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RESEARCH ARTICLE

PREPARATION, VIBRATIONAL AND ELECTRONIC STUDIES OF HEXACOORDINATED COMPLEXES OF IRON OCTOCARBOXYPHthalOCYANINE WITH PYRIDINE AXIAL LIGANDS AND SUBSTITUTED PYRIDINES, PHOSPHINE AND PHOSPHITES

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ABSTRACT

Iron phthalocyanine (FePc), iron octocarbonylphthalocyanine [(COOH)₈FePc] and their complexes carrying axial ligands were prepared and studied by vibrational and optical spectrometry. The ligands used are: pyridine and its derivatives 3-Rpyridine (with R = CH₃, OH, Cl and OHCH₂), 4-Rpyridine (with R = CH₃, OH, CN and SH), phosphites and phosphine P(OPh)₃, P(OMe)₃, HOP(OEt)₂ and PPh₃. Analysis of the infrared spectra made it possible to highlight, in the spectra of the complexes, new bands of vibration were attributed to the axial ligands; which reflects the fact that the expected reactions have been realized. In optical spectrometry, inter and intramolecular interactions are reflected in the spectra of octasubstituted compounds by a dominant electron-donor effect. The introduction of axial ligands results to major modifications: the appearance of new transition bands absent in the FePc and (COOH)₈FePc spectra and a significant decrease in the electron-donor effect of the COOH groups.

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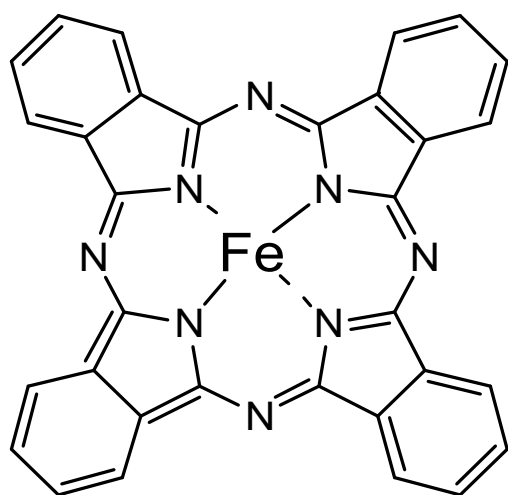
INTRODUCTION

Metallophthalocyanines possess particular properties that come largely from the high electron density due to having a system of eighteen π electrons delocalized over the entire molecule. This high electronic density adds a remarkable thermal and chemical stability. These properties are at the origin of the use of these complexes in the manufacture of paints and lithium batteries, in catalysis and in information storage (Sakamoto *et al.*, 2009; Shun-ichiro *et al.*, 2006). They are also studied for applications in photovoltaics (Lane *et al.*, 2000), in nanoelectronics (Tolbin *et al.*, 2008), in optoelectronics (Quintiliani *et al.*, 2005) and in medicine (Qiu *et al.*, 2009). In addition, phthalocyanine complexes are prominent in supramolecular chemistry whose development is concerned with the storage of information at the molecular level, its re-reading, transfer and transcription at the supramolecular level (Lahmani, 2006). Complexes of iron phthalocyanine have been the subject of many studies and are justified by the interest in iron complexes in general, because of their physical and chemical properties (catalysis, luminescence, redox properties etc).

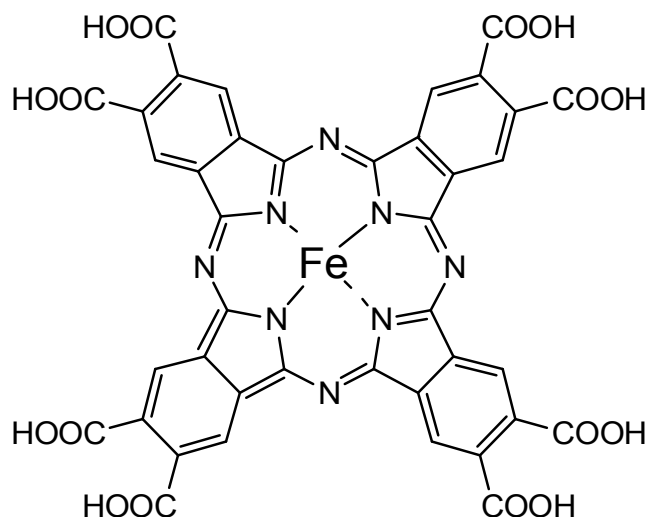
Iron phthalocyanine is likely to accept any donor heteroelement (S, N, O, ...) in the apical position. One of the essential characteristics of these complexes is their very wide range of stability, depending on the type of apical ligand (Zanguina *et al.*, 2002). The structural similarities of phthalocyanines and porphyrins with hemes caused researchers to investigate the reactivity of phthalocyanines having molecules with a free electron pair. The ligands generally used are amines, thiols, phosphines, phosphites, pyridine and substituted pyridines, nitrogen monoxide, chlorine (Kadish, 2003) etc. Thus, depending on the nature of the axial ligand used, the optical spectra of the hexacoordinated iron phthalocyanine complexes presents new bands of transitions attributable to metal-ligand charge transfer or ligand-metal charge transfer. The elucidation of the structure in order to explain the properties, especially the electronic conduction of the derived molecular solids, is the subject of numerous published works. On the other hand, there is very little work that explains whether the electron flux transits through the π system in only axial ligands or if the equatorial ligands are also involved (Metz *et al.*, 1984). The present work has introduced two factors that can modulate the electronic structure of FePc; the first factor being the introduction of equatorial substituents and the second being the attachment of axial ligands.

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Iron phthalocyanine



Iron octacarboxyphthalocyanine

Figure 1. Iron phthalocyanine (FePc) and Iron octacarboxyphthalocyanine ((COOH)₈FePc)

Indeed, we know that the possibility of changing the central metal, to make equatorial or axial substitutions can modulate the electronic properties of the macrocycle (Bawa *et al.*, 2017). We therefore propose to prepare and study, through the use of vibrational and electronic spectrometers, a series of complexes of Iron octacarboxyphthalocyanine and bearing in axial position two series of ligands: pyridine and its derivatives [3-Rpyridine (with R = CH₃, OH, Cl and OHCH₂), 4-Rpyridine (with R = CH₃, OH, CN and SH)], phosphine and phosphites [PPh₃, P(OPh)₃, P(OMe)₃ and HOP(OEt)₂]. The exploitation of our results could be an important contribution to the elucidation of the electronic structure of these complexes.

Experimental part

Preparation of the compounds.

Preparation of iron phthalocyanine.

FePc was prepared and purified as described in a previous work (Zanguina *et al.*, 2002).

Preparation of iron phthalocyanine complexes carrying axial ligands.

Complexes carrying the following ligands Py, 3MePy, 4MePy, 3HOCH₂Py

The complexes carrying the pyridine ligands Py and the substituted pyridines 3MePy, 4MePy, 3HOCH₂Py were obtained after refluxing in acetonitrile 20 mg (3.52x10⁻⁵mol) of FePc and an excess of the corresponding ligand. After three hours of heating, a green product was isolated and washed with ethanol.

Complexes carrying ligands 4HOPy, 3HOPy, 3ClPy and 4SHPy

When the ligands are 4HOPy, 3HOPy, 3ClPy and 4SHPy, the mixture of 20 mg (3.52x10⁻⁵mol) of FePc and the corresponding excess ligand in acetonitrile are refluxed for fifteen hours. After filtration, the isolated solid is washed with distilled water and then with petroleum ether for complexes carrying the 4HOPy and 3HOPy ligands and with ethanol for the complexes bearing the 3ClPy and 4SHPy ligands.

Complex carrying the 4CNPy ligand

The reaction product of FePc with the 4CNPy ligand was obtained by contacting the two compounds, 20 mg (3.52x10⁻⁵mol) of FePc and an excess of 4CNPy, in benzene. The mixture was refluxed for four days. The isolated solid was washed with ethanol and then dried.

Preparation of ((COOH)₈FePc

We prepared and purified ((COOH)₈FePc as described in the literature (Sakamoto K. *et al.*, 2009). *Preparation of Iron octacarboxyphthalocyanine complexes with axial ligands of pyridine and its derivatives.* In a single-necked flask of 100 cm³, 1 mg (1.1 × 10⁻⁵mol) of ((COOH)₈FePc and an excess of the corresponding ligand were successively introduced. The mixture was refluxed in the appropriate solvent; all the syntheses were done under the same conditions as before and the products were all isolated in solid form.

Preparation of iron octacarboxyphthalocyanine complexes carrying axial ligands of phosphine and phosphite
Complexes carrying the ligands PPh₃, P(OPh)₃ and HOP(OEt)₂

Mixtures of 15 mg (1.63x10⁻⁵mol) of ((COOH)₈FePc and 20 mg (7.63x10⁻⁵mol) of PPh₃, 0.5 mL (17x10⁻⁵mol) P(OPh)₃ or 0.5 mL (37x10⁻⁵mol) HOP(OEt)₂ in 5 mL of DMSO were respectively heated at 70°C with shaking for ten hours. After cooling, the products obtained were precipitated in dichloromethane. They were then filtered and washed extensively with ethanol and dried under P₂O₅.

Complex with the ligand P(OMe)₃

Stirring was done in 5 mL of DMSO at 70°C, a mixture of 0.5 mL (40x10⁻⁵mol) P(OMe)₃ and of 15 mg (1.63x10⁻⁵mol) of ((COOH)₈FePc. The heating lasted for one hour and thirty minutes. After cooling, the product obtained was precipitated in dichloromethane. It was then filtered and washed extensively with ethanol and dried under P₂O₅.

Table I: Vibration frequencies of the remarkable bands of (COOH)₆FePc in the 400 and 4000 cm⁻¹ range.

(COOH) ₆ FePc	430 l	482 m	501 m	543 m	581 m	627 m	662m	676 m	732 m	749 s	799 s
corresponding (COOH) ₆ FePc	Φ _{C-C} deformation of the macrocycle										
corresponding (COOH) ₆ FePc	918 s	1000 vs	1090vs	1143 l	1163 l	1180 l	1233 s	1268s	1317m	1369m	1437m
corresponding (COOH) ₆ FePc	M-N	β _{C-H}				V _{C-O}		V _{C-N}			
corresponding (COOH) ₆ FePc	1450m	1516m	1586 s	1628m	1703 vs	2500-3500w					
corresponding (COOH) ₆ FePc	V _{C-C}				V _{C=O}		V _{O-H}				

Legende: vs = very strong, s = strong, m = medium, l = low, w = wide.

Table II. Vibration frequencies of the remarkable bands of the complexes bearing the pyridine and substituted pyridine ligands in the 400 and 4000 cm⁻¹ range

Py	4CNPy	3CIPy	3HOCH ₂ Py	3MePy	4MePy	3HOPy	4HOPy	4SHPy	corresponding
431 l	433 m	430 l	446 l	437 l	438 l	430 l	445 l	417 l	Φ _{C-C} deformation of the macrocycle
458 m		469 m			469 l			457	
			489 l	481 l		482 l	481 l		
501 m	501 l	502 m	502 m	495 m	449 m	497 m		498 m	
547 m	538 m	546 m	537 m	546 m	546 m	544 m	538 m	541 m	
	600 l	598 l	599 m	599 m		598 m	593 m	597 m	
632 s	632 s	634 s	630 s	632 s	634 s	628 s	640 s	638 s	
			667 s		667 s			667 s	
						675 s			
688-697 s	695 m	689 s	681 s	693 m	694 s		688 s		
734 s	733 vs	734 vs	734 vs	734 s	733 vs	734 vs	729 vs	732 vs	V _{C-H}
750 l	750 s	750 s	748 s	750 m	751 m	747 m	742 m		
801 l	800 m	800 m	799 s	800 s	799 s	799 s	806 m	800 m	γ _{C-H}
825 m	826 m	835 m	826 m	831 m	826 m	850 m			
921 s	923 s	917 s	924 s	917 s	923 s	923 m	923 m	915 m	M-N
1008 s	1000 s	1013 s	1006 m	1000 m	1008 s	1005 vs		1000 s	
1090 s	1088 vs	1090 s	1088 vs	1090 vs	1087 vs	1087 vs	1066 vs 1109 m	1067-1092 s	β _{C-H}
1150 m	1155 m	1151 m	1142 s	1153 s	1147 s	1137 s		1133 s	β _{C-H}
-							1199 m		
1237 m	1242 m	1237 m	1238 m	1236 m	1235 m	1231 m		1233 m	V _{C=O}

Legende: vs = verystrong, s = strong, m = medium, l = low

Table II. Vibration frequencies of the remarkable bands of the complexes bearing the pyridine and substituted pyridine ligands in the 400 and 4000 cm⁻¹ range (continued)

Py	4CNPy	3CIPy	3HOCH ₂ Py	3MePy	4MePy	3HOPy	4HOPy	4SHPy	corresponding
1272 s	1270 s	1273 vs	1268 s	1272 m	1272 s	1272 s	1272 l	1263 s	V _{C-N}
1319 m	1316 m	1319 m	1319 m	1320 s	1318 m	1313 m	1311 vs	1313 vs	
1374 m	1369 m	1383 vs	1361 m	1373 m	1369 m	1362 m	1378 s	1361 s	
1452 s	1450 s	1453 s	1448 l 1472 l	1452 s	1453 s	1449 s			V _{C-C}
1498 m							1506 s		
1516 m	1516 m	1517 s	1516 s	1516 s	1516 s	1515 s		1515 m	
1583 m	1586 m	1585 m	1569 s	1585 s	1584 s	1572 s			
	1635 l	1633 m	1637 m	1636 m		1626 m	1621 m	1625 m	
1705 vs	1704 vs	1707 vs	1705 m	1704 m	1705 s	1705 vs	1706 vs	1704 vs	V _{C=O}
2500- 3500 w	2500-3500 w	2500-3500 w	2500- 3500 w	2500- 3500 w	2500- 3500 w	2500- 3500 w	2500- 3500 w	2500- 3500 w	V _{O-H}

Legende: vs = very strong, s = strong, m = medium, l = low, w = wide

Equipment

Infrared absorptionspectrometry:

The IR spectra were recorded in the range of 400 to 4000 cm⁻¹, using a Bruker TENSOR 27, ATR diamond-type spectrometer.

Optical absorptionspectrometry

The UV-visible spectra were recorded using a spectrometer of the type 190 DES Double Energy System in the range 300 and 900 nm from compounds dissolved in dimethylsulfoxide (DMSO) and benzene in the presence of an excess of ligand and for compounds carrying axial ligands.

RESULTS AND DISCUSSION

Infrared absorption spectrometry

Complexes carrying the pyridine axial ligands and its derivatives: In general, the binding of the pyridine and pyridine ligands substituted on (COOH)₆FePc is reflected in the infrared spectra by the appearance of new vibration bands, as well as the disappearance and the variation of the relative intensities of some of them. The most remarkable bands are grouped in Table II. On the whole, it can be seen that the frequencies of the characteristic bands of the macrocycle phthalocyanine (Pc) are little modified despite the fixation of the axial ligands. This shows the high stability of the C-C, C-N and C = N bonds of the macrocycle phthalocyanine (Bawa A. S. *et al.*, 2017).

Table III Remarkable vibration bands of the phosphite and phosphine complexes of $(\text{COOH})_8\text{FePc}$ between 400 and 4000 cm^{-1}

$(\text{COOH})_8\text{FePc}$	$\text{P}(\text{OMe})_3$	$\text{P}(\text{OPh})_3$	$\text{OHP}(\text{OEt})_2$	$\text{P}(\text{PPh})_3$	corresponding
430 l	429 f	425 m	428 s	420 m	$\Phi_{\text{C-C}}$ deformation of the macrocycle
	468 m		473 m	472 l	
482 m	486 f	491 m	484 m		
501 m	502 f		498 s		
543 m	548 m	540 m	539 s	539 s	
581 m	584 m	583 f			
	593 f	593 m	592 s	592 m	
627m	628 m	634 m			
			640 s	643 m	
662 m	665 m				
676 m		679 m			
	695 m		691 m	699 l	
732 vs	732 vs	730 vs	731 vs	734 vs	$\nu_{\text{C-H}}$
749 s	749 s				
	766 sh	772 l	775 l		$\delta(\text{P-O-C})$
799 s	799 s	799 m	800 m	800 m	
			880 l	885 l	$\gamma_{\text{C-H}}$
918 s	919 s	913 s	931 s	930 m	M-N
1000 s	1000 s	1000 s	1006 s	1000 s	
		1066 vs	1067 vs		
1090 vs	1087 vs	1091 s	1097 s	1091 s	
1143 l		1135 m	1133 m	1137 m	$\beta_{\text{C-H}}$ $\delta(\text{P-Ph})$
				1163 sh	
1180 l			1210 l	1208 l	
1233 s	1239 s	1237 l	1234 l	1240 l	$\nu_{\text{C-O}}$
1268 s	1267 s	1262 s	1273 m	1276 m	
1317 m	1314 m	1313 s	1314 vs		$\nu_{\text{C-N}}$
1369 m	1369 m	1362 m	1379 m		
1437 m	1443 m		1435 m	1430 m	
1450 m		1454 m			$\nu_{\text{C-C}}$
1516 m	1515 m	1514 s	1514 s	1517 s	
1586 s	1582 s	1584 m			
1628 m	1630 m	1634 l	1629 l	1622 s	
1703 vs	1701 vs	1703 vs	1704 vs	1705 vs	$\nu_{\text{C=O}}$ $\nu_{\text{O-H}}$
2500-3500 w	2500-3500 w	2500-3500 w	2500-3500 w	2500-3500 w	

Legende: vs = very strong s = strong, m = medium, l = low, sh = shoulder, w = wide.

Table IV. Maximum absorption wavelengths of UV-visible spectra of FePc solutions and FePc reaction compounds with pyridine and its derivatives in DMSO

Compounds	$\pi \rightarrow \pi^*$	$\text{Fe} \rightarrow$	L_{ax}	$L_{\text{ax}} \rightarrow$	Pc
FePc	649			-	
FePc(Py) ₂	653			406	
FePc(4CNPy) ₂	649	497		397	
FePc(3ClPy) ₂	650	548 sh		401	
FePc(3OHCH ₂ Py) ₂	653			409	
FePc(3MePy) ₂	653			407	
FePc(4MePy) ₂	656			406	
FePc(3OHPy) ₂	652			407	
FePc(4OHPy) ₂	653			417	
FePc(4SHPy) ₂	654			428	

Legende : sh = shoulder

Table V. Maximum absorption wavelengths of UV-visible spectra of solutions of $(\text{COOH})_8\text{FePc}$ and reaction compounds of $(\text{COOH})_8\text{FePc}$ with pyridine and its derivatives in DMSO

Compounds	$\pi \rightarrow \pi^*$	$\text{Fe} \rightarrow$	L_{ax}	$L_{\text{ax}} \rightarrow$	Pc
$(\text{COOH})_8\text{FePc}$	682				
$(\text{COOH})_8\text{FePc}(\text{Py})_2$	673			424	
$(\text{COOH})_8\text{FePc}(4\text{CNPy})_2$	669	574 sh		418	
$(\text{COOH})_8\text{FePc}(3\text{ClPy})_2$	670	591 sh		418	
$(\text{COOH})_8\text{FePc}(3\text{OHCH}_2\text{Py})_2$	677			427	
$(\text{COOH})_8\text{FePc}(3\text{MePy})_2$	672			427	
$(\text{COOH})_8\text{FePc}(4\text{MePy})_2$	675			428	
$(\text{COOH})_8\text{FePc}(3\text{OHPy})_2$	671			427	
$(\text{COOH})_8\text{FePc}(4\text{OHPy})_2$	676			451	
$(\text{COOH})_8\text{FePc}(4\text{SHPy})_2$	679			428	

Legende : sh = shoulder

The variation in the relative intensities may be due to the super positions of different modes of vibration of the macrocycle and axial ligands on the one hand and the strong couplings between the different motions of deformation of the macrocycle. Notable changes in the range 400 to 1000 cm^{-1} are the disappearance of some bands of vibration in some spectra. For example, there is the absence of the band around 581 cm^{-1} in all the spectra of the substituted complexes (Table 1 and 2). In addition, the presence of axial ligands also causes the appearance of new bands in this area. They appear respectively around 460, 600, 673 and 825 cm^{-1} . The band at 600 cm^{-1} was assigned to a vibration band of axial ligands. Indeed, K. BAYO (Socrates G. 2001) observed it while studying a series of complexes $(\text{COONa})_4\text{FePc-RPy}_2$ and attributed it to a vibration of the pyridine ligand. In the spectrum of free phenol appears a band of vibration of angular deformation OH out of the plane between 720 and 600 cm^{-1} (Emmanuel, 1988). The band which appears in the spectrum of the complex formed with the ligand 3OHPy at 675 cm^{-1} could be due to this vibration. Those at 460 cm^{-1} and between 825-850 cm^{-1} in the spectra of the substituted complexes are also attributable to the pyridine ligands, since they are absent in the $(\text{COOH})_8\text{FePc}$ spectrum. In the 1000-1700 cm^{-1} range, we observed the disappearance of the 1163, 1180 and 1437 cm^{-1} bands in the spectra of the $(\text{COOH})_8\text{FePc}$ reaction compounds with the RPy ligands. The $\nu\text{C-H}$ vibration band of pyridine at 1225 cm^{-1} in the $\text{FePc}(\text{RPy})_2$ complexes spectra (Ouedrago GV *et al.*, 1981) is not obvious in the spectra of the $(\text{COOH})_8\text{FePc}(\text{RPy})_2$ complexes. A new band was observed at 1472 cm^{-1} with the 3OHCH₂Py ligand. This can be attributed to the shearing of the -CH₂- entity compared to that observed at 1471 cm^{-1} in the spectrum of benzylalcohol (Socrates G. 2001).

Complexes bearing the phosphite and phosphine axial ligands

The presence of phosphite and phosphine ligands in the axial position results in the appearance of new vibration bands, the modulation of relative intensities and the disappearance of certain vibration bands of $(\text{COOH})_8\text{FePc}$. The changes observed in the spectra of the $(\text{COOH})_8\text{FePc}(\text{PX}_3)_2$ complex vary with axial ligand and probably reflect a reorganization of the crystal structure due to ligand coordination (Bawa *et al.*, 2017). The new vibration bands come mainly from the vibrations of axial ligands and / or structural changes. The 1163 cm^{-1} vibration band in the spectrum of the P(Ph)₃ ligand complex is attributable to the P-Ph deformation. It appears as a shoulder shape in the FePc spectra, complexed with the same ligand, at 1190 cm^{-1} (Zanguina A. *et al.*, 2002). As for the vibrations of the C-O-P bond in the complexes of P(OMe)₃, HOP(OEt)₃ and P(OPh)₃, they are observable around 770 cm^{-1} . In the spectra of free ligands, these vibrations appear in the 830-740 cm^{-1} intervals (Richard N. 2001) for the ligands P(OMe)₃ and HOP(OEt)₃, and between 740 and 790 cm^{-1} (Barbara H. 2004) for the ligand P(OPh)₃. Other vibration bands also attributable to axial ligands appear at 470 cm^{-1} , 640 cm^{-1} , 695 cm^{-1} , 880 cm^{-1} , and 1210 cm^{-1} in the spectra of the formed complexes.

Optical absorption spectrometry

Complexes carrying the axial ligands of pyridine and its derivatives. The wave lengths of the absorption maxima between 300 and 900 nm are grouped together in Tables IV

and V. The results obtained with the FePc series are consistent with those already published in the literature (Ouedrago *et al.*, 1981). The introduction of carboxylic acid groups at the periphery has significantly modified the electronic properties of the macrocycle. The whole is moved towards the long wavelengths. Inter and intramolecular interactions result in a dominant electron-donor effect (Figure 2); which is in accordance with the results of the literature (Sakamoto K. *et al.*, 2009). These displacements are attributed to interaction phenomena of dipolar nature or resulting from the formation of hydrogen bonds which stabilize the electron density around the macrocycle, thus weakening the energy required for electronic transitions. A new phenomenon, never observed in a previous work with these types of compound (Ouedrago *et al.*, 1981), appears in the spectra of the reaction of the compound $(\text{COOH})_8\text{FePc}$ with axial ligands. The introduction of axial ligands causes a significant increase in the transition energies of the main band π . It is quite possible that the phenomena which are at the origin of the electron-emitting effect resulting from the introduction of the -COOH groups are strongly attenuated by the fixing of the axial ligands; which constitutes a new result. FePc complexes with the ligands used are hex coordinated in the form of FePcL_2 (Zanguina *et al.*, 2002). In the optical spectra of these complexes, the essential modifications observed are as follows:

- The appearance of a new transition band absent in the FePc spectrum around 410 nm (Table IV) when the substituent on pyridine is an electron donor. This transition is attributed to a transition with charge transfer from the axial ligand to the macro cycle (TC L \rightarrow Pc);
- When the substituent on pyridine is electro attractant, a second new transition is observed around 520 nm. It is a transition with charge transfer from the central metal to the axial ligand (TC Fe \rightarrow L) ;
- Moreover, these new transitions evolve in correlation with the band Q. If the ligand is an electron donor, they evolve towards the low energies; if not, they move towards higher energies (Table IV).

In the present work, the attachment of the axial ligands causes identical modifications (Table V). The notable difference with previous results is the impossibility of establishing a correlation between the evolution of transition bands and charge transfer. (TC L \rightarrow Pc and TC Fe \rightarrow L) and the electron-withdrawing or electron-donating character of the axial ligands. Also, we could not establish with the evolution of the band Q.

The complexes carry the axial ligands of phosphine and phosphite: The wavelengths of the absorption maxima between 300 and 900 nm are grouped together in Tables VI, VII, VIII and IX. The results obtained with the FePc series are consistent with those already published in the literature (Zanguina *et al.*, 2002). In this series, the introduction of axial ligands has a limited influence on the Q-band. It is not as disturbed as with pyridine ligands and substituted pyridines, even though overall its energy increases. This reflects the fact that this phenomenon is closely related to the nature of the ligand. Spectral analysis of the reaction of compounds $(\text{COOH})_8\text{FePc}$ with the ligands PPh₃, P(OPh)₃, P(OMe)₃ and HOP(OEt)₂ highlights two new transition bands absent from the $(\text{COOH})_8\text{FePc}$ spectra.

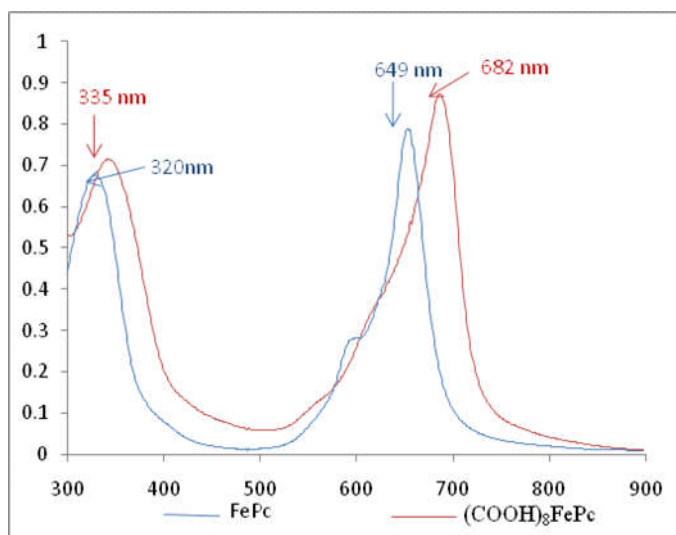


Figure 2. UV-visible spectra of $(\text{COOH})_8\text{FePc}$ and FePc in DMSO solution

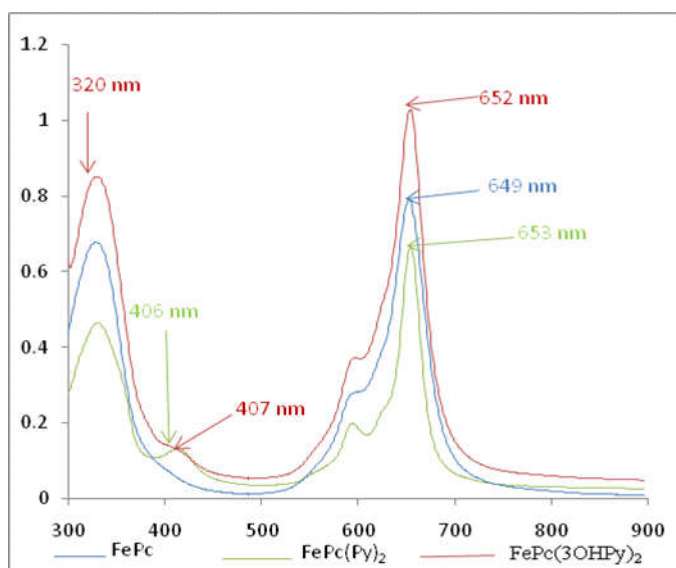


Figure 3. UV-visible spectra of FePc , $\text{FePc}(3\text{OHpy})_2$ and $\text{FePc}(\text{Py})_2$ in DMSO solution

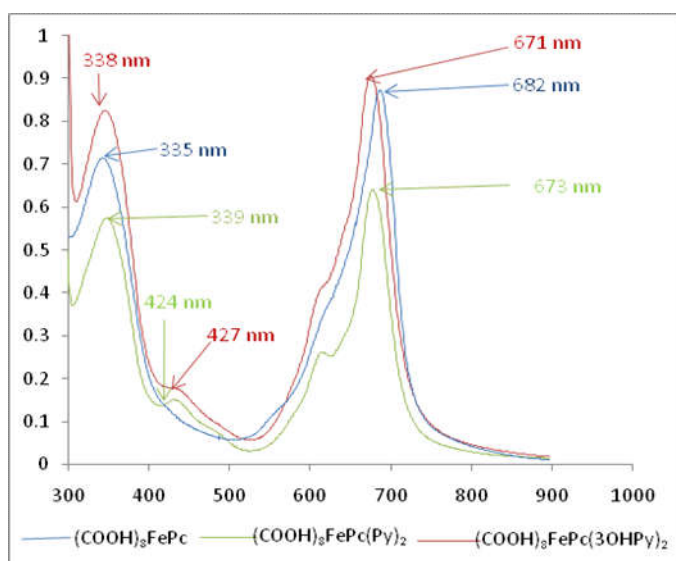


Figure 4. UV-Visible Spectra of $(\text{COOH})_8\text{FePc}$, $(\text{COOH})_8\text{FePc}(3\text{OHpy})_2$ and $(\text{COOH})_8\text{FePc}(\text{Py})_2$ in DMSO solution

Table VI. Maximum absorptionwavelengthsofthe UV-visible spectraof FePc and $\text{FePc}(\text{PX}_3)_2$ solutions in DMSO

Compounds	$\pi \rightarrow \pi^*$	$\text{Fe} \rightarrow$	L_{ax}	$L_{ax} \rightarrow$	Pc
FePc	652				
$\text{FePc}[\text{P}(\text{Ph})_3]_2$	654	400			
$\text{FePc}[\text{P}(\text{OPh})_3]_2$	652				
$\text{FePc}[\text{P}(\text{OMe})_3]_2$	655	410			
$\text{FePc}[\text{OHP}(\text{OEt})_2]_2$	654				

Table VII. Maximum absorption wavelength of UV-visible spectra of solutions of FePc and $\text{FePc}(\text{PX}_3)_2$ in benzene.

Compounds	$\pi \rightarrow \pi^*$	$\text{Fe} \rightarrow$	L_{ax}	$L_{ax} \rightarrow$	Pc
FePc	652				
$\text{FePc}[\text{P}(\text{Ph})_3]_2$	654	410			
$\text{FePc}[\text{P}(\text{OPh})_3]_2$	652	419			
$\text{FePc}[\text{P}(\text{OMe})_3]_2$	655	434		375	
$\text{FePc}[\text{OHP}(\text{OEt})_2]_2$	654	412			

Table VIII. Maximum absorption of the UV-visible spectra of $(\text{COOH})_8\text{FePc}$ and $(\text{COOH})_8\text{FePc}(\text{PX}_3)_2$ solutions in DMSO.

Compounds	$\pi \rightarrow \pi^*$	$\text{Fe} \rightarrow L_{ax}$	$L_{ax} \rightarrow \text{Fe}$
$(\text{COOH})_8\text{FePc}$	682		
$(\text{COOH})_8\text{FePc}[\text{P}(\text{Ph})_3]_2$	677		451
$(\text{COOH})_8\text{FePc}[\text{P}(\text{OPh})_3]_2$	678	469	424
$(\text{COOH})_8\text{FePc}[\text{P}(\text{OMe})_3]_2$	680	473	423
$(\text{COOH})_8\text{FePc}[\text{OHP}(\text{OEt})_2]_2$	681	521	425

Table IX. Maximum absorption of the UV-visible spectra of solutions of $(\text{COOH})_8\text{FePc}$ and $(\text{COOH})_8\text{FePc}(\text{PX}_3)_2$ in benzene

Compounds	$\pi \rightarrow \pi^*$	$\text{Fe} \rightarrow L_{ax}$	$L_{ax} \rightarrow \text{Fe}$
$(\text{COOH})_8\text{FePc}$	710		
$(\text{COOH})_8\text{FePc}[\text{P}(\text{Ph})_3]_2$	703		468
$(\text{COOH})_8\text{FePc}[\text{P}(\text{OPh})_3]_2$	706	488	452
$(\text{COOH})_8\text{FePc}[\text{P}(\text{OMe})_3]_2$	704	488	445
$(\text{COOH})_8\text{FePc}[\text{OHP}(\text{OEt})_2]_2$	708	572	

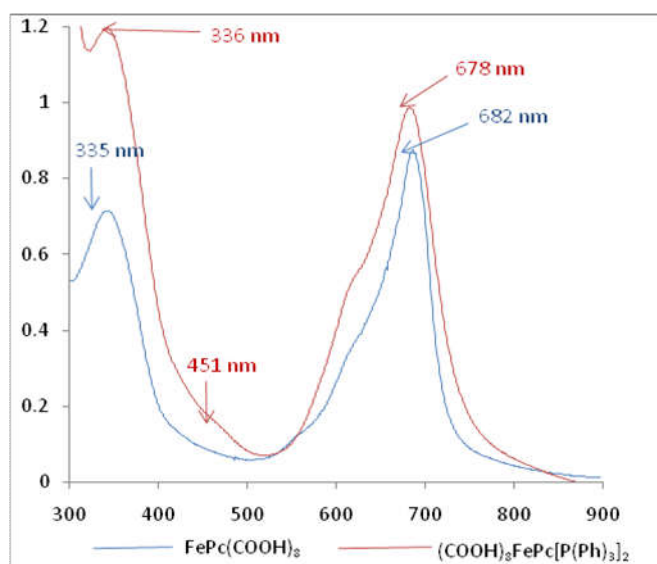


Figure 5. UV-visible spectra of $(\text{COOH})_8\text{FePc}$ and $(\text{COOH})_8\text{FePc}[\text{P}(\text{Ph})_3]_2$ in DMSO solution

The first appears around 425 nm; it is attributable to a transition with charge transfer from the axial ligand to the macrocycle (TC $L \rightarrow \text{Pc}$). As for the second transition, it appears around 480 nm and is attributable to a transition with charge transfer from the central metal to the axial ligand (TC $\text{Fe} \rightarrow L$).

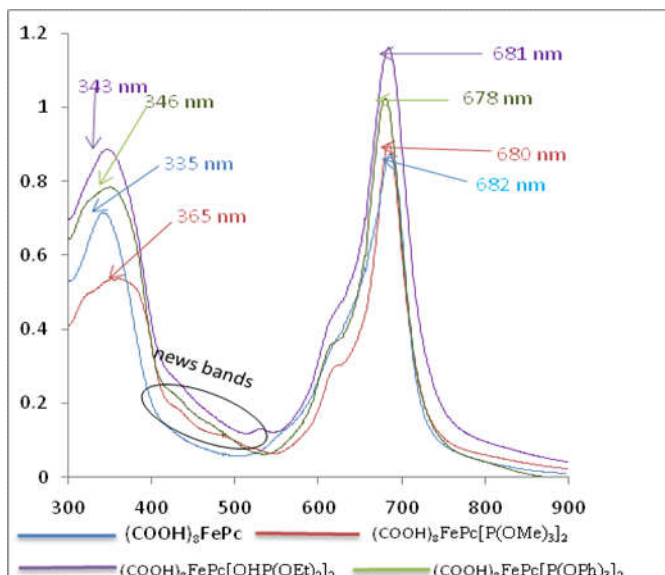


Figure 6. UV-visible spectra of $(\text{COOH})_8\text{FePc}$, $(\text{COOH})_8\text{FePc}[\text{P}(\text{OPh})_3]_2$, $(\text{COOH})_8\text{FePc}[\text{P}(\text{OMe})_3]_2$ and $(\text{COOH})_8\text{FePc}[\text{OHP}(\text{OEt})_2]_2$ in DMSO solution

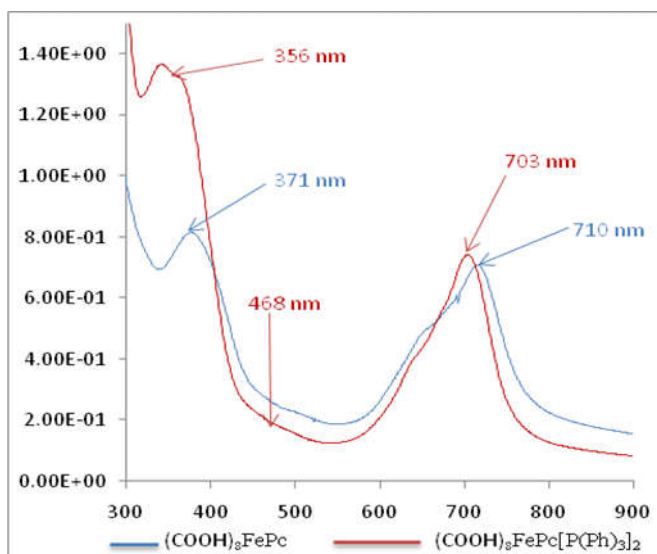


Figure 7. UV-visible spectra of $(\text{COOH})_8\text{FePc}$ and $(\text{COOH})_8\text{FePc}[\text{P}(\text{Ph})_3]_2$ in benzene solution

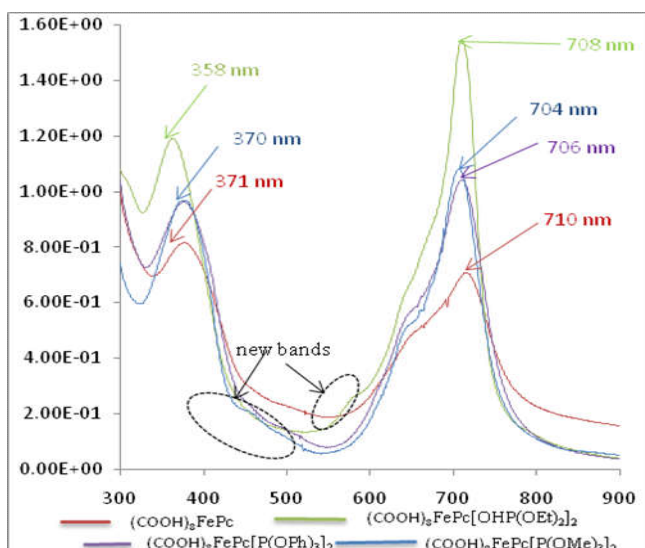


Figure 8. UV-Visible Spectra of $(\text{COOH})_8\text{FePc}$, $(\text{COOH})_8\text{FePc}[\text{P}(\text{OPh})_3]_2$, $(\text{COOH})_8\text{FePc}[\text{P}(\text{OMe})_3]_2$ and $(\text{COOH})_8\text{FePc}[\text{OHP}(\text{OEt})_2]_2$ in benzene solution

These results confirm those obtained with FePc with the same ligands (Zanguina *et al.*, 2002). The notable difference between the two series is the effect of the solvent. Indeed, with the FePc complexes, the charge transfer transition from the central metal to the axial ligand (TC Fe→L) was difficult to observe in DMSO. It was evident only in benzene. In the present work, it can be observed in the spectra of all complexes of $(\text{COOH})_8\text{FePc}$, with the same axial ligands, in DMSO. It can be deduced that its intensity is influenced by the equatorial substituents.

Conclusion

This work enabled us to prepare and isolate in solid form a series of complexes of iron octacarboxyphthalocyanine $(\text{COOH})_8\text{FePc}$ with the pyridine ligands and its derivatives 3-Rpyridine (with R = CH₃, OH, Cl and OHCH₂), 4-Rpyridine (with R = CH₃, OH, CN and SH), phosphites and phosphine P(OPh)₃, P(OMe)₃, HOP(OEt)₂ and PPh₃. The compounds were studied by optical and vibrational spectrometry; analysis of the spectrometric results allowed us to obtain new results and confirmed the results of previous work. The presence of vibration bands attributable to axial ligand vibrations in the complex spectra confirms that the expected reactions have been achieved. In optical spectrometry, we confirmed the results obtained with iron phthalocyanine, especially the transition bands with charge transfer TC L→Pc and TC Fe→L in the spectra of complexes. In addition, this work made it possible to demonstrate a new type of influence of the axial ligands on the Q band in the $(\text{COOH})_8\text{FePc}$ series. With the pyridine ligands, the band Q undergoes a significant hypsochrome displacement; the phenomenon remains observable with phosphite and phosphine ligands. This perturbation can be explained by the fact that the fixation of the axial ligands modifies the mode of association of the molecules in solution. This would result in a redeployment of the interactions between the π systems present. Also, the introduction of -COOH groups at the periphery highlights the influence of equatorial substituents on the intensity of the charge-coupled transition bands, especially with phosphines and phosphites. The addition of our results to those already published could constitute a significant progress of the debates on the knowledge of the electronic structure of these compounds.

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