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Journal of
Materials Chemistry

Cite this: *J. Mater. Chem.*, 2012, **22**, 20266

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PAPER

Naphthalene-substituted 2,3,4,5-tetraphenylsiloles: synthesis, structure, aggregation-induced emission and efficient electroluminescence†

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Received 14th July 2012, Accepted 8th August 2012
DOI: 10.1039/c2jm34621d

Two thermally stable naphthalene-substituted 2,3,4,5-tetraphenylsiloles, 1,1-dimethyl-2,5-bis[4-(naphthalen-1-yl)phenyl]-3,4-diphenylsilole (D-1-NpTPS) and 1,1-dimethyl-2,5-bis[4-(naphthalen-2-yl)phenyl]-3,4-diphenylsilole (D-2-NpTPS), have been synthesized and fully characterized. D-2-NpTPS shows redder absorption and emission than D-1-NpTPS due to the better conjugation between naphthalen-2-yl groups and phenyl rings at the 2,5-positions of the silole core. While they are weakly fluorescent in solutions, strong luminescence is induced when aggregated in poor solvents or fabricated into solid films, with high fluorescence quantum yields up to 99%, demonstrating their aggregation-induced emission (AIE) feature. Efficient non-doped organic light-emitting diodes utilizing D-1-NpTPS and D-2-NpTPS as light-emitting layers are fabricated. Remarkably high electroluminescence efficiencies of 10.5 cd A^{-1}, 7.3 lm W^{-1}, and 3.2% are acheived by the D-2-NpTPS device.

Introduction

Efficient luminescent materials are highly pursued and have been the subject of tremendous investigation due to their various potential applications in materials science and biological technology. For real-world application in optoelectronic devices such as organic light-emitting diodes (OLEDs), light emitters usually have to be fabricated into thin solid films. However, many chromophores that show good light emission when molecularly dispersed in solutions become weakly fluorescent or non-fluorescent when fabricated into nanoparticles or thin solid films, presenting an intractable problem of aggregation-caused quenching (ACQ).[1] This effect undermines device performance and remains a difficult issue for the evolution of OLEDs, although many chemical approaches and engineering techniques have been proposed.[2] It would be advantageous if novel chromophores that did not suffer from the notorious ACQ effect could be developed.

Siloles (silacyclopentadienes) are silicon-containing five-membered cyclic dienes which have drawn considerable research interest due to their unique electronic structures and potential technological applications. The effective interaction between the σ* orbital of the silicon–carbon bond and the π* orbital of the butadiene fragment results in a low-lying lowest unoccupied molecular orbital (LUMO) energy level, endowing siloles with high electron affinity and fast electron mobility.[3] Recent studies have revealed that propeller-like 2,3,4,5-substituted siloles possess an excellent attribute in light emission. While these siloles are almost non-fluorescent in solutions, they fluoresce strongly in the aggregate state, which is attributed to the restriction of intramolecular rotation in the condensed phase.[4] Such a novel phenomenon, named "aggregation-induced emission (AIE)", is exactly the opposite of the ACQ effect observed in most conventional chromophores, and paves a new avenue for the design and synthesis of efficient solid-state emitters. Thanks to their intriguing AIE characteristic, 2,3,4,5-substituted siloles with tailored molecular architectures have surmounted the ACQ problem and shown great potential in chemosensors,[5] fluorescent bioimaging,[6] supermolecular self-assembly,[7] *etc.* In particular, many researchers have demonstrated that they are extremely good light emitters for non-doped OLEDs,[8] which avoid the complicated and hard-to-control processes of the doping techniques used to alleviate the ACQ effect in OLED fabrication.[9] In order to develop efficient solid-state emitters for OLEDs and to determine the structure–property relationship in silole-based luminogens, in this contribution we wish to report the synthesis and characterization of two new naphthalene-substituted

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† Electronic supplementary information (ESI) available: General information, device fabrication, preparation of nanoaggregates and Fig. S1 and S2. CCDC numbers: 888228, 886291 and 886292. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2jm34621d

2,3,4,5-tetraphenylsiloles. The impact of the different methods of conjugation between the naphthalene substituents and the silole core on the photoluminescence (PL) and electroluminescence (EL) properties of the resultant luminogens is investigated and discussed. High-performance OLEDs are achieved based on the new siloles.

Results and discussion

Synthesis

Scheme 1 illustrates the synthetic routes to the naphthalene-substituted 2,3,4,5-tetraphenylsiloles. The detailed procedures and characterization data are given in the experimental section. The key compound 2,5-bis(4-bromophenyl)-1,1-dimethyl-3,4-diphenylsilole (**3**) was prepared in good yield (70%) from dimethylbis(phenylethynyl)silane by a one-pot reaction similar to the method described in previously published papers.[10] It is a very useful intermediate, whose 4-bromophenyl groups can undergo various coupling reactions such as Suzuki, Heck and Sonogashira coupling reactions to afford desired compounds with different conjugation patterns. The treatment of **3** with 1- and 2-naphthylboronic acids in the presence of a palladium catalyst in basic medium generated the target compounds 1,1-dimethyl-2,5-bis[4-(naphthalen-1-yl)phenyl]-3,4-diphenylsilole (D-1-NpTPS) and 1,1-dimethyl-2,5-bis[4-(naphthalen-2-yl)phenyl]-3,4-diphenylsilole (D-2-NpTPS) in 89 and 41% yields, respectively. Both silole derivatives are soluble in common organic solvents including THF, dichloromethane, chloroform, toluene, *etc.* but are insoluble in water.

Crystal structure

Single crystals of D-1-NpTPS and D-2-NpTPS were grown from a THF–ethanol mixture and a chloroform solution, respectively, and analyzed by X-ray diffraction crystallography. The crystal structures of D-1-NpTPS and D-2-NpTPS are displayed in Fig. 1, which verifies the structures of both compounds. The crystals of the intermediate compound **3** were also obtained from its THF–methanol mixture, and the crystal structure is shown in Fig. S1 in the ESI.† Fig. 2B illustrates the packing manner of D-2-NpTPS molecules in the crystalline state. No π–π stacking between aromatic rings is found due to the propeller-like shape of the molecule. Multiple C–H···π hydrogen bonds with distances ranging from 2.686 to 3.097 Å are formed between adjacent molecules. These hydrogen bonds have effectively rigidified the molecular conformation and restricted the rotation of the aromatic rings, particularly the phenyl rings attached at the 3,4-positions of the silole core, whose low frequency intramolecular motions can consume the excited state energy, resulting in the quite faint fluorescence of substituted siloles.[4d,7a] Therefore, these C–H···π hydrogen bonds are conducive to reducing nonradiative decay of the excited state and thus enhancement of emission efficiency.[4c,11] Similarly, multiple C–H···π hydrogen bonds are also observed in the crystals of D-1-NpTPS but no π–π stacking is found (Fig. 2A).

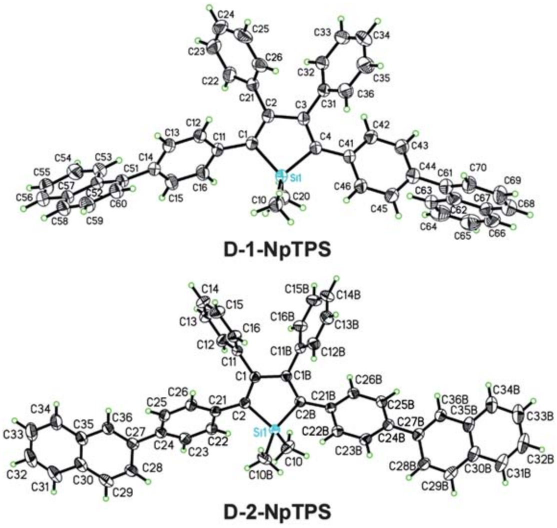
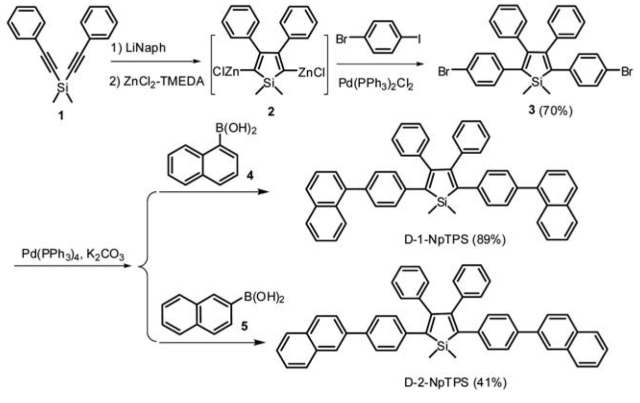


Fig. 1 ORTEP drawings of D-1-NpTPS (CCDC 886291) and D-2-NpTPS (CCDC 886292).



Scheme 1 Synthetic routes to naphthalene-substituted 2,3,4,5-tetraphenylsiloles.

Thermal stability

The thermal properties of D-1-NpTPS and D-2-NpTPS were examined by differential scanning calorimetry (DSC) and

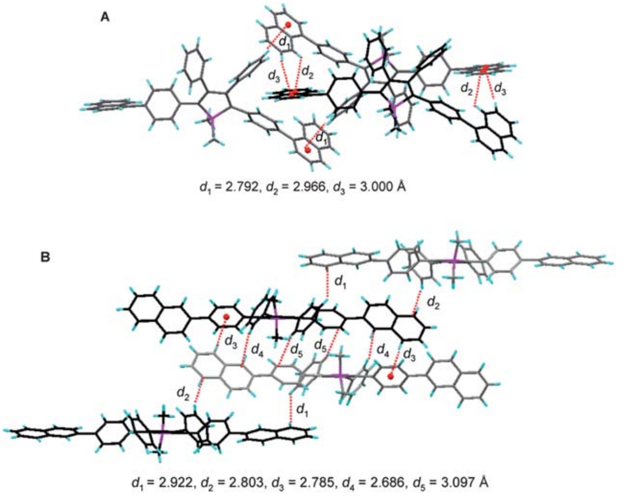


Fig. 2 Molecular packing of (A) D-1-NpTPS and (B) D-2-NpTPS in crystals, with C–H···π hydrogen bonds indicated.

thermogravimetric analysis (TGA) measurements. The DSC thermograms reveal that D-1-NpTPS has a glass-transition temperature (T_g) of 97 °C, while no T_g is detected for D-2-NpTPS. As shown in Fig. 3, both luminogens have good thermal stability and decompose at high temperatures (T_d) (408 °C for D-1-NpTPS and 396 °C for D-2-NpTPS), suggesting that they are thermally stable enough for vapor deposition for the film fabrication.

Optical properties

The UV-vis absorption spectra of D-1-NpTPS and D-2-NpTPS in THF solutions are shown in Fig. 4A. D-2-NpTPS exhibits an absorption maximum at 385 nm, which is red-shifted by 11 nm compared with that of D-1-NpTPS, suggesting that D-2-NpTPS has a longer conjugation length than D-1-NpTPS. The PL emissions of D-1-NpTPS and D-2-NpTPS in THF solutions are very weak. Only faint PL signals with maxima at 496 and 508 nm are recorded (Fig. 4B). The fluorescence quantum yields of D-1-NpTPS and D-2-NpTPS in dilute THF solutions are as low as 1.39 and 2.32%, respectively, measured using 9,10-diphenylanthracene ($\Phi_F = 90\%$ in cyclohexane) as a standard. Although the Φ_F values are low, they are much higher than those of the parent siloles without naphthalene substituents, 1,1-dimethyl-2,3,4,5-tetraphenylsilole (TPS), 1-methyl-1,2,3,4,5-pentaphenylsilole (MPPS) and 1,1,2,3,4,5-hexaphenylsilole (HPS), due to the elongated conjugation with additional aromatic hydrocarbons.[8e,f] Both siloles are highly emissive in the solid state. The films of D-1-NpTPS and D-2-NpTPS fluoresce intensely with emission maxima at 502 and 510 nm, respectively. Only slight bathochromic shifts are observed in the PL spectra of the films relative to those of the solutions, thanks to the propeller-like conformations that impede close π–π stacking between molecules. The Φ_F values of the films are as high as 99% and 92% for D-1-NpTPS and D-2-NpTPS, respectively, estimated by integrating sphere, which are greatly improved compared with that of the TPS parent, implying that the elongation of conjugation length is beneficial to the light emission of silole-based luminogens. The excellent solid-state Φ_F values reveal that both new luminogens are excellent light-emitting materials for non-doped OLEDs (Table 1).

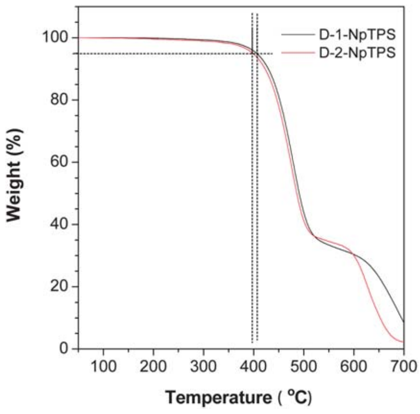


Fig. 3 TGA thermograms of D-1-NpTPS and D-2-NpTPS under nitrogen at a heating rate of 10 °C min^{-1}.

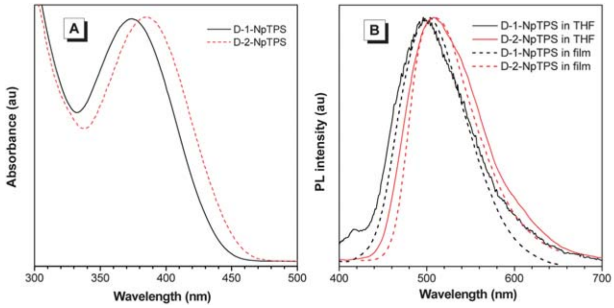


Fig. 4 (A) Absorption spectra of D-1-NpTPS and D-2-NpTPS in THF solutions. (B) PL spectra of D-1-NpTPS and D-2-NpTPS in THF solutions (10 μM) and in films. Excitation wavelength: 350 nm.

The drastically enhanced Φ_F values of the solid films suggest that the new silole derivatives have inherited the AIE feature from the TPS parent. To further confirm the AIE attribute, PL spectra of D-1-NpTPS and D-2-NpTPS in THF–water mixtures were measured. With the addition of water to the THF solution of D-1-NpTPS, the emission intensity starts to increase slightly. When the water fraction becomes higher ($f_w \geq 70$ vol%), the emission intensity enhances swiftly (Fig. 5). D-2-NpTPS exhibits similar emission behavior in THF–water mixtures (Fig. S2†). Since D-1-NpTPS and D-2-NpTPS are insoluble in water, their molecules must have aggregated in the aqueous mixtures with high water content. The intramolecular rotation process that is active in the solution state is restricted due to steric hindrance and C–H⋯π hydrogen bonds in the aggregate state, which blocks the nonradiative relaxation channel and promotes radiative decay of the excited state. These results demonstrate that both silole derivatives are indeed AIE-active.

Theoretical calculations

To gain a deep insight into the relationship between the optical properties and the conjugation pattern of the naphthalene substituents with TPS, density functional theory calculations were performed on D-1-NpTPS and D-2-NpTPS. The nonlocal density functional of B3LYP with 6-31G(d) basis sets was used for the calculation. The optimized structures and the orbital distributions of the HOMO and LUMO energy levels of D-1-NpTPS and D-2-NpTPS are shown in Fig. 6. As can be seen from the optimized structure, the dihedral angle between the planes of the naphthalene ring and the adjacent phenyl ring is 55.55° in

Table 1 Optical and thermal properties of naphthalene-substituted 2,3,4,5-tetraphenylsiloles

	λ_{abs} (nm)	λ_{em} (nm)		Φ_F (%)		
	Soln[a]	Soln[a]	Film[b]	Soln[c]	Film[d]	T_g/T_d (°C)
D-1-NpTPS	374	496	502	1.39	99	97/408
D-2-NpTPS	385	508	510	2.32	92	—/396

[a] In THF solution (10 μM). [b] Film drop-cast on a quartz plate. [c] Fluorescence quantum yields determined in THF solutions using 9,10-diphenylanthracene ($\Phi_F = 90\%$ in cyclohexane) as a standard. [d] Fluorescence quantum yields of the amorphous films measured by integrating sphere.

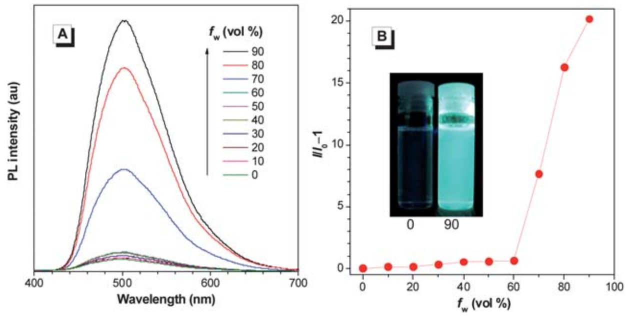


Fig. 5 (A) PL spectra of D-1-NpTPS in THF–water mixtures with different water fractions (f_w). (B) Plot of ($I/I_0 - 1$) values *versus* water fractions in THF–water mixtures of D-1-NpTPS. I_0 is the PL intensity in pure THF solution. Inset: photos of D-1-NpTPS in THF–water mixtures ($f_w = 0$ and 90%) taken under the illumination of a UV lamp.

D-1-NpTPS, while it is 36.70° in D-2-NpTPS, revealing that the naphthalene ring conjugates better with the TPS through its 2-position than the 1-position. Since D-2-NpTPS possesses a longer conjugation length than D-1-NpTPS, the calculated energy band gap of D-2-NpTPS (3.37 eV) is narrower than that of D-1-NpTPS (3.51 eV). These results are in accordance with the optical values obtained from the onset of absorption spectra ($E_g = 2.75$ eV for D-1-NpTPS and $E_g = 2.67$ eV for D-2-NpTPS). From the LUMOs it can be seen that an intense electron cloud is located on the exocyclic Si–C single bonds at the 1-position of the silole ring, indicating that effective σ*–π* conjugation exists in both luminogens. D-1-NpTPS and D-2-NpTPS have low-lying LUMO energy levels of −1.71 and −1.77 eV, respectively, which are lower than those of TPS, MPPS and HPS,[8e] implying that electron-injection is more favorable in these silole derivatives than their parent.

Electrochemical properties

The electrochemical properties of D-1-NpTPS and D-2-NpTPS were investigated by cyclic voltammetry (CV). Both luminogens exhibit similar CV curves with two irreversible oxidation peaks (Fig. 7). The oxidation onset potentials (E_{onset}) of D-1-NpTPS and D-2-NpTPS occur at 1.12 and 1.08 V, respectively, from which the HOMO energy levels are calculated to be −5.52 and −5.48 eV (HOMO = $-(4.4 + E_{\mathrm{onset}})$). Their LUMO energy levels can be obtained from the optical band gap energies (E_g) and the HOMO values (LUMO = $-(\mathrm{HOMO} + E_g)$), and are located at −2.77 and −2.81 eV. The CV measurement reveals that D-2-NpTPS possesses a slightly higher HOMO energy level and lower LUMO energy level in comparison with those of D-1-NpTPS, which agrees with the calculated results.

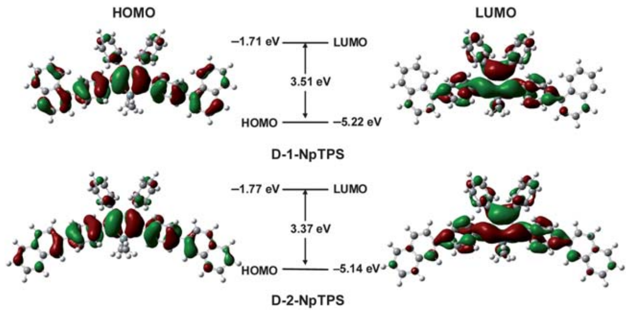


Fig. 6 B3LYP/6-31G(d) calculated molecular orbital amplitude plots of the HOMO and LUMO energy levels of D-1-NpTPS and D-2-NpTPS.

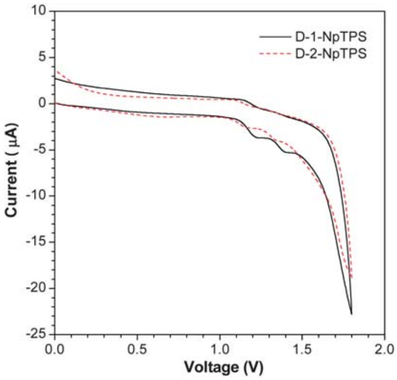


Fig. 7 Cyclic voltammograms of D-1-NpTPS and D-2-NpTPS measured in dichloromethane containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate. Scan rate: 100 mV s^{-1}.

Electroluminescence

The good thermal stability and efficient solid state PL emission of D-1-NpTPS and D-2-NpTPS encouraged us to examine their EL properties. Multilayer OLEDs with a configuration of ITO/NPB (60 nm)/D-1-NpTPS or D-2-NpTPS (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm) were fabricated, where D-1-NpTPS and D-2-NpTPS work as light-emitting layers, *N*,*N*-bis(1-naphthyl)-*N*,*N*-diphenylbenzidine (NPB) functions as the hole-transporting layer and 2,2′,2″-(1,3,5-benzinetriyl)tris(1-phenyl-1-*H*-benzimidazole) (TPBi) serves as the electron-transporting layer. The device performances are listed in Table 2 and the EL spectra and characteristic curves of the devices are shown in Fig. 8. D-1-NpTPS exhibits an EL emission maximum at 512 nm, which is slightly red-shifted by 10 nm compared to the PL in the film. The device of D-1-NpTPS is turned on at 4.7 V, corresponding to a luminance of 1 cd m^{-2}, and gives a maximum luminance ($L_{\max}$) of 15 700 cd m^{-2}. The maximum current efficiency ($\eta_{\mathrm{C,max}}$), power efficiency ($\eta_{\mathrm{P,max}}$), and external quantum efficiency ($\eta_{\mathrm{ext,max}}$) attained by the device are 4.9 cd A^{-1}, 1.8 lm W^{-1}, and 1.6%, respectively. The EL emission maximum of D-2-NpTPS is located at 536 nm, and a strong bathochromic shift is observed in comparison with the PL in the film, probably due to the microcavity effect. The D-2-NpTPS-based device shows a low turn-on voltage of 4.4 V, and a $L_{\max}$ of 9420 cd m^{-2}. The $\eta_{\mathrm{C,max}}$, $\eta_{\mathrm{P,max}}$ and $\eta_{\mathrm{ext,max}}$ obtained from the device of D-2-NpTPS are

Table 2 EL performances of D-1-NpTPS and D-2-NpTPS[a]

	EL (nm)	V_{on} (V)	$L_{\max}$ (cd m^{-2})	$\eta_{\mathrm{P,max}}$ (lm W^{-1})	$\eta_{\mathrm{C,max}}$ (cd A^{-1})	$\eta_{\mathrm{ext,max}}$ (%)
D-1-NpTPS	512	4.7	15 700	1.8	4.9	1.6
D-2-NpTPS	536	4.4	9420	7.3	10.5	3.2

[a] Abbreviations: V_{on} = turn-on voltage at 1 cd m^{-2}, $L_{\max}$ = maximum luminance, $\eta_{\mathrm{P,max}}$, $\eta_{\mathrm{C,max}}$, and $\eta_{\mathrm{ext,max}}$ = maximum power, current, and external quantum efficiencies, respectively.

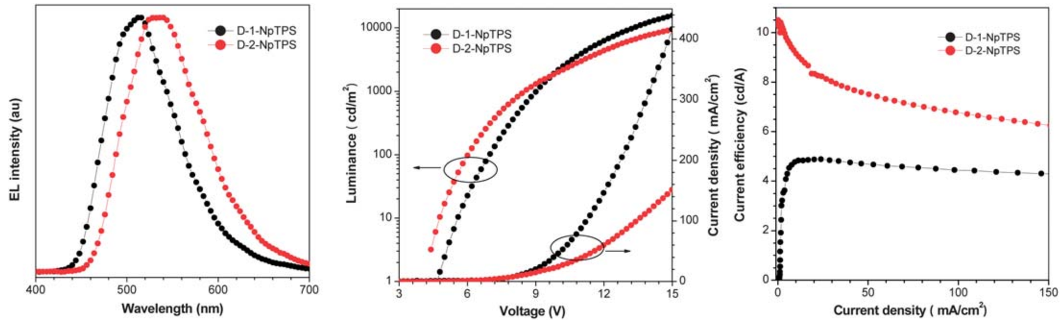


Fig. 8 (A) EL spectra of D-1-NpTPS and D-2-NpTPS, (B) change in luminance and current density with the applied voltage and (C) plots of current efficiency *versus* current density in multilayer devices with a configuration of ITO/NPB (60 nm)/emitter (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm).

10.5 cd A^{-1}, 7.3 lm W^{-1}, and 3.2%, respectively, which are increased more than two-fold with respect to those of the device of D-1-NpTPS, clearly demonstrating that D-2-NpTPS outperforms D-1-NpTPS as light-emitting material. Since the device configuration is yet to be optimized, the performances of the D-2-NpTPS-based device are slightly inferior to those of MPPS and HPS attained by their most efficient OLEDs. The performances, however, have progressed greatly in comparison with those of EL devices fabricated from other silole-based light emitters.[12] It is expected that more efficient non-doped OLEDs will be achieved through the exploration of new solid-state emitters based on siloles, as well as device configuration optimization. The $\eta_{C,max}$ value (10.5 cd A^{-1}) of the D-2-NpTPS-based device is among the most efficient of non-doped OLEDs in the literature,[13–15] indicating that D-2-NpTPS is a promising host emitter for OLEDs.

Conclusions

In summary, two thermally stable naphthalene-substituted silole derivatives (D-1-NpTPS and D-2-NpTPS) are synthesized and fully characterized. The attachment of 2-naphthyl groups leads to better conjugation than 1-naphthyl groups, and thus redder absorption and emission of the resultant luminogen. Both D-1-NpTPS and D-2-NpTPS possess an AIE feature and are highly emissive in the solid state, with high Φ_F values up to 99%. Multilayer devices fabricated using D-1-NpTPS and D-2-NpTPS as host emitters perform outstandingly, and remarkably high EL efficiencies ($\eta_{C,max}$ = 10.5 cd A^{-1}, $\eta_{P,max}$ = 7.3 lm W^{-1}, and $\eta_{ext,max}$ = 3.2%) are attained by the device of D-2-NpTPS, suggesting that they are excellent host emitters. These results demonstrate that chemical modification of the 2,3,4,5-substituted siloles is a feasible approach to creating efficient luminescent materials for non-doped OLEDs.

Experimental

Synthesis

2,5-Bis(4-bromophenyl)-1,1-dimethyl-3,4-diphenylsilole (3). A solution of lithium naphthalenide (LiNaph) was prepared by stirring a mixture of naphthalene (2.56 g, 20 mmol) and lithium granular (0.14 g, 20 mmol) in dry THF (30 mL) for 4 h at room temperature under nitrogen. A solution of bis(phenylethynyl) dimethylsilane (**1**) (1.3 g, 5 mmol) in THF (20 mL) was then added dropwise into the solution of LiNaph, and the resultant mixture was stirred for 1 h at room temperature. After the solution was cooled to −10 °C, $ZnCl_2$–TMEDA (6.3 g, 25 mmol) and 20 mL of THF were added. The fine suspension was stirred for 1 h at room temperature, and $Pd(PPh_3)_2Cl_2$ (210 mg, 0.3 mmol), 1-bromo-4-iodobenzene (3.5 g, 12.5 mmol), and 10 mL THF were then added. After refluxing for 12 h, the reaction was cooled to room temperature and terminated by the addition of 1 M hydrochloric acid. The mixture was poured into water and extracted with dichloromethane. The organic layer was washed successively with aqueous sodium chloride solution and water, and dried over magnesium sulfate. After filtration, the solvent was evaporated under reduced pressure and the residue was purified by silicon-gel column chromatography using *n*-hexane as the eluent. A yellow solid of **3** was obtained in 70% yield based on the amount of **1** used. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.25–7.23 (d, 4H, J = 8.0 Hz), 7.04–7.00 (m, 6H), 6.78–6.76 (m, 8H), 0.45 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 153.87, 140.14, 138.00, 137.53, 130.51, 129.72, 129.16, 126.96, 125.88, 118.91, −4.65. HRMS (MALDI-TOF): *m*/*z* 571.9918 (M^+, calcd 571.9994).

1,1-Dimethyl-2,5-bis[4-(naphthalen-1-yl)phenyl]-3,4-diphenylsilole (D-1-NpTPS). A mixture of **3** (0.57 g, 1 mmol), 1-naphthylboronic acid (0.41 g, 2.4 mmol), $Pd(PPh_3)_4$ (0.11 g, 0.1 mmol), and potassium carbonate (1.1 g, 8 mmol) in 150 mL of toluene/ethanol/water (8/1/1 v/v/v) was heated to reflux for 12 h under nitrogen. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using hexane/dichloromethane as the eluent. A yellow solid of D-1-NpTPS was obtained in 89% yield (0.59 g). ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.94–7.88 (m, 4H), 7.84–7.82 (d, 2H, J = 8.4 Hz), 7.52–7.40 (m, 8H), 7.29–7.27 (d, 4H, J = 7.6 Hz), 7.09–7.07 (d, 10H, J = 6.4 Hz), 6.93–6.92 (m, 4H), 0.65 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 153.74, 140.68, 139.51, 138.41, 138.10, 137.23, 133.21, 130.93, 129.40, 129.06, 128.15, 127.62, 126.92, 126.80, 126.22, 125.70, 125.44, 125.25, 125.05, 124.74, −4.02. HRMS (MALDI-TOF): *m*/*z* 666.2740 (M^+, calcd 666.2743).

1,1-Dimethyl-2,5-bis[4-(naphthalen-2-yl)phenyl]-3,4-diphenylsilole (D-2-NpTPS). The procedure was analogous to that described for D-1-NpTPS. Yellow solid, yield 41%. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.01 (s, 2H), 7.89–7.83 (m, 6H), 7.73–7.71 (d, 2H, J = 8.8 Hz), 7.54–7.46 (m, 8H), 7.08–7.06

(d, 10H, $J = 8.0$ Hz), 6.91–6.90 (m, 4H), 0.60 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 153.67, 140.54, 138.35, 138.28, 137.45, 137.30, 133.05, 131.88, 129.36, 128.83, 127.67, 127.51, 126.97, 126.20, 125.70, 125.57, 125.14, 124.68, 124.65, −4.07. HRMS (MALDI-TOF): m/z 666.2744 (M^+, calcd 666.2743).

X-ray crystallography

Crystal data for **3** (CCDC 888228): $C_{30}H_{24}Br_2Si\cdot CH_3OH$, $MW = 604.44$, monoclinic, $P2(1)/c$, $a = 20.6335(19)$, $b = 14.6119(13)$, $c = 9.6084(9)$ Å, $\beta = 103.327(2)°$, $V = 2818.9(4)$ Å^3, $Z = 4$, $D_c = 1.424$ g cm^{-3}, $\mu = 2.940$ mm^{-1} (MoKα, $\lambda = 0.71073$), $F(000) = 1224$, $T = 296(2)$ K, $2\theta_{max} = 55$ (99.5%)°, 24 638 measured reflections, 6440 independent reflections ($R_{int} = 0.0413$), GOF on $F^2 = 1.016$, $R_1 = 0.0987$, w$R_2 = 0.1756$ (all data), Δe 0.681 and −0.489 eÅ^{-3}.

Crystal data for D-1-NpTPS (CCDC 886291): $C_{50}H_{38}Si\cdot THF$, $MW = 739.00$, triclinic, $P\bar{1}$, $a = 10.9439(6)$, $b = 13.7898(7)$, $c = 14.4698(7)$ Å, $\alpha = 101.357(4)$, $\beta = 99.878(4)$, $\gamma = 97.211(4)°$, $V = 2080.31(19)$ Å^3, $Z = 2$, $D_c = 1.180$ g cm^{-3}, $\mu = 0.784$ mm^{-1} (MoKα, $\lambda = 1.5418$), $F(000) = 784$, $T = 173.00(14)$ K, $2\theta_{max} = 66.5$ (96.5%)°, 12 066 measured reflections, 7231 independent reflections ($R_{int} = 0.0311$), GOF on $F^2 = 1.017$, $R_1 = 0.0787$, w$R_2 = 0.1828$ (all data), Δe 0.809 and −0.244 eÅ^{-3}.

Crystal data for D-2-NpTPS (CCDC 886292): $C_{50}H_{38}Si$, $MW = 666.89$, monoclinic, $P2/c$, $a = 25.5955(3)$, $b = 10.43900(10)$, $c = 13.54670(10)$ Å, $\beta = 90.9540(10)°$, $V = 3619.06(6)$ Å^3, $Z = 4$, $D_c = 1.224$ g cm^{-3}, $\mu = 0.828$ mm^{-1} (MoKα, $\lambda = 1.5418$), $F(000) = 1408$, $T = 173.00(14)$ K, $2\theta_{max} = 66.5$ (99.0%)°, 21 793 measured reflections, 6474 independent reflections ($R_{int} = 0.0364$), GOF on $F^2 = 1.013$, $R_1 = 0.0421$, w$R_2 = 0.1041$ (all data), Δe 0.217 and −0.274 eÅ^{-3}.

Acknowledgements

We acknowledge financial support from the National Natural Science Foundation of China (21074028, 21104012 and 91127032), the Natural Science Foundation of Zhejiang Province (Y4110331), the Project of Zhejiang Key Scientific and Technological Innovation Team (2010R50017), the RPC and SRFI Grants of HKUST (RPC10SC13, RPC11SC09, and SRFI11SC03PG), the Research Grants Council of Hong Kong (604711, 603509, HKUST2/CRF/10, and N_HKUST620/11), the Innovation and Technology Commission (ITCPD/17-9) and the University Grants Committee of Hong Kong (AoE/P-03/08 and T23-713/11-1). Z.Z. thanks the financial support from the Initial Funding of Hangzhou Normal University (HSQK0085).

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