Anion Doping as a Probe of Cooperativity in the Molecular Spin-Crossover Compound $[FeL_2][BF_4]_2$ (L = 2,6-di{pyrazol-1-yl}pyridine)

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Electronic Supplementary Information

Figure S1. Observed and simulated magnetic data for the powder samples of **1**-**4** in warming mode, using the Slichter and Drickhamer model of phase transitions in solid solutions.

Figure S2. Variable temperature unit cell dimensions from single crystals of **2** and **3**, near their spin-transition temperatures.

Table S1. Selected bond lengths and angles (Å, °), and metric parameters for the intermolecular π-π interactions, for **1**-**3**.

Table S2. Selected bond lengths and angles (Å, °) for **4**.

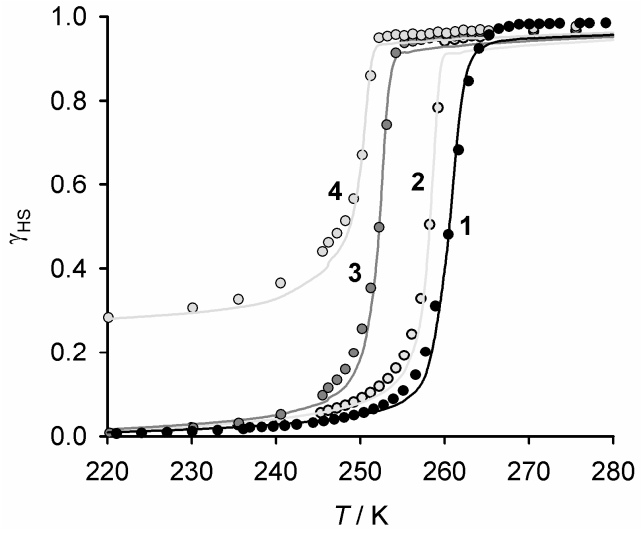

Figure S1. Observed (points) and simulated (line) magnetic data for the powder samples of **1**-**4** in warming mode, using the Slichter and Drickhamer model of solid state phase transitions.[1] γ_{HS} is the high-spin fraction of the sample at a given temperature. The values of the interaction energy Γ derived by this analysis are listed in Table 1 of the main paper.

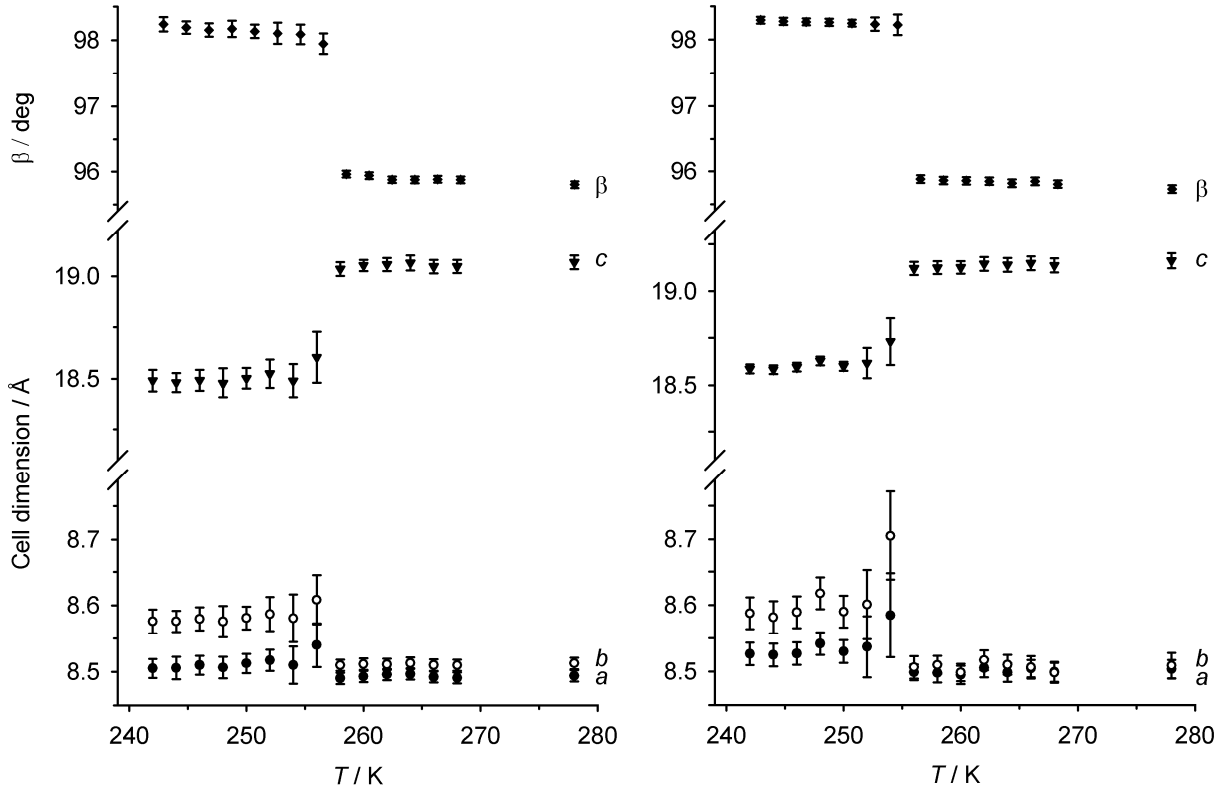

Figure S2 Variable temperature unit cell dimensions from single crystals of **2** (left) and **3** (right), near their spin-transition temperatures. Corresponding data for **1** are presented in ref. 2.

Table S1 Selected bond lengths and angles (Å, °), and metric parameters for the intermolecular π-π interactions, for **1**-**3**. Symmetry codes: (i) –1+*x*, *y*, *z* (**1** and **3**) or 1+*x*, *y*, *z* (**2**); (ii) *x*, 1+*y*, *z* (**1** and **3**) or *x*, –1+*y*, *z* (**2**). The codes for **2** are different because the crystal used was of the opposite hand to those of **1** and **3**.

	1		**2**		**3**	
	300 K	150 K	300 K	150 K	300 K	150 K
Fe(1)–N(2)	2.1390(14)	1.9049(15)	2.141(2)	1.907(2)	2.134(3)	1.911(2)
Fe(1)–N(9)	2.2063(17)	1.9913(17)	2.201(3)	1.987(3)	2.201(3)	1.989(2)
Fe(1)–N(14)	2.1865(19)	1.9751(17)	2.193(3)	1.976(3)	2.189(3)	1.973(2)
Fe(1)–N(18)	2.1402(15)	1.9097(16)	2.140(2)	1.914(2)	2.138(3)	1.914(2)
Fe(1)–N(25)	2.1964(19)	1.9912(18)	2.193(3)	1.994(3)	2.190(3)	1.996(2)
Fe(1)–N(30)	2.203(2)	1.9760(18)	2.202(3)	1.979(3)	2.212(4)	1.979(2)
N(2)–Fe(1)–N(9)	73.68(6)	79.97(7)	73.54(10)	79.86(10)	73.51(10)	79.80(9)
N(2)–Fe(1)–N(14)	73.23(6)	80.23(7)	73.31(10)	80.44(10)	73.45(11)	80.24(9)
N(2)–Fe(1)–N(18)	172.98(7)	178.15(8)	173.06(12)	178.14(12)	173.43(13)	177.95(11)
N(2)–Fe(1)–N(25)	113.16(7)	101.77(7)	113.17(11)	101.74(11)	112.82(13)	101.95(9)
N(9)–Fe(1)–N(30)	100.15(7)	98.08(7)	100.14(11)	98.32(10)	100.48(13)	98.15(9)
N(9)–Fe(1)–N(14)	146.88(7)	160.19(7)	146.82(11)	160.29(10)	146.91(12)	160.04(9)
N(9)–Fe(1)–N(18)	104.33(6)	100.80(7)	104.35(10)	100.76(10)	104.32(10)	101.01(8)
N(9)–Fe(1)–N(25)	98.35(7)	93.10(7)	98.32(10)	93.25(11)	98.20(11)	93.06(9)
N(9)–Fe(1)–N(30)	93.03(7)	92.15(7)	93.16(10)	92.33(10)	93.02(11)	92.28(9)
N(14)–Fe(1)–N(18)	108.32(6)	98.99(7)	108.40(10)	98.92(10)	108.32(11)	98.92(9)
N(14)–Fe(1)–N(25)	95.93(7)	91.30(7)	95.83(11)	91.21(11)	96.10(12)	91.48(9)
N(14)–Fe(1)–N(30)	91.23(7)	90.23(7)	91.26(11)	90.02(10)	91.18(12)	90.10(9)
N(18)–Fe(1)–N(25)	73.68(7)	79.91(7)	73.56(10)	80.00(11)	73.49(12)	79.92(9)
N(18)–Fe(1)–N(30)	73.10(7)	80.22(7)	73.23(11)	79.92(11)	73.30(12)	79.96(9)
N(25)–Fe(1)–N(30)	146.60(7)	160.06(6)	146.61(10)	159.82(10)	146.63(11)	159.81(9)
Intralayer π-π interactions:						
N(8)-C(12)...N(13^{i})-C(17^{i})						
Average interplanar spacing	3.593(8)	3.554(7)	3.588(12)	3.566(11)	3.606(15)	3.592(11)
Dihedral angle	8.28(14)	5.48(12)	7.8(2)	5.50(18)	6.9(3)	5.38(18)
Centroid offset	1.20	1.72	1.22	1.74	1.25	1.76
N(24)-C(28)...N(29^{ii})-C(33^{ii})						
Average interplanar spacing	3.443(8)	3.368(8)	3.446(12)	3.379(12)	3.483(15)	3.403(11)
Dihedral angle	4.96(14)	8.05(11)	4.1(2)	7.83(17)	3.7(3)	7.86(16)
Centroid offset	1.66	2.16	1.66	2.17	1.65	2.19
Interlayer spacing						
c/2	9.5770(9)	9.2150(8)	9.6042(7)	9.2482(4)	9.6676(4)	9.3044(3)

Table S2 Selected bond lengths and angles (Å, °) for **4**. See ref. 3 for the definition and discussion of the distortion angles θ and ϕ. Symmetry code: (iii) *–x*, *y*, ½*–z*.

Fe(1)–N(2)	2.1808(16)	Fe(1)–N(14)	2.2297(19)
Fe(1)–N(9)	2.1951(18)		
N(2)–Fe(1)–N(2^{iii}) (ϕ)	155.69(10)	N(9)–Fe(1)– N(9^{iii})	85.20(10)
N(2)–Fe(1)–N(9)	72.35(7)	N(9)–Fe(1)–N(14)	141.81(6)
N(2)–Fe(1)–N(9^{iii})	127.82(7)	N(9)–Fe(1)–N(14^{iii})	106.05(7)
N(2)–Fe(1)–N(14)	72.13(6)	N(14)–Fe(1)–N(14^{iii})	87.62(10)
N(2)–Fe(1)– N(14^{iii})	90.17(6)	θ	66.56 (2)

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