ChemComm

Covalently attached multilayer assemblies of diazo-resins and porphyrins

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Received (in Cambridge, UK) 2nd December 1998, Accepted 10th March 1999

Construction of highly stable covalently attached multilayer films containing porphyrins was achieved by UV irradiation of ionic self-assembled multilayer films of diazo-resins (DAR) and tetrasodium 5,10,15,20-tetraphenyl-21H,23H-porphine-P,P′,P″,P‴-tetrasulfonic acid (tpps$_4$).

Layered construction of porphyrins into organized systems has increasingly gained in importance due to its potential application in various disciplines ranging from voltaics, electrochromics to nonlinear optics. Many strategies have been exploited to fulfill this purpose, including Langmuir–Blodgett,[1] self-assembly[2] and electropolymerization techniques.[3] Recently, ourselves and others have developed a new method to fabricate porphyrin multilayer films based on electrostatic interactions as the driving force.[4] This technique has proven to be a rapid and experimentally very simple way to fabricate porphyrin containing films. However, porphyrin films fabricated by this technique are not robust enough and can be etched by solvents which limits applications in an extended range. Here we introduce a new method to fabricate covalently attached multilayer films containing porphyrins by UV photoreacting diazonium and sulfonate groups at the interface. This method combines the simplicity of the ionic self-assembly technique and the high stability of the covalently attached multilayer films. Thus it promises to be a very efficient method to prepare highly stable multilayer films containing porphyrins.

Diazo-resin (DAR) was kindly provided by Prof. Weixiao Cao (College of Chemistry and Molecular Engineering, Peking University, Beijing), and its synthesis has been reported previously.[5] The porphyrin tpps$_4$ was synthesized according to the literature.[6] A freshly cleaned quartz slide was first modified with a layer of (3-mercaptopropyl)trimethoxysilane (MPTS) from benzene, after which terminal –SH functional groups at the exposed surface were oxidized by 30% H_2O_2–HOAc *in situ* into sulfonic acid groups.[7] The sulfonic acid covered quartz slide was then alternately immersed in aqueous solutions of DAR (1.5 mg ml^{-1}) and tpps$_4$ (0.2 mg ml^{-1}) for 20 min, with an intermediate water washing and N_2 drying. Multilayer films can be formed by repeating the above step in a cyclic fashion. The above deposition process was conducted in the dark. Finally, irradiating the multilayer films with UV light for a given time is required to convert the ionic interaction of neighboring layers into covalent bonds.

UV–VIS spectroscopy was used to follow the fabrication process. Fig. 1(a) shows the UV–VIS absorption spectra of eight bilayers of DAR/tpps$_4$ assembled on a quartz slide. The absorbance at 380 nm is attributed to the π–π^* transition of the diazonium group, while the absorbance at 426 nm corresponds to the Soret band of porphyrin. It was found that the absorbances at 380 and 426 nm increase linearly with the number of layers, which demonstrates a progressive deposition process. UV–VIS spectroscopy also indicates that the Soret band of the porphyrin in the DAR/tpps$_4$ multilayer films is red-shifted by *ca*. 12 nm compared with that in solution, which is a consequence of formation of aggregates of chromophores in the films.

Owing to the well known photoreaction of diazonium and sulfonate groups, the above assembled films containing eight bilayers of DAR/tpps$_4$ were irradiated with a 30 W medium power mercury lamp at a distance of 20 cm. Fig. 1 shows the changes in UV–VIS spectra of the films with different irradiation times, from which, we can clearly see that the absorbance at 380 nm decreases dramatically due to the decomposition of the diazonium group, concomitantly, the absorbance at 290 nm increases gradually. Throughout the experiment, we found that the decomposition proceeded completely within 30 min. It was also found that at the same time the absorbance of the Soret band of tpps$_4$ decreases gradually with no change in peak position or shape. This decrease is caused by the decrease of the contribution of diazonium groups at this wavelength. The fact that the peak position and shape of the Soret band of tpps$_4$ did not change shows that no or few conformational changes took place during the reaction, which was consistent with the result of polarized UV–VIS spectroscopy.

We compared the stability of the multilayer films before and after UV irradiation by immersing the corresponding films into a ternary mixture of H_2O–DMF–$ZnCl_2$ (3 : 5 : 2, w/w/w). This ternary system was chosen because of the high solubility of the DAR/tpps$_4$ complex in it compared to other solutions, such as aqueous $ZnCl_2$ DMF, chloroform, *etc*. The UV–VIS spectra showed that before UV irradiation treatment, almost all the porphyrin and most of DAR can be dissolved after 5 min of immersion as seen the large decrease of the absorbance at 426 and 380 nm. However, for the UV irradiated films, the spectrum after immersion scarcely decreased showing that $< 10\%$ of the films dissolved. Thus the stability of the irradiated films was substantially improved.

From the change of the stability of the multilayer films before and after UV irradiation, it is proposed that a photoreaction takes place between the diazonium groups of DAR and sulfonate groups of tpps$_4$. As for the general reaction mechanism,[8] it is thought that DAR is first converted into its phenyl cationic form after release N_2 upon UV irradiation. Then an S_N1 type of nuclear displacement by sulfonate occurs as shown in Scheme 1. The fact that the photoreaction changes the

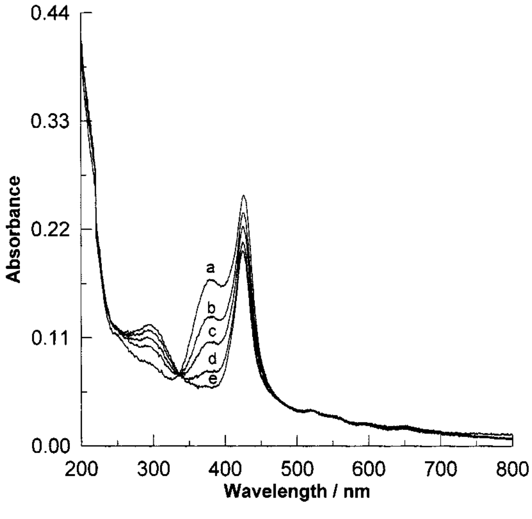
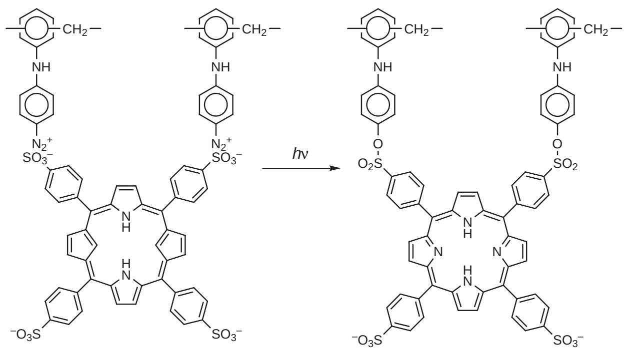


Fig. 1 UV–VIS absorption spectra of eight bilayers of DAR/tpps$_4$ upon irradiation with UV light for (a) 0, (b) 2, (c) 4, (d) 8 and (e) 15 min.



Scheme 1 Photoreaction of DAR and $tpps_4$ in one bilayer.

interactions not only between the neighboring layers, but also the first layer of DAR and the modified substrate from ionic to covalent is likely to be responsible for the improvement of the stability of the irradiated films.

The photoreaction of diazonium and sulfonate groups in multilayer films was further confirmed by IR spectroscopy. Three absorption peaks at 2220, 2163 and 1177 cm^{-1} are observed in the IR spectra of an 18-bilayer film of DAR/$tpps_4$ assembled on CaF_2 substrate [modified by cationic poly(diallyldimethyl ammonium chloride)] before UV irradiation. The first two originate from the stretching of $–CN_2$ and that at 1177 cm^{-1} from symmetric stretching of $–SO_3^-$. After UV irradiation, the absorptions at 2220 and 2163 cm^{-1} disappeared completely, indicating decomposition of the diazonium group. Meanwhile, a new absorption at 1170 cm^{-1} appeared which corresponds to the symmetric stretching of the sulfonate coupled with the phenyl group. In layer-by-layer multilayer films, the photoreaction should be facilitated to some extent by the close proximity of the diazonium and sulfonate groups. However, it is very difficult to determine the extent of reaction of diazonium with sulfonate groups. Further efforts to solve this problem are in progress.

Polarized UV–VIS spectroscopy was used to study the orientation of the planar porphyrin in the multilayer films before and after photoreaction. In both cases, no detectable changes were found when the multilayer films were examined at normal incidence using polarized light with its electric vector parallel or perpendicular to the plane of incidence, indicating that no in-plane anisotropy exists. When the film was examined at 30° incidence under the similar process, an obvious change of the spectra could be observed both before and after UV irradiation as shown in Fig. 2. We can calculate the orientation angle of the porphyrin plane by using the method described previously by us.[4] Herein, we presume the optical indices of the films before and after UV irradiation are the same and have a value of 1.5. The angle between the normal line of plane x and the substrate, *i.e.* θ, calculated before and after UV irradiation films is 53 and 49°. In other words, the oriented angle between the plane and horizon of the substrate are 53 and 49°, respectively, which show little conformational change of the porphyrin in multilayer films before and after UV irradiation.

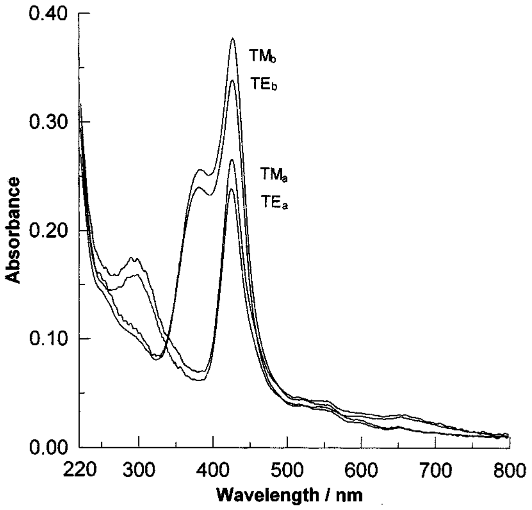


Fig. 2 Polarized UV–VIS spectra of a 12-bilayer DAR/$tpps_4$ film before (TE_b and TM_b) and after (TE_a and TM_a) UV irradiation for TE and TM polarisations. Incident angle = 30°.

In conclusion, a new method to fabricate covalently attached multilayers of porphyrin has been developed exploiting the ionic self-assembly technique and post UV-irradiation photoreaction of the diazonium and sulfonate groups in the multilayer assemblies. This technique is a simple but efficient method to prepare highly stable porphyrin-containing multilayer films.

This work was supported by National Natural Science Foundation of China.

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Communication 8/09419E