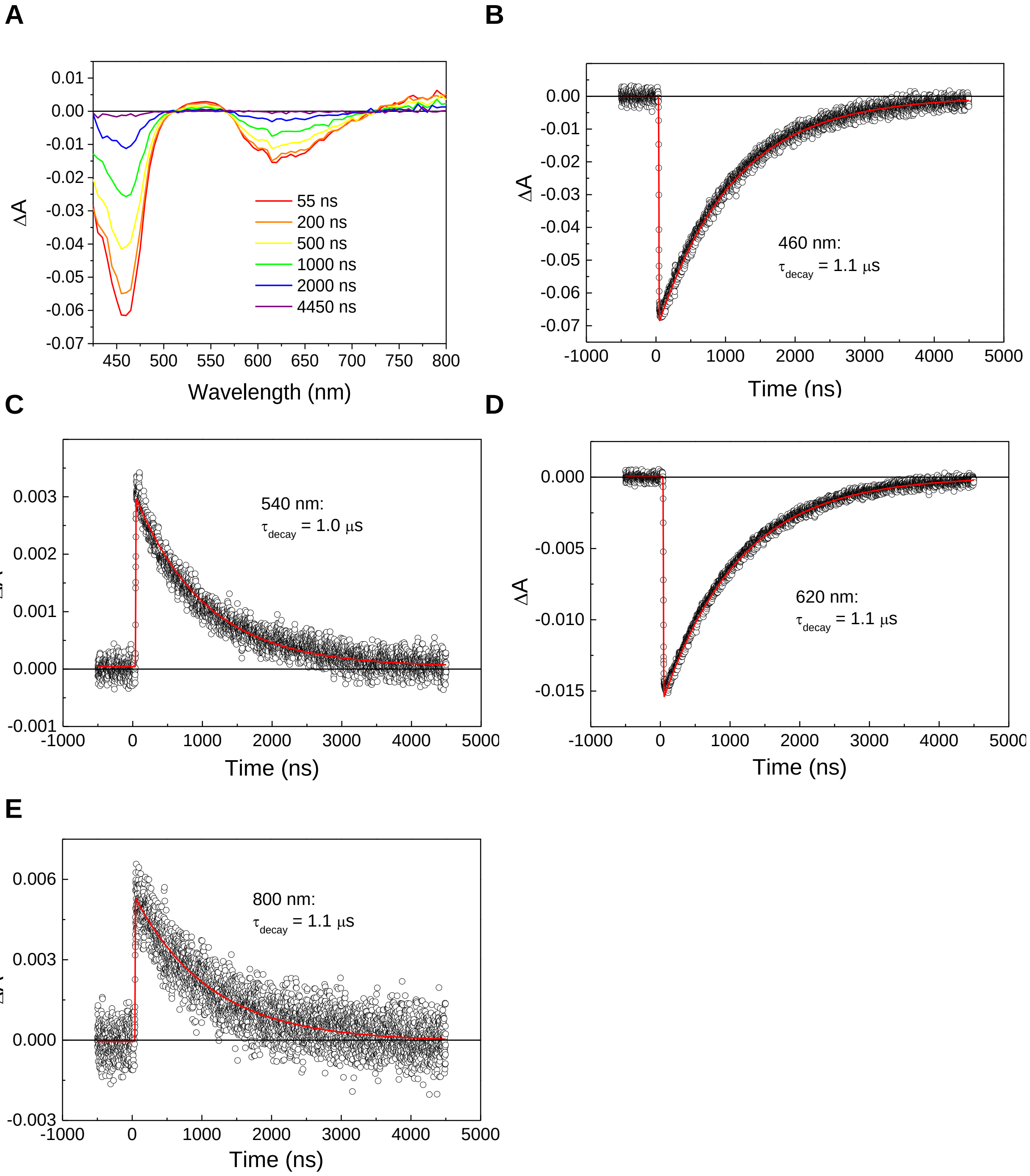


Figure S13. (A) Nanosecond transient absorption spectra of **3** following 416 nm excitation in acetonitrile. (B, C, D, and E) Transient kinetics at 460 nm, 540 nm, 620 nm, and 800 nm respectively.

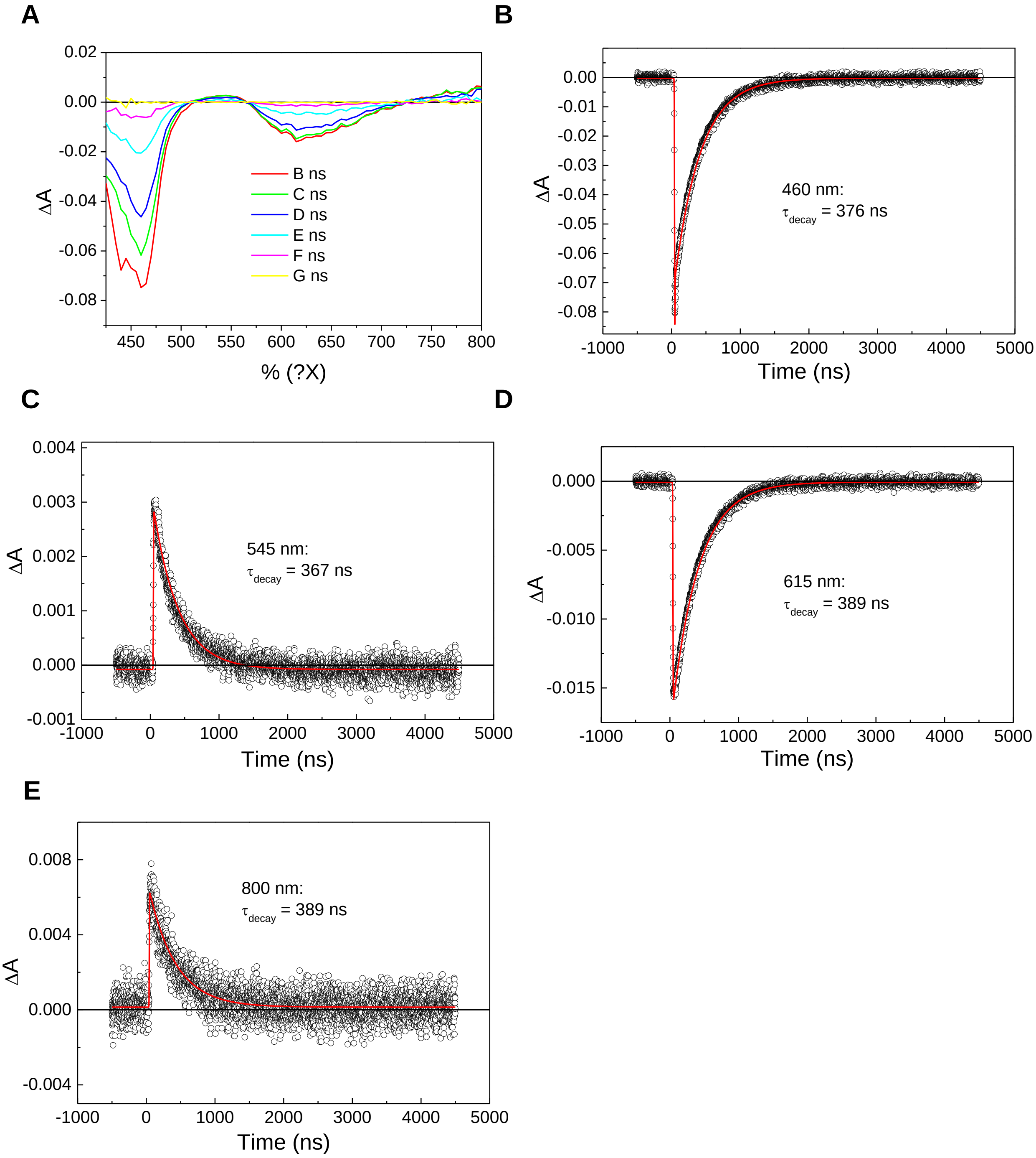


Figure S14. (A) Nanosecond transient absorption spectra of dyad **4** following 416 nm excitation in acetonitrile. (B, C, D, and E) Transient kinetics at 460 nm, 545 nm, 615 nm, and 800 nm respectively.

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