

一种含苯并菲侧基的“毛-棒”状梯形聚倍半硅氧烷 LB 膜研究*

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摘 要 一种新的含烷基取代的苯并菲侧基的“毛-棒”状(hairy-rod)梯形聚倍半硅氧烷(LPSQ)可以在空气-水界面形成稳定的单分子层,研究了温度、铺展溶剂和浓度对 π -A 等温曲线的影响.在适当的表面压下,以甲苯为铺展溶剂该单分子层可以被成功地转移至疏水的硅片或石英片上形成均一稳定的 Y-型 LB 膜,其紫外吸收强度在几个月内均保持不变,说明该 LB 膜具有良好的稳定性,AFM 图像表明其形成了均一致密的膜.通过偏振紫外光谱和荧光光谱研究了其面内各向异性,发现 LPSQ 的分子链采取了平行于拉膜方向的优先取向,最优取向因子 S 为 0.42.

关键词 梯形高分子, 聚硅氧烷, 苯并菲, LB 膜

STUDY ON THE LB FILMS OF A HAIRY-ROD LADDER POLYSILSESQUOXANE WITH TRIPHENYLENE SIDE GROUPS*

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Abstract A novel kind of “hairy-rod” ladder polysilsesquioxane (LPSQ) with alkyl substituted triphenylene side groups formed a stable monolayer on the air-water interface, and the effects of temperature, solvents and concentration of LPSQ solution on π -A isotherm curves were investigated. The monolayers of LPSQ can be successfully transferred onto hydrophobic surface of silicon wafer or quartz plate to develop a very stable and uniform Y-type Langmuir-Blodgett (LB) film when using toluene as the spreading solvent at proper surface pressure. High stability of LPSQ LB films is confirmed by the fact that the intensity of UV absorption does not decay within several months and AFM image shows uniform and compact films without noticeable defects. The in-plane anisotropy was monitored by the combination of polarized UV and fluorescence spectroscopy, revealing that the backbones of LPSQ adopted a preferential orientation parallel to the dipping direction with an optimum orientation parameter S of 0.42. Furthermore, the stable and uniform LB films of LPSQ with the triphenylene side groups promise to be a fine one-dimensional molecular/nano-wire material.

Keywords Ladder polymers, Polysiloxanes, Triphenylene, LB films

1 INTRODUCTION

Langmuir-Blodgett (LB) technique has been utilized as

an excellent fabrication method of ultrathin films well-defined at the molecular level by transferring Langmuir (L) monolayers onto different substrates. In the past

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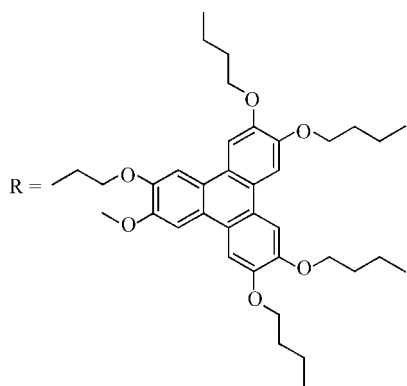
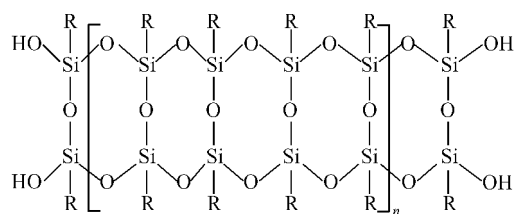
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few decades there have been intensive studies on the fabrication, structural characterization and functions of the LB films^[1~4].

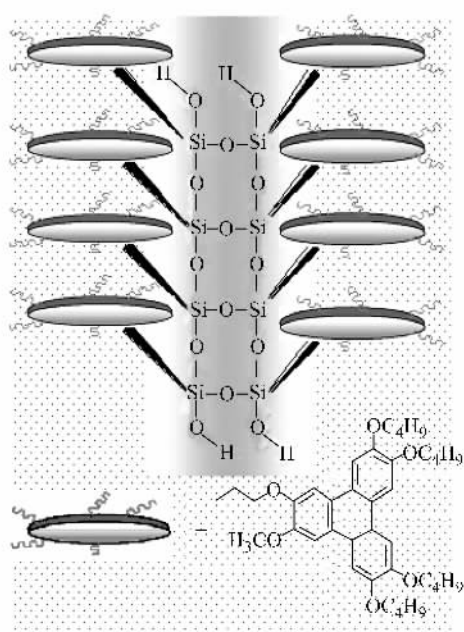
Generally, there are two approaches to the ultrathin films. The first one is to use amphiphilic polymers bearing both hydrophilic and hydrophobic substituents^[5]. However, the polymers which can provide stable LB films on a water surface can't inevitably yield oriented polymer films when the monolayers are transferred onto solid substrates. It is known that the great rigidity of polymer main chains is beneficial to assist in the orientation of the main chains in the film^[6]. Hence, the second one emerged to use a new class of “hairy-rod” polymers where the rigid main chain is decorated by side groups with conformational flexibility and minimal polarity^[7]. Typical examples of such LB film-forming polymers are certain substituted poly(glutamate)s in their helical conformation^[8,9] and poly(phthalocyanato-siloxane)s^[10~18]. Obviously, the ordered structure in LB films based-on the “hairy-rod” polymers mainly results from the combination of the rigid main chain as a backbone of material and the

flexible side chain as a soft component giving a liquid-like character to the monolayer at the air-water interface.

We reported a new approach to the first soluble, high molecular weight (M_w) and perfect *cis*-isotactic ladder polysilsesquioxane (LPSQ) (Fig. 1a), which was based on the self-organizing of α, ω -ditriphenylene tetrahydroxy-disiloxane (monomer M) by concerted π - π stacking and H-bonding to yield a perfect ladder polysilsesquioxane superstructure (LS)^[19]. In this case, the introduction of electro-rich triphenylene groups intensified the template role, resulting in formation of a supramolecular channel for confined covalent polycondensation of Ms. On the other hand, control over stereo-configuration of the LPSQ was well realized utilizing the interactions between π -conjugated discotic side groups. This new kind of LPSQ has extremely stiff double siloxane main chain (T_g ca. 258°C) bearing closely stacked triphenylene groups with flexible alkyl side chains, which is characteristic of “hairy-rod” polymers (schemed in Fig. 1b).



(a)



(b)

Fig. 1 Structure of LPSQ (a) and sketch map of hairy-rodlike LPSQ (b)

This paper aims to present the interesting thin film-forming ability of “hairy-rod” LPSQ with bulky electron-rich triphenylene side groups, which has promising applications as one-dimensional molecular/

nano-wire materials because of the expected high conductivity resulting from the compact π - π stacking between triphenylene side groups^[20~25]. It is well known that the LB film has not been commercially

utilized so far because of its low stability and defects. Here, we combined the self-assembly and LB techniques to fabricate stable and uniform film of LPSQ, in which all the electron-rich triphenylene groups are most closely stacked face to face with “edge-on” mode. For that, we examined the effects of temperature, solvents and concentration of LPSQ solution on fabrication of LB films, and investigated the orientation and morphological characteristics of deposited LB films by UV and fluorescence spectroscopic measurements and atom force microscopy (AFM) measurements.

2 EXPERIMENTAL

2.1 Materials and Measurements

LPSQ with alkyl substituted triphenylene side groups shown in Fig. 1(a) was synthesized as described previously^[19]. The weight-average molecular weight (M_w) was determined to be 8.2×10^5 by static light scattering method. Toluene, chloroform and *n*-hexane used were distilled three times before use to prepare spreading solutions with concentrations of approximately 0.2 mg/mL and 0.6 mg/mL. All of the samples were allowed to be placed for at least 24 h before use. UV spectra were recorded with a Perkin-Elmer Lambda-18 spectrometer. Fluorescence spectra were given with a Hitachi F-4500 fluorescence spectrometer at room temperature. All spectroscopic measurements were made in transmission geometry using nonfluorescent quartz slides (10 mm × 40 mm) as the substrate. The incident beam was polarizer with a Glan-Thompson polarizer to measure the anisotropy of UV and fluorescence spectra. The atomic force microscopy (AFM) was performed with a Nano Scope III a microscope (Digital Instruments), operating in tapping mode with silicon wafer as the substrate.

2.2 Langmuir and LB Films Formation

The surface pressure-area (π - A) isotherms were recorded on a KSV minitrough model 2000 (KSV Instrument Ltd., Helsinki, Finland). The trough was supplied with an electronic balance that used a Wilhelmy plate as the surface pressure sensor and has a sensitivity of 0.02 mN/m. π was measured by Wilhelmy plate and A was calculated by the equation:

$A = WRT/\pi M$ (W , mass of polymer; T , temperature; M , molecular weight of polymer). For monolayer compression, two symmetrically movable computer controlled barriers were used. The surface of the water which was purified by distilling deionized water was further cleaned by suctioning off potential impurities from the interface. LPSQ solutions were spread onto the water using a syringe of a 160 μ L volume, and the spreading solvents were allowed to evaporate by waiting about 10 min. The monomolecular layer was compressed by Teflon barrier at a rate of 8 mm/min to the desired surface pressure.

Quartz slides and silicon wafers were cleaned in piranha solution (7 : 3 V/V concentrated H_2SO_4 /30 wt% H_2O_2) for 2 h at 80 ~ 90°C, and washed thoroughly with boiling water for 1 h, and dried under a stream of nitrogen. Hydrophobic surfaces were obtained by treating the clean and dry substrates with a hot solution of dichlorodimethylsilane in CCl_4 (5%) for 10 min followed by washed with chloroform and drying under a stream of nitrogen. Monolayers were transferred onto the hydrophobic substrates by vertical dipping method with an optimum transfer ratio of a drawing speed of 5 mm/min at different surface pressure. During all the processes, the temperature of the subphase was kept at $(23 \pm 0.5)^\circ C$.

3 RESULTS AND DISCUSSION

3.1 Behaviors at the Air-Water Interface

The π - A isotherm of LPSQ with 0.2 mg/mL chloroform solution as the spreading solution at room temperature is shown in Fig. 2(a). A nil surface pressure followed by a slow lift from 1.55 ~ 1.00 nm² per repeat unit and a steep rise of surface pressure is observed in the region of 1.00 ~ 0.42 nm² per repeat unit. Although the isotherm of LPSQ does not show second transition, its linear region that corresponds to the solid-state film is relatively long. The limiting area per repeat unit is about 1.00 nm² obtained by the exploration of the solid phase to surface pressure zero, and the collapse pressure of the monolayer is 53 mN/m. It has been known that triphenylene groups can adopt two possible orientations at the air-water interface: “face-on” mode and “edge-on” mode. On the face-on mode, the

triphenylene groups lie flat on the subphase surface, while on the edge-on mode they are stacked together and the triphenylene disks are oriented perpendicular to the subphase surface. The size of LPSQ as determined by X-ray diffraction has a polymer width of 3.23 nm and a disk spacing of 0.36 nm^[19]. The limiting area per repeat unit of 1.00 nm² indicates that the triphenylene side groups of LPSQ adopt an edge-on mode on the water surface.

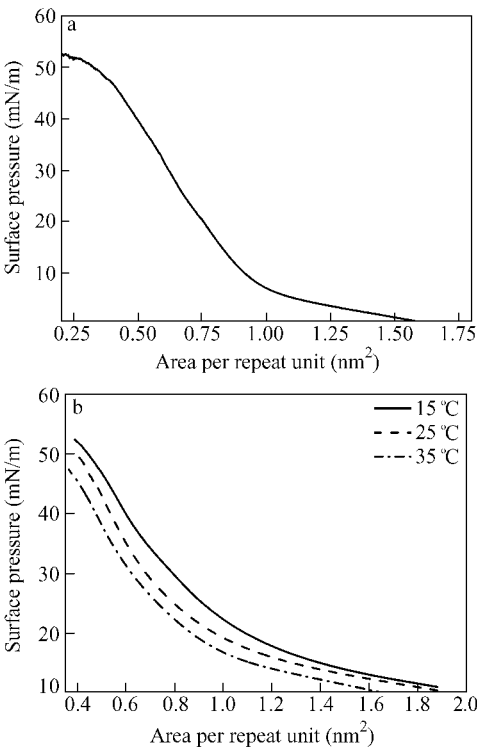


图 2 LPSQ 以 0.2 mg/mL 氯仿溶液为铺展溶液在不同温度下的表面压力-面积 (π -A) 等温线
a) 室温 (23°C); b) 15°C, 25°C, 35°C

Surface pressure-area isotherms recorded for LPSQ with subphase temperatures at 15°C, 25°C and 35°C, respectively, are shown in Fig. 2(b). It can be seen that the shape of π -A isotherms of LPSQ at different subphase temperatures remains the same, while the limiting area per repeat unit and the collapse pressure are both changed obviously. The limiting area per repeat unit becomes smaller with the increase in temperature, which can be attributed to better molecular packing as the mobility of LPSQ's rigid main chain tends to increase at higher temperatures. On the other hand, the collapse pressure decreases from 52

mN/m to 47 mN/m with the temperature increase from 15°C to 35°C in temperature, which coincides with the general pattern of the collapse pressure changes of most amphiphilic molecules.

The effects of solvents and concentrations of spreading solutions on π -A isotherms of LPSQ are also investigated. The isotherms of spreading solutions of three kinds of solvents: *n*-hexane, chloroform and toluene in two different concentrations (0.2 mg/mL and 0.6 mg/mL) are shown in Fig. 3. It can be seen that the π -A isotherms have distinct changes with the concentrations of LPSQ in each kind of solvents. The

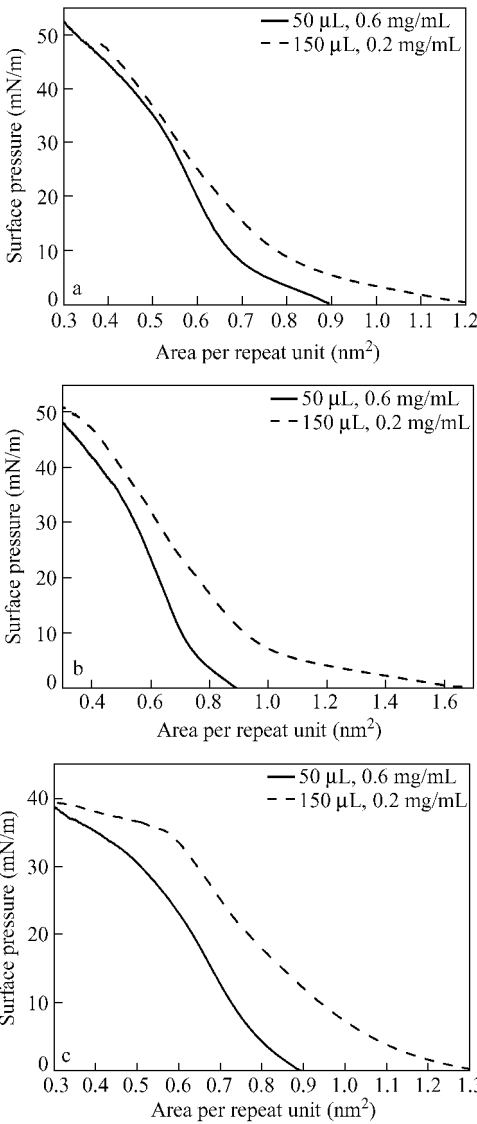


图 3 LPSQ 从不同浓度溶液铺展的表面压力-面积 (π -A) 等温线
a) *n*-Hexane 溶液; b) Chloroform 溶液; c) Toluene 溶液

limiting areas and collapse pressures data are listed in Table 1. The limiting area per repeat unit becomes smaller when the concentration increases from 0.2 mg/mL to 0.6 mg/mL, indicating a more close packing of molecules in the monolayer spread from solutions of higher concentrations. The change of limiting area per repeat unit is the biggest for toluene solutions. Moreover, the limiting areas per repeat unit of monolayers spread from three solutions are obviously different even if at the same concentration. The limiting area per repeat unit of monolayer spread from *n*-hexane solution is the smallest compared with those from chloroform and toluene solutions. This difference becomes larger when the concentration of spreading solution changes from 0.2 mg/mL to 0.6 mg/mL. The results indicate that the solvent of the spread solutions can affect the limiting areas per repeat unit of LPSQ monolayers, and this influence is more obvious when the concentration of the spread solution is high, which can be explained by the fact that LPSQ polymer has different chain conformation and aggregation state in different solvents and it adopted the most compact aggregation way in *n*-hexane than in chloroform and toluene.

Table 1 The limiting area per repeat unit and collapse pressures of monolayers spread from different solutions

Concentrations (mg/mL)	<i>n</i> -Hexane solutions		Chloroform solutions		Toluene solutions	
	<i>A</i> ₁ ^a	<i>π</i> _c ^b	<i>A</i> ₁	<i>π</i> _c	<i>A</i> ₁	<i>π</i> _c
0.2	0.85	49	1.00	51	1.12	39
0.6	0.72	52	0.78	48	0.82	38

^a *A*₁ represents the limiting area per repeat unit; ^b *π*_c represents collapse pressure

3.2 Deposition of LB Films

Monolayers of LPSQ at 20°C were successfully transferred onto the solid substrates at proper surface pressures with the transfer ratio between 1.0 ~ 1.2. Y-type LB films can be obtained by transferring the monolayers onto hydrophobic quartz slides or silicon wafers, while Z-type LB films are formed on hydrophilic substrates. Moreover, LB films on hydrophobic substrates are very stable, confirmed by the fact that the intensity of UV absorption does not decay within several months. While LB films on hydrophilic substrates are not very stable, confirmed by

the gradual decrease the intensity of UV absorption after a few days. Figure 4(a) shows the UV spectra of different layers of LB films on hydrophobic quartz slides. It can also be found that the UV absorbance of the triphenylene moiety in the built-up film increases linearly with the number of layers, indicating successfully layer-by-layer deposition. Furthermore, the maximum absorbance wavelength of LB films is 271 nm with a red shift compared to that of LPSQ solution alone (268 nm) due to a greater π -electronic delocalization in the solid film than in solution.

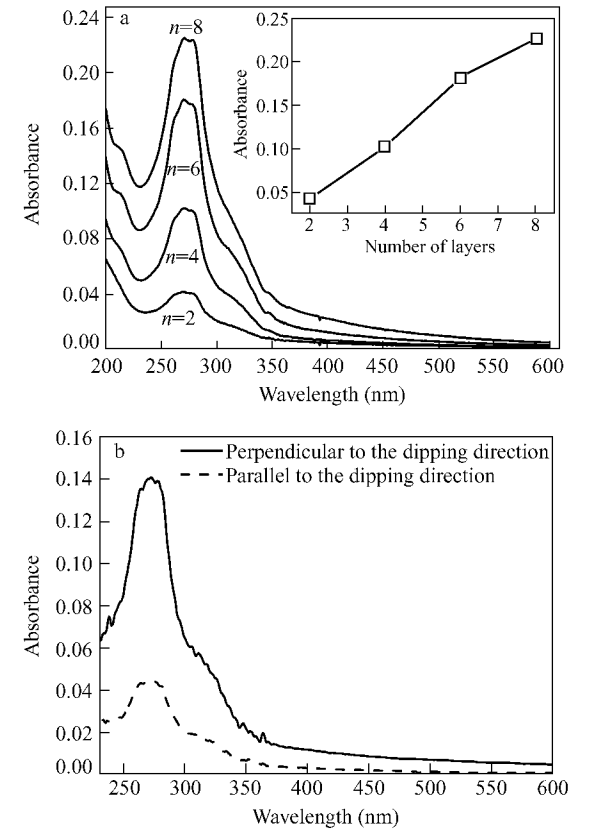


Fig. 4 UV spectra of multilayer-deposited (a) and polarized transmission UV spectra of LB films (b)
a) *n* represents numbers of layers; The inset displays the plot of absorbance at 271 nm against the number of layers

3.3 Polarized UV and Fluorescence Spectra

In-plane anisotropy was investigated by polarized transmission UV absorbance and fluorescence spectra. A large dichroism was observed in UV absorbance of LPSQ films, as shown in Fig. 4(b). The UV absorbance perpendicular to the dipping direction of the quartz slide is much larger than that parallel to the dipping direction, clearly indicating that the

triphenylene groups arranged in the edge-on mode on the solid substrate are preferentially perpendicular to the dipping direction as shown in Fig.5(a). According to our previous report^[19], the triphenylene disks are almost perpendicular to the plane of Si—O—Si double chains, in fact, so the backbones of LPSQ have been arranged prior to the dipping direction. The order parameter is expressed by the equation $S = (R - 1) / (R + 2)$, where R is the dichroic ratio defined by $R = A_{\perp} / A_{\parallel}$, and $A_{\perp} / A_{\parallel}$ are the absorbances at 268 nm measured with light polarized perpendicular and parallel to the dipping direction, respectively. In this case, the orientation parameter S is determined as 0.42, which is almost the same as that of the liquid crystals^[26].

This anisotropy also can be observed by polarized fluorescence spectra, which show the greater fluorescence intensity at the direction of perpendicular to the dipping direction. The order parameter S is

determined as 0.38 by the same equation, in which the dichroic ratio defined by the ratio between fluorescence intensities excited at 268 nm perpendicular and parallel to the dipping direction.

3.4 AFM Observations

AFM measurements were performed to investigate the morphology of the LB films of LPSQ. The AFM images of single-bilayer LB films of LPSQ on hydrophobic silicon wafers transferred from monolayer spread from different solvents at 25 mN/m are shown in Figs. 5(b) ~ (d). It can be seen that the uniform and compact LB film with the least defects is formed with toluene as the spreading solvent, while there are less uniformity in the LB films formed with chloroform and *n*-hexane as the spreading solvents at the same transferring surface pressure. Perfect LB films would be obtained at higher surface pressures for chloroform and *n*-hexane as spreading solvents.

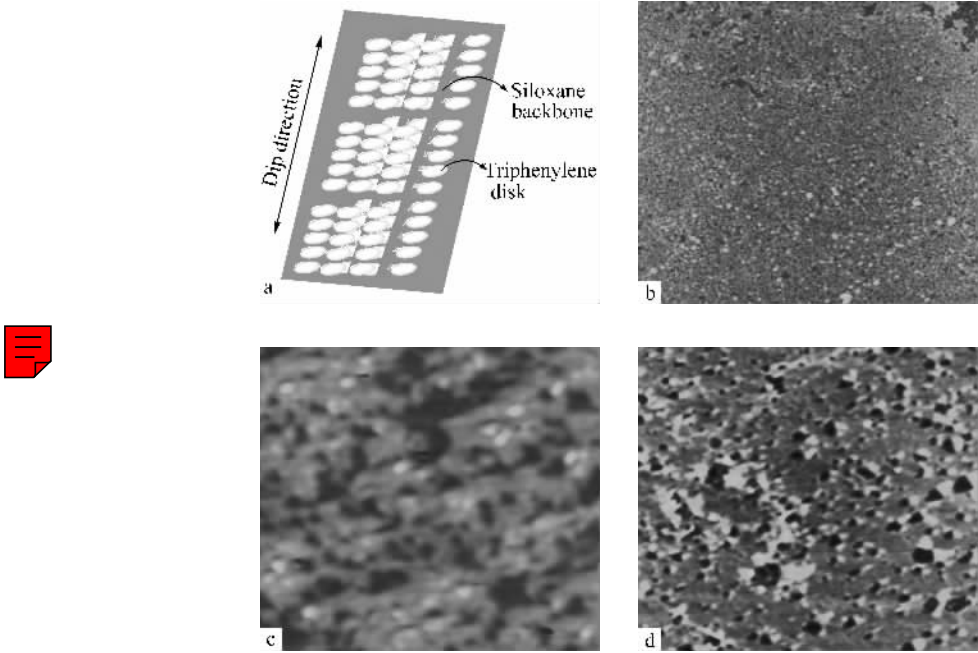


Fig. 5 (a) Sketch maps of the preferential arrangement way of LPSQ in LB film on quartz slides; (b ~ d) AFM images of single-bilayer LB films of LPSQ on hydrophobic silicon wafers transferred from monolayer spread from different solvents at 25 mN/m
b) Toluene spreading solution; c) Chloroform spreading solution; d) *n*-hexane spreading solution; The size of the images is 5 μm × 5 μm.

4 CONCLUSIONS

From the above studies, we can conclude that this newly synthesized “Hairy-rod” LPSQ with functional triphenylene side groups can form a stable monolayer on

the air-water interface. Moreover, very stable and uniform Y-type LB films in which the backbones of LPSQ have a preferential orientation parallel to the dipping direction can be prepared with the ordinary LB technique, confirmed by polarized UV and fluorescence

spectroscopic measurements and AFM morphology observations. Furthermore, the stable and uniform LB films of LPSQ with the triphenylene side groups promise to be a fine one-dimensional molecular/nano-wire

material.

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