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Electronic Supplementary Information

Pre-organization of clefts for Ag-π interactions in Zn(II) bisdipyrrin helicates for the construction of heterometallic networks

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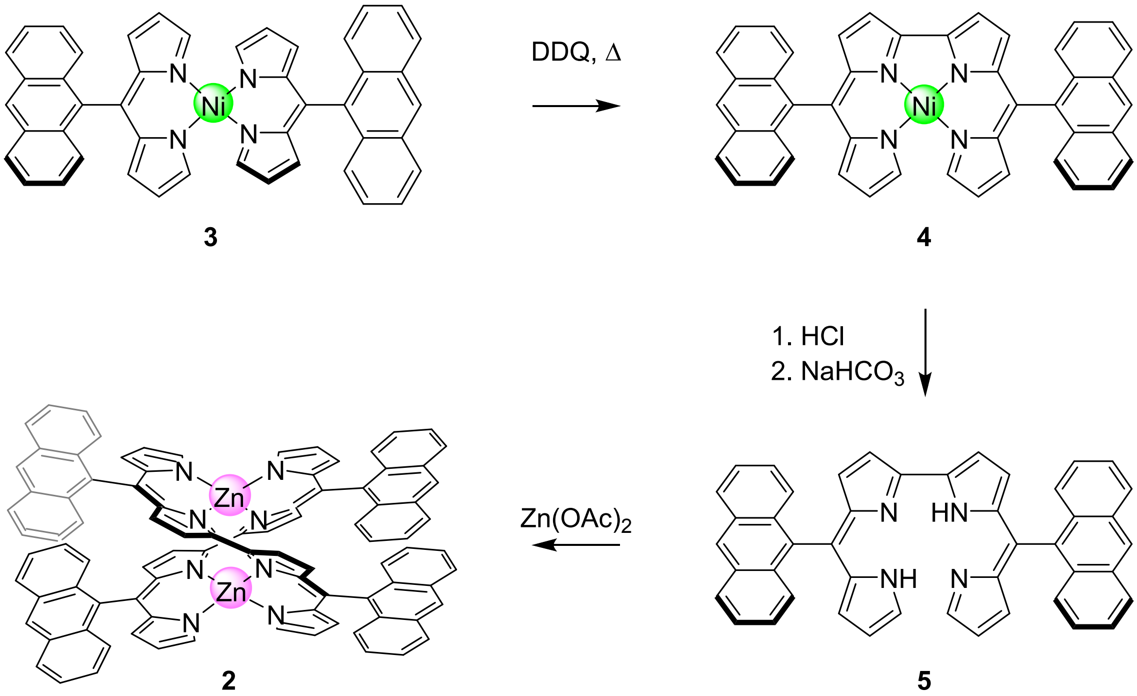

Scheme ESI1 Synthetic route for the preparation of [2+2] helicate **2**.

Synthesis

Ni(II) complex **3** was synthesized following the protocol described for the Zn(II) analogue.[1] ^{1}H and ^{13}C NMR spectra were recorded at 25 °C on a Bruker 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 **4**: To a toluene (225 mL) solution of complex **3** (0.600 g, 0.86 mmol), a toluene (75 mL) solution of DDQ (0.220 g, 0.97 mmol) was added and the mixture was heated at reflux overnight. After evaporation to dryness, the residue was purified by column chromatography (SiO_2, CH_2Cl_2/cyclohexane, 1/1) affording **4** as a brown solid (0.370 g, 62%). δ_H (500 MHz, $CDCl_3$) 6.11 (d, *J* = 4.2 Hz, 2H), 6.14 (s, 2H), 6.30 (dd, *J* = 1.2 and 4.2 Hz, 2H), 6.34 (dd, *J* = 1.2 and 4.2 Hz, 2H), 6.45 (d, *J* = 4.2 Hz, 2H), 7.43 (m, 4H), 7.49 (m, 4H), 7.97 (d, *J* = 8.5 Hz, 4H), 8.07 (d, *J* = 8.5 Hz, 4H), 8.59 (s, 2H). δ_C (125 MHz, $CDCl_3$) 115.7, 117.7, 125.4, 126.2, 127.0, 128.0, 128.2, 130.0, 130.2, 130.9, 131.4, 134.5, 137.5, 140.6, 140.8, 153.4, 161.7. λ_{max}(CH_2Cl_2)/nm (ε/mol^{-1} L cm^{-1}) : 333 (11600), 349 (17600), 368 (27000), 388 (33500), 412 (33000), 431 (28000, sh), 534 (9500), 571 (11000), 640 (3000, sh), 773 (5000). HRMS (ESI), *m*/*z*: $[M]^+$ calcd. for $C_{46}H_{28}N_4Ni$: 694.1662; found: 694.1642. Single crystals were obtained by slow evaporation of a $CHCl_3$solution of the complex.

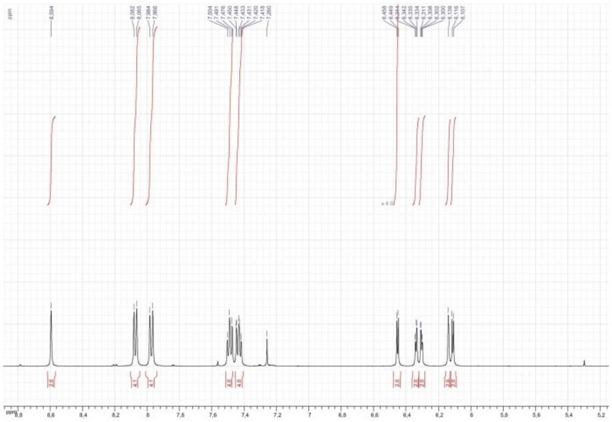

Fig. ESI1 ^{1}H NMR spectrum of complex **4** in $CDCl_3$.

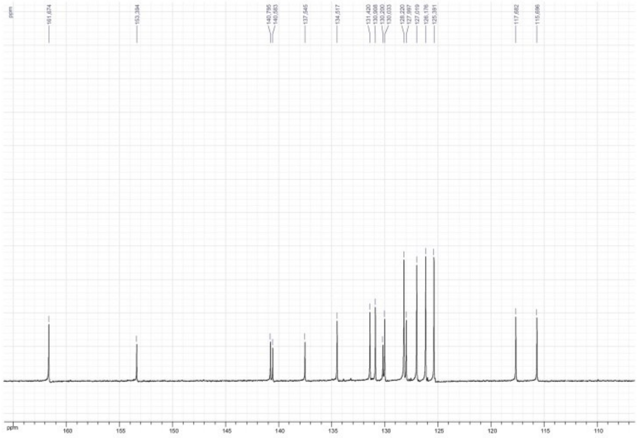

Fig. ESI2 ^{13}C NMR spectrum of complex **4** in $CDCl_3$.

Bis-dipyrrin **5**: To a $CHCl_3$ (30 mL) solution of complex **4** (0.300 g, 0.43 mmol), a 12 M solution of HCl (5 mL) was added and the heterogeneous mixture was stirred at room temperature overnight. Upon addition of a saturated $NaHCO_3$ 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 **5** as a dark blue solid (0.250 g, 91%). δ_H (500 MHz, CD_2Cl_2) 5.96 (d, J = 3.7 Hz, 2H), 6.18 (d, J = 4.3 Hz, 2H), 6.27 (dd, J = 1.7 and 4.3 Hz, 2H), 6.91 (d, J = 4.3 Hz, 2H), 7.39-7.43 (m, 4H), 7.48-7.51 (m, 4H), 7.69 (s, 2H), 7.94 (d, J = 8.8 Hz, 4H), 8.11 (d, J = 8.8 Hz, 4H), 8.64 (s, 2H). δ_C (125 MHz, CD_2Cl_2) 116.4, 120.9, 125.5, 126.0, 126.3, 126.6, 128.1, 128.5, 130.7, 131.2, 131.3, 131.5, 137.3, 138.9, 140.5, 147.4, 153.3. $\lambda_{max}(CH_2Cl_2)$/nm (ε/mol^{-1} L cm^{-1}): 332 (17000), 349 (23000), 367 (30000), 387 (35000), 412 (28000), 562 (31000), 590 (36000), 727 (11000). HRMS (ESI), m/z: $[M+H]^+$ calcd. for $C_{46}H_{31}N_4$: 639.2543; found: 639.2565. Slow evaporation of a CH_2Cl_2 solution of the ligand afforded single crystals suitable for X-Ray diffraction.

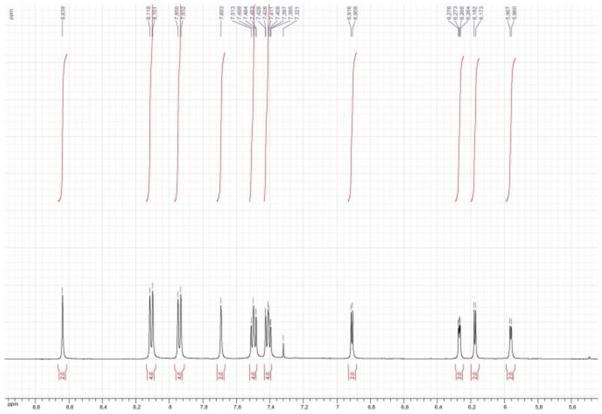

Fig. ESI3 ^1H NMR spectrum of bis-dipyrrin **5** in CD_2Cl_2.

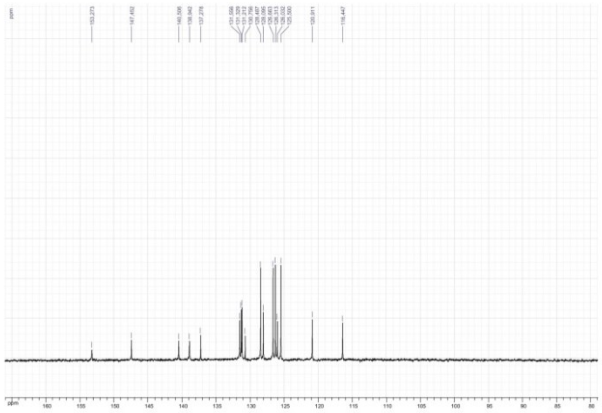

Fig. ESI4 ^{13}C NMR spectrum of bis-dipyrrin **5** in CD_2Cl_2.

Helicate **2**: A MeOH (15 mL) solution of $Zn(OAc)_2$ $(H_2O)_2$ (35 mg, 0.16 mmol) was added to a $CHCl_3$ (50 mL) solution of ligand **5** (100 mg, 0.16 mmol). The mixture was stirred for three days at room temperature. After evaporation under vacuum, the residue was purified by column chromatography (SiO_2, $CHCl_3$/cyclohexane, 1/1) affording **2** as a green solid (80 mg, 73%). δ_H (500 MHz, $CDCl_3$) 6.13 (dd, J = 0.8 and 4.2 Hz, 4H), 6.18-6.22 (m, 4H), 6.36 (d, J = 4.2 Hz, 4H), 6.62 (d, J = 4.2 Hz, 4H), 6.95 (t, J = 7.5 Hz, 4H), 7.09-7.12 (m, 8H), 7.34-7.37 (m, 4H), 7.43-7.46 (m, 4H), 7.85 (d, J = 8.4 Hz, 4H), 7.99 (d, J = 8.4 Hz, 4H), 8.06 (d, J = 8.4 Hz, 4H), 8.53 (s, 4H). δ_C (125 MHz, $CDCl_3$) 118.1, 118.8, 125.1, 125.3, 125.9, 126.1, 127.0, 127.1, 127.4, 127.5, 128.2, 130.6, 130.8, 131.1, 131.4, 131.7, 132.4, 133.1, 143.0, 143.3, 144.0, 149.3, 154.2. $\lambda_{max}(CH_2Cl_2)$/nm (ε/mol^{-1} L cm^{-1}): 351 (42800), 368 (58600), 389 (57400), 431 (91900), 487 (18000, sh), 634 (51500), 680 (67000), 740 (42000). HRMS (ESI), m/z: $[M]^+$ calcd. for $C_{92}H_{56}N_8Zn_2$: 1404.3192; found: 1404.3261. Single crystals were obtained by slow evaporation of a toluene solution of the helicate.

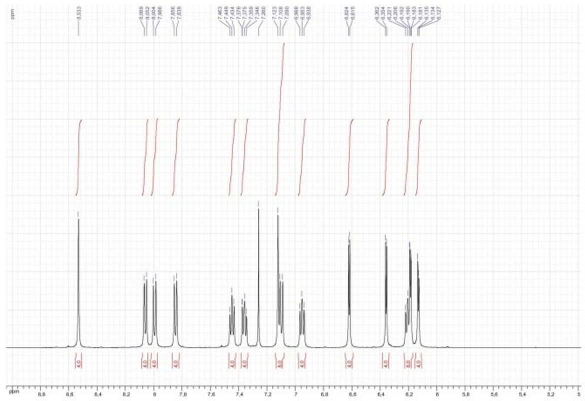

Fig. ESI5 ^{1}H NMR spectrum of helicate **2** in $CDCl_3$.

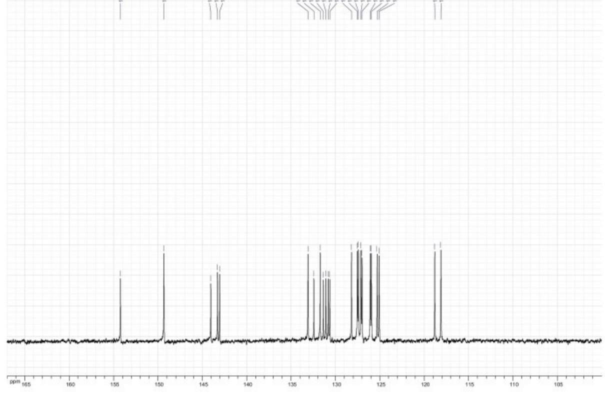

Fig. ESI6 ^{13}C NMR spectrum of helicate **2** in $CDCl_3$.

Networks **6** and **7**: An excess of Ag(TfO) was added to a toluene solution (3 mL) of helicate **1** (5 mg, 0.0049 mmol). The mixture was sonicated and filtered. Slow diffusion of Et_2O vapour into the filtrate afforded few crystals of **6** and **7** after few days.

Network **8**: An excess of Ag(TfO) was added to a *o*-xylene solution (4 mL) of helicate **2** (10 mg, 0.007 mmol). The mixture was sonicated and filtered. Slow diffusion of Et_2O vapour into the filtrate afforded crystals of **8** after several days (5.1 mg, 33%). Found: C, 58.81; H, 3.32; N, 5.81. $C_{94}H_{56}Ag_2F_6N_8O_6S_2Zn_2$ requires C, 58.86; H, 2.94; N, 5.84.

X-Ray diffraction

Single-crystal data (Tables ESI1 and ESI2) were collected on a Bruker SMART CCD diffractometer with Mo–Kα radiation at 173 K. The structures were solved using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-2014 with anisotropic thermal parameters for all non-hydrogen atoms.[2] The hydrogen atoms were introduced at calculated positions and not refined (riding model). In the structure of **2**, **3** and **7**, highly disordered molecules are present, the SQUEEZE command has been employed to account for the corresponding electron density.[3] In the structure of **8**, one diethyl ether molecule is disordered over two positions. The hydrogen atoms on this molecule have not been introduced but are taken into account in the compound formula.

CCDC 1506006-1506012 contain the supplementary crystallographic data for compounds **2**-**8**. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

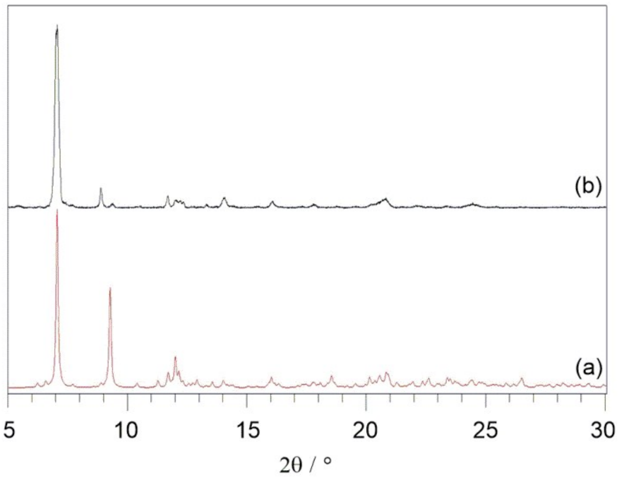

Fig. ESI7 Simulated (a) and experimental (b) PRXD pattern for network **8**. The difference in intensities results from preferential orientation.

Table ESI1 Crystallographic data for compounds **2-5**

	2	**3 (Toluene)**	**4**	**5**
Formula	$C_{92}H_{56}N_8Zn_2$	$C_{53}H_{38}N_4Ni$	$C_{46}H_{28}N_4Ni$	$C_{46}H_{30}N_4$
FW	1404.18	789.58	695.43	638.74
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2/c$	$P2/n$	$Pca2_1$	$C2/c$
a / Å	10.8018(6)	10.7748(4)	18.0300(8)	26.2435(13)
b / Å	17.3515(9)	11.5828(4)	11.0785(5)	13.5308(5)
c / Å	26.7953(16)	35.9716(11)	16.2510(7)	9.4070(4)
β / °	97.145(3)	93.971(2)		99.357(4)
V / Å^3	4983.2(5)	4478.6(3)	3246.1(2)	3295.9(3)
Z	4	4	4	4
T / K	173(2)	173(2)	173(2)	173(2)
μ/ mm^{-1}	0.521	0.472	0.640	0.076
Refls. coll.	97746	48069	41621	48796
Ind. refls. (Rint)	14675 (0.0625)	12232 (0.0446)	9244 (0.0823)	4850 (0.0456)
R_1 (I>2σ(I))^a	0.0586	0.0633	0.0491	0.0645
wR_2 (I>2σ(I))^a	0.1573	0.1724	0.1174	0.1632
R_1 (all data)^a	0.1039	0.1024	0.0689	0.1058
wR_2 (all data)^a	0.1836	0.1998	0.1244	0.1881
GOF	1.034	1.047	1.001	1.028

^{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 **6-8**

	6	**7**	**8**
Formula	$C_{136}H_{110}Ag_4F_{12}N_{16}O_{15}S_4Zn_4$	$C_{63}H_{40}Ag_3F_9N_8O_9S_3Zn_2$	$C_{216}H_{172}Ag_4F_{12}N_{16}O_{17}S_4Zn_4$
FW	3257.59	1774.56	4312.89
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	P-1
a / Å	9.4384(3)	11.3487(3)	15.4217(5)
b / Å	34.9486(12)	18.6122(5)	16.4449(5)
c / Å	20.3325(7)	33.9443(10)	22.1055(7)
α / °			69.989(2)
β / °	101.347(2)	95.100(2)	69.909(2)
γ / °			73.752(2)
V / Å^3	6575.8(4)	7141.5(3)	4863.4(3)
Z	2	4	1
T / K	173(2)	173(2)	173(2)
μ/ mm^{-1}	1.450	1.639	1.001
Refls. coll.	201092	242815	161393
Ind. refls. (Rint)	19535 (0.0704)	20962 (0.0411)	26162 (0.0496)
R_1 (I>2σ(I))^a	0.0562	0.0447	0.0536
wR_2 (I>2σ(I))^a	0.1128	0.1238	0.1388
R_1 (all data)^a	0.0928	0.0660	0.0882
wR_2 (all data)^a	0.1266	0.1363	0.1587
GOF	1.100	1.030	1.068

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

References

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