



Synthesis and photophysical properties of highly emissive compounds containing a dibenzosilole core

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ABSTRACT

A series of new rigid rod-like molecules consisting of a dibenzosilole core, ethynylene linkages, and different aryl end-groups has been synthesized by palladium-catalyzed Sonogashira cross-coupling reactions. These compounds exhibit intense blue to green emissions with high quantum efficiencies and good thermal stabilities.

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π -Conjugated rigid rod-like molecules containing ethynylene linkages have attracted considerable interest due to their fascinating properties relating to organic light-emitting devices (OLEDs),¹ phototransistors,² molecular wires,³ and chemosensors.⁴ Molecules with various fluorophores, such as fluorene,⁵ carbazole,⁶ benzothiadiazole,⁷ and siloles (silacyclopentadienes),⁸ have been constructed. Molecules of this class generally exhibit high photoluminescence efficiencies and maximum orientation as a consequence of their extremely stiff, linear backbones.⁹

On the other hand, in recent years, dibenzosiloles or 9-silafluorenes, the silicon-bridge containing analogs of fluorenes, have received increasing attention as building blocks for the construction of opto-electronic functional materials. A series of polymers containing dibenzosilole units¹⁰ has been developed, and some of them display high potential as thermally stable blue-light emitting materials,¹¹ as hosts for green electrophosphorescent emitters,¹² or as p-channel materials with excellent OFET performance.¹³ However, little attention has been paid to rigid rod-like molecules that combine ethynylene linkages with a dibenzosilole unit. In this Letter, we wish to report the synthesis of new rigid rod-like molecules consisting of a dibenzosilole core, ethynylene linkages, and different aryl end-groups. Their photophysical properties and thermal behavior are also discussed.

The synthetic route is outlined in Scheme 1. Based on a facile and efficient synthesis of 6,6'-diiodo-4,4'-dibromo-3,3'-dime-

thoxybiphenyl (**1**), Huang and co-workers developed a general synthetic method for the 2,7-dibromo-9-heterofluorenes, by which **2a** and **2b** were prepared in yields of 12% and 63%, respectively.¹⁴ By slightly modifying Huang's method in this work, **2a** and **2b** were obtained in higher yields of 93% and 68%, respectively.¹⁵

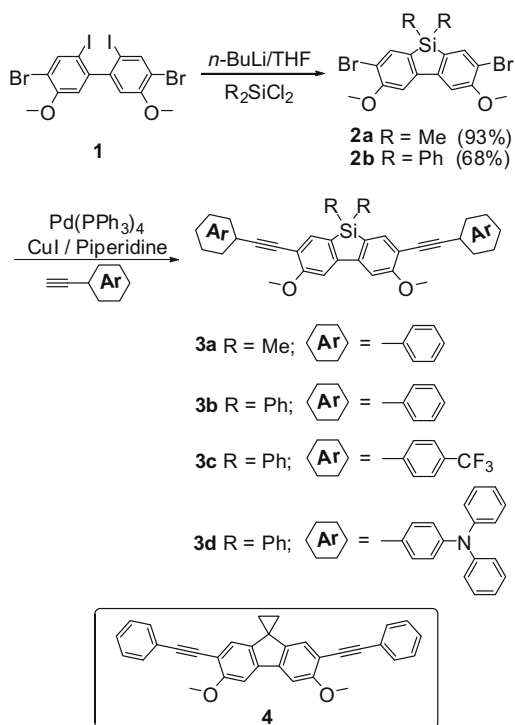
With **2a** and **2b** in hand, we then carried out the synthesis of the target molecules containing a dibenzosilole core and ethynylene linkages by Sonogashira cross-coupling reactions. Thus, the reaction of **2a** with phenylacetylene in piperidine solution at 80 °C with Pd(PPh₃)₄ and CuI as co-catalysts produced **3a** in 65% yield. Similarly, **3b**, **3c**, and **3d** were prepared by reactions of **2b** with different phenylacetylene derivatives¹⁶ in yields of 59%, 75%, and 83%, respectively.¹⁷ All of the new compounds were fully characterized by ¹H NMR, ¹³C NMR, and elemental analysis.

A single crystal of **3b** suitable for X-ray analysis was obtained from a solution in an ethanol/CH₂Cl₂ solvent mixture, and its structure is shown in Figure 1. Compound **3b** crystallizes in an orthorhombic crystal system with space group *Pbca*. One of the terminal phenyl rings (P1) is almost coplanar with the plane of the dibenzosilole core, with a torsion angle of 7.39°, while the other phenyl ring (P2) adopts a perpendicular arrangement relative to the core, with a torsion angle of 89.24°.¹⁸

The normalized UV–vis absorption and emission spectra of **3a–d** in acetonitrile solution are shown in Figure 2. Details of their photophysical and thermal properties are summarized in Table 1, together with those of compound **4**¹⁹ for comparison. In solution, all compounds containing a dibenzosilole core exhibit strong absorptions and intense emissions, with their absorption maxima

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Scheme 1. Synthesis of 2,7-bis(arylethynyl)-dibenzosiloles **3a–d**.

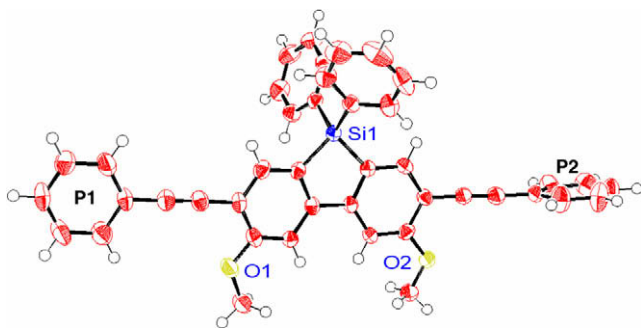


Figure 1. ORTEP diagram of compound **3b**.

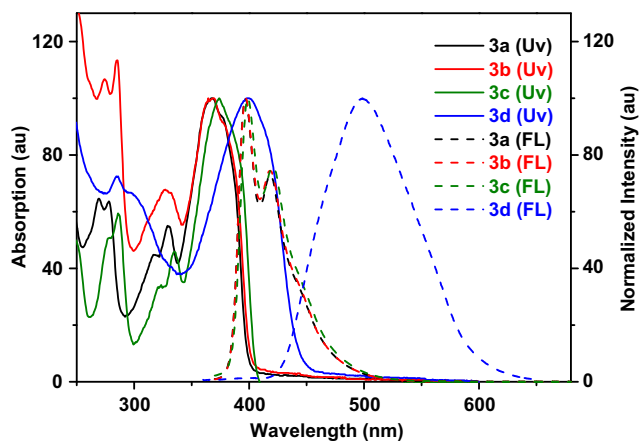


Figure 2. Normalized UV-vis and fluorescence spectra of **3a–d** in acetonitrile.

in the range 367–399 nm and their emission maxima in the range 397–499 nm. Compounds **3a** and **3b** exhibit almost identical

Table 1
Optical and thermal properties of compounds **3a–d**

| Compound | $\lambda_{\text{abs}}^{\text{max,a,b}}$ (nm) | $\log \epsilon$ | $\lambda_{\text{em}}^{\text{max,a,c}}$ (nm) | $\Phi_{\text{f}}^{\text{a,d}}$ | $T_{\text{m}}^{\text{e}}/T_{\text{d}}^{\text{f}}$ (°C) |
|-----------------------|--|-----------------|---|--------------------------------|--|
| 3a | 367 | 4.9 | 397, 418 | 0.89 | 208/346 |
| 3b | 368 | 4.7 | 397, 419 | 0.86 | 249/424 |
| 3c | 374 | 4.7 | 399, 421 | 0.75 | 307/412 |
| 3d | 399 | 4.9 | 499 | 0.46 | 294/445 |
| 4 ^g | 348 | — | 371, 391 | 1.00 | 186/302 |

^a In acetonitrile solution.

^b All compounds show vibronic absorption spectra. Only the longest absorption maxima are listed.

^c Excited at 350 nm.

^d Determined with anthracene as a standard.

^e Melting points measured by DSC under N_2 .

^f Decomposition temperatures (5% weight loss) measured by TGA under N_2 .

^g 2',7'-Bis(phenylethynyl)-spiro(cyclopropane-1,9'-fluorene) **4**, Ref. 19

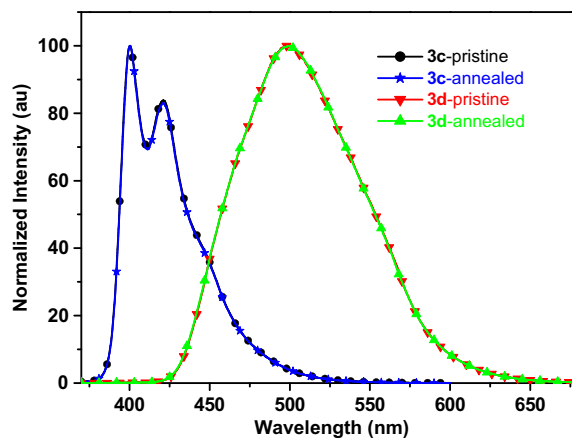


Figure 3. Fluorescence spectra of **3b** and **3d** (in acetonitrile) pristine, and annealed.

absorption and emission spectra, suggesting that substituents attached to the silicon atom have negligible influence on their photo-physical properties. Compared with those of **3b**, the absorption and emission maxima of compound **3c** are only slightly red-shifted, while significant bathochromic shifts are seen for those of **3d**. This indicates that although increasing either the electron-withdrawing or electron-donating character of the end-groups leads to either core-to-periphery or periphery-to-core intramolecular charge transfer,²⁰ the electron-donating groups show a more pronounced effect. In addition, both the absorption and emission bands of **3a** show significant red-shifts relative to those of analog **4** containing a fluorene core owing to the effective $\sigma^*(\text{Si-C})-\pi^*$ conjugation, while maintaining comparable fluorescence efficiency (fluorescence spectra of **3a** in different solvent were shown in Supplementary data).^{11,21} All of the molecules show intense emissions, with their fluorescence quantum yields ranging from 0.46 to 0.89 in acetonitrile solution.

To test their optical stabilities, powder samples of **3a–d** were annealed in air at 200 °C for 10 h. After annealing, the samples were each dissolved in acetonitrile and their fluorescence spectra were recorded. **Figure 3** shows the normalized fluorescence spectra of both pristine and annealed **3b** and **3d**. No new emission bands were detected for either of the annealed samples, each sample showing an identical spectrum to that of the corresponding pristine material. This suggests that these new compounds have good optical stabilities.²²

The thermal properties of **3a–d** under nitrogen atmosphere were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and the results are listed in **Table 1**. DSC analyses of **3a–d** showed relatively high melting

points, while no glass transition temperatures were observed. Broad exothermic peaks, which are typical of cross-linking reactions of acetylene groups, were observed in the DSC thermograms of each of the compounds, centered at 377, 381, 367, and 385 °C for **3a–d**, respectively (see Supplementary data).²³ The TGA results clearly indicate that all of the new compounds have good thermal stability. The decomposition temperatures (T_d) corresponding to 5% weight loss were measured as 346, 424, 412, and 445 °C for **3a–d**, respectively, which are much higher than that of their carbon analog **4**. This is consistent with the finding that thermal stability may be improved by increasing the molecular volume or incorporating a heteroatom such as silicon.²⁴

In conclusion, we have synthesized a series of new highly emissive compounds consisting of a dibenzosilole core, ethynylene linkages, and various peripheral chromophoric units. These compounds exhibit blue to green emissions with high fluorescence quantum efficiencies in solution. They also display good optical stabilities and high thermal stabilities. Further studies on the optoelectronic properties of the present compounds as well as the incorporation of ethynyl-linked dibenzosilole units into π -conjugated polymers are underway in our laboratory.

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Supplementary data

Supplementary data (fluorescence spectra of **3a** in different solvent, ¹H and ¹³C NMR spectra, TGA and DSC curves for all new compounds) associated with this article can be found in the online version, at doi:10.1016/j.tetlet.2009.11.074.

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- A typical procedure for the synthesis of compound **2b**: *n*-BuLi (2.5 mol/L in hexane, 7.0 mL, 17.5 mmol) was added over 45 min to a solution of **1** (5.0 g, 8.0 mmol) in dry THF (80 mL) dropwise at –90 °C. The reaction mixture was stirred for further 2 h at –90 °C. Then dichlorodiphenylsilane (3.4 mL, 16.0 mmol) was added and the mixture was allowed to room temperature for 0.5 h and gently refluxed for 6 h. After cooled to room temperature, the reaction mixture was quenched with a saturated NH₄Cl aqueous solution, and extracted with chloroform. The organic layer was washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The mixture was purified by recrystallization from chloroform/ethanol to give **2b** (3.0 g, 5.4 mmol) in 68% yield as colorless crystals, mp 266 °C (DSC data). Compound **2a**: colorless crystals, 93% yield, mp 221 °C (DSC data). All the spectroscopic data of **2a** and **2b** were identical to that reported.¹⁴
- For the synthesis of (4-ethynylphenyl)diphenylamine, see: McLlroy, S. P.; Cló, E.; Nikolajsen, L.; Frederiksen, P. K.; Nielsen, C. B.; Mikkelsen, K. V.; Gothelf, K. V.; Ogilby, P. R. *J. Org. Chem.* **2005**, *70*, 1134.
- A typical procedure for the synthesis of compounds **3a–d**: To a 25 mL flask was charged with dibromodibenzosilole (0.54 mmol), Pd(PPh₃)₄ (62 mg, 0.054 mmol), and CuI (21 mg, 0.11 mmol). Then piperidine (6 mL) and arylacetylene (1.62 mmol) were added. The mixture was stirred at 80 °C for 8 h. After concentrated, water (10 mL) was added and the mixture was extracted with dichloromethane. The combined organic layers were washed with brine (20 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography to afford the title compound. Compound **3a**: yield: 65%; ¹H NMR (400 MHz, acetone-*d*₆): δ 7.82 (s, 2H), 7.74 (s, 2H), 7.55 (d, *J* = 6.9 Hz, 4H), 7.41 (m, 6H), 4.03 (s, 6H), 0.46 (s, 6H); ¹³C NMR (100 MHz, acetone-*d*₆): δ 163.5, 150.4, 138.4, 132.2, 131.9, 129.4, 129.1, 124.8, 113.0, 105.5, 94.6, 87.6, 56.4, -3.1; MS (EI) *m/z* (%): 470 (M⁺, 100%); Anal. Calcd for C₃₂H₂₆O₂Si: C, 81.66; H, 5.57. Found: C, 81.44; H, 5.48. Compound **3b**: yield: 59%; ¹H NMR (400 MHz, acetone-*d*₆): δ 7.98 (s, 2H), 7.87 (s, 2H), 7.73 (dd, *J* = 1.4, 7.7 Hz, 4H), 7.55 (dd, *J* = 1.7, 7.7 Hz, 4H), 7.49–7.36 (m, 12H), 4.06 (s, 6H); ¹³C NMR (150 MHz, acetone-*d*₆): δ 163.0, 150.4, 138.3, 135.3, 132.6, 131.3, 130.3, 128.5, 128.3, 127.8, 123.7, 112.7, 105.1, 94.1, 86.4, 55.6; MS (EI) *m/z* (%): 594 (M⁺, 100%); Anal. Calcd for C₄₂H₃₀O₂Si: C, 84.81; H, 5.08. Found: C, 84.80; H, 5.08; Compound **3c**: yield: 75%; ¹H NMR (400 MHz, acetone-*d*₆): δ 8.03 (s, 2H), 7.91 (s, 2H), 7.76 (s, 8H), 7.73 (d, *J* = 7.5 Hz, 4H), 7.49–7.42 (m, 6H), 4.08 (s, 6H); ¹³C NMR (100 MHz, acetone-*d*₆): δ 164.2, 151.8, 139.5, 136.2, 133.3, 132.8, 131.2, 130.2, 129.9, 129.2, 128.9, 126.4, 123.8, 113.0, 106.2, 93.6, 90.0, 56.6; MS (EI) *m/z* (%): 730 (M⁺, 100%); Anal. Calcd for C₄₄H₂₈F₆O₂Si: C, 72.32; H, 3.86. Found: C, 72.65; H, 3.58; Compound **3d**: yield: 83%; ¹H NMR (400 MHz, CDCl₃): δ 7.86 (s, 2H), 7.66 (d, *J* = 6.7 Hz, 4H), 7.44–7.35 (m, 12H), 7.28 (t, *J* = 7.7 Hz, 8H), 7.12 (d, *J* = 7.8 Hz, 8H), 7.06 (t, *J* = 7.4 Hz, 4H), 7.00 (d, *J* = 8.6 Hz, 4H), 4.08 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 162.6, 149.9, 147.9, 147.4, 138.8, 135.6, 132.7, 132.6, 130.3, 129.5, 128.4, 128.3, 125.1, 123.6, 122.5, 116.6, 113.3, 104.0, 95.1, 85.6, 56.2; MALDI-TOF: calcd: 928.3, found: 928.7; Anal. Calcd for C₆₆H₄₈N₂O₂Si: C, 85.31; H, 5.21; N, 3.01. Found: C, 85.09; H, 5.38; N, 3.17.
- Crystallographic data for **3b** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 721777. Copies of the data may be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44(0)1223 336033 or email: deposit@ccdc.cam.ac.uk).
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