Supplementary Information for

Spin-Crossover Semiconductors Based on Homoleptic Tris-Diimine Fe(II) Complexes with Fractionally Charged TCNQ•$^{\delta-}$ Anions

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Table S1. Data collection and structure refinement parameters for [Fe(3tpH)$_3$](TCNQ)$_3$ (**1**) and [Fe(4bt)$_3$](TCNQ)$_3$ (**2**).

Compound	$FeS_3N_{21}C_{54}H_{27}$ (**1**)		$FeS_6N_{18}C_{54}H_{24}$ (**2**)		
Temperature, K	90 K	295 K	100 K	230 K	300 K
CCDC number	2433956	2433953	2433957	2433955	2433954
Formula weight	1121.99	1121.99	1173.12	1173.12	1173.12
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*
a, Å	33.5745(8)	33.677(1)	33.0830(6)	33.1267(8)	33.409(1)
b, Å	9.7164(2)	9.8498(3)	9.7943(2)	9.9158(2)	9.8946(4)
c, Å	15.4349(3)	15.4982(5)	15.7944(3)	15.8990(4)	15.9778(6)
α, deg	90	90	90	90	90
β, deg	98.048(2)	98.304(3)	99.523(2)	99.703(2)	99.860(3)
γ, deg	90	90	90	90	90
V, Å^3	4985.6(2)	5087.1(3)	5047.3(2)	5147.8(2)	5203.7(3)
Z	4	4	4	4	4
Crystal color	dark black	dark violet	dark violet	dark violet	dark violet
Crystal size, mm^3	0.32×0.12×0.08	0.68×0.27×0.17	0.29×0.21×0.11	0.35×0.25×0.10	0.30×0.28×0.10
d_{calc}, g cm^{-3}	1.491	1.465	1.544	1.514	1.497
μ, mm^{-1}	0.492	0.482	0.608	0.596	0.590
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073
$2\theta_{max}$, deg	59.15	56.56	61.02	61.02	54.97
Total reflections (R_{int})	32796 (0.029)	22209 (0.023)	49904 (0.056)	45635 (0.052)	19052 (0.056)
Unique reflections	6996	6273	7690	7852	5774
Parameters refined	529	492	490	486	486
Restraints used	442	17	0	13	17
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.097, 0.113	0.081, 0.105	0.043, 0.053	0.049, 0.064	0.058, 0.087
R_1, wR_2 (all data)	0.204, 0.210	0.218, 0.231	0.108, 0.114	0.128, 0.137	0.148, 0.166
Goodness of fit[b]	1.095	1.108	1.027	1.034	1.030
Diff. peak/hole, e Å^{-3}	0.44, –0.49	0.40, –0.48	0.61, –0.53	0.71, –0.49	0.43, –0.38

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; [b] Goodness-of-fit = $[\Sigma[w(F_o^2-F_c^2)^2]/(N_{obs}-N_{params})]^{1/2}$, based on all data.

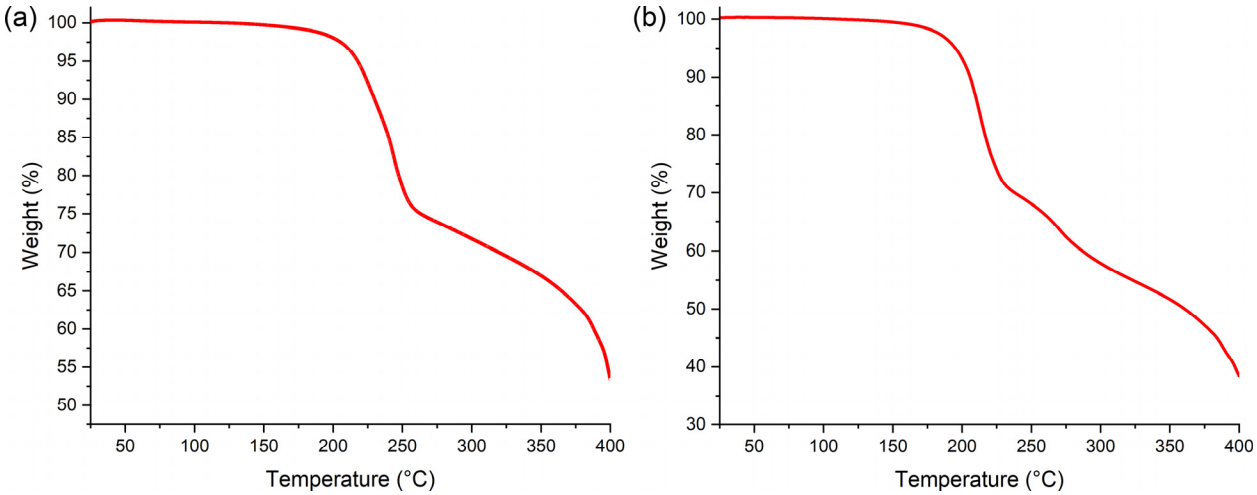


Figure S1. Thermogravimetric curves for **1** (a) and **2** (b) recorded at the heating rate of 10 K/min.

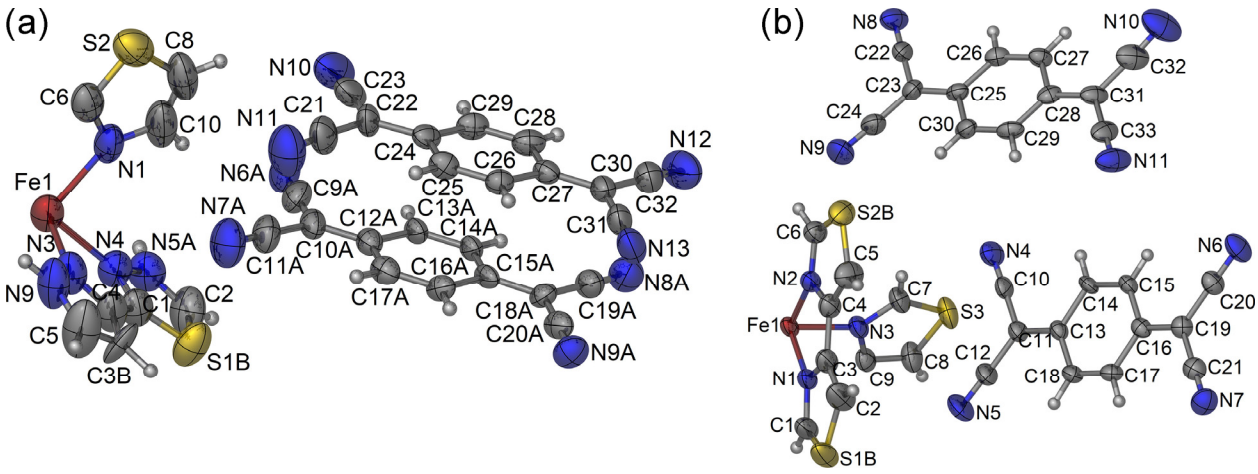


Figure S2. Asymmetric units in the crystal structures of **1** and **2**. The labels of H atoms are omitted for clarity.

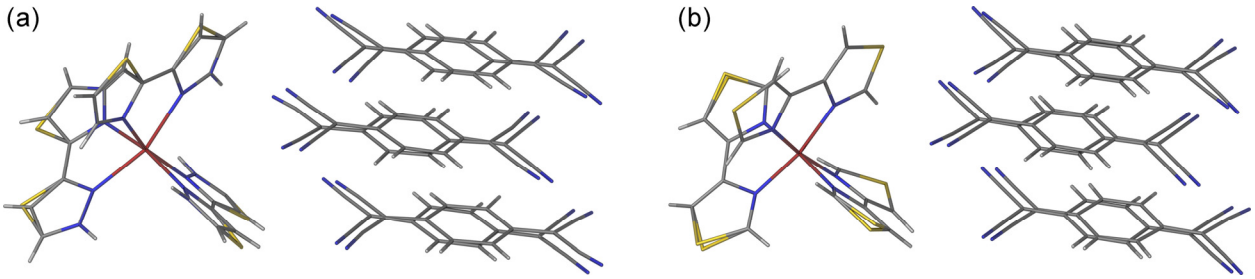
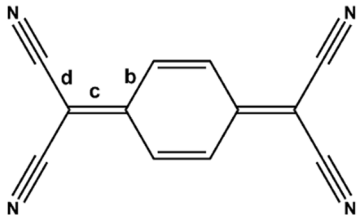


Figure S3. The view of formula units, $[FeL_3](TCNQ)_3$, in the crystal structures of **1** (L = 3tpH) and **2** (L = 4bt), showing the disorder of both the ligands and the $TCNQ^{\bullet\delta-}$ anions.



Scheme S1. The metric parameters used to estimate the charges on the TCNQ fragments from the crystal structures determined at 230 K.

Complex	TCNQ Fragment	*b*, Å	*c*, Å	*d*, Å	Charge (scaled)[a]
1 at 230 K	A	1.440	1.3835	1.4198	–0.56
	B	1.426	1.3865	1.426	–0.72
2 at 230 K	A	1.428	1.3965	1.4265	–0.68
	B	1.437	1.4005	1.429	–0.66

[a] For each compound, the charges on the TCNQ fragments were scaled to total –2, to match the +2 charge of the Fe(II) cationic complex.

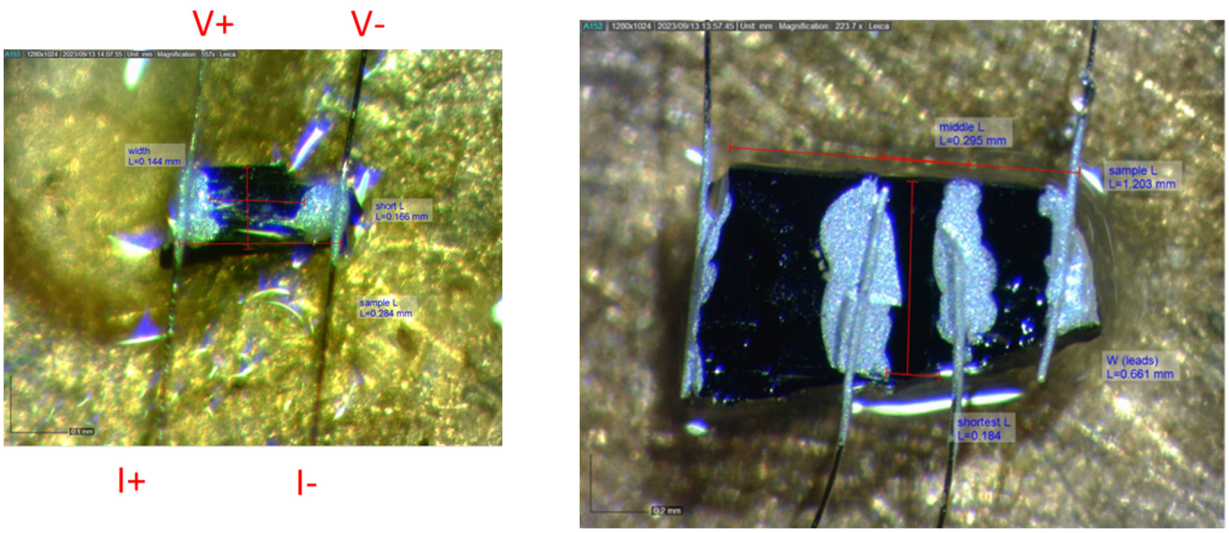


Figure S4. The 4-probe electrode configuration used to measure electric transport on the single-crystal samples of **1** (left) and **2** (right).

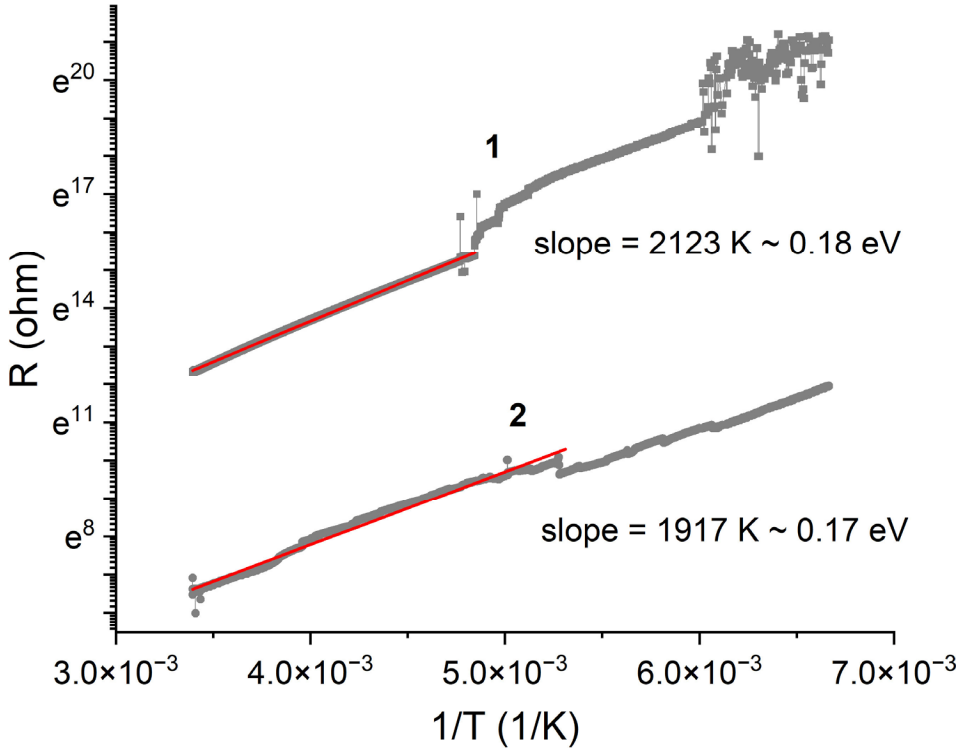


Figure S5. The dependence of logarithmic resistance on inverse temperature, from which the activation energy for charging hopping was determined for the single-crystal samples of **1** and **2**.