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Novel Covalently Linked Self-Assembled Films from a Functional Hyperbranched Conjugated Poly (Phenylene Vinylene)

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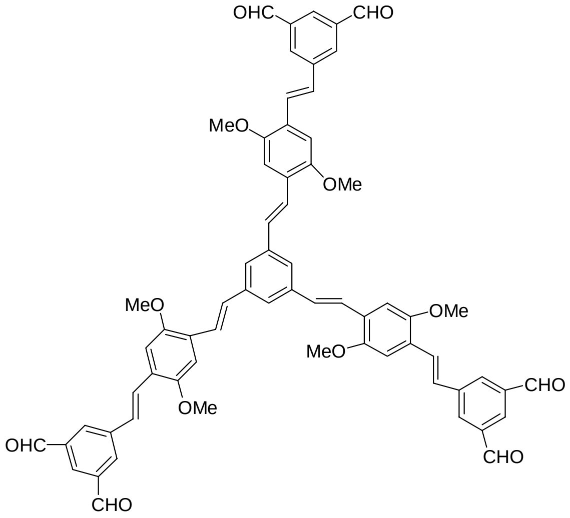
Abstract: A new self-assembled films of a functional dendritic molecule, hyperbranched conjugated poly (phenylene vinylene), is obtained through covalent bond linkage. The highly ordered and homogenous molecular films are obtained and characterized by UV-vis spectra, fluorescent spectra and atomic force microscopy.

Keywords: Self-assembly film, hyperbranched conjugated PPV.

The hotspot in the fields of molecular films focuses on highly ordered, ultrathin films with molecularly controllable surface properties. It is attractive to study supramolecular functional polymeric materials with suitable physical properties and abilities to form organized superstructures at the interfaces[1,2,3,4]. Dendritic macromolecules are a kind of materials which is capable of self-organizing into superstructures[5]. So a new dendrimer-like poly(phenylene vinylene)---hyperbranched conjugated poly(phenylene vinylene) (SPPV) has been studied as an optical functional molecule to form self-assembled (SA) films. The covalent linkage between the molecules in the films and the substrates is used to form SA films in this work instead of the widely used method that is based on the electrostatic attraction between opposite charges to create ultrathin films[6].

This hyperbranched conjugated PPV can be obtained through Wittig reaction between 1,3,5-benzene trimethanal and paramethyoxide benzene Ylide. Its molecular weight is *ca.* 2954. The details of the compound synthesis will be published elsewhere[7]. The structure of our target molecule (repeat units and one full branch for generation G1) is shown in **scheme 1**. As there are aldehyde groups around the out sphere of the molecule, it is suitable to form SA films by covalent bond through dehydration reaction between hydroxy groups on the substrates and SPPV molecules. The hydrophilic quartz is immersed in 0.16 mg/mL SPPV chloroform solution containing 0.2 mg/ml dicyclohexylcarbodiimide (DCC). Acetal formation can take place between the aldehyde groups of SPPV and the hydroxy groups on the surface of the substrates, so that SPPV is linked on the substrate through covalent bond. The films are then rinsed ultrasonicly 1 minute each time in chloroform for 2 times.

Scheme 1. The structure of hyperbranched conjugated poly(phenylene vinylene) (SPPV); repeat unit and one full branch for generation G1



The UV-vis spectra of SPPV in both the solution and the SA films on quartz are studied (as shown in **Figure 1**). The maximum absorption peaks of its chloroform solution are at 238 nm, 327 nm and 393 nm, while those of SA films are at 237 nm, 322 nm and 380 nm. This result indicates that the formation of the self-assembled films is succeeded. As SPPV, an analog of poly(4-phenylene vinylene), is a good light emission material, the fluorescent spectra are also studied (as shown in **Figure 2**). The maximum emission peak of SA films is at 439 nm while that of chloroform solution is at 490 nm. It is said that high quality films prepared on ultra smooth substrate are essential to observe the photo luminescence (PL) blue shift[8]. In our experiment, the maximum emission peak blue shifts about 50 nm after the formation of SA film, indicating that the self-assembled film is in good order compared to spin-coating films that exhibit normally red shifted peaks. From the phenomenon of the peak blue shifts in both the emission and absorption spectra, it is proposed that H-aggregate may be formed in the SA films. In order to understand the structure of dendritic molecules within films, mica substrates are used in atomic force microscopy (AFM) detection for investigating the morphology of SPPV SA films.

Figure 3 shows the topographic images of SPPV SA films prepared from 0.1mg/mL SPPV chloroform solution and 0.05 mg/mL that solution respectively. Thickness of SPPV films is measured by the SPM technique. The thickness of the film shown in **Figure 3a** is 12.7 nm, its microroughness is 5.1 nm, and the thickness of the film shown in **Figure 3b** is 3.7 nm, its microroughness is 2.1 nm. Although these films are prepared at different condition, they all form homogenous films on the substrate. The diameter of SPPV (generation 2) molecules is 3.6 nm, which is calculated by using MM2 method theoretically. It is concluded that when the concentration of SPPV solution is high, the G2 SPPV may form aggregates on the SA films. This may lead to the increasing of both the thickness and the microroughness of SA films.

Figure 1. UV-vis spectra of SPPV. — in self-assembled films on quartz, Λ in 0.16 mg/mL chloroform solution

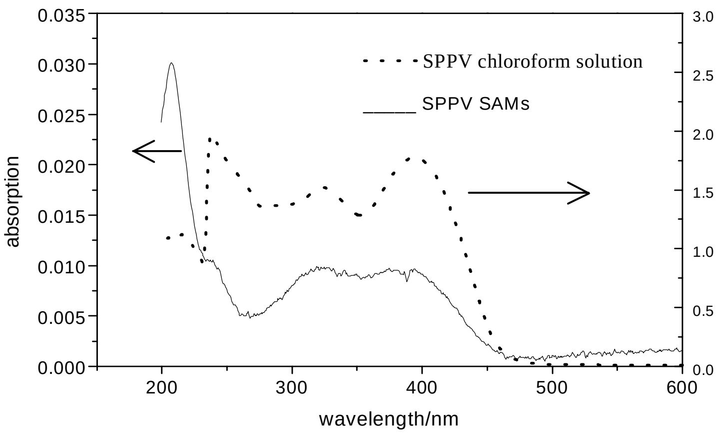
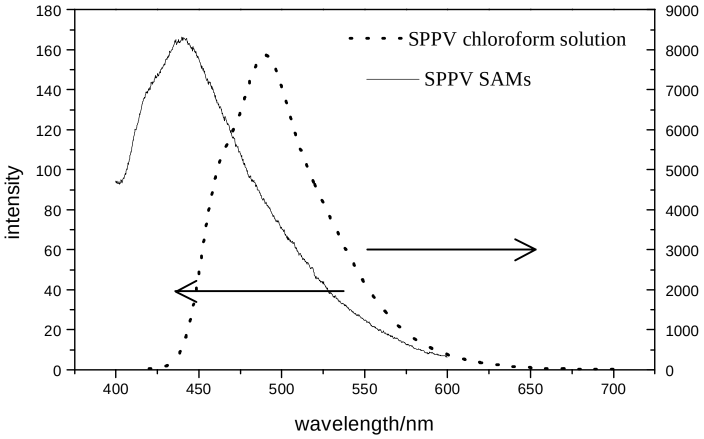
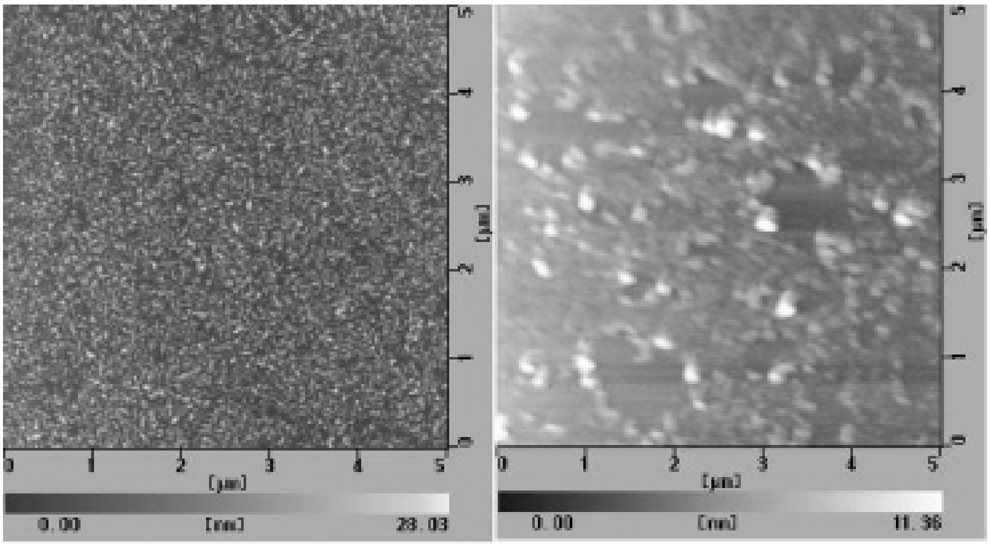


Figure 2 Fluorescent spectra of SPPV. — in self-assembled films on quartz, Λ in 0.16 mg/mL chloroform solution



In conclusion, a new self-assembled method using covalent bond as the linkage between the substrate and the functional hyperbranched molecule is proposed and a dendritic molecule SPPV with the good light emission property is used to form ordered homogenous films successfully. This method may have potential application in improving the charge injection at the interface between the electrode and organic thin films of OLED. Relating work is in progress in our laboratory.

Figure 3. AFM images of the self-assembled films of SPPV



a b

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References

1. A.Ulman, *Introduction to Ultrathin Organic Films*, Academic Press: San Diego, CA, **1991**.
2. V.V.Tsukruk, *Prog. Polym. Sci.*, **1997**, *22*, 247.
3. J.H.Fendler, F.C.Meldrum, *Adv. Mater.*, **1995**, *7*, 607.
4. V.V.Tsukruk, J.H.Wendorff, *Trends Polym. Sci.*, **1995**, *3*, 82.
5. V. V. Tsukruk, F. Rinderspacher, V.n. Bliznyuk, *Langmuir*, **1997**,*13*(8), 2171.
6. G.Decher, Y. Lvov, J. Schmitt, *Thin Solid Films*, **1994**, *244*, 772.
7. T. Lin, Q.He, F.Bai, L.Dai, *Thin Solid Films*, **2000**, *363*, 122.
8. H. Hong, D. Davidov, Y. Avny, H. Chayet, E.Z. Faraggi, R. Neumann, *Adv. Mater.*, **1995**, *7*(10), 846.

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