Progress in the Suzuki Polycondensation of Fluorene Monomers

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1. Procedures for monomer synthesis

\begin{center}
\begin{tikzpicture}
\path[use as bounding box, thick, draw=black, line width=0.2mm] (0,0) rectangle (3.5,3.5);
\end{tikzpicture}
\end{center}

\textbf{2,7-dibromo-9,9-bis(cyanopropyl)-fluorene}

A 100 mL three-neck, round bottom flask charged with 2,7-dibromo-9H-fluorene (2.00 g, 6.2 mmol) and 20 mL of DMSO was degassed (3 times) and heated at 60°C under nitrogen until complete dissolution. After slowly cooling to room temperature 50% aq. NaOH (4 mL, 50 mmol) and benzyltriethylammonium chloride (2.13 g, 10.0 mmol) in 10 mL of DMSO were slowly added and allowed to stir for 30 min. 4-Bromobutyronitrile (1.85 mL, 18.6 mmol) was added dropwise with a syringe and the reaction mixture was stirred for 6 hours at room temperature and monitored via TLC. Upon completion of the reaction, the mixture was diluted with water (100 mL) and neutralized with 1M HCl (aq.). The final yellow suspension was extracted with ethyl acetate (3 x 50 mL) and the combined organic layers were washed with 10% aq. HCl (2 x 25 mL), water (2 x 50 mL), sat. aq. NaHCO\textsubscript{3} (2 x 25 mL) and brine (2 x 50 mL). The organic phase was dried over MgSO\textsubscript{4} and the solvent was removed under vacuum. The resulting crude product was recrystalized (3 times) from n-butanol to yield the nitrile-decorated monomer (2.32 g, 82%) as bright yellowish crystals. mp 209 °C (from n-butanol). The nitrile garnished fluorene monomer is soluble in common solvents like chloroform, ethyl acetate, dichloromethane, tetrahydrofurane, dimethylsulfoxide, toluene and tetrachloroethane.

\begin{align*}
\delta_{\text{H}} (300 \text{ MHz, CDCl}_3): & 7.53 \text{ (m, 4H)}, 7.49 \text{ (s, 2H)}, 2.11 \text{ (m, 8H)}, 0.75 \text{ (m, 4H)}; \\
\delta_{\text{C}} (300 \text{ MHz, CDCl}_3): & 150.06, 139.17, 131.64, 126.14, 122.47, 122.12, 119.75, 54.73, 38.99, 20.12, 17.43.
\end{align*}

ESI-MS: (m/z) calculated for C\textsubscript{21}H\textsubscript{18}Br\textsubscript{2}N\textsubscript{2}Na [M+Na]\textsuperscript{+} 478.9734, found 478.9739.

Figure S1. \textsuperscript{1}H NMR spectrum of 2,7-dibromo-9,9-bis(cyanopropyl)-fluorene monomer. The signals of CDCl\textsubscript{3} (#) and \textsuperscript{13}C satellites (*) are marked.
2,7-dibromo-9,9-bis(tert-butyl(propyl-carbamate))-fluorene

The same procedure as above was applied starting from 2,7-dibromo-9H-fluorene (4.07 g, 12.56 mmol) and tert-butyl(3-chloropropyl)carbamate (7.3 g, 37.69 mmol). The resulting crude product was recrystallized (3 times) from a mixture of ethyl acetate and heptane (3:2) to yield the protected amino-decorated monomer (6.09 g, 76%) as pale yellow crystals. mp 159 °C (from ethyl acetate : heptane = 3:2). The (protected) amino garnished fluorene monomer is soluble in common solvents like chloroform, ethyl acetate, dichloromethane, tetrahydrofurane, dimethylsulfoxide, toluene and tetrachloroethane.

δ\textsubscript{H} (300 MHz, CD\textsubscript{3}SO): 7.82 (d, 2H), 7.67 (s, 2H), 7.55 (d, 2H), 6.61 (s, 2H), 2.66 (m, 4H), 1.97 (m, 4H), 1.31 (s, 18H), 0.58 (m, 4H).

δ\textsubscript{C} (300 MHz, CDCl\textsubscript{3}): 155.35, 150.98, 138.67, 130.39, 125.65, 121.50, 121.18, 78.73, 54.52, 40.14, 36.86, 28.10, 24.12.

ESI-MS: (m/z) calculated for C\textsubscript{29}H\textsubscript{39}Br\textsubscript{2}N\textsubscript{2}O\textsubscript{4} [M+H]\textsuperscript{+} 637.1277, found 637.1268.

Figure S2. \textsuperscript{1}H NMR spectrum of 2,7-dibromo-9,9-bis(tert-butyl(propyl-carbamate))-fluorene monomer. The signals of DMSO (\#) and \textsuperscript{13}C satellites (*) are marked.

1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene

A 2 L round bottom flask was charged with 47.60 g (287.1 mmol) of 1,4 - phenylenediboronic acid and 69.55 g ((588.6 mmol, 2.05 eq) of pinacol. The starting materials were dissolved in 1250 ml toluene and the reaction was heated along with a Dean-Stark apparatus over 24 hours. The solvent was removed in vacuum and the resulting crude solid was redissolved in diethylether. Hot filtration and subsequent crystallizations (3 times) yielded the desired product as colorless crystals (80.23 g, 84.7 %). mp 241 °C (from diethylether).

δ\textsubscript{H} (300 MHz, CDCl\textsubscript{3}): 7.81 (s, 4 H), 1.34 (s, 24 H) ppm. δ\textsubscript{C} (300 MHz, CDCl\textsubscript{3}): 134.22, 84.11, 25.02 (signal for the C atom next to B atom was not visible, as also reported by other authors).
Figure S3. $^1$H NMR spectrum of 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene monomer. The signals of CDCl$_3$ (β) and $^{13}$C satellites (*) are marked.

2. A typical procedure for Suzuki polycondensation (SPC)

A Schlenk flask was charged with precisely weighed in 1.00 g (2.182 mmol, 1.00 eq) of 2,7-dibromo-9,9-bis(cyanopropyl)-fluorene, 0.720 g (2.182 mmol, 1.00 eq) of 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene and 1.832 g of NaHCO$_3$ (10 eq). All weighing-vessels were carefully rinsed repeatedly with toluene to ensure complete transfer. In a glove box, 22.26 mg Pd[P(p-tolyl)$_3$]$_3$ (1 mol%) was weighed, dissolved in degassed toluene (1 mL) and added by syringe. The total amount of toluene was 25 mL, which was complemented with 10 mL of water. The reaction mixture was degassed by freeze-pump-thaw cycles, before (3 times) and after (2 times) the addition of Pd[P(p-tolyl)$_3$]$_3$. The reaction mixture was vigorously stirred at 90 °C for 96 h under nitrogen. After cooling to room temperature, 100 ml of toluene (or tetrachloroethane) were added to the mixture and the layers separated. The organic phase was washed with water (2 times), concentrated to be ca. 20 mL and poured into cold diethyl ether (200 mL). The resulting yellow precipitate was collected by filtration. The solid was redissolved (50 mL) and stirred with NaCN aq. solution (basic pH by NaHCO$_3$) for a minimum of 8h. The inorganic phase was separated and extracted with toluene. The combined organic phases were washed with dilute NaHCO$_3$ solution (2 times) and water (2 times), concentrated and precipitated from cold diethyl ether. The final precipitated product was collected by filtration and dried under vacuum to afford 588.4 mg (72%) of polymer CN as a bright yellow powder.

Note: The yield was calculated ignoring the presence of end functional groups whose nature is unclear. If any suspension was formed in the organic phase during workup it was heated close to reflux for at least 6h and any insoluble parts were filtered off after cooling and collected separately.

CN polymer: $\delta$H (500 MHz, C$_2$D$_2$Cl$_4$): 7.78 (s, 6H), 7.68 (s, 2H), 7.61 (s, 2H), 2.22 (broad, 4H), 2.02 (broad, 4H), 1.02 (broad, 4H).
NHBoc: 2,7-dibromo-9,9-bis(tert-butyl(propyl-carbamate))-fluorene (1 g, 1.566 mmol, 1.00 eq), 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (516.8 mg, 1.566 mmol, 1.00 eq), NaHCO3 (1314 mg, 15.66 mmol, 10 eq), Pd(dppf)Cl2 (12.5 mg, 1 mol%), toluene (15 mL) and water (10 mL) were used in the typical SPC procedure described above. The polymer was obtained as a dark yellow powder (677.8 mg, 78%).

NHBoc polymer: $\delta_{1H}$ (500 MHz, C2D2Cl4): 7.85-7.80 (broad, 6H), 7.70-7.65 (s, 4H), 4.33 (s, 2H), 2.93 (broad, 4H), 2.16-2.09 (broad, 4H), 1.36 (s, 18H), 0.94 (broad, 4H).

Figure S4. MALDI–TOF mass spectrum (in black) versus mMass simulated mass spectrum (flipped, colored, each colour corresponding to a different end group pattern) of the lower mass fraction of polymer CN. The inset shows a magnified region corresponding to the MALDI–TOF mass spectrum (in red) ad mMass simulated mass spectrum (in blue) of the C3 oligomer (3 repeating units, end group pattern: Tol – M6 – PO(Tol)2) with a difference between the two smaller than 0.15 m/z.
Figure S5. Fluorescence spectra of polymers NHBoc and CN at different concentrations in DMF solutions ($10^{-5} – 10^{-9}$ M).