Supporting Information

A Systematic Study of Prussian Blue Analogs as Cathode Materials for Calcium Ion Batteries and Interstitial Water Regulation: First-principles Calculations

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Table S1. The band gaps in $Ca_xMFe(CN)_6 \cdot nH_2O$ (M = Mn, Fe, and Co, $0 \leq x \leq 1$, $n = 0$ and 2).

band gap (eV)	$Ca_xMnFe(CN)_6$	$Ca_xMnFe(CN)_6 \cdot 2H_2O$	$Ca_xFeFe(CN)_6$	$Ca_xFeFe(CN)_6 \cdot 2H_2O$	$Ca_xCoFe(CN)_6$	$Ca_xCoFe(CN)_6 \cdot 2H_2O$
$x = 1$	1.59	2.76	1.44	2.56	1.51	1.88
$x = 0.5$	1.04	0.29	1.57	0.78	1.64	0.48
$x = 0$	1.02	0.00	1.26	0.94	1.39	0.36

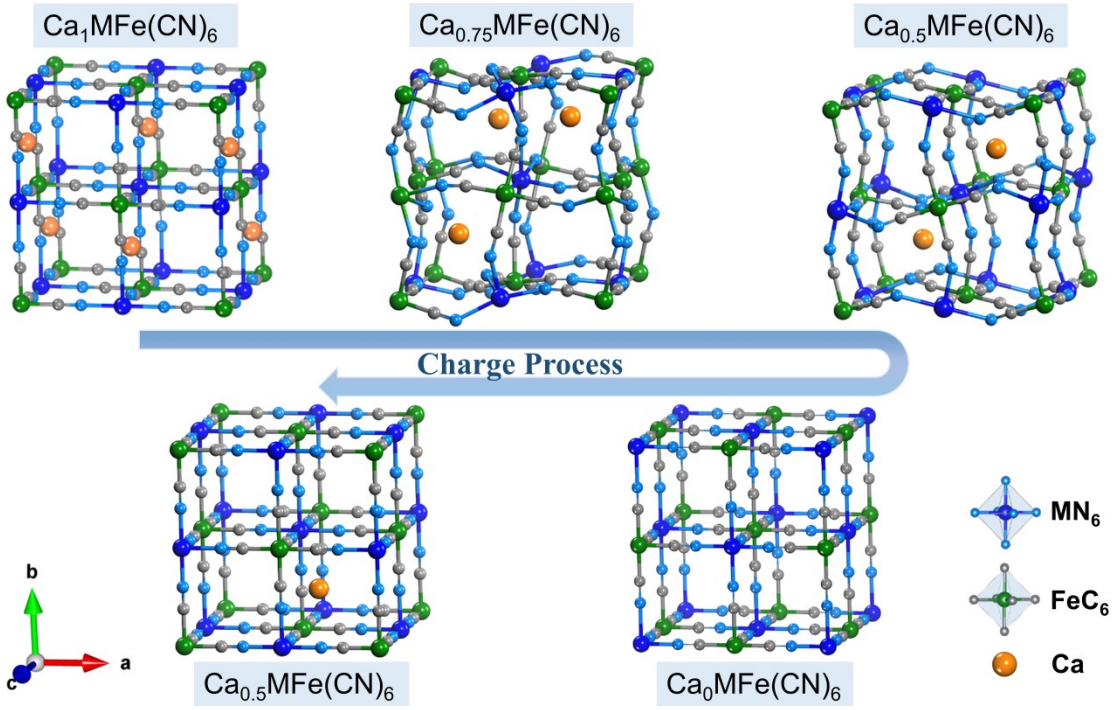

Figure S1. Schematic diagram of the lattice structure evolution during Ca^{2+} extraction in $Ca_xMFe(CN)_6$ (M = Mn, Fe, and Co; x = 1, 0.75, 0.5, 0.25, 0).

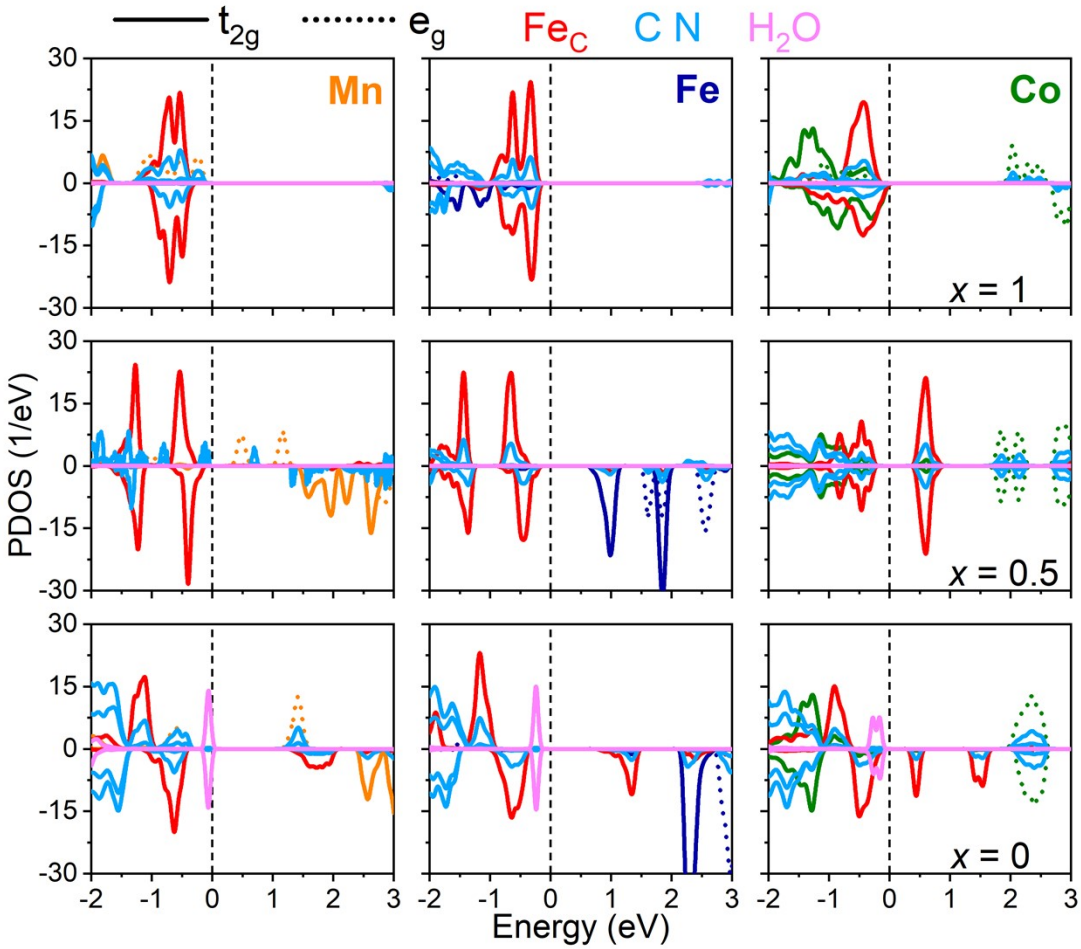

Figure S2. PDOS of $Ca_xMFe(CN)_6 \cdot 2H_2O$ (M = Mn, Fe, and Co; x = 1, 0.5, 0) containing interstitial water. The M in the left, middle, and right columns correspond to Mn, Fe, and Co, respectively. The top, middle, and bottom rows correspond to different cation contents x = 1, 0.5, and 0, respectively. The solid and dashed lines represent the t_{2g} and e_g orbitals, respectively. The Fermi level is set to zero.

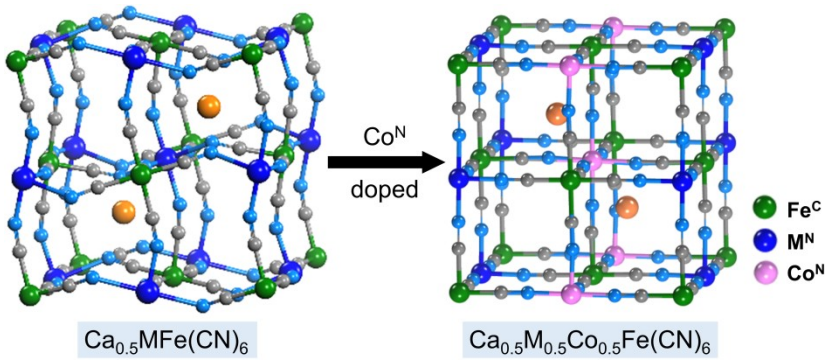

Figure S3. Schematic diagram of the lattice structure for the $Ca_{0.5}MFe(CN)_6$ (M = Mn and Fe) systems before and after Co doping.

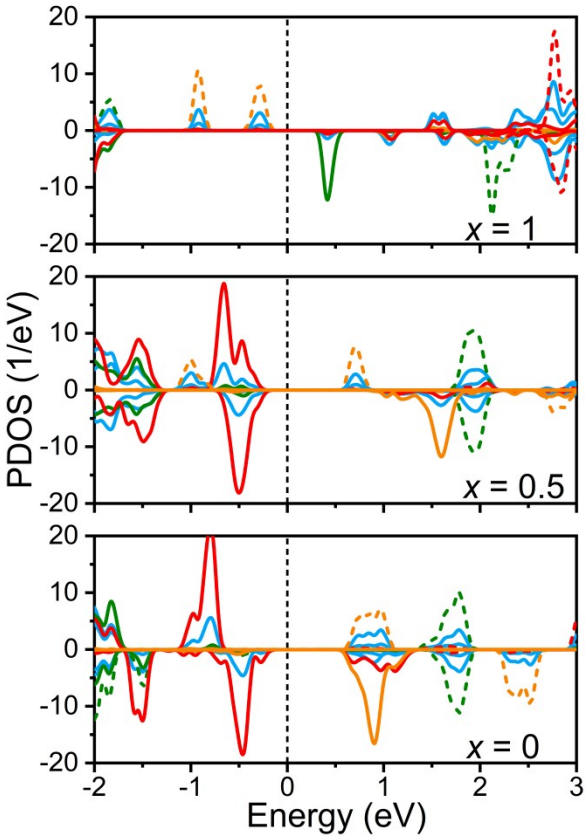

Figure S4. PDOS of $Ca_xCo_{0.5}Mn_{0.5}Fe(CN)_6$ (x = 1, 0.5, 0). The top, middle, and bottom rows correspond to different cation contents x = 1, 0.5, and 0, respectively. The solid and dashed lines represent the t_{2g} and e_g orbitals, respectively. The Fermi level is set to zero.

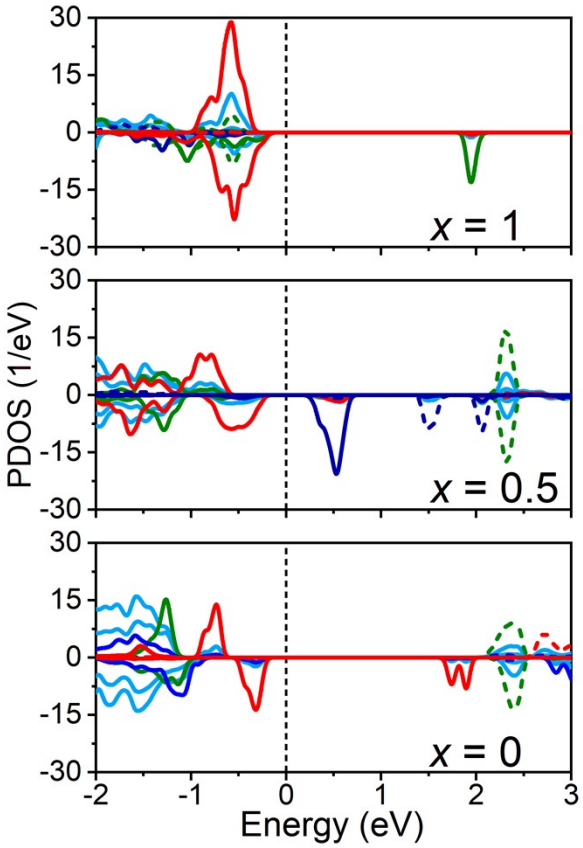

Figure S5. PDOS of $Ca_xCo_{0.5}Fe_{0.5}Fe(CN)_6$ (x = 1, 0.5, 0). The top, middle, and bottom rows correspond to different cation contents x = 1, 0.5, and 0, respectively. The solid and dashed lines represent the t_{2g} and e_g orbitals, respectively. The Fermi level is set to zero.