Macromolecules

Hydroxyalkylaminoalkylamide PIMs: Selective Adsorption by Ethanolamine- and Diethanolamine-Modified PIM-1

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Ⓢ *Supporting Information*

ABSTRACT: The polymer of intrinsic microporosity PIM-1 was modified by reaction with ethanolamine and with diethanolamine, and the modified polymers characterized by infrared spectroscopy, solid-state NMR spectroscopy, elemental analysis, thermogravimetric analysis and nitrogen adsorption. Various possible reaction products were considered, and the results indicated that hydroxyalkylaminoalkylamide structures were obtained. Gas adsorption measurements showed that ethanolamine modification increased the ideal CO_2/N_2 selectivity. Studies of dye adsorption from aqueous solution demonstrated that the reaction products showed strong selectivity for the anionic dye Orange II, compared to the cationic dye Safranin O. Mass uptakes of the anionic dye by ethanolamine-modified PIM-1 samples were up to 2 orders of magnitude higher than for the parent polymer.
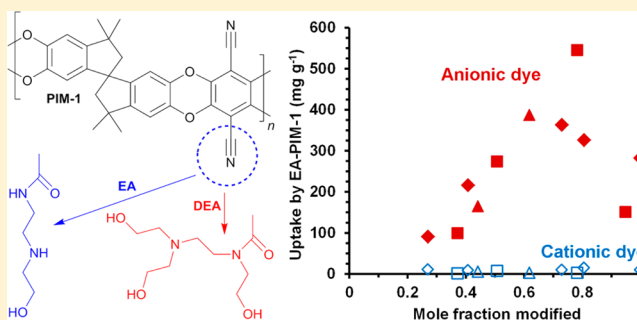
INTRODUCTION

The selective removal of organic compounds from aqueous media is relevant to the isolation of natural products,[1] to the recovery of biorefinery products,[2] and to the treatment of industrial wastewater.[3−5] A variety of separation processes may be employed, including adsorption, extraction, precipitation, and membrane processes, the latter being particularly amenable to continuous processing and *in situ* product recovery.[6] Neutral, cationic, and anionic dyes are useful model compounds for evaluating uptake by potential sorbents and membrane materials. Chemical modification provides a way of manipulating the selectivity of an adsorbent. Ethanolamine (also termed monoethanolamine), which has both a hydroxyl and an amine group and is widely used in absorption processes for carbon dioxide removal,[7,8] has previously been utilized for the chemical modification of mesoporous silica,[9] Merrifield resin,[10] poly-succinimide,[11] and polyacrylonitrile.[12−14]

Polymers of intrinsic microporosity (PIMs) exhibit a high affinity for organic species, coupled with the ability to form thin films in many cases.[15−17] PIMs have macromolecular backbones comprising fused ring sequences interrupted by sites of contortion, such as spiro-centers. They cannot pack efficiently in the solid state, and thus possess high free volume, giving rise to molecular sieve behavior, *i.e.*, they behave like microporous materials as defined by IUPAC[18] (pore dimensions <2 nm). The archetypal solution-processable PIM, referred to as PIM-1 (Figure 1a), shows strong interactions with neutral dyes.[19] Recently, we have demonstrated that the base-catalyzed hydrolysis of PIM-1 yields products with a mixture of amide and carboxylate functionality, and that increasing degree of carboxylation leads to a dramatic increase in the affinity for the cationic dye Safranin O (Figure 1b) and reduced affinity for the anionic dye Orange II (Figure 1c).[20] Here we report new chemical modifications of PIM-1, ethanolamine (EA) and diethanolamine (DEA) modified PIM-1, which show the reverse behavior, high affinity for the anionic dye and low affinity for the cationic. The samples investigated are summarized in Table 1.

EXPERIMENTAL SECTION

Materials. Dimethylformamide (DMF), dimethylacetamide (DMAc), toluene, methanol (MeOH), chloroform, dioxane, acetone, ethanolamine (EA, purified by redistillation, ≥ 99.5%), diethanolamine (DEA, reagent grade, ≥ 98.0%), Safranin O (>85% dye content), and Orange II sodium salt (>85% dye content) were purchased from Sigma-Aldrich and were used as received. Tetrafluoroterephthalonitrile (TFTPN, 98%, Aldrich) was purified by sublimation; it was heated to around 150 °C and the pure product collected without vacuum. 5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane (TTSBI, 98%, Alfa Aesar) was dissolved in methanol and reprecipitated from dichloromethane before use. Anhydrous potassium carbonate (K_2CO_3, 99.0%, Fisher) was dried in an oven at 110 °C overnight before use. Two batches of PIM-1 were used in this study, prepared as described below. Although they were prepared by different methods, and they differ slightly in their molar mass distribution (see Supporting Information), their properties are similar.

Synthesis of PIM-1 at 65 °C (SPIM).[16] All the glassware was washed with acetone before use and was dried in an oven overnight at 110 °C. Under a stream of dry N_2 gas, a mixture of TTSBI (10.01 g, 30 mmol) and TFTPN (6.02 g, 30 mmol) was dissolved in dry DMF
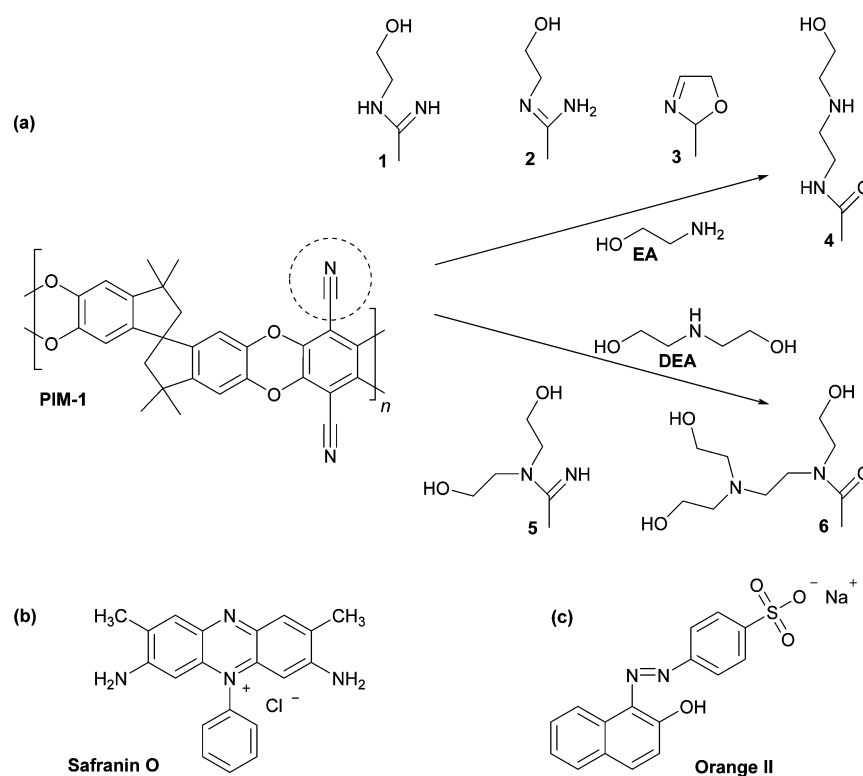
Figure 1. Chemical structures of (a) the polymer of intrinsic microporosity PIM-1 and possible products of reaction with ethanolamine (EA) and diethanolamine (DEA), (b) cationic dye Safranin O, and (c) anionic dye Orange II.

Table 1. Elemental Analysis, Mole Ratio of N to C ($r_{N/C}$), Fraction Modified (x_{mod}), BET Surface Area (S_{BET}), and Dye Uptake after 72 h for Reaction Products and the Corresponding Data for the Parent PIM-1 Samples

| | elemental analysis (wt %) | | | | | | | dye uptake (mg g^{-1}) | |
sample[a]	C	H	N	O[b]	$r_{N/C}$	x_{mod}	S_{BET} (m^2 g^{-1})	orange II	safranin O
SPIM	73.7	4.3	6.1	16.0	0.070	–	719	3	6
TPIM	74.2	3.4	6.1	16.2	0.071	–	750	3	–
ES120-3	70.4	4.8	6.7	18.1	0.082	0.27	421	91	11
ES120-6	67.5	4.9	6.9	20.8	0.087	0.41	374	216	9
ES120-12	66.2	5.8	7.7	20.3	0.099	0.73	26	363	10
ES120-24	65.2	6.0	7.8	21.1	0.102	0.81	10	326	15
ES120-48	65.1	6.2	8.2	20.5	0.108	1.00	–	282	10
ET105-6	70.6	4.9	7.1	17.5	0.086	0.37	534	99	1
ET105-12	69.3	5.0	7.4	18.3	0.091	0.51	441	274	7
ET105-24	67.4	5.4	7.9	19.4	0.101	0.78	–	545	2
ET105-36[c]	60.4	4.8	7.8	26.9	0.111	–	–	152	2
ET105-48	65.2	5.3	8.1	21.3	0.106	0.95	–	151	0
ET90-24	69.3	4.7	7.2	18.8	0.089	0.44	546	165	5
ET90-52	66.4	5.0	7.4	21.3	0.095	0.62	52	387	2
DT120-9	70.6	4.9	6.2	18.2	0.076	0.25	481	6	5
DT120-24	70.5	4.6	6.2	18.7	0.076	0.25	462	13	2
DT120-46	65.5	5.7	6.3	22.5	0.083	0.60	9	74	11
DT120-90	66.3	5.4	6.4	21.9	0.083	0.62	–	151	1
DT150-24	62.8	6.5	6.4	24.3	0.087	0.88	13	218	0
DT150-30	62.4	6.7	6.4	24.5	0.088	0.95	–	287	1
DT150-48	61.9	6.8	6.3	25.0	0.088	0.90	–	284	0

[a]Sample codes for reaction products: E = ethanolamine modification, D = diethanolamine modification, S = PIM-1 batch SPIM, and T = PIM-1 batch 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 measured C, H, and N values. [c]ET105-36 is impure as there was insufficient sample for a full washing sequence.

(200 mL) at 65 °C. After all monomers were dissolved, anhydrous K$_2$CO$_3$ (30 g, 61.8 mmol) was added to this solution and the reaction mixture was stirred for 72 h at 65 °C. The mixture was then cooled at room temperature for 20 min. It was poured into water (300 mL) and
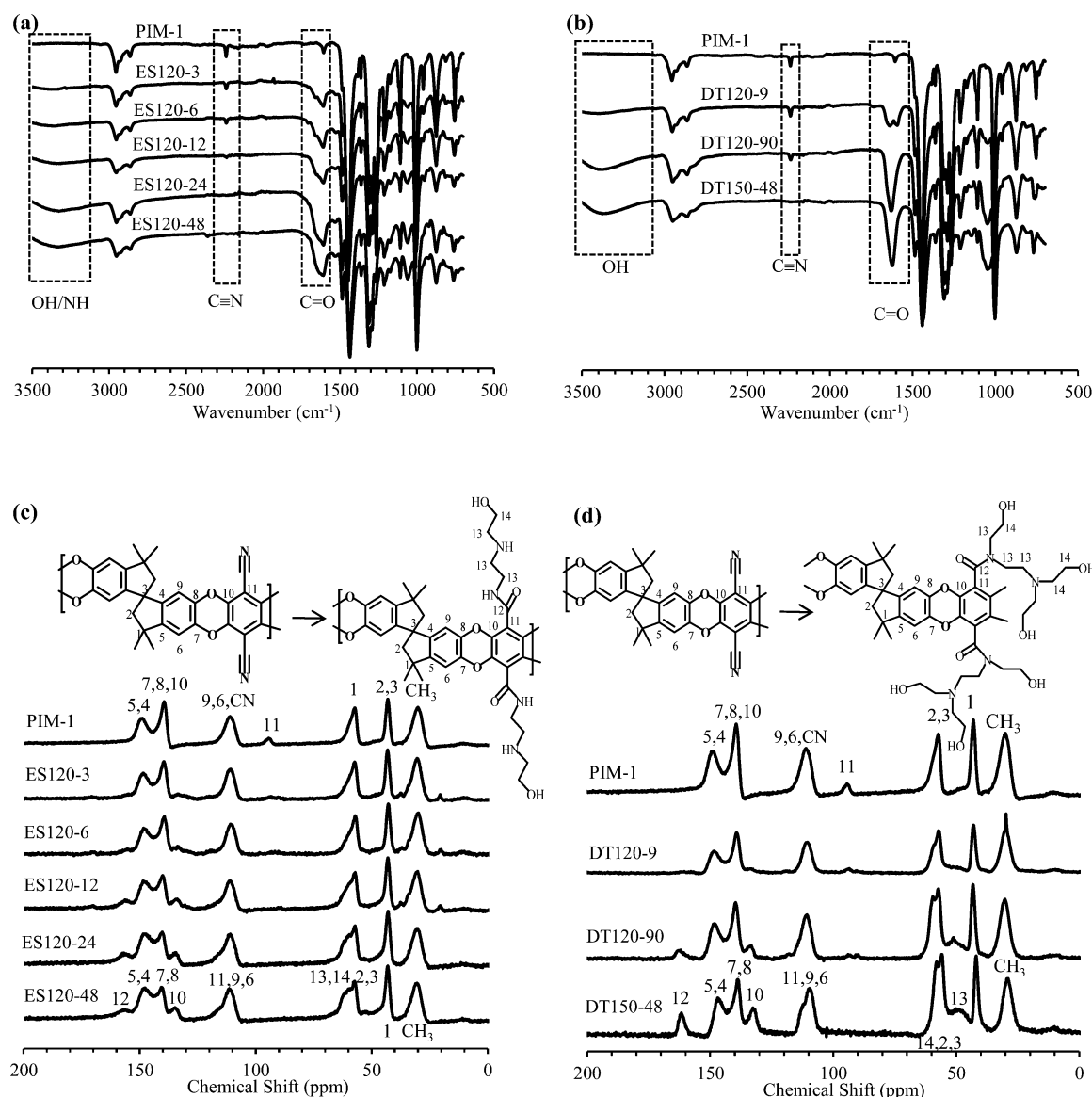
Figure 2. Infrared spectra of PIM-1 and products of reaction with (a) EA at 120 °C for 3 h (ES120-3), 6 h (ES120-6), 12 h (ES120-12), 24 h (ES120-24) and 48 h (ES120-48), and (b) DEA at 120 °C for 9 h (DT120-9), 120 °C for 90 h (DT120-90) and 150 °C for 48 h (DT150-48), and corresponding solid-state ^{13}C NMR spectra and peak assignments for (c) EA products and (d) DEA products.

the crude yellow product was collected by filtration under vacuum. It was stirred continuously for 15 min in water (700 mL), then filtered under vacuum. First, the product was allowed to dry at room temperature for 30 min, and then in an oven at 110 °C for 10 h. Dry polymer was washed on a funnel with dioxane (500 mL), acetone (200 mL), water (200 mL) and a further portion of acetone (200 mL). The solid product was obtained by filtration under vacuum and was dried at 110 °C in an oven for 2 days, giving 12.6 g (91.3% yield) of the fluorescent yellow polymer PIM-1. GPC: M_n = 52 000 g mol^{-1}, M_w = 194 000 g mol^{-1}, and M_w/M_n = 3.7. ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 6.75 (2H, s), 6.35 (2H, s), 2.26–2.09 (4H, dd), 1.40–1.10 (broad, 12H). ATR-IR (cm^{-1}): 2995, 2864, 2239, 1605, 1446, 1264. Anal. Calcd for C$_{29}$H$_{20}$N$_2$O$_4$ (wt %): C, 75.64; H, 4.37; N, 6.08. Found: C, 73.7; H, 4.3; N, 6.1.

Synthesis of PIM-1 at 160 °C (TPIM).[21] To a dry 1 L flange reactor equipped with a Dean−Stark trap and mechanical stirrer, under an inert atmosphere of nitrogen were added TTSBI (17.00 g, 0.05 mol) and TFTPN (10.005 g, 0.05 mol), anhydrous K$_2$CO$_3$ (20.05 g, 0.15 mol), DMAc (100 mL), and toluene (50 mL). The reaction temperature was set to 160 °C (heated before reaction) and carried out for a total of 45 min (5 min used to obtain equilibrium) under

reflux. At the end of the reaction, when stirring was stopped, the highly viscous solution immediately turned into a solid-like structure and a couple of milliliters of liquid had collected in the Dean−Stark trap. The crude polymer was poured into methanol (1 L). Following this, it was dissolved in chloroform (2 L) and reprecipitated from methanol (2 L). The product was refluxed for 6 h in deionized water and then dried at 110 °C for 2 days. This gave 19.9 g (86% yield) of PIM-1. GPC: M_n = 34 000 g mol^{-1}, M_w = 99 000 g mol^{-1}, and M_w/M_n = 2.9. ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 6.75 (2H, s), 6.35 (2H, s), 2.26–2.09 (4H, dd), 1.40–1.10 (broad, 12H). ATR-IR (cm^{-1}): 2995, 2864, 2239, 1605, 1446, 1264. Anal. Calcd for C$_{29}$H$_{20}$N$_2$O$_4$ (wt %): C, 75.64; H, 4.37; N, 6.08. Found: C, 74.2; H, 3.4; N, 6.1.

EA Modification of PIM-1. PIM-1 powder was put into a three-neck flask equipped with a reflux condenser, closed with a Suba Seal rubber septum with a needle to release pressure, under an inert atmosphere of nitrogen. EA was added and the reaction mixture stirred continuously at the set temperature. Reactions were carried out at 120, 105, and 90 °C. Samples were taken after various reaction times and poured into ethanol. After stirring for 15 min, the precipitate was filtered off, washed with deionized water, and dried in a vacuum oven at 110 °C. For each sample, details of the reaction conditions and
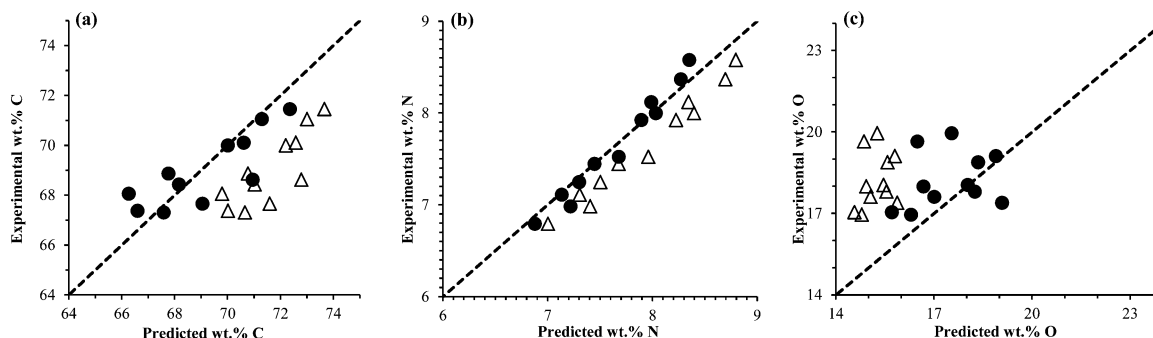
Figure 3. Comparison of experimental and predicted values of (a) wt % C, (b) wt % N, and (c) wt % O for structures **1** and **2** (△) and for structure **4** (●) for ethanolamine-modified PIM-1 products. The dashed line indicates prediction equal to experiment.

work-up procedure, and the visual appearance of the reaction mixture and product, are summarized in the Supporting Information.

DEA Modification of PIM-1. PIM-1 powder (0.23 g) was put into a three neck flask equipped with a reflux condenser, closed with a Suba Seal rubber septum with a needle to release pressure, under an inert atmosphere of nitrogen. DEA (6 g) was added and the reaction mixture stirred continuously at the set temperature. Reactions were carried out at 120 and 150 °C for various times. After cooling 15 min, ethanol (100 mL) was poured into the mixture and stirred for 15 min. The polymer was then filtered under vacuum and washed with water (500 mL). Following this, to get rid of any DEA trapped in the polymer, the product was placed in ethanol, stirred overnight, then filtered and washed with water again. The samples were dried in a vacuum oven at 110 °C overnight.

To see the effect on PIM-1 of treatment at 150 °C, the above procedure was followed without DEA for 48 h. The product was soluble in tetrahydrofuran, suggesting that no cross-linking of PIM-1 occurred under these conditions. Sample TPIM-150: Anal. Calcd for $C_{29}H_{20}N_2O_4$ (wt %): C, 75.64; H, 4.37; N, 6.08. Found: C, 74.55; H, 4.0; N, 6.1.

Methods. Infrared (IR) spectra of samples were recorded on a Thermo Scientific Nicolet iS5 FT-IR spectrometer with an attenuated total reflectance (ATR) accessory. Each sample was scanned 16 times at a resolution of 4 cm^{-1}.

[1]H nuclear magnetic resonance (NMR) spectra of the parent polymers were recorded using a Bruker Avance II 500 MHz instrument. Polymer solutions for NMR were prepared in CDCl$_3$. Signal peaks for the solvent were used as references.

High powered decoupling (Hpdec) magic angle spinning (MAS) solid state NMR spectra were collected using a Bruker Avance III 400 MHz instrument using an adamantane reference. A spinning rate of ~10 000 Hz was used with powder samples packed into a 4 mm zirconium rotor. Spectra were compiled from 6000 scans using a repetition time of 10 s and a spectral width of 200 ppm.

Average molar masses of the parent polymers were measured by multidetector gel permeation chromatography (GPC). Analysis was performed in CHCl$_3$ at a flow rate of 1 mL min^{-1} using a Viscotek VE2001 GPC solvent/sample module with two PL Mixed B columns and a Viscotek TDA302 triple detector array (refractive index, light scattering, viscosity detectors). The data were analyzed by the OmniSec program.

Thermogravimetric Analysis (TGA) was carried out using a Mettler Toledo Star System. Polymer samples were heated to 600−1000 °C at 10 °C min^{-1} under a nitrogen atmosphere.

N$_2$ adsorption isotherms at −196 °C were measured using a Micromeritics ASAP 2020 surface area and porosity analyzer. CO$_2$ and N$_2$ adsorption isotherms at 0 °C were measured using a Micromeritics ASAP 2050 surface area and porosity analyzer. A small amount of powdered sample (~0.1 g) was weighed into an analysis tube and degassed under high vacuum at 120 °C for 960 min. After reweighing the degassed sample, it was degassed again under high vacuum for a further 2 h to ensure all volatiles were removed before N$_2$ adsorption analysis. Samples were then degassed again for 2 h and a free space

measurement carried out using helium. Brunauer−Emmet−Teller (BET) surface areas were calculated from low temperature N$_2$ adsorption isotherms by multipoint analysis.

For dye adsorption studies, aqueous stock solutions of Orange II sodium salt (molecular formula, $C_{16}H_{11}N_2NaO_4S$; molecular weight, 350.32) and Safranin O (molecular formula, $C_{20}H_{19}ClN_4$; molecular weight, 350.84) were prepared in deionized water. Different concentrations were prepared by dilution of the stock solutions with deionized water. Calibration solutions were prepared from 50 to 0.39 mg L^{-1} and their absorbances were measured using a Shimadzu UV-1800 spectrometer. Values of λ_{max} for Orange II and Safranin O were taken as 484 and 509 nm, respectively. Specific absorption coefficients, a, were determined as 0.0597 L mg^{-1} cm^{-1} for Orange II and 0.0893 L mg^{-1} cm^{-1} for Safranin O. An exact amount of oven-dried adsorbent (~5.0 mg) was placed in 100 mL of 50 ppm dye solution. The dye solution (pH ∼ 6.4) containing the adsorbent was stirred well with a magnetic stirrer for 72 h, after which time there was little further uptake of dye. The 3 mL aliquots were taken by syringe and filtered through a PTFE hydrophobic filter (0.45 μm). The mass of dye adsorbed by the polymer, q_e (mg g^{-1}), was determined from the absorbance of the dye solution before contact with polymer, A_0, and the absorbance of the dye solution after reaching effective equilibrium with the polymer, A_e, using eq 1.

$$q_e = \frac{(A_0 - A_e)V}{alm} \tag{1}$$

where V is the total volume of dye solution, a is the specific absorption coefficient (see above), l is the path length in the spectrometer and m is the total mass of polymer.

■ RESULTS AND DISCUSSION

Characterization of Reaction Products. The reaction of EA or DEA with the nitrile groups in PIM-1 could yield various possible structures, as indicated in Figure 1a. The reaction products were insoluble in common organic solvents, which limited the range of characterization methods that could be employed.

Both ATR-IR spectroscopy (Figure 2a,b) and solid-state ^{13}C NMR spectroscopy (Figure 2c,d) showed loss of nitrile with increasing time of reaction with EA (Figure 2a,c) or DEA (Figure 2b,d). However, quantitative analysis of the degree of conversion by IR or NMR was difficult, because other peaks in the spectra also changed on chemical modification and there was no stable internal reference peak. Furthermore, neither technique could distinguish unambiguously between carbonyl (C=O) containing and imine (C=N) containing reaction products. For example, IR peaks that developed in the region 1700−1600 cm^{-1} could be attributed to either C=O or C=N.[22] The peak assignments given in Figure 2 are based on structures deduced from elemental analysis, as discussed below.
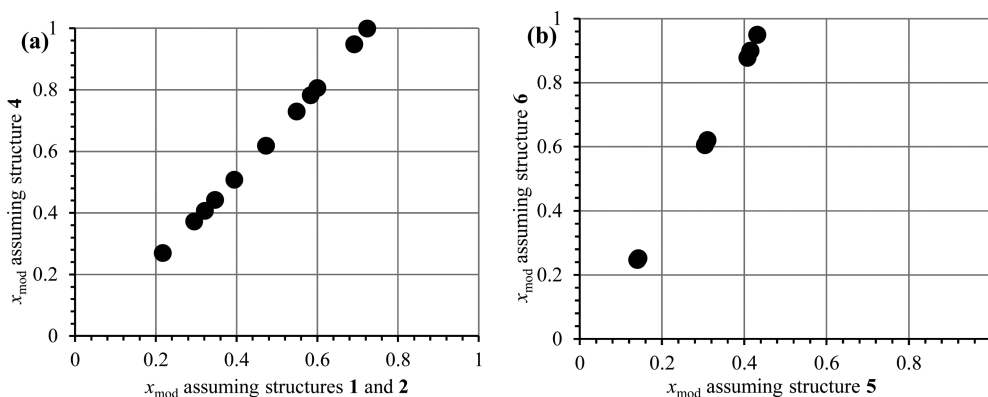
Figure 4. (a) Comparison of x_{mod} calculated assuming structure **4** with that assuming structures **1** and **2** for EA-modified PIM-1 products. (b) Comparison of x_{mod} calculated assuming structure **6** with that assuming structure **5** for DEA-modified PIM-1 products.
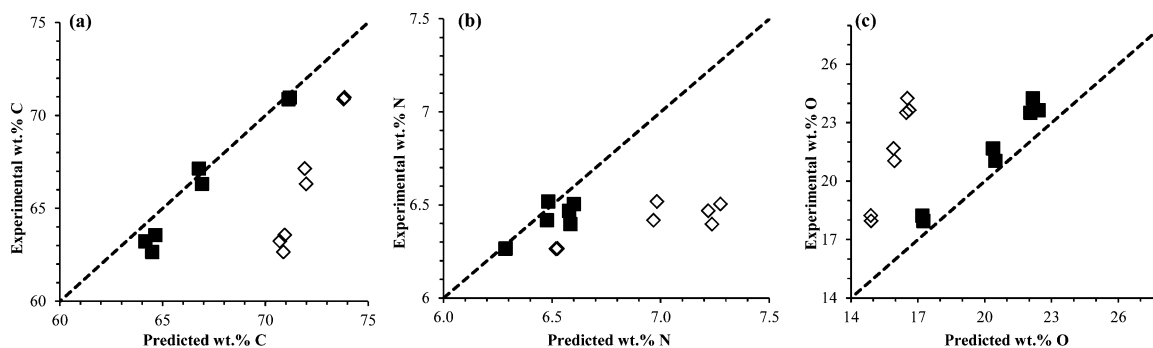
Figure 5. Comparison of experimental and predicted values of (a) wt % C, (b) wt % N, and (c) wt % O for structures **5** (◇) and **6** (■) for DEA-modified PIM-1 products. The dashed line indicates prediction equal to experiment.

Elemental analysis results for all samples are given in Table 1. The repeat unit of PIM-1 contains 29 C atoms and 2 N atoms. If full modification adds C_{add} additional C atoms and N_{add} additional N atoms to the repeat unit, then, for a mole fraction of modified groups x_{mod}, the mole ratio of N to C, $r_{N/C}$, is given by eq 2.

$$r_{N/C} = \frac{2 + x_{mod}N_{add}}{29 + x_{mod}C_{add}} \quad (2)$$

Thus, the mole fraction of modified groups for a partially modified sample is given by eq 3.

$$x_{mod} = \frac{2 - 29r_{N/C}}{C_{add}r_{N/C} - N_{add}} \quad (3)$$

For a given presumed structure, x_{mod} may be calculated from the experimental values of $r_{N/C}$ given in Table 1. Structures may then be differentiated on the basis of the absolute values of C and N content, as explained below. For the comparison of absolute values, a correction was applied to account for traces of moisture in the samples, based on small weight losses below 150 °C in thermogravimetric analysis (see Supporting Information).

For another nitrile-containing polymer, polyacrylonitrile, it has been suggested that modification with EA gives the tautomeric structures **1** and **2** (Figure 1a).[12−14] Values of wt % C, wt % N and wt % O predicted for structures **1** and **2** are compared with experimental results for extensively washed EA-modified PIM-1 products in Figure 3. It can be seen that the experimental C and N contents were consistently lower, and O contents consistently higher, than can be accounted for by

these structures for the $r_{N/C}$ ratios obtained. Reaction of EA with a nitrile may also produce an oxazoline structure **3** (Figure 1a),[23] but would give products with significantly lower N/C ratios than observed here; application of the above procedure for structure **3** gives unfeasible, negative, values of x_{mod}. The patent literature indicates that two moles of EA may react with a nitrile to give a hydroxyethylaminoethylamide structure, **4** (Figure 1a).[24] For this structure, it can be seen in Figure 3 that the predicted values of C, N, and O content were close to the experimental values, suggesting that this is the predominant structure.

Figure 4a shows the relationship between values of x_{mod} calculated assuming structure **4** with values calculated assuming structures **1** and **2**. It should be noted that if structure **4** is assumed, full modification is achieved, whereas if structures **1** and **2** are assumed, no greater than 72% modification is achieved. Since the infrared spectra in Figure 2a indicate complete loss of nitrile for the most fully reacted samples, this further supports the suggestion that the structure obtained on modification with EA is the hydroxyethylaminoethylamide structure **4**. Values of x_{mod} calculated for structure **4** are included in Table 1 for the EA-modified products.

For DEA-modified PIM-1, structure **5** (Figure 1a), from addition of one DEA per nitrile, and structure **6** (Figure 1a), from addition of two DEA per nitrile, were considered. It can be seen in Figure 5 that for the N/C ratios obtained, the C and N contents calculated for structure **5** were consistently higher, and the O contents lower, than the experimental values. However, for structure **6** the predicted values were close to the experimental values over the range of samples, suggesting this to be the predominant structure.
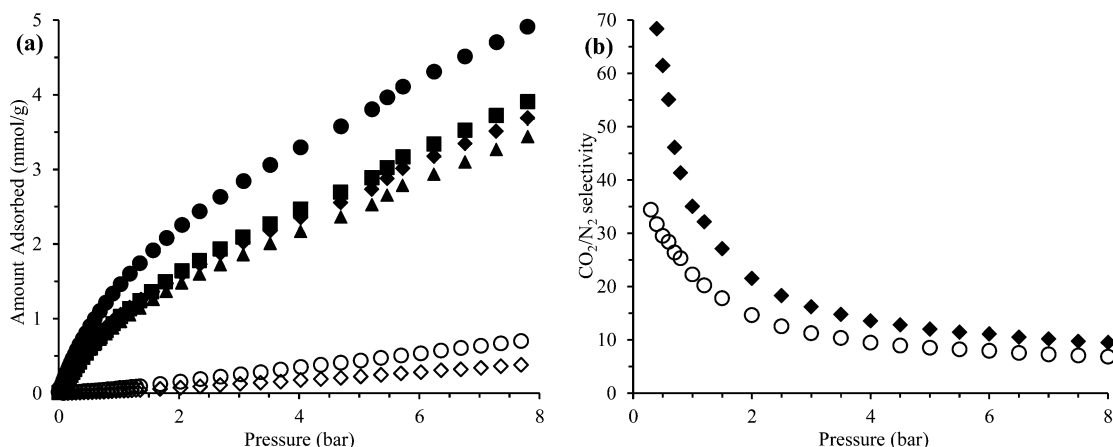
Figure 6. (a) CO_2 (filled symbols) and N_2 (open symbols) adsorption isotherms at 0 °C for PIM-1 powder sample SPIM-1 (●, ○) and for EA-modified powder samples ES120-24 (◆, ◇), ES120-6 (■) and ES120-3 (▲). (b) Pressure dependence of CO_2/N_2 ideal sorption selectivity at 0 °C for PIM-1 powder sample SPIM (○) and EA-modified powder sample ES120-24 (◆).

Figure 4b shows the relationship between values of x_{mod} calculated assuming structure **6** with values calculated assuming structure **5**. As discussed above for EA-modified samples, if structure **6** is assumed, a high degree of modification (95%) is achieved, whereas if structure **5** is assumed, only a low degree of modification (no greater than 43%) is achieved. Again, the loss of the nitrile peak in the infrared spectra (Figure 2b) suggests that much higher degrees of modification are attained in practice than can be accounted for by structure **5**. The hydroxyalkylaminoalkylamide structure **6** is fully consistent with the experimental evidence. Values of x_{mod} calculated for structure **6** are included in Table 1 for the DEA-modified products.

Thermogravimetric analysis (TGA) of PIM-1 shows little degradation below 450 °C. EA- and DEA-modified products exhibit weight losses in the temperature range 240−450 °C that correlate with the fraction modified as determined from elemental analysis (see Supporting Information).

Gas Adsorption. In a nitrogen adsorption experiment at liquid nitrogen temperature (−196 °C), PIM-1 exhibits high uptake at very low relative pressure,[15] which is characteristic of a microporous material.[25] This effective porosity is due to its high free volume in the glassy state, which in turn is a consequence of frustrated packing of its relatively rigid, contorted macromolecular backbone.[26−28] However, as with other polymers, a penetrant may lead to swelling or plasticization.[29,30] Thus, the interactions of small molecules with PIM-1 show aspects of the behavior expected with classical porous materials, commonly described in terms of "adsorption", and that expected with conventional polymers, commonly described in terms of "solution".

Table 1 includes values of BET surface area determined from nitrogen adsorption measurements at −196 °C. For PIM-1, apparent surface areas >700 m² g⁻¹ are obtained. Note that BET surface area cannot be equated to geometric surface area,[28] and is used only as a convenient comparative measure. Modification with EA or DEA adds relatively bulky groups which can fill the available free volume, thus reducing accessibility to a nitrogen probe. Hydrogen bonding may further tighten the structure, as has been suggested in the case of hydrolyzed PIM-1.[20,31] Thus, as can be seen in Table 1, for hydroxyalkylaminoalkylamide PIMs the apparent surface area, as measured by low temperature nitrogen adsorption, decreases

with increasing fraction modified, and is very low at values of $x_{mod} > 0.6$. However, despite the loss of accessibility to N_2 molecules at low temperature, a penetrant that has significant solubility in the modified polymer may nevertheless show high uptake at ambient temperature.

Figure 6a shows CO_2 and N_2 adsorption isotherms at 0 °C for a PIM-1 sample (SPIM) and for representative EA-modified products. In contrast to amine-modified PIM-1,[32] which shows enhanced affinity for CO_2 compared to the parent polymer, EA-modification, which adds significant mass to the repeat unit, leads to a reduction in the amount of CO_2 adsorbed per unit mass. However, a more pronounced reduction in the uptake of N_2 gives rise to an increase in the ideal CO_2/N_2 sorption selectivity, as can be seen in Figure 6b. For sample ES120-24, the ideal CO_2/N_2 sorption selectivity at 1 bar was 35.

Dye Adsorption. Mass uptakes after 72 h of the anionic dye Orange II (Figure 1c) and the cationic dye Safranin O (Figure 1b) from aqueous solution by powdered samples of PIM-1 and of EA- and DEA-modified PIM-1 are given in Table 1. Whereas uptake of the cationic dye is relatively low for all samples, uptake of the anionic dye increases dramatically with increasing degree of modification, as illustrated in Figure 7. The highest uptakes, 2 orders of magnitude higher than for the parent polymer PIM-1 under the conditions employed, were observed for EA-modified samples with values of x_{mod} in the
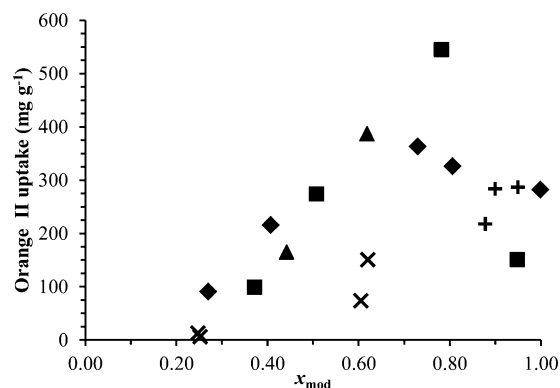
Figure 7. Uptake after 72 h of the anionic dye Orange II by the products of reaction of PIM-1 with EA at 120 °C (◆), 105 °C (■), and 90 °C (▲), and with DEA at 120 °C (✕) and 150 °C (+).

range 0.6−0.8. The pronounced selectivity for the anionic over the cationic dye is in marked contrast to hydrolyzed PIM-1,[20] which shows the reverse selectivity.

Dye uptake is expected to reflect the interplay of microporosity, which enhances adsorption through multiple wall interactions, and solubility, which may promote selective uptake. For EA-modified PIM-1, the increase in Orange II uptake with increasing degree of modification, up to values of x_{mod} ca. 0.6, may be attributed to selective interactions with the hydroxyalkylaminoalkylamide component, facilitated by residual microporosity. At higher values of x_{mod}, reduced uptake is most likely due to the effective loss of microporosity. Modification with the bulkier DEA does not give such high uptakes at x_{mod} ca. 0.6, but uptakes for the more fully modified samples are comparable for DEA- and EA-modified PIM-1.

CONCLUSIONS

The ability to tailor the sorption selectivity for gases and organic compounds, through chemical modification, opens up a host of possibilities for molecular separations on both the laboratory and the industrial scale. Modification of PIM-1 with ethanolamine or diethanolamine yields hydroxyalkylaminoalkylamide products. In adsorption from aqueous solution, they exhibit a high affinity for an anionic dye. This complements previous research that has demonstrated high uptake of neutral species by PIM-1,[19] and of cationic species by hydrolyzed PIM-1.[20] In gas adsorption, ethanolamine modification increases the CO_2/N_2 selectivity.

The present work focused on adsorption by powder samples of modified polymers. The modified polymers are insoluble in common organic solvents, and thus extension of this work to adsorption and permeation by membranes requires chemical modification of materials in the form of thin films. That will be the subject of further research.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.5b01196.

> (1) Characterization of PIM-1, (2) chemical modification of PIM-1, with reaction conditions and work-up procedures and visual appearance of reaction mixtures and products, (3) characterization of EA- and DEA-modified PIM-1 with ATR-IR and ^{13}C NMR spectroscopy and elemental analysis, and (4) thermogravimetric analysis for EA-modified PIM-1 and DEA-modified PIM-1 (PDF)

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Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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