Supplementary Information

Tetranuclear [FeII2FeIII2]2+ molecular switches: [FeII(bik)2(N-)2] spin-crossover complexescontaining [FeIII(Tp)(CN)3]- metalloligands as N- donor

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Figure S1. Cyclovoltammogram of PPh4[Fe(Tp\*)(CN)3] (5)

Table S1. Crystal data and structure refinement parameters for PPh4[Fe(Tp\*)(CN)3].CH3CN (5)

Figure S2. Perspective and top view of the anionic complex in PPh4[Fe(Tp\*)(CN)3].CH3CN

Table S2. Selected bond lengths (Å) and angles (°) for PPh4[Fe(Tp\*)(CN)3].CH3CN

Figure S3. Magnetic properties of 2 depicted as the *χMT versus T* curve (solvated and *in-situ* desolvated sample.

Figure S4. *χMT versus T* curves of 3 and 4 measured upon heating (from low temperature to 400 K) and upon cooling (from 400 K to low temperature).

Figure S5. *MT* *versus T* curves simulated using the Slicher Drickammer model.

Figure S6. Measurement of the χ*MT* product *versus* time at 10 K for the compound 4 under laser light irradiation



Figure S1. Cyclovoltammogram of PPh4[Fe(Tp\*)(CN)3] (5) at room temperature in dried acetonitrile (*vs* Fc/Fc+). Scan rate ν = 100 mV.s-1, Pt/[nBu4N][PF6]/Ag.

The redox process in PPh4[Fe(Tp\*)(CN)3] occurs at a half potential of E°1/2 = -1002 mV (Ep = 78 mV) a value lower than that found for PPh4[Fe(Tp)(CN)3] (E°1/2 = -824 mV *vs* [Fc]/[Fc]+ ).

Table S1. Crystal data and structure refinement parameters for PPh4[Fe(Tp\*)(CN)3].CH3CN (5)

|  |  |
| --- | --- |
| Compound | PPh4[Fe(Tp)\*(CN)3] · CH3CN |
| Molecular formula | C44H45BFeN10P |
| *M* [g·mol-1] | 811.54 |
| Crystal system | monoclinic |
| Space group | *P*21/*c* |
| *a* [Å] | 16.3287(5) |
| *b* [Å] | 9.8451(3) |
| *c* [Å] | 26.4596(8) |
| ** | 90.00 |
| ** | 103.2530(10) |
| ** | 90.00 |
| *V* [Å3] | 4140.3(2) |
| Crystal size | 0.160×0.120×0.100 |
| *µ* [mm-1] | 0.448 |
| *ρcalculated* [g·cm3] | 1.302 |
| *Z* | 4 |
| *T* [K] | 200 |
| 2*θmax* [°] | 60.23 |
| Collected reflexions | 41529 |
| Unique reflexions | 12087 |
| Number of parameters/restraints | 515/0 |
| R1 [I ≥ 2σ(I)] | 0.0541 |
| *wR2* (all data) | 0.1752 |
| Max/min residual electron density [e×Å-3] | 0.84/-0.80 |
| Radiation | Mo Kλ = 0.71073) |
| Diffractometer | Bruker Kappa Apex2 |



Figure S2. Perspective and top view of the anionic complex in PPh4[Fe(Tp\*)(CN)3].CH3CN

The complex PPh4[Fe(Tp\*)(CN)3].CH3CN (5) crystallises in the monoclinic space group P21/c, (Z = 4). Its crystal structure consists of a negatively charged tricyanido tris(3,5-dimethylpyrazolyl)borate iron(III) complex, its tetraphenyl phosphonium countercation and an acetonitrile molecule. It is isostructural to the literature-known PPh4[FeII(Tpm\*)(CN)3] · 2 MeCN,[[1]](#footnote-1) where the change in oxidation state of the iron ion compensates the replacement of the neutral scorpionate Tpm\* ligand ( ) by the negatively charged Tp\*. The Fe–C bond lengths exhibit a mean distance of 1.923 Å, which is typical for iron(III) cyanide complexes. The Fe–N bonds are about the same length with a mean value of 2.010 Å. This difference contributes to the elongation along the pseudo C3v symmetry axis (Fe···B). Selected bond lengths and angles are listed below.

Table S2. Selected bond lengths (Å) and angles (°) for PPh4[Fe(Tp\*)(CN)3].CH3CN (5)

|  |  |
| --- | --- |
| Fe1–C1 1.922(3)Fe1–C2 1.930(3)Fe1–C3 1.917(3) | Fe1–N11 2.025 (2)Fe1–N13 1.990(2)Fe1–N15 2.014(2) |
| C1-Fe1-C2 89.66(11),C1-Fe1-C3 87.19(12),C2-Fe1-C3 86.56(11),N11-Fe1-N13 89.96(9),N11-Fe1-N15 89.33(9),N13-Fe1-N15 88.36(9), | C1-Fe1-N11 90.84(10),C1-Fe1-N13 90.38(9),C2-Fe1-N11 90.58(11),C2-Fe1-N15 91.60(11),C3-Fe1-N13 92.27(11),C3-Fe1-N15 93.32(11), | Fe1-C1-N1 176.8(3)Fe1-C2-N2 178.8(3)Fe1-C3-N3 178.4(3) |



Figure S3. Magnetic properties of 2 depicted as the *χMT versus T* curve. The black curve represents the properties of the fresh sample (measured upon heating) while the orange curve represents the properties of the *in-situ* desolvated sample. Once dehydrated the sample show a well reproducible spin-transition (green curve).



Figure S4. *χMT versus T* curves of 3 and 4 measured upon heating (from low temperature to 400 K) and upon cooling (from 400 K to low temperature). In both cases, the *χMT* curve superimposed to each other showing that the loss of solvent (occurring when measuring upon heating under reduced He pressure) does not affect the spin crossover behaviour.

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| H = 24 kJ.mol-1.K; S = 105 J.mol-1.K;  = 1.6 kJ.mol-1.K | H = 23.5 kJ.mol-1.K; S = 105 J.mol-1.K;  = 1.0 kJ.mol-1.K |

Figure S5. *MT* *versus T* curves simulated using the Slicher Drickammer model. Experimental data are in black. The simulated data is in red.



Figure S6. Measurement of the χ*MT* product *versus* time at 20 K for compound 4 under laser light irradiation (ca. 5 mW/cm2) at 808 nm (red), 532 nm (green) and 405 nm (violet).

1. Shi, C.-C.; Chen, C.-S.; Hsu, S. C. N.; Yeh, W.-Y.; Chiang, M. Y.; Kuo, T.-S. *Inorg. Chem. Commun.* 2008, *11* (10), 1264–1266. [↑](#footnote-ref-1)