Ultra-robust, Highly Proton-conductive Polymer Carbon Dots Membranes through Bioinspired Complexation

Benbing Shi[a,b‡], Xiao Pang[a,b‡], Hong Wu[a,b], Jianliang Shen[a,b], Jingyuan Guan[a,b], Xiaoyao Wang[a,b], Chunyang Fan[a,b], Li Cao[a,b], Tianhao Zhu[a,b], Zhuoyu Yin[a,b], Yan Kong[a,b], Yiqin Liu[a,b], Sijia Wang[a,b], and Zhongyi Jiang[*a,b,c,d]

[a]Key Laboratory for Green Chemical Technology, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China.
[b]Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China.
[c]Joint School of National University of Singapore and Tianjin University, International Campus of Tianjin University, Binhai New City, Fuzhou, 350207, China.
[d]Zhejiang Institute of Tianjin University, Ningbo, Zhejiang 315201, China.
‡ These authors contributed equally.
E-mail: zhyjiang@tju.edu.cn

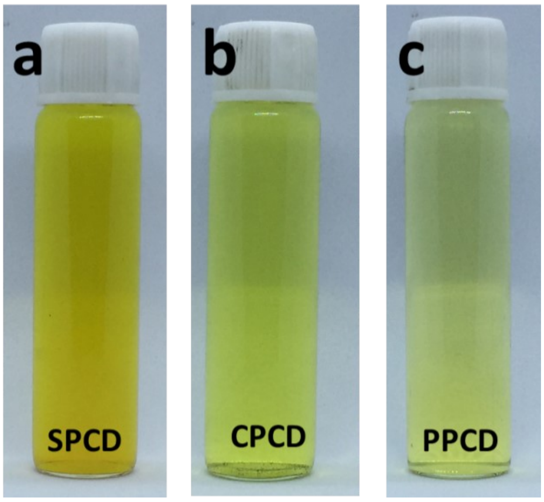

Fig. S1 Photograph of the PCD solution (SPCD(a), CPCD(b), PPCD(c)).

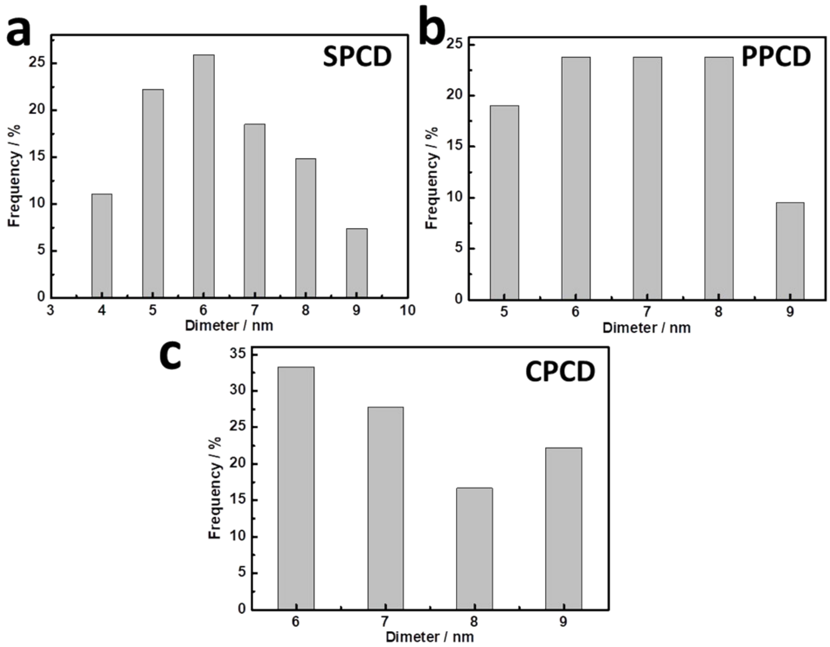

Fig. S2 Frequency distribution histogram of the size of the PCDs(SPCD(a), CPCD(b), PPCD(c)).

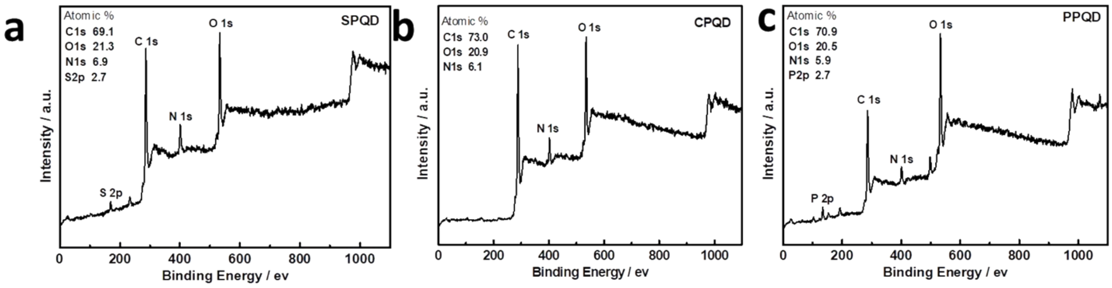

Fig. S3 XPS spectra and the element content of the PCDs (SPCD(a), CPCD(b), PPCD(c)).

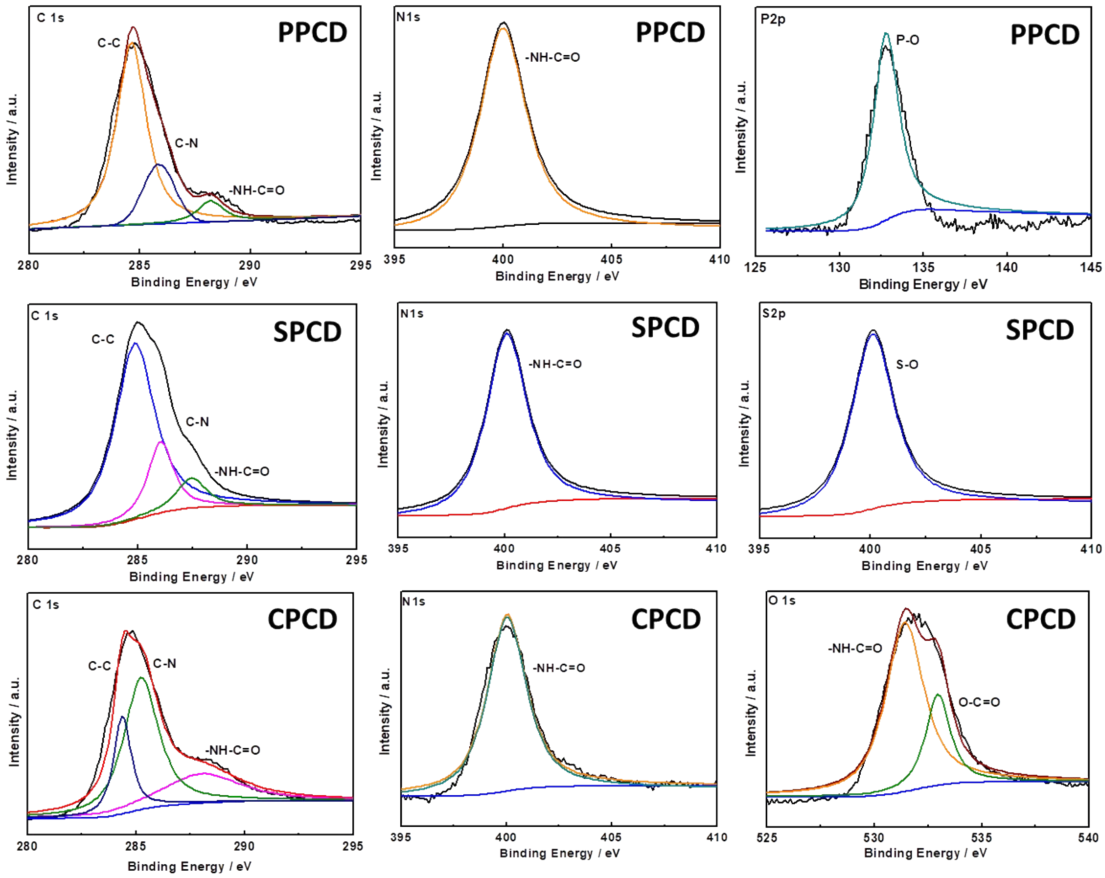

Fig.S4 High-resolution XPS spectra of PCDs

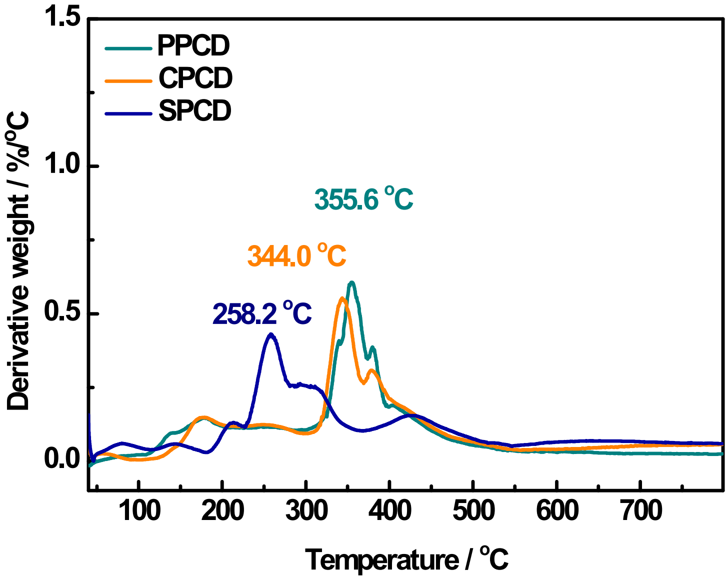

Fig. S5 DTG curves of the PCDs.

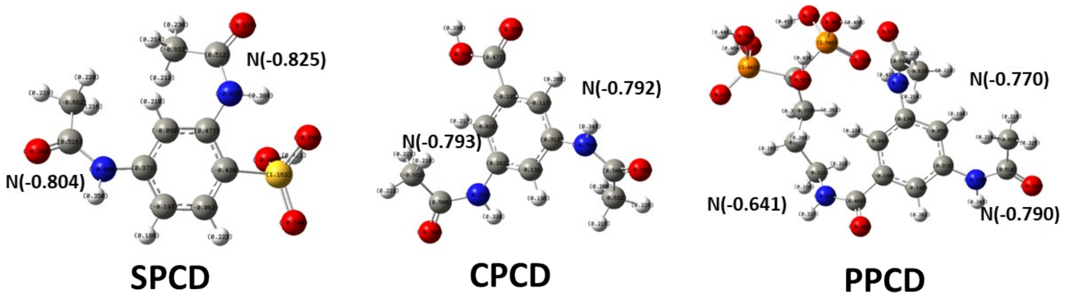

Fig. S6 The charge distribution of N atom in PCD.

The molecular electrostatic potential (MEP) values of the functional groups were calculated in the GAUSSIAN 09W package at the DFT/B3LYP level. The electron density on N atom was related to the charge distribution and higher negative charge indicates higher electron density, and vice versa.

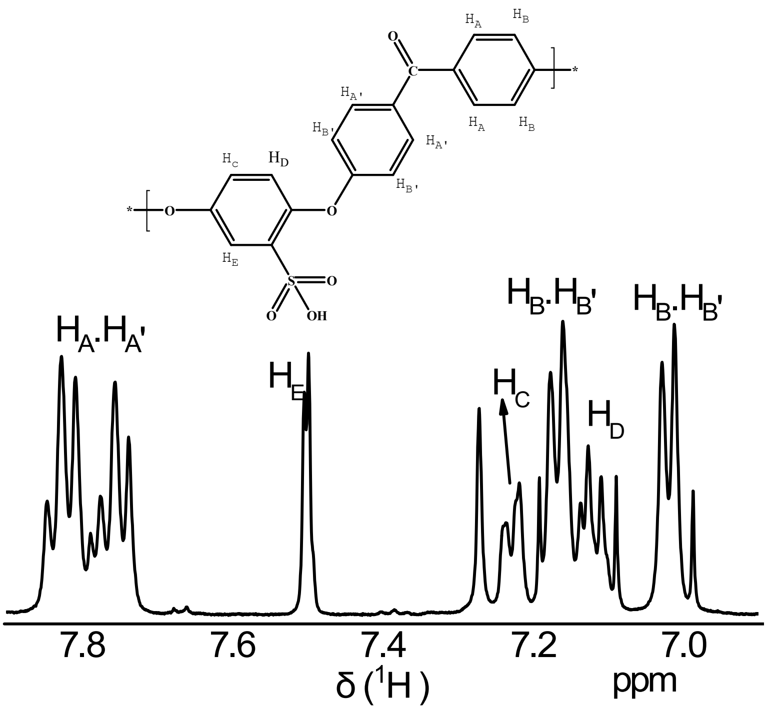

Fig. S7 H-NMR spectrum of the SPEEK.

Table S1 The weight loss of PCDs in PCDMs.

Sample	Weight loss (wt.%)
SPCDM-50	1.5
PPCDM-50	1.9
CPCDM-50	2.4
SPCDM-55	3.7
PPCDM-55	4.2
CPCDM-55	4.7

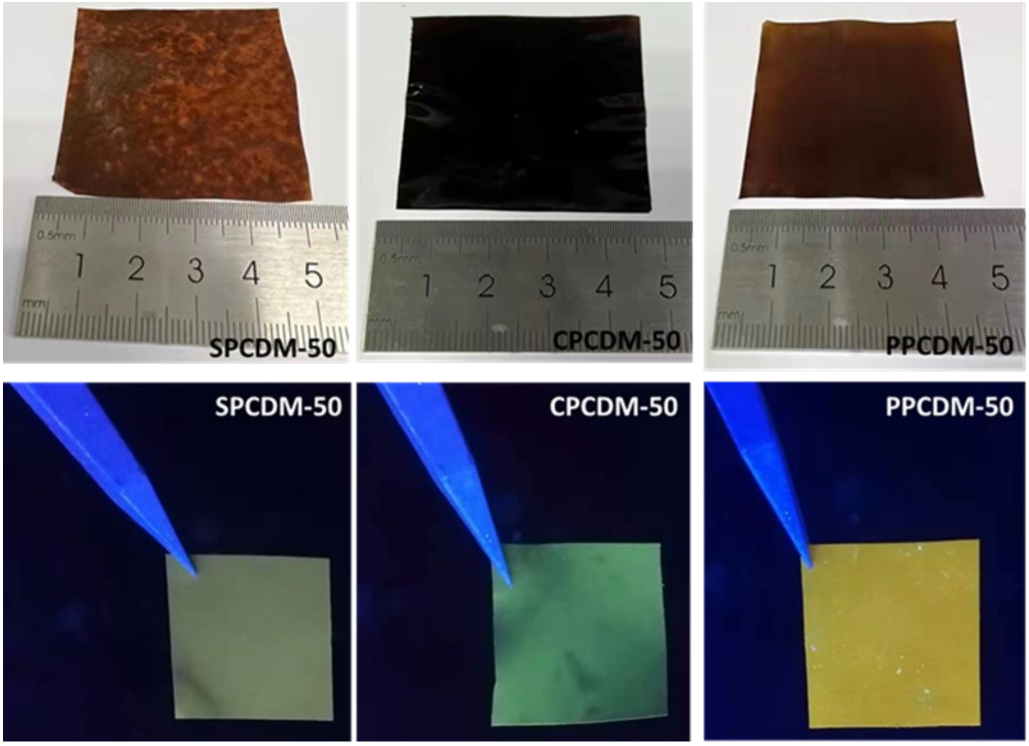

Fig. S8 Fluorescence phenomenon of the PCDMs under UV(365 nm).

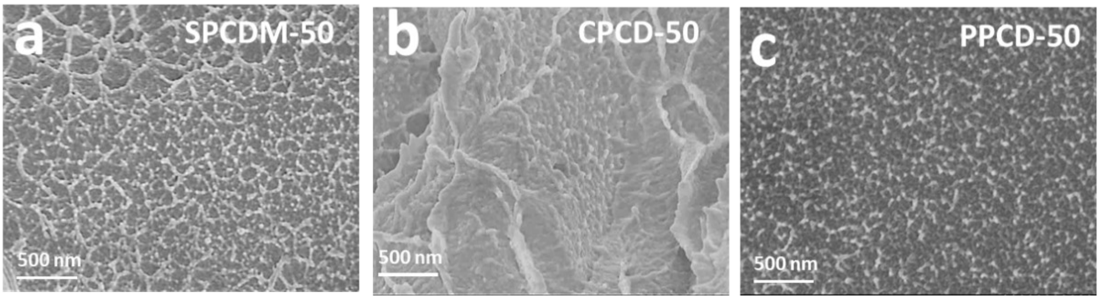

Fig. S9 SEM images of the cross section of the PCDMs.

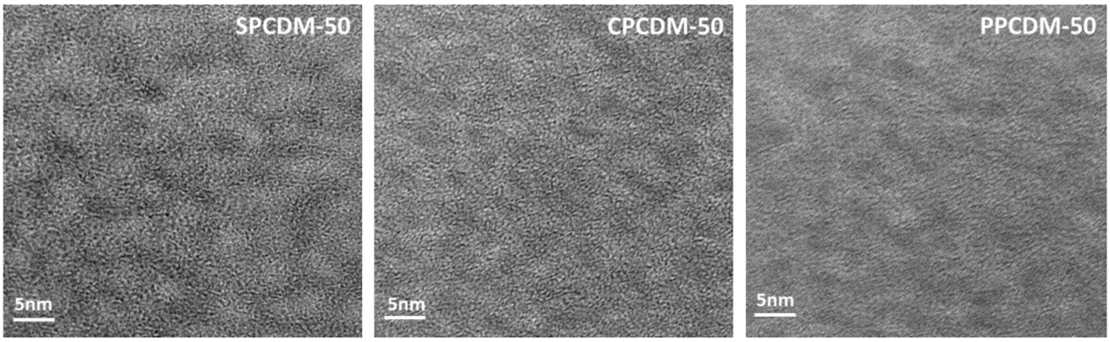

Fig. S10 TEM images of the PCDM.

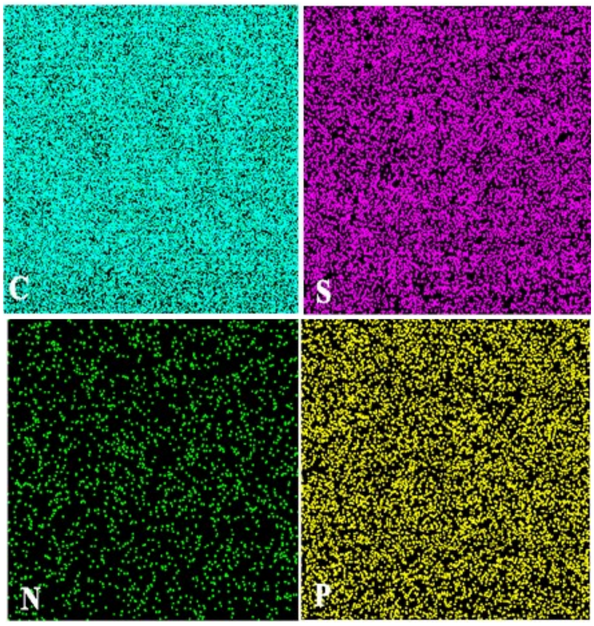

Fig. S11 Element distribution in PCDMs.

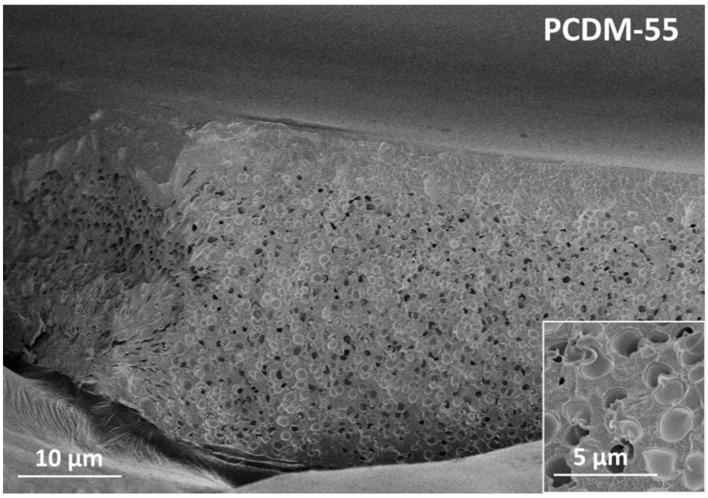

Fig. S12 SEM image of cross section the PCDM-55.

Table S2. Proton conductivity, IEC values, and mechanical stability of PCDMs and membranes in literature

Membrane	*IEC* values (mmol g^{-1})	Stress (MPa)	Proton conductivity(mS cm^{-1} (Temperature/ °C)	Reference
PTFE48/SPEEK65	1.44	27.2	183 (90)	1
Aq-PSUT（30%）	1.02	20	180(80)	2
Su-CNTs/Nafion	0.98	20.6	216 (99)	3
SPPESK-SF-7.5	1.62	31.4	226.7(90)	4
Nafion/CeO2-TiC(0.5 wt%)	0.87	46.9	90(90)	5
PTPBSH-90	2.44	51.2	119(90)	6
Nafion-ZrGdNR-1.5	0.909	22.5	164(80)	7
M-BC	1.75	25	90.2 (80)	8
GO-g-SPEEK/Nafion-33	1.45	8.6	219(90)	9
Me-m-SPEEK	1.78	55.4	173(100)	10
SPP-QP	2.6	34	220 (80)	11
SPEEK/S-UiO-66@GO-10	1.7	53.5	268(70)	12
SPAFT5	1.77	44.3	105(80)	13
SF-Nafion-1	0.932	13	130(80)	14
MIV	0.56	6.25	32(80)	15
SPAES-8-33	1.66	20.51	331(80)	16
6F-PAEK-SP22	1.77	29.5	148(100)	17
SPI-5-POSS	1.69	40.8	132(80)	18
C-SPAES-40	2.12	71.5	150.4(80)	19
PEEK-PEMs	3.08	14	431(80)	20
SPEKEBI-4	2.14	11	233(80)	21
SPAEK-100	1.49	45.34	159(100)	22
SPAES50	1.84	54.86	211.6 (80)	23
SPEEK/PANTs-3#-10	1.869	57.25	330(70)	24
poly(SHS-ddm)	3.13	32.49	154 (80)	25
SPAES 50	2.01	9.2	181(80)	26
SPES-3	1.51	27	131.4(100)	27
sPBT-PE57.5	2.55	49.2	130(80)	28
SPP-co-PAEK(5/1)	2.38	46	233(60)	29
PEM-OH	1.6	48	100(80)	30
Am-SPEEK-T	1.53	53.8	140 (80)	31
2-SPAES-80	1.73	53	258(80)	32
SPAEK	1.73	49	130(120)	33
PPCDM-50	2.53	56	264(80)	This work

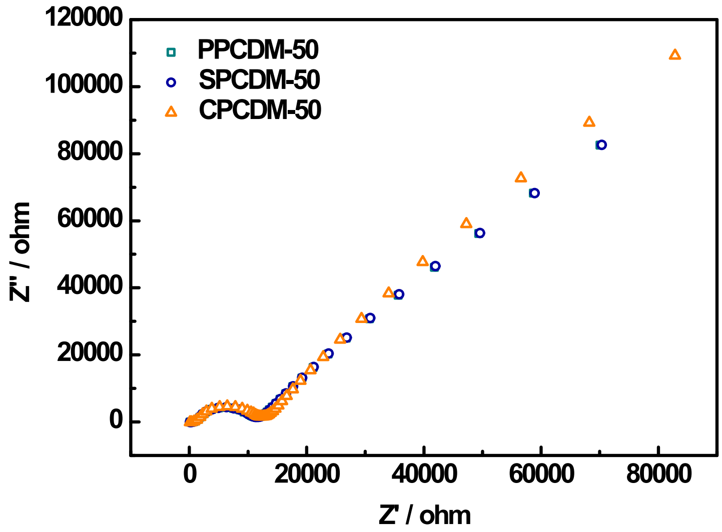

Fig.S13 Nyquist plot of the PCDMs at 30 °C under 100% RH.

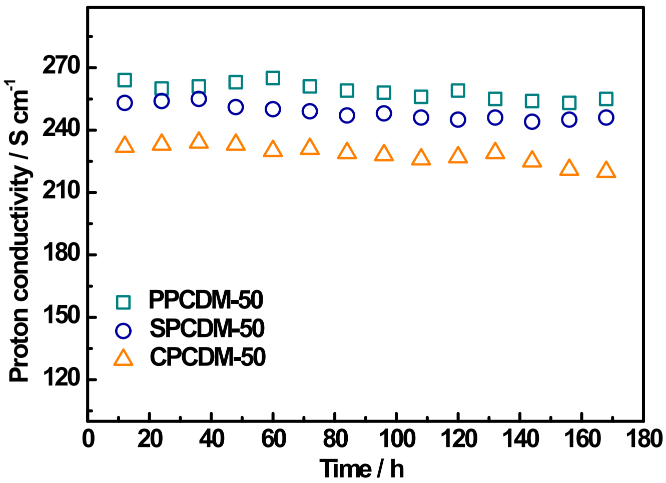

Fig. S14 Time dependent proton conductivity of PCDMs at 80 ^oC under 100% RH

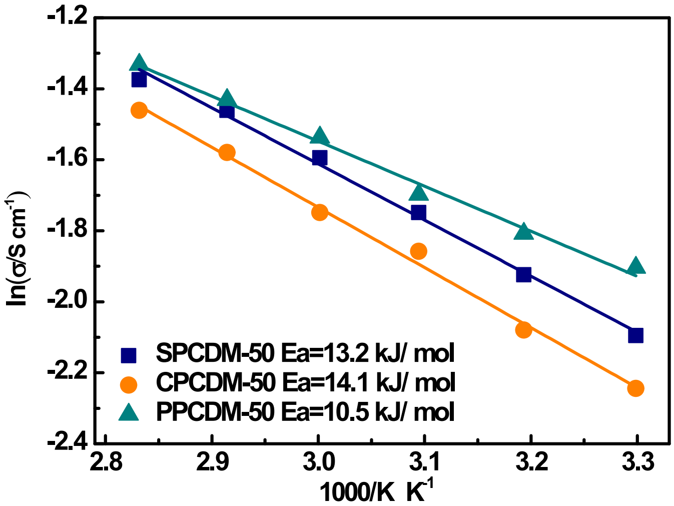

Fig. S15 Arrhenius plots of the proton conductivities of the membranes.

Table S3 H_2 permeability of the PCDM before and after water treatment

Sample	H_2 permeability / Barrier (without water treatment)	H_2 permeability / Barrier (water treatment)
SPCDM-50	22.33	9.67
CPCDM-50	59.97	22.2
PPCDM-50	35.43	13.11
SPCDM-55	1557.7	37.88

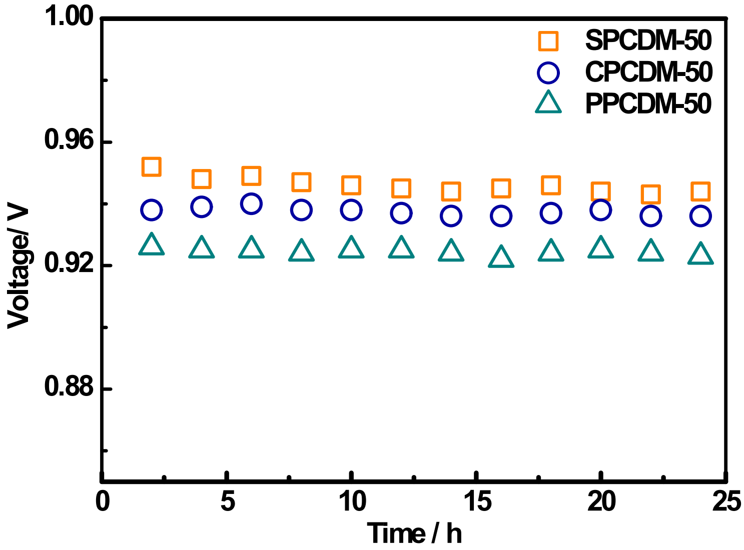

Fig. S16 Durability of the MEAs at 40 mA/cm^2.

References

1 G. C. Park and D. Kim, *Polymer*, 2021, **218**, 123506.

2 R. Sood, S. Giancola, A. Donnadio, M. Zatoń, N. Donzel, J. Rozière, D. J. Jones and S. Cavaliere, *Journal of Membrane Science*, 2021, **622**, 119037.

3 L. Qian, C. Yin, L. Liu, X. Zhang, J. Li, Z. Liu, H. Zhang, P. Fang and C. He, *Journal of Materials Science*, 2021, **56**, 6764–6779.

4 W. Chen, M. Chen, D. Zhen, T. Li, X. Wu, S. Tang, L. Wan, S. Zhang and G. He, *ACS Applied Materials and Interfaces*, 2020, **12**, 40740–40748.

5 M. Vinothkannan, S. Ramakrishnan, A. R. Kim, H. K. Lee and D. J. Yoo, *ACS Applied Materials and Interfaces*, 2020, **12**, 5704–5716.

6 A. Ghorai, A. K. Mandal and S. Banerjee, *Journal of Polymer Science*, 2020, **58**, 263–279.

7 D. Han, S. I. Hossain, B. Son, D. H. Lee and S. Shanmugam, *ACS Sustainable Chemistry and Engineering*, 2019, **7**, 16889–16899.

8 Y. Sui, Y. Du, H. Hu, J. Qian and X. Zhang, *Journal of Materials Chemistry A*, 2019, **7**, 19820–19830.

9 K. Oh, O. Kwon, B. Son, D. H. Lee and S. Shanmugam, *Journal of Membrane Science*, 2019, **583**, 103–109.

10 H. Zhang, R. J. Stanis, Y. Song, W. Hu, C. J. Cornelius, Q. Shi, B. Liu and M. D. Guiver, *Journal of Power Sources*, 2017, **368**, 30–37.

11 J. Miyake, R. Taki, T. Mochizuki, R. Shimizu, R. Akiyama, M. Uchida and K. Miyatake, *Science Advances*, , 2017, **3**.

12 H. Sun, B. Tang and P. Wu, *ACS Applied Materials and Interfaces*, 2017, **9**, 26077–26087.

13 P. Salarizadeh, M. Javanbakht and S. Pourmahdian, *RSC Advances*, 2017, **7**, 8303–8313.

14 J. Li, K. Fan, W. Cai, L. Ma, G. Xu, S. Xu, L. Ma and H. Cheng, *Journal of Power Sources*, 2016, **332**, 37–41.

15 L. Ahmadian-Alam, M. Kheirmand and H. Mahdavi, *Chemical Engineering Journal*, 2016, **284**, 1035–1048.

16 D. Liu, D. Tao, J. Ni, X. Xiang, L. Wang and J. Xi, *Journal of Materials Chemistry C*, 2016, **4**, 1326–1335.

17 J. Pang, X. Jin, Y. Wang, S. Feng, K. Shen and G. Wang, *Journal of Membrane Science*, 2015, **492**, 67–76.

18 Z. Wu, S. Zhang, H. Li, Y. Liang, Z. Qi, Y. Xu, Y. Tang and C. Gong, *Journal of Power Sources*, 2015, **290**, 42–52.

19 T. Ko, K. Kim, B. K. Jung, S. H. Cha, S. K. Kim and J. C. Lee, *Macromolecules*, 2015, **48**, 1104–1114.

20 T. Hamada, S. Hasegawa, H. Fukasawa, S. I. Sawada, H. Koshikawa, A. Miyashita and Y. Maekawa, *Journal of Materials Chemistry A*, 2015, **3**, 20983–20991.

21 M. Cui, Z. Zhang, T. Yuan, H. Yang, L. Wu, E. Bakangura and T. Xu, *Journal of Membrane Science*, 2014, **465**, 100–106.

22 H. Cheng, J. Xu, L. Ma, L. Xu, B. Liu, Z. Wang and H. Zhang, *Journal of Power Sources*, 2014, **260**, 307–316.

23 P. Wen, Z. Zhong, L. Li, F. Shen, X. D. Li and M. H. Lee, *Journal of Membrane Science*, 2014, **463**, 58–64.

24 G. He, L. Nie, X. Han, H. Dong, Y. Li, H. Wu, X. He, J. Hu and Z. Jiang, *Journal of Power Sources*, 2014, **259**, 203–212.

25 B. Yao, X. Yan, Y. Ding, Z. Lu, D. Dong, H. Ishida, M. Litt and L. Zhu, *Macromolecules*, 2014, **47**, 1039–1045.

26 D. M. Yu, S. Yoon, T. H. Kim, J. Y. Lee, J. Lee and Y. T. Hong, *Journal of Membrane Science*, 2013, **446**, 212–219.

27 S. Feng, K. Shen, Y. Wang, J. Pang and Z. Jiang, *Journal of Power Sources*, 2013, **224**, 42–49.

28 G. Wang, Y. Yao, G. Xiao and D. Yan, *Journal of Membrane Science*, 2013,

425–**426**, 200–207.
29 X. Zhang, Z. Hu, Y. Pu, S. Chen, J. Ling, H. Bi, S. Chen, L. Wang and K. I. Okamoto, *Journal of Power Sources*, 2012, **216**, 261–268.
30 K. Enomoto, S. Takahashi, R. Rohani and Y. Maekawa, *Journal of Membrane Science*, 2012, **415**–**416**, 36–41.
31 J. Wang, C. Zhao, L. Zhang, M. Li, J. Ni, S. Wang, W. Ma, Z. Liu and H. Na, *International Journal of Hydrogen Energy*, 2012, **37**, 12586–12596.
32 C. Wang, D. W. Shin, S. Y. Lee, N. R. Kang, Y. M. Lee and M. D. Guiver, *Journal of Membrane Science*, 2012, **405**–**406**, 68–78.
33 J. E. Kim and D. Kim, *Journal of Membrane Science*, 2012, **405**–**406**, 176–184.