

Supplementary Information

Concentration effects on spontaneous and amplified emission in benzo[c]fluorenes

K. Kazlauskas ^{a,*}, G. Kreiza ^a, E. Radiunas ^a, P. Adomėnas ^a, O. Adomėnienė ^a, K. Karpavičius ^a,
J. Bucevičius ^b, V. Jankauskas ^c, S. Juršėnas ^a

^a *Institute of Applied Research, Vilnius University, Saulėtekio 9-III, LT-10222 Vilnius, Lithuania*

^b *Department of Organic Chemistry, Faculty of Chemistry, Vilnius University, Naugarduko 24,
LT-03225 Vilnius, Lithuania*

^c *Department of Solid State Electronics, Vilnius University, Saulėtekio 9-III, LT-10222 Vilnius,
Lithuania*

* Corresponding author. Tel.: +370 5 2366032; fax: +370 5 2366059.

E-mail address: karolis.kazlauskas@ff.vu.lt (K. Kazlauskas).

2.1. Materials

The starting compounds, *i.e.*, indanone, aryl bromides, as well as various supplementary materials like NBS, hydrazine hydrate, ethyleneglycol etc were purchased from Sigma Aldrich and used as received.

2.1.1. 5,9-Dibromo-7,7-dimethyl-7H-benzo[c]fluorene

7,7-Dimethyl-7H-benzo[c]fluorene (40 g; 164 mmol) was dissolved in 200 ml dichloroethane, 0.5 g crystalline iodine was added. The mixture was cooled down to 5°C. Bromine (53 g; 330 mmol) was added to it at such rate, that the mixture temperature wouldn't exceed 15°C. After all bromine was introduced, the reaction mixture was stirred for 1.5 h, then poured into an aqueous sodium sulfite solution and extracted by dichloromethane. The organic solution was washed by water, the solvent evaporated, the remainder crystallized from hexane. 30 g product (yield 45.5%) obtained. White to off-white crystalline powder, m.p. 115-117°C. GC-MS: MW 402.0. C₁₉H₁₄Br₂, calculated: MW 402.12. ¹H-NMR (CDCl₃, 400MHz), δ, ppm: 8.695 (d, J=8.4 Hz, 1H), 8.409 (d, J=8.4Hz, 1H), 8.186 (d, J=8.4Hz, 1H), 7.935 (s, 1H), 7.8-7.46 (m, 4H), 1.564 (s, 6H). ¹³C-NMR (101 MHz, CDCl₃) δ, ppm: 156.76, 152.66, 138.70, 131.88, 130.60, 128.83, 127.87, 126.89, 126.35, 125.57, 124.64, 124.30, 123.48, 121.10, 47.339. 26.69.

2.1.2. 3-(9,9'-Dihexyl-9H-fluorenyl)boronic acid

3-Bromo-9,9'-dihexyl-9H-fluorene (26 g; 62 mmol) was dissolved in 200 ml anhydrous tetrahydrofuran (THF), the solution was cooled down to -70°C. 26 ml 25% butyllithium hexane solution (70 mmol) was added to it dropwise and stirred at this temperature for 1 h. Trimethylborate (10.4 g; 100 mmol) solution in 30 ml THF added dropwise to a resulting mixture and let to warm up to room temperature. To the stirred mixture 6 ml water, after this – 40 ml 10% sulphuric acid was added. The boronic acid was extracted by toluene (2 × 100 ml), evaporated, purified by flash-chromatography (silicagel, eluent hexane-ethyl acetate, 2:1). 13 g boronic acid was obtained, m.p. 150°C. Yield 55%.

2.1.3. 5,9-Diaryl-7,7-dimethyl-7H-benzo[c]fluorenes

5,9-Dibromo-7,7-dimethyl-7H-benzo[c]fluorene (0.402 g; 1 mmol) was dissolved in 20 ml toluene. Under argon atmosphere, 2 mmol corresponding boronic acid, 70 mg (0.1 mmol) palladium dichloride–triphenylphosphine complex, 55 mg (0.2 mmol) triphenylphosphine was added. The mixture was heated up to 70°C, 1 g sodium carbonate solution in 7 ml water was added. The mixture was refluxed under argon atmosphere for 6 h, then cooled down. 30 ml Toluene was added, the mixture was washed by water, layers separated. The palladium catalyst was removed from toluene layer by filtration, the solvent evaporated. The remainder was purified by column chromatography (silica-gel; eluent hexane-toluene, 12:1). Yield 60-70%.

2.1.4. 5,9-Bis-(4-ethoxyphenyl)-7,7-dimethyl-7H-benzo[c]fluorene (BF8)

M.p. 203-207°C. ¹H NMR (400 MHz, CDCl₃) δ 8.86 (d, *J* = 8.4 Hz, 1H), 8.40 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.74 – 7.49 (m, 9H), 7.10 – 7.03 (m, 4H), 4.16 (q, *J* = 7.6 Hz, 4H), 1.63 (s, 6H), 1.51 (t, *J* = 7.6 Hz, 6H). ¹³C NMR (101 MHz, C₆D₆) δ 158.52, 158.39, 155.41, 151.97, 138.93, 138.81, 133.77, 133.59, 132.39, 131.95, 131.33, 129.91, 128.17, 127.51, 126.40, 125.72, 125.02, 124.16, 123.22, 122.13, 120.71, 114.85, 114.31, 77.34, 77.02, 76.70, 63.59, 63.57, 46.87, 26.88, 14.95, 14.91.

2.1.5. 5,9-Bis-(4-biphenyl)-7,7-dimethyl-7H-benzo[c]fluorene (BF9)

M.p. 259°C. ¹H NMR (400 MHz, CDCl₃) δ 8.90 (d, *J* = 8.4 Hz, 1H), 8.48 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.86 – 7.70 (m, 13H), 7.68 – 7.41 (m, 10H), 1.67 (s, 6H).

2.1.6. 5,9-Bis-(9',9'-dihexylfluoren-3'-yl)-7,7-dimethyl-7H-benzo[c]fluorene (BF12)

The product was obtained in a glassy state. ¹H-NMR (CDCl₃, 400MHz), δ, ppm: 8.93 (1H, d, *J*=8.4 Hz), 8.51 (1H, d, *J*=8.4 Hz), 8.13 (1H, d, *J*=8.0 Hz), 8.09 (1H, d, *J*=1.4 Hz), 7.93–7.71(m, 8 H), 7.71-7.29 (m, 12 H), 2.08 (qnt, 8H), 1.72 (s, 6H), 1.19-1.12 (m, 25 H), 0.86-0.83 (m, 21H). ¹³C-NMR (101 MHz, CDCl₃) δ, ppm: 152.11, 151.16, 149.88, 141.80, 141.18, 141.01, 140.93, 140.13, 139.92, 139.72, 139.29, 132.59, 132.09, 129.98, 129.20, 129.06, 128.25, 127.71, 127.21, 126.80, 126.51, 126.31, 125.13, 124.20, 123.31, 123.19, 123.00, 122.93, 122.67, 122.26, 121.50, 121.28, 119.81, 119.78, 118.37, 55.04, 54.93, 47.04, 40.45, 31.59, 31.56, 29.84, 29.80, 26.98, 23.95, 23.87, 22.67, 22.63, 14.07, 14.05.

2.1.7. 2,7-Dibromo-9-(4-hexylphenyl)-9H-fluoren-9-ol

500 ml flask, connected with reflux condenser, dropping funnel and magnetic stirrer, was charged with 13.6 g (0.56 mol) magnesium turnings and 80 ml anhydrous tetrahydrofuran (THF), several drops dibromoethane added. 1-Bromo-4-hexylbenzene (125 g; 0.52 mol) solution in 250 ml THF was added dropwise to the said mixture, after this the resultant mixture heated to reflux for 2h, thus forming solution of Grignard reagent. An another 1L flask was charged with 2,7-dibromo-9H-fluoren-9-one (150 g; 0.44 mol) and 500 ml anhydrous THF. To this solution the above mentioned Grignard reagent was added dropwise at a rate, which maintained a slow boiling of the reaction mixture, then heated to reflux additionally 2-3 h. The mixture was cooled down and poured into 500 ml 2M hydrochloric acid, then extracted with dichloromethane (3 × 200 ml). The organic layer washed twice by water and evaporated. The obtained brown oil was used in the next step without a purification. 191 g (yield 87%) product was obtained.

2.1.8. 2,7-Dibromo-9-chloro-9-(4-hexylphenyl)-9H-fluorene

500 ml flask, connected with reflux condenser, stirred by a magnetic stirrer, was charged with crude 2,7-dibromo-9-(4-hexylphenyl)-9H-fluoren-9-ol (191 g; 0.382 mol) and 200 g (1.68 mol) thionyl chloride, heated at reflux for 16h. An excess of thionyl chloride was distilled off. The remainder – dark brown solid product – was used in the next step unpurified. Yield 160 g (80%).

2.1.9. 2,7-Dibromo-9-(4-hexylphenyl)-9H-fluorene

1 L flask, connected with reflux condenser and stirred by a magnetic stirrer, was charged with 300 ml glacial acetic acid and 160 g (0.308 mol) crude 2,7-dibromo-9-chloro-9-(4-hexylphenyl)-9H-fluorene. The mixture was heated to 60°C, zinc powder (60 g; 0.92 mol) was added to it portionwise during 8h. The reaction mixture was stirred for additional 8h at 60°C, then cooled down. A precipitate was formed, which was filtered off and washed by 2M hydrochloric acid (3 × 400 ml). The product was crystallized from 2-propanol. Yellow crystals, yield 105 g (70%), m.p. 114-116°C. ¹H-NMR (CDCl₃), δ, ppm: 0.906-0.952 (3H, t, -CH₃, J=6.9 Hz), 1.356-1.386 (6H, m), 1.588-1.644 (2H, m), 2.594-2.646 (2H, t, =C-CH₂-CH₂-, J=7.8 Hz), 5.011 (1H, s, -CH-), 6.976-7.003 92h, d, J=8.1Hz), 7.137-7.164 (2H, d, J=8.1 Hz), 7.465-7.556 (4H, m), 7.636-7.663 (2H, D, J=8.1Hz). ¹³C-NMR (CDCl₃) δ, ppm: 14.36, 22.86, 29.35, 31.65, 31.98, 35.91, 54.17, 121.49, 121.75, 128.34, 128.91, 129.26, 130.93, 136.99, 139.19, 142.45, 150.00.

2.1.10. 2,7-Dibromo-9-pentyl-9-(4-hexylphenyl)-9H-fluorene

100 ml flask, connected with reflux condenser and stirred by a magnetic stirrer, was charged with 40 ml DMSO, 5 g (10.3 mmol) 2,7-dibromo-9-(4-hexylphenyl)-9H-fluorene, 2.34 g (15.5 mmol) 1-bromopentane, 0.12 g (0.53 mmol) triethylbenzylammonium chloride and 40 g 50% aqueous sodium hydroxide solution. The mixture was stirred for 28 h at room temperature, then poured into 250 ml water, extracted with dichloromethane (3 × 50 ml). Organic layer washed by water 3 times, evaporated. The remainder was crystallized from 2-propanol. White crystals, m.p. 79-81°C. Yield 4.4 g (77%). ¹H-NMR (CDCl₃), δ, ppm: 0.780-1.616 (20H, m), 2.403-2.457 (2H, m, -C-CH₂-CH₂-), 2.557-2.609 (2H, t, =C-CH₂-CH₂-, J=7.8Hz), 7.042-7.108 (4H, m), 7.302-7.489 (2H, m), 7.516-7.625 (4H, m). ¹³C-NMR (CDCl₃), δ, ppm: 14.25, 14.36, 22.55, 22.86, 23.72, 29.39, 31.57, 31.98, 32.40, 35.75, 37.89, 59.13, 121.54, 122.02, 126.64, 127.85, 128.84, 130.74, 138.92, 140.71, 141.85, 154.22.

2.1.11. 2,7-Bis(9,9-dihexylfluoren-3-yl)-9-pentyl-9-(4-hexylphenyl)-9H-fluorene (BF14)

The synthesis was carried out in the same way as that of the benzofluorene derivatives. Yield 62%. The product was obtained in a glassy state. ¹H-NMR (CDCl₃, 400MHz), δ, ppm: 7.96 (2H, d, J=1.2 Hz), 7.92-7.90(2H, s), 7.81 (2H, d, J=6.4 Hz), 7.78 (2H, d, J=6.4 Hz), 7.75 (2H, d, J=6.4 Hz), 7.61-7.57 (6H, m), 7.43-7.38 (4H, dd), 7.37-7.09 (4H, dd), 2.66-2.56 (4H, m), 2.04-2.00 (8H, t, J=7.6Hz), 1.61-0.72 (69H, m).

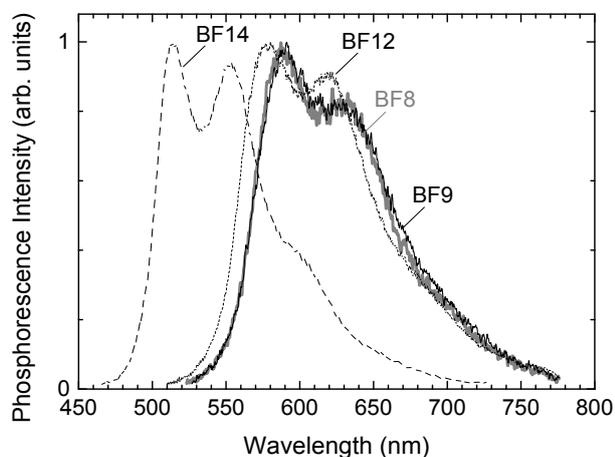


Fig. S1 Normalized phosphorescence spectra of the benzofluorenes **BF8**, **BF9**, **BF12**, and the reference compound **BF14** dispersed in PS matrix at the concentration of 1 wt %. The spectra measured at 20 K.

Triplet state energies (E_T) of the benzofluorenes were evaluated from the position of 0th vibronic band of the phosphorescence spectra measured at 20 K. The disagreement of experimental E_T values provided in Table 3 and the ones obtained by TD-DFT (see Table 2) is within 0.14-0.25 eV, which can be justified taking into account Stokes energy losses.¹ Generally, the phosphorescence spectra exhibited better resolved vibronic structure as compared to that observed in the fluorescence spectra due to the stronger localized wavefunction of the triplet excitons.² Similar E_{T1} ranging from 2.10 eV to 2.14 eV were obtained for all the benzofluorenes. For comparison, the fluorene-cored reference compound **BF14** displayed higher E_{T1} (2.41 eV) as a result of the reduced conjugation. Note that the measured absorption/fluorescence bands of **BF14** providing an estimate for singlet state energy were also shifted to higher energies due to the same reason. Experimentally revealed large singlet-triplet splitting (>0.8 eV) in the benzofluorenes, which was also confirmed by TD-DFT calculations, is obviously caused by the good overlap of HOMO and LUMO (see Fig. 2) as it is typical of well-conjugated compounds.²

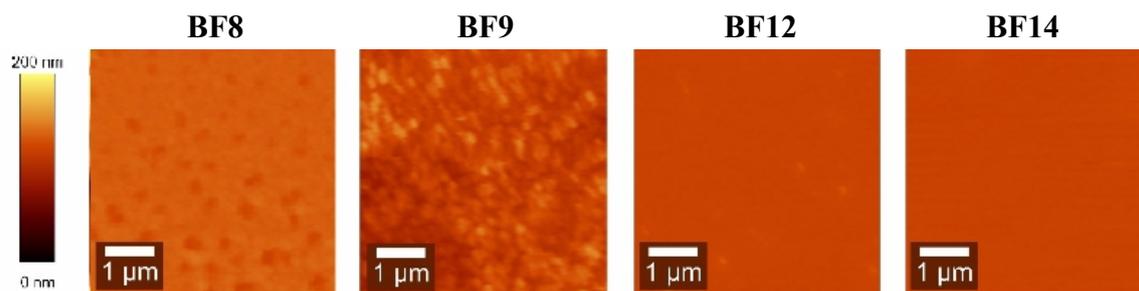


Fig. S2 AFM images of the neat films of **BF8**, **BF9**, **BF12** and **BF14**.

Atomic force microscopy measurements clearly evidence formation of aggregates for compounds **BF8** and **BF9**, meanwhile homogeneous films for **BF12** and **BF14** thus testifying their amorphous nature.

References

- 1 S. Huang, Q. Zhang, Y. Shiota, T. Nakagawa, K. Kuwabara, K. Yoshizawa and C. Adachi, *J. Chem. Theory Comput.*, 2013, **9**, 3872–3877.
- 2 A. Köhler and H. Bässler, *Mat. Sci. Eng. R*, 2009, **66**, 71–109.

Complete reference 35:

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision D. 01.*, Gaussian, Inc., Wallingford, CT, USA, 2009.