

## Supplementary Information

### **A Thianthrene-based small molecule as high-potential cathode for lithium-organic batteries**

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## Experimental section

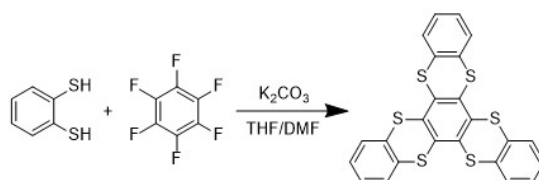
### Materials

All chemicals were purchased from commercial providers and used without further purification. Experiments with water- or oxygen-sensitive substances were carried out under an argon atmosphere using glassware dried by heating under vacuum and standard Schlenk techniques. All other solvents were distilled prior to use.

### Characterization

$^1\text{H}$  NMR was measured on Bruker AV400 spectrometer. FTIR spectra data was recorded using Bruker ALPHA spectrometer in the range of 400-4000  $\text{cm}^{-1}$ . SEM images were obtained by ZEISS Gemini 300. XRD was collected on X'Pert3 Powder instrument using  $\text{Cu K}\alpha$  X-ray radiation ( $\lambda=1.5406 \text{ \AA}$ ). Elemental analysis including C, H, N and S was carried out by Vario Micro Cube Elemental Analyzer. TGA analysis was recorded by a Pyris1 of PerkinElmer Instruments under  $\text{N}_2$  atmosphere with a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$ . MS spectrum was performed on Agilent 1100 LC/MSD Trap Spectrometer. EPR spectra were conducted at room temperature on a Bruker EMX nano spectrometer. XPS data was acquired by Thermo Fisher EscaLab 250Xi. UV-visible absorption spectra were recorded by Shimadzu UV-2600.

### Synthesis of BDBDT



**Scheme S1.** Synthetic route of BDBDT

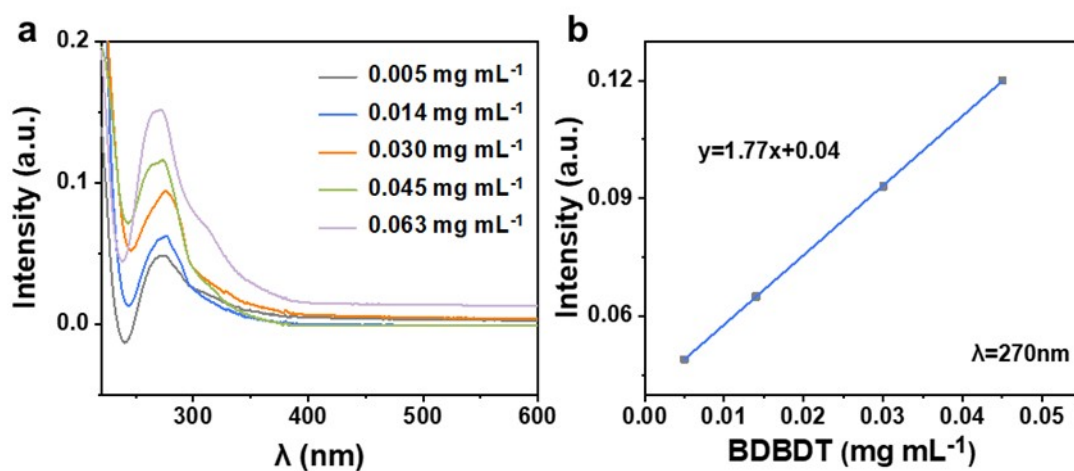
Benzo[5,6][1,4]dithiino[2,3-a]benzo[5,6][1,4]dithiino[2,3-c]thianthrene[BDBDT] was synthesized according to the procedure described in a previous report<sup>1</sup>. To a 50ml round bottom flask containing  $\text{K}_2\text{CO}_3$  (0.63 g, 4.5 mmol) was added DMF (10 mL), hexafluorobenzene (57  $\mu\text{L}$ , 0.5 mmol), 1,2-benzenedithiol (173  $\mu\text{L}$ , 1.5 mmol) and THF (10 mL) under argon atmosphere. The reaction was heated at  $120 \text{ }^\circ\text{C}$  for 2 days. The yellow mixture was concentrated and precipitated into an excess of aqueous 1 M HCl solution. The precipitate was filtered, washed with deionized water and methanol sequentially and finally dried under vacuum to afford a creamy-white solid (205 mg, 84%). The characterizations are consistent with the literature reported.  $^1\text{H}$  NMR (400 MHz, DMSO-

d<sub>6</sub>)  $\delta$  7.73 (dd, 6H), 7.43 (dd, 6H). Elemental analysis (%): C, 58.208; S, 39.036; H, 2.647.

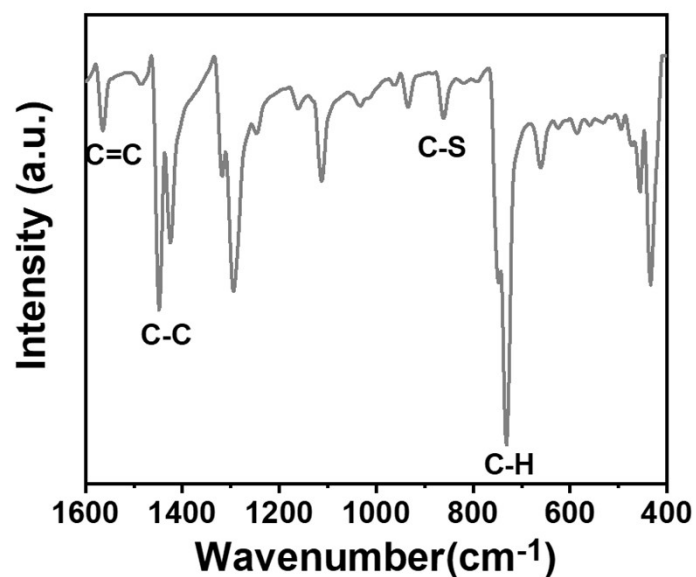
### **Electrochemical measurements**

The working electrode was prepared by mixing active material, CNT and PEDOT/PSS at a weight ratio of 5:4:1 in deionized water uniformly, if without special note. The slurry was then applied to Al foil and dried overnight at 80 °C under vacuum to remove water. The foil was cut into 14 mm diameter disks with an area mass loading of 0.8-2 mg cm<sup>-2</sup> of active material. In the Ar-filled glovebox, 2032 coin cells were assembled using Li metal as counter electrode, glass fiber membrane (Whatman, GF/B) and polypropylene (PP) membrane (Celgard2500) as separator and 1 M LiClO<sub>4</sub> in 1:1 (v/v) ethylene carbonate (EC) and diethyl carbonate (DEC) as the electrolyte. CNT half-cells were obtained similar to BDBDT half-cells. CNT and PEDOT/PSS were mixed uniformly with a weight ratio of 9:1 and coated on the surface of Al foil. The counter electrode, separator, and electrolyte were the same as BDBDT half-cells.

Galvanostatic discharge and charge and galvanostatic intermittent titration technique (GITT) tests were measured in the potential ranging from 3.0 to 4.5 V (vs. Li/Li<sup>+</sup>) at different current densities using LANHE-CT2001A system (Wuhan, China). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out by BioLogic VMP3 potentiostat system. CV tests were conducted in the potential range of 3.0 - 4.5 V (vs. Li/Li<sup>+</sup>). EIS was performed in the frequency ranging from 1 MHz to 10 mHz. GITT was tested at 0.2 A g<sup>-1</sup> in the potential range of 3.0 - 4.5 V (vs. Li/Li<sup>+</sup>) with a constant current pulse of 1.5 min and a relax of 0.5 h.



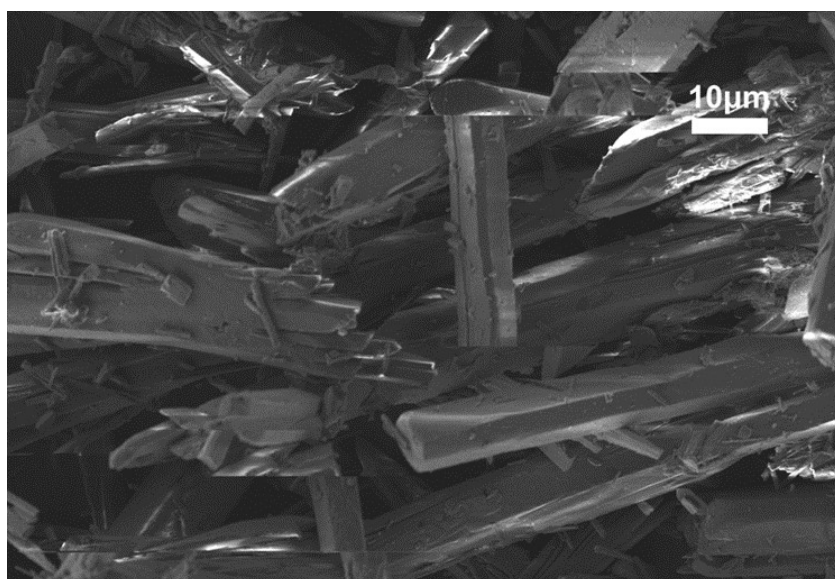
**Fig. S1.** (a) The UV-vis spectra of BDBDT dipping in 1 M LiClO<sub>4</sub> EC/DEC, (b) A linear fit of solubility in the UV and intensity of absorption peaks. According to the linear relationship  $y=1.77x+0.04$ , the maximum absorption peak intensity of 0.151 corresponds to a saturation concentration of 0.063 mg mL<sup>-1</sup> ( $\sim 10^{-5}$  M) in the electrolyte.



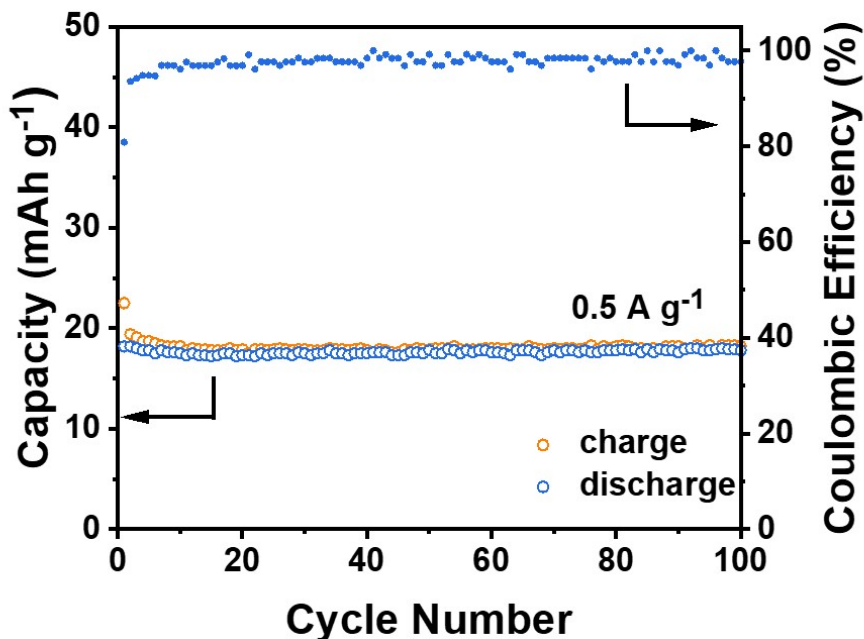
**Fig. S2** FTIR spectra of BDBDT

**Table S1.** Elemental analysis data of BDBDT ( $C_{24}H_{12}S_6$ )

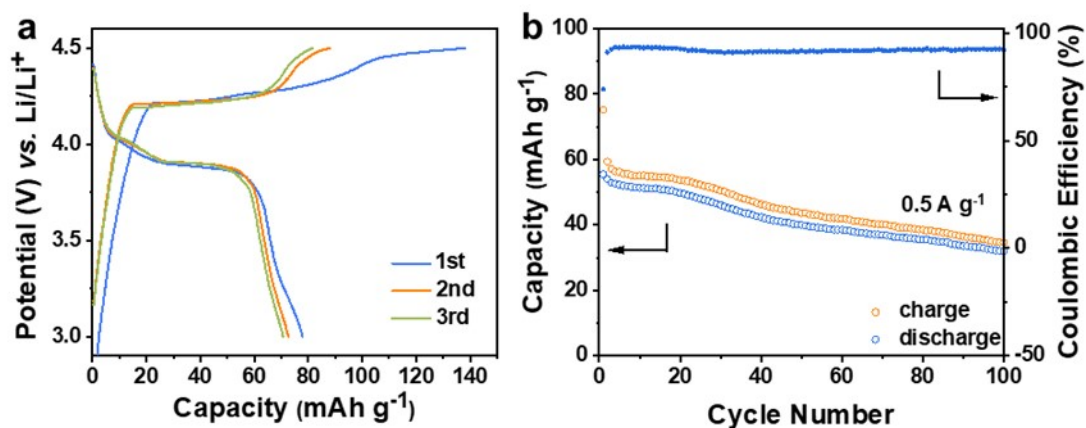
|                                  | C       | H      | S       |
|----------------------------------|---------|--------|---------|
| Calculated for $C_{24}H_{12}S_6$ | 58.50%  | 2.45%  | 39.04%  |
| Found                            | 58.208% | 2.647% | 39.036% |



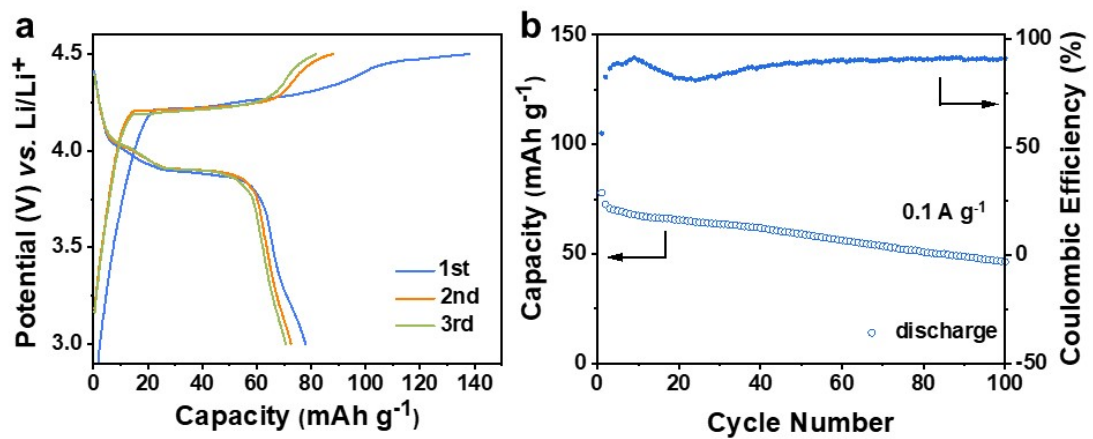
**Fig. S3** SEM images of BDBDT



**Fig. S4** The cycling performance at  $0.5 \text{ A g}^{-1}$  of CNT for LIBs in the potential range of 3.0-4.5V (vs  $\text{Li/Li}^+$ ).

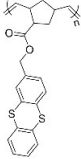
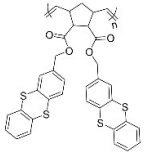
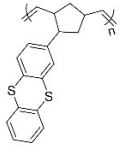
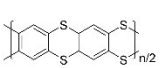
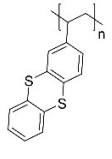
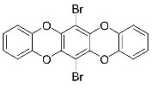
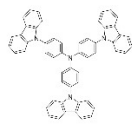
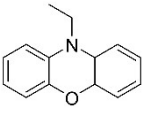
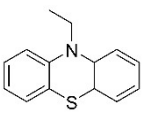


**Fig. S5.** (a) charge–discharge curves of BDBDT at different cycles at  $0.5 \text{ A g}^{-1}$ , (c) cycling performance at  $0.5 \text{ A g}^{-1}$ . The electrodes were prepared by mixing BDBDT, super P (conductive additive) and PVDF (binder) with a mass ratio 5:4:1. The performance based on super P and PVDF showed lower capacity and poorer cyclability than those based on CNT and PEDOT:PSS, probably due to the higher conductivity of PEDOT:PSS than PVDF and the intercrossing conductive channels forming by CNT.

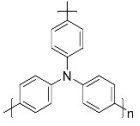
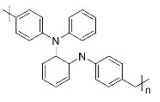


**Fig. S6.** (a) charge–discharge curves of BDBDT at different cycles at 0.1 A g<sup>-1</sup>, (c) cycling performance at 0.1 A g<sup>-1</sup>.

**Table S2.** Electrochemical performance of BDBDT and analogues as cathodes.

| Active material structure   | Content of active materials | Electrolyte                  | Discharge potential (V) | Average discharge potential (V) | Reversible capacity (mAh g <sup>-1</sup> ), current density (A g <sup>-1</sup> ) | Capacity retention (current (A g <sup>-1</sup> ), cycle number) | Ref.             |
|---|-----------------------------|------------------------------|-------------------------|---------------------------------|--|---|------------------|
| <b>BDBDT</b>  | <b>50%</b>                  | <b>1 M LiClO<sub>4</sub></b> | <b>3.9</b>              | <b>3.9</b>                      | <b>78, 0.1</b>   | <b>86.3%</b>  | <b>This work</b> |
|   |                             | <b>EC/DEC</b>                |                         |                                 | <b>73, 0.5</b>   | <b>(0.5 A g<sup>-1</sup>, 100)</b>                              |                  |
|   |                             | <b>(1:1 v/v)</b>             |                         |                                 |  |   |                  |
|    | 50%                         | 1 M LiPF <sub>6</sub>        | 4.01                    | -                               | 66, 0.073  | 30.3%   | 2                |
|   |                             | EC/DMC                       |                         |                                 |  | (0.5 A g <sup>-1</sup> , 100)                                   |                  |
|   |                             | (1:1 v/v)                    |                         |                                 |  |   |                  |
|    | 50%                         | 1 M LiPF <sub>6</sub>        | 3.96                    | -                               | -  | -   | 2                |
|   |                             | EC/DMC                       |                         |                                 |  |   |                  |
|   |                             | (1:1 v/v)                    |                         |                                 |  |   |                  |
|   | 50%                         | 1 M LiPF <sub>6</sub>        | 3.92                    | -                               | -  | -   | 2                |
|   |                             | EC/DMC                       |                         |                                 |  |   |                  |
|   |                             | (1:1 v/v)                    |                         |                                 |  |   |                  |
|  | 70%                         | 0.10 M                       | 3.9                     | -                               | 71, -  | -   | 3                |
|   |                             | [NBu <sub>4</sub> ]          |                         |                                 |  |   |                  |
|   |                             | [BF <sub>4</sub> ] in        |                         |                                 |  |   |                  |
|   |                             | CH <sub>3</sub> CN           |                         |                                 |  |   |                  |
|  | 40%                         | 1 M LiClO <sub>4</sub>       | 3.9                     | 3.85                            | 105, 0.106   | 81.5%   | 4                |
|   |                             | EC/DMC                       |                         |                                 |  | (0.106 A g <sup>-1</sup> , 250)                                 |                  |
|   |                             | (3:7 v/v)                    |                         |                                 |  |   |                  |
|   |                             | 1:1.1 (molar                 |                         |                                 |  |   |                  |
|   |                             | ratio)                       |                         |                                 |  |   |                  |
|  | 50%                         | LiFSI/DMC                    | 4.0, 4.4                | 3.8                             | 108, 0.12  | 66.1%   | 5                |
|   |                             |                              |                         |                                 |  | (0.6 A g <sup>-1</sup> , 50)                                    |                  |
|  | 63%                         |                              | 3.6                     | -                               | 92, 0.1  | 48%   | 6                |
|   |                             |                              |                         |                                 |  | (1.0 A g <sup>-1</sup> , 5000)                                  |                  |
|  | 40%                         | 5 m LiClO <sub>4</sub>       | 3.17, 3.82              | 3.4                             | 244, 0.3   | 86%   | 7                |
|   |                             | in EC/                       |                         |                                 |  | (0.3 A g <sup>-1</sup> , 100)                                   |                  |
|   |                             | DMC                          |                         |                                 |  |   |                  |
|  | 40%                         | 5 m LiClO <sub>4</sub>       | 3.2, 3.9                | 3.5                             | 185, 0.3   | 79%   | 7                |
|   |                             | in EC/                       |                         |                                 |  | (0.3 A g <sup>-1</sup> , 100)                                   |                  |
|   |                             | DMC                          |                         |                                 |  |   |                  |



|   |     |   |          |   |          |                                       |   |
|---|-----|---|----------|---|----------|---------------------------------------|---|
|  | 50% | 1 M LiPF <sub>6</sub><br>(EC/DMC/<br>DEC) | 3.7      | - | 94, 0.02 | 95%<br>(0.02 A g <sup>-1</sup> , 20)  | 8 |
|  | 70% | 1 M LiPF <sub>6</sub><br>(EC/DEC)         | 2.9, 3.7 | - | 146,     | 95%<br>(0.02 A g <sup>-1</sup> , 800) | 9 |

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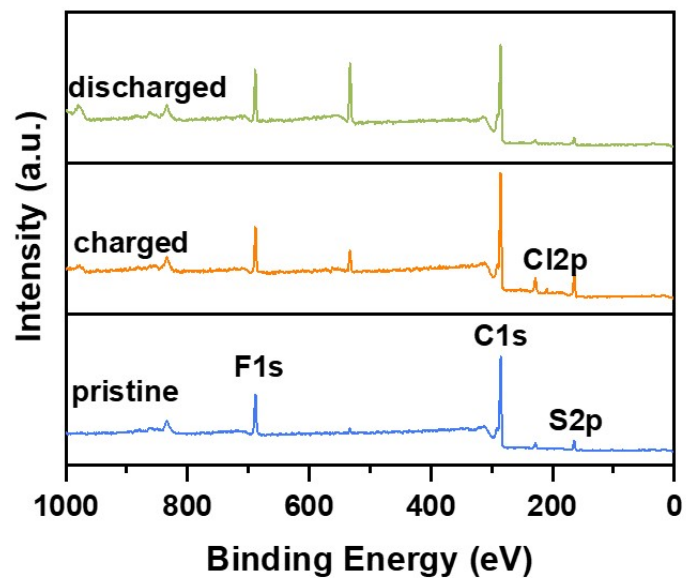


Fig. S7 XPS spectra of BDBDT cathode in different states.

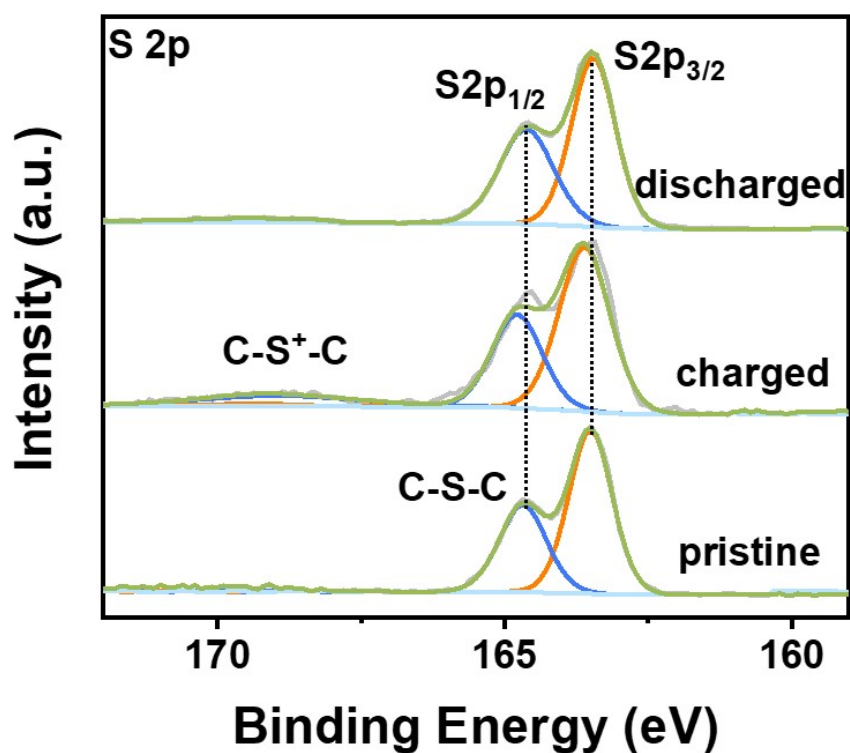
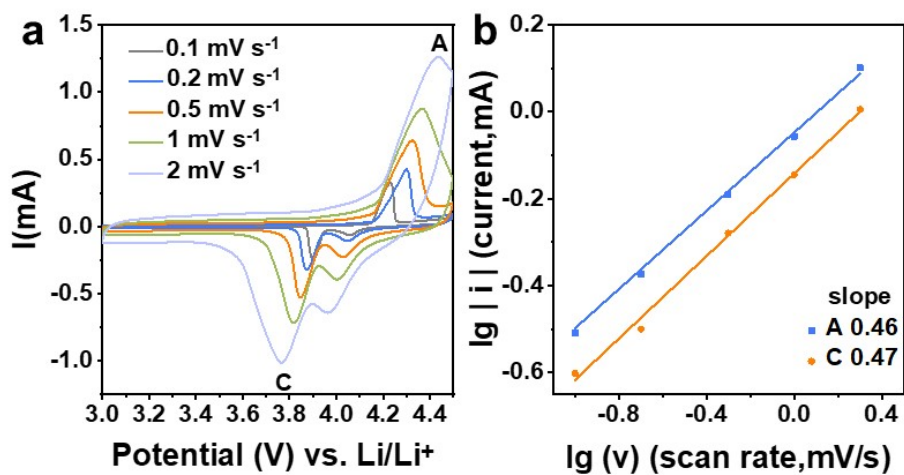


Fig. S8 High-resolution S 2p XPS spectra. Blue line: S 2p<sub>1/2</sub>, orange line: S 2p<sub>3/2</sub>.

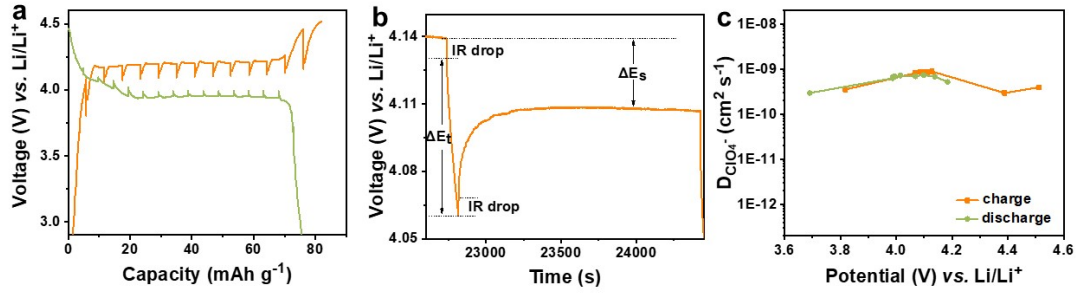


**Fig. S9** (a) CV curves at different scan rates, (b) log relationship between the absolute value of scan rate and peak current. After the analysis of the CV curves for different scan rates and according to the equations<sup>10, 11</sup>:

$$i = av^b$$

$$\log i = b \times \log v + \log a$$

where  $i$  is the test current,  $v$  is the scan rate,  $a$  and  $b$  are adjustable parameters, and if the slope  $b$  is close to 1, the electrochemical reaction is mainly controlled by capacitive effects, and if the slope  $b$  is close to 0.5, the process is controlled by ion diffusion.

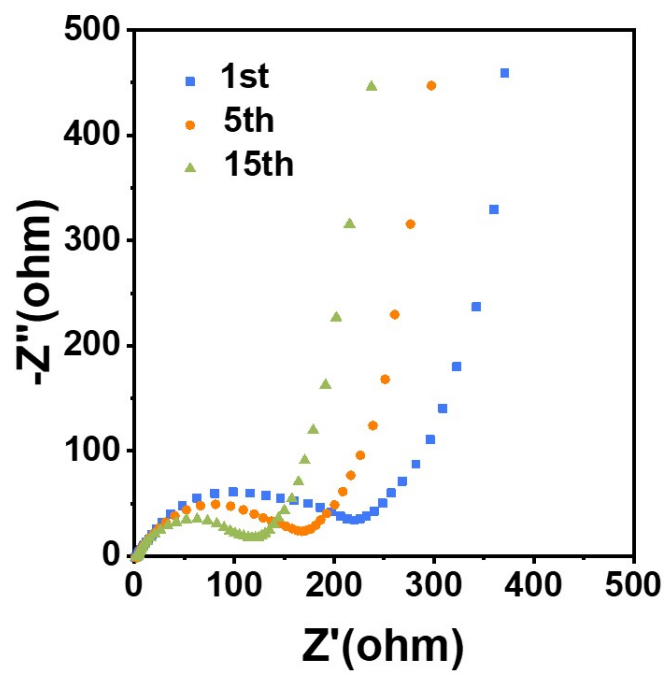


**Fig. S10** (a) Full charge-discharge cycle, (b) a typical step of discharge curve and (c) The  $\text{ClO}_4^-$  diffusion coefficient ( $D_{\text{ClO}_4^-}$ ) of BDBDT as cathode in LIBs.

The diffusion coefficients of  $\text{ClO}_4^-$  in BDBDT ( $D_{\text{ClO}_4^-}$ ) was calculated using the GITT diffusivity formula<sup>12</sup>:

$$D_{GITT} = \frac{4}{\pi\tau} \left( \frac{m_B V_M}{M_B S} \right)^2 \left( \frac{\Delta E_S}{\Delta E_t} \right)^2$$

$\tau$  is the pulse time;  $m_B$  is the active material loading of BDBDT (86 mg),  $V_M$  is the molar volume of BDBDT ( $0.0628 \text{ cm}^3$ ),  $S$  represents the electrode-electrolyte contact area, and  $M_B$  is the molar mass;  $\Delta E_S$  represents the pulse-induced potential change, which is the potential difference between the steady state and the initial state at each step;  $\Delta E_t$  is the potential change due to constant current charging (discharging), which is the total potential change, excluding the IR drop. The molar volume of each repetition unit ( $347.2 \text{ cm}^3/\text{mol}$ ) is calculated by measuring the mass and total volume of the pressed BDBDT flake.



**Fig. S11** Nyquist plots in a charged state after different numbers of cycles.

**Table S3.** Charge transfer resistance ( $R_{ct}$ ) of the battery after 1, 5, 15 charge-discharge cycles

| Cycle number          | 1st | 5th | 15th |
|-----------------------|-----|-----|------|
| $R_{ct}$ ( $\Omega$ ) | 220 | 168 | 120  |

## References

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