

Electronic Supporting Information

The CF₃TMS adduct of anthraquinone as a monomer for making polymers with potential as separation membranes

Kim Jiayi Wu,^a John M. Tobin,^a Anli Ji,^a Yang Shi,^a Chunchun Ye,^a Gary S. Nichol,^a Alessio Fuoco,^b Mariagiulia Longo,^b Johannes C. Jansen,^b Neil B. McKeown*^a

^a EaStChem, School of Chemistry, University of Edinburgh, David Brewster Road, Edinburgh, EH9 3FJ, UK.

^b Institute on Membrane Technology, National Research Council of Italy (CNR-ITM), via P. Bucci 17/C, Rende (CS), 87036, Italy.

Corresponding Author

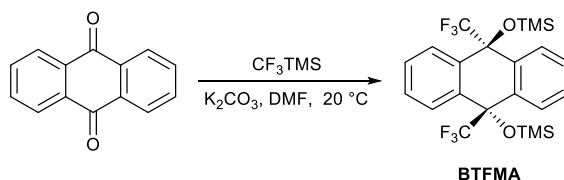
*N. B. McKeown E-mail: Neil.McKeown@ed.ac.uk

1. Methods and Materials

All reagents and starting materials employed in this work were commercially available and used without further purification unless otherwise stated. Melting points (Mp) measurements were recorded using Stuart Melting Point Apparatus (SPM10) and are uncorrected. Thin layer chromatography (TLC) was used aluminium-back plates coated with Merck TLC silica gel 60 GF254. Fourier-transform infrared spectra were obtained using powdered sample in the range of 4000-500 cm^{-1} using Shimadzu IRAffinity-1S FTIR spectrophotometer. Room temperature ^1H , ^{13}C and ^{19}F NMR spectra were acquired using chloroform-*d* (CDCl_3) and recorded using a 500 MHz Bruker Avance spectrometer. Variable temperature ^1H , ^{13}C , ^{19}F , ^1H -COSY, $^1\text{H}/^{13}\text{C}$ -HSQC and $^1\text{H}/^{13}\text{C}$ -HMBC were required using chloroform-*d* (CDCl_3) and N,N-dimethylformamide-*d*7 (DMF-*d*7) using a 400 MHz Bruker Avance III spectrometer. Low-resolution mass spectrometry (LRMS) for monomers were performed using a Fisons VG Platform II quadrupole instrument using electron impact ionization (EI) and electrospray ionisation (ESI). Low-temperature nitrogen adsorption/desorption isotherm at 77K and carbon dioxide adsorption isotherm at 273 K were obtained using a Quantachrome Quadrasorbevo automated surface area & pore size analyser. Gel permeation chromatography (GPC) of **BTFMA-DPE** polymers were analysed using a Malvern Viscotek GPCmax Model VE2001 with a RI detector. Samples were dissolved in CHCl_3 and operated at a flow rate of 1 mL min^{-1} at 35 $^\circ\text{C}$. Molecular weight and polydispersity index (PDI) were calculated based on polystyrene standards. Thermogravimetric analysis (TGA) measurement was carried out using a Discovery Thermogravimetric Analyzer 5500 (TA Instruments) with heating rate set at 10 $^\circ\text{C min}^{-1}$ to 600 $^\circ\text{C}$ on a platinum pan under nitrogen. Differential scanning calorimetry (DSC) measurement was carried out using a Discovery DSC 25 (TA Instruments) with heating rate set at 10 $^\circ\text{C min}^{-1}$ to 450 $^\circ\text{C}$ on a Tzero aluminum pan under nitrogen.

2. Experimental Procedures

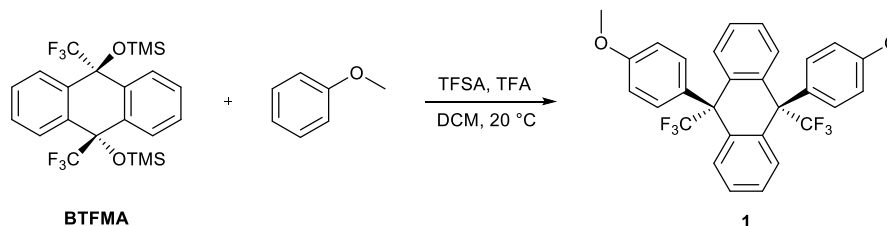
Synthesis of 9,10-bis(trifluoromethyl)-9,10-bis(trimethylsiloxy)-9,10-dihydroanthracene (BTFMA)



Prepared based on literature methods.¹ Briefly, to a nitrogen-flushed two-necked 100 ml round-bottom flask containing 9,10-anthraquinone (2.082 g, 10 mmol) and potassium carbonate (0.553 g, 4 mmol) was added DMF (20 mL) followed by CF_3TMS (3.3 mL, 22 mmol) slowly via a syringe at 0 $^\circ\text{C}$. The reaction was stirred at room temperature for 15 h. The solution was then poured into a mixture of saturated NH_4Cl (20 mL) and 1M HCl (5 mL) solution and extracted by Et_2O (3 x 40 mL). The organic phase was dried over Na_2SO_4 , filtered, and the solvent was removed under reduced pressure. The crude solid was washed with iced-cooled 2-propanol, filtered, and dried at 100 $^\circ\text{C}$ to obtain a pure white product (4.07 g, 8.2 mmol, 82%). Mp: 120 $^\circ\text{C}$; v_{max}

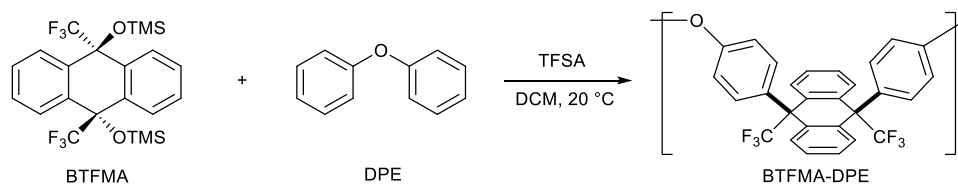
(cm^{-1}): 2968, 1447, 1412, 1234, 1157, 1070, 943, 839; ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.99-7.95 (m, 4H), 7.54-7.51 (m, 4H), -0.08 (s, 18H); ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 133.45, 129.70, 129.67, 129.65, 129.62, 128.72, 128.14, 125.83, 123.53, 121.23, 75.15, 74.93, -1.64; ^{19}F NMR (471 MHz, CDCl_3): δ (ppm) -78.02; LRMS (ESI, m/z): $[\text{M} + \text{Na}]$ calcd for $\text{C}_{22}\text{H}_{26}\text{O}_2\text{Si}_2\text{Na}$, 515.1268; found, 515.1279.

Synthesis of 9,10-Bis(3',4'-methoxybenzene)-9,10-Bis(trifluoromethyl) anthracene (1)



Trifluoroacetic acid (TFA) (1 mL) and trifluoromethylsulfonic acid (TFSA) (0.25 mL) were added to a 25 mL round bottom flask. Then, a solution of **BTfMA** (0.5 g, 1 mmol) and anisole (0.24 mL, 2.2 mmol) in DCM (10 mL) was added dropwise. The reaction was stirred at room temperature overnight. The mixture was then poured into ice-water (100 mL) and the product extracted with DCM (40 mL x 3). The organic phase was dried over Na_2SO_4 , filtered, and the solvent was removed under reduced pressure. The crude product was recrystallized from 2-propanol, filtered, and dried in air to obtain pure white crystals suitable for crystallography (0.294 g, 0.5 mmol, 50%). Mp: 245 $^\circ\text{C}$, ν_{max} (cm^{-1}): 1510, 1236, 1143, 1031, 827, 725; ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.22 (br, m, Ar H), 6.89 (br, d, Ar H), 3.85 (s, Me H); ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 158.06, 137.78, 135.26, 132.36, 130.16, 127.68, 113.69, 56.96, 55.23; ^{19}F NMR (471 MHz, CDCl_3): δ (ppm) -64.68; Mass spec LR-MS (ESI, m/z): $[\text{M} + \text{Na}]$ calcd for $\text{C}_{30}\text{H}_{22}\text{F}_6\text{O}_2\text{Na}_2$, 574.1269; found, 574.2143.

Optimised procedure for the synthesis of BTfMA-DPE (entry 7 in ESI Table 1)



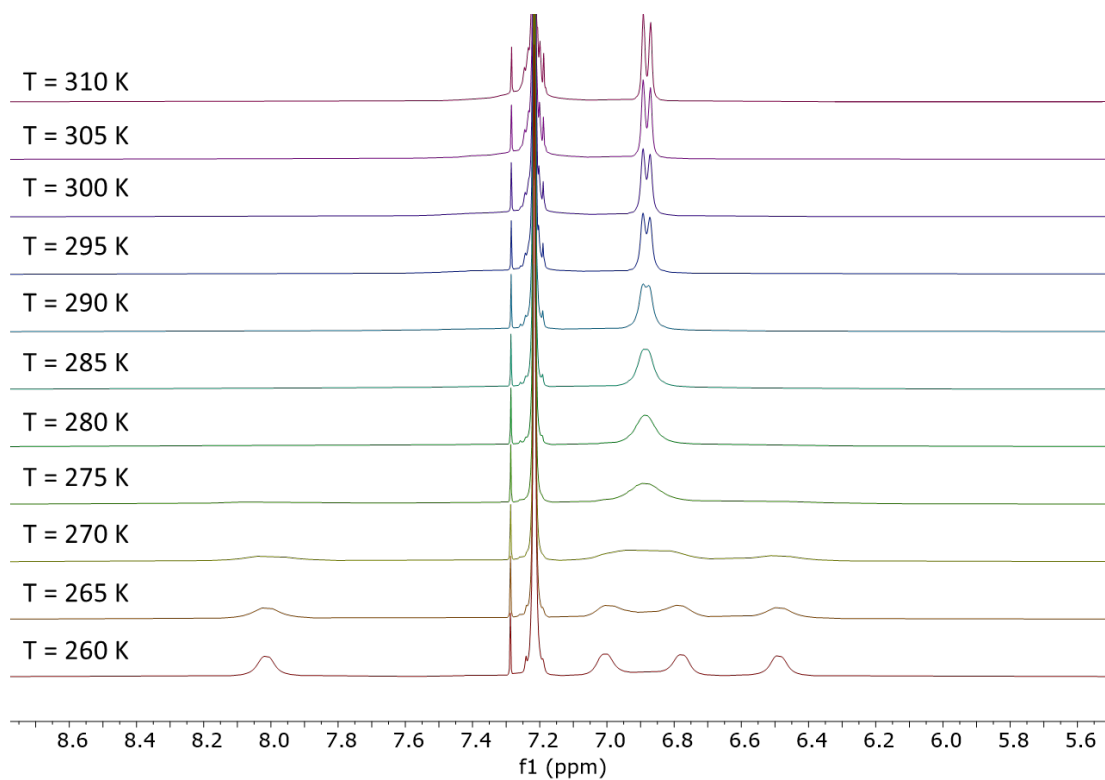
A two-neck round bottom flask equipped with a magnetic stirrer bar was charged with **BTfMA** (1.0 g, 2.03 mmol), **DPE** (0.35 g, 2.03 mmol), and DCM (4 mL). The solution was cooled to 0 $^\circ\text{C}$ followed by dropwise addition of TFSA (0.8 mL). The reaction mixture was stirred at room temperature for 0.5 h. The resulting viscous mixture was poured into water to precipitate a white solid. The solid was filtered, washed with water, sat. NaHCO_3 , and hot methanol, then dried in an oven at 100 $^\circ\text{C}$. The crude polymer was dissolved in chloroform and added dropwise to methanol, and the precipitated solid was collected under vacuum. The white fibrous polymer was refluxed in methanol, filtered, and then dried at 100 $^\circ\text{C}$. The yield was 0.92 g (94%). ν_{max} (cm^{-1}): 1500, 1238, 1143, 825, 727; ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.20 (br, s, Ar H), 6.97 (br, s, Ar H); ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 115.31, 140.60, 134.96, 132.38, 127.93; ^{19}F NMR δ (ppm) -64.67; GPC (CHCl_3): $M_n = 150,000 \text{ g mol}^{-1}$, $M_w = 310,000 \text{ g mol}^{-1}$; $S_{\text{ABET}} = 450 \text{ m}^2 \text{ g}^{-1}$, total pore volume = 0.31 mL g^{-1} at $P/P_0 = 0.98$

from N₂ adsorption at 77K; TGA analysis: peak degradation temperature for the initial mass loss was found at ~430 °C.

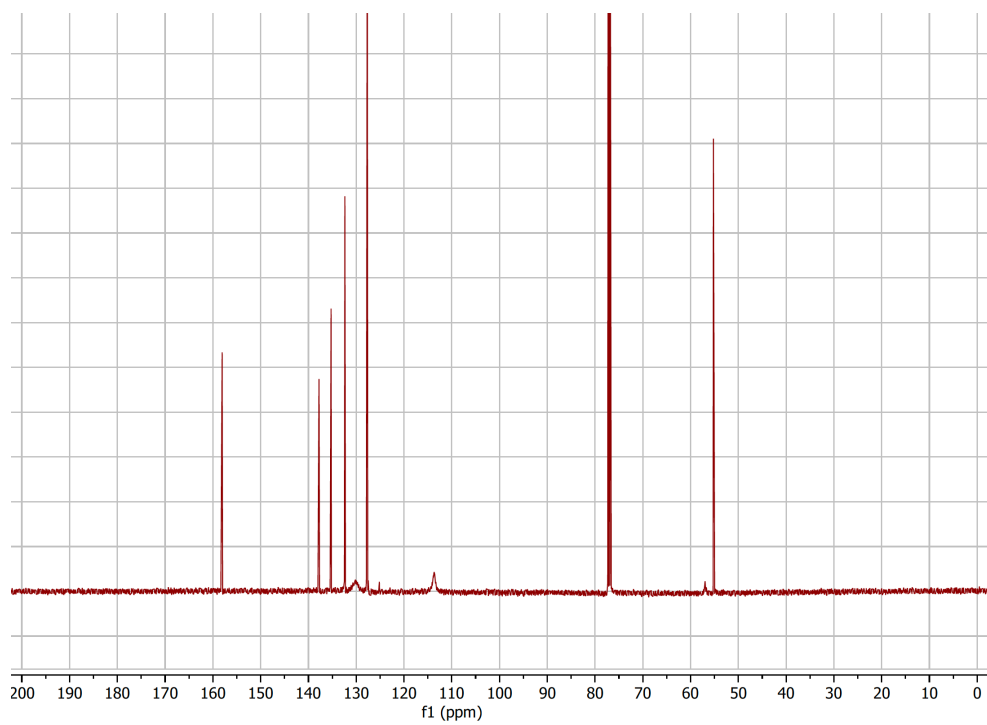
Membrane Formation

BTFMA-DPE polymer prepared using the optimized reaction conditions (ESI Table 1; entry 7) was dissolved (~0.30 g) in CHCl₃ (6.5 mL) to obtain a clear solution. The polymer solution was filtered through cotton to remove insoluble impurities and then casted on a glass petri dish (diameter = 5 cm). The **BTFMA-DPE** membrane was allowed to form by slow evaporation at room temperature for 36-48 h. Dry 100- μ m-thick membrane was peeled off from the petri dish and cut into required sizes for further measurements. Reported values for gas permeability were obtained 100 days after methanol treatment of the film using the methods and apparatus reported previously.³

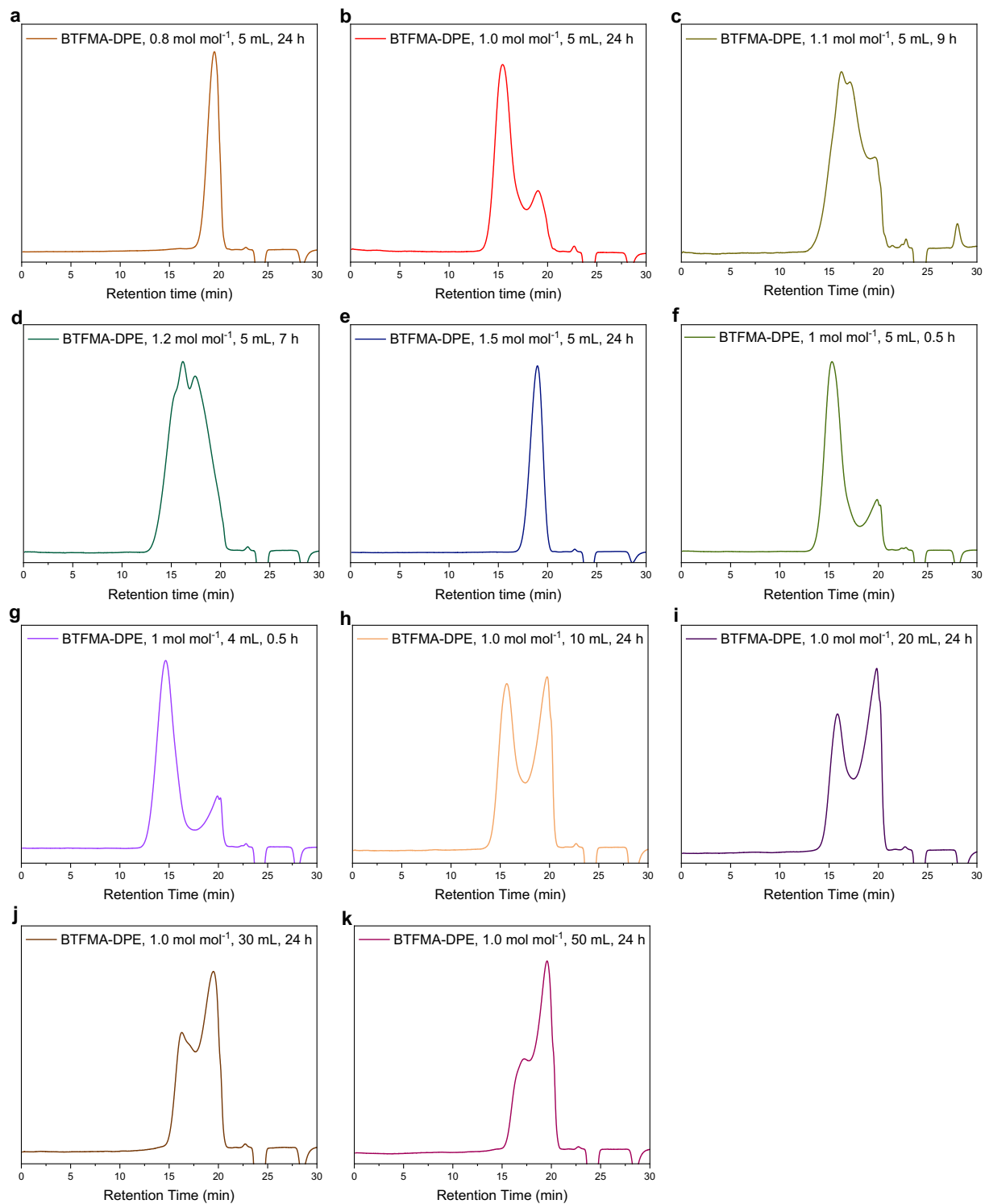
3. Supplementary Characterisation and Results



ESI Fig. 1a Variable-temperature ^1H NMR in CDCl_3 of model compound **1**.



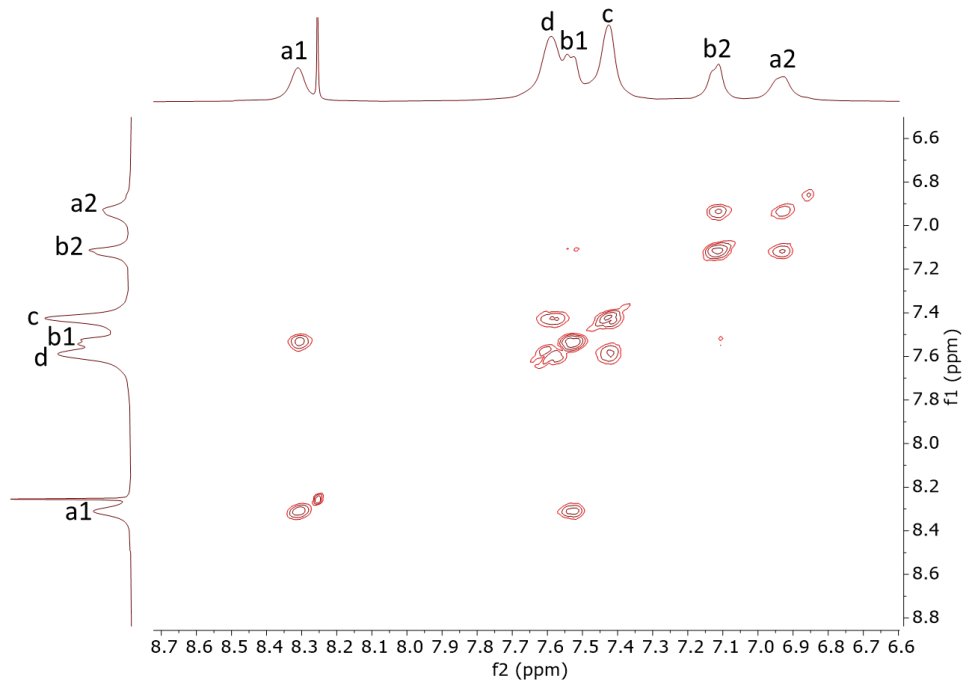
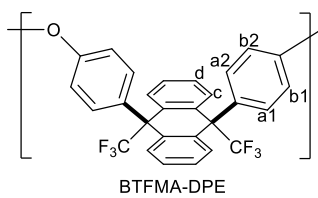
ESI Fig. 1b. Ambient temperature ^{13}C NMR in CDCl_3 of model compound **1**.



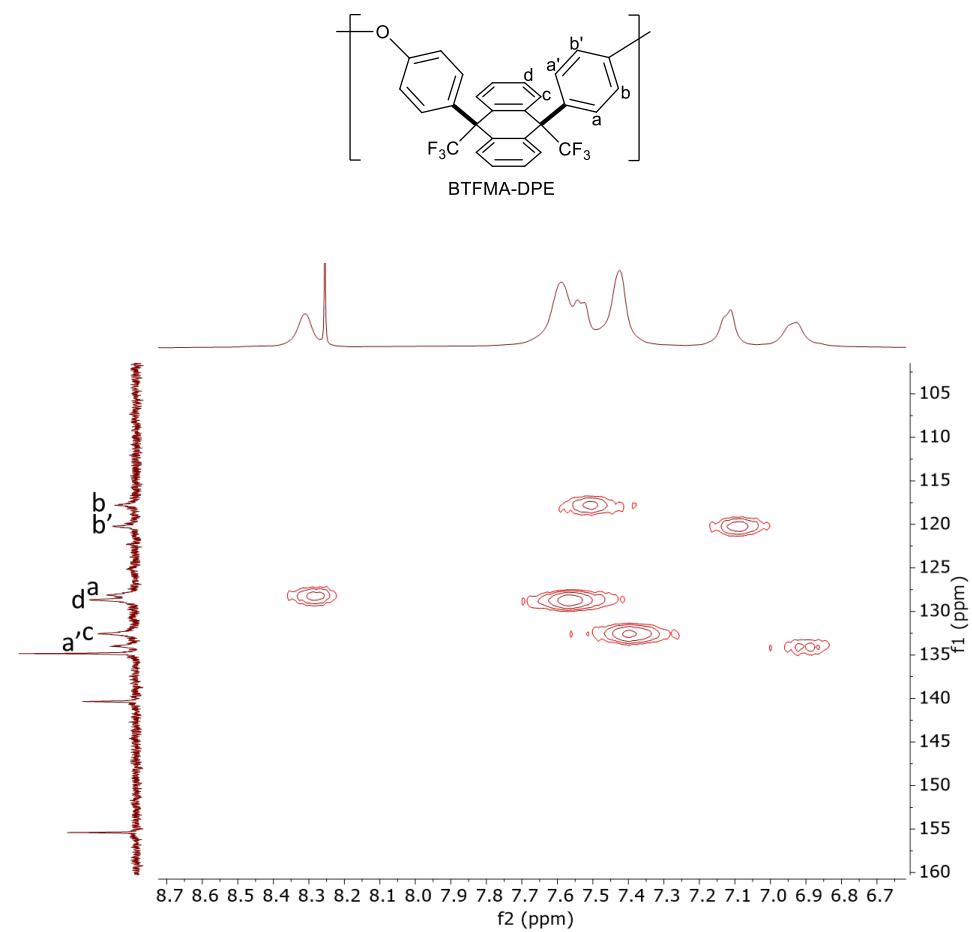
ESI Fig. 2 GPC traces of **BTFMA-DPE** polymer reactions in TFSA (0.8 mL) with different feed ratio of **BTFMA** and **DPE** (mol mol^{-1}), amount of solvent (mL) and reaction time (h). (a) – (k) ESI Table entries 1 – 11.

ESI Table 1. Results of polymerisation between **BTFMA** and **DPE** in TFSA (0.8 mL) using different feed ratio (mol mol⁻¹), amount of solvent (mL) and reaction time (h).

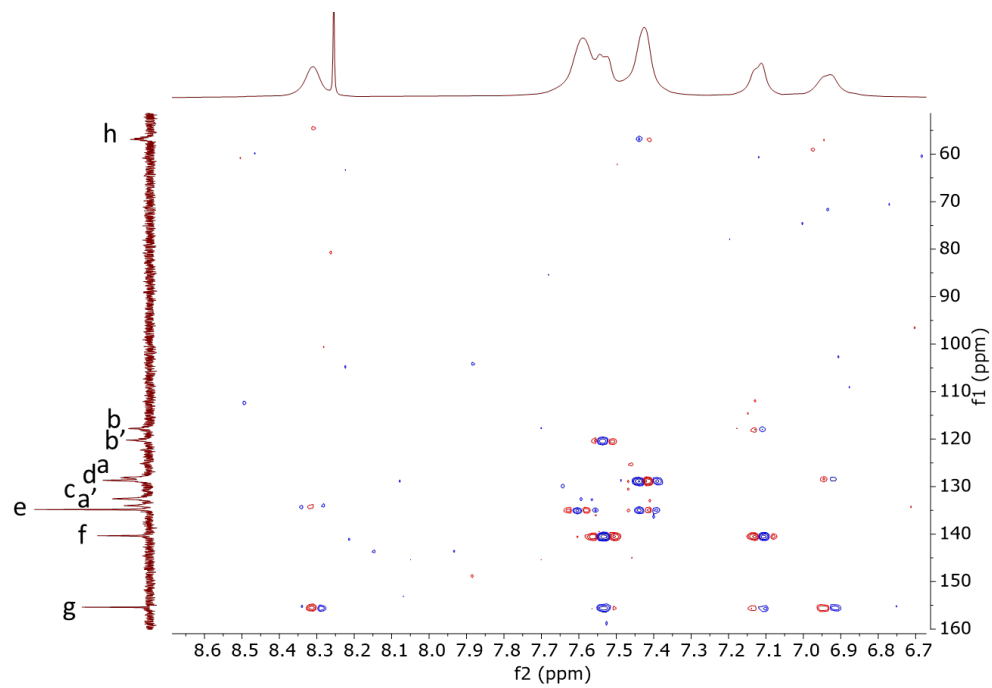
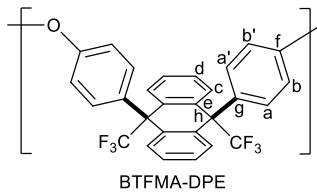
Entry	BTFMA/DPE (mol mol ⁻¹)	DCM (mL)	Time (h)	Yield (%)	Peak 1				Peak 2			
					Mn (g mol ⁻¹)	Mw (g mol ⁻¹)	PDI	Peak Wt Fr.	Mn (g mol ⁻¹)	Mw (g mol ⁻¹)	PDI	Peak Wt Fr.
1	0.8	5	24	65	2 044	2 610	1.3	1.0	-	-	-	-
2	1.0	5	24	90	59 532	122 563	2.1	0.79	2 680	3 642	1.4	0.21
3	1.1	5	9	91	6 398	59 355	9.3	1.0	-	-	-	-
4	1.2	5	7	86	9 043	82 305	9.1	1.0	-	-	-	-
5	1.5	5	24	62	3 375	4 571	1.4	1.0	-	-	-	-
6	1.0	5	0.5	93	66 572	138 963	2.1	0.83	1 803	2 443	1.4	0.17
7	1.0	4	0.5	94	149 189	310 150	2.1	0.82	1 806	2 615	1.4	0.18
8	1.0	10	24	88	58 237	104 359	1.8	0.51	2 160	3 355	1.6	0.49
9	1.0	20	24	76	53 496	88 876	1.7	0.43	2 127	3 452	1.6	0.57
10	1.0	30	24	77	32 442	50 434	1.6	0.40	2 351	3 467	1.5	0.60
11	1.0	50	24	82	24 076	33 867	1.4	0.31	2 212	3 249	1.5	0.69



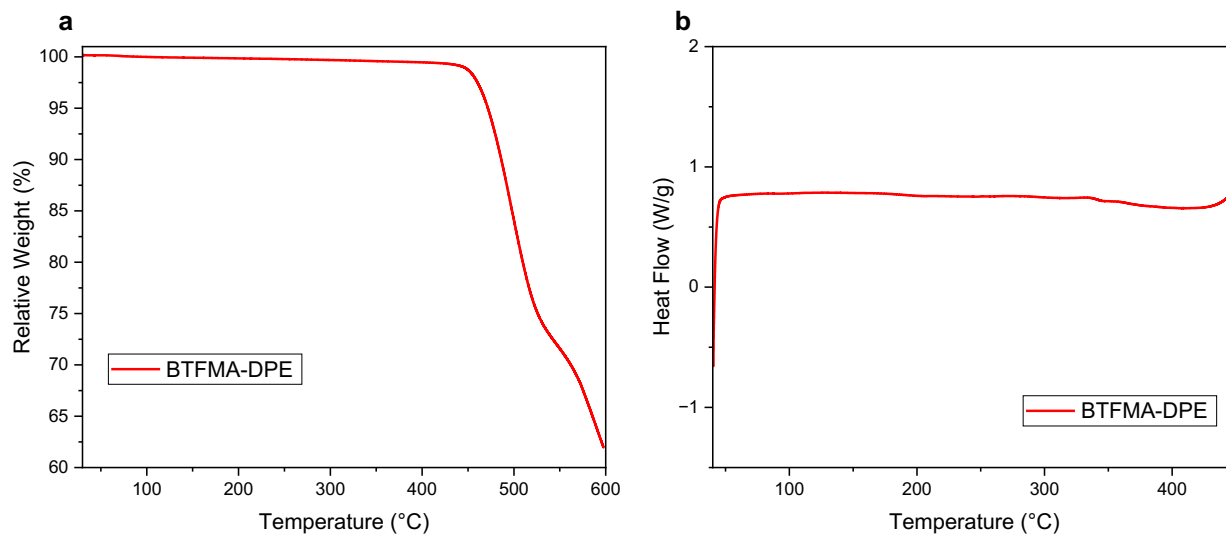
ESI Fig. 3 ^1H -COSY spectra and ^1H peak assignment of **BTFMA-DPE** polymer obtained in CDCl_3 at $-30\text{ }^\circ\text{C}$.



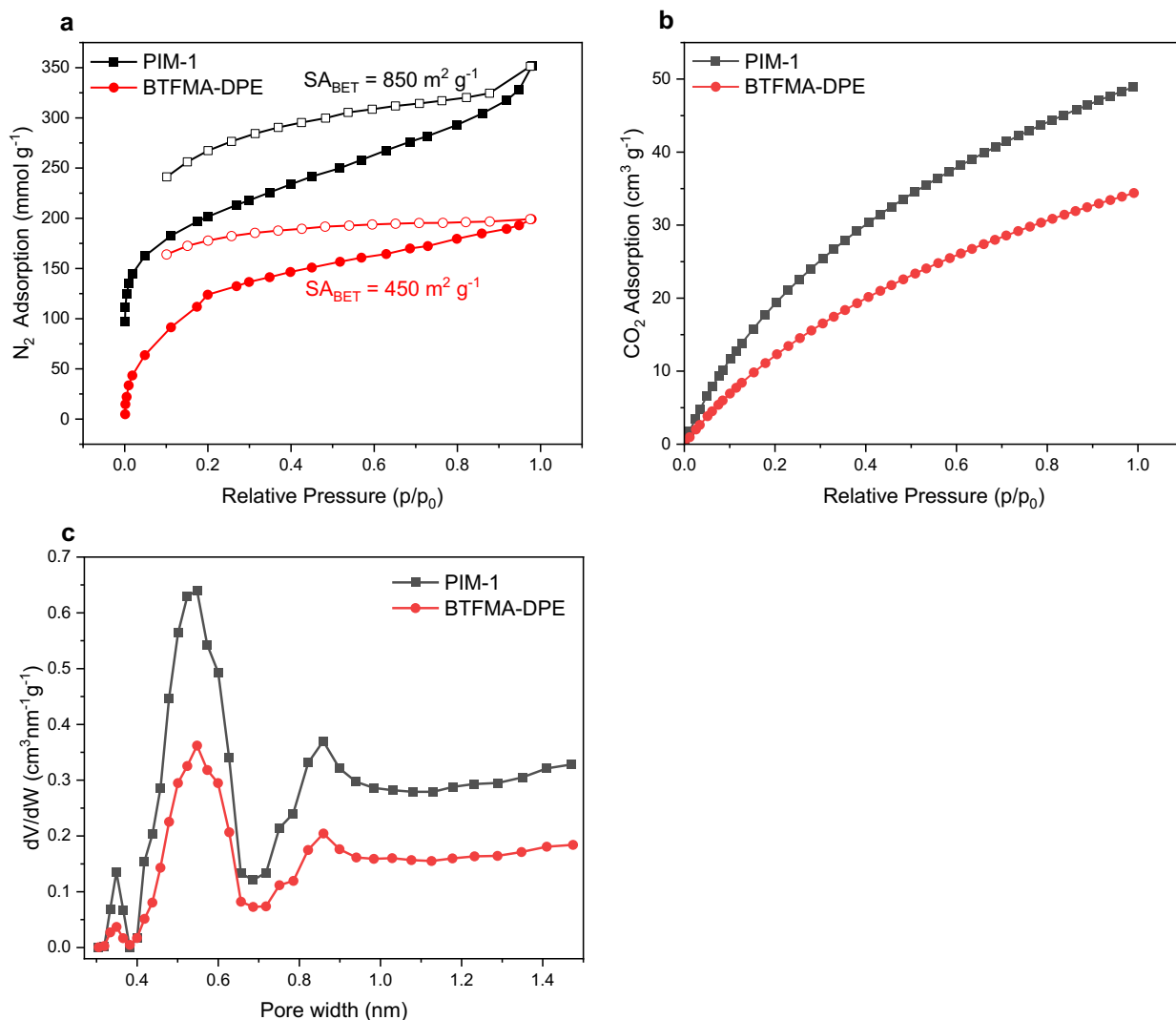
ESI Fig. 4 ¹H/¹³C-HSQC spectra and ¹³C peak assignment of **BTFMA-DPE** polymer obtained in CDCl₃ at -30 °C.



ESI Fig. 5 ¹H/¹³C-HMBC spectra and ¹³C peak assignment of **BTfMA-DPE** polymer obtained in CDCl₃ at -30 °C.



ESI Fig. 6 (a) TGA and (b) DSC of **BTFMA-DPE** polymer.



ESI Fig. 7. Gas sorption of polymer **BTFMA-DPE** compared with that of PIM-1, (a) N₂ adsorption-desorption isotherms at 77K. (b) CO₂ adsorption-desorption isotherms at 273K and (c) derived pore size distribution based on DFT calculations. Data points for polymer **BTFMA-DPE** are shown in red and PIM-1 in black with solid symbols: adsorption; open symbols: desorption.

5. ESI References

- 1) S. Yamada, K. Kinoshita, S. Iwama, T. Yamazaki, T. Kubota and T. Yajima, *RSC Advances* 2013, **3**, 6803-6806.
- 2) R. O. Iakovenko, A. Chicca, D. Nieri, I. Reynoso-Moreno, J. Gertsch, M. Krasavin, A. V. Vasilyev, *Tetrahedron*, 2019, **75** (5), 624-632.
- 3) B. Comesaña-Gándara, J. Chen, C. G. Bezzu, M. Carta, I. Rose, M.-C. Ferrari, E. Esposito, A. Fuoco, J. C. Jansen and N. B. McKeown, *Energy Environ. Sci*, 2019, **12**, 2733-2740.