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Supporting information for article:

Polymorphs of phenazine hexacyanoferrate(II) hydrate: supramolecular isomerism in a 2D hydrogen-bonded network

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Table S1 Parameters of hydrogen bonds present in **I**.

Hydrogen bond	***d*(D,H)/Å**	***d*(D,A)/Å**	***d*(A,H)/Å**	***ϕ*(D,H,A)/ °**
O1—H2···N15	0.838(8)	2.778(2)	1.940(8)	177.6(1.1)
O2—H3···N1	0.84(2)	3.122(4)	2.34(2)	155.1(1.5)
O2—H4···N13	0.839(11)	2.865(2)	2.14(2)	145.3(1.2)
N18—H7···N7	0.84(2)	2.690(3)	1.85(2)	172(2)
N20—H5···N9	0.94(2)	2.685(2)	1.75(2)	170(2)
N3—H8···O1	0.91(2)	2.550(3)	1.64(2)	173(2)
N22—H6···N1[a]	0.87(2)	2.727(2)	1.86(2)	175(2)
N11—H12···N5[b]	1.10(2)	2.580(2)	1.48(2)	176(2)
N10—H11···N8[c]	0.99(3)	2.628(3)	1.65(3)	171(2)
N2—H9···N4[d]	0.98(3)	2.600(3)	1.62(3)	176(2)
O1—H1··O2[e]	0.838(13)	2.684(3)	1.848(13)	176.0(1.4)
N6—H10···N12[f]	1.334(2)	2.571(2)	1.238(2)	177(3)

a) *x*, *y*+1, *z*; b) −*x*, −*y*+1, −*z*; c) *x*, −*y*+3/2, *z*+1/2; d) *x*, −*y*+1/2, *z*−1/2; e) −*x*, *y*+1/2, −*z*+1/2; f) –*x*+1, *y*−1/2, −*z*+1/2

Table S2 Parameters of hydrogen bonds present in **II**.

Hydrogen bond	***d*(D,H)/Å**	***d*(D,A)/Å**	***d*(A,H)/Å**	***ϕ*(D,H,A)/ °**
O1—H2···N19	0.86(3)	2.831(4)	1.97(3)	175(2)
N9—H9···O1	1.01(6)	2.565(5)	1.56(6)	174(5)
N13—H4···N4	0.95(4)	2.662(4)	1.73(4)	167(4)
N22—H8···N7	0.96(5)	2.688(4)	1.74(5)	170(4)
O2—H11···N15	0.86(3)	2.906(4)	2.09(3)	159(3)
O2—H12···N3	0.86(2)	3.269(5)	2.92(4)	106(2)
O2—H12···N4	0.86(2)	3.387(4)	2.76(3)	132(2)
O1—H3···O2[a]	0.86(2)	2.724(4)	1.87(2)	170.7(1.4)
N6—H6···N12[b]	1.19(5)	2.585(3)	1.39(5)	175(5)
N18—H7···N2[c]	1.08(4)	2.661(4)	1.58(4)	176(4)

N5—H11···N11[d]	1.35(4)	2.562(3)	1.22(4)	178(4)
N1—H1···N8[e]	1.07(4)	2.581(3)	1.52(4)	173(4)
N10—H10···N3[f]	1.31(4)	2.580(4)	1.28(4)	171(4)

a) –x+1, –*y*+2, –*z*+1; b) −*x*+1, −*y*+1, −*z*+1; c) *x*+1, *y*, *z*+1; d) −*x*, –*y*+2, −*z*+1; e) *x*–1, *y*, *z*; f) *x*, *y*, *z*+1

Table S3 Bond distances in hexacyanoferric anions in **I**.

Bond	***d*(Fe,C)/Å**	***d*(C,N)/Å**	**Hydrogen bonded to**
Fe1—C1—N1	1.914(2)	1.154(2)	$Hphen^+$ (N22)
Fe1—C2—N2	1.880(2)	1.142(2)	HCF (N4)
Fe1—C3—N3	1.866(2)	1.155(2)	H_2O (O1)
Fe1—C4—N4	1.906(2)	1.153(2)	HCF (N2)
Fe1—C5—N5	1.894(2)	1.149(2)	HCF (N11)
Fe1—C6—N6	1.898(2)	1.147(2)	HCF (N12)
Fe2—C7—N7	1.912(2)	1.160(2)	$Hphen^+$ (N18)
Fe2—C8—N8	1.912(2)	1.151(2)	HCF (N10)
Fe2—C9—N9	1.917(2)	1.160(2)	$Hphen^+$ (N20)
Fe2—C10—N10	1.882(2)	1.145(2)	HCF (N8)
Fe2—C11—N11	1.891(2)	1.143(2)	HCF (N5)
Fe2—C12—N12	1.887(2)	1.145(2)	HCF (N6)

Table S4 Bond distances in hexacyanoferric anions in **II**.

Bond	***d*(Fe,C)/Å**	***d*(C,N)/Å**	**Hydrogen bonded to**
Fe1—C1—N1	1.897(3)	1.154(4)	HCF (N8)
Fe1—C2—N2	1.912(4)	1.152(5)	$Hphen^+$ (N18)
Fe1—C3—N3	1.897(3)	1.160(4)	HCF (N10)
Fe1—C4—N4	1.912(4)	1.166(5)	$Hphen^+$ (N13)
Fe1—C5—N5	1.893(3)	1.156(3)	HCF (N11)
Fe1—C6—N6	1.893(3)	1.158(4)	HCF (N12)
Fe2—C7—N7	1.943(4)	1.152(5)	$Hphen^+$ (N22)
Fe2—C8—N8	1.911(3)	1.156(3)	HCF (N1)

Fe2—C9—N9	1.880(4)	1.160(5)	H_2O (O1)
Fe2—C10—N10	1.895(3)	1.148(4)	HCF (N3)
Fe2—C11—N11	1.890(3)	1.158(3)	HCF (N5)
Fe2—C12—N12	1.908(3)	1.155(3)	HCF (N6)

Table S5 Number of CSD entries with 1-8 chemically unique residues in the unit cell.

No. of residues	**Metal-organic**	**Organic**	**Metal-organic – non-ionic**	**Organic – non-ionic**	**Metal-organic – ionic**	**Organic – ionic**
1	248921	300193	248921	300193	0	0
2	198829	89901	120835	56645	77994	33256
3	85681	26714	15404	6351	70277	20363
4	18984	4612	1505	527	17479	4085
5	3087	731	119	35	2968	696
6	454	82	7	5	447	77
7	84	10	3	5	81	5
8	22	1	0	0	22	1

Table S6 Number of CSD entries with 1-8 chemically unique residues in the unit cell with the keyword ‘polymorph’.

No. of residues	**Metal-organic**	**Organic**	**Metal-organic – non-ionic**	**Organic – non-ionic**	**Metal-organic – ionic**	**Organic – ionic**
1	6283	11325	6283	11325	0	0
2	3552	3082	862	1470	2690	1612
3	923	749	57	54	866	695
4	166	60	1	1	165	59
5	9	6	0	0	9	6
6	1	0	0	0	1	0
7	0	0	0	0	0	0
8	0	0	0	0	0	0

Table S7 Number of CSD entries with 2-6 chemically unique residues in the unit cell with the keyword 'polymorph' which contain at least one water molecule.

No. of residues	Metal-organic	Organic	Metal-organic – non-ionic	Organic – non-ionic	Metal-organic – ionic	Organic – ionic
2	347	387	347	387	0	0
3	444	390	46	54	398	336
4	121	44	0	1	121	43
5	9	5	0	0	9	5
6	1	0	0	0	1	0

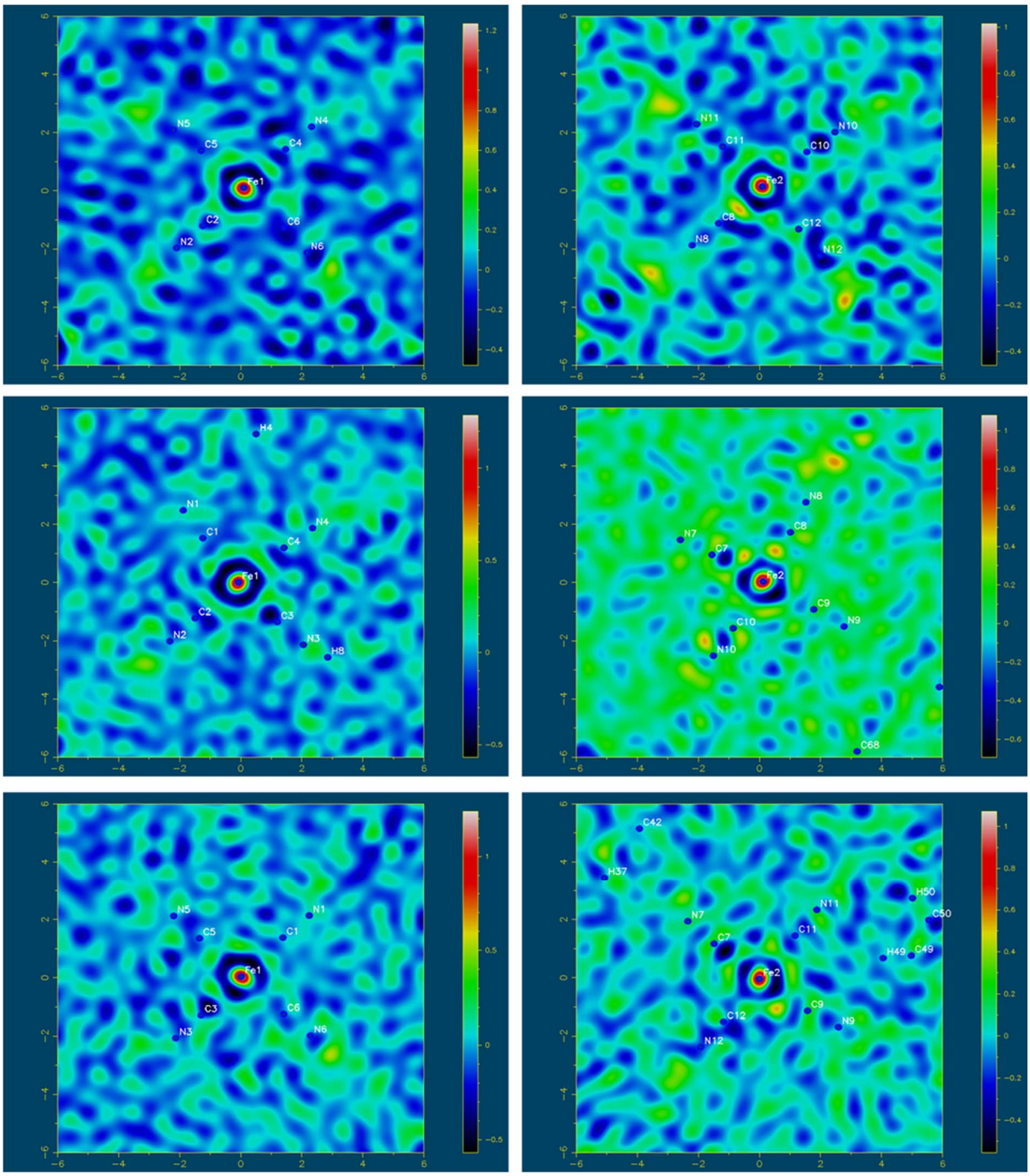

Figure S1 Differential electron density Fourier maps for planes defined by the hexacyanoferric nitrogen atoms in the crystal structure of **I** prior to locating the hexacyanoferric hydrogen atoms. Distances are in Å, and the color scheme represents electron density difference between F_o and F_c in e/Å^3. Atom N2 is hydrogen bonded to N4, N5 to N11, N6 to N12, and N8 to N10. Atoms N1, N7, and N9 form hydrogen bonds with phenazinium cations, and the atom N3 forms hydrogen bond with a water molecule.

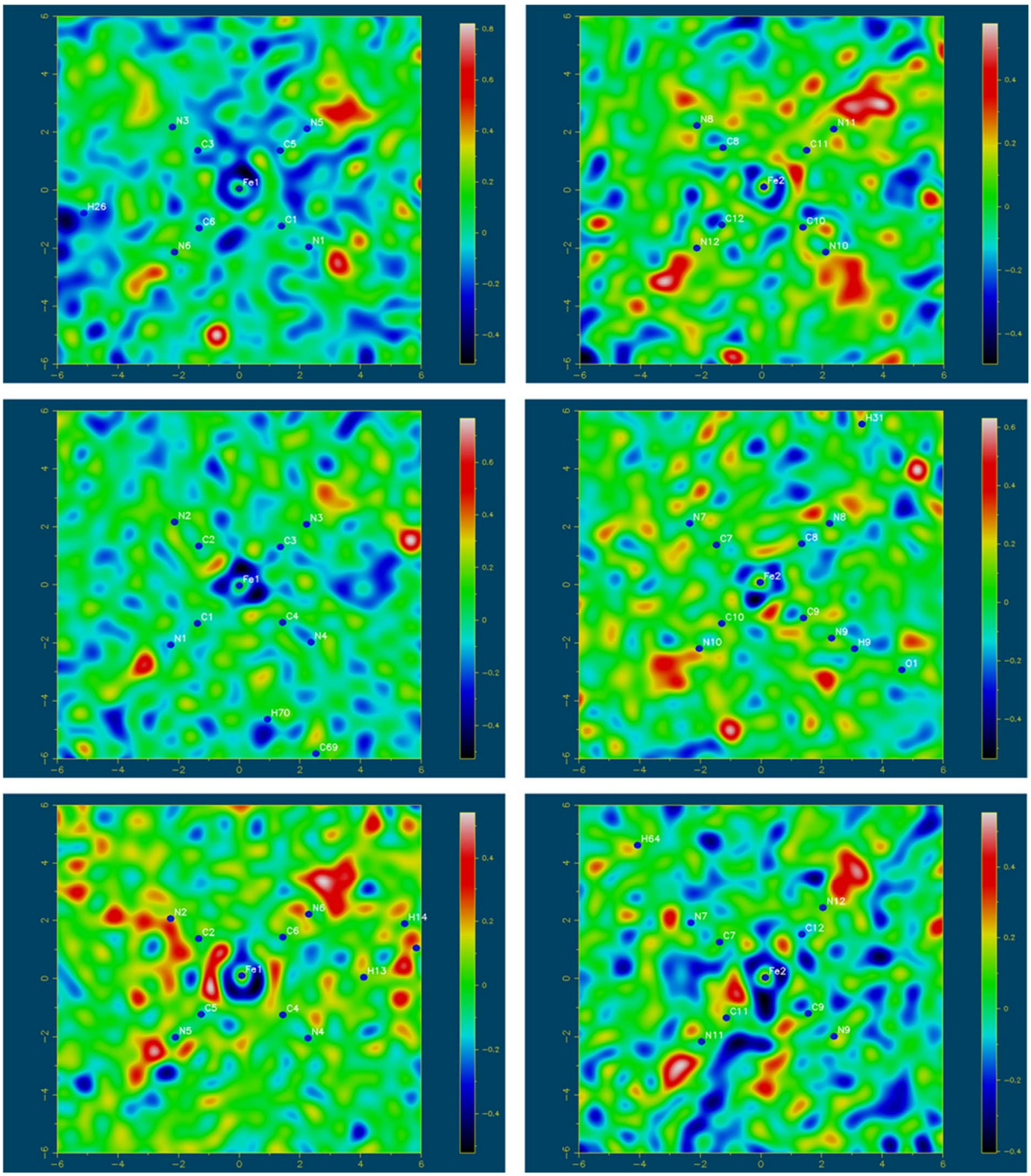

Figure S2 Differential electron density Fourier maps for planes defined by the hexacyanoferric nitrogen atoms in the crystal structure of **II** prior to locating the hexacyanoferric hydrogen atoms. Distances are in Å, and the color scheme represents electron density difference between F_o and F_c in e/Å^3. Atom N1 is hydrogen bonded to N8, N3 to N10, N5 to N11, and N6 to N12. Atoms N2, N4, and N7 form hydrogen bonds with phenazinium cations, and the atom N9 forms hydrogen bond with a water molecule.