

## **Supporting Information**

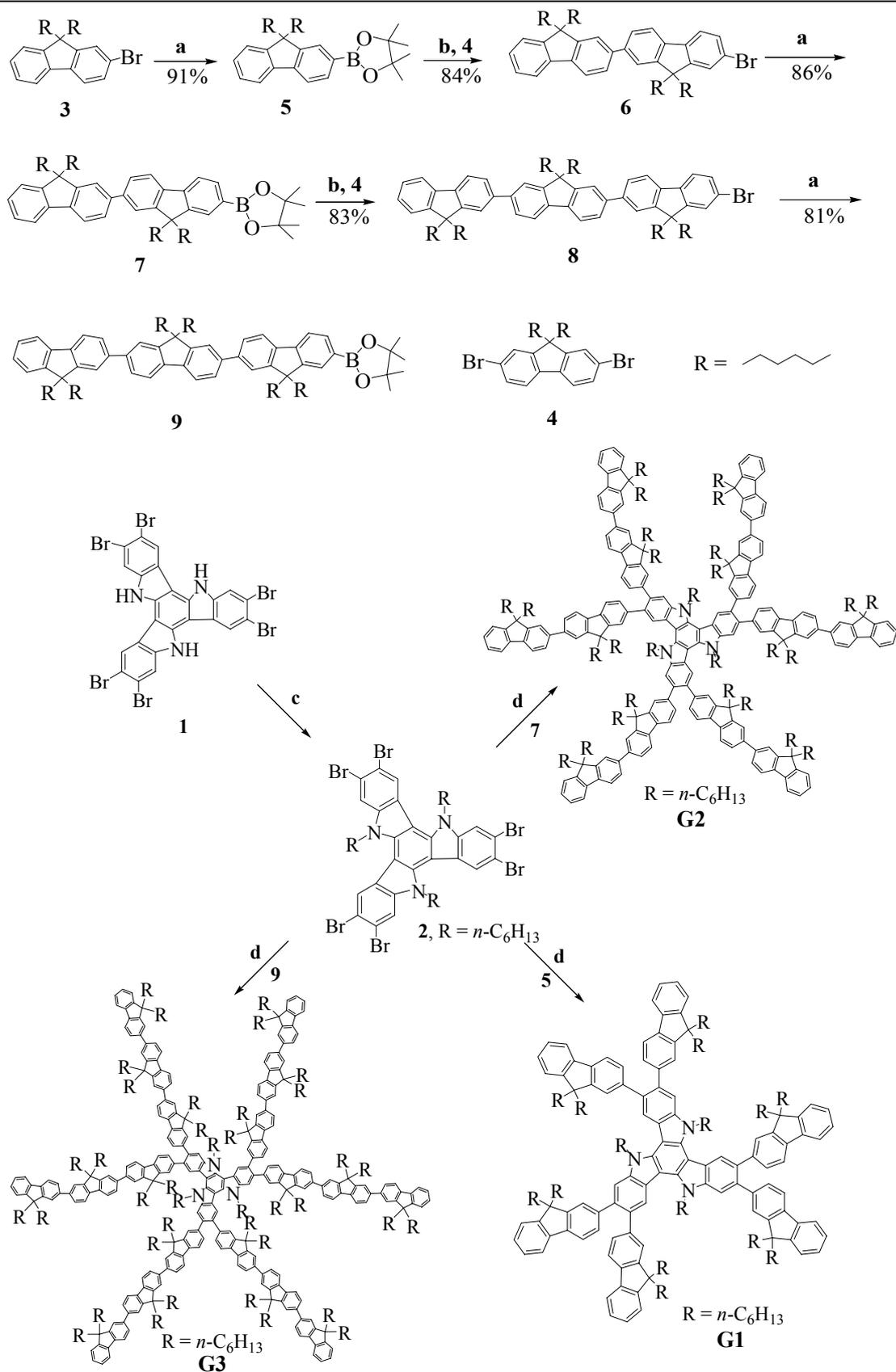
**For**

# **Microwave-Enhanced Multiple Suzuki Couplings toward Highly Luminescent Starburst Monodisperse Macromolecules**

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**Scheme 1.** Reagents and conditions: (a) (i)  $n\text{-BuLi}$ ,  $-78\text{ }^\circ\text{C}$ ; (ii) 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane,  $-78\text{ }^\circ\text{C}$  to rt. (b) Conventional heating,  $\text{Pd}(\text{PPh}_3)_4$ , 2 M  $\text{K}_2\text{CO}_3/\text{H}_2\text{O}$ , THF, reflux, 2 d. (c) Conventional heating,  $\text{KOH}$ , THF, reflux, 12 h. (d) Microwave heating, pressurized-vessel,  $\text{Pd}(\text{PPh}_3)_4$ , aqueous  $\text{K}_2\text{CO}_3\text{---THF}$ ,  $150\text{ }^\circ\text{C}$ , 15–30 min.

## Experimental Section.

Hexabromo-triazatruxene (**1**),<sup>1</sup> 2-bromo-9,9-dihexylfluorene (**3**),<sup>2</sup> 2,7-dibromo-9,9-dihexylfluorene (**4**),<sup>3</sup> 2-(2-bromo-9,9-dihexyl-9H-fluoren-7-yl)-9,9-dihexyl-9H-fluorene (**6**),<sup>4</sup> and 2-(2-bromo-9,9-dihexyl-9H-fluoren-7-yl)-9,9-dihexyl-7-(9,9-di-hexyl-9H-fluoren-2-yl)-9H-fluorene (**8**)<sup>4</sup> were obtained similarly to the procedures described in the literatures.

**General procedure for synthesis of oligofluorene boronates 5, 7, and 9.** Into a solution of the corresponding 2-bromofluorene derivatives (**3**, **6** or **8**) in anhydrous THF (12–15 mL per gram) was added dropwise *n*-BuLi (1.6 M solution in *n*-hexane, 1.1–1.3 equivalents) at  $-78\text{ }^{\circ}\text{C}$ , where the reaction mixture was stirred 1 h before adding 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.0 equiv.). The mixture was allowed to warm to room temperature and stirred for 12 h. It was poured onto crushed ice and extracted several times with ethyl ether. The extracts were washed with brine three times, and finally dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After filtration and evaporation of the solvents, the resulting product was purified by flash chromatography on a silica gel column with elution hexane/ethyl acetate (95:5) to afford oligofluorene boronates (**5**, **7**, or **9**).

**5:** Pale-yellow oil, yield 91%.  $^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ,  $\delta$ , ppm): 7.81–7.80 (d, 1H), 7.74–7.69 (m, 3H), 7.34–7.31 (m, 2H), 1.99–1.95 (m, 4H), 1.39 (s, 12H), 1.11–1.01 (m, 12H), 0.77–0.73 (t, 6H), 0.60–0.57 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz, DMSO,  $\delta$ , ppm): 151.5, 150.1, 144.3, 141.1, 133.9, 129.1, 127.7, 126.9, 123.1, 120.3, 119.6, 119.2, 83.9, 55.3, 40.5, 31.7, 29.9, 25.2, 25.0, 23.9, 22.8, 14.2. MALDI-TOF MS ( $m/z$ ): Calcd for  $\text{C}_{31}\text{H}_{45}\text{BO}_2$ , Exact Mass: 460.35, Mol. Wt.: 460.5; Found: 460.3 ( $\text{M}^+$ ).

**7:** White solid, yield 86%.  $^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ,  $\delta$ , ppm): 7.85–7.73 (m, 6H), 7.66–7.61 (m, 4H), 7.38–7.30 (m, 3H), 1.97–1.93 (m, 8H), 1.33 (s, 12H), 1.06–0.99 (m, 24H), 0.70–0.61 (m, 20H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 152.3, 151.7, 151.2, 150.4, 144.0, 141.2, 141.0, 140.7, 140.6, 140.3, 134.0, 129.2, 127.3, 127.1, 126.4, 123.2, 121.8, 120.7, 120.2, 120.0, 119.4, 84.1, 55.6, 55.5, 40.7, 40.6, 31.8, 30.0, 25.3, 24.1, 24.0, 22.9, 14.4. MALDI-TOF MS ( $m/z$ ): Calcd for  $\text{C}_{56}\text{H}_{77}\text{BO}_2$ , Exact Mass: 792.6, Mol. Wt.: 793.02; Found: 792.9 ( $\text{M}^+$ ).

**9:** White solid, yield 81%.  $^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ,  $\delta$ , ppm): 7.86–7.79 (m, 6H), 7.77–7.75 (d, 2H), 7.69–7.64 (m, 8H), 7.39–7.30 (m, 3H), 2.13–2.05 (m, 12H), 1.41 (s, 12H), 1.27–1.09 (m, 36H), 0.79–0.72 (m, 30H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 152.4, 152.1, 151.8, 151.3, 150.5, 144.2,

141.1, 140.8, 140.7, 140.5, 140.4, 140.3, 134.2, 129.2, 127.3, 127.1, 126.5, 126.4, 123.3, 121.9, 121.8, 120.7, 120.3, 120.2, 120.0, 119.4, 84.1, 55.7, 55.5, 40.7, 40.6, 31.8, 30.0, 25.3, 22.9, 14.4. MALDI-TOF MS ( $m/z$ ): Calcd for  $C_{81}H_{109}BO_2$ , Exact Mass: 1124.85, Mol. Wt.: 1125.54; Found: 1124.9 ( $M^+$ ).

**2.** A mixture of 2,3,7,8,12,13-hexabromo-5H-diindolo[3,2-a:3',2'-c]carbazole **1** (2.45 g, 3 mmol) and KOH (1.68 g, 30 mmol) was heated to reflux in THF (50 mL). Then, 1-bromohexane (2.23 g, 13.5 mmol) was added and the mixture was refluxing for 12 h before it was cooled to room temperature. The mixture was diluted with  $CH_2Cl_2$  and washed with 10% aqueous HCl solution and with saturated aqueous NaCl solution, dried ( $Na_2SO_4$ ) and evaporated. The resulting residue was purified by silica-gel column chromatography using hexane/ $CH_2Cl_2$  (8:1) as the eluent to give **2** as a white solid (2.96 g, 92%).  $^1H$  NMR (400 Hz,  $CDCl_3$ ,  $\delta$ , ppm): 8.02 (s, 3H), 7.55 (s, 3H), 4.08 (m, 6H), 1.74 (brs, 6H), 1.33–1.26 (m, 18H), 0.87–0.84 (m, 9H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ,  $\delta$ , ppm): 140.3, 138.9, 125.2, 123.1, 118.7, 115.4, 114.8, 101.5, 47.2, 31.7, 30.4, 26.4, 22.9, 14.2. MALDI-TOF MS ( $m/z$ ): Calcd for  $C_{42}H_{45}Br_6N_3$ , Exact Mass: 1064.87 Mol. Wt.: 1071.25; Found: 1069.0 ( $M^+$ ), 991.0 ( $[M-Br]^+$ ), 913.1 ( $[M-2Br]^+$ ), 833.2 ( $[M-3Br]^+$ ), 753.3 ( $[M-4Br]^+$ ), 675.3 ( $[M-5Br]^+$ ), 597.5 ( $[M-6Br]^+$ ).

**General procedure for synthesis of six-arm triazatruxenes G1–G3.** A solution of **2** (0.05 mmol), **5**, **7**, or **9** (0.39 mmol) and aqueous 2 M  $K_2CO_3$  (375  $\mu$ L, 0.75 mmol) in THF (3 mL for **5**, 4 mL for **7**, 5 mL for **9**) in a 10 mL pressurized vessel was carefully degassed before and after adding  $Pd(PPh_3)_4$  (0.03 mmol). The vessel was then sealed and heated in the CEM Discover system. The initial microwave power was set at 100 W. After the set temperature of 150  $^\circ$ C is reached, the microwave power regulated itself to keep that temperature for corresponding reaction hold time as listed in Table

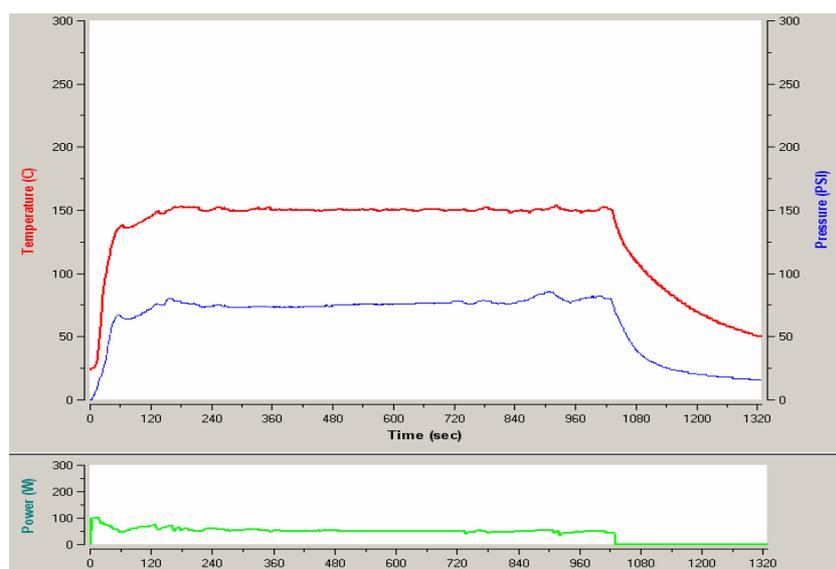
1 before cooling down to room temperature. The mixture was subsequently diluted with  $\text{CH}_2\text{Cl}_2$  and then washed with 1 M aqueous HCl and with saturated brine, dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated. The resulting residue was purified with column chromatography using hexane– $\text{CH}_2\text{Cl}_2$  as eluant to give the final product. The temperature was monitored using a calibrated infrared temperature control mounted under the reaction vessel. The pressure was controlled by a load cell connected to the vessel via the septum.

**G1:** Yield 89%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.44 (s, 3H), 7.71 (s, 3H), 7.64–7.62 (m, 9H), 7.57–7.55 (d, 3H), 7.45–7.43 (d, 3H), 7.39 (s, 3H), 7.35–7.33 (d, 3H), 7.30–7.20 (m, 21H), 5.05 (m, 6H), 2.15 (m, 6H), 1.89–1.74 (m, 24H), 1.26 (m, 36H), 1.20–1.18 (m, 9H), 1.08–0.87 (m, 54H), 0.77–0.56 (m, 60H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 151.1, 151.0, 150.8, 150.5, 142.1, 141.5, 141.2, 141.1, 140.9, 139.9, 139.5, 139.3, 136.7, 133.9, 129.3, 129.0, 127.1, 127.0, 126.9, 125.6, 125.2, 124.3, 123.0, 122.9, 119.9, 119.8, 119.5, 119.3, 112.4, 103.5, 55.1, 55.0, 47.6, 40.6, 32.2, 31.9, 30.0, 29.6, 26.9, 24.1, 22.9, 22.8, 14.4, 14.3, 14.2. MALDI-TOF MS ( $m/z$ ): Calcd for  $\text{C}_{192}\text{H}_{243}\text{N}_3$ , Exact Mass: 2590.91, Mol. Wt.: 2593; Found: 2592.0 ( $\text{M}^+$ ), 2507.6 ( $[\text{M}-\text{C}_6\text{H}_{13}]^+$ ), 2423.8 ( $[\text{M}-2\text{C}_6\text{H}_{13}]^+$ ). Anal. Calcd for  $\text{C}_{192}\text{H}_{243}\text{N}_3$ : C, 88.93; H, 9.45; N, 1.62. Found: C, 88.86; H, 9.48; N, 1.66.

**G2:** Yield 86%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.51 (s, 3H), 7.77–7.70 (m, 24H), 7.63–7.50 (m, 30H), 7.46 (s, 3H), 7.39–7.29 (m, 24H), 5.11 (m, 6H), 2.21–1.81 (m, 54H), 1.38–1.07 (m, 156H), 0.86–0.72 (m, 135H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 151.6, 151.2, 142.2, 141.6, 141.0, 140.8, 140.5, 140.4, 136.7, 133.9, 132.7, 127.1, 127.0, 126.2, 123.1, 121.6, 120.0, 103.5, 55.3, 40.6, 32.7, 31.8, 31.7, 29.9, 24.0, 22.9, 22.8, 20.3, 14.4, 14.3, 14.2. MALDI-TOF MS ( $m/z$ ): Calcd for  $\text{C}_{342}\text{H}_{435}\text{N}_3$ , Exact Mass: 4584.41, Mol. Wt.: 4588.13; Found: 4586.7 ( $\text{M}^+$ ), 4469.0 ( $[\text{M}-117.7]^+$ ), 4350.8 ( $[\text{M}-117.7-118.2]^+$ ). Anal. Calcd for  $\text{C}_{342}\text{H}_{435}\text{N}_3$ : C, 89.53; H, 9.56; N, 0.92. Found: C, 89.50; H, 9.63; N, 0.94.

**G3:** Yield 84%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.52 (s, 3H), 7.82–7.71 (m, 36H), 7.67–7.51

(m, 54H), 7.47 (s, 3H), 7.43–7.30 (m, 24H), 5.13 (m, 6H), 2.22–1.84 (m, 78H), 1.37–1.08(m, 228H), 0.90–0.75 (m, 195H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 152.1, 151.8, 151.3, 141.1, 140.8, 140.6, 140.3, 126.4, 126.3, 123.3, 121.8, 120.3, 120.0, 55.5, 40.7, 32.0, 31.8, 30.2, 30.0, 27.0, 24.1, 23.1, 22.9, 14.5, 14.4. MALDI-TOF MS ( $m/z$ ): Calcd for  $\text{C}_{492}\text{H}_{627}\text{N}_3$ , Exact Mass: 6577.92, Mol. Wt: 6583.26; Found: 6581.0 ( $\text{M}^+$ ), 6461.9 ( $[\text{M}-119.1]^+$ ), 6344.7 ( $[\text{M}-119.1-117.2]^+$ ). Anal. Calcd for  $\text{C}_{492}\text{H}_{627}\text{N}_3$ : C, 89.76; H, 9.60; N, 0.64. Found: C, 89.57; H, 9.58; N, 0.63.



**Fig. S1** Temperature, pressure, and power profile after optimization for the preparation of **G1** in aqueous  $\text{K}_2\text{CO}_3$ -THF heated under sealed-vessel microwave irradiation conditions. The maximum pressure in the reaction vessel was ca. 75 psi. After the set temperature of 150 °C is reached, the power regulates itself down to ca.50 W.

## References

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