Supplementary Information

Synthesis and Characterization of Diazafluorene-based Oligofluorenes and Polyfluorenes

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Experimental section

Chemicals. All the solvents and reagents were purchased from commercial suppliers and used without further purification, unless noted otherwise. All products were purchased by flash column chromatography which was carried out with Kanto Silica Gel 60N (40-63 μm). Spectrochemical-grade solvents were used for optical measurements. Tetra(triphenylphosphine) palladium(II), and n-butyllithium were obtained from Aldrich Chemical Co. Sulfuric acids, nitric acid, bromine, sulfur monochloride, N,N-dimethyl formamide, aliquat 336, potassium carbonate, magnesium sulphate, chloroform, and toluene were purchased from Sinopharm Chemical Reagent Co., LtdS without further purification. THF and toluene were dried over sodium benzophenone ketyl anion radical and distilled under a dry nitrogen atmosphere immediately prior to use. 2-boromo-4,5-diazafluoren-9-one (4), 2,7-dibromo-4,5-diazafluoren-9-one (1), 2,7-bis(1′,3′,2′-dioxaborolan-2′-yl)-9,9′-dioctyl-fluorene (5), 2,7-dibromo-9,9′-dioctyl-fluorene (6), 2-(1′,3′,2′-dioxaborolan-2′-yl)-9,9′-dioctyl-fluorene, were obtained according to the literatures.

Characterization. $^1$H-NMR and $^{13}$C-NMR were recorded on a Bruker 400 MHz spectrometer in $d$-CDCl$_3$ with tetramethylsilane (TMS) as the interval standard. Mass spectra were recorded on a Shimadzu GCMS 2010 PLUS. Element analyses were carried out on an Elementa Analysensysteme GmbH Vario EL III Instrument. Absorption spectra were measured with a Shimadzu UV-3150 spectrometer at 25°C, and emission spectra were recorded on a Shimadzu RF-530XPC luminescence spectrometer upon excitation at the absorption maxima. Differential scanning calorimetry (DSC) analyses were performed on a Shimadzu DSC-60A Instrument at a heating rate of 10°C/min. Thermogravimetric analyses (TGA) were conducted on a

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Shimadzu DTG-60H thermogravimetric analyzer under a heating rate of 10 °C/min. Cyclic Voltammetric (CV) studies were conducted at room temperature on the CHI660E system in a typical three-electrode cell with a platinum sheet working electrode, a platinum wire counter electrode, and a silver/silver nitrate (Ag/Ag⁺) reference electrode. All electrochemical experiments were carried out under a nitrogen atmosphere at room temperature in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in CH₂Cl₂ expect that polymers were coated on Platinum plate electrodes in acetonitrile at a sweeping rate of 0.1 V/s. According to the redox onset potentials of the CV measurements, the highest occupied molecular orbital (HOMO)/lowest unoccupied energy levels (LUMO) of the materials are estimated based on the reference energy level of ferrocene (4.8 eV below the vacuum): HOMO/LUMO = – (E_{onset} – 0.04 V) – 4.8 eV, where the value 0.04 V is for ferrocene vs Ag/Ag⁺.

Experimental details

2,7-dibromo-4,5-diazafluorene (2). A mixture of 2,7-dibromo-4,5-diazafluoren-9-one (680 mg, 2mmol) and NH₂NH₂·H₂O (5 mL) was heated at 150 °C for 5 h. After cooling, the mixture was extracted with chloroform (3 × 100 mL). The organic layer was combined and dried over anhydrous MgSO₄. Solvents were removed in vacuum. The crude products was purified by column chromograph (silica gel, EtOAc: hexane = 1:2). A brown solid was obtained with a yield of 80% (520 mg, 1.6 mmol). GC-MS (m/z): 325 (M⁺); ¹H NMR (400 MHz, d-CDCl₃, ppm) δ 8.80 (s, 2H), 8.03 (s, 2H), 3.88 (s, 2H); ¹³C NMR (100 MHz, d-CDCl₃, ppm) δ 156.42, 150.91, 138.71, 135.74, 120.32, 31.73.

2,7-dibromo-9,9-dioxyl-4,5-diazafluorene (3). 2,7-Dibromo-4,5-diazafluorene (486 mg, 1.5 mmol) and t-BuOK (896 mg, 8mmol) were dissolved in anhydrous THF in a round-bottomed flask. The appropriate alkyl bromide (5 mmol) was added in one portion. The mixture was refluxed for 4 h under argon, and then the reaction was quenched with water, extracted with Et₂O and dried over anhydrous MgSO₄. The target product was isolated by purification of crude product using column
chromatography (silica gel, EtOAc: hexane = 1:6) to give a white solid (330 mg, 0.6 mmol) in 40% yield. GC-MS (m/z): 550 (M⁺); ¹H NMR (400 MHz, d-CDCl₃, ppm) δ 8.75-8.74 (d, J = 2 Hz, 2H), 7.83-7.82 (d, J = 2.4 Hz, 2H), 1.98-1.93 (m, J = 4.2 Hz, 4H), 1.21-1.07 (m, 24H), 0.86-0.81 (t, J = 6.8 Hz, 6H); ¹³C NMR (100 MHz, d-CDCl₃, ppm) δ 156.04, 150.95, 146.60, 133.51, 120.80, 51.72, 39.00, 31.72, 29.76, 29.11, 29.09, 24.04, 22.58, 14.07.

**General Procedure for Suzuki reactions.** A typical preparation procedure is as follows. In a three-necked schlenk flask (150 mL), 2-bromo-4,5-diazafluorenone (261 mg, 1 mmol), 2-(9,9'-dioctylfluoren-2-yl)-1,3,2-dioxaborinane (640 mg, 1.3 mmol, 1.3 eq), tetra(triphenylphosphine) palladium (0) (80 mg) were added. The flask was evacuated and back-filled with nitrogen atmosphere over three times, after which degassed toluene (30 mL) and K₂CO₃ aqueous solution (2M, 5 mL, 10 eq) were injected into the flask through syringe. The mixture was heated up to 90 °C and stirred for 2 days. The solvent was removed under vacuum. The mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether, 1:5) to afford pale yellow oil (482 mg, 80%).

2-(9,9'-dioctylfluoren-2-yl)-4,5-diazafluorenone (NFF). Rᵣ = 0.52 (ethyl acetate/petroleum ether, 1:3). ¹H NMR (400 MHz, CDCl₃) δ 9.10 (d, J = 2.1 Hz, 1H), 8.82 (dd, J = 5.0, 1.4 Hz, 1H), 8.26 (d, J = 2.1 Hz, 1H), 8.02 (dd, J = 7.5, 1.5 Hz, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.76 (d, J = 7.5 Hz, 1H), 7.64 (dd, J = 7.8, 1.5 Hz, 1H), 7.59 (s, 1H), 7.36 (m, 4H), 2.02 (m, 4H), 1.22 – 0.92 (m, 24H), 0.79 (t, J = 7.1 Hz, 6H); ¹³C NMR (100 MHz, d-CDCl₃) δ 189.90, 163.50, 161.66, 155.32, 153.70, 152.08, 151.06, 142.19, 140.13, 138.73, 135.17, 131.55, 129.75, 129.62, 127.72, 126.97, 125.96, 124.52, 123.01, 121.27, 120.47, 120.11, 55.38, 40.36, 31.75, 29.98, 29.71, 29.20, 23.80, 22.58, 14.06; MALDI-TOF-MS (m/z) calcd for C₄₀H₄₆N₂O [M⁺] 570.81, found 571.87.

2,7-bis(9,9'-dioctylfluoren-2-yl)-4,5-diazafluorenone (F₂NF). The compound was prepared analogously, corresponding to the 2,7-dibromo-4,5-diazafluorenone (340 mg, 1 mmol, 1 eq), 2-(9,9'-dioctylfluoren-2-yl)-1,3,2-dioxaborinane (1405 mg, 2.5 mmol, 2.5 eq) and tetra(triphenylphosphine) palladium (0) (70 mg) to give pale
yellow solids (614 mg, 60%). $R_f = 0.48$ (ethyl acetate/petroleum ether, 1:3, added a drop triethylamine). $^1$H NMR (400 MHz, $d$-CDCl$_3$, ppm) $\delta$ 9.12 (d, $J = 2.0$ Hz, 1H), 8.29 (d, $J = 1.9$ Hz, 1H), 7.84 (d, $J = 7.9$ Hz, 1H), 7.76 (d, $J = 6.2$ Hz, 1H), 7.66 (d, $J = 8.6$ Hz, 1H), 7.61 (s, 1H), 7.42 – 7.32 (m, 3H), 2.10 – 1.96 (m, 4H), 1.29 – 0.99 (m, 24H), 0.80 (t, $J = 7.0$ Hz, 7H); $^{13}$C NMR (100 MHz, $d$-CDCl$_3$, ppm) $\delta$ 189.88, 161.70, 153.77, 152.09, 151.07, 142.18, 138.49, 135.22, 130.02, 129.66, 127.72, 126.98, 125.93, 123.01, 121.26, 120.48, 120.11, 55.39, 40.38, 31.76, 29.99, 29.21, 23.81, 22.59, 14.07; MALDI-TOF-MS (m/z) calcd for C$_{69}$H$_{86}$N$_2$O [M$^+$] 959.43, found 960.97.

2,7-bis[4,5-diazafluoren-2-yl]-9,9'-dioctylfluorene (NF2F). The compound was prepared analogously, corresponding to the 2-bromo-4,5-diazafluoren-9-one (626 mg, 2.4 mmol, 2.4 eq), 2,7-bis(1',3',2'-dioxaborinan-2'-yl)-9,9'-dioctyl-fluorene (562 mg, 1 mmol, 1 eq) and tetra(triphenylphosphine) palladium (0) (70 mg) to give yellow solids (495 mg, 63%). $R_f = 0.38$ (ethyl acetate/petroleum ether, 1:3). $^1$H NMR (400 MHz, $d$-CDCl$_3$) $\delta$ 9.12 (d, $J = 2.1$ Hz, 1H), 8.84 (dd, $J = 5.1$, 1.4 Hz, 1H), 8.29 (d, $J = 2.1$ Hz, 1H), 8.04 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.89 (d, $J = 7.9$ Hz, 1H), 7.69 (d, $J = 7.8$ Hz, 1H), 7.63 (s, 1H), 7.38 (dd, $J = 7.5$, 5.1 Hz, 1H), 2.10 (m, 2H), 1.08 (m, 12H), 0.77 (t, $J = 6.9$ Hz, 3H); $^{13}$C NMR (100 MHz, $d$-CDCl$_3$) $\delta$ 189.82, 163.42, 161.81, 155.35, 153.70, 152.43, 141.18, 138.52, 135.91, 131.62, 129.70, 129.65, 126.26, 124.62, 121.40, 120.97, 55.77, 40.36, 31.71, 29.92, 29.20, 29.16, 23.89, 22.57, 14.04; MALDI-TOF-MS (m/z) calcd for C$_{51}$H$_{50}$N$_4$O$_2$ [M$^+$] 750.97, found 752.36.

Poly((9,9-dioctyl-fluorene)-co-(4,5-diazafluoren-9-one-2,7-yl) (PFO-NO). 2,7-dibromo-4,5-diazafluoren-9-one (100 mg, 0.3 mmol) and 2,7-dibromo-9,9-dioctyl-fluorene (548 mg, 1 mmol) were added to a appropriate DMF (10 mL) and toluene (10 mL) solution containing Ni(COD)$_2$ (0.50 g, 1.82 mmol), 1,5-cyclooctadiene (COD) (0.24 ml, 1.82 mmol), 2,2'-bipyridine (0.28 g, 1.82 mmol) in a 50 mL Schlenk tube under argon, respectively. The reaction mixture were stirred 96 h at 85 °C to obtain dark blue solution. The 1-bromobenzene was added to solution for terminating reaction. After the mixture had cooled to room temperature, 10 mL THF and 1.0 mL hydrazine hydrate were added for quenching reaction. The
precipitate was separated by filtration. The solution should further purification to be subjected to Al₂O₃ column chromatography eluting with THF to afford PFO-NO as orange powder (397 mg, 70%). ¹H NMR (400 MHz, d-CDCl₃, ppm) δ 9.13 (br, ArH), 8.312 (br, ArH), 7.86-7.36 (br, ArH), 2.17 (br, CH₂), 1.25-1.14 (br, CH₂), 0.83-0.80 (br, CH₃).

General procedures of Suzuki polycondensation, taking PFO-N15 as an example

Under argon atmosphere, a solution of 2,7-dibromo-9,9-dioctyl-fluorene (382 mg, 0.7 mmol), 2,7-bis(1',3',2'-dioxaborolan-2'-yl)-9,9'-dioctyl-fluorene (530 mg, 1 mmol), 2,7-dibromo-9,9-dioctyl-4,5-diazafluorene (3) (164 mg, 0.3 mmol), and Pd(PPh₃)₄ (15 mg) in the mixture solution of toluene/THF (1:5) was stirred and heated to 80 °C. After 1 h, K₂CO₃ aqueous solution (5 mL, 2M) was added. The solution was kept in 85-95 °C with vigorous stirring under argon for 2 days. The end groups were capped by refluxing 6 h with phenylboronic acid and bromobenzene, respectively. After cooling, the precipitate was separated by filtration. The solution was further purified by column chromatography using THF as eluent. to give a yellow solid. The resulting polymers were precipitated into methanol (300 mL) and filtered off. Then, the polymer was was subjected to Soxhlet extraction with acetone. The solid was dried under vacuum for 1 fay to get the final product. The yields of the polymerization reactions were about 60%. ¹H NMR (400 MHz, d-CDCl₃, ppm) δ 9.06 (br, ArH), 7.98-7.48 (br, ArH), 2.17 (br, CH₂), 1.25-1.14 (br, CH₂), 0.83-0.80 (br, CH₃).

PFO-N5: 2,7-dibromo-9,9-dioctyl-fluorene (492 mg, 0.9 mmol), 2,7-bis(1',3',2'-dioxaborolan-2'-yl)-9,9'-dioctyl-fluorene (530 mg, 1 mmol), and monomer 3 (54.8 mg, 0.1 mmol) to obtain yellow powder with a yield of 75%. ¹H NMR (400 MHz, d-CDCl₃, ppm) δ 9.06 (br, ArH), 8.03-7.37 (br, ArH), 2.17 (br, CH₂), 1.26-1.13 (br, CH₂), 0.83-0.80 (br, CH₃);

PFO-N50: 2,7-bis(1',3',2'-dioxaborolan-2'-yl)-9,9'-dioctyl-fluorene (530 mg, 1 mmol), and monomer 3 (548 mg, 1 mmol) to obtain yellow powder with a yield of 70%. ¹H NMR (400 MHz, d-CDCl₃, ppm) δ 9.06-9.92 (br, ArH), 7.98-7.90 (br, ArH), 7.76-7.66 (br, ArH), 2.12 (br, CH₂), 1.25-1.14 (br, CH₂), 0.84-0.80 (br, CH₃).
Figure SI-1. $^1$H NMR spectra of 2

Molecular Weight: 325.99
Figure SI-2. $^1$H NMR and $^{13}$C NMR spectra of 3
Figure SI-3. $^1$H NMR and $^{13}$C NMR spectra of NFF
Figure SI-4. $^1$H NMR and $^{13}$C NMR spectra of F2NF
Figure SI-5. $^1$H NMR and $^{13}$C NMR spectra of NF2F
Figure SI-6. $^1$H NMR spectrum of PFO-NFO
Figure SI-7. MODI-TOF spectra of NFF

Figure SI-8. MODI-TOF spectra of F2NF
Figure SI-9. MODI-TOF spectra of NF2F
Figure SI-10. TGA and DSC curves of polymers
Figure SI-11. The UV-vis absorption and emission spectra of compound F2NF in different solvents (M = 10^{-5} \text{ mol/L})
Figure S1-12. The UV-vis absorption and emission spectra of compound NF2F in different solvents (M = 10⁻⁵ mol/L)
Figure SI-13. Changes in UV-vis absorption (a) and PL (b) spectra of PFO-N5 (2.0 × 10⁻⁵ M, repeating unit) in chloroform at various concentrations of TFA: [TFA] = 0, 5 × 10⁻⁴, 1 × 10⁻³, 2 × 10⁻³, 4 × 10⁻³, 6 × 10⁻³, 8 × 10⁻³, 1 × 10⁻², 2 × 10⁻² M).
**Figure SI-14.** Changes in UV-vis absorption (a) and PL (b) spectra of PFO-N15 (2.0 × 10⁻⁵ M, repeating unit) in chloroform at various concentrations of TFA: [TFA] = 0, 5 × 10⁻⁴, 1 × 10⁻³, 2 × 10⁻³, 4 × 10⁻³, 6 × 10⁻³, 8 × 10⁻³, 1 × 10⁻², 2 × 10⁻² M).
**Figure SI-15.** UV-vis (a) and PL spectra (b) of polymer PFO-N50 (2 × 10^{-5} M, repeating unit) and metal ions (1 × 10^{-3} M) in THF-methanol (4:1). The following metal salts were used: KNO_{3}, NaNO_{3}, Mn(NO_{3})_{2}, Ni(NO_{3})_{2}, Cd(NO_{3})_{2}, Al(NO_{3})_{3}, Pb(NO_{3})_{2}, Fe(NO_{3})_{3}, Co(NO_{3})_{2}, Cu(NO_{3})_{2}.