Silole–pyrrole co-oligomers: their synthesis, structure and UV–VIS absorption spectra[1]

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Silole–pyrrole co-oligomers (containing up to nine rings) are synthesized and found to have long UV–VIS absorption maxima in spite of their twisted structures.

The silole (silacyclopentadiene) ring is a new building unit for π-conjugated polymers. Several studies on silole-containing polymers have been reported.[2–5] For the molecular design of the new π-conjugated polymers, a particularly low-lying LUMO of the silole ring is especially useful.[6] Our recent study has demonstrated that the low-lying LUMO of silole is caused by the σ*–π* conjugation between the π-symmetrical σ* orbital of two exocyclic σ bonds on silicon and the π* orbital of the butadiene moiety.[6c] Here we compare the electronic structures of the silole ring with those of some other common cyclic dienes by preliminary *ab initio* calculations (HF/6–31G*).† The results depicted in Fig. 1 demonstrate that the silole ring has the smallest HOMO–LUMO energy gap as well as the lowest LUMO. The results also show the high-lying HOMO of pyrrole. We thus anticipated that combination of silole as the π-electron deficient ring with pyrrole as the π-electron rich ring would form new π-conjugated polymers with unique π-electron structures. Similar approaches using other ring systems have been recently reported by Yamamoto *et al.*,[7] ten Hoeve *et al.*[8] and our group.[3,9] Here we report the synthesis and properties of silole–pyrrole co-oligomers as models of their co-polymers.

As a monomer unit, pyrrole–silole–pyrrole three-ring compounds **3** were prepared by Pd⁰-catalysed cross-coupling of readily available dihalogenosiloles **1**‡[4] with 2-stannylpyrrole **2**, as shown in Scheme 1. The coupling reactions using trifurylphosphine[10] or triphenylphosphine as a ligand afforded the monomers **3** as air-stable yellow crystals in good yields.

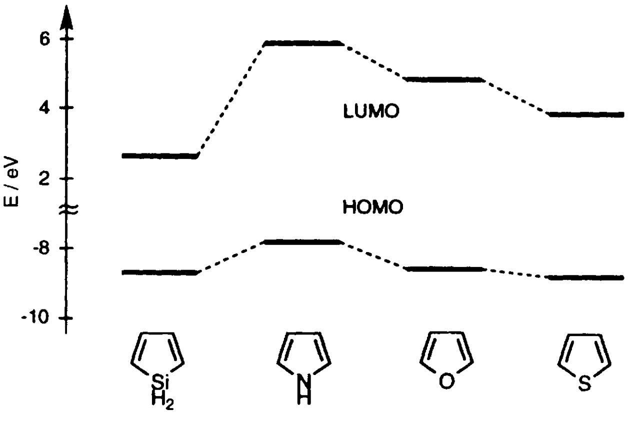
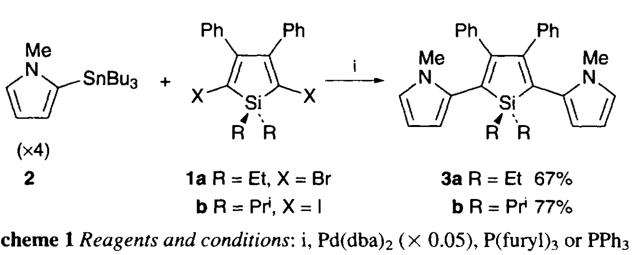


Fig. 1 Relative HOMO and LUMO energy levels for cyclic π-conjugated dienes, based on HF/6–31G* calculations

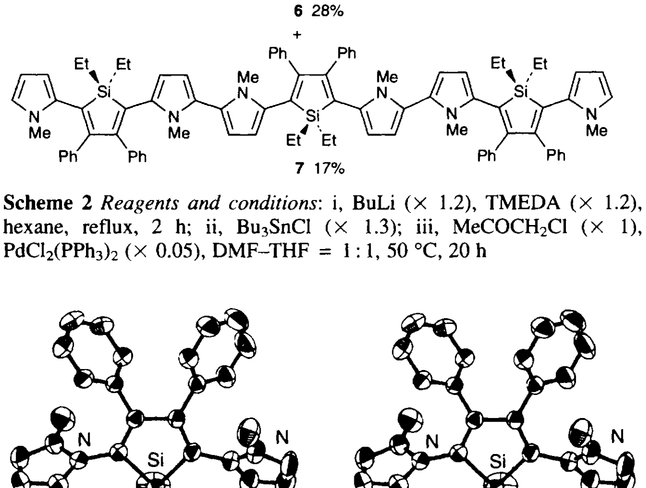


2   **1a** R = Et, X = Br   **3a** R = Et 67%
b R = Pr^i, X = I   **b** R = Pr^i 77%

Scheme 1 *Reagents and conditions*: i, Pd(dba)$_2$ (× 0.05), P(furyl)$_3$ or PPh$_3$ (× 0.10), DMF, 50 °C, 18–30 h

Oligomers of **3a** were prepared according to Scheme 2. Thus, monomer **3a** was lithiated with BuLi (1.2 equiv.)–TMEDA (1.2 equiv.) in refluxing hexane[11] and subsequently treated with tributylstannyl chloride to afford a mixture of mono- and distannylated compounds, **4** and **5**, 4.9 : 1, as determined by ^{1}H NMR. The mixture was isolated by preparative gel permeation chromatography (GPC) using 1,2-dichloroethane as eluent in 59% total yield based on **3a** and used in the next homo-coupling reaction without separation. The mixture was then subjected to oxidative coupling in the presence of PdCl$_2$(PPh$_3$)$_2$ (5 mol%) and chloroacetone (1 equiv. per stannyl functionality) under Kikukawa conditions,[12] to give the dimer **6** (six ring compound) as an orange powder in 28% yield and the trimer **7** (nine ring compound) as a red powder in 17% yield, along with higher oligomers; the yields were based on **3a**.§

The X-ray crystal structure of the monomer **3b** exhibits the highly twisted conformation of the pyrrole–silole–pyrrole skeleton, as shown in Fig. 2;¶ the tilt angles between the silole least-square plane and the two pyrrole least-square planes are 51.7 and 55.7° in opposite directions. This non-coplanarity may



Scheme 2 *Reagents and conditions*: i, BuLi (× 1.2), TMEDA (× 1.2), hexane, reflux, 2 h; ii, Bu$_3$SnCl (× 1.3); iii, MeCOCH$_2$Cl (× 1), PdCl$_2$(PPh$_3$)$_2$ (× 0.05), DMF–THF = 1 : 1, 50 °C, 20 h

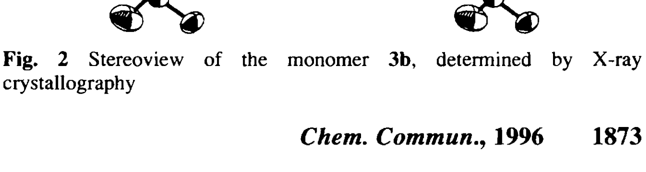


Fig. 2 Stereoview of the monomer **3b**, determined by X-ray crystallography

arise from the steric repulsion between the 3,4-diphenyl groups on silole and the methyl group on the pyrrole nitrogen atom.

UV–VIS spectral data are summarized in Table 1. The monomers **3** have absorption maxima at approximately 100 nm longer wavelength than terpyrrole derivatives (parent terpyrrole, 317 nm;[13] *N,N′,N″*-trimethylterpyrrole, 271 nm).[11] However, extension of the π-conjugated main chain from the monomer **3** to the trimer **7** causes a *ca.* 40 nm bathochromic shift, probably due to the non-coplanarity of the main chain along with the steric repulsion mentioned above.

The long wavelength band of the monomers **3** may be ascribed to the unique π-electronic structure developed by the combination of π-electron deficient silole with π-electron rich pyrrole, as expected. To elucidate the electronic structures, we performed *ab initio* calculations (HF/6–31G*) on coplanar conformers of both the parent pyrrole–silole–pyrrole and the parent terpyrrole for comparison.† The results shown in Fig. 3 indicate that while the HOMO of the pyrrole–silole–pyrrole is delocalized over the three rings like terpyrrole and lies in a comparable level with that of the parent terpyrrole, the LUMO of the former is almost localized on silole ring and lies at a much lower level than that of terpyrrole. As a consequence, the HOMO–LUMO energy gap of the former is about 1.3 eV smaller than that of the latter. The present results strongly suggest that the silole–pyrrole combination is promising for the development of novel low band gap π-conjugated polymers.

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Table 1 UV–VIS spectral data for silole–pyrrole co-oligomers[a]

Compound		λ_{max}/nm	log ε
monomer	**3a**	406	3.93
	3b	409	3.92
dimer	**6**	436	4.24
trimer	**7**	447	4.53

[a] In chloroform.

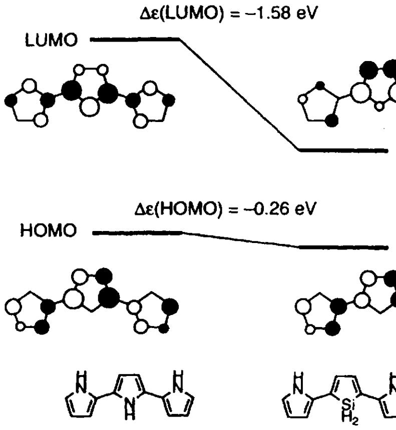
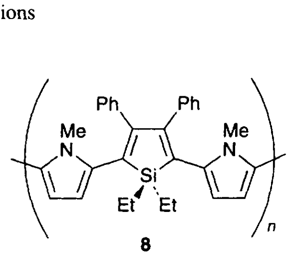


Fig. 3 Relative HOMO and LUMO energy levels for the parent pyrrole–silole–pyrrole and terpyrrole in co-planar conformation, based on HF/6–31G* calculations



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Footnotes

† Calculations were performed by using the GAUSSIAN 92 program.[14] Geometry optimizations for the one-ring compounds and the three-ring compounds were carried out within the C_{2v} and C_{2h} symmetry constraints, respectively.

‡ The 2,5-diiodosilole **1b** was prepared by the reaction of the corresponding dilithiosilole[4] with 1,2-diiodoethane.

§ The synthesis of the silole–pyrrole copolymer has also been attempted by oxidative coupling of the distannylated monomers **5** in the presence of $PdCl_2(PPh_3)_2$ (5 mol%) and chloroacetone (1 equiv.), giving the corresponding co-polymer (deep red powder) **8** in 70% crude yield after reprecipitation from ethanol [M_w = 8300, M_n = 4800, determined by GPC *vs.* polystyrene standard, λ_{max} ($CHCl_3$) = 463 nm]. The polymer, however, was contaminated with small amounts of uncharacterizable polymeric impurities which may have arisen from the tributylstannyl moiety, as judged from the NMR spectra. Many attempts at further purification of this polymer, which included repeated reprecipitation from hexane, preparative GPC isolation, and treatment with KF in aqueous THF, failed.

¶ *Crystal data* for **3b** (instrument; Rigaku AFC7R): $P2_1/c$ (no. 14); a = 10.464(1), b = 15.235(1), c = 18.4652(9) Å, β = 100.957(7)°, V = 2890.0(4) Å^3, Z = 4, D_c = 1.0960 g cm^{-3}, μ (Cu-Kα) = 8.61 cm^{-1}, temperature 20 °C, R = 0.043, R_w = 0.048 and S = 2.40; number of unique reflections = 3282. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/145.

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