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Supporting Information

Proton exchange membranes with perfluorobenzenesulfonic acid groups for vanadium redox flow battery applications

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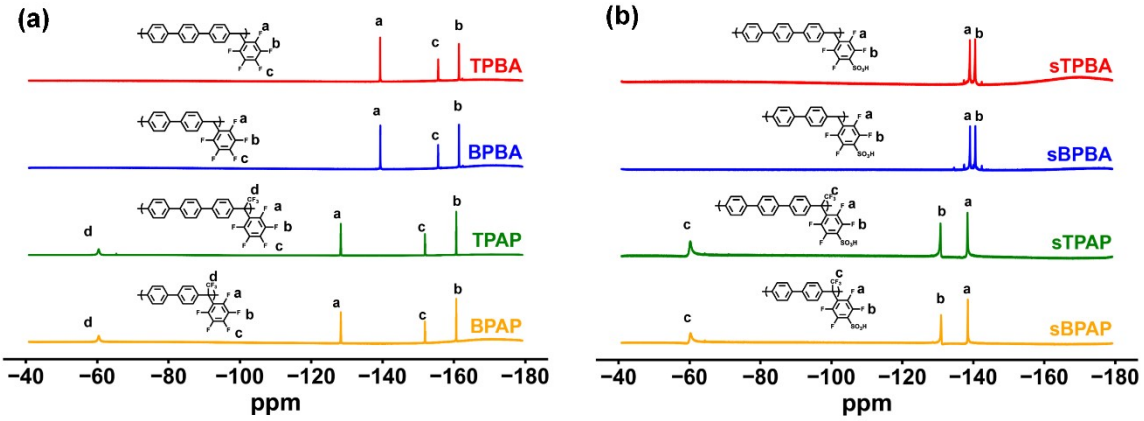

Figure S1. ^{19}F NMR spectra of the precursor (left) and sulfonated (right) polymers recorded using $CDCl_3$ and DMSO-d_6 solutions, respectively.

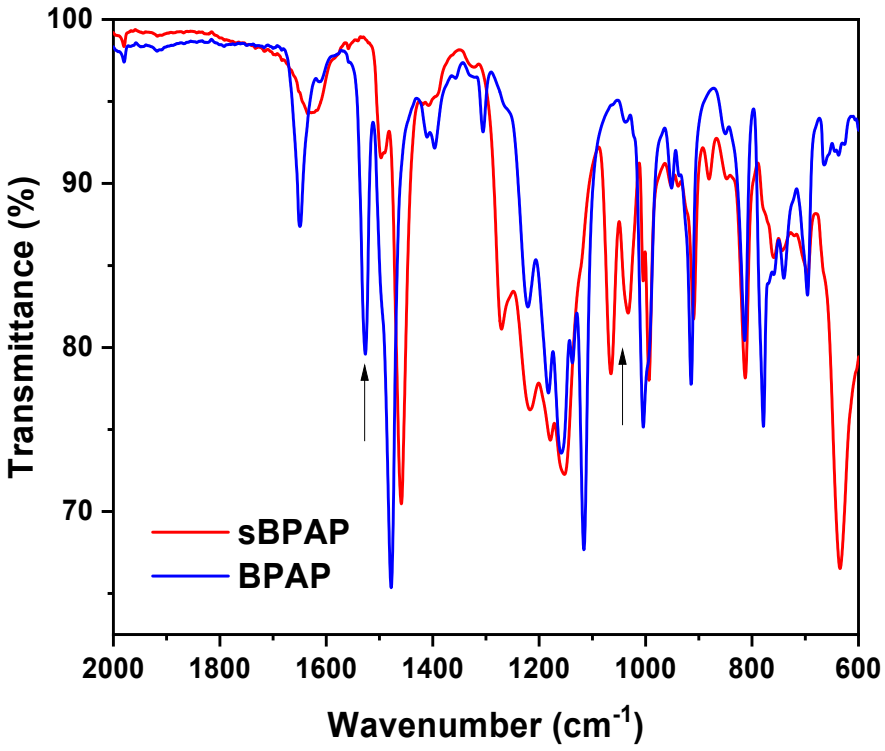

Figure S2. FTIR spectra of the sBPAP and BPAP polymers.

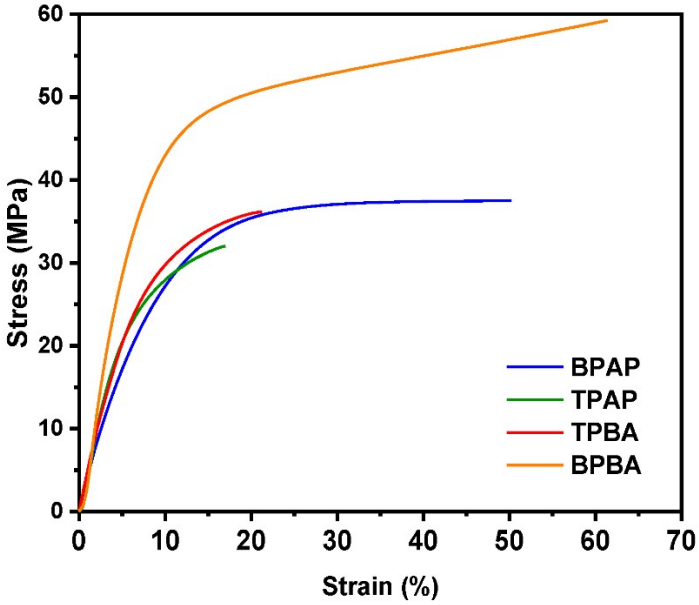

Figure S3. Stress-strain data of the TPBA, BPBA, TPAP and BPAP membranes in the dry state at 31 °C under a 0.3 N min^{-1} ramping force test.

Table S1 Data of the precursor polymers.

Sample	M_n (kg/mol)	M_w/M_n	T_g (°C)	$T_{d,onset}$ (°C)
TPBA	39	3.1	/	505
BPBA	86	6.8[a]	298	522
TPAP	46	1.8	/	465
BPAP	51	2.8	307	482

a. High dispersity arising from a bimodal distribution.

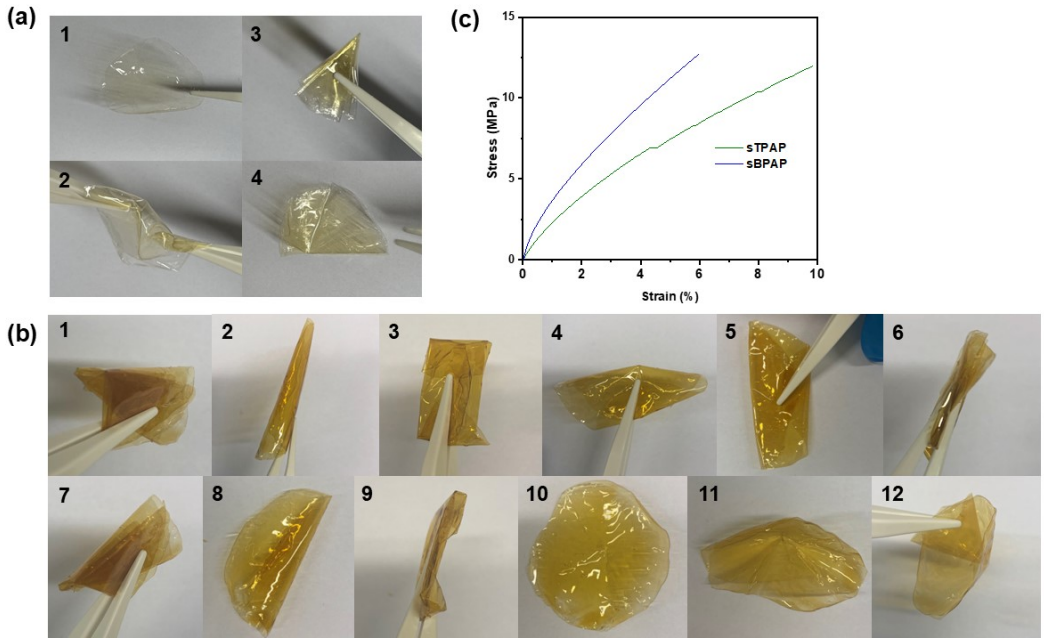

Figure S4. (a) Photographs of twisting(1,2) and folding (3,4) sBPAP membrane, (b) sequential photographs of a freestanding sTPAP membrane folded along different axes (longitudinal, transverse, diagonal, and radial), together with gently bent and unfolded configurations, illustrating its macroscopic flexibility, (c) stress-strain data of sTPAP and sBPAP recorded in the hydrated state at 31 °C under a 0.3 N min^{-1} ramping force test.

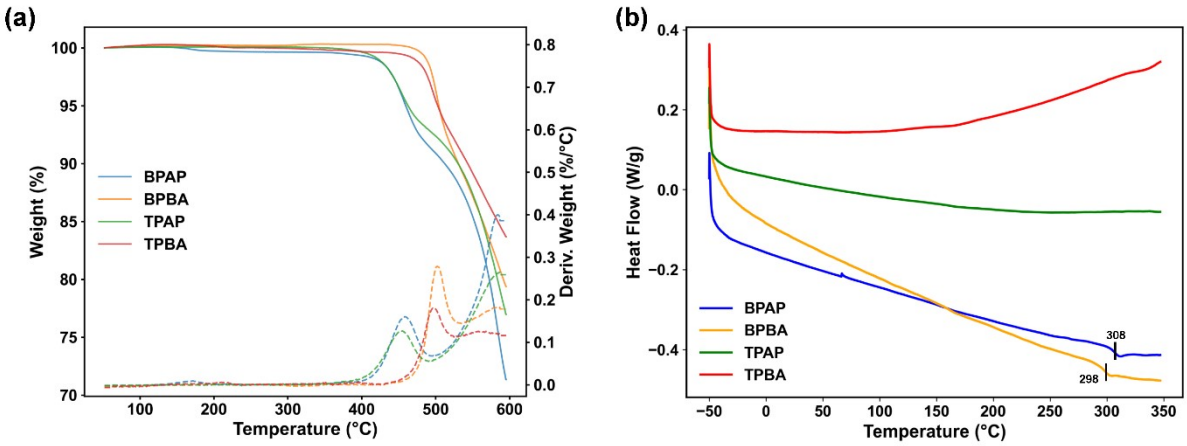

Figure S5. (a)TGA traces (solid lines) of TPBA, BPBA, TPAP and BPAP and the corresponding temperature derivatives (dashed lines), and (b) DSC second heating traces of the TPBA, BPBA, TPAP and BPAP polymers.

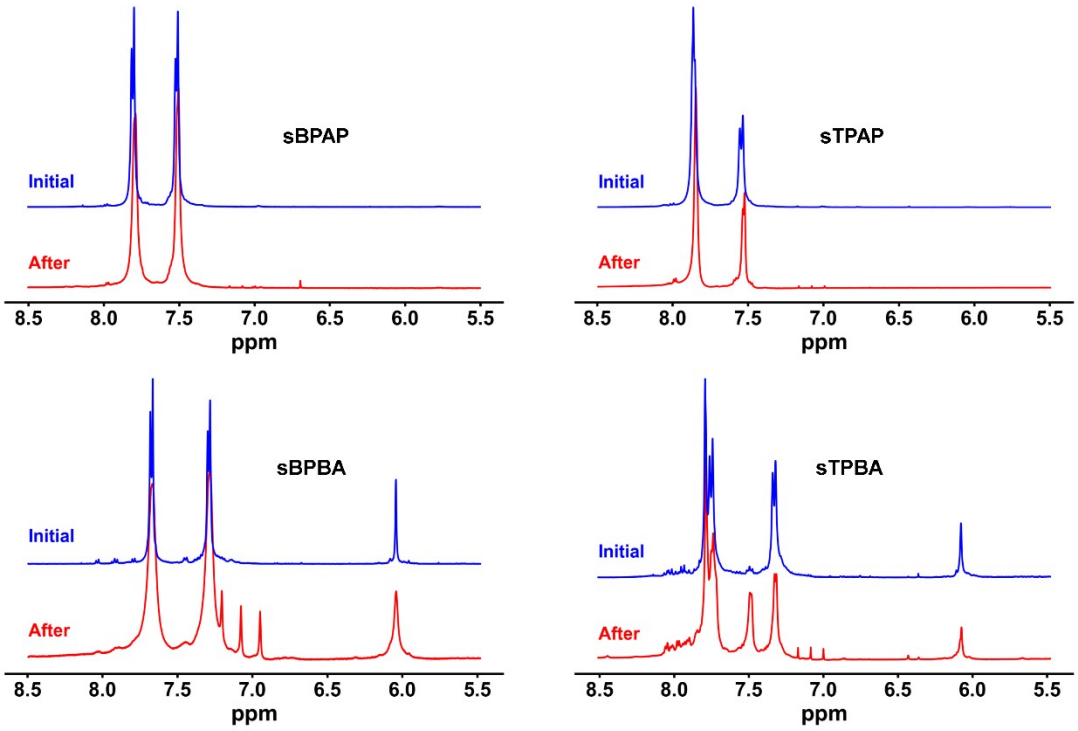

Figure S6. ^{1}H NMR spectra of sTPBA, sBPBA, sTPAP and sBPAP membrane polymers before and after treatment in an aqueous 1.5 M VO_2^+/3 M H_2SO_4 solution for 80 h.

Table S2. Summarizing data of the poly(arylene perfluorophenylsulfonic acid) PEMs.

Sample	Aromatic monomer	Backbone substitution	M_w/M_n	Proton conductivity (mS cm^{-1}) [a]	Ion selectivity (S min cm^{-3})	Oxidative stability (h)[b]	VRFB performance (cycle number) [d]
sTPBA	Terphenyl	–H	3.1	100	8.07×10^4	12	<50
sBPBA	Biphenyl	–H	6.8 [c]	152	4.72×10^4	12	100
sTPAP	Terphenyl	–CF_3	1.8	80	4.53×10^5	80	250
sBPAP	Biphenyl	–CF_3	2.8	97	2.03×10^4	60	400

[a]Intrinsic proton conductivity measured in water.
[b]Time required to reach 90% membrane mass loss.
[c]High dispersity arising from a bimodal distribution.
[d]Cycling performance evaluated at 100 mA cm^{-2}.