Luminescence

Modulation of Aggregation-Induced Emission and Electroluminescence of Silole Derivatives by a Covalent Bonding Pattern

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Abstract: The deciphering of structure–property relationships is of high importance to rational design of functional molecules and to explore their potential applications. In this work, a series of silole derivatives substituted with benzo[b]thiophene (BT) at the 2,5-positions of the silole ring are synthesized and characterized. The experimental investigation reveals that the covalent bonding through the 2-position of BT (2-BT) with silole ring allows a better conjugation of the backbone than that achieved though the 5-position of BT (5-BT), and results in totally different emission behaviors. The silole derivatives with 5-BT groups are weakly fluorescent in solutions, but are induced to emit intensely in aggregates, presenting excellent aggregation-induced emission (AIE) characteristics. Those with 2-BT groups can fluoresce more strongly in solutions, but no obvious emission enhancements are found in aggregates, suggesting they are not AIEactive. Theoretical calculations disclose that the good conjugation lowers the rotational motions of BT groups, which enables the molecules to emit more efficiently in solutions. But the well-conjugated planar backbone is prone to form strong intermoelcular interactions in aggregates, which decreases the emission efficiency. Non-doped organic lightemitting diodes (OLEDs) are fabricated by using these siloles as emitters. AIE-active silole derivatives show much better elecroluminescence properties than those without the AIE characterisic, demonstrating the advantage of AIE-active emitters in OLED applications.

Introduction

Since the pioneering work by Tang and co-workers in 1987,^[1] organic light-emitting diodes (OLEDs) have attracted considerable scientific and industrial interests because of their great potential in full-color flat panel displays and mercury-free solid-state lighting sources.^[2] Organic light emitters usually have to be fabricated into solid thin films in a real-world application, such as in OLEDs.^[3] Hence, the design and synthesis of robust organic materials that can fluoresce efficiently in the

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To address this issue, an abnormal emission phenomenon of aggregation-induced emission (AIE), firstly reported on propeller-like silole derivatives, such as 1-methyl-1,2,3,4,5-pentaphenylsilole (MPPS) and 1,1-dimethyl-2,3,4,5-tetraphenylsilole (DMTPS),^[7] has caught the attention of researchers. These silole derivatives are almost non-fluorescent in solutions but show strong fluorescence when assembled as nanoparticles or fabricated into solid films. The fact that light emission is enhanced rather than quenched by aggregate formation challenges the common knowledge of the ACQ effect. A series of designed experiments and theoretical calculations were performed and rationalized that restriction of intramolecular rotations (RIR) is the main working mechanism of this new photophysical phenomenon.^[8] This important finding paves a new avenue to create efficient solid-state emitters. Many luminescent materi-

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als bearing AIE-active units display high fluorescence efficiencies in solid films⁽⁹⁾ and exhibit promising application in OLEDs.^[10]

So far, a great many new AIE luminogens have been developed and studied worldwide, such as cyanostilbenes,^[11] tetraphenylethenes,^[12] diphenyldibenzofulvenes,^[13] phosphole and phosphindole oxides,[14] 9,10-distyrylanthracenes,^[15] and so on. As the archetypal AIE luminogens, siloles are still drawing considerable attention and have been applied to diverse research frontiers, such as chemosensors,^[16] bioprobes,^[17] and so on. Their highly efficient emissions in the solid state allow them to serve as light-emitting layers to construct high-performance OLEDs. In addition, siloles pos-



Scheme 1. Molecular structures and synthetic routes of the new silole derivatives. LiNaph = lithium naphthalenide, TMEDA = *N*,*N*,*N*-tetramethylethylenediamine.

sess unique low-lying LUMO levels owing to the $\sigma^*-\pi^*$ conjugation arising from the effective interaction between the σ^* orbital of two exocyclic single C–Si bonds and the π^* orbital of the butadiene moiety.^[18] Siloles hence show good electron affinity and fast electron mobility,^[19] and have been utilized as electron-transporting layers in the construction of OLEDs.^[20] The AIE characteristic and high electron mobility enables siloles to function as bifunctional materials for the fabrication of configuration-simplified OLEDs without sacrificing device performances.^[21]

The study of the structure-property relationship is fundamentally important as it helps us to understand the structure impacts on the properties, and thus further wisely design molecules for desired functionalities and applications. The emission wavelengths as well as the AIE characteristics of silole derivatives are also reported to be sensitive to the substituents.^[22] Some papers concluded that the substituents at the 1,1-positions of silole ring exert inductive effect primarily upon the absorption properties of the silole ring but have only a minor impact on fluorescence spectra.^[18,23,8a] The substituents at the 3,4-positions can affect the emission behavior of siloles mainly by the steric effect,^[24] and are considered to be crucial components to keep the AIE attribute of the silole derivatives. On the other hand, the substituents at the 2,5-positions can tune the electronic structures and photophysical properties of silole derivatives through π -conjugation with the silole ring.^[25] The π extended planar chromophores at the 2,5-positions of silole ring can increase the emission efficiency in solutions but decrease that in the solid state. To further depict how the covalent bonding pattern between substituents and silole ring impact the optical properties of siloles, a typical planar group, benzo[b]thiophene (BT), which is widely utilized to construct functional materials that are applied as active materials in photovoltaic cells, field-effect transistors, nonlinear optics, and OLEDs,^[26] is attached onto the silole ring through its different positions (-5 and -2). The 2,5-BT-substituted siloles (Scheme 1) were synthesized and fully characterized. The correlation between molecular structures and photoluminescence (PL) and electroluminescence (EL) properties of these new siloles is discussed based on the results from experimental measurements and theoretical calculations. It is demonstrated that different connection patterns between BT and silole ring impacts conjugation degree of the backbone, and alters the AIE characteristics of the silole derivatives. The AIE-active silole derivatives show superior EL performance compared with those without AIE characteristics, directly highlighting the advantage of AIE effect in OLED applications.

Results and Discussion

Synthesis

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Scheme 1 illustrates the synthetic routes to 2,5-BT-substituted silole derivatives. The starting materials **1a** and **1b**, which were facilely prepared according to the reported methods,^[27] underwent *endo–endo* intramolecular reductive cyclizations with treatment of lithium naphthalenide (LiNaph) and subsequent $ZnCl_2$ -*N*,*N*,*N*,'*N*-tetramethylethylenediamine (TMEDA) to yield 2,5-metalated silole intermediates (**2**).^[28] The palladium-catalyzed cross-couplings of **2** with 2-bromobenzo[b]thiophene or 5-bromobenzo[b]thiophene provided target silole derivatives. All of these final products are characterized by standard spectroscopic methods with satisfactory results. The detailed procedures and characterization data are given in Experimental section. They show good solubility in common organic sol-

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vents including THF, dichloromethane, chloroform, toluene, and so on, but are insoluble in water and ethanol.

Crystal structure

Single crystals of 5-BTDMS were grown from THF/ethanol mixtures and analyzed by using X-ray diffraction crystallography. The ORTEP drawing of the crystal structure of 5-BTDMS is displayed in Figure 1. The torsion angles between silole and 5-BT groups are 29.81°, which are smaller than those between silole and phenyl rings at the 2,5-positions in DMTPS (34.82– 48.79°).^[19d] Figure 2 illustrates the molecular packing manner of 5-BTDMS in the crystalline state. It can be seen that no close π - π stacking is found, owing to the twisted molecular conformation of 5-BTDMS, which prevents the strong redshift in the PL spectrum and emission quenching in the solid state. Multiple C–H··· π hydrogen bonds with a distance of 2.681 Å are



Figure 1. ORTEP drawing of the crystal structure of 5-BTDMS.^[34]



Figure 2. Molecular packing of 5-BTDMS in the crystalline state. Intermolecular C–H \cdots π hydrogen bonds are indicated (d=2.681 Å).

formed between the phenyl hydrogen atom in one molecule and the π -electron cloud of the phenyl ring of BT group in the adjacent molecule. The collective effect of these weak intermolecular interactions can help to rigidify the molecular conformation, lock the intramolecular motions, and thus, enhance the emission efficiency in the condensed phase.

Optical property

Figure 3A shows the absorption spectra of the new silole derivatives in dilute THF solutions. The spectral profiles of 5-BTDMS and 5-BTMPS are similar, and so are those of 2-BTDMS and 2-BTMPS. A close survey of the absorption spectra discloses that the absorption maximum of 5-BTMPS is located at 375 nm, associated with the π - π * transition, which is slightly redshifted by 5 nm relative to that of 5-BTDMS (370 nm). A similar small redshift is also observed by comparing the ab-

> sorption spectra of 2-BTMPS (437 nm) and 2-BTDMS (432 nm). This phenomenon is attributed to the inductive effect of the phenyl ring at the 1-position of silole ring.^[23,8a] On the other side, the absorption maxima of 2-BTDMS and 2-BTMPS are redshifted apparently with much larger molar absorptivities than those of 5-BTDMS and 5-BTMPS, suggesting that the former two silole derivatives own a better conjugation backbone.

> Figure 3B and C present the PL spectra of these silole derivatives in dilute THF solutions and in solid films, respectively. The emission maximum of 5-BTDMS in solid film is 494 nm, being slightly redshifted by 6 nm compared with that in THF solution (488 nm) on account of its propeller-like molecular conformation that can impede close π -stacking interactions. However, a large redshift of 19 nm is observed in the PL spectrum of 2-BTDMS in solid film (541 nm) relative to that in THF solution (522 nm), which suggests that strong π -stacking interactions occur in the solid film of 2-BTDMS. The PL spectra of 2-BTDMS in both solution and solid film are also redshifted relative to those of 5-BTDMS, owing to the better conjugation of 2-BTDMS. Similar emission trends are also observed for 2-BTMPS and 5-BTMPS. Like most silole derivatives in the literature, 5-BTDMS and 5-BTMPS emit weakly in THF solutions, with low fluorescence quantum yields ($\Phi_{\rm F}$) of 0.8 and 1.2%, respectively (Table 1). The $\Phi_{\rm F}$ values of 5-BTDMS and 5-BTMPS are increased to 60.4 and 53.0%, respectively, revealing that they are AIE-active, and are excellent solid-state emitters. What surprises us is that 2-BTDMS and 2-BTMPS exhibit quite different emission behaviors under the same conditions. They can fluoresce more strongly than 5-BTDMS and 5-BTMPS, with much higher $\Phi_{\rm F}$ values of 4.5 and 6.5% in THF solutions. However, their emission efficiencies in solid films are only 5.5 and 8.5%, being barely increased with regards to those in solutions. This should also be ascribed to the π -stacking interactions in solid



Figure 3. A) Absorption spectra in THF solutions and PL spectra, B) in THF solution (10^{-5} M), and C) in solid films of the silole derivatives.

film due to the planar conjugated backbones of 2-BTDMS and 2-BTMPS.

The PL properties of these new silole derivatives were further investigated in THF/water mixtures, in which THF was CHEMISTRY A European Journal Full Paper

used as a good solvent but water as a poor solvent for these silole derivatives. Figure 4A and B exemplify the PL spectra of 5-BTDMS and 2-BTDMS in THF/water mixtures, respectively. It can be seen that the PL emission of 5-BTDMS is very weak when the water fraction (f_w) is low. But the emission efficiency increases swiftly (Figure 4C) when the f_w becomes high. Since 5-BTDMS is insoluble in water, its molecules must have aggregated in the mixtures with a high f_{w} . The intramolecular rotation is active when 5-BTDMS molecularly dissolved in THF/ water mixtures with a low f_{w} which efficiently deactivates the excited state through the nonradiative relaxation channel. But in the aggregated state, the intramolecular rotations are restricted by steric constraint, and thus the nonradiative energy decay is blocked, rendering the molecules highly emissive. Thus, the result confirms that 5-BTDMS is AIE-active indeed. For 2-BTDMS, addition of a large amount of water ($f_w > 70\%$) into its THF solution causes obvious redshifts in the PL spectra (Figure 4B), which is consistent with those observed in solid films. As shown in Figure 4C, 2-BTDMS exhibits similar $\Phi_{
m F}$ values in both the isolated molecule and the aggregated state. Namely, 2-BTDMS does not possess a typical AIE characteristic. Clearly, although 5-BTDMS and 2-BTDMS are comprised of the same building blocks, the different connection manner has resulted in vastly varied optical properties.

Theoretical calculations

To gain a deeper insight into the significant distinctions in photophysical properties of these silole derivatives, theoretical calculations were performed using the Gaussian 09 program. Time-dependent density functional theory (TD-DFT) calculations (the Supporting Information, Table S1) show that the first singlet excited state (S₁) is dominated by the transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) for both isolated 5-BTDMS and 2-BTDMS molecules; that is, their photophysical properties are mainly determined by their HOMO and LUMO energy levels. As illustrated in Figure 5, the HOMOs and LUMOs are mainly located on the central silole ring and the BT substituents at the 2,5-positions. In addition, 2-BTDMS has a higher HOMO energy level but a lower LUMO one than those of 5-BTDMS, which is equal to a narrower energy band gap of 2.91 eV than that of 5-BTDMS (3.58 eV). This also reflects that 2-BTDMS has a better conjugation between silole and BT rings than 5-BTDMS.

As the saying goes, structure determines property. We thus investigated the optimized molecular structures of 5-BTDMS and 2-BTDMS in the isolated single-molecule state. The important geometrical parameters of the ground state (S_0) and S_1 for both isolated molecules are listed in Table 2. Two important structural diversities should be noted: 1) The lengths of single bonds C2–C2' and C5–C2" in 2-BTDMS are obviously shorter than the corresponding bond lengths (C2–C5' and C5–C5") of 5-BTDMS in both S_0 and S_1 ; 2) In S_0 , the dihedral angles Si-C2-C2'-C3' and Si-C5-C2"-C3" of 2-BTDMS (both –14.6°) are dramatically smaller than those of Si-C2-C5'-C6' and Si-C5-C5"'-C6'' in 5-BTDMS (both 49.9°). An identical trend is also found in S_1

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Figure 4. PL spectra of A) 5-BTDMS and B) 2-BTDMS in THF/water mixtures with different water fractions (f_w). Concentration: 10 μ M; excitation wavelengths: 370 nm for 5-BTDMS and 420 nm for 2-BTDMS. C) Plots of fluorescence quantum yields versus water fractions in THF/water mixtures. Fluorescence quantum yields were determined by a calibrated integrating sphere. Inset: photos of A) 5-BTDMS and B) 2-BTDMS in THF/water mixtures ($f_w = 0$ and 95%), taken under the illumination of a UV lamp (365 nm).

Table 1. Optical properties, thermal stabilities, and energy levels of the silole derivatives.									
	$\lambda_{ m abs}$ [nm] ^[a]	λ_{em} [nm]		$\Phi_{ extsf{F}}^{ extsf{[c]}}$ [%]		$T_{g}/T_{m}/T_{d}^{[d]}$ [°C]	HOMO/LUMO ^[e] [eV]	E _g [eV]	
		Soln ^[a]	Film ^[b]	Soln	Film				
5-BTDMS	370	488	494	0.8	60.4	n.d/198/305	-5.37/-2.58	2.79	
5-BTMPS	375	499	502	1.2	53.0	84/263/322	-5.55/-2.79	2.76	
2-BTDMS	432	522	541	4.5	5.5	n.d/262/315	-5.33/-2.85	2.48	
2-BTMPS	437	522	552	6.5	8.5	107/239/351	-5.35/-2.91	2.44	
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[a] In THF solution (10^{-5} M) . [b] Vacuum-deposited film. [c] Fluorescence quantum yield determined by a calibrated intergrating sphere. [d] n.d = not detectable. [e] Determined by cyclic voltammetry.



Figure 5. Calculated molecular orbital amplitude plots and energy levels of HOMOs and LUMOs of 5-BTDMS and 2-BTDMS.

of both molecules. These results directly indicate that the BT group conjugates better with the silole ring through its 2-position in 2-BTDMS. This is understandable because the thiophene

ring in BT is smaller than phenyl ring in size, and thus it can connect with silole ring in a more coplanar pattern with less steric congestion, which facilitates the π -electron delocalization. From S₀ to S₁, the changes of dihedral angles (Si-C2-C5'-C6' and Si-C5-C5"-C6") are 19.0° for 5-BTDMS, whereas those of 2-BTDMS are as low as 1.0°, revealing that the BT groups in 2-BTDMS experience only slight structural alteration upon photoexcitation. In other words, the rotational motions of the BT rings are lowered in isolated 2-BTDMS. However, the corresponding changes of C3-C4-C6-C7 and C4-C3-C8-C9 present a contrary tendency: 2.4° for 5-BTDMS and 12.3° for 2-BTDMS. This indicates that the rotations of the phenyl rings

at the 3,4-positions of silole ring are easier in isolated 2-BTDMS than in isolated 5-BTDMS.

It is generally known that the fluorescence quantum yield can be expressed as: $\Phi_{\rm F} = k_{\rm r}/(k_{\rm r}+k_{\rm nr}) = k_{\rm r}/(k_{\rm r}+k_{\rm ic}+k_{\rm isc})$, in which k_r is the radiative decay rate from S₁ to S₀, k_{ic} is the internal conversion rate from S_1 to S_0 , and k_{isc} is the intersystem crossing rate from S_1 to the first triplet excited state (T_1) .^[29] Since the spin-orbital coupling between S_1 and T_1 in these silole derivatives is very small,^[19d] the intersystem crossing process from S₁ to T₁ is reasonably negligible. Hence, $\Phi_{\rm F}$ is determined by the competition between k_r and k_{ir} . The radiative decay rate can be evaluated through the Einstein spontaneous emission relationship, which can be cast into a simple working formula $k_r = fE^2/1.499$, in which f is the oscillator strength of emission, E is the transition energy of emission (in cm^{-1}), and then k_r is in unit of s⁻¹. The calculated data of f and E are shown in Table S1 (the Supporting information). Consequently, the k_r value of isolated 2-BTDMS ($1.33 \times 10^8 \text{ s}^{-1}$) is slightly higher than that of isolated 5-BTDMS ($0.87 \times 10^8 \text{ s}^{-1}$) because of the better conjugation of 2-BTDMS, which could only marginally increase the $\Phi_{\rm F}$ of 2-BTDMS compared to 5-BTDMS. So the difference between 5-BTDMS and 2-BTDMS in $\Phi_{\rm F}$ values in

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Table 2. Selected bond lengths [Å], dihedral angles [°] of the S_0 and S_1 for isolated 5-BTDMS and 2-BTDMS molecules.								
Molecule	Structural parameter	S ₀	S ₁	$ \Delta(S_1-S_0) $	Crystal data			
	C2–C5′	1.479	1.448	0.031	1.475			
	C5–C5"	1.479	1.448	0.031	1.475			
	Si-C2-C5'-C6'	49.9	30.9	19.0	33.7			
S-BIDIVIS	Si-C5-C5"-C6"	49.9	30.9	19.0	33.7			
	C3-C4-C6-C7	58.0	55.6	2.4	61.9			
	C4-C3-C8-C9	58.0	55.6	2.4	61.9			
	C2–C2′	1.448	1.419	0.029				
	C5–C2"	1.448	1.419	0.029				
	Si-C2-C2'-C3'	-14.6	-15.6	1.0				
2-0101015	Si-C5-C2"-C3"	-14.6	-15.6	1.0				
	C3-C4-C6-C7	-73.6	-61.3	12.3				
	C4-C3-C8-C9	-73.6	-61.3	12.3				

the solution state is largely determined by the diversity of the internal conversion rate k_{ic} in the single-molecule state.

According to the previous researches,^[30,8c] the total reorganization energy of S₁ is a crucial factor in determining the k_{icr} in other words, a larger total reorganization energy predicatively leads to a higher k_{icr} which results in a smaller $\Phi_{\rm F}$ value. The calculated total reorganization energies of isolated 5-BTDMS and 2-BTDMS are given in Table 3. Evidently, 5-BTDMS has

Table 3. Selected calculated results for isolated 5-BTDMS and 2-BTDMS molecules.								
	$k_{r}^{[a]}$	$\lambda_{es}^{[b]}$	$\lambda_{2,5}^{[c]}$	$\lambda_{3,4}^{[d]}$				
	[s ⁻¹]	[cm ⁻¹]	[cm ⁻¹]	[cm ⁻¹]				
5-BTDMS	0.87×10^{8}	4640	1953 (42.1 %)	251 (5.4%)				
2-BTDMS	1.33×10^{8}	2549	8 (0.3 %)	572 (22.4%)				
[a] Calculated radiative decay rate from S_1 to S_0 . [b] The total reorganization energy of S_1 . [c] Contribution to the total reorganization energy from								

tion energy of S₁. [c] Contribution to the total reorganization energy from the BT ring rotations at 2,5-positions. [d] Contribution to the total reorganization energy from the phenyl ring rotations at 3,4-positions.

a much larger total reorganization energy of S_1 (4640 cm⁻¹) than that of 2-BTDMS (2549 cm⁻¹), revealing that the isolated 5-BTDMS possesses a higher k_{ic} , and hence a smaller Φ_F value in the solution state. In a word, it is the block of nonradiative channel, internal conversion process from S_1 to S_0 , that enhances the emission of 2-BTDMS in the solution state. In addition, the reorganization energies versus normal modes are plotted in Figure 6. It can be clearly seen that the contribution of the low frequency modes that represent the ring rotational motions to the total reorganization is suppressed in 2-BTDMS in comparison with that of 5-BTDMS. This suggests that the restriction of rotational motions is the main cause for blocking the nonradiative channel and enhancing the emission efficiency of 2-BTDMS in the solution state, which again offers a direct evidence to support the RIR mechanism of AIE phenomenon.

To further study the relationship between their emission behaviors and the molecular structures, we project their total reorganization energies into the structural parameter relaxations (Table 3). For isolated 5-BTDMS, the main contribution to the

total reorganization energy of S₁ is from the rotational motions of BT rings at the 2,5-positions (1953 cm⁻¹), accounting for 42.1% of the total reorganization energy, which is much higher than the contributions from phenyl rings at the 3,4-positions (5.4%). On the contrary, in isolated 2-BTDMS, the contribution from the rotational motions of phenyl rings at the 3,4-positions of silole ring takes a larger portion (22.4%, 572 cm⁻¹), whereas that from the BT groups is only 0.3% (8 cm⁻¹). It is also noteworthy that the reorganization energy from the rotational motions of BT rings for isolated 5-BTDMS is dramatically larger than that of 2-BTDMS (8 cm⁻¹, 0.3%), but the contributions of other motion modes for 5-BTDMS and 2-BTDMS (2657 vs. 2541 cm⁻¹) are comparable. These results are fully consistent with the above structural modification from S₀ to S₁.

Therefore, it is reasonable that the rotational motions are easier for the BT groups than for the phenyl rings at the 3,4positions, and are mainly responsible for the weak emission of 5-BTDMS in solution. In 2-BTDMS, the rotational motions of BT



Figure 6. The calculated reorganization energy versus the normal mode wavenumber for isolated molecules of A) 5-BTDMS and B) 2-BTDMS

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rings are lowered greatly by a good conjugation, and the rotational motions of the phenyl rings at the 3,4-positions are promoted to some extent. However, the former effect is dominative still, which allows the 2-BTDMS to emit more efficiently than 5-BTDMS in solutions.

Thermal stability

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The thermal properties of these silole derivatives were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). As shown in Figure 7, these com-



Figure 7. A) TGA and B) DSC thermograms of the silole derivatives recorded under nitrogen at a heating rate of A) 20 and B) $10 \,^{\circ}$ Cmin⁻¹.

pounds have good thermal stability with high decomposition temperatures (T_d) of 305–351 °C, according to 5% loss of initial weight. DSC analysis shows that all the compounds exhibit obvious melting temperatures (T_m) in the range of 198–263 °C. Glass-transition temperatures (T_g) of 5-BTMPS and 2-BTMPS are detected at 84 and 107 °C, respectively. One thing that should be pointed out is that the T_d and T_g become higher as the replacement of methyl group by phenyl ring at the 1,1-positions.

It is also noteworthy that the connection between silole ring and thiophene ring in BT (2-position of BT) endows the molecules with higher T_d and T_g than the connection between the silole ring with phenyl ring in BT (5-position) (Table 1). The good thermal and morphological stabilities enable these silole derivatives to be utilized as light-emitting materials for OLEDs.

Electrochemical property

The electrochemical properties of these silole derivatives were estimated by using cyclic voltammetry (CV) in acetonitrile solution with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte at a scan rate of 50 mV s⁻¹ and platinum as the working electrode and saturated calomel electrode (SCE) as the reference electrode. The voltammograms are presented in Figure S1 (the Supporting Information) and the obtained energy levels are summarized in Table 1. 5-BTDMS and 5-BTMPS show oxidation onset potentials (E^{ox}_{onset}) at 0.97 and 1.15 V, respectively, which are slightly higher than those of 2-BTDMS and 2-BTMPS (0.93 and 0.95 V, respectively). According to the following Equation: $HOMO = -(4.4 + E_{onset}^{ox})$ eV, the HOMO energy levels are calculated to be -5.37, -5.55, -5.33, and -5.35 eV for 5-BTDMS, 5-BTMPS, 2-BTDMS, and 2-BTMPS, respectively. The LUMO energy levels [LUMO = - (HOMO + E_{α}) eV] are determined by HOMO values and optical band gaps (estimated from the onset wavelength of their UV absorptions). The LUMO energy levels are -2.58, -2.79, -2.85, and -2.91 eV for 5-BTDMS, 5-BTMPS, 2-BTDMS, and 2-BTMPS, respectively.

Electroluminescence

As discussed above, the connection pattern between BT group and silole ring has impacted the PL property of the silole derivatives greatly, and an influence on the EL property of the molecules is also expected. Therefore, multilayer OLEDs with a configuration of ITO/NPB (60 nm)/EML (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm) were fabricated, in which the silole derivatives function as light-emitting layers (EML), N,N'-di(1-naphthyl)-N,N'-diphenyl-benzidine (NPB) acts as a hole-transporting layer (HTL) and 2,2',2"-(1,3,5-benzinetriyl)-tris(1-phenyl-1H-benzimidazole) (TPBi) serves as an electron-transporting layer (ETL). As illustrated in Figure 8A, 5-BTDMS and 5-BTMPS exhibit green EL with peaks located at 512 nm. 2-BTDMS and 2-BTMPS, however, emit yellow EL peaks at 548 and 560 nm, respectively. These EL peak positions are only slightly redshifted compared with those of the PL peak positions in solid films, confirming that the EL emissions are indeed from the emitting layers of the silole derivatives. The EL performance data of the devices are summarized in Table 4. The device of 5-BTDMS shows good performance with a turn-on voltage (V_{on}) of 4.4 V, a maximum luminance (L_{max}) of 20107 cd m⁻², a maximum current efficiency ($\eta_{C,max}$) of 10.29 cd A⁻¹, a maximum power efficiency ($\eta_{P,max}$) of 4.63 lm W⁻¹, and a maximum external quantum efficiency ($\eta_{\text{ext,max}}$) of 3.63%. The device of 5-BTMPS provides comparable EL performances, with an even lower V_{on} of 3.7 V, and a higher $\eta_{P,max}$ of 6.08 lm W⁻¹. However, the devices

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800 В Α С - 5-BTDMS 10 - 5-BTDMS 5-BTMPS 10 5-BTMPS - 2-BTDMS Ā 2-BTDMS Current Density (mA cm⁻²) 2-BTMPS Luminescence (cd m⁻²) Current Efficiency (cd A⁻¹) 2-BTMPS Intensity (a.u.) 10³ 5-BTDMS 5-BTMPS 10^{2} 2-BTDMS 4 2-BTMPS Е 200 10 2 0 0 490 560 630 700 10 12 60 120 180 240 300 420 Voltage (V) Wavelength (nm) Current Density (mA cm⁻²)

Figure 8. A) EL spectra, B) current density-voltage-luminance characteristics, and (C) changes in current efficiency with the current density in multilayer EL devices of these silole derivatives.

Table 4. EL performance of the new silole derivatives. ^[a]								
EML	λ _{εL} [nm]	V _{on} [V]	L _{max} [cd m ⁻²]	η_{C} [cd A^{-1}]	$\eta_{\scriptscriptstyle P}$ [lm W $^{-1}$]	EQE [%]	CIE [<i>x, y</i>]	
5-BTDMS	512	4.4	20107	10.29	4.63	3.63	[0.25, 0.49]	
5-BTMPS	512	3.7	27070	10.23	6.08	3.58	[0.25, 0.50]	
2-BTDMS	548	4.4	5010	3.66	1.64	1.22	[0.41, 0.56]	
2-BTMPS	560	5.2	3950	1.61	0.68	0.56	[0.43, 0.54]	
[a] With a	device c	onfigura	ation of IT(O/NPB/EML/	rpbi/lif/al.	Abbrevia	tions: EML=	

light-emitting layer; $\lambda_{EL} = EL$ maximum; $V_{on} = turn-on voltage at 1 cd m^{-2}$; $L_{max} = maximum$.

of 2-BTDMS and 2-BTMPS exhibit much inferior EL data (5010 cd m⁻², 3.66 cd A⁻¹, 1.64 lm W⁻¹ and 1.22% for 2-BTDMS; 3950 cd m⁻², 1.61 cd A⁻¹, 0.68 lm W⁻¹ and 0.56% for 2-BTMPS), which is rationally attributed to their poor solid-state PL emissions. Such a huge difference is virtually demonstrating the positive effect of AIE characteristic on the OLED device performance.

Conclusion

A series of silole derivatives substituted with BT groups through different covalent bonding patterns have been successfully synthesized and fully characterized. These new silole derivatives possess a similar molecular structure but a different conjugation degree, and thus, guite different absorption and emission behaviors. For instance, 5-BTDMS with a poorly conjugated backbone is weakly fluorescent in solution but becomes highly emissive in the aggregated state, presenting a typical AIE characteristic. 2-BTDMS that is of a high conjugation degree, however, does not exhibit the classical AIE effect: It has a much higher $\Phi_{\rm F}$ value than 5-BTDMS in THF solution but a much lower $\Phi_{\rm F}$ value in solid film. Combining the experimental results and theoretical calculations, it is concluded that the good conjugation between BT groups and silole ring lowers rotational motions of BT groups, and makes 2-BTDMS more fluorescent in the solution state. It is the restriction of rotational motions of BT rings that makes 5-BTDMS emit strongly in the aggregated state. However, the competition between the restriction of the rotational motions of phenyl rings at 3,4-positions of silole ring and intermolecular interactions between well-conjugated backbones makes 2-BTDMS present only a slight increase in emission efficiency in the aggregated state relative to that in solution. Multilayer OLEDs were fabricated by using these new siloles as emitters. The AIE-active 5-BTDMS and 5-BTMPS exhibit superior EL properties than 2-BTDMS and 2-BTMPS. The highest device performance was recorded with 5-BTMPS as the emitter, with V_{on} , L_{max} , $\eta_{C,max}$, $\eta_{P,max}$ and $\eta_{ext,max}$ of 3.7 V, 27 070 cd m⁻², 10.23 cd A⁻¹, 6.08 lm W⁻¹, and 3.58 %,

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respectively. The EL properties of these siloles once again demonstrate that AIE emitters have promising applications in OLEDs. The results presented here not only provide more evidences to support the RIR mechanism of the AIE phenomenon, but also offer a deeper insight into the structure–property correlation of silole derivatives, which is conducive for the further design of silole-based functional materials.

Experimental Section

Materials and instruments

THF was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. All other chemicals and reagents were purchased from J&K Scientific Ltd., and used as received without further purification. ¹H and ¹³C NMR spectra were measured on a Bruker AV 500 spectrometer in deuterated chloroform using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal reference. UV/ Vis absorption spectra were measured on a Shimadzu UV-2600 spectrophotometer. PL spectra were recorded on a Horiba Fluoromax-4 spectrofluorometer. High-resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operating in MALDI-TOF mode. Single-crystal X-ray diffraction intensity data were collected at 293 K on a Bruker-Nonices Smart Apex CCD diffractometer with graphite monochromated Mo_{Ka} radiation. Processing of the intensity data was carried out using the SAINT and SADABS routines, and the structure and refinement were conducted using the SHELTL suite of X-ray programs (version 6.10). TGA analysis was carried on a SHIMADZU TGA-50 under dry nitrogen at

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a heating rate of 20 °C min⁻¹. Thermal transitions were investigated by DSC using NETZSCH DSC-204(F1) instrument under dry nitrogen at a heating rate of 10° Cmin⁻¹.

Computational methods

The geometry optimization and harmonic vibrational frequency calculations of ground state (S_0) were carried out at the level of density functional theory (DFT). Then, for the first single excited state (S_1), the time-dependent density functional theory (TD-DFT) was applied. The B3LYP functional^[31] was applied with 6–31G(d,p) basis set. We have confirmed that all the frequencies obtained at the minima of S_0 and S_1 states are positive, namely, the optimized structures are stable. All these electronic structure calculations were performed with Gaussian 09 program package.^[32] The reorganization energy was obtained through the DUSHIN program, with the total reorganization energy projected to the molecular structure parameters relaxation.^[33]

Device fabrication

Glass substrates pre-coated with a 170 nm thin layer of indium tin oxide (ITO) with a sheet resistance of 10 Ω per square were thoroughly cleaned in ultrasonic bath of acetone, isopropyl alcohol, detergent, deionized water, and isopropyl alcohol and treated with O₂ 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 NPB was deposited. Next, a 20 nm thin of 5-BTDMS, 5-BTMPS, 2-BTDMS, or 2-BTMPS was deposited to form EML. Finally, a 40 nm thin ETL of TPBi was deposited to transport electrons, and to confine excitons in the emission zone. 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 mm×3 mm openings. Deposition rates are $1 \sim 2 \text{ A s}^{-1}$ for organic materials, 0.1 A s^{-1} for LiF, and 6 A 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.

Preparation of nanoaggregates

Stock THF solutions of the silole derivatives with a concentration of 10^{-4} M were prepared. Aliquots of the stock solution were transferred to 10 mL volumetric flasks. After appropriate amounts of THF were added, water was added dropwise under vigorous stirring to furnish 10^{-5} M solutions with different water contents (0–95 vol%). The PL measurements of the resultant solutions were then performed immediately.

Synthesis

2,5-Di(benzo[b)thiophen-5-yl)-1,1-dimethyl-3,4-diphenylsilole (5-BTDMS): A solution of lithium naphthalenide (LiNaph) was prepared by stirring a mixture of naphthalene (1.28 g, 10 mmol) and lithium granular (0.07 g, 10 mmol) in dry THF (30 mL) for 4 h at room temperature under nitrogen. A solution of bis(phenylethy-nyl)dimethylsilane (0.65 g, 2.5 mmol) in THF (20 mL) was then added 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, ZnCl₂-TMEDA (3.2 g, 12.5 mmol) and THF (20 mL) were added. The fine suspension was stirred for 1 h at room temperature, and [PdCl₂(PPh₃)₂] (105 mg, 0.15 mmol) and 5-bromobenzo[b]-thiophene (1.28 g, 6 mmol) were then added. After heating at

reflux for 12 h, the reaction mixture was cooled to room temperature and terminated by 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 anhydrous magnesium sulfate. After filtration, the solvent was evaporated under reduced pressure and the residue was purified by silica-gel column chromatography using *n*-hexane/dichloromethane as eluent. 5-BTDMS was obtained as green solid in 54% yield. ¹H NMR (500 MHz, CDCl₃): δ (TMS) = 7.59 (d, 2H, *J*=8.0 Hz), 7.45 (s, 2H), 7.35 (d, 2H, *J*=5.0 Hz), 7.16 (d, 2H, *J*=5.5 Hz), 7.03–6.98 (m, 6H), 6.89 (d, 2H, *J*=8.5 Hz), 6.86–6.84 (m, 4H), 0.53 ppm (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ (TMS) = 155.0, 142.9, 140.4, 139.1, 138.3, 133.4, 129.9, 128.3, 127.5, 124.3, 124.1, 123.9, 123.0, 121.9, -1.8 ppm; HRMS: *m/z* calcd for C₃₄H₂₆S₂Si: 526.1245 [*M*⁺]; found: 526.1224.

2,5-Bis(benzo[b]thiophen-2-yl)-1,1-dimethyl-3,4-diphenylsilole

(2-BTDMS): The procedure was analogous to that described for 5-BTDMS. Yellow solid, yield 36%. ¹H NMR (500 MHz, CDCl₃): δ (TMS) = 7.65 (d, 2 H, *J* = 8.0 Hz), 7.55 (d, 2 H, *J* = 8.0 Hz), 7.25–7.16 (m, 12 H), 7.05–7.03 (m, 4 H), 0.81 ppm (s, 6 H); ¹³C NMR (125 MHz, CDCl₃): δ (TMS) = 155.0, 142.9, 140.4, 139.1, 138.3, 133.4, 129.9, 128.3, 127.5, 124.3, 124.1, 124.0, 123.0, 121.9, –1.8 ppm; HRMS: *m*/*z* calcd for C₃₄H₂₆S₂Si: 526.1245 [*M*⁺]; found: 526.1221.

2,5-Bis(benzo[b]thiophen-5-yl)-1-methyl-1,3,4-triphenylsilole (**5-BTMPS**): The procedure was analogous to that described for 5-BTDMS. Green solid, yield 28%. ¹H NMR (500 MHz, CDCl₃): δ (TMS) = 7.69 (d, 2H, J = 8.0 Hz), 7.49 (d, 2H, J = 8.5 Hz), 7.40–7.35 (m, 5H), 7.29 (d, 2H, J = 5.0 Hz), 7.06–7.01 (m, 8H), 6.91–6.90 (m, 4H), 6.83 ppm (dd, 2H, J_1 = 8.5 Hz, J_2 = 1.5 Hz); ¹³C NMR (125 MHz, CDCl₃): δ (TMS) = 155.6, 140.4, 139.6, 138.9, 137.2, 135.7, 134.7, 133.5, 130.1, 129.9, 128.3, 127.6, 126.4, 126.0, 125.9, 124.0, 123.8, 121.7, –6.3 ppm; HRMS:): m/z calcd for C₃₉H₂₈S₂Si: 588.1402 [M^+]; found: 588.1522.

2,5-Bis(benzo[b]thiophen-2-yl)-1-methyl-1,3,4-triphenylsilole (2-BTMPS): The procedure was analogous to that described for 5-BTDMS. Yellow solid, yield 19%. ¹H NMR (500 MHz, CDCl₃): δ (TMS) = 7.90–7.89 (m, 2H), 7.53–7.46 (m, 7H), 7.25–7.23 (m, 6H), 7.19–7.10 (m, 8H), 7.02 (s, 2H), 1.10 ppm (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ (TMS) = 156.2, 142.4, 140.4, 139.0, 138.3, 134.7, 133.4, 132.5, 130.5, 129.9, 128.6, 128.3, 127.6, 124.6, 124.2, 123.9, 123.0, 121.8, -4.6 ppm; HRMS *m/z* calcd for C₃₉H₂₈S₂Si: 588.1402 [*M*⁺]; found: 588.1425.

X-ray crystallography

Crystal data for 5-BTDMS^[34]: C₃₄H₂₆S₂Si, M_w =526.76, monoclinic, P2/n, a=7.7430(15), b=10.568(2), c=17.025(3) Å, β =77.727(2)°, V=1388.9(5) Å³, Z=2, ρ_{cald} =1.260 g cm⁻³, μ =0.256 mm⁻¹ (Mo_{Kav}, λ =0.71073), F(000)=552, T=293(2) K, $2\theta_{max}$ =52.00°, 11590 measured reflections, 2728 independent reflections (R_{int} =0.0142), GOF on F^2 =0.994, R_1 =0.0373, wR_2 =0.1300 (all data), Δe 0.256 and -0.348 e Å⁻³.

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