Fluorofluorescent Perylene Bisimides

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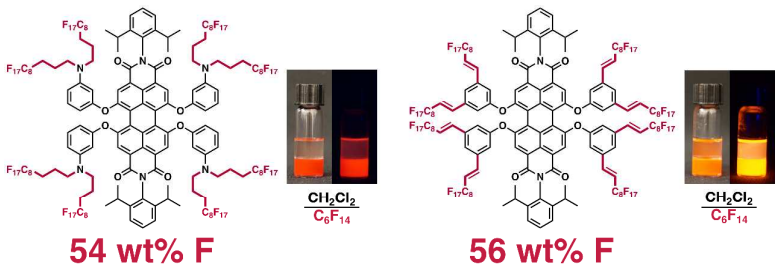

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Abstract Perfluorinated liquids can exhibit immiscibility with organic solvents and water, and provide orthogonal opportunities in chemistry. Examples of emissive dyes that display only fluorous phase solubility are limited, despite the many potential applications. Perylene bisimides are among the most versatile dyes and are known for their outstanding stability and high quantum yields. Herein, we report the synthesis of two new "fluorofluorescent" perylene bisimide dyes, designed to be soluble in the fluorous phases. These two dyes possess unique photophysical properties, including dramatic increases in fluorescence quantum yields when treated with Brønsted acids as well as aggregation in the fluorous phase.

Key words perylene bisimides, fluorines, Heck reaction, fluorescence, aggregation

The "fluorous" phase, which consists of perfluorinated alkanes, ethers, or amines, has found unique opportunities in chemistry as a result of the ability to phase-separate from polar and nonpolar phases.[1] The term "fluorous" was coined by Horváth and Rábai in 1994, when they demonstrated the utility of fluorous biphasic catalysis.[2] Fluorous molecules tend to exhibit improved photochemical, thermal, and chemical stability than their hydrocarbon counterpart.[3] Fluorous compounds have deserved popularity in applications[4] such as in coating materials,[5] organic electronics,[6] perfluorocarbon nanoemulsions for *in vivo* drug delivery[7] and cell tracking,[8] and fluorescent recognition in the fluorous phase.[9] These examples represent only a few unique highlights of the fluorous phase and new discoveries will be enabled by access to an expanded portfolio of fluorous materials.

Fluorous solubility depends mainly on the fluorine content of the molecule, typically requiring >50 weight percent fluorine (wt% F) and extended perfluoroalkyl chains.[1] Examples of dyes that exhibit fluorous solubility are extremely limited.[10] To address this shortage, our group has previously synthesized fluorous soluble conjugated polymers,[11] as well as an array of "fluorofluorophores", in which "fluoro" refers to both fluorescence and fluorination.[12] However, to date only a small parameter space has been explored and there are vast uncharted territories of electronic molecules to be discovered.

We targeted perylene bisimides (PBIs) as a result of their wide utility as organic semiconductors,[13] supramolecular building blocks,[14] and fluorophores.[15] Previous examples to incorporate fluorinated groups in PBIs have been demonstrated to show utility as air-stable n-type semiconductors,[6c-d,16] however the fluorine content of these examples were <50 wt% F. Examples of PBIs with higher wt% F have been reported to self-assemble into ordering structures.[17] However, their fluorous solubilities as well as photophysical properties of the fluorinated molecules were not studied in detail.

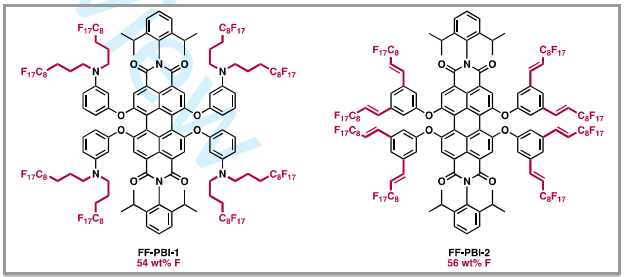
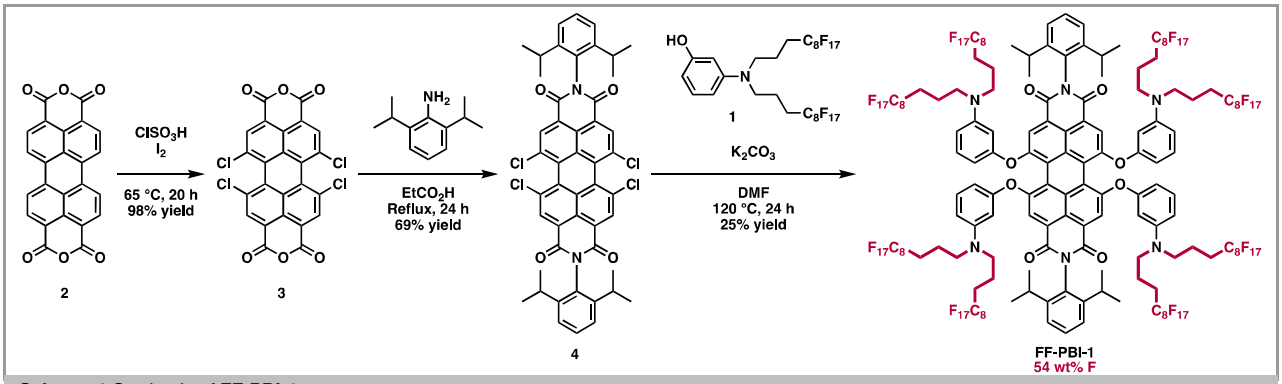


Figure 1 Chemical structures of fluorofluorescent PBIs in this report

Herein, we disclose two synthetic approaches to obtain fluorofluorescent PBI dyes **FF-PBI-1** and **FF-PBI-2**, both requiring only four facile steps from a common starting material. **FF-PBI-1**, which possesses 54 wt% F, initially shows moderate solubility in both organic and fluorous solvents, but the solubility in fluorous solvents is improved upon addition of a Brønsted acid. On the other hand, **FF-PBI-2**, which possesses 56 wt% F, shows good solubility in both organic and fluorous solvents. The photophysical properties of the two **FF-PBI**s are also distinctly unique; **FF-PBI-1** shows a response to acidity, whereas **FF-PBI-2** shows concentration dependence.

The synthesis of **FF-PBI-1** is shown in Scheme 1. Fluoroalkylated aminophenol **1**, compound **3**, and compound **4**

were prepared according to previous reports.[12,17b,18] An S_NAr reaction of **4** and **1**



Scheme 1 Synthesis of **FF-PBI-1**

produced the target perylene bisimide **FF-PBI-1** in 25% isolated yield.[19] The product was purified by chromatography on silica gel, but its poor solubility in most solvents presumably led to the low yield.[19,20] **FF-PBI-1** was fully characterized by ^1H, ^{19}F nuclear magnetic resonance (NMR) spectroscopy, matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI TOF-MS), and elemental analysis.

We sought to gain a better understanding of the solubility of **FF-PBI-1**, which showed moderate solubility (~1.0 mg/mL; ~2.1×10^2 μM) in organic solvents such as dichloromethane (CH_2Cl_2) (Figure 2(a)), toluene, chloroform, acetone, and ethyl acetate. Interestingly, when C_6F_{14} was added to a solution of **FF-PBI-1** in CH_2Cl_2, we visually observed the partition of **FF-PBI-1** in both CH_2Cl_2 and C_6F_{14} layers (Figure 2(a),(b)). Despite the high wt% F, **FF-PBI-1** was insoluble in pure fluorous solvents such as perfluorohexanes (C_6F_{14}) (Figure 2(d)), as well as perfluorodecalin.

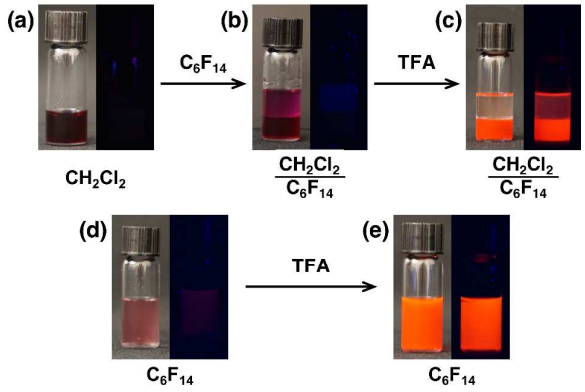


Figure 2 Demonstration of solubility of **FF-PBI-1** and its response to TFA under ambient light (left) and UV light (right, λ_{ex} = 365 nm). (a) Photographs of **FF-PBI-1** (0.5 mg) in CH_2Cl_2 (0.5 mL), (b) after adding C_6F_{14} (0.5 mL), and (c) after adding TFA. (d) Photographs of the heterogeneous mixture of **FF-PBI-1** (1.0 mg) and C_6F_{14} (1.0 mL) and (e) the sample after adding TFA.

To our surprise, we found that addition of a Brønsted acid improved the solubility of **FF-PBI-1** in fluorous solvents. For instance, when trifluoroacetic acid (TFA) was added to the solution of **FF-PBI-1** in CH_2Cl_2/C_6F_{14} mixture, the color of the CH_2Cl_2 layer turns from turbid purple to colorless transparent, while that of the C_6F_{14} layer turns from turbid purple to a brilliant fluorescent red (Figure 2(c)). When TFA was added to the heterogeneous mixture of **FF-PBI-1** (1.0 mg) and C_6F_{14} (1.0 mL), the mixture became homogeneously red and fluorescent, thereby confirming that this effect is not dependent on the organic solvent (Figure 2(d),(e)). Other Brønsted acids such as hydrochloric acid and perfluorononanoic acid also showed a

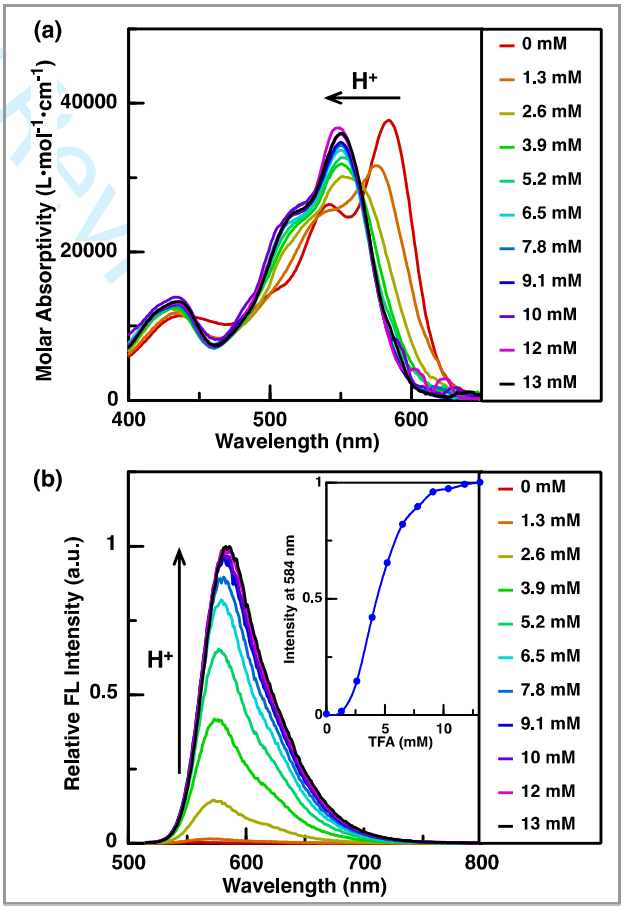


Figure 3 Photophysical properties of **FF-PBI-1**. (a) Absorbance spectra and (b) relative fluorescence spectra (λ_{ex} = 500 nm) of **FF-PBI-1** in CH_2Cl_2 at different concentrations of TFA. ((b) inset)

Fluorescence intensity at 584 nm at different concentrations of TFA. Black arrows indicate spectral change with increasing concentration of TFA.

similar phenomenon. **FF-PBI-1**'s fluorescence was also increased upon protonation with these other acids and it also exhibits preferential solubility for fluorous solvents over organic solvents under acidic conditions.

We further investigated the photophysical properties of **FF-PBI-1** in CH_2Cl_2 (2.1 μM) by monitoring the absorbance and fluorescence and the changes upon addition of TFA. The absorbance spectra showed a gradual hypsochromic shift (Figure 3(a)), and the fluorescence spectra showed an enhanced intensity (Figure 3(b)). The concentration of TFA plotted against the fluorescence intensity at 584 nm (Figure 3(b), inset) gives a sigmoidal shape. We observe a saturation of fluorescence intensity when the concentration of TFA was increased to ~9 mM. The quantum yield of **FF-PBI-1** in CH_2Cl_2 increased from 6.1% to 54% upon excess addition of TFA (Table 1). The quantum yield of **FF-PBI-1** in C_6F_{14} with excess TFA was 76%. The red shifted spectra and higher quantum yields in fluorous phases confirm the benefits of the fluorous environments (also see Figure S1).

Table 1 Photophysical Properties of **FF-PBI-1** in CH_2Cl_2 and C_6F_{14} (+ TFA)

Solvent	λ_{max}(Abs) (nm)	λ_{max}(Em) (nm)	Φ_F (%)
CH_2Cl_2	584	616[b]	6.1
CH_2Cl_2 + TFA[a]	549	584[c]	54
C_6F_{14} + TFA[a]	562	594[c]	76

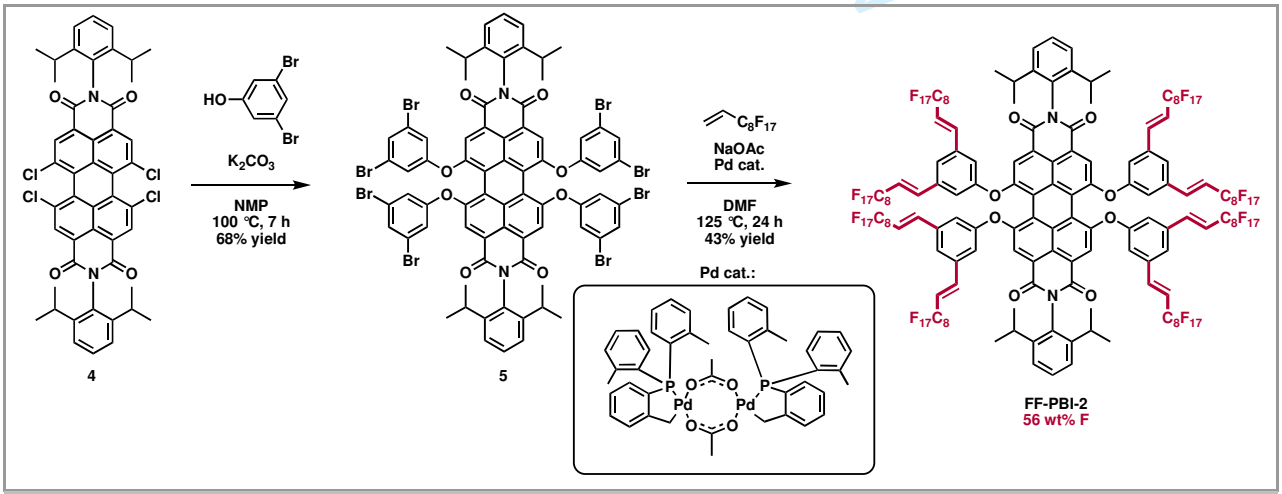
[a]Excess TFA was added to the sample. [b]λ_{ex} = 570 nm. [c]λ_{ex} = 500 nm.

We attribute the initial fluorescence quenching of **FF-PBI-1** to photo-induced electron transfer (PET) from the peripheral lone pairs of the nitrogen on the aminophenolic groups.[21] Upon addition of acid, PET is attenuated as a result of protonation of the aminophenolic group. This protonation also likely causes the absorbance to shift to a shorter wavelength, because the HOMO of **FF-PBI-1** is also lowered with the decreased electron donation by the protonated pendant aminophenolic groups. The proton induced photophysical change in **FF-PBI-1** is also reversible. Addition of triethylamine to the acidic sample reestablishes the original absorbance and fluorescence spectra (Figure S2).

Although the protonation of **FF-PBI-1** led to interesting properties such as improved fluorous solubility and fluorescence, we also embarked on the study of alternative structures of PBIs that lack basic nitrogens with high wt% F. Beginning with intermediate **4**, we synthesized octabrominated PBI **5** *via* an S_NAr reaction with 3,5-dibromophenol in 68% yield. We targeted compound **5** as a useful intermediate for subsequent metal-catalyzed cross-coupling reactions. Indeed, compound **5** successfully underwent an eight-fold Herrmann's palladacycle-catalyzed Heck reaction[22] between 1H,1H,2H-perfluoro-1-decene to smoothly provide the desired product **FF-PBI-2** in 43% yield.[23,24] **FF-PBI-2** was fully characterized by ^1H, COSY, ^{19}F NMR spectroscopy, MALDI TOF-MS, and elemental analysis. This efficient eight-fold reaction produces only the trans-alkene product, which is readily isolated in pure form.

In contrast to **FF-PBI-1**, **FF-PBI-2** showed good solubility (>1.0 mg/mL; >2.2×10^2 μM) in common organic solvents such as CH_2Cl_2, toluene, chloroform, acetone, and ethyl acetate. Intriguingly, **FF-PBI-2** also showed good solubility in perfluoroalkanes such as C_6F_{14} and perfluorodecalin. When C_6F_{14} was added to a solution of **FF-PBI-2** in CH_2Cl_2, we observed the extraction of **FF-PBI-2** into the C_6F_{14} layer (Figure 4). This result illustrates that **FF-PBI-2** has a higher preference towards fluorous solvents over organic solvents.

FF-PBI-2 exhibited concentration dependent photophysical properties in C_6F_{14}. Figure 5(a) shows the absorbance spectra of **FF-PBI-2** at different concentrations. A peak at 525 nm was observed in the dilute solution. However, a large bathochromic peak at 567 nm develops in concentrated solutions, which is characteristic of J-aggregate formation.[25] In the fluorescence spectra, in addition to the peak at 558 nm, a large bathochromic peak at 595 nm was observed when the concentration of the solution was increased (Figure 5(b)).



Scheme 2 Synthesis of **FF-PBI-2**

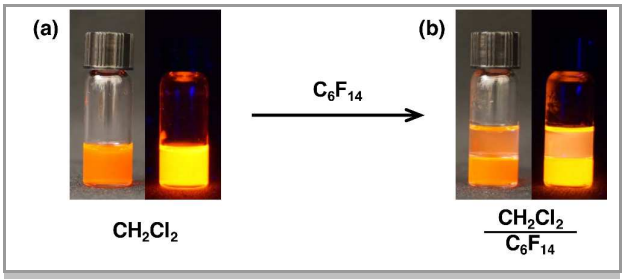


Figure 4 Photographs of **FF-PBI-2** under ambient light (left) and UV light (right, λ_{ex} = 365 nm). (a) Photographs of **FF-PBI-2** (0.5 mg) in CH_2Cl_2 (0.5 mL). (b) Photographs of the sample after adding C_6F_{14} (0.5 mL).

The quantum yields of **FF-PBI-2** in C_6F_{14} at different concentrations were maintained near 75% (Figure S3). The red shifted spectra, increase in the molar absorptivity, and the increased quantum yield for emission all support a J-aggregate formation. Similar measurements of **FF-PBI-2** in CH_2Cl_2 showed a completely different trend. In the absorbance spectra, no new peaks were observed when the concentration of the solution was increased (Figure 5(c)). In the fluorescence spectra, the peak at 595 nm simply gradually enhanced in intensity (Figure 5(d)). This suggests that the aggregation is exclusively observed in fluorous solvents. Recently, Cao and Sletten reported the first cyanine dye showing aggregation in the fluorous phase;[26] however, they utilize 1% CH_2Cl_2 and a mixture of methoxy- and ethoxynonafluorobutane as their solvent system. Therefore, **FF-PBI-2** presents a unique entry of aggregation in pure perfluorinated solvents.

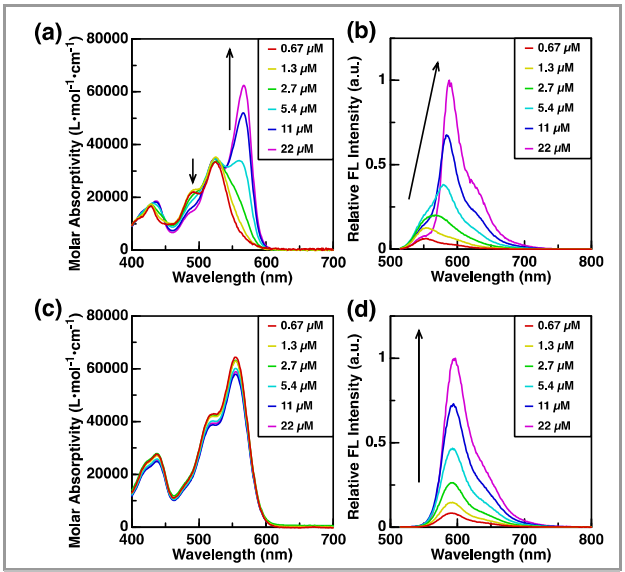


Figure 5 Photophysical properties of **FF-PBI-2** in C_6F_{14} and CH_2Cl_2. (a) Absorbance spectra and (b) relative fluorescence spectra (λ_{ex} = 500 nm) of samples at different concentrations in C_6F_{14}. (c) Absorbance spectra and (d) relative fluorescence spectra (λ_{ex} = 500 nm) of samples at different concentrations in CH_2Cl_2. Black arrows indicate spectral change with increasing concentration.

In conclusion, we have disclosed two synthetic methods to obtain fluorofluorescent perylene bisimides. **FF-PBI-1** only showed moderate solubility in both organic and fluorous solvents, but the solubility could be improved upon addition of Brønsted acid. On the other hand, **FF-PBI-2** showed useful solubility in both organic and fluorous solvents. Titration measurements of **FF-PBI-1** and concentration dependent measurements of **FF-PBI-2** demonstrate the interesting and potentially useful photophysical properties of the fluorofluorescent PBIs. We envision these properties will provide promising applications in the fluorous phase, including the incorporation of fluorofluorescent PBIs in the fluorous phase of dynamic complex emulsions.[27]

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Acknowledgment

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Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

NO (this text will be deleted prior to publication)

References and Notes

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(19) **Synthesis of 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_2CO_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 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_2Cl_2 (2:1 v/v) as an eluent, and the fraction containing **FF-PBI-1** (R_f = 0.50) was collected and evaporated to dryness to provide a purple solid (0.212 g, 0.0440 mmol, 25%). ^{1}H NMR (500 MHz, CD_2Cl_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). ^{19}F NMR (470 MHz, CD_2Cl_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 $C_{160}H_{102}F_{136}N_6O_8$ $[M+H]^+$: 4819.5678, found: 4819.80. Anal. calcd. for $C_{160}H_{102}F_{136}N_6O_8$ (%): C, 39.87; H, 2.13; N, 1.74. Found: C, 39.35; H, 2.08; N, 1.65.

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(24) **Synthesis of 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 freeze-pump-thaw cycles. 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 $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel using $CHCl_3$ as an eluent, and the fraction containing **FF-PBI-2** (R_f = 0.50) was collected and evaporated to dryness to provide a pink-red solid (0.517 g, 0.112 mmol, 43%). ^{1}H NMR (500 MHz, CD_2Cl_2, 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). ^{19}F NMR (470 MHz, CD_2Cl_2, 25 °C, α,α,α-trifluorotoluene was added as an internal standard and was referenced to -63.72 ppm): 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 $C_{152}H_{66}F_{136}N_2O_8$: 4630.2648, found: 4630.13. Anal. calcd. for $C_{152}H_{66}F_{136}N_2O_8$ (%): C, 39.41; H, 1.44; N, 0.60. Found: C, 39.40; H, 1.33; N, 0.60.

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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_2Cl_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-τ3 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).

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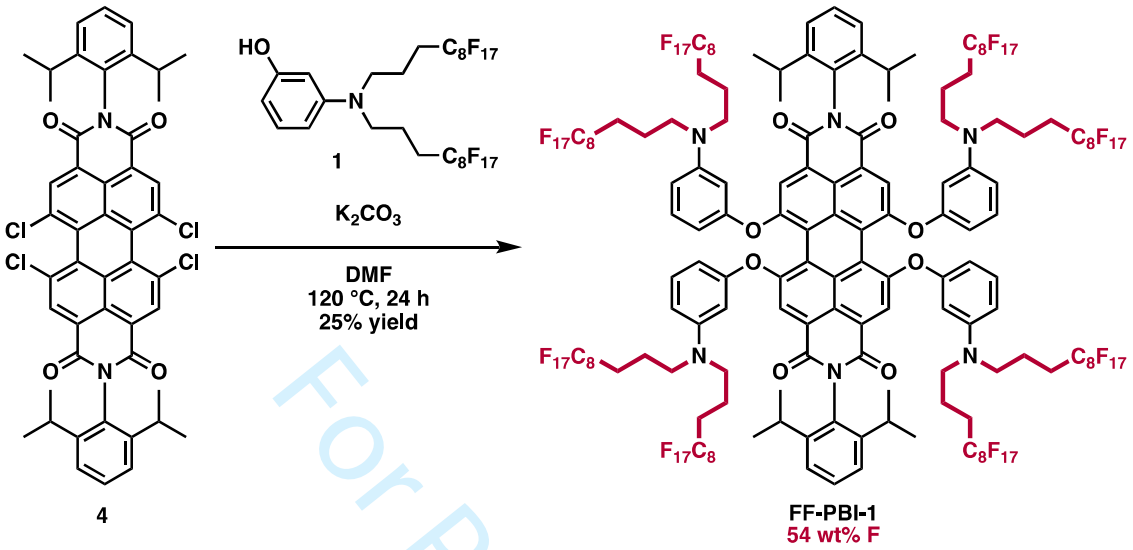
2. Synthetic Procedures



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_2CO_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_2Cl_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, 0.0440 mmol, 25%). ^{1}H NMR (500 MHz, CD_2Cl_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_2Cl_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 $C_{160}H_{102}F_{136}N_6O_8$ $[M+H]^+$: 4819.5678, found: 4819.80. Anal. calcd. for $C_{160}H_{102}F_{136}N_6O_8$ (%): C, 39.87; H, 2.13; N, 1.74. Found: C, 39.35; H, 2.08; N, 1.65.

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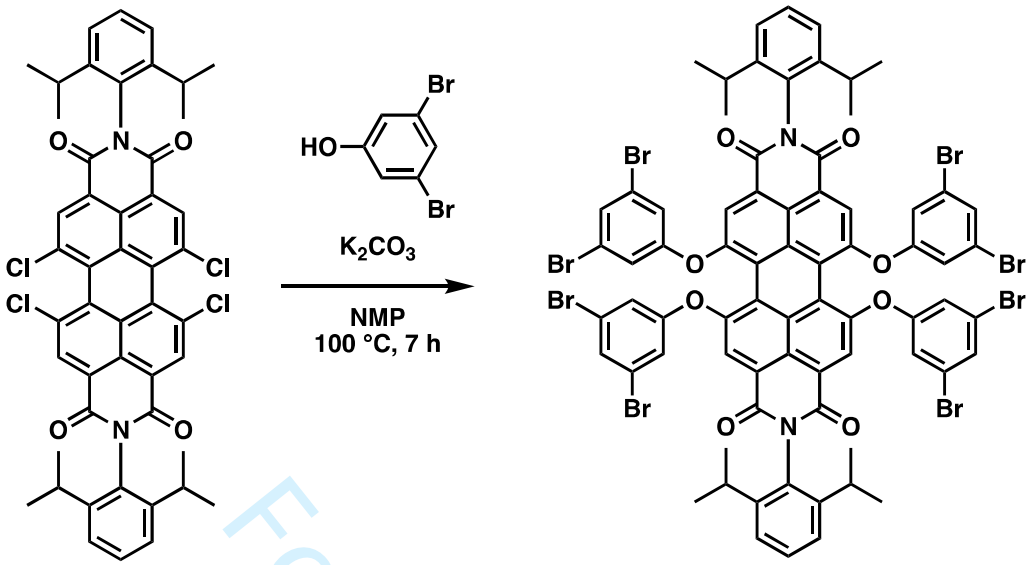
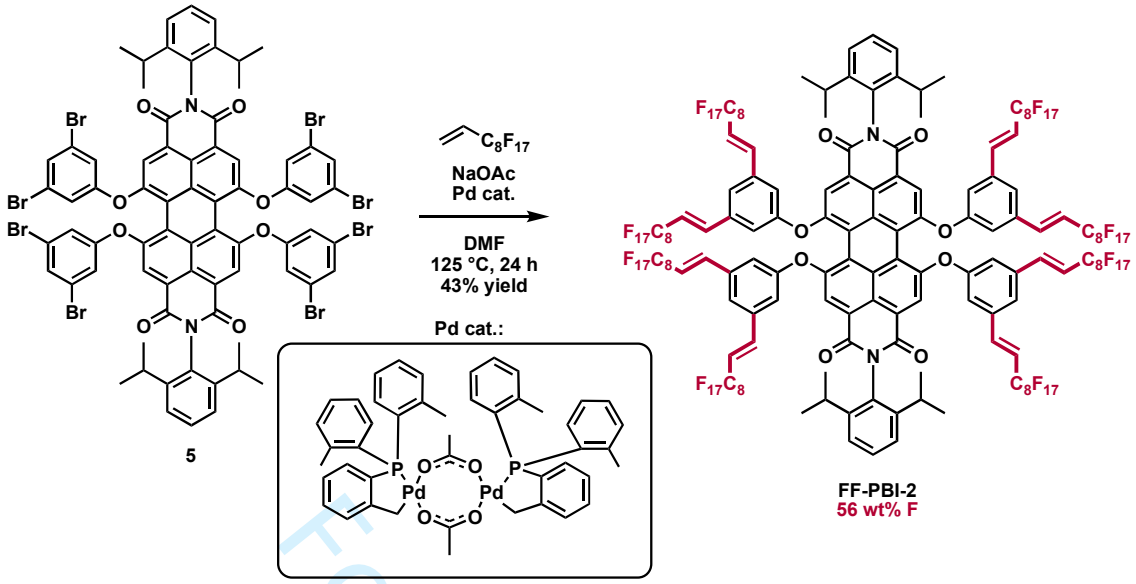


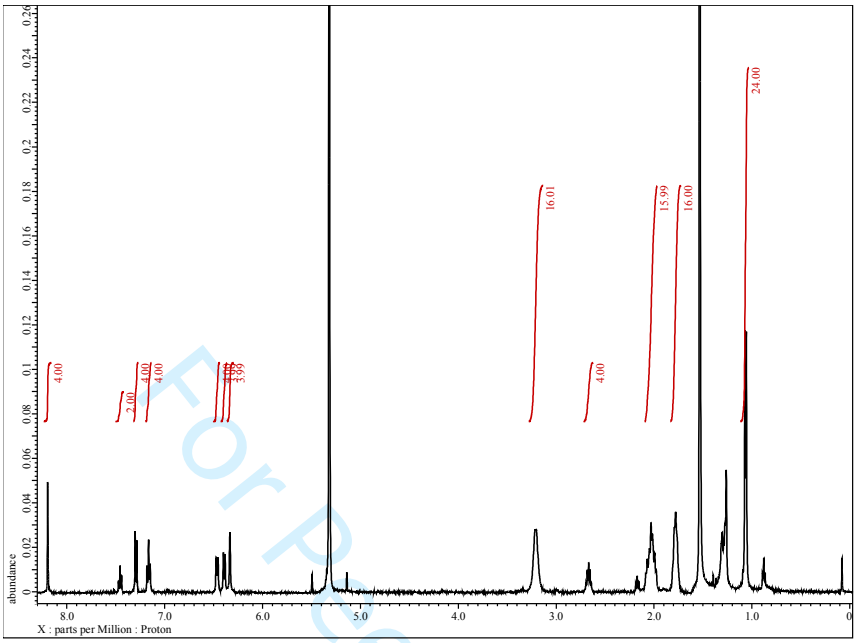
Synthesis of Compound 5. A mixture of compound **4** (0.320 g, 0.377 mmol), 3,5-dibromophenol (0.907 g, 3.60 mmol), and anhydrous K_2CO_3 (0.256 g, 1.85 mmol) in anhydrous 1-methyl-2-pyrrolidinone (NMP) (4 mL) was stirred at 100 °C under Ar for 7 h. Then, the reaction mixture was cooled to room temperature 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** (R_f = 0.70) was collected and evaporated to dryness under reduced pressure to provide a pink-red solid (0.440 g, 0.257 mmol, 68%). ^{1}H NMR (500 MHz, $CDCl_3$, 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). ^{13}C NMR (126 MHz, $CDCl_3$, 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 $C_{72}H_{50}Br_8N_2O_8$ $[M+H]^+$: 1710.7057, found:1710.7048.



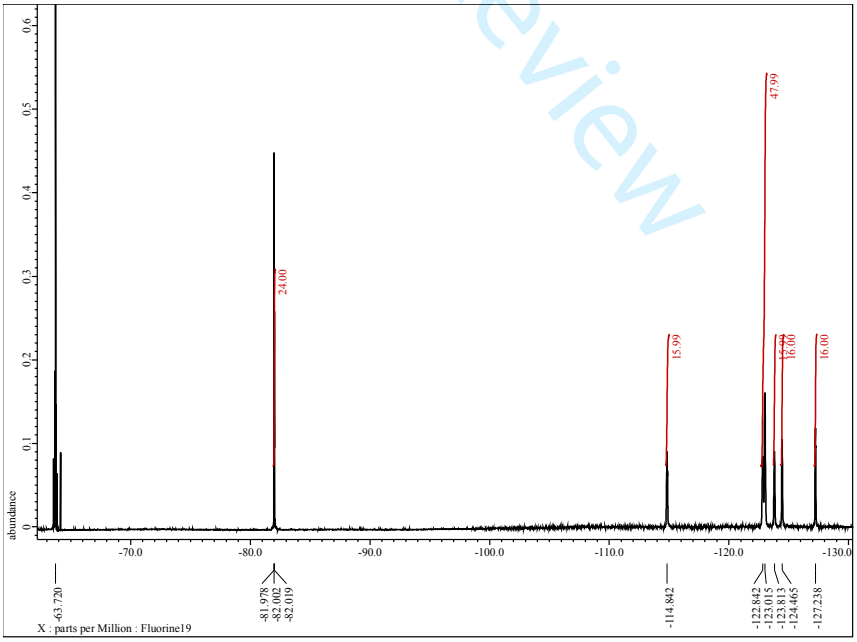
Synthesis of Compound FF-PBI-2. A mixture of compound **5** (0.439 g, 0.257 mmol), 1H,1H,2H-perfluoro-1-decene (1.44 g, 3.23 mmol), NaOAc (0.256 g, 3.04 mmol), and anhydrous DMF (5 mL) was treated with three cycles of freeze-pump-thaw. Then, Herrmann's catalyst (50.2 mg, 0.0535 mmol) was added to the 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 $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel using $CHCl_3$ as an eluent, and the fraction containing **FF-PBI-2** (R_f = 0.50) was collected and evaporated to dryness to provide a pink-red solid (0.517 g, 0.112 mmol, 43%). ^{1}H NMR (500 MHz, CD_2Cl_2, 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). ^{13}C NMR spectra could not be obtained due to low solubility. ^{19}F NMR (470 MHz, CD_2Cl_2, 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 $C_{152}H_{66}F_{136}N_2O_8$: 4630.2648, found: 4630.13. Anal. calcd. for $C_{152}H_{66}F_{136}N_2O_8$ (%): C, 39.41; H, 1.44; N, 0.60. Found: C, 39.40; H, 1.33; N, 0.60.

3. NMR Spectra

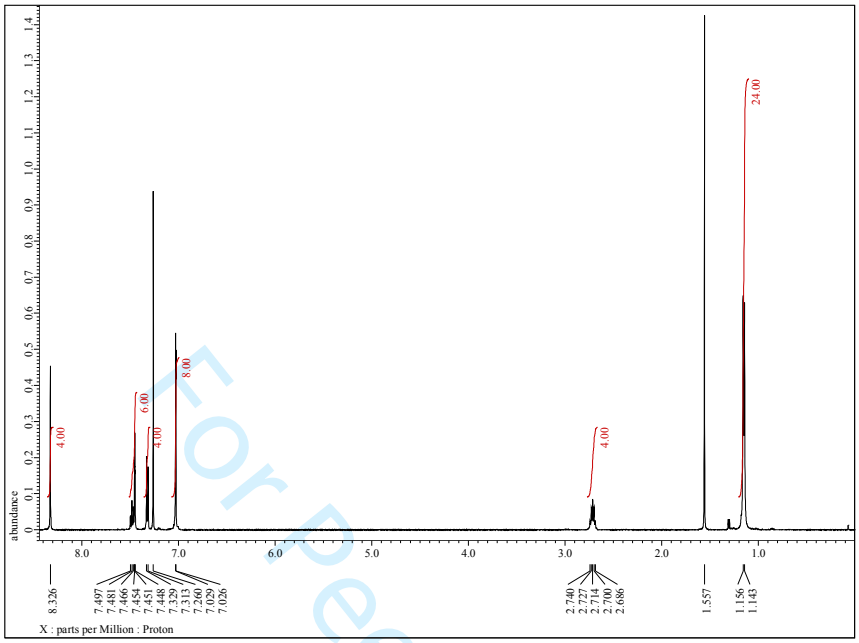
Compound **FF-PBI-1** ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C)



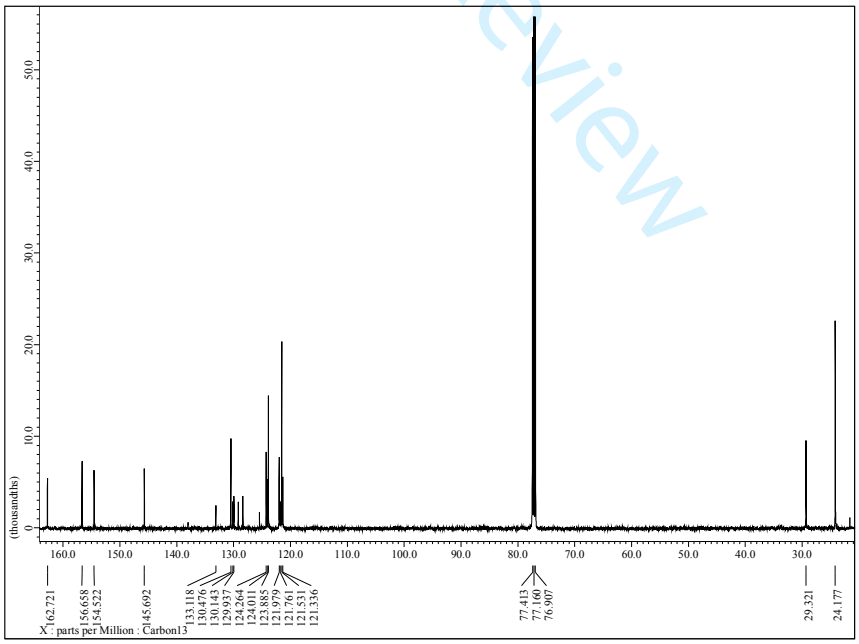
Compound **FF-PBI-1** ^{19}F NMR (470 MHz, CD_2Cl_2, 25 °C)



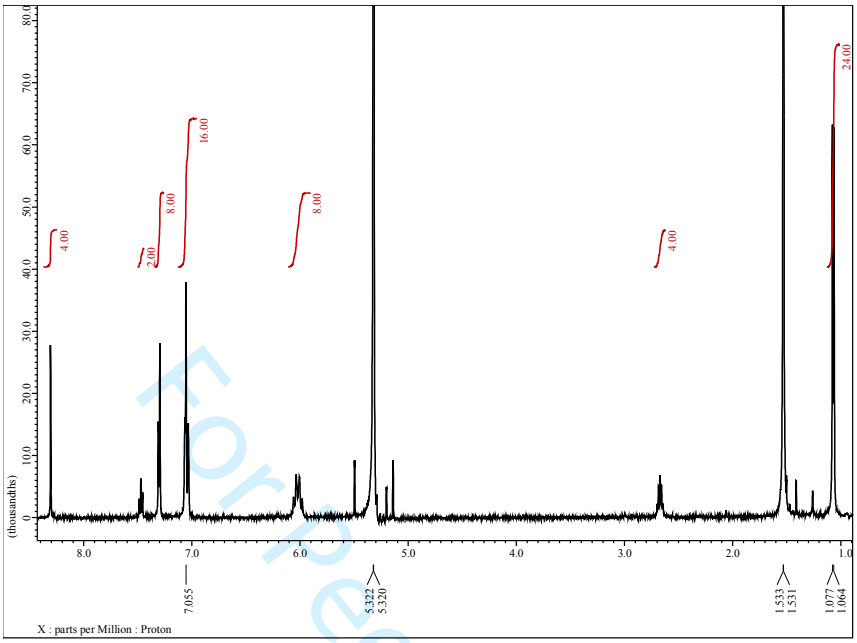
Compound **5** ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C)



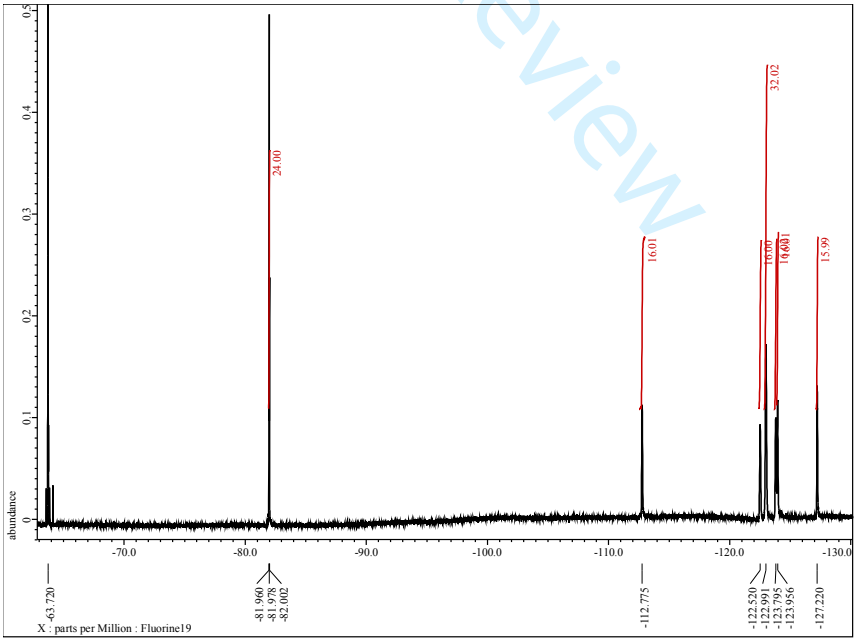
Compound **5** ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C)



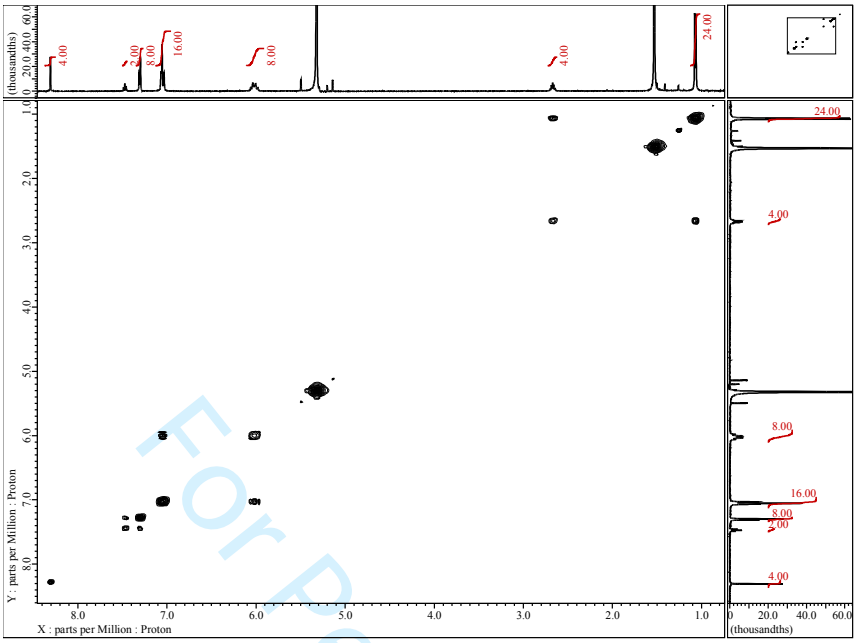
Compound **FF-PBI-2** ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C)



Compound **FF-PBI-2** ^{19}F NMR (470 MHz, CD_2Cl_2, 25 °C)



Compound **FF-PBI-2** COSY NMR (500 MHz, CD_2Cl_2, 25 °C)



4. Supporting Figures

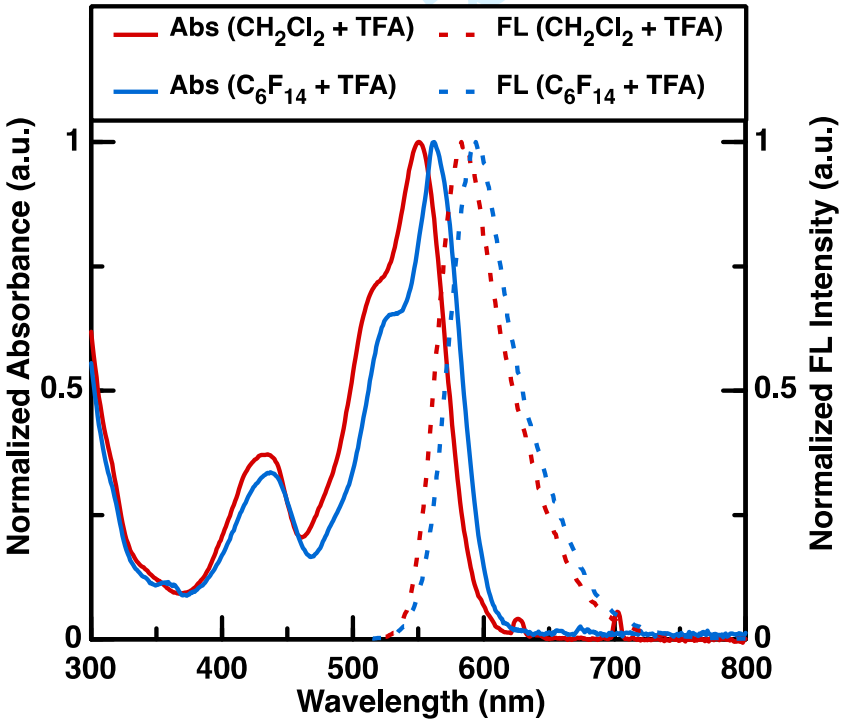


Figure S1: Normalized absorbance and fluorescence spectra of **FF-PBI-1** in CH_2Cl_2 + TFA and C_6F_{14} + TFA.

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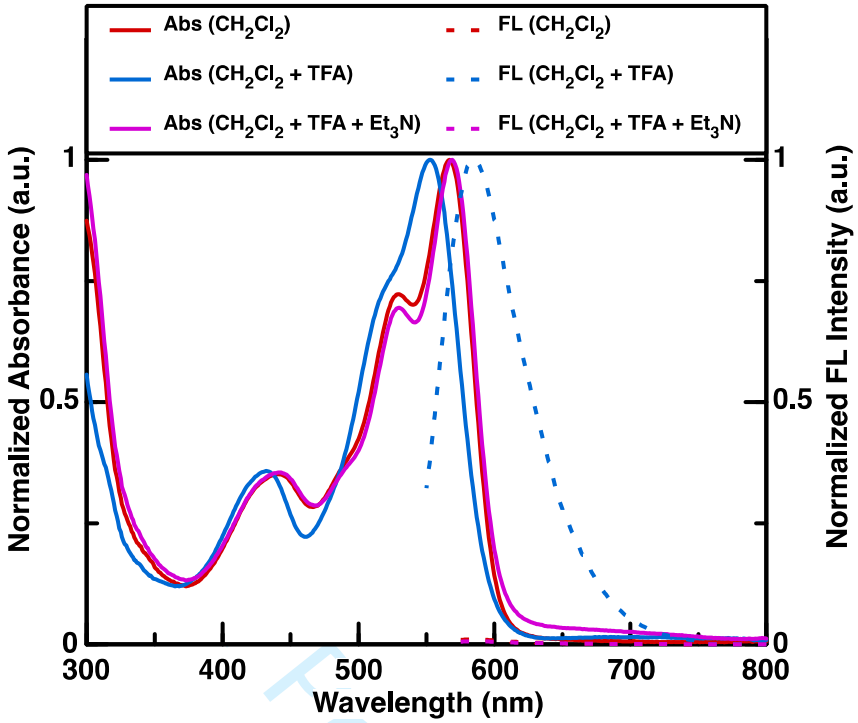

Figure S2: Normalized absorbance and fluorescence spectra of **FF-PBI-1** in CH_2Cl_2 and its change upon addition of TFA and Et_3N.

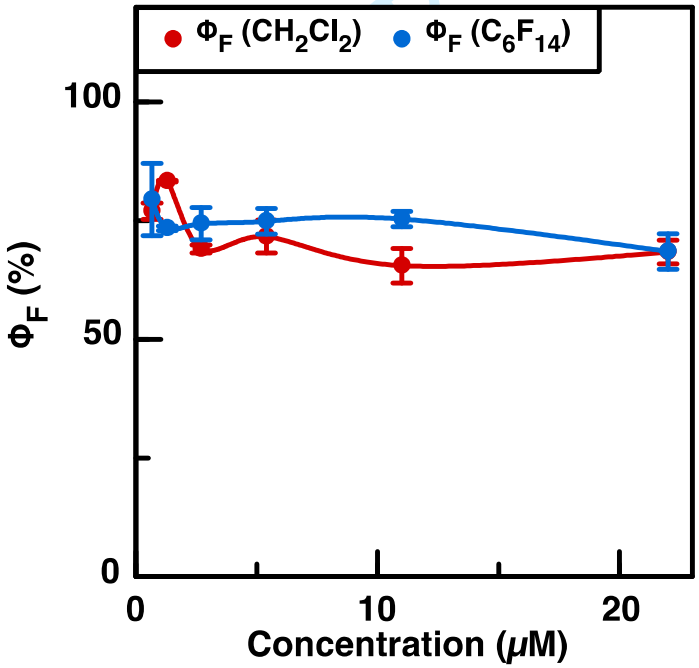

Figure S3: Quantum yield (Φ_F) of **FF-PBI-2** in CH_2Cl_2 and C_6F_{14} at different concentrations. Φ_F was determined by using an integrating sphere. The error bars represent values of Φ_F measured at three different excitation wavelengths.