

## Electrochemical and spectroscopic detection of self-association of octa-alkyl phthalocyaninato cadmium compounds into dimeric species

*Eleanor Fourie, Jannie C. Swarts,\* Isabelle Chambrier and Michael J. Cook\**

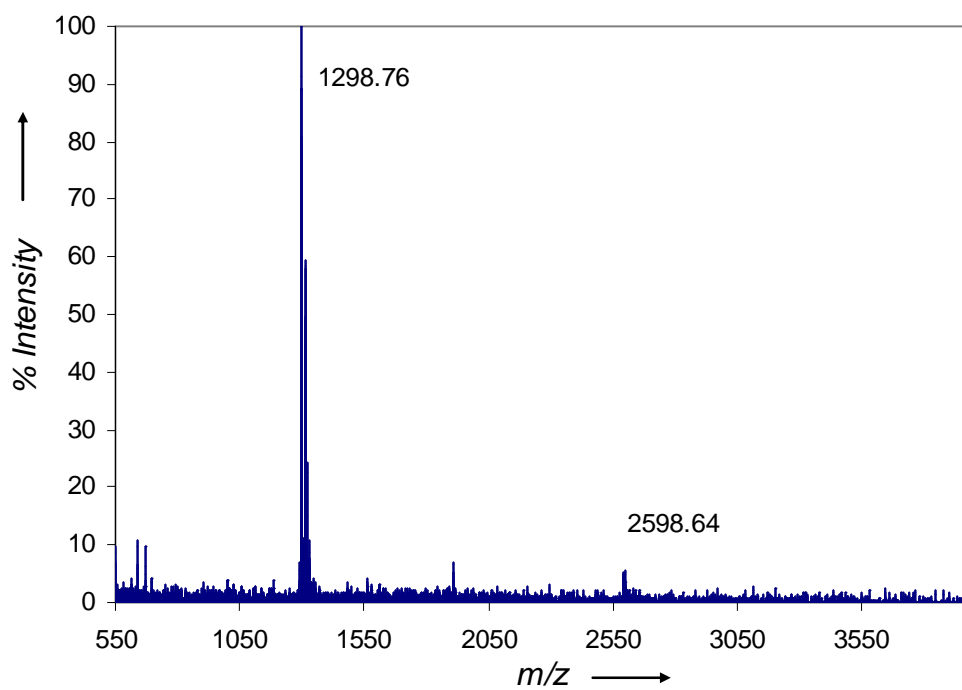
### 1. General

**Materials and techniques:** Dichloromethane was dried over calcium hydride during reflux under nitrogen; tetrahydrofuran was dried over Na metal.  $[N(n\text{-Bu})_4][B(C_6H_5)_4]$  was prepared as described elsewhere.<sup>1</sup>

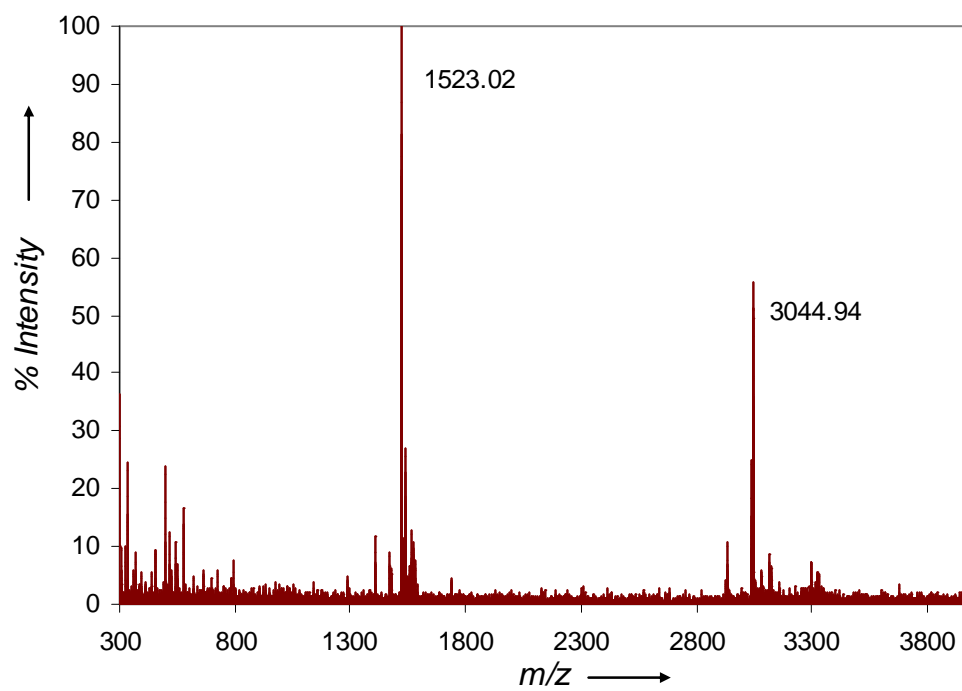
**Spectroscopy:** All solvents were analytical grade and were used as supplied.  $CHCl_3\text{-}d_1$  (>99.8 atom% D) deuterated solvent was purchased from Apollo Scientific Ltd. THF- $d_8$  (99.5 atom% D) was purchased from Cambridge Isotope Laboratories Inc. Pyridine- $d_5$  (99.5 atom% D) was purchased from Goss Scientific Instruments Ltd. The UV-vis. spectra were obtained on a Hitachi U-3000 spectrophotometer. Solutions were prepared at the required concentrations and the absorbance measured in 1 cm, 1 mm or 0.1 mm quartz cells in the stated solvents. The  $^1H$  NMR spectra were measured at 400 MHz on a Jeol Unityplus-400 spectrometer in the stated solvents.

**Electrochemistry:** Cyclic voltammetry, square wave voltammetry and linear sweep voltammetry experiments were performed on *ca.*  $5 \times 10^{-4}$  M solutions of **1-4** in dry  $CH_2Cl_2/0.1$  M  $[N(n\text{-Bu})_4][B(C_6F_5)_4]$  or THF/  $0.1$  M  $[N(n\text{-Bu})_4][B(C_6F_5)_4]$  utilising a standard three-electrode cell with circular glassy carbon electrode of surface area  $3.14$  mm<sup>2</sup> (pre-treated by polishing on a Buehler microcloth first with 1 micron and then  $\frac{1}{4}$  micron diamond paste), a Pt-wire counter electrode and a Ag/Ag<sup>+</sup> reference electrode. Because the working electrode was quickly contaminated, it was never used for more than six successive potential cycles before it was recleaned and polished. The Ag/Ag<sup>+</sup> reference electrode was constructed by immersing a Ag wire in an acetonitrile solution containing  $0.01$  M AgNO<sub>3</sub> and  $0.1$  M  $[N(n\text{-Bu})_4][B(C_6H_5)_4]$  in a thin inner Luggin capillary with vicor tip. This Luggin was immersed into a second Luggin capillary with vicor tip which contained  $0.1$  M  $[N(n\text{-Bu})_4][B(C_6H_5)_4]$  dissolved either in dichloromethane for experiments conducted in  $CH_2Cl_2$ , or in THF for experiments conducted in THF. Ferrocene and/or dexamethylferrocene (Fc\*) was at the end of each experiment added as internal standard to the bulk solution to enable data reporting versus the Fc/Fc<sup>+</sup> couple as recommended by IUPAC.<sup>2</sup> Under our conditions, the Fc/Fc<sup>+</sup> couple exhibited  $i_{pc}/i_{pa} = 0.98$ ,  $\Delta E_p = 70$  mV and  $E^{\circ'} = 0.220$  V versus Ag/Ag<sup>+</sup> in  $CH_2Cl_2$ , while in THF it exhibited  $i_{pc}/i_{pa} = 0.97$ ,  $\Delta E_p = 90$  mV and  $E^{\circ'} = 0.176$  V versus Ag/Ag<sup>+</sup>. The Fc\*/Fc\*<sup>+</sup> couple was at  $-0.610$  or  $-0.515$  V vs. Fc/Fc<sup>+</sup> in  $CH_2Cl_2$  or THF respectively.<sup>3</sup> As this study was especially concerned with formal reduction potentials under strong reducing conditions in THF, we chose to reference our results vs. Fc\*/Fc\*<sup>+</sup> at  $-0.610$  V in *both* solvents rather than vs. Fc/Fc<sup>+</sup>. We did this to allow better comparisons of obtained formal reduction potentials in THF and  $CH_2Cl_2$  at more negative potentials. This reference potential means that the  $CH_2Cl_2$  results is reported vs. Fc/Fc<sup>+</sup> as well, but not the THF results. Based on the experimentally determined Fc\*/Fc\*<sup>+</sup>  $\Delta E_p$  values, with respect to this study, all processes having  $\Delta E_p < ca.$  90 mV were considered as electrochemical reversible. Qualitatively, processes having  $\Delta E_p$  values in the range  $90 < \Delta E_p < 150$  mV were considered electrochemical quasi reversible, and those that exhibited  $\Delta E_p > 150$  mV were considered electrochemical irreversible.<sup>4</sup> An ideal one-electron electrochemical reversible process are characterised by  $\Delta E_p = 59$  mV.<sup>5</sup> All measurements were conducted under a blanket of argon thermostated at  $25.0 \pm 0.2$  °C in a Faraday cage connected to a BAS 100 B/W electrochemical workstation interfaced with a personal computer. Data, uncorrected for junction potentials, were collected with standard BAS 100 software and exported to Excel for manipulation and analyses. Successive experiments under the same experimental conditions showed that all formal reduction and oxidation potentials were reproducible within 5 mV. Blank experiments using solvent containing electrolyte but no phthalocyanines were performed to determine the usable potential window of each solvent and to confirm purity of each solvent/supporting electrolyte system.

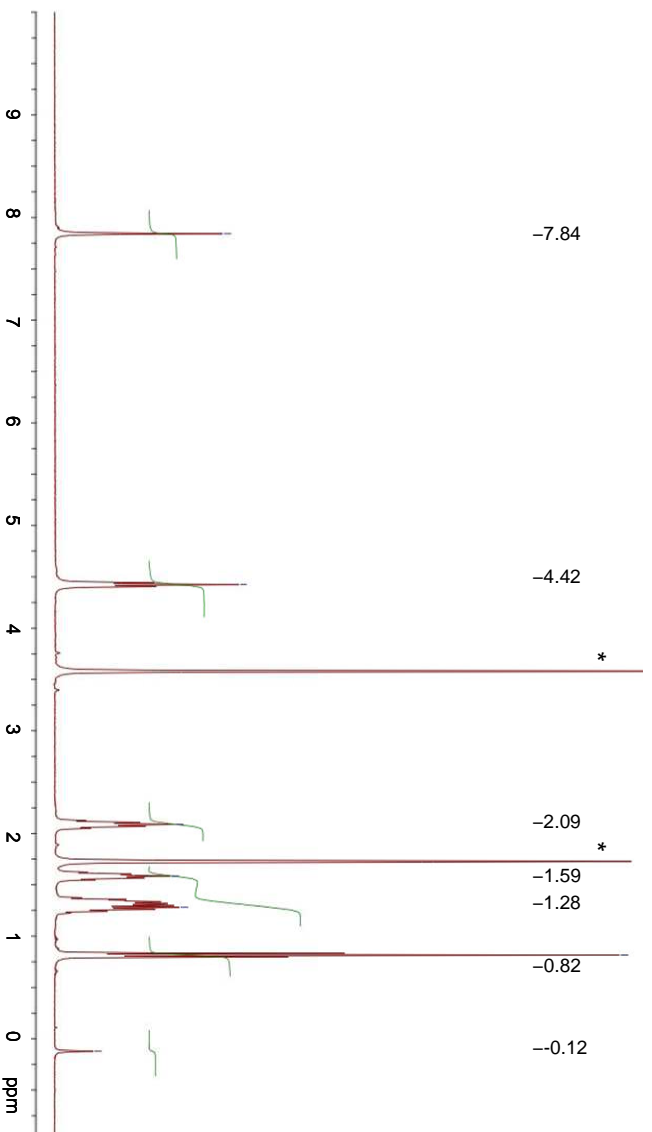
## 2. MALDI-TOF spectrum of compound 3



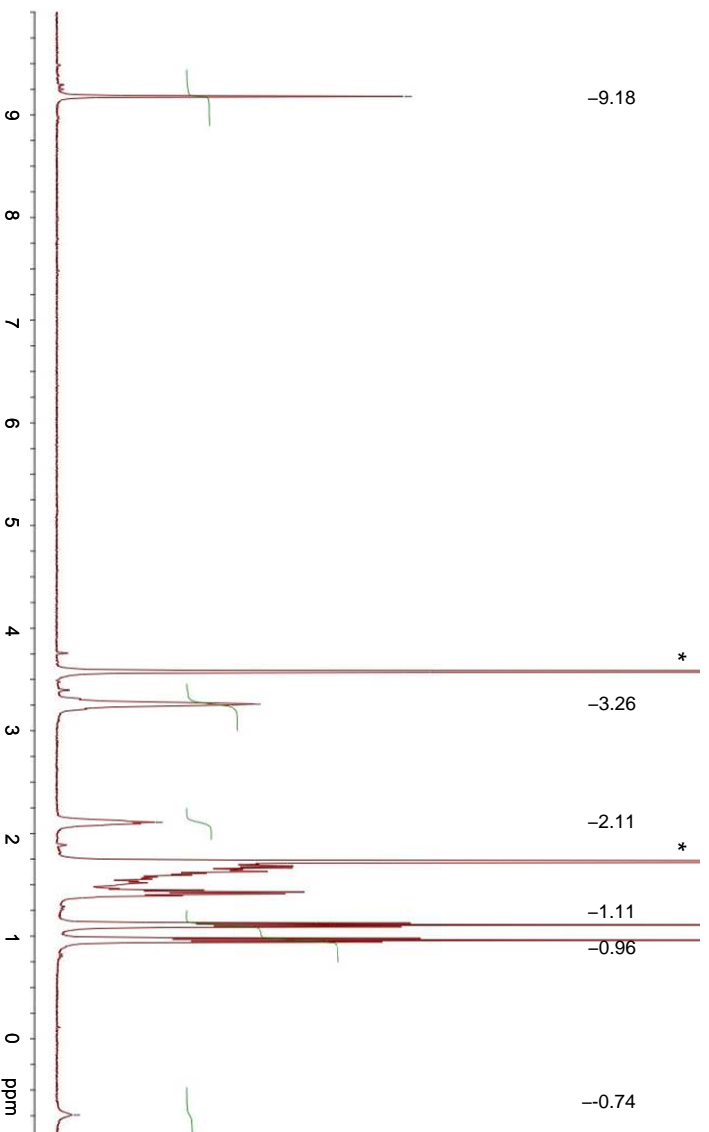
## 3. MALDI-TOF spectrum of compound 4



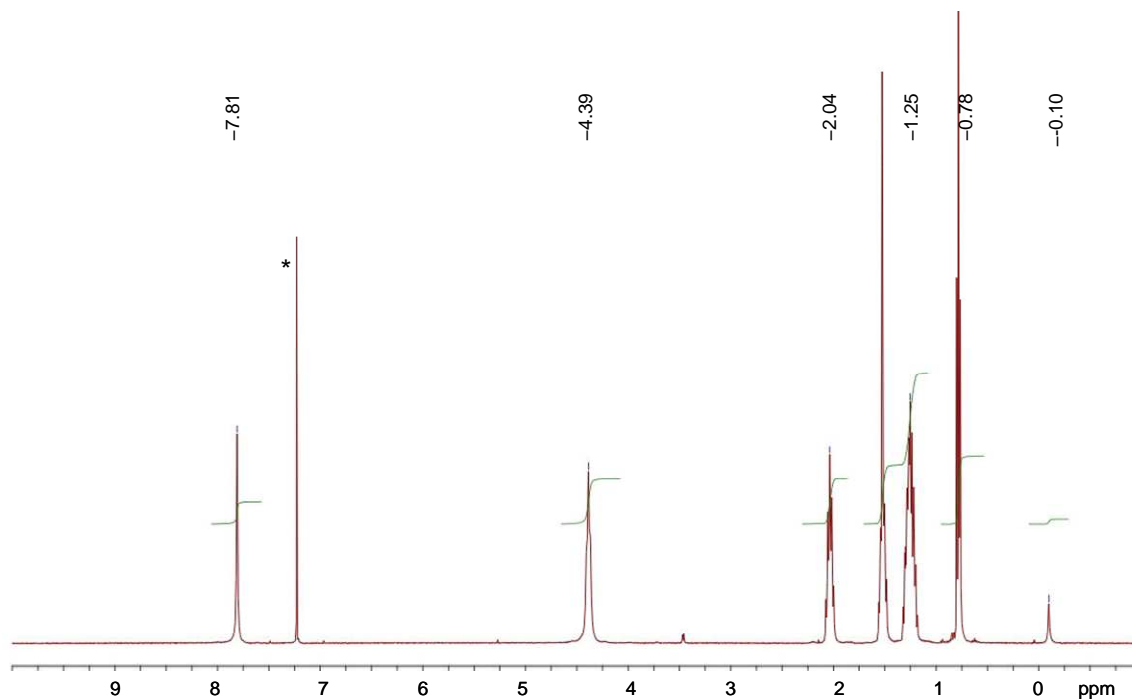
4.  $^1\text{H}$  NMR spectrum (400 MHz) of compound **1** in THF- $d_8$  (\* indicates solvent peaks)



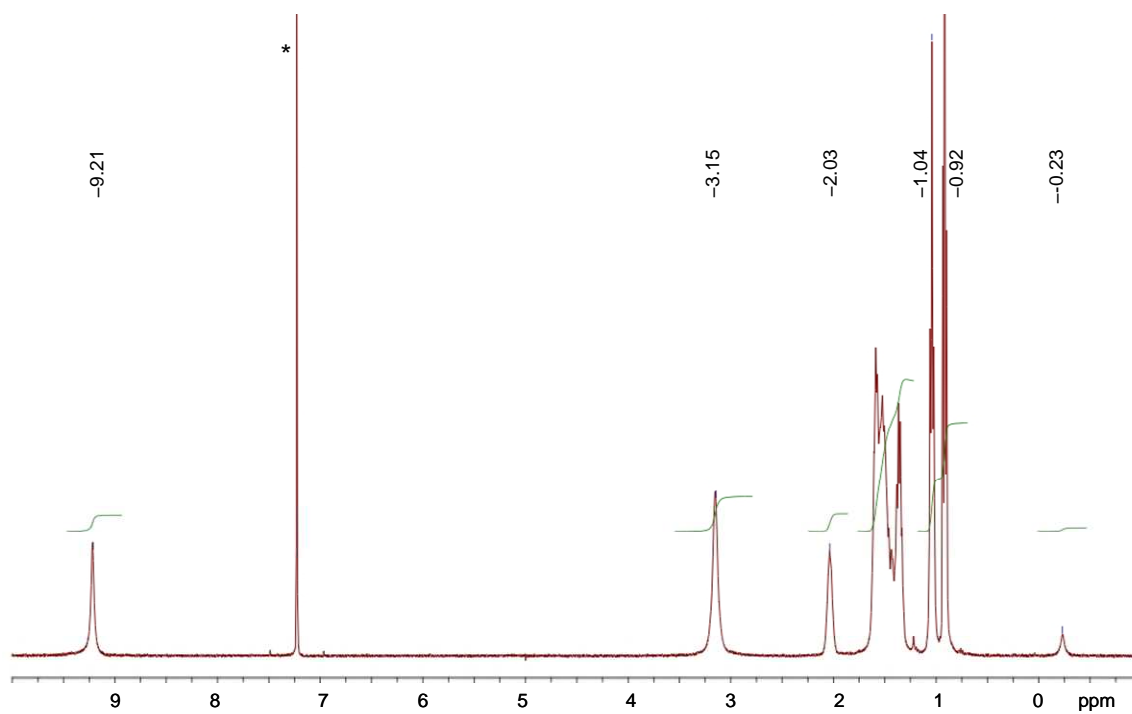
5.  $^1\text{H}$  NMR spectrum (400 MHz) of compound **2** in THF- $d_8$  (\* indicates solvent peaks)



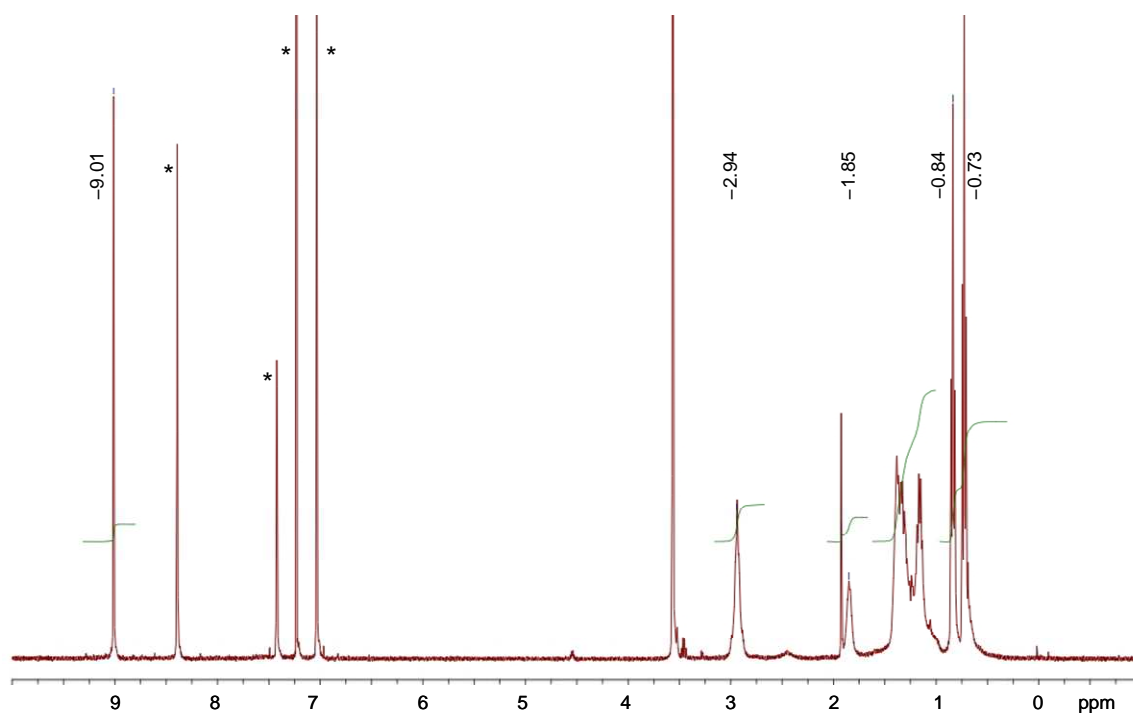
6.  $^1\text{H}$  NMR spectrum (400 MHz) of compound **1** in  $\text{CHCl}_3\text{-d}_1$  (\* indicates solvent peak)



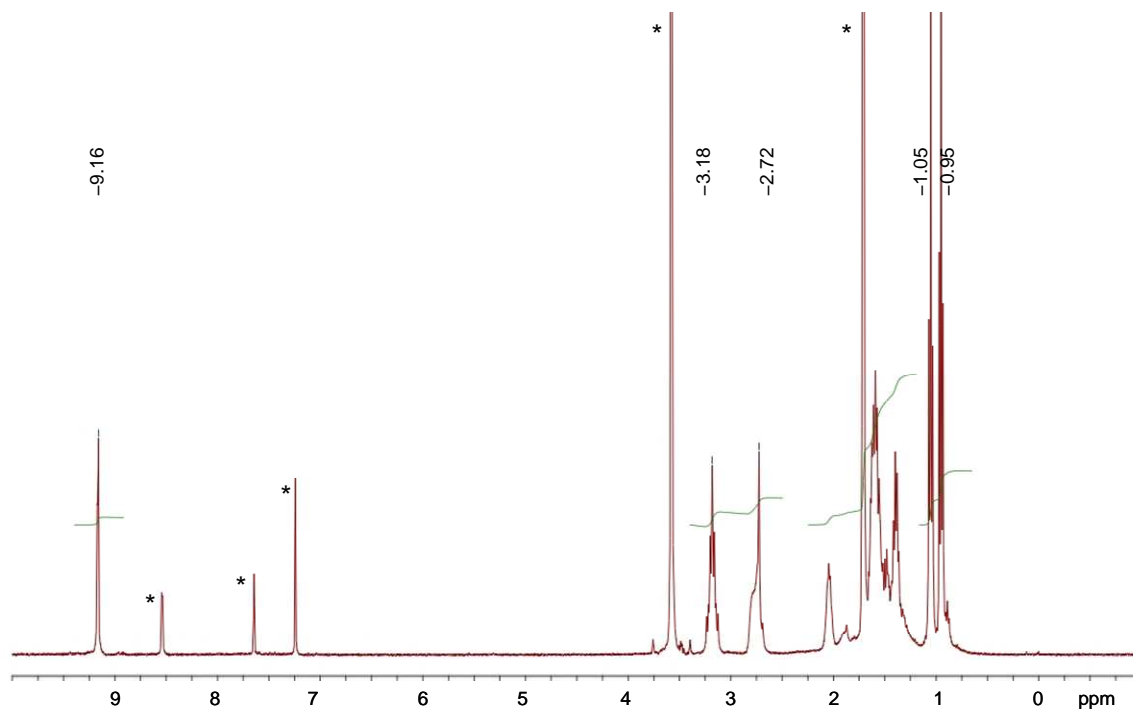
7.  $^1\text{H}$  NMR spectrum (400 MHz) of compound **2** in  $\text{CHCl}_3\text{-d}_1$  (\* indicates solvent peak)



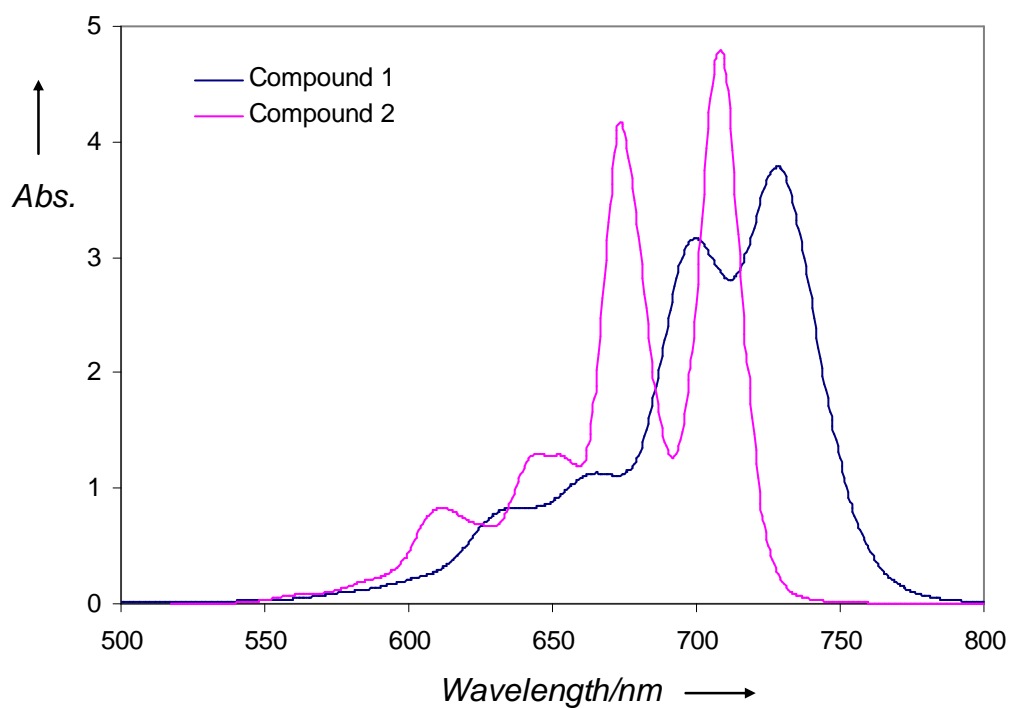
8.  $^1\text{H}$  NMR spectrum (400 MHz) of compound **4** in  $\text{CHCl}_3\text{-d}_1$  + pyridine- $\text{d}_5$  (\* indicates solvent peaks)



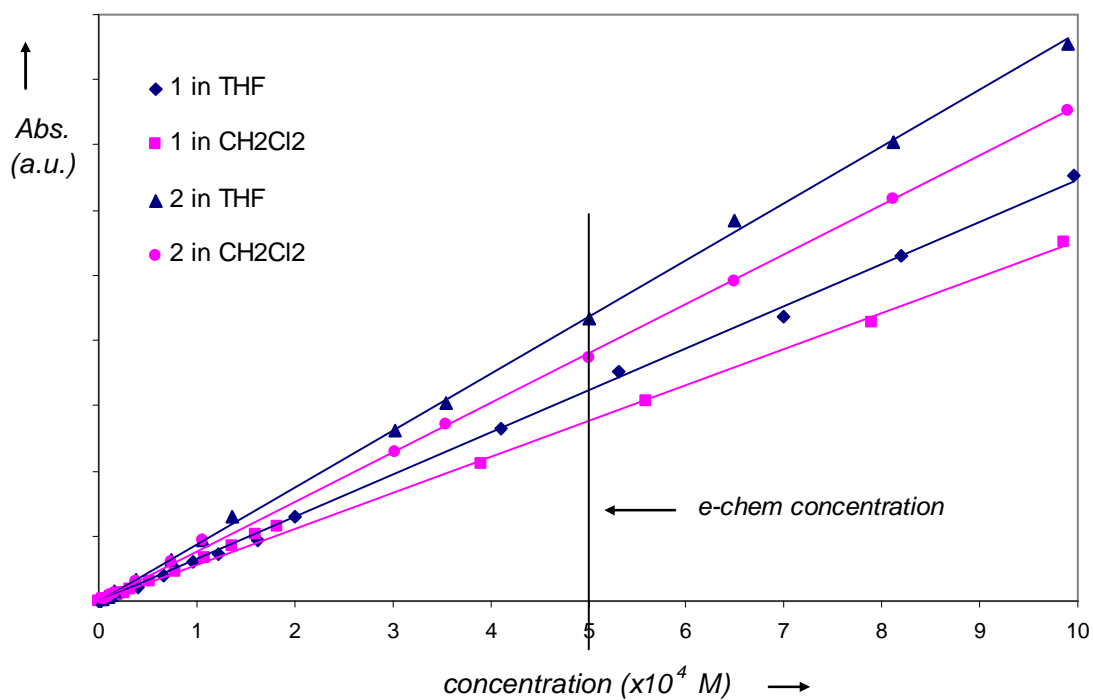
9.  $^1\text{H}$  NMR spectrum (400 MHz) of compound **4** in  $\text{THF-d}_8$  + pyridine- $\text{d}_5$  (\* indicates solvent peaks)



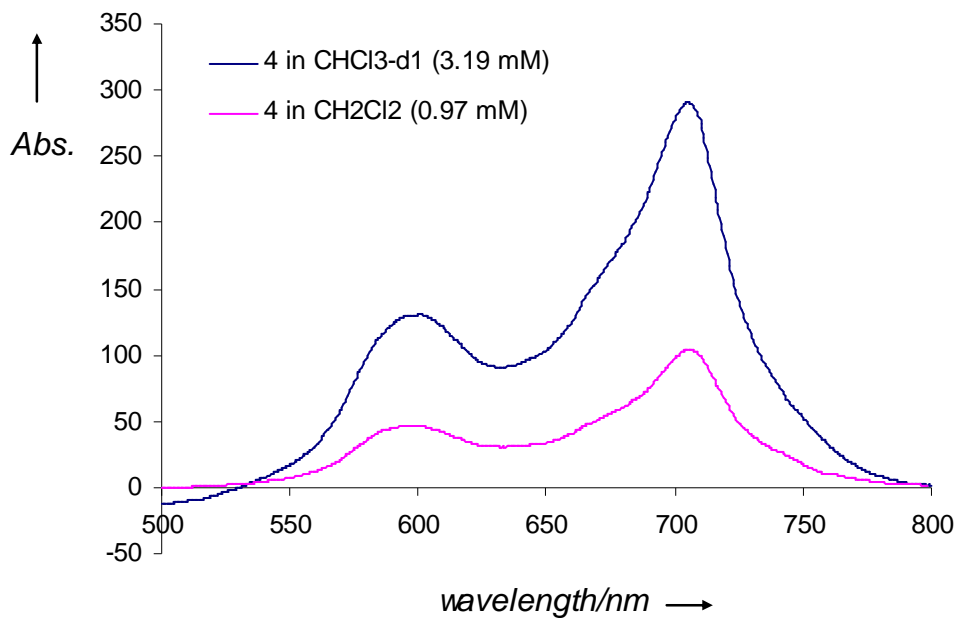
10. UV-Vis. spectra of compounds **1** ( $1.38 \times 10^{-5}$  M) and **2** ( $1.30 \times 10^{-5}$  M) in  $\text{CH}_2\text{Cl}_2$



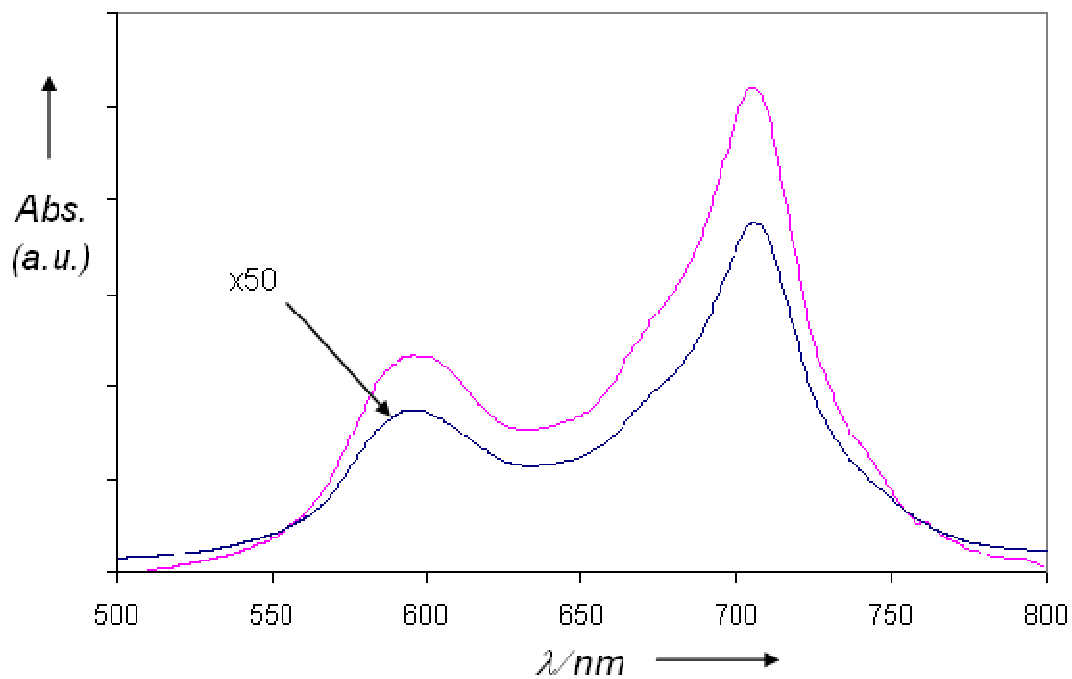
11. Beer-Lambert plots of compounds **1** and **2** in  $\text{CH}_2\text{Cl}_2$  and THF



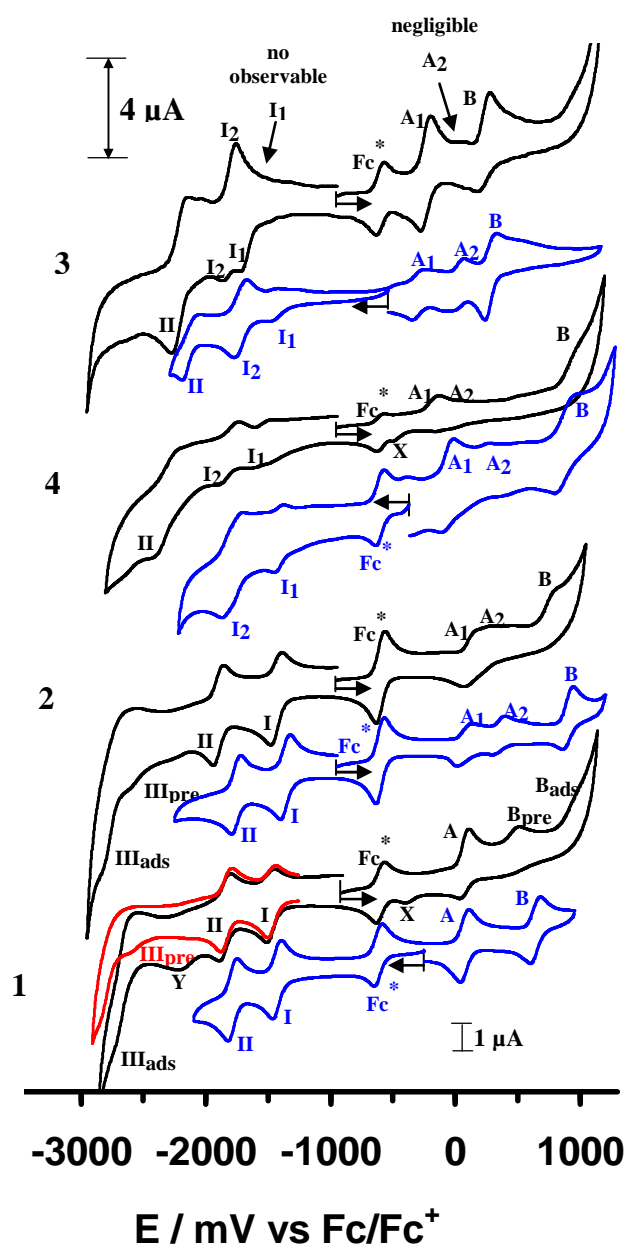
12. UV-Vis. spectra of compound **4** in  $\text{CH}_2\text{Cl}_2$  ( $0.97 \times 10^{-3}$  M) and in  $\text{CHCl}_3\text{-d}_1$  ( $3.19 \times 10^{-3}$  M)



13. UV-Vis. spectra of compound **4** in  $\text{CH}_2\text{Cl}_2$  at  $1.44 \times 10^{-5}$  M (blue) and  $0.93 \times 10^{-3}$  M (pink)



14. CVs at  $100 \text{ mV s}^{-1}$  in  $\text{CH}_2\text{Cl}_2$  (blue) and THF (black). Anodic (oxidation) processes are labelled A and B, cathodic (reduction) processes are labelled I through III. Numbering started from the resting redox state to synchronize wave number with sequential redox processes.  $\text{Fc}^*$  = the internal standard, decamethylferrocene, which has a potential of  $-610 \text{ mV vs. Fc/Fc}^+$  in  $\text{CH}_2\text{Cl}_2$ . Although the  $\text{Fc}^*/\text{Fc}^{*+}$  couple is at  $-515 \text{ mV vs. Fc/Fc}^+$  in THF, for consistency, we referenced here potentials in both solvents *vs. Fc\*/Fc\*+* at  $-610 \text{ mV}$  because the potentials at negative voltages are key results from this study and because THF is more likely to interact with substrates under oxidising conditions than under reducing conditions. Ads = adsorptive, pre = prewave, X and Y are peaks due to electrode fouling and are dependent on scan direction and initial potential. The arrows indicate the initial potential and scan direction.





## 15. References

- 1 R. J. LeSuer, C. Buttolph and W. E. Geiger, *Anal. Chem.*, 2004, **76**, 6395-6401.
- 2 G. Gritzner and J. Kuta, *Pure Appl. Chem.* 1984, **56**, 461-466.
- 3 M. J. Cook, I. Chambrier, G. F. White, E. Fourie and J. C. Swarts, *J. Chem. Soc. Dalton Trans.*, preceding paper.
- 4 A. Auger, A. J. Muller and J. C. Swarts, *J. Chem. Soc. Dalton Trans.*, 2007, 3623-3633.
- 5 D. H. Evans, K. M. O'Connell, R. A. Petersen and M. J. Kelly, *J. Chem. Educ.*, 1983, **60**, 290-293; P. T. Kissinger and W. R. Heineman, *J. Chem. Educ.*, 1983, **60**, 702-706; J. J. Van Benschoten, J. Y. Lewis and W. R. Heineman, *J. Chem. Educ.*, 1983, **60**, 772-776; G. A. Mabbot, *J. Chem. Educ.*, 1983, **60**, 697-702.