Supplementary Data

A Free-Base Dipyrrin Capable of Forming Extended Architectures Comparable to Those of Its Metal(II) Complex Counterparts

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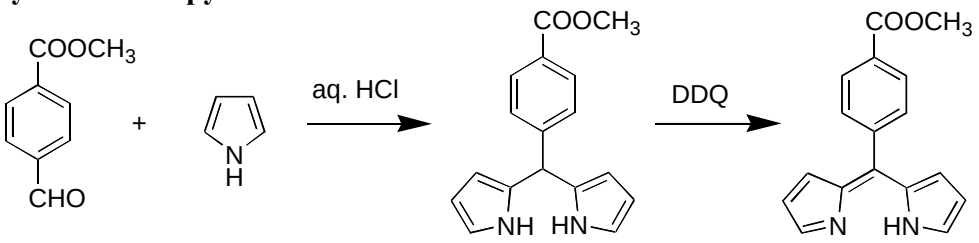
Contents:

General.

All reagents were obtained commercially from Sigma-Aldrich and used as received. Melting points were determined on a Electrothermal Digital Melting Point Apparatus. ^{1}H-and ^{13}C-NMR spectra were obtained with a Bruker AC 250 at 250 MHz (^{1}H) and 60 MHz (^{13}C) with residual solvents as internal reference. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz), and integration. UV/visible spectra were recorded on a SAFAS UV mc2 spectrophotometer (SAFAS MONACO), and IR spectra on a PerkinElmer 1725 X FTIR-spectrophotometer. Mass spectra were recorded either on an API-365 Perkin Elmer Sciex spectrometer (ESI), a DSQ Thermo Fisher Scientific spectrometer (EI and DCI NH_3), or a Waters Micromass MALDI micro MX™ spectrometer (MALDI-TOF).

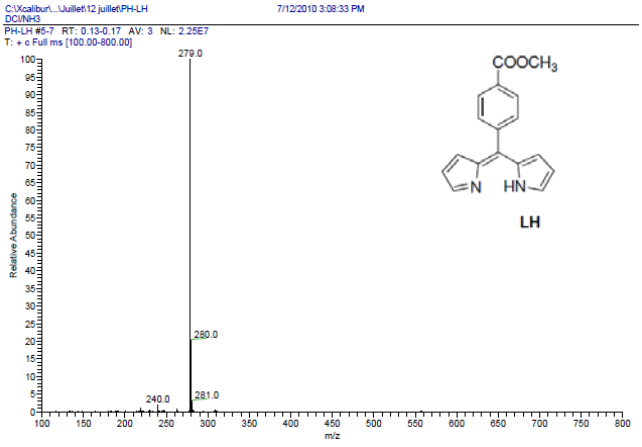
I. Synthesis of dipyrrin LH



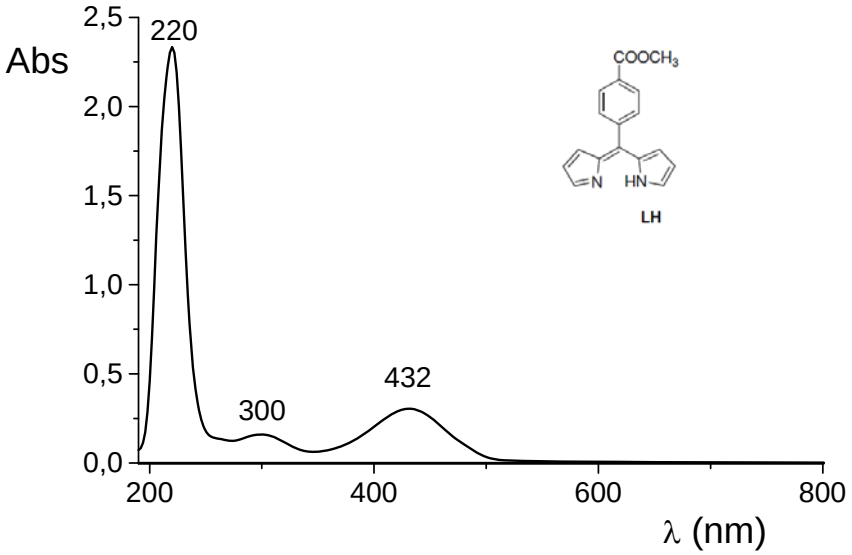
red-LH **LH**

5-(4-Methoxycarbonylphenyl)-4,6-dipyrromethene (LH). Dipyrromethane **red-LH** was synthesized as previously described from methyl 4-formylbenzoate and 3 equivalents of pyrrole in a 0.18 M aqueous hydrochloric acid solution.[1] Dipyrromethane **red-LH** (1.88 g, 6.71 mmol) was then dissolved in a mixture of $CHCl_3$ (70 mL) and acetone (30 mL) cooled to 0 °C (ice-bath), and a solution of 2,3-dichloro5,6-dicyano-1,4-benzoquinone (DDQ, 1.67 g, 7.36 mmol) in acetone (30 mL) was dropwise added. The resulted brown solution was kept at 0 °C for 1 h under magnetic stirring and then 15 min at room temperature. Solvents were then removed by evaporation under reduced pressure, and the dark brown residue was purified by chromatography on alumine (aluminium oxide 90 active neutral, Merck) using 1 % of methanol in dichloromethane as eluent to give **LH** (1.0 g, 54 %) as a yellow film. Crystals were obtained by allowing vapors of hexane to diffuse into a solution of **LH** in dichloromethane; mp 78-79 °C. UV-VIS (CH_3OH, 0.15% DMF) λ_{max} (log ε): 220 (5.41), 300 (4.25), 432 (4.52). IR (KBr): 1724, 1573, 1382, 1278, 1098, 1007 cm^{-1}. ^1H NMR ($CDCl_3$) δ (ppm) 3.97 (s, 3H), 6.40 (dd, J = 4.2 Hz and J = 1.5 Hz, 2H) , 6.52 (dd, J = 4.2 Hz and J = 1.1 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.66 (m, 2H), 8.12 (d, J = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm) 52.4, 118.0, 128.5, 128.9, 130.6, 130.8, 140.4, 140.6, 141.9, 144.1, 166.7. MS (DCI, NH_3) for $C_{17}H_{14}N_2O_2$: 279 [MH^+] (100 %), 280 (20 %).

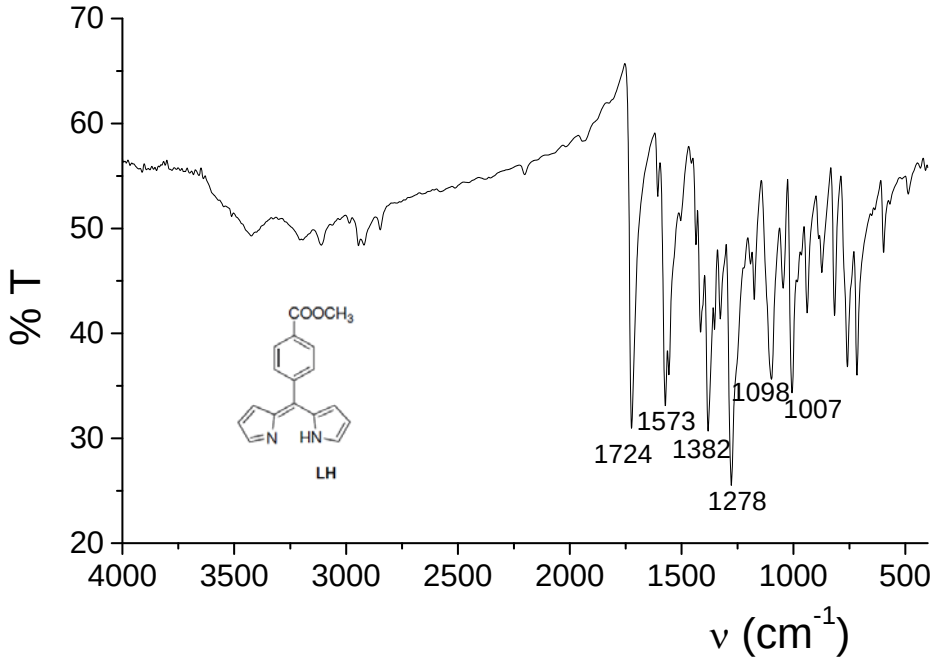
MS – DCI / NH_3



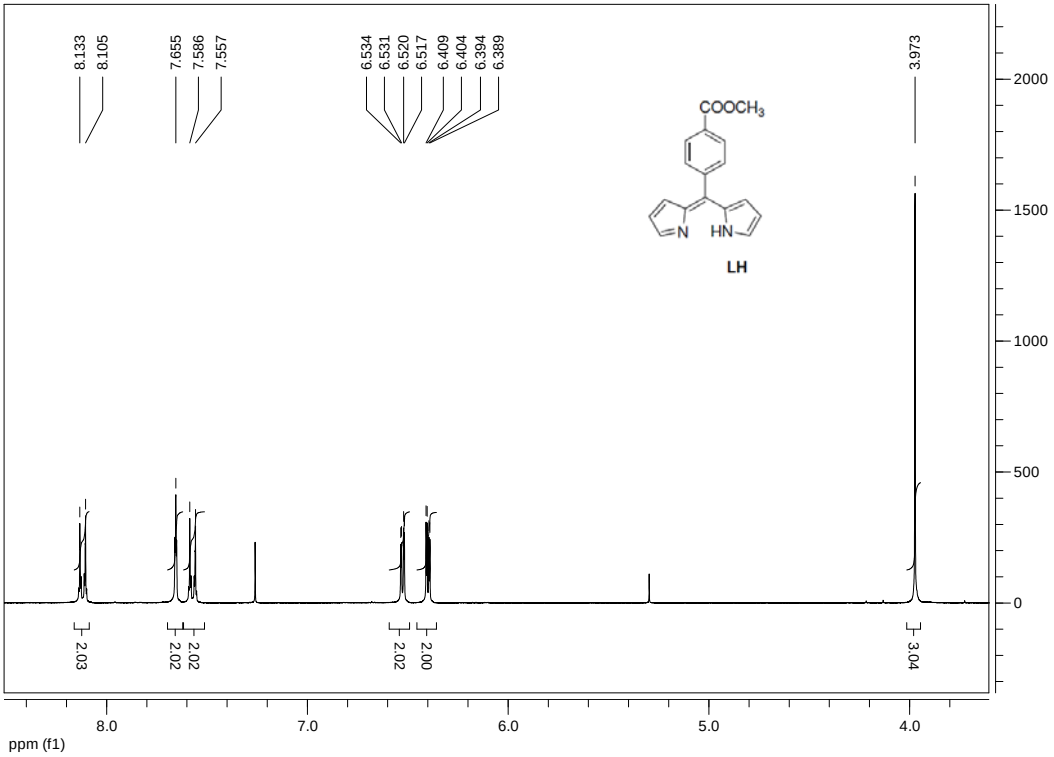
UV Visible ($CDCl_3$) (80 µM in CH_3OH + 3 % DMF)



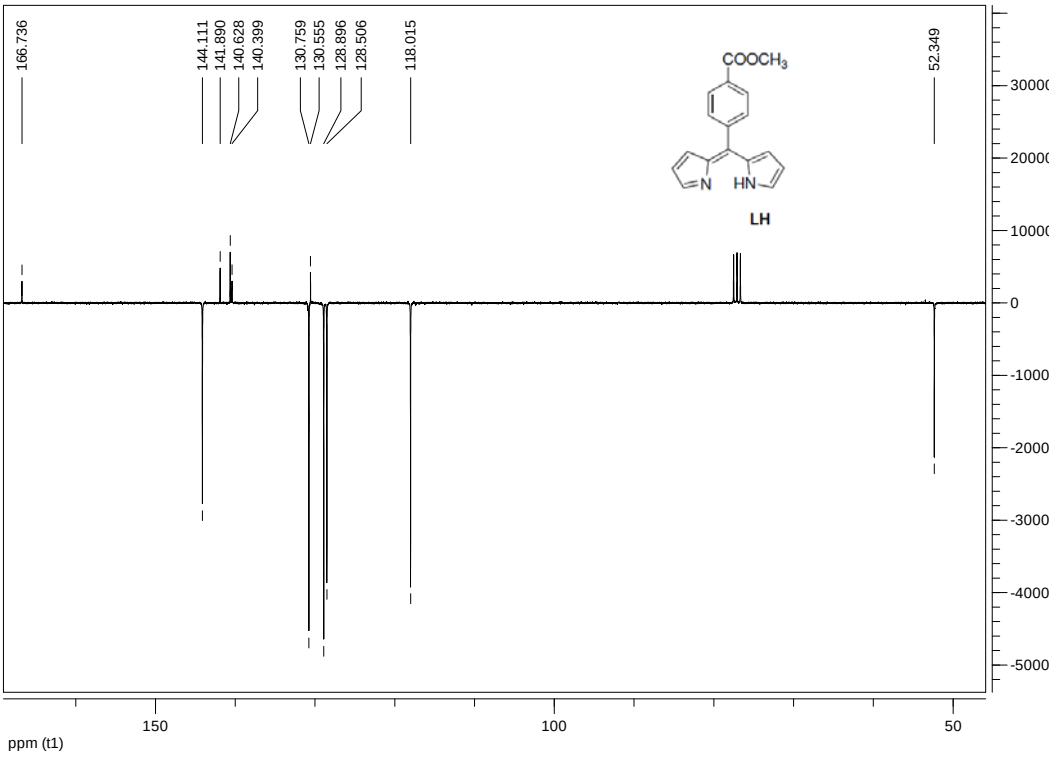
IR (KBr)



^{1}H NMR ($CDCl_3$)

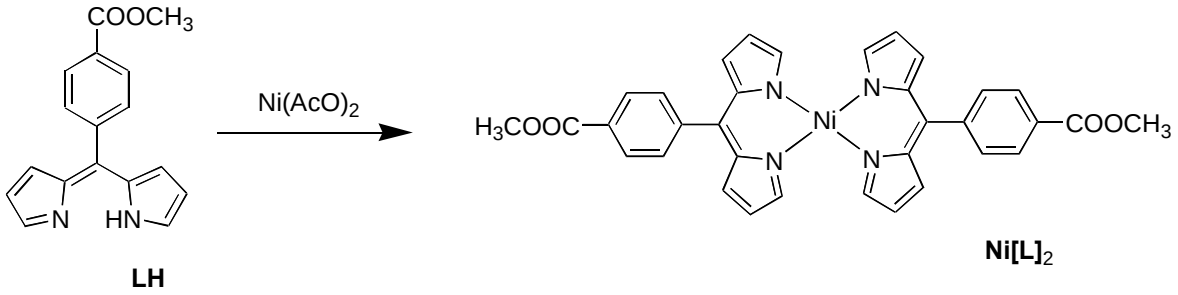


^{13}C NMR ($CDCl_3$)



II. Synthesis of Metal-complexes $M[L]_2$

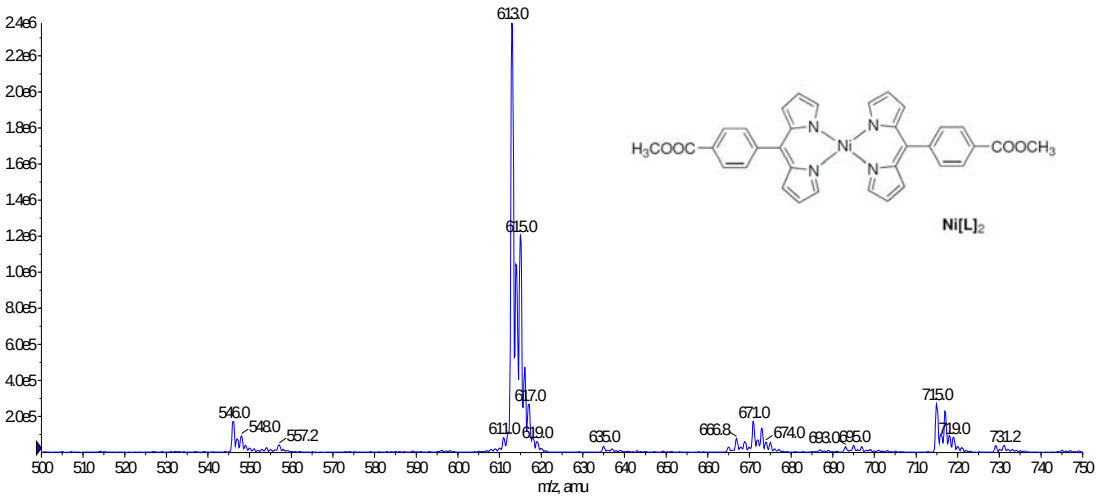
Bis[4-methoxycarbonylphenyl-4,6-pyrrinato]Ni(II) ($Ni[L]_2$)



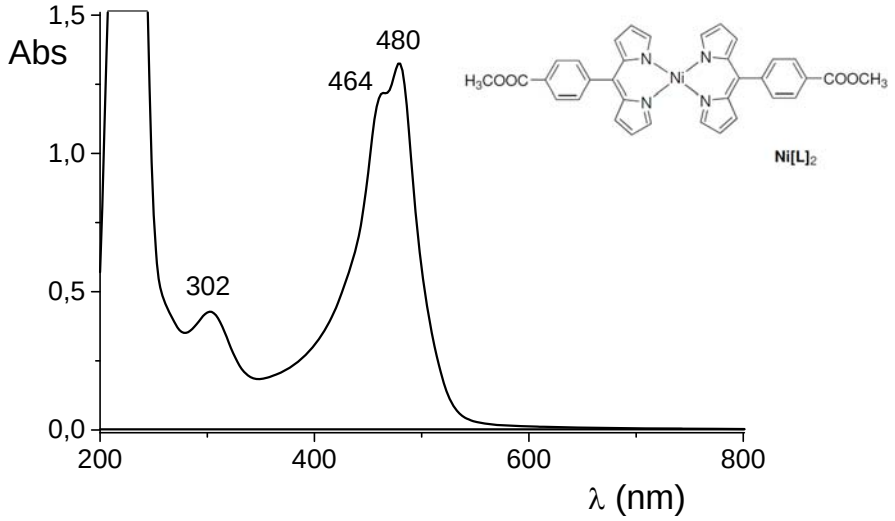
LH **$Ni[L]_2$**

To a solution of dipyrine **LH** (120 mg, 0.43 mmol) in methanol (100 mL) was added nickel(II) acetate tetrahydrate (55 mg, 0.22 mmol, 0.5 eq.) and the mixture was magnetically stirred at room temperature for 18 h. The dark precipitate was filtered off and air-dried to provide 84 mg (64 %) of analytically pure nickel complex **$Ni[L]_2$**. Crystallization from a slow evaporation of a solution of dichloromethane and ethanol (approx. 90 / 10) yielded green dichroic microcrystals with a metallic lustre; mp 290-292 °C. UV-VIS (CH_3OH, 3% DMF) λ_{max} (log ε): 302 (3.73), 464 (4.18), 480 (4.22). IR (KBr): 1723, 1544, 1377, 1278, 1243, 1027 cm^{-1}. ^1H NMR ($CDCl_3$) δ (ppm) 3.96 (s, 6H), 6.68 (d, J = 3.9 Hz, 4H) , 7.44 (d, J = 8.3 Hz, 4H), 8.04 (m, 4H), 8.06 (d, J = 8.3 Hz, 4H), 10.46 (br s, 4H). ^{13}C NMR ($CDCl_3$) δ (ppm) 52.4, 128.7, 130.6, 130.7, 137.9, 139.8, 141.2, 141.9, 150.5, 166.7, 177.1. MS (ESI) for $C_{34}H_{26}N_4O_4Ni$: m/e 613.0 [MH^+] (100 %), 614.0 (42 %), 615.0 (48 %), 616 (19 %).

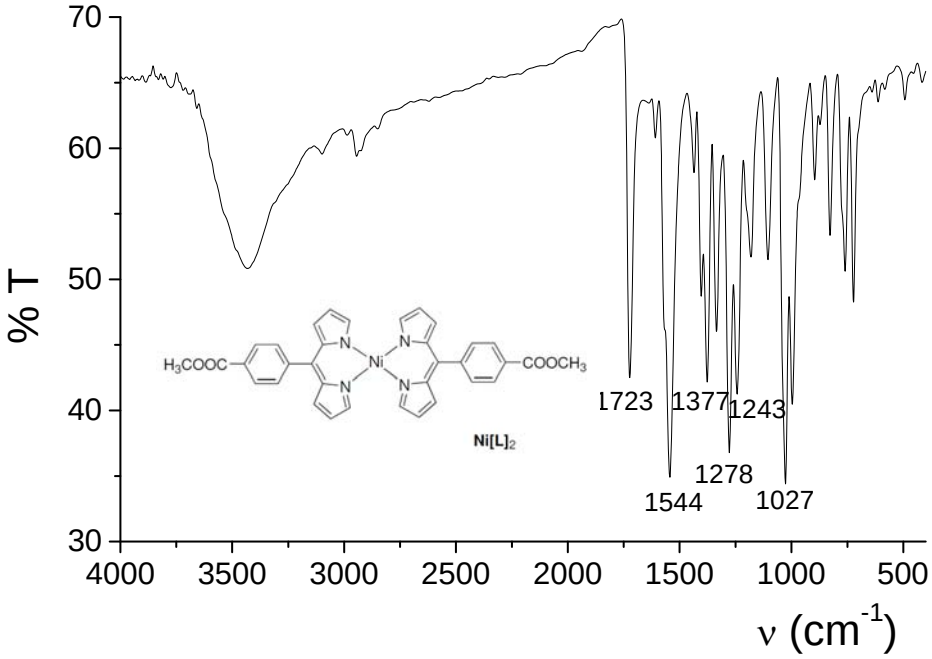
ESI – CH_2Cl_2 / CH_3OH



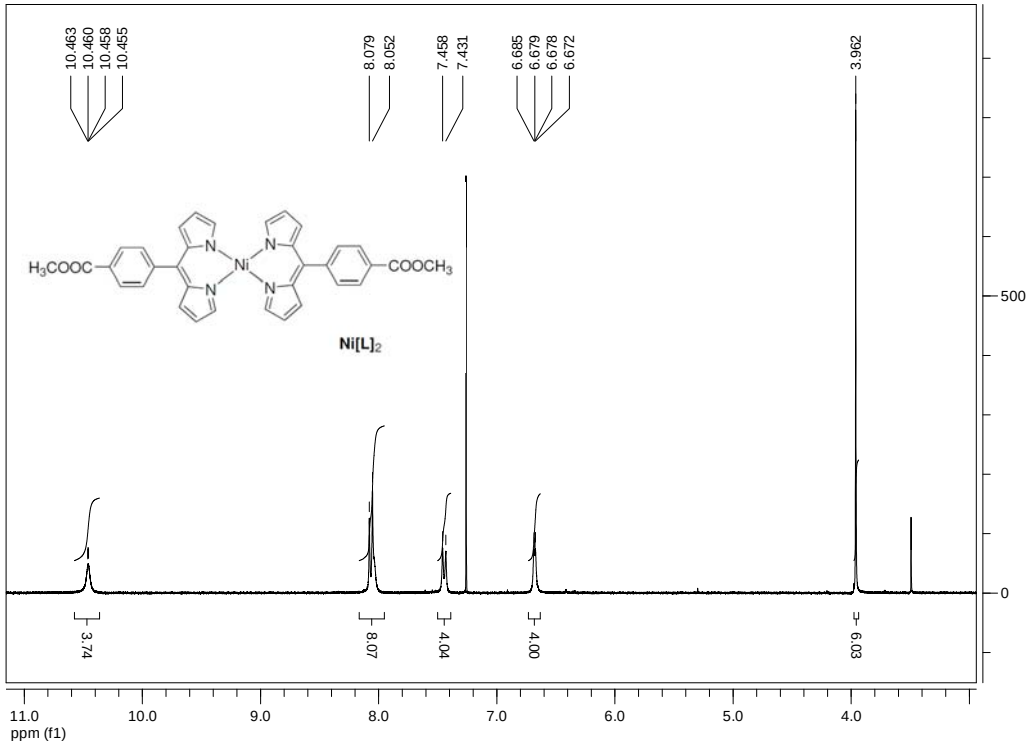
UV Visible ($CDCl_3$) (80 µM in CH_3OH + 3 % DMF)



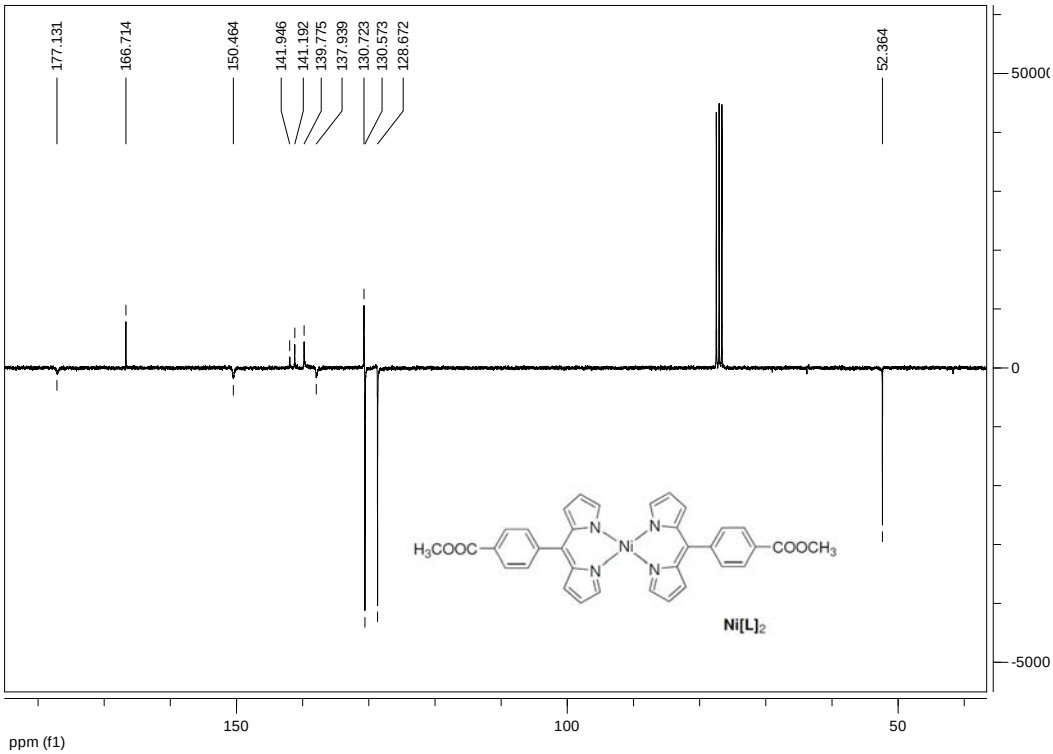
IR (KBr)



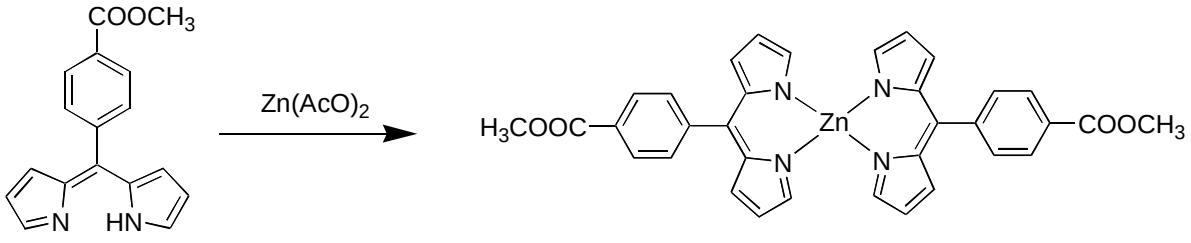
^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)



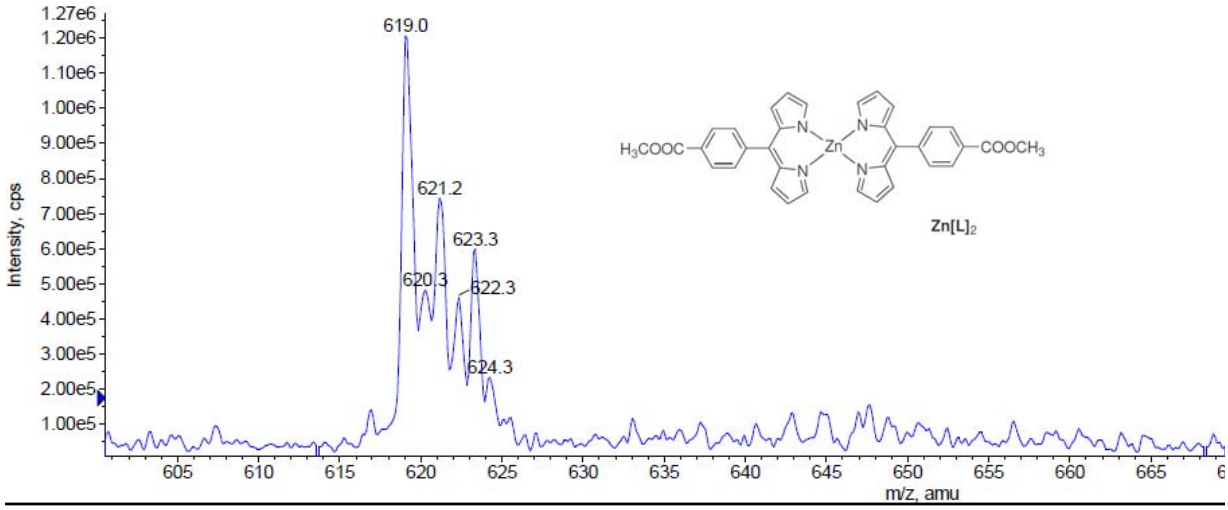
Bis[4-methoxycarbonylphenyl-4,6-pyrrinato]Zn(II) ($Zn[L]_2$)



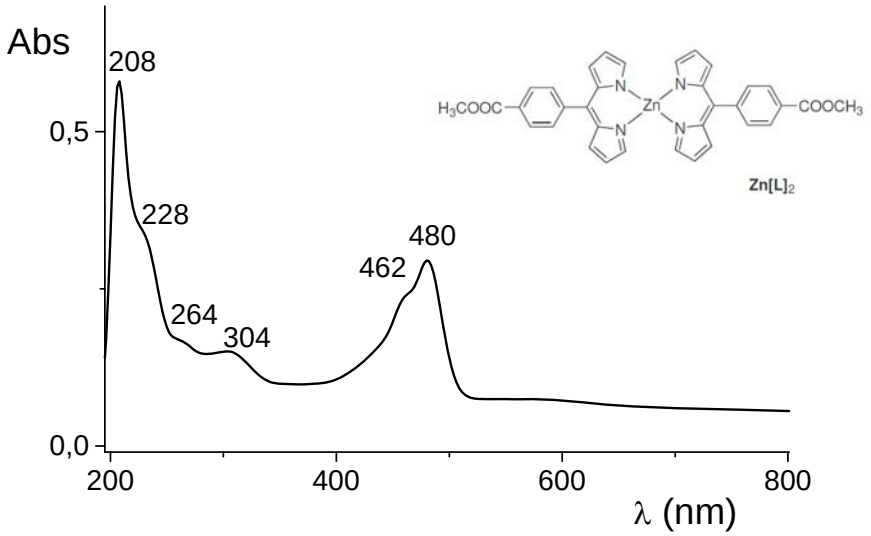
LH **$Zn[L]_2$**

To a solution of dipyrine **LH** (200 mg, 0.72 mmol) in methanol (50 mL) was added zinc(II) acetate (79 mg, 0.36 mmol, 0.5 eq.) and the mixture was magnetically stirred at room temperature for 2 h. The orange precipitate was filtered off and air-dried to provide 210 mg (94 %) of pure zinc complex **$Zn[L]_2$**. Crystallization from a slow evaporation of a solution of *N*,*N*-dimethylformamide yielded orange dichroic microcrystals; mp >350 °C. UV-VIS (CH_3OH, 0.3% CH_2Cl_2) λ_{max} (log ε): 208 (3.86), 264 (3.33), 304 (3.27), 462 (3.48), 480 (3.57). IR (KBr): 1724, 1539, 1403, 1374, 1335, 1281, 1244, 1190, 1106, 1030 cm^{-1}. ^1H NMR ($CDCl_3$) δ (ppm) 4.02 (s, 6H), 6.45 (dd, J = 1.5 and 3.2 Hz, 4H) , 6.66 (dd, J = 0.9 and 4.2 Hz, 4H), 7.58 (s, 4H), 7.67 (d, J = 8.1 Hz, 4H), 8.17 (d, J = 8.1 Hz 4H). MS (ESI) for $C_{34}H_{26}N_4O_4Zn$: m/e 619.0 [MH^+] (100 %), 621.0 (42 %), 623.0 (48 %).

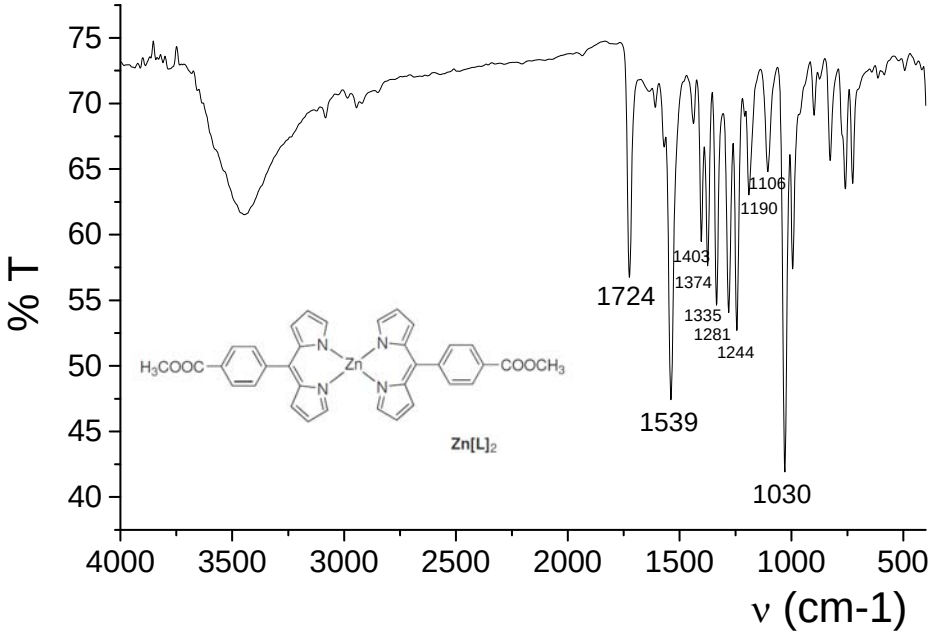
ESI – CH_2Cl_2 / CH_3OH



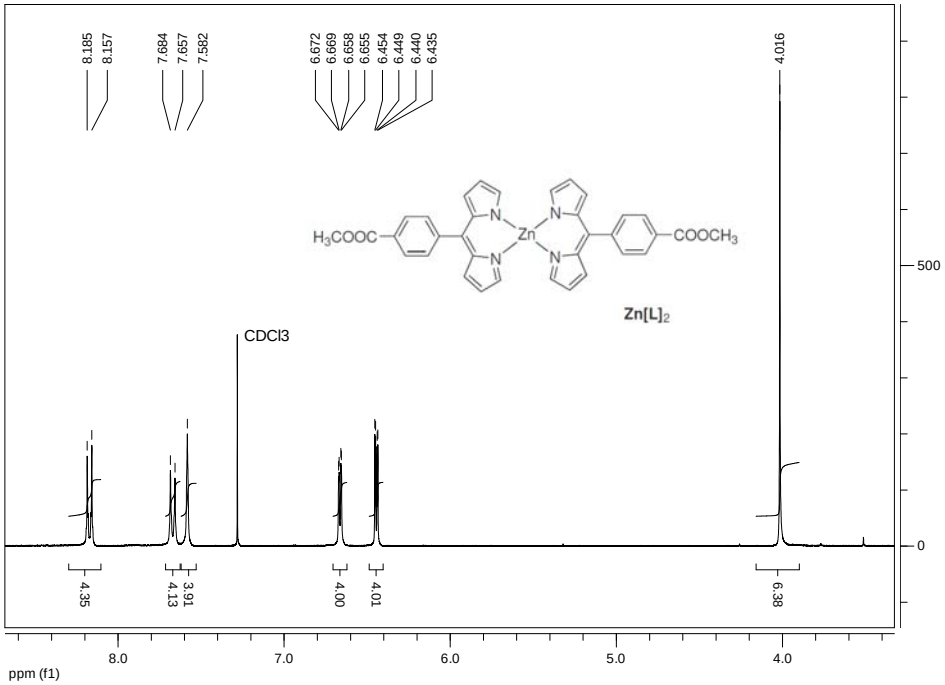
UV Visible ($CDCl_3$) (80 µM in CH_3OH + 3 % DMF)



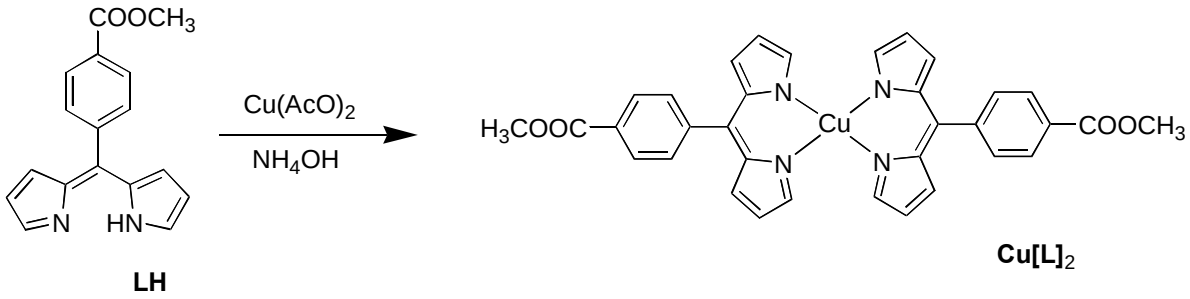
IR (KBr)



^{1}H NMR ($CDCl_3$)



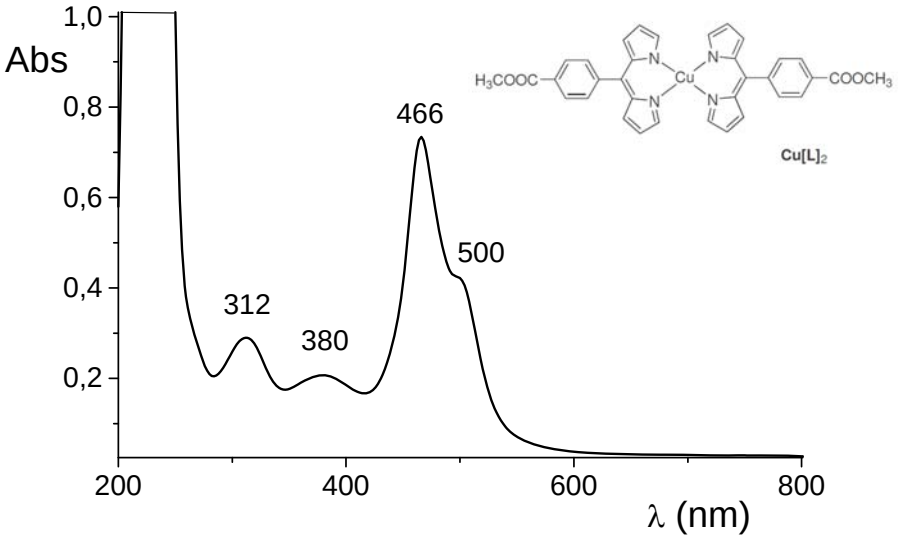
Bis[4-methoxycarbonylphenyl-4,6-pyrrinato]Cu(II) ($Cu[L]_2$)



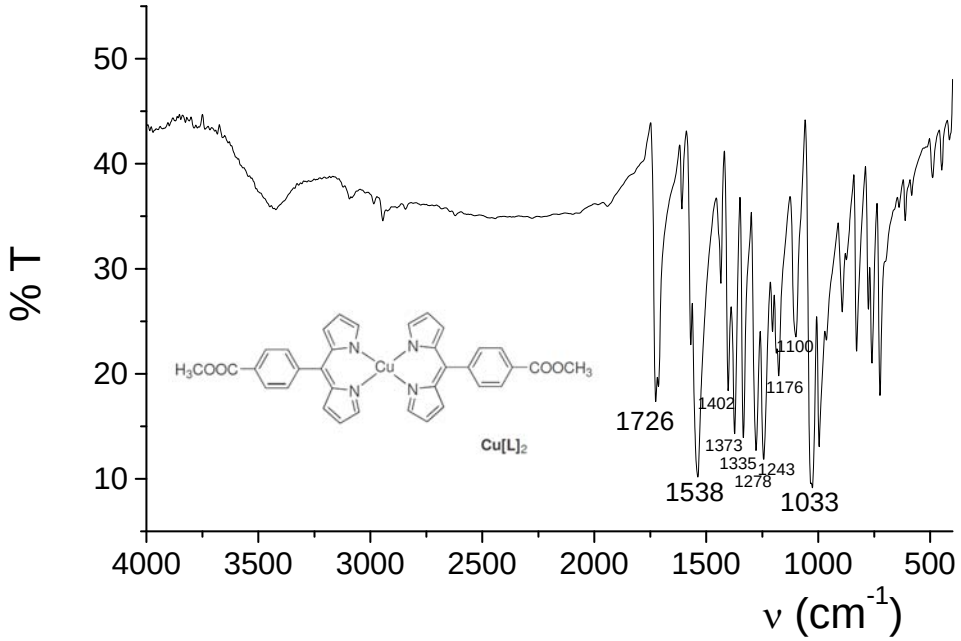
LH **$Cu[L]_2$**

To a solution of dipyrine **LH** (300 mg, 1.08 mmol, 1 eq.) in methanol (50 mL) was added a 28 % ammonium hydroxide solution (5 mL), and then slowly anhydrous copper(II) acetate (98 mg, 0.54 mmol, 0.5 eq.) and the mixture was magnetically stirred at room temperature for 1H30. The precipitate was then filtered off, washed with methanol, and purified by chromatography on silica gel (silica gel 60, 0.035-0.070 mm, ACROS Organics) using dichloromethane as eluent to give 205 mg (61 %) of analytically pure copper complex **$Cu[L]_2$**. Crystallization from a slow evaporation of a solution of dichloromethane yielded green dichroic microcrystals with a metallic lustre; mp 250-252 °C. UV-VIS (CH_3OH, 1% DMF) λ_{max} (log ε): 312 (3.08), 380 (2.94), 466 (3.48), 500 (3.24). IR (KBr): 1726, 1538, 1402, 1373, 1335, 1278, 1243, 1176, 1100, 1033 cm^{-1}. The NMR spectra could not be recorded (paramagnetic). MS (MALDI-TOF) for $C_{34}H_{26}N_4O_4Cu$: m/e 617.0 [MH^+] (100 %), 618.0 (40 %), 617.0 (43 %).

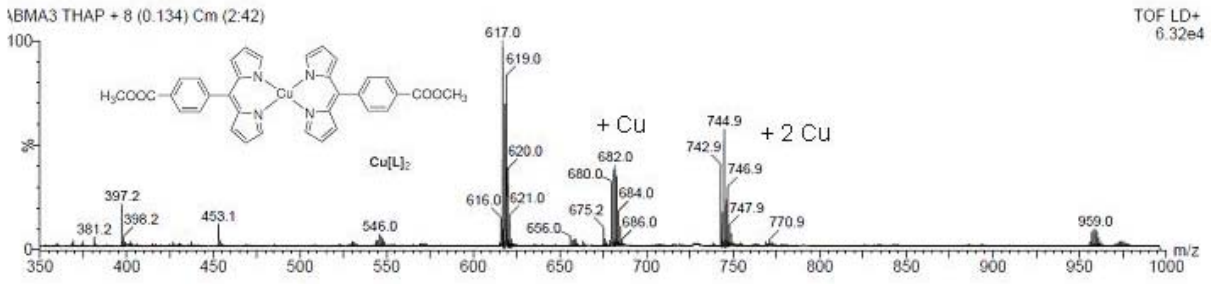
UV Visible ($CDCl_3$) (240 µM in CH_3OH + 1 % DMF)



IR (KBr)



MALDI – TOF



III. X-ray crystallographic details

Data were collected at low temperature (193 K) using an oil-coated shock-cooled crystal on a Bruker-AXS APEX II diffractometer with Mo Kα radiation (k = 0.71073 Å). The structures have been solved by Direct Methods using SIR 92[2], and all non hydrogen atoms were refined anisotropically using the least-squares method on F² with the aid of the program SHELXL 97[3] included in the software package WINGX version 1.63[4].

LH: $C_{17}H_{14}N_2O_2$, *M*=278.30, monoclinic, space group *P2/c*, a=11.4997(3)Å, b=11.1220(4)Å, c=22.5876(6)Å, β=91.285(2)°, *V*=2888.22(15)Å^3, *Z*=8, crystal size 0.42x 0.36 x 0.14 mm^3, 18848 reflections collected (5283 independent, R_{int}=0.0538), 387 parameters, *R*1 [I>2σ(I)]= 0.0505, *wR*2 [all data]= 0.1377, largest diff. peak and hole: 0.576 and -0.297 e.Å^{-3}.

Ni[L]2: $C_{34}H_{26}N_4NiO_4$, *M*=613.28, monoclinic, space group *C2/c*, a=22.9274(8)Å, b=21.1264(8)Å, c=23.1730(9)Å, β=90.436(2)°, *V*=11224.1(7)Å^3, *Z*=16, crystal size 0.40 x 0.12 x 0.02 mm^3, 67647 reflections collected (5365 independent, R_{int}=0.1809), 781 parameters, *R*1 [I>2σ(I)]= 0.0562, *wR*2 [all data]= 0.123, largest diff. peak and hole: 1.05 and -0.666 e.Å^{-3}.

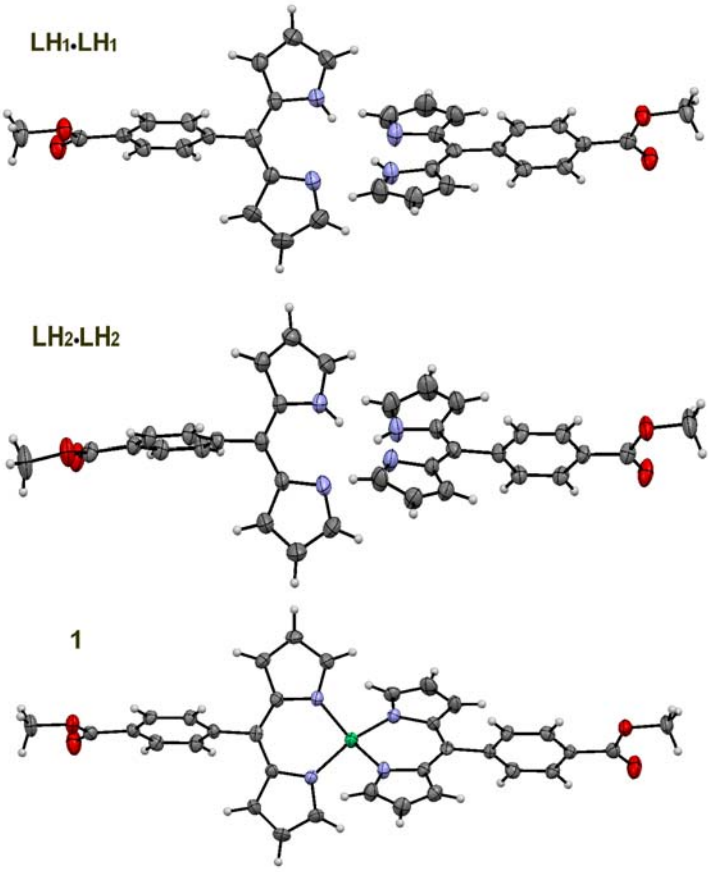
Zn[L]2: $C_{34}H_{26}N_4O_4Zn$, *M*=619.98, monoclinic, space group *P2/c*, a=11.5320(13)Å, b=11.0426(10)Å, c=22.891(3)Å, β=90.073(4)°, *V*=2915.0(6)Å^3, *Z*=4, crystal size 0.50 x 0.04 x

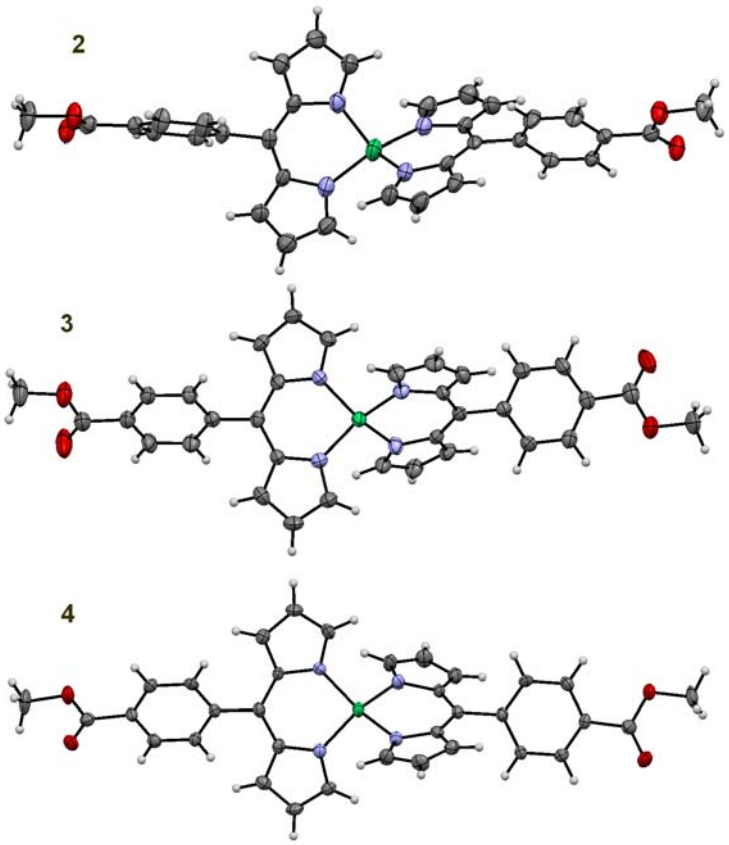
0.04 mm^3, 19463 reflections collected (5902 independent, R_{int}=0.0739), 391 parameters, *R*1 [I>2σ(I)]= 0.0486, *wR*2 [all data]= 0.1161, largest diff. peak and hole: 0.348 and -0.327 e.$Å^{-3}$.

Cu[L]$_2$: $C_{34}CuH_{26}N_4O_4$, *M*=618.14, monoclinic, space group *C2/c*, a=23.0164(6)Å, b=20.7890(6)Å, c=23.3891(7)Å, β=90.592(2)°, *V*=11190.8(5)$Å^3$, *Z*=16, crystal size 0.32 x 0.05 x 0.03 mm^3, 78344 reflections collected (11351 independent, R_{int}=0.1145), 781 parameters, *R*1 [I>2σ(I)]= 0.0481, *wR*2 [all data]= 0.1250, largest diff. peak and hole: 1.236 and -0.909 e.$Å^{-3}$.

Red-LH: $C_{17}H_{16}N_2O_2$, *M*=280.32, triclinic, space group *P-1*, a=5.6828(3)Å, b=7.6675(4)Å, c=16.4091(9)Å, β=95.194(4)°, *V*=703.87(6)$Å^3$, *Z*=2, crystal size 0.34x 0.3 x 0.02 mm^3, 5780 reflections collected (3201 independent, R_{int}=0.0409), 197 parameters, *R*1 [I>2σ(I)]= 0.0652, *wR*2 [all data]= 0.1762, largest diff. peak and hole: 0.264 and -0.268 e.$Å^{-3}$.

1 – Views of dimeric structure of dipyrrin **LH** and its **Ni**-complex analogues (**Ni[L]$_2$, 1-4**).

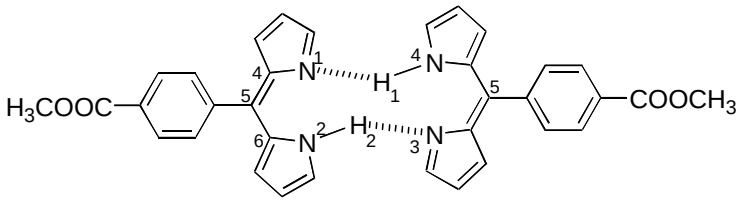




Interplane angle	**LH1•LH1**	**LH2•LH2**	**1**	**2**	**3**	**4**
Ph-Ph	13.53°	21.15°	10.64°	23.09°	46.65°	33.46°
Ph-Dipyr.	60.65°	57.90°	70.16°	63.09°	53.74°	50.69°
Dipyr-Dipyr	72.64°	86.27°	50.71°	83.52°	63.11°	67.87°

angle	**LH1•LH1**	**LH2•LH2**	**1**	**2**	**3**	**4**
$C_{para}NiC_{para}$	-	-	178.47°	155.10°	169.68°	175.50°
$C_{para}C_5C_{para}$	173.30°	172.68°	178.13°	164.47°	170.99°	175.32°

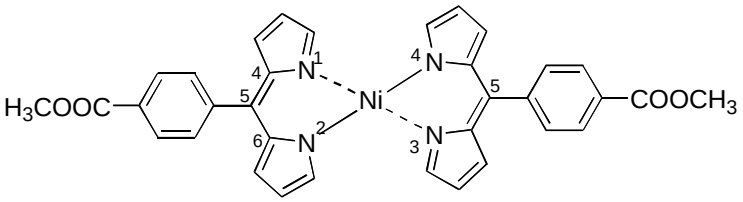
2 – Selected geometrical parameters of the dimeric structures of **LH**.



LH•LH

Distance (Å) or angle	**LH1•LH1**	**LH2•LH2**
N^1-N^2	2.770	2.865
N^1-N^3	3.076	3.266
N^2-N^4	3.076	3.266
N^1-N^4	3.733	2.960
N^2-N^3	3.179	2.966
N^1-H^1	2.247	2.317
N^1-H^2	2.493	2.680
N^3-H^1	2.493	2.680
N^3-H^2	2.247	2.317
C^5- C^5	6.634	6.392
<C^4-C^5-C^6>	124.95 °	125.06 °

3 – Selected geometrical parameters of **Ni[L_2]** complexes **1**-**4**.

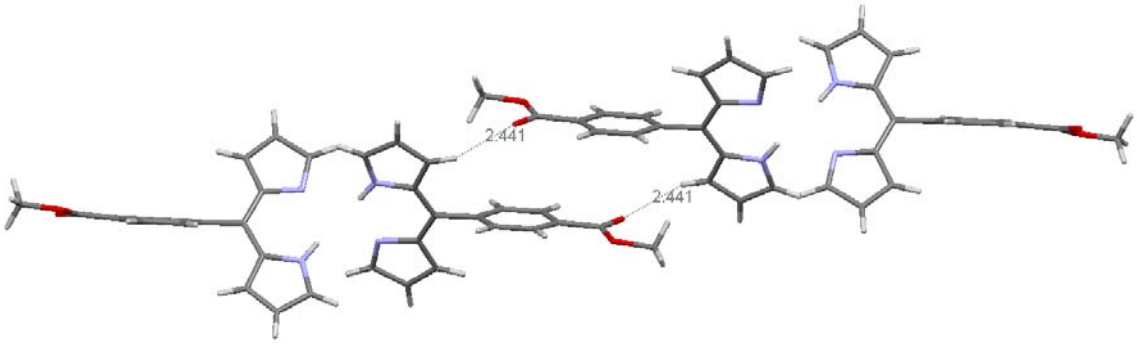


Ni[L_2]

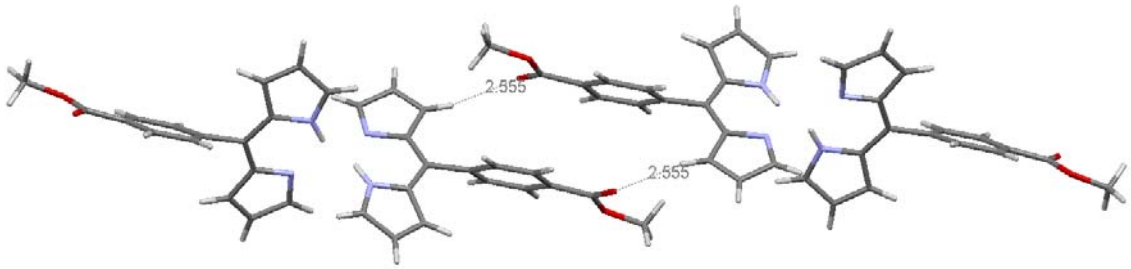
	Ni[L_2]			
Distance (Å) or angle	**1**	**2**	**3**	**4**
N^1-N^2	2.726	2.805	2.719	2.733
N^1-N^3	3.641	3.716	3.627	3.622
N^2-N^4	3.671	3.253	3.658	3.622
Ni-N^1	1.889	1.939	1.891	1.891
Ni-N^2	1.891	1.962	1.886	1.885
Ni-N^3	1.889	1.939	1.891	1.891
Ni-N^4	1.891	1.962	1.886	1.885
N^1-N^4	2.787	3.128	2.805	2.795
N^2-N^3	2.787	3.128	2.805	2.837
C^5- C^5	6.683	6.567	6.693	6.676
<C^4-C^5-C^6>	125.35 °	126.88 °	123.86 °	123.69 °

4– Interactions between **LH** dimers

[LH1●LH1] ●[LH1●LH1]

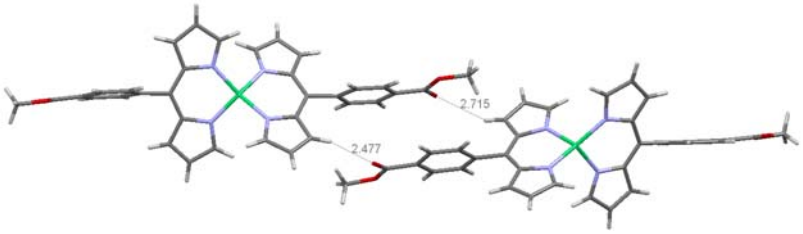


[LH2●LH2] ●[LH2●LH2]

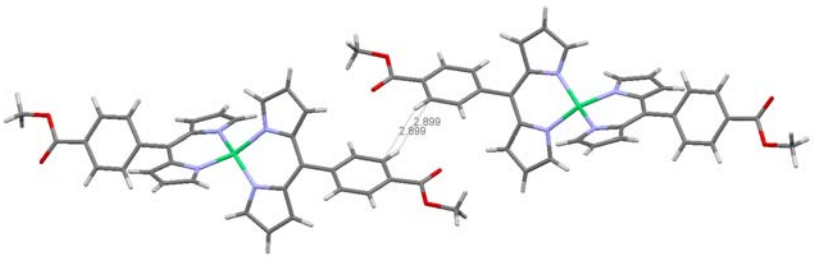


5 – Interactions between nickel complexes

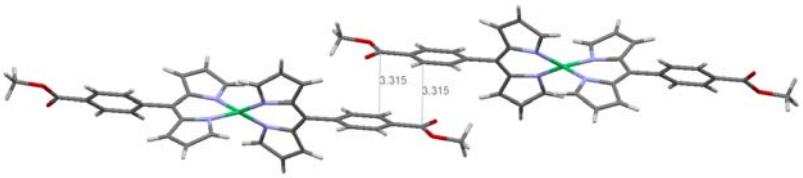
1●2



3●3

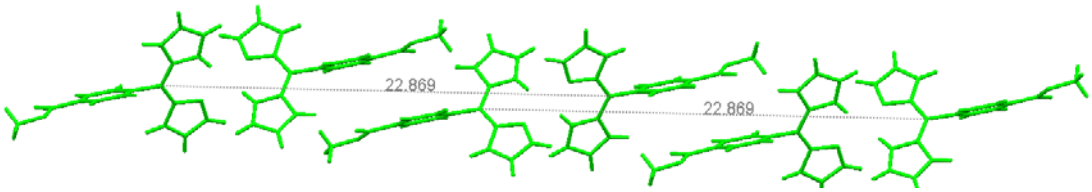


4●4

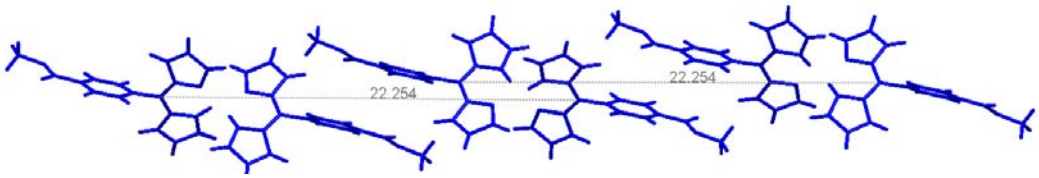


6 – C_5-C'_5 distances for **LH** and Ni complexes

$(LH1)_n$

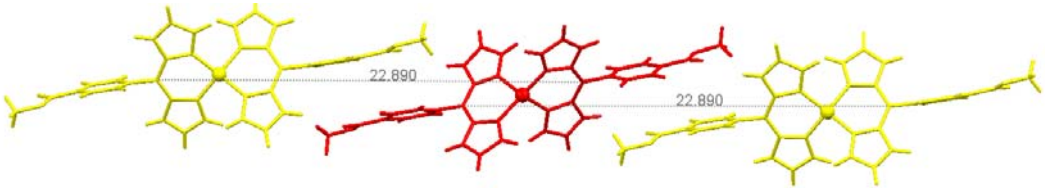


$(LH2)_n$

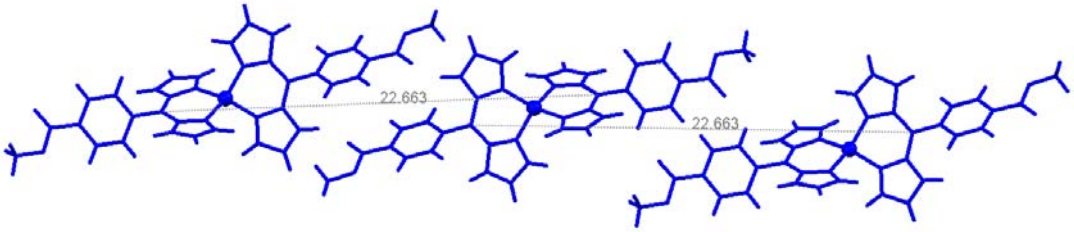


	$(LH1)_n$	**$(LH2)_n$**
$d^4_{C5\text{-}C5}$	22.869	22.254

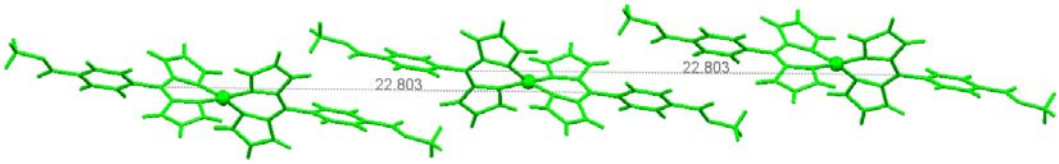
$(1\bullet2)_n$



$(3)_n$

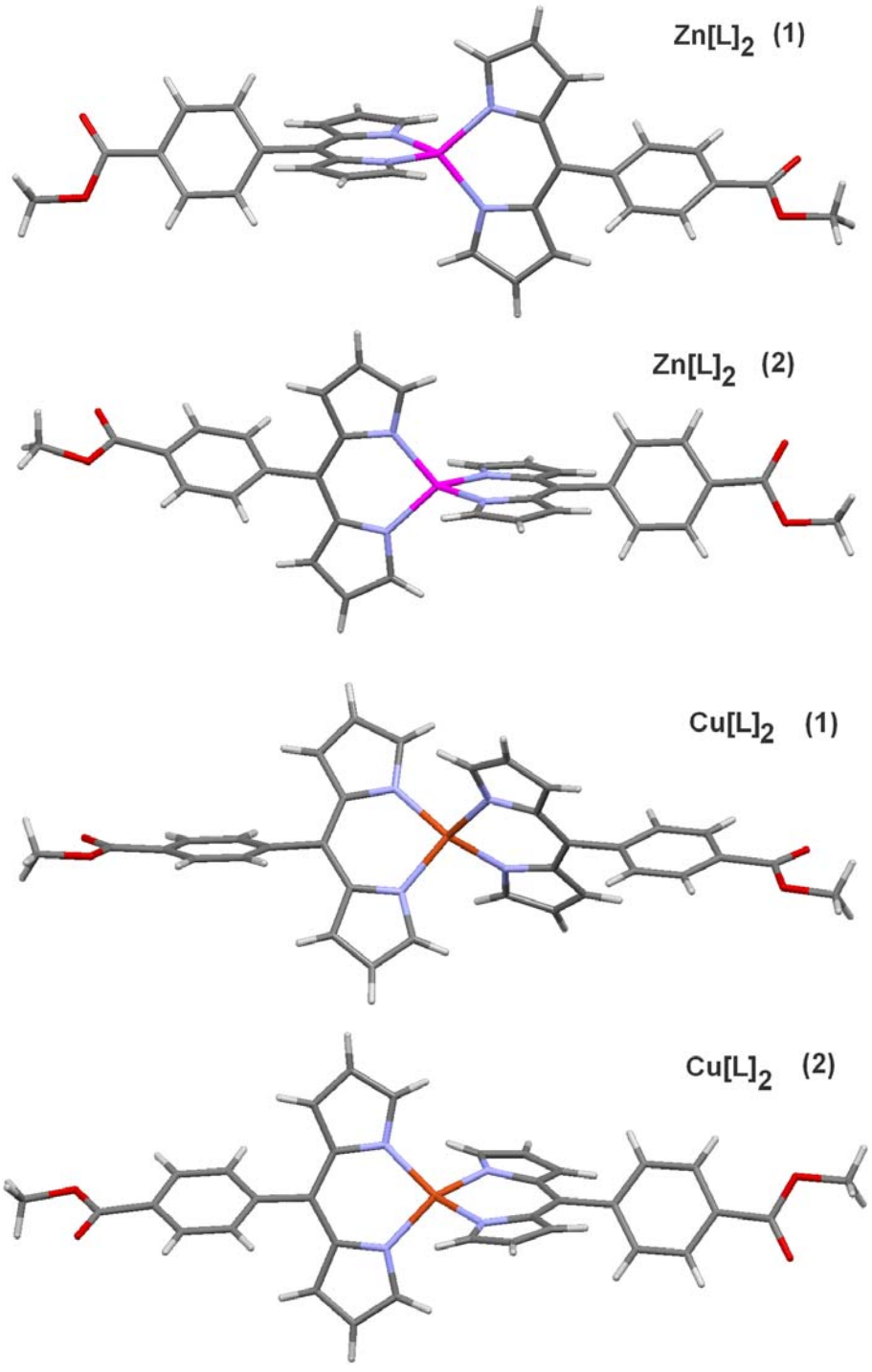


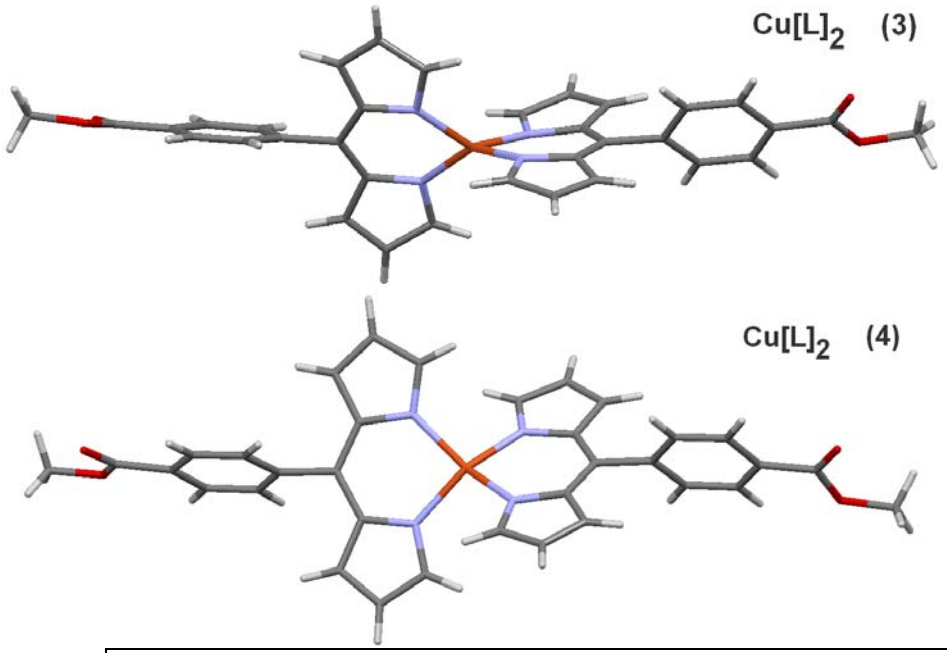
$(4)_n$



	$(1\bullet2)_n$	**$(3)_n$**	**$(4)_n$**
$d^4_{C5\text{-}C5}$	22.890	22.663	22.803

7 – Views of **Zn[L$_2$]** and **Cu[L$_2$]** complexes.



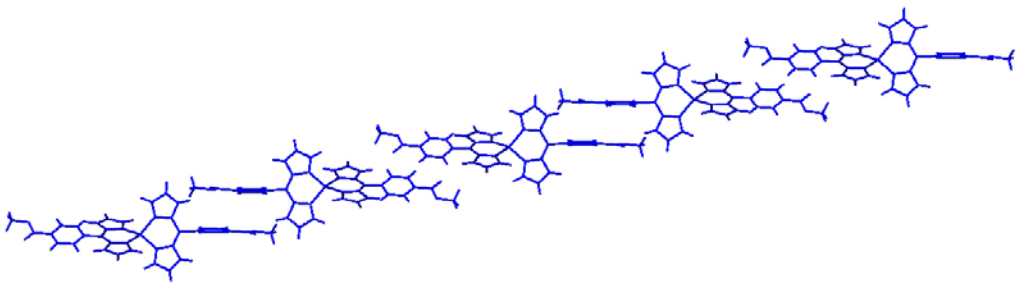


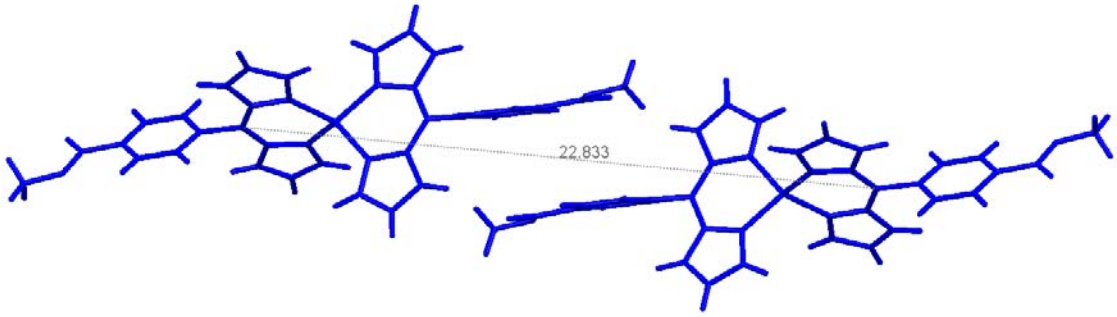
	Zn[L_2]			
	Zn-1	**Zn-2**	-	-
C^5- C^5 distance (Å)	6.650	6.681	-	-
Dipyr-Dipyr Interplane angle	83.95 °	83.14 °	-	-
	Cu[L_2]			
	Cu-1	**Cu-2**	**Cu-3**	**Cu-4**
C^5- C^5 distance (Å)	6.633	6.730	6.736	6.714
Dipyr-Dipyr Interplane angle	71.49 °	72.12 °	68.25 °	52.55 °

8 – Views and C_5-C'_5 distances for Zn and Cu complexes

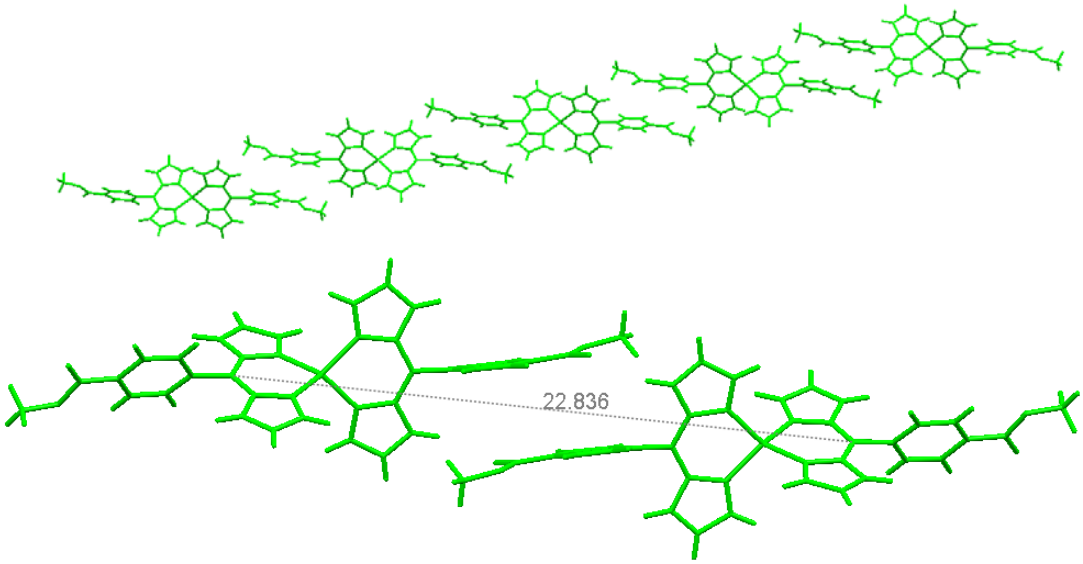
Zn[L_2] :

(Zn-1)$_n$

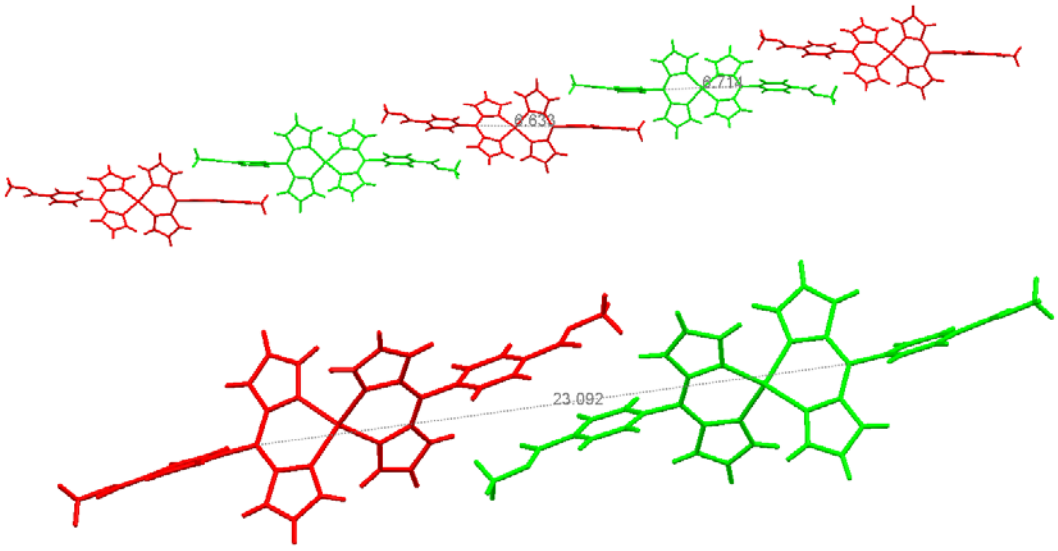




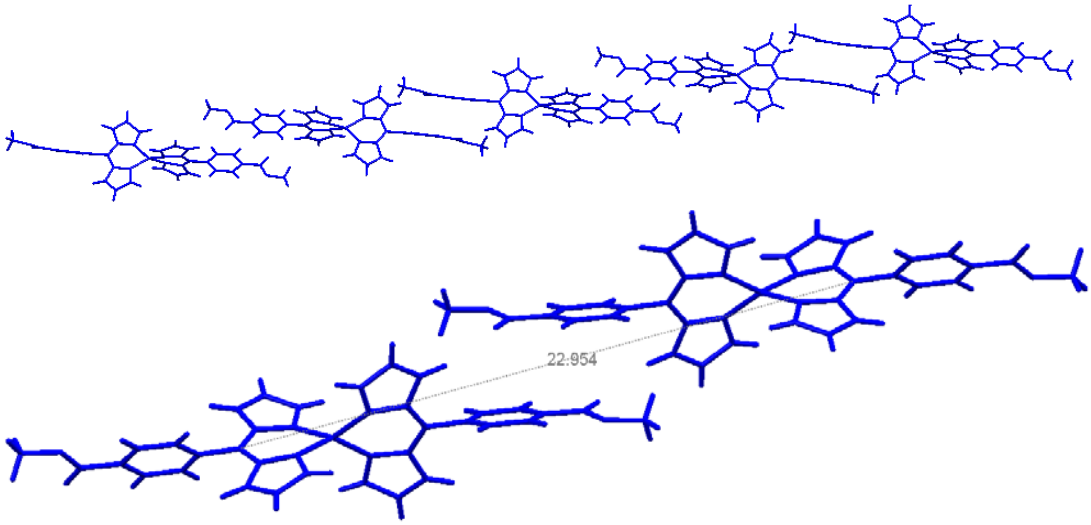
(Zn-2) $_n$



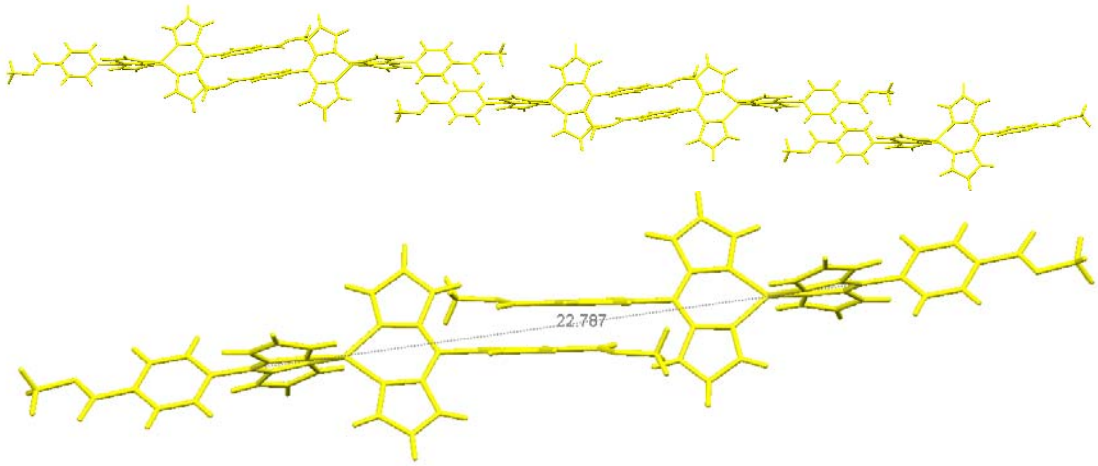
Cu[L$_2$] :
(Cu-1●Cu-4) $_n$



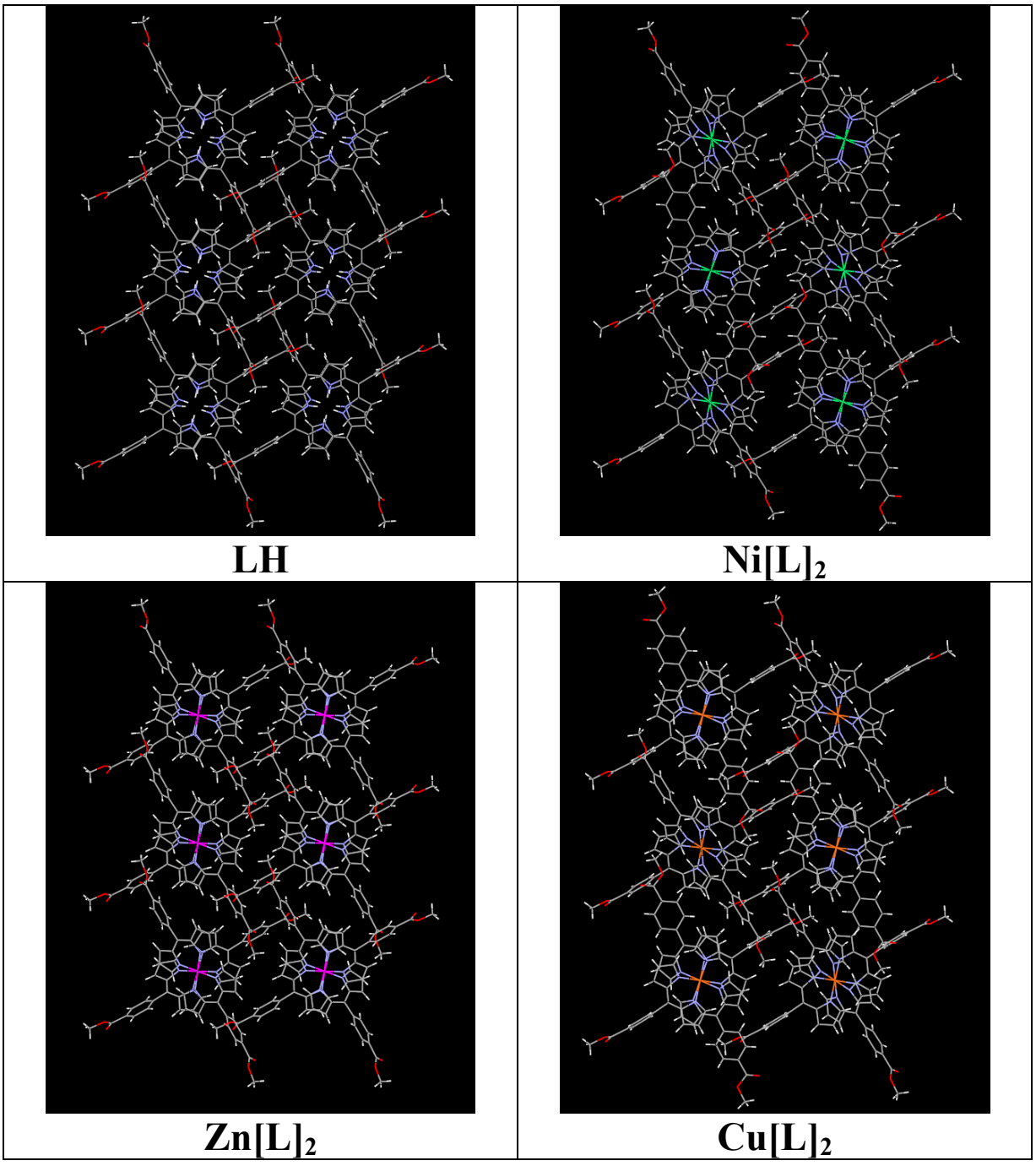
(Cu-2) $_n$



(Cu-3) $_n$



9 – Part of the crystal structures of **LH**, **Ni[L]$_2$**, **Zn[L]$_2$** and **Cu[L]$_2$** showing the close similarity in the 3D packing (along the *b* axis) of dipyrrin-based molecules substituted by the 4-methoxycarbonylphenyl moeity.



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