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Abstract. 2,3,4,5-Tetraarylsiloles are efficient solid-state luminescent materials with good electron-transporting ability. Substitution at the 2,5-positions of silole rings produce various outstanding functional materials that can be used as active layers in organic light-emitting diodes (OLEDs). In this work, two 2,5-dicarbazole-substituted siloles, (2-Cz)₂MTPS and (3-Cz)₂MTPS, are facilely synthesized and fully characterized. Their thermal, photophysical, electrochemical, and electroluminescent properties are investigated systematically. The results show that these 2,5-dicarbazole-functioned siloles are thermally stable and feature aggregation-enhanced emission characteristics with high solid-state photoluminescence efficiencies. Nondoped OLEDs [ITO/N,N'-di(1-naphthyl)-N,N'-diphenyl-benzidine (NPB) (60 nm)/emitter (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm)] fabricated by adopting (2-Cz)₂MTPS and (3-Cz)₂MTPS as light-emitting layers exhibit good performances, with high luminance of 28240 cd m⁻² and electroluminescence efficiency of 4.5 cd A⁻¹. © 2015 Society of Photo-Optical Instrumentation Engineers (SPIE) [DOI: [10.1117/1.JPE.5.053598](https://doi.org/10.1117/1.JPE.5.053598)]

Keywords: aggregation-induced emission; organic light-emitting diode; fluorescence quantum yield; silole; carbazole.

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1 Introduction

Organic light-emitting diodes (OLEDs) have attracted considerable attention due to their potential real-world applications in flat-panel displays and solid-state lighting.¹⁻³ Although numerous organic electroluminescent (EL) materials including polymers and small organic molecules are thoroughly studied for utilization in OLEDs, in recent years, most of them have encountered some stubborn problems. For instance, many conventional luminescent materials are highly fluorescent in good solvents but suffer from notorious aggregation-caused quenching (ACQ) when fabricated into solid films or nanoparticles, which limits their practical application in OLEDs. To address this issue, various chemical, physical, and engineering approaches have been proposed, but they can only partially solve the problem and often result in detrimental side effects.⁴⁻⁶ Therefore, the best way to mitigate the ACQ problem is to develop a system in which light emission is enhanced rather than quenched by the aggregate formation. Delightfully, the discovery of the intriguing phenomenon of aggregation-induced emission (AIE)⁷ from 1,2,3,4,5-pentaphenylsilole (MPPS) opens up a new avenue to conquer the ACQ problem. So far, plentiful organic materials featuring AIE characteristics have been synthesized and applied to nondoped

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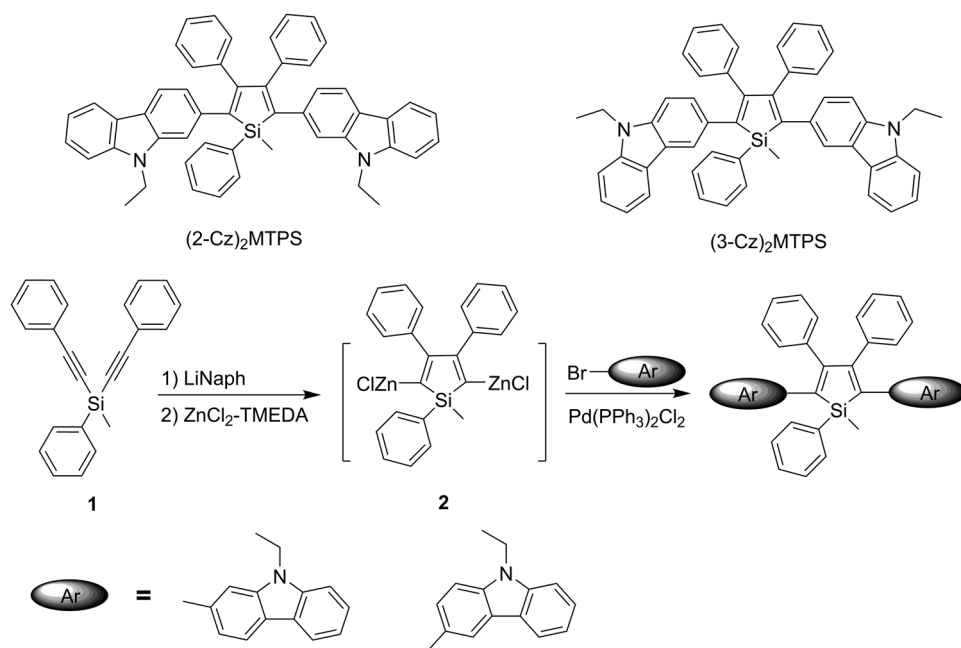


Fig. 1 Synthetic routes to $(2\text{-Cz})_2\text{MTPS}$ and $(3\text{-Cz})_2\text{MTPS}$. LiNaph = Lithium 1-naphthalenide; TMEDA = *N, N, N', N'*-tetramethylethylenediamine.

OLEDs as efficient light-emitting materials, which sheds light on a practically valid method to solve the ACQ problem of most conventional EL materials.^{8–14}

As one of the first reported AIE luminogens, siloles have become attractive building blocks for the design and synthesis of EL materials not only because of their high solid-state fluorescence efficiencies but also because of their unique electronic structures.^{15–22} The $\sigma^* - \pi^*$ conjugation between the σ^* orbitals of two exocyclic silicon-carbon bonds and the π^* orbital of the butadiene moiety contributes to the low-lying lowest unoccupied molecular orbital (LUMO) and high electron-transporting ability.^{23–26} Recently, Jorner et al.²⁷ have also described a new conceptual model of how substituents impact the excitation energies of siloles. The model is based on Baird's rule and the excited-state aromaticity and antiaromaticity, which can help to understand the electronic states of substituted siloles.^{27,28} Since the 2,5-substituents exert an important impact on the electronic and optical properties of siloles,²³ a great many silole-based materials have been designed and synthesized through the combination of the silole ring with functional substituents at the 2,5-positions. In our previous works, we had developed various 2,5-substituted siloles, which can function as excellent solid-state emitters or electron transporters.^{29–33} Herein, we report the synthesis and characterization of two new silole derivatives, $(2\text{-Cz})_2\text{MTPS}$ and $(3\text{-Cz})_2\text{MTPS}$, 2,5-substituted with carbazole moieties (Fig. 1). These two new siloles are composed of the same building blocks, but the connection patterns are different, which can cause different effective conjugation lengths, different electron donor–acceptor interactions, and, consequently, different optical properties. The thermal, photophysical, electrochemical, and EL properties of the new siloles are investigated systematically, providing useful information about the structure–property relationship of silole derivatives. The results also demonstrate that they are in the list of efficient AIE luminogens with potential applications in non-doped OLEDs.

2 Experimental Section

2.1 Materials and Instruments

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. Compound **1**²⁵ was prepared according to the method in the literature.

All the other chemicals and reagents were purchased from commercial sources and used as received without further purification. NMR spectra were obtained on a Bruker AV 500 spectrometer. High resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operating in MALDI-TOF mode. UV-visible absorption spectra were measured on a SHIMADZU UV-2600 spectrophotometer. Fluorescence spectra were recorded on a Horiba Fluoromax-4 fluorescence spectrophotometer. Fluorescence quantum yields were measured using a Hamamatsu absolute photoluminescence (PL) quantum yield spectrometer C11347 Quantaaurus_QY. Thermogravimetric analysis (TGA) was carried on a TA TGA Q5000 under dry nitrogen at a heating rate of $10^{\circ}\text{C min}^{-1}$. Thermal transitions were investigated by differential scanning calorimetry (DSC) using a NETZSCH DSC-204(F1) instrument under dry nitrogen at a heating rate of $10^{\circ}\text{C min}^{-1}$. Cyclic voltamograms were measured on a CHI 610E A14297.

2.2 Device Fabrication

Glass substrates precoated with a 170-nm thin layer of indium tin oxide (ITO) with a sheet resistance of 10Ω per square were thoroughly cleaned in an ultrasonic bath of acetone, isopropyl alcohol, detergent, deionized water, and isopropyl alcohol and treated with O_2 plasma for 20 min in sequence. Organic layers were deposited onto the ITO-coated substrates by high-vacuum ($<5 \times 10^{-4}$ Pa) thermal evaporation. A 60-nm thin hole-transporting layer (HTL) N,N'-di(1-naphthyl)-N,N'-diphenyl-benzidine (NPB) was deposited. Next, a 20-nm thin of emitter was deposited to form emitting layer (EML). Finally, a 40-nm thin electron-transporting layer (ETL) of TPBi was deposited. Cathodes, consisting of a 1-nm thin layer of LiF followed by a 100-nm thin layer of Al, were patterned using a shadow mask with an array of $3 \text{ mm} \times 3 \text{ mm}$ openings. Deposition rates are 1 to 2 \AA s^{-1} for organic materials, 0.1 \AA s^{-1} for LiF, and 6 \AA s^{-1} for Al, respectively. EL spectra were taken by an optical analyzer, Photo Research PR705. The current density and luminance versus driving voltage characteristics were measured by Keithley 2420 and Konica Minolta chromameter CS-200, respectively.

2.3 Synthesis

2,5-Bis(9-ethylcarbazol-2-yl)-1-methyl-1,3,4-triphenylsilole [(2-Cz)₂MTPS]: A solution of lithium 1-naphthalenide (LiNaph) was prepared by stirring a mixture of naphthalene (2.56 g, 20.0 mmol) and lithium granular (0.14 g, 20.0 mmol) in dry THF (30 mL) for 4 h at room temperature under nitrogen. A solution of **1** (1.61 g, 5.0 mmol) in dry THF (20 mL) was then added dropwise into the solution of LiNaph, and the resultant mixture was stirred for 30 min at room temperature. The solution was cooled to -10°C , into which ZnCl_2 -TMEDA (6.3 g, 25.0 mmol) and 20 mL of THF were added. After the fine suspension was stirred for 1 h, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (100 mg) and a solution of 2-bromo-9-ethyl-9H-carbazole (2.73 g, 10.0 mmol) in 10 mL THF were added. After reflux for 12 h, the reaction was cooled to room temperature and terminated by addition of 2 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 then dried over magnesium sulfate. After filtration, the solvent was evaporated under reduced pressure and the residue was purified by silica-gel column chromatography. (2-Cz)₂MTPS was obtained as a yellow solid in 51% yield. $^1\text{H NMR}$ (500 MHz, CD_2Cl_2), δ (ppm): 7.99 (d, 2H, $J = 7.5$ Hz), 7.90 to 7.88 (m, 2H), 7.83 (d, 2H, $J = 8.0$ Hz), 7.48 to 7.40 (m, 5H), 7.35 (d, 2H, $J = 8.0$ Hz), 7.19 to 7.10 (m, 12H), 6.96 (d, 2H, $J = 8.0$ Hz), 6.90 (s, 2H), 4.03 (q, 4H, $J = 7.0$ Hz), 1.13 (t, 6H, $J = 7.0$ Hz), 1.01 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3), δ (ppm): 155.54, 140.97, 140.35, 139.91, 139.81, 136.90, 134.72, 134.24, 130.06, 129.95, 128.31, 127.73, 126.40, 125.28, 122.64, 120.85, 120.76, 119.98, 119.49, 118.59, 109.08, 108.22, 37.13, 13.29, -6.26 . HRMS ($\text{C}_{51}\text{H}_{42}\text{N}_2\text{Si}$): m/z 710.3119 [M^+ , calcd 710.3117].

2,5-Bis(9-ethylcarbazol-3-yl)-1-methyl-1,3,4-triphenylsilole [(3-Cz)₂MTPS]: The procedure was analogous to that described for (2-Cz)₂MTPS. Yellow solid; yield 17%. $^1\text{H NMR}$ (500 MHz, CD_2Cl_2), δ (ppm): 7.90 to 7.89 (m, 2H), 7.75 to 7.73 (m, 2H), 7.64 to 7.63 (m, 2H), 7.48 to 7.42 (m, 5H), 7.39 (d, 2H, $J = 8.0$ Hz), 7.18 to 7.10 (m, 16H), 4.31 (q, 4H, $J = 7.5$ Hz), 1.40 (t, 6H, $J = 7.0$ Hz), 1.01 to 1.00 (m, 3H). $^{13}\text{C NMR}$ (125 MHz,

CDCl_3), δ (ppm): 154.49, 140.17, 140.16, 139.89, 138.31, 134.78, 134.62, 130.21, 130.17, 129.82, 128.26, 127.65, 127.48, 126.13, 125.43, 122.84, 122.54, 120.68, 119.91, 118.58, 108.37, 107.85, 37.50, 13.56, -6.18 . HRMS ($\text{C}_{51}\text{H}_{42}\text{N}_2\text{Si}$): m/z 710.3082 [M^+ , calcd 710.3117].

3 Results and Discussions

3.1 Synthesis

The target dicarbazole-functioned siloles, $(2\text{-Cz})_2\text{MTPS}$ and $(3\text{-Cz})_2\text{MTPS}$, were facilely synthesized according to the synthetic routes illustrated in Fig. 1. The detailed procedures and characterization data are given in Sec. 2. Briefly, treatment of **1** with lithium 1-naphthalenide (LiNaph) followed by addition of $\text{ZnCl}_2\text{-TMEDA}$ afforded 2,5-metalated silole intermediate (**2**). Without purification, **2** underwent a coupling reaction with arylbromide in the presence of a palladium catalyst, yielding the final products in moderate yields. $(2\text{-Cz})_2\text{MTPS}$ and $(3\text{-Cz})_2\text{MTPS}$ were fully characterized by NMR and mass spectroscopies, which verified their molecular structures. They are soluble in THF, dichloromethane, chloroform, etc., but insoluble in water.

3.2 Optical Property

As illustrated in Fig. 2(a), the absorption maxima of $(2\text{-Cz})_2\text{MTPS}$ and $(3\text{-Cz})_2\text{MTPS}$ in dilute THF solutions are 401 and 409 nm, respectively, being obviously red-shifted in comparison with their parent silole MPPS (363 nm),³⁴ due to the elongated conjugation across the 2,5-positions. Although connecting carbazole with silole ring via carbazole's 3-position results in a *meta*-linkage, and thus, limited conjugation in $(3\text{-Cz})_2\text{MTPS}$,³⁵ the absorption maximum of $(3\text{-Cz})_2\text{MTPS}$ is red-shifted by 8 nm compared with that of $(2\text{-Cz})_2\text{MTPS}$. The electron-donating effect of the nitrogen in the $(3\text{-Cz})_2\text{MTPS}$, where the nitrogen atom is in *para* position of the silole ring,³⁶ will cause stronger electron donor-acceptor interaction. Therefore, the slightly red-shifted absorption of $(3\text{-Cz})_2\text{MTPS}$ relative to $(2\text{-Cz})_2\text{MTPS}$ can be explained by the combined effects of less conjugation of the molecule, but stronger electron-donating ability of the nitrogen in carbazole to silole rings. The PL spectra of the new siloles in THF and in the solid state are shown in Fig. 2(b). $(2\text{-Cz})_2\text{MTPS}$ and $(3\text{-Cz})_2\text{MTPS}$ show identical PL peaks at 526 nm in dilute THF solutions, with low fluorescence quantum yields (Φ_F) of 6.0 and 2.3% (Table 1), respectively, which indicate that they are weakly fluorescent when dissolved in good solvents. The PL wavelengths are longer than that of MPPS (491 nm) and Φ_F values are higher than that of

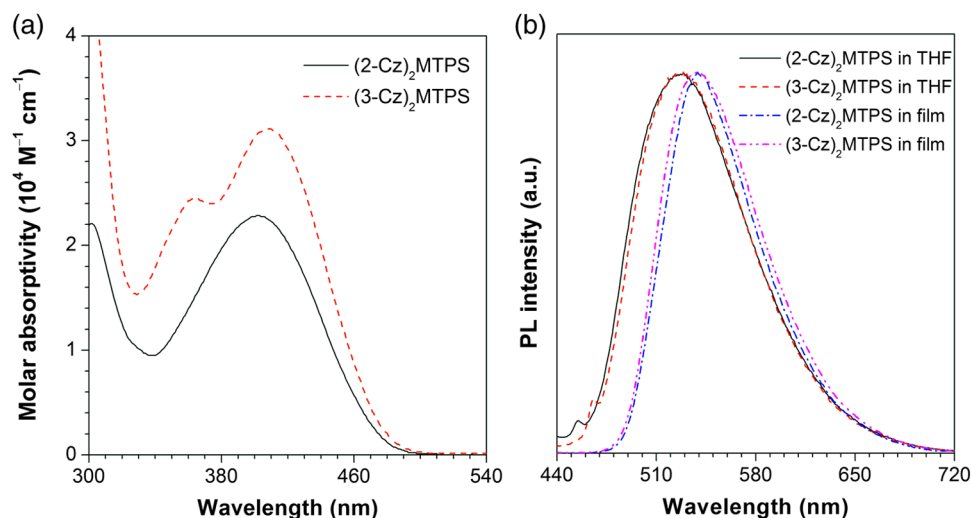


Fig. 2 (a) Absorption (in THF, $10\ \mu\text{M}$) and (b) photoluminescence (PL) spectra of $(2\text{-Cz})_2\text{MTPS}$ and $(3\text{-Cz})_2\text{MTPS}$. Excitation wavelength: 400 nm.

Table 1 Optical, electronic, and thermal properties of (2-Cz)₂MTPS and (3-Cz)₂MTPS.

Compounds	λ_{abs} (nm)	λ_{em} (nm)		$\Phi_{\text{F}}^{\text{b}}$ (%)		$T_{\text{g}}/T_{\text{d}}$ (°C)	HOMO/LUMO ^c (eV)	E_{g} (eV)
		THF	Film ^a	THF	powder			
(2-Cz) ₂ MTPS	401	526	540	6.0	65	112/396	-5.36/ -2.93	2.43
(3-Cz) ₂ MTPS	409	526	540	2.3	56	-/404	-5.15/ -2.70	2.45

Note: THF, tetrahydrofuran.

^aSpin-coated film.

^bAbsolute fluorescence quantum yield determined by a calibrated integrating sphere.

^cDetermined by cyclic voltammetry.

MPPS (0.09%), owing to the enhanced conjugation by substitution of the carbazole moieties. They become highly emissive in the solid state. The film of (2-Cz)₂MTPS fluoresces intensely with a PL peak at 540 nm as the same as that of (3-Cz)₂MTPS [Fig. 2(b)]. The negative effect of the conjugation across 2,5-positions and the positive effect of the electron-donating effect of the nitrogen in carbazole to silole rings in (3-Cz)₂MTPS coincidentally result in the same PL wavelengths as (2-Cz)₂MTPS in THF solution or in solid state. The Φ_{F} values of (2-Cz)₂MTPS and (3-Cz)₂MTPS in the solid state were estimated to be 65% and 56%, respectively. The significantly improved PL efficiencies of the new siloles in the solid state reveal that they practically have an aggregation-enhanced emission (AEE) feature. But the emission efficiencies of both new siloles in the solid state are lower than that of MPPS (85%), probably because of the intermolecular interaction between large planar carbazole substituents.

The AEE characteristics of these new silole derivatives were further confirmed by their emission behaviors in THF/water mixtures. Taking (3-Cz)₂MTPS as an example, its emission intensity increases swiftly at high water fractions (Fig. 3). Similar emission behaviors are also recorded from (2-Cz)₂MTPS in THF/water mixtures. Since these siloles are insoluble in water, they must have aggregated when the water content became high. Like most AIE luminogens, the intramolecular rotation that is active in good solvents is then restricted because of the steric hindrance in the condensed phase. The nonradiative relaxation of the excited state is thus blocked, rendering the molecules highly emissive. These results indicate that both new siloles are AEE-active indeed.

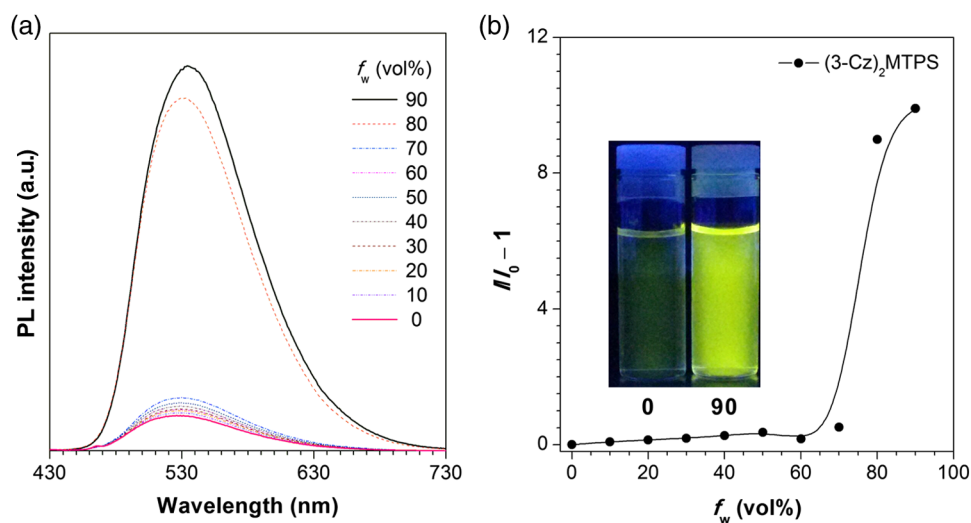


Fig. 3 (a) PL spectra of (3-Cz)₂MTPS in THF/water mixtures with different water fractions (f_w). (b) Plot of $(I/I_0 - 1)$ values versus water fractions in THF/water mixtures of (3-Cz)₂MTPS. I_0 is the PL intensity in pure THF solution. Inset: photos of (3-Cz)₂MTPS in THF/water mixtures ($f_w = 0$ and 90%), taken under illumination of a UV lamp (365 nm).

3.3 Thermal Property

The thermal property of $(2\text{-Cz})_2\text{MTPS}$ and $(3\text{-Cz})_2\text{MTPS}$ was investigated by thermogravimetric analysis and differential scanning calorimetry. The results show that they possess good thermal stability with high decomposition temperatures (T_d) of 396°C and 404°C, according to 5% loss of initial weight [Fig. 4(a)]. High glass-transition temperatures (T_g) of 112°C are also recorded for $(2\text{-Cz})_2\text{MTPS}$ [Fig. 4(b)], indicating it is morphologically stable. Although no obvious T_g could be found from $(3\text{-Cz})_2\text{MTPS}$, it is expected to have good thermal stability because of its similar decomposition temperature and chemical structure as $(2\text{-Cz})_2\text{MTPS}$. The good thermal and morphological stabilities enable them to serve as active materials for OLEDs.

3.4 Electrochemical Property

To evaluate the energy levels of the new siloles, their electrochemical property was investigated by cyclic voltammetry in dichloromethane solution with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte at a scan rate of 50 mV s^{-1} using platinum as the working electrode and saturated calomel electrode as the reference electrode. $(2\text{-Cz})_2\text{MTPS}$ and $(3\text{-Cz})_2\text{MTPS}$ exhibit a quasireversible oxidation process, with onset potentials of 0.96 and 0.75 V (Fig. 5). The energy levels of HOMO [$\text{HOMO} = -(4.4 + E_{\text{onset}})$] and LUMO [$\text{LUMO} = -(\text{HOMO} + E_g)$] are determined by onset potential of oxidation (E_{onset}) and optical band gap. Therefore, the HOMO energy levels of $(2\text{-Cz})_2\text{MTPS}$ and $(3\text{-Cz})_2\text{MTPS}$ are calculated to be -5.36 and -5.15 eV, and the LUMO energy levels are -2.93 and -2.70 eV, respectively (Table 1). The introduction of 9-ethylcarbazol-2-yl substituents results in much lower energy levels than the 9-ethylcarbazol-3-yl ones of the silole derivatives. The calculated LUMO energy levels of the new siloles are close to or even lower than those of widely used electron-transporting materials, such as 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBi, -2.7 eV),³⁷ demonstrating their potential electron-transporting ability in OLEDs.

3.5 Electroluminescence

Given the excellent thermal stabilities and high solid-state emission efficiencies, $(2\text{-Cz})_2\text{MTPS}$ and $(3\text{-Cz})_2\text{MTPS}$ were subjected to EL study in nondoped OLEDs. Trilayer OLEDs with a configuration of ITO/NPB (60 nm)/EML (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al were fabricated, in which $(2\text{-Cz})_2\text{MTPS}$ and $(3\text{-Cz})_2\text{MTPS}$ served as a light EML, NPB functioned as an HTL, and TPBi acted as an ETL. The EL spectra and characteristic curves of the devices are illustrated

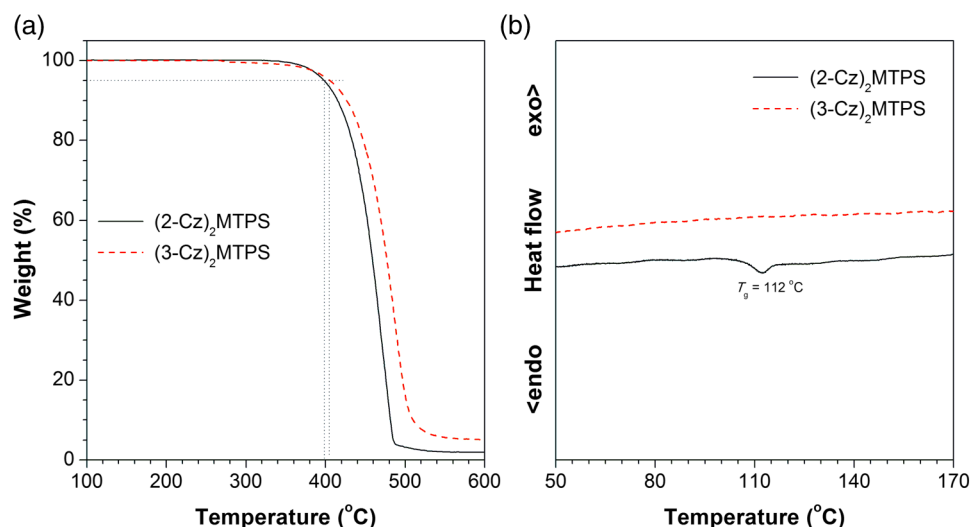


Fig. 4 (a) Thermogravimetric analysis and (b) differential scanning calorimetry curves of $(2\text{-Cz})_2\text{MTPS}$ and $(3\text{-Cz})_2\text{MTPS}$, recorded under nitrogen at a heating rate of $10^\circ\text{C min}^{-1}$.

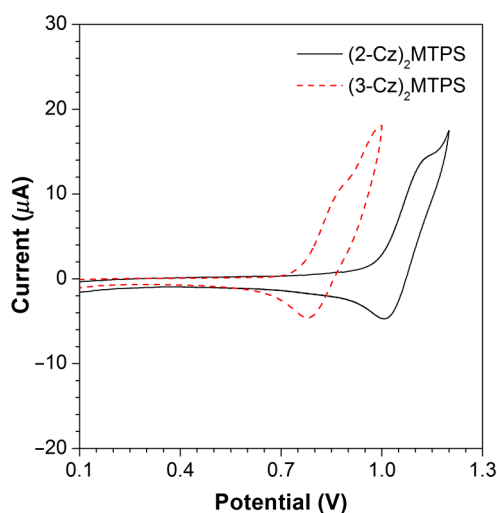


Fig. 5 Cyclic voltammograms of $(2\text{-Cz})_2\text{MTPS}$ and $(3\text{-Cz})_2\text{MTPS}$, measured in dichloromethane.

Table 2 Electroluminescent performances of organic light-emitting diodes based on $(2\text{-Cz})_2\text{MTPS}$ and $(3\text{-Cz})_2\text{MTPS}$.^a

Emitters	λ_{EL} (nm)	V_{on} (V)	L_{max} (cd m^{-2})	η_{c} (cd A^{-1})	η_{ext} (%)	η_{p} (lm W^{-1})	CIE (x, y)
$(2\text{-Cz})_2\text{MTPS}$	552	4.6	28240	4.50	1.44	1.91	(0.41, 0.56)
$(3\text{-Cz})_2\text{MTPS}$	548	4.6	17280	4.26	1.35	2.23	(0.39, 0.57)

^aAbbreviations: λ_{EL} , electroluminescence maximum; V_{on} , turn-on voltage at 1 cd m^{-2} ; L_{max} , maximum luminance; η_{c} , maximum current efficiency; η_{ext} , maximum external quantum efficiency; η_{p} , maximum power efficiency; CIE, Commission Internationale de l'Éclairage coordinates. Device configuration: ITO/NPB (60 nm)/emitter (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al.

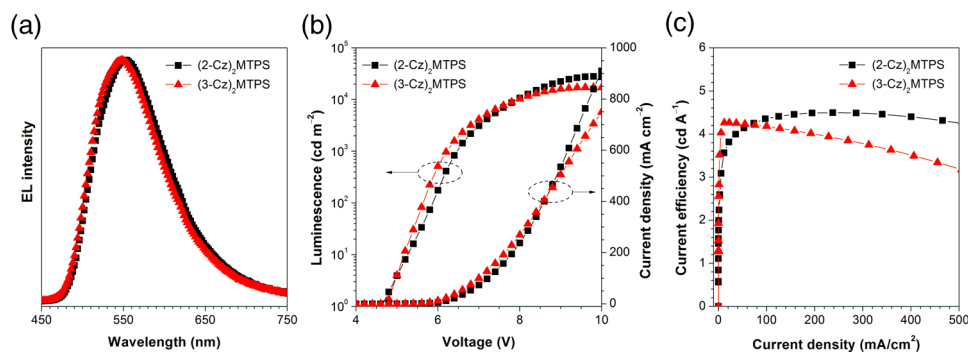


Fig. 6 (a) Electroluminescent (EL) spectra, (b) current density–voltage–luminance characteristics, and (c) current efficiencies with the current density in EL devices of $(2\text{-Cz})_2\text{MTPS}$ and $(3\text{-Cz})_2\text{MTPS}$.

in Fig. 6 and the device performance data are listed in Table 2. The devices of $(2\text{-Cz})_2\text{MTPS}$ and $(3\text{-Cz})_2\text{MTPS}$ show yellow emissions peaking at 552 and 548 nm, respectively, which are close to the PL emissions of their solid films. Both the devices are turned on at a low voltage of 4.6 V. The device adopting $(2\text{-Cz})_2\text{MTPS}$ as EML exhibits good performances with a maximum luminance of 28240 cd m^{-2} and maximum current efficiency of 4.50 cd A^{-1} . The device based on $(3\text{-Cz})_2\text{MTPS}$ shows a comparable performance with a maximum luminance of 17280 cd m^{-2} and maximum current efficiency of 4.26 cd A^{-1} . The good EL performances of the new siloles demonstrate that they are potential EL materials for nondoped OLEDs. Although $(2\text{-Cz})_2\text{MTPS}$

and (3-Cz)₂MTPS show no better EL performance than other 2,5-functioned siloles with yellow emissions in the literature,^{29–31,33,34} they are complementary to the silole families and provide useful information for structure-property relationship study of silole derivatives.

4 Conclusion

In summary, two thermally stable 2,5-dicarbazole-functioned siloles are facilely synthesized and fully characterized. The new siloles are weakly fluorescent in solution, but become highly emissive in the solid state, presenting AEE characteristics. Due to its low LUMO energy levels and high solid-state PL efficiencies, trilayer OLED adopting (2-Cz)₂MTPS as light EMLs shows good EL performances of 28240 cd m⁻² and 4.50 cd A⁻¹. It should also be noted that the devices have not yet been optimized thoroughly. Given the excellent optoelectronic property of the new siloles, highly efficient nondoped OLEDs are expected to be achieved through device engineering.

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