Electronic Supplementary Information

Sulfonated poly(arylene thioether phosphine oxide)s (sPTPO) and sPTPO/sulfonated polybenzothiazole blends as proton exchange membranes

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In order to analyze the chemical structure of sPTPO-60, sPTPO-100 and the model compound, *i.e.* bis(4-(*p*-tolylenethio phenyl) phenyl phosphine oxide (TTPPO), were synthesized. Their chemical structure is displayed in Scheme S1, and their dept135 and ^{13}C NMR spectra are exhibited in Fig. S1.

1. ***Synthesis of model compound (TTPPO):*** 0.5465 g (4.4 mmol) of *p*-toluenethiol, 0.6285 g (2.0 mmol) of BFPPO, 0.6689 g (4.84 mmol) of K_2CO_3, 8 mL NMP, and 8 mL toluene were added to a 150 mL three-necked round bottom flask, equipped with a mechanical stirrer, condenser, Dean-Stark trap and argon inlet/outlet. The sequent preparation procedure is similar to that of sPTPO-60, which was described in the main text.

Yield: 93%. ^1H NMR (DMSO-d_6, ppm): 7.64–7.56 (2H), 7.56–7.53 (2H), 7.53–7.51 (1H), 7.51–7.45 (4H), 7.44–7.39 (4H), 7.31–7.26 (4H), 7.22–7.17 (4H), 2.36–2.31 (6H). ^{13}C NMR (DMSO-d_6, ppm): 143.713, 139.678, 134.690, 133.05 (d, J_{CP} = 103 Hz), 132.664 (d, J_{CP} = 10.5 Hz), 132.510, 131.848 (d, J_{CP} = 9.8 Hz), 131.188, 129.936 (d, J_{CP} = 104 Hz), 129.214 (d, J_{CP} = 11.8 Hz), 127.440, 127.079 (d, J_{CP} = 12.2 Hz), 21.246. FT-IR (film, cm^{-1}): 2973 ($-CH_3$), 1192 (P=O).

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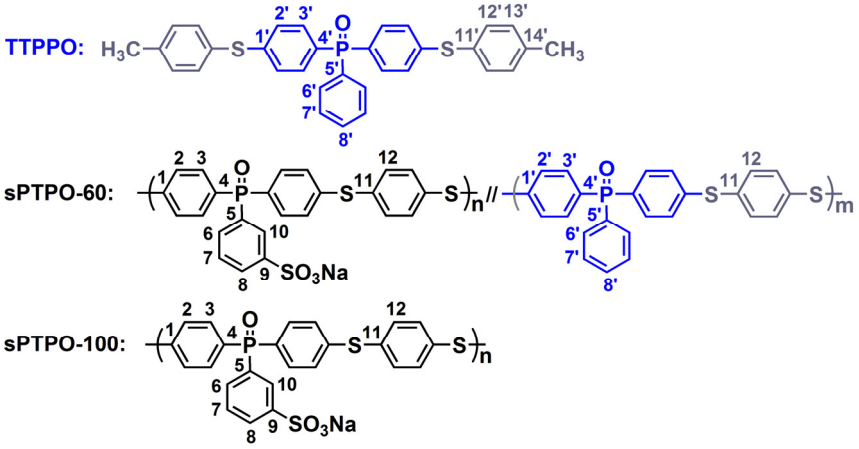
Scheme S1. Chemical structure of TTPPO, sPTPO-60, and sPTPO-100.



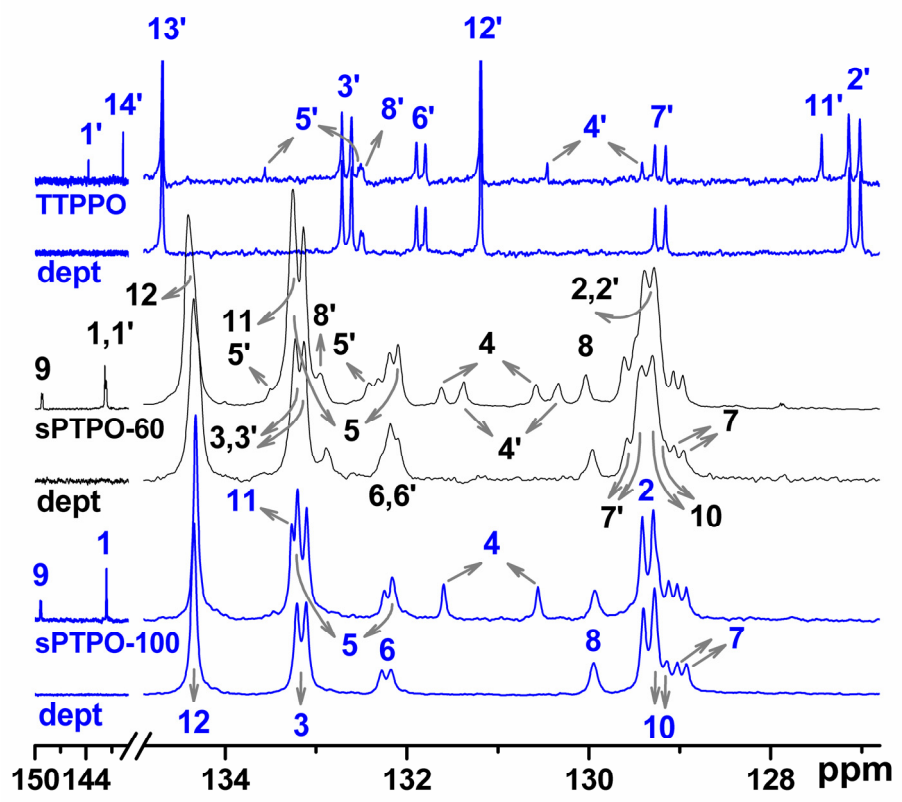


Fig. S1. Dept135 and ^{13}C NMR spectra of TTPPO, sPTPO-60, and sPTPO-100.

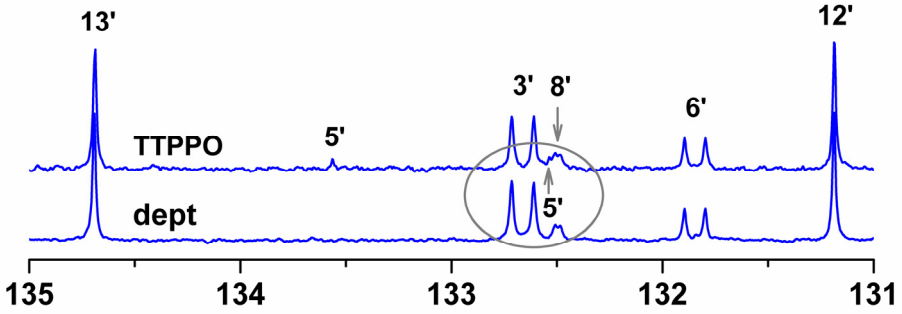


Fig. S2. Partial Enlarged image of the dept135 and ^{13}C NMR spectra of TTPPO

2. ***Assignment of the signal peaks of the dept135 and ^{13}C NMR spectra***

At first, the assignment of the signal peaks in the dept135 and ^{13}C NMR spectra of TTPPO was analyzed as follows. In the dept135 NMR spectrum of TTPPO, the signal peaks of the odd-carbon atoms ($C_{2'}$, $C_{3'}$, $C_{6'}$, $C_{7'}$, $C_{8'}$, $C_{12'}$ and $C_{13'}$) could be identified according to the chemical shift, coupling constant, and number of carbon atoms. Similarly, the signal peaks of the even-carbon atoms ($C_{1'}$, $C_{4'}$, $C_{5'}$, $C_{11'}$ and $C_{14'}$) could be assigned in the ^{13}C NMR spectra of TTPPO. Notably, it could be clearly seen that the right split peak of $C_{5'}$ was partly overlapped with the peak of $C_{8'}$ at 132.5 ppm in Fig. S2. The coupling constant (J_{CP}) of $C_{4'}$/P and $C_{5'}$/P was ~100 Hz, while the coupling constant (J_{CP}) of $C_{2'}$/P, $C_{3'}$/P, $C_{6'}$/P and $C_{7'}$/P was about 10 Hz. $C_{1'}$ and $C_{8'}$ almost showed no coupling constant (J_{CP}) with phosphine atom because the number of chemical bonds between them is larger than 3. $C_{11'}$, $C_{12'}$, $C_{13'}$ and $C_{14'}$ showed no coupling constant (J_{CP}) with phosphine atom because the number of chemical bonds between them is much larger than 3.

Similarly, the signal peaks in the dept135 and ^{13}C NMR spectra of sPTPO-100 could be assigned, as shown in Fig. S1. There were several overlapped signal peaks. The peak of C_{11} was partly overlapped with the left split peak of C_3. Moreover, it could be observed that the left split peak of C_3 was also overlapped with the left split peak of C_5 at 133.2 ppm and that the right split peak of C_5 was overlapped with the right split peak of C_6 at 132.1 ppm by comparing the dept135 and ^{13}C NMR spectra of sPTPO-100. In addition, the right split peak of C_2 was overlapped with the left split peak of C_{10} at 129.3 ppm. These overlapping of signal peaks could be verified by the coupling constant between the C and P atoms.

As indicated in Scheme S1, the chemical structure of the sulfonated repetitive unit of sPTPO-60 was exactly that of sPTPO-100, whereas the chemical structure of the triphenyl phosphine oxide moiety in the *non*-sulfonated repetitive unit of sPTPO-60 was similar to the one (*marked with blue*) in TTPPO. Therefore, the signal peaks in the dept135 and ^{13}C NMR spectra of sPTPO-60 could be assigned with the assistance of the ^{13}C NMR spectra of TTPPO and sPTPO-100. The detailed assignment of each carbon atom is displayed in Fig. S1.