



## Supporting Information

for

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# A Multiproperty Switching Molecular Array based on the Redox Behavior of a Ferrocenyl Polychlorotriphenylmethyl Radical

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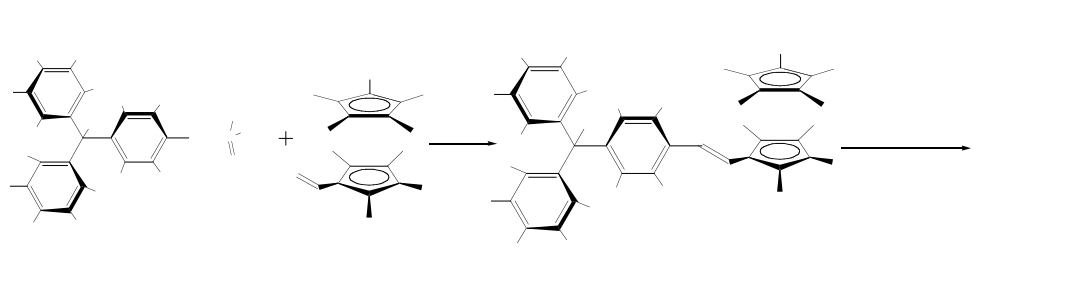
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**Chart S1.** Synthesis of radical **1** and salts  $K^+(18\text{-crown-}6)[1^-]$  and  $[1^+]BF_4^-$ .

## Experimental Section

### 1. General procedures:

All solvents were reagent grade from SDS and were used as received and distilled otherwise indicated. All reagents, organic and inorganic, were of high purity grade and obtained from E. Merck, Fluka Chemie and Aldrich Chemical Co. Elemental analyses were obtained in the Servei de Microanàlisi del CID (CSIC), Barcelona.

UV-Vis and NIR spectra were recorded using a Varian Cary 05E spectrophotometer. Infrared spectra were recorded on a FT-IR Perkin Elmer and  $^1\text{H}$ -NMR spectra on a Bruker AC250 spectrometer. Fluorescence measurements were performed in  $\text{CH}_2\text{Cl}_2$  with a KONTRON SFM-25 spectrofluorimeter

Hyper-Rayleigh scattering experiments were carried out with the compounds dissolved in  $\text{CH}_2\text{Cl}_2$ , which was previously saturated with nitrogen and passed through 0.2  $\mu\text{m}$  filters. To avoid decomposition of the compounds, all solutions were protected against light with an aluminium foil. Crystal Violet chloride ( $\chi = 338 \cdot 10^{-30}$  esu, in  $\text{CH}_3\text{OH}$ ) was used as external reference and standard local field correction factors were applied  $[(n_{\text{D}} + 2)/3]^3$ , where  $n$  is the refractive index of the solvent at the sodium D line]. A relative error of 5% is estimated due to the high laser stability.

Cyclic voltammograms were recorded with the conventional three-electrode configuration in  $\text{CH}_2\text{Cl}_2$  containing 0.1M  $^n\text{Bu}_4\text{N}^+\text{PF}_6^-$ , as supporting electrolyte, with Pt-electrodes and a Ag/AgCl electrode as the reference one. Resulting potentials were corrected vs. the  $\text{Fc}/\text{Fc}^+$  couple (+470 mV, see: N. G. Connelly, W.E. Geiger, *Chem. Rev.* **1996**, *96*, 877-910).

Chronoamperometric experiments were performed with an electrochemistry equipment from EG&G Princeton Applied

Research, using a platinum wire as working electrode and a Ag/AgCl electrode as the reference electrode. Anhydrous  $\text{CH}_2\text{Cl}_2$  was freshly distilled over  $\text{P}_2\text{O}_5$  under nitrogen. Anhydrous THF was freshly distilled over Sodium under Nitrogen. 0.1M Tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte.

EPR spectra were obtained on a Bruker ESP-300E spectrometer operating at X-band (9.3 GHz), equipped with a rectangular cavity T 102. Spectra were recorded in the 4 - 300 K range using a Bruker variable-temperature unit and an Oxford Instruments EPR-900 cryostat. The signal-to-noise ratio was increased by accumulation of scans using the F/F lock accessory Bruker ER 033M and a NMR gaussmeter Bruker ER 035M, to guarantee a high-field reproducibility. Precautions to avoid undesirable spectral line broadening such as that arising from microwave power saturation and magnetic field over-modulation were taken.

## 2. Crystal structure of radical 1:

X-ray structure analysis of  $\text{C}_{40}\text{H}_{29}\text{Cl}_{14}\text{Fe}$ ,  $M_r = 1061.78$ ; brown plates with the dimensions 0.25 x 0.06 x 0.03 mm; triclinic, space group  $P\bar{1}$  (no.2),  $a = 9.1198(8)$ ,  $b = 15.805(2)$ ,  $c = 17.310(2)$  pm,  $\alpha = 116.150(5)$ ,  $\beta = 95.495(7)$ ,  $\gamma = 99.661(7)$ deg,  $V = 2166.9(4)$  nm<sup>3</sup>,  $\rho_{\text{calcd}} = 1.627$  gcm<sup>-3</sup>,  $Z = 2$ ,  $T = 233(2)$  K,  $\mu(\text{Mo}_K\alpha) = 0.71703$ . Data were measured with a Nonius Kappa CCD, intensities were integrated with DENZO and scaled with SCALEPACK; 6943 measured reflections, of which 3738 with  $I > 2\sigma(I)$  were included in the structure refinement against  $F^2$  (SHELXL 97). The structure was solved by direct methods (SHELXS 97); heavy atoms with anisotropic temperature factors except C1 to C12 which were refined isotropically; hydrogen atoms were calculated. The ethylene bridge C11-C12 display an orientation disorder (1:1). Refinement with 449 variables with a GOF of 1.072. Final R-values for 2538

reflections with  $I > 2\sigma(I)$ :  $R_1 = 0.0878$  (against  $|F^2|$ ) and  $wR_2 = 0.1615$  (against  $|F|$ ). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC-191558. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>. Program for crystal structure solutions, Göttingen (Germany), 1997; G. M. Sheldrick, SHELXS-97.

### 3. Preparation of compound 1H:

Phosphonate **2** (637 mg, 0.726 mmol) was suspended in dry THF (20 mL) under argon. The solution was cooled down to  $-78^\circ\text{C}$  and potassium-tert-butoxide (190 mg, 1.69 mmol) was added. The orange-yellow ylide suspension that was formed immediately was stirred for 15 min after which the temperature was increased to  $0^\circ\text{C}$  by means of an ice bath and finally the nonamethylferrocenecarboxaldehyde **3** (271 mg, 0.800 mmol), dissolved in THF (5 mL) was added dropwise to the reaction mixture. Stirring was continued for 60 hours at room temperature after which the reaction mixture was quenched with HCl (5 mL, 2N) and extracted with chloroform (4 portions of 25 mL). The organic layer was washed with water (20 mL), dried over sodium sulfate and evaporated under reduced pressure. Chromatographic workup (silica, hexane/ether, 1/1) yielded 700 mg (90%) of pure **1H**. Characterization Data: Elemental Anal. Calc. for  $\text{C}_{40}\text{H}_{30}\text{Cl}_{14}\text{Fe}-\text{C}_6\text{H}_{14}$ : C, 46.7; H, 3.37; Found C, 46.52; H, 3.43; Cyclic Voltammetry in  $\text{CH}_2\text{Cl}_2$  and 0.1M tetrabutylammonium hexafluorophosphate as electrolyte:  $E_{\text{red}} = 0.090$  V vs. Ag/AgCl; FT-IR (KBr,  $\tilde{\nu}$  in  $\text{cm}^{-1}$ ): 2954; 2923; 2854; 1624;; 1536; 1451; 1423; 1373; 1299; 1241; 1135; 1028; 972; 809; 716; 683; 648; 529; 468; UV-Vis-NIR ( $\text{CH}_2\text{Cl}_2$ ,  $\lambda_{\text{max}}$  in nm ( $\epsilon$ )): 338 (12100); 519 (2200); EM-LDI-TOF

(negative mode):  $m/z$  (amu/e<sup>-</sup>) 1063, [M+1H]<sup>-</sup>; 1028 [M-1Cl]<sup>-</sup>; 992 [M-2Cl]<sup>-</sup>; 957; 870; 822; 679; 481; 311; NMR (CDCl<sub>3</sub>): <sup>1</sup>H:  $\delta$  7.01 (1H, s, CH), 6.92 (1H, d,  $J$  = 16.6Hz, CH=CH), 6.65 (1H, d,  $J$  = 16.6Hz, CH=CH), 1.90 (6H, s, CH<sub>3</sub>), 1.75 (6H, s, CH<sub>3</sub>), 1.65 (15H, s, CH<sub>3</sub>).

#### 4. Preparation of salt K<sup>+</sup>(18-crown-6)[1]<sup>-</sup>:

Compound **1H** (350 mg, 330  $\mu$ mol) was dissolved in dry THF (10 mL) under argon. 18-Crown-6 (100 mg, 375  $\mu$ mol) and finely grinded powder of potassium hydroxide (200 mg, 3.60 mmol) were added to the solution which was left with strong stirring for 24 hours. The solution was filtered and the solvent was reduced in volume to approximately 1 mL. The product precipitated on addition of dry n-hexane. It was filtered, redissolved in a few mL of dry CH<sub>2</sub>Cl<sub>2</sub> and reprecipitated with dry n-hexane two times more. Yield: 400 mg (89%) of K<sup>+</sup>(18-crown-6)[1]<sup>-</sup> as a dark violet powder. Characterization Data: Elemental Anal. Calc. for C<sub>52</sub>H<sub>53</sub>O<sub>6</sub>Cl<sub>14</sub>KFe: C, 45.75; H, 3.91; Found C, 45.6; H, 3.75; FT-IR (KBr,  $\nu$  in cm<sup>-1</sup>): 2913; 2857; 1631; 1472; 1453; 1373; 1352; 1335; 1283; 1249; 1107; 962; 838; 721; 663; 687; 649; 612; 584; 530; 523; UV-Vis-NIR (CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{max}$  in nm ( $\epsilon$ )): 534 (31350); (THF,  $\lambda_{max}$  in nm ( $\epsilon$ )): 534 (31300); EM-LDI-TOF (negative mode):  $m/z$  (amu/e<sup>-</sup>) 1061, [M(1<sup>-</sup>)]; 1026, [M-1Cl]<sup>-</sup>; 991, [M-2Cl]<sup>-</sup>; 956, [M-3Cl]<sup>-</sup>; 303.

#### 5. Preparation of radical 1:

The K<sup>+</sup>(18-crown-6)[1]<sup>-</sup> salt [200 mg, 146  $\mu$ mol] was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and solid AgBF<sub>4</sub> (30 mg, 150  $\mu$ mol) was added. After a few minutes the color of the solution changed from violet to dark-brown and grey precipitate of metallic silver was formed. The solution was left with strong stirring for 30min after which it was

filtered and evaporated. The product was redissolved in dry *n*-hexane, filtered again and the solvent was evaporated under reduced pressure. Yield: 108 mg (70%) of radical **1** as dark brown power. Characterization Data: Elemental Anal. Calc. for  $C_{40}H_{29}Cl_{14}Fe$ : C, 45.24; H, 2.75; Found C, 45.5 ; H, 2.85. FT-IR (KBr,  $\bar{\nu}$  in  $cm^{-1}$ ): 2901; 1612; 1505, 1474; 1420; 1375; 1351; 1335; 1262; 1108; 1084; 1029; 965; 838; 816; 736; 712; 667; 652; 530; UV-Vis-NIR ( $CH_2Cl_2$ ,  $\lambda_{max}$  in nm ( $\epsilon$ )): 346 (16900), 385 (23950), 497 (8000), 656 (3900), 1520 (1600); (THF,  $\lambda_{max}$  in nm ( $\epsilon$ )): 346 (15250), 385 (22800), 497 (8600), 656 (4400), 1540 (1700). EPR (THF at 300K),  $g_{iso} = 2.0024$ ;  $a(1H) = 1.6$  G;  $\Delta H_{1/2} = 1.4$  G. EPR (in frozen THF at 77 K),  $g_{\square} = 2.0022$ ;  $g_{//} = 2.0075$ . EM-LDI-TOF (positive mode):  $m/z$  (amu/ $e^-$ ) 1061,  $[M]^+$ ; 991,  $[M-2Cl]^+$ ; 956,  $[M-3Cl]^+$ ; 371; 303; 287; 242; 215; Cyclic voltammetry in  $CH_2Cl_2$  and 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte: (1/1-):  $E_{\square} = -238$  mV, (1/1+):  $E_{\square} = +86$  mV, (1+/1++):  $E_{\square} = \text{aprox. } 1800$  mV vs Ag/AgCl, corrected vs  $fc/fc^+$  couple.

## 6. Preparation of salt $[1]^+BF_4^-$ :

salt  $K^+(18\text{-crown-6})[1]^+$  (90 mg, 66  $\mu\text{mol}$ ) was dissolved in  $CH_2Cl_2$  (5 mL) and  $AgBF_4$  (27 mg, 137  $\mu\text{mol}$ ) was added. After a few minutes the color of the solution changed from violet to dark-yellow-brownish and a grey precipitate of metallic silver was formed. The solution was left with strong stirring for 30min after which it was filtered and reduced in volume to approximately 1mL. On addition of dry *n*-hexane small white needles appeared floating on the surface and then they were sucked off. On further addition of *n*-hexane the a brown powder precipitated which as filtered, redissolved in a few mL of dry  $CH_2Cl_2$  and then treated two times with dry *n*-hexane the same way as described before. Yield: 60 mg (79%) of salt  $[1]^+BF_4^-$  as a dark brown powder. Characterization Data: Elemental Anal. calc. for

$C_{40}H_{29}BCl_{14}F_4Fe$ : C, 41.83; H, 2.54; Found C, 42.3 ; H, 2.65 .  
 FT-IR (KBr,  $\lambda$  in  $cm^{-1}$ ): 2956; 2921; 2855; 1628; 1474, 1383;  
 1336; 1259; 1056; 816; 710; EPR (THF at 300K),  $g_{iso} =$   
 2.0024. EPR (in toluene/ $CH_2Cl_2$  1:1, at 4 K),  $g_{//} = 4.03$ ;  $g_{\perp} =$   
 1.65;  $|D'| = 155$  G;  $|E'| = 35$  G. UV-Vis-NIR ( $CH_2Cl_2$ ,  $\lambda_{max}$  in  
 nm ( $\epsilon$ )): 285 (33300), 324 (27300), 385 (36650), 425 (s,  
 15800), 565 (2050), 805 (850); (THF,  $\lambda_{max}$  in nm ( $\epsilon$ )): 285  
 (26450), 324 (21950), 385 (27750), 425 (s, 20800), 565  
 (1650), 804 (750).

#### **Non linear optical properties of **1**, **1**<sup>+</sup>, and **1**<sup>-</sup>:**

The  $\chi(800)$  values for **1**, **1**<sup>+</sup>, and **1**<sup>-</sup> are resonantly enhanced to a certain extent due to the closeness of the second harmonic wavelength of the excitation laser to an absorption band. Unfortunately, determination of static hyperpolarizability values  $\chi(0)$  using the simple two-level model is not straightforward for organometallic compounds since several charge transfer excitations may contribute to the observed  $\chi$  value. Furthermore, as it was recently pointed out, the two-level model is also inappropriate for open-shell molecules [1] and results in underestimated values for the static hyperpolarizability. To evaluate the influence of fluorescence in the nonlinear optical responses of the studied compounds, emission spectra when irradiated at a wavelength of 375 nm were recorded. No studied compounds show any emission at 400 nm, thus the contribution of fluorescence to the HRS signal is shown to be zero. In summary, it can be said that radical **1** gives an intense nonlinear optical response while this response is much lower in its reduced or oxidized forms.

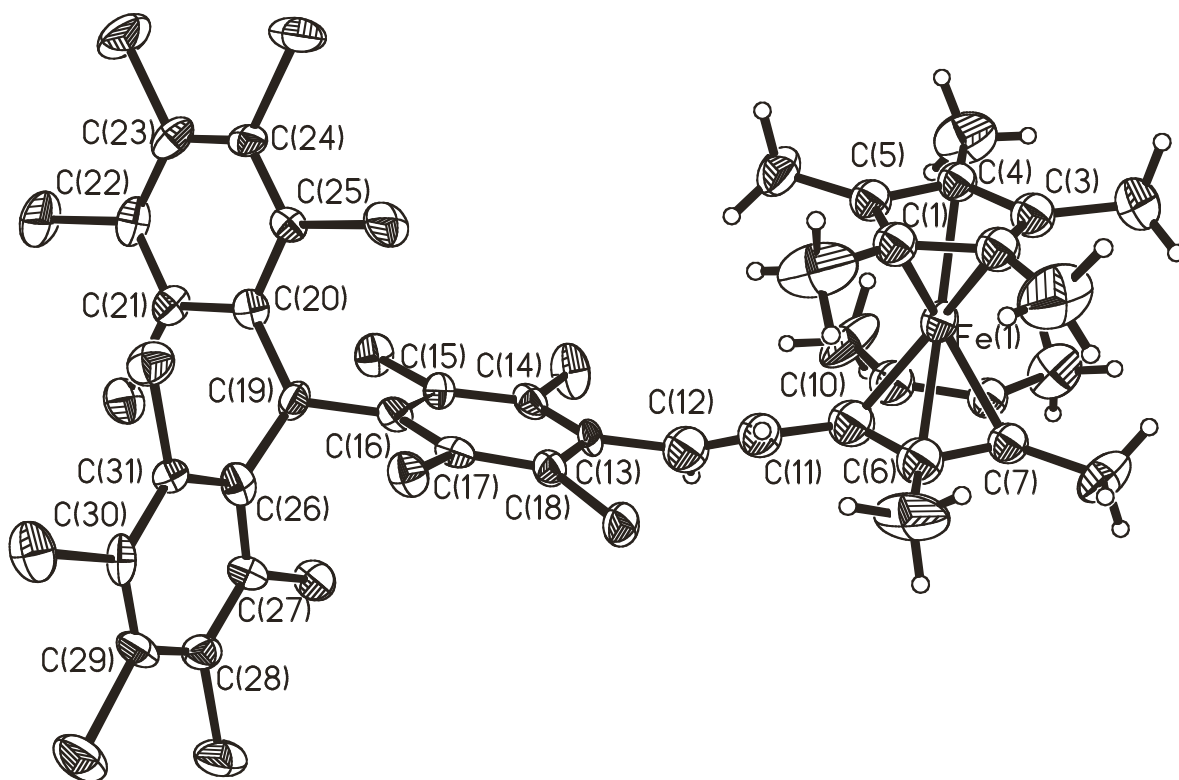
#### **EPR studies:**

The two paramagnetic compounds show difference in the magnetic properties in solution studied by EPR spectroscopy

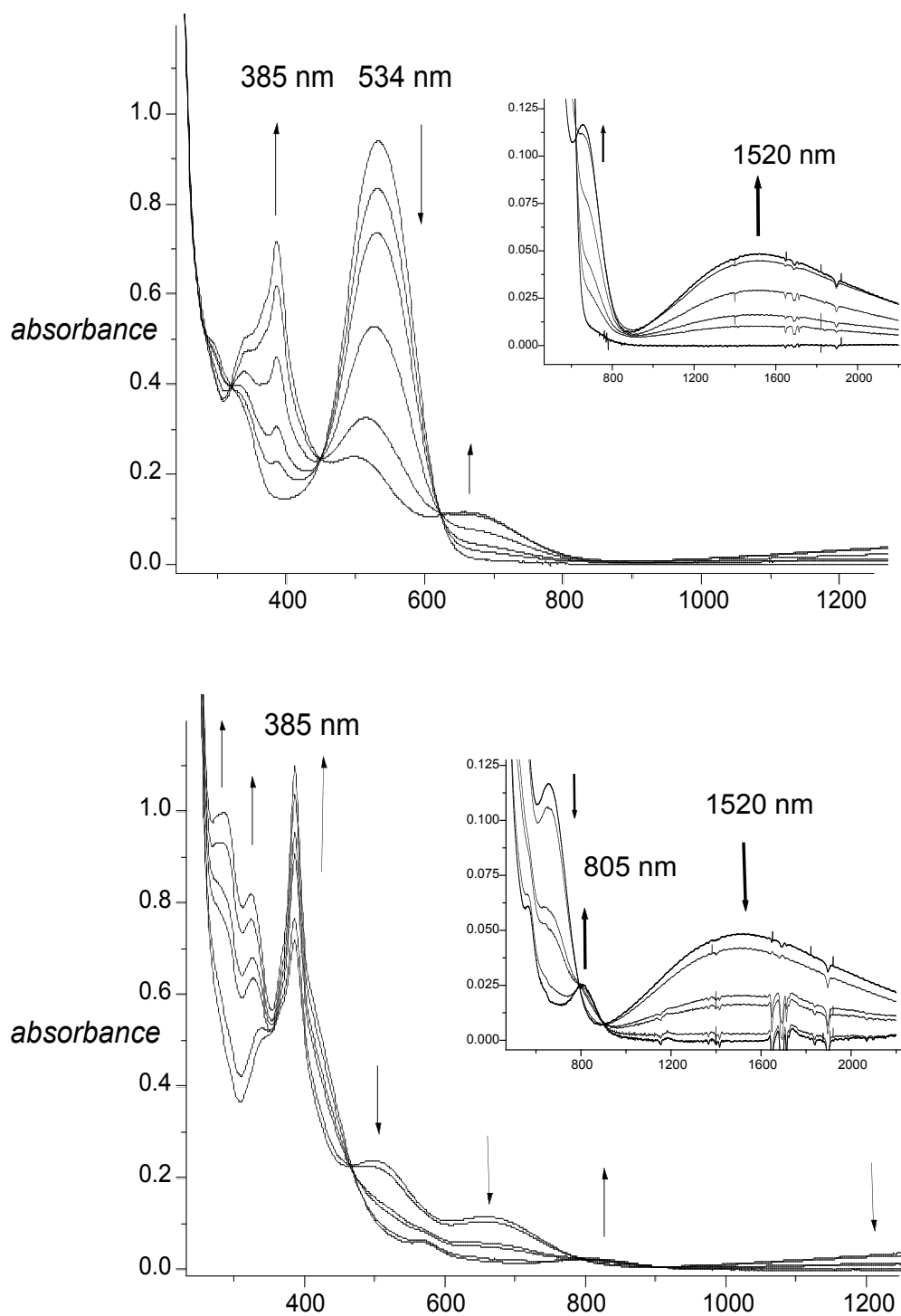


So, **1** exhibits at 300 K two main, symmetrical, partially overlapped lines, centered at  $g = 2.0024$ , that are caused by the hyperfine coupling with one H atom of the ethylene bridge with  $a(\text{H}) = 1.6$  G; as occurs for other vinyl substituted radicals of this family. [10] By contrast, **1**<sup>+</sup> displays under similar conditions an asymmetrical structured line at  $g = 2.0024$ . Spectral differences of these two open-shell species increase progressively by lowering the temperature becoming entirely different at very low temperatures. Thus, **1** shows at 4 K the typical spectrum of an organic radical with a very small magnetic anisotropy,  $g_{\parallel} = 2.0075$  and  $g_{\perp} = 2.0022$ , while **1**<sup>+</sup> exhibits the characteristic fine structure of a triplet species with zero-field splitting parameters of  $|D'| = 155$  Gauss and  $|E'| = 35$  Gauss with principal components of **g**-tensor being  $g_{\parallel} = 4.03$  and  $g_{\perp} = 1.65$ .

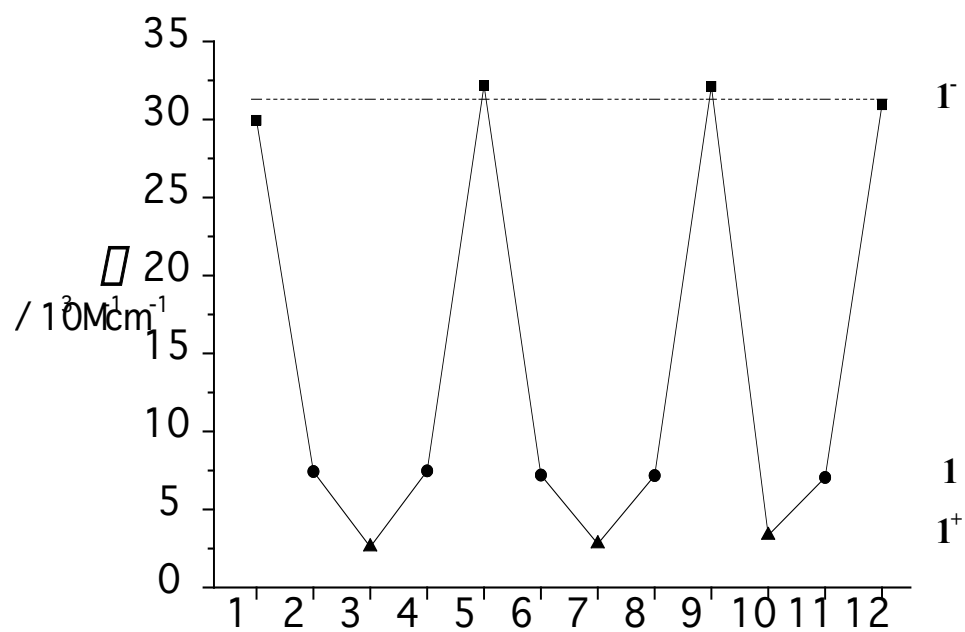
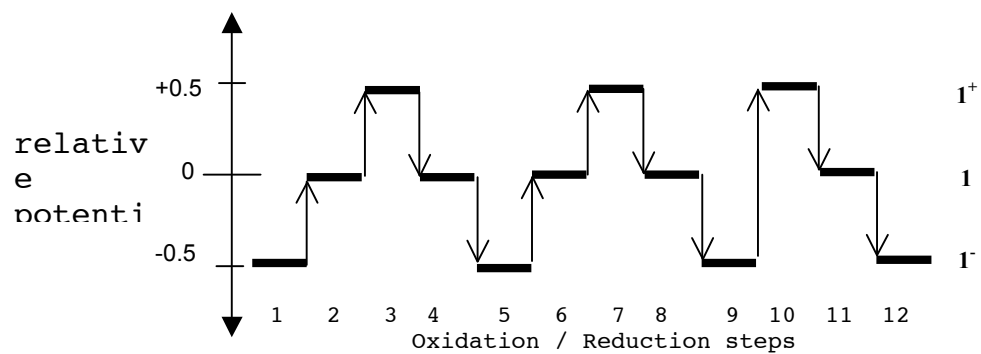
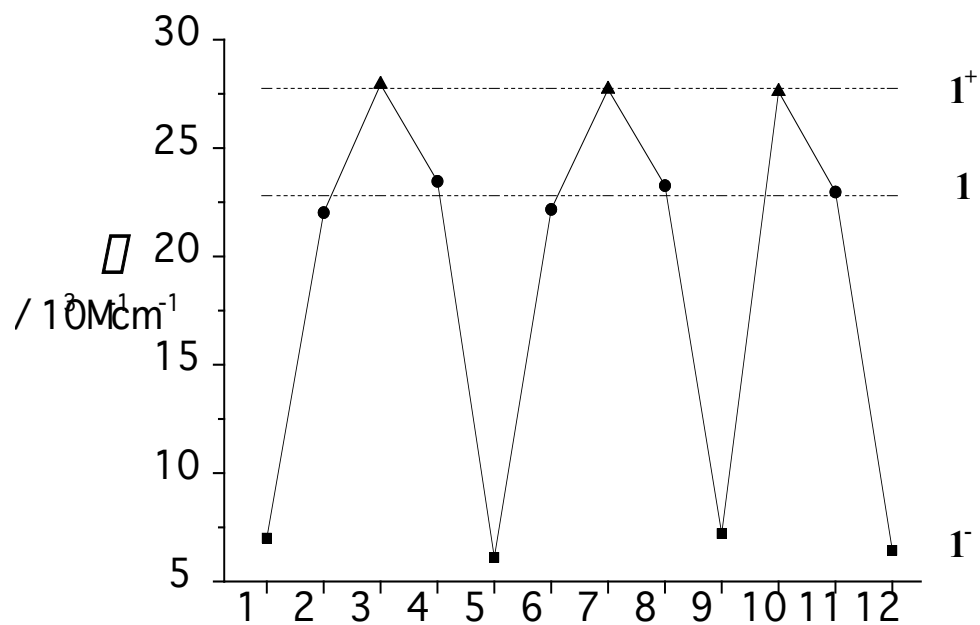
[1] S. diBella, I. Fragala, T. J. Marks, M. A. Ratner, *J. Am. Chem. Soc.* **1996**, *118*, 12747-12751.



**Figure S1.** Crystal structure of **1**. Thermal ellipsoids are shown at the 30% probability level.



**Figure S2** Spectroelectrochemical experiments showing the evolution of UV-Vis-NIR spectra during the oxidation of **1<sup>-</sup>** (*top*) and of radical **1** (*bottom*) in CH<sub>2</sub>Cl<sub>2</sub>. Trends of intensity changes are shown for a few particular bands with arrows pointing up and down.



**Figure S3.** Cyclic stepwise oxidations and reductions carried out in THF with a chronoamperometric technique following the changes by visible spectrometry. *Top:* Changes observed at a wavelength of 385 nm where **1** ( ) and **1**<sup>+</sup> (□) exhibit the strongest absorption and **1**<sup>-</sup> (▢) shows a very weak absorption. *Bottom:* Changes observed at 534 nm where **1** ( ) and **1**<sup>+</sup> (□) exhibit very weak absorptions while it is maximum for **1**<sup>-</sup> (▢). *Middle:* Fixed potentials used in the different steps of cyclic redox experiments.