

Supporting information:

## Prussian Blue: A New Framework of Electrode Materials for Sodium Batteries

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### Characterization

The structure and composition of Prussian blue analogues were characterized by Powder X-ray diffraction (XRD) obtained with a Philips X-ray diffractometer equipped with Cu K $\alpha$  radiation ( $\lambda=1.5418$  Å). The angular resolution in  $2\theta$  scans was  $0.02^\circ$  over a  $2\theta$  range of  $10-70^\circ$ . The temperature dependence of magnetic susceptibility was measured in the temperature range 5-300 K under a magnetic field  $H = 1$  T with a commercial Superconducting Quantum Interference Device (SQUID) magnetometer (Quantum Design).

A standard CR2032 coin cell was adopted to evaluate the electrochemical behavior of the Prussian blue analogues (PB) electrodes. The coin cell included a sandwich structure of a PB cathode, a Celgard<sup>®</sup> polypropylene separator, and a piece of sodium metal as anode. The PB electrode consisted of 75 wt.% PB analogues, 5 wt.% polytetrafluoroethylene (PTFE) binder, and 20 wt.% acetylene black. The electrode was rolled into a thin sheet and punched into circular discs. The typical electrode mass was  $2\pm 0.5$  mg. The electrolyte used for testing was the saturated NaClO<sub>4</sub> in 1:1 EC/DEC (vol.:vol.). All cells were assembled in an argon-filled glove box. The cells were aged for 5 h before charge/discharge to ensure full absorption of the electrolyte into the electrode. The cells were discharged first. All the cells are cycled between 2.0- 4.0 V at a current density of C/20.