Electronic Supplementary Material (ESI) for ChemComm.

High-Tc Superconducting Phases in Organic Molecular Intercalated Iron Selenides: Synthesis and Crystal Structures †

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Supplementary Information

Sample synthesis. All sample preparations were carried out in an argon-filled dry box with an O_2 and H_2O content below 1 ppm. Tetragonal $Fe_{1+\delta}Se$ was synthesized following the method described in Ref. 1. Anhydrous ethylenediamine (***En***), 1,3-diaminopropane (1,3-***DIA***), and putrescine (***PUT***) (Sinopharm Chemical Reagent, 99.0% purity) were further purified following the method described in Ref. 2. Polycrystalline samples in nominal compositions $Na_{0.5}(C_2N_2H_8)_yFe_2Se_2$, $Na_{0.5}(\mathit{1,3}\text{-}C_3N_2H_{10})_yFe_2Se_2$ and $Na_{1.0}(C_4N_2H_{12})_yFe_2Se_2$ were prepared by a sonochemical solution reaction. In a typical synthesis to obtain the En/sodium intercalated compound, 0.002 mole $Fe_{1+\delta}Se$ powder and 0.0005 mole Na pieces (Alfa Aesar, 99.97% purity) are ultrasonically reacted in the ultra-dried ethylenediamine solvent at 60 °C for 12 h, followed by thoroughly rinse with the dried solvent and removal of the remaining solvent under dynamic vacuum at room temperature. The crystallinity of the samples can be further enhanced by annealing 6 -12h below the boiling point of the solvent, before removal of the solvent under vacuum. ***Caution note:*** Ethylenediamine, diaminopropane and putrescine are skin and respiratory irritant. Unless tightly contained, liquid ethylenediamine, diaminopropane and putrescine will release toxic and irritating vapors into its surroundings, especially on heating.

Structural characterization and composition determination. NPD experiments were conducted using Ge 311 (λ=2.0775 Å) monochromators. Data were collected over the 2θ ranges 3.0-150.0° (Ge 311) with a step size of 0.05° at 295 K. The NPD experiments were carried out in the NIST Center for Neutron Research. Laboratory *in situ* PXRD measurements were made using a Panalytical X'pert PRO instrument (Co Kα1 radiation) equipped with an Anton Paar HTK-1200N Oven Sample stage (10^{-4} pa, RT-1200 °C). Time-dependent *in situ* X-ray diffractometry was performed in air atmosphere at intervals of 10 min (5° to 60°, with a scanning step width of 0.017°). Temperature-dependent *in situ* X-ray diffractometry was performed in the angular range from 5° to 65°. The room-temperature diffraction pattern (at 25 °C) was firstly obtained as a standard, the sample stage was then heated from 30 °C to 200 °C at intervals of 10 °C. Each diffraction pattern was obtained 5 min after the required temperature was reached. The sample composition (Na: Fe: Se) were determined by inductively coupled plasma mass spectrometry. The nitrogen contents in the samples were determined using an Oxygen and Nitrogen Analyzer (Senbao TN-306, Shanghai), with a stand deviation of 0.1 ppm and Nitrogen concentration range between 0.0005%～20%.

Magnetic susceptibility and resistivity. Magnetization and resistivity measurements were carried out using a SQUID PPMS-9 system (Quantum Design). Magnetic susceptibility measurements were made in *d.c.* fields of 10 Oe in the temperature range 10-300 K after cooling in zero applied field (ZFC) and in the measuring field (FC). Resistivity were measured using the standard four-probe configuration based on samples cold-pressed at a uniaxial stress of 400 kg cm^2.

NMR. The ^{23}Na NMR spectra of powdered crystals were obtained through Fourier transformation of spin−echo signal with a Bruker Avance III 400 HD spectrometer in a magnetic field of 9.39 T. Hahn echo pulse sequence was used with a typical delay of 1 s and the first pulse was 1.5 μs. All spectra were referred to 1 mol/L aquoes NaCl (-2.3 ppm).

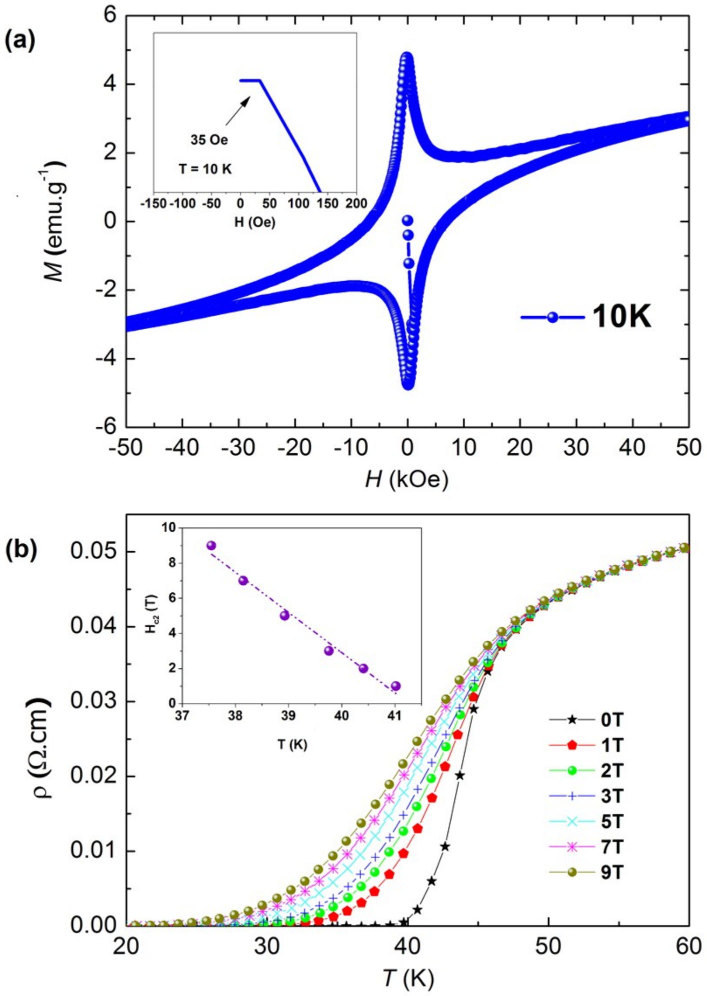

Fig. S1. Magnetization, electrical resistance of $Na_{0.39}(C_2N_2H_8)_{0.77}Fe_2Se_2$. a) The magnetic hysteresis measured at 10 K in the range -50 kOe to 50 kOe, respectively. Inset shows the point of deviation of M from the Meissner line for T = 10 K. b) Temperature dependence of electrical resistivity under magnetic fields of 0, 1, 2, 3, 5, 7, and 9 T, inset shows the temperature dependence of the upper critical magnetic field.

Table S1. Crystallographic parameters from indexing the PXRD data at 298 K.

Composition ‡	Symmetry	*a* (Å)	*b (Å)*	*c* (Å)
$Na_{0.39(1)}(C_2N_2H_8)_{0.77(1)}Fe_{2.02(1)}Se_2$	*I* 4/*m*	3.8145(7)		22.1954(8)
$Na_{0.33(1)}(C_3N_2H_{10})_{0.39(1)}Fe_{2.04(1)}Se_2$	*I* 222 *	3.7932(7)	3.8422(8)	20.356(3)
$Na_{1.03(1)}(C_4N_2H_{12})_{0.41(1)}Fe_{2.01(1)}Se_2$	*P* 4/*nmm* *	3.808(2)		12.464(2)

* The two space groups are proposed according to the extinction conditions.

‡ The Na:Fe:Se ratio is determined by inductively coupled plasma atomic emission spectrometry (ICP-AES), the organic species is determined by an Oxygen and Nitrogen Analyzer (ONA)

Table S2. Structural Parameters. Atomic coordinates for $Na_{0.39}(C_2N_2H_8)_{0.77}Fe_2Se_2$ from NPD refinement at 295 K. R_p = 5.32% and R_{wp} = 6.86%.

Atom	Wyckoff site	x	y	z	Occupation	Uiso(Å2)
N1	16i	-0.146(8)	0.011(8)	0.448(2)	0.096	0.092(5)
C1	16i	-0.330(6)	0.995(7)	0.506(2)	0.096	0.092(5)
C2	16i	-0.730(6)	0.998(8)	0.503(2)	0.096	0.092(5)
N2	16i	-0.881(5)	0.985(9)	0.564(2)	0.096	0.092(5)
H1	16i	-0.222(9)	0.231(9)	0.423(2)	0.096	0.092(5)
H2	16i	-0.206(11)	0.797(13)	0.421(2)	0.096	0.092(5)
H3	16i	-0.246(7)	0.218(8)	0.535(2)	0.096	0.092(5)
H4	16i	-0.241(6)	0.751(8)	0.530(2)	0.096	0.092(5)
H5	16i	-0.812(7)	0.779(9)	0.472(2)	0.096	0.092(5)
H6	16i	-0.817(8)	0.248(9)	0.481(2)	0.096	0.092(5)
H7	16i	-0.810(12)	0.205(9)	0.588(2)	0.096	0.092(5)
H8	16i	-0.798(13)	0.766(9)	0.589(2)	0.096	0.092(5)
Se	4e	0.500	0.500	0.316(1)	1.000	0.165(5)
Fe	4d	0.000	0.500	0.250	1.000	0.171(4)
Na	2a	0.500	0.500	0.500	0.39	0.077(5)

Space group: *I*4/m (No. 86); *a* = 3.812(1) Å, *c* = 22.075(2) Å, *V* = 320.78(12) Å^3, U_{iso} is the isotropic displacement parameter.

Table S3. Selected interatomic distances and interatomic angles for $Na_{0.39}(C_2N_2H_8)_{0.77}Fe_2Se_2$ from NPD refinement at 295 K.

Interatomic distances (Å)	
Fe–Se	2.40(1) Å
H12-Se13	2.60(5) Å
H6–Se13	2.81(5) Å
Na-N1	2.57(3) Å
Na-N2	2.74(3) Å
Interatomic angles (°)	
Se^{top}–Fe–Se^{top}	105.21(1) °
Se^{top}–Fe–Se^{bottom}	111.64(1) °
N2–Na–N1	122.4(8) °
N2–Na–N2	105.4(7) °
N1–Na–N1	101.5(1) °
N1–Na–N2	127.3(7) °

Reference:

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[2] R. R. Dewald, J. L. Dye, *J. Phys. Chem.,* 1964*,* ***68,*** 121.