Macromolecules **2005,** *38,* 4661−4665

Robust Polyaromatic Octasilsesquioxanes from Polybromophenylsilsesquioxanes, Br_xOPS, via Suzuki Coupling

Chad M. Brick,[†] Yuko Ouchi,[†,⊥] Yoshiki Chujo,[⊥] and Richard M. Laine*[,‡,§]

Departments of Chemistry and Materials Science and Engineering and the Macromolecular Science and Engineering Center, University of Michigan, Ann Arbor, Michigan 48109-2136, and Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto, Japan

Received January 18, 2005; Revised Manuscript Received March 22, 2005

ABSTRACT: Polybromophenylsilsesquioxane (Br_xOPS), where $x = 5.3$ ($p{:}m = 65{:}25$), because of its octahedral structure and nanometer size, represents a potentially very useful nanoconstruction site. We report here that $Br_{5.3}OPS$ reacts readily with borates of phenyl, biphenyl, naphthyl, 9,9-dimethylfluorene, and thiophene using standard Suzuki conditions to produce the corresponding polyaromatic and heteroaromatics with complete substitution of all bromines. The resulting materials, because of the 3-D octahedral structure, are completely soluble in a variety of common organic solvents. They are also stable to temperatures exceeding 400 °C in air, making them quite robust and easily processable. UV−vis spectra of these materials are red-shifted 20−30 nm from the simple organics, suggesting some conjugation with the silica cage core. Photoluminescence measurements show standard aromatic $\pi-\pi^*$ behavior with typical quantum efficiencies except for the 9,9-dimethylfluorene compound, which has an unexpectedly high quantum efficiency >95%. The resulting compounds offer potential for further functionalization.

Introduction

Highly conjugated compounds including polyaromatics are currently a subject of considerable study because of their potential utility in organic and molecular electronics for applications ranging from organic light-emitting diodes, to photovoltaics, to organic transistors.[1−4] In part, work in this area is driven by the ability to manipulate their HOMO/LUMO gaps extensively through changes in degree of conjugation and/or peripheral substituents. In part, their very robust nature makes them attractive for device manufacture using traditional microelectronics solid-state processing methods.

One drawback to using polyaromatics in particular for organic electronics (specifically for OLED applications) arises because of their propensity to form π-stacks (aggregate), which can cause undesirable exciplex emissions, force potentially unwanted crystallization, and also limit their solubility or volatility.[5,6] For example, syntheses of polyfluorenes, an important class of polymers for blue-light emission in light-emitting diodes, frequently generate a large proportion of insolubles.[5a] Considerable effort has been invested in introducing solubilizing substituents that also limit or control aggregation, without diminishing inherent properties.[1,5b,6] An alternate approach has been to affix polyaromatics to star or dendrimer structures[7−9] to improve their solubility by limiting/controlling their potential to π-stack without impairing their electronic/photonic properties. In some instances, improved performance is also observed.[9]

Unfortunately, dendrimer syntheses can be long and complicated, and aliphatic links can limit thermal stability. Furthermore, fully aromatic and/or conjugated dendrimers, with some notable exceptions, are not easily accessible.[6−8,10] We report here an alternate approach to polyaromatics with multiple advantages in terms of ease of synthesis, robustness, versatility in functionality, and high solubility.

Cubic octasilsesquioxanes (Figure 1) are novel compounds that have been used as model catalytic surfaces, molecular catalysts, porous media, NMR standards, fluoride encapsulants, and building blocks for nanocomposite materials.[11,12] We have explored their utility as building blocks for formulating nanocomposites with complete definition of their 3-D structures at nanometer length scales.[12] In these systems, each cube vertex can have a functional group. The orthogonal vertices place these functional groups in eight different octants in Cartesian space offering materials with high solubilities, limited opportunities to π-stack (aggregate) or crystallize, and therefore excellent processing properties.

The easily synthesized octavinyl (OVS) and octaphenyl (OPS) octasilsesquioxanes suggest that simple chemistries might be used to create star and branched molecules akin to dendrimers with exceptional degrees of functionality in early generations. Furthermore, the single crystal silica core offers the potential for good thermal and mechanical stability. Thus, we have begun to explore the utility of these types of silsesquioxanes as routes to highly functional materials for a variety of applications.[12,13]

Since our initial patent on the Heck functionalization of OVS to produce highly luminescent, high-T_g, amorphous, and thermally stable functionalized silsesquioxanes,[13] several groups have reported using cubic silsesquioxanes as end, pendant, and star core components to construct new luminescent materials. Of particular interest are four recent papers on polyfluorene systems that target improved solubility and resistance to aggregation.

[†] Department of Chemistry, University of Michigan.

[‡] Department of Materials Science and Engineering, University of Michigan.

[§] Macromolecular Science and Engineering Center, University of Michigan.

[⊥] Kyoto University.

10.1021/ma0501141 CCC: \$30.25

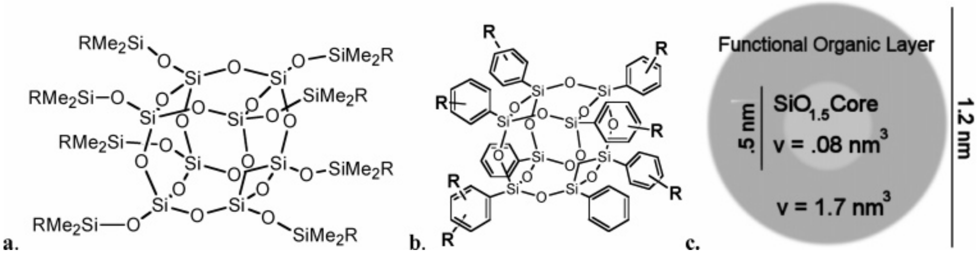
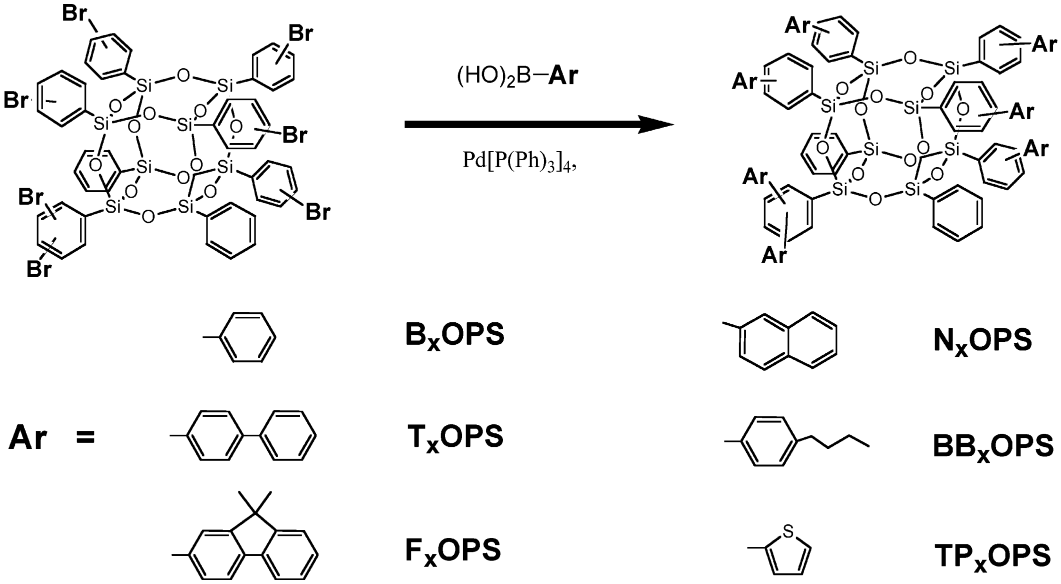


Figure 1. Cubic silsesquioxanes. (a) Q8 (Q = SiO_4); R = H, vinyl, epoxy, 3-hydroxypropyl, aminopropyl, glycidylepoxy, ethylcyclohexylepoxy, methacrylate, etc. (b) PhT8/OPS (T = carbon−$SiO_{1.5}$); R = Br, NH_2, alkyl, alkene, acetylene, acyl, azo, etc. R = same or mixed. (c) Typical sizes/volumes.

Scheme 1. Synthesis of Arylated Phenyloctasilsesquioxanes (Ar_xOPS)



Xiao et al. describe end-capping several luminescent oligomers, including poly(9,9-dioctylfluorene) (PFO) with *p*-(bromophenyl)hepta(cyclopentyl)octasilsesquioxane.[14] A second paper by Shim et al. describes the synthesis PFO with pendant hepta(cyclopentyl)octasilsesquioxanes.[15] Jen et al. use still a third format for coupling PFO with octa(*p*-bromophenethyl)octasilsesquioxane to produce an (PFO-phenethyl)octasilsesquioxane star polymer.[16] A fourth paper by Wei et al. uses 9,9-anilino groups as points of attachment to tether heptacylopentyloctasilsesquioxane units and include these units as comonomers in PFO copolymers.[17] A related paper by Huang et al. couples brominated OPS (Br_xOPS, where x is average number of bromines per molecule) with alkylated bromobenzenes and biphenyls via Grignard chemistry to form alkylated polyarylsilsesquioxanes (Ar_xOPS).[18] This report suggests that the resulting compounds act as organic quantum dots, a potentially exciting result. Furthermore, it suggests that Suzuki coupling does not work well for these systems.

We recently described the detailed synthesis and characterization of Br_xOPS compounds in a patent and a paper.[19] We find, contrary to the Huang et al. paper, Suzuki coupling worked quite well for the synthesis of a biphenyl derivative. Given our continuing interest in the use of silsesquioxanes as nanobuilding blocks for polyfunctional and luminescent materials, we decided to explore the use of Suzuki coupling as a route to these types of materials. Also, after examining the absorption and emission data for the biphenyl material we obtained, we did not observe the same luminescence behavior as reported previously,[18] providing further impetus for the efforts reported here.

We now report the Suzuki coupling of $Br_{5.3}$OPS to a variety of aryl borates, including phenyl, biphenyl, naphthyl, thiophene, and 9,9-dimethylfluorene (Scheme 1). These materials are very robust, highly soluble, and in the case of the fluorenyl derivative (F_xOPS) offer unexpected luminescence properties, but not properties consistent with quantum dots. The choice of $Br_{5.3}$OPS is predicated on the fact that it consists of a mixture of discrete octameric phenylsilsesquioxane cores containing three to eight bromines per molecule, with the average being 5.3. As reported elsewhere, detailed analysis of the bromination pattern indicates that substitution is primarily *para* (65%) and *meta* (25%) relative to the silica core with <3% dibromination. This is important because bromination beyond Br_8OPS changes the substitution pattern greatly, generating >80% *ortho, meta*, or 2,5-dibromophenyl groups, which can be expected to lead to much different luminescence behavior.

Experimental Section

Materials. Toluene was purchased from Fisher and distilled from Na/benzophenone under N_2 prior to use. Brominated phenylsilsesquioxane was produced by previously published methods.[20] 9,9-Dimethylfluorene-2-boronic acid was prepared according to the following literature procedure.[21] All other chemicals were purchased from Fisher or Aldrich and used as received.

General Suzuki Coupling of Br5.3OPS. To a dry 50 mL Schlenk flask under N_2 was added 0.500 g of $Br_{5.3}$OPS

(1.83 mmol of Br) and $Pd(PPh_3)_4$ (0.076 mmol, 26 mg, 4%). Dry toluene (15 mL) was then added by syringe, followed by 1.75 mL of K_2CO_3 saturated water, phase transfer catalyst Aliquat 336 (0.100 mL), and the arylboronic acid (5.76 mmol). The mixture was stirred at 100 °C for 24 h and then quenched by precipitation into 150 mL of hexane. The solution was then filtered, and the solid was redissolved in 10 mL of THF. This solution was then filtered through a 1 cm Celite column to remove bulk Pd particles and then was further purified by column chromatography (silica, 10:1 hexane:ethyl acetate) and dried in vacuo for 3 h.

All compounds were synthesized using this procedure except for naphthylboronic acid, which was done at half scale.

Analytical Methods. Thermogravimetric Analyses. All TGA analyses were performed on a Perkin-Elmer TGA-7 thermogravimetric analyzer (Perkin-Elmer Co., Norwalk, CT), under dry air with a flow rate of 60 mL/min and a heating rate of 10 °C/min. Alumel and iron supplied by the manufacturer were used to calibrate the system. Samples were dried under vacuum for a minimum of 3 h prior to analysis and heated to 120 °C for 10 min inside the TGA before analysis to remove adsorbed water.

Gel Permeation Chromatography. All GPC analyses were performed on a Waters 440 system equipped with Waters Styragel columns (7.8 × 300, HT 0.5, 2, 3, 4) with RI detection using an Optilab DSP interferometric refractometer and THF as solvent. The system was calibrated using polystyrene standards and toluene as reference.

Matrix-Assisted Laser Desorption/Time-of-Flight Spectrometry. MALDI−TOF was performed on a Micromass TofSpec-2E equipped with a 337 nm nitrogen laser in positive-ion reflection mode using poly(ethylene glycol) as the calibration standard, dithranol as the matrix, and $AgNO_3$ as the ion source. Samples were prepared by mixing solutions of five parts dithranol (10 mg/mL in THF), five parts sample (1 mg/mL in THF), and one part $AgNO_3$ (2.5 mg/mL in water) and blotting the mixture on the target plate.

UV−Vis Spectroscopy. Spectra were taken on a Shimadzu UV-1601 UV−vis transmission spectrometer in THF. Dried samples were weighed, dissolved in a known amount of THF, and diluted to a concentration (10^{-6}−10^{-7} M) where the absorption maximum was less than 10% for a 1 cm path length.

Photoluminescence Spectroscopy. Photoluminescent spectra were taken on a Fluoromax-2 fluorimeter in THF using 270 nm excitation. Samples from UV−vis spectroscopy were used at 31-fold dilution (10^{-7}−10^{-8} M) to avoid excimer formation and self-absorption.

PLE (Quantum Efficiency). PLE was determined by a modification of the relative method described by Demas and Crosby[22a] using anthracene[22b] and 1,10-diphenylanthracene[22c] as references. The adsorption at 270 nm was determined for each material at three different concentrations. These samples were then diluted 31-fold, and the total area of the emission spectrum was calculated. For each solution, adsorption and emission measurements were repeated a minimum of three times and averaged. The slope of a plot of emission vs adsorption was determined for each material, and the relative quantum efficiency calculated according to the equation

$$\Phi_{PL(x)} = (A_s/A_x)(F_x/F_s)(n_x/n_s)^2\Phi_{PL(s)}$$

where x is the sample to measured, s the reference, A the absorption at the excitation wavelength, F the total integrated emission, n the refractive index of the solvent, and Φ_{PL} the quantum yield.

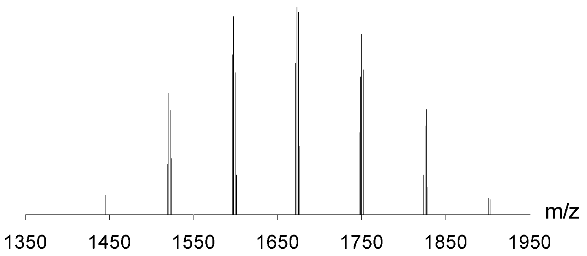


Figure 2. MALDI−TOF of B_xOPS (Ag^+ ion); B_6OPS(Ag^+) = 1597.2 g/mol.

Results and Discussion

Suzuki coupling was run using a variety of commercially available aryl borates and $Pd(PPh_3)_4$ as catalyst. The reaction solution was a biphasic water/toluene solution (see experimental) that reduced the potential for base-catalyzed ring-opening polymerization of the silsesquioxane cage. This approach affords >99% conversion of $Br_{5.3}$OPS to Ar_xOPS for all aryl borates tested. All of the compounds are highly soluble in common organic solvents such as THF, acetone, ethyl acetate, and toluene.

A variety of techniques were used to characterize these materials, including MALDI−TOF analysis. Figure 2 shows the MALDI−TOF analysis of B_xOPS as representative of the series (see SI for MALDI−TOF of other materials). The spectrum consists of a series of peaks separated by 76 amu, consistent with the sequential addition of phenyl units to OPS. The center and breadth of the distribution generally match the distribution found in the $Br_{5.3}$OPS precursor.

It is important to note that while the mass data for MALDI−TOF spectra are correct as determined by modeling of the isotope patterns, the derived distribution patterns are not perfectly quantitative. Slight differences in distribution can occur as a result of differing ionization potentials of particular molecular species, especially those with higher degrees of substitution. This generally weights the MALDI−TOF average distributions to larger values, as discussed elsewhere for the precursor $Br_{5.3}$OPS, which has an average degree of substitution of 5.7 when calculated by MALDI−TOF.[19] For Ar_xOPS compounds, MALDI−TOF-calculated average degrees of substitution were even higher, ranging from six to eight. This could be an artifact of the ionization potential differences or representations of true but small increases in "x" due to selectivity (e.g., higher solubility) during purification. In all cases, only small amounts of $x > 8$ were detected.

All samples were chromatographically purified to ensure the purities required for photoluminescence and eventually electroluminescence studies. Chromatographic yields ranged from 30 to 60% with the naphthyl

Table 1. GPC and TGA Data for Ar_xOPS Compounds ($x \approx 6$−8)

		MALDI Ar_6POS (Ag^+)		GPC				TGA	
molecule	yield (%)	found	calculated	M_n	M_w	PDI	$Td_{5\%}$	CY	calculated
F_xOPS	59	2295.0	2294.5	1521	1594	1.05	480	22.8	25.0
B_xOPS	49	1597.2	1597.2	904	920	1.02	440	35.2	33.5
T_xOPS	38	2054.0	2054.3	1231	1256	1.02	440	33.4	26.1
BBOPS	41	1934.2	1934.5	1312	1412	1.08	400	29.1	27.8
NP_xOPS	28	1896.8	1898.3	1181	1256	1.06	450	38.9	28.3
TP_xOPS	52	1632.7	1632.9	987	1018	1.03	510	26.4	32.8

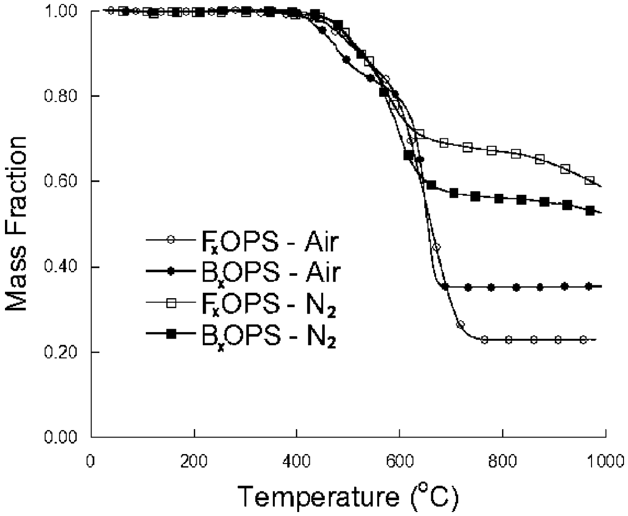


Figure 3. UV−vis spectra (dilute THF) of Ar$_x$OPS materials.

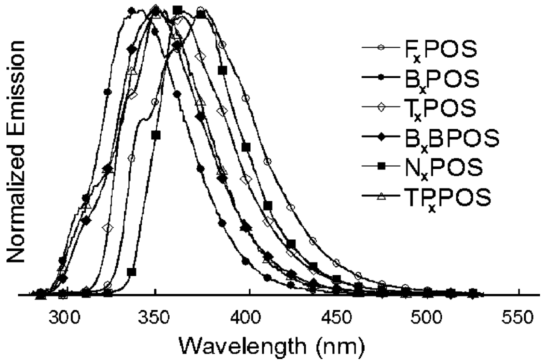


Figure 4. PL emission spectra (dilute THF) of Ar$_x$OPS materials.

substituents being the most problematic to isolate from the excess naphthylboronic acid. Table 1 provides pertinent analytical data for these materials. Note that the Td$_{5\%}$ (in air) values are quite high, indicating the robust nature of these materials. Indeed, there is no difference in air or N$_2$ for the decomposition of F$_x$OPS (Figure 3). For BB$_x$OPS, which contains alkyl chains, the TGA exhibits two distinct mass loss steps (Figure 3) that begin slightly earlier in air, corresponding first to loss of the alkyl chains followed by loss aryl fragments. For the purely aromatic B$_x$OPS, T$_x$OPS, and N$_x$OPS, the TGA ceramic yields in air are high because of the propensity of these materials to graphitize.

The measured values of M_n and M_w are smaller than expected from MALDI−TOF, but typical of GPC characterization of rigid spherical molecules using flexible, linear polystyrene standards.[11,12,19] The narrow PDIs found in GPC analyses additionally confirm the retention of the silica core and the lack of base promoted cage-opening polymerization.

Photophysical Properties. All of the Ar$_x$OPS materials exhibit absorption and emission spectra (Figures 4 and 5) similar to those expected for their small molecule analogues untethered to the silsesquioxane core. There appears to be a slight red shift of 20−30 nm from the free organic molecules. Given the electron-withdrawing nature of the SiO$_{1.5}$ unit,[23] one would normally expect a blue shift. We believe that these red shifts are related to some conjugation of the silicon vertex with the aromatic rings. However, this contrasts with stilbene−functional silsesquioxanes, which we will report on elsewhere, which show a 60−80 nm red shift relative to the corresponding small molecules.[24]

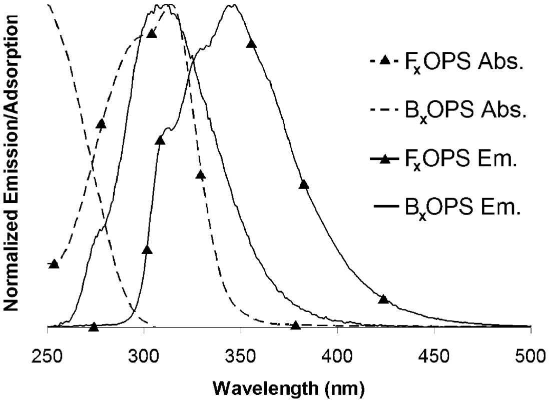


Figure 5. UV−vis and PL spectra of FOPS and BOPS.

Table 2. Spectral Data for Ar$_x$OPS and Related Materials

compound	ext coeff[a]	UV max (nm)	PL max (nm)	Φ_{PL} (%)[a]
F$_x$OPS	1.17×10^5	312	377	98
B$_x$OPS	3.43×10^4	250	342	10
T$_x$OPS	5.46×10^4	285	349	23
BB$_x$OPS	3.06×10^4	263	348	35
N$_x$OPS	2.13×10^5	291	362	38
TP$_x$OPS	3.81×10^4	271	350	9
PFO[16]		384	417	72
biphenyl[25]		251	313	17
terphenyl[25]		276	337	84

[a] Measured at maximum absorption wavelength in THF.

Photoluminescence quantum yields (Φ_{PL}) were calculated relative to anthracene and 9,10-diphenylanthracene standards and are reported (Table 2) as an average of three measurements. For the simplest material, B$_x$OPS, the observed $\Phi_{PL} = 10\%$ matches closely the reported value for biphenyl of 17%.[25] However, for the terphenyl[25] derivative, Φ_{PL} decreases markedly from 84% to 23% upon attachment to the silsesquioxane core. Incorporation of a naphthyl group provides a moderate red shift and a Φ_{PL} close to the 44% reported for the small molecule analogue.[26] Some improvements in efficiency from 10% to 35% were obtained with the addition of a *para n*-butyl group on the terminal ring (BB$_x$OPS), consistent with the findings of Huang et al.[18]

As the photoluminescent measurements were made in dilute solution ($\sim 10^{-7}$ M) and at several dilutions without a change in Φ_{PL}, it is unlikely that this effect is due to a decrease in molecular aggregation as suggested by Huang et al. for thin films of similar small molecules.

Figure 6 shows exemplary plots of the absorption and emission spectra of B$_x$OPS and F$_{5x}$OPS, which reveal normal 0−0 transitions typical of aromatic compounds and not the very narrow emissions reported by Huang et al. as suggesting quantum dot behavior.[18] This may be a consequence of a different substitution patterns in their original Br$_x$OPS, as their reported method of bromination differed from that used here, and no information was provided concerning the breadth of distribution or isomeric distribution pattern.

Perhaps the most significant finding of our studies is the Φ_{PL} observed for F$_x$OPS. It is substantially different than the other members of the series in both its spectra and quantum efficiency. The above-cited work on poly(9,9-*R,R*)fluorene/silsesquioxanes indicates that solution Φ_{PL} data range from 0.54 to 0.99 for the various materials[14−17] prepared with maximum emissions occurring at ≈420 nm. F_xOPS is structurally quite different from these materials in that there is direct conjugation with the vertex Si, which we believe can significantly change the emission wavelengths and Φ_{PL}. We hope to report further on this in the future.

The important issue here is that it may be possible to shift the emission wavelength closer to 420 nm without the need to form a polymer, perhaps using Br_{16}OPS, which we can make in high yield at the 100 g scale.[19] This offers the potential opportunity to avoid the green luminescence that competes with blue luminescence in typical polyfluorenes due either to aggregation or as the work of Wei et al. suggests due to oxidation of some of the materials.[17] The methyl substituents used here are much less susceptible to oxidation than the octyl groups currently used to increase solubility.

Conclusions

The use of polybromophenyloctasilsesquioxanes, which can be made at 100 g scales at room temperature, provides excellent nanoconstruction sites for the introduction of a number of functional groups. They also permit, through simple Suzuki coupling, complete conversion of all bromo substituents to aryl and heteroaromatic substituents on the OPS core. Furthermore, the resulting materials offer excellent solubility in multiple solvents, are stable to very high temperatures in air, and, in the case of the 9,9-dimethylfluorene derivative, offer unusually efficient photoluminescence behaviors. The resulting compounds can in principle be further functionalized to tailor a wide variety of properties, which represents the goal of current efforts.

Acknowledgment. We thank NSF IGERT (DGE-9972776), Matsushita Electric Ltd., Mayaterials Inc., Kuraray Inc., Delphi Inc., Nippon Shokubai, and Guardian Glass Science & Technology Center for support of this work.

Supporting Information Available: MALDI−TOF data for all Ar_xOPS compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Jenekhe, S. A. Special Issue on Organic Electronics. *Chem. Mater.* **2004***,* 16.

(2) (a) Hung, L. S.; Chen, C. H. *Mater. Sci. Eng., R* **2002***, 39*, 143. (b) Mitschke, U.; Bäuerle, P. *J. Mater. Chem.* **2000**, *10*, 1471.

(3) (a) Katz, H. E.; Bao, Z. *J. Phys. Chem. B* **2000**, *104* 671. (b) Afzali, A.; Dimitrakopoulos, C. D.; Breen, T. L. *J. Am. Chem. Soc.* **2002**, *124*, 8812.

(4) (a) Tan, L.; Curtis, M. D.; Francis, A. H. *Chem. Mater.* **2003**, *15,* 2272. (b) Liu, Y.; Yang, C.; Li, Y.; Li, Y.; Wang, S.; Zhuang, J.; Liu, H.; Wang, N.; He, X.; Li, Y.; Zhu, D. *Macromolecules*, in press.

(5) (a) Trimpin, S.; Grimsdale, A. C.; Rader, H. J.; Mllen, K. *Anal. Chem.* **2002**, *7*, 3777. (b) Wu, J.; Fechtenktter, A.; Gauss, J.; Watson, M. D.; Kastler, M.; Fechtenktter, C.; Wagner, M.; Mllen, K. *J. Am. Chem. Soc.* **2004**, *126*, 11311.

(6) (a) Mihov, G.; Scheppelmann, I.; Mllen, K. *J. Org. Chem.* **2004**, *69*, 8029. (b) Wiesler, U.-M.; Berresheim, A. J.; Morgenroth, F.; Lieser, G.; Mllen, K.; *Macromolecules* **2001**, *34*, 187.

(7) (a) Spetseris, N.; Ward, R. E.; Meyer, T. Y. *Macromolecules* **1998**, *31*, 3158. (b) Gaab, K. M.; Thompson, A. L.; Xu, J.; Martinez, T. J.; Bardeen, C. J. *J. Am. Chem. Soc.* **125**, 9288.

(8) (a) Devadoss, C.; Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996***, 118*, 9635. (b) Mikroyannidis, J. A. *Chem. Mater.* **2003**, *15* 1865.

(9) Freeman, A. W.; Koene, S. C.; Malenfant, P. R. L.; Thompson, M. E.; Frechet, J. M. M. *J. Am. Chem. Soc.* **2000**, *122*, 12385.

(10) (a) Lehmann, M.; Fischbach, I.; Spiess, H. W.; Meier, H. *J. Am. Chem. Soc.* **2004**, *126*, 774. (b) Deb, S. K.; Maddux, T. M.; Yu, L. *J. Am. Chem. Soc.* **1997**, *119*, 9097.

(11) (a) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 1741. (b) Feher, F. J.; Budzichowski, T. A.; Blanski, R. L.; Weller, K. J.; Ziller, J. W. *Organometallics* **1991**, *10*, 2526. (c) Feher, F. J.; Soulivong, D.; Eklud, A. G.; Wyndham, K. D. *Chem. Commun.* **1997**, 1185. (d) Feher, F. J.; Blanski, R. L. *J. Am. Chem. Soc.* **1992**, *114*, 5886. (e) Severn, J. R.; Duchateau, R.; van Santen, R. A.; Ellis, D. D.; Spek, A. L. *Organometallics* **2002**, *1*, 4. (f) Duchateau, R.; Abbenhuis, H. C. L.; van Santen, R. A.; Meetsma, A.; Thiele, S. K.-H.; van Tol, M. F. H. *Organometallics* **1998**, *26*, 5663. (g) Maxim, N.; Magusin, P. C. M. M.; Kooyman, P. J.; van Wolput, J. H. M. C.; van Santen, R. A.; Abbenhuis, H. C. L. *Chem. Mater.* **2001**, *13*, 2958. (h) Bonhomme, C.; Toledano, P.; Maquet, J.; Livage, J.; Bohnomme-Coury, L. *J. Chem. Soc., Dalton Trans.* **1997**, 1617. (i) Bassindale, A. R.; Pourny, M.; Taylor, P. G.; Hursthouse, M. B.; Light, M. E. *Angew. Chem., Int. Ed.* **2003**, *42*, 3488. (j) Bassindale, A. R.; Parker, D. J.; Pourny, M.; Taylor, P. G.; Horton, P. N.; Hursthouse, M. B. *Organometallics* **2004**, *23*, 4400. (k) Tsuchida, A.; Bollin, C.; Sernetz, F. G.; Frey, H.; Mülhaupt, R. *Macromolecules* **1997**, *30*, 2818. (l) Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem. Rev.* **1995**, *95*, 1409. (m) Provatas, A.; Matisons, J. G. *Trends Polym. Sci.* **1997**, *5*, 327. (n) Loy, D. A.; Shea, K. J. *Chem. Rev.* **1995**, *95*, 1431. (o) Voronkov, M. G.; Lavrent'yev, V. I. *Top. Curr. Chem.* **1982**, *102*, 199.

(12) (a) Tamaki, R.; Choi, J.; Laine, R. M. *Chem. Mater.* **2003**, *15*, 793. (b) Choi, J.; Tamaki, R.; Kim, S. G.; Laine, R. M. *Chem. Mater.* **2003**, *15*, 3365. (c) Laine, R. M.; Choi, J.; Lee, I. *Adv. Mater.* **2001**, *13*, 800. (d) Choi, J.; Yee, A. F.; Laine, R. M. *Macromolecules* **2003**, *15,* 5666.

(13) (a) Sellinger, A.; Laine, R. M. in United States Patent (Canon Kabushiki Kaisha (Tokyo, JP), USA, 2003. (b) Sellinger, A.; Tamaki, R.; Laine, R. M.; Ueno, K.; Tanabe, H.; Williams, E. Jabbour, G. E. Solution processable nanocomposites based on silsesquioxane cores for use in organic light emitting diodes (OLEDs), to be submitted for publication.

(14) Xiao, S.; Nguyen, M.; Gong, X.; Cao, Y.; Wu, H.; Moses, D.; Heeger, A. J. *Adv. Funct. Mater.* **2003**, *13*, 25.

(15) Lee, J.; Cho, H.-J.; Jung, B.-J.; Cho, N.-S.; Shim, H.-K. *Macromolecules* **2004**, *37,* 8523.

(16) Lin, W.-J.; Chen, W.-C.; Wu, W.-C.; Niu, Y.-H.; Jen, A.-K. *Macromolecules* **2004,** *37,* 2335.

(17) Chou, C. H.; Hsu, S. L.; Dinakaran, K.; Chiu, M.-Y.; Wei, K.-H. *Macromolecules,* in press.

(18) He, C.; Xiao, Y.; Huang, J.; Lin, T.; Mya, K.; Zhang, X. *J. Am. Chem. Soc.* **2004**, *126*, 7792.

(19) (a) Laine, R. M.; Tamaki, R.; Choi, J. WO 02/100867 A1 Dec 19, 2002. (b) Brick, C.; Tamaki, R.; Kim, S.-G.; Asuncion, M. Z.; Mark Roll, M.; Nemoto, T.; Ouchi, Y.; Laine R. M. *Macromolecules* **2005**, *38*, 4655.

(20) Li, R.; Lim, C. *J. Chem. Phys.* **1972**, *57*, 605.

(21) Suzuki, K.; Seno, A.; Tanabe, H.; Ueno, K. *Synth. Met.* **2004**, *143*, 89.

(22) (a) Demas, J.; Crosby, G. *J. Phys. Chem.* **1971**, *75*, 991. (b) *Standards for Fluorescence Spectrometry*; Miller, J. N., Ed.; Chapman and Hall: London, 1981. (c) Hamai, S.; Hirayama, F. *J. Phys. Chem.* **1983**, *87*, 83.

(23) Feher, F. J.; Budzichowski, T. A. *J. Organomet. Chem.* **1989***, 379,* 33.

(24) Laine, R. M.; Brick, C.; Tamaki, R.; Rush, J.; Asuncion, M. Z.; Neurock, M.; Filhol, J.-S.; Lee, C.-Y. Highly Red Shifted, Luminescent Emissions from Stilbeneoctasilsesquioxanes, to be submitted for publication.

(25) Nijegorodov, N. I.; Downey, W. S.; Danailov, M. B. *Spectrochim. Acta, Part A* **2000**, *56*, 783.

(26) Lentz, P.; Blume, H.; Schulte-Frohlinde, D. *Ber. Bunsen-Ges. Phys. Chem.* **1970**, *74*, 484.

MA0501141