

# Fusion of Nitro Isomers of Naphthoquinone Enhances Capacity and Cyclability in Zn-ion Batteries

## Supporting information

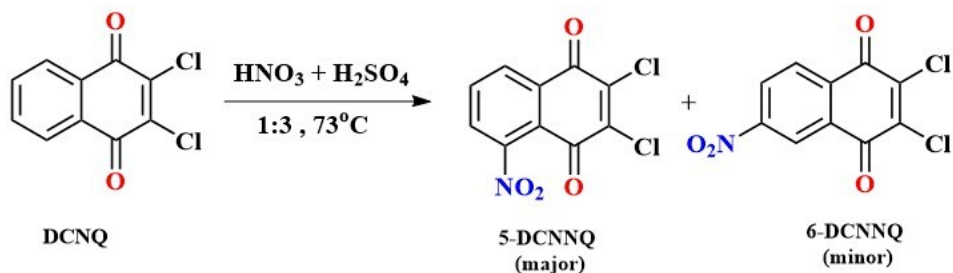
### S.1. Materials and characterisation:

98% pure 2,3-dichloro-1,4-naphthoquinone (DCNQ) was obtained from TCI chemicals. Sulfuric acid and nitric acid were purchased from Thermo Fisher Scientific. Super P carbon and PVDF were from Alfa Aesar Pvt. Ltd. Nafion ionomer solution (5 wt. %) and  $\text{Zn}(\text{OTf})_2$  were purchased from Sigma-Aldrich. All chemicals were used as received.  $^1\text{H}$  NMR of all active materials was recorded in 99% deuterated solvent or  $\text{CDCl}_3$ , purchased from Sigma-Aldrich, using a Bruker NMR spectrometer at 400 MHz. Melting points of the compounds were obtained by using the G LAB apparatus, and they were  $145\text{ }^\circ\text{C}$  ( $\pm 4$ ),  $175\text{ }^\circ\text{C}$  ( $\pm 3$ ), and  $170\text{ }^\circ\text{C}$  ( $\pm 3$ ) for 5-nitro 2,3-dichloro 1,4-naphthoquinone (5-DCNNQ), 6-nitro 2,3-dichloro 1,4-naphthoquinone (6-DCNNQ) and their mixture DCNNQmix, respectively. 5-DCNNQ crystals were obtained from a saturated solution of 5-DCNNQ in methanol (at  $50\text{ }^\circ\text{C}$ ) upon slowly cooling to room temperature, yielding colourless needle-like crystals. Single crystal X-ray diffraction was performed using Bruker D8 Venture diffractometer with PHOTON II detector operated with a molybdenum ( $\lambda(\text{MoK}\alpha) = 0.71073\text{ \AA}$ ) X-ray radiation. For structure solving, more than 4292 reflections are considered. APEX3-SAINT program (Bruker AXS) and SADABS program were used for preliminary determination of the cell constants, data collection, data refinement, and an absorption correction, respectively <sup>[1]</sup>. The data were acquired at 173 K, and the space group determination and structure solution was carried out using the SHELXT-2018/2 and SHELXL-2018/3 programs <sup>[2]</sup>. ORTEP-3 <sup>[3]</sup> for windows was used to draw the structure.

### S.2. Synthesis procedure of 5-nitro 2,3-dichloro 1,4-naphthoquinone (5-DCNNQ), 6-nitro 2,3-dichloro 1,4-naphthoquinone (6-DCNNQ):

The preparation 5/6-DCNNQ was done according to the literature report [4]. A mixture of fuming  $\text{HNO}_3$  (4.5 gm) and  $\text{H}_2\text{SO}_4$  (15 gm) was prepared in an ice bath. DCNQ (1.5 g, 0.66 mmol) was slowly added to the prepared solution and then heated at  $80^\circ\text{C}$  for 3 h. A dark brown solution was poured into the ice water (100 mL) to give a bright yellow precipitate. This yellow solid was filtered and washed with water and then collected by vacuum filtration. Column chromatography with ethyl acetate: hexane of 60:40 was used to separate the final product 5-DCNNQ (~ 69%, major) and 6-DCNNQ (~ 30%, minor).

5-DCNNQ:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.41 (d, 1H, ), 7.98 (t, 1H), 7.79 (d, 1H) pp. 6-DCNNQ:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  9.00 (d, 1H), 8.62 (dd, 1H), 8.42 (d, 1H).



**Scheme S1.** Synthesis scheme of 5-DCNNQ and 6-DCNNQ.

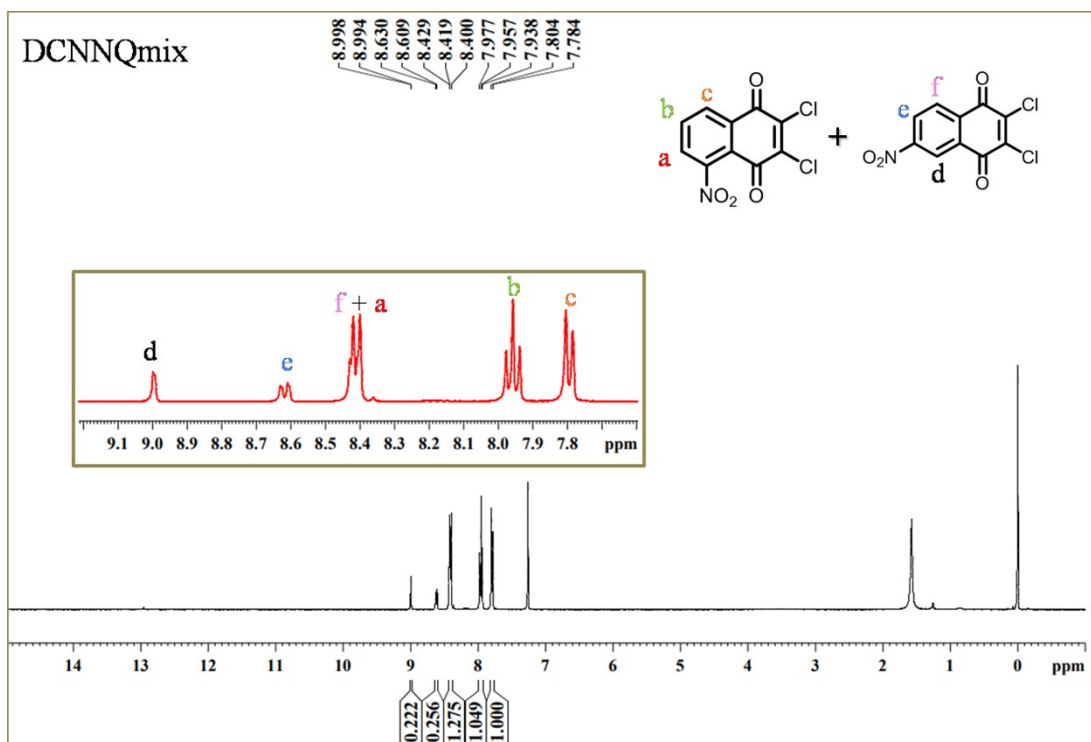


Fig. S1.  $^1\text{H-NMR}$  of the reaction mixture (DCNNQmix).

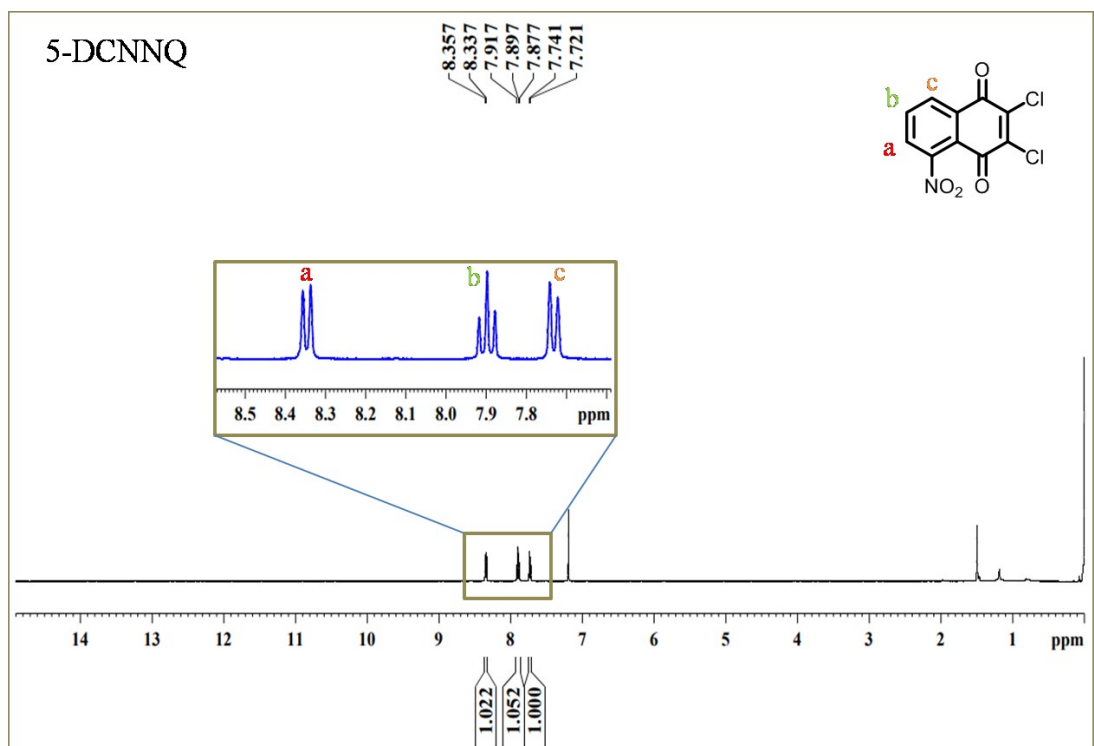
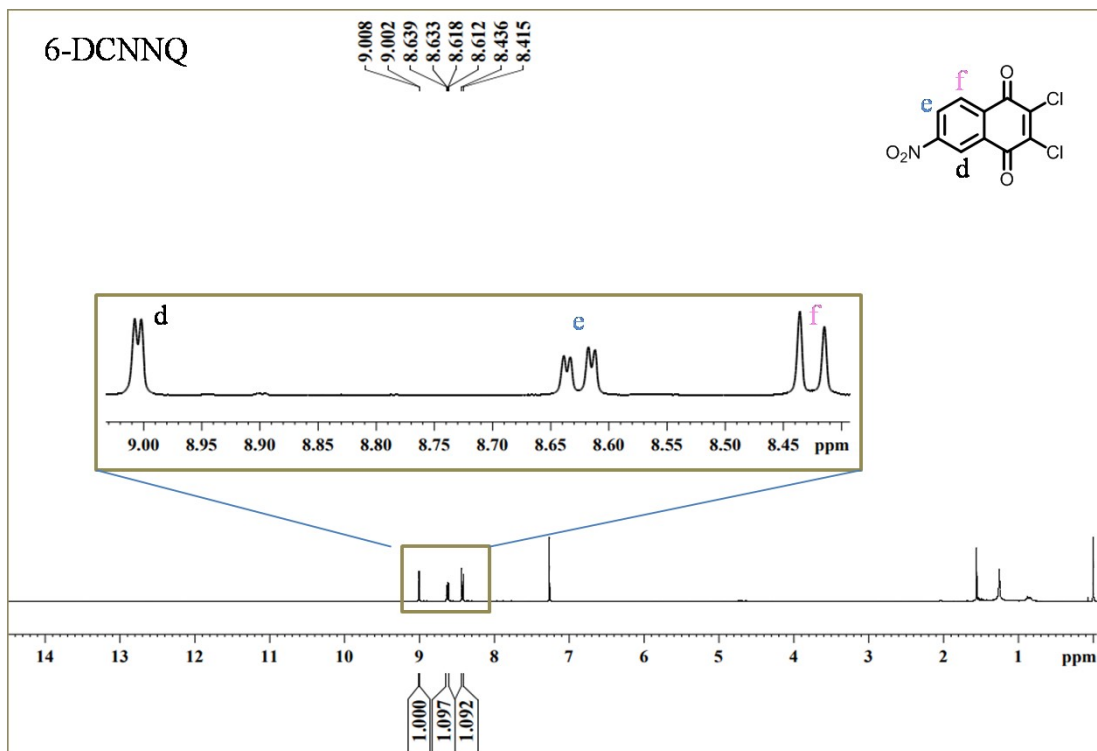


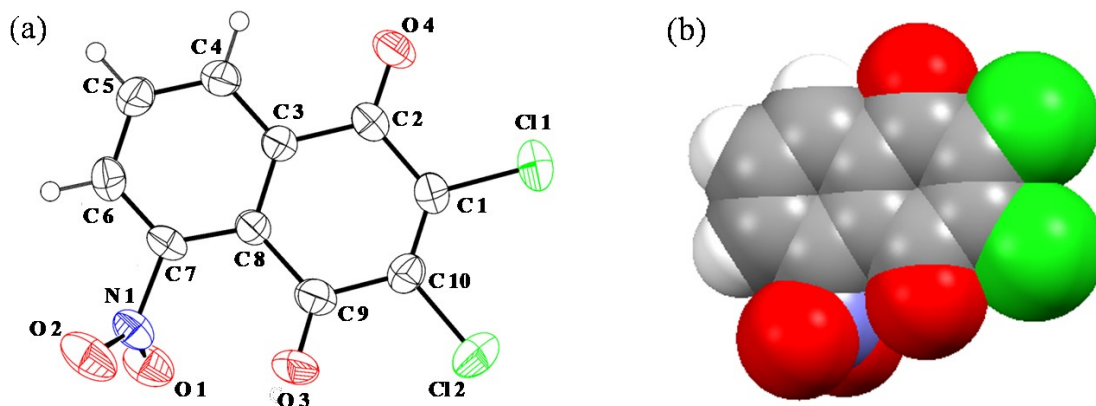
Fig. S2.  $^1\text{H-NMR}$  of 5-DCNNQ.



**Fig. S3.**  $^1\text{H-NMR}$  of 6-DCNNQ.

**Table S1.** Crystal structure parameters of 5-DCNNQ at low temperature.

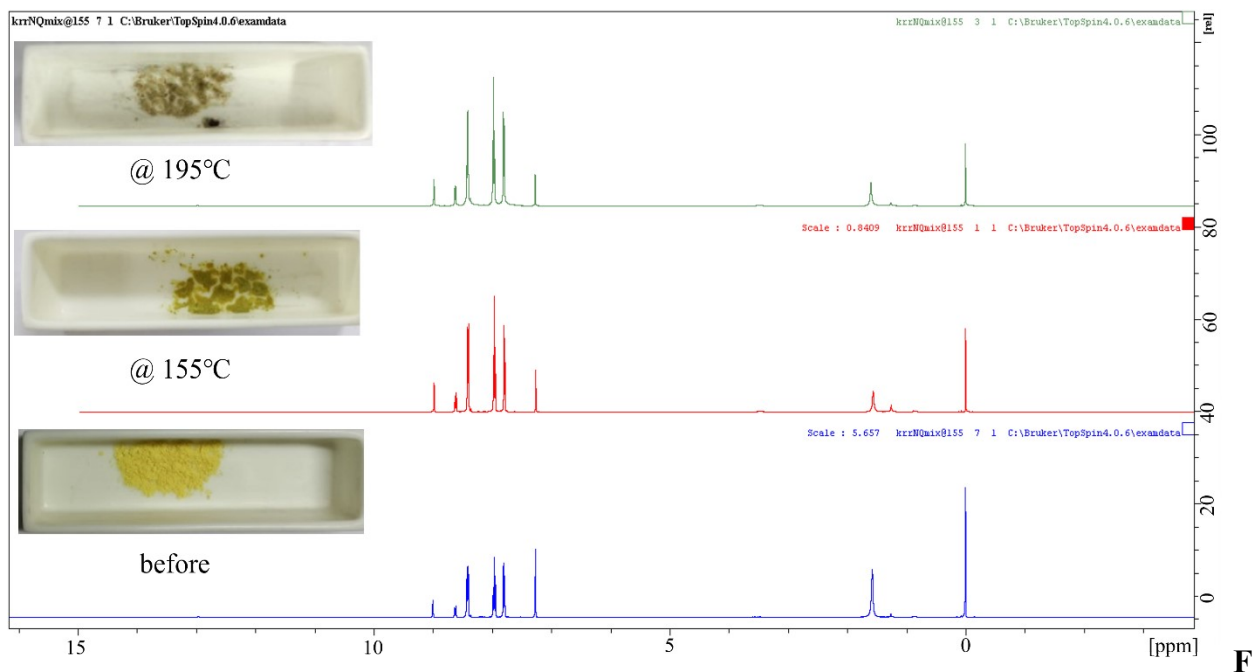
<b>CCDC number</b>	2325245
<b>Space group</b>	$P 2_1 / c$
<b>Crystal symmetry</b>	Monoclinic
<b>Cell parameters</b>	$a=9.1782 (18)$ , $b=14.990 (3)$ , $c=7.7606 (13)$ $\alpha = 90^\circ$ , $\beta = 102.925^\circ (6)$ , $\gamma = 90^\circ$ $V = 1040.7 \text{ \AA}^3$ $Z = 4$ Density = $1.736 \text{ g cm}^{-3}$ $R = 0.078$



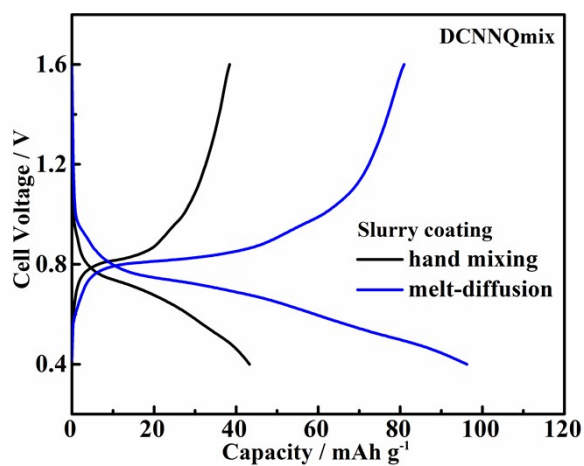
**Fig. S4.** Crystal structure of 5-DCNNQ (a) ORTEP diagram and (b) space fill form.



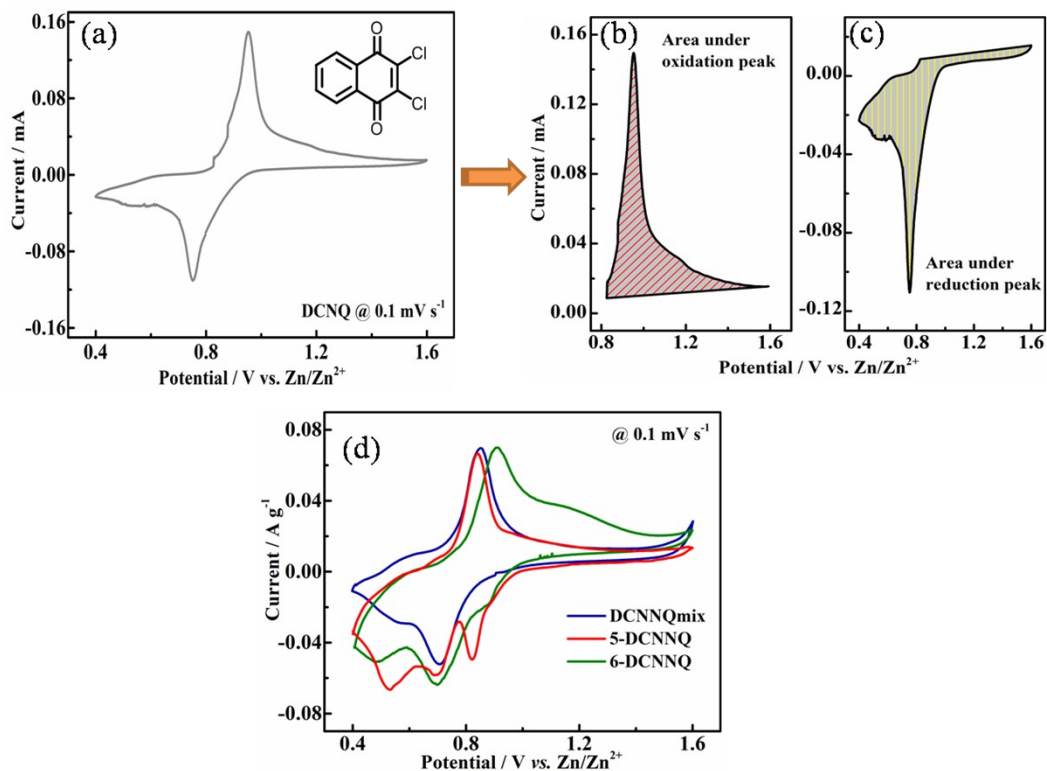
**Fig. S5.** Solubility tests of powder samples of 5-DCNNQ, DCNNQmix, and 6-DCNNQ in the electrolyte.



**ig. S6.** A comparative  $^1\text{H}$ -NMR of DCNNQmix before and after heating at 155 °C and 195 °C.



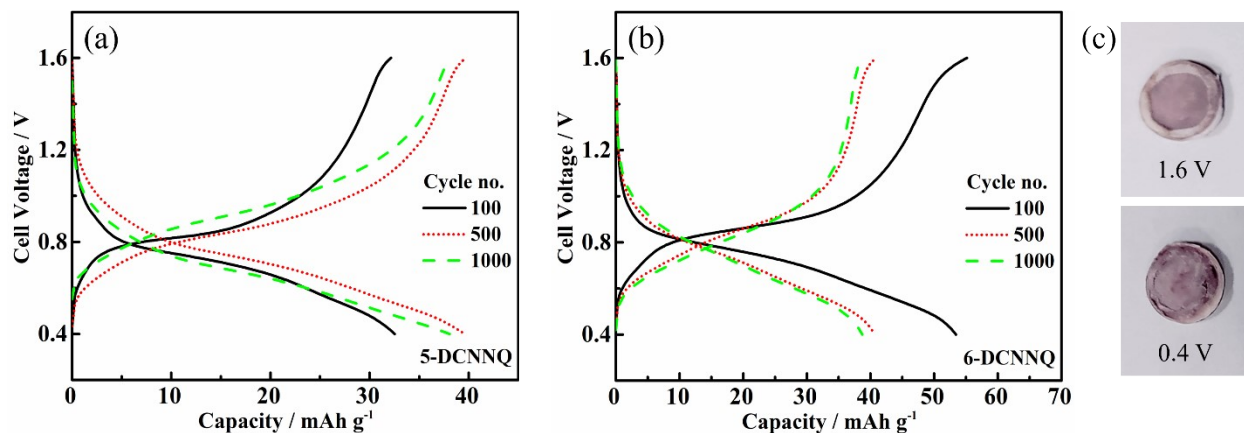
**Fig. S7.** Comparative charge-discharge plot (10<sup>th</sup> cycle) of Zn//DCNNQmix-Cathode cell at 0.1 A g<sup>-1</sup> of current density when slurry made with hand mixing and melt-diffusion technique.



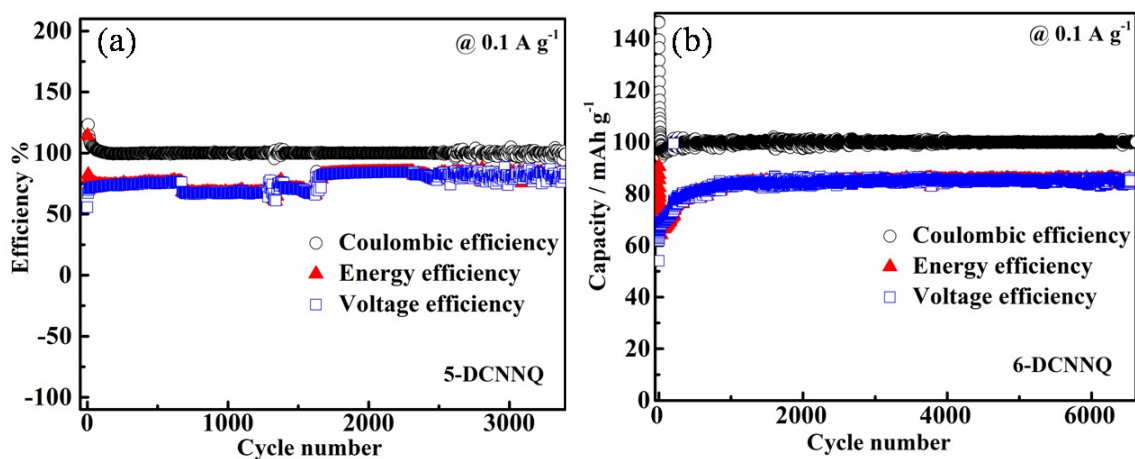
**Fig. S8.** Cyclic voltammetry (CV) of (a) DCNQ-Cathode recorded and its area under the (b) oxidation and (c) reduction peak at the scan rate of 0.1 mV s<sup>-1</sup>. (d) Comparative CV curve of 5-DCNNQ-Cathode, 6-DCNNQ-Cathode, and DCNNQmix-Cathode in two-electrode mode at the scan rate of 0.1 mV s<sup>-1</sup>.

**Table S2.** Depicts the area under the reduction and oxidation peaks and their ratio of 5- and 6-DCNNQ-Cathode and DCNNQmix-Cathode.

Electrode	Area under reduction peak ( $A_R$ ) / mW	Area under oxidation peak ( $A_o$ ) / mW	Ratio ( $A_R/A_o$ )
DCNQ	$2.316 \times 10^{-2}$	$1.944 \times 10^{-2}$	1.19
5-DCNNQ	$4.715 \times 10^{-2}$	$1.269 \times 10^{-2}$	3.7
6-DCNNQ	$3.885 \times 10^{-2}$	$1.553 \times 10^{-2}$	2.5
DCNNQmix	$2.063 \times 10^{-2}$	$8.203 \times 10^{-3}$	2.5

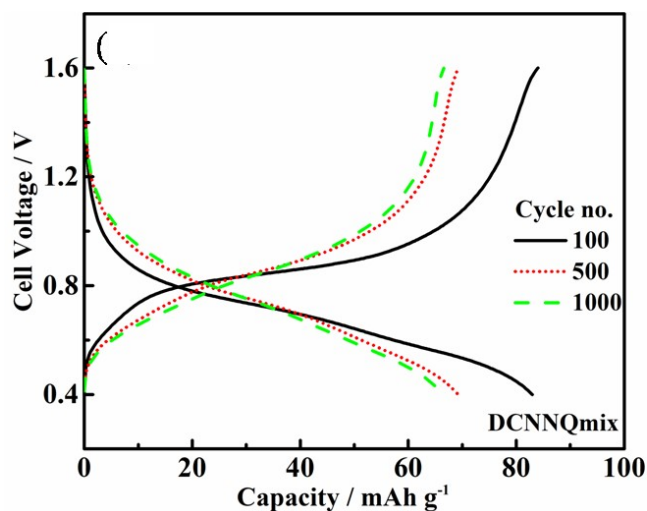


**Fig. S9.** Galvanostatic charge-discharge plot of (a) 5-DCNNQ-Cathode and (b) 6-DCNNQ-Cathode at the rate of  $0.1 \text{ A g}^{-1}$ . (c) Photographic image of GF membrane at 1.6 V and 0.4 V recovered after disassembling the Zn//DCNNQmix cell.



**Fig. S10.** Efficiency plot of (a) 5-DCNNQ-Cathode and (b) 6-DCNNQ-Cathode at the current density of  $0.1 \text{ A g}^{-1}$ .



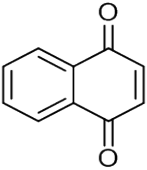
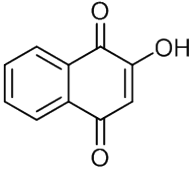
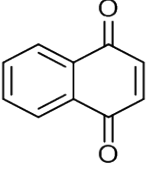
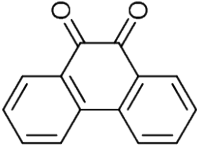



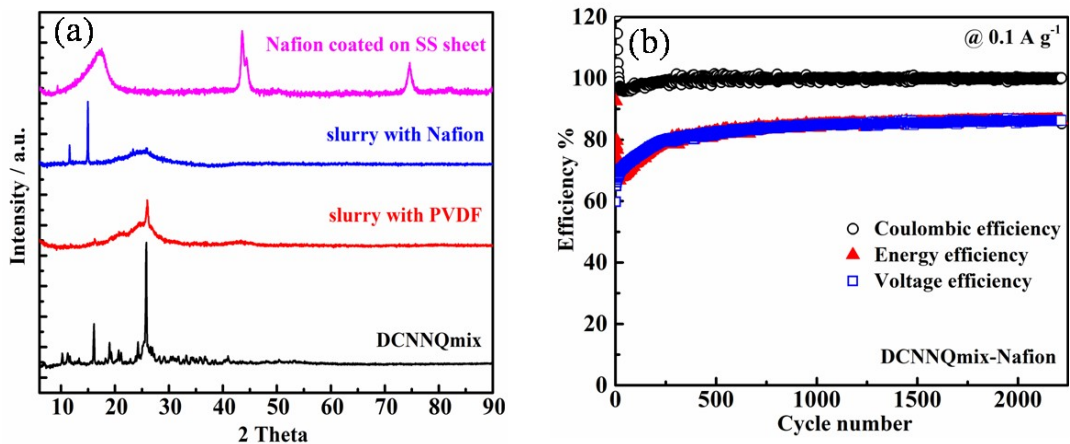
**Fig. S11.** Charge-discharge curve of DCNNQmix-PVDF cycled at the rate of 0.1 A g<sup>-1</sup>.

**Table S3.** Representation of unit charges experienced by >C=O and -NO<sub>2</sub> groups in 5-DCNNQ and 6-DCNNQ calculated using Natural Bond Orbital analysis.

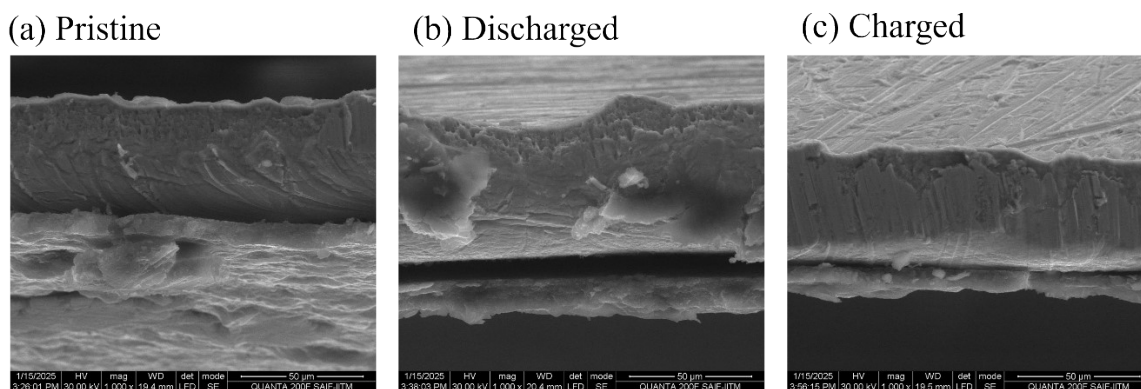
Active materials	Charges at >C=O at neutral states		Charge differences when reduced by 1e <sup>-</sup>	
	at >C=O	at -NO <sub>2</sub>	at >C=O	at -NO <sub>2</sub>
5-DCNNQ	ortho = 0.518	0.517	ortho = -0.119	0.008
	far = 0.518		far = -0.125	
6-DCNNQ	meta = 0.519	0.513	meta = -0.094	-0.016
	para = 0.517		para = -0.123	

**Table S4.** The table compares the quinone-based organic cathode materials for Zn-ion batteries.

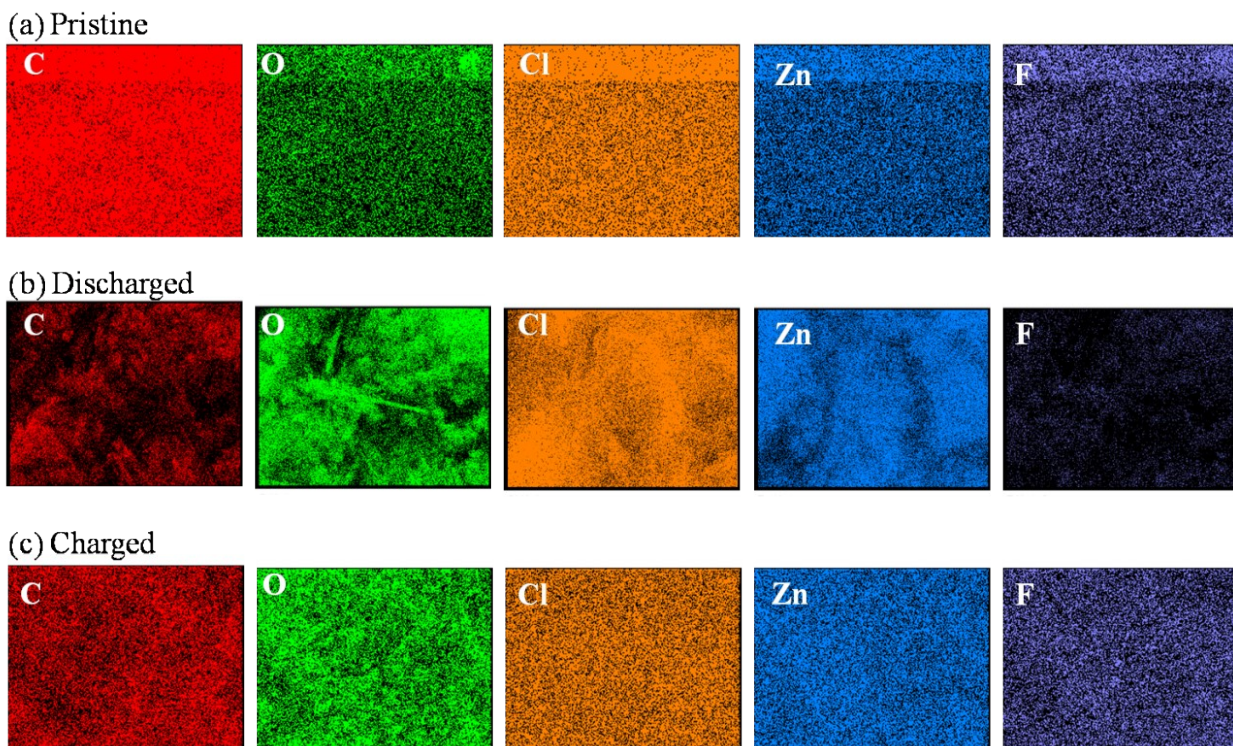
Active cathode materials	Conductive Carbon	Separator	Diffusion coefficient	Capacity / Capacity retention	Current density / Cycle number	Ref.
 1,4-NQ	Super P	Nafion-212		50 mAh g <sup>-1</sup> / 87%	0.02 A g <sup>-1</sup> /	20
 LS	Super P	Nafion-212	10 <sup>-13</sup> – 10 <sup>-14</sup> cm <sup>2</sup> s <sup>-1</sup>	50 mAh g <sup>-1</sup> / 50%	0.1 A g <sup>-1</sup> / 500	19
 NQ@CNT	CNT	Glass Fiber		137.2 mAh g <sup>-1</sup> / 41%	1 C / 1500	23
 PQ@AC	Active Carbon	Glass Fiber	10 <sup>-9</sup> cm <sup>2</sup> s <sup>-1</sup>	107.8 mAh g <sup>-1</sup> / 96%	5 A g <sup>-1</sup> / 36000	21
 DCNNQmix	Super P	Glass Fiber	10 <sup>-7</sup> cm <sup>2</sup> s <sup>-1</sup>	140 mAh g <sup>-1</sup> / 91.3%	0.1 A g <sup>-1</sup> / 9600	This work



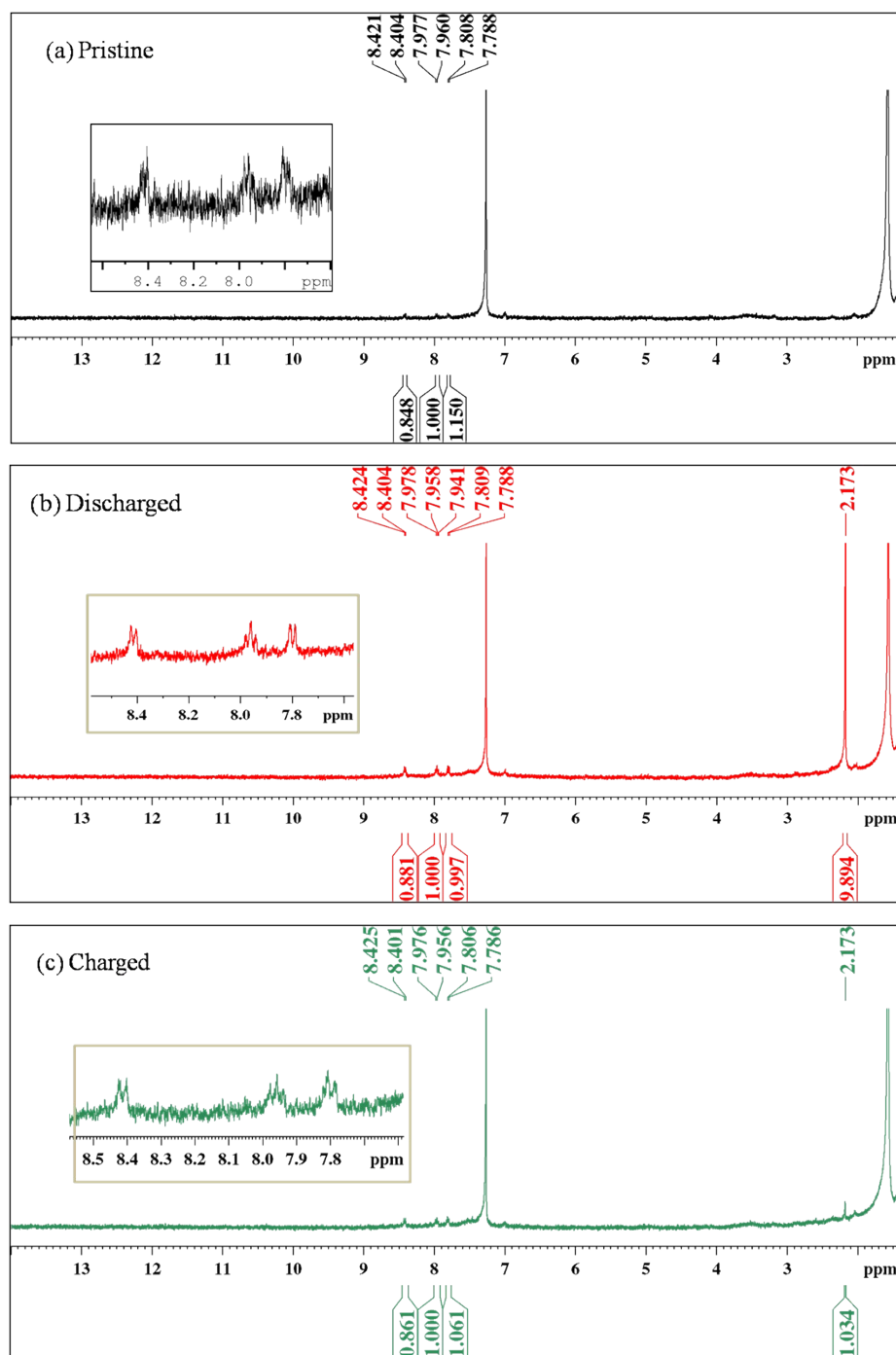
**Fig. S12.** (a) PowderXRD of DCNNQmix powder and its slurry with PVDF and Nafion binder, and Nafion solution coated on a stainless steel sheet. (b) Efficiency vs. cycle number plot of Nafion-based Zn//DCNNQ-Cathode for >2200 cycles at  $0.1 \text{ A g}^{-1}$ .



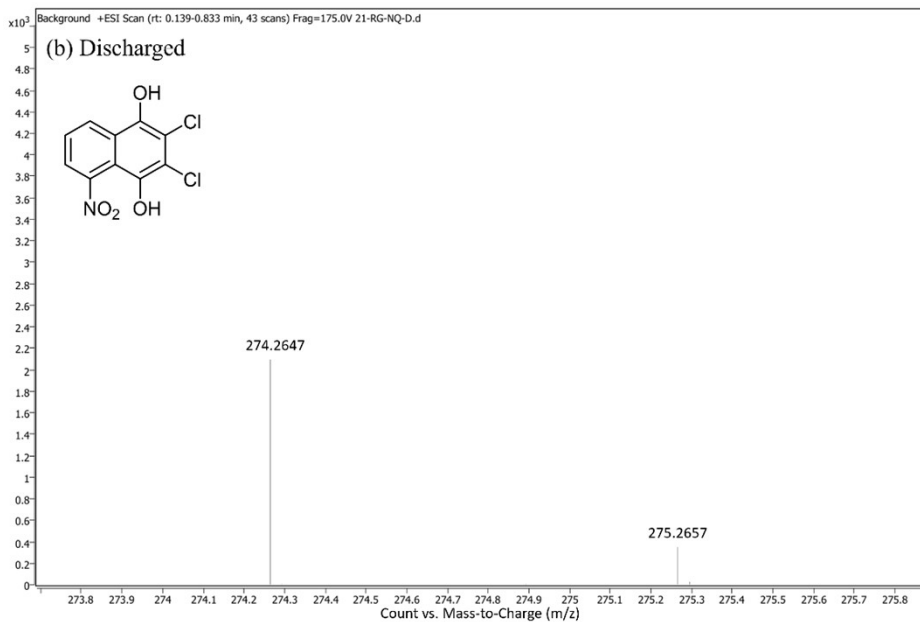
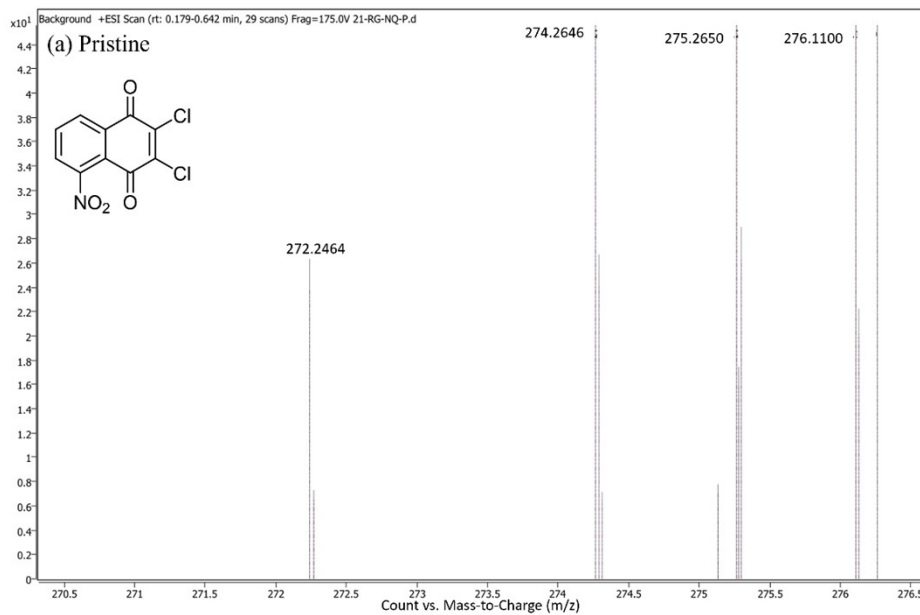
**Fig. S13.** HRSEM crosssection images of DCNNQ electrode at (a) pristine, (b) discharged, and (c) charged states.

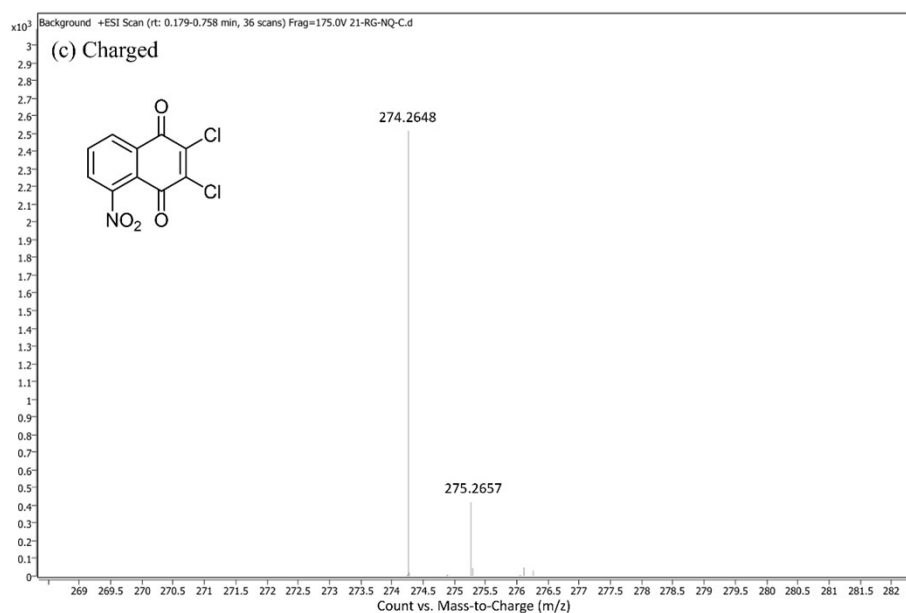


**Fig. S14.** HR-SEM coupled with EDX for elemental mapping of DCNNQmix electrodes at (a) pristine, (b) discharged, and (c) charged state of C, O, Cl, Zn, and F.

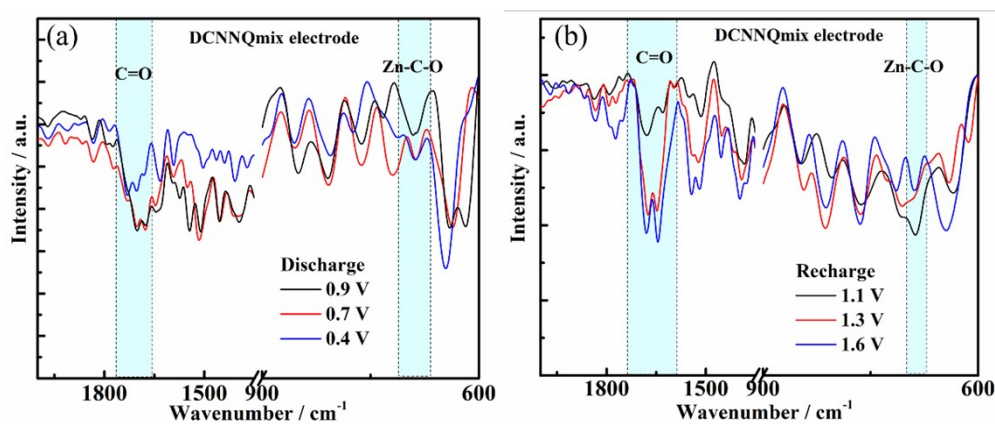


**Fig. S15.**  $^1\text{H-NMR}$  of DCNNQmix extracted from the electrodes at (a) pristine, (b) discharged, and (c) charged state using  $\text{CDCl}_3$ .





**Fig. S16.** Mass spectrum of DCNNQmix extracted from the electrodes at (a) pristine, (b) discharged, and (c) charged state.



**Fig. S17.** ATR-IR recorded of DCNNQmix electrodes at various cell voltage during (a) discharge and (b) charge of the cell.

## References

- [1] G. M. Sheldrick, *Sadabs* **1996**.
- [2] G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8.
- [3] L. J. Farrugia, *J. Appl. Crystallogr.* **2012**, *45*, 849–854.
- [4] E. G. Stoddard, B. J. Killinger, R. N. Nair, N. C. Sadler, R. F. Volk, S. O. Purvine, A. K. Shukla, J. N. Smith, A. T. Wright, *J. Am. Chem. Soc.* **2017**, *139*, 16032–16035.