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Unexpected cyclization of the monoribbed-functionalized iron(II) clathrochelate into the macrobicyclic complex with six-membered *N*,*S*-fusing moiety

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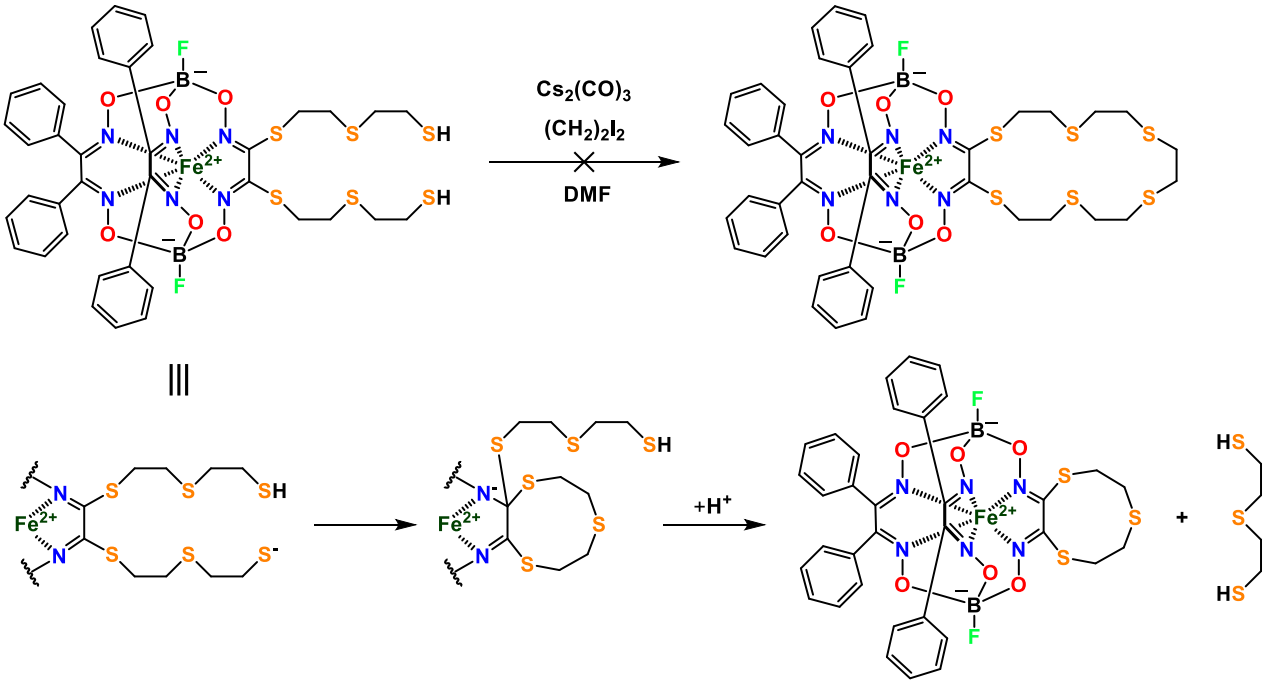
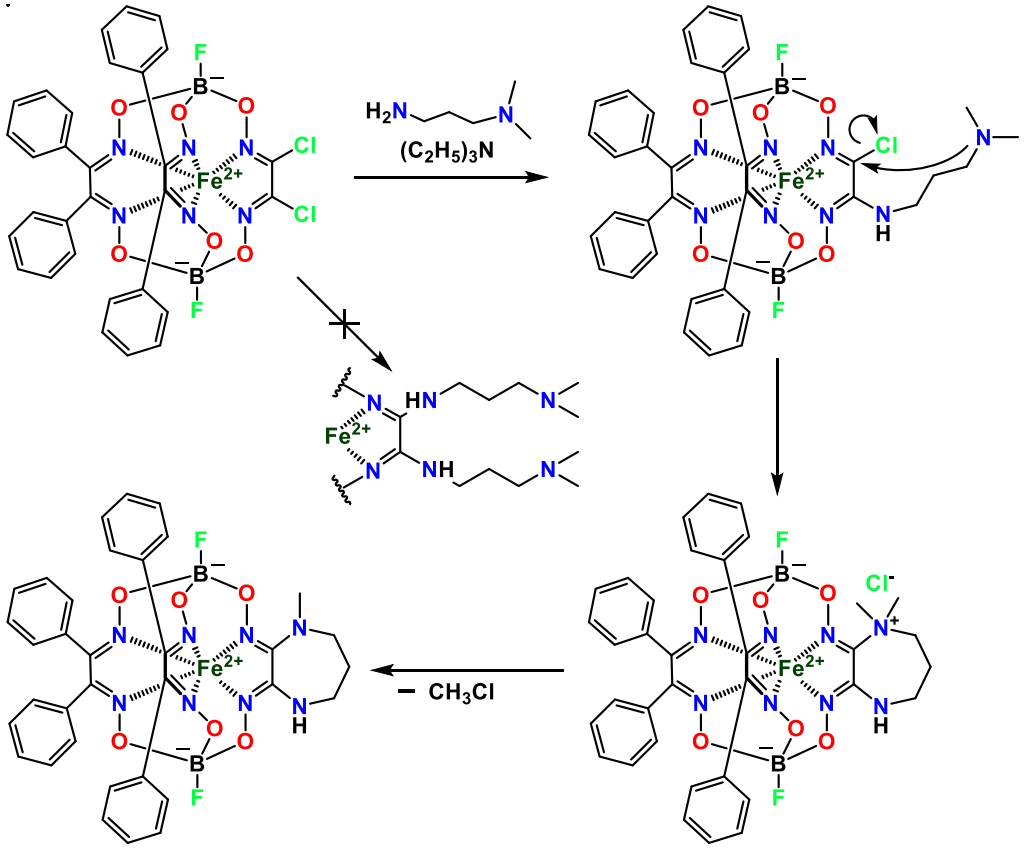
Experimental

The reagents used, $FeCl_2 \cdot 4H_2O$, *α*-benzil dioxime, $BF_3 \cdot O(C_2H_5)_2$, *o*-aminothiophenol, sorbents, organic bases and solvents were obtained commercially (SAF®). Dichloroglyoxime was obtained by known procedure [S1]. Bis-α-(benzil dioximate) dichloroclathrochelate precursor $FeBd_2(Cl_2Gm)(BF)_2$ (**2**) was prepared as described elsewhere [S2]. Synthesis of compounds **6a,b** and **7a,b** has been reported recently [S3].
Thin layer chromatography (TLC) was performed using a Silica Gel 60 F254 foil (Merck).
Analytical data (C, H, N contents) were obtained with a Carlo Erba 1106 microanalyzer.
MALDI-TOF mass spectrum of the obtained new iron(II) cage complex was recorded without matrix using a MALDI-TOF-MS Bruker Autoflex II (Bruker Daltonics) mass spectrometer in reflecto-mol mode. The ionization was induced by a UV-laser with a wavelength of 337 nm. Its sample was applied to a steel plate. The accuracy of measurements was 0.1%.
^1H and $^{13}C\{^1H\}$NMR spectra were recorded from its solutions in CD_2Cl_2 and $CDCl_3$ with a q-ONE AS400 Quantum I Plus spectrometer. The measurements were performed using the residual signals of these deuterated solvents.
Solution UV-vis spectrum in dichloromethane was recorded in the range 230 – 800 nm with a Varian Cary 60 spectrophotometer. Its individual Gaussian components were calculated using the Fityk program [S4].

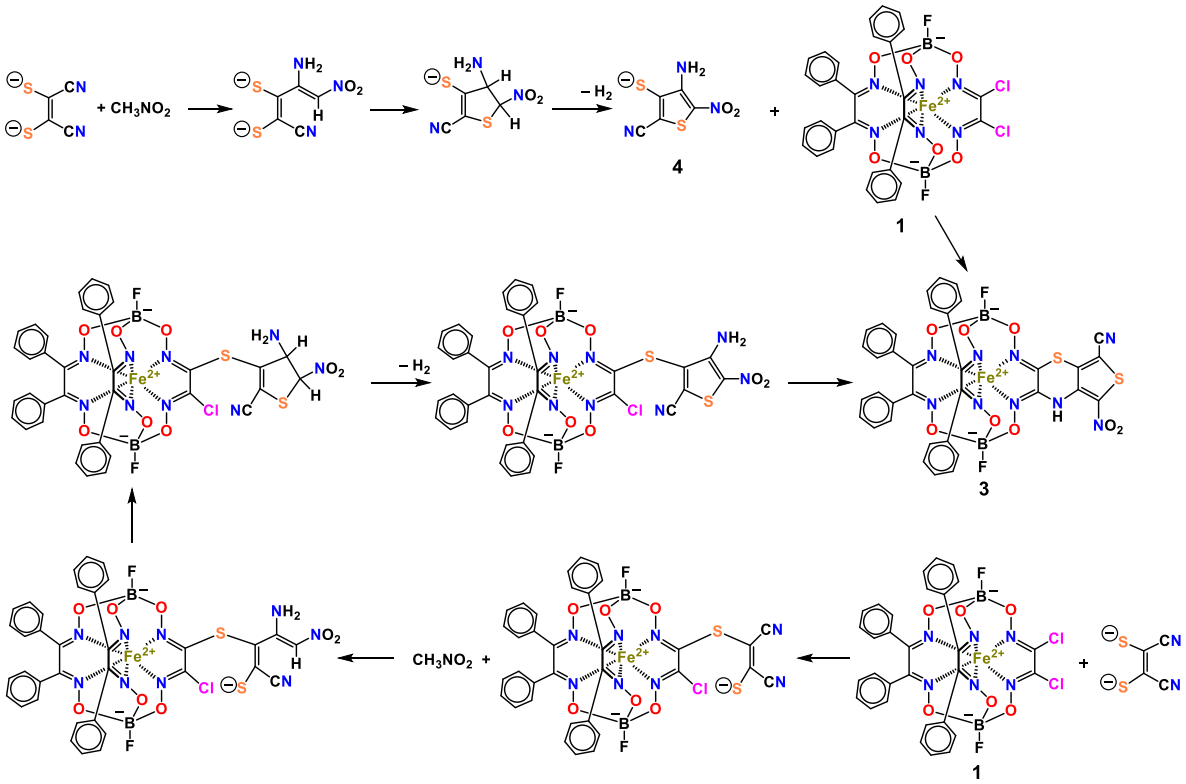
Synthesis of clathrochelate $FeBd_2((S\text{-}C_6H_4\text{-}NH)Gm)(BF)_2$ (**8**): Complex $FeBd_2(Cl_2Gm)(BF)_2$ (**2**) (0.05 g, 0.06 mmol), triethylamine (0.018 ml, 0.12 mmol) and *o*-aminothiophenol (0.008 g, 0.06 mmol) were dissolved in dichloromethane (2 ml) under intensive stirring. The reaction mixture was stirred for 2 h and then separated by column chromatography on silica gel (eluent: dichloromethane). The first eluate (R_f = 0.87) containing mainly the precursor **2**, was discarded; the second bright-red major eluate (R_f = 0.61) was collected and evaporated to dryness. The solid residue was washed with hexane and dried *in vacuo*. Yield: 0.037 g (78 %). Anal. Calc. for $C_{36}H_{25}B_2F_2FeN_7O_6S$ (%): C, 54.11, H, 3.15, N, 12.27. Found (%): C, 54.16, H, 3.09, N, 12.35. ^1H NMR ($CDCl_3$, δ, ppm): 7.63 (t, 1H, α-CH(Ph)), 7.39-7.29 (m, 20H, Ph(Bd)), 7.22 (t, 1H, α`-CH(Ph)), 6.75 (m, 2H, β-CH(Ph) + β`-CH(Ph)), 4.54 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ, ppm): 113.69 (α-CH(Ph)), 117.32(α`-CH(Ph)), 124.28 (β-CH(Ph)), 127.64 (β`-CH(Ph)), 128.56, 129.02, 129.39(S–C), 129.49(NH–C), 129.94, 130.52, 131.04, 131.14 (Ar), 132.53 (1-Ph), 132.60 (1-Ph`), 137.94(NHC=N), 139.63 (SC=N), 156.83, 157.3 (PhC=N). MS (MALDI-TOF) *m/z*: 799 $[M]^{+\bullet}$. Deconvoluted UV-vis (CH_2Cl_2): ν, cm^{-1} ($\varepsilon \cdot 10^{-3}$, $dm^3\ mol^{-1} \cdot cm^{-1}$): 44470 (29), 40510 (23), 37760 (16), 35112 (11), 32410 (9.7), 28060 (3.7), 24660 (1.4), 22000 (9.9), 20270 (17), 17170 (0.8).



Scheme S1 [S5]



Scheme S2 [S6]



Scheme S3 [S7]

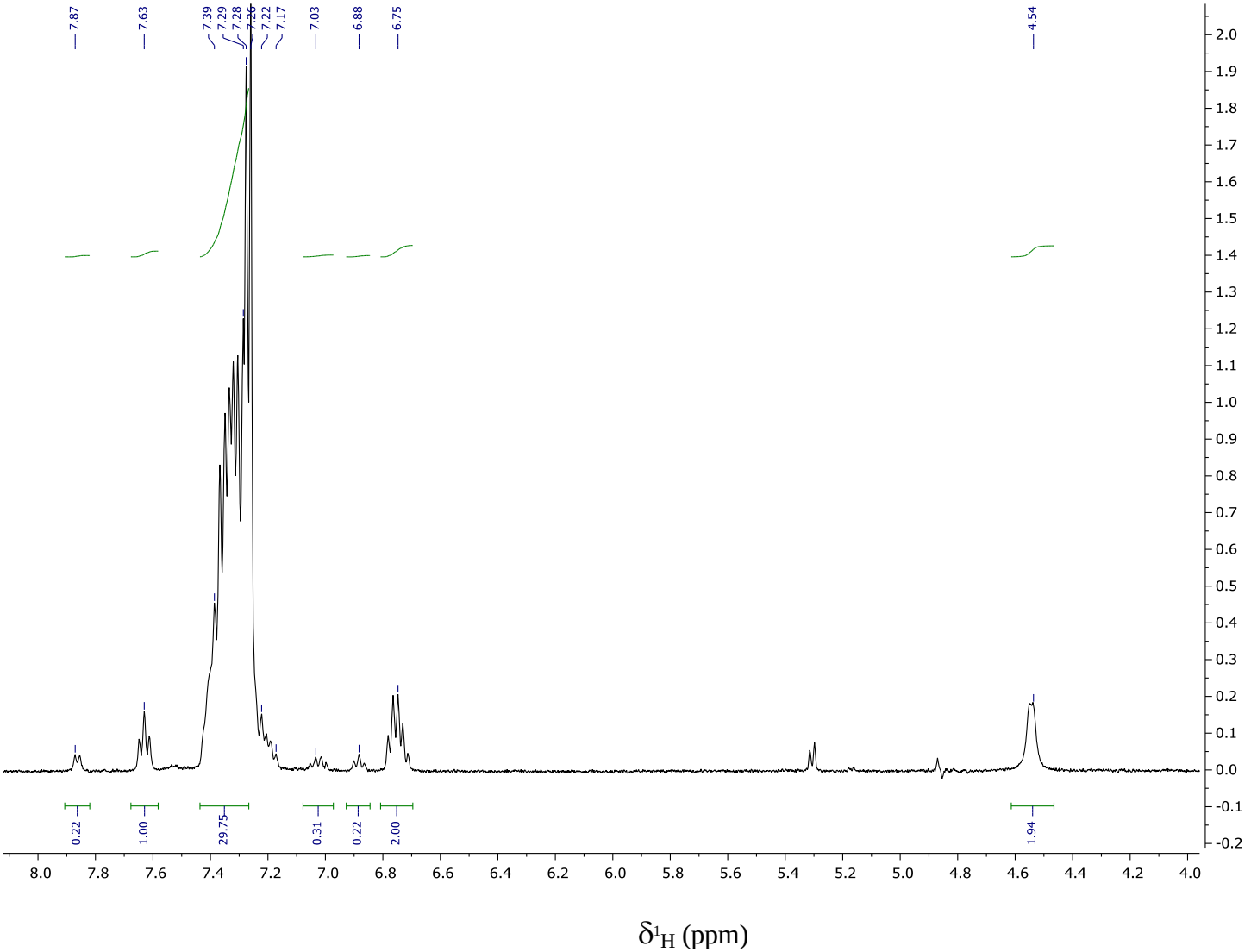


Figure S1. Fragment of the solution ^{1}H NMR spectrum of the complex $FeBd_2((S\text{-}C_6H_4\text{-}NH)Gm)(BF)_2$ (**8**) in $CDCl_3$

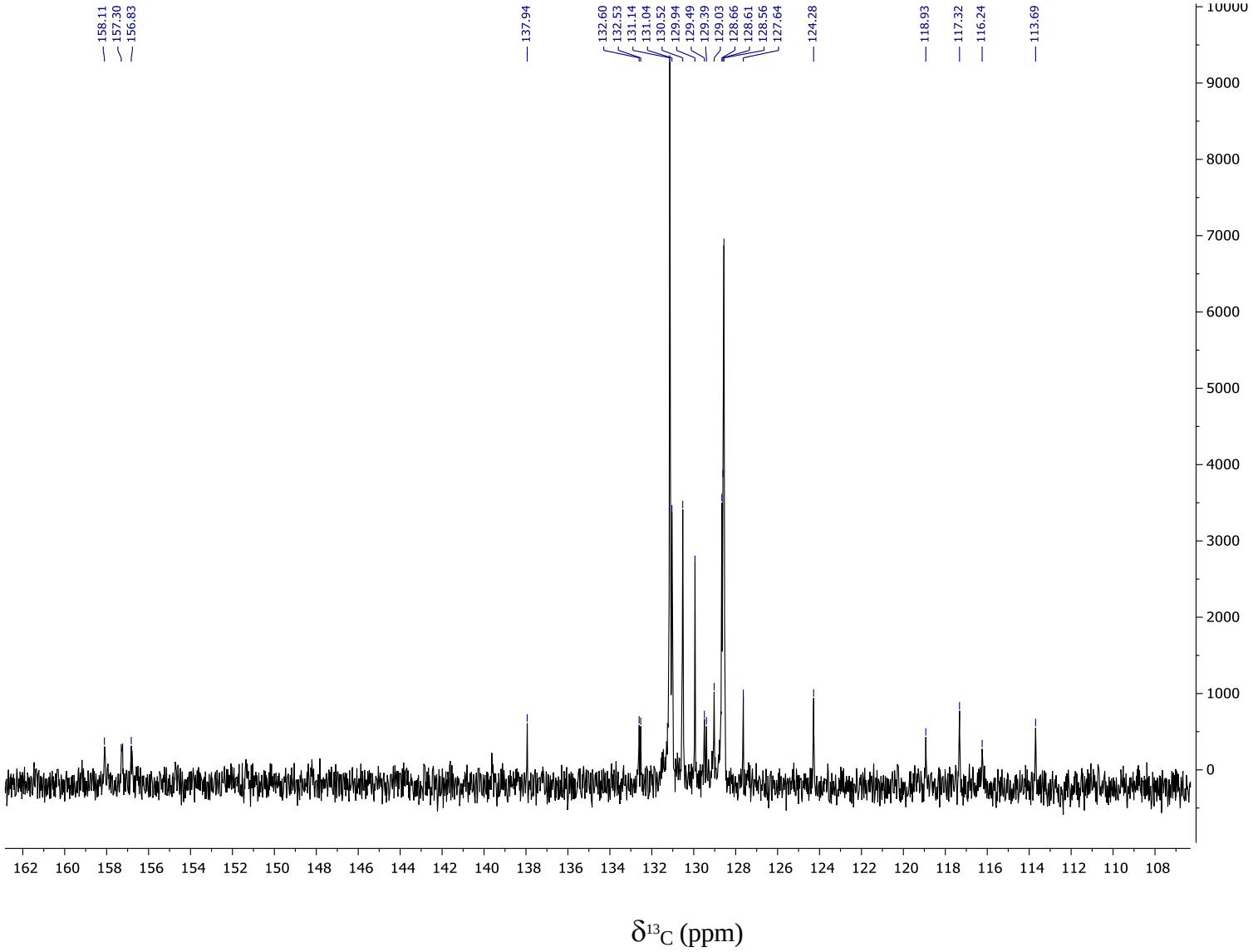


Figure S2. Fragment of the solution $^{13}C\{^{1}H\}$ NMR spectrum of the complex $FeBd_2((S\text{-}C_6H_4\text{-}NH)Gm)(BF)_2$ (**8**) in CD_2Cl_2

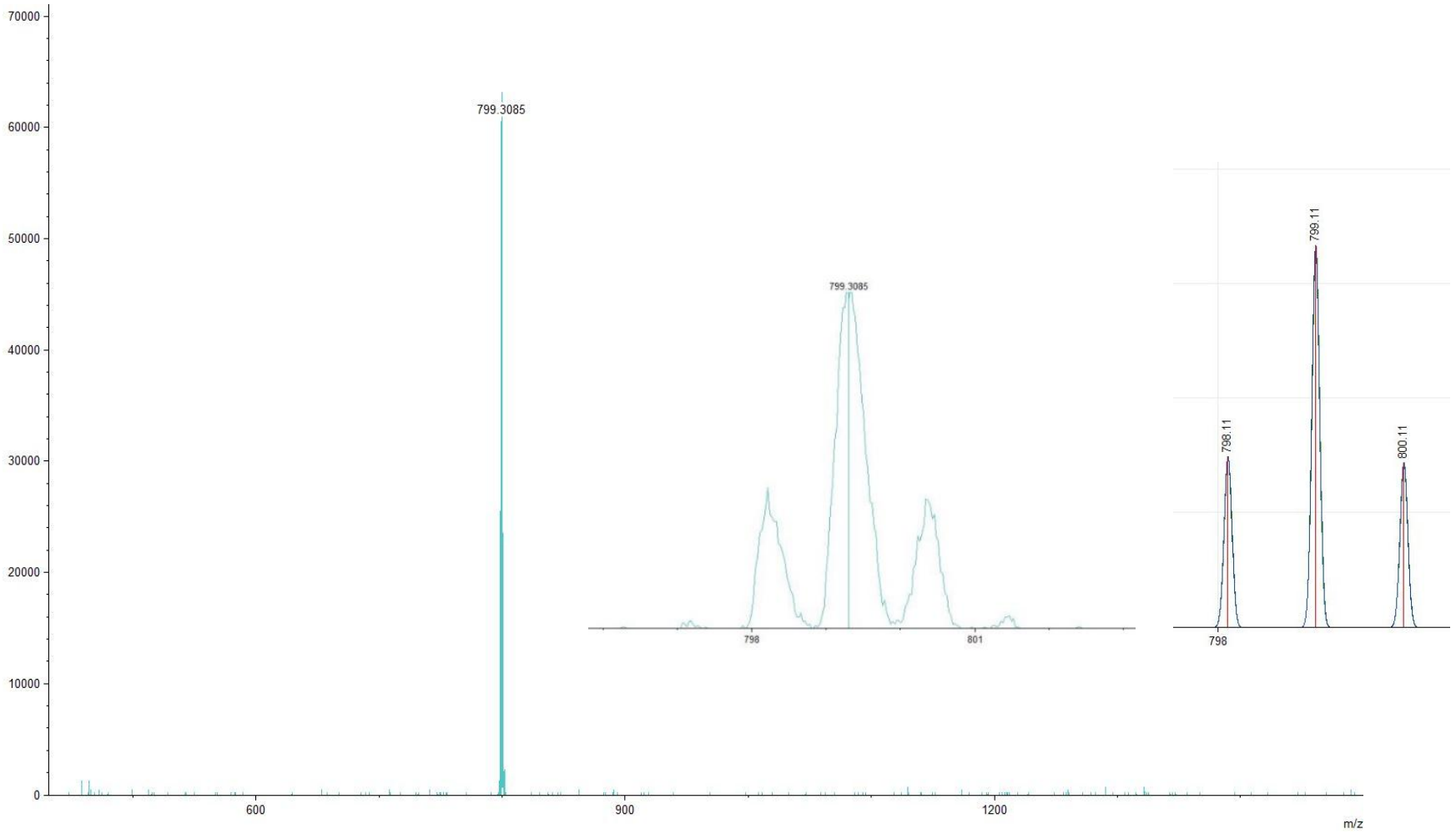


Figure S3 MALDI-TOF mass spectrum of complex $FeBd_2((S\text{-}C_6H_4\text{-}NH)Gm)(BF)_2$ (**8**). Inset: theoretically calculated (right) and experimentally observed (left) isotope distribution in its molecular ion.

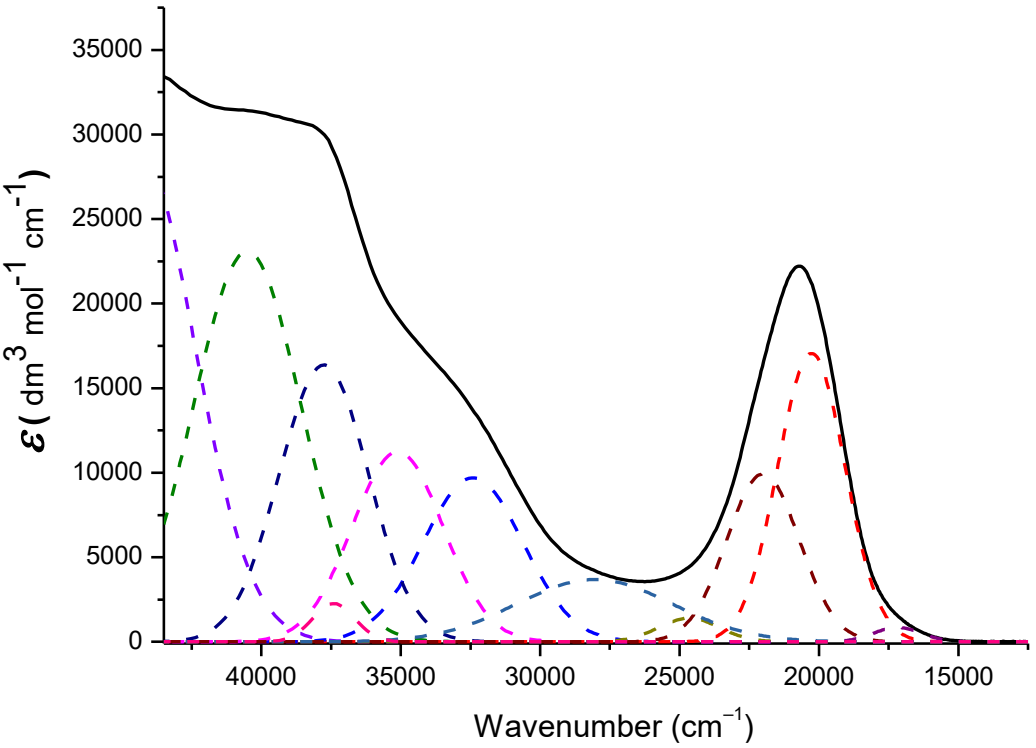


Figure S4 Solution UV-vis spectrum of clathrochelate $FeBd_2((S\text{-}C_6H_4\text{-}NH)Gm)(BF)_2$ (**8**) in dichloromethane (shown in black solid line) and its deconvolution into the Gaussian components (shown in color dashed lines).

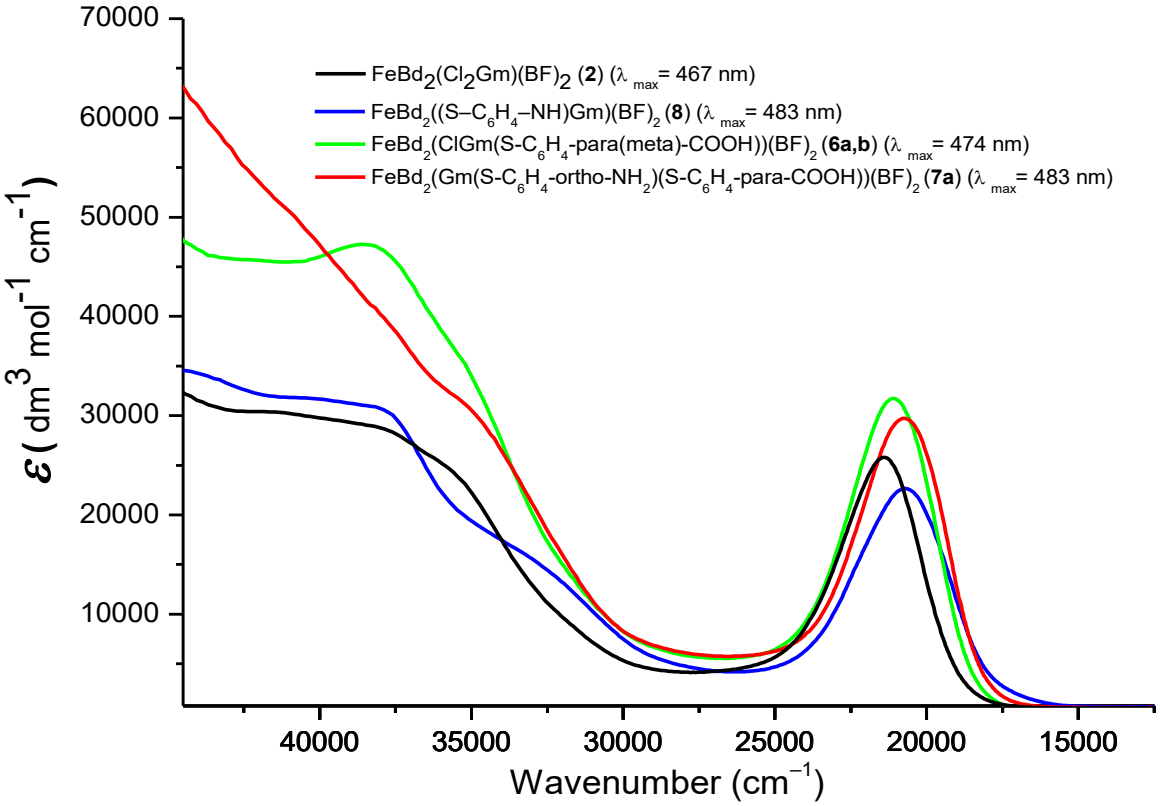


Figure S5 Comparison of the solution UV-vis spectra of several monoribbed-functionalized iron(II) clathrochelates (shown in colored lines) and that of their dichloroclathrochelate precursor $FeBd_2(Cl_2Gm)(BF)_2$ (**2**) (shown with black line)

Table S1. Deconvoluted solution UV-vis spectrum (ν, cm^{-1}, $\varepsilon \times 10^{-3}$, $dm^3\ mol^{-1} \cdot cm^{-1}$) of iron(II) clathrochelate **8**

Compound	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9	ν_{10}
$FeBd_2((S\text{-}C_6H_4\text{-}NH)Gm)(BF)_2$ (**8**)	44470 (29)	40510 (23)	37760 (16)	35112 (11)	32410 (9.7)	28060 (3.7)	24660 (1.4)	22000 (9.9)	20270 (17)	17170 (0.8)

Table S2. Solution UV-vis spectra (λ, nm, $\varepsilon \times 10^{-3}$, $dm^3\ mol^{-1} \cdot cm^{-1}$) of some iron(II) clathrochelates

Compound	λ_1	λ_2	λ_3
$FeBd_2((S\text{-}C_6H_4\text{-}NH)Gm)(BF)_2$ (**8**)	261 (30)	308 (13) sh	483 (22)
$FeBd_2(Cl_2Gm)(BF)_2$ (**2**)	239 (30)		467 (25)
$FeBd_2(ClGm(SC_6H_4\text{-}\textit{para}\text{-}COOH))(BF)_2$ (**6a**)	259 (47)		474 (32)
$FeBd_2(Gm(SC_6H_4\text{-}\textit{meta}\text{-}COOH)(SC_6H_4\text{-}\textit{ortho}\text{-}NH_2))(BF)_2$ (**7b**)		286 (30) sh	483 (29)

Supporting Information References

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