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Tetrakis((ethyl-4(4-butyryl)oxyphenyl)porphyrinato Zinc Complexes with 4,4'-bpyridin: Synthesis, Characterization, and its catalytic degradation of Calmagite

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Supporting information

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1. X-Ray

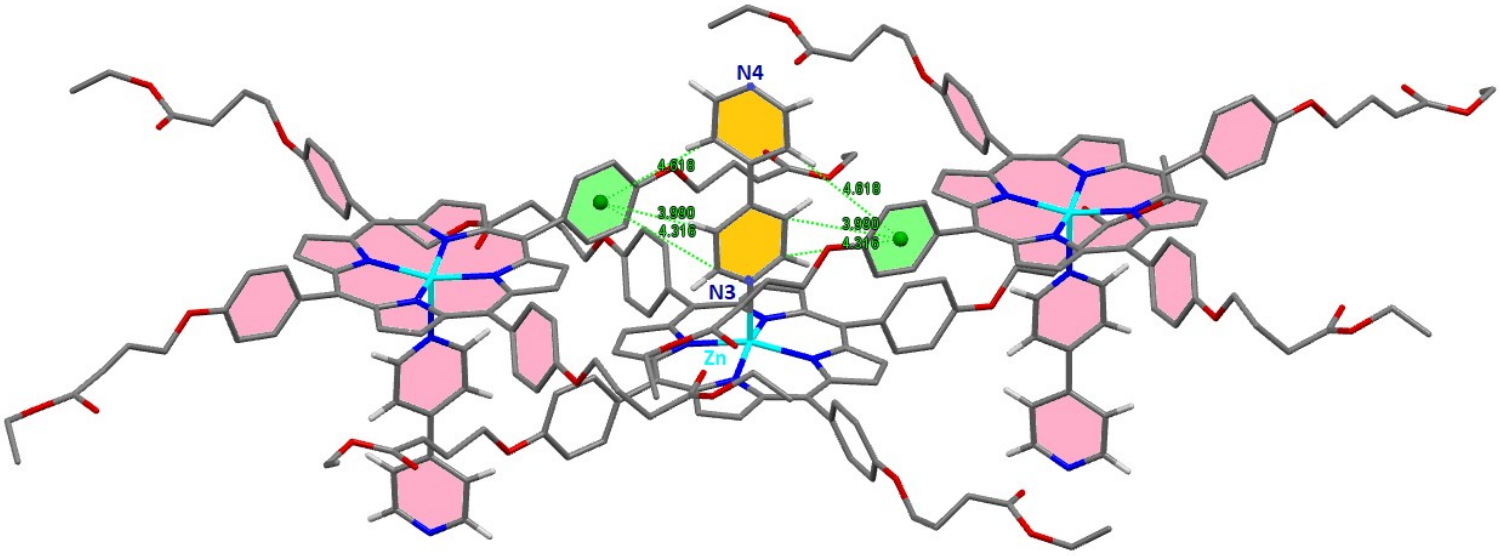

Figure S1. Schematic representation of the interactions involving the 4,4'-bipyridine axial ligand of complex **3**.

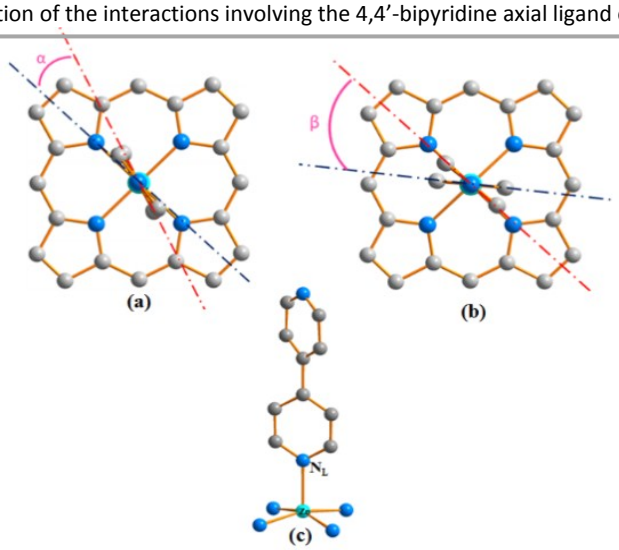

Figure S2. Drawings showing (**a**) : the α dihedral angle between the " Np-M-NL" plan (Np is the closeted pyrrole nitrogen atom) and the first pyridyl moiety of the 4,4'-bipyridine axial ligand, (**b**) : the β dihedral angle between the two pyridyl rings of the 4,4'-bipyridine and (**c**) : the coordination geometry of the Zn^{2+} cation in complex **3**.

Table S1. Crystal and refinement data of [Zn(TEBOP)(4,4'-bpy)] (**3**).

Parameters	**Complex 3**
Empirical formula	$C_{78}H_{76}N_6O_{12}Zn$
Formula weight	1354.87
Cryst. Sym	Monoclinic
Space group	C 2/c
a(Å)	25.890(5)
b(Å)	18.024(5)
c(Å)	18.699(5)
β (°)	127.821(5)
V (Å^3)	6893(3)
Z	4
Dcalc, (g/cm^3)	1.306
μ (mm^{-1})	0.424
Max./min. trans.	1.000/0.624
F(000)	2848
Crystal size (mm^3)	0.49 x 0.41x 0.27
T (K)	200(2)
Θ range (°)	2.55-26.37
Limiting indices	-32 ≤h ≤ 29, -21 ≤ k ≤ 22, -23 ≤ l ≤ 23
Reflec. collec/unique	46070/7020
Parameters	570
S [Goodness of fit]	1.119
R_1[a], wR_2 [Fo> 4σ(Fo)]	R_1 = 0.0798, wR_2 = 0.2129
R_1, wR_2[b] [all data]	R_1 = 0.1130, wR_2 =0.2634
Min./max. res. (eÅ^{-3})	0.956 and -0.875
CCDC	1060414

[a]: $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b]: $wR_2 = \left[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\right]^{1/2}$.

Table S2. Selected bond distances (Å) and angles (°) in the molecular structure s of [Zn(TEBOP)(4,4'-bpy)] (3).

Complex 3	
Zinc coordination polyhedron	
Zn–N1	2.057 (3)
Zn–N2	2.078 (3)
Zn–N3	2.152 (5)
N1—Zn—N2	88.62 (14)
N1—Zn—N3	97.69 (10)
N2—Zn—N3	99.73 (11)
4,4'-bipyridine ligand	
N3– C38	1.324 (6)
C38–C39	1.387 (7)
C39–C40	1.377 (7)
C40–C41	1.517 (11)
C41–C42	1.394 (10)
C42–C43	1.382 (11)
N4–C43	1.344 (12)

Table S3. Selected bond lengths (Å) and angles (°) for **3**, and some 4,4'-bipyridine porphyrinic and non-porphyrinic complexes.

Complexes	M—N_p[a]	Zn—N_L[b]	α (°)	β(°)	Ref.
		Zn-(4,4'-bpy) porphyrin complexes			
[Zn(TEBOP)(4,4'-bpy)] (**3**)	2.0675(3)	2.151(2)	37	36	Current work
$[Zn(TOHP)_2(4,4'\text{-bpy})]$[c]	2.041	2.134	3	1	[1]
	2.030	2.144			
$[Zn(TPP)_3(4,4'\text{-bpy})_2]$	2.049(8)	2.185(8)	23	24	[2]
	2.055	2.490	4		
$[Zn(TPP)_2(4,4'\text{-bpy})]$	2.065	2.169(6)	5	38	[2]
	2.081	2.270(7)	7	46	
		M-(4,4'-bpy) porphyrin complexes (M = Co, Fe)			
[Co(TPP)(4,4'-bpy)]	1.993	2.342	12	38	[3]
$\{[Co(TpivPP)(4,4\text{-bpy})_2]\}_n$[d]	1.984[e]	2.312[e,f]	19	38	[3]
	1.976[e]	2.311[e,f]	23	35	
[Fe(TPP)(bpy)]	1.990	1.985	33	30	[4]
		Zn-(4,4'-bpy) non-porphyrinc complexes			
$[Zn(4,4'\text{-bpy})_2(H_2O)_4](ClO_4)_2.(4,4'\text{-bpy})$	-	2.117(2)	-	2	[5]
$\{[Zn(\mu_2\text{-}4,4'\text{-bpy})(\mu_4\text{-BPTC})\}_n$[g]	-	2.044	-	0	[6]
$\{[Zn(\mu_2\text{-}4,4'\text{-bpy})_2(\mu\text{-FA})_2]\}_n$[h]	-	2.114[i]	-	48	[7]

[a] : Average equatorial zinc–nitrogen pyrrole distance.
[b] :N-coordinated zinc atom of the axial ligand L
[c] :TOHPP = 5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrinato.
[d] : TpivPP = *meso*-4-tetrapivalamidophenylporphyrinato.
[e]: The asymmrtic unit contains two $[Co(TpivPP)(4,4'\text{-bpy})_2]$ molecules.
[f] : Average values of the two Co—N(bpy) distances.
[g] : BPTC = biphenyl-3,3',5,5'-tetracarboxylato.
[h] : FA = format-O (CH_2O_2).
[i] :Average values of the two Zn__N(bpy) distances.

Table S4. Selected hydrogen bonds and intermolecular C–H...Cg π interactions of complex [Zn(TEBOP)(4,4'-bpy)] (3)

D[a]–H···A[b]	Symmetry of A	D···A (Å)	D –H···A (°)
C19–H19B···O1	x, y, z	2.825(11)	106
C21–H21b···O2	x, y, z	2.57(2)	103
C33A–H33B···O5A	x, y, z	2.85(5)	104
C37A–H37C···O5A	x, y, z	2.95(5)	113
C37A–H37C···O2	−x, y, −z+1/2	3.40(4)	139
C43–H43···O5A	−x+1/2,y+1/2, −z+3/2	3.37(3)	140
C15—H15···Cg1	x+3/2, y+1/2, z+1	3.503(5)	138
C18—H18A···Cg9	x+3/2, y+1/2, z+1	3.80(11)	170
C18—H18B···Cg2	−x+1/2, y+1/2, −z−1/	3.773(9)	138
C32A—H32A···Cg7	−x+1/2, −y+1/2, −z+1	3.543(11)	135
C32A—H32A···Cg7	x−1/2, −y+1/2, z−3/2	3.543(11)	135
C25B—H25B···Cg2	−x+1/2, −y+1/2, −z+1	3.34(2)	145
C37B—H37D···Cg9	−x, y, −z+1/2	3.82(3)	143

[a]: D = donor atom.
[b]: A = acceptor atom.
Complex **3**: Cg1, Cg2, Cg7 and Cg9 are the centroids of the N1-C1/C4, N2-C6/C9, N3-C38-C39-C40-C38A-C39A-C40A, C11/C16 rings respectively.

2. ^{1}H NMR

2.1. ^{1}H NMR Spectra of ethyl-4(4-butyryl)oxyphenylaldehyde

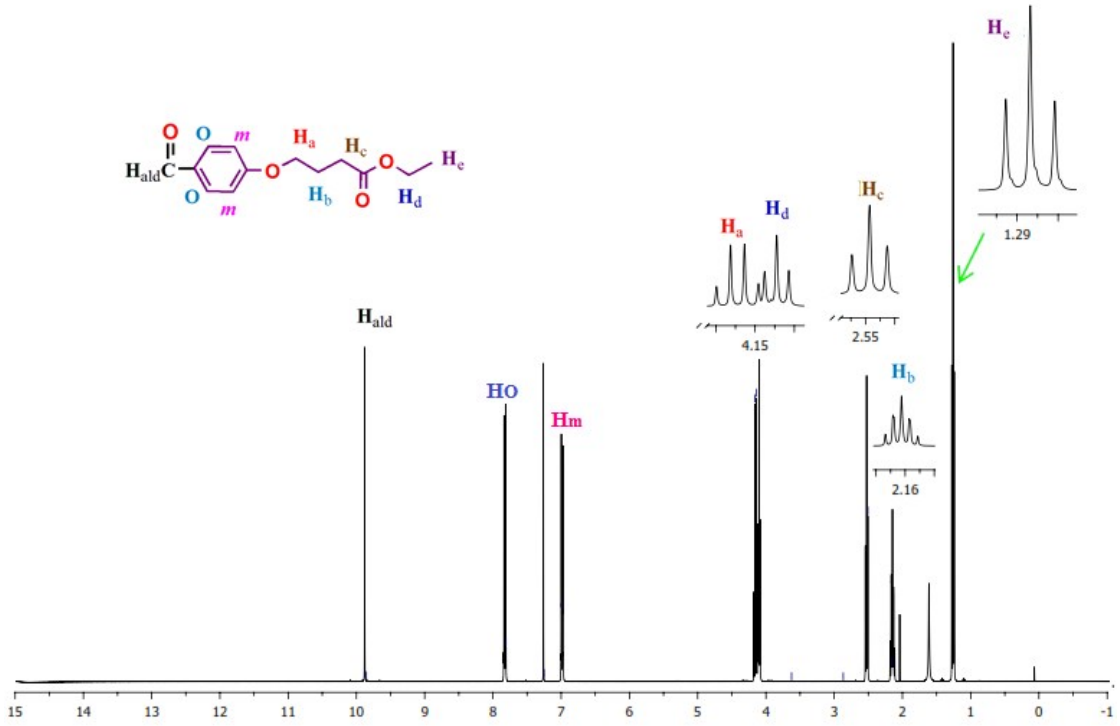

Figure S3. ^{1}H NMR spectrum of ethyl-4(4-butyryl)oxyphenylaldehyde in $CDCl_3$.

2.1. ^{1}H NMR Spectra of compound (3)

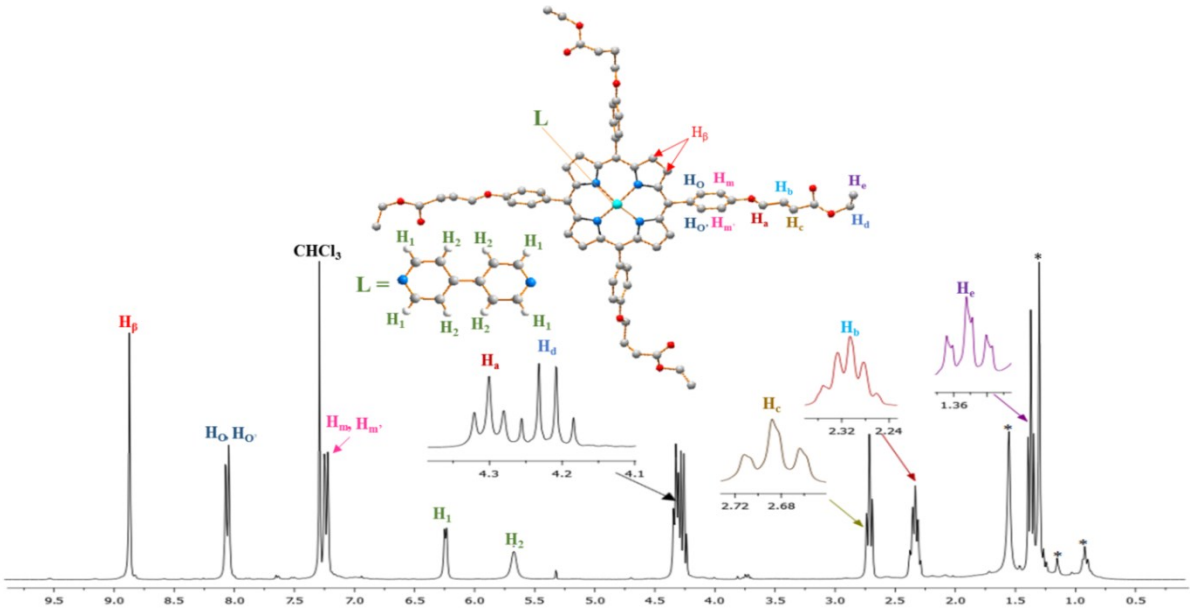

Figure S4. ^{1}H NMR spectrum of **complex 3** in $CDCl_3$

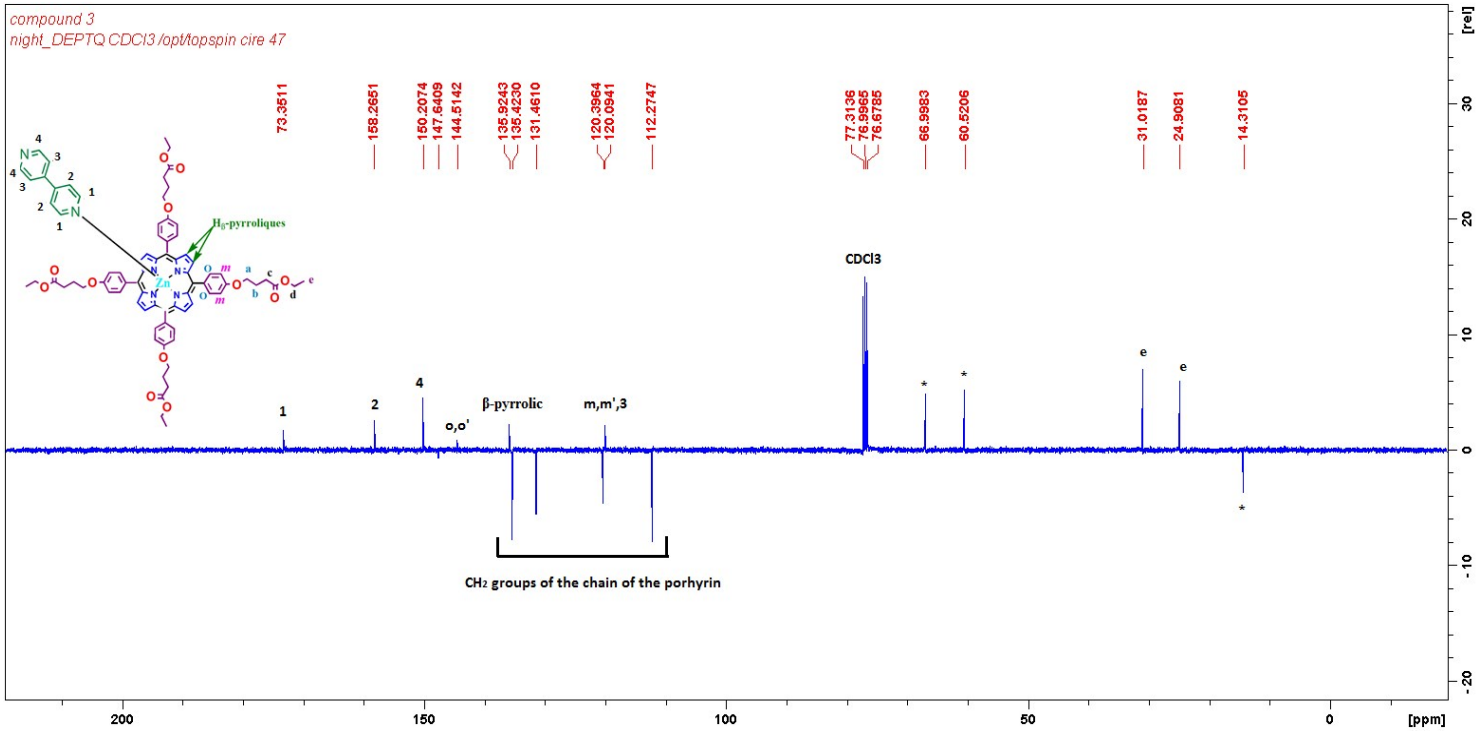

Figure S5. ^{13}C DEPT spectrum of **complex 3** in $CDCl_3$

Table S5. Electrochemical data for complex 3 and a selection of related zinc metalloporphyrins in dichloromethane (exceptions are indicated).

	Ring oxidations									Ring reductions						Ref
	1st oxidation (O1, R1)			2nd oxidation (O2, R2)			3th oxidation (O3, R3)			1st reduction			2nd reduction			
	E_{pa}[b]	E_{pc}[c]	$E_{1/2}$[d]	E_{pa}	E_{pc}	$E_{1/2}$	E_{pa}	E_{pa}	$E_{1/2}$	E_{pc}	E_{pa}	$E_{1/2}$	E_{pc}	E_{pa}	$E_{1/2}$	
H_2TPP	-	-	1.02	-	-	1.26	-	-	-	-	-	-1.20	-	-	-1.55	**[8]**
H_2TPP	-	-	1.08	-	-	1.35	-	-	-	-	-	-1.21	-	-	-	**[9]**
H_2TTP[e]	-	-	0.62	-	-	-	-	-	-	-	-	-1.12	-	-	-1.54	**[10]**
H_2TEBOP (**1**)	-	-	0.96	-	-	1.13	-	-	-	-	-	-1.26	-	-	-1.60	this work
[Zn(TPP)]	-	-	0.84*	-	-	1.13*	-	-	-	-	-	-1.31*	-	-	-1.75 *	**[11]**
[Zn(TEBOP)] (**2**)	-	-	0.64	-	-	0.94	-	-	-	-	-	-1.42	-	-	-	this work
[Zn(TDCPP)]	-	-	1.06	-	-	1.36	-	-	-	-	-	-1.20	-	-	-1.68 *	**[11]**
[Zn(TPFPP)][f]	-	-	1.37	-	-	1.58	-	-	-	-	-	-0.95	-	-	-1.37	**[11]**
[Zn(TEBOP)(4,4'-bpy)] (**3**)	0.68	0.61	0.64	0.98	0.90	0.94	1.41	1.25	1.33	-1.50	-1.42	-1.46	-	-	-	this work
[Zn(TPP)(HIm)]	-	-	0.70*	-	-	1.40*	-	-	-	-	-	-1.40*	-	-	-1.75 *	**[11]**
[Zn(TPP)(2-Meim)]	-	-	0.71*	-	-	1.37*	-	-	-	-	-	-1.45*	-	-	-1.75 *	**[11]**
[Zn(TMP)(HIm)]	-	-	0.63*	-	-	1.26*	-	-	-	-	-	-1.55*	-	-	-	**[11]**
[Zn(TPP)(2-Meim)]	-	-	0.63*	-	-	1.23*	-	-	-	-	-	-1.60*	-	-	-	**[11]**

[a] :The potentials are reported versus SCE.
[b] : Epa = anodic peak potential.
[c] : Epc = cathodic peak potential.
[d] : $E_{1/2}$ = half wave potential.
[e] : in THF.
[f]: TPFPP : is the dianion of the tetrapentafluorophenylporphyrin.
* : Irreversible wave.

Notes and references

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