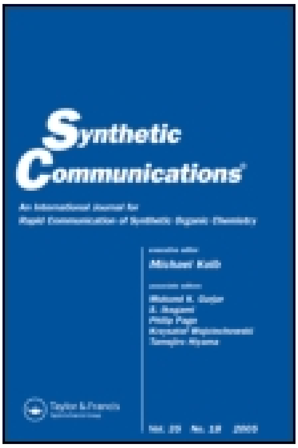


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Design and Synthesis of Dumbbell-Shaped POSS-C_{60} Dyads with Flexible Spacer

Fafu Yang [a] [b] , Congcong Li [a] , Hongyu Guo [a] , Jinqi Ye [a] & Ziyu Jiao [a]
[a] College of Chemistry and Materials Science, Fujian Normal University, Fuzhou, China
[b] Fujian Key Laboratory of Polymer Materials, Fuzhou, China

To cite this article: Fafu Yang , Congcong Li , Hongyu Guo , Jinqi Ye & Ziyu Jiao (2012): Design and Synthesis of Dumbbell-Shaped POSS-C_{60} Dyads with Flexible Spacer, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 42:24, 3664-3669

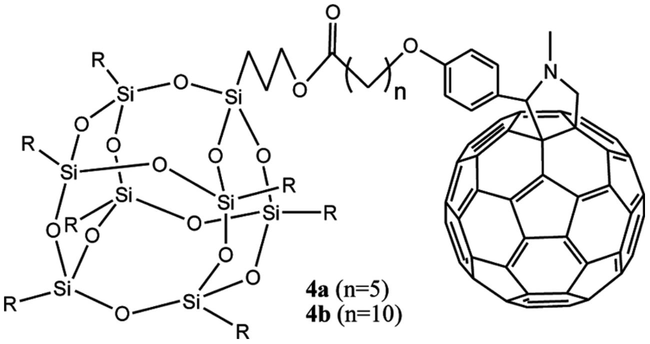
To link to this article: http://dx.doi.org/10.1080/00397911.2011.589562

Synthetic Communications®, 42: 3664–3669, 2012
Copyright © Taylor & Francis Group, LLC
ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2011.589562

DESIGN AND SYNTHESIS OF DUMBBELL-SHAPED POSS-C_{60} DYADS WITH FLEXIBLE SPACER

Fafu Yang,[1,2] Congcong Li,[1] Hongyu Guo,[1] Jinqi Ye,[1] and Ziyu Jiao[1]
[1]*College of Chemistry and Materials Science, Fujian Normal University, Fuzhou, China*
[2]*Fujian Key Laboratory of Polymer Materials, Fuzhou, China*

GRAPHICAL ABSTRACT



Abstract *Using polyhedral oligomeric silsesquioxane (POSS) as starting material, novel dumbbell-shaped POSS-C_{60} dyads with flexible spacers were designed and synthesized in good yields by esterification, subsequent etherification, and further 1,3-dipolar cycloaddition of azomethine ylide generated* in situ *from aldehyde and sarcosine to C_{60}.*

Keywords 1,3-Dipolar cycloaddition; fullerene; POSS; synthesis

INTRODUCTION

Fullerene has received much research interest because of its unique structure, interesting properties, and promising applications in a variety of fields, such as macromolecular materials, fuel cells, solar energy conversion and storage, and biomedical and life sciences.[1,2] However, their poor solubility and processability pose difficulties in utilizing fullerene for practical applications. To overcome these disadvantages, one method was to synthesize the fullerene-grafted polymers, some of which exhibited attractive properties,[3,4] for instance, fullerene-containing polyester

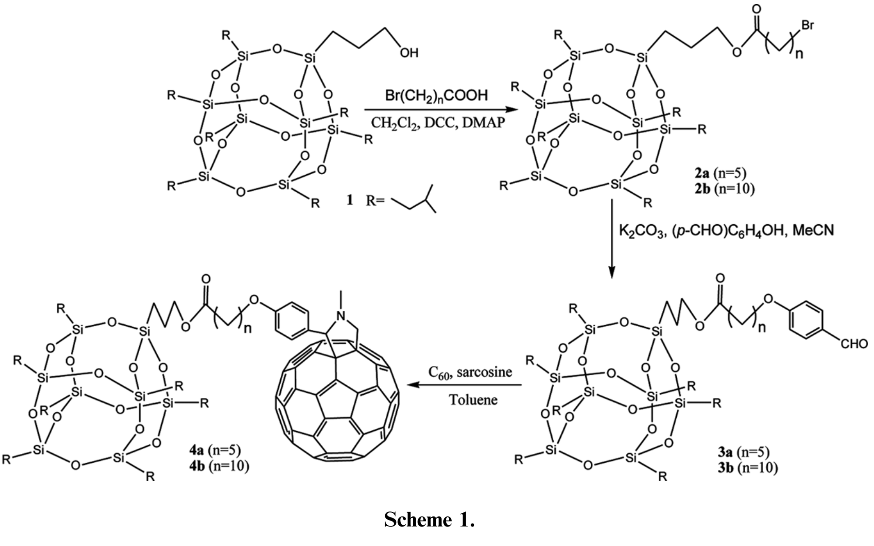
Received March 27, 2011.

Address correspondence to Fafu Yang, College of Chemistry and Materials Science, Fujian Normal University, Fuzhou 350007, China. E-mail: yangfafu@fjnu.edu.cn

and π-conjugated polymers,[5] fullerene-containing poly(propylene oxide) membrane.[6] However, the syntheses of these kinds of polymers were often complicated and the contents of fullerene in them were difficult to adjust for different applications. Another method was to prepare fullerene-doped polymers, such as sol-gel glasses,[7] polymethyl methacrylate (PMMA),[8] and glass-polymer composites.[9] However, the heterogeneous dispersion of fullerene in a polymetric matix often resulted in aggregation, which was the obstacle to obtaining stable and homogeneous materials.

The polyhedral oligomeric silsequioxane (POSS) macromer, consisting of a spherical inorganic silica core (Si_8O_{12}) surrounded by seven inert alkyl groups for solubility and one reactive group, is a well-defined cluster whose diameter is approximately 15 Å.[10] POSS can be regarded as the smallest possible silica particle surrounded by an organic surface.[11] Because of the special structure of POSS, the POSS-fullerene dyad, in theory, should not only exhibit the interesting properties based on fullerene units but also possess excellent homogenous dispersion in polymeric matries based on POSS units, preventing aggregation of fullerene and improving physical and mechanical properties.[12] Lately, Clarke et al. reported the first examples of POSS-fullerene derivative with short and rigid phenyl groups.[13,14] However, the short and rigid phenyl groups were not favorable for homogenous dispersion in polymers. The long and flexible aliphatic spacer would be an excellent candidate for preparing fullerene-POSS dyads possessing outstanding flexibility and compatibility with polymers. In this article, we designed and synthesized novel dumbbell-shaped polyhedral oligomeric silsesquioxane (POSS)-C_{60} dyads, in which POSS and C_{60} were linked with long and flexible aliphatic spacers for the first time.

The synthetic route is shown in Scheme 1. The esterification of mono-hydroxy POSS **1** was carried out by reacting mono-hydroxy POSS **1** with corresponding ω-bromo-substituted carboxylic acid, using N,N′-dicyclohexylcarbodiimide as condensating agent and 4-dimethylaminopyridine as catalyst. Mono-ω-bromo-substituted POSS **2a** and **2b** were obtained in yields of 85% and 78%, respectively. Subsequently, nucleophilic substitution of compound **2** with 4-hydroxybenzaldehyde



Scheme 1.

gave the desired mono-aldehyde-substituted POSS **3a** or **3b** in refluxing K_2CO_3/MeCN system in 88% or 86% after column chromatography. After further treating compound **3** with C_{60} and sarcosine, the novel dumbbell-shaped POSS-C_{60} dyad **4a** and **4b** were prepared by 1,3-dipolar cycloaddition of azomethine ylide generated in situ from aldehyde and sarcosine in yields of 55% and 61%, respectively. Although novel dumbbell-shaped POSS-C_{60} dyads **4a** and **4b** were prepared in multiple steps, the total yields of them were as high as 41% and 40%, respectively.

The structures of intermediate compounds **2** and **3** were characterized by elemental analyses, electrospray ionization–mass spectrometry (ESI-MS), and ^{1}H NMR spectra. All these data were in accordance with the structures of compounds **2** and **3**. The structures of target compounds of novel dumbbell-shaped POSS-C_{60} dyads **4a** and **4b** were confirmed by elemental analyses, ultraviolet (UV), infrared (IR), ESI-MS, ^{1}H NMR, and ^{13}C NMR spectra. The UV spectra showed the typical absorption features of mono-fulleropyrrolidine at 256, 308, and 430 nm. The ESI-MS spectra exhibited corresponding molecular ion peaks at 1840.34 and 1910.22, respectively. In the ^{1}H NMR spectra, all the protons were well assigned. Especially, the typical split of NCH_2 (a and a′) on a pyrrole ring and ArH (c and d) were observed clearly. All these spectral data were in accordance with the structures of fulleropyrrolidine derivatives in literatures.[1,2,13,14] Our further work will focus on preparing various polymers with compounds **4a** and **4b** to form stable and homogeneous hybrid materials containing C_{60} units and nanometer silica particles.

EXPERIMENTAL

C60, POSS, 6-bromocaproic acid, 11-bromoundecanoic acid, 4-hydroxybenzaldehyde, sarcosine, N,N′-dicyclohexylcarbodiimide, 4-dimethylaminopyridine, and KI were obtained from commercial suppliers and used without further purification. The other organic and inorganic reagents were purified according to standard methods before use. The analysis of thin-layer chromatography (TLC) was performed using precoated glass plates. Column chromatography was performed using silica gel (200–300 mesh). IR spectra were recorded on a Perkin-Elmer PE-983 IR spectrometer as KBr pellets with absorption in cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker-ARX 600 instrument at 30 °C, using, tetramethylsilane (TMS) as internal standard. The UV–vis absorption spectra were measured on a computer-controlled Shimadzu UV2501-PC spectrophotometer. ESI-MS spectra were obtained from DECAX-30000 LCQ Deca XP mass spectrometer. Elemental analyses were performed on a Vario EL III Elemental Analyzer.

Syntheses of Compounds 2a and 2b

Compound **1** (0.5 g, 0.57 mmol), corresponding ω-bromo-substituted carboxylic acid (0.60 mmol), N,N′-dicyclohexylcarbodiimide (0.13 g, 0.63 mmol), and 4-dimethylaminopyridine (0.02 g, 0.16 mmol) were dissolved in 10 mL CH_2Cl_2. The mixture was stirred for 4 h under room temperature. Then the solvent was evaporated under reduced pressure. The residue was precipitated in a 1:1 vol/vol mixture of methanol and water, separated by centrifugation, and dried under vacuum. The crude product was further purified by flash column chromatography on silica gel using a mixture of hexane–acetone (7:1) as eluant. Compounds **2a** and **2b** were obtained as white powder in yields of 85% and 78%, respectively.

Compound 2a. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm: 0.61 (m, 16H, $SiCH_2$), 0.97 (d, 42H, $J = 6.6$ Hz, CH_3), 1.43–1.74 [m, 8H, $\underline{(CH_2)}_3CH_2COO$ and $COOCH_2\underline{CH_2}$], 1.85 (m, 7H, $SiCH_2\underline{CH}$), 2.32 (t, 2H, $J = 7.2$ Hz, CH_2COO), 3.41 (t, 2H, $J = 6.6$ Hz, CH_2Br), 4.03 (t, 2H, $J = 6.6$ Hz, $COOCH_2$); MS *m/z* (%): 1051.71 (M^+, 100). Anal. calcd. for $C_{37}H_{79}BrO_{14}Si_8$: C, 42.25; H, 7.57. Found C, 42.20; H, 7.64.

Compound 2b. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm: 0.61 (m, 16H, $SiCH_2$), 0.97 (d, 42H, $J = 6.6$ Hz, CH_3), 1.30 [m, 12H, $\underline{(CH_2)}_6CH_2CH_2Br$], 1.43 (m, 2H, $\underline{CH_2}CH_2COO$), 1.56–1.72 (m, 4H, $COOCH_2\underline{CH_2}$ and $\underline{CH_2}CH_2Br$), 1.87 (m, 7H, $SiCH_2CH$), 2.30 (t, 2H, $J = 7.2$ Hz, CH_2COO), 3.42 (t, 2H, $J = 6.6$ Hz, CH_2Br), 4.04 (t, 2H, $J = 6.6$ Hz, $COOCH_2$); MS *m/z* (%): 1122.23 (M^+, 100). Anal. calcd. for $C_{42}H_{89}BrO_{14}Si_8$: C, 44.99; H, 7.99. Found: C, 44.93; H, 7.91.

Syntheses of Compounds 3a and 3b

Compounds **2a** or **2b** (0.35 mmol), and 4-hydroxybenzaldehyde (0.25 g, 2.0 mmol), and K_2CO_3 (0.27 g, 2.0 mmol) were refluxed in 50 mL MeCN overnight and purged with N_2. After cooling, the mixture was filtered and evaporated to dryness on a rotavapor. Then the mixture was further purified by column chromatography on silica gel using a mixture of petroleum ether–CH_2Cl_2(5:1, *v/v*) as eluant. The compounds **3a** and **3b** were obtained as grayish solids in yields of 88% and 86%, respectively.

Compound 3a. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm: 0.60 (m, 16H, $SiCH_2$), 0.95 (d, 42H, $J = 6.6$ Hz, CH_3), 1.51–1.87 [m, 15H, $\underline{(CH_2)}_3CH_2COO$, $COOCH_2\underline{CH_2}$ and $SiCH_2\underline{CH}$], 2.34 (t, 2H, $J = 7.2$ Hz, CH_2COO), 4.04 (m, 4H, $ArOCH_2$ and $COOCH_2$), 6.98 (d, 2H, $J = 8.4$ Hz, ArH), 7.83 (d, 2H, $J = 8.4$ Hz, ArH), 9.88 (s, 1H, ArCHO); MS *m/z* (%): 1092.82 (M^+, 100). Anal. calcd. for $C_{44}H_{84}O_{16}Si_8$: C, 48.34; H, 7.75. Found C, 48.43; H, 7.68.

Compound 3b. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm: 0.59 (m, 16H, $SiCH_2$), 0.94 (d, 42H, $J = 6.6$ Hz, CH_3), 1.21–1.88 [m, 25H, $\underline{(CH_2)}_8CH_2OAr$, $COOCH_2\underline{CH_2}$ and $SiCH_2CH$], 2.28 (t, 2H, $J = 7.2$ Hz, CH_2COO), 4.01–4.11 (m, 4H, CH_2OAr and $COOCH_2$), 6.98 (d, 2H, $J = 8.4$ Hz, ArH), 7.81 (d, 2H, $J = 8.4$ Hz, ArH), 9.87 (s, 1H, ArCHO); MS *m/z* (%): 1162.84 (M^+, 100). Anal. calcd. for $C_{49}H_{94}O_{16}Si_8$: C, 50.59; H, 8.15. Found: C, 50.68; H, 8.06.

Syntheses of Compounds 4a and 4b

A mixture of compounds **3a** or **3b** (0.23 mmol), C_{60} (0.18 g, 0.25 mol), and sarcosine (0.26 g, 3.0 mmol) in dry toluene (200 mL) was refluxed for 48 h. After the reaction mixture was cooled to room temperature, the solvent was removed under reduce pressure and the residue was further purified by column chromatography [SiO_2 200–300 mesh, petroleum ether/CH_2Cl_2(1:1, *v/v*) as eluant]. The compounds **4a** and **4b** were obtained as brown solids in yields of 55% and 61%, respectively.

Compound 4a. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm: 0.60 (m, 16H, $SiCH_2$), 0.95 (d, 42H, $J = 6.6$ Hz, CH_3), 1.23–1.88 [m, 15H, $(\underline{CH_2})_3CH_2OAr$, $COOCH_2\underline{CH_2}$ and $SiCH_2\underline{CH}$], 2.27 (t, 2H, $J = 7.2$ Hz, CH_2COO), 2.77 (s, 3H, NCH_3), 3.94 (t, 2H, $J = 6.6$ Hz, OCH_2), 4.02 (t, 2H, $J = 6.6$ Hz, CH_2OAr), 4.22 (d, 1H, $J = 9.6$ Hz, NCH_2), 4.87 (s, 1H, ArCH), 4.95 (d, 1H, $J = 9.6$ Hz, NCH_2), 6.92 (d, 2H, $J = 8.4$ ArH), 7.68 (bs, 2H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm: 8.56, 22.43, 22.65, 22.72, 24.07, 24.10, 24.98, 25.90, 25.93, 25.96, 29.27, 34.41, 40.22, 66.47, 67.80, 69.20, 70.21, 77.60, 83.40, 129.01, 136.01, 136.02, 136.80, 137.0, 139.80, 140.13, 140.34, 140.37, 141.76, 141.90, 142.05, 142.19, 142.23, 142.25, 142.30, 142.33, 142.35, 142.38, 142.48, 142.51, 142.76, 142.80, 142.89, 143.20, 143.36, 144.62, 144.84, 144.93, 145.36, 145.45, 145.49, 145.52, 145.55, 145.68, 145.71, 145.76, 146.0, 146.14, 146.16, 146.31, 146.35, 146.37, 146.43, 146.49, 146.52, 146.61, 146.75, 147.03, 147.51, 147.52, 153.90, 154.34, 156.60, 159.30, 173. FT-IR (KBr) ν/cm^{-1}: 3437, 2952, 1737, 1464, 1109, 836, 560, 481. UV-vis: 256, 308, and 429 nm. MS m/z (%): 1840.34 (M^+, 100). Anal. calcd. for $C_{106}H_{89}O_{15}Si_8N$: C, 69.16; H 4.87; N, 0.76. Found: C, 69.24; H, 5.73; N, 0.67.

Compound 4b. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm: 0.60 (m, 16H, $SiCH_2$), 0.95 (d, 42H, $J = 6.6$ Hz, CH_3), 1.24–1.86 [m, 25H, $(\underline{CH_2})_8CH_2OAr$, $COOCH_2\underline{CH_2}$ and $SiCH_2CH$], 2.28 (t, 2H, $J = 7.2$ Hz, CH_2COO), 2.77 (s, 3H, NCH_3), 3.93 (t, 2H, $J = 6.6$ Hz, OCH_2), 4.01 (t, 2H, $J = 6.6$ Hz, CH_2OAr), 4.22 (d, 1H, $J = 9.6$ Hz, NCH_2), 4.87 (s, 1H, ArCH), 4.95 (d, 1H, $J = 9.6$ Hz, NCH_2), 6.92 (d, 2H, $J = 8.4$ ArH), 7.69 (bs, 2H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm: 8.57, 22.43, 22.65, 22.72, 24.07, 24.10, 25.22, 25.89, 25.93, 26.32, 29.41, 29.51, 29.56, 29.63, 29.64, 29.75, 34.57, 40.22, 66.38, 68.19, 69.20, 70.22, 77.61, 83.42, 128.90, 136.01, 136.80, 136.99, 139.79, 140.11, 140.33, 140.37, 141.75, 141.89, 142.05, 142.19, 142.22, 142.25, 142.30, 142.33, 142.35, 142.38, 142.48, 142.51, 142.77, 142.80, 142.88, 143.20, 143.36, 144.61, 144.84, 144.92, 145.36, 145.45, 145.49, 145.52, 145.55, 145.68, 145.71, 145.76, 146.0, 146.13, 146.16, 146.31, 146.34, 146.37, 146.42, 146.48, 146.52, 146.62, 146.75, 147.04, 147.50, 147.52, 153.92, 154.35, 156.62, 159.41, 174.01. FT-IR (KBr) ν/cm^{-1}: 3440, 2952, 1737, 1464, 1108, 836, 572, 483. UV-vis: 256, 307, and 430 nm. MS m/z (%): 1910.22 (M^+, 100). Anal. calcd. for $C_{111}H_{99}O_{15}Si_8N$: C, 69.76; H, 5.22; N, 0.73. Found: C, 69.86; H, 5.17; N, 0.64.

ACKNOWLEDGMENTS

Financial support from the National Natural Science Foundation of China (No. 20402002), Fujian Natural Science Foundation of China (No. 2009J01019), and Program for Excellent Young Researchers in University of Fujian Province (JA10056) were greatly acknowledged. Thanks go to Prof. Lei Zhu at Case Western Reserve University for supplying the materials.

REFERENCES

1. Sawamura, M.; Kawai, K.; Matsuo, Y.; Kanie, K.; Kato, T.; Nakamura, E. Stacking of conical molecules with a fullerene apex into polar columns in crystals and liquid crystals. *Nature* **2002**, *419*, 702–705.

2. Michinobu, T.; Nakanishi, T.; Hill, J.; Funahashi, M.; Ariga, K. Room-temperature liquid fullerenes: An uncommon morphology of C60 derivatives. *J. Am. Chem. Soc.* **2006**, *128*, 10384–10387.
3. Segura, J. L.; Martín, N.; Guldi, D. M. Materials for organic solar cells: The C60/p-conjugated oligomer approach. *Chem. Soc. Rev.* **2005**, *34*, 31–47.
4. Kuang, L.; Chen, Q.; Sargent, E. H.; Wang, Z. Y. Fullerene-containing polyurethane films with large ultrafast nonresonant third-order nonlinearity at telecommunication wavelengths. *J. Am. Chem. Soc.* **2003**, *125*, 13648–13649.
5. Yu, H.; Gan, L. H.; Hu, X.; Venkatraman, S. S.; Tam, K. C.; Gan, Y. Y. A novel amphiphilic double-[60] fullerene-capped triblock copolymer. *Macromolecules* **2005**, *38*, 9889–9893
6. Sterescu, D. M.; Bolhuis-Versteeg, L.; Vegt, N. F. A.; Stamatialis, D. F.; Wessling, M. Novel gas separation membranes containing covalently bonded fullerenes. *Macromol. Rapid Commun.* **2004**, *25*, 1674–1681.
7. Maggini, M.; De Faveri, C.; Scorrano, G.; Prato, M.; Brusatin, G.; Guglielmi, M.; Meneghetti, M.; Signorini, R.; Bozio, R. Synthesis and optical-limiting behavior of hybrid inorganic–organic materials from the Sol–Gel processing of organofullerenes. *Chem. Eur. J.* **1999**, *5*, 2501–2510.
8. Kost, A.; Tutt, L.; Klein, M. B.; Dougherty, T. K.; Elias, W. Optical limiting with C_{60} in polymethyl methacrylate. *Opt. Lett.* **1993**, *18*, 334–336.
9. Gvishi, R.; Bhawalker, J. D.; Kumar, N. D.; Ruland, G.; Narang, U.; Prasad, P. N.; Reinhardt, B. A. Multiphasic nanostructured composites for photonics: Fullerene-doped monolith glass. *Chem. Mater.* **1995**, *7*, 2199–2202.
10. Hao, N.; Böhning, M.; Goering, H.; Schönhals, A. Nanocomposites of polyhedral oligomeric phenethylsilsesquioxanes and poly(bisphenol a carbonate) as investigated by dielectric spectroscopy. *Macromolecules* **2007**, *40*, 2955–2964.
11. Tamaki, R.; Tanaka, Y.; Asuncion, M. Z.; Choi, J.; Laine, R. M. Octa(aminophenyl) silsesquioxane as a nanoconstruction site. *J. Am. Chem. Soc.* **2001**, *123*, 12416–12417.
12. Costa, R. O. R.; Vasconcelos, W. L.; Tamaki, R.; Laine, R. M. Organic/inorganic nanocomposite star polymers via atom transfer radical polymerization of methyl methacrylate using octafunctional silsesquioxane cores. *Macromolecules* **2001**, *34*, 5398–5407.
13. Clarke, D. J.; Matisons, J. G.; Simon, G. R.; Samoc, M.; Samoc, A. Polyhedral oligomeric silsesquioxane bound fulleropyrrolidines. *Appl. Organometal. Chem.* **2008**, *22*, 460–465.
14. Clarke, D. J.; Matisons, J. G.; Simon, G. R.; Samoc, M.; Samoc, A. Polyhedral oligomeric silsesquioxane-bound iminofullerene. *Appl. Organometal. Chem.* **2010**, *24*, 184–188.