Supporting Information for:

Fluorofluorescent Perylene Bisimides

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1. General Methods and Materials

All chemical reagents were purchased from Sigma-Aldrich, Synquest Laboratories, or TCI, and used without purification unless noted otherwise. Thin layer chromatography was performed with Baker-flex Silica Gel 1B-F plates (JT Baker). Flash chromatography was performed using technical grade silica gel with 60 Å pores and 230–400 mesh particle size (Sigma-Aldrich, 717185).

$^1$H, $^{13}$C, and $^{19}$F NMR spectra were recorded on a JEOL model JNM-ECZ500R/S1 spectrometer operating at 500, 126, and 470 MHz, respectively. For $^1$H, $^{13}$C NMR spectra, deuterated solvent references were used as internal standards ($^1$H: 7.26 ppm for CDCl$_3$, 5.32 ppm for CD$_2$Cl$_2$; $^{13}$C: 77.16 ppm for CDCl$_3$). For $^{19}$F NMR spectra, α,α,α-trifluorotoluene was added as an internal standard and the spectra was referenced to −63.72 ppm. Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), septet (sep), multiplet (m). Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained at the Massachusetts Institute of Technology Biopolymers & Proteomics Core Laboratory. Electrospray ionization (ESI) high-resolution mass spectra (HRMS) were obtained at the MIT Department of Chemistry Instrumentation Facility. Elemental analysis data were obtained by Robertson Microlit Laboratories. Absorbance spectra were obtained at room temperature on a Cary 4000 UV/Vis spectrophotometer (Agilent Technologies) with a scan rate of 600 nm/min. The instrument was blanked on the solvent prior to obtaining a spectrum. Fluorescence spectra were obtained at room temperature on a Horiba Jobin Yvon SPEX Fluorolog-t3 fluorimeter (model FL-321, 450 W Xenon lamp). Quantum yields were determined by using Horiba Quanta-ϕ integrating sphere. Absorbance and fluorescence data were collected in a quartz cuvette (1 cm path length).
2. Synthetic Procedures

**Synthesis of Compound FF-PBI-1.** A mixture of compound 4 (0.150 g, 0.176 mmol), compound 1 (1.04 g, 1.01 mmol), and anhydrous K$_2$CO$_3$ (0.123 g, 0.892 mmol) in anhydrous N,N-dimethylformamide (DMF) (6 mL) was stirred at 120 °C under Ar for 24 h. Then, the reaction mixture was cooled to room temperature. The precipitated product was filtered under suction, washed three times with water (100 mL), and dried under vacuum. The residue was chromatographed on silica gel using hexanes/CH$_2$Cl$_2$ (2:1 v/v) as an eluent, and the fraction containing compound FF-PBI-1 (R$_f$ = 0.50) was collected and evaporated to dryness under reduced pressure to provide a purple solid (0.212 g, 0.044 mmol, 25%).

$^1$H NMR (500 MHz, CD$_2$Cl$_2$, 25 °C): δ (ppm) 8.20 (s, 4H), 7.46 (t, J = 7.5 Hz, 2H), 7.29 (d, J = 8.0 Hz, 4H), 7.17 (t, J = 8.0 Hz, 4H), 6.47 (d, J = 8.0 Hz, 4H), 6.39 (d, J = 8.0 Hz, 4H), 6.33 (s, 4H), 3.21 (d, J = 6.5 Hz, 16H), 2.67 (sep, J = 7.0 Hz, 4H), 1.96–2.10 (m, 16H), 1.72–1.83 (m, 16H), 1.06 (d, J = 6.5 Hz, 24H). $^{13}$C NMR could not be obtained due to low solubility. $^{19}$F NMR (470 MHz, CD$_2$Cl$_2$, 25 °C): δ (ppm) –82.00 (t, 9.4 Hz, 24F), –114.84 (br, 16F), –122.84 (br, 16F), –123.02 (br, 32F), –123.81 (br, 16F), –124.47 (br, 16F), –127.24 (br, 16F). MALDI-TOF MS: m/z calcd. for C$_{160}$H$_{102}$F$_{136}$N$_6$O$_8$ [M+H]$^+$: 4819.5678, found: 4819.80. Anal. calcd. for C$_{160}$H$_{102}$F$_{136}$N$_6$O$_8$ (%): C, 39.87; H, 2.13; N, 1.74. Found: C, 39.35; H, 2.08; N, 1.65.
**Synthesis of Compound 5.** A mixture of compound 4 (0.320 g, 0.377 mmol), 3,5-dibromophenol (0.907 g, 3.60 mmol), and anhydrous K₂CO₃ (0.256 g, 1.85 mmol) in anhydrous 1-methyl-2-pyrrolidinone (NMP) (4 mL) was stirred at 100 °C under Ar for 7 h. Then, the reaction mixture was cooled to room temperature and poured into hydrochloric acid (30 mL, 1 M). The precipitated product was filtered under suction, washed three times with water (100 mL), and dried under vacuum. The residue was chromatographed on silica gel using toluene as an eluent, and the fraction containing compound 5 (R₁ = 0.70) was collected and evaporated to dryness under reduced pressure to provide a pink-red solid (0.440 g, 0.257 mmol, 68%). **¹H NMR** (500 MHz, CDCl₃, 25 °C): δ (ppm) 8.33 (s, 4H), 7.48 (t, J = 8.0 Hz, 2H), 7.45 (t, J = 1.5 Hz, 4H), 7.32 (d, J = 8.0 Hz, 4H), 7.03 (d, J = 1.5 Hz, 8H), 2.71 (sep, J = 7.0 Hz, 4H), 1.15 (d, J = 7.0 Hz, 24H). **¹³C NMR** (126 MHz, CDCl₃, 25 °C): δ (ppm) 162.73, 156.66, 154.52, 145.70, 133.12, 130.48, 130.14, 129.94, 124.26, 124.01, 123.89, 121.98, 121.76, 121.53, 121.34, 29.32, 24.17. HRMS (ESI): m/z calcd. for C₇₂H₉₀Br₈N₂O₈ [M+H]+: 1710.7057, found: 1710.7048.
Synthesis of Compound FF-PBI-2. A mixture of compound 5 (0.439 g, 0.257 mmol), 1H,1H,2H-perfluoro-1-decene (1.44 g, 3.23 mmol), NaOAc (0.256 g, 3.04 mmol), and anhydrous DMF (5 mL) was treated with three cycles of freeze-pump-thaw. Then, Herrmann’s catalyst (50.2 mg, 0.0535 mmol) was added to the mixture and it was stirred for 24 h at 125 °C. Upon cooling the reaction mixture to room temperature, the residue was dissolved in AcOEt (100 mL) and HCl (1 M, 100 mL). The organic layer was separated, washed with water (100 mL × 3) and brine (100 mL), dried with MgSO₄, and evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel using CHCl₃ as an eluent, and the fraction containing FF-PBI-2 (Rf = 0.50) was collected and evaporated to dryness to provide a pink-red solid (0.517 g, 0.112 mmol, 43%). ¹H NMR (500 MHz, CD₂Cl₂, 25 °C): δ (ppm) 8.31 (s, 4H), 7.47 (t, J = 7.5 Hz, 2H), 7.30–7.31 (m, 8H), 7.03–7.06 (m, 16H), 5.98–6.06 (m, 8H), 2.67 (sep, 7.0 Hz, 4H), 1.07 (d, 7.0 Hz, 24H). ¹³C NMR spectra could not be obtained due to low solubility. ¹⁹F NMR (470 MHz, CD₂Cl₂, 25 °C): δ (ppm) −81.98 (t, 9.9 Hz, 24F), −112.78 (br, 16F), −122.52 (br, 16F), −122.99 (br, 32F), −123.80 (br, 16F), −123.96 (br, 16F), −127.22 (br, 16F). MALDI-TOF MS: m/z calcd. for C₁₅₂H₆₆F₁₃₆N₂O₈: 4630.2648, found: 4630.13. Anal. calcd. for C₁₅₂H₆₆F₁₃₆N₂O₈ (%): C, 39.41; H, 1.44; N, 0.60. Found: C, 39.40; H, 1.33; N, 0.60.
3. NMR Spectra

Compound FF-PBI-1 $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 25 °C)

Compound FF-PBI-1 $^{19}$F NMR (470 MHz, CD$_2$Cl$_2$, 25 °C)
**Compound 5** $^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

![NMR Spectrum](compound_5_1h_nmr.png)

**Compound 5** $^{13}$C NMR (125 MHz, CDCl$_3$, 25 °C)

![NMR Spectrum](compound_5_13c_nmr.png)
Compound **FF-PBI-2** $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 25 °C)

![Proton NMR spectrum of FF-PBI-2](image)

Compound **FF-PBI-2** $^{19}$F NMR (470 MHz, CD$_2$Cl$_2$, 25 °C)

![Fluorine NMR spectrum of FF-PBI-2](image)
Compound **FF-PBI-2** COSY NMR (500 MHz, CD$_2$Cl$_2$, 25 °C)

4. Supporting Figures

**Figure S1:** Normalized absorbance and fluorescence spectra of **FF-PBI-1** in CH$_2$Cl$_2$ + TFA and C$_6$F$_{14}$ + TFA.
**Figure S2**: Normalized absorbance and fluorescence spectra of **FF-PBI-1** in CH$_2$Cl$_2$ and its change upon addition of TFA and Et$_3$N.

**Figure S3**: Quantum yield ($\Phi_F$) of **FF-PBI-2** in CH$_2$Cl$_2$ and C$_6$F$_{14}$ at different concentrations. $\Phi_F$ was determined by using an integrating sphere. The error bars represent values of $\Phi_F$ measured at three different excitation wavelengths.