Supporting Information

Hydroxyalkylaminoalkylamide PIMs: Selective adsorption by ethanolamine- and diethanolamine-modified PIM-1

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1. Characterization of PIM-1

^{1}H and ^{13}C NMR spectra of SPIM and TPIM are shown in **Figure S1**. Molecular weight distributions from GPC are shown in **Figure S2**.

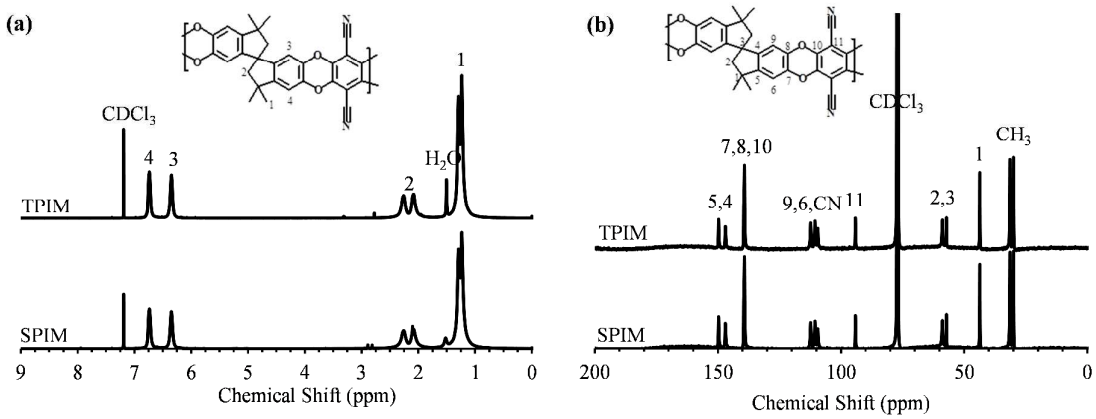

Figure S1. (a) ^{1}H-NMR spectra and (b) ^{13}C NMR spectra of PIM-1 samples SPIM (bottom spectra) and TPIM (top spectra), and peak assignments.

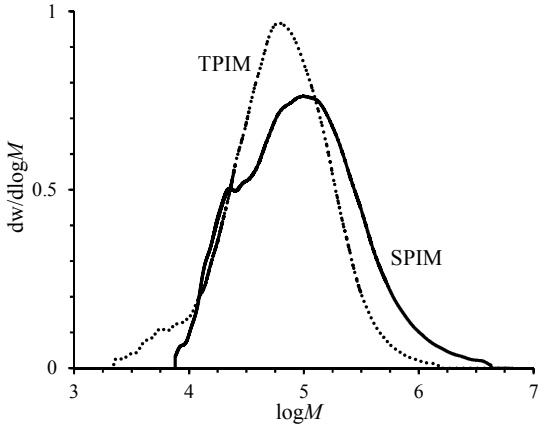

Figure S2. Weight distributions of log*M* from multi-detector GPC for SPIM (solid line) and TPIM (dashed line).

2. Chemical modification of PIM-1

2.1 Reaction conditions and work-up procedure

Details of reaction conditions and work-up procedures for each sample are listed in **Table S1**.

Table S1. Amounts of reagents, temperature and time of reaction for modification of PIM-1 with ethanolamine (EA) and diethanolamine (DEA), volume of aliquots taken from reaction, and volumes of ethanol and water used for washing.

			Reaction conditions					Work-up procedure			
Sample	Internal code	PIM-1	Weight PIM-1/g	Amine	Amount amine	*T*/°C	*t*/h	Aliquot taken/mL	Vol. ethanol/ mL	Vol. water/ mL	No. of wash cycles
ES120-3	EAP10-1	SPIM	1.07	EA	35 mL	120	3	*ca.* 7	20	100	3
ES120-6	EAP10-2	SPIM	1.07	EA	35 mL	120	6	*ca.* 7	20	100	3
ES120-12	EAP10-3	SPIM	1.07	EA	35 mL	120	12	*ca.* 7	20	100	2
ES120-24	EAP10-4	SPIM	1.07	EA	35 mL	120	24	*ca.* 7	20	100	2
ES120-48	EAP10-5	SPIM	1.07	EA	35 mL	120	48	residue	20	100	2
ET105-6	EAPA-1	TPIM	1.15	EA	30 mL	105	6	*ca.* 5	20	100	2
ET105-12	EAPA-2	TPIM	1.15	EA	30 mL	105	12	*ca.* 5	20	100	2
ET105-24	EAPA-3	TPIM	1.15	EA	30 mL	105	24	*ca.* 5	20	100	2
ET105-36	EAPA-4	TPIM	1.15	EA	30 mL	105	36	*ca.* 5	20	100	1
ET105-48	EAPA-5	TPIM	1.15	EA	30 mL	105	48	residue	20	100	1
ET90-24	EAP22	TPIM	0.23	EA	10 mL	90	24	all	20	100	2
ET90-52	EAP24	TPIM	0.23	EA	10 mL	90	52	all	20	100	2
DT120-9	DEA9	TPIM	0.23	DEA	6 g	120	9	all	100	500	2
DT120-24	DEA24	TPIM	0.23	DEA	6 g	120	24	all	100	500	2
DT120-46	DEA46	TPIM	0.23	DEA	6 g	120	46	all	100	500	2
DT120-90	DEA90	TPIM	0.23	DEA	6 g	120	90	all	100	500	2
DT150-24	DEA10	TPIM	0.23	DEA	6 g	150	24	all	100	500	2
DT150-30	DEA11	TPIM	0.23	DEA	6 g	150	30	all	100	500	2
DT150-48	DEA12	TPIM	0.23	DEA	6 g	150	48	all	100	500	2

2.2 Visual appearance of reaction mixtures and products

PIM-1 does not readily dissolve in ethanolamine (EA) or diethanolamine (DEA), and no solvent was used in the chemical modification of PIM-1, so the reaction mixtures were suspensions at the start of the reaction period. However, over extended periods of reaction, a more homogeneous mixture was obtained. For each sample, the visual appearance of the reaction mixture at the time the sample was recovered, and of the isolated product, is summarised in **Table S2**. None of the products, once recovered, could be redissolved in the amine.

Table S2: Modification of PIM-1 with ethanolamine (EA) and diethanolamine (DEA): Appearance and colour of reaction mixture at end of reaction period, and colour of reaction products after addition to ethanol (EA products) or addition of ethanol (DEA products), and after drying in the oven.

Sample	Appearance of reaction mixture	Colour of reaction mixture	Colour of product after ethanol.	Colour of oven-dried sample
ES120-3	Suspension	Yellow-greenish	Yellow	Yellow
ES120-6	Suspension	Yellow-greenish	Yellow	Yellow
ES120-12	Suspension	Yellow-greenish	Yellow	Yellow
ES120-24	Solution	Dark green	Yellow-green	Brown
ES120-48	Solution	Dark green	Yellow-green	Brown
ET105-6	Suspension	Yellow	Yellow	Yellow
ET105-12	Suspension	Yellow	Yellow	Yellow
ET105-24	Suspension	Yellow-brown	Yellow	Yellow
ET105-36	Suspension	Brownish	Yellow	Brown
ET105-48	Solution	Brownish	Brown	Brown
ET90-24	Suspension	Yellow	Yellow	Yellow
ET90-52	Suspension	Yellow	Yellow	Yellow
DEA-modified samples	Gel-like Suspension	Yellow	Pale-yellow	Pale-Yellow

3. Characterization of ethanolamine- and diethanolamine-modified PIM-1

3.1 ATR-IR and ^{13}C-NMR spectroscopy

ATR-IR infrared spectra and solid-state ^{13}C NMR spectra are shown in **Figures S3** and **S4**, respectively, for samples for which the spectra are not included in **Figure 2** of the paper.

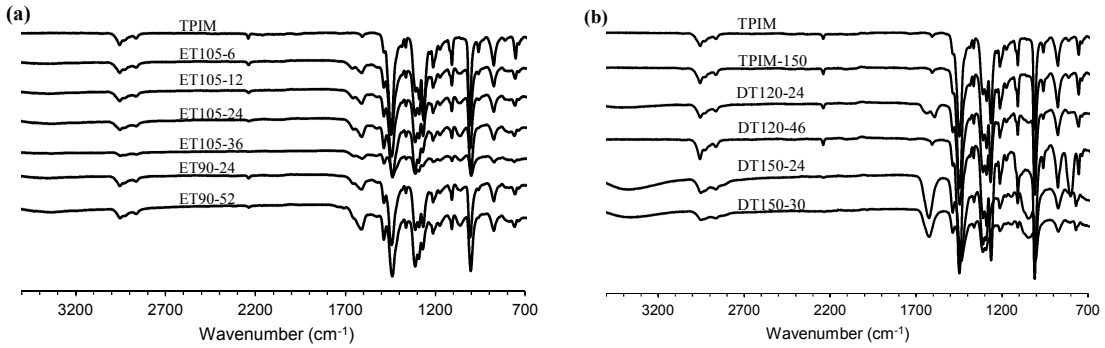

Figure S3. ATR-IR Spectra of (a) TPIM and ethanolamine-modified PIM-1 samples, (b) TPIM, heat-treated TPIM (TPIM-150), and diethanolamine-modified PIM-1 samples.

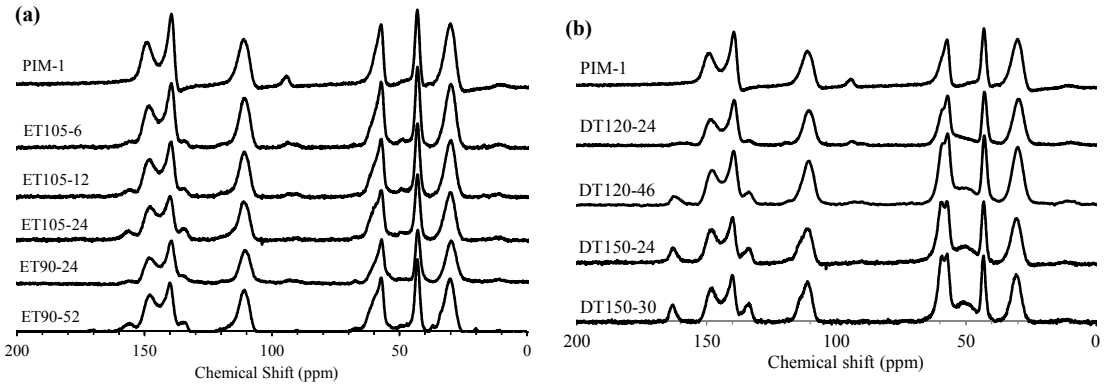

Figure S4. Solid-state ^{13}C-NMR spectra of (a) SPIM and ethanolamine-modified PIM-1 samples, (b) SPIM and diethanolamine-modified PIM-1 samples.

3.2 Elemental analysis

For the purposes of structural prediction, the elemental analysis results were corrected for the moisture content of the samples, determined as the weight loss below 150 °C by thermogravimetric analysis (see below). Original and corrected elemental analysis results are listed in **Table S3**. The correction does not affect the N/C ratio, and thus does not affect the calculated values of x_{mod}.

Table S3. Modification of PIM-1 with ethanolamine (EA) and diethanolamine (DEA): Elemental analysis of reaction products and values corrected for moisture in the samples, based on the weight loss below 150 °C by thermogravimetric analysis.

Sample[a]	Original elemental analysis (wt.%)				Corrected elemental analysis (wt.%)			
	C	H	N	O[b]	C	H	N	O[b]
ES120-3	70.4	4.8	6.7	18.1	71.5	4.7	6.8	17.0
ES120-6	67.5	4.9	6.9	20.8	68.6	4.8	7.0	19.6
ES120-12	66.2	5.8	7.7	20.3	68.4	5.6	7.9	18.0
ES120-24	65.2	6.0	7.8	21.1	67.3	5.8	8.0	18.9
ES120-48	65.1	6.2	8.2	20.5	68.1	6.0	8.6	17.4
ET105-6	70.6	4.9	7.1	17.5	71.0	4.9	7.1	16.9
ET105-12	69.3	5.0	7.4	18.3	70.0	4.9	7.4	17.6
ET105-24	67.4	5.4	7.9	19.4	68.9	5.2	8.1	17.8
ET105-36[c]	60.4	4.8	7.8	26.9	62.4	4.6	8.1	25.0
ET105-48	65.2	5.3	8.1	21.3	67.4	5.1	8.4	19.1
ET90-24	69.3	4.7	7.2	18.8	70.1	4.7	7.2	18.0
ET90-52	66.4	5.0	7.4	21.3	67.7	4.9	7.5	20.0
DT120-9	70.6	4.9	6.2	18.2	70.9	4.9	6.3	17.9
DT120-24	70.5	4.6	6.2	18.7	71.0	4.5	6.3	18.2
DT120-46	65.5	5.7	6.3	22.5	66.3	5.6	6.4	21.7
DT120-90	66.3	5.4	6.4	21.9	67.1	5.3	6.5	21.0
DT150-24	62.8	6.5	6.4	24.3	63.6	6.5	6.5	23.5
DT150-30	62.4	6.7	6.4	24.5	63.2	6.6	6.5	23.6
DT150-48	61.9	6.8	6.3	25.0	62.7	6.7	6.4	24.3

[a]Sample codes for reaction products: E = ethanolamine modification, D = diethanolamine modification; S = SPIM, T = TPIM; first number = temperature of reaction in °C; Second number = time of reaction in h. E.g., Sample ES120-3 is the product of reaction of ethanolamine with SPIM at 120 °C for 3 h.
[b]Oxygen content calculated from C, H and N values.
[c]ET105-36 is impure as there was insufficient sample for a full washing sequence.

4. Thermogravimetric analysis

4.1. Ethanolamine-modified PIM-1

TGA curves for selected ethanolamine-modified PIM-1 samples are shown in **Figure S5(a)**. Weight losses below 150 °C (**Table S4**) may be attributed to moisture in the samples. The weight loss in the range 240-450 °C was determined for every sample (**Table S4**), and is plotted against the mole fraction of modified groups, x_{mod}, in **Figure S5(b)**. A clear correlation is seen with the degree of modification.

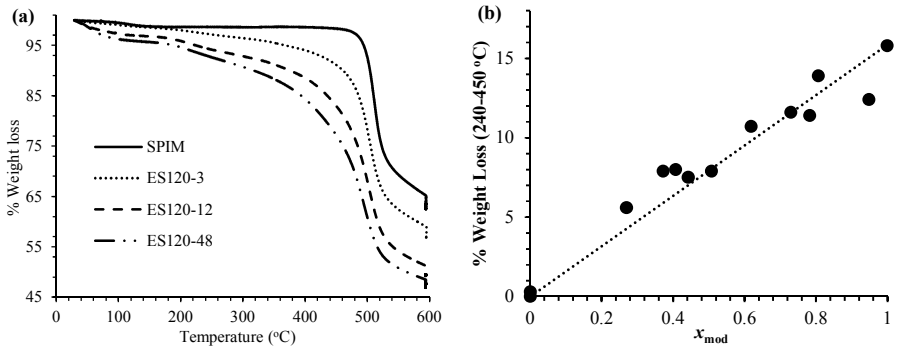

Figure S5. (a) TGA curves for SPIM and for ethanolamine-modified samples ES120-3, ES120-12 and ES120-48. (b) Correlation between the weight loss in the temperature range 240-450 °C and the mole fraction of modified groups.

4.2. Diethanolamine-modified PIM-1

TGA curves for selected diethanolamine-modified PIM-1 samples are shown in **Figure S6(a)**. The weight loss in the range 245-450 °C was determined for every sample (**Table S4**), and is plotted against the mole fraction of modified groups, x_{mod}, in **Figure S6(b)**. A clear correlation is seen with the degree of modification.

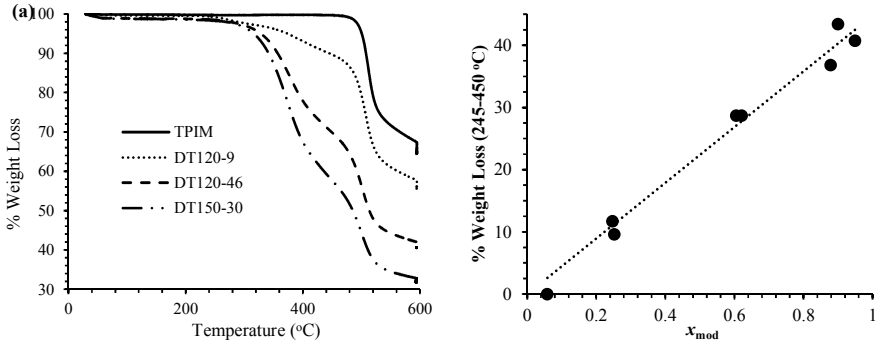

Figure S6. (a) TGA curves for TPIM and for diethanolamine-modified samples DT120-9, DT120-46 and DT150-30. (b) Correlation between the weight loss in the temperature range 245-450 °C and the mole fraction of modified groups.

Table S4. Percentage weight loss by thermogravimetric analysis below 150 °C (attributed to loss of sorbed water) and in the temperature range 240-450 °C for EA-modified samples or 245-450 °C for DEA-modified samples (attributed to degradation associated with modified groups).

Sample	% weight loss		
	<150 °C	240-450 °C	245-450 °C
ES120-3	1.5	5.6	
ES120-6	1.6	8	
ES120-12	3.2	11.6	
ES120-24	3.1	13.9	
ES120-48	4.4	15.8	
ET105-6	0.7	7.9	
ET105-12	1.0	7.9	
ET105-24	2.2	11.4	
ET105-36	3.1	11.7	
ET105-48	3.2	12.4	
ET90-24	1.2	7.5	
ET90-52	1.9	10.7	
DT120-9	0.4		9.6
DT120-24	0.7		11.7
DT120-46	1.2		28.7
DT120-90	1.2		28.7
DT150-24	1.2		36.8
DT150-30	1.3		40.7
DT150-48	1.2		43.4