Supporting information

Quinone-amine polymers prepared by simple precipitation polymerization and used as cathodes for aqueous zinc-ion batteries and electrochromic materials

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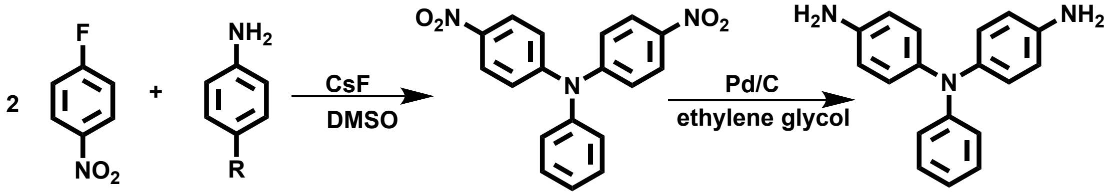
Experimental section

Synthesis of monomer：The process used to create the monomer is depicted in Figure 1. First, p-fluoronitrobenzene(10 mol, 1.41g) and aniline(5 mol, 0.47 g) were reacted with dimethylsulfoxide solution(100 mL) and cesium fluoride(10 mol, 1.02 g) under catalysis for 48 hours at 140°C. After the reaction was finished, the mixture was poured into iced water while being stirred and filtered to produce 4,4'-dinitrotriphenylamine(yield: 87%, 1.46 g). Next, 4,4'-dinitrotriphenylamine(4.35 mol, 1.46 g) was reduced in a palladium (1mol, 0.11 g)and hydrazine hydrate(10 mL) in ethylene glycol solution(100 mL) at 120°C for eight hours. Finally, 4,4'-diamino triphenylamine was obtained by filtering the palladium carbon and adding it to iced water while stirring and filtering(yield: 57.7%, 2.51 mol, 0.69 g). To obtain a white crude product, the crude product was first refined using silica gel column chromatography (petroleum ether: dichloromethane = 1:1) and then further refined by recrystallization. (ether: dichloromethane = 2:1) and subsequently refined further via recrystallization, yielding a white solid in 57% of the sample, ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.13 – 6.94 (m, 2H), 6.80 (d, J = 8.2 Hz, 4H), 6.69 – 6.43 (m, 7H), 4.96 (s, 4H).



Scheme 1. Synthetic reaction pathway of TPA.

Synthesis of polymer：PQAH and PQACl were synthesized using a straightforward chemical polymerization process. In an ethanol solvent, BQ and TCB, respectively, were reacted with 4,4'-diamino triphenylamine at 80 °C for 8 hours. The mixture finished product was added to ice-cold methanol, mixed, filtered, and then extracted using methanol by Soxhlet extraction.

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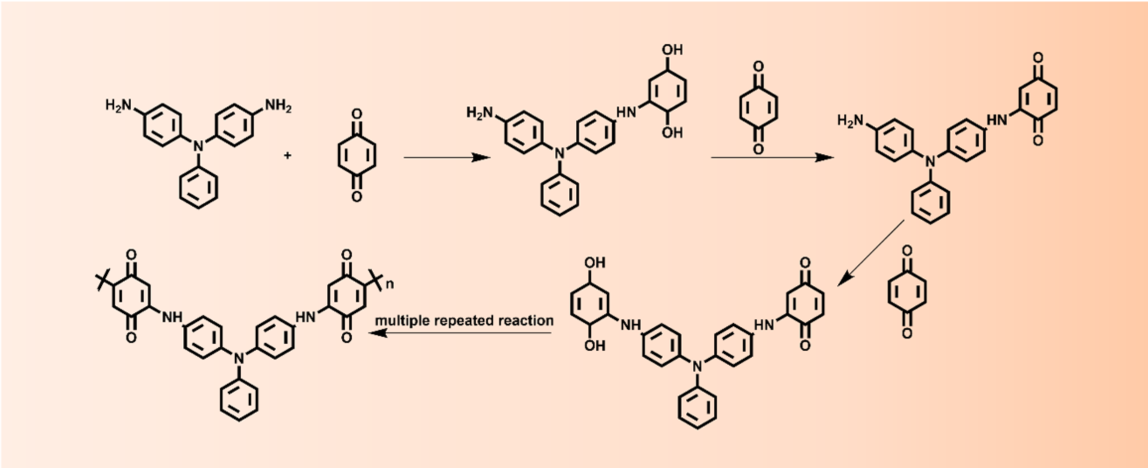

Figure S1. The detailed reaction flow chart of PQAH.

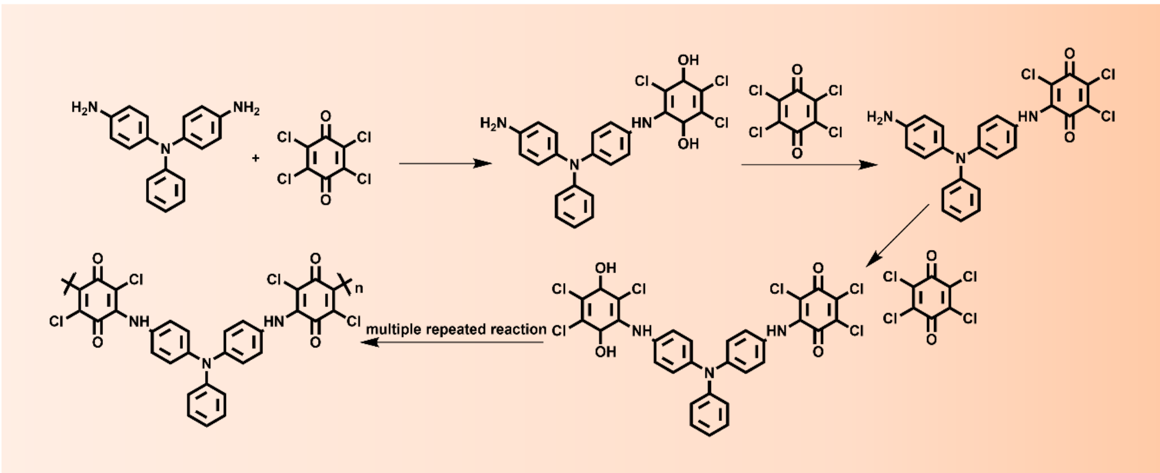

Figure S2. The detailed reaction flow chart of PQAH.

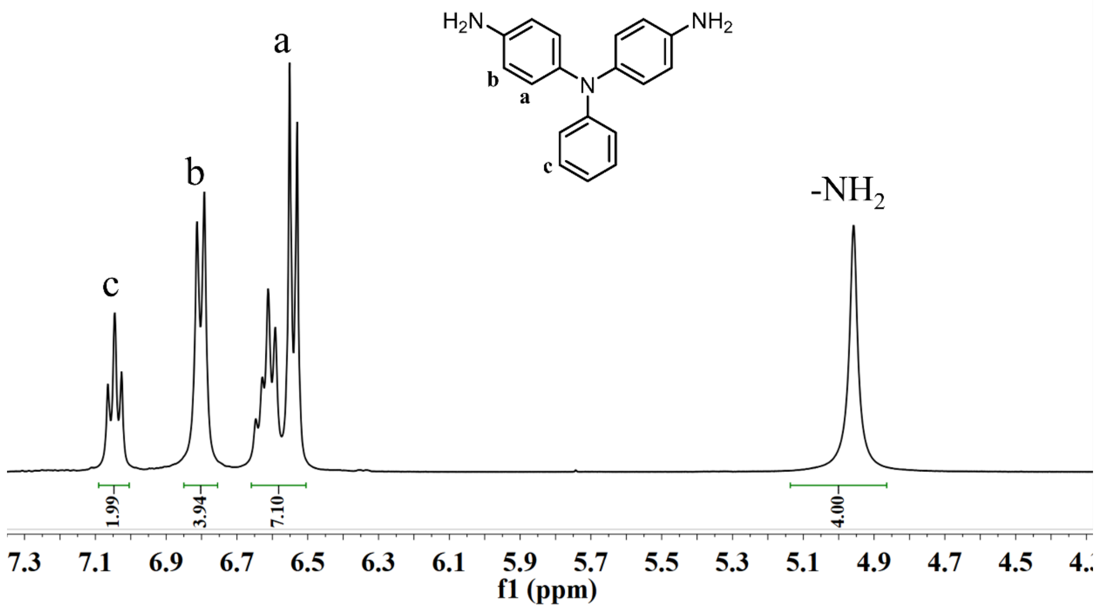

Figure S3. [1]H NMR spectrum of 4,4'-diamino triphenylamine.

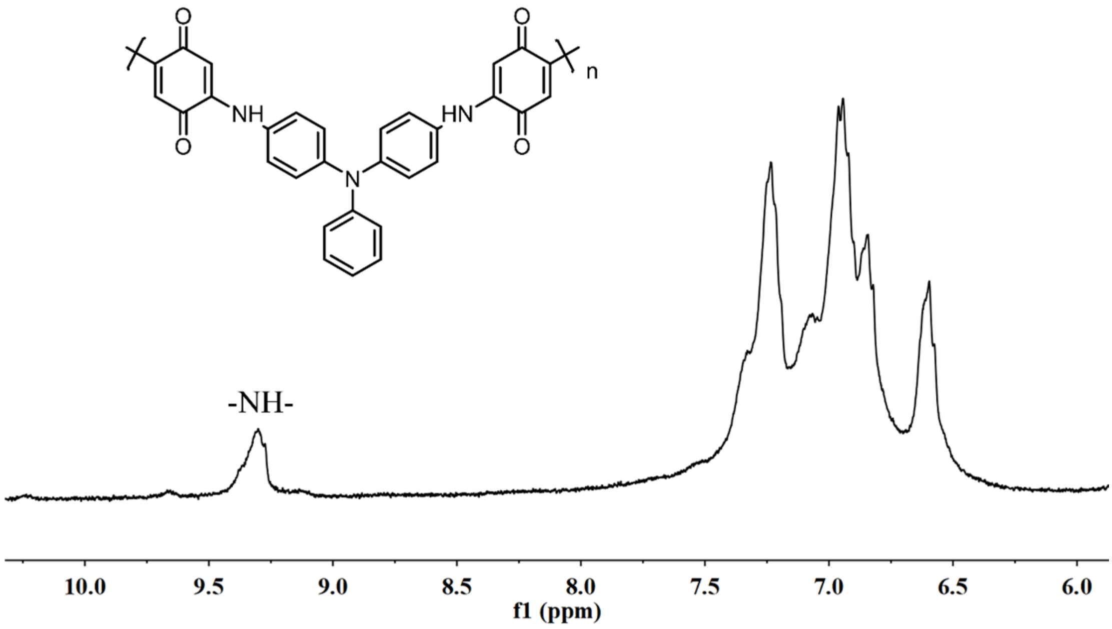

Figure S4. [1]H NMR spectrum of PQAH.

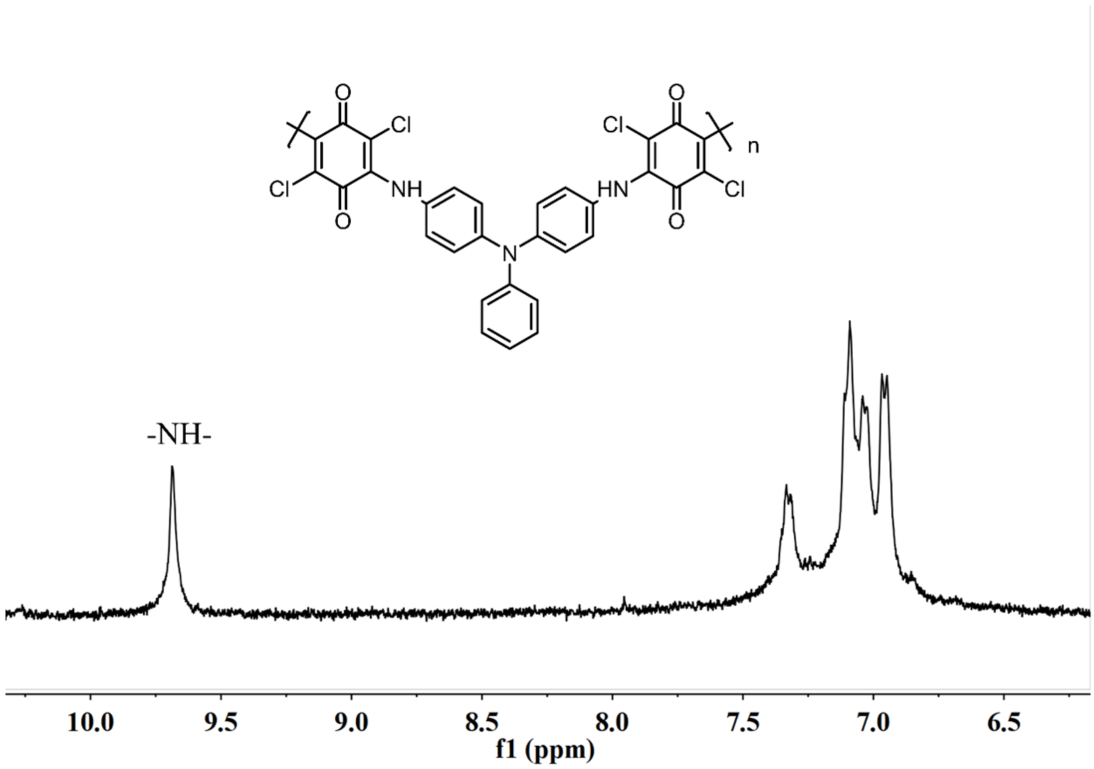

Figure S5. ^{1}H NMR spectrum of PQACl.

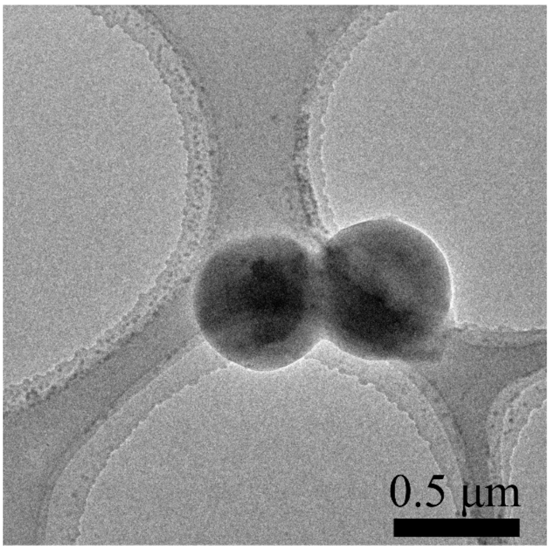

Figure S6. TEM image of PQAH.

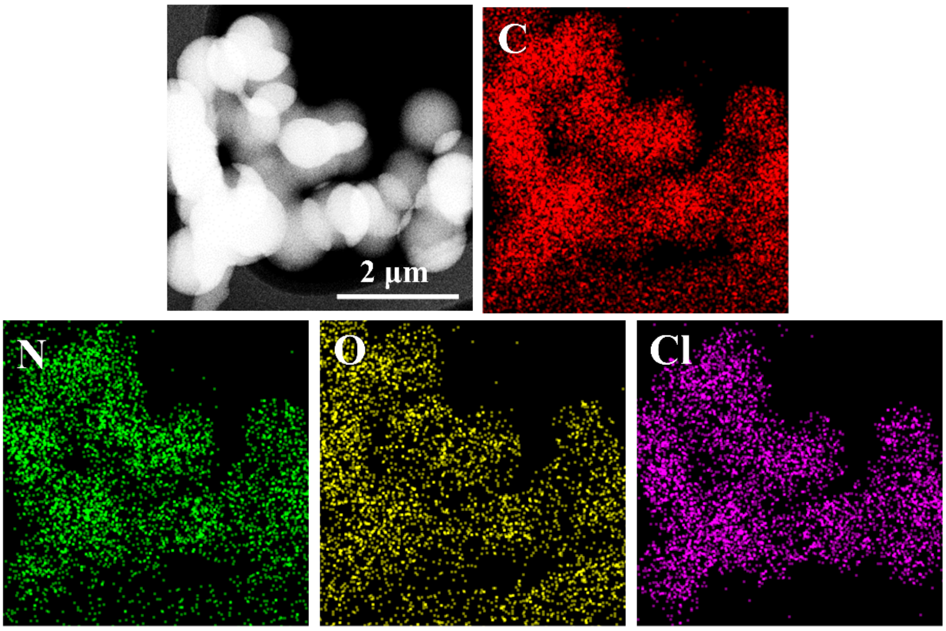

Figure S7. TEM-mapping images of PQACl.

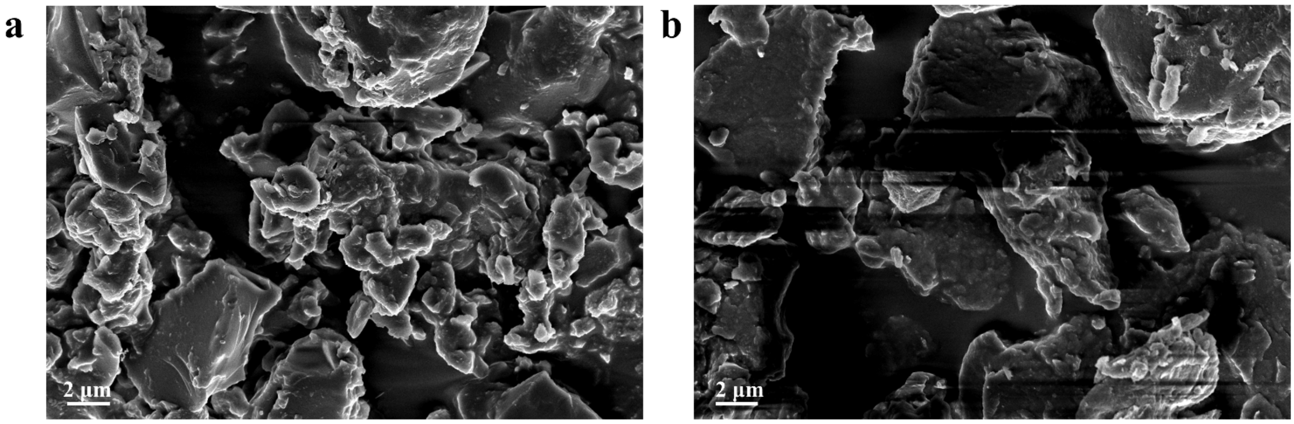

Fig S8. SEM images of PQAH (a) and PQACl (b)

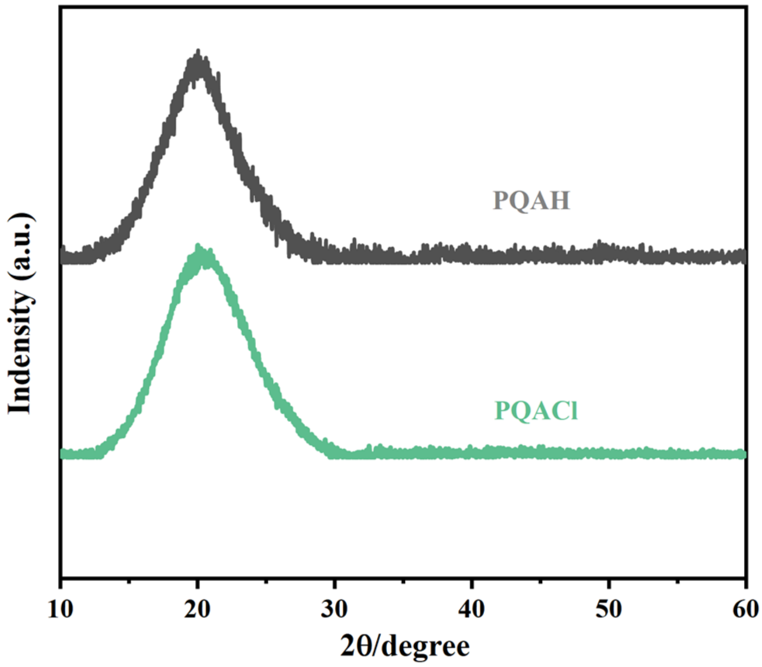

Fig S9. The characterizations of PQAH and PQACl XRD.

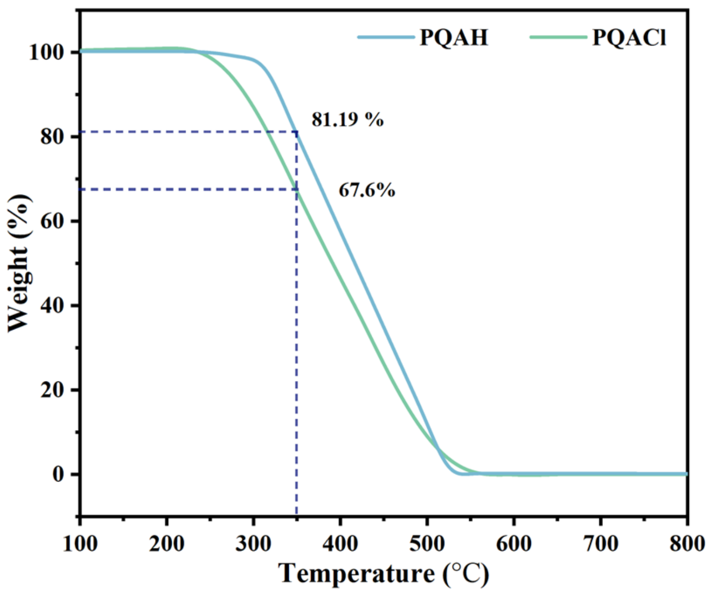

Fig S10. Thermogravimetric curve of PQAH and PQACl

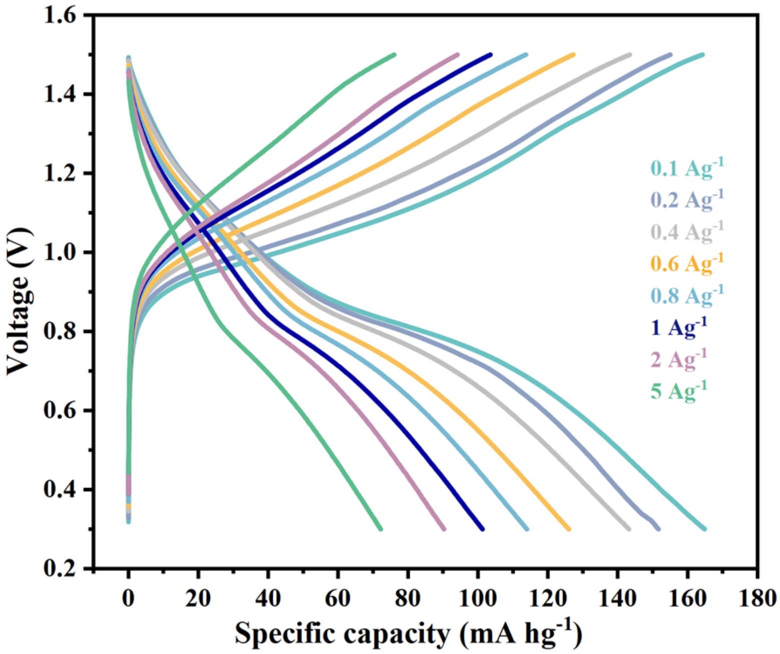

Fig S11. Charge-discharge curves of PQACl at different current densities.

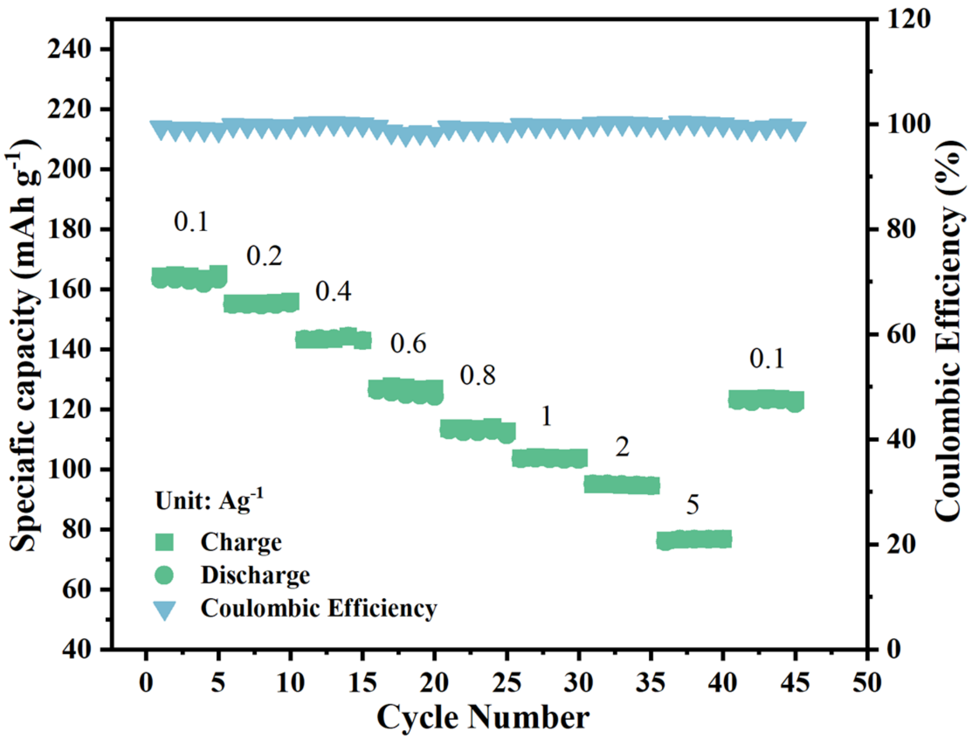

Fig S12. PQACl with varying current densities rate performance.

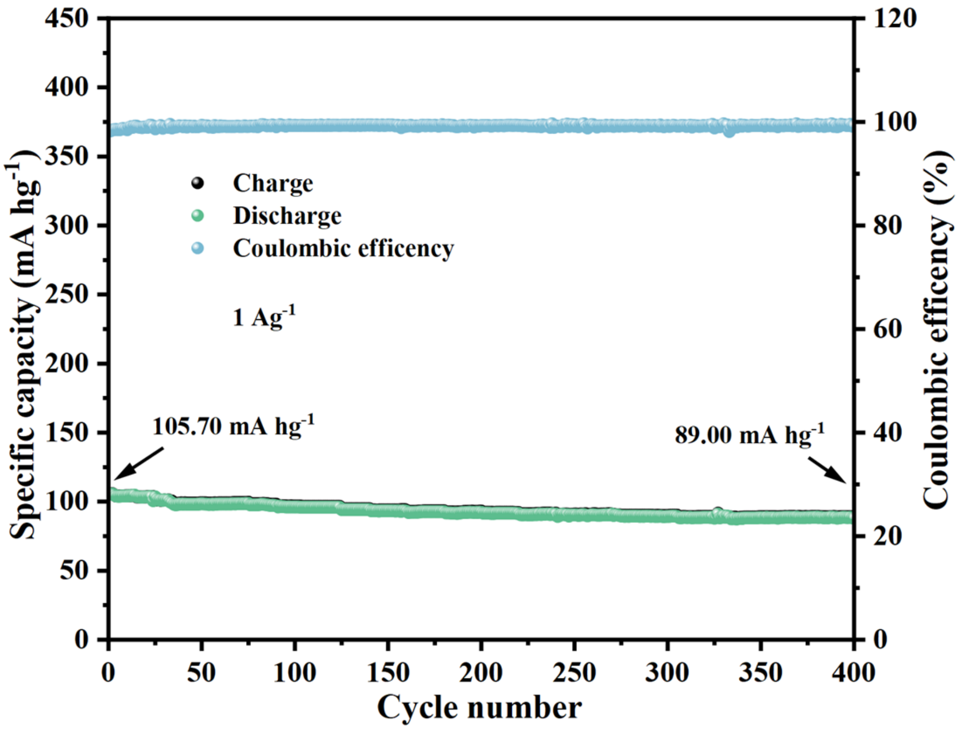

Fig S13. Cycle stability of PQACl running at 1 A g^{-1}.

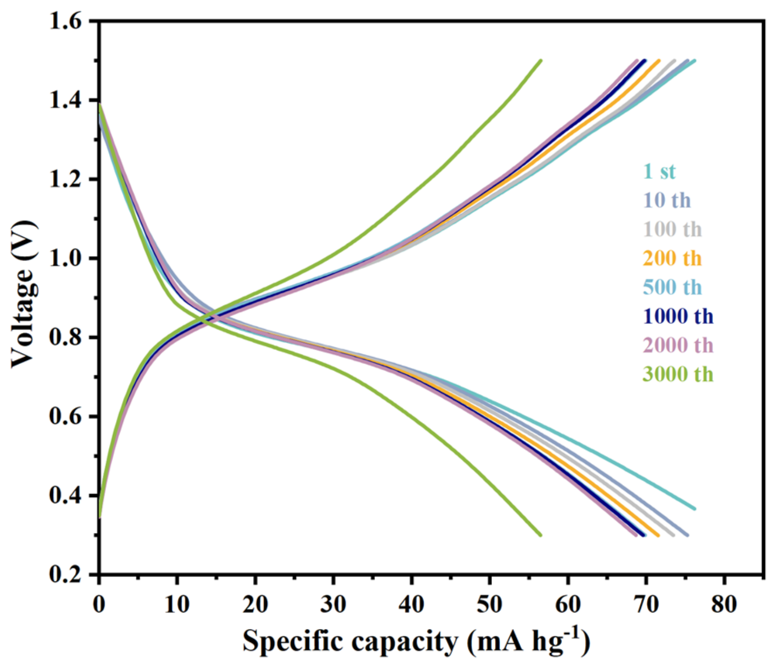

Fig S14. Discharge–charge curves of PQACl half-cell running at 5 A g^{-1}

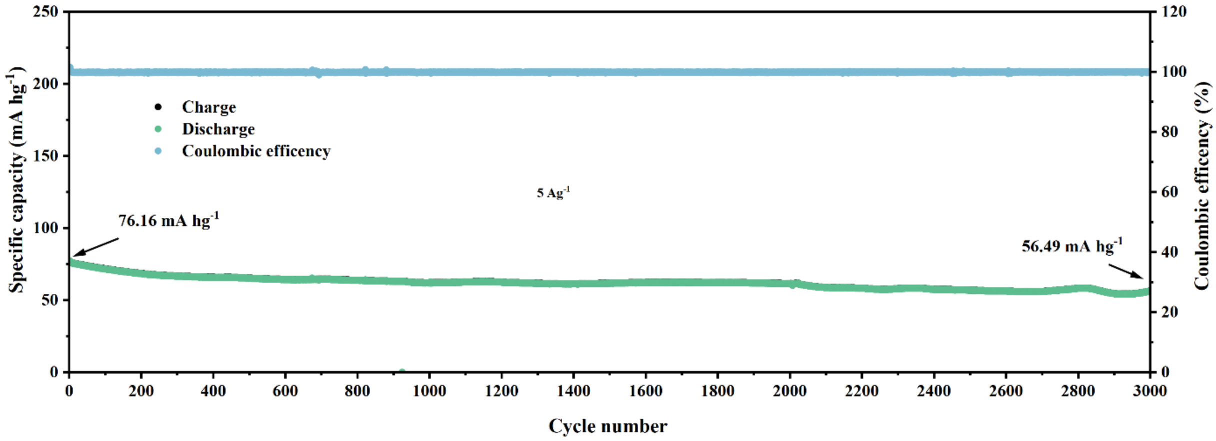

Fig S15. Cycling long life of PQACl half-cell running at 5 A g^{-1}

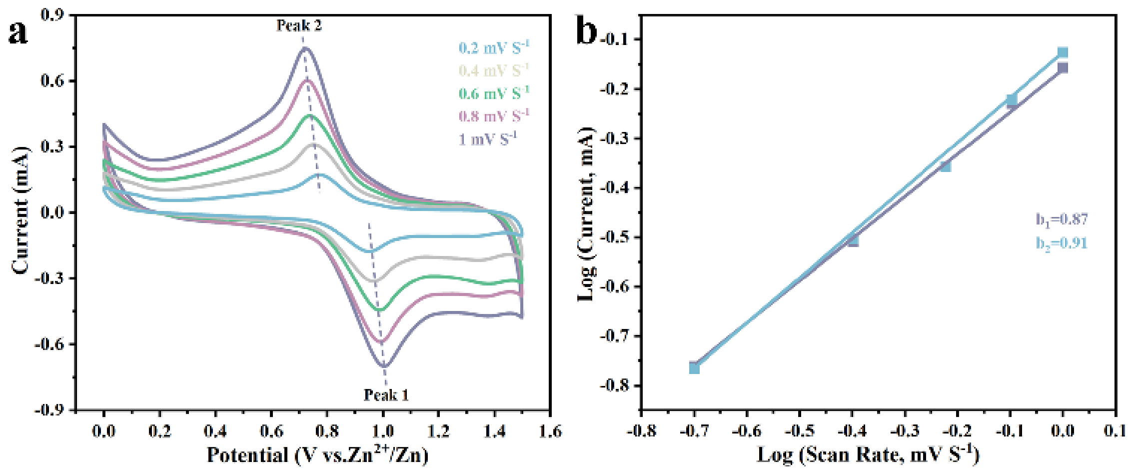

Fig S16. PQACl half cell (a) CV curves at the scan rates ranging from 0.2 to 1.0 mV s^{-1}. (b) b values calculated via log(i) and log(v) linear fit plots.

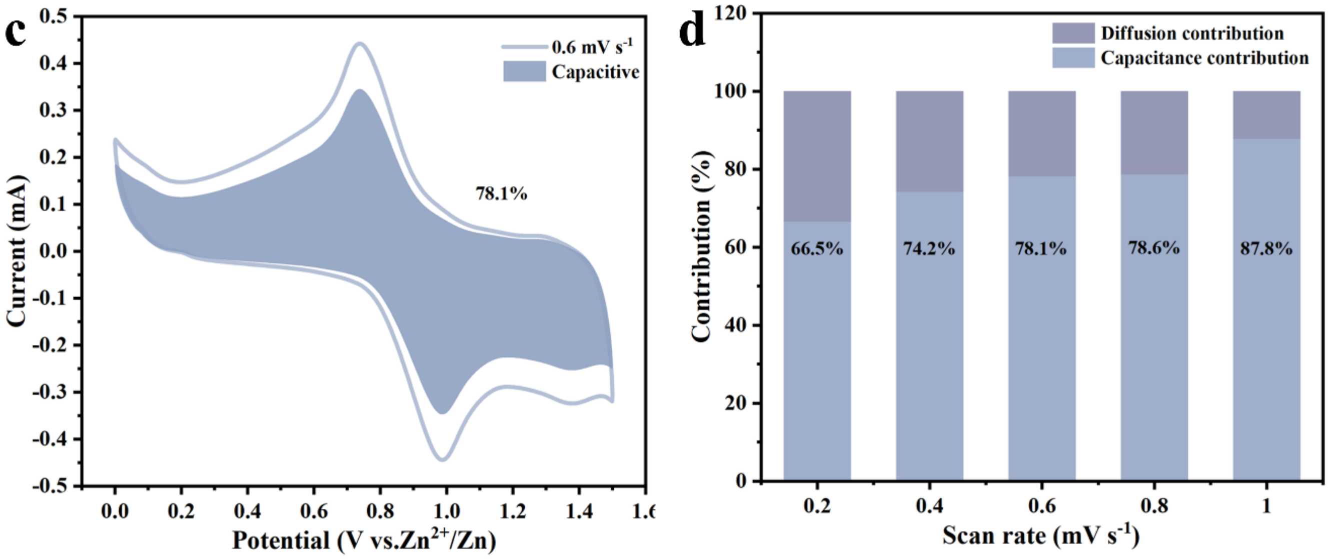

Fig S17. PQACl half cell (a) contribution of capacitive and diffusion control running under 0.6 mV s $^{-1}$ and (b) under the scan rates ranging from 0.2 to 1.0 mV s $^{-1}$.

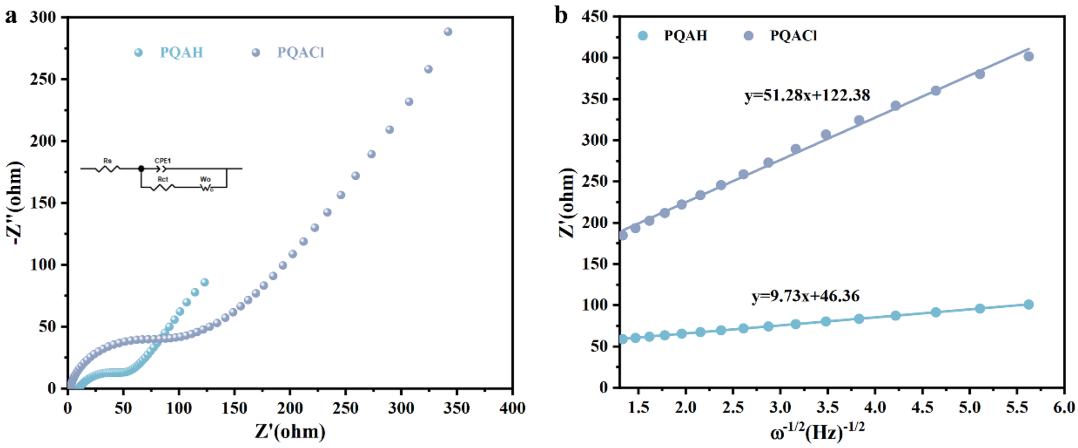

Fig S18. (a) Impedance spectra collected at open-circuit voltage of PQAH and PQACl; (b) The relation between Z_{re} and $\omega^{-1/2}$ at low frequency of PQAH and PQACl.

Table S1. Electrochemical properties of the PQAH and PQACl.

Polymers Code	λ_{onset}^{Abs} [a] (nm)	E_{onset} [b]	$E_{1/2}$ [c] (v)	$E_{electro}$ [d] (eV)			$E_{quantum}$ [e] (eV)		
				E_{HOMO}	E_{LUMO}	E_g	E_{HOMO}	E_{LUMO}	E_g
PQAH	568	0.66	1.03	-5.09	-2.91	2.18	-5.19	-3.40	1.79
PQACl	582	0.75	0.89	-5.18	-3.13	2.05	-5.20	-3.84	1.36

[a] λ_{onset} of polymers in NMP solution (1×10^{-5} mol·L^{-1}).

[b] Onset potential (vs Ag/AgCl) of the polymers was calculated from CV curve in 0.1 M LiTFSI in CH_3CN.

[c] $E_{1/2}$ of polymers is the average potential of the redox couple peaks.

[d] $E_{LUMO} = E_{HOMO} + E_g$; $E_g = 1240/\lambda_{onset}$ (nm).

[e] Quantum theoretical calculation of the polymers.

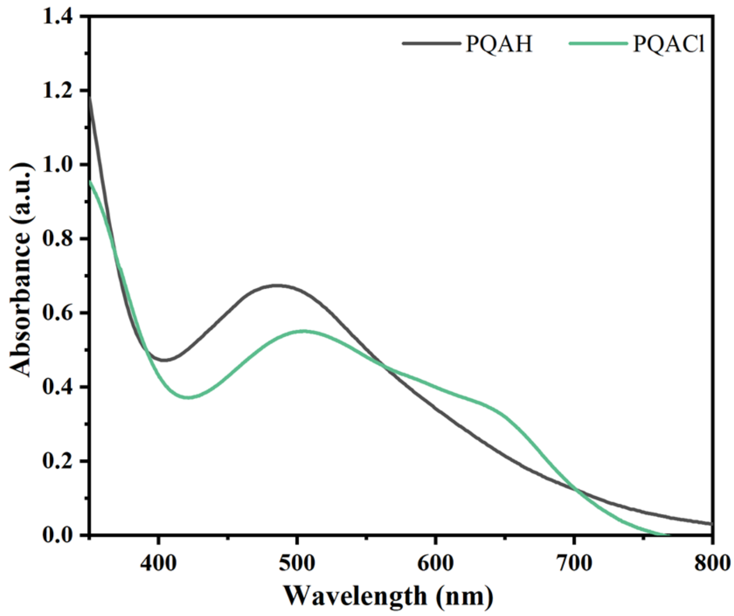

Fig S19. UV-Vis absorption spectra of PQAH and PQACl in DMF solution

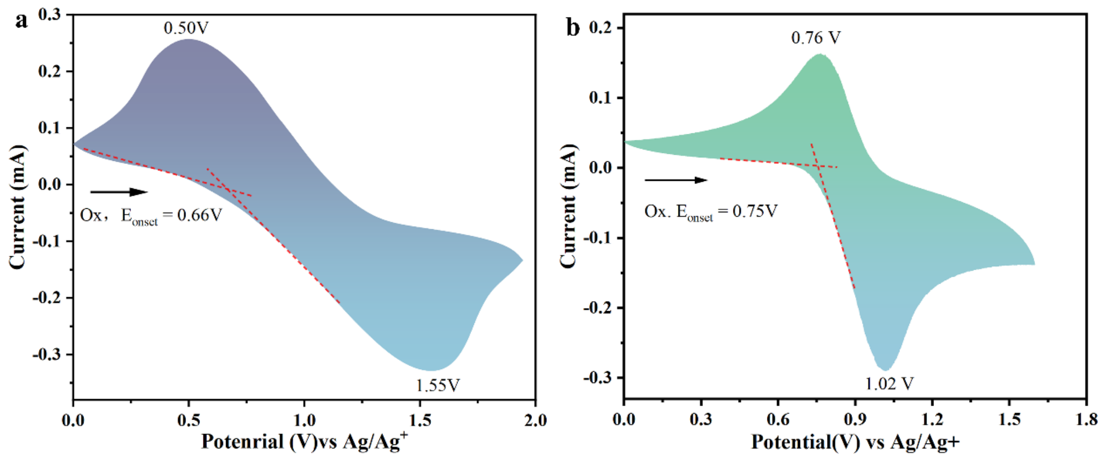

Fig S20. The CV curves of PQAH (a), PQACl (b) on the ITO-coated glass substrate in 0.1 mol L^{-1} LiTFSI/ACN solution at a scan rate of 50 mV s^{-1}.

Table S2. EC properties of the polymers.

Polymers Code	λ^a (nm)	ΔT (%)	Response time [b]		ΔOD^c	Q_d [d] ($mC\cdot cm^{-1}$)	CE[e] ($mC\cdot cm^{-1}$)
			t_c (s)	t_b (s)			
P1	418	38.2	1.5	1.6	0.319	1.62	233.9
P2	440	44.2	0.5	1.1	0.336	1.94	173.2

[a] Maximum absorption wavelength of polymers films.

[b] The time for the polymers film to reach 90% of the full-absorption change.

[c] Optical density (ΔOD) = $\log(T_{blenched}/T_{colored})$, where T_b and T_c are the transmittances in the bleached state and colored state, respectively.

[d] Q_d is ejected charge.

[e] $CE = \Delta OD/Q_d$.

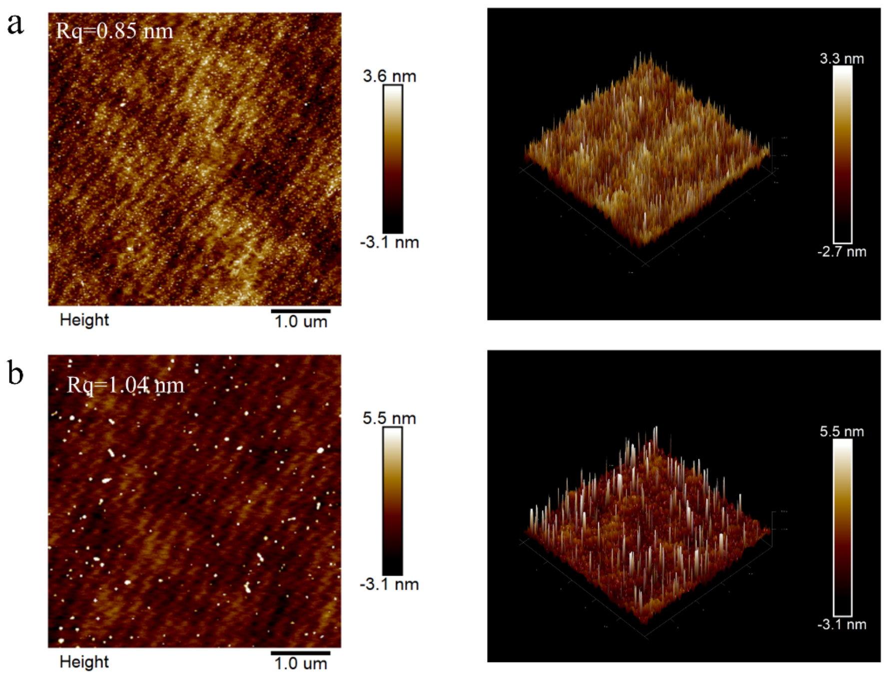

Fig S21. AFM images of PQAH(a) and PQACl(b) polymer films.

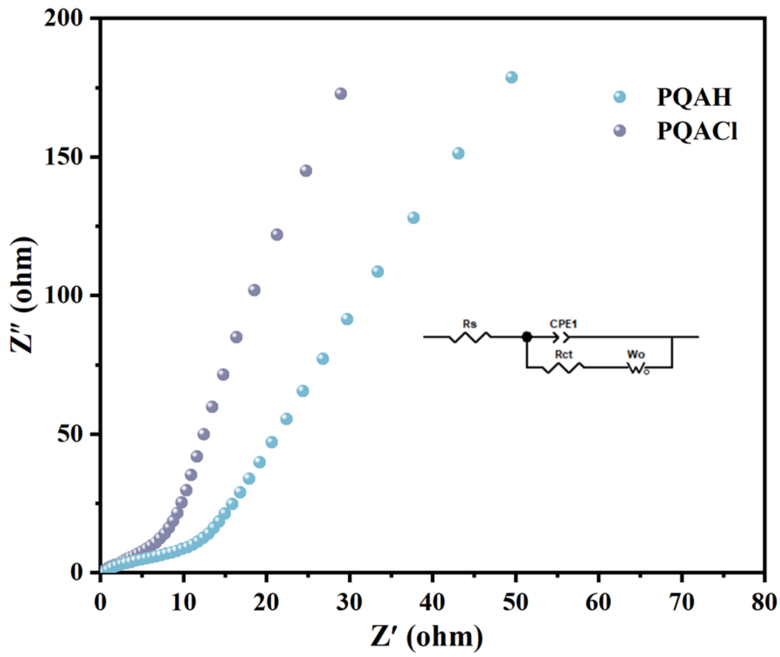

Fig S22. Impedance spectra of PQAH and PQACl films collected at open circuit voltage.