Supramolecular assembly of alternating porphyrin and phthalocyanine layers based on electrostatic interactions

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A new type of self-assembled porphyrin/phthalocyanine multilayer film is prepared by alternating deposition of oppositely charged rigid planar molecules; the deposition process and photochemical and photophysical properties are studied in detail.

Recently, increasing attention has been given to the assembly of porphyrins and phthalocyanines into organized supramolecular functional systems[1,2] due to their potential application in fields such as photovoltaics, electrochromics and nonlinear optics. Here, we report a new type of self-assembled porphyrin/phthalocyanine film employing a novel film growth technique, introduced by Decher and coworkers.[3–5] In this regard, oppositely charged polyelectrolytes were alternately adsorbed onto an ionic substrate with electrostatic interactions acting as the driving force. This technique is a rapid and experimentally very simple way to produce complex layered structures with precise control of layer composition and thickness. The limitation of this technique is the relatively low order of the resulting films compared with other types of ultrathin films such as LB films. Herein, we employed two compounds, sodium (phthalocyaninetetrasulfonato)cobalt, $Na_4[Co(TsPc)]$, and [tetrakis(*N*,*N*,*N*-trimethyl-4-aniliniumyl)porphine]cobalt, $[Co(TAP)]Br_4$, whose ionic structures make them suitable for film growth as described above. By alternating deposition of the anionic phthalocyanine and the cationic porphyrin, we achieved a new type of functional multilayer film composed of purely rigid planar molecules.

UV–VIS spectra were obtained using a Shimadzu 3100 UV–VIS–NIR spectrophotometer. The quartz crystal microbalance (QCM) experiment was performed with an AT-cut, 6 MHz quartz crystal plate (0.502 cm^2) on each side of which a 0.23 cm^3 Ag electrode had been deposited and a home-made oscillator designed to drive the quartz at its resonance frequency. Surface photovoltage spectroscopy (SPS) experiments were carried out with a photovoltaic cell ITO/sample/ITO. The principle and setup diagram have been described in detail elsewhere.[6]

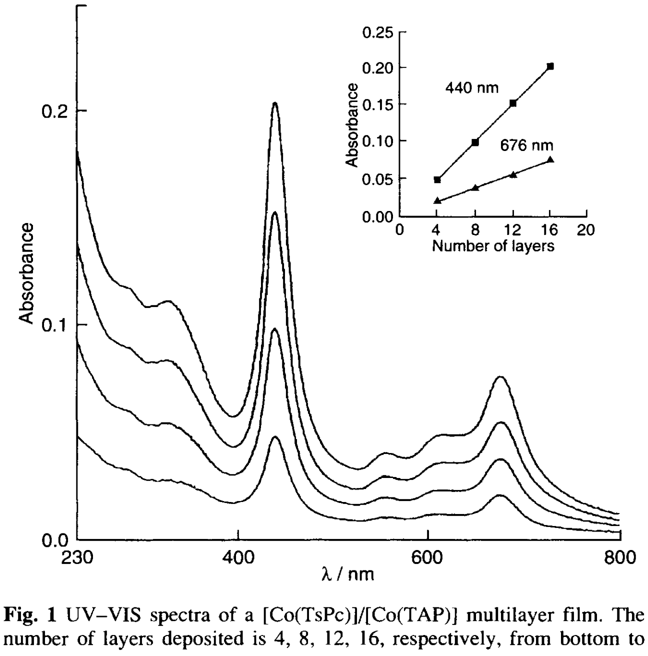

Fig. 1 UV–VIS spectra of a [Co(TsPc)]/[Co(TAP)] multilayer film. The number of layers deposited is 4, 8, 12, 16, respectively, from bottom to top.

$Na_4[Co(TsPc)]$ was provided by Professor M. L. Wang and $[Co(TAP)]Br_4$ by Professor C. B. Hang, which were synthesized following the literature.[7,8] For deposition, 2 mg per 10 ml aqueous solution was used for each of the compounds.

Substrates were incubated in a 5 mass% solution of the appropriate anchoring agent (4-aminobutyldimethylmethoxysilane for silicon and quartz, 12-sulfanyldodecaneamine for silver electrode) for *ca.* 15 h under dry N_2 to obtain a self-assembled film. Afterwards, the modified substrate was dipped into 0.1 mol dm^{-3} HCl to obtain a positively charged surface.

The multilayer film was fabricated as follows. A solid substrate with a positively charged surface was first immersed in the [Co(TsPc)] solution for 30 min, in this way the substrate was covered with one layer and its surface charge was reversed. After rinsing with Milli-Q water, the substrate was transferred into a [Co(TAP)] solution for 30 min, thus adding a second layer and restoring the original charge. An alternating multilayered [CoTsPc]/[CoTAP] film can be obtained by repeating these two steps in a cyclic fashion. The resulting assemblies showed high mechanical stability. An intense rinsing process caused no more than 5% loss of the materials once they were adsorbed onto the substrate (UV–VIS spectra).

Both the porphyrin and phthylocyanine have characteristic absorptions in the UV–VIS region and UV–VIS spectroscopy was used to follow the deposition process (Fig. 1). Two absorption peaks are found at 440 and 676 nm, which correspond to the porphyrin Soret band and the phthalocyanine Q band, respectively. The linear increase of the absorbance with

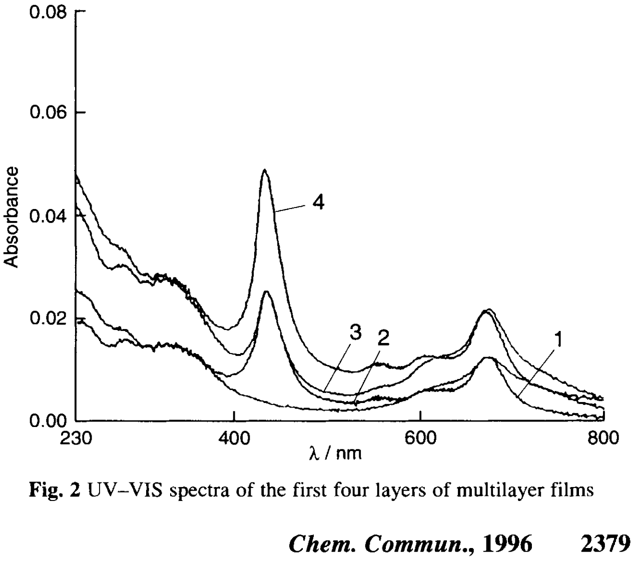

Fig. 2 UV–VIS spectra of the first four layers of multilayer films

the number of layers demonstrates that the consecutive absorption is uniform and regular. Both porphyrin and phthalocyanine absorption peaks in the self-assembled films are red-shifted by *ca.* 10 cm compared to the solution spectra, which results from the formation of aggregates of chromophores within the layer.

In order to observe the deposition process more closely, we focused on the deposition of the first several layers. Fig. 2 shows the absorption process of the first four layers, from which we can clearly see that the two photoactive molecules were deposited alternately.

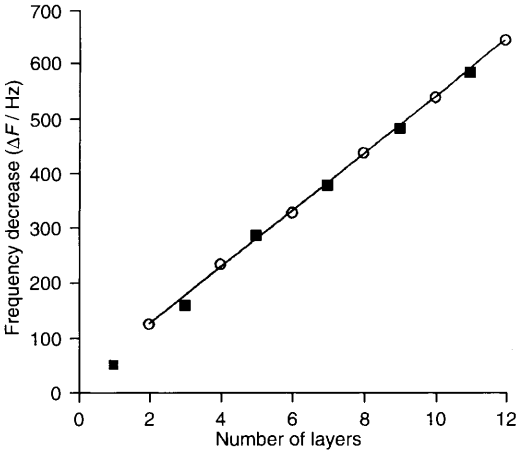

Fig. 3 Dependence of QCM frequency shifts on the number of layers deposited. Open circles correspond to the [Co(TAP)] terminal layer and filled squares correspond to the [Co(TsPc)] terminal layer.

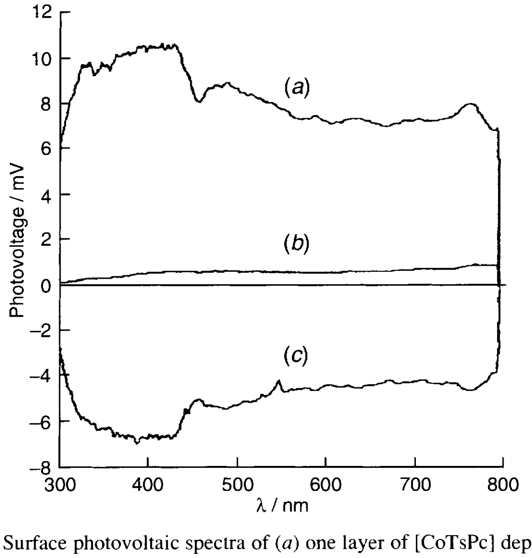

Fig. 4 Surface photovoltaic spectra of (*a*) one layer of [CoTsPc] deposited on the cationic n-Si substrate; (*b*) pure n-Si plate and (*c*) [CoTAP]/[CoTsPc] bilayer deposited on the cationic n-Si substrate

The uniform and regular deposition process is also confirmed by quartz crystal microbalance (QCM) measurements, which can detect the adsorption of material onto quartz electrodes with a precision of 1 ng. Fig. 3 shows the dependence of the frequency shift on the number of layers deposited. Linear growth was obtained during the 12 steps of the alternating assembly and the average mass changes per layer were calculated to be 112 ng for porphyrin and 101 ng for phthalocyanine, following the literature.[9] The estimated surface densities of porphyrin and phthalocyanine are calculated to be 2.72×10^{-7} and 2.44×10^{-7} mmol cm^{-2} from the QCM data, which indicate monolayers of macrocycle molecules.

Polarized UV–VIS spectra were used to study the orientation of the planar molecules in the multilayered films. No significant change was found when the self-assembled film was examined at normal incidence, using polarized light with its electric vector parallel or perpendicular to the plane of incidence, indicating that in-plane anisotropy is only slight. When the film was examined at 30° incidence, the order parameter, S, defined as $(A_{\perp} - A_{\|})/(A_{\perp} + A_{\|})$, is 0.06 for phthalocyanine and 0.05 for porphyrin. The above results mean that there is a slight out-of-plane anisotropy for the planar molecules.

This new type of porphyrin/phthalocyanine self-assembled film shows unique photophysical and photochemical properties. Their surface photovoltaic spectra (SPS) were measured and are shown in Fig. 4, from which we can see that when one layer of [Co(TsPc)] was deposited on the substrate, the SPS response increased by an order of magnitude compared with that of the pure n-Si plate, which means that the [Co(TsPc)] layer has a strong effect on the SPS response of the substrate. Furthermore, when the [Co(TsPc)] modified substrate was layered with [Co(TAP)], the response of bilayer [Co(TAP)]/[Co(TsPc)] modified n-Si was significantly reversed. This phenomenon confirms that efficient charge transfer occurred between the [Co(TsPc)] and [Co(TAP)] layers,[6] and that the photophysical and photochemical properties of the Si substrate can be dramatically changed using the above film growth technique.

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