Supplementary Materials

Syntheses, Structures and Magnetic Properties of a Novel *mer*-$[(bbp)Fe^{III}(CN)_3]^{2-}$ Building Block (bbp: bis(2-benzimidazolyl)pyridine dianion) and Its Related Heterobimetallic Fe(III)-Ni(II) Complexes

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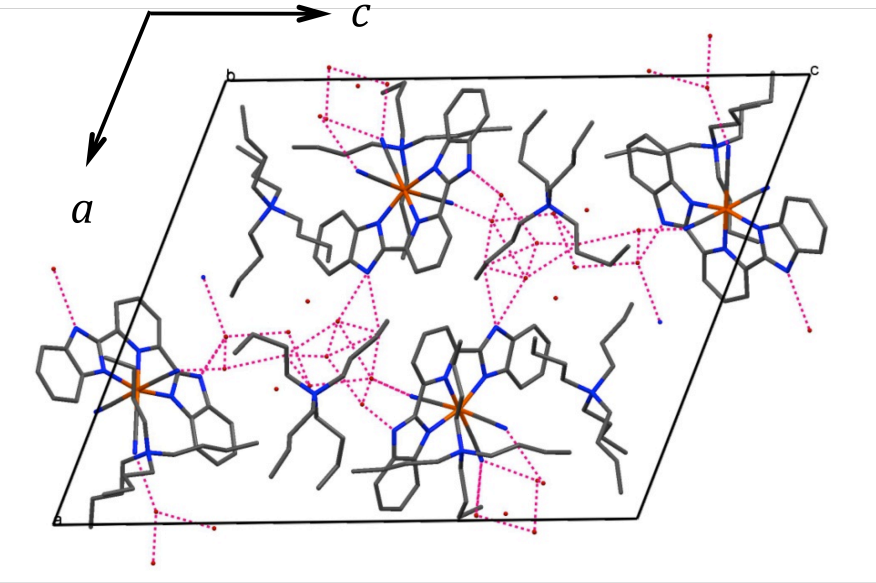

Figure S1. Asymmetric unit for complex **1** viewed perpendicular to the *b* axis.

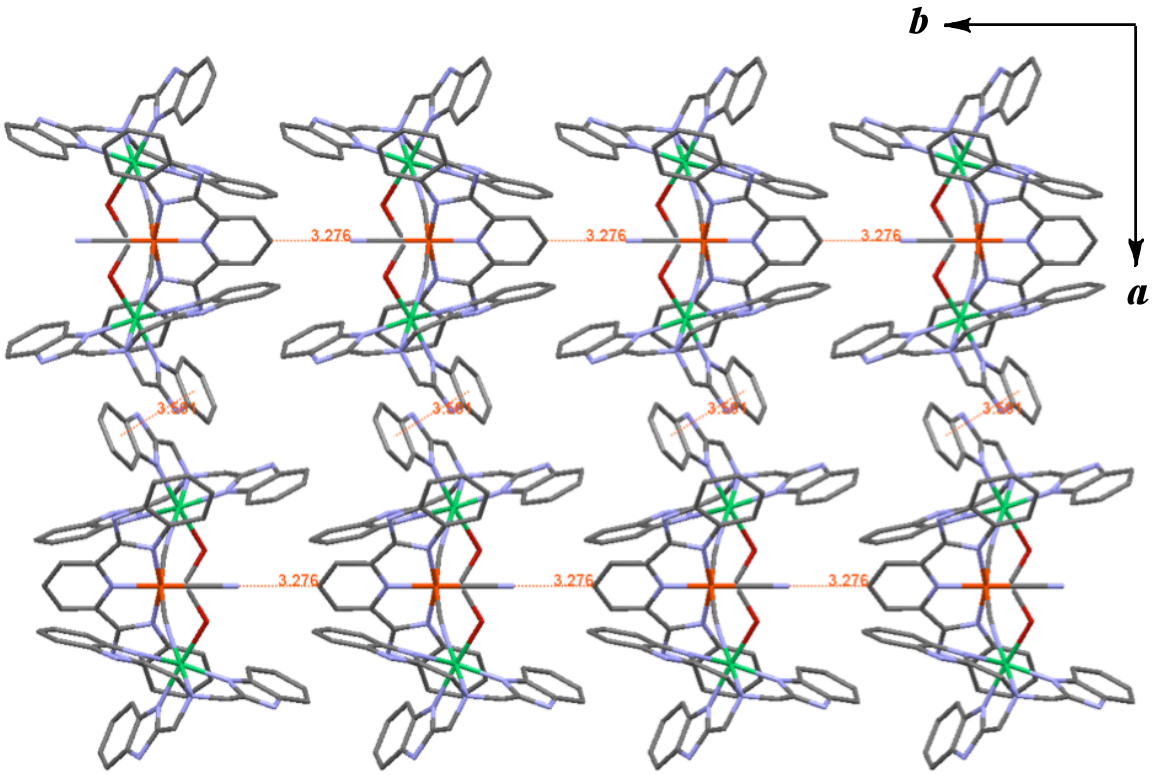

Figure S2. Molecular packing of complex **2** in the *ab* plane showing hydrogen bonding and π-π stacking.

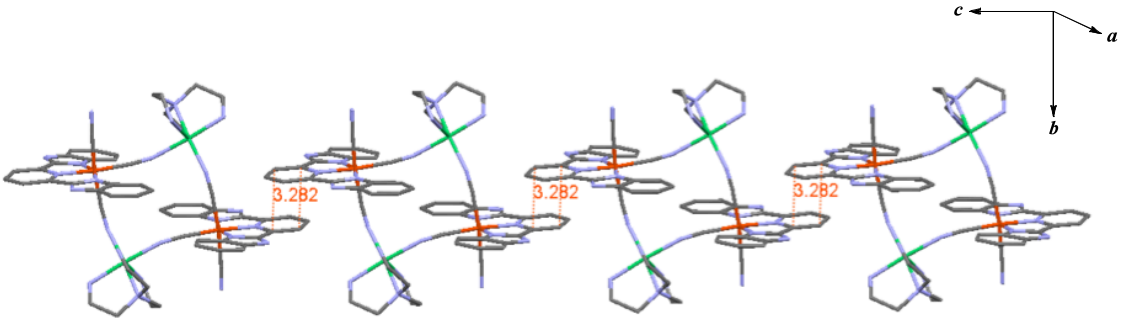

Figure S3. Supramolecular chain of complex **3** running along the *c* axis.

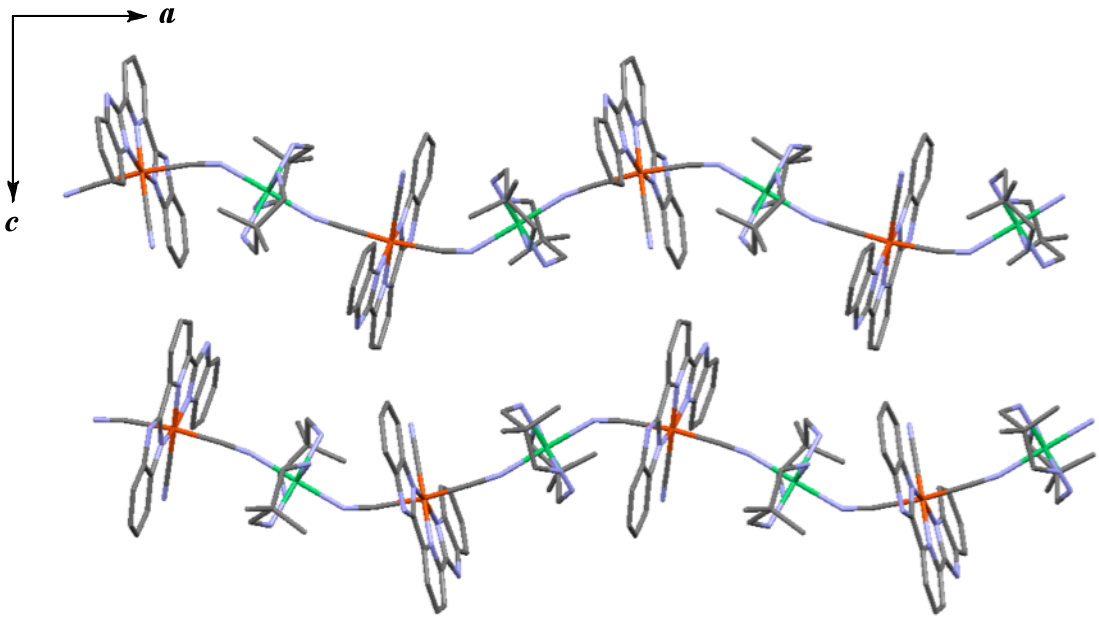

Figure S4. One dimensional coordination polymer observed in **4** running parallel to the *a* axis.

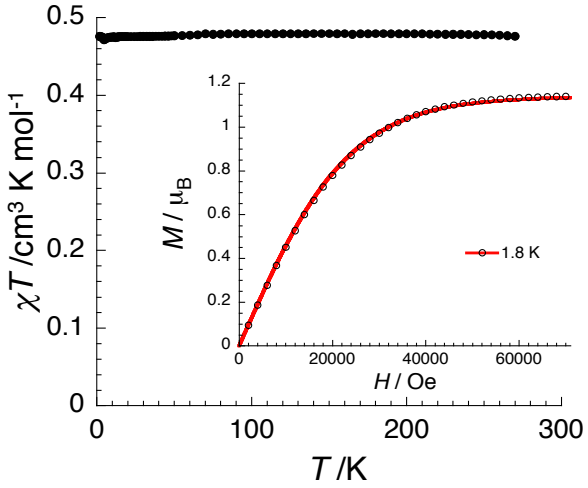

Figure S5. Temperature dependence of the χT product for compound **1** (where $\chi = M/H$ per complex) measured at 0.1 T. Inset: field dependence of the magnetization versus H at 1.8 K. The solid red line is the best fit of the experimental data to the $S = 1/2$ Brillouin function $g_{Fe} = 2.29$.

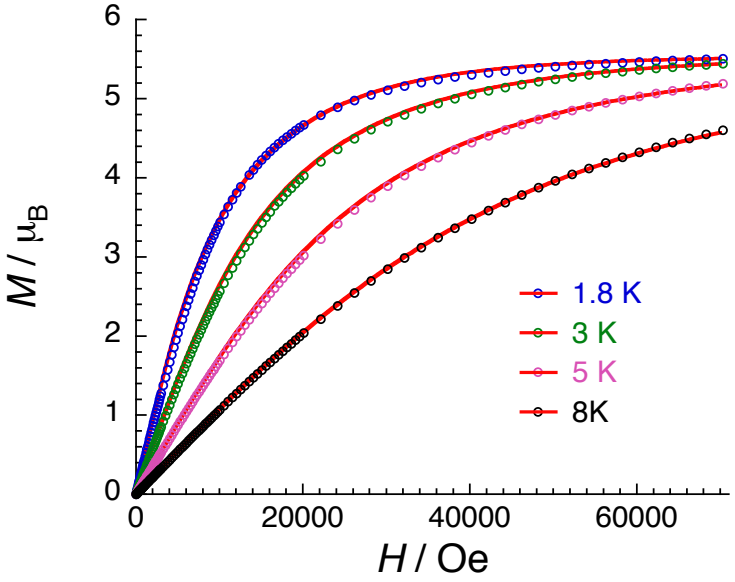

Figure S6. Field dependence of the magnetization at 1.8, 3, 5 and 8 K for compound **2**. The solid red lines are the best simulation obtained with the MAGPACK program[1] using the Hamiltonian $\hat{\boldsymbol{H}} = -2J\boldsymbol{S}_{Fe(III)}\cdot(\boldsymbol{S}_{Ni(II)} + \boldsymbol{S}_{Ni(II)}) + D_{Ni}\,(S^2_{z,Ni1} + S^2_{z,Ni2})$ with the parameters $g_{Ni} = 2.21(1)$, $g_{Fe} = 2.29(1)$, $J/k_B = 12.4(2)$ K, and $D_{Ni}/k_B = -4(1)$ K.

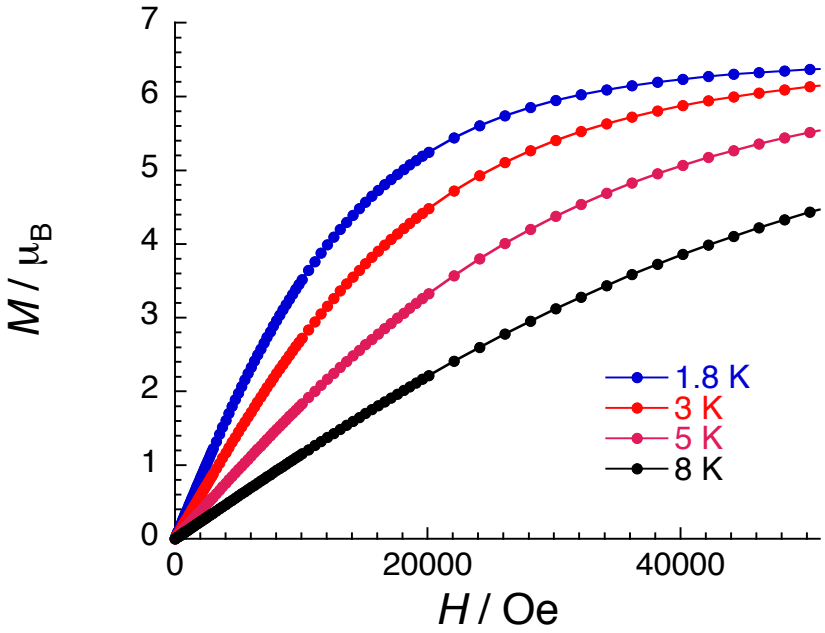

Figure S7. Field dependence of the magnetization at 1.8, 3, 5 and 8 K for **3** (the lines are eye guides).

Table S1. Selected magneto-structural data for related heterobimettallic $Fe^{III}_{LS}(\mu\text{-CN})Ni^{II}$ compounds.

Compounds	Structure	Ni–NC (°)	Ni···Fe (Å)	*g*	*J*/K	Ref.
$[(Tp)_2Fe_2(CN)_6Ni(cyclam)]\cdot 2H_2O$	trinuclear	171.5(3)	5.132(2)	2.37	24.6	2a
$[(Tp)_2Fe_2(CN)_6Ni(en)_2]$	trinuclear	153.8(3)	5.0669(11)	2.25	1.7	2b
$[Ni(L1)][Fe(bpb)(CN)_2]_2\cdot H_2O$	trinuclear	160.2(7)	5.093(2)	2.5	9.14	2c
$[Ni(L3)][Fe(bpb)(CN)_2]_2\cdot 7H_2O$	trinuclear	163.2(2)	5.110(1)		7.8	2c
$[Ni(L4)][Fe(bpb)(CN)_2]_2\cdot 4H_2O$	trinuclear	173.4(5)	5.133(1)		11.1	2c
$[Ni(L5)][Fe(bpb)(CN)_2]_2$	trinuclear	157.0(2)	5.068(1)		8.81	2c
$[(pzTp)_2Fe_2(CN)_6Ni(L)]\cdot 1/2CH_3OH$	trinuclear	149.2(6)-150.7(6)	4.900(2)-4.910(2)	2.5	1.3	2d
$[(pzTp)_2Fe_2(CN)_6Ni(bipy)_2]\cdot 2H_2O$	square	169.8(4)	5.080(1)	2.31	7.0	2d
$[TpFe(CN)_3]_2[Ni(DMSO)_4]$	trinuclear	165.4(3)	5.020(4)	2.30	3.8	2e
$\{[Tp^*Fe(CN)_3Ni(DMF)_4]_2[OTf]_2\}\cdot 2DMF$	square	176.4(3)	5.1144(9)-5.0963(8)	2.20	7.5	3a
$\{[(Tp^{*Bn})Fe(CN)_3]_2[Ni(DMF)_4]\}\cdot 2DMF$	trinuclear	173.3(3)	5.0422(6)	2.30	7.1	3b
$[TpFe(CN)_2(\mu\text{-}CN)Ni(dmphen)_2]_2(ClO_4)_2\cdot 2CH_3OH$	square	169.5(2)-168.6(2)	5.170(6)-5.166(8)	2.30-2.21	15.3-13.8	3c
$[(pzTp)Fe(CN)_2(\mu\text{-}CN)Ni(dmphen)_2]_2(ClO_4)_2\cdot 2CH_3OH$	square	170.3(3)-171.6(3)	5.150(6)-5.168(5)	2.39-2.20	12.1-8.9	3c
$[(pzTp)Fe(CN)_3]_4[NiL]_4[OTf]_4\cdot 10DMF\cdot Et_2O$	cube	177.4(8)-179.1(2)	5.120(3)	2.20	9.5	4a
$\{[(Tp^{*Me})Fe(CN)_3]_4[Ni(DMF)_3]_2\}\cdot 4DMF\cdot H_2O$	hexanuclear	170.2(3)-177.1(3)	5.0986(8)-5.0571(9)	2.30	9.0	4b
$\{[(Tp^{*Me})Fe(CN)_3]_6[Ni(MeOH)_3]_2[Ni(MeOH)_2]\}\cdot 3H_2O\cdot 8MeOH$	nonanuclear	157.5(4)-172.8(4)1	5.0458(7)-5.0775(8)	2.50	9.0	4b
$\{(MeTp)_2Fe_2(CN)_6Ni[(1R,2R)\text{-chxn}]_2\}$	square	163.0(5)-167.1(5)	5.096(1)-5.081(1)	2.34	4.16	5a
$\{[(Tp^{*Me})Fe(CN)_3]_4[Ni(tren)]_4[ClO_4]_4\}\cdot 7H_2O\cdot 4MeCN$	octanuclear	158.7(4)-170.6(3)	5.0859(9)-5.093(1)-5.1188(8)	2.40	9.5	5b
$[(pzTp)_2Fe_2Ni_2(dpa)_2(CN)_6](ClO_4)_2\cdot 2CH_3OH\cdot 6H_2O$	square	171.2(6)-174.4(5)	5.100(1)	2.23	10.1	5c
$\{[TpFe(CN)_3]_2[Ni(dpt)]\}_n\cdot 3nH_2O$	chain	159.5(2)-172.0(3)	5.066-5.188	2.30	16.3	5d
$[(PhTp)Fe(CN)_3Ni(tren)]_2(ClO_4)_2$	square	160.3(4)-173.6(4)	5.016- 5.157	2.284	6.0	6
$[(MeTp)Fe(CN)_3Ni(tren)]_2(ClO_4)_2\cdot 2H_2O$	square	161.6(8)-177.2(8)	5.047-5.153	2.305	4	6
$[(i\text{BuTp})Fe(CN)_3Ni(tren)]_2(ClO_4)_2\cdot 2H_2O\cdot 2CH_3OH$	square	164.7(4)-175.2(4)	5.047–5.189	2.285	7.8	6
$[(pzTp)Fe(CN)_3]_4[NiL^1]_4[OTf]_4$	cube	179.0(1)-177.0(1)	5.188(5)	2.30	9.5-8.5	7
$[TpFe(CN)_3Ni(tren)]_2(ClO_4)_2\cdot 2H_2O$	square	161.7(3)-173.8(3)	5.042-5.156	2.22	6.4	8a
$[TpFe(CN)_3Ni(bipy)_2]_2[TpFe(CN)_3]_2\cdot 6H_2O$	square	169.8(2)-171.7(2)	5.090-5.100	2.67	10.5	8a
$\{[Tp^*Fe(CN)_3Ni(bipy)_2]_2[OTf]_2\}\cdot 2H_2O$	square	167.1(4)-171.9(3)	5.097(1)	2.29	9.4	8b
catena-[Ni((R)-pabn)][TpFe $(CN)_3$]$PF_6\cdot 2$MeOH	chain	164.9(3)-160.0(3)	5.0654(8)-4.9853(8)	2.40	9.14	8c

$[TpFe(CN)_3(NiL^2)_2]_2 \cdot 2ClO_4 \cdot 6H_2O$	square	175.5(3)-177.9(2)	5.135(4)	2.14	6.1	9
$[(i\text{-BuTp})Fe(CN)_3Ni(L^3)_2]_2 \cdot 2ClO_4 \cdot 6H_2O$	square	175.5(3)-177.9(2)	4.978(9)	2.14	6.0	9
$[(Tp)_2Fe_2(CN)_6Ni(L^4)_2] \cdot 8H_2O$	square	159.6(4)	4.978(9)	2.34	5.9	9
$\{[Ni(ntb)(MeOH)]_2[Fe(bbp)(CN)_3][ClO_4]_2\} \cdot 2MeOH$ **2**	trinuclear	176.5(3)	5.0817(4)	2.22	12.4	This work
$\{[Ni(tren)]_2[Fe(bbp)(CN)_3]_2\} \cdot 7MeOH$ **3**	square	149.4(2)-164.3(2)	4.9443(5)-5.1107(5)	2.23	4.4	This work
$\{[Ni(dpd)_2]_2[Fe(bbp)(CN)_3]_2\} \cdot 9MeOH \cdot 3H_2O$ **4**	chain	148.6(4)-167.3(4)	4.9239(8)-5.0839(9)	2.30	18.5	This work

Tp = hydrotris(pyrazol-1-yl)borate, Tpm^{Me} = tris(3,5-dimethyl-1-pyrazolyl)methane), cyclam = 1,4,8,11-tetraazacyclotetradecane, en = ethylenediamine, , pzTp = tetra(pyrazol-1-yl)borate, L = 1,5,8,12-tetraazadodecane, bipy = 2,2'-bipyridine, Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate, OTf = trifluoromethanesulfonate, Tp^{*Bn} = tris(3,5-dimethyl-4-benzyl)pyrazolylborate, L1 = 1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane, L3 = 1,8-dihydroxyethyl- l,3,6,8,10,13-hexaazacyclotetradecane, L4 = 3,10-bis(2-phenylethyl)-1,3,5,8,10,12-hexaazacyclotetradecane, L5 = 3-methyl-1,3,5,8,12-pentaazacyclotetradecane, dmphen = 2,9-dimethyl-1,10-phenanthroline, MeTp = methyltris(pyrazolyl)borate, bpb = 1,2-Bis(pyridine-2-carboxamido)benzenate, chxn = 1,2-diaminocyclohexane, Tp^{*Me} = tris(3,4,5-trimethylpyrazolyl)borate, phen = phenanthroline, PhTp = tris(pyrazolyl)phenylborate, *i*BuTp = 2-methylpropyltris(pyrazolyl)borate, L^1 = 1-S(acetyl)-tris(pyrazolyl)hexane, pabn = N^2,$N^{2'}$-bis(pyridin-2-ylmethyl)-1,10-binaphthyl-2,2'-diamine, cyclen = 1,4,7,10-tetraazacyclododecane, L^2 = 4,5-[1′,4′]dithiino[2′,3′-b]quinoxaline-2-bis(2-pyridyl)methylene-1,3-dithiole, L^3 = dimethyl-2-[di(pyridin-2-yl)methylene]-1,3-dithiole-4,5-dicarboxylate, L^4 = 4,5-bis(methylthio)-2-bis(2-pyridyl)methylene-1,3-dithiole, dpt = dipropylenetriamine.

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