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-Bu)4][B(C6H5)4] was prepared as described elsewhere.1

Spectroscopy: All solvents were analytical grade and were used as supplied. CHCl3-d5 (>99.8 atom% D) deuterated solvent was purchased from Apollo Scientific Ltd. THF-d5 (99.5 atom% D) was purchased from Cambridge Isotope Laboratories Inc. Pyridine-d5 (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 Cambridge Isotope Laboratories Inc. Pyridine-d5.

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2. MALDI-TOF spectrum of compound 3

3. MALDI-TOF spectrum of compound 4
4. $^1$H NMR spectrum (400 MHz) of compound 1 in THF-d$_8$ (* indicates solvent peaks)

5. $^1$H NMR spectrum (400 MHz) of compound 2 in THF-d$_8$ (* indicates solvent peaks)

4. $^1$H NMR spectrum (400 MHz) of compound 1 in THF-d$_8$ (* indicates solvent peaks)
6. $^1$H NMR spectrum (400 MHz) of compound 1 in CHCl$_3$·d$_1$ (* indicates solvent peak)

7. $^1$H NMR spectrum (400 MHz) of compound 2 in CHCl$_3$·d$_1$ (* indicates solvent peak)
8. $^1\text{H}$ NMR spectrum (400 MHz) of compound 4 in CHCl$_3$-d$_1$ + pyridine-d$_5$ (* indicates solvent peaks)

9. $^1\text{H}$ NMR spectrum (400 MHz) of compound 4 in THF-d$_8$ + pyridine-d$_5$ (* indicates solvent peaks)
10. UV-Vis. spectra of compounds 1 (1.38x10^{-5} \text{ M}) and 2 (1.30x10^{-5} \text{ M}) in CH\textsubscript{2}Cl\textsubscript{2}.

![UV-Vis. spectra](image)

11. Beer-Lambert plots of compounds 1 and 2 in CH\textsubscript{2}Cl\textsubscript{2} and THF.

![Beer-Lambert plots](image)
12. UV-Vis. spectra of compound 4 in CH$_2$Cl$_2$ (0.97x10$^{-3}$ M) and in CHCl$_3$-d$_1$ (3.19x10$^{-3}$ M)

13. UV-Vis. spectra of compound 4 in CH$_2$Cl$_2$ at 1.44x10$^{-5}$M (blue) and 0.93x10$^{-3}$M (pink)
14. CVs at 100 mV s\(^{-1}\) in CH\(_2\)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. Fc\(^*\) = the internal standard, decamethylferrocene, which has a potential of -610 mV vs. Fc/Fc\(^+\) in CH\(_2\)Cl\(_2\). Although the Fc\(^*/Fc^{*+}\) couple is at -515 mV vs. Fc/Fc\(^+\) in THF, for consistency, we referenced here potentials in both solvents vs. Fc\(^*/Fc^{*+}\) at -610 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