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Polyhedral oligomeric silsesquioxane bound fulleropyrrolidines

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The first reported examples of polyhedral oligomeric silsesquioxane (POSS) cages containing a fulleropyrrolidine species are reported herein. Monosubstituted POSS-dioxalane species were synthesized through the hydrosilylation of a silyl-dioxalane with mono-vinyl substituted POSS. Subsequent deprotection yielded the desired aldehyde functionality. An alternative synthetic pathway, involving the nucleophilic substitution of mono-benzyl chloride POSS with 4-hydroxybenzaldehyde yielded the desired aldehyde functionality. Each mono-aldehyde POSS was then reacted with *N*-methylglycine and C_{60} to yield the desired POSS fulleropyrrolidines. The prepared compounds were characterized by multinuclear NMR, electrospray mass spectrometry, elemental analysis, UV–vis, fluorescence and optical power limiting measurements. Copyright © 2008 John Wiley & Sons, Ltd.

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Keywords: silsesquioxane; fullerene; optical limiting; hydrosilylation

Introduction

The use of lasers is prevalent in a variety of scientific, industrial, medical and military fields. The emission wavelength of lasers can be tuned from the visible to the near-infrared (NIR) region and the radiation can be emitted either as continuous wave or in a pulsed mode, with pulse duration ranging from microseconds to femtoseconds. Protection of operating personnel and technical components against pulsed tunable lasers is a high priority. Eye protection is critical, as the retina is vulnerable in the visible and NIR spectral range.[1]

An ideal optical limiter exhibits linear transmission below a certain input light fluence threshold, but above the threshold the output light fluence is fixed at a constant level. Promising optical limiting materials, also known as reverse saturable absorbers (RSA), are those that exhibit strong nonlinear absorptions. The primary mechanism for nonlinear absorptive optical limiting is a large ratio of excited-state to ground-state absorption cross sections. Thus, potent RSAs are usually molecules with weak ground-state absorptions, such as metallophthalocyanines, mixed metal complexes and clusters, and fullerenes.[2]

It is well established that C_{60} solutions exhibit optical limiting behaviour derived from a RSA mechanism.[1,3] C_{60} exhibits a broad absorption spectrum, characterized by strong absorptions in the ultraviolet region and weaker absorptions that extend over the majority of the visible region.[4] These weak absorptions allow for optical pumping using a broad range of laser wavelengths. The excited state dynamics and the large quantum yield for intersystem crossing allow for population build-up in either the singlet or triplet excited states, depending on the duration of the laser pulse. C_{60} also possesses excited state absorption cross sections that are larger than those of the ground state over the complete visible section.[3] Different fullerene derivatives, such as methanofullerenes and fulleropyrrolidines, exhibit diverse electronic properties. The ground state absorptions of such derivatives vary in the UV–vis region, as methanofullerenes display a major absorption band at 500 nm, whilst fulleropyrrolidines display reduced absorption in this spectral region. However, the triplet-triplet absorption is stronger for methanofullerenes than fulleropyrrolidines, thus making them equally useful for optical limiting purposes.[5]

Fullerene solutions are efficient optical limiters; however the use of solid devices is preferred for practical applications. Crystalline films of C_{60} have previously been studied, but were found to be inefficient against pulses longer than tens of picoseconds. This is ascribed to the fast de-excitation of the excited state due to interactions of neighbouring C_{60} molecules in the solid phase. Studies have shown that C_{60} retains optical limiting properties after inclusion in solid matrices, such as sol–gel glasses,[6–11] PMMA[12] and glass–polymer composites;[13] however the optical responses of C_{60} in PMMA are much weaker than those displayed in solution. This difference in performance has been attributed to the fact that different optical limiting mechanisms occur in the solution and solid phases.[2] A modified optical limiting mechanism has been proposed, detailing the contribution of bimolecular processes,

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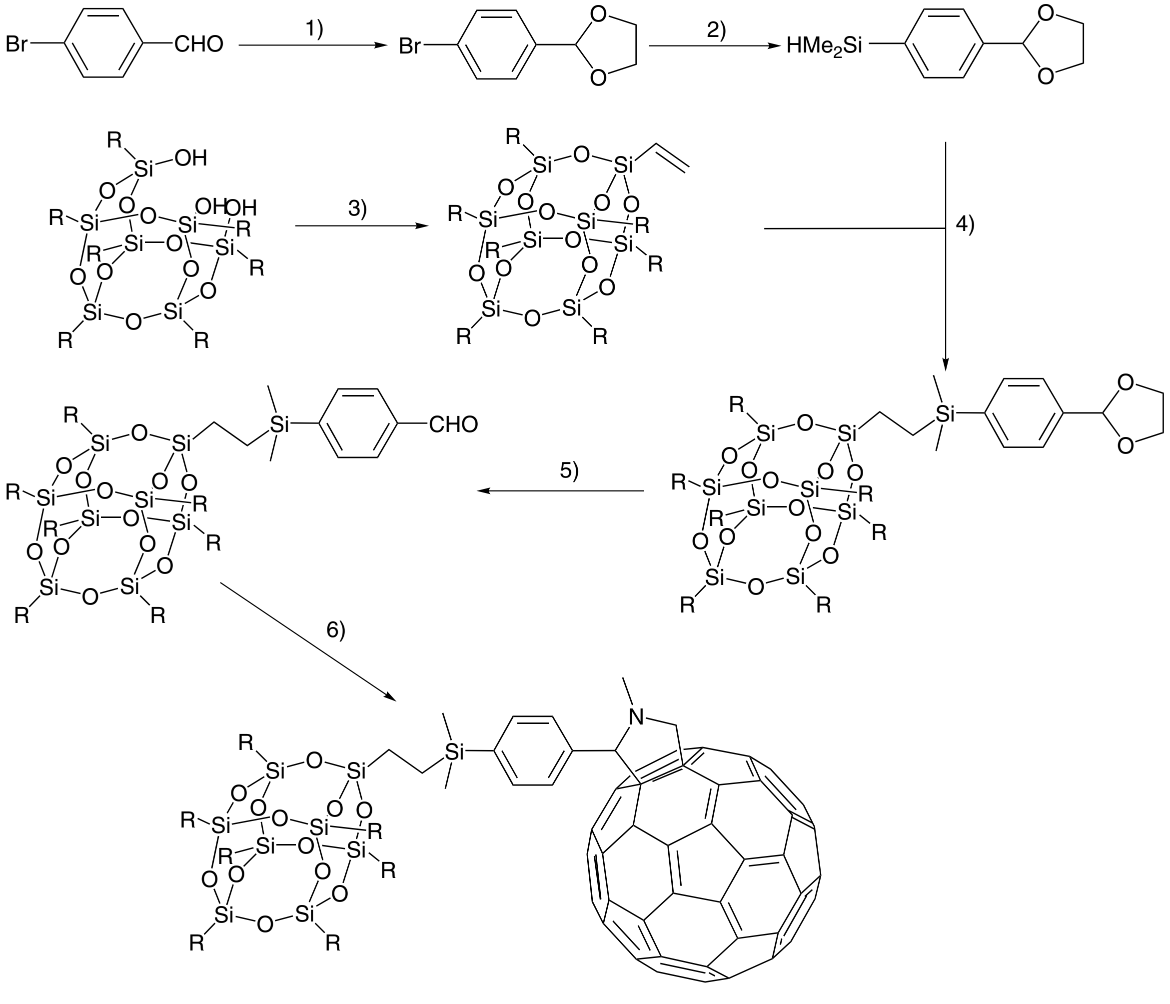
such as self-quenching of the fullerene excited triplet state by ground state fullerene molecules and triplet–triplet annihilation.[2]

Fullerene derivatives covalently linked to polyhedral oligomeric silsesquioxanes can, in theory, be homogenously dispersed in a polymeric matrix, preventing aggregation of fullerene in the final polymer. Whilst this separation will reduce the optical activity of the polymer, the incorporation of POSS cages into the polymeric systems should lead to significant improvements in physical and mechanical properties, such as temperature and oxidative and reduction resistance, surface hardening and reduced flammability.[14–17] It is not trivial to effectively covalently couple two such dissimilar nanoparticles, the fullerene and the silsesquioxane (POSS), as such compounds have not been previously reported in the literature. A widely accessible pathway to fullerene substitution is through generation of azomethine ylides in situ, via the reaction of an aldehyde and an amino glycine, followed by[6,6] cycloaddition to C_{60}, to yield the desired fulleropyrrolidine,[18] the synthesis and characterization of which are the subject of this paper.

Results and Discussion

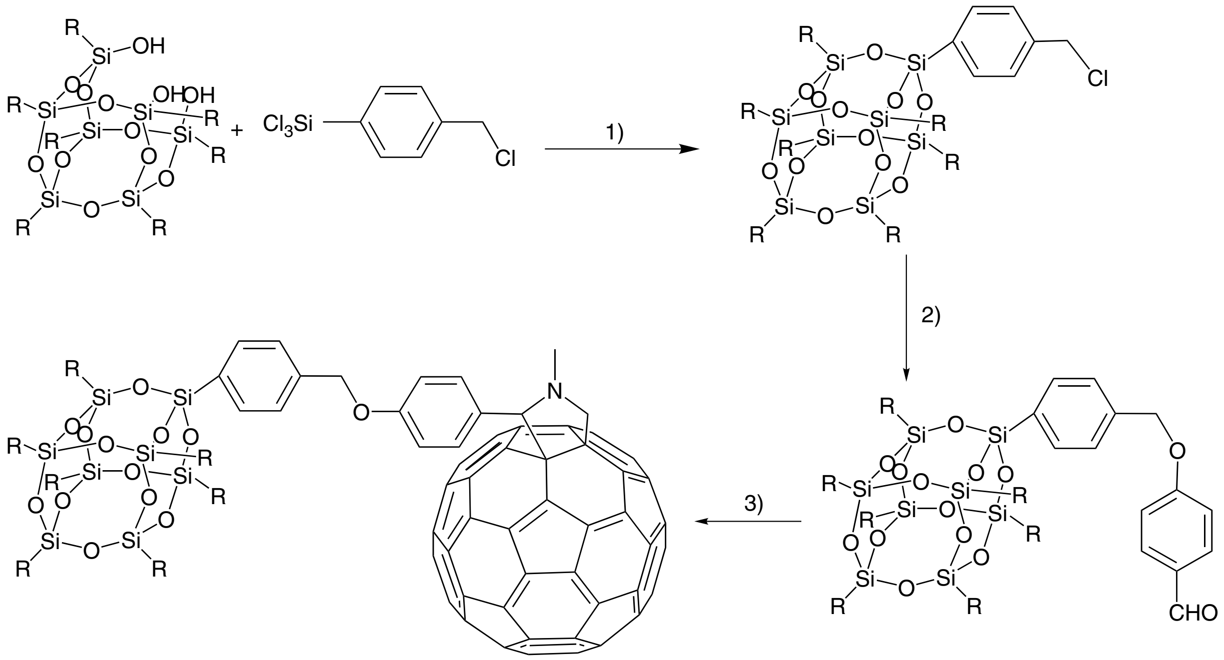
Synthetic pathway 1 is depicted in Fig. 1, and is described herein. Monosubstituted POSS aldehydes have been synthesized previously by the hydrosilylation of a silyl dioxalane, [2-(4-dimethylsilyl)phenyl]-1,3-dioxalane, which was synthesized according to literature procedures[19] to mono-vinyl POSS. Mono-vinyl POSS was synthesized by the reaction of vinyltrichlorosilane with $R_7Si_7O_9(OH)_3$, (R = iBu and Ph).[20] Platinum-catalyzed hydrosilylation was then performed with [2-(4-dimethylsilyl)phenyl]-1,3-dioxalane and mono-vinyl POSS. Subsequent deprotection with pyridinium *p*-toluenesulfonate yielded the desired POSS aldehyde.[19] The aldehyde was reacted with *N*-methylglycine and C_{60} to yield the desired POSS fulleropyrrolidine after purification by column chromatography.

The presence of the pyrrolidine structure was confirmed by NMR and mass spectrometry, with the example of R = iBu discussed herein. ^{1}H NMR exhibited resonances of the pyrrolidine moiety, with a singlet at δ 4.93 and an AB quartet, consisting of doublets at 4.27 and 4.99, which is indicative of coupling occurring



1) Ethylene Glycol, p-toluenesulfonic acid, C_6H_6; 2) Mg, $HSiMe_2Cl$, Et_2O; 3) $CH_2{=}CHSiCl_3$, Et_3N, Et_2O; 4) Karstedt's catalyst, 5) Et_2O; Pyridinium p-toluenesulfonate, acetone; 6) C_{60}, sarcosine, toluene
R = iBu, Ph

Figure 1 Synthesis of POSS fulleropyrrolidines (synthetic pathway 1).



1) Et_3N, THF; 2) K_2CO_3, NaI, (*p*-CHO)C_6H_4OH, 3) C_{60}, sarcosine, toluene

R = iBu, Cp

Figure 2 Synthesis of POSS fulleropyrrolidines (synthetic pathway 2).

between the protons at the 5 position on the pyrrolidine ring. ^{13}C NMR exhibited resonances at δ 40.26 (NCH_3), 69.25 (CH_2), 70.25 (sp^3 C) and 83.78 (CH), as well as resonances of the fullerene from 127.75 to 156.41. ^{29}Si NMR exhibited resonances typical of a monosubstituted POSS cage, with resonances apparent at δ −1.66 (SiR_4), −67.65, −68.13 and −68.40 ($RSiO_3$). −68.13 and ESI mass spectrometry exhibited a peak at 1754.3872 $[M + Na]^+$−68.40 ($RSiO_3$), compared with the theoretical value of 1754.3888. Elemental analysis provided further confirmation of the formation of the desired compound, with good correlation of the experimental results (C, H, N; 69.10, 4.77, 0.80) with the theoretical (C, H, N; 69.81, 5.67, 0.46).

Synthetic pathway 2 is depicted in Fig. 2 and is detailed herein. Monosubstituted POSS aldehydes have previously been synthesized through the nucleophilic substitution of mono-benzyl chloride POSS.[21] Mono-benzyl chloride POSS was synthesized through the reaction of trichloro[4-(chloromethyl)phenyl]silane with trisilanol POSS.[21] Nucleophilic substitution of the chloride functionality with 4-hydroxybenzaldehyde yielded the POSS aldehyde, which was reacted with *N*-methylglycine and C_{60} to yield the desired POSS fulleropyrrolidine after purification by column chromatography. These fulleropyrrolidines uniquely represent the first attachment of a carbon based nanoparticle to silica-based nanoparticles.

The presence of the pyrrolidine structure was again confirmed by NMR and mass spectrometry, with the example of R = iBu discussed herein. ^1H NMR (R = iBu) exhibited resonances at δ 0.65–0.66, 0.96–1.01, 1.86–1.93, 2.80 (NCH_3), 4.25–4.27 (CH_2), 4.91 (CH), 4.96–5.21 (CH_2), 6.85–7.07, 7.43–7.50 and 7.68–7.84. The broad pyrrolidine and phenyl resonances were associated with restricted rotation around the pyrrolidine-phenyl bond, with similar broadness evident on a variety of compounds containing phenyl rings adjacent to the pyrrolidine ring.[11] ^{13}C NMR exhibited resonances at δ 22.62, 22.71, 24.02, 25.86, 40.14 (NCH_3), 69.15 (CH), 70.12 (CH_2O) 83.32 (CH), 70.12, 115.14 and resonances of the fullerene sphere apparent from δ 126.75–159.00. The peak broadness associated with the restricted rotation of the phenyl rings observed in the ^1H NMR spectra was again evident in the broad resonance at δ 115.14. The remaining resonances of the phenyl carbons were obscured by the large number of resonances associated with the fullerene. ^{29}Si NMR exhibited resonances at δ −67.65 and −68.26 ($RSiO_3$). ESI mass spectrometry exhibited a peak at 1774.3790 $[M + Na]^+$, compared with the theoretical value of 1774.3739. Elemental analysis provided further confirmation of the formation of the desired compound, with good correlation of the experimental results (C, H, N; 69.81, 5.01, 0.77) with the theoretical (C, H, N; 70.36, 4.48, 0.79).

The absorption spectra of the fulleropyrrolidine derivatives in toluene are depicted in Fig. 3, and exhibit an absorption band at 433 nm, and a broad band at approximately 705 nm due to the triplet–triplet absorption. These features are characteristic of[6,6] ring-closed fullerene derivatives, which exhibit a singlet-triplet quantum yield near unity, like C_{60}.[22]

Excitation of the fulleropyrrolidines (λ_{exc} = 335 nm) displayed weak emission bands with maxima at approximately 719 nm (Fig. 4), which correspond to the fullerene excited singlet state emission ($^1C_{60}{}^*$), which is characteristic of a fullerene-based emission.[23–27]

Power-limiting measurements were performed using a diode-Q-switched Nd–YLF laser which after frequency doubling of the output provided ~25 ns 523 nm pulses of microjoule energies. The experimental setup was constructed to be similar to the standard

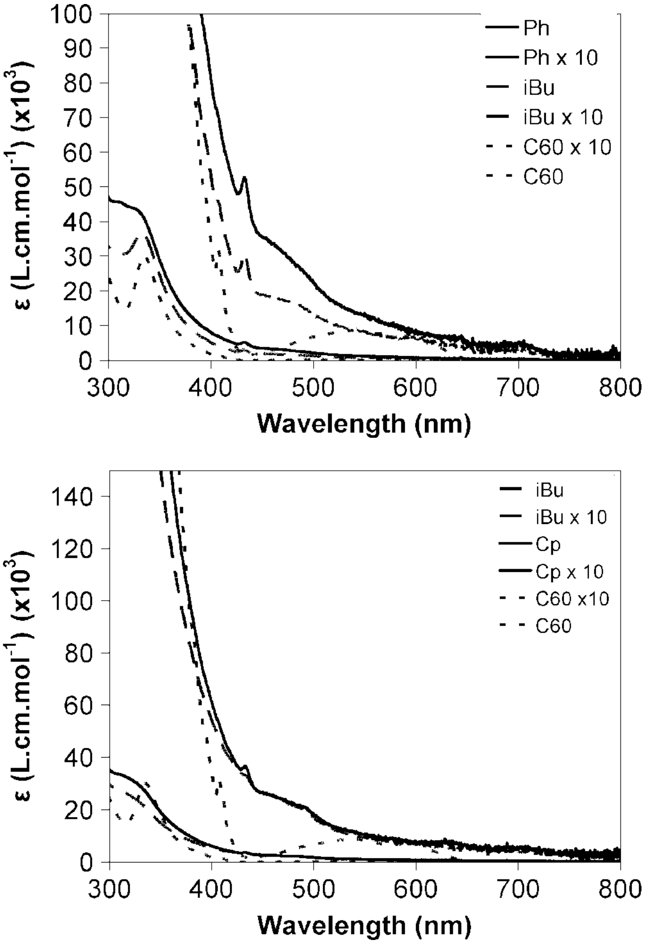


Figure 3 UV-vis spectra of POSS fulleropyrrolidines of synthetic pathways 1 (top).

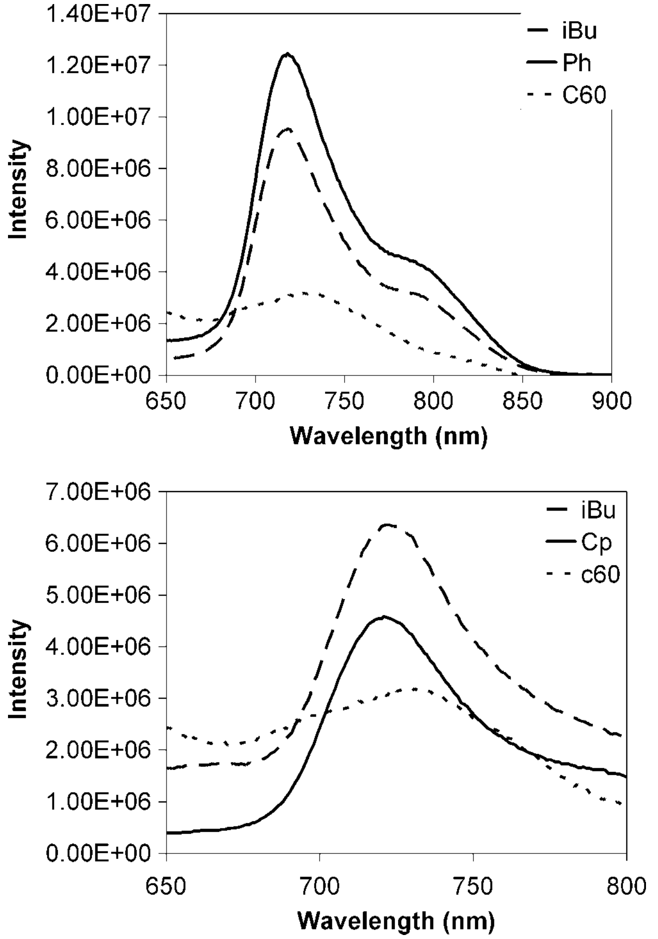


Figure 4 Fluorescence spectra of POSS fulleropyrrolidines of synthetic pathways 1 (top) and 2 (bottom).

f/5 test bed used in the literature[28] and toluene solutions of the investigated compounds with concentrations adjusted to provide ~70% transmission at 523 nm were examined in 1 mm glass cells.

The transmission vs fluence curves were each constructed from several runs in which the incident pulse energy was manipulated and the fluence was additionally varied by scanning the sample position along the *z*-axis. The shapes of open and closed aperture *Z*-scans obtained in such a way were used to calculate the fluence values. Figure 5 shows the results obtained for R = iBu synthesised via synthetic pathway 1. In the cases examined, for solutions of C_{60} and POSS fulleropyrrolidines, there is distinct power limiting of the transmission with the onset of approximately 200 mJ cm^{-2}. In each experiment strong thermal effects were seen at fluences above ca 1 J cm^{-2}, evident from increased scattering which contributed to the power limiting effect. The power-limiting properties of the two POSS compounds investigated were essentially identical to those of C_{60}.

Experimental

Synthetic pathway 1

2-[4-(Dimethylsilyl)phenyl]-1,3-dioxalane was synthesised according to the literature procedure detailed by Morris *et al.*[19] Mono-vinyl POSS compounds were synthesized according to the literature procedure detailed by Shockey *et al.*[9] The mono-functionalized POSS aldehydes were synthesized via slight modification of the literature procedure for the octa-aldehyde POSS.[20] Mono POSS-aldehyde (137 mg, 0.14mmol) was added to a solution containing C_{60} (100 mg, 0.14 mmol), *N*-methylglycine (25 mg, 0.28 mmol) and toluene (100 ml). The solution was then refluxed overnight. The solvent was removed *in vacuo* and the residue extracted with toluene and separated with flash chromatography (toluene or hexane–dichloromethane). Evaporation of the brown fraction yielded the POSS-fulleropyrrolidine product as a brown solid.

R = iBu

Yield = 20 mg (9 %); FTIR (KBr, cm^{-1}): 2957m, 2870m, 2700m, 1463m, 1429w, 1401w, 1104vs, 1022s, 801s, 744m, 706w; ^{1}H NMR ($CDCl_3$): δ 0.24 ($SiCH_3$), 0.55–0.59 (m, 14H, iBu CH_2), 0.91–0.96 (m, 42H, iBu CH_3), 1.75–1.90 (m, 7H, iBu CH), 2.82 (s, 3H, NCH_3), 4.27 (d, 1H, $^3J_{H-H}$ = 14.1 Hz, NCH), 4.93 (s, 1H, NCH), 4.99 (d, $^3J_{H-H}$ = 14.1 Hz, 1H, NCH), 7.42 (d, $^3J_{H-H}$ = 11.4 Hz, 2H, CH), 7.76 (d, $^3J_{H-H}$ = 11.4 Hz, 2H, CH); ^{13}C NMR ($CDCl_3$): δ −3.56 and −3.47 ($SiCH_3$), 4.57 ($SiCH_2$), 7.09 (CH_2Si), 22.62, 24.00, 25.87 (iBu), 40.26 (NCH_3), 69.25 (CH_2), 70.25 (sp_3 C), 83.78 (CH), 127.75, 128.10, 128.35, 128.77, 129.69, 130.54, 134.00, 136.00, 136.87, 137.59, 139.56, 139.73, 139.99, 140.33, 141.66, 141.84, 142.10, 142.28, 142.72, 143.28, 144.55, 144.86, 145.42, 145.71, 145.92, 146.09,

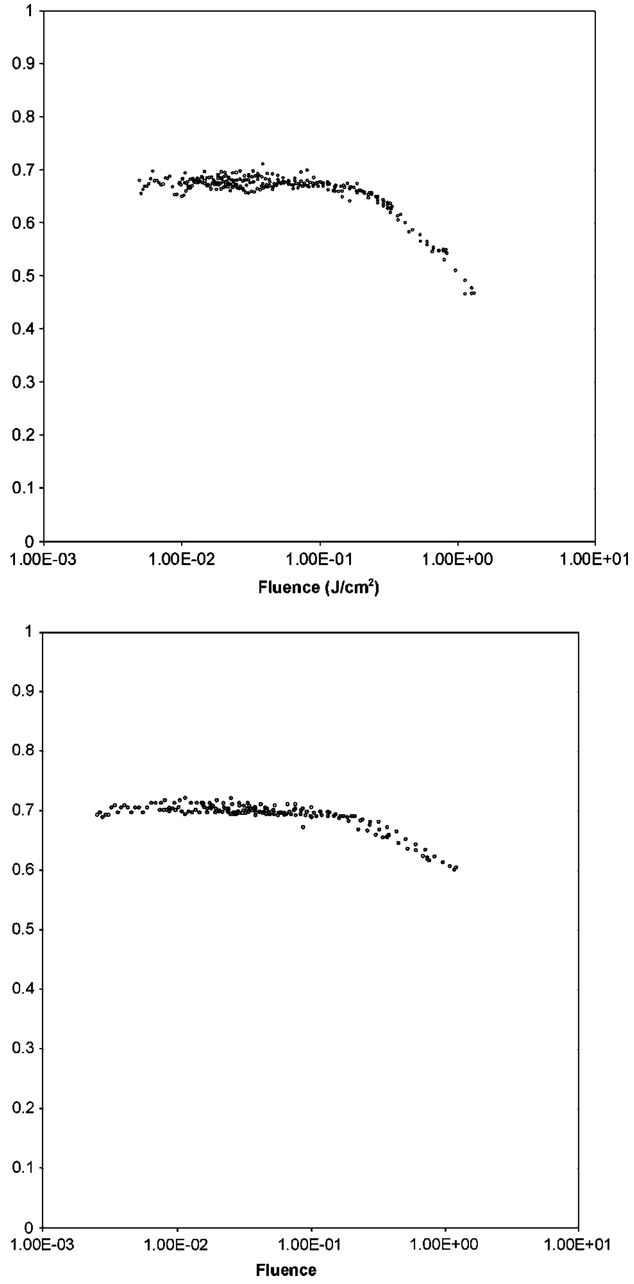


Figure 5 Power Limiting results of C_{60} (top) and POSS fulleropyrrolidine (R = iBu, synthetic pathway 1, bottom).

146.04, 146.65, 147.00, 147.47, 153.62, 154.27, 156.41; ^{29}Si NMR ($CDCl_3$): δ −1.66 (SiC_4), −67.65, −68.13, −68.40 ($RSiO_3$); $[M]^+$ 1754.3888 (1754.3872 theory); elemental analysis: calcd (%) 69.81, 5.67, 0.46; found 69.10, 4.77, 0.80; UV–vis λ_{max} (nm) [ε (M^{-1} cm^{-1})] (toluene) 433 (3005), 705 (235); Fluorescence (λ_{exc} = 335 nm, toluene) 719 nm.

R = Ph

Yield = 34 mg (14%); FTIR (KBr, cm^{-1}): 3072w, 3050w, 3028w, 2953m, 2923m, 2780w, 1666w, 1594w, 1463w, 1430m, 1261w, 1247w, 1203w, 1134vs, 1109s, 1029m, 998m, 837w, 797w, 744m, 697m; ^{1}H NMR ($CDCl_3$): δ 0.23 (s, 6H, $SiCH_3$), 0.53–0.59 (m, 2H, $SiCH_2$), 0.82–0.90 (m, 2H, CH_2Si), 2.83 (s, 3H, NCH_3), 4.25–4.28 (m, 1H, NCH_2), 4.92 (s, 1H, NCHR), 4.98–5.00 (m, 1H, NCH_2), 7.34–7.49 (m, 25H, CH), 7.70–7.74 (m, 15H, CH); ^{13}C NMR ($CDCl_3$): δ −3.56 ($SiCH_3$), 4.21 ($SiCH_2$), 7.04 (CH_2Si), 40.14 (NCH_3), 68.84 (CH_2), 69.77 (sp^3 C), 83.47 (CH), 127.80, 128.60, 130.25, 130.45, 130.74, 133.91, 134.18, 134.20, 135.65, 136.76, 139.26, 139.81, 140.04, 141.09, 141.37, 141.57, 141.57, 141.72, 141.81, 142.05, 142.05, 142.12, 142.37, 142.44, 142.49, 142.59, 142.76, 142.91, 143.00, 144.21, 144.28, 144.46, 144.58, 145.11, 145.21, 145.41, 145.53, 145.60, 145.75, 145.79, 146.03, 146.17, 146.23, 147.19, 153.02; ^{29}Si NMR ($CDCl_3$): δ −1.19 (SiC_4), −65.28, −78.85, −78.92, −79.19 ($RSiO_3$); $[M]^+$ 1894.1723 (1894.1681 theory); elemental analysis: calcd (%) 70.29, 3.12, 0.75; found 72.87, 2.92, 0.74; UV–vis λ_{max} (nm) [ε (M^{-1} cm^{-1})] (toluene) 432 (4935), 705 (343); fluorescence (λ_{exc} = 335 nm, toluene) 719 nm.

Synthetic pathway 2

Mono-aldehyde POSS was synthesized according to the method detailed by Wei *et al.*[21] POSS-fulleropyrrolidines were synthesized according analogously to the procedure detailed for synthetic pathway 1.

R = iBu

Yield = 80 mg (54%); FTIR (KBr, cm^{-1}): 2954m, 2905m, 2870m, 2779w, 1698w, 1600m, 1577w, 1512m, 1382w, 1366w, 1332w, 1261m, 1229m, 1110vs, 1035m, 833m, 803m, 743m; ^{1}H NMR ($CDCl_3$): δ 0.65–0.66 (m, 16H, iBu CH_2), 0.96–1.01 (m, 42H, iBu CH_3), 1.86–1.93 (m, 7H, iBu CH), 2.80 (s, 3H, NCH_3), 4.26–4.27 (m, 1H, NCH_2), 4.91 (s, 1H, NCH), 4.96–5.21 (m, 3H, CH_2O and NCH_2), 6.85–7.07 (m, 4H, CH), 7.43–7.50 (m, 2H, CH), 7.68–7.84 (m, 4H, CH); ^{13}C NMR ($CDCl_3$): δ 22.62, 22.71, 24.02, 25.86, 40.14, 69.15, 70.12, 83.32, 115.14, 126.75, 128.42, 128.50, 129.75, 129.91, 131.68, 132.54, 134.47, 135.95, 136.00, 136.74, 136.96, 139.07, 139.13, 139.19, 139.75, 140.09, 140.34, 141.32, 141.44, 141.72, 141.85, 142.01, 142.14, 142.21, 142.29, 142.43, 142.73, 142.84, 143.16, 143.32, 144.34, 144.80, 144.85, 145.32, 145.42, 145.45, 145.49, 145.65, 145.72, 145.95, 146.10, 160.30, 146.38, 146.48, 146.52, 146.68, 146.97, 147.47, 153.80, 154.27, 156.56, 159.04; ^{29}Si NMR ($CDCl_3$): δ −67.65, −68.26; $[M + Na]^+$ 1774.3790 (1774.3739 theory); elemental analysis: calcd (%) 69.81, 5.01, 0.77; found 70.36, 4.48, 0.79; UV–vis λ_{max} (nm) [ε (M^{-1} cm^{-1})] (toluene) 432 (2695), 706 (214); fluorescence (λ_{exc} = 335 nm, toluene) 723 nm.

R = Cp

Yield = 171 mg (60%); FTIR (KBr, cm^{-1}): 2949m, 2865m, 1699m, 1601m, 1579w, 1508m, 1451m, 1400w, 1321w, 1252m, 1114, 914m, 830m, 806m, 700w; ^{1}H NMR ($CDCl_3$): δ 1.03 (m, 7H, Cp), 1.54 (m, 42H, Cp), 1.78 (m, 14H, Cp), 2.80 (m, 3H, NCH_3), 4.25–4.27 (m, 1H, CH_2), 4.91–5.13 (m, 3H, CH and CH_2), 7.04 (m, 2H, CH), 7.43 (m, 4H, CH), 7.69 (m, 2H, CH); ^{13}C NMR ($CDCl_3$): δ 22.40, 27.13, 27.18, 27.46, 40.13, 69.12, 70.13, 83.28, 115.10, 126.75, 129.47, 129.88, 130.65, 132.02, 134.67, 135.92, 135.96, 136.71, 136.93, 138.94, 139.71, 120.06, 140.29, 141.42, 141.68, 141.81, 141.97, 142.11, 142.17, 142.25, 142.40, 142.69, 142.81, 143.13, 143.28, 144.53, 144.76, 144.85, 145.28, 145.38, 145.44, 145.61, 145.68, 145.91, 146.07, 146.26, 146.34, 146.43, 146.49, 146.65, 146.93, 147.23, 147.44, 153.76, 154.23, 156.50, 159.00; ^{29}Si NMR ($CDCl_3$): δ −66.22, −66.55; $[M + Na]^+$ 1880.3600 (1880.3603 theory); elemental analysis: calcd (%) 70.24, 4.82, 0.78; found 71.70, 4.28, 0.75; UV–vis λ_{max} (nm) [ε (M^{-1} cm^{-1})] (toluene) 433 (3028), 704 (260); fluorescence (λ_{exc} = 335 nm, toluene) 721 nm.

Conclusions

POSS-bound fulleropyrrolidines were synthesized and characterized by FTIR, NMR, ESI UV–vis and fluorescence, which confirmed that the desired fulleropyrrolidine structure was present. The optical properties of the compounds in solution were investigated with power-limiting measurements, indicating that the power limiting of the POSS fulleropyrrolidines was essentially identical to that of C_{60}. In order to incorporate the POSS fulleropyrrolidines into a range of polymeric systems, a polymerizable group on the nitrogen atom of the fulleropyrrolidine is desired. It is envisaged that this will be obtained through the preparation of a suitably N-functionalized amino glycine and subsequent reaction with the mono POSS aldehyde in the presence of C_{60}, allowing for the covalent attachment of the desired polymerizable group and incorporation into the desired polymeric systems for characterization of the optical limiting properties in the solid state.

Supplementary material

Supplementary electronic material for this paper is available in Wiley InterScience at http://www.interscience.wiley.com/jpages/0268-2605/suppmat/

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