meta- and *para*-Functionalized Thermally Crosslinkable OLED-Materials through Selective Transition-Metal-Catalyzed Cross-Coupling Reactions

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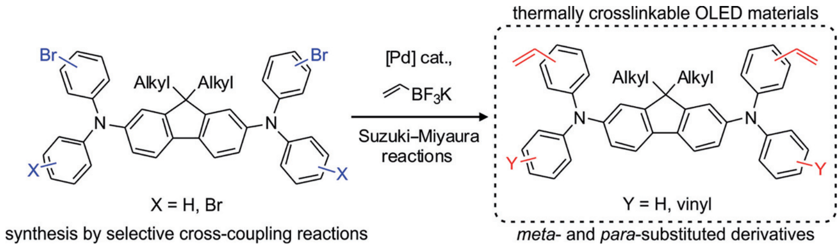

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Abstract Herein, a synthetic approach using selective transition-metal-catalyzed cross-coupling reactions to thermally crosslinkable OLED materials based on vinyl-functionalized arylamines is reported. In a modular approach, 9,9-dialkyl-2,7-diiodo-9*H*-fluorene underwent a selective Ullmann cross-coupling reaction with bromo-substituted-diphenylamines to give 9,9-dialkyl-2,7-bis(bromo-substituted-diphenylamino)-9*H*-fluorenes that underwent end-functionalization by the Suzuki–Miyaura reaction using potassium vinyltrifluoroborate to give the corresponding 9,9-dialkyl-2,7-bis(vinyl-substituted-diphenylamino)-9*H*-fluorenes. Novel *meta*-functionalized materials were synthesized, which are difficult to prepare by traditional synthetic pathways. The thermal behavior of the compounds was investigated by DSC measurements, indicating a lower thermal sensitivity of the *meta*-substituted materials than their *para*-functionalized analogues.

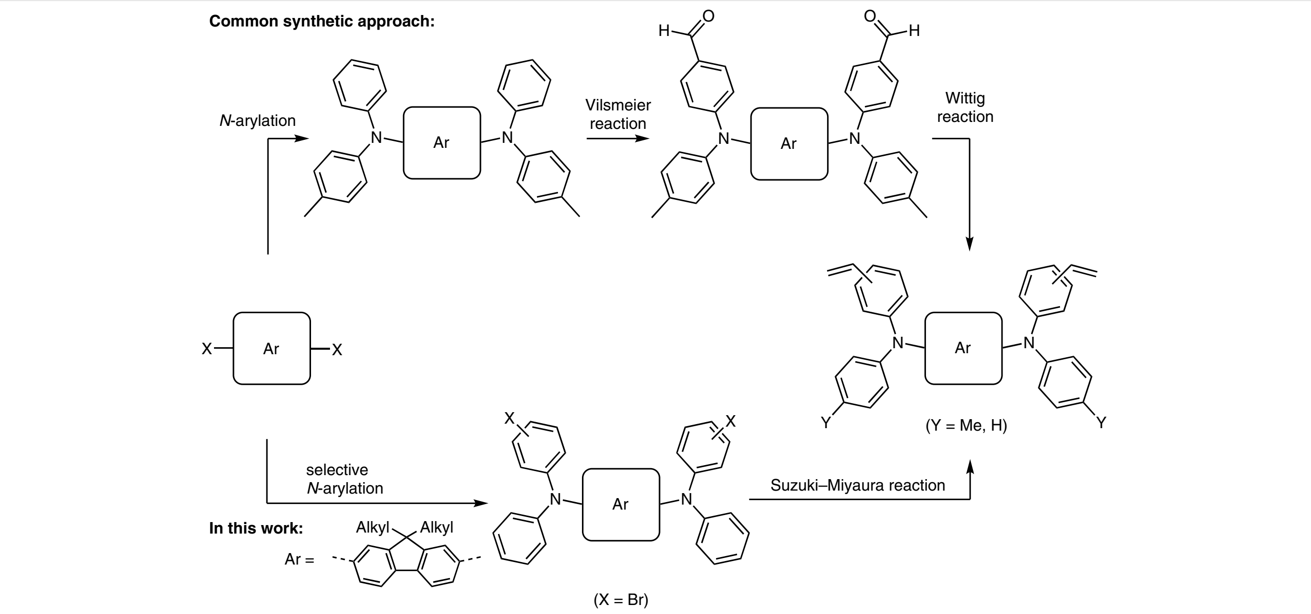
Key words cross-link, vinylation, OLED materials, Suzuki–Miyaura, solution-processing, DSC

One key challenge for the production of high-efficiency organic light-emitting diodes (OLEDs) by low-cost solution based processes is the fabrication of well-defined multilayer architectures. During successive deposition of layers, the preceding layers can be affected by dissolution, swelling, or intermixing of the functional organic materials, resulting in undefined interfaces and significantly reduced device efficiencies. One effective strategy to avoid this problem is the use of crosslinkable materials, rendering deposited layers insoluble before further processing.

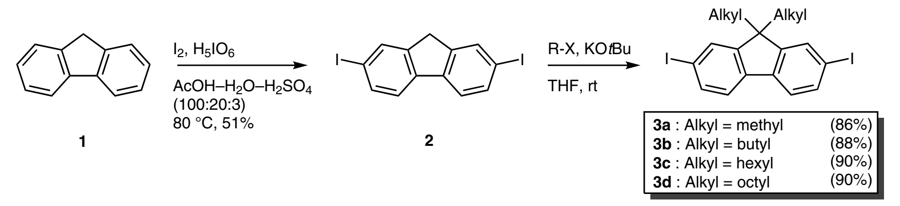
In this context, reactive moieties, such as trifluorovinyl ethers,[1] benzocyclobutanes,[2] cinnamates,[3] acrylates,[4] azides,[5–7] or oxetanes,[8–10] have been applied in the field of organic electronics. Furthermore, organic materials have been functionalized with styrene groups for thermal, self-initiated crosslinking of thin films.[11–13] The attachment of styrene groups to the molecular backbone has been realized either by the formation of benzylic ethers with corresponding styrene segments[14,15] or by *de novo* synthesis which most commonly involves Vilsmeier formylation, followed by a Wittig reaction (Scheme 1).[16–18] Unfortunately, this strategy has several drawbacks: (1) the reaction sequence suffers from poor atom economy, (2) only *para*-substituted derivatives are accessible, and (3) the insufficient regioselectivity of the Vilsmeier reaction, especially when functionalizing more complex molecules. Therefore, this synthetic approach often comprises the additional necessity of blocking reactive molecular positions, thus limiting the scope of the functionalization method.

In this work we demonstrate a strategy to overcome the aforementioned limitations. Retrosynthetically, the attachment of the thermolabile vinyl moieties could be achieved by key Suzuki–Miyaura reactions using potassium vinyltrifluoroborate, introduced by Genêt and Molander et al.[19,20] In this way the corresponding halogenated precursor molecules, obtained following a selective modular synthetic approach, undergo a transition-metal-catalyzed cross-coupling reaction. Thereby, even *meta*-functionalized materials are obtainable, which are not accessible by electrophilic aromatic substitution reactions. In addition to this, modulation of the thermal properties of the materials was achieved by varying the length of the attached alkyl chains. The thermal behavior, as well as the crosslinkability of the derivatives synthesized, was investigated by differential scanning calorimetry (DSC).

Synthesis of the materials was accomplished by coupling of a central fluorene segment and lateral diphenylamine components. The central fluorene core was synthesized in a two-step reaction sequence, starting with selective iodination[21] of 9*H*-fluorene (**1**) using iodine and periodic acid (Scheme 2). Thereafter, geminal dialkylation reactions[22] yield the fluorene components **3a–d** with diverse alkyl chain length.

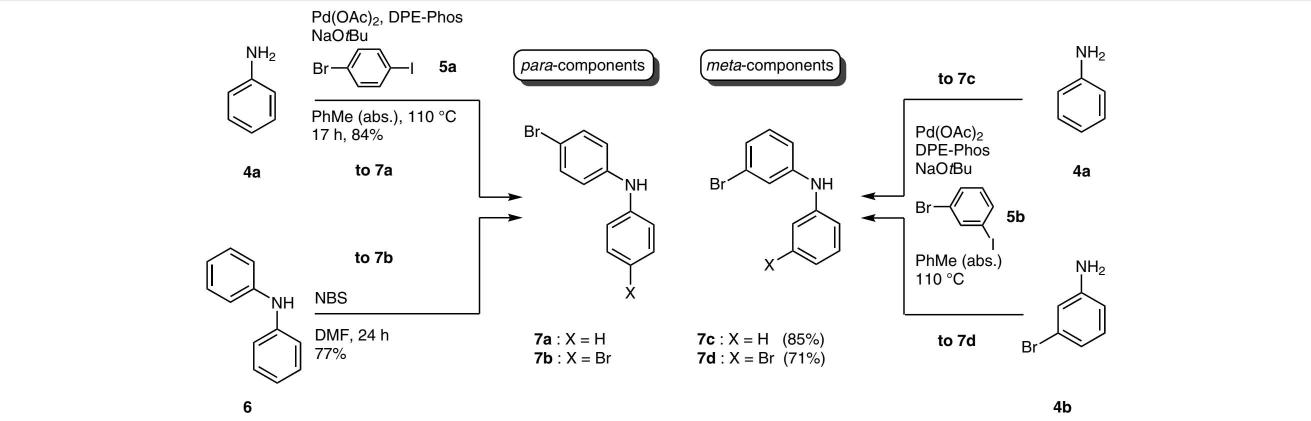


Scheme 1 Synthetic approach

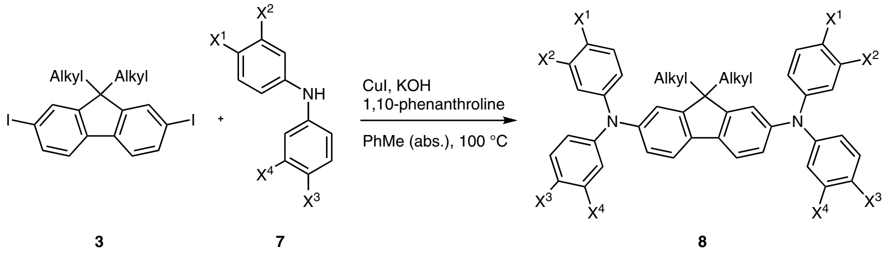


Scheme 2 Synthesis of alkylated 2,7-diiodofluorenes **3a–d**

The synthesis of the halogenated secondary arylamines was achieved by Buchwald–Hartwig cross-coupling reactions of anilines with 1-bromo-4- or -3-iodobenzenes **5a**,**b**, selecting iodine over bromine (Scheme 3). Using the bidentate ligand DPE-Phos,[23,24] diphenylamine components **7a**, **7c**, and **7d**, respectively, were obtained in good yields (71–85%). The synthesis of the bis(4-bromophenyl)amine (**7b**) was achieved more conveniently by dibromination of diphenylamine (**6**) using NBS as reported by Ishow et al.[25]



Scheme 3 Synthesis of brominated diphenylamine components by selective Buchwald–Hartwig cross-coupling



Scheme 4 Synthesis of brominated precursor molecules **8** by selective Ullmann coupling

Table 1 Results of Synthesis of Compounds **8**

Entry	Fluorene (alkyl)	Amine	X^1	X^2	X^3	X^4	Product	Yield (%)
1	**3a** (Me)	**7a**	Br	H	H	H	**8a**	90
2	**3a** (Me)	**7b**	Br	H	Br	H	**8b**	75
3	**3b** (Bu)	**7b**	Br	H	Br	H	**8c**	69
4	**3c** (hexyl)	**7b**	Br	H	Br	H	**8d**	52
5	**3d** (octyl)	**7b**	Br	H	Br	H	**8e**	74
6	**3a** (Me)	**7c**	H	Br	H	H	**8f**	64
7	**3a** (Me)	**7d**	H	Br	H	Br	**8g**	76

Table 2 Results of Synthesis of Compounds **10**

Entry	Fluorene	R^1	R^2	R^3	R^4	Product	Yield (%)
1	**8a**	vinyl	H	H	H	2V-Methyl (**10a**)	34
2	**8b**	vinyl	H	vinyl	H	4V-Methyl (**10b**)	41
3	**8c**	vinyl	H	vinyl	H	4V-Butyl (**10c**)	18
4	**8d**	vinyl	H	vinyl	H	4V-Hexyl (**10d**)	–
5	**8e**	vinyl	H	vinyl	H	4V-Octyl (**10e**)	–
6	**8f**	H	vinyl	H	H	m2V-Methyl (**10f**)	68
7	**8g**	H	vinyl	H	vinyl	m4V-Methyl (**10g**)	60

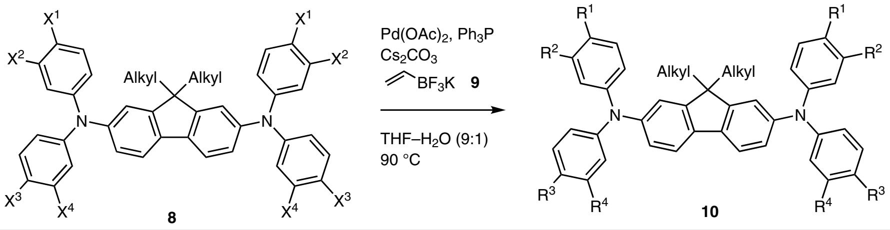
Following the modular approach, the synthesis of the halogenated precursor molecules **8** was accomplished by the twofold Ullmann cross-coupling reaction of the diiodofluorenes **3a**–**d** with the diphenylamines **7a**–**d**, thereby selecting iodine over the bromine-substituent of the electron-rich diphenylamine components (Scheme 4, Table 1). The compounds were obtained in acceptable to excellent yields.

The vinylation of the halogenated precursor molecules **8** was achieved by Suzuki–Miyaura cross-coupling reactions using potassium vinyltrifluoroborate (**9**) (Scheme 5, Table 2).[20] The crosslinkable compounds **10a**–**c**,**f**,**g** were isolated in moderate to good yields, provided care is taken due to the thermal instability of compounds **10** and their minacious polymerization under work-up conditions.

This tendency is even more pronounced in case of the derivatives bearing longer alkyl chains and therefore, the compounds 4V-Hexyl **10d** and 4V-Octyl **10e** could not be isolated.

The thermal behavior and crosslinkability of the vinylated derivatives **10** was investigated by DSC measurements (Figure 1). The thermograms of the first heating cycles show endothermic signals, which were assigned to the melting of the non-crosslinked molecules. It can be seen that the number of vinyl groups per molecule has only a minor impact on the melting temperature. In comparison to the *para*-substituted derivatives, the *meta*-functionalized analogues m2V-Methyl **10f** and m4V-Methyl **10g** tend to melt at lower temperatures. By substituting the fluorene segment with longer alkyl chains, the melting temperature of the functional materials can be lowered even further, e.g. **10c**.

At higher temperatures the thermograms of all derivatives **10** feature a broad and intense exothermic signal in their first heating cycles, which is caused by the progressing thermal crosslinking reaction. The absence of any exothermic behavior at those temperatures in the course of subse-



Scheme 5 Functionalization of precursor molecules **8** by Suzuki–Miyaura cross-coupling

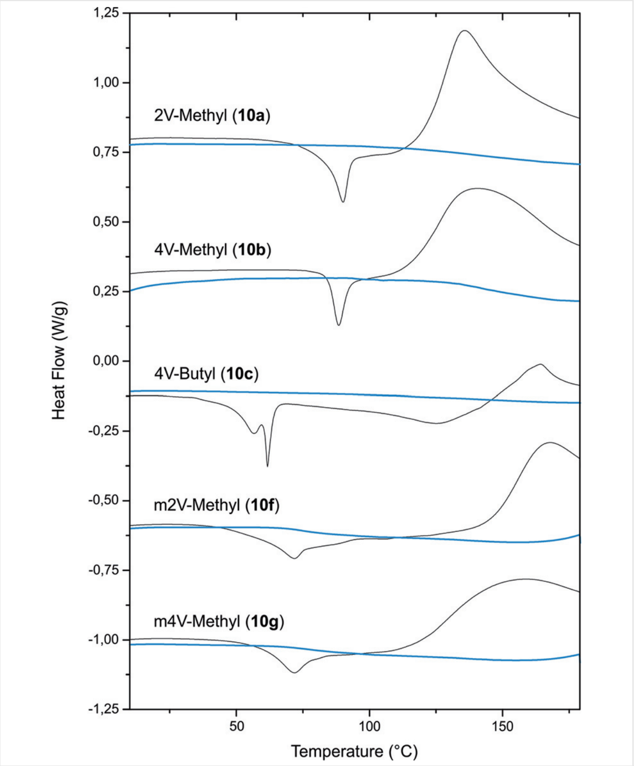


Figure 1 DSC measurements of thermally crosslinkable derivatives **10** (N_2 atmosphere, 10 K/min, black line: first heating cycle, blue line: second heating cycle). The traces have been shifted vertically for clarity.

quent heating cycles indicates complete crosslinking in the first place. The *meta*-substituted derivatives are generally less sensitive towards thermal crosslinking than the *para*-substituted compounds. This results in higher onset- and peak-maxima temperatures of the corresponding signals. A possible explanation of this behavior can be found in the mechanism of the self-initiated radical polymerization of styrene derivatives, involving an initial dimerization step via Diels–Alder reaction, followed by a subsequent radical transfer step.[26–28] The resulting benzylic radical initiates the chain growth reaction. Because of the distinct steric and electronic situations of the vinyl groups in the case of the *meta*- and *para*-functionalization, different reactivities of the derivatives in both initiation steps are plausible as experimentally observed in the DSC thermograms.

In conclusion, we have demonstrated a synthetic approach to thermally crosslinkable model compounds based on selective transition-metal-catalyzed cross-coupling reactions. The strategy features the end-functionalization of halogenated precursor molecules **8** by Suzuki–Miyaura reaction with potassium vinyltrifluoroborate (**9**), introducing the thermolabile, crosslinkable vinyl moiety in the very last step of the synthesis. Thus, novel *meta*-substituted materials were obtained for the first time. In addition to this, the described cross-coupling chemistry does not suffer from regioselectivity restrictions associated with the electrophilic aromatic substitution reactions of earlier preparations.

The thermal behavior and crosslinkability of the reported derivatives was investigated by DSC measurements. The synthetic strategy described in this paper should be easily transferable to more complex functional molecules and presents an attractive alternative to the traditional synthetic approach towards this kind of crosslinkable materials.

Solvents and reagents: THF and toluene were distilled from Na/benzophenone under an argon atmosphere. Reagents were obtained from commercial sources and were used without further purification. Moisture and/or air sensitive experiments were conducted using flame-dried glassware under argon atmosphere. NMR: ^{1}H NMR spectra were recorded on Bruker ARX 300 and DRX 500 spectrometers operating at 300 and 500 MHz, respectively at 300 K and ^{13}C NMR spectra were recorded on the same instruments at 75 and 125 MHz, both were referenced against the residual solvent signal as reported in the literature.[29] Assigned peaks are indicated by numbering used in the corresponding figure. Flash chromatography was carried out on silica gel 60 (15–40 μm) by Merck KGaA at a pressure of 2–3 bar. Mass spectra: EI-MS and EI-HRMS were recorded on a double focusing mass spectrometer MAT 95. Elemental analysis were performed by the service of Technische Universität Darmstadt on a Vario El by Elementar. Differential scanning calorimetry (DSC) was performed on a DSC1 by Mettler-Toledo.

2,7-Diiodo-9*H*-fluorene (2)

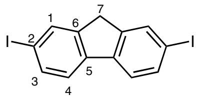


Figure 2

In a modification of the literature procedure,[21] fluorene (**1**, 50.00 g, 300.81 mmol) was suspended in a mixture of glacial AcOH (800 mL), H_2O (165 mL), and concd H_2SO_4 (25 mL). The suspension was initially heated to 95 °C and then cooled to 80 °C. At this temperature, H_5IO_6 (25.00 g, 109.68 mmol, 0.36 equiv) and I_2 (50.50 g, 198.97 mmol, 0.66 equiv) were added and the resulting mixture was vigorously stirred for 4 h. Then the mixture was cooled to r.t. The resulting precipitate was filtered and washed with aq sat. $NaHCO_3$ solution and water. The solid was dried and then recrystallized (*n*-hexane) to give the product (Figure 2) as colorless needles; yield: 64.49 g (154.29 mmol, 51%).

Analytical data match data reported in the literature.[21]

^{1}H NMR ($CDCl_3$, 300 MHz, 300 K): δ = 3.831 (s, 2 H, 7-H), 7.491 (d, 2 H, 4-H), 7.706 (d, 2 H, 3-H), 7.879 (s, 2 H, 1-H); $^3J_{3,4}$ = 8.1 Hz.

9,9-Dialkyl-2,7-diiodo-9*H*-fluorenes 3; General Procedure

In a modification of the literature procedure,[30] in a flame-dried flask, 2,7-diiodo-9*H*-fluorene (**2**) was dissolved in abs THF (2 mL/mmol) and the resulting solution was cooled to 0 °C. The solution was slowly mixed with KO*t*Bu (2.70 equiv) and the mixture was stirred at r.t. for 2 h. The mixture was cooled to 0 °C, mixed with the haloalkane (3.00

equiv) and the mixture was stirred at r.t. for 24 h. The mixture was filtered through silica gel and the solvent was removed in vacuo. The resulting solid was purified by recrystallization.

2,7-Diiodo-9,9-dimethyl-9*H*-fluorene (3a)

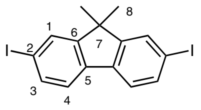


Figure 3

According to the general procedure using **2**, (50.00 g, 119.60 mmol), KO*t*Bu (36.24 g, 322.96 mmol, 2.70 equiv), and MeI (22.44 mL, 358.00 mmol, 3.00 equiv) gave a solid that was purified by recrystallization (toluene) to give the product (Figure 3) as colorless crystals; yield: 45.67 g (102.38 mmol, 86%); mp 203 °C.

Analytical data matched data reported in the literature.[31]

^{1}H NMR (CDCl$_3$, 300 MHz, 300 K): δ = 1.451 (s, 6 H, 8-H), 7.443 (d, 2 H, 4-H), 7.664 (d, 2 H, 3-H), 7.744 (s, 2 H, 1-H); $^4J_{1,3}$ = 1.53 Hz, $^3J_{3,4}$ = 7.94 Hz.

MS (EI): *m*/*z* (%) = 446 (100, [M]$^+$]), 431 (45, [M – CH$_3$]$^+$), 319 (10, [M – I]$^+$), 304 (20, [M – I – CH$_3$]$^+$), 192 (5, [M – I$_2$]$^+$).

Anal. Calcd for C$_{15}$H$_{12}$I$_2$: C, 40.39; H, 2.71. Found: C, 40.40; H, 2.81.

9,9-Dibutyl-2,7-diiodo-9*H*-fluorene (3b)

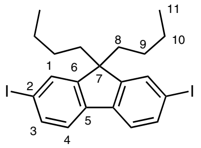


Figure 4

According to the general procedure using **2** (30.00 g, 71.77 mmol), KO*t*Bu (21.74 g, 193.77 mmol, 2.70 equiv), and BuI (24.50 mL, 215.30 mmol, 3.00 equiv) gave a solid that was purified by column chromatography (silica gel, cyclohexane/*n*-hexane, 1:1) and recrystallized (EtOH/EtOAc) to give the product (Figure 4) as colorless crystals; yield: 33.44 g (63.07 mmol, 88%); mp 137 °C.

^{1}H NMR (CDCl$_3$, 500 MHz, 300 K): δ = 0.578 (m, 4 H, 9-H), 0.697 (t, 6 H, 11-H), 1.092 (m, 4 H, 10-H), 1.907 (m, 4 H, 8-H), 7.409 (d, 2 H, 4-H), 7.649 (s, 2 H, 1-H), 7.659 (d, 2 H, 3-H); $^3J_{3,4}$ = 7.00 Hz.

^{13}C NMR (CDCl$_3$, 125 MHz, 300 K): δ = 13.89 (11-C), 23.08 (10-C), 25.98 (9-C), 40.08 (8-C), 55.60 (7-C), 93.27 (2-C), 121.64 (4-C), 132.19 (1-C), 136.19 (3-C), 139.91 (5-C), 152.65 (6-C).

MS (EI): *m*/*z* (%) = 530 (100, [M]$^+$]), 473 (40, [M – C$_4$H$_9$]$^+$), 417 (30, [M – 2 (C$_4$H$_9$)]$^+$), 346 (50, [M – C$_4$H$_9$ – I]$^+$).

HRMS (EI): *m*/*z* [M] calcd for C$_{21}$H$_{24}$I$_2$: 529.9966; found: 529.9927.

Anal. Calcd for C$_{21}$H$_{24}$I$_2$: C, 47.57; H, 4.56. Found: C, 47.56; H, 4.56.

9,9-Dihexyl-2,7-diiodo-9*H*-fluorene (3c)

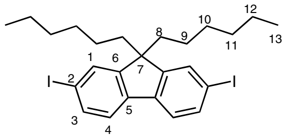


Figure 5

According to the general procedure using **2** (30.00 g, 71.77 mmol), KO*t*Bu (21.74 g, 193.77 mmol, 2.70 equiv), and 1-bromohexane (30.22 mL, 215.31 mmol, 3.00 equiv) gave a solid that was purified by column chromatography (silica gel, cyclohexane/*n*-hexane, 1:1) and recrystallized (EtOH) to give the product (Figure 5) as colorless crystals; yield: 37.68 g (64.27 mmol, 90%); mp 60 °C.

^{1}H NMR (CDCl$_3$, 500 MHz, 300 K): δ = 0.599 (m, 4 H, 9-H), 0.790 (t, 6 H, 13-H), 1.000–1.093 (m, 8 H, 10-H, 11-H), 1.124 (m, 4 H, 12-H), 1.897 (m, 4 H, 8-H), 7.405 (d, 2 H, 4-H), 7.645 (s, 2 H, 1-H), 7.654 (d, 2 H, 3-H).

^{13}C NMR (CDCl$_3$, 125 MHz, 300 K): δ = 14.13 (13-C), 22.69 (12-C), 23.78 (9-C), 29.69 (10-C or 11-C), 31.56 (10-C or 11-C), 40.23 (8-C), 55.68 (7-C), 93.24 (2-C), 121.63 (4-C), 132.20 (1-C), 136.17 (3-C), 139.61 (5-C), 152.65 (6-C).

MS (EI): *m*/*z* (%) = 586 (100, [M]$^+$]), 501 (25, [M – C$_6$H$_{13}$]$^+$), 417 (30, [M – 2 (C$_6$H$_{13}$)]$^+$), 374 (35, [M – C$_6$H$_{13}$ – I]$^+$).

HRMS (EI): *m*/*z* [M] calcd for C$_{25}$H$_{32}$I$_2$: 586.0592; found: 586.0634.

Anal. Calcd for C$_{25}$H$_{32}$I$_2$: C, 51.21; H, 5.50. Found: C, 51.25; H, 5.49.

2,7-Diiodo-9,9-dioctyl-9*H*-fluorene (3d)

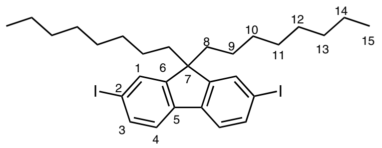


Figure 6

According to the general procedure using **2** (30.00 g, 71.77 mmol), KO*t*Bu (21.74 g, 193.77 mmol, 2.70 equiv), and 1-bromooctane (37.46 mL, 215.31 mmol, 3.00 equiv) gave a solid that was purified by column chromatography (silica gel, cyclohexane/*n*-hexane, 1:1) and recrystallized (EtOH) to give the product (Figure 6) as colorless crystals; yield: 41.47 g (64.54 mmol, 90%); mp 58 °C.

^{1}H NMR (CDCl$_3$, 500 MHz, 300 K): δ = 0.596 (m, 4 H, 9-H), 0.841 (t, 6 H, 15-H), 1.014–1.188 (m, 16 H, 10-H, 11-H, 12-H, 13-H), 1.223 (m, 4 H, 14-H), 1.896 (m, 4 H, 8-H), 7.404 (d, 2 H, 4-H), 7.646 (s, 2 H, 1-H), 7.655 (d, 2 H, 3-H).

^{13}C NMR (CDCl$_3$, 125 MHz, 300 K): δ = 14.22 (15-C), 22.75 (14-C), 23.76 (9-C), 29.25 (CH$_2$), 29.30 (CH$_2$), 31.90 (CH$_2$), 40.20 (8-C), 55.69 (7-C), 93.25 (2-C), 121.62 (4-C), 132.20 (1-C), 136.17 (3-C), 139.91 (5-C), 152.66 (6-C).

MS (EI): *m*/*z* (%) = 642 (100, [M]$^+$]), 529 (20, [M – C$_8$H$_{17}$]$^+$), 417 (25, [M – 2 (C$_8$H$_{17}$)]$^+$), 402 (35, [M – C$_8$H$_{17}$ – I]$^+$).

HRMS (EI): *m*/*z* [M] calcd for C$_{29}$H$_{40}$I$_2$: 642.1218; found: 642.1184.

Anal. Calcd for C$_{29}$H$_{40}$I$_2$: C, 54.22; H, 6.28. Found: C, 54.17; H, 6.26.

4-Bromo-*N*-phenylaniline (7a)

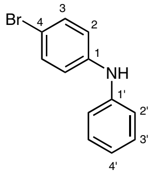


Figure 7

According to the literature procedure,[32] in a flame-dried Schlenk-flask 1-bromo-4-iodobenzene (**5a**, 14.50 g, 51.25 mmol), aniline (**4a**, 4.68 mL, 51.25 mmol, 1.00 equiv), DPE-Phos (1.66 g, 3.08 mmol, 0.06 equiv), and Pd(OAc)$_2$ (0.469 g, 2.05 mmol, 0.04 equiv) were suspended in abs toluene (25 mL) and the mixture was stirred for 20 min at r.t. Then NaO*t*Bu (5.23 g, 56.38 mmol, 1.10 equiv) was added and the dark red suspension was stirred at 110 °C for 17 h. After cooling to r.t., the mixture was filtered through a pad of silica gel and the solvent was removed in vacuo. The residue was purified by column chromatography (silica gel, petroleum ether/Et$_2$O, 8:1 + 3 vol% Me$_2$NEt), to give the product (Figure 7) as a colorless solid; yield: 10.67 g (43.00 mmol, 84%); mp 87 °C.

Analytical data match data reported in the literature.[32]

^{1}H NMR (CDCl$_3$, 300 MHz, 300 K): δ = 5.690 (br, N–H), 6.928 (t, 1 H), 6.958 (t, 1 H), 6.966–7.014 (m, 1 H), 7.037–7.092 (m, 2 H), 7.255–7.331 (m, 2 H), 7.338 (m, 1 H), 7.367 (m, 1 H).

MS (EI): m/z (%) = 249 (97, [M$_{\mathrm{Br(81)}}$]$^+$]), 247 (100, [M$_{\mathrm{Br(79)}}$]$^+$), 167 (100, [M – Br]$^+$).

HRMS (EI): m/z [M] calcd for C$_{12}$H$_{10}$BrN: 246.9997; found: 247.0004.

Anal. Calcd for C$_{12}$H$_{10}$BrN: C, 58.09; H, 4.06; N, 5.65. Found: C, 58.09; H, 4.00; N, 5.61.

Bis(4-bromophenyl)amine (7b)

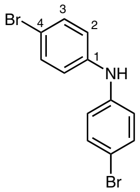


Figure 8

According to a literature procedure,[25] Ph$_2$NH (**6**, 60.00 g, 354.56 mmol) was dissolved in DMF (200 mL) and cooled to 0 °C. Under vigorous stirring, a solution NBS (126.88 g, 712. mmol, 2.01 equiv) in DMF (400 mL) was added dropwise and the mixture was stirred at r.t. for 48 h. Then, the mixture was poured into H$_2$O (1.5 L) and the resulting precipitate was filtered. The solid was recrystallized (EtOH/H$_2$O) to give the product (Figure 8) as colorless crystals; yield: 89.77 g (274.5 mmol, 77%); mp 107.5 °C.

Analytical data match data reported in the literature.[25]

^{1}H NMR (CDCl$_3$, 500 MHz, 300 K): δ = 5.624 (br, N–H), 6.915 (d, 4 H, 2-H), 7.362 (d, 4 H, 3-H).

$^3J_{2,3}$ = 8.70 Hz.

MS (EI): m/z (%) = 327 (100, [M]$^+$]), 247 (10, [M – Br]$^+$), 167 (50, [M – 2 Br$_2$]$^+$).

Anal. Calcd for C$_{12}$H$_9$Br$_2$N: C, 44.07; H, 2.77; N, 4.28. Found: C, 44.10; H, 2.82; N, 4.32.

3-Bromo-*N*-phenylaniline (7c)

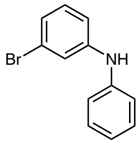


Figure 9

In a flame-dried flask and under argon atmosphere, a mixture of aniline (**4a**, 1.83 mL, 20 mmol), 1-bromo-3-iodoaniline (**5b**, 2.56 mL, 20 mmol, 1.00 equiv), Pd(OAc)$_2$ (22.6 mg, 0.10 mmol, 0.005 equiv), and DPE-Phos (81.2 mg, 0.15 mmol, 0.0075 equiv) was dissolved in abs toluene (20 mL) and the mixture was stirred for 1 h at r.t. Then NaO*t*-Bu (2.69 g, 28 mmol, 1.40 equiv) was added and the mixture was heated to 110 °C for 2 h. After cooling to r.t., the mixture was filtered through a pad of silica gel and the solvent was removed in vacuo. The residue was purified by kugelrohr distillation under reduced pressure to give the product (Figure 9) as a yellow oil; yield: 4.19 g (16.9 mmol, 85%).

Analytical data match data reported in the literature.[33]

Anal. Calcd for C$_{12}$H$_{10}$BrN: C, 58.09; H, 4.06; N, 5.65. Found: C, 58.16; H, 4.09; N, 5.64.

Bis(3-bromophenyl)amine (7d)

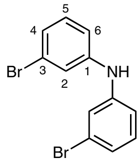


Figure 10

In a flame-dried flask and under argon atmosphere, a mixture of 3-bromoaniline (9.80 mL, 15.50 g, 90 mmol), 1-bromo-3-iodoaniline (11.5 mL, 25.50 g, 90 mmol, 1.00 equiv), Pd(OAc)$_2$ (507 mg, 2.26 mmol, 0.025 equiv), and DPE-Phos (1.82 g, 3.38 mmol, 0.038 equiv) was dissolved in abs toluene (90 mL) and the mixture was stirred for 1 h at r.t. Then NaO*t*Bu (12.10 g, 126 mmol, 1.40 equiv) was added and the mixture was heated to 110 °C for 2 h. After cooling to r.t., the mixture was filtered through a pad of silica gel and the solvent was removed in vacuo. The residue was purified by kugelrohr distillation under reduced pressure to give the product (Figure 10) as a colorless oil; yield: 20.80 g (63.5 mmol, 71%).

^{1}H NMR (CDCl$_3$, 500 MHz, 303 K): δ = 5.690 (br, N–H), 6.978 (ddd, 2 H, 4-H), 7.089 (ddd, 2 H, 6-H), 7.136 (‘t’, 2 H, 5-H), 7.199 (‘t’, 2 H, 2-H); $^4J_{2,4}$ = 1.7 Hz, $^4J_{2,6}$ = 2.1 Hz, $^3J_{4,5}$ = 7.9 Hz, $^4J_{4,6}$ = 1.2 Hz, $^3J_{5,6}$ = 7.9 Hz.

^{13}C NMR (CDCl$_3$, 125 MHz, 303 K): δ = 116.62 (4-C), 120.89 (2-C), 123.18 (3-C), 124.58 (6-C), 130.72 (5-C), 143.78 (1-C).

Anal. Calcd for C$_{12}$H$_9$Br$_2$N: C, 44.07; H, 2.77; N, 4.28; Br, 48.87. Found: C, 44.10; H, 2.92; N, 4.19.

Synthesis of Halogen-Substituted *N*^{2},*N*^{2},*N*^{7},*N*^{7}-Tetraaryl-9*H*-fluorene-2,7-diamines 8; General Procedure

In a flame-dried flask and under an argon atmosphere, a mixture of alkyl-substituted 2,7-diiodo-9*H*-fluorene **3**, brominated diphenylamine **7** (2.00 equiv), CuI (21 mol%), and 1,10-phenanthroline (40 mol%) was suspended in abs toluene (2 mL/mmol). Then, finely ground KOH (8.00 equiv) was added and the resulting mixture was heated to 100 °C until the reaction was complete. After cooling to r.t., the mixture was filtered through a pad of silica gel and the solvent was removed in vacuo. The remaining solid was purified by column chromatography (silica gel) or by recrystallization.

N^2,*N*^{7}-Bis(4-bromophenyl)-9,9-dimethyl-*N*^{2},*N*^{7}-diphenyl-9*H*-fluorene-2,7-diamine (8a)

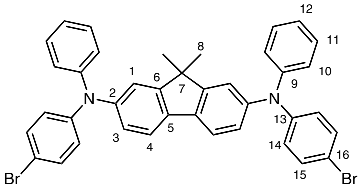


Figure 11

According to the general procedure using **3a** (800 mg, 1.79 mmol), **7a** (890 mg, 3.59 mmol, 2.00 equiv), CuI (73.6 mg, 0.38 mmol, 0.21 equiv), 1,10-phenanthroline (129.3 mg, 0.72 mmol, 0.40 equiv), and KOH (805 mg, 14.35 mmol, 8.00 equiv) gave the product (Figure 11) as a yellow glass; yield: 1.103 g (1.61 mmol, 90%); mp 215.5 °C.

^{1}H NMR (CDCl$_3$, 500 MHz, 300 K): δ = 1.352 (s, 6 H, 8-H), 6.988 (d, 8 H, 14-H), 7.042 (t, 2 H, 12-H), 7.115 (d, 2 H, 3-H), 7.133 (s, 2 H, 1-H), 7.271 (t, 4 H, 11-H), 7.343 (d, 4 H, 14-H), 7.503 (d, 2 H, 4-H); $^3J_{3,4}$ = 7.9 Hz, $^3J_{14,15}$ = 8.6 Hz.

^{13}C NMR (CDCl$_3$, 125 MHz, 300 K): δ = 27.13 (8-C), 46.99 (7-C), 114.80 (16-C), 119.06 (1-C), 120.37 (4-C), 123.26 (3-C), 123.86 (12-C), 124.38 (10-C), 125.18 (14-C), 129.45 (11-C), 132.28 (15-C), 134.52 (5-C), 146.44 (2-C), 147.31 (13-C), 147.64 (9-C), 155.35 (6-C).

MS (EI): *m*/*z* (%) = 688 (49, [M$_{\mathrm{Br(81)}}$]$^+$]), 686 (100, [M$_{\mathrm{Br(79)}}$]$^+$), 671 (10, [M – CH$_3$]$^+$), 606 (10, [M – Br]$^+$), 591 (5, [M – Br – CH$_3$]$^+$).

HRMS (EI): *m*/*z* [M] calcd for $C_{39}H_{30}Br_2N_2$: 684.0776; found: 684.0804.

Anal. Calcd for $C_{39}H_{30}Br_2N_2$: C, 68.23; H, 4.40; N, 4.08. Found: C, 67.44; H, 4.28; N, 4.27.

N^2,*N*^{2},*N*^{7},*N*^{7}-Tetrakis(4-bromophenyl)-9,9-dimethyl-9*H*-fluorene-2,7-diamine (8b)

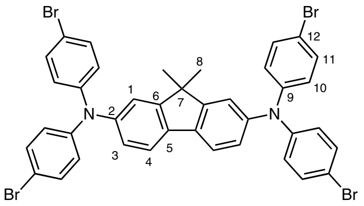


Figure 12

According to the general procedure using **3a** (5.097 mg, 11.426 mmol), **7b** (7.313 g, 22.363 mmol, 1.96 equiv), CuI (431 mg, 2.264 mmol, 0.20 equiv), 1,10-phenanthroline (836 mg, 4.636 mmol, 0.41 equiv), and KOH (5.106 g, 91 mmol, 7.97 equiv) gave a solid that was purified by column chromatography (silica gel, cyclohexane/petroleum ether/Et$_2$O, 1000:998:2) to give the product (Figure 12) as a colorless solid; yield: 7.205 g (8.534 mmol, 75%); mp 144.0–146.0 °C.

^{1}H NMR (CDCl$_3$, 500 MHz, 300 K): δ = 1.360 (s, 6 H, 8-H), 6.983 (d, 8 H, 10-H), 7.008 (d, 2 H, 3-H), 7.115 (s, 2 H, 1-H), 7.358 (d, 8 H, 11-H), 7.519 (d, 2 H, 4-H); $^4J_{1,3}$ = 1.6 Hz, $^3J_{3,4}$ = 8.1 Hz, $^3J_{10,11}$ = 8.6 Hz.

^{13}C NMR (CDCl$_3$, 125 MHz, 300 K): δ = 27.12 (8-C), 47.09 (7-C), 115.52 (12-C), 119.14 (1-C), 120.60 (4-C), 123.56 (3-C), 125.44 (10-C), 132.49 (11-C), 135.74 (5-C), 146.05 (2-C), 146.81 (9-C), 155.48 (6-C).

MS (EI): *m*/*z* (%) = 844 (100, [M]$^+$), 765 (10, $C_{39}H_{28}Br_3N_2$).

HRMS (EI): *m*/*z* [M] calcd for $C_{39}H_{28}Br_4N_2$: 839.8985; found: 839.8944.

N^2,*N*^{2},*N*^{7},*N*^{7}-Tetrakis(4-bromophenyl)-9,9-dibutyl-9*H*-fluorene-2,7-diamine (8c)

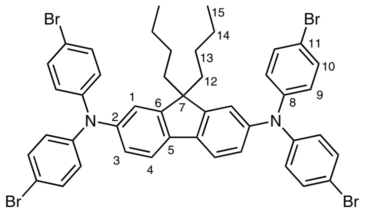


Figure 13

According to the general procedure using **3b** (14.00 g, 26.40 mmol), **7b** (17.23 g, 52.81 mmol, 2.00 equiv), CuI (1.08 g, 5.54 mmol, 0.21 equiv), 1,10-phenanthroline (1.903 g, 10.56 mmol, 0.40 equiv), and KOH (11.85 g, 211.23 mmol, 8.00 equiv) with purification by recrystallization (CH$_2$Cl$_2$/petroleum ether) gave the product (Figure 13) as yellow crystals; yield: 16.89 g (18.19 mmol, 69%); mp 213.5 °C.

^{1}H NMR (CDCl$_3$, 500 MHz, 300 K): δ = 0.642 (m, 4 H, 13-H), 0.719 (t, 6 H, 15-H), 1.028–1.119 (m, 4 H, 14-H), 1.778 (m, 4 H, 12-H), 6.895–7.006 (br, 10 H, 9-H, 3-H), 7.022 (br, 2 H, 1-H), 7.346 (d, 8 H, 10-H), 7.498 (br, 2 H, 4-H).

^{13}C NMR (CDCl$_3$, 125 MHz, 300 K): δ = 14.13 (15-C), 23.07 (14-C), 26.32 (13-C), 19.80 (12-C), 55.24 (7-C), 115.46 (11-C), 119.63 (1-C), 120.34 (4-C), 123.97 (3-C), 125.31 (9-C), 132.44 (10-C), 136.87 (5-C), 145.86 (2-C), 146.76 (8-C), 152.60 (6-C).

MS (EI): *m*/*z* (%) = 928 (100, [M]$^+$]), 828 (20, [M – 2 (C$_4$H$_9$)]$^+$).

Anal. Calcd for $C_{45}H_{40}Br_4N_2$: C, 58.21; H, 4.34; N, 3.02. Found: C, 58.32; H, 4.34; N, 3.07.

N^2,*N*^{2},*N*^{7},*N*^{7}-Tetrakis(4-bromophenyl)-9,9-dihexyl-9*H*-fluorene-2,7-diamine (8d)

According to the general procedure using 3c (10.00 g, 17.06 mmol), 7b (17.28 g, 52.84 mmol, 3.10 equiv), CuI (1.08 g, 5.54 mmol, 0.21 equiv), 1,10-phenanthroline (1.93 g, 10.71 mmol, 0.40 equiv), and KOH (7.66 g, 136.44 mmol, 8.00 equiv) with purification by recrystallization (CH$_2$Cl$_2$/petroleum ether) gave the product (Figure 14) as fine crystals; yield: 8.67 g (8.80 mmol, 52%); mp 208 °C.

^{1}H NMR (CDCl$_3$, 500 MHz, 300 K): δ = 0.659 (m, 4 H, 13-H), 0.838 (t, 6 H, 17-H), 1.011–1.112 (m, 8 H, 14-H, 15-H), 1.161 (m, 4 H, 16-H), 1.773 (m, 4 H, 12-H), 6.965 (d, 8 H, 9-H), 6.984 (d, 2 H, 3-H), 7.021 (s, 2 H, 1-H), 7.341 (d, 8 H, 10-H), 7.503 (d, 2 H, 4-H); $^3J_{9,10}$ = 8.5 Hz.

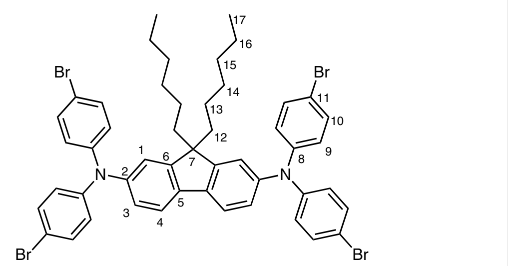


Figure 14

^{13}C NMR (CDCl$_3$, 125 MHz, 300 K): δ = 14.23 (17-C), 22.67 (16-C), 24.01 (13-C), 29.69 (15-C), 31.72 (14-C), 40.16 (12-C), 55.33 (7-C), 115.37 (11-C), 119.72 (1-C), 120.33 (4-C), 124.01 (3-C), 125.23 (9-C), 132.45 (10-C), 136.87 (5-C), 145.87 (2-C), 146.82 (8-C), 152.58 (6-C).

HRMS (EI): *m*/*z* [M] calcd for $C_{49}H_{48}{}^{79}Br_4N_2$: 980.0546; found: 980.0555.

Anal. Calcd for $C_{49}H_{48}Br_4N_2$: C, 59.78; H, 4.91; N, 2.85. Found: C, 59.76; H, 4.89; N, 2.72.

N^2,N^2,N^7,N^7-Tetrakis(4-bromophenyl)-9,9-dioctyl-9*H*-fluorene-2,7-diamine (8e)

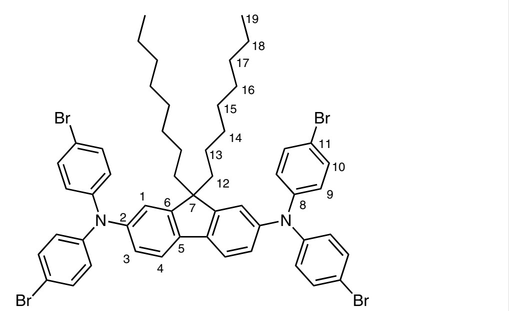


Figure 15

According to the general procedure using **3d** (17.00 g, 26.46 mmol), **7b** (17.31 g, 52.92 mmol, 2.00 equiv), CuI (1.08 g, 5.56 mmol, 0.21 equiv), 1,10-phenanthroline (1.93 g, 10.71 mmol, 0.40 equiv), and KOH (11.87 g, 211.69 mmol, 8.00 equiv) with purification by recrystallization (EtOAc) gave the product (Figure 15) as fine, colorless crystals; yield: 20.49 g (19.69 mmol, 74%); mp 185.5 °C.

^{1}H NMR (CDCl$_3$, 500 MHz, 300 K): δ = 0.658 (m, 4 H, 13-H), 0.874 (t, 6 H, 19-H), 0.991–1.236 (m, 16 H, 14-H, 15-H, 16-H, 17-H), 1.269 (m, 4 H, 18-H), 1.772 (m, 4 H, 12-H), 6.964 (d, 8 H, 9-H), 6.983 (d, 2 H, 3-H), 7.023 (s, 2 H, 1-H), 7.346 (d, 8 H, 10-H), 7.504 (d, 2 H, 4-H); $^3J_{9,10}$ = 8.7 Hz.

^{13}C NMR (CDCl$_3$, 125 MHz, 300 K): δ = 14.30 (19-C), 22.80 (18-C), 24.10 (13-C), 29.41 (15-C or 16-C), 29.52 (15-C or 16-C), 30.09 (14-C), 31.96 (17-C), 40.17 (12-C), 55.35 (7-C), 115.37 (11-C), 119.69 (1-C), 120.36 (4-C), 123.97 (3-C), 125.23 (9-C), 132.44 (10-C), 136.88 (5-C), 145.86 (2-C), 146.81 (8-C), 152.57 (6-C).

HRMS (EI): *m*/*z* [M] calcd for $C_{53}H_{56}Br_4N_2$: 1036.1172; found: 1036.1172.

Anal. Calcd for $C_{53}H_{56}Br_4N_2$: C, 61.17; H, 5.42; N, 2.69. Found: C, 61.18; H, 5.49; N, 2.62.

N^2,N^7-Bis(3-bromophenyl)-9,9-dimethyl-N^2,N^7-diphenyl-9*H*-fluorene-2,7-diamine (8f)

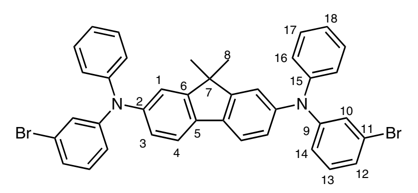


Figure 16

According to the general procedure using **3a** (11.90 g, 26.60 mmol), **7c** (15.30 g, 61.80 mmol, 2.30 equiv), CuI (435 mg, 2.28 mmol, 0.086 equiv), 1,10-phenanthroline (413 mg, 2.29 mmol, 0.086 equiv), and KOH (14.30 g, 216 mmol, 8.10 equiv) with purification by column chromatography (silica gel, petroleum ether/Et$_2$O) and recrystallization (cyclohexane/*n*-hexane) gave the product (Figure 16) as colorless crystals; yield: 11.60 g (16.90 mmol, 64%); mp 206–207 °C.

^{1}H NMR (CDCl$_3$, 500 MHz, 303 K): δ = 1.361 (s, 6 H, 8-H), 6.970–7.040 (m, 2 H, 3-H), 7.040–7.100 (m, 6 H, 1-H, 13-H, 18-H), 7.131 (d, 4 H, 16-H), 7.287 (‘t’, 4 H, 17-H), 7.537 (d, 2 H, 4-H), 6.97–7.04, 7.21–7.25, 7.14–7.17 (m, 6 H, 10-H, 12-H, 14-H); $^3J_{3,4}$ = 8.0 Hz, $^3J_{16,17}$ = 7.6 Hz.

^{13}C NMR (CDCl$_3$, 125 MHz, 303 K): δ = 26.95 (8-C), 46.89 (7-C), 119.30 (C-H), 120.34 (4-C), 121.40 (3-C), 122.80 (11-C), 123.42 (18-C), 124.06 (C-H), 124.56 (16-C), 124.83 (1- C), 125.62 (C-H), 129.41 (17-C), 130.31 (13-C), 134.59 (5-C), 146.13 (2-C), 147.29 (15-C), 149.52 (9-C), 155.26 (6-C).

MS (EI): *m*/*z* (%) = 686 (100, [$C_{39}H_{30}N_2Br_2$]$^+$), 607 (2, [$C_{39}H_{30}N_2Br$]$^+$).

HRMS (EI): *m*/*z* [M] calcd for $C_{39}H_{30}N_2Br_2$: 684.0776; found: 684.0788.

N^2,N^2,N^7,N^7-Tetrakis(3-bromophenyl)-9,9-dimethyl-9*H*-fluorene-2,7-diamine (8g)

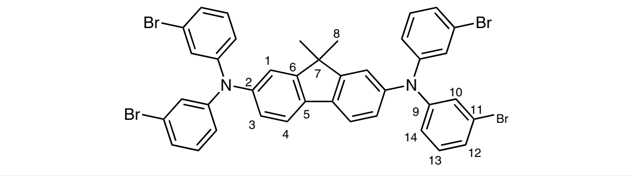


Figure 17

According to the general procedure using **3a** (18.70 g, 41.80 mmol), **7d** (31.40 g, 69.20 mmol, 2.30 equiv), CuI (804 mg, 4.22 mmol, 0.10 equiv), 1,10-phenanthroline (767 mg, 4.26 mmol, 0.010 equiv), and KOH (21.50 g, 216 mmol, 7.80 equiv) with purification by column chromatography (silica gel, cyclohexane/petroleum ether/Et$_2$O) and recrystallization (cyclohexane/*n*-hexane) gave the product (Figure 17) as colorless crystals; yield: 26.70 g (31.60 mmol, 76%); mp 239 °C

^{1}H NMR (CDCl$_3$, 500 MHz, 303 K): δ = 1.376 (s, 6 H, 8-H), 6.970–7.060 (m, 2 H, 3-H), 7.090–7.180 (m, 6 H, 1-H, 13-H), 7.21–7.25 (m, 4 H, 10-H), 7.562 (d, 2 H, 4-H), 6.970–7.060, 7.090–7.180 (m, 8 H, 12-H, 14-H); $^3J_{3,4}$ = 8.1 Hz.

^{13}C NMR (CDCl$_3$, 125 MHz, 303 K): δ = 26.91 (8-C), 46.99 (7-C), 119.58 (C-H), 120.65 (4-C), 122.18 (C-H), 122.95 (11-C), 124.37 (C-H), 125.90 (C-H), 126.46 (10-C), 128.77 (C-H), 130.55 (C-H), 135.04 (5-C), 145.68 (2-C), 148.83 (9-C), 155.48 (6-C).

MS (EI): m/z (%) = 844 (100, $[C_{39}H_{28}N_2Br_4]^+$), 764 (5, $[C_{39}H_{28}N_2Br_3]^+$), 747 (4, $[C_{38}H_{25}N_2Br_3]^+$).

HRMS (EI): m/z [M] calcd for $C_{39}H_{28}N_2Br_4$: 839.8985; found: 839.8992.

End-Functionalization by Suzuki–Miyaura Cross-Coupling; General Procedure

In modification of the literature procedure,[20] in a flame-dried flask and under an argon atmosphere, a mixture of the halogenated precursor molecule **8**, potassium vinyltrifluoroborate (1.75 equiv,/halide), Cs_2CO_3 (1.75 equiv/halide), $Pd(OAc)_2$ (0.03 equiv/halide), and Ph_3P (0.09 equiv/halide) was suspended in a degassed mixture of THF (3.6 mL/mmol) and H_2O (0.4 mL/mmol). Under vigorous stirring, the suspension was heated to 90 °C until the reaction was complete. The mixture was cooled to r.t., and then it was filtered through a pad of silica gel and the solvent was removed in vacuo. The residue was purified by column chromatography (silica gel).

9,9-Dimethyl-*N*^{2},*N*^{7}-diphenyl-*N*^{2},*N*^{7}-bis(4-vinylphenyl)-9*H*-fluorene-2,7-diamine (2V-Methyl) (10a)

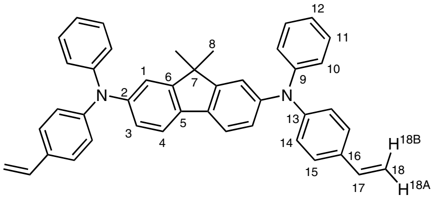


Figure 18

According to the general procedure, a mixture of **8a** (6.00 g, 8.74 mmol), potassium vinyltrifluoroborate (4.10 g, 30.59 mmol, 3.50 equiv), Cs_2CO_3 (9.97 g, 30.59 mmol, 3.50 equiv), $Pd(OAc)_2$ (118 mg, 0.52 mmol, 0.06 equiv), and Ph_3P (413 mg, 1.57 mmol, 0.18 equiv) were suspended in a degassed mixture of THF (31.5 mL) and H_2O (3.50 mL). Purification by column chromatography gave the product (Figure 18) as a yellow glass; yield: 1.70 g (2.93 mmol, 34%).

^{1}H NMR ($CDCl_3$, 500 MHz, 300 K): δ = 1.255 (s, 6 H, 8-H), 5.066 (d, 2 H, 18A-H), 5.552 (d, 2 H, 18B-H), 6.581 (dd, 2 H, 17-H), 6.923 (d, 2 H, 3-H), 6.935 (t, 2 H, 12-H), 6.973 (d, 4 H, 14-H), 7.042 (d, 4 H, 10-H), 7.069 (s, 2 H, 1-H), 7.163 (t, 4 H, 11-H), 7.206 (d, 4 H, 15-H), 7.403 (d, 2 H, 4-H); $^3J_{3,4}$ = 8.0 Hz, $^3J_{14,15}$ = 8.5 Hz, $^3J_{17,18A}$ = 10.9 Hz, $^3J_{17,18B}$ = 17.6 Hz, $^2J_{18A,18B}$ = 0.6 Hz.

^{13}C NMR ($CDCl_3$, 125 MHz, 300 K): δ = 27.15 (8-C), 46.99 (7-C), 112.19 (18-C), 119.1 (1-C), 120.23 (4-C), 122.94 (12-C), 123.57 (14-C), 123.86 (3-C), 124.36 (10-C), 127.21 (15-C), 129.38 (11-C), 131.90 (16-C), 134.36 (5-C), 136.43 (17-C), 146.59 (2-C), 147.83 (13-C), 147.94 (9-C), 155.25 (6-C).

MS (EI): m/z (%) = 580 (100, $[M]^+$]), 554 (15, $[M - (C_2H_3)]^+$), 371 (5, $[M - N(C_6H_5)(C_8H_7) - (CH_3)]^+$).

HRMS (EI): m/z [M] calcd for $C_{43}H_{36}N_2$: 580.2879; found: 580.2832.

Anal. Calcd for $C_{43}H_{36}N_2$: C, 88.93; H, 6.25; N, 4.82. Found: C, 88.49; H, 6.30; N, 4.58.

9,9-Dimethyl-*N*^{2},*N*^{2},*N*^{7},*N*^{7}-tetrakis(4-vinylphenyl)-9*H*-fluorene-2,7-diamine (4V-Methyl) (10b)

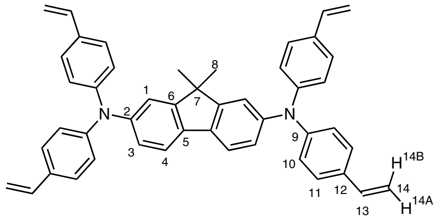


Figure 19

According to the general procedure, a mixture of **8b** (2.02 g, 2.39 mmol), potassium vinyltrifluoroborate (2.57 g, 19.00 mmol, 7.95 equiv), Cs_2CO_3 (6.27 g, 19.22 mmol, 8.04 equiv), $Pd(OAc)_2$ (60 mg, 0.27 mmol, 0.11 equiv), and Ph_3P (198 mg, 0.75 mmol, 0.32 equiv) was suspended in a degassed mixture of THF (45 mL) and H_2O (5 mL). Purification by column chromatography (cyclohexane/petroleum ether/Et_2O, 1000:998:2) gave the product (Figure 19) as a yellow solid; yield: 617 mg (0.98 mmol, 41%).

^{1}H NMR ($CDCl_3$, 500 MHz, 300 K): δ = 1.364 (s, 6 H, 8-H), 5.183 (d, 4 H, 14A-H), 5.669 (d, 4 H, 14B-H), 6.689 (dd, 4 H, 13-H), 7.037 (d, 2 H, 3-H), 7.087 (d, 8 H, 10-H), 7.176 (s, 2 H, 1-H), 7.317 (d, 8 H, 11-H), 7.513 (d, 2 H, 4-H); $^4J_{1,3}$ = 1.8 Hz, $^3J_{3,4}$ = 8.2 Hz, $^3J_{10,11}$ = 8.2 Hz, $^3J_{13,14A}$ = 10.8 Hz, $^3J_{13,14B}$ = 17.4 Hz, $^2J_{14A,14B}$ = 0.6 Hz.

^{13}C NMR ($CDCl_3$, 125 MHz, 300 K): δ = 27.12 (8-C), 47.01 (7-C), 112.34 (14-C), 119.18 (1-C), 123.84 (10, 3-C), 127.22 (11-C), 132.17 (12-C), 134.46 (5-C), 136.36 (13-C), 146.35 (2-C), 147.51 (9-C), 155.27 (6-C).

MS (EI): m/z (%) = 632 (100, $[M]^+$), 605 (20, $C_{45}H_{37}N_2$).

HRMS (EI): m/z [M] calcd for $C_{47}H_{40}N_2$: 632.3192; found: 632.3207.

9,9-Dibutyl-*N*^{2},*N*^{2},*N*^{7},*N*^{7}-tetrakis(4-vinylphenyl)-9*H*-fluorene-2,7-diamine (4V-Butyl) (10c)

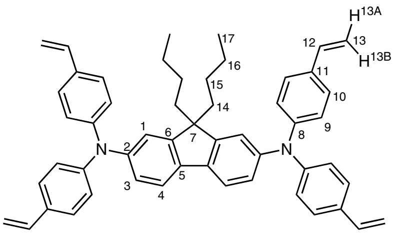


Figure 20

According to the general procedure, a mixture of **8c** (8.00 g, 8.62 mmol), potassium vinyltrifluoroborate (8.08 g, 60.32 mmol, 7.00 equiv), Cs_2CO_3 (19.65 g, 60.32 mmol, 7.00 equiv), $Pd(OAc)_2$ (193 mg, 0.86 mmol, 0.10 equiv), and Ph_3P (678 mg, 2.59 mmol, 0.30 equiv) was suspended in a degassed mixture of THF (38.8 mL) and H_2O (4.31 mL). Purification by column chromatography gave the product (Figure 20) as a yellow solid; yield: 1.10 g (1.53 mmol, 18%).

^{1}H NMR ($CDCl_3$, 500 MHz, 300 K): δ = 0.651 (m, 4 H, 15-H), 0.743 (t, 6 H, 17-H), 1.048–1.137 (m, 4 H, 16-H), 1.784 (m, 4 H, 14-H), 5.178 (d, 4 H, 13A-H), 5.660 (d, 4 H, 13B-H), 6.686 (dd, 4 H, 12-H), 7.029 (d, 2 H, 4-H), 7.081 (d, 8 H, 9-H), 7.094 (s, 2 H, 1-H), 7.305 (d, 8 H, 10-H), 7.501 (d, 2 H, 3-H); $^3J_{3,4}$ = 8.2 Hz, $^3J_{9,10}$ = 8.6 Hz, $^3J_{12,13A}$ = 10.8 Hz, $^3J_{12,13B}$ = 17.54 Hz, $^2J_{13A,13B}$ = 0.9 Hz.

^{13}C NMR (CDCl$_3$, 125 MHz, 300 K): δ = 14.09 (17-C), 23.10 (16-C), 24.01 (13-C), 26.31 (15-C), 30.50 (14-C), 39.87 (12-C), 55.17 (7-C), 112.31 (13-C), 119.78 (1-C), 120.03 (3-C), 123.67 (9-C), 123.98 (4-C), 127.19 (10-C), 132.11 (11-C), 136.39 (12-C), 136.65 (5-C), 146.19 (2-C), 147.52 (8-C), 152.31 (6-C).

MS (EI): *m*/*z* (%) = 716 (60, [M]$^+$]), 690 (10, [M – C_2H_3]$^+$), 220 (30, [N(C_8H_7)$_2$]$^+$).

9,9-Dimethyl-*N*^{2},*N*^{7}-diphenyl-*N*^{2},*N*^{7}-bis(3-vinylphenyl)-9*H*-fluorene-2,7-diamine (*m*2V-Methyl) (10f)

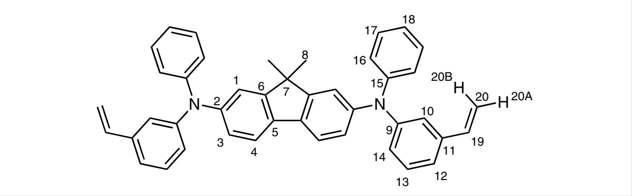


Figure 21

According to the general procedure, a mixture of **8f** (6.00 g, 8.74 mmol), potassium vinyltrifluoroborate (4.11 g, 30.60 mmol, 3.50 equiv), Cs_2CO_3 (9.97 g, 30.60 mmol, 3.50 equiv), Pd(OAc)$_2$ (118 mg, 0.52 mmol, 0.06 equiv), and Ph$_3$P (413 mg, 1.57 mmol, 0.18 equiv) was suspended in a degassed mixture of THF (31.5 mL) and H_2O (3.5 mL). Purification by column chromatography gave the product (Figure 21) as an off-white solid; yield: 3.48 g (5.99 mmol, 68%).

^{1}H NMR (CDCl$_3$, 500 MHz, 303 K): δ = 1.352 (s, 6 H, 8-H), 5.188 (dd, 2 H, 20A-H), 5.636 (dd, 2 H, 20B-H), 6.618 (dd, 2 H, 19-H), 6.98–7.29 (m, 22 H, 1-H, 3-H, 16-H, 17-H, 18-H, 10-H, 12-H, 13-H, 14-H), 7.503 (d, 2 H, 4-H); $^3J_{3,4}$ = 7.9 Hz, $^3J_{19,20B}$ = 17.5 Hz, $^3J_{19,20A}$ = 10.9 Hz, $^2J_{20A,20B}$ = 0.6 Hz.

^{13}C NMR (CDCl$_3$, 125 MHz, 303 K): δ = 26.98 (8-C), 46.81 (7-C), 113.98 (20-C), 120.04 (4- C), 134.10 (5-C), 136.69 (19-C), 138.71 (11-C), 146.58 (2-C), 155.04 (6-C), 118.85, 120.34, 121.69, 122.60, 123.38, 123.58, 124.02, 129.20, and 129.29 (1-C, 3-C, 10-C, 12-C, 13-C, 14-C, 16-C, 17 C, 18-C), 147.92 and 148.30 (9-C, 15-C).

MS (EI): *m*/*z* (%) = 580 (96, [$C_{43}H_{36}N_2$]$^+$), 565 (5, [$C_{42}H_{33}N_2$]$^+$), 554 (2, [$C_{41}H_{34}N_2$]$^+$), 371 (3, [$C_{28}H_{21}N_2$]$^+$), 28 (100, [C_2H_4]$^+$).

HRMS (EI): *m*/*z* [M] calcd for $C_{43}H_{36}N_2$: 580.2879; found: 580.2897.

Anal. Calcd for $C_{43}H_{36}N_2$: C, 88.93; H, 6.25; N, 4.82. Found: C, 88.77; H, 6.34; N, 4.56.

9,9-Dimethyl-*N*^{2},*N*^{2},*N*^{7},*N*^{7}-tetrakis(3-vinylphenyl)-9*H*-fluorene-2,7-diamine (*m*4V-Methyl) (10g)

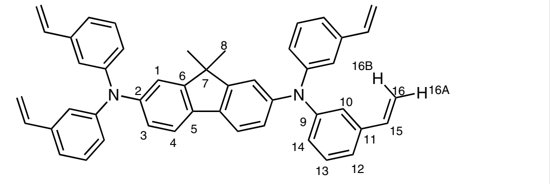


Figure 22

According to the general procedure, a mixture of **8g** (9.00 g, 10.60 mmol), potassium vinyltrifluoroborate (9.99 g, 74.60 mmol, 7.00 equiv), Cs_2CO_3 (24.3 g, 74.60 mmol, 7.00 equiv), Pd(OAc)$_2$ (239 mg, 1.07 mmol, 0.10 equiv), and Ph$_3$P (839 mg, 3.20 mmol, 0.30 equiv) was suspended in a degassed mixture of THF (48 mL) and H_2O (5.3 mL). Purification by column chromatography gave the product (Figure 22) as an off-white solid; yield: 4.05 g (6.40 mmol, 60%).

^{1}H NMR (CDCl$_3$, 500 MHz, 303 K): δ = 1.360 (s, 6 H, 8-H), 5.193 (d, 4 H, 16A-H), 5.645 (d, 4 H, 16B-H), 6.624 (dd, 4 H, 15-H), 6.97–7.30 (m, 20 H, 3-H, 4-H, 10-H, 12-H, 13-H, 14-H), 7.518 (br, 2 H, 1-H); $^3J_{15,16B}$ = 17.1 Hz, $^3J_{15,16A}$ = 10.7 Hz.

^{13}C NMR (CDCl$_3$, 125 MHz, 303 K): δ = 26.96 (8-C), 46.82 (7-C), 114.03 (16-C), 120.08 (1- C), 134.13 (5-C), 136.37 (15-C), 138.75 (11-C), 146.51 (2-C), 148.11 (9-C), 155.05 (6-C), 118.83, 120.47, 121.81, 123.57, and 129.33 (3-C, 4-C, 10-C, 12-C, 13-C, 14-C).

MS (EI): *m*/*z* (%) = 632 (100, [$C_{47}H_{40}N_2$]$^+$), 617 (5, [$C_{26}H_{37}N_2$]$^+$), 605 (3, [$C_{45}H_{38}N_2$]$^+$), 397 (3, [$C_{30}H_{23}N$]$^+$), 28 (14, [C_2H_4]$^+$).

HRMS (EI): *m*/*z* [M] calcd for $C_{47}H_{40}N_2$: 632.3192; found: 632.3219.

Anal. Calcd for $C_{47}H_{40}N_2$: C, 89.20; H, 6.37; N, 4.43. Found: C, 88.92; H, 6.50; N, 4.09.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1590824.

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