Supplementary information

Block poly(arylene ether sulfone) copolymers tethering aromatic side-chain quaternary ammonium as anion exchange membranes

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1. Experimental Part

Synthesis of DFDM

2,6-Difluorophenyl [3-[(3,5-dimethyl phenyl) methyl]-5-methylphenyl] methanone (DFDM) was prepared according to our reported method, [36] the procedure is as follows.

25.91 g of 1-bromo-3,5-dimethylbenzene (0.14 mol) in 100 mL absolute diethyl ether was dropwised slowly into 100 mL absolute diethyl ether containing 3.41 g of magnesium (0.14 mol) under N_2 protection to prepare 3,5-dimethylphenyl magnesium bromide. Then 100 mL of absolute diethyl ether solution of 2,6-difluorobenzonitrile (19.47 g, 0.14 mol) was added slowly with stirring and refluxing. After completion of the reaction, the system was quenched by 80 mL of 0.1 M HCl solution. The separated ether layer was hydrolysed at reflux for 6 h with 1 M HCl solution, then washed to neutral. The obtained crude product was distilled to obtain 5-(2,6-difluorobenzyl)-1,3-dimethylbenzene (DFDB).

To 50 mL of chloroform, 0.50 g of DFDB (2.03 mmol), 1.23 g of *N*-bromosuccinimide (6.90 mmol) and 0.06 g of 2,2-azobisisobutyronitrile (0.37 mmol) were added under stirring and refluxed for 4.5 h. Then the solvent was evaporated and the residue was purified via column chromatography (petroleum ether/ethyl acetate (PE/EA) of 100/1) to give 5-(2,6-difluorobenzyl)-1-methyl-3-bromomethyl benzene (DFMBB).

To a solution mixture of tetrahydrofuran (72 mL) and distilled water (24 mL), 1.00 g of DFMBB (3.08 mmol), 0.80g of 3,5-dimethylphenylboronic acid (5.33 mmol), 0.70 g of sodium carbonate (6.60 mmol), 0.20 g of trtrakis(triphenylphosphine) palladium (0.17 mmol), and 0.05 g of tetrabutyl ammonium bromide (0.16 mmol) were added and stirred at reflux for 12 h under N_2 protection. Then the system was extracted with methylene chloride and the separated organic layer was dried over anhydrous magnesium sulfate. The resultant residue was purified via column chromatography (PE/EA of 100/1) to obtain DFDM.

Table s1. Comparison of IEC, WU, σ, P_M and φ among AEMs.

	Membrane	IEC (mequiv g^{-1})	*WU* [a] (%)	σ (mS/cm) [b] 25 °C	σ (mS/cm) [b] 80 °C	P_M [c] ($10^{-7}cm^2s^{-1}$)	~~10^{-4}~~ φ (S s cm^{-3})	Ref.
	bQPAES-x7y32-1	1.15	48.8	30.4	86.3	5.2	5.8×10^4	This
	bQPAES-x4y20-1	1.11	45.8	26.4	81.8	4.8	5.5×10^4	This
	bQPAES-x7y24	0.81	33.5	23.6	58.9	4.1	5.7×10^4	This
	bQPAES-x4y15	0.79	30.9	20.3	54.8	3.7	5.4×10^4	This
R1	rQPAES	1.20	30.1	21.0	50.4	4.8	4.4×10^4	This
R2	rQPE	1.88	95(30 °C)	20	40	—	—	31
R3	QBPES-60	1.86	52	27.5	52.1	—	—	37
R4	QPAES–X20Y18	1.54	57.2	13.3	64.1	—	—	34
R5	QBPES-40	1.62	36	29	48	—	—	38
R6	SEBS-TMA	2.41	211(25 °C)	45(30 °C)	102	—	—	39
R7	QPE-X16Y11	1.93	112(30 °C)	96	144	—	—	31
R8	bQAPDHTPE-OH20	1.66	32(30 °C)	18(40 °C)	21	—	—	40
R9	mPES-X6.7Y11.1	2.82	57.50	14.2	29(60°C)	—	—	41
R10	QPAE-X15Y15	1.91	25(60 °C)	20.3	45.4	—	—	42
R11	QPAE-a	2.38	63	25(20 °C)	64.7	—	—	12
R12	QPPO-PAES-QPPO-1.14	1.83	70	63	129	—	—	43
R13	AMBPE-76	2.74	170	56(30 °C)	85(70°C)	—	—	44
R14	ImPEEK-94	2.24	63.31	25(30 °C)	57.80	46.1	1.37×10^4	45
R15	ImPPESN-2.92	2.10	70(60 °C)	35(30 °C)	70	—	—	46
R16	ImPESN-19-22	2.07	23(60 °C)	50(30 °C)	110	—	—	47
R17	PI-cPES-50	1.21	6.21	30	90	4.72	6.3×10^4	48
R18	ImPSf-A	1.75	102 (60 °C)	19.68 (20 °C)	55	—	—	49

[a] At 80 °C. [b] In water at 25 (or 30) and 80 °C. [c] At 32 wt% methanol solution and 25 °C.

Table s2. Comparison of alkaline stability among AEMs.

	Membrane	IEC (mequiv g^{-1})	Condition (conc./base. /temp.)	Time (h)	σ remaining [a] (%)	Ref.
	bQPAES-x7y32-1	1.15	4M/NaOH/80 °C	144	49.7	This
			1M/KOH/80 °C	144	84.1	This
	bQPAES-x4y20-1	1.11	4M/NaOH/80 °C	144	47.8	This
	bQPAES-x7y24	0.81	4M/NaOH/80 °C	144	51.5	This
	bQPAES-x4y15	0.79	4M/NaOH/80 °C	144	52.8	This
R1	rQPAES	1.20	1M/NaOH/80 °C	144	38.0	This
			4M/NaOH/80 °C	144	24.7	This
R3	QBPES-60	1.26	1M/KOH/60 °C	240	23.7(60 °C)	37
R4	QPAES–X20Y18	1.57	1M/NaOH/60 °C	168	72.1(60 °C)	34
R8	bQAPDHTPE-OH20	1.89	1M/NaOH/60 °C	240	60.8	40
R10	QPAE-X15Y15	1.91	1M/KOH/60 °C	168	91.7(60 °C)	42
R15	ImPPESN-2.92	2.10	2M/NaOH/60 °C	200/600	57.0/51.0 (30 °C)	46
R16	ImPESN-19-22	2.07	2M/NaOH/60 °C	200/600	70.0/60.0 (20 °C)	47
R17	PI-cPES-50	1.21	2M/KOH/60 °C	240/840	100/93.3 (25 °C)	48
R18	ImPSf-A	1.75	3M/NaOH/25 °C	168	82.4(25 °C)	49

[a] At 80 °C.

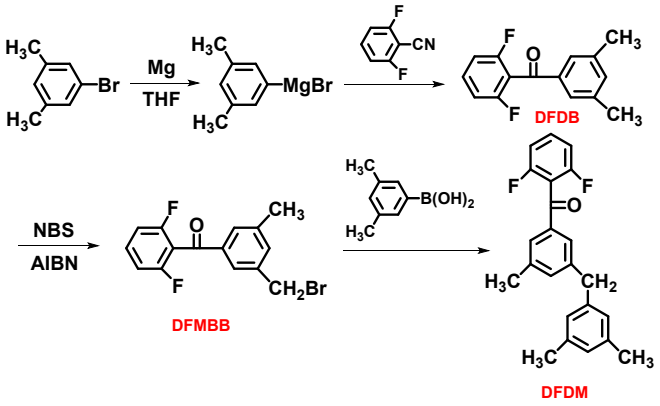

Figure s1. Synthesis of DFDM.

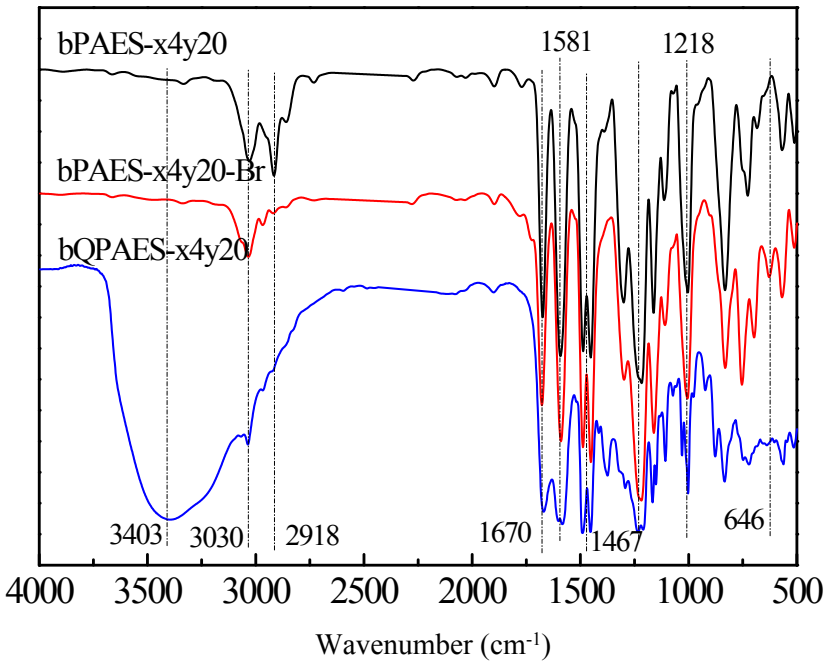

Figure s2. IR spectra of bPAES-x4y20, bPAES-x4y20-Br and bQPAES-x4y20.

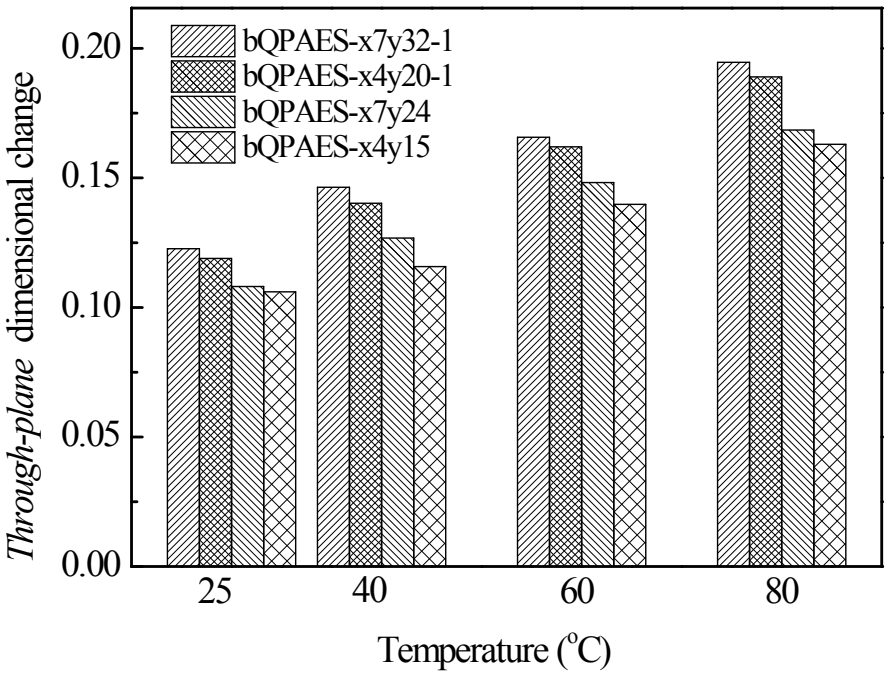

Figure s3. *Through-plane* dimensional change of block bQPAES.

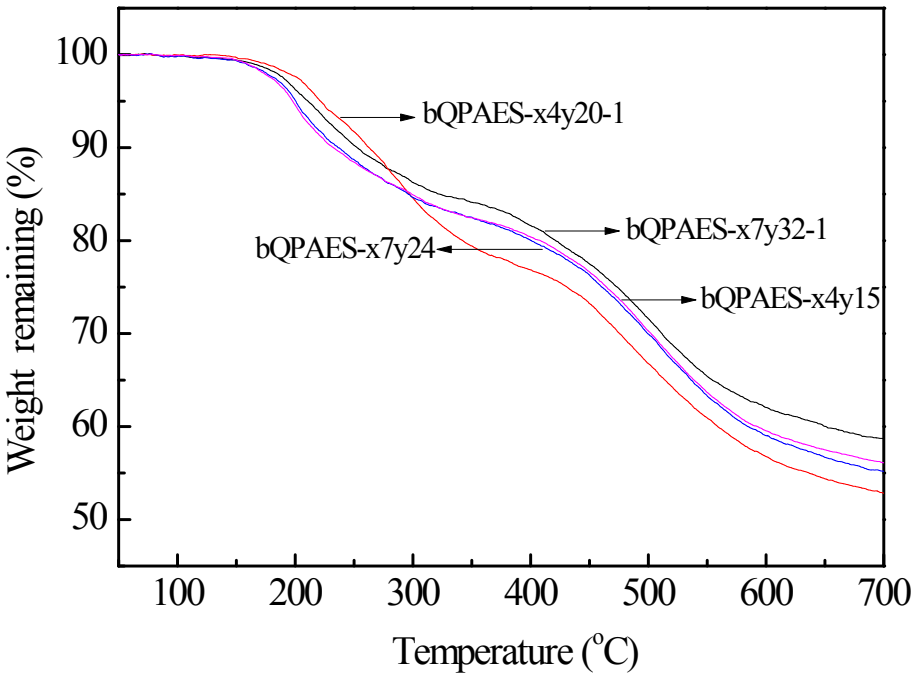

Figure s4. TGA curves of block bQPAES.

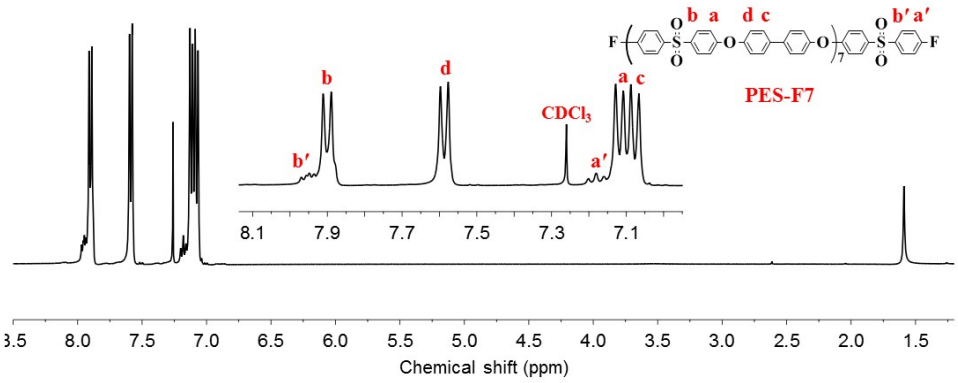

Figure s5. ^{1}H-NMR spectra of PAES-F7.

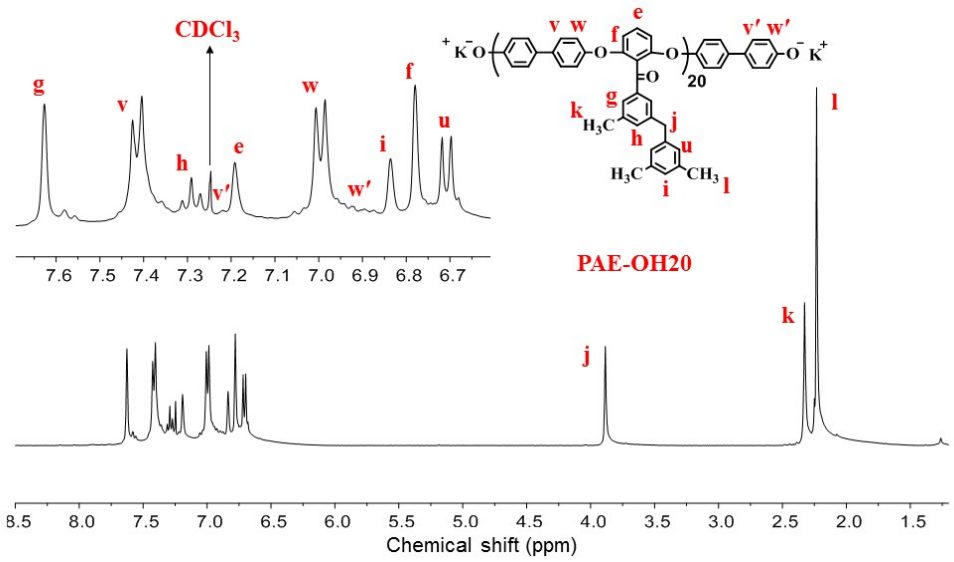

Figure s6. ^{1}H-NMR spectra of PAE-OH20.

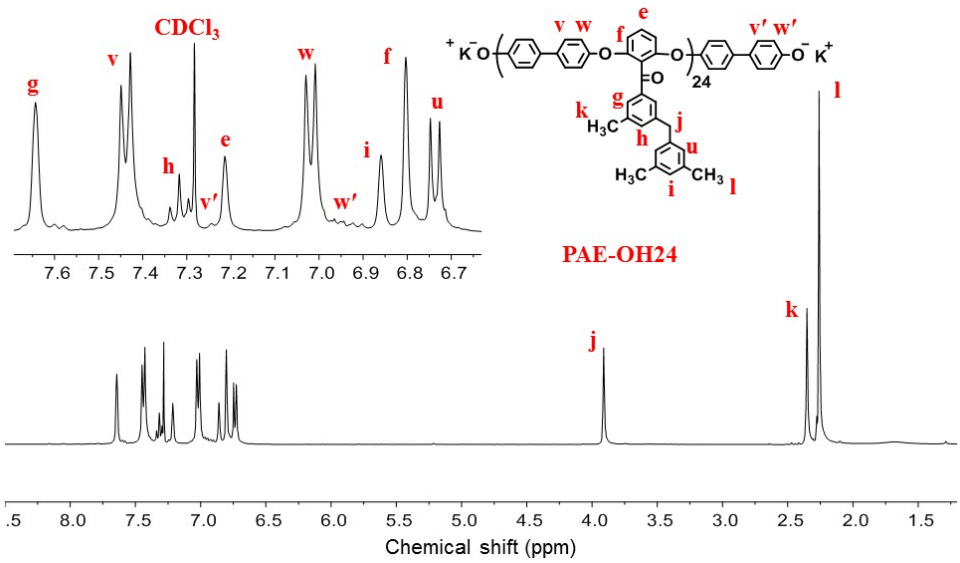

Figure s7. ^{1}H-NMR spectra of PAE-OH24.

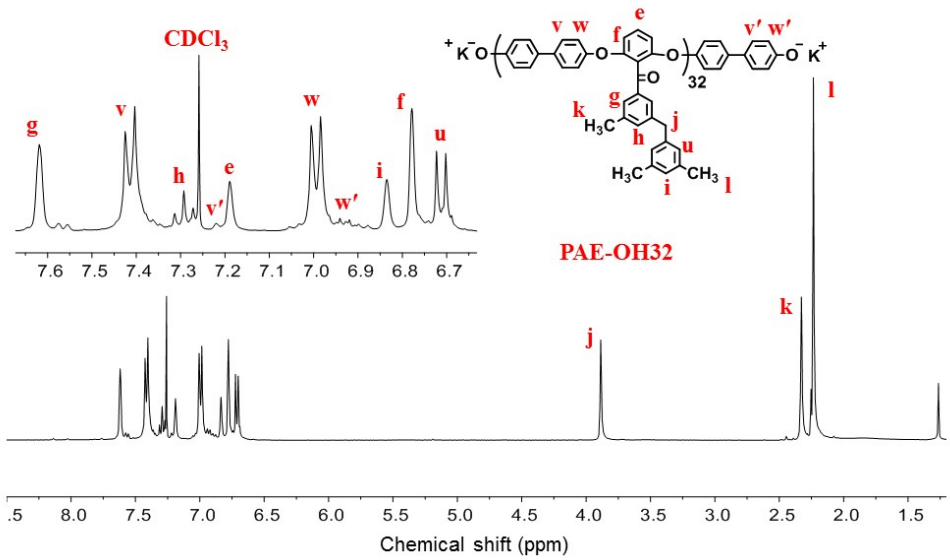

Figure s8. ^{1}H-NMR spectra of PAE-OH32.