

## **Dimethyldihydropyrene-Cyclophanediene Photochromic Couple**

### **Functionalized with Terpyridyl Metal Complexes as Multi-Addressable Redox-and Photo-Switches**

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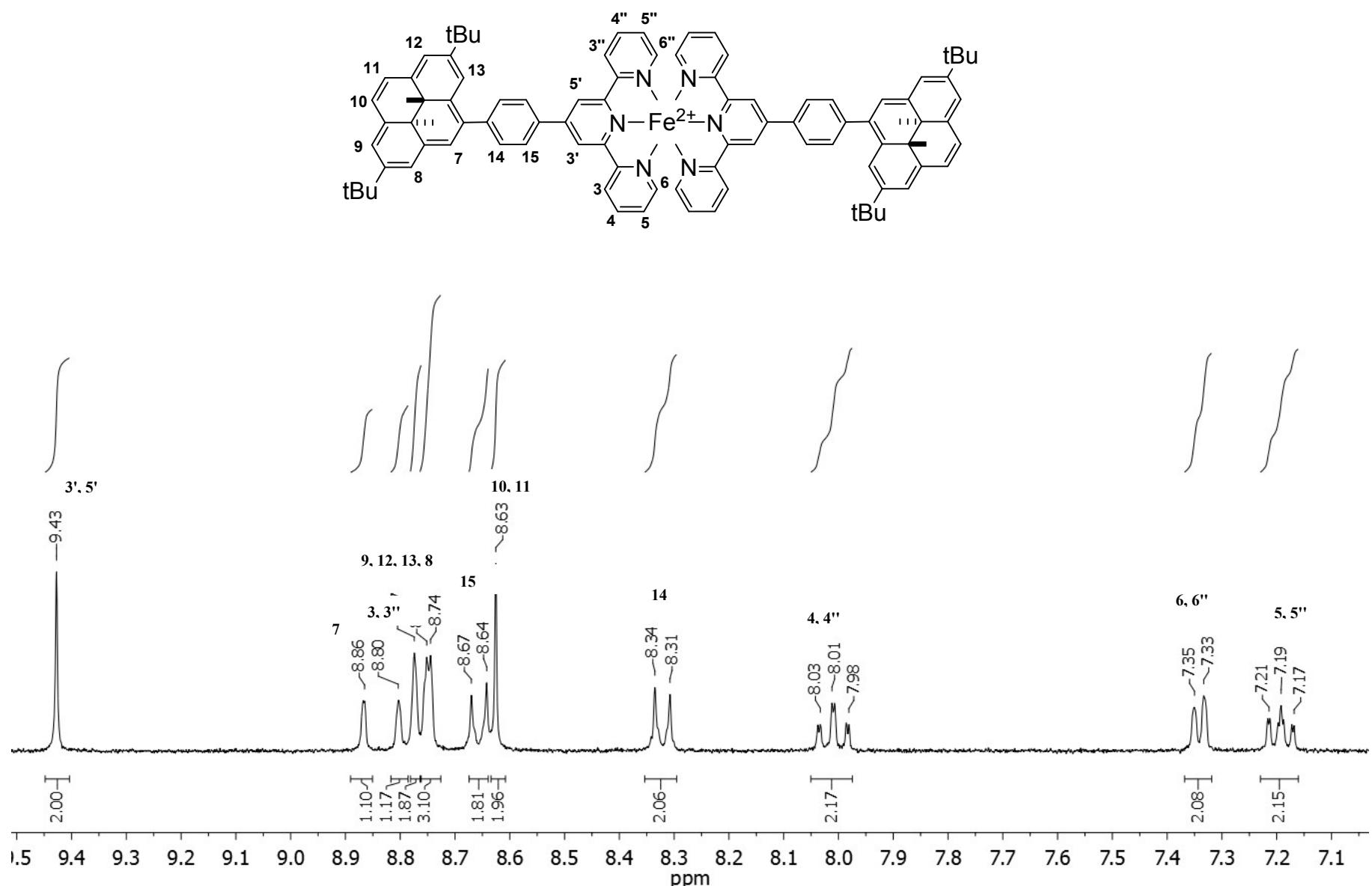
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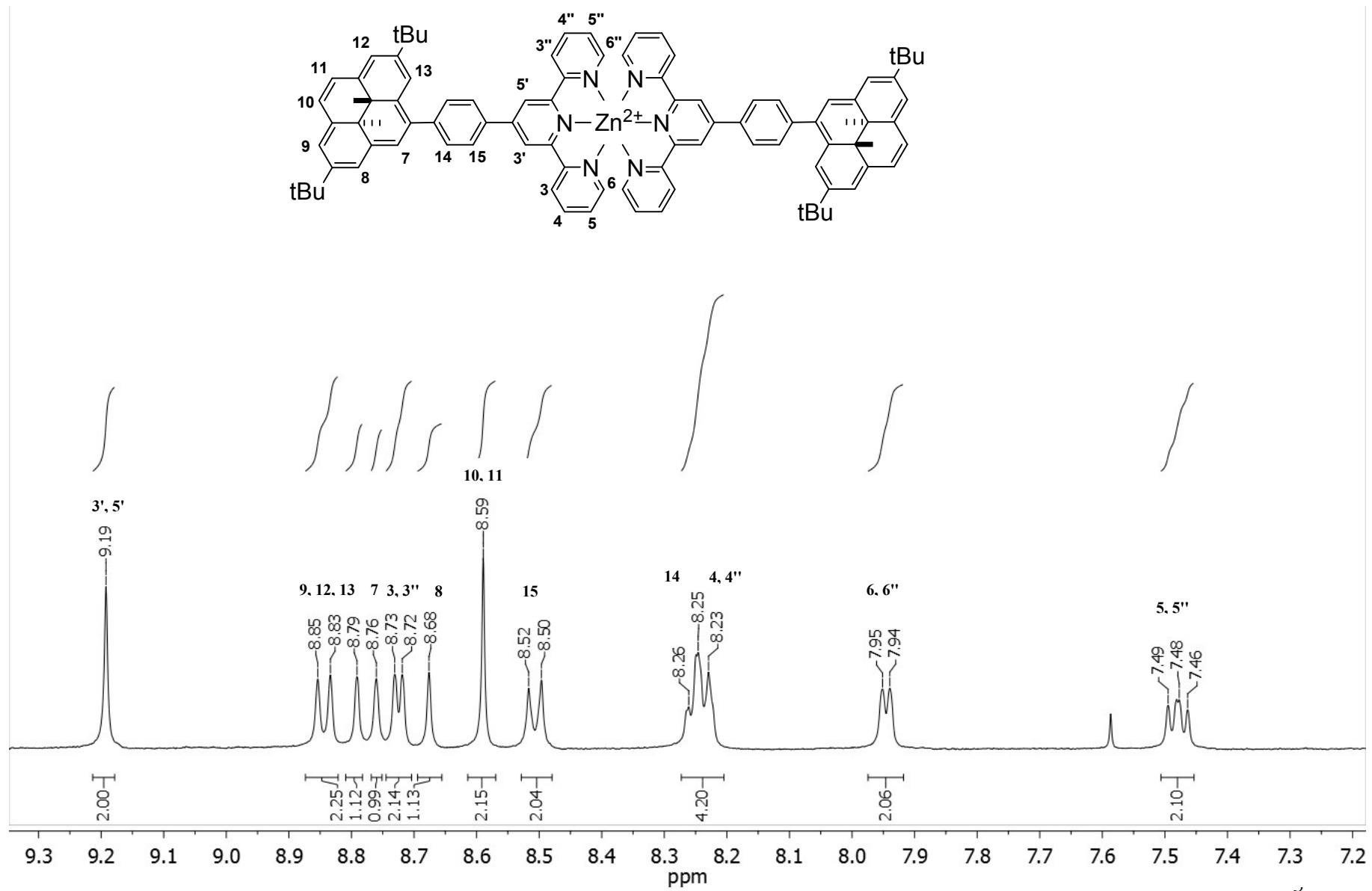
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## 1. Additional NMR spectra

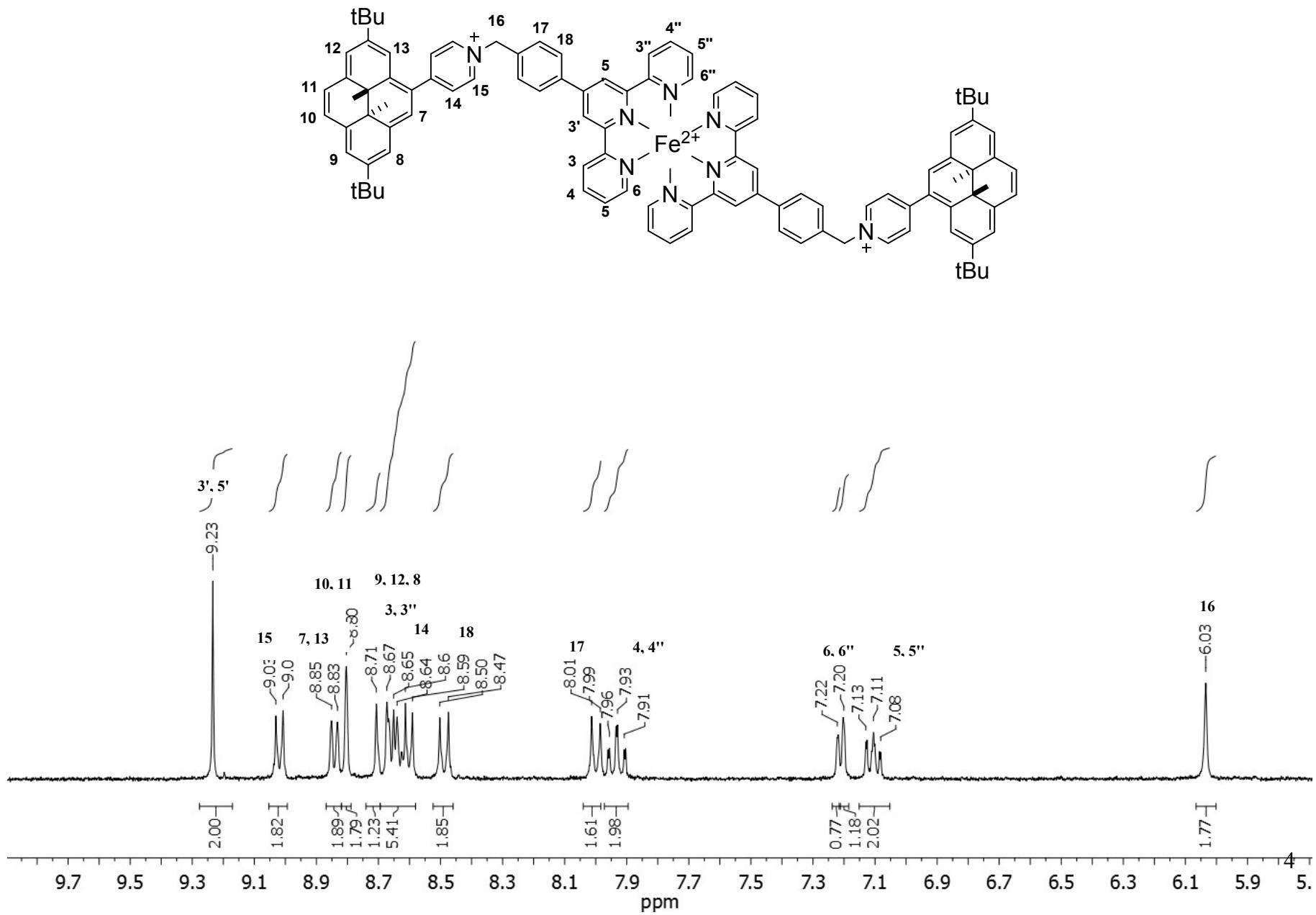
**Figure ESI 1 :**  $^1\text{H}$  NMR spectrum of  $\text{Fe}(1_c)_2^{2+}$



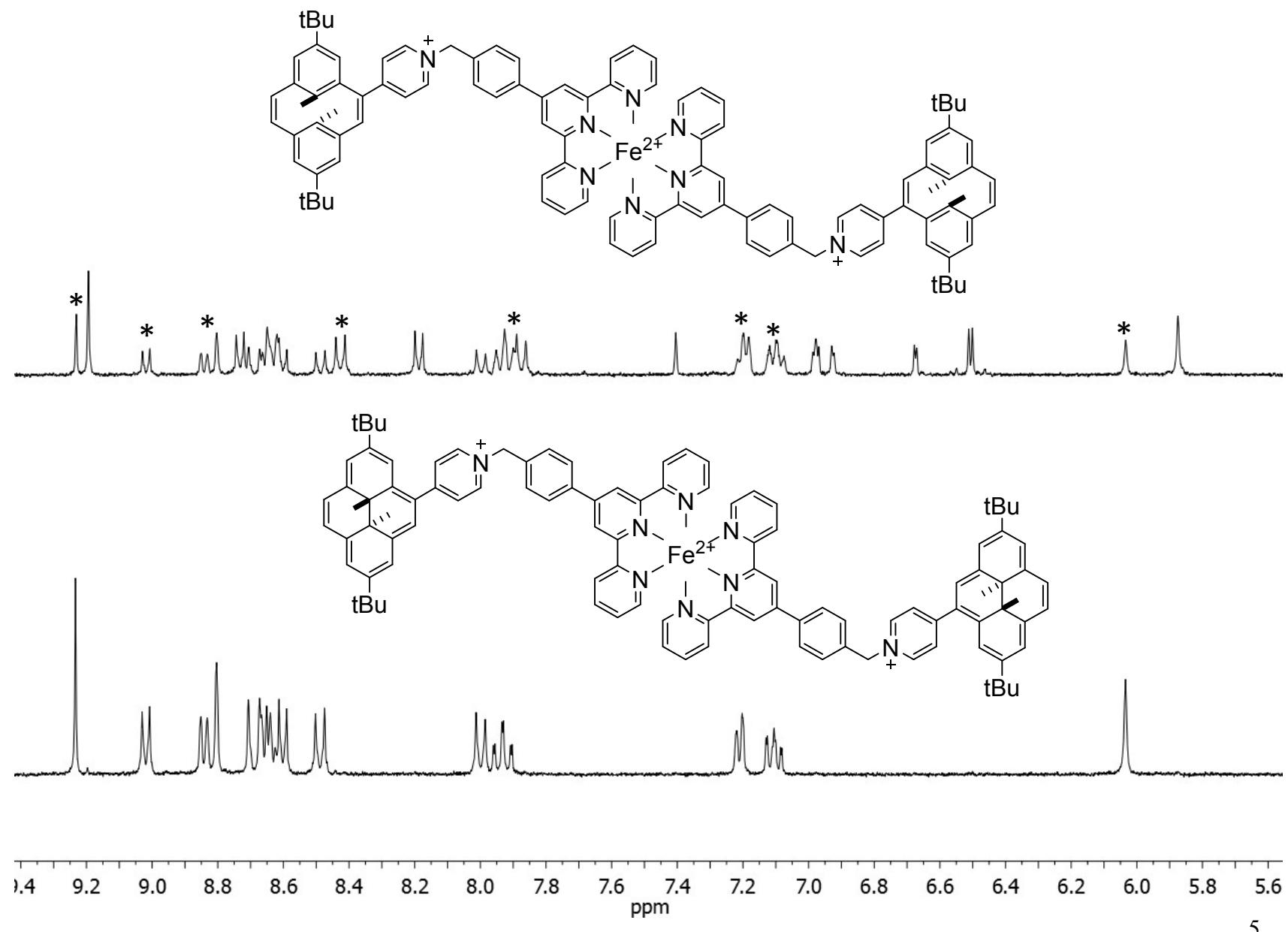
**Figure ESI 2 :**  $^1\text{H}$  NMR spectrum of  $\text{Zn}(1_c)_2^{2+}$



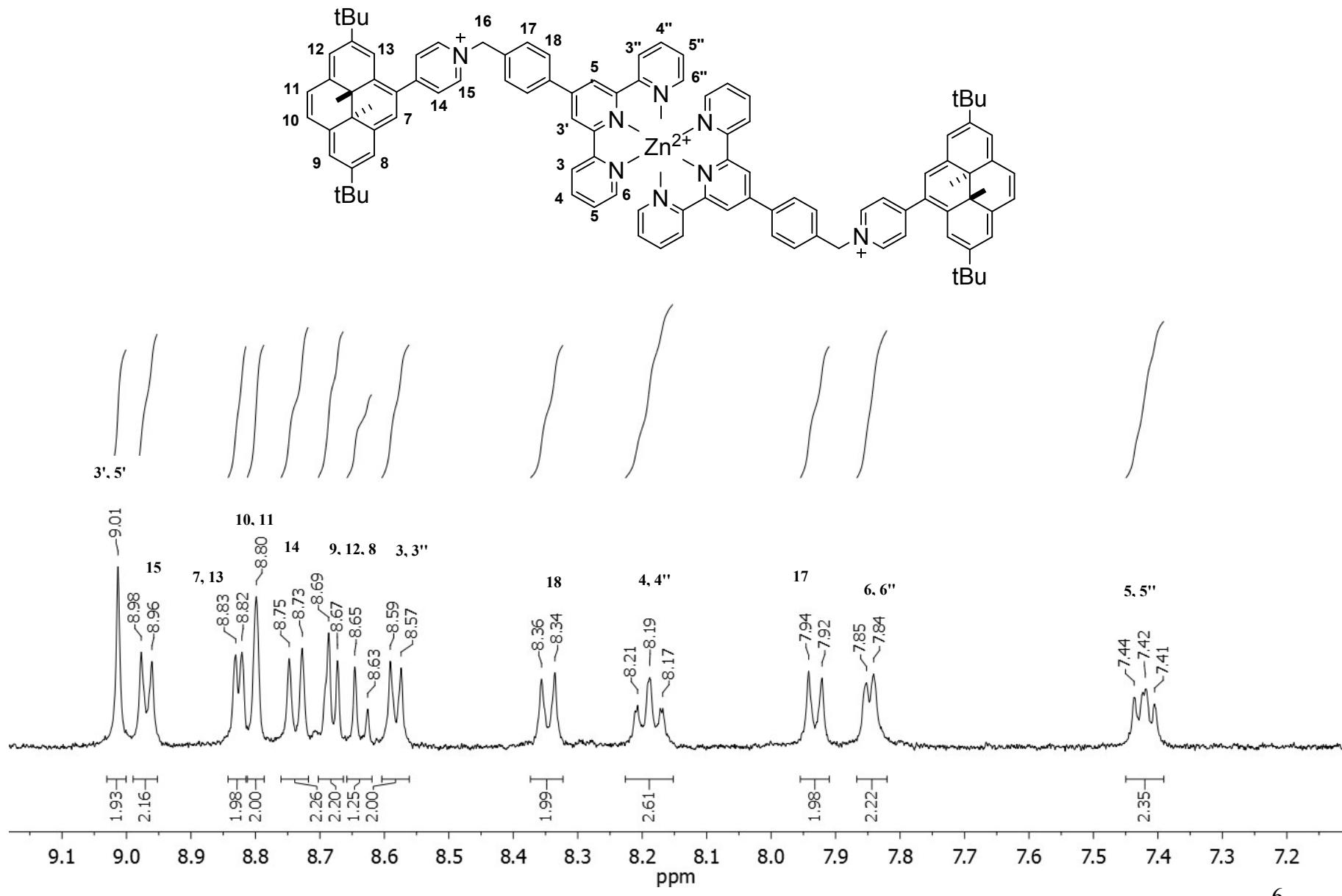
**Figure ESI 3 :**  $^1\text{H}$  NMR spectrum of  $\text{Fe}(\text{2c})_2^{4+}$

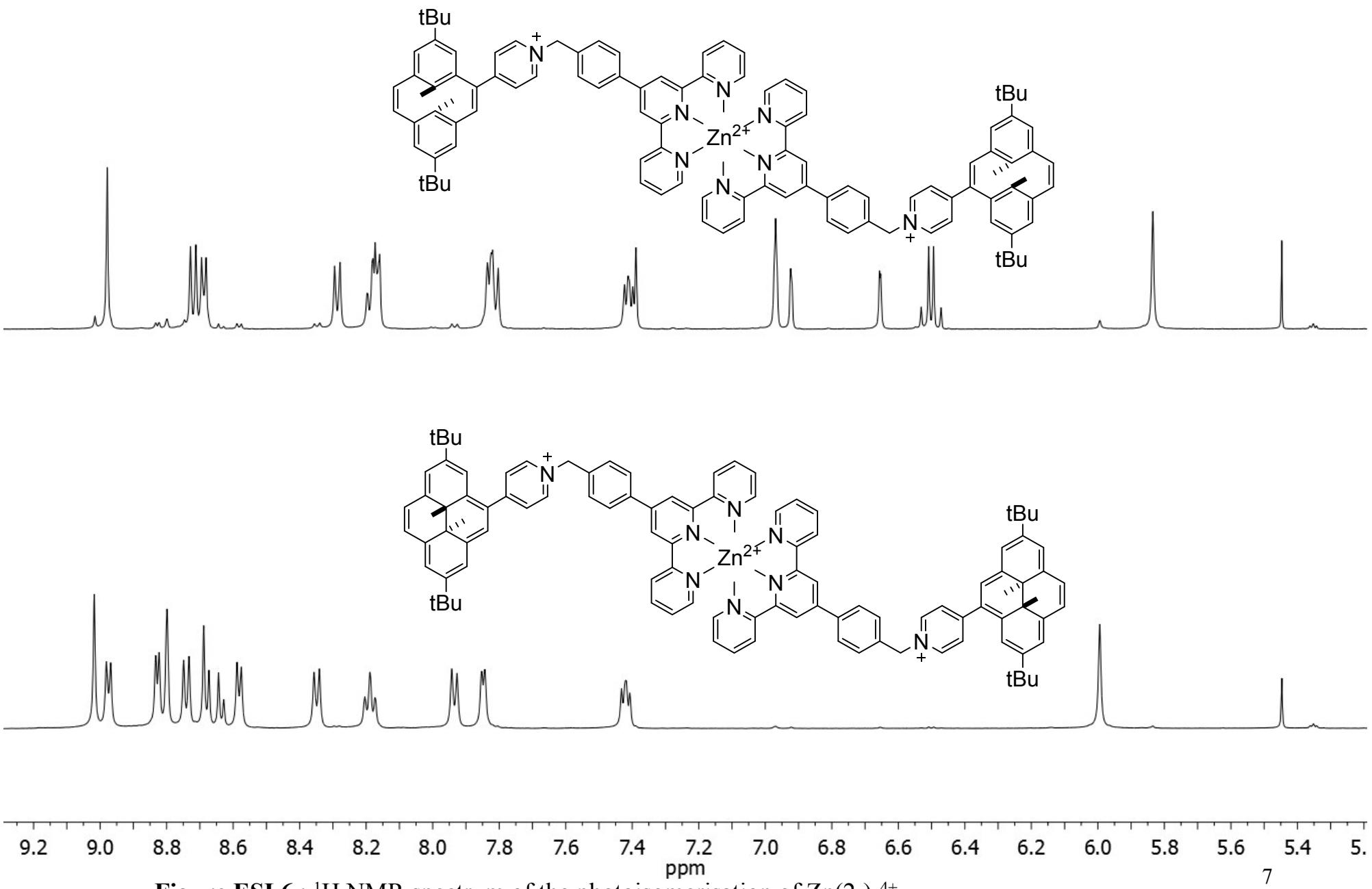


**Figure ESI 4 :**  $^1\text{H}$  NMR spectrum of the photoisomerisation of  $\text{Fe}(2_c)_2^{4+}$



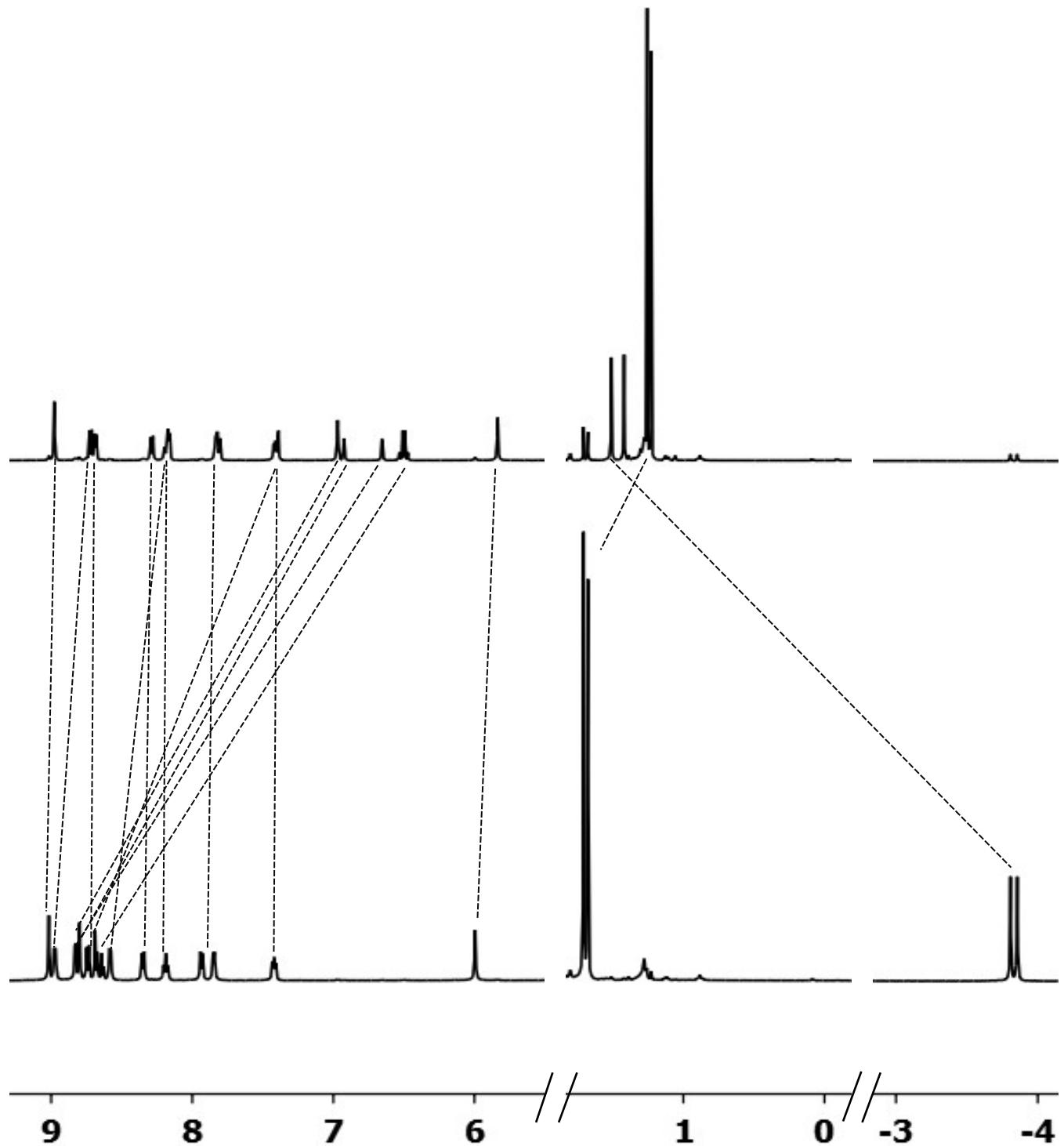
**Figure ESI 5 :**  $^1\text{H}$  NMR spectrum of  $\text{Zn}(\text{2}_c)_2^{4+}$





**Figure ESI 6 :**  $^1\text{H}$  NMR spectrum of the photoisomerisation of  $\text{Zn}(2\text{c})_2^{4+}$

**Figure ESI 7 :**  $^1\text{H}$  NMR spectrum correlation of  $\text{Zn}(2_c)_2^{4+}$  and  $\text{Zn}(2_o)_2^{4+}$



## 2. Cyclic voltammetry data of compounds

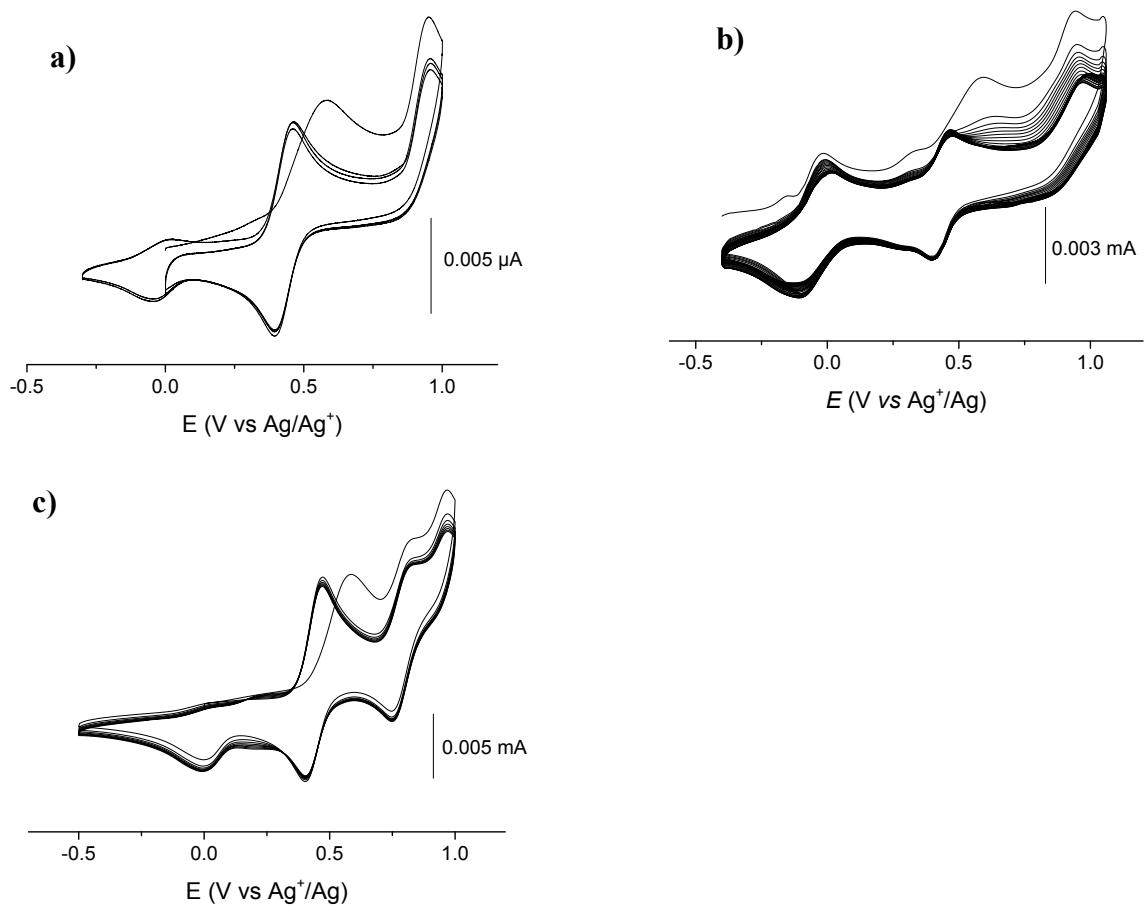


Figure ESI 7: Repeated cyclic voltammograms of the photogenerated solutions of (a)  $\text{Zn}(\text{2}_\text{o})_2^{4+}$ , (b)  $\text{Co}(\text{2}_\text{o})_2^{4+}$  and (c)  $\text{Fe}(\text{2}_\text{o})_2^{4+}$ , black line 1<sup>st</sup> cycle.  $[\text{C}] = 1 \text{ mmol}$  in 0.1M TBAP/CH<sub>3</sub>CN. Scan rate: 100 mV.s<sup>-1</sup>. Potentials are referred to the formal potential of the Ag<sup>+</sup>/Ag redox couple.

	tpy <sup>+</sup> /tpy <sup>2-</sup>	tpy/ tpy <sup>+</sup>	E <sub>1/2</sub> (DHP <sup>0/-</sup> )	E <sub>1/2</sub> (Py <sup>+/-</sup> )	E <sub>1/2</sub> (DHP <sup>+/-</sup> )	E <sub>pa</sub> (DHP <sup>2+/-</sup> ) <sup>c</sup>	E <sub>1/2</sub> (M <sup>III</sup> /M <sup>II</sup> )	E <sub>1/2</sub> (M <sup>II</sup> /M <sup>I</sup> )
<b>DHP(tpy<sup>+</sup>tpy)</b>	-2.175(100)	-1.99(170)		-1.40 (210)	0.47 (200)	1.17 <sup>b</sup>		
<b>Co(1<sub>c</sub>)<sub>2</sub><sup>2+</sup></b>		-1.85(50)		-	0.31 (70)	0.88 <sup>b</sup>	-0.08 (60)	-1.05 (70)
<b>Fe(1<sub>c</sub>)<sub>2</sub><sup>2+</sup></b>	-1.63(60)	-1.51(60)		-	0.29(60)	0.82 <sup>b,c</sup>	0.82 <sup>c</sup>	
<b>Zn(1<sub>c</sub>)<sub>2</sub><sup>2+</sup></b>	-1.69(abs)	-1.53(60)		-	0.3 (70)	0.84 <sup>b</sup>		
<b>Co(2<sub>c</sub>)<sub>2</sub><sup>4+</sup></b>	-1.96 <sup>b</sup>	-1.85	-2.28(60)	-1.36(60)	0.43(60)	0.95 <sup>b</sup>	-0.05 (40)	-1.03 (60)
<b>Fe(2<sub>c</sub>)<sub>2</sub><sup>4+</sup></b>	-1.60 <sup>b</sup>	-1.50	-1.93(60)	-1.35(60)	0.43(60)	0.97 <sup>b</sup>	0.79 (70)	
<b>Zn(2<sub>c</sub>)<sub>2</sub><sup>4+</sup></b>	-1.65(60)	-1.5	-2.97(80)	-1.37(60)	0.42(60)	0.95 <sup>b</sup>		

<sup>a</sup>All potentials are given in volts referred to the Ag<sup>+</sup>/Ag (10<sup>-2</sup> M in CH<sub>3</sub>CN) reference electrode in CH<sub>3</sub>CN + TBAP 0.1 M, at a stationary vitreous carbon electrode ( $\varnothing=3$  mm). E<sub>1/2</sub>=(E<sub>pa</sub>+E<sub>pc</sub>)/2 at 0.1 V s<sup>-1</sup>; ΔEp= E<sub>pa</sub>-E<sub>pc</sub>. <sup>b</sup> peak potential (irreversible system).

<sup>c</sup> superimposed waves.

### 3. Crystal data

**Table S1.** Crystal Data and Structure Refinement for Zn(1c)<sub>2</sub><sup>2+</sup>

Formula	C <sub>99.24</sub> H <sub>113.02</sub> B <sub>1.50</sub> Cl <sub>0.50</sub> F <sub>6.02</sub> N <sub>6</sub> O <sub>7.47</sub> Zn
Fw (g mol <sup>-1</sup> )	1722.96
Crystal system	triclinic
Space group	P-1
<i>a</i> (Å)	9.4857(19)
<i>b</i> (Å)	16.519(3)
<i>c</i> (Å)	30.909(6)
$\alpha$ (deg.)	103.94(2)
$\beta$ (deg.)	91.56(5)
$\gamma$ (deg.)	91.38(4)
<i>V</i> (Å <sup>3</sup> ) / <i>Z</i>	4696.4(16)
<i>Dx</i> (g cm <sup>-3</sup> )	1.218
$\mu$ (cm <sup>-1</sup> )	0.344
Crystal dim. (mm)	0.28x0.24x0.20
<i>T</i> (K)	200
$\theta$ range for coll. (deg.)	1,36 -25,26
nb. of rflns. coll.	28336
Data/restraints/parameters	10944/1930/1514
R ( <i>I</i> ) <sup>a</sup> all/R[ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	20.38% / 16.36%
Goodness of fit S	1.090
$\Delta\rho_{\min}/\Delta\rho_{\max}$ (e Å <sup>-3</sup> )	-0.617 / 0.962

$$^aR = \frac{\sum|I_o| - |I_c|}{\sum|I_o|}.$$

