

## Electronic Supplementary Information

### Sulfonated poly(arylene ether phosphine oxide)s with various distribution and content of pendant sulfonic acid groups synthesized by direct polycondensation

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#### 1. Assignment of the NMR spectra of DSPPO

The dept135 and <sup>13</sup>C NMR spectra of DSPPO are indicated in Fig. S1a. As shown,

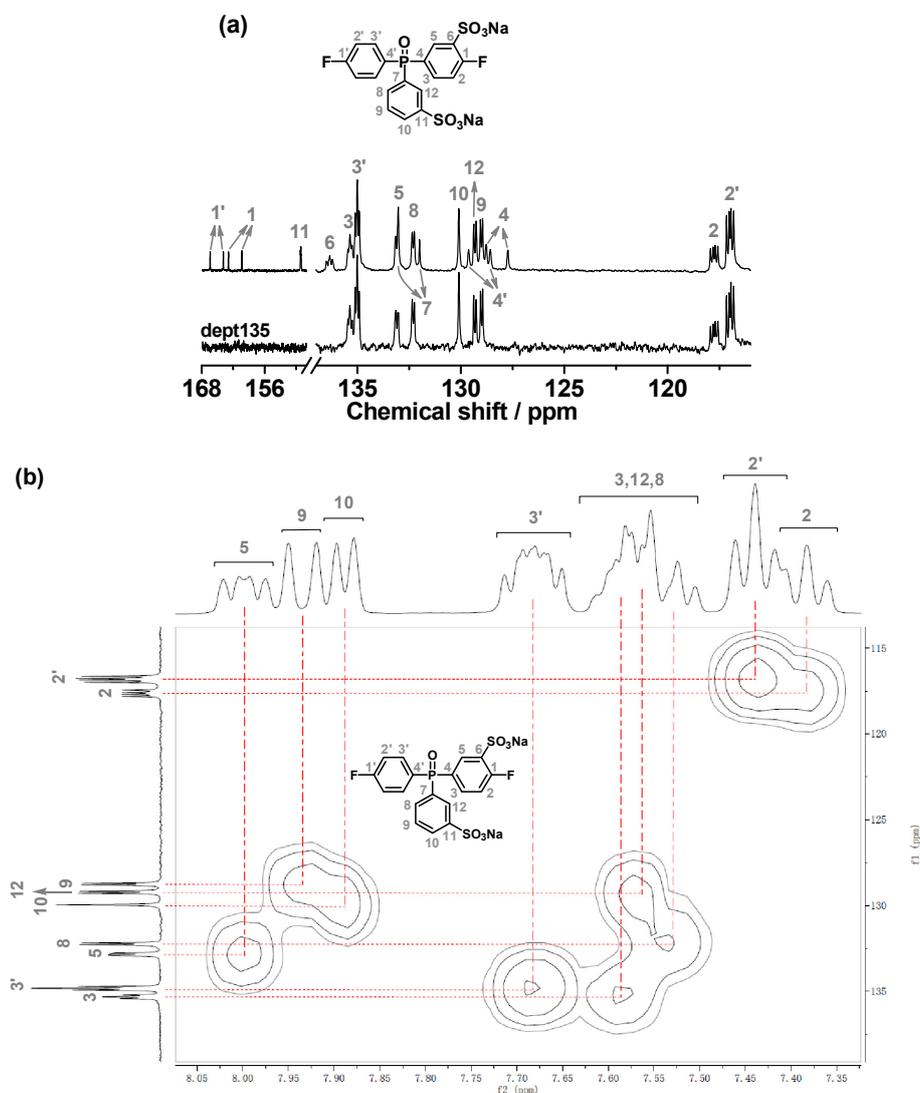


Fig. S1. Dept135, <sup>13</sup>C NMR (a) and HMQC (b) spectra of DSPPO

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the signal peaks of the carbon atoms of DSPPO were well assigned. Carbon 1 and 1' displayed a C/F coupling constant of ~256 Hz. Carbon 4, 4' and 7 exhibited a C/P coupling constant of about 100 Hz, which is equivalent to that of the carbon atoms with similar chemical environments.<sup>[1]</sup>

The HMQC spectrum of DSPPO is presented in Fig. S1b. The signals of the odd carbon atoms of DSPPO in the HMQC spectrum was determined as above, so the signal peaks of the hydrogen atoms of DSPPO could be assigned by the HMQC spectrum, which were indicated in Fig. S1b.

## 2. Assignment of the <sup>1</sup>H NMR spectra of polymers

The chemical structure of PEPOF, msPEPOF-100, dsPEPOF-100 and tsPEPOF-130 is displayed in Fig. S2a. The <sup>1</sup>H NMR spectrum of PEPOF was assigned in our previous report as indicated in Fig. S2b,<sup>[2]</sup> which was used to assist the analysis of the <sup>1</sup>H NMR spectra of the three ionomers. msPEPOF-100 is a homopolymer, its signal peaks in the <sup>1</sup>H NMR spectrum could be well assigned (Fig. S2b). On the other hand, as indicated in Figure S2a, the non-sulfonated repetitive unit of tsPEPOF-130 is exactly the repetitive unit of PEPOF. Moreover, tsPEPOF-130 and msPEPOF-100 also possess identical structural moieties, *i.e.* benzenesulfonate side groups and hexafluoroisopropylidene diphenyl moieties. These hydrogen atoms with similar chemical environments have approximate chemical shift.<sup>[3]</sup> Therefore, on the basis of the assignment of the <sup>1</sup>H NMR spectra of PEPOF and msPEPOF-100, the assignment of the <sup>1</sup>H NMR spectrum of tsPEPOF-130 could be determined, which was presented in Fig. S2b. Similarly, the assignment of the <sup>1</sup>H NMR spectrum of dsPEPOF-100 was also resolved by the assistance of the <sup>1</sup>H NMR spectra of PEPOF, msPEPOF-100 and tsPEPOF-130. Hence, all the <sup>1</sup>H NMR spectra of the three ionomers were determined.

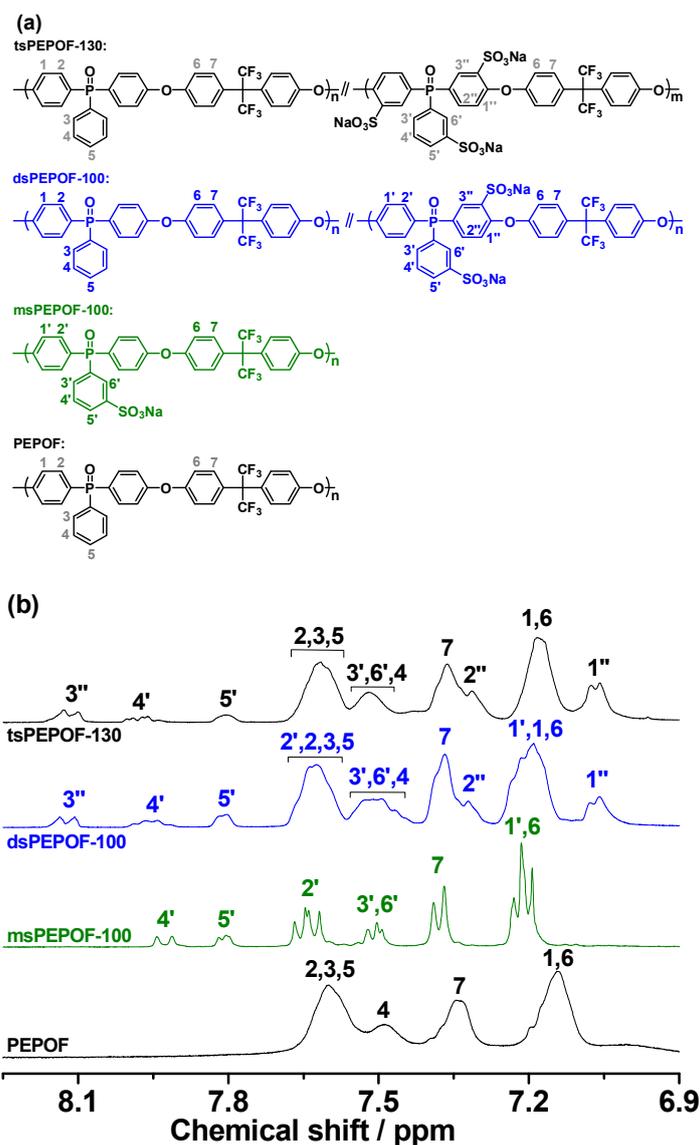


Fig. S2. Chemical structures (a) and <sup>1</sup>H NMR spectra (b) of PEPOF, msPEPOF-100, dsPEPOF-100 and tsPEPOF-130.

Table S1. Mechanical properties and methanol permeability of membranes.

Membranes	Mechanical properties			Methanol permeability ( $\times 10^{-7}$ cm <sup>2</sup> /s)
	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)	
msPEPOF-100	40.4	1.10	6.2	2.4
dsPEPOF-100	43.3	1.11	10	2.2
dsPEPOF-110	42.4	1.13	8.2	2.7
dsPEPOF-120	44.4	0.94	7.4	3.3
tsPEPOF-100	41.3	1.08	6.0	1.2
tsPEPOF-110	43.4	1.13	7.0	1.4
tsPEPOF-120	46.5	1.09	6.7	2.0
tsPEPOF-130	37.8	0.77	9.0	2.5
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## References

1. L. C. Fu, G. Y. Xiao, D. Y. Yan, *J. Mater. Chem.*, 2012, **22**, 13714–13722.
2. H. Y. Liao, G. Y. Xiao, D. Y. Yan, *Chem. Commun.*, 2013, **49**, 3979–3981.
3. N. Tan, G. Y. Xiao, D. Y. Yan, *Chem. Mater.*, 2010, **22**, 1022–1031.