Supporting Information

D-A type polymer as Organic Cathode Material for Sodium-based Dual-ion Battery with 3.0 V Output Voltage

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Experimental Section

Synthesis of BPyPZ

The synthetic route was referenced to the pervious reported with some modifications [1, 2]. Buchwald-Hartwig coupling reaction was carried out in an oven-dried 200 mL glass Schleck round-bottom flask equipped with a reflux condenser and a magnetic stirring bar under Ar. 5,10-dihydrophenazine (273 mg, 1.00 eqv.), 2,5-dibromopyridine (355 mg 1.00 eqv.), Ruphos (14 mg, 0.03 eqv.), Ruphos Pd G2 (23 mg, 0.03 eqv.) and *t*-BuONa (720 mg, 5.0 eqv.) were added into the above-mentioned Schleck flask under Ar. Thereafter, 80 mL of xylenes were added into the flask through a syringe. The mixture was heated to reflux at 140 °C for 3 days. During this process, the solution became dark and green solid appeared. The precipitate was separated and successively washed with dichloromethane, warm deionized water, methanol and acetone. The crude product BPyPz was obtained as a green powder after extracted in Soxhlet extractor with THF and dried in vacuum oven at 90 °C (456 mg, yield, 72.6%).

Synthesis of TPyPz

The synthesis of TPyPz was similar to BPyPz. 5,10-dihydrophenazine (273 mg, 1.0 eqv.) 2,4,6-tribromopyridin (211 mg, 0.67 eqv.), Ruphos (14 mg, 0.03 eqv.), Ruphos Pd (23 mg, 0.03 eqv.) G2 and *t*-BuONa (720 mg, 5.0 eqv.) and 80 mL xylenes, respectively. The reaction lasted for 4 days at 140 °C. And the purification process is similar to that of BPyPz, and TPyPz was obtained dark green powder (322 mg, yield,

66.5%).

Electrochemical measurements

The galvanostatic cycling test was carried on a CT-4008T instrument (Shen Zhen NEWARE electronic Co.) at 25 °C. CVs were tested on a CHI instrument electrochemical work-station (CS 310s) between 1.5 and 4.3 V (vs. Na^+ /Na) for half-cell and between 1.0 and 4.0 V for full-cell.

Half-cell assembly

The BPyPz/TPyPz cathodes were fabricated by 70 wt.% BPyPz, 20 wt.% Super-P and 10 wt.% PVDF (binder). The loading mass of BPyPz/TPyPz on Al foil were above 1-1.2 mg cm^{-2}. The electrolyte consists of 1.0 M 1 M $NaClO_4$ in ethylene carbonate (EC): diethyl carbonate (DEC)=1: 1 (Vol%) with 5% fluoroethylene carbonate (FEC), with the used volume of 90 μL mg^{-1} versus the electrode in every cell. The Bi anode was fabricated by 45 wt.% Bi, 50 wt.% Super-P and 10 wt.% PVDF. The loading mass of Bi on Al was foil was above 0.7-0.85 mg cm^{-2}. The electrolyte consists of 1.0 M 1 M $NaClO_4$ in ethylene carbonate (EC): diethyl carbonate (DEC)=1: 1 (Vol%) with 5% fluoroethylene carbonate (FEC), with the used volume of 60 μL mg^{-1} versus the electrode in every cell. The separator was Whatman glass fiber. All half-cell (CR2032) were assembled in an argon filled glove box with oxygen level below 0.1 ppm.

Full-cell assembly

To remove the side reactions such as solid-electrolyte interphase (SEI) on the anode and cathode-electrolyte interphase (CEI) on cathode, both the cathode and anode were

tested for 3 cycles (at 100mA/g). When the cathodes were charged to 4.3 V and the anodes were discharged to 0.1 V, the half cells were subsequently disassembled in the Ar-filled glove box, and the cathodes and anodes were taken out to fabricate full cells. The electrolyte content of the full cells was consistent with that of the BPyPz half cells. The negative/positive capacity ratio was about 1.05 :1.

Material characterizations

The Fourier transform infrared spectrometer (FT-IR) was recorded using KBr pellets on a Nicolet Nexus 670 with the wavenumber range of 400-4000 cm^{-1}. The morphology images of the samples were collected by field-emission scanning electron microscope (FE-SEM, JEOL, JSM-7800F) and X-ray diffraction (XRD, SHIMADZU XRD-7000).

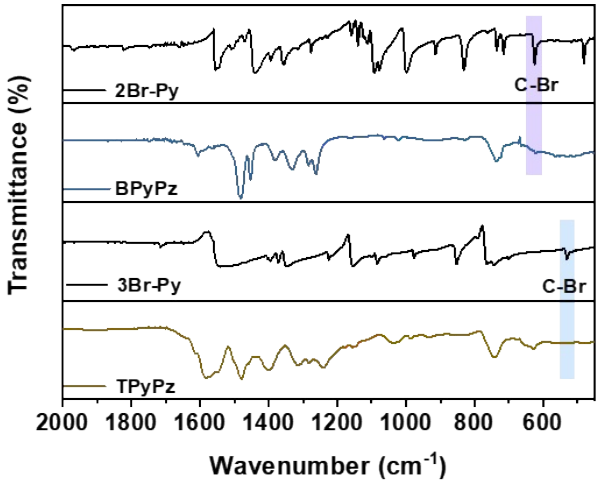

Figure S1. FTIR comparison of reactants (2Br-Py and 3Br-Py) and products (BPyPz and TPyPz).

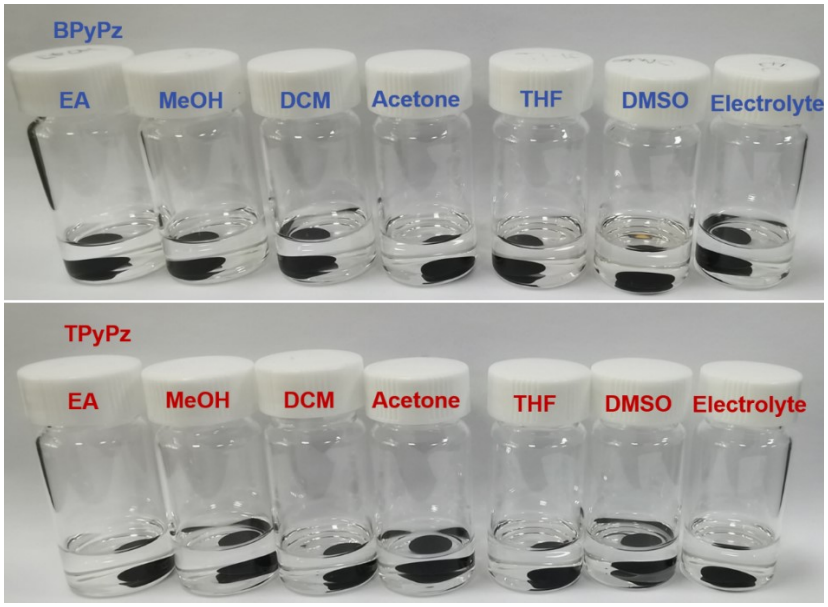

Figure S2. BPyPz and TPyPz electrodes soaked in common organic solvents for 72 h.

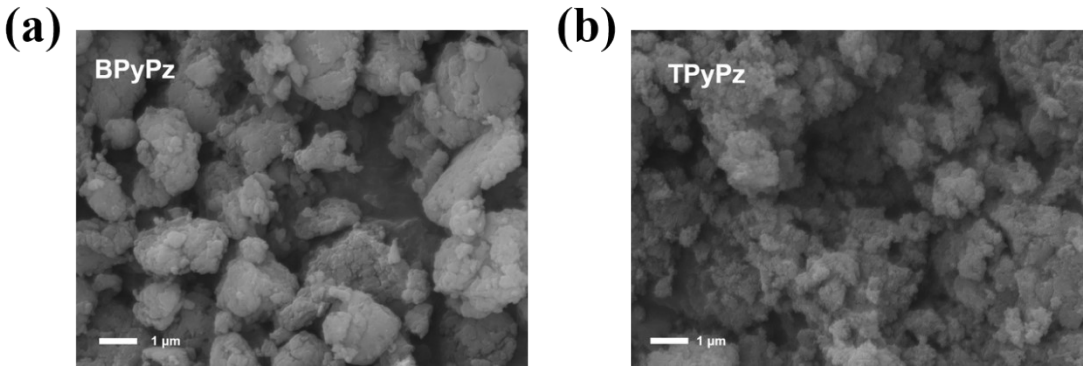

Figure S3. FE-SEM image of BPyPz (a) and TPyPz (b).

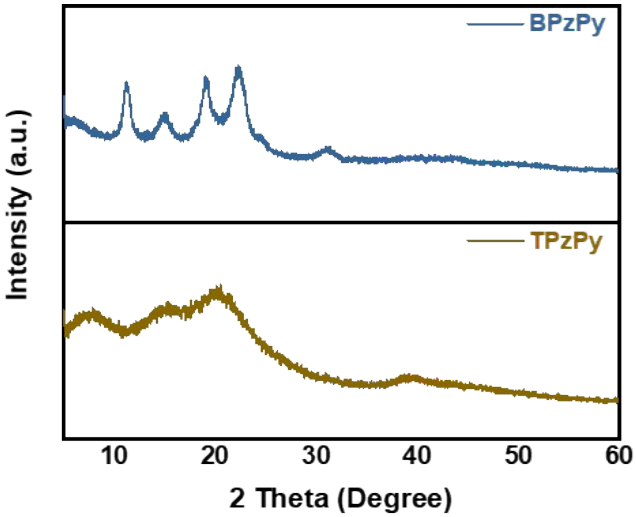

Figure S4. PXRD of BPyPz and TPyPz.

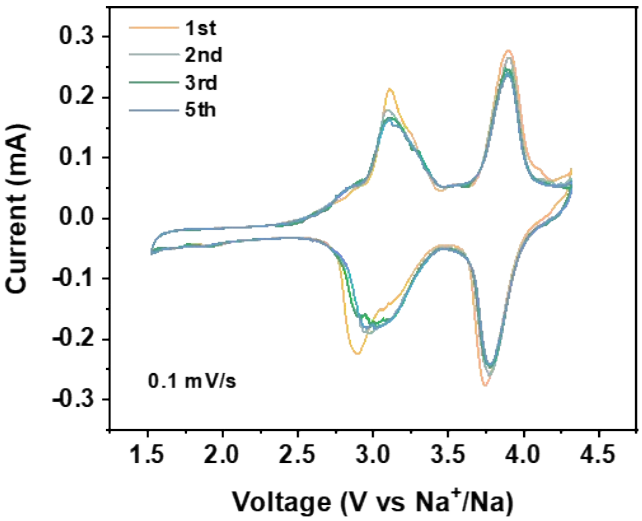

Figure S5. CV curves of BPyPz at a scan rate of 0.1 mV s^{-1}.

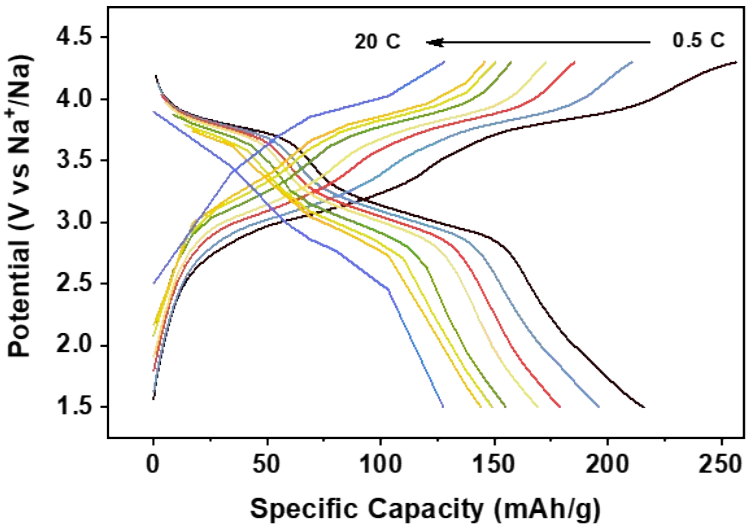

Figure S6. The GCD curves from 0.5 C to 20 C.

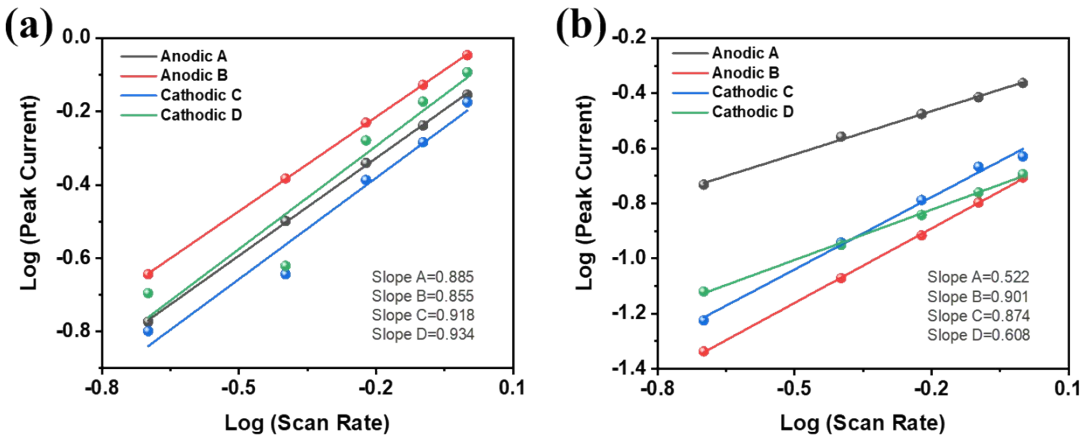

Figure S7. The fitting line of b-value of BPyPz (a) and TPyPz (b).

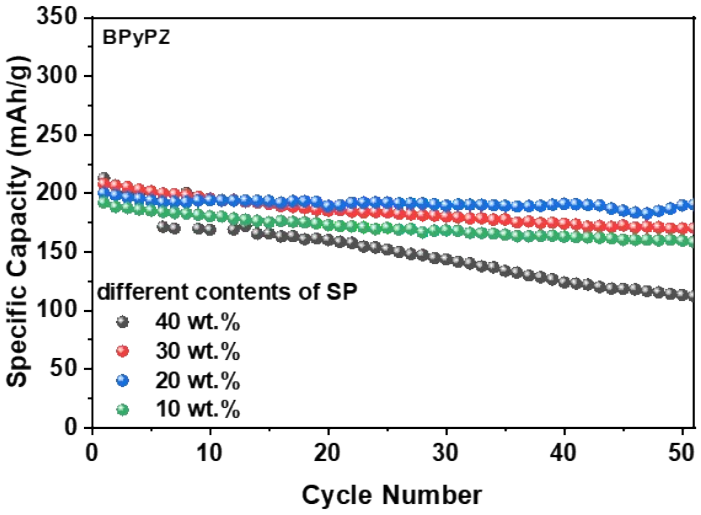

Figure S8. the cycle performance of BPyPz cathode was tested with different contents of conductive agent super P (SP) (from 40 wt% to 10 wt%).

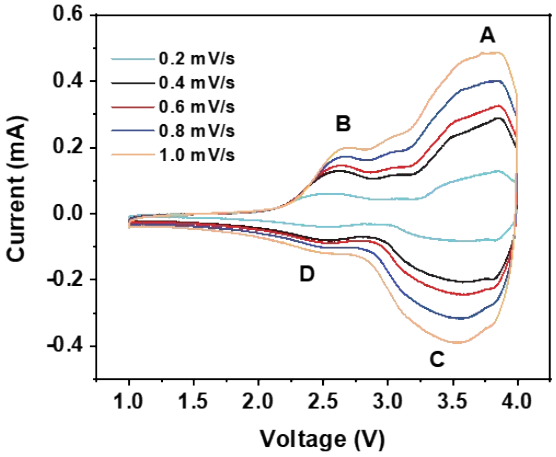

Figure S9. CV curves of the full-cell at various scan rates from 0.2 to 1 mV s^{-1}.

Figure S10. The LED light board driven under the voltage of 2.2-2.4 V

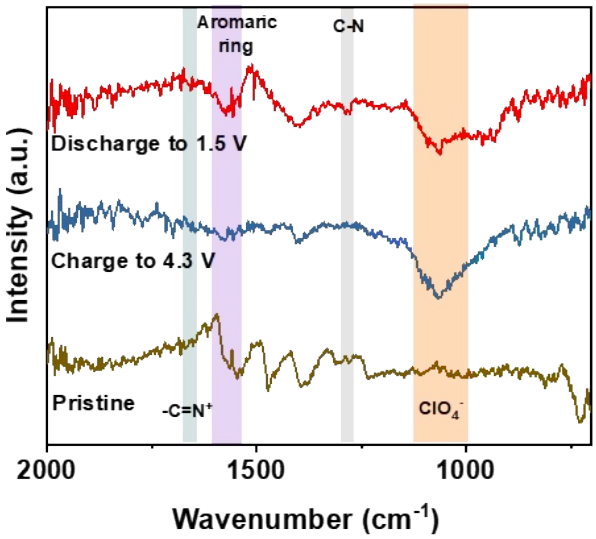

Figure S11. Ex-Situ FTIR spectra of TPyPz. The mechanism of TPyPz is similar to that of BPyPz, with Pz N as the active site and reversible storage of ClO_4^-.

The redox mechanism of TPyPz: The absorption peak at 1278 cm^{-1} is attributed to the C-N stretching. When charged from 1.5 to 4.3 V, the peak gradually decreases, while -C=N^+- peak appeared at 1647 cm^{-1}, indicating that the tertiary amine groups were oxidized to the N-radical cations to store anions. At the same time, the appearance and increased intensity of the peak at 1067cm^{-1} represents the storage of ClO_4^-.

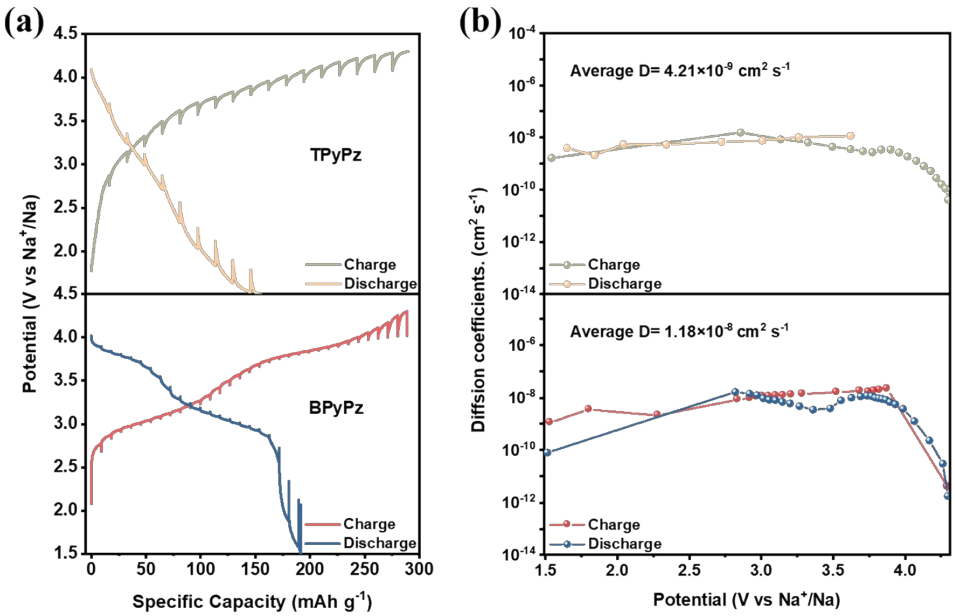

Figure S12. (a) Gitt curves of BPyPz and TPyPz. (b) the calculated ClO_4^- diffusion coefficients for BPyPz and TPyPz in half cells.

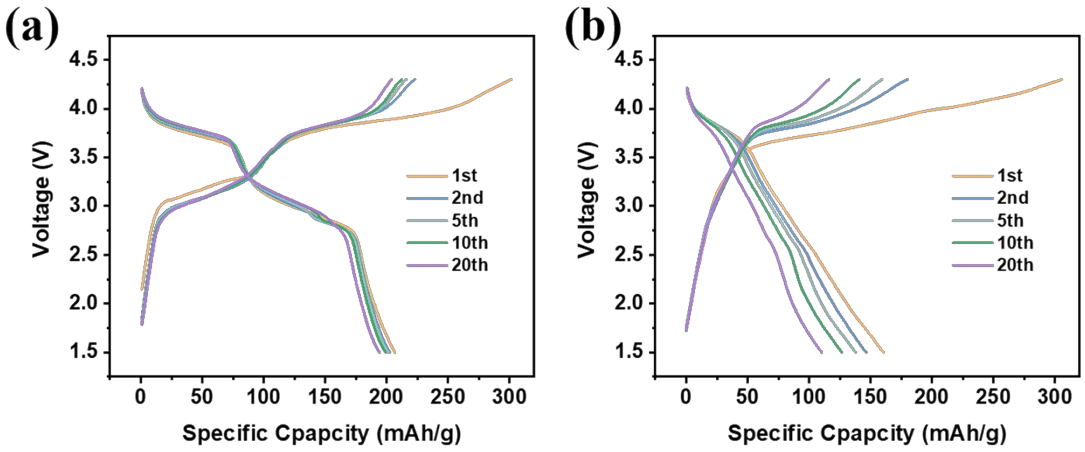

Figure S13. Discharge/charge curves in selected cycles in a voltage window at 1.5-4.3V (a) BPyPz, (b)TPyPz.

Table S1. Elements analysis results of BPyPz and TPyPz.

	Materials	C (%)	H (%)	N (%)	Total (%)
Experimental	BPyPz	74.471	4.034	14.338	92.843
Calculated		79.05	4.68	16.27	100
Experimental	TPyPz	74.45	4.141	13.91	92.501
Calculated		79.35	4.52	16.13	100

Table S2. A comparison for electrochemical performance of organic cathodes in full-cells.

Cathode II Anode	Voltage (V)	Capacity (mAh/g)	Rate performance	Type	Ref.
PAQB II Bi	1.30	172	113 (5 A $g^{-1}_{cathode}$)	Na-based	[3]
PTCDI-DAQ II Bi	1.25	203	142 (20 A $g^{-1}_{cathode}$)	Na-based	[4]
Na_4DHTPA II Na_4DHTPA	1.8	220	78 (1.9 A $g^{-1}_{cathode}$)	Na-based	[5]
CuTAPc II CuTAPc	2.15	110.9	22.5 (1 A $g^{-1}_{cathode}$)	Na-based	[6]
P-PANI II N-PDHC	2.9	161	50 (5 A $g^{-1}_{cathode}$)	Na-based	[7]
PAQDPZ II LiC_6	2.4	228	147 (2 A $g^{-1}_{cathode}$)	Li-based	[8]
$P(TMA_{0.95}\text{-co-}AQ_{0.05})_{1610}$ II Ag_2TP	2.8	185	50 (0.7 A g^{-1}_{anode})	Li-based	[9]
BPyPz II Bi	**3.0**	**162**	**112 (2 A $g^{-1}_{cathode}$)**	**Na-based**	**This work**

References

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