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A New Synthetic Procedure to 2,8-Diaminoindeno[1,2-*b*]fluorene as a Blue Light Emitting Material

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Conjugated aromatic compounds are potential candidates as organic semiconductors for use in thin-film transistors (TFTs) and light-emitting diodes (LEDs),[1] among which the fluorene-based compounds (Fig. 1) have received most attention owing to their good availability and processability.[2-4] Therefore, the synthesis of indenofluorene derivatives draws significant interest for their proper supply in both designing a new derivative and manufacturing.[1,5-7] Recently, 2,8-bis(diphenylamino)-6,6,12,12-tetramethyl-6,12-dihydroindeno[1,2-*b*]fluorene (**1**) has been reported to have a good luminous efficiency and excellent life time, and good operation lifetime of its OELD device.[8] These results prompted us to scale-up the synthesis of **1** for its further applications using the reported procedures as shown in Scheme 1.[1,6-8] However we found a couple of problems in the reported synthesis, such as low yield, harsh reaction conditions and the formation of side products. Herein, we report an improved synthetic route to **1** which overcomes the problems found in the reported procedures.

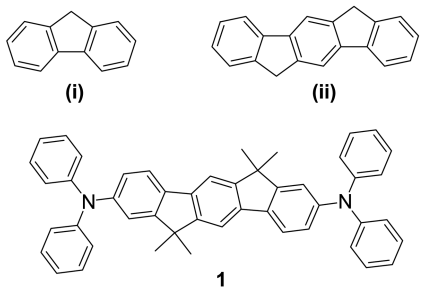
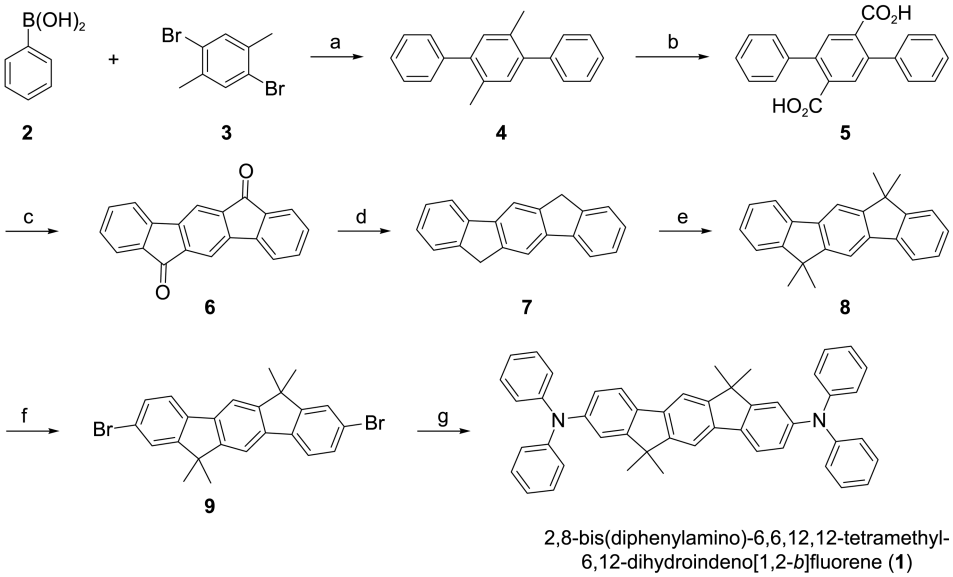
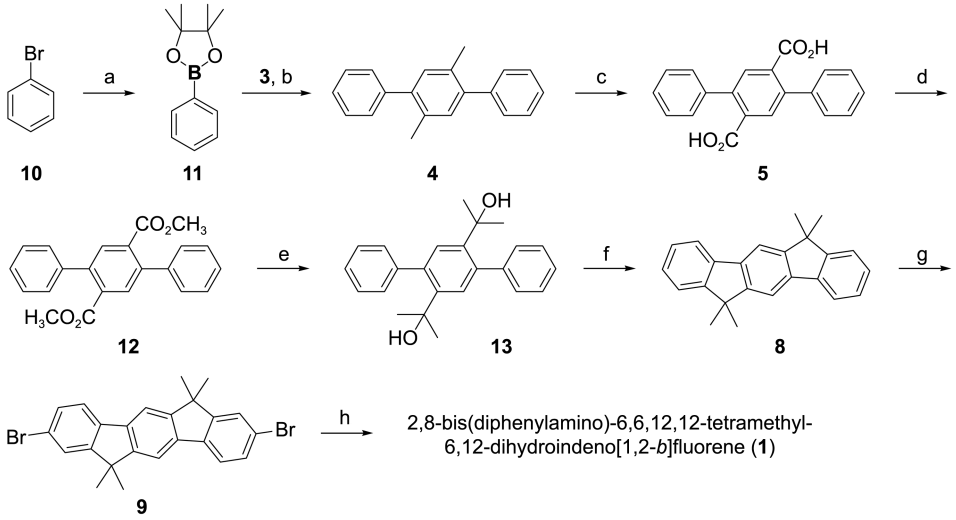


Figure 1. Structures of fluorine (**i**), indenofluorene (**ii**), and 2,8-diaminoindenofluorene (**1**).

When we repeated the reported procedures (Scheme 1), we found three major synthetic problems. They are (i) formation of decarboxylated side products in the cyclization of **5** into **6** for parent indeno[1,2-*b*]fluorene ring; (ii) use of harsh reaction conditions of Wolff-Kishner reduction of **6** which are not suitable for large-scale preparation; and, (iii) low yield at the tetra-methylation of **7**. In particular, when the tetra-methylation reaction of **7** was carried out by using *n*-BuLi and CH_3I condition, tetrabutylindenofluorene was



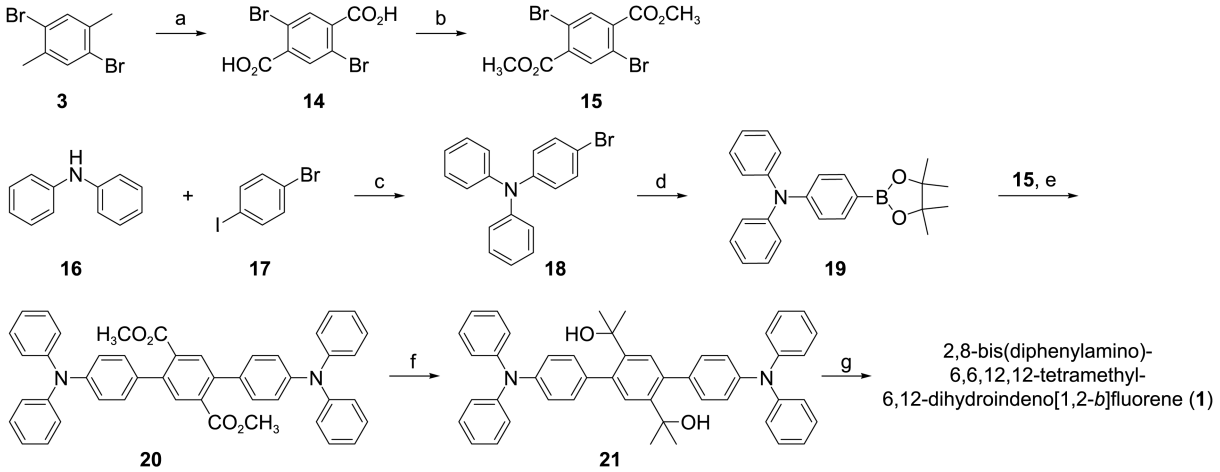
Scheme 1. Reported reagents and conditions[1,6-8]: (a) $Pd(OAc)_2$, K_2CO_3, *n*-Bu_4NBr, H_2O, 70 °C, 2 h, > 98%; (b) $KMnO_4$, H_2O, pyridine, reflux, 24 h, then *conc*. HCl, 72-96%; (c) concentrated H_2SO_4, rt, 2 h, 78-96%; (d) $N_2H_4{\cdot}H_2O$, KOH, diethylene glycol, reflux, 48 h, 76-79%; (e) Me_2SO_4, NaOH, DMSO (86%) or MeI, *t*-BuONa, DMSO (96%) or *n*-BuLi, CH_3I, THF, −78 °C to rt, (27%); (f) $FeCl_3$, Br_2, $CHCl_3$, 0 °C, 24 h, (74%) or Br_2, Na_2CO_3, H_2O, CH_2Cl_2, (97%) or Br_2, 1,1,2,2-tetrachloroethane (TCE), rt, 12 h, (77%); (g) diphenylamine, $Pd(OAc)_2$, *t*-BuONa, P(*t*-Bu)$_2$Cl, toluene, reflux, 6 h, 81%.



Scheme 2. Reagents and conditions: (a) *n*-BuLi, THF, −78 to −40 °C then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 90%; (b) $Pd(PPh_3)_4$, THF, 2 M K_2CO_3, reflux, 18 h; (c) $KMnO_4$ (12 equiv), pyridine, H_2O, reflux, 24 h, 92% (two steps); (d) $SOCl_2$ (4 equiv), CH_3OH, reflux, 5 h, quantitative; (e) CH_3MgBr (8 equiv), THF, N_2, reflux, 10 h, 96%; (f) concentrated HCl, CH_2Cl_2, reflux, 5 h, 80%; (g) $CuBr_2$ on Al_2O_3, CCl_4, reflux, 18 h, 80%; (h) diphenylamine, CuI, 1,10-phenanthroline, KOH, toluene, reflux, 48 h, 65%.

obtained as a major product instead of tetramethylindenofluorene (**8**) which would be stemmed from the metal exchange between *n*-BuLi and CH_3I. In the cases of using lithium diisopropylamine (LDA) or potassium *tert*-butoxide (*t*-BuOK) as another base, the desired **8** was obtained only in low yield.

As a key modification to **1**, we envisaged that the introduction of four methyl groups of **8** could be accomplished by the cyclization of tertiary alcohol **13** under acid-catalysis (Scheme 2). This strategy in particular avoids the harsh reaction conditions of Wolff-Kishner reduction step of low yield and furthermore, overcomes the low yield of the tetraalkylation step of the reported synthesis. Reaction of bromobenzene (**10**) with *n*-BuLi for at −78 °C, followed by addition of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, afforded **11** in 90% yield.[9] Suzuki coupling reaction of **11** with 2,5-dibromo-*p*-xylene (**3**) afforded **4**, which was oxidized by $KMnO_4$ to provide 2,5-diphenylterephthalic acid (**5**) in 92% yield over two steps. Esterification of **5** with $SOCl_2$ in methanol provided methyl 2,5-diphenylterephthalate (**12**) in quantitative yield. Reaction of **12** with CH_3MgBr (8 equiv) in dry THF at reflux yielded bis(tertiary alcohol) **13** in 96% yield. The ring closure of **13** by concentrated HCl at reflux afforded 6,6,12,12-tetramethyl-6,12-dihydroindeno[1,2-*b*]fluorene (**8**) in 80% yield.[10,11] Regioselective bromination of **8** using Mitsuo Kodomari's method ($CuBr_2$ on Al_2O_3, CCl_4, reflux, 18 h)[12] gave 2,8-dibromoindenofluorene (**9**) in 80% yield. Finally, Cross coupling of **9** with diphenylamine using CuI and 1,10-phenanthroline in dry toluene with dried KOH for 48 h at reflux provided **1** in 65% after workup and flash chromatographic purification (toluene/hexane = 4/1).



Scheme 3. Reagents and conditions: (a) CrO_3 (8 equiv), concentrated H_2SO_4, HOAc, rt, 24 h, 90%; (b) $SOCl_2$, CH_3OH, reflux, 5 h, quantitative; (c) CuI, 1,10-phenanthroline, KOH, toluene, reflux, 48 h, 70%; (d) *n*-BuLi, THF, −78 to −40 °C, 1 h, then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, −78 °C to rt, 90%; (e) $Pd(PPh_3)_4$, THF, 2 M K_2CO_3, reflux, 24 h, 80%; (f) CH_3MgBr (8 equiv), THF, reflux 10 h, quantitative; (h) concentrated H_2SO_4, rt, 2 h, 80%.

Although the first modification improved the reported synthesis significantly, there is still room for further refinements, particularly for the convergence of the synthesis. In this context, we decided to couple **15** and **19** in convergent fashion, after which the introduction of the four methyl groups using Grignard reagent followed by acid catalyzed cyclization provides the target compound **1** (Scheme 3). Oxidation of 2,5-dibromo-*p*-xylene (**3**) with chromic acid afforded 2,5-dibromoterephthalic acid (**14**) in 90% yield, which was treated with $SOCl_2$ in methanol to afford methyl 2,5-dibromoterephthalate (**15**) in quantitative yield. The cross coupling of diphenylamine (**16**) with 1-bromo-4-iodobenzene (**17**) was accomplished in the presence of Cu (I) catalyst[13] and the mixture was purified by chromatography with *n*-hexane only to provide (4-bromophenyl)diphenylamine (**18**) in 70% yield. Lithiation by *n*-BuLi followed by the addition of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane afforded 2-[*p*-(diphenylamino)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**19**) in 90% yield. Suzuki coupling reaction of **15** with **19** provided **20** in 80% yield, which was treated with excess CH_3MgBr in dry THF to afford precursor **21** in quantitative yield. The ring closure of **21** was accomplished with concentrated H_2SO_4 at room temperature to provide the target compound **1** in 80% yield.

In summary, two synthetic routes to 2,8-diaminoindeno-[1,2-*b*]fluorene (**1**) are described. Device of the tetramethylation of terephthalate (**12** & **20**) using Grignard reagent and the subsequent ring closure reaction of tertiary alcohol (**13** & **21**) catalyzed by acid overcame the problems of harsh reaction conditions and low yields encountered in the previous synthesis. In particular, the second modified procedure is highly convergent-only five straightforward steps from commercially available **15**.

Experimental Section

2,8-Bis(diphenylamino)-6,6,12,12-tetramethyl-6,12-dihydroindeno[1,2-*b*]fluorene (1). To a solution of compound **20** (1.36 g, 2.00 mmol) in anhydrous THF (30 mL) was added a 3.0 M solution of CH_3MgBr in diethyl ether (5.3 mL, 16 mmol), then heated at reflux for 10 h under an atmosphere of argon. After cooling in an ice bath, the resulting solution was poured into aqueous NH_4Cl solution and the mixture was extracted with ethyl acetate. The combined extracts were washed with brine and dried over $MgSO_4$. Evaporation of the solvent afforded the tertiary alcohol **21** as a yellow solid in quantitative yield. Without further purification, the compound **21** was dissolved in concentrated sulfuric acid (20 mL) in an ice bath. After removing an ice bath, the reaction mixture was stirred for 2 h and poured into fine ice to provide a purple solid, which was added to a mixed solution of aqueous 5% NaOH (100 mL) and toluene (100 mL) with well stirring. The toluene phase was separated, dried over $MgSO_4$, concentrated, and subjected to column chromatography (silica, hexane/toluene = 7/2) to afford the target compound **1** (1.03 g, 80%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.59 (m, 4H), 7.30-7.24 (m. 8H), 7.21-7.19 (m, 2H), 7.14-1.12 (m, 8H), 7.03-7.00 (m, 6H), 1.41 (s, 6H), 1.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.49, 153.17, 148.03, 146.95, 134.60, 129.19, 123.99, 123.57, 122.52, 120.17, 118.85, 113.49, 46.53, 29.72, 27.32; HRMS/FAB *m/z* 644.3191 (calculated), 644.3189 (observed).

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References and Notes

1. Hadizad, T.; Zhang, J.; Wang, Z. Y.; Gorjanc, T. C.; Py, C. *Org. Lett*. **2005**, *7*, 795.
2. Wong, K. T.; Chien, Y. Y.; Chen, R. T.; Wang, C. F.; Lin, Y. T.; Chiang, H. H.; Hsieh, P. Y.; Wu, C. C.; Chou, C. H.; Su, Y. O.; Lee, G. H.; Peng, S. M. *J. Am. Chem. Soc*. **2002**, *124*, 11576.
3. Katsis, D.; Geng, Y. H.; Ou, J. J.; Culligan, S. W.; Trajkovska, A.; Chen, S. H.; Rothberg, L. J. *Chem. Mater*. **2002**, *14*, 1332.
4. Beaupre, S.; Ranger, M.; Leclerc, M. *Macromol. Rapid Commun*. **2002**, *21*, 1013.
5. Harvey, R. G.; Pataki, J.; Cortez, C.; Raddo, P. D.; Yang, C. *J. Org. Chem*. **1991**, *56*, 1210.
6. Merlet, S.; Birau, M.; Wang, Z. Y. *Org. Lett*. **2002**, *4*, 2157.
7. Choi, I. W.; Kim, C. S.; Shin, H. N.; Lee, M. A.; Shin, H. S.; Kwak, M. Y.; Kim, N. K.; Kim, B. O.; Kim, S. M. WO 086,701 A1, 2007.
8. Vestweber, H.; Heil, H.; Stoessel, P.; Buesing, A.; Parham, A. H.; Fortee, R. U.S. Patent 0220,285 A1, 2008.
9. Kwon, H. J.; Cho, Y. J.; Yoon, S. S.; Kim, B. O.; Kim, S. M. WO 061,218 A1, 2007.
10. Anchel, M.; Blatt, A. H. *J. Am. Chem. Soc*. **1941**, *63*, 1948.
11. To achieve high conversion, the reaction was monitored by GC/MS (*m/z* = 310).
12. Kodomari, M.; Satoh, H. Yoshitomi, S. *J. Org. Chem*. **1988**, *53*, 2094.
13. Kelkar, A. A.; Patil, N. M.; Chaudhari, R. V. *Tetrahedron Lett*. **2002**, *43*, 7143.