

Monolayer Formation and In-Plane Anisotropy of an Amphiphilic Block Molecule

Lidong Qin, Lixin Wu,* Hongbo Li, Xueliang Hou, Dengli Qiu, and Jiacong Shen

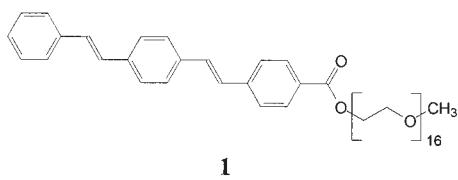
Key Laboratory for Supramolecular Structure and Materials of Ministry of Education, Jilin University, Changchun 130023, P. R. China

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Coverage controlled monolayer nano-sheets with homogeneous height were fabricated by casting aqueous solution of amphiphilic rod-coil diblock molecule **1** on mica surface. The monolayer sheet was anisotropic, due to the asymmetric arrangement of the diblock molecule on surface, confirmed by polarization-dependent fluorescence spectra.

Supramolecular structures formed by the self-assembly of functional molecular building blocks are very important for material science and nano technology.¹ A typical example is provided by rod-coil diblock oligomers, where the phase-separation between the covalently connected segments leads to self-assembly into lamellar, cylindrical, spherical, and other structures, due to the incompatibility and volume fraction of the both blocks.^{2,3} One more interesting case is the self-assembly of the amphiphilic rod-coil oligomers on surfaces, which is additionally related with the substrate and the process of film casting and solvent evaporation.^{4,5} If photo-electronic segments are employed, the morphology, molecular packing, and the structural properties of these thin films will be also essential for optical properties and charge transportation.

The present work focuses on casting aqueous solution of amphiphilic diblock molecule **1** onto mica substrate and drying the film. **1** contains oligo (phenylene vinylene) (OPV) dimer as rod segment and poly (ethylene oxide) (PEO with average $M_w = 750$) as coil segment. Since PEO could be complexed with metal ions and shows conductive properties and OPV could be applied to electro-luminescent devices,^{6,7} the study of **1** on surface will be valuable for exploring the behavior of this kind of organic semi-conductors. Monolayer nano-sheets were observed by Tapping Mode Atomic Force Microscopy (AFM). The coverage of the sheets could be controlled by changing the quantity of the added sample. The monolayer sheets with the aligned OPV segments, which emit polarized light, will be particularly useful as electronic light-emitting devices.



Synthesis of **1** is similar to our previous work⁸ and the target molecule was characterized by NMR, IR, GPC and MALDI-TOF mass spectroscopy.⁹ The films were prepared by casting aqueous solution of **1** onto freshly cleaved mica wafer. AFM observation of the cast film was carried with commercial instruments (Digital Instrument, Nanoscope III, Dimension 3000TM and Multi-modeTM), operating in tapping mode in air. The error of the measured height in our experiment is in the range of $0.2 \sim 0.5$ nm.

When we cast $10 \mu\text{l}$ of 1.04×10^{-5} mol/l aqueous solution of **1** onto 1 cm^2 sized mica wafer and dried the film, we could obtain nano-sheet structure with the coverage about 16% as shown in Figure 1a. The average height of the sheet is 5.8 nm and the diameter is about 330 nm, which were measured over 50 different sheets. Interestingly, the height of the sheet structure is very homogeneous as the section analysis shown in Figure 1b. Because the fully extended molecular length is 7.6 nm,¹⁰ while the measured height here is 5.8 nm, the sheet should be composed of monolayer of **1** with OPV outside, due to the hydrophilic interaction between PEO and mica substrate.

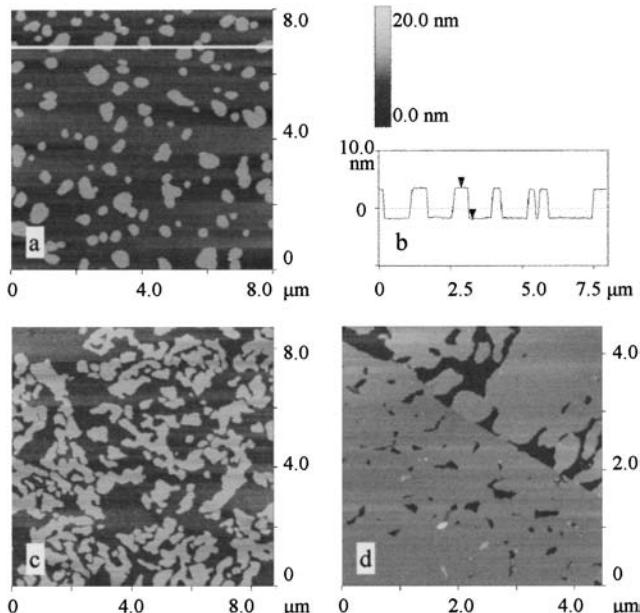


Figure 1. Tapping mode AFM height images of cast films of **1**, coverage versus sample volume. (a) The coverage of the sheet morphology is 16% and the average height 5.8 nm; (b) Section analysis of a; (c) The coverage is 48% and the average height 5.7 nm; (d) The coverage is 94% and the height 5.4 nm. The volumes of the sample added are $10 \mu\text{l}$ of 1.04×10^{-5} mol/l aqueous solution for (a), $30 \mu\text{l}$ of 1.04×10^{-5} mol/l for (c) and $30 \mu\text{l}$ of 2.08×10^{-5} mol/l for (d).

In fact, the homogeneous height of the nano-sized sheet is extraordinary for cast films. We suggest that there are at least three original impetuses. The first is the phase separation of the both blocks, which is just advantageous for lamellar structure¹¹ and makes the formation of a sheet-like structure possible; the second is the high tendency of the OPV segment to aggregate and order through $\pi-\pi$ overlaps, which makes the top of the monolayer flat; The third is the flexible and hydrophilic PEO segment, which firmly adsorbs onto mica substrate and acts as a cushion-like amorphous layer for the crystallized OPV layer.¹²

Thus the monolayer sheets are the most possible result for the asymmetric diblock molecule **1** on mica surface.

Interestingly, when we cast more solution onto mica surface, for example, 30 μ l of 1.04×10^{-5} mol/l aqueous solution onto the 1 cm^2 sized mica substrate, the nano-sheets structure could also be observed with a larger coverage of 48%, as shown in Figure 1c. The average size of the sheets is also enlarged and lengthened. But the height is still homogeneous with the average value equal to 5.7 nm. We can calculate the molecular area on the cast film from the amount of added sample and the coverage of the monolayer. The value was 0.25 nm^2 , which was close to that of OPV dimer in a herringbone mode (0.20 nm^2)¹³ and in a Langmuir monolayer (0.24 nm^2).¹⁴ The results above offered an attempt to obtain full-covered monolayer sheet if we add more sample on mica surface. Figure 1d showed an image with coverage of 94%. The film was obtained by casting 30 μ l of 2.08×10^{-5} mol/l aqueous solution. It also had a homogeneous height of 5.4 nm.

The above-mentioned films are very useful. The surface structure is simple and easy to be measured by AFM, which would be significant for model system of luminescent materials. And, because OPV segment are ordered and orientated on the surface, the films offered an opportunity to obtain polarized emission of the luminescent group.

Photoemission of the cast film with the morphology shown in Figure 1d, excited at 300 nm, produced a typical spectrum for poly(phenylene vinylene): a fluorescent band at 462 nm with two small shoulders at about 433 and 492 nm derived from low-energy vibronic sidebands.^{13,15-17} To certificate the anisotropic property of the cast film, linear dichroism experiments were performed. The measurements were done under parallel and perpendicular of the angle between the pump polarization and probe polarization.^{18,19} Figure 2 shows the polarization dependent photoemission of the cast film. The dichroitic ratio at 462 nm between the parallel and perpendicular directions is 2.3 : 1. Thus we can conclude that the molecule dipole is oriented in the cast film. However, from our experiments it is difficult to derive an exact value for the inclination angle between OPV axis and the mica surface.

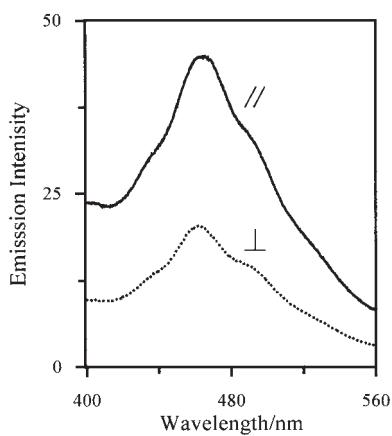


Figure 2. Polarized Photoemission spectra of the cast film with the morphology shown in Figure 1d excited at 300 nm.

In conclusion, we therefore present that coverage controlled

nano sheets could be fabricated by controlling the volume of the aqueous solution casting onto the mica substrate. These nano structures were highly anisotropic and had a potential application in polarized light-emitting devices. This work offered an accessible approach to fabricate oriented nano structures on surface.

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- 9 The characterization data for EO16OPV: $^1\text{H-NMR}$ (400 MHz, CDCl_3): 8.048 (d, 2H, $J = 8$ Hz), 7.577 (d, 2H, $J = 8$ Hz), 7.540 (s, 4H), 7.536 (d, 2H, $J = 8$ Hz), 7.375 (t, 2H, $J = 8$ Hz), 7.275 (t, 1H, $J = 8$ Hz), 7.251–7.132 (q, 2H, $J = 15.6$ Hz), 7.184–7.092 (q, 2H, $J = 16$ Hz), 4.486 (t, 2H, $J = 4.8$ Hz), 3.838 (t, 2H, $J = 4.8$ Hz), 3.8–3.5 (m, 60H), 3.379 (s, 3H). IR (KBr, cm^{-1}): 3052, 3080 cm^{-1} , aromatic CH stretching; 3024 cm^{-1} , trans C=C double bond CH stretching; 962 cm^{-1} , trans C=C double bond CH wagging; 2870, 2917 cm^{-1} , CH_2 symmetric and anti-symmetric stretching mode; 1716 cm^{-1} , C=O stretching mode of aryl ester; 1603 cm^{-1} , symmetric benzyl ring stretching; 1109 cm^{-1} , C–O–C out-of-plane bending. $^1\text{H-NMR}$ and IR also testified that the two double bonds in OPV block are both trans configuration. The rod-coil molecule shows a narrow molecular weight distribution with polydispersity index of 1.06 from GPC result. Mass spectrum indicated a close match between calculated and experiment molecular weights. Fine peaks in the mass spectrum varied by the mass of one ethylene oxide unit ($M_w = 44.05$), indicating that the polydispersity of the copolymer mirrors that of the PEO used in the synthesis.
- 10 The length of the rod is 1.9 nm obtained from Cerius² molecule dynamic mimic and the fully extended length of the coil is 5.7 nm calculated by imaging the molecules taking a planar zigzag conformation as reference: Y. Takahashi, I. Sumita, and H. Todokord, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 2113 (1973).
- 11 The inference is based on an X-ray Diffraction of a thick cast film, which gives a lamellar structure with a d-spacing equal to 6.2 nm.
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