Supplementary Information (SI) for Journal of Materials Chemistry A.
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Supporting Information for:

π-Extended Dihydrophenazine Based Redox Responsive Polymers of Intrinsic Microporosity

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Keywords: PIMs, dihydrophenazine, gas separation, membranes

Summary

1. General Remarks

1.1 Instrumentation

Thin layer chromatography (TLC) was conducted on Sigma Aldrich pre-coated aluminum sheets (0.25 mm layer thickness, 60 Å porosity and fluorescent indicator GF254) and were visualized using 254 or 365 nm light. Flash column chromatography was carried out using Merck Gerduran silica gel 60 (particle size 40-63 µm). ***Melting points*** (M.P.) were measured on a Gallenkamp apparatus. All of melting points have been measured in open capillary tubes and have not been corrected. ***Nuclear magnetic resonance*** (NMR) ^{1}H, and ^{13}C spectra were obtained on Varian Inova spectrometer (500 MHz ^{1}H, 126 MHz ^{13}C and 50.66 MHz ^{15}N) or Varian 400 MHz NMR spectrometer (400 MHz ^{1}H, 101 MHz ^{13}C and 376 MHz ^{19}F). Chemical shifts were reported in ppm according to tetramethylsilane using the solvent residual signal as an internal reference ($CDCl_3$: $\delta_H = 7.26$ ppm, $\delta_C = 77.16$ ppm, CD_2Cl_2: $\delta_H = 5.32$ ppm, $\delta_C = 53.84$ ppm, MeOD: $\delta_H = 3.31$ ppm, $\delta_C = 49.00$ ppm, CD_3CN: $\delta_H = 1.94$ ppm, $\delta_C = 1.32$, 118.26 ppm, DMSO-*d6*: $\delta_H = 2.50$ ppm, $\delta_C = 39.52$ ppm). Coupling constants (*J*) were given in Hz. Resonance multiplicity was described as s (singlet), d (doublet), t (triplet), m (multiplet), br (broad signal), dd (doublet of doublets), dt (doublet of triplets). Carbon spectra were acquired with a complete decoupling for the proton, unless specified. All spectra were recorded at 25 °C unless specified. ^{1}H-^{15}N HMBC spectra were recorded at 50.664 MHz a ^{15}N spectral width of -200 to 0 ppm (reference $MeNO_2$) and a multiple bond Jnxh of 5 Hz. **Solid-state ^{13}C NMR spectra** were recorded using a Bruker Avance III spectrometer equipped with a wide-bore 9.4 T magnet (Larmor frequencies of 100.9 MHz for ^{13}C). Samples were packed into standard zirconia rotors with 4 mm outer diameter and rotated at a magic angle spinning (MAS) rate of 12.5 kHz. Spectra were recorded with cross polarization (CP) from ^{1}H using a contact pulse (ramped for ^{1}H) of 1.5 ms. High-power ($\nu_1 \approx 100$ kHz) TPPM-15 decoupling of ^{1}H was applied during acquisition to improve resolution. Signal averaging was carried out for 6144 transients with a recycle interval of 2 s. Chemical shifts are reported in ppm relative to $(CH_3)_4Si$ (TMS) using the CH_3 signal of L-alanine ($\delta = 20.5$ ppm) as a secondary solid reference. ***Infrared spectra*** (IR) were recorded on a Shimadzu IR Affinity 1S FTIR spectrometer in ATR mode with a diamond mono-crystal. Selected absorption bands are reported in wavenumber (cm^{-1}). ***ESI-High resolution mass spectrometry*** (ESI-HRMS). ESI-HRMS was performed at University of Trieste Chemistry department, High resolution mass spectra (HRMS) were obtained on Bruker micrOTOF-Q (ESI-TOF). ***Photophysical analysis***: Absorption spectra of compounds were recorded on air equilibrated solutions at room temperature with an Agilent Cary 5000 UV-Vis spectrophotometer, using quartz cells with path length of 1.0 cm. **Thermal gravimetric analysis**: TGAs were performed using the Perkin Elmer Thermal Analyzer STA 6000 at a heating rate of 10 °C/min from 30 to 995 °C. SEM images were recorded with a Hitachi S-4800 field emission (~1 nm resolution). **Gas adsorption and porosity analysis**: Low temperature N_2 (77 K and 298 K) and CO_2 (195 K, 273 K and 298 K) adsorption/desorption measurements of polymer powders were made using a Anton Paar Nova 600. Samples were degassed over 8 h at 80 °C under high vacuum prior to analysis. The gases were supplied by BOC and used without any further purification (N_2 purity > 99.999, CO_2 purity > 99.995%. The data were analyzed with the software Kaomi for Nova provided with the instrument. The BET surface area was calculated form the N_2 isotherms at a relative pressure P/P0 <

0.1. NLDFT analysis was performed to calculate the pore size distribution and volume, considering a carbon equilibrium transition kernel from CO_2 isotherms at 273 K based on a slit-pore model; the kernel is based on a common, one center, Lennard-Jones model. Heats of adsorption were calculated from the CO_2 curves measured at 273 K and 298 K. The data were analyzed with the Anton Paar Kaomi software and fitted with the Langmuir-Freundlich equation and calculated via the Clausius-Clapeyron equation. **Scanning Electron Microscopy**: (SEM) analysis iSEM images were recorded with a Hitachi S-4800 field emission (~1 nm resolution**)**. **IAST Selectivity Calculation**: The ideal adsorption solution theory (IAST) of Myers and Prausnitz1 is typically used to calculate the selectivity of binary mixtures of gases from the single isotherms. The isotherms were fitted with Dual-Site Langmuir-Freundlich using the software IAST++ 2 and the selectivity (S) was calculated according to the formula:

$$S = \frac{Q_{CO_2}}{Q_{N_2}} \times \frac{P_{N_2}}{P_{CO_2}}$$

Where

P_{CO2} is the partial pressure of CO_2

P_{N2} is the partial pressure of N_2

Q_{N2} is the N_2 uptake

Q_{CO2} is the CO_2 uptake

Pure gas permeation measurement: Permeation tests were carried out at 25 °C and at 1 bar of feed gas pressure on a fixed volume/pressure increase instrument, designed by Helmholz Zentrum Geesthacht and constructed and customized by Elektro & Elektronik Service Reuter (Geesthacht,Germany). Prior to the permeability measurements, the films were soaked in methanol for 24 h to remove residual solvent and then dried for 24 h in air. The samples were evacuated and degassed for at least 1 h before the measurements, and the baseline evaluated with preliminary O_2 permeation tests. Between two consecutive measurements, the membrane is evacuated by a turbomolecular pump for at least ten times the time lag of the previously measured gas, in order to guarantee a complete degassing. 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.

AFM Force spectroscopy: A Multimode 8 AFM system equipped with a Nanoscope V controller was employed to perform the mechanical properties. The measurements were performed at room temperature using a cantilever with an elastic constant of 25 N m^{-1} and a spherical colloidal tip with a nominal radius of 2 µm. In order to ensure statistical relevance, as described in previous studies[1,2] 60 force–distance (FD) curves were collected per each membrane in three distinct regions with a scan rate of ca 400 nm s^{-1}. The Young's modulus was determined fitting each individual FD curve with the Hertz model. Data analysis was performed using NanoScope Analysis 1.5 software, and statistical evaluation was carried out with Microsoft Excel.

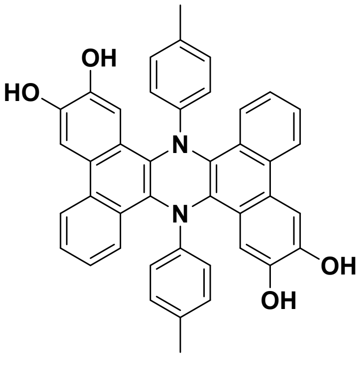
1.2 Materials and methods

Chemicals were purchased from Sigma Aldrich, TCI, Alfa Aesar and Fluorochem and were used as received unless otherwise stated. Solvents were purchased from Sigma Aldrich and Alfa Aesar, while deuterated solvents from Eurisotop and Sigma Aldrich. Anhydrous conditions were achieved by repeated cycles of flaming with a heat gun under vacuum and purging with Argon (Ar). The inert atmosphere was maintained using Argon-filled balloons equipped with a syringe and needle that was used to penetrate the silicon stoppers used to close the flask's necks. Additions of liquid reagents were performed using plastic syringes. Degassing of solutions was performed by bubbling argon in the reaction under sonication for at least 10 minutes or alternatively by 3 freeze pump thaw cycles. The latter were performed by freezing the solution with liquid N_2 and keeping the frozen solvent under vacuum for 5 to 10 min., followed by thawing. Dry solvents were obtained commercially or via treatment on activated molecular sieves. Activation of MS was carried out by multiple cycles of heating under vacuum and the solvents were left over MS for at least 24 h. MilliQ water was obtained from a Millipore Milli-Q Plus 185 apparatus and presented a resistivity of 18.2 MΩcm. MilliQ water was always used unless otherwise specified. K_2CO_3 for polymer synthesis was stored at 80°C in an oven. Dihydrophenazine **1** was synthesized according to a published literature procedure.[3] ^1H-^{15}N HMBC for **1** was recorded in DMSO-*d6* resulting in a ^{15}N chemical shift of δ: -94.30.

All the gases used for pure gas permeation tests, H_2, He, CO_2, N_2, CH_4, and O_2, were supplied by Sapio at a minimum purity of 99.9995%.

2 Synthetic procedures and spectral data

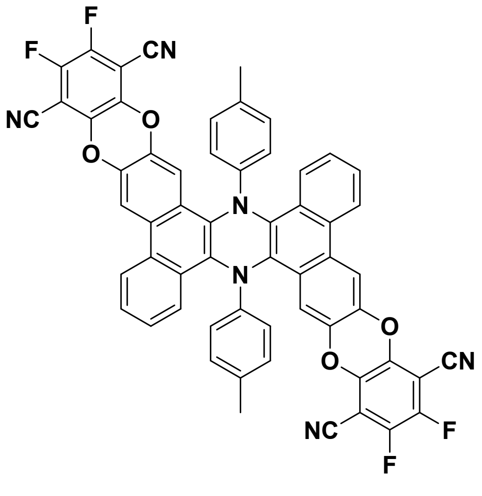
2.0 Synthesis of 2



In a double necked flask, 9-Bromo-2,3-dimethoxyphenanthrene (1.42 g, 4.5 mmol), toluidine (528 mg, 4.92 mmol), $Pd_2(dppf)Cl_2$ (164 mg, 0.22 mmol) and dppf (122 mg, 0.22 mmol) were added and purged with Ar (3 × vacuum/Ar cycles). Anhydrous toluene (20 ml) was then added, and the resulting suspension degassed for 10 min. with Ar bubbling and sonication. NaOtBu (947 mg, 9.86 mmol) was then added in one portion under Ar and the reaction degassed for further 10 min. The resulting dark suspension was then placed in a preheated silicon oil bath at 100°C and stirred for 2 h at the same temperature. At this point, a compressed air inlet equipped with a 12 cm needle was used to bubble air (passed on a column filled with drierite™) in the reaction solution at 100°C for 2 h. After complete conversion of the intermediate from the previous step, the reaction was diluted with PE (100 mL) and filtered on a silica plug (PE 100% to CH_2Cl_2 100%). The obtained material was transferred in a 100 mL single necked round bottom flask and dissolved in CH_2Cl_2 (20 mL) under Ar. The solution was cooled to 0°C, DDQ (586 mg, 2.58 mmol) added in one portion and the black reaction stirred at r.t. for 2 h. The resulting suspension was diluted with CH_2Cl_2 (50 mL) and filtered on a silica plug using CH_2Cl_2 as eluent. The organic phase was evaporated and the resulting solid (1.1g) directly added in a single necked flask and dissolved in CH_2Cl_2 (40 mL). The reaction was then cooled to 0°C and BBr_3 (9.66 mL, 1.0 M in CH_2Cl_2) slowly added. The reaction was then allowed to react r.t. and stirred for 1 h. The reaction was then slowly quenched by slow addition of H_2O and diluted with EtOAc (100 mL). The resulting mixture was then washed with H_2O (100 mL × 2), an aq. Solution of $Na_2S_2O_4$ (1g × 100 mL) followed by brine (50 mL × 1). The organic solution was then dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was finally purified by reprecipitation from CH_2Cl_2 (3 ×, 6000 rpm, 2 min.) to afford **2** as a grey powder (474 mg, 34%, respectively to the phenanthrene).

^{1}H NMR (400 MHz, CD_3CN) δ: 8.63 (d, *J* = 7.8 Hz, 2 H), 8.30 (dd, *J* = 7.4 Hz, 2 H), 8.20 (s, 2 H), 7.77 (s, 2 H), 7.69-7.62 (m, 4 H), 7.40 (s, 2 H), 7.27 (s, 2 H), 6.71 (d, *J* = 8.3 Hz, 4 H), 6.51 (d, *J* = 8.7 Hz, 4 H), 2.05 (s, 6 H). ^{13}C NMR (101 MHz, DMSO-*d6*) δ 147.30, 147.19, 145.03, 139.92, 137.33, 128.83, 128.52, 128.45, 127.71, 126.38, 125.76, 124.15, 123.91, 123.54, 122.90, 114.50, 108.13, 107.94, 19.84. ^{1}H-^{15}N HMBC (50.664 MHz, DMSO) δ: -93.15. IR (ATR) ν (cm^{-1}): 3339, 3028, 2907, 1611, 1537, 1503, 1441, 1337, 1260, 1159, 1040, 868, 808, 777, 760, 743, 584, 538, 480. ESI-HRMS: $[M+Na]^+$ calc. for $[C_{42}H_{30}N_2O_4Na]^+$: 649.2098; found 649.2097.

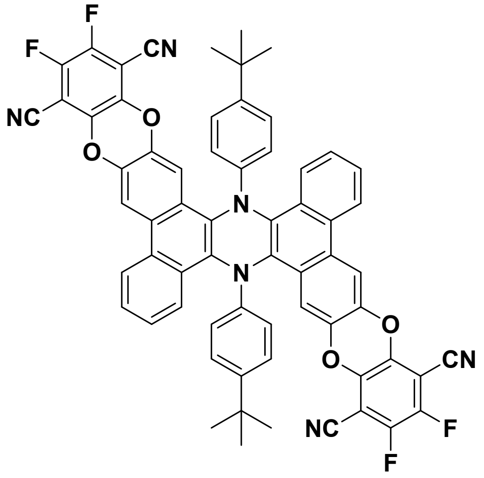
2.1 Synthesis of 4



In a flame dried Schlenk tube **5** (24 mg, 0.12 mmol) was added together with **2** (25 mg, 0.04 mmol). The solids were purged 3 times with vacuum and Ar and then dry DMF (2 mL) was added followed by 3 freeze-pump-thaw cycles. Anhydrous K_2CO_3 (23 mg, 0.17 mmol) was then added, and the reaction was immediately placed in a pre-heated oil bath at 60°C followed by stirring at the same temperature for 4 h. After this time, the reaction was dropped in H_2O (10 mL) filtered (0.45 µm PTFE) and washed with ACN and Et_2O. The residue was then purified on a silica plug (CH_2Cl_2 100%) to give **4** as a yellow solid (37 mg, qnt.).

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.57 (d, *J* = 8.3 Hz, 2 H), 8.53 (d, *J* = 8.1 Hz, 2 H), 8.39 (s, 2 H), 8.05 (s, 2 H), 7.83 (t, *J* = 7.5 Hz, 2 H), 7.77 (t, *J* = 7.6 Hz, 2 H), 6.66 (d, *J* = 8.5 Hz, 4 H), 6.43 (d, *J* = 8.6 Hz, 4 H), 2.07 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.32 (d, *J* = 268.1 Hz, 1 C), 145.17, 142.71, 140.77 (m, 1 C), 140.43, 139.12, 138.73, 130.88, 129.98, 129.24, 128.82, 128.55, 128.31, 125.32, 123.31, 115.35, 111.78, 111.15, 107.89 (d, *J* = 11.1 Hz, 1 C), 106.03, 100.09, 20.37. ^{1}H-^{15}N HMBC (50.664 MHz, $CDCl_3$) δ: -94.60. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -134.14. IR (ATR) ν (cm^{-1}): 3034, 2926, 2866, 2241, 1612, 1501, 1472, 1450, 1414, 1358, 1306, 1261, 1202, 1013, 991, 949, 912, 883, 808, 797, 777, 760, 718, 650, 453, 419, 407. Product does not ionize enough for ESI-MS analysis.

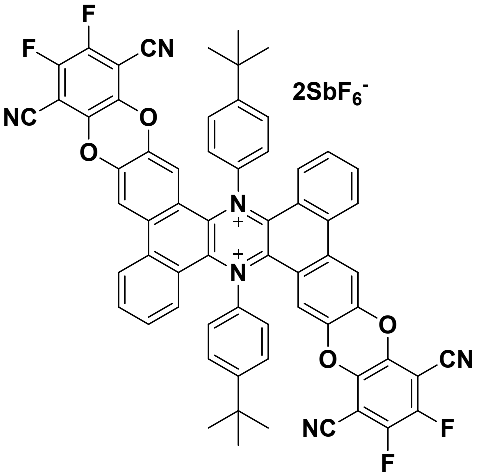
2.2 Synthesis of 3



In a flame dried Schlenk tube **5** (84 mg, 0.42 mmol), **1** (100 mg, 0.14 mmol) and K_2CO_3 (78 mg, 0.56 mmol) were added, the solids were purged 3 times with vacuum and Ar and then dry DMF (4 mL) was added followed by 3 freeze-pump-thaw cycles. The reaction was immediately placed in a pre-heated oil bath at 60°C followed by stirring at the same temperature for 4 h. After this time, the reaction was evaporated under reduced pressure and filtered on a silica plug (CH_2Cl_2 100%), followed by reprecipitation from MeOH, affording **3** as a yellow powder (145 mg, 99%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ: 8.62 (dd, *J* = 7.2, 2.3 Hz, 2 H), 8.58 (d, *J* = 7.2 Hz, 2.3 Hz, 2 H), 8.45 (s, 2 H), 8.12 (s, 2 H), 7.80 (m, 4 H), 6.84 (d, *J* = 9.0 Hz, 4 H), 6.46 (d, *J* = 9.0 Hz, 4 H), 1.06 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.02 (ddd, *J* = 262.4, 15.8, 5.8 Hz, 1 C), 145.43, 143.45, 143.18, 140.83, 140.8 (m, 1C), 139.14, 138.72, 131.03, 129.37, 128.76, 128.57, 128.23, 127.91, 125.32, 125.26, 123.27, 115.31, 111.75, 111.11, 107.91 (d, *J* = 11.8 Hz), 97.03 (m, 1C), 33.85, 31.34. ^{1}H-^{15}N HMBC (50.664 MHz, $CDCl_3$) δ: -95.30. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -134.18. IR (ATR) ν (cm^{-1}): 3070, 2961, 2866, 2245, 1612, 1512, 1476, 1450, 1412, 1358, 1308, 1261, 1236, 1198, 1169, 1011, 988, 949, 887, 814, 775, 764, 434, 419. Product does not ionize enough for ESI-MS analysis.

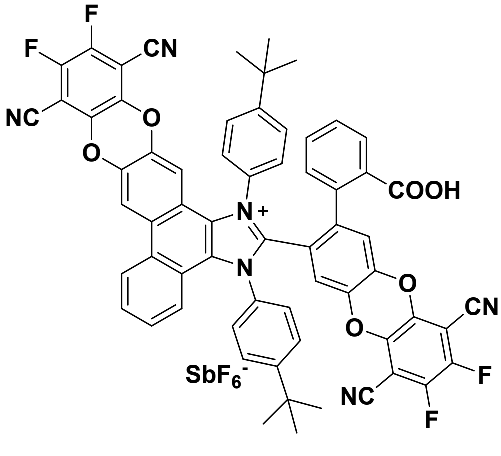
2.3 Synthesis of 3^{2+}

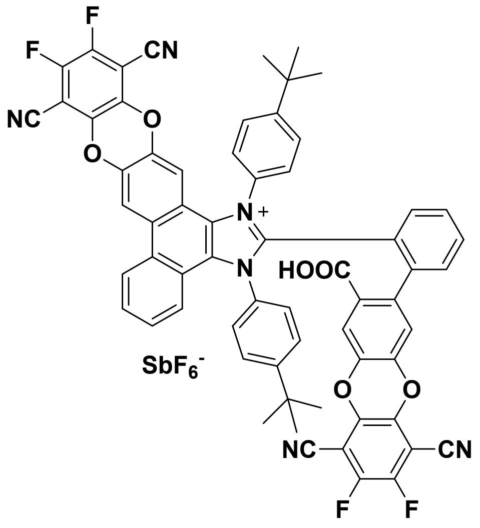


3 mg of **3** are added in a screw cap glass vial and dissolved in anhydrous DCE (1 mL). An excess of $NOSbF_6$ was then added under Ar followed by 2 min of sonication with Ar bubbling. The resulting dark green solution was then left standing under Ar for 30 min followed by evaporation under reduced pressure. The dark green residue was dissolved in CD_2Cl_2 and directly analyzed *via* NMR.

^{1}H NMR (500 MHz, CD_2Cl_2) δ: 8.43 (d, *J* = 8.2 Hz, 2H), 8.19 (s, 2H), 7.95 (t, *J* = 7.7 Hz, 2H), 7.86 – 7.81 (m, 4H), 7.77 (dd, *J* = 8.9, 2.6 Hz, 2H), 7.69 (dd, *J* = 8.9, 2.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 2H), 6.64 (s, 2H), 1.47 (s, 18H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 160.05, 144.55, 142.07, 139.65, 139.07, 135.87, 135.78, 134.18, 130.19, 130.08, 128.87, 128.16, 127.96, 125.25, 120.05, 118.28, 117.83, 113.01, 106.78, 43.91, 35.74, 30.91. (Some signals not visible due to F coupling and dilution). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -131.19 (d, *J* = 20.4 Hz), -132.16 (d, *J* = 20.4 Hz).

2.4 Synthesis of 3^{deg}





In a found bottom flask, **3** (50 mg, 0.05 mmol) is dissolved in anhydrous DCE (5 mL). $NOSbF_6$ (29 mg, 0.11 mmol) is then added, and the dark green solution is sonicated with Ar bubbling for 10 min, followed by stirring for 1 h. The solution is then diluted with ACN (10 mL) and H_2O (0,1 mL) followed by stirring for 1h.

Evaporation and reprecipitation from CH_2Cl_2/PE 1/1 affords clean **3^{deg}** as a pale solid (60 mg, 92%). The sample is composed by a mixture of isomers.

^{1}H NMR (500 MHz, DMSO-*d6*) δ: 9.13-9.10 (m, 1H), 8.90 (d, *J* = 5.8 Hz, 1H), 8.19-6.13 (m, 18H), 1.38 (s, 18H). ^{13}C NMR (126 MHz, DMSO-*d6*) δ: 166.70, 164.66, 148.13, 146.30, 146.00, 143.98, 140.93, 140.70, 140.67, 140.53, 140.52, 140.34, 139.95, 139.74, 139.61, 139.09, 138.92, 137.76, 136.38, 136.02, 134.28, 132.48, 132.29, 132.07, 131.84, 129.37, 129.13, 129.05, 128.80, 128.69, 127.91, 127.82, 127.57, 127.46, 127.36, 127.32, 126.13, 125.75, 121.54, 121.48, 121.17, 120.65, 119.83, 119.80, 119.68, 119.32, 118.95, 118.38, 118.36, 116.07, 115.09, 112.64, 112.59, 108.37, 108.08, 95.65, 34.98, 31.00, 30.95, 30.92. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -136.37, -136.56, -136.61, -136.71, -136.96, -137.01, -137.11, -137.17, -148.37. ESI-HRMS: $[M]^+$ calc. for $[C_{64}H_{39}F_4N_6O_6]^+$: 1063.2862; found 1063.2861.

2.5 Synthesis of Phen-PIM-2

In a flame dried Schlenk tube, **5** (128 mg, 0.64 mmol) was added together with **2** (400 mg, 0.64 mmol). The solids were purged 3 times with vacuum and Ar, and then dry DMF (22 mL) was added followed by 3 freeze-pump-thaw cycles. Anhydrous K_2CO_3 (370 mg, 2.7 mmol) was then added, and the reaction was immediately placed in a pre-heated oil bath at 65°C followed by stirring at the same temperature for 70 h. After this time, the reaction was dropped in H_2O (100 mL) and filtered on a 0.45 µm PTFE filter. The obtained solid was then washed with H_2O (200 mL), MeOH (100 mL), Acetone (100 mL), THF (100 mL) and Et_2O (100 mL) After the complete procedure 415 mg of a yellow/brown powder are obtained, corresponding to an 87% yield.

The sample used for BET analysis was further purified by stirring at 80 °C for 1h in 10 mL DMF, followed by filtration on a 0.45 µm PTFE filter and washing with DMF (10 mL) and THF (10 mL). Then by stirring at 80 °C for 1h in 10 mL THF, followed by filtration on a 0.45 µm PTFE filter and washing with THF (10 mL) and $CHCl_3$ (10 mL). Then by stirring at 80 °C for 1h in 10 mL $CHCl_3$, followed by filtration on a 0.45 µm PTFE filter and washing with $CHCl_3$ (10 mL) and MeOH (10 mL). And finally, by stirring at 80 °C for 18h in 10 mL MeOH, followed by filtration on a 0.45 µm PTFE filter and washing with MeOH (10 mL). After the complete procedure 323 mg of a yellow powder are obtained.

2.6 Synthesis of Phen-PIM-1

In a flame dried Schlenk tube, TFTPN (260.3 mg, 1.3 mmol) was added together with **1** (924.7 mg, 1.3 mmol). The solids were purged 3 times with vacuum and Ar, and then dry DMF (47 mL) was added followed by 3 freeze-pump-thaw cycles. Anhydrous K_2CO_3 (755 mg, 5.5 mmol) was then added, and the reaction was immediately placed in a pre-heated oil bath at 65°C followed by stirring at the same temperature for 70 h. After this time, the reaction was dropped in H_2O (250 mL), filtered on a 0.45 µm PTFE filter and subsequently washed with 100 mL MeOH. The resulting material was then transferred to a falcon tube and suspended with sonication in Acetone (50 mL), followed by centrifugation (6000 rpm, 10 min.). The same procedure was repeated with THF and Et_2O.

The sample used for BET analysis was further purified by stirring at 80 °C for 1h in 10 mL DMF, followed by centrifugation and washing with DMF (20 mL) and THF (10 mL). Then by stirring at 80 °C for 1h in 20 mL THF, followed by centrifugation and washing with THF (20 mL) and $CHCl_3$ (20 mL). Then by stirring at 80 °C for 1h in 20 mL $CHCl_3$, followed by centrifugation and washing with $CHCl_3$ (20 mL) and MeOH (20 mL). And finally, by stirring at 80 °C for 18h in 20 mL MeOH, followed by filtration on a 0.45 µm PTFE filter and washing with MeOH (20 mL). After the complete procedure 1.06 g of a yellow powder are obtained, corresponding to a 98% conversion by mass.

2.7 Synthesis of Phen-PIM-1^{ox}

In a flame dried Schlenk tube under Ar, **Phen-PIM-1** (100 mg) was added and placed under vacuum for 10 min. At this point Anhydrous DCE (5 mL) was added, and the resulting suspension sonicated for 5 min with Ar bubbling. $NOSbF_6$ (81 mg) was then added while sonicating and Ar bubbling was kept for a couple of minutes (reaction turns immediately dark green), followed by stirring at 500 rpm for 2h at r.t. under Ar. The reaction was then poured in a falcon, diluted to 8 mL with CH_2Cl_2 and 2 mL PE added. The suspension was then centrifuged for 5 min at 6000 rpm. Then again 8 mL CH_2Cl_2 and 2 mL PE were added, and the procedure repeated for a total of 3 times. The greenish material was suspended in CH_2Cl_2, evaporated and the resulting black powder kept under vacuum for 2h. A total of 150 mg (96% yield by mass) of **Phen-PIM-1^{ox}** were collected.

2.8 Synthesis of Phen-PIM-2^{ox}

In a flame dried Schlenk tube under Ar, **Phen-PIM-2** (100 mg) was added and placed under vacuum for 10 min. At this point Anhydrous DCE (5 mL) was added, and the resulting suspension sonicated for 5 min with Ar bubbling. $NOSbF_6$ (94 mg) was then added while sonicating and Ar bubbling was kept for a couple of minutes (reaction turns immediately dark green), followed by stirring at 500 rpm for 2h at r.t. under Ar. The reaction was then poured in a falcon, diluted to 8 mL with CH_2Cl_2 and 2 mL PE added. The suspension was then centrifuged for 5 min at 6000 rpm. Then again 8 mL CH_2Cl_2 and 2 mL PE were added, and the procedure repeated for a total of 2 times. The greenish material was suspended in CH_2Cl_2, evaporated and the resulting black powder kept under vacuum for 2h. A total of 163 mg (99% yield by mass) of oxidized **Phen-PIM-2^{ox}** were collected.

2.9 Synthesis of Phen-PIM-1^{deg}

In a flame dried Schlenk tube under Ar, **Phen-PIM-1** (200 mg) was added and placed under vacuum for 10 min. At this point, Anhydrous DCE (10 mL) was added, and the resulting suspension sonicated for 5 min with Ar bubbling. $NOSbF_6$ (162 mg) was then added while sonicating and Ar bubbling was kept for a couple of minutes (reaction turns immediately dark green), followed by stirring at 500 rpm for 2h at r.t. under Ar. The reaction was then evaporated under vacuum and suspended in 30 mL ACN containing 1 mL of H_2O, followed by stirring at r.t. for 18h. The reaction was then dropped in 1M NaCl (100 mL) and sonicated for 30 min. The resulting suspension was then filtered on a 0.45 µm PTFE filter and the residue washed with 50 mL MeOH and 100 mL Et_2O. For the BET measurement the sample was further purified by refluxing in MeOH (20 mL) for 6h followed by hot filtration on a 0.45 μm PTFE filter and washing with 100 mL Et_2O resulting in 201 mg (93% yield by mass) of **Phen-PIM-1^{deg}** as a beige solid.

2.10 Phen-PIM-1^{red} oxidation reduction

In a flame dried Schlenk tube under Ar, **Phen-PIM-1** (100 mg) was added and placed under vacuum for 10 min. At this point, Anhydrous DCE (5 mL) was added, and the resulting suspension sonicated for 5 min with Ar bubbling. $NOSbF_6$ (81 mg) was then added while sonicating and Ar bubbling was kept for a couple of minutes (reaction turns immediately dark green), followed by stirring at 500 rpm for 2h at r.t. under Ar. The reaction was then poured in a falcon, diluted to 10 mL with Et_2O and centrifuged for 5min at 6000 rpm. Then, again 10 mL Et_2O were added, and the procedure repeated for a total of 2 times. The residue was dried under vacuum and suspended in 20 mL CH_2Cl_2, and 100 mg PPh_3 added, and the reaction was sonicated for 15 min. under Argon. The reaction undergoes discoloration immediately. The resulting suspension was then left stirring under Ar for 18 h followed by filtration on a 0.45 μm PTFE filter after diluting with Et_2O (20 mL) followed by washing with MeOH (20 mL) and again H_2O (100 mL), MeOH (100 mL) and Et_2O (20 mL). Finally, the sample for the BET measures was refluxed in MeOH (20 mL) for 6h followed by hot filtration and wash with 20 mL Et_2O resulting in the isolation of 100 mg (100% yield by mass) of **Phen-PIM-1^{red}** as a yellow solid.

2.11 Preparation of Phen-PIM-1 self-standing defect free membrane

Phen-PIM-1 (0.5 g) was solubilized in NMP (20 mL). The solution was poured into a glass Petri dish (7 cm diameter), which was placed on top of a levelled hotplate and the temperature was raised to 50 °C. The Petri dish was covered with a large glass funnel to allow slow evaporation and avoid air drafts. After 5 days the film was formed, and it was soaked for 1 h into MeOH to wash traces of casting solvent. The MeOH treatment was repeated 3 times then the solvent was removed and the film allowed to dry at room temperature in a covered Petri dish.

3 NMR and HRMS spectroscopic characterization

3.1 Derivative 1

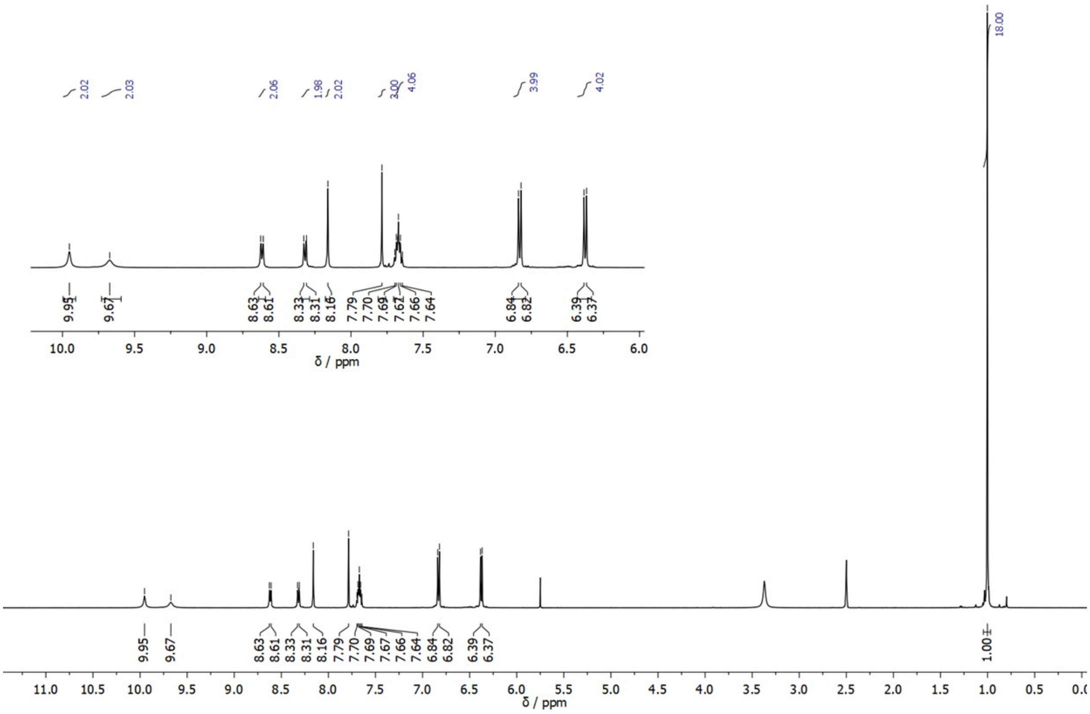


Figure S1. 500 MHz ^{1}H NMR of **1** in DMSO-*d6*.

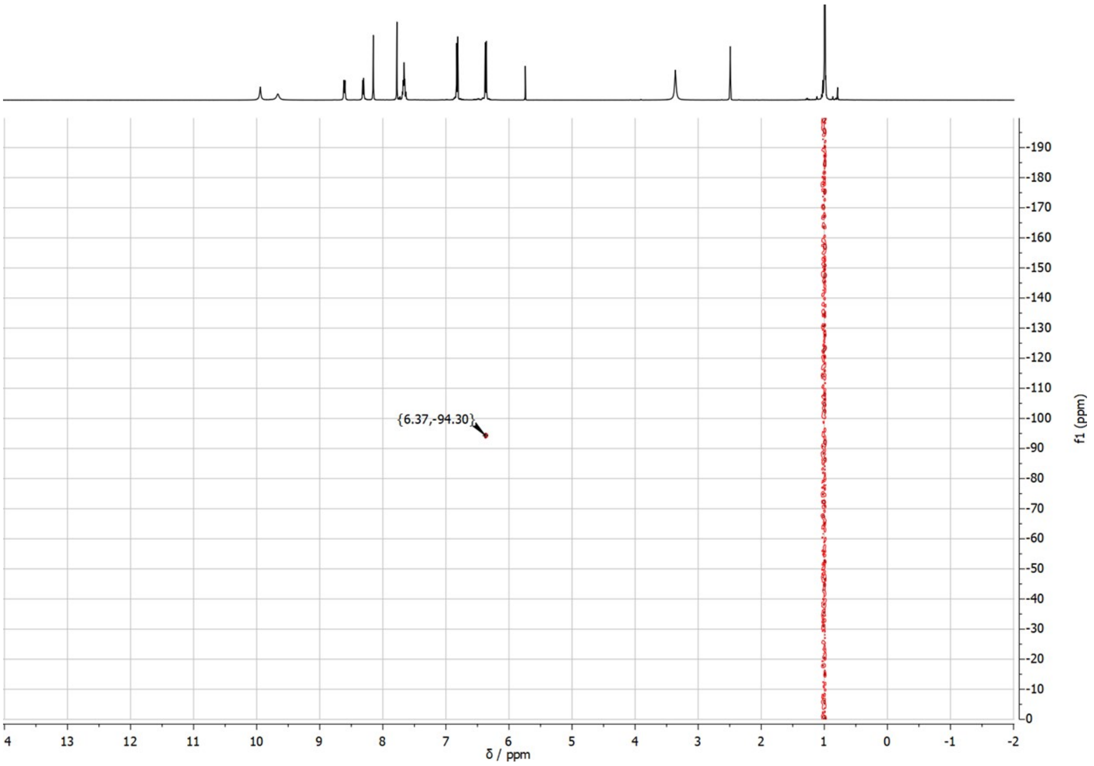


Figure S2. 50.664 MHz ^{1}H-^{15}N HMBC NMR of **1** in DMSO-*d6*.

3.2 Derivative 2

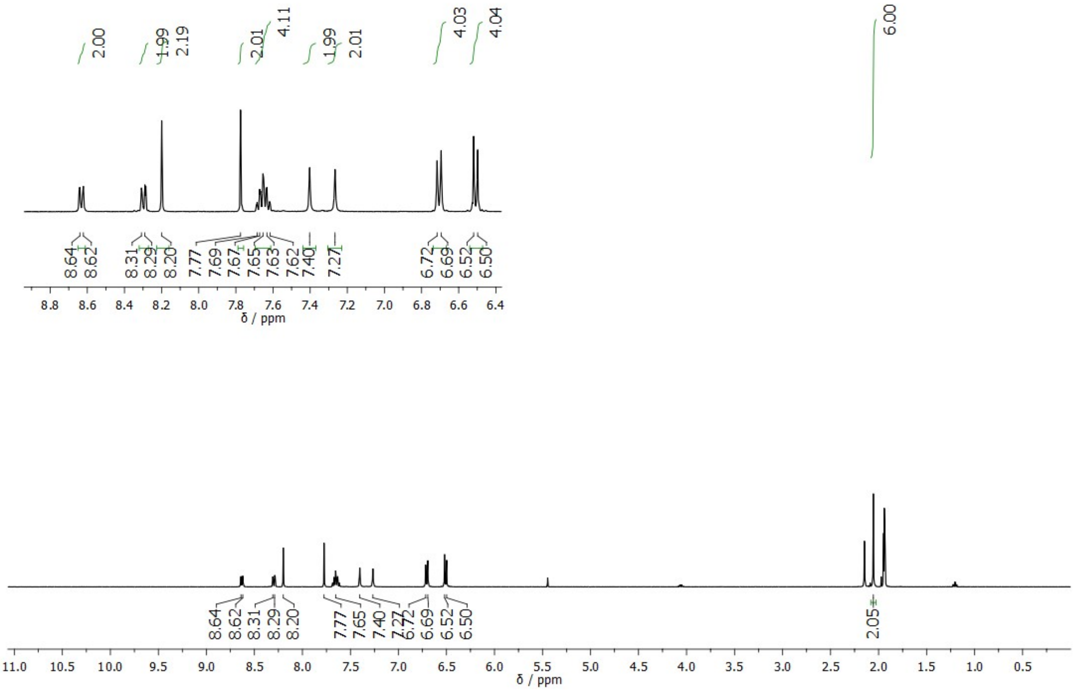


Figure S3. 400 MHz ^{1}H NMR of **2** in ACN.

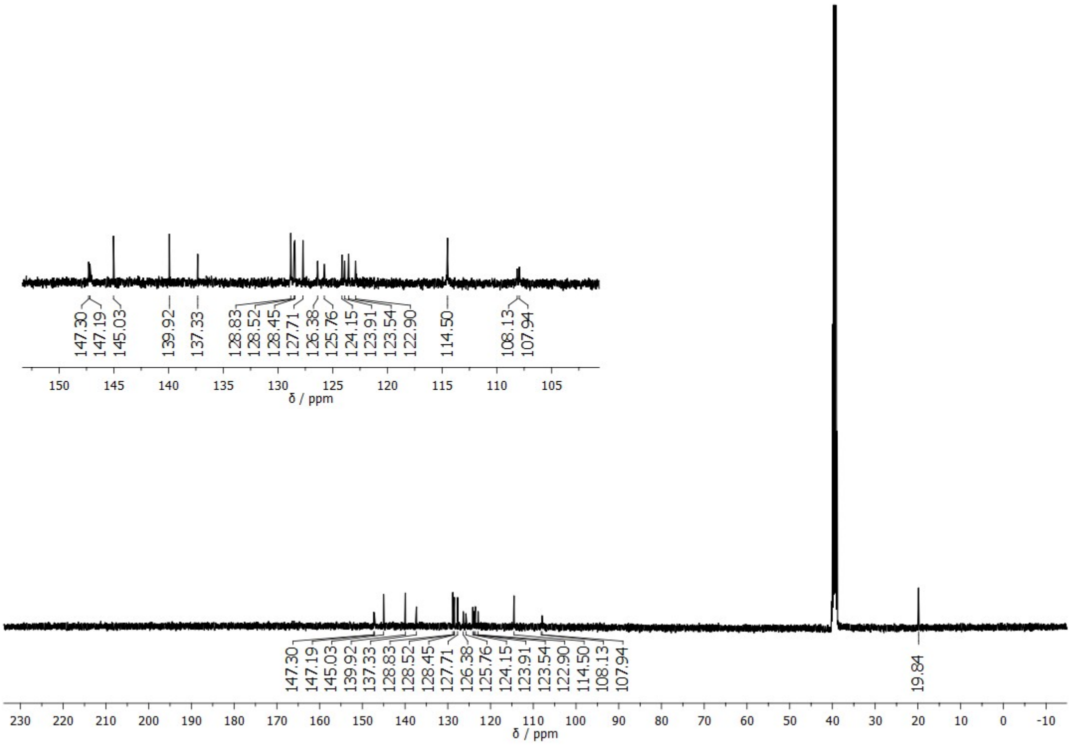


Figure S4. 101 MHz ^{13}C NMR of **2** in DMSO-*d6*.

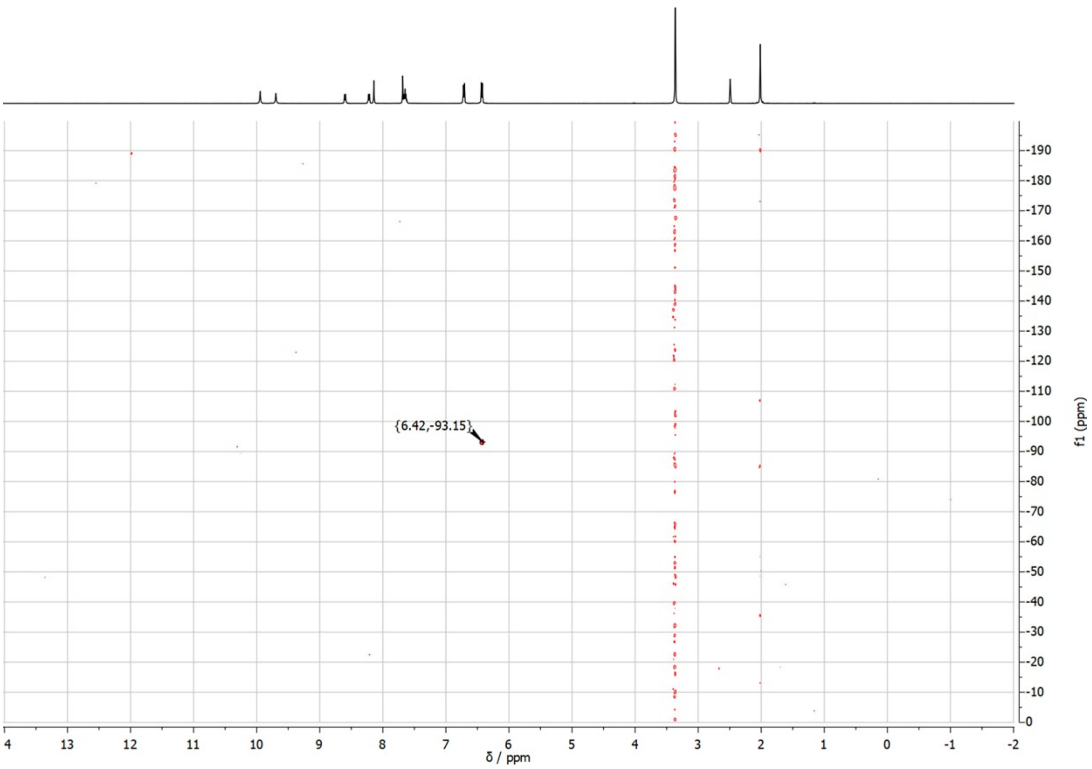


Figure S5. 50.664 MHz ^{1}H-^{15}N HMBC NMR of **2** in DMSO-*d6*.

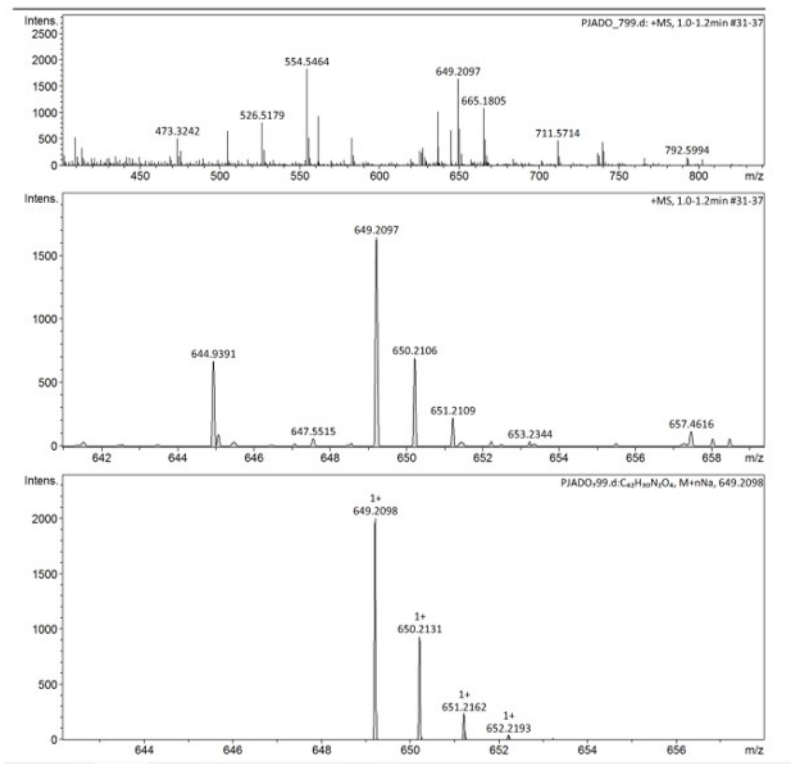


Figure S6. ESI-HRMS of **2**, top) full spectra, middle) zoom and bottom) simulated.

3.3 Derivative 4

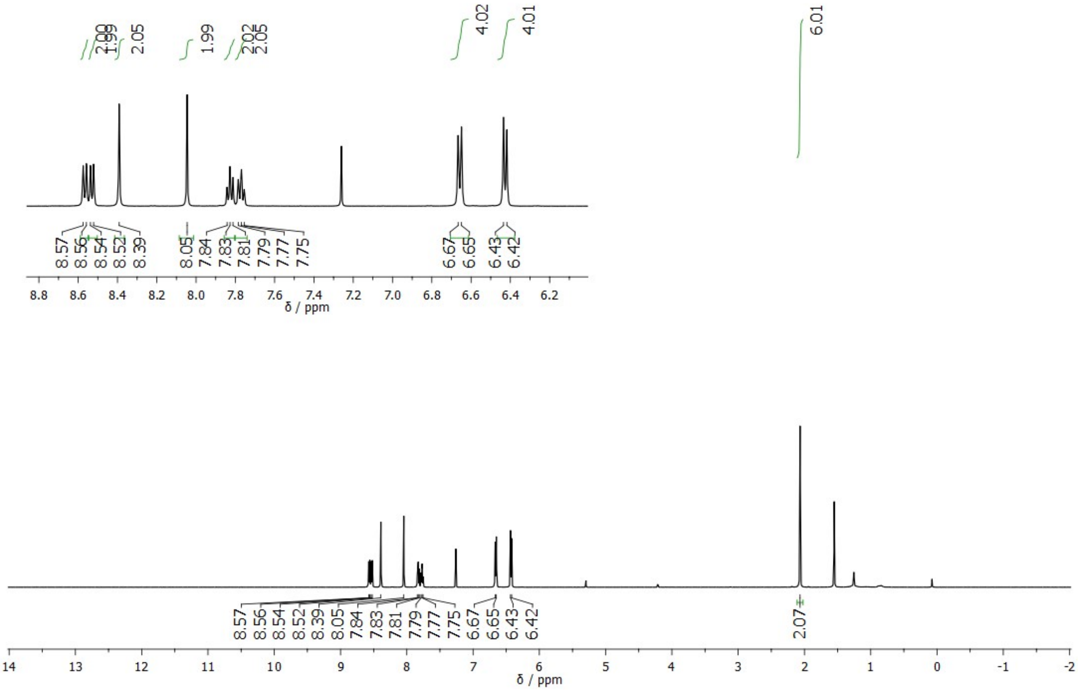


Figure S7. 500 MHz ^{1}H NMR of **4** in CDCl$_3$.

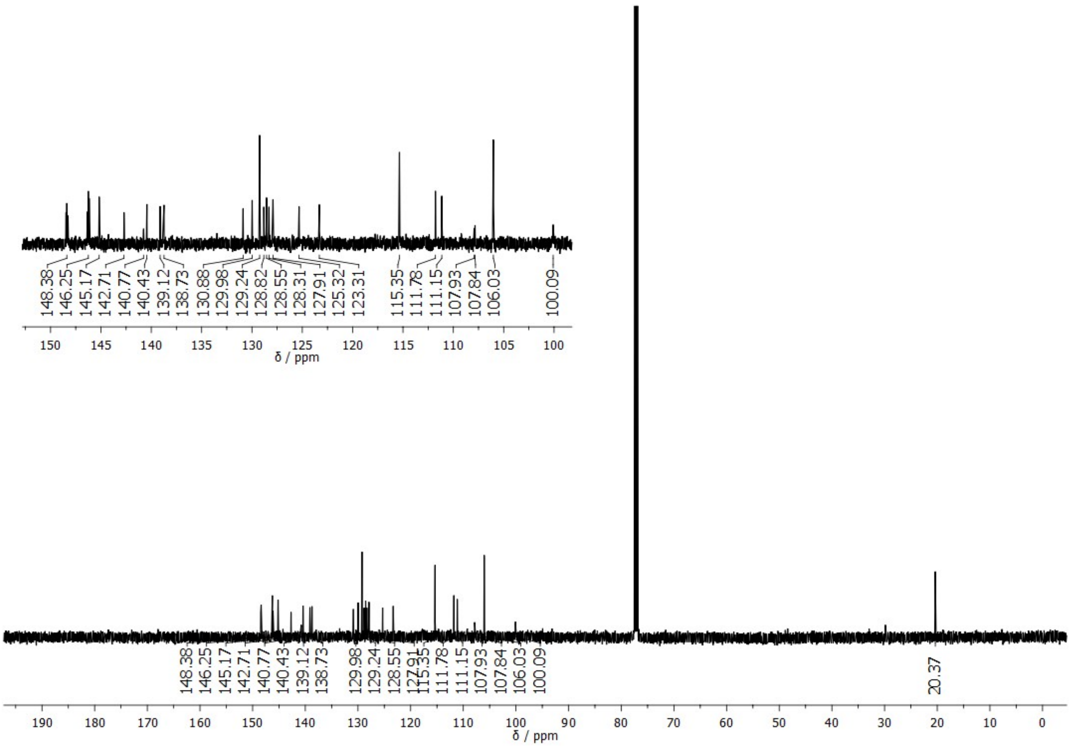


Figure S8. 126 MHz ^{13}C NMR of **4** in CDCl$_3$.

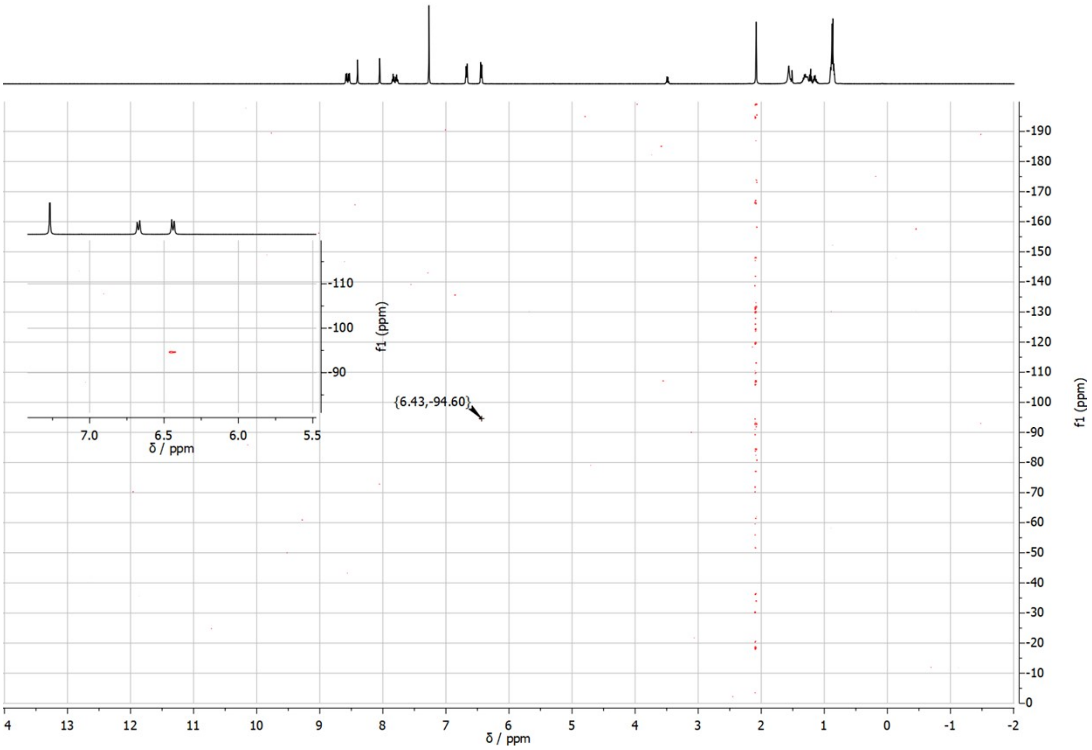


Figure S9. 50.664 MHz ^{1}H-^{15}N HMBC NMR of **4** in CDCl$_3$.

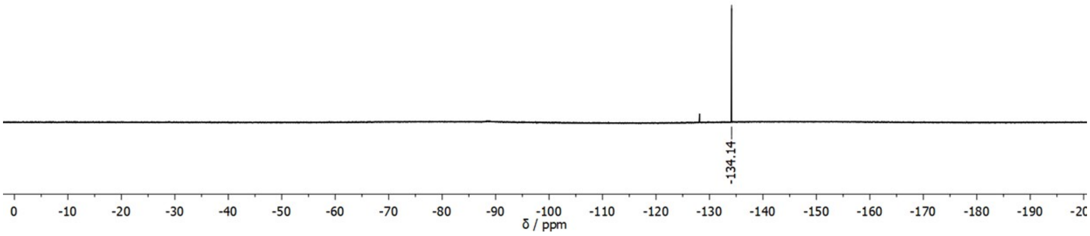


Figure S10. 377 MHz ^{19}F NMR of **4** in CDCl$_3$.

3.4 Derivative 3

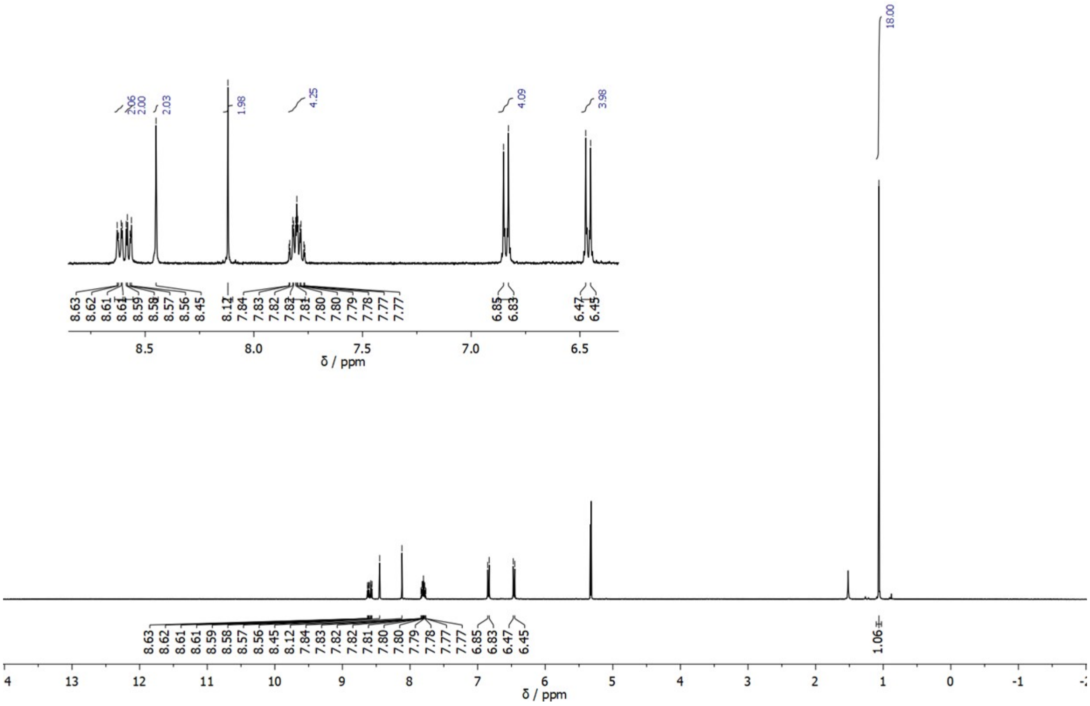


Figure S11. 400 MHz ^{1}H NMR of **3** in CD_2Cl_2.

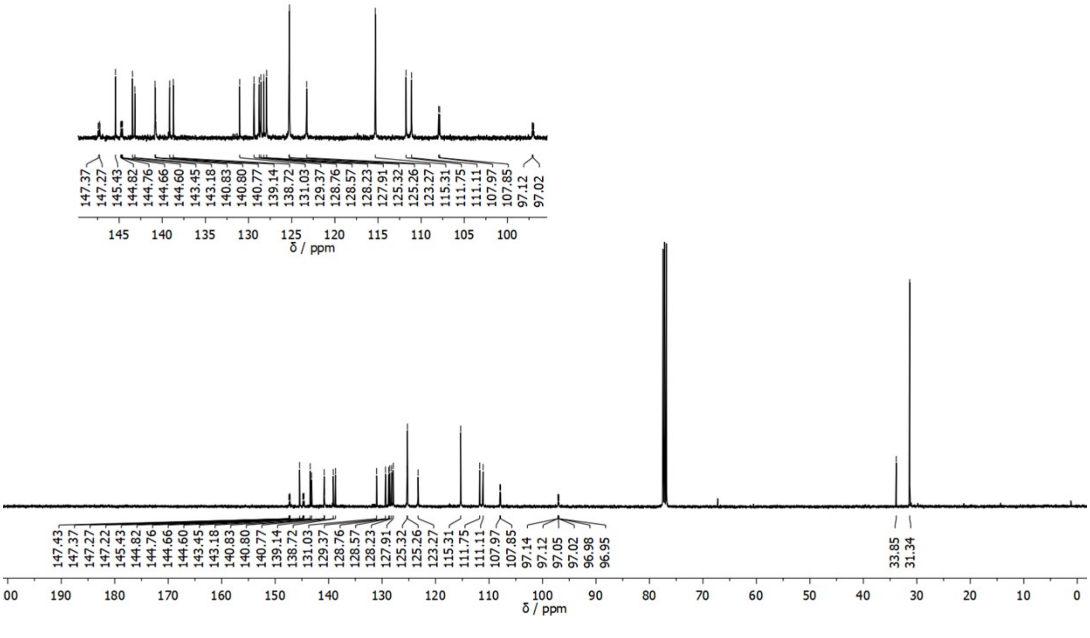


Figure S12. 101 MHz ^{13}C NMR of **3** in $CDCl_3$.

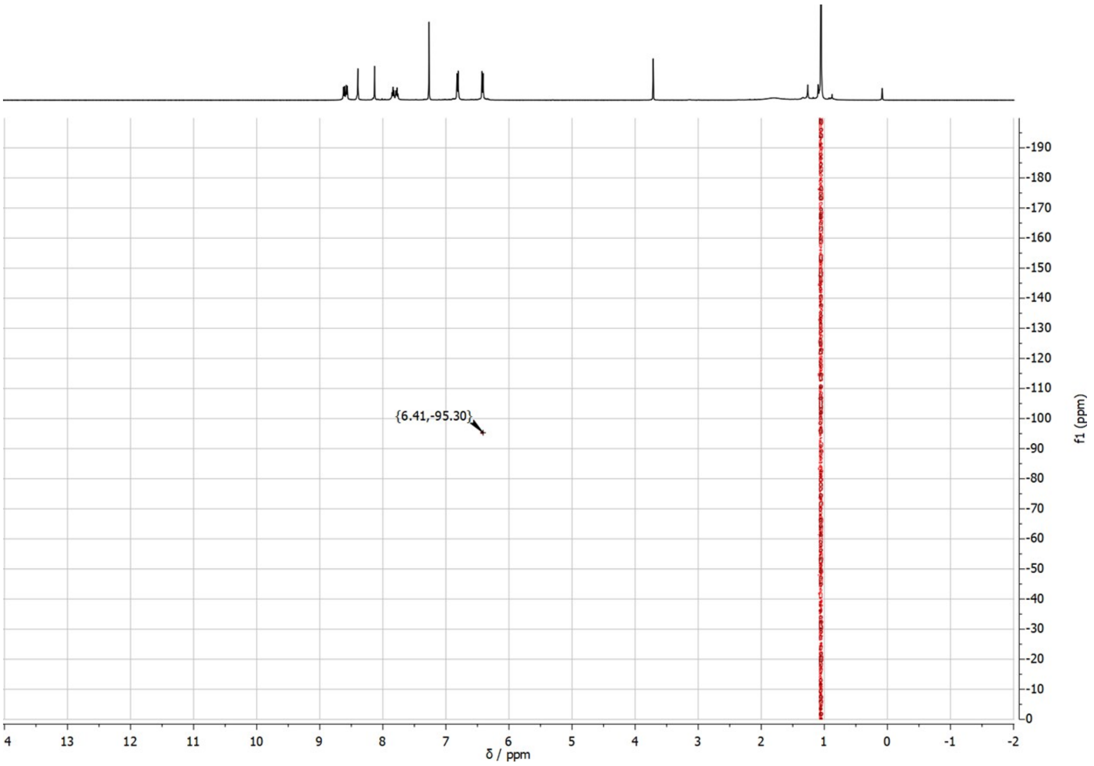


Figure S13. 50.664 MHz ^{1}H-^{15}N HMBC NMR of **3** in $CDCl_3$.

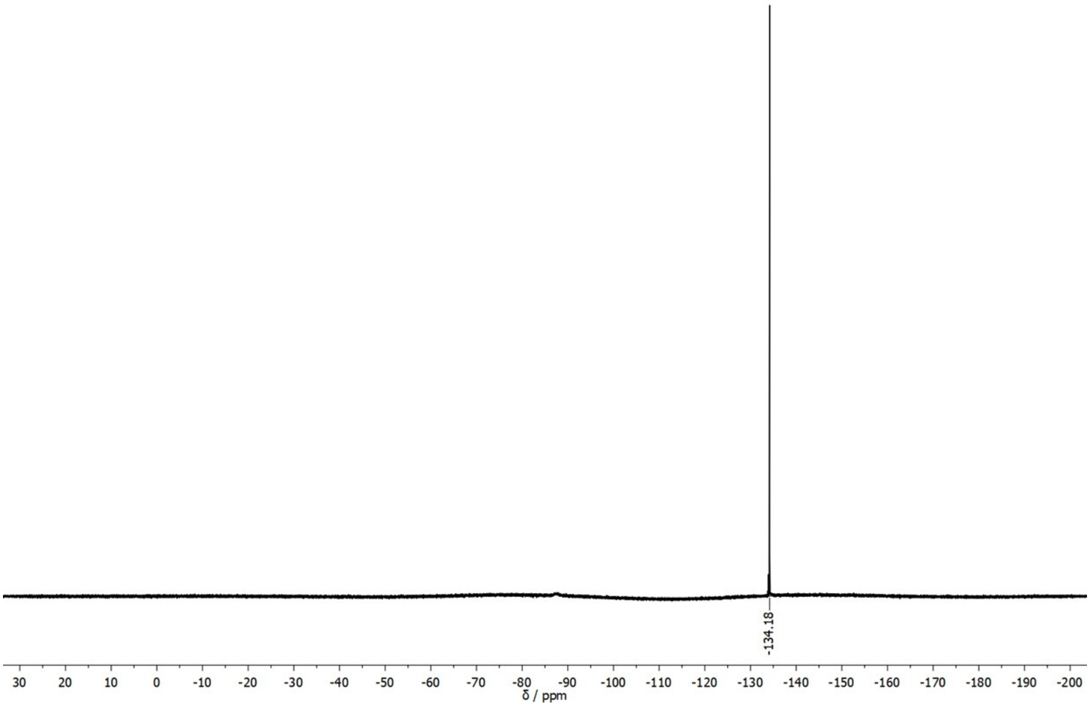


Figure S14. 377 MHz ^{19}F NMR of **3** in $CDCl_3$.

3.5 Derivative 3^{2+}

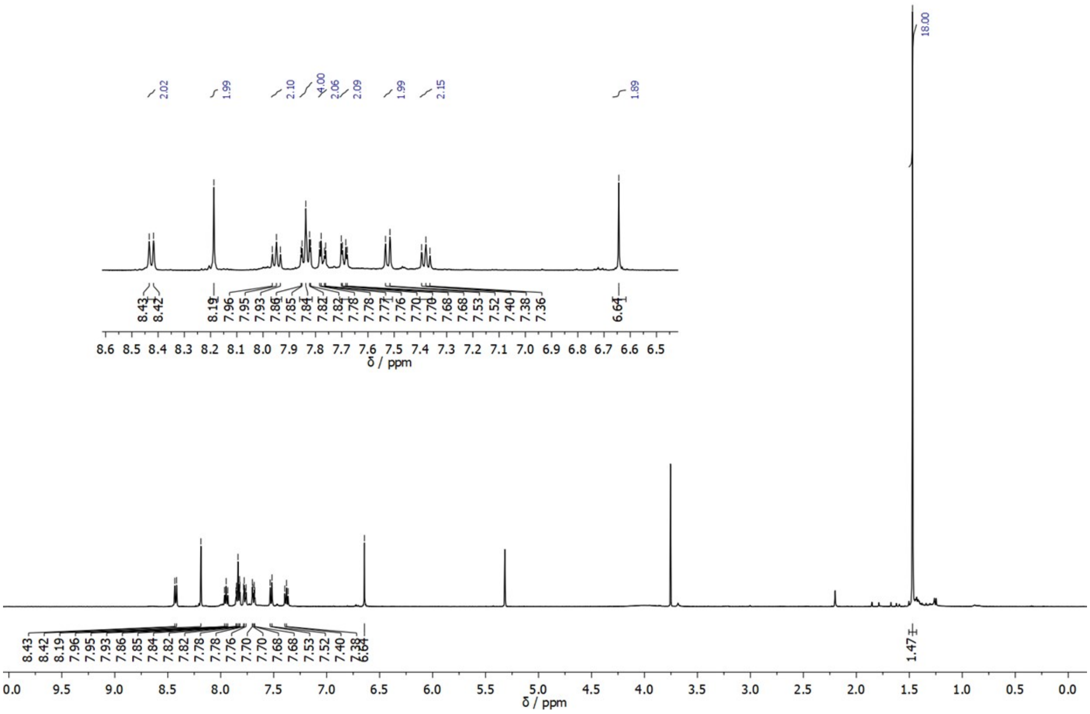


Figure S15. 500 MHz ^{1}H NMR of $\mathbf{3}^{2+}$ in CD_2Cl_2. Signal at 3.76 ppm is residual DCE.

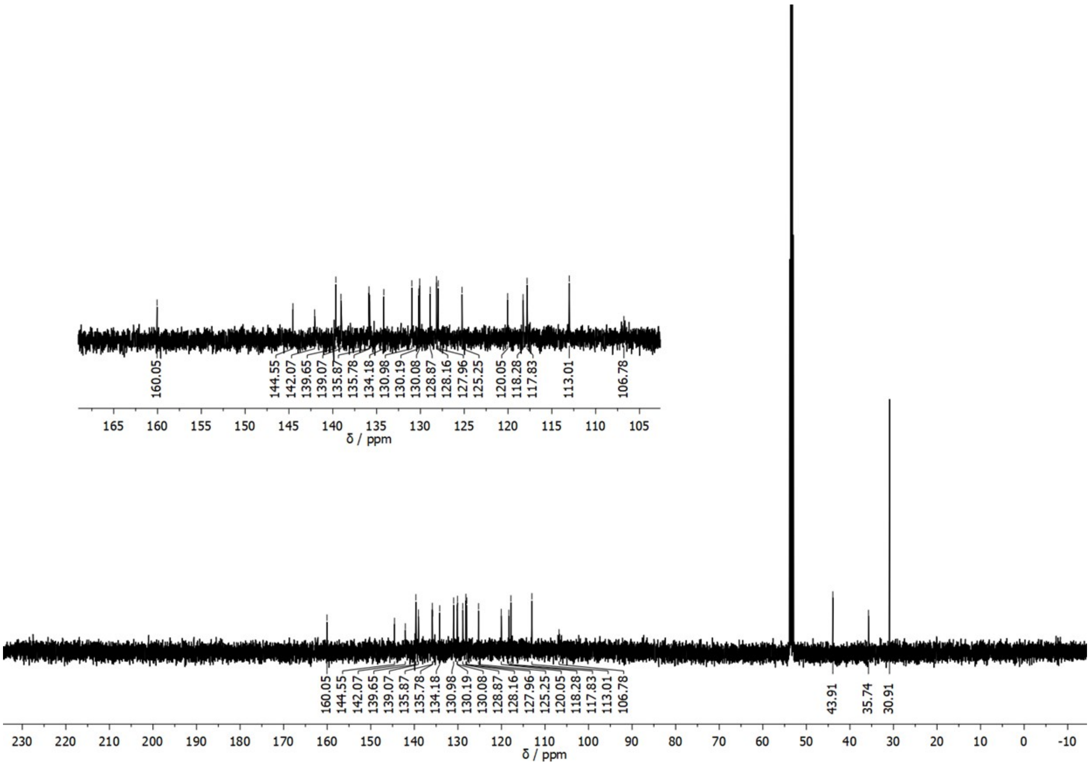


Figure S16. 126 MHz ^{13}C NMR of $\mathbf{3}^{2+}$ in CD_2Cl_2.

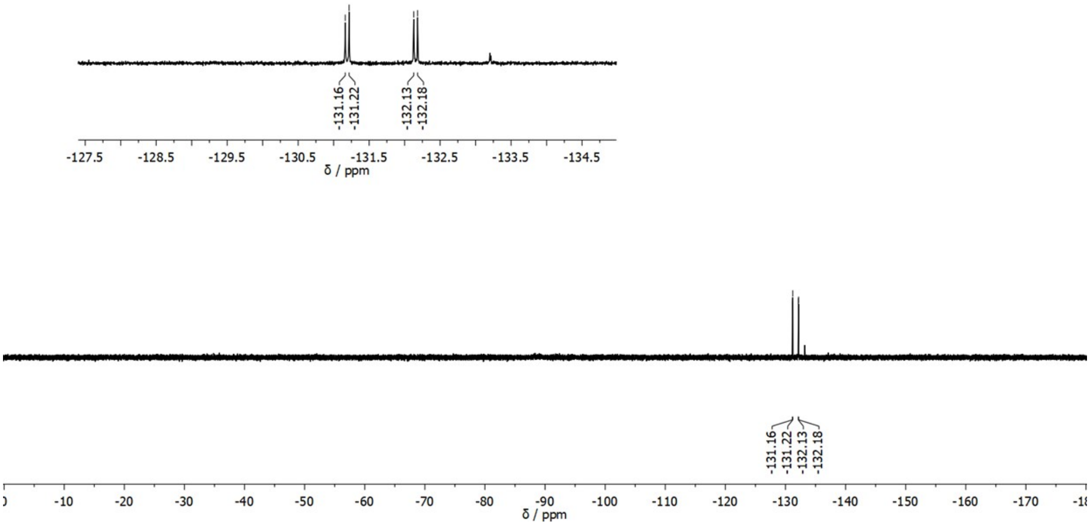


Figure S17. 377 MHz ^{19}F NMR of $\mathbf{3}^{2+}$ in $CDCl_3$.

3.6 Derivative $\mathbf{3}^{\mathbf{deg}}$

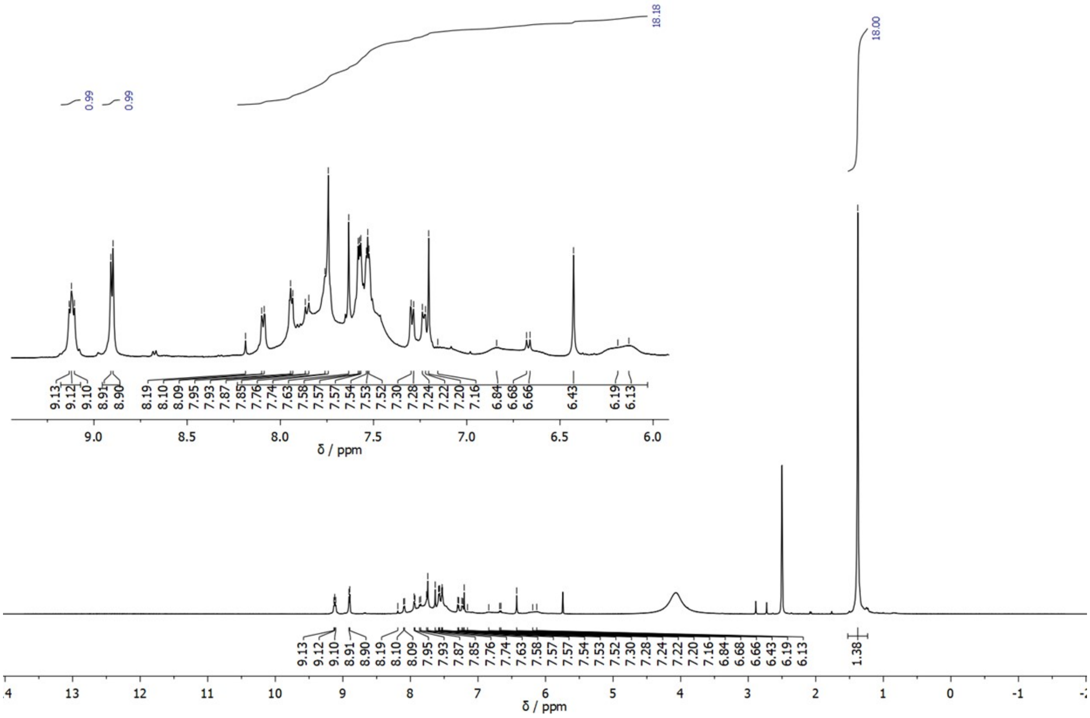


Figure S18. 500 MHz ^{1}H NMR of $\mathbf{3}^{\mathbf{deg}}$ in DMSO-*d6*.

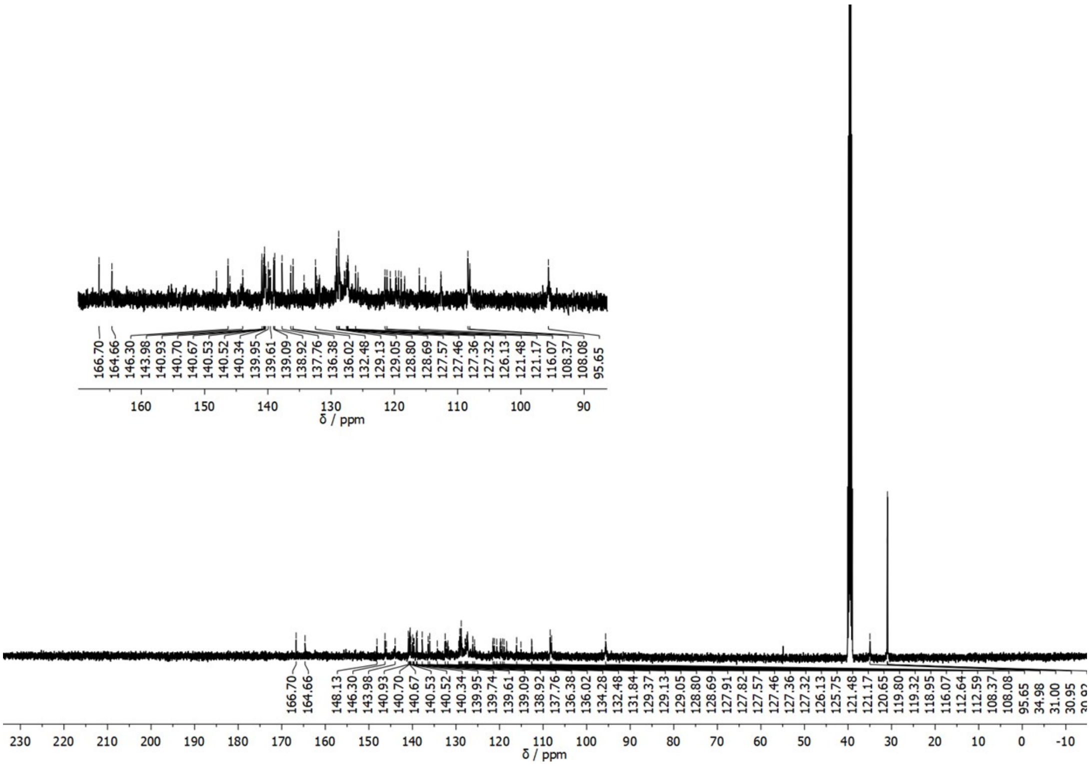


Figure S19. 126 MHz ^{13}C NMR of **3$^{\mathbf{deg}}$** in DMSO-*d6*.

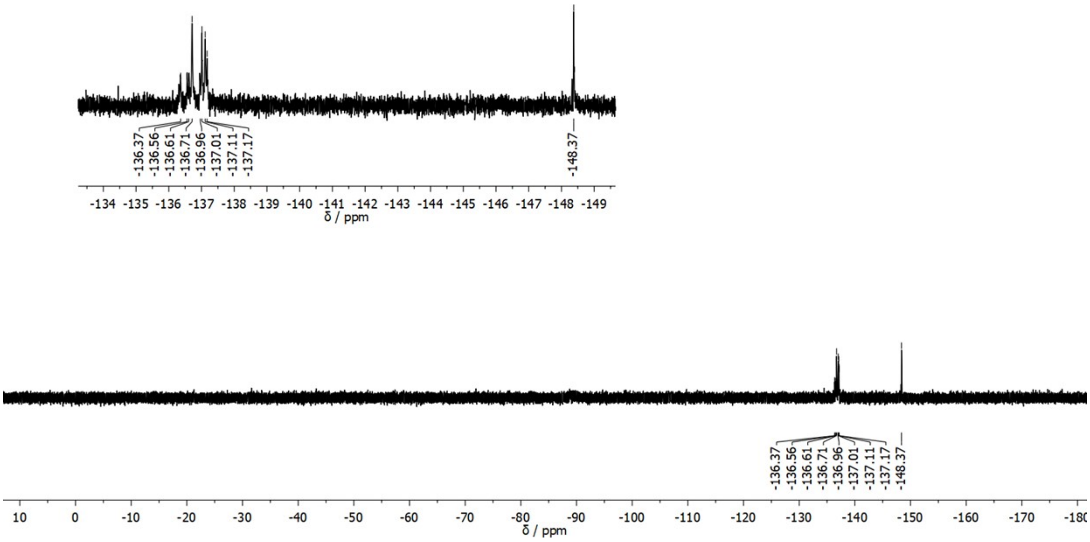


Figure S20. 377 MHz ^{19}F NMR of **3$^{\mathbf{deg}}$** in DMSO-*d6*.

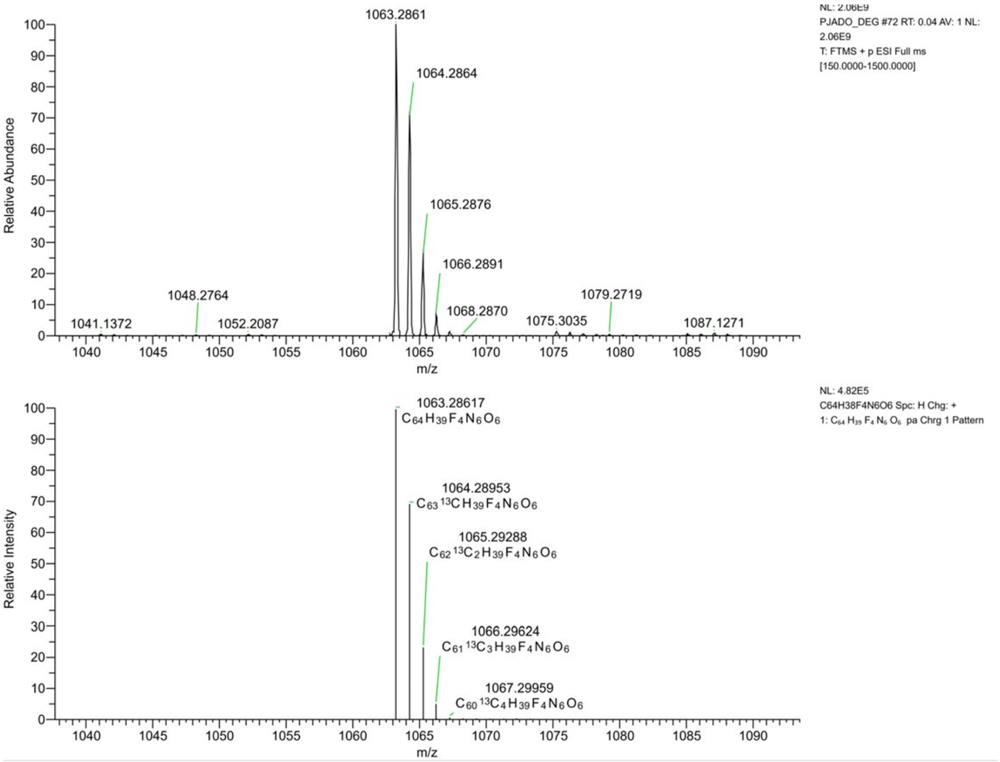


Figure S21. ESI-HRMS of **3^{deg}** top) experimental and bottom) simulated spectra.

4 Solid State NMR Study of polymers

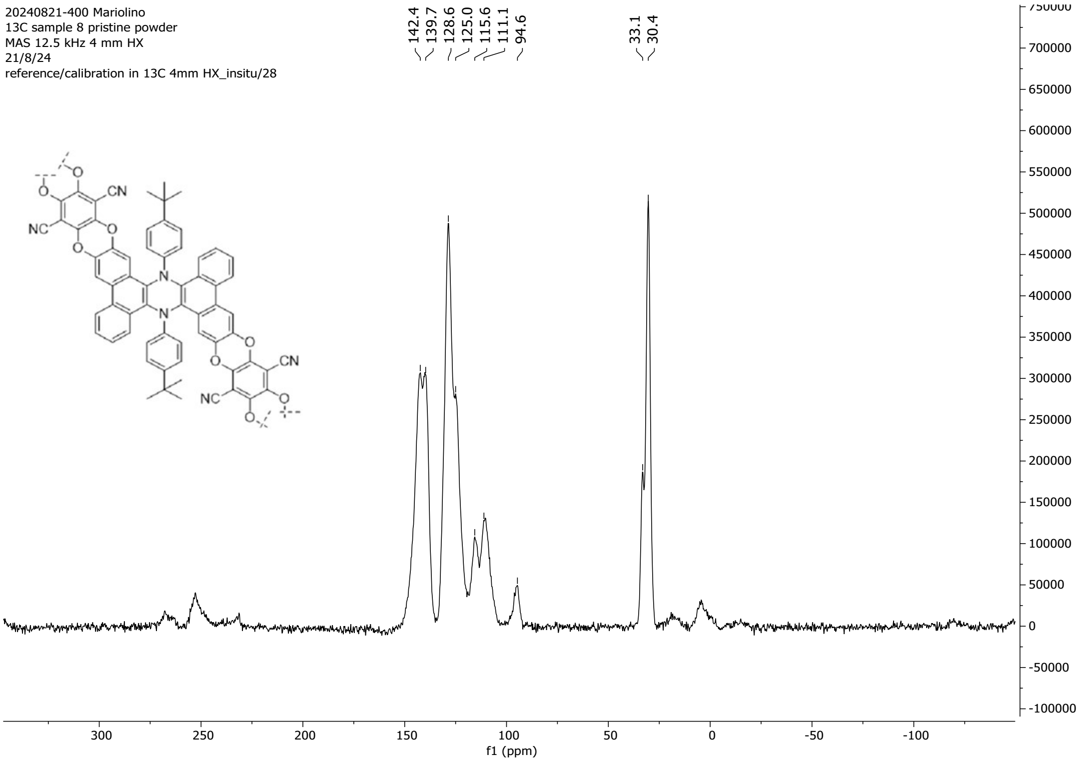


Figure S22. ^{13}C SSNMR of **Phen-PIM-1**

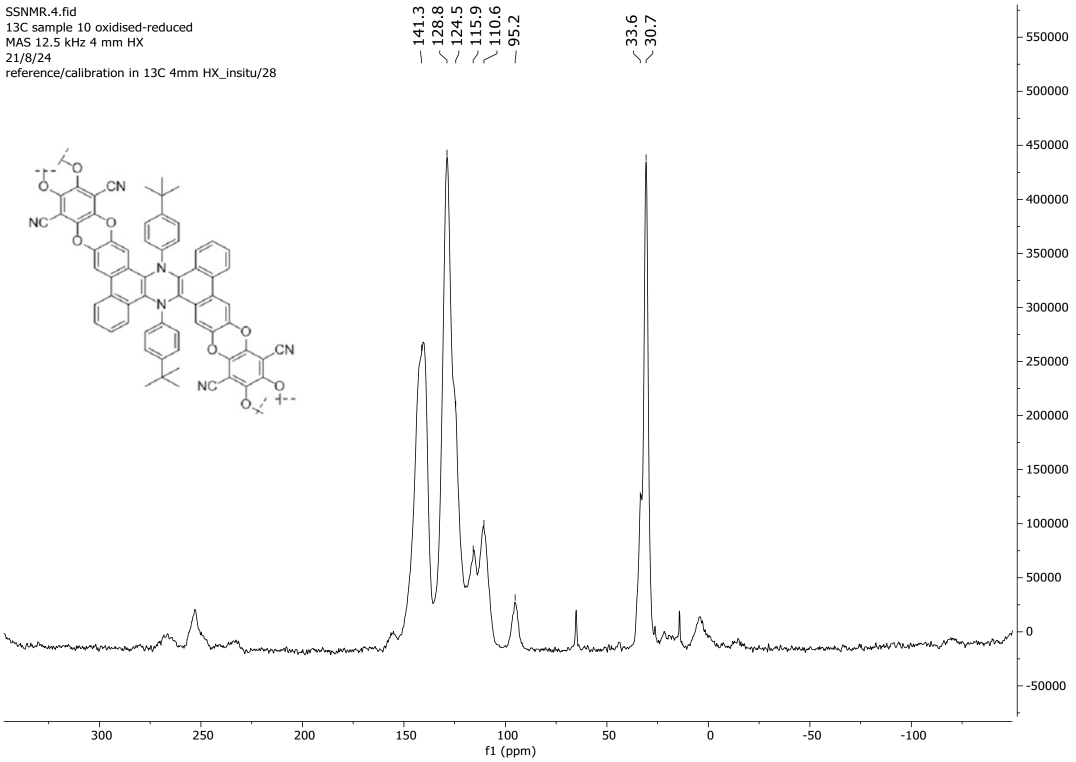


Figure S23. ^{13}C ssNMR of **Phen-PIM-1$^{\text{ox-red}}$**.

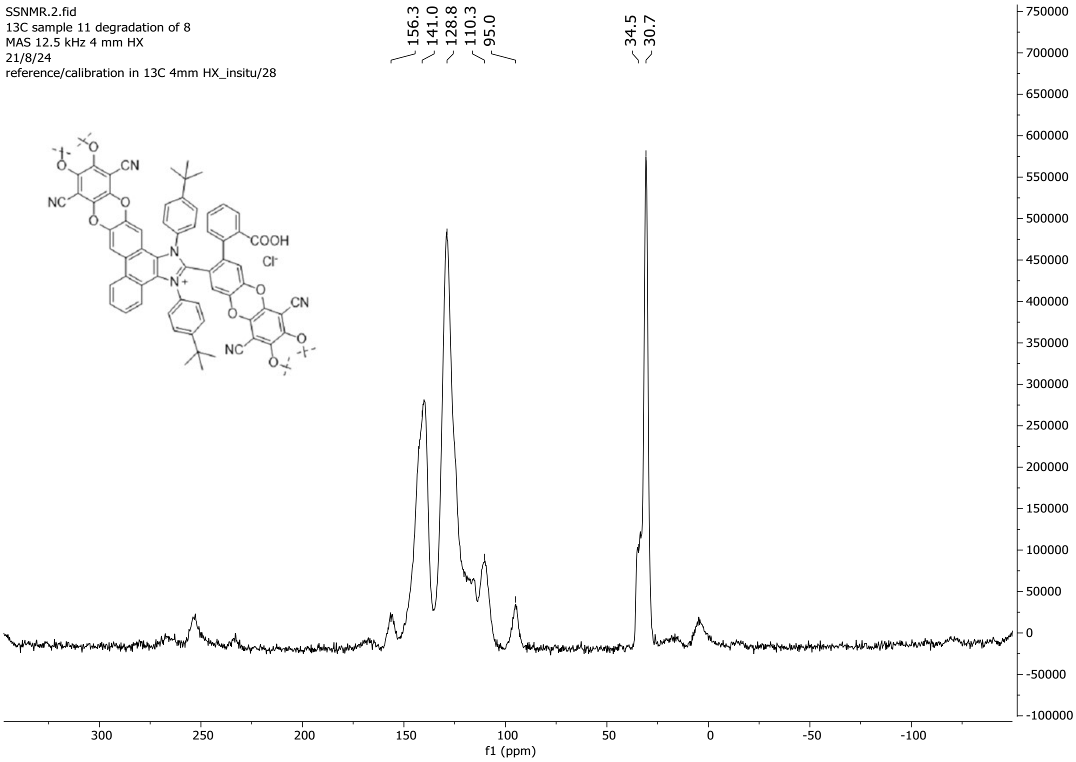


Figure S24. ^{13}C ssNMR of **Phen-PIM-1$^{\text{deg}}$**.

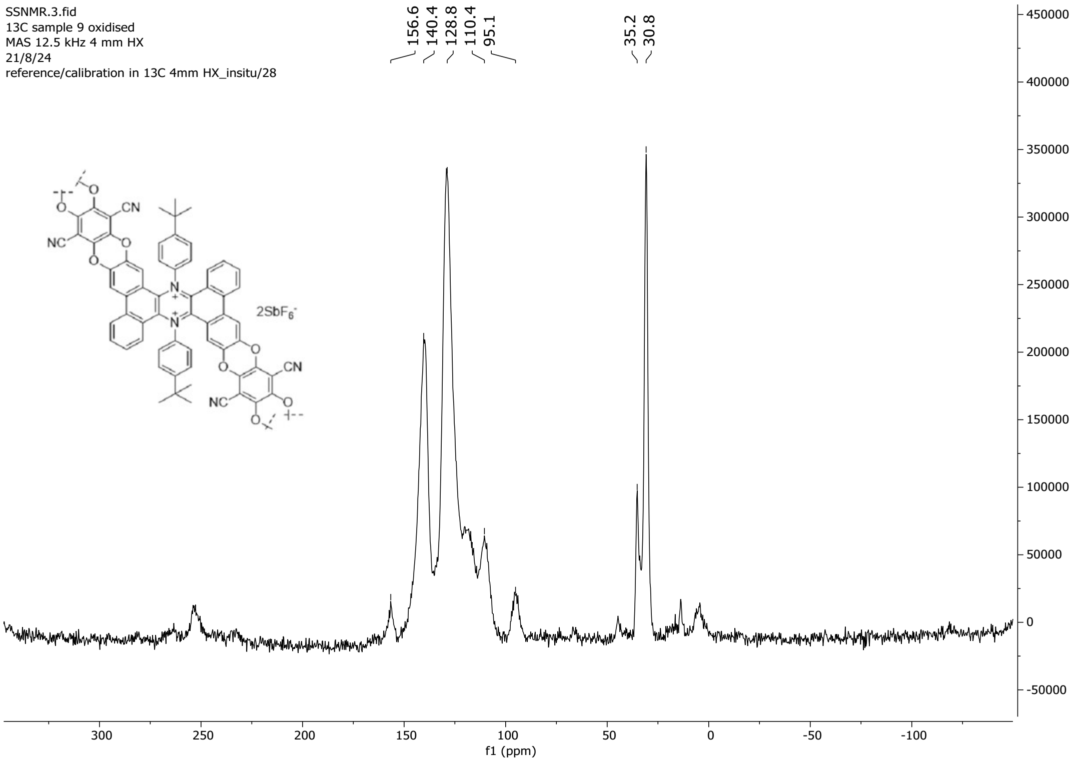


Figure S25. ^{13}C ssNMR of **Phen-PIM-1^{ox}**.

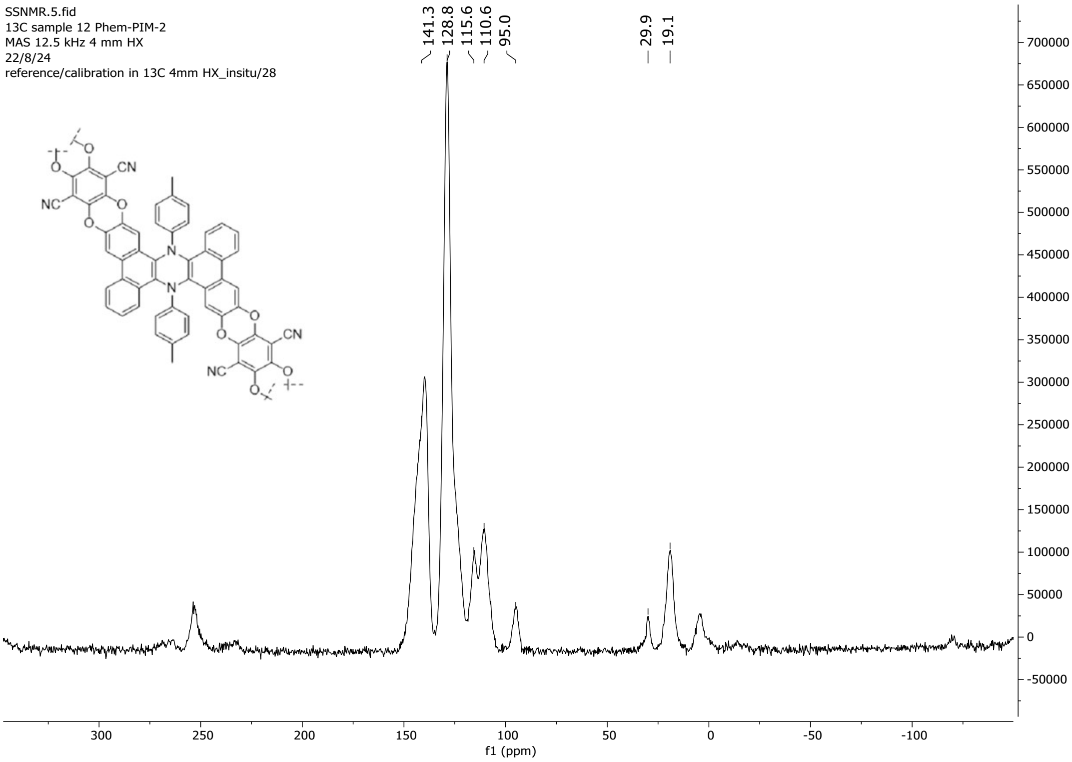


Figure S26. ^{13}C ssNMR of **Phen-PIM-2**.

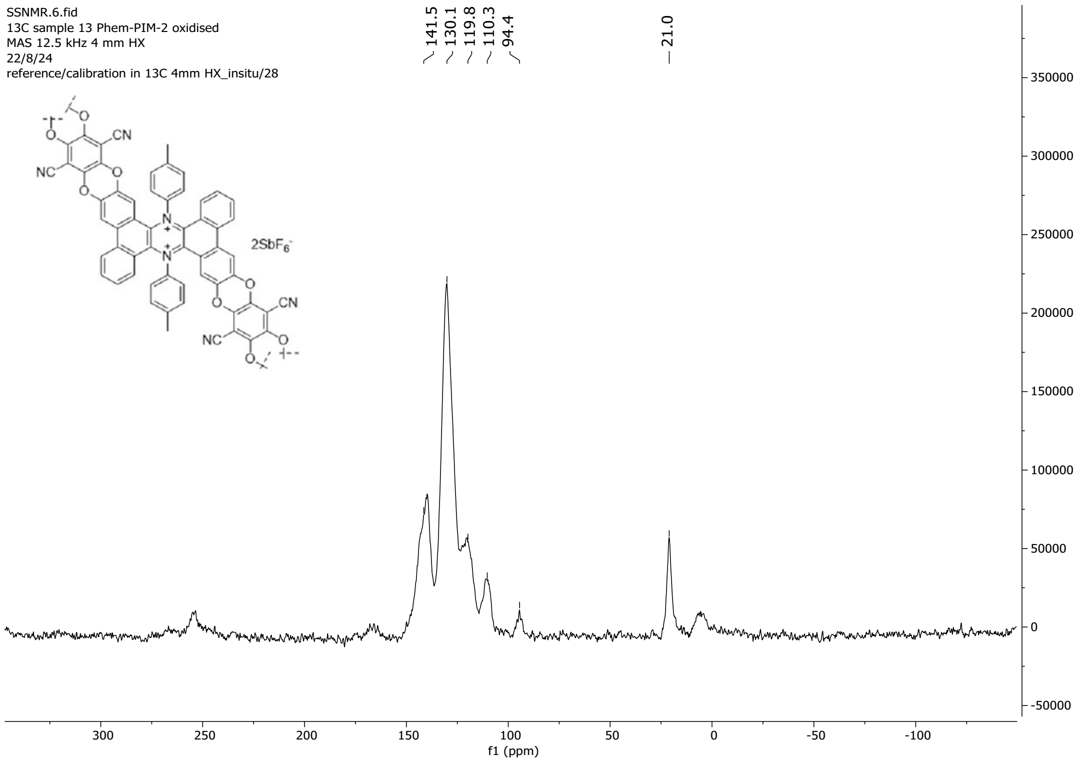


Figure S27. ^{13}C ssNMR of **Phen-PIM-2^{ox}**.

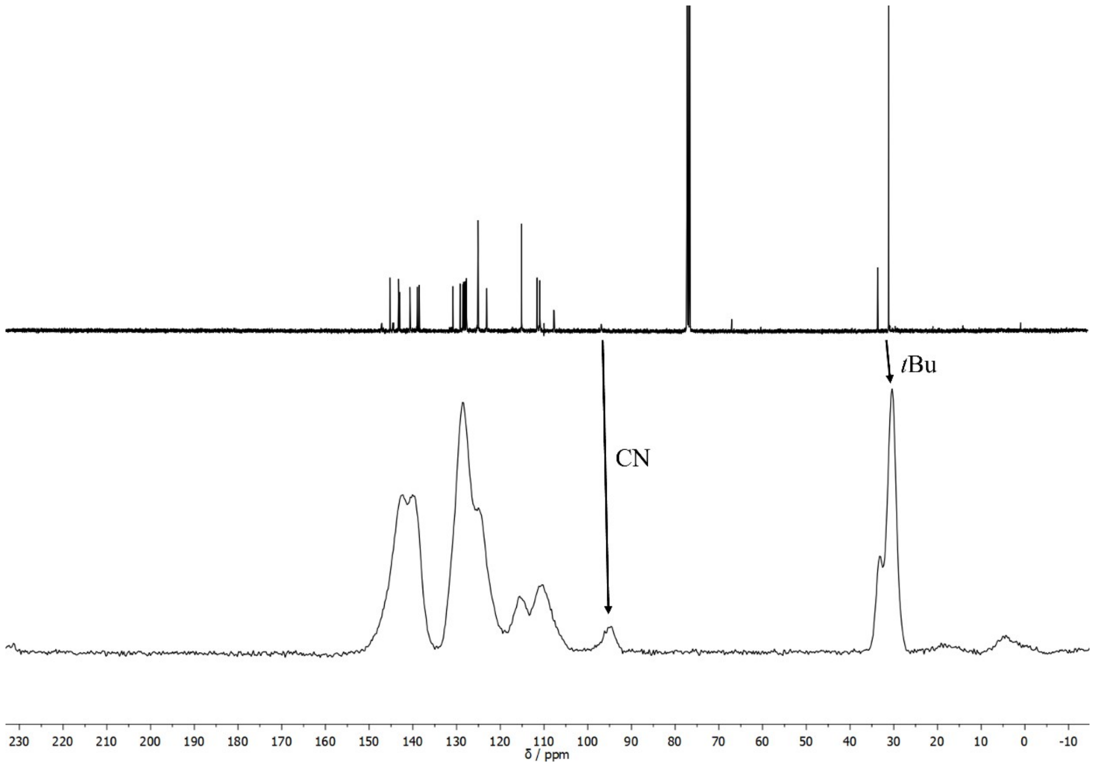


Figure S28. Comparison of top) 101 MHz ^{13}C NMR of **3** in CDCl$_3$. Bottom) ssNMR of **Phen-PIM-1**.

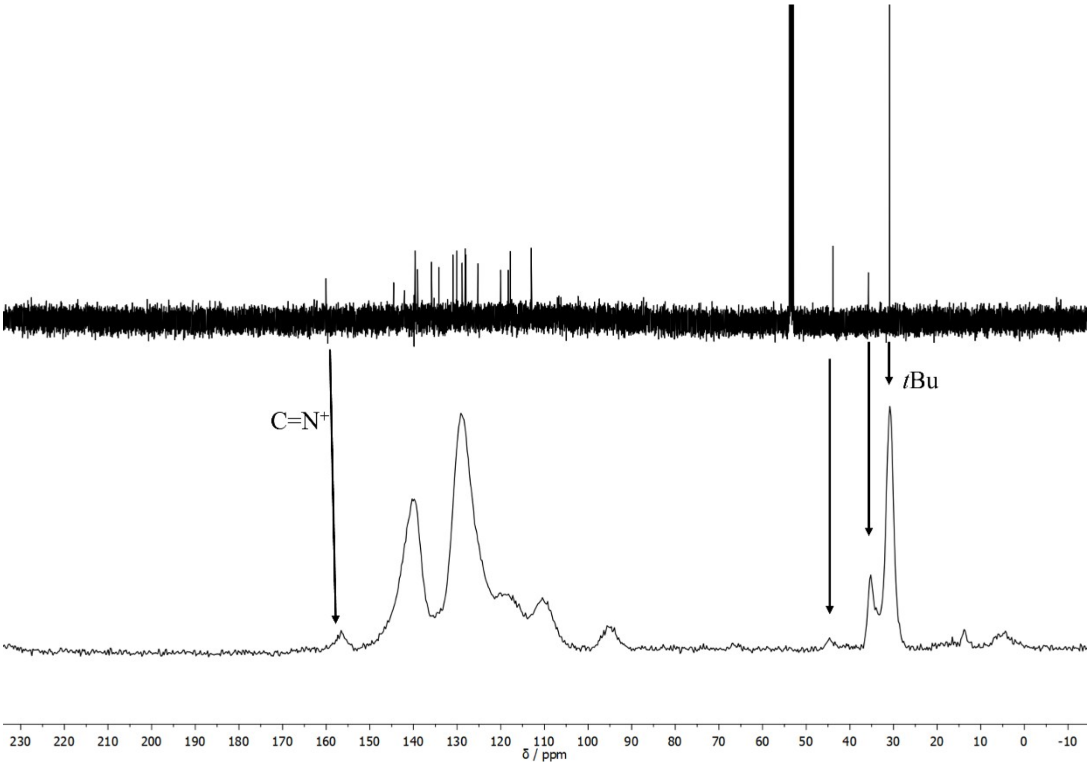


Figure S29. Comparison of top) 101 MHz ^{13}C NMR of **3^{ox}** in CDCl$_3$. Bottom) ssNMR of **Phen-PIM-1^{ox}.**

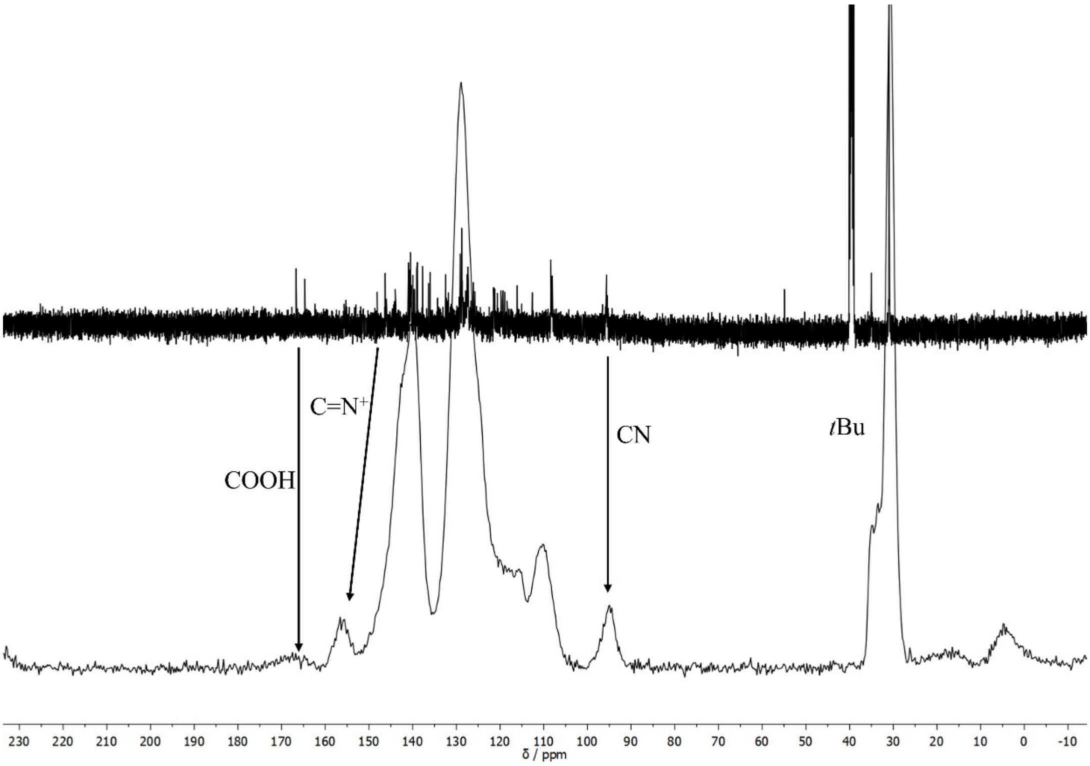


Figure S30. Comparison of top) 126 MHz ^{13}C NMR of **3^{deg}** in CDCl$_3$. Bottom) ssNMR of **Phen-PIM-1^{deg}.**

5 UV-Vis Analysis of monomer and polymers

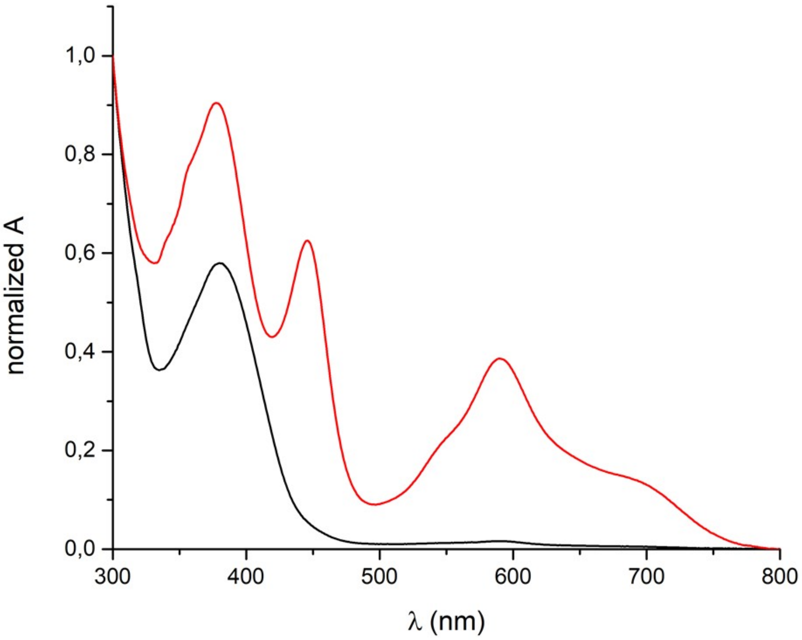


Figure S31. Normalized steady state absorption of **3** (black) and $\mathbf{3}^{2+}$ (red, after addition of an excess of $NOSbF_6$) in CH_2Cl_2.

6 ATR-IR spectra of materials

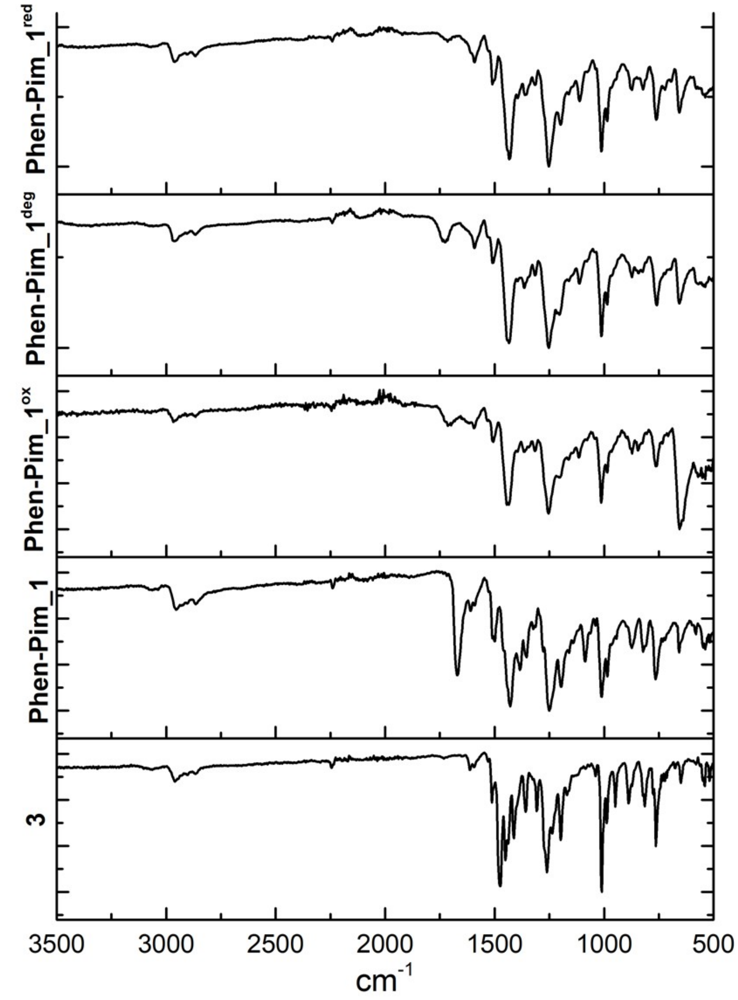


Figure S32. ATR-IR stacked spectra of materials described in this study. Carbonyl signal at 1675 cm^{-1} in **Phen-PIM-1** is residual DMF trapped in the polymer pores.

7 TGA measurements on polymeric materials

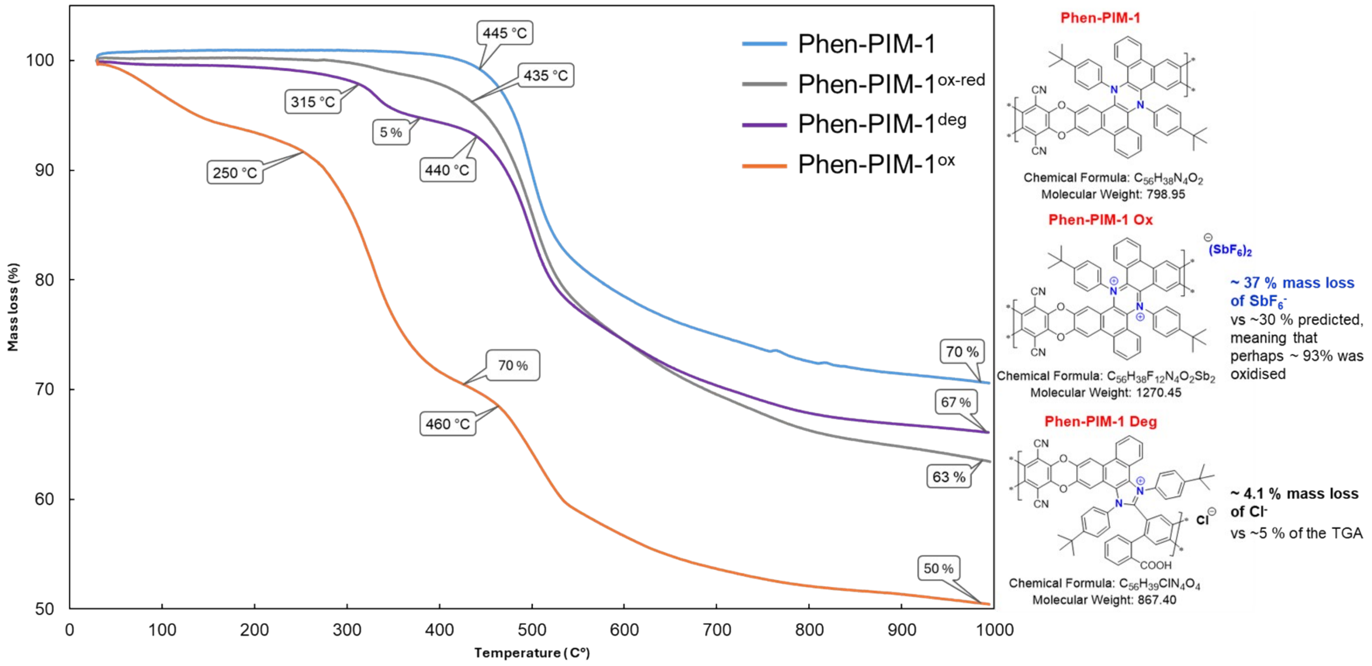


Figure S33. TGA traces overlay of pristine **Phen-PIM-1** (light blue); **Phen-PIM-1^{ox-red}** (grey); **Phen-PIM-1^{ox}** (orange) and **Phen-PIM-1^{deg}** (purple).

8 Absorption isotherms on polymeric materials

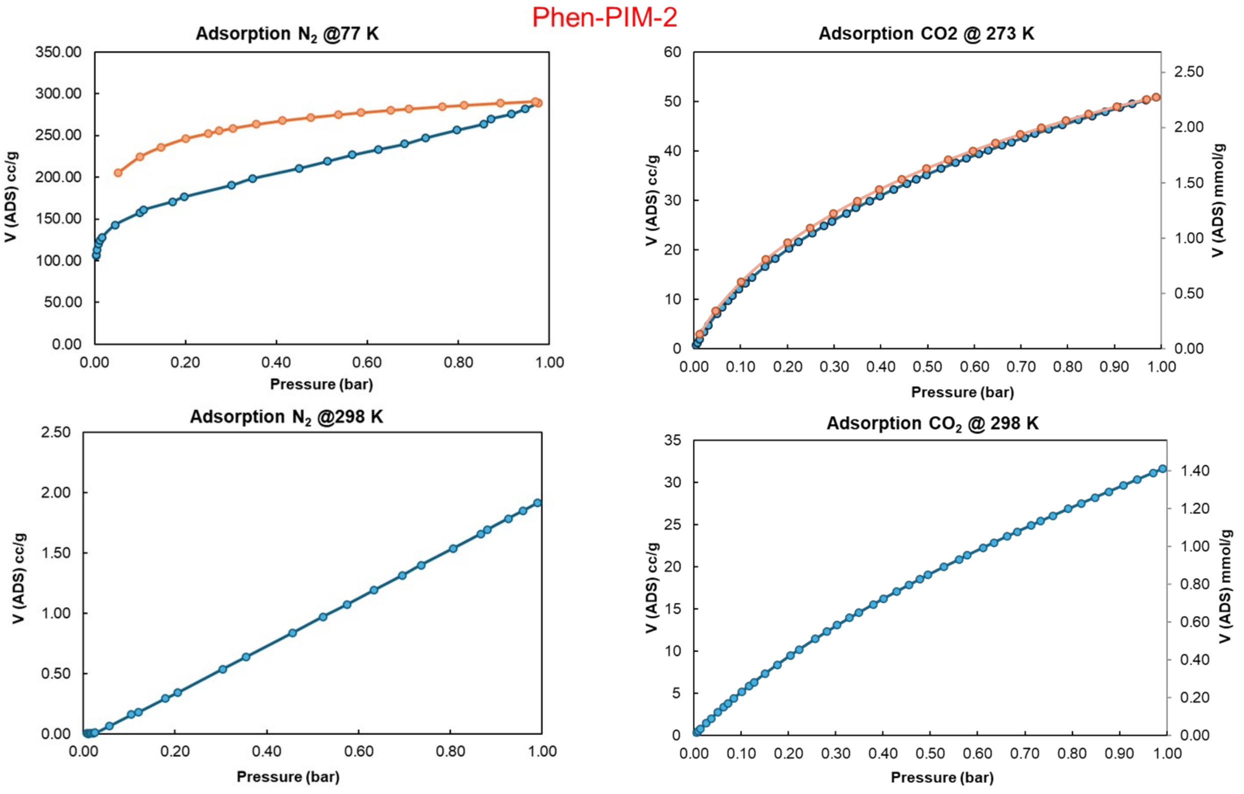


Figure S34. Adsorption isotherms for **Phen-PIM-2**.

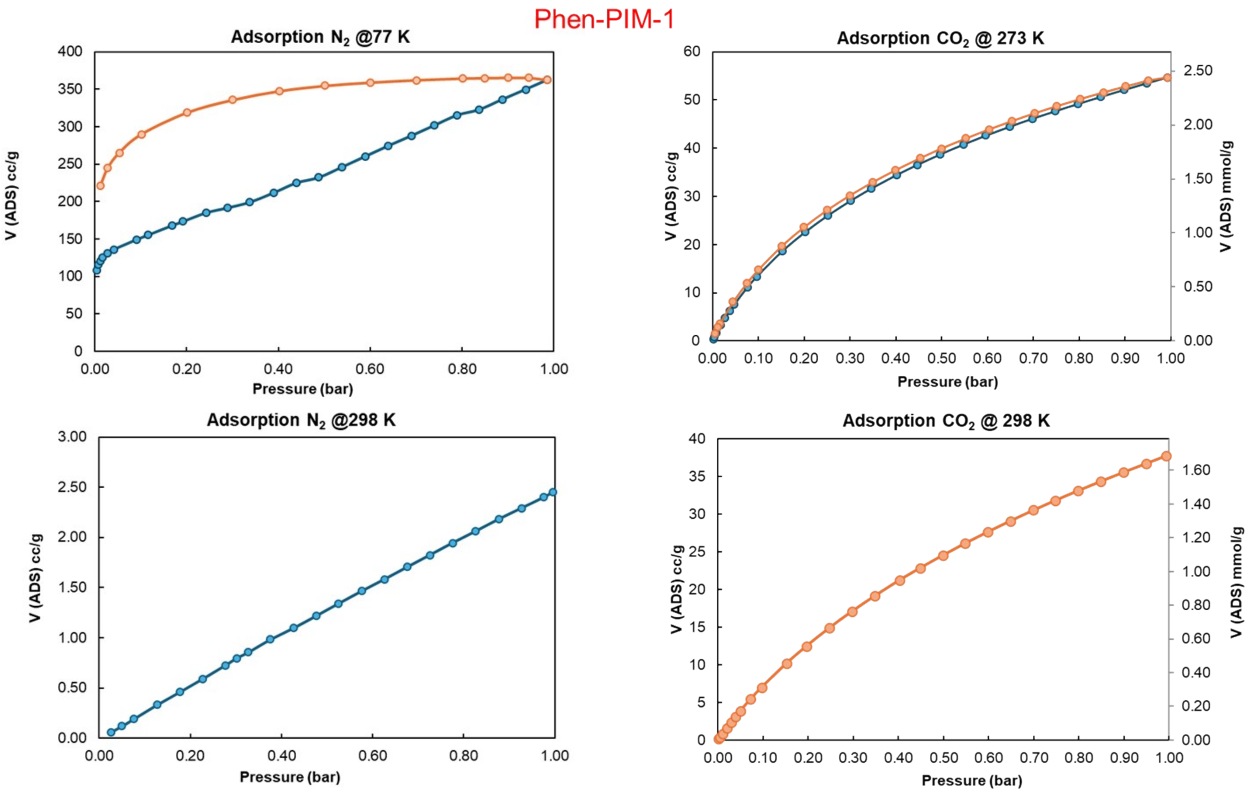


Figure S35. Adsorption isotherms for **Phen-PIM-1**.

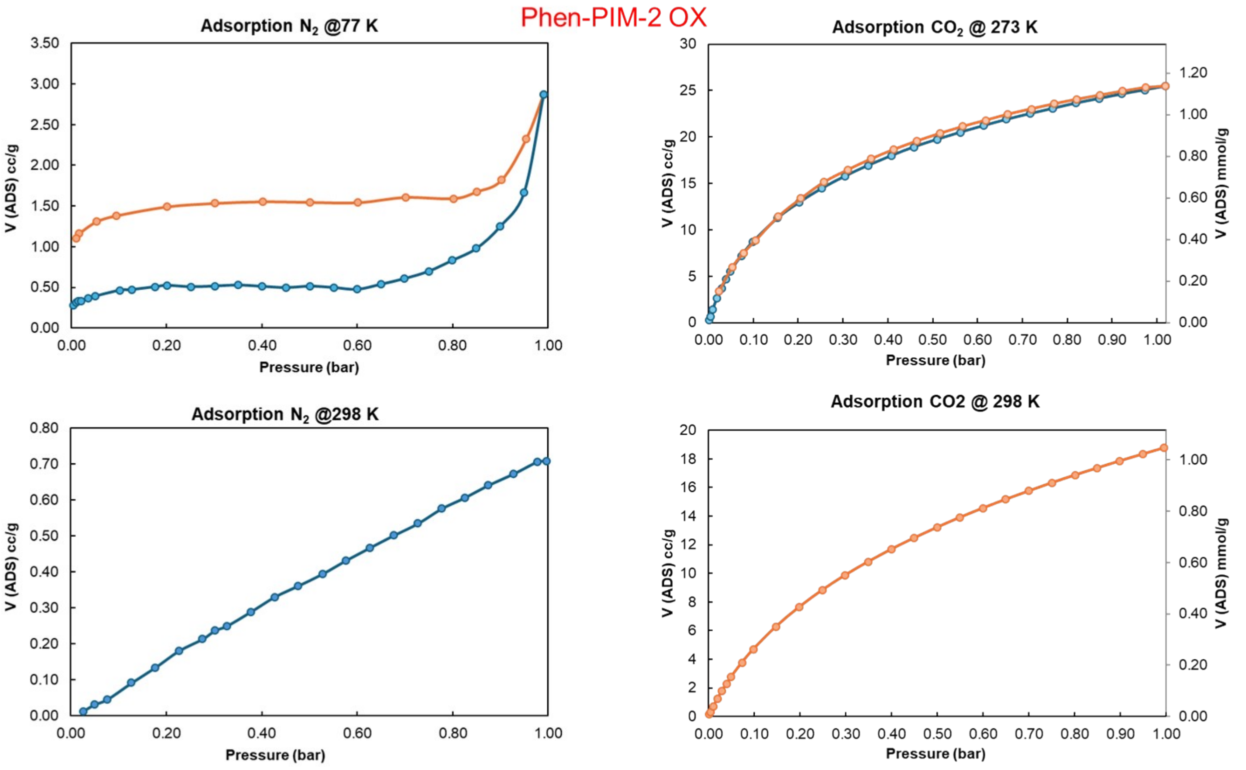


Figure S36. Adsorption isotherms for **Phen-PIM-2^{ox}**.

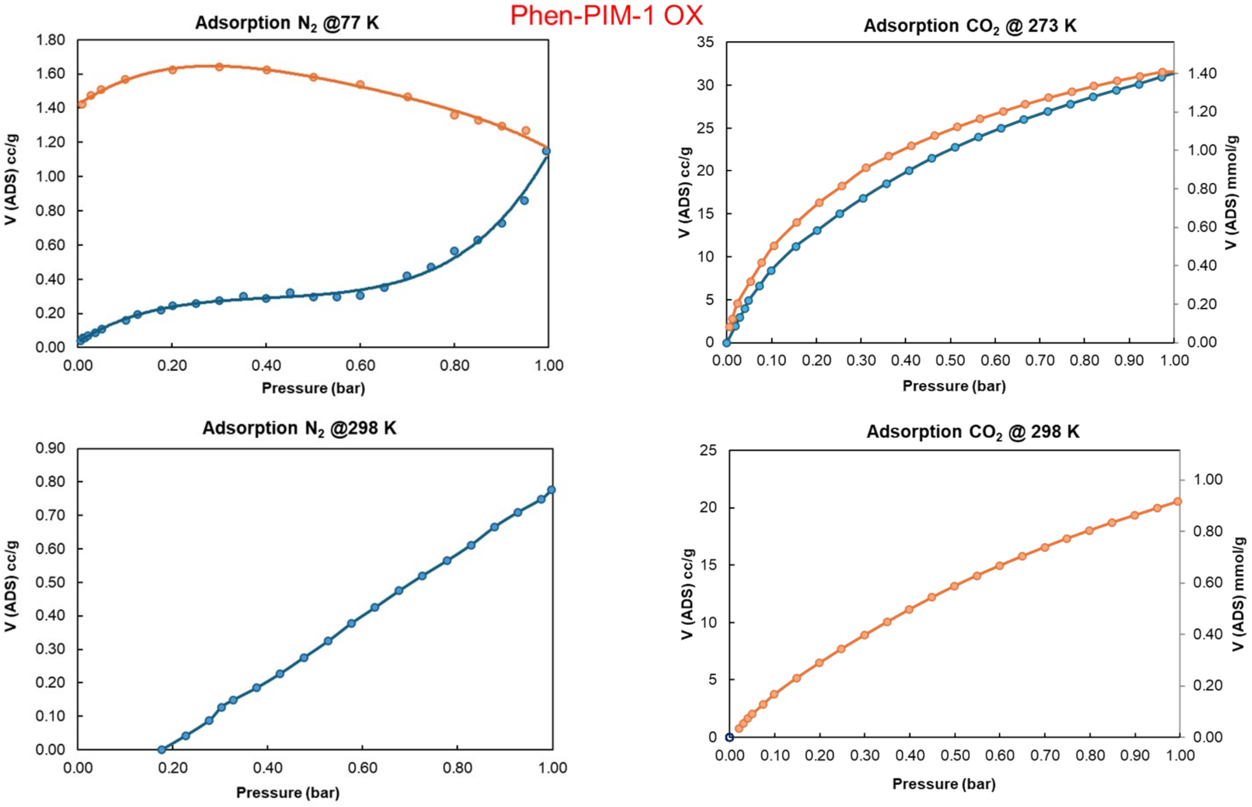


Figure S37. Adsorption isotherms for **Phen-PIM-1^{ox}**.

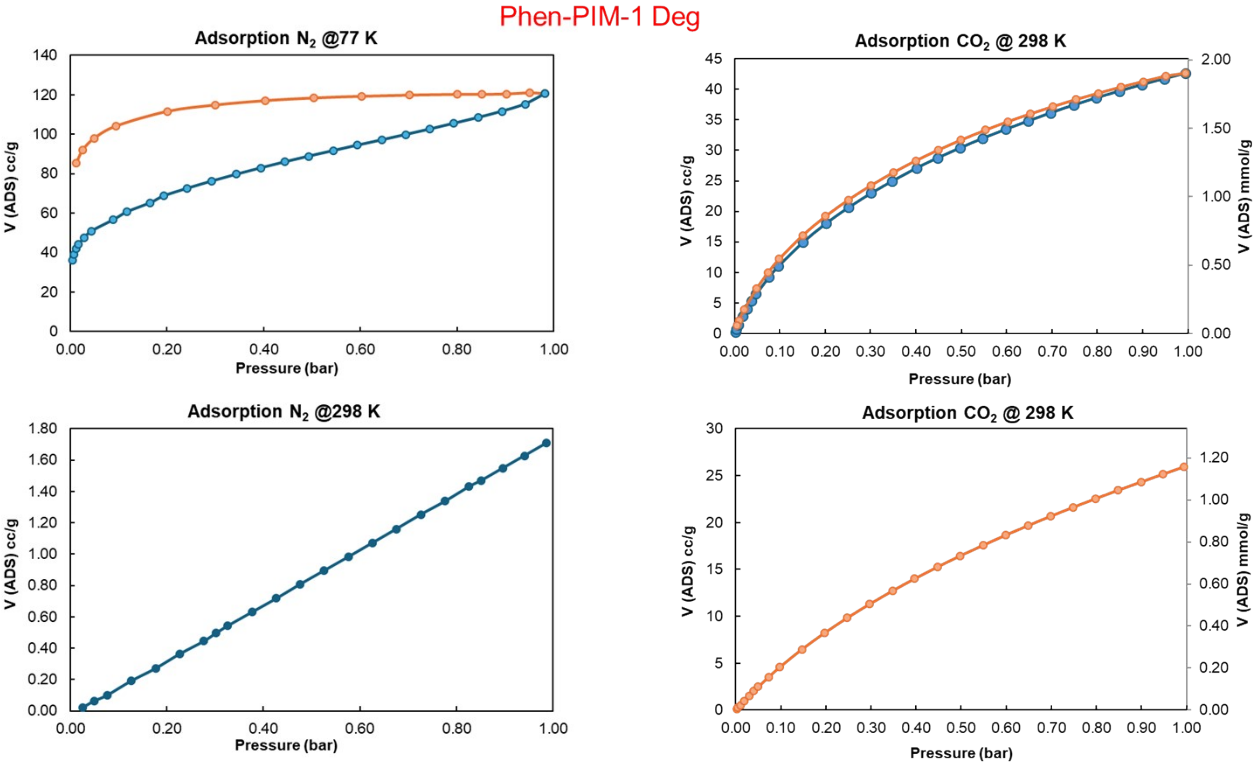


Figure S38. Adsorption isotherms for **Phen-PIM-1^{deg}**.

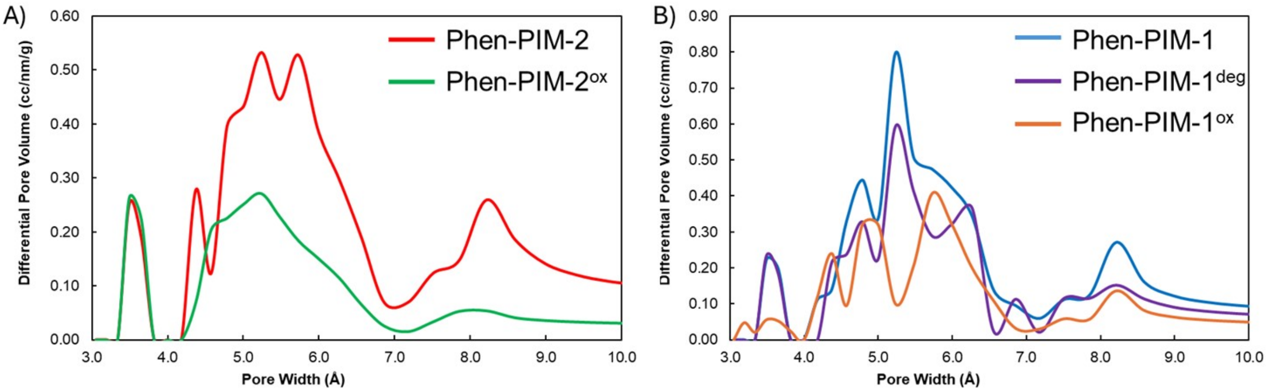


Figure S39. Pore size distribution calculated from CO_2 adsorption at 273 K and via NLDFT. A) **Phen-PIM-2**; B) **Phen-PIM-1**.

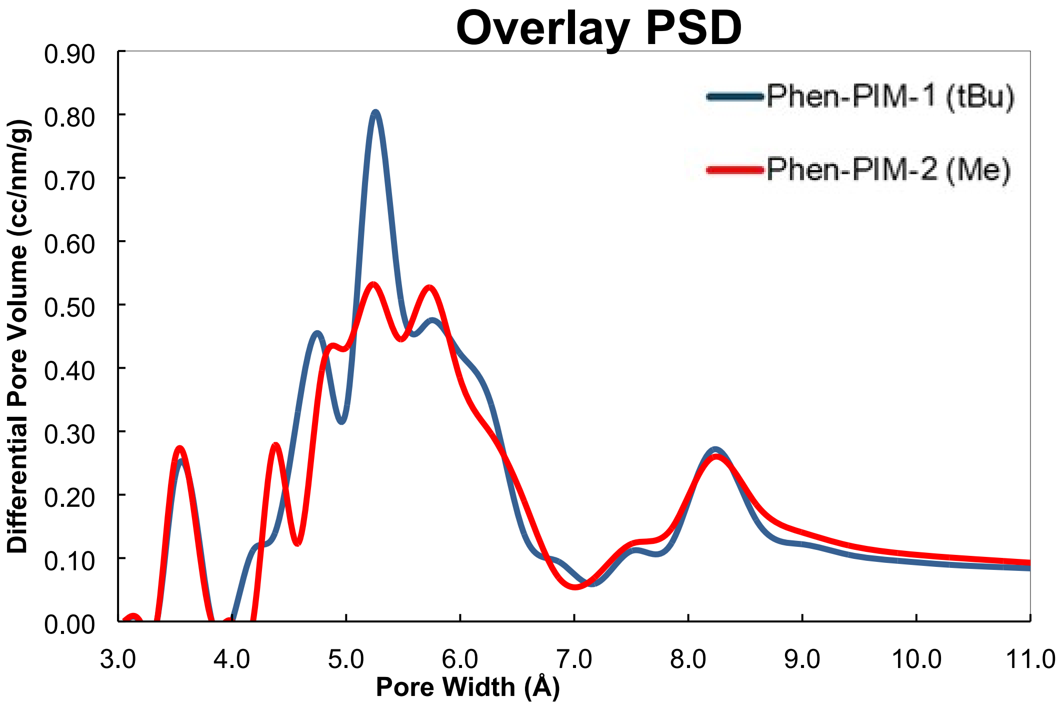


Figure S40. Overlay of PSD of **Phen-PIM-1** and **Phen-PIM-2**

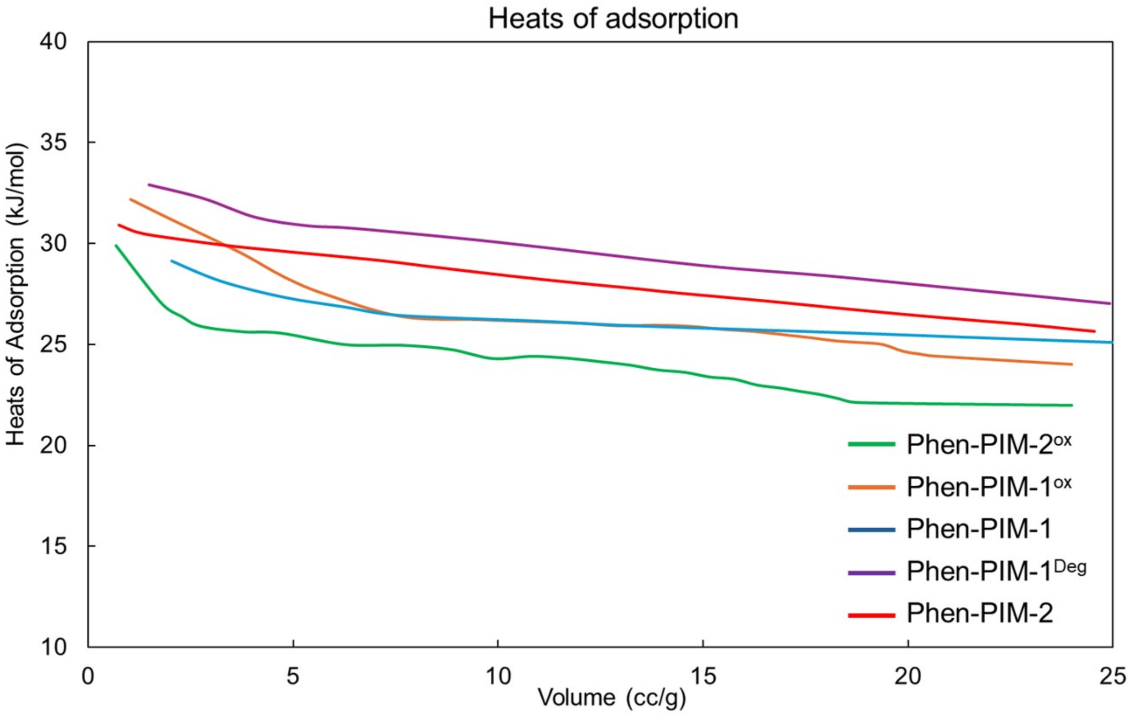


Figure S41. Isosteric heats of adsorption of all **Phen-PIMs**.

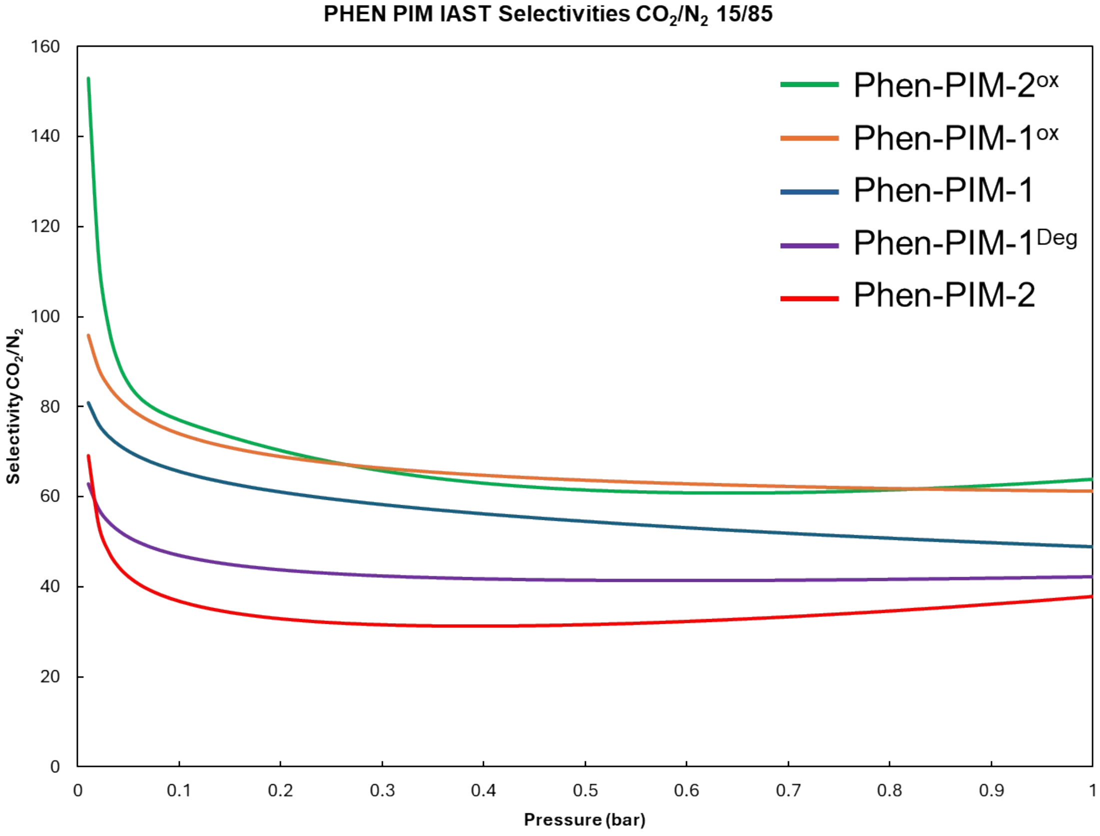


Figure S42. Ideal Selectivity of all **Phen-PIMs** calculated according to IAST at 298 K and 1 bar.

9 Gas diffusion coefficients via time-lag method

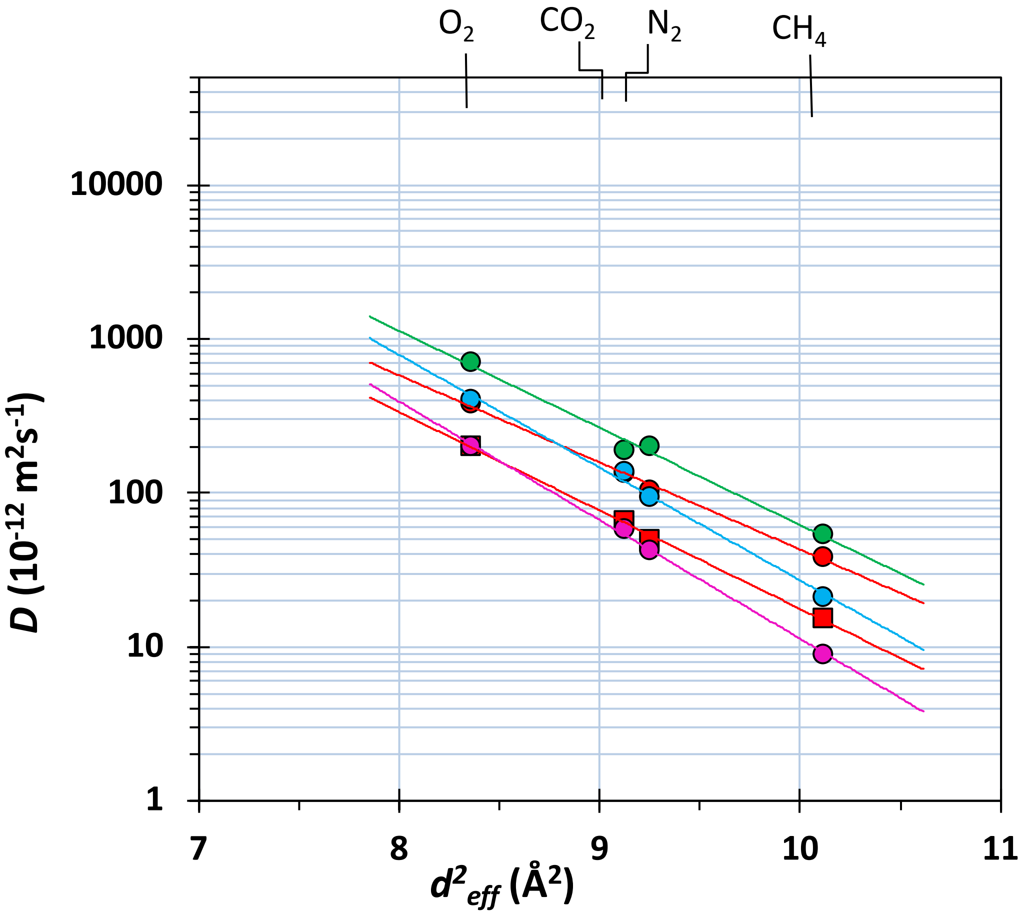


Figure S43. Diffusion coefficients as a function of the squared effective diameter of the gases [4] of interest for **Phen-PIM-1** in red (circle ● fresh and square 🟥 aged), for PIM-SBF-5 in blue (●),[5] for PIM-TOT-SBF-5 in green (●),[6] for DPt-TMPD in pink (●).[7]

10 AFM force spectroscopy

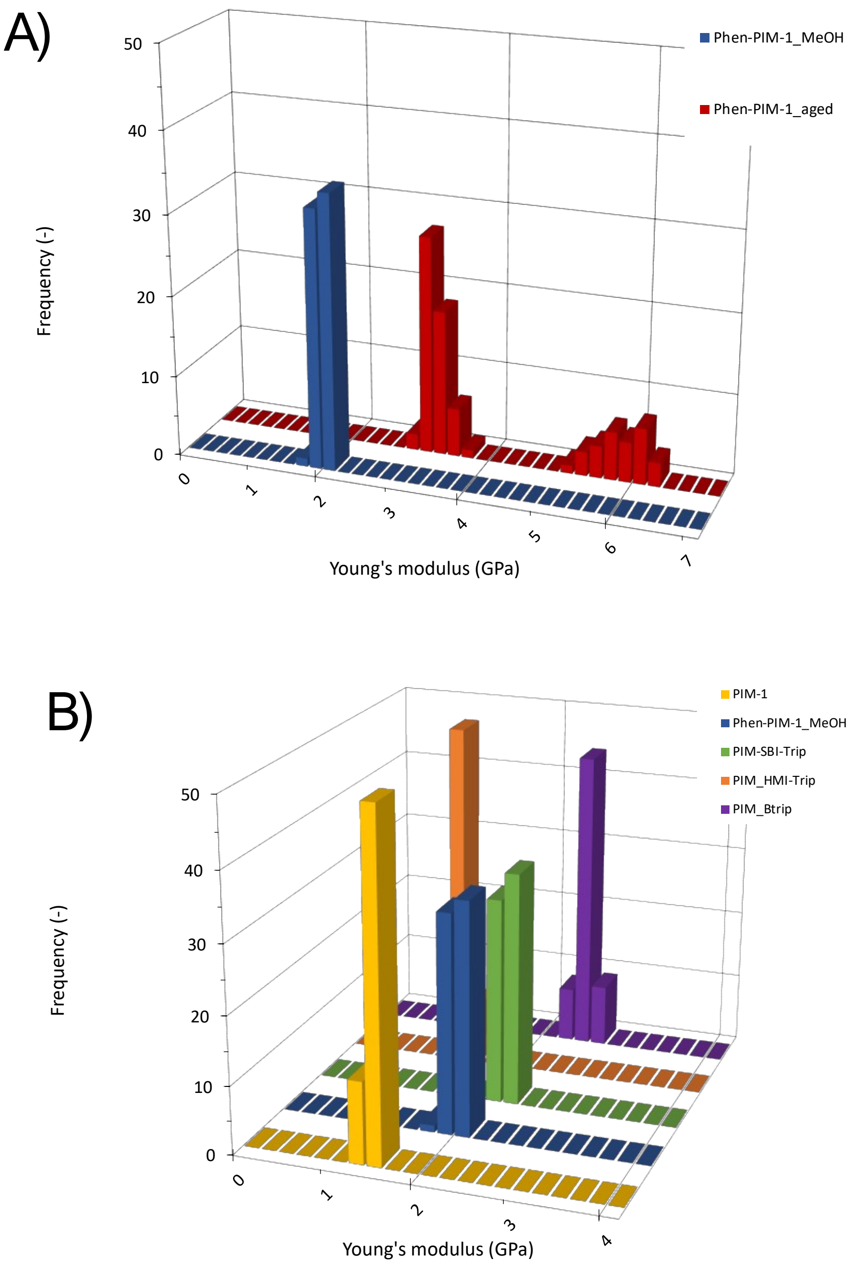


Figure S44. Distribution of the local Young's modulus for a total of 60 individual force spectroscopy measurements on A) **Phen-PIM-1** after methanol treatment and after aging and B) **Phen-PIM-1** after methanol treatment in comparison with other PIMs.[2,8]

11 Bibliography

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