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Peripherally-substituted polydimethylsiloxane phthalocyanines: a novel class of liquid materials

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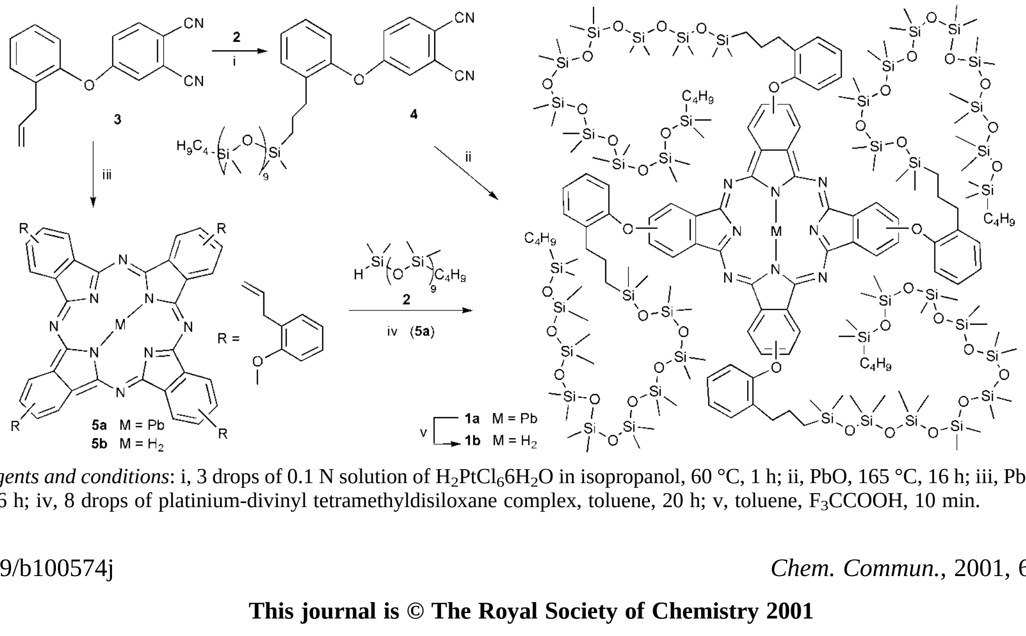
Isotropic liquid phthalocyanine compounds with peripheral polydimethylsiloxane oligomer substitution were synthesized and found to have a unique combination of thermorefractive and nonlinear optical properties along with unusual metal substitution reactivity and aggregation behavior.

Polydimethylsiloxane oligomer substitution at the periphery of a phthalocyanine ring generates a liquid material with exceptional optical properties and chemical behavior. This material is designed to have the rheological and thermorefractive properties of a silicone fluid[1] and the nonlinear optical properties characteristic of the phthalocyanine chromophore.[2] Structure **1** in Scheme 1 combines these molecular features coupled through an aromatic ether linkage. The motivation for this design is to combine two mechanisms important to an optical limiting application[2] into a single compound: a large fluence dependent, refractive index;[1] and a reverse saturable optical absorption.[2] The aromatic ether linkage further incorporates an enhanced photo-oxidative stability. Cloaking of the phthalocyanine ring in a silicone covering has important implications for the chemistries of aggregation and metal substitution. To our knowledge, no examples of peripheral silicone substituted phthalocyanines have been previously reported. In this communication we report synthesis and preliminary characterization of a new class of liquid phthalocyanine (Pcs) materials.

Two routes for the synthesis of the lead and metal-free phthalocyanine compounds are depicted in Scheme 1. Starting reagents for both routes are prepared in the first step. The butyl capped hydrosilyl terminated poly(dimethylsiloxane) (PDMS) oligomer (**2**) (DP = 9 in this example) is synthesized by an anionic ring opening polymerization of hexamethylcyclotrisiloxane.[3] The allylphenoxyphthalonitrile (**3**) is prepared by a nitroaromatic displacement reaction of 4-nitrophthalonitrile[4] with 2-allylphenol. In the preferred route, the PDMS oligomer is first coupled to the allylphenoxyphthalonitrile by a hydrosilylation reaction. Next the allylphenoxyphthalonitrile–PDMS adduct (**4**) is cyclotetramerized in the presence of lead oxide to yield the phthalocyanine **1a**. The alternate route is to first conduct the cyclotetramerization yielding the tetrakis(allylphenoxy)phthalocyanine (**5**) then to perform the hydrosilylation to yield the phthalocyanine product (**1**). This route has the disadvantage of a more arduous purification (as a consequence of a required large excess of **2** to ensure a quantitative conversion of the allyl groups) and the use of a heterogeneous non-acidic hydrosilylation catalyst (to avoid displacement of a labile metal from the phthalocyanine cavity).

Structures **1**–**5** are consistent with spectroscopic characterization.† The phthalocyanine materials have both a mixed isomer and polydisperse character. The phthalocyanine forming reaction produces a statistical mixture of four possible isomers.[5] The polydispersity is a result of the manner in which the butyl capped PDMS oligomer (**2**) is prepared.[6] These features are regarded as advantages in discouraging liquid crystal formation. In an analogous phthalocyanine system with polyethylene oxide oligomer substituents it was found that a monodisperse system is liquid crystalline[7] while that with a polydisperse system is an isotropic liquid.[8] Liquid crystallinity is detrimental for applications where optical transparency is required.

The PDMS chains determine the liquid character of these materials, which are viscous liquids at room temperatures. The glass transition temperatures, *T*g, for the Pb (**1a**), H_2 (**1b**) phthalocyanine compounds and the phthalonitrile precursor (**4**) are 3, 16, and 14 °C respectively. This narrow range of glass transition temperatures is a consequence of the dominant effect of the siloxane chains. A similar trend of a slightly increasing *T*g, when progressing from lead to metal-free phthalocyanine with epoxy substituted phthalocyanine glasses, has previously been observed.[9] This trend correlates with a greater tendency of the metal-free phthalocyanine to aggregate relative to the lead phthalocyanine.[10] At rt these phthalocyanine materials will fill short length (~4 μm) optical cells by capillary action over several hours. At elevated temperatures (~100 °C) the viscosity



Scheme 1 *Reagents and conditions*: i, 3 drops of 0.1 N solution of $H_2PtCl_66H_2O$ in isopropanol, 60 °C, 1 h; ii, PbO, 165 °C, 16 h; iii, PbO or hydroquinone, 165–180 °C, 16 h; iv, 8 drops of platinium-divinyl tetramethyldisiloxane complex, toluene, 20 h; v, toluene, F_3CCOOH, 10 min.

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is much lower, the aggregation is reduced (spectroscopic detection), and the filling of the cell is much more rapid.

The refractive index of a thin film of the lead phthalocyanine compound (**1a**) was measured by ellipsometry and also by measuring the angle of total internal reflection for a thin film on a prism of known refractive index. Over a temperature range of 24 to 95 °C the refractive index at 1550 nm decreased from 1.492 to 1.465. This corresponds to a decrease of $4 \pm 1 \times 10^{-4}$ per degree Centigrade and correlates well with the d*n*/d*T* reported (4×10^{-4} °C^{-1}) for linear dimethylsiloxane oligomers.[1] This decrease also indicates that the temperature dependence of the refractive index of silicone substituted phthalocyanines is dominated by PDMS chains. Relative to other polymers, polydimethylsiloxane has an exceptionally large d*n*/d*T*,[11] and this combination with the phthalocyanine structure demonstrates a successful coupling of this property and this chromophore.

Z-scan and optical limiting measurements were performed on the lead phthalocyanine compound (**1a**) to characterize the nonlinear optical properties. The Z-scan of a 20.2 mM sample of **1a** in a 50.5 μm sample cell at 532 nm is shown in Fig. 1. The material is a strong reverse saturable absorber at 532 nm. An estimate of the excited state cross section from this Z-scan and from a nonlinear transmission experiment on the same sample gave a value of the excited state cross section of ~ 20 times that of the ground state at 532 nm. This implies that the material is a very good reverse saturable absorber. The nonlinear absorbing properties are similar to those found in lead tetrakis(cumylphenoxy)phthalocyanine, PbPc(CP)$_4$.[12] The strong nonlinear absorption, in combination with the large d*n*/d*T* reported above, makes this a superior optical limiter material.

Finally, the silicone chains covering the phthalocyanine chromophore impart some unusual chemical behavior, particularly with regard to metal substitution reactions and aggregate formation. When the siloxane–phthalonitrile precursor (**4**) is subjected to the Linstead conditions of lithium pentoxide–pentan-1-ol for conversion to lithium phthalocyanine,[13] a product with a Q-band diagnostic of the dilithium substituted phthalocyanine (675 nm) is obtained. However, it is very difficult to displace the normally very labile lithium with protons. Normally, this occurs under very mild acidic conditions. We find that normal and progressively more severe acid exchange conditions were unsuccessful.‡ Treatment with concentrated HCl and heating resulted in conversion being first observed at 90 °C which became quantitative after 2 h at this temperature. However, once the lithium ion is displaced by the proton, subsequent metal ion substitution reactions proceed under normal conditions.§

The other aspect of unique chemical behavior is in the aggregation tendency. Phthalocyanine compounds aggregate as a concentration dependent association of phthalocyanine rings. The dimerization constant is a useful measure of this aggregation tendency. Typical dimerization constants for phthalocyanine compounds range from 10^4 to 10^6 M^{-1}.[14] Preliminary analysis of concentration dependence of the Q-band absorption using a monomer–dimer equilibrium model indicates that the dimerization constant for **1b** is 150 ± 100 M^{-1}. This is significantly less than the range for phthalocyanine dimerization constants mentioned above. We attribute this result to the nature of the siloxane chain and the ortho substitution of the phenylene ether linkage to the phthalocyanine ring.

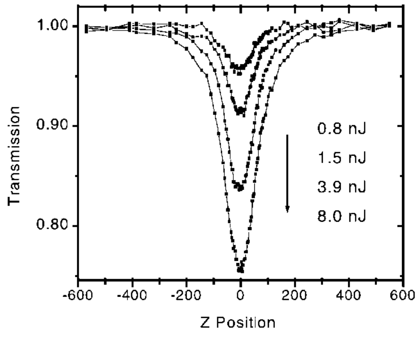

Fig. 1 A Z-scan of a 20.2 mM sample of **1a** at increasing input energy.

In summary, the incorporation of PDMS oligomers as phthalocyanine peripheral substituents combines the desirable rheological and refractive properties of a silicone fluid with the nonlinear optical properties associated with the phthalocyanine. The long silicone substituents further impart unique chemical behavior with respect to the phthalocyanine synthesis and aggregation.

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Notes and references

† *Selected data* for **1a**; λ(toluene)/nm 721, 648, 365; ν(NaCl)/cm^{-1} 2959 (CH), 1608 and 1492 (C–C), 1253 (SiCH$_3$), 1091 and 1014 (SiOSi), 800 (SiC). For **1b** λ(toluene)/nm 703, 666, 638, 605, 346; ν(NaCl)/cm^{-1} 3295 (NH), 2959 (CH), 1615 and 1479 (C–C), 1259 (SiCH$_3$), 1091 and 1027 (SiOSi), 807 (SiC); *m*/*z* 4500–2200 consists of peaks separated by 74 amu due to –Si(CH$_3$)$_2$O– degradation which is common to mass spectra of PDMS oligomers.[6] For **2**: δ_H(CDCl$_3$, 300 MHz)/ppm 0.04–0.07 (54H, br s, SiCH$_3$), 0.19 (6H, m, SiCH$_3$), 0.53 (2H, m, SiCH$_2$), 0.89 (3H, t, CH$_3$), 1.32 (4H, m, CH$_2$), 4.70 (1H, sept, SiH); ν(NaCl)/cm^{-1} 2972 (CH), 2132 (SiH), 1272 (SiCH$_3$), 1098 and 1027 (SiOSi), 800 (SiC). For **3**: δ_H(CDCl$_3$, 300 MHz)/ppm 3.23 (2H, d, CH$_2$), 4.95 (2H, dd, =CH$_2$), 5.78 (1H, m, =CH), 6.95 (1H, d, H$_{arom}$), 7.12–7.33 (5H, m, H$_{arom}$), 7.68 (1H, d, H$_{arom}$); δ_C(CDCl$_3$, 75 MHz) 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; ν(NaCl)/cm^{-1} 3082 (=CH$_2$), 2229 (CN), 1615 (C=C), 1595 and 1486 (C–C), 1246; For **4**: δ_H(CDCl$_3$, 300 MHz)/ppm 0.012–0.064 (60H, m, SiCH$_3$), 0.51 (4H, m, SiCH$_2$), 0.86 (3H, t, CH$_3$), 1.29 (4H, m, CH$_2$), 1.58 (2H, m, CH$_2$), 2.49 (2H, t, CH$_2$), 6.95 (1H, d, H$_{arom}$), 7.14–7.31 (5H, m, H$_{arom}$), 7.68 (1H, d, H$_{arom}$); ν(NaCl)/cm^{-1} 2966 (CH), 2229 (CN), 1602 and 1492 (C–C), 1254 (SiCH$_3$), 1098 and 1033 (SiOSi), 806 (SiC); For **5a** λ(toluene)/nm 721, 650, 346; ν(NaCl)/cm^{-1} 3076 (=CH$_2$), 2919 (CH), 1638 (C=C), 1608, 1485 (C–C), 1239. For **5b** λ(toluene)/nm 703, 667, 639, 605, 350; ν(NaCl)/cm^{-1} 3295 (NH), 3075 (=CH$_2$), 1638 (CH=CH$_2$), 1611 and 1467(C–C), 1228; δ_H(CDCl$_3$, 300 MHz)/ppm −4.1 (s, NH), 3.6 (m, CH$_2$), 5.1 (m, =CH$_2$), 6.1 (m, CH=), 6.8–7.7 (m, H$_{arom}$); *m*/*z* 1091.

‡ Unsuccessful lithium displacement conditions: aliquot addition of trifluoroacetic acid (10 min); second aliquot addition of trifluoroacetic acid (30 min); aliquot addition of conc. HCl (10 min).

§ Copper and lead ions were substituted into the metal-free phthalocyanine using the acetate salts and refluxing for 2 h in pentan-1-ol–THF.

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