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Zirconium Phosphonate/1,4,5,8-Naphthalenediimides Self-Assembled Films

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ABSTRACT

The formation and characterization of self-assembled films of zirconium phosphonate / N,N'-di(2-phosphonoethyl)-1,4,5,8-naphthalenediimide (DPN) is presented. The films were produced on glass substrates by deposition of alternating layers of Zr^{+4} and DPN. Films containing up to 16 layers on each side of the substrate were obtained and monitored by absorption spectroscopy and ellipsometry. When irradiated, the initially colorless films turned to a persistent pinky color reminiscent of that of DPN anion radical. These films are a promising material to the development of photovoltaic devices.

Key words: zirconium phosphonates, naphthalenediimides, self-assembled films.

INTRODUCTION

Naphthalenediimides are a group of compounds that have become increasingly important in the past few years, due to their use in a series of applications, ranging from the biomedical area to the science of materials (Green & Fox 1995, Barros *et al.* 1997, Kheifets *et al.* 1977, Saito *et al.* 1990). Chemical or electrochemical reduction of 1,4,5,8-naphthalenediimides gives rise to a stable anion radical, making them very attractive for the construction of conducting materials (Miller *et al.* 1993) and for artificial photosynthesis (Greenfield *et al.* 1996). For most applications a fine control of the spatial organization of the system is required. Thus the incorporation of aromatic-diimides in a number of macromolecular systems has been investigated (Jazwinski *et al.* 1987, Hamilton *et al.* 1998, Brochsztain & Politi 1999).

A way to achieve a fine level of control over the properties of the system is to assemble the molecules in thin films. Here it is reported the preparation and characterization of self-assembled thin films of N,N'-di(2-phosphonoethyl)-1,4,5,8-naphthalenediimide (DPN) /zirconium phosphonate (Lee *et al.* 1988a, Lee *et al.* 1988b).

MATERIAL AND METHODS

The films were assembled on glass substrates (BK-7) and on silicon wafers by depositing alternating layers of DPN (Chae *et al.* 1998, Rodrigues *et al.* 1999) and Zr^{+4} (Scheme 1). The substrates were previously treated by known procedure (Katz *et al.* 1991). The treatment resulted in a surface rich in phosphonate groups, which adsorbed a layer of Zr^{+4} when exposed to an aqueous solution of $ZrOCl_2$.

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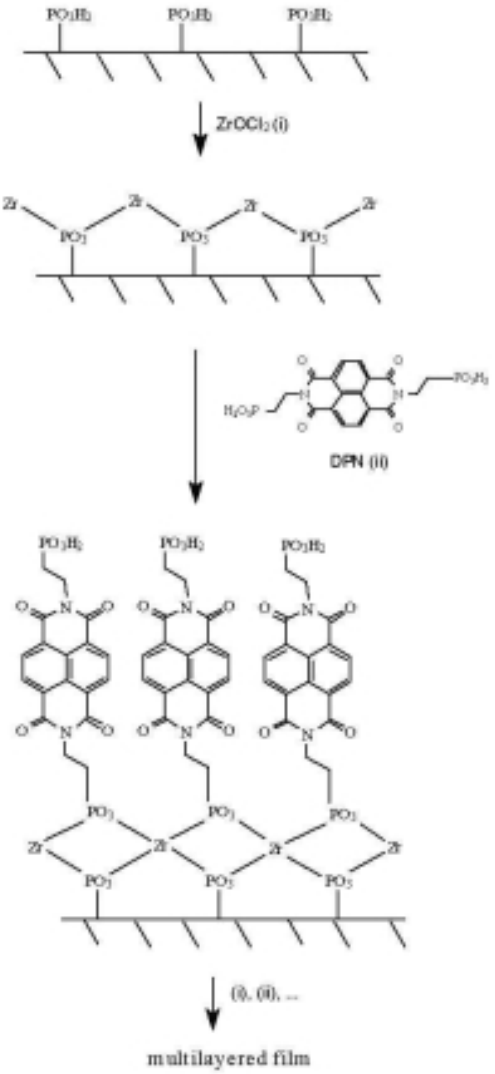
The zirconated surface is then exposed to an aqueous solution of DPN. Multilayers are obtained by sequential treatment with $ZrOCl_2$ and DPN solutions.

SCHEME 1



RESULTS AND DISCUSSION

Film formation was followed by electronic spectroscopy and by ellipsometry. A plot of the absorbance at 360 nm versus the number of DPN layers deposited was linear up to 16 layers (Fig. 1A). In parallel a plot of the ellipsometric thickness versus the deposition number was linear having a thickness of 10.2 Å per layer (Fig. 1B).

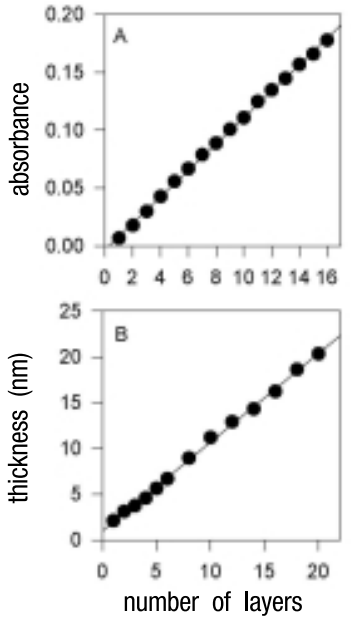


Fig. 1 – (A) Absorbance of a DPN film (at 360 nm) as a function of the number of deposited layers on both sides of a glass substrate. (B) Ellipsometric thickness of a DPN film as a function of the number of layers deposited on one side of a silicon wafer.

The absorption spectra of films with different thickness are shown in Fig. 2. The spectra of DPN in water and acetonitrile solutions are also shown for comparison. The spectrum in water is typical of monomeric 1,4,5,8-naphthalenediimides (Barros *et al.* 1997, Brochsztain & Politi 1999), showing well-defined vibrational structure. In acetonitrile, on the other hand, loss in the vibrational structure is seen which is attributed to aggregated DPN (Brochsztain & Politi 1999). The spectra of the film show the same trends observed in the acetonitrile spectrum, suggesting that the diimide rings are stacked in the films.

The emission spectrum of a DPN film is shown in Fig. 2B. The red-shifted, unstructured, excimer-like emission band observed for the film is in sharp contrast to the emission of DPN in water solution.

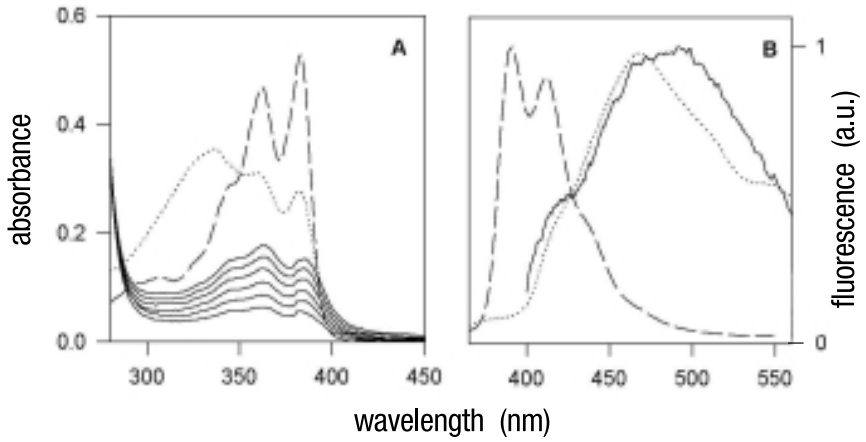


Fig. 2 – (A) Absorption spectra of DPN films with 6, 8, 10, 12, 14 and 16 layers on each side of a glass slide (—) and of DPN ([4×10^{-6} M]) solutions (5 cm path length) in CH_3CN ($\cdots$) and water (- - -). (B) Emission spectra of a DPN film with 16 layers on each side of a glass slide (—) and of DPN ([5×10^{-6} M])solution in water (- - -). The emission spectrum of a suspension of microcrystalline N,N'-dibutyl-1,4,5,8-naphthalenediimide in water is also shown ($\cdots$). Spectra are normalized to I_{max} = 1, and $\lambda_{ex} = 310$nm in all cases.

The emission spectrum of the film was very similar to that of a suspension of microcrystalline N,N-dibutyl-1,4,5,8- naphthalenediimide in water (Barros *et al*. 1997) (Fig. 2B). In either case the spectra can be attributed to emission from stacked chromophoric units in the solids, a typical case of a self-trapped exciton (Rashba 1987). Thus, both absorption and emission measurements point to a stacked arrangement of the aromatic rings within the films.

The DPN/zirconium phosphonate films photoactivity was observed when a 16-layer film (on each side of a glass slide) was irradiated under steady state or flash photolysis conditions. Thus, irradiation of the films with a Hg lamp (20 h) resulted in persistent spectroscopic changes, with the decrease of the diimide absorption band and the appearance of a tail extending to longer wavelengths. When the films were photolyzed with a pulsed Nd:YAG laser (355 nm), a long-lived bleaching of the DPN absorption band was observed, together with the appearance of a transient absorption at longer wavelengths. Both signals did not decay within the time scale of the experiment (up to 100μs). In these experiments, the appearance of a slightly pink color on the slide could be observed. We are presently investigating the nature of this photochemical process and in particular the possibility that stable imide radicals were formed. In conclusion the self assemble of DPN on zirconated glass surfaces and the initial steps towards its characterization and utilization are presented.

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