SUPPLEMENTARY INFORMATION

Discriminating octahedral transition metal ions: Highly selective tripodal tris-(2,2´-bipyridine) functionalized piperazine cyclophane receptor for Cu^{2+} ions†

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Experimental

General

All chemicals and solvents were analytical reagent grade, purchased commercially and used as such. Analytical grade metal salts were used in a UV/VIS absorption experiments. Cyclophanes **3** and **4** were prepared previously from the reaction of piperazine and 1,3-bis(bromomethyl)-2-nitrobenzene under the high-dilution conditions followed by reduction of nitro-groups with stannous(II)chloride.[1] Melting points were measured with Mettler Toledo FP62 apparatus. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance DRX 500 FT NMR spectrometer operating at 500 MHz and 125 MHz by using CD_3OD as a solvent at -40 ºC. Mass spectra were obtained on a Micromass (ESI-TOF) spectrometer. Elemental analyses were performed with Elementar Analysesysteme GmbH VariolEL. UV/VIS spectra were recorded with Perkin Elmer Lambda 650 UV/VIS spectrophotometer.

Synthesis

1: diethyl 2,2'-bipyridine-5,5'-dicarboxylate was prepared according to the previously published procedure[2] from ethyl nicotinate in 10 % of palladium carbon. Yield: 7.2 g (6%) of colourless needles; m.p. 149 °C (lit.,[2] 145 – 157 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.43 (t, 6H), 4.44 (q, 4H), 8.42 (d, 2H), 8.57 (d, 2H), 9.28 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 126 MHz, CDCl3): δ = 14.5, 61.7, 121.5, 126.8, 138.3, 150.8, 158.5, 165.4 ppm.

2: Powdered KOH (0.56 g, 10 mmol) was dissolved in ethanol (65 ml) and added drop wise into the refluxing ethanol solution (40 ml) of **1** (3.0 g, 10 mmol). Insoluble potassium salt of 5'-(ethoxycarbonyl)-2,2'-bipyridine-5-carboxylic acid precipitated after few minutes. The bulk white solid was refluxed for additional 2 h, stirred at RT overnight and then collected by filtration. The crude product was mixed in dry dichloromethane (20 ml) and filtered again to obtain potassium (ethoxycarbonyl)-2,2'-bipyridine-5-carboxylate. The potassium salt was mixed into thionyl chloride (20 ml) and refluxed under nitrogen for 4 h. The clear solution was cooled and evaporated to dryness. The crude product was dissolved in dry dichloromethane (30 ml) and the insoluble residues were filtered off. The filtrate was collected and evaporated to dryness to obtain **2** as yellowish oil. Yield 1.76 g (60 %); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.45 (t, 3H), 4.55 (q, 2H), 8.40 – 8.54 (m, 2H), 8.58 – 8.72 (m, 2H), 9.25 – 9.37 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 126 MHz, $CDCl_3$): δ = 14.50, 61.92, 121.99, 122.11, 127.46, 129.69, 138.62, 139.92, 150.80, 151.83, 157.40, 160.15, 165.11, 167.05 ppm.

5: A mixture of **2** (1.40 g, 4.82 mmol) and dry dichloromethane (60 ml) was added into the stirred solution of cyclophane **3** (0.700 g, 1.15 mmol), triethylamine (0.550 g, 5.44 mmol) and dichloromethane (20 ml) at RT. The reaction mixture was poured into the dropping funnel and extracted with aqueous K_2CO_3 solution (100 ml). The organic layer was collected and dried by using K_2SO_4 and evaporated to dryness. The crude product was purified with flash chromatography by using DCM:MeOH:TEA (50:1:1) as eluent to obtain **5** as a white powder. Yield 1.47 g (93 %); ^{1}H NMR (500 MHz, -40 ºC, $CDCl_3$): δ = 1.44 (t, 9H), 1.51 (t, 3H), 1.84 (t, 3H), 2.17 (t, 6H), 2.47 (t, 3H), 2.53 (t, 3H), 2.96 (d, 3H), 3.02 (d, 3H), 3.20 (d, 6H), 3.92 (d, 3H), 3.98 (d, 3H), 4.42 (q, 6H), 7.01 (d, 3H), 7.10 (t, 3H), 7.62 (d, 3H), 8.38 – 8.55 (m, 12H), 9.21 (s, 3H), 9.28 (s, 3H), 11.54 (s, 3H) ppm; ; ^{13}C NMR ($CDCl_3$, 126 MHz, -40 ºC, $CDCl_3$): δ = 14.22, 50.78, 53.78, 54.95, 58.01, 61.67, 121.12, 125.78, 126.01, 128.33, 129.19, 129.34, 133.93, 135.01, 136.01, 138.26, 148.48, 150.34, 157.26, 157.52, 163.14, 165.09 ppm; ESI-MS (m/z): 1372.42 $[M+H]^+$, 1394.37 $[M+Na]^+$, 1410.37 $[M+K]^+$; Elemental analysis; calculated form $(C_{78}H_{81}N_{15}O_9)_5\cdot CH_2Cl_2\cdot CH_3OH$: C = 67.36, H = 6.01, N = 14.95 %; found: C = 67.45, H = 5.95, N = 15.05 %.

6: A mixture of **2** (0.172 g, 0.591 mmol) and dry dichloromethane (25 ml) was added into the stirred solution of cyclophane **4** (0.117 g, 1.15 mmol), triethylamine (0.073 g, 0.72 mmol) and dichloromethane (5 ml) at RT. The reaction mixture was poured into the dropping funnel and extracted with aqueous Na_2CO_3 solution (20 ml). The organic layer was collected and dried with Na_2SO_4 and evaporated to dryness. The crude product was purified with flash chromatography with DCM:MeOH:TEA (50:1:1) as eluent to obtain **6** as a white powder. Yield 0.25 g (95 %); ^{1}H NMR (500 MHz, -40 ºC, $CDCl_3$): δ = 1.41 (t, 12H), 1.81 (t, 4H), 2.03 (t, 4H), 2.30 – 2.65 (m, 16H), 2.81 (d, 4H), 3.05 (d, 4H), 3.21 (t, 8H), 3.92 (dd, 8H), 4.41 (q, 8H), 7.06 (d, Hz, 4H), 7.17 (t, 4H), 7.72 (d, 4H), 8.38 – 8.70 (m, 16H), 9.22 (s, 4H), 9.28 (s, 4H), 11.33 (s, 4H) ppm; ^{13}C NMR ($CDCl_3$, 126 MHz, -40 ºC, $CDCl_3$): δ = 14.20, 51.43, 54.40, 57.63, 61.66, 62.24, 121.10, 121.79, 125.70, 126.07, 127.50, 127.89, 129.47, 129.79, 133.77, 134.90, 136.90, 138.32, 148.26, 150.49, 157.53, 157.72, 162.56, 165.04 ppm; ESI-MS (m/z): 1830.70 $[M+H]^+$, 1851.66 $[M+Na]^+$, 1867.81 $[M+K]^+$; Elemental analysis; calculated form $C_{104}H_{108}N_{20}O_{12}\cdot CH_2Cl_2\cdot CH_3OH$: C = 67.15, H = 6.08, N = 15.02 %; found: C = 67.26, H = 5.93, N = 14.99 %.

7: A suspension of **5** (0.123 g, 0.09 mmol), powdered KOH (0.500 g, 8.91 mmol) and ethanol (4 ml) was stirred at 75 ºC for 12 h. The clear mixture was cooled and carefully neutralized with conc. HCl. The resulted white precipitate was collected by filtration and washed abundantly with water and ethanol and recrystallized form $FeSO_4$ solution to obtain red prisms. Yield 0.63 g; ESI-MS (m/z): 428.1 $[M-3H]^{3-}$.

UV/VIS spectroscopy

Job's plot: The measurements were carried out in 0.35 M (pH 2.6) acetic acid solutions at 21.7 °C. Job's plot was prepared from the absorption spectra of eleven mixtures, where the mole fraction of the ligand $\boldsymbol{x}_\mathbf{L}$ was varied from 0 to 1, while the total concentration ($c[\mathbf{5}]_{aq} + c[Fe^{2+}]_{aq} + c[\mathbf{5}\cdot Fe]^{2+}_{aq}$ = 0,203 mM and $c[\mathbf{6}]_{aq} + c[Fe^{2+}]_{aq} + c[\mathbf{6}\cdot Fe]^{2+}_{aq}$ = 0,265 mM) was kept constant (Figures S1 and S2). The absorption maxima (**A**) for each spectrum was recorded (574 nm). Assuming that only one $[\mathbf{L_n}\cdot M]^{2+}_{aq}$ complex is formed, the value of $\boldsymbol{n}$ was calculated from the equation $\boldsymbol{n} = \boldsymbol{x}_\mathbf{max}/1-\boldsymbol{x}_\mathbf{max}$, where the $\boldsymbol{x}_\mathbf{max}$ is the mole fraction of the ligand ($x[\mathbf{5}]$ or $x[\mathbf{6}]$) at the absorption maxima (Figures S3 and S4).

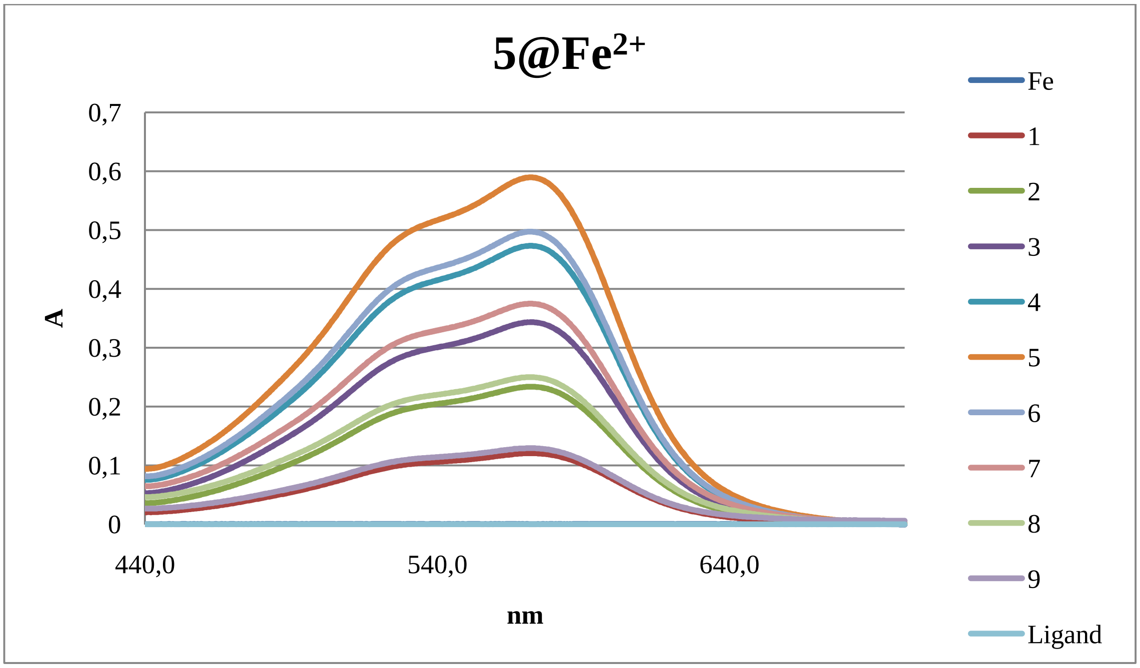


Figure S1. UV/VIS measurement of the complex of **5** (*Ligand*) and $Fe(BF_4)_2$ (*Fe*), showing increment of absorption at 574 nm, where the samples 1 to 9 represents the molar fractions from 1:9 to 9:1 of [**5**]:[Fe^{2+}].

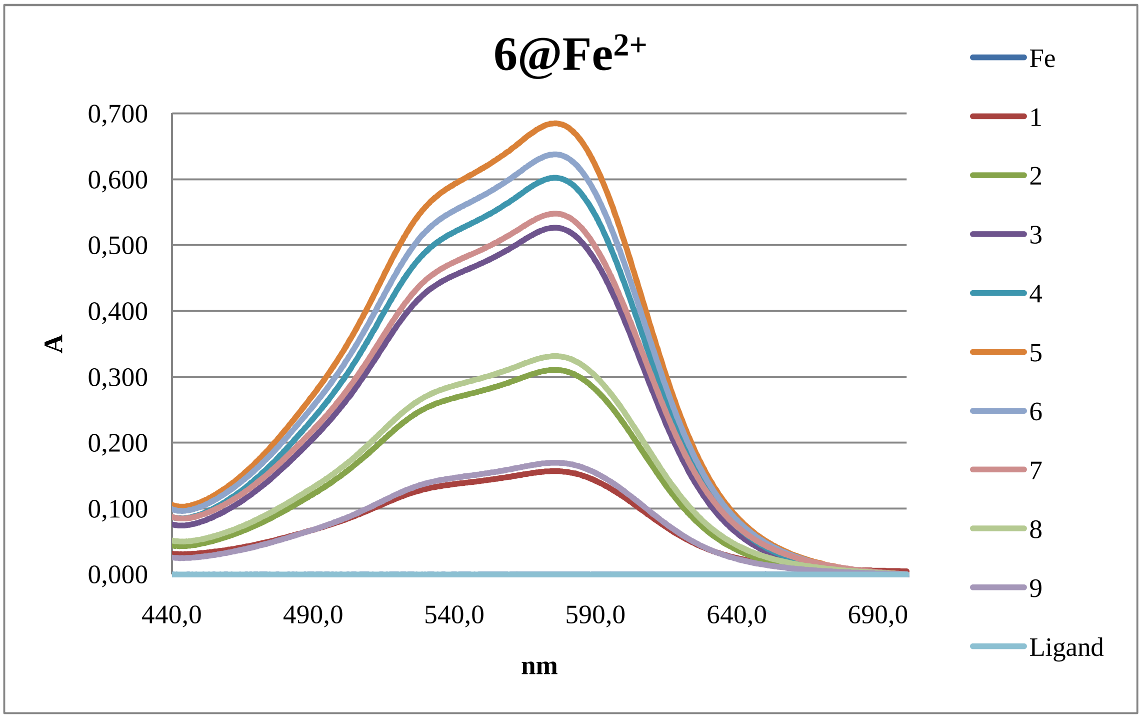


Figure S2. UV/VIS measurement of the complex of **6** (*Ligand*) and $Fe(BF_4)_2$ (*Fe*), showing increment of absorption at 574 nm, where the samples 1 to 9 represents the molar fractions from 1:9 to 9:1 of [**6**]:[Fe^{2+}]

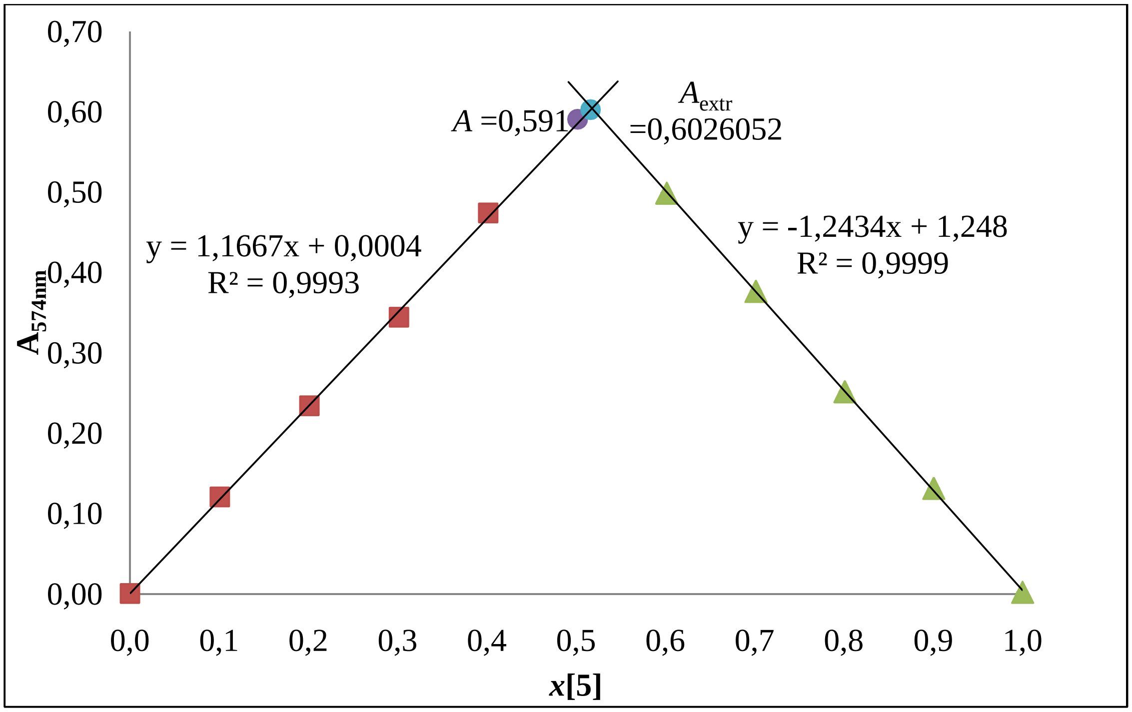


Figure S3. Job's plot in 0.35 M acetic acid solution showing the maximum absorption A, and extrapolated absorption A_{extr} for [**5**·Fe]$^{2+}_{aq}$ (above).

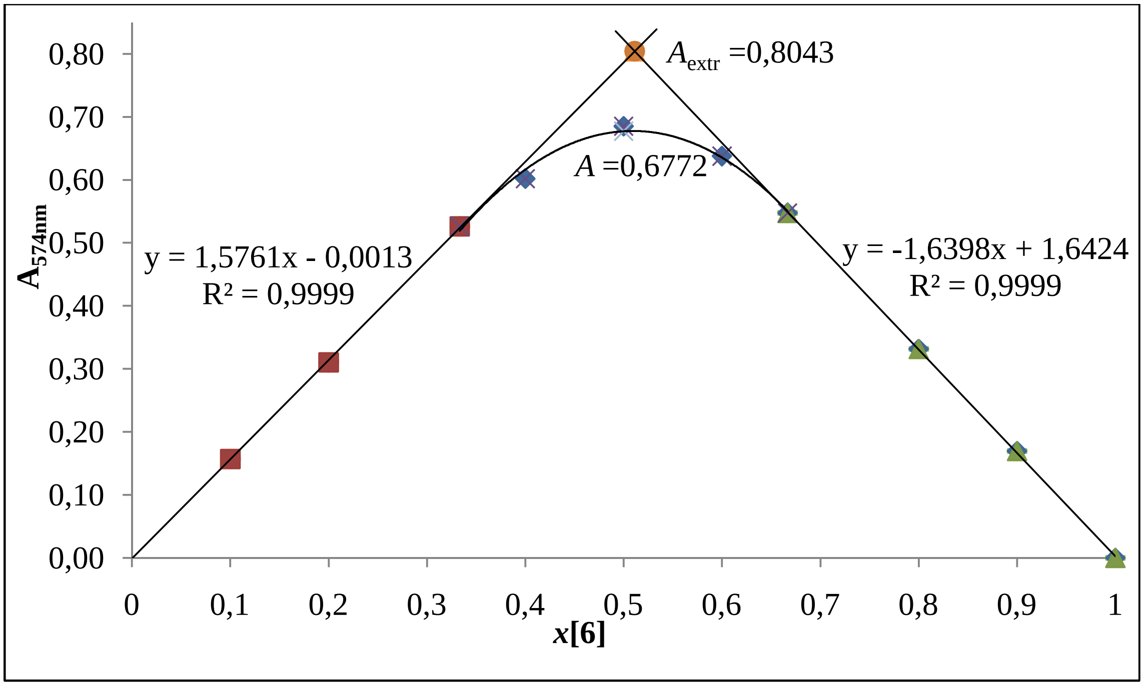


Figure S4. Job's plot in 0.35 M acetic acid solution showing the maximum absorption A, and extrapolated absorption A_{extr} for [**6**·Fe]$^{2+}_{aq}$.

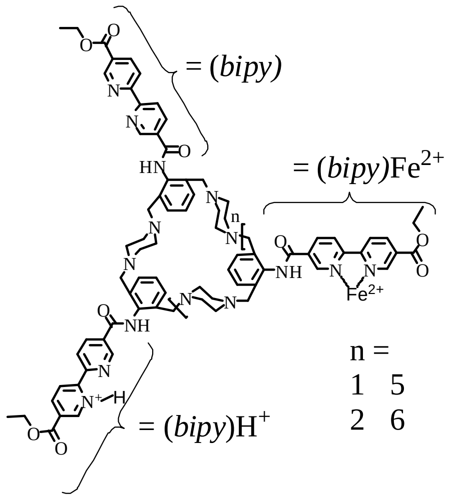
Determination of complex stability constants log$K_{(5)}$, log$K_{(6)}$ and the relative stability $R_{(5/6)}$ from the Job's plots of $[5\cdot Fe]^{2+}_{aq}$ and $[6\cdot Fe]^{2+}_{aq}$.

Under the acidic (pH 2.61) experimental conditions, each 2,2'-bipyridine groups (*bipy*) in ligands **5** and **6** were assumed to be protonated once. During the complexation, the pyridines were also assumed to coordinate Fe^{2+} ion independently (bidentate, tetradentate or octadentate binding).

$$\left.\begin{aligned} (bipy)H^+ &\xrightarrow{K_a} (bipy)+H^+\\ (bipy)H^+ &\xrightarrow{K_a} (bipy)+H^+\\ (bipy)H^+ &\xrightarrow{K_a} (bipy)+H^+ \end{aligned}\right\} = K_a \times K_a \times K_a$$

$$\left.\begin{aligned} (bipy)+Fe^{2+} &\xrightarrow{K_1} (bipy)Fe^{2+}\\ (bipy)+(bipy)Fe^{2+} &\xrightarrow{K_2} (bipy)_2Fe^{2+}\\ (bipy)+(bipy)_2Fe^{2+} &\xrightarrow{K_3} (bipy)_3Fe^{2+} \end{aligned}\right\} = K_i$$

$$\overline{3(bipy)H^+ + Fe^{2+} \longrightarrow (bipy)_3Fe^{2+} + 3H^+ \,\|\, K_i^{tot}}$$



K_i is the stability constant $\boldsymbol{K_{(5)}}$ and $\boldsymbol{K_{(6)}}$ of the ligands **5** and **6**. The same pH (= 2,61) was used in all experiments. *logK_a* values for each 2,2´-bipyridine moieties in **5** and **6** were approximated to be equal with 2,2´-bipyridine (logK_a = 4.30) (equation 1).

$$(1) \qquad K_i = K_i^{tot} \times \frac{1}{(K_a)^3} = \frac{[(bipy)_3Fe^{2+}]_i}{[(bipy)H^+]_i^3 \times [Fe^{2+}]_i} \times \frac{[H^+]^3}{[K_a]^3}$$

***R*$_{5/6}$** is the ratio of the stability constants $\boldsymbol{K_{(5)}}$ and $\boldsymbol{K_{(6)}}$ of the ligands **5** and **6** (equation 2).

$$(2) \qquad i = 5,6 \Rightarrow \qquad R_{5/6} = \frac{K_5}{K_6} = \frac{[(bipy)_3Fe^{2+}]_5 \times [(bipy)H^+]_6^3 \times [Fe^{2+}]_6}{[(bipy)H^+]_5^3 \times [Fe^{2+}]_5 \times [(bipy)_3Fe^{2+}]_6}$$

The concentration of the complex $[(\mathit{bipy})_3\mathrm{Fe}^{2+}]_i$ (i = 5, 6) can be calculated from the ration of the A/$\mathrm{A}_{\mathrm{extr}}$ and the initial concentration of the ligand (or $\mathrm{Fe(BF_4)_2}$) (equation 3).

$$(3)\qquad \left[(bipy)_3 Fe^{2+}\right]_i = \left(\frac{A}{A_{extr}}\right)_i \times C_i^{(bipy)_3 Fe^{2+}}$$

Where A is the measured maximum absorbance and A_{extr} is the extrapolated absorbance (see job's plots in Figures S3 and S4 and the reference 3). $C_i^{(bipy)_3 Fe^{2+}}$ Represents the theoretical maximum concentration of the complex $[(\mathit{bipy})_3\mathrm{Fe}^{2+}]_i$.

The concentration of the free 2,2´-*bipy* groups $[(\mathit{bipy})H^+]_i$ and iron(II) $[\mathrm{Fe}^{2+}]_i$ (i = 5, 6) can be calculated from the concentration of the complex $[(\mathit{bipy})_3\mathrm{Fe}^{2+}]_i$ (i = 5, 6) (equations 4 and 5).

$$(4)\qquad \left[Fe^{2+}\right]_i = C_i^{Fe^{2+}} - \left[(bipy)_3 Fe^{2+}\right]_i$$

$$(5)\qquad \left[(bipy)H^{+}\right]_i = 3C_i^{Lig.} - 3\left[(bipy)_3 Fe^{2+}\right]_i$$

Where $C_i^{Lig.}$ and $C_i^{Fe^{2+}}$ (i = 5, 6) are the initial concentration of the ligand (**5** or **6**) and $\mathrm{Fe(BF_4)_2}$, respectively. Each ligand ($C_i^{Lig.}$) provides three 2,2´-bipy moieties *(bipy)*.

Results are collected in table S1.

Table S1. The absorbances and concentrations [mM] for the calculations of $\boldsymbol{K_{(5)}}$, $\boldsymbol{K_{(6)}}$ and $\boldsymbol{R_{(5/6)}}$.

	A_{extr}	A	$\left[(bipy)_3Fe^{2+}\right]_i$	$C_i^{Fe^{2+}}$	$C_i^{Lig.}$	$\left[(bipy)H^+\right]_i$	$\left[Fe^{2+}\right]_i$
5	0.6026	0.5907	0.09890 mM	0.1009 mM	0.1015 mM	0.007838 mM	0.00199 mM
6	0.8043	0.6772	0.11165 mM	0.1327 mM	0.1326 mM	0.062863 mM	0.02110 mM

$$c\left[H^+\right] = 10^{-2,61} M \qquad K_a = \frac{[2,2'\!-\!bipy]\times\left[H^+\right]}{\left[2,2'\!-\!bipyH^+\right]} = 10^{-4,3} M$$

$$\Rightarrow \frac{\left[H^+\right]^3}{\left[K_a\right]^3} = \frac{(10^{-2,61} M)^3}{(10^{-4,3} M)^3} = 10^{5,07}$$

$$K_{(5)} = \frac{[0.09890]_5}{[0.007838]_5^3 \times [0.00199]_5} \times \frac{10^{-3} M}{(10^{-3})^4 M} \times 10^{5.07} = 10^{22.08} M^{-3}$$

$$K_{(6)} = \frac{[0.11165]_6}{[0.062863]_6^3 \times [0.02110]_6} \times \frac{10^{-3} M}{(10^{-3})^4 M} \times 10^{5.07} = 10^{18.39} M^{-3}$$

$$\log K_{(5)} = 22.08$$

$$\log K_{(6)} = 18.39$$

$$\log R_{(5/6)} \approx 3.69$$

The competition experiment: Five stock solutions ***a* – *e*** (8.855 ± 0.003 mM) of each metal ion $\mathbf{M}^{2+}$ (Fe^{2+}(***a***), Ni^{2+}(***b***), Co^{2+}(***c***), Cu^{2+}(***d***), Zn^{2+}(***e***)) were prepared from the sulphate salt (Table S2). Stock solutions ***a* – *e*** (1.000 ml of each) where then mixed to the six 20 ml flasks to obtain following mixtures: ***a***, ***a* + *b***, ***a* + *c***, ***a* + *d***, ***a* + *e*** and ***b* + *c* + *d* + *e*,** followed by acidification with HAc (0.400 ml, 99 %) and then dilution to the volume of 20 ml ($c[\mathbf{M}^{2+}]$ = 0.4428 ± 0.0004 mM) (Table S3). Stock solution of **5** was prepared by dissolving **5** (12.154 mg, 0.00885 mmol) in HAc (0.400 ml) and diluting the solution to the volume of 20 ml (*c*[**5**] = 0.4427 mM). Stock solution of reference ligand 5,5´-dimethyl-2,2´-bipyridine (**L**) was prepared in a analogical manner (24.474 mg, 0.13284 mmol, *c*[**L**] = 1.3284 mM) (Table S4). Twelve solution (six for **5** and another six for **L**) for the UV-VIS spectroscopy were prepared by adding 1 ml of solution containing the mixture of metals (see table S3), 1 ml of ligand solution (**5** or **L**) and diluted with 1 ml of 0.35 M HAc solution ($c[\mathbf{5}] = c[\mathbf{M}^{2+}] = c^{1}/_{3}[\mathbf{L}]$ = 0.1476 *mM*) (Table S5).

Table S2. The stock solutions.

Solution		**m[mg]**	**M[g/mol]**	**n[mmol]**	***c*[mM]**
a	$Fe(SO_4)\bullet 7H_2O$	123.1	278.01	0.4428	8.856
b	$Co(SO_4)\bullet 7H_2O$	124.5	281.10	0.4429	8.858
c	$Ni(SO_4)\bullet 6H_2O$	116.4	262.85	0.4428	8.857
d	$Cu(SO_4)\bullet 5H_2O$	110.5	249.69	0.4425	8.851
e	$Zn(SO_4)\bullet 7H_2O$	127.3	287.55	0.4427	8.854

Table S3. The metal mixtures.

	Concentration of metal ion [mM]				
Mixture	***c*[Fe^{2+}]**	***c*[Co^{2+}]**	***c*[Ni^{2+}]**	***c*[Cu^{2+}]**	***c*[Zn^{2+}]**
b* + *c* + *d* + *e	-	0.4429	0.4428	0.4425	0.4427
a	0.4428	-	-	-	-
a* + *b	0.4428	0.4429	-	-	-
a* + *c	0.4428	-	0.4428	-	-
a* + *d	0.4428	-	-	0.4425	-
a* + *e	0.4428	-	-	-	0.4427

Table S4. The stock solution of the ligands **5** and **L**.

	m [mg]	**M [g/mol]**	**n [mmol]**	***c*[mM]**
5	12.154	1372.61	0.00885	0.4427
L (5,5-dimethyl-2,2´-bipy)	24.474	184.24	0.13284	1.3284

Table S5. Samples for the UV/VIS experiments.

	Concentration of the ligand and metal ions [mM]					
Sample	***c*[Fe^{2+}]**	***c*[Co^{2+}]**	***c*[Ni^{2+}]**	***c*[Cu^{2+}]**	***c*[Zn^{2+}]**	***c*[Lig.]**
[**L**]:[Fe]	0.1476	-	-	-	-	0,4427
[**L**]:[Fe]:[Co]	0.1476	0.1476	-	-	-	0,4427
[**L**]:[Fe]:[Ni]	0.1476	-	0.1476	-	-	0,4427
[**L**]:[Fe]:[Cu]	0.1476	-	-	0.1475	-	0,4427
[**L**]:[Fe]:[Zn]	0.1476	-	-	-	0.1476	0,4427
[**L**]:[Co]:Ni]:[Cu]:[Zn]	-	0.1476	0.1476	0.1475	0.1476	0,4427
[**5**]:[Fe]	0.1476	-	-	-	-	0.1476
[**5**]:[Fe]:[Co]	0.1476	0.1476	-	-	-	0.1476
[**5**]:[Fe]:[Ni]	0.1476	-	0.1476	-	-	0.1476
[**5**]:[Fe]:[Cu]	0.1476	-	-	0.1475	-	0.1476
[**5**]:[Fe]:[Zn]	0.1476	-	-	-	0.1476	0.1476
[**5**]:[Co]:Ni]:[Cu]:[Zn]	-	0.1476	0.1476	0.1475	0.1476	0.1476

X-Ray crystallography

Suitable crystals of **I**, **V** (Figure S5) and **VII** (Figure S6) for the single crystal X-ray diffraction analyses were selected and analyses were performed by using a Bruker Kappa Apex II diffractometer with graphite-monochromatized Mo-K_α (λ = 0.71073 Å) radiation for **I** and **VII**, and Cu-K_α (λ = 1.54184 Å) radiation for **V**. Collect software[4] was used for the data collection and DENZO-SMN[5] for the data reduction. The structures were solved by direct methods with SIR97[6] and refined by full-matrix least-squares methods with WinGX-software,[7] which utilizes the SHELXL-97.[8] All C–H hydrogen positions were calculated in the idealized positions by using a riding atom model after the anisotropic refinement of all non-hydrogen atoms of the structure. If possible, all N–H hydrogens were located from the electron density map and refined with restrained bond distances using isotropic displacement parameters of $1.2U_{eq}$ of the attached N-atom. Most of the O–H hydrogens were located from the electron density map and refined as a rotating group by using the same ($1.2\ U_{eq}$) isotropic displacement parameters. In case of **VII**, the water O–H hydrogens could not be located from the electron density map. Detailed crystallographic data for **I**, **V** and **VII** is depicted in Table S6.

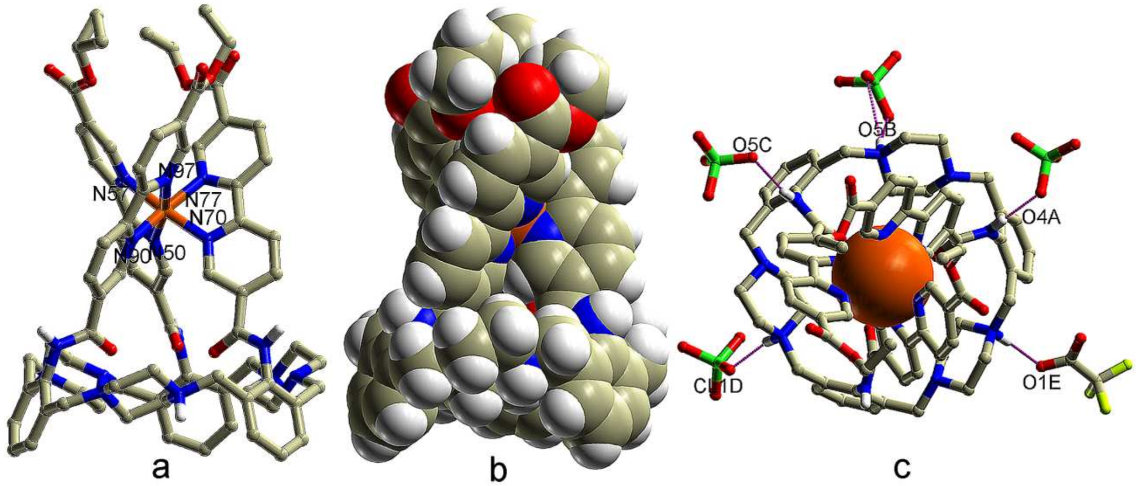


Figure S5 A view of the crystal structure of **V**; solvent molecules and counter ions are omitted for clarity (**a**) and the top view of the complex (**b**) with the counter ions. Distances and angles for the six N–H···O H-bonds; 2.742(13) Å and 144.5º [N8-H···O5D], 3.031(16) and 171.5 [N22-H···O5B], 2.731(13) and 161.5 [N36-H···O1E], 3.000(13) and 155.9 [N43-H···O3D*], 2.822(14) and 157.9 [N63-H···O5C], 2.955(13) and 167.3 [N83-H···O4A] (*another symmetrically equivalent site).

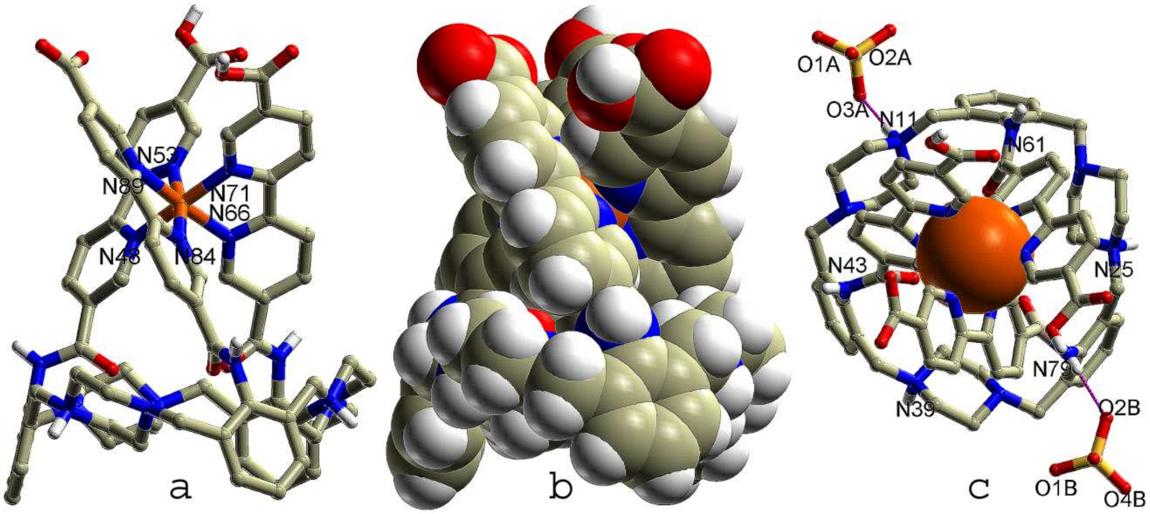


Figure S6 A view of the crystal structure of **VII**; solvent molecules and counter ions are omitted for clarity (**a**) and the top view of the complex (**b**) with the counter ions. Distances and angles for the six N–H···N and the two carboxyl H-bonds; 2.751(4) Å and 168.9º [N11-H···O3A], 2.755(4) Å and 170.1º [N25-H···O1A*], 2.768(4) Å and 170.5º [N39-H···O2A*], 2.947(6) Å and 157.4º [N43-H···O4B*], 2.993(5) Å and 162.5º [N61-H···O1B*], 2.983(6) Å and 165.7º [N79-H79···O2B], 2.553(4) Å and 163.1º [O59-H···O2A*], 2.504(5) Å and 168.8º [O78-H···O3] (* another symmetrically equivalent site).

Table S6 Crystallographic data for **I**, **V** and **VII**.

Crystal	**I**	**V**	**VII**
Formula	$C_{56}H_{65}Cl_2\ N_7O_2Fe$	$C_{81}H_{86}Cl_4F_3N_{15}O_{28}Fe$	$C_{72}H_{71}N_{15}O_{43}S_2Fe$
space group	*P* 21/*c*	*P* -1	*C c*
***a* [Å]**	14.9147(2)	13.6922(14)	13.8873(2)
***b* [Å]**	24.5620(4)	18.3992(14)	24.0212(3)
***c* [Å]**	16.5450(2)	19.312(2)	31.2772(4)
***α* [º]**	90	110.059(4)	90
***β* [º]**	94.707(1)	91.044(6)	101.126(1)
***γ* [º]**	90	94.961(6)	90
***V* [Å3]**	6040.5(2)	4547.0(7)	10237.6(2)
Z	4	2	4
T [K]	123(2)	173(2)	123(2)
D_{calc} [Mg/m^3]	1.428	1.441	1.268
μ [mm^{-1}]	0.421	3.206	0.278
F[0.0.0]	2712	2044	4040
***θ* max [º]**	25.0	63.32	27.50
***θ* comp.[%]**	99.8	94.6	99.5
refl. collect. / uniq.	70828 /10625	12686 / 12686	64949 / 23401
parameters	795	1232	1250
restrains	0	249	16
***R*1 [I>2σ(I)]**	0.0630	0.1204	0.0778
w*R*2 [I>2σ(I)]	0.1265	0.2774	0.2163
GOF on F^2	1.050	1.055	1.089
ΔF_{max} [$eÅ^3$]	0.968	1.236	1.186
ΔF_{min} [$eÅ^3$]	-0.660	-1.126	-1.510

Table S7. Selected bond lengths [Å] and angles [º] for **Fe@I**, **VI** and **VII**.

Fe@V		**Fe@VII**		**Fe@I**	
Bond distance	**[Å]**	**Bond distance**	**[Å]**	**Bond distance**	**[Å]**
Fe-N(70)	1.965(9)	Fe-N(84)	1.963(3)	Fe-N(54)	1.962(3)
Fe-N(97)	1.979(9)	Fe-N(53)	1.967(4)	Fe-N(32)	1.967(3)
Fe-N(57)	1.992(9)	Fe-N(48)	1.968(3)	Fe-N(61)	1.969(3)
Fe-N(90)	1.978(8)	Fe-N(66)	1.968(3)	Fe-N(39)	1.969(3)
Fe-N(50)	1.979(9)	Fe-N(71)	1.971(3)	Fe-N(10)	1.972(3)
Fe-N(77)	1.999(9)	Fe-N(89)	1.979(4)	Fe-N(17)	1.978(3)
Bond angle	**[º]**	**Bond angle**	**[º]**	**Bond angle**	**[º]**
N(70)-Fe-N(97)	94.3(3)	N(84)-Fe-N(66)	95.10(14)	N(54)-Fe-N(39)	89.40(13)
N(70)-Fe-N(50)	94.8(4)	N(84)-Fe-N(48)	93.53(14)	N(54)-Fe-N(10)	91.42(13)
N(70)-Fe-N(90)	92.3(3)	N(84)-Fe-N(89)	80.96(14)	N(54)-Fe-N(32)	96.01(13)
N(90)-Fe-N(97)	80.4(3)	N(53)-Fe-N(66)	92.12(15)	N(32)-Fe-N(39)	81.85(13)
N(90)-Fe-N(50)	96.1(3)	N(53)-Fe-N(71)	93.32(15)	N(32)-Fe-N(17)	89.91(13)
N(90)-Fe-N(57)	96.0(3)	N(53)-Fe-N(89)	92.44(16)	N(32)-Fe-N(10)	96.58(13)
N(77)-Fe-N(70)	80.9(4)	N(48)-Fe-N(89)	93.14(14)	N(61)-Fe-N(54)	81.88(13)
N(77)-Fe-N(50)	94.6(3)	N(48)-Fe-N(66)	94.08(14)	N(61)-Fe-N(39)	94.67(13)
N(77)-Fe-N(97)	90.0(3)	N(48)-Fe-N(53)	81.18(14)	N(61)-Fe-N(10)	86.93(13)
N(50)-Fe-N(50)	81.0(4)	N(71)-Fe-N(84)	92.54(14)	N(17)-Fe-N(39)	97.53(12)
N(50)-Fe-N(97)	90.4(4)	N(71)-Fe-N(66)	80.79(14)	N(17)-Fe-N(10)	81.78(13)
N(50)-Fe-N(77)	91.5(3)	N(71)-Fe-N(89)	92.35(15)	N(17)-Fe-N(61)	92.56(13)

References

1 K. Raatikainen, J. Huuskonen, E. Kolehmainen, K. Rissanen, *Chem. Eur. J.*, 2008, **14**, 3297.

2 G. R. Newkome, J. G. Patri, A. K. Patri, *J. Org. Chem.*, 1997, **62**, 3013

3 Huang C. Y., *Methods in enzymology*, 1982, **87**, 509; Job, P., *Ann. Chim.*, 1928, **9**, 113; M. M Krunz, L. B. Pfendt, Lidija B, Microchemical Journal, 1983, **28**, 162.

4 R. W. Hooft, COLLECT, Nonius BV, Delft (The Netherlands), **1998.**

5 Z. Otwinowski, W. Minor, *Methods in Enzymology*, 1997, **276**, *Macromolecular Crystallography*, Part A, 307.

6 A. Altomare M. C. Burla M. Camalli G. L. Cascarano C. Giacovazzo A. Guagliardi A. G. G. Moliterni G. Polidori R. Spagna, *J. Appl. Crystallogr*. 1999, **32**, 115.

7 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.

8 G. M. Sheldrick, Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.