www.publish.csiro.au/journals/ajc

# **Organosilicon Compounds with Blue Photoluminescence Properties**

Guorong Zheng,<sup>A</sup> Wei Li,<sup>A</sup> Zixing Wang,<sup>A</sup> and Ping Lu<sup>A,B</sup>

<sup>A</sup> Department of Chemistry, Zhejiang University, Zhejiang 310027, P.R. China.

<sup>B</sup> Author to whom correspondence should be addressed (e-mail: pinglu@zju.edu.cn).

A series of  $\pi$ -conjugated compounds and related Si compounds with blue photoluminescent properties have been prepared. Structures of products were confirmed by NMR spectra and mass spectrometry. Photoluminescent properties are discussed. Based on luminescent properties, these Si compounds might find utility as emitters in organic light-emitting diode displays.

Manuscript received: 5 March 2004. Final version: 18 May 2004.

# Introduction

Electroluminescence (EL) devices have been studied because of their potential application in full-colour flat-panel displays.<sup>[1]</sup> Compared to other display technologies, organic light-emitting diodes (OLEDs) show unique advantages, for example, low driving voltage, wide viewing angle, easy processing, high brightness, and ultra-thin layers.<sup>[2–5]</sup> However, the lifetimes of OLEDs limit their application in large-area displays. The synthesis of new organic materials with better properties is an effective way to solve this restrictive problem. Organic compounds and polymers based on an sp<sup>2</sup>-hybridized carbon skeleton<sup>[6,7]</sup> have been developed for this purpose. Compared to polymers, organic compounds are easier to purify by sublimation, have exact molecular weight, and give rise to high colour purity.<sup>[6]</sup>

With sp<sup>2</sup>-conjugated systems, there are at least three practical considerations. The rigidity of the molecule will definitely influence device fabrication. The solubility of the molecule will affect its preparation and purification. Finally, a red shift of the absorption and emission is observed as the molecular weight increases. To investigate these, several organosilicon compounds have been synthesized:<sup>[7]</sup> silicon has empty d orbitals that can conjugate with carbon p orbitals to form d–p conjugation. Silicon partially interrupts the conjugated systems. The net result is that the absorption and emission could be blue-shifted and the colour purity improved. On the other hand, these molecules are more flexible and easier to fabricate.

A new type of organic light-emitting material with silicon inserted into an sp<sup>2</sup>-hybridized carbon skeleton has been synthesized by a Wittig–Horner reaction in moderate yields (Scheme 1). Both the absorption and emission  $\lambda_{max}$  of **2a** and **2b** are blue-shifted. In the case of **2c** the absorption is blue-shifted, while the emission  $\lambda_{max}$  is split into two peaks (see Fig. 3). Based on their relative lower melting points (Table 1), 2a, 2b, and 2c are more flexible than 1a, 1b, and 1c.

# **Results and Discussion**

## Synthesis and Thermal Properties

The synthetic routes are described in Scheme 1. A Grignard reaction between p-tolylmagnesium bromide and dichlorodimethylsilane yields dimethylditolylsilane **3**. Treatment of **3** with *N*-bromosuccinimide and dibenzoyl peroxide in carbon tetrachloride yields the corresponding bis(bromomethyl)phenyldimethylsilane **4**. Bis[4-(diethoxy phosphoryl)methyl]phenyldimethylsilane **5** was prepared by an Arbuzov reaction between **4** and triethylphosphite in toluene.

Conjugated compounds **1a–1c** were synthesized by a Wittig–Horner reaction between the appropriate carbonyl compound and bis[4-(diethoxyphosphoryl)methyl]biphenyl in good yield. Products were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and mass spectrometry (MS). Compounds **1a**, **1b**, and **1c** show poor solubility and high thermal stability. Analogous silicon-containing compounds (**2a**, **2b**, and **2c**) were highly soluble in common organic solvents.

# **Photoluminescence** Properties

Table 1 lists the  $\lambda_{max}$  for the UV absorption and photoluminescence (PL) spectra of six compounds in tetrahydrofuran (THF). As shown, the absorption  $\lambda_{max}$  arising from the  $\pi - \pi^*$  transition of the diphenyl-based conjugated compounds (1a, 1b, and 1c) ranged from 364 to 369 nm, while the absorption  $\lambda_{max}$  of the silicon-containing compounds (2a, 2b, and 2c) ranged from 327 to 336 nm. These were blue-shifted an average of 35 nm compared to those of the diphenyl-based compounds (1a, 1b, and 1c). In the PL spectra, the emission  $\lambda_{max}$  of 1a, 1b, and 1c ranged from 416 to 439 nm, while those



Scheme 1. Synthesis of organic emitters.

 
 Table 1. Properties of organic emitters with or without silicon insertion

| Compound no. | mp [°C]    | Absorption $\lambda_{max}$ [nm] | Emission<br>λ <sub>max</sub> [nm] | Quantum<br>yield |
|--------------|------------|---------------------------------|-----------------------------------|------------------|
| 1a           | 280 (dec.) | 369                             | 416, 439                          | 0.55             |
| 1b           | 280 (dec.) | 365                             | 416, 438                          | 0.21             |
| 1c           | 260-262    | 364                             | 428                               | 0.0075           |
| 2a           | 185-186    | 335                             | 391                               | 0.061            |
| 2b           | 138-140    | 327                             | 378                               | 0.016            |
| 2c           | 110-112    | 336                             | 418, 438                          | 0.0052           |

of **2a**, **2b**, and **2c** are between 378 and 438 nm, respectively (Figs 1 and 2).

Luminescence was observed for both 1c and 2c (Fig. 3) although the quantum yields were low, being 0.0075 and 0.0052, respectively. As previously reported,<sup>[8]</sup> no luminescence was found when the linkage was a 1,4-phenylene ring.

In the case of the silicon compounds, the backbone is more flexible. This may be because of the longer Si–C bond (1.91 Å) compared to the C–C bond (1.53 Å). This will



Fig. 1. UV-vis and emission spectra of 1a and 2a.

disturb the coplanarity of the  $\pi$ -conjugated compounds and reduce their crystallinity. In other words, the compounds with silicon insertion should be good candidates for blue emitters in OLED displays.



Fig. 2. UV-vis and emission spectra of 1b and 2b.



Fig. 3. UV-vis and emission spectra of 1c and 2c.

# Conclusion

In conclusion, a series of blue emitters were synthesized in moderate yields by a Wittig–Horner reaction, and fully characterized by spectroscopy. Their thermal and optical properties were investigated. The results indicated that these new silicon-inserted compounds are highly promising materials for the development of stable, blue, electroluminescent emitters. Further investigation of the thermal behaviour and photoluminescence properties of these new molecules is in progress.

#### **Experimental**

#### Instruments

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a Bruker AVANCE DMX500 spectrometer operating in the FT mode. Five percent w/v solutions in CDCl<sub>3</sub> or (CD<sub>3</sub>)<sub>2</sub>SO were used to obtain NMR spectra. Tetramethylsilane (TMS) was used as an internal standard. A Hewlett Packard 5989B electron-impact mass spectrometer was used to obtain mass spectra. Fluorescence measurements were made with an RF-5301 spectrofluorometer (Shimadzu, Kyoto, Japan) equipped with a xenon lamp. UV-vis absorption spectra were recorded on a Shimadzu UV-265 spectrophotometer. Quantum yields are calculated based on POPOP (1,4-bis(5-phenyloxazol-2-yl)benzene) as standard.<sup>[9]</sup>

# *Typical Procedure for the Synthesis of Symmetrical Compounds* (*1a*, *1b*, and *1c*)

4,4'-Bis[(diethoxyphosphoryl)methyl]biphenyl (4 mmol) and a carbonyl compound (8 mmol, see Scheme 1) were dissolved in 30 mL of toluene. The mixture was heated under stirring to  $110^{\circ}$ C. To this solution, solid potassium *tert*-butoxide (12 mmol) was added in one portion. After refluxing for 3 h, solvent was removed by rotary evaporation. The residue was dissolved in chloroform, precipitated from methanol, and filtered. The product was purified by recrystallization from chloroform/methanol.

Compound **1a**, yield 85%, decomposition above 280°C (Found: C 78.0, H 4.8. Calc. for C<sub>24</sub>H<sub>18</sub>S<sub>2</sub>: C 77.8, H 4.9%).  $\delta_{\rm H}$  ((D<sub>6</sub>)DMSO) 7.00 (2H, d, *J* 16.3), 7.08 (2H, dd, *J*<sub>1</sub> 4.6, *J*<sub>2</sub> 3.7), 7.24 (2H, d, *J* 3.7), 7.47 (2H, d, *J* 4.6), 7.50 (2H, d, *J* 16.3), 7.66 (4H, d, *J* 8.3), 7.72 (4H, d, *J* 8.3); *m/z* (EI) 370 (100%, M<sup>+</sup>).

Compound **1b**, yield 84%, decomposition above 280°C (Found: C 84.9, H 5.4. Calc. for C<sub>24</sub>H<sub>18</sub>O<sub>2</sub>: C 85.2, H 5.4%).  $\delta_{\rm H}$  ((D<sub>6</sub>)DMSO) 6.56–6.58 (4H, m), 7.04 (2H, d, *J* 16.4), 7.19 (2H, d, *J* 16.4), 7.66 (4H, d, *J* 8.4), 7.72 (6H, d, *J* 8.4).  $\delta_{\rm C}$  (CDCl<sub>3</sub>) 110.1, 112.8, 117.5, 126.6, 127.3, 127.6, 136.6, 139.2, 143.7, 153.5. *m/z* (EI) 338 (100%, M<sup>+</sup>).

Compound **1c**, yield 80%, mp 260–262°C (Found: C 95.0, H 5.8. Calc. for C<sub>40</sub>H<sub>26</sub>: C 94.8, H 5.2%).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 7.11 (2H, dd,  $J_1$  7.9, 7.2), 7.34 (4H, dd, J 7.3, 7.2), 7.40 (2H, t, J 7.2), 7.72–7.76 (12H, m), 7.82 (6H, dd, J 6.4, 7.9).  $\delta_{\rm C}$  119.9, 120.1, 120.5, 124.7, 126.9, 127.1, 127.3, 128.5, 128.9, 130.2, 130.3, 136.5, 136.8, 137.0, 139.5, 139.9, 140.4, 141.7. *m/z* (EI) 506 (23.15%, M<sup>+</sup>).

#### Synthesis of 2a and 2b

Bis[4-(diethoxyphosphoryl)methyl]phenyldimethylsilane (5 mmol) and a carbonyl compound (10 mmol, Scheme 1) were dissolved in 30 mL of toluene. Potassium *tert*-butoxide (12 mmol) was added. The mixture was stirred at room temperature for 4 h and the solvent was removed. The residue was purified by column chromatography (silica gel) using *n*-hexane/dichloromethane (20:1); **2a** and **2b** were obtained.

Compound **2a**, yield 72%, mp 185–186°C (Found: C 72.4, H 5.8. Calc. for C<sub>26</sub>H<sub>24</sub>S<sub>2</sub>Si: C 72.9, H 5.6%).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 0.56 (6H, s), 6.92 (2H, d, *J* 16.1), 6.99–7.00 (2H, m), 7.06 (2H, d, *J* 3.4), 7.18 (2H, d, *J* 5.0), 7.26 (2H, d, *J* 16.1), 7.44 (4H, d, *J* 7.9), 7.50 (4H, d, *J* 7.9).  $\delta_{\rm C}$  (CDCl<sub>3</sub>) –0.007, 124.5, 126.8, 128.0, 128.6, 129.9, 130.6, 136.9, 139.9, 140.1, 145.2. *m/z* (EI) 428 (73.62%, M<sup>+</sup>).

Compound **2b**, yield 76%, mp 137–140°C (Found: C 78.5, H 5.9. Calc. for C<sub>26</sub>H<sub>24</sub>O<sub>2</sub>Si: C 78.8, H 6.1%).  $\delta_{\rm H}$  (CDCl<sub>3</sub>, TMS) 0.55 (6H, s), 6.34–6.41 (4H, m), 6.92 (2H, d, *J* 16.3), 7.02 (2H, d, *J* 16.3), 7.39 (2H, s), 7.43 (4H, d, *J* 7.9), 7.49 (4H, d, *J* 7.9).  $\delta_{\rm C}$  (CDCl<sub>3</sub>, TMS) 0.002, 111.2, 114.1, 119.3, 128.1, 129.4, 136.9, 139.9, 140.1, 144.6, 155.6. *m/z* (EI) 396 (77.84%, M<sup>+</sup>).

#### Synthesis of 2c

Compound 2c was prepared as above except that the mixture was stirred at  $110^{\circ}$ C for 10 min.

Compound **2c**, yield 70%, mp 110–112°C (Found: C 89.3, H 5.9. Calc. for  $C_{42}H_{32}Si$ : C 89.3, H 5.7%).  $\delta_{H}$  (CDCl<sub>3</sub>) 0.67 (6H, s), 7.07 (2H, dd,  $J_1$  3.05,  $J_2$  3.07), 7.29–7.36 (8H, m), 7.59–7.62 (4H, m), 7.65–7.67 (6H, m), 7.70 (4H, d, J 7.55), 7.77 (2H, d, J 7.45).  $\delta_{C}$  (CDCl<sub>3</sub>) 0.9, 122.9, 123.0, 123.5, 127.7, 129.9, 130.3, 130.4, 131.5, 131.9, 132.0, 137.6, 139.8, 139.9, 141.0, 141.5, 142.5, 142.8, 144.6. *m/z* (EI) 564 (8.02%, M<sup>+</sup>).

# Acknowledgments

P.L. thanks the National Science Foundation (20074032, 20374045) and the Ministry of Education of China for financial support.

## References

- [1] C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.* **1987**, *51*, 913. doi:10.1063/1.98799
- [2] A. Kraft, A. C. Grimsdale, A. B. Holmes, Angew. Chem. Int. Ed. 1998, 37, 402. doi:10.1002/(SICI)1521-3773(19980302)37:4<402::AID-ANIE402>3.0.CO;2-9
- [3] G. Grem, G. Leditzky, B. Ullrich, G. Leising, *Adv. Mater.* **1992**, *4*, 36.
- [4] Z. Yang, I. Sokolik, F. E. Karasz, Macromolecules 1993, 26, 1188.
- [5] T. Zyung, D. H. Hwang, I. N. Kang, H. Shim, K. L. Hwang, W. Y. Kim, *Chem. Mater.* **1995**, *7*, 1499.
- [6] P. Lu, H. Hong, G. P. Cai, P. Djurovich, W. P. Weber, M. E. Thompson, J. Am. Chem. Soc. 2000, 122, 7480. doi:10.1021/JA000354Q
- [7] K. D. Kim, J. S. Park, H. K. Kim, T. B. Lee, K. T. No, *Macromolecules* 1998, 31, 7267. doi:10.1021/MA980349V
- [8] J. M. Kauffman, G. Moyna, J. Org. Chem. 2003, 68, 839. doi:10.1021/JO020333+
- [9] M. Mardelli, J. Olmsted, J. Photochem. 1977, 7, 277. doi:10.1016/0047-2670(77)85005-3