Build-up of a New Type of Ultrathin Film of Porphyrin and Phthalocyanine based on Cationic and Anionic Electrostatic Attraction

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A new type of self-assembled multilayer film, a molecular deposition (MD) film composed of *meso*-tetra(4-sulfenyl)porphyrin ($tppS_4$) or copper phthalocyaninetetrasulfonic acid, tetrasodium salt (CuTsPc), alternating with a bipolar pyridine salt has been achieved and its structure studied in detail.

Both $tppS_4$ and CuTsPc are planar molecules containing a large π conjugate system. Studies concerned with the physical and chemical properties[1,2] of these molecules have lead to supramolecular structures of $tppS_4$ (or CuTsPc) by using (Langmuir–Blodgett) techniques.[7,4] We have tried to build a new type of self-assembled multilayer film, a molecular deposition (MD)[5,6] film, composed of $tppS_4$ (or CuTsPc) alternating with a bipolar pyridine salt based on cationic and anionic electrostatic attraction as the driving force. The resulting films were characterised by both UV–VIS and polarized UV–VIS spectroscopy and small-angle XRD which confirmed the stepwise deposition process and the ordered structure.

The bipolar pyridine salt (PyC_6BPC_6Py) was synthesized and its structure confirmed by elemental analysis, ^1H NMR† and FTIR. CuTsPC was obtained from Aldrich and $tppS_4$ was synthesized according to the literature.[7]

A hydroxylated substrate (quartz or silicon) was prepared to react with the vapour of 3-aminopropyltriethoxysilane in xylene so that it was modified with one layer of aminopropylsilane.[8] Contact angle measurement showed that a well-ordered surface can be obtained in this way.

The substrate was first dipped into 0.1 mol dm^{-3} HCl to obtain a positively charged surface followed by immersion in a solution containing 1 mg $tppS_4$ (or CuTsPc) in 10 ml H_2O for 30 min; in this way the substrate was covered with one layer and its surface charge was reversed. After rinsing with Milli-Ω water, the substrate was transferred into a solution containing 5 mg of the bipolar pyridine salt in 10 ml H_2O for 30 min, thus adding a second layer and restoring the original surface charge. A well-ordered multilayer $tppS_4$ (or CuTsPc) MD film can be obtained by repeating these two steps in a cyclic fashion.

UV–VIS spectroscopy indicates that the Soret bond (423 nm) of porphyrin in the $tppS_4$–PyC_6BPC_6Py MD film is shifted into the red region by 9 nm compared with that of the solution, which results from the formation of aggregates of chromophores in the films. The maximum absorption in MD films is not shifted with increasing deposited layer, which means that

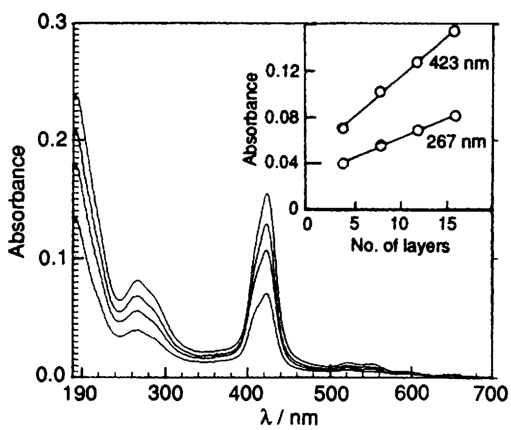


Fig. 1 UV–VIS spectra of MD film of $tppS_4$ alternating with bipolar pyridinium salt with different number of layers, 4, 8, 12, 16

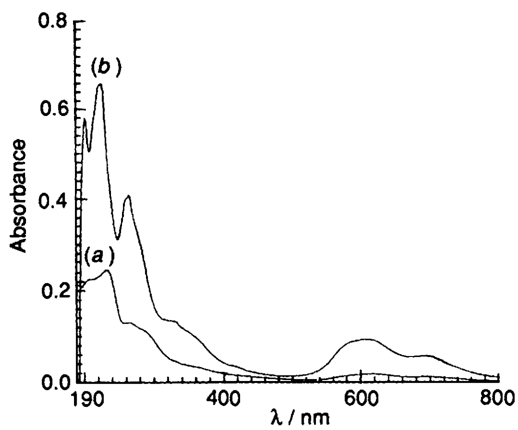


Fig. 3 UV–VIS absorption spectra of (*a*) MD film at CuTsPc–PyC_6BPC_6Py (20 layers) and (*b*) a simulated solution of CuTsPc–PyC_6BPC_6Py (molar ratio 1:2)

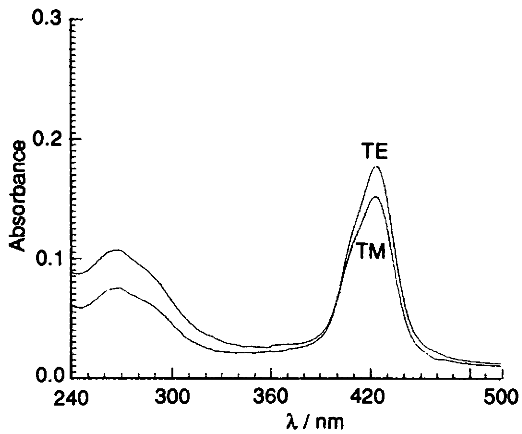


Fig. 2 Polarized UV–VIS spectra of $tppS_4$–PyC_6BPC_6Py MD films (20 layers) for TE and TM polarisations. Incident angle 30°.

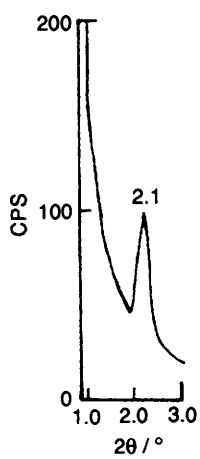


Fig. 4 XRD of a multilayer MD film composed of 23 alternating layers of CuTsPc and PyC_6BPC_6Py

there is no aggregation between the layers. The linear increase of the absorbance with the number of layers demonstrates that the consecutive absorption is uniform and regular (Fig. 1).

$$\frac{A_{\text{TM}}(i)}{A_{\text{TE}}(i)} = \left(\frac{n_1 \cos i + n_3 \cos r}{n_1 \cos r + n_3 \cos i}\right)$$

$$\left(\cos i \cos r + \frac{2n_1{}^3 n_3 \times \sin^2 i}{n_2{}^4} + \frac{<\sin^2 \theta>}{2 - <\sin^2 \theta>}\right) \quad (1)$$

From eqn. (1),[9] where i is the angle of incidence, r the angle of refraction in the substrate ($n_1 \sin i = n_3 \sin r$), n_1 n_2 and n_3, the optical indices of air, MD film and substrate respectively, θ the

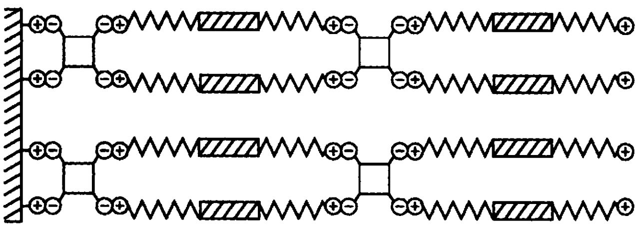
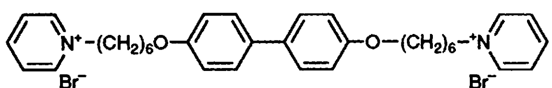
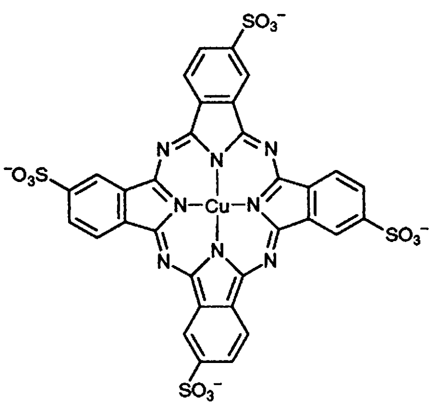


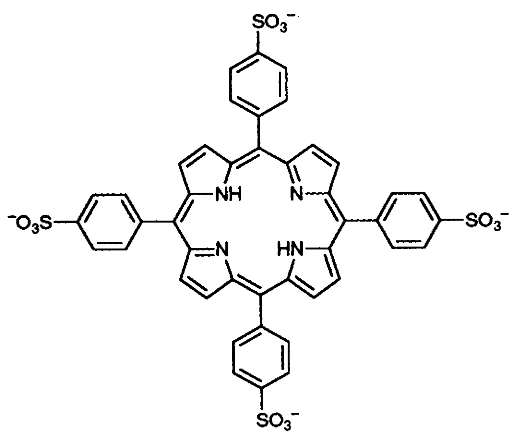
Fig. 5 Ideal model of multilayer MD films containing porphyrin or phthalocyanine



(PyC6BPC6Py)



(CuTsPc)



(tppS4)

angle between the normal line of plane x and the substrate, TE and TM the mean transverse electrical and transverse magnetic linear polarizations respectively (electric field perpendicular or parallel to the plane of incidence) and using the Soret band of tppS$_4$ (423 nm) as a working λ, for $n_1 = 1.00$, $n_2 = 1.43$, $n_3 = 1.47$, $i = 30$, $A_{\text{TM}}(i) = 0.152$. $A_{\text{TE}}(i) = 0.177$, then $\sin\theta = 0.5475$ and $\theta = 33°$ were obtained *i.e.*, the oriented angle between the plane and normal line of the substrate is 57°.

The CuTsPc–PyC$_6$BPC$_6$Py ultrathin MD film was similarly prepared and studied. It was found that the characteristic UV-VIS absorption of phthalocyanine in the CuTsPc–PyC$_6$BPC$_6$Py MD film is similar to that of the solution (Fig. 3). That both the absorption of monomer (693 nm) and dimer (613 nm) exist means that phthalocyanine is deposited as the monomer and dimer, although more of the dimer is present. As for the MD film of CuTsPc, the linear increase of the absorbance of the film with the number of the layers is also observed. Polarized UV-VIS spectroscopy shows little difference in the characteristic absorption peak of phthalocyanine, so it is difficult to calculate the oriented angle precisely. But we can conclude from the absorbance change of phenyl in phthalocyanine that there is a preferred orientation in the film. A diffraction peak can also be seen at 2.1° (2θ) in small-angle XRD and a *d*-spacing of 4.2 nm is calculated (Fig. 4). Thus, the MD film composed of CuTsPc is confirmed to have a well-ordered laminar structure.

In conclusion a new type of multilayer MD film containing tppS$_4$ (or CuTsPc), an ideal model or general way to fabricate these large plane conjugated molecules, is proposed as shown in Fig. 5 Owing to their excellent physical and chemical properties, we expect a wide range of applications in the fields of nonlinear optics, gas sensors, data storage, solar energy exchange and so forth.

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Footnotes

† *Selected spectroscopic data* for bipolar pyridine salt: ^{1}H NMR δ $(CD_3)_2SO$ 1.43–1.72 (m, 16 H), 3.97 (t, 4 H), 4.62 (t, 4 H), 6.99–7.46 (AB, 8 H), 8.15 (t, 4 H), 8.61 (t, 2 H), 9.07 (d, 4 H).

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