Electronic Supporting information

(ESI)

Design of 3d-4f Molecular Squares through the $[Fe\{(HB(pz)_3)\}(CN)_3]^-$ Metalloligand

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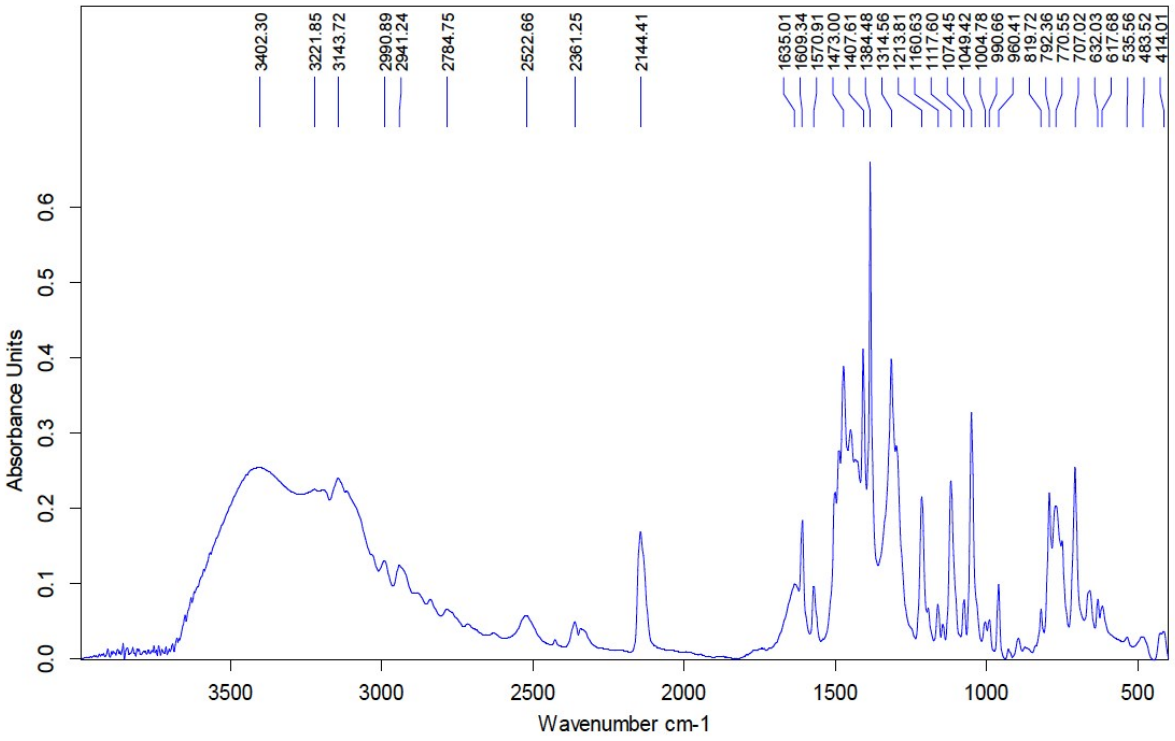

Figure S1. FTIR spectrum for compound **1**

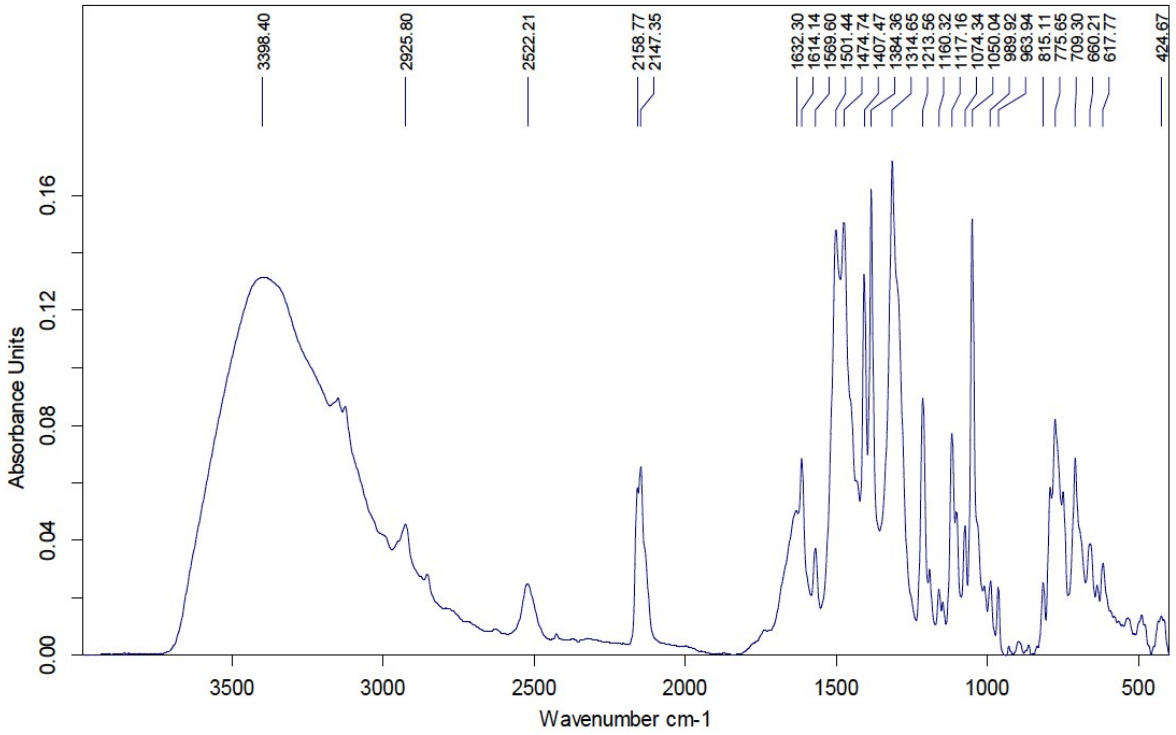

Figure S2. FTIR spectrum for compound **2**

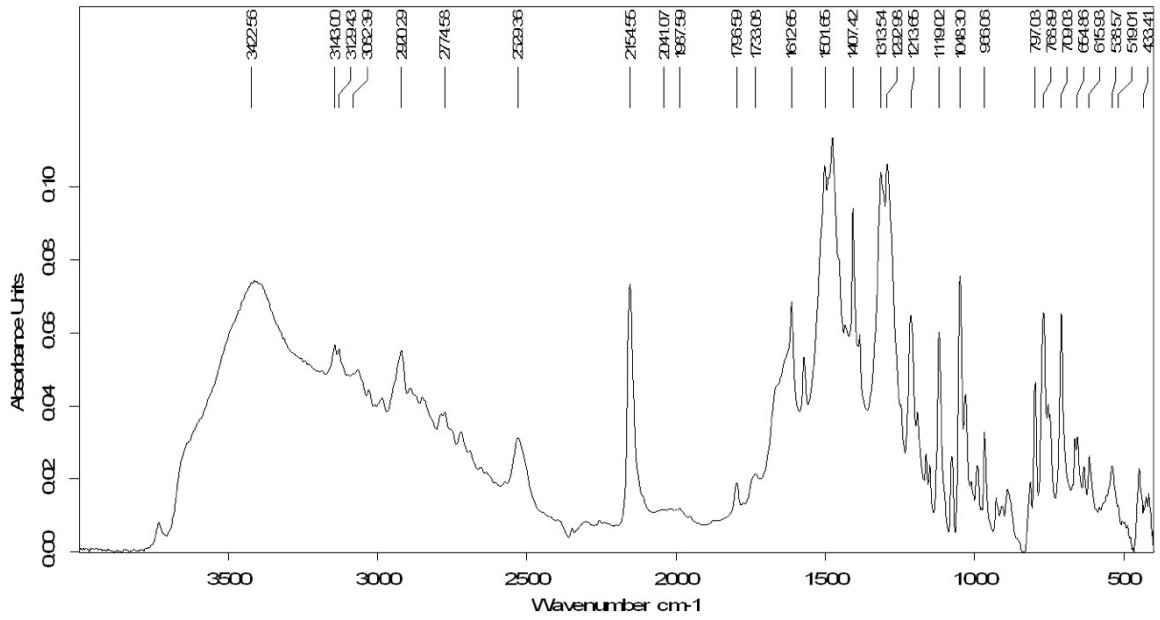

Figure S3. FTIR spectrum for compound **3**

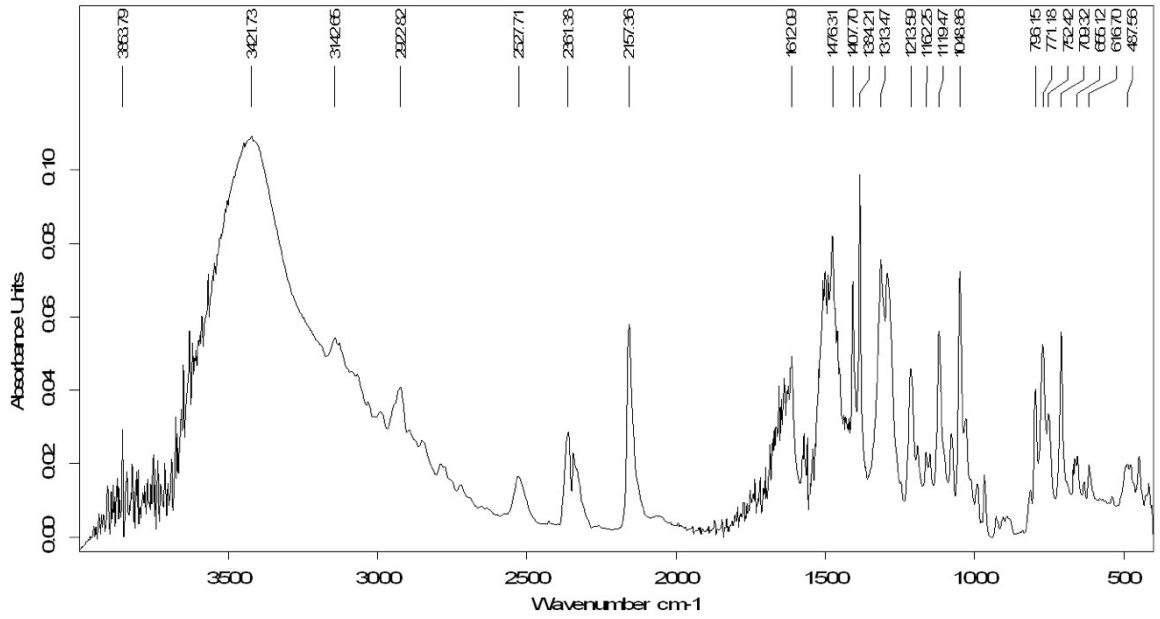

Figure S4. FTIR spectrum for compound **4**

Table S1. Bond Lengths (Å) and angles (deg) of the environments of the iron(III) and lanthanum(III) ions in **1**

				1			
Fe1-N1	1.970(5)	N3-Fe1-C11	90.1(2)	N12-La1-O5	82.65(15)	N15-La1-N8	133.38(16)
Fe1-N3	1.977(5)	N3-Fe1-C12	177.9(2)	N13-La1-O1	102.26(15)	O1-La1-N7a*	160.74(15)
Fe1-N5	1.983(5)	N5-Fe1-C10	176.9(2)	N13-La1-O2	65.91(14)	O1-La1-N8	118.11(17)
Fe1-C10	1.930(6)	N5-Fe1-C11	92.1(2)	N13-La1-O4	111.78(14)	O2-La1-N7	132.42(15)
Fe1-C11	1.926(6)	N5-Fe1-C12	89.4(2)	N13-La1-O5	140.34(14)	O2-La1-N8	77.94(16)
Fe1-C12	1.936(7)	C10-Fe1-C11	86.8(2)	N15-La1-O1	67.08(15)	O4-La1-N7a*	66.03(15)
La1-N7a*	2.625(5)	C10-Fe1-C12	87.7(2)	N15-La1-O2	76.03(16)	O4-La1-N8	135.47(16)
La1-N8	2.609(5)	C11-Fe1-C12	88.6(3)	N15-La1-O4	74.13(15)	O5-La1-N7a*	112.98(16)
La1-N10	2.757(5)	Fe1-C10-N7	177.2(5)	N15-La1-O5	79.42(15)	O5-La1-N8	146.53(15)
La1-N12	2.647(5)	Fe1-C11-N8	178.5(6)	O1-La1-O2	47.87(15)		
La1-N13	2.810(5)	Fe1-C12-N9	176.3(6)	O4-La1-O5	47.82(14)		
La1-N15	2.623(5)	N10-La1-N12	61.82(16)	O1-La1-O4	104.37(15)		
La1-O1	2.712(5)	N13-La1-N15	61.15(15)	O1-La1-O5	62.69(16)		
La1-O2	2.606(4)	N10-La1-N13	139.21(15)	O2-La1-O4	145.95(14)		
La1-O4	2.675(5)	N10-La1-N15	145.36(16)	O2-La1-O5	110.55(15)		
La1-O5	2.638(5)	N12-La1-N13	128.27(16)	La1-N7-C10	175.5(5)		
		N12-La1-N15	135.70(16)	La1-N8-C11	160.1(5)		
N1-Fe1-N3	88.8(2)	N10-La1-O1	116.51(15)	N10-La1-N7a*	77.48(15)		
N1-Fe1-N5	88.7(2)	N10-La1-O2	133.90(15)	N10-La1-N8	77.68(16)		
N3-Fe1-N5	89.0(2)	N10-La1-O4	71.70(15)	N12-La1-N7a*	130.47(15)		
N1-Fe1-C10	93.9(2)	N10-La1-O5	73.64(15)	N12-La1-N8	68.67(16)		
N1-Fe1-C11	178.6(2)	N12-La1-O1	68.67(15)	N13-La1-N7a*	68.55(15)		
N1-Fe1-C12	92.6(2)	N12-La1-O2	73.01(15)	N13-La1-N8	73.07(16)		
N3-Fe1-C10	93.9(2)	N12-La1-O4	119.86(15)	N15-La1-N7a*	93.83(16)		

a = *-x*, *-y*, *-z*

Table S2. Bond Lengths (Å) and angles (deg) of the environments of the iron(III) and lanthanide(III) ions in **2-4**

	2	**3**	**4**		**2**	**3**	**4**
Fe1-N1	1.955(12)	1.971(5)	1.964(4)	Ln1-N9a-C12	166.4(11)	165.9(6)	167.0(5)
Fe1-N3	1.970(11)	1.967(6)	1.962(5)	N10-Ln1-N8	77.6(4)	69.40(18)	69.39(14)
Fe1-N5	1.976(13)	1.963(6)	1.974(5)	N12-Ln1-N8	85.8(4)	85.8(2)	85.78(15)
Fe1-C10	1.939(17)	1.912(8)	1.910(7)	N10-Ln1-N9a*	77.6(4)	77.8(2)	77.65(15)
Fe1-C11	1.916(14)	1.920(7)	1.925(6)	N12-Ln1-N9a*	137.4(4)	137.5(2)	137.60(15)
Fe1-C12	1.908(15)	1.914(7)	1.927(5)	N3-Fe1-C12	92.8(5)	93.4(3)	93.1(2)
Ln1-N8	2.452(13)	2.436(5)	2.428(5)	N10-Ln1-O1	125.2(3)	126.07(18)	126.13(14)
Ln1-N9a*	2.446(13)	2.432(6)	2.426(4)	N10-Ln1-O2	150.5(4)	150.18(19)	150.57(13)
Ln1-N10	2.632(12)	2.633(6)	2.620(5)	N10-Ln1-O4	114.6(3)	113.74(16)	113.92(13)
Ln1-N12	2.471(12)	2.445(5)	2.436(4)	N10-Ln1-O5	73.2(3)	72.50(16)	72.75(13)
Ln1-O1	2.489(10)	2.491(5)	2.478(4)	N10-Ln1-O1W	130.6(3)	131.43(18)	131.89(13)
Ln1-O2	2.472(11)	2.455(5)	2.454(4)	N12-Ln1-O1	145.5(4)	146.78(19)	146.48(14)
Ln1-O4	2.512(9)	2.515(4)	2.517(4)	N12-Ln1-O2	136.7(4)	136.37(19)	136.15(14)
Ln1-O5	2.476(11)	2.464(5)	2.465(4)	N12-Ln1-O4	70.9(3)	71.04(18)	70.83(14)
Ln1-O1W	2.347(9)	2.365(5)	2.357(3)	N12-Ln1-O5	77.3(3)	77.61(18)	77.30(14)
				N12-Ln1-O1W	76.7(4)	77.65(19)	77.75(14)
N1-Fe1-N3	89.8(5)	89.4(2)	89.75(18)	N8-Ln1-O1	71.4(4)	72.6(2)	72.72(15)
N1-Fe1-N5	89.3(5)	89.2(2)	89.26(18)	N8-Ln1-O2	122.4(4)	123.9(2)	123.42(16)
N3-Fe1-N5	87.1(5)	87.6(2)	87.9(2)	N8-Ln1-O4	150.1(4)	150.65(18)	150.34(13)
Fe1-C10-N7	179.7(19)	179.2(7)	178.8(5)	N8-Ln1-O5	142.6(4)	141.90(19)	142.12(14)
Fe1-C11-N8	173.3(13)	176.7(6)	175.8(4)	N8-Ln1-O1W	77.3(4)	78.53(18)	78.67(14)
Fe1-C12-N9	173.5(13)	175.3(7)	175.0(5)	N9a-Ln1-O1	74.0(4)	72.5(2)	72.92(15)
C10-Fe1-C11	87.5(6)	87.4(3)	87.4(2)	N9a-Ln1-O2	73.6(4)	73.7(2)	74.04(15)
C10-Fe1-C12	85.5(6)	86.0(3)	86.4(2)	N9a-Ln1-O4	108.6(4)	109.43(19)	109.39(14)
C11-Fe1-C12	85.1(6)	84.3(3)	84.9(2)	N9a-Ln1-O5	71.9(4)	72.29(19)	72.59(15)
N1-Fe1-C10	91.9(5)	91.1(3)	91.1(2)	N9a-Ln1-O1W	145.9(4)	144.8(2)	144.65(15)
N3-Fe1-C10	92.2(6)	91.7(3)	91.6(2)	O1-Ln1-O2	51.7(3)	51.90(19)	51.45(14)
N5-Fe1-C10	178.6(5)	179.3(3)	179.4(2)	O1-Ln1-O4	118.6(3)	118.19(17)	118.03(14)
N1-Fe1-C11	92.3(5)	92.8(2)	92.25(19)	O1-Ln1-O5	135.7(3)	134.26(18)	134.66(13)
N3-Fe1-C11	177.9(5)	177.6(3)	177.78(19)	O1-Ln1-O1W	73.3(3)	73.55(18)	73.09(13)
N5-Fe1-C11	93.1(6)	93.3(3)	93.1(2)	O2-Ln1-O4	69.8(3)	68.99(18)	69.25(14)
N1-Fe1-C12	176.4(6)	176.0(3)	176.2(2)	O2-Ln1-O5	91.6(4)	90.48(19)	91.05(15)
N3-Fe1-C12	92.8(5)	93.4(3)	93.1(2)	O2-Ln1-O1W	78.7(4)	78.30(19)	77.42(14)
N5-Fe1-C12	93.3(6)	93.8(3)	93.3(2)	O4-Ln1-O5	50.9(3)	51.15(15)	50.85(12)
N10-Ln1-N12	65.6(4)	64.84(18)	65.21(14)	O4-Ln1-O1W	79.2(3)	79.04(16)	78.73(13)
Ln1-N8-C11	168.2(11)	168.3(5)	168.7(4)	O5-Ln1-O1W	129.0(3)	129.28(16)	128.70(12)

* (*a*) = 1-*x*, -*y*, -*z* (**2**, **4**); (*a*) = -1-*x*, -1-*y*, -1-*z* (**3**)

Table S3. Summary of SHAPE analysis for $[LaN_6O_4]$ fragment in complex **1**[a]

CN = 10			La(III)
DP-10	36.408	D_{10h}	Decagon
EPY-10	23.589	C_{9v}	Enneagonal pyramid
OBPY-10	16.348	D_{8h}	Octagonal bipyramid
PPR-10	11.235	D_{5h}	Pentagonal prism
PAPR-10	12.860	D_{5d}	Pentagonal antiprism
JBCCU-10	13.545	D_{4h}	Bicapped cube J15
JBCSAPR-10	6.058	D_{4d}	Bicapped square antiprism J17
JMBIC-10	6.537	C_{2v}	Metabidiminished icosahedron J62
JATDI-10	16.664	C_{3v}	Augmented tridiminished icosahedron J64
JSPC-10	**3.136**	C_{2v}	**Sphenocorona J87**
SDD-10	5.254	D_2	Staggered Dodecahedron (2:6:2)
TD-10	4.482	C_{2v}	Tetradecahedron (2:6:2)
HD-10	10.703	D_{4h}	Hexadecahedron (2:6:2) or (1:4:4:1)

[a]The listed values correspond to the deviation between the ideal and real coordination polyhedra, the lowest values are given in bold.

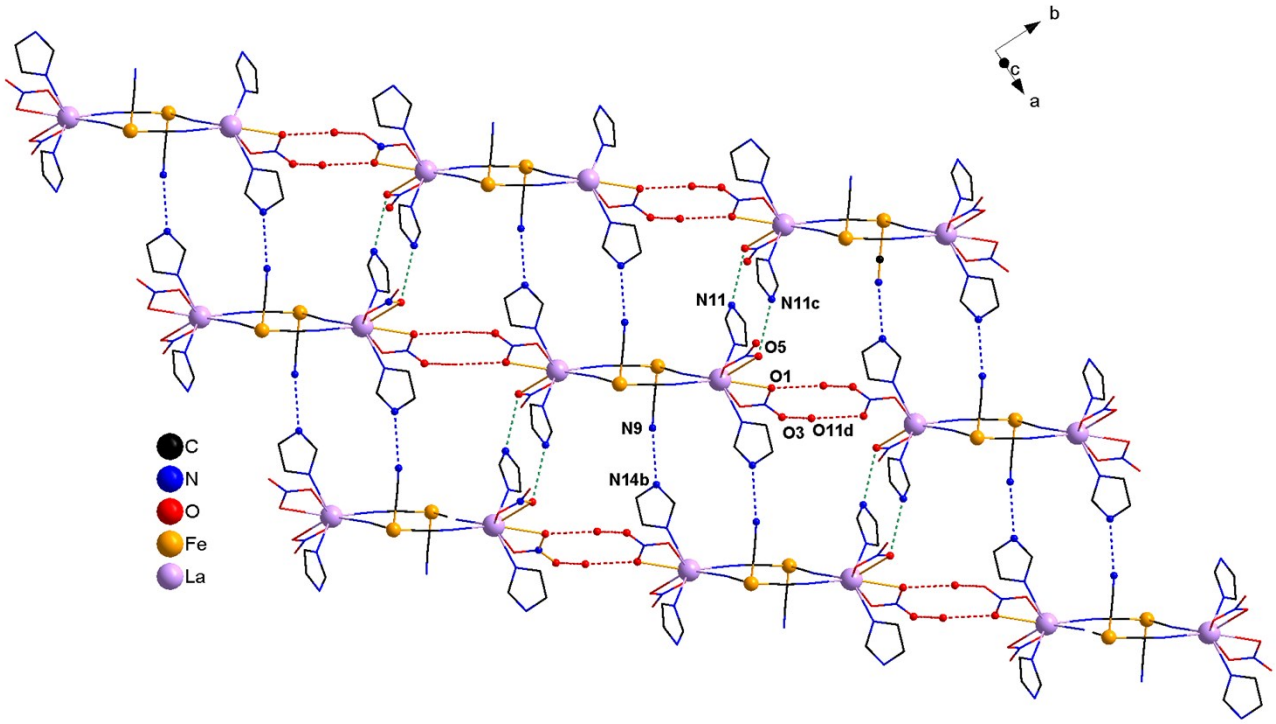

Figure S5. View in the crystallographic *ab* plane showing the supramolecular layers formed through hydrogen bonds for compound **1** (the pyridyl (pyim) and pyrazolyl ($\{HB(pz)_3\}^-$) rings were omitted for the sake of clarity. Symmetry codes: (*b*) = 1-*x*, -*y*, -*z*; (*c*) = -*x*, 1-*y*, -*z*; (*d*) = 1+*x*, *y*, *z*).

Table S4. Selected intermolecular contacts (Å) for compound **1***

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	Angle D-H···A
N14-H14*A*···N9^{iii}	0.88	2.00	2.868(8)	167
N11-H11···O5^{iv}	0.88	2.16	2.917(7)	144

*Symmetry code: (*iii*) = -*x*+1, -*y*, -*z*; (*iv*) = -*x*, -*y*+1, -*z*.

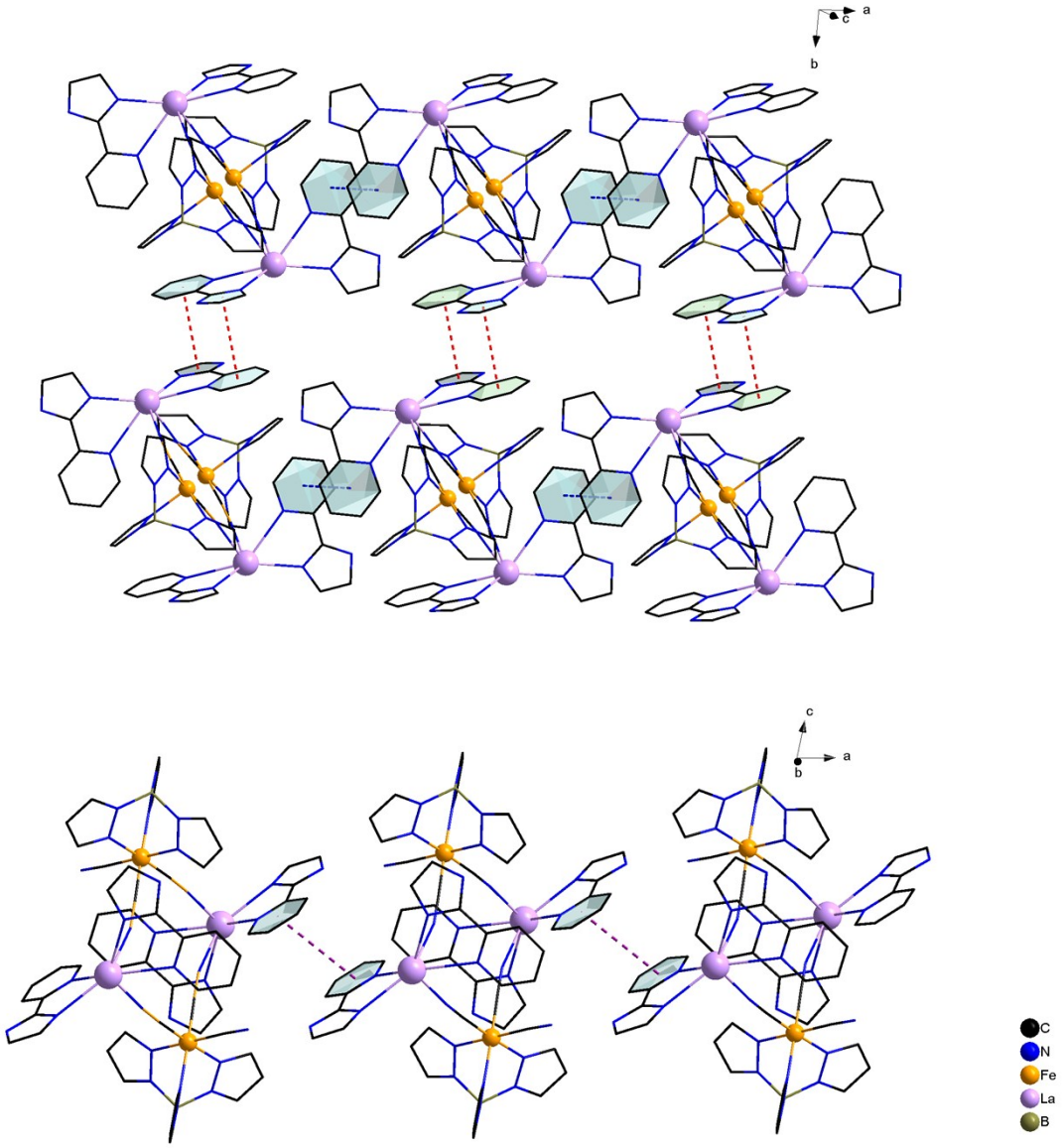

Figure S6. Up: View in the crystallographic *ab* plane of the supramolecular layers built through pyridyl-pyridy and pyridy-imidazole $\pi\cdots\pi$ stacking interactions in compound **1.** Bottom: Detail of the supramolecular layers showing the pyim-pyim stacking interactions, after an axis parallel to the crystallographic *a* axis, established between the pyridyl rings of pyim molecules from neighbouring tetranuclear units. The nitrate ligands were omitted for the sake of clarity.

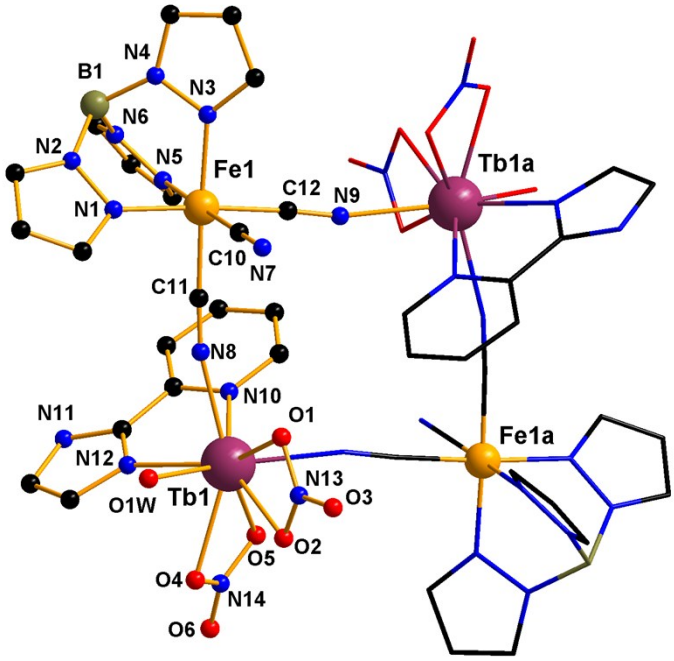

Figure S7. Perspective view of the molecular structure of **3** together with the atom labelling scheme. The molecular fragment resulted through inversion symmetry operation are represented with wires and sticks [Symmetry code: (*a*) = -1-*x*, -1-*y*, -1-*z*)].

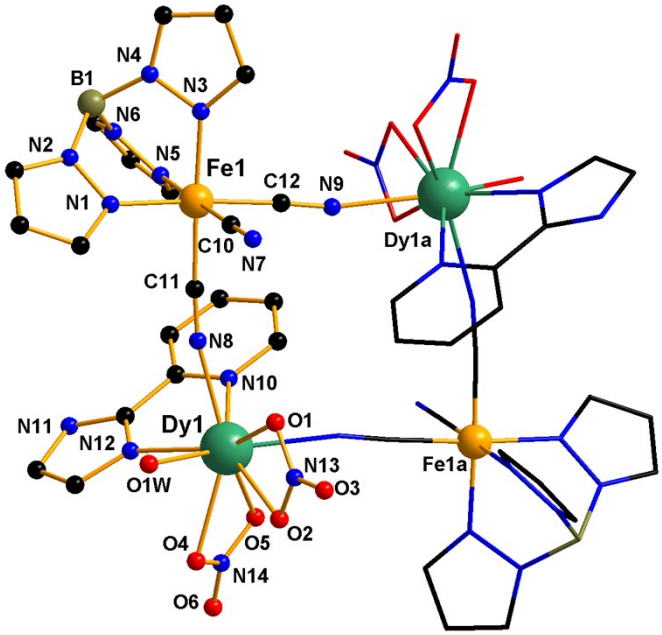

Figure S8. Perspective view of the molecular structure of **4** together with the atom labelling scheme. The molecular fragment resulted through inversion symmetry operation are represented with wires and sticks [Symmetry code: (*a*) = 1-*x*, -*y*, -*z*].

Table S5. Summary of SHAPE analysis for the [LnN_4O_5] fragment in **2-4** [Ln = Gd (**2**), Tb (**3**) and Dy (**4**)][a]

CN = 9[b]	Gd(III)	Tb(III)	Dy(III)
EP-9	34.083	34.361	34.288
OPY-9	22.221	22.387	22.459
HBPY-9	15.091	15.252	15.197
JTC-9	15.505	15.446	15.365
JCCU-9	9.106	9.012	9.082
CCU-9	8.077	7.973	8.053
JCSAPR-9	3.629	3.237	3.236
CSAPR-9	2.423	2.425	2.450
JTCTPR-9	3.425	3.278	3.304
TCTPR-9	2.848	2.744	2.822
JTDIC-9	13.636	13.575	13.599
HH-9	7.612	7.771	7.717
MFF-9	**1.986**	**1.949**	**1.975**

[a]The listed values correspond to the deviation between the ideal and real coordination polyhedra, the lowest values being given in bold. [b]EP-9, D_{9h}, enneagon; OPY-9, C_{8v}, octagonal pyramid; HBPY-9, D_{7h}, heptagonal bipyramid; JTC-9, C_{3v}, Johnson triangular cupola J3; JCCU-9, C_{4v}, capped cube J8; CCU-9, C_{4v}, spherical-relaxed capped cube; JCSAPR-9, C_{4v}, capped square antiprism; CSAPR-9, C_{4v}, spherical capped square antiprism; JTCTPR-9, D_{3h}, tricapped trigonal prism J51; TCTPR-9, D_{3h}, spherical tricapped trigonal prism; JTDIC-9, C_{3v}, tridiminished icosahedron; HH-9, C_{2v}, hula-hoop; MFF-9, C_s, muffin.

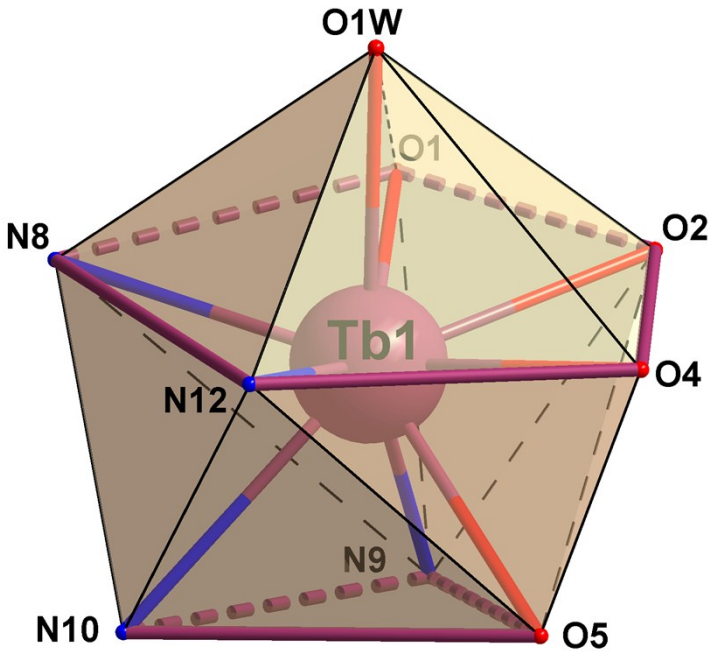

Figure S9. Muffin-like geometry for the Tb^{III} ion in **3**.

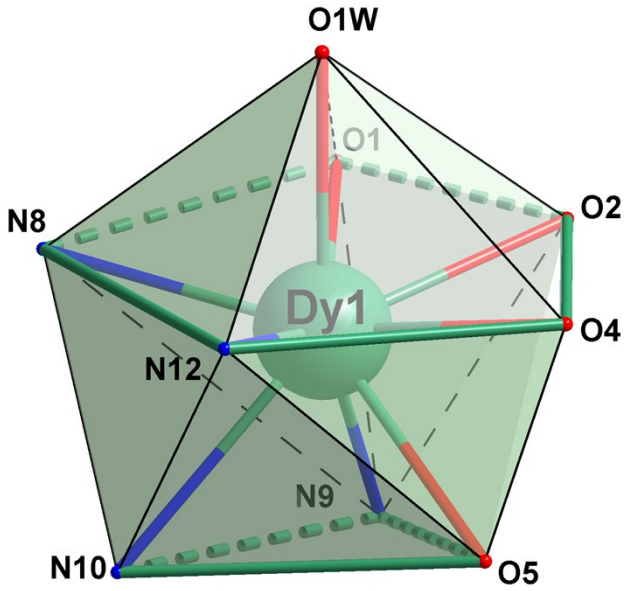

Figure S10. Muffin-like geometry for the Dy^{III} ion in **4**.

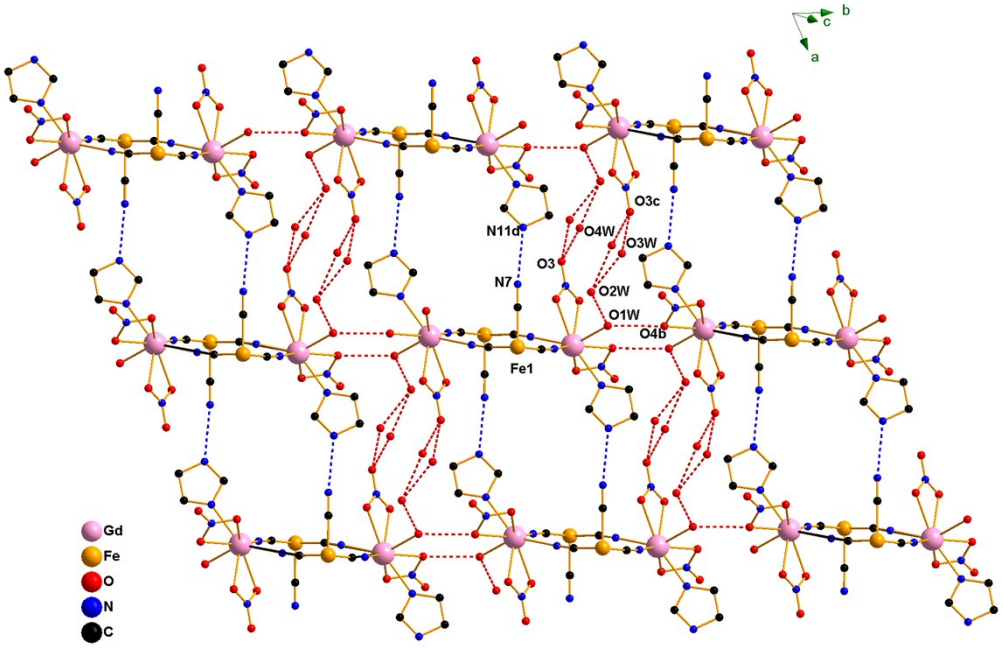

Figure S11. View in the crystallographic *ab* plane of the supramolecular layers for compound **2** built through O···O (red dotted lines; the O atoms belong to crystallization water molecules, aqua and nitrate ligands) and N···N type hydrogen bonds (blue dotted lines; the N atoms belong to the imidazole ring of pyim molecule and the terminal cyanide ligand). The pyridyl ring of the pyim molecule as well as the pyrazolyl rings of the $HB(pz)_3^-$ ligands were omitted for the sake of clarity. Symmetry codes: (*b*) = 1-*x*, 1-*y*, -*z*; (*c*) = -*x*, 1-*y*, -*z*.

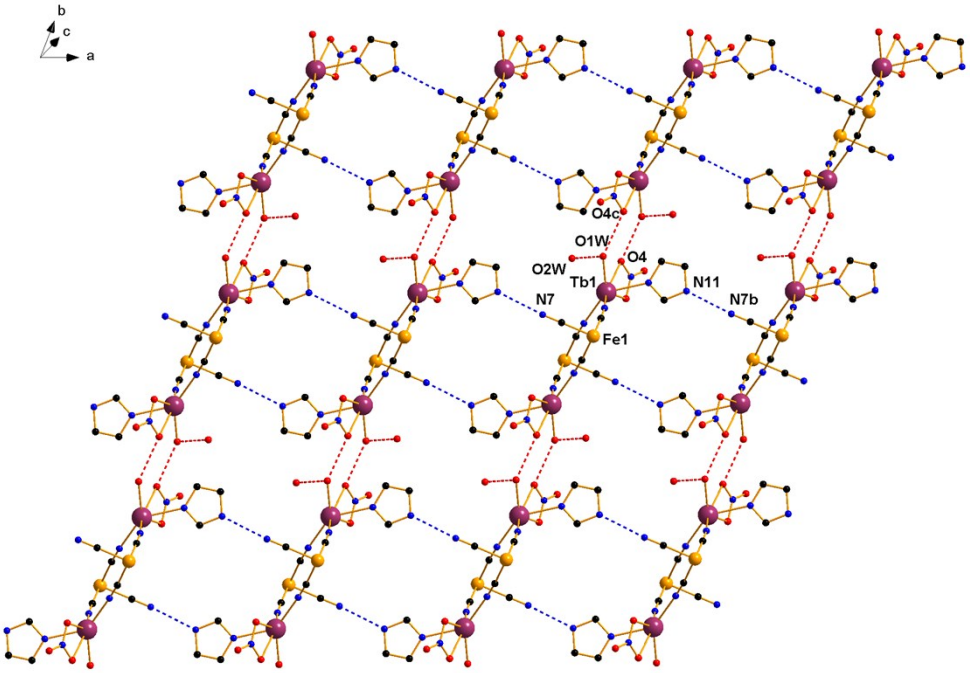

Figure S12. View in the crystallographic *ab* plane of the supramolecular layers for compound **3** built through O···O (red dotted lines; the O atoms belong to crystallization water molecules, aqua and nitrate ligands) and N···N type hydrogen bonds (blue dotted lines; the N atoms belong to the imidazole ring of pyim molecule and the terminal cyanide ligand). The pyridyl ring of the pyim molecule as well as the pyrazolyl rings of $\{HB(pz)_3\}^-$ ligands and one nitrate group were omitted for the sake of clarity. Symmetry codes: (*b*) = 1+*x*, *y*, *z*; (*c*) = -1-*x*, -*y*, -1-*z*.

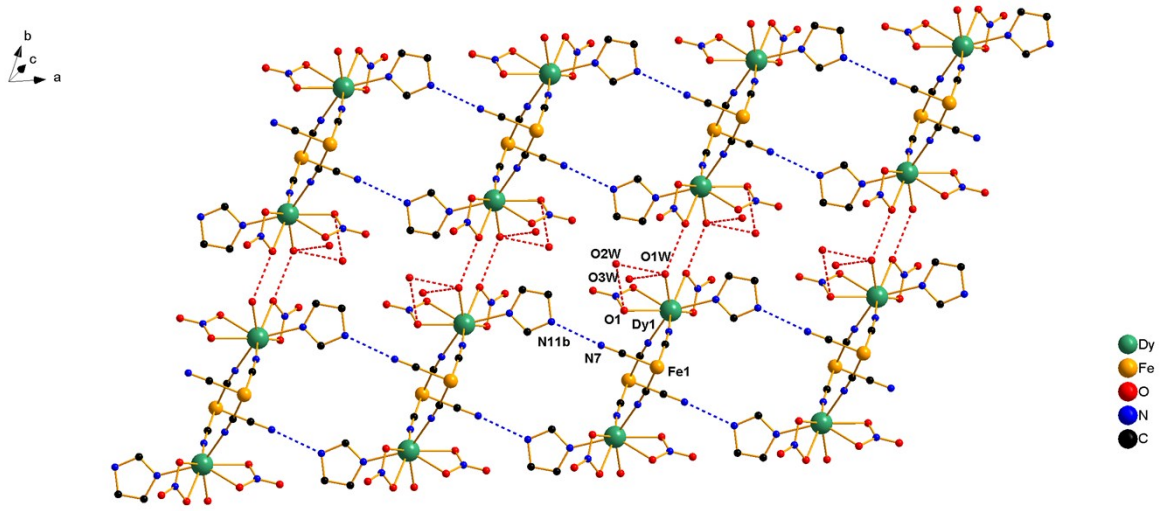

Figure S13. View in the crystallographic *ab* plane of the supramolecular layers for compound **4** built through O···O (red dotted lines; the O atoms belong to crystallization water molecules, aqua and nitrate ligands) and N···N type hydrogen bonds (blue dotted lines; the N atoms belong to the imidazole ring of pyim molecule and the terminal cyanide ligand). The pyridyl ring of the pyim molecule as well as the pyrazolyl rings of the $\{HB(pz)_3\}^-$ ligands were omitted for the sake of clarity. Symmetry code: (*b*) = -1+*x*, *y*, *z*.

Table S6. Selected intermolecular contacts (Å) for compounds **2**-**4**[&]

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	Angle D-H···A
		Compound **2**		
O1W-H1W*c*···O2W	0.85	1.84	2.69(2)	171
O1W-H1A···O4*b**	0.87	2.13	2.796(17)	134
O4W-H4WA···O3*c**	0.85	2.12	2.83(5)	140
O2W-H2WA···O3W	0.85	1.99	2.67(5)	137
O2W-H2WA···O4W	0.85	2.03	2.76(5)	142
O3W-H3WA···O3*c**	0.85	2.16	2.97(4)	157
N11-H11···N7*d**	0.86	1.97	2.83(2)	170
		Compound **3**		
O1W-H1WA···O2W**	0.85	2.28	2.663(18)	108
O1W-H1WB···O4*b***	0.85	2.02	2.804(8)	153
O2W-H2W···O1	0.86	2.29	3.110(15)	160
N11-H11···N7*c***	0.86	1.96	2.811(13)	171
		Compound **4**		
O1W-H1WA···O4*b****	0.85	2.39	2.792(6)	109
O1W-H1WB···O3W	0.85	1.87	2.681(12)	159
O1W-H1WB···O2W	0.85	2.23	2.80(5)	124
N11-H1WB···N7*c****	0.86	1.96	2.817(10)	172
O3W-H3WB···O1	0.85	2.47	3.110(12)	132

[&]Symmetry codes: (**b*) = 1-*x*, 1-*y*, -*z*; (**c*) = -*x*, 1-*y*, -*z*; (**d*) = 1+*x*, *y*, *z*; (***b*) = -1-*x*, -*y*, -1-*z*; (***c*) = 1+*x*, *y*, *z*; (****b*) = 1-*x*, 1-*y*, 1-*z*; (****c*)= 1+*x*, *y*, *z*.

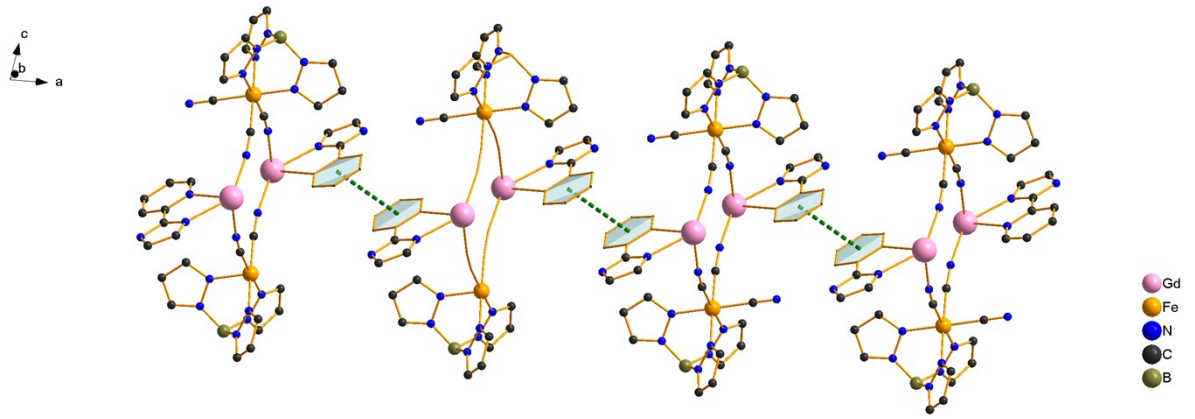

Figure S14. Representation of the supramolecular chain assembled, after a direction parallel to the crystallographic *a* axis, through $\pi\cdots\pi$ stacking interactions established between the pyridyl rings of pyim molecules in **2**. The nitrate and aqua ligands were omitted for the sake of clarity.

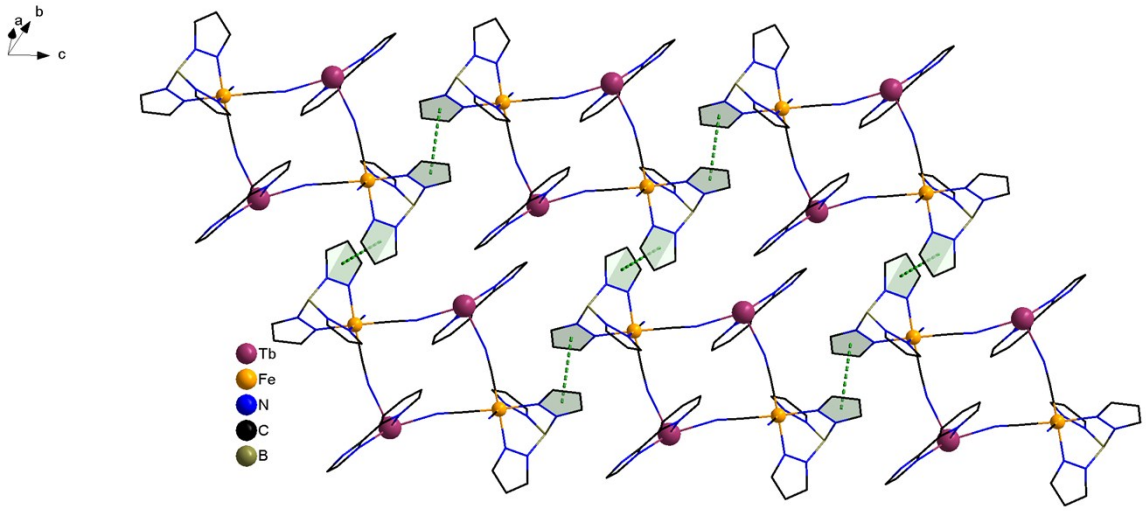

Figure S15. View in the crystallographic *bc* plane of the supramolecular layers developed through two sets of $\pi\cdots\pi$ stacking interactions established between the pyrazolyl rings of the $\{HB(pz)_3\}^-$ ligands for **3**. The nitrate and aqua ligands were omitted for the sake of clarity.

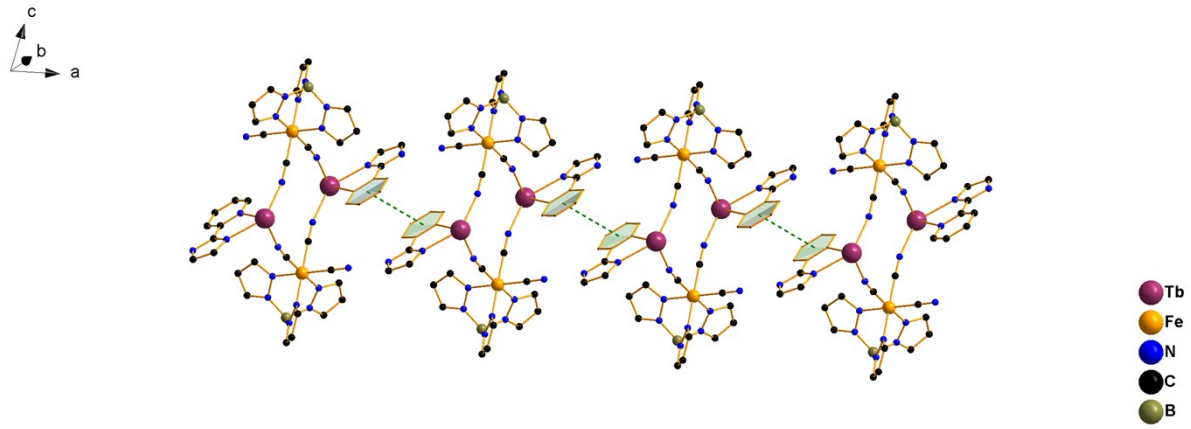

Figure S16. Representation of the supramolecular chain assembled, after a direction parallel to the crystallographic *a* axis, through $\pi\cdots\pi$ stacking interactions established between the pyridyl rings of the pyim molecules in **3**. The nitrate and aqua ligands were omitted for the sake of clarity.

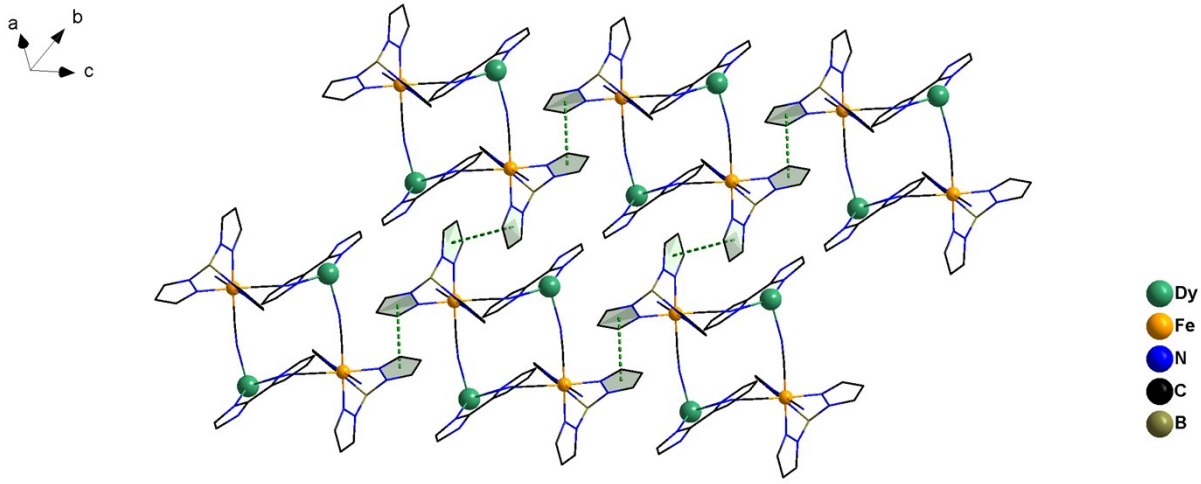

Figure S17. View in the crystallographic *bc* plane of the supramolecular layers developed through two sets of $\pi\cdots\pi$ stacking interactions established between the pyrazolyl rings of the $HB(pz)_3^-$ ligands for **4**. The nitrate and aqua ligands were omitted for the sake of clarity.

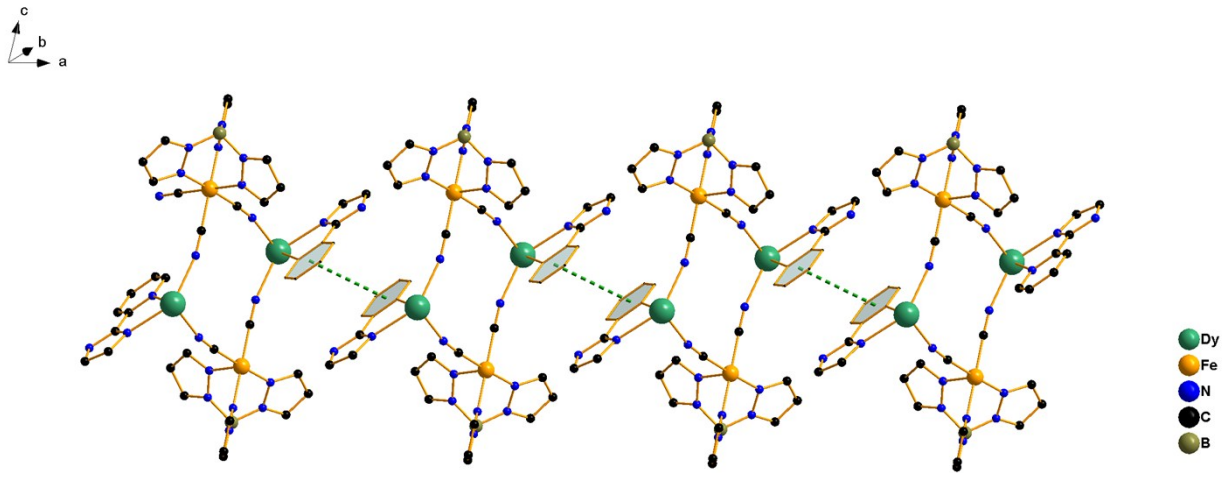

Figure S18. Representation of the supramolecular chain assembled, after a direction parallel to the crystallographic *a* axis, through $\pi\cdots\pi$ stacking interactions established between pyridininc rings of pyim molecules in compound **4**. The nitrate, terminal cyanide and aqua ligands were omitted for the sake of clarity.