Supporting Information for

Construction of Semi-Fluorinated Polyimide with Perfluorocyclobutyl Aryl Ether-Based Side Chains

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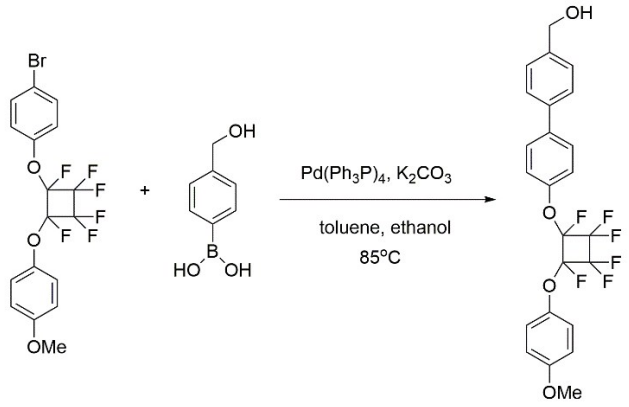
S1. Materials

All chemicals were purchased from Aldrich and used as received unless otherwise specified. 1-Methyl-2-pyrrolidinone (NMP) was distilled over CaH_2 under reduced pressure prior to use.

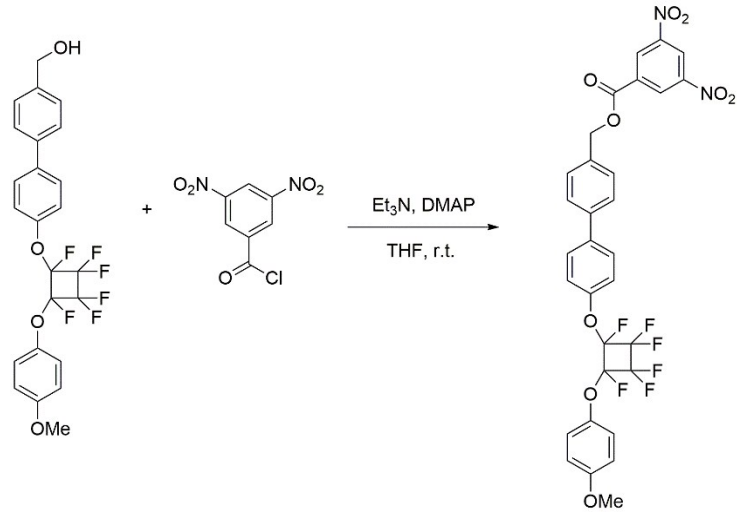
S2. Synthetic Procedures and Characterization Data for the Intermediates and Diamines

PF_1OH



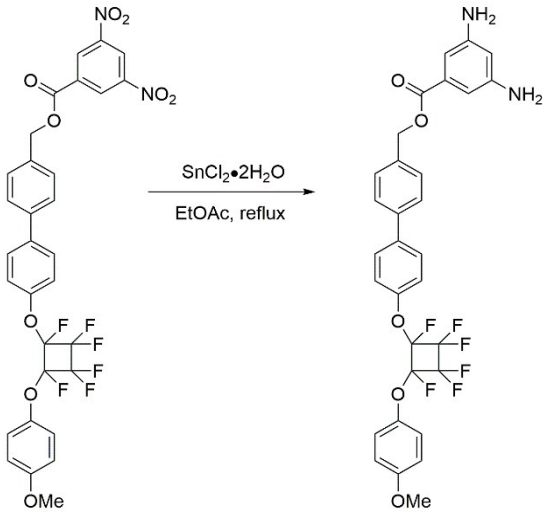
Into a 500 mL round-bottom flask were added $BrPF_1OMe$ (5.0 g, 10.9 mmol), 4-hydroxmethylphenylboronic acid (2.2 g, 14.5 mmol), tetrakis(triphenylphosphine)-palladium(0) (0.5 g, 0.43 mmol), and K_2CO_3 (6.0 g, 43.4 mmol). Next, 50 mL of ethanol and 150 mL of toluene were added into the flask. The resulting mixture was heated at 85°C for 4 h under Ar. The solvents were removed by rotary evaporation, and the residue was subjected to column chromatography using a mixture of hexane and ethyl acetate (v:v = 1:1) to afford PF_1OH as a white solid (5.2 g, 98% yield). ^1H NMR ($CDCl_3$): δ (ppm): 3.76 (s, 3H), 4.73 (s, 2H), 6.81-6.85 (m, 2H), 7.08-7.25 (m, 4H), 7.42-7.55 (m, 6H). ^{13}C NMR ($CDCl_3$): δ (ppm): 157.30, 157.10, 152.22, 152.07, 152.05, 146.30, 146.09, 140.26, 140.24, 139.50, 139.48, 138.20, 137.95, 128.45, 128.39, 127.64, 127.29, 127.28, 120.39, 119.96, 119.94, 118.95, 118.93, 118.60, 118.58, 114.79, 114.73, 65.16, 55.73, 55.70. ^{19}F NMR ($CDCl_3$): δ (ppm): -128.37~ -131.78 (PFCB). MALDI-TOF-MS (M^+ calcd as $C_{24}H_{18}F_6O_4$ = 484.11) m/z (%): 484.2 (8), 468.2 (22), 467.2 (100).

PF_1DN



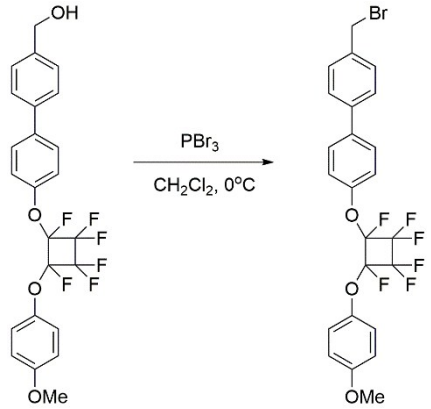
Into PF_1OH (2.0 g, 4.1 mmol) in 40 mL of extra dry tetrahydrofuran (THF) were added 3,5-dinitrobenzoyl chloride (1.13 g, 4.9 mmol) and 4-dimethylaminopyridine (0.05 g, 0.41 mmol). The resulting system was placed into an ice-water bath to be cooled. Triethylamine (TEA, 1.15 mL, 8.2 mmol) was introduced into the system through a syringe. The resulting mixture was warmed to room temperature and allowed to stir for another 5 h. Water was added to quench the reaction. THF was removed by rotary evaporation, and the residue was extracted using 150 mL of CH_2Cl_2. The organic phase was washed with 5% aqueous K_2CO_3 (150 mL×2) as well as brine (150 mL×2), dried over anhydrous $MgSO_4$ and filtered. After CH_2Cl_2 was evaporated, the crude product was purified using column chromatography (hexane/ ethyl acetate, v:v = 5:1) to afford PF_1DN as a pale yellow solid (2.49 g, 89% yield). ^1H NMR ($CDCl_3$): δ (ppm): 3.76 (s, 3H), 5.51 (s, 2H), 6.81-6.84 (m, 2H), 7.07-7.13 (m, 2H), 7.19-7.26 (m, 2H), 7.53-7.62 (m, 6H), 9.17-9.18 (m, 2H), 9.21-9.22 (m, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm): 162.56, 157.32, 157.11, 152.48, 152.33, 152.31, 148.55, 146.25, 146.06, 140.91, 137.70, 137.45, 133.96, 133.83, 133.80, 129.64, 129.56, 128.56, 128.49, 127.59, 127.57, 122.61, 120.36, 119.93, 119.91, 118.98, 118.97, 118.66, 118.64, 114.79, 114.73, 68.43, 55.73, 55.70. ^{19}F NMR ($CDCl_3$): δ (ppm): -128.30~ -131.92 (PFCB).

PF_1DA



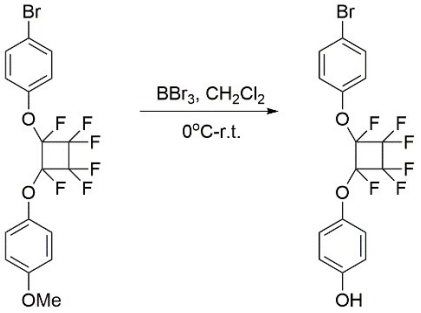
Into PF_1DN (3.0 g, 4.4 mmol) in 40 mL of ethyl acetate was added stannous chloride dihydrate (10.0 g, 44.3 mmol). The resulting mixture was stirred at reflux for 2 h under Ar. Next, aqueous K_2CO_3 was added into the system to adjust the pH to basicity. The product was extracted using ethyl acetate (150 mL×2). The organic phase was combined, washed with brine (150 mL×2), dried over anhydrous $MgSO_4$ and filtered. After ethyl acetate was evaporated, the crude product was subjected to column chromatography using ethyl acetate as eluent to afford PF_1DA as a pale yellow solid (2.6 g, 96% yield). ^{1}H NMR (DMSO-d_6): δ (ppm): 3.73 (s, 3H), 5.01 (s, 4H), 5.29 (s, 2H), 6.04-6.05 (m, 1H), 6.48-6.49 (m, 2H), 6.97-7.00 (m, 2H), 7.17-7.21 (m, 2H), 7.29-7.33 (m, 2H), 7.50-7.53 (m, 2H), 7.68-7.70 (m, 2H), 7.75-7.78 (m, 2H). ^{13}C NMR (DMSO-d_6): δ (ppm): 166.62, 157.14, 156.96, 151.29, 151.05, 149.43, 145.10, 144.85, 138.45, 137.55, 137.27, 135.98, 135.94, 130.48, 128.65, 128.59, 128.50, 126.79, 126.76, 120.06, 119.84, 118.61, 118.38, 115.13, 115.06, 103.79, 103.66, 65.24, 55.47, 55.45. ^{19}F NMR (DMSO-d_6): δ (ppm): -127.91~ -130.99 (PFCB). FT-IR (KBr): ν (cm^{-1}): 3469.28, 3377, 1713, 1605, 1504, 1318, 1245, 1188, 1107, 962, 814. MALDI-TOF-MS (M^+ calcd as $C_{31}H_{24}F_6N_2O_5$ = 618.16) m/z (%): 622.1 (8.1) , 621.1 (46.9), 620.1 (25.5), 619.1 (100), 618.1 (63.9), 467.9 (17.7), 466.9 (87.0).

PF_1MBr



In a 250 mL round-bottom flask, PF_1OH (8.5 g, 17.5 mmol) was dissolved in 100 mL of dry CH_2Cl_2. The resulting system was placed into an ice-water bath, and after it was cooled, PBr_3 (0.67 mL, 7.1 mmol) was injected into the system slowly. The resulting mixture was stirred for another 1 h. Next, 100 mL of 5% aqueous K_2CO_3 was added to quench the reaction. The product was extracted using CH_2Cl_2 (100 mL×2). The organic phase was combined, washed with brine (100 mL×2), dried over anhydrous $MgSO_4$ and filtered. CH_2Cl_2 was evaporated to afford PF_1MBr as a white solid (9.5 g, 99% yield). The product was used without further purification. ^1H NMR ($CDCl_3$): δ (ppm): 3.75 (s, 3H), 4.53 (s, 2H), 6.81-6.84 (m, 2H), 7.07-7.13 (m, 2H), 7.18-7.24 (m, 2H), 7.44-7.54 (m, 6H). ^{13}C NMR ($CDCl_3$): δ (ppm): 157.29, 157.08, 152.39, 152.22, 146.26, 146.04, 140.21, 137.77, 137.51, 137.16, 137.13, 129.72, 128.49, 128.44, 127.51, 120.39, 119.92, 118.96, 118.59, 114.77, 114.72, 55.72, 55.69, 33.34. ^{19}F NMR ($CDCl_3$): δ (ppm): -128.35~ -131.84 (PFCB). ESI-MS (M^+ calcd as $C_{24}H_{17}BrF_6O_3$ = 546.03) m/z (%): 468.1 (19), 467.1 (100).

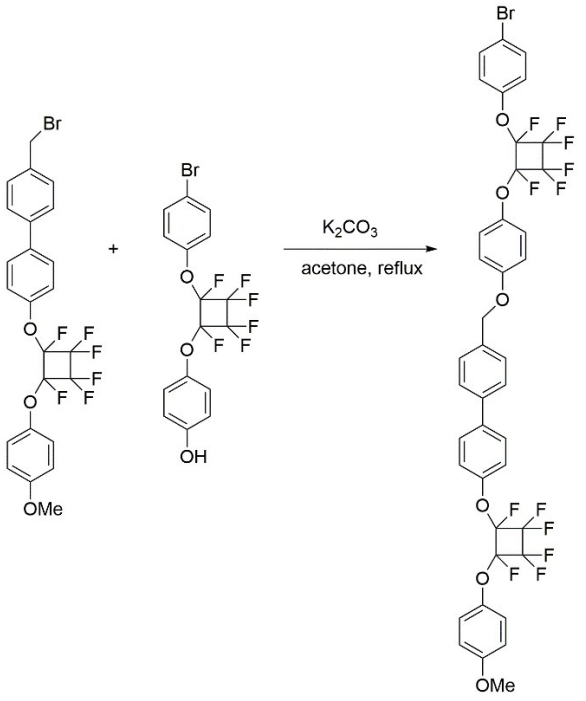
$BrPF_1OH$



In a 500 mL round-bottom flask seated in an ice-water bath, $BrPF_1OMe$ (20 g, 43.8

mmol) was dissolved in 200 mL of dry CH_2Cl_2. Next, BBr_3 (4 M solution in CH_2Cl_2, 22 mL, 88 mmol) was added slowly through a syringe. The resulting solution was warmed to room temperature and stirred overnight. Afterwards, 200 mL of 5% aqueous K_2CO_3 was added to quench the reaction. The product was extracted using CH_2Cl_2 (200 mL×2). The organic phase was combined, washed with brine (200 mL×2), dried over anhydrous $MgSO_4$ and filtered. CH_2Cl_2 was evaporated to afford $BrPF_1OH$ as a pale white solid (17.5 g, 91% yield). The product was used without further purification. ^{1}H NMR ($CDCl_3$): δ (ppm): 4.96 (br, 1H), 6.75-6.79 (m, 2H), 6.99-7.05 (m, 4H), 7.42-7.47 (m, 2H). ^{13}C NMR ($CDCl_3$): δ (ppm): 153.37, 153.09, 151.81, 151.61, 146.27, 146.06, 132.91, 132.85, 120.68, 120.57, 120.55, 120.09, 118.57, 118.20, 116.31, 116.27. ^{19}F NMR ($CDCl_3$): δ (ppm): -128.27~-132.44 (PFCB).

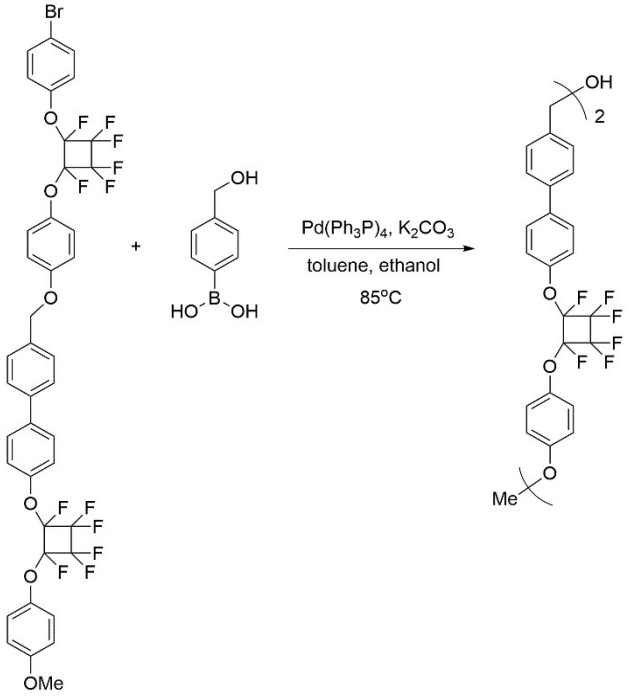
PF_2Br



Into a 250 mL round-bottom flask were added PF_1MBr (9.6 g, 17.5 mmol), $BrPF_1OH$ (9.3 g, 21.1 mmol), K_2CO_3 (4.85 g, 35.1 mmol), and 100 mL of acetone. The resulting mixture was stirred at reflux under Ar for 12 h. Acetone was removed via rotary evaporation and the residue was subjected to column chromatography

(hexane/ethyl acetate, v:v = 7:1) to afford PF_2Br as a clear viscous liquid (13.2 g, 83% yield). ^1H NMR ($CDCl_3$): δ (ppm): 3.75 (s, 3H), 5.06 (s, 2H), 6.81-6.85 (m, 2H), 6.90-6.93 (m, 2H), 7.00-7.14 (m, 6H), 7.19-7.24 (m, 2H), 7.41-7.58 (m, 8H). ^{13}C NMR ($CDCl_3$): δ (ppm): 157.33, 157.12, 156.55, 156.29, 152.33, 152.16, 151.84, 151.64, 146.42, 146.30, 146.20, 146.09, 139.98, 138.06, 137.81, 136.01, 135.98, 132.90, 132.85, 128.50, 128.44, 128.19, 128.16, 127.38, 120.61, 120.50, 120.40, 120.10, 119.95, 119.90, 118.98, 118.63, 115.83, 114.80, 114.75, 50.31, 55.73, 55.70. ^{19}F NMR ($CDCl_3$): δ (ppm): -128.13~ -132.03 (PFCB).

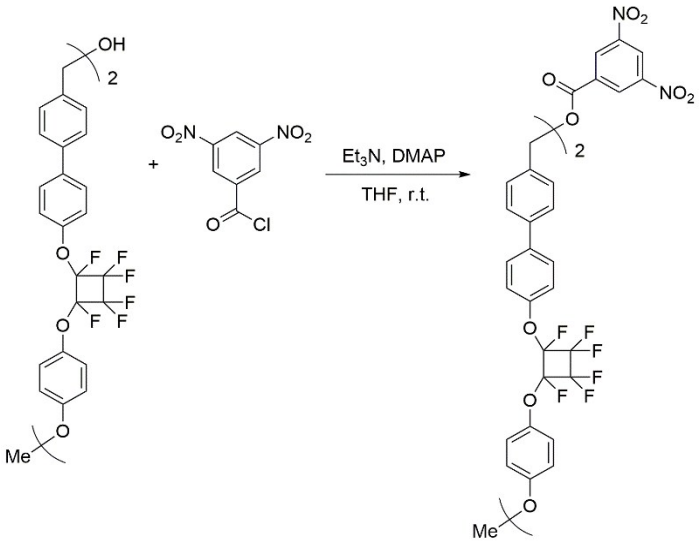
PF_2OH



Into a 250 mL round-bottom flask were added PF_2Br (2.0 g, 2.20 mmol), 4-hydroxmethylphenylboronic acid (0.43 g, 2.83 mmol), tetrakis(triphenylphosphine)-palladium(0) (0.1 g, 0.09 mmol), and K_2CO_3 (1.2 g, 8.8 mmol). Next, 30 mL of ethanol and 100 mL of toluene were added into the system. The resulting mixture was heated at 85°C for 4 h under Ar. The solvents were removed by rotary evaporation, and the residue was subjected to column chromatography using a mixture of hexane and ethyl acetate (v:v=1:1) to afford PF_2OH as a white solid (1.8 g, 87% yield). ^1H NMR ($CDCl_3$): δ (ppm): 3.75 (s, 3H), 4.73 (s, 2H), 5.02 (s, 1H), 5.06 (s, 1H), 6.81-

6.84 (m, 2H), 6.89-6.94 (m, 2H), 7.07-7.13 (m, 4H), 7.17-7.24 (m, 4H), 7.41-7.57 (m, 12H). ^{13}C NMR ($CDCl_3$): δ (ppm): 157.30, 157.09, 156.43, 156.20, 152.30, 152.20, 152.13, 152.04, 146.54, 146.29, 146.07, 140.28, 140.25, 139.94, 139.46, 138.23, 138.04, 137.95, 137.80, 136.03, 136.00, 135.97, 128.48, 128.44, 128.39, 128.15, 127.65, 127.35, 127.29, 127.27, 120.45, 120.39, 119.95, 119.02, 118.97, 118.58, 115.78, 114.78, 114.73, 70.28, 70.24, 65.16, 55.73, 55.69. ^{19}F NMR ($CDCl_3$): δ (ppm): -128.34~ -131.78 (PFCB). MALDI-TOF-MS (M^+ calcd as $C_{47}H_{32}F_{12}O_7$ = 936.2) m/z (%): 920.3 (48), 919.3 (100).

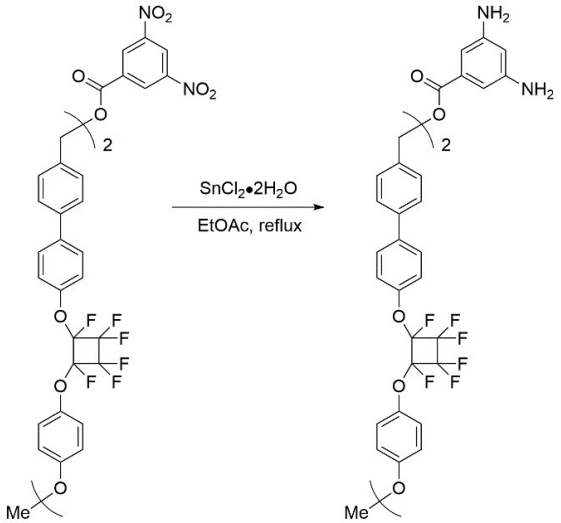
PF_2DN



Into PF_2OH (3.0 g, 3.2 mmol) in 40 mL of extra dry THF were added 3,5-dinitrobenzoyl chloride (0.75 g, 3.3 mmol) and 4-dimethylaminopyridine (0.04 g, 0.33 mmol). The resulting system was placed into an ice-water bath to be cooled. TEA (0.89 mL, 6.4 mmol) was then introduced into the system through a syringe. The resulting mixture was warmed to room temperature and allowed to stir for another 5 h. Afterwards, water was added to quench the reaction. THF was removed by rotary evaporation and the residue was extracted using 150 mL of CH_2Cl_2. The organic phase was washed with 5% aqueous K_2CO_3 (150 mL×2) as well as brine (150 mL×2), dried over anhydrous $MgSO_4$ and filtered. After CH_2Cl_2 was evaporated, the crude product was purified using column chromatography (hexane/ethyl acetate, v:v = 5:1)

to afford PF_2DN as a pale yellow solid (2.9 g, 81% yield). ^1H NMR ($CDCl_3$): δ (ppm): 3.76 (s, 3H), 5.04 (s, 1H), 5.06 (s, 1H), 5.50 (s, 2H), 6.81-6.84 (m, 2H), 6.90-6.94 (m, 2H), 7.07-7.14 (m, 4H), 7.18-7.25 (m, 4H), 7.45-7.61 (m, 12H), 9.16-9.18 (m, 2H), 9.20-9.22 (m, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm): 162.56, 157.32, 157.11, 156.46, 156.23, 152.47, 152.31, 152.14, 148.85, 146.54, 146.31, 146.07, 140.92, 139.95, 139.93, 138.03, 137.74, 137.47, 136.03, 136.00, 135.98, 133.96, 133.95, 133.84, 133.81, 129.64, 129.58, 128.57, 128.50, 128.47, 128.41, 128.15, 127.61, 127.58, 127.35, 122.61, 120.40, 119.95, 119.05, 118.96, 118.62, 115.81, 114.79, 114.74, 70.30, 70.26, 68.44, 55.74, 55.70. ^{19}F NMR ($CDCl_3$): δ (ppm): -128.33~ -131.80 (PFCB).

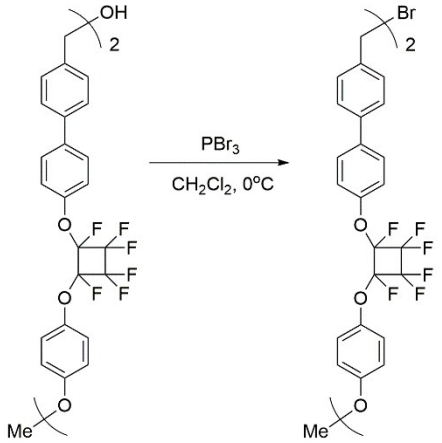
PF_2DA



Into PF_2DN (2.0 g, 1.77 mmol) in 40 mL of ethyl acetate was added stannous chloride dihydrate (4.0 g, 17.7 mmol). The resulting mixture was stirred at reflux for 2 h under Ar. Aqueous K_2CO_3 was added into the system to adjust the pH to basicity. The product was extracted using ethyl acetate (150 mL×2). The organic phase was combined, washed with brine (150 mL×2), dried over anhydrous $MgSO_4$ and filtered. After ethyl acetate was evaporated, the crude product was subjected to column chromatography using ethyl acetate as eluent to afford PF_2DA as a pale yellow solid (1.5 g, 79% yield). ^1H NMR ($CDCl_3$): δ (ppm): 3.64 (br, -NH_2), 3.75 (s, 3H), 5.02 (s, 1H), 5.06 (s, 1H), 5.34 (s, 2H), 6.17-6.19 (m, 1H), 6.81-6.85 (m, 4H), 6.89-6.94 (m,

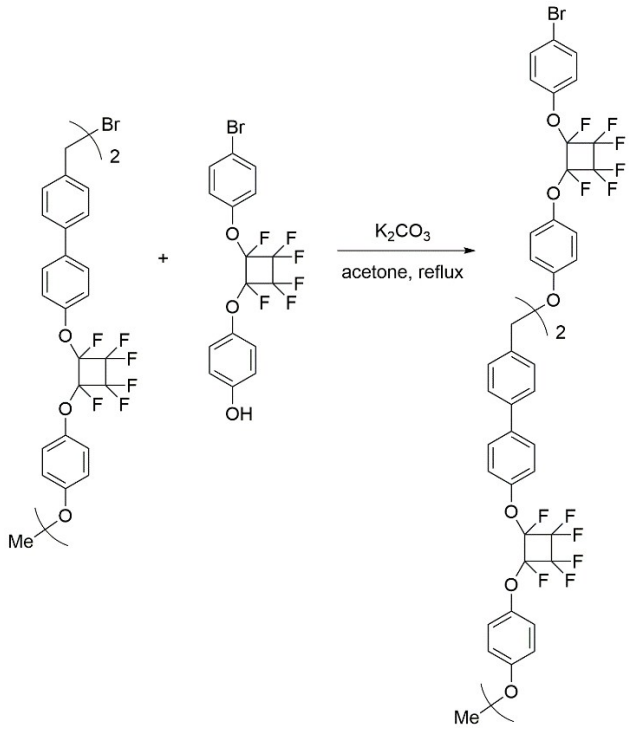
2H), 7.08-7.14 (m, 4H), 7.18-7.23 (m, 4H), 7.44-7.57 (m, 12H). ^{13}C NMR ($CDCl_3$): δ (ppm): 166.82, 157.30, 157.09, 156.44, 156.21, 152.28, 152.11, 147.66, 146.53, 146.29, 146.06, 139.98, 139.95, 139.93, 138.10, 138.05, 137.83, 137.80, 136.03, 136.00, 135.97, 135.64, 135.60, 132.12, 128.83, 128.49, 128.43, 128.16, 127.35, 127.30, 127.28, 120.47, 120.38, 119.95, 119.04, 118.95, 118.58, 115.77, 114.79, 114.73, 107.15, 105.91, 70.30, 70.25, 66.34, 55.74, 55.70. ^{19}F NMR ($CDCl_3$): δ (ppm): -128.37~-131.79 (PFCB). FT-IR (KBr): ν (cm^{-1}): 3469, 3377, 1713, 1605, 1504, 1318, 1245, 1188, 1107, 962, 814. MALDI-TOF-MS (M^+ calcd as $C_{54}H_{38}F_{12}N_2O_8$ = 1070.24) m/z (%): 1074.5 (8.3), 1073.5 (26.1), 1072.5 (41.6), 1071.5 (100), 1070.5 (42.9), 921.4 (11.9), 920.4 (29.8), 919.4 (61.6).

PF_2MBr



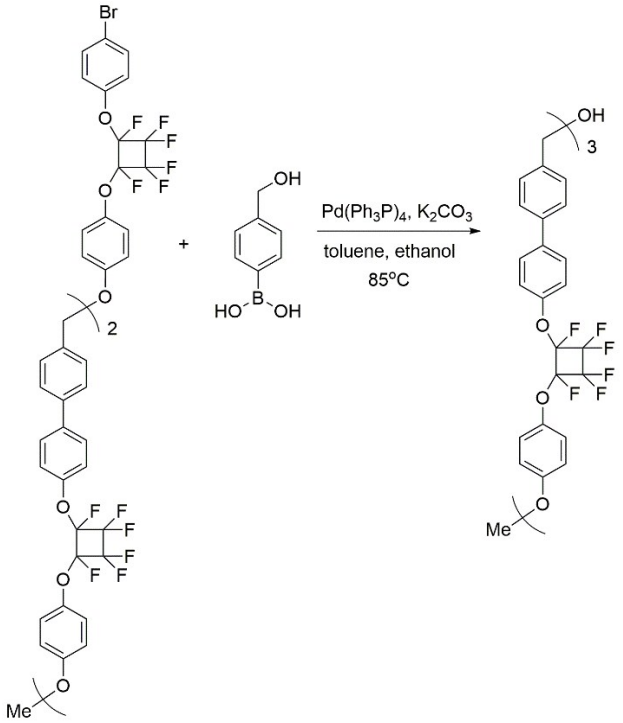
In a 250 mL round-bottom flask, PF_2OH (4.7 g, 5.0 mmol) was dissolved in 100 mL of dry CH_2Cl_2. The resulting system was placed into an ice-water bath, and after it was cooled, PBr_3 (0.2 mL, 2.1 mmol) was injected into the system slowly. The resulting solution was stirred for another 1 h. Afterwards, 100 mL of 5% aqueous K_2CO_3 was added to quench the reaction. The product was extracted using CH_2Cl_2 (100 mL×2). The organic phase was combined, washed with brine (100 mL×2), dried over anhydrous $MgSO_4$ and filtered. CH_2Cl_2 was evaporated to afford PF_2MBr as a white solid (3.6 g, 72% yield). The product was used without further purification. ^{1}H NMR ($CDCl_3$): δ (ppm): 3.76 (s, 3H), 4.54 (s, 4H), 6.81-6.84 (m, 2H), 7.07-7.25 (m, 10H), 7.45-7.52 (m, 12H). ^{19}F NMR ($CDCl_3$): δ (ppm): -127.82~-131.93 (PFCB).

PF_3Br



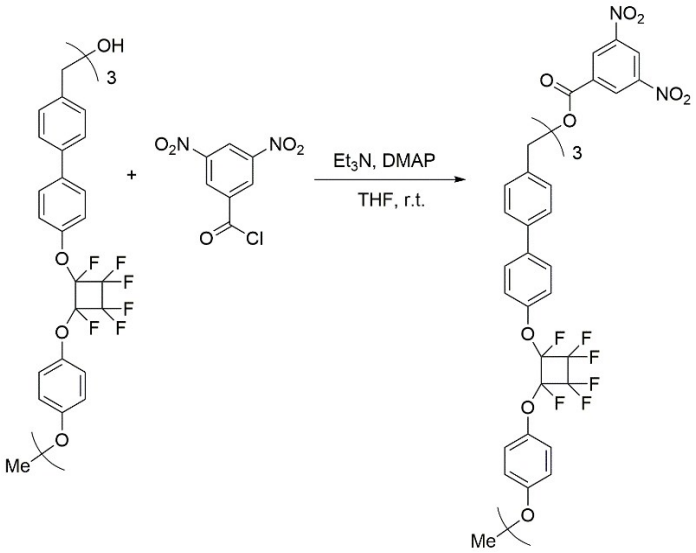
Into a 250 mL round-bottom flask were added PF_2MBr (3.6 g, 3.6 mmol), $BrPF_1OH$ (1,9 g, 4.3 mmol), K_2CO_3 (1.0 g, 7,2 mmol), and 100 mL of acetone. The resulting mixture was stirred at reflux under Ar for 12 h. Then acetone was removed via rotary evaporation and the residue was subjected to column chromatography (hexane/ethyl acetate v:v = 7:1) to afford PF_3Br as a clear viscous liquid (4.3 g, 86% yield). ^1H NMR ($CDCl_3$): δ (ppm): 3.75 (s, 3H), 5.02-5.06 (m, 4H), 6.81-6.84 (m, 2H), 6.89-6.93 (m, 4H), 7.00-7.14 (m, 8H), 7.18-7.23 (m, 4H), 7.41-7.57 (m, 14H). ^{13}C NMR ($CDCl_3$): δ (ppm): 157.30, 157.11, 152.31, 152.14, 151.83, 151.64, 146.56, 146.42, 146.31, 146.20, 146.08, 139.96, 138.09, 138.06, 137.81, 136.02, 132.91, 132.85, 128.49, 128.43, 128.20, 128.16, 127.36, 120.68, 120.60, 120.49, 120.40, 120.10, 119.96, 119.90, 119.06, 119.98, 118.60, 115.80, 114.80, 114.74, 70.30, 55.73, 55.69. ^{19}F NMR ($CDCl_3$): δ (ppm): -128.12~-132.12 (PFCB).

PF_3OH



Into a 500 mL round-bottom flask were added PF_3Br (5.5 g, 4.0 mmol), 4-hydroxmethylphenylboronic acid (0.8 g, 5.3 mmol), tetrakis(triphenylphosphine)-palladium(0) (0.19 g, 0.16 mmol), and K_2CO_3 (2.2 g, 16.0 mmol). Next, 50 mL of ethanol and 150 mL of toluene were added into the system. The resulting mixture was heated at 85°C for 4 h under Ar. Afterwards, the solvents were removed via rotary evaporation, and the residue was subjected to column chromatography using a mixture of hexane and ethyl acetate (v:v = 3:1) to afford PF_3OH as a white solid (4.3 g, 77% yield). ^1H NMR ($CDCl_3$): δ (ppm): 3.75 (s, 3H), 4.73 (s, 2H), 5.01-5.05 (m, 4H), 6.81-6.84 (m, 2H), 6.89-6.94 (m, 4H), 7.07-7.13 (m, 6H), 7.17-7.23 (m, 6H), 7.41-7.57 (m, 18H). ^{13}C NMR ($CDCl_3$): δ (ppm): 157.28, 157.07, 156.42, 156.18, 152.28, 152.19, 152.12, 152.02, 146.53, 146.28, 146.05, 140.26, 140.23, 139.92, 139.46, 138.21, 138.07, 138.02, 137.93, 137.78, 136.00, 135.98, 128.48, 128.42, 128.39, 128.16, 127.65, 127.35, 127.29, 127.27, 120.45, 120.38, 119.95, 119.01, 118.94, 118.56, 115.75, 114.77, 114.72, 70.26, 70.23, 65.17, 55.73, 55.69. ^{19}F NMR ($CDCl_3$): δ (ppm): -128.34~-131.79 (PFCB).

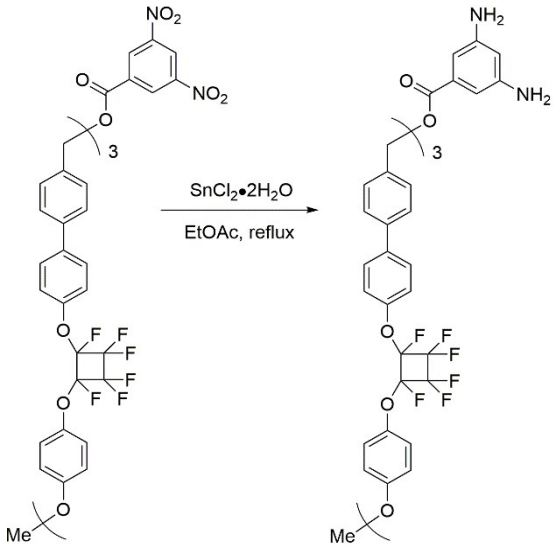
PF_3DN



Into PF_3OH (2.0 g, 1.4 mmol) in 40 mL of extra dry THF were added 3,5-dinitrobenzoyl chloride (0.4 g, 1.7 mmol) and 4-dimethylaminopyridine (0.02 g, 0.16 mmol). The resulting system was placed into an ice-water bath to be cooled. TEA (0.4 mL, 2.8 mmol) was then introduced into the system through a syringe. The resulting mixture was warmed to room temperature and allowed to stir for another 5 h. Afterwards, water was added to quench the reaction. THF was removed by rotary evaporation and the residue was extracted using 150 mL of CH_2Cl_2. The organic phase was washed with 5% aqueous K_2CO_3 (150 mL×2) as well as brine (150 mL×2), dried over anhydrous $MgSO_4$ and filtered. After CH_2Cl_2 was evaporated, the crude product was purified using column chromatography (hexane/ethyl acetate, v:v = 5:1) to afford PF_3DN as a pale yellow solid (1.5 g, 66% yield). ^1H NMR ($CDCl_3$): δ (ppm): 3.75 (s, 3H), 5.02-5.06 (m, 4H), 5.50 (s, 2H), 6.81-6.84 (m, 2H), 6.90-6.93 (m, 4H), 7.07-7.13 (m, 6H), 7.17-7.25 (m, 6H), 7.44-7.61 (m, 18H), 9.16-9.17 (m, 2H), 9.20-9.21 (m, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm): 162.55, 157.32, 157.11, 156.46, 156.22, 152.48, 152.31, 152.13, 148.55, 146.54, 146.31, 146.07, 140.92, 139.93, 138.05, 137.80, 137.74, 137.47, 136.01, 133.96, 133.84, 133.81, 129.64, 129.57, 128.57, 128.50, 128.48, 128.42, 128.15, 127.61, 127.58, 127.35, 122.61, 120.41, 119.96, 119.04, 118.97, 118.62, 118.60, 115.80, 114.79, 114.74, 70.30, 70.26, 68.44, 55.74,

55.70. ^{19}F NMR ($CDCl_3$): δ (ppm): -128.34~-131.80 (PFCB).

PF_3DA



Into PF_3DN (1.4 g, 0.88 mmol) in 40 mL of ethyl acetate was added stannous chloride dihydrate (2.0 g, 8.8 mmol). The resulting mixture was stirred at reflux for 2 h under Ar. Aqueous K_2CO_3 was added into the system to adjust the pH to basicity. The product was extracted using ethyl acetate (150 mL×2). The organic phase was combined, washed with brine (150 mL×2), dried over anhydrous $MgSO_4$ and filtered. After ethyl acetate was evaporated, the crude product was subjected to column chromatography using ethyl acetate as eluent to afford PF_3DA as a pale yellow solid (1.1 g, 82% yield). ^{1}H NMR ($CDCl_3$): δ (ppm) 3.65 (br, 4H), 3.75 (s, 3H), 5.02 (s, 2H), 5.05 (s, 2H), 5.33 (s, 2H), 6.17-6.18 (m, 1H), 6.81-6.84 (m, 4H), 6.89-6.93 (m, 4H), 7.08-7.13 (m, 6H), 7.17-7.23 (m, 6H), 7.45-7.56 (m, 18H). ^{13}C NMR ($CDCl_3$): δ (ppm): 166.82, 157.31, 157.10, 156.45, 156.22, 152.29, 152.11, 147.68, 146.54, 146.30, 146.07, 139.97, 139.92, 138.11, 138.05, 137.83, 137.81, 136.01, 135.65, 135.62, 132.13, 128.83, 128.48, 128.43, 128.16, 127.35, 127.30, 127.28, 120.47, 120.39, 119.96, 119.05, 118.96, 118.59, 115.78, 114.79, 114.74, 107.16, 105.90, 70.29, 70.25, 66.33, 55.73, 55.69. ^{19}F NMR ($CDCl_3$): δ (ppm): -128.33~ -131.78 (PFCB). FT-IR (KBr): ν (cm^{-1}): 3469, 3377, 1713, 1605, 1504, 1318, 1245, 1188, 1107, 962, 814. MALDI-TOF-MS (M^+ calcd as $C_{77}H_{52}F_{18}N_2O_{11}$ = 1523.24) m/z (%): 1526.8 (5.1), 1525.8 (7.6), 1524.8 (6.0), 1523.8 (10.6), 1522.8 (7.5), 1373.7 (6.1),

1372.7 (13.9), 1371.7 (16.8), 921.5 (19.0), 920.5 (50.0), 919.5 (100).

S3. General Synthetic Procedure and Characterizations for Polyimides with Various Side Chains.

To an NMP solution (*ca*. 20% solid content) containing PFCBBPDA and PF_nDA with a certain feeding ratio was added 6FDA. The resulting solution was stirred at room temperature for 18 h under inert atmosphere. The obtained viscous polyamic acid solution was casted on a dry glass plate placed on an adjustable horizontal table and flowed naturally to uniformity. Evaporation of the solvent and the following imidization were conducted in a Muffle furnace. The heating program was 70°C for 1 h, 150°C for 1 h, 250°C for 0.5 h, and 300°C for 1 h. No control over the cooling process was carried out after the heating process. The polyimide film was peeled off from the glass plate immediately after immersion in water and dried at 55°C *in vacuo* for 24 h. FT-IR (KBr): ν (cm^{-1}): 1785 (C=O asymmetric stretch), 1725 (C=O symmetric stretch), 1378 (C-N stretch), 960 (PFCB ring), 722 (imide ring deformation). Solid ^{13}C NMR: δ (ppm): 165.8 (carbonyl carbon), 152.4, 138.3, 132.2, 127.5, 118.2 (PFCB ring carbon), 108.5, 65.5 (methylene carbon), 54.3 (methyl carbon). Solid ^{19}F NMR: δ (ppm): -61.7 (CF_3), -106.3, -135.5, -164.1 (PFCB).

S4. Spectra for Diamines and Polyimides

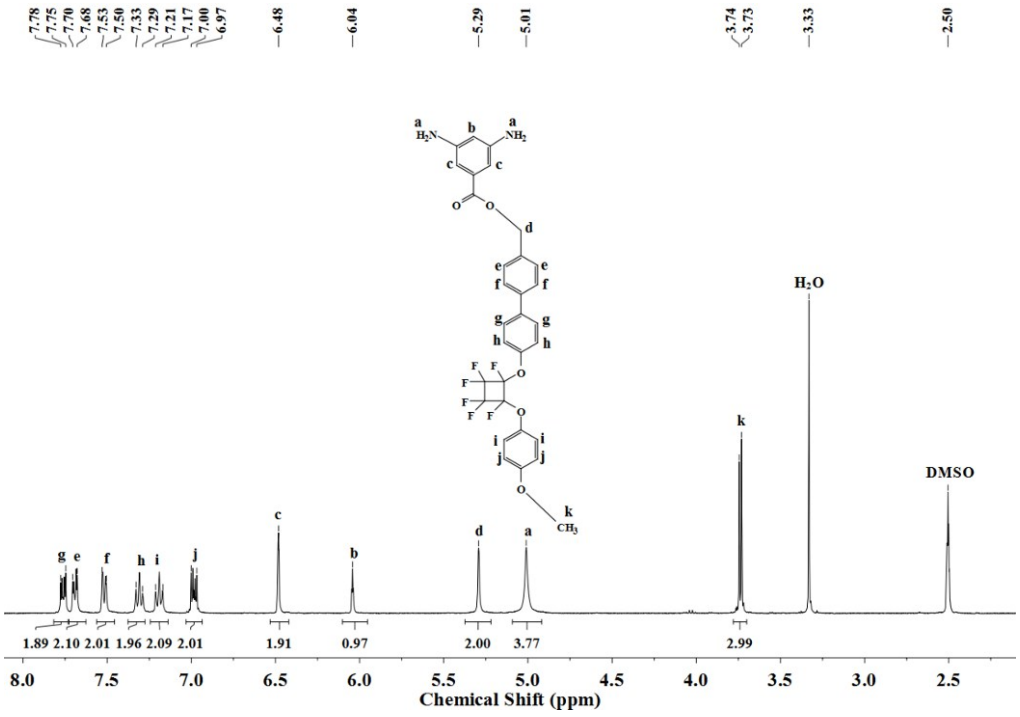


Figure S1. ^{1}H NMR spectrum of PF_1DA in DMSO-d_6.

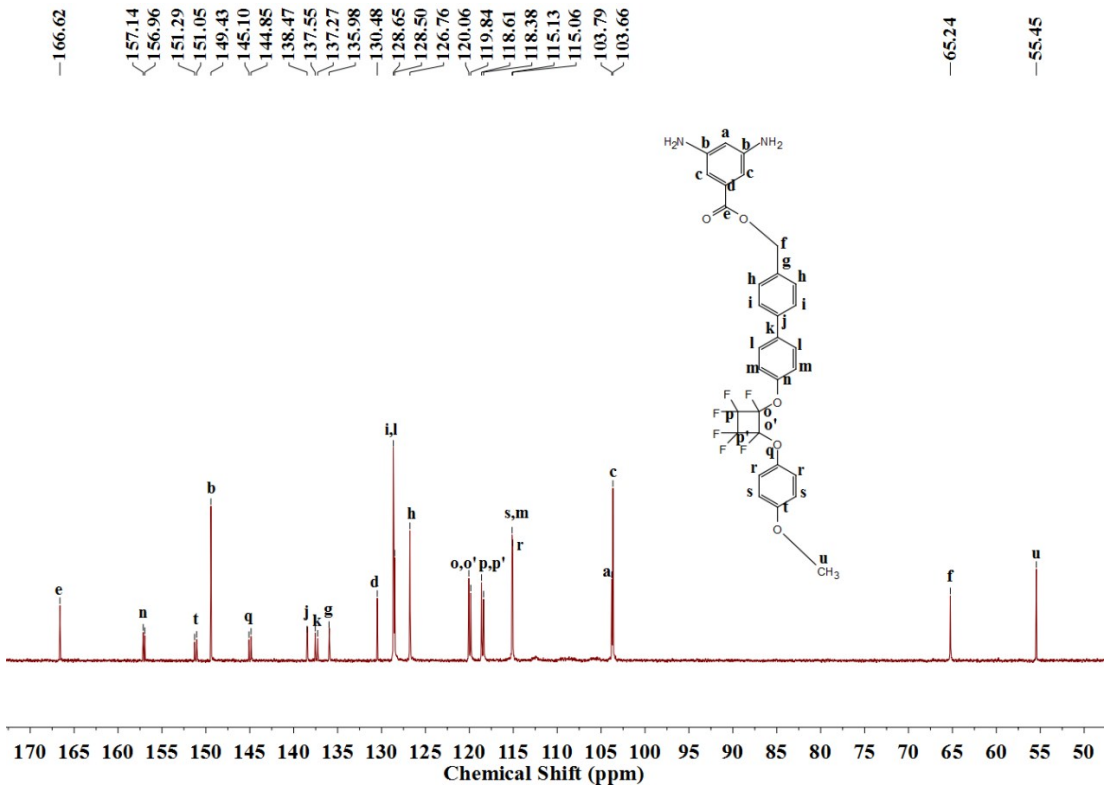


Figure S2. ^{13}C NMR spectrum of PF_1DA in DMSO-d_6.

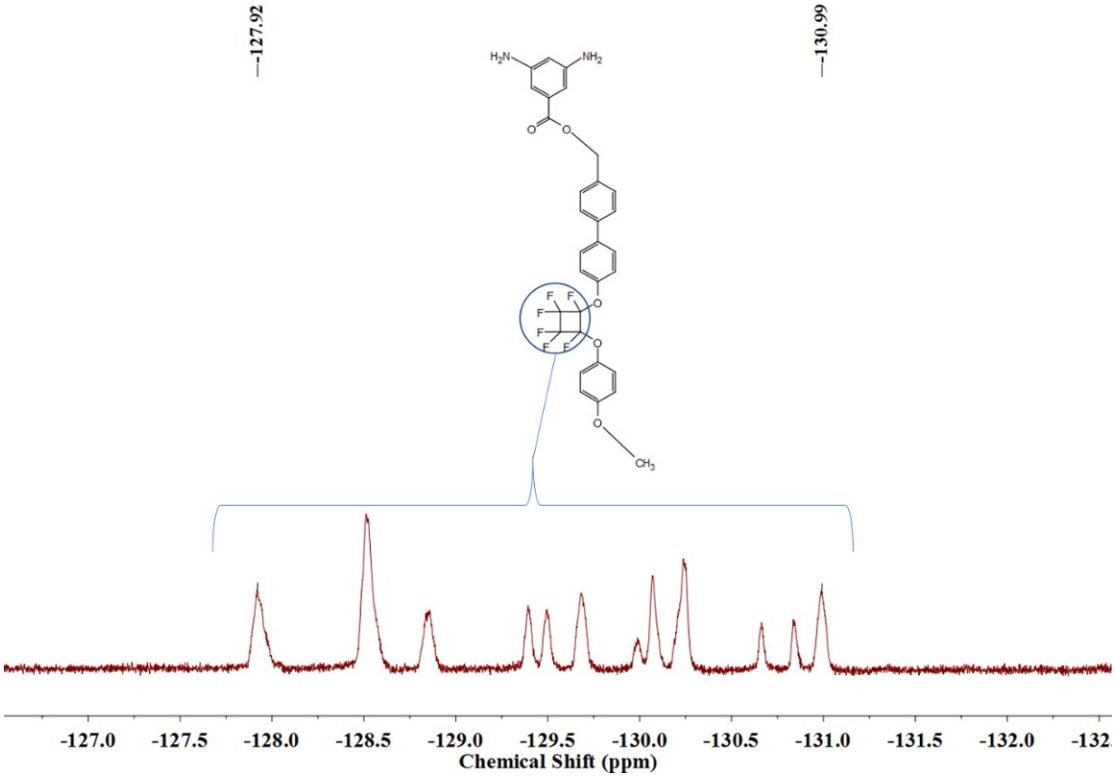


Figure S3. ^{19}F NMR spectrum of PF_1DA in DMSO-d_6.

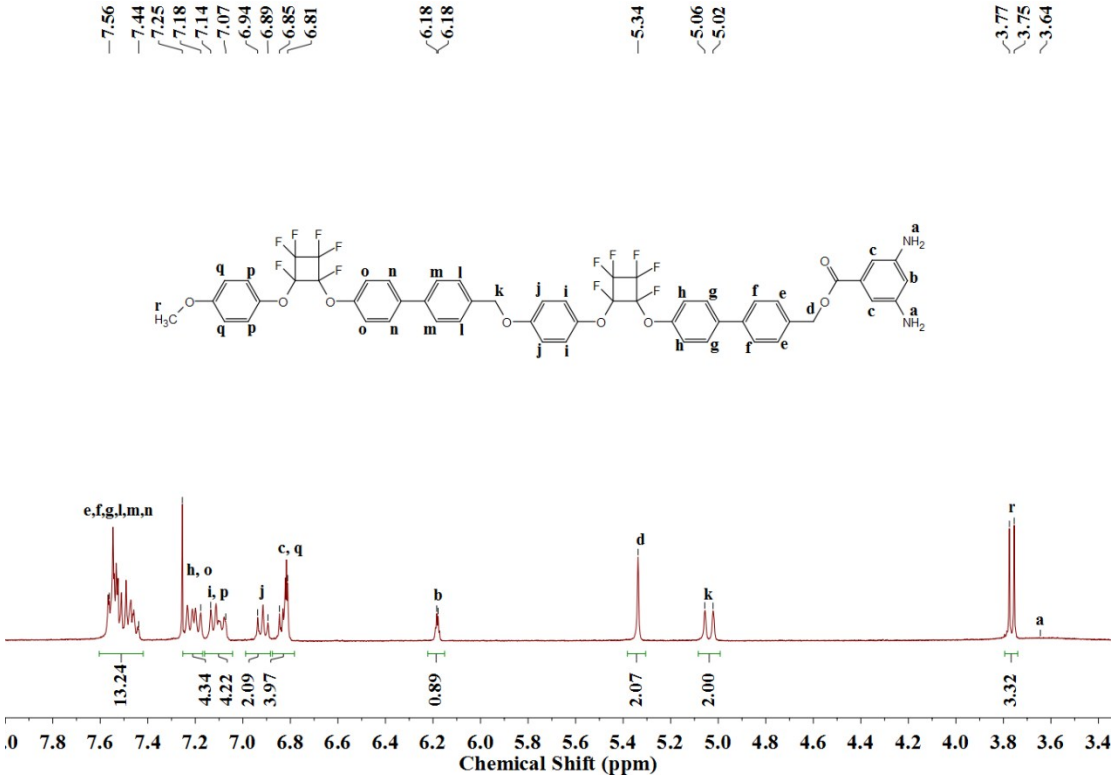


Figure S4. ^{1}H NMR spectrum of PF_2DA in $CDCl_3$.

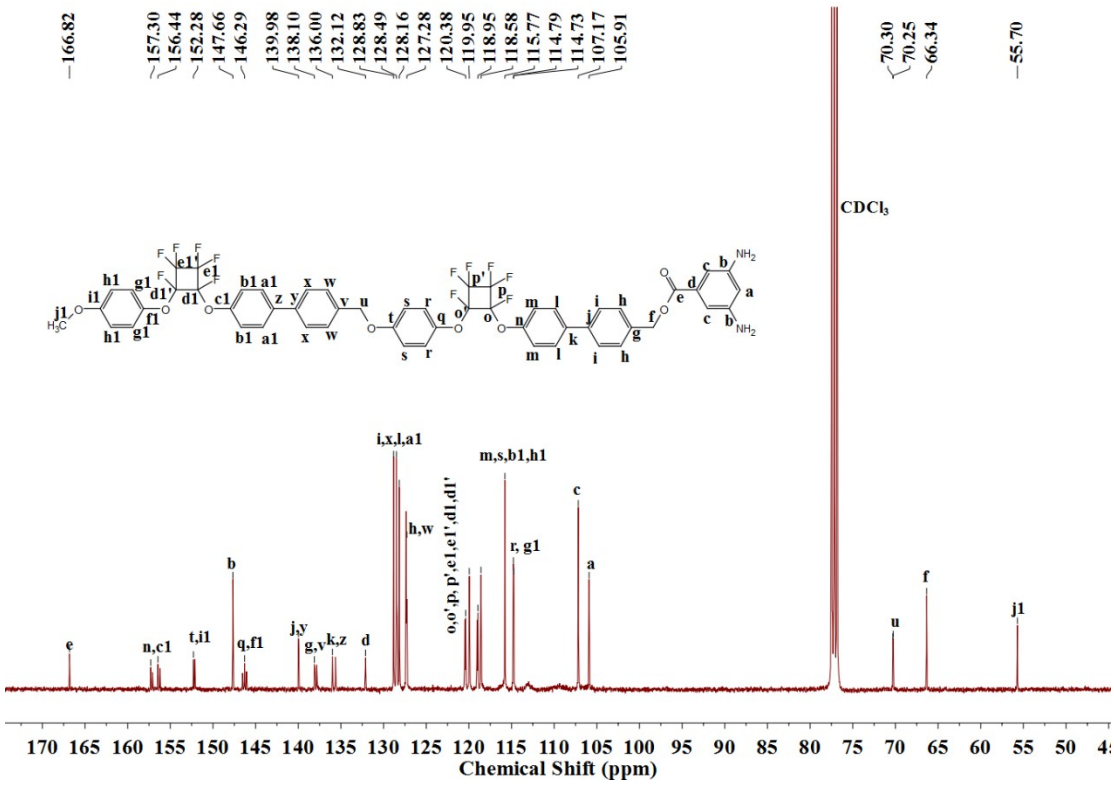


Figure S5. ^{13}C NMR spectrum of PF_2DA in $CDCl_3$.

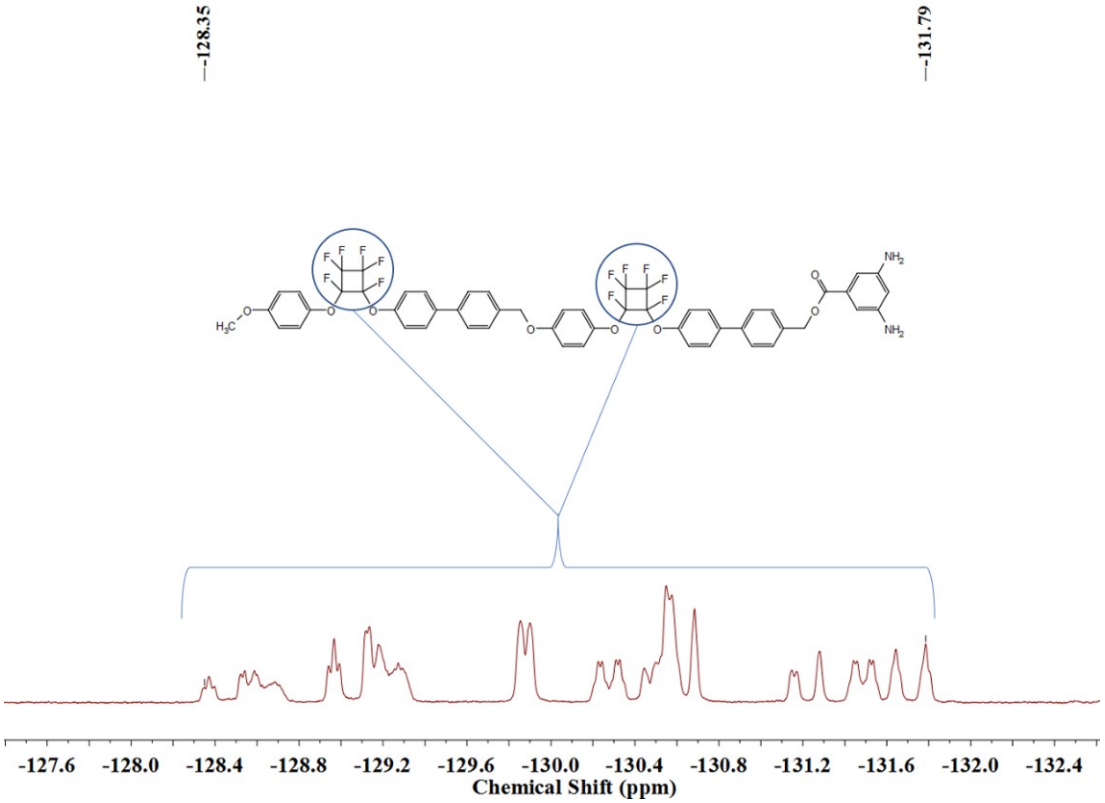


Figure S6. ^{19}F NMR spectrum of PF_2DA in $CDCl_3$.

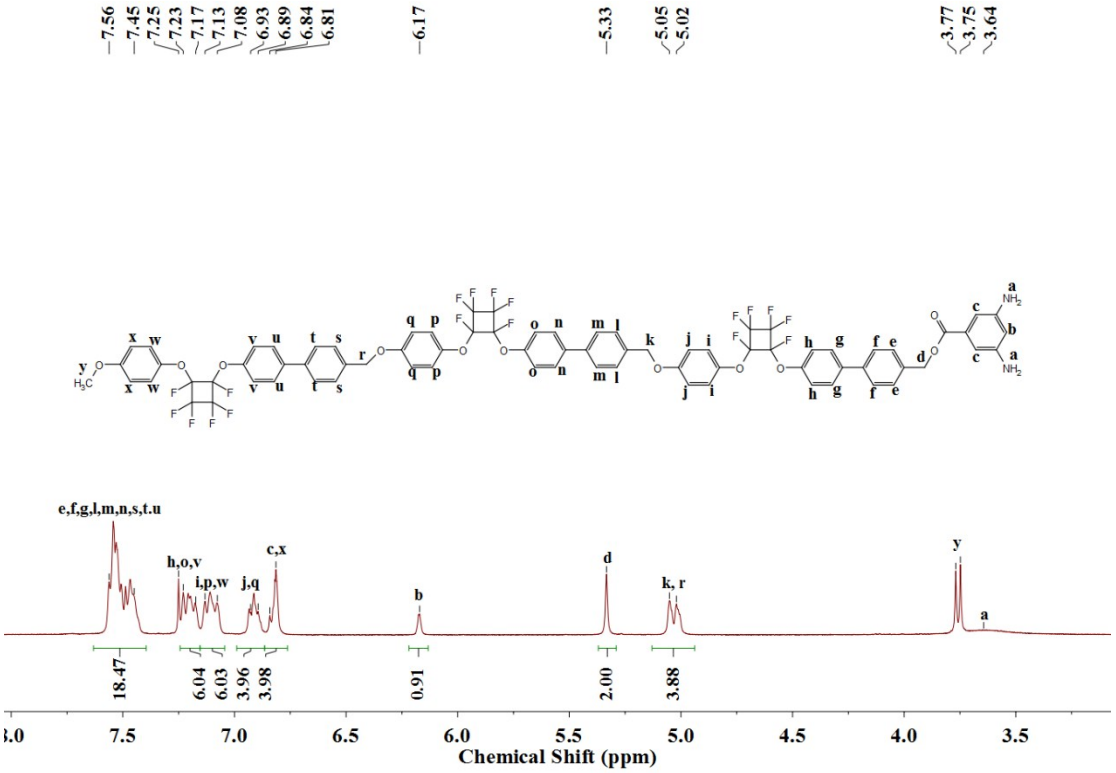


Figure S7. ^{1}H NMR spectrum of PF_3DA in $CDCl_3$.

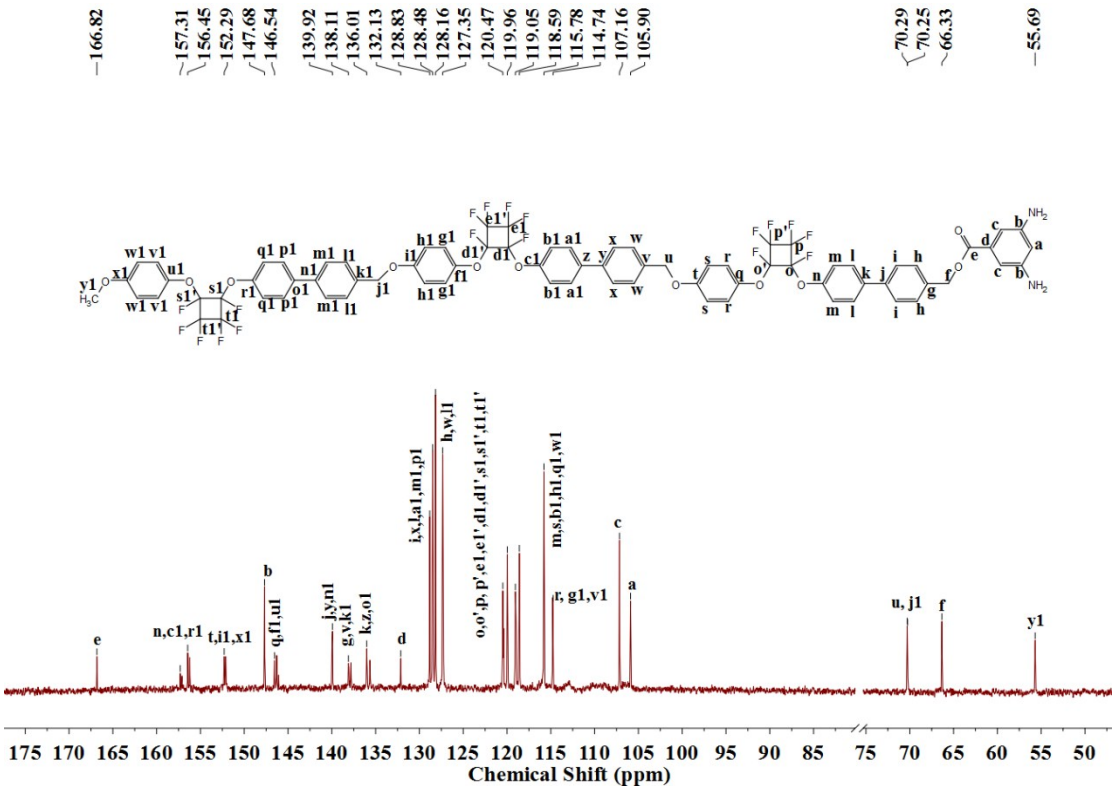


Figure S8. ^{13}C NMR spectrum of PF_3DA in $CDCl_3$.

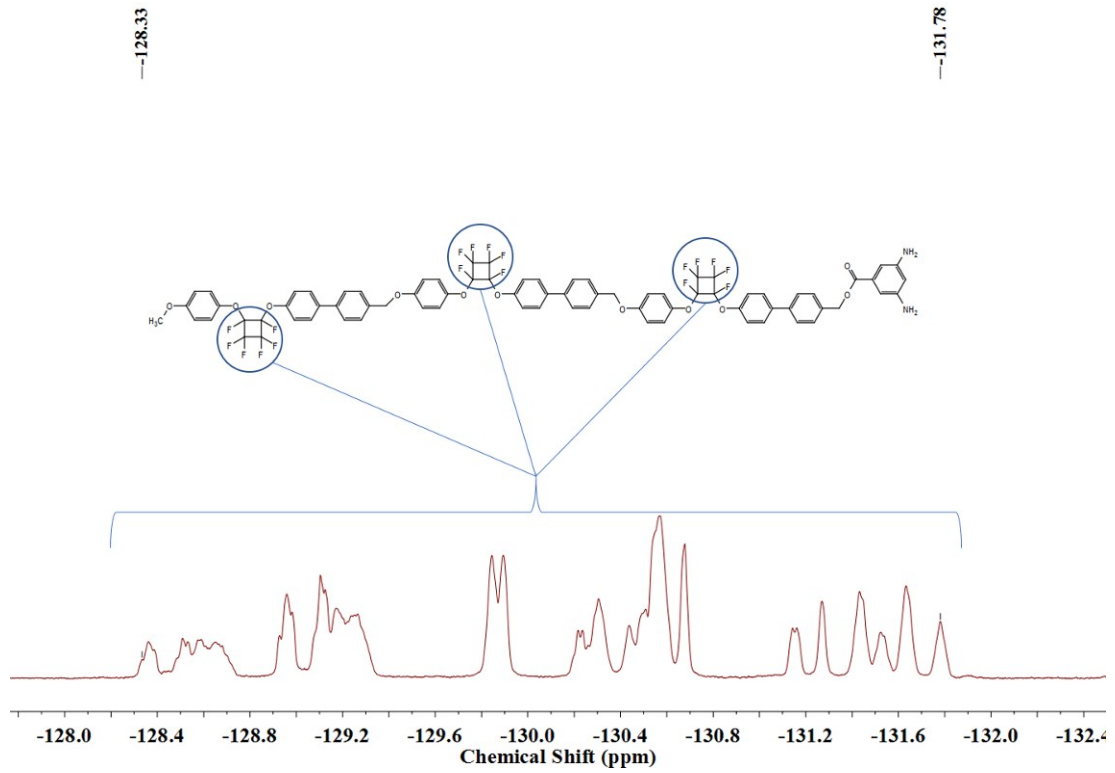


Figure S9. ^{19}F NMR spectrum of PF_3DA in $CDCl_3$.

S5. Instruments and Methods

^{1}H, ^{13}C, and ^{19}F NMR spectra of intermediates were recorded on a JEOL resonance ECZ 400S spectrometer (400 MHz) in $CDCl_3$ or DMSO-d_6. Tetramethylsilane (TMS) and $CDCl_3$ (or DMSO-d_6) were used as internal standards for ^{1}H and ^{13}C NMR, respectively; CF_3CO_2H was used as an external standard for ^{19}F NMR. Solid-state ^{13}C cross-polarization/magic angle spinning (CP/MAS) spectra were collected on an Agilent DD2 600 Solid system (600 MHz), equipped with a 3.2 mm HFXY MAS probe. Hartmann-Hahn conditions of CP experiment were obtained at a 15 kHz MAS spinning speed with a contact time of 2.0 ms and a recycle delay time of 5 s. ^{13}C chemical shifts were externally referenced to TMS (δ = 0.0 ppm). ^{19}F MAS spectra were obtained on an Agilent DD2 600 solid System operating at 564 MHz, using a 5 s delay between pulses and 3us 90° pulses. Samples with a diameter of 3.2 mm were spun at 15,000 Hz using a commercial high-speed magic-angle spinning probe. ^{19}F chemical shifts were externally referenced to TMS (δ = 0.0 ppm).

Electrospray ionization mass spectrometry (ESI-MS) was measured by an Agilent FTMS-7.0 Fourier transformation mass spectrometer, and matrix-assisted laser desorption time-of-flight mass spectrometry (MALDI-TOF-MS) was conducted on an IonSpec 4.7T Fourier transformation mass spectrometer using α-cyano-4-hydroxycinnamic acid (α-CHCA) as the matrix. Number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) were obtained on a conventional gel permeation chromatography (GPC) system equipped with a Waters 515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel

columns (HR3 (500-30,000), HR4 (5,000-600,000), and HR5 (50,000-4,000,000), 7.8×300 mm, particle size: 5 μm). GPC measurement was carried out at 35°C using dimethyl formamide (DMF) as eluent with a flow rate of 1.0 mL/min. The system was calibrated with linear polystyrene standards. FT-IR spectra were recorded on a Nicolet AVATAR-360 FT-IR spectrophotometer with a resolution of 4 cm^{-1}.

The capacitances at 1 MHz were measured on an HP4194A impedance-gain phase analyzer. Silver adhesive with a volume resistivity of $1\sim3\times10^{-4}$ Ω·cm was coated on double surfaces of the film, and measurements were conducted at a relative humidity of 40% after the adhesive fully cured. The dimension of samples was 0.075×10×10 mm^3. The contact angle of water on the film was measured by a JC2000C instrument at 20±1°C using a sessile drop method.

Positron annihilation lifetime spectroscopy (PALS) was conducted on an ORTEC PLS-SYSTEM positron lifetime picosecond timing system and the measurements were performed as follows: A position source was prepared by depositing *ca*. 1.1 MBq of aqueous ^{22}NaCl on a Kapton® foil with a thickness of 7 μm and an area of 10×10 mm. After drying, the foil was covered with the same size of foil, and the edges were glued with epoxy resin. The source was further sealed in a 3 μm Mylar foil and then sandwiched by two identical samples for positron annihilation measurements. The diameter of the spot of ^{22}Na source was *ca*. 2 mm. During the measurement, samples were kept in a vacuum cell. The positron lifetime is determined from the time delay between the emission of the birth gamma (1.28 MeV) and one of 0.511 MeV annihilation photons; lifetime measurements were conducted

using a fast-fast coincidence system with a time resolution of *ca*. 220 ps and a channel width of 12.6 ps. Spectra were recorded every hour, and about 1-2 million events were stored in each spectrum. The lifetime spectra were analyzed using the data processing program PATFIT.

Thermogravimetry analysis (TGA) was conducted on a TA Discovery TGA 55 thermal analysis system in N_2 with a heating rate of 10^{o}C/min. Hardness and elastic modulus of polyimide films were conducted on a CSM UNHT/NST nanomechanics integrated test system. The cross-section dimension of the base of Berkovich indenter is 6×6 μm^2. The maximum applied load is 1 mN, with loading and unloading times of 20 s, respectively; the waiting time was 5 s for the nanoindentation experiments. Four experiments were conducted for each sample.