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SUPPORTING INFORMATION

Synthesis, Crystal Structures and Semiconducting Properties of New Hexacyanidometallates

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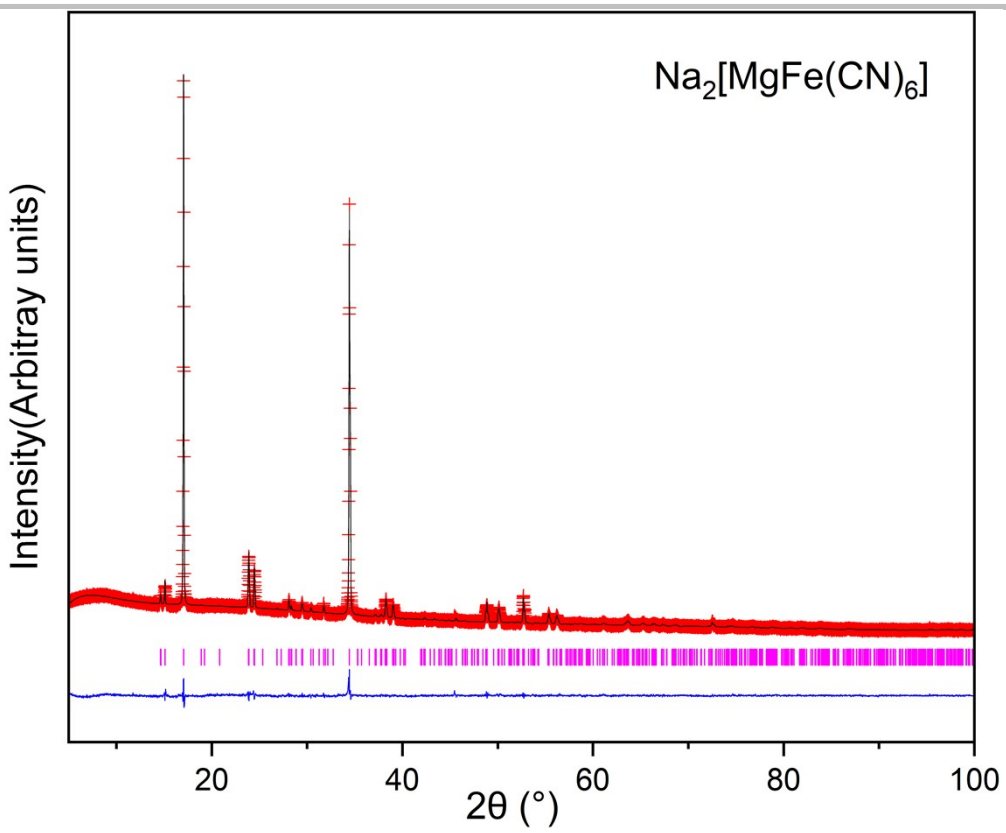

Figure S1. Rietveld fit of $Na_2[MgFe(CN)_6]$ to PXRD data, showing in observed (red), calculated (black), and difference (blue) intensities. Bragg positions of $Na_2[MgFe(CN)_6]$ (pink) are denoted by vertical markers.

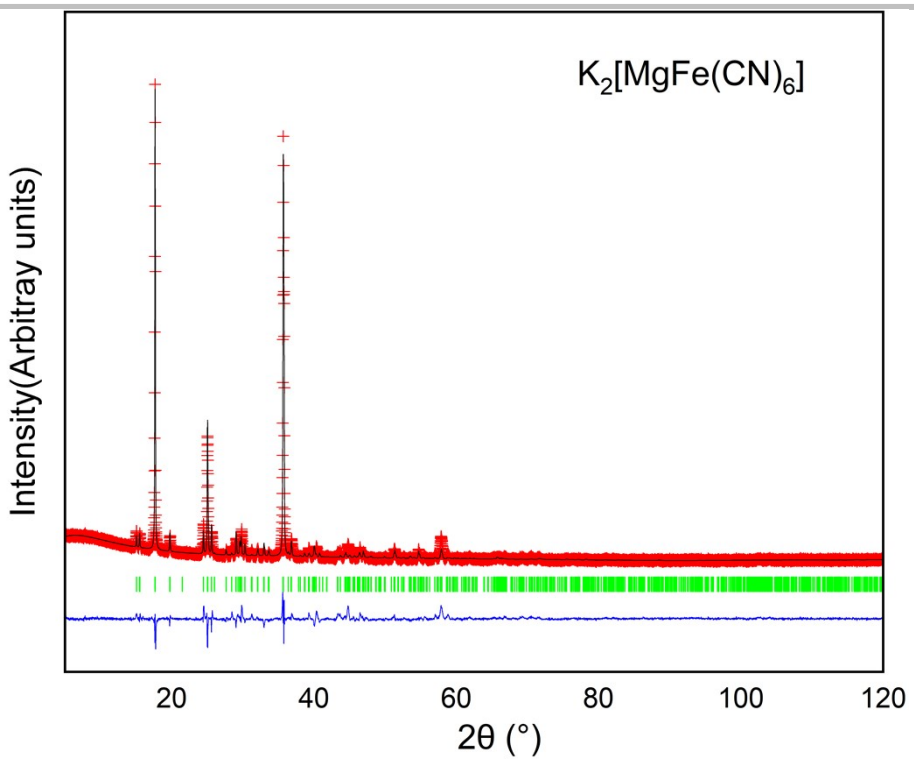

Figure S2. Rietveld fit of $K_2[MgFe(CN)_6]$ to PXRD data, showing in observed (red), calculated (black), and difference (blue) intensities. Bragg positions of $K_2[MgFe(CN)_6]$ (green) are denoted by vertical markers.

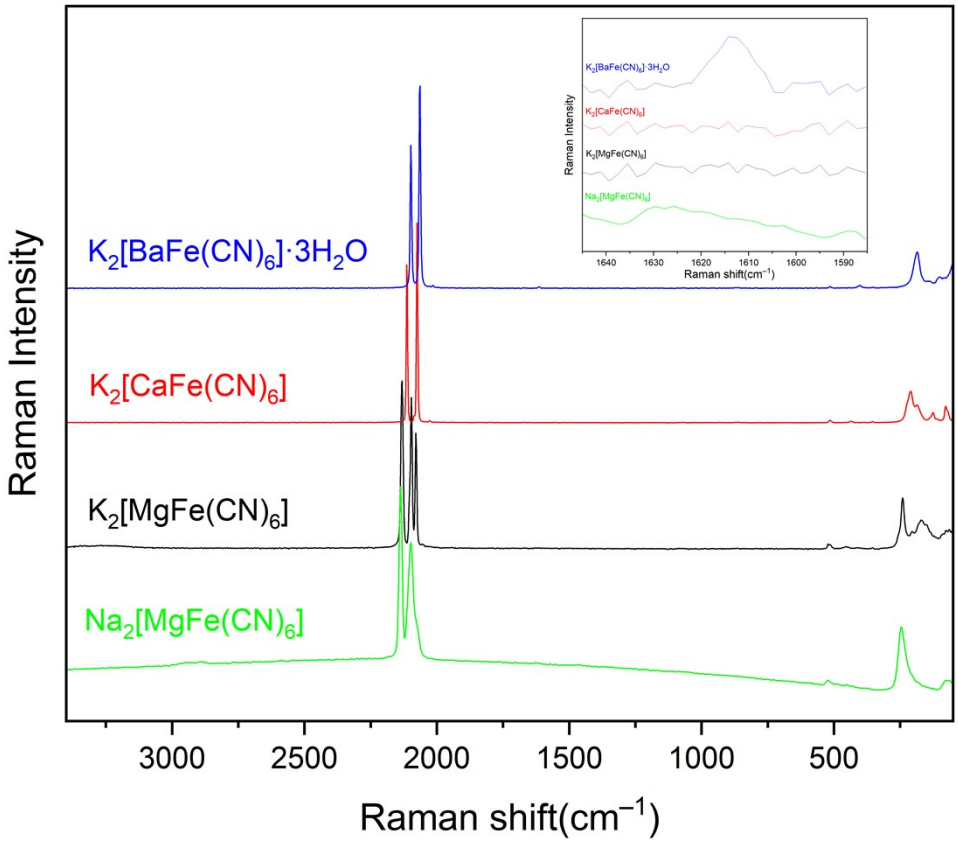

Figure S3. Comparison of the Raman spectra of $Na_2[MgFe(CN)_6]$, $K_2[MgFe(CN)_6]$, $K_2[CaFe(CN)_6]$ and $K_2[BaFe(CN)_6]\cdot 3H_2O$.

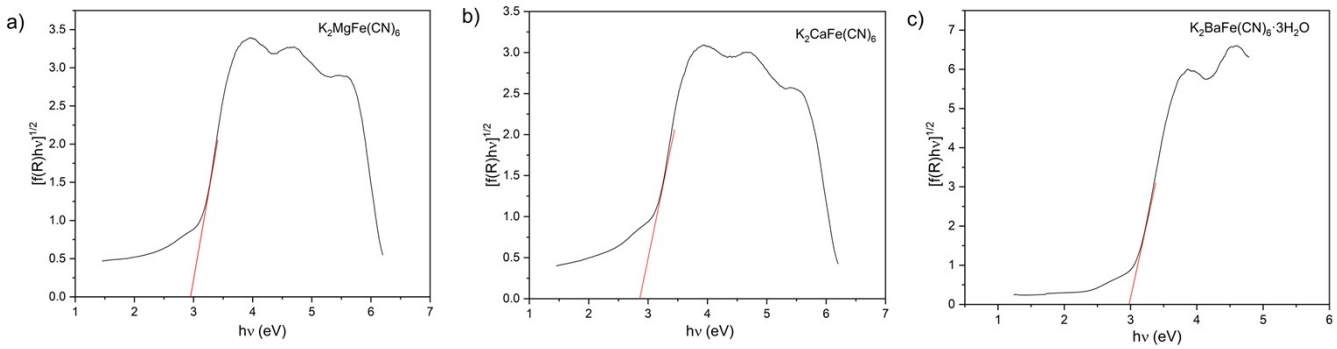

Figure S4. Tauc plot for the $K_2[MgFe(CN)_6]$, $K_2[CaFe(CN)_6]$ and $K_2[BaFe(CN)_6]\cdot 3H_2O$ electron showing the electronic band gap.

Table S1. Crystallographic data and fractional coordinates for $Na_2[MgFe(CN)_6]$.

Atom	Wyckoff site	*x*	*y*	*z*	U_{iso} (Å^2)
Na	4*e*	0.2476(10)	0.4539(23)	0.0119(19)	0.0542(31)
Mg	2*a*	½	½	½	"
Fe	2*d*	½	0	0	"
C1	4*e*	0.5270(20)	0.1696(28)	0.8195(30)	0.0073(28)
C2	4*e*	0.2075(19)	0.4541(32)	0.528(4)	"
C3	4*e*	0.4820(19)	0.2146(29)	0.1680(28)	"
N1	4*e*	0.4996(13)	0.2796(23)	0.7453(29)	"
N2	4*e*	0.2800(14)	0.4920(31)	0.459(3)	"
N3	4*e*	0.5108(14)	0.2909(24)	0.2916(28)	"

[a] Standard deviations are given in parentheses. Monoclinic, $P2_1/n$ (No. 14), Z = 2, a = 10.4320(2) Å, b = 7.4754(2) Å, c = 7.2842(3) Å, and β = 91.748(3)°; R_{wp} = 1.86%, R_p = 1.32%, χ^2 = 2.56.

Table S2. Crystallographic data and fractional coordinates for $K_2[MgFe(CN)_6]$.

Atom	Wyckoff site	*x*	*y*	*z*	U_{iso} (Å^2)
K	4*e*	0.7536(8)	0.9469(11)	0.4863(11)	0.091(25)
Mg	2*d*	0	½	½	"
Fe	2*a*	0	0	0	"

C1	4*e*	0.5021(17)	0.619(4)	0.2558(20)	0.169(31)
C2	4*e*	0.9958(17)	0.8112(18)	0.1946(21)	"
C3	4*e*	0.6962(7)	0.4677(18)	0.5700(30)	"
N1	4*e*	0.4870(13)	0.2808(14)	0.8822(26)	"
N2	4*e*	0.0563(10)	0.3348(12)	0.7646(12)	"
N3	4*e*	0.2084(6)	0.4729(14)	0.4030(15)	"

[a]Standard deviations are given in parentheses. Monoclinic, $P2_1/n$ (No. 14), Z = 2, a = 10.0720(15) Å, b = 7.2919(13) Å, c = 6.9644(14) (2) Å, and β = 90.241(5) °; Rwp = 5.83%, Rp = 3.27%.

Table S3. Crystallographic data and fractional coordinates for $K_2[CaFe(CN)_6]$.

Atom	Wyckoff site	*x*	*y*	*z*	U_{iso} (Å^2)
K	4e	0.7440(7)	0.9291(5)	0.4824(8)	0.0464(11)
Ca	2d	0	½	½	"
Fe	2a	0	0	0	"
C1	4e	0.529(3)	0.5968(24)	0.2277(28)	0.060(3)
C2	4e	0.9533(29)	0.7508(27)	0.1001(23)	"
C3	4e	0.6719(16)	0.542(4)	0.624(5)	"
N1	4e	0.4361(22)	0.2704(20)	0.8139(23)	"
N2	4e	0.0468(22)	0.3067(20)	0.7567(22)	"
N3	4e	0.2216(16)	0.4654(29)	0.374(3)	"

[a] Standard deviations are given in parentheses. Monoclinic, $P2_1/n$ (No. 14), Z = 2, a = 10.3012(3) Å, b = 7.5148(2) Å, c = 7.0677(2) Å, and β = 90.3221(8) °; R_{wp} = 2.60%, R_p = 2.00%, χ^2 = 1.16.

Table S4. Crystal data, data collection parameters and convergence results for $Na_2[CaFe(CN)_6]\cdot 2H_2O$, $K_2SrFe(CN)_6$, $K_2CaFe(CN)_6\cdot 2H_2O$ and $K_2BaFe(CN)_6\cdot 3H_2O$.

Empirical formula	$Na_2CaFe(CN)_6\cdot 2H_2O$	$K_2SrFe(CN)_6\cdot H_2O$	$K_2[CaFe(CN)_6]\cdot 2H_2O$	$K_2[BaFe(CN)_6]\cdot 3H_2O$
M	334.06	395.81	343.21	481.56
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Rhombohedral
Space group (No.)	$P2_1/n$ (No.14)	$P2_1/c$ (No.14)	*Pnma* (No.62)	$R\bar{3}c$ (No.167)
a/Å	7.4638(10)	13.8435(6)	12.8405(10)	7.2611(5)
b/Å	7.6331(9)	7.7597(3)	13.7735(12)	7.2611(5)

c/Å	10.9182(16)	12.0631(6)	10.9182(16)	45.873(5)
β/°	≈ 90	112.628(5)	90	90
V(Å^3)	622.03(14)	1196.08(10)	1297.40(19)	2094.6(4)
Z	2	4	4	6
μ/mm^{-1}	1.69	6.36	2.01	4.45
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4215, 1592, 1138	11024, 2932, 2296	5056, 1639, 1385	2538, 582, 512
R_{int}	0.029	0.024	0.051	0.016
(sinθ/λ)max (Å^{-1})	0.72	0.667	0.666	0.667
$R1$ ($F^2 > 2\sigma(F^2)$), $wR2$ (F^2)	0.027, 0.047	0.029, 0.074	0.053, 0.171	0.014, 0.037

Table S5. Fractional coordinates for the non-hydrogen atoms and equivalent isotropic displacement parameters for $Na_2[CaFe(CN)_6]\cdot 2H_2O$ and $K_2[SrFe(CN)_6]\cdot H_2O$. Standard deviations are given in parentheses.

Atom	x	y	z	U_{eq} (Å^2)
$Na_2[CaFe(CN)_6]\cdot 2H_2O$				
Na	0.20569(11)	0.29778(8)	0.25197(8)	0.0209(2)
Ca	0	0	½	0.00795(12)
Fe	0	0	0	0.00758(10)
C1	0.1379(2)	0.2110(2)	0.00138(17)	0.0110(4)
C2	0.0010(2)	0.0048(2)	0.17400(17)	0.0103(4)
C3	0.2145(3)	–0.1361(2)	–0.00039(17)	0.0109(4)
N1	0.2210(2)	0.33790(17)	0.00829(16)	0.0172(4)
N2	0.3415(2)	–0.22230(18)	0.00172(16)	0.0169(4)
N3	0.0125(2)	0.01249(18)	0.27906(15)	0.0162(4)
O1	0.0438(2)	0.5683(2)	0.25365(16)	0.0301(4)
$K_2SrFe(CN)_6\cdot H_2O$				
K1	0.41213(4)	0.10000(6)	0.65182(5)	0.02080(13)

K2	0.10277(4)	0.41534(7)	0.38399(5)	0.02327(14)
Sr	0.25341(2)	–0.00274(2)	0.25012(2)	0.01048(8)
Fe1	½	½	½	0.00897(11)
Fe2	0	0	½	0.00961(11)
C1	0.58191(16)	0.3691(3)	0.63936(18)	0.0117(4)
C2	0.45989(16)	0.2857(3)	0.41623(18)	0.0123(4)
C3	0.38146(17)	0.4770(3)	0.54198(19)	0.0125(5)
C4	–0.06821(16)	0.2181(3)	0.45774(17)	0.0122(4)
C5	0.05376(17)	0.0261(3)	0.3778(2)	0.0146(5)
C6	0.12238(17)	0.1126(3)	0.61194(19)	0.0137(5)
N1	0.62894(15)	0.2821(2)	0.72017(16)	0.0177(4)
N2	0.43365(14)	0.1543(2)	0.36803(16)	0.0182(4)
N3	0.30953(15)	0.4566(3)	0.56734(17)	0.0192(4)
N4	–0.10862(15)	0.3504(2)	0.43109(16)	0.0193(4)
N5	0.08897(15)	0.0437(3)	0.30507(17)	0.0196(4)
N6	0.19502(15)	0.1835(2)	0.67896(17)	0.0223(5)
O1	0.28555(13)	–0.1250(2)	0.47052(15)	0.0242(4)

Table S6. Fractional coordinates for the non-hydrogen atoms and equivalent isotropic displacement parameters for $K_2[CaFe(CN)_6]\cdot 2H_2O$ and . Standard deviations are given in parentheses.

Atom	*x*	*y*	*z*	U_{eq} (Å^2)
K	0.3340(2)	0.4115(2)	0.9735(5)	0.0712(9)
Ca	0.15954(13)	¼	0.4963(2)	0.0091(3)
Fe	½	½	½	0.0072(3)
C1	0.3837(5)	0.4134(5)	0.4905(10)	0.0225(14)
C2	0.5822(5)	0.4128(4)	0.3541(9)	0.0184(13)
C3	0.4508(5)	0.5662(5)	0.2842(9)	0.0173(12)
N1	0.3105(5)	0.3617(5)	0.4927(10)	0.0360(17)
N2	0.6331(5)	0.3610(5)	0.2706(10)	0.0318(15)
N3	0.4216(5)	0.6074(5)	0.1582(9)	0.0320(15)
O1	0.2222(6)	¼	0.8298(10)	0.0264(16)
O2	–0.0431(6)	¼	0.4116(12)	0.0310(17)

Table S7. Fractional coordinates for the non-hydrogen atoms and equivalent isotropic displacement parameters for $K_2[BaFe(CN)_6]\cdot 3H_2O$. Standard deviations are given in parentheses.

Atom	*x*	*y*	*z*	U_{eq} (Å^2)
K	⅓	⅔	0.31898(3)	0.0265(3)
Ba	⅓	⅔	0.416667	0.01204(10)
Fe	⅔	⅓	⅓	0.01179(13)
C1	0.6231(2)	0.5251(2)	0.35706(3)	0.0154(3)
N1	0.5997(2)	0.6460(2)	0.37098(3)	0.0239(3)
O1	–0.0591(3)	⅔	0.416667(3)	0.0495(7)

Table S8. Theoretical gaps with different calculation methods for $K_2[MgFe(CN)_6]$, $K_2[CaFe(CN)_6]$.

Band gap (eV) with different function	$K_2[MgFe(CN)_6]$	$K_2[CaFe(CN)_6]$
PBE	4.29 (indirect)	3.92 (indirect)
PBE+*U* (*U* = 4)	4.75 (indirect)	4.63 (indirect)
HSE	6.14 (indirect)	6.04 (indirect)