

Supporting Information

Comb-shaped cardo poly(arylene ether nitrile sulfone) anion exchange membranes: significant impact of nitrile group content on morphology and properties

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Section S1 Characterization and measurement

S1.1 Nuclear magnetic resonance (NMR), FT-IR spectroscopy and gel permeation chromatography (GPC)

The ^1H NMR spectra were recorded on a Bruker 500 MHz/Avance III NMR spectrometer, using deuterated chloroform (CDCl_3) or dimethyl sulfoxide- d_6 ($\text{DMSO-}d_6$) as solvents and tetramethylsilane (TMS) as the internal standard. The FT-IR spectra were obtained from a Thermo Scientific Nicolet iS50 with an accumulation of 32 scans in the range 500–4000 cm^{-1} . GPC of the copolymers was performed on a Waters 1515 system, where a HPLC grade tetrahydrofuran (THF) was used as the eluent with a flow rate of 1.0 $\text{mL}\cdot\text{min}^{-1}$ and polystyrene as the standard.

S1.2 Ionic exchange capacity (IEC), water uptake (WU) and swelling ratio (SR)

The IEC of the CCPENS-x AEMs was measured by the back-titration method. The membranes in OH^- form were first dried at 60 $^\circ\text{C}$ under vacuum for 48 h. Then the samples were immersed in a 0.1 M HCl solution for 48 h, followed by back titrating with a 0.05 M standard KOH solution. The IEC value ($\text{meq}\cdot\text{g}^{-1}$) is calculated using Equation (1).

$$IEC = \frac{M_{o,HCl} - M_{e,HCl}}{m_d} \times 100\% \quad (1)$$

where $M_{o,HCl}$ and $M_{e,HCl}$ (meq) are the milliequivalents of HCl before and after equilibrium, respectively, and m_d (g) is the weight of the dried membrane sample.

For measuring WU and SR, the square AEM samples (approximately 3 cm \times 3 cm) were soaked in deionized water (DI water) at different temperatures every 24 h. During this period, the AEMs and DI water were kept in a chamber which was charged with flowing N_2 gas for protecting from air. The mass (M_{wet}) and length (L_{wet}) of the wet membrane samples were measured immediately after being

wiped with filter papers. The samples were then dried at 60 °C under vacuum for 48 h to measure the corresponding dry mass (M_{dry}) and length (L_{dry}). The WU and SR were calculated by Equation (2) and (3), respectively.

$$WU = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100\% \quad (2)$$

$$SR = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\% \quad (3)$$

The number of absorbed water molecules per ion group, designated as λ , was calculated by Equation (4).

$$\lambda = \frac{WU}{M_{H_2O}} \times \frac{1000}{IEC} \quad (4)$$

where M_{H_2O} is the molecular weight of water (18.02 g mol⁻¹).

SI.3 Ionic conductivity, scanning electron microscopy (SEM) and atomic force microscopy (AFM)

The ionic conductivity of the AEMs (OH⁻ form) was detected on an electrochemical system (Parstat 2273, Ametek Inc., USA) by the two-electrode AC impedance spectroscopy method under fully hydrated condition. Before testing, the membrane samples were immersed in DI water at 25 °C for 24 h. The measurements were performed on the OH⁻ form membranes in DI water at various temperatures (from 30 °C to 80 °C) in a chamber. The chamber was charged with flowing N₂ gas for protecting from air during the measurement. The ionic conductivity (σ , mS·cm⁻¹) was calculated by Equation (5).

$$\sigma = \frac{l}{AR} \quad (5)$$

where l (cm) refers to the distance between the two electrodes, A (cm²) is the cross-sectional area of the membrane, and R (Ω) represents the AEM resistance.

The SEM images of the AEMs were recorded using a field emission scanning electron microscope (SEM, S-4800, Hitachi, Japan). Before observation, the samples were fractured with liquid nitrogen and then coated with gold.

The surface morphology measurements of the AEMs were performed on an AFM5500 (Agilent Technologies) instrument using tapping mode and ambient condition. Before testing, the samples were equilibrated at 25 °C and 60% RH for 24 h.

S1.4 Mechanical property, thermal stability and alkaline stability

The mechanical properties of the membranes in full wet state were measured on a WD-300K universal material testing system with a stretching speed of 5 mm·min⁻¹ at 25 °C and 60% RH. Before testing, the membrane samples in 15 mm width were kept in DI water at 25 °C for 24 h and taken out to wipe off the surface water by a filter paper.

The thermal stability of the AEMs was measured on a SHIMADZU DTG-60H thermogravimetric analyzer (TGA) at a heating rate of 10 °C·min⁻¹ in nitrogen atmosphere. Before testing, the samples were dried at 60 °C under vacuum for 24 h.

The alkaline stability was evaluated by immersing the membrane samples (OH⁻ form) into a 1 M KOH solution at 80 °C for 480 h. During this period, the solution was kept in a chamber which was charged with flowing N₂ gas for protecting from air. The changes in both the ionic conductivity and IEC of the AEMs were investigated.

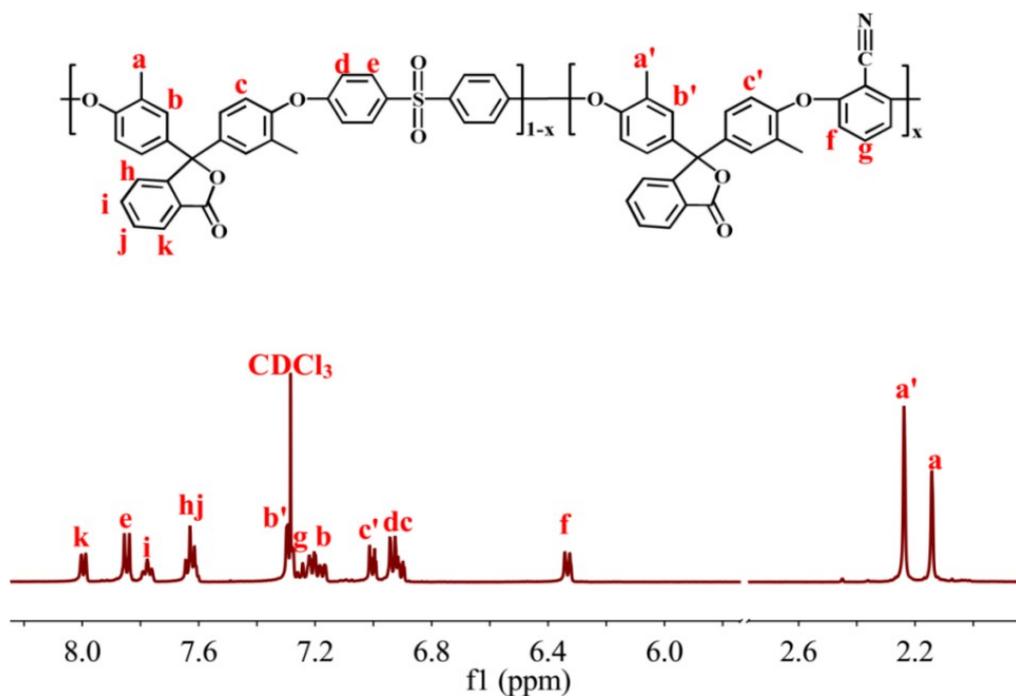


Figure S1 ^1H NMR spectra of CPENS-0.6.

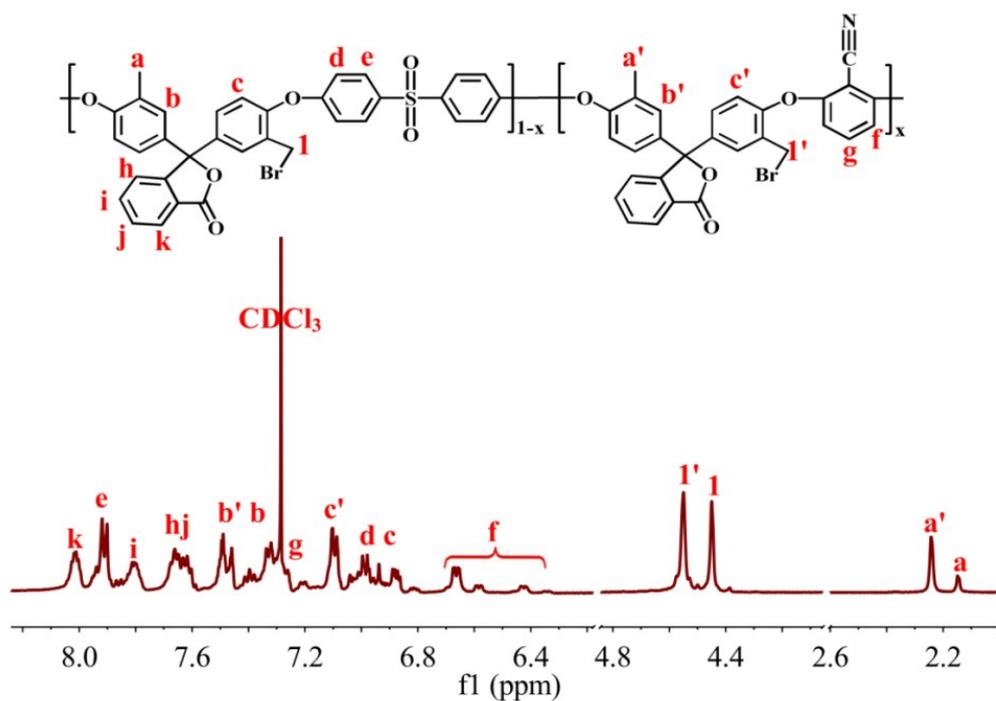


Figure S2 ^1H NMR spectra of BCPENS-0.6.

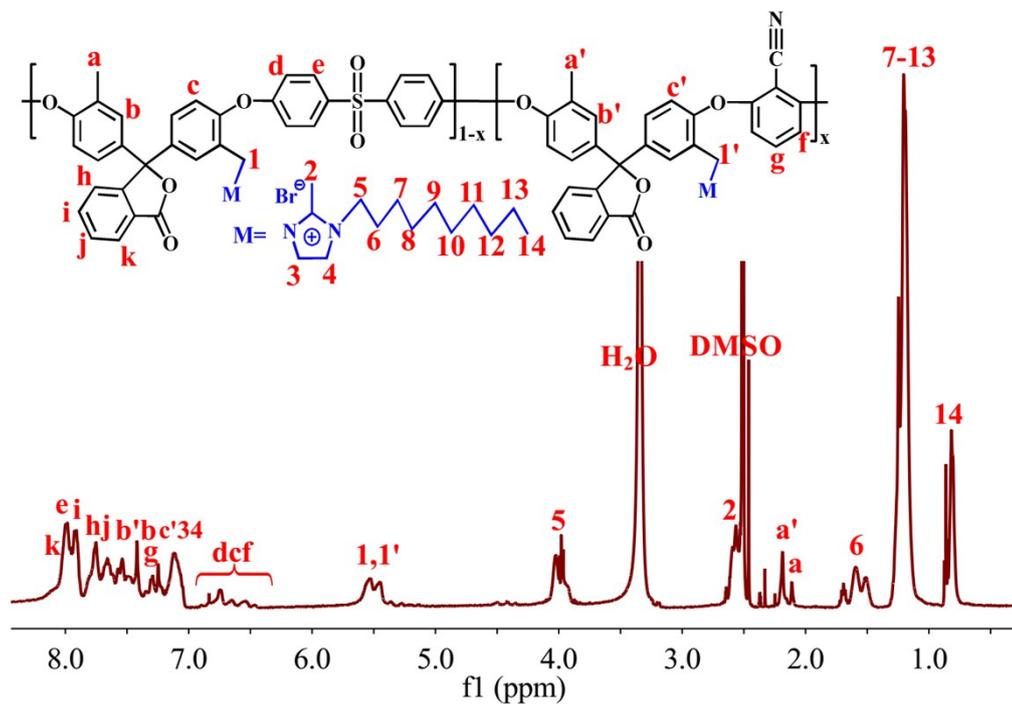


Figure S3 ^1H NMR spectra of CCPENS-0.6.

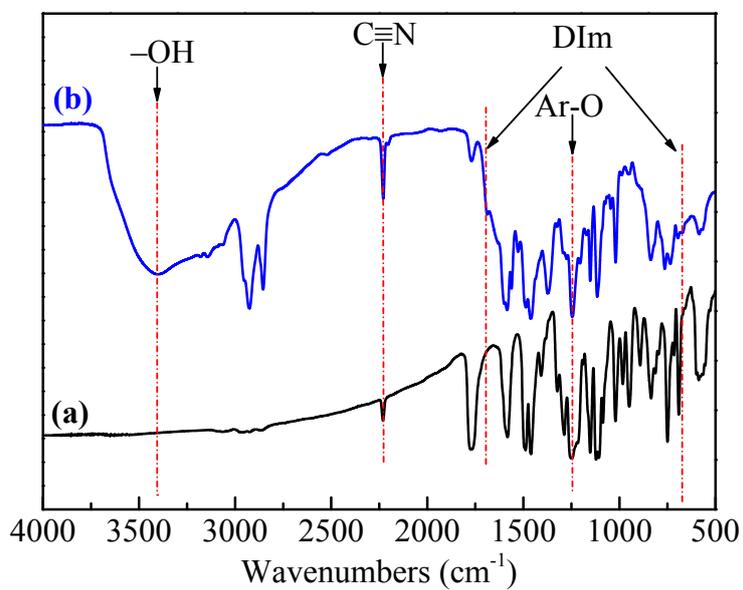


Figure S4 FT-IR spectra of (a) CPENS-0.6 and (b) CCPENS-0.6.

Table S1 The performance of AEMs reported in the literature and this work.

AEMs	IEC (meq g ⁻¹)	σ^a (mS cm ⁻¹)	Swelling ratio ^a (%)	Tensile strength ^b (MPa)	Elongation at break ^b (%)
CCPENS-x (this work)	1.56~1.65	58.6~83	12.7~9.2	24.2~27.6	4.8~6.1
BI-cPES-4 [1]	1.2	61	7.1	56.49	4.44
PES-PPH-Py(OH)-100 [2]	1.46	59	17	39.00	8.90
QPAES-X20Y8 [3]	1.57	69.5	44	-	-
CPAES-Q-90 [4]	1.64	57.5	22.5	23.6 ± 3.1	27.0 ± 1.6
QBz-PEEK-70.2% [5]	1.64	90	21.5	50	35
MM-PES-1.5-1 [6]	1.69	78.3	33.3	38.9	4.9
QPAE-a [7]	1.73	49.1	17.8	-	-
BQA-SPEK-50 [8]	1.79	67.8	27.8	71.3	6.9
QA-(PS ₁₄₀ -PDVPPA ₆₀ -PS ₁₄₀) [9]	1.81	86	31	12.6 ± 2.2	6.4 ± 0.7
FPAES-Im-52 [10]	1.92	83.1	16.9	18.6	12.5
C18BQAPPO-3 [11]	1.98	85	25	8.4	27.5
PPO-5.4 [12]	2.01	74	23.3	~35	~40
DQRPES-2.4OH [13]	2.2	30	27	26.4	16.0

^a Measured at 80 °C.

^b Measured in full wet state.

References

- [1] A. H. N. Rao, S. Y. Nam and T. H. Kim, *RSC Adv.*, 2016, 6, 16168–16176.
- [2] F. Gong, R. Wang, X. Chen, P. Chen, Z. An and S. Zhang, *Polym. Chem.*, 2017, 8, 4207–4219.
- [3] X. Li, Q. Liu, Y. Yu and Y. Meng, *J. Membr. Sci.*, 2014, 467, 1–12.
- [4] G. Nie, X. Li, J. Tao, W. Wu and S. Liao, *J. Membr. Sci.*, 2015, 474, 187–195.
- [5] Z. Zhang, X. Xiao, X. Yan, X. Liang and L. Wu, *J. Membr. Sci.*, 2019, 574, 205–211.
- [6] S. Kwon, A. H. N. Rao and T. H. Kim, *J. Power Sources*, 2018, 375, 421–432.
- [7] X. Li, Q. Liu, Y. Yu and Y. Meng, *J. Mater. Chem. A*, 2013, 1, 4324–4335.
- [8] X. L. Gao, Q. Yang, H. Y. Wu, Q. H. Sun, Z. Y. Zhu, Q. G. Zhang, A. M. Zhu and Q. L. Liu, *J. Membr. Sci.*, 2019, 589, 117247.
- [9] M. Zhu, M. Zhang, Q. Chen, Y. Su, Z. Zhang, L. Liu, Y. Wang, L. An and N. Li, *Polym. Chem.*, 2017, 8, 2074–2086.
- [10] B. Shen and H. Pu, *Int. J. Hydrogen Energy*, 2019, 44, 11057–11065.
- [11] Y. He, J. Si, L. Wu, S. Chen, Y. Zhu, J. Pan, X. Ge, Z. Yang and T. Xu, *J. Membr. Sci.*, 2016, 515, 189–195.
- [12] B. Lee, H. Lim, J.E. Chae, H.J. Kim and T.H. Kim, *J. Membr. Sci.*, 2019, 574, 33–43.
- [13] X. Dong, D. Lv, J. Zheng, B. Xue, W. Bi, S. Li and S. Zhang, *J. Membr. Sci.*, 2017, 535, 301–311.