

# Formation and Spectroelectrochemical Characterization of Multilayer and Submonolayer Thin Films of 2,3,9,10,16,17,23,24-Octa(2-benzyloxyethoxy) Phthalocyaninato Copper (CuPc(OC<sub>2</sub>OBz)<sub>8</sub>)<sup>†</sup>

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**ABSTRACT:** We review here the self-assembly, electrochemical and spectroelectrochemical properties of 2,3,9,10,16,17,23,24-octa(2-benzyloxyethoxy) phthalocyaninato copper (CuPc(OC<sub>2</sub>OBz)<sub>8</sub>), where terminal benzyl groups on the eight ethylene oxide side chains assist in forming unusually ordered, mechanically rigid thin films. New spectroscopic characterization of cast CuPc(OC<sub>2</sub>OBz)<sub>8</sub> films is discussed in comparison with cast films of its metal-free analogue H<sub>2</sub>Pc(OC<sub>2</sub>OBz)<sub>8</sub> and similar copper and dihydrogen phthalocyanines with benzyl-terminated triethylene oxide substituents, CuPc((OC<sub>2</sub>O)<sub>3</sub>Bz)<sub>8</sub>, and H<sub>2</sub>Pc((OC<sub>2</sub>O)<sub>3</sub>Bz)<sub>8</sub>, which do not demonstrate the same degree of ordering as CuPc(OC<sub>2</sub>OBz)<sub>8</sub>. AFM studies of horizontally transferred LB films of CuPc(OC<sub>2</sub>OBz)<sub>8</sub> show column-column distances of *ca* 2.8 nm and confirm the high degree of ordering previously surmised from spectroscopic characterization of multilayer thin films. The oxidative electrochemistry of multilayer thin films prepared from these Pcs is strongly dependent on the chemical identity of the supporting electrolyte anion and on annealing of the thin films. Compliance of the films to counter-ion transport limits the extent of electrochemical doping. Preliminary studies of the oxidative electrochemistry of isolated CuPc(OC<sub>2</sub>OBz)<sub>8</sub> aggregates (diluted into an electroinactive methyl arachidate thin film) on an electroactive, integrated optic waveguide (EA-IOW) are also presented. Monitoring the change in absorbance at 633 nm on the waveguide surface allows the determination of the onset potential for oxidation of the isolated aggregates, which appears to be less positive in potential versus that observed for multilayer Pc assemblies. Copyright © 1999 John Wiley & Sons, Ltd.

**KEYWORDS:** phthalocyanines; spectroelectrochemistry; self-assembly; AFM; integrated optic waveguides

## INTRODUCTION

Peripherally substituted phthalocyanines are of interest because of their tendency to aggregate in columnar assemblies, many with discotic liquid crystalline properties, with the prospect for molecular electronic, photonic and chemical sensor applications [1–13]. Insuring coherence in these assemblies over tens of

nanometers or longer is a significant challenge, especially because small variations in molecular architecture of the phthalocyanine assembly may ultimately control the optical, electrical and electrochemical properties of the material. Coherence of cofacial Pc assemblies can be assured for polysilicon phthalocyaninato (PcPS) materials on the length scale of the polymer chains. Axial polymerization of the central silicon atoms provides the possibility to create ordered thin films with up to 100 Pc units per monomer unit within the film [7–11]. Creation of thin films composed of linear cofacial Pc aggregates from simple self-assembling monomers, while more attractive from a processing point of view, has not provided nearly this type of coherent assembly [1–6, 14–17]. Crystalline Pcs with a tendency toward formation of

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perfectly cofacial aggregates (e.g. the FAIPc system) can be vacuum deposited as epitaxial layers on single-crystal substrates (e.g. freshly cleaved SnS<sub>2</sub>) to form very highly ordered cofacial aggregates, but again the processing conditions are not simple [18, 19].

We have recently produced a new class of phthalocyanines with eight benzyl-terminated ethylene oxide side chains per Pc monomer. 2,3,9,10,16,17,23,24-Octakis(2-benzyloxyethoxy) phthalocyaninato copper (CuPc(OC<sub>2</sub>OBz)<sub>8</sub>) and its related zinc (ZnPc(OC<sub>2</sub>OBz)<sub>8</sub>) and metal-free (H<sub>2</sub>Pc(OC<sub>2</sub>OBz)<sub>8</sub>) analogues have been prepared [20–23]. CuPc(OC<sub>2</sub>OBz)<sub>8</sub> is illustrated in the schematic shown in Fig 1(b). The simple modification of the ethylene oxide side chains with a terminal benzyl group leads to a supramolecular material with unique properties. Stable monolayer and bilayer thickness LB films are readily formed from CuPc(OC<sub>2</sub>OBz)<sub>8</sub> and H<sub>2</sub>Pc(OC<sub>2</sub>OBz)<sub>8</sub> using a horizontal transfer method (Schaffer method [24], and multilayer films show unprecedented long-range order [25–27]. As shown below, when the number of ethylene oxide units in the benzyl-terminated side chain is increased from one to three, as in the octa(tri(ethylene oxide)) Pcs CuPc(O(CO<sub>2</sub>)<sub>3</sub>Bz)<sub>8</sub> and H<sub>2</sub>Pc(O(CO<sub>2</sub>)<sub>3</sub>Bz)<sub>8</sub>, the aggregation tendencies in solution are weakened. Increased side chain motion, possible in the longer-chain materials, reduces the stability of the aggregate assemblies. The unusual stability of the mono(ethylene oxide)-linked materials is lost, as is the ability to form well-ordered LB thin films and to transfer these films with the efficiency noted for both CuPc(OC<sub>2</sub>OBz)<sub>8</sub> and H<sub>2</sub>Pc(OC<sub>2</sub>OBz)<sub>8</sub>.

The cofacial aggregation or axial polymerization of Pcs influences their redox properties, generally lowering the first oxidation potential for the assembly versus the monomeric material [28–36]. Electrochemical ‘doping’ of these assemblies to increase conductivity, in a manner similar to that previously reported for crystalline Pc complexes [1, 37–41], becomes accessible for thin films of these materials [13]. For the polymerized silicon phthalocyanine systems the effect of placing the Pcs in close proximity is substantial, with up to a 650 mV decrease in first oxidation potential between the monomer and the trimer oligomers and a somewhat larger decrease in oxidation potential for the PcPS polymer versus the monomer [28–30]. CuPc(OC<sub>2</sub>OBz)<sub>8</sub> multilayer thin films appear to show a decrease in first oxidation potential versus that expected for the monomer, although not as large an effect as the SiPc oligomers or polymers [20–23, 25–27].

Incorporation of counter-ions into the Pc film must accompany the oxidation events. Film structure must be sufficiently compliant to facilitate counter-ion injection without disruption of columnar order in the film structure [42, 43]. For the oxidation of CuPc(OC<sub>2</sub>OBz)<sub>8</sub> thin films, as shown in this paper, there is a strong dependence of the onset for oxidation and the shape of the voltammetric peaks on the chemical identity of the counter-anion species in solution. These counter-ion dependences on redox behavior have been previously noted for PcPS thin films [13] and are consistent with the behavior noted for the electrochemical doping of vacuum-deposited crystalline Pc thin films [21, 42, 43].

Ultimately it is desirable to use columnar polymers or aggregates of these Pcs to span electrical contacts on the distance scale approaching 50–100 nm, and to be able to ‘tune’ the conductivity of these molecular wires through chemical or electrochemical doping [44–46]. Heroic efforts to arrange individual PcPS ‘wires’ across metal contacts on this distance scale have been reported, and the resultant assembly imaged by scanning tunneling microscopy [44–46]. It is useful to understand the electrochemical properties of isolated Pc polymers or aggregates in order to better control doping, such that specific electronic material properties are accessible. In ultrathin films, where the Pc assemblies are monolayer or less in coverage, the rate of ion transport should not be limiting. Both PcPS and CuPc(OC<sub>2</sub>OBz)<sub>8</sub> assemblies can be diluted into monolayers of an electroinactive matrix such as poly(isopentyl) cellulose (IPC) or an LB amphiphile such as methyl arachidate (MA) [44–47]. Normal electrochemical methods of characterization, however, lack sufficient sensitivity to monitor a redox event involving less than 10% of a monolayer of the Pc in question. Spectroelectrochemical methods can be used productively if the molecules being investigated undergo significant absorbance changes during the redox event.

We have recently introduced an integrated optic waveguide technology, the electroactive integrated optic waveguide (EA-IOW), which is capable of monitoring redox events involving certain adsorbed chromophores at coverages near 1% of a monolayer [48, 49]. Monitoring the absorbance changes occurring in such thin films as a function of potential may ultimately allow for the reconstruction of a voltammetric response, or at least the determination of onset potentials for redox activity. This spectroscopic response is insensitive to the non-faradaic background currents which limit the sensitivity of normal voltam-

metric investigations involving low-coverage redox-active molecules [48, 49]. This technology can be productively applied to the characterization of the redox chemistries of low surface coverages of both  $\text{CuPc}(\text{OC}_2\text{OBz})_8$  and PcPS, and we present here our first results using the EA-IOW in the characterization of  $\text{CuPc}(\text{OC}_2\text{OBz})_8$  aggregates diluted into MA thin films and deposited by LB vertical dipping technologies onto the EA-IOW surface.

## EXPERIMENTAL

The synthesis and purification of  $\text{CuPc}(\text{OC}_2\text{OBz})_8$  and its related analogues have been described previously [20–22]. The Pcs were each created from phthalonitrile derivatives, modified in the 3,4-positions by the appropriate benzyl-terminated ethylene oxide. LB films of this molecule were created from chloroform solutions of the pure Pc or solutions containing both the Pc and MA. After dispersal on the trough surface, films were allowed to stand for 20 min prior to the onset of compression.

For the spectroscopic studies of aggregation during solvent evaporation, a fiber optic probe spectrophotometer (Spectral Instruments SI400) was used to obtain absorbance spectra in real time during the evaporation of drops of the chloroform solution (volumes *ca* 50  $\mu\text{L}$ , initial Pc concentration *ca*  $10^{-7}$  M). Solutions were placed in a microscope depression slide located in the spectrometer light path. Spectra were collected at intervals of 15 s, in reflection mode, during the full evaporation of these solvent drops. The path length and distribution of Pc in the light path change dramatically as film formation on the surface of the depression slide proceeds. This redistribution of material accounts, in part, for the loss of absorbance intensity during the course of the experiment. In addition, the molar absorptivity of monomeric Pc is greater than that of aggregated Pc assemblies.

LB films were created on a Riegler–Kiersten trough using a standard Wilhelmy balance [22]. Films were compressed to the appropriate surface pressure, creating either a monolayer or a bilayer thickness film (see below). An appropriately hydrophobized substrate was lowered horizontally onto the trough, picking up the Pc film via the Schaeffer method. Highly ordered multilayer films were prepared by utilizing a film stabilization baffle positioned in the subphase, which cuts the film into stabilized segments as the Langmuir film is lowered. The segmented film can then be horizontally transferred in sequence to the

appropriate substrate without disruption of neighboring film segments [25–27].

AFM studies of multilayer films of  $\text{CuPc}(\text{OC}_2\text{OBz})_8$ , deposited by the horizontal transfer method on either freshly cleaved HOPG surfaces or hydrophobized Si(100) surfaces, were conducted with a Digital Instruments Nanoscope III. Images were generated in aqueous fluid tapping mode using oxide-sharpened silicon nitride tips [50]. The images were processed in both height and deflection modes and were enhanced through a convolution/deconvolution algorithm which heightened the contrast in topology [25–27].

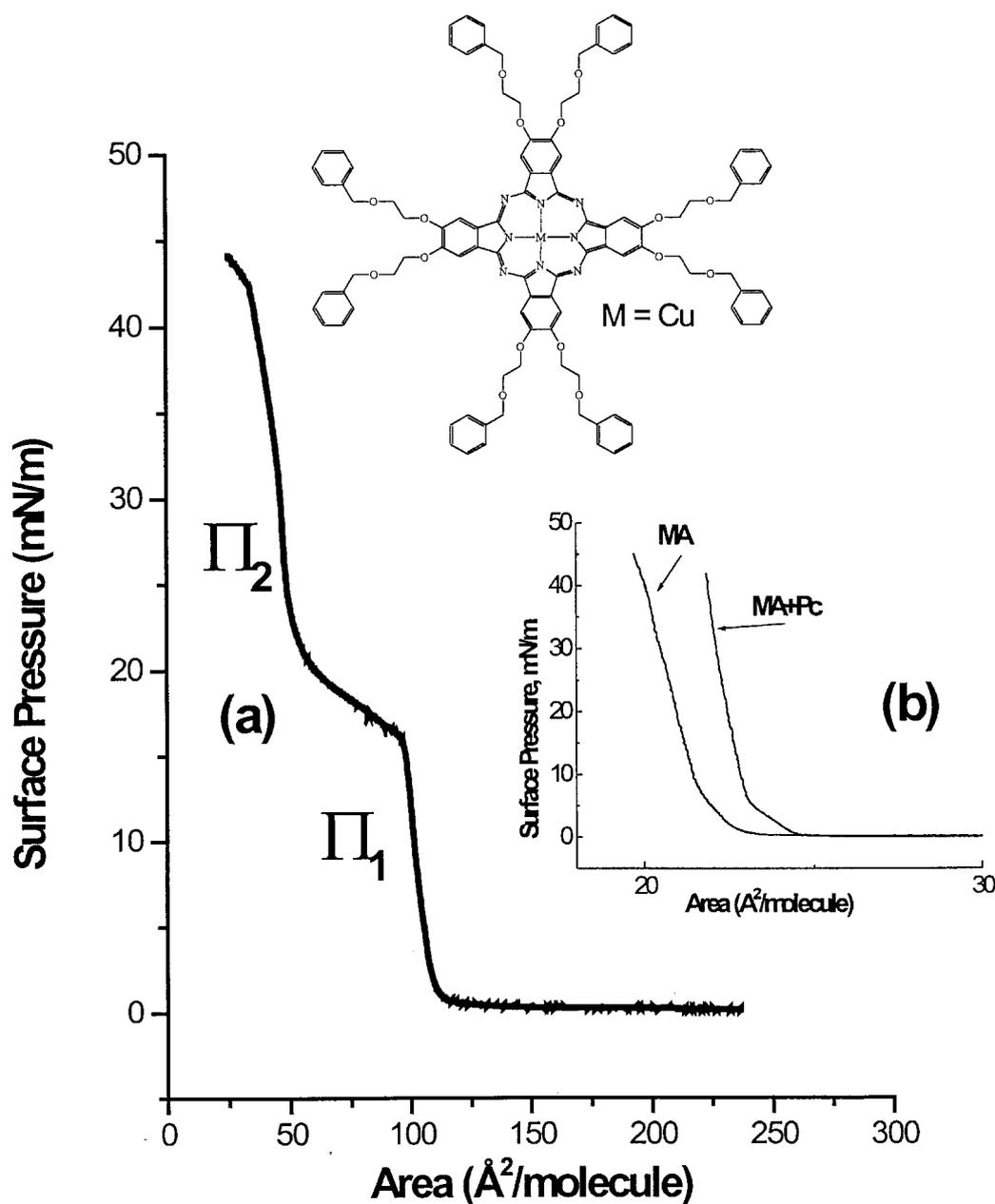
Electrochemical studies were conducted on multilayer films of  $\text{CuPc}(\text{OC}_2\text{OBz})_8$  on hydrophobized indium tin oxide (ITO) substrates as discussed previously [22]. The electrolytes were all aqueous solutions, 0.1 M in the supporting electrolyte. Spectroelectrochemical studies were carried out in the same electrochemical cell as that used for the normal voltammetric studies [22], using the Spectral Instruments fiber probe spectrometer discussed above for the droplet evaporation studies.

The construction of the EA-IOW technology used in this study has been reviewed recently [48, 49]. A schematic of the EA-IOW is shown in Fig 7. A single mode of light from the He–Ne laser source (633 nm) is coupled into this step-index waveguide structure, so that a fraction of the evanescent tail is present in the outer ITO film and interacts with molecules adsorbed to the ITO surface at low coverages. The degree of this interaction is a strong function of the thickness of the Corning 6059 waveguide layer, the thickness of the silica buffer layer, the thickness of the ITO, and the refractive index of all the waveguide components and the superstrate materials. The entire EA-IOW assembly was housed in an electrochemical cell which permits solutions to be introduced and changed at will. The incident He–Ne laser source was modulated at a frequency of 1 kHz, and the outcoupled light, after striking a photodiode with a preamplifier and subsequently demodulated, was corrected for changes in absorbance background which accompany all voltammetric processes on the EA-IOW surface [48, 49].

## RESULTS AND DISCUSSION

### LB Thin Films and AFM Studies of $\text{CuPc}(\text{OC}_2\text{OBz})_8$

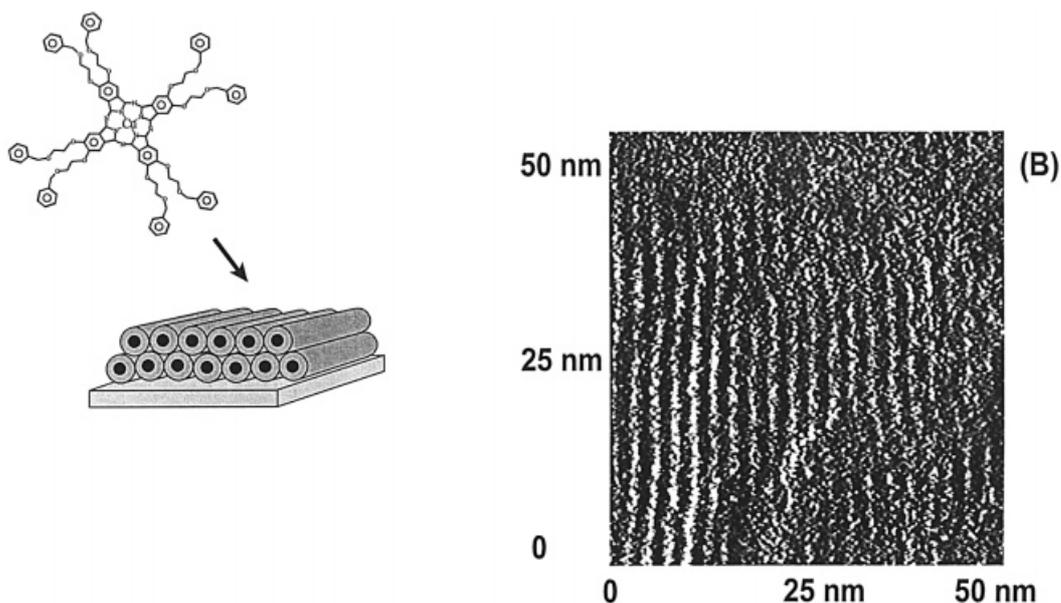
Figure 1(a) shows a typical pressure–area isotherm for



**Fig. 1.** Schematic view of CuPc(OC<sub>2</sub>OBz)<sub>8</sub>: (a) pressure–area isotherm observed for this molecule on a pure water subphase, showing pressures for both monolayer film transfer (Π<sub>1</sub>) and bilayer film transfer (Π<sub>2</sub>); (b) pressure–area isotherms for a methyl arichidate monolayer and for same monolayer with *ca* 10 mol% of CuPc(OC<sub>2</sub>OBz)<sub>8</sub> diluted into it.

CuPc(OC<sub>2</sub>OBz)<sub>8</sub> [22]. The two phase transitions associated with compression of this molecule are clearly seen, corresponding to the formation of a close-packed single monolayer (Π<sub>1</sub>) and a close-packed bilayer film (Π<sub>2</sub>) [22]. Previous AFM studies at the submicron lateral resolution scale, along with recent X-ray reflectometry studies of multilayer

versions of these thin films, confirm that both monolayer and bilayer thickness film transfers are possible and that the horizontal transfer method is capable of producing thin films with unusually high coherence [22, 25–27]. We are aware of only one other octasubstituted Pc system which exhibits this kind of clear transition between monolayer thickness films



**Fig. 2.** Schematic view of columnar assemblies and their hexagonal close packing as a bilayer film, and tapping mode AFM image of such a thin film (in water), showing parallel, coherent columns spaced at *ca* 2.8 nm.

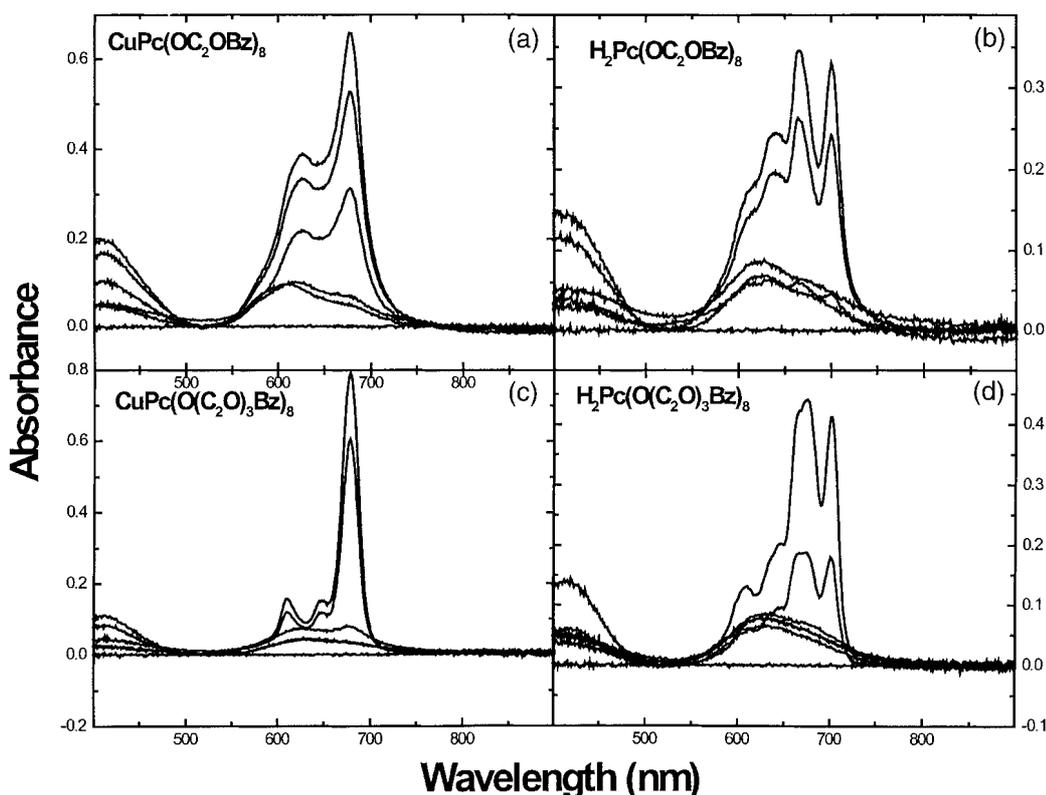
and bilayer thickness films [6]. Nolte and co-workers have reported two-phase isotherm behavior for Pcs with branched and optically active alkoxy substituent groups, and associated the phases with monolayer and bilayer film formation on the trough surface. The branched substituent chains introduce a chiral center which is expected to influence the liquid crystalline properties and enhance the self-assembly of these materials into more rigid thin films. Unlike our materials, however, these branched substituent chain Pcs were difficult to transfer to substrates.

Recent tapping mode AFM studies of CuPc(OC<sub>2</sub>OBz)<sub>8</sub> films in contact with water confirm that these films consist of parallel coherent columnar assemblies with lengths of up to 50 nm and a column-column spacing of *ca* 2.8–3.0 nm (Fig 2) [25–27]. This column spacing is somewhat shorter than that expected for the Pcs with their side chains fully extended (*ca* 3.2–3.5 nm) and suggests some canting of the Pcs with respect to the long axis of the column and some relaxation of the side chains due to their interactions [20, 25]. Note that the column axes of the Pc assemblies in Fig 2 lie parallel to the compression barriers used on the LB trough to create these thin films. This result also suggests that columnar order is achieved on the trough through film compression and that horizontal transfer does not destroy that column ordering. Previously reported studies of these thin films utilizing vertical transfer methods produced

poorly ordered films [20]. Comparable alignment of Pc columns has been achieved for the polysilicon phthalocyaninato (PcPS) system, but these molecules generally align along the vertical dipping axis, as the process of inserting and withdrawing the substrate through the LB film causes the rigid rod molecules to align along flow profiles [7–11, 13].

#### Spectroscopic Characterization of Cast Thin Films

Absorbance spectra taken of CuPc(OC<sub>2</sub>OBz)<sub>8</sub> thin films before and during compression on the LB trough suggest that large-scale aggregate assemblies develop immediately upon distribution of the chloroform solutions on the trough surface [22]. Figures 3 and 4 illustrate the solution spectral properties of this material, and the spectral changes which occur upon solvent evaporation during the formation of cast films as would be expected on the LB trough. These figures also show the spectral properties of related materials, including H<sub>2</sub>Pc(OC<sub>2</sub>OBz)<sub>8</sub> and two new triethylene oxide side chain derivatives of this molecule, CuPc((OC<sub>2</sub>O)<sub>3</sub>Bz)<sub>8</sub> and H<sub>2</sub>Pc((OC<sub>2</sub>O)<sub>3</sub>Bz)<sub>8</sub> [26]. In Fig 3 we show spectra of *ca* 10<sup>-7</sup> M solutions of each of these Pcs in chloroform, before and during evaporation of the solvent to create a cast thin film. Since the concentrations of each Pc solution used in these studies were approximately equal, and similar volumes were distributed in each case, we can



**Fig. 3.** Q band absorbance spectra of chloroform solutions of CuPc(OC<sub>2</sub>OBz)<sub>8</sub>, H<sub>2</sub>Pc(OC<sub>2</sub>OBz)<sub>8</sub>, CuPc(O(C<sub>2</sub>O)<sub>3</sub>Bz)<sub>8</sub> and H<sub>2</sub>Pc(O(C<sub>2</sub>O)<sub>3</sub>Bz)<sub>8</sub> just after deposition as a droplet and at equal time intervals during drop evaporation and formation of final cast film.

compare the aggregation tendencies of these materials directly. In all cases the absolute absorbance dropped as solvent evaporated, owing to a change in oscillator strength in the Q band region due to the perturbation of molecular orbitals influenced by aggregate formation [20, 23]. Additional reduction in the absolute absorbance intensity can be ascribed to a reduction of path length and redistribution of the chromophores in the light path that accompanies the evaporation of solvent.

The effect of lengthening the ethylene oxide side chains from one ethylene oxide unit to three is immediately apparent on comparing the absorbance spectra in Figs 3(a) and 3(c), and this effect must transfer to the aggregation tendencies of these materials on the LB trough. It is clear that the aggregation of CuPc(OC<sub>2</sub>OBz)<sub>8</sub> at the same solution concentration is much greater than for CuPc(O(C<sub>2</sub>O)<sub>3</sub>Bz)<sub>8</sub>, in as much as there is significantly more broadening and blue shifting of the Q band for the shorter-chain material [20]. Previously we have estimated the aggregation constant in chloroform

solutions for CuPc(OC<sub>2</sub>OBz)<sub>8</sub> to be  $K_{\text{agg}} = 2.9 \times 10^2$  [20], and we estimate the aggregation constant for CuPc(O(C<sub>2</sub>O)<sub>3</sub>Bz)<sub>8</sub> to be at least an order of magnitude smaller [20]. For CuPc(O(C<sub>2</sub>O)<sub>3</sub>Bz)<sub>8</sub>, in fact, there is little difference between the Q band spectrum at the initial solution concentration and that expected for a purely monomeric solution of Pc [2, 20]. Monomeric spectral features were still observable as the solvent neared complete evaporation and the solution concentration of the Pc approached molar levels. Sensitivity-enhanced versions of the spectra, for the fully evaporated films in Figs 3(a) and 3(c), and cast films on glass (Fig 4), also suggest that there is considerably more disorder in the CuPc(O(C<sub>2</sub>O)<sub>3</sub>Bz)<sub>8</sub> film, as evidenced by the width of the Q band spectrum [20]. Previous studies of vacuum-deposited, well-ordered cofacial columnar aggregates of FA1Pc, where the Pc–Pc spacing is comparable with that of the aggregates shown here, have shown a Q band  $\lambda_{\text{max}}$  of *ca* 615–630 nm and an FWHM of this Q band of *ca* 80 nm [18, 19]. Only the CuPc(OC<sub>2</sub>OBz)<sub>8</sub> aggregates, as deposited using our hor-

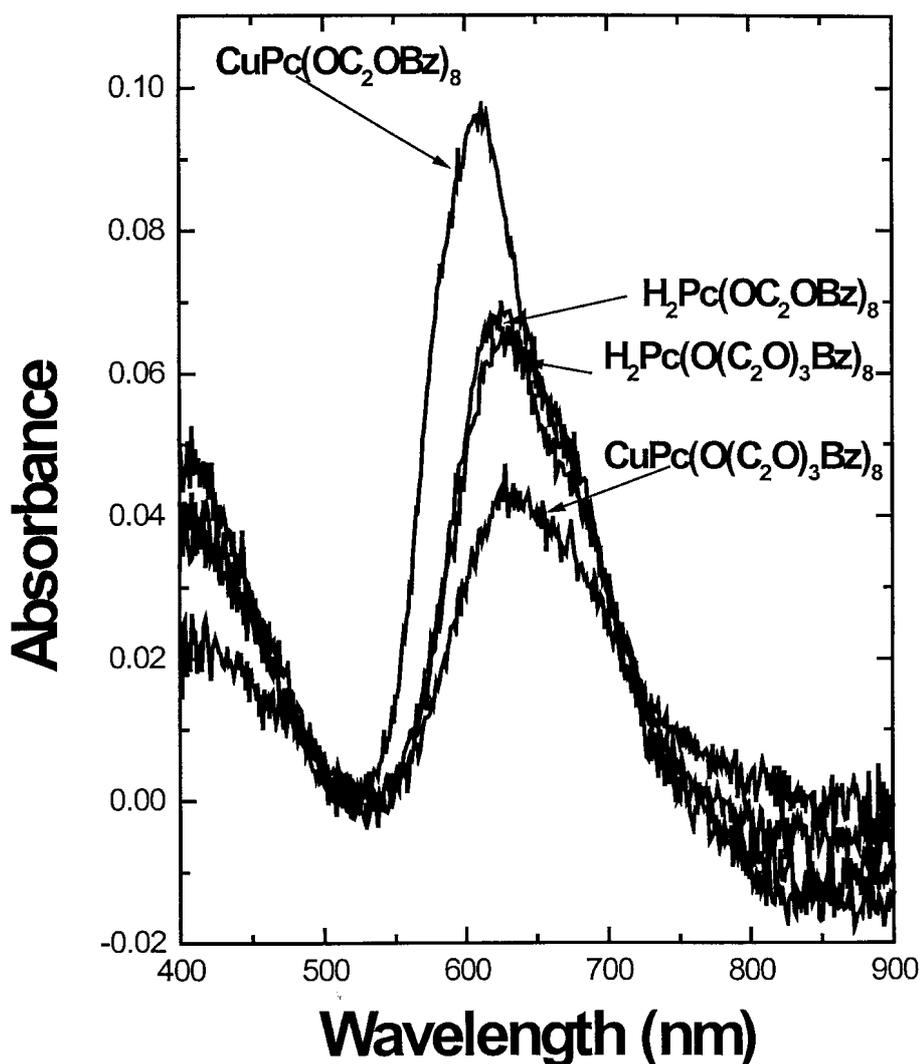
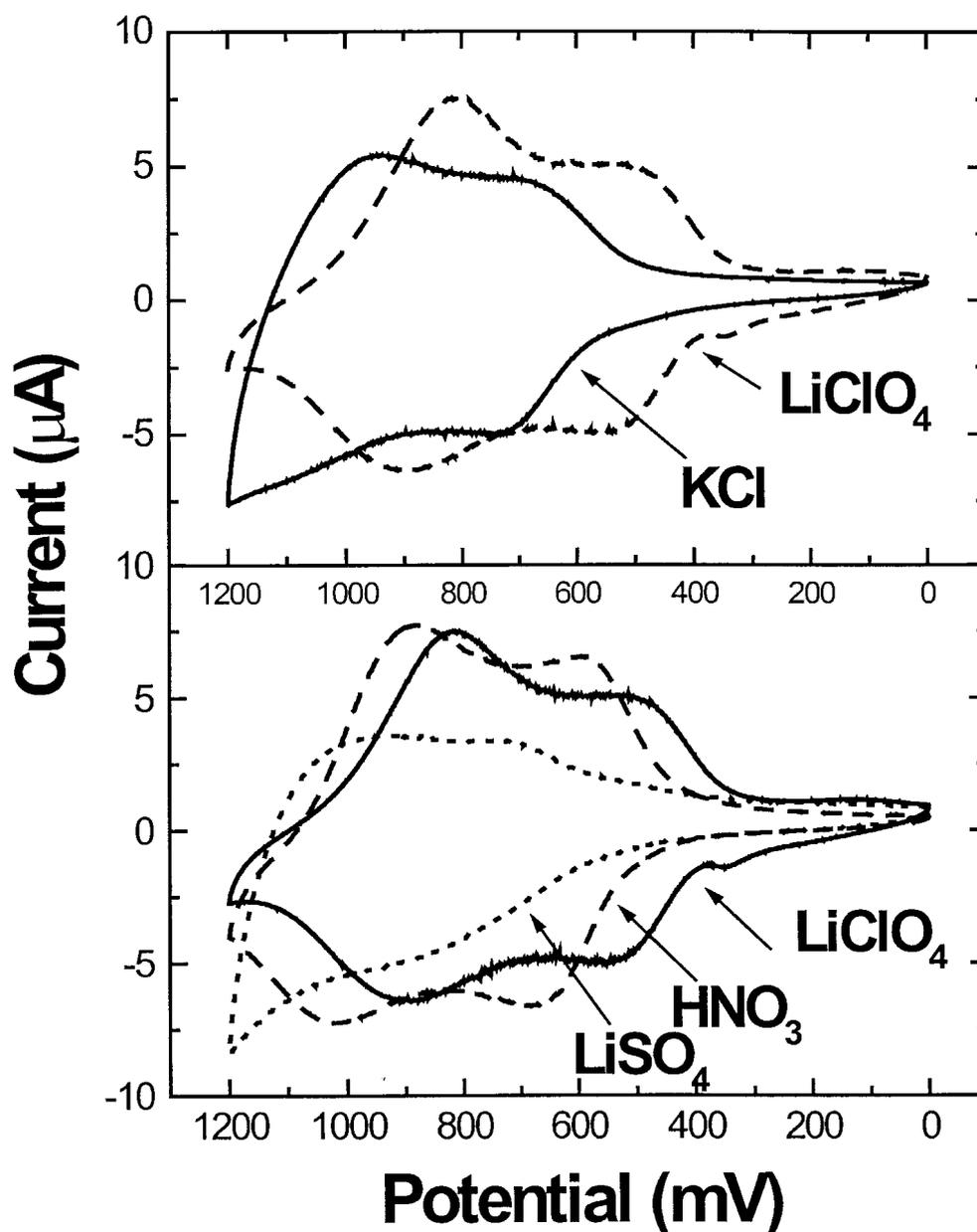


Fig. 4. Q band absorbance spectra of phthalocyanines in Fig 3 as cast thin films on glass.

horizontal transfer method from the LB trough, approach this level of blue shifting and narrowing of the Q band lineshape. For the metal-free versions of these Pcs, the degree of aggregation in solution for  $\text{H}_2\text{Pc}(\text{OC}_2\text{OBz})_8$  is somewhat higher than for  $\text{H}_2\text{Pc}(\text{O}(\text{C}_2\text{O})_3\text{Bz})_8$ , as evidenced by the broadening of the Q band spectrum, but the behavioral difference is not as clear as in the case of the copper-centered materials. Features consistent with monomeric Pcs could be clearly seen for both Pcs as the solvent neared complete evaporation and the solution concentrations approached nearly molar values [26].

These spectroscopic studies are consistent with the degree of ordering observed in thin films deposited on the LB trough, and with our ability to transfer well-

ordered films to hydrophobized substrates. Only  $\text{CuPc}(\text{OC}_2\text{OBz})_8$  and  $\text{H}_2\text{Pc}(\text{OC}_2\text{OBz})_8$  produced the two-phase LB isotherms shown in Fig 1(a). Clear transitions between monolayer thickness and bilayer thickness films were most easily observed for  $\text{CuPc}(\text{OC}_2\text{OBz})_8$ , consistent with its higher degree of aggregation in concentrated solutions and cast films. The longer-chain Pcs both gave poorly defined pressure–area isotherms, expected of amphiphilic phthalocyanines which do not achieve significant order on the LB trough [2–4, 12]. For both  $\text{CuPc}(\text{O}(\text{C}_2\text{O})_3\text{Bz})_8$  and  $\text{H}_2\text{Pc}(\text{O}(\text{C}_2\text{O})_3\text{Bz})_8$  we were unable to achieve efficient transfer from the LB trough, using either vertical or horizontal transfer techniques, and only cast thin films and poorly defined inhomogeneous



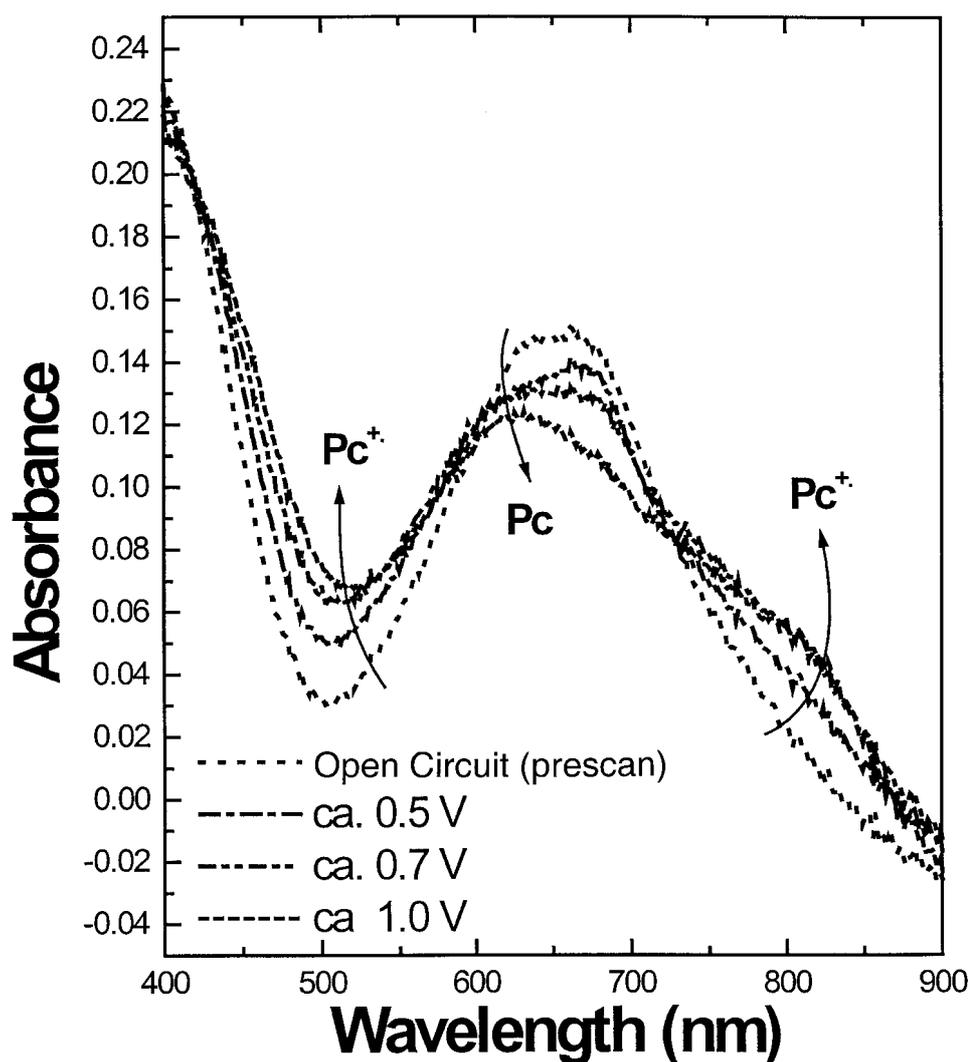
**Fig. 5.** Cyclic voltammetric scans for oxidation of four-bilayer thick films of CuPc(OC<sub>2</sub>OBz)<sub>8</sub> in presence of 0.1 M solutions of LiClO<sub>4</sub>, KCl, HNO<sub>3</sub> and LiSO<sub>4</sub>. 0.1 M solutions of NaBF<sub>4</sub> were also investigated (not shown) and gave voltammetric responses entirely comparable with those seen for LiClO<sub>4</sub>.

LB films could be examined for their spectroscopic and electrochemical properties [26].

#### Electrochemical/Spectroelectrochemical Studies of CuPc(OC<sub>2</sub>OBz)<sub>8</sub> Thin Films

Figure 5 shows the voltammetric responses of four-

bilayer thick (*ca* 23 nm) films of CuPc(OC<sub>2</sub>OBz)<sub>8</sub>, horizontally deposited on hydrophobized ITO substrates [22, 26], in contact with 0.1 M solutions of several different supporting electrolytes— LiClO<sub>4</sub>, KCl, LiSO<sub>4</sub> and HNO<sub>3</sub>. Comparable responses were obtained with thin films created from H<sub>2</sub>Pc(OC<sub>2</sub>OBz)<sub>8</sub> [26]. In general, we have found no significant difference in the electrochemical response of these



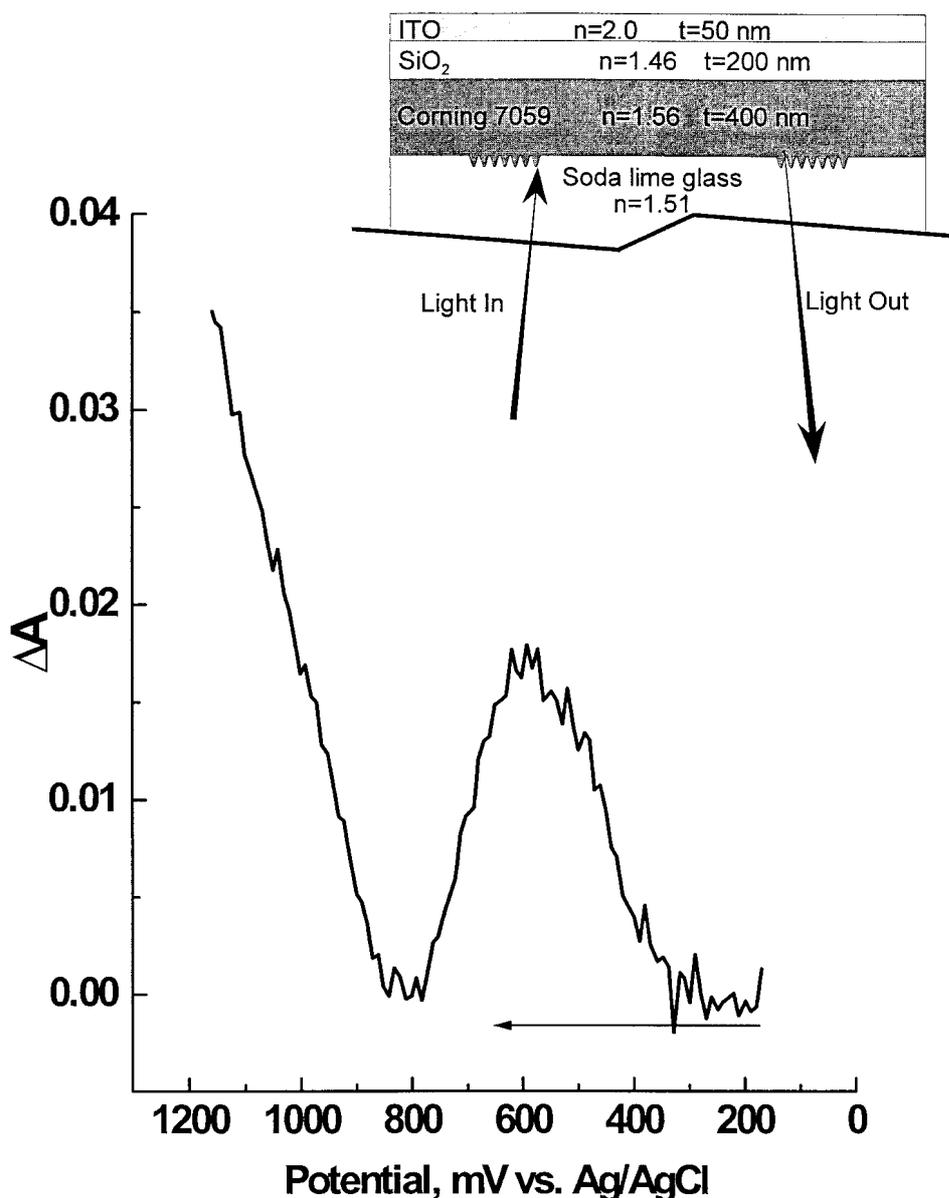
**Fig. 6.** Q band absorbance spectra obtained during oxidation in 0.1 M LiClO<sub>4</sub> of a 10-bilayer thick film of CuPc(OC<sub>2</sub>OBz)<sub>8</sub>. The increases in absorbance due to Pc cation radical formation and the decrease in absorbance of the starting material are shown with the added arrows.

films as a function of changing the cation (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>) in the supporting electrolyte. Significant differences are observed as a function of changing the identity of the anion. Similar effects have been observed for the electrochemical oxidation of PcPS thin films, and for thin films of various electroactive polymers which can be oxidatively 'doped' [13, 51].

At the voltammetric sweep rates used in these studies, the electrochemical oxidation event appears to resolve itself into two broad voltammetric peaks: (a) a peak spanning *ca.* 0.4–0.7 V in LiClO<sub>4</sub> and in NaBF<sub>4</sub> (not shown, but essentially identical to the responses seen in LiClO<sub>4</sub>), and (b) an even broader peak positive

of 0.7 V. Coulometric analysis of these voltammetric peaks suggests that, at potentials of *ca.* 1.0 V in LiClO<sub>4</sub> and NaBF<sub>4</sub> electrolytes, up to 85% of the Pc rings in the thin film are oxidized [22, 26].

The transmission spectroelectrochemical data in Fig 6, as discussed previously [22], show that oxidation of the film involves a complicated combination of processes. Formation of the Pc cation radical state is observed concurrently with the loss of Q band absorbance due to the Pc aggregate. While the counter-ion identity affects the energetics of the oxidation process, it does not influence significantly the types of oxidation products formed. At the onset



**Fig. 7.** Schematic of EA-IOW (see text) and absorbance change noted for voltammetric oxidation of *ca* 10% of a monolayer of CuPc(OC<sub>2</sub>OBz)<sub>8</sub>, diluted in an MA monolayer, as a function of applied potential.

of oxidation of the multilayer film, there is a clear loss of absorbance at the peak of the Q band for the aggregate (*ca* 620–630 nm), in parallel with the growth of absorbance in the 500 and 800 nm spectral regions. By comparison with solution oxidation studies of these Pcs and related materials, these new absorbance features are assigned to the broad absorbance bands of the Pc<sup>+</sup> cation radical [22, 26, 52, 53]. The absorbance features in the region from 630 to 700 nm, however, remain constant, or

even slightly increase in absorbance up to potentials applied of 0.7 V or less. Higher applied bias voltages then cause the loss of absorbance at longer wavelengths in the Q band region, with continued growth of absorbance intensity in the *ca* 500 and 800 nm spectral regions. We have surmised from these data that, beyond 0.7 V bias, the Pc films become less aggregated, developing a monomer-like structure due to counter-ion penetration, followed by the oxidation of this material [22].

The electrochemical behavior of these CuPc(OC<sub>2</sub>OBz)<sub>8</sub> and H<sub>2</sub>Pc(OC<sub>2</sub>OBz)<sub>8</sub> thin films suggests considerable stability after oxidation of up to *ca* 50% of the Pc rings in the assembly. For cast thin films created from CuPc(O(C<sub>2</sub>O)<sub>3</sub>Bz)<sub>8</sub> and H<sub>2</sub>Pc(O(C<sub>2</sub>O)<sub>3</sub>Bz)<sub>8</sub>, however, two poorly resolved electrochemical oxidation processes were observed, but without the electrochemical stability observed in Fig 5. Once the oxidation events had been initiated, there was a clear deterioration of the cast films of CuPc(O(C<sub>2</sub>O)<sub>3</sub>Bz)<sub>8</sub> and H<sub>2</sub>Pc(O(C<sub>2</sub>O)<sub>3</sub>Bz)<sub>8</sub>, and the currents observed on the reduction side of these voltammograms were less than 50% of those seen on the oxidation side of the voltammograms. After more than one oxidation/reduction cycle, there was a clear physical deterioration of the cast thin films of CuPc(O(C<sub>2</sub>O)<sub>3</sub>Bz)<sub>8</sub> and H<sub>2</sub>Pc(O(C<sub>2</sub>O)<sub>3</sub>Bz)<sub>8</sub>. Such electrochemical behavior underscores the importance of film ordering and coherence in stabilizing the Pc oxidation products in CuPc(OC<sub>2</sub>OBz)<sub>8</sub>.

It has recently been of interest to determine the extent to which the electrochemical properties of CuPc(OC<sub>2</sub>OBz)<sub>8</sub> are unique to multilayer, close-packed thin films. If the electrochemical processes are independent of the bulk film properties, they will be observed as well in thin film formats where the Pc aggregate is embedded in an electroinactive thin film. As seen in Fig 1(b), methyl arachidate (MA) shows the pressure–area isotherm expected of a classic amphiphile, with one phase transition observed with increasing compression. MA was chosen for this study because of this amphiphilic behavior, and because there are no electrochemically active metal ions present in the LB layer or subphase, as might be necessary in using other amphiphiles such as stearic acid. Addition of CuPc(OC<sub>2</sub>OBz)<sub>8</sub>, at concentrations which would produce coverages of *ca* 1%–10% of a full monolayer, produced the pressure–area isotherm shown in Fig 1(b). For the mixed films the projected area per molecule increased systematically and predictably as the mole fraction of Pc increased. This type of increase in projected area is consistent with incorporation of the Pc aggregate into the MA thin film, rather than ejection of the Pc so that it rests on the MA film surface, or beneath it in the subphase. Attempts to image these Pc aggregates embedded in the MA thin film are under way, but preliminary studies suggest that the Pc aggregates imbedded in MA films possess lengths of less than 10 nm and are not as coherent as those shown in Fig 2. Nevertheless, our spectroelectrochemical characterization of their electrochemical oxidation suggests some similarities

between the energetics of the oxidation process in the submonolayer and multilayer assemblies.

Figure 7 shows the change in absorbance experienced by a submonolayer coverage of CuPc(OC<sub>2</sub>OBz)<sub>8</sub> diluted into the MA thin film, deposited on the EA-IOW surface, in contact with a 0.1 M KCl solution. The EA-IOW structure provides the opportunity to monitor absorbance changes occurring at 633 nm as a function of applied potential during the voltammetric sweep. Absorbance changes are due only to species adsorbed to the ITO/solution interface [47–49]. The sensitivity of this spectroelectrochemical approach is such that, for many strongly absorbing organic dyes, optical changes such as those shown in Fig 7 can be followed during the voltammetric process, for dye coverages of only a few per cent of a monolayer. The changes in optical properties of the ITO layer are generally superimposed upon the optical changes of the organic thin film and have been removed from the plot in Fig 7. It should be noted that the first derivative of this plot of absorbance change with potential,  $\delta A/\delta E$ , if corrected for changes in molar absorptivity, would be directly proportional to the faradaic current flowing as a function of potential [48, 49, 54].

It can be seen that the onset for oxidation of the Pc entrapped in this MA film is at *ca* 0.4 V vs Ag/AgCl, which is *ca* 0.2 V negative of the onset for oxidation of the multilayer film in the same electrolyte. A second oxidation event apparently begins positive of 0.8 V, as is observed for the multilayer voltammogram. These spectroelectrochemical data suggest that counter-ion transport limitations do contribute as much as 0.2 V in added potential required to oxidize the multilayer CuPc(OC<sub>2</sub>OBz)<sub>8</sub> film versus the submonolayer coverage aggregate. Oxidation is accompanied in this case, however, by an increase in absorbance at 633 nm, suggesting very different spectral properties of the Pc aggregates and their oxidation products when entrapped in the MA film, as opposed to their properties in the cofacially aggregated multilayer film. Such differences in optical properties are not unexpected if the degree of aggregation is altered in these MA films, and requires investigations using multiple-wavelength (broadband) interrogation of the electrochemical events on the EA-IOW surface [55].

In PcPS thin films diluted into IPC matrices, multiple-wavelength experiments were conducted on the EA-IOW, and shifts in Q band spectra and in cation radical absorbance spectra were noted with increasing oxidation, but those essentially mimic the changes observed in multilayer versions of PcPS

[13, 47]. In the case of these polymerized Pc chains we have to conclude that the optical properties are unaffected by dilution into another matrix. The fact that the onset potential for oxidation of PcPS films appears to be unaffected by coverage or dilution into another matrix, while the oxidation of CuPc(OC<sub>2</sub>OBz)<sub>8</sub> films is dependent on these changes, suggests that counter-ion incorporation is made easier by loss of aggregation associated with dilution of CuPc(OC<sub>2</sub>OBz)<sub>8</sub> into the MA film.

The recent work of Jansen and Beck, characterizing the electrochemical oxidation of crystalline, vacuum-deposited thin films of CuPc, NiPc, FePc and CoPc, provides some additional insight into the redox activity of our multilayer materials [42, 43]. They have shown that the voltammetric oxidation of both CuPc and NiPc films in the presence of ClO<sub>4</sub><sup>-</sup> in acetonitrile proceeds through two sharp (FWHM ≤ 100 mV) and well-resolved processes separated by *ca* 0.4 V. The first process produces an 'insertion complex' (CuPc<sup>+</sup>/ClO<sub>4</sub><sup>-</sup>) which appears to be directly related to similar complexes prepared through chemical doping of these Pcs [37–41]. When prepared chemically, these insertion complexes appear to involve oxidation of the Pc macrocycle, resulting in parallel rows of oxidized Pcs and incorporated counter-anions, with approximately 30%–40% of the Pc rings oxidized in the stable product. In the case of the voltammetric oxidation in Fig 5, this is very close to the charge transferred in the first oxidation wave of the CuPc(OC<sub>2</sub>OBz)<sub>8</sub> thin films in contact with the aqueous 0.1 ClO<sub>4</sub><sup>-</sup> solutions. The second voltammetric oxidation wave in Fig 5 is more positive than the first by nearly the same potential, as seen by Jansen and Beck for the oxidation of the crystalline CuPc films [42, 43]. For these crystalline unsubstituted Pc films the second oxidation process caused dissolution of the thin film.

In the case of our materials, this second voltammetric peak does not in general lead to the loss of Pc from the electrode surface, provided that the electrode potential is not held positive of 1.0 V for extended periods of time. Films in contact with KHP as the supporting electrolyte did, however, degrade when the potential was cycled beyond the first oxidation process [26]. These results suggest that the higher oxidation products of CuPc(OC<sub>2</sub>OBz)<sub>8</sub> are stabilized by the interaction of the substituent chains which contribute to the structural integrity of the columnar assemblies noted above. In the case of the KHP anion insertion complex we assume that the presence of the aromatic moiety destabilizes the columnar assemblies and

results in dissolution of the Pcs, similar to that seen in the work of Jansen and Beck [42, 43]. We can hypothesize that the differences seen in the onset for oxidation of these films, as a function of anion identity, are due primarily to the differences in stability of the insertion complexes formed, and that, as with the crystalline materials, the perchlorate complexes are the most stable of the anions thus far investigated [37–41]. This now appears to govern the electrochemical doping of our thin film materials, and the PcPS system, at coverages above one or two monolayers.

## CONCLUSIONS

CuPc(OC<sub>2</sub>OBz)<sub>8</sub> represents an unusual phthalocyanine aggregate where the process of cofacial aggregation on the surface of the LB trough provides a pathway for the formation of extremely highly ordered thin films through self-assembly. From the experiments shown here and from studies published elsewhere [20–23, 25–27], we can confirm the balance of interactions which contribute to this ordered film formation. Copper as a central metal in the Pc rings appears to assist in the aggregation, through interactions between aza nitrogens on one Pc ring and the metal atom in the adjacent ring, causing a tilt of the Pc rings with respect to the aggregate column axis [20]. The metal-free version H<sub>2</sub>Pc(OC<sub>2</sub>OBz)<sub>8</sub> is not as strongly aggregated in solution, but forms films with physical and electrochemical properties nearly indistinguishable from the copper-centered material [25–27].

The length of the ethylene oxide side chains is critical to the stability of the columnar assemblies. As discussed here, longer side chains produce a more disordered, liquid crystalline-like material not well suited to LB film formation methods. We have also noted that the substitution of methyl groups for the benzyl groups on the termini of these side chains significantly decreases the ordering tendencies of these materials, confirming the importance played by arene–arene interactions in these terminal benzyl groups [26].

The electrochemical and spectroelectrochemical properties of these assemblies suggest that they can be oxidatively 'doped' to increase their conductivities in a fashion reminiscent of the crystalline Pcs, which have been oxidized as vacuum-deposited thin films or as slurries in non-aqueous solvents [37–43]. Earlier work on phthalocyanines such as NiPc and silicon

phthalocyanine oligomers and polymers showed that these materials could be chemically oxidized to the point where about 30% of the Pc rings were in the cation radical state, producing a highly conductive material. Electrochemically doped films with *ca* 75% of the Pc rings oxidized have been reported, although at large positive overpotentials [37–41]. The CuPc(OC<sub>2</sub>OBz)<sub>8</sub> system shows itself to be amenable to this same kind of oxidative doping at potentials less than 1.0V versus the Ag/AgCl reference electrode. Earlier electrochemical doping studies suggested that the energetics of anion incorporation were determined by the size and charge density of the anion, and that the lowest oxidation potential for the Pc assembly would occur with anions (X<sup>-</sup>) which were the easiest geometrically to incorporate into the Pc<sup>+</sup>X<sup>-</sup> lattice [37–41]. The work reported here, especially with regard to the electrochemical oxidation of submonolayer levels of CuPc(OC<sub>2</sub>OBz)<sub>8</sub>, and our other recent electrochemical studies of submonolayer levels of PcPS suggest that anion incorporation into the oxidized assembly may not control the energetics for oxidation as much as previously thought for these side-chain-modified Pcs [13]. Transport of these ions clearly does affect the rates for oxidation, as we have observed in sweep rate dependences of the oxidation of these CuPc(OC<sub>2</sub>OBz)<sub>8</sub> films and thin films of PcPS, but the onset for oxidation of both materials appears to be independent of film thickness and probably depends more on the solubility of the counter-ion in the 'solvent' environment created by the side chains, the energetics of contact ion pair formation, and the relative stability of Pc<sup>+</sup>X<sup>-</sup> [51, 56].

This work is now being extended to include different metals and modifications to the terminal benzyl groups of the CuPc(OC<sub>2</sub>OBz)<sub>8</sub> and related molecules, to allow for further stabilization of the assembly through polymerization. The prospect now appears good for creating Pc aggregate thin films which can be patterned over small areas, doped to provide increases in conductivity, and which exhibit substantial long-range order and dichroism in both their electrical and optical properties [25–27].

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