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

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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 π-conjugated polymers.[1-4] A silole ring is conspicuous by its low-lying LUMO level due to the σ*-π* conjugation in the ring.[1c] Based on this electronic structure, silole-containing π-conjugated systems reported so far, *i.e.*, silole-thiophene copolymers,[1a,c] silole-pyrrole cooligomers,[1d] and silole homo-oligomers,[1b] 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 π-electronic system with an acetylene π-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,[5] 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,[6] as shown in Scheme 1.[7] Thus, 2,5-dibromosiloles **1**, readily available by our new silole synthesis,[1b] were allowed to react with various ethynylstannanes **2a**-**2e** using a Pd(dba)$_2$/P(furyl)$_3$ catalyst system[8] to give **3a**-**3e** in 58-82% isolated yields.[9] These products are all stable in the air.[10]

The crystal structure of bis(butadiynyl)silole **3b** has been determined by X-ray crystallography, as shown in Figure 1.[11] 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 moiety are in the normal range.

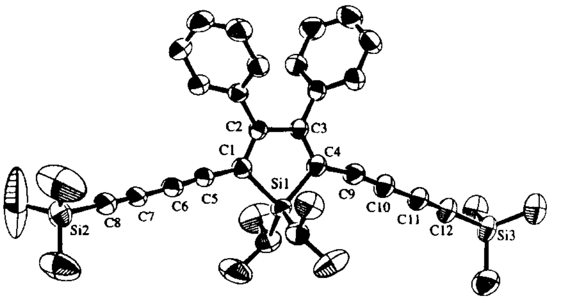
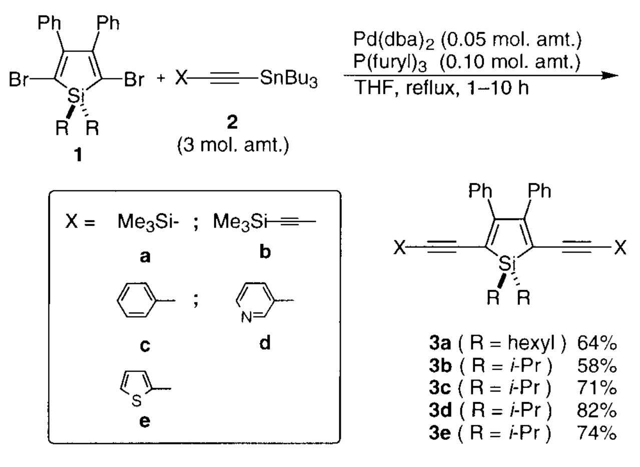


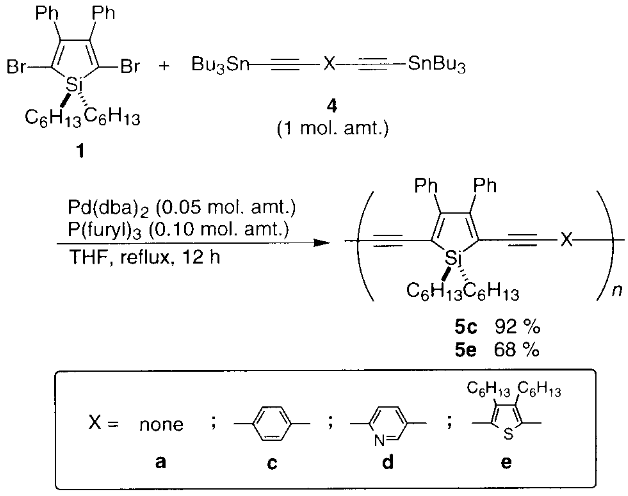
Figure 1. *ORTEP* drawing of **3b** (50% probability thermal ellipsoids). Selected bond lengths [Å] and angles[deg]: Si1-C1 1.880(3), C1-C2 1.362(4), C2-C3 1.495(3), C1-C5 1.406(3), C5-C6 1.199(3), C6-C7 1.376(3), C7-C8, 1.207(4), C8-Si2 1.824(3), C1-Si1-C4 90.0(1), Si1-C1-C2 109.2(2), C1-C2-C3 115.3(2), Si1-C1-C5 124.6(2), C1-C5-C6 175.8(3), C5-C6-C7 175.8(3), C-6-C7-C8 177.1(3), C7-C8-Si2 175.8(3).

Scheme 1.



We next examined the synthesis of diethynylsilole-based π-conjugated polymers using a similar Stille coupling reaction of **1** with bis(stannylethynyl)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$_3$ to give a reddish orange solution and an ink-blue solution, respectively. However, the coupling of **1** with distannyldiacetylene **4a** or bis(stannylethynyl)pyridine **4d** only

Scheme 2.



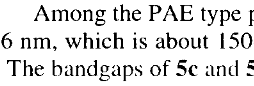
gave insoluble polymeric materials and thus further purification and characterization failed.

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**,[12] with poly(phenyleneethynylene) **8**[5e] and poly(thienyleneethynylene) **9**,[5d] 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 π-electronic systems. Trimethylsilyl-capped bis(butadiynyl)silole **3b** has a 60 nm red-shifted absorption maximum in comparison with **3a**, due to the extended π-conjugation. The λ_{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[a]

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

[a] In $CHCl_3$, unless otherwise stated. [b] Estimated from the onsets of absorptions. [c] In THF. Ref. 5c. [d] Ref. 5d.



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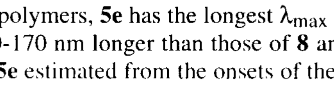

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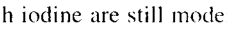

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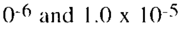

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Among the PAE type polymers, **5e** has the longest λ_{max} at 576 nm, which is about 150-170 nm longer than those of **8** and **9**. The bandgaps of **5c** and **5e** estimated from the onsets of their absorptions are rather small, 2.07 and 1.77 eV, respectively. Despite these features, however, their conductivities upon doping with iodine are still moderate, 6.0 x 10^{-6} and 1.0 x 10^{-5} S cm^{-1} for **5c** and **5e**, respectively. Further investigation of other properties of these silole-acetylene π-electronic systems, such as electrochemical behavior and nonlinear optical properties is now in progress.

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9 The compound **3c** has already been prepared by the similar coupling reaction. See ref. 1b.

10 An attempt to synthesize a parent 2,5-diethynylsilole by desilylation from **3a** with K_2CO_3/MeOH failed due to ring-opening of the silole ring even under such a mild basic condition.

11 Crystal data of **3b** (instrument: Rigaku RAXIS IV): $C_{36}H_{42}Si_3$, 0.40 x 0.30 x 0.30 mm, triclinic, $P\bar{1}$ (#2); a = 15.279(1) Å, b = 17.112(1) Å, c = 7.8326(5) Å, α = 103.066(4)°, β = 99.005(3)°, γ = 110.185(4)°, V = 1809.76 Å^3, Z = 2, D_c = 1.026 g cm^{-3}, μ (Mo Kα) = 1.51 cm^{-1}, temperature 20 °C, R = 0.047, R_w = 0.072, and GOF = 1.29; number of unique reflections = 6333.

12 Compounds **6** and **7** were prepared by the coupling reaction of 2,5-dibromothiophene with trimethylsilylacetylene under Sonogashira conditions.[7a]