

## Supporting Information

# Furan-based Organic Cathode Materials for High-performance Sodium Ion batteries

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## Experimental Section

### Synthesis of 2,5-bis-(*p*-dimethoxybenzene) furan BFBOMe

Suzuki cross-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. 2,5-dimethoxyphenylboronic Acid (9.43 mmol, 2.2 eqv.), Cs<sub>2</sub>CO<sub>3</sub> (15.01 mmol 3.5 eqv.) and tetrakis (triphenylphosphine) palladium (0.214 mmol, 0.05 eqv.) was added into above mentioned Schleck flask under Ar. Thereafter, 960 mg 2,5-dibromofuran (4.29 mmol, 1.0 eqv.), 70 mL THF, 9 mL H<sub>2</sub>O was added into the flask through a syringe. The mixture was heated to reflux at an oil bath at 70 °C for 72 hours. Approximately 100 mL of brine solution was added the solution was extract with ethyl acetate (90 mL) for three times. The organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated. The pure produce was obtained through purifying the crude over silica gel using dichloromethane: petroleum ether (1:2) in 1.14 g, 78% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.48 (s, 2H), 7.23 (d, *J* = 2.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.81 (d, *J* = 2.9 Hz, 1H), 6.79 (d, *J* = 2.9 Hz, 1H), 3.90 (d, *J* = 13.3 Hz, 6H), 3.83 (s, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 149.12 (s), 145.61 (s), 134.59 (s), 121.13 (s), 119.74 (s), 109.29 (s), 108.61 (s), 108.41 (s), 51.72 (s), 51.10 (s).

### Synthesis of 2,5-bis-(*p*-benzoquinonyl) furan (QFQ)

The synthesis of QFQ was according to previous reports with some modifications. To a solution of 200 mg BFBOMe (0.59 mmol 1 eqv.) in MeCN (15 mL) round-bottom

flask equipped with a magnetic stirred under Ar. And the solution was cooled to 0 °C. Then, a solution of 1.93 g  $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$  (3.54 mmol 6 eqv.) in 4 mL water added drop by drop during 20 min. Therefore, warming to 35 °C, the mixture was stirred for 3 days. During this process, the solution became dark and yellow solid appeared. Add deionized water to the reaction flask and sonicate for 30 min. The precipitate was separated by suction filtration, washed with dichloromethane and warm deionized water, and dried to give crude product QFQ as a yellow powder. The QFQ was obtained through recrystallization form 1,1,2,2-tetrachloroethane in 0.127 g, 77 % yield.

#### **Synthesis of 1,4-bis(2,5-dimethoxyphenyl) benzene (BBBOMe)**

The synthesis of BBBOMe was similar to BFBOMe. 3.0 g 1,4-Dibromobenzene (12.72 mmol, 1 eqv.), 2,5-dimethoxyphenylboronic Acid (30.52 mmol, 2.4 eqv.), tetrakis (triphenylphosphine) palladium (0.636 mmol, 0.05 eqv.) and  $\text{Cs}_2\text{CO}_3$  (44.51 mmol, 3.5 eqv.), respectively. The time for reflux was 48 hours at 70 °C. The pure produce was obtained through purifying the crude over silica gel using dichloromethane: petroleum ether (1:2.5), in 3.9 g, 88 %.

#### **Synthesis of 1,4-bis(*p*-benzoquinonyl) benzene (BBQB)**

The synthesis of BBQB was similar to QFQ. 1.000 g BBBOMe (2.857 mmol) was added. Finally add deionized water to the reaction flask and sonicate for 30 min. The precipitate was separated by suction filtration, washed with dichloromethane and warm deionized water, and dried to give crude product BBQB as a orange powder. The QFQ was obtained through recrystallization form 1,1,2,2-tetrachloroethane in 0.671g, 81 % yield.

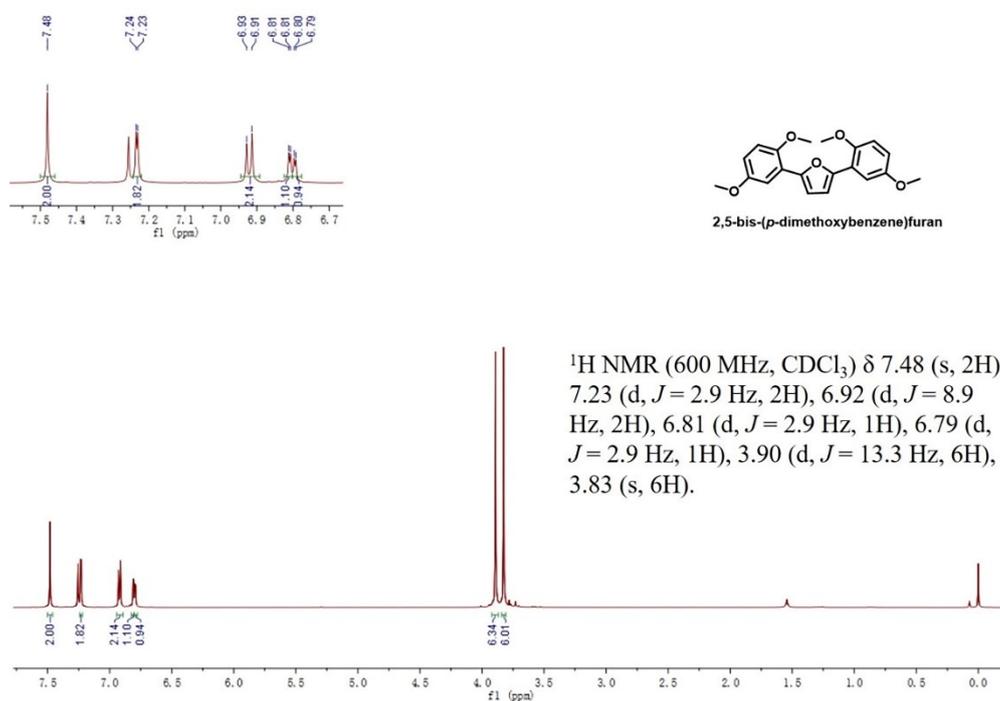
## **Electrochemical measurements**

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 working electrode was fabricated from a slurry of 60 wt.% active material ( $\sim 1.0 \text{ mg/cm}^2$ ), 30 wt.% ketjin black (KB) and 10 wt.% PVDF as the binder. These slurries were blade cast onto aluminum current collector and dried at 60 °C for 8 hours before battery assembling. The cells were assembled with an electrolyte of 1 M NaPF<sub>6</sub> in 1,2-dimethoxyethane (DME) (100 VOL%), a separator of Whatman glass fiber. For the full cell the anode was prepared similarly as the cathode with Na-CPP that reported by our group as active material. The specific capacity of full cells was based on the mass of the cathode only. Both cathode and anode were electrochemically pre-sodiated for 3 cycles (at 100 mA g<sup>-1</sup>). 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) at a scan rate of 0.1 mV s<sup>-1</sup> between 1.0 and 3.9 V (vs. Na<sup>+</sup>/Na). The EIS test was measured by a CHI instrument electrochemical workstation in the frequency range of 0.01–10<sup>5</sup> Hz at the amplitude of 5 mV. All the tests were performed at room temperature.

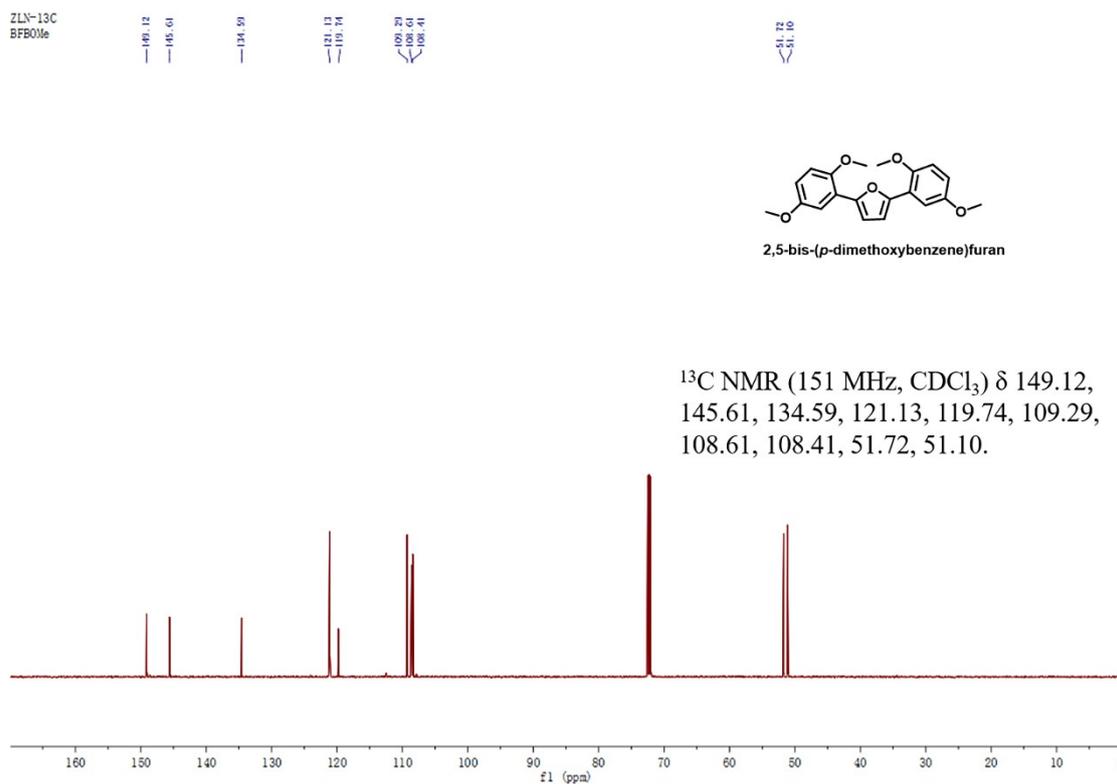
## **Material characterizations**

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<sup>-1</sup>. The <sup>1</sup>H and <sup>13</sup>C Nuclear Magnetic Resonance (NMR) was performed on Bruker 600 MHz. The

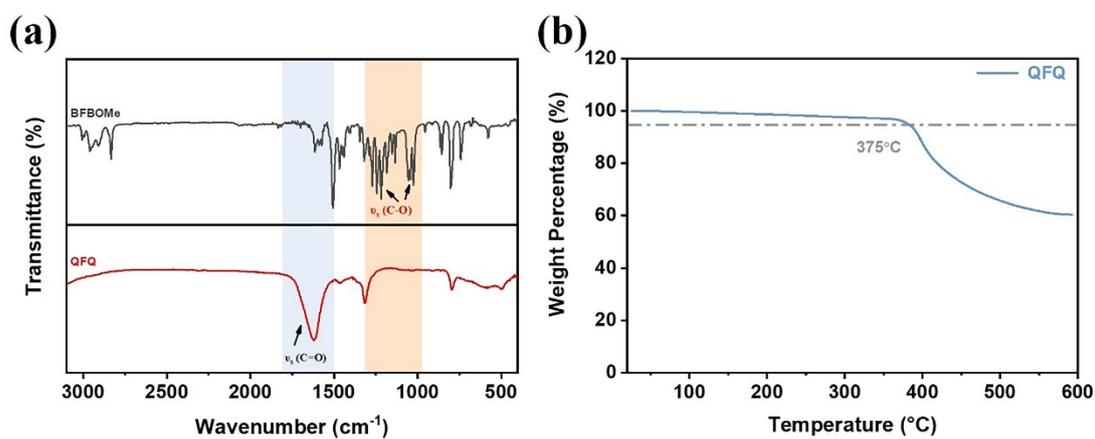
morphology images of the samples were collected by field-emission scanning electron microscope (FE-SEM, JEOL, JSM-7800F) and X-ray diffraction (XRD, SHIMADZU XRD-7000).



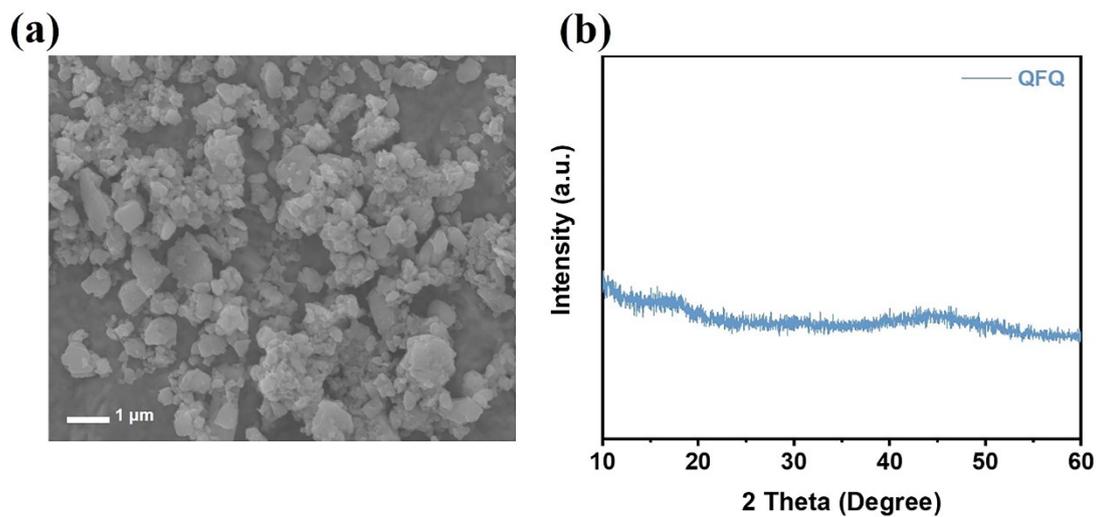
**Fig. S1.**  $^1\text{H NMR}$  spectrum of BFBOMe in  $\text{CDCl}_3$ .



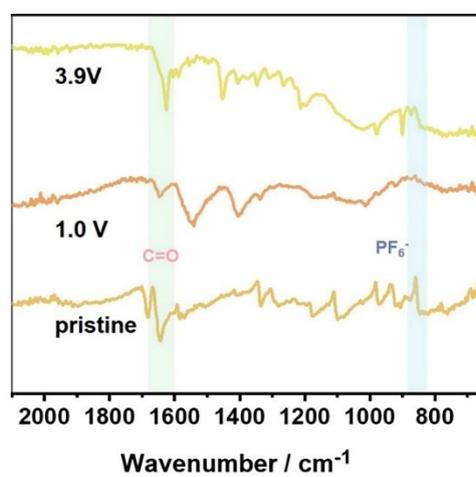
**Fig. S2.**  $^{13}\text{C}$  NMR spectrum of BFBOMe in  $\text{CDCl}_3$ .



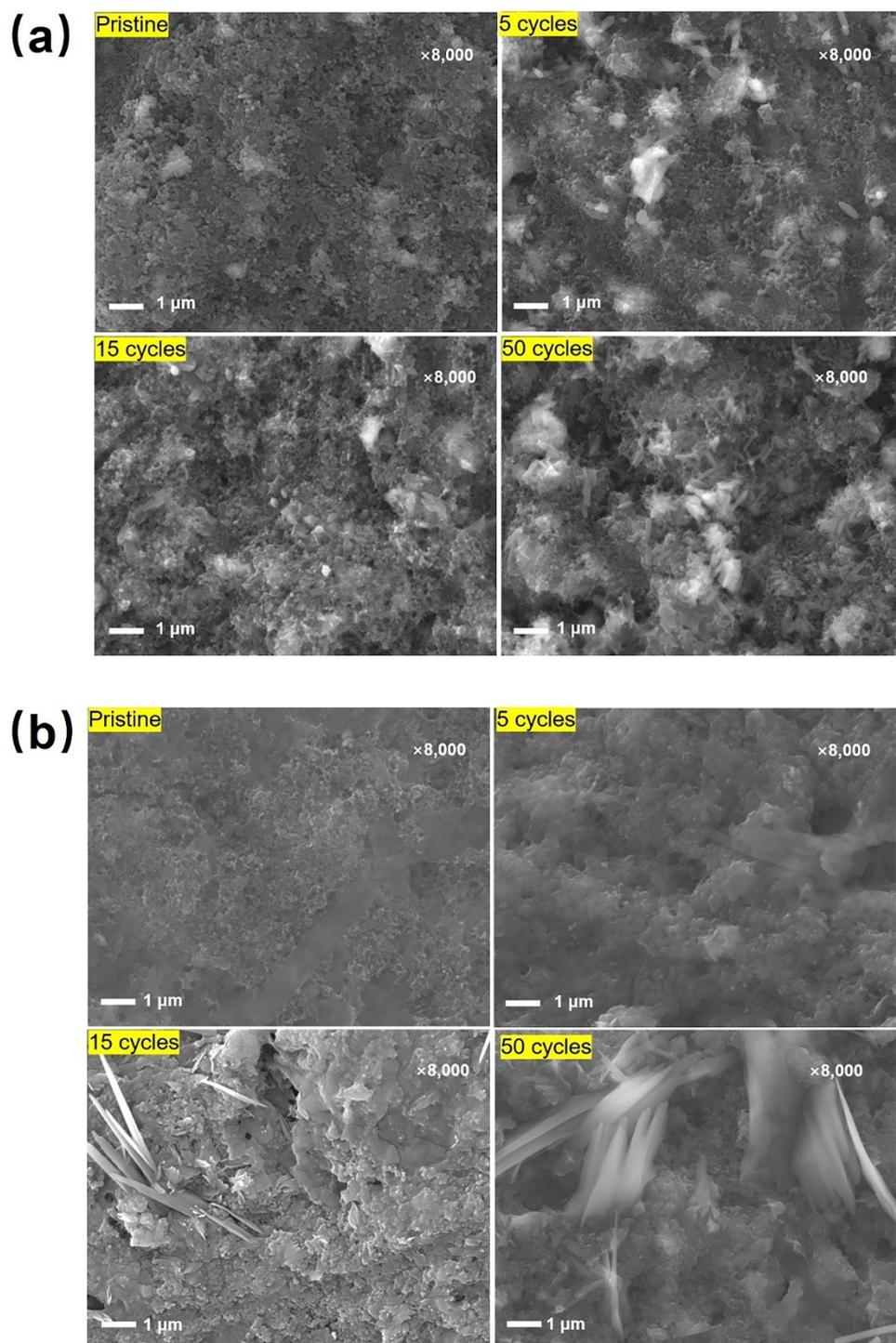
**Fig. S3.** Fourier Transform infrared spectroscopy of BFBOMe and QFQ (a), and Thermal Gravimetric Analyzer curve of QFQ (b).



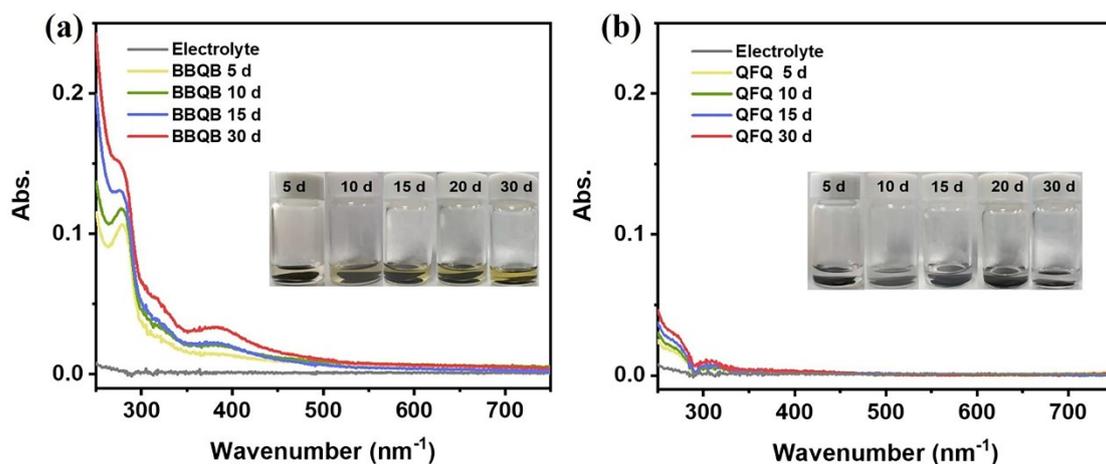
**Fig. S4.** FE-SEM image of QFQ (a). Characterized of QFQ by XRD (b).



**Fig. S5.** Ex-Suit FTIR of BBQB.



**Fig. S6.** FESEM images of QFQ (a) and BBQB (b) at different cycles.



**Fig. S7.** UV-vis spectra of solubility experiments with (a) BBQB and (b) QFQ electrode sheet

immersed in 1M NaPF<sub>6</sub> in DME.

In the UV test, in order to ensure that the absorbance is within the reasonable detection range of the instrument, we take 50  $\mu$ L electrolyte of the immersed electrode sheets and dilute with 2 mL DME.

**Table S1.** Solubility of QFQ and BBQB in DME.

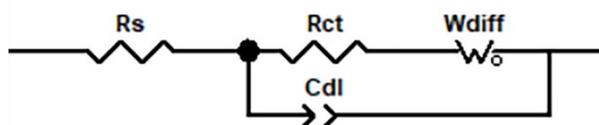
Materials	Solubility (mg/mL)
QFQ	<0.005 mg/mL
BBQB	0.059 mg/mL

**Table S2.** The calculated Solvation free energy ( $\Delta G$  in kcal mol<sup>-1</sup>) of QFQ and BBQB.

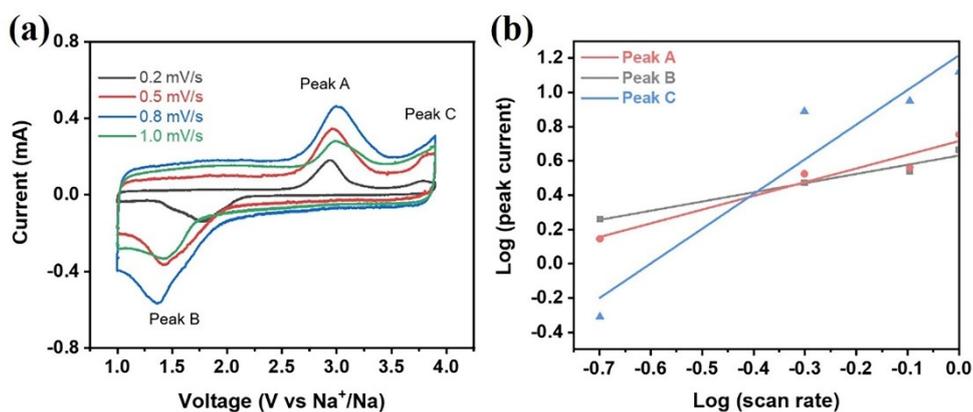
	$\Delta G_{(\text{diethylether})} / \text{kcal mol}^{-1}$	$\Delta G_{(1,4\text{-dioxane})} / \text{kcal mol}^{-1}$
QFQ	-6.07	-3.94

**Table S3.** The summary of  $R_s$  and  $R_{ct}$  ( $\Omega$ ) of QFQ and BBQB at different cycles.

Cycle	QFQ			BBQB		
	Pristine	1	80	Pristine	1	80
$R_s$ ( $\Omega$ )	14.44	6.328	10.22	3.786	7.920	21.33
$R_{ct}$ ( $\Omega$ )	53.31	71.46	79.25	76.88	114.8	358.7



**Fig. S8.** EIS equivalent circuit.



**Fig. S9.** (a) CV curves of QFQ cathode at various scan rates from 0.2 to 1 mV s<sup>-1</sup>. (b) Dependence

of peak current on different scan rates.

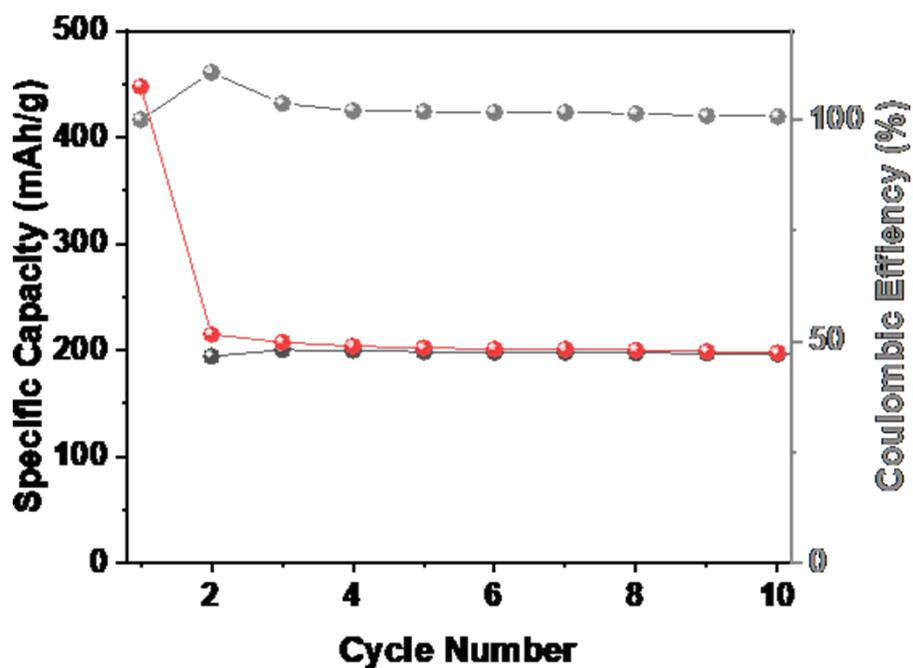


Fig. S10. Galvanostatic charge-discharge profiles of Na-CPP at  $100\text{mA g}^{-1}$ .

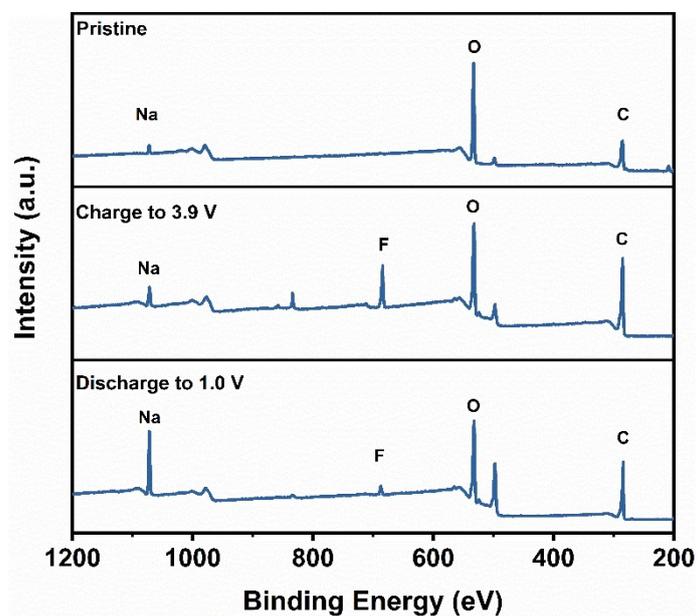


Fig. S11. The full XPS spectra of QFQ during charging and discharging (SA as a binder).

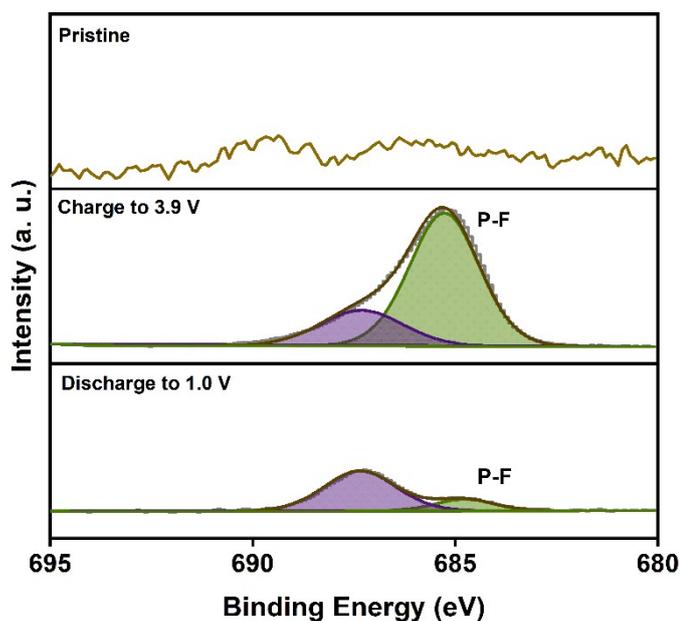


Fig. S12. F1s spectra during charging and discharging (SA as binder).

**Table S4.** Summary of reported All-organic Na-ion batteries based on small molecular cathode material.

Cathode	Anode	Type	Voltage (V)	Capacity (mAh/g)	Stability	Ref
Na <sub>4</sub> DHTPA	Na <sub>4</sub> DHTPA	SIBs	0.2-2.6	142 <sub>Cathode</sub>	76%/100th cycles (100 mA g <sup>-1</sup> )	1
Na <sub>2</sub> AQ26DS	Na <sub>2</sub> TP	SIBs	0-3.1	68 <sub>Cathode</sub>	52%/100th cycles (100 mA g <sup>-1</sup> )	2
Na <sub>6</sub> C <sub>6</sub> O <sub>6</sub>	Na <sub>2</sub> TP	SIBs	0-3.1	426 <sub>Cathode</sub>	85%/30th cycles (50 mA g <sup>-1</sup> )	3
PFS1	PMDA	SIBs	0-2.0	85 <sub>Cathode</sub>	74%/200th cycles (550 mA g <sup>-1</sup> )	4
PTCDA/NC/CNT	Na <sub>4</sub> TPC/CNT	SIBs	0.8-3.0	64 <sub>Cathode</sub>	85 %/200th cycles (200 mA g <sup>-1</sup> )	5
AQ26ONa	Na <sub>2</sub> TP	SIBs	0.01-3.0	142 <sub>Cathode</sub>	70 %/50th cycles (50 mA g <sup>-1</sup> )	6
<b>QFQ</b>	<b>Na-CPP</b>	<b>SIBs</b>	<b>0.1-3.0</b>	<b>117<sub>Cathode</sub></b>	<b>90%/200th cycles</b> <b>(100 mA g<sup>-1</sup>)</b>	<b>This work</b>

## References

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