Zinc(II) Triazole *meso*-arylsubstituted Porphyrins for UV-visible chloride and bromide detection. Adsorption and Catalytic Degradation of Malachite Green Dye

Mouhieddinne Guergueb [a], Jihed Brahmi [a], Soumaya Nasri [a,b*], Frédérique Loiseau [c], Kaïss Aoudi [d], Vincent Guerineau [e], Shabir Najmudin [f], Habib Nasri [a]

[a]: University of Monastir, Laboratoire de Physico-chimie des Matériaux, Faculté des Sciences de Monastir, Avenue de l'environnement, 5019 Monastir, Tunisia.
[b]: Department of Chemistry, College of Science Al-Zulfi, Majmaah University, Saudi Arabia.
[c]: Département de Chimie Moléculaire, 301 rue de la Chimie, Université Grenoble Alpes, CS 40700, 38058 Grenoble Cedex 9, France.
[d]: Department of Chemistry, College of Science, Qassim University-, , Buraidah 51452, Saudi Arabia
[e]: Institut de Chimie des Substances Naturelles CNRS, Avenue de la Terrasse, F-91198 Gif-sur-Yvette.
[f] : Randall Centre for Cell and Molecular Biophysics, 3rd floor New Hunt's House, Faculty of Life Sciences and Medicine, King's College, London SE1 1UL, UK.

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Part 1: Method and Materials

All commercially available reagents were reagent grade and were used without further purification. UV-visible absorption spectra and titration were recorded on a WinASPECT PLUS (validation for SPECORD PLUS version 4.2) scanning spectrophotometer. All anions used for selectivity tests were in the form of the tetrabutylammonium salt.

Fourier-transformed IR spectra were recorded on a PerkinElmer Spectrum Two FT-IR spectrometer. ^{1}H NMR spectra were recorded on Bruker DPX 400 spectrometer and chemical shifts (δ) are reported in ppm downfield from internal tetramethylsilane (TMS).

Emission spectra were recorded in dichloromethane at room temperature on a Horiba Scientic Fluoromax-4 spectrofluorometer. Samples were placed in 1 cm path length quartz cuvettes. Luminescence lifetime measurements were performed after irradiation at λ = 430 nm obtained by the second harmonic of a titanium: Sapphire laser (picosecond Tsunami laser spectra physics 3950-M1BB + 39868-03 pulse picker doubler) at an 800 kHz rate of repetition. For the decay acquisition, Fluotime 200 (AMS technologies) was utilized consisting of a GaAsmicro channel plate photomultiplier tube (Hamamatsu model R3809U-50) followed by a time-correlated single photon counting system from Picoquant (PicoHarp300). The ultimate time resolution of the system is close to 30 ps. Luminescence decays were analyzed with FLUOFIT software available from Picoquant. Emission quantum yields were determined at room temperature in dichloromethane solutions using the optically dilute method. [Zn(TPP)] in air-equilibrated dichloromethane solution was used as quantum yield standard ($\phi_f = 0.031$) [1]. The instrumental uncertainties are as follows: absorption maxima, 2 nm; molar absorption, 20%; emission maxima, 5 nm; emission lifetimes, 10%; emission quantum yields, 20%. The fluorescence quantum yield (ϕ_f) was measured using the following equation (Eq. I) : [2]

$$Q_f = \emptyset_{f(std)} \frac{F.A_{std}.n^2}{F_{sdt}.A.n_{std}^2} \qquad \text{(Eq. I)}$$

Where $\phi_{f(std)}$ is the fluorescence quantum standard (in dichloromethane) ($\phi_{f(std)} = 0.03$), the reference used is [Zn(TPP)] as mentioned above. F and F_{std} are the areas of the fluorescence emission plots for both the sample and the standard. A, n, A_{std} and n^2_{std} are the relative absorbance of the sample and the refractive indices of the solvents for the sample and standard at the excitation wavelength.

Electrospray (ESI) spectra were obtained using an amaZon speed instrument. The samples were made by a 5.10^{-5} M in dichloromethane.

An UltrafleXtreme mass spectrometer (Bruker Daltonics, Bremen) was used for all MALDI-TOF analyses. Acquisitions were performed in reflector positive ion mode. The laser intensity was set just above the ion generation threshold to obtain peaks with the highest possible signal-to-noise (S/N) ratio without significant peak broadening. The mass spectrometer was externally calibrated using PEG1500-2000. All data were processed using the program FlexAnalysis (Bruker Daltonics, Bremen).
Trans-2-[3-(4-ter-Butylphenyl)-2-propenylidene] malonitrile (DCTB), used as the matrix for MALDI-TOF MS, was of the highest grade available and used without further purification). It was purchased from Sigma Aldrich Co.
The samples were made as 3.10^{-3} M in tetrahydrofuran (THF), then diluted to 5.10^{-5} M in methanol.
Electrochemistry : Cyclic voltammetry (CV) experiments were performed with a CH-660B potentiostat (CH Instruments). All analytical experiments were conducted at room temperature under an argon atmosphere (argon stream) in a standard one-compartment, three-electrode electrochemical cell. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was used as the supporting electrolyte (0.1 M) in a mixture dichloromethane acetonitrile 4/1. An automatic Ohmic drop compensation procedure was systematically implemented before the CV data were recorded with electrolytic solutions containing the studied compounds at concentrations of ca. 10^{-3} M. CH Instruments vitreous carbon (ϕ = 3 mm) working electrodes were polished with 1 μm diamond paste before each recording. The $Ag/AgNO_3$ 0.01 M (in CH_2Cl_2/CH_3CN) redox couple was used as the reference electrode. For comparison with previously published data, all potentials given in the text and in Table 3 have been converted to values relative to the saturated calomel electrode (SCE) by using the following relationship: $E(SCE) = E(Ag/AgNO_3) + 298$ mV.

Adsorption and oxidation degradation of the malachite green dye (MG dye) : The experiments were carried out at room temperature using 5 mg of **4a-c** free base porphyrins and the corresponding zinc(II) complexes **5a-c**-complexes and 5 mL of an aqueous solution of the MG dye (at pH = 8). The agitation was kept at 150 rpm. The resultant mixture was filtrated and the concentration was then determined by measuring the absorption at 618 nm. The adsorbed amount q_t (mg/g) was calculated according to the following formula (Eq. II):

$$Q(mg/g) = (C_o - C_t).(V/m) \qquad \text{(Eq. III)}$$

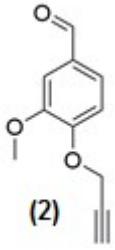
where C_o and C_t are the dye concentration before and after the adsorption, respectively. V is the volume of the dye used and m is the mass of the adsorbent. The oxidation degradation of the malachite green dye in the presence of our synthetic zinc(II) porphyrin species **5a-c** as catalysts was performed with the utilization of an aqueous solution of H_2O_2 (6 $mg.L^{-1}$). After filtration of the obtained mixture, concentration of the resultant solution was made by measuring the absorption at λ_{max} = 618 m.

Part 2: Synthetic procedures

Synthesis of 3-methoxy-4-(prop-2-ynl-yloxy)benzaldehyde (2)

3-hydroxy-3-methoxy-benzaldehyde (**1**) (10 g, 65.76 mmol, 1 eq) was dissolved in acetone (200 mL) then, 36.28 g of K_2CO_3 (263.07 mmol, 4 eq) was added and heated under reflux. 19.93 mL, of propargyl bromide (263.07 mmol, 4 eq) were added dropwise. The reaction mixture was stirred at 68 °C, under air, for 4 hours and then cooled at room temperature. The mixture was extracted with dichloromethane and the combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to afford 11.35 g (yield = 90.79 %) of the compound **2** as pale yellow solid.

Compound 2: $C_{11}H_{10}O_3$ (190.06): calcd. C, 69.46; H, 5.30; found C 69.36, H 5.34.^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 9.86 (s, 1 H Aldehyde), 7.46 (d, 1 H, J = 8.3 Hz), 7.42 (m, 1 H), 7.14 (d,1 H, J = 8.1 Hz), 4.84 (d, 2 H, J = 2.4 Hz, OCH_2), 3.93 (s, 3 H, OCH_3), 2.55 (t, 1 H alkyne, J = 2.4 Hz). FTIR:($solide, \bar{\nu}$, cm^{-1}) = 3254 (CH alkyne), 3088 (CH aldehyde), 2123 (C≡C Alkyne), 1600 (C=O Aldehyde), 1264 (CH_3–O vanillin).


(2)

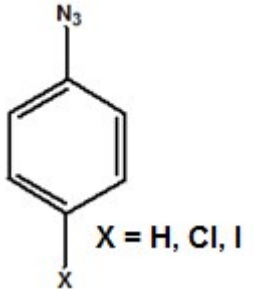
Synthesis of azidobenzene, 1-azido-4-Chlorobenzene and 1-azido-4-Iodobenzene

Aniline (5 g, 53.73 mmol, 1 eq.) was dissolved in (15 mL) 1:1 ratio of HCl/H_2O and taken in a round bottom flask equipped with stirrer. The reaction was stirred at 0°C for 20 min. Sodium nitrite (3.7 g, 53.73 mmol, 1 eq.) was dissolved in 5 mL of water and added to the mixture. Then, sodium azide (3.49 g, 53.73 mmol, 1 eq.) was dissolved in 5 mL of water and added dropwise and the reaction mixture stirred for 30 min at 0°C. The residue was extracted with dichloromethane and washed successively with water. The combined organic layers were dried over anhydrous $MgSO_4$ and evaporated to the azidobenzene product.

The 1-azido-4-Chlorobenzene and the 1-azido-4-Iodobenzene were prepared using the same procedure as that used for the azidobenzene.

Azidobenzene: $C_6H_5N_3$ (119.05), FTIR (solid, $\bar{\nu}$, cm^{-1}): = 2915 (CH phenyl), 2130 and 2090 ν_{as}(N=N=N azido).

1-azido-4-Chlorobenzene: $C_6H_4N_3Cl$ (153.01), FTIR (solid, $\bar{\nu}$, cm^{-1}): $\bar{\nu}$ = 2930 (CH phenyl), 2120 and 2080 ν_{as}(N=N=N azido), 780 (C-Cl), **1-azido-4-Iodobenzene:** $C_6H_4N_3I$ (244.95), FTIR (solid, $\bar{\nu}$, cm^{-1}) 2922 (CH phenyl), 2115 and 2080 ν_{as}(N=N=N azido),580 (C-I).



Synthesis of 3-methoxy-4-(3-phenyl-3H-[1,2,3]triazol-4-ylmethoxy)-benzaldehyde (3a), 4-[3-(4-chloro-phenyl)-3H-[1,2,3]triazol-4-ylmethoxy]-3-methoxy-benzaldehyde (3b) and the (4-iodo-phenyl)-3H-[1,2,3]triazol-4-ylmethoxy]-3-methoxy-benzaldehyde (3c)

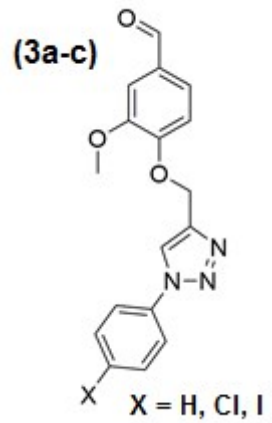
3-methoxy-4-(prop-2-ynl-yloxy)benzaldehyde (**2**) (3g, 15.78 mmol, 1 eq.), copper iodide (0.5 eq.), diisopropylethylamine (DIPEA) (6 eq.), and 100 mL of toluene were introduced in a round bottom flask. The reaction mixture was stirred at 70°C for 20 min. Then a solution of azido derivative (1 eq. per alkyne) in toluene (3 mL) was added to the mixture. The reaction was carried out in a microwave (400 W) for 1 hour. The resulting reaction was diluted with EtOAc (100 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and evaporated. The crude product was purified by flash silica gel column chromatography using (EtOAc/cyclohexane 60/40) as eluent to afford the 3-methoxy-4-(3-phenyl-3H-[1,2,3]triazol-4-ylmethoxy)-benzaldehyde compound (**3a**). The chloro and the iodo derivatives (**3b-c**) were prepared using the same procedure. The masse obtained of the 3a-c are 4.15 g (Yield = 90%), 4.66 g (Yield = 86%) and 5.65 g (Yield 82%) respectively.

Compound 3a: $C_{17}H_{15}N_3O_3$ (309.11): calcd. C, 66.01; H, 4.89; N, 13.58; found C, 66.05; H, 4.85; N, 13.55. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 9.81 (s, 1 H Aldehyde), 8.05 (s, 1 H triazole), 7.7 (d, J = 8.4 Hz, 1 H), 7.38 (d, J = 8.3 Hz, 1 H), 7.51 (t, J = 8.3 Hz,1H), 7.33 (d, J = 7.5 Hz, 1 H), 7.32 (m, 1 H), 7.17 (d, J = 7.6 Hz, 1 H), 5.34 (s, 2 H, OCH_2), 3.84 (s, 3 H, OCH_3).. FTIR (solid, $\bar{\nu}$, cm^{-1}) 3160

(CH triazole), 3088 (CH aldehyde), 1726 (C=N, N=N triazole), 1605 (C=O Aldehyde), 1266 (CH_3–O vanillin),

Compound 3b: $C_{17}H_{14}ClN_3O_3$ (343.07): calcd. C, 49.4; H, 4.11; N 12.22; found C, 49.42; H, 4.05; N, 12.25. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 9.64 (s, 1 H Aldehyde) ,8.12 (s, 1 H-Triazole), 7.66 (d, *J* = 8.4 Hz, 1 H), 7.38 (d, J = 8.3 Hz, 1 H), 7.33 (d, J = 7.6 Hz, 1 H), 7.31 (m, 1 H), 7.16 (d, J = 7.7 Hz, 1 H), 5.35 (s, 2 H, OCH_2),3.82 (s, 3 H, OCH_3). FTIR (solid, $\bar{\nu}$, cm^{-1}) 3162 (CH triazole), 3090 (CH aldehyde), 1705 (C=N, N=N triazole), 1599 (C=O Aldehyde), 1260 (CH3–O vanillin), MS (ESI^+, CH_2Cl_2): *m*/*z* = 366.06 $[3b]^+$ Na^+ Found 366.87.

Compound 3c: $C_{17}H_{14}IN_3O_3$ (435.007): calcd. C 46.92, H 3.24, N 9.66; found C 46.85, H 3.2, N 9.59. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 9.7 (s, 1 H Aldehyde) , 8.02 (s, 1 H-Triazole), 7.61 (d, *J* = 8.2 Hz, 1 H), 7.43 (d, J = 8.3 Hz, 1 H), 7.37 (d, J = 7.9 Hz, 1 H), 7.31 (m, 1 H), 7.15 (d, *J* = 7.8 Hz, 1 H), 5.32 (s, 2 H, OCH_2), 3.80 (s, 3 H, OCH_3). FTIR (solid, $\bar{\nu}$, cm^{-1}) 3155 (CH triazole), 3095 (CH aldehyde), 1730 (C=N, N=N triazole), 1625 (C=O Aldehyde), 1245 (CH_3–O vanillin).



Synthesis of *meso*-tetrakis-[3-methoxy-4-(3-phenyl-3H-[1,2,3]triazol-4-ylmethoxy)-phenyl]-porphyrin (4a), *meso*-tetrakis-{4-[3-(4-chloro-phenyl)-3H-[1,2,3]triazol-4-ylmethoxy]-3-methoxy-phenyl}-porphyrin (4b) and *meso*-tetrakis-{4-[3-(4-iodo-phenyl)-3H-[1,2,3]triazol-4-ylmethoxy]-3-methoxy-phenyl}-porphyrin (4c).

The *meso*-porphyrins were prepared using a slightly modified Adler-Longo procedure. [3] In a 250 mL two-necked flask, aldehyde **3a** (4 g, 12.94 mmol, 4eq) was dissolved in propionic acid (150 mL). The solution was heated under reflux. Freshly distilled pyrrole (0.89 mL, 12.94 mmol, 4eq.) was then added

dropwise and the mixture was stirred for 35 min. The mixture was cooled overnight at 4°C and filtered under vacuum. The crude residue was purified by column chromatography (SiO_2, chloroform as eluent). A dark blue solid of the porphyrin **4a** was obtained and dried under vacuum (820 mg, yield 18%).

The chloro (**4b**) [H_2T_{AzP}-ClVP)] and the iodo (**4c**) [H_2T_{AzP}-IVP)] *meso*-porphyrins were prepared using the same procedure as that of the porphyrin **4a**. The porphyrin **4b** was obtained as a dark green solid 840 mg, Yield = 17%) and the porphyrin **4c** is a dark-brown solid (985 mg, yield = 16%).

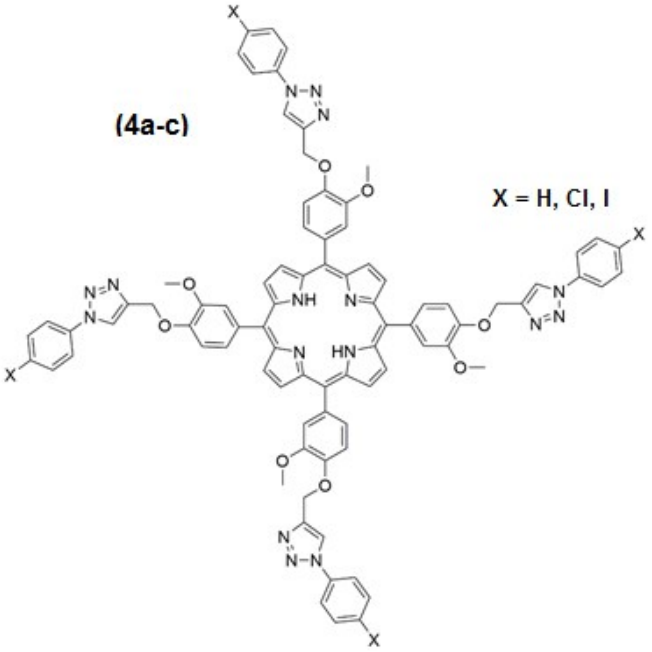
Porphyrin 4a: $C_{84}H_{66}N_{16}O_8$ (1426.52): calcd. C, 70.67; H, 4.66; N ,15.7; found C, 70.61; H, 4.7; N, 15.67. UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-3}$, L.mmol^{-1}.cm^{-1}) = 420 (565),517 (42), 554 (19), 593 (15),650 (13) (nm). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 8.8 (s, 8 H, H-pyrrole),8.09 (s, 4 H-triazole), 7.71 (d, J = 8.6 Hz, 8 H), 7.53 (t, J = 8.2 Hz, 4 H), 7.48 (d, J = 8.3, 8 H),7.35 (m, 4 H), 7.31 (s, 4 H),7.24 (d, J = 4.8 Hz, 4 H), 5.48 (s, 8 H, OCH_2), 3.93 (s, 12 H, OCH_3) -2.68 (s, 2H, H-pyrrole).

. MS (ESI$^+$, CH_2Cl_2): *m*/*z* = 1426.52 [4a-H]$^+$ Found 1427.57. FTIR (solid, $\bar{\nu}$, cm^{-1}) 3280 (NH porphyrin), 3070 (CH triazole), 2955-2854(CH porphyrin), 1726 (C=N, N=N triazol), 1600 (C=C.C=N Porphyrin), 1268 (CH_3–O vanillin) ,966 [δ(CCH) porphyrin].

Porphyrin 4b: $C_{84}H_{62}Cl_4N_{16}O_8$ (1562.36): calcd. C, 64.45; H, 3.99; N, 14.32; found C, 64.4; H, 4.01; N, 14.35. UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-3}$, L.mmol^{-1}.cm^{-1}) = 422(551), 518(35), 555(26), 594(15), 651(17) nm. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 8.92 (s, 8 H, H-pyrrole), 8.17 (s, 4 H-triazol), 7.67 (d, J = 7.9 Hz, 8 H), 7.49 (d, J = 8.2 Hz, 8 H), 7.43 (m, 4 H), 7.38 (s, 4 H),7.27 (d, J = 7.6 Hz, 4 H), 5.44 (s, 8 H, OCH_2), 3.93 (s, 12 H, OCH_3) , -2.73 (s, 2H, H-pyrrole).

MS (ESI$^+$, CH_2Cl_2): *m*/*z* = 1564.36 [4b-H]$^+$ found 1565.41. FTIR (solid, $\bar{\nu}$, cm^{-1}) 3295 (NH porphyrin), 3070 (CH triazole), 1716 (C=N, N=N triazole), 2965-2859 (CH porphyrin), 1600 (C=C.C=N Porphyrin), 1268 (CH_3–O vanillin), 951 [δ(CCH) porphyrin].

Porphyrin 4c: $C_{84}H_{62}I_4N_{16}O_8$ (1930.11): calcd. C, 52.24; H, 3.24; N, 11.61; found C, 52.2; H, 3.27; N, 11.60. UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-3}$, L.mmol^{-1}.cm^{-1}) = 424 (576), 520 (46), 555 (29), 595 (24), 652 (18) nm. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 8.85 (s, 8 H, H_ pyrrole), 8.01 (s, 4 H-triazol), 7.61 (d, J = 8.09 Hz, 8 H), 7.43 (d, J = 8.1 Hz, 8 H7.33 (m, 4 H), 7.328 (s, 4 H), 7.17 (d, J = 7.5 Hz, 4 H) , 5.39 (s, 8 H, OCH_2), 3.85 (s, 12 H, OCH_3), -2.71 (s, 2H, H-pyrrole). MS (ESI$^+$, CH_2Cl_2): *m*/*z* = 1930.11 [4c-H]$^+$ found 1931.15. FTIR (solid, $\bar{\nu}$, cm^{-1}) 3283 (NH porphyrin), 3050 (CH triazole), 1710 (C=N, N=N triazole), 2965-2859(CH porphyrin), 1600 (C=C.C=N Porphyrin), 1268 (CH_3–O vanillin), 976 [δ(CCH) porphyrin].



Synthesis of the zinc(II) porphyrin complexes 5a, 5b and 5c.

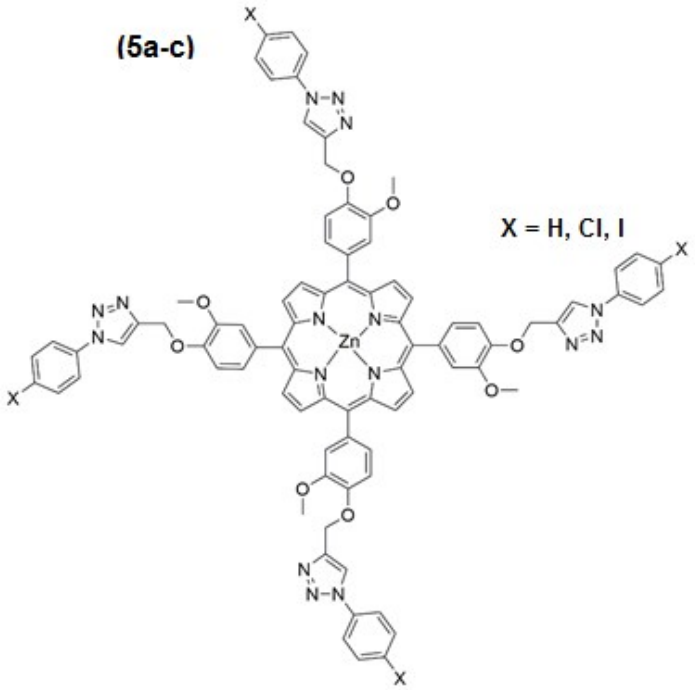
A mixture of the porphyrin **4a** [$H_2(T_{AzP}$-HVP)] (400 mg, 0.28 mmol, 1eq.) and [$Zn(OAc)_2$].$2H_2O$ (51.4 mg, 0.28 mmol,1 eq) in a chloroform-methanol (9-1) (100 mL) was stirred at room temperature overnight. The solvents were removed and a dark blue solid of complex **5a** ([$Zn(T_{AzP}$-HVP)]) was obtained (390 mg, 93%). The other two zinc(II) porphyrin complexes **5b** ([$Zn(T_{AzP}$-ClVP)]) and **5c** ([$Zn(T_{AzP}$-IVP)]) were obtained using the same procedure as that used for complex **5a**. Complexes **5b** and **5c** were obtained as dark purple powders with yield (415 mg, 91%) and yield (490 mg, 88%).

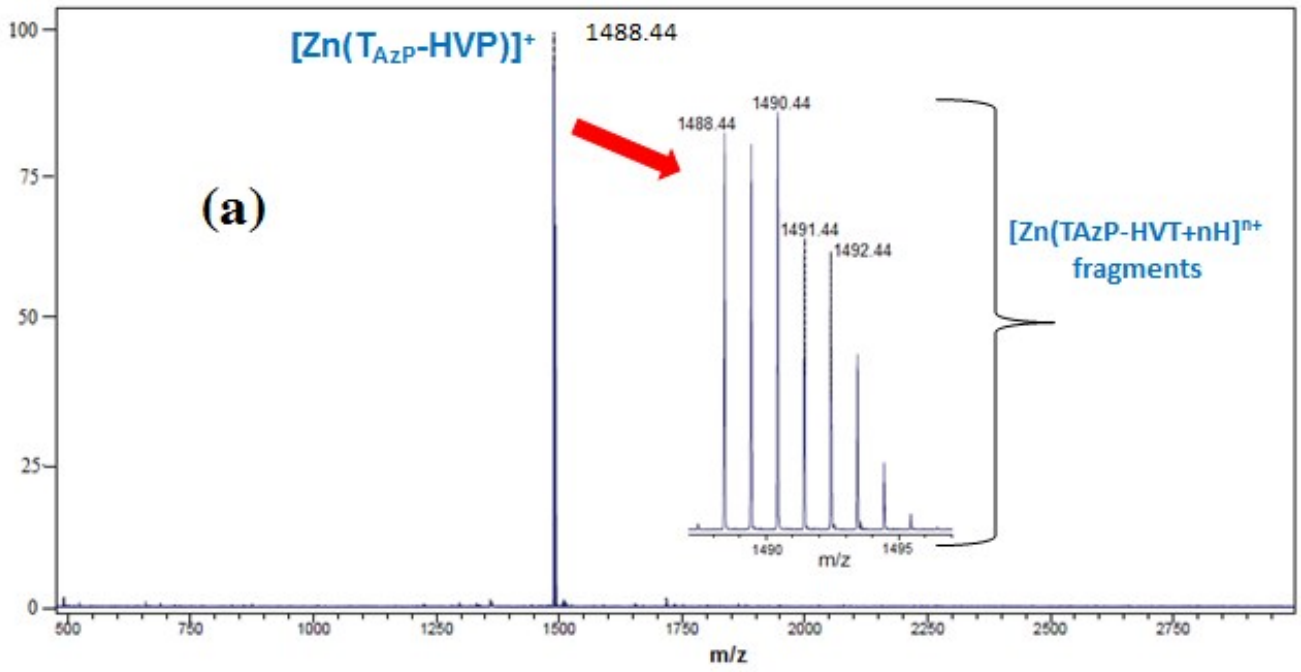
Zn-complex 5a: $C_{84}H_{64}N_{16}O_8Zn$ (1488.43): calcd. C, 67.67; H, 4.23; N, 15.03; found C, 67.81; H, 4.15; N, 15.11. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 9.11 (s, 8 H, H_ pyrrole),8.13 (s, 4 H Triazole), 7.71 (d, J = 8.6 Hz, 8 H), 7.55 (t, J = 8.2 Hz, 4 H), 7.47 (d, J = 8.5,4 H), 7.34 (m, 4 H),7.31 (s, 4 H), 7.25 (d, J = 7.9 Hz, 4 H), 5.47 (s, 8 H, OCH_2), 3.94 (s, 12 H, OCH_3).UV/Vis (CH_2Cl_2): λ_{max} (ε × 10^{-3}, L $mmol^{-1}.cm^{-1}$) = 424 (530), 551 (26), 592 (10) nm. MS (MALDI-TOF, THF, DCTB matrix): *m*/*z* = 1488.43 $[5a\text{-}H]^+$. Found 1489.44. FTIR (solid, $\bar{\nu}$, cm^{-1}) 3062 (CH triazole), 2957-2854 (CH porphyrin), 1725 (C=N, N=N), 1268 (CH_3–O vanillin), 1002 [(*δ*CCH porphyrin].

Zn-complex 5b: $C_{84}H_{60}Cl_4N_{16}O_8Zn$ (1624.28): calcd. C, 61.95; H, 3.71; N,13.76; found C, 61.9; H, 3.75; N, 13.22. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) δ = 9.18 (s, 8 H, H-pyrrole), 8.14 (s, 4 H triazole), 7.67 (d, J = 7.9 Hz, 8 H), 7.51 (d, J = 8.2 Hz, 8 H), 7.43 (m, 4H), 7.27 (s, 4H), 7.24 (d, J = 8.2 Hz, 4 H), 5.45 (s, 8 H, OCH_2), 3.93 (s, 12 H, OCH_3). UV/Vis (CH_2Cl_2): λ_{max} (ε × 10^{-3}, L.$mmol^{-1}.cm^{-1}$) = 425

(523), 552 (31), 593 (15) nm. MS (MALDI-TOF, THF, DCTB matrix): *m*/*z* = 1626.27 [**5b**]$^+$ found 1627.28. FTIR (solid, $\bar{\nu}$, cm^{-1}) 3005 (CH triazole), 2907-2869 (CH porphyrin), 1725 (C=N, N=N), 1260 (CH_3–O vanillin), 1002 [δ(CCH porphyrin].

Zn-complex 5c: $C_{84}H_{60}I_4N_{16}O_8Zn$ (1992.02): calcd. C, 50.59; H, 3.03; N, 11.24; found C, 50.65; H, 3.01; N, 11.20. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 9.06 (s, 8 H, H-pyrrole), 8.02 (s, 4 H-triazole), 7.61 (d, *J* = 8.1 Hz, 8 H), 7.45 (d, J = 8.1 Hz, 8 H), 7.37 (m, 4 H), 7.22 (s, 4 H) 7.19 (d, *J* = 7.8 Hz, 4 H), 5.39 (s, 8 H, OCH_2), 3.87 (s, 12 H, OCH_3). UV/Vis (CH_2Cl_2): λ_{max} (ε × 10^{-3}, L.mmol^{-1}.cm^{-1}) = 426 (532), 558 (29), 597 (12) nm. MS (MALDI-TOF, THF, DCTB matrix): *m*/*z* = 1992.02 [4c]$^+$ Found 1992.02. FTIR (solid, $\bar{\nu}$, cm^{-1}) (CH triazole), 2968-2859 (CH porphyrin), 1724 (C=N, N=N), 1268 (CH_3–O vanillin), 1002 [δCCH porphyrin].





Part 3: Mass spectrometry data

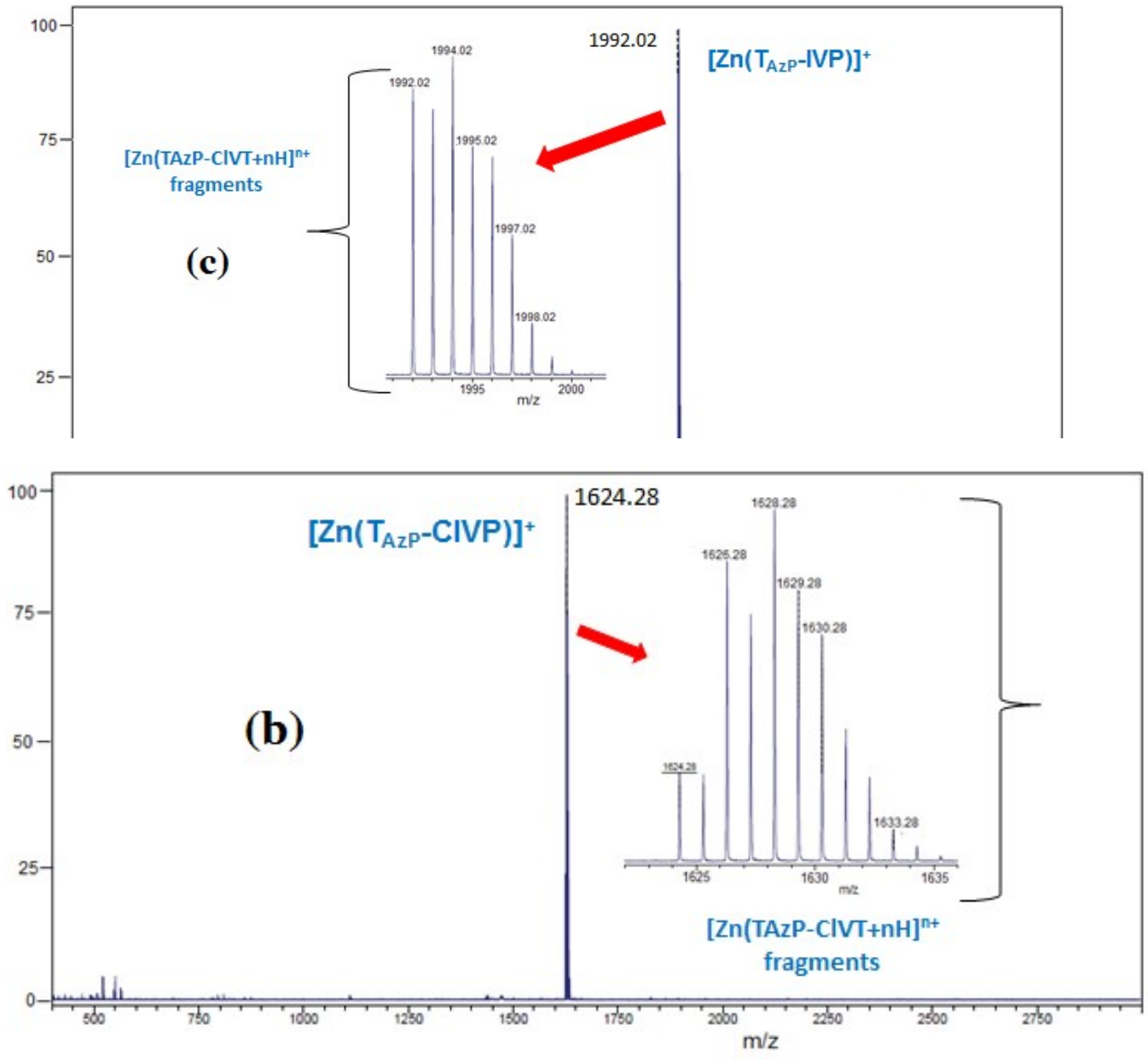


Figure SI-1. MALDI-TOF full spectrum of complex **5a (a)**, **5b (b)** and **5c (c)**. The insets show enlarged views. The solvent used is the THF with a concentration of 5.10^{-3} M.

Part 4: FT-IR and ^{1}H NMR data

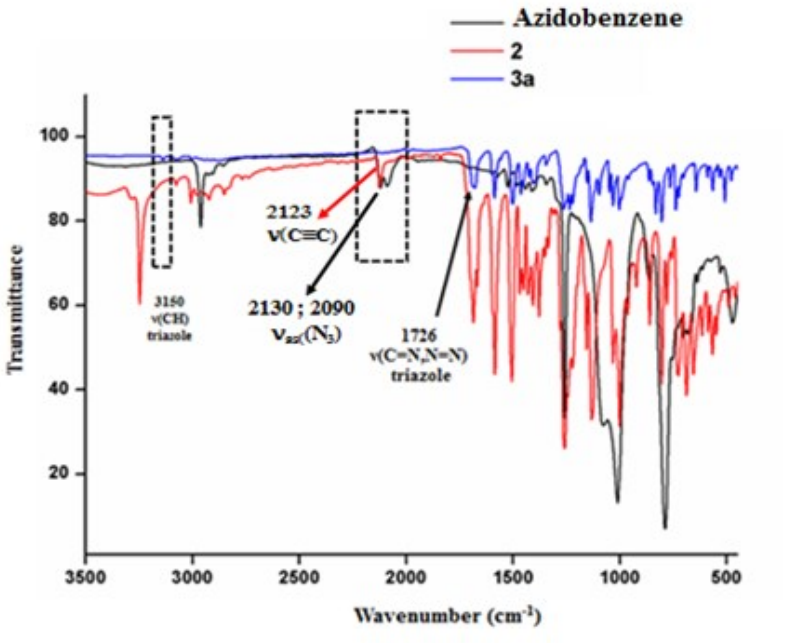


Figure SI-2. IR spectra (solid state) the azidobenzene reagent (black spectrum), compound **2** (red spectrum) and compound **3a**.

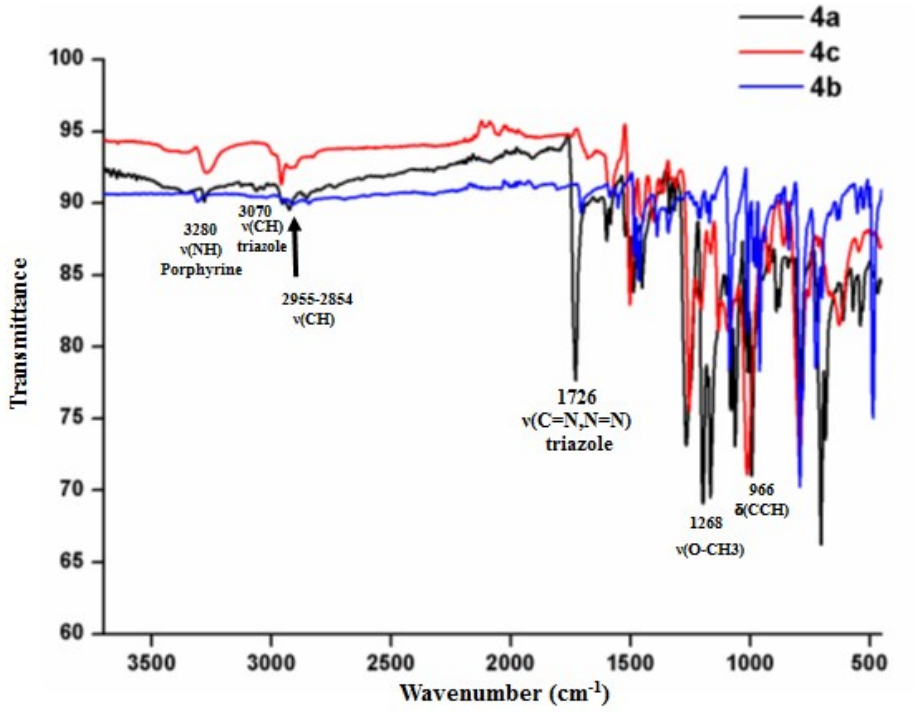


Figure SI-3. IR spectra (solid state) of the porphyrin $H_2(T_{AzP}$-HVP) (**4a**) (black color), the porphyrin $H_2(T_{AzP}$-ClHP) (**4b**) (blue color) and the porphyrin $H_2(T_{AzP}$-IVP) (**4c**) (red color).

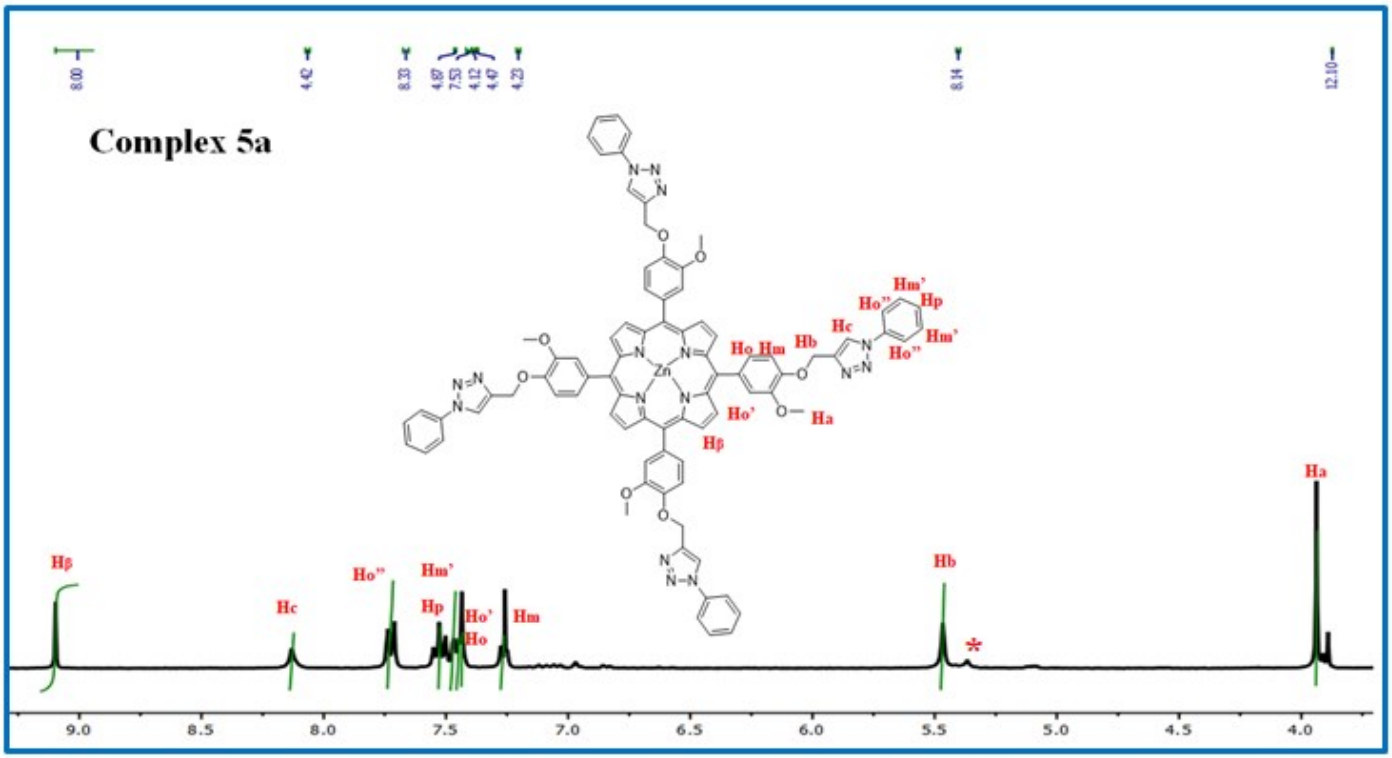


Figure SI-4. ^{1}H NMR (400 MHz) spectra in $CDCl_3$ of complex **5a**. The concentration is ~ 10^{-3} M.

* = impurities (CH_2Cl_2).

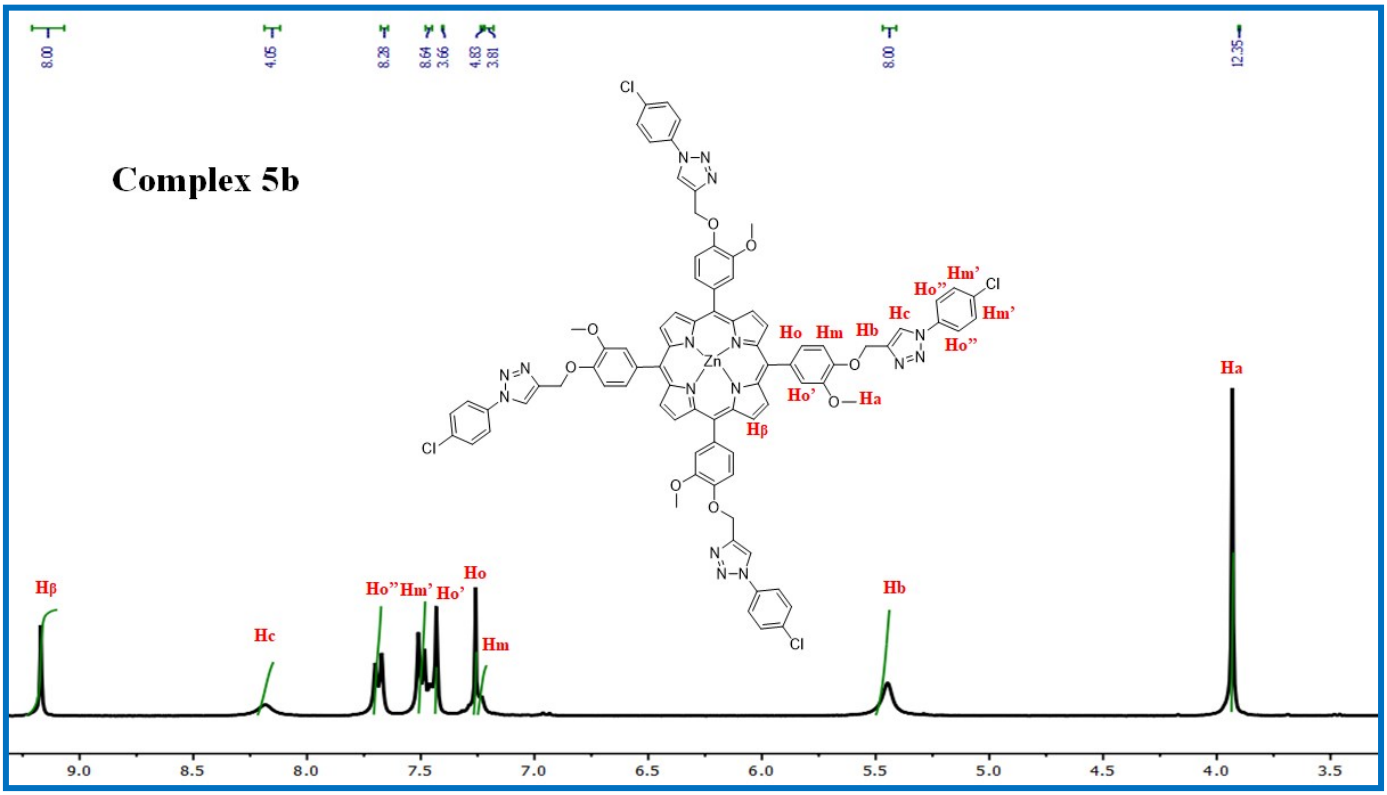


Figure SI-5. ^{1}H NMR (400 MHz) spectra in $CDCl_3$ of complex **5b**. The concentration is ~ 10^{-3} M.

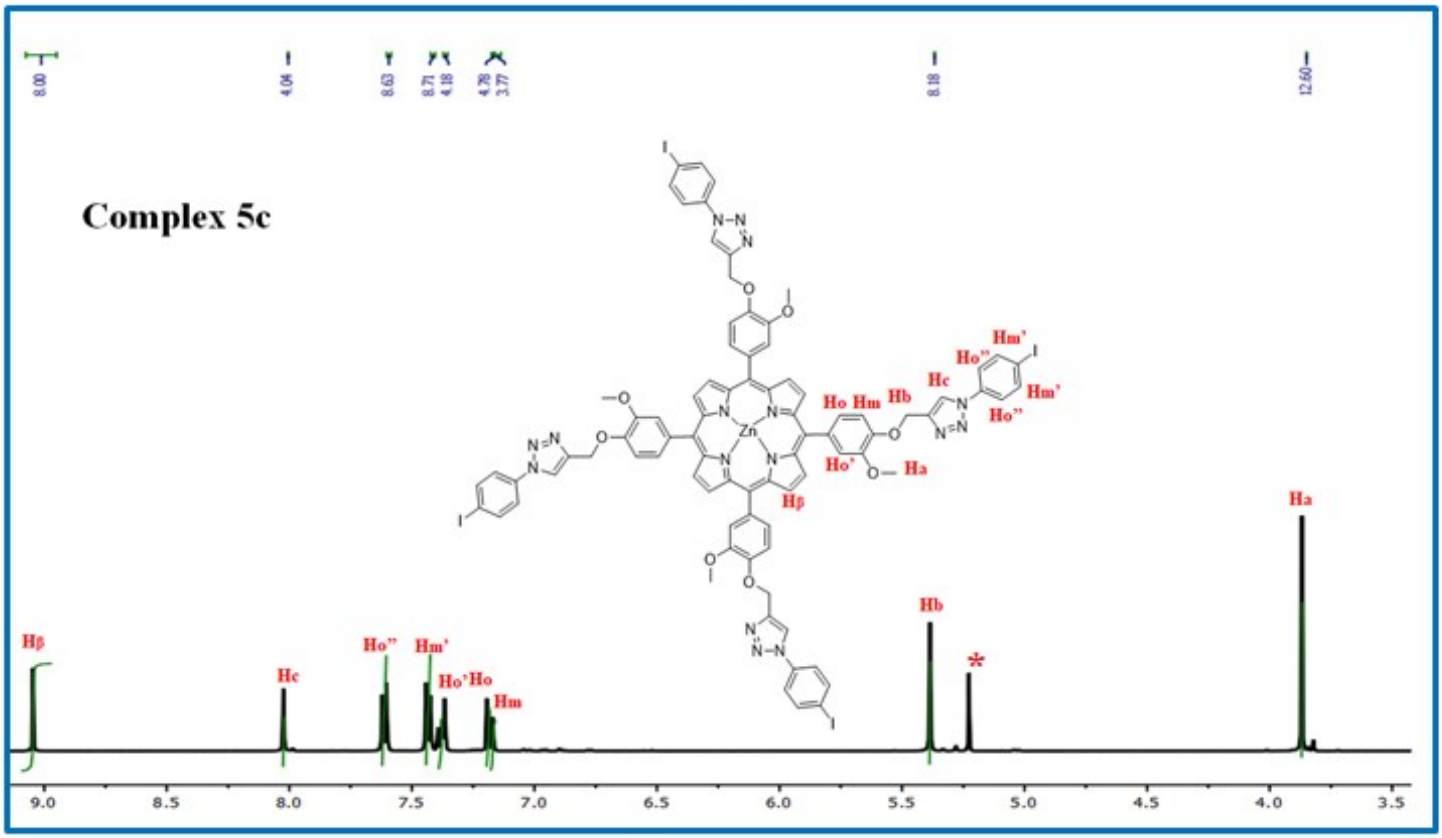


Figure SI-6. ^{1}H NMR (400 MHz) spectra in $CDCl_3$ of complex **5c**. The concentration is ~ 10^{-3} M. * = impurities (CH_2Cl_2).

Part 5: Photophysical data

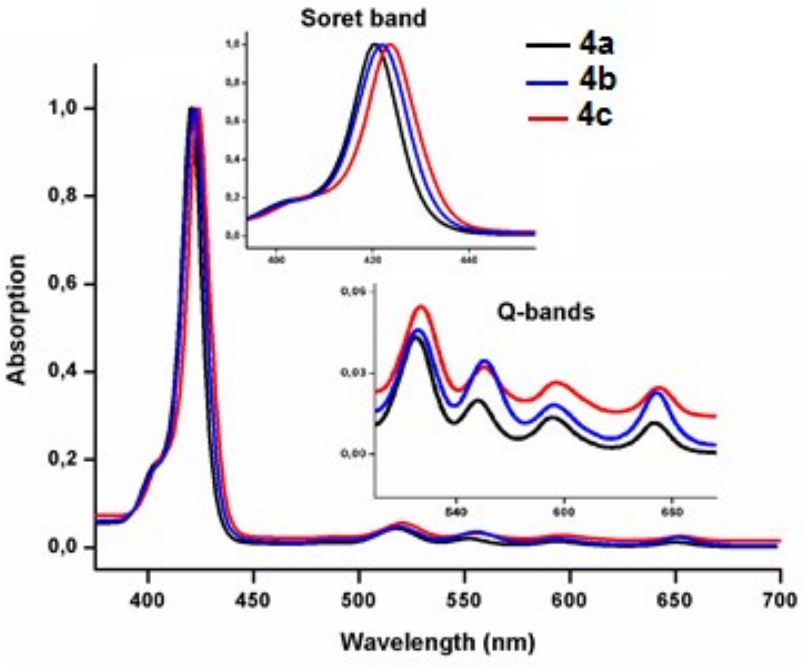


Figure SI-7. UV-visible spectra of the **4a-c** free base porphyrins: **4a** (black color), **4b** (blue color) and **4c** (red color). The spectra were recorded in the dichloromethane with a concentration ~ 10^{-6} M. The inset shows enlarged view.

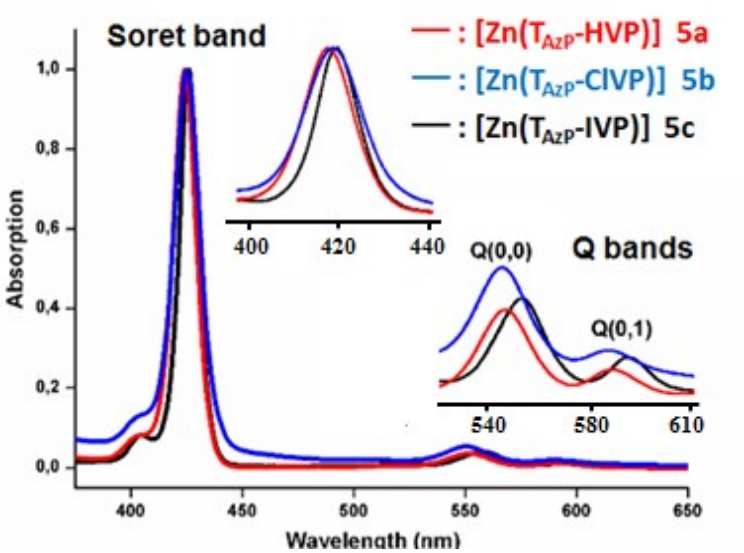


Figure SI-8. UV-visible spectra of the **5a-c** zinc complexes; **5a**: in red color, **5**b: in blue color and **5c**: in black color. The spectra were recorded in the dichloromethane with a concentration ~ 10^{-6} M. The insets show enlarged views.

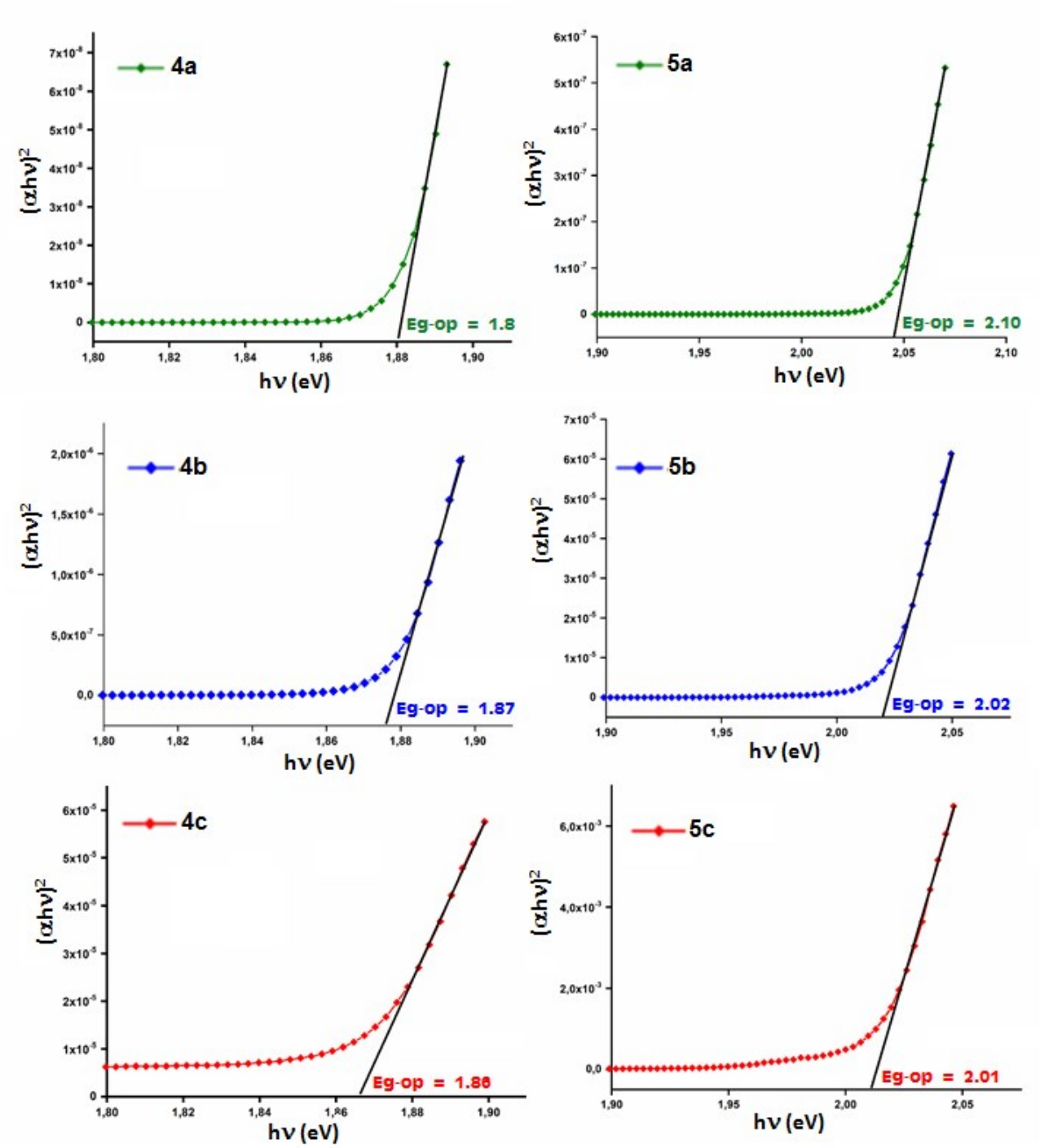


Figure SI-9. Curves of $(\alpha h\upsilon)^2$ against photon energy *E* of compounds **4a-c** and **5a-c**.

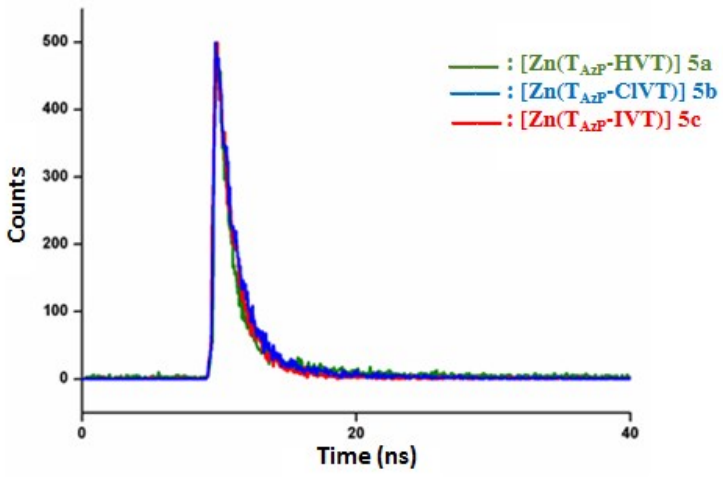
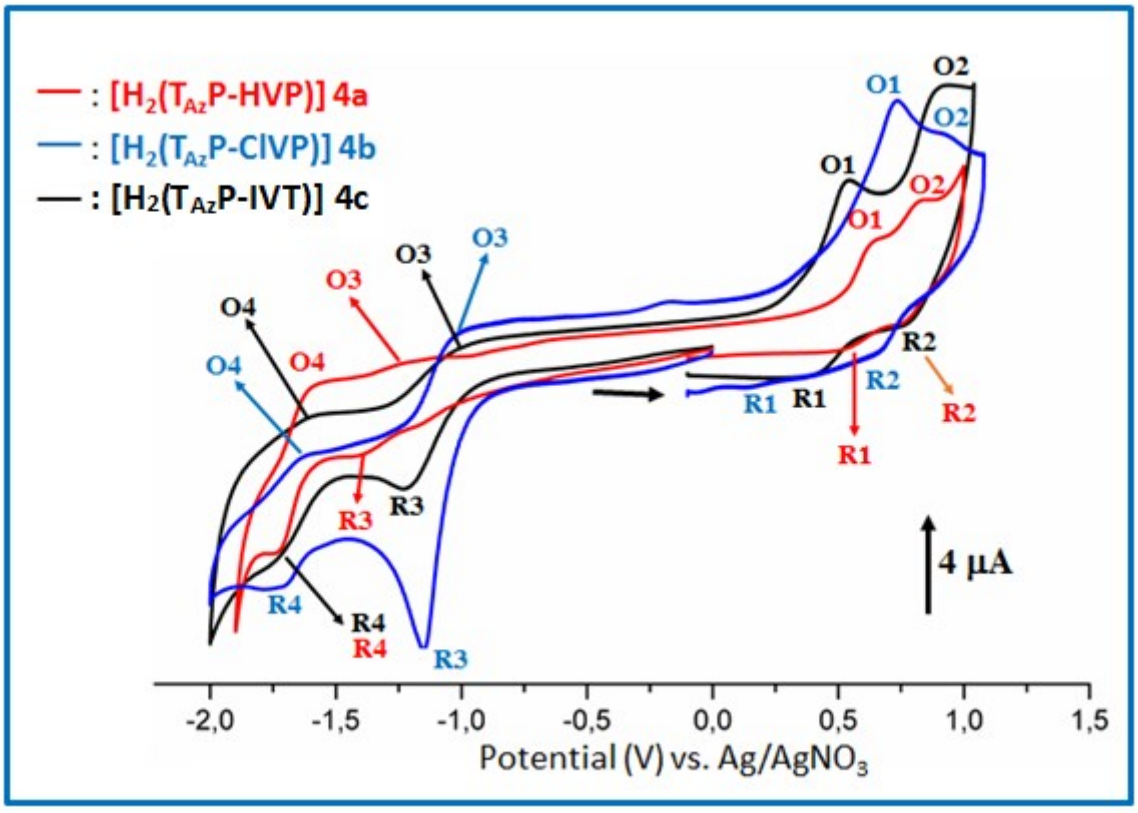


Figure SI-10. Fluorescence decay profiles of **5a-c** coordination compounds.



Part 6: Cyclic voltammetry data

Figure SI-11. Cyclic voltammograms of the free bases **4a-c**. The solvent is a mixture of dichloromethane and acetonitrile (4/1) and the concentration is ca. 10^{-3} M in 0.1 M $TBAPF_6$, 100 mV/s, vitreous carbon working electrode (Ø = 2 mm).

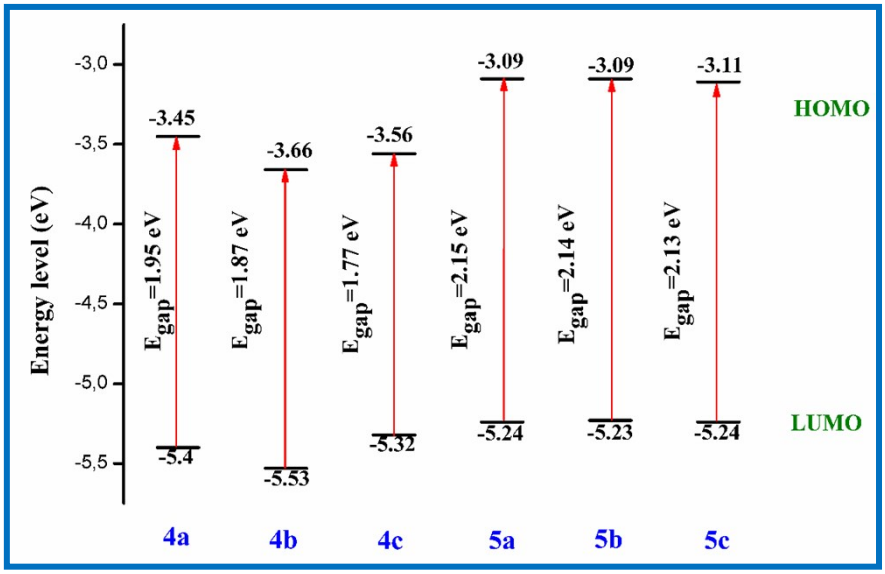


Figure SI-12. HOMO-LUMO energy levels of **4a-c** and **5a-c** and energy gaps of these species.

Part 7: UV-visible titration data

To calculate the associate constants K_{as} of complexes 5a-c, we used the " strong interactions" method (Equation **1*)*** : [4]

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

where F_c is the molar fraction : $F_c = \Delta_{Abs} / (A_{complex} - A_0)$.
- Δ_{Abs} is the absorption variation: $\Delta_{Abs} = A_{mes} - A_0$.
- A_0 is the initial absorption of [Zn(Porph)] (**5a-c**)before adding halide anion (Cl^- or Br^-)
$A_{complex}$ is the absorption of the complex (**5a-c**).
A_{mes} is the absorption of the complex (**5a-c**) after each addition of axial aza ligand *L*.
R is the concentration of the complex (**5a-c**).
S is the concentration of the halide ion.

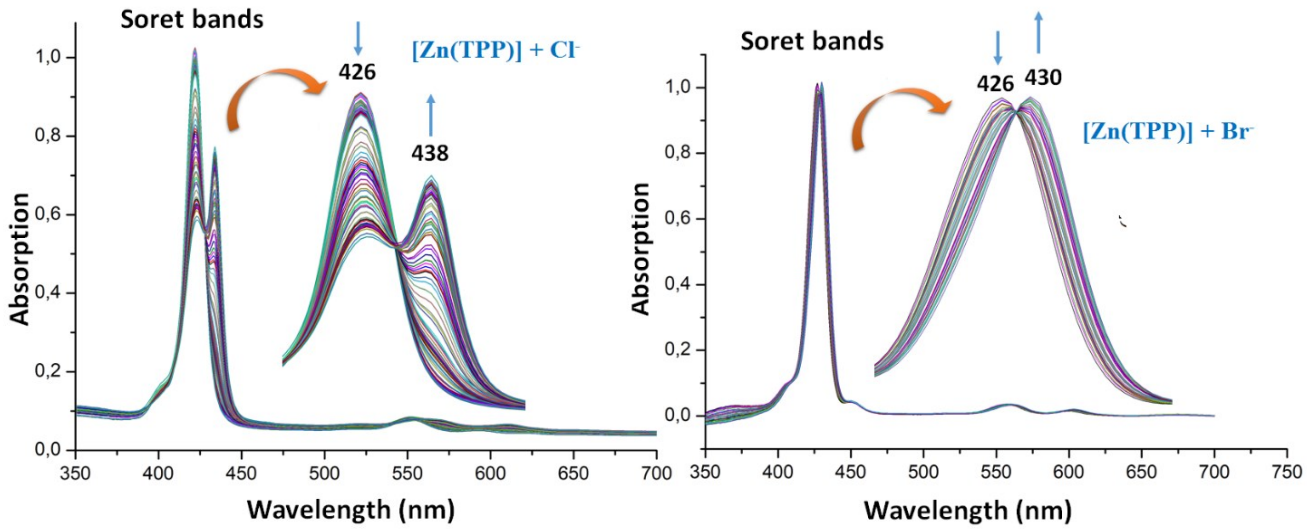


Figure SI-13. Changes in the absorption spectra in the Soret band region of [Zn(TPP] (~10^{-6} M) recorded in dichloromethane, upon addition of Cl^- (**left**) and Br^- (**right**). The insets show enlarged views.

Table SI-1. Values of the association constants (K_{as}) and $logK_{as}$ for complexes **5b-c**, [Zn(TPP)] and [Zn(PC)] [5,6] coordination compounds.

Complex	TBACl[a]		TBABr[b]	
	Kas	$logK_{as}$	K_{as}	$logK_{as}$
[Zn(T_{AzP}-ClVP)] (**5b**)	$1.1015.10^4$	4.0245	$0.3550.10^4$	3.5512
[Zn(T_{AzP}-IVP)] (**5c**)	$4.1486.10^4$	4.6179	$1.1392.10^5$	5.0566
[Zn(TPP)]	$0.6987.10^2$	1.8443	$1.7971.10^3$	3.2132
[Zn(PC)][c]	$1.2191.10^4$	4.0860	< 50	-

[a]: TBACl = the tetrabutylammonium chloride salt, [b]: TBABr = the tetrabutylammonium bromide salt, [c]: PC = the "cage porphyrin" nammely : *meso*-((3,3',3",3'"-(Benzene-1,2,4,5-tetrayltetrakis (carbonyloxymethanediyl-1H-1,2,3-triazole-4,1-diylmethanediyl))tetraphenyl)porphyrinato).

Part 8: Adsorption dye data

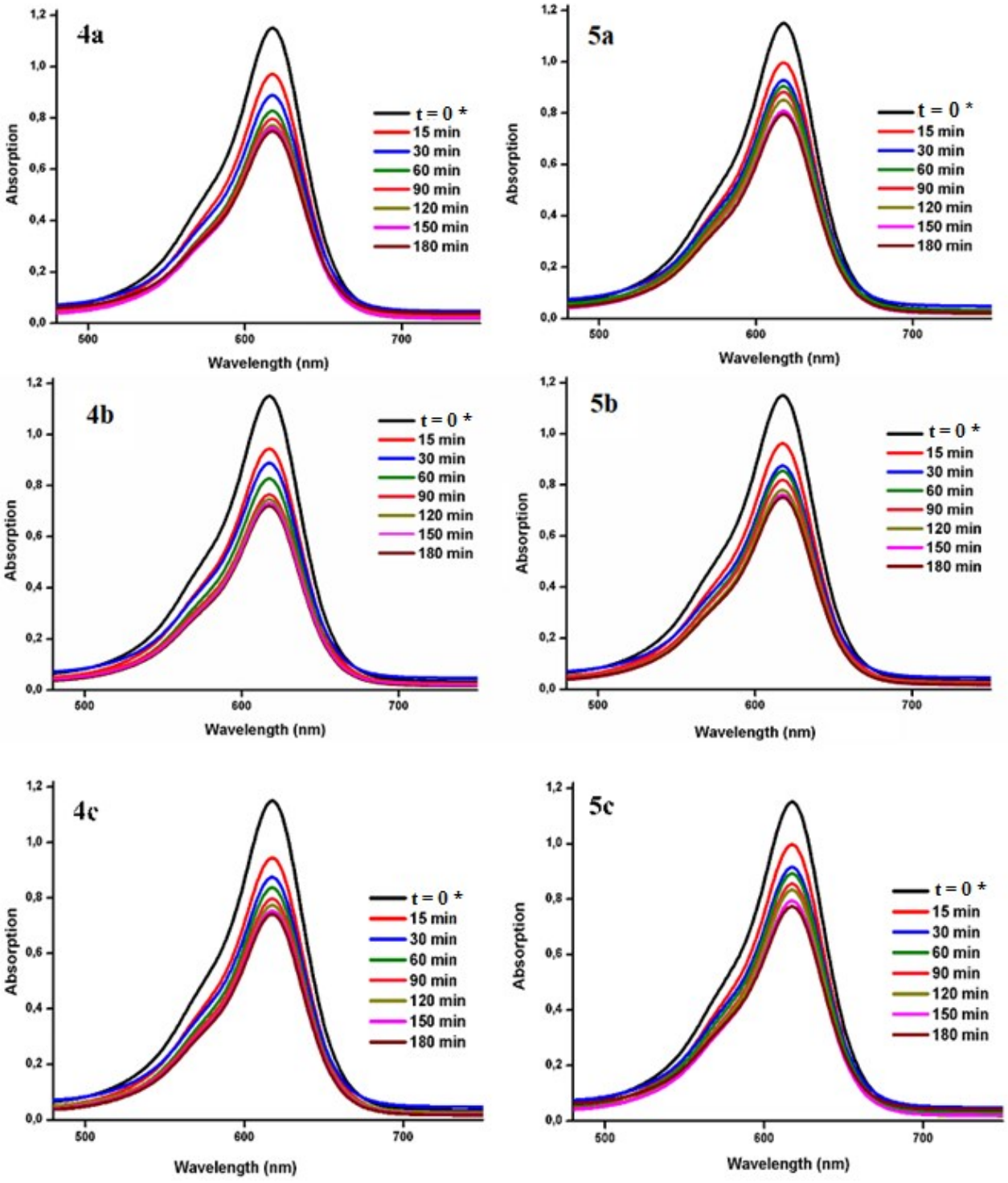


Figure SI-14. Variation of the λ_{max} values of the absorption bands of MG in aqueous solution in the presence of **4a-c** free base porphyrins (5 mg) (**left**) and **5a-c** zinc(II) complexes (**right**) (5 mg). The concentration of MB is 20 mg.$L^{-1}$and pH = 8. *: before adding the **4a-c** and **5a-c** adsorbents.

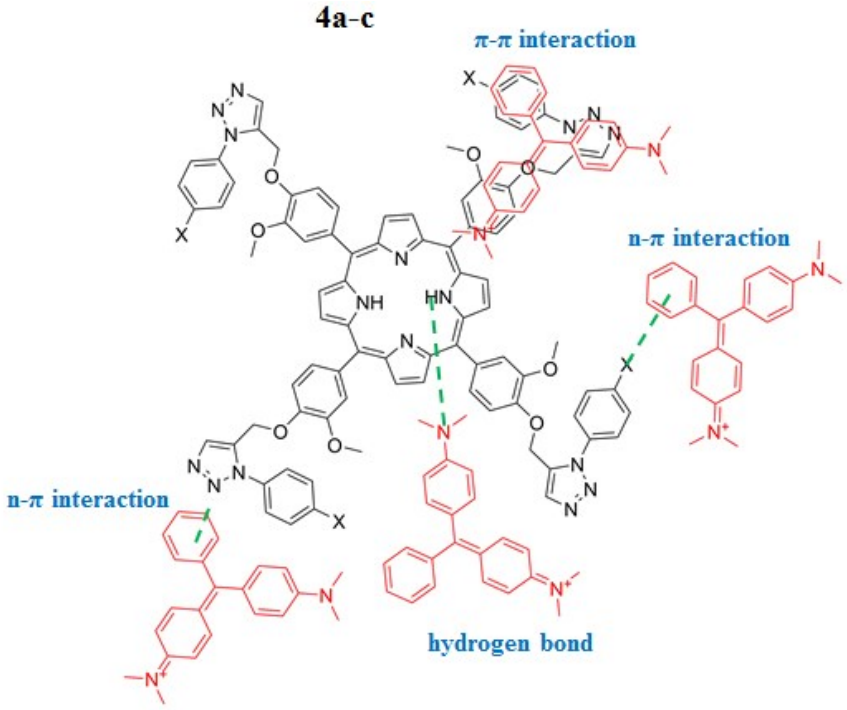


Figure SI-15. Schematic representation of interactions between the MG dye molecules with one triazole-*meso*-arylporphyrin derivative (**4a**, **4b** or **4c**).

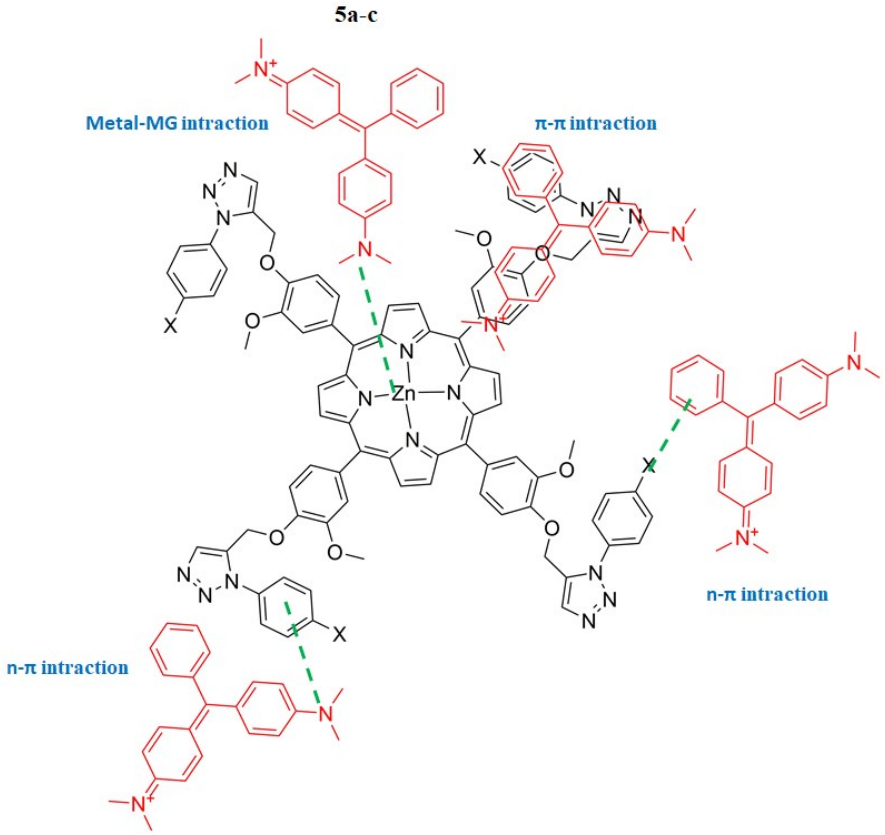


Figure SI-16. Schematic representation of interactions between the MG dye molecules with one zinc(II) porphyrin adsorbent (**5a**, **5b** or **5c**).

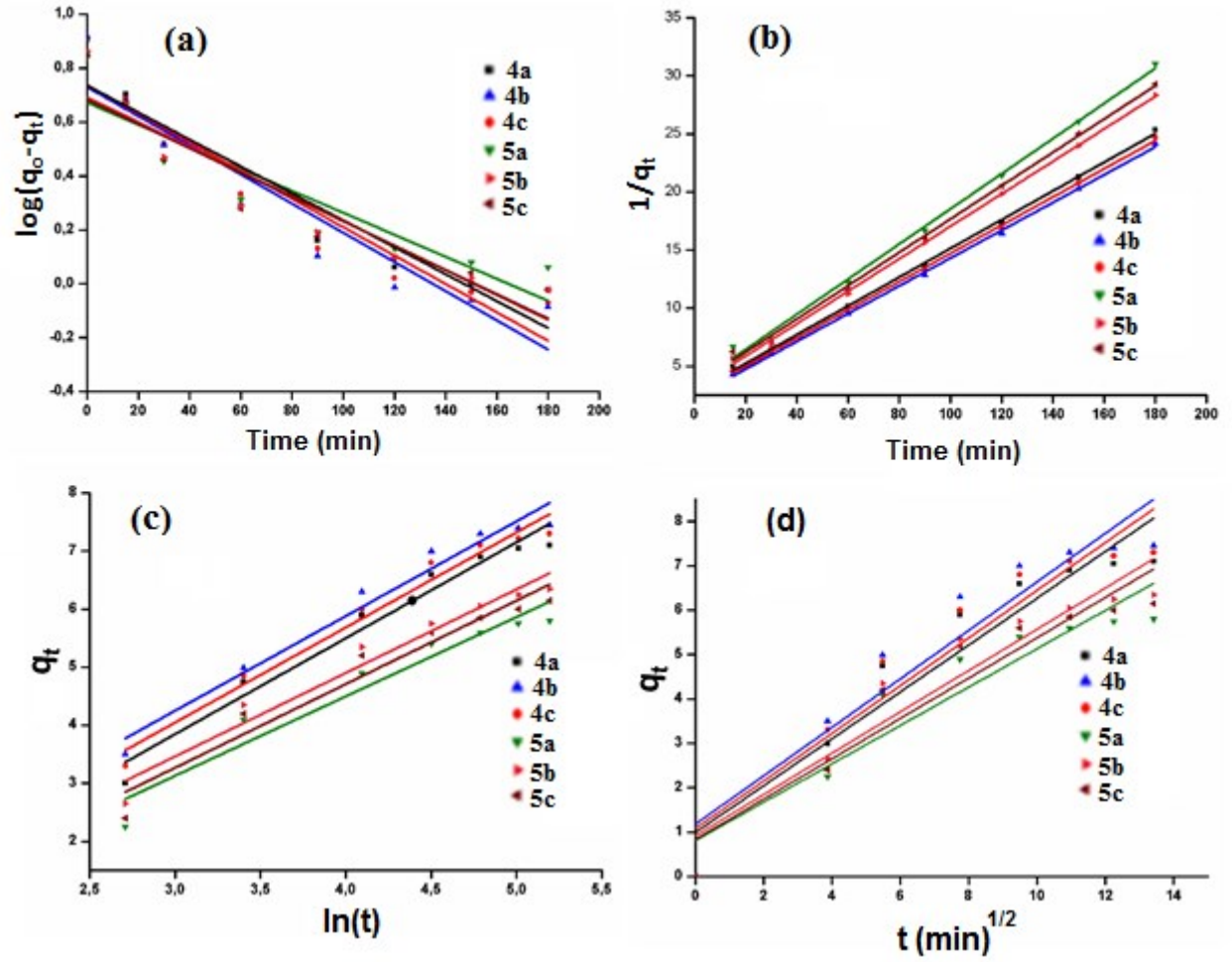


Figure SI-17. Kinetic modeling for the adsorption of MG dye in the presence of compounds **4a-c** and **5a-c**. **(a):** Pseudo first order kinetic model, **(b):** Pseudo second order kinetic model, **(c):** Elovich kinetic model and **(d)**: Intra-particular diffusion kinetic model.

Table SI-2. Kinetic data for the adsorption of MG dye for compounds **4a-c** and **5a-c**.

Calculated parameters	**4a**	**4b**	**4c**	**5a**	**5b**	**5c**
q_{exp} (mg.g^{-1})	8.05	8.15	8.27	6.75	7.1	7.3
Pseudo first Order						
k_1 (min^{-1})	0.0115	0.0122	0.0124	0.0104	0.0104	0.0106
q (mg.g^{-1})	5.4400	5.4576	5.3716	4.5160	4.8195	4.9238
R^2	0.8960	0.9054	0.8940	0.8670	0.8825	0.8917
Pseudo second order						
k_2 (min^{-1})	0.0055	0.0057	0.0061	0.0067	0.0062	0.0064
q_{cal} (mg.g^{-1})	8.0775	8.2372	8.3542	6.6050	6.9638	7.1530
R^2	0.9989	0.9993	0.9993	0.9967	0.9977	0.9990

Elovich						
α (mg.g^{-1}.min^{-1})	0.2633	0.3984	0.5703	0.3614	0.3180	0.4207
β (mg.g^{-1}.min^{-1})	0.6050	0.6108	0.6129	0.7312	0.6947	0.6949
R^2	0.9651	0.9741	0.9689	0.9336	0.9459	0.9580
Intra-particular diffusion						
K_d (mg.g^{-1}.min$^{-1/2}$)	0.5275	0.5365	0.5457	0.4318	0.4538	0.4651
R^2	0.9123	0.9125	0.903	0.8969	0.9037	0.9057
C (mg.g^{-1})	0.995	1.083	1.1812	0.8137	0.8399	0.9194

k_1 : the pseudo first order rate constant (min^{-1}), k_2 : the pseudo second order rate constant (g.mg^{-1}.min^{-1}), α (mg.g^{-1} min^{-1}) : the initial adsorption rate, β (g.mg^{-1}): the desorption constant related to the extent of surface coverage and activation energy for chemisorption, k_d : the Intra-particle diffusion rate constant (g. mg^{-1}.min$^{-1/2}$), *C (mg.g^{-1})*: represents the thickness of the limited diffusion layer.

Part 9: Degradation dye data

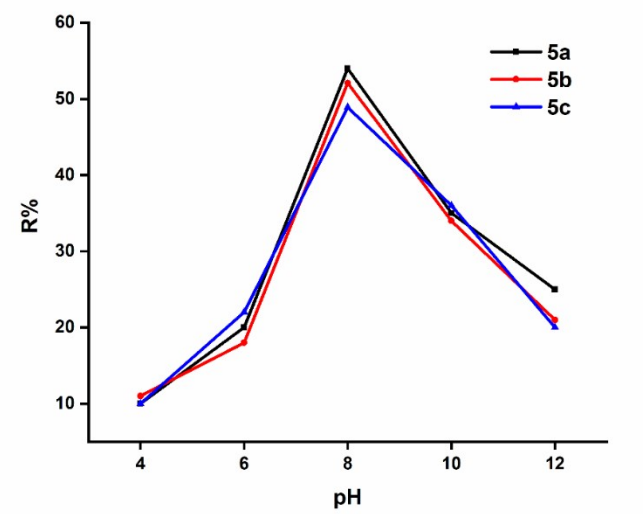


Figure SI-18. Evolution of the degradation efficiency (R%) of the MG dye versus pH using the same mass of **5a-c** (5 mg) as catalysis. Experiment conditions: time contact = 180 min, T = 25°C, [MG] = 20 mg/L and [H_2O_2]= 6 mg.L^{-1}.

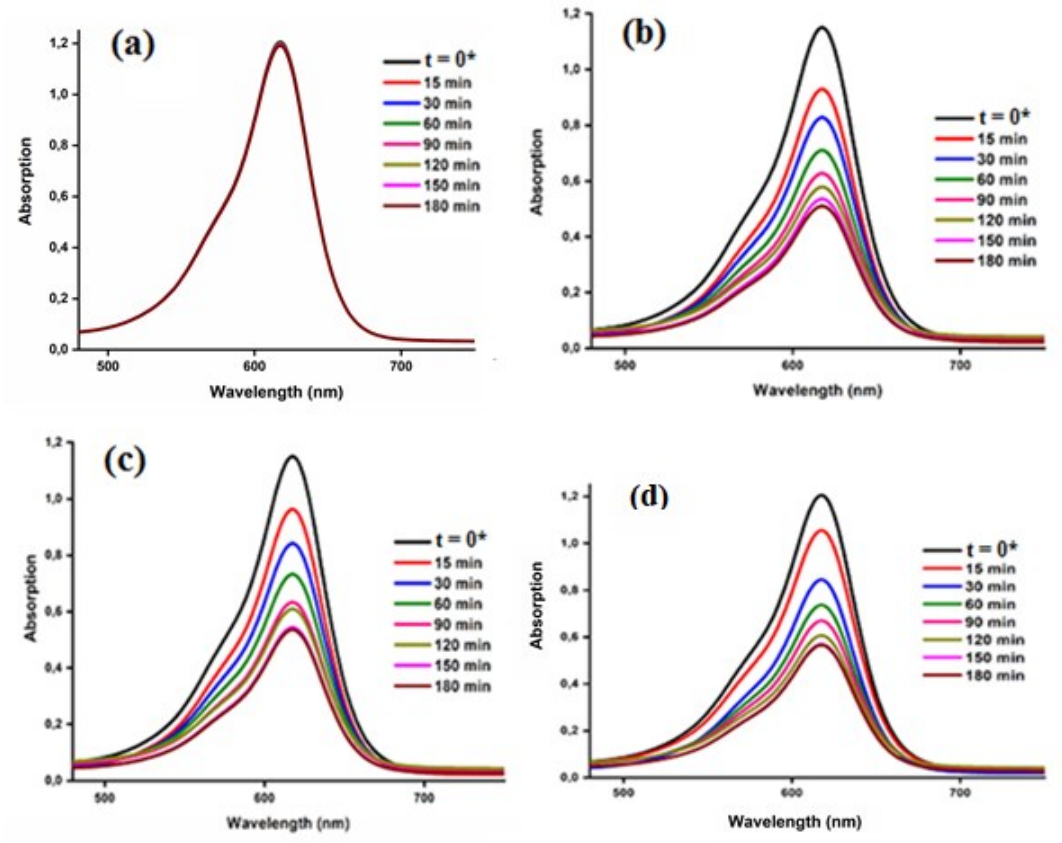


Figure SI-19. Variation of the λ_{max} values of the absorption bands of MG dye and an aqueous H_2O_2 solution (6 mg.L^{-1} and pH = 8). **(a):** blank test (without **5a-c** catalysts), **(b):** in the presence of **5a** (5 mg), **(c):** in the presence of **5b** (5 mg) and **(c):** in the presence of **5c** (5 mg). The concentration of MG is 20 mg.L^{-1} and pH = 8. *: before adding the **5a-c** catalysts.

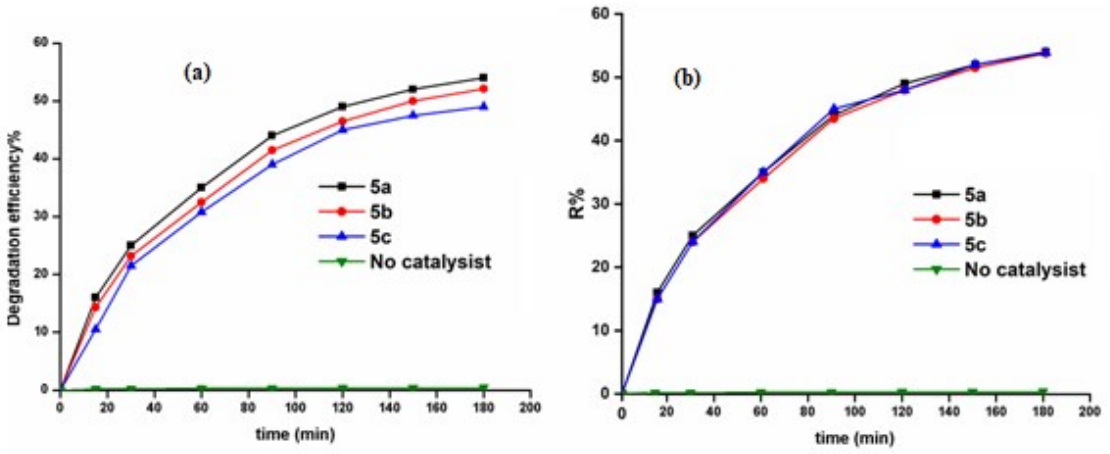


Figure SI-20. Degradation removal efficiency for complexes **5a-c**. **(a):** mass of the **5a-c** catalysts m_o = 5 mg, **(b):** number of moles of the **5a-c** catalysts $n_o = 3.35.10^{-6}$ mol. Experimental concentration: the concentration of MG is 20 mg.L^{-1}.

Part 10: References

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