Ladder polysilsesquioxane for wide-band semiconductors: synthesis, optical properties and doped electrophosphorescent device†

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A ladder polysilsesquioxane with side chain 3-methyl-1,5-diphenylbenzene groups (Tp-LPSQ) is synthesized successfully and confirmed by the MALDI-TOF MS, ²⁹Si-NMR and ¹H-NMR. DSC, TGA, AFM and PL spectra reveal its good film-forming property, high thermal and morphological stability and good miscibility to the dopant FIrpic. In addition, it also shows a high triplet energy and a wide bandgap. Thus Tp-LPSQ may act as a host for the blue light emitting iridium complex FIrpic. The electrophosphorescent device based on Tp-LPSQ as the active layer exhibits typical blue emission and the performance of device is superior to other reported polymeric host materials.

Introduction

Organic light-emitting diodes (OLED) are now considered to be one of the most promising candidates for next-generation lighting and flat display panel systems.¹,² In the development of high efficiency OLED, employing phosphorescent dyes in the electroluminescent light-emitting layer is an important method to realize high efficiency OLED because phosphorescent dyes, such as iridium bis(4,6-difluorophenyl)pyridinato-N,C²-picolinate (FIrpic), enable the internal quantum efficiency to be as high as 100% conversion of both singlet and triplet excitons into photons.³,⁴ In general, dopant–host systems are used for electrophosphorescent OLED to restrain the annihilation of both triplet–triplet and triplet–polaron.⁵ High efficiency host materials for green and red phosphorescent OLEDs have been realized,⁶-⁸ but further studies are still requisite for blue phosphorescence emitting host materials. An ideal host for blue-light electrophosphorescence should essentially meet the following: high enough singlet and triplet energy levels (E₁) to confine singlet and triplet excitons, high charge mobility, and wide energy gap (E₂).⁹ In addition, good chemical and thermal stabilities of the host materials are also of great importance. Several low molecular weight host materials for blue electrophosphorescent OLED using FIrpic as the dopant, such as carbazole derivatives CBP,¹⁰ mCP,¹¹ CDBP¹² and so on, have been studied. As an example, Kido’s research group¹³ has recently reported very efficient blue phosphorescent host materials of FIrpic and the device showed a power efficiency of 55 lm/W and external quantum efficiency of 26% at a practical luminance of 100 cd m⁻².¹⁴ On the other hand, polymeric host materials have attracted much more attention in the fabrication of OLED devices since they exhibit better mechanical strength and stability than those of low molecular weight materials, and furthermore have better adhesion properties to a substrate. A few polymer hosts have been researched, such as poly(N-vinylcarbazole)(PVK),¹⁵ conjugated polymer poly(9,9’-diethyl-3,6-silafluorene)¹⁶ and poly(9,9’-bis(2-ethylhexyl)fluorene).¹⁷ However, PVK is prone to form exciplex and its high resistivity leads to a high operating voltage and the conjugated polymer host has a relatively low E₁. Therefore, a real challenge, and still the main target, is to develop suitable polymer hosts for blue-light emitters.

Polysiloxane is a special kind of semiconductor, exhibiting good optical properties, good solubility in common organic solvents, a good film-forming ability, and fair adhesion to various substrates.¹⁷-¹⁹ Comparing to the single chain polysiloxane, the ladder polysilsesquioxanes possess incomparable comprehensive merits because of the unique double-stranded molecular structure, such as the excellent resistances to thermal, chemical and irradiation degradation.²⁰-²² These unique properties promise great opportunities for application in OLED. Taking those into account, we designed a ladder polysilsesquioxane backbone with chromophore groups introduced into its side chains. One advantage of the polysiloxane-based double chain structure is the prevention of aggregation leading to quenching of the fluorescence.²³,²⁴ In addition, the silicon-containing low conjugation structure may give a high E₁.

In this study, we report the synthesis of a 3-methyl-1,5-diphenylbenzene containing ladder polysilsesquioxane (Tp-LPSQ)
with a wide bandgap of \(\text{ca.} 4.0\ \text{eV}\), showing photoluminescence (PL) and electroluminescence (EL) emission peaking at around 357 and 475 nm, respectively. It also shows a high \(E_T\), high thermal stability, good film-forming properties and morphological stability, excellent miscibility to the dopant and a high quantum efficiency. Thus Tp-LPSQ may be a potential host material for blue-light emitting triplet emitters such as Firpic. Moreover, preliminary results of a phosphorescent device have also been obtained.

**Results and discussion**

**Synthesis and properties of the precursor and Tp-LPSQ**

The synthetic routine to monomer and polymer Tp-LPSQ are outlined in Scheme 1. The monomer \(\text{M1}\) was synthesized via hydrosilylation reaction of 1,1,3,3-tetramethyldisiloxane and 3,5-diphenyl-4-allyloxytoluene using \(\text{Cp}_2\text{PtCl}_2\) as a catalyst. For this reaction the 3,5-diphenyl-4-allyloxytoluene must be excessive for the complete addition of the Si–H groups of 1,1,3,3-tetramethyldisiloxane. It can be found from the \(^1\text{H}-\text{NMR}\) spectrum (Fig. 1) of \(\text{M1}\) that the above-mentioned hydrosilylation reaction leads to the almost exclusive formation of the \(\beta\)-adduct product. The reason for the absence of the \(\alpha\)-adduct is possibly the higher steric hindrance in the formation of the \(\alpha\)-adduct than the \(\beta\)-adduct. \(^{29}\text{Si}-\text{NMR}\) of \(\text{M1}\) shows a single peak at \(-51.3\ \text{ppm}\) with a peak width at half-height as small as \(-0.5\ \text{ppm}\), also indicating \(\text{M1}\) was produced successfully. \(\text{M2}\) was obtained by hydrolysis of \(\text{M1}\) in a dilute THF–HCl solution under \(0\ ^\circ\text{C}\). Low temperature could suppress the undesired condensation between the formed silanols. As shown in Fig. 1, the \(^1\text{H}-\text{NMR}\) spectrum of \(\text{M2}\) shows a new peak at \(5.41\ \text{ppm}\), assigned to the proton of the Si–OH groups, and the peak at \(3.34\ \text{ppm}\) assigned to the protons of Si-OCH\(_3\), disappears, indicating the complete hydrolysis of \(\text{M1}\). In addition, the \(^{29}\text{Si}-\text{NMR}\) of \(\text{M2}\) shifts to \(-55.1\ \text{ppm}\), suggesting that \(\text{M1}\) reacts completely into \(\text{M2}\). (Fig. 1) The desired polymer Tp-LPSQ was obtained by the supramolecular template directed coupling polymerization. On the basis of what is known from the literature and our previous work,\(^{25–27}\) \(\text{M2}\) is able to spontaneously assemble into the ladder supramolecule (LS) via synergistic interactions of the silanols’ square planar H-bonding and the diphenylbenzene’s \(\pi\)–stacking (Scheme 1). The non-covalent LS is then used for the direct condensation of the reactive silanol groups to form the target Tp-LPSQ.

As a weak supramolecular dynamic assembly based-on \(\pi\)–stacking aided by hydrogen-bonding, LS is very susceptible to the ambient environment such as temperature and polarity or donor-electron capability of solvents.\(^{28}\) Any actions dealing with LS are during the polymerization done in mild conditions and thus ensuring the formation of high-ordered Tp-LPSQ instead of branched or crosslinking products. After carefully choosing the reaction conditions, we found that the polymerization performed in THF–dioxane (v/v 1/1) mixture under \(40\ ^\circ\text{C}\) is preferred. We supposed that THF–dioxane mixture solvent has a low polarity and a low electrodonating ability. Williams\(^{29}\) has pointed out that an acidic environment is favorable for the formation of H-bonding between the silanols. Moreover, an acidic catalyst is good for the condensation of silanols with electrodonating groups,\(^{29}\) and so sulfuric acid was chosen as the condensation catalyst. To stabilize Tp-LPSQ, Me\(_3\)SiCl was used to cap the Si–OH end groups at the end of polymerization.

In the \(^1\text{H}-\text{NMR}\) of Tp-LPSQ (Fig. 1), the peak at \(5.41\ \text{ppm}\) assigned to the proton of the Si–OH groups disappears, indicating the complete polymerization of the Si–OH groups. The \(^{29}\text{Si}-\text{NMR}\) spectrum of Tp-LPSQ displays a single peak at \(-66.9\ \text{ppm}\), suggesting that chemical environment of all the silicon atoms is similar and the high ladder regularity of Tp-LPSQ. This was also shown in the matrix-assisted laser desorption ionization mass spectroscopy (MALDI-TOF MS) of Tp-LPSQ (Fig. 2). Although the maximum molecular weight of \(\text{ca.} 4500\) was observed because of the degree of ionization, the detector’s saturation effect and so on, we still obtained convincing structure information from it. The spectrum bears the characteristic shape of a condensation polymer, which is made up of clusters of isotopic peaks.\(^{30}\) The nominal separation between these alternate
major clusters, 706 Daltons, is exactly equal to the repeat unit of Tp-LPSQ, indicating that the synthesis proceeded as expected to give a double chain ladder structure without a side reaction. What’s more, the adjacent major clusters attribute to the Me₃SiO- and HO-capped Tp-LPSQ respectively. Tp-LPSQ solubility testing found that Tp-LPSQ is readily soluble in toluene, THF, dichloromethane, and so forth. The weight average molecular weight (Mw) of Tp-LPSQ was determined to be 35.2 kDa with PDI = 1.16 by GPC in THF with polystyrene as standard (Fig. S1†).

The UV-visible absorption and photoluminescence (PL) spectra of Tp-LPSQ in dichloromethane solution (10⁻⁶ M) and thin film are shown in Fig. 3. The absorption spectrum in dichloromethane solution and thin film features two peaks at 241 and 296 nm attributed to the 3-methyl-1,5-diphenylbenzene groups. The optical band gap is 3.94 eV, calculated from the onset of optical absorption. The PL spectra of Tp-LPSQ were recorded with 310 nm excitation (Fig. 3B), and show an emission peak at 364 nm in dichloromethane solution and thin film. We found that 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 state packing. This phenomenon may be caused by the confined ladder structure.

The PL emission of Tp-LPSQ at low temperature was also measured to calculate $E_T$. A new emission band with a maximum peak at 439 nm determined at 77 K (Fig. S2), indicates that $E_T$ reaches 2.82 eV, which 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 the Tp-LPSQ−FiRpic system. In addition, the PL quantum efficiency of Tp-LPSQ film is 61% with 8-hydroxyquinoline aluminum (AlQ₃) used as a reference by an integrating sphere.

Properties of a FIrpic-doped thin film of Tp-LPSQ

As a potential host for the blue light emitter FIrpic, the PL spectrum of a Tp-LPSQ film blended with 8 wt% FIrpic by casting from dichloromethane solution was determined. As shown in Fig. 6, the PL spectrum shows a maximum emission peak at 469 nm and a shoulder peak at 496 nm, typical for FIrpic, with no trace of the host Tp-LPSQ left at ca. 364 nm, (Fig. 2B-c), indicating an efficient energy transfer from Tp-LPSQ to FIrpic and that the back transfer from the FIrpic to Tp-LPSQ does not occur at all. To investigate the thermal stability of doping 8 wt% FIrpic film of Tp-LPSQ, the film was annealed at 120 °C in air for 4 h, and the PL spectrum shows little variation, as shown in the Fig. 6b. This result demonstrates that Tp-LPSQ is free of low energy defects (e.g., caused by crystallization) and has great thermal and color stability.

The film-forming ability, morphological stability of Tp-LPSQ and miscibility to the dopant FIrpic were also investigated by...
atomic force microscopy (AFM). Because of a good solubility in organic solvents, Tp-LPSQ can be easily fabricated into films by casting, spin-coating, and dipping techniques. The topographical image of Tp-LPSQ with 8 wt% doped FIrpic reveals that the surface is smooth and uniform, with 0.6 nm surface roughness, is free of pinholes, particle aggregation, or phase separation as shown in Fig. 7a. Moreover, it is thermally stable as confirmed by annealing the film at 120 °C for 4 h (Fig. 7b) and the surface roughness is nearly unchanged. High thermal and morphological stability as well as good miscibility to FIrpic may be attributed to the ladder polysilsesquioxane skeleton.

Performance of an electroluminescence (EL) device

To investigate the EL properties of Tp-LPSQ as host for phosphorescent materials, the OLED of Tp-LPSQ doping blue light FIrpic as an active emitting layer was fabricated. As shown in Fig. 8a, the device was designed according to a stepped progression of the HOMO and LUMO energy levels of the hole-transport material, host material, and electron-transport material layer. As shown in Fig. 8a, it includes a configuration of [the polyethylenedioxythiophene(PEDT) decorated indium tin oxide (ITO)], a poly(N-vinylcarbazole) (PVK) layer, an 8 wt% FIrpic doped Tp-LPSQ layer, a 1,3,5-tris(9-phenylbenzimidazol-2-yl)benzene (TPBI) layer, and LiF/Al. The PVK was spin-coated from a chloroform solution as the hole transporting layer, 8 wt% FIrpic doped Tp-LPSQ was spin-coated from a toluene solution to form the emitting layer, TPBI was used as the electron-transporting and hole-blocking layer, while the ITO and LiF/Al were used as the anode and cathode, respectively.

The EL spectrum of the device displays a bluer emission with an emission peak at 468 nm and a shoulder peak at 491 nm, with a narrow full-width at the half maximum of 53 nm, as shown in Fig. 8b. Commission International de L’Eclairage (CIE) coordinates are (0.17, 0.30). Moreover, the light-emitting color is unchanged by increasing the driving voltage, as shown in Fig. S3.† The current density-voltage-luminance (J-V-L) characteristics of the device are displayed in Fig. 9a. The turn-on voltage of device is 5.8 V, which is lower than that of reported polymer host materials such as poly(9,9'-bis(2-ethylhexyl)-3,6-fuorene) (13.3V). The luminance efficiency vs. current density characteristics of the device is presented in Fig. 9b. The efficiency of the device decreases as the driving voltage is increased. The device reaches a maximum brightness of 883 cd m⁻² at 13 V and shows a maximum luminous efficiency of 8.7 cd A⁻¹ or a maximum power efficiency of 3.1 lm/W, which is superior to that of the reported polymer hosts poly(9,9'-bis(2-ethylhexyl)-3,6-fuorene)¹⁵ and PVK,¹³ and is even comparable to the small molecule host 4,4'-bis(9-carbazolyl)biphenyl (CBP).³² The external quantum efficiency of the device is 4.6%, which is the highest of any blue light polymer host for FIrpic reported so far.
fluorescence spectra were recorded on a Shimadzu UV-3100 as the ionizing and matrix reagents, respectively. UV-vis and resonance spectra were obtained at room temperature by using a Bruker Biflex III spectrometer, using a laser of 337 nm.

Conclusions

In summary, a novel ladder polysilsesquioxanes Tp-LPSQ has been successfully designed and synthesized. As a host for the blue light emitter FIrpic, it shows a good film-forming property, high thermal and morphological stability, and good miscibility to the dopant FIrpic, in addition it also has a high triplet energy and wide bandgap. An electrophosphorescent device can be produced based on the Tp-LPSQ as the active layer exhibits typical blue emission and high performance. We believe this work paves the way to prepare ladder polysilsesquioxane hosts and that high efficiency materials may be obtained by tuning the chromophore groups of ladder polysilsesquioxanes.

Experimental

Materials

All starting materials were obtained from commercial suppliers (Alfa Aesar) and used without further purification; solvents were purified according to standard procedures.

Characterizations

Fourier transform infrared (FTIR) spectra were recorded using a Perkin Elmer SP100 Fourier transform infrared spectrometer in the range of 400–4000 cm⁻¹. ¹H and ²⁹Si Nuclear Magnetic Resonance spectra were obtained at room temperature by using Bruker DX400 and Bruker DX300 spectrometers at 400 MHz and 59.6 MHz, respectively, with tetramethylsilane as the reference. The DSC investigation was carried out on a NETZSCH thermal analyzer under a 50 ml min⁻¹ nitrogen flow. The samples were heated from 25 to 800 °C at a rate of 10 °C min⁻¹ under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed on a NETZSCH TGA-Q500 thermal analyzer under a 50 ml min⁻¹ nitrogen flow. The samples were heated from 25 to 800 °C at a rate of 10 °C min⁻¹. Gel permeation chromatography (GPC) analysis was also performed by a Hitachi/Merrick L-7100 pump, a Waters 2414 refractive index detector, a Hitachi/Merrick L-7100 detector, in combination with a Waters 486 ultraviolet detector, in combination with a Hersteller MZ-Gel SDplus 5 µm, porosity 100 A, 10³ A, 10⁴ A, and 10⁵ A. THF with 1 g L⁻¹ LiBr was used as eluent at a flow rate of 1 ml min⁻¹ at 35 °C. Elemental analysis was conducted by a Heraeus CHN-RAPID, DATEL System, Inc. (Germany). Matrix Assisted Laser Desorption–Ionization Time-of-Flight Mass Spectra (MALDI-TOF MS) were obtained with a Bruker Biflex III spectrometer, using a laser of 337 nm and potassium chloride and 4-hydroxy-α-cyanocinnamic acid as the ionizing and matrix reagents, respectively. UV-vis and fluorescence spectra were recorded on a Shimadzu UV-3100 spectro-photometer and a Shimadzu RF-5301PC spectro-photometer, using 1 cm path length quartz cells, respectively. Atomic force microscopy images were recorded on a Agilent 550 AFM (Agilent Technologies) in tapping mode, using silicon cantilevers with spring constants of 20–30 N m⁻¹; the resonance frequencies were set as 140–160 kHz and the scan speed varied from 0.5–1.0 line/s. Electrochemical measurements were performed with a BAS 100W Bioanalytical System, using a glass–carbon disk electrode as the working electrode, a Pt wire as the counter electrode, Ag/AgCl as the reference electrode and Bu₄NClO₄ (0.1 M) in acetonitrile as the electrolyte. Chromaticity coordinates were measured with a SpectraScan PR650 photometer and J–V–L measurements were recorded simultaneously using a Keithley 2400 semiconductor parameter analyzer. External quantum efficiency was calculated from the luminance, current density, and EL spectrum. Photoluminescence (PL) quantum efficiency is determined by an integrating sphere (PTI C-701 time resolution spectro-photometer) with Alq₃ used as reference.

Device fabrication

In a general procedure, ITO-coated glass substrates were etched, patterned, and cleaned in an ultrasonic bath with acetone, ethanol, isopropanol and deionized water, respectively and then dried with nitrogen, and finally irradiated in an UV-ozone chamber. PEDT was spin-coated to smooth the ITO surface, and then PVK and organic emitting materials were sequentially spin-coated from the chloroform and toluene solutions. Finally a LiF buffer layer (0.5 nm) and Al (100 nm) cathode were deposited onto the organic films. The layer thickness of the cathode material was monitored in situ using an oscillating quartz thickness monitor.

Synthesis

Synthesis of 3,5-diphenyl-4-allyloxytoluene. A mixture of 2,6-diphenyl-4-methylphenol (3.9 g, 15 mmol), allyl bromide (3 ml, 34.5 mmol), K₂CO₃ (7.5 g, 55 mmol) and acetone (360 ml) were refluxed for 24 h. The solvent was removed by rotary evaporation, and the crude product was crystallized with ethanol to give the crystal. (3.6 g, 80%). ¹H-NMR (400 MHz; CDCl₃; Me₄Si) δ_H (ppm): 2.40 (s, 3H; CH₃), 3.70 (d, J = 6 Hz, 2H; OCH₂), 4.83 (t, J = 12 Hz, 2H; CH), 5.40 (m, J = 6 Hz, 1H; CH₂), 7.16 (s, 2H; Ar H), 7.33 (t, J = 8 Hz, 2H; Ar H), 7.41 (t, J = 8 Hz, 4H; Ar H), 7.61 (d, J = 8 Hz, 2H; Ar H).

Synthesis of 1,1,3,3-tetramethyldisiloxane (TMDS). To a mixture of trimethoxysiloxane (58 ml), THF (100 ml) and a drop of 0.5 M HCl were dropped with water (3.8 ml) and THF (20 ml) under stirring at room temperature. The reaction was continued for a further 2 h at room temperature after complete addition. The solvent was removed and the crude product was distilled by reduced pressure to give viscous oil. (8 ml, 30%). FTIR (KBr): 2947, 2845 cm⁻¹ (strong, δ CH₃), 2218 cm⁻¹ (strong, ν Si–H), 1000–1200 cm⁻¹ (strong, ν Si–O–Si), 843 cm⁻¹ (γ Si–H). ¹H-NMR (400 MHz; CDCl₃; Me₄Si) δ_H (ppm): 4.28 (s, 2H; SiH), 3.58 (s, 12H; OCH₃). ²⁹Si-NMR (300 Hz; toluene; Me₄Si) δ_Si (ppm): −64.8.

Fig. 9 a) Current density-voltage-luminance curve and b) luminous efficiency and power efficiency as a function of current density of device.
1,1,3,3-Tetramethoxy-\(\chi,\omega\)-(propoxyl-3,5-diphenyltoluene)disiloxane M1. A mixture of 3,5-diphenyl-4-allyloxytoluene (0.54 g, 1.8 mmol), 4.5 mg \(\text{Cp}_2\text{PtCl}_2\), anhydrous toluene (20 ml) and TMDS (0.12 g, 0.6 mmol) was heated to 90 °C for 96 h. After that, the solvent was removed and the crude product was purified by chromatography on silica gel with petroleum ether–dichloromethane (1 : 6) to give the title compound as a viscous oil. (0.75 g, 84%). 1H-NMR (400 MHz; CDCl\(_3\); Me\(_4\)Si) \((\delta_{\text{H}} \text{ppm})\): 0.11 (br, 4H; SiCH\(_2\)), 1.03–1.27 (br, 4H; CH\(_2\)), 2.35 (br, 6H; CH\(_3\)), 3.12 (br, 4H; OCH\(_2\)), 7.14–7.33 (br, 16H; Ar H), 7.55–7.56 (br, 8H, Ar H). 29Si-NMR (300 Hz; toluene; Me\(_4\)Si) \(\delta_{\text{Si}}\) ppm: –51.3. MALDI-TOF MS [M + Na\(^+\)] \(m/z\) = 821.5. Anal. Calcd for C\(_{44}\)H\(_{46}\)O\(_7\)Si\(_2\): C 71.13, H 6.24; found: C 71.28, H 6.18.

Preparation of Tp-LPSQ. 0.69g 1,1,3,3-tetrahydroxy-\(\chi,\omega\)-(propoxyl-3,5-diphenyltoluene) disiloxane was dissolved in 1.4-dioxane (20 ml); THF (20 ml) and two drops of concentrated H\(_2\)SO\(_4\). The mixture was heated to 80 °C for 96 h and then tri-methylchlorosilane (0.1 ml) and triethylamine (10 ml) were added with THF (30 ml), water (1 ml) and two drop of 1 M HCl under ice bath. After that the reaction was continued for a further 24 h at room temperature. The solution was concentrated to 20 ml and 100 ml of ethyl ether was added. The organic layer was washed three times with 15 ml of water and dried over Na\(_2\)SO\(_4\). The ethyl ether was removed and precipitated by n-hexane. A white solid was obtained. (0.69 g, 92%) 1H-NMR (400 MHz; CDCl\(_3\); Me\(_4\)Si) \((\delta_{\text{H}} \text{ppm})\): 0.11 (br, 4H; SiCH\(_2\)), 1.03–1.27 (br, 4H; CH\(_2\)), 2.35 (br, 6H; CH\(_3\)), 3.12 (br, 4H; OCH\(_2\)), 7.14–7.33 (br, 16H; Ar H), 7.55–7.56 (br, 8H, Ar H). 29Si-NMR (300 Hz; toluene; Me\(_4\)Si) \(\delta_{\text{Si}}\) ppm: –55.1. Anal. Calcd for C\(_{44}\)H\(_{46}\)O\(_7\)Si\(_2\): C 71.13, H 6.24; found: C 71.28, H 6.18.

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Notes and references