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Synthesis, aggregation behavior and nonlinear absorption properties of lead phthalocyanines substituted with siloxane chains

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The synthesis and characterization of polysiloxane substituted metal-free and lead phthalocyanines are described. These materials form a class of isotropic liquid phthalocyanines that combine a large nonlinear absorption with an exceptionally large nonlinear thermal refractive effect. These materials effectively couple the nonlinear absorption characteristics of the phthalocyanine (Pc) moiety with the thermorefractive properties typical of siloxanes. The room temperature index of these phthalocyanines can be varied by the choice of the siloxane substituent. Furthermore, the siloxane substituents are effective at inhibiting aggregation of the phthalocyanine rings. The observed aggregation constants in toluene solutions are very small and only a small degree of aggregation is observed even in the pure liquid phthalocyanines. Nonlinear transmission, z-scan, transient absorption and degenerate four-wave mixing studies confirm that the Pb substituted materials possess a broad spectral region of induced absorption with nonlinear absorption coefficients similar to that observed from other lead substituted phthalocyanines. The observed ground state molar absorption coefficients of the siloxy phthalocyanines are somewhat smaller than comparable alkyl substituted phthalocyanines. Taken together, these properties make these materials very useful for practical nonlinear optical applications. The coupling of siloxane chains to the Pc rings represents a promising way to achieve some important properties that are difficult to achieve by other means.

Introduction

One of the goals of materials science and chemistry is to incorporate new functionalities into existing materials without altering the fundamental response mechanisms that made the material originally interesting. This paper describes a realization of that goal. We have recently synthesized a series of polysiloxane phthalocyanines that were specifically designed to possess useful nonlinear optical properties. In addition to their nonlinear optical properties, these materials are designed to be viscous, thermorefractive, isotropic liquids that form optically clear thin films, which facilitates their use in practical optical applications.

While the materials described in this paper were designed to possess enhanced nonlinear optical and optical limiting responses, the unique properties of these new materials may prove useful in other applications. In addition to being among the best nonlinear materials for optical limiting applications,^{1–3} phthalocyanines are an important class of commercial dyes and coloring agents. They have been used as laser dyes,⁴ as photoreceptors in color copiers and color laser printers and as a photoactivator in several brands of CD-R discs.

Optical limiters are nonlinear optical devices whose transmission decreases with increasing applied intensity. These devices require materials with appropriate nonlinear optical response mechanisms, in particular nonlinear absorption and nonlinear refraction. The nonlinear absorption properties of many dyes have been investigated.⁵ It has been found that materials that have higher absorption cross sections in the excited state than they do in their ground state yield positive nonlinear absorption coefficients. This effect is sometimes called reverse saturable absorption (RSA). A number of dye materials, primarily phthalocyanines and porphyrins, with large positive nonlinear absorption coefficients have been reported. The desirability of materials with a large intensity or fluence dependent refractive index in such applications has been recognized.^{5–7} We know of few examples of materials that are strong nonlinear absorbers and also possess a large non-linear refractive index. In most previous cases the refractive response was dominated by that of the solvent. An intrinsic, fluence dependent refractive index is desirable when the non-linear material is used pure or as a thin film.

The peripherally substituted silicone phthalocyanines (Pc's) reported here combine large nonlinear absorption and nonlinear refraction coefficients. The source of the fluence dependence of the refractive index is thermal. Our hypothesis is that the silicone-substituted phthalocyanines can couple the large refractive index variation with temperature (dn/dT) characteristic of the siloxane structure⁸ with the large nonlinear absorption (reverse saturable absorption) characteristic of the phthalocyanine ring.¹

In addition to the nonlinear response characteristics, these silicone phthalocyanines possess other useful properties: optical transparency over a relatively broad region, photo-oxidative stability, as evidenced by the invariance of the UV-vis absorption spectrum over a period of months, and processability as a solution, glass or liquid. In previous materials, some of these properties have been achieved. Peripheral substitution of arylethers at the phthalocyanine ring,^{5,9} for example, introduction of cumylphenoxy substituents, generates effective optical limiting materials with excellent solubility and photooxidative stability.¹ However, this material is a solid in pure form and does not readily form transparent films. The introduction of an alternative peripheral substituent group, phenylglycidylether, allowed the formation of optically clear thin films of the pure material.¹⁰ These thin films are glassy and were found to have relatively low damage thresholds.¹¹ Attachment of ethyleneoxide oligomer substituents to the Pc core, yields intrinsic liquids which also form optically clear films that have the ability to self heal if optically damaged.¹² Unfortunately, the material with the best nonlinear absorption characteristics, a lead substituted version, was found to be unstable upon dilution in common solvents.

Another important feature in phthalocyanine design for nonlinear optical applications is the control over aggregation. Phthalocyanines tend to form aggregates in solution and films. Aggregation reduces the excited state lifetime and hence the effective nonlinear optical absorption coefficients. Strategies to reduce aggregation include incorporation of long alkyl chains in the α position of the phthalocyanine ring^{12–15} or substitution at the β position with bulky groups such as large dendritic substituents.¹⁶ We postulated that the substitution of the Pc ring with poly(dimethylsiloxane) chains (10 repeat units length) would also be effective for suppression of aggregation in solution.⁷

In this paper the preparation and properties of some peripheral silyloxy substituted phthalocyanines and their lead substituted analogs are described in detail. We show that silyloxy substitution gives a novel class of isotropic liquid phthalocyanines with an exceptionally large thermorefractive effect combined with a large nonlinear absorption. Aggregation studies of these compounds are reported and preliminary data on the nonlinear optical properties are given. The synthesis of a lead phthalocyanine with phenyl substituted siloxane chains is also described to demonstrate the variability of the linear refractive index of the material. The coupling of siloxane chains to the Pc rings represents a promising way to achieve some important properties that are difficult using more common substituents.

Experimental

General

Reagents (Gelest, Aldrich, Fisher) were used without further purification unless otherwise noted. Dry THF were used after refluxing under nitrogen over lithium aluminium hydride and distillation just prior to use. Chromatographic purifications were performed on silica gel columns (Fluka AG 60, activity 2-3). NMR spectra were recorded on a Bruker AC 300 spectrometer (300 MHz for ¹H and 75 MHz for ¹³C). Deuterated acetone or chloroform were used as solvents, and the chemical shifts are internally referenced to CD₃COCD₃ (2.04 and 29.8 ppm) or to CDCl₃ (7.26 and 77 ppm) for the respective ¹H and ¹³C nuclei. Infrared spectra were obtained from samples deposited as thin films on NaCl plates and the spectra were recorded using a Nicolet Magna FTIR 750. UV-VIS spectra were measured using either a Perkin Elmer Lambda 5 or Lambda 9 spectrophotometer. Differential scanning calorimetry (DSC) data were recorded on a DuPont 2100 thermal analysis system/910 DSC module. Melting points were determined in an electro-thermal melting point apparatus and are uncorrected. Refractive indices of colorless compounds were measured with a Bausch & Lomb Abbe-3L refractometer (589 nm; 20 °C) and those of phthalocyanine compounds were measured via both a Woolam spectroscopic ellipsometer and a Metricon Model 2010 prism coupler.

The experimental apparatus for the nonlinear optical characterization has been described.³ Briefly, the laser source for the nanosecond experiments was an optical parametric oscillator (Continuum Surelite) pumped by the third harmonic of a Nd/YAG laser. The pulse width of this laser was 2.5

nanoseconds. Some of the nanosecond experiments at 532 nm used a doubled Nd/YAG (Spectra-Physics) laser with a pulse width of 8 nanoseconds. The beam was spatially filtered and the experiments were performed used f/5 focusing optics. The experiments were conducted at 10 Hz for lower fluences but at higher fluences, where persistent thermal effects are possible, the repetition rate was reduced to 0.5 Hz. At the highest fluences, the sample was translated between the shots so that each data point was on a fresh sample. The picosecond time resolved experiments included degenerate four-wave mixing (DFWM) studies and spectrally resolved transient absorption. They were performed using a dye laser that is synchronously pumped by the second harmonic of a CW mode-locked Nd:YAG laser. The dye laser output is amplified in a threestage dye amplifier pumped by the second harmonic of a regenerative Nd:YAG amplifier seeded with the fundamental of the mode-locked Nd:YAG laser. The 10 Hz output of this laser system provides 1.2 ps FWHM pulses with energies up to 1 mJ. For these experiments the laser system was tuned between 589-606 nm.

Synthetic procedures

4-(2-allylphenoxy)phthalonitrile, 3. To a 250 mL two-neck flask fitted with a magnetic stirring bar and nitrogen inlet tube, was added 25 mL of Me₂SO, 5 g (0.028 mol) of 4-nitrophthalonitrile (1) and 3.94 g (0.029 mol) of 2-allylphenol (2). The mixture was stirred at room temperature while 6.57 g (0.047 mol) of anhydrous potassium carbonate were added in 0.54 g quantities at 0.5 h intervals over a 6 h period. The reaction mixture was stirred overnight under nitrogen. The reaction was worked up by filtering and concentrating at reduced pressure to near dryness. The brown oil obtained was extracted with 100 mL CH₂Cl₂ and washed twice with 100 mL of water. The CH₂Cl₂ phase was separated and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the oil was passed through an alumina column using toluene elution. Yield 4.45 g (61%). $M.p = 49-51 \degree C$; ¹H NMR (CDCl₃) δ ppm 3.23 (2H, d, CH₂), 4.95 (2H, dd, =CH₂), 5.78 (1H, m, =CH), 6.95 (1H, d, H_{arom}), 7.12–7.33 (5H, m, H_{arom}), 7.68 (1H, d, H_{arom}); ¹³C NMR (CDCl₃) δ ppm 34.0, 108.5, 114.9 and 115.4 (CN), 116.7, 117.6, 120.8, 120.9, 121.0, 126.7, 128.5, 131.6, 132.4, 135.3, 135.4, 151.1, 161.7; IR (NaCl) v cm⁻¹ 3082 (=CH₂), 2229 (CN), 1615 (C=C), 1595 and 1486 (C-C), 1246 (C-O-C).

Butyl capped hydrosilyl terminated polydimethylsiloxane (PDMS) oligomers, 5a-b. The procedure was adopted from Holohan et al.¹⁷ A solution of hexamethylcyclotrisiloxane (4a) in THF (33% w/v) was prepared by passing 6 g (0.027 mol) of hexamethylcyclotrisiloxane through an alumina column under nitrogen. Dry THF was passed through the column until 18 g of solution was collected in a preflamed flask equipped with a magnetic stirring bar placed at the end of the column. The flask was immediately closed and immersed in an ice-water bath. A solution of BuLi in hexane was added with stirring. For compound 5a 3.59 mL (9 mmol) of BuLi were used, and for compound 5b 1.79 mL, (4.5 mmol) were used. After initiation, the polymerization was allowed to proceed at room temperature for between 15 and 20 h. The reaction was terminated by the slow addition of chlorodimethylsilane at -78 °C (for 5a 4 mL (0.036 mol) (CH₃)₂SiHCl and for **5b** 2 mL (0.018 mol) (CH₃)₂SiHCl). This mixture was stirred for 30 min at -78 °C and two hours at room temperature during which time a precipitate of LiCl formed. THF, hexane and excess chlorodimethylsilane were removed by rotary evaporation. LiCl was then removed by filtration. Further purification of the oligomer was carried out by heating under vacuum at 120 °C.

5a (Bu^{n} - $PDMS_{10}$ -H). Yield: 5.50 g (78%); Tg = -134 °C; $n_{\rm D} = 1.4008$; ¹H NMR (D₃CCOCD₃) δ ppm 0.05 (6H, d, -SiCH₃), 0.19 (54H, m, -SiCH₃), 0.53 (2H, m, CH₂), 0.89 (3H, t, CH₃), 1.32 (4H, m, CH₂), 4.70 (1H, q, SiH); IR (NaCl) ν cm⁻¹ 2972.2 (CH), 2132 (SiH), 1272 (SiCH₃), 1098 and 1027 (SiOSi), 800 (SiC).

5b (Buⁿ-PDMS₁₉-H). Yield: 5.61g (86%); Tg = -130 °C; n_D = 1.4020; ¹H NMR (D₃CCOCD₃) δ ppm 0.07 (114H, m, -SiCH₃), 0.58 (2H, m, CH₂), 0.89 (3H, t, CH₃), 1.37 (4H, m, CH₂), 4.71 (1H, q, SiH); IR (NaCl) ν cm⁻¹ 2970 (CH), 2132 (SiH), 1266 (SiCH₃), 1104 and 1033 (SiOSi), 807 (SiC).

Butyl capped hydrosilyl terminated polymethylphenylsiloxane, 5c (Buⁿ-PMPhS₁₀-H). A solution of trimethyltriphenylcyclotrisiloxane (4b) in THF (33% w/v) was prepared by passing 7 g (0.017 mol) of trimethyltriphenylcyclotrisiloxane through an alumina column under nitrogen. Dry THF was passed through the column until 21.2 g of solution were collected in a preflamed flask equipped with a magnetic stirring bar placed at the end of the column. The flask was immediately closed and immersed in an ice-water bath. A 2.5 M solution of BuLi in hexane (2.25 mL, 5.6 mmol) was added with stirring. After initiation, the polymerization was allowed to proceed at room temperature for between 15 and 20 h. The reaction was terminated by the slow addition of 2.55 mL (0.022 mol) of (CH₃)₂SiHCl at -78 °C. This mixture was stirred for 30 min at -78 °C and two hours at room temperature during which time a precipitate of LiCl formed. THF, hexane and excess chlorodimethylsilane were removed by rotary evaporation. LiCl was then filtered. The product was further purified by heating under vacuum at 120 °C to yield 4.51 g (60%) of colorless oil. Tg = -69 °C; $n_D = 1.5255$; ¹H NMR (D₃CCOCD₃) δ ppm 0.11–0.55 (33H, m, -SiCH₃), 0.83 (5H, m, -CH₃, CH₂), 1.31 (4H, m, CH₂), 4.77 (1H, q, SiH), 7.19–7.69 (45H, m, H_{arom}); IR (NaCl) v cm⁻¹ 3069, 2972 and 2897 (CH), 2125 (SiH), 1595 and 1440 (SiPh), 1259 (SiCH₃), 1130 and 1072 (SiOSi), 910 (SiC), 794 and 729 (PhSi CH₃).

Butyl capped polysiloxane methylene phenoxy phthalonitriles, 6a–c. General procedure. To a flask equipped with a magnetic stirring bar were added 1 g (3.85 mmol) of 2-allylphenoxyphthalonitrile **3** and 3 drops of a 0.1 M solution of hydrogen hexachloroplatinate(v) hydrate (H₂PtCl₆) in isopropanol. The mixture was heated at 60 °C and 3.85 mmol of the corresponding butyl capped hydrosilyl terminated polysiloxane oligomer (**5a–c**) were added followed by 1 h stirring. The light brown oil obtained was purified by column chromatography on silica with toluene as the eluent to give a colorless oil.

6a. Yield: 1.40 g (35%); $Tg = -111 \degree C$; $n_D = 1.4482$; ¹H NMR (D₃CCOCD₃) δ ppm 0.012–0.064 (60H, m, -SiCH₃), 0.54 (4H, m, -SiCH₂), 0.86 (3H, t, CH₃), 1.29 (4H, m, CH₂), 1.58 (2H, m, CH₂), 2.49 (2H, t, CH₂), 6.95 (1H, d, H_{arom}), 7.14–7.31 (5H, m, H_{arom}), 7.68 (1H, d, H_{arom}); ¹³C NMR (D₃CCOCD₃) δ ppm 0.37 (Si(CH₃)₂C), 1.39 (OSi(CH₃)₂O), 14.08 (CH₃), 18.51 and 18.71 (SiCH₂), 23.90, 24.80 and 26.9 (CH₂), 34.1 (PhCH₂), 109.22 and 115.85 (C_{arom}), 116.26 (CN), 118.21, 121.90, 121.99, 122.08, 127.19, 128.90, 132.29 (CH_{arom}), 135.50 (C_{arom}), 136.81 (CH_{arom}), 155.12 and 161.08 (C–O–C); IR (NaCl) ν cm⁻¹ 2959 (CH), 2234 (CN), 1608 and 1492 (C–C), 1259 (SiCH₃), 1098 and 1033 (SiOSi), 806 (SiC).

6b. Yield: 3.49 g (53%); Tg = -122 °C; $n_D = 1.4317$; ¹H NMR (D₃CCOCD₃) δ ppm 0.016–0.084 (114H, m, -SiCH₃), 0.54 (4H, m, -SiCH₂), 0.88 (3H, t, CH₃), 1.32 (4H, m, CH₂), 1.55 (2H, m, CH₂), 2.50 (2H, t, CH₂), 6.95 (1H, d, H_{arom}), 7.15–7.32 (5H, m, H_{arom}), 7.70 (1H, d, H_{arom}); ¹³C NMR (D₃CCOCD₃) δ ppm 0.55 (Si(CH₃)₂C), 1.54 (OSi(CH₃)₂O), 13.80 (CH₃), 17.96 and 18.19 (SiCH₂), 24.01, 25.46 and 26.38 (CH₂), 33.53 (PhCH₂), 108.53 and 114.97 (C_{arom}), 115.40 (CN), 117.73, 120.75, 121.02, 126.65, 128.06 and 131.57

(CH_{arom}), 134.86 (C_{arom}), 135.40 (CH_{arom}), 151.29 and 162.03 (C–O–C); IR (NaCl) ν cm⁻¹ 2966 (CH), 2235 (CN), 1608 and 1492 (C–C), 1272 (SiCH₃), 1098 and 1033 (SiOSi), 800 (SiC).

6c. Yield: 4.43 g (72%); Tg = -42 °C; $n_D = 1.5398$; ¹H NMR (D₃CCOCD₃) δ ppm 0.13–0.52 (m, -SiCH₃), 0.91 (m, CH₃), 1.24 (m, CH₂), 1.65 (m, CH₂), 2.50 (m, CH₂), 7.21–7.88 (m, H_{arom}); ¹³C NMR (D₃CCOCD₃) δ ppm 0.17 (Si(CH₃)₂C), 0.23 (OSi(CH₃)₂O), 13.97 (CH₃), 17.56 and 18.66 (SiCH₂), 24.69, 26.03 and 26.93 (CH₂), 34.43 (PhCH₂), 109.17 and 115.93 (C_{arom}), 116.35 (CN), 127.20, 128.52, 128.65, 128.90, 130.17, 130.51, 130.60, 132.31, 133.95, 134.05 and 134.13 (CH_{arom}), 135.44 (C_{arom}), 136.82 (CH_{arom}), 152.51 and 162.82 (C-O-C); IR (NaCl) ν cm⁻¹ 3076, 2966 and 2869 (CH), 2242 (CN), 1602, 1505 and 1427 (SiPh), 1266 (SiCH₃), 1136 and 1085 (SiOSi), 807 (SiC), 790 and 730 (PhSiCH₃).

Tetra(butyl capped polysiloxane methylene phenoxy) lead phthalocyanines, 7a–c. General procedure. A 10×75 mm tube was charged with 0.5 mmol of the corresponding butyl capped polysiloxane methylene phenoxy phthalonitrile (6a–c), 0.082 g (0.37 mmol) of yellow PbO (Fisher) and a stirring bar, degassed under vacuum (~1 torr) with gentle warming (5 min), sealed under vacuum and heated at 165–170 °C with stirring for 12 h. In the case of phthalonitrile 6c, the reaction was maintained for 48 h. The crude product was dissolved in 10 mL of toluene filtered and purified by passing through a silica column with toluene elution. The first fractions were contaminated with a triazine byproduct¹⁸ and discarded. Subsequent fractions were concentrated and vacuum dried (2 h at 80 °C) to yield a green liquid.

7a (*PbPc*(*BuⁿPDMS*₁₀)₄). Yield: 0.220 g (40%); *T*g = -122 °C; UV (toluene) λ nm 721, 648, 365; IR (NaCl) ν cm⁻¹ 2959 (CH), 1608 and 1492 (C–C), 1253 (SiCH₃), 1091 and 1014 (SiOSi), 800 (SiC).

7b $(PbPc(Bu^nPDMS_{I9})_4)$. Yield: 0.317 g (36%); Tg = -121 °C; UV (toluene) λ nm (ε) 719 (84947), 648 (17845), 365 (27415); IR (NaCl) ν cm⁻¹ 2966 (CH), 1621 and 1486 (C–C), 1266 (SiCH₃), 1091 and 1033 (SiOSi), 800 (SiC).

7c $(PbPc(Bu^nPMPhS_{10})_4)$. Yield: 0.372 g (45%); Tg = -46 °C; UV (toluene) λ nm (ε) 719 (2.9 × 10⁴), 646 (5.8 × 10³), 368 (8.5 × 10³); IR (NaCl) ν cm⁻¹ 3069, 2966 and 2869 (CH), 1610, 1595 and 1427 (SiPh), 1266 (SiCH₃), 1130 and 1085 (SiOSi), 794 (SiC), 730 and 720 (PhSiCH₃).

Tetra(butyl capped polysiloxane methylene phenoxy) metal free phthalocyanine, 8. Two drops of trifluoroacetic acid were added to a solution of 0.100 g of lead phthalocyanine PbPc(BuⁿPDMS₁₀)₄ in 5 mL of CH₂Cl₂ followed by 10 min stirring at 20 °C. The CH₂Cl₂ solution was extracted twice with 10 mL of 5% Na₂CO₃, washed twice with distilled water and dried (anh MgSO₄) to yield 0.081 g (85%) of a blue liquid. Tg = -115 °C; UV (toluene) λ nm 703, 666, 638, 605, 346; IR (NaCl) ν cm⁻¹ 3295 (NH), 2959 (CH), 1615 and 1479 (C–C), 1259 (SiCH₃), 1091 and 1027 (SiOSi), 807 (SiC); MS *m/z* 4500–2200.

Tetraallylphenoxy lead phthalocyanine, 9. A 10×75 mm tube was charged with 0.500 g (1.92 mmol) of allylphenoxy phthalonitrile (3), 0.329 g (1.47 mmol) of PbO (Fisher) and a stirring bar, degassed under vacuum (~1 torr) with gentle warming (5 min), sealed under vacuum and heated at 165–170 °C with stirring for 12 h. The crude product was dissolved in 10 mL of CH₂Cl₂, filtered and purified by passing through an alumina column (ICN EcoCrom, activity 1) with CH₂Cl₂ elution. The first fractions were contaminated with a triazine byproduct¹⁸ and discarded. Subsequent fractions were concentrated and vacuum dried (2 h at 80 °C) to yield a green solid. Yield; 0.61 g (42%); mp > 300 °C; UV (toluene) λ nm 721, 650, 346; IR (NaCl) ν cm⁻¹ 3076 (=CH₂), 2919 (CH), 1638 (C=C), 1608, 1485 (C–C), 1239 (C–O–C).

Tetraallylphenoxy metal free phthalocyanine, 10. A 10×75 mm tube was charged with 0.500 g (1.92 mmol) of allylphenoxy phthalonitrile (3), 0.052 g (0.48 mmol) of hydroquinone and a stirring bar, degassed under weak vacuum (~ 20 torr/5 min), sealed under vacuum and heated at 165-170 °C with stirring for 12 h. The crude product was dissolved in 10 mL of CHCl₃, filtered and purified by passing through an alumina column (ICN EcoCrom, activity 1) with CHCl₃ elution, concentrated and precipitated into methanol to yield a blue solid. This compound can also be prepared by displacement of the lead ion following the procedure described for the synthesis of the metal free phthalocyanine H₂Pc(BuⁿPDMS₁₀)₄. Yield; 0.293 g (56%); mp > 300 °C; ¹H NMR (CDCl₃) δ ppm -4.1 (s, NH), 3.6 (m, CH₂), 5.1 (m, =CH₂), 6.1 (m, CH=), 6.8-7.7 (m, H-arom); UV (toluene) λ nm 703, 667, 639, 605, 350; IR (NaCl) ν cm⁻¹ 3295 (NH), 3075 (=CH₂), 1638 (CH=CH₂), 1611 and 1467 (C-C), 1228 (C-O-C); MS m/z 1091.

Results and discussion

Synthesis and characterization

The peripherally substituted siloxane phthalocyanines PbPc- $(Bu^nPDMS_{10})_4$, PbPc $(Bu^nPDMS_{19})_4$ and PbPc $(Bu^nPMPhS_{10})_4$ were synthesized according to Scheme 1.

In the first step the base-catalyzed nucleophilic aromatic nitro displacement¹⁹ of 4-nitrophthalonitrile (1) with 2-allylphenol afforded 4-(2-allylphenoxy)phthalonitrile, (3), and the butyl capped hydrosilyl terminated poly(dimethylsiloxane) (Buⁿ-PDMS-H) oligomers (5a,b) were synthesized by an anionic ring opening polymerization of hexamethylcyclotrisiloxane (D_3) (4a) with butyl lithium (BuLi).¹⁷ To obtain PDMS oligomeric chain lengths of 9 and 18, polymerizations were carried out using 3:1 or 6:1 mole ratios of D₃ and BuLi. The butyl capped methylphenyl oligomer 5c was prepared by using a 3:1 molar ratio of trimethyltriphenylcyclotrisiloxane (4b) and BuLi. All reactions were terminated by the slow addition of chlorodimethylsilane. The number average chain length of the PDMS and PMPhS oligomers and their hydrosilyl group functionality were determined from the ¹H NMR spectroscopy integrals of the butyl, hydrosilyl and silylmethyl proton resonances. A 1:1 butyl:hydrosilyl ratio was obtained for each oligomer, and the oligomer chain lengths determined are consistent with those calculated from the Holohan reference. The butyl capped hydride terminated siloxane oligomers (5a-b) were then coupled to the 4-(2-allylphenoxy)phthalonitrile 3 by a hydrosilylation reaction using hydrogen hexachloroplatinate hydrate (H₂PtCl₆) as catalyst. The reaction's progress was followed spectroscopically (IR and ¹H



Scheme 1 Preferred PbPc(BuⁿPDMS_m)₄ synthesis route.

NMR) by disappearance of the Si-H (2128 cm⁻¹; 4.70 ppm) and allyl (1615 cm⁻¹; 3.23, 4.95 and 5.78 ppm) functional groups.

In the next step, the butyl capped siloxane lead phthalocyanines (7a-c) were prepared by reacting the corresponding phthalonitriles (6a-c) with a stoichiometric quantity of lead oxide in a sealed tube.^{20,21} In addition to phthalocyanine formation, small amounts of tris(phenylcyano)triazine were obtained in all cases as a by-product.¹⁸ The triazine derivatives were easily detected by IR (a weak -CN absorption at 2221 cm^{-1} and strong triazine ring absorptions at 1520 and 1360 cm^{-1}). The phthalocyanines were purified by column chromatography on silica gel using toluene elution. The IR spectra of the purified lead phthalocyanines PbPc(BuⁿPDMS₁₀)₄, $PbPc(Bu^{n}PDMS_{19})_{4}$ and $PbPc(Bu^{n}PMPhS_{10})_{4}$ were free of the triazine and phthalonitrile precursor (2234 cm⁻¹) bands and displayed the bands associated with the dimethylsiloxane structure (1253 cm⁻¹ Si-CH₃ symmetric deformation, 1091 and 1014 cm⁻¹ Si-O-Si stretching vibrations and 800 cm⁻¹ Si-C stretching and CH₃ rocking). The IR spectrum of the PbPc(BuⁿPMPhS₁₀)₄ displayed additional bands due to the phenyl groups attached to the siloxane chain (1610, 1595 and 1427 cm^{-1} Si-Ph stretching and 730 and 720 cm⁻¹ Ph-Si-CH₃ stretching).

NMR spectra are particularly useful in monitoring the transformations of the allylphenoxyphthalonitrile **3** to the *n*-butyl terminated siloxane functionalized phthalonitrile **6** and subsequently to the phthalocyanine analog **7**. The spectra also provide a good internal stoichiometry check between the siloxane chain and the phthalonitrile or phthalocyanine structures and an observation of phthalocyanine ring current effects on peripheral structures. As an example, spectra of the transformations of **3** to **6a** to **7a** are presented in Fig. 1. The allyl group in **3** is transformed *via* the hydrosilylation reaction to the trimethylene group in **6a** as represented by the *a*, *b*, *c* peak assignments. This transformation also attaches an *n*-butyl terminated polydimethylsiloxane chain. Integration of resonances assigned to the *n*-butyl group (*d*, *e*, *f*, *g*) are consistent with a 1:1 stoichiometry with the trimethylene group as

required by the structure of **6a**. Transformation of **6a** to the phthalocyanine **7a** results in a broadening and shifting of the aromatic resonances as well some of the aliphatic resonances. The broadening and shifting is most pronounced for the protons situated closest to the phthalocyanine ring. The broadening is due to a mixed isomer character of the phthalocyanine compound and to longer relaxation times associated with the larger rigid structure. Phthalonitriles substituted at the 4-position generate four possible phthalocyanine isomers, and these have recently been separated with respective NMR assignments made.²² The downfield shifting is attributable to the phthalocyanine ring current effect with the stronger effects being observed on the aromatic proton resonances (*a'* and *b'*) although shifting is also observed for the trimethylene resonances. Similar effects were also observed for ethyleneoxide oligomer substituted phthalocyanine compounds.²³

The lead ion complexed in the phthalocyanine cavity is not stable toward conditions for mass spectral analysis. In order to obtain mass spectral characterization of the phthalocyanine with this peripheral structure, the metal free phthalocyanine $H_2Pc(Bu^nPDMS_{10})_4$ was also prepared by treatment of the corresponding lead Pc, PbPc(BuⁿPDMS_{10})_4, with trifluoro-acetic acid. The mass spectrum of this compound is consistent with the assigned structure⁷ and consists of peaks separated by 74 amu due to $-Si(CH_3)_2$)O- degradation which is characteristic of the mass spectra of PMDS oligomers.²⁴

As further confirmation of product, an alternative route wherein phthalocyanine formation occurs prior to attachment of the peripheral silicone pendant groups was followed (Scheme 2). In this scheme, the tetrakis(allylphenoxy) lead phthalocyanine **9** is prepared by cyclotetramerization of 4-(2allylphenoxyphthalonitrile) **3** in the presence of lead oxide^{20,21} in a sealed tube. In the second step the hydrosilylation reaction was conducted using an excess of oligomer **5a** and platinumdivinyl tetramethylsiloxane complex as catalyst to yield the Buⁿ-PDMS lead phthalocyanine PbPc(BuⁿPDMS₁₀)₄. This route can also be used to prepare the corresponding Buⁿ-PDMS metal free phthalocyanine by hydrosilylation reaction over the tetrakis(allylphenoxy) metal free phthalocyanine (**10**).



Fig. 1 NMR spectra of compounds 3, 6a and 7a. The resonance assignments shown are discussed in the text.



Scheme 2 Alternative $PbPc(Bu^nPDMS_m)_4$ synthesis route.

This phthalocyanine was prepared by reacting the corresponding phthalonitrile **3** with a stoichiometric quantity of hydroquinone in a sealed tube.¹⁸ This second route has the disadvantage of a more arduous purification because of the required excess of oligomer **5a** to ensure the conversion of all allyl groups. In addition, a heterogeneous non-acidic catalyst is necessary to avoid the displacement of the lead ion.

The success of the methods developed lie in the use of butyl capped hydride terminated oligomers (**5a**–c) instead of commercial α, ω -dihydride terminated PDMS. We have observed when using commercial dihydride terminated oligomers,²⁵ polymeric species can be formed due to the coupling tendency of the Si–H group which makes the synthesis, purification and handling more difficult.

Fig. 2 shows the UV-vis spectra of dilute toluene solutions of the new PbPc's PbPc(Bu"PDMS₁₀)₄, PbPc(Bu"PDMS₁₉)₄ and PbPc(Bu"PMPhS₁₀)₄. All three compounds display a Q-band characteristic of lead phthalocyanine in both shape and wavelength maximum (719 nm). Molar absorption coefficients (ε) obtained for the polydimethylsiloxane lead phthalocyanines PbPc(Bu"PDMS₁₀)₄ and PbPc(Bu"PDMS₁₉)₄ are 0.79 and 0.80 × 10⁵ 1 mol⁻¹ cm⁻¹ respectively. The polymethylphenylsiloxane lead phthalocyanine PbPc(Bu"PMPhS₁₀)₄ shows a lower molar absorption coefficient of 0.3 × 10⁻⁵ 1 mol⁻¹ cm⁻¹. All values are somewhat smaller than those reported for phthalocyanines containing other peripheral oligomer pendant



Fig. 2 Electronic spectra of $PbPc(Bu^nPDMS_{10})_4$, $PbPc(Bu^nPDMS_{19})_4$ and $PbPc(Bu^nPMPhS_{10})_4$ in dilute toluene solutions.

groups such as oxyethylene chains ($\varepsilon = 1 \times 10^5 \, \mathrm{I \, mol^{-1} \, cm^{-1}}$),¹² oxyethylenealkoxy chains ($\varepsilon = 2 \times 10^5 \, \mathrm{I \, mol^{-1} \, cm^{-1}}$),²⁶ or octadecyl chains ($\varepsilon = 1.64 \times 10^5 \, \mathrm{I \, mol^{-1} \, cm^{-1}}$).²⁷ These results indicate that the siloxane chains, particularly polymethylphenyl siloxane chains, have an effect on the optical absorption intensity of the phthalocyanines.

All of the silicone lead phthalocyanines, PbPc-(Bu"PDMS₁₀)₄, PbPc(Bu"PDMS₁₉)₄ and PbPc(Bu"PMPhS₁₀)₄ are isotropic viscous green liquids at room temperature. No birefringence is observed under crossed polarizers. The respective glass transition temperatures as determined by differential scanning calorimetry (DSC) measurements are -122 °C, -121 °C and -46 °C (Fig. 3). Similar glass transitions are measured for the phthalonitrile precursors (6ac) indicating that the siloxane chains determine the liquid character of these materials. PDMS materials whether they be oligomeric, high molecular weight, cyclic or networked have a narrow Tg range (-120 to -125 °C) reflecting the high dynamic flexibility of the dimethylsilicone chain.²⁸ Substitution of a phenyl group for a methyl group in the siloxane polymer stiffens the siloxane chain and elevates the Tg and viscosity. The polymethylphenylsiloxane substituted phthalocyanine PbPc(BuⁿPMPhS₁₀)₄ is a more viscous material with higher Tg value (-46 °C) than PbPc(BuⁿPDMS₁₀)₄ and $PbPc(Bu^{n}PDMS_{19})_{4}$. This trend in Tg values correlates well with the data reported in the literature for varying degrees of phenyl for methyl substitution in the PDMS chain.²⁹

Refractive index and thermorefractive properties

The refractive index of each of the lead substituted siloxy phthalocyanines is measured with a prism coupling instrument. The temperature dependence of the refractive index of a thin film of PbPc(BuⁿPDMS₁₀)₄, is deduced from ellipsometric measurements and is shown in Fig. 4.³⁰ The refractive index derived from ellipsometry at 24 °C is within experimental error of that measured on the prism coupling instrument at 532 nm, 1064 nm, and 1550 nm. The measured refractive index at 1550 nm decreases from 1.492 to 1.465 over a temperature range of 24 to 95 °C. This corresponds to a *dn/dT* = $-4 \pm 1 \times 10^{-4} \circ C^{-1}$. The measured *dn/dT* is within experimental error of this value between 1100 nm and 1550 nm. In the regions of strong absorption, the variation of index with temperature is not simple partially due to the temperature dependence of the monomer–dimer equilibrium (see below).

The observed dn/dT of PbPc(BuⁿPDMS₁₀)₄ is close to the dn/dT reported (-4 × 10⁻⁴ °C⁻¹) for linear dimethylsiloxane



Fig. 3 Differential scanning calorimetry thermograms of PbPc-(BuⁿPDMS₁₀)₄, PbPc(BuⁿPDMS₁₉)₄ and PbPc(BuⁿPMPhS₁₀)₄.



Fig. 4 Temperature dependence of the refractive index of PbPc(Buⁿ-PDMS₁₀)₄ as deduced from spectroscopic ellipsometry measurements.

oligomers alone.⁸ The temperature dependence of the refractive index of silicone substituted phthalocyanines is apparently dominated by the PDMS chains. Polydimethylsiloxane has an exceptionally large dn/dT,³¹ relative to other polymers. The observed dn/dT for the siloxy phthalocyanine demonstrates that we were successful at introducing the large siloxane dn/dT with a phthalocyanine chromophore.

The room temperature refractive indices for two different siloxy phthalocyanine compounds are shown in Table 1. PbPc(BuⁿPMPhS₁₀)₄, with methylphenyl substitution shows a higher refractive index than the polydimethylsiloxane lead phthalocyanine, PbPc(BuⁿPDMS₁₀)₄, at each of the measured wavelengths. This variation correlates with an expected effect of the phenyl group substituted in place of one of the methyl groups in the PDMS oligomer chain. Depending on the wavelength this refractive index variation ranges from 0.020 to 0.027. By comparison the refractive index variations for the

Table 1 Wavelength dependence of the refractive indices

Wavelength/nm	PbPc(Bu"PDMS ₁₀) ₄ refractive index	PbPc(Bu ⁿ PMPhS ₁₀) ₄ refractive index
1550	1.496	1.523
1319	1.500	1.527
1064	1.511	1.531

respective hydride and phthalonitrile terminated siloxaneoligomer analog precursors are 0.125 and 0.092 (see n_D 589 nm measurements in the Experimental section). While this comparison is not quantitative due to the difference of wavelength in the measured refractive indices, a qualitative effect of phthalonitrile termination and particularly phthalocyanine termination on diminishing this refractive index difference between the PDMS and PMPhS system is observed and is indicative of the large contribution of the phthalocyanine ring polarizability to the refractive index of this material. However, the dn/dT is dominated by the siloxane oligomer as described above.

Aggregation studies

Aggregation is the association of the phthalocyanine molecules to form dimers, trimers and higher oligomers. The formation of coaxial stacks of the rings is easy to visualize. The rings can also be offset as far as side-by-side. For nonlinear optical applications such as optical limiting, aggregation is of particular importance because the aggregates can have different optical properties from the monomer.³² Various techniques have been used to study aggregation in solution including UV-Vis^{33–35} and NMR³⁶ spectroscopy. Here, the concentration dependence of the UV-Vis spectra is used to examine the aggregation behavior of the polydimethylsiloxane lead phthalocyanines PbPc(BuⁿPDMS₁₀)₄ and PbPc(BuⁿPDMS₁₉)₄ as well as the metal free derivative H₂Pc(BuⁿPDMS₁₀)₄.

Fig. 5 shows the concentration dependence of the observed molecular absorption coefficients for PbPc(BuⁿPDMS₁₀)₄ in toluene solution. At low concentrations, the spectrum is dominated by the strong π - π^* absorption of the monomer near 719 nm, usually called the Q-band. There is also a weaker vibronic satellite band at a shorter wavelength. As the concentration is increased, the apparent molar absorption coefficients of the monomer Q-band absorption decrease with the appearance of a species with a broader, overlapping absorbance to the red. The band to the red of the monomer Q-band can be assigned to the dimer. The appearance of an isosbestic point at 743 nm is consistent with a two-component equilibrium in the concentration range depicted in Fig. 5.



Fig. 5 Variation of the molar absorption coefficient of PbPc(Bu"PDMS₁₀)₄ in toluene as a function of concentration. The concentrations range from 6.2×10^{-7} M (top trace) to 4.7×10^{-2} M (lower trace). The arrow shows the location of the isosbestic point.

A simple monomer–dimer equilibrium model may apply over an appropriate concentration range with the attending basic equations for conservation of mass (eqn. 1), mass-action (eqn. 2) and additivity of optical absorbances (eqn. 3) used for the determination of the dimerization constant:³⁷

$$Pc_{1} + Pc_{1} \stackrel{K_{d}}{\nleftrightarrow} Pc_{2}$$

$$C_{0} = [Pc_{1}] + 2[Pc_{2}] x = \frac{[Pc_{1}]}{C_{0}} 1 - x = \frac{2[Pc_{2}]}{C_{0}}$$
(1)

$$K_d = \frac{[Pc_2]}{[Pc_1]^2} = \frac{1-x}{2C_0 x^2}$$
(2)

$$\varepsilon = \left(\frac{[Pc_1]}{C_0}\right)\varepsilon_1 + \left(\frac{2[Pc_2]}{C_0}\right)\varepsilon_2 = (\varepsilon_1 - \varepsilon_2)x + \varepsilon_2 \tag{3}$$

where K_d is the dimerization constant, C_0 is the analytical concentration of phthalocyanine, $[Pc_1]$ and $[Pc_2]$ are the respective equilibrium concentrations of phthalocyanine monomer and dimer, x is the mole fraction of phthalocyanine monomer, and ε is the observed analytical molar absorption coefficient per phthalocyanine structural unit, with ε_1 and ε_2 being the respective monomer and dimer molar absorption coefficients per phthalocyanine structural unit. In this work K_{d} is utilized as a measure of aggregation tendency. The data handling to determine K_d involves iterative plots of ε vs. x according to eqn. 3 wherein calculated values of x are obtained from the experimental values of C_0 and trial values of K_d according to eqn. 2. Of the various trial K_d values, the one that provides the best conformity with a straight line (maximum correlation coefficient determined by a plot of K_d vs correlation coefficient) is the one that best fits the data to the monomerdimer equilibrium model. To determine that the concentration range is appropriate for this model, the data points corresponding to the most concentrated solutions are successively removed from the data set and the iterative determination of K_d redone until the K_d value becomes independent of concentration.

Fig. 6 depicts the concentration dependence of the Q-band molar absorption coefficient maxima for the PDMS lead phthalocyanines PbPc(Bu"PDMS10)4 and PbPc(Bu"PDMS19)4. A drop in the molar absorption coefficient indicates the onset of dimerization. The higher the concentration at which this occurs, the lower the aggregation tendency. The corresponding dimerization constants of the silicone phthalocyanine compounds are 2 M^{-1} for PbPc(BuⁿPDMS₁₀)₄ and 5 M^{-1} for PbPc(BuⁿPDMS₁₉)₄. For typical phthalocyanines compounds $K_{\rm d}$ ranges from 10^3 to 10^6 M⁻¹, depending on the peripheral group substituent, complexed metal ion, solvent and temperature.³⁷ The observed K_d values indicate a very small tendency for aggregate formation for these compounds. More specifically, the observed K_d values are significantly smaller than that observed for lead tetracumylphenoxy phthalocyanine $(PbPc(CP)_4)$ which had an aggregation constant of 400 M⁻¹ Both PbPc(BuⁿPDMS₁₀)₄ and PbPc(BuⁿPDMS₁₉)₄ remain essentially monomeric in toluene up to concentrations of about 5 mM.

Molecular aggregation in the metal free derivative $H_2Pc(Bu''PDMS_{10})_4$ was also studied. Fig. 6b shows the concentration dependence of the molar absorption coefficient of $H_2Pc(Bu''PDMS_{10})_4$ at the peak of one component of the Q-band at 703 nm. A similar plot for the tetracumylphenoxy metal free phthalocyanine ($H_2Pc(CP)_4$), an example of a moderately aggregated phthalocyanine compound¹⁵ is also shown for comparison. The effective molar absorption coefficient at the peak of the Q-band for $H_2Pc(Bu''PDMS_{10})_4$ diminishes at higher concentrations than does the effective molar absorption coefficient for the comparable $H_2Pc(CP)_4$ solutions. $H_2Pc(Bu''PDMS_{10})_4$ has a much weaker tendency to form aggregates than $H_2Pc(CP)_4$. Quantitatively, the dimerization



Fig. 6 Molar absorption coefficients at the Q-band maxima as a function of concentration for $PbPc(Bu^nPDMS_{10})_4$, $PbPc(Bu^nPDMS_{19})_4$, $H_2Pc(Bu^nPDMS_{10})_4$ and $H_2Pc(CP)_4$.

constant for H₂Pc(Bu^{*n*}PDMS₁₀)₄ was 31 M⁻¹, about a factor of 225 smaller than for H₂Pc(CP)₄ ($K_d = 7000 \pm 50 \text{ M}^{-1}$). The aggregation constant of the metal free material is larger than for the lead phthalocyanine. This is consistent with other phthalocyanines where the introduction of a lead atom into the Pc cavity yields smaller aggregation constants.²¹

Fig. 7 shows a comparison of the molar absorption coefficient of a 0.033 M solution with that of the pure PbPc- $(Bu^{n}PDMS_{10})_{4}$ (trace A) with the spectra of a 4 µm films of pure PbPc $(Bu^{n}PDMS_{10})_{4}$ (trace B) and of PbPc $(Bu^{n}PDMS_{19})_{4}$



Fig. 7 Comparative electronic spectra for A) 0.033 M PbPc(Bu^{*n*}PDMS₁₀)₄ in toluene to B) the pure material. Also shown is C) the molar absorption coefficient spectrum of pure PbPc(Bu^{*n*}PDMS₁₉)₄. The inset is C) on an expanded scale.

(trace C and the inset). The molar absorption coefficients of the pure materials were found by estimating the density of the pure materials. The spectral changes are distinctly different from those observed upon aggregation in solution displayed in Fig. 5. Comparing traces A and B, the Q-band near 715 nm for the pure material is broader. Also, there is a loss in integrated intensity and some evidence for an absorption near 680 nm, to the blue of the main Q-band. This could be due to intermolecular interactions in the pure state different from aggregation observed in solution.

The most notable difference in the two thin film spectra in Fig. 7 is that the Q-band of pure PbPc(BuⁿPDMS₁₉)₄ is considerably less intense than that of pure PbPc(BuⁿPDMS₁₀)₄. We saw in Fig. 2 that in dilute solution, the molar absorption coefficients of PbPc(BuⁿPDMS₁₀)₄ and PbPc(BuⁿPDMS₁₉)₄ are similar, so the difference is characteristic of the pure material. The peak absorption is shifted very little, but the integrated absorption coefficient is a little smaller in PbPc(BuⁿPDMS₁₀)₄. However, the Q-band absorption of pure PbPc(BuⁿPDMS₁₀)₄ is a factor of 4.5 weaker than that of PbPc(BuⁿPDMS₁₀)₄ and more than an order of magnitude less intense than the same material in dilute solution.

The origin of the decrease in the molar absorption coefficients of the Q-bands in the pure $PbPc(Bu^nPDMS_{19})_4$ material is not obvious. The small equilibrium constants for dimerization in toluene demonstrate that the polydimethyl-siloxane substitution is very effective at reducing the tendency of the phthalocyanines to aggregate. It seems unlikely that increasing the length of the siloxy chains in going from compound $PbPc(Bu^nPDMS_{10})_4$ to $PbPc(Bu^nPDMS_{19})_4$ would increase the tendency to aggregate. If the decrease in molar absorption coefficient is due to aggregation, the structure of the aggregate in the pure material may be different from that in toluene solution.

Different geometries for the aggregates are suggested by the observation that in toluene solution, the dimer absorption band is to the red of the monomeric Q-band, whereas in the pure material, the aggregate absorption is mainly to the blue. The spectral shift upon aggregation is related to the exciton splitting in the dimer, which, in turn depends on the aggregate structure. The shift is proportional to³⁸

$$M^2 \frac{\left(1 - 3\cos^2\theta\right)}{R^3} \tag{4}$$

where M is the transition dipole of the phthalocyanine, θ is the angle between the transition dipole of the two adjacent molecules in the dimer with respect to the axis through the centers of the molecule and R is the distance between the centers of the molecule. The observed shift between the monomer Q-band and dimer in toluene compared to that in the pure material could imply that in toluene, the phthalocyanine rings aggregate with the rings offset, *i.e.* the angle between the centers of the rings is greater than 57 degrees, whereas in the pure material, this angle is smaller and the rings are closer to vertically stacked. Such different spectral shifts have been reported for two similar phthalocyanines that pack differently: *i.e.* a blue shift for vertically stacked rings and a red shift for a side-by-side configuration.³⁹ While the spectra are consistent with different dimer structures, it is also possible that the differences in the observed spectra arise for other reasons, such as multiple dimeric structures.

Nonlinear optical properties

As noted above, the principal motivation for the synthesis of the polydimethylsiloxane lead phthalocyanines $PbPc(Bu^nPDMS_{10})_4$ and $PbPc(Bu^nPDMS_{19})_4$, was to examine their potential for nonlinear optical applications including optical limiting. The Pb phthalocyanine chromophore is a very efficient nonlinear absorber and the isotropic liquid character of the pure material enables the preparation of nonscattering thin films of high optical quality. Here we evaluate the potential of the pure lead polydimethylsiloxane phthalocyanine films for such applications. More detailed studies of the nonlinear optical properties are in progress.

In order to verify that these materials were nonlinear absorbers (reverse saturable absorbers) picosecond timeresolved transient absorption studies were performed. In these experiments, the sample is excited at 606 nm and the absorption spectrum is recorded with a continuum probe before and at several times after the sample is excited. Representative transient absorption spectra of PbPc(BuⁿPDMS₁₀) are shown Fig. 8. At negative time, when the continuum probe pulse arrives before the excitation pulse, the plot of change in optical density (delta OD) with wavelength is flat indicating that there is no change in the observed absorption spectrum. The trace at 20 ps after excitation shows that there is an immediate appearance of a broad region of induced absorption. This is a direct measurement of the spectral region over which the excited state absorption coefficients exceed those of the ground state. The breadth of this region is comparable to that observed in other PbPcs^{1,2} and several InPcs.³ The other two traces in the figure show that this induced absorption remains strong at 493 ps and at 1160 ps after excitation. The 500 nm to 600 nm spectral region shows little change for at least 1.2 ns after excitation. The apparent excited state lifetime for the carrier of the absorption in this region is longer than 2.5 ns. Estimates of the excited state cross sections from this data indicate that they are comparable to those observed for other PbPcs and InPcs.¹⁻³ Between 440 and 500 nm the induced absorption increases from 3 ps to 0.5 ns and then decays somewhat between 0.5 and 1.2 ns. The origin of this spectral evolution is not fully understood but may be due either to participation of multiple excited states or may have to do with conformational changes of the bulky peripheral polydimethylsiloxane chains.

Picosecond time resolved degenerate four-wave mixing (DFWM) experiments verify that the excited state lifetime is longer that 5 ns. Fig. 9 shows time resolved DFWM data obtained from a grating excited by orthogonally polarized 606 nm pump pulses. An immediate rise of the signal is apparent. More importantly the signal does not appreciably decay over the 1.2 ns duration of the experiment. Neither excited state nor chromophore reorientational mechanisms decay on this time scale. This confirms that the lifetime for the induced absorption in this region is much longer than 5 ns. In contrast, the metal free siloxy Pc, $H_2Pc(Bu^nPDMS_{10})_4$, has a lifetime measured to be 100 ps. The short excited state lifetime of



Fig. 8 Transient absorption spectra of $PbPc(Bu^nPDMS_{10})_{4}$. The legend shows the time after excitation.



Fig. 9 Degenerate four-wave mixing signal from $PbPc(Bu^nPDMS_{10})_4$. The grating is written with cross polarized laser beams at 606 nm.

 $H_2Pc(Bu^nPDMS_{10})_4$ means it is practical as an optical limiter only for pulses shorter than 100 ps.

Nanosecond nonlinear absorption and optical limiting experiments were performed on thin films of the lead phthalocyanines PbPc(Bu"PDMS₁₀)₄ and PbPc(Bu"PDMS₁₉)₄ in cells with path lengths of 4.22 μ m and 3.82 μ m respectively. The liquid character made it possible to fill these short path length cells by capillary action.

The visible spectrum of the phthalocyanine films is shown in Fig. 7. The weak, relatively broad Q-band absorption in the PbPc(BuⁿPDMS₁₉)₄ film is notable. This is partly because the molecular volume per chromophore is larger in the PbPc-(BuⁿPDMS₁₉)₄, because of the long peripheral groups, but even when normalized for the concentration, the absorption coefficient of the Q-band in the pure thin film is more than an order of magnitude smaller. The absorption coefficient of PbPc(BuⁿPDMS₁₉)₄ was sufficiently small that it was also possible to perform nonlinear absorption experiments in a cell with a path length of 48.2 µm.

The nonlinear transmission and optical limiting curves for compound PbPc(Bu^nPDMS_{10})₄ taken at 532 nm are compared in Fig. 10. The difference between the experiments is that nonlinear transmission is measured with collection optics such that all of the light is collected while optical limiting is measured with an f/5 aperture inserted before the collection lens. Nonlinear transmission experiments measure only the



Fig. 10 Optical limiting and nonlinear transmission measurements for PbPc(BuⁿPDMS₁₀)₄ at 532 nm.



Fig. 11 Open aperture z-scans for $PbPc(Bu''PDMS_{19})_4$ at 532 nm. The legend indicates the relative fluence for each trace in the experiment.

absorptive part of the response while the optical limiting experiments have contributions from both refractive and absorptive responses. The results show that at low excitation energies both curves are superimposable; nonlinear absorption dominates the low fluence response. At excitation energies above 10 nJ the two curves deviate with the optical limiting experiment reaching lower transmittances than the nonlinear transmission. The threshold for optical limiting where $T(I)/T_0$ = 0.5 is 25 nJ which compares to 8 nJ observed for a chloroform solution of PbPc(CP)₄.¹ The high fluence behavior shows that refractive mechanisms significantly contribute to the optical limiting response consistent with the large values of dn/dT discussed above. Similar data is observed from cells containing pure PbPc(BuⁿPDMS₁₉)₄. In addition, there was evidence for higher order nonlinear absorption processes contributing to the nonlinear absorption in this material.

To examine the nonlinear refractive response in $PbPc(Bu''PDMS_{19})_4$, a series of z-scans were carried out at different excitation energies. Fig. 11 shows the open aperture results. These results are typical of a strong nonlinear absorber. Fig. 12 shows the results from derived from closed aperture z-scans where the nonlinear absorption contribution has been removed and hence shows only the refractive part of the response. At low excitation energies the data show the signature of a positive refractive component. The refractive index of the excited state is greater than that of the ground state. At higher excitation energies, the shape of the z-scan trace becomes more complex, with evidence of an increasingly strong negative refractive response building in with increasing



Fig. 12 Refractive component deduced from the closed aperture z-scans for $PbPc(Bu''PDMS_{19})_4$ at 532 nm. The legend indicates the relative fluence for each trace in the experiment.

fluence. The negative sign of this second component of the response is consistent with the expected thermorefractive response superimposed on the excited state response. It is also consistent with the large dn/dT coefficient measured in static experiments above. The different z dependence of the two components of the refractive response has been observed previously. It is consistent with a thermal nonlinearity giving rise to the negative component of the nonlinear refractive response.^{3,40} We conclude that the enhancement in the optical limiting response seen in Fig. 10 at high fluences is largely due to the thermal response of the PDMS side chains.

Conclusions

This paper has described the synthesis and characterization of three polysiloxane substituted lead phthalocyanines. These new materials are isotropic liquids at room temperature that combine desirable optical properties of the phthalocyanines with those of the siloxanes in a single material. The variation of the refractive index with temperature indicates a large negative thermorefractive coefficient similar in magnitude to that observed from neat siloxanes. Measurements of the variation of the molar absorption coefficient as a function of concentration show that there is little evidence of aggregation in toluene solutions and only a small degree of aggregation in the neat liquid. The spectra at high concentrations in toluene compared to that in pure materials indicate that the structure of the aggregate in toluene could differ from that of the pure material.

Transient absorption studies of the neat liquid lead substituted materials show a broad spectral region of induced absorption similar to that observed from other lead phthalocyanines. That broad region of induced absorption persists for at least many nanoseconds. DFWM studies verify that the excited state lifetime is long compared to nanosecond pulses used to do optical limiting. Nonlinear transmission, optical limiting and z-scan results show that these siloxy materials possess a nonlinear absorption coefficient similar to that found in other lead substituted phthalocyanines. The nonlinear response has the additional feature of a large thermal nonlinear refractive response that contributes strongly to optical limiting at high fluence.

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References

- J. S. Shirk, R. G. S. Pong, F. J. Bartoli and A. W. Snow, *Appl. Phys. Lett.*, 1993, 63, 1880–1882.
- 2 J. W. Perry, K. Mansour, I. Y. S. Lee, X. L. Wu, P. V. Bedworth, C. T. Chen, D. Ng, S. R. Marder, P. Miles, T. Wada, M. Tian and H. Sasabe, *Science*, 1996, **273**, 1533–1536.
- 3 J. S. Shirk, R. G. S. Pong, S. R. Flom, H. Heckmann and M. Hanack, J. Phys. Chem. A, 2000, 104, 1438–1449.
- 4 P. P. Sorokin and J. R. Lankard, *IBM J. Res. Develop.*, 1966, **10**, 162.
- 5 H. S. Nalwa and J. S. Shirk, in *Phthalocyanines: Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH Publishers Inc., New York, 1996, vol. 4, p. 79.

- 6 M. Hanack, T. Schneider, M. Barthel, J. S. Shirk, S. R. Flom and R. G. S. Pong, *Coord. Chem. Rev.*, 2001, 219, 235–258.
- 7 E. M. Maya, J. S. Shirk, A. W. Snow and G. L. Roberts, *Chem. Commun.*, 2001, 615–616.
- 8 J. Dugas, P. Michel, L. Martin and J. M. Cariou, *Appl. Opt.*, 1986, 25, 3807–3808.
- 9 Phthalocyanines: properties and applications, ed. C. C. Leznoff and A. B. P. Lever, VCH, New York, 1989–93, vol. 1–4.
- R. D. George and A. W. Snow, *Chem. Mater.*, 1994, 6, 1587–1588.
 R. D. George, A. W. Snow, J. S. Shirk, S. R. Flom and
- R. G. S. Pong, *Mater. Res. Soc. Symp. Proc.*, 1995, **374**, 275.
 12 A. W. Snow, J. S. Shirk and R. G. S. Pong, *J. Porphyr.*
- Phthalocyanines, 2000, 4, 518–524.
 J. C. Swarts, E. H. G. Langner, N. Krokeide-Hove and M. J. Cook, J. Mater. Chem., 2001, 11, 434–443.
- 14 M. Brewis, B. M. Hassan, H. Li, S. Makhseed, N. B. McKeown and N. Thompson, J. Porphyr. Phthalocyanines, 2000, 4, 460–464.
- 15 R. D. George, A. W. Snow, J. S. Shirk and W. R. Barger, J. Porphyr. Phthalocyanines, 1998, 2, 1–7.
- 16 M. Kimura, K. Nakada, Y. Yamaguchi, K. Hanabusa, H. Shirai and N. Kobayashi, *Chem. Commun.*, 1997, 1215–1216.
- 17 A. T. Holohan, M. H. George, J. A. Barrie and D. G. Parker, *Macromol. Chem. Phys.*, 1994, **195**, 2965–2979.
- 18 A. W. Snow, J. R. Griffith and N. P. Marullo, *Macromolecules*, 1984, 17, 1614–1624.
- 19 T. M. Keller, T. R. Price and J. R. Griffith, *Synthesis*, 1980, 613–613.
- 20 P. A. Barret, C. E. Dent and R. P. Linstead, J. Chem. Soc., 1938, 1157.
- 21 A. W. Snow and N. L. Jarvis, J. Am. Chem. Soc., 1984, 106, 4706– 4711.
- 22 M. Sommerauer, C. Rager and M. Hanack, J. Am. Chem. Soc., 1996, **118**, 10085–10093.
- 23 D. D. Dominguez, A. W. Snow, J. S. Shirk and R. G. S. Pong, J. Porphyr. Phthalocyanines, 2001, 5, 582–592.
- 24 S. K. Pollak and A. M. Morgan, ACS Polymer Preprints, 2000, 41, 631.
- 25 S. R. Flom, J. S. Shirk, R. G. S. Pong, A. W. Snow and E. M. Maya, ACS Polymeric Materials: Science and Engineering, 2000, 83, 224.
- 26 J. M. Kroon, R. B. M. Koehorst, M. vanDijk, G. M. Sanders and E. J. R. Sudholter, *J. Mater. Chem.*, 1997, 7, 615–624.
- 27 M. J. Cook, I. Chambrier, S. J. Cracknell, D. A. Mayes and D. A. Russell, *Photochem. Photobiol.*, 1995, **62**, 542–545.
- 28 S. J. Clarson, K. Didgson and J. A. Semlyn, *Polymer*, 1985, 26, 930–934.
- 29 M. K. Lee and D. J. Meier, Polymer, 1993, 34, 4882-4892.
- 30 Ellipsometry measurements performed by C. Bungay at J.A. Woolam Co. Inc., Lincoln, Nebraska, USA.
- 31 J. M. Cariou, J. Dugas, L. Martin and P. Michel, *Appl. Opt.*, 1986, 25, 334–336.
- 32 S. R. Flom, J. S. Shirk, J. R. Lindle, F. J. Bartoli, Z. H. Kafafi, R. G. S. Pong and A. W. Snow, *Mater. Res. Soc. Symp. Proc.*, 1992, 247, 271.
- 33 W. F. Law, K. M. Lui and D. K. P. Ng, J. Mater. Chem., 1997, 7, 2063–2067.
- 34 S. Tai and N. Hayashi, J. Chem. Soc., Perkin Trans. 2, 1991, 1275–1279.
- 35 M. T. M. Choi, P. P. S. Li and D. K. P. Ng, *Tetrahedron*, 2000, 56, 3881–3887.
- 36 M. J. Chen and J. W. Rathke, J. Porphyr. Phthalocyanines, 2001, 5, 528–536.
- 37 A. W. Snow, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Elsevier Science, Amsterdam, 2003, Chapter 109.
- 38 M. Kasha, H. R. Rawls and M. A. El-Bayoumi, *Pure Appl. Chem.*, 1965, **11**, 371.
- 39 A. Chakrabarti, A. Schmidt, V. Valencia, B. Fluegel, S. Mazumdar, N. Armstrong and N. Peyghambarian, *Phys. Rev. B*, 1998, **57**, R4206–R4209.
- 40 P. Brochard, V. Grolier-Mazza and R. Cabanel, J. Opt. Soc. Am. B, 1997, 14, 405.

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