JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Subscriber access provided by American Chemical Society

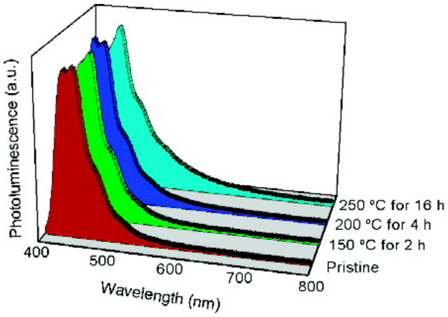
Communication

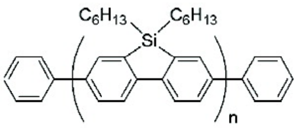
Poly(2,7-dibenzosilole): A Blue Light Emitting Polymer

Khai Leok Chan, Mary J. McKiernan, Carl R. Towns, and Andrew B. Holmes

J. Am. Chem. Soc., **2005**, 127 (21), 7662-7663• DOI: 10.1021/ja0508065 • Publication Date (Web): 05 May 2005

Downloaded from http://pubs.acs.org on March 25, 2009





More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 28 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

High quality. High impact.

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Published on Web 05/05/2005

Poly(2,7-dibenzosilole): A Blue Light Emitting Polymer

Khai Leok Chan,[†,§] Mary J. McKiernan,[‡] Carl R. Towns,[‡] and Andrew B. Holmes*[,†,§]

Melville Laboratory for Polymer Synthesis, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, United Kingdom, Cambridge Display Technology Limited, Building 2020, Cambourne Business Park, CB3 6DW, United Kingdom, and Bio21 Institute, University of Melbourne, Parkville, Victoria 3010, Australia

Received February 7, 2005; E-mail: aholmes@unimelb.edu.au

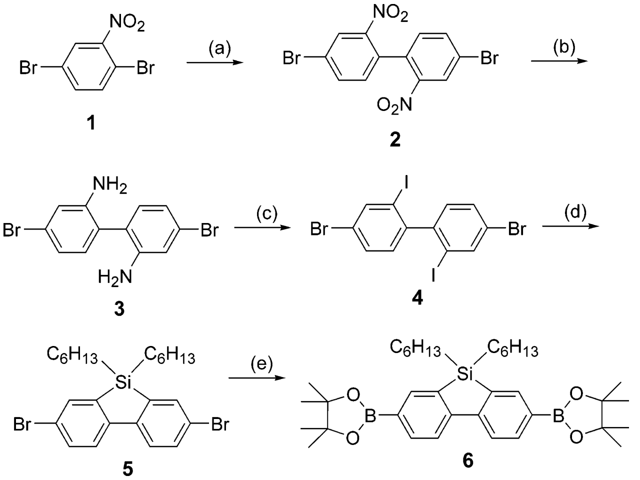
Since the discovery of electroluminescence from conjugated polymers, real progress has been made toward the development of materials for commercially viable display devices.[1−3] Polyfluorene and derivatives have emerged as the dominant class of polymers for commercial applications.[4] They have been shown to exhibit high luminescence quantum efficiencies, thermal stability, and good solubility. However, under certain circumstances, they develop an unwanted long wavelength emission that has most recently been attributed to the formation of carbonyl groups at the C-9 position.[5] In light of this, we decided to explore polymers in which the vulnerable C-9 carbon in polyfluorene is replaced by a heteroatom, such as silicon. A further attraction of such a polymer is the expected enhancement of electron affinity owing to the $\sigma^*-\pi^*$ conjugation, as observed in analogous molecular and polymeric siloles.[6]

In this Communication, we report the preparation of 2,7-functionalized dibenzosilole monomers **5** and **6** and their Suzuki cross-coupling to prepare poly(9,9-dihexyl-2,7-dibenzosilole) **7**. The physical and optoelectronic properties of polydibenzosilole are compared with those of an analogous polyfluorene and an alternating copolymer of the two.

The known Ullmann coupling product **2** was reduced to the corresponding diamine **3**[7] which was diazotized with nitrosylsulfuric acid in concentrated sulfuric acid.[8] Sandmeyer reaction of the resulting diazonium salt with concentrated KI solution gave 4,4′-dibromo-2,2′-diiodobiphenyl **4** in 30% yield. Conventional diazotization with nitrous acid followed by Sandmeyer reaction afforded a much poorer yield (15%) of **4**. The low yield for this reaction is presumably a consequence of intramolecular cyclization of the first formed iodo substituent onto the neighboring 2′-position by the decomposition of the second diazonium substituent to give a dibenzoiodonium iodide salt.[9] This was minimized by use of a 10-fold excess of KI.

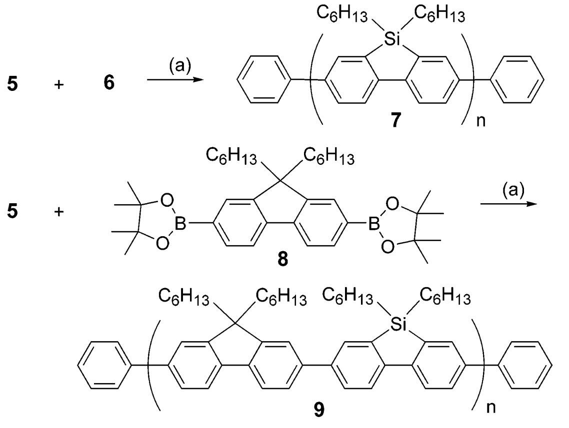
The most direct route to the corresponding dibenzosilole would be the selective trans-lithiation of the 2,2′-iodo substituents in the presence of the apparently more accessible 4,4′-bromo substituents and subsequent cyclization with a dialkyldihalosilane.[10] In the event, treatment of **4** with 4 equiv of *t*-BuLi in THF followed by addition of dichlorodihexylsilane gave 2,7-dibromo-9,9-dihexyldibenzosilole **5** in 52% yield. The counterpart for the cross-coupling reaction, the dibenzosilole-2,7-diboronic ester **6**, was readily prepared by double lithiation of **5** followed by the formation of the bis(boronate) ester **6**, as shown in Scheme 1.

Scheme 1. Synthesis of Monomers **5** and **6**[a]



[a] Reagents and conditions: (a) Cu, DMF, 125 °C, 88%; (b) Sn, HCl, EtOH, 110 °C (bath temp.), 72%; (c) nitrosylsulfuric acid, concentrated H_2SO_4, 0 °C, then aq. KI, −10 to 50 °C, 30%; (d) *t*-BuLi (4 equiv), THF, −90 to −78 °C, then $(C_6H_{13})_2SiCl_2$, 25 °C, 52%; (e) *t*-BuLi, diethyl ether, −78 °C, then 2-isopropoxy-4,4′,5,5′-tetramethyl-1,3,2-dioxaboralane, 25 °C, 86%.

Scheme 2. Synthesis of the Homopolymer **7** and Copolymer **9**[a]



[a] Reagents and conditions: (a) $Pd(OAc)_2$, tricyclohexylphosphine, NEt_4OH, toluene, 90 °C, then $PhB(OH)_2$, then PhBr. Yield **7** (93%), **9** (94%).

The Suzuki polycondensation of the dibromide **5** with the diboronic ester **6** (Scheme 2) was carried out under basic conditions with the $Pd(OAc)_2$/tricyclohexylphosphine catalyst system in a biphasic system of toluene and aqueous tetraethylammonium hydroxide[11] with phenyl group endcapping to afford poly(9,9-dihexyl-2,7-dibenzosilole) **7** in 93% yield; the molecular weight of **7** was determined by GPC analysis with polystyrene standards, $M_w = 220\,000$ and $M_n = 31\,000$ (DP ≈ 90). Copolymers can similarly be prepared between **1** or **2** and their correspondingly functionalized aromatic partners. For instance, the alternating copolymer **9** was prepared in 94% yield from the dibromide **5** and

---

[†] Melville Laboratory for Polymer Synthesis.
[‡] Cambridge Display Technology Limited.
[§] Bio21 Institute.

10.1021/ja0508065 CCC: $30.25 © 2005 American Chemical Society

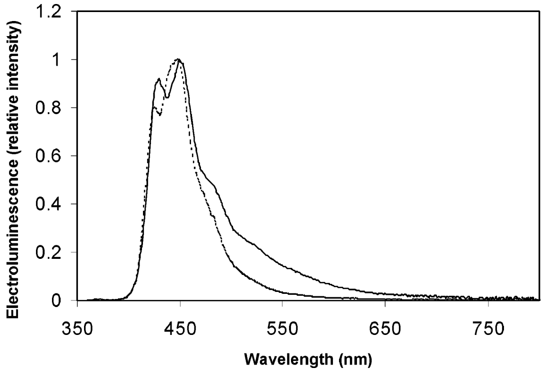


Figure 1. Electroluminescence emission spectra of polymer **7** (—) and PF8 (- - -).

the fluorene bis(boronate) **8** (Scheme 2) under similar reaction conditions; $M_w = 425\,000$ and $M_n = 109\,000$ (DP ≈ 160). Both polymers **7** and **9** are completely soluble in common organic solvents, such as chloroform and THF.

The optical properties of polymer **7** are remarkably similar to those of poly(9,9-dioctyl-2,7-fluorene) (PF8). The absorption maximum in the UV−vis spectrum of a thin film of **7** ($\lambda_{max} = 390$ nm) is comparable with that of PF8 ($\lambda_{max} = 389$ nm), and the optical band gaps, determined from the λ_{0-0} band edges, are 2.93 eV for both polymers. The photoluminescence (PL) emission maximum (excitation at 325 nm) of a film of polymer **7** at 425 nm and its two vibronic sidebands at 449 and 482 (*CIE* coordinates $x = 0.15$, $y = 0.11$, PL efficiency = 62%) are all within 3 nm of the corresponding bands for PF8 (PL efficiency = 60%). These observations suggest that the extent of π-conjugation within the two polymers is comparable and indicate the similarity of the poly-*p*-phenylene backbones as chromophores.

Preliminary results for the electroluminescence emission spectrum of the homopolymer **7** were measured on a single layer device in the configuration ITO/PEDOT/polymer(65 nm)/Ba/Al and showed very promising device characteristics with emission maxima at 431 and 451 nm and an efficiency slightly superior to that of the corresponding device fabricated with a single layer of PF8 (Figure 1).[12]

To test the thermal stability, films of polymer **7** ($T_g = 149$ °C) and PF8 were annealed under air and ambient light, and the PL emission spectra were recorded (Figure 2). Films of PF8 degraded as evidenced by the appearance of a broad green band centered at 535 nm in the photoluminescence spectrum. In contrast, **7** maintained its color integrity even after annealing at 250 °C for 16 h. The HOMO and LUMO energy levels of **7** in thin film were determined by cyclic voltammetry to be −5.77 and −2.18 eV, respectively. These are about 0.1 eV lower than the corresponding levels for PF8 when measured under the same conditions with a potential advantage of lowering the energy barrier for electron injection.

In summary, the successful synthesis of 2,7-functionalized dibenzosilole building blocks has opened the door to a new class of high energy gap light emitting polymers with the potential to avoid development of unwanted long wavelength emission under operation.

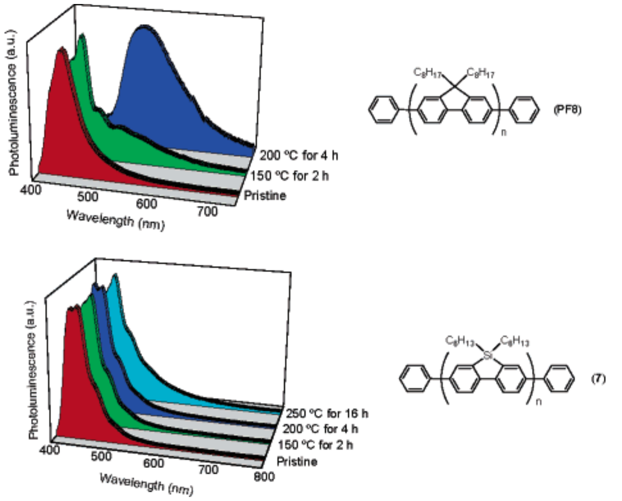


Figure 2. Effect of thermal aging on PL spectrum of **7** and PF8 under air and ambient light.

Acknowledgment. We thank the Gates Cambridge Trust and the Universities UK (scholarships to K.L.C.), the Engineering and Physical Sciences Research Council (UK), the European Commission, the Australian Research Council and VESKI for generous financial support. We thank Drs. S. Watkins, I. Grizzi, C. Murphy, A. Goodsell, and S. Goddard (CDT) for their interest in this work.

Supporting Information Available: Experimental procedures and characterization of **2**−**7** and **9**, UV−vis, PL, EL, DSC, and TGA data for **7** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

(2) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402.

(3) Friend, R. H.; Gymer, W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121.

(4) (a) Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. *Adv. Mater.* **2000**, *12*, 1737. (b) Leclerc, M. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2867. (c) Scherf, U.; List, E. J. W. *Adv. Mater.* **2002**, *14*, 477. (d) Rees, I. D.; Robinson, K. L.; Holmes, A. B.; O'Dell, R.; Towns, C. R. *MRS Bull.* **2002**, *27*, 451.

(5) (a) List, E. J. W.; Güntner, R.; Scanducci de Freitas, P.; Scherf, U. *Adv. Mater.* **2002**, *14*, 374. (b) Lupton, J. M.; Craig, M. R.; Meijer, E. W. *Appl. Phys. Lett.* **2002**, *80*, 4489. (c) Gaal, M.; List, E. J. W.; Scherf, U. *Macromolecules* **2003**, *36*, 4236.

(6) (a) Yamaguchi, S.; Endo, T.; Uchida, M.; Izumizawa, T.; Furukawa, K.; Tamao, K. *Chem.*—*Eur. J.* **2000**, *6*, 1683. (b) Palilis, L. C.; Mäkinen, A. J.; Uchida, M.; Kafafi, Z. H. *Appl. Phys. Lett.* **2003**, *82*, 2209.

(7) Patrick, D. A.; Boykin, D. W.; Wilson, W. D.; Tanious, F. A.; Spychala, J.; Bender, B. C.; Hall, J. E.; Dykstra, C. C.; Ohemeng, K. A.; Tidwell, R. R. *Eur. J. Med. Chem.* **1997**, *32*, 781.

(8) We thank Mr. S. Y. Cho for drawing our attention to this commonly used diazotizing agent for dyestuff chemistry.

(9) Lothrop, W. C. *J. Am. Chem. Soc.* **1941**, *63*, 1187.

(10) (a) Gilman, H.; Gorsich, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 1883. (b) Liu, Y.; Stringfellow, T. C.; Ballweb, D.; Guzei, I. A.; West, R. *J. Am. Chem. Soc.* **2002**, *124*, 49.

(11) Towns, C. R.; O'Dell, R. PCT Int. Appl. 2000 WO200053656-A1 20000914; *Chem. Abstr.* **2000**, *133*, 238529.

(12) We thank Drs. C. Murphy and I. Grizzi (CDT) for these data.

JA0508065