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Switching of the Rate-limiting Step in the Electrochromic Reduction of Fluorinated Phthalocyanine Thin Films by Decreased Intermolecular Coupling

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ABSTRACT

Thin solid films (5-120 nm) of the electron deficient perfluorinated phthalocyanine 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadeca-fluorophthalocyaninato copper(II) ($F_{16}PcCu$) and the perfluoroalkyl-substituted perfluorophthalocyanine 1,4,8,11,15,18,22,25-octakis-fluoro-2,3,9,10,16,17,23,24-octakis-perfluoro(isopropyl) phthalocyaninato copper(II) ($F_{64}PcCu$) have been prepared by physical vapor deposition onto a glass substrate coated with a transparent conductor (indium-tin-oxide, ITO). Cyclic voltammetry, chronoamperometry and spectroelectrochemical UV-vis spectroscopy studies revealed that the films were readily reduced and re-oxidized at potentials slightly negative of the Ag/AgCl reference electrode confirming a significant stabilization of the produced anions by the electron-withdrawing fluorinated substituents. A significant color change accompanied the change of the molecular redox states. Electroneutrality of the films was ensured by intercalation of K^+-counter ions upon reduction and their ejection upon re-oxidation. Molecules of $F_{64}PcCu$ were reduced by one electron, those of $F_{16}PcCu$ by up to two, for thin films subjected to slow charging rates. In addition to a decisive influence on the electronic structure of the inner ring π-system of the metal complexes the steric hindrance of the fluorinated ligands influence the extent of intermolecular coupling. The perfluoroalkyl, R_f, groups in $F_{64}PcCu$ thereby led to widely decoupled electronic states of the molecules in the thin films as detected by the observed optical absorption spectra. The bulky R_f groups also led to facile diffusion of the K^+-counter ions into the films, as well as to a significantly reduced electrical conductivity of $F_{64}PcCu$ relative to $F_{16}PcCu$. Time-resolved measurements served to analyze the interplay of the two mandatory transport processes. Interestingly, the variability in steric hindrance results in a qualitative change in the rate-limiting steps of the reduction. Thus, in the case of $F_{64}PcCu$ the transport of electrons in the molecular films is rate-limiting, as opposed to counter ion diffusion in the case of $F_{16}PcCu$. This switch underlines the importance of structural parameters for the tuning of the observed reduction and re-oxidation of organic thin films via intermolecular interactions.

1. Introduction

Electronic redox changes of thin films coupled with changes in absorption wavelengths or molar extinction coefficients have found numerous technological applications. For example, the so-called smart windows, i.e. transparent devices, exhibit transmission that can be tuned using electricity and thus can contribute significantly to saving energy in buildings by controlled inlet or reflection of solar radiation depending on the need for heating, cooling and lighting in a room. Further applications may be seen in a controllable privacy or visual accessibility ("smart curtain") or controlled reflection (e.g. in car mirrors). Different techniques can

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[2] JW performed the film preparation, characterization, electrochemical experiments and data analysis. AL synthesized and characterized $F_{64}Pc$. SMG supervised and coordinated the synthetic work and molecular characterization. DS supervised the film preparation, characterization, electrochemical experiments, data analysis and coordinated the discussion leading to this article. All authors actively participated in the scientific discussion of this work and in the writing of the manuscript.

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be used to construct smart windows. Aside from the most promising electrochromic devices, layers that change color upon reaction with a gas environment, upon illumination (photochromic) or upon temperature changes (thermochromic), as well as approaches using a switchable scattering power by use of liquid crystals, the use of electrophoretic or suspended-particles have also been reported [1]. As an alternative to classical inorganic electrochromic layers like tungsten oxide, thin films of organic pigments and dyes like phthalocyanines are of interest as electrochromic layers because of their high molar extinction coefficients and a large change of color upon redox reactions [2,3] They are also of interest as organic semiconductor films [4–6] in organic light-emitting diodes (OLED), organic field-effect transistors (OFET) and organic photovoltaic cells (OPV). In all these applications the position of the frontier energy levels (HOMO- highest occupied molecular orbital; LUMO- lowest unoccupied molecular orbital) is of high relevance since not only their redox potentials, but also contact characteristics, conduction type and readiness to dopant interactions are determined by these levels [7–9]. Electron-withdrawing substituents, e.g., decrease the electron density in the central π-system [10,11]. The electron energy of both the HOMO and LUMO levels is lowered [12] leading to a more positive redox potential (easier reduction) [10,11,13] and hence to the dominance of n-type doping [11,14,15]. Whereas the oxidation of unsubstituted phthalocyanine films in contact with aqueous electrolytes suffered from extensive degradation [16], films of substituted phthalocyanines with electron- withdrawing substituents showed reversible electrochromic reductions [2,17–22].

Based on the high molar extinction coefficient of phthalocyanines as well as on the significant spectral change upon reduction of films a significant coloration efficiency can be reached for films of only about 50–100 nm thickness compared to the classic μm-thick films of tungsten oxide [23,24]. Considerably faster switching speeds for the substituted phthalocyanines can be envisaged provided that sufficiently fast rates of electron transport and of counter-ion intercalation for charge neutrality can be established. Aside from electron transport in the films, charge-compensating counter-ion intercalation is needed to preserve electroneutrality [2]. Cation intercalation during reduction of films was observed for octacyanophthalocyanines [17], tetrapyrazinotetraazaporphyrins [19,20], 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadeca-fluorophthalocyaninatozinc(II) (F_{16}PcZn) [21] and tetrapyridotetraazaporphyyrins [18,22]. The intercalation of counter-ions was found to be in some cases fast, supported by a high diffusion coefficient D [17,19,20,22], or slow, limited by a small D in other cases, thus hindering the electrochromic redox reaction [17,19–21].

Considering the above requirements, F_{16}PcZn and, to an even larger extent, the zinc-, copper- and vanadyl-complexes of 1,4,8,11,15,18,22,25-octakis-fluoro-2,3,9,10,16,17,23,24-octakis-perfluoro(isopropyl) phthalocyanine (F_{64}PcVO, F_{64}PcCu, F_{64}PcZn) turned out to be very promising electrochromic materials [21,25,26]. F_{64}Pc can serve as a prototype organic scaffold for phthalocyanines whose macrocycle is substituted with perfluoroalkyl (R_f) groups. R_f groups have been reported to exhibit the strongest electron deficiency since they show an overall higher electron-withdrawing ability than fluorine atoms attached to aromatic rings [27–32]. Perfluoroalkylated phthalocyanines are characterized by an additional shift of the redox potential in solution towards the positive direction, about 0.4 V vs. the molecules based on the F_{16}Pc scaffold, caused by the partial removal of π-back bonding pathways [25,26,28,29]. The F_{64}Pc-based molecules are stable under ambient conditions and under illumination, even while producing reactive oxygen species [30,33]. Thin films of F_{64}Pc, similar to those of F_{16}Pc can be conveniently prepared by physical vapor deposition [34]. Their study has revealed that in addition to their electronic stabilization effect, perfluoro-isopropyl-groups exert a strong steric effect due to their bulkiness, largely suppressing intermolecular interactions as evidenced by minimum intermolecular spin couplings and decreased splitting of optical absorption bands [25,26,31,34]. Such decreased intermolecular electronic coupling does lead to lower electron mobility in films of F_{64}Pc relative to those of F_{16}Pc as explicitly shown for the Cu complexes [34]. The lower electron mobility, however, does not necessarily mean lack of redox activity. Thus, a faster diffusion of cations in the films might be possible since smaller lattice energies have to be overcome in order to allow ionic movement [25,26]. Indeed, switching times of the electrochromic reaction in the range of about a second were determined for a 40 nm thin film of F_{64}PcCu in contact to aqueous LiCl [25]. Incomplete reactions were, however, observed for thicker films, due to limited diffusion of the Li^+ counter-ions. A comprehensive investigation and modeling of the rate-limiting step in the electrochromic reduction and re-oxidation of these promising materials is still missing.

Detailed electrochemical experiments have been proposed to determine the rate-limiting step in the reduction or oxidation of thin films [2,35]. In cyclic voltammetry, peak current densities j_{pc} and j_{pa} depending linearly on the sweep rate ν are expected for redox reactions of monolayers or films sufficiently thin to still allow a transport of electrons and ions in the films that is fast relative to all other steps involved in the reaction (e.g., charge transfer and transport in an electrolyte). Furthermore, if a redox reaction occurs in a thermodynamically reversible way, a negligible separation of the cathodic and anodic peak potentials (E_{pc} and E_{pa}, respectively) is expected. In contrast, for thermodynamically reversible reactions limited by the diffusion of a reactant (as it is often the case for redox reactions in solutions at a catalytic electrode surface) a constant difference of peak potentials $\Delta E_p = E_{pa} - E_{pc} = 56.5/n$ mV is expected, with n being the number of electrons transferred per reactant in a given reaction (often provided in F/N_a, multiples of Faradays constant per mol of reactant). Peak current densities proportional to the square-root of ν are also expected, according to the Randles-Sevcik-equation [35]. Electrochemical characteristics close to thermodnamic reversibility have been observed for thin films of octacyanophthalocyanines [17], a transition from reversibility to diffusion control has been observed for films of tetrapyrazinotetraazaporphyrins [19] while diffusion-controlled processes have been observed for thin films of F_{16}PcZn [21] and F_{64}PcCu [25] at, however, quite low ν. The diffusion limitation has been attributed to a redox reaction limited by counter-ion diffusion in the thin films as opposed to an interfacial charge transfer or electron transport in the films. A value of the diffusion coefficient $D = 3.5 \times 10^{-12}\,cm^2\,s^{-1}$ has been determined for K^+-uptake by F_{16}PcZn [21] and of $D = 2.6 \times 10^{-12}\,cm^2\,s^{-1}$ for Li^+-uptake by F_{64}PcCu [25] from the square-root dependence of j on ν [35] in, however, a quite limited range of ν.

The role of counter-ion diffusion in films is further revealed by chronoamperometry since, according to the Cottrell-equation, the current density is expected to decay inversely proportional to the square root of time ($j \sim t^{-1/2}$) following a potential-step beyond the equilibrium potential of a reaction [35]. This way, $D = 4.0 \times 10^{-12}\,cm^2\,s^{-1}$ has been determined for K^+-uptake by a film of F_{16}PcZn [21], but the signals obtained for F_{64}PcCu could not be evaluated based on the classical Cottrell-approach indicating that other limiting factors for the reaction than simple ion diffusion exist [25].

For thin films, in which the electron-transfer from the contact electrode into the film and among the molecules in the films can not be assumed to be fast compared with the ion transport in the film, models have been developed to analyze the rate-limiting