## **Supplementary information**

# Multi-block copolymers with fluorene-containing hydrophilic segments densely functionalized by side-chain quaternary ammonium groups as anion exchange membranes

Liuhong Li,<sup>ab</sup> Xi Yue,<sup>ab</sup> Wenjun Wu,<sup>ab</sup> Wuxin Yan,<sup>ab</sup> Mingjian Zeng,<sup>ab</sup> You Zhou,<sup>ab</sup> Shijun Liao<sup>ab</sup> and Xiuhua Li<sup>\*ab</sup>

<sup>a</sup> School of Chemistry & Chemical Engineering, South China University of Technology, Guangzhou 510641, P. R. China.

<sup>b</sup> The Key Laboratory of Fuel Cell Technology of Guangdong Province, South China University of Technology, Guangzhou 510641, P. R. China.

### **Corresponding Author**

\* Tel & Fax: 8620 – 22236591. E-mail: <u>lixiuhua@scut.edu.cn</u>

## I. Figures and tables

## II. Experimental section

### I. Figures and tables

**Fig. S1** <sup>1</sup>H NMR spectra of the oligomer-Fs (a) X = 5 and (b) X = 7.

**Fig. S2** <sup>1</sup>H NMR spectra of oligomer-OHs (a) Y = 10, (b) Y = 13 and (c) Y = 17.

**Fig. S3** <sup>1</sup>H NMR spectra of (a) BrMPAES-X5Y10, (b) BrMPAES-X5Y13, (c) BrMPAES-X5Y17, (d) BrMPAES-X7Y10, (e) BrMPAES-X7Y13 and (f) BrMPAES-X7Y17.

Fig. S4 AFM pattern of QMPAES-X5Y10

 $\label{eq:stable} \textbf{Table S1} \quad \mathsf{IEC}_{\mathsf{m}}, \, \mathsf{IECv}_{\mathsf{wet}}, \, \sigma, \, \sigma/\mathsf{IEC}_{\mathsf{m}}, \, \sigma/\mathsf{IECv}_{\mathsf{wet}} \, of \, the \, \mathsf{QMPAESs} \, membranes \, and \, some \, reported \, \mathsf{AEMs}.$ 



Fig. S1  $^{1}$ H NMR spectra of the oligomer-Fs (a) X = 5 and (b) X = 7.



Fig. S2  $^{1}$ H NMR spectra of oligomer-OHs (a) Y = 10, (b) Y = 13 and (c) Y = 17.



**Fig. S3** <sup>1</sup>H NMR spectra of (a) BrMPAES-X5Y10, (b) BrMPAES-X5Y13, (c) BrMPAES-X5Y17, (d) BrMPAES-X7Y10, (e) BrMPAES-X7Y13 and (f) BrMPAES-X7Y17.



200 nm

Fig. S4 AFM pattern of QMPAES-X5Y10

Membrane	IEC <sub>m</sub> (meg g <sup>-1</sup> )	IECv <sub>wet</sub> (meg.cm <sup>-3</sup> )		σ (mS cm <sup>-1</sup> )		σ/IEC <sub>m</sub> (mS g/(cm mmol))		σ/IECv <sub>wet</sub>	
	(meq 6 /	30 °C	80 °C	30 °C	, 80 °C	30 °C	80 °C	30 °C	80 °C
QMPAES-X7Y10	1.28	0.52	0.51	27.4	85.0	21.4	66.4	52.7	166.7
QMPAES-X7Y13	1.02	0.70	0.64	27.2	51.9	26.7	50.9	38.9	81.1
QMPAES-X7Y17	0.90	0.72	0.68	11.6	38.7	12.9	43.0	16.1	56.9
QMPAES-X5Y10	1.06	0.78	0.74	21.4	58.0	20.2	54.7	27.4	78.4
QMPAES-X5Y13	0.83	0.56	0.56	16.5	44.1	19.9	53.1	29.5	78.8
QMPAES-X5Y17	0.81	0.64	0.61	9.7	23.0	12.0	28.4	15.2	37.7
QPAES-X8Y8 <sup>1</sup>	1.60	1.12ª	1.05	18.3ª	75.8	11.4ª	47.4	16.3ª	72.2
QPAES-X16Y8 <sup>1</sup>	1.24	0.62ª	0.56	26.1ª	51.5	21.0ª	41.5	42.1ª	92.0
QPAES-X16Y10 <sup>1</sup>	1.15	0.85ª	0.77	11.8ª	37.8	10.3ª	32.9	13.9ª	49.1
	1.45	0.96ª	0.84	15.4ª	54.5	10.6ª	37.6	16.0ª	64.9
QPAES-X20Y18 <sup>1</sup>	1.54	0.98ª	0.87	13.3ª	64.1	8.6ª	41.6	13.6ª	73.7
QPAE-X15Y8 <sup>2</sup>	1.13	0.90ª	0.77 <sup>c</sup>	9.8ª	27.6 <sup>c</sup>	8.7ª	24.4 <sup>c</sup>	10.9ª	35.8 <sup>c</sup>
QPAE-X25Y21 <sup>2</sup>	1.45	1.07ª	0.86 <sup>c</sup>	16.9ª	37.3 <sup>c</sup>	11.7ª	25.7 <sup>c</sup>	15.8ª	43.4 <sup>c</sup>
QPE-X16Y11 <sup>3</sup>	0.79	d	d	d	8.8 <sup>c</sup>	d	11.1 <sup>c</sup>	d	d
	1.13	d	d	d	47.0 <sup>c</sup>	d	41.6 <sup>c</sup>	d	d
	1.38	d	d	d	52.0 <sup>c</sup>	d	37.7 <sup>c</sup>	d	d
QPE-X22Y11 <sup>3</sup>	0.86	d	d	d	25.0 <sup>c</sup>	d	29.1 <sup>c</sup>	d	d
ds-PAES-75 <sup>4</sup>	1.49	1.27 <sup>b</sup>	1.03	21.9 <sup>b</sup>	47.3	14.7 <sup>b</sup>	31.7	17.2 <sup>b</sup>	45.9
4(X35) <sup>5</sup>	1.01	1.14ª	d	15ª	24.6	14.9ª	24.4	13.2ª	d
4(X50) <sup>5</sup>	1.32	1.40ª	d	26ª	40.0	19.7ª	30.3	18.6ª	d
ImPES-0.55 <sup>6</sup>	0.98	1.29	d	21.9	51.7	22.3	52.8	17.0	d
ImPES-0.70 <sup>6</sup>	1.23	1.48	d	32.6	69.2	26.5	56.3	22.0	d
PAES-Q-12 <sup>7</sup>	1.65	d	d	22.9ª	54.0	13.9ª	32.7	d	d
QA-PSf-g-PEG350 <sup>8</sup>	1.36	d	d	24.9ª	70.2	18.3 ª	51.6	d	d
<sup>a</sup> Determined at 20 °C. <sup>b</sup> Determined at 25 °C. <sup>c</sup> Determined at 60 °C. <sup>d</sup> Not reported in the literature.									

**Table S1**IEC $\sigma$ ,  $\sigma$ /IEC $\sigma$ ,  $\sigma$ /IEC $\sigma$ ,  $\sigma$ /IEC $\sigma$  $\sigma$ \sigma $\sigma$ 

#### **II. Experimental section**

#### <sup>1</sup>H NMR characterization.

<sup>1</sup>H NMR spectras were recorded on a Bruker AVANCE 400S with tetramethylsilane (TMS) as the standard and CDCl<sub>3</sub> or DMSO-d<sub>6</sub> as the solvent.

#### Atomic Force Microscopy (AFM) characterization.

Tapping mode Atomic Force Microscopy (AFM) was performanced on a Bruker Multimode 8 scanning probe microscopy with a probe of MPP-11100-10 (40 N/m, 300 kHz). The scanning frequency is 1 Hz. The sample was equilibrated at 60% RH for more than 24 h before test.

#### References

- 1 X. Li, Q. Liu, Y. Yu and Y. Meng, J. Membr. Sci., 2014, 467, 1-12.
- 2 X. Li, Y. Yu, Q. Liu and Y. Meng, J. Membr. Sci., 2013, 436, 202-212.
- 3 M. Tanaka, K. Fukasawa, E. Nishino, S. Yamaguchi, K. Yamada, H. Tanaka, B. Bae, K. Miyatake and M. Watanabe, J. Am. Chem. Soc., 2011, **133**, 10646-10654.
- 4 X. Li, G. Nie, J. Tao, W. Wu, L. Wang and S. Liao, ACS Appl. Mater. Interfaces, 2014, 6, 7585-7595.
- 5 N. Li, Q. Zhang, C. Wang, Y. M. Lee and M. D. Guiver, *Macromolecules*, 2012, **45**, 2411-2419.
- 6 Y. Zhuo, A. Lai, Q. Zhang, A. Zhu and M. Ye, Q. Liu, J. Mater. Chem. A, 2015, 3, 18105-18114.
- 7 C. Wang, B. Shen, C. Xu, X. Zhao and J. Li, J. Membr. Sci., 2015, 492, 281-288.
- 8 S. He and C.W. Frank, J. Mater. Chem. A, 2014, 2, 16489-16497.