

## Silole-Acetylene $\pi$ -Electronic Systems with Low Bandgaps: Synthesis, Structure, and UV-vis Absorption Spectra of 2,5-Diethynylsiloles Derivatives and Their Polymers

Shigehiro Yamaguchi, Kazuo Imura, and Kohei Tamao\*  
*Institute of Chemical Research, Kyoto University, Uji, Kyoto 611*

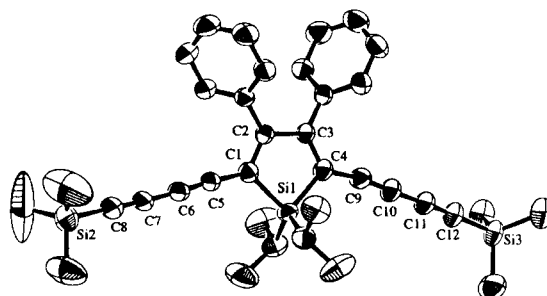
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A series of 2,5-diethynylsilole derivatives and their polymers, prepared by the Stille coupling reaction, show unique optical properties such as long-wavelength absorptions in their UV-vis absorption spectra.

Silole (silacyclopentadiene) now represents a new building unit of  $\pi$ -conjugated polymers.<sup>1-4</sup> A silole ring is conspicuous by its low-lying LUMO level due to the  $\sigma^*$ - $\pi^*$  conjugation in the ring.<sup>1c</sup> Based on this electronic structure, silole-containing  $\pi$ -conjugated systems reported so far, *i.e.*, silole-thiophene copolymers,<sup>1a,c</sup> silole-pyrrole cooligomers,<sup>1d</sup> and silole homooligomers,<sup>1b</sup> show unique optical properties such as long-wavelength absorptions in their UV-vis absorption spectra. We are now interested in the combination of a silole  $\pi$ -electronic system with an acetylene  $\pi$ -electronic system. Herein reported are the synthesis, structure, and optical properties of 2,5-diethynylsilole derivatives and their polymers. While poly(aryleneethynylene) (PAE) type polymers normally have relatively large bandgaps of about 2.1–2.6 eV,<sup>5</sup> our diethynylsilole-based polymers show significantly narrower bandgaps up to 1.8 eV.

A series of 2,5-diethynylsilole derivatives **3** having various terminal groups have been prepared by the Stille coupling reaction,<sup>6</sup> as shown in Scheme 1.<sup>7</sup> Thus, 2,5-dibromosiloles **1**, readily available by our new silole synthesis,<sup>1b</sup> were allowed to react with various ethynylstannanes **2a-2e** using a Pd(dba)<sub>2</sub>/P(furyl)<sub>3</sub> catalyst system<sup>8</sup> to give **3a-3e** in 58–82% isolated yields.<sup>9</sup> These products are all stable in the air.<sup>10</sup>

The crystal structure of bis(butadiynyl)silole **3b** has been determined by X-ray crystallography, as shown in Figure 1.<sup>11</sup> While the endo-cyclic bond angle C1–Si1–C4 90.0(1)° is the smallest so far found for silole angles (90.5°–97°), all other bond lengths and angles of the acetylene moieties and silole

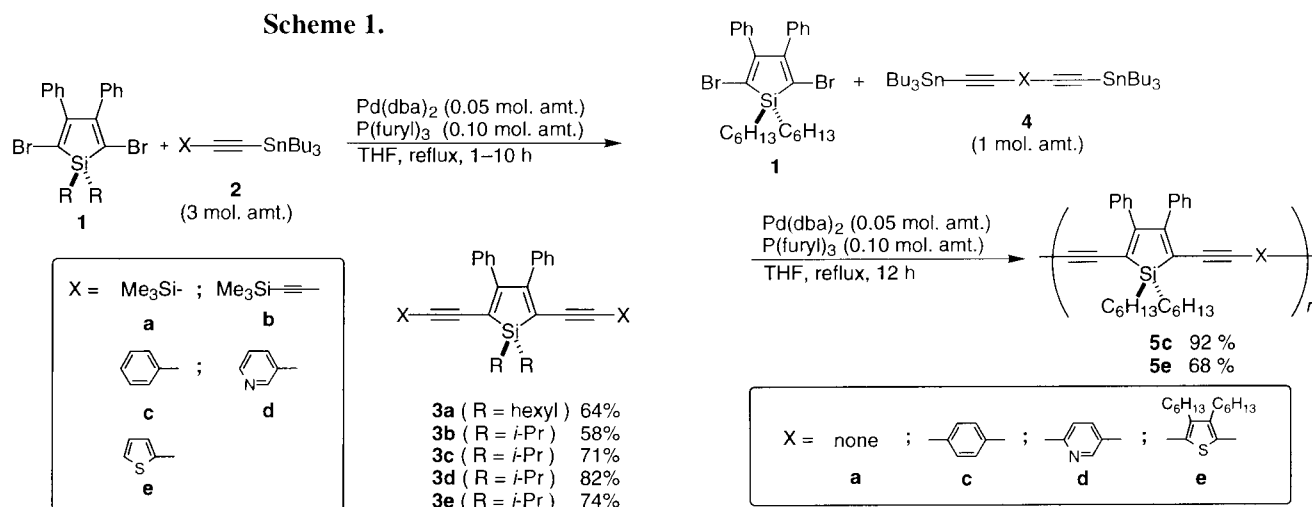


**Figure 1.** ORTEP drawing of **3b** (50% probability thermal ellipsoids). Selected bond lengths [Å] and angles[deg]: Si1–C1 1.880(3), C1–C2 1.362(4), C2–C3 1.495(3), C1–C5 1.406(3), C5–C6 1.199(3), C6–C7 1.376(3), C7–C8 1.207(4), C8–Si2 1.824(3), C1–Si1–C4 90.0(1), Si1–C1–C2 109.2(2), C1–C2–C3 115.3(2), Si1–C1–C5 124.6(2), C1–C5–C6 175.8(3), C5–C6–C7 175.8(3), C6–C7–C8 177.1(3), C7–C8–Si2 175.8(3).

moiety are in the normal range.

We next examined the synthesis of diethynylsilole-based  $\pi$ -conjugated polymers using a similar Stille coupling reaction of **1** with bis(stannyethynyl)arenes **4**, as shown in Scheme 2. When the phenylene and thienylene derivatives, **4c** and **4e**, were employed, the coupling reactions smoothly proceeded to give a red polymer **5c** and a deep violet polymer **5e** in 92% and 68% yields, respectively. Molecular weight approximations by GPC using polystyrene standards show  $M_w = 64,000$ ,  $M_n = 9,000$  for **5c** and  $M_w = 63,000$ ,  $M_n = 13,000$  for **5e**. Both polymers are air-stable and soluble in common organic solvents such as THF and CHCl<sub>3</sub> to give a reddish orange solution and an ink-blue solution, respectively. However, the coupling of **1** with distannyldiacetylene **4a** or bis(stannyethynyl)pyridine **4d** only

### Scheme 2.



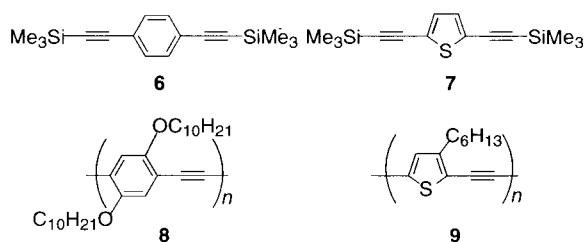
gave insoluble polymeric materials and thus further purification and characterization failed.

The UV-vis absorption spectral data for the 2,5-diethynylsilole derivatives **3** and their polymers **5** are summarized in Table 1, which also contains the data for bis(trimethylsilylethynyl)benzene **6** and -thiophene **7**,<sup>12</sup> with poly(phenyleneethynylene) **8**<sup>5c</sup> and poly(thienyleneethynylene) **9**,<sup>5d</sup> for comparison. Trimethylsilyl-capped diethynylsilole **3a** has its absorption maximum at 395 nm, which is considerably longer than those of the phenylene and thienylene analogs, **6** and **7**, and comparable to that of polymer **9**. This is a clear indication of the unique electronic structure of the present silole-acetylene  $\pi$ -electronic systems. Trimethylsilyl-capped bis(butadiynyl)silole **3b** has a 60 nm red-shifted absorption maximum in comparison with **3a**, due to the extended  $\pi$ -conjugation. The  $\lambda_{\max}$  of **3b** is comparable to those of phenyl- or pyridyl-capped diethynyl-siloles, **3c** or **3d**. The longest absorption maxima is observed for the thienyl-capped diethynylsilole **3e**.

**Table 1.** UV-vis Absorption Spectral Data for Diethynylsilole Derivatives and Their Related Compounds<sup>a</sup>

compound	$\lambda_{\max}$ / nm (log $\epsilon$ )	bandgap / eV <sup>b</sup>
<b>3a</b>	395 (4.06)	
<b>3b</b>	430 (4.32), 452 (sh, 4.32)	
<b>3c</b>	430 (4.41)	
<b>3d</b>	428 (4.44)	
<b>3e</b>	452 (4.49)	
<b>5c</b>	505, 527	2.07
<b>5e</b>	576, 605(sh)	1.77
<b>6</b>	279 (4.67), 288 (4.51), 294 (4.75)	
<b>7</b>	311 (4.40), 316 (4.39), 325 (4.35), 331 (4.37)	
<b>8<sup>c</sup></b>	429	2.53
<b>9<sup>d</sup></b>	403	2.38

<sup>a</sup> In CHCl<sub>3</sub>, unless otherwise stated. <sup>b</sup> Estimated from the onsets of absorptions. <sup>c</sup> In THF. Ref. 5c. <sup>d</sup> Ref. 5d.



Among the PAE type polymers, **5e** has the longest  $\lambda_{\max}$  at 576 nm, which is about 150-170 nm longer than those of **8** and **9**. The bandgaps of **5c** and **5e** estimated from the onsets of their absorptions are rather small, 2.07 and 1.77 eV, respectively. Despite these features, however, their conductivities upon doping with iodine are still moderate,  $6.0 \times 10^{-6}$  and  $1.0 \times 10^{-5}$  S cm<sup>-1</sup>

for **5c** and **5e**, respectively. Further investigation of other properties of these silole-acetylene  $\pi$ -electronic systems, such as electrochemical behavior and nonlinear optical properties is now in progress.

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- Coupling reaction of **1** with terminal acetylenes using PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>/CuI catalyst system in amine,<sup>7a</sup> which is a useful methodology for preparation of PAE type polymers,<sup>5</sup> gave only a complex mixture. a) K. Sonogashira, Y. Tohda, and N. Hagihara, *Tetrahedron Lett.*, **16**, 4467 (1975).
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- The compound **3c** has already been prepared by the similar coupling reaction. See ref. 1b.
- An attempt to synthesize a parent 2,5-diethynylsilole by desilylation from **3a** with K<sub>2</sub>CO<sub>3</sub>/MeOH failed due to ring-opening of the silole ring even under such a mild basic condition.
- Crystal data of **3b** (instrument: Rigaku RAXIS IV): C<sub>36</sub>H<sub>42</sub>Si<sub>3</sub>, 0.40 x 0.30 x 0.30 mm, triclinic, P1 (#2); *a* = 15.279(1) Å, *b* = 17.112(1) Å, *c* = 7.8326(5) Å,  $\alpha$  = 103.066(4)°,  $\beta$  = 99.005(3)°,  $\gamma$  = 110.185(4)°, *V* = 1809.76 Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.026 g cm<sup>-3</sup>,  $\mu$  (Mo K $\alpha$ ) = 1.51 cm<sup>-1</sup>, temperature 20 °C, *R* = 0.047, *R<sub>w</sub>* = 0.072, and GOF = 1.29; number of unique reflections = 6333.
- Compounds **6** and **7** were prepared by the coupling reaction of 2,5-dibromothiophene with trimethylsilylacetylene under Sonogashira conditions.<sup>7a</sup>