

## Supplementary Information

### **Napthalene Diimide Derivative Based Organic Cocystal Frameworks as Cathode Electrodes for Stable Lithium Batteries**

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## Experimental Procedures

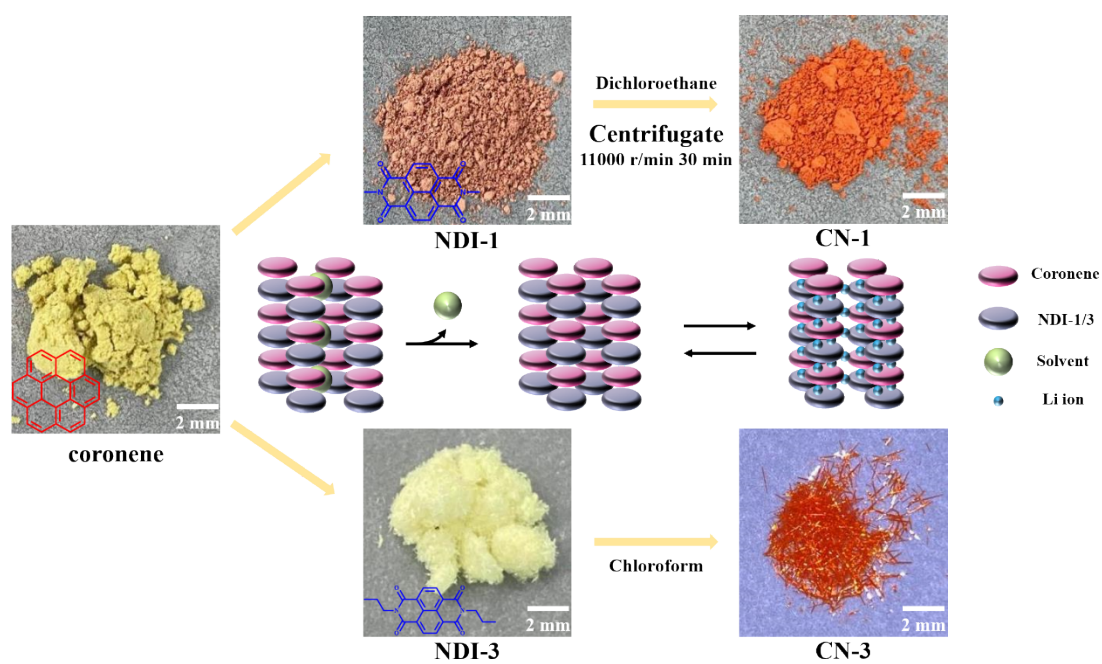
**Synthesis of CN-1 and CN-3.** First, NDI-R (R = Methyl or Propyl group) was firstly dissolved in dichloroethane (R = Methyl) or chloroform (R = Propyl group) with coronene in a molar ratio of 1:1 at the total concentration of about 4 mg/mL. Thanks to the good solubility of parent components, it was a very quick process to get a limpid solution without extra sonication. Then, plenty of two designed cocrystals in orange ribbon-shape were obtained by centrifugation at 11000 rpm for about 30 min, washed with ethanol and dried under vacuum for later electrode preparation. 30 min centrifugal process could generate at least 300 mg complexes using 60 mL mixed solution.

**Cocrystal Electrode Fabrication and Coin Cell Assembly.** Mixtures of the electroactive cocrystal, conductive carbon black and poly-(vinylidene difluoride) (PVDF) binder in a mass ratio of 8:1:1 were grinded completely in a mortar, and then uniform slurry were prepared by stirring for 12 h after adding some N-Methylpyrrolidone (NMP). The slurry was evenly scraped on the copper foil with a 100  $\mu\text{m}$  coating scraper and dried in a vacuum oven at a temperature of 60  $^{\circ}\text{C}$  for about 0.5 h. The dried copper foil with active material was cut into disk electrodes with a diameter of 12 mm. The 2032-type coin cells were assembled with Li metal disk (thickness of 1.1 mm) as anode, 1.0 M LiTFSI in DME:DOL 1:1 Vol% with 2.0%  $\text{LiNO}_3$  as the electrolyte and trilayer membrane (Celgard 2320) as the separator. For a long solubility test (~one day), the solubility of CN-1' in the electrolyte is less than 0.1 mg/mL, and CN-3 is about 0.35 mg/mL.

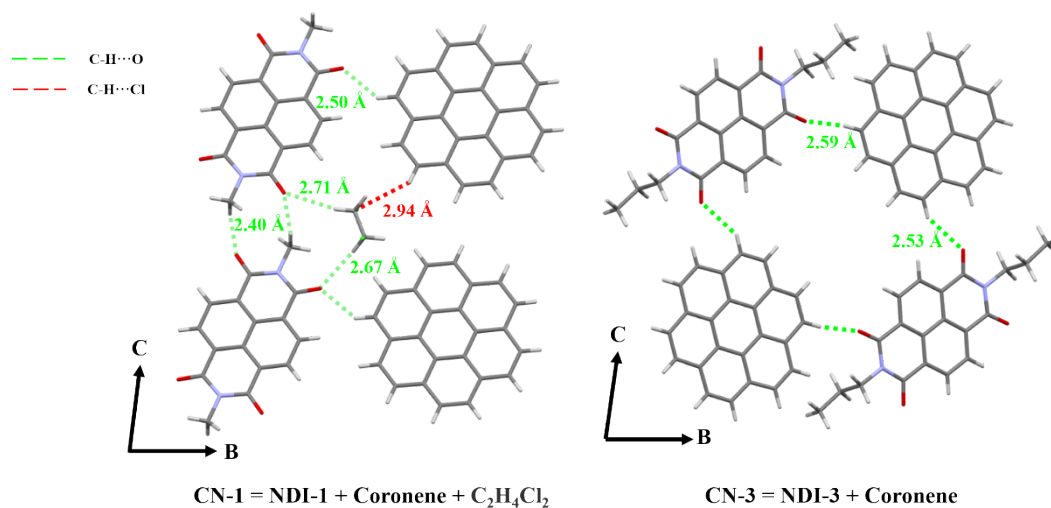
**Material Characterization.** The data of powder X-ray diffractometry (XRD) pattern was recorded with a scan rate of 0.2 s in the region from 3 to 30 $^{\circ}$  using Cu K $\alpha$  radiation on an X-ray powder diffractometer (Burger D8 Advance A25). Single crystal X-ray diffractometry of the two cocrystal were conducted via Bruker D8 Quest. Thermo-gravimetry/differential thermal analyses (TG/DSC) of cocrystals were tested in the atmosphere of air from 25 to 800  $^{\circ}\text{C}$  at a heating rate of 10  $^{\circ}\text{C}\cdot\text{min}^{-1}$ . The morphology and surface element composition were characterized by SEM (Hitachi S4800) and XPS (KRATOS Axis Supra). The titration experiments for CN-1 and CN-3 were carried out in dichloroethane and chloroform, respectively, for the fluorescence emission tracking, to figure out the association constants. Li-ion adsorption models were calculated by sorption module.

**Electrochemical Characterization.** The cycling stability and rate capability tests were performed using a Land battery testing system. The cell was characterized by cyclic voltammetry (CV) at multistep sweeping rates and galvanostatic cycling.

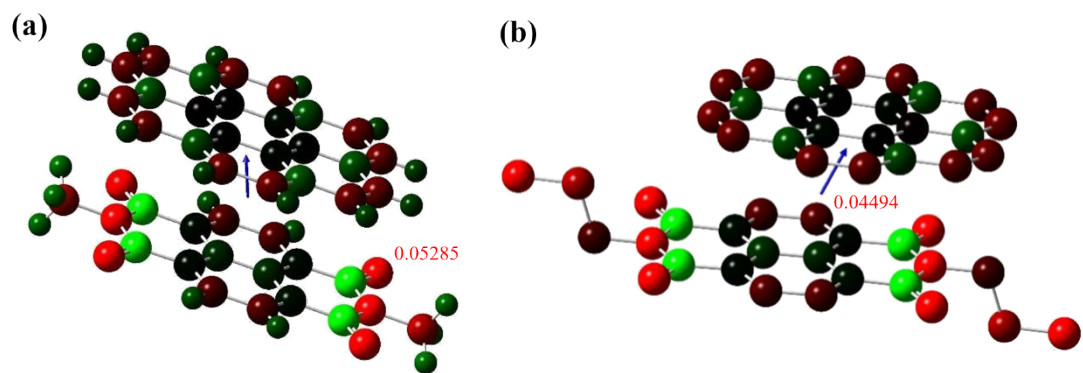
## Results and Discussion



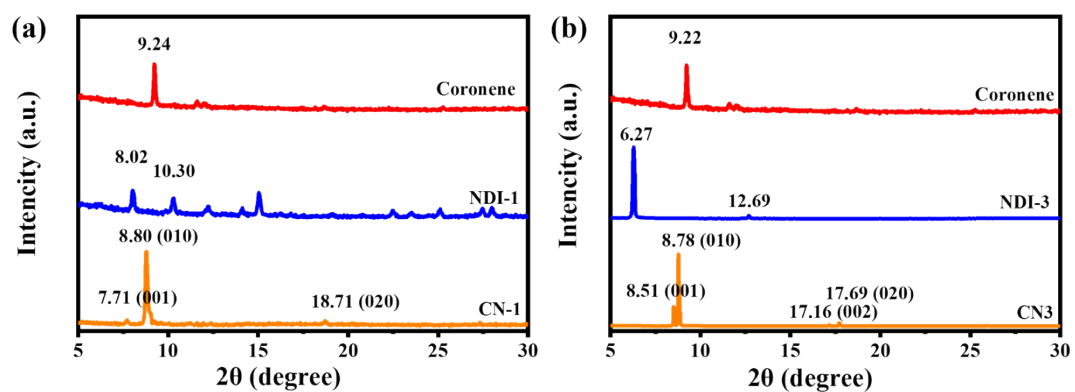
**Fig. S1** Schematic diagram of cocystal preparation and lithiation.



**Fig. S2** Short contacts in CN-1 and CN-3 cocrystals.



**Fig. S3** The calculated mulliken charge distribution of (a) CN-1 and (b) CN-3 cocrystals at the DFT level with B3LYP/6-31G\*.



**Fig. S4** XRD patterns of CN-1 and CN-3 cocrystals. It demonstrates the complete transition into complex from parent single-components.

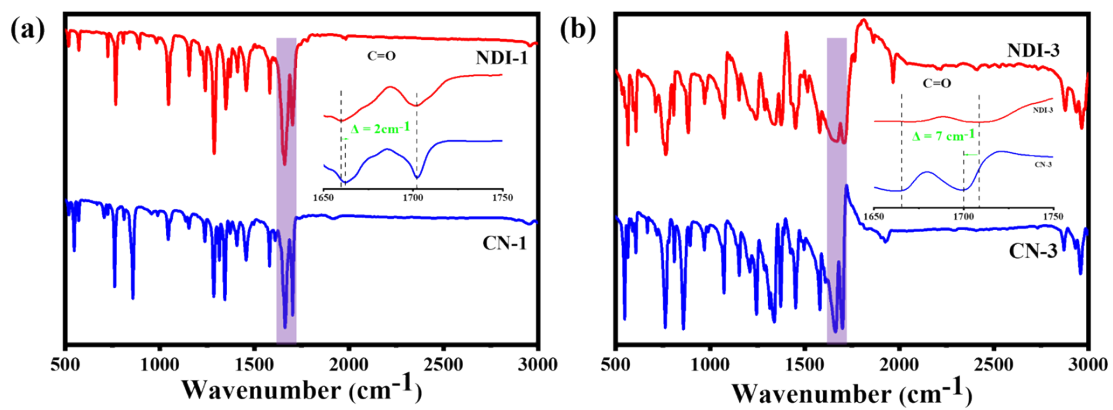
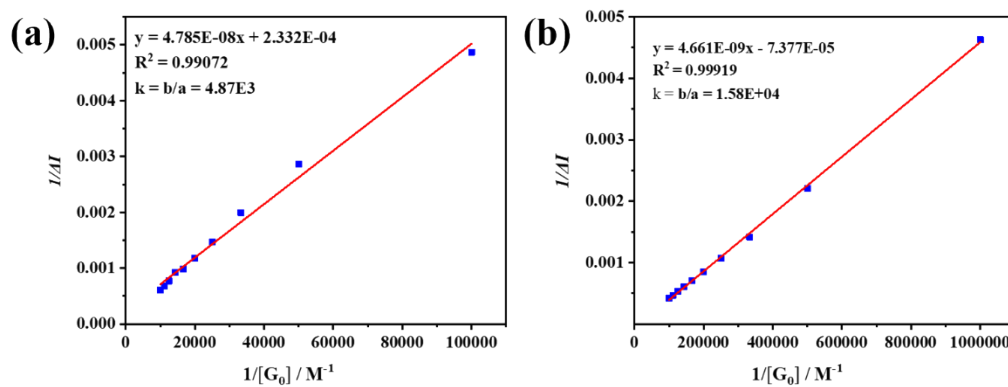
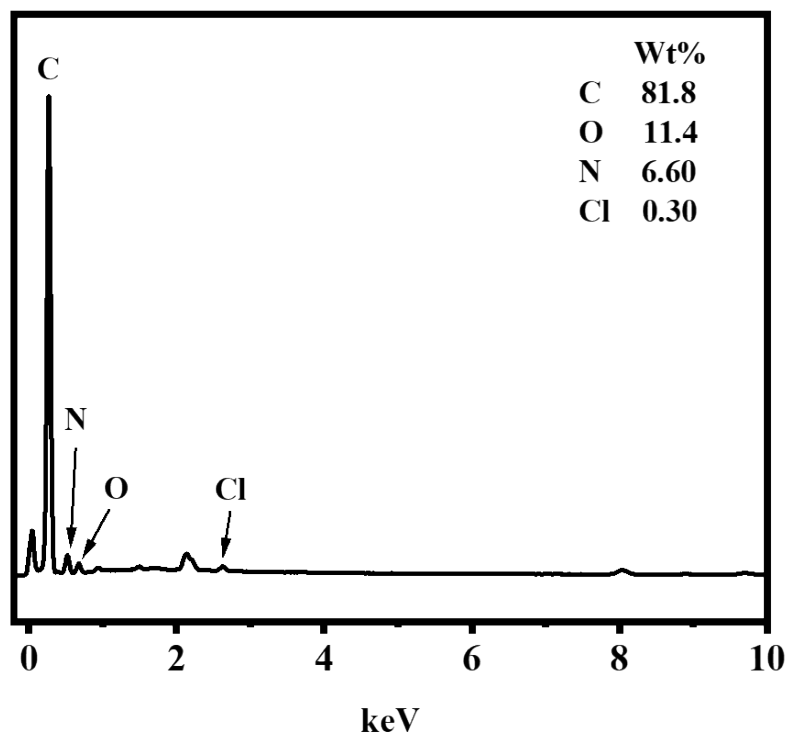


Fig. S5 FT-IR spectra of (a) CN-1 and (b) CN-3 cococrystals.

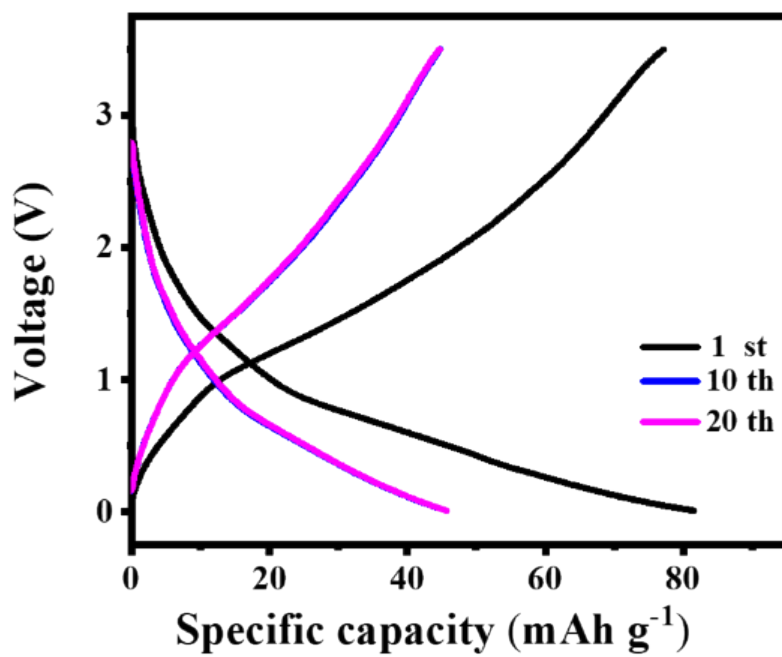




**Fig. S6** The fitting diagrams of CN-1 and CN-3 systems.



**Fig. S7** EDS of main element in CN-1 electrode. (Cl in CN-1 cocystal is 8 Wt%)



**Fig. S8** Voltage-capacity profile and cycling performance of CN-3 at 0.5 A·g<sup>-1</sup>.

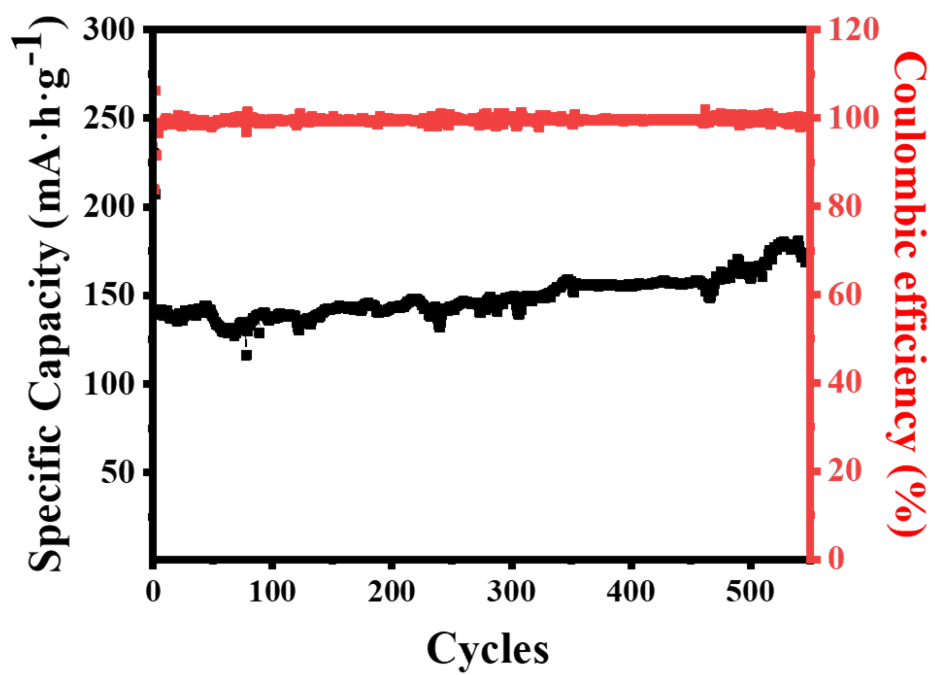
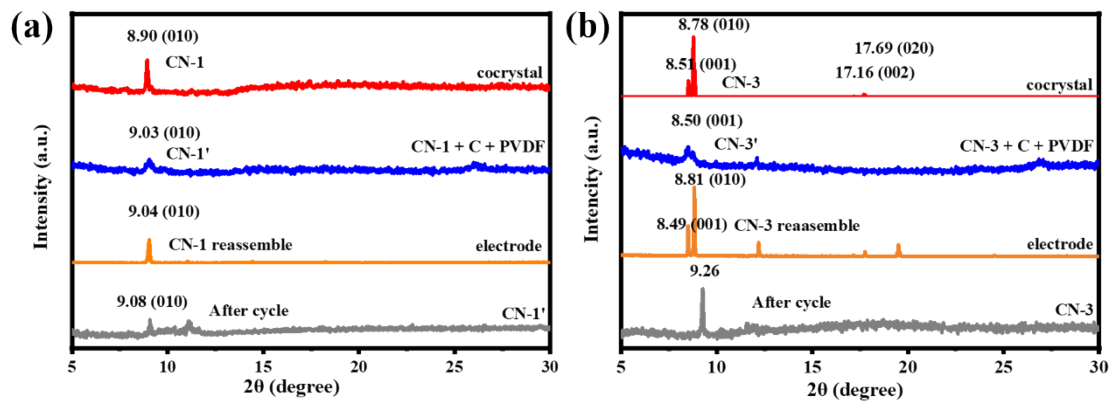
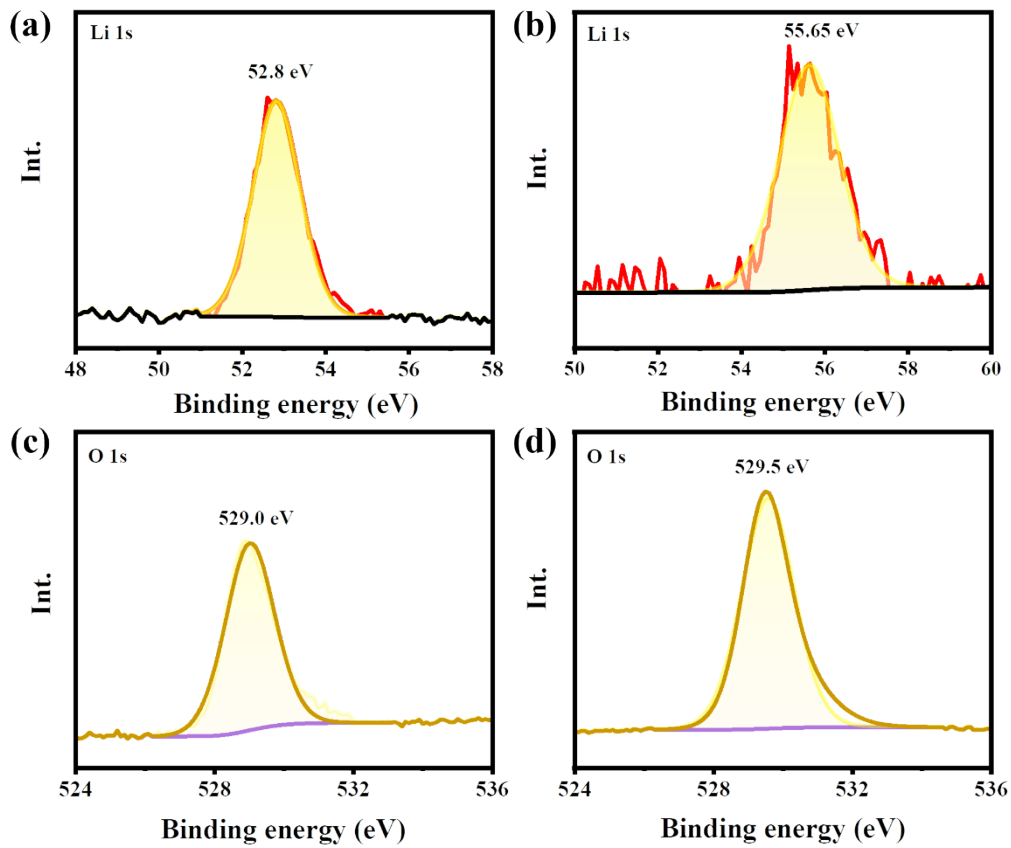


Fig. S9 Cycling performance of CN-1' at 0.5 A·g<sup>-1</sup>.



**Fig. S10** XRD pattern of (a) CN-1' and (b) CN-3 before and after cycle.



**Fig. S11** Li 1s XPS spectra of (a) CN-1 and (b) CN-3 samples, and O 1s XPS spectra of CN-1 sample (c) before and (d) after cycling.

**Table S1.** Crystal data and structure refinements for CN-1, and CN-3 cocrystals.

	CN-1	CN-3
Formula	C <sub>42</sub> H <sub>26</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	C <sub>44</sub> H <sub>30</sub> N <sub>2</sub> O <sub>4</sub>
Formula weight	693.55	650.70
Temperature (K)	197.00	193.00
Wavelength (Å)	0.71073	0.71076
Crystal system	triclinic	triclinic
space group	P-1	P-1
<b>Unit cell dimensions</b>		
<i>a</i> (Å)	7.200(9)	7.551(9)
<i>b</i> (Å)	10.109(13)	10.097(13)
<i>c</i> (Å)	11.007(14)	10.507(13)
$\alpha$ (°)	94.520(9)	86.191(5)
$\beta$ (°)	94.515(8)	76.039(5)
$\gamma$ (°)	103.410(8)	79.920(5)
Volume (Å <sup>3</sup> )	772.95(17)	765.18(17)
<i>Z</i>	1	1
Density (calculated) (g/cm <sup>3</sup> )	1.490	1.412
Absorption coefficient (mm <sup>-1</sup> )	2.307	0.091
<i>F</i> (000)	358.0	340.0
Crystal size (mm)	0.13 × 0.12 × 0.10	0.15 × 0.13 × 0.08
$\theta$ range (°)	2.648 to 24.989	5.636 to 55.068
Limiting indices	-8 ≤ <i>h</i> ≤ 7 -12 ≤ <i>k</i> ≤ 12 -13 ≤ <i>l</i> ≤ 13	-9 ≤ <i>h</i> ≤ 9 -13 ≤ <i>k</i> ≤ 13 -13 ≤ <i>l</i> ≤ 13
Reflections collected	9604	12719
<i>R</i> (int)	0.0469	?
Absorption correction	Semi-empirical from equivalents Absorption correction	
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup> Refinement method	
Data / restraints / parameters	2832 / 0 / 227	12719 / 0 / 228
<i>R</i> [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0613 <i>wR</i> <sub>2</sub> = 0.1674	<i>R</i> <sub>1</sub> = 0.0700 <i>wR</i> <sub>2</sub> = 0.1546
<i>R</i> (all data)	<i>R</i> <sub>1</sub> = 0.0718 <i>wR</i> <sub>2</sub> = 0.1788	<i>R</i> <sub>1</sub> = 0.1226 <i>wR</i> <sub>2</sub> = 0.1862
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.062	1.019
CCDC NO.	2190909	2190910

**Table S2.** Performances of NDI derivatives and NDI-1 cocrystal as the cathode electrodes.

material	$C_i$ (mAh·g <sup>-1</sup> )	cycling stability
NDIH <sup>[1]</sup>	170	20% after 10 cycles at 0.5 C
NDILi <sup>[2]</sup>	131	89% after 100 cycles at 0.5 C
NDIMe <sup>[2]</sup>	167	12% after 40 cycles at 0.5 C
NTCDI(MeCarb-Na) <sub>2</sub> <sup>[3]</sup>	157	93% after 50 cycles at 0.1 C
NTCDI(EtSulf-Na) <sub>2</sub> <sup>[3]</sup>	117	96% after 50 cycles at 0.1 C
DP-NTCDI-250 <sup>[4]</sup>	170	70% after 100 cycles at 0.1 C
CN-1(this work)	230	78% after 600 cycles at 0.5 A·g <sup>-1</sup>



## Reference

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