

# A design concept of long-wavelength fluorescent analogs of rhodamine dyes: replacement of oxygen with silicon atom

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**Replacement of the oxygen with a silicon atom on the rhodamine framework produces a strong red-emission fluorophore which has a high molar extinction coefficient and 90 nm red shift relative to rhodamine dye PY.**

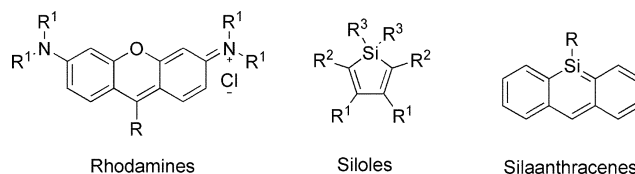
Long-wavelength fluorescent dyes have been extensively applied in life science in recent years.<sup>1</sup> The advantage of long-wavelength fluorophores over the shorter ones, lies in that they can effectively avoid the interference from the biological background fluorescence. However, among numerous fluorophores, long-wavelength ones with high fluorescence quantum yields amount to an extremely small portion. Although a few novel long wavelength fluorophores have been developed,<sup>2</sup> most of them are based on structural modification of conventional short wavelength fluorophores<sup>3</sup> in which the rhodamine type cationic dyes (as shown in Scheme 1) play a very important role. The rhodamines are widely used as fluorescent probes and molecular markers in chemistry and biochemistry.<sup>4</sup> However, the absorption and emission wavelengths of most rhodamine derivatives are well below 600 nm. In order to get longer wavelength rhodamine derivatives, many efforts have been made, including extending the conjugation by fusing heteroaromatic ring moieties to the rhodamine precursor,<sup>5</sup> substituting the central carbon by nitrogen,<sup>6</sup> or introducing electron-withdrawing groups, such as cyano, on the central carbon atom,<sup>7</sup> etc. Analogs developed by the above methods have some disadvantages such as synthetic difficulties, decrease in absorption or fluorescence intensity, and so on. Another important strategy to get tunable spectroscopic properties of rhodamine-relative dyes is to replace the oxygen bridge atom by other elements, such as N, C, S, Se and Te. However, only C substitution leads to a 50 nm bathochromic shift, other substitutions resulting in small bathochromic shift or even hypochromic shift.<sup>8</sup>

Recently, the silico-cyclic conjugated compounds, siloles and silaanthracenes, (shown in Scheme 1), have attracted much attention on their syntheses and properties. Siloles, which have extremely low LUMO energy, fast electron mobility and unique aggregation induced emission (AIE) properties, are extensively used in organic electroluminescent devices

(OLEDs)<sup>9</sup> and organic field-effect transistors (OFETs).<sup>10</sup> Some green emission and even red emission silole derivatives have been reported very recently.<sup>11</sup> Most silaanthracene compounds show relatively weak absorption bands in the range of 270–550 nm and emission bands centered around 550 nm,<sup>12</sup> and have poor stability at room temperature except those with bulky substituents on the silicon atom.<sup>13</sup> So far, there is no report on designing long-wavelength fluorophores by directly utilizing the spectral tuning (lowering LUMO energy) ability of silicon atom. Encouraged by the significant achievements on siloles and silaanthracenes, we believed it was feasible to obtain a long-wavelength and strongly emitting silaanthracene derivative using the silicon atom as the functional element to modify the rhodamine framework.

In this paper, the first red-emission silaanthracene fluorophore: 2,7-*N,N,N',N'*-tetramethyl-9-dimethyl-10-hydro-9-silaanthracene (TMDHS) was synthesized as shown in Scheme 2.<sup>14</sup> From the starting material, 3-bromoaniline, a two-step procedure<sup>15</sup> was adopted to prepare bis(2-bromo-4-*N,N*-dimethylphenyl)methane. Then, from this key intermediate, a facile one-pot synthesis process, the consecutive operations of lithiation, silylanization and oxidation, gave TMDHS with a good yield up to 80%. Unlike many other silaanthracene compounds, TMDHS is stable under ambient conditions. With the rhodamine-like cationic dye framework, TMDHS exhibits intriguingly strong absorption and emission. The properties of the TMDHS were studied in comparison with the rhodamine counterpart ( $R = H$ ,  $R^1 = Me$ , commercial name pyronine Y, PY).

The spectral properties of TMDHS and PY are shown in Fig. 1 and Table 1. TMDHS has very strong and sharp absorption and emission bands in the red region of the spectrum. For example, in dichloromethane, the maximum absorption wavelength is at 641 nm, with a 90 nm bathochromic shift compared with PY. The extinction coefficient ( $\epsilon$ ) is very high,  $10^5 \text{ M}^{-1} \text{ cm}^{-1}$ , and twice that of PY ( $\epsilon \approx 5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). The emission band peaked at 659 nm is very narrow (30 nm FWHM). The fluorescence quantum yield ( $\Phi_F$ )



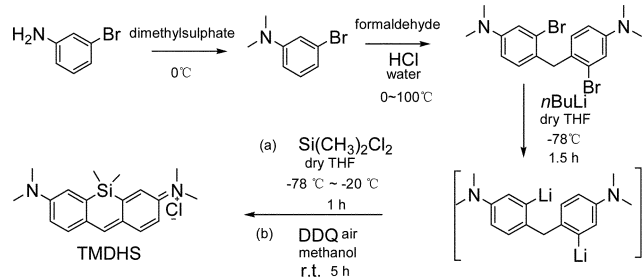
**Scheme 1** The molecular structures of rhodamines, siloles and silaanthracenes.

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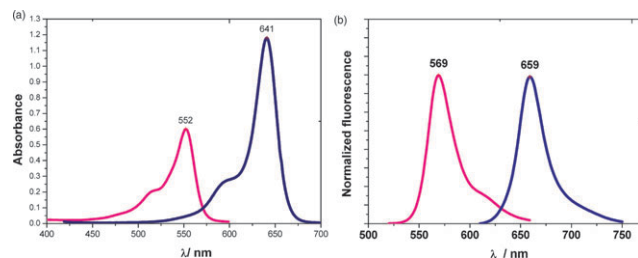
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**Scheme 2** The synthesis process of TMDHS.



**Fig. 1** The absorption (a) and emission (b) spectra of 11.5  $\mu\text{M}$  TMDHS (blue line) and PY (magenta line) in  $\text{CH}_2\text{Cl}_2$ .

**Table 1** The spectral properties of TMDHS in different solvents

Solvent	$\lambda_{\text{abs}}/\text{nm}$	$\epsilon/\text{M}^{-1} \text{cm}^{-1}$	$\lambda_{\text{em}}/\text{nm}$	$\Phi_{\text{F}}^a$
Dichloromethane	641	102 623	659	0.39
Acetone	637	103 285	660	0.29
Ethanol	636	43 646	655	0.26
Water	634	64 191	653	0.18

<sup>a</sup> Quantum yields were measured using rhodamine B ( $\Phi_{\text{F}} = 0.49$  in ethanol) as the standard.

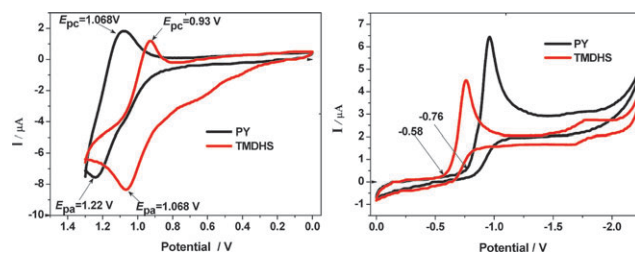
of TMDHS is 0.39 in  $\text{CH}_2\text{Cl}_2$  and 0.18 in water. The values of  $\epsilon$  and  $\Phi_{\text{F}}$  decrease in protic solvents considerably. Considering a similar tendency was also observed for PY, we speculated that such a special solvent effect might involve the interactions of solvent molecules with the electron-deficient central CH position of the cationic dyes, where the positive charge is partially localized. We believed that such a solvent effect could be eliminated by introducing blocking substituents on the carbon atom, such as aryl groups as in the case of the rhodamines. The high quantum yield and the long absorption and emission wavelength of the TMDHS confirmed our design concept. To the best of our knowledge, this is the first time where the introduction of a silicon atom to the key position of a conventional dye has successfully tuned the spectral properties.

It is amazing that, from rhodamine dye PY to TMDHS, a single atom change leads to a large red shift up to 90 nm, and such a significant effect has never been obtained before

**Table 2** Electrochemical data<sup>a</sup> of TMDHS and PY

Compd.	$E_{\text{ox}}/\text{V}$	$E_{\text{red}}/\text{V}$	$E_{\text{HOMO}}/\text{eV}$	$E_{\text{LUMO}}/\text{eV}$	$E_{\text{g}}/\text{eV}$	$\lambda_{\text{abs}}/\text{nm}$	$E_{\text{og}}/\text{eV}$
PY	1.14	-0.76	-5.64	-3.74	1.90	552	1.82
TMDHS	1.00	-0.58	-5.50	-3.92	1.58	641	1.61

<sup>a</sup> The electrochemical data were estimated on the basis of ferrocene (measured  $E_{1/2\text{FC}} = 0.30 \text{ V}$  vs.  $\text{Ag}/\text{AgNO}_3$ ), and  $E_{\text{ox}} = 1/2(E_{\text{pa}} + E_{\text{pc}})$ .  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  energy levels were calculated according to  $E_{\text{HOMO}}/E_{\text{LUMO}} = -4.8 - e(E_{\text{ox/red}} - E_{1/2\text{FC}}) \text{ eV}$ , respectively.<sup>17</sup>



**Fig. 2** Cyclic voltammetry of TMDHS and PY. The CV was carried out at a glass carbon electrode in dichloromethane solution containing 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte, Pt wire as auxiliary electrode and  $\text{Ag}/\text{AgNO}_3$  as the reference electrode. The concentration of the compounds used in this experiment was 1 mM and the scan rate was  $100 \text{ mV s}^{-1}$ .

through the bridge atom replacement strategy. To understand the effect of silicon on the spectral properties, electrochemical measurement was applied. The cyclic voltammetry (CV) curves of TMDHS and PY are similar (Fig. 2). Both show a pair of reversible oxidation peaks and an irreversible reductive peak. The electrochemical data are listed in Table 2. The original oxidation potential, the average of the anodic and cathodic peak potentials of TMDHS, is located at 1.00 V (vs.  $\text{Fc}/\text{Fc}^+$ ) and gives a HOMO value of  $-5.50 \text{ eV}$ . The original reductive potential investigated as the onset potential is at  $-0.58 \text{ V}$  and gives a LUMO value of  $-3.92 \text{ eV}$ . Similarly, PY has an oxidation potential at 1.14 V and a reductive potential at  $-0.76 \text{ V}$ , which gives a HOMO value of  $-5.64 \text{ eV}$  and a LUMO value of  $-3.74 \text{ eV}$ . The energy gap values  $E_{\text{g}}$  of the two compounds are 1.58 and 1.90 eV, respectively, which is consistent with the optical results  $E_{\text{og}}$  obtained from the absorption onset wavelength. Compared with PY, the HOMO of TMDHS increases by 0.14 eV, while the LUMO of TMDHS decreases by 0.18 eV. This result indicates that the substitution of oxygen by silicon affects the HOMO and LUMO energy level simultaneously, and thus a smaller energy gap is obtained and large red shift is achieved. Similar to that of siloles,<sup>16</sup> the low-lying LUMO energy level of the TMDHS is caused by the special  $\sigma^*-\pi^*$  conjugation, with the contribution of the  $\sigma^*$  of the silicon atom and  $\pi^*$  of the adjacent carbons. The HOMO energy increase of the TMDHS is ascribed to the inductive electron-donating effect of the dimethylsilyl group relative to oxygen.

In summary, TMDHS, a new strong fluorescence silaanthracene dye in the red region has been developed through substitution of the rhodamine oxygen bridge atom by silicon, which results in a 90 nm red shift. This is the first case where silicon atom is adopted as the functional element into the key position of a conventional excellent dye to successfully modulate the spectral properties. The electrochemical studies

indicate that the smaller energy gap of TMDHS results from both energy decrease of LUMO and energy increase of HOMO. Further derivation on TMDHS for efficient sensors is now in progress.

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- The authors had already patented this work in China, the patent number is ZL2006100459446. The synthesis procedure was described as follows: to a stirred solution of bis(2-bromo-4-*N,N*-dimethylphenyl)methane (237 mg, 0.57 mmol) in dry THF (6 mL) at  $-78^{\circ}\text{C}$  under  $\text{N}_2$  atmosphere, was quickly added 750  $\mu\text{L}$  (1.2 mmol) solution of *n*-BuLi (1.6 M). After the mixture solution was stirred for additional 1 h at the same temperature, 70  $\mu\text{L}$  (0.57 mmol) dichlorodimethylsilane ( $\text{SiMe}_2\text{Cl}_2$ ) was added dropwise over 15 min into the reaction solution with stirring at  $-78^{\circ}\text{C}$ . The mixture was warmed slowly to  $-20^{\circ}\text{C}$  and stirred for an additional 20 min, and then the mixture solution warmed to room temperature and stirred overnight. 5 mL methanol and 226 mg (1 mmol) DDQ (dichlorodicyanoquinone) were added to the reaction solution and stirred in air for 12 h. The mixture was evaporated *in vacuum*, and the residue was dissolved in  $\text{CH}_2\text{Cl}_2$ , filtered, the filtrate was concentrated in vacuum and purified by column chromatography on silica gel with methanol–dichloromethane (1 : 15) as the eluent to give 144 mg of a blue solid. Yield: 81%. MS:  $m/z$  [ $\text{M} - \text{Cl}]^+$ : calculated for  $\text{C}_{19}\text{H}_{25}\text{N}_2\text{Si}^+$ : 309.1787, found: 309.1778.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  7.83 (s, 1H), 7.68 (d, 2H,  $J = 9.2$  Hz), 7.29 (s, 2H), 6.95 (d, 2H,  $J = 9.2$  Hz), 3.32 (s, 12H), 0.490 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  161.2, 156.7, 148.9, 144.5, 128.9, 122.2, 115.2, 41.1,  $-1.3$ .
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