Electronic Supplementary Information
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Enhancing the selectivity of Nafion membrane by incorporating a novel functional skeleton molecule to improve the performance of direct methanol fuel cell

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Electronic supplementary information for:

1. ^{1}H NMR spectrum of DMNF. (Fig. S1)
2. TGA curves of membranes. (Fig. S2)
3. Cross-sectional SEM imagines of different membranes. (Fig. S3)
4. Photographs of composite membranes. (Fig. S4)
5. Nyquist plots of single cells impedance spectra. (Fig. S5)
6. Liquid uptake and swelling ratio of membranes. (Table S1, Table S2, Table S3)
7. The polarization and power density curves of membranes at 25 °C. (Fig. S6)

1. ^{1}H NMR spectrum of DMNF.

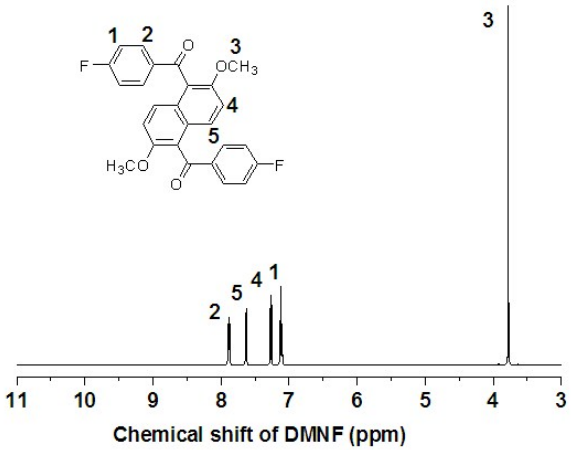


Figure S1. ^{1}H NMR spectrum of DMNF.

DMNF was prepared by Friedel-Crafts acylation, catalyzed by anhydrous ferric chloride. Pure DMNF is white acicular crystal.

2. TGA curves of recast Nafion and SDF-PAEK@Nafion-x membranes.

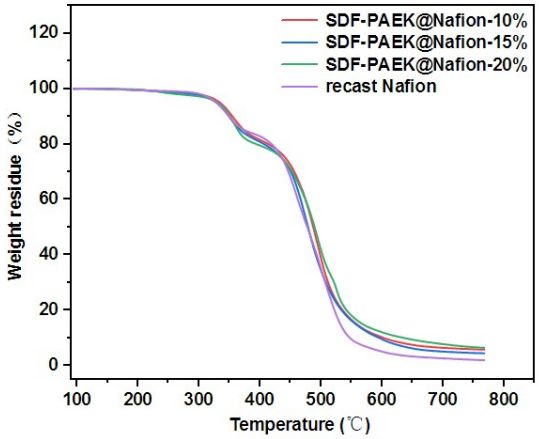
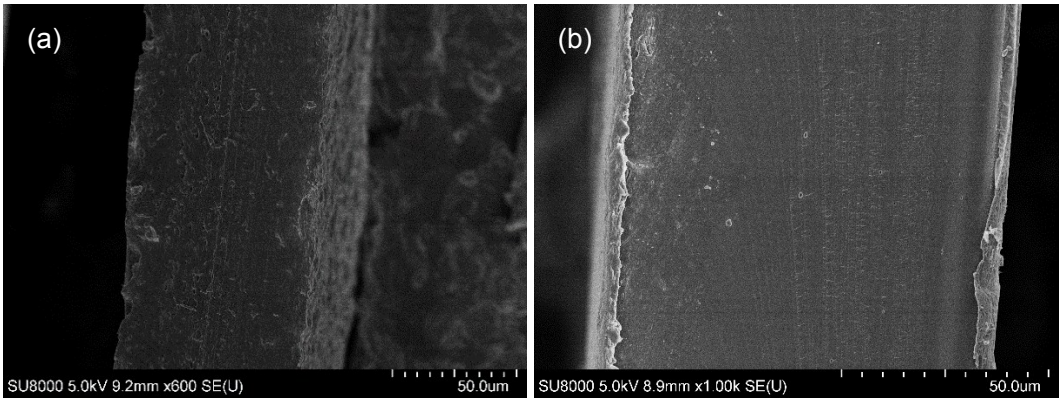


Figure S2. TGA curves of recast Nafion membrane and composite membranes.

To evaluate the effect of incorporating SDF-PAEK to Nafion matrix on the thermal stabilities, samples were heated from 100 to 800 °C at a speed of 10 °C raised per minute under nitrogen atmosphere. As clearly shown in Fig. S2, there were two two-step degradation patterns of membranes. From 300 to 400 °C, the first degradation step stood for the decomposition of side-chain sulfonic acid groups. The second step, from 400 to 600 °C, assigned to the decomposition of the main polymer chain. In summary, after the incorporation of skeleton molecule, the thermodynamic stability of membranes was slightly improved. All the membranes can display excellent thermal stability as the temperature is reduced below 200 °C and meet the thermal stabilities requirement for medium DMFCs applications.

3. Cross-sectional SEM imagines of different membranes.



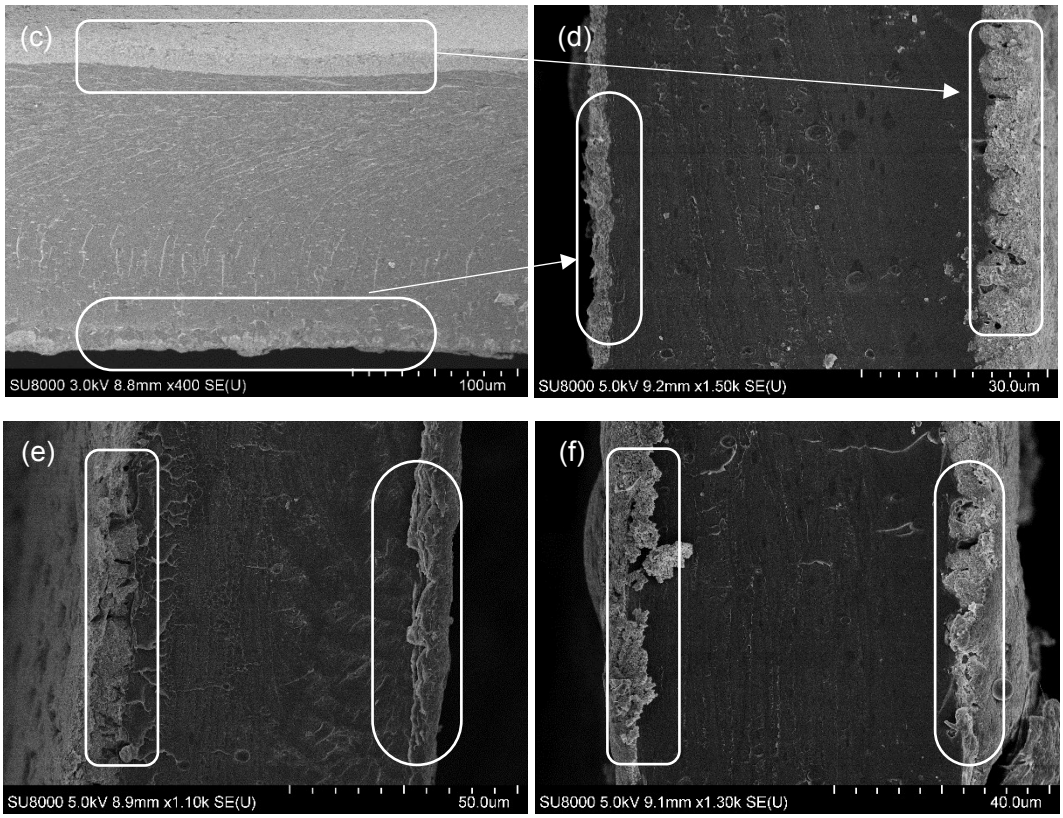


Figure S3. Cross-sectional SEM imagines of (a), (b) SDF-PAEK@Nafion-15%; (c) SDF-PAEK@Nafion-15% with catalyst; (d) SDF-PAEK@Nafion-15% with catalyst after single-cell test, (e) SDF-PAEK@Nafion-10% with catalyst after single-cell test, (f) SDF-PAEK@Nafion-20% with catalyst after single-cell test.

The cross-sectional SEM images are given in Fig. S3, and we can find that all the composite membranes were uniform. The pores and texture of membranes were generated by the nitrogen overflowed in the process of making SEM test samples in liquid nitrogen. And after single-cell test, the membranes bonded with catalyst layers firmly, without appeared separation. Catalysts in Fig. S3(c) were smoother than that in Fig. S3(d), which was due to the fuel scoured in the process of single-cell test. Fig. S3(e) and Fig. S3(f), show the cross-sectional SEM imagines of SDF-PAEK@Nafion-10% and SDF-PAEK@Nafion-20% with catalyst after single-cell test.

4. Photographs of composite membranes.

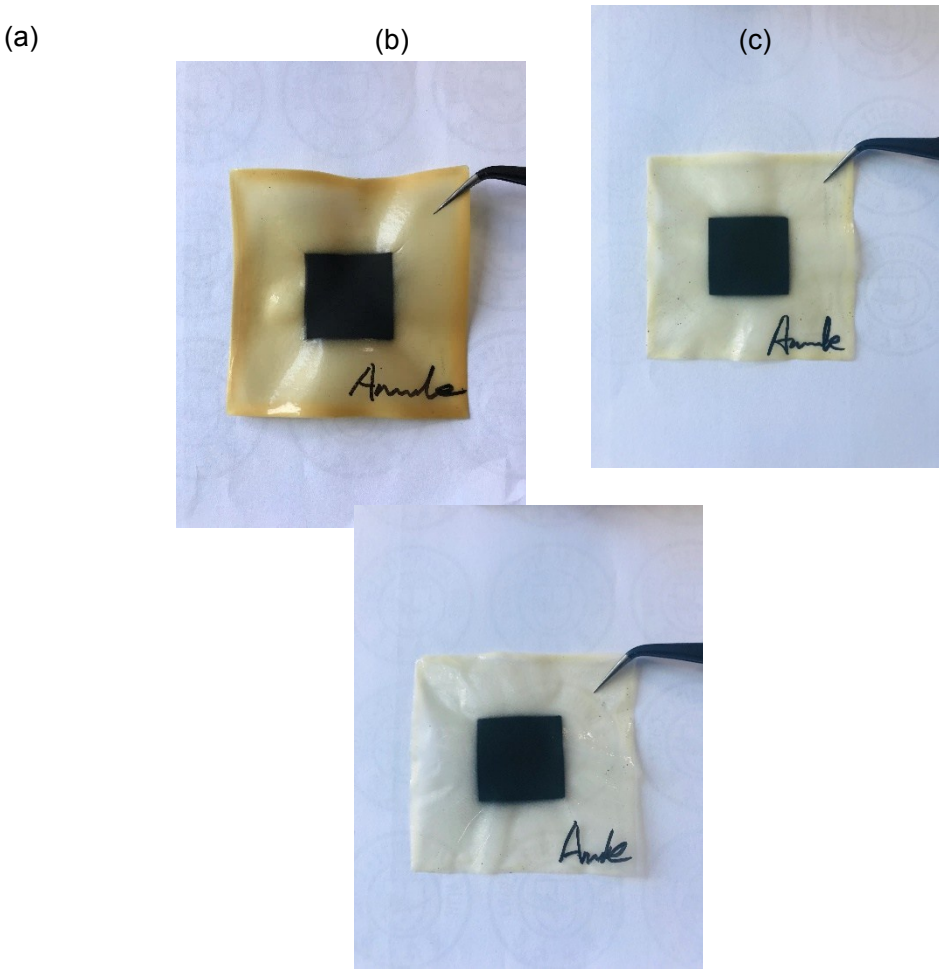


Figure S4. Photographs of composite membranes: SDF-PAEK@Nafion-20% (a); SDF-PAEK@Nafion-15% (b); SDF-PAEK@Nafion-10% (c).

Composite membranes are transparent in Fig. S4, which indicates the skeleton molecules exhibits the good consistency with the matrix consisting of the similar molecule sizes, structures, and physicochemical properties. During the process of spraying catalyst and single cell test, the membranes need to be heated, so the colour of them are brown, especially SDF-PAEK@Nafion-20%.

5. Nyquist plots of SDF-PAEK@Nafion-15% single cells impedance spectra.

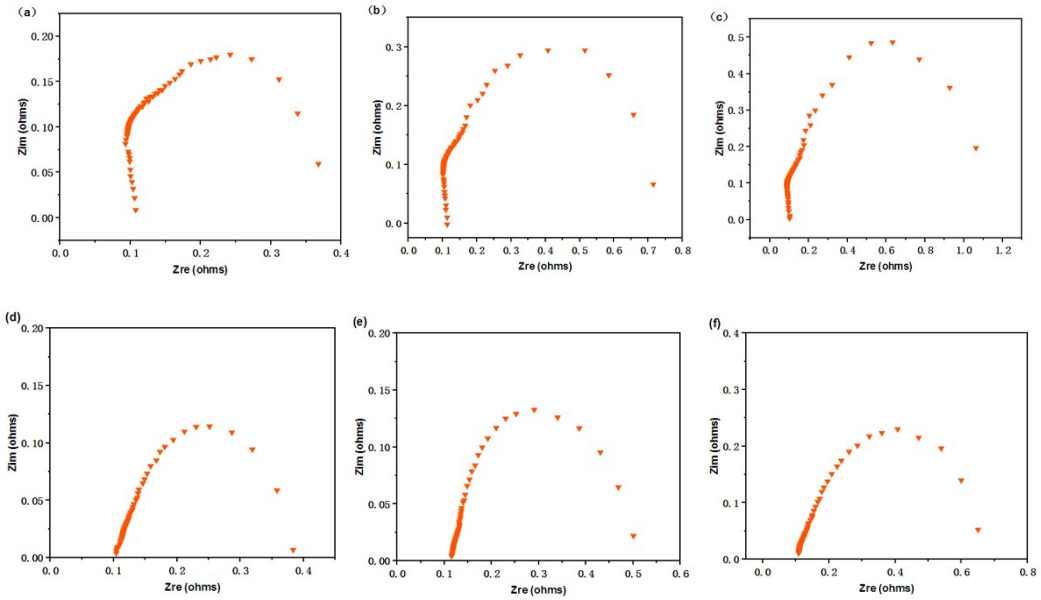


Figure S5. Nyquist plots of SDF-PAEK@Nafion-15% single cells impedance spectra. 1M: (a), (b), and (c); 2M: (d), (e), and (f).

6. Liquid uptake and swelling ratio of membranes.

Table S1 Liquid uptake and swelling ratio of membranes in 0 M methanol aqueous solution (deionized water).

Samples	Liquid uptake (%)		Swelling ratio in thickness (%)		Swelling ratio in area (%)	
	25 °C	80 °C	25 °C	80 °C	25 °C	80 °C
SDF-PAEK@Nafion-10%	24.81±1.91	59.23±2.11	12.02±1.55	23.41±1.55	15.92±1.37	52.11±1.57
SDF-PAEK@Nafion-15%	26.54±1.73	61.87±1.93	13.51±1.65	25.04±1.91	18.81±1.39	54.59±1.58
SDF-PAEK@Nafion-20%	30.71±1.61	64.54±2.22	16.32±1.67	23.81±2.54	21.73±1.40	62.99±1.63
Recast Nafion	36.53±1.43	57.13±1.87	8.28±0.91	23.57±0.91	30.72±1.69	58.76±1.86

Table S2 Liquid uptake and swelling ratio of membranes in 1 M methanol aqueous solution.

Samples	Liquid uptake (%)		Swelling ratio in thickness (%)		Swelling ratio in area (%)	
	25 °C	80 °C	25 °C	80 °C	25 °C	80 °C
SDF-PAEK@Nafion-10%	30.51±1.83	63.93±2.12	21.87±1.53	26.25±0.88	18.97±2.08	55.08±2.38
SDF-PAEK@Nafion-15%	32.67±1.43	65.72±1.65	26.84±1.64	30.87±1.64	21.55±2.11	60.18±2.42

SDF-PAEK@Nafion-20%	36.81±1.34	68.68±1.73	28.02±1.56	31.21±0.91	27.66±2.16	61.65±2.43
Recast Nafion	55.43±1.33	82.78±1.83	27.74±1.58	30.32±0.91	42.83±2.28	86.05±2.61

Table S3 Liquid uptake and swelling ratio of membranes in 2 M methanol aqueous solution.

Samples	Liquid uptake (%)		Swelling ratio in thickness (%)		Swelling ratio in area (%)	
	25 °C	80 °C	25 °C	80 °C	25 °C	80 °C
SDF-PAEK@Nafion-10%	37.67±1.08	73.98±1.39	34.93±2.56	39.72±1.67	23.02±1.64	81.05±1.99
SDF-PAEK@Nafion-15%	40.33±2.31	76.05±2.02	30.33±1.63	42.21±1.63	26.18±1.66	88.77±2.03
SDF-PAEK@Nafion-20%	45.44±2.22	79.47±1.97	30.62±2.33	40.62±1.53	33.71±1.47	91.01±1.76
Recast Nafion	67.67±1.23	100.91±1.41	33.95±1.74	41.35±1.74	52.28±1.82	129.72±2.24

7. The polarization and power density curves of membranes at 25 °C.

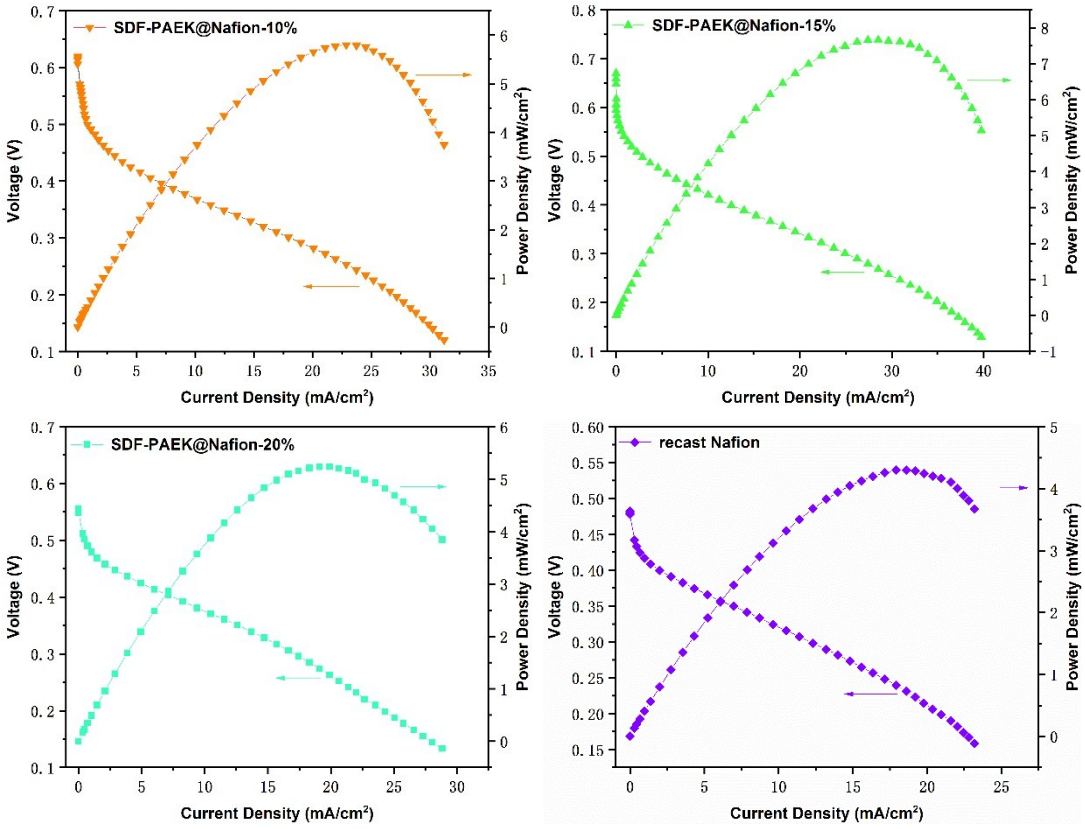


Figure S6. The polarization and power density curves of membranes at 2 M methanol solution at 25 °C.