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# The synthesis, chain-packing simulation and long-term gas permeability of highly selective spirobifluorene-based polymers of intrinsic microporosity

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## S1. Computational models and methods

### S1.1 Molecular models

Molecular dynamics (MD) simulations were conducted using the Large-scale Atomic/Molecular Massively Parallel Simulator LAMMPS software package.[1] The parameters from the transferable potential for phase equilibria united atom (TraPPE-UA)[2-8] were used for non-bonded interactions, and bonded interactions were modeled using the generalized amber force field (GAFF).[9] The partial charges for the polymer framework were derived using *ab initio* calculations using HF/6–31G* level of theory followed by a restrained electrostatic potential (RESP) charge fitting procedure[10-11] using Gaussian 03[12] and AMBER[13] programs. Partial charges, and coordinates for the monomer repeat units of PIM-SBF-1, PIM-SBF-2, PIM-SBF-5, PIM-SBF-6, and PIM-SBF-7. For MD simulations, the shifted Lennard-Jones (LJ) 12–6 potential was used, where interaction energies that have pair distance larger than 15 Å were set to zero, with long–range electrostatics calculated using the particle-particle particle-mesh solver.[14] The cross interaction LJ parameters were determined using the Lorentz−Berthelot combining rules.[15] All MD simulations were conducted with a time step of 1 fs using the velocity–Verlet algorithm. Five independently generated samples were used for analysis.

PIM-SBF samples were constructed using the Polymatic simulated polymerization algorithm[16-17] and the compression/decompression scheme.[18] The PIM-SBF structure generation consists of three steps: (1) random packing of respective PIM-SBF 100 repeat monomers into a simulation box under periodic boundary conditions at a low arbitrary density of 0.3–0.4 g/cm$^3$, (2) polymerization via Polymatic simulated polymerization algorithm and (3) compression/decompression of the polymerized sample, '21-steps' to generate a final simulation box at relevant experimental conditions.[18] During the polymerization steps, (1) additional charges on 'reactive atoms' ($q_{polym} = \pm 0.5e$) were used to accelerate the polymerization process, (2), 'reactive atoms' on neighboring monomers within a cutoff distance of 6 Å or less were bonded together, and (3) additional charges on 'reactive atoms' ($q_{polym} = \pm 0.5e$) were taken out after bonding.[16] Next, the polymerized systems was compressed/decompressed using the '21–step' MD simulation protocol with $T_{max} = 1000$ K, $P_{max} = 5 \times 10^4$ atm, $T_{final} = 300$ K, and $P_{final} = 1$ atm.[18]

### S1.2 Gas adsorption

Unary gas adsorption of $CO_2$ and $N_2$ on PIM-SBF frameworks were conducted using the Cassandra Monte Carlo (MC) simulation software.[19] The LJ parameters for $CO_2$ and $N_2$ were obtained from the TraPPE force field.[20] Adsorption simulations were conducted using the isobaric-isothermal (*NPT*) version of the Gibbs Ensemble Monte Carlo (*NPT*-GEMC)[21-22] technique which holds the total number of particles, pressure and temperature constant while allowing the volume of the gas box to fluctuate. During MC simulations, several moves were conducted: molecule translation, rotation, volume changes and particle swaps between two simulation boxes (PIM-SBF frameworks were held rigid during MC simulations, and only gas molecules were allowed to translate, rotate and swap between simulation boxes). The simulations consist of equilibration and production periods with at least $5\times10^6$ and $1\times10^7$ MC steps respectively.

### S1.3 Structural analysis

The pore size distributions (PSDs) within polymer frameworks were calculated using the Poreblazer software.[23] The PSDs were measured as follow:

$$PSD = -\frac{\mathrm{d}V_{\mathrm{void}}(D)}{\mathrm{d}D} \qquad (1)$$

where $V_{\mathrm{void}}$ is the void volume at a specific probe diameter ($D$). We also measured the $SA_{\mathrm{BET}}$ using the $N_2$ adsorption isotherms at 77K using the BET equation:[24]

$$\frac{p/p_0}{n(1-p/p_0)} = \frac{1}{n_{\mathrm{m}}\mathrm{C}} + \frac{C-1}{n_{\mathrm{m}}\mathrm{C}}\frac{p}{p_0} \qquad (2)$$

where $p$ is the absolute pressure, $p_0$ is the saturation pressure, $n$ is the amount of nitrogen adsorbed, and $n_{\mathrm{m}}$ is the BET monolayer capacity. After $n_{\mathrm{m}}$ is obtained using $N_2$ adsorption isotherms, the $SA_{\mathrm{BET}}$ can be calculated using the following relationship:

$$SA_{\mathrm{BET}} = n_{\mathrm{m}}N_{\mathrm{a}}\sigma \qquad (3)$$

where $N_{\mathrm{a}}$ is the Avogadro's number, and $\sigma$ is the area occupied by $N_2$ molecule in a monolayer. A more detailed description of the procedure for applying BET theory for calculation of $SA_{\mathrm{BET}}$ is provided in previous work done by Hart *et al.*[25]

## S.2 Materials and Methods

### S2.1 General methods and equipment.

Commercially available reagents were used without further purification. Anhydrous dichloromethane and tetrahydrofuran were obtained from a Solvent Purification System. Anhydrous N,N-dimethylformamide was bought from Sigma Aldrich. All reactions using air/moisture sensitive reagents were performed in oven-dried or flame-dried apparatus, under a nitrogen atmosphere. TLC analysis refers to analytical thin layer chromatography, using aluminium-backed plates coated with Merck Kieselgel 60 $GF_{254}$. Flash chromatography was performed on silica gel 60 Å (35-70 micron) chromatography grade (Fisher Scientific). Melting points were recorded using a Stuart Digital Melting Point Apparatus and are uncorrected. $^{1}H$ NMR spectra were recorded in the solvent stated using an Avance Bruker DPX 400 (400 MHz) or DPX 500 (500 MHz) instruments, with $^{13}C$ NMR spectra recorded at 100 MHz or 125 MHz respectively. The solid state $^{13}C$ NMR were obtained at the EPSRC Solid State NMR Research Service at Durham University using a Varian VNMRS spectrometer operating at 100.56 MHz. Low-resolution mass spectrometric data were determined using a Fisons VG Platform II quadrupole instrument using electron impact ionization (EI) unless otherwise stated. High-resolution mass spectrometric data were obtained in electron impact ionization (EI) mode unless otherwise reported, on a Waters Q-TOF micromass spectrometer. The TGA was performed using the device Thermal Analysis SDT Q600 at a heating rate of 10 °C/min from room temperature to 1000 °C. Low-temperature (77 K) $N_2$ adsorption/desorption isotherms were obtained using a Coulter SA3100 surface area analyser. The powder samples were degassed for 800 mins at 125 °C under high vacuum prior to analysis. $CO_2$ (273 K) sorption data were acquired using a Quantachrome Autosorb iQ. The powder samples were degassed for 600 min at 120 °C before the experiment. Gel permeation chromatography (GPC) analyses were performed on chloroform solutions (1 mg ml$^{-1}$) using a GPC MAX 1000 system equipped with two Viscotek CLM3012 LT 5000L columns and a RI(VE3580) detector, operating at a flow rate of 1 ml min$^{-1}$. Calibration was achieved using Viscotek polystyrene standards (Mw 1000 – 1,000,000 g mol$^{-1}$).

### S2.2 General procedures

**General procedure A. Synthesis of biphenyls via Suzuki coupling.** The appropriate phenylboronic acid (1 equivalent), the appropriate phenyl bromide (1 equivalents), and $K_2CO_3$ (2 equivalents) were added to a degassed solution of $H_2O$ (10 ml per g of reagent) and THF (10 ml per g of reagent). The solution was heated to 80 °C and $Pd(PPh_3)_4$ (0.7% eq.) added. After 36 h, the reaction mixture was allowed to reach r.t., the THF was removed under *vacuum* and the product extracted with dichloromethane (DCM). The solution was dried over anhydrous $MgSO_4$ and filtered then the solvent was evaporated under reduced pressure. The resulting solid was filtered through a plug of silica gel eluting firstly with hexane and then with DCM. Further purification by recrystallization from methanol afforded the product as colourless crystals.

**General procedure B. Bromination of biphenyls.** The appropriate 3,4-dimethoxybiphenyl (1 equivalent) precursor was dissolved in $CHCl_3$ (20 ml per g of reagent). Neat bromine (1.1 equivalents) was added drop-wise with stirring at 0 ºC. The reaction was stirred for 24 h at room temperature then poured into water. The organic layer was separated then washed with an aqueous solution of sodium thiosulfate to eliminate excess of bromine, dried over anhydrous $MgSO_4$, filtered and the solvent evaporated under *vacuum*. The crude compound was recrystallized from methanol affording white crystals.

**General procedure C. Synthesis of carboxylic biphenyl precursor**. The appropriate bromo-biphenyl precursor (1 equivalent) was dissolved in anhydrous THF (20 ml per g of precursor) under inert atmosphere. A solution of butyl lithium (1.25 equivalents, 2.5 M in Hexane) was added at -78 °C and left under stirring for 1 hour. Dry gaseous $CO_2$ was bubbled through the solution for 2 hours. The reaction was quenched with ice water (10 ml per g of precursor) and the THF evaporated under *vacuum*. To the resulting product was added water (20 ml per g of precursor). After washing with DCM (3 x 15 ml) the aqueous layer was carefully acidified until pH 5 and the resulting white precipitate collected under suction to afford the acid precursor as white solid.

**General procedure D. Synthesis of fluorenones**. The appropriate carboxylic biphenyl precursor was dissolved into methane sulfonic acid ($MeSO_3H$, 10 g per g of precursor) and stirred for 3 hours. The reaction was quenched with iced water and the resulting precipitate collected under suction and recrystallized from methanol affording a yellow/orange solid.

**General procedure E. Synthesis of SpiroBiFluorenes (SBFs)**. *n*-Butyl lithium solution in hexane (2.5 M 1.2 equivalents) was added drop-wise to a solution of the appropriate bromo-biphenyl (1.1 equivalents) in anhydrous THF (20 ml per g of bromo-biphenyl) at -78 °C. After 1.5 hour, the appropriate fluorenone (1 equivalent) was added to the reaction mixture, which was allowed to slowly reach r.t. and stirred for 12 hours then quenched with water. The THF was evaporated under *vacuum*, and the aqueous layer extracted with DCM. The organic extracts were washed with water, dried with anhydrous $MgSO_4$, filtered and the solvent evaporated under reduced pressure. The crude pale yellow carbinol precursor was triturated in methanol then filtered to afford a white solid. The obtained solid was dissolved in cold glacial acetic acid (20 ml per g of carbinol) and conc. hydrochloric acid (0.5 ml per g of carbinol) was added drop-wise to the solution, which was then refluxed for 3h. After cooling the mixture was poured into water and the precipitate was filtered off then triturated in methanol to afford the pure product as white solid.

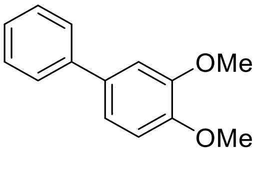
**General procedure F. Demethylation of the SBFs**. Neat $BBr_3$ (3 equivalents) was slowly added to a solution of appropriate spirobifluorene (1 equivalent) in anhydrous DCM (10 ml per equivalent of precursor) at 0 °C under $N_2$ atmosphere. The reaction mixture was stirred for 2 hours at room temperature then poured into water (20 ml per g of precursor). The DCM was allowed to evaporate and the white solid formed was filtered and washed with water. The product was then dried under high *vacuum* to give the product as a white powder.

**General procedure G. Synthesis of PIMs-SBF polymers.**

A mixture of the appropriate SBF (1 equivalent) and 2,3,5,6-tetrafluoroterephthalonitrile (1 equivalent) in anhydrous DMF (15 ml per g of reagent) was stirred under a dry nitrogen atmosphere. The mixture was heated to 30 °C and anhydrous $K_2CO_3$ (8 equivalents) added. The temperature was then raised to 65 °C and the mixture stirred for 96 h. After cooling, the reaction mixture was poured into water (150 ml), the precipitate filtered off and washed repeatedly with water and acetone and dried in a vacuum oven. The solid was purified by reprecipitation from $CHCl_3$ solution (60 mL), which was filtered through cotton wool then poured into a flask containing a mixture of acetone/methanol (2/1, 180 ml). If the polymer was not soluble it was refluxed and filtered off under suction respectively with THF, $CHCl_3$, acetone and methanol. The product was collected by filtration and dried under high vacuum overnight to give the final product as yellow solid

### S2.3 Monomers synthesis

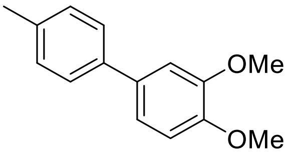
### (1a) 3,3-Dimethoxybiphenyl[26]



Phenylboronic acid (4.35 g, 35.7 mmol), 4-bromoveratrole (9.30 g, 42.8 mmol), and $K_2CO_3$ (9.80 g, 71.4 mmol) were reacted in presence of $Pd(PPh_3)_4$ (0.28 g, 0.25 mmol) according to the general procedure A to obtain the desired product (7.17 g, 93%) as colourless crystals; mp 68-70 °C, (lit.[27] 68-69 °C); $^1H$ NMR (400 MHz, $CDCl_3$, δ): 7.57 (d, $J$ = 7.3 Hz, 2 H), 7.43 (t, $J$ = 7.6 Hz, 2 H), 7.32 (t, $J$ = 7.3 Hz, 1 H), 7.16 (dd, $J$ = 8.2, 1.9 Hz, 1 H), 7.12 (d, $J$ = 1.9 Hz, 1 H), 6.96 (d, $J$ = 8.2 Hz, 1 H), 3.96

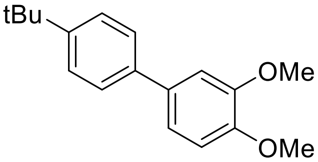
(s, 3H), 3.93 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, *δ*): 149 .3, 148.7, 141.1, 134.3, 128.8, 126.9, 126.9, 119.4, 111.5, 110.5, 56.0, 56.0; APCIMS (m/z (%)): 215.11 (100) [M + $H^+$].

**(1b) 3,4-Dimethoxy-4'-methyl-1,1'-biphenyl**



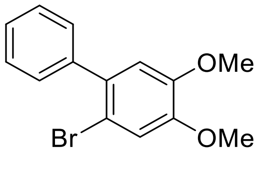
3,4-Dimethoxyphenylboronic acid (5.00 g, 29.0 mmol), 4-bromotoluene (5.95 g, 34.8 mmol) and $K_2CO_3$ (8.00 g, 58.0 mmol) were reacted in presence of $Pd(PPh_3)_4$ (0.23 g, 0.20 mmol) according to the general procedure A to obtain the desired product (6.00 g, 91%) as colourless crystals. mp 63-65 °C (lit.[28] 62-64 °C); $^1$H NMR (400 MHz, $CDCl_3$, δ): 7.37 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.02 (m, 2H), 6.85 (d, *J* = 8.2 Hz, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 2.30 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, *δ*): 149.2, 148.5, 138.2, 136.6, 134.3, 129.4, 126.7, 119.2, 111.6, 110.5, 56.0, 55.9, 21.0; HRMS (EI, m/z): [$M^+$] calcd for $C_{15}H_{16}O2$, 228.1150; found, 228.1145.

**(1c) 3,4-Dimethoxy-4'-*t*-butyl-1,1'-biphenyl**



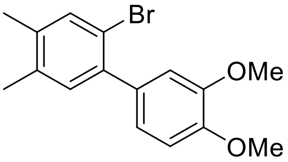
3,4-Dimethoxyphenylboronic acid (4.25 g, 23.4 mmol) and 4-*t*-butyl-bromotoluene (5.00 g, 23.4 mmol) and $K_2CO_3$ (6.45 g, 46.8 mmol) were reacted in presence of $Pd(PPh_3)_4$ (0.19 g, 0.16 mmol) according to the general procedure A to obtain the desired product (6.00 g, 95%) as colourless crystals. mp 60-62 °C; $^1$H NMR (400 MHz, $CDCl_3$, δ): 7.51 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H), 7.14 (dd, J = 8.2, 2.1 Hz, 1H), 7.11 (d, J = 2.0 Hz, 1H), 6.94 (d, J = 8.3 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 1.36 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$, *δ*): 150.0, 149.2, 148.5, 138.4, 134.3, 126.7, 125.9, 119.4, 111.6, 110.5, 56.2, 56.1, 34.7, 31.6; HRMS (EI, m/z): [$M^+$] calcd for $C_{18}H_{22}O2$, 270.1620; found, 270.1625.

**(2a) 2-Bromo-4,5-dimethoxy-biphenyl[26]**



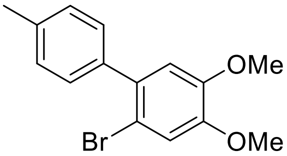
3,3-Dimethoxybiphenyl (9.30 g, 43.5 mmol) and bromine (7.60 g, 47.9 mmol) were reacted according to the general procedure B, affording the product as white crystals (10.40 g, 92%); mp 110-112 °C; $^1$H NMR (400 MHz, $CDCl_3$, δ): 7.42 (m, 5H), 7.13 (s, 1H), 6.84 (s, 1H), 3.92(s, 3H), 3.87 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, *δ*): 148.7, 148.2, 141.0, 134.7, 129.5, 127.9, 127.4, 115.7, 113.8, 112.4, 56.2, 56.0; EIMS (m/z, (%)) 292.01(35%) [$^{79}$Br M+], 294.01(35%) [$^{81}$Br $M^+$].

### (2b) 1-Bromo-2-(3,4-dimethoxyphenyl)-4,5-dimethylbenzene



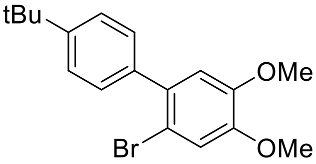
3,4-Dimethoxyphenylboronic acid (5.00 g, 18.9 mmol), 1,2-dibromo-4,5-dimethylbenzene (3.45 g, 18.9 mmol), $PPh_3$ (0.15 g, 0.57 mmol), $K_2CO_3$ (7.82 g, 56.7 mmol) and $Pd(PPh_3)_4$ (0.33 g, 0.28 mmol) were added to a degassed solution of $H_2O$ (30 ml) and THF (20 ml). The solution was heated to 80 °C. After 36 h, the reaction mixture was allowed to reach r.t., the THF was removed under *vacuum* and the product extracted with dichloromethane (DCM). The solution was dried over anhydrous $MgSO_4$ and filtered then the solvent was evaporated under reduced pressure. The resulting solid was purified by column chromatography on silica, eluting with hexane/ethyl acetate (9/1). Further purification by recrystallization from methanol afforded the product as colourless crystals (4.1 g, 67%). mp 70-72 °C; $^1$H NMR (400 MHz, $CDCl_3$, δ): 7.44 (s, 1H), 7.12 (s, 1H), 6.94 (m, 3H), 3.93 (s, 3H), 3.91 (s, 3H), 2.28 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$, δ): 148.4, 148.3, 139.6, 137.5, 136.0, 133.9, 133.9, 132.5, 121.8, 119.4, 113.1, 110.7, 56.0, 56.0, 19.3, 19.2; HRMS (EI, m/z): [$M^+$] calcd for $C_{16}H_{17}{}^{79}BrO_2$, 320.0412; found, 320.0405.

### (2c) 1-Bromo-3,4-dimethoxy-4'-methyl-1,1'-biphenyl



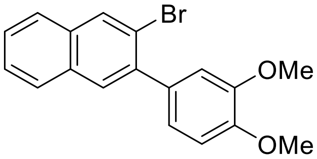
3,4-Dimethoxy-4'-methyl-1,1'-biphenyl (4.90 g, 21.46 mmol) and bromine (3.77 g, 23.61 mmol) were reacted according to the general procedure B, affording the product as white crystals (6.22 g, 95%); mp 100-102 °C; $^1$H NMR (400 MHz, $CDCl_3$, δ): 7.31 (d, $J$ = 8.1 Hz, 2H), 7.24 (d, $J$ = 7.9 Hz, 2H), 7.12 (s, 1H), 6.83 (s, 1H), 3.91 (s, 3H), 3.86 (s, 3H), 2.41 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $\delta$): 148.7, 148.3, 138.3, 137.2, 134.8, 129.4, 128.7, 115.9, 114.1, 112.6, 56.3, 56.1, 21.2; HRMS (EI, m/z): [$M^+$] calcd for $C_{15}H_{15}O_2{}^{79}Br$, 306.0255; found, 306.0252.

### (2d) 1-Bromo-3,4-dimethoxy-4'-*t*-butyl-1,1'-biphenyl



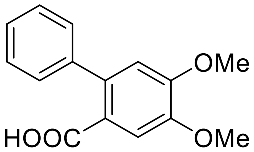
3,4-dimethoxy-4'-*t*-butyl-1,1'-biphenyl (5.50 g, 20.41 mmol) and bromine (3.59 g, 22.45 mmol) were reacted according to the general procedure B, affording the product as white crystals (6.97 g, 98%); mp 70-72 °C; $^1$H NMR (400 MHz, $CDCl_3$, δ): 7.44 (d, $J$ = 8.5 Hz, 2H), 7.35 (d, $J$ = 8.5 Hz, 2H), 7.12 (s, 1H), 6.85 (s, 1H), 3.91 (s, 3H), 3.86 (s, 1H), 1.37 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$, *δ*): 150.3, 148.7, 148.3, 138.1, 134.8, 129.1, 124.9, 115.9, 114.2, 112.5, 56.3, 56.1, 34.6, 31.4; HRMS (EI, m/z): [$M^+$] calcd for $C_{18}H_{21}O_2{}^{79}Br$, 348.0725; found, 348.0732.

**(2e) 2-Bromo-3-(3,4-dimethoxyphenyl)-naphthalene**



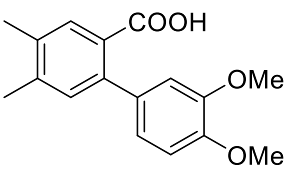
3,4-Dimethoxyphenylboronic acid (1.69 g, 9.3 mmol), freshly prepared 2,3-dibromonaphthalene[29] (2.65 g, 9.3 mmol), triphenylphosphine (0.07 g, 0.28 mmol) and $K_2CO_3$ (3.84 g, 27.9 mmol) and $Pd(PPh_3)_4$ (0.16 g, 0.14 mmol) were added to a degassed solution of $H_2O$ (18 ml) and THF (12 ml). The solution was heated to 80 °C. After 36 h, the reaction mixture was allowed to reach r.t., the THF was removed under *vacuum* and the product extracted with dichloromethane (DCM). The solution was dried over anhydrous $MgSO_4$ and filtered, then the solvent was evaporated under reduced pressure. The resulting solid was purified by column chromatography on silica, eluting with hexane/ethyl acetate (85/15). Further purification by recrystallization form methanol afforded the product as colourless crystals (1.9 g, 60%). mp 118-120 °C; $^1$H NMR (400 MHz, $CDCl_3$, δ): δ 8.19 (s, 1H), 7.80 (m, 3H), 7.51 (m, 2H), 7.05 (m, 2H), 6.96 (d, *J* = 8.8 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$, δ): 148.7, 148.3, 139.9, 133.8, 133.5, 132.4, 131.7, 130.0, 127.9, 126.9, 126.8, 122.2, 121.3, 113.3, 110.7, 56.1, 56.0.; HRMS (EI, m/z): [$M^+$] calcd for $C_{18}H_{15}{}^{79}BrO_2$, 342.02499; found 342.02475.

**(3a) 4,5-Dimethoxy-2-phenylbenzoic acid**



2-Bromo-4,5-dimethoxy-biphenyl (4.50 g, 15.41 mmol) and n-butyl lithium (7.7 ml of a solution 2.5 M in hexane, 19.26 mmol) were reacted according to the general procedure C to obtain a yellow oil (2.98 g, 75%). $^1$H NMR (400 MHz, $CDCl_3$, δ): 7.53 (s, 1H), 7.36 (m, 5H), 6.78 (s, 1H), 3.95 (s, 3H), 3.92 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, *δ*): 172.2, 152.0, 147.8, 141.5, 138.75, 128.8, 128.1, 127.3, 120.4, 114.1, 113.6, 56.3, 56.2; HRMS (EI, m/z): [$M^+$] calcd for $C_{15}H_{14}O_4$, 258.0892; found, 258.0898.

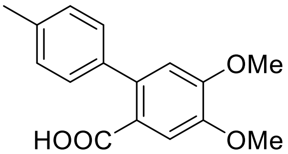
**(3b) 2-(3,4-Dimethoxyphenyl)-4,5-dimethylbenzoic acid**



1-Bromo-2-(3,4-dimethoxyphenyl)-4,5-dimethylbenzene (3.00 g, 9.3 mmol) and n-butyl lithium (4.1

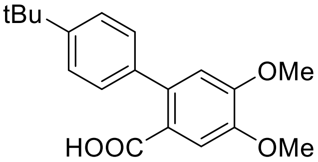
ml of a solution 2.5 M in hexane, 10.3 mmol) were reacted according to the general procedure C to obtain a white solid (2.36 g, 89%). $^1$H NMR (400 MHz, CDCl$_3$, δ): 7.73 (s, 1H), 7.13 (s, 1H), 6.87 (m, 2H), 6.84 (m, 1H), 3.91 (s, 3H), 3.86 (s, 3H), 2.33 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$, *δ*): 173.1, 148.5, 148.4, 141.5, 140.8, 135.7, 133.9, 132.7, 132.0, 126.5, 120.9, 112.3, 110.9, 56.0, 56.0, 20.0, 19.4; HRMS (EI, m/z): [M$^+$] calcd for $C_{15}H_{14}O_4$, 286.1206; found, 286.1205.

**(3c) 4,5-Dimethoxy-2-(4-methylphenyl)benzoic acid**



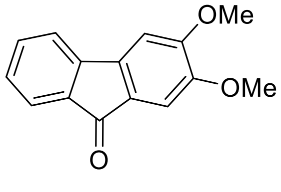
1-Bromo-3,4-dimethoxy-4'-methyl-1,1'-biphenyl (3.00 g, 9.76 mmol) and butyl lithium (4.9 ml of a solution 2.5 M in Hexane, 12.2 mmol) were reacted according to the general procedure C to obtain a yellow oil (1.85 g, 75%). m.p. 208-210 °C; $^1$H NMR (400 MHz, CDCl$_3$, δ): 7.53 (s, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 6.77 (s, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 2.40 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, *δ*): 171.5, 152.1, 147.8, 138.7, 138.6, 137.1, 128.9, 128.7, 120.5, 114.3, 113.9, 56.3, 56.2, 21.3; HRMS (EI, m/z): [M$^+$] calcd for $C_{16}H_{16}O_4$, 272.1049; found, 272.1046.

**(3d) 2-(4-Tert-butylphenyl)-4,5-dimethoxybenzoic acid**



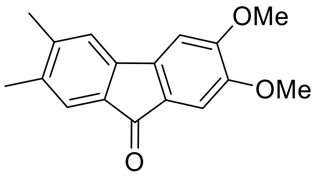
1-Bromo-3,4-dimethoxy-4'-*t*-butyl-1,1'-Biphenyl (4.50 g, 12.88 mmol) and butyl lithium (6.45 ml of a solution 2.5 M in Hexane, 16.1 mmol) were reacted according to the general procedure C to obtain a white solid (3.46 g, 85%). m.p. 120-122 °C; $^1$H NMR (400 MHz, CDCl$_3$, δ): 7.53 (s, 1H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 6.79 (s, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 1.36 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$, *δ*): 172.1, 152.0, 150.2, 147.7, 138.6, 138.4, 128.5, 125.0, 120.5, 114.3, 113.8, 56.3, 56.2, 34.7, 31.5; HRMS (EI, m/z): [M$^+$] calcd for $C_{19}H_{22}O_4$, 314.1518; found, 314.1512.

**(4a) 2,3-Dimethoxy-9H-fluoren-9-one**



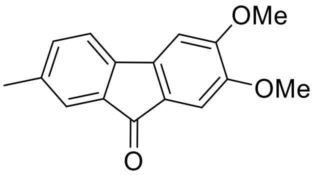
4,5-Dimethoxy-2-phenylbenzoic acid (2.00g, 7.74 mmol) and MeSO$_3$H (20 ml) were reacted according to the general procedure D to obtain an orange solid (1.45 g, 78%). m.p. 159-161 °C (lit.[30] 160-161 °C); $^1$H NMR (400 MHz, CDCl$_3$, δ): 7.55 (dd, *J* = 7.3, 0.7 Hz, 1H), 7.40 (td, *J* = 7.4, 1.1 Hz, 1H), 7.35 (m, 1H), 7.18 (m, 2H), 7.00 (s, 1H), 4.01 (s, 3H), 3.93 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, *δ*): 193.4, 154.8, 149.9, 144.1, 139.7, 134.9, 134.4, 128.4, 127.1, 123.9, 119.3, 107.4, 103.6, 56.5, 56.4; HRMS (EI, m/z): [$M^+$] calcd for $C_{15}H_{12}O_3$, 240.0786; found, 240.0786.

**(4b) 2,3-Dimethoxy-6,7-dimethyl-9H-fluoren-9-one**



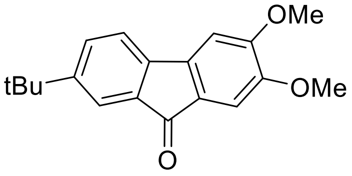
2-(3,4-Dimethoxyphenyl)-4,5-dimethylbenzoic acid (2.36 g, 8.24 mmol) and $MeSO_3H$ (25 ml) were reacted according to the general procedure D to obtain an orange solid (2.10 g, 95%). m.p. 144-146 °C; $^1$H NMR (400 MHz, $CDCl_3$, δ): 7.32 (s, 1H), 7.15 (s, 1H), 7.13 (s, 1H), 6.94 (s, 1H), 4.00 (s, 3H), 3.91 (s, 3H), 2.29 (s, 3H), 2.24 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, *δ*): 193.6, 154.4, 149.4, 143.6, 142.1, 139.8, 136.6, 133.0, 127.3, 125.4, 121.0, 107.3, 103.3, 56.4, 56.4, 20.8, 19.9; HRMS (EI, m/z): [$M^+$] calcd for $C_{17}H_{16}O_3$, 268.1099; found 268.1101.

**(4c) 2,3-Dimethoxy-7-methyl-9H-fluoren-9-one**



4,5-Dimethoxy-2-(4-methylphenyl)benzoic acid (1.90 g, 6.95 mmol) and $MeSO_3H$ (20 ml) were reacted according to the general procedure D to obtain an orange solid (1.41 g, 80%). m.p. 190-192 °C; $^1$H NMR (400 MHz, $CDCl_3$, δ): 7.36 (s, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.16 (s, 1H), 6.95 (s, 1H), 4.00 (s, 3H), 3.91 (s, 3H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, *δ*): 193.5, 154.8, 149.6, 141.4, 139.9, 138.4, 135.2, 134.6, 127.1, 124.8, 119.1, 107.4, 103.5, 56.5, 56.4, 21.4; HRMS (EI, m/z): [$M^+$] calcd for $C_{16}H_{14}O_3$, 254.0943; found, 254.0944.

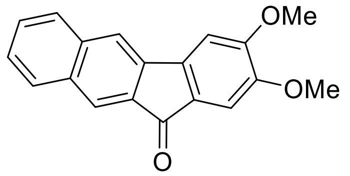
**(4d) 2,3-Dimethoxy-7-*t*-butyl-9H-fluoren-9-one**



2-(4-Tert-butylphenyl)-4,5-dimethoxybenzoic acid (3.20 g, 10.17 mmol) and $MeSO_3H$ (30 ml) were reacted according to the general procedure D to obtain an orange solid (2.56 g, 85%). m.p. 160-162 °C; $^1$H NMR (400 MHz, $CDCl_3$, δ): 7.62 (d, *J* = 1.8 Hz, 1H), 7.42 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.27 (d, *J* = 7.8, 1H), 7.18 (s, 1H), 6.97 (s, 1H), 4.01 (s, 3H), 3.92 (s, 3H), 1.33 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$, *δ*):

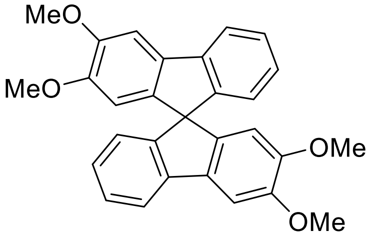
193.8, 154.8, 152.1, 149.7, 141.4, 139.9, 135.1, 130.9, 127.4, 121.4, 118.9, 107.5, 103.5, 56.5, 56.4, 35.1, 31.3; HRMS (EI, m/z): [M$^+$] calcd for $C_{19}H_{20}O_3$, 296.1412; found, 296.1418.

### (4e) 2,3-dimethoxybenzo[b]fluoren-11-one



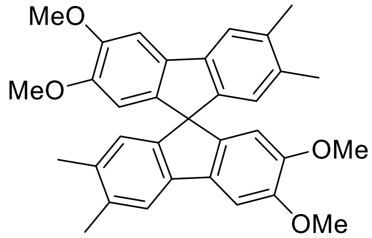
2,3-dimethoxybenzo[b]fluoren-11-one was prepared according to a reported procedure.[31] A methanol (60 ml) solution of *o*-phthalaldehyde (1.40 g, 10.4 mmol) and 5,6-dimethoxy-1-indanone was refluxed for 30 minutes, then 20 ml of a 30% solution of KOH in methanol were added dropwise and refluxing continued for 6 hours. The product crashed out as an orange crystalline material (1.92 g, 64%). m.p. 204-206 °C; $^1$H NMR (400 MHz, CDCl$_3$, δ ): 7.98 (s, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.61 (s, 1H), 7.48 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 7.40 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 7.18 (s, 1H), 7.08 (s, 1H), 4.02 (s, 3H), 3.92 (s, 3H).$^{13}$C NMR (100 MHz, CDCl$_3$, *δ*): 192.2, 155.3, 150.3, 140.1, 138.3, 136.9, 133.7, 133.4, 130.8, 129.4, 128.9, 128.6, 126.7, 124.9, 117.6, 106.4, 103.3, 56.5, 56.3; HRMS (EI, m/z): [M$^+$] calcd for $C_{17}H_{16}O_3$, 290.0943; found 290.0938.

### (5a) 2,2',3,3''-Tetramethoxy-9,9'-spirobifluorene[26]



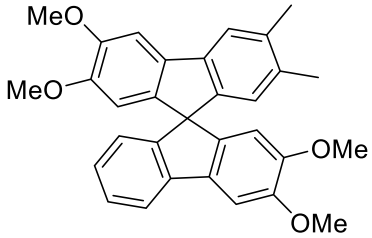
*n*-Butyl lithium solution in hexane (2.5 M; 5.2 ml, 13 mmol), 2-bromo-4,5-dimethoxybiphenyl (2.92 g, 10 mmol) and 2,3-dimethoxy-9H-fluoren-9-one (2.00 g, 8.3 mmol) in anhydrous THF (60 ml) were reacted according to the general procedure E to afford the pure product as white solid (2.70 g, 75%); mp 221- 223 ºC; $^1$H NMR (400 MHz, CDCl$_3$, δ): 7.72 (d, *J* = 7.5 Hz, 2H), 7.35 (s, 2H), 7.32 (dd, *J* = 7.5, 1.0 Hz, 2H), 7.03 (td, *J* = 7.5, 1.0 Hz, 2H), 6.66 (d, *J* = 7.5 Hz, 2H), 6.24 (s, 2H), 4.03 (s, 6H), 3.64 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$, *δ*): 149.6, 149.4, 149.2, 142.0, 140.9, 134.4, 127.6, 126.7, 123.7, 118.9,106.9, 103.0, 65.9, 56.3, 56.1; HRMS (EI, m/z): [M$^+$] calcd for $C_{29}H_{24}O_4$, 436.1675; found 436.1682.

**(5b) 2,2',3,3'-Tetramethoxy-6,6',7,7'-tetramethyl-9,9'-spirobifluorene**



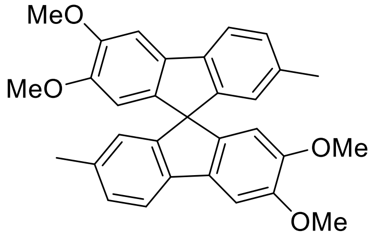
*n*-Butyl lithium solution in hexane (2.5 M; 4.5 ml, 11.20 mmol), 1-bromo-2-(3,4-dimethoxyphenyl)-4,5-dimethylbenzene (3.30 g, 10.26 mmol) and 2,3-dimethoxy-6,7-dimethyl-9H-fluoren-9-one (2.50 g, 9.33 mmol) in anhydrous THF (70 ml) were reacted according to the general procedure E to afford the pure product as white solid (4.00 g, 88%); mp 238-240 ºC; $^1$H NMR (400 MHz, CDCl$_3$, δ): 7.50 (s, 2H), 7.30 (s, 2H), 6.44 (s, 2H), 6.20 (s, 2H), 4.02 (s, 6H), 3.64 (s, 6H), 2.34 (s, 6H), 2.08 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$, *δ*): 149.2, 149.0, 147.2, 141.4, 139.8, 135.8, 135.1, 134.6, 124.8, 120.1, 107.1, 102.6, 65.4, 56.2, 56.2, 20.3, 20.1; HRMS (EI, m/z): [M$^+$] calcd for $C_{33}H_{32}O_4$, 492.22951; found 492.22938.

**(5c) 2,2',3,3'-Tetramethoxy-6,7-dimethyl-9,9'-spirobifluorene**



*n*-Butyl lithium solution in hexane (2.5 M; 2.04 ml, 5.10 mmol), 1-bromo-2-(3,4-dimethoxyphenyl)-4,5-dimethylbenzene (1.50 g, 4.67 mmol) and 2,3-dimethoxy-9H-fluoren-9-one (1.14 g, 4.74 mmol) in anhydrous THF (50 ml) were reacted according to the general procedure E to afford the pure product as white solid (1.70 g, 78%); mp 252-254 ºC; $^1$H NMR (400 MHz, CDCl$_3$, δ): 7.72 (d, *J* = 7.5 Hz, 1H), 7.50 (s, 1H), 7.32 (m, 3H), 7.03 (td, *J* = 7.5, 0.8 Hz, 1H), 6.66 (d, *J* = 7.5 Hz, 1H), 6.43 (s, 1H), 6.25 (s, 1H), 6.20 (s, 1H), 4.03 (s, 3H), 4.02 (s, 3H), 3.66 (s, 3H), 3.63 (s, 3H), 2.34 (s, 3H), 2.09 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, *δ*): 149.7, 149.5, 149.3, 149.3, 149.1, 146.8, 141.9, 141.4, 140.9, 139.9, 135.9, 135.2, 134.7, 134.3, 127.5, 126.6, 124.8, 123.8, 120.1, 118.9, 107.0, 107.0, 102.9, 102.7, 65.7, 56.3, 56.2, 56.2, 56.2, 20.3, 20.1; HRMS (EI, m/z): [M$^+$] calcd for $C_{31}H_{28}O_4$, 464.1988; found 464.1990.

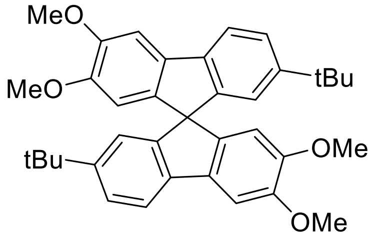
**(5d) 2,2',3,3'-Tetramethoxy-6,6'-dimethyl-9,9'-spirobifluorene**



*n*-Butyl lithium solution in hexane (2.5 M; 2.9 ml, 7.20 mmol), 1-bromo-3,4-dimethoxy-4'-methyl-1,1'-

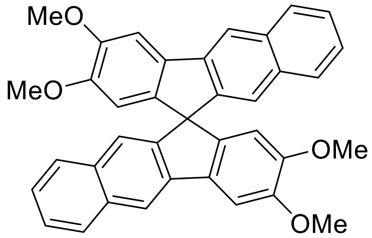
biphenyl (2.04 g, 6.65 mmol) and 2,3-dimethoxy-7-methyl-9H-fluoren-9-one (1.41 g, 5.54 mmol) in anhydrous THF (60 ml) were reacted according to the general procedure E to afford the pure product as white solid (1.93 g, 75%); mp 155-157 ºC; $^1$H NMR (400 MHz, CDCl$_3$, δ): 7.53 (d, *J* = 7.0 Hz, 2H), 7.27 (m, 2H), 7.07 (d, *J* = 7.0 Hz, 2H), 6.40 (s, 2H), 6.14 (s, 2H), 3.95 (s, 6H), 3.57 (s, 6H), 2.12 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$, *δ*): 149.6, 149.3, 149.1, 140.9, 139.2, 136.4, 134.4, 128.3, 124.4, 118.4, 107.2, 102.8, 67.5, 56.2, 56.1, 21.4; HRMS (EI, m/z): [M$^+$] calcd. for $C_{31}H_{28}O_4$, 464.1988; found 464.1984.

**(5e) 2,2',3,3'-Tetramethoxy-6,6'-*t*-butyl-9,9'-spirobifluorene**



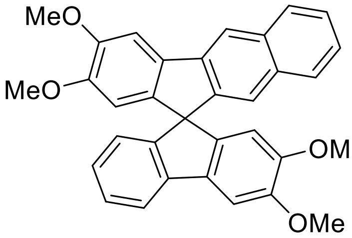
*n*-Butyl lithium solution in hexane (2.5 M; 4.05 ml, 7.75 mmol), 1-bromo-3,4-dimethoxy-4'-*t*-butyl-1, 1'-biphenyl (3.25 g, 9.30 mmol) and 2,3-dimethoxy-7-*t*-butyl-9H-fluoren-9-one (2.29 g, 7.75 mmol) in anhydrous THF (60 ml) were reacted according to the general procedure E to afford the pure product as white solid (2.38 g, 75%); mp 120-122 ºC; $^1$H NMR (400 MHz, CDCl$_3$, δ): 7.64 (d, *J* = 8.0 Hz, 2H), 7.38 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.31(s, 2H), 6.64 (d, *J* = 1.6 Hz, 2H), 6.19 (s, 2H), 4.03 (s, 6H), 3.63 (s, 6H), 1.15 (s, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$, *δ*): 150.1, 149.6, 149.3, 149.3, 141.8, 139.6, 134.6, 124.5, 120.9, 118.2, 107.2, 102.9, 66.2, 56.3, 56.2, 34.9, 31.6; HRMS (EI, m/z): [M$^+$] calcd for $C_{37}H_{40}O_4$, 548.2927; found 548.2931.

**(5f) 2,2',3,3'-Tetramethoxy-11,11'-spirobi[benzo[b]fluorene]**



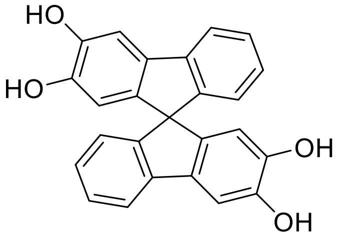
*n*-Butyl lithium solution in hexane (2.5 M; 2.10 ml, 5.2 mmol), 2-bromo-3-(3,4-dimethoxyphenyl)-naphthalene (1.50 g, 4.37 mmol) and 2,3-dimethoxybenzo[b]fluoren-11-one (1.15 g, 3.97 mmol) in anhydrous THF (50 ml) were reacted according to the general procedure E to afford the pure product as white solid (1.67 g, 78 %); mp 266-268 ºC; $^1$H NMR (400 MHz, CDCl$_3$, δ): 8.16 (s, 2H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.52 (s, 2H), 7.51(d, *J* = 8.1 Hz, 2H), 7.43 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 2H), 7.31 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 2H), 7.14 (s, 2H), 6.27 (s, 2H), 4.10 (s, 6H), 3.63 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$, *δ*): 150.5, 149.8, 148.8, 142.7, 140.6, 133.8, 133.5, 133.1, 128.3, 128.0, 125.9, 125.3, 122.7, 116.6, 107.0, 103.3, 64.9, 56.3, 56.1; HRMS (EI, m/z): [M$^+$] calcd for $C_{37}H_{28}O_4$, 536.1988; found 536.1990.

**(5g) 2,2',3,3'-Tetramethoxyspiro[benzo[b]fluorene-11,9'-fluorene]**



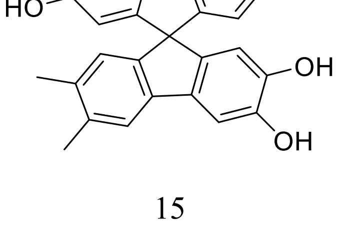
*n*-Butyl lithium solution in hexane (2.5 M; 2.69 ml, 6.72 mmol), 2-bromo-4,5-dimethoxy-biphenyl (1.82 g, 6.2 mmol) and 2,3-dimethoxybenzo[b]fluoren-11-one (1.5 g, 5.17 mmol) in anhydrous THF (60 ml) were reacted according to the general procedure E to afford the pure product as white solid (2.20 g, 87 %); mp 238-240 °C; $^1$H NMR (400 MHz, $CDCl_3$, δ): 8.11 (s, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.48 (s, 1H), 7.37 (m, 4H), 7.10 (s, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.70 (d, *J* = 7.5 Hz, 1H), 6.27 (s, 1H), 6.23 (s, 1H), 4.07 (s, 3H), 4.05 (s, 3H), 3.66 (s, 3H), 3.61 (s, 3H);$^{13}$C NMR (100 MHz, $CDCl_3$, *δ*): 150.4, 150.3, 149.8, 149.7, 149.5, 147.8, 142.0, 141.8, 141.8, 140.8, 134.2, 133.8, 133.7, 133.1, 128.3, 127.9, 127.7, 126.76, 125.9, 125.3, 124.1, 122.4, 119.0, 116.6, 107.1, 106.8, 103.3, 103.0, 65.4, 56.3, 56.2, 56.1; HRMS (EI, m/z): [$M^+$] calcd for $C_{33}H_{26}O_4$, 486.1831; found 486.1821.

**(1a) 2,2’,3,3’’-Tetrahydroxy-9,9'-spirobifluorene[26]**



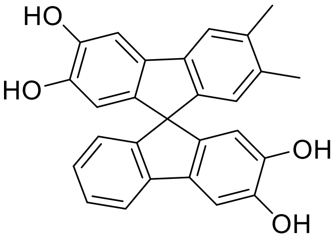
$BBr_3$ (1.74 g, 6.9 mmol) and 2,2’,3,3'-tetramethoxy-9,9'-spirobifluorene (1.00 g, 2.3 mmol) in anhydrous DCM (20 ml) were reacted according to the general procedure F to give the product (0.80 g, 92%) as a white powder; m.p. decomposes before melting; $^1$H NMR (400 MHz, acetone $D_6$, δ): 8.03 (br s, 2H), 7.97 (br s, 2H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.40 (s, 2H), 7.29 (s, 2H), 7.00 (s, 2H), 6.59 (d, *J* = 7.5 Hz, 2H), 6.17 (s, 2H); $^{13}$C NMR (100 MHz, acetone-$D_6$, δ): 150.0, 146.1, 146.0, 142.9, 141.4, 134.2, 128.0, 126.7, 123.9, 119.5, 111.0, 107.4, 65.7; HRMS (ESI-, m/z): [M-$H^+$] calcd for $C_{25}H_{15}O_4$, 379.0970; found 379.0975.

**(1b) 2,2',3,3'- Tetrahydroxy -6,6',7,7'-tetramethyl-9,9'-spirobifluorene**



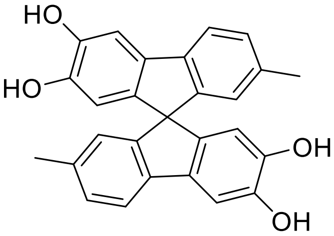
$BBr_3$ (4.6 g, 18.45 mmol) and 2,2',3,3'-tetramethoxy-6,6',7,7'-tetramethyl-9,9'-spirobifluorene (3.00 g, 6.15 mmol) in anhydrous DCM (60 ml) were reacted according to the general procedure F to give the product (2.60 g, 97%) as a white powder; m.p. decomposes before melting; $^1$H NMR (400 MHz, MeOD, δ): 7.39 (s, 2H), 7.18 (s, 2H), 6.30 (s, 2H), 6.05 (s, 2H), 2.30 (s, 6H), 2.06 (s, 6H); $^{13}$C NMR (100 MHz, MeOD, δ): 148.8, 146.2, 146.1, 142.6, 141.3, 136.4, 135.4, 135.2, 125.5, 120.6, 111.6, 107.2, 65.9, 20.1, 19.9; HRMS (EI, m/z): [$M^+$] calcd for $C_{29}H_{24}O_4$, 436.1675; found 436.1672

**(1c) 2,2',3,3'- Tetrahydroxy -6,7-dimethyl-9,9'-spirobifluorene**



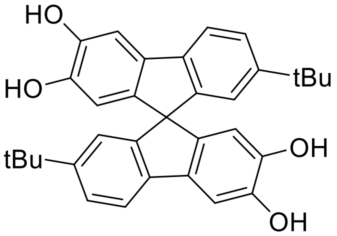
$BBr_3$ (2.58 g, 10.32 mmol) and 2,2',3,3'-tetramethoxy-6,7-dimethyl-9,9'-spirobifluorene (1.6 g, 3.44 mmol) in anhydrous DCM (40 ml) were reacted according to the general procedure F. The product was extracted with $Et_2O$ and dried over $MgSO_4$. After evaporation of the solvent the white solid product was dried under high vacuum but residual $Et_2O$ was observed and its amount evaluated by $^1$H NMR (1.35 g, 97%); m.p. decomposes before melting; $^1$H NMR (400 MHz, MeOD, δ): 7.62 (d, *J* = 7.6 Hz, 1H), 7.40 (s, 1H), 7.24 (m, 2H), 7.19 (s, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.53 (d, *J* = 7.6 Hz, 1H), 6.31 (s, 1H), 6.07 (s, 1H), 6.05 (s, 1H), 2.30 (s, 3H), 2.06 (s, 3H);$^{13}$C NMR (100 MHz, MeOD, δ): 151.2, 148.4, 146.7, 146.4, 146.3, 146.2, 143.5, 142.6, 142.2, 141.4, 136.5, 135.5, 135.2, 134.8, 128.2, 126.9, 125.5, 124.5, 120.7, 119.5, 111.6, 111.5, 107.5, 107.3, 66.9, 20.1, 19.9; HRMS (EI, m/z): [$M^+$] calcd for $C_{27}H_{20}O_4$, 408.1362; found 408.1370

**(1d) 2,2',3,3'- Tetrahydroxy -6,6'-dimethyl-9,9'-spirobifluorene**



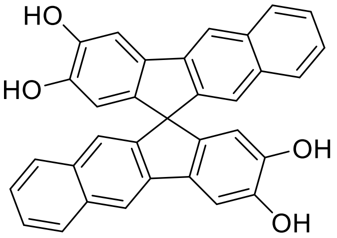
$BBr_3$ (2.34 g, 9.68 mmol) and 2,2',3,3'- tetramethoxy -6,6'-dimethyl-9,9'-spirobifluorene (1.50 g, 3.22 mmol) in anhydrous DCM (30 ml) were reacted according to the general procedure F to give the product (1.20 g, 92%) as a white powder; m.p. decomposes before melting; $^1$H NMR (400 MHz, acetone-$D_6$, δ): 8.01 (s, 2H), 7.93 (s, 2H), 7.59 (d, *J* = 7.7 Hz, 2H), 7.32 (s, 2H), 7.10 (d, *J* = 7.7 Hz, 2H), 6.39 (s, 2H), 6.13 (s, 2H), 2.15 (s, 6H); $^{13}$C NMR (100 MHz, acetone-$D_6$, δ): 150.8, 146.2, 145.9, 141.7, 140.5, 136.5, 134.6, 129.0, 124.8, 119.5, 111.3, 107.3, 65.8, 21.3; HRMS (ESI+, m/z): [$M$-$H^+$] calcd for $C_{27}H_{20}O_4$, 408.1362; found 408.1367.

### (1e) 2,2',3,3'- Tetrahydroxy -6,6'-t-butyl-9,9'-spirobifluorene



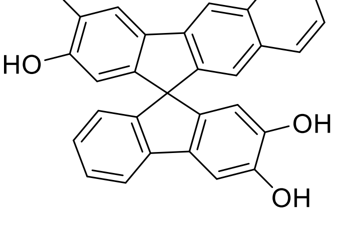
$BBr_3$ (1.61 g, 6.45 mmol) and 2,2',3,3'-tetramethoxy-6,6'-*t*-butyl-9,9'-spirobifluorene (1.18 g, 2.15 mmol) in anhydrous DCM (20 ml) were reacted according to the general procedure F to give the product (1.08 g, 92%) as a white powder; m.p. decomposes before melting; $^1H$ NMR (400 MHz, acetone-$D_6$, δ): 7.96 (s, 2H), 7.86 (s, 2H), 7.64 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.33 (s, 2H), 6.65 (s, 2H), 6.11 (s, 2H), 1.13 (s, 18H); $^{13}C$ NMR (100 MHz, acetone-$D_6$, δ): 150.6, 150.1, 146.1, 145.9, 142.5, 140.8, 134.4, 125.3, 121.0, 119.2, 111.3, 107.5, 66.4, 35.3, 31.8; HRMS (ESI-, m/z): [M-H$^+$] calcd for $C_{33}H_{31}O_4$, 491.2222; found 491.2220.

### (1f) 2,2',3,3'- Tetrahydroxy -11,11'-spirobi[benzo[b]fluorene]



$BBr_3$ (2.23 g, 8.94 mmol) and 2,2',3,3'-tetramethoxy-11,11'-spirobi[benzo[b]fluorene] (1.60 g, 2.98 mmol) in anhydrous DCM (30 ml) were reacted according to the general procedure F to give the product (1.40 g, 98%) as a white powder; m.p. decomposes before melting; $^1H$ NMR (400 MHz, acetone-$D_6$, δ): 8.21 (s, 2H), 8.09 (s, 2H), 8.01 (s, 2H), 7.95 (d, $J = 8.2$ Hz, 2H), 7.61 (d, $J = 8.2$ Hz, 2H), 7.59 (s, 2H), 7.43 (m, 2H), 7.30 (m, 2H), 7.14 (s, 2H), 6.24 (s, 2H). $^{13}C$ NMR (100 MHz, acetone-$D_6$, δ): 150.3, 147.4, 146.8, 143.6, 141.8, 134.9, 133.9, 133.7, 128.9, 128.7, 126.6, 125.9, 123.0, 117.3, 111.5, 108.1, 65.1; HRMS (EI, m/z): [M$^+$] calcd for $C_{33}H_{20}O_4$, 480.1362; found 480.1361.

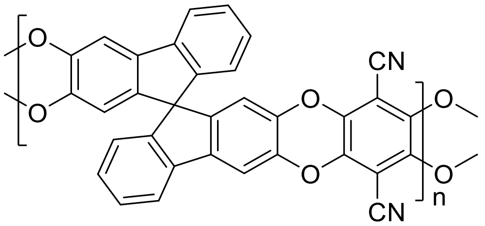
### (1g) 2,2',3,3'-Tetrahydroxyspiro[benzo[b]fluorene-11,9'-fluorene]



$BBr_3$ (2.46 g, 9.87 mmol) and 2,2',3,3'-tetramethoxyspiro[benzo[b]fluorene-11,9'-fluorene] (1.60 g, 3.29 mmol) in anhydrous DCM (40 ml) were reacted according to the general procedure F to give the product (1.34 g, 95%) as a white powder; m.p. decomposes before melting; $^1H$ NMR (400 MHz, Acetone D6, δ): 8.17 (s, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.54 (s, 1H), 7.42 (m, 2H), 7.32 (m, 2H), 7.07 (s, 1H), 7.01 (m, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 6.22 (s, 1H), 6.18 (s, 1H). $^{13}$C NMR (126 MHz, Acetone-D6, δ): 151.3, 149.2, 147.2, 146.7, 146.4, 143.0, 142.8, 142.6, 141.9, 134.8, 134.4, 133.9, 133.8, 128.8, 128.7, 128.4, 127.1, 126.5, 125.8, 124.4, 122.6, 119.8, 117.2, 111.5, 111.2, 108.0, 107.7, 65.5; HRMS (EI, m/z): [M$^+$] calcd for $C_{29}H_{018}O_4$, 430.1205; found 430.1210.

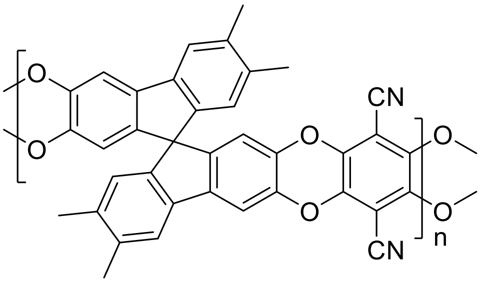
**S2.4 Polymers synthesis**

**PIM-SBF-1**[26]



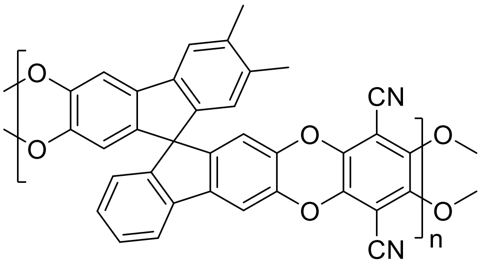
2,2′,3,3′-Tetrahydroxy-9,9′-spirobifluorene (1.14 g, 3.00 mmol), and 2,3,5,6-tetrafluoroterephthalonitrile (0.60 g, 3.00 mmol) in anhydrous DMF (15 mL) were reacted according to the general procedure G to give the final product as yellow solid (1.30 g, 86% based on the molecular weight of the repeated unit); $^1$H NMR (500 MHz, $CDCl_3$ , δ ): 7.72 (br s, 2H), 7.41 (br s, 4H), 7.14 (br s, 2H), 6.71 (br s, 2H), 6.38 (br m, 2H); BET surface area = 803 m$^2$ g$^{-1}$; total pore volume = 0.74 cm$^3$ g $^{-1}$ at $p/p_0$ = 0.98, from $N_2$ adsorption at 77 K; GPC ($CHCl_3$) $M_n$ = 38000 g mol$^{-1}$, $M_w$ = 89000 g mol $^{-1}$; TGA analysis (nitrogen): 2% loss of weight occurred at ~ 350 °C. Initial weight loss due to thermal degradation commences at ~565 °C.

**PIM-SBF-2**



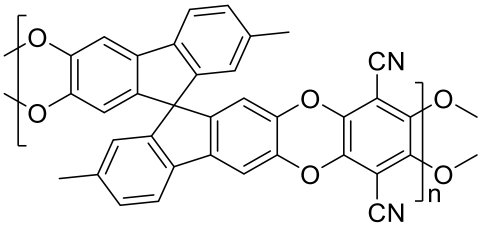
2,2',3,3'-Tetrahydroxy -6,6',7,7'-tetramethyl-9,9'-spirobifluorene (1.14 g, 2.29 mmol), and 2,3,5,6-tetrafluoroterephthalonitrile (0.46 g, 2.29 mmol) in anhydrous DMF (13 mL) were reacted according to the general procedure G to give the final product as yellow solid (1.10 g, 86% based on the molecular weight of the repeated unit); $^1$H NMR (400 MHz, $CDCl_3$ , δ): 7.49 (br s, 2H), 7.37 (br s, 2H), 6.49 (br s, 2H), 6.33 (br s, 2H), 2.33 (br s, 6H), 2.11 (br s, 6H); $^{13}$C NMR (100 MHz, *solid state*, δ) 146.2, 139.4, 124.6, 120.8, 112.3, 107.6, 95.1, 66.0, 18.9; BET surface area = 938 m$^2$ g$^{-1}$ ; total pore volume = 0.69 cm$^3$ g $^{-1}$ at $p/p_0$ = 0.98, from $N_2$ adsorption at 77 K; GPC ($CHCl_3$ ); GPC ($CHCl_3$ ) $M_n$ = 40000 g mol$^{-1}$, $M_w$ = 95000 g mol $^{-1}$; TGA analysis (nitrogen): 1.6% loss of weight occurred at ~ 325 °C. Initial weight loss due to thermal degradation commences at ~510 °C.

**PIM-SBF-3**



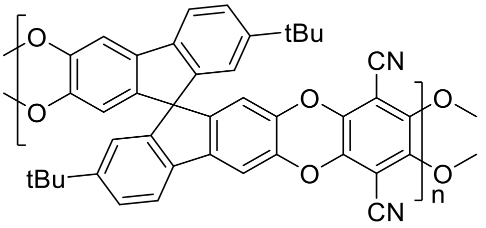
2,2',3,3'-Tetrahydroxy-6,7-dimethyl-9,9'-spirobifluorene (1.17 g, 2.86 mmol), and 2,3,5,6-tetrafluoroterephthalonitrile (0.58 g, 2.86 mmol) in anhydrous DMF (15 mL) were reacted according to the general procedure G to give the final product as yellow solid (1.45 g, 95% based on the molecular weight of the repeated unit); $^1$H NMR (500 MHz, $CDCl_3$, δ) 7.72 (br s, 1H), 7.47 (br s, 2H), 7.39 (br s, 2H), 7.13 (br s, 1H), 6.72 (br s, 1H), 6.48 (br s, 1H), 6.36 (br s, 2H), 2.33 (br s, 3H), 2.11 (br s, 3H); $^{13}$C NMR (100 MHz, *solid state*) δ 145.6, 139.6, 127.6, 124.1, 120.7, 111.5, 108.1, 95.3, 66.1, 18.6; BET surface area = 794 $m^2$ $g^{-1}$ ; total pore volume = 0.54 $cm^3$ $g^{-1}$ at $p/p_0$ = 0.98, from $N_2$ adsorption at 77 K; GPC ($CHCl_3$ ) $M_n$ = 43000 g $mol^{-1}$, $M_w$ = 76000 g $mol^{-1}$; TGA analysis (nitrogen): 1.4% loss of weight occurred at ~ 315 °C. Initial weight loss due to thermal degradation commences at ~485 °C.

**PIM-SBF-4**



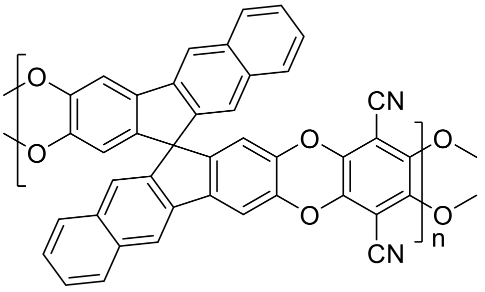
2,2',3,3'-Tetrahydroxy-6,6'-dimethyl-9,9'-spirobifluorene (1.15 g, 2.81 mmol), and 2,3,5,6-tetrafluoroterephthalonitrile (0.563 g, 2.81 mmol) in anhydrous DMF (15 ml) were reacted according to the general procedure G to give the final product as yellow solid (1.19 g, 80% based on the molecular weight of the repeated unit); $^1$H NMR (500 MHz, $CDCl_3$ , δ ): 7.60 (br s, 2H), 7.39 (br s, 2H), 7.19 (br s, 2H), 6.52 (br s, 2H), 6.37 (s, 2H), 2.21 (br s, 6H); $^{13}$C NMR (100 MHz, *solid state*, δ) 148.6, 144.4, 139.7, 138.5, 128.7, 123.8, 119.5, 110.9, 108.2, 94.7, 20.4; BET surface area = 752 $m^2$ $g^{-1}$ ; total pore volume = 0.59 $cm^3$ $g^{-1}$ at $p/p_0$ = 0.98, from $N_2$ adsorption at 77 K; GPC ($CHCl_3$ ) $M_n$ = 40000 g $mol^{-1}$, $M_w$ = 75000 g $mol^{-1}$; TGA analysis (nitrogen): 2% loss of weight occurred at ~300 °C. Initial weight loss due to thermal degradation commences at ~530 °C.

**PIM-SBF-5**



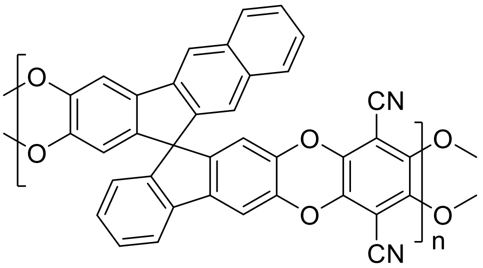
2,2',3,3'-Tetrahydroxy-6,6'-*t*-butyl-9,9'-spirobifluorene (1.818 g, 3.690 mmol), and 2,3,5,6-tetrafluoroterephthalonitrile (0.738 g, 3.690 mmol) in anhydrous DMF (25 ml) were reacted according to the general procedure G to give the final product as yellow solid (1.80 g, 80% based on the molecular weight of the repeated unit); $^1$H NMR (500 MHz, $CDCl_3$ , δ ): 7.65 (br s, 2H), 7.43 (br s, 4H), 6.70 (br s, 2H), 6.32 (br s, 2H), 1.17 (br s, 18H); $^{13}$C NMR (100 MHz, *solid state*, δ) 152.2, 139.6, 124.7, 120.0, 112.1, 108.0, 30.5; BET surface area = 882 $m^2$ $g^{-1}$ ; total pore volume = 0.73 $cm^3$ $g^{-1}$ at $p/p_0$ = 0.98, from $N_2$ adsorption at 77 K; GPC ($CHCl_3$ ) $M_n$ = 46000 g $mol^{-1}$, $M_w$ = 110000 g $mol^{-1}$; TGA analysis (nitrogen): 2% loss of weight occurred at ~300 °C. Initial weight loss due to thermal degradation commences at ~490 °C.

**PIM-SBF- 6**



2,2',3,3'-Tetrahydroxy-11,11'-spirobi[benzo[b]fluorene] (0.80 g, 1.67 mmol), and 2,3,5,6-tetrafluoroterephthalonitrile (0.33 g, 1.67 mmol) in anhydrous DMF (13 mL) were reacted according to the general procedure G to give the final product as yellow solid (0.81 g, 81% based on the molecular weight of the repeated unit); $^{13}$C NMR (100 MHz, *solid state*, δ) 146.8, 139.7, 133.9, 126.5, 118.1, 108.0, 94.2, 65.2; BET surface area = 768 $m^2$ $g^{-1}$ ; total pore volume = 0.46 $cm^3$ $g^{-1}$ at $p/p_0$ = 0.98, from $N_2$ adsorption at 77 K; TGA analysis (nitrogen): 1.6% loss of weight occurred at ~ 315 °C. Initial weight loss due to thermal degradation commences at ~562 °C.

**PIM-SBF-7**



2,2',3,3'-Tetrahydroxyspiro[benzo[b]fluorene-11,9'-fluorene] (1.10 g, 2.55 mmol), and 2,3,5,6-tetrafluoroterephthalonitrile (0.51 g, 2.55 mmol) in anhydrous DMF (18 mL) were reacted according to the general procedure G to give the final product as yellow solid (1.10 g, 78% based on the molecular weight of the repeated unit); $^{13}$C NMR (100 MHz, *solid state*, δ) 147.5, 140.0, 134.0, 127.4, 119.1, 108.4, 94.5, 66.0; BET surface area = 727 $m^2$ $g^{-1}$ ; total pore volume = 0.50 $cm^3$ $g^{-1}$ at $p/p_0 = 0.98$, from $N_2$ adsorption at 77 K; TGA analysis (nitrogen): 1.6% loss of weight occurred at ~ 415 °C. Initial weight loss due to thermal degradation commences at ~580 °C.

## S2.5 GPC of soluble SBF PIMs.

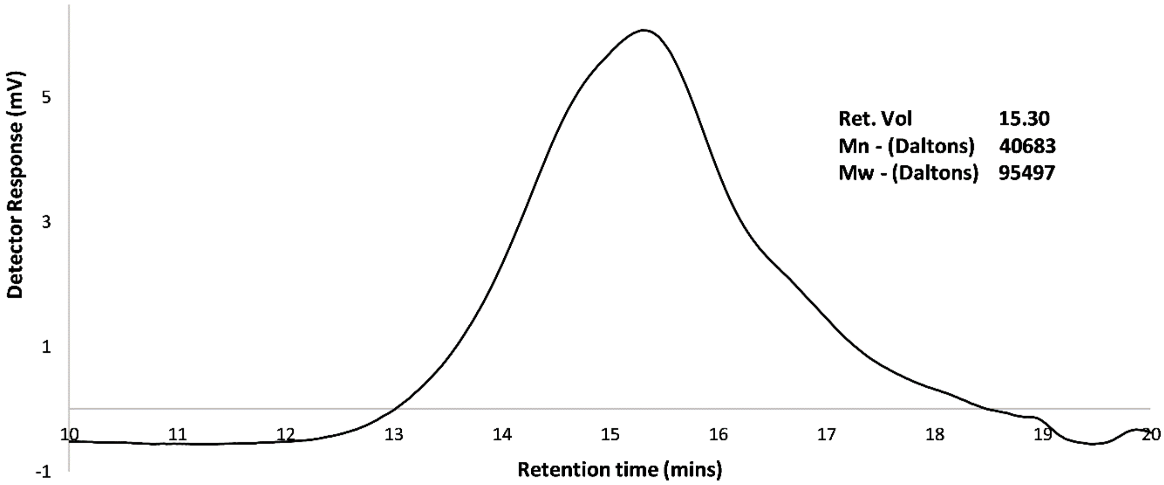


**Figure S1.** GPC trace for PIM-SBF-2.

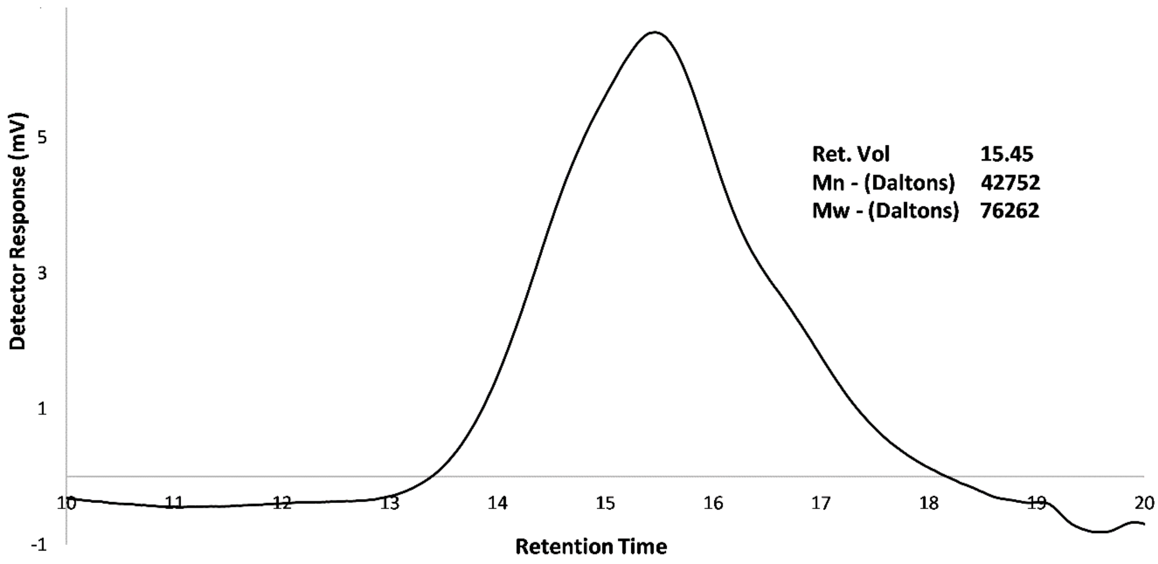


**Figure S2.** GPC trace for PIM-SBF-3.

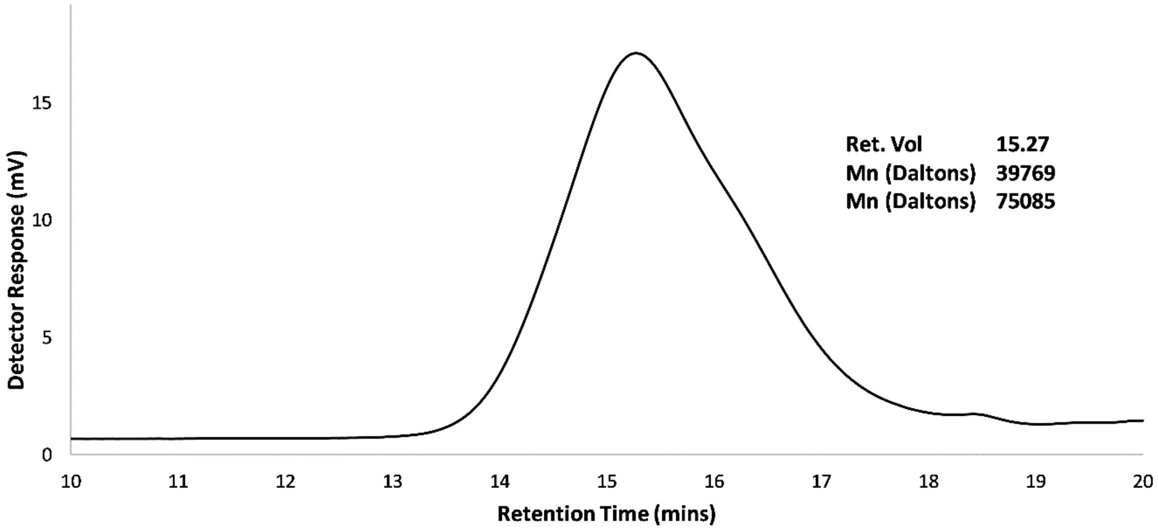


**Figure S3.** GPC trace for PIM-SBF-4.

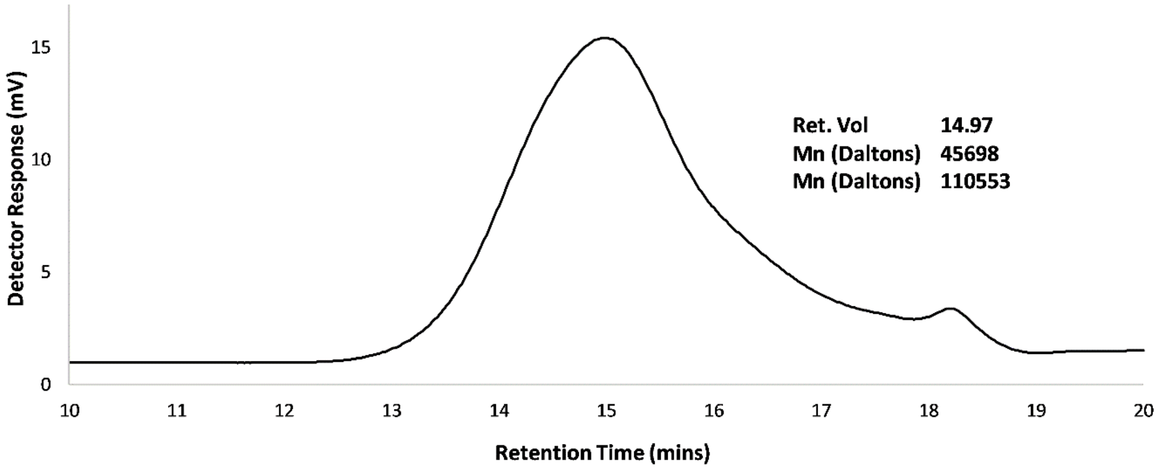


**Figure S4.** GPC trace for PIM-SBF-5.

## S2.6 $N_2$ Isotherms of SBF PIMs

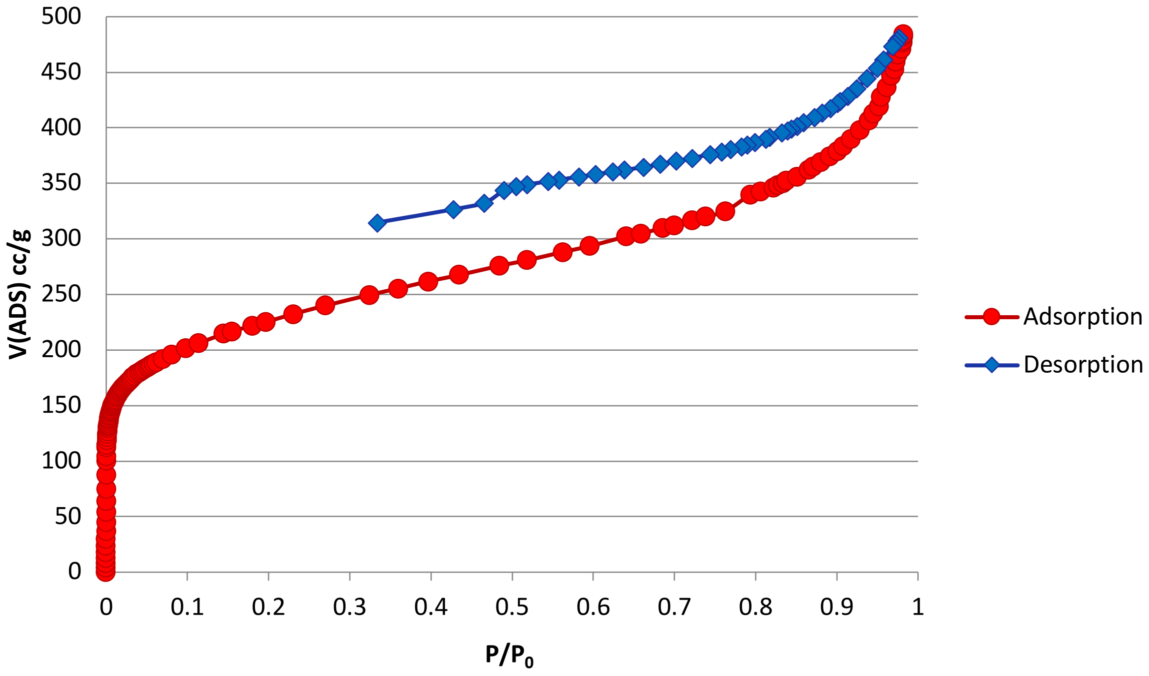


**Figure S5.** The $N_2$ adsorption and desorption isotherms for PIM-SBF-1.

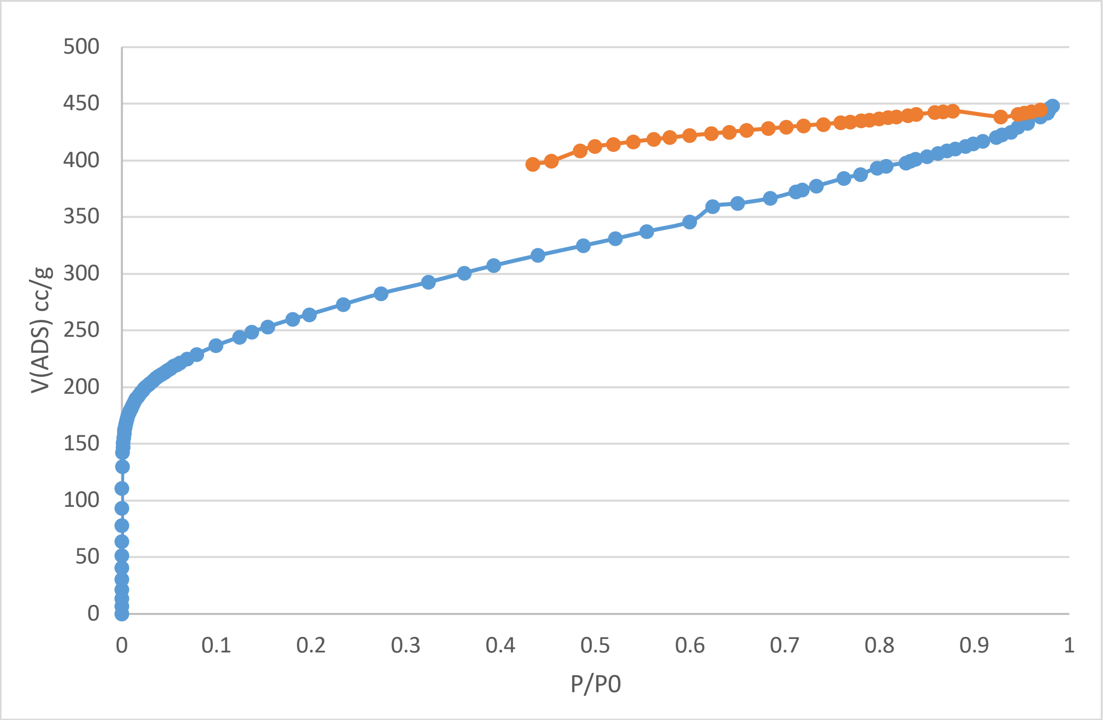


**Figure S6.** The $N_2$ adsorption and desorption isotherms for PIM-SBF-2.

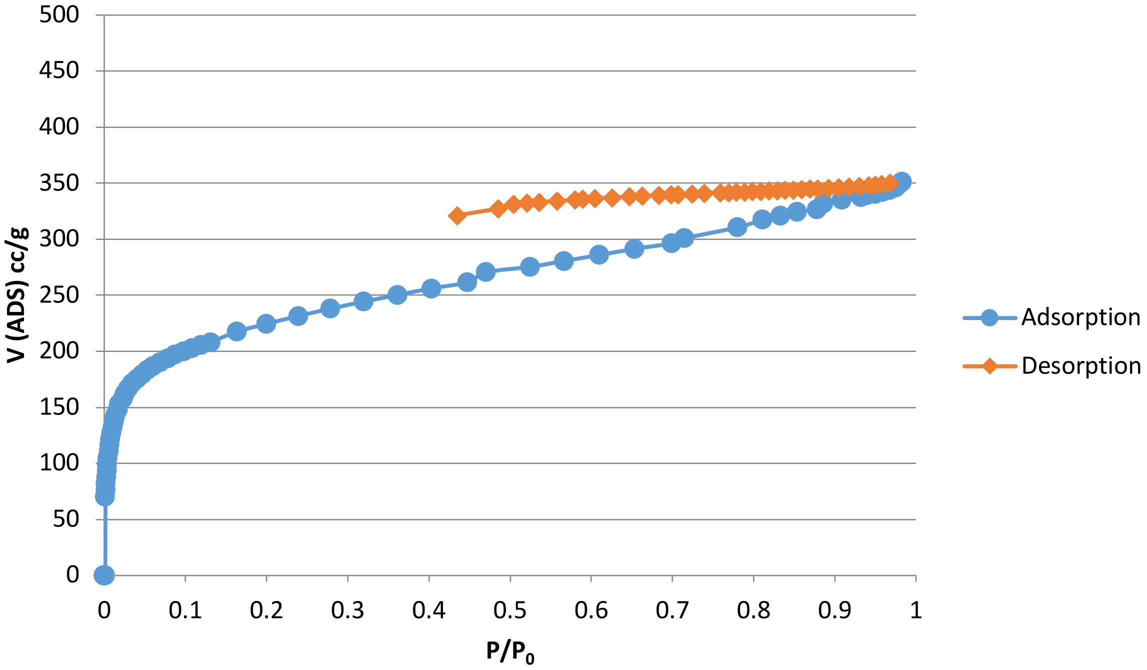


**Figure S7.** The $N_2$ adsorption and desorption isotherms for PIM-SBF-3.

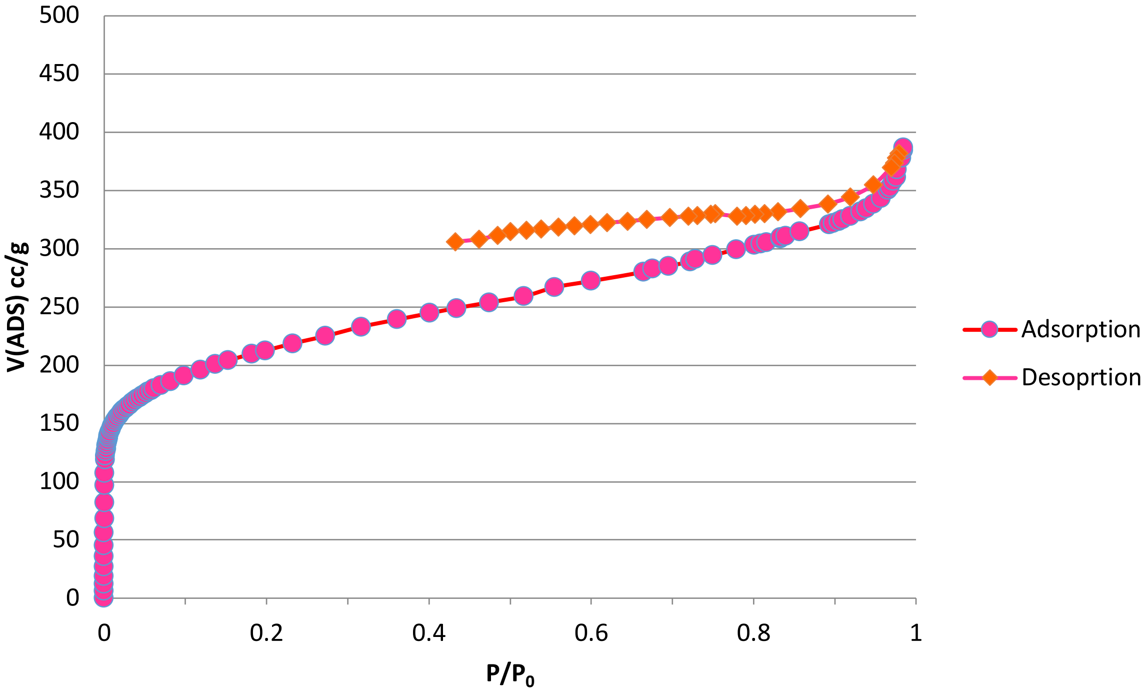


**Figure S8.** The $N_2$ adsorption and desorption isotherms for PIM-SBF-4.

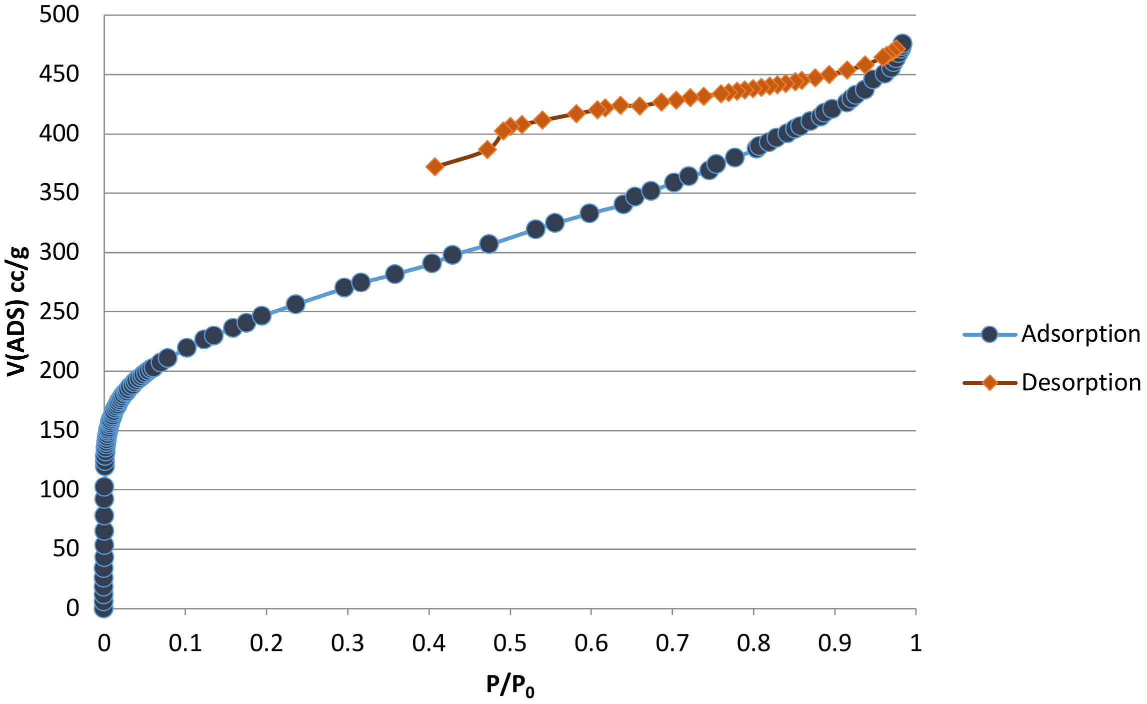


**Figure S8.** The $N_2$ adsorption and desorption isotherms for PIM-SBF-5.

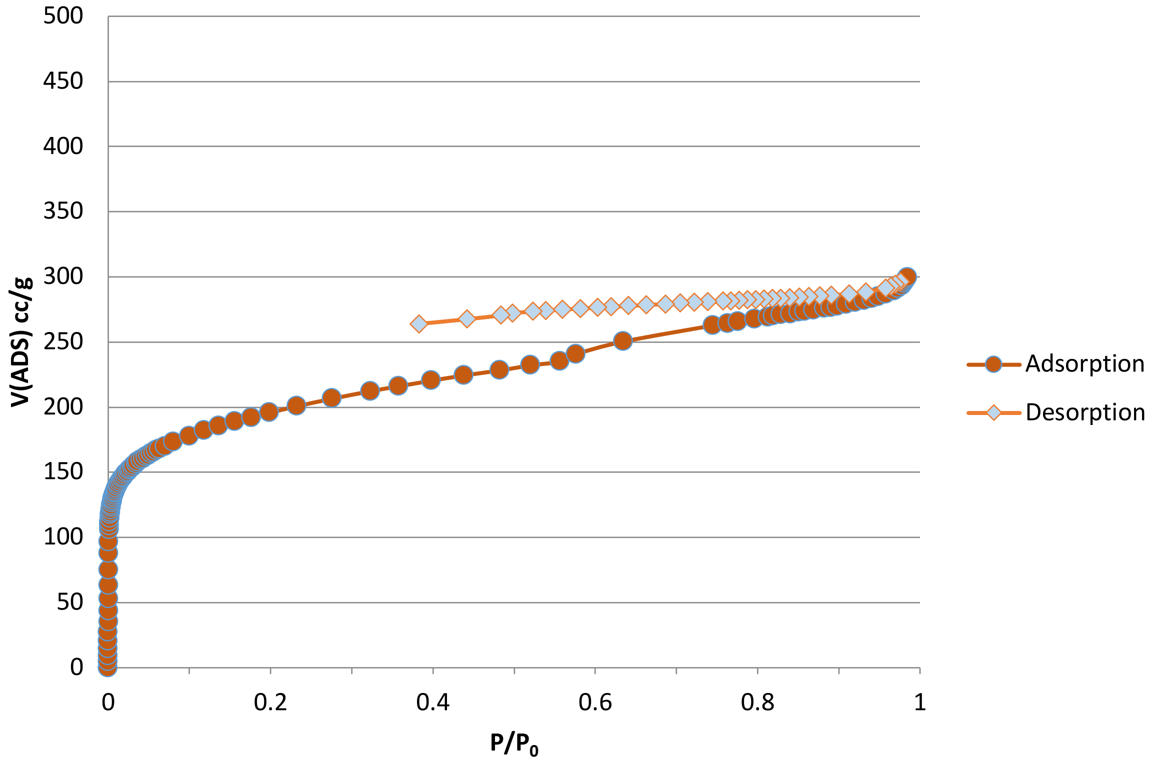


**Figure S9.** The $N_2$ adsorption and desorption isotherms for PIM-SBF-6.

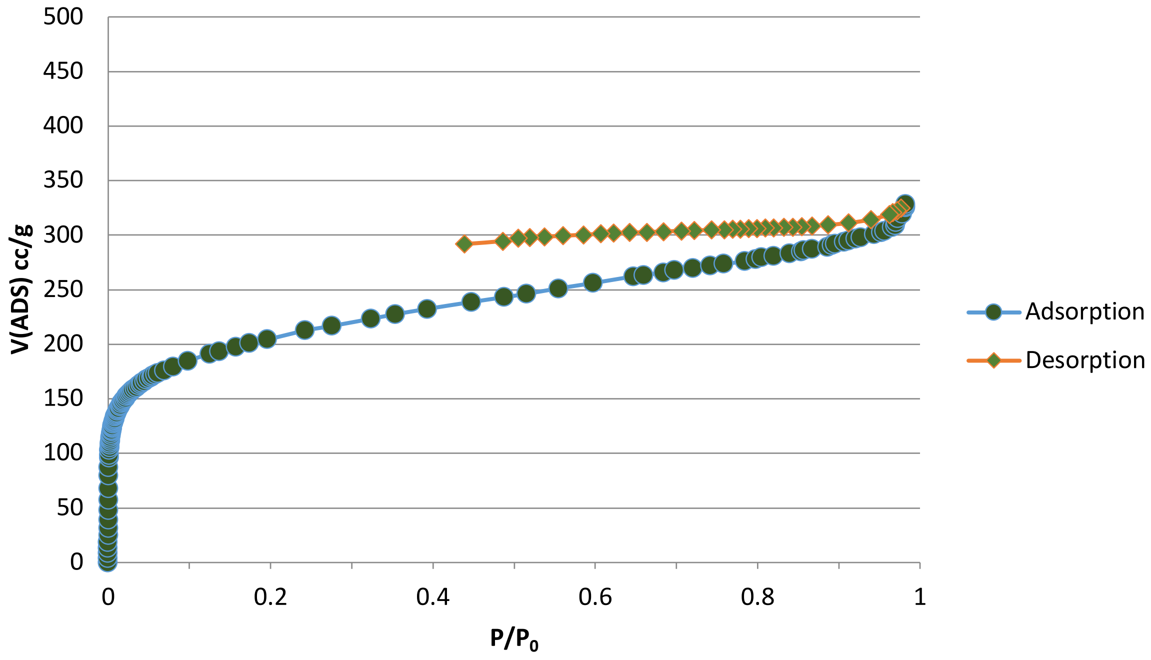


**Figure S10.** The $N_2$ adsorption and desorption isotherms for PIM-SBF-7.

### S2.7 $CO_2$ adsorption of SBF PIMs at 273K

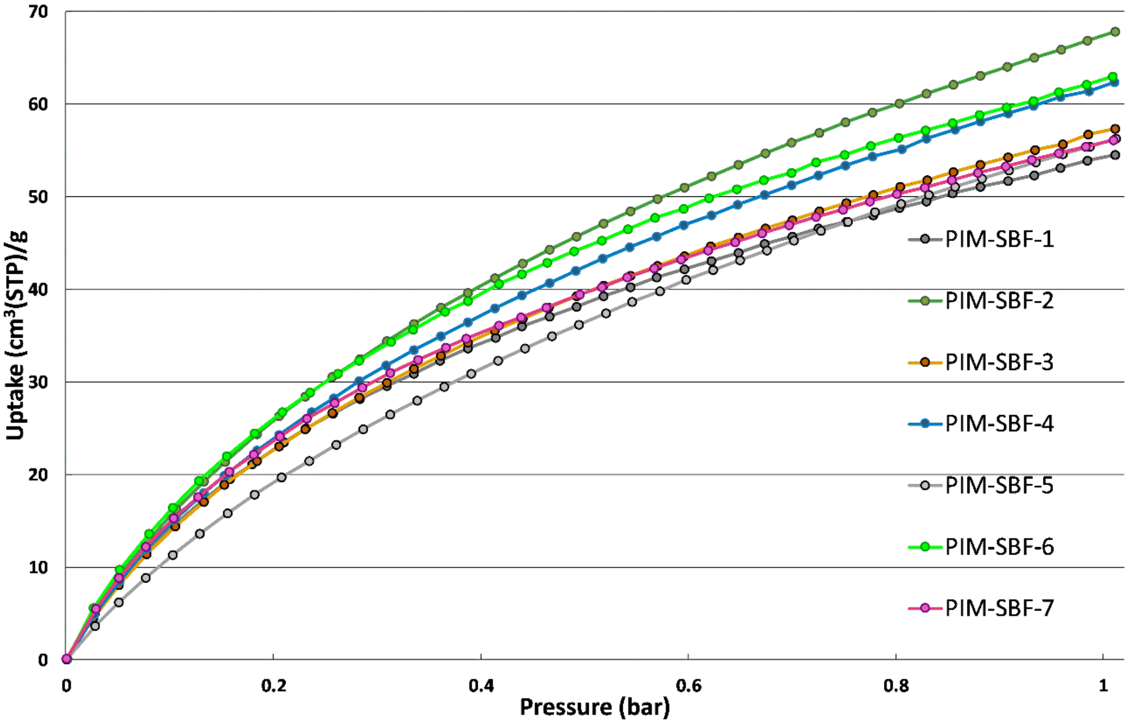


**Figure S11.** $CO_2$ adsorption isotherms for PIM-SBF polymers.

### S2.8 Pore size distribution from $CO_2$ adsorption data calculated using DFT of PIM-SBF polymers

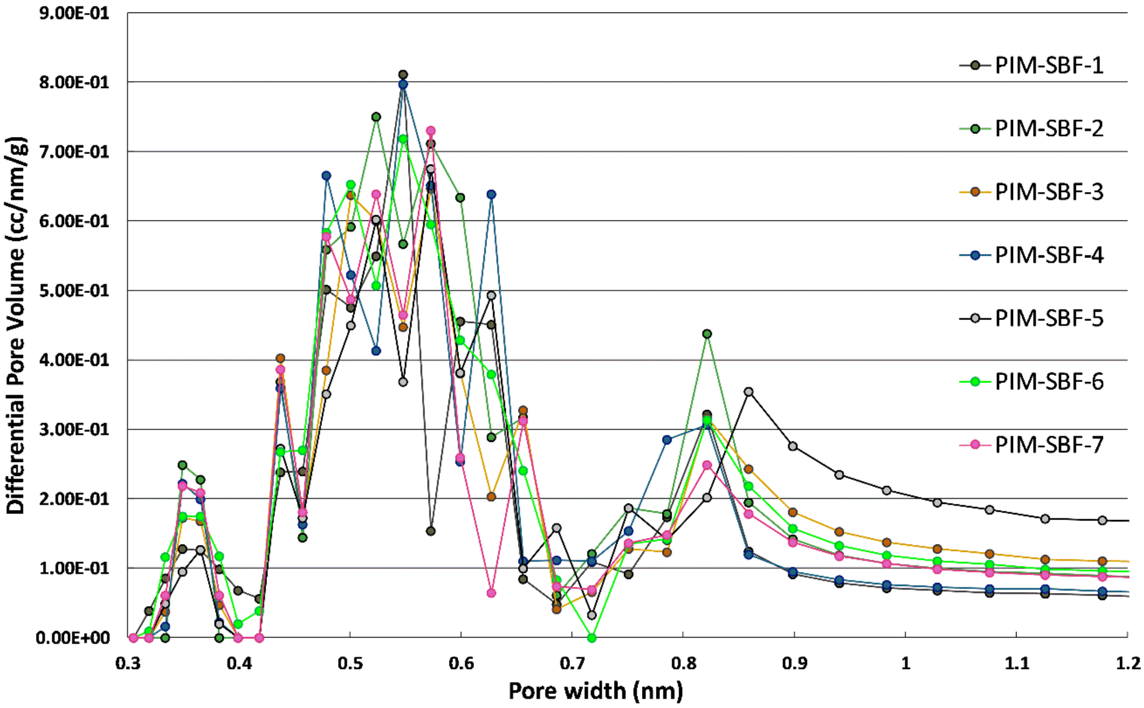


**Figure S12.** Pore size distribution for PIM-SBF polymers calculated from $CO_2$ adsorption at 273K using DFT.

## S3. Gas permeability measurements

### S3.1 Pure gas permeation measurements

All the gases used for pure and mixed gas permeation tests were supplied by Sapio at a minimum purity of 99.9995%. Permeation tests were carried out at 1 bar of feed gas pressure and at a constant temperature of 25 ± 1 °C on a fixed volume/pressure increase instrument, constructed and customized by Elektro & Elektronik Service Reuter (Geesthacht, Germany). Between two consecutive measurements, the membrane is evacuated for at least ten times the time lag of the previously measured gas, in order to guarantee a complete degassing. Before the first measurement the membrane is degassed for approximately 1 hour, or more if needed, to guarantee complete removal of absorbed species. The degassing of the membranes is performed under high vacuum conditions by a turbomolecular pump.

The permeability coefficient, *P*, is expressed in Barrer (1 Barrer = $10^{-10}$·cm$^3$(STP)·cm·cm$^{-2}$·s$^{-1}$·cm Hg$^{-1}$) and calculated from the steady state of the permeation curve. Diffusion is calculated by the so-called time-lag method and the approximate gas solubility coefficient by assuming the validity of the diffusion-solution model. A more detailed description of the method and calculation procedures is reported elsewhere.[32,33]

**Table SI 1:** pure gas permeability data of sample PIM-SBF-1

| **PIM-SBF 1 freshly MeOH treated** | | | | | | |
|---|---|---|---|---|---|---|
| **Transport parameter** | **$N_2$** | **$O_2$** | **$CO_2$** | **$CH_4$** | **$H_2$** | **He** |
| **$P_x$ [Barrer]** | ***340*** | ***1420*** | ***8850*** | ***532*** | ***4330*** | ***1560*** |
| **$\alpha(P_x/PN_2)$** | | 4.16 | 26.0 | 1.56 | 12.7 | 4.58 |
| **$D_x$ [$10^{-12}$ m$^2$s$^{-1}$]** | ***59.7*** | ***241*** | ***90.6*** | ***19.0*** | ***4960*** | ***6010*** |
| **$\alpha\ (D_x/DN_2)$** | - | 4.04 | 1.52 | 0.32 | 83.1 | 101 |
| **$S_x$ [cm$^3_{STP}$ cm$^{-3}$ bar$^{-1}$]** | ***4.28*** | ***4.41*** | ***73.3*** | ***21.0*** | ***0.66*** | ***0.19*** |
| **$\alpha\ (S_x/SN_2)$** | - | 1.03 | 17.1 | 4.92 | 0.15 | 0.05 |
| **PIM-SBF 1 aged for 2088 days** | | | | | | |
| **Transport parameter** | **$N_2$** | **$O_2$** | **$CO_2$** | **$CH_4$** | **$H_2$** | **He** |
| **$P_x$ [Barrer]** | ***87.5*** | ***486*** | ***2410*** | ***102*** | ***2190*** | ***914*** |
| **$\alpha(P_x/PN_2)$** | - | 5.56 | 27.5 | 1.17 | 25.0 | 10.4 |
| **$D_x$ [$10^{-12}$ m$^2$s$^{-1}$]** | ***16.5*** | ***86.2*** | ***26.0*** | ***4.7*** | ***2790*** | ***4390*** |
| **$\alpha\ (D_x/DN_2)$** | - | 5.21 | 1.57 | 0.28 | 168 | 265 |
| **$S_x$ [cm$^3_{STP}$ cm$^{-3}$ bar$^{-1}$]** | ***3.96*** | ***4.23*** | ***69.5*** | ***16.5*** | ***0.59*** | ***0.16*** |
| **$\alpha\ (S_x/SN_2)$** | - | 1.07 | 17.53 | 4.16 | 0.15 | 0.04 |

**Table SI 2:** pure gas permeability data of sample PIM-SBF-2

| **PIM-SBF 2 freshly MeOH treated** | | | | | | |
|---|---|---|---|---|---|---|
| **Transport parameter** | **$N_2$** | **$O_2$** | **$CO_2$** | **$CH_4$** | **$H_2$** | **He** |
| **$P_x$ [Barrer]** | ***1150*** | ***3820*** | ***22300*** | ***2020*** | ***9160*** | ***3110*** |
| **$\alpha(P_x/PN_2)$** | - | 3.31 | 19.4 | 1.75 | 7.96 | 2.70 |
| **$D_x$ [$10^{-12}$ $m^2s^{-1}$]** | ***278*** | ***812*** | ***308*** | ***116*** | ***8860*** | ***12200*** |
| **$\alpha\ (D_x/DN_2)$** | - | 2.92 | 1.11 | 0.42 | 31.8 | 43.8 |
| **$S_x$ [$cm^3_{STP}$ $cm^{-3}$ $bar^{-1}$]** | ***3.10*** | ***3.52*** | ***54.2*** | ***13.1*** | ***0.78*** | ***0.19*** |
| **$\alpha\ (S_x/SN_2)$** | - | 1.14 | 17.5 | 4.22 | 0.25 | 0.06 |
| **PIM-SBF 2 aged for 1295 days** | | | | | | |
| **Transport parameter** | **$N_2$** | **$O_2$** | **$CO_2$** | **$CH_4$** | **$H_2$** | **He** |
| **$P_x$ [Barrer]** | ***166*** | ***910*** | ***3870*** | ***184*** | ***4240*** | ***1700*** |
| **$\alpha(P_x/PN_2)$** | - | 5.48 | 23.3 | 1.11 | 25.6 | 10.2 |
| **$D_x$ [$10^{-12}$ $m^2s^{-1}$]** | ***38.8*** | ***191*** | ***54.6*** | ***9.6*** | ***5720*** | ***9600*** |
| **$\alpha\ (D_x/DN_2)$** | - | 4.93 | 1.41 | 0.25 | 148 | 248 |
| **$S_x$ [$cm^3_{STP}$ $cm^{-3}$ $bar^{-1}$]** | **3.21** | **3.58** | **53.10** | **14.3** | **0.56** | **0.13** |
| **$\alpha\ (S_x/SN_2)$** | - | 1.11 | 16.5 | 4.45 | 0.17 | 0.04 |

**Table SI 3:** pure gas permeability data of sample PIM-SBF-3

| **PIM-SBF 3 freshly MeOH treated** | | | | | | |
|---|---|---|---|---|---|---|
| **Transport parameter** | **$N_2$** | **$O_2$** | **$CO_2$** | **$CH_4$** | **$H_2$** | **He** |
| **$P_x$ [Barrer]** | ***463*** | ***1820*** | ***10900*** | ***878*** | ***5460*** | ***1971*** |
| **$\alpha(P_x/PN_2)$** | - | 3.94 | 23.5 | 1.90 | 11.8 | 4.26 |
| **$D_x$ [$10^{-12}$ $m^2s^{-1}$]** | ***100*** | ***349*** | ***129*** | ***33.8*** | ***5180*** | ***5610*** |
| **$\alpha\ (D_x/DN_2)$** | - | 3.49 | 1.29 | 0.34 | 51.8 | 56.0 |
| **$S_x$ [$cm^3_{STP}$ $cm^{-3}$ $bar^{-1}$]** | ***3.47*** | ***3.92*** | ***63.2*** | ***19.5*** | ***0.79*** | ***0.26*** |
| **$\alpha\ (S_x/SN_2)$** | - | 1.13 | 18.2 | 5.62 | 0.23 | 0.08 |
| **PIM-SBF 3 aged for 1294 days** | | | | | | |
| **Transport parameter** | **$N_2$** | **$O_2$** | **$CO_2$** | **$CH_4$** | **$H_2$** | **He** |
| **$P_x$ [Barrer]** | ***213*** | ***965*** | ***4850*** | ***248*** | ***3370*** | ***1270*** |
| **$\alpha(P_x/PN_2)$** | - | 4.53 | 22.8 | 1.16 | 15.8 | 5.97 |
| **$D_x$ [$10^{-12}$ $m^2s^{-1}$]** | ***40.6*** | ***182*** | ***61.8*** | ***11.2*** | ***4110*** | ***6260*** |
| **$\alpha\ (D_x/DN_2)$** | - | 4.48 | 1.52 | 0.28 | 101 | 154 |
| **$S_x$ [$cm^3_{STP}$ $cm^{-3}$ $bar^{-1}$]** | ***3.94*** | ***3.98*** | ***58.9*** | ***16.6*** | ***0.61*** | ***0.15*** |
| **$\alpha\ (S_x/SN_2)$** | - | 1.01 | 15.0 | 4.23 | 0.16 | 0.04 |

**Table SI 4:** pure gas permeability data of sample PIM-SBF-4

| **PIM-SBF 4 freshly MeOH treated** | | | | | | |
|---|---|---|---|---|---|---|
| **Transport parameter** | **$N_2$** | **$O_2$** | **$CO_2$** | **$CH_4$** | **$H_2$** | **He** |
| **$P_x$ [Barrer]** | ***474*** | ***1760*** | ***10600*** | ***834*** | ***4900*** | ***1930*** |
| **$\alpha(P_x/PN_2)$** | - | 3.71 | 22.3 | 1.76 | 10.3 | 4.08 |
| **$D_x$ [$10^{-12}$ m$^2$s$^{-1}$]** | ***96.3*** | ***346*** | ***134*** | ***29.2*** | ***6190*** | ***7580*** |
| **$\alpha(D_x/DN_2)$** | - | 3.59 | 1.39 | 0.30 | 64.3 | 78.8 |
| **$S_x$ [cm$^3_{STP}$ cm$^{-3}$ bar$^{-1}$]** | **3.70** | **3.81** | **59.4** | **21.4** | **0.59** | **0.19** |
| **$\alpha(S_x/SN_2)$** | - | 1.03 | 16.1 | 5.80 | 0.16 | 0.05 |
| **PIM-SBF 4 aged for 1428 days** | | | | | | |
| **Transport parameter** | **$N_2$** | **$O_2$** | **$CO_2$** | **$CH_4$** | **$H_2$** | **He** |
| **$P_x$ [Barrer]** | ***286*** | ***1260*** | ***6410*** | ***331*** | ***3960*** | ***1470*** |
| **$\alpha(P_x/PN_2)$** | - | 4.42 | 22.4 | 1.16 | 13.9 | 5.14 |
| **$D_x$ [$10^{-12}$ m$^2$s$^{-1}$]** | ***47.0*** | ***205*** | ***70.1*** | ***13.2*** | ***4160*** | ***5920*** |
| **$\alpha(D_x/DN_2)$** | - | 4.37 | 1.49 | 0.28 | 88.6 | 126 |
| **$S_x$ [cm$^3_{STP}$ cm$^{-3}$ bar$^{-1}$]** | **4.57** | **4.62** | **68.6** | **18.8** | **0.72** | **0.19** |
| **$\alpha(S_x/SN_2)$** | - | 1.01 | 15.0 | 4.12 | 0.16 | 0.04 |

**Table SI 5:** pure gas permeability data of sample PIM-SBF-5

| **PIM-SBF 5 freshly MeOH treated** | | | | | | |
|---|---|---|---|---|---|---|
| **Transport parameter** | **$N_2$** | **$O_2$** | **$CO_2$** | **$CH_4$** | **$H_2$** | **He** |
| **$P_x$ [Barrer]** | ***1080*** | ***2750*** | ***16400*** | ***2480*** | ***5590*** | ***2060*** |
| **$\alpha(P_x/PN_2)$** | - | 2.55 | 15.2 | 2.29 | 5.17 | 1.91 |
| **$D_x$ [$10^{-12}$ m$^2$s$^{-1}$]** | ***239*** | ***670*** | ***293*** | ***139*** | ***6710*** | ***10200*** |
| **$\alpha(D_x/DN_2)$** | - | 2.80 | 1.22 | 0.58 | 28.1 | 42.5 |
| **$S_x$ [cm$^3_{STP}$ cm$^{-3}$ bar$^{-1}$]** | ***3.39*** | ***3.08*** | ***42.1*** | ***13.4*** | ***0.62*** | ***0.15*** |
| **$\alpha(S_x/SN_2)$** | - | 0.91 | 12.4 | 3.95 | 0.18 | 0.04 |
| **PIM-SBF 5 aged for 1439 days** | | | | | | |
| **Transport parameter** | **$N_2$** | **$O_2$** | **$CO_2$** | **$CH_4$** | **$H_2$** | **He** |
| **$P_x$ [Barrer]** | ***550*** | ***1870*** | ***10000*** | ***925*** | ***4710*** | ***1830*** |
| **$\alpha(P_x/PN_2)$** | - | 3.41 | 18.2 | 1.68 | 8.57 | 3.32 |
| **$D_x$ [$10^{-12}$ m$^2$s$^{-1}$]** | ***133*** | ***418*** | ***169*** | ***55.7*** | ***5360*** | ***7850*** |
| **$\alpha(D_x/DN_2)$** | - | 3.14 | 1.27 | 0.42 | 40.3 | 59.0 |
| **$S_x$ [cm$^3_{STP}$ cm$^{-3}$ bar$^{-1}$]** | ***3.10*** | ***3.37*** | ***44.5*** | ***12.4*** | ***0.66*** | ***0.17*** |
| **$\alpha(S_x/SN_2)$** | - | 1.09 | 14.4 | 4.02 | 0.21 | 0.06 |

### S3.2 Mixed Gas permeation measurements

Mixed gas permeation experiments were carried out on a constant pressure/variable volume instrument. The custom made instrument is equipped with a modified Millipore permeation cell, and the permeate composition is determined by means of a Mass Spectrometric (MS) device equipped with a quadrupole mass filter (Hiden Analytical, HPR-20 QIC Benchtop residual gas analysis system, max. 200 AMU) and a sampling capillary with a typical flow rate of ca. 12 cm$^3$ min$^{-1}$ argon at ambient pressure. The feed (200 cm$^3$ min$^{-1}$) and the sweep (30 cm$^3$ min$^{-1}$) flow rates were controlled by EL-FLOW electronic Mass Flow Controllers (Bronkhorst) and an EL-PRESS electronic back pressure controller was used to control the feed pressure (0-5 bar(g)). All measured data were recorded with the MASsoft software package supplied with the mass spectrometer and with the FlowPlot software supplied with the pressure and mass flow controllers. The measured data were processed by a self-written elaboration program. More detailed descriptions of the setup and of data fitting is reported in previous works. [32,33]

Before each analysis, the membrane was flushed at both sides with two argon streams until that a sufficiently stable signal was detected by the MS. In one set of experiments, the argon flux at the feed side was replaced by a $CO_2/CH_4$ (35/65 v/v) mixture, and the feed pressure was stepwise changed from 1 to 5 bar (g) and back. In each step, the feed pressure was maintained constant for sufficiently long time intervals to reach steady state permeation. In the second set of experiments, the feed composition was changed from 10 to 50 % of $CO_2$.

**Table SI 6:** Mixed gas permeability and selectivity of PIM-SBF-1 and PIM-SBF-5 as a function of the feed pressure with a mixture of 35 vol.% $CO_2$ in $CH_4$ and argon as a sweeping gas.

| PIM-SBF-1 | | | | PIM-SBF-5 | | | |
|---|---|---|---|---|---|---|---|
| | **Permeability** | | | | **Permeability** | | |
| **Total pressure (bar(a))** | **$CH_4$ (Barrer)** | **$CO_2$ (Barrer)** | **$CO_2/CH_4$ selectivity (-)** | **Total pressure (bar(a))** | **$CH_4$ (Barrer)** | **$CO_2$ (Barrer)** | **$CO_2/CH_4$ selectivity (-)** |
| 1.02 | 95.0 | 3170 | 33.3 | 1.01 | 853 | 12400 | 14.5 |
| 2.00 | 90.8 | 2900 | 32.0 | 1.99 | 945 | 11700 | 12.4 |
| 3.00 | 89.9 | 2780 | 30.9 | 2.99 | 932 | 11100 | 11.9 |
| 4.00 | 89.8 | 2700 | 30.0 | 3.99 | 921 | 10600 | 11.5 |
| 5.00 | 90.1 | 2610 | 28.9 | 4.99 | 904 | 10200 | 11.3 |
| 6.00 | 91.2 | 2540 | 27.9 | 5.99 | 900 | 9850 | 10.9 |
| 5.50 | 92.5 | 2600 | 28.1 | 5.49 | 905 | 10000 | 11.1 |
| 4.50 | 93.5 | 2700 | 28.8 | 4.49 | 917 | 10600 | 11.5 |
| 3.50 | 93.6 | 2790 | 29.8 | 3.49 | 932 | 1100 | 11.8 |
| 2.50 | 93.9 | 2910 | 30.9 | 2.49 | 941 | 11600 | 12.3 |
| 1.50 | 93.8 | 3000 | 32.0 | 1.49 | 951 | 12300 | 13.0 |
| 1.02 | 92.0 | 3040 | 33.1 | 1.01 | 913 | 12700 | 13.9 |

## S4. References

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