Electronic Supporting Information

A stable and strongly luminescent dinuclear Cu(I) helical complex prepared from 2-diphenylphosphino-6-methylpyridine

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Experimental section

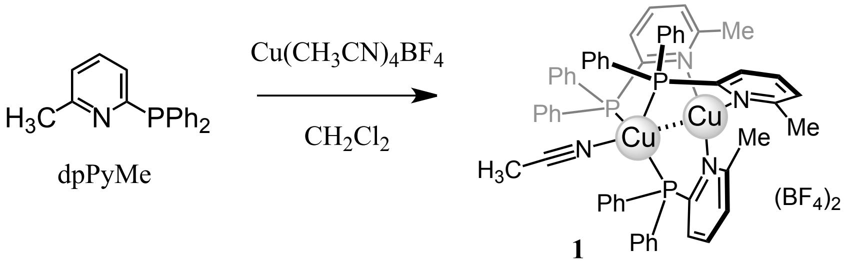
General. Dichloromethane (CH_2Cl_2) was distilled over CaH_2 under Ar. All reactions were performed in standard glassware under an inert Ar atmosphere. Evaporation and concentration were done at water aspirator pressure and drying in vacuo at 10^{-2} Torr. Column chromatography: silica gel 60 (230-400 mesh, 0.040-0.063 mm) was purchased from E. Merck. Thin Layer Chromatography (TLC) was performed on aluminum sheets coated with silica gel 60 F_{254} purchased from E. Merck. IR spectra (cm^{-1}) were recorded on a Perkin–Elmer Spectrum One Spectrophotometer. NMR spectra were recorded on a Bruker AC 300 or AC 400 with solvent peaks as reference. ESI-MS mass spectra were carried out on a Bruker MicroTOF spectrometer.

Electrochemistry. The electrochemical measurements were carried out with a potentiostat Autolab PGSTAT100. Experiments were performed at room temperature in a homemade airtight three–electrode cell connected to a vacuum/argon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a platinum wire of *ca*. 1 cm^2 apparent surface. The working electrode was a Pt microdisk (0.5 mm diameter). The supporting electrolyte $n\mathrm{Bu_4NBF_4}$ (Fluka, 99% electrochemical grade) was used as received and simply degassed under argon. Dichloromethane was freshly distilled over CaH_2 prior to use. The solutions used during the electrochemical studies were typically 10^{-3} M in compound and 0.1 M in supporting electrolyte. Before each measurement, the solutions were degassed by bubbling Ar and the working electrode was polished with a polishing machine (Presi P230). Under these experimental conditions, Fc/Fc^+ is observed at +0.55 ± 0.01 V *vs*. SCE.

Photophysical studies. Dichloromethane (Carlo Erba, spectrofluorimetric grade) was used as solvent without further purification. Absorption spectra were recorded with a Perkin-Elmer Lambda 950 UV/vis/NIR spectrophotometer. For luminescence experiments, the solution samples were placed in fluorimetric 1-cm path cuvettes and, when necessary, they were deoxygenated in a special cuvette by bubbing argon for 20 min.; solid state measurements were carried out with discs, prepared by finely grinding the samples with KBr (Sigma Aldrich, puriss) and pressed. Uncorrected emission spectra were obtained with an Edinburgh FLS920 spectrometer equipped with a peltier-cooled Hamamatsu R928 photomultiplayer tube

(185–850 nm). An Edinburgh Xe900 450 W Xenon arc lamp was used as exciting light source. Corrected spectra were obtained via a calibration curve supplied with the instrument. Luminescence quantum yields (Φ_{em}) in solution obtained from spectra on a wavelength scale [nm] were measured according to the approach described by Demas and Crosby[1] using air-equilibrated $Ru(bpy_3)_3Cl_2$ in water solution, $\Phi_{em} = 0.028$, as standard. The solid state Φ_{em} have been calculated by corrected emission spectra obtained from an apparatus consisting of barium sulfate coated integrating sphere (6 in.), with the same light source and detector stated above, following the procedure described by De Mello et al.[2] Fluorescence lifetimes were measured with an IBH 5000F time-correlated single-photon counting spectrometer using pulsed NanoLED excitation sources at 331 nm. Analysis of the luminescence decay profiles against time was accomplished with the Decay Analysis Software DAS6 provided by the manufacturer. The luminescence spectra at 77 K were measured using a Perkin-Elmer LS-50B spectrofluorimeter equipped with a pulsed Xe lamp. The rigid matrices were prepared by filling the sample solutions in glass tubes and subsequently inserted into special quartz dewar, filled up with liquid nitrogen to cool down the solution temperature to 77 K. Experimental uncertainties are estimated to be ± 8% for lifetime determinations, ± 20% for emission quantum yields, ± 2 nm and ± 5 nm for absorption and emission peaks respectively.

Compound 1



A solution of $Cu(CH_3CN)_4BF_4$ (227 mg, 0.721 mmol) and dpPyMe (300 mg, 1.08 mmol) in CH_2Cl_2 (40 mL) was stirred at room temperature. After 3 h, the solvent was evaporated. Recrystallization by vapor diffusion of Et_2O into a CH_2Cl_2 solution of the crude product gave **1** (351 mg, 83%). Colourless crystals. ^{1}H-NMR (CD_2Cl_2, 300 MHz, 293 K): 7.56 (t, $J = 7$ Hz, 3H), 7.42 (m, 6H), 7.31 (m, 12H), 7.10 (m, 15H), 6.91 (d, $J = 7$ Hz, 3H), 2.40 (s, 9H), 1.92 (s,

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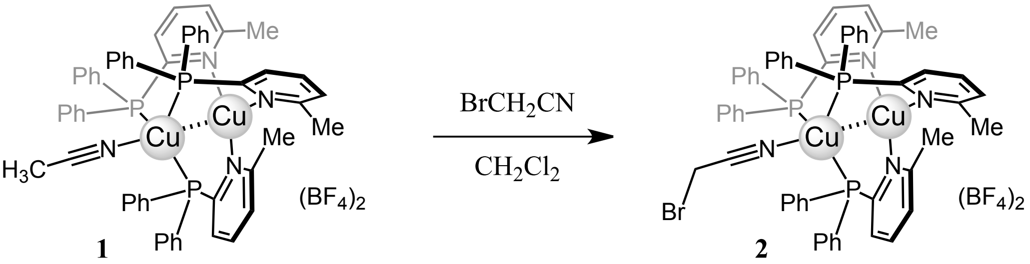
[1] G. A. Crosby and J. N. Demas, *J. Phys. Chem.*, 1971, **75**, 991.
[2] J. C. de Mello, H. F. Wittmann and R. H. Friend, *Adv. Mater.,* 1997, **9**, 230.

3H). $^{31}P\{^{1}H\}$-NMR (CD_2Cl_2, 293 K, 162 MHz): 2.09. ESI-MS: 340.04 (97%, $[Cu(dpPyMe)]^{+}$), 617.17 (100%, $[Cu(dpPyMe)_2]^{+}$), 894.29 (16%, $[Cu(dpPyMe)_3]^{+}$). Anal. Calcd for $C_{56}H_{47}N_4P_3Cu_2B_2F_8.1/2CH_2Cl_2$: C, 55.80; H, 4.31; N, 4.61. Found: C, 55.73; H, 4.40; N, 4.30.

Compound 2



A solution of **1** (150 mg, 0.128 mmol) and 2-bromoacetonitrile (16 mL, 0.135 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 30 min. and evaporated to dryness. The resulting solid was dissolved in CH_2Cl_2 (20 mL) and the solution evaporated (3 X). The resulting solid was dried under high vacuum. Recrystallization by vapor diffusion of Et_2O into a CH_2Cl_2 solution of the crude product gave **2** (130 mg, 81%). Colourless crystals. 7.62 (t, J = 7 Hz, 3H), 7.44 (m, 6H), 7.18 (m, 12H), 7.10 (m, 15H), 6.98 (d, J = 7Hz, 3H), 3.78 (s, 2H), 2.45 (s, 9H). $^{31}P\{^{1}H\}$-NMR (CD_2Cl_2, 293 K, 162 MHz): 3.10. ESI-MS: 340.05 (100%, $[Cu(dpPyMe)]^{+}$), 617.17 (55%, $[Cu(dpPyMe)_2]^{+}$), 894.29 (15%, $[Cu(dpPyMe)_3]^{+}$). Anal. Calcd for $C_{56}H_{46}BrN_4P_3Cu_2B_2F_8$: C, 53.87; H, 3.71; N, 4.49. Found: C, 53.59; H, 3.66; N, 4.34.

X-Ray crystal structure of 1.

Crystals suitable for X-ray crystal-structure analysis were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of **1**. Data were collected at 173 K on a Nonius KappaCCD diffractometer (Mo-Kα radiation, λ = 0.71073 Å). The structure was solved by direct methods (SHELXS-97) and refined against F^2 using the SHELXL-97 software. The non-hydrogen atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. Crystallographic data: formula: $C_{56}H_{51}Cu_2N_4P_3.(BF_4)_2(CH_2Cl_2)_2$ (M =

1343.47 g.mol^{-1}); colourless crystal, 0.18 × 0.15 × 0.07 mm; crystal system: monoclinic, space group P2$_1$/1; a = 20.8139(5) Å; b = 12.7855(4) Å; c = 21.9411(5) Å; α = 90°; β = 94.614(2)°; γ = 90°; V = 5820.0(3) Å^3; Z = 4; F(000) = 2736; a total of 32994 reflections collected; 1.84° < θ < 27.44°, 13271 independent reflections with 8524 having I > 2σ(I); 734 parameters; Final results : R$_1$(F^2) = 0.0599; wR$_2$(F^2) = 0.1274, Goof = 1.060. Full data collection parameters and structural data are available as CIF file (Cambridge Crystallographic Data Centre deposition number CCDC 908234).

Table S1. Selected bond distances (Å) and bond angles (°) within the coordination sphere of the $[Cu_2(\mu\text{-dpPyMe})_3(CH_3CN)]^{2+}$ dication in **1**.$(CH_2Cl_2)_2$ (see Fig. S1 for the numbering).

Selected bond lengths		Selected bond angles	
Cu(1)-N(1)	2.051(3)	N(1)-Cu(1)-N(2)	119.23(12)
Cu(1)-N(2)	2.027(3)	N(1)-Cu(1)-N(3)	116.22(12)
Cu(1)-N(3)	2.029(3)	N(2)-Cu(1)-N(3)	122.46(12)
Cu(2)-P(1)	2.3256(10)	P(1)-Cu(2)-P(2)	113.39(4)
Cu(2)-P(2)	2.3168(10)	P(1)-Cu(2)-P(3)	112.72(4)
Cu(2)-P(3)	2.3323(10)	P(1)-Cu(2)-N(4)	103.33(9)
Cu(2)-N(4)	2.036(3)	P(2)-Cu(2)-P(3)	115.03(4)
		P(2)-Cu(2)-N(4)	106.81(10)
		P(3)-Cu(2)-N(4)	104.19(9)

Fig. S1. (A) Two views of the X-ray crystal structure of **1** showing the details of the coordination sphere around the two metal centers. (B) View along the Cu(1)-Cu(2) axis showing the shielding of Cu(1) due to the presence of the CH_3 groups.

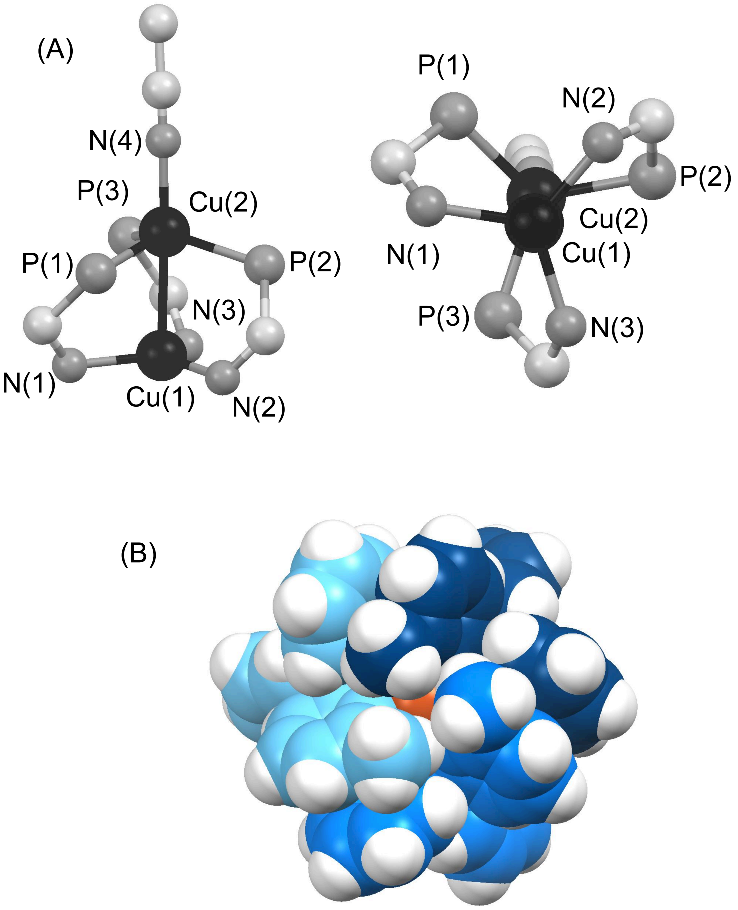


Fig. S2. ^{1}H (top) and ^{31}P (bottom) NMR spectra of compound **1** recorded in CD_2Cl_2 at room temperature.

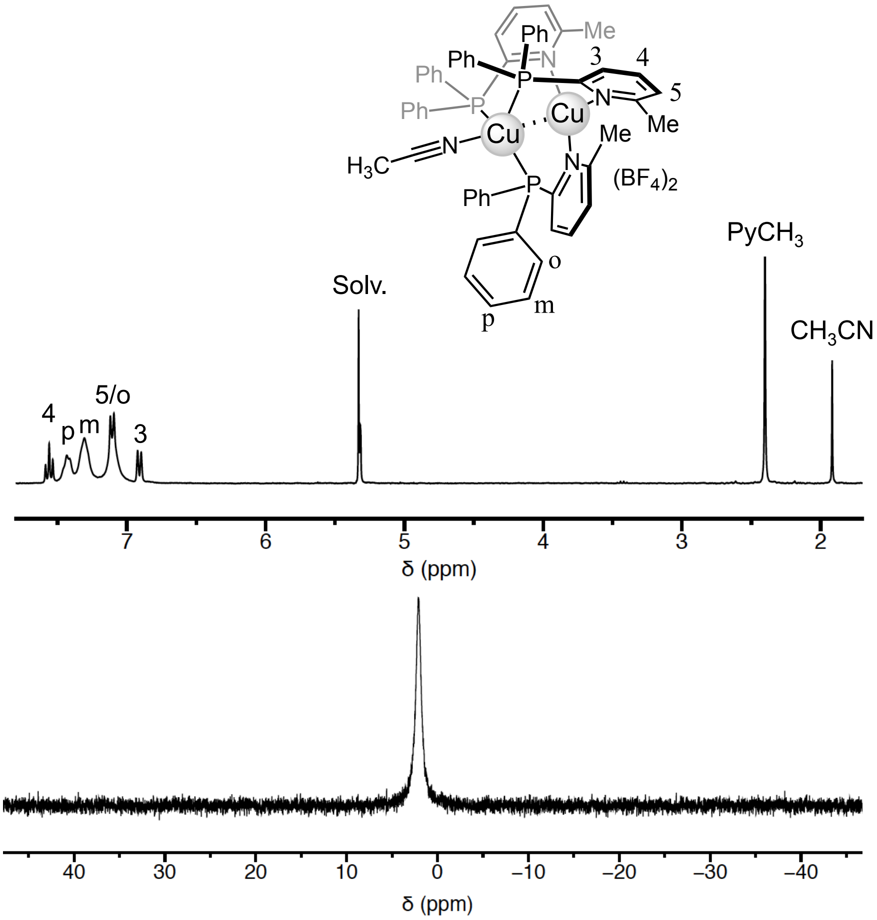


Fig. S3. ^{1}H NMR spectra of **2** recorded at different temperatures in CD_2Cl_2 (*: Et_2O).

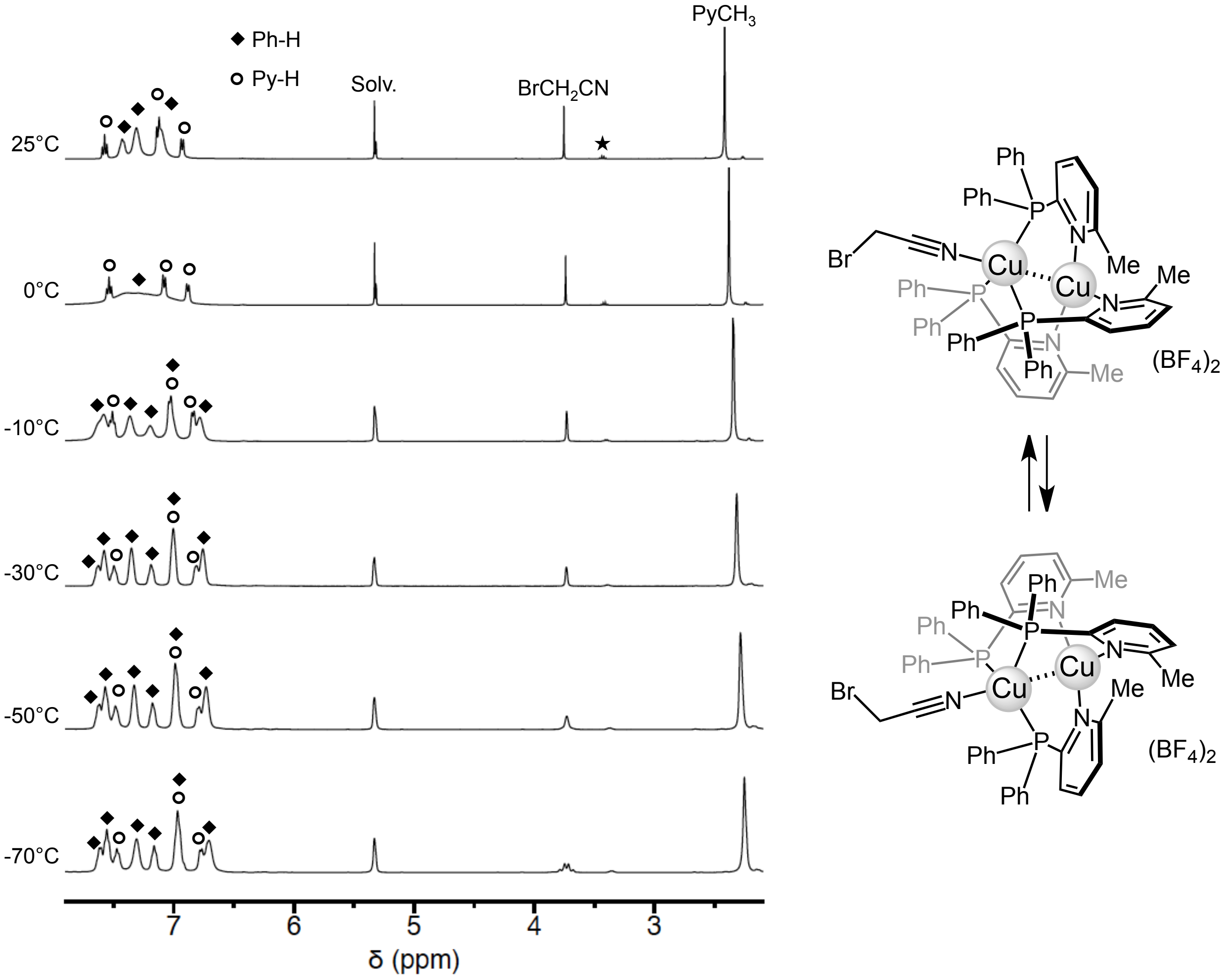


Fig. S4. ^{31}P NMR spectra of **2** recorded at different temperature (top: 25°C, bottom: -70°C).

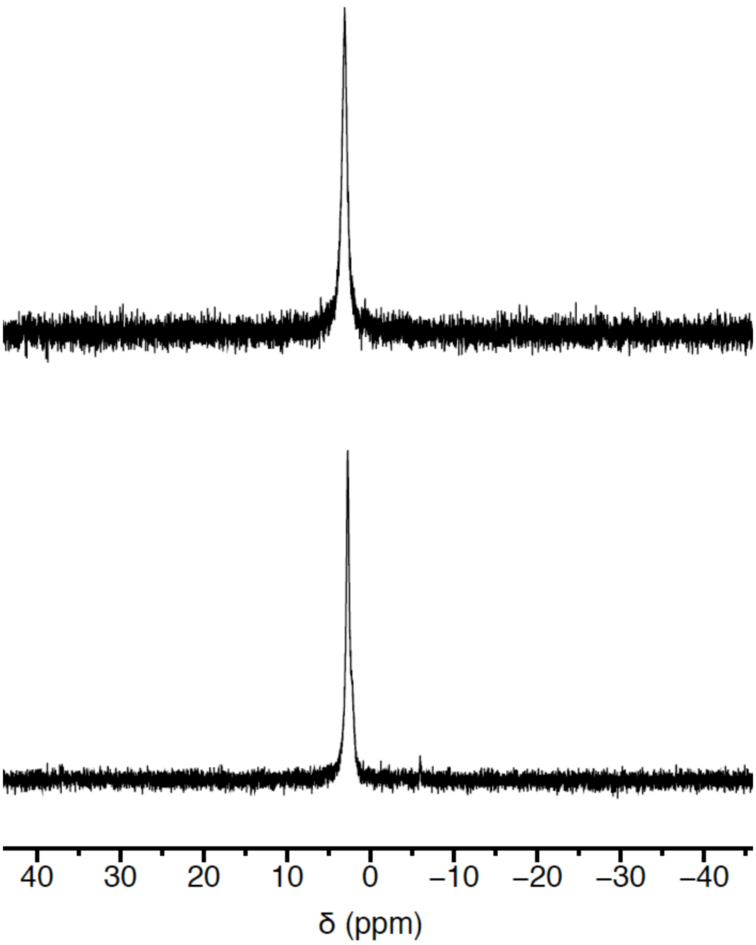


Fig. S5A. OSWVs (anodic and cathodic scans) of compound **1** ([**1**] = 10^{-3} M) on a Pt electrode in CH_2Cl_2 + 0.1 M $n$$Bu_4NBF_4$ at room temperature using a sweep widht of 20 mV, a frequency of 10 Hz, and a step potential of 5 mV; Fc/Fc^+ is observed at +0.55 ± 0.01 V under these conditions.

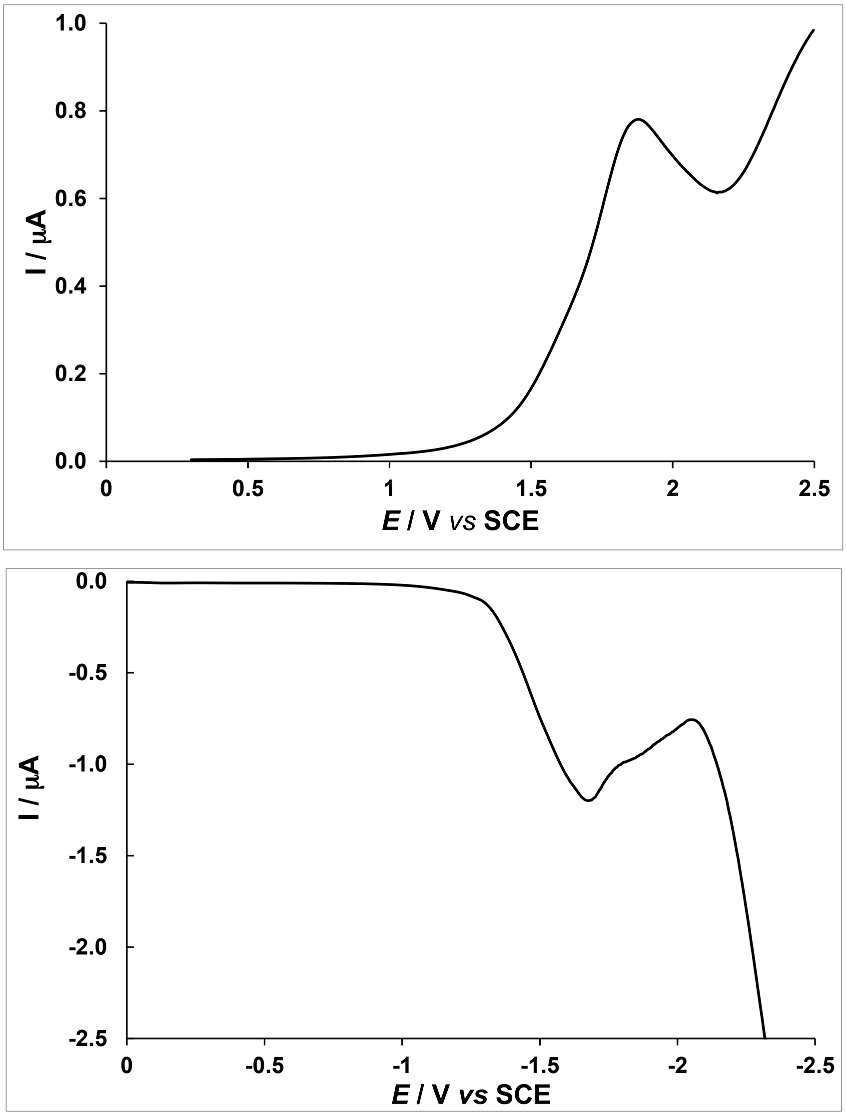
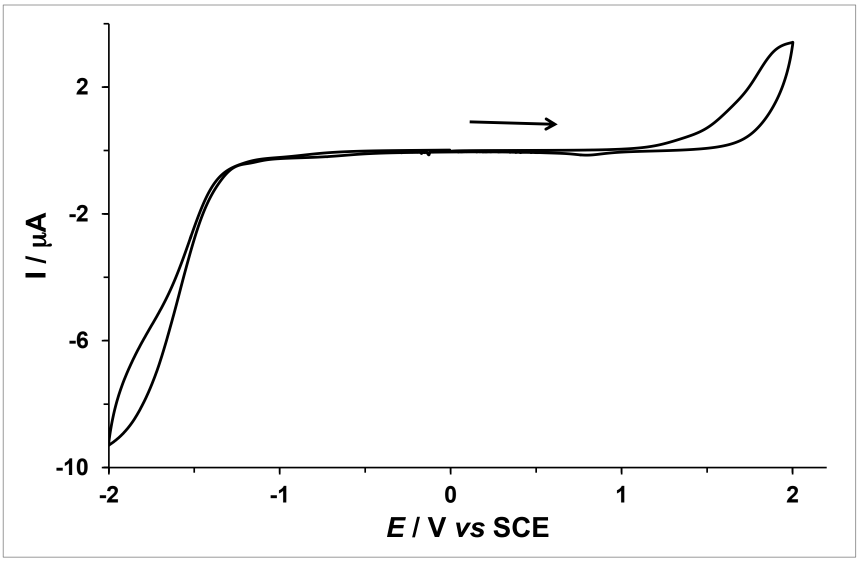


Fig. S5B. CVs of compound **1** ([**1**] = 10^{-3} M) on a Pt electrode in CH_2Cl_2 + 0.1 M *n*Bu_4NBF_4 at room temperature (v = 100 mV/s).



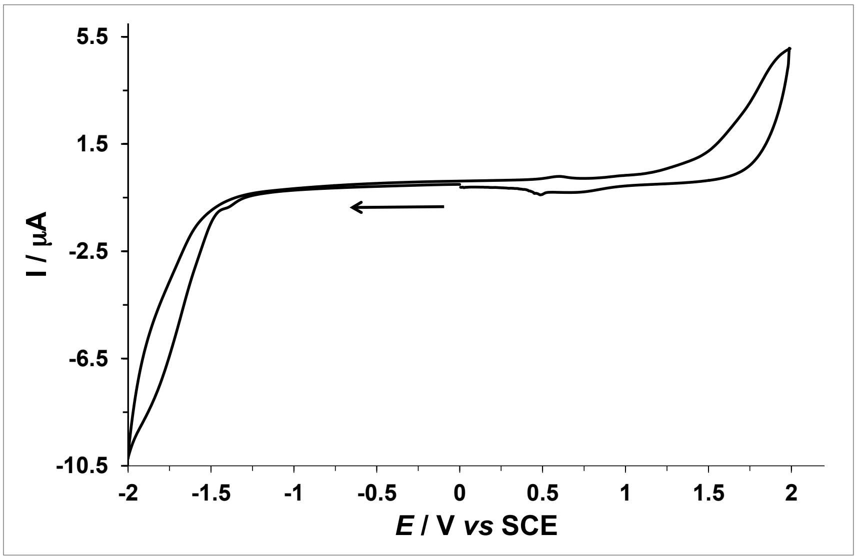


Fig. S6. The electronic absorption spectra of **1** collected at different time intervals in CH_2Cl_2.

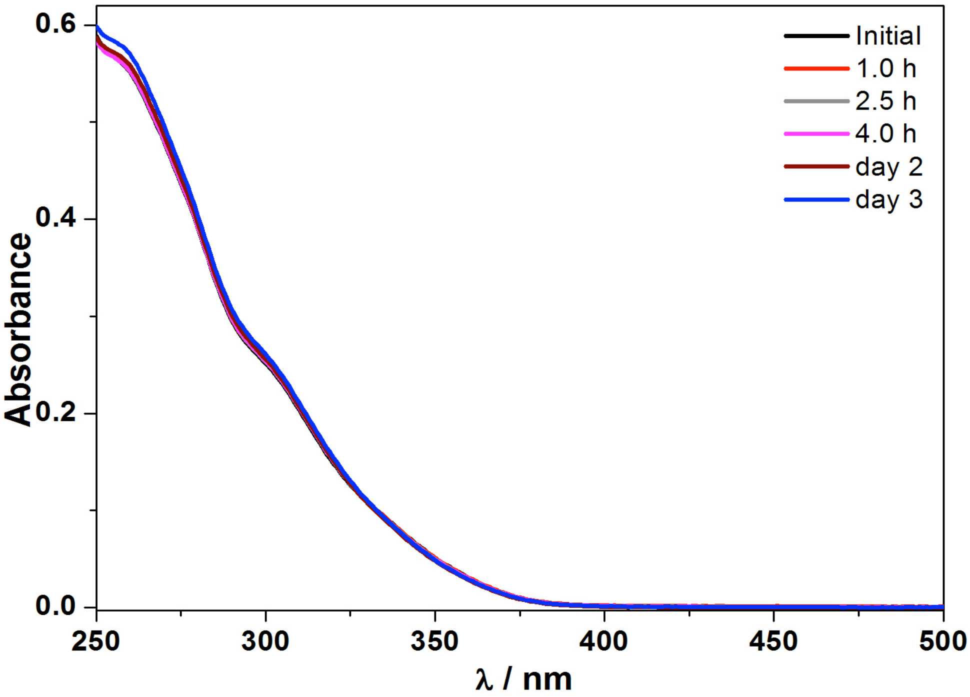


Fig. S7. The emission decay curve of **1** collected at the corresponding emission maximum in aerated CH_2Cl_2. (λ_{exc} = 331 nm)