Electronic Supplementary Information (ESI)

4,5-Diazafluorene co-oligomers as electron-deficient light-emitting materials and selective fluorescence sensors for mercury(II) cations

Sanjay Ghosh, Abdulaziz S. Alghunaim, Mohammed H. Al-mashhadani, Michal P. Krompiec, Megan Hallett, and Igor F. Perepichka*

School of Chemistry, Bangor University, Bangor, LL57 2UW, UK

*E-mail: i.perepichka@bangor.ac.uk; i_perepichka@yahoo.com; Tel: +44–(0)1248–382386

Materials and Instrumentations

All chemicals and solvents were purchased from either Aldrich, Alfa Aesar or Fischer Scientific and were used without further purification unless stated otherwise. Tetrahydrofuran (THF) was refluxed over sodium benzophenone ketyl (sodium metal + benzophenone) under argon and distilled off directly prior using the solvent for cyclic voltammetry and absorption/emission spectral measurements. Manual purification of the products was performed by column chromatography silica gel LC60 (40–60 μM). Some products were purified using Telydyne Isco automatic flash chromatograph, model Combiflash Rf 200 using Biotage disposable PTFE columns, hand-filled with silica gel LC60 (40–60 μM). For monitoring the progress of the reactions and control the products, thin layer chromatography (TLC) on pre-coated silica gel (Merck, 20 × 20 cm, Silica gel 60 F254) was used.

1H NMR, 13C NMR and DEPT-135 C NMR spectra were recorded either on a Bruker Avance 400 MHz or Bruker Avance 500 MHz in CDCl3 or DMSO-d6. Chemical shifts are reported in ppm, relative to tetramethylsilane (TMS) reference (δ = 0.00 ppm). The following abbreviations were used to assign NMR spectra: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, td = doublet of triplet. Mass spectra were recorded on GC-MS 5890 (Hewlett Packard Series II) or microTOF LC Bruker Daltonics mass spectrometers. Microwave assisted reactions were performed on a CEM Discover SP microwave reactor. Spin-coated films were prepared using spin coater from Laurel Technologies, Model WS-650Mz-23NPP/LITE.

Absorption and emission spectra, and the photoluminescence quantum yields

Shimadzu UV-3600 UV-Vis-NIR spectrophotometer and Horiba Yvon Fluoromax-4 spectrofluorometer were used for recording absorption and photoluminescence spectra at room temperature. Absorption and emission spectra in solutions were measured using HPLC grade solvents in 10 mm path length quartz cells. Solid state measurements were performed for spin-coated films deposited on 12.5 mm circular quartz windows. The films were prepared by spin coating from oligomer solutions (1–3 mg per 1 mL of DCM) at 3000–4000 rpm. Photoluminescence quantum yields (PLQY, ΦPL) in solutions for all oligomers were measured in HPLC grade dichloromethane (DCM) at room temperature according to the described method. The values of ΦPL were calculated according to the following formula:

ΦPL = Φr × (A/Ar) × (OD/OD) × (n²/nr²)

where ΦPL is a photoluminescence quantum yield, A is an integral intensity of the emission, OD is an optical density, and n is a refractive index of the used solvent. The subscript r refers to the reference fluorophore of known quantum yield [9,10-diphenylanthracene (DPA), diluted solution in cyclohexane, Φr = 90%). The solutions were deoxygenated by bubbling with argon for about 10 minutes before the measurements. Corrected emission and absorption spectrum was used to
calculate the quantum yields. Absolute $\Phi_{PL}$ in solutions and in the solid state were measured for spin-coated films on quartz substrates using calibrated integrating sphere Horiba F-3018 on Horiba Jobin Yvon Fluromax-4 spectrofluorometer at room temperature, and calculated by Horiba Yvon quantum yield calculator software. CIE 1931 color space have been calculated using OSRAM Color Calculator v. 7.23.

**Table S1** Determination of photoluminescence quantum yields (PLQY, $\Phi_{PL}$) of oligomers in degassed DCM.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Integral intensity of the emission A ($\lambda_{ex} = 350$ nm)</th>
<th>Optical density OD (a.u.)</th>
<th>PLQY, $\Phi_{PL}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9,10-DPA$^a$</td>
<td>$7.53 \times 10^7$</td>
<td>0.05</td>
<td>(90)</td>
</tr>
<tr>
<td>FNoF$^b$</td>
<td>$9.75 \times 10^5$</td>
<td>0.05</td>
<td>1</td>
</tr>
<tr>
<td>FFNFF</td>
<td>$1.04 \times 10^8$</td>
<td>0.07</td>
<td>84</td>
</tr>
<tr>
<td>FNF</td>
<td>$1.13 \times 10^8$</td>
<td>0.07</td>
<td>93</td>
</tr>
<tr>
<td>SNS</td>
<td>$1.21 \times 10^8$</td>
<td>0.07</td>
<td>101</td>
</tr>
<tr>
<td>NSN</td>
<td>$8.54 \times 10^7$</td>
<td>0.05</td>
<td>89</td>
</tr>
</tbody>
</table>

$^a$ Diluted solution of DPA in degassed cyclohexane ($\Phi_r = 90\%$) was used as fluorophore standards.$^2$

$^b$ $\lambda_{ex} = 370$ nm

**Experimental procedure for the metal cations sensing study of FNF.**

The metal salts used in these studies LiClO$_4$, NaClO$_4$, AgClO$_4$, Mg(ClO$_4$)$_2$, Ba(ClO$_4$)$_2$, Cu(BF$_4$)$_2$, Ni(NO$_3$)$_2$, Pb(ClO$_4$)$_2$ and Hg(ClO$_4$)$_2$ were dried under high vacuum (10$^{-3}$ mbar) for at least 24 hours prior to using them for preparation of solutions in dry THF [hygroscopic salts were preliminary dried in an oven at 170 °C for several hours]. The stoichiometry of the coordination complex with Hg$^{2+}$ was determined using Job's method.$^{3,4}$ The absorption and photoluminescence spectra for titration of FNF with HgClO$_4$ are shown in Figure S10. The corresponding Job's plot using both fluorescence and absorption intensity (Figure S11) reveal 2:1 ($\text{FNF}:\text{Hg}^{2+}$, mole ratio) stoichiometry for the [FNF-Hg$^{2+}$] adduct. The corresponding structure of the possible complex formation is shown on Figure S12.

Measurements of known concentrations of 2[FNF]:Hg$^{2+}$ complex emission intensity can be used to determine the unknown concentration of Hg$^{2+}$ in a given sample by plotting calibration graph of the emission intensity vs concentration. Photoluminescence titration of FNF with Hg$^{2+}$ ions showed that an intensity of the long wavelength emission band at 507 nm of FNF-Hg$^{2+}$ complex gradually increased with an increase of Hg$^{2+}$ ions up to certain limit that corresponds to the 2:1 ratio (Figure S13b). Linear increase in the fluorescence intensity with an increase of Hg$^{2+}$ concentration added to the FNF solution in THF is observed in the range of ca. 0 – 2.5 μM that allowed to estimate the detection limit to be ca. 1.5–2 × 10$^{-7}$ M.

**Cyclic voltammetry**

Cyclic voltammetry experiments were conducted in a standard three-electrode configuration, using Metrohm Autolab PGSTAT-302N potentiostat/galvanostat, with iR drop compensation. Platinum disk electrode (d = 1.5 or 2 mm) and platinum wire (d = 0.2 mm) were used as the working and counter electrodes, respectively. The reference electrode was Ag/Ag$^+$ (silver wire immersed in a mixture of 0.01 M AgNO$_3$ and 0.1 M Bu$_4$NPF$_6$ in acetonitrile, separated from the solution by a Vycor frit). Potentials are referenced to half-wave potential ($E_{1/2}$) of ferrocene, which was used as an internal standard. The average potentials of Fc/Fc$^+$ vs Ag/Ag$^+$ in our conditions were $E_{1/2} = 0.20–0.22$ V (in DCM) and 0.19–0.21 V (in THF). Oxidation scans were performed in DCM containing 0.2 M Bu$_4$NPF$_6$, reduction scans were carried out in a freshly distilled THF containing 0.2 M Bu$_4$NPF$_6$, under argon. The CV were recorded at the scan rate of 100 mV/s.
**Computational studies**

All the computational studies were performed with Gaussian 09 package of programs\(^5\) using the density functional theory method (DFT). The hybrid functional B3LYP, which combines Becke's exchange\(^6\) and Lee, Yang, Paar's correlation functional\(^7\) with 6-31G or 6-311G basis sets supplemented by (d) or (d,p) polarization functions were used for calculations. The calculations were performed either in a gas phase or in acetonitrile (using polarizable continuum model, PCM). The restricted Hartree-Fock formalism was used. No constraints were used and all structures were free to optimize. The force constants and vibrational frequency for stationary points have been calculated after optimizations to check that they are true minima. To decrease the computation time, all the oligomers geometries were optimized with ethyl substituents at the positions 9,9- of fluorene and 4,5-diazafluorene (instead of longer hexyl or octyl substituents in experimental work). This was shown have no effect on the HOMO/LUMO energy levels of the co-oligomers. The visualization of the orbital coefficients was performed with GaussView 5.0 software.

![Optimized structures of conjugated oligomers calculated at DFT/B3LYP/6-31G(d) level.](image)

**Figure S1.** Optimized structures of conjugated oligomers calculated at DFT/B3LYP/6-31G(d) level. For simplicity, H atoms are omitted and tube framework used with colors blue = nitrogen, red = oxygen, and yellow = sulphur atoms using GaussView 05 software.

**Table S2.** Dipole moments of the optimized geometries of studied co-oligomers calculated by DFT/B3LYP using different basis sets in a gas phase and in ACN.

<table>
<thead>
<tr>
<th>Compound</th>
<th>6-31G(d) gas phase</th>
<th>6-31G(d,p) ACN</th>
<th>6-311G(d,p) gas phase</th>
<th>6-311G(d,p) ACN</th>
</tr>
</thead>
<tbody>
<tr>
<td>FNoF</td>
<td>0.02</td>
<td>0.16</td>
<td>0.07</td>
<td>0.10</td>
</tr>
<tr>
<td>FFNFF</td>
<td>3.50</td>
<td>5.43</td>
<td>3.47</td>
<td>5.38</td>
</tr>
<tr>
<td>FNF</td>
<td>3.44</td>
<td>5.06</td>
<td>3.43</td>
<td>5.01</td>
</tr>
<tr>
<td>SNS</td>
<td>12.54</td>
<td>17.44</td>
<td>12.76</td>
<td>18.23</td>
</tr>
<tr>
<td>NSN</td>
<td>11.51</td>
<td>18.88</td>
<td>11.51</td>
<td>17.08</td>
</tr>
</tbody>
</table>
Figure S2. HOMO and LUMO orbital coefficients of 4,5-diazafluorene co-oligomers FNoF, FFNFF, FNF, SNS, and NSN by DFT/B3LYP/6-31G(d) calculations in a gas phase (surface isovalue = 0.02).
Figure S3 Frontier orbitals energy levels of 4,5-diazafluorene co-oligomers by DFT/B3LYP/6-31G(d) calculations in a gas phase.

Figure S4 HOMO, LUMO (a) and HOMO–LUMO gaps, $E_g$ (b) of 4,5-diazafluorene co-oligomers calculated by DFT/B3LYP using different basis sets and polarization functions [6-31G(d), 6-31G(d,p) and 6-311G(d,p)] in a gas phase and in acetonitrile, ACN (by PCM model).
Figure S5. Photoluminescence spectra of FNF in the solid state (spin-coated-films from chloroform solution) before and after thermal annealing on an air. The measurements have been performed on an integrating sphere (the shown spectra have not corrected on the sphere background).

Table S3. Absorption and photoluminescence maxima of FNF, FFNFF and FNoF co-oligomers in different solvents.\(^a\)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>FNF</th>
<th>FFNFF</th>
<th>FNoF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{abs}}$ (nm)</td>
<td>$\lambda_{\text{PL}}$ (nm)</td>
<td>$\lambda_{\text{abs}}$ (nm)</td>
</tr>
<tr>
<td>Hexane</td>
<td>358.5</td>
<td>398, 418, 445sh</td>
<td>324, 372</td>
</tr>
<tr>
<td>Toluene</td>
<td>363</td>
<td>404.5, 426, 450sh</td>
<td>326, 377</td>
</tr>
<tr>
<td>DCM</td>
<td>366</td>
<td>409, 430sh</td>
<td>328, 378</td>
</tr>
<tr>
<td>THF</td>
<td>365</td>
<td>404, 426, 450sh</td>
<td>–</td>
</tr>
<tr>
<td>ACN</td>
<td>364</td>
<td>407, 424, 450sh</td>
<td>–</td>
</tr>
<tr>
<td>EtOH</td>
<td>367</td>
<td>415, 430sh</td>
<td>327, 379</td>
</tr>
</tbody>
</table>

\(^a\) The data are from the spectra shown on Figures 2a,b, 3a-c and 6a,b.

Figure S6. Solvatochromic shifts of the emission maxima ($\nu_{\text{PL}}^{\text{max}} = 1/\lambda_{\text{PL}}^{\text{max}}$) for FNF against the solvent polarity parameter [Lippert-Mataga equation, $\Delta \nu = (\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(n^2 + 1)$, where $\varepsilon$ is a dielectric permittivity and $n$ is a refractive index of a solvent].
Figure S7 Changes in UV-Vis absorption (a) and photoluminescence (b) spectra of FNF [~10 μM] in THF at various concentrations of methanesulfonic acid (0.05 – 40 mM).

(c) As seen in Figure S7b, the intensity of PL (at λPL = 510 nm) of the protonated FNF is lower than PL intensity of the neutral FNF (λPL ~ 410 nm). This is, partially, because the absorption of FNF at the excitation wavelength (λex = 365 nm) is decreased on protonation (see Figure S7a). Therefore, on the graph (c) we have corrected PL spectra to their absorption intensities at 365 nm: the intensities of PL have been multiplied by \[\frac{\text{Abs}^{365}(\text{FNF} + \text{CH}_3\text{SO}_3\text{H})}{\text{Abs}^{365}(\text{FNF})}\] and normalized to PL intensity of FNF.

(d,e) The bottom photographs show changes of the color of FNF solution in THF upon addition of a large excess of CH₃SO₃H: (e) under day light illumination [from colorless to light yellow] and (f) under 366 nm UV-lamp irradiation [from deep blue to green fluorescence].
Figure S8. CIE 1931 color space diagrams of the emission spectra of FNF [~1.4 μM] solutions in THF in presence of various metal cations [~14 μM]. The PL spectra have been taken from Figures 7b (left diagram) and Figure 7d (right diagram). Triangle corresponds to sRGB gamut.
For PL spectra, excitations are at the wavelengths close to the absorption maxima: $\lambda_{ex} = 365$ nm (cation-free, Li$^+$, Na$^+$, Cu$^{2+}$, Mg$^{2+}$, Ba$^{2+}$), 367 nm (Ag$^+$), 371 nm (Ni$^{2+}$), 379 nm (Pb$^{2+}$), 395 nm (Hg$^{2+}$).

Figure S9. Changes in the absorption (a,c) and photoluminescence (b,d) spectra of FNF [~10 μM] solutions in THF in presence of Hg(ClO₄)₂ to demonstrate the reversibility of complexation.

(a,b) Concentration of Hg(ClO₄)₂ was increased for 0 to 6.5 μM:
(a) an absorption of FNF at 365 nm disappear on the cost of an appearance of red-shifted absorption of the complex FNF/Hg²⁺ at 405 nm;
(b) no emission is observed for an excitation of FNF 415 nm; and addition of Hg(ClO₄)₂ results in an appearance of emission at ~515 nm (OFF ⇒ ON).

(c,d) The {FNF [-10 μM] + Hg(ClO₄)₂ [6.5 μM]} from experiments (a,b) was diluted with a solution of FNF [-10 μM]. This kept the concentration of FNF constant, but the concentration of Hg(ClO₄)₂ was decreased from 6.5 μM to <1 μM:
(c) long-wavelength absorption of the complex FNF/Hg²⁺ is decreased and an absorption of free FNF is growing;
(d) on decrease of the concentration of Hg(ClO₄)₂, the emission of the complex is decereased and then disappear.
Figure S10. (a) UV-Vis absorption and (b) emission spectra of mixtures of equal concentrations (20 μM each) of FNF and Hg(ClO₄)₂ in different ratios (in THF) keeping the total volume of the solution $V_{\text{FNF}} + V_{\text{Hg(ClO₄)₂}} = 10$ mL; $\lambda_{\text{ex}} = 415$ nm.
Figure S11. Job's plots for the mixtures of FNF (20 μM) and Hg(ClO₄)₂ (20 μM) at different ratios in THF: (a) absorption intensities at 415 nm; (b) PL intensities at 510 nm (λ<sub>ex</sub> = 415 nm). The values have been taken from the data in Figure S5a,b.

Figure S12. (Top) The reaction scheme of 2[FNF]:Hg<sup>2+</sup> complex formation. (Bottom) The photographs show changes of the color of FNF solution in THF upon addition of Hg(ClO₄)₂: (left) under day light illumination [from colorless to light yellow] and (right) under 365 nm UV-lamp irradiation [from deep blue to green fluorescence].
**Figure S13**  
(a) Changes in the photoluminescence spectra of FNF (10 µM) on titration with Hg(ClO₄)₂ (0 - 54.2 µM) in THF (excited at 410 nm). (b) PL intensity measured at 510 nm versus concentration of Hg(ClO₄)₂ (0-54.25 µM), (PL max is observed at [FNF]:[Hg(ClO₄)₂] ~2:1). (c) Linear dependence of the intensity of PL measured at 510 nm versus [Hg(ClO₄)₂] at low concentrations of 0 - 2.54 µM.
**Figure S14** Absorption and photoluminescence spectra of THF solutions of FNF [~10 μM] and Hg(ClO₄)₂ [~5 μM]} in presence of NaClO₄, Cu(BF₄)₂ and Ba(ClO₄)₂ salts to show the interference of Hg²⁺ detection by other cations (Na⁺, Cu²⁺ and Ba²⁺).
Figure S15  Absorption and photoluminescence spectra of THF solutions of FNF [~10 μM] and Hg(ClO₄)₂ [~5 μM] in presence of Mg(ClO₄)₂, AgClO₄ and Ni(NO₃)₂ salts to show the interference of Hg²⁺ detection by other cations (Mg²⁺, Ag⁺ and Ni²⁺).
Figure S16  Absorption (a,b) and photoluminescence (c,d) spectra of FFNFF (a,c) FNoF (b,d) in THF in cation-free solutions and in presence of Hg(ClO$_4$)$_2$.

The photographs of FFNFF (e) and FNoF (f) solutions in THF under 365 nm UV-lamp irradiation before (left photographs) and after (right photographs) addition of Hg(ClO$_4$)$_2$. CIE 1931 color space diagrams on the top of the photographs show the changes of the emission colors (calculated from Figures S16c,d) of FFNFF and FNoF (circles) upon addition of Hg(ClO$_4$)$_2$ (squares).
Synthesis

Synthesis of intermediate compounds 1 – 8. 9,9-Dihexylfluoren-2-yl boronic acid 2, 8, 2,7-dibromo-4,5-diazafluoren-9-one 3, compounds 4, 8, 5 and 7 were obtained as described previously. Synthesis of compound 6 and 8 was performed similar to literature procedure 10 with slight modification described below.

2,7-Dibromo-9,9-dihexylfluorene-4,5-diazafluorene (1)

Under nitrogen, to a stirred solution of of 2,7-dibromo-4,5-diazafluorene (1a) (1.00 g, 3.06 mmol) in dry THF (20 mL), n-iodohexane (0.95 mL, 6.44 mmol) was added at -5 °C. After that, a solution of potassium tert-butoxide (720 mg, 6.44 mmol) in dry THF (15 mL) was added over a period of 50 min keeping the temperature at -5 °C. The reaction mixture was allowed to warm up slowly to room temperature and stirred at room temperature for 32 hours. The solvent was removed on rotary evaporator and the residue was purified by column chromatography on silica gel (column size = 2 × 20 cm) eluting with isooctane:ethyl acetate(EA) = 10:1, v/v to afford the crude product (1.21 g) as a yellow solid. The crude product was further purified by recrystallization from a mixture of isopropanol:water, 5:1 (25 mL) to yield compound 1 (1.04 g, 69%) as a light yellow solid.

1H NMR (400 MHz, CDCl3): δ (ppm) 8.75 (2H, d, J = 2.0 Hz), 7.84 (2H, d, J = 2.0 Hz), 2.06–1.87 (4H, m, CH2C5H11), 1.22–0.97 (12H, m, CH2(C2H4(CH2)3CH3), 0.79 (6H, t, J = 7.1 Hz, C5H10CH3), 0.73–0.60 (4H, m, CH2CH2C4H9).

13C NMR (101 MHz, CDCl3): δ (ppm) 155.93, 150.93 (CH), 146.59, 133.50 (CH), 120.79, 51.70 (C-9), 39.01 (CH2C5H11), 31.35 (C2H4CH2C3H7), 29.45 (C3H6CH2C2H5), 24.01 (CH2CH2C4H9), 22.49 (C4H8CH2CH3), 13.93 (C5H10CH3).

MS (ESI+) m/z: 491.97 ([M+H]+, 50%, 79Br/81Br), 494.00 ([M+H]+, 100%, 79Br/81Br), 495.92 ([M+H]+, 51%, 81Br, 81Br). Calcd. for C23H30Br2N2: 492.08.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzothiophenes-S,S-dioxide (6)

Under argon, a two-necked flask (100 mL) was charged with 3-bromodibenzothiophene-S,S-dioxide (1b) (1.01 g, 3.39 mmol), bis(pinacolato)diboron (1.29 g, 5.08 mmol), anhydrous KOAc (1.25 g, 12.73 mmol), 1,1'-bis(diphenylphosphino)ferrocene (dpff) (70 mg, 0.13 mmol) and dry dioxane (50 mL). The mixture was degassed by bubbling with argon for 15 minutes before Pd(dpff)Cl2·DCM (104 mg, 3 mol%) was added and the mixture was degassed for another 15 minutes. The mixture was heated at 100 °C for 32 hours under argon atmosphere. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was diluted with water (50 mL). The aqueous solution was then extracted with DCM (2 × 50 mL), washed with water (2 × 20 mL) and dried over anhydrous MgSO4. The DCM solution (dark color) was then passed through a short silica gel bed eluting with DCM (100 mL) to give a clear solution which was concentrated to afford the product 6 as an off white solid (1.05 g, 91%). According to 1H NMR, the purity of the sample is >80%, with the main other component being the unreacted excess of bis(pinacolato)diboron. The product was used in the next reaction step without further purification.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.28 (1 H, s), 8.05 (1 H, dd, $J = 7.7, 0.7$ Hz), 7.80 (3 H, m), 7.64 (1 H, td, $J = 7.7, 1.0$ Hz), 7.54 (1H, td, $J = 7.6, 0.8$ Hz), 1.36 (12 H, s).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ (ppm) 140.12, 138.10, 137.13, 133.81, 133.80, 132.03(br.), 131.54, 130.75, 128.34, 122.16, 121.93, 120.75, 84.56, 24.87.

DEPT-135 $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ (ppm) 140.12(CH), 138.10, 137.13, 133.81(CH), 131.54, 130.75(CH), 128.35(CH), 122.17(CH), 121.93(CH), 120.75(CH), 83.50, 24.87(CH$_3$).

MS (EI) $m/z$: 341.99 ([M]$^+$, 100%). Calcd. for C$_{18}$H$_{19}$BO$_4$S: 342.11.

3,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzothiophene-S,S-dioxide (8)

Under nitrogen, a two-necked flask (100 mL) was charged with 3,8-dibromodibenzothiophene-S,S-dioxide (1c)$^8$ (1.01 g, 2.70 mmol), bis(pinacolato)diboron (1.49 g, 5.88 mmol), anhydrous KOAc (1.57 g, 15.99 mmol), dppf (89 mg, 0.16 mmol) and dry dioxane (50 mL) and degassed with argon for 15 min. Pd(dppf)Cl$_2$·DCM (131 mg, 0.16 mmol) was added and the mixture was degassed for another 15 min. The mixture was heated at 100 °C for 32 hours under argon atmosphere. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was diluted with water (50 mL). The aqueous solution was extracted with DCM (2 × 50 mL), washed with water (2 × 20 mL) and dried with anhydrous MgSO$_4$. The DCM solution (dark color) was then passed through a short silica gel bed eluting with dichloromethane (100 mL) to give a clear solution which was concentrated to afford the product 8 as an off white solid (1.01 g, 85%).

$^1$H NMR (400 MHz, CDCl$_3$):$\delta$ (ppm) 8.28 (1H, s), 8.05 (1H, d, $J = 8.1$ Hz), 7.80 (1H, d, $J = 7.7$ Hz), 1.36 (12H, s).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ (ppm) 140.05 (CH), 137.50, 133.73, 132.37 (br.), 128.33 (CH), 121.09 (CH), 84.56, 24.87 (CH$_3$).

DEPT-135 $^{13}$C NMR (101 MHz, CDCl$_3$):$\delta$ (ppm) (101 MHz, CDCl$_3$) 140.05 (CH), 137.49 , 133.73, 128.33 (CH), 121.09 (CH), 84.56, 24.87 (CH$_3$).

MS (EI) $m/z$: 468.12 ([M]$^+$, 100%). Calcd. for C$_{24}$H$_{30}$B$_2$O$_6$S: 468.19.

**Synthesis of the oligomers.** General procedure of Pd-catalyzed C–C coupling in the synthesis of conjugated oligomers: under inert atmosphere, flame heated three-neck flask fitted with argon (or nitrogen inlet) was charged with aryl boronic acid (or ester), arylbromide, base and degassed solvents. The mixture was degassed with argon for 15 minutes before adding Pd catalyst and degassed again for another 15–20 minutes. The degassed mixture was stirred under reflux for a required time. After cooling, the solvent was removed under reduced pressure on a rotary evaporator. The residue was dissolved in EA/DCM, washed with water, dried over MgSO$_4$, and evaporated to afford the crude product, which was then purified by flash/column chromatography on silica gel eluting with appropriate solvents.

3,7-Bis(9,9-dihexylfluoren-2-yl)-9,9-dihexyl-4,5-diazafluorene (FNF)
Under nitrogen, to a mixture of 2,7-dibromo-9,9-dihexy-4,5-diazafluorene (1) (245 mg, 0.49 mmol), 9,9-dihexylfluorene-2-boronic acid (2) (382 mg, 1.01 mmol) and Pd(PPh₃)₃Cl₂ (7 mg, 2 mol%), degassed 2M aqueous K₂CO₃ (4 mL, 8 mmol) and 1,4-dioxane (10 mL) were added via syringe. The mixture was stirred under nitrogen with heating at 110 °C (oil bath) for 24 hours with protection from the sunlight. The mixture was cooled down to room temperature and the resulting slurry was poured into 5% NaCl aqueous solution (50 mL). The precipitate was collected by filtration, washed with water (3 × 20 mL), dried in vacuo to afford the crude product (448 mg, 88%) as a brown solid. The crude product was purified by column chromatography on silica gel, eluting first with PE to remove byproducts and then with PE:EA mixture, with gradual increase of EA contents from 2% to 6%, to yield product FNF (353 mg, 70.5%) as a yellow solid.

1H NMR (500 MHz, CDCl₃): δ (ppm) 9.01 (2H, d, J = 1.9 Hz), 7.93 (2H, d, J = 2.0 Hz), 7.83 (2H, d, J = 7.8 Hz), 7.78–7.76 (2H, m), 7.67–7.63 (4H, m), 7.40–7.34 (6H, m), 2.16–2.12 (4H, m), 2.08–2.03 (8H, m), 1.24–1.01 (36H, m), 0.89–0.82 (4H, m), 0.81–0.64 (26H, m).

13C NMR (100 MHz, CDCl₃): δ (ppm) 151.92, 151.07, 148.38 (CH), 145.72, 141.47 (× 2), 140.37 (× 2), 136.78, 128.93 (CH), 127.45 (CH), 126.91 (CH), 126.32 (CH), 123.01 (CH), 121.53 (CH), 120.26 (CH), 119.96 (CH), 55.33, 51.63, 40.29, 39.23, 31.44, 31.35, 29.62, 29.52, 24.13, 23.77, 22.52, 22.45, 13.97, 13.93.

DEPT-135 13C NMR (100 MHz, CDCl₃): δ (ppm) 151.87, 151.05, 148.72 (CH), 145.42, 141.32, 140.42, 137.05, 136.52, 128.66 (CH), 127.40 (CH), 126.90 (CH), 126.32 (CH), 123.01 (CH), 121.48 (CH), 120.23 (CH), 119.94 (CH), 55.31 (C-9), 40.30, 39.29, 31.46, 31.39, 29.64, 29.56, 24.13, 23.77, 22.54, 22.48, [14.00, 13.96 (CH₃)].

MS (ESI+) m/z: 1001.76 ([M + H]+, 100%). Calcd. for C₇₃H₉₆N₂: 1000.76.

9,9-Dihexyl-2,7-bis(9,9,9’,9’-tetrahexyl-9H,9H-[2,2’-bifluoren]-7-yl)-9H-4,5-diazafluorene (FFNFF)

Under nitrogen, to a mixture of 2,7-dibromo-9,9-dihexyl-4,5-diazafluorene (1) (10 mg, 0.02 mmol), 9,9,9’,9’-tetrahexyl-2,2’-bifluoren-7-yl-boronic acid (4) (41 mg, 0.057 mmol), Pd(PPh₃)₂Cl₂ (3 mg, 10 mol%), 10% K₂CO₃ aqueous solution (0.5 mL, 0.4 mmol), ethanol (0.5 mL) and toluene (3 mL) were added. The reaction mixture was degassed for 15 minutes with argon and then irradiated with microwave (150 W) keeping the temperature at 150 °C in a microwave reactor for 4 hours. The reaction mixture was cooled down to room temperature and the solvent was evaporated. The residual slurry was poured into 5% NaCl aqueous solution, the product was extracted with chloroform (2 × 15 mL), the combined organic layers were washed with water until pH = 7, dried over anhydrous MgSO₄ and the solvent was evaporated to afford the crude product (45 mg) as a yellowish solid. The crude product was purified by flash chromatography on silica gel, eluting first with PE, then with PE:EA mixture, 4:1 to yield pure product FNF (21 mg, 61%) as a light yellow solid.

1H NMR (400 MHz, CDCl₃): δ (ppm) 9.04 (2H, d, J = 1.8 Hz), 7.96 (2H, d, J = 1.8 Hz), 7.89–7.63 (20H, m), 7.39–7.29 (6H, m), 2.18–1.98 (20H, m), 1.22–1.02 (60H, m), 0.92–0.64 (50H, m).
$^{13}$C NMR (101 MHz, CDCl$_3$): δ 157.22, 152.20, 151.84, 151.52, 151.02, 148.73, 145.55, 141.05, 141.01, 140.76, 140.45, 140.37, 139.57, 137.02, 136.55, 128.68, 127.05, 126.81, 126.44, 126.28, 126.07, 122.95, 121.61, 121.59, 121.46, 120.32, 120.20, 119.92, 119.75, 55.48, 55.19, 51.51, 40.38, 40.29, 39.32, 31.48, 31.44, 31.41, 29.70, 29.61, 29.58, 24.16, 23.85, 23.79, 22.57, 22.54, 22.50, 14.02, 13.98.

DEPT-135 $^{13}$C NMR (101 MHz, CDCl$_3$): δ 157.21, 152.20, 151.84, 151.52, 151.02, 148.73 (CH), 145.55, 141.05, 141.01, 140.76, 140.45, 140.37, 139.57, 137.02, 136.55, 128.68 (CH), 127.05 (CH), 126.81 (CH), 126.44 (CH), 126.27 (CH), 126.07 (CH), 122.95 (CH), 121.60 (CH), 121.59 (CH), 121.46 (CH), 120.32 (CH), 119.92 (CH), 119.75 (CH), 55.48, 55.19 (C-9), 51.51 (CH$_2$), 40.38, 40.29, 39.32 (CH$_2$), 31.48, 31.44, 31.41 (CH$_2$), 29.70, 29.61, 29.58 (CH$_2$), 24.16, 23.85, 23.79 (CH$_2$), 22.57, 22.54, 22.50 (CH$_2$), 14.02, 13.98 (CH$_3$).

MS (MALDI TOF) m/z: 1666.81 ([M + H]$^+$, 100%). Calcd. for $C_{123}H_{160}N_2$: 1665.26.

3,7-Bis(9,9-dihexylfluoren-2-yl)-4,5-diazafluoren-9-one (FNoF)

Under nitrogen, to a three-necked flask containing 2,7-dibromo-4,5-diazafluoren-9-one (3) (201 mg, 0.581 mmol), 9,9-dihexylfluoren-2-boronic acid (2) (453 mg, 1.20 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (9 mg, 2 mol%), degassed 2M aqueous K$_2$CO$_3$ (4 mL, 8 mmol) and 1,4-dioxane (10 mL) were added via a syringe. The reaction mixture was stirred under reflux (oil bath, 110 °C) for 24 hours under nitrogen, with protection from the sunlight. The reaction mixture was cooled down to room temperature and the resulting slurry was poured into 5% NaCl aqueous solution. The product was extracted with DCM (2 × 25 mL), the combined organic layer was washed with water until pH = 7, dried over anhydrous MgSO$_4$, filtered off and the solvent was evaporated to afford the crude product (405 mg, 79%) as a yellow solid. The crude product was purified by flash chromatography on silica gel, eluting first with PE and then with PE:DCM mixture (gradient from 1:1 to 1:4 v/v ratio) to yield pure product FNoF (252 mg, 49%) as a yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 9.12 (2H, d, $J = 2.1$ Hz), 8.28 (2H, $J = 2.1$ Hz, s), 7.83 (2H, d, $J = 7.9$ Hz), 7.77–7.75 (2H, m), 7.65 (2H, dd, $J = 7.8$, 1.5 Hz), 7.60 (2H, d, $J = 1.2$ Hz), 7.40–7.36 (6H, m), 2.06–2.02 (8H, m, CH$_2$C$_5$H$_{11}$), 1.13–1.02 (24H, m, C$_2$H$_4$(CH$_2$)$_3$CH$_3$), 0.77 (12H, t, $J = 6.8$ Hz, CH$_3$), 0.70–0.61 (8H, m, CH$_2$CH$_2$C$_4$H$_9$).

$^{13}$C NMR (100MHz, CDCl$_3$): δ (ppm) 190.18 (CO), 161.71, 153.77 (CH), 152.08, 151.07, 142.18, 140.15, 138.50, 135.23, 130.02, 129.65 (CH), 127.72 (CH), 126.98 (CH), 125.95 (CH), 123.00 (CH), 121.27 (CH), 120.48 (CH), 120.11 (CH), 55.38 (C-9), 40.39, 31.49, 29.66, 23.79, 22.56, 13.99 (CH$_3$).

DEPT-135 $^{13}$C NMR (100MHz, CDCl$_3$): δ (ppm) 161.73, 153.79 (CH), 152.09, 151.08, 142.18, 140.16, 138.51, 135.25, 130.03, 129.66 (CH), 127.72 (CH), 126.99 (CH), 125.95 (CH), 123.01 (CH), 121.28 (CH), 120.48 (CH), 120.11 (CH), 55.39 (C-9), 40.40 (CH$_2$), 31.49 (CH$_2$), 29.67 (CH$_2$), 23.79 (CH$_2$), 22.57 (CH$_2$), 14.00 (CH$_3$).

MS (ESI$^+$) m/z: 847.55 ([M+H]$^+$, 100%). Calcd. for $C_{61}H_{70}N_2O$: 846.55.
3,7-Bis(9,9-dioctyl-4,5-diazafluoren-2-yl)dibenzothiophene-S,S-dioxide (NSN)

Under nitrogen, to a three-necked flask containing 2-bromo-9,9-dioctyl-4,5-diazafluorene (7) (402 mg, 0.854 mmol), 3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzothiophene-S,S-dioxide (8) (200 mg, 0.427 mmol), 2M aqueous K₂CO₃ (4 mL, 8 mmol), 1,4-dioxane (20 mL) and ethanol (2 mL) were added. The mixture was degassed with argon for 15 minutes before adding Pd(PPh₃)₂Cl₂ (10 mg, 0.014 mmol, 3 mol%) and then degassed for another 15 minutes. The mixture was stirred under reflux (oil bath, 115 °C) for 24 hours under nitrogen atmosphere. After cooling to room temperature, the solvent was evaporated under reduced pressure on a rotavapor. The residue was dissolved in ethyl acetate (100 mL), washed with water (2 × 50 mL), dried over anhydrous MgSO₄, filtered off and evaporated to afford the crude product (788 mg) as a brown oil. The crude product was purified by flash chromatography on silica gel eluting with PE:EA (gradient from 1:1 to 1:9) to afford pure oligomer NSN as a yellow solid (152 mg, 59%).

1H NMR (400 MHz, CDCl₃): δ (ppm) 9.00 (2H, d, J = 2.0 Hz), 8.74 (2H, dd, J = 4.8, 1.2 Hz), 8.16 (2H, d, J = 0.8), 8.05–7.99 (4H, m), 7.95 (2H, d, J = 2.0 Hz), 7.76 (2H, dd, J = 7.6, 4.8 Hz), 7.33 (2H, dd, J = 7.6, 4.8 Hz), 2.10–2.06 (8H, m, CH₂C₇H₁₅), 1.25–0.98 (40H, m, C₂H₄(CH₂)₅CH₃), 0.81 (12H, t, J = 7.2 Hz, C₇H₁₄CH₃), 0.72–0.66 (8H, m, CH₂CH₂C₆H₁₃).

13C NMR (100MHz, CDCl₃): δ (ppm) 159.01, 157.78, 149.88 (CH), 148.18 (CH), 145.64, 145.55, 141.17, 139.00, 133.65, 132.87 (CH), 130.79, 130.65 (CH), 128.66 (CH), 123.35 (CH), 122.52 (CH), 121.03 (CH), 51.66 (C-9), 39.31 (CH₂), 31.72 (CH₂), 29.90 (CH₂), 29.18 (CH₂), 29.14 (CH₂), 24.16 (CH₂), 22.58 (CH₂), 14.05 (CH₃).

DEPT-135 13C NMR (100 MHz, CDCl₃): δ (ppm) 159.01, 157.82, 149.91 (CH), 148.20 (CH), 145.61, 145.52, 141.19, 138.98, 133.63, 132.86 (CH), 130.76, 130.64 (CH), 128.66 (CH), 123.35 (CH), 122.51 (CH), 121.03 (CH), 51.66 (C-9), 39.35 (CH₂), 31.72 (CH₂), 29.18 (CH₂), 29.14 (CH₂), 24.16 (CH₂), 22.57 (CH₂), 14.05 (CH₃).

MS (ESI⁺) m/z: 1020.42 ([M+Na]⁺, 100%). Calcd. for C₆₆H₈₄N₄O₂S: 996.63.

2,7-Bis(dibenzothiophene-S,S-dioxide-3-yl)-4,5-diazafluorene (SNS)

A three-necked flask (50 mL) was charged with 2,7-dibromo-9,9-dioctyl-4,5-diazafluorene (5) (150 mg, 0.272 mmol), 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzothiophene-S,S-dioxide (6) (373 mg, 1.090 mmol), 2M aqueous K₂CO₃ (4 mL, 8 mmol), dioxane (20 mL) and ethanol (4 mL) and degassed with argon for 15 minutes. Then Pd(PPh₃)₂Cl₂ (6 mg, 0.008 mmol) was added and the mixture was degassed for another 15 minutes. The mixture was stirred under reflux (oil bath, 115 °C) for 32 hours under nitrogen atmosphere. After cooling to room temperature, the mixture was diluted with water (15 mL) and then extracted with DCM (2 × 100 mL). The combined DCM layers...
were washed with water (2 × 20 mL), dried with anhydrous MgSO4, filtered off and evaporated on a rotavapor to afford the crude product (580 mg) as a brown oil. The crude product was purified by flash chromatography on silica gel eluting with DCM:MeOH mixture (gradient ratio of 100:1 to 100:2) to afford pure oligomer SNS as an off yellow solid (60 mg, 26%).

1H NMR (400 MHz, CDCl3): δ (ppm) 9.03 (2H, d, J = 1.9 Hz), 8.15 (2H, d, J = 1.1 Hz), 8.00–7.95 (6H, m), 7.89 (4H, d, J = 8.0 Hz), 7.72 (2H, t, J = 7.5 Hz), 7.60 (2H, t, J = 7.6 Hz), 2.16–2.12 (4H, CH2C7H15), 1.24–0.98 (20H, m, C2H4(CH2)5CH3), 0.79 (6H, t, J = 6.0 Hz, C7H14CH3), 0.78–0.69 (4H, m, CH2CH2C6H13).

13CNMR (100MHz, CDCl3): δ (ppm) 158.14, 148.50 (CH), 146.13, 140.73, 138.92, 137.92, 134.16, 134.12 (CH), 132.70 (CH), 131.19, 130.69 (CH), 128.79 (CH), 122.42 (CH), 122.33 (CH), 121.86 (CH), 120.92 (CH), 51.94, 39.39 (CH2), 31.63 (CH2), 29.29 (CH2), 29.19 (CH2), 29.16 (CH3), 24.30 (CH2), 22.57 (CH2), 14.04 (CH3).

DEPT-135 13C NMR (100MHz, CDCl3): δ (ppm) 158.14, 148.50 (CH), 146.13, 140.73, 138.92, 137.92, 134.16, 134.12 (CH), 132.70 (CH), 131.19, 130.69 (CH), 128.79 (CH), 122.42 (CH), 122.33 (CH), 121.86 (CH), 120.92 (CH), 51.94, 39.39 (CH2), 31.70 (CH2), 29.17 (CH2), 24.29 (CH2), 22.57 (CH2), 14.04 (CH3).

MS (ESI+) m/z: 843.39 ([M+Na]+, 100%). Calcd. for C51H52N2O4S2: 820.34.

References
$^{1}H$ NMR (400 MHz, CDCl$_3$) of FFNFF

$^{13}C$ NMR (101 MHz, CDCl$_3$) of FFNFF
$^{13}$C NMR (101 MHz, CDCl$_3$) of NSN

NSN

DEPTQ NMR (100MHz, CDCl$_3$) of NSN

NSN
$^1$H NMR (400 MHz, CDCl$_3$) of SNS

DEPTQ NMR (100MHz, CDCl$_3$) of SNS
$^{13}\text{C NMR (101 MHz, CDCl}_3\text{) of comp. 3}$

$^{1}\text{H NMR (400 MHz, CDCl}_3\text{) of comp. 1}$
$^{13}$C NMR (101 MHz, CDCl$_3$) of comp. 1

DEPT-135 $^{13}$C NMR (101 MHz, CDCl$_3$) of comp. 1
$^1$H NMR (400 MHz, CDCl$_3$) of comp. 5

$^{13}$C NMR (101 MHz, CDCl$_3$) of comp. 5
DEPT-135 $^{13}$C NMR (101 MHz, CDCl$_3$) of comp. 5

$^1$H NMR (500 MHz, CDCl$_3$) of comp. 7
$^{13}$C NMR (126 MHz, CDCl$_3$) of comp. 7

$^1$H NMR (400 MHz, CDCl$_3$) of comp. 6
$^{13}$C NMR (101 MHz, CDC$_3$) of comp. 6

DEPT-135 $^{13}$C NMR (101 MHz, CDC$_3$) of comp. 6
$^1$H NMR (400 MHz, CDCl$_3$) of comp. 8

$^{13}$C NMR (101 MHz, CDCl$_3$) of comp. 8
DEPT-135 $^{13}$C NMR (101 MHz, CDCl$_3$) of comp. 8

FNF