

Supporting information

A Robust Conductive Covalent Organic Framework for Ultra-Stable Potassium Storage

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Experimental Section

Ni-TTF Synthesis

Ni-bis(dithiolene)tetrabenzaldehyde [Ni(bded)₂] was synthesized tetra(aminophenyl)-tetrathiafulvalene (TTFNH₂) as reported.^{1,2}

Synthesis of **Ni-TTF COF**: Ni-TTF was synthesized according to reported method¹ with a slight modification. Ni(bded)₂ (0.02 mmol, 13.1 mg), TTFNH₂ (0.02 mmol, 11.4 mg) and ammonium acetate (0.1 mmol, 7.7 mg) were charged into a Pyrex tube with a mixture of 1.5 mL *o*-DCB and 0.5 mL BuOH. The mixture was sonicated for 5 minutes, and then 6 M HOAc was added, followed by sonication for another 5 minutes. The mixture was cooled with liquefied nitrogen, degassed by freeze-pump-thaw cycles, flame sealed, heated to 120°C and kept for 5 days. After the reaction, the precipitate was collected by filtration, washed with DMF until the filtrate was colorless, and then Soxhlet extracted with THF for 24 hours. Afterwards, the resulting powder was dried and activated by heating at 100°C under vacuum to obtain Ni-TTF as a dark green powder with a yield of 74% (17.2 mg). The obtained Ni-TTF was further dried and activated at 300 °C for 5 h under Ar flow.

General Methods

All chemicals are commercially available. All reactions were carried out in a Schlenk line under the protection of N₂. An X-ray powder diffractometry study of the complex was performed on a Bruker D8 ADVANCE diffractometer (Cu K α radiation) with an exposure of 1.5 s deg⁻¹ and a step of 0.01 degrees at room temperature. FT-IR spectra were recorded on a Tensor II Bruker spectrophotometer in the 4000-400 cm⁻¹ region. UV-Vis-NIR spectra were recorded on a UV-2600 SHIMADZU spectrophotometer. The morphology was characterized by a field-emission scanning electron microscope (Hitachi Regulus 8100) and transmission electron microscope (FEI Talos F200x G2). Gas adsorption/desorption isotherms were measured using an ASAP 2020 (Micromeritics Instrument Corp USA). TGA data were obtained on an STA449C thermal analysis system at a heating rate of 10°C min⁻¹ under air atmosphere. Temperature-dependent conductivity was measured with a keysight 2902A measure unit and Lakeshore TTPX probe station at a heating rate of 5°C/min.

Electrochemical Measurement

The electrochemical performances were tested with CR2032 coin cells (half-cell) at room temperature. The active materials were mixed with carbon black (Super P) and a binder (CMC/SBR with a mass ratio of 1:1) in a mass ratio of 60:30:10 and mixed to form a slurry. This slurry was then coated onto a carbon-coated copper foil and dried under vacuum conditions at 70°C for 12 hours to prepare the working electrode. The active material loading on the electrode surface was 0.8-1.2 mg cm⁻². CR2032 coin cells were assembled in an argon-filled glovebox (O₂ and H₂O levels < 0.1 ppm), with active material as the working electrode, a glass fiber separator (Whatman) as the separator, 5 M KFSI in EC:EMC (v:v=1:1) as the electrolyte, and a metallic potassium plate (Sigma Ltd) as the counter electrode. Charge and discharge tests were performed in a LAND Battery Testing system (CT-3002A). Cyclic voltammetry (CV) tests were performed on CHI760E and Metrohm Autolap electrochemical workstations. All tests were conducted at room temperature.

Theoretical Calculation

All calculations were achieved by density functional theory (DFT) of the GGA-PBE method³ at the Gamma point in Cambridge Serial Total Energy Package (CASTEP) modules in the Materials Studio 2018 program.⁴ The initial model of Ni-TTF was taken from the X-ray crystallography data directly, and the structural relaxation was performed on the unit cell with the freezing cell parameters. The ELE function and the mapped surface were

calculated based on the optimized wavefunction of Ni-TTF. The K^+ ion accommodation structures were calculated based on a $1 \times 1 \times 2$ supercell model of Ni-TTF and achieved by adding K^+ ions and electrons to the Ni-TTF model step by step. The geometry optimizations were performed when the changes in energy, max force and max displacement converged to 5.0×10^{-5} eV/atom, 1.0×10^{-1} eV/Å and 5.0×10^{-3} Å, respectively. The plane wave cutoff energy was 400 eV, and OTFG ultrasoft pseudopotentials were used for all atoms.

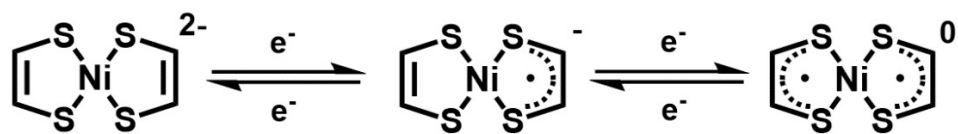


Fig.S1. Proposed reversible redox process of Ni-bis(dithiolene) for energy storage.

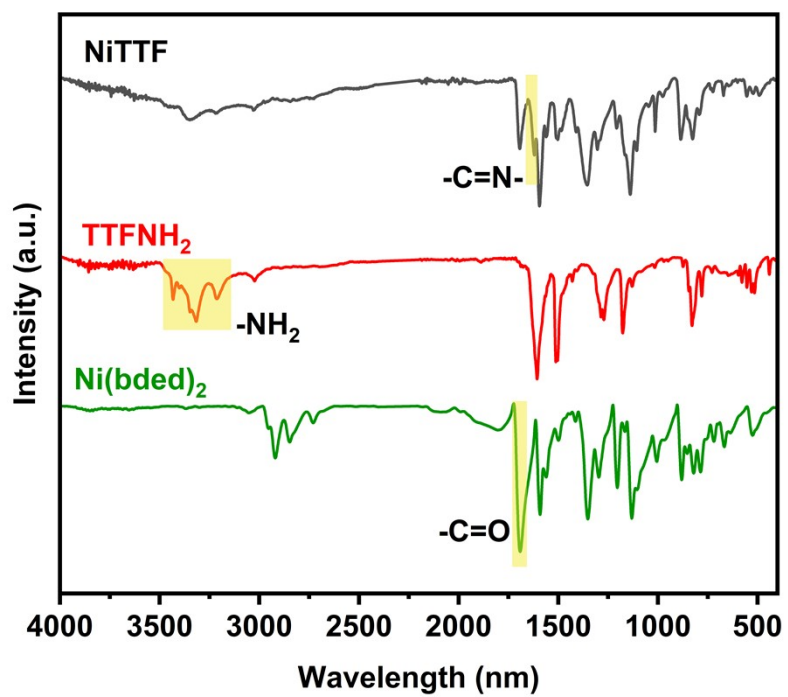


Fig. S2. FT-IR spectrum of Ni-TTF, TTFNH₂ and Ni(bded)₂.

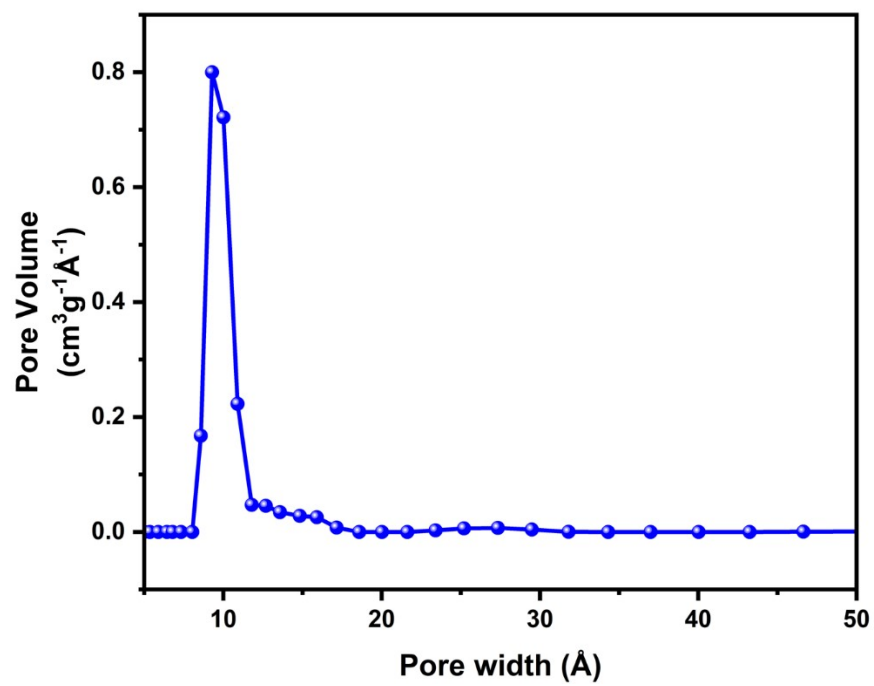


Fig. S3. Pore width distribution of Ni-TTF.

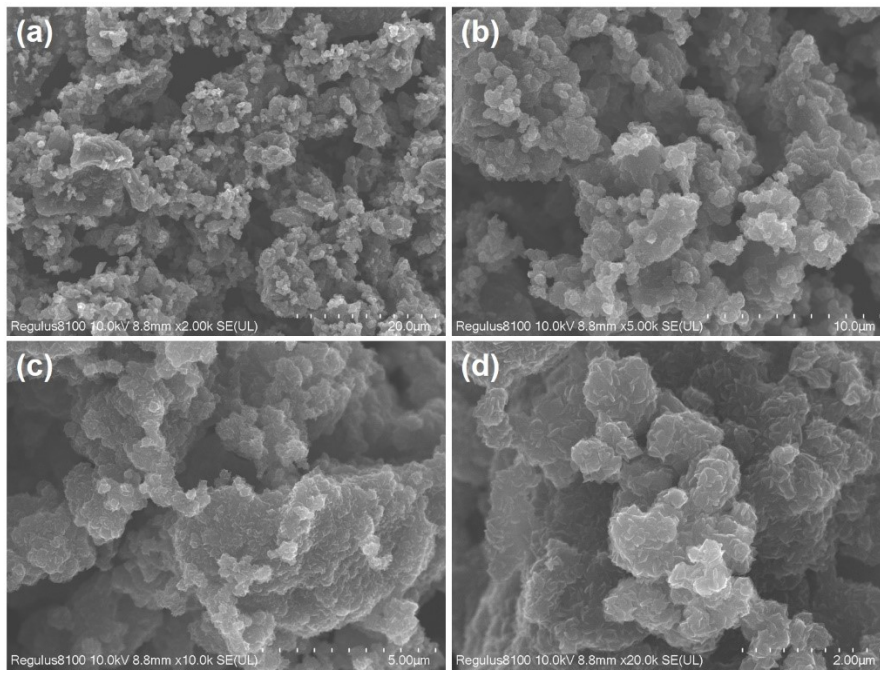


Fig. S4. SEM images of Ni-TTF of different magnification.

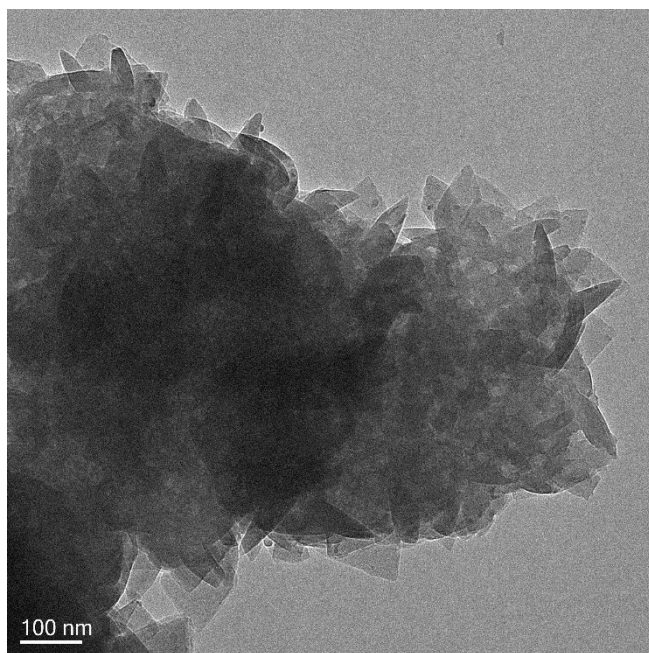


Fig. S5. TEM image of Ni-TTF.

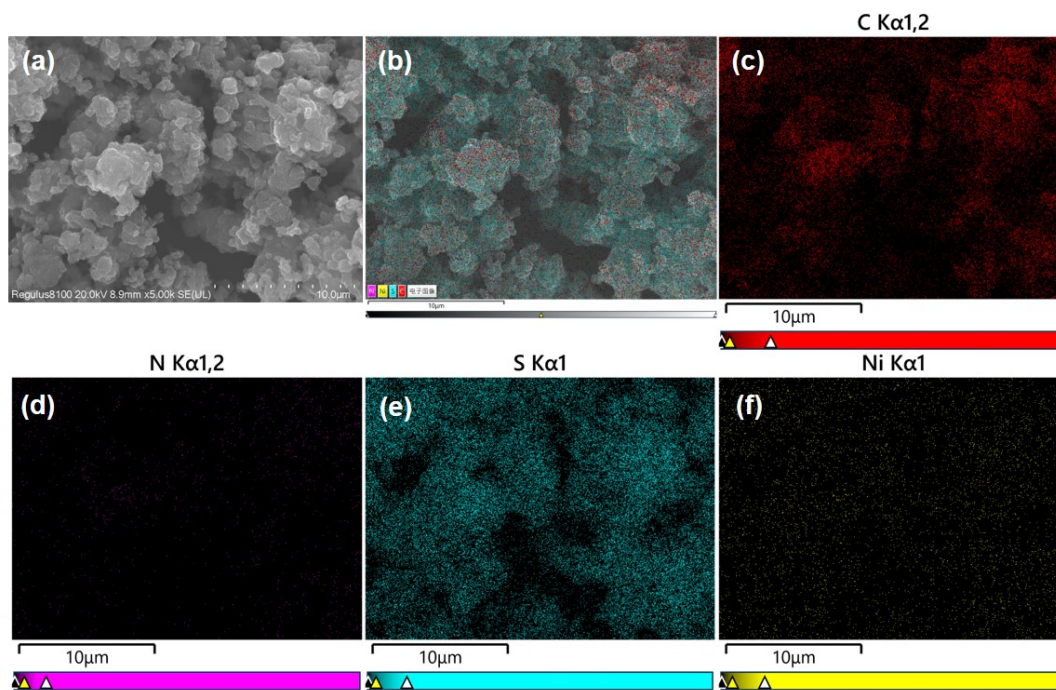


Fig. S6. The energy dispersive spectroscopy (EDS) of Ni-TTF showed the even distribution of C, N, S and Ni.

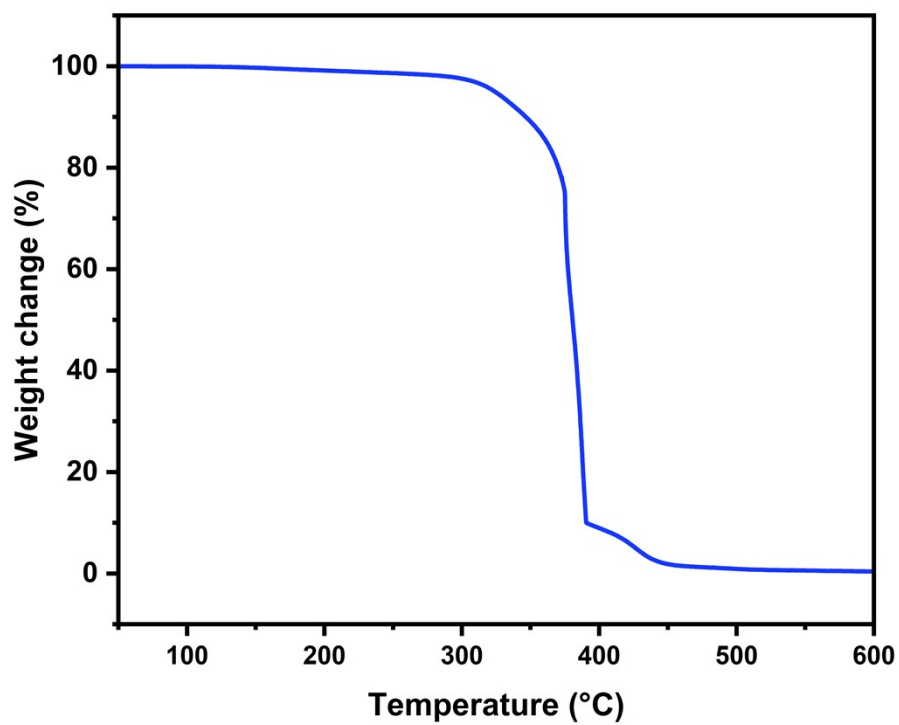


Fig. S7. TGA of Ni-TTF under air atmosphere within the temperature range between 50 and 600°C under a heating rate of 10°C min⁻¹.

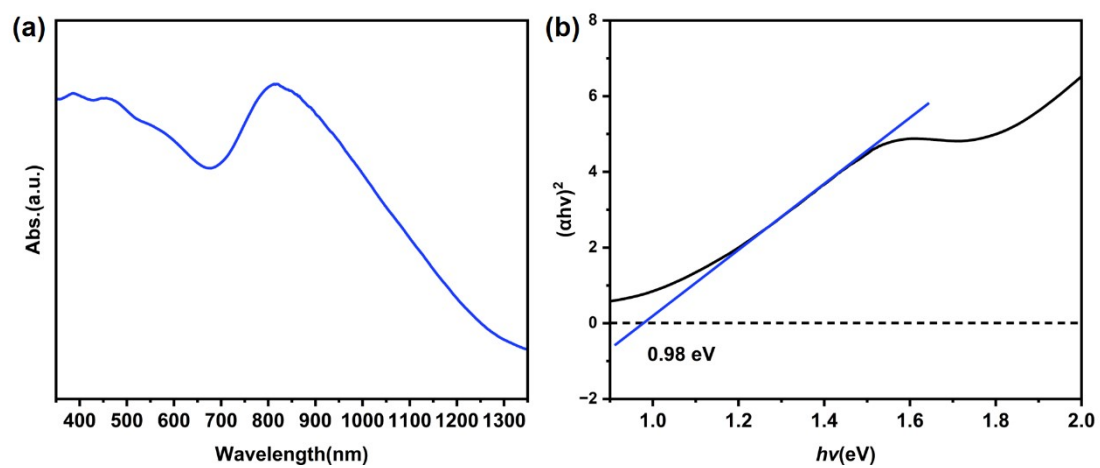


Fig. S8. (a) UV-vis spectrum and (b) Tauc plot of Ni-TTF.

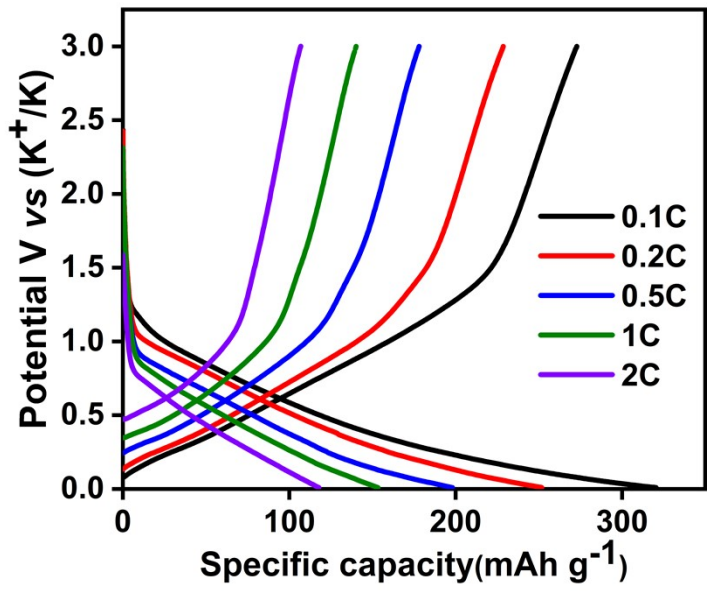


Fig. S9. Charge and discharge curves of Ni-TTF at various current densities.

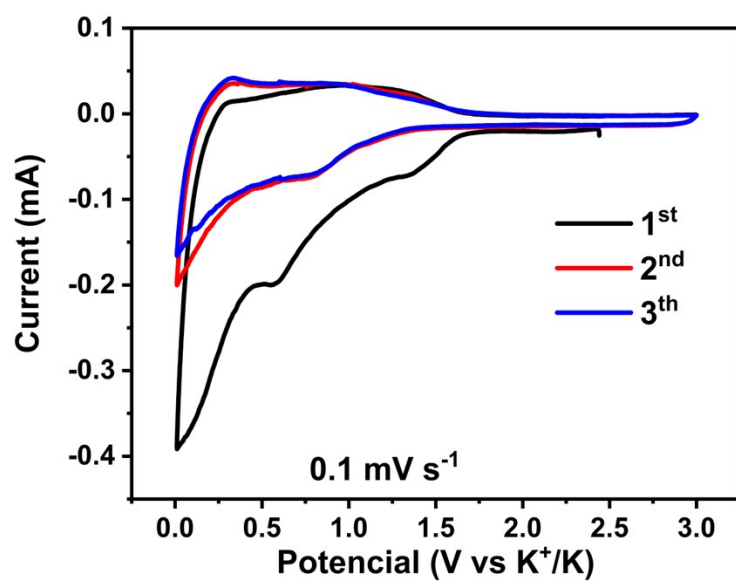


Fig. S10. CV curve of Ni-TTF between 0.01-3 V at a scan rate of 0.1 mV s⁻¹.

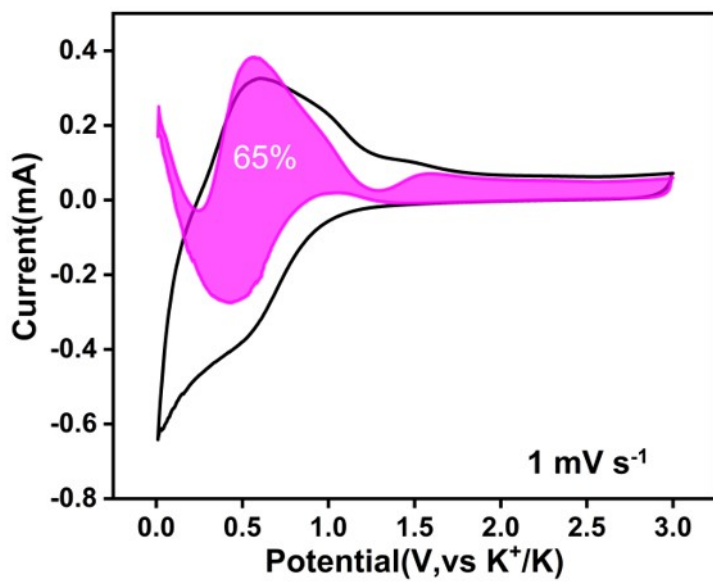


Fig. S11. Capacitive contribution calculation during charging/discharging at a scan rate of 1 mV s⁻¹.

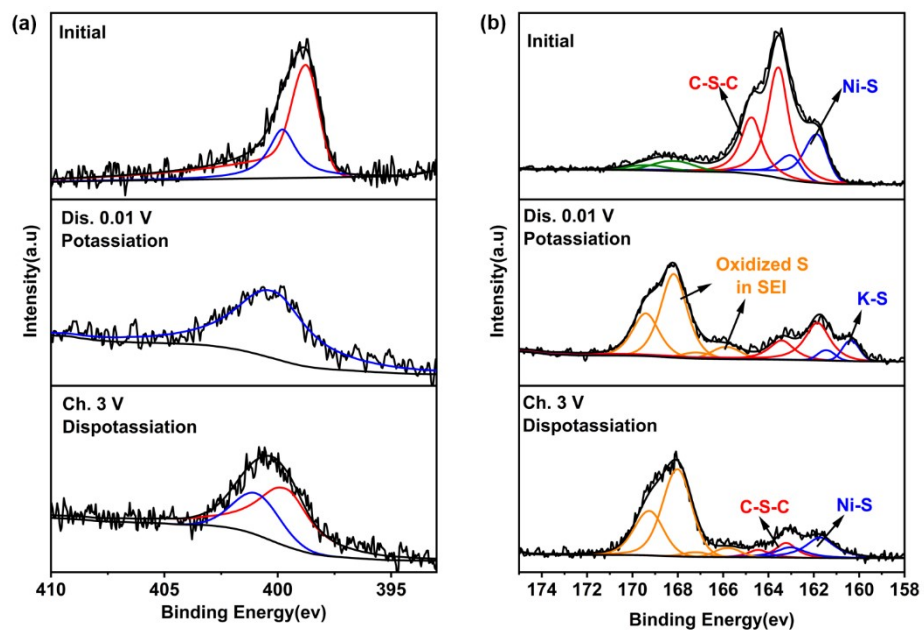


Fig. S12. Ex situ XPS a) N 1s and b) S 2p, S2p3/2 and S 2p1/2 spectra of Ni-TTF at fully charged and fully discharged states.

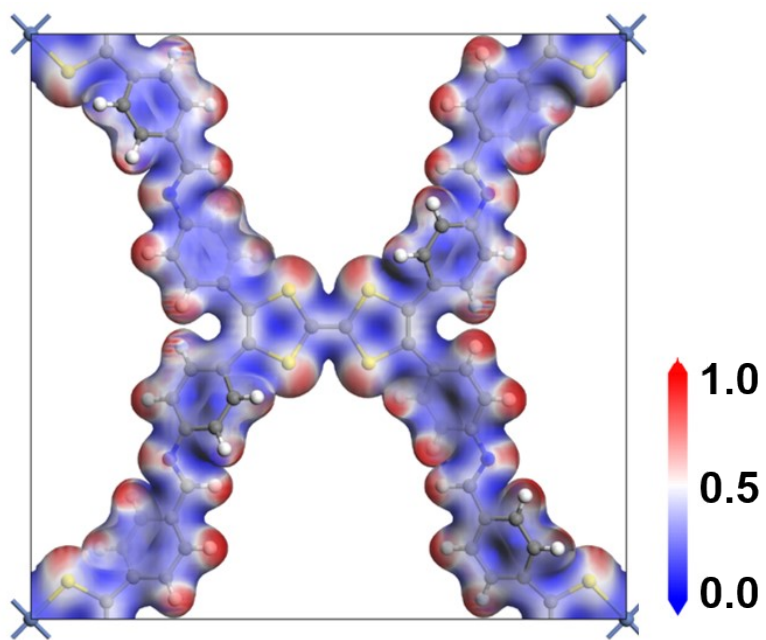


Fig. S13. Electron localization function (ELF) values on the van der Waals surface of Ni-TTF. A unit cell is shown.

Table S1. Comparison of KIB anode performance of Ni-TTF with previous publication.

Materials	Reversible Capacity	Capacity retention ratio	Cycle number	Ref.
Ni-TTF	150 mAh g ⁻¹ at 0.6 Ag ⁻¹	>100%	2500	This work
	223 mAh g ⁻¹ at 0.3Ag ⁻¹	> 100%	800	
(P-COF@SWCNT)	114 mAh g ⁻¹ at 0.7 Ag ⁻¹	56%	1400	5
CTF-0	113 mAh g ⁻¹ at 0.1 Ag ⁻¹	73%	200	6
TP-COF HS	203 mAh g ⁻¹ at 0.3Ag ⁻¹	81.2%	500	7
TP-COF/CNTs	220 mAh g ⁻¹ at 0.2Ag ⁻¹	86%	500	8
K-MOF	115 mAh g ⁻¹ at 0.1Ag ⁻¹	92%	300	9
Polypyrene	190 mAh g ⁻¹ at 0.5Ag ⁻¹	~63.3%	1000	10
K ₄ PTC@CNT	50 mAh g ⁻¹ at 0.5Ag ⁻¹	68.5%	2500	11

References

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