Electronic Supplementary Information

On Zn(II) 2,2‘-Bis-dipyrrin Circular Helicates

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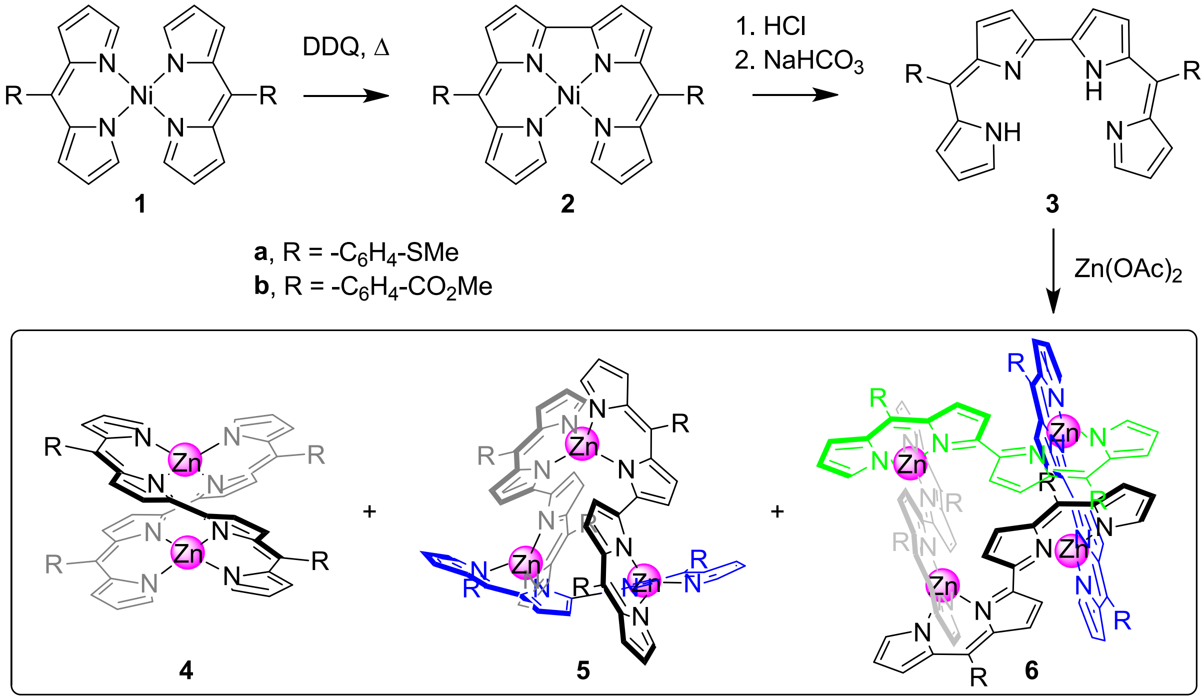


Scheme ESI1 Synthetic route for the formation of [2+2] helicate **4**, tri- [3+3] and tetra-nuclear [4+4] complexes **5** and **6**

Synthesis

Ni(II) complex **1a** was synthesized following the protocol described for the Cu(II) analogue.[1] Complex **1b** was prepared according to a reported procedure.[2] ^{1}H and ^{13}C NMR spectra were recorded at 25 °C on a Bruker AV300 (300 MHz), AV400 (400 MHz) or AV500 (500 MHz) with the deuterated solvent as the internal reference. NMR chemical shifts and *J* values are given in parts per million (ppm) and in Hertz, respectively. Mass spectrometry was performed by the Service commun d’analyse (University of Strasbourg).

Complex **1a**: To a $CHCl_3$ (750 mL) solution of the corresponding dipyrromethane (3 g, 11.1 mmol), a benzene (750 mL) solution of DDQ (2.60 g, 11.4 mmol) was added dropwise. After stirring at room temperature for 2 hours, a THF (100 mL) solution of $Ni(BF_4)_2(H_2O)_6$ (1.6 g, mmol) was added. The mixture was left to stir for 3 days. After evaporation to dryness, purification by column chromatography (SiO_2, $CHCl_3$ to $CHCl_3$/AcOEt 1/1) afforded complex **1a** as a red-green dichroic solid (1.23 g, 36 %). δ_H (500 MHz, CD_2Cl_2) 2.55 (s, 6H), 6.81 (d, J = 4.6 Hz, 4H), 7.27-7.29 (m, 4H), 7.35-7.37 (m, 4H), 7.44 (br s, 4H), 9.23 (br s, 4H). δ_C (125 MHz, CD_2Cl_2) 15.1, 124.7, 130.6, 131.4, 133.3, 138.5, 140.9, 143.4, 143.6, 167.5. $\lambda_{max}(CH_2Cl_2)$/nm (ε/mol^{-1} L cm^{-1}): 256 (42500), 380 (25500), 475 (45500). Single crystals were obtained by *n*-pentane vapor diffusion into a solution of the complex in $CHCl_3$.

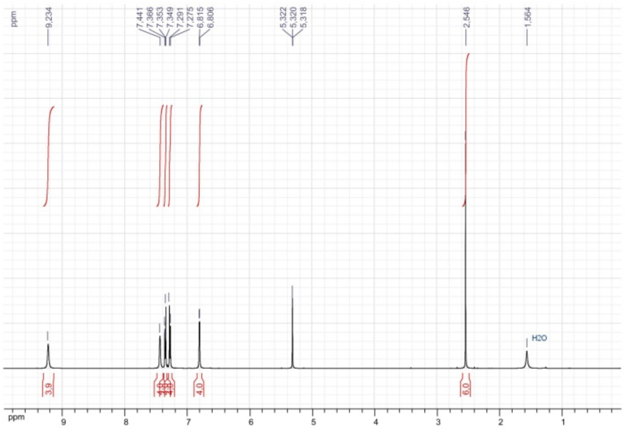


Fig. ESI1 ^{1}H NMR spectrum of complex **1a** in CD_2Cl_2.

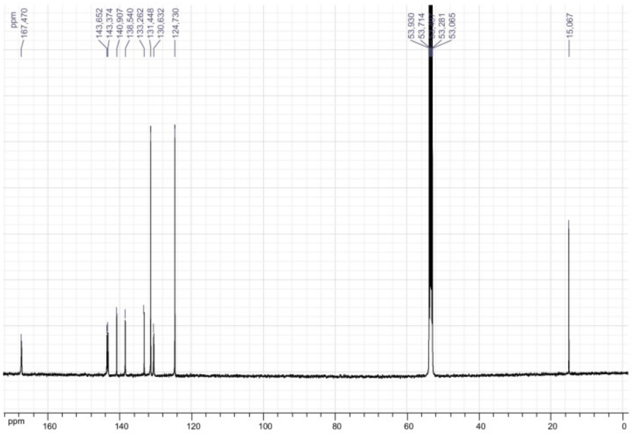


Fig. ESI2 ^{13}C NMR spectrum of complex **1a** in CD_2Cl_2.

Complex **2a**: A toluene (100 mL) solution of DDQ (0.339 g, 1.5 mmol) was added to a toluene (300 mL) solution of complex **1a** (0.800 g, 1.3 mmol) and the mixture was heated at reflux overnight. TLC (SiO_2, $CHCl_3$) revealed the presence of unreacted complex and DDQ (160 mg, 0.7 mmol) was added. After reflux for an additional day, the mixture was evaporated to dryness and the residue was purified by column chromatography (SiO_2, $CHCl_3$) affording **2a** as a brown solid (0.552 g, 69%). δ_H (500 MHz, $CDCl_3$) 2.55 (s, 6H), 5.96 (m, 2H), 6.41 (dd, J = 1.4 and 4.1 Hz, 2H), 6.60 (d, J = 4.4 Hz, 2H), 6.75 (d, J = 4.4 Hz, 2H), 6.78 (d, J = 4.1 Hz, 2H), 7.31 (d, J = 8.0 Hz, 4H), 7.48 (d, J = 8.0 Hz, 4H). δ_C (125 MHz, $CDCl_3$) 15.5, 115.3, 117.1, 125.1, 129.9, 131.5, 133.4, 134.6, 135.8, 138.8, 140.5, 143.2, 153.6, 160.6. λ_{max}(CH_2Cl_2)/nm (ε/mol^{-1} L cm^{-1}): 257 (33000), 373 (19000), 419 (37500), 565 (11000), 760 (5000), 838 (10000). HRMS (ESI), *m*/*z*: $[M]^+$ calcd. for $C_{34}H_{24}N_4NiS_2$: 586.0790; found: 586.0738. Single crystals were obtained by Et_2O vapor diffusion into a solution of the complex in CH_2Cl_2.

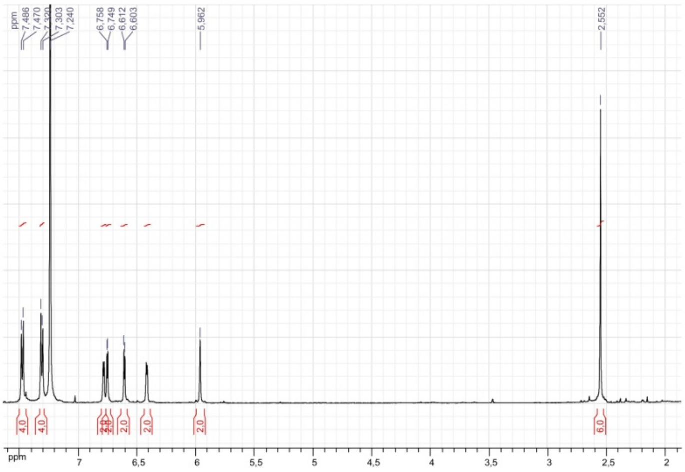


Fig. ESI3 ^{1}H NMR spectrum of complex **2a** in $CDCl_3$.

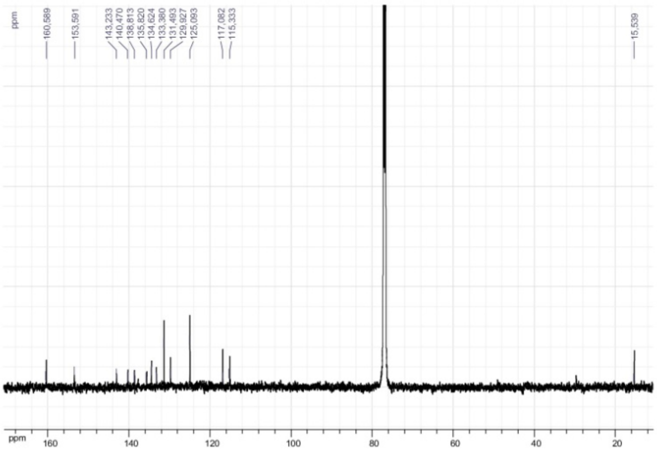


Fig. ESI4 ^{13}C NMR spectrum of complex **2a** in $CDCl_3$.

Bis-dipyrrin **3a**: To a $CHCl_3$ (75 mL) solution of complex **2a** (0.515 g, 0.88 mmol), a 12 M solution of HCl (5 mL) was added and the mixture was stirred at room temperature for 5 hours. Upon addition of a saturated Na_2CO_3 solution, the organic layer turned from green to dark blue. The organic phase was recovered and washed with H_2O (2x100 mL). The organics were dried over Na_2SO_4 and evaporated to dryness to afford ligand **3a**($CHCl_3$) as a dark blue solid (0.510 g, 89%). δ_H (500 MHz, CD_2Cl_2) 2.57 (s, 6H), 6.43 (dd, J = 1.8 and 4.8 Hz 2H), 6.61 (dd, J = 1.1 and 4.1 Hz 2H), 6.83 (d, J = 4.1 Hz, 2H), 7.32 (s, 1H, $CHCl_3$), 7.34-7.36 (m 4H), 7.47-7.49 (m, 4H), 7.61 (br s, 2H). δ_C (125 MHz, CD_2Cl_2) 15.1, 115.6, 120.2, 125.0, 126.1, 131.5, 132.1, 133.6, 137.9, 138.6, 140.3, 140.6, 145.8, 153.4. λ_{max}(CH_2Cl_2)/nm (ε/mol^{-1} L cm^{-1}): 262 (24000), 347 (11500), 411 (29000), 560 (32000), 594 (37000), 730 (2600). HRMS (ESI), *m/z*: $[M+H]^+$ calcd. for $C_{32}H_{27}N_4S_2$: 531.1672; found: 555.1678. Single crystals were obtained by slow evaporation of a $CHCl_3$ solution of the bis-dipyrrin.

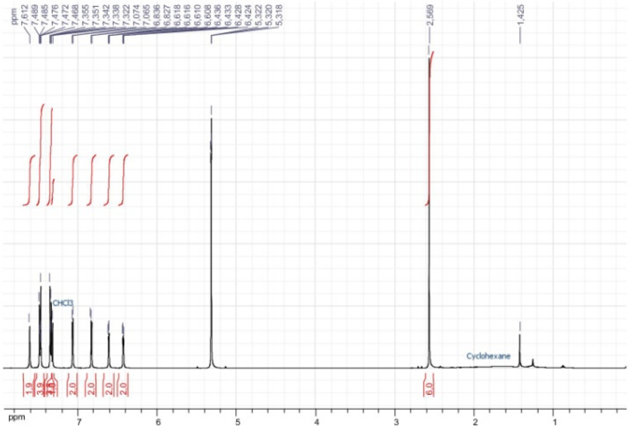


Fig. ESI5 ^1H NMR spectrum of bis-dipyrrin **3a** in CD_2Cl_2.

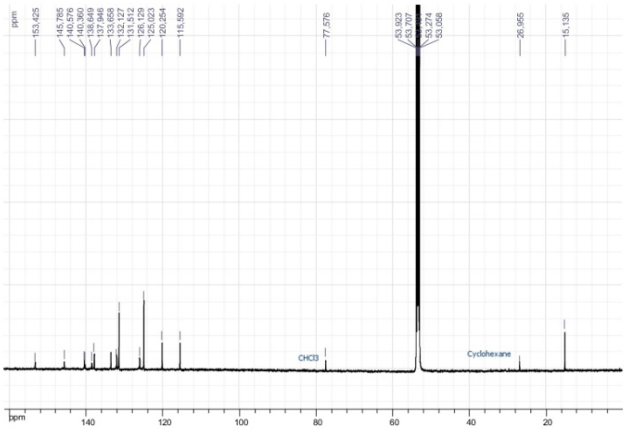


Fig. ESI6 ^{13}C NMR spectrum of bis-dipyrrin **3a** in CD_2Cl_2.

Helicate **4a**: A MeOH (20 mL) solution of $Zn(OAc)_2 (H_2O)_2$ (85 mg, 0.38 mmol) was added to a $CHCl_3$ (70 mL) solution of ligand **3a**($CHCl_3$) (200 mg, 0.31 mmol). The mixture was stirred overnight at room temperature. After evaporation under vacuum, the residue was washed with MeOH (3x30 mL) to afford helicate **4a** (168 mg, 92%). δ_H (300 MHz, $CDCl_3$) . 2.58 (s, 12H), 6.28 (dd, J = 1.0 and 4.2 Hz, 4H), 6.36 (d, J = 4.2 Hz, 4H), 6.42 (d, J = 4.2 Hz, 4H), 6.60 (d, J = 1.0 and 4.2 Hz, 4H), 6.98 (m, 8H), 7.09 (dd, J = 1.4 and 8.0 Hz, 4H), 7.25 (dd, J = 1.4 and 8.0 Hz, 4H, overlap with solvent), 7.39 (dd, J = 1.4 and 8.0 Hz, 4H). $\lambda_{max}(CH_2Cl_2)$/nm (ε/mol^{-1} L cm^{-1}): 260 (48000), 300 (20000), 381 (51000), 426 (110000), 468 (24000), 582 (41000), 639 (50000). HRMS (ESI), m/z: $[M]^+$ calcd. for $C_{64}H_{48}N_8S_4Zn_2$: 1184.1462; found: 1184.1469. Single crystals were obtained by slow evaporation of a $CHCl_3$ solution of the helicate.

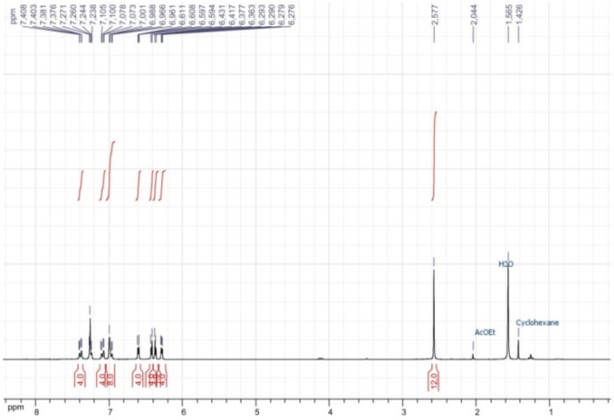
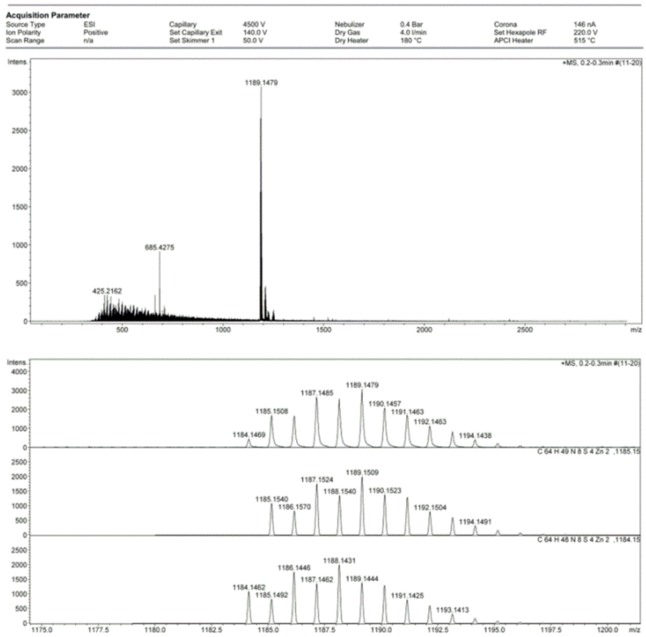


Fig. ESI7 ^{1}H NMR spectrum of helicate **4a** in $CDCl_3$.



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Scan Range	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	515 °C

Fig. ESI8 ESI mass spectrum of helicate **4a**.

Tri- and tetra-nuclear complexes **5a** and **6a**: Addition of a MeOH (30 mL) solution of Zn(OAc)$_2$ (H$_2$O)$_2$ (21 mg, 0.09 mmol) to a CH$_2$Cl$_2$ (6 mL) solution of ligand **3a**(CHCl$_3$) (60 mg, 0.09 mmol) resulted in the immediate formation of a precipitate. The mixture was stirred for 30 min at room temperature and the solid was recovered by centrifugation. It was suspended in AcOEt (150 mL). Filtration of the suspension allowed the isolation of helicate **4a** as a solid (35 mg, 64%). The filtrate was concentrated and purified by column chromatography (SiO$_2$, Cyclohexane/AcOEt 1/1) to afford complex **5a** (13 mg, 24%) and **6a** as traces. Analytical data for **5a**: δ_H (400 MHz, CD$_2$Cl$_2$) 2.70 (s, 18H), 6.28 (d, *J* = 4.4 Hz, 6H), 6.37 (d, *J* = 4.4 Hz, 6H), 6.45 (dd, *J* = 1.2 and 4.2 Hz, 6H), 6.70 (dd, *J* = 1.2 and 4.2 Hz, 6H), 7.03 (dd, *J* = 1.2 and 7.8 Hz, 6H), 7.24 (dd, *J* = 1.4 and 7.8 Hz, 6H), 7.32 (dd, *J* = 1.2 and 8.0 Hz, 6H), 7.39 (dd, *J* = 1.5 and 8.0 Hz, 6H), 7.61 (t, *J* = 1.2 Hz, 6H). HRMS (ESI), *m*/*z*: [M+Na]$^+$ calcd. for C$_{96}$H$_{72}$N$_{12}$NaS$_6$Zn$_3$: 1799.2094; found: 1799.2126. Single crystals were obtained by slow diffusion of *n*-pentane vapour in an AcOEt solution of the complex.

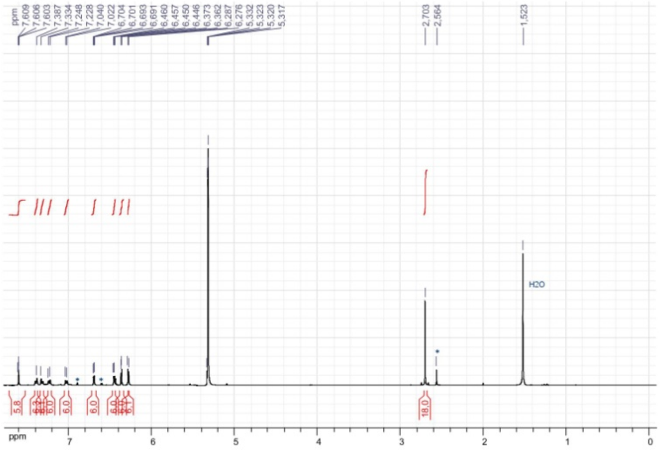
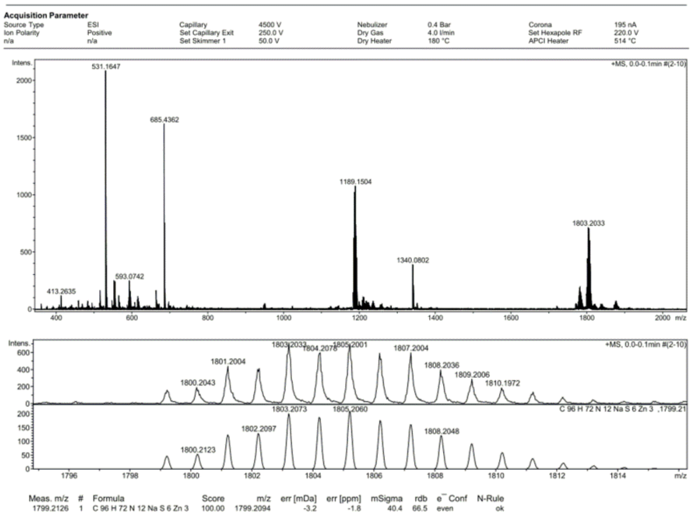


Fig. ESI9 ^{1}H of trinuclear complex **5a** in CD$_2$Cl$_2$. * denotes traces of the linear helicate.



Acquisition Parameter

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n/a	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	514 °C

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1799.2126	1	C 96 H 72 N 12 Na S 6 Zn 3	100.00	1799.2094	-3.2	-1.8	40.4	66.5	even	ok

Fig. ESI10 ESI mass spectrum of trinuclear complex **5a**.

Complex **2b**: A toluene (300 mL) solution of DDQ (0.820 g, 3.6 mmol) was added to a toluene (300 mL) solution of complex **1b** (2.0 g, 3.3 mmol). Upon heating at reflux temperature for 48 hours, the mixture turned from red to brown. After evaporation of the solvent under vacuum, the residue was purified by column chromatography (SiO_2, $CHCl_3$) affording **2b** as a brown solid (0.717 g, 36%). δ_H (500 MHz, $CDCl_3$) 3.96 (s, 6H), 5.92 (d, *J* = 1.0 Hz, 2 H), 6.42 (dd, *J* = 1.2 and 4.4 Hz, 2H), 6.60 (d, *J* = 4.4 Hz, 2H), 6.66 (d, *J* = 4.4 Hz, 2H), 6.71 (dd, *J* = 1.0 and 4.5 Hz, 2H), 7.60-7.62 (m, 4H), 8.11-8.13 (m, 4H). δ_C (125 MHz, $CDCl_3$) 55.4, 115.7, 117.5, 128.9, 129.9, 130.7, 130.9, 134.6, 135.5, 138.6, 141.3, 142.1, 153.9, 161.5, 166.7. $\lambda_{max}(CH_2Cl_2)$/nm (ε/mol^{-1} L cm^{-1}): 308 (18000), 353 (21000), 417 (35000), 432 (32500), 570 (12000), 770 (5200), 848 (9600). HRMS (ESI), *m*/*z*: $[M]^+$ calcd. for $C_{34}H_{24}N_4NiO_4$: 610.1146; found: 610.1139. Single crystals were obtained by *n*-pentane vapor diffusion into a solution of the complex in $CHCl_3$.

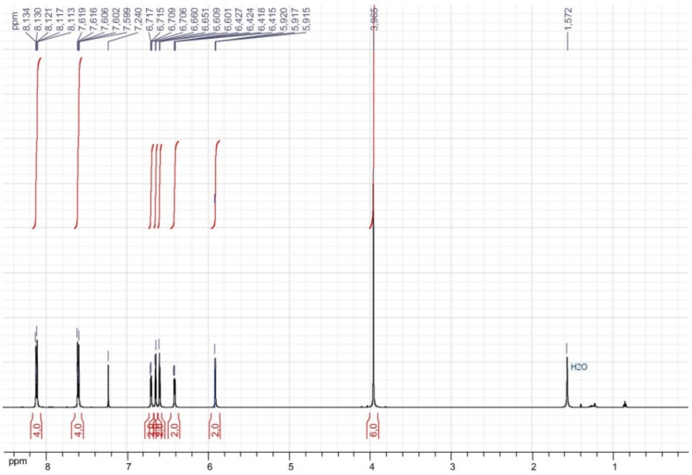


Fig. ESI11 ^1H NMR spectrum of complex **2b** in $CDCl_3$.

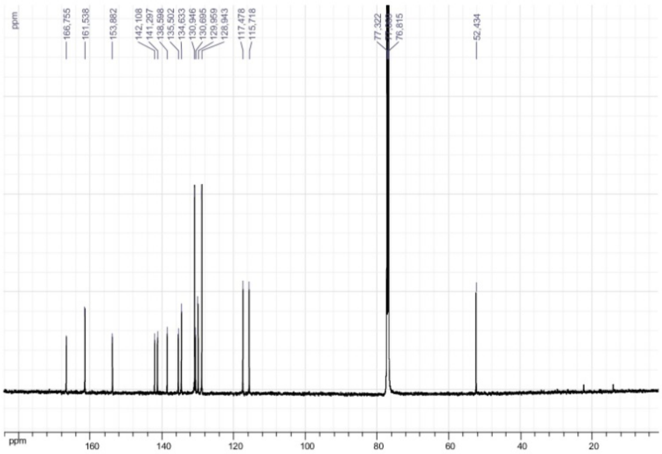


Fig. ESI12 ^{13}C NMR spectrum of complex **2b** in $CDCl_3$.

Bis-dipyrrin **3b**: To a $CHCl_3$ (50 mL) solution of complex **2b** (0.700 g, 1. 1 mmol), a 12 M solution of HCl (8 mL) was added and the mixture was stirred at room temperature for 5 hours. Upon addition of a saturated Na_2CO_3 solution, the organic layer turned from green to dark blue. The organic phase was recovered and washed with H_2O (2x100 mL). The organics were dried over Na_2SO_4, and evaporated to dryness to afford ligand **3b** as a dark blue solid (0.556 g, 89%). δ_H (500 MHz, CD_2Cl_2) 3.96 (s, 6H), 6.42-6.44 (m, 2H), 6.53 (d, J = 4.1 Hz, 2H), 6.74 (d, J = 4.1 Hz, 2H), 7.06 (d, J = 4.1 Hz, 2H), 7.61-7.63 (m, 6H), 8.13-8.15 (m, 4H). δ_C (125 MHz, CD_2Cl_2) 52.3, 116.2, 120.7, 126.3, 129.0, 130.8, 131.1, 131.9, 138.7, 138.8, 139.4, 141.8, 145.7, 153.6, 166.6. λ_{max}(CH_2Cl_2)/nm (ε/mol^{-1} L cm^{-1}): 330 (22500), 412 (23500), 560 (34000), 590 (39000). HRMS (ESI), *m*/*z*: $[M+H]^+$ calcd. for $C_{34}H_{27}N_4O_4$: 555.2027; found: 555.2050. Single crystals were obtained by slow evaporation of a $CHCl_3$ solution of the bis-dipyrrin.

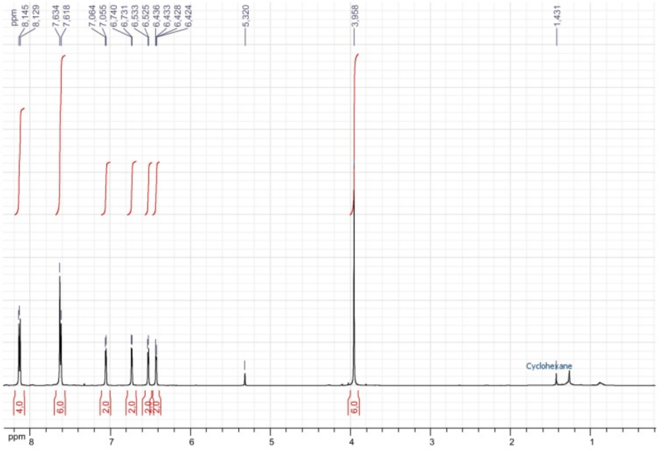


Fig. ESI13 ^{1}H NMR spectrum of bis-dipyrrin **3b** in CD_2Cl_2.

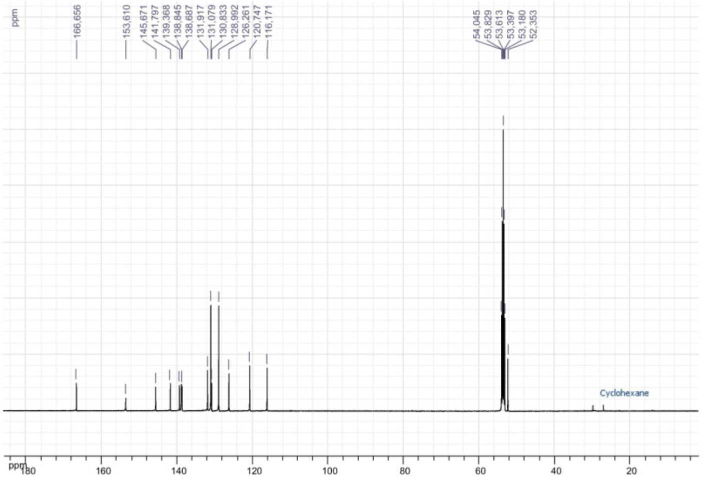


Fig. ESI14 ^{13}C NMR spectrum of bis-dipyrrin **3b** in CD_2Cl_2.

Helicate **4b**: A MeOH (10 mL) solution of $Zn(OAc)_2 (H_2O)_2$ (25 mg, 0.11 mmol) was added to a $CHCl_3$ (20 mL) solution of ligand **3b** (60 mg, 0.11 mmol). The mixture was stirred overnight at room temperature. After evaporation under vacuum, the residue was washed with MeOH (5x15 mL) to afford helicate **4b** (66 mg, 98%). δ_H (300 MHz, CD_2Cl_2) 3.97 (s, 12H), 6.30 (dd, *J* = 1.4 and 4.1 Hz, 4H), 6.38 (d, *J* = 4.1 Hz, 4H), 6.47 (d, *J* = 4.1 Hz, 4H), 6.53 (dd, *J* = 1.1 and 4.1 Hz, 4H), 6.93 (t, *J* = 1.1 Hz, 4H), 7.13 (dd, *J* = 1.4 and 8.0 Hz, 4H), 7.56 (dd, *J* = 1.4 and 8.0 Hz, 4H), 7.90 (dd, *J* = 1.5 and 8.0 Hz, 4H), 8.08 (dd, *J* = 1.5 and 8.0 Hz, 4H). $\lambda_{max}(CH_2Cl_2)$/nm (ε/mol^{-1} L cm^{-1}): 283 (35000), 338 (40000), 428 (87000), 468 (19000), 583 (36000), 635 (47000). HRMS (ESI), *m*/*z*: $[M+H]^+$ calcd. for $C_{68}H_{49}N_8O_8Zn_2$: 1233.2251; found: 1233.2176. Single crystals were obtained by slow diffusion of a MeOH solution of $Zn(OAc)_2 (H_2O)_2$ into a $CHCl_3$ solution of the ligand **3b**.

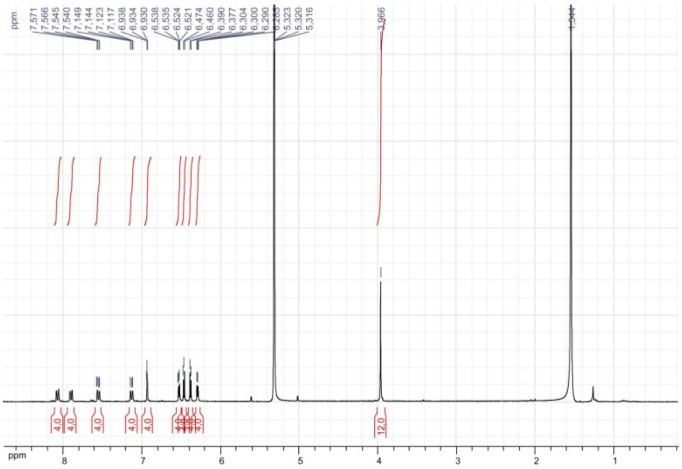
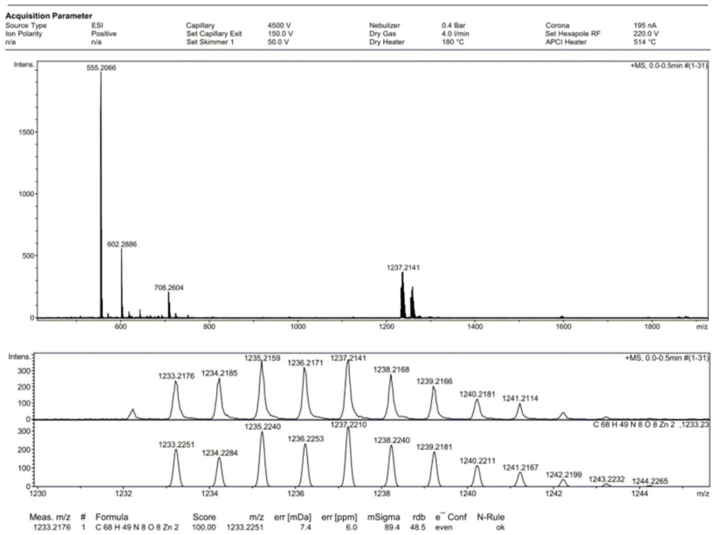


Fig. ESI15 ^1H NMR spectrum of helicate **4a** in CD_2Cl_2.



Acquisition Parameter

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Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1233.2176	1	C 68 H 49 N 8 O 8 Zn 2	100.00	1233.2251	7.4	6.0	89.4	48.5	even	ok

Fig. ESI16 ESI mass spectrum of the helicate **4b**.

Tri- and tetra-nuclear complexes **5b** and **6b**: Addition of a MeOH (120 mL) solution of $Zn(OAc)_2$ $(H_2O)_2$ (95 mg, 0.43 mmol) to a CH_2Cl_2 (24 mL) solution of ligand **3b** (240 mg, 0.43 mmol) resulted in the immediate formation of a precipitate. The mixture was stirred for 40 min at room temperature and the solid was recovered by centrifugation and washed with MeOH (40 mL). It was suspended in AcOEt (500 mL). Filtration of the suspension allowed the isolation of helicate **4b** as a solid (211 mg, 61%). The filtrate and the MeOH solution were concentrated and purified by column chromatography (SiO_2, Cyclohexane/AcOEt 1/1) to afford complex **5b** (39 mg, 15%) and **6b** (25 mg, 9%) Analytical data for **5b**: δ_H (400 MHz, CD_2Cl_2) 4.11 (s, 18H), 6.21 (d, $J = 4.3$ Hz, 6H), 6.37 (d, $J = 4.3$ Hz, 6H), 6.46 (dd, $J = 1.2$ and 4.3 Hz, 6H), 6.62 (dd, $J = 1.0$ and 4.3 Hz, 6H), 7.19 (m, 6H), 7.56 (m, 6H), 7.65 (t, $J = 1.2$ Hz 6H), 8.11 (m, 12H). $\lambda_{max}(CH_2Cl_2)$/nm (ε/mol^{-1} L cm^{-1}): 275 (52000), 336 (46000), 353 (54000), 433 (17000), 463 (22000), 614 (245000), 656 (183000), 697 (135000). HRMS (ESI), *m*/*z*: $[M+Na]^+$ calcd. for $C_{102}H_{72}N_{12}NaO_{12}Zn_3$: 1871.3159; found: 1871.3065. Single crystals were obtained by slow diffusion of *n*-pentane vapour in a $CHCl_3$ solution of **5b**.

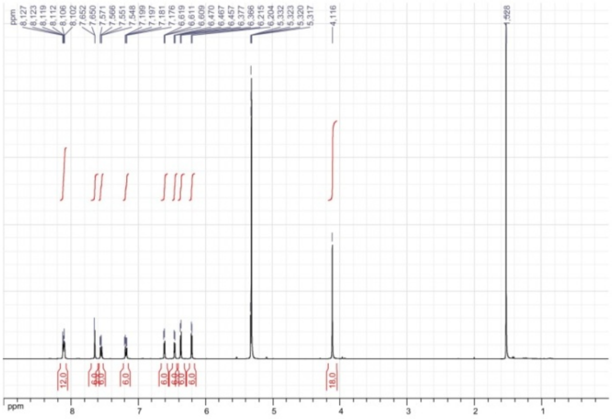
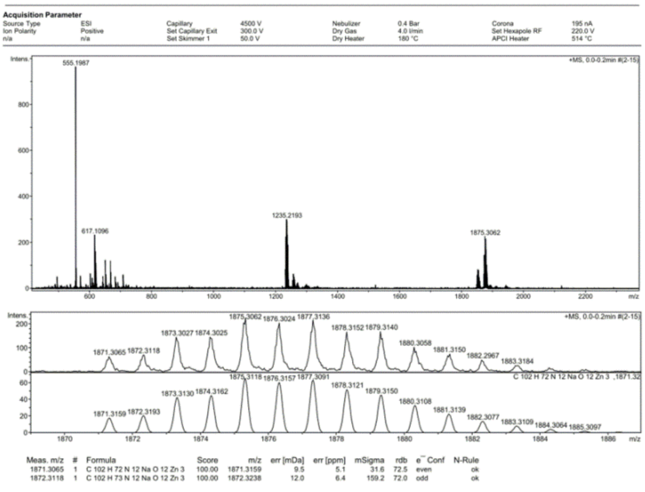


Fig. ESI17 ^{1}H NMR spectrum of trinuclear complex **5b** in CD_2Cl_2.



Acquisition Parameter

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n/a	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	514 °C

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1871.3065	1	C 102 H 72 N 12 Na O 12 Zn 3	100.00	1871.3159	9.5	5.1	31.6	72.5	even	ok
1872.3118	1	C 102 H 73 N 12 Na O 12 Zn 3	100.00	1872.3238	12.0	6.4	159.2	72.0	odd	ok

Fig. ESI18 ESI mass spectrum of the trinuclear complex **5b**.

Analytical data for **6b**: δ_H (400 MHz, CD_2Cl_2) 4.06 (s, 12H), 4.17 (s, 12H), 5.46 (d, *J* = 4.2 Hz, 4H), 5.74 (d, *J* = 4.2 Hz, 4H), 6.24 (d, *J* = 4.2 Hz, 4H), 6.32 (dd, *J* = 1.1 and 4.2 Hz, 4H), 6.36 (dd, *J* = 1.1 and 4.2 Hz, 4H), 6.40 (dd, *J* = 1.1 and 4.2 Hz, 4H), 6.48 (dd, *J* = 1.1 and 4.2 Hz, 4H), 6.70 (dd, *J* = 1.4 and 8.0 Hz, 4H), 7.22 (dd, *J* = 1.4 and 7.8 Hz, 4H), 7.34 (m, 8H), 7.46 (dd, *J* = 1.2 and 7.8 Hz, 4H), 7.55 (m, 8H), 8.07 (dd, *J* = 1.4 and 7.7 Hz, 4H), 8.15 (dd, *J* = 1.6 and 7.7 Hz, 4H), 8.22 (dd, *J* = 1.4 and 8.0 Hz, 4H). $\lambda_{max}(CH_2Cl_2)$/nm (ε/mol^{-1} L cm^{-1}): 279 (75000), 332 (63500), 360 (75000), 466 (64500), 483 (56000), 606 (261000), 649 (231000), 676 (209000). HRMS (ESI), *m/z*: $[M+Na]^+$ calcd. for $C_{136}H_{94}N_{16}NaO_{16}Zn_4$: 2494.4230; found: 2494.3934. Single crystals were obtained by slow diffusion of Et_2O vapour in a toluene solution of **6b**

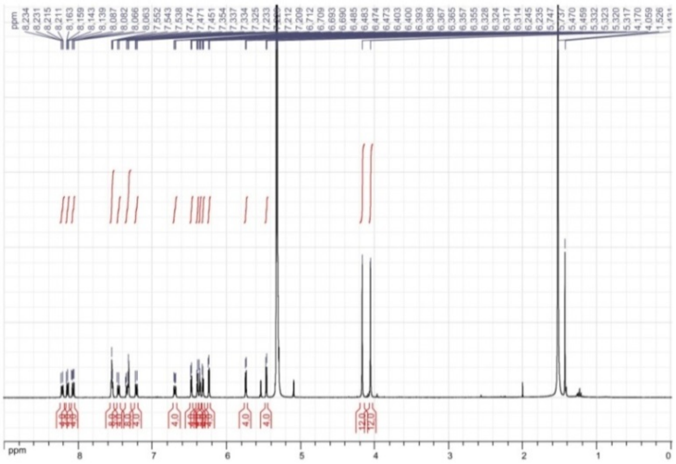
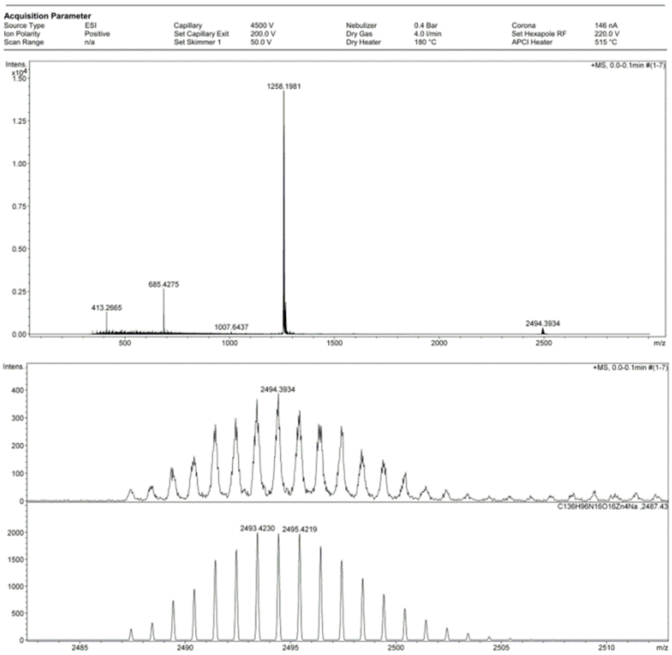


Fig. ESI19 ^{1}H NMR spectrum of tetranuclear complex **6b** in CD_2Cl_2.



Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	146 nA
Ion Polarity	Positive	Set Capillary Exit	200.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	220.0 V
Scan Range	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	515 °C

Fig. ESI20 ESI mass spectrum of tetranuclear complex **6b**.

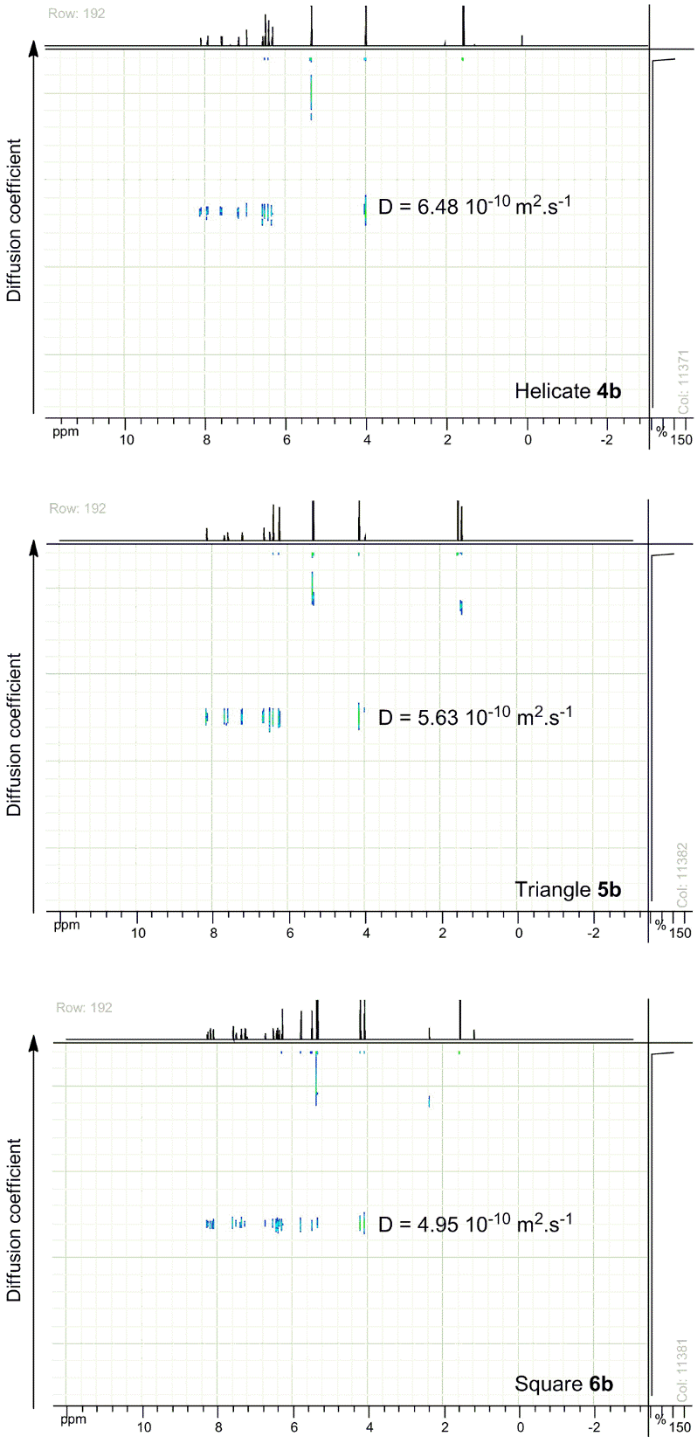


Fig. ESI21 DOSY NMR spectra in CD_2Cl_2 of pure **4b** (top), **5b** (middle) and **6b** (bottom) at 25°C.

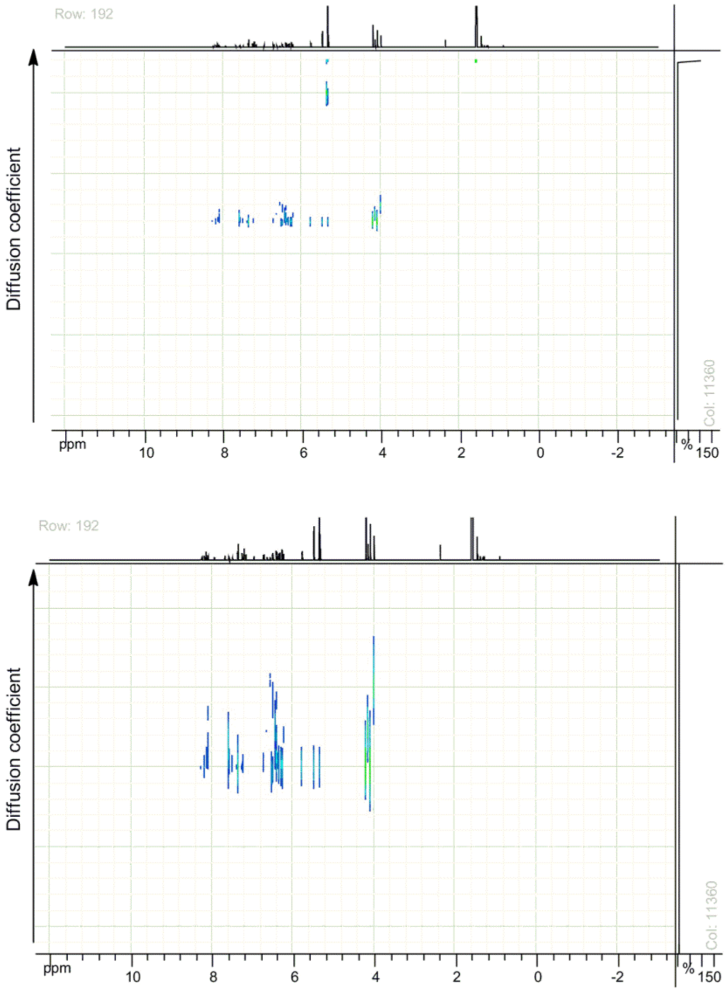
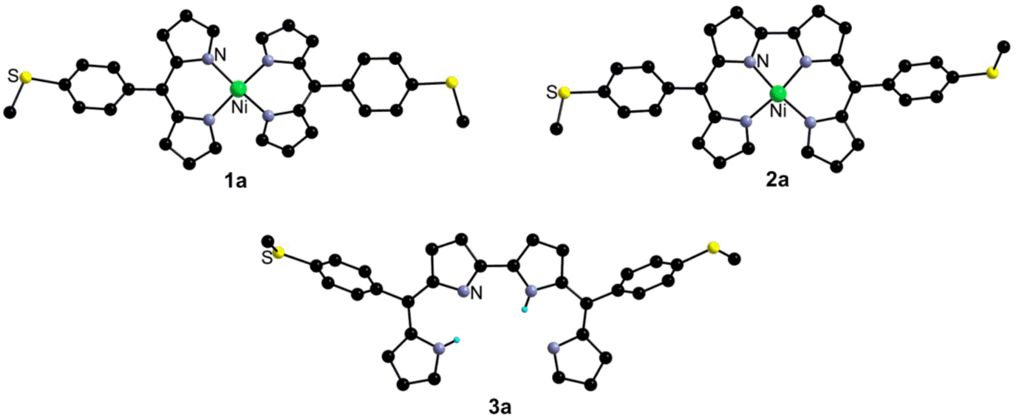


Fig. ESI22 DOSY NMR spectra in CD_2Cl_2 of a mixture of **4b**, **5b** and **6b** (top) and zoom showing the three different diffusion coefficients observed for the three compounds (bottom).

X-Ray diffraction

Single-crystal data (Tables ESI1 and ESI2) were collected on a Bruker SMART CCD diffractometer with Mo–Kα radiation at 173 or 190 K. The structures were solved using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-97 with anisotropic thermal parameters for all non-hydrogen atoms.[3] The hydrogen atoms were introduced at calculated positions and not refined (riding model). In the structure of **5a**, the carbon atom of two methyl groups of peripheral thioether moieties are disordered over two positions. Furthermore, the *n*-pentane solvent molecule is also disordered. This has been taken into account using the PART command. The hydrogen atoms on this molecule have not been introduced but are taken into account in the compound formula. For **3b**, one carbonyl group shows disorder over two positions, modeled using the PART command. In the structure of **4b**, two phenyl groups show positional disorder. For both *P*-**6b** and *M*-**6b**, toluene molecules present in the crystal are heavily disordered. The SQUEEZE command has been employed to account for the corresponding electron density.[4]

CCDC 1040034-1040046 contain the supplementary crystallographic data for compounds **1a**-**5a** and **1b**-**6b**. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.



1a

2a

3a

Fig. ESI 23. Crystal structures of compounds **1a**-**3a**. CH hydrogen atoms and solvent molecules are not presented for clarity.

Table ESI1 Crystallographic data for compounds **1a**-**5a**

	α-1a	**β-1a**	**2a**	**3a(CHCl$_3$)**	**4a**	**(5a)$_2$(AcOEt)$_2$(*n*-pentane)**
Formula	$C_{32}H_{26}N_4NiS_2$	$C_{32}H_{26}N_4NiS_2$	$C_{32}H_{24}N_4NiS_2$	$C_{33}H_{27}Cl_3N_4S_2$	$C_{64}H_{42}N_8S_4Zn_2$	$C_{205}H_{172}N_{24}O_4S_{12}Zn_6$
FW	589.40	589.40	587.38	650.06	1188.19	3812.61
Crystal system	Orthorhombic	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	*P*bca	*P*-1	*P*-1	*P*-1	$P2_1$/n	*P*-1
a / Å	18.0049(9)	9.7891(2)	9.9075(2)	8.9232(2)	15.1355(4)	13.3649(5)
b / Å	9.0457(4)	11.7331(2)	12.331(3)	12.3869(3)	14.9332(4)	18.2896(6)
c / Å	32.7494(15)	12.5712(3)	12.4360(3)	14.6782(4)	24.9048(5)	18.8109(7)
α / °		104.4860(10)	64.1490(10)	75.7490(10)		96.448(2)
β / °		99.6890(10)	69.8930(10)	75.0970(10)	106.3990(10)	99.538(2)
γ / °		102.5310(10)	79.4820(10)	86.5210(10)		64.693(2)
V / Å^3	5333.8(4)	1326.30(5)	1283.19(5)	1519.57(7)	5400.0(2)	4482.1(3)
Z	8	2	2	2	4	1
T / K	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
μ/ mm^{-1}	0.914	0.919	0.950	0.470	1.094	0.995
Refls. coll.	32789	26383	26379	30752	62112	81271
Ind. refls. (Rint)	7802 (0.0615)	7063 (0.0310)	6911 (0.0364)	8155 (0.0385)	15675 (0.0710)	24097 (0.0764)
R_1 (I>2σ(I))^a	0.0417	0.0366	0.0344	0.0517	0.0517	0.0631
wR_2 (I>2σ(I))^a	0.1042	0.0895	0.0762	0.1213	0.1310	0.1602
R_1 (all data)^a	0.0739	0.0455	0.0490	0.0875	0.1008	0.1384
wR_2 (all data)^a	0.1267	0.0947	0.0828	0.1394	0.1580	0.2003
GOF	1.089	1.072	1.028	1.034	1.064	1.018

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum wF_o^4]^{1/2}$

Table ESI2 Crystallographic data for compounds **1b-6b**

	1b	**2b**	**3b**	**4b**	**5b(CHCl$_3$)$_3$**	***P*-6b**	***M*-6b**
Formula	$C_{34}H_{26}N_4NiO_4$	$C_{34}H_{24}N_4NiO_4$	$C_{34}H_{26}N_4O_4$	$C_{68}H_{48}N_8O_8Zn_2$	$C_{105}H_{75}Cl_9N_{12}O_{12}Zn_3$	$C_{136}H_{96}N_{16}O_{16}Zn_4$	$C_{136}H_{96}N_{16}O_{16}Zn_4$
FW	613.30	611.28	554.59	1235.88	2211.93	2471.77	2471.77
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	*P*-1	*C*2/c	*P*2/c	*C*2/c	*C*2/c	*I*222	*I*222
a / Å	9.2124(3)	34.4732(8)	20.8248(7)	23.8065(15)	18.1355(4)	15.3648(9)	15.3370(6)
b / Å	11.1476(3)	9.8680(2)	7.2192(2)	16.6644(11)	21.5289(5)	19.7305(11)	19.7279(14)
c / Å	14.7168(5)	7.9143(2)	19.4469(7)	42.744(3)	25.5659(6)	23.6393(13)	23.6518(12)
α / °	86.1660(10)						
β / °	76.5000(10)	100.7240(10)	105.8250(10)	100.563(2)	100.0080(10)		
γ / °	70.6820(10)						
V / Å^3	1386.77(8)	2645.28(11)	2812.81(16)	16670.1(18)	9830.0(4)	7166.4(7)	7156.2(7)
Z	2	4	4	12	4	2	2
T / K	173(2)	173(2)	173(2)	173(2)	173(2)	190 (2)	190 (2)
μ/ mm^{-1}	0.748	0.784	0.088	0.932	1.040	0.723	0.724
Refls. coll.	26775	28830	41843	110709	57850	24227	50642
Ind. refls. (Rint)	7382 (0.0255)	3688 (0.0270)	7843 (0.0406)	22429 (0.0925)	14449 (0.0631)	10413 (0.0404)	10481 (0.0627)
R_1 (I>2σ(I))^a	0.0419	0.0310	0.0544	0.0775	0.0615	0.0425	0.0480
wR_2 (I>2σ(I))^a	0.1010	0.0879	0.1259	0.1884	0.1619	0.0899	0.0958
R_1 (all data)^a	0.0545	0.0369	0.1032	0.1386	0.1187	0.0566	0.0731
wR_2 (all data)^a	0.1189	0.1003	0.1538	0.2190	0.2011	0.0941	0.1021
GOF	1.027	1.141	1.023	1.056	1.039	0.953	0.954

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum wF_o^4]^{1/2}$

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