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How do substituents affect silole emission?†

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Introduction

Siloles or silacyclopentadienes are a group of organometallic molecules with novel molecular structures and electronic properties. Siloles enjoy a unique $\sigma^*-\pi^*$ conjugation arising from the orbital interaction of the σ^* orbitals of their silylene moieties and the π^* orbitals of their butadiene fragment, which significantly lowers their LUMO energy levels and increases their electron affinity.^{1,2} As a matter of fact, siloles possess the highest electron-accepting ability,^{3,4} in comparison to other heterocycles such as pyrroles and thiophenes, and have been utilized as luminescent materials for the construction of

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Researchers are in constant pursuit of solid-state emitters with high emission efficiency, excellent photostability and large Stokes shift. Among them, siloles are good representatives. In this paper, we report the effect of substituent on the emission of silole. 1,1,3,4-Tetraphenylsilole (TPS) is weakly emissive at 392 nm in both solution and aggregated states. Progressive attachment of the trimethylsilylethynylphenyl (TMSEP) group to the 2,5-positions of TPS generates TPE–TMSEP and TPS–2TMSEP, which emit intensely at 491 nm and 517 nm, respectively, in the condensed phase despite their solutions giving almost no light upon photoexcitation. High solid-state quantum yields of up to 91% are deduced from their solid powders, demonstrating a phenomenon of aggregation-induced emission (AIE). Restriction of the low-frequency motions is proved to be the main cause of the AIE effect. Conformational study and theoretical calculation show that the steric and electronic effects contributed by the 3,4- and 2,5-substituents are crucial for the silole emission.

chemosensors,⁵⁻⁷ biological probes,^{8,9} electroluminescence devices,¹⁰⁻¹³ *etc.*

The photophysical property of a fluorophore is sensitive to its substituents. Deciphering the substituent effect on its light emission process is important as it helps in further molecular design and exploration of its high-tech applications. However, such investigation has not been comprehensively conducted on siloles and until now, there are only a few of such papers available in the literature. Yamaguchi et al. studied the influence of 1,1-substituent on the photoluminescence (PL) of siloles' rings and concluded that they mainly affect silole emission through an inductive effect.3 Pagenkopf et al. synthesized a silole molecule with different substituents at the 2,5-positions and successfully tuned its electronic and physical structures through push-pull interaction.14,15 The above studies are all conducted in the solution state. For most real-world applications, the luminogenic materials are utilized as solid films. Thus, it is more desirable if the study is carried out in the solid state though it is much less examined due to the involvement of complex intramolecular interactions such as π - π stacking, hydrogen bonding, *etc.*

We recently observed a novel phenomenon of aggregationinduced emission (AIE) in siloles.^{16,17} Instead of quenching as observed in most conventional fluorophores, aggregate formation has turned on their light emission, changing them from weak fluorophores in solution to strong emitters in the condensed phase. Systematic studies show that restriction of intramolecular motion is the main cause of the AIE effect.¹⁸⁻²⁰ In solution, the active intramolecular motion (IMR) of the silole molecules serves as a nonradiative relaxation channel for the excited state to decay. In the aggregated state, such rotation is restricted due to the physical constraint on the molecular

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[†] Electronic supplementary information (ESI) available: PL spectra of TPS-TMSEP in different solvents at different excitation wavelengths, UV and PL excitation spectra of TPS-TMSEP in THF and THF-water mixtures with different water factions and summary of crystal data and intensity collection parameters for TPS, TPS-TMSEP and TPS-2TMSEP. CCDC 933862, 933863 and 933864. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3tc30880d

Because the AIE phenomenon is of great scientific value and technological implications, our group has worked on the creation of new silole derivatives and systematically investigated their PL in both solution and aggregated states. For example, we have prepared a series of 2,3,4,5-tetraphenylsiloles with different 1,1-substituents (Chart 1)18 and found that with an increase in their electronegativity, the absorption and PL spectra of the luminogens shift bathochromically. This is consistent with the results from Yamaguchi et al.3 Though the effect is small, as suggested by the small emission wavelength change from 481 nm to 507 nm when the two methyl substituents $(X = Y = CH_3)$ are converted to a phenyl ring and a hydroxyl group. Instead, much larger emission variation was observed by varying the 2,5-substituents. For example, when the R groups at the 2,5-positions of 2 (Chart 1) were replaced from methyl to isopropyl, the PL maximum shifts from 520 nm to 495 nm accompanied by an almost 3-fold increase in the PL quantum yield (from 27% to 77%).²¹ Since all the molecules of 2, regardless of the type of substituent, are AIE-active and the substituent change occurs only at a remote distance, deeper insight into the substituent effect is not achieved. With such regard, in this paper, we report the preparation of 1,1,3,4-tetraphenylsiloles with no (TPS), one (TPS-TMSEP) and two (TPS-2TMSEP) substituent(s) at the 2,5 positions (Chart 1) and investigate the effect of molecular structure on their optical properties. Compared with previous investigation, such a structural change is more clear-cut and dramatic, and is thus anticipated to create large optical transformation. This is indeed the case: while TPS is a weakly emissive UV fluorophore in both solution and aggregated states, the nanoaggregates and solid powders of TPS-TMSEP and TPS-2TMSEP emit strong light with high quantum yields of up to 91% despite their solutions being almost non-fluorescent. This result offers insight into the underlying emission mechanism of siloles and provides valuable information for the development of efficient solid-state emitters.



Chart 1 Molecular structures of the silole luminogens with different substituents at the 1,1-and 2,5-positions.

Results and discussion

Synthesis and structural characterization

TPS, TPS-TMSEP and TPS-2TMSEP were prepared according to the synthetic routes shown in Scheme 1. Diphenylbis(2-phenylethynyl)silane (3) was prepared by reaction of dichlorodiphenylsilane with sodium phenylacetylide, which underwent intramolecular reductive cyclization by treatment with lithium naphthalenide to form 2,5-dilithiosilole (4).^{22,23} Compound 4 was transformed to 2,5-dizincsilole (5) by transmetalation with $ZnCl_2 \cdot TMEDA$ (TMEDA = N, N, N', N'-tetramethylethylenediamine). The subsequent reaction of 4 in the presence or absence of 4-(2-trimethylsilylethynyl)-1-bromobenzene (6) catalyzed by Pd(Ph₃)₂Cl₂ generated TPS, TPS-TMSEP and TPS-2TMSEP with no, one and two substituent(s), respectively at the 2,5-positions. All the compounds were characterized by ¹H NMR, ¹³C NMR and high-resolution mass spectroscopies, and elemental analysis, from which satisfactory data corresponding to their structures and purities were determined (see Experimental section for details). Single crystals of TPS, TPS-TMSEP and TPS-2TMSEP were grown from their dichloromethane-methanol mixture and characterized by X-ray diffraction. Their crystal structures are given in Fig. 1, while the crystal data are summarized in Table S1(ESI[†]). All the molecules take a nonplanar or twisted conformation due to the steric repulsion between the periphery phenyl rings.



Scheme 1 Synthetic routes to TPS, TPS–TMSEP and TPS–2TMSEP.

Paper



Fig. 1 Crystal structures of TPS, TPS–TMSEP and TPS–2TMSEP.

Optical properties

The dilute THF solution of TPS exhibits an absorption maximum at 288 nm (Fig. 2). Incorporation of a trimethylsilylethynylphenyl (TMSEP) substituent to the 2-position of the silole ring gives TPS-TMESP, which largely red-shifts the UV spectrum by \sim 70 nm, due to the enhancement in the molecular conjugation. Addition of a second TMSEP group at the 5 position further moves the absorption maximum to longer wave-lengths and the UV spectrum of TPS-2TMSEP now peaks at 383 nm. The absorption shift (30 nm) caused by the second substituent is much less than the first one (70 nm), presumably due to the loss of π -conjugation caused by the increase in the steric repulsion between the substituents.

TPS is a weak fluorophore, emitting faint UV light at 392 nm in both solution and solid states (data not shown here). Such behaviour may be ascribed to its poor conjugation. In contrast, TPS-TMSEP exhibits a distinctly different optical property. The PL spectrum of TPS-TMSEP in THF solution shows an emission peak centred at 392.5 nm (Fig. 3A). The PL intensity drops progressively and remains unchanged when up to 75% of water is added into the THF solution. Afterwards, the PL maximum shifts to 490 nm and the spectrum was intensified gradually with increasing water content. At 95% water fraction, the PL intensity is \sim 57-fold higher than that in pure THF solution (Fig. 3B). Since TPS-TMSEP is not soluble in water, its molecules must have been aggregated in an aqueous mixture with



Fig. 2 UV spectra of TPS, TPS–TMSEP and TPS–2TMSEP in THF solutions. Concentration: 10 μ M.

high water content. Clearly, TPS–TMSEP is AIE-active. The photographs shown in Fig. 3C also demonstrate the AIE feature of TPS–TMSEP. While no or weak PL was observed in aqueous mixtures with low water contents, intense blue light was emitted when the molecules aggregate in the presence of a large amount of water. The UV and PL excitation spectra exert little change when the TPS–TMSEP molecules aggregate in the presence of water, revealing that the same species dominate the absorption and light emission processes (Fig. S1[†]).

Now, what is the origin of the emission peak at 392.5 nm? Is it originating from the molecule or the artefact as the Raman scattering effect of the excitation light, which arises from the inelastic scattering of photons, can also result in the appearance of such a "false" peak. The Raman scattering peak will shift when the excitation wavelength is varied. In contrast, according to Kasha's rule, a "real" emission peak does not change with the excitation wavelength. As shown in Fig. S2A,† changing the excitation wavelength in pure THF solution from 280 nm to 353 nm causes variation in the emission intensity but exerts no shift in the PL maximum. This suggests that the peak at 392.5 nm arises really from TPS-TMSEP. Similar results are obtained when the investigations are carried out in the THF-water mixture (40/60, v/v) and chloroform although in the latter solvent, an additional vibronic band is observed at \sim 370 nm (Fig. S2B and S2C[†]).

Fluorescence lifetime refers to the average time a molecule stays in its excited state before emitting a photon. The lifetime for a typical fluorescence process lies in the nanosecond range. Measurement of the lifetime will help us differentiate further the true peak from the artefacts, which generally have shorter lifetimes. The weighted mean lifetime of TPS–TMSEP in the THF–water mixture (5/95, v/v) at 490 nm is 1.65 ns, which falls within the range for fluorescence emission (Fig. 4A). A similar value of 1.83 ns was deduced in pure THF solution, further proving that the peak at 390 nm really stems from fluorescence transition rather than an artefact (Fig. 4B).

Considering that the small peak locates at a wavelength where the TPS emits, we envisioned that this small peak may arise from the TPS skeleton of TPS-TMSEP. Siloles 1 and 2 are also constructed from TPS but their PL spectra exhibit no peak at 390 nm. One possibility is that these molecules possess higher conjugation than TPS-TMSEP such that their absorption spectra overlap well with the emission spectrum of the TPS core. This leads to more efficient energy transfer and thus quenches completely the PL peak at 390 nm. When aggregate forms, the TPS-TMSEP molecules are in close proximity to each other, which may enhance the energy transfer process. That may account for the gradual decrease in the peak intensity at 390 nm and its complete removal in the THF-water mixture with increasing water content (Fig. 5).

TPS-2TMSEP, which carries two TMSEP groups at the 2,5positions of the silole ring, is also AIE-active. In THF, TPS-2TMSEP is practically non-emissive. The emission remains weak when up to 60% of water is added into the THF solution. Thereafter, the PL intensity starts to rise. The higher the water content, the stronger is the light emission. At 95% water content, the PL intensity is 50-fold higher than that in pure THF



Fig. 3 (A) PL spectra of TPS–TMSEP in THF–water mixtures with different water fractions (f_w). Excitation wavelength: 353 nm; concentration: 10 μ M. (B) Plot of peak intensity at 491 nm and 392.5 nm *versus* the composition of the THF–water mixture of TPS–TMSEP. (C) Photographs of THF–water mixtures of TPS–TMSEP with different f_w values taken under UV illumination from a hand-held UV lamp.



Fig. 4 Time-resolved fluorescence spectra of TPS–TMSEP in (A) THF–water mixture (5/95, v/v) at 490 nm and (B) THF solution at 390 nm. $\langle \tau \rangle$ = weighted mean lifetime determined from $\langle \tau \rangle = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$, where A_i and τ_i are the fractions and lifetimes of the shorter (1) and longer (2)-lived species, respectively.

solution. To have a quantitative picture, the quantum yields $(\Phi_{\rm F})$ of the molecules in THF-water mixtures with different water fractions were measured using quinine sulphate in 0.1 N sulphuric acid ($\Phi_{\rm F} = 54.6\%$) as the standard (Fig. 6). TPS shows very low quantum yields in both solution and aggregated states (0.021% and 0.07%, respectively). The $\Phi_{\rm F}$ values of TPS-TMSEP and TPS-2TMSEP are also low in pure THF solution (0.26% for TPS-TMSEP and 0.45% for TPS-2TMSEP) but become higher when aggregates start to form at 70% water content. The maximum $\Phi_{\rm F}$ values are attained at 95% water fraction, being 45- and 60-fold higher than the solution values (Table 1). The

extent of emission enhancement or AIE effect can be quantified by the following equation

$$\alpha_{\rm AIE} = \frac{\Phi_{\rm F,A}}{\Phi_{\rm F,Soln}} \tag{1}$$

where $\Phi_{\rm F,A}$ and $\Phi_{\rm F,Soln}$ are the quantum efficiencies in the aggregated and solution states, respectively. The $\alpha_{\rm AIE}$ values for TPS, TPS–TMSEP and TPS–2TMSEP are determined to be 0.3, 45.7 and 59.7. Since all the molecules are weakly emissive in solutions, the larger $\alpha_{\rm AIE}$ of TPS–2TMSEP is mainly attributed to its higher $\Phi_{\rm F,A}$ value, which arises from its better conjugation contributed by the additional TMESP group at the 5 position. The $\Phi_{\rm F}$ values of solid powders of TPS, TPS–TMSEP and TPS–2TMSEP are also measured using a calibrated integrating sphere and are equal to 16.77%, 54.80% and 90.88% respectively.

To gain further insight into their photophysical properties, theoretical calculations were performed. Based on their crystal structure, the HOMO and LUMO energy levels of TPS, TPS–TMSEP, and TPS–2TMSEP were calculated using the B3LYP/6-31G* basis set. The HOMO and LUMO orbitals of TPS are mainly located on the central silole core and the 3,4-substituents, while the phenyl rings at 1,1-positions make little contribution (Fig. 7). On the other hand, the central silole ring and 2,5 substituents contribute largely to the orbitals of HOMO and LUMO of TPS–TMSEP and TPS–2TMSEP. This orbital distribution results in a long, linear conjugation, accounting for their redder absorption and emission. The band gaps of TPS,



Fig. 5 (A) PL spectra of TPS–2TMSEP in THF–water mixtures with different water fractions (f_w). Excitation wavelength: 383 nm; concentration: 10 μ M. (B) Plot of relative PL intensity (I/I_0) at 517 nm *versus* the composition of the THF–water mixture of TPS–2TMSEP. (C) Photographs of THF–water mixtures of TPS–2TMSEP with different f_w values taken under UV illumination from a hand-held UV lamp.



Fig. 6 Plot of quantum yield *versus* the composition of the THF–water mixtures of TPS, TPS–TMSEP and TPS–TMSEP. Excitation wavelength (nm): 283 (TPS), 353 (TPS–TMSEP) and 383 (TPS–2TMSEP).

TPS-TMSEP and TPS-2TMSEP are calculated to be 4.27 eV, 3.69 eV and 3.68 eV, which are consistent with the results from UV spectroscopy.

Mechanism

We have previously shown that the restriction of the IMR process is the main cause of the AIE effect.¹⁸ To decipher the influence of low-frequency motion on the emission of TPS,

TPS-TMSEP and TPS-2TMSEP, Shuai's method was employed,24-26 from which the vertical emission energy and oscillator strength of 2.56 eV, 2.21 eV and 2.07 eV, and 0.0032, 0.245 and 0.668 are deduced for TPS, TPS-TMSEP and TPS-2TMSEP, respectively (Table 1). These results are well correlated with the experimental results, revealing the good applicability of the method. The low oscillator strength of TPS suggests that the probability of its excitons to undergo radiative decay is low, which makes it weakly emissive in both solution and aggregated states. The histograms of reorganization energy versus wavenumber for TPS-TMSEP and TPS-2TMSEP are shown in Fig. 8. The lines at high frequency or wavenumber are ascribed to the stretching of C=C and C-C, which are insensitive to aggregate formation, while the low frequency lines are related to the torsional and twisting motions of the peripheral phenyl rings, which can be restricted in the aggregated state. In both molecules, the low frequency lines constitute a large fraction of the reorganization energy. These results suggest that the AIE phenomenon of TPS-TMSA and TPS-2TMSA really originates from the restriction of the IMR process. Once it is deactivated, the excitons can dissipate their energy radiatively, which makes the dye molecule highly emissive.

From the above results, we deduced the effect of substituents on the optical properties of siloles. DPS (Chart 2) was reported to be emissive in the solution state, with a $\Phi_{\rm F}$ value of 29%.²⁷ Due to the absence of a steric effect from the 3,4-substituents, DPS takes a coplanar conformation with a small dihedral angle of 14° between the silole ring and the phenyl rings at 2,5-positions (Table 2).²⁸ To facilitate the discussion, the phenyl rings in

Luminogen	$\lambda_{\mathrm{em}} \left(\mathrm{nm} \right)$	$E_{\rm em,exp}$ (eV)	$\Phi_{\mathrm{F,A}}\left(\% ight)$	${arPhi_{ m F,S}}\left(\% ight)$	$lpha_{ m AIE}$	$E_{\rm em,vertical}$ (eV)	Oscillator strength
TPS	392	2.94	0.07	16.77	0.3	2.56	0.0032
TPS-TMSEP	491	2.49	11.73	54.80	45.7	2.21	0.245
TPS-2TMSEP	517	2.21	26.78	90.88	59.7	2.07	0.668

^{*a*} Abbreviation: λ_{em} = experimental emission wavelength, $E_{em,exp}$ = experimental emission energy, $\Phi_{F,A}$ = quantum yield in THF-water mixtures (5/ 95, v/v) determined using quinine sulphate as the standard, $\Phi_{F,S}$ = quantum yield of the solid powders determined by a calibrated integrating sphere, and $E_{em,vertical}$ = vertical emission energy.





Chart 2 Molecular structures of DPS and HPS with numbered phenyl rings.

 Table 2
 Dihedral angles between the numbered phenyl and silole rings in DPS,

 TPS, TPS–TMSEP and TPS–2TMSEP determined by single-crystal X-ray diffraction

	Dihedral angle (deg)					
Phenyl ring	DPS	TPS	TPS-TMSEP	TPS-2TMSEP		
2	14		42.46	54.82		
3		49.03	61.61	57.84		
4		40.63	43.07	57.84		
5	14			54.18		

positions. Since the conjugation is maximized when the dihedral angle equals zero, the more twisted 2,5-substituents thus explain well the smaller red-shift in the absorption and emission wavelengths caused by the incorporation of the second TMSEP group. Comparison between these molecules depicts that without 3,4-substituents, the 2,5-substituents will lie on the same plane with the silole ring. Addition of substituents at the 3,4-positions twists the 2,5-substituents due to the steric hindrance. On the other hand, the 3,4-substituents locate out of the plane of the silole ring no matter whether there are substituents at the 2,5-positions. Through such analyses, it becomes clear that the 3,4 substituents affect siloles' emission through steric repulsion, while the 2,5-substituents play an important role in molecular conjugation and hence affect the emission wavelength and efficiency.

Conclusion

In this paper, 1,1,3,4-tetraphenylsiloles (TPS, TPS–TMSEP and TPS–2TMSEP) without and with one or two TMSEP group(s) at the 2,5-positions are synthesized, and the effect of molecular structure on their PL properties was investigated in both

Fig. 7 Molecular orbital amplitude plots of HOMO and LUMO energy levels of TPS, TPS–TMSEP and TPS–2TMSEP calculated using the B3LYP/6-31G* basis set.

HPS are numbered as shown in Chart 2. Moving the two phenyl rings from 2,5-positions (DPS) to 3,4-positions (TPS) of the silole ring alters largely the PL of the resulting luminogen. As described above, TPS gives almost no light in both solution and aggregated states. The dihedral angles between the 3,4-substituents and the silole core are 49.03° and 40.63° respectively, revealing that TPS takes a twisted conformation and is poorly conjugated. Attachment of one TMSEP group at the 2-position of the silole ring increases not only the molecular conjugation but also the steric hindrance, as revealed by the large increase in the dihedral angle at the 3-position in order to relieve the overcrowdedness. Addition of another TMSEP group at the 5-position increases the dihedral angles at both 2- and 4-



Fig. 8 Calculated reorganization energy versus the normal mode wavenumber for (A) TPS-TMSEP and (B) TPS-2TMSEP.

solution and aggregated states. With gradual addition of substituents at the 2,5-positions, the absorption and emission of the luminogen shifts bathochromically. TPS is weakly emissive in the UV region in both solution and aggregated states. While the solutions of TPS-TMSEP and TPS-2TMSEP also give no light upon photoexcitation, their nanoparticle suspensions in poor solvents and solid powders emit intense visible light with high $\Phi_{\rm F}$ values of up to 91%, demonstrating a phenomenon of AIE. Restriction of the low-frequency intramolecular motions is further proved to be the cause of the AIE effect. Through conformational study and theoretical calculation, both 3,4- and 2,5-substituents are crucial for the emission of siloles. While the PL process of siloles is affected by the steric effect contributed by the former, the latter is important for the molecular conjugation and affects the emission wavelength and efficiency.

Experimental section

General information

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl immediately prior to use. Lithium wire, naphthalene, dichlorobis(triphenylphosphine)palladium(π), ZnCl₂·TMEDA, and other chemicals and solvents were all purchased from Aldrich and used as received without further purification.

¹H and ¹³C NMR spectra were recorded on a Bruker ARX 400 NMR spectrometer using chloroform-d as solvent and tetramethylsilane (TMS) as the internal reference. UV absorption spectra were recorded on a Milton Ray Spectronic 3000 array spectrophotometer. Elemental analysis was performed on a Thermo Finnigan Flash EA1112. High-resolution mass spectra (HRMS) were recorded on a Finnigan MAT TSQ 7000 Mass Spectrometer System operating in a MALDI-TOF mode. Timeresolved fluorescence spectra were collected on an Edinburgh FLSP920 spectrophotometer. Crystals of TPS, TPS-TMSEP and TPS-2TMSEP with quality suitable for X-ray diffraction (XRD) analysis were grown from their dichloromethane-methanol mixture. Single crystal XRD intensity data were collected at 173 K on a Bruker-Nonius Smart Apex CCD diffractometer with graphite monochromated Mo-Ka radiation. The data were processed using the SAINT and SADABS routines, and the structure solution and refinement were carried out by the SHELXTL suite of X-ray programs (version 6.10). Melting point of three compounds was measured on a Barnstead Electrothermal 9100. PL spectra were recorded on a Perkin Elmer LS 55 spectrofluorometer. Emission efficiencies of the solid powders were measured by a calibrated integrating sphere. The solution $\Phi_{\rm F}$ values were estimated using quinine sulfate in 0.1 N sulfuric acid ($\Phi_{
m F}=54.6\%$) as the standard. The absorbance of the solutions was kept between 0.04 and 0.06 to avoid the internal filter effect. Molecular orbital amplitude plots of HOMO and LUMO energy levels of the silole molecules were calculated using the B3LYP/6-31G* basis set. The equilibrium geometries of the investigated compounds were optimized at the level of closed-shell Kohn-Sham density functional theory (DFT). Timedependent density functional theory (TD-DFT) was applied to optimize the equilibrium geometries in the first excited states

and calculate the excitation energies and the corresponding oscillator strength. The B3LYP functional and a split valence plus polarization basis set 6-31G* were used. All the calculations for reorganization energy were performed using a TUR-BOMOLE 6.3 program package.

Materials preparation

1,1,3,4-tetraphenyl-2,5-bis{4-[2-(trimethylsilyl)ethynyl]phenyl}silole (TPS-2TMSEP). TPS-2TMSEP was synthesized according to the literature with some modifications.23 A solution of lithium naphthalenide (LiNp) was prepared by stirring a mixture of naphthalene (2.05 g, 16 mmol) and lithium granular (0.13 g, 16 mmol) in THF (16 mL) at room temperature for 3 h under a nitrogen atmosphere. The resulting dark green mixture was transferred to a pre-deoxygenated two-necked flask via a cannula as soon as possible. A solution of diphenylbis(2-phenylethynyl)silane (3, 1.54 g, 4 mmol) in THF (10 mL) was added dropwise to the solution of LiNp, and the resulting mixture was stirred for 1 h at room temperature. After the solution was cooled to 0 °C, ZnCl₂ ·TMEDA (4.00 g, 16 mmol) and 40 mL of THF were added. The fine suspension was stirred for 1 h and then 160 mg of Pd(PPh₃)₂Cl₂ and 4-(2-trimethylsilylethynyl)-1bromobenzene (6, 2.13 g, 8.4 mmol) in THF (20 mL) were added quickly to this system. Afterward, the mixture was refluxed overnight. The mixture was then extracted with dichloromethane. The organic layer was washed successively with brine and dried over magnesium sulphate. After filtration, the solvent was evaporated under reduced pressure and the residue was purified by silica-gel column chromatography using petroleum ether as eluent to give a yellow solid in 47% yield. ¹H NMR (400 MHz, CDCl₃): δ (TMS, ppm) 7.63-7.60 (dd, 4H), 7.48-7.43 (m, 2H), 7.39-7.43 (m, 4H), 7.13-7.09 (m, 4H), 7.05-7.00 (m, 6H), 6.86-6.83 (m, 4H), 6.82-6.78 (m, 4H), 0.18 (s, 18H). ¹³C NMR (100 MHz, CDCl₃): δ (TMS, ppm) 157.4, 140.3, 139.7, 138.5, 136.2, 131.8, 131.2, 130.6, 130.1, 129.2, 128.6, 127.8, 126.9, 120.2, 105.6, 94.4, 0.2. Anal. calcd for C50H46Si3: C, 82.13; H, 6.34. Found: C, 81.98; H, 6.34. HRMS (MALDI-TOF): m/z 730.2902 [M⁺, calcd 730.2907]. m.p.: 209.1–210.7 °C.

1,1,3,4-Tetraphenyl-2-{4-[2-(trimethylsilyl)ethynyl]phenyl}-1*H***silole (TPS-TMSEP).** This compound was synthesized using a similar procedure described above using half the amount of **6**. A pale yellow solid was obtained in 40% yield. ¹H NMR (400 MHz, CDCl₃): δ (TMS, ppm) 7.61–7.58 (m, 4H), 7.47–7.42 (m, 2H), 7.39–7.34 (m, 4H), 7.16–7.12 (m, 4H), 7.08–7.02 (4H), 6.85–6.82 (m, 2H), 6.79–6.75 (m, 2H), 6.50 (s, 1H), 0.20 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ (TMS, ppm) 164.6, 155.1, 141.2, 141.0, 138.2, 135.9, 131.8, 131.8, 130.4, 130.2, 129.2, 128.5, 128.4, 128.3, 127.9, 127.6, 127.3, 127.0, 120.2, 105.7, 94.3, 0.2. Anal. calcd for C₃₉H₃₄Si₂: C, 83.82; H, 6.13. Found: C, 83.55; H, 6.13. HRMS (MALDI-TOF): *m/z* 558.2208 [M⁺, calcd 558.2199]. m.p.: 183.2–184.2 °C.

1,1,3,4-Tetraphenyl-silole (TPS). The procedure for its synthesis was similar to that described above but in the absence of **6**. A white powder was obtained in 56% yield. ¹H NMR (400 MHz, CDCl₃): δ (TMS, ppm) 7.73–7.70 (m, 4H), 7.49–7.39 (m, 6H), 7.23–7.17 (m, 6H), 7.15–7.11 (m, 4H), 6.54 (s, 1H). ¹³C NMR

(100 MHz, CDCl₃): δ (TMS, ppm) 162.7, 140.7, 135.8, 132.4, 130.3, 130.1, 128.3, 128.2, 127.7, 127.4. Anal. calcd for C₃₉H₃₄Si₂: C, 87.00; H, 5.74. Found: C, 86.56; H, 5.72. HRMS (MALDI-TOF): *m/z* 386.1491 [M⁺, calcd 386.1491]. m.p.: 137.8–139.1 °C.

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