Luminescent Materials

Improving Quantum Efficiencies of Siloles and Silole-Derived Butadiene Chromophores through Structural Tuning**

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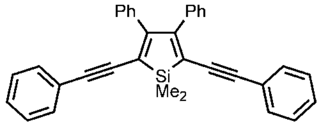
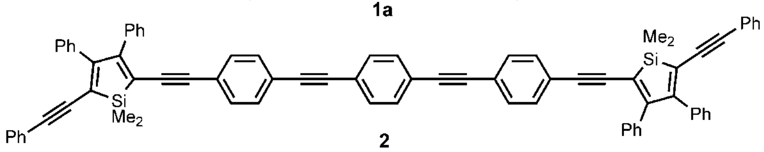
Over the last decade, Tamao's *endo-endo* cycloreduction of bis(phenylethynyl)silanes has emerged as a powerful tool for generating 2,5-dilithiosiloles that can be trapped by various electrophiles in situ.[1] The strategy has been used for the construction of various silole-containing monomeric, oligomeric, and polymeric systems,[2] but a significant structural limitation for cycloreduction is the requirement for arene rings at the alkyne termini. Unfortunately, 3,4-diarylsiloles are virtually non-emissive in solution, exhibiting low quantum efficiencies from 0.1–11 %.[3,4] Their poor luminescence has been ascribed directly to effects arising from 3,4-substitution, given that the corresponding unsubstituted systems consistently show greater emission intensities.[5] The lackluster luminescence of 3,4-diarylsilole chromophores condemns them to a dark future, which is unfortunate given the ease with which they can be prepared by cycloreduction methods.

We recently observed from silole **1a** a curiously high quantum efficiency of 9 %,[6] and in our studies of conjugated silole oligomers[7] we observed a 20 % quantum efficiency from the silole-capped extended chromophore **2**. The emission intensities of **1a** and **2** suggested that silole luminescence attenuation classically ascribed to the 3,4-diphenyl rings can be circumvented by manipulation of the C2, C5, and Si substituents. Increased chromophore rigidity often leads to improved luminescence by dually facilitating electron delocalization and minimizing vibrational–rotational events in the excited state.[8] With consideration of the silole nucleus, it seemed likely that increasing steric bulk about silicon and the 2,5-substituents would increase the energy barriers for non-emissive decay processes and ultimately result in increased photoluminescence. Thus, we explored synthetically practical silole modifications intended to impart "rigidity" to analogues of the parent chromophore **1a**. Herein, we report the structural optimization of a series of siloles ultimately resulting in the first highly luminescent 3,4-diphenylsilole chromophores.



1a



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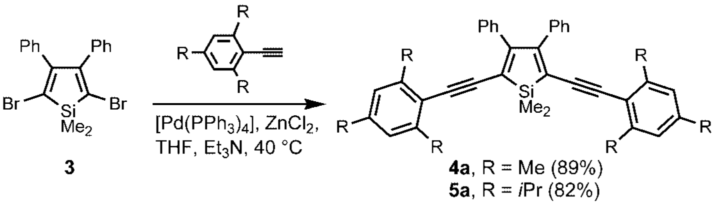
The dimethylsilolene chromophores (**4a** and **5a**) were prepared by Negishi cross-coupling reactions with dibromide **3**[6] (Scheme 1). These new siloles were crystalline solids that were purified by recrystallization from the crude reaction mixtures.



Scheme 1. Synthesis of 1,1-dimethylsilole fluorophores.

For the synthesis of di-*tert*-butylsilolene systems (Scheme 2) we found that isolation of dibromide intermediate **7** was not necessary and good yields were obtained by carrying out the entire reaction sequence from silane **6** through to siloles **1b**, **4b**, or **5b**. As with **4a** and **5a**, this simple process provided the desired siloles as crystalline solids that could be purified by recrystallization from the crude product mixtures.

Chlorosilole **10** was prepared via known intermediate **9**[6] in 72 % overall yield from silane **8** (Scheme 3). Cross-coupling with phenylacetylene provided asymmetric "mixed" silole **11a** in 86 % isolated yield after recrystallization. Similarly, bromosilole **12** was used en route to "mixed" silole **11b**.

We found that treatment of the 1,1-dimethylsiloles with Bu_4NF in THF accomplished stereospecific[9] desilylation in nearly quantitative yield after only a few minutes at room temperature (Scheme 4). As can be seen from X-ray crystal structures (Figure 1), the backbone of the chromophore achieves a nearly completely planar orientation upon removal of the silolene moiety and, as expected, the butadiene moiety adopts an *s-trans* conformation. The efficiency and simplicity of this desilylation method provided **1c**, **4c**, and **5c** essentially gratis.[10]

All of the new silole chromophores absorb in the visible region (Table 1) and have moderate molar absorptivities. In comparison with **1a**, siloles bearing larger arenes (**11a**, **4a**, and **5a**) display sequential bathochromic shifts in absorption maxima consistent with having greater electron density.

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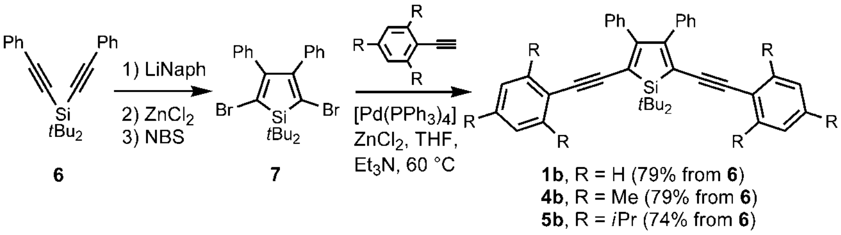
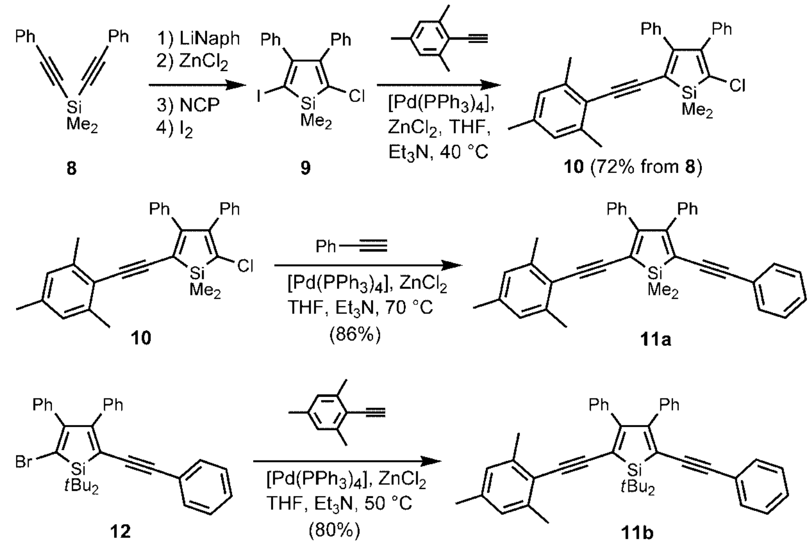
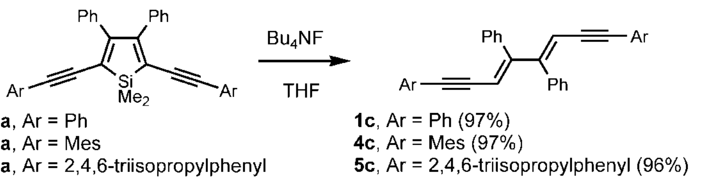


Scheme 2. Synthesis of 1,1-di-*tert*-butylsilole fluorophores; NBS = 1-bromo-2,5-pyrrolidinedione.



Scheme 3. Synthesis of asymmetric silole fluorophores; NCP = *N*-chlorophthalimide.



Scheme 4. Protiodesilylation for synthesis of butadiene chromophores.

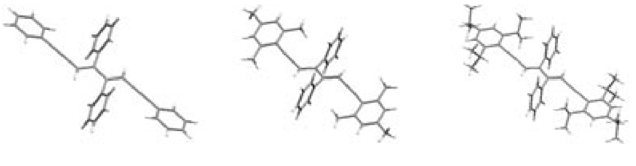


Figure 1. X-ray structures of siloles **1c** (left), **4c** (middle), and **5c** (right).

Increasing steric bulk about silicon alone causes a small hypsochromic shift in the absorption maxima (**1a** vs. **1b**, **4a** vs. **4b**, **5a** vs. **5b**, **11a** vs. **11b**). Relative to the least hindered silole **1a**, a hypochromic shift (decrease in absorption intensity) is observed for each of the bulkier systems suggesting a decrease in planarity. In all cases, desilylation causes nearly equivalent hypsochromic shifts (that is, blue shifts) in absorption maxima (**1a**→**1c** $\Delta\lambda_{max} = -66$ nm; **4a**→**4c** $\Delta\lambda_{max} = -64$ nm, **5a**→**5c** $\Delta\lambda_{max} = -66$ nm, Table 1) as a result of the loss of butadiene tethering and electronic interactions with the silicon atom. Increasing the size of the alkyl groups on the terminal arenes (i.e. **4c** and **5c** vs. **1c**) also causes longer wavelength absorption maxima and decreased molar absorptivity for the butadienes. Notably, blue emission was obtained from both **4c** and **5c**, which emit with 20% and 25% efficiency, respectively.

These structural modifications resulted in significant stepwise increases in quantum efficiencies (Φ_f) with minimal impact on emission wavelengths (Figure 2, Table 1). Compared with the parent silole **1a** ($\Phi_f = 9\%$), emission intensities improved when larger terminal arenes were employed. Replacing a single phenyl group on **1a** ($\Phi_f = 9\%$) with a mesityl (**11a**, $\Phi_f = 10$) had a marginal effect, but exchanging both phenyl groups for mesityl groups results in a marked increase in luminescence (**4a**, $\Phi_f = 30\%$). Replacing the mesityl groups with triisopropylphenyl groups gave only slight enhancement (**5a**, $\Phi_f = 41\%$). Substituting the dimethylsilolene for a di-*tert*-butylsilolene has a greater influence on Φ_f than changes to the terminal arene units. For the parent silole **1a** ($\Phi_f = 9\%$), the exchange brought Φ_f to 25% (**1b**). Incorporation of a single mesityl group again lead to only a modest improvement (**11b**, $\Phi_f = 32\%$), but when two mesityl groups were used in combination with the di-*tert*-butylsilolene (**4b**) a quantum efficiency of 63% was observed. No further increase was observed, however, with silole **5b** ($\Phi_f = 56\%$). To our knowledge, these quantum efficiencies are the highest ever reported for 3,4-diphenylsilole chromophores in solution.

Table 1: Electronic absorption and emission data in solution.

Silole	Butadiene	Absorption		Emission	
		λ_{max}	log(ε)	λ_{max}	Φ_f[b]
1a	–	429	4.74	520	0.09
1b	–	428	4.36	516	0.25
4a	–	443	4.49	532	0.30
4b	–	439	4.48	529 (536)[a]	0.63
5a	–	447	4.43	523	0.41
5b	–	439	4.51	507 (512)[a]	0.56
11a	–	436	4.42	532	0.10
11b	–	434	4.43	522	0.32
–	**1c**	363	5.03	428	0.02[c]
–	**4c**	379	4.99	448	0.20[c]
–	**5c**	381	4.85	426	0.25[c]

[a] Emission maxima of thin films given in parentheses. [b] Determined with reference to fluorescein unless stated otherwise. [c] Determined with reference to 9,10-diphenylanthracene.

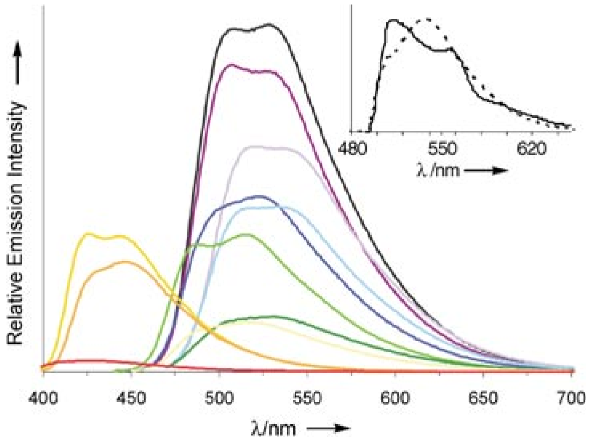


Figure 2. Photoluminescence spectra in CH_2Cl_2 at room temperature. **4b** (——), **5b** (——), **5a** (——), **11b** (——), **4a** (——), **1b** (——), **11a** (——), **1a** (——), **5c** (——), **4c** (——), **1c** (——). Inset: normalized emission spectra of thin films of **4b** (dashed line) and **5b** (solid line).

Although the solution photoluminescence (PL) efficiency is a good first measure of performance and is paramount in areas such as nitroaromatic detection,[11] the solid-state behavior will more likely dictate the feasibility of deploying these compounds in electronic devices. In this regard, thin-films of **4b** and **5b** were prepared by spin-coating,[12] and their PL spectra examined (Figure 2, inset). Intense green light emission was observed from the thin film of each fluorophore and the emission spectra revealed slight bathochromic shifts in the solid state relative to the solution PL spectra.

In conclusion, simple structural modifications have provided new luminescent silole chromophores with the highest quantum efficiencies for fully substituted monomeric siloles in solution. Importantly, these discoveries welcome siloles prepared by practical cycloreduction methods into the fold of useful fluorophores. The PL intensity was selectively modified without impact on the emission wavelength. This work establishes structure–property relationships that refute the notion that 3,4-disubstituted siloles possess intrinsically low quantum efficiencies, and illustrates enhanced performance through substituent tuning at C2, C5, and Si.

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