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Hysteretic Four-Step Spin-Crossover in a 3D Hofmann-type Metal-Organic Framework with Aromatic Guest

Cui-Juan Zhang, Kai-Ting, Guo-Zhang Huang, Sukhen Bala, Zhao-Ping Ni*, and Ming-Liang Tong

Key Laboratory of Bioinorganic and Synthetic Chemistry of Ministry of Education, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, P. R. China

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Experimental Details

General Procedure

All the reagents were commercially available and used as received. The powder XRD patterns were recorded on a Rigaku Smartlab X-Ray diffractometer with $Cu_{K\alpha}$ ($\lambda = 1.54178$ Å) radiation. Thermogravimetric analyses (TG) were recorded on TG209 F1 Libra. The C, H, and N microanalyses were performed for the dry crystals on an Elementar Vario-ELCHNS elemental analyzer. Differential Scanning Calorimetry (DSC) measurement was performed by cooling and heating the humid sample in an aluminium crucible using a NETZSCH5, which was carried out at sweeping rate of 10 K min⁻¹ under liquid nitrogen. Magnetic susceptibility measurements for the humid samples were performed on a Quantum Design PPMS instrument operating under a field of 1000 Oe. Diamagnetic correction was performed based on Pascal's coefficients.

Synthesis

[Fe(dpoda){Ag(CN)₂}₂]•1.5benzene (1·1.5bz) was prepared through a vial-invial slow diffusion technique. A solution of Fe(ClO₄)₂·6H₂O (0.05 mmol, 18 mg) in EtOH (1 mL) was dripped into a mixture of dpoda (0.05 mmol, 12 mg) and KAg(CN)₂ (0.1 mmol, 20 mg) in DMF (1 mL). The guest benzene (10 mL) was placed in a large vial. The small vial was placed in the large one and then both of them were carefully filled with ethanol. The yellow block crystals were collected after one week. Yield: 60%. Anal. Calcd for C_{24.4}H_{16.4}N₈OFeAg₂ (1·1.4bz): C 41.32, H 2.33, N 15.80. Found: C, 41.00; H, 2.47; N, 15.59. Part of the benzene guest was lost during the preparation of dry sample for EA analysis. FT-IR (KBr): *v* 3402(br), 3233(s), 2164(s), 2056(w), 1640(s), 1618(s), 1400(s), 1089(w), 837(w), 747(w), 718(w), 681(w), 624(w), 479(w) cm⁻¹.

 $[Fe(dpoda){Ag(CN)_2}_2]$ •1.5naphthalene (1·1.5naph) was prepared through a vial-in-vial slow diffusion technique. A solution of $Fe(ClO_4)_2$ ·6H₂O (0.05 mmol, 18 mg) in EtOH (1 mL) was dripped into a mixture of dpoda (0.05 mmol, 12 mg) and KAg(CN)₂ (0.1 mmol, 20 mg) in DMF (1 mL). The small vial was placed in the large

vial. The large vial was then filled with the EtOH (20 mL) solution of naphthalene (2.5 mmol, 320 mg). The yellow block crystals were collected after one week. Yield: 60 %. Anal. Calcd for C₂₉H_{18.4}N₈OFeAg₂ (**1**·**1.3naph**): C, 45.44; H, 2.42; N, 14.62. Found: C, 45.22; H, 2.58; N, 14.39. Part of the naphthalene guest was lost during the preparation of dry sample for EA analysis. FT-IR (KBr): v 3413(br), 3234(s), 2167(s), 2061(w), 1638(s), 1620(s), 1400(s), 1089(w), 836(w), 786(w), 707(w), 681(w), 618(w), 484(w) cm⁻¹.

 $[Fe(dpoda){Ag(CN)_2}_2]$ •anthracene (1·anth) was prepared by a similar method of 1·1.5naph except using the anthracene as the guest. Yield: 20%. Anal. Calcd for $C_{25.8}H_{15}N_8OFeAg_2$ (1·0.7anth): C, 42.76; H, 2.09; N, 15.46. Found: C, 42.76; H, 2.16; N, 15.75. Part of the anthracene guest was lost during the preparation of dry sample for EA analysis. FT-IR (KBr): v 3414(br), 3235(s), 2167(s), 2111(w), 2031(w), 1639(s), 1618(s), 1400(s), 1088(w), 839(w), 727(w), 623(w), 472(w) cm⁻¹.

X-ray Crystallography

Single-crystal diffraction data were recorded on a Bruker D8 QUEST diffractometer with $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation in sequence at 120 K and 273 K for **1**·**1**.5bz, at 150 K, 188 K, 211 K, 239 K and 298 K for **1**·**1**.5naph, at 120 K and 298 K for **1**·anth, respectively. The current unit cell for **1**·**1**.5naph at 188 K in Table

$$\begin{array}{cccc} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{array}$$

S2 resulted from the transformation matrix $\begin{bmatrix} -1 & 0 & 0 \end{bmatrix}$ upon its respective original triclinic unit cells. The current unit cell for 1.1.5naph at 211 K in Table S2

$$\begin{bmatrix} 0 & -1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{bmatrix}$$

was the result of the transformation matrix l - 1 = 0 = 0] upon its original triclinic unit cell. The crystal structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL 2014/7 program.¹ Hydrogen atoms on organic ligands were generated by the riding mode. The refinement details can be found in "_refine_special_details" within each .cif file. The responses to the alerts from checkCIF are quoted within the validation response form. CCDC 1913107 (120 K), 1913108 (273 K) for **1**·1**.5bz**, 1913109 (150 K), 1913110 (188 K), 1913111 (211 K), 1913112 (239 K), 1913113 (298 K) for **1.1.5naph** and 1913114 (120 K), 1913115 (298 K) for **1.anth** contain the supplementary crystallographic data for this paper. These data could be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[1] a) Sheldrick, G. M.SHELXS-97, Program for Crystal Structuresolution.University of Göttingen, Germany 1997. b) Sheldrick, G. M.SHELXL-97, Program for Crystal Structure Refinement. University of Göttingen, Germany 1997. c) Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Crystallogr. C* 2015, *71*, 3–8.

Parameter	1·1.5b)Z
<i>T</i> /K	120(2)	273(2)
Chemical Formula	$C_{25}H_{17}N_8OFeAg_2$	C ₂₅ H ₁₇ N ₈ OFeAg ₂
Mr	717.05	717.05
Crystal system	monoclinic	monoclinic
Space group	C2/c	C2/c
a/Å	28.645(2)	28.6573(19)
b/Å	13.5949(11)	14.3191(10)
c/Å	14.3880(11)	14.5629(9)
$lpha/^{\circ}$	90	90
$eta/^{\circ}$	108.176(3)	105.924(2)
$\gamma/^{\circ}$	90	90
V/Å ³	5323.5(7)	5746.5(7)
Ζ	8	8
μ (Mo K α)/mm ⁻¹	2.028	1.879
Radiation	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)
Reflections collected	52455	60633
Independent reflections	$6150 [R_{int} = 0.0761]$	6623 [$R_{int} = 0.0449$]
Goodness-of-fit on F ²	1.048	1.052
Final <i>R</i> indexes [$I \ge 2\sigma(I)$]	$R_1^a = 0.0466, wR_2 = 0.1177$	$R_1 = 0.0388, wR_2 = 0.1116$
Final R indexes [all data]	$R_1 = 0.0704, wR_2^b = 0.1296$	$R_1 = 0.0631, wR_2 = 0.1257$
Largest diff. peak/hole / e Å-	³ 2.04/-1.10	1.31/-0.72

 Table S1. Crystallographic data for 1.1.5bz.

 ${}^{a}R_{1} = \sum |F_{o}| - |F_{c}|| / \sum |F_{o}|; {}^{b}wR_{2} = \{ [\sum w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})^{2}] \}^{1/2}.$

Parameter			1·1.5naph		
T/K	150(2)	188(2)	211(2)	239(2)	298(2)
Chemical Formula	$C_{31}H_{20}N_8OFeAg_2 \\$	$C_{124}H_{80}N_{32}O_4Fe_4Ag_8\\$	$C_{62}H_{40}N_{16}O_2Fe_2Ag_4\\$	$C_{31}H_{20}N_8OFeAg_2 \\$	$C_{31}H_{20}N_8OFeAg_2$
Mr	792.14	3168.56	1584.28	792.14	792.14
Crystal system	monoclinic	triclinic	triclinic	monoclinic	monoclinic
Space group	C2/c	P^{1}	P^1	C2/c	C2/c
a/Å	20.3664(13)	27.8418(18)	15.5150(19)	20.8653(12)	21.0563(2)
b/Å	28.302(3)	17.5236(14)	17.552(2)	28.7182(18)	28.9371(17)
c/Å	13.7232(9)	13.7996(9)	13.9024(16)	13.9679(8)	14.1011(14)
$\alpha/^{\circ}$	90	67.033(2)	67.038(4)	90	90
$eta / ^{\circ}$	131.844(2)	76.138(2)	90.558(4)	131.492(2)	131.4150(10)
$\gamma/^{\circ}$	90	87.708(3)	64.872(4)	90	90
$V/Å^3$	5892.9(8)	6007.6(7)	3085.4(7)	6269.3(7)	6443.4(8)
Ζ	8	2	2	8	8
μ (Mo K α)/mm ⁻¹	1.842	1.807	1.759	1.731	1.685
Radiation	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)
Reflections collected	66089	133997	51532	64850	41739
Independent reflections	6788 [$R_{\rm int} = 0.0897$]	27609 [$R_{\rm int} = 0.1655$]	14107 [$R_{int} = 0.0993$]	7206 [$R_{\rm int} = 0.0815$]	7353 [$R_{\rm int} = 0.0601$]
Goodness-of-fit on F^2	1.017	1.023	1.096	1.148	1.092
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1^a = 0.0344, wR_2 = 0.0524$	${}^{4}R_{1} = 0.0798, wR_{2} = 0.1207$	$R_1 = 0.1040, wR_2 = 0.2601$	$R_1 = 0.0672, wR_2 = 0.1299$	$R_1 = 0.0531, wR_2 = 0.1157$
Final <i>R</i> indexes [all data]	$R_1 = 0.0656, wR_2^{b} = 0.0589$	$R_1 = 0.2182, wR_2 = 0.1531$	$R_1 = 0.1571, wR_2 = 0.2843$	$R_1 = 0.1076, wR_2 = 0.1430$	$R_1 = 0.0939, wR_2 = 0.1311$
Largest diff. peak/hole / e Å	³ 0.46/-0.65	1.48/-1.84	2.91/-3.45	0.88/-1.01	0.83/-0.81

 Table S2. Crystallographic data for 1.1.5naph.

^{*a*} $R_1 = \sum |F_0| - |F_c|| / \sum |F_0|; {}^{b} w R_2 = \{ [\sum w (F_0^2 - F_c^2)^2] / \sum [w (F_0^2)^2] \}^{1/2}.$

Parameter		
Т/К	120(2)	298(2)
Chemical Formula	$C_{30}H_{18}N_8OFeAg_2 \\$	$C_{30}H_{18}N_8OFeAg_2$
Mr	778.11	778.11
Crystal system	monoclinic	monoclinic
Space group	C2/c	C2/c
a/Å	28.695(3)	28.679(4)
b/Å	13.6288(10)	14.1905(17)
c/Å	14.3844(10)	14.5490(15)
$\alpha/^{\circ}$	90	90
$eta/^{\circ}$	107.917(4)	105.919(6)
γ/°	90	90
$V/\text{\AA}^3$	5352.6(7)	5693.9(12)
Ζ	8	8
μ (Mo K α)/mm ⁻¹	2.026	1.905
Radiation	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)
Reflections collected	54074	54949
Independent reflections	$6146 [R_{int} = 0.0465]$	6468 [$R_{int} = 0.0719$]
Goodness-of-fit on F^2	1.101	1.055
Final <i>R</i> indexes [$I \ge 2\sigma(I)$]	$R_1 = 0.0786, wR_2 = 0.1784$	$R_1 = 0.0790, wR_2 = 0.2252$
Final R indexes [all data]	$R_1 = 0.0922, wR_2 = 0.1853$	$R_1 = 0.1255, wR_2 = 0.2636$
Largest diff. peak/hole / e Å	³ 4.58/-1.40	1.94/-1.48

 Table S3. Crystallographic data for 1·anth.

 $\overline{{}^{a} R_{1} = \sum |F_{o}| - |F_{c}|| / \sum |F_{o}|; {}^{b} w R_{2} = \{ \sum w (F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w (F_{o}^{2})^{2}] \}^{1/2}.$

Parameter	120(2)	273(2)
<fe–n>^a</fe–n>	1.963(4)	2.170(3)
$Ag \cdots Ag^b$	3.0874(6)	3.1758(5)
Fe…Fe ^c	13.8783(12)	14.1803(11)
$\mathrm{Fe}^{\dots}\mathrm{Fe}^{\mathrm{d}}$	9.8749(11)	10.1802(8)
	9.9200(11)	10.2433(8)
∑Fe ^e	8.07(16)	10.75(12)
Fe–N–C ^f	174.8(4)	168.0(3)
θ^{g}	86.752(7)	89.032(5)
dihedral angle ^h	26.6(1)/27.3 (1); 51.8(1)	21.2 (1)/25.0(1); 44.2(1)
dihedral angle ⁱ	75.46(3)	61.19 (6)

 Table S4. Selected structural parameters for 1.1.5bz at different temperatures.

^aThe average Fe–N bond lengths (Å); ^bThe argentophilic interactions (Å); ^cThe Fe…Fe distance (Å) linked by the dpoda ligand; ^dThe Fe…Fe distance (Å) linked by the $[Ag(CN)_2]^-$ unit; ^eOctahedral distortion parameters (°); ^f The average Fe–N–C angles within the Hofmann layer; ^gThe acute angle between neighboring Fe(II) sites within the Hofmann layer; ^hIn the dpoda ligand, the dihedral angles between the oxadiazole and each pyridine ring as well as the dihedral angle between the pyridine rings; ⁱThe dihedral angle between the up and down pyridine rings coordinated to Fe(II) site.

Parameter	150(2)	188(2)	211(2)	239(2)	298(2)
<fe–n>a</fe–n>	1.962(2)	<fe1-n> 1.995(10)</fe1-n>	<fe1-n> 1.988(10)</fe1-n>	2.105(6)	2.166(5)
		<fe2–n> 1.946(9)</fe2–n>	<fe2–n> 2.151(10)</fe2–n>		
		<fe3–n> 1.999(10)</fe3–n>			
		<fe4–n> 2.094(11)</fe4–n>			
$Ag \cdots Ag^b$	3.0207(5)	3.0250(15)	3.0581(15)	3.0732(12)	3.0922(10)
	3.2383(5)	3.2452(15)	3.2639(15)	3.2577(12)	3.2794(11)
		3.0324(17)			
		3.2539(16)			
Fe···Fe ^c	14.1510(17)	14.1451(26)	14.3001(27)	14.3591(15)	14.4686(12)
		14.1523(25)	14.3137(27)		
		14.2678(27)			
		14.2704(26)			
Fe···Fe ^d	10.2842(9)	10.2202(29)	10.3432(28)	10.4127(19)	10.6440(13)
	10.2041(12)	10.2808(21)	10.3882(28)	10.4526(19)	10.5495(16)
	10.2656(9)	10.3045(29)	10.4607(24)	10.5312(13)	10.6417(13)
	10.1624(12)	10.4335(21)	10.4724(24)	10.5265(13)	10.5068(16)
		10.1764(28)			
		10.4194(21)			
		10.3433(29)			
ΣFe ^e	7.29(10)	ΣFe1 5.4(4)	ΣFe1 10.6(4)	12.5(2)	14.05(18)
		ΣFe2 6.9(4)	ΣFe2 16.2(4)		
		ΣFe3 13.9(4)			
		ΣFe4 14.0(4)			

Table S5. Selected structural parameters for 1.1.5naph at different temperatures.

Fe-N-C ^f	175.3(2)	Fe1-N-C 174.0(11)	Fe1-N-C176.2(12)	174.0(6)	173.2(5)
		Fe2–N–C 175.4(9)	Fe2–N–C172.7(11)		
		Fe3-N-C 175.8(10)			
		Fe4–N–C 173.4(11)			
$\theta^{\!\!\!\!*}$	84.198(6)	Fe1 83.43(2)	83.81(2)	83.66(1)	83.633(8)
	84.313(6)	Fe2 84.62(2)	83.64 (2)	83.49(1)	83.417(8)
	95.558(6)	Fe3 83.31(2)	96.10 (2)	96.29 (1)	96.353(9)
	95.931(6)	Fe4 83.31(2)	96.45(2)	96.56 (1)	96.597(9)
dihedral angle ^h	15.61(6)/9.34(8); 13.53(2)	Fe1O1:7.5(4)/15.8 (3);12.9(2)	Fe1O1:7.3(4)/14.3(4);12.4(4)	14.1(2)/7.0(2); 12.0(2)	13.5(2)/6.3(2)
		Fe2O2:8.0(4)/15.1 (4);11.7 (3)	Fe2O2:8.0(4)/14.6(5);11.6 (4)		12.2(2)
		Fe3O3:8. 2(3)/15.0 (4);12.3(3)			
		Fe4O4:8.2(4)/15.3(4);12. 5(3)			
dihedral angle ⁱ	8.550	Fe1: 9.3 (2)	Fe1: 7.7(4)	8.8(2)	8.9(2)
		Fe2: 8.6(3)	Fe2: 9.2(5)		
		Fe3: 7.8(3)			
		Fe4: 9.4(4)			

^aThe average Fe–N bond lengths (Å); ^bThe argentophilic interactions (Å); ^cThe Fe…Fe distance (Å) linked by dpoda; ^dThe Fe…Fe distance (Å) linked by $[Ag(CN)_2]^-$; ^eOctahedral distortion parameters (°); ^fAverage Fe–N–C angles within Hofmann layer; ^gThe acute angle between neighboring Fe(II) sites within the Hofmann layer; ^hIn the ligand dpoda, the dihedral angles between the oxadiazole and each pyridine ring as well as the dihedral angle between the pyridine rings; ⁱThe dihedral angle between the up and down pyridine rings coordinated to Fe(II) site.

Parameter	120(2)	298(2)
<fe–n>^a</fe–n>	1.961(7)	2.153(7)
$Ag \cdots Ag^b$	3.0871(10)	3.1484(14)
Fe…Fe ^c	13.9316(20)	14.1887(24)
Fe…Fe ^d	9.8903(18)	10.1404(18)
	9.9252(18)	10.1832(18)
∑Fe ^e	7.5(3)	10.1(3)
Fe-N-C ^f	175.4(7)	167.6(9)
θ^{g}	86.91(1)	88.57(1)
	86.91(1)	88.57(1)
	92.88(1)	91.18(1)
	93.30(1)	91.68(1)
dihedral angle ^h	24.9 (3)/25.9(3); 49.5(3)	20.5 (3)/24.7 (3); 43.8(3)
dihedral angle ⁱ	75.6(3)	66.0(3)

 Table S6. Selected structural parameters for 1·anth at different temperatures.

^aThe average Fe–N bond lengths (Å); ^bThe argentophilic interactions (Å); ^cThe Fe…Fe distance (Å) linked by dpoda; ^dThe Fe…Fe distance (Å) linked by $[Ag(CN)_2]^-$; ^cOctahedral distortion parameters (°); ^fAverage Fe–N–C angles within Hofmann layer; ^gThe acute angle between neighboring Fe(II) sites within the Hofmann layer; ^hIn the ligand dpoda, the dihedral angles between the oxadiazole and each pyridine ring as well as the dihedral angle between the pyridine rings; ⁱThe dihedral angle between the up and down pyridine rings coordinated to Fe(II) site.

120 K	$ heta^{\mathrm{b}}$	Z^{c}	d^{d}	r ^e	$lpha^{ m f}$	l g
bz1 and py1 ^a	12.838	3.6053	3.2022	1.6565		
bz1 and bz2 ^a	80.276	5.4569	4.5339	3.0367	160.181	3.2120
273 K						
bz1 and py1 ^a	12.203	3.8123	3.3753	1.7723		
bz1 and bz2 ^a	75.780	5.7142	4.5195	3.4966	153.160	3.5811

Table S7. $\pi \cdots \pi$ interactions in 1.1.5bz at different temperatures.

^abz1: C23-C28, -x, y, -1/2-z; bz2: C17-C22, -x, 1-y, -1-z; py1: C12-C16, N8, x, y, z; ^bThe dihedral angle between two aromatic rings (°); ^cThe distance between the centroids of aromatic rings (Å); ^dThe perpendicular distance between two aromatic rings (Å); ^eThe offset distance between two aromatic rings (Å); ^fThe angle of π -H··· π (°), in which the H atom have ^gthe shortest distance of H-to-ring center (Å).

Table S8. $\pi \cdots \pi$ interactions in **1** anth at different temperatures.

120 K	$ heta^{ ext{b}}$	Zc	d^{d}	r ^e	$lpha^{ m f}$	lg
anth1 and py1 ^a	65.163	4.8841	4.6569	1.4723	128.427	3.1254
anth2 and py1 ^a	15.220	3.7532	3.1817	1.9908		
anth1 and anth2 ^a	52.400	4.6577	4.4500	1.3754	139.289	2.6271
298 K						
anth1 and py1 ^a	57.515	4.9634	4.6692	1.6834	130.191	3.2113
anth2 and py1 ^a	9.320	3.8871	3.2785	2.0883		
anth1 and anth2 ^a	50.144	4.9190	4.6003	1.7418	141.680	2.9163

^aanth1: C17-C24, 1-x,y,3/2-z; anth2: C25-C31, 1-x, 1-y, 1-z; py1: C5-C9, N5, x, y, z; ^bThe dihedral angle between two aromatic rings (°); ^cThe distance between the centroids of aromatic rings (Å); ^dThe perpendicular distance between two aromatic rings (Å); ^eThe offset distance between two aromatic rings (Å); ^fThe angle of π -H··· π (°), in which the H atom have ^gthe shortest distance of H-to-ring center (Å).

150 K	$ heta^{ ext{b}}$	Z^{c}	d^{d}	r ^e	$lpha^{ m f}$	l ^g	
naph1 and oda1 ^a	2.516	3.7654	3.2146	1.9608			
naph1 and py1 ^a	9.139	3.7342	3.2134	1.9022			
naph2 and oda1 ^a	2.155	3.4210	3.2901	0.9373			
naph2 and py1 ^a	9.423	3.6613	3.3324	1.5167			
naph3 and py1 ^a	84.040	4.8961	4.7568	1.1596	131.190	3.0894	
239 K	$ heta^{ ext{b}}$	Zc	d^{d}	r ^e	$\alpha^{ m f}$	l ^g	
naph1 and oda1 ^a	2.591	3.8632	3.2743	2.0502			
naph1 and py1 ^a	7.281	3.7996	3.2913	1.8985			
naph2 and oda1 ^a	2.596	3.5020	3.3606	0.9851			
naph2 and py1 ^a	8.122	3.6951	3.3787	1.4960			
naph3 and py1 ^a	84.768	5.0661	4.8966	1.2995	134.972	3.2026	
298 K	$ heta^{ ext{b}}$	Zc	d^{d}	r ^e	$lpha^{ m f}$	lg	
naph1 and oda1 ^a	2.974	3.8979	3.2955	2.0817			
naph1 and py1 ^a	7.191	3.8286	3.3186	1.9092			
naph2 and oda1 ^a	2.241	3.5443	3.3876	1.0422			
naph2 and py1 ^a	7.368	3.7234	3.4328	1.4421			
naph3 and py1 ^a	84.007	5.1272	4.9261	1.4219	135.994	3.2613	
^a naph1: C17-C26,	x, y, z; nap	oh2: C17-C2	6, x, 1-y, ¹ /	∕₂+z; naph3:	C27-C31, 1-x	, 1-y, 1-z;	
oxadiazole(oda1): N	16-N7, C10-C	211, O1, x, y,	z; py1: C12-	C16, N8, x, y	, Z.		
211 K L1-O1	$ heta^{ ext{b}}$	Z^{c}	d^{d}	r ^e	α^{f}	lg	
naph1 and $oda1^{h}$	2.742	3.8402	3.2746	2.0060			
naph1 and py1 ^h	6.679	3.7565	3.2855	1.8212			
naph2 and $oda1^{h}$	2.227	3.4950	3.3451	1.0126			
naph2 and py1 ^h	7.477	3.6832	3.3861	1.4492			
naph3 and py1 ^h	85.845	5.0169	4.8787	1.1694	135.849	3.1491	
211 K L2-O2							
naph4 and oda2 ^h	2.294	3.8120	3.2507	1.9911			
naph4 and $py2^{h}$	8.843	3.7784	3.2465	1.9330			
naph5 and $oda2^{h}$	1.211	3.4788	3.3346	0.9912			
naph5 and $py2^{h}$	8.474	3.7049	3.4065	1.4567			
naph6 and py2 ^h	82.014	5.0496	4.8403	1.4387	131.565	3.2180	
^h naph1: C17-C26, x, y, z; naph2: C48-C57, 1-x, 1-y, 2-z; naph3: C27-C31, -x, 2-y, 1-z; naph4:							
C48-C57, x, y, z; naph5: C17-C26, 1-x, 1-y, 1-z; naph6: C58-C62, 2-x, -y, 2-z; oxadiazole(oda1):							
N6-N7, C10-C11, C	01, x, y, z; oc	la2: N14-N15	5, C41-C42,	02, x, y, z; p	oy1: C12-C16,	N8, x, y, z;	
py2: C43-C47, N16	, x, y, z.						
188 K L1-O1	$ heta^{ ext{b}}$	Zc	d^{d}	r ^e	$\alpha^{ m f}$	lg	

Table S9. $\pi \cdots \pi$ interactions in **1**·**1.5naph** at different temperatures.

naph1 and $oda1^i$ 2.476 3.7982 3.2155 2.0216 naph1 and py1ⁱ 8.227 3.7388 3.2289 1.8849 naph2 and oda1ⁱ 1.677 3.3065 0.9854 3.4502 naph2 and py1ⁱ 8.307 3.6875 3.3582 1.5232 naph3 and $py1^i$ 4.9396 4.8099 85.645 1.1245 134.673 3.0777

188 K L2-O2						
naph4 and oda2 ⁱ	2.611	3.7870	3.2408	1.9592		
naph4 and py2 ⁱ	7.983	3.7417	3.2495	1.8550		
naph5 and $oda2^i$	2.382	3.4444	3.3129	0.9426		
naph5 and $py2^i$	8.926	3.6903	3.3491	1.5498		
naph6 and $py2^i$	85.549	4.8823	4.7621	1.0767	132.825	3.0381
188 K L3-O3						
naph7 and oda3 ⁱ	2.574	3.7775	3.2169	1.9802		
naph7 and $py3^i$	8.808	3.7624	3.2322	1.9258		
naph8 and $oda3^i$	2.426	3.4497	3.3202	0.9363		
naph8 and py3 ⁱ	9.233	3.6652	3.3402	1.5089		
naph9 and py3 ⁱ	83.137	4.9345	4.7541	1.3221	130.784	3.1365
188 K L4-O4						
naph10 and $oda4^i$	3.075	3.7874	3.2007	2.0248		
naph10 and $py4^i$	9.724	3.7621	3.2150	1.9538		
naph11 and oda4 ⁱ	2.703	3.4497	3.3201	0.9367		
naph11and py4 ⁱ	9.757	3.6660	3.3400	1.5113		
naph12 and py4 ⁱ	82.172	5.0001	4.7972	1.4099	131.71	3.1896

ⁱnaph1: C17-C26, x, y, z; naph2: C110-C119, 1-x, 2-y, 1-z; naph3: C27-C31, -x, 2-y, -z; naph4: C48-C57, x, y, z; naph5: C79-C88, 1-x, -y, -z; naph6: C58-C62, 1-x, 1-y, -z; naph7: C79-C88, x, y, z; naph8: C48-C57, 1-x, -y, 1-z; naph9: C89-C93, 1-x, -1-y, 1-z; naph10: C110-C119, x, y, z; naph11: C17-C26, 1-x, 2-y, -z; naph12: C120-C124, 2-x, 2-y, 1-z; oxadiazole(oda1): N6-N7, C10-C11, O1, x, y, z; oda2: N14-N15, C41-C42, O2, x, y, z; oda3: N22-N23, C72-C73, O3, x, y, z; oda4: N30-N31, C103-C104, O4, x, y, z; py1: C12-C16, N8, x, y, z; py2: C43-C47, N16, x, y, z; py3: C74-C78, N24, x, y, z; py4: C105-C109, N32, x, y, z;.

^bThe dihedral angle between two aromatic rings (°); ^cThe distance between the centroids of aromatic rings (Å); ^dThe perpendicular distance between two aromatic rings (Å); ^eThe offset distance between two aromatic rings (Å); ^fThe angle of π -H··· π (°), in which the H atom have ^gthe shortest distance of H-to-ring center (Å).



Figure S1. Powder X-ray diffraction data of **1**·**1.5bz** (a), **1**·**1.5naph** (b) and **1**·**anth** (c) at room temperature.



Figure S2. Thermogravimetric analyses of 1.1.5bz (black), 1.1.5naph (red) and 1.anth (blue). The weight loss of 1.1.5bz (16.57 %), 1.1.5naph (22.69 %), and 1.anth (18.55 %) are similar to the weight percent of 1.5 bz (16.34 %), 1.38 naph (22.77 %) and 0.76 anth (18.42%).



Figure S3. The first order differentiation of $\chi_M T$ versus T plots for 1.1.5bz (a), 1.1.5naph (b) and 1.anth (c) on cooling (blue) and heating (red).



Figure S4. Variable-temperature magnetic measurements of two sequential cycles for **1**·**1.5bz** (a), **1**·**1.5naph** (b) and **1**·**anth** (c).



Figure S5. Differential scanning calorimetry (DSC) measurements of (a) **1**·**1.5bz**, (b) **1**·**1.5naph** and (c) **1**·**anth** at 10 K min⁻¹.



Figure S6. Asymmetric unit of **1**·**1.5bz** at 120 K. Thermal ellipsoids are drawn at the 30 % probability. Hydrogen atoms are omitted for clarity.









Figure S7. Asymmetric unit of **1**•**1.5naph** at 150 K (a), 188 K (b), 211 K (c), 239 K (d), 298 K (e). Thermal ellipsoids are drawn at the 30 % probability. Hydrogen atoms are omitted for clarity.



Figure S8. Asymmetric unit of **1**•**anth** at 120 K. Thermal ellipsoids are drawn at the 30 % probability. Hydrogen atoms are omitted for clarity.



Figure S9. View of two-fold interpenetrated frameworks and the corresponding pcu topological network of 1.1.5naph.



Figure S10. The argentophilic interactions between two layers in **1**·**1.5naph**: (a) four sets of Ag···Ag interactions at 188 K: 3.2539 Å (green), 3.2452 Å (blue), 3.0324 Å (pink), 3.0249 Å (red); (b) two sets of Ag···Ag interactions at 211 K: 3.2716 Å (red), 3.0482 Å (blue).



Figure S11. 1D channel along the *c* axis in (a) $1 \cdot 1.5bz$ (at 273 K) and (b) $1 \cdot anth$ (at 298 K)



Figure S12. 2D channel along the *ac* plane in $1 \cdot 1.5$ naph (a) and the view along the *c* axis (b) at 298 K.



Figure S13. Offset face-to-face (pink dash lines) and edge-to-face (turquoise dashed lines) $\pi \cdots \pi$ interactions in **1**·**1.5bz** (at 273 K) along the *c* axis. Green dashed lines represent the argentophilic interactions.



Figure S14. Offset face-to-face (pink dash lines) and edge-to-face (turquoise dashed lines) $\pi \cdots \pi$ interactions in **1** anth (at 298 K) along the *c* axis. Green dashed lines represent the argentophilic interactions.



Figure S15. Offset face-to-face (pink dash lines) and edge-to-face (turquoise dashed lines) $\pi \cdots \pi$ interactions in **1**·**1.5naph** (at 298 K) along the *b* axis.



Figure S16. (a) Arrangement of Fe1 (red), Fe2 (pink), Fe3 (orange) and Fe4 (yellow) sites within one Hofmann layer for **1**·**1.5naph**, showing the ordering of each Fe site along the *c*-axis at 188 K. (b) View of one set of 3D framework for **1**·**1.5naph**, showing the ordering of each Fe site with respective colored blocks along the *bc* plane. (c) View of full twofold-interpenetrated 3D framework for **1**·**1.5naph**, showing the ordering of Fe2 (pink) and Fe4 (yellow) sites along the *bc* plane. Hofmann-type layers from two sets of 3D framework are represented with red and blue squares, respectively. These layers with the same colored squares are connected by ligands, which are omitted for clarity.



Figure S17. (a) Arrangement of Fe1 (red) and Fe2 (yellow) sites within one Hofmann layer for $1 \cdot 1.5$ naph, showing the ordering of each Fe site along the *c*-axis at 211 K. (b) View of one set of 3D framework for $1 \cdot 1.5$ naph, showing the ordering of each Fe site with respective colored blocks along the *bc* plane. (c) View of full twofoldinterpenetrated 3D framework for $1 \cdot 1.5$ naph, showing the ordering of Fe1 and Fe2 in the whole 3D framework. Hofmann-type layers from two sets of 3D framework are represented with red and blue squares, respectively. These layers with the same colored squares are connected by ligands, which are omitted for clarity. The HS Fe2 sites are marked with yellow blocks.



Figure S18. Ligand orientations within one cubic (a), one set of 3D framework (b) and twofold-interpenetrated 3D framework (c) in **1**·**1.5naph** at 150 K. The ligands with opposite orientations are marked by dark yellow and pink, respectively.