Synthesis of a Novel Zinc(II) Porphyrin Complex, Halide Ions Reception, Catalytic Degradation of Dyes and Optoelectronic Application

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CONTENTS

1. Synthetic procedures

1.1.Synthesis of the 4α-*Meso*-tetra(*o*-aminophenylporphyrin (4α-H_2TNH_2PP) (1)

8 g of *Meso*-tetra-(*o*-nitrophenyl) porphyrin (H_2TNO_2PP) (0.01 mol) was dissolved in 400 mL of HCl (37%). 33 g of $SnCl_2{\cdot}2H_2O$ (0.14 mol) dissolved in 40 mL of a concentrated hydrochloric acid was added under magnetic stirring. The stirring was maintained at room temperature for 90 min, then the temperature was raised to 60 °C within 10 min and maintained for 1 hour. The solution was cooled in an ice bath and the reaction mixture was then neutralized carefully by adding slowly and in small portions, 400 mL of 30% NH_4OH. The pH was then adjusted to >10 with NH_4OH. The biphasic basic brown solution was then stirred vigorously in the presence of 600 mL of $CHCl_3$, for 12 hours. After few minutes of stirring, the beginning of settling was observed. The organic phase was washed several times with an aqueous solution of NH_4OH at pH 8-9 then with water. Using the rotary evaporator, the organic phase was evaporated to 250 mL. The product crystallizes by successive concentrations in the rotary evaporator and addition of ethanol. The obtained crystals were washed with 4 portions of 10 mL ethanol and dried under vacuum for 12 hours. The desired product was obtained with a 71% yield (5 g).

The obtained product is made by a mixture of four atropisomers of the H_2TNH_2PP porphyrin. In order to increase the yield of the 4α-H_2TNH_2PP atropisomer, a recycling process was performed. This process consists of shifting the conformational equilibrium to the 4α-H_2TNH_2PP atropisomer by its adsorption onto silica. 5 g of four mixed atropisomers of the H_2TNH_2PP porphyrin (0.007 mol) were dissolved in a 1 liter of $CHCl_3$ in the presence of 450 g of silica (7.5 mol). The solution was then mechanically stirred under argon bubbling (to avoid any oxidation of the amines) and maintain under reflux for 48 hours. The solution was then cooled to room temperature and filtered. The silica was washed with small fractions of $CHCl_3$ until the eluents are very pale. The 4α-H_2TNH_2PP atropisomer was extracted from the silica using an acetone-ether 1/1 mixture. In order to avoid any subsequent isomerization, the temperature should not exceed 30°C. The 4α-H_2TNH_2PP atropisomer was then separated from the other three isomers by chromatography due to its strong polarity. A first fraction of this atropisomer was first separated by chromatography on silica column. The three other atropisomers were separated by the $CHCl_3$-ether mixture, while the fraction containing the 4α isomer was separated by the 1/1 acetone-ether mixture. This fraction was evaporated to dryness and passed over a second $CHCl_3$-mounted silica chromatographic column. On this column, the residues of the three atropisomers (which are the least polar) were separated using a toluene-ether 1/1 mixture. The pure 4α-H_2TNH_2PP atropisomer was then extracted with acetone-ether 1/1 eluent. A 750 mg of 4α-H_2TNH_2PP was obtained with a yield of 15%.

Anal (%) calcd for $C_{44}H_{34}N_8$ (674.79): C, 78.32, H, 5.08, N, 16.61, found: C, 78.19, H, 5.19; N, 16.75; UV-visible [CH_2Cl_2]: λ_{max} ($\varepsilon.10^{-3}M^{-1}.cm^{-1}$): 424(545), 514(434), 552(414), 592(409), 677(424).^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm), 8.91 (s, 8H, β-pyrrole), 7.85 (d, *J* = 7.6 Hz, 4H, ArH), 7.60 (d, *J* = 6.8 Hz, 4H ArH), 7.13 (d, *J* = 7.2 Hz 8H, ArH), 3.55 (s, 8H, NH-amino), -2.70 (NH-pyrolic). FTIR (solid, $\bar{\nu}$, cm^{-1}); 3356 [ν(NH) porphyrin], 2912 [ν(CH) porphyrin], 1601 [ν(C=N), ν(C=C)porphyrin], 965 [δ(CCH) porphyrin].

1.2.Synthesis of the *Meso*-tetra-(*o*-azidophenyl)porphyrin (4α-H_2TN_3PP) (2)

300 mg of the 4α-H_2TNH_2PP porphyrin (0.44 mmol) was dissolved in 15 mL of HCl/H_2O solution (1:1) at 0°C for 20 min with magnetic stirring. 75 mg of $NaNO_2$ (1.15 mmol) dissolved in 15 mL distilled water at 0°C was then added dropwise. After 20 minutes, a solution of 75 mg (1.15 mmol) of NaN_3 dissolved in 12 mL of distilled water was added dropwise. After 2 hours of stirring, the obtained mixture was separated using dichloromethane as solvent. The required compound was produced with a yield of 43% (250 mg).

Anal (%) calcd for $C_{44}H_{26}N_{16}$ (778.78): C, 67.86, H, 3.36, N, 28.78; found: C, 67.69; H, 3.41; N, 28.91; UV-visible [CH_2Cl_2]: λ_{max} ($\varepsilon.10^{-3}$ $M^{-1}.cm^{-1}$): 424(525), 514(34), 552(41), 592(40), 677(42). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm), 8.67 (s, 8H, β-pyrrole), 8.05 (d, *J* = 6.8 Hz, 4H ArH), 7.85 (d, *J* = 7.3 Hz, 4H ArH), 7.57 (d, *J* = 7.1 Hz, 8H, ArH), -2.68 (NH-Pyrolic). FTIR (solid, $\bar{\nu}$, cm^{-1}); 3298 [ν(NH) porphyrin], 2964 [ν(CH) porphyrin], 2130-2085 [ν(N_3)], 1497 [ν(C=N), ν(C=C) porphyrin], 980 [δ(CCH) porphyrin].

1.3.Synthesis of the [4α-*Meso*-tetra(2-azidophenyl)porphyrinate]zinc(II)(4α-[Zn(TN_3PP)]) (3)

250 mg (0.32 mmol) of 4α-H_2TN_3PP and 500 mg (2.7 mmol.) of zinc acetate $Zn(OAc)_2{\cdot}2H_2O$ were dissolved in 100 mL of chloroform/ethanol mixture. After 12 hours of stirring at room temperature the new zinc(II) metalloporphyrin **(3)** was obtained with a yield of 66 % (180 mg).

Anal (%) calcd for $C_{44}H_{24}N_{16}Zn$ (842.16): C, 62.75, H, 2.87, N, 26.61; found: C, 62.89; H, 2.91; N, 26.81; UV-visible [CH_2Cl_2]: λ_{max} ($\varepsilon.10^{-3}$ $M^{-1}.cm^{-1}$): 432(525), 560(41), 598(36). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm), 8.80 (s, 8 H β-pyrrole), 8.07 (d, *J* = 7.0 Hz,4H, ArH), 7.85 (d, *J* = 6.8 Hz4H, ArH), 7.61 (d, *J* = 7.4 Hz, 8H, ArH).FTIR (solid, $\bar{\nu}$, cm^{-1}); 2955-2915 [ν(CH) porphyrin],2133-2098 [ν(N_3),1517 [ν(C=N) , ν(C=C) porphyrin], 1011 [δ(CCH) porphyrin].

1.4. Synthesis of the [4α-*Meso*-tetra-(1,2,3-triazolyl)phenylporphyrinato]zinc(II)(4α-[Zn(TAzPP)] (4)

In a 250 mL flask, 50 mg of complex (**3**) (0.059 mmol), 45 mg of copper iodide (0.7 mmol) and 4.5 mL of trimethylamine (0. 2 mmol) were dissolved in a mixture of acetonitrile / THF (2/1). After 30 minutes of stirring, 2 mL of phenylacetylene (0.089 mmol) was added to the reaction mixture and left for 3 hours. The product was then obtained by extraction with chloroform/ether mixture (9/1) and purified by chromatography. The obtained yield is 42% (30 mg).

Anal (%) calcd for $C_{76}H_{48}N_{16}Zn$ (1250.69): C, 72.98, H, 3.87, N, 17.92, found: C, 73.69, H, 3.95, N, 17.78); UV-visible [CH_2Cl_2]: λ_{max} ($\varepsilon.10^{-3}$ $M^{-1}.cm^{-1}$): 430(544), 56(39), 601(32). ^1H NMR (400 MHz, $CDCl_3$) δ(ppm), 8.81 (s, 8H, β-pyrrole), 7.77 (d, J = 7.2 Hz, 8H, ArH), 7.61 (d, J = 7.2 Hz4H, ArH), 6.94 (s, 4H, Triazole-H), 6.68 (20H, ArH), FTIR (solid, $\bar{\nu}$, cm^{-1}); 2961 [ν(CH) porphyrin], 1731 [ν(C=C), ν(C=N) triazole], 1492 [ν(C=C), ν(C=N) porphyrin], 1063[δ(CCH) porphyrin].

2. IR spectroscopy

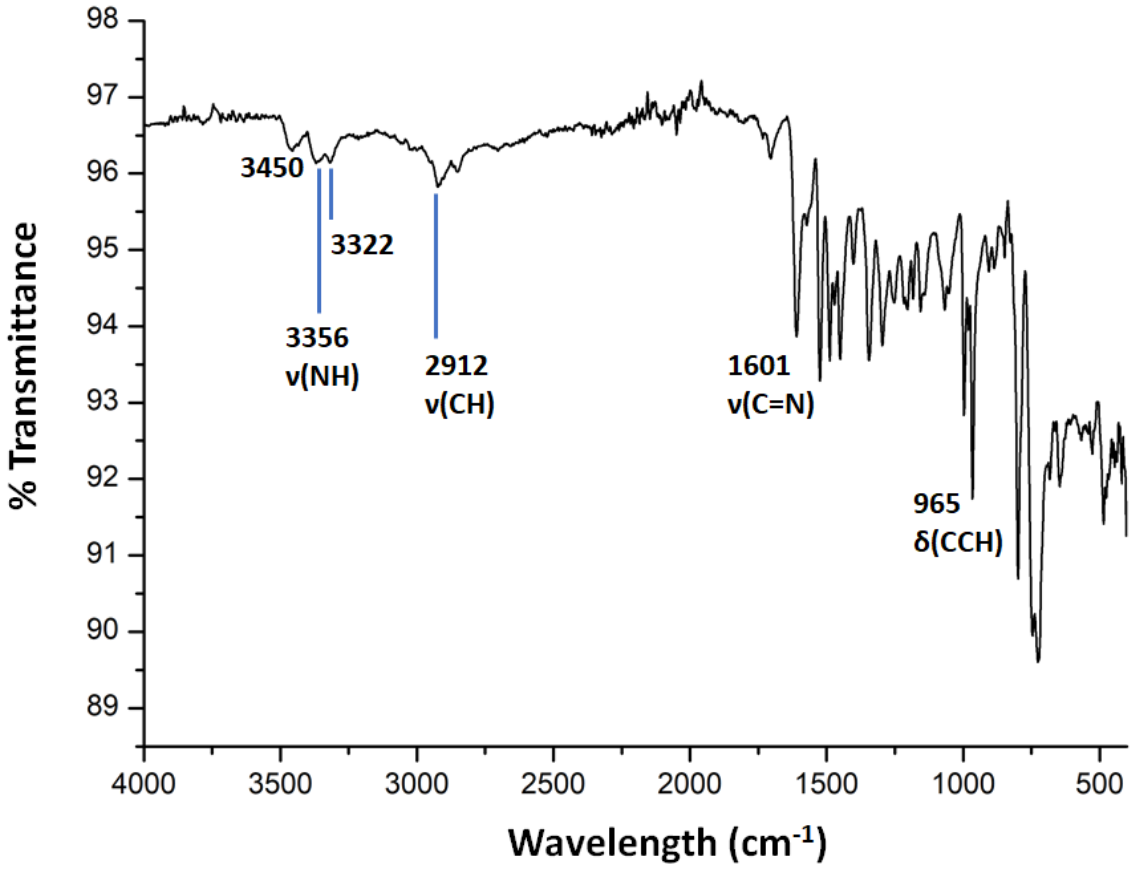

Figure S1. IR spectrum of the free base porphyrin (4α-H_2TNH_2PP) (**1**).

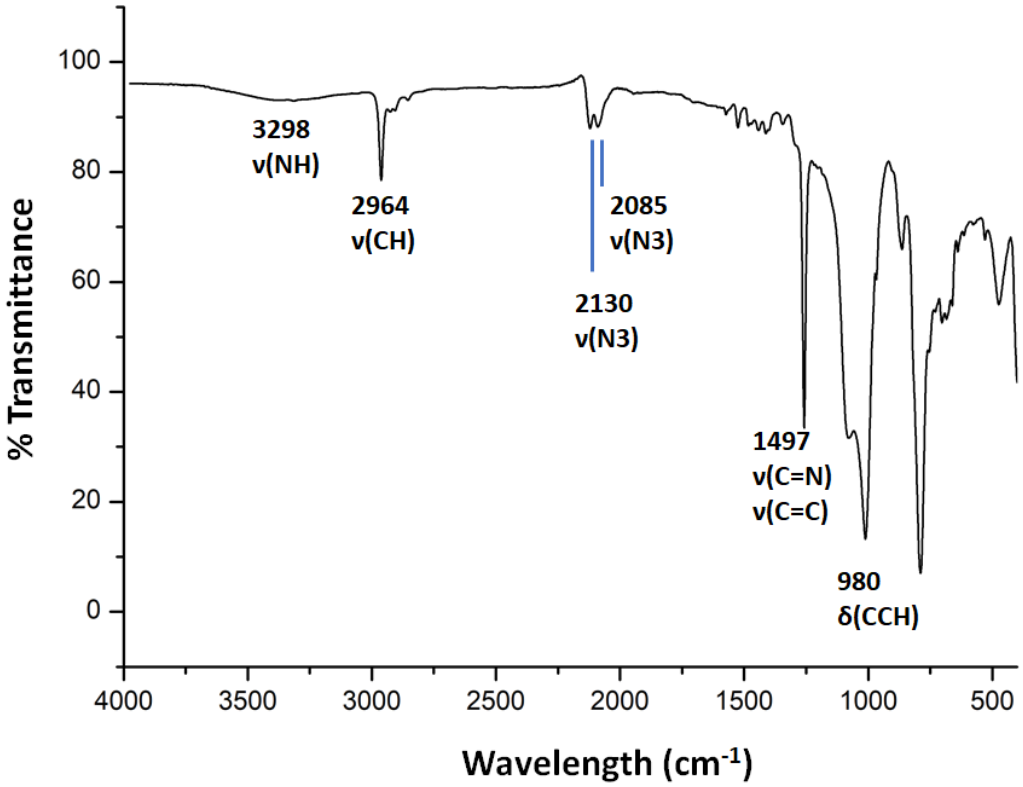

Figure S2. IR spectra of the free base porphyrin 4α-H_2TN_3PP (**2**).

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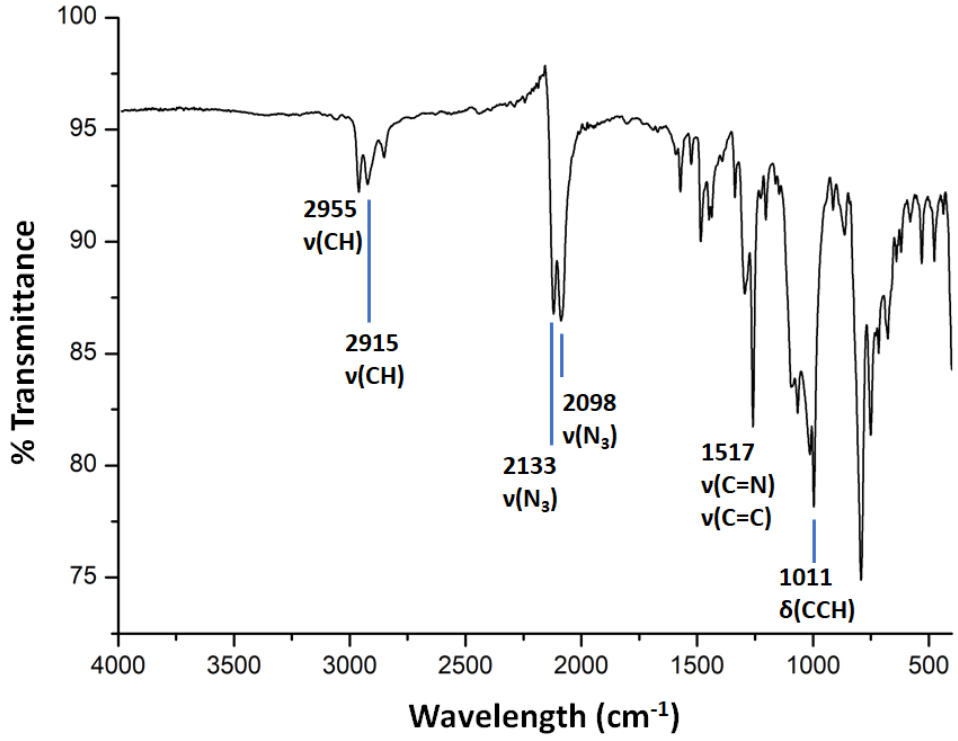

Figure S3. IR spectra of the complex 4α-[Zn(TN_3PP)]) (**3**).

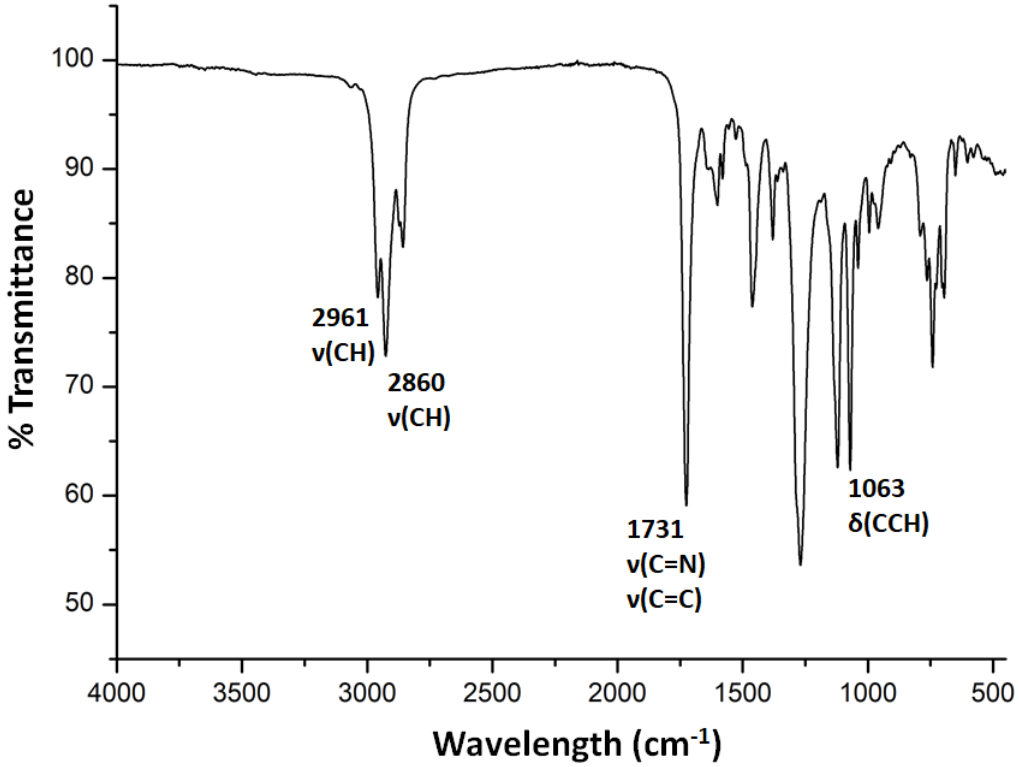

Figure S4. IR spectra of complex 4α-[Zn(TAzPP)] (**4**).

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3. ^{1}H NMR spectroscopy

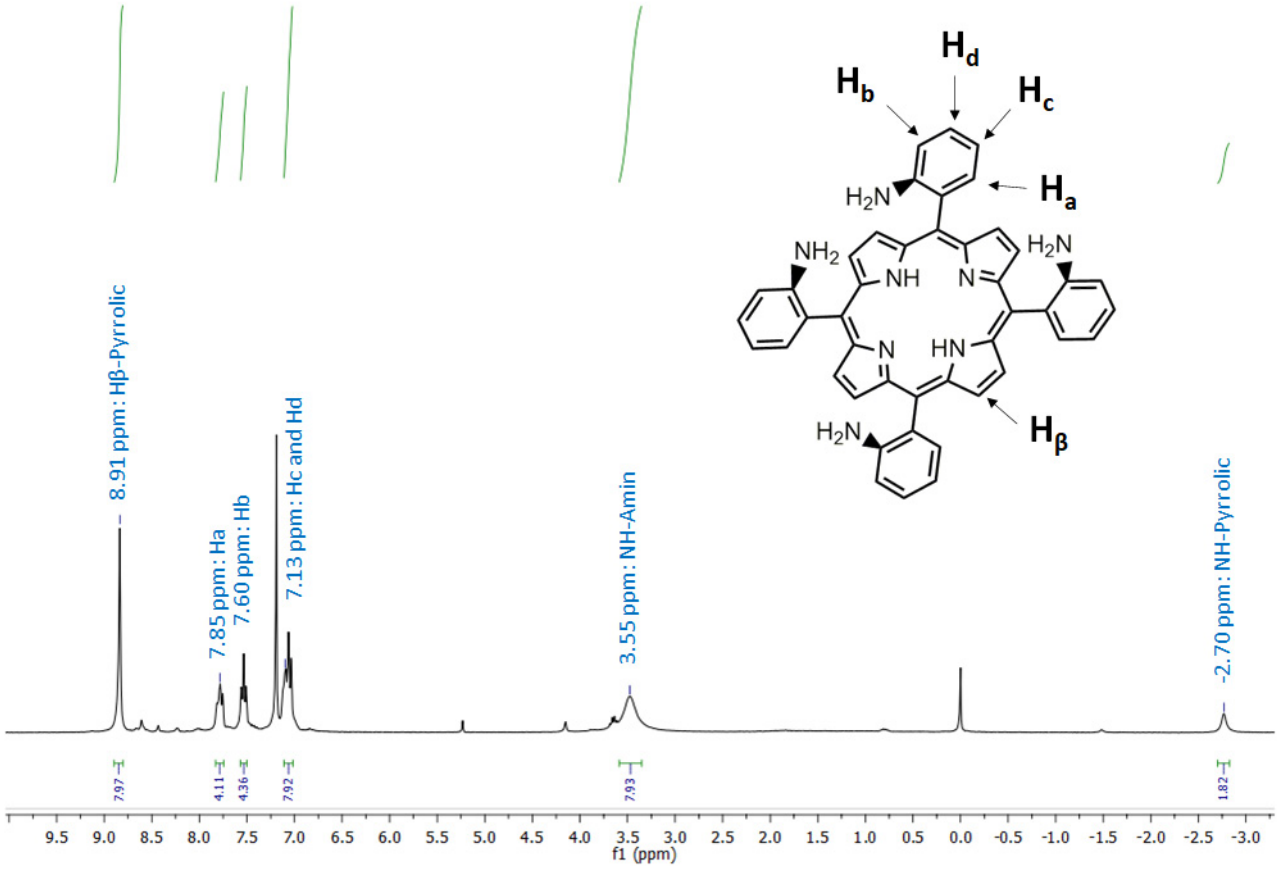

Figure S5. ^{1}H NMR spectrum of the free base porphyrin 4α-$H_2T_{NH2}PP$ (**1**)(400 MHz, $CDCl_3$).

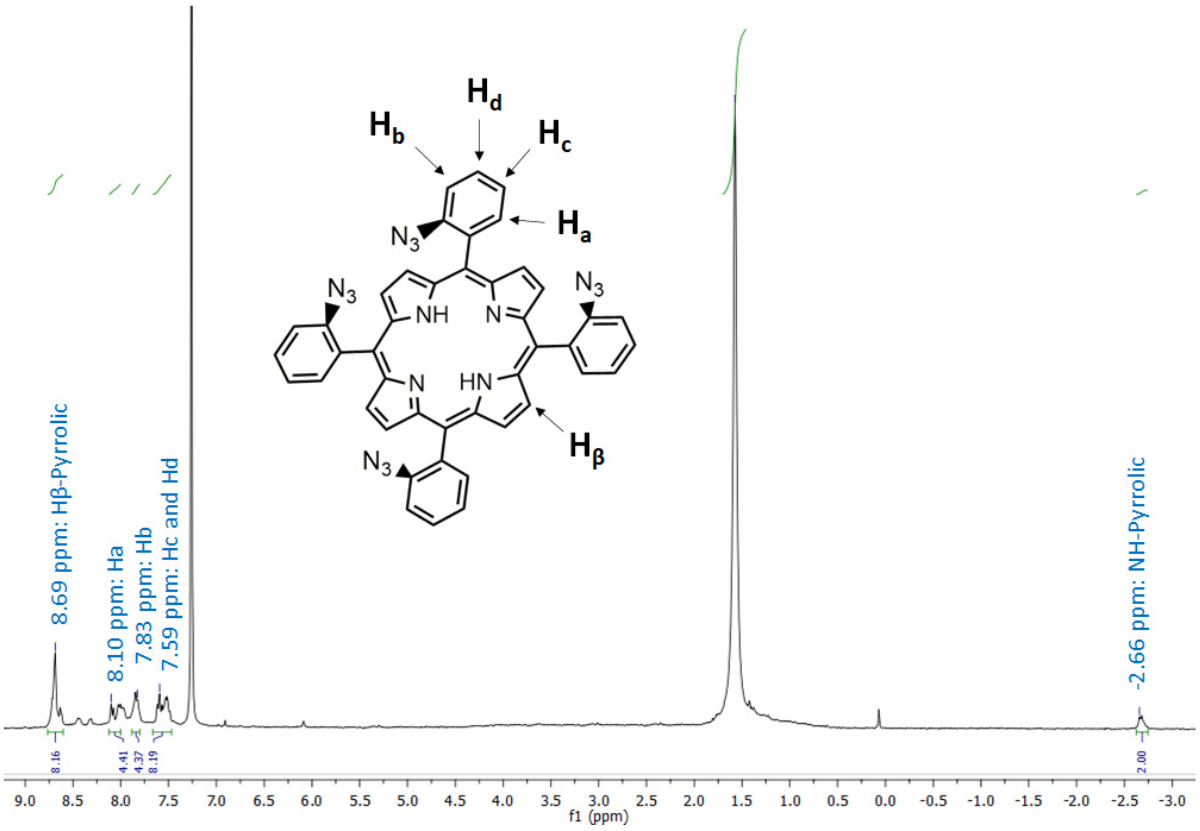

Figure S6. ^{1}H NMR spectrum of free base porphyrin 4α-H_2TN_3PP (**2**)(400 MHz, $CDCl_3$).

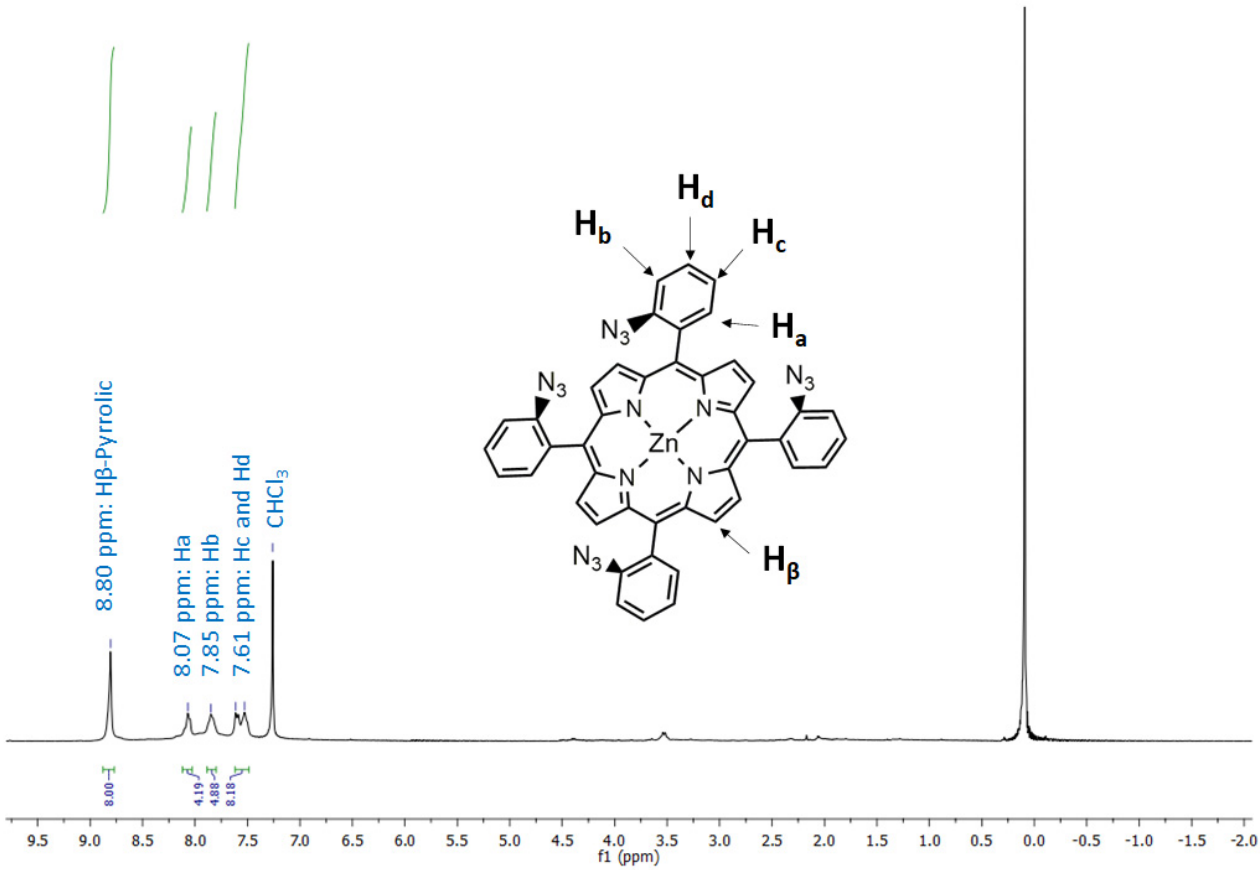

Figure S7. ^{1}H NMR spectrum of 4α-[Zn(TN$_3$PP)] (**3**)(400 MHz, CDCl$_3$).

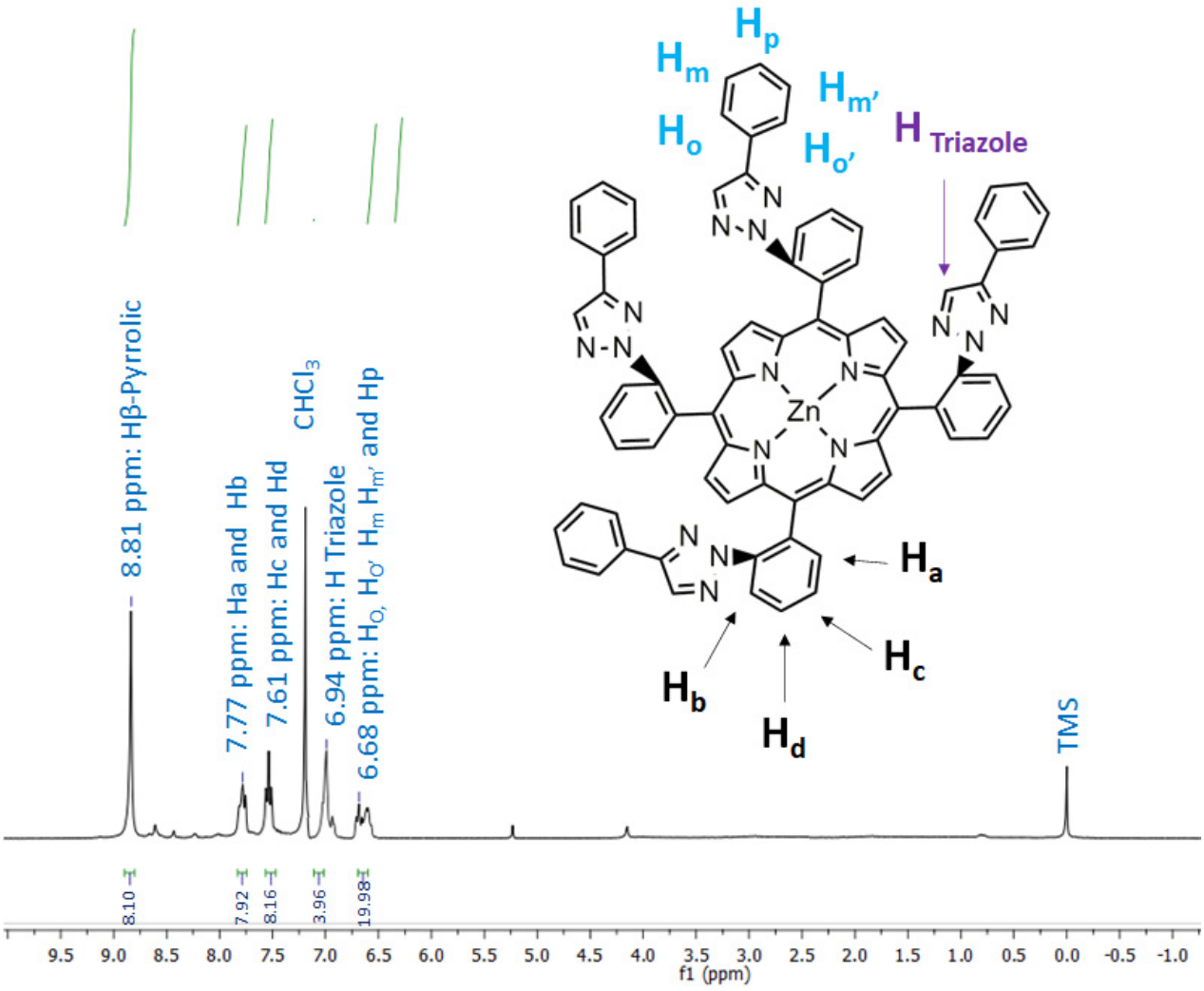

Figure S8. ^{1}H NMR spectrum of α$_4$-[Zn(T$_{AZ}$PP)] compound (**4**)(400 MHz, $CDCl_3$).

4. UV-visibletitration

To calculate the associate constants $K_{as}$of [Zn(TAzPP)Br] and [Zn(TAzPP)Cl] complexes **,** we used both the Benesi-Hildebrand method [56] for "weak interactions" (Equation **1**) and the "strong interactions" method (Equation **2*)*** [56] :

$$\bullet([Zn(TAZPP)]_0.[X]_0)/\Delta_{Abs} = \frac{1}{qK_{as}} + \frac{1}{q}.\left([Zn((TAZPP))]_0 + [X]_0\right)$$ **(Equation 1)**

Where $[Zn(TAZPP)]_0$ is the concentration of [Zn(TAzPP)] at t = 0.

$[X]_0$ = concentration of the halide axial ligand (Cl^- or Br^-) at t = 0.

$q = \varepsilon_{halide\text{-}complex} - \varepsilon_{[Zn(TAZPP)]}$

$\Delta_{Abs} = A_{exp} - (\varepsilon_{[Zn(TAzPP)]} \text{ x } [Zn(TAzPP)]_0)$

• $K_{as} = \frac{F_C}{(1-F_C)(S-R.F_C)}$ **(Equation 2)**

Where:

- F_c is the molar fraction : $F_c = \Delta_{Abs} / (A_{\text{halide-complex}} - A_0)$.
- Δ_{Abs} is the absorption variation: $\Delta_{Abs} = A_{mes} - A_0$.
- A_0 is the initial absorption of [Zn(TAzPP)] before adding the halide axial ligand *Cl- or Br-*.
- $A_{\text{halide-complex}}$ is the absorption of the [Zn(TAzPP)Br] complex or [Zn(TAzPP)Cl].
- A_{mes} is the absorption of [Zn(TAzPP)Br] complex or [Zn(TAzPP)Cl] after each addition of axial ligand *Cl- or Br-*.
- R is the concentration of the [Zn(TAzPP)Br] complex or [Zn(TAzPP)Cl].
- S is the concentration of the axial ligand *Cl- or Br-*.