Supplementary Information (SI) for Inorganic Chemistry Frontiers.

Design of D−A type Alternating Copolymer as Electrodes for Efficient Symmetric Sodium-Dual-ion Batteries

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Experimental Section

Synthesis of PDQZ

The synthetic route was referenced to the pervious reported methods with some modifications. Buchwald-Hartwig coupling reaction was carried out in an oven-dried 200 mL Schleck flask equipped with a magnetic stirring bar under Ar. 5,10-dihydrophenazine (150 mg, 1.0 eqv.), 1,10-Phenanthroline-5,6-Dione,3,8-Dibromo (302.90 mg 1.0 eqv.), Ruphos (15.4 mg, 0.04eqv.), Ruphos Pd G2 (25.63 mg, 0.04 eqv.) and *t*-BuONa (395.55 mg, 5.0 eqv.) were added into the aforementioned Schleck flask under Ar atmosphere. Thereafter, 60 mL xylenes were added into the flask through a syringe. The mixture was heated to reflux in an oil bath at 140 ℃ for 4 days. During this process, the solution became black solid appeared. The precipitate was separated by suction filtration, and washed with dichloromethane, warm deionized water, methanol, acetone, respectively. Dry the residue in a vacuum oven at 90 ℃ to obtain the dark brown solid product PDQZ (173mg, yield: 38.2%).

Ex-situ characterization

The electrode sheets at different charging and discharging state were taken out from the batteries in a glove box filled with Ar (O_2 and H_2O content < 0.1 ppm), and then washed with DME to remove the residual electrolyte. Next, the electrodes were dried in vacuum for 2 hours, at 60 ℃. After that, the electrodes were marked and stored in Ar-filled glove box. The samples were exposed in air when ex-situ FTIR test conducted, and they were tested using the ATR pattern. For ex-situ XPS tests, the samples were prepared in a stream of Ar-flow, and then the ex-situ XPS measurement was carried

out.

Electrochemical measurements

Device measurements were conducted in CR 2032-coin cell casings, which were assembled in an argon filled glove box with oxygen level below 0.1 ppm. The anode was sodium metal and the PDQZ was fabricated from a slurry of 70 wt.% active material, 20 wt.% Ketjin black and 10 wt.% PVDF as the binder. The loading mass of PDQZ on Al foil were above 1.2-1.5 mg cm^{-2}. These slurries were blade cast onto aluminum current collector and dried at 60 ℃ for 8 hours before battery assembling. The cells were assembled with an electrolyte of 1 M $NaPF_6$ in DME (120 μl), a separator of Whatman glass fiber. For the symmetric-cell: PDQZ as the active material to assembly cathodes and anodes, then directly assembled into a full cell for testing. The galvanostatic cycling test was carried on a CT-4008T instrument (Shen Zhen NEWARE electronic Co.) at 25 ℃. CVs were tested on a CHI instrument electrochemical work-station (CS 310m) at a scan rate of 2.0 mV s^{-1} between 0.5 and 4.0 V (vs. Na^+ /Na). The EIS test was measured by a CHI instrument electrochemical workstation in the frequency range of 0.01–10^5 Hz at the amplitude of 5 mV. The above tests were conducted at room temperature. The galvanostatic cycling test at 60℃ was conducted on MHW200 instrument (Shenzhen NEWARE Electronics Co., Ltd.), and the galvanostatic cycling test at -10℃ was conducted on AP-HX-80C3 instrument (Guangdong Aipei Testing Equipment Co., Ltd).

Computational details

Chemical structures and the optimized molecular orbital distribution of PDQ, DPZ, and PDQZ dimers were fully optimized using B3LYP at the 6-31G (d, p) levels. The energies of all of the obtained geometries are ensured to be the lowest because the optimized structures do not exhibit imaginary frequency. The calculations of ground-state geometry and energy on DFT were carried out by the Gaussian 09 program.

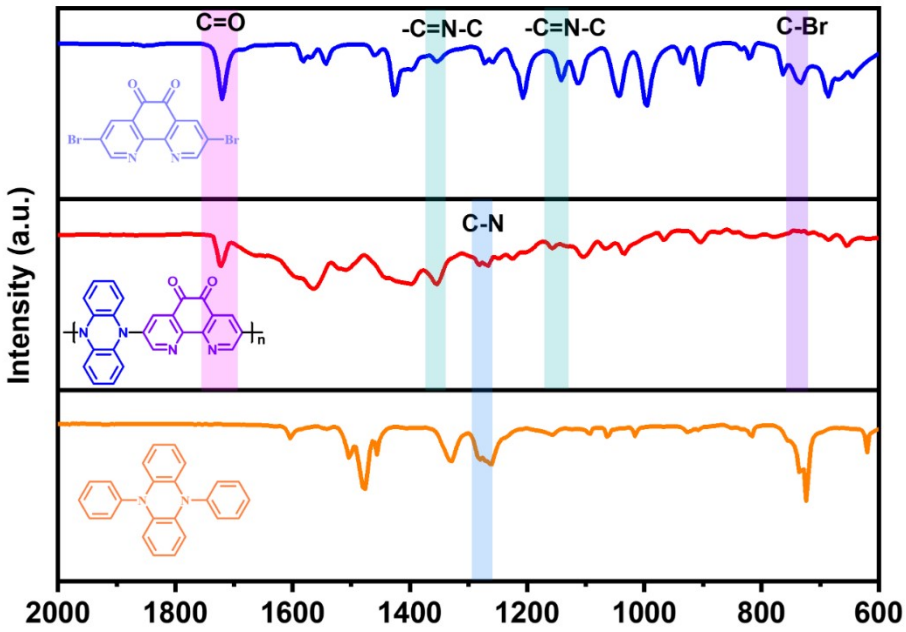

Figure S1. FT-IR of the BPQ, PDQZ and DPZ.

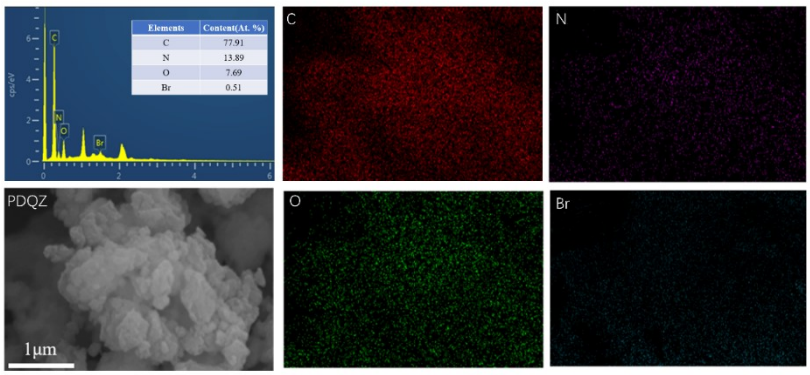

Figure S2. EDS analysis of PDQZ.

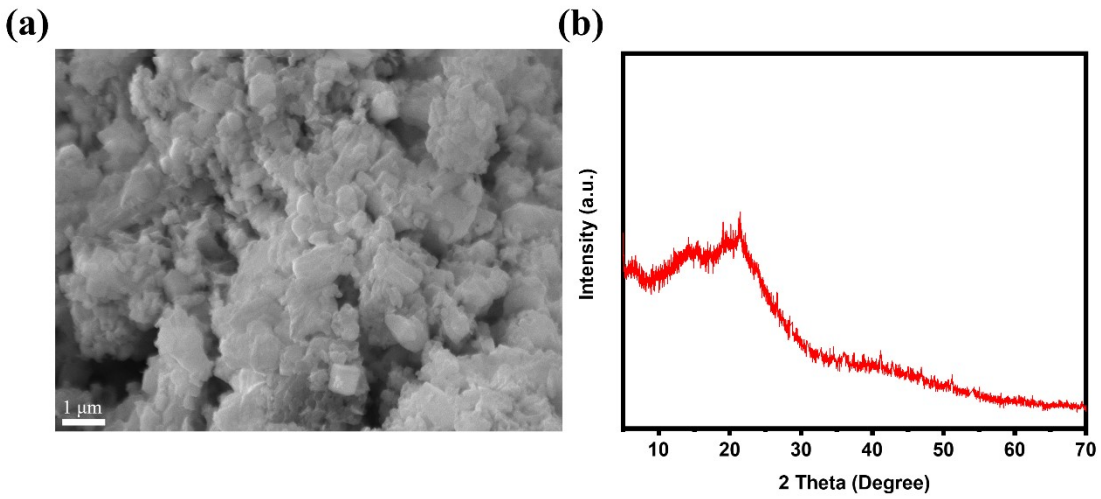

Figure S3. Characterized PDQZ: (a) FE-SEM images; (b) XRD

Figure S4. DPZ, PDQ, and PDQZ were soaked in electrolyte solvent for 7 days.

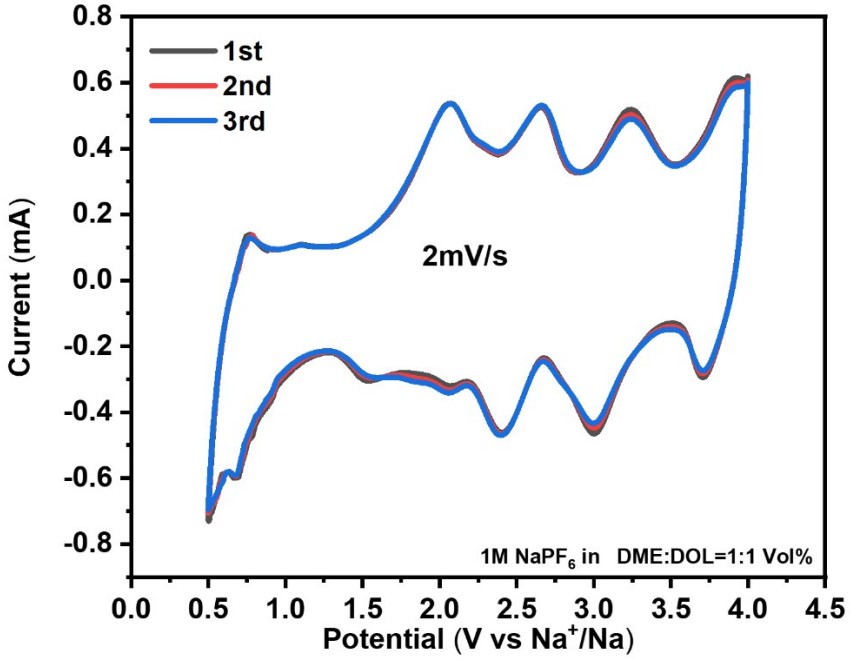

Figure S5. CV of PDQZ in 1M NaPF6 in DME: DOL=1:1 Vol% electrolyte.

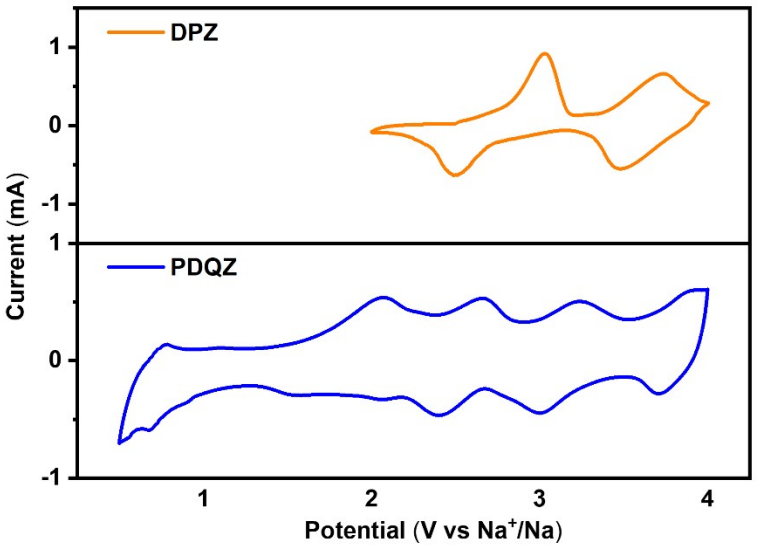

Figure S6. CV curves of DPZ and PDQZ.

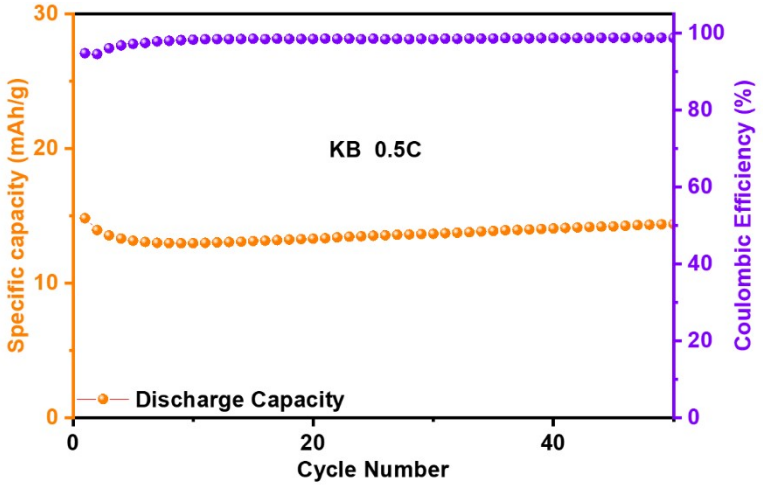

Figure S7. The cyclic performance of KB at 0.5C (for PDQZ)

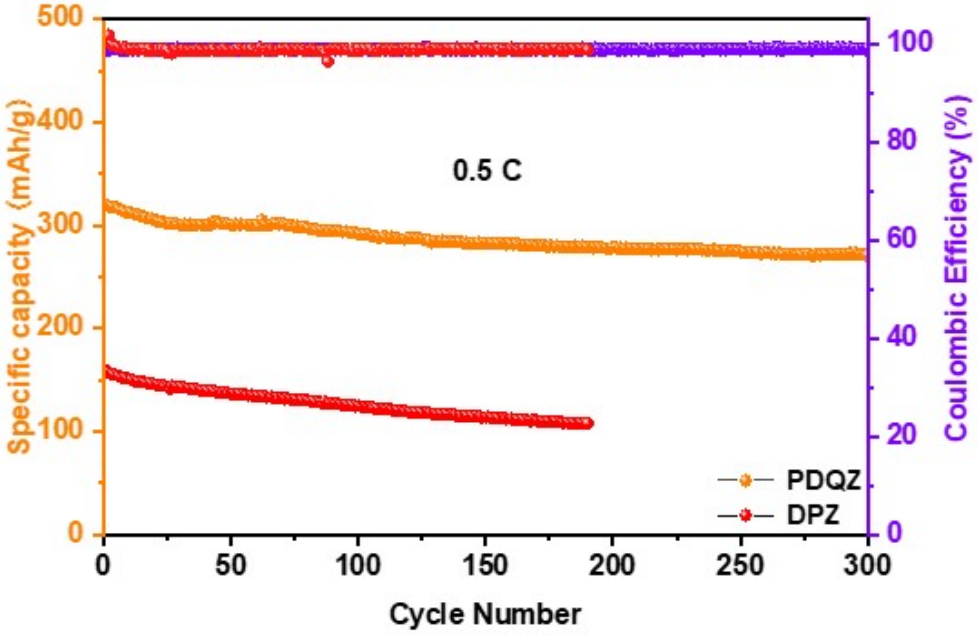

Figure S8. Cycling performance at 0.5 C of PDQZ and DPZ.

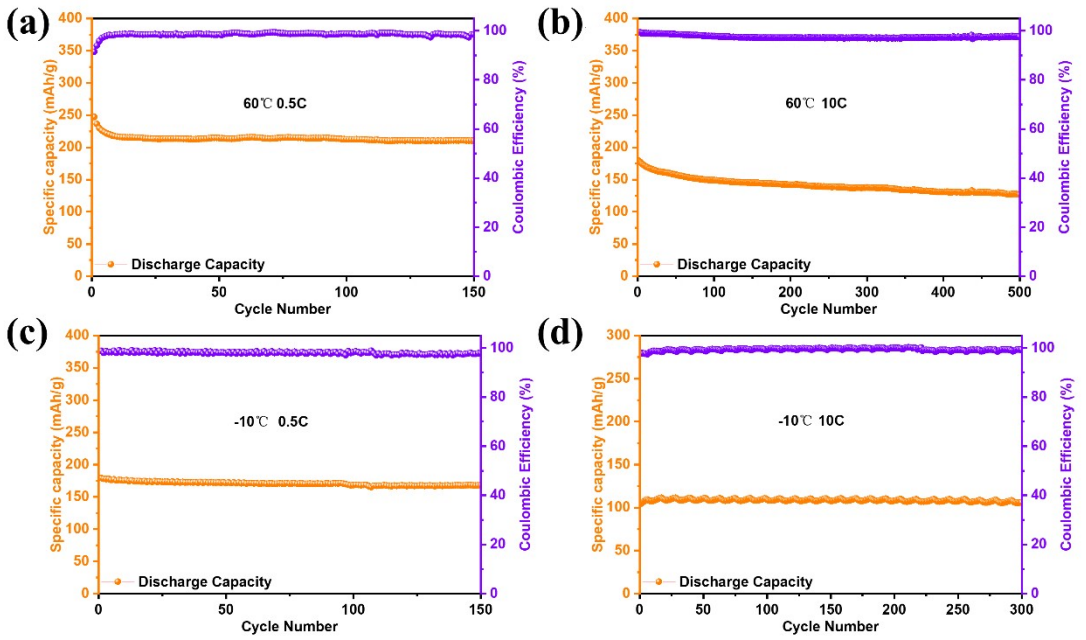

Figure S9. The cycling performance of half cells is a) 60 ℃, 0.5C, b) 60 ℃, 10C, c) -10 ℃, 0.5C, d) -10 ℃, 10C.

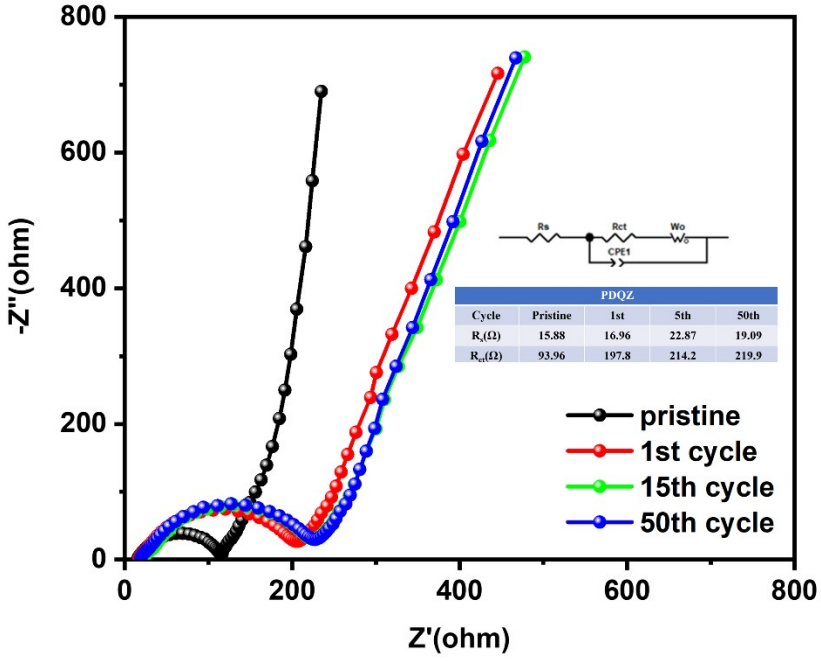

Figure S10. EIS of PDQZ at different cycles. Inset: the equivalent circuit and the of R_{ct} *and* R_{ct} values at different cycles.

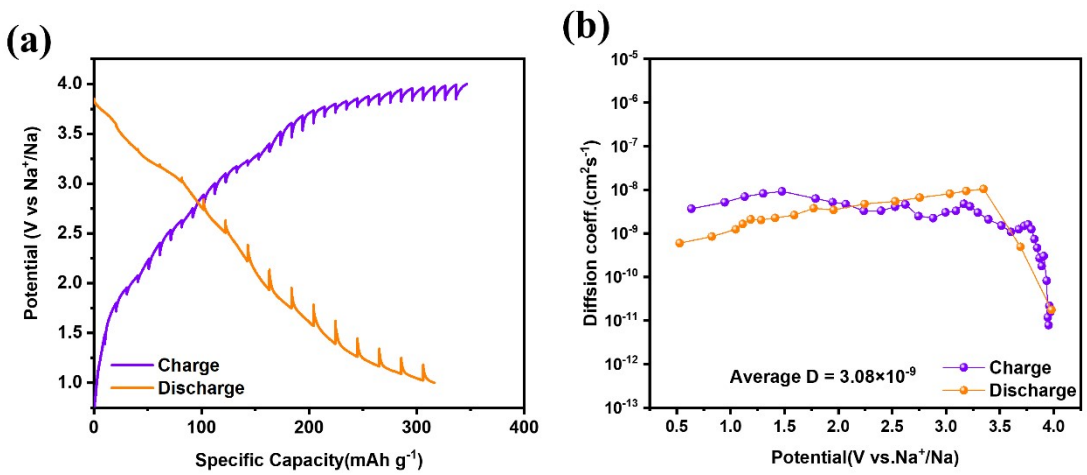

Figure S11. (a) GITT and (b) the calculated ions diffusion coefficients for PDQZ in half cells.

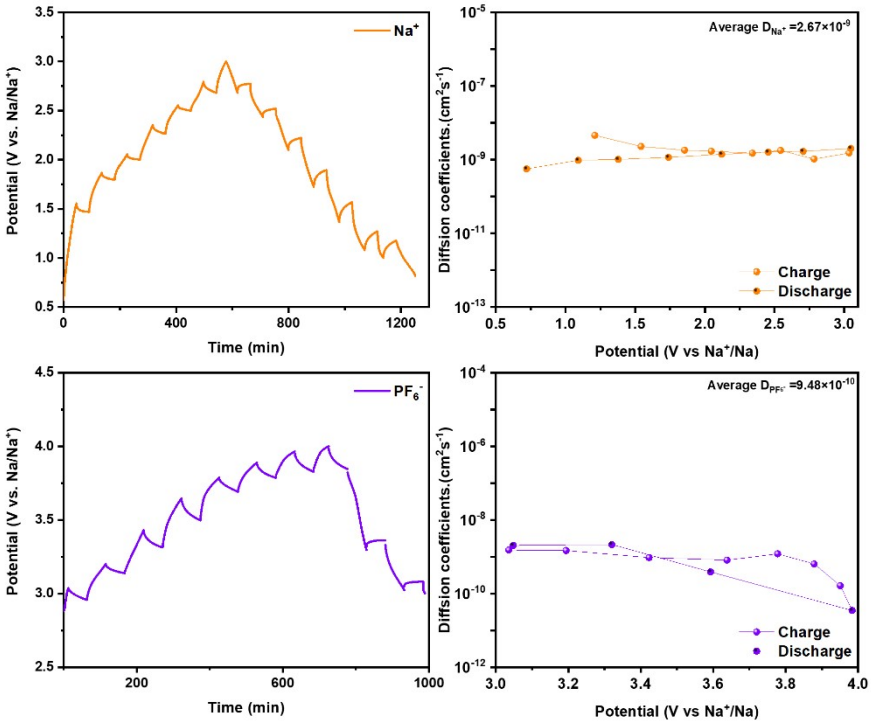

Figure S12. GITT curves of PQPZ for (a) cation (Na^+) and (c) anion (PF_6^-) diffusion process. Diffusion coefficients at different potentials during (b) sodiation-desodiation and (d) PF_6^- insertion and deinsertion in PQPZ.

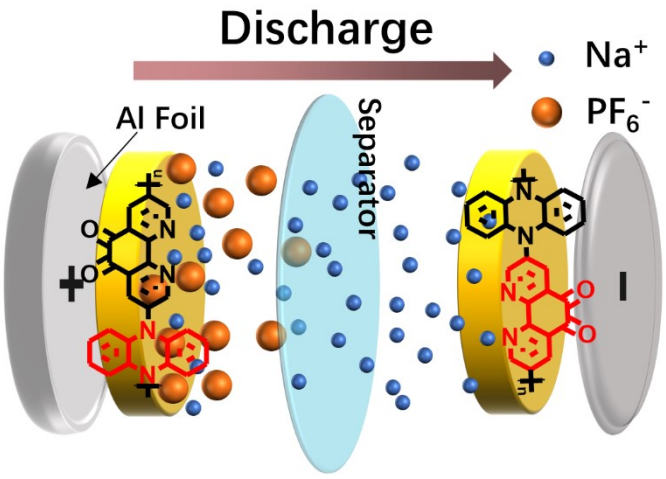

Figure S13. Illustration of symmetric organic full-cells.

Table S1. Compare the electrochemical performance of our symmetric battery with related works.

Materials	Cycling performance (capacity (mAh/g), current density)	Cycle number, average capacity decay rate per cycle	Reference
TPSZ	106, 100 mA/g	100, 0.15%	Energy Storage Materials 66 (2024) 9.[1]
PAD@MX	93, 500 mA/g	500, 0.06%	Advanced Functional Materials 34(13) (2024) 10.[2]
IDT	65, 2 A/g	600, 0.0035%	Advanced Functional Materials 34(34) (2024) 11.[3]
DAQ-DPZ	88, 1A/g	5000, 0.0081%	Chemical Engineering Journal 474 (2023) 9.[4]
TAPT	198, 1A/g	500, 0.062%	Angewandte Chemie-International Edition 61(33) (2022) 9.[5]
BDMI-CTF	75, 1 A/g	1000, 0.032%	Journal of Colloid and Interface Science 660 (2024) 1039-1047.[6]
Poly-BQ1	200, 500 mA/g	400, 0.038%	Nano Energy 86 (2021) 9.[7]
BPZT	114, 5 A/g	20000, 0.0005%	Advanced Science 11(30) (2024) 10.[8]
CNT@PMAQ	200, 100 mA/g	50, 0.8%	Advanced Functional Materials 33(5) (2023) 13.[9]
CNT@CPAN	123, 500 mA/g	1000, 0.0264%	Angewandte Chemie-International Edition 63(19) (2024) 10.[10]
PDQZ	112, 1 A/g	2000, 0.02%	This work

Table S2. Elements analysis results of PDQZ.

Weight Ratio	**C (%)**	**H (%)**	**O (%)**	**N (%)**	**Total (%)**
Experimental Results	72.412	4.22	11.45	6.67	94.752
Calculated Results	74.63	4.34	13.39	7.65	100

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