Manganese Carbonyl Terpyridyl Complexes. Their Synthesis, Characterization and Potential Application as CO-Release Molecules.

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Electronic Supplementary Information

• Experimental Section

Syntheses

All commercially available reagents were used as purchased without further purifications. Due to the complexes being highly light-sensitive, all the reaction mixtures were kept in the dark using Al foils.

fac-[Mn(terpy-$\kappa^2 N^1,N^2$)$(CO)_3$Br] (**1a**): [Mn$(CO)_5$Br] (200 mg, 0.73 mmol) and 2,2':6',2"-terpyridine (120 mg, 0.51 mmol) are dissolved in 30 mL of diethyl ether. The resulting solution is refluxed for 3 h, and allowed to cool down to RT before the dark yellow solid is filtered. Excess of [Mn$(CO)_5$Br] is eliminated by vigorously stirring the crude product in 50 mL of diethyl ether for 30 min, filtering and thoroughly washing with diethyl ether. Yield: 201 mg (87% /terpy). **FTIR** (KBr pellets, C≡O stretching region): ν/cm^{-1} = 2032(s); 1937(s); 1914(s). **^{1}H-NMR** (300 MHz, CD_3CN): δ/ppm = 9.24 (1H, d, J=5.2 Hz); 8.79 (1H, d, J=4.5 Hz); 8.40 (2H, d, J=7.8 Hz); 8.17 (2H, m); 7.98 (1H, m); 7.81 (1H, d, J=7.8 Hz); 7.72 (1H, d, J=7.8 Hz); 7.58 (2H, m). **^{13}C-NMR** (75 MHz, CD_3CN): δ/ppm = 164.4; 159.7; 158.2; 158.0; 154.2; 150.6; 140.2; 140.0; 138.1; 128.3; 127.0; 126.0; 125.8; 124.7; 123.2. **UV-Vis** (CH_3CN): λ_{max}/nm (ε/M^{-1} cm^{-1}) = 302 (17000); 373 (2200,sh); 409 (2400). **Anal. calc.** for $C_{18}H_{11}BrMnN_3O_3$: C 47.8; H 2.4; N 9.3; Br 17.7; Mn 12.1; Found: C 47.3; H 2.7; N 9.2; Br

17.8; Mn 12.1. Single crystals suitable for X-ray diffraction were grown by slow vapor diffusion of diisopropyl ether into a solution of **1a** in DMF.

fac-[Mn(terpy–κ^2*N*^{1},*N*^{2})(CO)$_3$(MeCN)](PF$_6$) (**1b**): **1a** (100 mg, 0.22 mmol) is dissolved in 10 mL of acetonitrile, then a solution of AgPF$_6$ (56 mg, 0.22 mmol) in 2 mL of acetonitrile is added. After stirring for 30 min at RT, the silver bromide precipitate is eliminated by filtration through celite. The filtrate is evaporated under reduced pressure with moderate heating (35 °C) to obtain **1b** as a yellow-green solid. Yield: 117 mg (95% /**1a**). **FTIR** (KBr pellets, C≡O stretching region): ν/cm^{-1} = 2043(s), 2026(m,sh), 1978(s), 1946(s). **^{1}H-NMR** (300 MHz, CD$_3$CN): δ/ppm = 9.18 (1H, d, *J*=5.4 Hz); 8.81 (1H, d, *J*=4.5 Hz); 8.48 (2H, m); 8.28 (2H, m); 8.03 (1H, m); 7.82 (2H, m); 7.72 (1H, m); 7.61 (1H, m). **^{13}C-NMR** (75 MHz, CD$_3$CN): δ/ppm = 164.7; 159.2; 157.8; 157.5; 155.0; 150.7; 141.3; 141.1; 138.5; 129.4; 128.1; 126.3; 125.8; 125.3; 123.8. **UV-Vis** (CH$_3$CN): λ_{max}/nm (ε/M^{-1} cm^{-1}) = 280 (1.4×10^4); 296 (1.4×10^4); 370 (2800). **Anal. calc.** for $C_{20}H_{14}F_6MnN_4O_3P$: C 43.0; H 2.5; N 10.0; F 20.4; Mn 9.9; P 5.6; Found: C 42.4; H 2.8; N 9.0; F 20.6; Mn 10.3; P 5.4.

mer,cis-[Mn(terpy-κ^3*N*^{1},*N*^{2},*N*^{3})(CO)$_2$(MeCN)](PF$_6$) (**2**): In a Schlenk flask protected from light (Al foils), 100 mg of **1b** are dissolved in a mixture of 20 mL of water and 10 mL acetonitrile under vigorous stirring. The system is kept at 30 °C and set under vacuum. After 6 h of stirring the solvent is evaporated, before the resulting solid is dissolved in acetonitrile. After the few insoluble impurities have been eliminated by centrifugation, the solvent is evaporated to obtain **2** as a dark green powder, which is then dried under vacuum for several hours. Yield: 70 mg (74% /**1b**). **FTIR** (KBr pellets, C≡O stretching region): ν/cm^{-1}= 1957(s), 1951(s), 1872(s,sh), 1864(s). **^{1}H-NMR** (300 MHz, CD$_3$CN): δ/ppm = 8.57 (2H, d, *J*=5.4 Hz); 8.39 (3H, m); 8.26 (2H, d, *J*=8.0 Hz); 7.97 (2H, m); 7.37 (2H, m). **^{13}C-NMR** (75 MHz, CD$_3$CN): δ/ppm = 157.8; 157.3; 156.8; 140.4; 139.3; 128.0; 124.1; 122.9. **UV-Vis** (CH$_3$CN): λ_{max}/nm (ε/M^{-1} cm^{-1}) = 280 (1.6×10^4); 323 (2.0×10^4); 380 (2200); 456 (2400); 617 (870). **Anal. calc.** for $C_{19}H_{14}F_6MnN_4O_2P$: C 43.0; H 2.6; N 10.6; F 21.5; Mn 10.4; P 5.9; Found: C 42.3; H 2.3; N 10.3; F 20.8; Mn 10.4; P 5.5.

Instrumentation

All characterizations were performed as much as possible in the absence of light. ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker Avance 300 spectrometer; chemical shifts are quoted against TMS. IR spectra were recorded on a Perkin-Elmer Spectrum GX FT-IR spectrometer using pressed KBr pellets. UV-Vis spectra were recorded on either a Varian Cary-300 or a Zeiss MCS-501 UV-NIR spectrophotometer using conventional quartz cuvettes of optical path length l = 1 cm or 2 mm. Elemental analyses were performed by the Service Central d'Analyses – Institut des Sciences Analytiques du CNRS, 69100 Villeurbanne, France.

Single crystal X-ray diffraction: intensity data collections were carried out with a Bruker KAPPA APEX 2 DUO diffractometer equipped with a CCD bidimensional detector using Mo Kα monochromatized radiation (λ=0.71073 Å). The measurement was performed at 100 K. The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELX-TL package.[1] **Crystal data for 1a:** $C_{18}H_{11}BrMnN_3O_3$, Mr = 452.15, monoclinic, space group $P2_1/c$, a = 15.8469(3) Å, b = 6.99830(10) Å, c = 16.9166(3) Å, β = 115.8320(10)°, V = 1688.61(5) Å^3, Z = 4, ρ_{calcd} = 1.779 Mg m^{-3}, T = 100(2) K, μ(Mo$_{K\alpha}$) = 3.172 mm^{-1}. 19066 reflections were measured, of which 5168 were unique (R_{int} = 0.0316). R_1 = 0.0258 [$I>2\sigma(I)$]; wR_2 = 0.0616 (all data). The hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C–H = 0.95 Å, and U_{iso} = 1.2 U_{eq}(parent atom). CCDC 961705 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Photoirradiation experiments: photoirradiation was performed with either a Hamamatsu Lightnincure LC8 lamp or a Dolan-Jenner Fiber-Lite DC950 quartz halogen lamp, equipped with filters centered on 372 or 417 nm depending on the experiment. Measurements done in the absence of O_2 were performed in a tight-closed quartz cell purged by an argon flow for 30 min, in the dark, prior to irradiation. Gas chromatography (GC) was performed on a Perkin-

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[1] G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112.

Elmer Clarus 500 gas chromatograph equipped with a Clarus 560 S mass spectrometer, using an external standard from Air Liquide France Industrie for CO quantification.

Quantum yield of the decarbonylation reaction was determined by monitoring the increase of the characteristic absorption bands of product **2** (λ_{max} = 456 and 617 nm), when irradiating a solution of **1b** in CH_3CN at λ_{irr} = 372 nm, in a 1 cm path length tight-sealed quartz cell purged with argon prior to experiment. The quantum yield ϕ is then given by equation (E1):

$$\frac{dA}{dt} = \varepsilon I_a \phi \qquad \text{(E1)}$$

where ε is the molar absorption coefficient at the observed wavelength (see the synthesis section), and I_a the light absorption intensity. We have assumed I_a to be constant as long as the conversion yield remains relatively low ([**2**]/[**1b**] < 10%). I_a has been determined by irradiating in the same conditions a solution of *trans(Cl)*-[Ru(bpy)(CO)$_2$Cl$_2$], and monitoring the increase of the absorption A_{ref} of the photoproduct [Ru(bpy)(CO)(MeCN)Cl$_2$] at λ_{max} = 460 nm, according to equation (E2):

$$I_a = \frac{1}{\varepsilon_{ref}\phi_{ref}} \frac{dA_{ref}}{dt} \qquad \text{(E2)}$$

with $\varepsilon_{\mathrm{ref}}$(460 nm) = 1530 M^{-1} cm^{-1} and $\phi_{\mathrm{ref}} = 1$, according to previously reported results.[2]

Electrochemistry: cyclic voltammogramms (CVs) were recorded under argon atmosphere at RT in a conventional three-electrodes cell, using a SP300 potentiostat/galvanostat controlled by an EC-Lab software, or an EG & Princeton Applied Research Model 173 potentiostat/galvanostat equipped with a Sefram TGM 164 X-Y recorder. The electrolyte was 0.1 M tetrabutylammonium perchlorate (TBAP). The working electrode was a glassy carbon disk (3 mm diameter) cleaned by polishing with 2 µm diamond compound (Diamantmittel Mecaprex Presi), the counter electrode a platinum plate, isolated from the electrolytic working solution through an CH_3CN + 0.1 M TBAP solution bridge, the reference a Ag/AgNO$_3$ (10 mM) electrode in CH_3CN + 0.1 M TBAP. All the potentials are quoted vs. Ag/Ag$^+$. In all experiments the potential scan rate was 100 mV s^{-1}. Electrocatalysis experiments are run at RT under CO_2 in a conventional three-electrode cell made airtight with vacuum grease (M. Apiezon). The total volume occupied by the gas in this cell is about 146 mL. Exhaustive electrolysis are carried out with a 28 x 28 x 2 mm CV plate (Goodfellow). During the

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[2] M.-N. Collomb-Dunand-Sauthier, A. Deronzier and R. Ziessel, *J. Organomet. Chem.*, 1993, **444**, 191.

electrolysis the gas is sampled directly from the electrochemical cell to the GC through injection of 100µL of sample using a gas-tight syringe. Gases (CO, H_2, CO_2) are analyzed on a Perkin Elmer 500 gas chromatograph equipped with a PDIP detector and a 30 m Carboplot 1010 column (Antelia). The concentration of produced gases is calculated by using standard gas mixture (Air liquide). Helium is used as the carrier gas.

• Figures

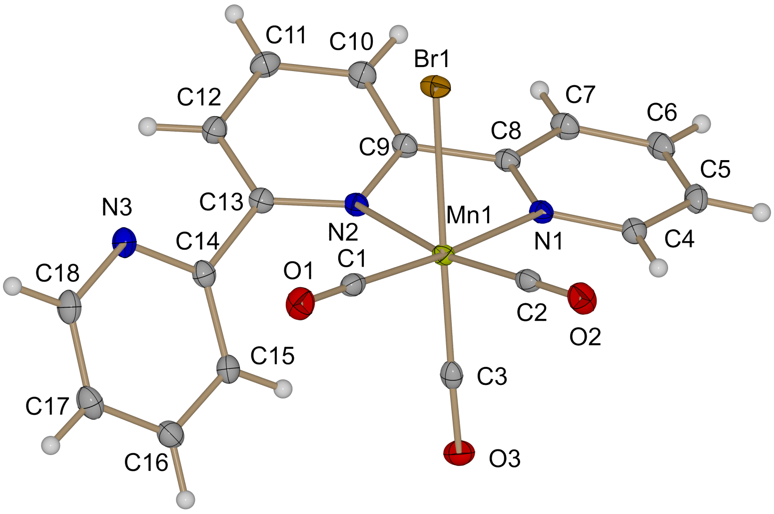

Figure S1. Representation of the crystallographic structure of **1a** as thermal ellipsoids (50% probability) with atoms labeling scheme. H atoms (white spheres) were positioned geometrically and constrained to ride on their parent atoms (see experimental section for details).

Table S1. Selected bond lengths (Å) and angles (°) for **1a.**

Br(1)-Mn(1)	2.5492(3)
Mn(1)-C(3)	1.7908(18)
Mn(1)-C(2)	1.8082(18)
Mn(1)-C(1)	1.8209(17)
Mn(1)-N(1)	2.0454(14)
Mn(1)-N(2)	2.1050(14)
C(2)-Mn(1)-C(1)	86.74(8)
N(1)-Mn(1)-N(2)	78.84(6)
C(3)-Mn(1)-Br(1)	176.94(6)

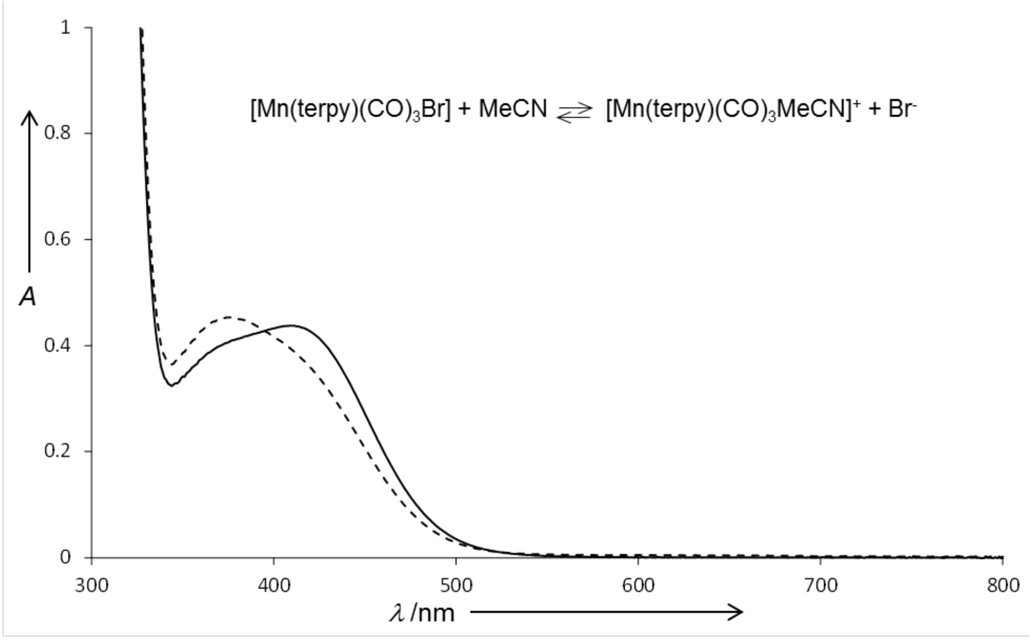

Figure S2. UV-Vis spectra of an acetonitrile solution of **1a**, 60 s after dissolution (solid line) and 6 h later (dotted line). The system eventually reaches an equilibrium between coordinated bromine and free bromide anions in solution. *C* = 1 mM, optical path length *l* = 2.00 mm.

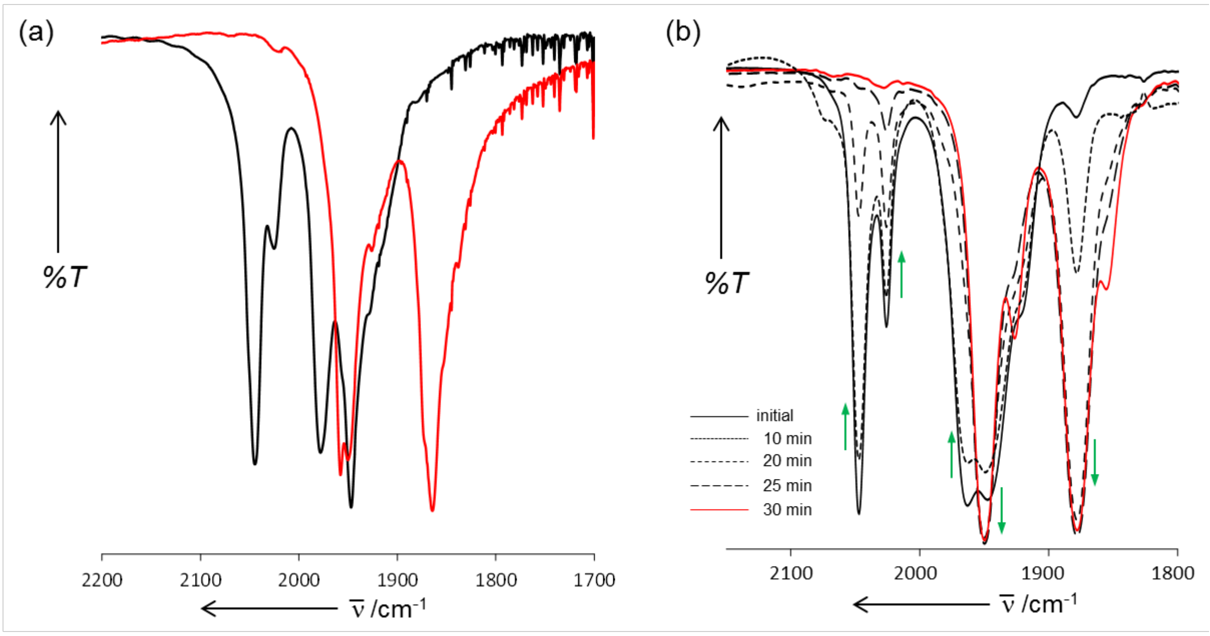

Figure S3. (a) FT-IR spectra (KBr pellets) of **1b** (black) and **2** (red) in the C≡O stretching region, showing the conversion of the tricarbonyl complex into the dicarbonyl one; (b) evolution of the FT-IR spectrum of a solution of **1b** in acetonitrile (C ≈ 10 mM) under irradiation at λ_{irr} = 370 nm.

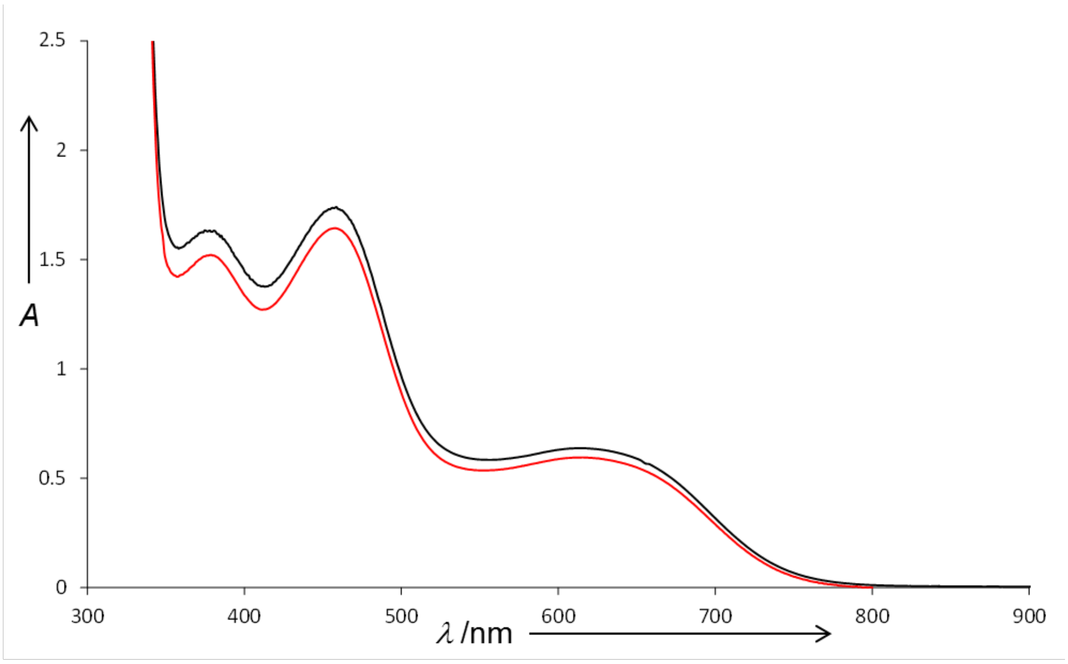

Figure S4. UV-Vis spectra of a photoirradiated solution of **1b** in acetonitrile (λ_{irr} = 370 nm, black), and of **2** dissolved in acetonitrile (red). C = 0.74 mM, optical path length l = 1.00 cm.

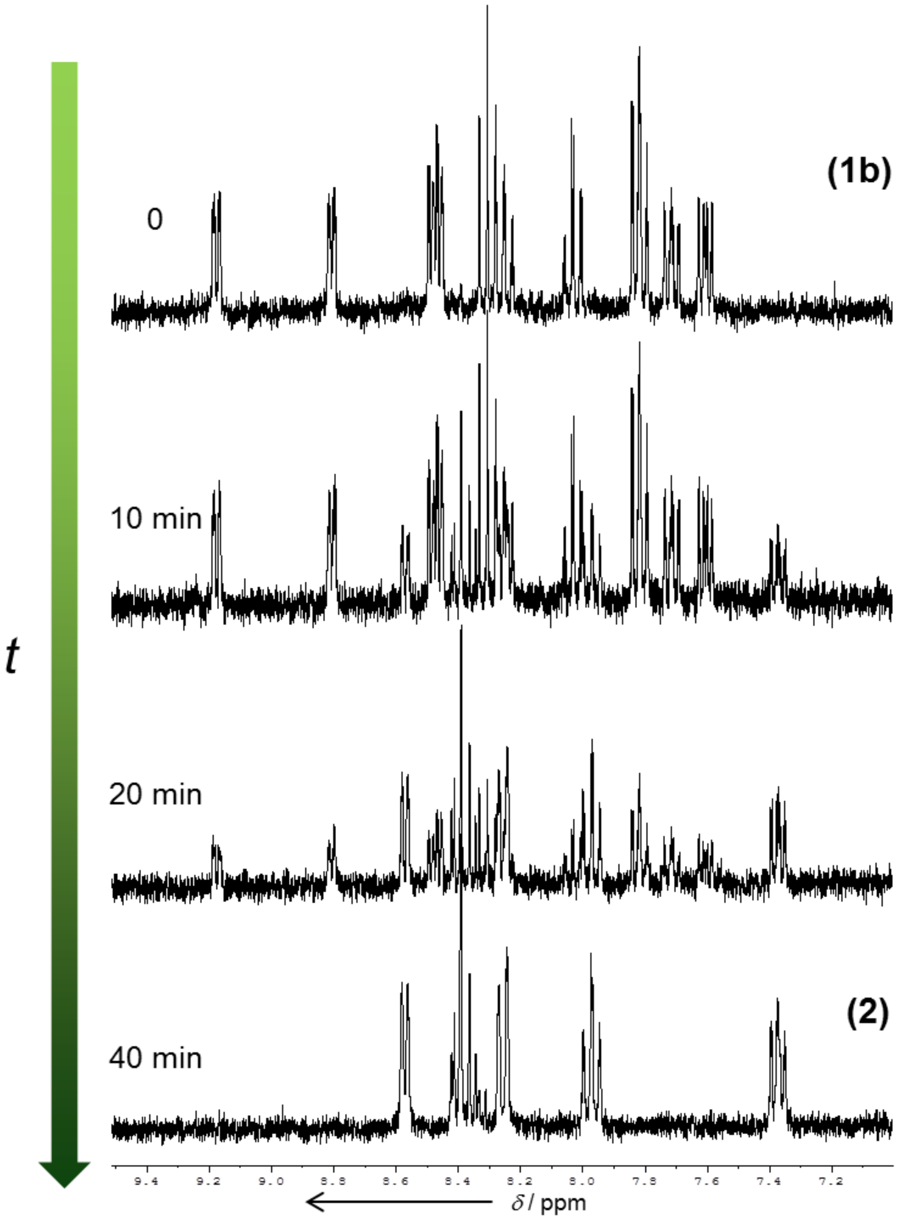

Figure S5. Evolution of the ^{1}H NMR spectrum (7.0 – 9.5 ppm region) of a solution of **1b** in CD_3CN ($C \approx 0.8$ mM) under irradiation at $\lambda_{irr} = 370$ nm.

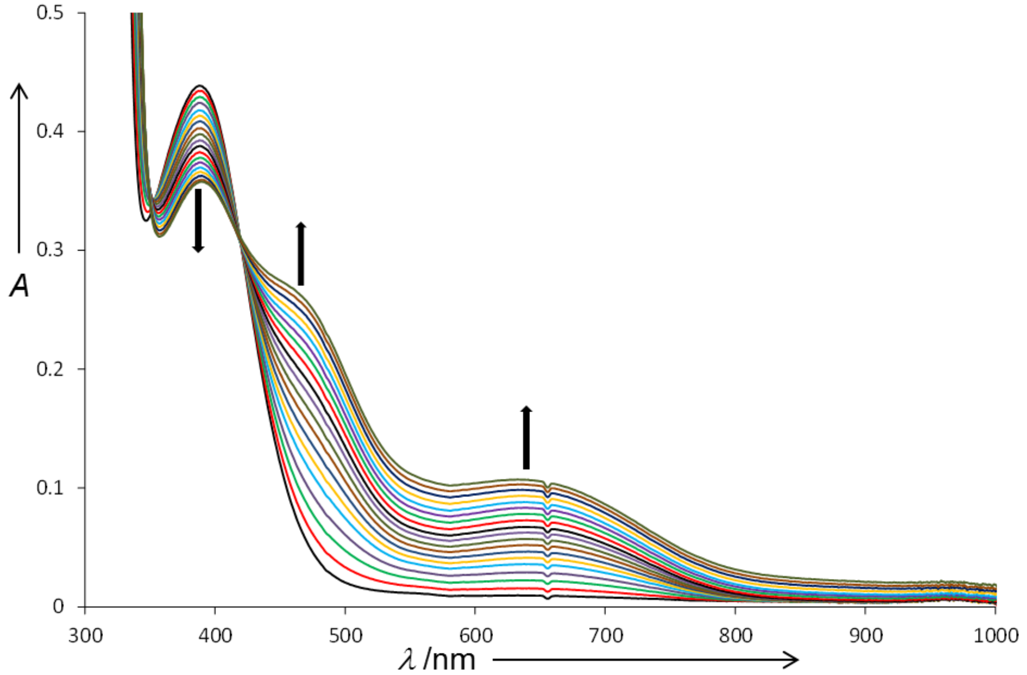

Figure S6. UV-Vis spectra showing the evolution of a solution of **1b** in water (C = 0.20 mM) under irradiation at λ_{irr} = 417 nm.
One spectrum recorded every 20 s, optical path length l = 1.00 cm.

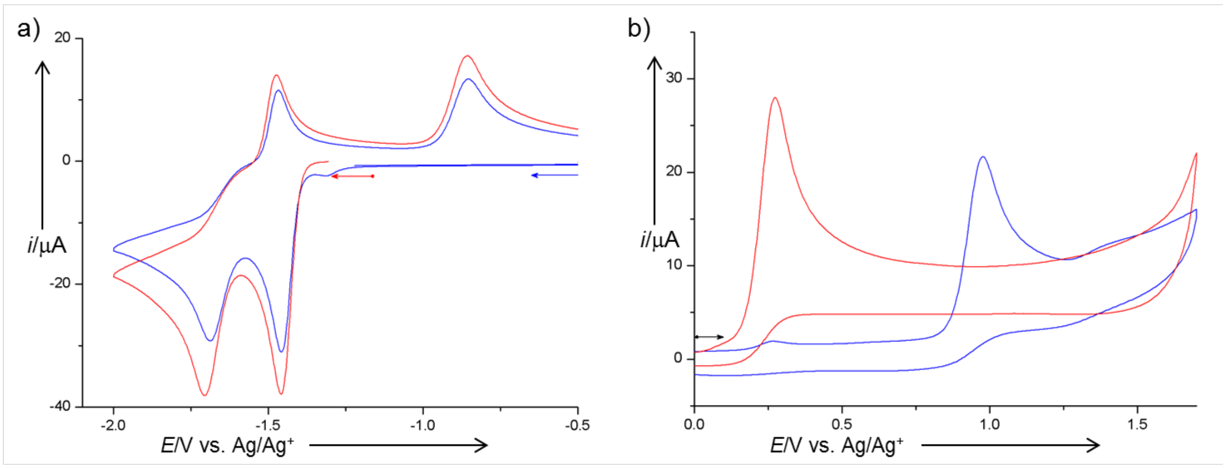

Figure S7. CVs of **1b** (blue, C = 1.1 mM) and **2** (red, C = 1.2 mM), (a) towards reduction and (b) towards oxidation, in acetonitrile + 0.1 M TBAP. Working electrode 3 mm diameter glassy carbon, reference Ag/Ag$^+$, scan rate v = 100 mV s^{-1}.

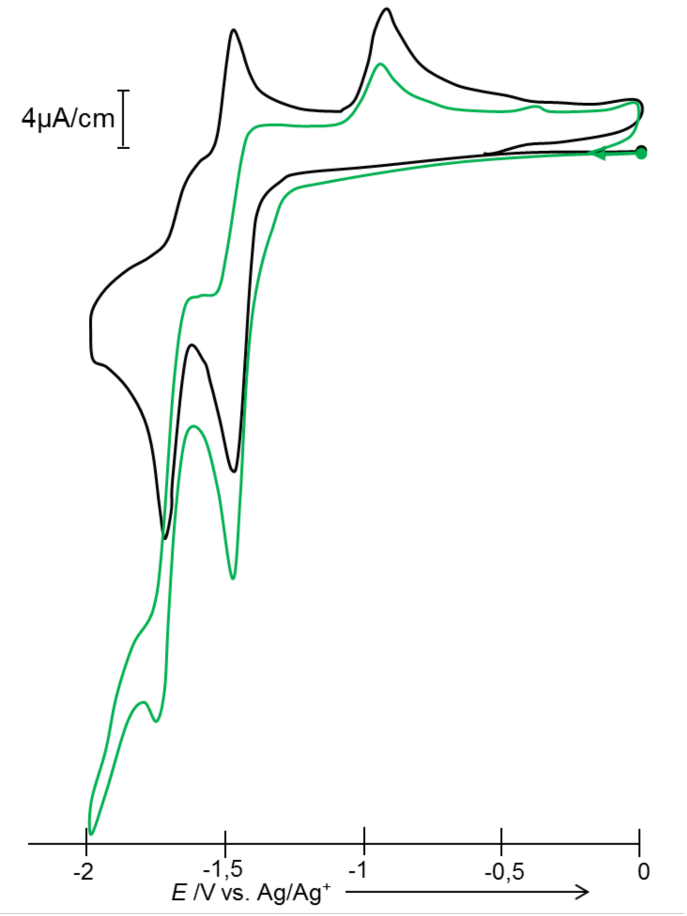

Figure S8. CVs of 1 mM solutions of **1a** in acetonitrile + 0.1 M TBAP; black: under Ar, green: under CO_2 + 5% H_2O. v = 100 mV s^{-1}.