Synthesis, Structure, Aggregation-Induced Emission, Self-Assembly, and **Electron Mobility of 2,5-Bis(triphenylsilylethynyl)-3,4-diphenylsiloles**

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Abstract: 2,5-Bis(triphenylsilylethynyl)-3,4-diphenylsiloles with different 1,1-substituents [XYSi(CPh)₂(C-C=C- $SiPh_3)_2$ (Ph = phenyl) were synthesized in high yields by the Sonogashira coupling of 2,5-dibromo-3,4-diphenylsiloles with triphenylsilylacetylene, and two of these were characterized crystallographically. Crystal structures and theoretical calculations showed that the new silole molecules had higher conjugation than 2,5-diarylsiloles. They possessed low HOMO and LUMO energy levels due to the electron-withdrawing effect of the triphenylsilylethynyl groups. Cyclic voltammetry analysis revealed low electron affinities, which were comparable to those of perfluoroarylsiloles. B3LYP/6-31* calculations demonstrated that the new siloles possessed large reorganization energies for electron and hole transfers and high electron mobilities. A mobility of up to $1.2 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ was obtained by transient electroluminescence the method, which was about fivefold higher than that of tris(8-hydroxyquinolinato)aluminum a widely used electron-transport material, under the

Keywords: electron transport electronic structure · fluorescence · self-assembly • silole

same conditions. All of the silole molecules possessed high thermal stability. Although, their solutions were weakly emissive, their nanoparticle suspensions and thin films emitted intense bluegreen light upon photoexcitation, demonstrating a novel feature of aggregation-induced emission (AIE). Polarized emissions were observed in the silole crystals. The addition of solvents, which did not dissolve the silole molecules, into silole-containing solutions caused self-assembly of the molecules, which produced macroscopic fibrils with strong light emissions.

occupied molecular orbital (LUMO) energy level.^[1] As a

result, siloles exhibit high electron affinity and fast electron

mobility.^[2] Recently, great efforts have been made to functionalize siloles and utilize them as electron-transport mate-

rials,^[3] light emitters,^[4] building blocks for conducting poly-

mers,^[5] fluorescence sensors,^[6] solar cells,^[7] electrochemilu-

minescence,^[8] and so forth. Meanwhile, many theoretical

studies have been conducted in order to better understand

the substitution effect on their electronic structures and op-

One-dimensional (1D) self-assembly of functional materi-

als has attracted increasing interest for the fabrication of

nanoscale electronic and optoelectronic devices, in which

the device miniaturization requires small channel materi-

als.^[10] In particular, macroscopic self-assembled materials

constructed from small molecules often show more unique

and/or enhanced properties than their molecular compo-

nents.^[11] The driving force of the supramolecular self-assem-

bly can be hydrogen bonding and/or other weak interac-

tions, such as π - π stacking, van der Waals forces, and elec-

trostatic forces. Recent investigations suggest that π - π

stacking between planar, rigid, organic small molecules and

oligomers is an effective way for aromatic molecules to as-

semble into materials with a 1D columnar nanostructure.

Such processes have increased the charge carrier mobility of

the organic semiconductors due to strong electronic cou-

toelectronic properties.^[9]

Introduction

Siloles (silacyclopentadienes) are silicon-containing fivemembered cyclic dienes that have attracted extensive attention due to their unique electronic properties and potential high-technological applications. They are considered novel $\sigma^* - \pi^*$ conjugated materials, in which the σ^* orbital of the silicon–carbon bond effectively interacts with the π^* orbital of the butadiene fragment, leading to a low-lying lowest un-

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- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201003382.



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pling between the molecules and polarized fluorescence arising from anisotropy in different directions.^[12] However, it is generally known that chromophore aggregation can quench light emission due to increased excited state relaxation through nonradiative pathways.^[13] Thus, the synthesis of fluorophores with strong emissions in the aggregate states through 1D self-assembly is intriguing, although such materials are seldom reported. Recently, Park prepared several organogels by the self-assembly of low-molecular-weight fluorophores and found that the emission is induced or enhanced along the stacking direction.^[14] This may open a new avenue for the development of columnar self-assembling materials with efficient light emissions.

During our search for highly luminescent materials, we were attracted by a group of propeller-shaped molecules called siloles. The structures of some molecules are shown in Scheme 1. These molecules are nonluminescent in solution



Scheme 1. Chemical structures of 2,3,4,5-tetraphenylsiloles.

but emit intensely in the solid-phase.^[15] We coined this novel phenomenon as "aggregation-induced emission" (AIE) because the nonemissive silole molecules are induced to emit intensely by aggregate formation. Mechanistic studies by different approaches reveal that the AIE effect is attributed to the restriction of intramolecular rotation (RIR).^[16,17] Utilizing the AIE characteristics, we have fabricated light-emitting diodes (LEDs) using siloles as active layers and obtained outstanding device performances. An external quantum efficiency of 8% was achieved in an organic light-emitting diode (OLED) device of MPPS MPPS = 1-methyl-1,2,3,4,5-pentaphenylsilole), (Scheme 1; approaching the limit of the possible.^[18] Technological applications of silole molecules as environmental sensors and biological probes were also explored.

Siloles are unique materials, and, therefore, preparation of new siloles is of academic and practical value. Studying their structure–property relationship will give valuable information on the synthesis of new molecules with novel molecular structures and properties. Due to its linear geometry and rich chemistry, triple bonds have been used as functional bridging groups to link aromatic rings together. In this work, we designed and synthesized new silole molecules by attaching triphenylsilyl groups to the silole core at the 2,5-positions through triple-bond functionalities (Scheme 2). The substitution effect at the 2,5-positions on their crystal and electronic structures were investigated. Thanks to the triphenylsilylethynyl groups, 1a-1c showed higher thermal stability and electron mobility than HPS and MPPS (Scheme 1; HPS=1,1,2,3,4,5-hexaphenylsilole). The addition



Scheme 2. Synthesis of 2,5-bis(triphenylsilylethynyl)-3,4-diphenylsiloles. Np = naphthyl, TMEDA = tetramethylethylenediamine. NBS = N-bromosuccinimide.

of solvents, which do not dissolve the silole molecules, into solutions of **1c** caused self-assembly of the molecules and produced fluorescent fibrils with macroscopic sizes.

Results and Discussion

Synthesis: To enlarge the library of silole molecules, we prepared three 2,5-bis(triphenylsilylethynyl)-3,4-diphenylsiloles with different 1,1-substituents according to Scheme 2. The one-pot synthesis of 2,5-extended siloles from 2,5-dilithiosiloles generally results in many side reactions, making the purification of the desired products a painful task. However, Sonogashira coupling of aromatic halides with alkynes is more efficient and much "cleaner" and has been widely used to construct conjugated monomers and oligomers.^[19] Thus, we prepared the 2,5-dibromosiloles (4a-4c) intermediates according to the literature methods,^[16c, 19] by bromination of 2,5-dilithiosiloles with N-bromosuccinimide (NBS). Single crystals of 4a and 4c were grown from their methanol/dichloromethane mixtures. The ORTEP plots of 4a and 4c are shown in Figure S1 in the Supporting Information and their crystal data are summarized in Table S1. Coupling of 4a-4c with triphenylsilylacetylene in the presence of $[Pd(PPh_3)_4]$ (PPh_3=triphenylphosphine) and CuI furnished the desired products 1a-1c in high yields. The new silole molecules were soluble in common organic solvents such as THF, dichloromethane, chloroform, and toluene, but were insoluble in ethanol, methanol, and water.

Crystal structures: The effect of bulkiness of the triphenylsilyl groups on the molecule structures of 1a-1c was investigated by single-crystal X-ray diffraction. The crystals of siloles 1a and 1b were grown from solutions of the complexes in methanol or *n*-hexane/dichloromethane mixtures as yellow blocks and yellow needles, respectively. Crystals of 1c were, however, not obtained under similar conditions. Suitable specimens for crystallography were mounted in air

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on glass fibers and their X-ray diffraction intensity data were collected on a diffractometer. The ORTEP drawings of **1a** and **1b** are shown in Figure 1 and their crystallographic data are summarized in Table S2 in the Supporting Information. The geometric parameters for the crystal structures of both siloles are listed in Table 1. Siloles **1a** and **1b** crystallized in the monoclinic system with space groups of $P2_1/n$ and $P2_1/c$, respectively. Both molecules exhibited an almost planar silacyclopentadiene ring with low torsion angles down to 1.1°. Similar observations were also found in our previous investigations on siloles with the same substituents



Figure 1. a) and b) ORTEP drawings of **1a** and **1b**, respectively. c) π - π interactions between phenyl groups of adjacent molecules of **1a**. d) B3LYP/6-31G* calculated molecular orbital amplitude plots of HOMO and LUMO energy levels of **1a**.

Table 1. Experimental and calculated structural parameters for $1\,a$ and $1\,b.$

	1:	1	1b		
	X-ray	calcd	X-ray	calcd	
bond lengths [Å]					
endocyclic Si1-C1	1.868(13)	1.889	1.864(3)	1.890	
endocyclic Si1-C4	1.871(13)	1.892	1.867(3)	1.887	
endocyclic C1-C2	1.361(17)	1.377	1.356(4)	1.376	
endocyclic C2-C3	1.508(18)	1.496	1.502(4)	1.497	
exocyclic Si1-C31	1.861(14)	1.892	1.852(3)	1.884	
exocyclic Si1-C	1.862(14) ^[a]	$1.878^{[a]}$	$1.844(3)^{[b]}$	$1.881^{[b]}$	
exocyclic C1-C5	1.419(17)	1.406	1.426(4)	1.405	
exocyclic C2-C11	1.486(17)	1.486	1.489(4)	1.486	
exocyclic C5-C6	1.208(18)	1.227	1.205(4)	1.227	
bond angles[°]					
C1-Si1-C4	90.7(6)	90.532	90.1(14)	90.569	
C2-C1-Si1	109.4(9)	109.066	110.2(2)	109.229	
C3-C4-Si1	109.9(9)	109.181	109.9(2)	109.105	
C1-C2-C3	115.5(11)	115.733	114.7(3)	115.420	
C4-C3-C2	114.5(11)	115.441	114.9(3)	115.628	
C1-C2-C11	121.3(11)	122.413	123.2(3)	122.483	
C2-C1-C5	125.0(12)	126.596	126.1(3)	127.239	
C6-C5-C1	175.6(14)	174.922	172.6(3)	174.336	
C5-C6-Si2	175.7(13)	178.448	177.1(3)	178.802	
torsion angle [°]					
Si1-C1-C2-C3	1.1(14)	1.599	5.1(4)	1.706	
C1-C2-C3-C4	0.01(16)	-2.512	-2.6(4)	-2.631	
C3-C2-C11-C16	-124.0(14)	-129.831	-58.7(4)	-48.292	
C2-C3-C21-C22	-142.9(13)	-131.868	-60.0(4)	-47.938	

[a] Si1–C41. [b] Si1–C30.

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at the 1,1-positions.^[17] Both **1a** and **1b** showed highly twisted conformations of the phenyl groups at the ring carbons of the silole skeletons. The phenyl substituents of **1a** and **1b** were twisted out of the plane of silacyclopentadiene, with dihedral angles to the phenyl planes of -124 and -58.7° at the C2 ring carbon atoms and -142.9 and -60° at the C3 position, respectively. The extent of the twisting was, however, small, when compared with HPS and MPPS at the same positions. It is worth noting that the phenyl blades of the triphenylsilyl groups of adjacent molecules of **1a** are arranged in a parallel fashion with a interplanar distance of 3.518 Å

(Figure 1 c). Such spacing implies π - π stacking and interactions,^[9e,20] which enables tight packing of the molecules in the three-dimensional crystal lattice.

The endocyclic C–C single bond lengths (e.g., C2–C3 = 1.508 Å) of **1a** were much longer than the endocyclic C=C double bonds (e.g., C1=C2 = 1.361 Å) and exocyclic C–C single bonds (C2–C11=1.486 and C1–C5=1.419 Å). The endocyclic Si–C single bond lengths were also longer than the exocyclic Si–C single bonds. Silole **1b** also exhibited similar behavior. The Si–C single bonds of **1a** were somewhat stretched due to the steric

effect of its two bulky phenyl groups, whereas in **1b**, this effect was lessened because it had only one phenyl group at the 1-position. The bond angles of the silole rings of **1a** and **1b** varied slightly, with a typical pattern of a relatively small angle about the silicon C1-Si1-C4 (90.7° for **1a** and 90.1° for **1b**), with standard angles of 109.4–110.2° at C1 and C4, and wider angles of 114.5–115.5° between C2 and C3. The bond angles at sp carbons (C6-C5-C1 and C5-C6-Si2, for example) were in the range of 172.6–177.1°, and those between the sp carbons and the silole ring sp² carbons (C2-C1-C5) were 125.0° in **1a** and 126.1° in **1b**, which indicated that the C=C triple bonds were well conjugated with the silole ring.

Electronic structures: Silole absorbs more into the red region than cyclopentadiene.^[21] Tamao investigated the structure of silole and compared it with cyclopentadiene by HF/6-31G* calculations to evaluate the role of the silicon atom in the electronic properties of the silole molecule. Results showed that silole had low-lying HOMO and LUMO energy levels, which were about 0.4 and 1.3 eV lower than those of cyclopentadiene, respectively. PM3 calculations revealed that the low-lying LUMO energy level arose from $\sigma^*-\pi^*$ conjugation between σ^* orbitals of the exocyclic σ bonds on silicon and π^* orbitals of the butadiene skeleton. Such effects give siloles unusual optical properties.^[22] Tamao

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also investigated the properties of siloles with different substituents at the ring silicon atom^[23] and 2,5-positions of the silole ring.^[9f] Both modifications were found to have strong influences on the electronic structures and energy levels of the silole molecules.

To evaluate the substituent effect on the electronic structures of 2,5-bis(triphenylsilylethynyl)-3,4-diphenylsiloles, we carried out theoretical calculations of 1a and 1b. The ground-state geometries were optimized using density functional theory (DFT) with B3LYP hybrid functional at the basis set level of 6-31G*, and the unrestricted formalism (UB3LYP) was adopted for the ion-state geometries. All of the calculations were performed using the Gaussian 03 package in a power leader workstation. The calculated values for the pertinent geometrical parameters were comparable to the experimental values determined from X-ray crystallography (Table 1). The optimized bond lengths and angles were slightly longer, but were still in good agreement with the experimental values. However, the torsion angles showed a large variation. This was in some senses expected because the packing effect was not included in the calculation, which offered the silole molecules a more open and less spherically compressed molecular structure. The torsion angles of 1a and 1b at the 3,4-positions were almost the same, revealing that the substituents at the 1,1-positions had no pronounced effects on the configurations of the phenyl groups at the 3,4positions. The optimized structures of 1a and 1b also showed that their phenyl groups at the 3,4-positions were less twisted and the silole rings were more planar than HPS and MPPS.^[17] This may be due to the triple bond functional bridge groups, which showed steric hindrance between the silole cores and the triphenylsilyl groups.^[16c,24]

The HOMOs and LUMOs of **1a** and **1b** displayed almost identical surfaces. Figure 1 d depicts the HOMO and LUMO of **1a** as an example. The HOMO and LUMO are mainly dominated by orbitals originating from the silole ring and two C=C triple bonds at the 2,5-postions. The two C=C triple bonds had significant contributions to both HOMOs and LUMOs due to efficient orbital overlapping. On the other hand, the phenyl groups at the 3,4-positons participated and contributed little to the energy levels. A contribution was not found for the phenyl groups attached to the Si2 and Si3 atoms. Owing to the $\sigma^*-\pi^*$ conjugation, the LUMOs had significant orbital density at the two exocyclic Si1–C bonds, which were identical to those of HPS, MPPS, and other silole derivatives.^[24]

The calculated HOMO energy levels for **1a** and **1b** were nearly identical (-5.42 eV for **1a** and -5.44 eV for **1b**). These values were lower than those of 1,1-dimethyl-2,3,4,5tetraphenylsilole (DMTPS, -5.29 eV), 2,5-dipyridylsilole (PySPy, -5.28 eV),^[9b] and 2,5-bis(trialkylsilylethynyl)-3,4-diphenylsiloles (from -5.28 to -5.39).^[16c] The LUMO energy levels for **1a** and **1b** were -2.29 eV and were much lower than DMTPS (-1.59 eV), PySPy (-1.82 eV), and other silole derivates determined using the same method,^[9b,c,f] indicating that the new silole derivatives were more electron affinitive. This also suggested that the triphenylsilylethynyl groups worked better than the trialkylsilylethynyl groups at lowering the energy levels of the silole molecules. Although, compared with the HOMO, the LUMO might play a more important role in determining the electronic properties of siloles. The lower LUMO energy level of **1a** than HPS may be one of the key reasons for the difference in electron-transport properties. The calculated band gap of **1a** and **1b** were $\approx 0.6 \text{ eV}$ lower than HPS (3.7 eV).

Redox activity: Hole and electron injections in electronic devices strongly influence the device efficiency. It is important to assess hole and electron injection barriers at the interfaces of various materials in designing device configurations. Such parameters can be estimated by comparing the ionization potentials (IPs) and electronic affinities (EAs) of the molecular components with each other and/or with Fermi energies of inorganic electrode materials.^[25] These data can be obtained through electrochemical measurements.

We investigated the redox behaviors of **1a–1c** in the solution state by cyclic voltammetry using ferrocene as the internal reference. As illustrated in Figure 2, all of the 2,5-bis(tri-



Figure 2. Cyclic voltammograms of 1a-1c in dichloromethane containing $0.1 \text{ M Bu}_4\text{NPF}_6$.

phenylsilylethynyl)-3,4-diphenylsiloles exhibited only one irreversible reduction peak at about -1.75 V. Similar to other silole derivatives,^[4b] an oxidation peak was not found. This means that hole injection is more difficult than electron injection in these siloles. According to references [4b,9c,d,26], the solid-state EA of a molecular species can be estimated by comparing its electrochemical potential for the $M^{0/-}$ couple with that for a commonly used electron-transport material (e.g., tris(8-hydroxyquinolinato)aluminum (Alq₃)), for which the solid-state EA and reduction potential have been determined. Thus, the EAs of **1a–1c** can be calculated by the following equation [Eq. (1)].

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$$EA(M) - EA(Alq_3) = E_{\frac{1}{2}}(Alq_3^{0/-}) - E_{\frac{1}{2}}(M^{0/-})$$
(1)

Taking the values of $E_{1/2}(Alq_3^{0/-}) = -2.30 V^{[27]}$ and EA- $(Alq_3) = -2.0$ to -2.5 eV,^[28] and assuming that $E_{1/2}$ was similar to $E_{\rm re}$ (-1.75 V), the EAs of **1a-1c** are in the range from -2.55 to -3.05 eV. These values are ≈ 0.5 eV lower than HPS (-1.95 to -2.45 eV),^[9c] and close to those of 2,5-diperfluoroarylsiloles (-2.58 to -2.93 eV).^[4b] This showed that the triphenylsilylethynyl substituents have a similar effect to the perfluoroaryl groups (e.g., C₆F₅, C₁₂F₉) for electron injection. The values were also $\approx 0.5 \text{ eV}$ lower than that of Alq₃ and were comparable to *n*-type conducting materials with the lowest EA energies.^[29] The low EA values of **1a-1c** might thus allow the molecules to find an array of applications in electronics. One aspect should be clarified that the EAs of the silole molecules estimated by the above procedures were only rough values. The main reason was that the reduction potential value was irreversible and was not equal to the real half-wave reduction potential. Nevertheless, the comparisons were performed based on the same method and data reported in the literature.

Cation and anion properties: To investigate if 1a-1c can be employed as charge transport materials in organic electronic devices, geometry optimizations for both the radical anion and radical cation states (i.e., a neutral molecule in the presence of an extra electron and a hole) were performed. Table 2 lists the calculated variations of the structural parameters in both states. Similar to HPS, MPPS, and other si-

Table 2. Calculated variations in the structural parameters of **1a** and **1b** in the cationic and anionic states.

	1 a		1	1b		
	cation	anion	cation	anion		
bond length [Å]						
endocyclic Si1-C1	0.0175	-0.0225	0.0126	-0.0203		
endocyclic Si1-C4	0.0118	-0.0235	0.0127	-0.0197		
endocyclic C1-C2	0.0365	0.0478	0.0383	0.0468		
endocyclic C2-C3	-0.0424	-0.058	-0.0417	-0.0579		
exocyclic Si1-C31	-0.0135	0.0195	-0.0067	0.0127		
exocyclic Si1-C	$-0.0111^{[a]}$	$0.0185^{[a]}$	$-0.013^{[b]}$	0.0213 ^[b]		
exocyclic C1-C5	-0.0233	-0.0173	-0.0238	-0.0182		
exocyclic C2-C11	-0.0083	-0.0026	-0.0095	-0.0022		
exocyclic C5-C6	0.0085	0.0117	0.0087	0.0121		
bond angle [°]						
C1-Si1-C4	-2.3755	1.2721	-2.2204	1.0497		
C2-C1-Si1	-1.3237	-0.6754	-0.1491	-1.3005		
C3-C4-Si1	1.7738	-0.9592	1.6951	-0.7944		
C1-C2-C3	-0.6057	0.2127	-0.5767	0.3714		
C4-C3-C2	-0.5196	0.3711	-0.5402	0.2063		
C1-C2-C11	-0.7156	-1.5236	-0.797	-1.6266		
C2-C1-C5	-1.2841	0.4943	-1.3907	0.2542		
C6-C5-C1	-0.2354	0.9031	0.1739	1.1654		
C5-C6-Si2	0.3524	0.9883	-1.9362	0.3652		
torsion angle [°]						
Si1-C1-C2-C3	-1.3237	-0.6754	-0.1491	-1.3005		
C1-C2-C3-C4	1.1139	0.6332	0.4602	1.1041		
C3-C2-C11-C16	1.9801	2.5573	3.963	2.6495		
C2-C3-C21-C22	2.7244	2.7539	2.7568	2.8894		

[a] Si1-C41. [b] Si1-C30.

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loles,^[9b,d,18] the geometric modifications for **1a** and **1b** upon carrier-injection were primarily localized within the central portion of the molecular system, the silole ring with two triple bonds. When an electron was injected (anion), the exocyclic Si1-C bond lengths were increased, and the ring Si1-C bond lengths shortened. The cis-butadiene portion of the central ring underwent a significant decrease in the bond length alternation as the C-C bonds adjusted to the presence of the extra electron. Meanwhile, the total lengths of the exocyclic C-C single bonds and the C=C triple bonds decreased significantly to stabilize the additional charge. The addition of a hole into 1a and 1b shortened the exocyclic Si1-C bond, but lengthened the ring Si1-C bond. Similar to the anion case, there was a significant change in the bond-length alternation pattern of the C-C bonds in the central ring and the C=C triple bonds at the 2,5-positions. However, the effect of electron addition on the lengths of exocyclic Si1-C single and C=C triple bonds was more profound than that of hole. With regard to the bond angle, the anion had larger endocyclic C-Si-C and smaller exocyclic C-Si-C bond angles than the neutral molecules. The cation exhibited the opposite behavior. Both the cation and the anion exhibited smaller torsion angles of the phenyl groups at the 3,4-positions and shorter bridge bond lengths than those of the neutral molecule, indicating that both the cation and the anion possess less twisted structures with higher conjugation. Overall, upon charge injection into 1a and 1b, geometry relaxation took place mainly in the silole ring and the adjacent C=C triple bonds at the 2,5-positions.

Reorganization energy and carrier mobility: Many reports have showed that siloles have higher electron mobility than Alq₃.^[2,17] To prove that it also holds for our new silole molecules, we calculated the barriers for electron and hole transfers in the radical anion and cation species and the carrier mobility of 1a and 1b. To describe the charge transport in the crystal state, we considered an incoherent hopping model, in which the charge could only transfer between the adjacent molecules. Viewing each hopping event as a nonadiabatic electron transfer reaction, we used standard Marcus theory^[30] to express the rate of charge motion between the neighboring molecules (W) in terms of the reorganization energy (λ) and the coupling matrix element (V). Assuming that the temperature is sufficiently high that vibrational modes can be treated classically, we obtained Equation (2), in which $k_{\rm B}$ is the Boltzmann constant and T is the temperature (298 K). Given the hopping rate between the two neighbors, the diffusion coefficient can be evaluated according to Equation (3), in which n is the dimensionality, W_i is the hopping rate due to charge carrier to the *i*th neighbor, r is the distance to neighbor *i*, and *P* is the relative probability for charge carrier to a particular *i*th neighbor [Eq. (4)]. In Equation (2), when n=1 the diffusion coefficient is in a special direction, and 2n=6, summing over all possible hops, leads to the averaged diffusion coefficient. The drift mobility of hopping, μ , is then evaluated from the Einstein relation [Eq. (5)], in which *e* is the electronic charge. Only when the intermolecular transfer integral (V) and the reorganization energy (λ) have been calculated, can the average drift mobility be evaluated using Equations (2)–(5). A direct dimer Hamiltonian method was adopted to calculate the intermolecular transfer integral (V). It can be written as given in Equation (6), in which $\langle \phi_{HOMO/LUMO}^{0,site 1} \rangle$ and $|\phi_{HOMO/LUMO}^{0,site 2} \rangle$ represents the HOMO/LUMO wave functions of two isolated molecules at different sites. F^0 is the Fock matrix constructed from the density matrix of the noninteracting dimer, which can be evaluated as $F=SC\varepsilon C^{-1}$, in which S is the overlap matrix of the dimer, and the Kohn–Sham orbital coefficients C and energy Eigen value ε are obtained by onestep diagonalization without iteration.

$$W = \frac{V^2}{\hbar} \left(\frac{\pi}{\lambda k_{\rm B}T}\right)^{\frac{1}{2}} \exp\left(-\frac{\lambda}{4k_{\rm B}T}\right)$$
(2)

$$D = \frac{1}{2n} \sum_{i} r^2 W_i P_i \tag{3}$$

$$P_i = \frac{W_i}{\sum_i W_i} \tag{4}$$

$$\mu = \frac{e}{k_{\rm B}T}D\tag{5}$$

$$V_{+/-} = \langle \phi_{\text{HOMO/LUMO}}^{0,\text{site 1}} | F^0 | \phi_{\text{HOMO/LUMO}}^{0,\text{site 2}} \rangle \tag{6}$$

The reorganization energy (λ) can be separated into the sum of two primary components: 1) the medium reorganization energy that arises from the modifications to the polarization of the surrounding medium due to the presence of excess charge (λ_s) and 2) the intramolecular reorganization energy (λ_i) , which corresponds to the sum of geometry relaxation energies upon going from the neutral-state geometry to the charged-state geometry and vice versa. Hence, λ for hole and electron transfers is given by Equation (7), in which $E_{\rm ng}^{+/-}$ and $E_{\rm ng}$ are the energies of the charged-state and neutral-state with the neutral-state geometry, and $E_{cg}^{+/-}$ and E_{cg} are the energies of the charged-state and neutralstate with the charged-state geometry. Considering the negligible medium reorganization energy in the solid state, we calculated the intramolecular contribution to the total reorganization energies for electron and hole transfers, and the

results are compared in Table 3 and the charge-hopping pathways are illustrated in Figures S2 and S3 in the Supporting Information.

$$\lambda_{+/-} = (E_{\rm ng}^{+/-} - E_{\rm cg}^{+/-}) + (E_{\rm cg} - E_{\rm ng})$$
(7)

The total reorganization energies for electron transfer (λ_{-}) were 0.574 and 0.541 eV for **1a**

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and **1b**, respectively, which were higher than the previously reported values for HPS, MPPS, and other silole derivatives.^[9b] The energies for hole transfer (λ_{+}) were 0.486 and 0.519 eV, respectively. The λ_{-} energy of **1a** was much higher than HPS (0.49 eV), fluorine-containing HPS (0.56 eV),^[9c] and other pyridine-substituted siloles ($\approx 0.50 \text{ eV}$),^[9b] and was approximately twice the value for Alq₃ (0.276 eV) calculated at the same level.^[31] The λ_{+} was also appreciably high, being four to five times larger than pentacene^[32] and more than twofold higher than that of N,N'-diphenyl-N,N'bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine, a widely used hole transport material.^[33] The geometric modifications that occurred during the reduction and oxidation of the new 2,5-bis(triphenylsilylethynyl)-3,4-diphenylsiloles were primarily localized at the central portion of the molecules, particularly in the silole ring, two C=C triple bonds, and exocyclic Si1-C bonds. This localization was mainly responsible for the relatively large reorganization energy of 1a and 1b.

The calculated hole mobility of **1a** and **1b** was as low as 3.30×10^{-7} and 3.08×10^{-7} cm²V⁻¹s⁻¹, respectively. However, they exhibited reasonably high electron mobility. The value for 1a was $2.92 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, which was about tenfold higher than that for **1b** $(3.84 \times 10^{-6} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1})$. The much higher electron mobility of 1a might be attributed to its more symmetrical structure, which encouraged a more compact stacking of molecules. This resulted in shorter intermolecular distances and, hence, promoted larger electronic coupling. Moreover, the π - π intermolecular interactions between the phenyl rings of the triphenylsilyl groups in the crystals of 1a might be helpful to increase the electron hopping rate,^[9b,e] which thus gave the molecule a higher electron mobility than those of 1,1,3,4-tetraphenylsioles with smallsized trialkylsilylethynyl substituents at the 2,5-positions $(1.33 \times 10^{-5} - 4.06 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}).^{[24a]}$

Thermal stability: The thermal properties of **1a–1c** were examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under nitrogen at a heating rate of 20 Kmin⁻¹. Table 4 summarizes the results and their TGA thermograms are given in Figure S4 in the Supporting Information. For comparison, the thermograms of HPS, MPPS, and DMTPS are also provided in the same figure.^[17] The melting points of **1a–1c** were 251, 248, and 194°C, re-

	Reorganization energy [eV]		Pathway Dimer distance [Å		Transfer integral [eV]		Drift mobility $[cm^2V^{-1}s^{-1}]$	
	λ+	λ_{-}			V_+	V_{-}	μ_+	μ_{-}
1a	0.486	0.574	Ι	9.761	4.92×10^{-5}	2.42×10^{-3}	3.30×10^{-7}	2.92×10^{-5}
			II	17.672	1.17×10^{-4}	2.20×10^{-4}		
			III	9.020	2.48×10^{-5}	3.17×10^{-4}		
			IV	8.650	1.35×10^{-4}	2.64×10^{-5}		
1b	0.519		Ι	8.402	4.30×10^{-6}	9.30×10^{-5}	3.08×10^{-7}	3.84×10^{-6}
		0.541	II	18.875	1.43×10^{-5}	1.34×10^{-5}		
		0.541 II IV	III	8.811	2.06×10^{-4}	8.20×10^{-4}		
			IV	18.063	2.35×10^{-5}	1.10×10^{-4}		

Table 3. Calculated transport characteristics of **1a** and **1b**.

Table 4. Optical properties of 1 in solution (Soln),^[a] crystalline (Cryst), and amorphous (Amor) states and their thermal properties.^[b]

	λ_{abs} [nm]	$\lambda_{\rm em}$ [nm]		$arPsi_{ m F}$	$E_{\rm g}$	$T_{\rm m}/T_{\rm d}$	
	$(\epsilon \times 10^4 [\text{m}^{-1} \text{cm}^{-1}])$	soln	cryst	amor	[%]	[eV]	[°C]
1a	405 (1.23)	490	487	491	18.1 (2.3)	2.75	251/412
1b	400 (1.24)	486	484	489	28.3 (1.0)	2.77	248/401
1c	397 (1.12)	483	-	490	34.6 (0.7)	2.79	194/396

[a] Dilute solutions in THF (10 μ M). [b] Abbreviations: λ_{abs} = absorption maximum, ε = molar absorption, λ_{em} = emission maximum, Φ_F = fluorescence quantum yield of the film determined by integrating sphere (data given in the parentheses were determined in THF solutions using 9,10-diphenylanthracene with a Φ_F value of 90% in cyclohexane as standard), E_g = energy band gap determined from the UV/Vis spectra, T_m = melting point, T_d = decomposition onset temperature.

spectively. They demonstrated high thermal stability with onset decomposition temperatures at 412, 401, and 396 °C for **1a–1c**, respectively. Such values were much higher than those of HPS, MPPS, and DMTPS, probably due to the thermally stable, bulky triphenylsilylethynyl groups, which gave the present molecules high resistance to thermolysis.

UV/Vis absorption: Figure 3 shows the UV/Vis absorption spectra of 1a-1c in THF. All of the molecules exhibited an absorption band at approximately 260 nm arising from the phenyl groups of the triphenylsilyl units as well as ones attached to the silole rings. The conjugated silole core absorbed at longer wavelengths and showed a blueshift from 405 nm in 1a to 397 nm in 1c. Similar phenomenon have been observed by Tamao^[23] and us^[15b, 16c] and were attributed to the change in the inductive effect by varying the substituents at the 1,1-positions. The absorption maxima of 1a-1c showed a \approx 40 nm redshift from those of HPS, MPPS, and DMTPS (366, 363, and 361 nm, respectively)^[17] with higher molar absorptions. The band gaps estimated from the onsets of their absorption spectra were, however, smaller. These results agreed well with the data obtained from the theoretical calculations that 1a-1c possessed higher conjugation. Due to steric hindrance, the phenyl groups at the 2,5-positions of HPS, MPPS, and DMTPS, were twisted out of the plane of



Figure 3. UV/Vis absorption spectra of 1a-1c in THF solutions.

the silole ring, which hampered their electronic communication and resulted in larger band gaps.

Light emission: Similar to the previously reported siloles, the wet spots of **1a-1c** on TLC plates were nonluminescent under the illumination of a UV lamp, but became visible when the solvent evaporated. Their dilute solutions in THF (10 µM) exhibited weak photoluminescence (PL) at 483-490 nm when photoexcited at 370 nm. The fluorescence quantum yields ($\Phi_{\rm F}$) of **1a–1c** in THF were measured to be 2.3, 1.0, and 0.7%, respectively (Table 4). Previous studies showed that the active intramolecular rotation of the phenyl rings around the axes of the single bond linked to the silole ring had annihilated the excitons, thus making the silole molecules weakly emissive in the dilute solutions.^[9a,f,18] Although the triphenylsilyl groups were bulky, it seemed that they could not efficiently restrict the intramolecular rotations of **1a–1c**, resulting in low $\Phi_{\rm F}$ values in solution. However, their thin films were highly emissive at the same excitation wavelength. The $\Phi_{\rm F}$ values of their thin solid films were 18.1, 28.3, and 34.6% (Table 4), respectively, revealing that their emissions, similar to other silole derivatives, were induced by aggregate formation or in other words, they exhibited a novel characteristic of AIE.

To confirm whether 1a-1c were really AIE active, we added different amounts of water, in which the silole molecules are insoluble, to their solutions in THF and studied the PL change. The final concentration of the mixtures was kept at the same value of $10 \,\mu\text{M}$ to allow standard comparison. Figure 4a shows the PL spectra of 1a in THF/water mixtures with different water fractions. The PL intensity remained virtually unchanged when up to $\approx 60\%$ of water was added. Afterward, it swiftly increased. Compound 1a is insoluble in water; therefore, its molecules must have aggregated in the mixtures with high water contents. The population of the aggregates and hence the PL intensity continued to increase with subsequent increases in the water content. Clearly, 1a was AIE active. Similar behaviors were also observed in 1b and 1c (Figure 4b).

To prove that aggregates of **1a–1c** were formed when large amounts of water was present in their THF solutions, we carried out particle size analysis. The aggregates of **1a** were nanodimensional and their average diameters decreased from 441 to 42 nm when the water fraction in the mixture was increased from 70 to 99.5% (Figure S5a in the Supporting Information). The particle size was further confirmed by transmission electron microscopy (TEM). An example of a TEM image of nanoaggregates of **1a** in a THF/ water mixture with 90% water is given in Figure S5. Similar phenomena were observed in our previous work.^[34] In mixtures with higher water contents, the molecules might agglomerate quickly to form smaller aggregates, while at lower water contents, the molecules of **1a** might slowly assemble in an ordered fashion to form larger clusters.

Polarized emission is generally originated from an ordered alignment of molecules in the solid state. However, the strong π - π interactions in the aggregated and crystal

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Figure 4. a) PL spectra of **1a** in THF/water mixtures with different water fractions; concentration: $10 \,\mu$ M; excitation wavelength: 370 nm. b) Plots of $(I/I_0)-1$ versus water fractions in THF/water mixtures, in which I_0 was the PL intensity in pure THF.

states of most conventional luminophores significantly quench their PL. Due to their AIE characteristics, the aggregates and solid films of 1a-1c can emit intense light

upon photoexcitation. It would be even better if the silole molecules could exhibit polarized emission. Therefore, we investigated the PL of crystals of **1a** and **1b** in vertical and horizontal directions. Interestingly, the crystals of **1a** and **1b** showed emission anisotropy with strong PL intensity in the vertical direction (Figures 5a and 5b). The reproducible polarization ratios (I_v/I_h)

were 4.49 and 4.75, and the degrees of polarization $[P=(I_v-I_h)/(I_v+I_h)]$ were calculated to be 0.64 and 0.65, respectively. These values, although preliminary, were quite high and close to that of single crystalline CdSe nanorods, highly fluorescent inorganic semiconductors.^[35]

Self-assembly: Although we failed to obtain crystals of 1c, we found that it exhibited a facile one-dimensional self-assembling ability. When a poor solvent, such as methanol, was added slowly into its dichloromethane solution (1 mgmL⁻¹) in a glass tube, thin 1D nanorods started to form at the solvent interface. Figures 6A and 6B show the scanning electron microscopy (SEM) images of the fibrils obtained from the methanol/dichloromethane mixture. The fibrils were elongated in shape with diameters of $\approx 50 \text{ nm}$ and lengths of several tens of micrometers (Figure 6A). After standing at ambient conditions for several days, more nanocables were formed and their association afforded fibrils with micrometer sizes (Figure 6B). Bundles of 1c were formed by further gathering of microrods. It is worth noting that parallel bands normal to the director of the microrods were clearly seen, suggesting that the microfibrils were constructed by side-by-side self-assembling of the nanorods. Analysis by TEM showed that the ropes possessed a uniform inner structure, as shown in Figure S6 in the Supporting Information.

After solvent evaporation, large gatherings of microrods were obtained at the bottom of the tube. The majority of the rods were arranged uniformly in a parallel fashion. Analysis by powder X-ray diffraction showed that these microrods were crystalline in nature (Figure S7 in the Supporting Information). Irrespective of the size, all of the cables emitted intensive green light upon photoexcitation, especially at the cross sections (Figure 6C). It is truly amazing that the silole molecules can spontaneously self-assemble into materials with well-organized morphological structures by simple evaporation methods. Together with their strong light emission, such materials are promising candidates in the fabrication of miniature electronic and photonic devices.



Figure 5. Polarized emissions from crystals of a) **1a** and b) **1b** and c) microrods of **1c**. Abbreviations: $I_v = PL$ intensity in the vertical direction, $I_h = PL$ intensity in the horizontal direction, P = degree of polarization calculated by $(I_v - I_h)/(I_v + I_h)$, r = fluorescence anisotropy calculated by $(I_v - I_h)/(I_v + 2I_h)$.

Chem. Eur. J. 2011, 17, 5998-6008

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Figure 6. A) and B) SEM micrographs of fibrils of **1c** obtained from methanol/dichloromethane mixtures; C) and D) fluorescent micrographs of microrods of **1c**.

We measured the PL of these microrods to get some preliminary information about their internal structures. The emission peak was located at 488 nm, similar to the emission in THF. The ordered stacking of nanorods into fibrils with macroscopic sizes should make the molecular conformation more rigid and restrict the rotation of the phenyl rings. Thus, it was anticipated that the cables would efficiently emit and show polarized emission. The absolute $\Phi_{\rm F}$ value of the microrods was 26.8%, which was more than twofold higher than that of the solid film and comparable to some of the highly emissive organic nanowires previously reported.^[36] The polarized PL spectrum of the microrods of 1c is shown in Figure 5c. The emission polarization in the microrods was 2.2. Taking into the account that the microrods were arranged in random directions, we believed this result demonstrates a reasonably high degree of molecular order.

Electron mobility: Our previous studies revealed that HPS and MPPS possessed higher electron mobility than Alq₃.^[17] Calculation showed that **1a-1c** were more conjugated with lower LUMO energy levels and larger reorganization energies than HPS and MPPS; therefore, they might exhibit even higher electron-transport abilities. Thus, we investigated the electron mobility of 1a-1c using the transient electroluminescence (EL) method. Figure 7 shows the voltage dependence on the transient EL of ITO/NPB)/1a/Al (ITO= indium tin oxide, NPB = N,N'-bis(1-naphthyl)-N,N'-diphenylbenzidine) device with the applied rectangular voltage pulse. With an increase in the applied voltage, the delay time (t_d) became shortened and a steep rise in the EL was observed. The t_d value was lowered because the charge carrier took less time to travel across the organic layers. This also meant that the carrier mobility of the organic molecules was enhanced with increasing electrical field.



Figure 7. Voltage dependence on the transient EL of 1a with a device configuration of ITO/NPB/1a/Al with the applied rectangular voltage pulse.

Figure 8 shows the change in the electron mobility of 1a and 1b against the square root of the bias field. The data for HPS and MPPS are also included in Figure 8 for comparison. All of the siloles showed higher mobilities at higher electric fields. This kind of field-dependence phenomenon is typical in organic EL materials. The electron mobility of 1b was $5.0 \times 10^{-6} - 1.2 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and **1a** was $3.1 \times 10^{-6} - 1.2 \times 10^{-6} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ $6.3 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The mobility of **1a** and **1b**, particularly 1b, was steadily increased with increasing field strength. The value for 1c was comparatively low $(2.0 \times 10^{-6} - 5.2 \times 10^{-6})$ $10^{-6} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$), which is only about half of that for **1b**. The electron mobility of 1a and 1b was superior to HPS, MPPS,^[17] and Alq₃, a commonly used electron-transport material with an electron mobility of $2.3 \times 10^{-6} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ under the same conditions.^[37] Recent reports showed that the excellent electron-transport properties of tetraphenylsi-



Figure 8. Plot of electron mobility of **1a** and **1b** versus the square root of the bias field. Data for HPS and MPPS are shown for comparison.

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loles stem from their large electron affinities, which originate from the $\sigma^*-\pi^*$ conjugation, and the stability of the resultant anionic species.^[2a] These factors might also be possible reasons for the high mobility of **1a** and **1b**. Noteworthy is that the experimental values for all of the siloles as well as Alq₃ are quite different from their calculated values, which demonstrates that besides molecular reorganization energy, the intermolecular electronic coupling, packing pattern, and morphology also play important roles in determining the electron mobility of a material.^[9c] Although the results obtained above are preliminary, it shows that the new 2,5-bis(triphenylsilylethynyl)-3,4-diphenylsiloles are promising electron-transport materials for electronic applications.

Conclusion

In this paper, new 2,5-bis(triphenylsilylethynyl)-3,4-diphenylsiloles were synthesized in high yields by Sonogashira coupling of 2,5-dibromo-3,4-diphenylsiloles with triphenylsilylacetylene. Single-crystal X-ray diffraction and theoretical calculations showed that when compared with 2,5-diarylsiloles, the present molecules were less twisted because the steric hindrance between the triphenylsilyl units and silole cores was lessened by the acetylene linkages. The electronwithdrawing effect of the triphenylsilylethynyl groups gave 1a-1c low HOMO and LUMO energy levels. Analysis by cyclic voltammetry revealed that the silole molecules exhibited low electron affinities, which were comparable to those of perfluoroarylsiloles. Calculations of the reorganization energies for electron-transfers showed that the 2,5-bis(triphenylsilylethynyl)-3,4-diphenylsiloles had higher electron mobilities than HPS, MPPS, and Alq₃. Values up to 1.2× $10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ were measured by the transient EL method. All of the siloles were thermally stable, losing little of their weight when heated up to 400°C. Although their solutions were weakly emissive, their nanoaggregates in poor solvents and thin films emitted intense blue-green light upon photoexcitation. The bulky triphenylsilylethynyl groups had efficiently suppressed the close packing of the silole molecules in the condensed phase and, hence, prevented a redshift in the emission spectra as observed in 2,5-bis(trialkysilylethynyl)siloles.^[16c] Polarized emission was observed in the crystalline aggregates of **1a-1c**. The addition of poor solvents to their THF solutions self-assembled their molecules, evaporation of which generated macroscopic fibrils with efficient emissions. With these novel properties, similar to the previously prepared AIE molecules such as HPS and MPPS, the new silole molecules are anticipated to find an array of applications in electronics and optics.

Experimental Section

For experimental details, please see the Supporting Information.

Acknowledgements

We thank the Research Grants Council of Hong Kong (603509, 601608, CUHK2/CRF/08, and HKUST2/CRF/10), the Innovation and Technology Commission (ITP/008/09NP and ITS/168/09), the University Grants Committee of Hong Kong (AoE/P-03/08), and the National Science Foundation of China (20974028). B.Z.T. is grateful to Cao Gaungbiao Foundation of Zhejiang University.

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Received: November 24, 2010 Published online: April 13, 2011

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