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### COMMUNICATION



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Two new strongly AEE active  $(I/I_0 \approx 94)$  tetraphenylsilolecontaining cyclosiloxanes with cyan emissions ( $\lambda_{em} = 500$  nm) and ~100% solid state fluorescence quantum yields are reported. The intra- and intermolecular C-H••• $\pi$  interactions in the crystal play a major role in the observed high solid state fluorescence quantum yields.

#### Introduction

Organic conjugated molecules have been the subject of active research in advanced materials due to their unique optical and electronic properties. They have been found to have a wide variety of applications in fundamental electron/energy transfer studies,<sup>1</sup> biological fluorescent probes,<sup>2</sup> photovoltaic devices,<sup>3</sup> field-effect transistors,<sup>4</sup> and organic light-emitting diodes (OLEDs).<sup>5</sup> Among these compounds, five-membered aromatic heterocycles with a silicon atom, siloles, have been shown to be excellent electron transporting materials for OLEDs. Silole possesses a low-energy LUMO due to the interaction between the  $\sigma^*$  orbital of its two exocyclic Si-C bonds and the  $\pi^*$  orbitals of the butadiene moiety.<sup>6</sup> Moreover, silole derivatives exhibit high thermal and air stability, relatively good solubility, easily tunable photophysical properties and good efficiency in electroluminescence (EL) devices.<sup>7</sup>

Since high-performance optoelectronic materials are commonly used as thin films in their real world applications, <sup>8</sup> materials with high electron mobility and very high photoluminescence quantum yield ( $\Phi_{PL}$ ) in the solid state are desirable. For realizing high  $\Phi_{PL}$  in solid state, doping a highly fluorescent material (guest) into the

approach.9 Although doping offers high  $\Phi_{\text{PL}}$  and other advantages such as an improvement of temperature dependence of external electroluminescence (EL) quantum efficiency  $(\Phi_{PL})$ ,<sup>10</sup> it complicates the fabrication process and may increase production cost of OLEDs. Thus, it would be ideal if one could achieve very high  $\Phi_{PL}$  in undoped solid thin films.<sup>10</sup> Apart from a few exceptions tetraphenylsilole and silafluorene derivatives are known to exhibit low  $\Phi_{PL}$  in solution.<sup>11</sup> On the other hand, fluorescent materials comprised of silole-containing compounds show strong AEE (aggregation enhanced emission) effects that usually enhance their quantum yields  $(\Phi_{Pl})$  by up to two order of magnitude upon aggregation,<sup>12</sup> making them promising materials for solid state (thin film) applications. However, to date, only a few silole basedcompounds with very high quantum yield ( $\Phi_{PL} > 90\%$ ) suitable for application in OLEDs are known.<sup>13a</sup> Notably, in 2002 Kafafi et al reported highly efficient MOLED (molecular organic light-emitting diodes) with superior external electroluminescence quantum efficiency ( $\eta_{FI}$ ) of 4.8 % and luminous power efficiency of 9 lm/W fabricated using 1,2-bis(1-methyl-2,3,4,5tetraphenylsilacyclopentadienyl)ethane, a silole derivative exhibiting blue-green fluorescence with an absolute quantum yield of 97% in the solid state.<sup>13a</sup> In 2009, Tang et al reported the of 1,1-dimethyl-2,5-bis(trialkylsilylethynyl)-3,4synthesis diphenylsiloles with a solid-state quantum yield of 99.9%.13b Although our research group has recently reported the synthesis and photophysical properties of two further silole-based derivatives displaying solid-state quantum yields ( $\Phi_{PL}$ ) over 80%, <sup>13c, d</sup> a careful analysis of their spectroscopic data indicates that the quinaldinate ligand in these molecules plays a certain role in the observed enhancement of the fluorescence quantum yield in the solid state.

emitting layer (host) has been accepted as the most effective

As optical and photophysical properties of silole-based compounds in the solid state are primarily influenced by their molecular packing, modification of optical properties in the solid state as compared to solution is mainly due to reduction of rotationally induced non-radiative deactivation processes, dissipation of excitation energy into various vibrational modes, but most importantly, the nature of the intermolecular interactions. For example, the quenching of excited states via non-radiative

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<sup>&</sup>lt;sup>+</sup> Electronic Supplementary Information (ESI) available: synthesis, experimental and excited state calculation details, NMR, single crystal X-ray crystallography, IR, UV-Vis and fluorescence spectra. The crystal structures are available free of charge from the Cambridge Crystallographic Data Center. The CCDC codes are 1010361, 1010362, and 1010355 for compounds **1a**, **1b**, and **2**, respectively. See DOI: 10.1039/c00000x/

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processes in the solid-state often originates from  $\pi$ - $\pi$  interactions encountered in the unit cell of planar conjugated molecules.  $^{14}$   $\pi$ - $\pi$  Interactions lead to the formation of aggregates in the ground-state and excimers in the excited state that usually diminish photoluminescence efficiency.  $^{15}$  One strategy to prevent such undesirable type of intermolecular interactions between adjacent molecules in the solid state is to introduce bulky substituents in the molecules impeding their aggregation.  $^{16}$  An alternative strategy would be incorporating fluorophores into a bulky and/or space-filling rigid framework that would effectively prevent dense packing of the molecules in the cell thus resulting in high solid state quantum yields.  $^{13}$ 

Combining these two approaches, we have used a simple condensation reaction of the suitable precursor 1,1-dihydroxy-2,3,4,5-tetraphenylsilole with appropriate dichlorosilane derivatives to incorporate a well-known silole derivative – tetraphenylsilole – into a siloxane framework to generate ring-shaped compounds displaying high solid-state fluorescence quantum yields. Here, we report the synthesis, characterization, and photophysical properties of two cyan-emitting ring-shaped silole derivatives **1-2** with solid state fluorescence quantum yields ~100%.

#### **Results and discussion**

The synthetic routes to compounds 1-2 are shown in Scheme 1. The hydrolysis of 1,1-dichloro-2,3,4,5-tetraphenylsilole at -20°C followed by condensation reaction with dichlorophenylmethylsilane or dichlorotetramethyldisiloxane at -20°C gives compounds 1 and 2, in raw yields of 50% and 40%, respectively. Lower reaction temperatures (0°C ~ -20°C) and using triethylamine in these reactions favor the formation of the cyclic structures of tetraphenylsilole derivatives. Compound 1 has trans and cis isomers. Although cis isomer 1b cannot be isolated pure neither by column chromatography nor chiral gas chromatography nor supercritical fluid chromatography (because of its high boiling point (over 300°C) and bad solubility in EtOH), it readily crystalizes in form of pale yellow crystals together with the trans isomer 1a from Et<sub>2</sub>O. The trans isomer 1a can be isolated by column chromatography and subsequent crystallization in hexane/THF mixture upon solvent evaporation.



**Scheme 1** Condensation reactions between 1,1-dihydroxy-2,3,4,5-tetraphenylsilole and dichlorosilane or dichlorosiloxane.

The isolated compounds **1a** and **2** were characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, <sup>29</sup>Si-NMR, IR, UV-Vis spectroscopy and electrospray ionization-time of flight mass spectroscopy. Their structures were determined by single-crystal X-ray diffraction (see ESI, Table S1<sup>+</sup> for details). The crystal structure of **1a**, **2** and **1b** are shown in Fig. 1, Fig. 2 and ESI-Fig.S12<sup>+</sup>, respectively. All the bond lengths and bond angles of the silole unit in these compounds are within the typical range of those tetraphenylsilole derivatives found in the Cambridge Structural Database (ESI, Table S2<sup>+</sup>). In general, the cyclosiloxane in these compounds has nearly planar ring structures.

Pure crystals of **1a** and **2** were used in the photoluminescence property studies. Fig.3 displays the photophysical properties of **1a** in THF solution. The maximum of UV-Vis absorption is at 367 nm, which is attributed to the  $\pi$ - $\pi$ \* transition (*vide infra*) from the tetraphenylsilole fluorophores. Compound **1a** in THF solution emits cyan light with emission maximum at 497 nm. There is no red or blue shift of the emission maximum for compound **1a** in solid state (ESI, Fig.S17†) as compared to in solution. This indicates that no  $\pi$ - $\pi$ stacking exists in **1a** in the crystalline state (*vide infra*).<sup>17</sup> Similar photophysical properties are found for compound **2**, these results are summarized in Table **1**.







**Fig. 2** Thermal ellipsoids drawing of compound **2** (all atoms are shown as 50% thermal probability ellipsoids, all H atoms are omitted for clarity).



**Fig. 3** (a) Normalized UV absorption of **1a** in THF solution; (b) Normalized fluorescence emission of **1a** in THF solution,  $\lambda_{ex}$ = 370 nm; (c) Normalized fluorescence excitation spectrum of **1a** in THF solution,  $\lambda_{activation}$ =497 nm.

The extinction coefficients of compounds 1a and 2 in THF solution do not differ greatly (Table 1). The solution quantum yields of these compounds are close to zero (ESI, Figures S15, S16<sup>+</sup>), which can be predicted because there are known tetraphenylsilole compounds with zero solution quantum yields.<sup>13</sup> In this case, as long as a compound contains a tetraphenylsilole fluorophore, its solution quantum yield is close to zero. The rotation of phenyl moieties in this fluorophore in solution can serve as the main relaxation channel of fluorescence quenching.<sup>12</sup> However, in line with our expectations, the solid state quantum yields of 1a and 2 as crystals are significantly higher (97±2% for 1a and 99±2% for 2), which means that these compounds emit almost the exact number of photons as they absorb. These exceptional photophysical properties (500 nm cyan emission and ~100% solid state quantum yields) can be hardly found in other compounds containing fluorophores such silafluorene, phenyl substituted silafluorene, as tetraphenylethylene and aluminodiquinaldinate (-AlQ<sub>2</sub>), etc.  $^{13, 18, 19}$ 

To better understand the different emission intensities of these compounds between the solution and crystalline state, we also studied the aggregation enhanced emission (AEE) behavior of **1a** and **2** by comparing their fluorescence in pure THF and THF/H<sub>2</sub>O mixtures.<sup>12,13</sup> These results are shown in Fig.4 and ESI-Fig.S14<sup>+</sup>. Addition of water to THF solutions of **1a** and **2** causes little change in the spectral profiles. Both compounds show strong AEE with ~94-fold increases in I/I<sub>0</sub> ratio when water fraction is over 70%. The mechanism of AEE (fluorophores have weak emission in solution but strong emission in aggregated state) or AIE (aggregation induced emission: fluorophores have no emission in solution but strong emission in aggregated state) can be explained by the restriction of intramolecular motions (RIM) in compounds in the aggregated state, which facilitates the emission efficiency of the fluorophores.<sup>19</sup>

**Table 1** Photoluminescent properties of **1a** and **2** ( $\lambda$  given in [nm]).

	$UV\lambda_{max}$	fluorescence $\lambda_{max}$		log <sub>10</sub> ε <sup>[b]</sup>	$\Phi_{fl}{}^{[a]}$		
	soln [c]	soln	crystal	soln	soln	crystal	
1a	367	497 <sup>[d]</sup>	500 <sup>[e]</sup>	3.98 <sup>[f]</sup>	0.00 <sup>[g]</sup>	0.99 <sup>[e]</sup>	
2	373	500 <sup>[d]</sup>	501 <sup>[e]</sup>	3.59 <sup>[f]</sup>	$0.00^{[g]}$	0.97 <sup>[e]</sup>	

[a] Fluorescence quantum yield. [b] c, Extinction coefficient. [c] THF solution of compounds 1a and 2; [d] Excitation wavelength 370 nm; [e] Excitation wavelength 325 nm; [f]  $\log_{10}\epsilon$  at 325 nm; [g] Excitation wavelength 350 nm.



**Fig. 4** (A) Fluorescence Emission Spectra of  $10^{-3}$  mg/mL compound **1a** in THF/H<sub>2</sub>O mixtures with different fractions of H<sub>2</sub>O. (B) Plot of I/I<sub>0</sub> at 502 nm versus the water fraction, where I<sub>0</sub> is the fluorescence emission intensity in pure THF solution,  $\lambda_{ex}$ =370 nm. (C) Photograph of **1a** in THF/H<sub>2</sub>O mixtures containing different volume fractions of water taken under illumination of a UV lamp at 365 nm; from left to right: water fractions 0%-95%.

Packing style and interactions, to a large extent, are related to the solid state quantum yields.<sup>12d,14b</sup> Typically, a C-H··· $\pi$  interaction (~4.2 KJ/mol) has the interaction distance less than 2.9 Å, a  $\pi$ - $\pi$  interaction (~2 KJ/mol) has the interaction distance less than 3.8 Å.<sup>20</sup> While the former interaction can reduce the exciton-vibronic coupling, the latter one can lead to a red shift in the emission spectra and fluorescence decay by increasing the exciton-phonon coupling.<sup>14a,16d,21</sup>

Whereas the X-ray crystal structures of compounds **1a**, **1b** and **2** do not contain any notable  $\pi$ - $\pi$  interactions (Figures 5-7), each structure does contain C-H··· $\pi$  interactions. Compound **1a** (Fig. 5) contains two strong intramolecular C-H··· $\pi$  interactions (distances: 2.663(4) Å, 2.800(4) Å; angles: 142.7(4)°, 161.1(4)°) and one intermolecular C-H··· $\pi$  interaction (distance: 2.570(3) Å; angle: 159.6(10)°) per molecule. Compound **1b** (Fig. 6) contains two intramolecular C-H··· $\pi$  interactions (distances: 2.750(3) Å; 2.872(3) Å; angles: 159.1(3)°, 149.9(3)°) and one weak intermolecular C-H··· $\pi$  interaction (distance: 2.750(3) Å, 2.872(3) Å; angles: 159.1(3)°, 149.9(3)°) and one weak intermolecular C-H··· $\pi$  interaction (distance: 2.849(4) Å; angle: 147.3(4)°). Compound **2** (Fig. 7) does not contain intramolecular C-H··· $\pi$  interactions; it only contains three intermolecular C-H··· $\pi$  interactions (distances: 2.7559(16) Å, 2.8130(14) Å, 2.8925(14) Å; angles: 147.68(13)° 156.44(13)°, 142.97°) per molecule in the asymmetric unit.



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Fig. 5 Intra- and intermolecular interactions (distances in Å) in compound 1a.



Fig. 6 Intra- and intermolecular interactions (distances in Å) in compound  ${\bf 1b}.$ 



As intramolecular C-H··· $\pi$  interactions can more readily stabilize a structure's conformation than intermolecular C-H··· $\pi$  interactions can, the molecules having inter- and intramolecular C-H··· $\pi$  interactions lead to a much higher fluorescence quantum yield compared to the compounds having only intermolecular C-H··· $\pi$  interactions. In part, we attribute the higher solid state fluorescence behavior of **1a** to this effect.

Actually, for tetraphenylsilole fluorophores, it is not easy to form  $\pi$ - $\pi$  stacking. Because the phenyls on 2,3,4,5 positions of silole unit prefer to form certain degree of angles to the silole plane (e.g. dichlorotetraphenylsilole: 52°, 54°, 58°, 31°), which inhibits the  $\pi$ - $\pi$  stacking of siloles and enlarges the distance between siloles. Compared to compounds **1a** and **2**, the starting material dichlorotetraphenylsilole as crystals has an emission peak at 522 nm with the solid state quantum yield only 5% (ESI, Figure S19<sup>+</sup>). The packing analysis shows that there are no effective C-H… $\pi$  and  $\pi$ - $\pi$  interactions in the dichlorotetraphenylsilole crystal structure.<sup>22</sup>

In an attempt to gain more insight into electronic structure of compounds **1a**, **1b** and **2** and explore possible fluorescence

mechanisms among them, MO and excited state UV-Vis calculations were performed employing the Gaussian 09 package (see ESI<sup>†</sup> for detail).<sup>23</sup> The calculated geometrical parameters of the optimized molecules of **1a**, **1b** and **2** in the ground states agree very well with the X-ray crystal structure (for optimized geometries, see ESI-Tables S4-S6<sup>†</sup>). The first five energetically lowest-lying excited states (S<sub>1</sub>-S<sub>5</sub>) and corresponding oscillation strengths for **1a**, **1b** and **2** were calculated from the geometry optimized single molecules. The results are summarized in ESI-Tables S3<sup>+</sup>.

The UV-Vis calculations indicate that compound **2** has three optically allowed excited states  $(S_1, S_2, S_5)$ , two of which  $(S_1 \text{ and } S_2)$  correspond roughly to  $(\pi-\pi^*)$  HOMO  $\rightarrow$  LUMO  $(S_1)$  and HOMO-1  $\rightarrow$  LUMO  $(S_2)$  transitions. The excited state  $S_5$  can be adequately described as a HOMO  $\rightarrow$  LUMO+1 transition. While both HOMO and HOMO-1 in compound **2** are widely spread over the  $\pi$ -systems of the silole moiety and appurtenant phenyl rings, the LUMO is mainly located on the  $\pi$ -system of the silole ring with minor contribution of its phenyl rings'  $\pi$ -systems (ESI, Figure S22<sup>+</sup>).

The electronic situations in compounds 1a and 1b do not show any significant differences. The results of the UV-Vis excited state calculations for both 1a and 1b predict three optically allowed excited states  $(S_2, S_3 \text{ and } S_5)$ . They further indicate that the experimentally observed absorption spectra correspond to a transition into the second excited state rather than first, since the first excited state is optically forbidden in both 1a and 1b (ESI, table S3<sup>+</sup>). Predicted excitation energies are remarkably close to the experimentally observed ones. The second excited state wave function (S<sub>2</sub>) in 1a and 1b has significant contributions from configurations arising from HOMO  $\rightarrow$  LUMO and HOMO  $\rightarrow$ LUMO+1 transitions. All aforementioned MOs in 1a and 1b are almost exclusively localized on the  $\pi$ -systems of the silole ring and (with a smaller contribution) appurtenant phenyl substituents on the silole moieties (Fig.8, ESI-Figures S20-S22<sup>+</sup>). Notably, phenyl groups of the PhMe-Si-moieties in both 1a and 1b show absolutely no contribution to the frontier orbitals and thus to the observed absorption spectra.



Fig. 8 (a) HOMO; (b) LUMO; (c) LUMO+1 in compound 1a.

#### Conclusions

In summary, we synthesized tetraphenylsilole cyclosiloxane compounds with  ${\sim}100\%$  solid state fluorescence quantum

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yields. These compounds can emit cyan light with emission maxima at around 500 nm both in THF solution and as crystals. The AEE studies reveal that all these cyclic tetraphenylsilole derivatives are strongly AEE active with  $I/I_0 \approx 94$ . Packing analysis suggests that the intramolecular C-H… $\pi$  interactions combined with the intermolecular C-H $\cdots\pi$  interactions in the crystal structure can stabilize the lattice which reduces the exciton-vibronic and exciton-phonon coupling, resulting in less fluorescence decay and high solid state quantum yield. Excited state UV-Vis calculations predict that the observed absorption maxima most likely correspond to HOMO→LUMO and HOMO → LUMO+1 transitions. MO calculations demonstrate that all MOs relevant for fluorescence processes of 1-2 are located on tetraphenylsilole units. These findings can be very useful in photophysical applications, and important guides for designing new highly efficient photoluminescent materials.

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