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Supporting Information

Synthesis, Structure, and Transport Property of Perfluorinated Oligofluorenes

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General. Melting points were obtained on a Büchi melting point apparatus B-540. ^{1}H and ^{19}F NMR spectra were recorded on a JEOL JNM-LA 500 at 500 and 470.4 MHz, respectively. Chemical shifts were reported as δ values (ppm) relative to internal tetramethylsilane (^{1}H NMR) or hexafluorobenzene (^{19}F NMR). Elemental analyses were measured on a Yanaco CHN corder MT-6. EI mass spectra were collected on a Shimadzu GCMS-QP5050A and a JEOL JMS-700V at 70 eV. UV-vis spectra were recorded on a JASCO V-570 spectrophotometer. Emission spectra were collected on a JASCO FP-6600 spectrofluorophotometer. The calorimetric data were obtained on a TA Instruments DSC-Q100 at a scanning rate 10 °C min^{-1} under a flow (50 mL min^{-1}) of argon. Cyclic voltammetries were recorded on a BAS-100B/W electrochemical analyzer. Analytical TLCs were performed on commercial Merck plates coated with silica gel 60 F254. Flash chromatographic separations were carried out on Yamazen Hi-Flash column using a Yamazen YFLC purification system.

Materials. Anhydrous ether, THF, DMF, dioxane, and toluene were used as received from Kanto Chemicals Co. Anhydrous copper(I) bromide was dried at 120 °C for 2 h under reduced pressure before use. All other reagents and solvents were used without further purification.

Bis(2-bromo-3,4,5,6-tetrafluorophenyl)methanol (1). A 1.6 M *n*BuLi in hexane (100 mL, 16 mmol) was added to a solution of 1,2-dibromo-3,4,5,6-tetrafluorobenzene (50.8 g, 165 mmol) in dry ether (300 mL) at -80 °C. The mixture was stirred under argon at -80 °C for 30 min, and ethyl formate (5.68 g, 76.7 mmol) was added. The reaction mixture was allowed to warm to room temperature over 4 h and poured into water. The organic layer was extracted with ether, washed with brine, dried with Na_2SO_4, and evaporated. The residue was purified by silica gel chromatography with *n*-hexane/ethyl acetate (90:10) to give **1** as a colorless oil (32.0 g, 85%). Recrystallization from hexane gave the analytical sample as a colorless solid: mp 92-94 °C; ^{19}F NMR ($CDCl_3$) δ 34.97-35.04 (m, 2F), 21.80-21.84 (m, 2F), 9.87 (t, J = 18.8 Hz, 2F), 7.49 (t, J = 18.8 Hz, 2F); ^{1}H NMR ($CDCl_3$) δ 6.46 (d, J = 10.0 Hz, 1H), 3.18 (dt, J = 10.0, 5.0 Hz, 1H); MS (EI) *m/z* 484, 486, 487, 488, 489 (M^+, 29.7, 59.6, 7.5, 28.5, 4.4), 405, 407, 408 (M^+-Br, 34.8, 40.3, 5.0), 387, 388, 389, 390 (M^+-

Br-F, 15.4, 2.3, 9.4, 1.7), 306, 307, 309 (M^+-Br_2-F, 20.7, 18.0, 31.9), 257, 258, 259, 260 (M^+-$C_6Br_2F_4$, 100, 30.5, 78.1, 9.1). Anal. Calcd for $C_{13}H_2Br_2F_8O$: C, 32.13; H, 0.41. Found: C, 32.27; H, 0.59.

Bis(2-bromo-3,4,5,6-tetrafluorophenyl)methane (2). A mixture of **1** (35.2 g, 72.4 mmol), red phosphorus (44.9 g, 1.45 mol), and 52% hydroiodic acid (500 g) was refluxed for 24 h. After cooling to room temperature, the reaction mixture was poured into a mixture of water (200 mL) and chloroform (100 mL). The combined phases were filtered through Celite. The organic layer was separated, washed with water, dried with Na_2SO_4, and filtered. After evaporation of the filtrate, the residue was chromatographed on silica gel with *n*-hexane to give **2** (29.2 g, 85%) as a colorless solid: mp 47-49 °C; ^{19}F NMR ($CDCl_3$) δ 34.12-34.19 (m, 2F), 24.34-24.40 (m, 2F), 7.57 (t, J = 18.8 Hz, 2F), 6.18 (t, J = 18.8 Hz, 2F); ^{1}H NMR ($CDCl_3$) δ 4.35 (s, 2H); MS (EI) *m/z* 468, 470, 471, 472, 473 (M^+, 41.5, 75.7, 11.4, 39.9, 6.2), 389, 390, 391, 392 (M^+-Br, 34.4, 5.7, 32.9, 4.6), 309, 310, 311 (M^+-Br_2, 64.1, 81.0, 20.1), 291, 292 (M^+-Br_2-F, 100, 23.2). Anal. Calcd for $C_{13}H_2Br_2F_8$: C, 33.22; H, 0.43. Found: C, 33.24; H, 0.43.

1,2,3,4,5,6,7,8-Octafluorofluorene (3). In a sealed tube, **2** (6.00 g, 12.8 mmol) and copper bronze (4.90 g, 77.1 mmol) were heated to 200 °C for 5 days. After the tube was cooled to room temperature, the reaction mixture was dissolved in CH_2Cl_2 and filtered. The filtrate was washed with 3 M HCl and brine. The CH_2Cl_2 solution was dried with Na_2SO_4 and filtered. After evaporation of the solvent, the residue was chromatographed on silica gel with *n*-hexane to give **3** (2.88 g, 72%) as a colorless solid: mp 113-114 °C (lit. 112.5-114.5°C)[1]; ^{19}F NMR ($CDCl_3$) δ 26.66-26.69 (m, 2F), 20.26-20.30 (m, 2F), 7.03-7.24 (m, 4F); ^{1}H NMR ($CDCl_3$) δ 4.10 (s, 2H); MS (EI) *m/z* 310, 311 (M^+, 61.3, 8.1), 291, 292 (M^+-F, 100, 15.9). Anal. Calcd for $C_{13}H_2F_8$: C, 50.34; H, 0.65. Found: C, 50.37; H, 0.79.

2-Bromo-1,3,4,5,6,7,8-heptafluorofluorene (5). A 100-mL, three-necked, and round-bottomed flask fitted with Ar inlet was charged with **3** (1.00 g, 3.22 mmol), hydrazine monohydrate (360 mg, 7.19 mmol), and ethanol (10 mL). The mixture was refluxed for 24 h, and then the solvent was

removed on a rotary evaporator. The resulting solid was filtered and washed with *n*-hexane to give crude 2-hydrazino-1,3,4,5,6,7,8-heptafluorofluorene (**4**). A mixture of this crude product, copper(II) bromide (3.60 g, 16.1 mmol), and 48% hydrobromic acid (10 mL) was heated under reflux for 3 h. The reaction mixture was poured into water and filtered. The resulting solid was chromatographed over silica gel with *n*-hexane. Recrystallization from ethanol and train sublimation gave **5** (560 mg, 47%) as a colorless solid: mp 136-137 °C; ^{19}F NMR ($CDCl_3$) δ 47.87 (d, J = 18.8 Hz, 1F), 35.37 (d, J = 18.8 Hz, 1F), 27.12 (dtd, J = 70.6 and 18.8 and 4.7 Hz, 1F), 25.86 (dt, J = 70.6 and 18.8 Hz, 1F), 20.44 (t, J = 18.8 Hz, 1F), 8.22 (t, J = 18.8 Hz, 1F), 7.13 (t, J = 18.8 Hz, 1F); ^{1}H NMR ($CDCl_3$) δ 4.09 (s, 2H); MS (EI) *m/z* 370, 372, 373 (M^+, 24.6, 25.0, 2.9), 351, 353 (M^+-F, 6.2, 6.6), 291, 292 (M^+-Br, 100, 13.0), 271, 272, 273 (M^+-Br-F, 18.1, 10.8, 1.4). Anal. Calcd for $C_{13}H_2BrF_7$: C, 42.08; H, 0.54. Found: C, 42.07; H, 0.69.

2-Bromo-1,3,4,5,6,7,8-heptafluoro-9,9-bis(trifluoromethyl)fluorene (7). General Procedure for Trifluoromethylation. A 100-mL, three-necked, round-bottomed flask fitted with Ar inlet, and rubber septum was charged with 55% NaH (150 mg, 3.38 mmol) and DMF (5 mL). After the mixture was cooled in an ice bath, **5** (500 mg, 1.35 mmol) and 15-crown-5 (750 mg, 3.38 mmol) in DMF (10 mL) was added dropwise. The reaction mixture was stirred at room temperature for 30 min. After the mixture was cooled to -40 °C, a suspension of 5-(trifluoromethyl)dibenzothiophenium tetrafluoroborate (**6**) (1.20 g, 3.38 mmol) and DMF (15 mL) was added. The reaction mixture was stirred for 1 h and warmed to room temperature over a period of 4 h. To the reaction mixture was added ether and water. The organic layer was washed with brine, dried with Na_2SO_4, and evaporated. The residue was purified by silica gel chromatography with *n*-hexane to give **7** (364 mg, 53%) as a colorless oil: ^{19}F NMR ($CDCl_3$) δ 96.52 (t, J = 23.5 Hz, 6F), 59.65-59.89 (m, 1F), 44.36 (dd, J = 18.8 and 3.3 Hz, 1F), 30.74-31.26 (m, 2F), 29.52 (dt, J = 98.8 and 18.8 Hz, 1F), 14.86 (td, J = 18.8 and 9.4 Hz, 1F), 13.29 (t, J =18.8 Hz, 1F); MS (EI) *m/z* 506, 507, 508, 509 (M^+, 83.0, 16.8, 83.2, 15.0), 487, 489, 490 (M^+-F, 9.5, 11.7, 1.8), 437, 439, 440 (M^+-CF_3, 86.8, 100, 12.2), 387, 389, 390 (M^+-

CF_3-CF_2, 71.4, 76.8, 9.8), 358, 359 (M^+-Br-CF_3, 27.9, 3.8), 308, 309 (M^+-Br -CF_3-CF_2, 46.4, 8.6), 289, 290 (M^+-Br -2CF_3, 51.5, 4.4). HRMS Calcd for $C_{15}BrF_{13}$: 505.8976. Found: 505.8970.

PF-2F. In a sealed tube, **7** (1.10 g, 2.17 mmol) and copper bronze (830 mg, 13.0 mmol) were heated to 200 °C for 5 days. After the tube was cooled to room temperature, the reaction mixture was dissolved in CH_2Cl_2 and filtered. The filtrate was washed with 3 M HCl and brine. The CH_2Cl_2 solution was dried with Na_2SO_4 and filtered. After evaporation of the solvent, the residue was purified by column chromatography on silica gel with *n*-hexane/ethyl acetate (95:5) and train sublimation to give **PF-2F** (2.88 g, 72%) as a colorless solid: mp 143-145 °C; ^{19}F NMR ($CDCl_3$) δ 96.58 (t, *J* = 23.5 Hz, 12F), 53.98-54.22 (m, 2F), 38.51-38.59 (m, 2F), 31.66 (dm, *J* = 98.8 Hz, 2F), 30.96-31.26 (m, 2F), 28.45 (dt, *J* = 98.8 and 18.8 Hz, 2F), 15.13 (td, *J* = 18.8 and 9.4 Hz, 2F), 14.21 (t, *J* = 18.8 Hz, 2F); MS (EI) *m/z* 854, 855, 856 (M^+, 85.1, 27.5, 4.9), 835, 836 (M^+-F, 11.1, 4.2) , 785, 786, 787 (M^+-CF_3, 73.7, 24.1, 4.0), 735, 736 (M^+-CF_3-CF_2, 23.0, 7.2), 716, 717 (M^+-2CF_3, 8.2, 3.1), 666, 667 (M^+-2CF_3-CF_2, 29.6, 9.4), 647, 648 (M^+-3CF_3, 13.9, 3.6), 616, 617 (M^+-2CF_3-2CF_2, 24.3, 8.0), 578, 579 (M^+-4CF_3, 11.3, 3.8), 427 (M^{2+}, 10.2), 340 (M^{2+}-CF_3, 68.7), 290 (M^{2+}-CF_3-CF_2, 100), 271 (M^{2+}-2CF_3, 16.5). Anal. Calcd for $C_{30}F_{26}$: C, 42.18. Found: C, 41.68. HRMS Calcd for $C_{30}F_{26}$: 853.9585. Found: 853.9597.

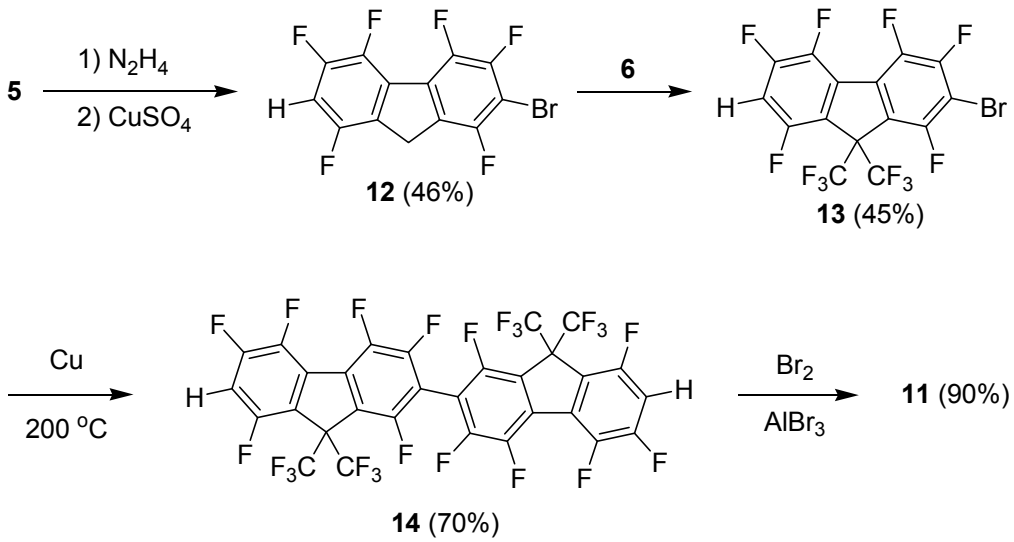
2,7-Dibromo-1,3,4,5,6,8-hexafluorofluorene (8). A 100-mL, three-necked, and round-bottomed flask fitted with Ar inlet was charged with **5** (900 mg, 2.43 mmol), hydrazine monohydrate (240 mg, 4.85 mmol), and dioxane (20 mL). The mixture was refluxed for 24 h, and then the solvent was evaporated. The resulting solid was washed with *n*-hexane to give crude 2-bromo-7-hydrazino-1,3,4,5,6,8-hexafluorofluorene. This crude product was heated under reflux with copper(II) bromide (2.71 g, 112 mmol) and 48% hydrobromic acid (20 mL) for 3 h. The reaction mixture was poured into water and filtered. The resulting solid was chromatographed over silica gel with *n*-hexane. Recrystallization from ethanol and train sublimation gave **8** (400 mg, 38%) as a colorless solid: mp 203-204 °C; ^{19}F NMR ($CDCl_3$) δ 47.99 (t, *J* = 9.4 Hz, 2F), 35.61 (t, *J* = 9.4 Hz, 2F), 26.19-26.27 (m, 2F); ^{1}H NMR ($CDCl_3$) δ 4.08 (s, 2H); MS (EI) *m/z* 430, 431, 432, 433, 434, 435 (M^+, 38.6, 9.7, 66.5,

12.2, 33.8, 4.7), 351, 352, 353, 354 (M^+-Br, 100, 20.0, 91.5, 12.8), 271, 272, 273 (M^+-Br_2, 30.8, 83.0, 10.9), 253, 254 (M^+-Br_2-F, 38.3, 5.7). Anal. Calcd for $C_{13}H_2Br_2F_6$: C, 36.15; H, 0.47. Found: C, 36.04; H, 0.56.

2,7-Dibromo-1,3,4,5,6,8-hexafluoro-9,9-bis(trifluoromethyl)fluorene (9). This compound was synthesized using the general procedure for trifluoromethylation with **8** (1.00 g, 2.32 mmol), 15-crown-5 (1.28 g, 5.79 mmol), 55% NaH (230 mg, 5.33 mmol), **6** (1.97 g, 5.79 mmol), and DMF (50 mL). Flash column chromatography over silica gel with *n*-hexane and train sublimation gave **9** (670 mg, 50%) as a colorless solid: mp 99-102 °C; ^{19}F NMR ($CDCl_3$) δ 96.75 (t, J = 23.5 Hz, 6F), 60.08-60.27 (m, 2F), 44.37-44.43 (m, 2F), 29.83-29.91 (m, 1F); MS (EI) *m/z* 566, 568, 569, 570, 571 (M^+, 48.5, 100, 18.2, 44.7, 8.5), 549, 551 (M^+-F, 8.7, 4.4), 497, 499, 500, 501, 502 (M^+-CF_3, 39.7, 77.6, 13.3, 36.0, 5.4), 447, 449, 450, 451, 452 (M^+-CF_3-CF_2, 27.9, 57.0, 8.5, 27.2, 3.7), 418, 420, 421 (M^+-Br-CF_3, 20.0, 23.9, 3.4), 368, 370, 371 (M^+-Br -CF_3-CF_2, 25.7, 31.3, 4.1), 349, 351, (M^+-Br -2CF_3, 5.9, 5.8), 320, 321 (M^+-2Br -CF_3-F, 16.5, 2.4), 289, 290 (M^+-2Br -CF_3-CF_2, 48.9, 7.1), 270, 271 (M^+-2Br -2CF_3, 16.5, 2.2). HRMS Calcd for $C_{15}Br_2F_{12}$: 565.8175. Found: 565.8171.

PF-3F. General Procedure for the Cross-Coupling Reaction. A 200-mL, three-necked, round-bottomed flask fitted with a reflux condenser, Ar inlet, and rubber septum was charged with **7** (3.00 g, 5.90 mmol) and THF (30 mL). After the mixture was cooled in an ice bath, 1.0 M ethylmagnesium bromide in THF (5.9 mL, 5.9 mmol) was added dropwise, and the reaction mixture was stirred for 1 h. After the mixture was stirred for 1 h at room temperature, anhydrous copper(I) bromide (1.69 g, 11.8 mmol) was added. The gray suspension was stirred at room temperature for 2 h, and dioxane (7.5 mL) was added. The resulting gray suspension was stirred at room temperature for 1 h. To the suspension was added a solution of **9** (840 mg, 1.47 mmol) in toluene (30 mL). The mixture was stirred at 90 °C for 4 days and filtered through Celite. The solvent was removed on a rotary evaporator. The residue was dissolved in toluene, and the solution was washed with 3 M HCl and brine. The toluene solution was dried with Na_2SO_4 and filtered. After evaporation of the solvent, the residue was purified by column chromatography on silica gel with *n*-hexane/ethyl acetate (95:5) and

train sublimation to give **PF-3F** (980 mg, 52%) as a colorless solid: mp 280 °C (DSC); ^{19}F NMR ($CDCl_3$) δ 96.83 (t, *J* = 23.5 Hz, 6F), 96.63 (t, *J* = 23.5 Hz, 12F), 54.60-54.76 (m, 2F), 54.13-54.26 (m, 2F), 38.71-38.84 (m, 4F), 31.75 (dm, *J* = 98.8 Hz, 2F), 31.02-31.32 (m, 2F), 29.37-29.45 (m, 2F), 28.58 (dt, *J* = 98.8 and 18.8 Hz, 2F), 15.23 (td, *J* = 18.8 and 9.4 Hz, 2F), 14.33(t, *J* = 18.8 Hz, 2F); MS *m/z* 1262, 1263, 1264, 1265 (M^+, 100.0, 51.5, 11.2, 1.7), 1243, 1244, 1245 (M^+-F, 10.0, 7.1, 2.4), 1193, 1194, 1195 (M^+-CF_3, 39.6, 21.0, 4.1), 1124, 1125 (M^+-2CF_3, 5.5, 2.8), 1005, 1006 (M^+-3CF_3-CF_2, 7.6, 3.2), 631 (M^{2+}, 1.6), 562, 563 (M^{2+}-CF_3, 3.3, 1.9). Anal. Calcd for $C_{45}F_{38}$: C, 42.81. Found: C, 42.47.



2-Bromo-1,3,4,5,6,8-hexafluorofluorene (12). A 100-mL, three-necked, and round-bottomed flask fitted with Ar inlet was charged with **5** (3.00 g, 8.09 mmol), hydrazine monohydrate (810 mg, 16.2 mmol), and dioxane (30 mL). The mixture was refluxed for 24 h, and then the solvent was evaporated. The resulting solid was washed with *n*-hexane to give crude 2-bromo-7-hydrazino-1,3,4,5,6,8-hexafluorofluorene. This crude product was heated under reflux with copper(II) sulfate pentahydrate (4.26 g, 17.1 mmol) and water (120 mL) for 3 h. The reaction mixture was poured into water and filtered. The resulting solid was chromatographed over silica gel with *n*-hexane. Recrystallization from ethanol and train sublimation gave **12** (1.34 g, 46%) as a colorless solid: mp 132-133 °C; ^{19}F NMR ($CDCl_3$) δ 45.75 (d, *J* = 18.8 Hz, 1F), 43.00 (dd, *J* = 18.8 and 8.0 Hz, 1F), 35.07 (d, *J* = 18.8 Hz, 1F), 28.23 (dd, *J* = 18.8 and 10.0 Hz, 1F), 26.06 (dtd, *J* =70.6 and 18.8 and

18.8 Hz, 1F), 22.53 (dtd, J = 70.6 and 18.8 and 5.0 Hz, 1F); ^{1}H NMR ($CDCl_3$) δ 7.03 (ddd, J = 10.0 and 8.0 and 5.0 Hz, 1H), 4.03 (s, 2H); MS (EI) *m/z* 352, 353, 354, 355 (M^+, 26.3, 6.2, 20.9, 3.1), 333, 335 (M^+-F, 3.9, 4.4), 273, 274 (M^+-Br, 100, 10.5), 253, 254 (M^+-Br-F, 19.4, 8.4). Anal. Calcd for $C_{13}H_3BrF_6$: C, 44.22; H, 0.86. Found: C, 44.40; H, 1.04.

2-Bromo-1,3,4,5,6,8-hexafluoro-9,9-bis(trifluoromethyl)fluorene (13). This compound was synthesized using the general procedure for trifluoromethylation with **12** (700 mg, 1.98 mmol), 15-crown-5 (1.10 g, 4.96 mmol), 55% NaH (220 mg, 4.96 mmol), **6** (1.69 g, 4.96 mmol), and DMF (40 mL). Flash column chromatography over silica gel with *n*-hexane gave **13** (440 mg, 45%) as a colorless oil: ^{19}F NMR ($CDCl_3$) δ 96.59 (t, J = 23.5 Hz, 6F), 59.72-59.97 (m, 1F), 54.09-54.37 (m, 1F), 43.97 (dd, J = 18.8 and 5.0 Hz, 1F), 36.05 (td, J = 18.8 and 9.4 Hz, 1F), 29.75 (ddd, J = 98.8 and 18.8 and 18.8 Hz, 1F), 26.76 (dtd, J = 98.8 and 18.8 and 5.0 Hz,1F); ^{1}H NMR ($CDCl_3$) δ 7.16 (td, J = 9.5 and 5.0 Hz, 1H); MS (EI) *m/z* 488, 489, 490, 491 (M^+, 63.4, 11.5, 61.8, 9.5), 469, 471, 472 (M^+-F, 7.4, 8.7, 1.2), 419, 421, 422 (M^+-CF_3, 87.7, 100, 13.4), 369, 371, 372 (M^+-CF_3-CF_2, 60.8, 67.2, 8.9), 340, 341 (M^+-Br-CF_3, 28.6, 4.2), 290, 291 (M^+-Br -CF_3-CF_2, 54.6, 7.2), 271, 272 (M^+-Br -2CF_3, 39.5, 4.2). HRMS Calcd for $C_{15}HBrF_{12}$: 487.9070. Found: 487.9081.

1,3,4,5,6,8,1',3',4',5',6',8'-Dodecafluoro-9,9,9',9'-tetra(trifluoromethyl)-[2,2']bifluorene (14). In a sealed tube, **13** (1.36 g, 2.80 mmol) and copper bronze (1.10 g, 17.3 mmol) were heated to 200 °C for 5 days. After the tube was cooled to room temperature, the reaction mixture was dissolved in CH_2Cl_2 and filtered. The filtrate was washed with 3 M HCl and brine. The CH_2Cl_2 solution was dried with Na_2SO_4 and filtered. After evaporation of the solvent, the residue was chromatographed on silica gel with *n*-hexane/ethyl acetate (95:5) to give **14** (800 mg, 70%) : ^{19}F NMR ($CDCl_3$) δ 96.53 (t, J = 23.5 Hz, 12F), 53.96-54.43 (m, 4F), 38.01-38.09 (m, 2F), 36.16 (dt, J = 18.8 and 9.4 Hz, 2F), 28.48 (dt, J = 98.8 and 18.8 Hz, 2F), 27.25 (dtd, J = 98.8 and 18.8 and 5.0 Hz, 2F); ^{1}H NMR ($CDCl_3$) δ 7.21 (td, J =10.0 and 5.0 Hz, 2H); MS (EI) *m/z* 818, 819, 820 (M^+, 43.8, 7.1, 2.1), 799, 800 (M^+-F, 5.4, 1.7), 749, 750, 751 (M^+-CF_3, 53.7, 16.0, 2.2), 699, 700 (M^+-CF_3-CF_2,

9.2, 3.1), 680, 681 (M^+-$2CF_3$, 6.4, 1.9), 630, 631 (M^+-$2CF_3$-CF_2, 17.7, 4.0), 580, 581 (M^+-$2CF_3$-$2CF_2$, 12.7, 4.4), 542, 543 (M^+-$4CF_3$, 6.7, 1.4), 409 (M^{2+}, 9.5), 340 (M^{2+}-CF_3, 68.7), 290 (M^{2+}-CF_3-CF_2, 100), 271 (M^{2+}-$2CF_3$, 16.5). HRMS Calcd for $C_{30}H_2F_{24}$: 817.9773. Found: 817.9758.

7,7'-Dibromo-1,3,4,5,6,8,1',3',4',5',6',8'-dodecafluoro-9,9,9',9'-tetra(trifluoromethyl)-[2,2']bifluorene (11). A mixture of **14** (800 mg, 0.978 mmol), bromine (3.20 g, 20.0 mmol), 60% fuming sulfuric acid (0.7 mL), and aluminum bromide (80 mg, 0.60 mmol) was stirred at 60 °C for 3 days. The reaction mixture was carefully poured into crashed ice. The resulting solid was filtered and washed with sodium carbonate, sodium bisulfite, and water. Flash chromatography over silica gel with *n*-hexane/ethyl acetate (95:5) and train sublimation gave **11** (870 mg, 90%) as a colorless solid: mp 191-193 °C; ^{19}F NMR ($CDCl_3$) δ 96.74 (t, J = 23.5 Hz, 12F), 60.20-60.44 (m, 2F), 54.26-54.60 (m, 2F), 44.55-44.64 (m, 2F), 38.52-38.57 (m, 2F), 30.40 (dt, J = 98.8 and 18.8 Hz, 2F), 28.73 (dt, J = 98.8 and 18.8 Hz, 2F); MS (EI) *m/z* 974, 975, 976, 977, 978, 979, 980 (M^+, 45.5, 17.4, 100, 32.9, 51.0, 14.9, 2.6), 905, 906, 907, 908, 909, 910 (M^+-CF_3, 18.6, 5.7, 40.5, 9.3, 19.9, 7.7), 895, 896, 897, 898 (M^+-Br, 11.0, 3.8, 9.0, 4.2), 855, 857, 858, 859 (M^+-CF_3-CF_2, 2.7, 6.4, 1.7, 3.3), 826, 827, 828, 829 (M^+-Br-CF_3, 9.3, 4.1, 9.2, 2.5), 786, 788, 789, 790 (M^+-$2CF_3$-CF_2, 4.2, 9.7, 3.5, 5.7), 707, 708, 709, 710 (M^+-Br-$2CF_3$-CF_2, 9.2, 2.8, 7.8, 2.6), 487, 488, 489 (M^{2+}, 3.3, 6.2, 3.4), 418, 419, 420 (M^{2+}-CF_3, 4.1, 10.3, 5.5), 368, 369, 370 (M^{2+}-CF_3-CF_2, 4.2, 8.3, 4.9). HRMS Calcd for $C_{30}Br_2F_{24}$: 973.7983. Found: 973.7994.

PF-4F. The general procedure for the cross-coupling reaction described above was followed using **7** (2.20 g, 4.40 mmol), THF (20 mL), 1.0 M ethylmagnesium bromide in THF (4.4 mL, 4.4 mmol), anhydrous copper(I) bromide (1.27 g, 8.85 mmol), dioxane (5.5 mL), **11** (1.09 g, 1.10 mmol), and toluene (35 mL). The mixture was stirred at 90 °C for 4 days. Flash chromatography over silica gel with *n*-hexane/ethyl acetate (9:1) and train sublimation gave **PF-4F** (860 mg, 46%) as a colorless solid: ^{19}F NMR ($CDCl_3$) δ 96.85 (t, J = 23.5 Hz, 12F), 96.64 (t, J = 23.5 Hz, 12F), 54.65-54.86 (m, 4F), 54.14-54.32 (m, 2F), 38.86-38.98 (m, 2F), 38.66-38.75 (m, 4F), 31.76 (dm, J = 98.8 Hz, 2F), 31.04-31.32 (m, 2F), 29.41-29.51 (m, 4F), 28.58 (dm, J = 98.8 Hz, 2F), 15.22 (td, J = 18.8 and 9.4

Hz, 2F), 14.33 (t, J = 18.8 Hz, 2F); MS *m/z* 1670, 1671, 1672, 1673 (M^+, 100, 58.9, 19.7, 4.1), 1651, 1652, 1653 (M^+-F, 10.3, 11.3, 4.5), 1601, 1602, 1603 (M^+-CF_3, 28.1, 16.1, 5.1), 1532, 1533 (M^+-$2CF_3$, 4.1, 2.5), 835, 836 (M^{2+}, 5.0, 2.8), 766, 767 (M^{2+}-CF_3, 8.6, 5.0). Anal. Calcd for $C_{60}F_{50}$: C, 43.14. Found: C, 42.68.

Electron-Mobility Measurement. The electron mobilities were measured by the conventional time-of-flight technique. The samples were prepared by vacuum deposition on ITO-coated glass substrates. A thin layer of Alq_3 (30 nm) was deposited on the ITO for photocarrier generation, and a thick layer of **PF-3F** (5.6 μm) (or **PF-4F**, 3.8 μm) was deposited on the Alq_3 layer. An aluminum electrode (100 nm) was then deposited on the **PF-3F** layer. The transient photocurrent due to the electron transit through the **PF-3F** layer was observed by an irradiation of N_2 pulse laser (wavelength: 337 nm). The photocurrent was characterized by a sharp pulse at t = 0, a plateau, and a dispersive tail. The transit time was defined at the demarcation point between the plateau and the dispersive tail. The electron mobility was calculated from the transit time.

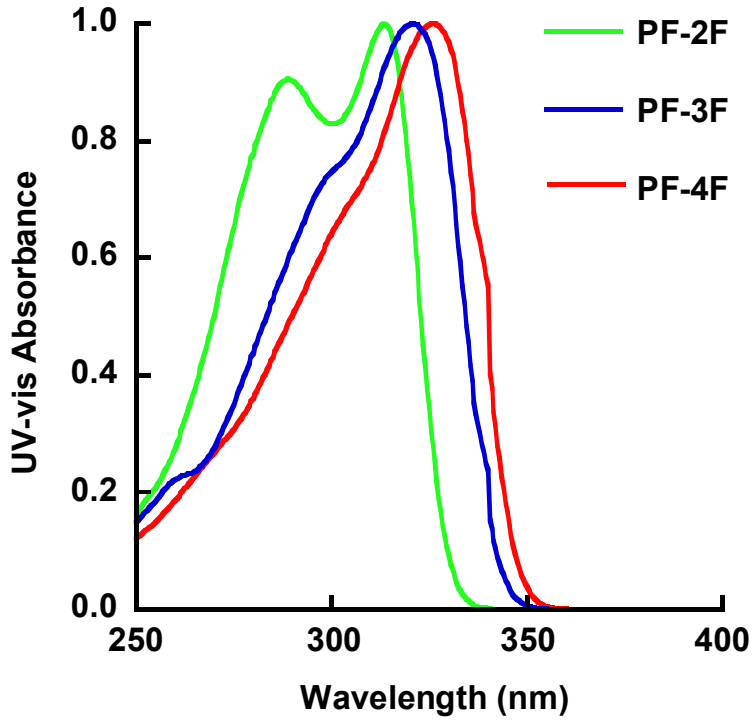


Figure 1. Absorption spectra of **PF-2F**, **PF-3F**, and **PF-4F** in chloroform.

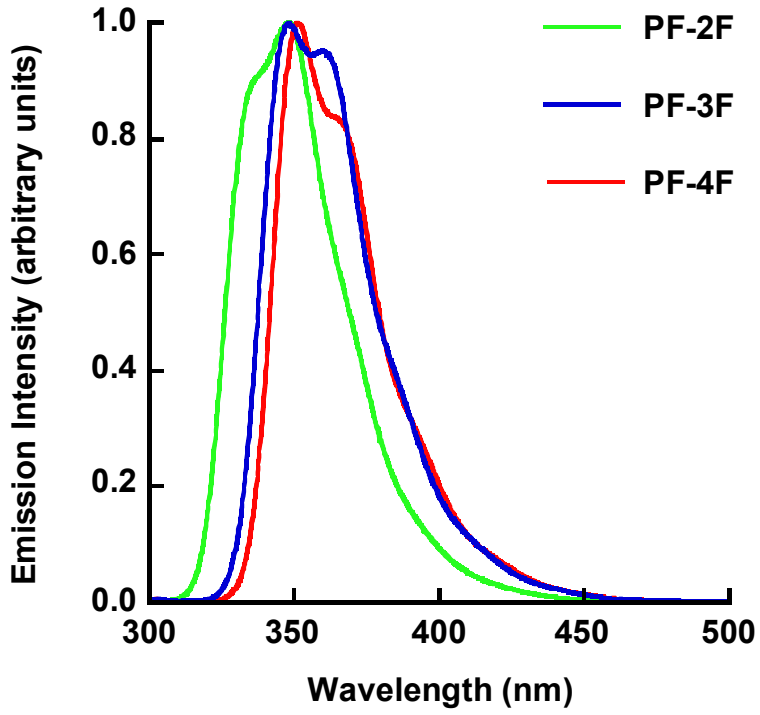


Figure 2. Emission spectra of **PF-2F**, **PF-3F**, and **PF-4F** in chloroform.

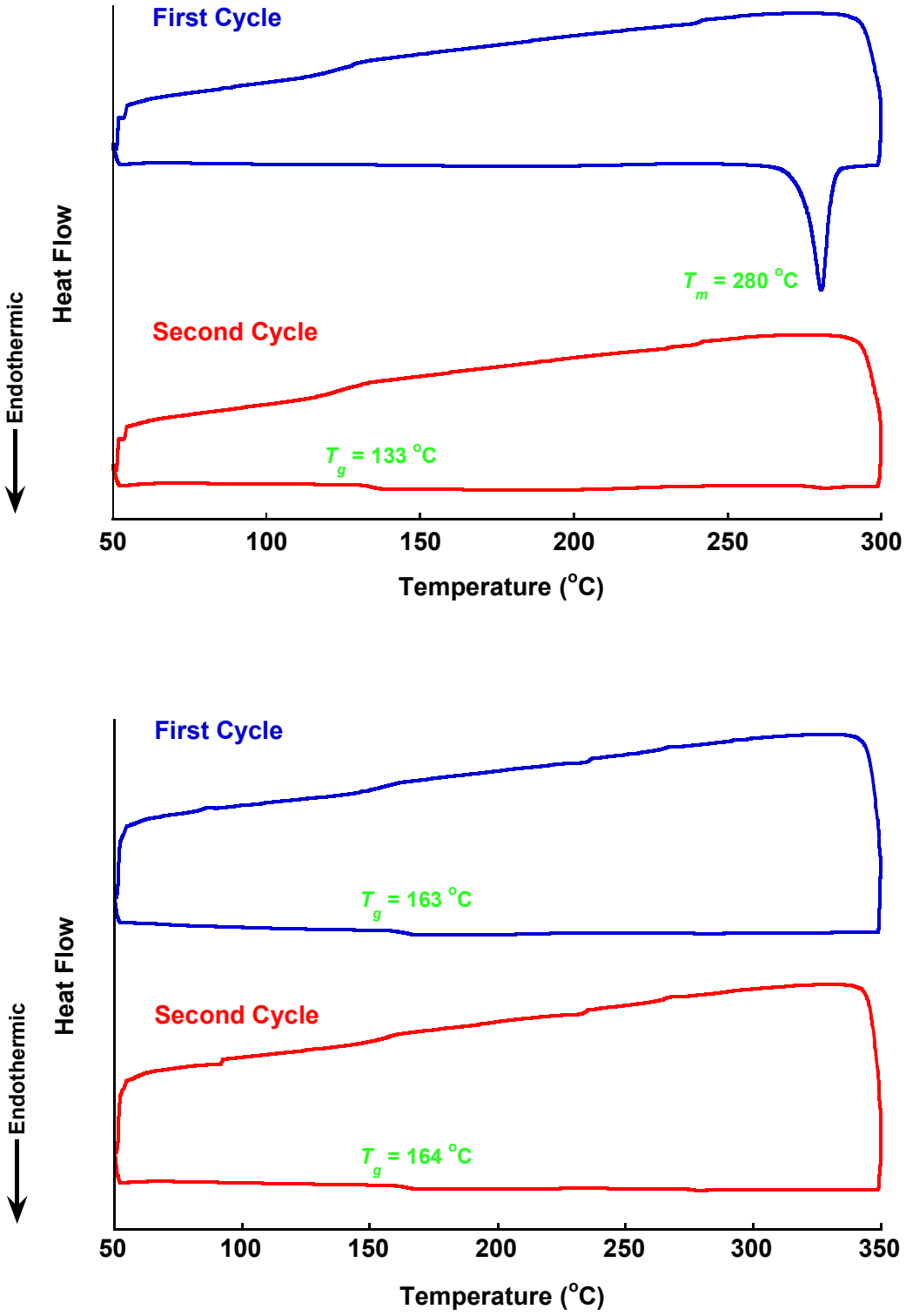


Figure 3. DCS traces of **PF-3F** (top) and **PF-4F** (bottom). The heating rate is 10 °C min^{-1}, and the cooling rate is 40 °C min^{-1}.

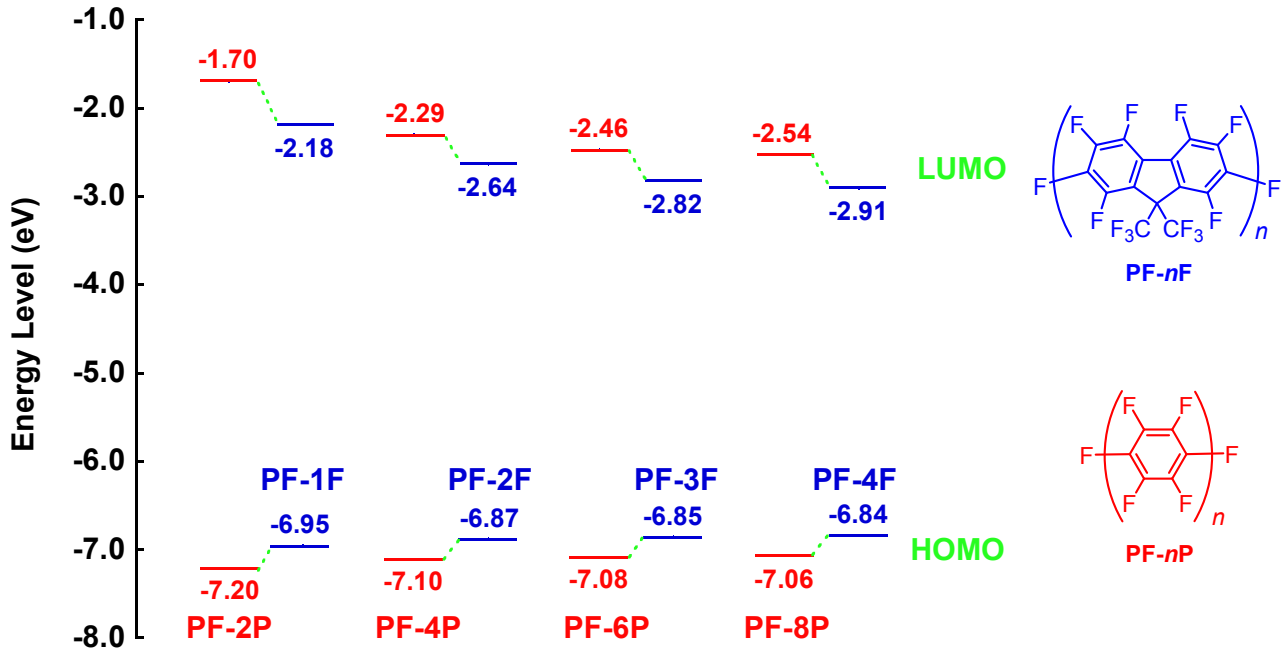


Figure 4. Energy diagrams calculated at the B3LYP/6-31G(d) level for **PF-*n*P**s and **PF-*n*F**s.[2]

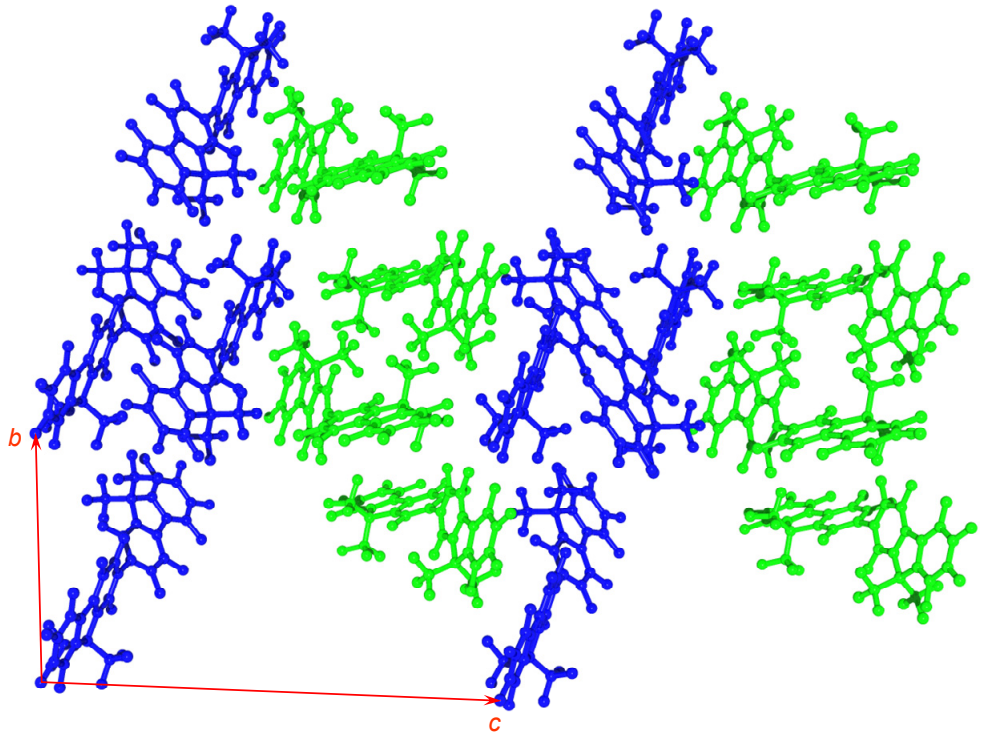


Figure 5. Molecular packing diagram of **PF-2F** with a view down the *a* axis.

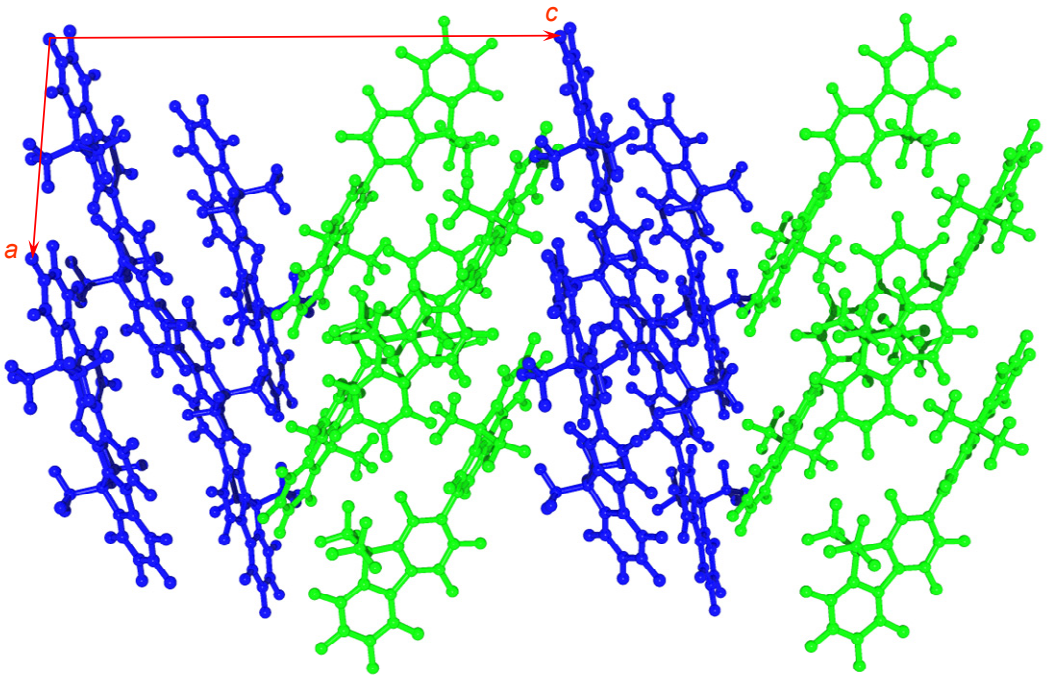


Figure 6. Molecular packing diagram of **PF-2F** with a view down the *b* axis.

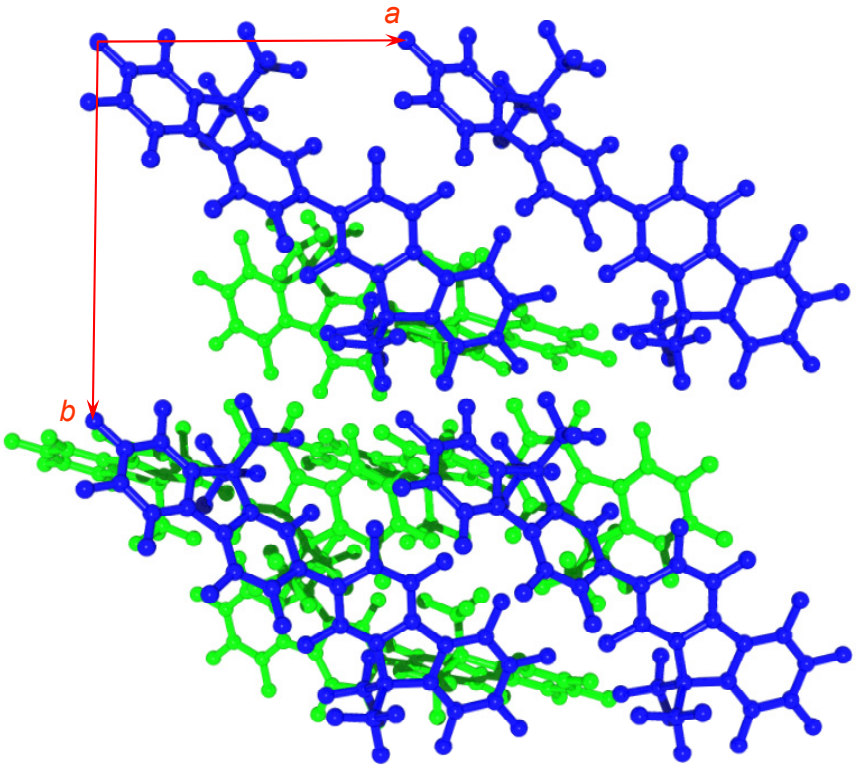


Figure 7. Molecular packing diagram of **PF-2F** with a view down the *c* axis.

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