

Organic/Inorganic Self-Assembled film based on a Perylenetetracarboxylic Diimide Derivative/CdS

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Abstract. A perylenetetracarboxylic diimide derivative, N,N,N',N'-tetra(hydroxyethyl)-1,7-di(4-tert-butylphenol)perylene-3,4:9,10-tetracarboxylic diimide(THPDI), was synthesized and covalently self-assembled as a monolayer on the modified a quartz surface. UV-vis absorption and IR spectra revealed the *H*-aggregate nature of THPDI molecules in the obtained thin solid film. With this thin solid film as a template, CdS nanoparticles were deposited on it in situ, which were characterized by electronic absorption, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The morphology of CdS nanoparticles is disklike, and the diameter is ca. 150 nm as determined by AFM. The present result provides an effective and new method toward directed growth of specific morphologies of the nanoparticles. It is believed helpful for designing and preparing molecular-based nano-electronic and nano-optoelectronic devices with good performance.

Introduction

Organic-inorganic nanocomposite material has been widely recognized as one of the most promising and rapidly emerging research areas for advanced materials with desirable optical, electrical and magnetic properties. The combined unique properties offered by both organic and inorganic components on a nanoscale level make such nanocomposites attractive for a wide range of applications including next-generation optics, optoelectronic nanodevices, thin-film field-effect transistors [1], chemical or biological sensors, and catalysts [2]. Recently, the self-assembly technique has emerged as a powerful technique of processing functional organic molecules into ultra thin films with controlled thickness and controlled molecular architecture [3-5]. As an important functional dye with outstanding photo and chemical stability as well as interesting photophysical and photochemical properties, perylenetetracarboxylic diimide derivatives (PDIs) have been intensively studied for several decades [5-7].

Because of their great potential application as organic semiconductors in different molecular electronic devices, the fabrication of ordered thin solid films of this functional molecular material has become an attracting research area. In this letter, we report a facile approach to the fabrication of an organic/inorganic hybrid thin film composed of N,N,N',N'-tetra(hydroxyethyl)-1,7-di(4-tert-butylphenol)perylene-3,4:9,10-tetracarboxylic diimide (THPDI, Fig. 1) and CdS, which involves the covalent immobilization of THPDI, on a quartz surface and the in situ deposition of CdS nanoparticles on the thin solid film of surface-bound THPDI. THPDI/CdS hybrid film was characterized by electronic absorption spectra, atomic force microscopy (AFM), and X-ray

photoelectron spectroscopy (XPS). This research provided a new way to preparing organic and inorganic nanostructures with a controlled molecular packing mode, which may be found potential applications in nano-electronic and nano-optoelectronic devices.

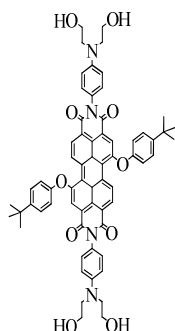


Fig. 1 The molecular structure of THPDI

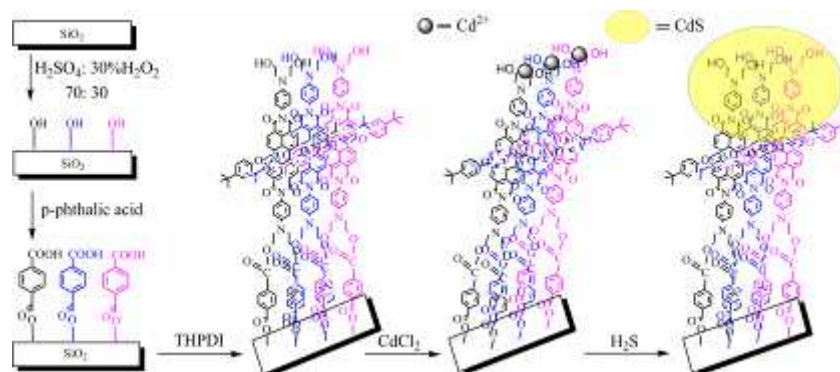


Fig. 2 Procedures for the fabrication of the THPDI, THPDI-Cd²⁺ and THPDI-CdS SA Film

Experimental Section

Reagents and Apparatus. The THPDI was synthesized according to published procedures [7,8]. Dichloromethane was freshly distilled from CaH₂ under nitrogen. Other reagents are used as received. Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. AFM images were collected under ambient conditions using tapping mode with a Nanoscope III/Bioscope scanning probe microscope from Digital Instruments. The XPS spectra were taken using PHI 5300 ESCA System (Perkin-Elmer, USA). The excitation source is Al K α radiation.

Preparation of the THPDI, THPDI-Cd²⁺ and THPDI-CdS SA Film (Fig. 2). (i) **THPDI SA film:** A mixture of p-phthalic acid (1.3 mg, 0.0078 mmol) and dicyclohexyl carbodimide (DCC) (1.6 mg, 0.0078 mmol) were dissolved in 5 ml of bromobenzene (solution 1). Another mixture of THPDI (8.14 mg, 0.0078 mmol) and DCC (1.6 mg, 0.0078 mmol) was dissolved in 5 ml of dichloromethane (solution 2). The substrates were first cleaned with “piranha” solution at 80 °C for 1 h and then left to cool to room temperature. They were repeatedly rinsed with double-distilled water and immersed in H₂O:30% H₂O₂:NH₃ 5:1:1 v/v/v mixture at room temperature for 40 min, washed again with doubly distilled water, and dried under vacuum just before the deposition of the coupling reagent. The newly treated quartz substrates were immersed in solution 1 at room temperature for 12 h and then into solution 2 for 24 h after being washed with dichloromethane to remove any residual unreacted THPDI. (ii) **THPDI-Cd²⁺ SA film:** THPDI SA film was dipped into a CdCl₂ aqueous solution (0.14 mmol/L) for 12 h. After being washed with water, the thin film was subjected to drying in air. (iii) **THPDI-CdS SA film:** THPDI-CdS SA film was obtained by putting THPDI-Cd²⁺ SA film in an atmosphere of H₂S gas liberated from thioacetamide aqueous solution at reduced pressure.

Results and discussion

UV-vis absorption spectra. As shown in Fig. 3a, the UV-vis absorption spectrum of THPDI in CH₂Cl₂ solution showed two absorption maxima at 549 and 518 nm, which correspond to 0-0 and 0-1 vibrational band of the S₀-S₁ transition, respectively. The observed absorption band around 404 nm is attributed to the electronic S₀-S₂ transition [4]. The peak positions of the absorption of THPDI correspond well to those of known PDIs with a similar substitution pattern at the bay positions

[3,4,7]. In the SA film, the characteristic electronic absorption band of THPDI significantly became broad (Fig.3b), due to a relatively close alignment of THPDI molecules in SA film caused by crystal field effect. In comparison with that in CH_2Cl_2 , an enhanced 0-1 vibronic band along with a significant blue-shift from 518 to 509nm is observed for THPDI SA film, Fig. 3b. Such a spectral change implies strong molecular stacking between the PDI skeletons and the formation of face-to-face π stacks (*H*-aggregate) [2]. This result is in good agreement with a study on thin films of analogous PDI derivatives reported by Würthner and co-workers [1]. Consistent with the absorption measurement of THPDI SA film, the absorption spectrum of THPDI- Cd^{2+} SA film also shows an enhanced 0-1 vibronic band with a blue-shift of the absorption maxima by 5 nm as compared to that in solution, Fig. 3c, indicating the similar stacking mode of THPDI molecules in both the THPDI SA film and THPDI- Cd^{2+} SA film. However, the fact that the blue shift in the THPDI- Cd^{2+} SA film is smaller than that of THPDI SA film suggests that the π - π interaction between the THPDI molecules in the THPDI- Cd^{2+} SA film is weakened owing to the coordination interaction between hydroxyethyl groups of the THPDI molecules and Cd^{2+} cations. On the other hand, by comparing the UV-vis spectra of the THPDI and the THPDI-CdS SA film (Fig. 3b,3d), one can see that the THPDI-CdS SA film exhibits a higher absorption intensity in the wavelength region below 445nm, which is very similar to the absorption of alkylated dendrimer-stabilized CdS nanoplatelets [9], but different from that of bulk CdS material (the absorption edge is near 590nm) [10], suggesting the CdS nanostructures have been formed in THPDI-CdS SA film. Furthermore, the 0-0 and 0-1 peaks of both THPDI SA film and the THPDI-CdS SA film did not show a significant change, suggesting similar packing behavior of THPDI molecules in a covalently attached monolayer before and after CdS nanoparticles deposition.

XPS analysis. The success in preparing THPDI SA film modified by CdS nanoparticles was further confirmed by the XPS spectra shown in Fig. 4. The peaks of XPS spectra appeared at 161.6, 405.3 and 412.1 eV, which correspond to S 2p, Cd 3d_{5/2}, and Cd 3d_{3/2}, respectively [11]. These further confirm that the THPDI-CdS SA film is composed of high purity CdS [11].

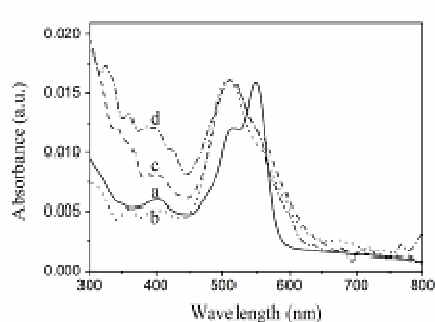


Fig. 3 UV-vis spectra of THPDI in solution(a) and the SA film for THPDI(b), THPDI- Cd^{2+} (c) and HPDI-CdS (d).

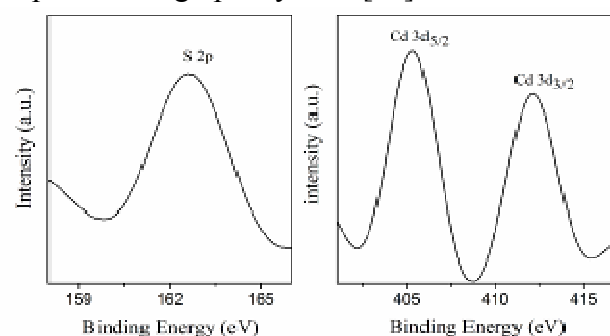


Fig. 4 High-resolution XPS patterns of THPDI-CdS SA film: S 2p and doublet Cd 3d_{5/2} and Cd 3d_{3/2}.

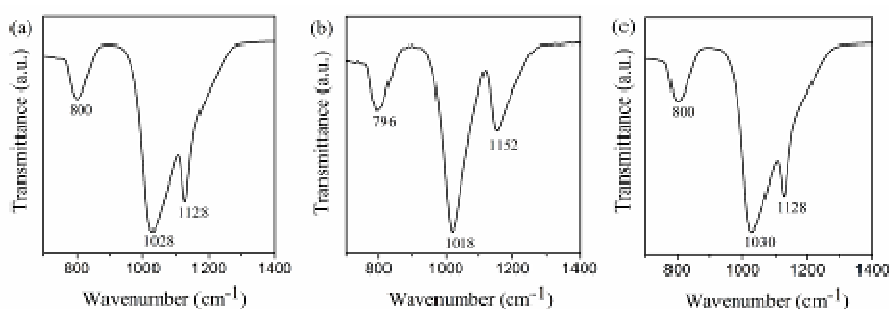


Fig. 5 ATR-IR spectrum of the SA film for THPDI (a) THPDI- Cd^{2+} (b) THPDI-CdS(c)

ATR-IR spectra. In order to further evaluate the perylene ring configuration and packing to the changes in film structure, ATR-FTIR spectroscopic measurements were carried out for the three types of SA films, Fig. 5. In line with that of perylene analogous [3], the principal out-of-plane band at $796\text{--}800\text{ cm}^{-1}$ has been assigned as the wagging modes of C-H on perylene ring, while the bands at both $1018\text{--}1030$ and $1128\text{--}1152\text{ cm}^{-1}$, correspond to the C-H bend mode. Very interesting, the bands from THPDI-CdS SA films (Fig. 5c) were at the almost same position as those from THPDI SA film, implying that the extent of the perylene-perylene interaction between THPDI molecules is very similar in the two types of films. A comparison of the peak frequencies for the C-H bend modes on perylene ring reveals that a definite trend toward higher peak frequencies follows the order THPDI SA film < THPDI-Cd²⁺ SA film. Therefore, the perylene-perylene interaction between THPDI molecules in THPDI-Cd²⁺ SA film is weaker than that in THPDI SA film. These are well consistent with the observation by UV-vis spectra. However, no any meaningful spectra for principal in-plane bands (which were expected to exist at ca. $1660\text{--}1700$ and $1500\text{--}1600\text{ cm}^{-1}$ correspond to the O=C-N stretches and the C=C aromatic stretches) on perylene were detected (because the signals of the in-plane bands of the ultrathin film are too weak to be recorded). For transmission, the polarization of the incident radiation always lies along the substrate surface. Therefore, only bands with a change in dipole moment parallel to the substrate surface will be intensified while the bands perpendicular to the substrate surface will be comparatively weak. Obviously, the out-of-plane wagging vibration is the more intense than in-plane vibrations in present case. Since the intensity is proportional to the dot product of the electric field and the dynamic dipole, the average PDI plane of the THPDI molecule should perpendicular to the substrate surface, suggesting an co-facial orientation (*H*-aggregation) for the THPDI molecules in SA films. This is also in line with the results of UV-vis spectra.

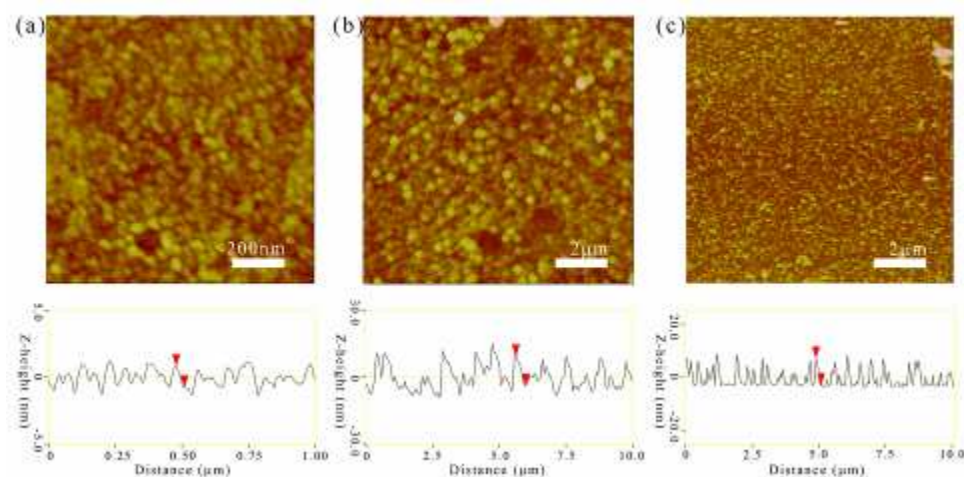


Fig. 6 Series of tapping-mode AFM images of three types of SA film for THPDI and corresponding section analysis(a), THPDI-Cd²⁺ and corresponding section analysis(b), and THPDI-CdS and corresponding section analysis(c).

The morphology of the thin film. AFM provided information on the aspect of the SA films. As can be found in Fig. 6, depending mainly on the intermolecular $\pi\text{--}\pi$ interaction incorporation with the van der Waals interaction as well as metal-ligand coordination, the continuous films (consisting of a high density of nano-particles) for the three types of SA film have been formed. Elongated domains of THPDI SA film can be observed with $50\text{--}70\text{ nm}$ in length around $20\text{--}40\text{ nm}$ in width (Fig. 6a), whereas square nano-particles of the THPDI-Cd²⁺ SA film exhibited a relatively uniform size distribution with average width of ca. 330 nm (Fig. 6b). Comparing the morphologies of three types

of SA film (Fig. 6), it can be seen directly that CdS nanoparticles are grown on the surface of the THPDI SA film with the average dimension of ca.150 nm. As shown in Fig. 6c, the average thickness of the CdS nanoparticles on the modified THPDI SA film is ca. 12 nm. Considering the thickness of the organic SA film (about 2.0 nm, Fig. 6a), the average thickness of the CdS nanoparticles on the THPDI SA film should be about 10 nm, which is much less than the average grain diameter, therefore, the disk-shaped CdS nanoparticles are obtained.

Summary

A monolayer of THPDI molecules covalently self-assembled on the modified a quartz surface was obtained successfully. With this thin solid film as a template, CdS nanoparticles were deposited on it in situ, which were characterized by electronic absorption, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). It is demonstrated that *H*-aggregates of the THPDI compound have been formed in both THPDI and THPDI-CdS SA film. The morphology of CdS nanoparticles is disklike, and the diameter is ca. 150 nm. The present result provides an effective approach towards directed growth of specific morphologies of nanoparticles.

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References

- [1] F. Würthner, C. Thalacker, S. Diele and C. Tschierske: Chemistry - A European Journal Vol. 7 (2001), p. 2245
- [2] M. Kasha, H. R. Rawls and M.A. El-bayoumi: Pure Appl. Chem. Vol. 11 (1965), p. 371
- [3] Y. Chen, Y. Kong, Y. Wang, P. Ma, M. Bao and X. Li: J. Colloid Interface Sci Vol. 330 (2009), p. 421
- [4] Y. Chen, L. Chen, G. Qi, H. Wu, Y. Zhang, L. Xue, P. Zhu, P. Ma and X. Li: Langmuir Vol. 26 (2010), p. 12473
- [5] L. Zang, Y. Che and J. S. Moore: Acc. Chem. Res. Vol. 41 (2008), p. 1596
- [6] X. Li, L.E. Sinks, B. Rybtchinski and M.R. Wasielewski: J. Am. Chem. Soc. Vol. 126 (2004), p. 10810
- [7] Y. Wang, Y. Chen, R. Li, S. Wang, W. Su, P. Ma, M. R. Wasielewski, X. Li and J. Jiang: Langmuir Vol. 23 (2007), p. 5836
- [8] C. Zhao, Y. Zhang, R. Li, X. Li and J. Jiang: J. Org. Chem. Vol.72 (2007), p. 2402
- [9] J.J.J.M. Donners, R. Hoogenboom, A.P.H.J. Schenning, P.A. Hal, R.J.M. Nolte, E.W. Meijer and N.A.J.M. Sommerdijk: Langmuir Vol.18 (2002), p. 2571
- [10] B. Ray: II-VI Compounds (Pergamon Press, Oxford, U.K., 1969)
- [11] S. Rodriguez-Llorente, R. Aroca, J. Duff and J.A. de Saja: Thin Solid Films Vol. 317 (1998), p. 129

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