

**Tri-aryls boron-based A- $\pi$ -A vs nitrogen-based D- $\pi$ -D quadrupolar compounds for single & two-photon excited fluorescences**

Zhi-Qiang Liu, Qi Fang\*, Du-Xia Cao, Dong Wang, Gui-Bao Xu

State Key laboratory of Crystal Materials, Shandong University, 250100 Jinan, P. R. China

E-mail: [fangqi@icm.sdu.edu.cn](mailto:fangqi@icm.sdu.edu.cn)

## **Experimental**

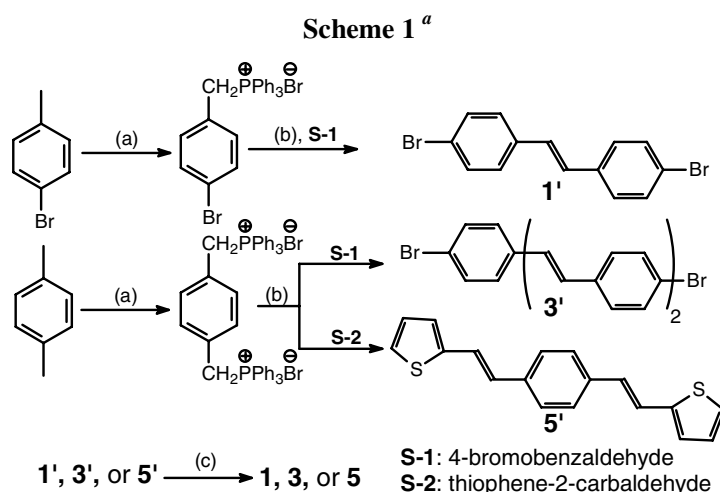
### **Synthesis and Characterization**

$^1\text{H}$  NMR spectra of the compounds were recorded on an FX-90Q Spectrometer. Electron Impact (EI, 70 eV) mass spectra were obtained on an Agilent 5973N MSD Spectrometer. The melting points were measured on a METTLER-TOLEDO DSC822e differential scanning calorimeter at a heating rate of  $20^\circ\text{C min}^{-1}$  under nitrogen atmosphere. Elemental analyses were obtained on a PE 2400 autoanalyser.

2-Thiophene-carboxaldehyde was purchased from Acros Ltd. Starting materials 4-(N, N-diphenylamino)benzaldehyde was prepared *via* the standard Vilsmeier reaction. Phosphonium salts was prepared in our lab as shown in Scheme 1. Dimesitylboron fluoride,  $\text{BF}(\text{Mes})_2$ , was purchased from the Aldrich Inc. The other reagents, such as *p*-bromo-benzaldehyde and *p*-bromo-toluene, were purchased from Shanghai Reagents Ltd. HPLC grade THF was freshly distilled with sodium-sand before use. All the chemical reactions were carried out under  $\text{N}_2$  atmosphere. Compounds **2** and **4** were synthesized according to published procedures<sup>[1,2]</sup>. Our synthesis strategy for boron-containing compound **1**, **3**, and **5** is outlined in Scheme 1.

**General procedure of Wittig reaction.** A mixture of phosphonium salt and aldehyde were suspended in about 50 mL freshly distilled THF, then BuOK in THF was added dropwise with stirring in an ice-bath. The mixture was continuously stirred at room temperature for further 20 h. All of the reactants were poured into 200 mL distilled water, and then the pH value was adjusted to 7.0 by addition of 0.1 M hydrochloric acid. The product was extracted with  $\text{CH}_2\text{Cl}_2$  twice. Then the organic layer was dried with anhydrous  $\text{MgSO}_4$  overnight. The solvent was removed by a rotary evaporator to get the crude product. To get the pure object compound with *trans*-conformation, the crude product was isomerized by dissolving in toluene and refluxing with trace amount of iodine for 4 h. After the solvent being removed, the residue was purified through column chromatography on silica gel using chloroform-petroleum ether (1: 3) as eluent.

**General procedure for the organoboron compounds 1, 3 and 5.** n-Butyl-lithium (1.6 M in hexane, 3 equivalent) was added slowly into a suspension of precursor (**1'**, **3'** and **5'**, 1 equivalent) in anhydrous THF at -78°C. One hour later, the temperature was allowed to naturally rise to room temperature and continuously stirred for further 1 h. Then the reactants were cooled to -78°C again, and dimesitylboron fluoride (2 equivalent) in appropriate quantity of THF was injected. The solution turned to dark-green at once, and finally to a clear fluorescent green color. The mixture was stirred overnight without cooling-bath. Then all the solvents were removed under reduced pressure. The residue was hydrolyzed and the product was extracted with chloroform. The organic layer was separated out and the solvent was removed to obtain viscous oil. This crude product was purified through column chromatography on silica gel using chloroform-petroleum ether (1: 5) as eluent.



<sup>a</sup> Reagents and condition: (a) i: NBS/BPO/CCl<sub>4</sub>/reflux/3 h; ii: PPh<sub>3</sub>/toluene/reflux/3 h; (b) t-KOBu/THF/0°C-RT/24 h; (c) n-LiBu/FB(Mes)<sub>2</sub>/THF/-78°C-RT/24 h.

***E*-4, 4'-Bis-(B, B-dimesitylboryl)-stilbene (1):** white powder. m. p. 128-131 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz) δ: 2.01 (s, 24H, *o*-CH<sub>3</sub>), 2.30 (s, 12H, *p*-CH<sub>3</sub>), 6.82 (s, 8H), 7.23 (s, 2H), 7.49 (s, 8H); MS (70 ev) *m/z* (%): 676(M<sup>+</sup>, 100); Anal. calcd for C<sub>50</sub>H<sub>54</sub>B<sub>2</sub>: C 88.76, H 8.04, found C 88.71, H 7.92.

**(*E, E*)-1, 4-Bis[4'-(B, B-dimesitylboryl) styryl]-benzene (3):** pale yellow powder. m. p. 134-138 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz) δ: 2.02 (s, 24 H, *o*-CH<sub>3</sub>), 2.31 (s, 12 H, *p*-CH<sub>3</sub>), 6.82 (s, 8 H), 7.11-7.49 (m, 16 H); MS (70 ev) *m/z* (%): 778(M<sup>+</sup>, 100); Anal. calcd for C<sub>58</sub>H<sub>60</sub>B<sub>2</sub>: C 89.46, H 7.77; found C 89.06, H 7.59.

**(*E, E*)-1, 4-Bis {2'-[5'-(B, B-dimesitylboryl) thiophen-2-yl]vinyl}-benzene (5):** yellow powder with yield 40 %. m. p. 176-180°C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz) δ: 2.14 (s, 24H), 2.31 (s, 12H), 6.83 (s, 8H), 7.09 ~ 7.40 (m, 12H); MS: *m/z* (%) 790 (5, M<sup>+</sup>); Anal. calcd for C<sub>54</sub>H<sub>56</sub>B<sub>2</sub>S<sub>2</sub>: C 82.02, H 7.14, S 8.11; found C 81.52, H 7.01, S 8.23.

## Optical measurement

All the solvents used for absorption spectra and fluorescence measurements were HPLC grade. For diluted solutions of  $C = 5.0 \times 10^{-6}$  mol/L, in quartz cuvettes of 1 cm path length, linear absorption spectra were recorded on a PE lambda 35 UV-VIS spectrometer. Steady state SPEF spectra and SPEF decay curves were recorded on an Edinburgh FLS920 fluorescence spectrometer equipped with a 450 W Xe lamp and a time-correlated single photon counting (TCSPC) card. All the SPEF spectra are corrected. Reconvolution fit of the decay profiles were made with F900 analysis software to get the lifetime value. To measure the quantum yields of these compounds,  $5.0 \times 10^{-6}$  mol/L fluorescein in 0.1 mol/L NaOH aquatic solution was used as the standard.

The TPEF emission spectra, TPEF excitation spectra and other TPEF properties were measured by a Coherent Mira 900 femtosecond Ti:sapphire laser as a pump source, and by a streak camera (Hamamatsu, model: C5680) in conjunction with an imaging spectrograph (Hamamatsu, model: C5094) as a recorder (see Figure 1). The laser beam was focused into the sample ( $C = 5.0 \times 10^{-4}$  mol/L) by a lens. The frequency up-converted fluorescence was collected at a direction perpendicular to the pump beam. To minimize the re-absorption, the excitation beam was focused as closely as possible to the quartz cell wall, which faced the slit of imaging spectrograph. The pulse width and repetition rate of the laser are 200 fs and 76 MHz respectively.

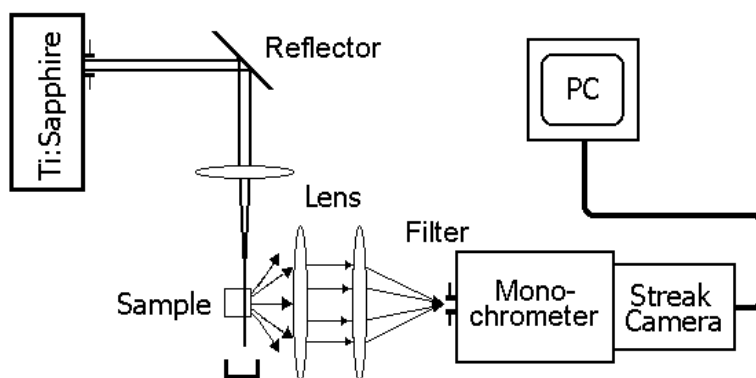


Figure1 . Experimental setup for TPEF measurement

1 Wang, X. M.; Wang, D.; Zhou, G. Y.; Yu, W. T.; Zhou, Y. F.; Fang, Q.; Jiang, M. H. *J. Mater. Chem.* **2001**, *11*, 1600.

2 Spangler, C. W.; Elandaloussi, E. H.; Ozer, B.; Ashworth, K.; Madrigal, L.; Reeves, B. *Mat. Res. Soc. Symp. Proc.* **2000**, *597*, 369.