Supporting Information

for

Induced chirality of the cage metal complexes switched by their supramolecular and covalent bindings

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Synthetic procedure [1] for the clathrochelate **1** (Scheme 2).

The complex $FeBd_2(ClGmH)(BF)_2$ (0.20 g, 0.28 mmol) and *para*-mercaptobenzoic acid (0.056 g, 0.37 mmol) were dissolved/suspended in dichloromethane (4 ml), and a solution of triethylamine (0.17 ml, 1.21 mmol) in dichloromethane (2 ml) was added dropwise to the stirring reaction mixture under argon. The reaction mixture was stirred for 24 h, then washed with 6% aqueous acetic acid (40 ml) and water (100 ml, in two portions), and dried with $CaCl_2$. The dichloromethane solution was flash chromatographed through a silica gel Silasorb SPH-300 {30-mm layer, eluents: dichloromethane (first), methanol (second)}. The methanol eluate was evaporated to dryness. The solid residue was dissolved in dichloromethane (2 ml) and precipitated with hexane. The precipitate was filtered off, washed with hexane and dried in vacuo.

$FeBd_2((para\text{-}HOOCC_6H_4S)GmH)(BF)_2$ Yield: 0.130 g (56%). Anal. Calc. for $C_{37}H_{26}N_6O_8B_2F_2FeS$: C, 53.53; H, 3.14; N, 10.13. Found: C, 53.69; H, 3.28; N, 9.87%. ^1H NMR (CD_2Cl_2) δ, ppm: 7.20–7.30 (m, 21H, Ph + HC=N), 7.72 (br. s, 2H, Ar), 8.10 (br. s, 2H, Ar). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ, ppm: 130.0 (s, *m*-Ph), 130.9 (s, *ipso*-Ph), 132.2 (s, *p*-Ph), 132.4, 132.5 (s, *o*-Ph), 133.6, 136.7 (two s, *o*-Ar + *m*-Ar), 144.9 (s, HC=N), 149.7 (s, SC=N), 158.4, 158.7 (two s, PhC=N) . IR (KBr) ν/cm^{-1}: 930, 1001, 1015, 1062, 1109, 1130 ν(N–O), 1215 m ν(B–O) + ν(B–F), 1547, 1595m ν(C=N), 1716 ν(C=O). MS (MALDI–TOF) m/z (I, %): (negative range) –830 $[M]^-$; (positive range) 830 [M]+ (100), 853 $[M+Na^+]^+$ (20), 869 $[M+K^+]^+$ (35). UV–Vis (CH_3OH) λ_{max}, nm (ε × 10^{-3}, $Lmol^{-1}cm^{-1}$): 247(31), 265(8.1), 282(15), 300(11), 332(4.1), 387(3.0), 442(6.3), 476(21), 483(5.9).

Synthetic procedure [1] for the clathrochelate **2**. (Scheme 2).

This clathrochelate was synthesized like the previous one except that *meta*-mercaptobenzoic acid was used instead of *para*-mercaptobenzoic acid.

$FeBd_2((meta\text{-}HOOCC_6H_4S)GmH)(BF)_2$ Yield: 0.110 g (47%). Anal. Calc. for $C_{37}H_{26}N_6O_8B_2F_2FeS$: C, 53.53; H, 3.14; N, 10.13. Found: C, 53.40; H, 3.21; N, 10.04%. ^1H NMR (CD_2Cl_2) δ, ppm: 7.15–7.31 (m, 21H, Ph + HC=N), 7.53 (br. s, 1H, Ar-5), 7.83, 8.13 (two br. s, 1H, Ar-4 + Ar-6), 8.31 (br. s, 1H, Ar-2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ, ppm: 130.0 (s, m-Ph), 131.00, 131.03 (two s, *ipso*-Ph), 132.19, 132.21 (two s, p-Ph), 132.5, 132.6 (two s, *o*-Ph), 129.9, 131.3, 131.5, 131.9, 132.0, 134.5 (all s, Ar), 144.8 (s, HC=N), 150.8 (s, SC=N), 158.3, 158.7 (two s,

PhC=N). IR (KBr) ν/cm^{-1}: 930, 1001, 1031, 1062, 1110, 1131 ν(N–O), 1214m ν(B–O) + ν(B–F), 1538, 1575m ν(C=N), 1695 ν(C=O). MS (MALDI-TOF) m/z (I, %): (negative range) –830 [M]$^-$; (positive range) 830 [M]$^+$ (100), 853 [M+Na$^+$]$^+$ (30), 869 [M+K$^+$]$^+$ (35). UV–Vis (CH_3OH) λ_{max}, nm (ε × 10^{-3}, Lmol^{-1}cm^{-1}): 252(24), 285(18), 317(3.9), 347(1.4), 389(3.2), 428(2.5), 450(7.5), 477(18), 492(6.7).

Synthetic procedure [1] for the clathrochelate **3** (Scheme 2).

This clathrochelate was synthesized like the previous one except that *ortho*-mercaptobenzoic acid was used instead of metamercaptobenzoic acid

$FeBd_2$((*ortho*-$HOOCC_6H_4S$)GmH)$(BF)_2$ Yield: 0.085 g (37%). Anal. Calc. for $C_{37}H_{26}N_6O_8B_2F_2FeS$: C, 53.53; H, 3.14; N, 10.13. Found: C, 53.47; H, 3.11; N, 9.99%. ^{1}H NMR ($(CD_3)_2CO$) δ, ppm: 7.34–7.44 (m, 20H, Ph), 7.53 (d, 1H, Ar, *J* = 12 Hz), 7.59 (m, 1H, Ar), 7.68 (m, 1H, Ar), 7.95 (d, 1H, HC=N), 8.12 (d, 1H, Ar, *J* = 12 Hz). ^{13}C{^{1}H} NMR ($(CD_3)_2CO$) δ, ppm: 127.92, 127.96 (two s, *m*-Ph), 128.9 (s, Ar), 129.45, 129.48 (two s, *ipso*-Ph), 130.0 (br. s, *p*-Ph), 130.7 (br. s, *o*-Ph), 131.3, 131.6, 132.1, 132.9, 133.0 (all s, Ar), 145.7 (s, HC=N), 147.9 (s, SC=N), 156.5, 156.7 (two s, PhC=N), 166.7 (s, COOH). IR (KBr) ν/cm^{-1}: 930, 1001, 1061, 1111, 1129 ν(N–O), 1213m ν(B–O) + ν(B–F), 1533, 1581m ν(C=N), 1698 ν(C=O). MS (MALDI–TOF) m/z (I, %): (negative range) –830 [M]$^-$; (positive range) 830 [M]$^+$ (40), 853 [M+Na$^+$]$^+$ (100), 869 [M+K$^+$]$^+$ (30). UV–Vis (CH_3OH) λ_{max}, nm (ε × 10^{-3}, Lmol^{-1}cm^{-1}): 243(24), 277(20), 313(1.2), 331(3.3), 389(3.7), 436(4.8), 469(18), 495(7.3).

Synthetic procedure for the clathrochelate **4**. (Scheme 3).

The complex $FeBd_2(Cl_2Gm)(BF)_2$ (0.20 g, 0.27 mmol) and *para*-mercaptobenzoic acid (0.09 g, 0.59 mmol) were dissolved/suspended in dichloromethane (4 ml), and a solution of triethylamine (0.17 ml, 1.21 mmol) in dichloromethane (2 ml) was added dropwise to the stirring reaction mixture under argon. The reaction mixture was stirred for 24 h, then washed with 6% aqueous acetic acid (40 ml) and water (100 ml, in two portions), and dried with $CaCl_2$. The dichloromethane solution was flash chromatographed through a silica gel Silasorb SPH-300 {30-mm layer, eluents: dichloromethane (first), methanol (second)}. The methanol eluate was evaporated to dryness. The solid residue was dissolved in dichloromethane (2 ml) and precipitated with hexane. The precipitate was filtered off, washed with hexane and dried in vacuo.

$FeBd_2((para\text{-}HOOCC_6H_4S)_2Gm)(BF)_2$ Yield: 0.136 g (51%). Anal. Calc. for $C_{44}H_{30}N_6O_{10}B_2F_2FeS_2$: C, 53.79; H, 3.06; N, 8.56. Found: C, 53.25; H, 3.17; N, 8.40%. ^{1}H NMR (DMSO-d_6): δ, ppm: 6.73–6.84 (m, 22H, Ar + Ph), 7.08 (m, 2H, Ar), 7.34–7.48 (m, Ar). $^{13}C\{^1H\}$ NMR (DMSO-d_6) δ, ppm: 126.6 (s, Ar), 128.5 (s, *m*-Ph), 128.9 (s, Ar), 129.2 (s, *ipso*-Ph), 130.8 (s, *p*-Ph), 130.9 (s, Ar), 131.0 (s, *o*-Ph), 137.4 (s, Ar), 146.6 (s, SC=N), 158.0 (s, PhC=N), 167.01 (s, COOH). MS (MALDI–TOF) m/z (I, %): (negative range) –982 $[M]^-$; (positive range) 982 $[M]^+$ (45), 1005 $[M+Na^+]^+$ (100), 1021 $[M+K^+]^+$ (40).

Synthetic procedure [1] for the clathrochelate **5** (Scheme 3).

This clathrochelate was synthesized like the previous one except that *meta*-mercaptobenzoic acid was used instead of *para*-mercaptobenzoic acid.

$FeBd_2((meta\text{-}HOOCC_6H_4S)_2Gm)(BF)_2$ Yield: 0.088 g (33%). Anal. Calc. for $C_{44}H_{30}N_6O_{10}B_2F_2FeS_2$: C, 53.79; H, 3.06; N, 8.56. Found: C, 53.64; H, 3.09; N, 8.51%. ^{1}H NMR ($(CD_3)_2CO$) δ, ppm: 7.34–7.49 (m, 22H, Ar-5 + Ph), 7.59 (d, 2H, Ar-4, J = 8 Hz), 7.75 (s, 2H, Ar-2), 7.90 (d, 2H, Ar-6, J = 8 Hz). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$) δ, ppm: 127.9 (s, m-Ph), 129.0 (s, Ar-6), 129.3 (s, Ar-5), 129.6 (s, *ipso*-Ph), 130.2 (s, *p*-Ph), 130.3 (s, Ar-3), 130.7 (s, *o*-Ph), 132.0 (s, Ar-2), 132.5 (s, Ar-1), 134.0 (s, Ar-4), 147.1 (s, SC=N), 157.9 (s, PhC=N), 165.9 (s, COOH). IR (KBr) m/cm^{-1}: 930, 1001, 1066, 1107, 1155 m(N–O), 1219m ν(B–O) + ν(B–F), 1597m ν(C=N), 1699 ν(C=O). MS (MALDI–TOF) m/z (I, %): (negative range) –981 $[M–H^+]^-$; (positive range) 982 $[M]^+$ (100), 1005 $[M+Na^+]^+$ (50), 1021 $[M+K^+]^+$ (40). UV–Vis (CH_3OH) λ_{max}, nm (ε × 10^{-3}, Lmol^{-1}cm^{-1}): 243(27), 278(14), 299(6.1), 399(3.3), 455(6.4), 476(12), 509(10).

Synthetic procedure [1] for the clathrochelate **6** (Scheme 3).

The complex $FeBd_2(Cl_2Gm)(BF)_2$ (0.20 g, 0.27 mmol) and *ortho*-mercaptobenzoic acid (0.09 g, 0.59 mmol) were dissolved/suspended in dichloromethane (4 ml), and a solution of triethylamine (0.17 ml, 1.21 mmol) in dichloromethane (2 ml) was added dropwise to the stirring reaction mixture under argon. The reaction mixture was stirred for 24 h and the precipitate that formed was filtered off, dissolved in acetone, precipitated with hexane and dried in vacuo. An additional portion of the target clathrochelate was obtained from the filtrate. The filtrate was washed with 6% aqueous acetic acid (40 ml) and water (100 ml, in two portions), and dried with CaCl2. The dichloromethane solution obtained was treated like the previous one.

$FeBd_2((ortho\text{-}HOOCC_6H_4S)_2Gm)(BF)_2$ Total yield: 0.188 g (71%). Anal. Calc. for $C_{44}H_{30}N_6O_{10}B_2F_2FeS_2$: C, 53.79; H, 3.06; N, 8.56. Found: C, 53.66; H, 3.11; N, 8.51%. ^{1}H NMR ($(CD_3)_2CO$) δ, ppm: 7.00 (d, 2H, Ar, J = 6 Hz), 7.32–7.52 (m, 24H, Ar + Ph), 8.05 (d, 2H, Ar, J = 6 Hz). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$) δ, ppm: 126.3 (s, Ar), 128.0 (s, *m*-Ph), 128.2 (s, Ar), 129.4 (s, *ipso*-Ph), 130.2 (s, *p*-Ph), 130.7 (s, *o*-Ph), 131.6, 132.9, 133.0, 136.3 (all s, Ar), 149.0 (s, SC=N), 157.4 (s, PhC=N), 166.7 (s, COOH). IR (KBr) ν/cm^{-1}: 929, 1063, 1106, 1152 ν(N–O), 1214m ν(B–O) + ν(B–F), 1587m ν(C=N), 1699 ν(C=O). MS (MALDI-TOF) m/z (I, %): (negative range) –982 $[M]^-$; (positive range) 982 $[M]^+$ (100), 1005 $[M+Na^+]^+$ (35), 1021 $[M+K^+]^+$ (40). UV–Vis (CH_3OH) λ_{max}, nm (ε × 10^{-3}, Lmol^{-1}cm^{-1}) 246(31), 291(15), 366(4.2), 429(3.9), 458(8.8), 483(11), 506(11).

Synthetic procedure for the clathrochelate **7** (Scheme 3).

Complex $FeBd_2(Cl_2Gm)(BF)_2$ (1.2g, 1.6mmol) and mercaptopropionic acid (0.34g, 3.60mmol) were dissolved in dry dichloromethane (200mL). The reaction mixture was cooled to 0°C and a solution of triethylamine (1mL, 7.20mmol) in dichloromethane (40mL) was added dropwise to the stirring reaction mixture. This mixture was stirred for 5 h at r.t.; the reaction course was controlled by TLC (eluent: dichloromethane). Then the reaction mixture was washed with 0.1% aqueous hydrochloric acid (500 mL) and water (500 mL). The dichloromethane extract was evaporated to dryness and the solid residue was separated by column chromatography on silica gel (eluent: dichloromethane – *iso*-propylamine 99:1). The major elute was collected and evaporated to dryness. The solid residue was extracted with dichloromethane and the extract was precipitated with hexane. The precipitate was filtered off, washed with hexane and dried *in vacuo*.

$FeBd_2((HOOC(CH_2)_2S)_2Gm)(BF)_2$ Yield: 1.1 g (77%). ^{1}H NMR (DMSO), δ, ppm: 2.54 – 2.65 (br s, 2H, OH), 3.35 (d, 4H, CH_2), 7.31 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR (DMSO) δ, ppm: 45.64 (s, CH_2), 54.9 (s, CH_2), 127.97(s, *meta*-Ph), 128.93(s, *ipso*-Ph), 130.11(s, *para*-Ph), 130.43(s, *ortho*-Ph), 149.55 (s, SC=N), 156.95(s, PhC=N). UV–Vis (THF) λ_{max}, nm (ε × 10^{-3}, Lmol^{-1}cm^{-1}) 247(46), 287(1.7), 297(3), 311(2.5), 405(6.2), 486(31).

Synthetic procedures for the clathrochelate **8** (Scheme 4) with terminal methoxyl groups.

1. New synthetic protocol for its preparation

Complex **5** (0.5g, 0.49mmol) was dissolved in dry DMF (5ml) under argon and N-ethyldiisopropylamine (0.4mL, 4.17 mmol) was added to the stirring solution. The reaction mixture was stirred for 10 min at room temperature and then methyl iodide (0.4mL, 1.24mmol) was added.

The reaction mixture was stirred for 3 h and precipitated with 3% acetic acid (40 ml). The precipitate was filtered off, washed with water, and extracted with dichloromethane. The extract was precipitated with hexane, the precipitate was filtered off, washed with hexane and dried *in vacuo*. Yield: 0.43 g (85%).

2. The synthetic protocol [2] for its preparation

Complex $FeBd_2(Cl_2Gm)(BF)_2$ (0.3 g, 0.4 mmol) was dissolved/suspended in dichloromethane (10 ml) at 0°C, and methyl ester of *meta*-mercaptobenzoic acid (0.016 g, 0.9 mmol) and triethylamine (0.15 ml, 1.2 mmol) were added under argon. The reaction mixture was stirred for 12 h at r.t., then washed with a diluted aqueous hydrochloric acid and dried with Na_2SO_4. This dichloromethane solution was flash-chromatographically separated on silica gel (50-mm layer, eluent: dichloromethane – hexane 1:2 mixture). The major elute was evaporated to a small volume (approximately 5 ml) and precipitated with hexane (20 ml). The precipitate was filtered off, washed with hexane and dried *in vacuo*. Yield: 0.32g (80%).

$FeBd_2((meta\text{-}CH_3OOCC_6H_4S)_2Gm)(BF)_2$. Calc. for $C_{46}H_{34}N_6B_2F_2FeO_{10}S_2$: C, 54.68; H, 3.39; N, 8.32. Found (%): C, 54.63; H, 3.53; N, 8.17. MS (MALDI-TOF): *m/z*: 1010 $[M]^{+\bullet}$. ^{1}H NMR ($CDCl_3$, δ, ppm): 3.86 (s, 6H, OCH_3), 7.32 (m, 24H, Ph+Ar), 7.51 (m, 2H, Ar), 7.84 (m, 2H, Ar), 7.91 (m, 2H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 52.42 (s, OCH_3), 128.04, 129.07, 129.43, 129.45, 130.39, 130.96, 131.41, 132.00, 132.06, 135.49 (all s, Ph+Ar), 147.43 (s, SC=N), 157.50 (s, PhC=N), 166.01 (s, COOMe). UV-vis (CH_2Cl_2), λ_{max}, nm($\varepsilon \cdot 10^{-3}$, $Lmol^{-1}cm^{-1}$) 242(38), 264(2.2), 284(3.1), 289(18), 351(4.5), 401(2.3), 482(26), 511(1.2).

Synthetic procedure for the clathrochelate **9** (Scheme 4) with terminal amide groups.

Complex **4** (1g, 1 mmol) was dissolved in dry DMSO (5 ml) under argon and CDI (0.486 g, 3 mmol) was added to the stirring solution. The reaction mixture was stirred at 40°C until the finishing of evolution of the gaseous products. Then the reaction mixture was cooled to 20°C and 700mL (10.5mmol) of dry gaseous ammonia was bulbed through the mixture in 20 min. The reaction mixture was stirred at room temperature for 1 h and precipitated with 2% aqueous hydrochloric acid (25 ml). The precipitate was filtered off, washed with water and extracted with dichloromethane. The extract was precipitated with hexane thus giving the crude product with a purity of approximately 90%. This product was flash-chromatographically separated on silica gel (eluent: dichloromethane – *iso*-propanol 97:3). Three major elutes were collected and the second of them was evaporated to dryness. The solid residue was extracted with dichloromethane and the

extract was precipitated with hexane. The precipitate was filtered off, washed with hexane and dried *in vacuo*.

$FeBd_2$((*meta*-$H_2NOCC_6H_4S)_2$Gm)$(BF)_2$ Yield: 0.64 g (64%). ^{1}H NMR (DMSO, δ, ppm): 7.34 (m, 24H, Ph+NH_2), 7.53 (s, 2H, Ar), 7.64 (s, 2H, Ar), 8.04 (s, 2H, Ar). $^{13}C\{^1H\}$ NMR (DMSO) δ, ppm: 127.09 (s, *meta*-Ph), 128.49 (s, Ar), 129.24(s, Ar), 129.86 (s, *ipso*-Ph), 130.31 (s, *para*-Ph), 130.75(s, Ar), 130.99 (s, *ortho*-Ph), 132.08 (s, Ar), 132.19 (s, Ar), 135.83 (s, Ar), 147.59 (s, SC=N), 158.06 (s, PhC=N), 167.01 (s, $CONH_2$). UV–Vis (THF) λ_{max}, nm (ε × 10^{-3}, $Lmol^{-1}cm^{-1}$) 232(50), 292(8.6), 311(4.3), 347(4.9), 484(24), 514(1.3).

General synthetic procedure for the clathrochelates **10 – 12** (Scheme 4) with terminal optically active amide groups.

The corresponding dicarboxyl-terminated clathrochelate precursor (**4**, **5** or **6**, 1 mmol) was dissolved in dry DMSO (5 ml) under argon and CDI (0.486 g, 3 mmol) was added to the stirring solution. The reaction mixture was stirred at 40°C until the finishing of evolution of the gaseous products. Then the reaction mixture was cooled to 20°C and R(+)1-phenylethylamine (0.36 g, 3 mmol) was added. The reaction mixture was stirred at room temperature for 1 h and precipitated with 2% aqueous hydrochloric acid (25 ml). The precipitate was filtered off, washed with water and extracted with dichloromethane. The extract was precipitated with hexane thus giving the crude product with a purity of approximately 90%. This product was flash-chromatographically separated on silica gel (eluent: dichloromethane – isopropanole 99:1). Three elutes were collected and the second of them was evaporated to dryness. The solid residue was extracted with dichloromethane and the extract was precipitated with hexane. The precipitate was filtered off, washed with hexane and dried *in vacuo*.

$FeBd_2$((*para*-R(+)$PhCH(CH_3)NHOCC_6H_4S)_2$Gm)$(BF)_2$

4-((1-phenylethyl)carbamoyl)phenyl-functionalized iron(II) clathrochelate **10**.

Yield: 0.6 g (48%). ^{1}H NMR (CD_3CN, δ, ppm): 1.55 (d, 6H, CH_3), 5.20 (q, 2H, CH), 7.30 (d, 4H, Ar), 7.39 (m, 32H, Ph+NH), 7.75 (d, 2H, Ar). $^{13}C\{^1H\}$ NMR (CD_3CN) δ, ppm: 21.57 (s, CH_3), 49.49 (s, CH), 126.11, 126.91, 128.18, 128.19, 128.25 (s, all Ar), 128.46 (s, *meta*-Ph), 129.29 (s, *ipso*-Ph), 129.4 (s, *ipso*-Ph), 130.31 (s, *para*-Ph), 130.40 (s, *ortho*-Ph), 134.21, 135.06, 144.65 (all s, Ar), 146.8 (s, SC=N), 157.56(s, PhC=N), 165.37 (s, CONH). MS (MALDI-TOF) m/z (I, %): (positive range) 1188 [M]$^{+\bullet}$ (100), 1211 [M+Na^+]$^+$ (90), 1227 [M+K^+]$^+$ (40).UV–Vis (CH_2Cl_2)

λ_{max}, nm ($\varepsilon \times 10^{-3}$, $Lmol^{-1}cm^{-1}$) 244(49), 264(6.2), 284(2.0), 290(2.6), 365(3.8), 403(2.1), 481(27), 511(1.3).

$FeBd_2$((*meta*-R(+)$PhCH(CH_3)NHOCC_6H_4S)_2Gm)(BF)_2$

3-((1-phenylethyl)carbamoyl)phenyl-functionalized iron(II) clathrochelate **11**.

Yield: 0.6 g (48%). ^1H NMR (CD_3CN, δ, ppm): 1.51 (d, 6H, CH_3), 5.20 (q, 2H, CH), 7.30 (t, 2H, Ar), 7.39 (m, 32H, Ph), 7.49 (d, 2H, Ar), 7.61 (br s, 2H, NH), 7.69 (d, 2H, Ar). $^{13}C\{^1H\}$ NMR (CD_3CN) δ, ppm: 21.60 (s, CH_3), 49.57 (s, CH), 126.07, 126.62, 126.92, 128.10 (all s, Ar), 128.46 (s, *meta*-Ph), 128.96, 129.32 (all s, Ar), 129.43 (s, *ipso*-Ph), 130.35 (s, Ar), 130.39(s, *para*-Ph), 131.99 (s, *ortho*-Ph), 132.84, 135.97, 144.55 (all s, Ar), 147.5 (s, SC=N), 157.79(s, PhC=N), 165.11 (s, CONH). MS (MALDI-TOF) m/z (I, %): (positive range) 1188 $[M]^{+\bullet}$ (100), 1211 $[M+Na^+]^+$ (60), 1227 $[M+K^+]^+$ (75). UV–Vis (CH_2Cl_2) λ_{max}, nm ($\varepsilon \times 10^{-3}$, $Lmol^{-1}cm^{-1}$) 264(1.7), 285(3.5), 298(1.8), 385(4.0), 482(30), 511(0.7).

$FeBd_2$((*ortho*-R(+)$PhCH(CH_3)NHOCC_6H_4S)_2Gm)(BF)_2$

2-((1-phenylethyl)carbamoyl)phenyl-functionalized iron(II) clathrochelate **12**.

Yield: 0.55g (43%). ^1H NMR (CD_3CN, δ, ppm): 1.42 (d, 6H, CH_3), 5.12 (m, 2H, CH), 7.30 (d, 4H, Ar), 7.39 (m, 32H, Ph+NH), 7.75 (d, 2H, Ar). $^{13}C\{^1H\}$ NMR (CD_3CN) δ, ppm: 21.77 (s, CH_3), 49.54 (s, CH), 126.03, 126.85, 127.42, 128.01, 128.14 (all s, Ar), 128.42 (s, *meta*-Ph), 129.38, 130.32 (s, Ar), 130.35 (s, *para*-Ph), 130.92 (s, *ortho*-Ph), 131.27, 136.70, 144.31 (all s, Ar), 149.25 (s, SC=N), 157.30, 157.43 (both s, PhC=N), 166.99 (s, CONH). MS (MALDI-TOF) m/z (I, %): (positive range) 1188 $[M]^{+\bullet}$ (100), 1211 $[M+Na^+]^+$ (50), 1227 $[M+K^+]^+$ (30). UV–Vis (CH_2Cl_2) λ_{max}, nm ($\varepsilon \times 10^{-3}$, $Lmol^{-1}cm^{-1}$): 263(3.7), 286(3.8), 299(2.5), 369(3.8), 407(2.2), 483(33), 509(1.4).

To 2.5. Computer simulation.

The initial conformations of the clathrochelates **10–12** were obtained by the orientation of their ribbed substituents in such a manner that they can form the intramolecular interactions under study, followed by optimization of their geometry using the semi-empiric method PM7 [3] from MOPAC program [4], and by final optimization using *ab initio* PBE functional with def2-SVP basis set on all atoms except Fe (def2-TZVP basis set), and the atom-pairwise dispersion correction with the Becke–Johnson damping scheme [5–12]. All calculations were performed with a cage framework, obtained from the direct single crystal X-ray experiment for the iron(II) clathrochelate **8**. We performed an optimization of all the constitutional isomers **10** – **12** of the corresponding amide-terminated cage complex. For the optimized structures, an inversion of all these molecules, followed by inversion of a chiral centre of a low-molecular chiral inductor *via* a changing of the positions of its methyl group and the corresponding hydrogen atom, and, then, a further optimization of the obtained molecular structures, were performed.

The optimized structures of the clathrochelates **13** and **14** were evaluated basing on the corresponding single crystal X-ray diffraction data with PBE0 functional and def2-TZVP basis set. All *ab initio* calculations were carried out using ORCA program package [13].

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Table S1. Comparison of the experimental X-ray diffraction data and the calculated ones for the clathrochelate **13**.

Parameter	Calculated using PBE0 D3 def2-TZVP	Experimental value
Fe–N distance (Å)	1.91	1.92
Chelate angle N–Fe–N (°)	79	78
Distortion angle φ (°)	24	13
Dihedral angle ψ (°)	7.25	5.05

Table S2. Comparison of the experimental X-ray diffraction data and the calculated ones for the clathrochelate **14**.

Parameter	Calculated using PBE0 D3 def2-TZVP	Experimental value
Fe–N distance (Å)	1.92	1.91
Chelate angle N–Fe–N (°)	79	79
Distortion angle φ (°)	26	29
Dihedral angle ψ (°)	9.4	13.8
Twist angle ω (°)	37–38	43–55

Table S3. Main intramolecular interactions in the clathrochelate molecules **10** – **12** and their calculated energies (kcal·mol^{-1}).

Compound	Type of interaction	Conformation	E_{Δ}	E_{Λ}	ΔE
10	intraribbed	10A(1)1	0	0.25	–0.25
	interribbed	10B,C(1,3)1	–6.1	–5.3	–0.79
11	intraribbed	11A(1,3)1	–0.54	0.31	–0.85
	intraribbed	11C(1)1	–20	–12	–8.5
	dispertion	11C(2)1	–3.7	–5.4	1.7
12	hydrogen bond	12B(3)1	–0.62	–14	13
	intraribbed		–7.9		