Supporting Information

Bindone-Based Polymer for Colorimetric Detection of Volatile Amines

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Contents

1. General Methods

Reagents and solvents were purchased from either Merck® or Fluorochem®. TLCs were performed using Merck silica gel 60 covered aluminium plates F254. Reaction temperatures: room temperature refers to 20–25 °C.

Mass spectrometry and elemental analysis were obtained from the mass spectrometry service at the University of Glasgow. NMRs were recorded on either Bruker Avance III 400. The ^{1}H and ^{19}F spectra were recorded at 400 MHz with TMS as internal standard. NMR spectra were analysed using MNova®. Signals in ^{1}H-NMR spectra are described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), multiplet (m), broad (b) or a combination of these, which refers to the spin-spin coupling pattern observed.

Absorbance spectrometry was performed using a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer. Qualitative fluorescence spectroscopy was performed using a Shimadzu RF-5301PC spectrofluorimeter. All the spectroscopic data was processed using Origin Pro 8.5 software suite.

Thermogravimetric analysis was carried out on a Netzsch TG 209 F3 Tarsus Thermogravimetric Analyser. The experiments were run under a flow of nitrogen with a heating rate of 10 K min^{-1} between 25 °C – 550 °C. Differential scanning calorimetry was carried out on a Netzsch DSC 214 Polyma instrument under nitrogen. The scans were carried out at a heating/cooling rate of 10 K min^{-1} with the maximum temperature 350°C.

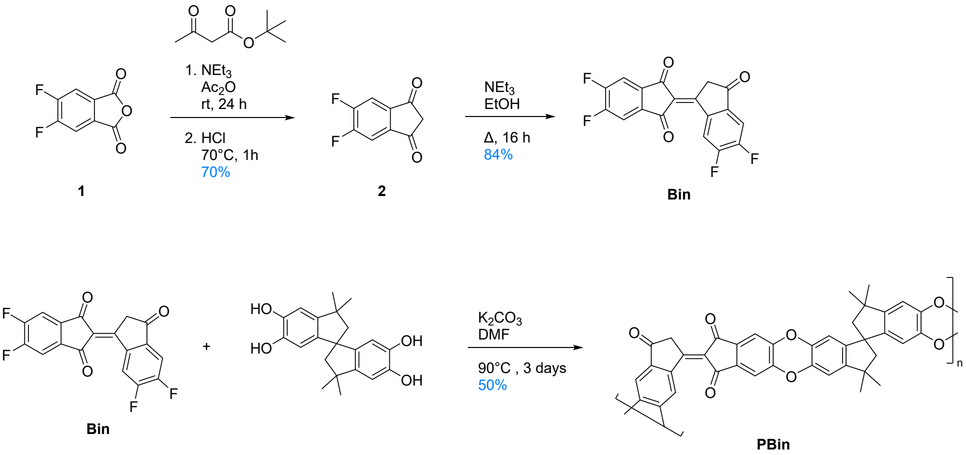
Gel permeation chromatography was performed on the polymer material using an Agilent 1260 Infinity II system with a PLgel 5 µm mixed-d dual column set up and polystyrene used as reference standard.

CO_2 and N_2 gas sorption isotherms of **PBin** were obtained at 273 and 77 K respectively using a Quantachrome Quandrasorb Evo surface area analyser. Samples were outgassed at 100 °C under vacuum for 24 h using a Quantachrome FLOVAC degasser prior to each gas sorption measurement. The pore size distribution was determined using the CO_2 gas adsorption isotherm by applying non-local density functional theory (NLDFT).

Scanning Electron Microscopy was carried out using TESCAN CLARA Ultra High Resolution Scanning Electron Microscope (UHR-SEM) with Field Emission Gun electron source. Samples were sputtered with Gold using Polaron SC7640 auto/manual high resolution sputter coater before imaging.

Computational calculations were performed using Gaussian '16 software suite.[1] Molecular geometries were initially optimized semi-empirically (PM6) and then re-optimized by DFT (B3LYP/6- 311G dp). Energy minima were confirmed by the absence of imaginary frequencies from vibrational frequency calculations.

2. Synthesis



*Scheme S1: Synthesis of **Bin** and **PBin***

Tetrafluorobindone (**Bin**)

Compound **2** (1.0 g, 5.4 mmol) was dissolved in ethanol (150 mL) and triethylamine (1 drop) was added. The reaction mixture was heated under reflux for 16h. The reaction mixture was cooled to room temperature and added to water (150 mL) and neutralised to pH 7 with HCl (1M aq). The precipitate was filtered and washed with water (100 mL) and petroleum ether (100 mL) yielding a beige solid (0.8 g, 84%). mp = 220-222 °C. ν_{max}/cm^{-1} 1481, 1569, 1678, 1724, 2908, 3047. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.64 (dd, J = 11.5, 7.3 Hz, 1H), 7.84 (dd, J = 8.2, 6.8 Hz, 1H), 7.77 (dd, J = 8.1, 6.8 Hz, 1H), 7.71 (t, J = 7.8 Hz, 1H), 4.13 (s, 2H). ^{19}F NMR (400 MHz, CD_2Cl_2, proton decoupled) δ -123.24 (d, J = 18.2 Hz), -123.37 (d, J = 18.3 Hz), -123.89 (d, J = 19.7 Hz), -124.45 (d, J = 19.7 Hz). MS (ESI-): m/z = 345.0181 [M-H]- (calculated for $[C_{18}H_7F_4O_3]^-$ = 345.0180).

Polytetrafluorbindone (**PBin**)

Bin (0.8 g, 2.4 mmol), 3,3,3′,3′-tetramethyl-1,1′-spirobiindane-5,5′,6,6′-tetraol (0.8 g, 2.4 mmol) and potassium carbonate (3.0 g, 24 mmol) were added to dimethylformamide (30 mL) and heated to 90 °C for 3 days. After cooling to room temperature, the reaction mixture was added to water (80 mL) and the neutralised to pH 7 with HCl (1M aq). The precipitate was filtered and washed with water (100 mL) and petroleum ether (100 mL). The crude material was added to water (50 mL) and heated under reflux for 2 h then filtered. The material was further purified *via* consecutive Soxhlet extractions with dichloromethane and methanol to yield a brown solid (0.8 g, 50%wt). Elemental Analysis found: C, 73.5; H, 4.5. Calc. for $C_{39}H_{26}O_7$: C, 77.2; H, 4.3% ν_{max}/cm^{-1} 1303, 1480, 1586, 1700, 2947. ^{1}H NMR (400 MHz, DMSO-d6) δ 9.00 – 6.00 (m, 8H), 3.01 – 2.61 (m, 2H), 2.37 – 2.04 (m, 4H), 1.54 – 0.90 (m, 12H). GPC m_w = 8470 $gmol^{-1}$ PDI = 1.4.

3. Characterisation

3.1 NMR

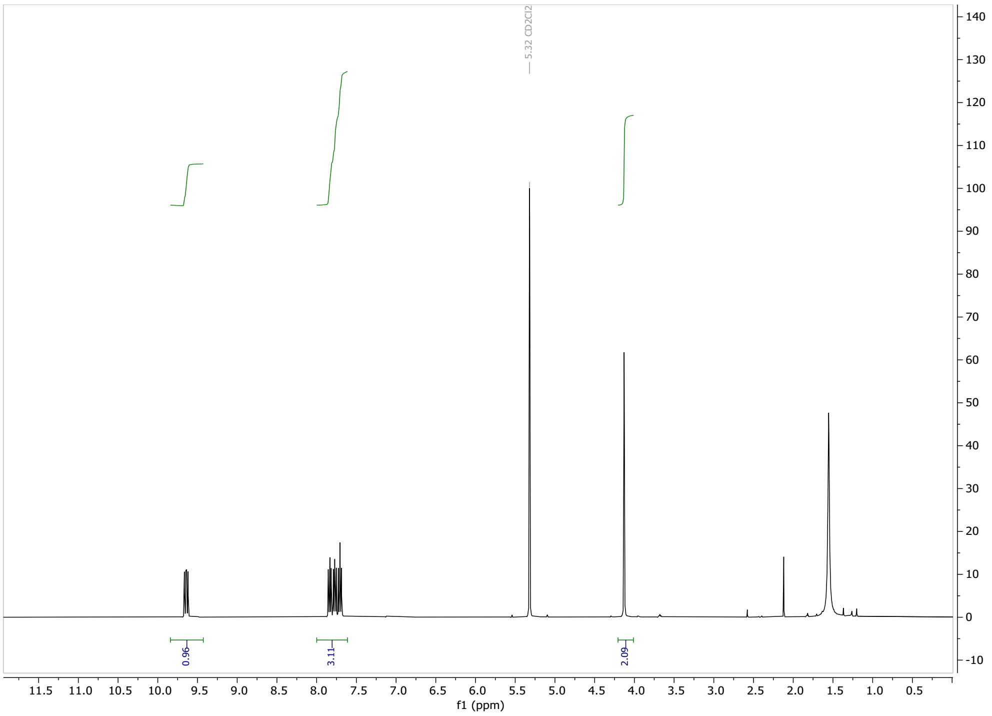


*Figure S1: ^{1}H NMR spectrum of **Bin** (dichloromethane-d2)*

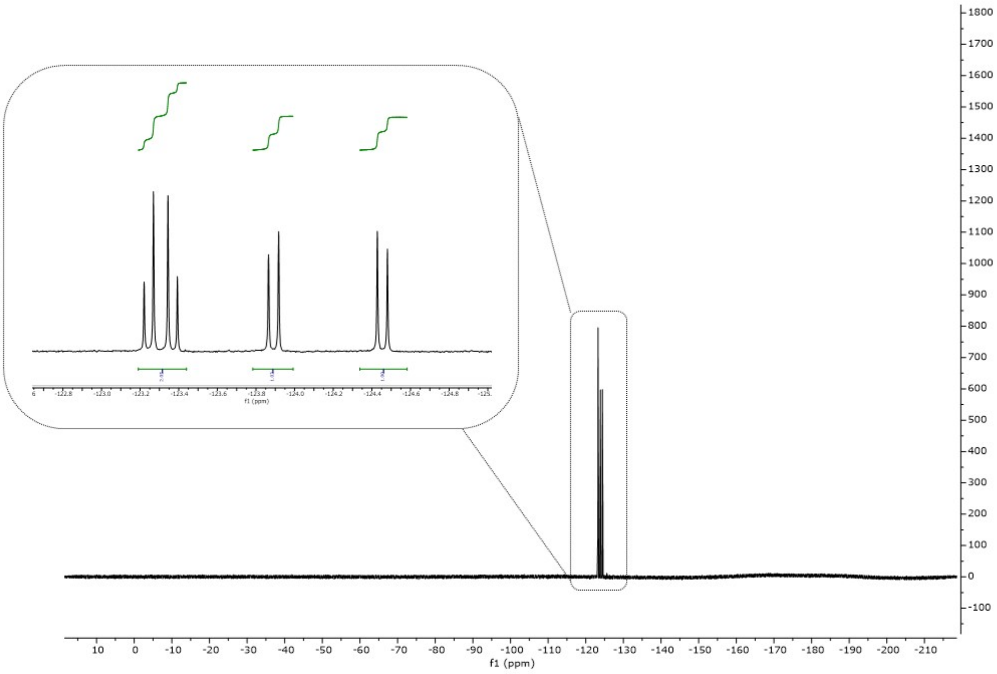


*Figure S2: ^{19}F NMR spectrum of **Bin** (dichloromethane-d2)*

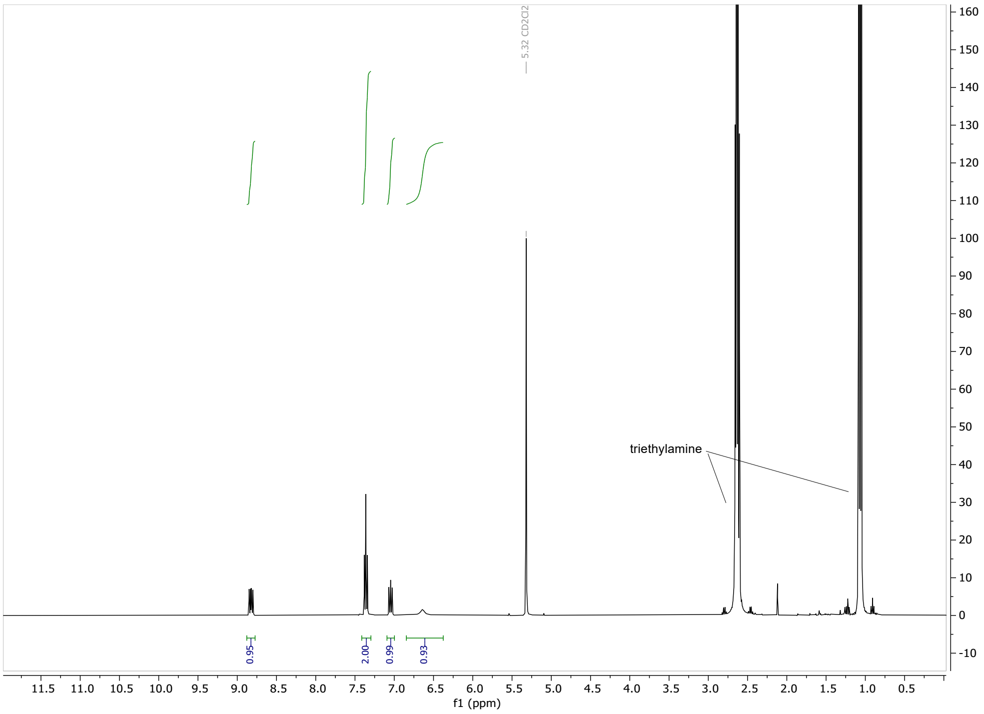


*Figure S3: ^{1}H NMR spectrum of **Bin** after addition of triethylamine (dichloromethane-d2)*

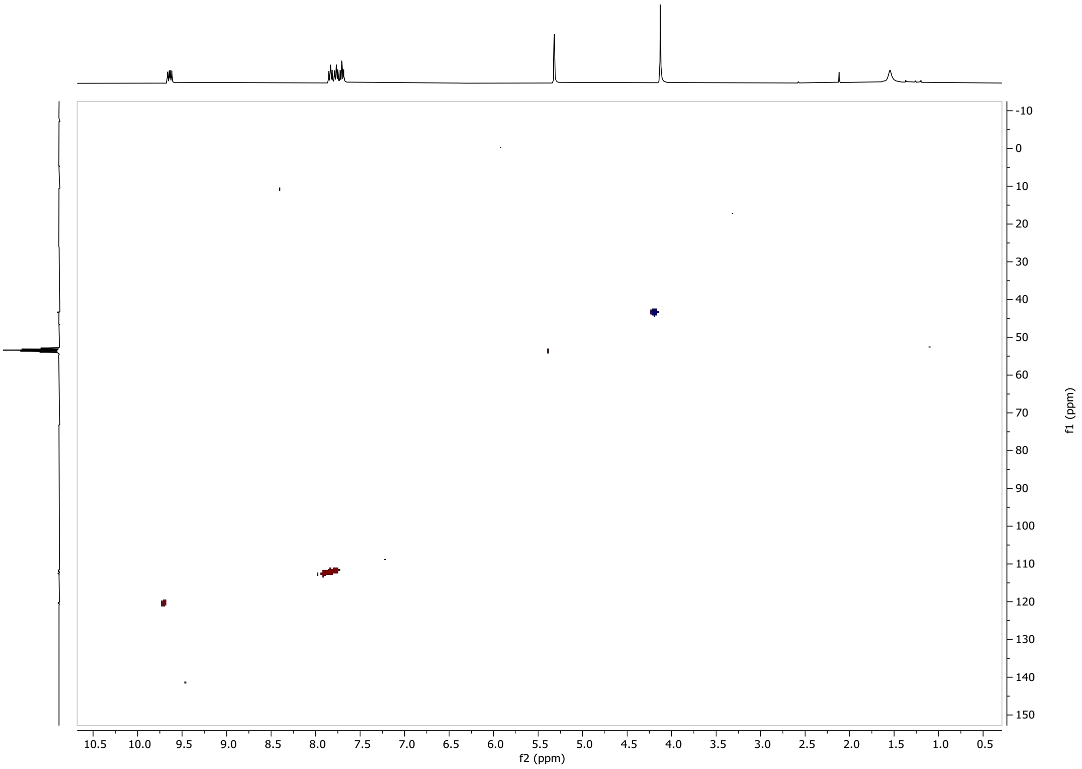


*Figure S4: HMQC NMR spectrum of **Bin** (CH and CH_3 red, CH_2 blue) (dichloromethane-d2)*

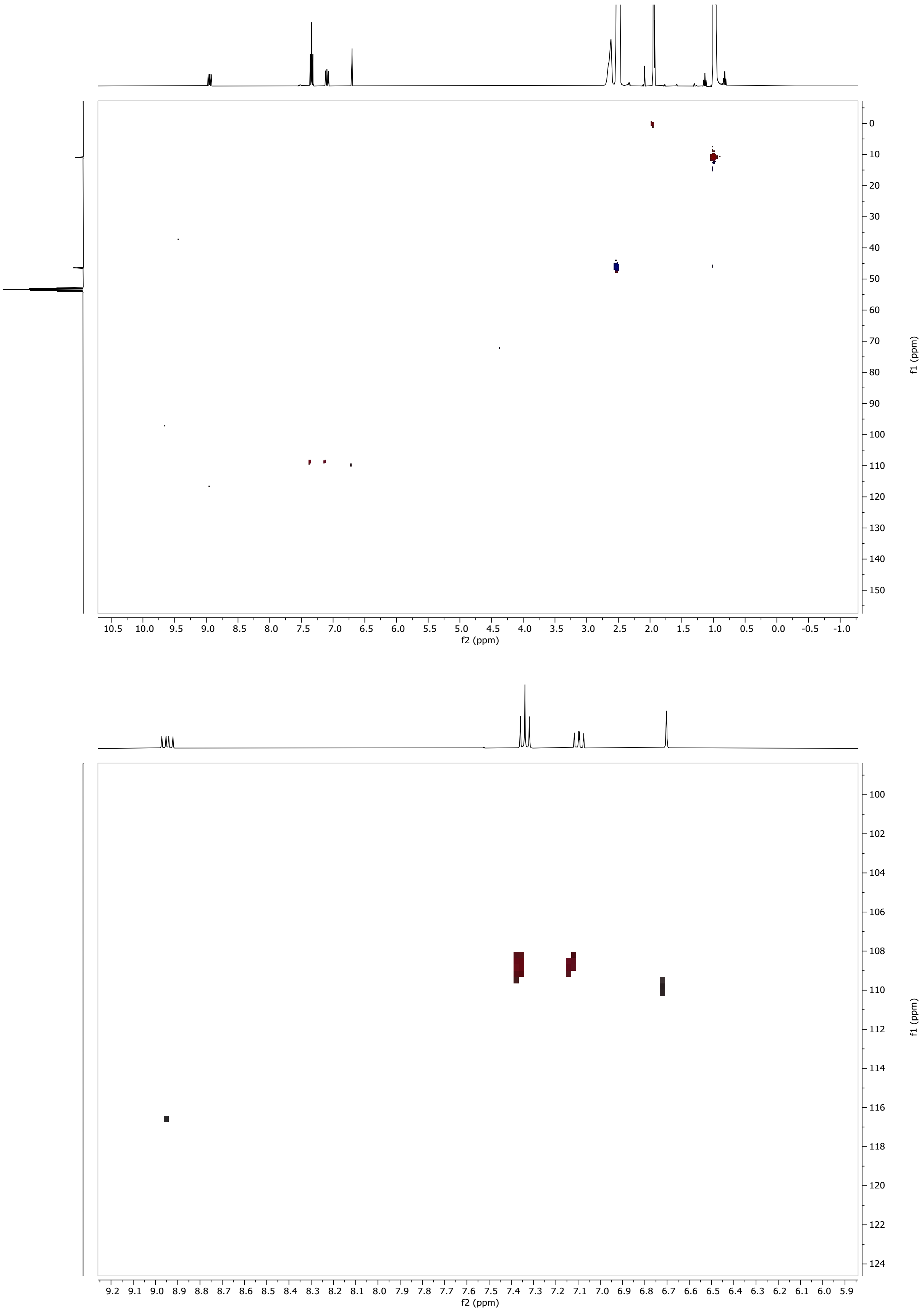


*Figure S5: HMQC NMR spectra (top: full, bottom: zoomed) of **Bin** after addition of triethylamine (CH and CH_3 red, CH_2 blue) (acetonitrile-d3)*

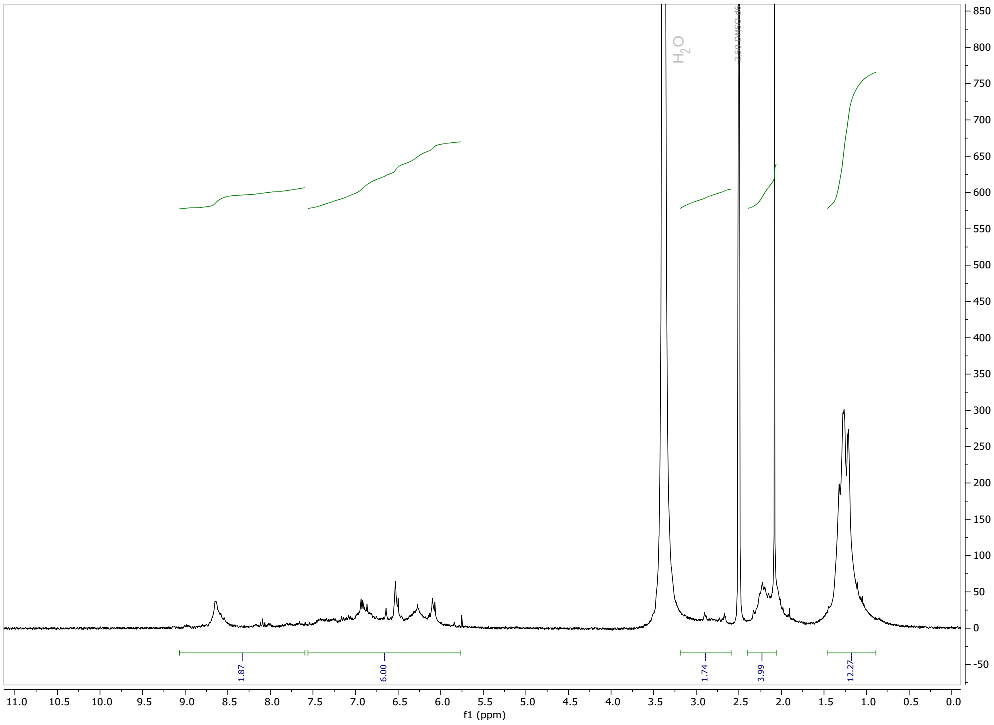
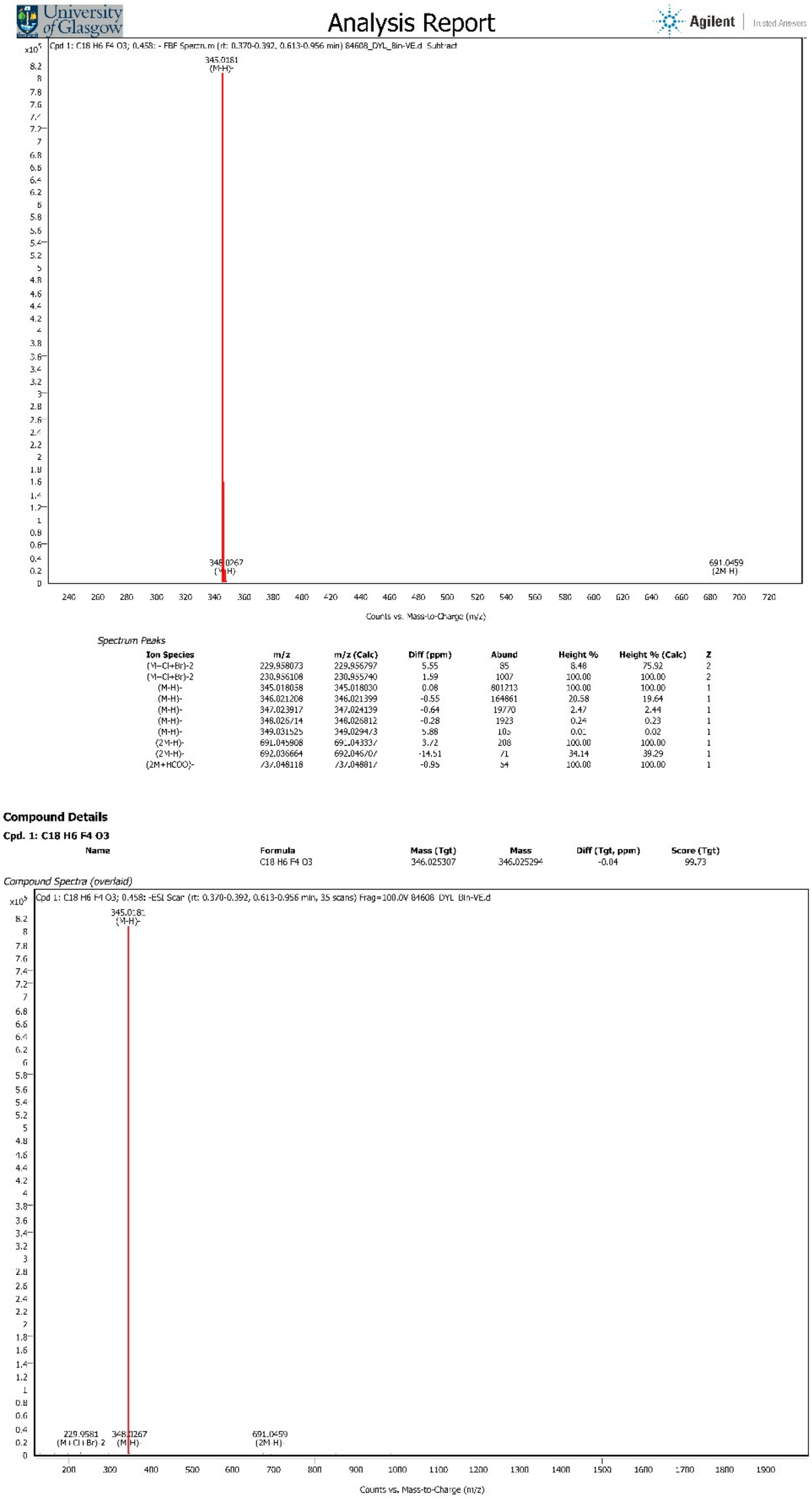


*Figure S6: ^{1}H NMR spectra of **PBin** (dimethylsulfoxide-d6)*

3.2 MS



Analysis Report

Cpd 1: C18 H6 F4 O3; 0.458: - FBF Spectrum (rt: 0.370-0.392, 0.613-0.956 min) 84608_DYL_Bin-VE.d Subtract

Spectrum Peaks

Ion Species	m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Z
(M−Cl+Br)-2	229.958073	229.956797	5.55	85	8.48	75.92	2
(M−Cl+Br)-2	230.956108	230.955740	1.59	1007	100.00	100.00	2
(M-H)-	345.018038	345.018030	0.08	801213	100.00	100.00	1
(M-H)-	346.021208	346.021399	-0.55	164861	20.58	19.64	1
(M-H)-	347.023917	347.024139	-0.64	19770	2.47	2.44	1
(M-H)-	348.026714	348.026812	-0.28	1923	0.24	0.23	1
(M-H)-	349.031525	349.029473	5.88	105	0.01	0.02	1
(2M-H)-	691.045908	691.043337	3.72	208	100.00	100.00	1
(2M-H)-	692.036664	692.046707	-14.51	71	34.14	39.29	1
(2M+HCOO)-	737.048118	737.048817	-0.95	54	100.00	100.00	1

Compound Details

Cpd. 1: C18 H6 F4 O3

Name	Formula	Mass (Tgt)	Mass	Diff (Tgt, ppm)	Score (Tgt)
	C18 H6 F4 O3	346.025307	346.025294	-0.04	99.73

Compound Spectra (overlaid)

Cpd 1: C18 H6 F4 O3; 0.458: -ESI Scan (rt: 0.370-0.392, 0.613-0.956 min, 35 scans) Frag=100.0V 84608_DYL_Bin-VE.d

*Figure S7: Mass spectrum of **Bin***

3.3 IR

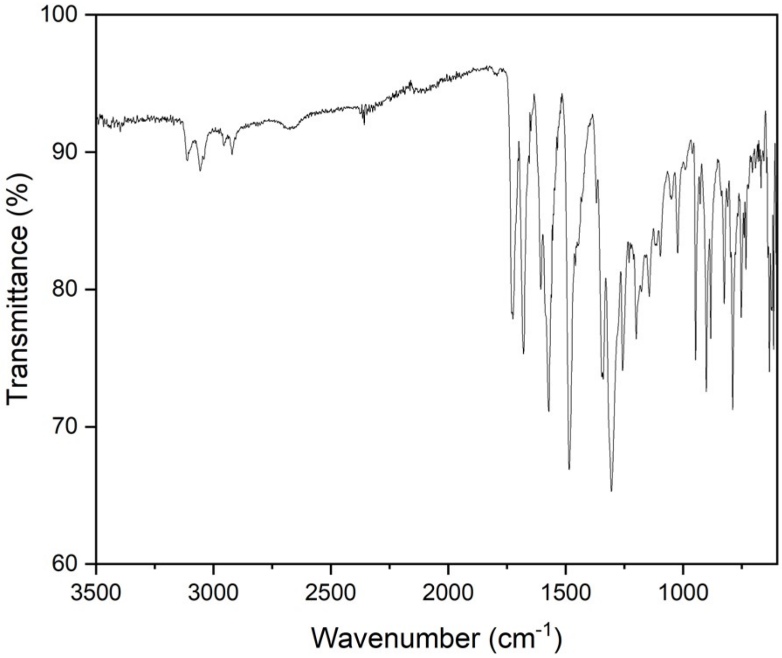


*Figure S8: IR spectra of **Bin***

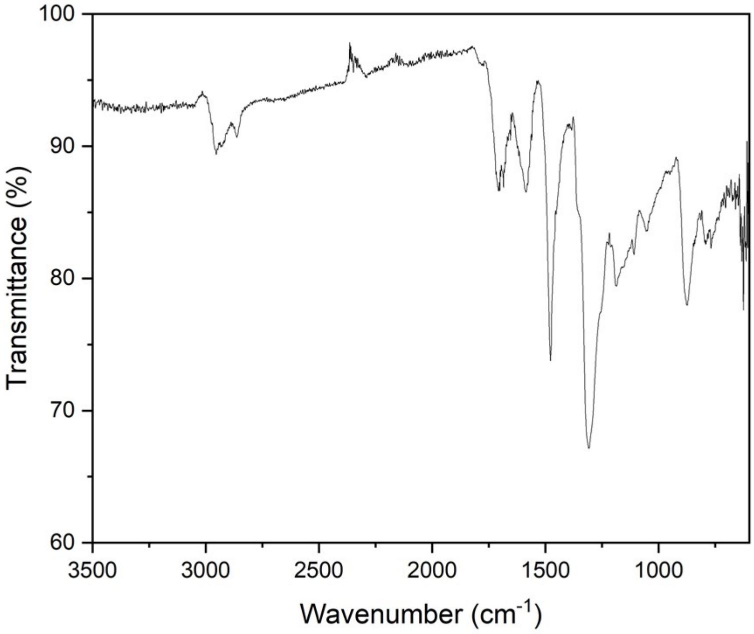


*Figure S9: IR spectra of **PBin***

3.4 Thermal Analysis

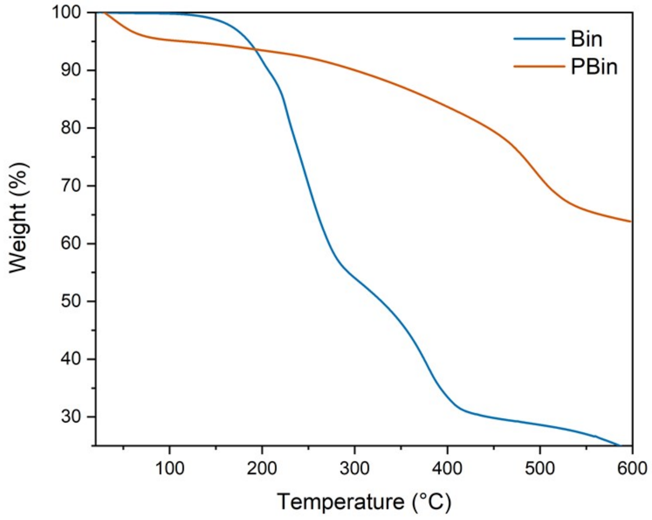


Figure S10: Thermal gravitational analysis of ***Bin*** *and* ***PBin.***

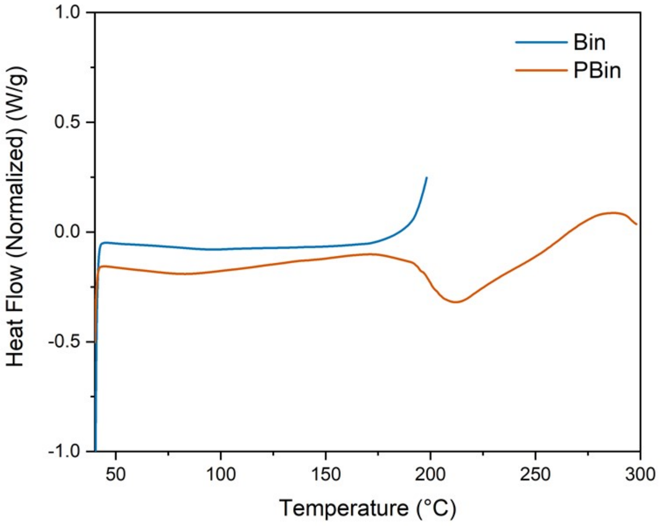
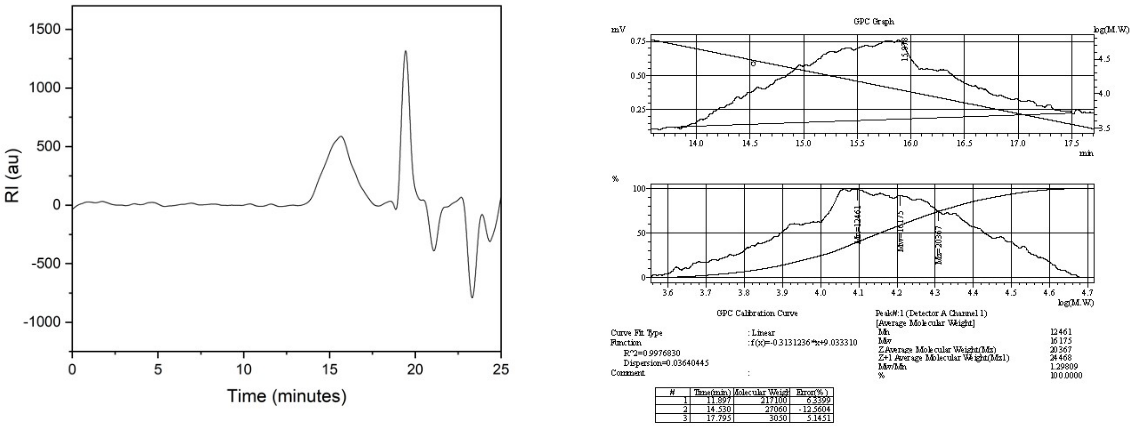


Figure S11: Differential scanning calorimetry of ***Bin*** *and* ***PBin*** *displaying glass transition temperature (Tg) of* ***PBin*** *at 210 °C.*

3.5 GPC



GPC Calibration Curve

Curve Fit Type : Linear
Function : f(x)=-0.3131236*x+9.033310
R^2=0.9976830
Dispersion=0.03640445
Comment :

#	Time(min)	Molecular Weigh	Error(%)
1	11.897	217100	6.3399
2	14.530	27060	-12.5604
3	17.795	3050	5.1451

Peak#:1 (Detector A Channel 1)
[Average Molecular Weight]

Mn	12461
Mw	16175
Z Average Molecular Weight(Mz)	20367
Z+1 Average Molecular Weight(Mz1)	24468
Mw/Mn	1.29809
%	100.0000

Figure S12: GPC spectra of ***PBin***

3.6 Gas Adsorption Analysis

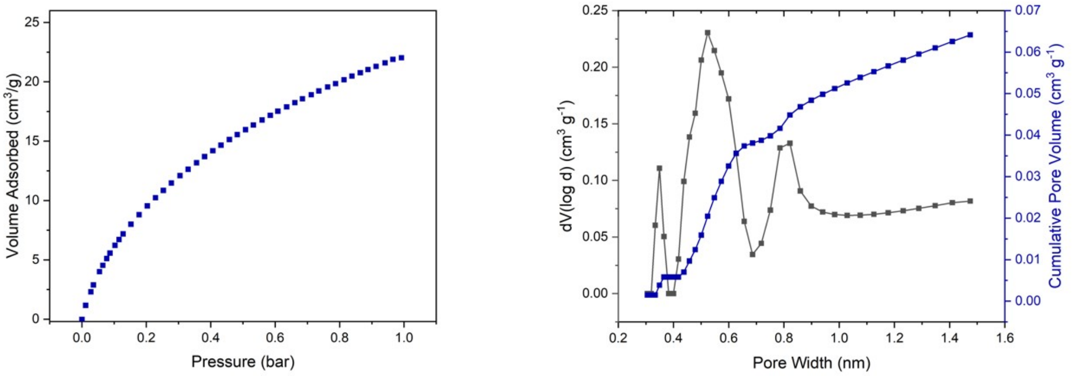


*Figure S13: CO_2 adsorption isotherm of **PBin** displaying 22 cm^3g^{-1} CO_2 uptake at 1 bar, and pore size distribution derived using CO_2 isotherm calculated through NLDFT.*

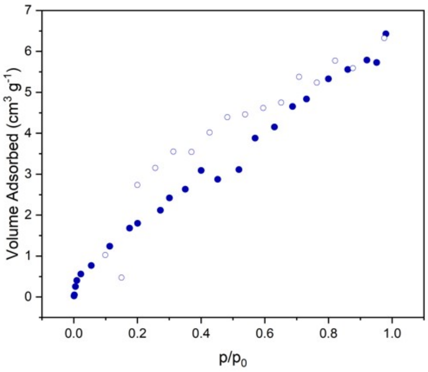


*Figure S14: N_2 adsorption isotherm of **PBin** revealing low uptake. Isotherm not well defined.*

3.7 SEM Images

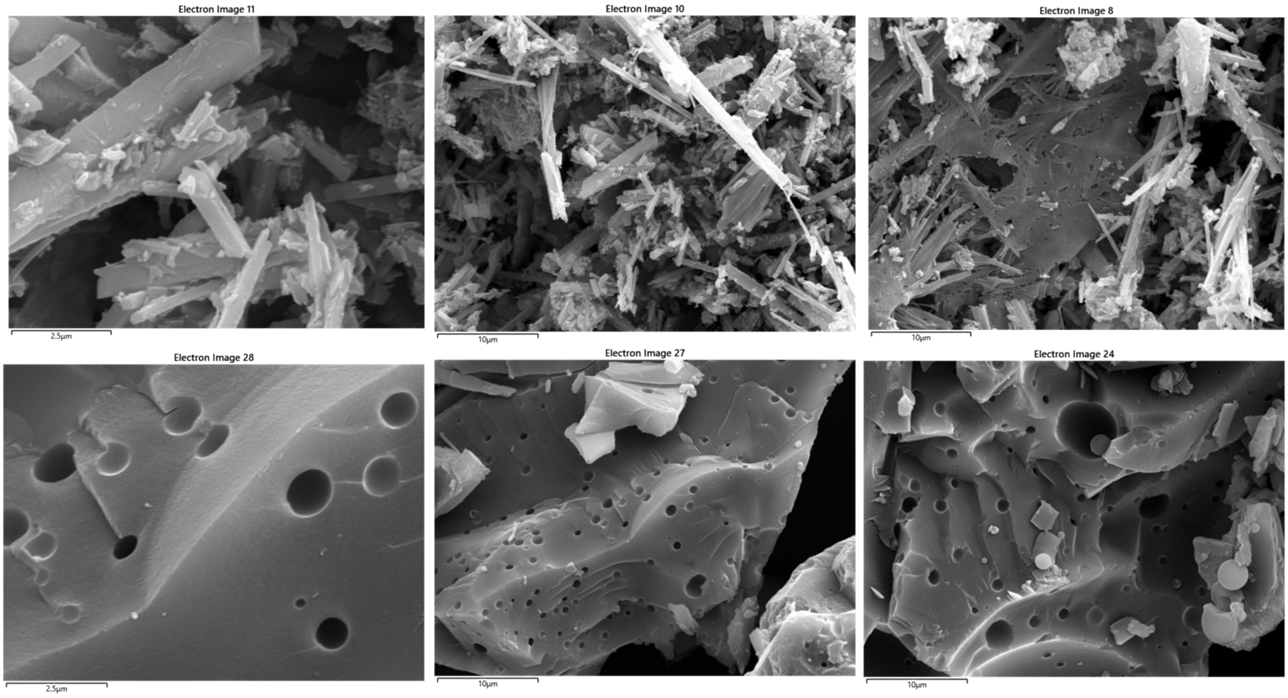


*Figure S15: SEM images of powder samples of **Bin** (above) and **PBin** (below) displaying macropores in **PBin***

3.8 Fluorescence

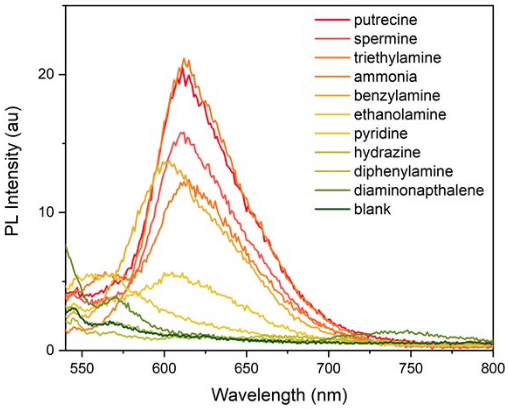


Figure S16: Fluorescence spectra of ***Bin*** *(1x10^{-5} mol L^{-1}) THF solution after addition of 0.1 equivalents of selected amines.*

3.9 Anion Sensing

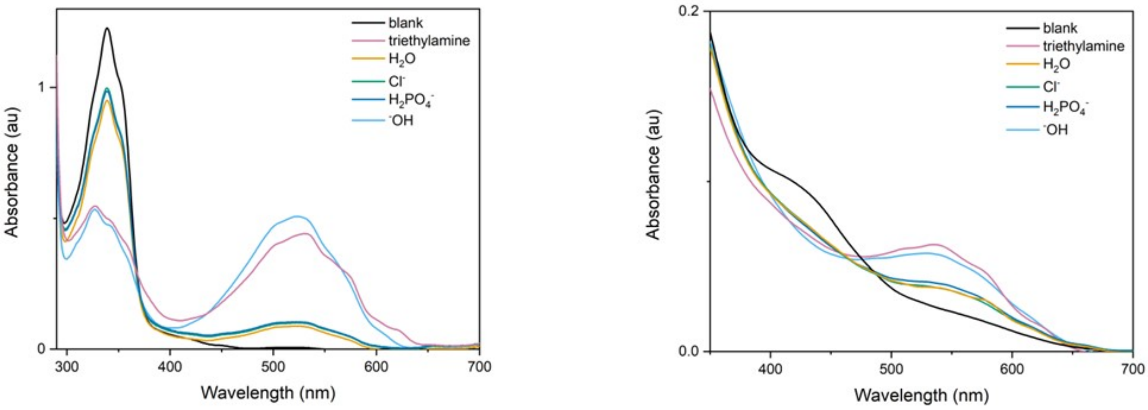
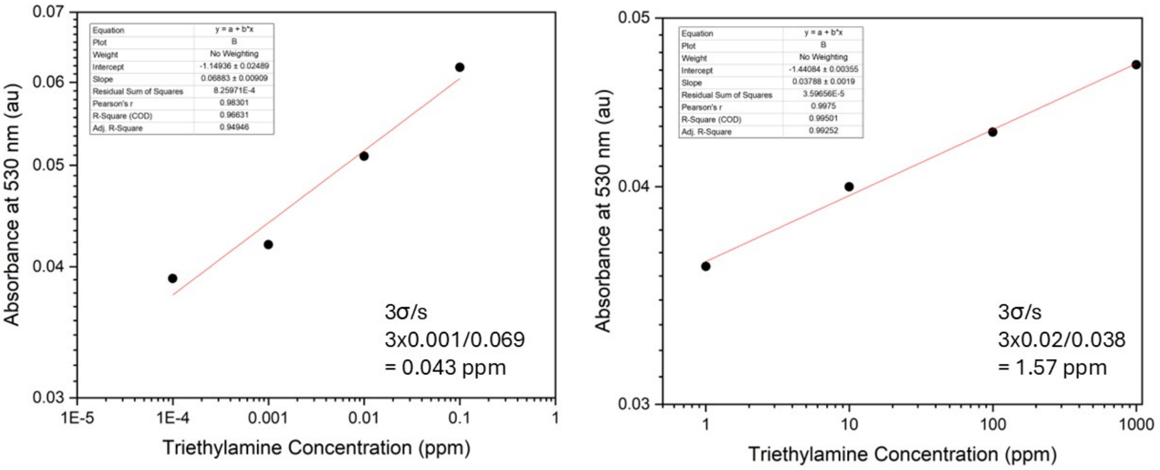


Figure S17: UV/Vis spectra of (a) ***Bin*** *$1x10^{-5}$ mol L^{-1} and (b)* ***PBin*** *0.1 mg mL^{-1} THF solution after adding to 0.1 equivalent of water, sodium chloride, potassium phosphate and sodium hydroxide, compared with a blank and triethylamine.*

3.10 Limit of Detection Calculation



Equation	y = a + b*x
Plot	B
Weight	No Weighting
Intercept	-1.14936 ± 0.02489
Slope	0.06883 ± 0.00909
Residual Sum of Squares	8.25971E-4
Pearson's r	0.98301
R-Square (COD)	0.96631
Adj. R-Square	0.94946

3σ/s
3x0.001/0.069
= 0.043 ppm

Equation	y = a + b*x
Plot	B
Weight	No Weighting
Intercept	-1.44084 ± 0.00355
Slope	0.03788 ± 0.0019
Residual Sum of Squares	3.59656E-5
Pearson's r	0.9975
R-Square (COD)	0.99501
Adj. R-Square	0.99252

3σ/s
3x0.02/0.038
= 1.57 ppm

*Figure S18: Absorbance at 530 nm vs. concentration of triethylamine added for **Bin** and **PBin** solutions used to calculate the limit of detection (LOD) using LOD=3σ/s where σ is the standard deviation of 4 blank runs and s is the slope of the calibration curve.*

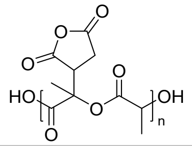
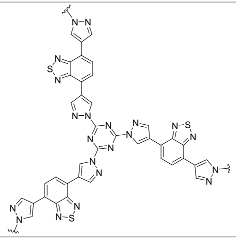
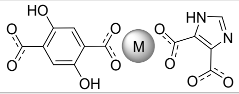
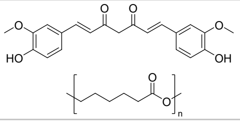
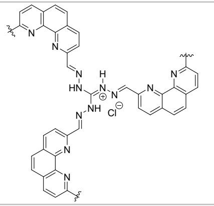
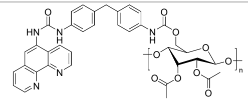
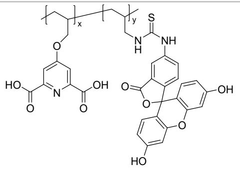
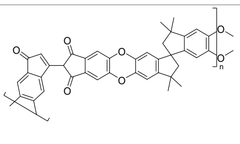
4. Amine pKaH

Table S1: pKa values of the conjugate acid (pKaH) of selected amines used as an indirect measure of basicity.[2]

Amine	**pKa (conjugate acid)**
Ammonia	9.2
Triethylamine	10.8
Spermine	8.3 [3]
Putrescine	9.3
Benzylamine	9.3
Ethanolamine	9.5
Diphenylamine	0.8
1,5-diaminonaphthalene	4.2
Hydrazine	8.1
Pyridine	5.1

5. Amine Sensor Comparison

*Table S2: Comparison of polymer structure, LOD and detection method between **PBin** and recently reported amine sensing polymers.*

Name, Description	**Structure**	**Analyte**	**Detection**	**LOD (ppm)**	**Ref**
PLA-*g*-SAh polylatic acid		methylamine	colorimetric	150	[4]
P1, conjugated polymer network		aniline, 1,4-phenylenediamine	fluorescence	0.16, 0.02	[5]
$[Cd_2(dht)(idc)(H_2O)_4]$, MOF		methylamine	colorimetric	279	[6]
PCLCU1, small molecule doped polycaprolactone		dimethylamine	colorimetric	2.37	[7]
TGH+.PD, COF		ammonia	fluorescence	0.002	[8]
Phen-MDI-CA, functionalised cellulose		triethylamine, aniline	fluorescence	0.09, 0.04	[9]
poly(FITC-co-DBA), co-polyalkene		cadaverine	Colorimetric, fluorescence	0.022	[10]
PBin		triethylamine	colorimetric	1.57	This work

6. Computational Study

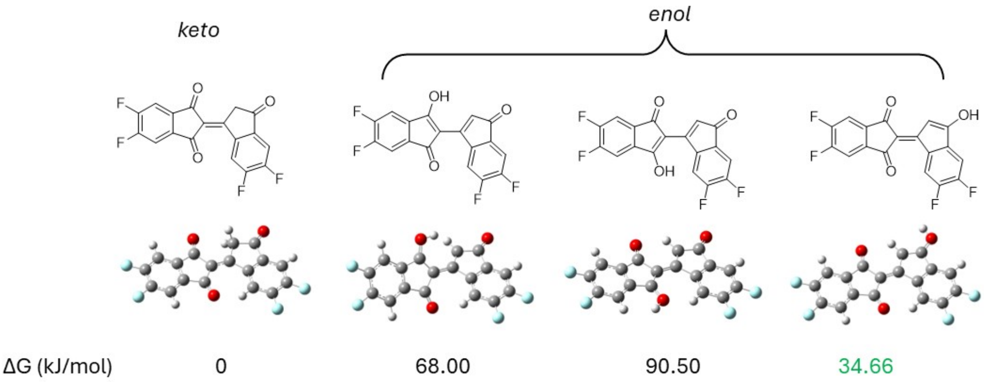


Figure S19: Free energy of enol isomers of ***PBin*** *relative to keto isomer calculated using DFT B3LYP 6311G (d,p).*

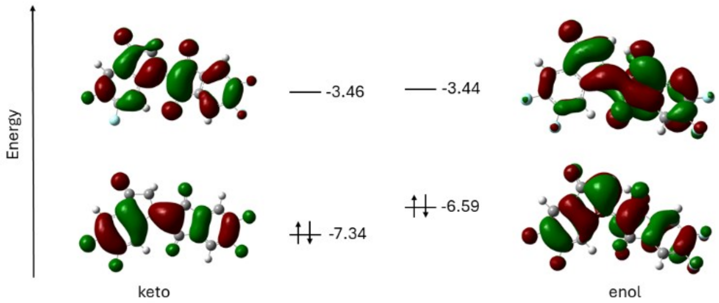


Figure S20: Frontier molecular orbital diagrams and energy levels of ***Bin**$_{keto}$* *and* ***Bin**$_{enol}$* *calculated using B3LYP 6311G (d,p).*

7. Reference

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