Electronic Supplementary Material (ESI) for CrystEngComm.
This journal is © The Royal Society of Chemistry 2015

Electronic Supplementary Information

The first cyano-bridged polynuclear coordination compounds derived from paramagnetic $[Mn(H_2daptsc)]^{2+}$ and photochromic $[Fe(CN)_5NO]^{2-}$ building blocks

Valentina D. Sasnovskaya,[a] Leokadiya V. Zorina,[b*] Sergey V. Simonov,[b] Artem D. Talantsev,[a] Roman B. Morgunov,[a] Atrem A. Mikhailov,[c] Gennadiy A. Kostin,[c] and Eduard B. Yagubskii[a*]

[a] *Institute of Problems of Chemical Physics, RAS, 1 Academician Semenov ave., Chernogolovka, Moscow District, 142432 Russia. E-mail: yagubski@gmail.com*
[b] *Institute of Solid State Physics, RAS, 2 Academician Ossipyan str., Chernogolovka, Moscow District, 142432 Russia. E-mail: zorina@issp.ac.ru*
[c] *Nikolaev Institute of Inorganic Chemistry, SB RAS, 3 Academician Lavrentieva ave., Novosibirsk, 630090 Russia*

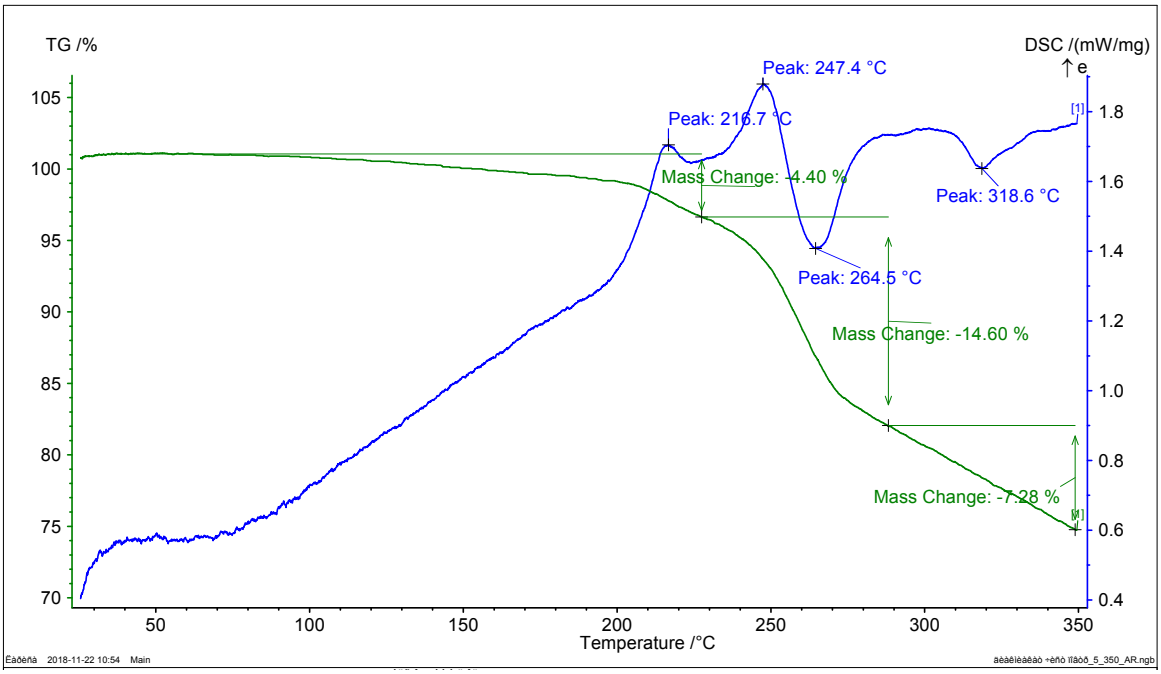


Fig S1. TG-DSC curves for complex **1**.

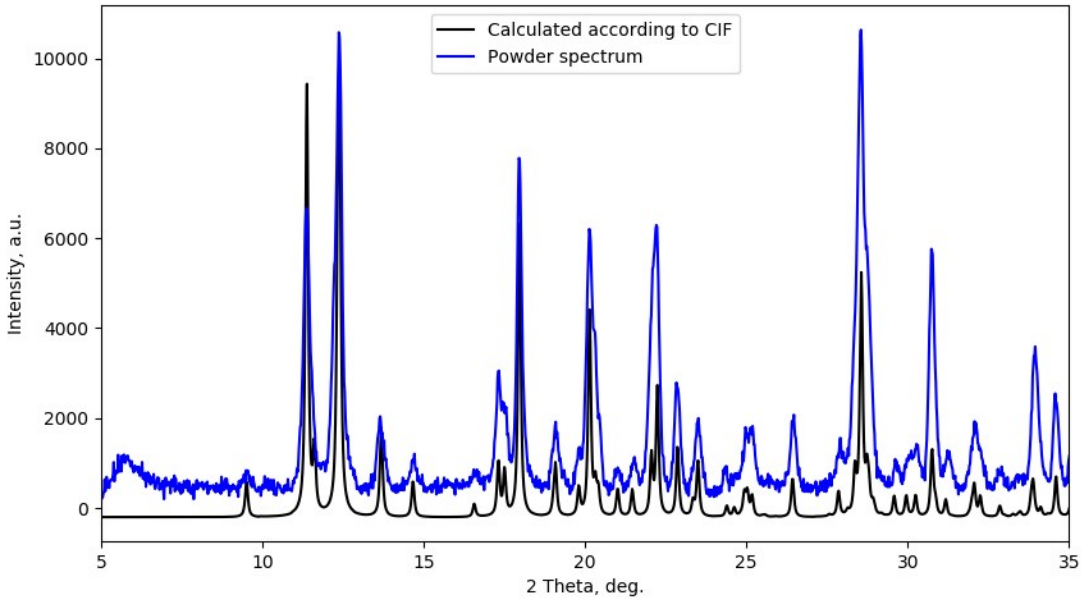


Fig. S2. Powder X-ray diffraction profile of **1** together with a simulation from the single crystal data.

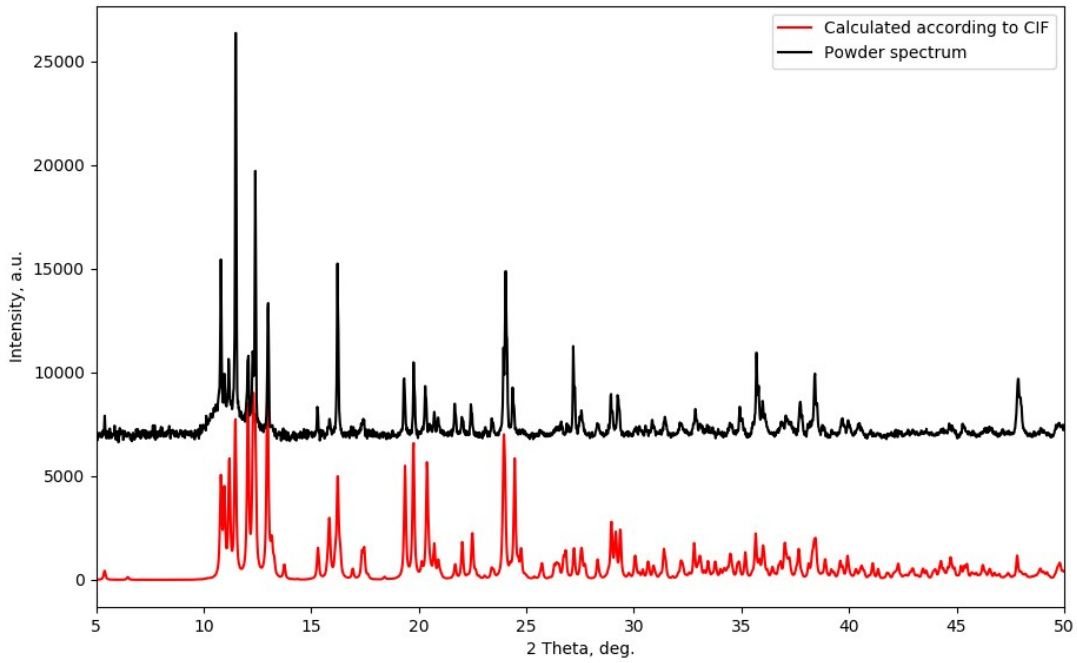


Fig. S3. Powder X-ray diffraction profile of **4** together with a simulation from the single crystal data.

Table S1. Selected bond lengths (Å) and angles (°) in **1** and **3.**

1		**3**			
Mn(1)-S(1)	2.6075(7)	Mn(1)-S(1)	2.6315(4)	Mn(2)-S(3)	2.6638(4)
Mn(1)-S(2)	2.6652(7)	Mn(1)-S(2)	2.6380(5)	Mn(2)-S(4)	2.6437(4)
Mn(1)-N(2)	2.345(2)	Mn(1)-N(2)	2.3944(12)	Mn(2)-N(22)	2.3616(12)
Mn(1)-N(4)	2.357(2)	Mn(1)-N(4)	2.3505(12)	Mn(2)-N(24)	2.3783(12)
Mn(1)-N(3)	2.269(2)	Mn(1)-N(3)	2.2823(12)	Mn(2)-N(23)	2.2916(12)
Mn(1)-N(12)	2.277(2)	Mn(1)-N(12)	2.2337(13)	Mn(2)-N(32)	2.2159(13)
Mn(1)-N(13)[a]	2.254(2)	Mn(1)-N(13)[b]	2.2129(13)	Mn(2)-N(33)[b]	2.2313(13)
Fe(1)-C_{CN}	1.932(2)-1.937(2)	Fe(1)-C_{CN}	1.9212(13)-1.9445(15)	Fe(2)-C_{CN}	1.9315(14)-1.9424(16)
Fe(1)-N(17)	1.657(2)	Fe(1)-N(17)	1.6609(13)	Fe(2)-N(37)	1.6628(13)
S(1)-Mn(1)-S(2)	76.52(2)	S(1)-Mn(1)-S(2)	78.85(1)	S(3)-Mn(2)-S(4)	78.48(1)
S(1)-Mn(1)-N(2)	73.56(5)	S(1)-Mn(1)-N(2)	72.64(3)	S(3)-Mn(2)-N(22)	72.49(3)
S(2)-Mn(1)-N(4)	72.44(5)	S(2)-Mn(1)-N(4)	72.92(3)	S(4)-Mn(2)-N(24)	72.76(3)
N(2)-Mn(1)-N(3)	68.68(7)	N(2)-Mn(1)-N(3)	68.38(4)	N(22)-Mn(2)-N(23)	68.30(4)
N(4)-Mn(1)-N(3)	69.19(7)	N(4)-Mn(1)-N(3)	68.83(4)	N(24)-Mn(2)-N(23)	68.22(4)
N(12)-Mn(1)-N(13)[a]	168.1(1)	N(12)-Mn(1)-N(13)[b]	170.69(5)	N(32)-Mn(2)-N(33)[b]	171.17(5)
Mn(1)-N(12)-C(12)	138.3(2)	Mn(1)-N(12)-C(12)	145.49(12)	Mn(2)-N(32)-C(32)	157.00(12)
Mn(1)-N(13)[a]-C(13)[a]	145.4(2)	Mn(1)-N(13)[b]-C(13)[b]	155.88(12)	Mn(2)-N(33)[b]-C(33)[b]	144.71(12)
Fe(1)-C(12)-N(12)	174.7(2)	Fe(1)-C(12)-N(12)	173.17(14)	Fe(2)-C(32)-N(32)	177.51(13)
Fe(1)-C(13)-N(13)	176.9(2)	Fe(1)-C(13)-N(13)	176.79(14)	Fe(2)-C(33)-N(33)	175.33(14)
C(12)-Fe(1)-C(13)	172.6(1)	C(12)-Fe(1)-C(13)	170.59(6)	C(32)-Fe(2)-C(33)	169.96(6)

Symmetry codes: [a] (*x*, *y*, *z*+1), [b] (*x*-1, *y*, *z*).

Table S2. Selected bond lengths (Å) and angles (°) in **2.**

2					
Mn(1)-S(1)	2.628(2)	Mn(2)-S(3)	2.631(2)	Mn(3)-S(5)	2.625(2)
Mn(1)-S(2)	2.646(2)	Mn(2)-S(4)	2.653(2)	Mn(3)-S(6)	2.626(2)
Mn(1)-N(2)	2.353(5)	Mn(2)-N(22)	2.372(5)	Mn(3)-N(42)	2.366(5)
Mn(1)-N(4)	2.345(5)	Mn(2)-N(24)	2.346(5)	Mn(3)-N(44)	2.358(5)
Mn(1)-N(3)	2.266(5)	Mn(2)-N(23)	2.280(5)	Mn(3)-N(43)	2.266(5)
Mn(1)-N(8)	2.269(5)	Mn(2)-N(28)	2.264(5)	Mn(3)-N(48)	2.288(5)
Mn(1)-N(9)[c]	2.295(5)	Mn(2)-N(29)[c]	2.229(5)	Mn(3)-N(49)[c]	2.293(5)
Fe(1)-C_{CN}	1.936(6)-1.945(6)	Fe(2)-C_{CN}	1.926(6)-1.945(6)	Fe(3)-C_{CN}	1.937(5)-1.956(6)
Fe(1)-N(13)	1.655(5)	Fe(2)-N(33)	1.666(5)	Fe(3)-N(53)	1.665(5)
S(1)-Mn(1)-S(2)	75.42(5)	S(3)-Mn(2)-S(4)	75.91(5)	S(5)-Mn(3)-S(6)	76.28(5)
S(1)-Mn(1)-N(2)	73.6(1)	S(3)-Mn(2)-N(22)	73.5(1)	S(5)-Mn(3)-N(42)	72.8(1)
S(2)-Mn(1)-N(4)	73.3(1)	S(4)-Mn(2)-N(24)	73.4(1)	S(6)-Mn(3)-N(44)	72.7(1)
N(2)-Mn(1)-N(3)	68.8(2)	N(22)-Mn(2)-N(23)	68.3(2)	N(42)-Mn(3)-N(43)	69.38(16)
N(4)-Mn(1)-N(3)	68.9(2)	N(24)-Mn(2)-N(23)	68.9(2)	N(44)-Mn(3)-N(43)	69.03(16)
N(8)-Mn(1)-N(9)[c]	173.0(2)	N(28)-Mn(2)-N(29)[c]	174.5(2)	N(48)-Mn(3)-N(49)[c]	167.5(2)
Mn(1)-N(8)-C(12)	151.5(5)	Mn(2)-N(28)-C(32)	143.4(5)	Mn(3)-N(48)-C(52)	152.9(4)
Mn(1)-N(9)[c]-C(13)[c]	140.3(5)	Mn(2)-N(29)[c]-C(33)[c]	154.2(5)	Mn(3)-N(49)[c]-C(53)[c]	139.3(5)
Fe(1)-C(12)-N(8)	175.4(5)	Fe(2)-C(32)-N(28)	174.2(5)	Fe(3)-C(52)-N(48)	175.7(5)
Fe(1)-C(13)-N(9)	172.6(5)	Fe(2)-C(33)-N(29)	175.3(6)	Fe(3)-C(53)-N(49)	173.2(5)
C(12)-Fe(1)-C(13)	170.9(3)	C(32)-Fe(2)-C(33)	171.3(3)	C(52)-Fe(3)-C(53)	171.4(2)

Symmetry code: [c] (*x*, *y*-1, *z*).

Table S3. Selected bond lengths (Å) and angles (°) in **4.**

4			
Mn(1)-S(1)	2.6494(9)	Mn(2)-S(3)	2.6683(9)
Mn(1)-S(2)	2.6458(9)	Mn(2)-S(4)	2.6325(9)
Mn(1)-N(2)	2.364(3)	Mn(2)-N(12)	2.337(3)
Mn(1)-N(4)	2.337(3)	Mn(2)-N(14)	2.330(2)
Mn(1)-N(3)	2.290(2)	Mn(2)-N(13)	2.279(2)
Mn(1)-N(21)	2.224(3)	Mn(2)-N(22)	2.264(3)
Mn(1)-Cl(1)	2.5626(9)	Mn(2)-Cl(2)	2.5824(9)
Fe(1)-C_{CN}	1.930(3)-1.949(3)	Fe(1)-N(26)	1.656(3)
S(1)-Mn(1)-S(2)	77.27(3)	S(3)-Mn(2)-S(4)	76.41(3)
S(1)-Mn(1)-N(2)	72.42(7)	S(3)-Mn(2)-N(12)	72.71(6)
S(2)-Mn(1)-N(4)	73.37(6)	S(4)-Mn(2)-N(14)	73.47(6)
N(2)-Mn(1)-N(3)	68.40(9)	N(12)-Mn(2)-N(13)	68.88(9)
N(4)-Mn(1)-N(3)	68.67(9)	N(14)-Mn(2)-N(13)	68.84(9)
N(21)-Mn(1)-Cl(1)	170.25(8)	N(22)-Mn(2)-Cl(2)	170.14(8)
Mn(1)-N(21)-C(41)	152.6(3)	Mn(2)-N(22)-C(42)	143.2(3)
Fe(1)-C(41)-N(21)	175.8(3)	Fe(1)-C(42)-N(22)	174.9(3)
C(41)-Fe(1)-C(42)	172.22(13)	Fe(1)-N(26)-O(1)	177.8(3)

Table S4. Selected bond lengths (Å) and angles (°) in **5** and **6.**

5		**6**	
Mn(1)-S(1)	2.6309(9)	Mn(1)-S(1)	2.6973(3)
Mn(1)-S(2)	2.6108(9)	Mn(1)-S(2)	2.6265(3)
Mn(1)-N(2)	2.356(2)	Mn(1)-N(2)	2.3873(9)
Mn(1)-N(4)	2.348(2)	Mn(1)-N(4)	2.3763(10)
Mn(1)-N(3)	2.265(2)	Mn(1)-N(3)	2.2960(9)
Mn(1)-N(12)	2.244(3)	Mn(1)-N(12)	2.2287(10)
Mn(1)-N(13)[a]	2.267(3)	Mn(1)-N(14)[b]	2.1836(10)
Fe(1)-C_{CN}	1.933(3)-1.946(3)	Fe(1)-C_{CN}	1.9264(11)-1.9478(12)
Fe(1)-N(17)	1.660(3)	Fe(1)-N(17)	1.6657(10)
S(1)-Mn(1)-S(2)	76.23(3)	S(1)-Mn(1)-S(2)	80.34(1)
S(1)-Mn(1)-N(2)	72.86(6)	S(1)-Mn(1)-N(2)	71.60(2)
S(2)-Mn(1)-N(4)	73.61(6)	S(2)-Mn(1)-N(4)	72.79(2)
N(2)-Mn(1)-N(3)	69.18(9)	N(2)-Mn(1)-N(3)	67.85(3)
N(4)-Mn(1)-N(3)	68.52(9)	N(4)-Mn(1)-N(3)	68.32(3)
N(12)-Mn(1)-N(13)[a]	170.8(1)	N(12)-Mn(1)-N(14)[b]	167.97(4)
Mn(1)-N(12)-C(12)	153.2(3)	Mn(1)-N(12)-C(12)	154.83(9)
Mn(1)-N(13)[a]-C(13)[a]	150.2(2)	Mn(1)-N(14)[b]-C(14)[b]	160.71(10)
Fe(1)-C(12)-N(12)	178.3(3)	Fe(1)-C(12)-N(12)	176.21(10)
Fe(1)-C(13)-N(13)	176.3(3)	Fe(1)-C(14)-N(14)	178.31(10)
C(12)-Fe(1)-C(13)	171.5(1)	C(12)-Fe(1)-C(14)	88.24(5)

Symmetry codes: [a] (*x*, *y*, *z*-1), [b] (0.5-*x*, *y*-0.5, 0.5-*z*).

Table S5. Hydrogen bond geometry in **1**.

D	H	A	Symmetry code for A	D-H, Å	H…A, Å	D…A, Å	D-H…A, º
N1	H1	N14	1+x, 1+y, 1+z	0.82(3)	2.24(3)	3.030(4)	161(3)
N6	H6A	N14	1+x, 1+y, 1+z	0.82(4)	2.28(4)	3.053(4)	156(4)
N5	H5	N15	x-1, y-1, z	0.82(3)	2.17(3)	2.936(4)	157(3)
N7	H7A	N15	x-1, y-1, z	0.86(4)	2.42(4)	3.157(4)	144(4)
N6	H6B	N16	x, 1+y, 1+z	0.84(4)	2.15(4)	2.925(5)	155(4)
O1W	H1W	S1	x, y, z-1	0.85(9)	2.90(7)	3.672(6)	151(6)
O1W	H2W	N14	x, 1+y, z	0.86(10)	2.27(12)	2.982(7)	140(10)
N7	H7A	O1W	x-1, y-1, z	0.86(4)	2.37(4)	3.091(7)	143(4)
O1S	H1S	N12	x, y, z	0.88(9)	2.29(11)	3.113(9)	154(12)
C7	H7	O1S	x, y-1, z	0.95	2.34	3.268(9)	165

Table S6. Hydrogen bond geometry in **2**.

D	H	A	Symmetry code for A	D-H, Å	H…A, Å	D…A, Å	D-H…A, º	type
N1	H1	N11	1+x, y, z	0.85(5)	2.13(5)	2.938(8)	157(6)	intralayer
N6	H6A	N11	1+x, y, z	0.85(6)	2.24(7)	3.026(7)	153(6)	intralayer
N6	H6B	O3S	1+x, y, z	0.84(3)	2.18(4)	2.975(7)	156(7)	
N5	H5	N10	x-1, y-1, z	0.83(5)	2.27(5)	2.976(8)	143(4)	intralayer
N7	H7A	N10	x-1, y-1, z	0.84(6)	2.25(6)	2.988(8)	147(6)	intralayer
N7	H7B	O2S	x, y, z	0.85(4)	2.03(4)	2.876(7)	177(12)	
N21	H21	N31	x-1, y-1, z	0.84(5)	2.18(5)	2.936(8)	151(6)	intralayer
N26	H26A	N31	x-1, y-1, z	0.84(7)	2.24(7)	3.027(7)	156(6)	intralayer
N26	H26B	O4S	x-1, y-1, z	0.84(3)	2.18(4)	2.947(7)	152(8)	
N25	H25	N30	1+x, y, z	0.83(5)	2.24(5)	3.009(8)	155(6)	intralayer
N27	H27A	N30	1+x, y, z	0.84(6)	2.17(5)	2.977(9)	160(5)	intralayer
N27	H27B	O1S	x, y, z	0.85(3)	2.05(4)	2.889(7)	175(7)	
N41	H41	N12	x,y,1+z	0.84(5)	2.29(6)	3.052(7)	152(6)	interlayer
N46	H46A	N12	x,y,1+z	0.84(5)	2.51(5)	3.297(8)	156(6)	interlayer
N46	H46B	O7S	x,y,1+z	0.84(6)	2.05(6)	2.872(7)	166(6)	
N45	H45	N32	x-1, y-1, z	0.83(5)	2.25(6)	3.008(7)	152(6)	interlayer
N47	H47A	N32	x-1, y-1, z	0.85(3)	2.32(3)	3.108(7)	154(6)	interlayer
C46	H46	N51	1+x, y, z	0.95	2.45	3.358(9)	159	intralayer
C47	H47	N28	x, y, z	0.95	2.59	3.352(7)	137	interlayer
O1S	H1S	O1	x, y, z	0.82(4)	2.44(2)	3.071(8)	135(1)	
O2S	H2S	O2	x, y, z	0.81(3)	2.31(2)	3.095(8)	162(2)	
O7S	H7S	N9	x, y, z	0.82(6)	2.46(7)	3.238(8)	158(9)	
O8S	H8S	N28	x, y, z	0.83(4)	2.41(3)	3.153(9)	150(1)	
O1S	H1S	O6S	x, y, z	0.82(4)	2.09(3)	2.773(9)	142(1)	
O3S	H3S	O2S	x, y, z	0.82(2)	2.08(3)	2.689(7)	131(2)	
O5S	H5S	O4S	x, y, z	0.81(4)	1.88(4)	2.689(10)	171(1)	
O6S	H6S	O3S	x, y, z	0.81(3)	2.08(2)	2.680(9)	131(2)	
O4S	H4S	O1S	x, y, z	0.83(4)	1.89(4)	2.698(7)	168(2)	
C48	H48	O8S	x, y, z	0.95	2.37	3.291(9)	164	

Table S7. Hydrogen bond geometry in **3**.

D	H	A	Symmetry code for A	D-H, Å	H…A, Å	D…A, Å	D-H…A, º	type
N1	H1	N14	x, 1/2-y, 1/2+z	0.82(2)	2.15(2)	2.936(2)	160(2)	intralayer
N6	H6A	N14	x, 1/2-y, 1/2+z	0.86(2)	2.35(2)	3.120(2)	150(2)	intralayer
N6	H6B	N35	x, 1/2-y, 1/2+z	0.81(2)	2.37(2)	3.150(2)	164(2)	interlayer
N5	H5	N15	x-1, 1/2-y, z-1/2	0.82(2)	2.08(2)	2.869(2)	162(2)	intralayer
N7	H7A	N15	x-1, 1/2-y, z-1/2	0.85(2)	2.35(2)	3.099(2)	148(2)	intralayer
N21	H21	O1W	x-1, 1/2-y, z-1/2	0.82(2)	2.00(2)	2.782(2)	160(2)	
N26	H26A	O1W	x-1, 1/2-y, z-1/2	0.82(2)	2.32(2)	3.046(2)	148(2)	
N26	H26B	S1	-x, y-1/2,1/2-z	0.82(3)	2.71(3)	3.515(2)	169(2)	interlayer
N25	H25	N34	1-x, -y, 1-z	0.82(2)	2.10(1)	2.893(2)	162(2)	intralayer
N27	H27A	N34	1-x, -y, 1-z	0.82(2)	2.51(2)	3.201(2)	143(2)	intralayer
N27	H27B	N16	1-x, -y, 1-z	0.82(2)	2.14(2)	2.944(2)	167(2)	interlayer
C28	H28	N12	x, y, z	0.95	2.46	3.267(2)	143	interlayer
O1W	H1W	O1S	x, y, z	0.84(2)	2.02(2)	2.839(2)	166(2)	
O1W	H2W	N35	x, 1/2-y, 1/2+z	0.85(2)	2.08(2)	2.862(2)	153(2)	
O1S	H1S	N32	1-x,1/2+y,1/2-z	0.85(3)	2.51(2)	3.149(2)	133(2)	

Table S8. Hydrogen bond geometry in **4**.

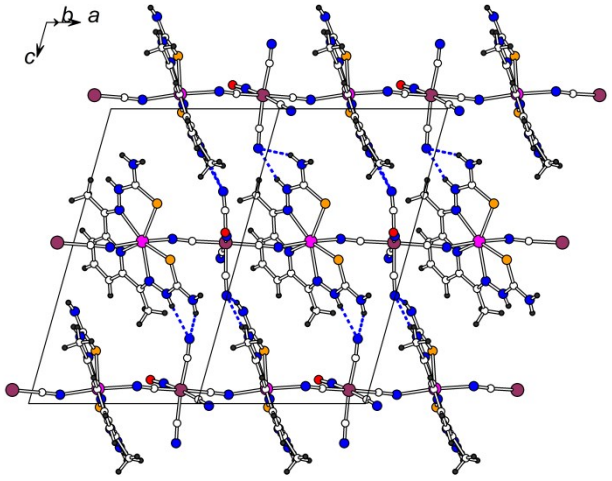
D	H	A	Symmetry code for A	D-H, Å	H…A, Å	D…A, Å	D-H…A, º
N(1)	H(1)	N(23)	2-x, 1-y, -z	0.82(4)	2.33(4)	3.075(4)	152(4)
N(6)	H(6A)	N(23)	2-x, 1-y, -z	0.80(4)	2.36(4)	3.066(5)	148(4)
N(6)	H(6B)	N(25)	1+x, y, z	0.80(4)	2.60(4)	3.241(5)	139(4)
N(5)	H(5)	Cl(1)	2-x, 1-y, 1-z	0.80(3)	2.46(4)	3.188(3)	153(4)
N(7)	H(7A)	Cl(1)	2-x, 1-y, 1-z	0.85(4)	2.51(4)	3.264(3)	149(4)
N(7)	H(7B)	Cl(2)	2-x, -y, -z	0.85(5)	2.45(5)	3.268(3)	164(4)
N(11)	H(11)	N(24)	2-x, -y, -z	0.83(4)	2.20(4)	2.970(4)	154(4)
N(16)	H(16A)	N(24)	2-x, -y, -z	0.82(5)	2.27(5)	3.005(5)	149(4)
N(15)	H(15)	Cl(2)	1-x, -y, -1-z	0.80(3)	2.48(3)	3.222(3)	155(3)
N(17)	H(17A)	Cl(2)	1-x, -y, -1-z	0.82(4)	2.46(5)	3.208(3)	153(5)
N(17)	H(17B)	Cl(1)	2-x, 1-y, -z	0.83(5)	2.40(5)	3.215(3)	166(4)
C(11)	H(11B)	Cl(1)	x-1, y, z	0.98	2.79	3.721(4)	159
C(23)	H(23B)	S(1)	2-x, -y, -z	0.98	2.90	3.679(3)	137
C(23)	H(23C)	N(24)	x, y, z	0.98	2.61	3.488(5)	149
C(31)	H(31B)	Cl(2)	x-1, y, z	0.98	2.67	3.571(4)	154

Table S9. Hydrogen bond geometry in **5**.

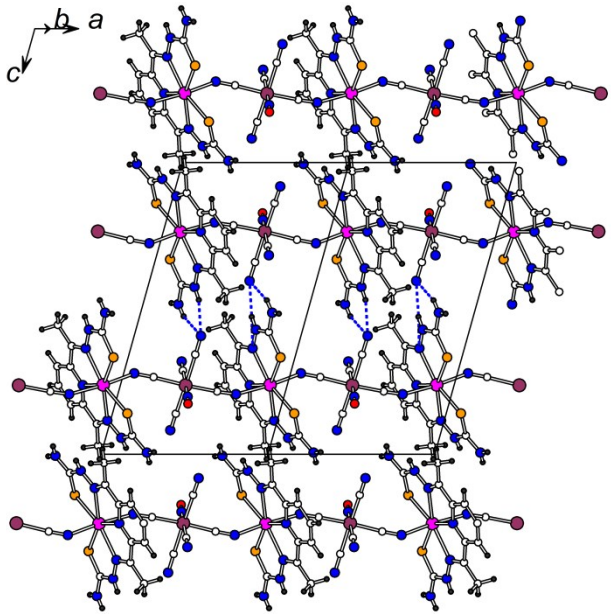
D	H	A	Symmetry code for A	D-H, Å	H…A, Å	D…A, Å	D-H…A, º
N6	H6A	N16	x, y-1, z	0.83(5)	2.30(5)	2.931(4)	133(4)
N7	H7B	N13	1+x, y, z-1	0.81(4)	2.38(4)	3.133(4)	153(4)
N1	H1	O1S	x, y, z	0.83(3)	2.14(3)	2.933(4)	160(4)
N5	H5	O2S	x, y, z	0.82(3)	2.08(3)	2.847(3)	155(3)
N7	H7A	O2S	x, y, z	0.81(4)	2.12(4)	2.869(4)	154(4)
O1S	H1S1	N15	x-1, y-1, z	0.84(4)	2.09(5)	2.910(4)	167(5)
O1S	H1S2	S1	x-1, y, z	0.85(4)	2.65(4)	3.483(3)	174(5)
O2S	H2S1	N14	1+x, 1+y, z-1	0.85(4)	2.02(4)	2.861(4)	172(4)
O2S	H2S2	N15	x, y, z-1	0.85(4)	2.45(5)	3.045(4)	128(4)
O2S	H2S2	N16	1+x, y, z-1	0.85(4)	2.46(5)	3.003(4)	123(4)

Table S10. Hydrogen bond geometry in **6**.

D	H	A	Symmetry code for A	D-H, Å	H…A, Å	D…A, Å	D-H…A, º
N1	H1	N15	1+x, y, z	0.82(2)	2.18(2)	2.956(2)	157(2)
N6	H6A	N15	1+x, y, z	0.82(2)	2.35(2)	3.058(2)	146(2)
N6	H6B	N16	1/2+x, 1/2-y, z-1/2	0.82(2)	2.21(2)	2.975(2)	155(2)
N5	H5	N13	-1/2-x, y-1/2, 1/2-z	0.84(2)	2.07(2)	2.869(2)	159(2)
N7	H7A	N13	-1/2-x, y-1/2, 1/2-z	0.83(2)	2.42(2)	3.130(2)	145(2)
N7	H7B	S1	-x, -y, -z	0.84(2)	2.65(2)	3.495(1)	178(1)
C7	H7	S2	1/2+x, 1/2-y, 1/2+z	0.95	2.80	3.686(1)	155
C11	H11C	N13	-1/2-x, y-1/2, 1/2-z	0.98	2.63	3.320(2)	128
O1S	H1S	N12	x, y, z	0.94(2)	2.30(2)	3.202(2)	160(2)



(a)



(b)

Fig. S4. View of the layer A (a) and B (b) along [-1 1 0] in the structure **3**. Intralayer N-$H_{H2daptsc}$…N_{NP} hydrogen bonds are shown by dashed lines (see Table S7 for details).