Electronic Supplementary Information.

Control of the Alkali Cation Alignment in Prussian Blue Framework

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1. Rietveld refinement conditions for $Rb_{0.85}Cu[Fe(CN)_6]_{0.95}\cdot 1.3H_2O$:

We indexed the diffraction pattern of $Rb_{0.85}Cu[Fe(CN)_6]_{0.95}\cdot 1.3H_2O$ in an orthorhombic *Pmna* (Z = 4) cell. We performed Rietveld analysis, starting with the usual Prussian blue framework, i.e. —Cu—NC—Fe—CN—Cu—NC—Fe— network, and two types of Rb ion in the interstitial sites (Rb1-site and Rb2-site). According to the formula, the occupancy (g) for Fe, C, and N atoms are assumed to be 0.95. The O atoms of ligand water molecules coordinated to Cu ions are assumed to occupy the site of N atoms with g of 0.05. The O atoms of zeolitic water molecules are assumed to occupy the interstitial sites; O7 and O8 occupy at the Rb1-site and Rb-2 site, respectively. The equivalent displacement parameters (U) for Fe2, Cu1, and Cu2 is fixed at the value of Fe1, while those for C2–6, N1–6, and O1–8 are fixed at the value of C1. U for Rb2 is fixed at the value of Rb1. Restraints for the bond length of Fe—C, C—N, and N—Cu, and bond angles of C—Fe—C and Fe—C—N are employed to keep appropriate values. At first, g values for Rb2, O7 and O8 are assumed to be $(1.0 - g_{Rb1})$, $(0.5 - 0.5 \times g_{Rb1})$, $(0.5 \times g_{Rb1})$, respectively, where g_{Rb1} is g of Rb1. However, this constraints makes the g value for Rb2 negative, and hence, g values for Rb1, Rb2, O7 and O8 are fixed at the values of 0.85, 0, 0.075, and 0.425.

2. Atomic coordinates, occupancy *g*, and equivalent displacement parameters *U* of $Rb_{0.85}Cu[Fe(CN)_6]_{0.95}\cdot 1.3H_2O$:

Table S1. Atomic coordinates, occupancy *g*, and equivalent displacement parameters *U*. The crystal structure is orthorhombic (*Pmna*, $Z = 4$). The reliability factor the reliability factors are $R_{wp} = 4.97\%$ and $R_B = 4.97$ %. Lattice parameters are $a = 10.1194(6)$, $b = 10.9598(6)$, $c = 10.0735(7)$ Å, respectively.

Atom	Site	*g*	*x*	*y*	*Z*	*U*
Rb1	4g	0.85	1/4	0.2366(9)	1/4	0.056(2)
Fe1	2b	0.95	1/2	0	0	0.0221(12)
Fe2	2d	0.95	0	1/2	0	0.0221
Cu1	2a	1	0	0	0	0.0221
Cu2	2c	1	1/2	1/2	0	0.0221
C1	4h	0.95	0	0.519(14)	0.19(2)	0.020(3)
C2	4h	0.95	0	0.319(8)	0.047(10)	0.020
C3	4h	0.95	0	0.172(7)	0.485(8)	0.020
C4	4f	0.95	0	0.008(10)	0.69(2)	0.020
C5	4e	0.95	0.31(3)	0	0	0.020
C6	4f	0.95	0.19(3)	1/2	0	0.020
N1	4e	0.95	0	0.531(10)	0.298(12)	0.020
N2	4h	0.95	0	0.214(5)	0.048(10)	0.020
N3	4h	0.95	0	0.278(5)	0.461(9)	0.020
N4	4f	0.95	0	0.023(6)	0.201(10)	0.020
N5	4h	0.95	0.20(2)	0	0	0.020
N6	4h	0.95	0.30(2)	1/2	0	0.020
O1	4e	0.05	0	0.531	0.299	0.020
O2	4h	0.05	0	0.214	0.048	0.020
O3	4h	0.05	0	0.278	0.461	0.020
O4	4f	0.05	0	0.023	0.201	0.020
O5	4h	0.05	0.20	0	0	0.020
O6	4h	0.05	0.30	1/2	0	0.020
O7	8i	0.082(3)	0.46(2)	0.25(5)	0.320(14)	0.020
O8	8i	0.418	0.263(12)	0.833(2)	0.210(5)	0.020

3. The bond lengths of $Rb_{0.85}Cu[Fe(CN)_6]_{0.95}\cdot 1.3H_2O$:

Table S2. The bond lengths (Å) of $Rb_{0.85}Cu[Fe(CN)_6]_{0.95}\cdot 1.3H_2O$.

Fe1—C3	1.89(8)	C1—N1	1.13(14)
Fe1—C4	1.9(2)	C2—N2	1.15(11)
Fe1—C5	1.9(3)	C3—N3	1.19(11)
Fe2—C1	1.9(2)	C4—N4	1.17(14)
Fe2—C2	2.04(9)	C5—N5	1.19(14)
Fe2—C6	1.9(3)	C6—N6	1.18(13)

4. Crystal structure of $Rb_{0.85}Cu[Fe(CN)_6]_{0.95}\cdot 1.3H_2O$:

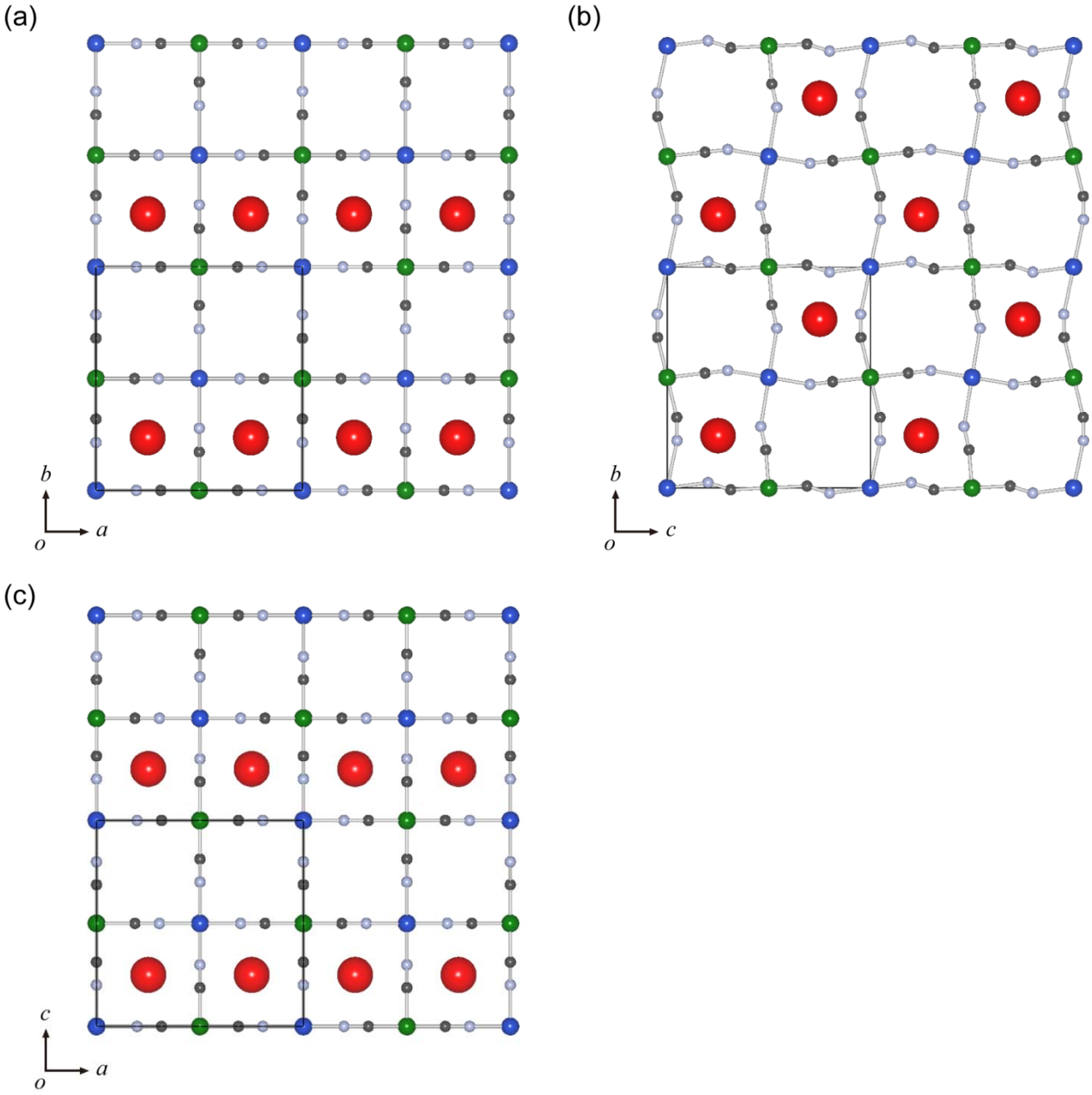

Figure S1. The crystal structure of $Rb_{0.85}Cu[Fe(CN)_6]_{0.95}\cdot 1.3H_2O$. (a) The projection in the *ab* plane. (b) The projection in the *bc* plane. (c) The projection in the *ac* plane.

5. Rietveld refinement condition of $Cs_{0.97}Cu[Fe(CN)_6]_{0.99}\cdot 1.1H_2O$:

We performed Rietveld analysis based on the usual tetragonal Prussian blue framework. According to the formula, the occupancy (g) for Fe, C, and N atoms are assumed to be 0.99. The O atoms of ligand water molecules coordinated to Cu ion are assumed to occupy the sites of N atoms with g of 0.01. g for Cs2 is assumed to be $(0.97 - g_{Cs1})$, where g_{Cs1} is g of Cs1. The O atoms of zeolitic water molecules are assumed to occupy 4f (0 1/2 z) position; O3, and O4 occupies at Cs1-site and Cs2-site, respectively. g for O4 is assumed to be $(0.26 - g_{O3})$, where g_{O3} is g of O3 The equivalent displacement parameters (U) for Cu1 is fixed at the value of Fe1, while those for C2, N1–2, and O1–4 are fixed at the value of C1. U for Cs2 is fixed at the value of Cs1. Restraints for the bond length of Fe—C, C—N, and Cu—N are employed to keep appropriate values.

6. Atomic coordinates, occupancy *g*, and equivalent displacement parameters *U* of $Cs_{0.97}Cu[Fe(CN)_6]_{0.99}\cdot 1.1H_2O$:

Table S3. Atomic coordinates, occupancy *g*, and equivalent displacement parameters *U*. The crystal structure is tetragonal ($I\bar{4}m2$, $Z = 2$). The reliability factor the reliability factors are $R_{wp} = 6.74\%$ and $R_B = 2.95$ %. Lattice parameters are $a = 7.1702(2)$, $c = 10.9843(5)$ Å, respectively.

Atom	Site	*g*	*x*	*Y*	*z*	*U*
Cs1	2d	0.619(6)	1/2	0	1/4	0.0440(14)
Cs2	2c	0.351	1/2	0	3/4	0.0440
Fe1	2a	0.99	0	0	0	0.0148(10)
Cu1	2b	1	1/2	1/2	0	0.0148
C1	4e	0.99	0	0	0.1729(19)	0.014(2)
C2	8g	0.99	0.180(2)	0.180	0	0.014(2)
N1	4e	0.99	0	0	0.2777(17)	0.014(2)
N2	8g	0.99	0.2990(18)	0.2990	0	0.014(2)
O1	4e	0.01	0	0	0.2777	0.014(2)
O2	8g	0.01	0.2990	0.2990	0	0.014(2)
O3	4f	0.12(2)	1/2	0	0.365(10)	0.014(2)
O4	4f	0.14	1/2	0	0.697(8)	0.014(2)

7. The bond lengths of $Cs_{0.97}Cu[Fe(CN)_6]_{0.99}\cdot 1.1H_2O$:

Table S4. The bond lengths (Å) of $Cs_{0.97}Cu[Fe(CN)_6]_{0.99}\cdot 1.1H_2O$.

Fe1—C1	1.83(2)	C1—N1	1.15(2)
Fe1—C2	1.90(2)	C2—N2	1.20(1)