

Formation of Covalently Linked Self-Assembled Films of a Functional Hyperbranched Conjugated Poly(Phenylene Vinylene)

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Received: June 5, 2000; In Final Form: February 2, 2001

A novel self-assembled (SA) film of a functional dendritic molecule, hyperbranched conjugated poly(phenylene vinylene) (SPPV), is obtained through the covalent bond linkage on a hydrophilic substrate (e.g., mica). The self-assembling process of the film is investigated in detail by UV–vis and fluorescence spectroscopy, and the morphology of the films are observed by atomic force microscopy. Hyperbranched molecules require longer times for forming highly ordered and homogeneous molecular films (several days) compared to small molecules. Excimers formed from the excited state of SPPV in these SA films can be detected by their fluorescence properties. The difference of fluorescence properties between the SPPV SA film and spin-coating film shows that the SA film is ordered and homogeneous. Finally, the photovoltaic response is reported for these SA films.

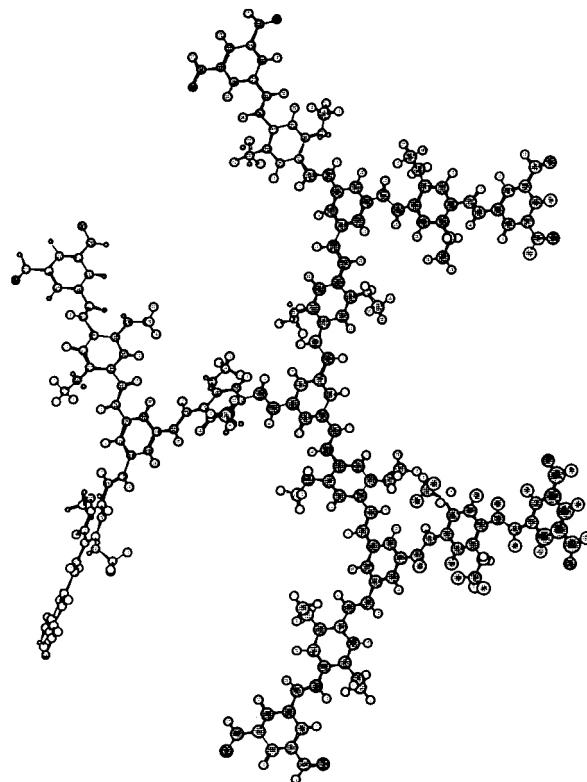
Introduction

Future device configuration for electronic, photonic, or other “intelligent” application requires nanofabrication, -manipulation, and -functionalization techniques of supramolecular aggregates and assemblies. It is very important to control structure, order, and dynamic behavior at the molecular/atomic level.^{1,2} Spin-coating, which is the conventional method for the deposition of polymer films, gives the films without the accurate thickness, and the film’s repetition is a problem for high-technique use (such as optical electronic devices). Furthermore, this method cannot give the covalently bonded films that may enhance electron transfer or injection into its supporting substrates.

Self-assembled monolayers have witnessed tremendous growth in synthetic sophistication and depth of characterization.^{3,4} The process of self-assembly of small molecules, such as organo-silicon and organosulfur, was investigated by using AFM and STM techniques.^{5–14} Recently, the self-assembly technique has emerged as a powerful technique for processing conjugated polymers into ultrathin films with controlled thickness and controlled molecular architecture.^{15–18} Alternating adsorption of anionic and cationic polyelectrolytes^{19–21} has been proved to be a powerful method in fabricating a multilayer nanostructure at interfaces. This method has been used in some fields such as OLEDs and polyelectrolyte-modified electrodes.^{22,23} It was also reported that this method was used to make self-assembled films of dendritic macromolecules.²⁴ Actually, the driving force for the self-assembled films of polymers does not have to be electrostatic force. Recently, there are some reports using hydrogen bonds and coordination bonds to make self-assembled films of poly(4-vinylpyridine) (PVP)^{25,26} and co(p-HydroxyV–PV) conjugated polymers.²⁷ To develop self-assembly methods for functional polymers, we introduced covalent bonding in our system.

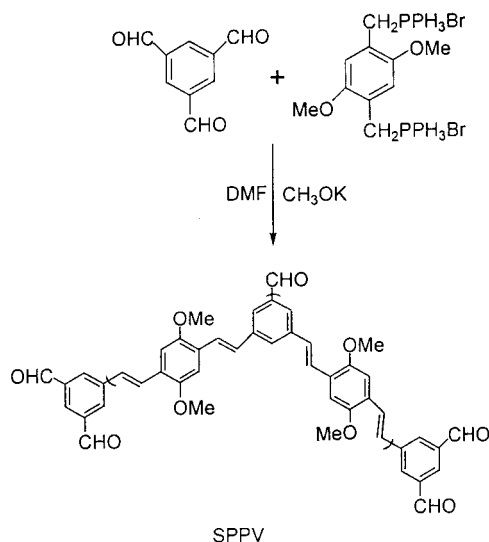
The functional polymer we used here is a dendritic molecule, a hyperbranched conjugated poly(phenylene vinylene) (SPPV), and the molecular structure is shown in Scheme 1. These hyperbranched materials demonstrate characteristics such as supermolecular assembly and micellar properties.^{28–30} As an

SCHEME 1: Structure of Hyperbranched Conjugated Poly(Phenylene Vinylene) (SPPV) Calculated by MM2 Method^a



^a Repeat unit and one full branch for generation G2.

analogue of poly(1,4-phenylene vinylene) (PPV), SPPV is a good fluorescence material. It has an extended π – π conjugation structure in two dimensions, which is expected to be useful in optical-electrical devices. In this paper, the aldehyde groups at the exterior of the polymer are used to form self-assembled films through organic reactions. To understand the structure of

SCHEME 2: Synthesis Route of SPPV through Wittig Reaction

dendritic macromolecules within molecular films, we used atom force microscopy (AFM), UV-vis spectra, and fluorescence spectra for investigating the morphology and microstructure of the film. The fluorescence properties of SPPV SA film and spin-coating film are compared. In addition, the photoinduced electron-transfer process is detected by surface photovoltage spectroscopy (SPS).

Experiment

Materials. The hyperbranched conjugated PPV was obtained through Wittig reaction (shown in Scheme 2). The details of the compound synthesis will be published elsewhere.³¹ The molecular weight is ca. 2954. All the other chemicals are A.R. grades.

Instruments. The UV-vis spectra are obtained by a HITACHI U-3010 Spectrophotometer, and the fluorescence spectra are obtained by a HITACHI F-4500 Fluorescent Spectrophotometer. The substrates used for spectroscopy studies are quartz.

AFM images are taken with a commercial AFM setup (Seiko SPA 3800N instrument) under ambient conditions. All the images shown here are obtained in constant height mode, while precise height information is obtained from simultaneous constant force mode images. A triangular-shaped Si_3N_4 cantilever with a spring constant of 0.02 N m^{-1} is used to acquire images in contact mode. The applied force is typically 0.1 nN .³² All structural parameters discussed below are obtained for several independently fabricated films, at randomly selected surface areas. The substrates used here are newly peeled mica.

SPS measurements are carried out with a solid junction photovoltaic cell indium tin oxide (ITO)/sample/ITO, a light source, a monochromator, and a lock-in detection technique. Monochromatic light is obtained by passing light from a 500-W xenon lamp through a double-prism monochromator (Higher and Watts, D300). A lock-in amplifier (Brookdeal, 9503-SC), synchronized with a light chopper, is used to amplify the photovoltage signal.³³

Film Assembling. The strategy of acetal formation through the reaction of aldehyde group and alcohol group is used in this preparation. Film construction is carried out on a hydrophilic pretreated quartz slide in $3.3 \times 10^{-5} \text{ M}$ SPPV chloroform solution (where the chloroform is newly distilled) containing 0.1 mg/mL DCC to help the dehydration. The immersion time

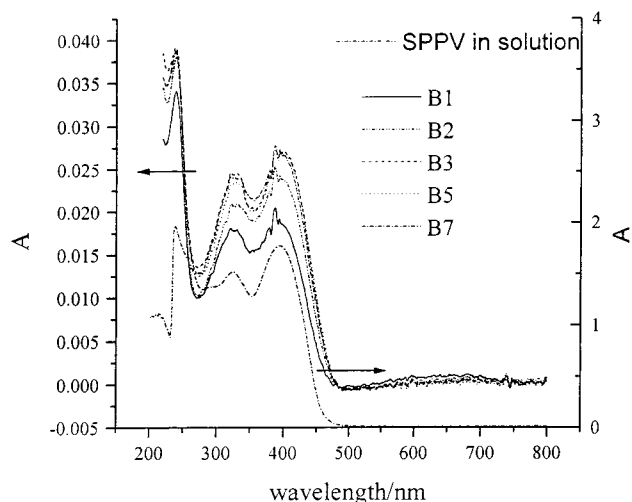
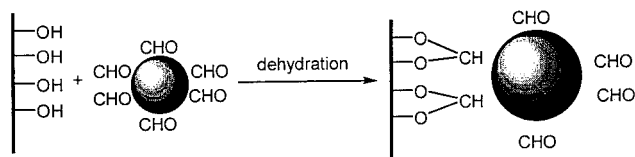


Figure 1. UV-vis spectra of SPPV. Right: 0.16 mg/mL SPPV chloroform solution. Left: SPPV SA films prepared for 1, 2, 3, 5, and 7 days, respectively.

SCHEME 3: Self-Assembling Procedure of SPPV

varied from 1 to 7 days, and the resulted films are denoted as film B_n ($n = 1, 2, 3, 5, 7$). When this self-assembly finishes, the substrates are taken out, rinsed ultrasonically for 1 min, and rinsed with chloroform. The procedure in this kind of film preparation is shown in Scheme 3.

Result and Discussion

1. UV-Vis Spectra and Contact Angle Characterization of the SA Film Formation. Hydrogen bond,³⁴ hydrophobic interaction,³⁵ and π - π interaction³⁶ may play roles in the formation of aggregates. The spectroscopic technique is an appropriate tool for studying the aggregates if the molecules bear chromophores. So the assembling process is generally monitored by UV-vis absorption spectroscopy. Figure 1 shows the UV-vis spectra of SPPV both in the CHCl_3 solution and the SA films. The maximum absorption peaks of SPPV chloroform solution and its SA films are both at 238, 327, and 393 nm. This similarity of both spectra in Figure 1 indicates the formation of the expected film of SPPV. As there is no change in the maximum absorption peaks in UV-vis spectra when the concentration of SPPV increases from 10^{-6} to 10^{-3} M (the figure is not shown here), the SPPV molecules are not aggregated in these concentrations. The time dependence of the absorption at 390 nm (shown in Figure 2) demonstrates that the film of SPPV actually is completed when the immersion time reaches 3 days. Because the diffusion rate of our large dendrimeric molecule may be slow, the formation time of its SA films is longer than that of the small molecules.³

The contact angle is one of the efficient characterization methods of surface properties and is widely used for studying the condition of the SA film-modified surface on gold, quartz, silicon, mica, and so on. To study the deposition process, we should carry out contact angle measurements for SA film formation.³⁷ The contact angles of SPPV SA films on mica prepared at different times are shown in Table 1. It is well-known that mica surface is a highly hydrophilic, with a contact

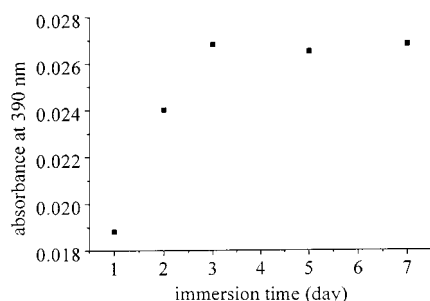


Figure 2. Maximum absorbance at 390 nm vs the immersion times.

TABLE 1: Contact Angles of SPPV SA Films on Mica with Different Immersion Times

immerse time (day)	contact angle (deg)
0	0
1	4.3
3	6.7
5	7.2
7	11.8

angle of 0° . When the mica substrate is immersed in 3.3×10^{-5} M SPPV chloroform solution for 1 day, the contact angle increases to 4.3° . As the immersion time is increased, the contact angle increased from 4.3° to 11.9° . Combined with the results of UV–visible spectra, it may be concluded that the SA film forms in two steps: First, the coverage on mica is small, so the contact angle is not large. Then, the coverage on mica increases, and as a result, the contact angles increase. We will discuss below how the changes in the contact angles from 0° to 6.7° represent the increase in the density of SPPV molecules in the self-assembled film and how the changes from 6.7° to 11.9° represent the later rearrangement process of the SA film. To understand this process in detail, we will follow the process of the SA film formation by AFM and fluorescence measurement.

2. Investigation of the Formation Process of SPPV SA Films by AFM Technique. Three concentrations of SPPV chloroform solutions (6.6×10^{-5} , 3.3×10^{-5} , and 1.6×10^{-5} M) are used to prepare the SA films on mica, and their AFM images are obtained. At the lower concentration, the molecules attached on the substrate are not uniform, and the network-like structure is formed, while for the higher concentration, aggregated islands are formed. High-quality films cannot be obtained at these two concentrations. Only when the concentration is 3.3×10^{-5} M can highly ordered SA films be obtained. According to the UV–vis spectra, we choose the films prepared at 1 day and 3 days to investigate their morphologies by AFM. Figure 3 shows the topographic images of SPPV SA films prepared from 3.3×10^{-5} M SPPV chloroform solution for 1 day (Figure 3a) and 3 days (Figure 3b). Obviously, the coverage of film B3 is ca. 94%, which is larger than that of film B1 (ca. 70%), representing the forming of the SA film. The statistic distributions (100 points for each Figure) of grain size in Figure 3a,b are shown in Figure 4. The average grain size of film B1 is 143 nm, and that of film B3 is 50 nm. This phenomenon indicates that the film formation process can be divided into two processes: (i) The aggregated domains are first formed on the hydrophilic substrates just after covalent bonds are formed. This leads to the large grain sizes we have observed. (ii) The aggregates in the SA films rearrange to form ordered homogeneous films, and the grain sizes become smaller.

3. Fluorescence Study of SPPV SA Films. Fluorescence spectroscopy is a sensitive method for studying molecular interactions, and we use it herein to investigate the formation process of SPPV SA films. The fluorescence spectra of different

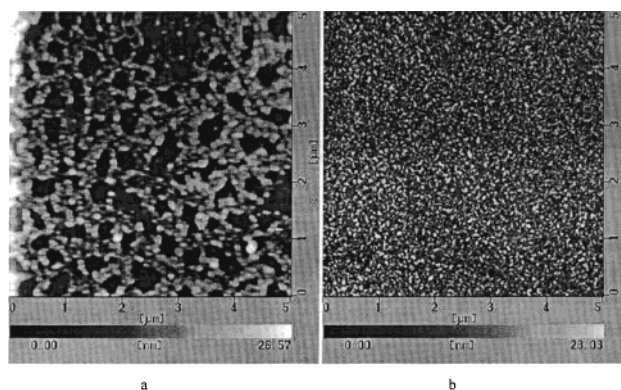


Figure 3. AFM image of the self-assembled films of SPPV. Surface morphology of the monolayer with light grainy structure, scan size $5 \mu\text{m}$. The concentration is 3.3×10^{-5} M SPPV chloroform solution. (a) The immersing time is 1 day. (b) The immersing time is 3 day.

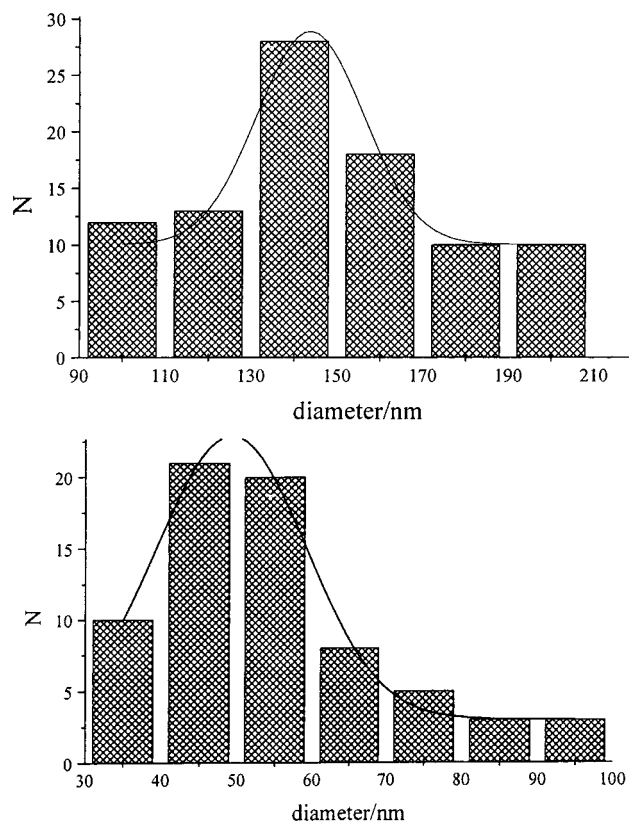


Figure 4. Statistic distribution of the grain sizes in film B1 (a) and film B3 (b). 100 points are collected in each graph.

concentrations of SPPV chloroform solution and that of SA films prepared at different immersing times are shown in Figure 5. As is seen in Figure 5a, the wavelength of emission peak is red-shifted with self-absorption when the concentration of SPPV increased, as the peak at 461 nm decreased while the peak at 492 nm increased under this experimental condition. There is no change in UV–vis spectra when the concentration of SPPV increases (not shown here), and its emission peak red-shifted with decreased fluorescence at the short wavelength. This phenomenon is typical of the emission of excimers.³⁸ According to the theory of self-quenching in concentrated solution, there may exist strong interaction between the ground state and the excited state, and excimers should be formed. We attribute the emission peak at 492 nm as the emission of an excimer. As to SPPV SA film, the two peaks in the emission spectrum are at 492 and 464 nm, respectively. One interesting phenomenon is

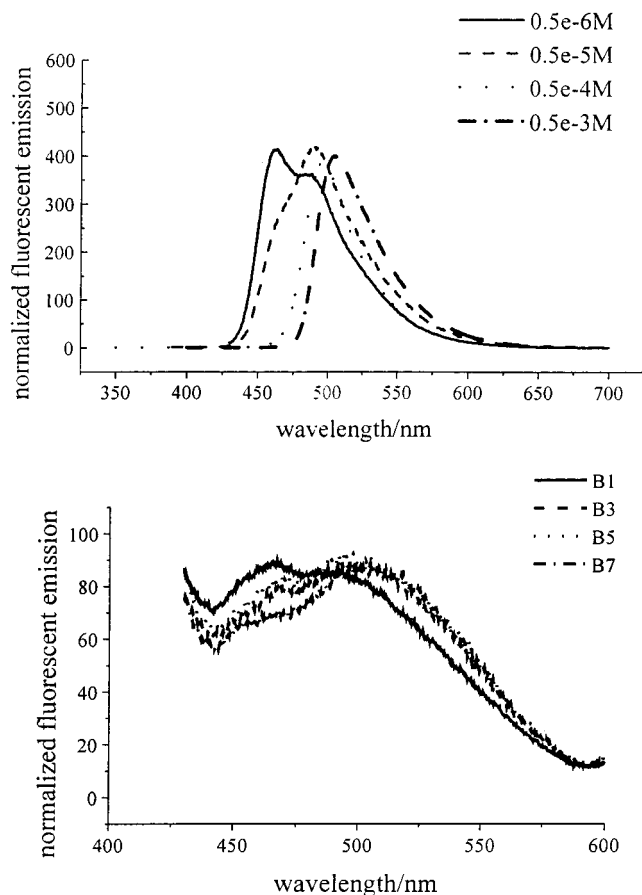


Figure 5. Fluorescence spectra of SPPV. (a) The concentrations of SPPV chloroform solution are 0.5×10^{-6} , 0.5×10^{-5} , 0.5×10^{-4} , and 0.5×10^{-3} M, respectively. (b) SPPV SA films prepared for 1, 3, 5, and 7 days, respectively.

that the main emission peak changes from 460 nm in film B1 to 492 nm in film B7 with the increase of the immersion time. Like other polymer films, optical excitation of the chromophore in chain may result in formation of an excimer³⁹ because of the fast energy transfer to the excimer site, which is the energy trap. On the other hand, the changes of the positions of the main emission peaks from 460 nm in film B1 to 492 nm in film B3 corresponds to an increase in the surface concentration (or surface coverage) of SPPV molecules as determined by the UV-vis spectra of SPPV SA films. The changes in the shapes of the main emission peaks of film B3 to film B7 correspond to the rearrangement of the SA film. At the same time, the density of excimer site should be changed with these processes mentioned above. So from the fluorescence properties of SPPV SA film, a two-step film formation process is detected.

To understand the molecular behavior in different physical state, we studied the fluorescence properties of SPPV SA film, a spin-coated film, and its chloroform solution. Figure 6 shows the fluorescence spectra of SPPV SA film, a spin-coated film, and SPPV solution. Because there is no change in their UV-vis spectra (not shown here), it means no significant intermolecular interactions at the ground state. The emission peaks of SPPV solution are at 461 and 485 nm, while those of SPPV SA film are at 464 and 492 nm. The fine structures of these two spectra can be seen clearly, but the emission band of SPPV SA film is broadened. The emission peak of the SPPV spin-coating film is at 506 nm, which is red-shifted compared with SA film and chloroform solution, and the peak shows no fine structure. In addition, the morphology of SPPV spin-coating

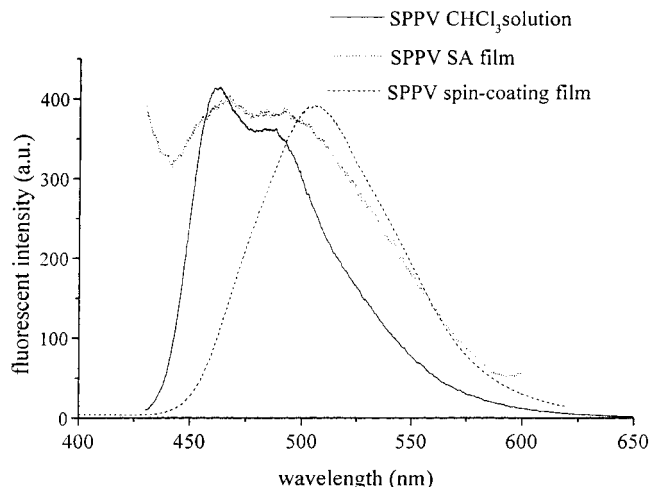


Figure 6. Fluorescence spectra of SPPV chloroform solution, SA film, and spin-coating film.

film is also observed by AFM technique. From the AFM image (not shown), the grain size is from 200 to 400 nm, and the thickness is nonuniform. So the molecules in spin-coated film are in an aggregated state, and this film is irregular compared with the self-assembly film. From these phenomena, it can be deduced that the state of SPPV molecules in SA film is different from the free state in solution and the irregular morphology found in the spin-coated film.

As the SPPV molecules are in an irregular state in the spin-coated film, their intermolecular interactions at the excited state are strong, and there may be more excimer-forming sites compared with the other two states. Because the energy level of excimer sites is lower than that of monomers, energy may transfer to the excimer-forming site easily in spin-coated film. This can be reflected by the red shift of the emission peak, and this emission peak can be attributed to the emission of the excimer. Although the emission peaks of molecules in SA film are almost the same as that of SPPV solution, the extension of the emission band indicates the existence of the molecular interaction at the excited state. We believe that the emission band at 464 nm comes from the monomer band and the emission at 492 nm belongs to the excimer band in the SPPV SA film. Because the molecules in SA film are covalently bonded on the substrate, it is difficult to meet the perfect excimer requirement geometry structure; e.g., the chromophore could not relax the face to face geometry structure. In addition, as the amount of molecules is less than that in spin-coated film, there are less excimer-forming sites in self-assembly films. So the fluorescence behavior of SPPV SA film is different from that of SPPV solution and spin-coated film. By comparison with the fluorescence spectra, it can be concluded that the molecular behavior of SPPV molecules in solution, in SA films, and in spin-coated film are different. The SPPV SA film is a stable and ordered solid one, and the molecular interaction at the excited state is strong enough to induce new physical property of films.

4. Photoinduced Electron-Transfer Property of the SPPV SA Film. The surface photovoltage effect, which consists of a change at the surface potential barrier caused by illumination, has been applied successfully to the investigation of electronic processes in semiconductors.⁴⁰ As a luminescent dye, SPPV is linked on the hydrophilic ITO substrate through covalent bonding, and the surface photovoltage spectra (SPS) can be obtained. Figure 7 is the SPS spectra of SPPV SA film. The maximum photovoltage peak is at 400 nm, which corresponds

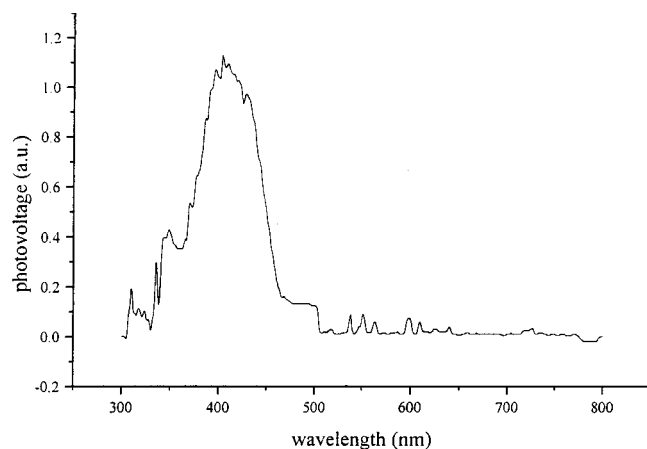


Figure 7. SPS spectra of SPPV SA film.

to the band-band transition. (This coincides with the absorption spectra of SPPV SA film.) The threshold is at 500 nm, corresponding to a band gap of 2.48 eV. This photovoltaic response indicates that the SPPV molecule is acting like an organic semiconductor. When the SA film is irradiated, charge separation takes place, and an electron-hole pair can be formed. As the lifetime of this exciton is long and the photoinduced electron transfer is vectorize, an electric field is formed between two ITO electrodes.

Conclusion

In summary, a new self-assembled method using covalent bonds as the linkage between the hydrophilic substrate and a functional hyperbranched molecule (SPPV) is used to form ordered homogeneous films. This film formation is very easy and controllable. Comparing the morphologies and fluorescence properties of self-assembly film and spin-coating film, it is found out that SPPV SA film linked through covalent bond is more homogeneous and stable. The film formation process of self-assembly is studied in detail by AFM and spectroscopy techniques. The excimers of SPPV in both the solution and SA films can be observed, indicating the strong interactions between the excited state of SPPV molecules in solution and in the solid state. Furthermore, the SPPV SA film modified electrode demonstrates a photovoltage. Related research work is progressing in our lab.

Acknowledgment. This work was supported by National Nature Science Foundation of China (29992530, 29873060), CAS, China Postdoctoral Science Foundation, and State Key Project for Fundamental Research (G 1999064504). The authors thank Miss J. Jin and Mr. T. F. Xie for their kind help in AFM scanning and the SPS experiment.

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