

## Supporting information for: ***Elegant Synthesis towards Soluble Polyfluorenone***

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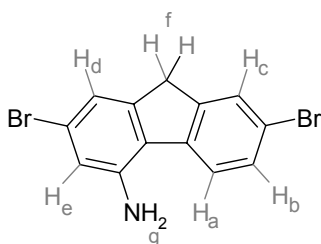
### Experimental section

#### *General Methods:*

Chemicals were obtained from Fluka, Aldrich, and Merck and used as received if not specified otherwise.  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra were recorded in  $\text{CD}_2\text{Cl}_2$  using a Bruker DPX 250 and Bruker 300 AMX spectrometers with use of the solvent proton or carbon signal as an internal standard. Field Desorption (FD) mass spectra were obtained on a VG Instruments ZAB 2-SEFPD. Elemental analysis was carried out on a Foss Heraeus Vario EL in the Institute for Organic Chemistry at the Johannes Gutenberg University, Mainz. The optical absorption measurements were performed at ambient temperature in a THF solution using a UV/Vis/NIR Perkin-Elmer Lambda 900 spectrometer. DSC was measured by Mettler DSC 30 with a heating rate of 10 K/min from  $-150\text{ }^\circ\text{C}$  to  $250\text{ }^\circ\text{C}$ . Gel permeation chromatography (GPC) analysis was performed with PL gel columns ( $10^3$  and  $10^4$  Å pore widths) connected to a UV/vis detector. The calibration was based on poly-*para*-phenylene standards with narrow weight distribution.

#### *Synthesis:*

##### ***2,7-Dibromo-4-amino-fluorene***



6.3 g 2,7-Dibromo-4-nitro-fluorene (17.1 mmol) were mixed with 30 mL concentrated, aqueous HCl and 80 mL ethanol. 8.1 g Tin powder (68.3 mmol) was added slowly, and the mixture was heated to reflux for 30 minutes. The reaction was poured into ice, extracted with ethyl acetate, washed with sodium carbonate, dried over magnesium sulfate, and the solvents removed *in vacuo* to yield 5.0 g of the title compound as a white powder (87 %).

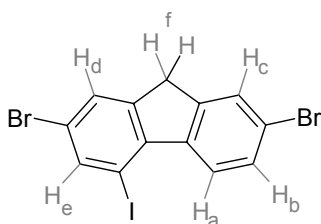
MS (FS, 8kV):  $m/z$  (%) = 337.4 (100%,  $M^+$ ) (calc. for  $C_{13}H_9Br_2N$  = 339.03 g mol<sup>-1</sup>)

<sup>1</sup>H-NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 7.67 (s, 1H,  $H_c$ ), 7.56 (d, 1H,  $^3J(H,H)$  = 8.10 Hz,  $H_a$ ), 7.51 (d, 1H,  $^3J(H,H)$  = 8.26 Hz,  $H_b$ ), 7.13 (s, 1H,  $H_d$ ), 6.88 (s, 1H,  $H_e$ ), 4.18 (s (broad), 2H,  $H_g$ ), 3.87 (s, 2H,  $H_f$ ).

<sup>13</sup>C-NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 146.84, 145.28, 143.86, 140.03, 130.11, 128.38, 125.67, 122.72, 121.69, 119.68, 118.92, 117.92, 37.28.

Elemental Analysis: 46.03% C, 3.03% H (calc. 46.06 % C, 2.68 % H).

### ***2,7-Dibromo-4-iodo-fluorene***



5.0 g 2,7-Dibromo-4-amino-fluorene (14.7 mmol) were dissolved in a mixture of 75 mL water and 75 mL sulphuric acid and cooled to 0 °C. Afterwards a solution of 1.06 g sodium nitrite in 10 mL water were added slowly, while the temperature was kept below 5 °C. The mixture was stirred for additional 30 minutes, before 5.4 g potassium iodide, dissolved in 10 mL water, were put in. The cloudy solution was brought to reflux and cooled down again. The precipitate was collected by filtration and purified by washing with 2M sodium hydroxide solution and water to afford 4.6 g of the desired product as an off-white crystalline material (70 %).

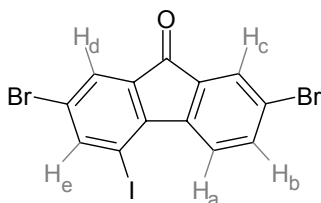
MS (FS, 8kV):  $m/z$  (%) = 450.4 (100%,  $M^+$ ) (calc. for  $C_{13}H_7Br_2I$  = 449.91 g mol<sup>-1</sup>)

<sup>1</sup>H-NMR (300 MHz, THF):  $\delta$  = 8.67 (d, 1H,  $^3J(H,H)$  = 8.49,  $H_a$ ), 8.05 (s, 1H,  $H_e$ ), 7.74 (s, 2H,  $H_d$ ,  $H_c$ ), 7.60 (d, 1H,  $^3J(H,H)$  = 8.49 Hz,  $H_b$ ), 3.94 (s, 2H,  $H_f$ ).

<sup>13</sup>C-NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 147.55, 146.30, 140.90, 140.48, 139.83, 128.84, 128.04, 127.88, 123.32, 121.64, 120.43, 87.51, 36.27.

Elemental Analysis: 34.66% C, 1.52% H (calc. 34.71 % C, 1.57 % H).

**2,7-Dibromo-4-iodo-9-fluorenone**



4.2 g 2,7-Dibromo-4-iodo-fluorene (9.3 mmol) were dissolved in 100 mL pyridine. 10 mL of a 1M *tert*-Butyl ammonium hydroxide solution in methanol was added, and the solution stirred with bubbling air for 3 days. 1M HCl was added until an approximately neutral solution was achieved, and the mixture was poured into water and filtered. The product was isolated by column chromatography (silica gel, eluent: hexane: ethylacetate = 4:1), and washed with ethyl acetate, to give 5.0 g of the title compound as a yellow powder (87 %).

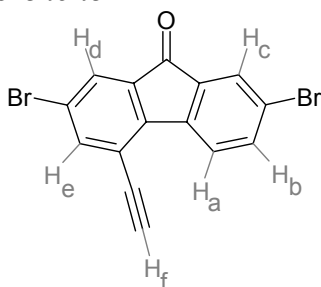
MS (FS, 8kV):  $m/z$  (%) = 464.3 (100%,  $M^+$ ) (calc. for  $C_{13}H_5Br_2IO$  = 463.90 g mol<sup>-1</sup>)

<sup>1</sup>H-NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 8.49 (d, 1H,  $^3J(H,H)$  = 8.23 Hz,  $H_a$ ), 8.11 (d, 1H,  $^4J(H,H)$  = 1.80 Hz,  $H_c$ ), 7.80 (d, 1H,  $^4J(H,H)$  = 1.98 Hz,  $H_d$ ), 7.76 (d, 1H,  $^4J(H,H)$  = 1.75 Hz,  $H_e$ ), 7.74 (d, 1H,  $^3J(H,H)$  = 8.24 Hz,  $^4J(H,H)$  = 1.98 Hz,  $H_b$ )

<sup>13</sup>C-NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 189.72, 148.05, 144.38, 142.98, 137.30, 135.80, 127.96, 127.58, 124.32, 123.58, 123.40, 88.86.

Elemental Analysis: 33.64% C, 1.16% H (calc. 33.66 % C, 1.09 % H).

**2,7-Dibromo-4-ethynyl-9-fluorenone**



527 mg 2,7-Dibromo-4-iodo-9-fluorenone (1.14 mmol), 560 mg trimethylsilylacetylene (5.7 mmol), 6 mg (22  $\mu$ mol) triphenylphosphine, and 4.3 mg copper (I) iodide (22  $\mu$ mol) were dissolved in a mixture of 30 mL triethylamine and 5 mL THF and degassed. Afterwards 16 mg bis(triphenylphosphin)palladium(II)chloride (22  $\mu$ mol) were added and the reaction was stirred at room temperature over night. The solvent was removed *in vacuo* and

the residue was purified by using preparative column chromatography (silica gel, hexane: ethyl acetate = 4:1,  $R_f$  = 0.6) to yield 720 mg of the desired product as a yellow crystalline material (81%, 1.66 mmol). To 0.4 g 2,7-dibromo-4-trimethylsilylethynyl-9-fluorenone (0.92 mmol) dissolved in 10 mL THF and 1 mL water, 1.5 g potassium carbonate was added. The resulting green solution was stirred for 2 hours, neutralized with 2M HCl, extracted with dichloromethane, washed with aqueous sodium carbonate solution, dried over magnesium sulfate, and the solvents removed *in vacuo* to yield 0.28 g of the title compound as a yellow powder (84 %).

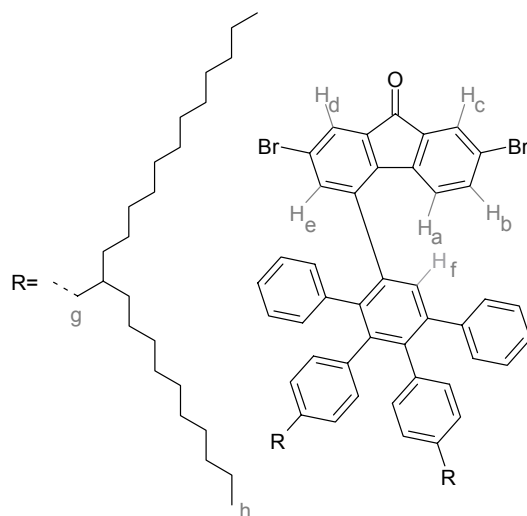
MS (FS, 8kV):  $m/z$  (%) = 362.4 (100%,  $M^+$ ) (calc. for  $C_{15}H_6Br_2O$  = 362.02 g mol<sup>-1</sup>)

<sup>1</sup>H-NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 8.17 (d, 1H,  $^3J(H,H)$  = 8.09 Hz,  $H_a$ ), 7.79 (d, 1H,  $^4J(H,H)$  = 1.94 Hz,  $H_c$ ), 7.75 (d, 1H,  $^4J(H,H)$  = 1.82 Hz,  $H_d$ ), 7.74 (d, 1H,  $^3J(H,H)$  = 1.85 Hz,  $H_d$ ), 7.69 (d, 1H,  $^3J(H,H)$  = 8.09 Hz,  $^4J(H,H)$  = 1.92 Hz,  $H_b$ ), 3.65 (s, 1H,  $H_f$ ).

<sup>13</sup>C-NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 190.18, 142.20, 141.48, 137.98, 135.77, 135.63, 132.24, 128.21, 127.81, 124.83, 124.18, 122.76, 84.94, 79.77.

Elemental Analysis: 49.73% C, 1.78% H (calc. 49.77% C, 1.67% H).

**2,7-Dibromo-4-(2,5-diphenyl-3,4-di(4-(2-decyl-tetradecyl)phenyl)phenyl)-9-fluorenone**



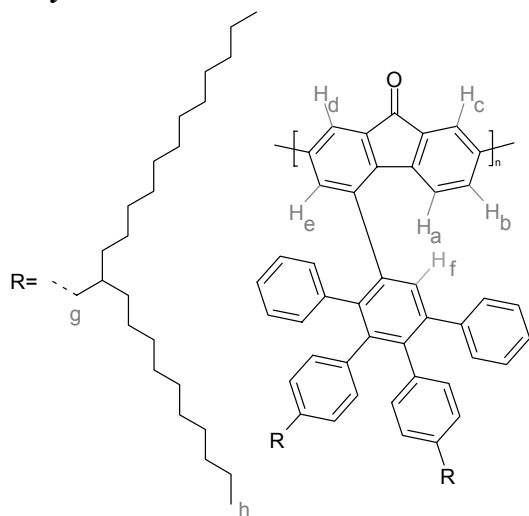
200 mg 2,7-Dibromo-4-ethynyl-9-fluorenone (552  $\mu\text{mol}$ ) and 2,5-diphenyl-3,4-bis-(4-(2-decyl-tetradecyl)-phenyl)-cyclopenta-2,4-dienone were dissolved 1 mL *o*-xylene. The reaction mixture was heated to 160  $^{\circ}\text{C}$  in a closed tube. After the reaction, the solvent was removed *in vacuo* and the residue was purified utilizing preparative column chromatography (silica gel, eluent: low boiling petroleum ether: dichloromethane = 7:3,  $R_f$  = 0.49) to afford 520 mg of the title compound (68%).

**MS** (FS, 8kV):  $m/z$  (%) = 1393.6 (100%,  $M^+$ )(calc. for  $\text{C}_{91}\text{H}_{122}\text{Br}_2\text{O}$  = 1391.79  $\text{g mol}^{-1}$ )

**$^1\text{H-NMR}$**  (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 7.71 (d, 1H,  $^4J(\text{H,H})$  = 1.83 Hz,  $H_c$ ), 7.58 (d, 1H,  $^4J(\text{H,H})$  = 1.86 Hz,  $H_d$ ), 7.52 (d, 1H,  $^3J(\text{H,H})$  = 8.05 Hz,  $^4J(\text{H,H})$  = 1.94 Hz,  $H_b$ ), 7.50 (s, 1H,  $H_f$ ), 7.41 (d, 1H,  $^4J(\text{H,H})$  = 1.85 Hz,  $H_e$ ), 7.2-6.6 (m, 19H,  $H_a$ ,  $H_{\text{arom}}$ ), 2.38 (d, 2H,  $^3J(\text{H,H})$  = 7.07 Hz,  $H_g$ ), 2.32 (d, 2H,  $^3J(\text{H,H})$  = 7.04 Hz,  $H_g$ ), 1.5-1.0 (m, 82H, - $\text{CH}_2$ -), 0.90 (t, 12H,  $^3J(\text{H,H})$  = 5.88 Hz,  $^4J(\text{H,H})$  = 1.75 Hz,  $H_h$ ).

**$^{13}\text{C-NMR}$**  (75 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 211.48, 163.69, 162.23, 162.039, 162.01, 161.01, 160.73, 160.66, 160.31, 160.23, 160.02, 159.98, 159.84, 157.86, 157.82, 157.77, 157.74, 157.70, 157.66, 156.80, 156.53, 156.00, 152.51, 152.27, 151.58, 151.44, 151.09, 150.24, 148.85, 148.81, 148.52, 148.20, 147.98, 147.66, 147.33, 147.16, 147.13, 145.70, 144.76, 143.67, 142.84, 156.81, 60.71, 53.71, 53.62, 52.79, 51.59, 51.24, 50.90, 50.57, 50.23, 49.87, 47.23, 44.22, 43.53, 35.12, 34.33, 47.91, 54.25, 53.54, 52.99, 52.11, 52.05, 49.53, 46.57, 42.84.

***Polymer :***



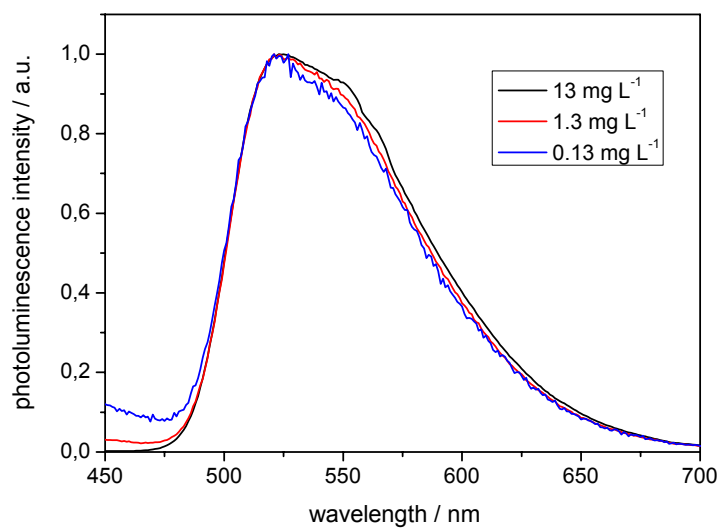
Ni(COD)<sub>2</sub> (112 mg, 0.4 mmol), 2,2'-bipyridyl (64 mg, 0.4 mmol) and COD (0.05 mL, 0.4 mmol) was mixed with 2 mL dry DMF and 0.5 mL dry toluene in a glove box. The purple solution was heated to 80 °C for 30 minutes. 2,7-Dibromo-4-(2,5-diphenyl-3,4-di(4-(2-decyl-tetradecyl)phenyl)phenyl)-9-fluorenone (240 mg, 0.17 mmol) in 3 mL of dry toluene was added, and the solution stirred under argon in absence of light for 2 days, before 0.5 mL of bromobenzene was added. The reaction mixture was precipitated in a methanol/HCl solution (4:1), filtered, subjected to Soxhlet extraction for 2 days in acetone, dissolved in THF, precipitated in methanol then filtered to give the title compound as a yellow solid. 170 mg (85%).

<sup>1</sup>H-NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 7.87-7.32 (m, 6H), 7.16-6.61 (m, 17H), 2.32-2.25 (m, 4H), 1.42-0.83 (m, 106H).

GPC:  $M_n = 2.7 \times 10^4 \text{ g mol}^{-1}$ ,  $M_w = 7.0 \times 10^4 \text{ g mol}^{-1}$ , and  $D = 2.6$  (against PPP standard).

Elemental Analysis: 87.74% C, 9.23% H (calc. 88.72% C, 9.98% H).

### Concentration dependent photoluminescence spectroscopy



**Figure 1. Concentration dependent emission spectrum of 7 in toluene.**