Ferrocene–Amino Acid Macrocycles as Hydrazone–Based Receptors for Anions

Sophie R. Beeren and Jeremy K. M. Sanders

Supporting Information

S1 Experimental

S1.1 General Experimental Procedures

All chemicals, unless otherwise stated, were purchased from Aldrich, Alfa Aesar, Lancaster or NovaBioChem and used as received. All solvents were distilled prior to use with the exception of deuterated solvents and HPLC or LC-MS grade solvents. CD_3OD-d_4, DMSO-d_6 and $CDCl_3$ were purchased from Euriso-top. The $CDCl_3$ was filtered through Alumina (Merck) immediately prior to use for analysis of hydrazones. Where reactions were carried out under a N_2 (g) MeOH was freshly distilled over CaH_2 in a N_2 (g) atmosphere. The HPLC and LC-MS grade MeOH were purchased from Fisher. The water used in the eluent was purified by a Millipore system. HPLC-grade formic acid was purchased from Romil and LC-MS grade formic acid was purchased from Fluka. Column chromatography was carried out using silica gel 60 F (Merck).

^{1}H and ^{13}C-NMR spectra were recorded on a Bruker DPX-400 spectrometer, operating at 400 MHz (^{1}H), 100 MHz (^{13}C), a Bruker DMX-500 spectrometer operating at 500 MHz (^{1}H) and 125 MHz (^{13}C) and a Bruker Cryoprobe TCI-500 operating at 500 MHz (^{1}H) and 125 MHz (^{13}C). Unless specified otherwise, all spectra were obtained at 298 K and are referenced to the internal solvent residue. Chemical shifts (δ) are quoted in ppm and have uncertainties of ± 0.01 ppm for ^{1}H, and ± 0.05 ppm for ^{13}C. Coupling constants (J) are listed in Hz. The following abbreviations are used for convenience in reporting the multiplicity for NMR resonances: s, singlet; d, doublet; t, triplet; q, quartet; sep, septet; m, multiplet and br, broad. Amino acid protons are labelled according to the traditional scheme: α, β, γ, and δ. The NMR data was processed using Bruker Topspin 2.0. Assignment of all ^{1}H and ^{13}C resonances was achieved using standard 2D NMR techniques; COSY, NOESY, HMQC and HMBC.

UV/Vis spectroscopy was carried out on a Varian Cary 400 instrument, using quartz cuvettes and operating a room temperature. Absorption maxima, λ_{max} and molar absorptivities, ε are given in nm and M^{-1} cm^{-1}, respectively. Circular Dichroism (CD) spectroscopy was performed on a Chirascan at operating at 25 °C, using 0.5 cm and 1 cm

quartz cuvettes. Ellipticity maxima (θ_{max}) are given in nm. Molar ellipticity coefficients M_θ were calculated as $M = 100 \times \theta / c \times l$, where ellipticity ($\theta$) is in degrees, concentration in mM and pathlength (l) in cm, thus giving deg mM^{-1} cm^{-1}. Fischer HPLC-grade solvent was used to prepare all samples for UV/Vis and CD spectroscopy. Melting points were measured using a Gallenkamp apparatus and are uncorrected. Exact masses were recorded using a Waters Micromass LCT Premier mass spectrometer.

HPLC analysis was performed on an Agilent Technologies 1200 Series system coupled to a diode array UV/Vis detector. LC-MS was carried out on an Agilent 1100 LC/MSD trap XCT system operating in alternating ultrascan mode with nebuliser, 25 psi; dry gas, 8 $lmin^{-1}$; dry temperature, 340 °C; capillary 3500 V; skimmer 40 V; capillary exit, 241 V; Oct1 DC, 12V; Oct 1 DC, 4.45 V; Trap drive 167.9 V; Oct RF 210.4 Vpp; lens 1, -5; lens 2, -60; scan range, 100-2200 m/z; max accumulation time, 200 ms and smart target 50000.

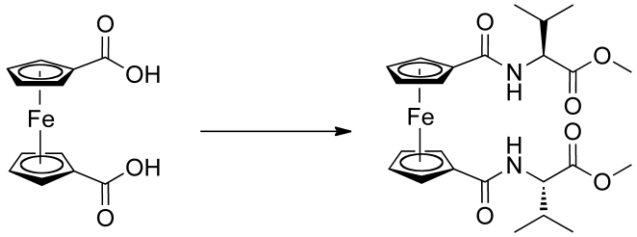
Separations were achieved using a Waters Symmetry C_{18} 3.5 µm 4.6 × 150 mm column maintained at 45 °C. The mobile phase solutions prepared were 0.1% formic acid in H_2O (A) and 0.1% formic acid in MeOH (B). Analysis of macrocycle mixtures was achieved using the method outlined below.

Injection Volume: 10 µl

Time / min	% Solution A	% Solution B
0	50	50
3	30	80
10	27	83
17	0	100
20	0	100

S1.2 Synthesis of Building Block Fc-[CO-Val-NHNH$_2$]$_2$ (V)

*Fc-[CO-Val-OMe]$_2$ (**1**)*[1]



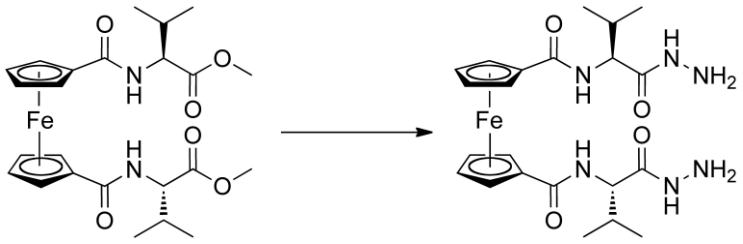
Fc-[COOH]$_2$ (2.00 g, 7.37 mmol), HOBt hydrate (2.64 g, 15.6 mmol (~20% H_2O)) and EDC (3.74 g, 19.5 mmol) were dissolved in DMF (120 ml) under an atmosphere of N_2 (g) to form a red solution. Et_3N (6.6 ml, 47 mmol) and then H-Val-OMe.HCl (3.27 g, 19.5 mmol) were added. The suspension formed was stirred overnight under an atmosphere of N_2 (g). Brine (150 ml) and H_2O (50 ml) were then added and the mixture was extracted with ethyl acetate (3 × 100 ml). The combined organic extracts were washed with $NaHCO_3$ (aq.) (2 × 150 ml), dried over Na_2SO_4, filtered and evaporated *in vacuo* to leave an orange solid. The crude material was purified by column chromatography (silica, crude material adsorbed on silica, hexane: ethyl acetate (1:1) to ethyl acetate) to yield the product as an orange solid. Yield: 2.64 g, 72 %. M.p.: 189-190 °C.

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.51 (d, ^3J = 8.4 Hz, 2H, N**H**), 4.85 (s, 2H, Cp-C**H**), 4.76 (s, 2H, Cp-C**H**), 4.66 (dd, ^3J = 7.9 Hz, 2H, α**H** of Val), 4.52 (s, 2H, Cp-C**H**), 4.36 (s, 2H, Cp-C**H**), 3.80 (s, 6H, OC**H**$_3$), 2.23-2.14 (m, 2H, β**H** of Val), 1.00 (d, ^3J = 3.1 Hz, 6H, γ**H** of Val), 0.99 (d, ^3J = 3.1 Hz, 6H, γ**H** of Val).

HR-MS (ESI): *m/z* = 501.1697 $[M + H]^+$ (calc. for $C_{24}H_{33}FeN_2O_6$: 501.1688).

CD (2 mM, $CHCl_3$:MeOH (96:4)): λ_{max} = 479 nm (M_θ = +6.9 deg mM^{-1} cm^{-1}), 358 nm (M_θ = –7.7 deg mM^{-1} cm^{-1}), 314 nm (M_θ = +12.2 deg mM^{-1} cm^{-1}).

*Fc-[CO-Val-NHNH$_2$]$_2$ (**V**)*



To a solution of Fc-[CO-Val-OMe]$_2$ (**1**) (2.00 g, 4.00 mmol) dissolved in MeOH (50 ml) under N_2 (g) atmosphere was added $N_2H_4.H_2O$ (20 ml) and the solution was stirred for two days. The yellow precipitate that formed was collected by vacuum filtration, washed with cold MeOH and dried *in vacuo*. Yield: 1.54 g, 77 %. M.p.: 220 °C (decomp.).

^{1}H-NMR (400 MHz; $CDCl_3$:CD_3OD (96:4): δ 8.89 (s, 2H, hydrazide N**H**), 7.98 (d, J = 8.3 Hz, 2H, amide N**H**), 4.75 (s, 2H, Cp-C**H**), 4.65 (s, 2H, Cp-C**H**), 4.45 (s, 2H, Cp-C**H**), 4.33 (s, 2H, Cp-C**H**), 4.08 (m, 2H, α**H** of Val), 2.20 (m, 2H, β**H** of Val), 1.02 (d, J = 6.6 Hz, 6H, γ**H** of Val), 0.94 (d, J = 6.6 Hz, 6H, γ**H** of Val). ^{13}C-NMR (100 MHz; $CDCl_3$:CD_3OD (9:1): δ 173.0 (**C**=O), 171.4 (**C**=O), 77.4 (Cp-**C**H), 76.0 (Cp-**C**), 72.1 (Cp-**C**H), 71.8 (Cp-**C**H), 70.2 (Cp-**C**H), 59.2 (α**C** of Val), 29.4 (β**C** of Val), 19.7 (γ**C** of Val), 19.4 (γ**C** of Val).

HR-MS (ESI): *m/z* = 523.1713 $[M + Na]^+$ (calc. for $C_{22}H_{32}FeN_6NaO_4$: 523.1732).

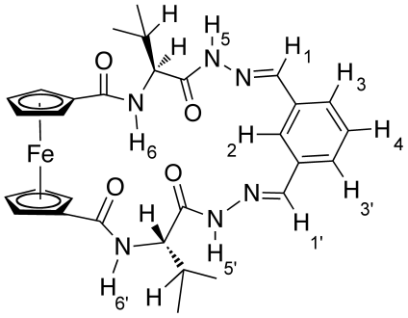
CD (2 mM, $CHCl_3$:MeOH (96:4)): λ_{max} = 483 nm (M_θ = +5.8 deg mM^{-1} cm^{-1}), 359 nm (M_θ = –5.5 deg mM^{-1} cm^{-1}), 312 nm (M_θ = +11.0 deg mM^{-1} cm^{-1}).

S1.3 Synthesis and Isolation of Macrocycles (VI), (VI)$_2$, (VI)$_3$ and (VI)$_4$

Fc-[CO-Val-NHNH$_2$]$_2$ (**V**) (200 mg, 0.40 mmol) and isophthalaldehyde (**I**) (54 mg, 0.40 mmol) were dissolved in a solution of $CHCl_3$ (400 ml) and acetic acid (4 ml) and stirred for 5 days. The solution was then washed with $NaHCO_3$ (aq.) (3 × 200 ml) and brine (1 × 200 ml), dried over Na_2SO_4, filtered and evaporated to yield a yellow solid. The material was purified by column chromatography (silica, crude material absorbed on Celite). From the first column (CH_2Cl_2 to MeOH:CH_2Cl_2 (1:9)) were isolated three fractions containing **(VI)** and **(VI)$_2$** together, **(VI)$_3$** and **(VI)$_4$**. A second column (isocratic, MeOH:Et_3N:CH_2Cl_2 (5:2.5:92.5)) was required to separate **(VI)** and **(VI)$_2$**. The isolated fractions were first washed with Na_2CO_3 (aq.) and then dried over Na_2SO_4 before evaporation *in vacuo* to yield as pale yellow solids: **(VI)** (17 mg, 7 %); **(VI)$_2$** (30 mg, 13 %); **(VI)$_3$** (14 mg, 6 %) and

(VI)$_4$ (6 mg, 2.5 %). The mixture of macrocycles in solution, and the isolated samples were analysed using HPLC.

(VI)



M.p.: 260 °C (decomp.).

^{1}H-NMR (500 MHz, CD_2Cl_2:CD_3OD (9:1), 278 K): δ 10.29 (s, 1H N**H**5/N**H**5′), 9.98 (br m, 2H, N**H**5/N**H**5′ and N**H**6), 8.79 (s, 1H, **H**2), 7.81 (s, 2H, **H**1 and **H**1′), 7.40 (dd apparent t, 1H, **H**4), 7.33 (br m, 3H, **H**3, **H**3′ and N**H**6′), 5.45 (br m, 1H α**H**′ of Val), 4.68 (br s, 1H, Cp-C**H**), 4.54 (br s, 1H Cp-C**H**), 4.39-4.20 (m, 6H, Cp-C**H**) , 4.00 (br m, 1H, α**H** of Val), 2.91 (br m, 1H, β**H** of Val), 2.25 (br m, 1H, β**H**′ of Val), 1.25 (br m, 3H, γ**H** of Val), 1.08 (br m, 3H, γ**H** of Val), 1.05 (d, ^3J = 6.7 Hz, 6H, γ**H**′ of Val) ppm.

HR-MS (ESI): *m/z* = 621.1890 $[M + Na]^+$ (calc. for $C_{30}H_{34}FeN_6NaO_4$: 621.1889).

UV/Vis: λ_{max} = 278 nm (ε = 40 000 M^{-1} cm^{-1}), 434 nm (ε = 100 M^{-1} cm^{-1}).

CD (1 mM $CHCl_3$:MeOH (9:1)): λ_{max} = 427 nm (M_θ = +0.4 deg mM^{-1} cm^{-1}), 340 nm (M_θ = +3.5 deg mM^{-1} cm^{-1})

(VI)$_2$

M.p.: 260 °C (decomp.).

HR-MS (ESI): *m/z* = 1219.3837 $[M + H]^+$ (calc. for $C_{60}H_{68}Fe_2N_{12}NaO_8$: 1219.3874).

UV/Vis: λ_{max} = 288 nm (ε = 80 000 M^{-1} cm^{-1}), 449 nm (ε = 290 M^{-1} cm^{-1}).

CD (0.5 mM $CHCl_3$:MeOH (9:1)): λ_{max} = 483 nm (M_θ = +3.0 deg mM^{-1} cm^{-1}), 418 nm (M_θ = –2.3 deg mM^{-1} cm^{-1}), 359 nm (M_θ = –1.7 deg mM^{-1} cm^{-1}).

(VI)$_3$

M.p.: 250 °C (decomp.).

UV/Vis: λ_{max} = 286 nm (ε = 95 000 M^{-1} cm^{-1}), 449 nm (ε = 570 M^{-1} cm^{-1}).

CD (0.33 mM $CHCl_3$:MeOH (9:1)): λ_{max} = 483 nm (M_θ = +7.5 deg mM^{-1} cm^{-1}), 418 nm (M_θ = –4.7 deg mM^{-1} cm^{-1}), 359 nm (M_θ = –5.3 deg mM^{-1} cm^{-1}).

(VI)$_4$

UV/Vis: λ_{max} = 286 nm (ε = 100 000 M^{-1} cm^{-1}), 449 nm (ε = 640 M^{-1} cm^{-1}).

CD (0.25 mM $CHCl_3$:MeOH (9:1)): λ_{max} = 483 nm (M_θ = +6.4 deg mM^{-1} cm^{-1}), 418 nm (M_θ = –2.8 deg mM^{-1} cm^{-1}), 359 nm (M_θ = –4.9 deg mM^{-1} cm^{-1}).

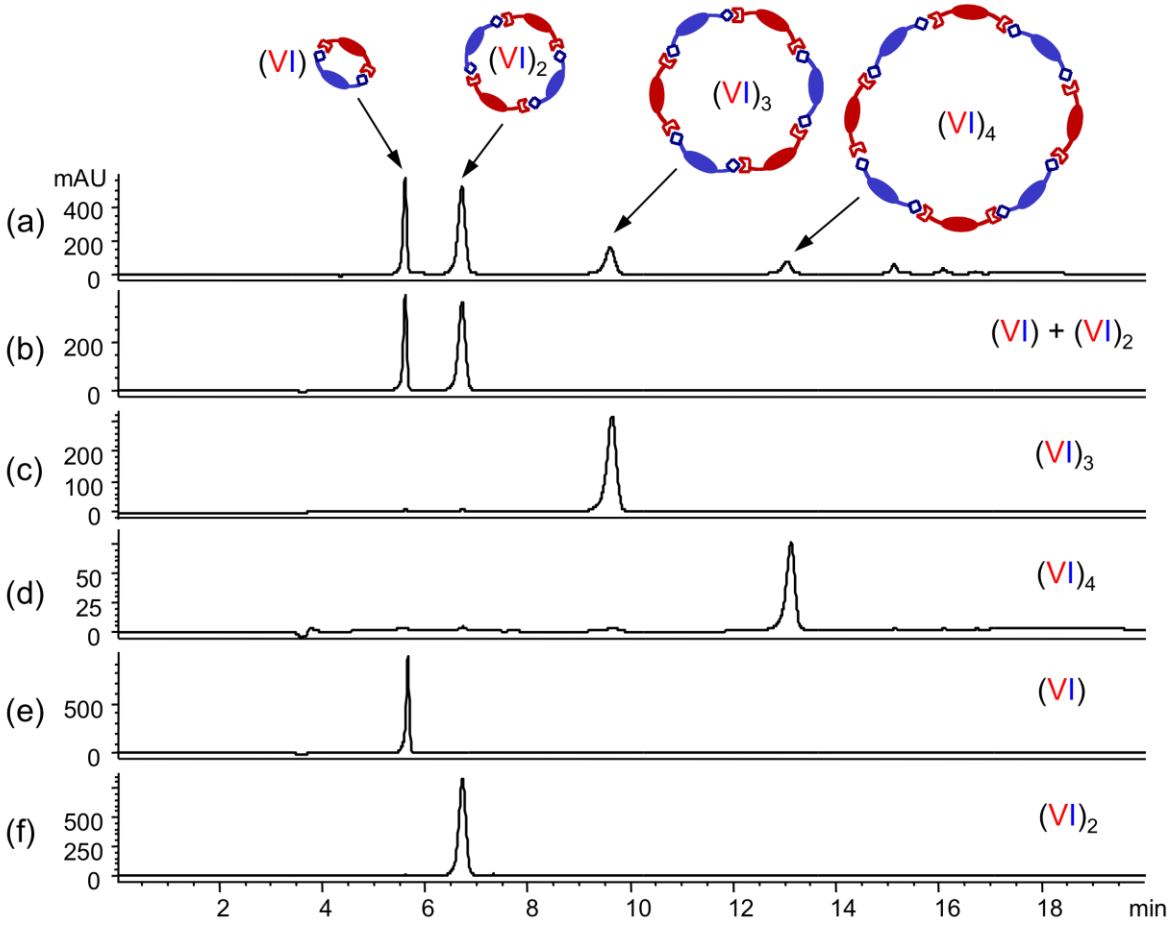


Figure S1. HPLC chromatograms (290 nm) showing (a) a preparative-scale library formed from Fc-[CO-Val-$NHNH_2$]$_2$ (**V**) and isophthalaldehyde (**I**) in chloroform with 0.5 % acetic acid and three fractions isolated *via* column chromatography (CH_2Cl_2 – CH_2Cl_2:MeOH (9:1)): (b) **(VI)** and **(VI)$_2$**; (c) **(VI)$_3$**; (d) **(VI)$_4$** and two fractions separated by a second column (CH_2Cl_2:MeOH:Et_3N (92.5:5:2.5)): (e) **(VI)** and (f) **(VI)$_2$**.

S1.4 UV/Vis Titrations

UV/Vis titrations were performed to determine binding constants for eight different anions with macrocycles **(VI)**, **(VI)$_2$**, **(VI)$_3$** and **(VI)$_4$**. A general procedure is described below.

Solutions of each macrocycle either in $CHCl_3$:MeOH (96:4) or $CHCl_3$ (100 ml) were prepared. These solutions were used to prepare solutions containing the macrocyclic host and the anionic guest together. The UV/Vis spectrum of the macrocycle solution was recorded from 240 nm to 400 nm on a 2 ml solution in a 1 cm quartz cuvette. Small aliquots of macrocycle + anion solution were added (5 μl and then 10 μl up to a total of 150 μl for **(VI)$_2$**, **(VI)$_3$** and **(VI)$_4$** and 10 μl and then 20 μl up to a total of 300 μl for **(VI)**). The UV/Vis spectrum was recorded after each addition. The solution of each macrocycle and of each macrocycle + anion mixture were prepared at the following concentrations:

- [**(VI)**]: 25 μM (100 ml)
- [**(VI)$_2$**]: 13 μM (100 ml)
- [**(VI)$_3$**]: 7.9 μM (100 ml)
- [**(VI)$_4$**]: 6.3 μM (100 ml)
- [anion] in **(VI)** + anion solution: ~ 1 mM (4 ml)
- [anion] in **(VI)$_2$** + anion solution: ~ 1 mM (4 ml)
- [anion] in **(VI)$_3$** + anion solution: ~ 0.7 mM (6 ml)
- [anion] in **(VI)$_4$** + anion solution: ~ 0.5 mM (7 ml)

The changes in absorbance at 289 nm (for **(VI)**, **(VI)$_2$** and **(VI)$_4$**) or 286 nm (for **(VI)$_3$**) were plotted against the concentration of added anion to generate a binding isotherm. Data fitting was carried out using the fitting programme, *Sci Davis* 0.2.3. Binding isotherms were fitted to a 1:1 binding model (*Equation S1*) using a Scaled Levenberg-Marquardt algorithm to determine the association constant *K*.

$$y = \frac{Bx}{1 + Kx} \qquad \textit{Equation S1}$$

y = change in absorbance at λ_{max}

x = concentration of added guest

B is a function of the difference in extinction between the complex and the unbound host and includes *K*; it is determined in the fitting.

S1.5 UV/Vis Job Plots

Solutions of macrocycle were prepared in $CHCl_3$:MeOH (96:4) in the same manner as for UV/Vis titrations. For each job plot with a specific macrocycle, an anion solution in $CHCl_3$:MeOH (5 ml) was prepared at the same concentration.

- For Job plots with **(VI)**, a solution of anion (25 mM, 1 ml) was prepared and then diluted 1/1000, to produce an anion solution (25 μM, 5 ml).
- For Job plots with **$(VI)_2$,** a solution of anion (13 mM, 1 ml) was prepared and then diluted 1/1000 to produce an anion solution (13 μM, 5 ml).
- For Job plots with **$(VI)_3$,** a solution of anion (7.9 mM, 1 ml) was prepared and then diluted 1/1000 to produce an anion solution (7.9 μM, 5 ml).
- For Job plots with **$(VI)_4$,** a solution of anion (12.6 mM, 1 ml) was prepared and then diluted 1/2000 to produce an anion solution (6.3 μM, 5 ml).

The UV/Vis spectrum of the macrocycle solution (2 ml) was recorded from 240 nm to 340 nm in a 1 cm quartz cuvette. Then aliquots of anion solution were added up to a total volume of 4 ml, recording the UV/Vis spectrum after each addition. The spectrum of the anion solution (2 ml) was then recorded. Aliquots of the macrocycle solution, up to a total volume of 4 ml, were added, again recording the spectrum after each addition. Plotting $\Delta A \times$ [macrocycle] against [macrocycle] / ([macrocycle] + [anion]) generated the Job plots.

S1.6 NMR Titrations

(VI) + $Bu_4NH_2PO_4$

Two solutions were prepared in $CDCl_3$:CD_3OD (96:4) as follows:

I. **(VI)** (4.0 mM, 1.8 ml);

solution I was then used to prepare solution II

II. $Bu_4NH_2PO_4$ (48 mM) and **(VI)** (4.0 mM) in 1 ml.

Solution I (600 μl) was transferred to an NMR tube, and the ^{1}H-NMR spectrum was acquired. Aliquots of solution (II) (beginning with 5 μl and gradually increasing to 60 μl until the concentration of $Bu_4NH_2PO_4$ reached 20 mM), were added and the ^{1}H and ^{31}P-NMR spectra were acquired after each addition, after shaking the NMR tube.

$(VI)_2$ + Bu_4NHSO_4

Two solution were prepared in $CDCl_3$:CD_3OD (9:1) as follows:

I. $\mathbf{(VI)_2}$ (2.0 mM, 1.9 ml);

solution I was used to prepare solution II

II. Bu_4NHSO_4 (240 mM) and $\mathbf{(VI)_2}$ (2.0 mM) in 1 ml.

Solution I (600 μl) was transferred to an NMR tube and the ^{1}H-NMR spectrum was recorded. Aliquots of solution (II) (beginning with 5 μl and gradually increasing to 60 μl until the concentration of Bu_4NHSO_4 reached 140 mM) were added. The tube was shaken and the ^{1}H-NMR spectrum was acquired after each addition.

1.7 Reaction Monitoring of Macrocycle Formation

A solution of Fc-[CO-Val-$NHNH_2$]$_2$ (**V**) (0.5 mM) and isophthalaldehyde (**I**) (0.5 mM) in acetic acid (0.5%) in $CHCl_3$ (10 ml) was prepared. It was sonicated to ensure complete dissolution and then stirred for 3 days. Aliquots of reaction mixture (200 μl) were removed from the flask and combined with a solution of Et_3N (200 μL, 1.5% in $CHCl_3$) at the following intervals: 0.25, 0.5, 0.75, 1, 1.5, 3, 4, 5, 6, 7, 8, 16, 24, 42.5, 52 and 70 hours. The collected aliquots were each analysed by HPLC using within 3 hours of their quenching with Et_3N.

S2 NMR Spectra

S2.1 Fc-[CO-Val-NHNH$_2$]$_2$

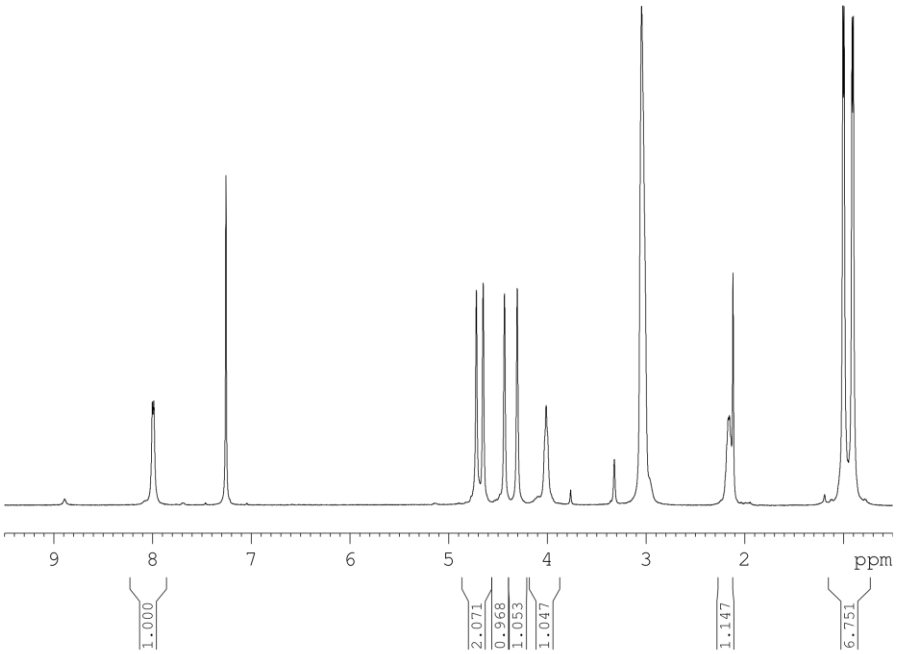


Figure S2. ^{1}H-NMR spectrum of Fc-[CO-Val-NHNH$_2$]$_2$ (**V**) in CDCl$_3$:CD$_3$OD (96:4).

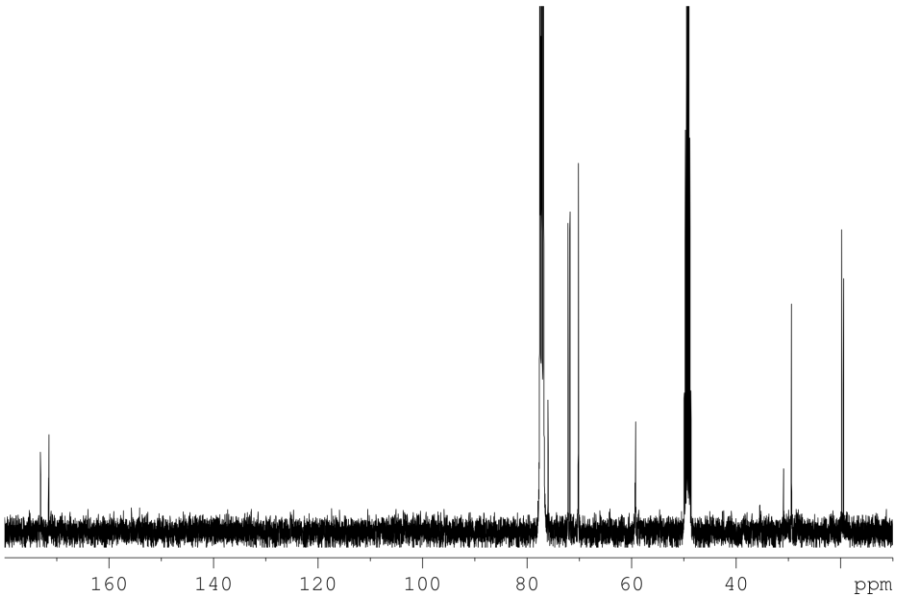


Figure S3. ^{13}C-NMR spectrum of Fc-[CO-Val-NHNH$_2$]$_2$ (**V**) in CDCl$_3$:CD$_3$OD (9:1).

S2.2 (VI)

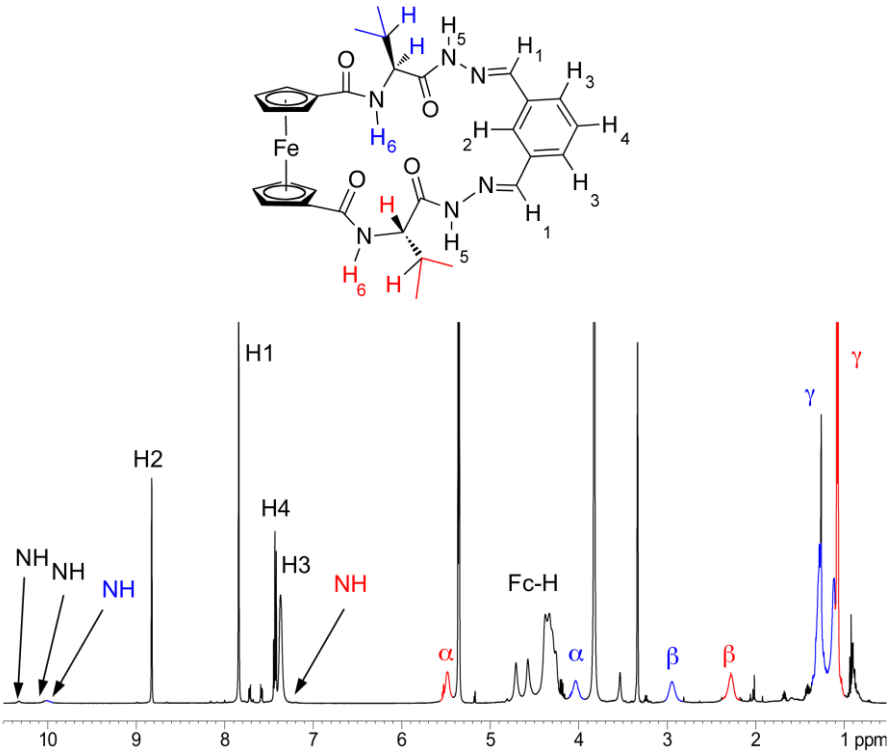


Figure S4. ^{1}H-NMR spectrum of **(VI)** in CD_2Cl_2:CD_3OD (9:1) at 278 K. In red and blue are labelled nonequivalent protons from opposite sides of the macrocycle.

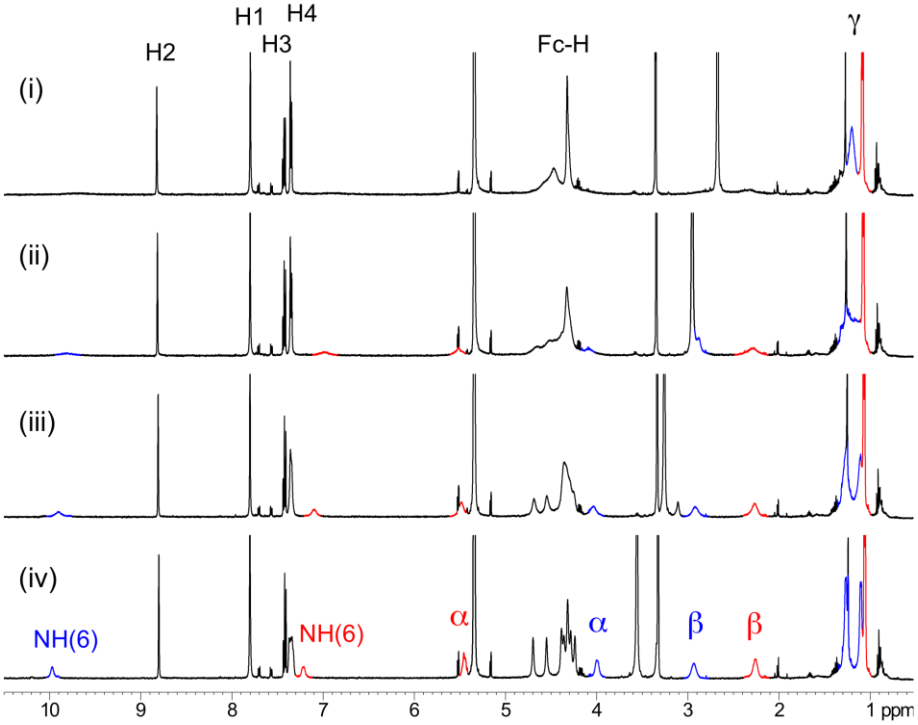


Figure S5. ^{1}H-NMR spectra of **(VI)** in CD_2Cl_2:CD_3OD (9:1) at (i) 300 K, (ii) 290 K, (iii) 280 K and (iv) 270 K.

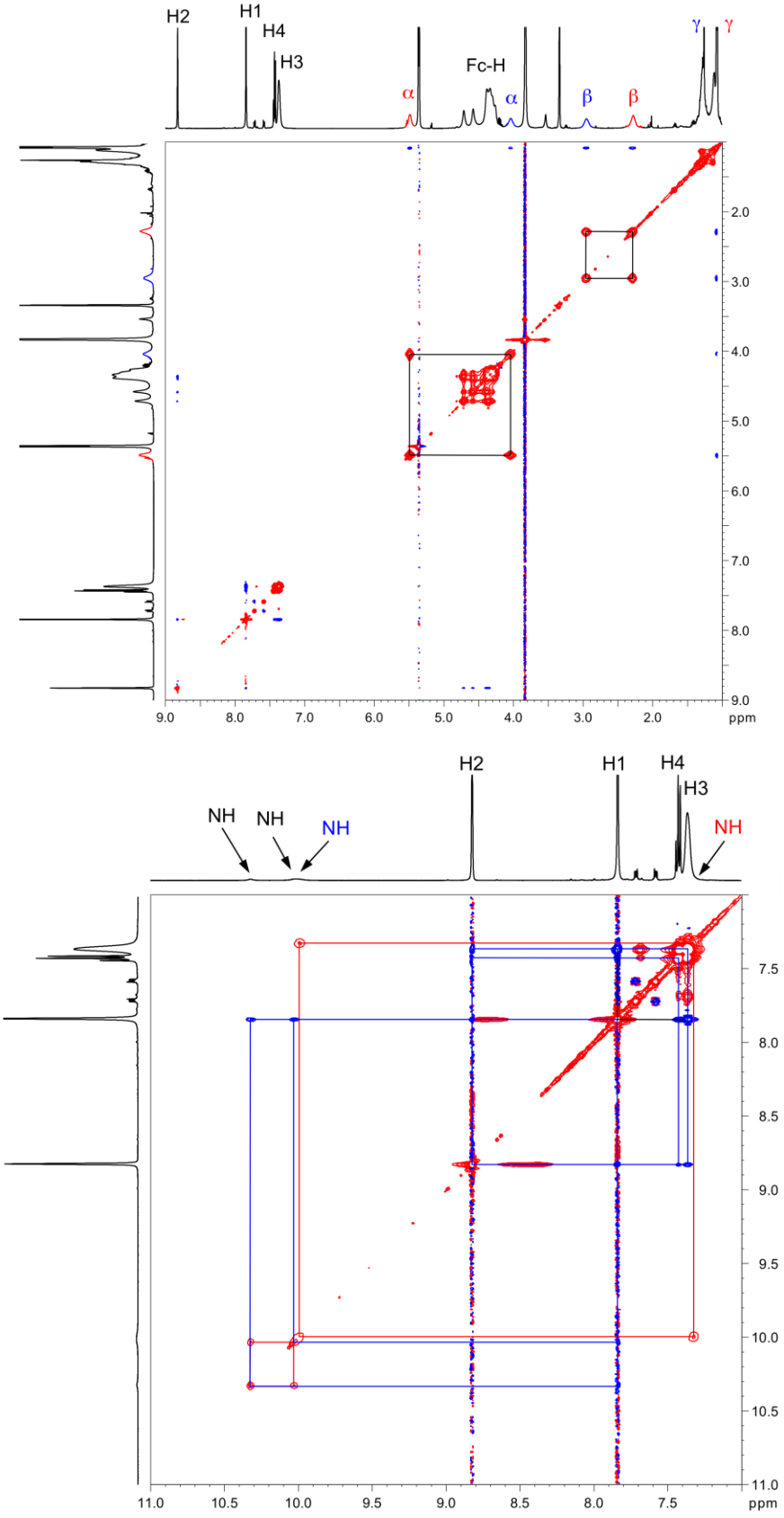


Figure S6. NOESY spectra of **(VI)** in CD_2Cl_2:CD_3OD (9:1) at 278 K. NOe cross peaks appear in blue, exchange cross peaks appear in red: (a) full spectrum; (b) aromatic region.

S2.3 $(VI)_2$

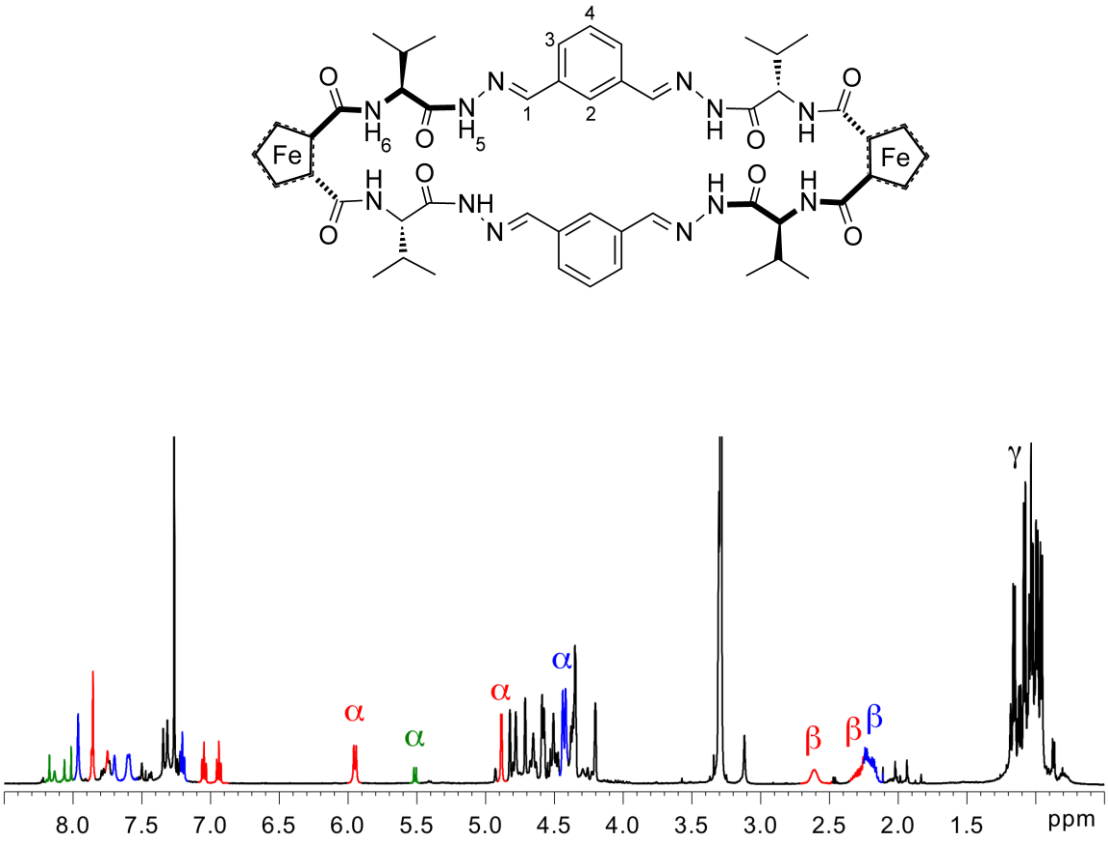
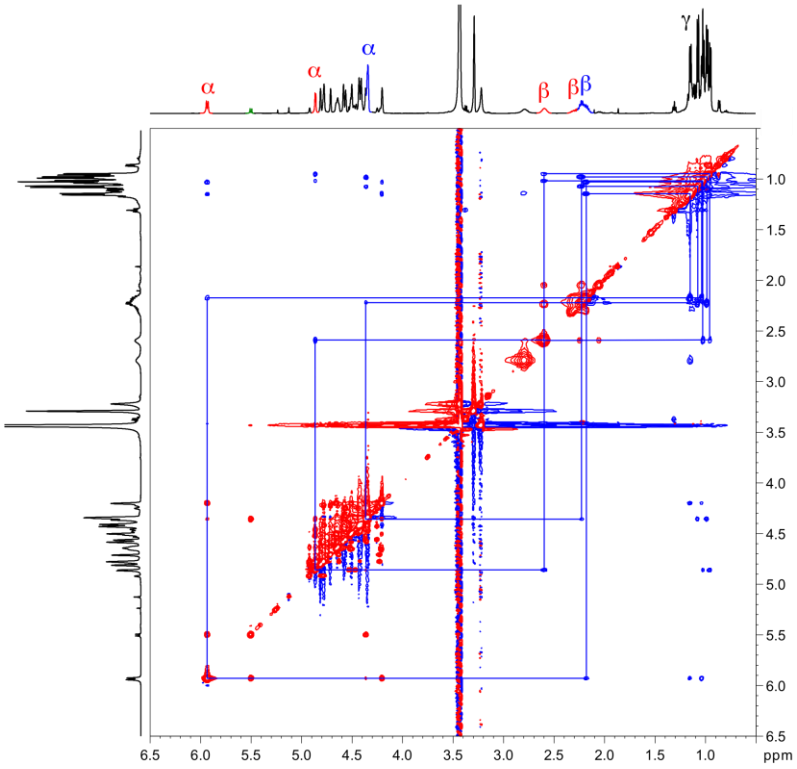


Figure S7. ^{1}H-NMR spectrum of **$(VI)_2$** in $CDCl_3$:CD_3OD (9:1) at 298 K. Selected signal from conformers A, B and C are coloured in blue, red and green, respectively.

(a)



(b)

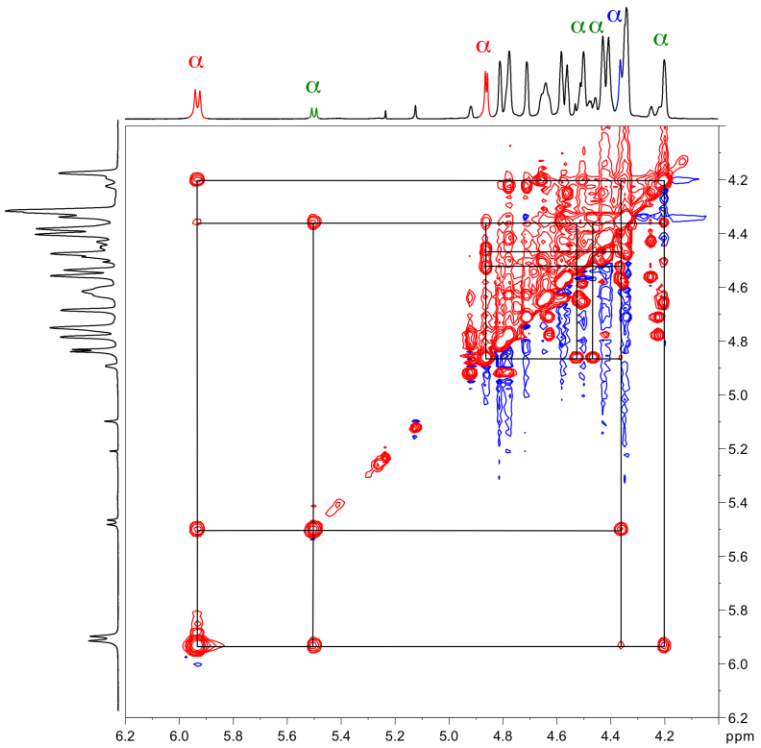
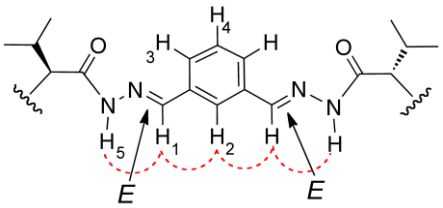
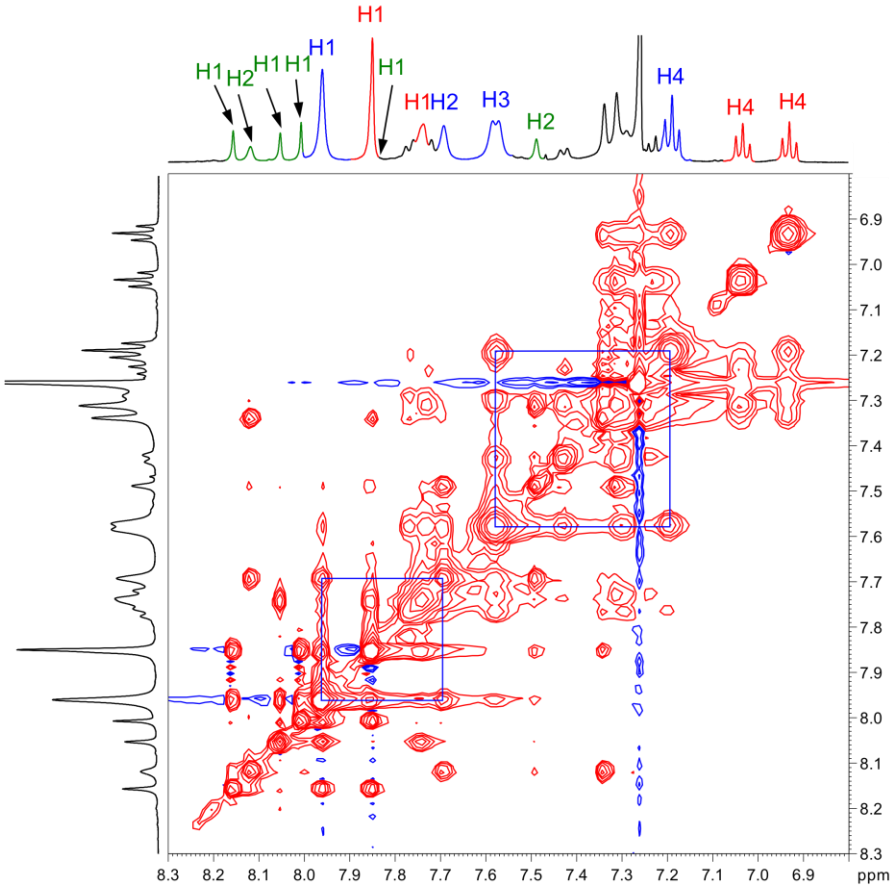


Figure S8. Partial NOESY spectra of **(VI)$_2$** in $CDCl_3$:CD_3OD (9:1) at 298 K: (a) highlighting nOe cross peaks between α, β and γ protons of valine moieties for conformations A (D_2, blue) and B (C_2, red); (b) highlighting the exchange cross peaks between α-protons of the three conformers.



(a)



(b)

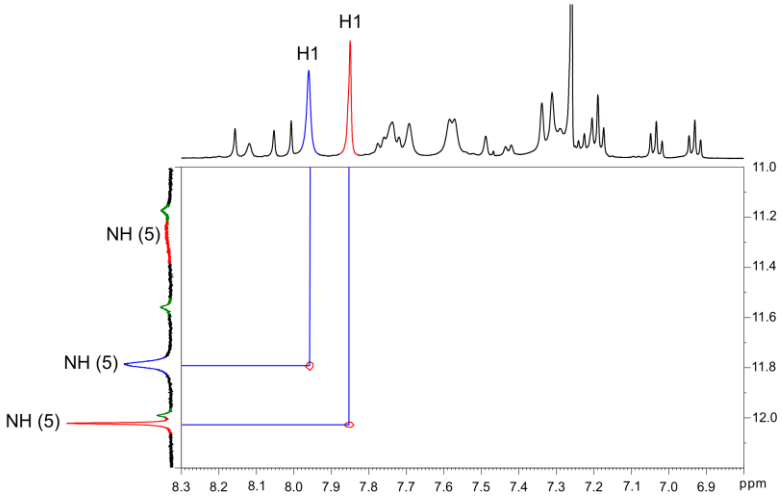


Figure S9. NOESY spectra of **$(VI)_2$** in $CDCl_3$:CD_3OD (9:1) at 298 K with nOe correlations highlighted with blue lines: (a) aromatic region; (b) NH region.

S2.4 $(VI)_3$

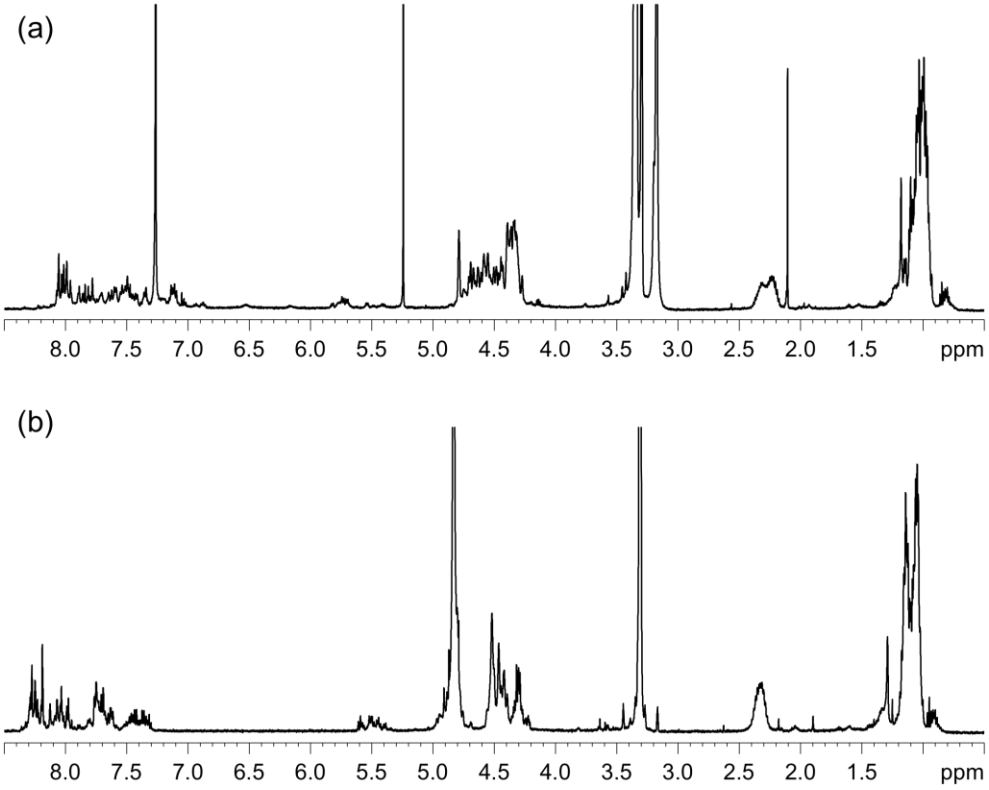


Figure S10. ^{1}H-NMR spectra of **$(VI)_3$** at 300 K in (a) $CDCl_3$:CD_3OD (9:1) and (b) CD_3OD.

S2.5 $(VI)_4$

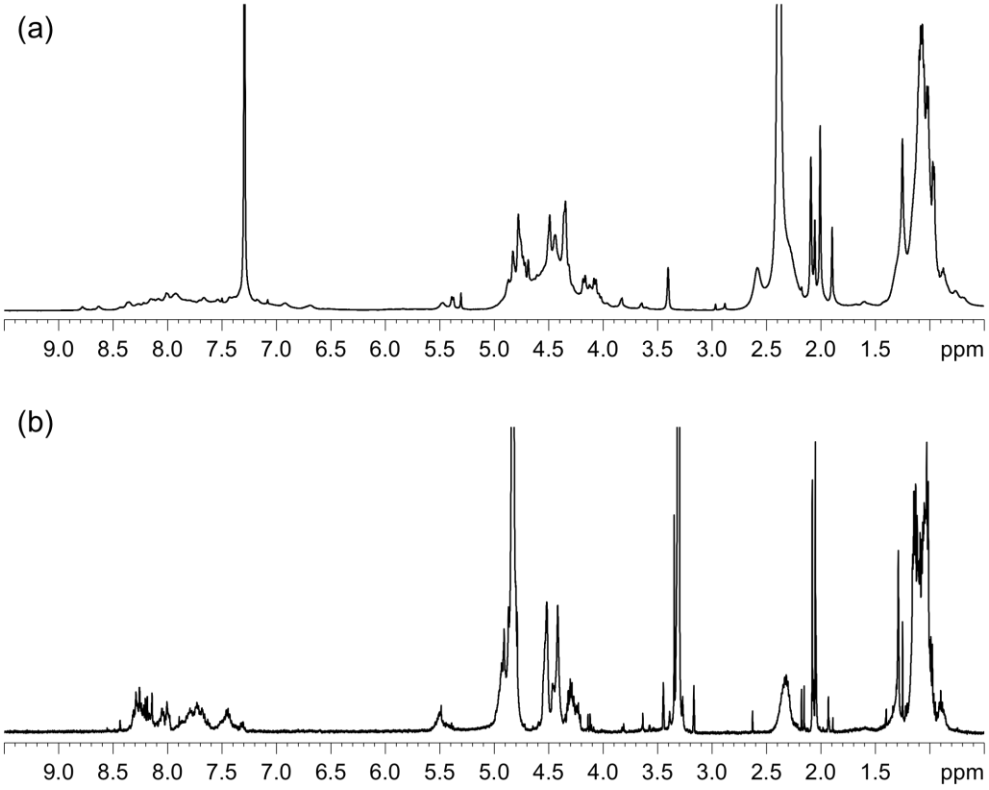
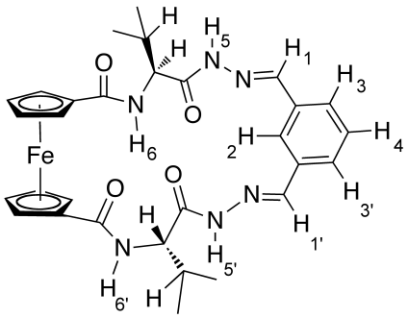


Figure S11. ^{1}H-NMR spectra of **$(VI)_4$** at 300 K in (a) $CDCl_3$:CD_3OD (9:1) and (b) CD_3OD.

S2.6 NMR Titration: (VI) + $Bu_4NH_2PO_4$



(a) (b)

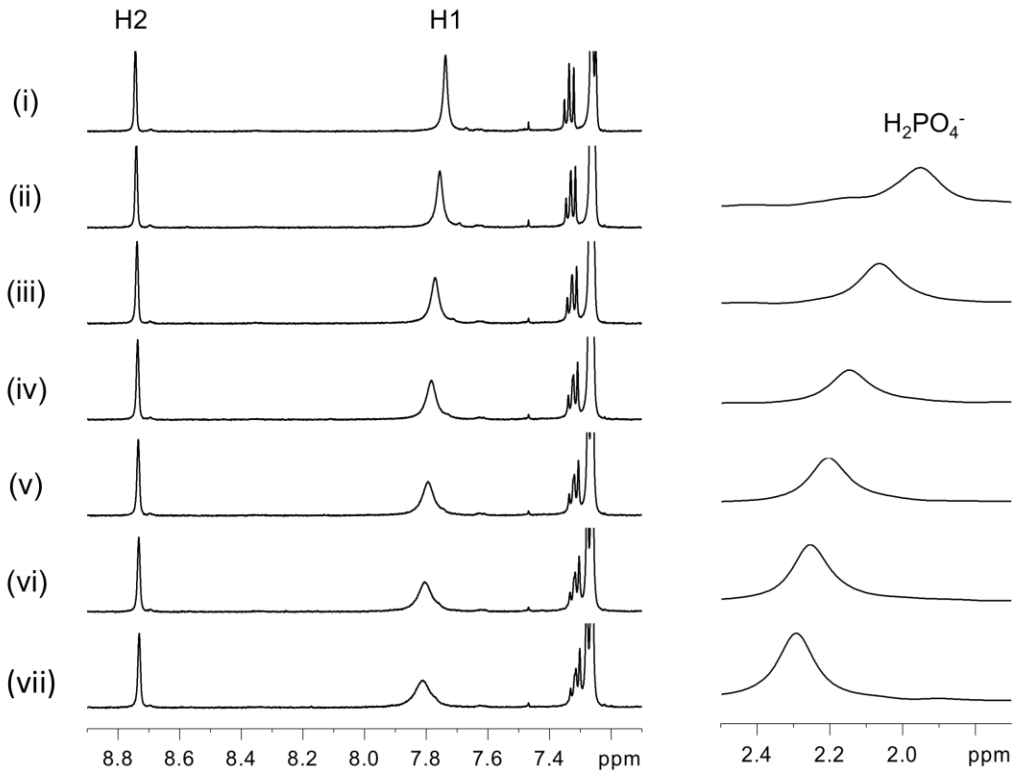


Figure S12. Partial ^{1}H-NMR (a) and ^{31}P-NMR (b) spectra of **(VI)** (4 mM) in $CDCl_3$:CD_3OD (96:4) at 298 K in the presence of $Bu_4NH_2PO_4$: (i) 0 mM, (ii) 4 mM, (iii) 8 mM, (iv) 12 mM, (v) 16 mM, **(VI)** 20 mM and (vii) 24 mM.

S3 UV/Vis Spectra and Curves

The UV/Vis spectra recorded during titrations with $BzEt_3NBr$, the fitted binding isotherms and Job plots are shown below as a representative sample. Very similar changes in UV/Vis spectrum were observed for titrations with the other anions studied.

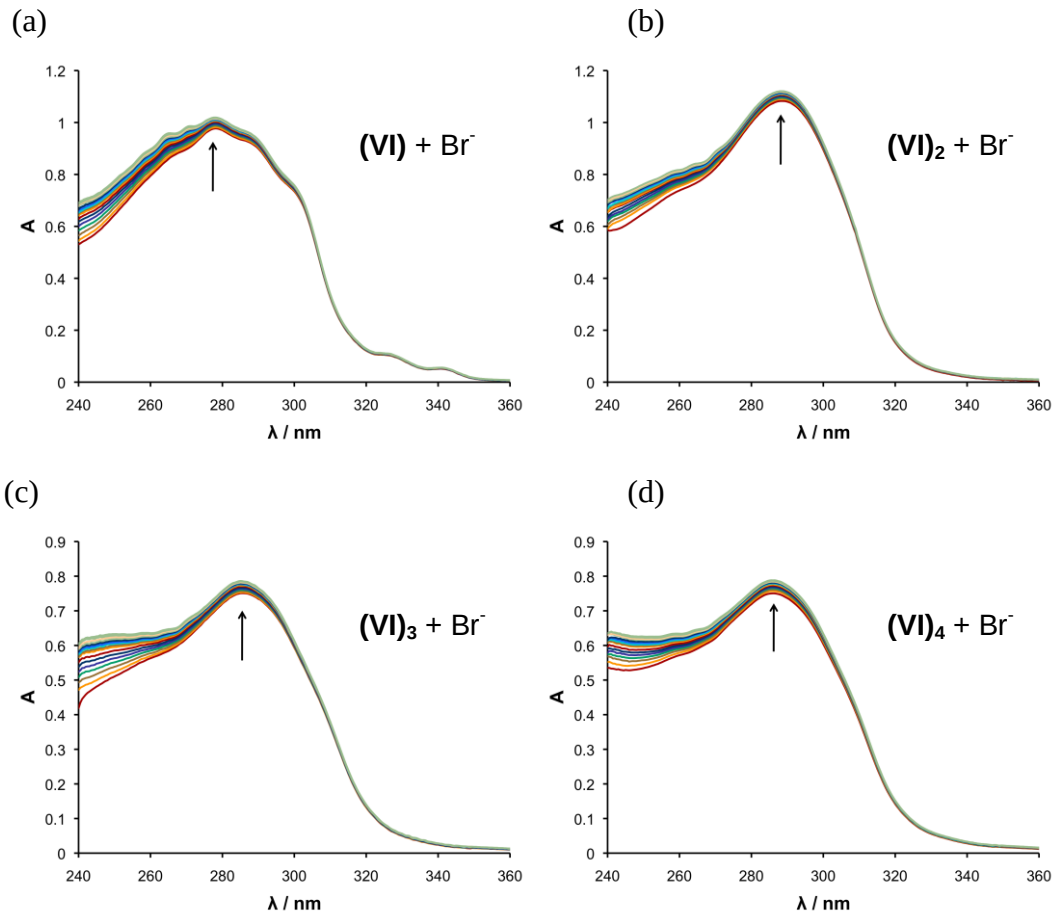


Figure S13. UV/Vis spectra depicting the hyperchromic shift on the absorbance at ~290 nm observed when $BzEt_3NBr$ was titrated into solutions of (a) **(VI)** (25 μM), (b) **$(VI)_2$** (13 μM), (c) **$(VI)_3$** (7.9 μM) and (d) **$(VI)_4$** 6.3 (μM) in $CHCl_3$:MeOH (96:4).

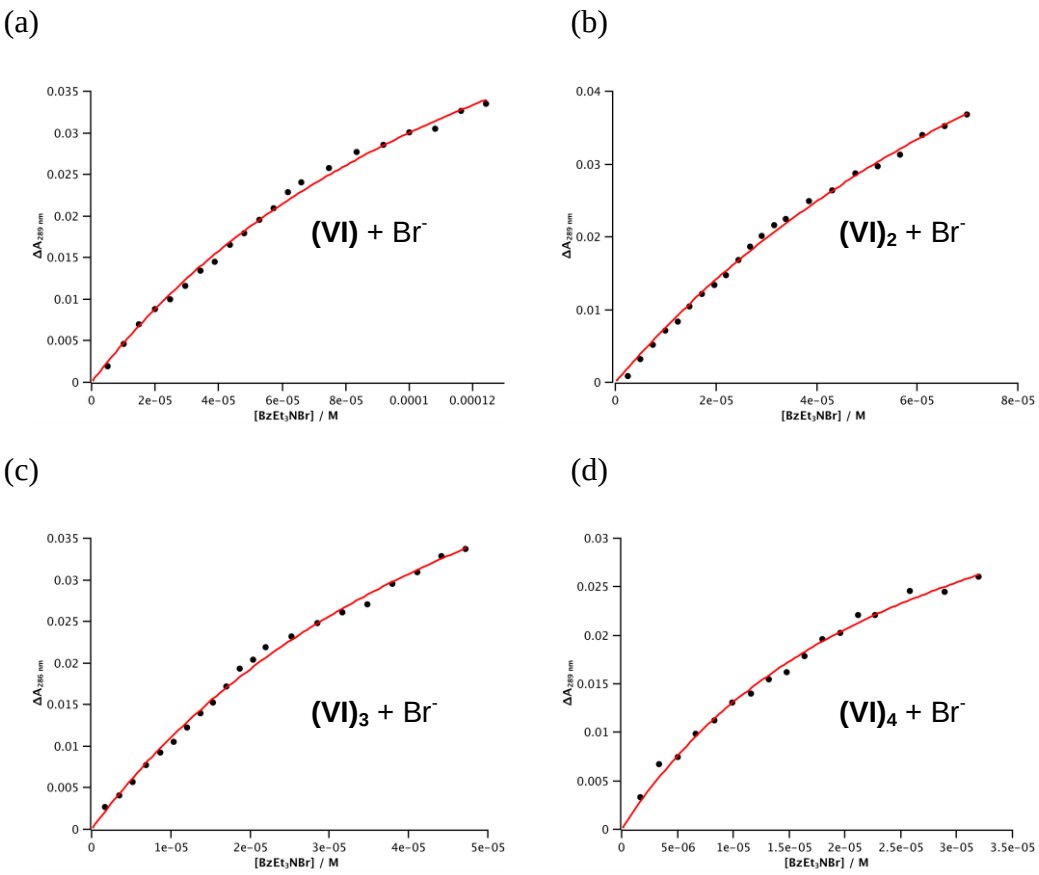


Figure S14. Fitted binding isotherms from UV/Vis titrations of $BzEt_3NBr$ into (a) **(VI)** (25 μM), (b) **(VI)$_2$** (13 μM), (c) **(VI)$_3$** (7.9 μM) and (d) **(VI)$_4$** (6.3 μM) in $CHCl_3$:MeOH (96:4).

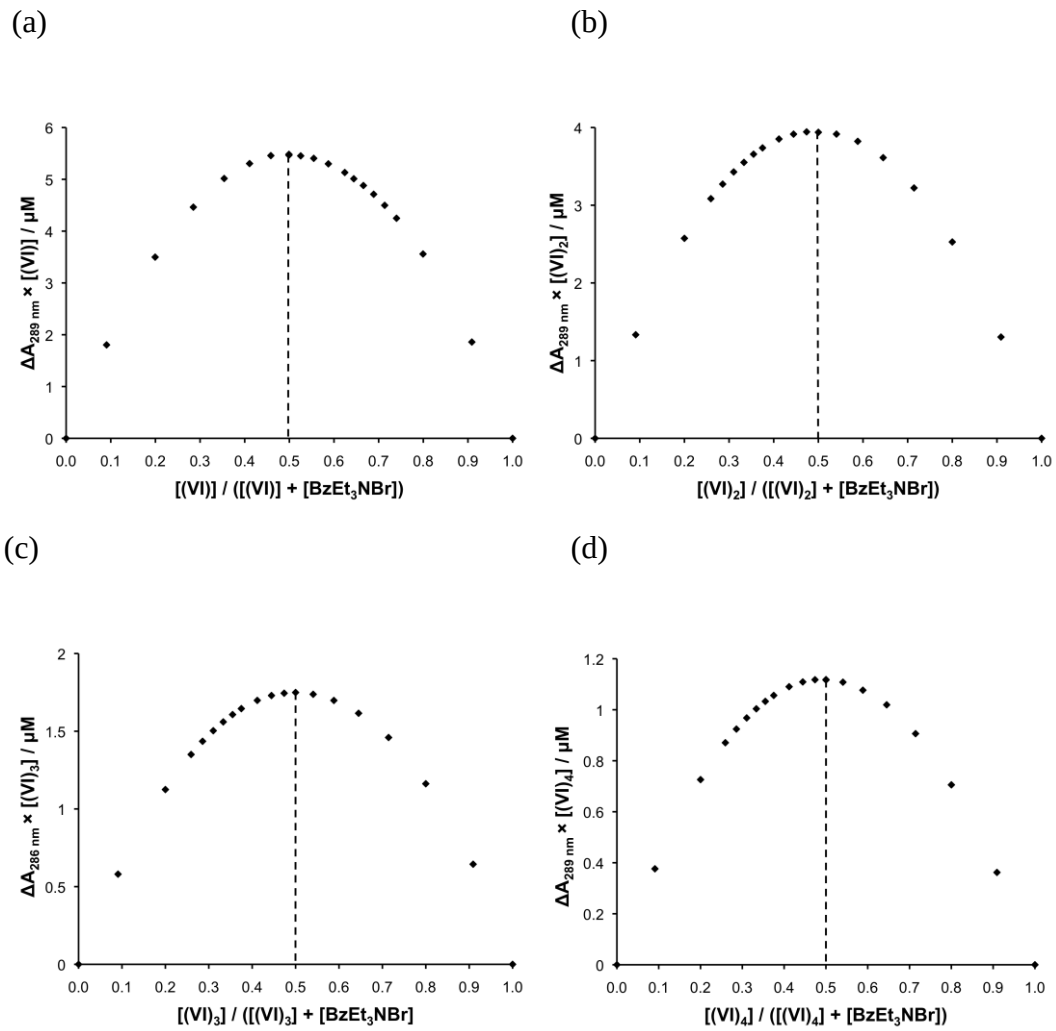


Figure S15. UV/Vis spectroscopy Job plots for the complexation of $BzEt_3NBr$ with (a) **(VI)** (25 μM), (b) **$(VI)_2$** (13 μM), (c) **$(VI)_3$** (7.9 μM) and (d) **$(VI)_4$** (6.3 μM) in $CHCl_3$:MeOH (96:4).

[1] M. Oberhoff, L. Duda, J. Karl, R. Mohr, G. Erker, R. Frohlich and M. Grehl, *Organometallics*, **1996**, *15*, 4005-4011.