Simple acid–base hydrolytic chemistry approach to new materials for second-order non-linear optics

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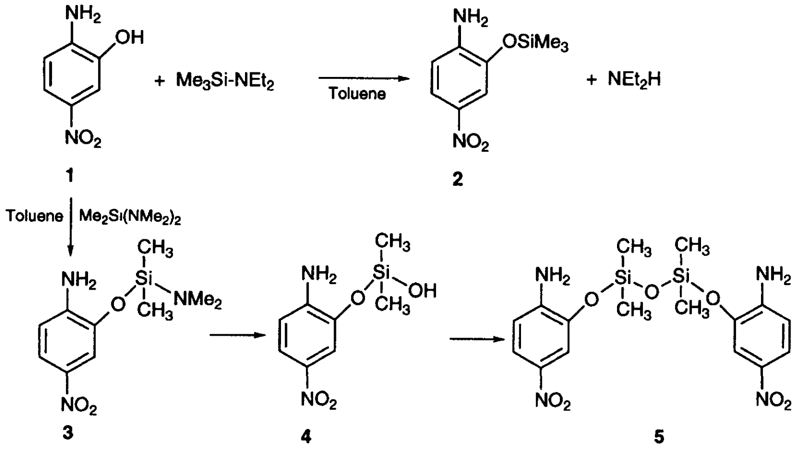
Acid–base hydrolysis of aminosilanes with NLO-active chromophores containing terminal acidic protons provides a facile synthetic route to robust dimeric, polymeric and molecularly self-assembled thin-film materials for second-order non-linear optics.

Second-order non-linear optics continues to attract much attention owing to its potential applications in the new materials industry for photonic-based devices.[1–2] The design strategy for such materials requires an adequate number density of 'push–pull' molecules which possess high second-order molecular hyperpolarizabilities (β); this can be achieved by covalently anchoring high-β molecules into the backbone of a polymer, by the preparation of Langmuir–Blodgett thin films and by molecular self-assembly. For the polymeric materials, ease of preparation, solubility in common solvents and high mechanical stability are important performance issues for any practical applications.[1–4] For the construction of robust and highly organized second-order non-linear optical (NLO) thin films, the availability of the desired chromophores and the simplicity of their chemical deposition on solid substrates can contribute significantly to the development of molecularly self-assembled materials. We report herein a new synthetic route, based on simple acid–base hydrolytic chemistry, to chromophore-functionalized dimeric and polymeric siloxanes, and molecularly self-assembled thin-film second-order NLO materials. In the former, incorporation of dimethylsiloxane linkages in the backbone provides improved processability and dimensional stability, as demonstrated by the high solubility and thermal stability of the polymer.

The hydrolysis of aminosilanes (*e.g.* $Me_3Si\text{-}NEt_2$), which can be prepared easily using chlorosilanes ($Me_3Si\text{-}Cl$) and excess amines (NEt_2H), with organic acids has been well documented.[5] The acid–base reaction of $Me_3Si\text{-}NEt_2$ with commercially available 2-amino-5-nitrophenol **1** is extremely facile and quantitative, yielding the corresponding silylated product, 2-amino-5-nitrotrimethylsilylphenol **2** (Scheme 1).† When **1** is treated with dimethylsilylbis(dimethylamine), the resulting 2-amino-5-nitrotrimethylsilyldimethylamine **3** reacts with molecular water to give the corresponding hydroxysilyl compound **4**. The latter undergoes co-condensation with another molecule of **4** yielding dimer **5**, which has been structurally characterized (Fig. 1).‡ The asymmetric unit consists of half the molecule in which the central oxygen [O(1)] sits on a two-fold axis of symmetry. The two phenyl rings of the NLO chromophores are parallel to each other. The NO_2 group shows a strong tendency to lie on top of the phenyl ring of the opposite



Scheme 1

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† *Selected data.* **2**: ^1H NMR (200 MHz, C_6D_6) δ 0.11 [s, $(CH_3)_3Si$], 6.20 (s, NH_2), 6.62 (d, C_6H_3, $J_{H-H}=8.6$ Hz), 7.60 (m, C_6H_3). MS (CI) 227. UV–VIS ($CHCl_3$) λ_{max}/nm 376. **5**: ^1H NMR (200 MHz, DMSO) δ 0.31 [s, $(CH_3)_2Si$], 6.39 (s, NH_2), 7.60 (d, C_6H_3, $J_{H-H}=8.6$ Hz), 7.71 (d, C_6H_3, $J_{H-H}=8.5$ Hz), 7.76 (d, C_6H_3, $J_{H-H}=8.6$ Hz). MS (EI) 438. UV–VIS ($CHCl_3$) λ_{max}/nm 376. Anal. Calcd. for $C_{16}H_{22}N_4O_7Si_2$: C, 43.84; H, 5.02; N, 12.72. Found C, 44.05; H, 5.07; N, 12.74. **6**: ^1H NMR (200 MHz, $CDCl_3$) δ 1.59 (s, OH) 1.90 (m, CH_2), 3.60 (t, CH_2, $J_{H-H}=7.3$ Hz), 3.75 (t, CH_2, $J_{H-H}=6.1$ Hz), 6.80 (d, C_6H_4, $J_{H-H}=7.3$ Hz), 8.11 (d, C_6H_4, $J_{H-H}=7.4$ Hz). MS (EI) 254. UV–VIS ($CHCl_3$) λ_{max}/nm 396. **7**: ^1H NMR (200 MHz, $CDCl_3$) δ 0.12 [s, $(CH_3)_3Si$], 1.74 (m, CH_2), 3.51 (m, CH_2), 3.62 (m, CH_2), 6.80 (d, C_6H_4, $J_{H-H}=9$ Hz), 8.03 (d, C_6H_4, $J_{H-H}=9$ Hz). MS (EI) 398. UV–VIS ($CHCl_3$) λ_{max}/nm 398. **9**: ^1H NMR (200 MHz, $CDCl_3$) δ 0.09 [s, $(CH_3)_2Si$], 1.73 (m, CH_2), 3.46 (br, CH_2), 3.67 (br, CH_2), 6.73 (br, C_6H_4), 7.96 (br, C_6H_4, $J_{H-H}=9$ Hz). UV–VIS ($CHCl_3$) λ_{max}/nm 398.

‡ Monoclinic, space group $C2/c$, $a=13.100(3)$, $b=10.611(3)$, $c=16.293(3)$ Å, $\beta=112.362(16)°$, $Z=4$. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/4.

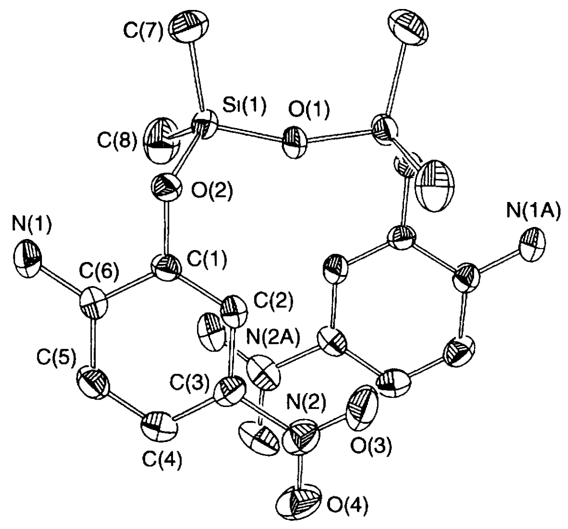

Fig. 1 ORTEP diagram of the molecular structure of dimer 5

molecule In an approximate arrangement of the dipoles in the dimer along the lines joining N(1) and N(1A), N(1), C(6) and C(3), and N(1A), C(6A) and C(3A) with an angle of *ca* 30°, the dipoles cancel out in the *x* direction ($-1\cos 30° + 1\cos 30° = 0$), but there is a net dipole moment in the *y* direction ($1\sin 30° + 1\sin 30° = 1$) However, since the crystal packing is centrosymmetric, the overall dipole moment is zero

The bifunctional chromophore 1-bis(3-hydroxypropyl)amino-4-nitrobenzene **6**, which is the polymer precursor, was prepared by reacting 1-fluoro-4-nitrobenzene with diallylamine, followed by treatment of the resulting 1-diallylamino-4-nitrobenzene with an excess of 9-BBN (9-borabicyclononane) and subsequent hydrolysis with H_2O_2–NaOH Compound **6** undergoes facile acid-base hydrolysis with 2 equivalents of Me_3Si-NEt_2 (Scheme 2) yielding the corresponding silylated product **7** † In a similar reaction, the polymer precursor **6** reacts with $Me_2Si(NMe_2)_2$ in concentrated DMSO solution to give **8**, which yields the desired polymer **9** upon hydrolysis and siloxane condensation The latter polymer ($M_w = 6200$, $M_n = 2300$ by gel permeation chromatography) was found to be extremely soluble in common organic solvents The thermal stability of the polymer was determined by thermogravimetry (TG), and it was found to decompose at 329 °C The high thermal stability is ascribed to the mechanical strength provided by the siloxane linkages in the backbone The UV–VIS absorption spectra of monomer **7** and the corresponding polymer **9** in chloroform were found to be similar in their peak positions ($\lambda_{max} = 398$ nm)

Thin films containing NLO chromophores were prepared using an analogous acid–base chemistry route The clean glass or quartz substrates were treated with (i) $SiCl_4$ using a 10% solution by volume in toluene at room temperature for 14 h, (ii) dry NEt_2H in a 5–10% solution by volume in toluene at room temperature for 10 h, followed by (iii) (*a*) 2-amino-5-nitrophenol, and (*b*) dye, Disperse Red 1§ (Scheme 3) The thin-film deposition process was monitored by contact angle goniometry, UV–VIS absorption, X-ray photoelectron spectroscopies and second-harmonic generation ¶ The surface density in the latter monolayer was estimated[6] as $1\,2 \times 10^{-10}$ mol cm^{-2} using UV–VIS absorption spectra of Disperse Red 1 in solution and of its monolayer on quartz, Beer–Lambert's law and the molar absorption coefficient of the above dye in solution ($\lambda_{max} = 482$ nm in $CHCl_3$, $\varepsilon_{482} = 4\,41 \times 10^7$ dm^3 mol^{-1} cm^{-1}) The second-harmonic generation characteristics of a thin film of Disperse Red 1 of an estimated thickness of 25 Å were examined at 1064 nm using quartz as a reference The $\chi^{(2)}_{zzz}$ for the latter thin film was calculated to be 8×10^{-8} esu with a chromophore tilt angle of *ca* 38° This SHG efficiency is comparable to the molecularly self-assembled chromophoric thin films prepared using other routes[7]

In conclusion, robust and extremely soluble dimeric and polymeric siloxanes, and molecularly self-assembled thin films containing second-order NLO chromophores are

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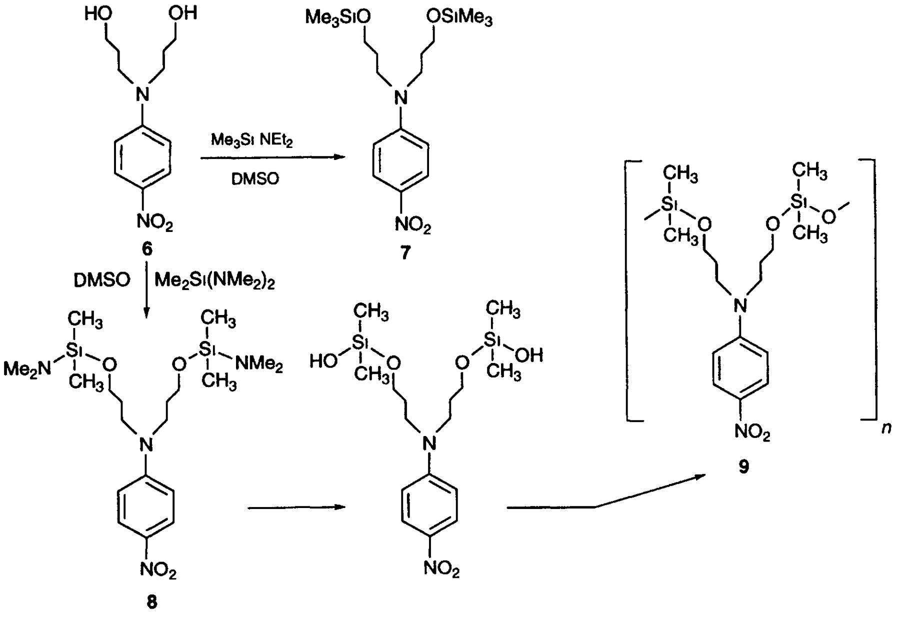
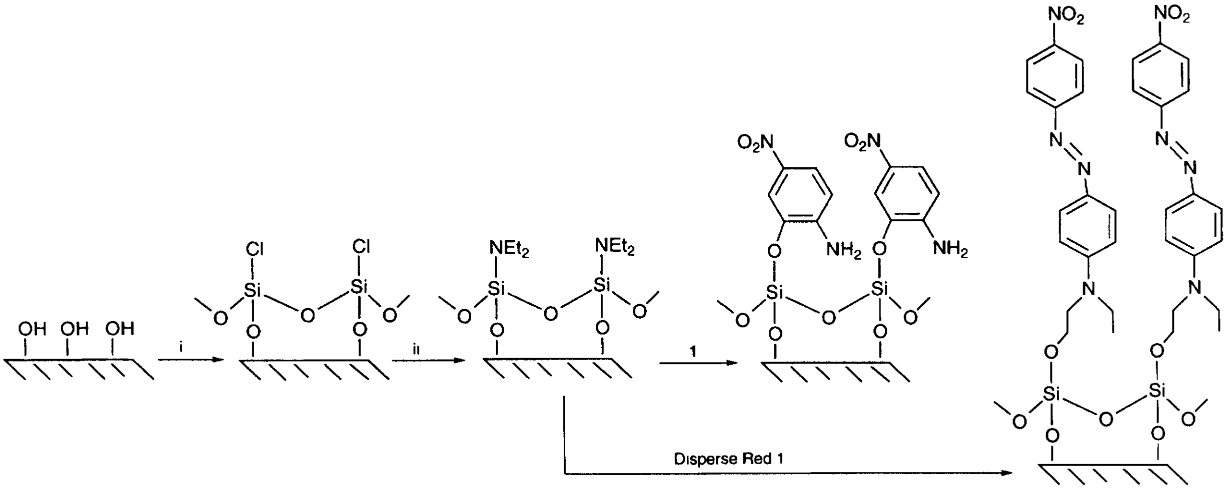
§ Disperse Red 1 reacts quantitatively with one equivalent of Me_3Si-NEt_2 yielding the corresponding silylated product with the elimination of diethylamine ^1H NMR (200 MHz, C_6D_6) δ 0 04 [s, $(CH_3)_3Si$], 0 82 (t, CH_2CH_3, $J_{H-H} = 7$ Hz), 3 00 (m, CH_2OSiMe_3), 3 12 (t, CH_2CH_3, $J_{H-H} = 6$ Hz), 3 44 (t, NCH_2OSiMe_3, $J_{H-H} = 6$ Hz), 6 53 (d, C_6H_4, $J_{H-H} = 9$ Hz), 7 76 (d, C_6H_4, $J_{H-H} = 7$ Hz), 7 95 (d, C_6H_4, $J_{H-H} = 9$ Hz), 8 13 (d, C_6H_4, $J_{H-H} = 9$ Hz) MS (EI) 386

¶ Static contact angles using water clean glass slide, 18°, glass slides functionalized with **1** and Disperse Red 1, 80 and 82° respectively UV–VIS absorption spectra of Disperse Red 1 in $CHCl_3$, λ_{max}/nm 482, on quartz, λ_{max}/nm 486, were similar except for some broadening on the surface X-Ray photoelectron spectra of a thin film of **1** on glass Si (2s, 157 1 eV, 2p, 106 8 eV), C (1s, 286 8 eV), N (2p, 401 1 eV), O (1s, 531 7 eV)



Scheme 2



Scheme 3 Reagents: i, $SiCl_4$; ii, NEt_2H

easily accessible using simple acid–base hydrolytic chemistry. Further elaboration of this synthetic approach to include other high-β molecules into polymers, bifunctional chromophores leading to multilayer thin films, and a detailed study of the NLO properties of these materials are currently being pursued.

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