PAPER

Spectroscopic and electrochemical studies on platinum and palladium phthalocyanines

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The synthesis, spectroscopy and electrochemical characterisation of palladium and platinum phthalocyanines is reported. Electrochemical techniques were used in conjunction with electronic absorption spectroscopy to analyse the reduced and oxidised phthalocyanine species in solid films and in solution, and significant and extensive excitonic coupling resulting in broadening of the Q-band was observed in the film phase. The Q-band was also shown to be affected by the electrolyte, changes in potential concomitant with the redox properties of the films and structural changes of the phthalocyanines within the films.

Introduction

Precious metal phthalocyanines[1] have been known for many years, but such materials are of increasing interest in catalysis[2,3] and electrochemistry.[4–8] Electronic absorption spectroscopy is an excellent tool for phthalocyanine investigation and characterisation. Interpretation of the spectra is possible by analogy with the 18π electron configuration of the porphyrin system and the mapping of the electronic molecular orbitals of standard metallophthalocyanines by, for instance, extended Huckel calculations.[9] The technique is amenable to *in situ* electrochemical studies as the profound affect on electronic structure after electrochemical oxidation and reduction should be easily apparent. Through analysis of excitonic coupling theory,[10] which is still in its infancy for the spectra of thin films, information about the structure and the long-range order of the films may be obtained.

Although significant work has been performed on the electrochemistry of soluble phthalocyanine materials, there are a large number of materials that have not been studied due to their low solubility in most common solvents. Due to the difficulty in preparing suitable thin films of phthalocyanines on conductive substrates, there are relatively few reports of the solid state electrochemistry of phthalocyanine films. Such electrochemistry may be expected to be significantly different from that of the soluble materials, as there is significant intermolecular interaction between the individual phthalocyanine molecules within the film.

In this work, we describe the synthesis, purification, spectroscopic and electrochemical characterisation of palladium and platinum phthalocyanines. As far as we are aware, this is the first time that electrochemical techniques have been used in conjunction with electronic absorption spectroscopy to study reduced or oxidised platinum and palladium phthalocyanine species in solid films.

Results and discussion

Synthesis and purification

The synthesis of the metal-containing phthalocyanines utilised the reaction of phthalonitrile with the appropriate metal

chloride, at high temperatures (though a method starting from lithium phthalocyanine also gave similar yields), based on the original methods of Linstead *et al.*[11] However, ultra-pure samples were required so the crude products obtained were subjected to sublimation at (i) 140 °C and at atmospheric pressures to remove unreacted phthalonitrile and (ii) in a tubular vacuum furnace at 550–650 °C and 10^{-3} mm Hg to allow collection of highly purified phthalocyanines. The synthetic routes gave reasonable yields, though exhaustive sublimation lowered these values to *ca.* 20%. The sublimed products were microcrystalline, enabling easier application onto the electrode surface than the usual powdered samples.

Electronic absorption spectroscopy

Appleby *et al.*[12] were the first to attempt to correlate the spectroscopic properties of absorbed iron phthalocyanine with their catalytic activities. Yeager *et al.*[13] reported the reflectance spectra of monolayers of tetra-sulfonated transition metal phthalocyanines adsorbed on electrode surfaces. Gavrilov *et al.*[14] have studied the absorption spectra and the electrochemistry of the tetra-*t*-butyl derivative of cobalt, zinc and lutetium phthalocyanines by 'wiping' the compounds on optically transparent electrodes and observed completely reversible electrochemical and spectro-electrochemical transitions for all three of the compounds under test.

Minami[15] has recorded photocurrent and UV-vis. spectra for CuPc, ZnPc, NiPc, VOPc, PbPc and H_2Pc. A significant change was observed for the absorption spectra of the metallophthalocyanines when they were in contact with aqueous solution. Free base analogues of metallophthalocyanines have often been studied in the literature,[16,17] both electrochemically and spectroscopically, to provide a better indication of the mechanisms of Pc redox chemistry. Several studies[18–20] have investigated the electrochromism of transition metal phthalocyanines, especially CuPc.

Few studies have measured the absorption spectra of PtPc. Hamnett *et al.*[7] measured the absorption spectra before electrochemical polarisation of a vacuum sublimed 200 nm PtPc film on a gold/carbon substrate. The result was a sharp absorption peak at about 620 nm with only a small shoulder at longer wavelengths suggesting a predominantly α-phase in the deposited film. Kogan and Yakushi[21,22] have fabricated a composite electrode from PtPc and inert, conductive organic

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binders and carbon. The spectra show significant excitonic coupling within the electrodes and a dramatic change upon oxidation of the composite. By contrast, little study has been carried out on PdPc. Its crystallographic forms were described by Kempa *et al.*[23] and the redox behaviour suggested by Nyokong.[24] However in this paper, its electrochemical behaviour and the effect on UV-vis. spectroscopy is discussed fully.

Film and solution spectra

A listing of the wavelengths at which Q-band absorption occurs for the phthalocyanines in α-chloronaphthalene solution and as solid thin films prior to polarisation is shown in Table 1. It is clear that the nature of the phthalocyanine and its physical state has a significant bearing on the wavelength of the Q-band and even how many peaks are seen. In solution, just one Q-band transition is observed for PtPc and PdPc. The free-base phthalocyanine (H_2Pc) shows two absorptions in solution owing to the lower symmetry of the compound and the splitting in the π–π* transition that this induces. The small peaks observed for PtPc, PdPc and H_2Pc at lower wavelengths than the main Q-band are additional components of the Q-band resulting from vibronic fine structure. It is known that vibronic structure in phthalocyanines is sensitive to the deviation of the phthalocyanine ring from planarity.[25] Co-ordination of a metal to the phthalocyanine ring (as opposed to free base Pc) shifts the Q-band to shorter wavelengths (known as a 'hypsochromic shift'). This has been interpreted as a strong metal d-orbital interaction with the phthalocyanine[26] (strong metal to ligand π back-bonding). This interaction then increases the separation between the phthalocyanine HOMO and LUMO orbitals. The effects of applying the phthalocyanines as solid thin films is quite pronounced resulting in multiple Q-band peaks and peak broadening owing to extensive excitonic coupling. This phenomenon is often referred to as 'Davydov splitting'. This effect is clearly seen when the solution and solid phase spectra are displayed together. This has been completed for the phthalocyanines under study and the results are shown below (Fig. 1). The absorptions have been normalised for easy comparison between the spectra. PdPc solution and film spectra are virtually identical to those for PtPc.

A cofacial arrangement and interaction of molecules leads to a blue-shift in absorption, whereas an edge-to-edge configuration leads to a red-shift. The interaction of the transition moments (dimer interactions) of molecules at an angle to each other leads to the observation of both red-shifted and blue-shifted bands. The Q-band is no longer degenerate and two distinct transitions can be observed. This theory can be extended to describe the absorption of infinite stacks, but the interactions are often more complicated. Bayliss *et al.*[27] have observed different contributions of these two Q-band transitions for α- and β-H_2Pc phases grown under UHV conditions which are well explained by Davydov splitting. The additional
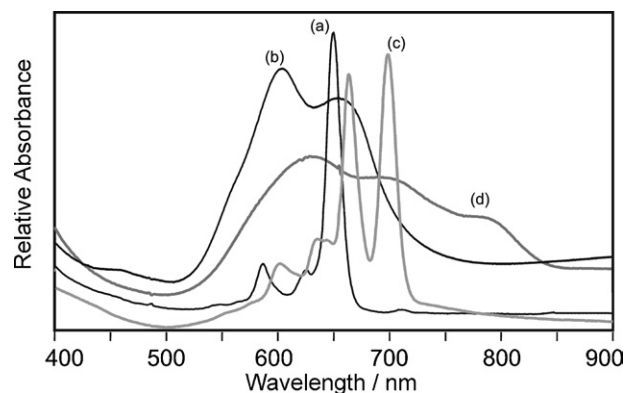

Fig. 1 Absorption spectra for α-chloronaphthalene solutions of PtPc (a) and H_2Pc (c) and as thin solid films of PtPc (b) and H_2Pc (d) deposited by mechanical abrasion on F-doped SnO coated glass.

splitting of the free base phthalocyanine Q-band owing to the lowered symmetry compared to an MPc is not great enough to be directly distinguished but is probably responsible for significant broadening of the absorption peaks. Indeed the H_2Pc film shows significantly more extensive broadening with three peaks observed whilst, the MPc films show two distinct peaks. This is thought to be a function of their polycrystalline/disordered structure. Chau *et al.*[28] note that any significant disorder within such layers will lead to additional exciton splitting patterns. These spectra also suggest that there may be significant longer range interaction between non-adjacent Pc molecules. The shape of the absorption spectra for these films is consistent with literature examples.[29,18,19] Peak fitting of the H_2Pc film absorption spectrum by Bayliss[30] suggests that at least 5 discrete absorptions are observed in the Q-band. Despite this, the structural interpretation of polycrystalline Pc films has been previously attempted in the literature.[31]

The electrochemistry of similarly deposited PtPc films has been extensively studied in both non aqueous[32–35] and aqueous electrolytes.[36] It is noteworthy that after electrochemical cycling the absorbance of the films is generally lower. This occurs over the first few electrochemical scans (always more extensively for PdPc) and then the absorbance remains constant. Since electrically disconnected phthalocyanine should still absorb even if it does not participate in the electrochemistry, this is an indication of two possibilities. It is possible that material is physically lost from the substrate, which is common during colour switching,[37] or that changes occur in the film structure during electrochemistry, which result in different spectral characteristics and a different extinction coefficient per unit length. It is suggested that both of these factors contribute to the observed changes. Conversely, Kogan and Yakushi[22] observed an increase in the absorption for their composite PtPc electrodes upon repetitive scanning. Toshima[18] observes a decrease in the absorption of the phthalocyanine layer depending on the extent of its reversibility.

Spectral changes with potential

The fact that the electrolyte has some effect on the wavelength of maximum absorption after electrochemical cycling shows that intercalation of solution into the film has an effect on the structure, packing and intermolecular interactions of the phthalocyanine molecules. It is also possible that the phthalocyanine molecule may have its symmetry altered by this process. Indeed, there is a universal negative shift in λ_{MAX} from the pre-electrochemical cycling Q-band absorption of 605 nm for PtPc and 612 nm for PdPc. This suggests that less intermolecular interaction and less dense phthalocyanine packing is seen after electrolyte intercalation. The concentration of electrolyte seems to have little effect on λ_{MAX}, although these measurements were all taken after several electrochemical cycles

Table 1 Listing of the Q-band absorption maxima for several phthalocyanines in α-chloronaphthalene solution and as thin sold films. (sh) refers to the presence of a shoulder rather than a distinct peak and the λ_{MAX} has thus been estimated (no meaningful extinction coefficients could be obtained due to insolubility problems)

Phthalocyanine	Solution phase Q-band absorption, λ_{MAX}/nm	Solid phase Q-band absorption, λ_{MAX}/nm
PtPc	650	605, 658
PdPc	660	612, 667
H_2Pc[40]	664, 699	632, 694, 782 (sh)
LiPc[34]	—	690, 632 (sh)

and any over-swelling phenomena occurring on the first sweep may have dissipated.

Fig. 2 shows the absorption spectra recorded on the oxidative sweep for PtPc film on F-doped SnO_2-coated glass in 0.2 M sulfuric acid. As expected, the shape of the spectra shows little change until the first bulk oxidation at 1.1 V. However the intensity of the λ_{MAX} peak decreases slightly and the spectrum becomes slightly broader from about 0.6 V to 1.0 V coinciding with the intra-domainal intercalation of anions and solvent and the oxidation of loosely attached crystals. After the first oxidation peak, the absorption shows a dramatic change in shape with the peaks moving to lower wavelength. In addition, the absorption intensity decreases and the peak width increases markedly. This change continues until the first oxidation is complete at 1.2 V. Ignoring for the moment the structural changes that will definitely be occurring within the film, one would expect a shift of the Q-band absorption to lower wavelengths since the positive charge and electron deficiency of the phthalocyanine ring increases the HOMO–LUMO separation. In this way more energy is now required to facilitate the π–π* transition. These changes in absorption continue as the second oxidation is traversed from 1.2 V to 1.4 V. Additionally, the shoulder observed at longer wavelengths after the first oxidation disappears after the second oxidation suggesting further structural changes. One may conclude that since the absorption spectra at 1.2 V is an intermediate step of the shape observed at 1.4 V, the two oxidation peaks in the cyclic voltammetry represent different extents of the same process. A clear isobestic point can be observed up until 1.1 V. After this potential no isobestic point is obvious. This has been previously[19] taken as evidence that the film may be oxidised reversibly until 1.1 V. During the oxidative sweep the film is seen to change from a dark purple to a sky blue colour.

The main features of the absorption response over the reductive part of the voltammetry are shown in Fig. 3. As the potential decreases the peak at about 560 nm decreases and a new peak grows at about 610 nm. Soon after the reduction peak at 1.15 V this new peak increases in height over that of the peak at 560 nm. This new peak shows a slight increase in intensity and little change in λ_{MAX} until the reduction peak at 0.6 V, after which a large increase in intensity is observed and the peak shifts down in wavelength to 594 nm (the original λ_{MAX}) and there is growth of a shoulder at about 660 nm. This result is particularly interesting as the absorption spectra (and thus structure) of the film is significantly different at the same extents of oxidation depending on whether the potential is being stepped positively or in the negative direction. This phenomenon is shown in Fig. 4 and suggests the structure of the film is exhibiting some hysteresis behaviour.
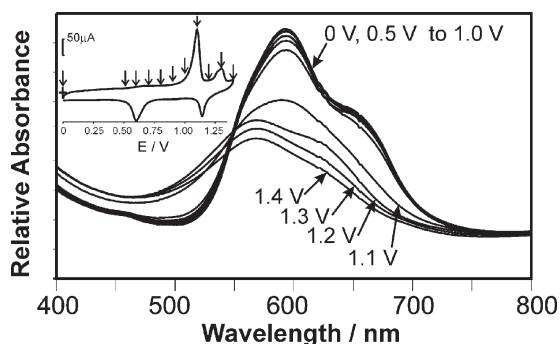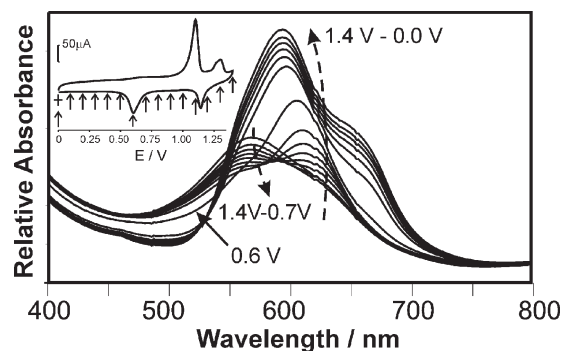

Fig. 3 Absorption spectra for a PtPc film on F-doped SnO coated glass in 0.2 M sulfuric acid, polarised at 1.4 V then at 100 mV increments down to 0.0 V. Inset is the cyclic voltammogram for this material in the same electrolyte showing the points at which measurements were made.

The λ_{MAX} (which gives an indication of where the bulk of the Q-band absorption lies) shows little change with potential until the first bulk oxidation peak after which it drops significantly to about 570 nm indicating a greater proportion of cofacial intermolecular interaction than seen in the fully reduced film. This then stays almost unchanged until the first reduction peak when λ_{MAX} increases to approximately 615 nm strongly suggesting that the film is now exhibiting edge-to-edge packing to a greater extent than observed in the original film. Upon the second reduction peak, the value of λ_{MAX} returns to its value in the original reduced film indicating that the structural changes occurring during scanning are reversible despite the fact that the film may physically deteriorate and lose material since the absorption intensity is not completely reversible.

The effect of electrolyte

Toshima *et al.*[19] postulate that the electrochromic behaviour of the phthalocyanine films they studied, prepared by vacuum sublimation, could be placed in four categories. The materials we have studied seem to broadly fall within this framework. The first category included those films showing no reversible electrochemistry and no changes in absorption spectra with potential. The second type also show no reversible electrochemistry and a decrease in the intensity of absorption without a change in shape after the first electrochemical scan. The third type observes irreversible electrochromism whilst the fourth category describes those films showing at least partly reversible electrochromism. The films examined in this work would appear to fall only into the second or fourth categories. This restriction may be because the studies have been confined to non-first row transition metal phthalocyanines. These categories are not definitive though. The behaviour of the PtPc
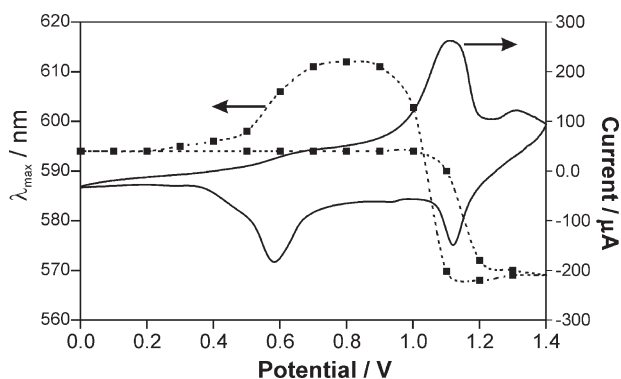

Fig. 2 Absorption spectra for a PtPc film on F-doped SnO coated glass in 0.2 M sulfuric acid, polarised at 0 V, then 0.5 V, then at 100 mV increments up to 1.4 V. Inset is the cyclic voltammogram for this material in the same electrolyte showing the points at which measurements were made.

Fig. 4 Current response (solid line) and λ_{MAX}/nm against potential for a PtPc film on F-doped SnO coated glass in 0.2 M sulfuric acid.

films in HCl falls between the second and third categories. Electrochemical studies have shown that in HCl electrolyte, a large irreversible oxidation peak is observed and then very little further electrochemistry on subsequent scans. However, the absorption spectra of the PtPc film in HCl shows slight changes even on the third scan. These results are shown below (Fig. 5).

Upon polarisation to more positive potentials the peak absorption intensity of the Q-band at 600 nm decreases slightly. This intensity recovers when the potential is stepped back to −0.3 V. Fig. 5 indicates that the PtPc film in HCl undergoes only very minor and superficial structural changes at oxidative potentials. It is suggested that it is just the loosely attached PtPc that is taking part here since the size of the anion is not as important to the loosely packed material. However, the system essentially shows almost no electrochromic or electrochemical behaviour.

Clearly this behaviour is in stark contrast to the reversibility shown by the PtPc films in sulfuric acid. Similar reversible behaviour is observed in perchloric acid.[36] However the electrochemistry in perchloric acid is not as well-defined but the trends in the absorption of the film with potential remain similar. It is observed however that variations in intensity occur more continuously than the sharp changes seen in sulfuric acid. This is simply a consequence of more well-defined phase transitions occurring in sulfuric acid. It is noteworthy that upon reduction of the film the absorbance returns to almost exactly the same value as before the oxidation, indicating that no material has been lost and film degradation is less severe than that experienced in sulfuric acid.

Differences in absorption spectra with different electrolytes are thought to be caused by the different sizes of the Stokes radii associated with different anions,[38] although it is difficult to explicitly relate these sizes to the structural changes within the film. The effect of an electrolyte with a larger cation on the electrochemistry of the phthalocyanine films has been described. The effect of the cation on the UV-vis. properties of the film is less pronounced. These results suggest that it is the anion that is responsible in the major part for controlling structural changes accompanying redox processes.

It seems that the PdPc films experience a greater drop in absorption intensity with cycling than their PtPc counterparts. This clearly suggests that the PdPc films are more susceptible to film degradation upon intercalation suggesting structural packing differences between the PtPc and PdPc crystals. This is certainly a feature where the differences between the PtPc and PdPc films are most apparent. Apart from this observation, the UV-vis. absorption behaviour of the two films is almost identical. However, the variation of λ_{MAX} of the PdPc absorption against potential shows some additional differences seen with changes in electrolyte concentration, again ascribed to the greater swelling caused by the less concentrated

electrolyte. The λ_{MAX} of absorption is seen to change even in the absence of phthalocyanine electrochemistry *i.e.* in the inert regions of the cyclic voltammogram especially between 1.1 V and 0.5 V on the reverse scan. This may be taken as unequivocal evidence that purely structural changes are occurring within these films with potential and the spectral changes are not solely governed by the onset of redox processes within the film.

Conclusion

The platinum and palladium Pcs synthesised show a high degree of purity and the solids are microcrystalline, thus providing useful extra roughness for mechanical application onto the electrode. The UV-vis. study of the phthalocyanine system has centred on the nature of the Q-band transition. It has been clearly shown that the solution phase spectra are very different from the spectra obtained from thin solid films. The absorption spectra of the films show significant and extensive excitonic coupling resulting in extensive broadening of the Q-band.

The Q-band absorptions have been shown to shift slightly to shorter wavelengths after electrochemical cycling. This effect has been attributed to structural changes induced in the film by the intercalation of electrolyte between and within the Pc microcrystals. The nature of the electrolyte's anion has been shown to have significant effect on changes in the Q-band absorption. This effect seems to be much greater than that of the cation.

Investigation of the change of the absorption spectra with potential has shown additional changes in the absorption spectra occurring concomitantly with redox processes within the film. These changes have been attributed to further structural changes in the film accompanying the redox processes. Shifts of the Q-band absorption to shorter wavelengths upon oxidation have been explained by an increased gap between the HOMO and LUMO orbitals. More energy is then required for the π–π* transition. Interesting hysteresis has been observed in the λ_{MAX} against potential between the spectra obtained whilst stepping to positive and to negative potentials. This has been attributed to structural hysteresis within the film during the redox processes. This is thought to be caused by changes in the herringbone crystal structure of the Pc as electrolyte intercalates within the film.

Experimental

General

The solvents used were commercial grade and used as supplied (unless otherwise stated, when they were dried and distilled over standard drying agents). The precious metal salts were provided by Johnson Matthey plc and organic reagents were purchased from Aldrich or Lancaster Chemical Companies and used without further purification. Aerobic reaction conditions were normally used, unless otherwise stated where a nitrogen atmosphere was employed. ^{1}H NMR spectra were taken using a Jeol EX 270 MHz Delta upgrade spectrometer and referenced to each solvent *i.e.* DMSO-d^6 (2.70 ppm) and D_2O (4.82 ppm). Infrared spectra were recorded using either a KBr disc or Nujol mull on a Mattson Polaris Fourier Transform IR spectrometer. All microanalyses were carried out using Scientific Analysis and Consultancy Services, University of North London.

Synthesis (based on literature methods[11] but including extra purification)

Platinum phthalocyanine. Platinum chloride (1 g, 3.8 mmol) and excess phthalonitrile (20 g, 156 mmol) were ground and
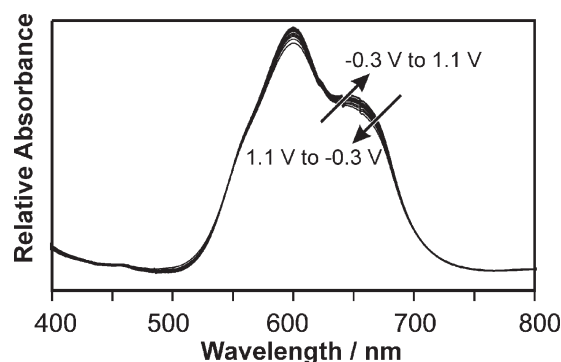

Fig. 5 Absorption spectra for a PtPc film on F-doped SnO coated glass in 0.2 M hydrochloric acid, polarised at −0.3 V then at 100 mV increments up to 1.1 V and then back down to −0.3 V.

mixed thoroughly and placed in a 100 mL round-bottomed flask fitted with a reflux condenser. The temperature was quickly raised to 200 °C and held there for 1 h. The blue solid formed was cooled and washed with methanol (100 mL) to remove soluble impurities. The crude mixture was placed in a laboratory sublimation vessel, packed with dry ice and acetone, and unreacted phthalonitrile was removed by sublimation at 140 °C and atmospheric pressures. Following this, the crude product (*ca.* 50% yield) was subjected to sublimation in a high vacuum furnace. Optimal conditions were 550 °C, 1×10^{-3} mm Hg and 8 h and the sublimation process was most efficient when using small batches (0.25 g) of material. The purified phthalocyanine, which was violet with a metallic lustre, was isolated in *ca.* 20% yield.

Mp. > 360 °C; (Found: C, 54.32; H, 2.28; N, 15.84. $C_{32}H_{16}N_8Pt$ requires C, 54.52; H, 2.23; N, 16.02%); ν cm^{-1} (KBr) 3046, 3010, 2921, 2852 (C=N), 1511–1290 (C=C, C–N), 1170–1076 (C–H) 725 (C–H out-of-plane); δ_H (D_2SO_4/D_2O) 9.39 (1H, s, H-peripheral), 8.39 (1H, s, H-non-peripheral).

Palladium phthalocyanine. An analogous method was applied here, though using palladium dichloride. The yields were slightly lower and the optimal sublimation conditions were 650 °C, 1×10^{-3} mm Hg and 8 h.

Mp. > 360 °C; (Found: C, 61.94; H, 2.53; N, 17.98. $C_{32}H_{16}N_8Pt$ requires C, 62.13; H, 2.61; N, 18.13%); ν cm^{-1} (KBr) *ca.* 3000 (C=N), 1612, 1508, 1288, 914 (C=C, C–N), 1168–1072 (C–H) 723 (C–H out-of-plane); δ_H (D_2SO_4/D_2O) 9.39 (1H, s, H-peripheral), 8.39 (1H, s, H-non-peripheral).

Electrochemical studies

The working electrode was generally a 30×8 mm piece of fluorine-doped tin oxide coated glass. Electrical contact was made by means of a copper wire joined to the glass with silver conductive paint and shielded from the electrolyte by an epoxy resin or silicone sealant covering. The electrode was housed in a $20 \times 20 \times 40$ mm quartz cuvette with a platinum flag counter electrode resting on the cuvette's bottom and a calomel reference electrode in solution contact with the electrolyte from above. The assembly was placed in a Hewlett Packard 8453 UV-vis. spectrometer with the cuvette face and the working electrode's face orthogonal to the path of the incident light. Phthalocyanine layers were applied by means of mechanical abrasion of the microcrystals onto the electrode surface. All electrolytes were saturated with argon (> 99.9%) by bubbling the gas through the solution for 30 min prior to each experiment and keeping a positive pressure above the solution during experiments. Potentiostatic control was achieved with an Oxford Electrodes manual potentiostat and sweep generator. The experiments were conducted in a sequential potential stepping fashion by polarising the electrode at a given potential (monitored by a digital voltmeter attached to the voltage output channel of the potentiostat) and recording the Electronic absorbance spectra approximately 5 s after each step. The applied potential was then increased/decreased to the next measurement point. Generally spectra were recorded at intervals of 100 mV.[39] Potentials are reported referenced to the saturated calomel reference electrode (SCE).

Acknowledgements

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