

# Synthesis, Electronic Spectroscopy, Cyclic Voltammetry, Photophysics and Electric Properties and X-ray Molecular Structures of the *dabco*, *pyz*, *4,4'-bpy*, *4-CNpy*, *4,4'-mda* Aza Ligands *Meso*-tetrakis[4-(benzoyloxy)phenyl]porphyrinato Complexes

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#### Abstract:

The synthesis of the new meso-porphyrin namely, tetrakis[4-(benzoyloxy)phenyl]porphyrin (H2TPBP), the meso-(tetrakis[4-(benzoyloxy)phenyl]porphyrinato)zinc(II) starting material complex [Zn(TPBP)] (1) and the 1,4-diazabicyclo[2.2.2]octane (dabco), pyrazine (pyz), 4,4'-bipyridine (4,4'-bpy), 4,4'diaminodiphenylmethane (4,4'-mda) and the 4-cyanopyridine (4-CNpy) coordination compounds with the TPBP porphyrinate complexes (2-7 respectively) are described. The preparation of the dabco derivative in chlorobenzene leads a crystalline material of a monomer five-coordinated zinc-porphyrin species (2) while the synthesis in dichloromethane gives in solid state a fivecoordinated zinc metalloporphyrin dimer (3). The pyrazine derivative crystallizes as bis-pyrazine six-coordinated zinc metalloporphyrin (4). Complex 5 is present in solid state as a dimer with the 4,4'-bpy

#### Introduction

Zinc porphyrins have been studied since the forties of the last century but for the last two decades a significant revivals of these investigations have been notice. This great interest concerning zinc porphyrins is explained by the use of these derivatives in many domains that extend from medicine, biology, chemistry and physics. Indeed, these applications include photodynamic therapy, photodynamic destructions of viruses,<sup>[11]</sup> chemical sensors,<sup>[22]</sup> semiconductors,<sup>[31]</sup> catalysis,<sup>[4]</sup> nonlinear optics,<sup>[5]</sup> photovoltaic materials.<sup>[6]</sup> Metalloporphyrin-base molecular systems are also of interest in the field of molecular electronic devices such as optoelectric memory devices <sup>[7]</sup> and

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acting as a bridging ligand while in solid state, the 4,4'-mda species (6) is a five-coordinated monomer zinc derivative. All structures of 2-6 possess cavities with different dimensions where are located the solvent molecules. The solution UV/Vis spectra of 2-7 exhibit redshifted Soret bands indicating that these derivatives in solution are five-coordinated zinc(II) porphyrin complexes. The UV/Vis titrations show that the values of the association constants of 2-7 are close to those of known five-coordinated zinc(II) *meso*-porphyrins. The proton NMR of these species confirms this deduction. The photophysical proprieties of 1-7 are similar to those of zinc(II) *meso*-porphyrins related species. The cyclic voltammetry of the H<sub>2</sub>TPBP free base and 1-7 present a third one-electron reversible oxidation wave. Single-layer diode devices of the [iridium tin oxide / zinc porphyrins (1-7) / aluminum] configurations show relatively low turn-on voltages.

light emitting diodes.<sup>[8]</sup> Understanding the effects of axial ligands and the type of the peripheral groups of the porphyrin core of zinc

metalloporphyrins on the electronic, redox, structural and photophysical as well as other physical properties is very important in order to use these species in the different applications mentioned above. In this context, an important number of investigations were carried out on the synthesis and characterization of new porphyrins with different substituents on the porphyrin core with different donor, attractor as well as sterically hindered characters.<sup>[9,10,11,12]</sup>

On the other hand, a number of zinc porphyrin complexes involving monodentate N-donor neutral ligands such as imidazole, pyridine <sup>[13,14]</sup> and anionic ligand such as N<sub>3</sub>, NCS and CN are reported in the literature.<sup>[15]</sup> Bidentate neutral Ndonor ligands (denoted aza ligands) such as 1,4diazabicyclo[2.2.2]octane (dabco), 4,4-bpyridine (4,4'-bpy), 4cyanopyridine (4-CNpy) and pyrazine (pyz) were also used in many studies involving zinc metalloporphyrins.[16,17,18,19] It is important to mention that several investigations were carried out on zinc dimers and trimers where the porphyrins are related together by different moieties known as spacers and the zinc ions of these dimers or trimers (known as tweezers) are coordinated to a bidentate ligand (dabco, pyz, ...) (Scheme 1).<sup>[20,21,22,23, 24, 25]</sup> Despite the important number of research devoted to zinc porphyrin with bidentate aza ligands, a complete characterization of these species are not found in the literature. Herein, we describe, the synthesis of a new meso-porphyrin with

an ester group (acting as  $\sigma$ -donor group) in para-positions of the the porphyrin: the meso-tetrakis[4phenvls of (benzoyloxy)phenyl] porphyrin (H<sub>2</sub>TPBP), the starting material [Zn(TPBP)] (1) and the zinc derivatives with the dabco, pyz, 4,4'and 4-CNpy aza ligands (complexes 2-7 bov. 4-mda respectively) (Scheme 2). These species are characterized by UV/Vis, IR, <sup>1</sup>H NMR spectroscopy and mass spectrometry (MS MALDI-TOF and MS ESI). The association constants (Kas) values of 2-7 are also reported. We shall also report the cyclic voltammetry and the fluorescence results for all species that we prepared. In addition, the electrical properties and the X-ray molecular structures of the zinc metalloporphyrins with the dabco, pyz, 4,4'-bpy and 4,4'-mda aza bidentate ligands are reported. Notably, the 4,4'-mda derivative is the first report of a zinc-porphyrin with this ligand and that a very few number of sixcoordinated structures of zinc metalloporphyrins with two Ndonor axial ligands are reported in the literature.



Scheme 1. Schematic representations of different zinc-porphyrin / N-donor bidentate ligands (L) coordination types.



Scheme 2. N-donor bidentate ligands (aza ligands) used in this work.

#### Results and Discussion Synthesis of 2-7

Complexes 2-7 were prepared by addition of an excess of the Ndonor aza ligands (*dabco*, *pyz*, *4*,*4'-bpy*, *4*,*4'-mda* and *4-CNpy*) to a solution of the [Zn(TPBP)] (1) staring material. It is noteworthy that the *dabco*-zinc(II) derivatives 2 and 3 were made using the same synthetic procedures except that 2 is prepared in chlorobenzene while **3** was prepared in dichloromethane. The crystallization of these two species in chlorobenzene (for **2**) and dichloromethane (for **3**) using n-hexane as non-solvent leads to crystals of a monomer species type 1/1-M (for **2**) and a dimer derivative type 2:1-D (for **3**) as determined by X-ray molecular structures.

#### UV/Vis spectroscopy

As shown in Table 1, the free bases meso-porphyrins, including the new H<sub>2</sub>TPBP porphyrin, present in solution similar UV/Vis spectra with  $\lambda_{max}$  values of the Soret band at ca. 420 nm and four Q bands at ca. 515, 550, 590 and 650 nm. The [Zn(Porph)] (Porph = meso-porphyrin) starting materials, exhibit similar solution electronic spectra, which are slightly redshifted compared to those of the free bases, with Soret bands at ca. 424 nm and Q(1,0) and Q(0,0) bands at ca. 550 and 590 nm respectively. If we neglect the solvent effect, we notice that the UV/Vis data of the free base meso-porphyrins and the corresponding [Zn(Porph)] complexes didn't depend on the nature of the group of atom(s) in the para positions of the phenyl rings of the meso-porphyrins (Table 1). Early investigations by Valentine *et coll*.<sup>[13]</sup> on zinc(II) *meso*-tetraphenylporphyrin (TPP) complexes with N-donor neutral monodentate ligand such as pyridine and imidazoles (L) show that in solution, only the fivecoordinated [Zn(TPP)(L)] species are formed. Later on, several studies have been reported in literature on monomeric zinc(II) metalloporphyrins (type 1:1-M) (Scheme 2) and especially on dimeric, trimeric (types 2:1-D and 3:2-T) and tweezer zinc porphyrin derivatives (type 1:1-Tw).<sup>[20,22,26]</sup> These investigations show that upon addition of N-donor bidentate ligands such as dabco, pyz, 4,4'-bpy, to the tetra-coordinated zinc-porphyrin starting material [Zn(Porph)], a bathochromic shift of about 10 nm is an indication of the formation of a monomer/L (type 1:1-M) species while a redshift of about 5 nm indicates the formation of 1:1 tweezer/L (type 1:1-Tw) sandwich complex but in both cases the zinc is five-coordinated.

The narrowing of the HOMO-LUMO gap is mainly due to the deformation of the porphyrin core leading to redshifted Soret and Q bands for porphyrins and metalloporphyrins.<sup>[27]</sup> The redshift of the Soret and Q bands of the zinc(II) metalloporphyrins is also related to the electron-withdrawing groups at the meso and βpyrrolic positions of the porphyrin and to the nature of the metal ion.<sup>[28,29,30,31]</sup> The normalized absorption spectra of the starting material [Zn(TPBP)] (1) and complexes 2-7 recorded in chloroform are shown in Figure 1. The spectra were obtained by dissolving crystals of 1-7 in chloroform. The  $\lambda_{\text{max}}$  Soret band values of these derivatives are practically the same (430 - 432 nm) which are redshifted by about 6 nm compared of the [Zn(TPBP)] starting material (1). Therefore, since the redshifts values of 2-7 are between 5 and 10 nm and according to what has been mentioned above, it is not clear to tell from the redshift values of the Soret bands whether 2-7 are monomer/L (type 1:1-M) or dimer/L (type 2:1-D) species. Nevertheless, these UV/vis data indicate that 2-7 are five-coordinated zinc(II) metalloporphyrins. In order to calculate the values of the association constants Kas of 2-7, titrations by UV/vis spectroscopy were carried out in chloroform with concentrations

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of about 10<sup>-6</sup> M for the Soret region and 10<sup>-5</sup> M for the Q bands region. The titrations spectra of the [Zn(TBPP)] complexes by the *dabco*, *pyz*, *4,4'-byp*, *4,4'-mda* and *4-CNpy* ligands are reported as supplementary information (Figures SI-1-10) along with the estimated K<sub>as</sub> values of **2-7** (Tables IS-1-2). The titration data were analyzed using the non-linear regression analysis program GWBASIC to determine the estimated K<sub>as</sub> values for complexes **2-7**. The *4,4'-bpy* derivative (**5**) exhibits the highest value of K<sub>as</sub> (2.72.10<sup>6</sup>), the smallest value of K<sub>as</sub> is shown by the *4,4'-mda* species (**6**) (0.59.10<sup>3</sup>) while the K<sub>as</sub> values of the *pyz* and *4-CNpy* derivatives (**4** and **7**) are 1.67.10<sup>3</sup> and 2.57.10<sup>3</sup> respectively. These titrations indicate a simple binding process with the formation of monomer/L (type 1:1-M. These values are in the range of the related species [Zn(TPP)(L)] (L = pyridine, imidazole) for which the K<sub>as</sub> values

are 2.52.10<sup>4</sup> and 6.61.10<sup>4</sup>.<sup>[32,33]</sup>. By the other hand, the UV/Vis titrations of the [Zn(Porph-Ia)] and [Zn(Porph-Ib)] complexes (Porph-Ia and Porph-Ib are the two 5-phenyl-10-(2-hydroxynaphthyl)-15-[4-hydroxyphenyl] porphyrinato enantiomers) with a pair of amino acid esters (L- and D-Phe-OMe) leads to an estimated values of K<sub>as</sub> of ~ 2.0.10<sup>4</sup> <sup>[34]</sup> which are comparable to those of our zinc(II) metalloporphyrins (2-7). The optical band gap (Eg-op) corresponds to the energy difference between the levels of the HOMO and LUMO orbitals of the metalloporphyrin (supplementary information Figure SI-11). The values of Eg-op were obtain from the chloroform UV/Vis spectra of 1-7 using the tauc'plot method. These values in chloroform solution are ~ 1.97 eV which are higher than that of the H<sub>2</sub>TPBP free base (1.82 eV) (Table 1).

Table 1. UV/Vis data of several free base meso-porphyrins, complexes 1-7 and a selection of zinc meso-metalloporphyrins.

Compound		$\lambda_{\max}$ (	nm) (ε.10 <sup>-3</sup> )				E <sub>og</sub> (eV)	Ref.
Free base meso-porphyrins	Solvent	Soret band	Q bands	S				
H₂TPP <sup>a</sup> H₂TTP <sup>b</sup> H₂TPBP	$\begin{array}{c} CH_2CI_2\\ CH_2CI_2\\ CHCI_3 \end{array}$	419 420 420 (513)	516 516 516 (17)	552 552 552 (7)	594 594 591 (5)	645 650 646 (4)	- - 1.82	[35] [36] this work
[Zn(Porph)] complexes		Soret band	Q(0,0) band	Q(0,0) b	and			
[Zn(TPP)] [Zn(TTP)] [Zn(TMP)] [Zn(TPBP)] ( <b>1)</b>	Toluene CH <sub>2</sub> Cl <sub>2</sub> CH <sub>2</sub> Cl <sub>2</sub> CHCl <sub>3</sub>	422 (578) 421 (524) 420 425 (546)	549 (23) 550 (21) 550 554 (24)	588(4 591 (2 586 596 (9	.) 25) 9)		- - - 1.99	[37] [35] [12] this work
<i>L-zinc metalloporphyrins</i> ( <i>L</i> = dabco. pyz. 4,4'-bpy, 4-CNpy and	4,4'-mda)	Soret band	Q(1,0) band	Q(0,	.0) band			
$\begin{split} & [Zn(TPP)(3-AP)]^{c} \\ & [Zn(TPP)(4-AP)]^{d} \\ & [Zn(TPP)(pyO] \\ & [Zn(TPP)(pyCCPh)]^{e} \\ & [Zn(TPP)(pyCCPh)]^{e} \\ & [Zn(TPBP)(dabco)].C_{6}H_{5}Cl (2) \\ & [\{Zn(TPBP)\}_{2}(\mu_{2}-dabco)] \\ & .4(CH_{2}Cl_{2}).2(C_{6}H_{14}) (3) \\ & [Zn(TPBP)(py2]_{2}].CHCl_{3} (4) \\ & [Zn(TPBP)]_{2}(\mu_{2}-4, 4-bpy)].2CHCl_{3} (5) \\ & [Zn(TPBP)(4, 4-mda)] (6) \\ & [Zn(TPBP)(4-CNpy)](4-CNpy) (7) \end{split}$	$\begin{array}{c} CH_2CI_2\\ CH_2CI_2\\ CH_2CI_2\\ Toluene\\ CHCI_3\\ CHCI_3\\ CHCI_3\\ CHCI_3\\ CHCI_3\\ CHCI_3\\ CHCI_3\\ CHCI_3\\ CHCI_3\end{array}$	428 428 429 431 (502) 432 (498) 430 (445) 430 (483) 431 (544) 430 (571)	563 564 562 - 564 (21) 563 (20) 561(18) 563 (20) 563 (27) 561 (23)	603 604 602 601 603 604 604 603 604 603	(12) (12) (9) (12) 18) (11)		- - - 1.97 1.97 1.99 1.97 1.94 1.98	[17] [17] [12] [38] this work this work this work this work this work this work

 $a^{\circ}$ : H<sub>2</sub>TPP = *meso*-tetraphenylporphyrin.  $b^{\circ}$ : *meso*-tetratolylporphyrin.  $c^{\circ}$ : 3-AP = 3-aminopyridine.  $d^{\circ}$ : 4-AP = 4-aminopyridine.

<sup>e</sup> : pyCCPh = 4-phenylethynyl-pyridine.



10<sup>-6</sup> M, recorded in chloroform. The inset shows enlarged views.

#### IR and <sup>1</sup>H NMR spectroscopy

The IR spectra of **2-7** confirm the presence of the axial ligands. Indeed, the 1:1-M and 2:1-D *dabco*-zinc deivatives **2** and **3** respectively exhibit sharp and medium intensity bands at ca. 3030 cm<sup>-1</sup> attributed to  $v_s(CH)$  of the methylene group of the *dabco* ligand. This absorption band is shifted to higher frequency compared to the free *dabco* molecule (2885 cm<sup>-1</sup>) indicating the coordination of this ligand to [Zn(TPBP)]. The presence of the pyrazine ligand of complex **4** is confirmed by the absorption bands at 2990 cm<sup>-1</sup>, 1416 cm<sup>-1</sup> and 1040 cm<sup>-1</sup>. The absorption bands of the C–H stretching frequencies of the starting material [Zn(TPBP)] (**1**) and those of the *4,4'-bpy* derivative (**5**) are superposed (3063 cm<sup>-1</sup> and 3034 cm<sup>-1</sup>) while the absorption

band at 1650 cm<sup>-1</sup> is attributed to v(C=C) of the 4,4'-bpy ligand. For the 4,4'-mda-zinc derivative (6), the absorption bands at 3337 cm<sup>-1</sup>, 3282 cm<sup>-1</sup>, 1621 cm<sup>-1</sup> and 818 cm<sup>-1</sup> are attributed to the coordinated 4-4'-mda ligand while the band at 494 cm<sup>-1</sup> corresponds to the stretching frequency v[Zn-N(4,4'-mda)].<sup>[39]</sup> For 7, the IR spectrum exhibits a weak absorption band at 2238 cm<sup>-1</sup> attributed to the nitrile stretching frequency v(C=N). The value of this band is almost identical to the one of the free 4cyanopyridine (2236 cm<sup>-1</sup>) which could be attributed both to the 4-CNpy ligand or the free 4-CNpy molecule in 7 because, this band is usually not affected by the coordination of the 4cyanopyridine.<sup>[40]</sup>

The proton NMR spectra of **1-7** are given as supplementary materials (Figures SI-13-20). Several investigations involving <sup>1</sup>H NMR titrations of tweezer-*dabco* zinc porphyrins reviled that when less than 0.3 equiv is added to the zinc-porphyrin starting material, the methylene protons of the *dabco* adduct appears as sharp signal at ~ -5.00 ppm but for further addition of this ligand, this signal is broadened and finally disappears.<sup>[41]</sup> The NMR spectra of the *dabco*-zinc porphyrin species **2-3** didn't show any signals attributed to the methylene protons of the *dabco* ligand. This could be explained by a fast exchange equilibrium between the coordinated and the non-coordinated *dabco* to the [Zn(TBPP)] species.

For complex 4 where Zn(II) is coordinated to a pyrazine ligand, a weak singlet signal appears at 6.93 ppm which is upfield shifted compared to the free pyrazine molecule ( $\delta$  = 8.59 ppm). Notably, the <sup>1</sup>H NMR titration of a tweezer-*pyz* zinc porphyrin shows that the coordinated pyrazine ligand appears at 6.12 ppm corresponding to a tweezer/pyz type 1:1-Tw derivative.  $\ensuremath{^{[42]}}$  The very close chemical shift values of 4 and the tweezer/pyz derivative is an indication that in solution, complex 4 is a fivecoordinated zinc metalloporphyrin. The 4,4'-bpy noncoordinated ligand presents two signals at 8.75 ppm (for the 1.4,6,7-H protons) and 7.53 (for the 2,3,5,8-H protons) (Scheme 2) ppm respectively. The protons of this ligand in complex 5 are shielded and resonate at 6.25 ppm and 6.53 ppm. For the monomer (1:1-M type) [Zn(TCIPP)(4,4'-bpy)] (TCIPP = mesotetrakis[4-chlorophenyl]porphyrinato) <sup>[42]</sup> related species, the  $\delta$ values of the 1,4,6,7-H and 2,3,5,8-H protons are 6.20 ppm and 5.60 ppm respectively. By the other hand, the 4,4'-bpy protons of the dimer/4.4-bpy (2:1-D type) species [Zn(TCIPP)<sub>2</sub>(4,4'-bpy)] <sup>[42]</sup> are much more shielded at 4.30 ppm and 5.66 ppm. Thus, the NMR data indicate that complex 5 in solution is a fivecoordinated zinc porphyrin derivative. For complex 6, the protons of the 4,4'-mda ligand are slightly upfield shifted compare to the free 4.4'-mda molecule for which the NH<sub>2</sub>, 1,4,7,8-H and 2,3,6,9-H protons (Scheme 2) resonate at ~ 4.00, 6.34 ppm, 6.81 and 3.81 ppm respectively. For 6, the chemical shift values of the 4,4'-mda ligand are 2.63 ppm, 6.00 ppm, 6.75 ppm and 3.63 ppm respectively. The proton NMR of our 4-CNpy-zinc(II) derivative (7) presents two doublets at 7.96 ppm (for the 2,6-H protons, Scheme 2) and 8.75 ppm (for the 3,5-H3 protons) attributed to the non-coordinated 4-CNpy molecule. The presence of a non-coordinated 4-CNpy in the lattice is confirmed by the X-ray molecular structure (see crystallographic section). The coordinated 4-CNpy ligand of 7 are upfield shifted and resonate at 6.85 ppm for the 2,6-H protons and 6.28 for the 3,5-H3 protons. These values are close to those of the related magnesium(II) *4-CNpy* with the tetranitrooctaethylporphyrin complex.<sup>[43]</sup>

As indicated by the <sup>1</sup>H NMR data, the axial ligand protons of **2-7** are upfield shifted which is due to the shielding effect of the porphyrin ring current.<sup>[43]</sup>

#### Fluorescence Spectroscopy

The fluorescence spectra of the H<sub>2</sub>TPBP and complexes 1-7 were recorded at room temperature in dilute dichloromethane solution (~10<sup>-6</sup> M) which show two bands Q(0,0) and Q(0,1)(Figure 2). In Table 2 are summarized the maxima of the fluorescence of the Q(0,0) and Q(0,1) bands, the fluorescence quantum yields  $(\Phi_f)$  and the fluorescence lifetimes  $(T_f)$  of the species just mentioned above and those of several related species. The major difference between the zinc complexes 1-7 compared to their corresponding free base H<sub>2</sub>TPBP is the remarkable hypsochromic shift of ~ 50 nm for the strongest emission band Q(0,0) (except complex 2 where the blue shift is ~ 40 nm) and between 70 and 55 nm for the Q(0,1) band. This shift is mainly due to the metalation of the porphyrin and it seems that the axial ligand have minor effect except for complex 2 where the shift differ from those of the other zinc porphyrin derivatives. By the other hand, the  $\lambda_{max}$  values of the Q(0,0) and Q(0,1) bands of 1-7 are close to those of the related zinc porphyrin derivatives (Table 2). The fluorescence quantum yiels of H<sub>2</sub>TPBP and complexes 1-7 are in the range [0.021 - 0.055] which are close to the related zinc metalloporphyrins.[44] The Stokes shifts for 1-7 and H<sub>2</sub>TPBP, which are very small, are

typical of a fluorescence emission with no significant conformation change between the fundamental and excited states. The singlet excited state lifetime was measured by single-photon counting technique and the fluorescence decays of **1-7** species were fitted

to single exponentials.



Figure 2. The fluorescence spectra of  $H_2TPBP$  and complexes **1–7** in  $CH_2Cl_2$  (concentration ~10<sup>-6</sup> M). The excitation wavelength is 540 nm.

The representative fluorescence decays for the free base H<sub>2</sub>TPBP and complex **1** are shown in Figure 3 while the curves of **2-7** are not shown as they resembles to complex **1**. The  $\tau_f$  values of the free base H<sub>2</sub>TPBP (~ 8 ns) is as expected much higher than those of zinc metalloporphyrins **1-7** which are at ca. 1.6 ns except complex **2** which has the smaller  $\tau_f$  value of 1.3 ns. Therefore, the life time value of zinc metalloporphyrins didn't depend on the axial ligand as shown also for the related species

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 $[Zn(TPP)(\textit{IQNO})] \ ^{[45]} (IQNO = isoquinoline N-oxide) and <math display="inline">[Zn(TPP)(\textit{1,4-dioxane})_2].^{[9]}$ 



Figure 3. (a) : Fluorescence decay profile of the free base H<sub>2</sub>TPBP (dark grey) and [Zn(TPBP)] (1) (light grey).

Table 2. Emission data of several meso-porphyrins and a selection of zinc meso-metalloporphuyrins,  $\lambda_{max}$  in nm and  $\tau_f$  in ns.

Compound	Q(0,0)	Q(0,1)	$\Phi_{f}$	$\tau_{\text{f}}$	Solvent	Ref.
Meso-porphyrins						
H₂TPP	654	712	0.11	-	CH <sub>2</sub> CI	[46,47]
H <sub>2</sub> TPP	656	717	0.09	-	$CH_2CI_2$	[48]
H <sub>2</sub> TPP	653	722	0.12	9.6	DMF <sup>a</sup>	[49]
H <sub>2</sub> TPBP	653	715	0.038	8.2	CH <sub>2</sub> Cl <sub>2</sub> th	nis work
Meso-porphyrin zinc(II) co	mplexe	s				
[Zn(TPP)]	597	647	0.033	1.9	$CH_2CI_2$	[36]
[Zn(TTP)]	600	648	0.03	1.6	$CH_2CI_2$	[15]
[Zn(TTP)( <i>mbpy~py</i> )] <sup>b</sup>	611	652	0.021	-	$CH_2CI_2$	[50]
[Zn(TPP)(IQNO)] <sup>c</sup>	~602	656	-	1.9	et-acet d	[51]
$[Zn(TPP)(N_3)]$	594	643	0.036	1.7	$CH_2CI_2$	[15]
[Zn(TPP)(CN)]	594	643	0.055	1.7	$CH_2CI_2$	[15]
[Zn(TPP)(1.4-dioxane)2]	604	655	-	1.8	dioxane	[15]
[Zn(TPBP)] (1)	606	654	0.027	1.6	$CH_2CI_2$	this work
[Zn(TPBP)(dabco)].						
C <sub>6</sub> H <sub>5</sub> Cl (2)	612	660	0.039	1.3	$CH_2CI_2$	this work
$[{Zn(TPBP)}_2(\mu_2 - dabco)]$						
.4(CH <sub>2</sub> Cl <sub>2</sub> ). <sub>2</sub> (C <sub>6</sub> H <sub>14</sub> ) (3)	606	654	0.046	1.6	$CH_2CI_2$	this work
$[Zn(TPBP)(pyz)_2].$						
CHCl <sub>3</sub> (4)	596	644	0.049	1.6	$CH_2CI_2$	this work
[{Zn(TPBP)}2(µ2-4.4-bpy)]						
3CHCl <sub>3</sub> (5)	596	645	0.044	1.5	$CH_2CI_2$	this work
[Zn(TPBP)(4,4'-mda)] (6)	606	654	0.039	1.7	$CH_2CI_2$	this work
[Zn(TPBP)(4-CNpy)]						
.4-CNpy (7)	596	645	0.041	1.5	$CH_2CI_2$	this work

<sup>a</sup> DMF = *N*.*N*-dimethylformamide. <sup>b</sup> : mbpy~py = 4'-methyl-4-[2-(4-pyridyl) ethenyl]-2.2'-bipyridine <sup>c</sup> : IQNO = isoquinoline N-oxide. <sup>d</sup> et-acet = ethyl acetate

#### Cyclic voltammetry

The electrochemical behavior of the H<sub>2</sub>TPBP porphyrin and **1–7** was studied by cyclic voltammetry (CV) with tetra-nbutylammonium perchlorate (TBAP) as the supporting electrolyte (0.1 M) in the non-coordinating solvent CH<sub>2</sub>Cl<sub>2</sub> under an argon atmosphere. The CV curves of H<sub>2</sub>TPBP and **1-7** are depicted in Figure 4. The electrochemical data for H<sub>2</sub>TPBP, complexes **1–7** along with those of several related species are collected in Table 3. The free base H<sub>2</sub>TPBP exhibits two oneelectron reduction reversible waves and three one-electron oxidation reversible waves which correspond to the reduction and the oxidation of the porphyrin ring. The E<sub>1/2</sub> values of H<sub>2</sub>TPBP are close to close of *meso*-tetraphenylporphyrins (H<sub>2</sub>TPP)] (Table 3). <sup>[49,45]</sup> Metallation of these porphyrins in [Zn(Porph)] leads to a shift to more negative values of the reduction and oxidation characteristic potentials.<sup>[12,51]</sup>

Thereby, for H<sub>2</sub>TPBP, the values of the half potential waves are 0.95, 1.36, and 1.48 V for the first, second and third oxidations waves respectively while those of complex **1** are 0.81, 1.11 and 1.40 V. The values of the  $E_{1/2}$  of the first, the second and the third reduction waves of **1** are -1.48 V and -1.67 V respectively compared to -1.12 V and -1.53 V for H<sub>2</sub>TPBP.

The coordination of the N-donor ligands (*dabco*, *pyz*, *4,4'-bpy*, *4,4'-mda* and *4-CNpy*) leading to complexes **2-7** have a minor effect on the oxidation and the reduction potentials compared with the starting material [Zn(TPBP)] (Table 3).

This is also the case for other zinc-porphyrin derivatives type  $[Zn(Porph)(X)]^{\pm m}$  (Porph = TPP, TMP and X = neutral or anionic monodentate ligand, m = 0 or -1) (Table 3). The zinc-porphyrin HOMO-LUMO gap can be expressed as the potential difference of the first oxidation and the first reduction (supplementary information Figure SI-12).<sup>[52]</sup> This energy gap is known as the electrochemical gap (Eg-el). The calculated values of the energy gap for 1-7 are in the range [2.15- 2.37] eV. These values are close to the usual value of 2.25  $\pm$  0.15 eV for metalloporphyrins <sup>[53]</sup> and to the theoretical value of 2.18 eV given by Gouterman and coll.<sup>[54]</sup> We notice that for 1-7, the values of the electrochemical gap (Eg-el) are quite higher compared to those of the optical dap (Eg-op).



Figure 4. Cyclic voltammograms of H<sub>2</sub>TPBP and 1 (the inset shows enlarged view): (a), complexes 2, 4 and 5: (b), complexes 3, 6 and 7: (c). The solvent is  $CH_2CI_2$  and the concentration is ca.  $10^{-3}$  m in 0.2 M TBAP, 50 mV/s, vitreous carbon working electrode ( $\emptyset = 3$  mm).

Table 3. Electrochemical data <sup>a</sup> (in dichloromethane solvent) for complexes 1-7 and a selection of meso-porphyrins and zinc(II) metalloporphyrins.

		Ring Oxidations					Ring Reductions									
	1 <sup>st</sup> oxidation 2 <sup>nd</sup> oxidation (O1, R1) (O2, R2)		3 <sup>th</sup> oxidation (O3, R3)			1 <sup>st</sup> reduction (R4, O4)			2 <sup>nd</sup> reduction (R5, O5)			Ref				
	E <sub>pa</sub> <sup>b</sup>	E <sub>pc</sub> <sup>c</sup>	$E_{1/2}^{d}$	E <sub>pa</sub>	E <sub>pc</sub>	E <sub>1/2</sub>	E <sub>pa</sub>	E <sub>pc</sub>	E <sub>1/2</sub>	E <sub>pa</sub>	E <sub>pc</sub>	E <sub>1/2</sub>	E <sub>pa</sub>	E <sub>pc</sub>	E <sub>1/2</sub>	
H <sub>2</sub> TPP	-	-	1.02	-	-	1.26	-	-	-	-	-	-1.20	-	-	-1.55	[50]
H <sub>2</sub> TPP	-	-	1.08	-	-	1.35	-	-	-	-	-	-1.21	-	-	-	[47]
H <sub>2</sub> TPBP	1.09	0.81	0.95	1.31	1.40	1.36	1.54	1.41	1.48	-1.17	-1.07	-1.12	-1.44	-1.62	-1.53	this work
[Zn(TPP)]	-	-	0.82	-	-	-	-	-	-	-	-	-1.20	-	-	-	[36]
[Zn(TPP)]	-	-	0.89*	-	-	1.18*	-	-	-	-	-	-1.26*	-	-	-1.70*	[12]
[Zn(TMP)]	-	-	0.83*	-	-	1.16*	-	-	-	-	-	-1.44*	-	-	-	[12]
[Zn(TTP)	-	-	0.74	-	-	-	-	-	-	-	-	-1.22	-	-	-	[12]
(1)	0.84	0.78	0.81	1.15	1.06	1.11	1.35	1.44	1.40	-1.44	-1.53	-1.48	-1.63	-1.70	-1.67	this work
[Zn(TPP)( <i>Him</i> )] <sup>†</sup>	-	-	0.65*	-	-	1.35*	-	-	-	-	-	-1.35*	-	-	-1.70*	[12]
[Zn(TPP)(2-Meim)] <sup>9</sup>	-	-	0.66*	-	-	1.32*	-	-	-	-	-	-1.40*	-	-	-1.75*	[12]
[Zn(TMP)(Him)]	-	-	0.58*	-	-	1.21*	-	-	-	-	-	-1.50*	-	-	-	[12]
[Zn(TMP)(2-Meim)]	-	-	0.58*	-	-	1.18*	-	-	-	-	-	-1.55*	-	-	-	[12]
[Zn(TPP)(N <sub>3</sub> )]	-	-	0.71	-	-	1.15	-	-	1.40	-	-	-1.53	-	-	-1.76	[15]
[Zn(TPP)(CN)]	-	-	0.65	-	-	1.06	-	-	1.38	-	-	-1.51	-	-	-1.77	[15]
(2)	0.92	0.75	0.84	1.20	1.04	1.12	1.44	-	-	-1.36	~ -1.3	0 ~ -1.33	-	-	-	this work
(3)	0.85	0.78	0.80	1.12	1.05	1.09	1.38	1.30	1.34	~ -1.3	8		-	-	-	this work
(4)	0.90	0.74	0.82	1.19	1.04	1.12	1.43	~ 1.33	3 ~ 1.38	~ -1.3	4*		-	-	-	this work
(5)	0.86	0.75	0.81	1.17	1.06	1.13	1.44	~ 1.34	4~1.39	-1.30*			-	-	-	this work
(6)	0.84	0.79	0.81	1.28	*	-	1.28*	-	-	-1.31	-1.35	-1.38	-1.62	-1.75	-1.69	this work
(7)	0.84	0.78	0.81	1.14	1.05	1.10	1.37	1.34	1.36	-1.47	-1.50	-1.52	-1.64	-1.84	-1.74	this work

<sup>a</sup>:The potentials are reported versus SCE. <sup>b</sup>:  $E_{pa}$  = anodic peak potential. <sup>c</sup>:  $E_{pc}$  = cathodic peak potential. <sup>d</sup>:  $E_{1/2}$  = half wave potential. <sup>e</sup>:  $H_2TMP$  = *meso*-tetramesitylporphyrin. <sup>f</sup>: Him = imidazole. <sup>g</sup>: 2-Meim = 2-methylimidazole. <sup>\*</sup>: denotes an irreversible wave.

#### Current-voltage measurements

As seen by the energy gaps values of **1-7** which are around 1.87 eV for the optical gap and in the range [2.15 – 2.36] eV for the electrochemical energy gap, these species are considered as semi-conductor materials which is the case of porphyrins and metalloporphyrins. In order to have an idea about the electrical properties of complexes **1-7**, the following study was carried out. Single-layer devices with the [ITO/ZnP(i)/AI] (i = 1-7 for complexes **1-7** respectively) configuration were made to investigate the current–voltage (*I-V*) characteristics of the zinc-porphyrin species **1-7**. Figure 5 displays the *I-V* curve measured at room temperature, which exhibit diode-like with relatively low turn-on voltages of 0.33, 0.70, 0.48, 0.40, 0.46, 0.65 and 0.35 V. From the slope of *I-V* curves, the room temperature resistance is estimated to be about 6.10, 52.80, 14.20, 9.00, 11.31, 56.56 and 116.00 k $\Omega$  for complexes **1-7** respectively.



Figure 5. Current-voltage curves of [ITO/ZnP(i)/Al] (i =1-7 for complexes 1-7 respectively).

These features make these compounds promising active materials for zinc metalloporphyrins-based OLEDs. The higher conductivity of the staring material [Zn(TPBP)] complex (1) compare to **2-7** could be explain by the absence of an axial ligand in **1**. This allows a better  $\pi$ - $\pi$  overlap between the  $\pi$ -conjugated zinc-porphyrin derivatives compared to the five-coordinated species. Notably, the crystal structures of **2-6** present voids with different dimensions while the crystal packing of complex **7** shows supramolecular channels parallel to the *c* axis (see crystallographic section) <sup>[54]</sup> which are for probably responsible of the electric properties of **1-7**. More studies are underway to understand the disparity in the turn-on voltage and the conductivity propriety of our zinc-porphyrin derivatives **1-7**.

#### X-ray Structures of 2-6

Complexes 2, 5 and 6 crystallize in the triclinic crystal system with the space group P-1 which is also the case of complex 7 <sup>[54]</sup>. Complex 2 crystallizes in the monoclinic crystal system (P21/n space group) while complex 4 crystallizes in the tetragonal crystal system ( $I4_1/a$  space group) where the zinc lies on a four-fold rotoinversion axis. The asymmetric unit of 2 is made by one [Zn(TPBP)(dabco)] complex and one chlorobenzene solvent molecule while the asymmetric unit of 3 contains one half [ $\{Zn(TPBP)\}_2(\mu_2 - dabco)$ ] of a dimer complex, two dichloromethane and one n-hexane molecules. For complexes 4-6, the asymmetric units is made by one-quarter of the  $[Zn(TPBP)(pyz)_2]$  complex and one-quarter of a chloroform molecule for the former complex, one half  $[{Zn(TPBP)}_2(\mu_2-4-4'$ bpy)] of a dimer complex and one chloroform molecule for complex 5 and one [Zn(TPBP)(4-4'-mda)] molecule for the later complex (6). As shown in Table 4, zinc metalloporphyrins with monodentate axial ligands are present in solid state as fivecoordinated species type  $[Zn(Porph)(X)]^{+m}$  (X = neutral or anionic ligand and m = 0 or 1)] (monomer type 1:1-M) in most cases and as six-coordinated derivative type [Zn(Porph)(L)2] (L = neutral axial monodentate ligand) (monomer type 1:2-M) in few [31]  $[Zn(TPP)(py)_2]$ and  $[Zn(TPP)(NH_2Ph)_2]$ cases i.e. complexes.[56]

A search of the Cambridge Structural Database (CSD, Version 5.37) <sup>[57]</sup> revealed (i) *dabco*-zinc metalloporphyrins are present as monomer/L type 1:1-M and tweezer/L type 1:1-Tw but there is no reported *dabco*-zinc metalloporphyrins as dimer/L type 2:1-D, (ii) reported structures of zinc metalloporphyrins with *pyz* ligand are monomers type 1:1-M, dimers type 2:1-D or six-coordinated monomers type 1:2-M, (iii) the reported *4,4'-bpy*-zinc porphyrin derivatives are dimer type 2:1-D, trimer type 3:2-D or polymers (type P), (iv) there is no *4,4'-mda* zinc metalloporphyrin reported in the literature.

The ORTEP drawings of 2-6 are illustrated by Figures 6-7. The X-ray molecular structure of 2 is a monomer type 1:1-M zincdabco species with the formula [Zn(TPBP)(dabco)].C<sub>6</sub>H<sub>5</sub>Cl while complex 3 is a dimer type 2:1-D zinc-dabco derivative with the formula  $[{Zn(TPBP)}_2(\mu_2 - dabco)].4(CH_2Cl_2).2(C_6H_{14}).$ For complex 2, the Zn(II) cation is chelated by four pyrrole N atoms of the porphyrinate anion and coordinated by nitrogen atom of the *dabco* axial ligand in a distorted square-pyramidal geometry. The dabco ligand in complex 3 links two [Zn(TPBP)] moieties leading to a 2:1-D dimer species. The Zn-N(dabco) bond lengths are very close (2.185 (2) Å and 2.182 (4) Å for 2 and 3 respectively) which are practically the same to the [Zn(OEP)(dabco)] (OEP = octaethylporphyrinate) with a Zn-N(dabco) distance of 2.182 (2) Å. [58] These values are quite different from those of zinc non-porphyrinic species (Table 4). Our pyrazine zinc porphyrin derivative (4) is six-coordinated with a Zn-N(pyz) distance of 2.459 (5) Å even though, in solution, this species is five-coordinated as discussed in the UV/Vis section. This value is considerably longer than those of the related pyz-zinc porphyrins (Zn-N(pyz ~ 2.000 Å) and those of pyz-zinc non-porphyrinic complexes where the Zn-N(pyz) distance values range between 2.014 (4) <sup>[59]</sup> and 2.118 (2) Å <sup>[60]</sup>. Nevertheless, the high Zn-N(pyz) distance of 4 is close to that of the 3-methoxypyrazine-zinc six-coordinated porphyrin species  $[Zn(TPP)(Me-pyz)_2]$  (MeO-pyz = 3-methoxypyrazine) with a Zn-N(Meo-pyz) distance of 2.467 Å (Table 4). Complex 5 is present in solid state as a dimer zinc metalloporphyrin type 2:1-D where the 4,4'-bpy ligand is the bridging ligand. The Zn-N(4,4'-bpy) bond length [2.178 (6) Å] is in the range [2.054 (4) - 2.270 (7) Å] of related species (Table 4). The 4,4'diamiadiphenylmethane zinc complex (6) is the first example of a zinc metalloporphyrin species presenting a 4,4'-mda axial ligand. This complex exhibits Zn-N(4,4'-mda) bond length value of 2.208 (5) Å which is quite longer than the related nonporphyrinic polymer complex  $\{[Zn(\mu_2-L)(\mu_2-4,4'-mda)]\}_n$  (L= 5carboxybenzene-1,3-dicarboxylato) (Table 4). The coordination geometries of 2-6 are reported as supplementary material (Figure SI-29). The Zn-Zn distances in the two 2:1-D dimers (3 and 5) are 6.9567 (11) Å for the *dabco* derivative and 11.323 (2) Å for the 4,4'-bpy species.



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Figure 6. ORTEP diagrams of complex 2 : (a), complex 3 : (b) and complex 4 : (c). Ellipsoids are drawn at the 50% for 2 and 40% for 3 and 4.



Figure 7. ORTEP diagrams of complex 5:(a) and complex 6:(b). Only one orientation of the disordered fragments is shown. Ellipsoids are drawn at the 40% for 5 and 30% for 6.

Formal diagrams of the porphyrinato cores of 2-6 showing the displacements of each atom from the mean plane of the 24atom porphyrin macrocycle in units of 0.01 Å are illustrated in Figure 8. The porphyrin macrocycle of the dabco-zinc monomer derivative (2) presents a major saddle and ruffling deformations and a moderate *doming* and *waving* distortions. The saddle deformation is due to the displacement of the pyrrole rings alternately above and below the mean porphyrin macrocycle so that the pyrrole nitrogen atoms are out of the mean plane. The *ruffling* distortion is indicated by the high values of the displacement of the meso-carbon atoms above and below the porphyrin mean plane. The doming deformation is originated by the displacement of the metal atom out of the mean plane and the nitrogen atoms are displaced toward the axial ligand. For the waving distortions, the four fragments "(β-carbon)-(α-carbon)-(meso-carbon)-(αcarbon)-(β-carbon)" are alternatively above and below the 24atoms of the  $C_{20}N_4$  least squares plane  $(\mathsf{P}_C \text{ plane})^{[87]}.$  The porphyrin core of the dabco-zinc dimer species (3) is less disordered than that of complex 2 with presents a moderate saddle, ruffling. doming and waving deformations. The pyrazine Zn(II) derivative (4), exhibits important ruffling, waving and saddle deformations of the porphyrin ring. The porphyrin cores of 5 and 6 are slightly disordered. It has been noticed that for five-coordinated metalloporphyrins, the average equatorial Metal-ion N(pyrrole) distance (M-Np) (M = metal ion) and the distance between the metal atom and the mean plane made by the 24-atom core of the porphyrin  $(M-P_c)$  are related <sup>[88]</sup> (Table 4). This is also true for our synthetic zinc porphyrins. Indeed, for the dabco derivatives (2 and 3), the Zn-Np and Zn-Pc values are very close: 2.078 (2) Å / 0.415 (1) Å and 2.075 (4) / 0.415 (1) Å respectively. The 4,4'-bpy and the 4,4'-mda derivatives (5 and 6) exhibit close Zn-Np / Zn-P<sub>c</sub> values which are 2.063 (6) Å / 0.329 (2) Å and 2.064 (4) Å / 0.331 (1) Å respectively. The sixcoordinated bis(pyrazine) zinc(II) derivative (4) presents the shortest Zn-Np distance value (2.027 (3) Å) and the Zn(II) ion is in the plane of porphyrin core as is the case for sixcoordinated metalloporphyrins. By the other hand, for fivecoordinated metalloporphyrins, a higher value of the Metal-Pc distance is an indication of a better tendency of coordination of an axial ligand to the central metal. Indeed, for the five-coordinated zinc-derivatives 2, 3, 5, 6 and 7 complexes, the Zn-Pc increase in the order : dabco (2-3) [0.415(1) Å] > 4,4'-mda (6) ~ 4,4'-bpy (5) [0.331(1) Å and]0.329(2) Å respectively] > 4-CNpy (7) [0.319(1) Å] species [55]. This indicates that the dabco ligand have the best coordination tendency to Zn(II) compared to the other aza ligands.

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Figure 8. Formal diagrams of the porphyrinato cores of complexes 2-6. The displacements of each atom from the 24-atom core plane in units of 0.01 Å are illustrated.

Table 4. Selected bond lengths [Å] and angles [°] for **2-6** and some *dabco*, *pyz*, *4,4'-bpy* and *4,4'-mda* complexes.

Complex	Type <sup>a</sup>	M—N <sub>p</sub> <sup>b</sup>	M-N <sup>c</sup>	M-Pc <sup>d</sup>	Ref
dab	co-porphyrii	n complexes			
[Co <sup>ll</sup> (OEP)( <i>dabco</i> )] <sup>e</sup>	1:1-M	1.996 (5)	2.292 (7)	0.284	[58]
[{Os(TTP)(CO)}2(µ2-dabco)]	2:1-D	2.056	2.353	0.093	[61]
$[{Ru(TTP)(CO)}_2(\mu_2-dabco)]$	2:1-D	2.059 (5)	2.343 (5)	0.069	[60]
[Zn(OEP)(dabco)]	1:1-M	2.091 (6)	2.182 (2)	0.572	[58]
$[Zn_2(\mu_2-P1)(\mu_2-dabco)]^{f}$	1:1-Tw	2.085	2.227	0.338	[62]
$[Zn(TPBP)(dabco)].C_6H_5CI(2)$	1:1-M	2.078 (2)	2.185(2)	0.4324(5)	this work
$[{Zn(TPBP)}_2(\mu_2 - dabco)]$					
.4(CH <sub>2</sub> Cl <sub>2</sub> ).2(C <sub>6</sub> H <sub>14</sub> ) (3)	2:1-D	2.075 (4)	2.182(4)	0.4151(1)	this work
dabo	co-Zn(II) no	n-porphyrinic	complexes		
[{Zn(L1)} <sub>2</sub> (µ <sub>2</sub> - <i>dabco</i> )] <sup>9</sup>	2 :1-D	-	2.0123 (3)	-	[63]
			2.123 (3)		
[Zn(L2)( <i>dabco</i> )] <sup>9</sup>	1:1-M	-	2.123 (3)	-	[64]
[{Zn(L3) <sub>4</sub> } <sub>2</sub> (µ <sub>2</sub> - <i>dabco</i> )] <sup>9</sup>	2:1-D	-	2.297 (5)	-	[65]
[ZnL4(dabco)]	1:1-M	-	2.117 (3)	-	[66]
			2.116 (3)		
{[{Zn( <i>Et</i> ) <sub>2</sub> }(µ <sub>2</sub> - <i>dabco</i> )]} <sub>n</sub>	Р	-	2.24 / 2.37*	-	[67]
pyz-	Zn(II) porpł	nyrin complexe	es		
[Zn(TPP)( <i>pyz</i> )]	1:1-M	2.062	2.210	0.282	[56]
[{Zn(TPP)} <sub>2</sub> (µ <sub>2</sub> - <i>pyz</i> )]	2:1-D	2.064 (2)	2.211 (2)	0.352	[68]
		2.057 (2)	2.179 (2)	0.339	
[Fe <sup>III</sup> (TPP)( <i>pyz</i> ) <sub>2</sub> ]	1:2-M	1.994 (3)	2.036 (2)	0.043	[69]
[Zn(TPP)( <i>MeO-pyz</i> ) <sub>2</sub> ] <sup>h</sup>	1:2-M	2.060	2.467	0.000	[56]
$[Zn_2(\mu_2-P2)(\mu_2-pyz)]^{l}$	2:1-D	2.065 (6)	2.190 (6)	0.190	[70]
		2.057 (5)	2.235 (6)	0.100	
$[Zn(TPBP)(pyz)_2].CHCl_3$ (4)	1:2-M	2.027 (3)	2.459(5)	0.012 (2)	this work
pyz-	non-porphy	rinic zinc com	plexes		
[{Zn(L5)(L6)} <sub>2</sub> (µ <sub>2</sub> - <i>pyz</i> )] <sup>9</sup>	2:1-D	-	2.118 (2)	-	[60]
[{Zn(L7)(L8)} <sub>2</sub> (µ <sub>2</sub> -pyz)] <sup>9</sup>	2:1-D	-	2.072 (3)	-	[71]
$[Zn_7(OAc)(O)(pyz)_2]^l$	1:1-M	-	2.072 (4)	-	[72]
{[{Zn(sac) <sub>2</sub> (H <sub>2</sub> O)} <sub>2</sub> (µ <sub>2</sub> -pyz)]} <sub>n</sub> <sup>k</sup>	Р	-	2.014	-	[59]
4,4'-	bpy porphy	rinic zinc com	plexes		
[{Zn(TOHPP)}2(µ2-4,4'-bpy)] <sup>l</sup>	2:1-D	2.032	2.134	0.306	[73]
		2.097	2.144	0.308	-

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[{Zn(OEP)} <sub>2</sub> (µ <sub>2</sub> -4,4'-bpy)]	2:1-D	2.080 (3)	2.173 (4)	0.517	[74]
[{Zn(TPP)} <sub>2</sub> (µ <sub>2</sub> -4,4'-bpy)]	2:1-D	2.081 (2)	2.169 (6)	0.327	[75]
		2.065 (1)	2.270 (7)	0.286	
{[Zn(TMP)(4,4'-bpy)]} <sub>n</sub>	Р	2.059	2.371	0.011	[76]
[{Zn(TPP)} <sub>3</sub> {µ <sub>2</sub> -4,4'-bpy)} <sub>2</sub> ]	3:2-T	2.049 (8)	2.185 (8)	-	[75]
		2.058	2.490		
[{Co <sup>II</sup> (TPP)} <sub>2</sub> (µ <sub>2</sub> -4,4'-bpy)]	2:1-D	1.985 (3)	2.223 (3)	0.138	[77]
{[{Co <sup>II</sup> (TPP) <sub>2</sub> (µ <sub>2</sub> -4,4'-bpy)]} <sub>n</sub>	Р	1.993	2.311	0.066	[78]
			2.342		
[{Zn(TPBP)} <sub>2</sub> (µ <sub>2</sub> -4,4-bpy)].					
3CHCl <sub>3</sub> (5)	2:1-D	2.063 (6)	2.178(6)	0.329 (2) thi	is work
4,4'-b	py non-porp	hyrinic zinc com	plexes		
[Zn(4,4'-bpy)(H <sub>2</sub> O) <sub>4</sub> ]	1:1-M	-	2.117	-	[79]
[{Zn(L9) <sub>2</sub> } <sub>2</sub> (µ <sub>2</sub> -4,4'-bpy)] <sup>9</sup>	2:1-D	-	2.085 (2)	-	[80]
[Zn(L10) <sub>2</sub> (4,4'-bpy) <sub>2</sub> ] <sup>9</sup>	1:1-M	-	2.054 (4)	-	[81]
		-	2.104 (4)		
$\{[\{Zn(NO_2)(H_2O)_2\}_2(4,4'-bpy)]\}_n$	Р	-	2.127	-	[82]
4.4-dr	na non-porp	ohyrinic zinc com	nplexes		
[Cd(OAc) <sub>2</sub> (4,4-dma) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>I</sup>	1:1-M	-	2.388	-	[83]
[Mn <sup>II</sup> Cl <sub>2</sub> (4,4-dma) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	1:1-M	-	2.293	-	[84]
[{Cu <sup>II</sup> Cl(L11)} <sub>2</sub> (µ <sub>2</sub> -4,4-dma) <sub>2</sub> ] <sup>9</sup>	2:1-D	-	2.023 (6)	-	[85]
		-	2.087 (5)	-	
{[Zn(µ2-L12)(µ <sub>2</sub> - <i>4,4-dma</i> )]} <sub>n</sub>	Р	-	2.035 (3)	-	[86]
			2.085 (3)		
[Zn(TPBP)(4,4-dma)] (6)	1:1-M	2.064 (4)	2.208 (5)	0.331 (1) this	s work

<sup>a</sup>: See Scheme 2. <sup>b</sup>: Average equatorial metal-nitrogen pyrrole distance. <sup>c</sup>: Distance between the metal and the nitrogen of the N-donor ligand. <sup>d</sup>: Distance between the metal atom and the mean plane made by the 24-atom core of the porphyrin (P<sub>c</sub>). <sup>e</sup>: OEP = octaethylporphyrinato. <sup>f</sup>:  $\mu_2$ -P1=  $\mu_2$ .1<sup>2</sup>,1<sup>8</sup>,1<sup>12</sup>,1<sup>18</sup>,8<sup>2</sup>,8<sup>8</sup>,8<sup>12</sup>,8<sup>18</sup>-octahexyl-13,17,113, 117,83.87,813,817-octamethyl-2,7,9,14(1,3) tetrabenzena-1,8(5,15)diporphyrina-4,5,11,12-tetrathiacyclotetradecaphane. g: Ln Ligands with L1 = (N,N-diethyl-dithiocarbamato-S,S'), L2 = acenaphthylene-1,2-dione bis(4-ethylthiosemicarbazonato). L3 = O,O'-di-isopropyl dithiophosphato-S,S'). L4 = bis(4-Allyl-3 thiosemicarbazonato) acenaphthenequinone. L5 = tri-t-butoxy silanethiolato-O,S. L6 = tri-t-butoxy silanethiolato-S, L7 = O,O'-di-isopropyl dithiophosphato-S,S'. L8 = O,O'-di. Isopropyldithiophosphato-S. L9 = 1,3-di-phenyl-1,3-propanedionato). L10 = hydrogenphthalate. L11 = chloro-malonic acid and L12 = 5-carboxybenzene-1,3-dicarboxylato. h: *MeO-pyz* methoxypyrazin. i:  $\mu_2$ -P2 =  $\mu_2$ -5,5'-(3,4,diethylpyrrol-2,5dyldimethylene)bis(2,3,7,8,12, 13,17,18-octaethylporphyrinate. j: OAc = acetate ligand.I:TOHPP=*meso*-tetrakis(4-hydroxyphenyl) porphyrinato. k: sac = saccharinato. \*:minimum / maximum of the six Zn-N(*dabco*)

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The conventional and non-conventional hydrogen bonds and the C–H<sup> $\dots$ </sup> $\pi$  intermolecular interactions of complexes **2-6** are listed in Table S-1 (supplementary materials). The crystal packing of **2** is stabilized by non-conventional C–H<sup> $\dots$ </sup>O and C–H<sup> $\dots$ </sup>N hydrogen bonds and by C–H<sup> $\dots$ </sup> $\pi$  intramolecular and intermolecular interactions involving pyrrole and phenyl rings of the porphyrins (supplementary information Table SI-3). Figure 9 illustrates the crystal packing of **2** shown that the chlorobenzene solvents occupy the voids between [Zn(TPBP)(*dabco*)] complexes. In Figure 10 is shown the contents of the unit cell for complex **3** where we can see that the disordered *dabco* axial ligand occupies the center and the summits of the cell. Within the crystal structure of **3**. The [Zn(TPBP)(*dabco*)] complexes are linked together via weak non-classical C–H<sup> $\dots$ </sup>O hydrogen bonds and by C–H<sup> $\dots</sup><math>\pi$ </sup> intermolecular interactions involving phenyl rings of the porphyrins (supplementary information Table SI-3).</sup>

The molecular structure of **4** shows the presence of non-classic C–H<sup>...</sup>O, C–H<sup>...</sup>N and C–H<sup>...</sup>Cl hydrogen bonds as well as C–H<sup>...</sup> $\pi$  intramolecular and intermolecular interactions (supplementary information Table SI-3). Notably, the chloroform solvents are weakly linked to four adjacent metalloporphyrins via C23–H23<sup>...</sup>Cl2 leading to three-dimensional framework (Figure 11). For complex **5**, the zinc-4,4'-bpy dimers with formula [{Zn(TPBP)}<sub>2</sub>( $\mu_2$ -4,4-bpy)] are linked together by weak C–H<sup>...</sup>O non-conventional hydrogen bonds and C–H<sup>...</sup> $\pi$  intermolecular interactions (supplementary information Table SI-3). The chloroform molecules are located near the 4,4'-bpy axial ligand inside the dimers (Figure 12).

A drawing showing the crystal packing of complex **6** along the [100] direction is illustrated by Figure 13. The [Zn(TPBP)(4,4'-mda)] complexes are linked together via weak non-classical C—H<sup> $\cdots$ </sup>O hydrogen bonds and by C—H<sup> $\cdots$ </sup> $\pi$  intermolecular interactions involving pyrrole and phenyl rings of the porphyrins (supplementary information Table SI-3). Noteworthy the presence of weak oxygen-oxygen non-contact interaction between the oxygens O8 of two adjacent metalloporphyrins (O8<sup> $\cdots$ </sup>O8 distance is 2. 919 Å). It is noteworthy that the crystal structures of **1-7** possess voids with different dimensions where are located the solvent molecules in the case of complexes **2-4** and **7**.



Figure 9.The crystal structure of **2** showing the chlorobenzene solvents occupying the voids between the [Zn(TPBP)(*dabco*)] molecules.



Figure 10. Projection along the [010] direction showing the contents of the unit cell for complex **3**.



Figure 11. Projection of the crystal lattice of **4** down the *a* axis. The disordered chloroform molecules (drawing in yellow) are located between the [Zn(TPBP)(*pyz*)] complexes.



Figure 12. A packing diagram of **5** showing the arrangement of the

[ $\{Zn(TPBP)\}_2(\mu_2-4,4-bpy)$ ] dimers and the chloroform molecules.



Figure 13. View down [100] showing the  $O^-H^{-}O$  hydrogen bonds linking adjacent [Zn(TPBP)(4,4'-mda)] complexes via the oxygen atoms of the TPBP porphyrinates.

#### CONCLUSION

We have successfully synthesized and characterized the new meso-porphyrin : tetrakis[4-(benzoyloxy)phenyl]porphyrin, the [Zn(TPBP)] starting material (1) and six zinc(II) species with this porphyrin where the central atom is coordinated to the dabco, pyz, 4,4'-bpy, 4,4'-mda and 4-CNpy aza ligands (complexes 2-7 respectively). The X-ray molecular structures of 2-6 show that the zinc(II)-dabco derivatives (2-3) are monomer type 1:1-M (for 2) and dimer type 2:1-D (for 3). Complex 4 is present in solid state as six-coordinated zinc(II)bis(pyrazine) species type 1:2-M. The zinc(II)-4,4'-bpy and the zinc(II)-4,4'-mda derivatives (5-6) in solid state are dimer type 2:1-D and monomer type 1:1-M respectively. The molecular structure of the [Zn(TPBP)(4,4'-mda)] is the first published structure of a zinc metalloporphyrin derivative with the 4,4'-mda ligand. The crystal structure of these metalloporphyrins show the presence of voids of different dimensions where are located the solvents in the case of complexes 2-4 and 7. The crystal packing of 2-6 are stabilized by weak C-H-O, C-H-N and C-H-Cl hydrogen bonds and by N–H<sup>...</sup>  $\pi$  and C–H<sup>...</sup> $\pi$  intermolecular interactions involving phenyl and pyrrole centroid rings. In solution, the UV/Vis and <sup>1</sup>H NMR spectroscopy show that 2-7 are fivecoordinated zinc(II) metalloporphyrins which is confirmed by UV/Vis titrations were the 4,4'-bpy zinc metalloporphyrin species presents the highest association constant (Kas) value while the 4,4'-mda and the pyz derivatives exhibit the smallest values of Kas. The photophysical properties of 1-7 are normal for zinc(II) metalloporphyrins. The cyclic voltammetry investigation on these species show similar voltammograms and that the half-wave potential values are close to those of the related  $[Zn(Porph)(L)]^{\pm m}$  species (Porph = mesoporphyrinato, L = neutral or anionic ligand and m = 0, -1). Nevertheless, a third reversible one-electron oxidation wave is shown for the H<sub>2</sub>TPBP free base and 1-7 which is not always the case for other meso-porphyrines and zinc metallporphyrins. The electrical propriety of 1-7 were tested using single-layer diode type [TIO/Zn-porphyrin/Al] devices

show relatively turn-on voltages between 0.33 and 0.70 V. These proprieties could be explained by the presence of voids in the crystal lattices of **1-7**.

#### Experimental

#### General

All solvents and reagents were purchased from commercial supplies and used without further purifications. <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic characterization were performed with a Bruker DPX 300 spectrometer. Chemical shifts are reported as  $\delta$  (parts per million), downfield from internal TMS. MALDI-TOF mass spectrometer (PerSeptive Biosystems, Framingham, MA, USA), equipped with a 337 nm pulsed nitrogen laser (20 Hz) and an Acqiris 2 GHz digitizer board, was used for all experiments. These spectra were obtained in the positive mode with the following settings: accelerating voltage 20 kV, grid voltage 62% of accelerating voltage, extraction delay time 100 ns. 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. All data were processed by using the Data Explorer software package (Applied Biosystems). Mass spectra were also recorded with a MicrOTOF Q Bruker instrument (ESI, positive and negative modes). The mass spectra of the H<sub>2</sub>TPBP and complexes 1-7 are reported as supplementary materials (Figures SI-21-28). Fourier-transformer IR spectra were recorded on a PerkinElmer Spectrum Two FT-IR spectrometer. UV/Vis spectra and titrations were recorded with a WinASPECT PLUS (validation for SPECORD PLUS version 4.2) scanning spectrophotometer. The emission spectra were recorded with a Horiba Scientific Fluoromax-4 spectrofluorometer with samples in dichloromethane at room temperature. The samples were placed in 1 cm path length quartz cuvettes. The luminescence lifetime measurements were performed after irradiation at  $\lambda$  = 400 nm obtained by the second harmonic of a titanium:sapphire laser (picosecond Tsunami Spectra Physics 3950-M1BB laser with a 39868-03 pulse picker doubler) at a 8 MHz repetition rate. A Fluotime 200 spectrometer from AMS technologies was used for the decay acquisition. It consists of a GaAs microchannel 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. The luminescence decays were analyzed with the FLUOFIT software from Picoguant. The emission guantum yields were determined at room temperature by the optically dilute method with samples in CH2CI2 solutions.[89] [Zn(TPP)] in air-equilibrated  $CH_2CI_2$  solution was used as a quanum yield standard ( $\phi = 0.033$ ).<sup>[36]</sup> The experimental uncertainties were as follows: absorption maxima, 2 nm; molar absorption, 20%; emission maxima, 5 nm; emission lifetimes, 10%; emission quantum yields, 20%. Electrochemical measurements were performed with an Voltalab PGZ 40. All experiments were performed with a conventional three-electrode system comprising a modified GCE working electrode (3 mm in diameter), a platinum wire auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. For the electrical experiments, single-layer devices were elaborated as sandwich structure between an aluminum (AI) cathode and an indium tin oxide (ITO) anode. The zinc metalloporphuyrins compounds solutions (3.10<sup>-</sup> <sup>2</sup> M in chloroform) were spin-coated onto ITO glass. A thin aluminum layer was deposited by thermal evaporation at 3.10<sup>-6</sup> Torr.

#### Synthesis Synthesis of the 4-formylphenylbenzoate

Benzoic acid (6 g, 0.049 mol.), 4-hydroxybenzaldehyde (6 g, 0,049 mol) and dimethylaminopyridin (DMAP) (0.6 g, 0.0049 mol.) were dissolved at 0 °C in 20 mL of dichloromethane. To this solution 10 g (0.040 mol.) dissolved in 30 mL of dichloromethane was added dropwise and stirred at 0 °C and then at room temperature for 12 h.

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Upon completion, the reaction mixture was filtered and the dichloromethane was removed by rotary evaporator. The solution was poured into water than the solid was filtered, washed with water than hexanes and dried under vacuum to afford 9.3 g yellow-pale powder (yield 86%), mp = 83 - 85°C,  $C_{14}H_{10}O_3 : C$  74.33, H 4.46%; found : C 74.81, H 4.35%. Spectroscopic analysis: <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$ (ppm) 10.04 (s, 1H), 8.17 (d, 2H, *J* = 6.2 Hz), 8.04 (d, 2H, *J* = 9.1 Hz), 7.80 (m, 1H), 7.64 (m, 2H), 7.56 (d, 2H, *J* = 8.9 Hz). <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>)  $\delta$ (ppm): 192.1 (C=O of CHO), 164.1 (C=O of ester),155.2, 134.3, 134.0, 131.1, 129.9, 129.0, 128.5, 122.9.

# Synthesis of the meso-tetrakis[4-(benzoyloxy)phenyl]porphyrin (H\_2TPBP)

In a 100 mL two-necked flask, 4-formylphenylbenzoate (4.5 g, 19.9 mmol) were dissolved in 50 mL of propionic acid. The solution was heated under reflex at 140 °C. Freshly distilled pyrrole (1.4 mL, 19.9 mmol) was then added dropwise and the mixture stirred for another 40 min. The mixture was cooled over night at 4 °C and filtered under vacuum. The crude product was purified using column chromatography (chloroform / petroleum ether = 4/1 as an eluent). A purple solid was obtained and tried under vacuum (1.18 g, yield 21%).  $C_{72}H_{46}N_4O_8$  : C 78.96 H 4.23, N 5.12 %; found : C 78.14, H 4.34, N 5.21 %. Spectroscopic analysis: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ(ppm) 8.97 (s, 8H, Hβ-pyrrol), 8.41 (d, 8H, J = 7.6 Hz), 8.32 (d, 8H, J = 8.3 Hz), 7.74 (t, J = 7.4, 4H), 7.65 (m, 16H), -2.74 (s, 2H, Hpyrrol). UV/vis  $(CHCl_3)$ ,  $\lambda_{max}$  (nm) ( $\epsilon$ .10<sup>-3</sup> L.mmol<sup>-1</sup>.cm<sup>-1</sup>) 420 (513), 516 (17), 552 (7), 591 (5), 646 (4). MS (ESI+, dichloromethane): m/z = 1095.16 [H<sub>2</sub>(TPBP)]<sup>+</sup>. FTR-IR cm<sup>-1</sup>: 3316 (NH porphyrin), 2960 (CH porphyrin), 1736 (C=O ester), 1263-1263 (C-O ester), 967 (δ<sub>CCH</sub> porphyrin).

Synthesis of the (meso-tetrakis[4-(benzoyloxy) phenyl] porphyrinato)zinc(II) complex [Zn(TPBP)] (1)



In a 100 mL one-necked round-bottomed flask, a mixture of the H<sub>2</sub>TPBP porphyrin (400 mg, 0.365 mmol) and Zn(OAc)<sub>2.2</sub>H<sub>2</sub>O (700 mg, 3.650 mmol) in a solution of CHCl<sub>3</sub> (30 mL) and CH<sub>3</sub>OH (5 mL) were stirred at room temperature overnight. The mixture was washed with water then the organic layer was dried over anhydrous MgSO<sub>4</sub> and concentrated. A light purple solid of the [Zn(TPBP)] complex was obtained (350 mg, yield 87.5%). C<sub>72</sub>H<sub>44</sub>N<sub>4</sub>O<sub>8</sub>Zn : C 74.64, H 3.83, N 4.84 %; found : C 74.81, H 3.94, N 4.98 %. Spectroscopic analysis: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ (ppm) 9.05 (s, 8H, Hβ-pyrrol), 8.41 (d, *J* = 6.3 Hz, 8H), 8.32 (d, *J* = 8.8 Hz, 8H), 7.73 (t, *J* = 9.0 Hz, 8H), 7.65 (m, 16H). UV/vis (CHCl<sub>3</sub>),  $\lambda_{max}$  (nm) (ε.10<sup>-3</sup> L.mmol<sup>-1</sup>.cm<sup>-1</sup>) 425 (546), 554 (25), 596 (9). MS (ESI-, dichloromethane): m/z = 1193.40

$$\label{eq:constraint} \begin{split} & [Zn(TPBP)CI]^{\text{T}}. \ FTR-IR \ cm^{-1}: \ 2960 \ (CH \ porphyrin), \ 1736 \ (C=O \ ester), \\ & 1264-1064 \ (C-O \ ester), \ 997 \ (\delta_{\text{CCH}} \ porphyrin). \end{split}$$

### Synthesis and crystallization of $[Zn(TPBP)(dabco)].C_6H_5CI (2),$ [ $\{Zn(TPBP)\}_2(\mu_2-dabco)] (3), [Zn(TPBP)(pyz)_2].CHCl_3 (4),$ [ $\{Zn(TPBP)\}_2(\mu_2-4,4'-bipy)].2CHCl_3 (5), [Zn(TPBP))(4,4'-diam)] (6) and [Zn(TPBP)(4-CNpy)].(4-CNpy) (7)$

Complex 1 (0.086 mmol) was mixed with 2.2 equiv of the bidentate ligand (*dabco, pyz, 4,4'-bpy, 4,4'-mda* and *4-CNpy*) (0.190 mmol) in 5 mL of the solvents (CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> or chlorobenzene). The reaction mixture was stirred at room temperature for 2 hours. Crystals of the desired complex were obtained by slow diffusion of n-hexane through the chloroform, dichloromethane or chlorobenzene solution.



Complex **2** :  $C_{84}H_{61}CIN_6O_8Zn$  : C 72.94, H 4.44, N 6.08 %; %; found : C 73.10, H 4.32, N 6.19%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ (ppm) : 8.93 (s, 8H), 8.40 (d, J = 9.1 Hz, 8H), 8.17 (d, J = 5.9 Hz, 8H), 7.75 (t, J = 6.2 Hz, 4H), 7.65 (m, 16H), 7.37 (m, 5H).  $\lambda_{max}$  (nm) ( $\epsilon$ .10<sup>-3</sup> L.mmol<sup>-1</sup>.cm<sup>-1</sup>) 433 (502), 564 (21), 604 (12). MS (ESI+, dichloromethane): m/z = 1270.40 [Zn(TPBP)(*dabco*)]<sup>+</sup>. FTR-IR cm<sup>-1</sup>: 2920 (CH porphyrin), 1735 (C=O ester), 1260-1060 (C-O ester), 992 ( $\delta_{CCH}$  porphyrin), 3030 (CH *dabco*).



Complex **3** :  $C_{166}H_{136}CI_{18}N_{10}O_{16}Zn_2$  : C 67.78, H 4.66, N 4.76 %; found : C 78.02, H 4.88, N 4.51%. <sup>1</sup>H NMR (300 MHz, CDCI<sub>3</sub>)  $\delta$ (ppm) : 8.92 (s, 8H), 8.40 (d, *J* = 8.2 Hz, 8H), 8.21 (d, *J* = 8.7 Hz, 8H), 7.72 (t, *J* = 8.9 Hz, 4H), 7.64 (m, 16H).  $\lambda_{max}$  (nm) ( $\epsilon$ .10<sup>-3</sup> L.mmol<sup>-1</sup>.cm<sup>-1</sup>) 431(485), 563(20), 604(12). MS (ESI+, dichloromethane): 1270,3

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 $[Zn(TPBP)(dabco)]^{+}$ . FTR-IR cm<sup>-1</sup>: 2921 (CH porphyrin), 1736 (C=O ester), 1258-1055 (C-O ester), 993 ( $\delta_{CCH}$  porphyrin), 3031 (CH dabco).



Complex **4** :  $C_{81}H_{53}CI_3N_8O_8Zn$  : C 67.65, H 3.71, N 7.79 %; found : C 68.02, H 3.90, N 7.59 %. <sup>1</sup>H NMR (300 MHz, CDCI<sub>3</sub>)  $\delta$ (ppm) : 9.01 (s, 8H), 8.40 (d, *J* = 8.3 Hz, 8H), 8.26 (d, *J* = 8.2 Hz, 8H), 7.73 (t, *J* = 6.1 Hz, 4H), 7.65 (m, 16H), 6.93 (s, 4H).  $\lambda_{max}$  (nm) ( $\epsilon$ .10<sup>-3</sup> L.mmol<sup>-1</sup>.cm<sup>-1</sup>) 430 (445), 561 (18), 601 (9). MS (MALDI-TOF(+), dichloromethane, with matrix): m/z = 1158.55 [Zn(TPBP)] <sup>+</sup> and m/z = 1238.27 [Zn(TPBP)(pyz)]<sup>+</sup>. FTR-IR cm<sup>-1</sup>: 2927 (CH porphyrin), 1734 (C=O ester), 12561-1058 (C-O ester), 994 ( $\delta_{CCH}$ porphyrin), 2990, 1416 1040 (*pyz* ligand).



Complex **5** ::  $C_{156}H_{98}Cl_6N_{10}O_{16}Zn_2$  : C 69.09, H 3.64, N 5.16 %; found : C 69.31, H 3.78, N 5.39%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ (ppm) : 8.97 (s, 8H), 8.67 (m, 4H), 8.40 (m, 8H), 8.25 (d, *J* = 7.2 Hz, 8H), 7.94 (d, *J* = 8.3 Hz, 4H), 7.73 (m, 4H), 7.62 (m, 16H), 6.62 (d, *J* = 5.1 Hz, 5H), 6.25 (m, 4H).  $A_{max}$  (nm) ( $\epsilon$ .10<sup>-3</sup> L.mmol<sup>-1</sup>.cm<sup>-1</sup>) 430 (483), 563 (20), 603 (12). MS (MALDI-TOF, dichloromethane, with matrix): m/z = 1158.55 [Zn(TPBP)]<sup>+</sup> and m/z = 1237.55 [Zn(TPBP)(py)]<sup>+</sup>. FTR-IR cm<sup>-1</sup>: 2925 (CH porphyrin), 1735 (C=O ester), 1257-1063 (C-O ester), 995 ( $\delta$ <sub>CCH</sub> porphyrin), 3063, 3034 and 1650 (*4*,*4*<sup>-</sup>*bpy* ligand).



Complex **6** :  $C_{85}H_{57}N_6O_8Zn$  : C 75.30, H 4.24, N 6.20%; found : C 75.61, H 4.31, N 6.39%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ (ppm) : 8.98 (s, 8H), 8.41 (d, *J* = 7.8 Hz, 8H), 8.27 (d, *J* = 8.2 Hz, 8H), 7.73 (t, *J* = 8.4 Hz, 4H), 7.70 (m, 16H), 6.75 (d, *J* = 8.2 Hz, 4H), 6.00 (d, *J* = 8.4 Hz, 4H), 3.64 (s, 2H), 2.63 (s, 2H). UV-vis (CHCl<sub>3</sub>),  $\lambda_{max}$  (nm) ( $\epsilon$ .10<sup>-3</sup> L.mmol<sup>-1</sup>.cm<sup>-1</sup>) 431 (544), 563 (27), 604 (18). MS (ESI+, dichloromethane): m/z = 1356.8 [Zn(TPBP)(*4*,*4'*-*mda*]]<sup>+</sup>. FTR-IR cm<sup>-1</sup>: 2920 (CH porphyrin), 1731 (C=O ester), 12562-1060 (C-O ester), 993 ( $\delta_{CCH}$  porphyrin), 3337, 3282, 1621 and 818 (*4*,*4'*- *mda* ligand) at 494 cm<sup>-1</sup> (v[Zn-N(*4*,*4'*-*bpy*]]).



Complex **7** :  $C_{84}H_{52}N_8O_8Zn$  : C 73.82, H 3.83, N 8.20 %; found : C 73.69, H 3.71, N 8.39%. <sup>1</sup>H NMR (300 MHz, CDCI<sub>3</sub>)  $\delta_H$ , (ppm) : 9.01(s, 8H), 8.75 (d, J = 9.1 Hz, 2H), 8.42 (d, J = 6.3 Hz, 8H), 8.28 (s, 8H), 7.96 (d, J = 8.9 Hz, 2H), 7.74 (t, J = 9.2 Hz, 4H), 7.65 (m, 16H), 6.85 (d, J = 6.3 Hz, 2H), 6.28 (s, 2H).  $\lambda_{max}$  (nm) ( $\epsilon$ .10<sup>-3</sup> L.mmol<sup>-1</sup>.cm<sup>-1</sup>) 430 (571), 561 (23), 601 (11). MS (ESI+, dichloromethane): m/z = 1262.66 [Zn(TPBP)(4-CNpy)]<sup>+</sup>. FTR-IR cm<sup>-1</sup>: 2966 (CH porphyrin), 1736 (C=O ester), 1061 (C-O ester), 996 ( $\delta_{CCH}$  porphyrin), 2238 (*4-CNpy* ligand).

#### Crystallography

The data collections for **2** and **5** were performed with a D8 VENTURE, Bruker, diffractometer, the data for **3** and **4** were measured with an APEXII, Bruker-AXS diffractometer while data for complex **6** were collected using an Eos KM4, Oxford Diffraction, diffractometer equipped with a graphite-monochromated Mo-K $\alpha$  radiation source ( $\lambda$  = 0.71073 Å). The intensity data for all compounds were collected by

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the narrow-frame method at low temperature for complexes 2-5 and at room temperature for complex 6. The unit-cell parameters were calculated and refined from the full data sets. The reflections were scaled and corrected for absorption effects by using SADABS program version 2.10 (Bruker AXS 2001) for complexes 2-5 [90] and SCALE3 ABSPACK in CrysAlis PRO program for complex 6 [91]. All structures were solved by direct methods using SIR-2004 program [48] and refined by full-matrix least-squares techniques on F<sup>2</sup> by using the SHELXL-97 program <sup>[92]</sup>. For 3, the *dabco* ligand is disordered on two positions (C96-C97-C98 and C99-C100-101) with equal occupancies (50%/50%) and one dichloromethane solvent is disordered in three positions (C74A-Cl3A-Cl4A, C74B-Cl3B-Cl4B and C74C-Cl3C-Cl4C) with occupancy factors 0.382(3), 0.445(3) and 0.174(3) respectively. The anisotropic displacement ellipsoids (ADP) of the disordered dichloromethane and the n-hexane are very elongated, which indicates that there is static disorder in the molecular structure of 3. For fragments involving these atoms, the DFIX, DANG and SIMU constraint commands in the SHELXL-97 software were used [93]. Complex 5 exhibits two disorder problems : the first, concerns one arm of the TPBP porphyrinate where the « O7A-C66A-O8A-C67A-C68A-C69A-C70A-C71A-C72A » and « O7B-C66B-O8B-C67B-C68B-C69B-C70B-C71B-C72B » fragments presents the occupancy factors 0.526(11) and 0.474(11) respectively. The second disordered of 5 concerns the chloroform molecule which presents four positions: « C78A-CI1-CI2-CI3 », « C78B-CI4-CI5-CI6 », « C78C-CI7-CI8-CI9 » and « C78D-Cl10-Cl11-Cl12» with occupancy factors of 0.426(3) 0.285(3), 0.151(3) and 0.137(3) respectively. For these disordered fragments, the ADP of these atoms are very elongated, which required the use of DFIX, DANG and SIMU constraint commands.

For complex **6**, the TPBP porphyrinate presents three disordered arms. One of them is completely disordered in two positions : « C21-C22-C23- the ester group: « C53-O6-C54-C55-C56-C57-C58-C59 » and « C53-O6-C54-C55-C56-C57-C58-C59 » with major position occupancy of 0.613(15). The ester group of a third arm of the TPBP moiety is also disordered in two positions: « C66-O8-C67-C68-C56-C69-C70-C71 » and « C66A-O8A-C67A-C68A-C56A-C69A-C70A-C71A» with refined occupancy coefficients converged to 0.732(8) for the major position. The ADP factors of these disordered fragments are very elongated which required the use of the DFIX, DANG, FLAT and SIMU constraint commands. All these disorders encountered during the refinements of the structure of **6** explain the huge number of restraints used. The crystallographic data, the structural refinement details and a selected bond lengths and angles for **2–6** are reported as supplementary

information (Tables SI-4(a,b) and Table SI-5).

CCDC-1473580-1473584 contain the supplementary crystallographic data of complexes **2-6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

**Supplementary information** (see footnote on the first page of this article):

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### **Table of Contents**

Key Topic\*: zinc porphyrin



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(benzoyloxy)phenyl]porphyrin (H<sub>2</sub>TPBP), the [Zn(TPBP)] starting material and the *dabco, pyz, 4,4'-bpy, 4,4'-mda* and *4-CNpy* zinc(II) complexes with the H<sub>2</sub>TPBP porphyrin are described. These species were characterized by spectroscopy, cyclic voltammetry and X-ray molecular structures. The electric properties of these derivatives were also described.

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