

Synthesis and Electronic Properties of Donor–Acceptor  $\pi$ -Conjugated Siloles

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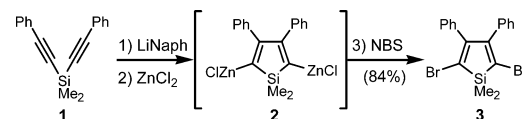
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Siloles are being increasingly recognized as promising and desirable  $\pi$ -conjugated materials for potential device applications, and important contributions have been made in the areas of electro- and photoluminescence<sup>1</sup> and nitroaromatic sensors.<sup>2</sup> They are also strong candidates for NLO applications based on the theoretical works of Matsuzaki<sup>3</sup> and Bakhshi<sup>4</sup> and the successes with related arylene materials.<sup>5</sup> The ability to control the electronic nature of the silole chromophore by varying the functional groups at the silole termini will be critical to fine-tuning and optimizing their properties. Access to silole systems bearing electron donating and accepting groups peripherally at the C(2) and C(5) positions has been impeded by the challenges of synthesizing desymmetrized siloles.

The synthesis of functionalized 2,5-silole extended chromophores is notoriously complicated by the incompatibility of the silole ring with traditional alkyne protecting groups. For example, the nucleophilic nature of the reaction conditions present during removal of conventional orthogonal alkyne protecting groups (e.g., Me<sub>3</sub>Si vs <sup>t</sup>Pr<sub>3</sub>Si vs Me<sub>2</sub>COH) successfully employed in the synthesis of other acetylenic systems<sup>6</sup> results in rapid desilylation of the silole moiety.<sup>1f,7</sup> In pioneering investigations, Tamao prepared asymmetric siloles suitable for further functionalization by monolithiation of a symmetrical 2,5-dibromosilole, followed by electrophilic trapping.<sup>8</sup> We sought a more direct route to obtain asymmetric siloles through site-specific cross-coupling methodology. Utilizing ZnCl<sub>2</sub> as an oxidizing agent for residual LiNaph, an approach that has proven advantageous in Negishi silole cross-couplings involving aryl halides,<sup>1f</sup> provided a satisfying 84% isolated yield of 2,5-dibromosilole **3** (Scheme 1).<sup>9</sup>

However, our efforts to desymmetrize the dibromosilole **3** by selective single cross-coupling reactions failed, and formation of the undesired biscoupled product along with unreacted starting material was the usual result. Attempts to desymmetrize the dizinc intermediate **2** by low temperature monobromination were stymied by formation of only the dibromosilole. We suspected that chlorination might be superior to bromination given the greater deactivating effect expected from a monochlorosilole on the nucleophilicity of the second vinyl zinc. However, chlorination of **2** using *N*-chlorosuccinimide gave fickle results with poor ratios of mono- to dichlorosilole (1.1:1, 84% combined yield). In contrast, successful monochlorination (16.2:1 ratio) was achieved using *N*-chlorophthalimide (NCP), and the intermediate 2-chloro-5-metallosilole **4** could be further functionalized by iodination with I<sub>2</sub> to afford the new chloriodosilole **5** in 81% yield (Scheme 2). The high light sensitivity of **5** complicated its isolation and storage, but through extensive optimization we have found in situ cross-coupling reactions to be extraordinarily useful for asymmetric silole synthesis. The best results were obtained by engaging the electron-poor acceptor alkyne in the first cross-coupling event at 40 °C, and when complete (ca. 14 h), the donor moieties were allowed to react at 70 °C. In this way, donor–acceptor (DA) systems **7–15** have each been prepared by an operationally simple process requiring only a single purification step (Scheme 2 and Table 1).<sup>10</sup> Specifically, the entire sequence consisting of cycloreduction,

Scheme 1



Scheme 2

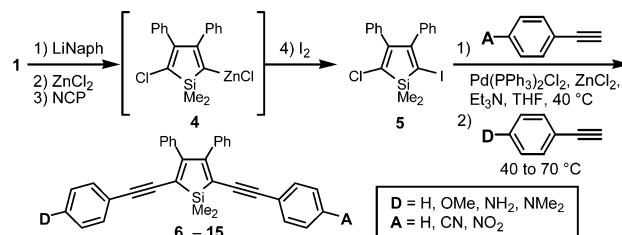


Table 1. Summary of Data for Donor–Acceptor Siloles

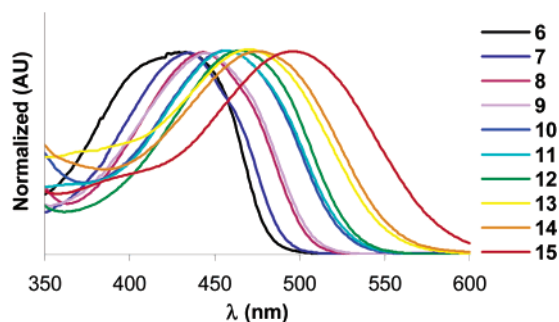
silole	donor	acceptor	absorption $\lambda_{\max}$ (log $\epsilon$ )	emission $\lambda_{\max}$ ( $\Phi_F \times 10^{-2}$ ) <sup>a</sup>	yield <sup>b</sup>	space group
<b>6</b>	H	H	429 (4.74)	520 (8.97)	82 <sup>c</sup>	— <sup>d</sup>
<b>7</b>	OCH <sub>3</sub>	H	435 (4.33)	528 (4.06)	65	Pbnc
<b>8</b>	OCH <sub>3</sub>	CN	443 (4.33)	559 (0.70)	54	P2 <sub>1</sub> /c
<b>9</b>	NH <sub>2</sub>	H	445 (4.51)	558 (2.57)	62	— <sup>d</sup>
<b>10</b>	OCH <sub>3</sub>	NO <sub>2</sub>	456 (4.44)	649 (0.44)	55	P1
<b>11</b>	NH <sub>2</sub>	CN	457 (4.44)	594 (1.80)	58	Pna2 <sub>1</sub>
<b>12</b>	NMe <sub>2</sub>	H	465 (4.25)	598 (2.12)	55	— <sup>d</sup>
<b>13</b>	NH <sub>2</sub>	NO <sub>2</sub>	471 (4.11)	613 (0.11)	56	Pna2 <sub>1</sub>
<b>14</b>	NMe <sub>2</sub>	CN	476 (4.53)	611 (2.94)	58	P2 <sub>1</sub> /c
<b>15</b>	NMe <sub>2</sub>	NO <sub>2</sub>	496 (4.37)	nd <sup>e</sup>	54	P2 <sub>1</sub> /c

<sup>a</sup> Determined with reference to fluorescein. <sup>b</sup> Isolated yields based on diethynylsilane **1**. <sup>c</sup> Isolated yield based on dibromosilole **3**. <sup>d</sup> Suitable crystals not yet obtained. <sup>e</sup> Photoluminescence not detected.

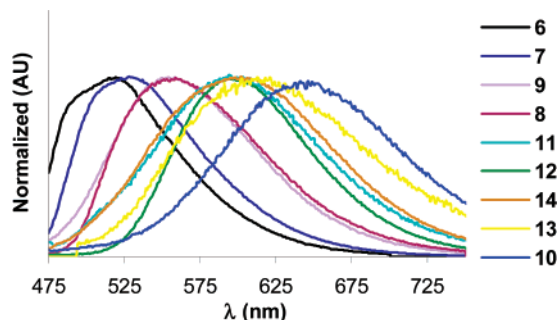
transmetalation, chlorination, iodination, and two sequential cross-couplings produced asymmetric siloles **7–15** in 54–65% isolated overall yield based on diyne **1**.

These materials are the first silole-containing extended chromophores bearing electronically dissimilar functional groups at C(2) and C(5) prepared by direct cross-coupling methodology. In this regard, a disincentive to large-scale silole synthesis by cross-coupling methodology was its previous reliance on stoichiometric tin reagents<sup>11</sup> for Stille-type<sup>12</sup> chemistry. Alkyne cross-couplings with 2,5-dihalo siloles under related Sonogashira conditions<sup>13</sup> proved fickle in our hands, as observed by others.<sup>7,14</sup> To the best of our knowledge, this communication constitutes the first successful alkyne cross-couplings under Negishi conditions.<sup>15</sup>

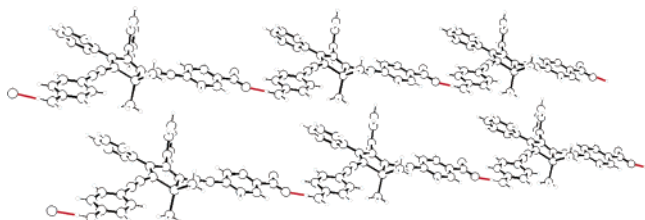
The electronic absorption spectra of DA siloles **7–15**, along with the parent compound **6**,<sup>10</sup> are shown in Figure 1. All of the compounds absorb in the visible region, and absorption maxima strongly depend on the nature of the push–pull substituents of the chromophore. Sequentially increasing the degree of electron delocalization from the parent silole **6** (A = D = H) to the most polar silole (**15**) results in a stepwise bathochromic shift in the electronic absorption spectra from 429 to 496 nm. These results demonstrate experimentally that silole chromophores can be electronically fine-



**Figure 1.** Electronic absorption spectra of donor-acceptor siloles in  $\text{CH}_2\text{Cl}_2$ .



**Figure 2.** Photoluminescence spectra of donor-acceptor siloles in  $\text{CH}_2\text{Cl}_2$ .



**Figure 3.** X-ray structure of silole **13**. Hydrogen bonds are shown in red.

tuned by the manipulation of peripheral DA functional groups. This advance brings siloles into the family of electronically tunable DA chromophores.

The consequences of varying the nature of the DA groups are also manifested in the photoluminescence spectra (Figure 2). Interestingly, silole **10** ( $\text{D} = \text{OCH}_3$ ,  $\text{A} = \text{NO}_2$ ) exhibits only the fifth longest wavelength absorption in this series, but displays the longest wavelength emission at 649 nm.<sup>16</sup> This is the longest wavelength emission for a compound possessing only a single silole in the chromophore.<sup>1f</sup> The moderate silole quantum efficiencies (Table 1) are consistent with previous observations.<sup>1f</sup>

Siloles **7**, **8**, **10**, **11**, and **13–15** gave crystals suitable for X-ray analysis (Table 1). Curiously, only **11** and **13** packed in a noncentrosymmetric space group ( $\text{Pna}2_1$ , Figure 3).<sup>17</sup> Within these crystals, two sheets of siloles intersect at  $45^\circ$ , and the orientation of the dimethylsilylene moiety is unidirectional throughout. The DA groups within a sheet reinforce the induced dipole by aligning in a head-to-tail fashion, and the intersecting sheet is oriented in an electrostatically complementary direction. In contrast, the remaining compounds packed in centrosymmetric space groups in which the dimethylsilylene moiety and the DA groups pack in a head-to-head orientation that minimizes dipoles.

We speculate that hydrogen bonding facilitates noncentrosymmetric packing in **11** and **13**. The average hydrogen bond distances and bond angles in **11** and **13** are 2.122 Å,  $170^\circ$  and 2.107 Å,  $148^\circ$ , respectively. In contrast, dipole-directed packing will favor cen-

trosymmetric space groups. This is particularly evident in comparing the amino siloles (**11** and **13**) with the dimethylamino counterparts (**14** and **15**) in which a hydrogen bond donor is absent. Further exploitation of hydrogen bonding directed crystal packing with other DA systems is currently underway in our laboratory.

In summary, we have developed a new and efficient method for the synthesis of novel donor-acceptor silole chromophores by direct cross-coupling reactions. The ability to manipulate the electronic and physical properties of siloles through judicious combinations of peripheral functional groups was also demonstrated. The entire synthetic sequence from silane **1** to DA systems is achieved efficiently in two steps with only a single purification process. Silole alkene cross-couplings and utilization of **5** to prepare second-generation siloles will be described elsewhere.

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**Supporting Information Available:** Detailed experimental procedures (PDF) and characterization of all new compounds (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (17) It is encouraging that both aminosiloles display noncentrosymmetric packing, which is a requirement for second-harmonic generation in the solid state; see ref 5.

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