# Polymers containing backbone acetylene, anthracene and tetra-, penta- or hexa-coordinate silicon units: UV–visible, photoluminescence and solution $\chi^{(3)}$ non-linear optical properties

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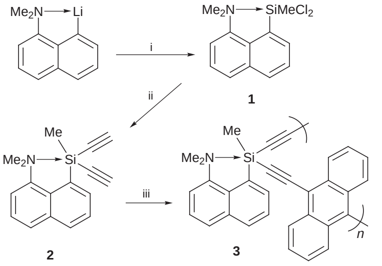
**Poly(aryleneethynylenesilylene)s of general structure $(C\equiv CSiR_2C\equiv CX)_n$ (X = 9,10-anthrylene) containing tetra-, penta- or hexa-coordinate silicon exhibit high $\chi^{(3)}$ values, the absorbance and emission spectra being red-shifted with respect to those for the corresponding monomers $R_2Si(C\equiv CAr)_2$ (Ar = 9-anthryl); these properties are consistent with extensive through-Si conjugation along the backbone.**

As recently reviewed, conjugated poly(aryleneethynylene)s are of current interest on account of their photo- and electroluminescent properties and large third order harmonic generation, the $\chi^{(3)}$ values being similar to those for poly(diacetylene)s.[1] The incorporation of electron-rich anthracene units into poly(aryleneethynylene)s has been found to have a marked influence on the luminescence properties,[2] and is particularly effective in π-electron delocalisation along the backbone of such polymers containing Pt.[3] The silicon-containing analogues $(C\equiv CSiR_2C\equiv CX)_n$ [poly(aryleneethynylenesilylene)s] have been known for some years,[4] those where X is phenylene exhibiting blue photoluminescence[5] with a solution $\mathrm{Re}(\chi^{(3)})$ value of $-9.3 \times 10^{-13}$ esu.[6] Few polymers containing hypercoordinate silicon are known although the latter exhibits very different chemical and electronic behaviour from tetracoordinate silicon.[7] Recently we prepared poly(aryleneethynylenesilylene)s containing backbone hexacoordinate silicon groups,[8] and the series has now been extended to the corresponding polymers with pentacoordinate silicon incorporating the 8-dimethylamino-1-naphthyl (NpN) ligand known to give stable hypercoordinate species.[9]

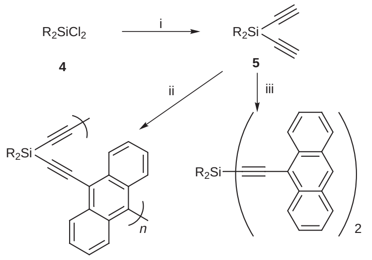
The pentacoordinate compounds were obtained from the previously characterized[10] dichlorosilane **1** which was treated with monoethynyl Grignard reagent (Scheme 1) to give the new (4 + 1)-coordinate[11] diethynylsilane **2**.‡ Likewise, tetracoordinate monomer **5** with two 1-naphthyl groups was prepared from dichlorosilane **4** (Scheme 2), the spectral data being similar to those for $Ph_2Si(C\equiv CH)_2$.[4,12]

Monomers **2** and **5** undergo palladium-catalysed cross-coupling polymerization with 9,10-dibromoanthracene affording, respectively, **3** containing pentacoordinate Si (Scheme 1) and **6** with tetracoordinate $(1\text{-Np})_2Si$ groups (Scheme 2), the latter being similar to the $Ph_2Si$ analogue **7**.[13] Size exclusion chromatography (SEC) showed both materials to be low molecular weight polymers (Table 1) similar to previously reported polymer **8** containing hexacoordinate Si.[8] Reflecting the change in the electronic environment, the Si*C*≡C $^{13}C$ and $^{29}Si$ NMR resonances are shifted upfield with increasing coordination number, there being little effect on the $\nu_{C\equiv C}$ IR absorbance (Table 1).



**Scheme 1** *Reagents and conditions*: i, excess $MeSiCl_3$, $Et_2O$, room temp., 5 h; ii, HC≡CMgBr, THF, −78 °C to room temp.; iii, 9,10-dibromoanthracene, $(PPh_3)_2PdCl_2$, CuI, $PPh_3$, $Et_3N$, PhMe, 4 h, 89 °C

Model monomers **9** and **10** containing tetracoordinate Si were prepared by palladium-catalysed cross-coupling with 9-bromoanthracene (Scheme 2, Table 2). The spectral data are similar to those for the analogous polymers (Table 1), the second IR $\nu_{C\equiv C}$ band in the polymers appearing in the monomers as an ill-defined shoulder around 2150 $cm^{-1}$.



**6** R = 1-naphthyl
(**7** R = Ph)
(**8** R = NpN)

**9** R = 1-naphthyl
(**10** R = Ph)

**Scheme 2** *Reagents and conditions*: i, HC≡CMgBr, THF, −78 °C to room temp.; ii, 9,10-dibromoanthracene, $(PPh_3)_2PdCl_2$, CuI, $PPh_3$, $Et_3N$, PhMe, 16 h, 89 °C; iii, 9-bromoanthracene, $(PPh_3)_2PdCl_2$, CuI, $PPh_3$, $Et_3N$, PhMe, 4 d, 89 °C

**Table 1** Properties of polymers

| | | | | | | | | $\delta_C$ [d] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Si Coord. no. | Polymer | Colour | $M_w$ [a] | $M_w/M_n$ [a] | $n$ [b] | $\nu_{C\equiv C}/cm^{-1}$ [c] | $\delta_{Si}$ [d] | Si*C*≡C [e] | SiC≡*C* [e] | $\Phi_f$ [f] |
| 4 | **7** | red | 23 500 | 3.2 | 56 | 2124 | −47.4 | 102.2 | 106.1 | 0.15 |
| 4 | **6** | orange | 8 800 | 2.8 | 17 | 2130 | −48.0 | 103.1 | 107.3 | 0.41 |
| 5 | **3** | red | 12 400 | 2.7 | 28 | 2129 | −54.9 | 102.2 | 110.1 | 0.01 |
| 6 | **8** | orange | 20 000 | 3.2 | 34 | 2128 | −61.0 | 90.8 | 103.1 | 0.02 |

[a] Determined by SEC with reference to polystyrene standards. [b] Number of units calculated from value of $M_w$. [c] In Nujol mull. [d] In $CDCl_3$ solution. [e] Assigned by analogy with results of $^{13}C$–$^{1}H$ coupling experiments on $(1\text{-Np})_2Si(C\equiv CPh)_2$. [f] Quantum yield, $\Phi_f$, determined in THF solution with an excitation wavelength of 370 nm and with reference to 9,10-diphenylanthracene standard.

**Table 2** Properties of model monomers

| Monomer | Colour | $\nu_{C\equiv C}$/cm$^{-1}$ [a] | $\delta_{Si}$[b] | $\delta_C$[b] SiC≡C[c] | SiC≡C[c] | $\Phi_f$[d] |
|---|---|---|---|---|---|---|
| **9** | red | 2122, 2142 | −48.1 | 101.1 | 107.7 | 0.65 |
| **10** | orange–red | 2122, 2148 | −47.2 | 100.1 | 106.6 | 0.88 |

[a] In Nujol mull. [b] In $CDCl_3$ solution. [c] Assigned by analogy with results of $^{13}C$–$^1H$ coupling experiments on $(1\text{-}Np)_2Si(C{\equiv}CPh)_2$. [d] Quantum yield, $\Phi_f$, determined in THF solution at an excitation wavelength of 370 nm with reference to 9,10-diphenylanthracene standard.

The UV–VIS spectra in $CH_2Cl_2$ solution [Fig. 1(A)] show intense absorption bands with fine structure most probably arising from transitions similar to those for anthracene. With respect to the bands in anthracene, those for **9** and **10** are red-shifted with increased extinction coefficients, the bathochromic shift being greater than for 9-ethynylanthracene.[14,15] The corresponding bands in the polymers are further red-shifted with respect to those in (i) **9** and **10**, (ii) 9,10-diethynylanthracene ($\lambda_{max}$, 356, 377, 423 nm),[16] and (iii) 9,10-bis(trimethylsilylethynyl)anthracene ($\lambda_{max}$, 391, 414, 439 nm). In addition, the polymers (except **6**) show a new broad absorption peak around 520 nm tailing off towards 575 nm, corresponding to an optical gap of *ca.* 2.2 eV. Monomers **9** and **10** show a similar new absorption occurring at lower wavelength than for the polymers (*e.g.* **9**: $\lambda_{max}$ 451 nm). These properties suggest the presence of through-Si conjugation.

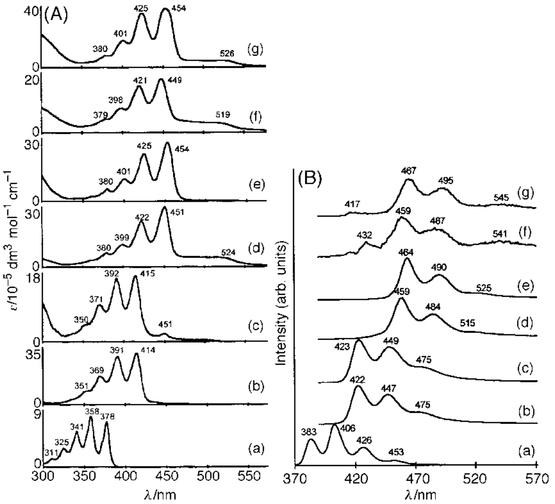


**Fig. 1** (A) UV–VIS spectra in $CH_2Cl_2$ solution and (B) fluorescence spectra in THF solution at an excitation wavelength of 370 nm of (*a*) anthracene, (*b*) **10**, (*c*) **9**, (*d*) **7**, (*e*) **6**, (*f*) **3** and (*g*) **8**

Likewise, the fluorescence spectra [Fig. 1(B)] show a red-shift on going from anthracene to **9** and **10** and then a further such shift on going to the polymers, the apparent Stokes shifts[17] lying in the range 8–13 nm (*cf.* anthracene 5 nm). For the polymers, the low energy band at *ca.* 540 nm is probably due to excimer formation since (i) the relative intensity is concentration dependent, and (ii) anthracene compounds are known to dimerize on absorbing 320–400 nm light.[18] A picosecond time-resolved photoluminescence study of **7** (1 g l$^{-1}$ in THF) at 532 nm showed maximum emission at 470 nm and a decay time constant of *ca.* 6 ns. Unlike polymers **3**, **7**, **8** and poly(*p*-phenyleneanthryleneethynylene)s,[19] **9** and **10** are highly emissive (*cf.* anthracene: $\Phi_f$ = 0.32[20]).

The sign and the magnitude of the real and imaginary parts of $\chi^{(3)}$ were determined for polymers **3**, **7** and **8** by solution Z-scan measurements[21] in the near-resonant region at 1064 nm (Table 3),§ the polymers being of sufficient chain length for the $\chi^{(3)}$ effects to be at a maximum.[22] High activity was found [in particular Im($\chi^{(3)}$) for **3** containing pentacoordinate Si], the value of Re($\chi^{(3)}$) being comparable to that determined in the resonant region at 590 nm for poly(phenyleneethynylenesilylene).[6] At 595 nm, a rather fast dominant relaxation time of *ca.* 20 ps was observed for the three polymers;¶ under non-resonant conditions the materials are expected to be considerably faster.

**Table 3** Solution $\chi^{(3)}$ properties[a]

| Si Coord. no. | Polymer | $\beta$/cm GW$^{-1}$ | Im($\chi^{(3)}$)/esu | $n_2$/cm$^2$ W$^{-1}$ | Re($\chi^{(3)}$)/esu |
|---|---|---|---|---|---|
| 4 | **7** | 0.27 | $1.8 \times 10^{-13}$ | $5.0 \times 10^{-15}$ | $4.0 \times 10^{-13}$ |
| 5 | **3** | 1.20 | $8.0 \times 10^{-13}$ | — | — |
| 6 | **8** | 0.27 | $1.8 \times 10^{-13}$ | $5.0 \times 10^{-15}$ | $4.0 \times 10^{-13}$ |

[a] Z-scan measurements in $CHCl_3$ solution (50 g l$^{-1}$) at 1064 nm, pulse duration 140 ps, intensity 20 GW cm$^{-2}$.

In conclusion, the UV–VIS, photoluminescence and high $\chi^{(3)}$ properties of the polymers are consistent with extensive through-Si conjugation along the backbone.

## Notes and References

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‡ *Selected data* for **2**: 76%; mp 102.4–104.3 °C; $\delta_{Si}(CDCl_3)$ −56.6; $\delta_C(CDCl_3)$ 91.3 (SiC≡*C*), 93.0 (Si*C*≡C); $\nu_{C\equiv C}$(Nujol)/cm$^{-1}$ 2036, 2021.

§ The values of $n_2$ were extracted from the Z-scan results with large uncertainties since the data could not be fitted well (no satisfactory result could be obtained for **3**).

¶ Excite-probe experiments on dilute polymer solutions with 0.6 ps pulses at 595 nm showed appreciable linear absorption and bleaching nonlinearity or saturable absorption. The relaxation dynamics could not be described with a single excited-state lifetime.

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