

Luminescent tetraphenylethene-substituted silanes*

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Abstract: Tetraphenylethene (TPE)-substituted silanes $[(\text{Ph}_4\text{C}=\text{C})_m\text{Si}(\text{Ph})_n]$, $m = 3-1$, $n = 3-1$ are designed and synthesized, and their optical, thermal, and electrochemical properties are studied. Whereas they are nonluminescent in solutions, they become highly emissive when aggregated in poor solvents (such as water) or fabricated into thin films, demonstrating a novel phenomenon of aggregation-induced emission (AIE). Their amorphous films exhibit high fluorescence quantum yields (54.6–63.7 %). They enjoy high thermal stability with 5 % weight loss occurring at 320–420 °C. Multilayer electroluminescence (EL) devices (ITO/NPB/emitter/TPBi/LiF/Al) utilizing the silanes as emitting layers are fabricated, which give deep blue EL with maximum luminance and external quantum efficiency of 5672 cd/m², and 1.6 %, respectively.

Keywords: aggregation; fluorescence; light-emitting diodes; silanes; tetraphenylethene.

INTRODUCTION

Since the development of the first efficient organic light-emitting diodes (OLEDs) by Tang and VanSlyke [1], significant attention has been paid to the production of full-color flat panel displays. To realize full-color OLED displays, red-, green-, and blue-emitting materials are required. Whereas red and green luminescent materials have been achieved in high luminance and efficiency, efficient blue emitters are still rare [2,3]. One problem associated with the dye emission in the solid state is aggregation-induced quenching: in the condensed phase, the molecules are located in immediate vicinity, which favors the formation of aggregates with ordered or random structures [4,5]. The excited states of the aggregates often decay via nonradiative pathways, which is a thorny problem in the development of effi-

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cient OLEDs. We and other groups have, however, found that certain luminophors show the opposite phenomenon. An example is given by tetraphenylethene (TPE) and its derivatives [6]. While they are weakly emissive or nonluminescent in the solution state, they become strong emitters when aggregated as nanoparticle suspensions in poor solvents (e.g., water) or as thin films in the solid state. Such novel phenomenon is coined as aggregation-induced emission (AIE) [7,8] because the nonemissive molecules are induced to emit by aggregate formation. OLEDs using the AIE luminogens as active layers are fabricated, which exhibit high external quantum efficiencies up to 8 %. Thus, they are outstanding light-emitting materials and warrant further exploration. TPE is a blue luminophor, and silane derivatives show not only good blue light-emitting properties [9,10] but also are utilized as hole-blocking [11,12] and host materials [13–15] in blue OLEDs. Combining the two components into one system may result in luminophors with novel optical properties. Thus, in this paper, we combined TPE with silane and obtained blue materials with efficient solid-state photoluminescence (PL) and electroluminescence (EL).

EXPERIMENTAL

Materials and instrumentations

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. All the chemicals and other reagents were purchased from Aldrich and used as received without further purification.

^1H and ^{13}C NMR spectra were measured on a Bruker AV 300 spectrometer in CD_2Cl_2 using tetramethylsilane (TMS; $\delta = 0$) as internal reference. UV spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. PL spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. The matrix-assisted laser desorption/ionization with time-of-flight (MALDI-TOF) mass spectra were recorded on a GCT premier CAB048 mass spectrometer. Thermogravimetric analysis (TGA) was carried out on a TA TGA Q5000 under dry nitrogen at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Thermal transitions were investigated by differential scanning calorimetry (DSC) using a TA DSC Q1000 at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Cyclic voltammetry was carried on a Princeton Applied Research (model 273A) potentiostat. The working and reference electrodes were glassy carbon and Ag/AgNO_3 (0.1 M in acetonitrile), respectively.

Device fabrication

Multilayer EL devices (ITO/NPB/emitter/TPBi/LiF/Al) were fabricated in the usual manner with sequential vacuum evaporation of various layers on 80 nm indium-tin oxide (ITO)-coated glass substrates with a sheet resistance of $25\ \Omega/\square$. The samples were transferred to the organic chamber with a base pressure of 7×10^{-7} Torr for the deposition of *N,N*-bis(1-naphthyl)-*N,N*-diphenylbenzidine (NPB), emitter, and 2,2',2''-(1,3,5-benzinetriyl)tris(1-phenyl-1-*H*-benzimidazole) (TPBi). The current density-voltage characteristics of the devices were measured by a HP4145B semiconductor parameter analyzer. The forward direction photons emitted from the devices were detected by a calibrated UDT PIN-25D silicon photodiode. The luminance and external quantum efficiencies of the devices were inferred from the photocurrent of the photodiode. The EL spectra were obtained by a PR650 spectrophotometer.

Synthesis

1-(4-Bromophenyl)-1,2,2-triphenylethene (2): To a solution of diphenylmethane (2.02 g, 12 mmol) in dry THF (50 ml) was added dropwise 1.6 M solution of *n*-butyllithium in hexane (7.5 ml, 12 mmol) at $0\text{ }^\circ\text{C}$ under a nitrogen atmosphere. The resultant orange-red solution was stirred for 1 h and then transferred slowly to a solution of 4-bromobenzophenone (2.6 g, 10 mmol) in THF (20 ml) at $0\text{ }^\circ\text{C}$. The reaction mixture was allowed to warm to room temperature and stirred for 6 h. The reaction was

quenched by adding an aqueous solution of ammonium chloride. The organic layer was extracted with dichloromethane, and the combined organic layers were washed with a saturated brine solution and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the resultant crude alcohol containing excess diphenylmethane was dissolved in ~80 ml of toluene and a catalytic amount of *p*-toluenesulfonic acid (0.5 g, 2.6 mmol) was added. After heating to reflux for 6 h, the mixture was cooled to room temperature and washed with a saturated brine solution and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using *n*-hexane as eluent. White solid of **2** was obtained in 86 % yield (3.5 g). ^1H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 7.20 (d, 2H, $J = 6.0$ Hz), 7.12–7.07 (m, 9H), 7.02–6.98 (m, 6H), 6.88 (d, 2H, $J = 6.3$ Hz). ^{13}C NMR (75 MHz, CD_2Cl_2), δ (TMS, ppm): 143.37, 143.28, 143.18, 142.66, 141.55, 139.61, 132.94, 131.26, 131.20, 131.18, 130.81, 127.84, 127.74, 127.64, 126.66, 126.61, 126.55, 120.40. MS (MALDI-TOF): m/z 412.0680 (M^+ , calcd. 412.0650).

4-(1,2,2-Triphenylvinyl)phenyltriphenylsilane (TPESiPh₃): *n*-Butyllithium (1.6 M in hexane, 3.8 ml, 6 mmol) was added dropwise into a solution of **2** (2 g, 5 mmol) in dry THF (50 ml) at -78 °C. After the reaction was kept at -78 °C for 3 h, 1.4 g (4.8 mmol) of chlorotriphenylsilane was added into the reaction. The mixture was allowed to warm to room temperature and then stirred for 12 h. The reaction was terminated by adding hydrochloric acid (2 M, 10 ml), and the mixture was then poured into water and extracted with dichloromethane. The organic layer was washed by water and dried over magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using *n*-hexane/dichloromethane as eluent. White solid of TPESiPh₃ was obtained in 88 % yield (2.5 g). ^1H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 7.50–7.26 (m, 15 H), 7.24 (d, 2 H, $J = 8.1$ Hz), 7.12–7.00 (m, 17 H). ^{13}C NMR (75 MHz, CD_2Cl_2), δ (TMS, ppm): 146.0, 144.4, 144.3, 144.1, 137.0, 136.3, 134.9, 132.0, 131.9, 131.3, 130.3, 128.6, 128.4, 128.3, 127.2. MS (MALDI-TOF): m/z 590.3459 (M^+ , calcd. 590.8263). Anal. calcd. for $\text{C}_{44}\text{H}_{34}\text{Si}$: C, 89.45; H, 5.80. Found: C, 89.35; H, 5.81.

Bis[4-(1,2,2-triphenylvinyl)phenyl]diphenylsilane [(TPE)₂SiPh₂]: The procedure was analogous to that described for TPESiPh₃. White solid; yield 64 %. ^1H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 7.46–7.31 (m, 10 H), 7.23 (d, 4 H, $J = 8.1$ Hz), 7.12–7.00 (m, 34 H). ^{13}C NMR (75 MHz, CD_2Cl_2), δ (TMS, ppm): 145.9, 144.4, 144.2, 142.3, 141.6, 137.0, 136.3, 135.0, 132.7, 132.0, 131.9, 131.3, 130.3, 128.5, 128.4, 128.3, 127.2. MS (MALDI-TOF): m/z 845.3454 (M^+ , calcd. 845.1514). Anal. calcd. for $\text{C}_{64}\text{H}_{48}\text{Si}$: C, 90.95; H, 5.72. Found: C, 90.73; H, 5.61.

Tris[4-(1,2,2-triphenylvinyl)phenyl]phenylsilane [(TPE)₃SiPh]: The procedure was analogous to that described for TPESiPh₃. White solid; yield 38 %. ^1H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 7.40–7.32 (m, 5 H), 7.17 (d, 6 H, $J = 8.1$ Hz), 7.11–6.99 (m, 51 H). ^{13}C NMR (75 MHz, CD_2Cl_2), δ (TMS, ppm): 145.9, 144.4, 144.2, 142.2, 141.6, 136.9, 136.3, 135.1, 132.8, 131.9, 131.3, 130.3, 128.5, 128.4, 128.3, 127.2. MS (MALDI-TOF): m/z 1099.6750 (M^+ , calcd 1099.4766). Anal. calcd. for $\text{C}_{84}\text{H}_{62}\text{Si}$: C, 91.76; H, 5.68. Found: C, 91.55; H, 5.72.

RESULTS AND DISCUSSION

Synthesis of TPE-substituted silanes

To enrich the research field of blue EL material, we synthesized three silane derivatives substituted with TPE according to Fig. 1. The key intermediate, 1-(4-bromophenyl)-1,2,2-triphenylethene (**2**), was synthesized according to the reference method [16] with minor modifications. Lithiation of **2** followed by reaction with chlorosilanes gave the target products, in which the yield was lowered with an increase in the TPE unit in the molecule due to the involved steric effect. TPESiPh₃, (TPE)₂SiPh₂, and (TPE)₃SiPh possess good processability. They are soluble in toluene, chloroform, dichloromethane, THF, etc., but are insoluble in methanol, acetonitrile, and water.

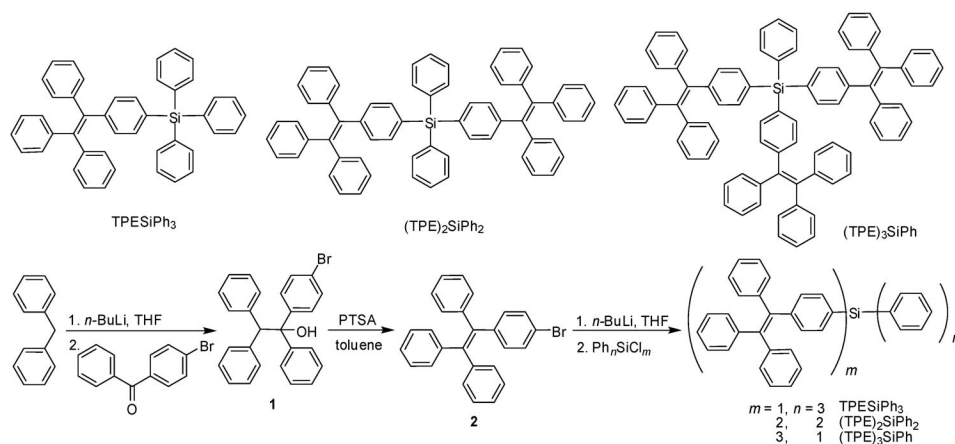


Fig. 1 Structures of TPE-substituted silanes and their synthetic route.

Optical properties

Figure 2 shows the absorption spectra of TPESiPh₃, (TPE)₂SiPh₂, and (TPE)₃SiPh in THF solutions. All the molecules exhibit an absorption maximum at ~315 nm associated with the π - π^* transitions of the TPE moiety. Figure 3A shows the PL spectra of TPESiPh₃ in THF/water mixtures with different water contents. The PL spectrum in pure THF is virtually a flat line parallel to the abscissa; that is, TPESiPh₃ is a weak emitter when molecularly dissolved in solution. The PL spectrum remains unchanged when up to 70 % of water is added but starts to increase afterwards. The emission intensity reaches its maximum at a water content of 99.5 %. Similar phenomena are also observed in (TPE)₂SiPh₂ and (TPE)₃SiPh. Clearly, similar to TPE, the emissions of the present molecules are induced by aggregate formation, thus truly verifying their AIE feature. In the dilute solution, rotations of multiple phenyl peripheries against the olefin double bonds of the molecules may have efficiently non-radiatively deactivated their excitons. Restriction of intramolecular rotations in the aggregates blocks the channel of nonradiative decay, hence changing the dyes to strong emitters.

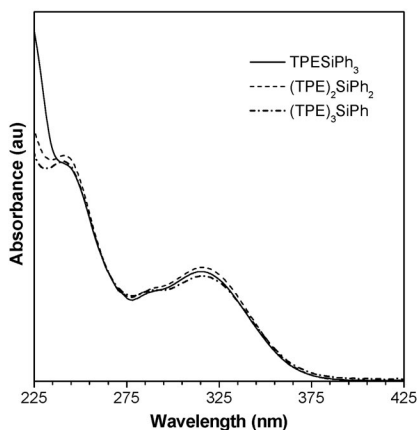


Fig. 2 Absorption spectra of TPESiPh₃, (TPE)₂SiPh₂, and (TPE)₃SiPh in THF solutions.

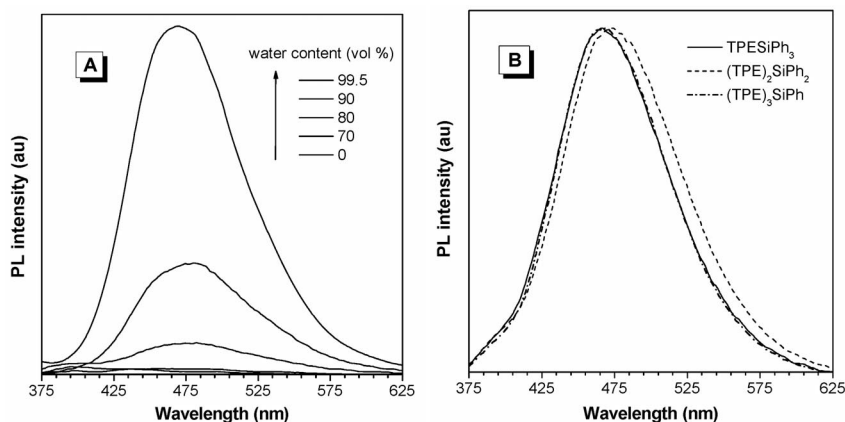


Fig. 3 PL spectra of (A) TPESiPh₃ in THF/water mixtures and (B) amorphous films of TPESiPh₃, (TPE)₂SiPh₂, and (TPE)₃SiPh. Solution concentration: 10 μM; excitation wavelength: 350 nm.

The spin-coated amorphous films of TPESiPh₃, (TPE)₂SiPh₂, and (TPE)₃SiPh also emit at similar wavelengths (Fig. 3B) to those in solutions with fluorescence quantum yields (Φ_F 's) of 63.7, 61.5, and 54.6 %, respectively, measured by integrating sphere. With an increase in the number of TPE unit, more rotors are present in the molecules. Efficient restriction of their motions would become difficult in the aggregate state, thus resulting in a gradual decrease in the Φ_F value from TPESiPh₃ to (TPE)₂SiPh₂, and then (TPE)₃SiPh.

Thermal stability

The thermal properties of the TPE-substituted silanes are examined by DSC and TGA analyses. Figures 4A,B show the TGA and DSC thermograms of TPESiPh₃, (TPE)₂SiPh₂, and (TPE)₃SiPh, respectively, recorded under nitrogen at a heating rate of 10 °C/min. All the molecules enjoy high thermal stability with 5 % weight loss occurring at 320–420 °C. The melting points of TPESiPh₃, (TPE)₂SiPh₂, and (TPE)₃SiPh measured by DSC are 202, 248, and 234 °C, respectively. (TPE)₂SiPh₂ shows the highest glass-transition temperature of 108 °C, while those for TPESiPh₃, and (TPE)₃SiPh are observed at 77 and 80 °C, respectively (Fig. 4B).

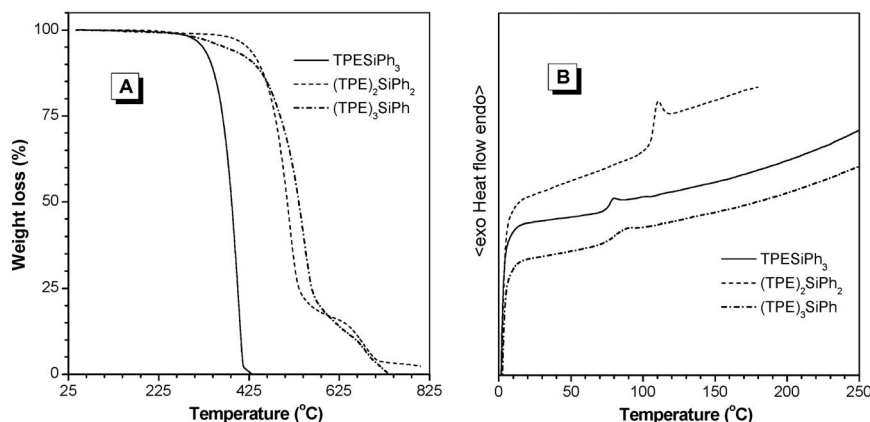


Fig. 4 (A) TGA and (B) DSC thermograms of second heating cycle of TPESiPh₃, (TPE)₂SiPh₂, and (TPE)₃SiPh recorded under nitrogen at a heating rate of 10 °C/min.

Redox activity

The dye molecules show almost the same electrochemical properties, irrespective of the number of TPE unit. No obvious reduction peaks are observed, while two oxidation peaks are observed for each molecule (Fig. 5). The first one is irreversible and found at ~ 0.9 V. On the contrary, the second peak is quasi-reversible and located at ~ 1.2 V. The onset oxidation potentials (E_{onset}) of all molecules are ~ 0.8 V, from which their highest occupied molecular orbital (HOMO) energy levels are calculated to be -5.2 eV by the equation $\text{HOMO} = -(E_{\text{onset}} + 4.4)$ [17]. The energy band gaps (E_g) of the TPE-substituted silanes calculated from the onset wavelengths of their absorption spectra are ~ 3.4 eV. From the equation lowest unoccupied molecular orbital (LUMO) = $-(\text{HOMO} + E_g)$, the LUMO energy levels are found at -1.8 eV. The large bandgap values of the molecules suggest that they are good candidates as host materials [13,14].

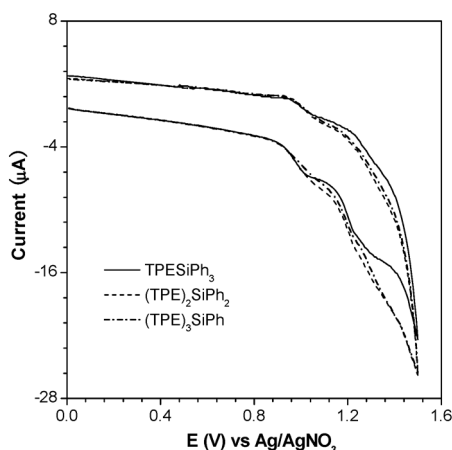


Fig. 5 Cyclic voltammograms of TPESiPh₃, (TPE)₂SiPh₂, and (TPE)₃SiPh in dichloromethane containing 0.1 M Bu₄NPF₆. Scan rate: 100 mV/s.

Electroluminescence

The high thermal stability and efficiency PL emission in the solid states of the TPE-substituted silanes encourage us to investigate their EL properties. We fabricated multilayer devices with a configuration of ITO/NPB(60 nm)/emitter(40 nm)/TPBi(20 nm)/LiF(1 nm)/Al(100 nm) by vapor deposition processes, in which TPESiPh₃, (TPE)₂SiPh₂, or (TPE)₃SiPh serves as emitting layer, NPB functions as hole-transport layer, and TPBi functions as electron-transport layer, respectively.

Figures 6 and 7 show the EL spectra, and the variation in the luminance and current density of the EL devices with the applied voltage, respectively. TPESiPh₃ shows a deep blue EL at 452 nm, which is 14 nm blue-shifted from the PL of its amorphous film. Since we found that the crystalline aggregates of some AIE-active molecules emit bluer PL than their amorphous counterparts, this suggests that the film of TPESiPh₃ is partially crystalline. The device shows a low turn-on voltage (5 V) and exhibits a maximum luminance of 5672 cd/m² at 18 V. The current and power efficiencies at 100 cd/m² are 2.1 cd/A and 1.1 lm/W, respectively (Table 1). The maximum external quantum efficiency attained by the device is 1.6 %. The emission of TPESiPh₃ is close to that of TPE (445 nm) but its EL performance is much better, suggesting that the EL properties of luminogenic silanes can be readily turned by molecular engineering endeavors [6]. Surprisingly, increasing the number of TPE unit from one in TPESiPh₃ to two and three in (TPE)₂SiPh₂ and (TPE)₃SiPh, respectively, has decreased the EL efficiency. Unlike TPESiPh₃, the ELs of (TPE)₂SiPh₂ and (TPE)₃SiPh are observed at longer wavelengths

than the PLs of their solid films, probably due to the microcavity effect or the formation of exci- or electroplexes between the emitter and the charge-transport layer [18–21]. The EL results, although preliminary, suggest that the TPE-substituted silanes are better blue emitters than most planar fluorophore-substituted silanes [9,10] and are promising luminescent materials to be useful in OLEDs.

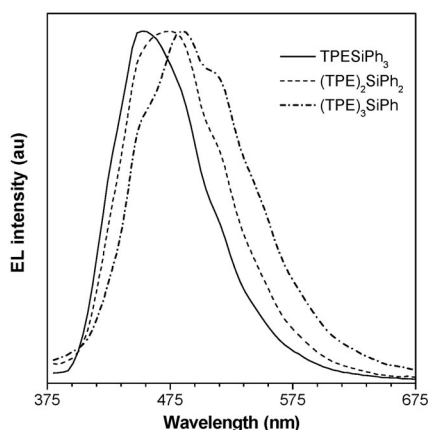


Fig. 6 EL spectra of multilayer EL devices of TPESiPh₃, (TPE)₂SiPh₂, and (TPE)₃SiPh with a configuration of ITO/NPB/emitter/TPBi/LiF/Al.

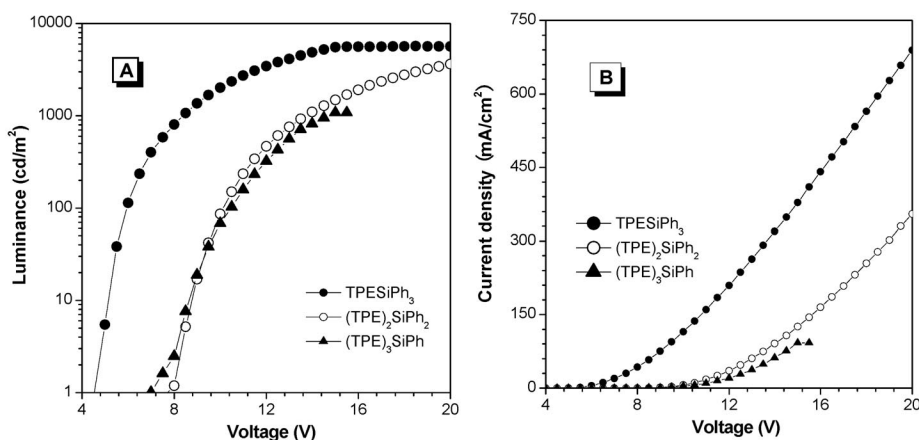


Fig. 7 (A) Luminance and (B) current density vs. voltage curves of multilayer EL devices of TPESiPh₃, (TPE)₂SiPh₂, and (TPE)₃SiPh with a configuration of ITO/NPB/emitter/TPBi/LiF/Al.

Table 1 EL performances of the TPE-substituted silanes^a.

Compound	λ_{EL} (nm)	V_{on} (V)	L_{max} (cd/m ²)	PE (lm/W)	CE (cd/A)	EQE_{max} (%)
TPESiPh ₃	452	5	5672	1.1	2.1	1.6
(TPE) ₂ SiPh ₂	472	8	3635	0.4	1.4	0.7
(TPE) ₃ SiPh	484	7	1081	0.47	1.6	0.8

^aAbbreviations: λ_{EL} = EL maximum, V_{on} = voltage at 1 cd/m², L_{max} = maximum luminance, PE and CE = power and current efficiencies at 100 cd/m². EQE_{max} = maximum external quantum efficiency.

CONCLUSION

In summary, we synthesized silane derivatives containing different numbers of TPE unit. These compounds show AIE feature and emit blue light in high fluorescence quantum yields in the solid states. They enjoy high thermal stability. Multilayer OLEDs utilizing the new molecules are fabricated, which give deep blue EL with maximum luminance and external quantum efficiencies of 5672 cd/m² and 1.6 %, respectively.

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