

Electronic Supplementary Information (ESI)

An organic cathode with tailored working potential for aqueous Zn-ion battery

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Experimental Section and Methods

AQ and TCNQ were purchased from Sigma Aldrich and directly applied as active cathode materials without any further treatment. The morphologies of the materials were studied by scanning electron microscopy (FESEM and EDS, SIGMA, ZEISS 20 kV). IR spectra were recorded on a Nicolet IS10 spectrometer from Thermo Electron. The ^1H NMR (400 MHz) data were recorded on BRUKER AVANCE III HD 400M using DMSO- d_6 as solvent at room temperature. X-ray photoelectron spectroscopy (Thermo Scientific, Escalab250Xi) were carried out using Al- $K\alpha$ as radiation source.

The electrochemical properties were studied using CR2016-type coin cells. The cathodes were made by mixing AQ (TCNAQ or TCNQ), Super P (Timcal) carbon, polytetrafluorethylene (PTFE) in 60:30:10 weight ratio, then the mixture was ground thoroughly in deionized water until a well-distributed and homogeneous slurry was got. The slurry was then evenly coated on graphite foil (Alfa Aesar, 99.8%) and dried at 100°C for 12h under vacuum. The dried film was punched into 1cm² coins with an average mass loading of 3-10 mg. The cells were fabricated in air using Zn foil ($\geq 99.9\%$, Sigma-Aldrich) as the counter/reference electrode, 2M ZnSO₄ ($\geq 99.9\%$, Sigma-Aldrich) aqueous solution as electrolyte, and glass fiber (Waterman® Glass microfiber filter) as separator.

The galvanostatic discharge/charge performance was studied at various current densities by LAND CT2001A battery testing system (Wuhan, China). CV was carried out on the CHI660E electrochemical workstation (Shanghai, China) at a scan rate of 0.1 mV s⁻¹.

Synthesis of 11,11',12,12'-tetracyanoanthraquinodimethane (TCNAQ)

A 500 mL 3-neck round bottomed flask equipped with two constant pressure drop funnels and a condenser (with a drying tube on the top) was assembled under a generous dry nitrogen flow. Under an ice bath, 6.6 g (0.1 mol) malonitrile and 8.3 g (0.04 mol) anthraquinone in 250 mL dry CHCl_3 were added in turn into the flask. Then 21 mL (0.2 mol) TiCl_4 and 60 mL pyridine was added dropwise successively with stirring and cooling. The ice bath was removed and the mixture was left stirring overnight under the room temperature. The solvent was removed. A yellow precipitate was recrystallized with acetic acid to give 10 g (0.033 mol, 82 %) of a light-yellow powder. $^1\text{H NMR}$ (DMSO-d_6) δ 7.67 (br, 4H), 8.25 (br, 4H); IR (KBr): 2222, 1605, 1503, 1383, 1344 cm^{-1} .

Computational Method:

Geometrical optimizations for isolated molecules of AQ, TCNQ and TCNAQ in the vacuum state were performed at the B3LYP/6-31+G(d,p) level using the Gaussian 09W software package.

Calculations of specific energy density and specific power density:

(1) Specific energy density

$$E_{spe} = \frac{C \times V}{m_{TCNAQ} + m_{Zn}}$$

where E_{spe} is specific energy density (Wh kg^{-1}); C is the discharge capacity (mAh); V is average discharge voltage (V); m_{TCNAQ} is the mass (g) of cathode (TCNAQ); m_{Zn} is the mass (g) of anode (the consumed Zn, $m_{zn} = C \div 820 \text{ mA h g}^{-1}$).

(2) Specific power density

$$P_{spe} = \frac{i \times V}{m_{TCNAQ} + m_{Zn}}$$

where P_{spe} is specific power density ($W\ kg^{-1}$); i is applied current (mA); V is average discharge voltage (V); m_{TCNAQ} is the mass (g) of cathode (TCNAQ); m_{Zn} is the mass (g) of anode (the consumed Zn, $m_{zn} = C \div 820\ mA\ h\ g^{-1}$).

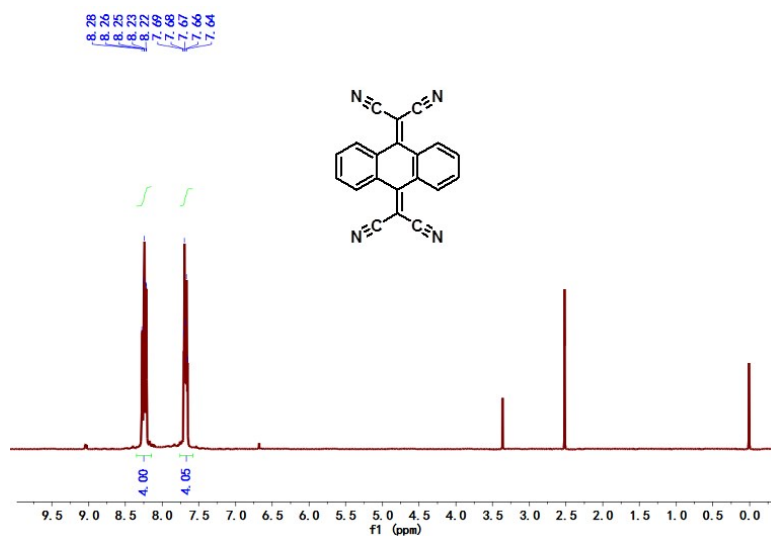


Fig. S1 ^1H NMR spectrum (400 MHz, DMSO- d_6) of as-prepared TCNAQ material.

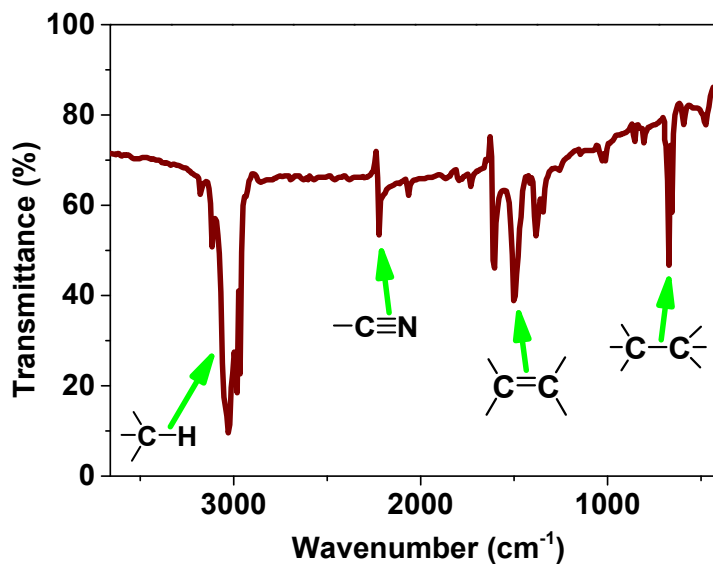


Fig. S2 FTIR spectra of as-prepared TCNAQ material. The C-H stretches at about 3000 cm^{-1} , $\text{C}\equiv\text{N}$ stretches at about 2222 cm^{-1} , C=C stretches at about 1503 cm^{-1} , and C-C stretches at about 680 cm^{-1} .

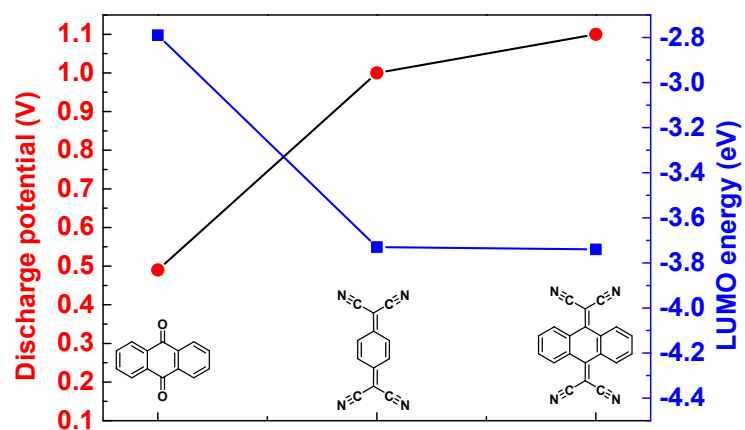


Fig. S3 Discharge potential and LUMO energy of the AQ, TCNQ and TCNAQ.

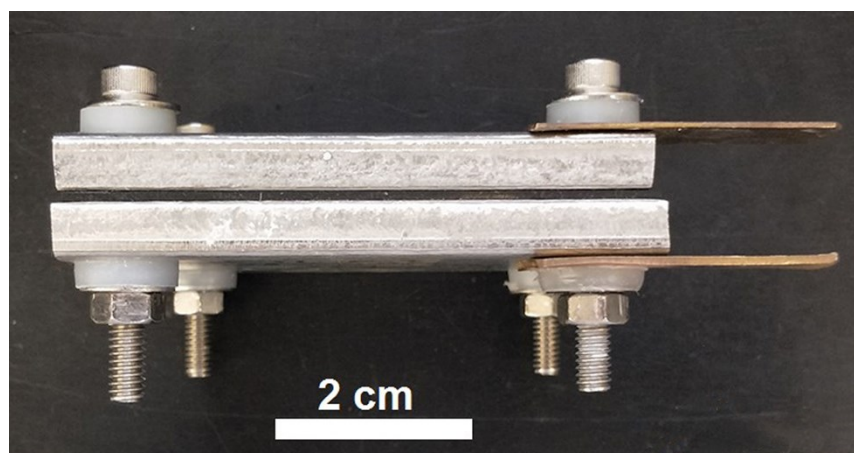


Fig. S4. A large battery made for electrochemical tests, using two stainless steel square sheet as outer shells and thermal conductive rubber as spacer. The area of cathode and anode is 4 cm^2 . A mass loading of 80 mg TCNAQ (about 20 mg cm^{-2}) are applied for the cathode.

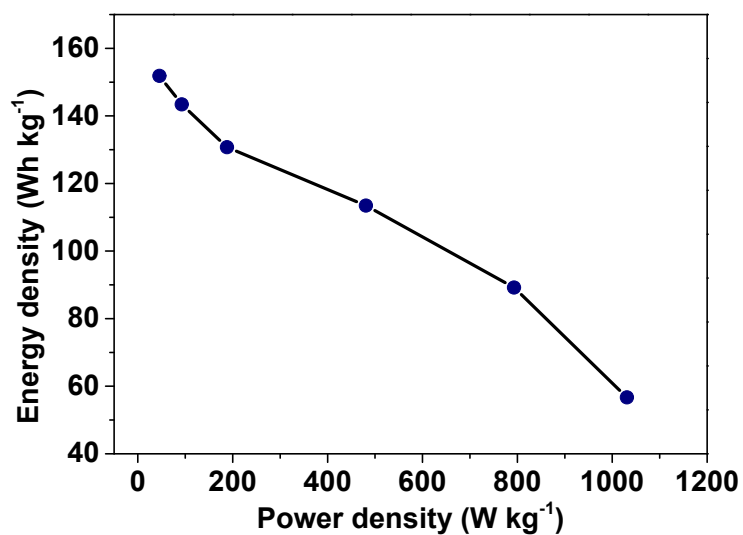


Fig. S5 Ragone plot of the assembled Zn//TCNAQ battery.

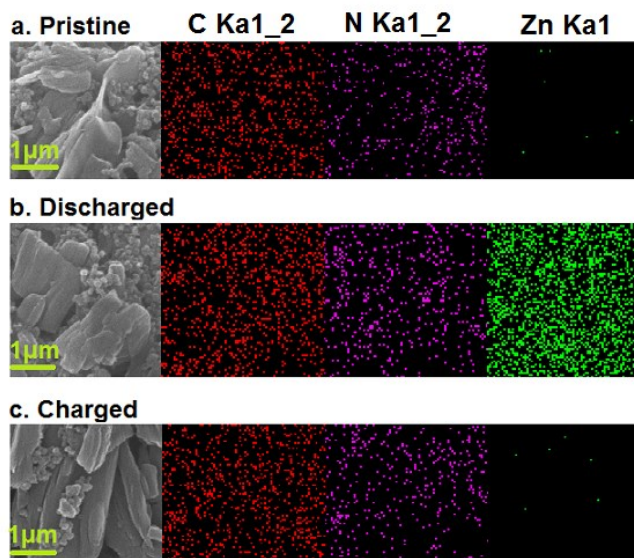
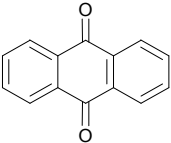
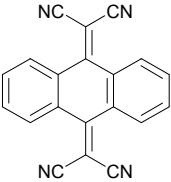
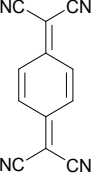


Fig. S6 *Ex situ* SEM-EDS mapping images of the TCNAQ cathode at (a) pristine stage, (b) deeply discharged stage and (c) fully recharged stage.

Table S1 Comparison of the molecular weight, theoretical specific capacity (C_{the}), initial experimental discharge specific capacity (C_{exp}),^a Coulombic efficiency (CE),^a discharge potential for the AQ, TCNAQ and TCNQ.

Entry	Compound name	Molecular structure	Molecular weight	C_{the} [mAhg ⁻¹]	C_{exp} [mAhg ⁻¹]	CE(%)	Discharge potential (V)
1	AQ		208.21	257	188	98	0.49
2	TCNAQ		304.3	176	169	98.5	1.1
3	TCNQ		204.19	262	192	97	1

^a The current density is 20 mA g⁻¹.