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# Ladder Polysiloxanes for Optoelectronic Applications

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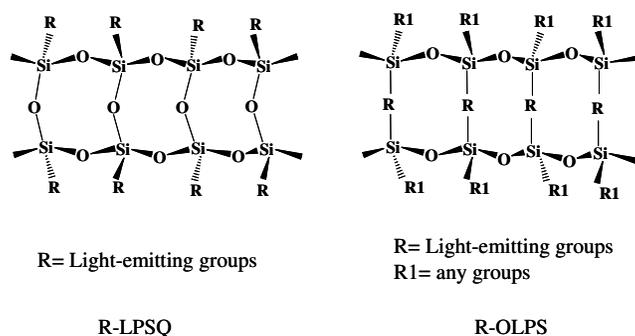
## 1. Introduction

Electroluminescence (EL) of conjugated polymers was first reported in 1990 with poly(*p*-phenylenevinylene) by Burroughes et al. (Burroughes et al., 1990) Since then polymer light-emitting diodes (PLED) have attracted the attention of many researchers and many efforts have been made to develop PLED in recent years (Kido et al., 1995; Service, 2005; Holder et al., 2005; D'Andrade & Forrest, 2004) because of the significant advantages that PLED present for displays, especially for flat panel displays. Those advantages include highly luminous efficiency, wide viewing angle, low operating voltage, high brightness, vivid color, low cost, light weight, and particular flexibility. Many approaches have been used in attempts to improve the performance of PLED device, for instance, improving deposition technologies (de Gans & Schubert, 2003; Singhet al., 2010) and controlling the interfacial microstructure of multilayer- structured devices (Segalman et al., 2009) in the process of preparing the devices; improving the electrical and optical properties of the light-emitting material layer (Grimsdale et al., 2009) and so on. Especially, the light-emitting material layer is crucial to get a high performance PLED device.

Considerable efforts have been devoted to developing conjugated materials as the active layers in PLED. (Gather et al., 2010; Wang et al., 2009; Xiao et al., 2010) The ongoing preparation of new light-emitting materials has produced in higher efficiencies, enhanced brightness, and longer lifetimes of optoelectronic devices. (Martin & Diederich, 1999; van Hutten & Hadziioannou, 2000; Müllen & Wegner, 1999) However, the stability of these materials under operating conditions needs further improvement if they are to be widely used in real products, some common causes resulting in degradation of PLED still remain to be unsolved. For instance, molecular aggregation induced by the  $\pi$ - $\pi$  stacking of polymer chain results in quenching of fluorescence; (Wu, et al., 2002; Amrutha & Jayakannan, 2007) poor film-forming property and poor morphological stability; low thermal stability (Weinfurtner et al., 2000) and so on.

For the first case, controlling the  $\pi$ - $\pi$  stacking induced molecular aggregation of the polymer chains is one of important tasks in the development of ideal PLED devices. To solve this problem, one method is that units of structural asymmetry are introduced in order to limit the ability of chains to pack effectively in the solid state. For example, Son et al. (Son, et al., 1995) controlled the distribution of *cis*-linkages in poly(phenylenevinylene) chains, the *cis*-linkages interrupt conjugation and interfere with the packing order of the polymer chains. Liao et al

(Liao et al., 2001) introduced a *meta*-linkage in the conjugated polymer chain, which reduced the conjugation length and allowed the polymer to blend and twisted more effectively than that of *para*-linkage. Another approach is to end-cap conjugation polymer, such as polyfluorenes, with a bulky group, (Klaerner et al., 1998, 1999; Setayesh et al., 2001) a crosslinkable moiety (Chen et al., 1999) or a charge-transporting moiety. (Yu et al., 1999) The third method is to prepare the dendronized polymer as the EL layer materials. It has been demonstrated that adding dendritic bulky moieties can effectively suppress the formation of aggregation (Ego et al., 2002; Marsitzky et al., 2001) and reduce self-quenching of luminescence due to intermolecular interactions. (Pogantsch et al., 2002) In addition, a good film-forming ability, a good morphological stability and a high thermal stability also are crucial to the practical application of PLED. (Smith et al., 1998; Fenter et al., 1997) They can be improved by increasing the molecular weight of the EL polymer materials or introducing, compounding the thermostable groups or molecules into the EL polymer materials. It is reported that semiconducting polymers containing polyhedral oligosilsesquioxanes (POSS) segments, when used in PLED devices, exhibit the better thermal stability, higher brightness, and higher external quantum efficiency as compared to the corresponding parent polymers. (Imae et al., 2005; Froehlich et al., 2007; Xiao et al., 2003; Yang et al., 2009, 2010; Singh et al., 2009) However, a light-emitting material with outstanding comprehensive performance still is few. Thus, to synthesize a new kind of materials, which features both preventing the intermolecular aggregation and possessing the excellent thermal stability, is especially important. In addition, polymer solar cells active materials have the similar requirements with that of PLED.



Scheme 1. Schematic structure of R-LPSQ and R-OLPS.

Toward this goal, we incorporate light-emitting units into polymer backbone forming well-defined ladder or double-stranded structure. Ladder structure with limited conformational freedom is expected to reduce the electron delocalization of conjugated polymer and thus suppress the formation of aggregation. Fortunately, among the ladder polymers, both the ladder organo-bridged polysiloxanes (R-LPSQ) and ladder polysilsesquioxanes (R-LPSQ) possess incomparable comprehensive merits, which can be readily used to prepare thin film devices. These merits are the good solubility in common organic solvents, good film-forming ability, fair adhesion to various substrates and the excellent resistances to thermal, chemical and irradiation degradation of the thin film. (Unno et al., 2002; Shea & Loy, 1995, 2001) Therefore, we introduce the light-emitting groups into the side chains of R-LPSQ or into the bridge of R-OLPS to prepare novel light-emitting materials as shown in Scheme 1.

During the last three decades, our research group proposed a supramolecular template strategy named "supramolecular architecture-directed stepwise coupling and polymerization", (Zhou et al., 2008; R. B. Zhang et al., 1999) by which a series of well-

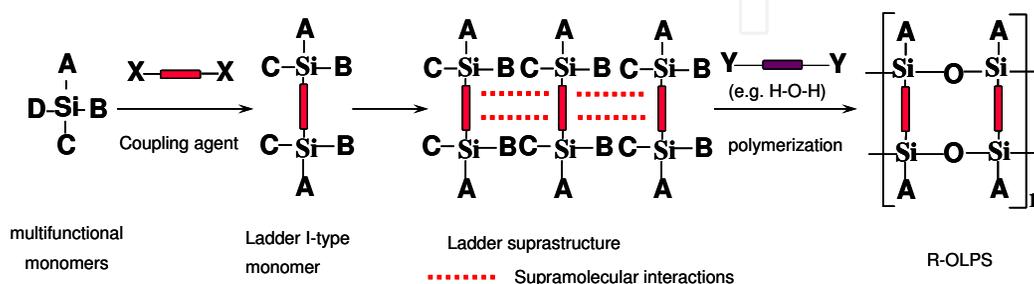
defined organo-bridged ladder polysiloxanes R-OLPS and ladder polysilsesquioxanes R-LPSQ have been prepared. (Wan et al., 2006; Sun et al., 2003a, 2003b; Guo et al., 2002; Li et al., 2002; Liu et al., 2000) The synthesis, properties and applications of ladder polysiloxanes materials would be discussed in detail in the following sections.

## 2. General synthetic method and characterization of ladder polysiloxanes

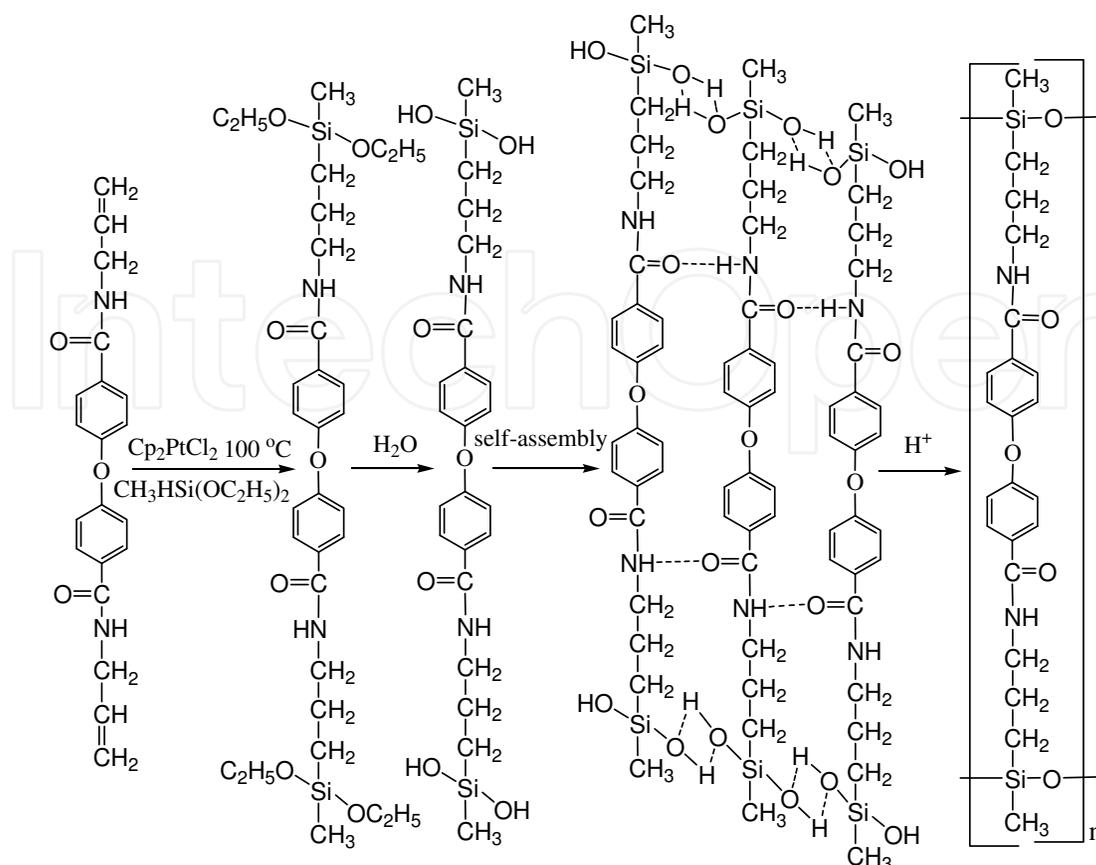
For carbon based ladder polymer, two general routes have been used to prepare ladder type materials: (Scherf et al., 1995, 1998, 1999) (1) the polymerization of multifunctional monomers, in which both the strands of ladder structure are generated in a single reaction; and (2) the cyclization of suitably functionalized open-chain (single-stranded) precursor polymers in a polymer-analogous process. Both strategies pre-suppose certain essentials to arrive at structurally defined ladder polymers, especially the exclusion of side-reactions and an almost quantitative conversion of the starting materials. For ladder polysiloxanes, these routes also are feasible and we adopt the method one to synthesize them, i.e. polymerization from the multifunctional monomers. As mentioned in the introduction section, the ladder polysiloxanes contains the R-LPSQ and R-OLPS, so we will introduce the synthesis and characterization of them respectively.

### 2.1 Synthesis and characterization of R-OLPS

The preparation of R-OLPS generally starts from the multifunctional monomer containing Si-X ( $x = F, Cl, Br$ ) or Si-OH groups. Because of the silicon atom has bigger atomic radius and smaller electro-negativity than carbon atom, Si-X or Si-OH bonds have the bigger polarity and higher reactivity than that of carbon. Thus to obtain the high molecular weight R-OLPS with any single uniform structure would be extremely difficult because of branches and crosslinking are often unavoidable. The traditional polymer synthetic methods usually emphasized chemical reactivity of monomers and ignored other strategies such as lately developed supramolecular concept, i.e., confining reactive monomer within a supramolecular assembly, which can be used as template to direct polymerization. As Bailey (Bailey, 1990) pointed out, the most desirable type of reaction for the formation of a real ladder is one in which both sides of the ladder should be formed simultaneously. Therefore, the problem may only be solved if the precursors' configuration can be effectively controlled during the whole polymerization process like the formation of biopolymers. Towards this goal, we developed a supramolecular template strategy named "supramolecular architecture-directed stepwise coupling and polymerization", which emphasized directive role of the weak supramolecular assembly and thus the polymerization could proceed in the confined environment.



Scheme 2. Illustration of synthesizing R-OLPS by supramolecular architecture-directed stepwise coupling and polymerization



Scheme 3. Synthetic route to ladder polymer A-LPMS.

Synthesizing R-OLPS by supramolecular architecture-directed stepwise coupling and polymerization are illustrated as shown in Scheme 2. Firstly, a silicon monomer, trifunctional silane (e.g.,  $\text{MeSiCl}_3$ ) or potentially tetrafunctional silane (e.g.,  $\text{HSiCl}_3$  or  $\text{CH}_2=\text{CHSiCl}_3$ ), reacts with a coupling agent X-X (e.g., phenylenediamine) to form a separable coupled ladder monomer. Then ladder monomer is self-assembled to form the ladder suprastructure by means of the concerted noncovalent interactions, including hydrogen bonding,  $\pi$ - $\pi$  stacking, and donor-acceptor effects. Next, the ladder suprastructure reacts with the second coupler Y-Y (e.g. H-O-H) to form a covalent ladder polymer R-OLPS. The method has been confirmed by the following practical reactions.

Tang et al. (Tang et al., 2002) reported the preparation of a template, N, N'-diallyl-[4,4'-oxybis(benzyl amide)] as shown in Scheme 3, which possesses strong intermolecular amide hydrogen bonding. Firstly, ladder monomer was synthesized via a hydrosilylation reaction of the template with methyltriethoxysilane. And then ladder monomer was hydrolyzed and further formed the ladder suprastructure by the hydrogen bonding of  $\text{C}=\text{O}\cdots\text{H}-\text{N}$  and  $\text{Si}-\text{OH}$  themselves. Lastly, the ladder suprastructure was condensed with concentrated  $\text{H}_2\text{SO}_4$  as catalyst to form a highly ordered aryl amide-bridged ladder polymethylsiloxane (A-LPMS). X-ray diffraction (XRD) analysis is an effective method to characterize ordered structures and it was successfully applied to characterize ladder structure. Brown (Brown et al., 1960) pointed out that the diffraction peak in the small-angle region represented the intermolecular chain-to-chain distance of the ladder polymer (*i.e.* the ladder width) and the diffusion peak in the wide-angle region was the thickness of the macromolecular chain (*i.e.* the ladder thickness). There are two distinct peaks representing ladder width (2.40 nm) and

ladder thickness (0.48 nm) in the XRD spectrum of polymer A-LPMS, indicating the ladder structure formed as shown in Fig. 1. Moreover, the regularity of ladder can be inferred from  $^{29}\text{Si}$ -NMR. It was known that the smaller peak width at half-height for  $^{29}\text{Si}$ -NMR peak in solution, the higher the ladder regularity of the polysiloxane. As shown in Fig. 2, except for the peak at 6.9 ppm for the external standard hexamethyldisiloxane and peak at 12.4 ppm for the trimethylsiloxyl end-capping group, a peak with the narrower half-peak width (less than 1ppm) at -18.8 ppm emerge, indicating A-LPMS has high ladder regularity and excluding the presence of the branch structure. In addition, the radius of gyration ( $R_g$ )/the radius of hydrodynamic ( $R_h$ ) = 1.6-1.8 of A-LMPS determined by static light scattering, indicating it is not like a flexible coil but like a semi-rigid soft ladder.

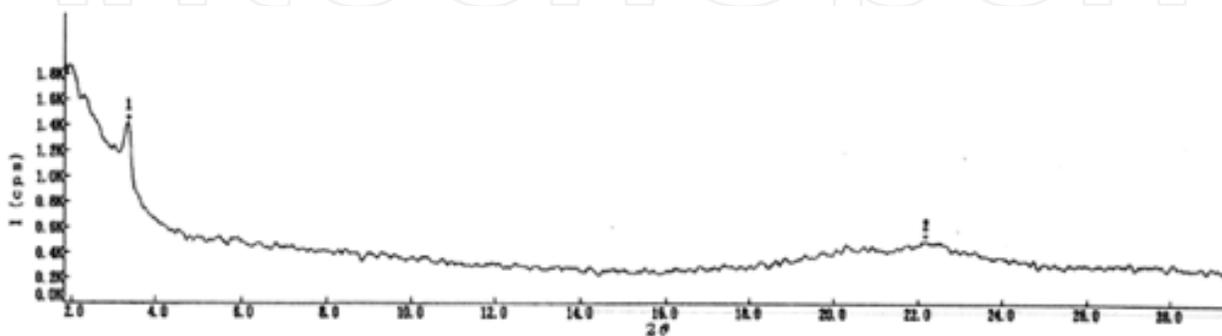


Fig. 1. XRD spectrum of polymer A-LPMS.

Usually, the Mark-Houwink-Sakurada equation is used to express the intrinsic viscosity as a function of the molar mass.

$$[\eta] = K M^\alpha \quad (1)$$

$K$  and  $\alpha$  are constants for a given polymer-solvent system at a given temperature. The exponent  $\alpha$  is characteristic for the polymer topology and reaches from  $\alpha = 0$  (solid spheres) over  $\alpha = 0.5$  (random coil under  $\theta$  conditions) to  $\alpha = 2$  (rigid rod). (Vanhee et al., 1996; Okoshi et al., 2005) The viscosity index ( $\alpha$ ) of A-LPMS can be roughly estimated by the slope of the plots ( $\log [\eta]/\log Mw$ ) and was 1.15, indicating the greater stiffness of the ladder chain. The glass transition temperature of A-LPMS is as high as 125.2°C, revealing its relative stiff backbone.

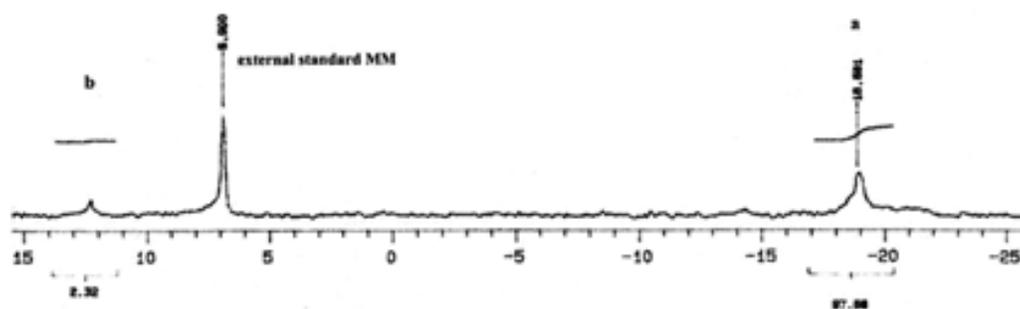
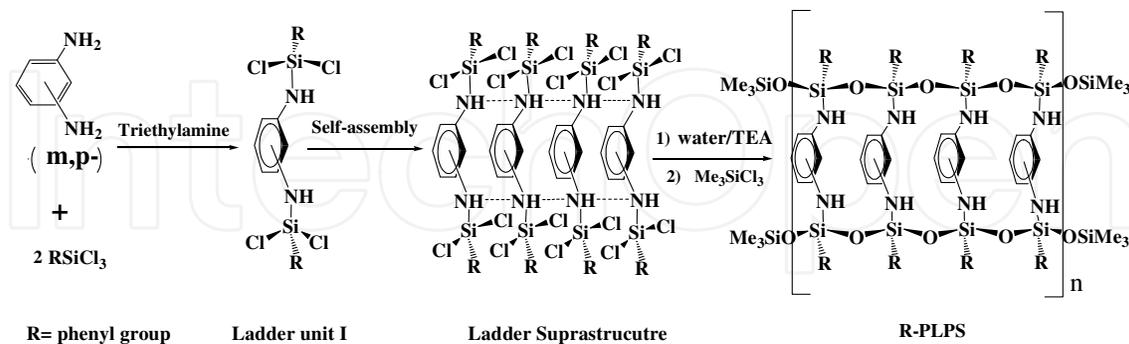


Fig. 2.  $^{29}\text{Si}$ -NMR spectrum of polymer A-LPMS.

Zhang et al. (T. Zhang et al., 2006) synthesized a perfect *p*-phenylenediimino-bridged ladder polyphenylsiloxane as shown in Scheme 4. The first step involves a reaction of phenyltrichlorosilane with the coupler *m* or *p*-phenylenediamine to form a separable

coupled ladder unit, which is self-assembled by a concerted interaction of N-H and Si-OH hydrogen bonding to ladder suprastructure. Then the ladder suprastructure underwent a novel stoichiometric hydrolysis/dehydrochlorination–condensation reaction leading to the desired Ph-PLPS.



Scheme 4. Synthetic route to ladder polymer Ph-PLPS.

Ladder structure also has been confirmed as follows: 1) there are two reflection peaks in XRD spectrum representing the ladder width and thickness, which were consistent with that calculated by molecular simulation. 2) as shown in Fig. 3, Ph-PLPS displays a extremely sharp absorption peak with small half-peak width (less than 0.3ppm) in  $^{29}\text{Si}$ -NMR spectrum, suggesting the presence of the perfect ladder structure. 3) the results of FI-IR, Fluorescence spectroscopy and the glass transition temperature also indicate successful preparation of ladder Ph-PLPS.

It should be noted that the tacticity of R-OLPS mainly depends on the intensity of the supramolecular interaction; in general, a stronger interaction leads to a more regular ladder structure. As shown in Fig. 3, when a hydrogen-bonding blocking reagent urea is added into the ladder suprastructure system, half-peak width of the final polymer becomes as large as 4 ppm in  $^{29}\text{Si}$ -NMR spectrum, indicating the resultant polymer Ph-PLPS became more irregular.

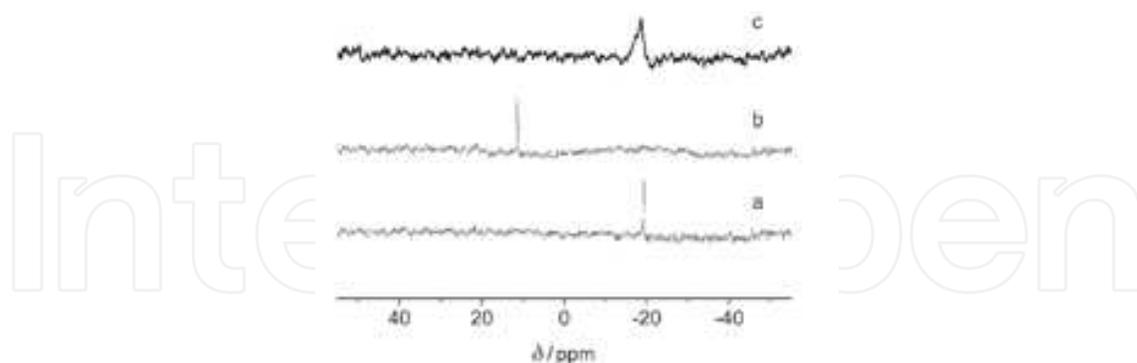
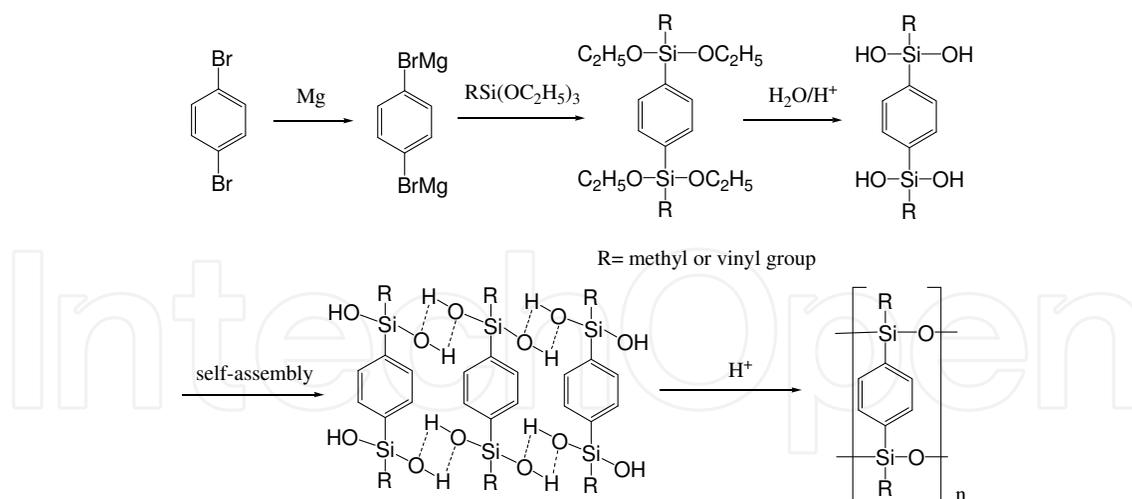


Fig. 3.  $^{29}\text{Si}$ -NMR spectra of a) polymer Ph-PLPS, b) ladder suprastructure, and c) the polymer Ph-PLPS derived from the ladder suprastructure adding urea.

Liu et al. (Liu et al, 2000) adopted another method to prepare ladder phenylene-bridged polymethylsiloxane and polyvinylsiloxane as shown in Scheme 5. Firstly, 1, 4-dibromobenzene reacts with magnesium give the Grignard reagent, which then reacts with methyltriethoxysilane or vinyltriethoxysilane to produce the ladder unit. The ladder unit is hydrolyzed and then condensed subsequently to get the target ladder polymer Me-PLPS or Vi-PLPS.



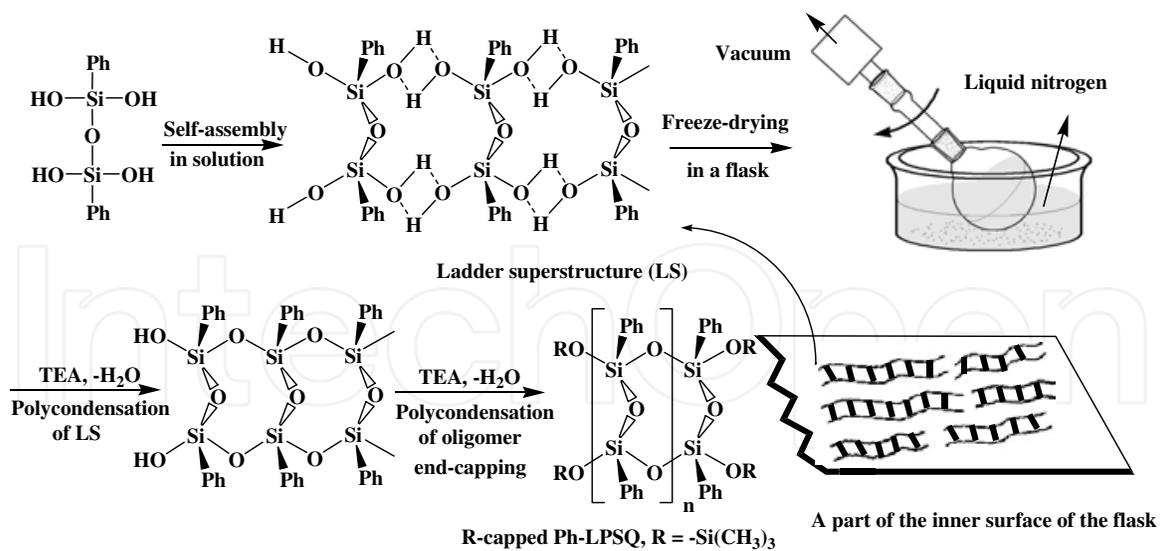
Scheme 5. Synthetic route to ladder polymer Me-PLPS or Vi-PLPS.

In summary, the preparation of ladder R-OLPS by supramolecular architecture-directed stepwise coupling and polymerization was confirmed to be feasible. And more ladder R-OLPS also have been synthesized by this method.

## 2.2 Synthesis and characterization of R-LPSQ

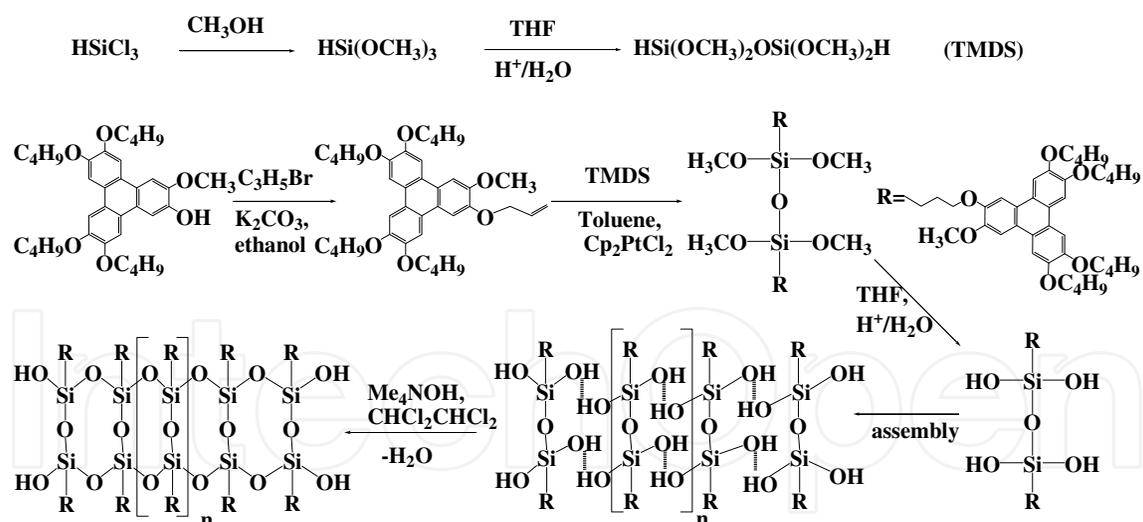
In 1960, Brown et al. (Brown et al., 1960) first reported a high molecular weight ( $M_w$ ) ladder polyphenylsilsesquioxane (Ph-LPSQ) via “equilibration polycondensation”. Nevertheless, its structure was refuted later by Frye *et al.* (Frye & Klosowski, 1971) who indicated that the so-called Ph-LPSQ actually was “partially opened polycyclic cages and short-range order but random on large scale”. In 2004, Yamamoto et al. (Yamamoto et al., 2004) reported an oligomeric polyphenylsilsesquioxane ladder with low ladder regularity. Lately, Brook (Brook, 2000) mentioned that the high  $M_w$  ladder polysilsesquioxanes reported are generally random networks, but the ladder structure may be obtained under certain controlled conditions. Similar to the preparation of R-OLPS, R-LPSQ also could be synthesized by supramolecular architecture-directed stepwise coupling and polymerization. The typical example will be introduced in the following section.

Zhang et al. (Z. X. Zhang et al., 2008) synthesized a well-defined ladder polyphenylsilsesquioxane (Ph-LPSQ) via a three-step approach: pre-organizing in solution, freeze drying, surface confined polycondensation as shown in Scheme 6. In the first step, ladder superstructure was formed by self-assembly of 1, 3-diphenyl-tetrahydroxy-disiloxane monomer in an acetonitrile solution. In the second step, lyophilization was realized by rotating a flask containing monomer/acetonitrile solution, while the flask was immersed in liquid nitrogen. This results in the formation of a continuous thin layer on the inner surface of the rotating flask (Scheme 6). In the third step, the self-assembled ladder superstructure immobilized in the solid thin layer was further converted into covalent ladder polymer by dehydrating polycondensation under TEA atmosphere. The rotation of the flask induced the orientation of ladder superstructures. Lyophilization fixed their orientation and structure. These factors promoted the confined polycondensation and prevented the cyclization and gelation side reactions, resulting in the formation of a soluble, high molecular-weight, and highly regular Ph-LPSQ.



Scheme 6. Systematic representation of the preparation of Ph-LPSQ via monomer self-organization-lyophilization-surface-confined polycondensation.

<sup>29</sup>Si-NMR analysis showed a very narrow peak (peak width at half-height of 2.5 ppm) at -78.5 ppm assigned to a Ph-SiO<sub>3/2</sub> unit, indicating a high degree of regularity of the Ph-LPSQ structure. The XRD profile of Ph-LPSQ also demonstrated two distinct peaks at 2θ around 7.0° (ladder width, 12.1 Å) and 20.0° (ladder thickness, 4.5 Å), respectively. Ren et al. (Ren et al., 2010) synthesized a well-defined triple-chain ladder polyphenylsiloxane by the similar strategy.



Scheme 7. synthetic route to the ladder triphenylene-containing polysilsesquioxane.

Zhang et al. (X. J. Zhang et al, 2006) reported a soluble, high  $M_w$  and perfect ladder triphenylene-containing polysilsesquioxane (LP) by a confined synthesis method as shown in Scheme 7. The self-organization of  $\alpha,\omega$ -ditriphenylene tetrahydroxy-disiloxane (M) by concerted  $\pi$ - $\pi$  stacking and H-bonding yield a high regular ladder superstructure (LS), and then LS converted into LP by dehydration condensation. In this case, introduction of electro-rich triphenylene groups intensified the supramolecular interactions and resulted in a supramolecular channel for a confined synthesis.

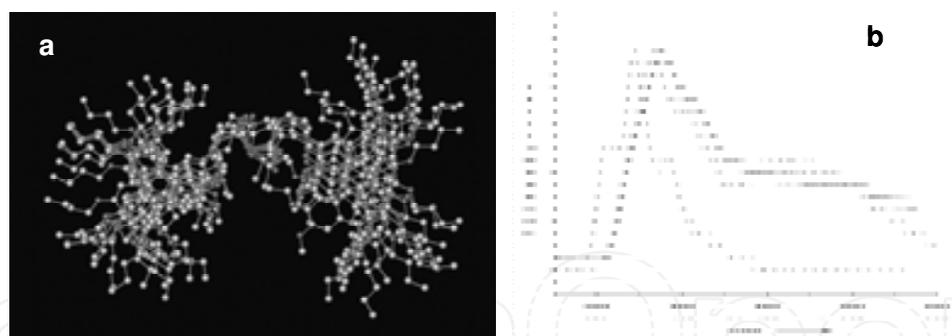


Fig. 4. (a) Top view of the molecular simulated ladder chain of LP with six repeat units (Hyper Chem 7.0 geometry optimization with RMS gradient of  $0.1 \text{ kcal.mol}^{-1}$ ). (b) Fluorescence emission spectra of M (dotted line), LS (dashed line), and LP (solid line) in n-hexane solution ( $10^{-6} \text{ M}$ ).

$^{29}\text{Si}$ -NMR and XRD measurements indicated the LP is prepared successfully. The top view of the molecular simulation of the chain (Fig. 4a) shows that all the triphenylene units are arranged on the same side of the ladder backbone and LP has a cis-isotactic structure. The regular stereoconfiguration of LP is also supported by fluorescence emission spectra as shown in Fig. 4b. In comparison to M, a new emission band at 493 nm appears in the spectrum of LS and LP, which is attributed to the excimer formed by the face to face  $\pi$ - $\pi$  stacking of the triphenylene side groups. It is also found that the ratio of the fluorescence emission intensities ( $I_m/I_e$ ) at 390 nm ( $I_m$ ) and at 493 nm ( $I_e$ ) is independent of the concentration of LP, and no red-shift of the emission spectra occurs as the concentration is changed. The existence of the intramolecular excimer further confirms the cis-isotactic structure.

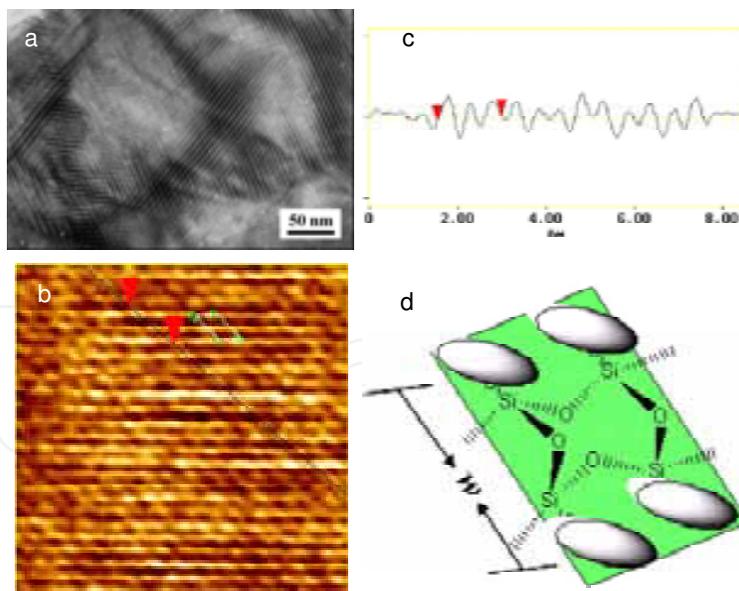
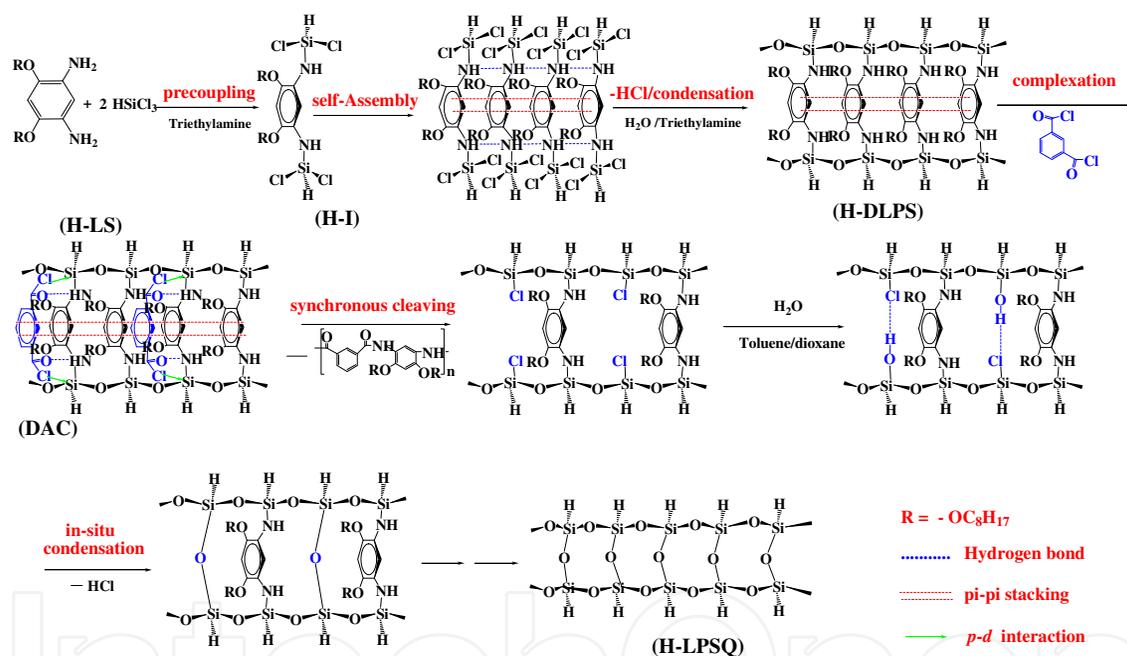


Fig. 5. TEM and AFM images of LP: (a) A bright-field TEM image obtained by freeze-drying a benzene solution; (b) high-resolution AFM image of a spin-coated film obtained from benzene solution; (c) AFM section analysis; (d) schematic representation of the ladder structure observed by AFM and the average value of  $w$  is 1.30 nm.

The transmission electronic microscopy (TEM) image (Fig. 5a) shows domains with dark lamellae with widths of about 2.5 nm, which are in agreement with the XRD results of LP.

However, high-resolution atomic force microscopy (AFM) images of a spin-coated film of LP on mica (Fig. 5b,c) show clear features (three parallel bright lines) of extended ladder chains (shown schematically in Fig. 5d): double chains align on the surface with the triphenylene side groups at the edge—the bright lines of two sides correspond to stacked triphenylene cores, and the middle one corresponds to the main chain of the ladder silsesquioxane. Careful observation shows the disc plane is aligned tilted to the chain axis. Section analysis gives the width of the repeat ladder unit  $w=1.30$  nm, which is reasonable for the distance between the centers of the triphenylene cores at the two sides.

Ren et al. (Ren et al., 2009) prepared a reactive and purely inorganic high Mw perfect ladder polyhydrosilsesquioxane (H-LPSQ) under direction of the two imperative supramolecular architectures: ladder superstructure (H-LS) and donor-acceptor complex (DAC) as shown in Scheme 8. It includes two steps: 1) precoupling and H-LS based synthesis of sacrificial 1,5-diimino-2,4-bis(octyloxy)-phenylene-bridged ladder polyhydrosiloxanes (H-DLPS) and 2) DAC based synchronous cleavage of the bridge and in-situ condensation. It is necessary to emphasize that H-LS and DAC are two imperative supramolecular architectures determining ladder regularity of H-LPSQ.



Scheme 8. Synthetic route to H-LPSQ

For the first step, the preparation of H-DLPS is similar to R-OLPS. The key for successfully conversion of H-DLPS to H-LPSQ is DAC based synchronous cleavage of the bridge and in-situ condensation. To achieve “synchronous cleavage”, isophthaloyl dichloride (IPC) was selected as the cleaving agent. It is proposed that when IPC is added into H-DLPS, it can form DAC with the diamino-phenylene-bridge by a synergy of hydrogen bonding between carbonyl and amino groups, benzene ring's  $\pi$ - $\pi$  stacking and  $d\pi$ - $p\pi$  interaction of p-electrons of Cl-atom and d-orbital of Si-atom. The Cl-atom of IPC then links to Si-atom, and breaks the Si-N bonds of the bridge and further transfer them into two Si-Cl bonds. The formation of DAC ensures the synchronous break of the two Si-N bonds on the same bridge, so that Si-O-Si can be formed in situ by hydrolysis and dehydrochlorination condensation of the two new-born Si-Cl bonds. The formation of a stable donor-accept complex (DAC) of

IPC with H-DLPS also was confirmed. As shown in Fig. 6, when IPC and H-DLPS were mixed with equal mole of IPC/the bridge, a low-energy absorbance at 386 nm emerged, which is different from the characteristic peaks of IPC and H-DLPS. That suggests the formation of DAC adducts apparently.

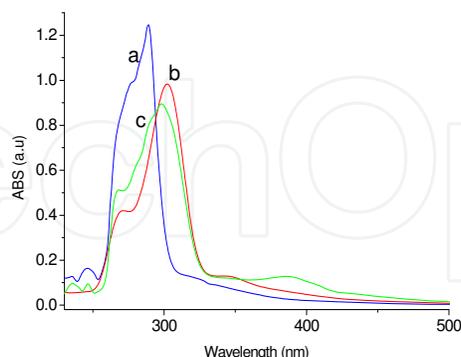


Fig. 6. UV spectra of (a) IPC; (b) H-DLPS; (c) H-DLPS and IPC (IPC and the bridge of H-DLPS is in equal mole)

The perfect ladder structure of H-LPSQ was also confirmed by elemental analysis, IR spectrum, XRD,  $^{29}\text{Si}$ -NMR and so on. Moreover, ladder H-LPSQ was functionalized by the hydrosilylation of cyclohexylene catalyzed by  $\text{Cp}_2\text{PtCl}_2$  to get ladder polycyclohexylsilsesquioxane (Ch-LPSQ). The perfection of Ch-LPSQ further demonstrates the perfection of the precursor H-LPSQ. The successful preparation of Ch-LPSQ also verifies the high reactivity of Si-H groups on H-LPSQ.

Using the similar method, the Ladder Polyphenylsilsesquioxanes (Ph-LPSQ) with a high regularity was prepared. MALDI-TOF-MS spectrum of Ph-LPSQ confirmed its ladder structure. As shown in Fig. 7, due to measuring mechanism, there was only the information of polymers with  $M_w < 6500$  Daltons. It bears the characteristic shape of a condensation polymer and make up of clusters of isotopic peaks. The nominal separation between these alternate major clusters, 258 Daltons, is exactly equal to the Ph-Si(O) $_{2/2}$ -O-Si(O) $_{2/2}$ -Ph repeat unit, indicating that the synthesis proceeded as expected to give double chain ladder structure without other side reactions. The displacement of the major clusters is attributed to the  $\text{Me}_3\text{SiO}$ - and  $\text{HOSiO}$ -capped Ph-LPSQ respectively, because the precursor was capped by trimethylchlorosilane in the end of polycondensation.

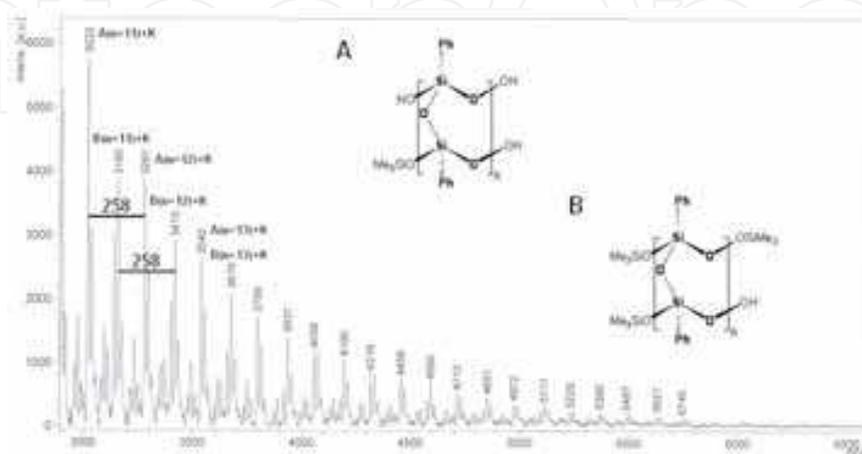


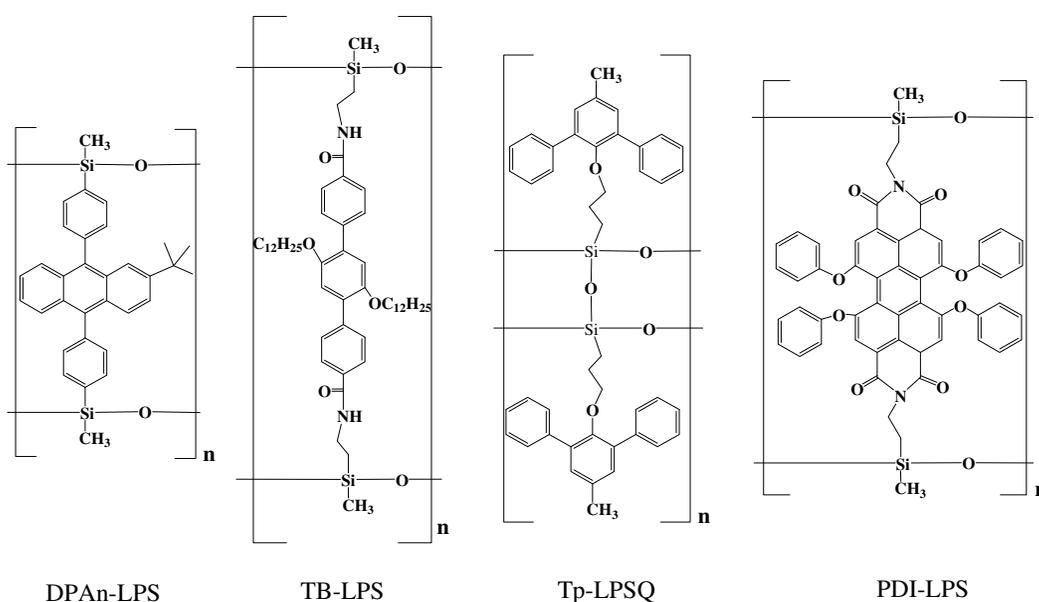
Fig. 7. MALDI-TOF MS of Ph-LPSQ.

### 3. Application of ladder polysiloxanes in polymer light-emitting diodes (PLED)

#### 3.1 Fluorescent materials

As mentioned in the introduction section, ladder polysiloxane is expected to reduce the electron delocalization of conjugated polymer and thus suppress the formation of aggregation. In fact, it was found that it could effectively prevent the aggregation of conjugated light-emitting groups so as to obtain stable, high efficiency and good film-forming materials.

It is well known that anthracene is typical for self-quenching of luminescence due to intermolecular aggregation. Zhang et al. (J. T. Zhang et al., 2010) introduced 9,10-Diphenylanthryl groups into the polysiloxanes skeleton to synthesize a 9,10-diphenylanthryl-bridged ladder polysiloxane (DPAn-LPS) as shown in Scheme 9.



Scheme 9. Chemical structure of DPAn-LPS, TB-LPS, Tp-LPSQ and PDI-LPS.

DPAn-LPS exhibits an emission band around 430 nm and absorption peaks in the range of 260-420 nm as shown in Fig. 8a. Note that there is only less than 2 nm red shift for UV-vis and photoluminescence spectra (PL) when the sample was varied from solution to film states, suggesting no aggregation of chromophore during film preparation. We suppose that the negligible variation of spectra between solution and film was due to confinement of 9,10-diphenylanthryl moieties within individual double-stranded ladder structure. Post-solution processing did not induce substantial change of local rearrangement of 9,10-diphenylanthryl units, which as return offered good film-forming property. PL spectra of DPAn-LPS show little variation after heating the film at 200 °C in air for 2 h as shown in Fig. 8b. This result demonstrates that DPAn-LPS is free of low energy defects (e.g., caused by crystallization) and has great thermal and color stability.

The fluorescence quantum efficient yield ( $\Phi_F$ ) of DPAn-LPS in THF is found to be 0.89 using 9,10-diphenylanthracene as a reference standard (cyclohexane solution,  $\Phi_F=0.9$ ). This value is notably higher than the reported values for some anthracene-containing compounds, such as 0.47 of 2-tert-butyl-9,10-bis[4-(iminostilbenyl)phenyl]anthracene (Danel et al., 2002) and 0.44 of 9-phenyl-10-(4-triphenylamine)anthracene. (Hamai & Hirayama, 1983)

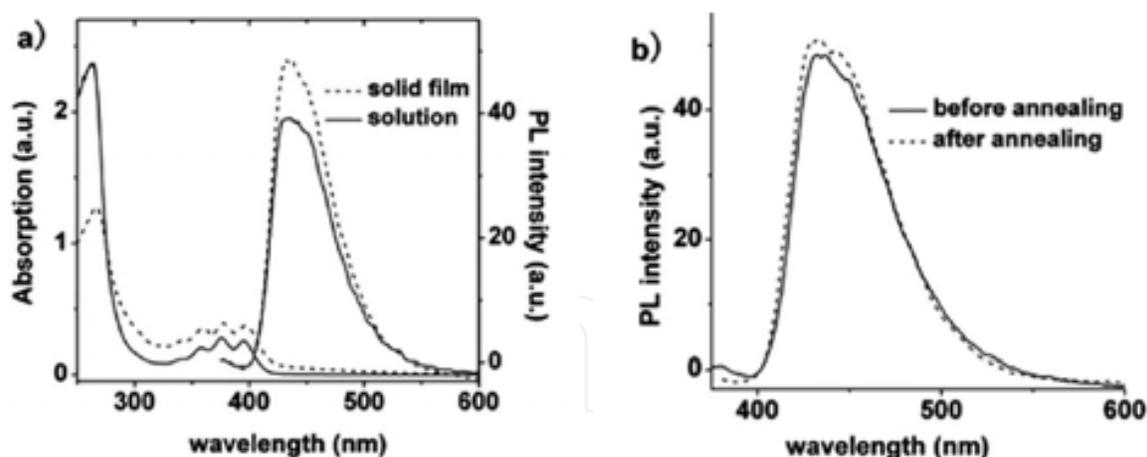


Fig. 8. (a) Absorption and photoluminescence emission spectra of DPAn-LPS in THF solution and thin film; (b) emission intensity of the spin-coated DPAn-LPS film before and after annealing at 200 °C for 2 h.

As expected, DPAn-LPS has the good emission stability at high temperature with high fluorescence quantum efficient yield because intramolecular aggregation of chromophores is effectively prevented by the rigid ladder structure.

Zhou et al. (Zhou et al., 2008) prepared a novel blue-light emitting terphenyl-bridged ladder polysiloxane (TB-LPS) as shown in Scheme 9. TB-LPS emits narrow blue light (420 nm) as shown in Fig. 9a with high quantum yields (0.96) in diluted solution. Comparing the solution state, TB-LPS shows no evident fluorophore aggregation in the solid state, indicating that the terphenyls are well isolated due to confinement of the ladder rungs. In addition, TB-LPS exhibits 5% weight loss at ca. 350 °C, and  $T_g$  of 143 °C revealing by thermogravimetric analysis and differential scanning calorimetry, indicating a good thermal stability. TB-LPS has the excellent color emission stability at high temperature based on annealing in air at 200 °C for 2 h as shown in Fig. 9b. Overall, TB-LPS can be considered as a potential material for fabricating stable and high-efficiency blue-light emitting optoelectronic devices.

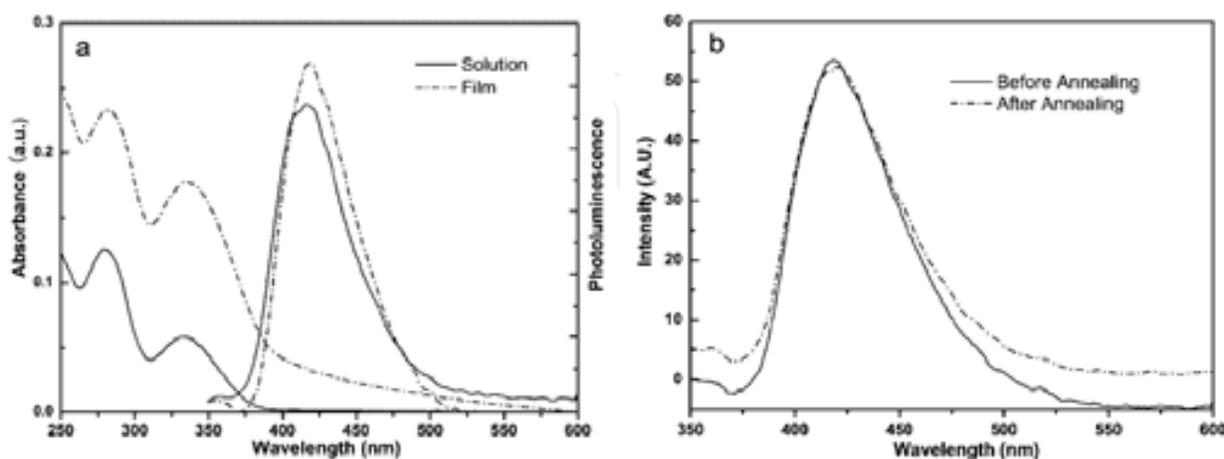


Fig. 9. (a) Absorption and photoluminescence emission spectra of TB-LPS in THF solution and in film. (b) Emission intensity of the spin-coated TB-LPS film before and after annealing at 200 °C for 2 h.

### 3.2 Phosphorescent host materials

In the development of high efficiency PLED, employing phosphorescent dyes in the electroluminescent light-emitting layer is an important method to realize high efficiency PLED because of the phosphorescent dyes, such as iridium bis(4,6-difluorophenyl)pyridinato-*N,C*<sup>2</sup>picolinate (FIrpic), can enable the internal quantum efficiency as high as 100% converting of both singlet and triplet excitons into photons. (Kawamura et al, 2005; Lamansky et al., 2001) In general, dopant/host systems are used for electrophosphorescent PLED to resolve the annihilation of both triplet-triplet and triplet-polaron. (Baldo et al., 2000) High efficiency host materials for green and red phosphorescence have been realized, but the research for blue phosphorescence emitting and host materials still are demanding. An ideal host for blue-light electrophosphorescence should essentially meet the follows: high enough singlet and triplet energy levels ( $E_T$ ) to confine singlet and triplet excitons, high charge mobility, and wide energy gap ( $E_g$ ). Of course, good chemical and thermal stabilities of the host materials are also of great importance. Ladder polysiloxane shows high thermal stability, good film-forming property. In addition, silicon-containing low conjugation structure may give a high  $E_T$ . Thus it may be a potential host material for blue-light emitting triplet emitter.

Ren et al. synthesized 3-methyl-1,5-diphenylbenzene containing ladder polysiloxane (Tp-LPSQ) with a wide bandgap of ca. 4.0 eV as shown in Scheme 9. The absorption spectrum of Tp-LPSQ in dichloromethane solution and thin film features two peaks at 241 nm and 296 nm as shown in Fig. 10A. The PL spectrum of Tp-LPSQ shows an emission peak at 364 nm in dichloromethane solution and thin film (Fig. 10B). The absorption and PL spectra of Tp-LPSQ thin film are almost identical to that in solution without any bathochromic shift, indicating negligible intermolecular interactions between Tp-LPSQ molecules in the solid packing state. The PL emission of Tp-LPSQ at low temperature was also measured to calculate  $E_T$ , which reaches to 2.82 eV. It is much higher than that of FIrpic ( $E_T = 2.62$  eV). So the generated triplet excitons could be confined in the emissive layer for Tp-LPSQ/FIrpic doped system.

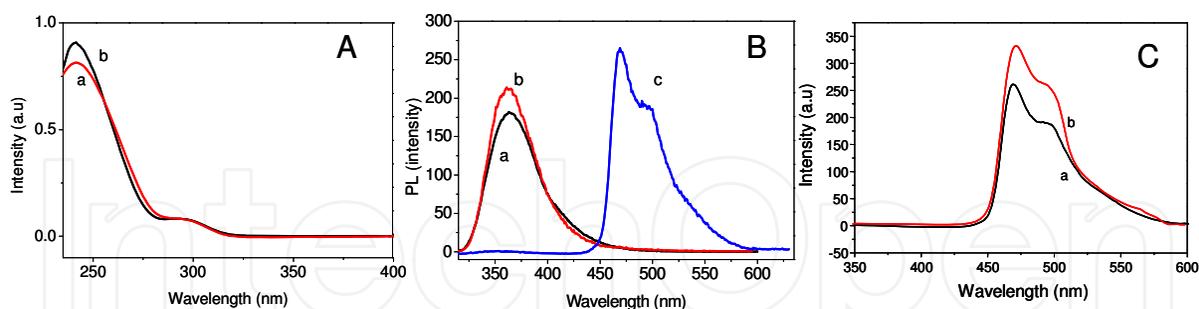


Fig. 10. (A) UV-vis spectra of Tp-LPSQ a) film; b) solution; (B) PL spectra of a) Tp-LPSQ solution; b) Tp-LPSQ film. c) Tp-LPSQ film doped with 8 wt % FIrpic. (C) PL spectra of Tp-LPSQ a) doped 8 wt% FIrpic and b) doped 8 wt% FIrpic aging 120 °C for 4h.

PL spectrum of Tp-LPSQ film blended with 8 wt% FIrpic shows a maximum emission peak at 469 nm and a shoulder peak at 496 nm, typical for FIrpic, with no trace of host Tp-LPSQ left at ca. 364 nm, (Fig. 10C) which indicate an efficient energy transfer from Tp-LPSQ to FIrpic and back transfer from the FIrpic to Tp-LPSQ does not occur at all. The PL spectrum shows the little variation after annealing at 120 °C in air for 4h, as shown in the Fig. 10B, suggesting Tp-LPSQ is free of low energy defects (e.g., caused by crystallization) and has great thermal and color stability.

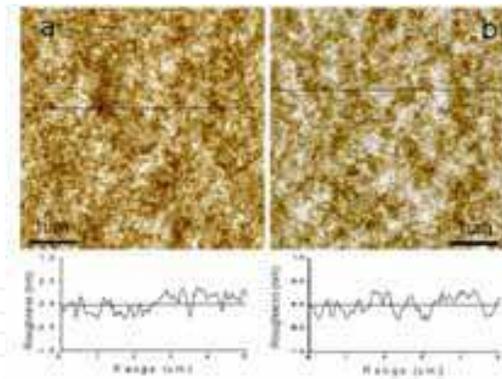


Fig. 11. AFM images and surface roughness of (a) Tp-LPSQ film doped with 8 wt% Firpic and (b) Tp-LPSQ film doped with 8 wt% Firpic after heating at 120 °C for 4h.

The film-forming ability, morphological stability of Tp-LPSQ and miscibility to the dopant Firpic also were investigated by the atomic force microscopy (AFM) as shown in Fig. 11. The topographical image of Tp-LPSQ with 8 wt % doped Firpic reveals that surface is smooth and uniform with 0.6 nm surface roughness, free of pinholes, particle aggregation, or phase separation as shown in Fig. 11a. Moreover, it is thermally stable as confirmed by annealing the film at 120 °C in air for 4h and the surface roughness is nearly unchanged.

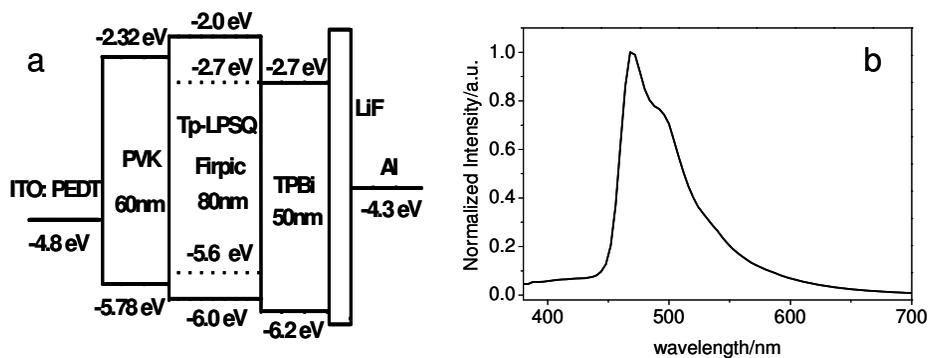


Fig. 12. (a) Energy level diagram for the device and (b) EL spectra of Tp-LPSQ doped with 8 wt% Firpic at 10V

The PLED of Tp-LPSQ doping blue light Firpic as active emitting layer was fabricated. As shown in Fig. 12a, the device configuration is [polyethylenedioxythiophene(PEDT) fabricated indium tin oxide (ITO)/poly(N-vinylcarbazole) (PVK) /8 wt % Firpic doped Tp-LPSQ /1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBI) /LiF/Al]. The EL spectra of the device displays bluer emission with an emission peak at 468 nm and a shoulder peak at 491 nm with a narrow full-width at half maximum of 53nm as shown in Fig. 12b. Commission International de L'Eclairage (CIE) coordinates is (0.17, 0.30).

As shown in Fig. 13, the turn-on voltage of device is 5.8 V, which is lower than that of reported polymer host materials. The device reaches the maximum brightness of 883 cd/m<sup>2</sup> at 13 V and shows a maximum luminous efficiency of 8.7 cd/A or the maximum power efficiency of 3.1 lm/W, which is superior to that of the reported polymer host (9,9'-bis(2-ethylhexyl)-3,6-fuorene) (Wu et al., 2008) and PVK, (Kido et al., 1993) even comparable to the small molecule host 4,4'-bis(9-carbazolyl)biphenyl (CBP). (Hu et al., 2009) The external quantum of the device is 4.6% ph/el, which is best blue light polymer host for Firpic reported so far.

In summary, ladder polysilsesquioxanes shows good film-forming property, high thermal and morphological stability, and good miscibility to the dopant Flrpic, in addition it has high triplet energy and wide band-gap. Therefore it may be potential host for phosphorescence emitter. We believe high efficiency materials may be obtained by tuning chromophore groups of ladder polysilsesquioxanes.

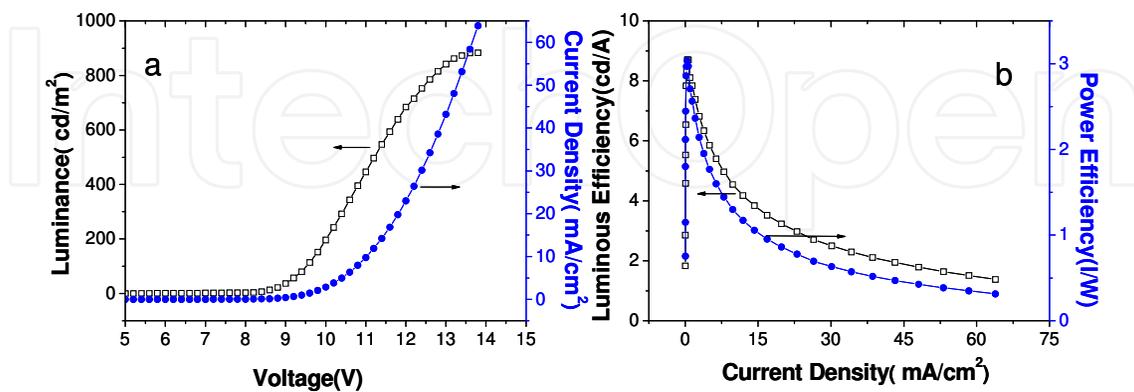


Fig. 13. (a) current density-voltage-luminance curve and (b) luminous efficiency and power efficiency as a function of current density of device.

#### 4. Application of ladder polysiloxane in polymer solar cells materials

Polymer solar cells (PSCs) are being extensively studied because of their great potential application. Compared with inorganic materials based solar cells, PSCs can be easily fabricated via spincoating, enabling the manufacture of large area, flexible, lightweight, inexpensive, and renewable devices. Generally, all of the solar cell devices require both hole-transporting (p-type) and electron-transporting (n-type) materials. From the view of improving performance the PSCs, controlling the metal/polymer semiconductor interfaces may lower the open circuit potential, and engineering the nanoscale morphology of the polymer semiconductor thin film may improve the mobility of the charge carriers. Apart from the necessity for efficiency improvement, stability is another problem for PSCs. Especially under light illumination and by simultaneous exposure to oxygen or water vapor, a rapid photooxidation/degradation occurs. Protection from air and humidity is necessary to achieve long device lifetimes (Günes et al., 2007).

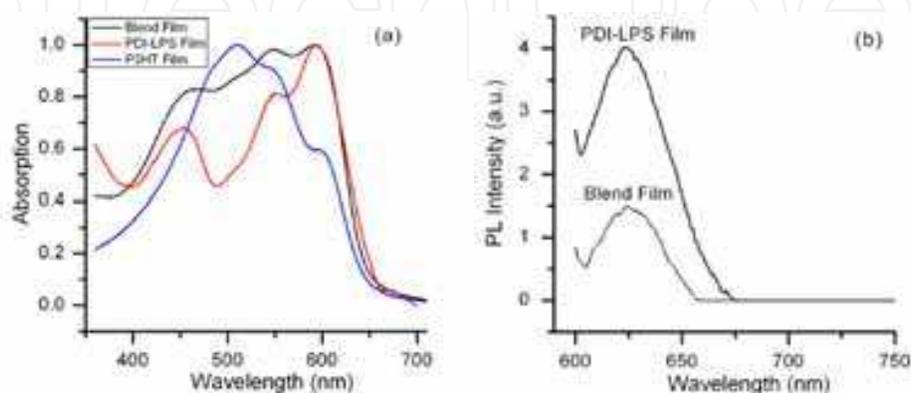


Fig. 14. (a) UV-vis spectra of blend film, PDI-LPS and P3HT films. (b) Fluorescence emission spectra.

The better film-forming ability, thermal stability, fair adhesion to various substrates and the excellent resistances to thermal, chemical and irradiation degradation of ladder polysiloxanes thin film may benefit the PSCs.

Perylene and its derivatives show an n-type, electron conducting behaviour and commonly serve as electron-acceptor materials of PSCs. Fu et al. (Fu et al., 2011) introduced a perylenediimide derivative into the central bridge of ladder polysiloxane to form PDI-LPS as shown in Scheme 9. Through chemically incorporating perylenediimide derivative (PDI) into ladder polymer backbone, it is expected to minimize the conglomeration of PDI and improve materials' thermostability and solubility while retaining its optoelectronic properties.

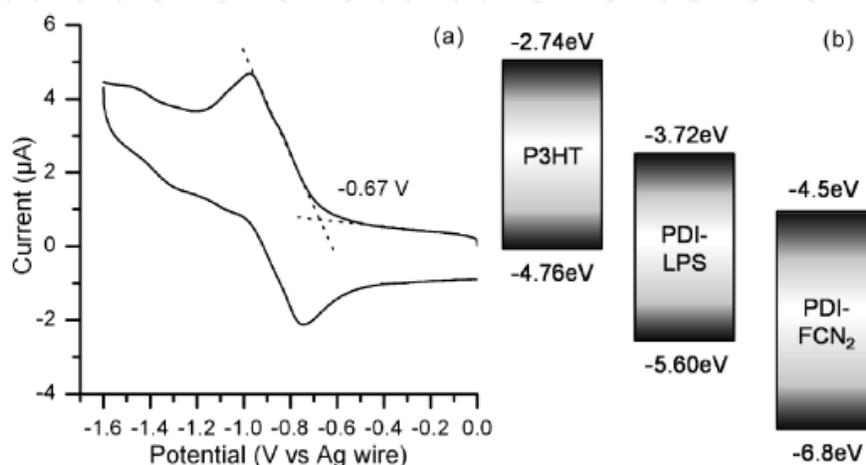


Fig. 15. (a) Cyclic voltammetry curve of PDI-LPS. (b) Energy levels diagram of ITO/PEDOT:PSS/P3HT:PDI-LPS:PDI-FCN<sub>2</sub>.

The PDI-LPS began to decompose at 442 °C and lost ca. 5 wt % at ca. 430 °C by TGA. The DSC curve shows that the PDI-LPS does not have any melting peaks, and its T<sub>g</sub> locates at ca. 310 °C, which is much higher than that of the low molar mass PDI derivatives. (Shin et al., 2006) The higher T<sub>g</sub> is due to the excellent regular ladder structure of the PDI-LPS and the double-strained structure could provide PDI-LPS with excellent thermal property and dimensional stability due to the minimized movements of chain segments.

It is well known that P3HT is as good p-type, hole conducting materials that works as electron donor. As a potential electron acceptor of PSCs, PDI-LPS was blended with P3HT and their optoelectronic properties were determined. As shown in Fig. 14a, UV-vis absorption edge of PDI-LPS extends to 660 nm and its corresponding optical energy gap is 1.88eV. Moreover, it is found the blends of PDI-LPS and P3HT (1:1) showed enhanced absorption areas spectrum compared to their precursors. Photoluminescence showed the blended thin film had strong fluorescence quenching indicating efficient energy transfer from P3HT to PDI-LPS as shown in Fig. 14b. The HOMO and LUMO energy levels of PDI-LPS were determined using cyclic voltammetry. As shown in Fig. 15, PDI-LPS has the proper HOMO and LUMO level with P3HT. Compared with the low molar mass PDI derivatives (e.g., PDI-FCN<sub>2</sub>), PDI-LPS has higher LUMO level, which could help the solar cell device to own higher open circuit voltage.

Especially the ladder polysiloxanes film is hydrophobic and it could resist photooxidation/degradation by simultaneous exposure to oxygen or water vapor. Thus the PSCs devices may achieve long device lifetimes.

## 5. Conclusion and perspectives

In summary, the ladder polysiloxanes have been successfully prepared by a supramolecular template strategy named "supramolecular architecture-directed stepwise coupling and polymerization". The ladder polysiloxanes displays good solubility in common organic solvents, good film-forming ability, fair adhesion to various substrates and the excellent resistances to thermal, chemical and irradiation degradation. Thus they offer great potentials in engineering the PLED and the PSCs. Except improving the thermal stability of the PLED and PSCs, the ladder polysiloxanes also could control the  $\pi$ - $\pi$  stacking induced molecular aggregation of the polymer chains. Therefore, high performance PLED and PSCs would be obtained by tuning the chemical structure of the ladder polysiloxanes and controlling the interface micro-structure of devices and it may be a kind of promising optoelectronic materials.

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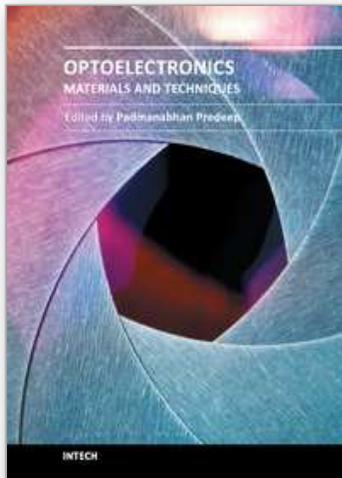
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