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A Redox- & Photo-responsive Quadri-state Switch based on Dimethyldihydropyrene -appended Cobalt Complexes

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1. Additionnal procedures and methods

All purchased chemicals were used as received. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance-500 MHz spectrometer in CD_3CN. ^{1}H and ^{13}C chemical shifts (ppm) are referenced to residual solvent peaks. High-resolution mass spectrometry analyses were conducted at High Resolution Mass Spectra (HRMS, Bruker maXis mass spectrometer) and were performed in positive Electrospray Ionisation (ESI+) mode by the Mass Spectrometry service of the ICOA (Institut de Chimie Organique et Analytique), Orléans, France.

Visible irradiations experiments have been carried out with a Xe-Hg lamp, using a 630 nm cut-off filter and the samples have been placed in a water bath at 281 K. Samples have been placed at a distance of 15 cm of the visible lamp.

Absorption spectra were recorded using a Varian Cary 50 Scan UV-Visible spectrophotometer equipped with a temperature controller unit. Absorption measurements over the spectral range from 250 to 800 nm were carried out in *quartz cells* having an optical *path length* of *1 cm.*

Electrochemical measurements were conducted in a glove box in a standard one-compartment, three-electrode electrochemical cell using a Bio-logic SP300 potentiostat. Investigations were carried out in anhydrous CH_3CN containing tetra-*n*-butylammonium perchlorate (0.1 M) as supporting electrolyte. An automatic ohmic drop compensation procedure was systematically implemented prior to recording CV data. CH-instrument vitreous carbon (Ø=3 mm) working electrodes were polished with 1 mm diamond paste before each recording. A CH instrument Ag|Ag+ electrode ($[Ag^+]=10^{-2}M$) was used as a reference. A platinum wire was used as the counter electrode. The reference electrode was calibrated with respect to the formal potential of the Ferrocenium/Ferrocene (Fc^+/Fc) couple in CH_3CN, which was estimated as 0.450 V under our experimental conditions.

UV/Vis spectroelectrochemical experiments were carried out with a photodiode array UV-visibleNIR spectrometer MCS 501 UV-NIR (Carl Zeiss). The light sources were halogen CLH 500 (20 W) and deuterium CLD 500 lamps with an optical fiber 041.002-UV SN 012105 or using an additional 1 mm quartz immersion probe (Hellma) and an automatic shutter.

DHP was used as a primary or secondary standard to determine photo-opening isomerization quantum yield of the compounds. The change in absorption upon irradiation at 480 nm (band-pass filter) during specific time periods for all the compounds was compared to the change in absorption for the actinometer irradiated at the same wavelength. The monitoring wavelengths were selected according the studied samples. The compounds were dissolved in acetonitrile and the concentration was such that the absorbance at 480 nm was higher than 2. The absorption spectra for each compound were recorded after each irradiation time without further handling and the total time was such that the isomerization of the compound was less than 10%. The ring opening quantum yields ϕ_x were calculated according to equation (1):

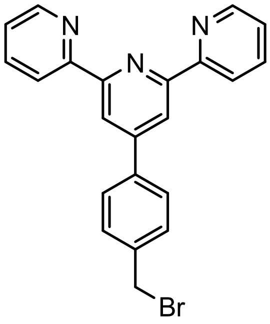
$$\phi_x = \frac{\phi_s \varepsilon_s \Delta A_x V_x t_s}{\varepsilon_x \Delta A_s V_s t_x} \qquad \text{eq. (1)}$$

where ϕ_s is the quantum yield of the standard, ε is the molar extinction coefficient at the monitoring wavelength, ΔA is the change in absorbance at the monitoring wavelength, V is the volume of solution and t is the irradiation time. The subscripts s and x refer to the standard and the compound of unknown quantum yield respectively.

Synthesis

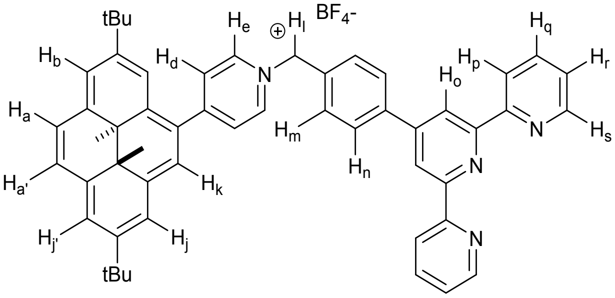
The synthesis of 2,7-di-tert-butyl-trans-10b,10c-dimethyl-10b,10c-dihydropyrene from 4-tert-butyl-toluene was performed following slight modifications of the procedure described by Mitchell (Mitchell, et al, JACS, 125, 2974–2988, 2003). 4-bromo-2,7-di-tert-butyl-trans-10b,10c-dimethyl-10b-10c dihydropyrene was synthesized, using the synthesis previously described by our group (Vilà, N., et al, Inorg Chem. 50, 10581–10591, 2011). All the DHP derivatives have been obtained as a racemic mixture of trans isomers as there is no asymmetric step in the synthetic route.

4’-(4-bromomethylphenyl)-2,2’:6’,2’’-terpyridine.



4’-(4-methylphenyl)-2,2’:6’,2’’-terpyridine (2 g, 6.18 mmol), N-bromosuccinimide (1.12 g, 6.29 mmol) and 2-2'-Azoisobutyronitrile (45 mg, 0.27 mmol) were dissolved into 40 mL of degassed CCl_4. The mixture was then stirred under reflux in an inert atmosphere for 4 hours. It was cooled down to room temperature and filtered. The filtrate was concentrated under reduced pressure and an orange solid precipitated. The yellow-orange crude was recrystallized in a 1:2 (vol:vol) acetone:ethanol mixture. The crystals were collected, washed 3 times with a cold 1:2 acetone:ethanol mixture and dried under vacuum. 4’-(4-bromomethylphenyl)-2,2’:6’,2’’-terpyridine was obtained as white crystals (yield 82%, 1.81 g, 5.07 mmol). ^1H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.73 (m, 4H), 8.65 (d, J = 7.9 Hz, 2H), , 7.91 (m, 4H), 7.56 (d, J = 7.9 Hz, 2H), 7.38 (ddd, J = 7.5, 4.9, 1 Hz, 2H), 4.58 (s, 2H). ^{13}C NMR (75 MHz, CD_3CN) δ/ppm: 156.07, 155.95, 149.50, 149.09, 138.62, 138.57, 136.94, 129.63, 127.76, 123.89, 121.38, 118.82, 32.96. HRMS: m/z calcd for $C_{22}H_{17}N_3Br$: 402.0606 $[M+H]^+$, found: 402.0600.

2,7-di-tert-butyl-4-(N-(4’-(4-methylphenyl)-2,2’:6’,2’’-terpyridin-yl)pyridin-4-yl)-trans-10b,10c-dimethyl-10b,10c-dihydropyrene tetrafluoroborate (L_c^+).



A degassed solution of 4’-(4-bromomethylphenyl) -2,2’:6’,2’’-terpyridine (57 mg, 0.142 mmol) in 5 mL of CH_2Cl_2 was added dropwise to a degassed solution of 4_f (50 mg, 0.18 mmol) in CH_3CN (40 mL),. The resulting solution was stirred and refluxed under an inert atmosphere for 12 hours. The red solution was cooled down to room temperature. It was concentrated under reduced pressure to one fourth of the initial volume. Diethyl ether was then added and 2_c(Br) precipitated. The solid was collected upon filtration and dissolved in a minimum amount of hot CH_3OH. Upon the dropwise addition of an aqueous concentrated KPF_6 solution, $2_c(PF_6)$ precipitated as a red powder. It was then collected by filtration, washed with water, and dried under vacuum. Finally the ligand was subjected to an anion exchange procedure to afford the targeted pyridinium salt Lc+, BF_4- isolated as a red powder. (yield 42%, 41 mg).

L_c^+: ^{1}H NMR (500 MHz, CD_3CN) δ/ppm: 8.94 (d, 2H, J = 6.5 Hz, i), 8.82 (m, 8H, b, m, a, e, f and q), 8.75 (m, 3H, c, n), 8.67 (m, 2H, d and g), 8.53 (d, 2H, J = 6.5 Hz, h), 8.12 (d, 2H, J = 8 Hz, l), 8.01 (t, 2H, o), 7.82 (d, J = 8 Hz, 2H, k), 7.50 (t, 2H, p), 5.94 (s, 2H, j), 1.69 (s, 9H, A), 1.64 (s, 9H, A’), -3.85 (s, 3H, B), -3.89 (s, 3H, B’). (100 MHz, CD_3CN) δ /ppm: 160.22, 157.36, 156.59, 150.37, 150.22, 150.08, 148.38, 144.68, 140.83, 140.05, 138.30, 138.04, 137.11, 135.22, 134.76, 131.22, 130.58, 129.22, 127.98, 126.10, 125.41, 125.08, 124.67, 124.23, 123.05, 122.10, 119.49, 118.94, 64.07, 37.19, 36.75, 31.98, 31.84, 31.48, 30.27, 15.42, 15.08. IR ν (ATR): 2958, 1628, 1602, 1584, 1567, 1548, 1466, 1442, 1389, 758 cm^{-1}. HRMS: m/z calcd for $C_{53}H_{51}N_4^+$: 743.4108 [M-BF_4]$^+$, found: 743.4099.

L_o^+: ^{1}H NMR (500 MHz, CD_3CN) δ/ppm: ^{1}H NMR (500 MHz, 298 K, CD_3CN) d (ppm) : 1.21 (s, 9H), 1.25 (s, 9H), 1.41 (s, 3H), 1.48 (s, 3H), 5.72 (s, 2H), 6.48 (s, 1H), 6.49 (s, 1H), 6.90 (br, 2H), 6.94 (br, 2H), 7.34 (s, 1H), 7.67 (br, 6H), 8.10 (d, 2H), 8.62 (d, 2H), 8.72 (br, 8H).

Preparation of $Co(L_c)_2^{4+}$

10^{-5} mol of **L_c^+** are dissolved in 10 ml of deoxygenated acetonitrile. A 0.5 equivalent of metal salt previously solubilized in 1mL of acetonitrile is added to the ligand solution. The mixture is refluxed for 2 h at 70 °C. Then the solution is concentrated on a rotary evaporator up to 1 ml, the complex is precipitated by addition of 15 ml of diethyl ether. The solution is filtered and the solid was washed with additional 5 ml of diethyl ether. The resulting powder was then dried under vaccum.

$Co(2_c)_2^{4+}$: 15.8 mg (6.78×10^{-6} mol, yield : 90 %) dark red powder. IR ν (ATR): 2961, 1629, 1558, 1507, 1473, 1436, 1406, 1054, 785, 765, 750 cm^{-1}. HRMS: m/z calcd for $C_{106}H_{102}N_8Co^{4+}$: 386.4384 [M-4BF_4^-]$^{4+}$, found: 386.4388.

2. Additional NMR spectra

Figure ESI 1 : ^{1}H NMR spectrum of $\mathbf{L_c}^+$.

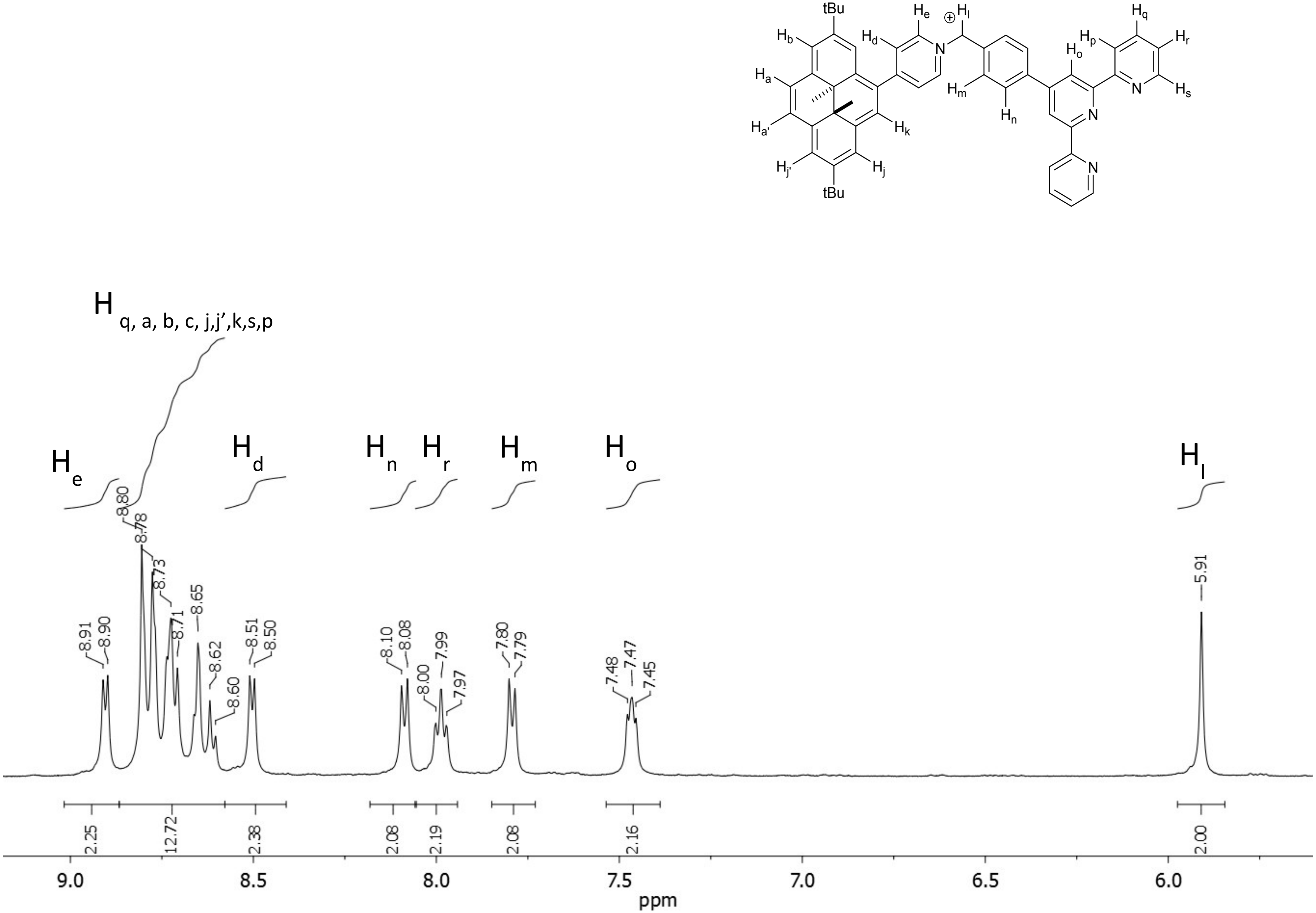


Figure ESI 2 : COSY ^1H -^1H NMR spectrum of $\mathbf{L_c}^+$.

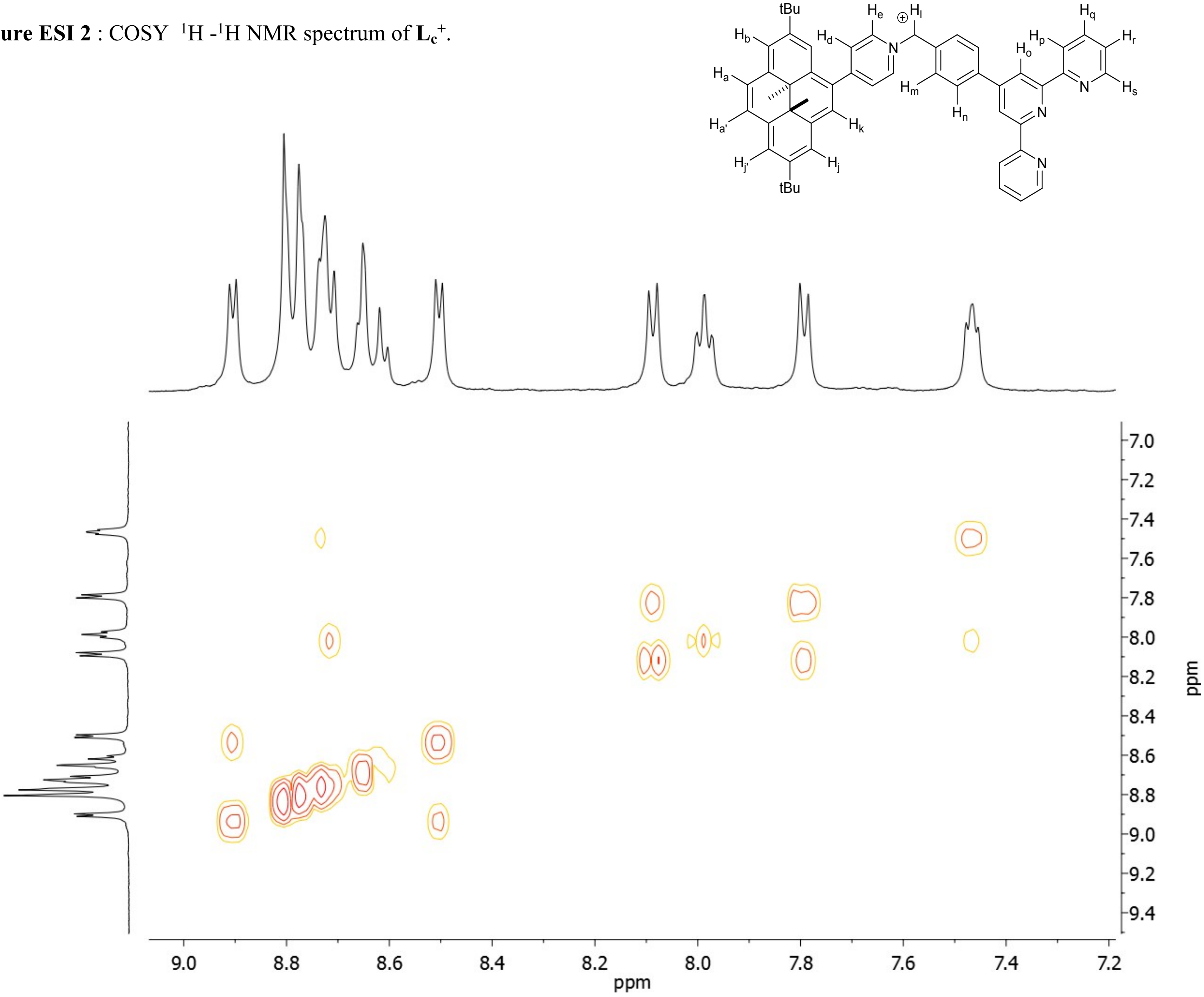
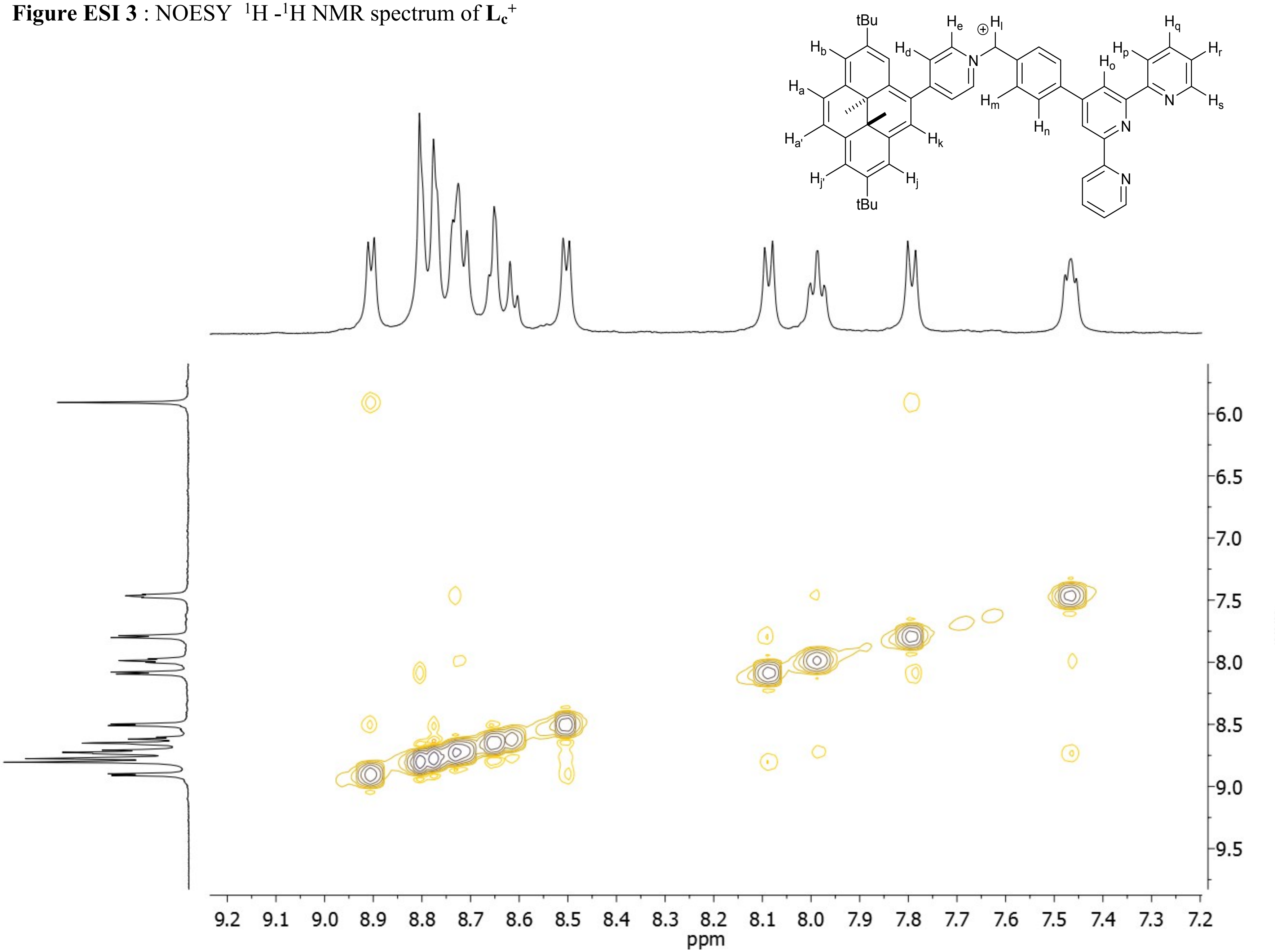


Figure ESI 3 : NOESY ^1H -^1H NMR spectrum of $\mathbf{L_c}^+$



3.Thermal closing process

Key kinetic parameters corresponding to the thermal conversion process from the open form to the closed forms were estimated by UV-Visible spectroscopy measurements conducted at different temperatures.

A $1\cdot10^{-5}$ M solution of the photochromic species in CH_3CN was irradiated with visible light (at $\lambda \geq 630$ nm) to afford the opened form in quantitative yield. The evolution of the absorption at λ_{max} was monitored over time at different temperatures (308K, 318K and 328K). The conversion of the UV-Vis data to a concentration was done using Lambert Beer law (1) where **A** is the absorption, **ε** is the molar absorptivity, **l** is the path length and **c** is the concentration. The total concentration ($\mathbf{c}_{total}$) is obtained in the initial scan (before irradiation) and corresponds to the completely closed compound.

$$\mathbf{A}=\boldsymbol{\varepsilon}\mathbf{lc} \qquad (1)$$

$$\mathbf{A}= \boldsymbol{\varepsilon}_{DHP}\mathbf{lc}_{DHP} + \boldsymbol{\varepsilon}_{CPD}\mathbf{lc}_{CPD} \qquad (2)$$

$$\mathbf{c}_{total}=\mathbf{c}_{DHP} + \mathbf{c}_{CPD} \qquad (3)$$

$$\text{and } \boldsymbol{\chi}_{CPD}=(\mathbf{c}_{CPD}/\mathbf{c}_{total}) \qquad (4)$$

	T/K	E_a (kcal/mol)	k (10^{-5} s^{-1})	$t_{1/2}$/h
$\mathbf{5_o}^{+}$	298	19± 6	1.11 ± 0.33	17.3
	318		3.55 ± 0.03	5.4
	328		20.5 ± 0.43	1.0
$Co(\mathbf{5_o})_2^{4+}$	298	21± 5	1.71 ± 0.01	11.3
	318		3.72 ± 0.03	5.2
	328		18.6 ± 0.2	1.0

4. Electrochemical ring closure

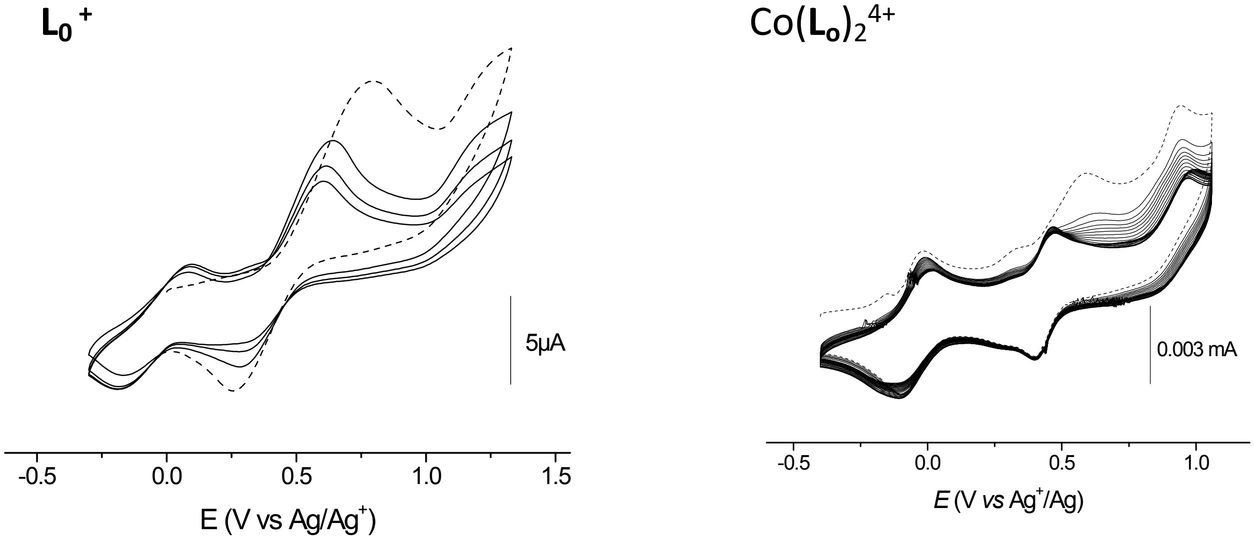


Figure ESI 4: Repeated cyclic voltammogramms of the photogenerated solution of $\mathbf{L_c}^+$ and Co($\mathbf{L_c}$)$_2^{4+}$ (1 mmol) in 0.1M TBAP/CH_3CN at 100 mv.s^{-1}. (Potentials are referred to the formal potential of the Ag/Ag$^+$ redox couple). In dashed open form after visible irradiation. ($\lambda > 630$ nm).

5. Emission spectra of $\mathbf{L_c}^+$ and Co($\mathbf{L_c}$)$_2^{4+}$

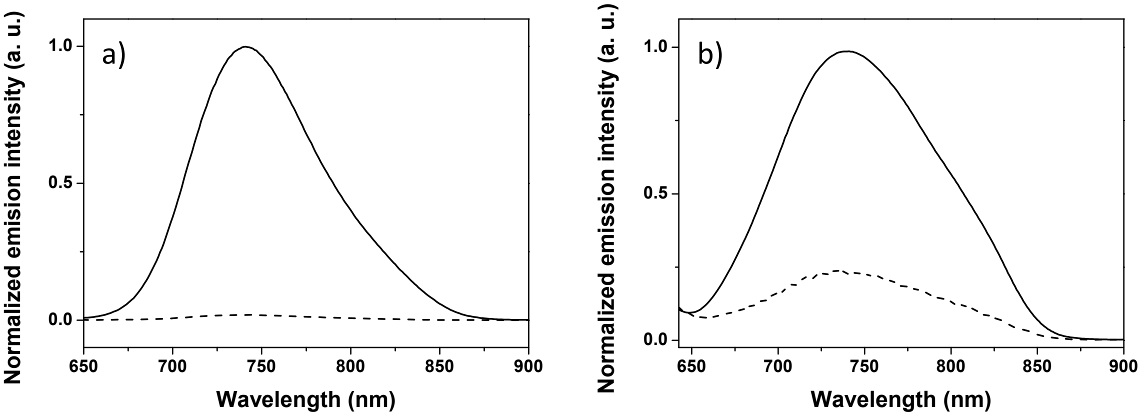


Figure ESI 5: Normalized emission spectra in acetonitrile at 293 K of $\mathbf{L_c}^+$ (a) and Co($\mathbf{L_c}$)$_2^{4+}$ complex (b). Excitation wavelength = 430 nm. (solid line closed form , dashed line opened form)

6. Fatigue resistance of cobalt complex

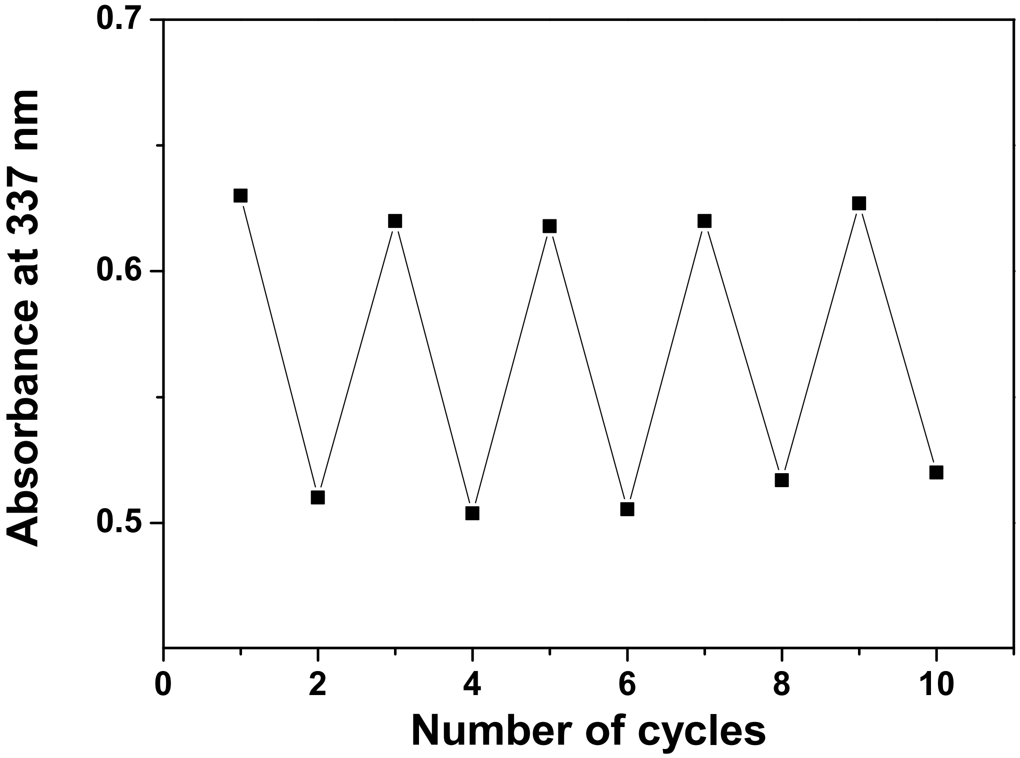


Figure ESI 6: Optical response of the Co($\mathbf{L_c}$)$_2^{4+}$ / Co($\mathbf{L_o}$)$_2^{4+}$ switch during 10 consecutive cycles, in CH_3CN. (Opening : irradiation at λ>630 nm for 15 min of Co($\mathbf{L_c}$)$_2^{4+}$, back process: heating at 318K during 30 min.)