Electronic Supplementary Information

for

Copper(I)- and copper(0)-promoted homocoupling and homocoupling–hydrodehalogenation reactions of dihalogenoclathrochelate precursors for C–C conjugated iron(II) bis-cage complexes

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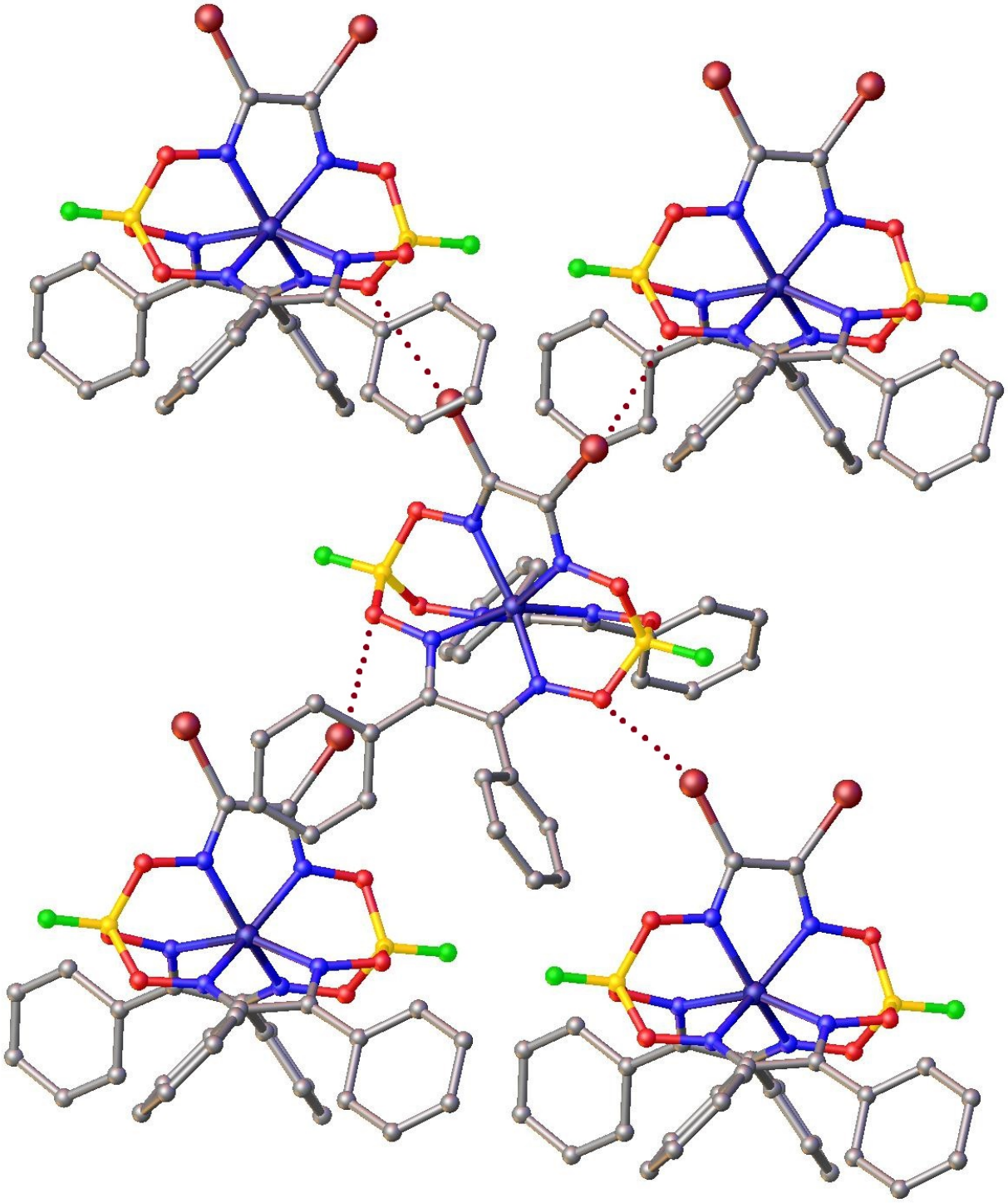

Figure S1. Fragment of C–Br...O bonded layers in the crystal of polymorph I of the complex $FeBd_2(Br_2Gm)(BF)_2 \cdot CH_2Cl_2$. Hydrogen atoms are omitted for clarity.

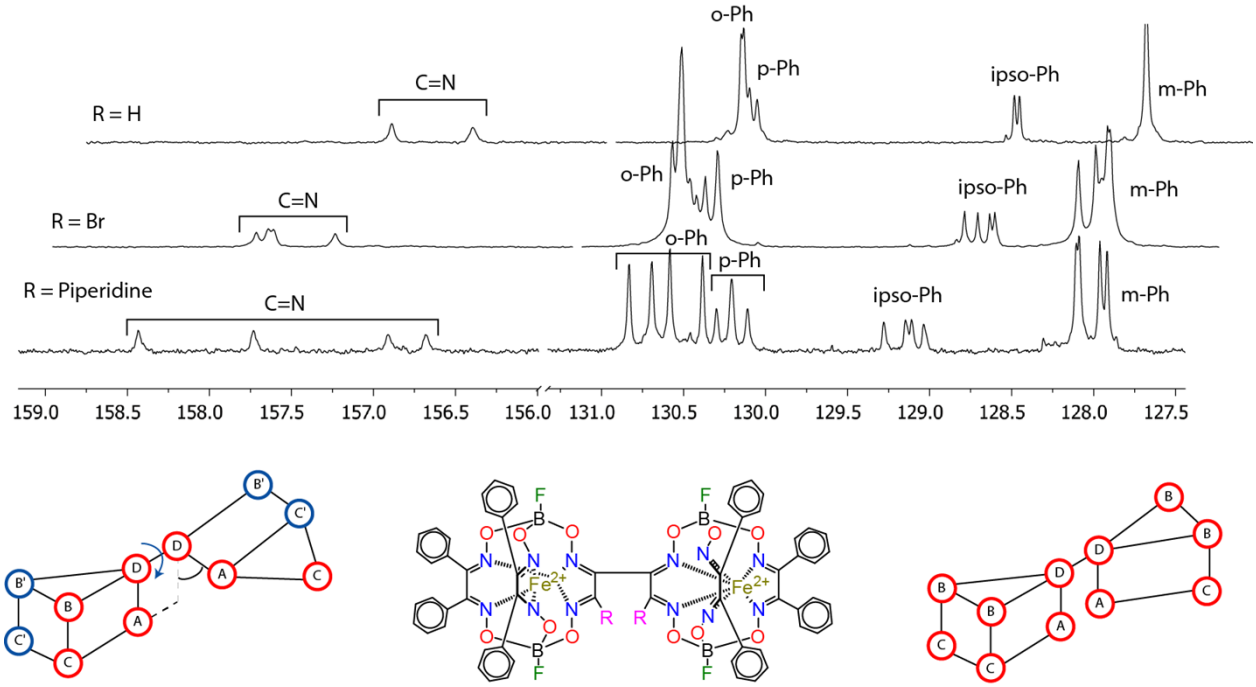

Figure S2. The selected $^{13}C\{^{1}H\}$ NMR spectra of bis-clathrochelates with different conformational lability.

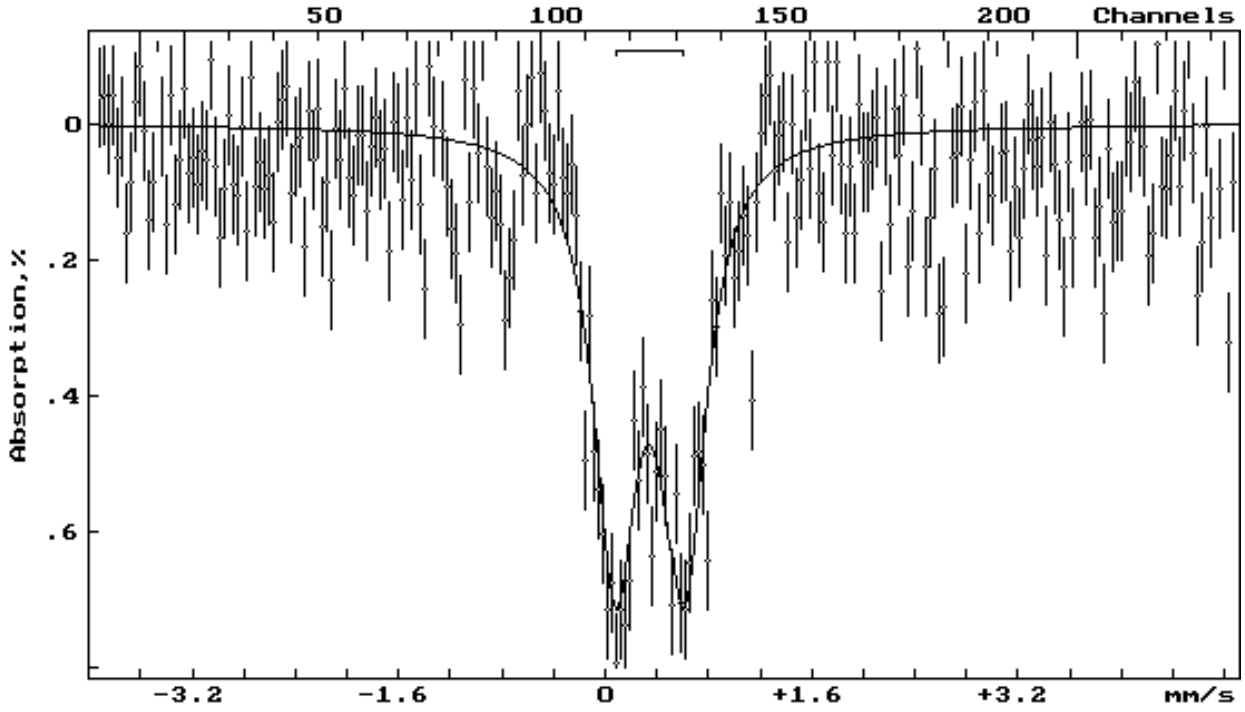

Figure S3. ^{57}Fe Mössbauer spectrum of $\{FeBd_2(BrGm)(BF)_2\}_2$

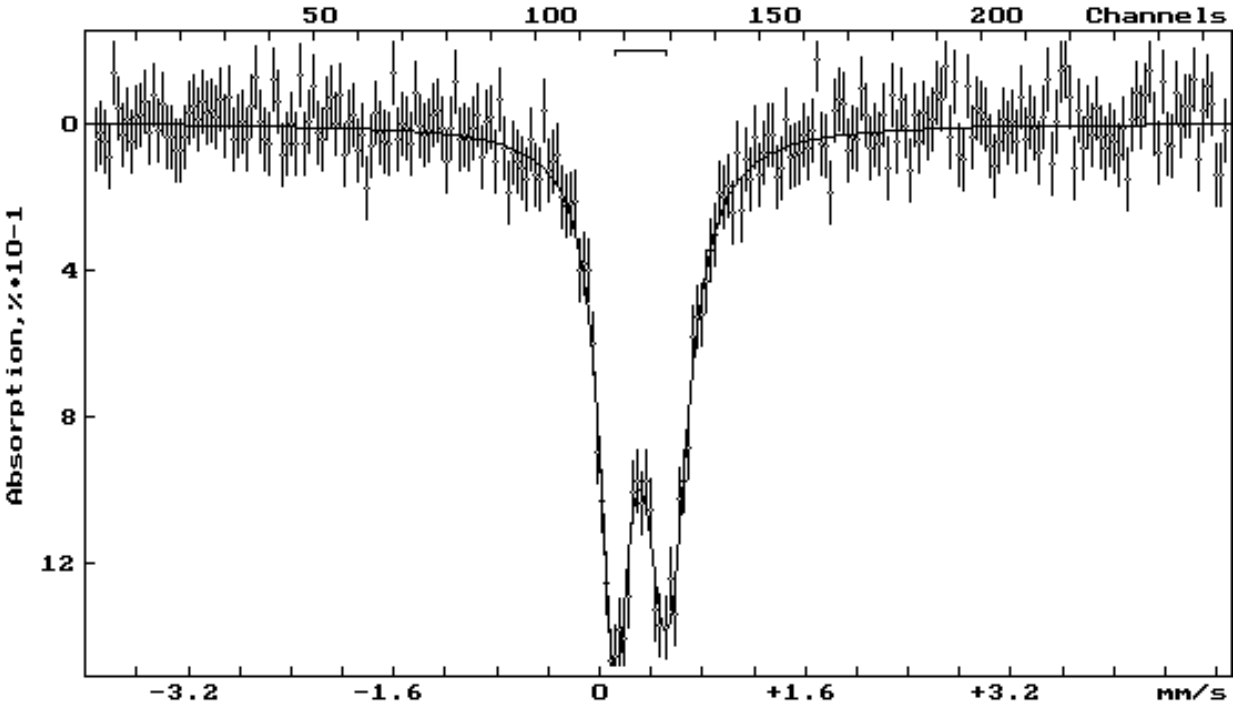

Figure S4. ^{57}Fe Mössbauer spectrum of $\{FeBd_2(IGm)(BF)_2\}_2$

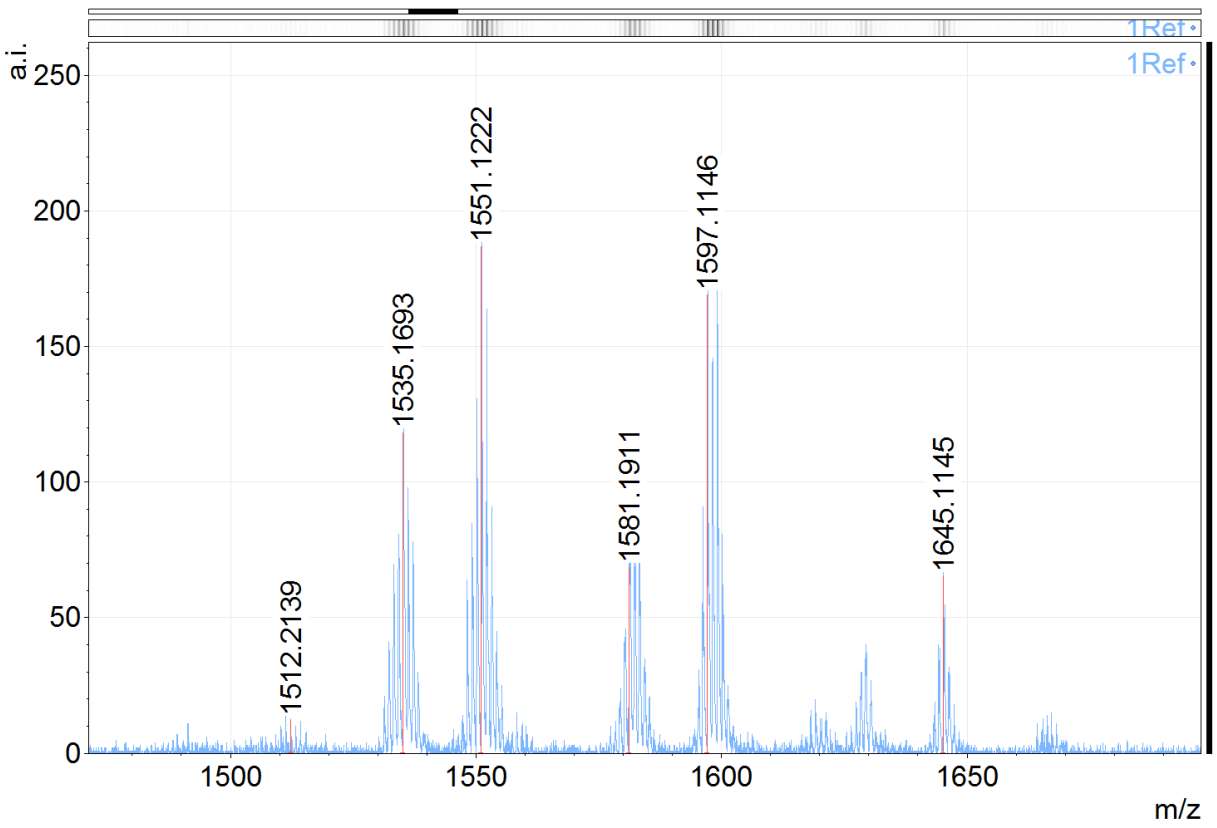

Figure S5. MALDI-TOF mass spectrum of $\{FeBd_2(BrGm)(BF)_2\}_2$

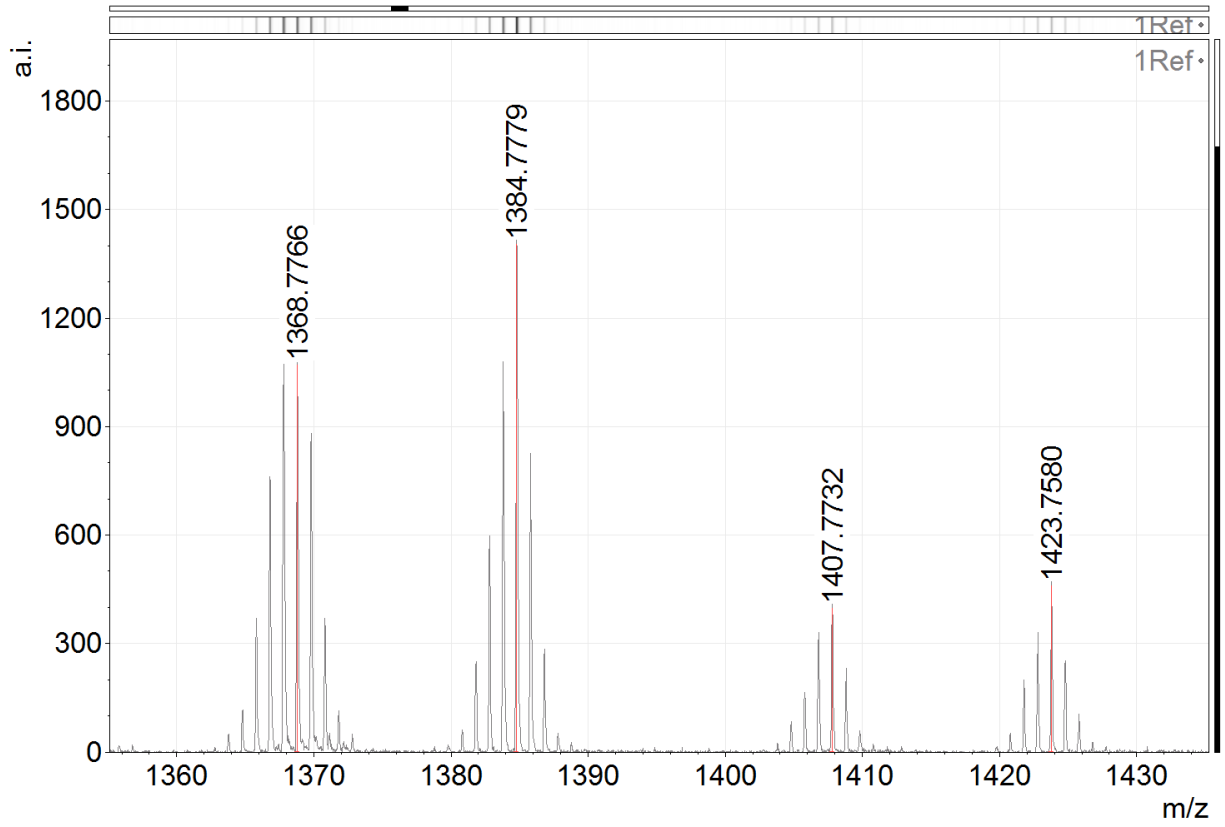

Figure S6. MALDI-TOF mass spectrum of $\{FeBd_2(NH_2Gm)(BF)_2\}_2$

Table S1. Crystallographic data and experimental details for the C–C conjugated iron(II) *bis*-clathrochelates and two polymorphs of their dibromomonoclathrochelate precursor

	$FeBd_2(Br_2Gm)(BF)_2 \cdot CH_2Cl_2$		$\{FeBd_2(HGm)(BF)_2\}_2 \cdot$	$\{FeBd_2(IGm)(BF)_2\}_2 \cdot$	$\{FeBd_2(BrGm)(BF)_2\}_2 \cdot$	$\{FeBd_2((CH_2)_5Gm)(BF)_2\}_2 \cdot$
	polymorph I (this work)	polymorph II [2]	$\cdot 3C_6H_6$	$\cdot 6C_6H_5Cl$	$\cdot 3\ C_6H_6$ [2]	$\cdot 5\ C_6H_6$ [2]
Empirical formula	$C_{31}H_{22}B_2Br_2Cl_2F_2FeN_6O_6$	$C_{31}H_{22}B_2Br_2F_2FeN_6O_6Cl_2$	$C_{78}H_{60}B_4F_4Fe_2N_{12}O_{12}$	$C_{96}H_{70}B_4Cl_6F_4Fe_2I_2N_{12}O_{12}$	$C_{78}H_{58}B_4Br_2F_4Fe_2N_{12}O_{12}$	$C_{100}H_{90}B_4F_4Fe_2N_{14}O_{12}$
Formula weight	920.74	920.74	1588.32	2281.08	1746.12	1910.80
Color, habit	Red, prism	Red, prism	Red, plate	Red-Violet, prism	Red, needle	Red, needle
Crystal size (mm)	0.50 × 0.35 × 0.30	0.32 × 0.15 × 0.13	0.24 × 0.19 × 0.06	0.48× 0.32 0.21	0.22 × 0.10 × 0.08	0.28 × 0.06 × 0.05
a (Å)	10.552 (2)	13.913 (2)	16.233 (3)	33.569 (4)	28.3891 (12)	12.040 (7)
b (Å)	22.452 (4)	17.521 (2)	14.490 (2)	17.048 (2)	28.3891 (12)	19.399 (12)
c (Å)	15.059 (3)	16.0443 (17)	33.279 (6)	23.737 (3)	18.8932 (17)	23.44 (2)
β (°)	93.750 (4)	96.463 (4)	100.199 (3)	128.290 (3)	90	96.646 (13)
V (Å^3)	3359.9 (11)	3886.1 (9)	7704 (2)	10662 (2)	15226.8 (16)	4891 (6)
Z	4	4	4	4	8	2
Crystal system	Monoclinic	monoclinic	Monoclinic	Monoclinic	tetragonal	triclinic
Space group	$P2_1/n$	$P2_1/n$	$C\ 2/c$	$C\ 2/c$	$I4_1/a$	$P\bar{1}$
D_{cal} (g cm^{-3})	1.718	1.574	1.369	1.421	1.523	1.299
μ (mm^{-1})	2.882	2.64	0.455	1.070	1.51	0.37
Reflections collected	37639	57472	35481	67324	82003	41467
Independent reflections (R_{int})	8976 (0.081)	9354 (0.030)	7560 (0.068)	10433 (0.032)	8696 (0.145)	17181 (0.141)
Obs.refl./restraints/ parameters	4914 / 0 / 469	7867 / 4 / 468	5552 / 0 / 426	8069 / 0 / 560	4872 / 0 / 454	4953 / 543 / 914
R,[a] % [$F^2 > 2\sigma(F^2)$]	0.048	0.067	0.089	0.080	0.048	0.119
R_w,[b] % (F^2)	0.106	0.195	0.223	0.228	0.103	0.289
GOF	1.00	1.00	1.01	0.99	1.00	1.02
Largest diff. peak and hole (e Å^{-3})	1.05 and -0.50	2.71 and – 1.64	0.90 and -0.74	2.48 and -1.70	1.05 and – 1.11	1.30 and – 1.25
F(000)	1824	1824	3264	4568	7072	1984

[a] $R = \Sigma \big|\, |F_o| - |F_c| \,\big| / \Sigma |F_o|$. [b] $R_w = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2))]^{1/2}$. [c] $\mathrm{GOF} = [\Sigma w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{1/2}$

Table S2. Intermolecular interactions in two polymorphs of the complex $FeBd_2(Br_2Gm)(BF)_2 \cdot CH_2Cl_2$

Type of A/Z interaction [a]	Polymorph I [b] (this work)	Polymorph II [b] [2]	$^{>1}\phi_{A/Z}$ [c]
Fe/B	2	2	0
F/O	12	12	0
O/H	4	4	0
O/C	15	17	2
O/O	6	6	0
O/N	6	6	0
O/Br	2	2	0
N/H	6	4	2
N/C	9	10	1
N/N	11	11	0
N/B	6	6	0
C/C	40	39	1
C/H	70	69	1
C/Br	2	2	0
H/H	20	19	1
Br/Br	1	1	0
Sum	212	210	8

[a] The interacting pairs are denoted as A/Z

[b] A number of their intramolecular interactions of such A/Z type

[c] $^{>1}\phi_{A/Z}$ is a module of the difference between the corresponding numbers for polymorphs 1 and II.

The full details of such procedure a comparison of the conformation polymorphs are described in [7].

Table S3. Maxima of the UV-vis spectra (λ_{max}/nm, $\varepsilon \cdot 10^{-3}$ mol^{-1}·L·cm^3) of the dihalogenomacrobicyclic precursors, the bis-clathrochelate derivatives and their monoclathrochelate analogs in the range 230–900 nm

Compound	λ_1	λ_2	λ_3	λ_4	λ_5	λ_6	λ_7	λ_8	λ_9	λ_{10}
$FeBd_2(Br_2Gm)(BF)_2$ [2]	264(28)	285(6.2)	299(10)	329(3.4)	386(3.5)	440(3.4)	470(30)			
$\{FeBd_2BrGm(BF)_2\}_2$ [2]	239(33)	263(21)	282(18)	301(12)	388(7.0)	435(9.8)	461(18)	509(25)		
$FeBd_2(I_2Gm)(BF)_2$ [5]	253(38)		281(23)	310(6.8)	345(3.8)	414(4.5)	447(9.8)	475(23)	503(9.4)	
$\{FeBd_2IGm(BF)_2\}_2$	262(44)		283(18)	298(19)	368(7.9)	428(9.7)	462(26)	495(23)	516(7.5)	
$FeBd_2(Cl_2Gm)(BF)_2$ [9]	264(14)		285(7.7)	311(3.6)	399(3.2)	448(3.5)	470(19)			
$FeBd_2(ClGmI)(BF)_2$ [17]	247(23)	271(11)	285(7.7)	303(6.5)	377(3.2)	436(4.5)	461(8.8)	479(18)		
$\{FeBd_2ClGm(BF)_2\}_2$	262(45)		283(20)	304(17)	390(8.7)	445(13)	465(26)	519(25)		
$FeBd_2Gm(BF)_2$ [S1]	265(1.6)	271(17)	282(1.2)	331(3.6)		460(6.0)	465(17)			
$\{FeBd_2HGm(BF)_2\}_2$	262(19)		279(27)	305(14)	346(6.0)	415(6.9)	465(26)	529(15)	567(24)	
$\{FeBd_2(((CH_2)_5N)Gm)(BF)_2\}_2$ [2]	253(41)	266(4.3)	288(31)	310(10)	399(7.0)	477(12)	489(21)	545(18)		
$FeBd_2((meta\text{-}HOOCC_6H_4S)_2Gm)(BF)_2$ [1]	246(27)	278(14)	299(6.1)		399(3.3)	455(6.4)	476(12)	509(10)		
$\{FeBd_2(meta\text{-}HOOCC_6H_4SGm)(BF)_2\}_2$ [1]	245(42)	270(28)	296(21)		358(6.8)	442(14)	465(17)	519(11)	526(16)	
$FeBd_2((para\text{-}HOOCC_6H_4S)_2Gm)(BF)_2$[1]	265(17)		288(7.6)	306(6.7)	403(2.9)	450(4.0)	475(7.8)	508(8.3)		
$\{FeBd_2(para\text{-}HOOCC_6H_4SGm)(BF)_2\}_2$ [2]	238(12)	269(35)	302(10)	362(4.7)		416(4.6)	458(15)	512(13)	530(5.8)	
$FeBd_2((NH_2)_2Gm)(BF)_2$ [1]	248(17)	266(7.9)	291(13)	338(3.1)	374(2.9)	425(5.3)	475(5.8)	511(12)	576(1.0)	
$\{FeBd_2(NH_2Gm)(BF)_2\}_2$ [2]	264(27)	285(10)	296(18)	323(9.0)	382(6.4)	442(8.7)	478(20)	508(14)	568(18)	598(5.8)
$\{FeBd_2(CH_3O(CH_2)_2NHGm)(BF)_2\}_2$ [2]	251(28)	276(34)	292(8.4)		357(9.1)	427(9.0)	474(140)	500(22)	555(12)	645(4.1)

Supplementary Information references

S1. O.A. Varzatskii, I.N. Denisenko, A.S. Belov, A.V. Vologzhanina, Y.N. Bubnov, S.V. Volkov, Y.Z. Voloshin, *Inorg. Chem. Commun*., 2014, **44**, 134.