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Use of a porphyrin platform and 3,4-HPO chelating units to synthesize ligands with N_4 and O_4 coordination sites

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ABSTRACT

Piperazine and 1,2-diaminobenzene have been previously used as anchoring molecules to synthesize 3-hydroxy-4-pyridinone (3,4-HPO) tetradentate ligands affording ligands with different flexibility and coordination properties. In order to have a relatively rigid and hindered structure, a porphyrin platform was selected to anchor one or two 3,4-HPO chelating units. This platform provides an additional N_4 coordination sphere and also very interesting optical properties to the synthesized conjugates. Depending on the metal ion present in the porphyrin core, conjugates with different spectroscopic properties are obtained. EPR spectroscopy has been used to characterize the copper(II) metalloporphyrins and to monitor and identify the species formed upon addition of copper(II) to solutions of two porphyrin conjugates with one and two 3,4-HPO arms. The porphyrin conjugates having two 3,4-HPO units are ligands that provide two separate binding sites with N_4 and O_4 coordination spheres, which allow accommodation of two metal ion centers that may be distinguished by spectroscopic methods.

1. Introduction

Porphyrin-type macrocycles keep on catching the attention of researchers in coordination chemistry.[1] Indeed, these compounds have assumed an important role in numerous areas of chemistry, biology, medicine, catalysis, and material science.[2]

Typically, porphyrin macrocycles, which are characterized by the presence of a central N_4 core, are excellent metal-complexing ligands. However their coordination chemistry is not restricted to the metal ion bound to the porphyrin central core and may be extended to the porphyrin periphery through the attachment of additional metal chelating units. For instance pyridylporphyrins, in which the pyridine ring is directly attached to the porphyrin forming a relatively rigid system, have been used in the construction of supramolecular coordination complexes.[3] The pyridyl group can be also introduced through sulfonamide linkage in order to achieve less rigid systems.[4] In the similar way, porphyrins bearing pyrazolyl, imidazolyl, and hydroxyl substituents have been applied as scaffolds for the building of multiporphyrin arrays and other supramolecular structures.[5]

Besides the coordination properties, the porphyrin framework presents very interesting and useful photophysical properties, including high absorption coefficients in the visible region, tunable fluorescence emission, and high stability against light and chemical reactions.[6] Because of this set of peculiar binding/optical properties, porphyrins have been utilized in the construction of highly sensitive and selective fluorescent chemosensors for copper(II) and zinc(II), through a metal ion bound mechanism to the porphyrin central core.[7] In order to improve the response of the sensor to the presence of these and others metal ions, the porphyrin chemosensor can be covalently immobilized to the surface of Au at SiO_2 core/shell nanoparticles[8] or to other matrices.[9] Porphyrins and metalloporphyrins bearing additional chelating units, such as 2-(oxymethyl)pyridine,[10] 2,2′-dipyridylamine,[11] and bipyridine units[12] have been also employed as efficient chemosensors for the detection of copper(II) and zinc(II). In these cases, the porphyrin or metalloporphyrin acts as a fluorophore due to their excellent photophysical properties and the peripheral group acts as a recognition and binding site for the metal ions.

An additional important feature of the porphyrin macrocycle is the fact that it provides a planar or quasi-planar platform to bind other chelating molecules thus allowing the synthesis of polydentate ligands based on bidentate units. Our group has reported, very recently, the preparation of three tetradentate 3,4-HPO

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chelators, which exhibit different flexibility due to the use of two anchor molecules, piperazine, and 1,2-diaminobenzene, and diverse length of the 3,4-HPO.[13] These ligands revealed to have a very rich coordination chemistry involving the formation of binuclear metal ion species, which we are presently exploring in more detail. In this context we used a porphyrin core as a platform to anchor 3,4-HPO bidentate units thus obtaining bidentate and tetradentate ligands based on a planar platform, which may include an additional coordination site. Moreover, the combination of the electronic and spectroscopic features of porphyrins with the chelating properties of 3,4-HPO expands the functionality of the system and provides the synthesis of novel conjugates with enhanced or complementary electronic, photophysical, and/or coordination properties.

Previously, 3,4-HPOs and other related families, have been used in the synthesis of diverse macrocyclic chelators to obtain mono- and bimetallic complexes in order to mimic the active site of multinuclear metalloenzymes.[14–17] Now, in this work a series of novel porphyrin and metalloporphyrin conjugates containing one and two 3,4-HPO chelating units in the periphery of the macrocycle (Fig. 1), were synthesized using an efficient and selective metal coordination strategy. This approach relies on the synthesis of mono- and di-substituted porphyrins with 3,4-HPO protected ligands, followed by metalation of the porphyrin core and selective removal of benzyl protecting groups via hydrogenolysis, leading to the desired peripherally containing 3,4-HPO metalloporphyrins **P2**, **P3**, **P5**, and **P6**. Metal-free porphyrin conjugates **P1** and **P4** were prepared using the same strategy but without metalation.

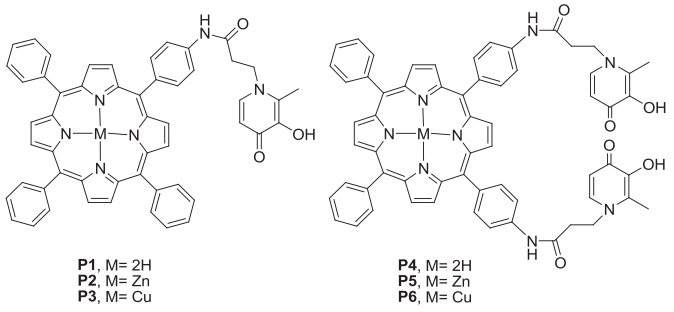


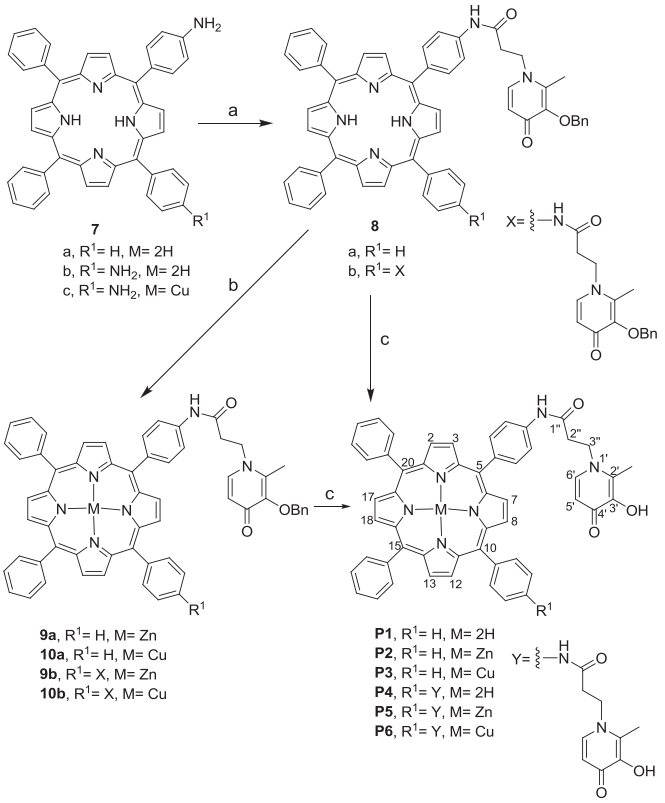
Fig. 1. Porphyrin conjugates containing one and two peripheral 3,4-HPO units (**P1**–**P6**).

2. Results and discussion

2.1. Synthesis

Bidentate 3,4-HPO ligands show a high affinity toward M(III) and M(II) metal ions forming complexes of general formula ML_3 and ML_2. The aim of the present work is to synthesize porphyrin conjugates with one and two 3,4-HPO arms in order to produce macrocyclic ligands with additional chelating functions. To achieve this goal 3,4-HPO units with a flexible spacer were attached to the porphyrin phenyl rings through amide bonds as its shown in Scheme 1.

Firstly, the amide coupling reaction of 5-(4-aminophenyl)-10,15,20-triphenylporphyrin **7a** with 3-benzyloxy-1-(3′-carboxypropyl)-2-methyl-4-pyridinone was performed in dry DMF at room temperature, during 24 h, through in situ generation of the corresponding activated ester using *N*,*N*′-dicyclohexylcarbodiimide (DCC) and 1-hydroxybenzotriazole (HOBt) as coupling reagents. After purification by flash chromatography and crystallization, porphyrin **8a** was obtained in 68% yield. This porphyrin was then metalated with $Zn(OAc)_2$ and $Cu(OAc)_2$, in a mixture of dichloromethane and methanol to give the desired Zn(II) and Cu(II)



Conditions: (a) 3-benzyloxy-1-(3'-carboxypropyl)-2-methyl-4-pyridinone, DCC, HOBt, DMF (b) $Zn(OAc)_2$ or $Cu(OAc)_2$, CH_2Cl_2/ MeOH, reflux; (c) H_2, 10% Pd/C cat.

Scheme 1. Synthesis of porphyrin conjugates (**P1**–**P6**).

complexes **9a** and **10a** in good yields (80–90%). The deprotection final sequence required the use of a selective methodology for removal of benzyl protecting group of the pyridinone skeleton without exclusion of the metal ion from the core of the macrocycle.

In fact, when the removal of the benzyl group was tried with the very labile Zn(II) complex **9a** using a solution of BCl_3 in dichloromethane, the reaction lead to the corresponding metal-free debenzylated conjugate **P1**. In order to use a non-acidic methodology, the catalytic hydrogenolysis was carried out with $H_2(g)$ in the presence of 10% Pd/C catalyst. Using these conditions the reaction afforded the desired Zn(II) conjugate **P2**, in a very good yield. Similarly, when the same catalytic hydrogenolysis was applied to Cu(II) complex **10a**, conjugate **P3** was also obtained in a very good yield. Even knowing that certain porphyrins can be reduced to porphyrinogens using H_2 and Pd/C catalyst,[18] in the present case no porphyrinogen was obtained. These results show that hydrogenolysis can be used as a selective and efficient methodology to remove the benzyl protecting groups from this set of porphyrin and metalloporphyrin conjugates. The metal-free conjugate **P1** was prepared using a similar strategy but without metalation. Furthermore, such synthetic strategy was successfully extended to di-substituted porphyrins allowing the synthesis of conjugates **P4**–**P6**.

The new compounds were characterized by mass spectrometry, NMR, absorption, and fluorescence spectroscopy and EPR in the case of copper(II) containing porphyrins.

2.2. Mass spectrometry

Mass spectrometry, particularly the electrospray ionization tandem mass spectrometry (ESI-MS/MS) is an important tool in the

structural characterization of porphyrins and metalloporphyrins.[19] In the present work, the ESI-MS spectra of porphyrin conjugates having one or two 3,5-HPO units were obtained in positive ion mode showed the corresponding protonated molecules $[M+H]^+$. For porphyrin conjugates **P1**–**P3** having one 3,4-HPO unit, the MS/MS spectra revealed several product ions that can be formed by cleavage in three possible points of fragmentation (a_1–a_3). The most intense peak observed corresponds to the fragmentation a_1 formed by heterolytic cleavage of the CH_2–N bond with the lost of the pyridinone ring with migration of one proton. The homolytic cleavage of the CO–CH_2 bond corresponds to a_2 fragmentation. Fragmentation a_3 corresponds to the cleavage of the amide bond between the C=O and the NHR group, is a common fragmentation of amides and its present in all MS/MS spectra. Similarly, the corresponding porphyrin conjugates having two 3,4-HPO units show the same fragmentation patterns.

2.3. NMR spectroscopy

The NMR spectra of porphyrin conjugates having one 3,4-HPO unit are relatively identical, showing the presence of one porphyrin macrocycle per pyridinone unit. For Zn(II) conjugate **P2** the most characteristic signals observed in the aromatic region of the ^{1}H NMR spectrum in DMSO are: (i) a broad singlet at 10.47 ppm due to the resonance of NH proton of the amide bond; (ii) a multiplet around 8.80 ppm due to the resonance of the β-pyrrolic protons of the porphyrin and (iii) two doublets at 6.22 and 7.71 ppm corresponding to the resonance of H-5′ and H-6′ protons of the pyridinone. While H-5′ shows HMBC correlation with a signal at 145.4 ppm assigned as C-3′ (C–OH), H-6′ shows HMBC correlation with a signal at 168.7 ppm assigned to C-4′ (C=O). In the aliphatic region of the spectrum is clear the presence of one singlet at 2.45 ppm corresponding to the methyl group of the pyridinone and two triplets at 2.97 and 4.40 ppm for the C_2H_5 spacer. As expected, the ^{1}H NMR spectra of the corresponding metal-free conjugate **P1** is very similar with the characteristic signal of the pyrrole NH protons at δ=−2.92 ppm, which is absent in zinc(II) conjugate **P2**. The NMR spectra of porphyrin conjugates having two 3,4-HPO units show a similar profile to those of mono-substituted porphyrins, revealing the presence of one porphyrin macrocycle per two pyridinone units, which are equivalent.

2.4. Electronic spectroscopy

Absorption spectra: The absorption spectra of all synthesized porphyrin conjugates are quite similar under the same experimental conditions thus indicating that the number of substituents does not significantly influence the absorption properties, which are also similar in the two solvents used (DMSO and acetonitrile, see Supplementary data). The spectra of the metal-free porphyrins (**P1** and **P4**) in DMSO show the typical Soret band and four Q bands with absorption maxima very similar for the two porphyrins. The band ca. 420 nm was assigned to the Soret band arising from the transition $a_{1u}(\pi)$–$e_g^*(\pi)$, and the other four absorption maxima (516, 553, 594, and 648 nm) were attributed to the Q bands (Qy(1,0), Qy(0,0), Qx(1,0), Qx(0,0)) that correspond to the $a_{2u}(\pi)$–$e_g^*(\pi)$ transition.[20] The substituents do not change the transition mode of the porphyrin molecules. For the metalloporphyrins (**P2**, **P3**, **P5**, and **P6**) the spectra are also typical of porphyrin complexes of the two metal ions used. For metalloporphyrins, due to the easy flow of electrons within the delocalized π system and to the increase of the molecular symmetry, the UV–vis spectra exhibit one Soret band and either one or two Q bands. For Cu(II) porphyrins, their delocalized π bonds decreased the average electron density on the metalloporphyrins thus increasing the energy available for electron transition. As a result, a hypsochromic shift of the Soret bands occurs and only one component of the Q bands is observed. However, the delocalized π bands of the Zn(II) porphyrins increased the average electron density of the porphyrin, which lowered the energy for electron transition, leading to a bathochromic shift in the Soret band and two components of the Q band are observed.[20] In Fig. 2 is depicted absorption spectra of porphyrins with one 3,4-HPO unit (**P1**–**P3**) measured in DMSO at room temperature.

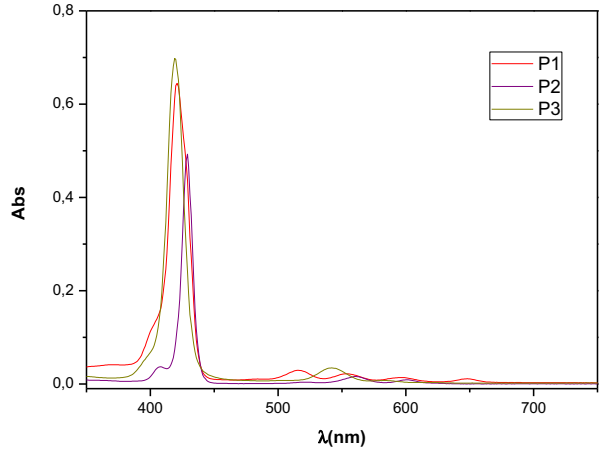


Fig. 2. Electronic absorption spectra of porphyrins **P1**–**P3** obtained in a DMSO solution.

Fluorescence spectra: The fluorescence spectra of porphyrins **P1**–**P3** are depicted in Fig. 3 and spectra of porphyrins **P4**–**P6** in Fig. 4.

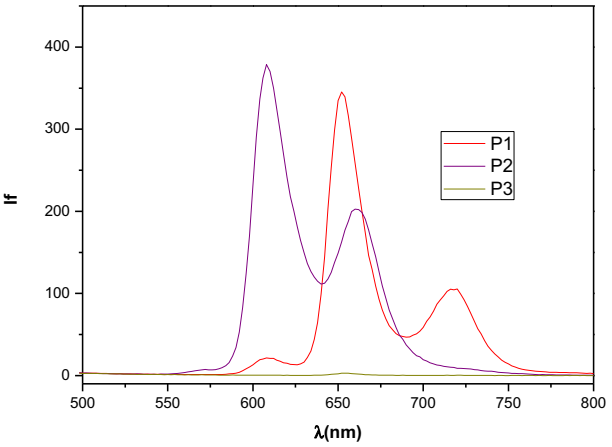


Fig. 3. Fluorescence spectra of porphyrins **P1**–**P3** obtained in a 2.5×10^{-7} M DMSO solution.

The fluorescence spectra of the free porphyrins (**P1** and **P4**) show Q(0,0) and Q(0,1) bands (Figs. 3 and 4). The asymmetric porphyrin **P1** shows a third component of the Q band and that can be assigned to a Q(1,0) transition, which is observed as a consequence of a decrease in molecular symmetry. The fluorescence spectra observed for the metalloporphyrins (**P2**, **P3**, **P5**, **P6**) illustrate the usual variation upon metal ion chelation. For the paramagnetic Cu(II) metalloporphyrins (**P3**, **P6**) fluorescence is quenched, a result, that is, in agreement with Gouterman's theory confirming the purity of the copper complexes synthesized in this work.[6] The fluorescence spectra of the diamagnetic Zn(II) metalloporphyrins (**P2**, **P5**) display fluorescence originated from the first excited singlet state, S1 or Q state. This Q band has two peaks at about 605.0 (Q(0,0)) and 655.0 nm (Q(0,1)) for porphyrins **P2** and

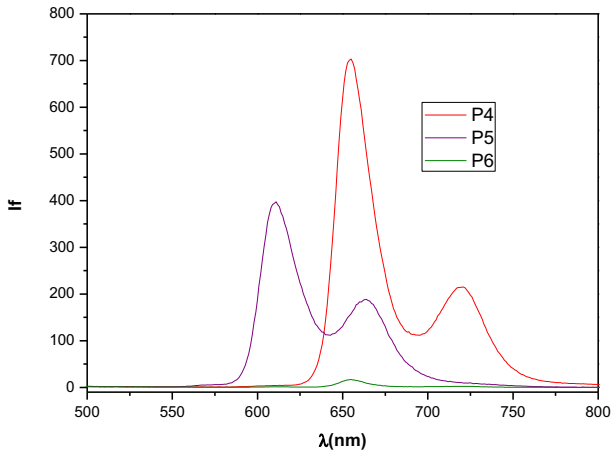


Fig. 4. Fluorescence spectra of porphyrins **P4**–**P6** obtained in a 2.5×10^{-7} M DMSO solution.

P5, respectively. The fluorescence maxima of these porphyrins show the usual hypsochromic shift relative to the free porphyrin.[21] For the asymmetric zinc(II) porphyrin **P2** the fluorescence intensity lies within the same order of magnitude of the free porphyrin while for the symmetric porphyrin **P5** a slight decrease is observed.

2.5. EPR spectroscopy

The EPR spectroscopy has been utilized to characterize the copper(II) metalloporphyrins (**P3**, **P6** and **7c**, see Fig. 1 and Scheme 1) and also to get information about the species formed upon addition of copper(II) to solutions of the porphyrin–pyridinone conjugates. The spectra of compounds **P3**, **P6**, and **7c**, which are, respectively, the copper complexes of the mono- and di-functionalized porphyrins and the non-derivatized starting porphyrin, are very similar and the X-band EPR spectrum of porphyrin **P6** obtained in a toluene frozen matrix is depicted in Fig. 5. The spectrum is typical of an one electron (S=1/2) system and clearly exhibits lines due to the hyperfine interaction of the unpaired electron with the copper nucleus (I=3/2) and with the four nitrogen (I=1) nuclei. The computer simulation of the spectrum was obtained considering the interaction of the unpaired electron with one copper nucleus and two sets of equivalent nitrogen atoms in the porphyrin ring. The values of the Spin-Hamiltonian parameters obtained upon simulation are registered in Table 1 and are consistent with a d_{x2-y2} ground state. These parameters are identical to those obtained for porphyrin **P3** and virtually identical those of porphyrin **7c** thus indicating that the functionalization of the porphyrin core with the pyridinone arms does not significantly change the electronic density on the copper ion. Porphyrin **7c** has a higher symmetry, which is reflected in the coincident values of g_{xx} and g_{yy}.

In order to characterize the EPR signal characteristic of a copper (II) complex formed by chelation with the 3,4-HPO arms of the porphyrins we prepared the copper complex of **P5**, which bears two 3,4-HPO arms and in which the porphyrinic center is occupied by zinc(II), designated as porphyrin **11**. The spectrum obtained in a DMSO matrix is depicted in Fig. 6. The signal is clearly different from that shown in Fig. 5 and very similar to the EPR spectra obtained for copper(II) complexes of *N*-alkyl-3-hydroxy-4-pyridinone bidentate ligands.[22] The spectrum is typical of a (S=1/2) system and only exhibits lines due to the interaction of the unpaired electron with the copper nucleus (I=3/2) as expected for the O_4 coordination sphere provided by the two 3,4-HPO bidentate ligands. The values of the Spin-Hamiltonian parameters obtained upon simulation are registered in Table 1 and are consistent with a d_{x2-y2} ground state.

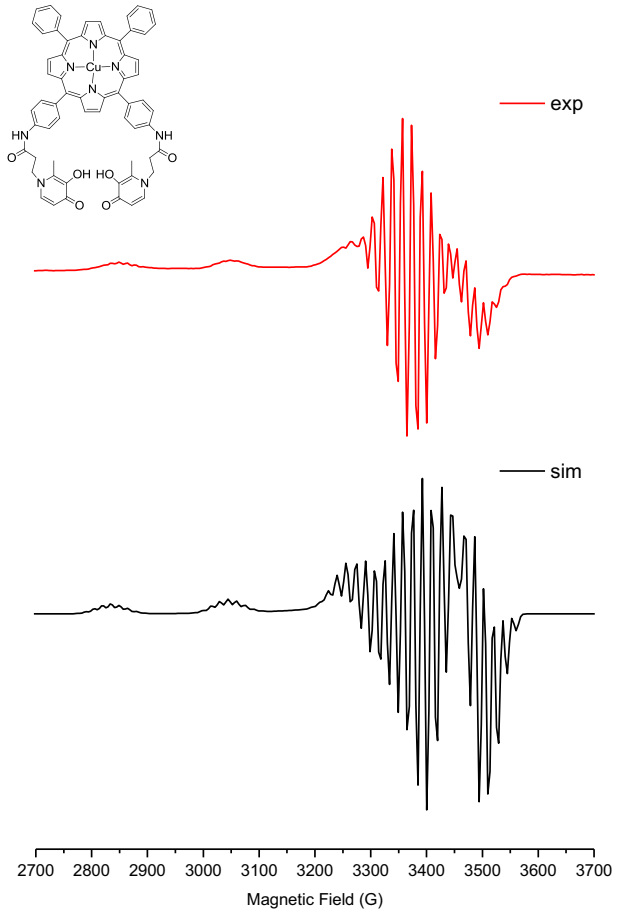


Fig. 5. Frozen solution EPR spectrum of porphyrin **P6** obtained in toluene at 77 K and computer simulation.

Table 1
Spin-Hamiltonian parameters for copper(II) porphyrins. The components of the hyperfine tensor are expressed in Gauss

Porphyrin		g_{xx}	g_{yy}	g_{zz}
7c		2.045	2.045	2.190
		A_{xx}	A_{yy}	A_{zz}
	^{63}Cu	50	50	210
	$^{14}N_{1,3}$	19	15	15
	$^{14}N_{2,4}$	15	19	15
P6		g_{xx}	g_{yy}	g_{zz}
		2.069	2.065	2.188
		A_{xx}	A_{yy}	A_{zz}
	^{63}Cu	35	35	210
	$^{14}N_{1,3}$	19	15	15
	$^{14}N_{2,4}$	15	19	15
11		g_{xx}	g_{yy}	g_{zz}
		2.055	2.06	2.264
		A_{xx}	A_{yy}	A_{zz}
	^{65}Cu	10	10	211
	^{63}Cu	10	10	182

Chelation properties of porphyrin conjugates toward copper(II): In order to understand the chelation properties of the new ligands toward copper(II), we registered EPR spectra of solutions of some of the porphyrin conjugates upon addition of copper(II) in 1:1, 1:2, and 1:4 molar ratios. We started with the metal free porphyrin **P4** that possesses two different coordination sites provided by the porphyrin ring (N_4 coordination sphere) and by the 3,4-HPO bidentate ligands (O_4 coordination sphere). The spectra obtained upon addition of copper(II) to a porphyrin **P4** DMSO solution are depicted in Fig. 7. In this figure the black line is the spectrum obtained upon addition of copper(II) in a 1:1 molar ratio, which

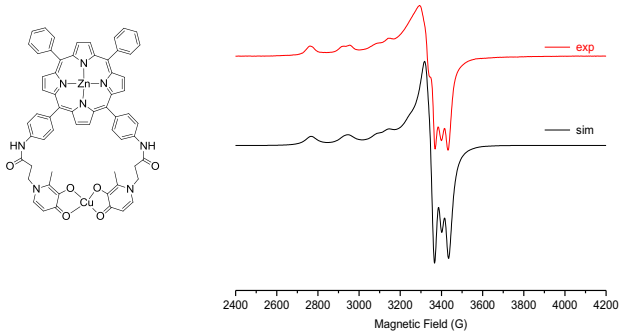


Fig. 6. Frozen solution EPR spectrum of the copper complex of porphyrin **11** obtained in DMSO at 77 K and computer simulation.

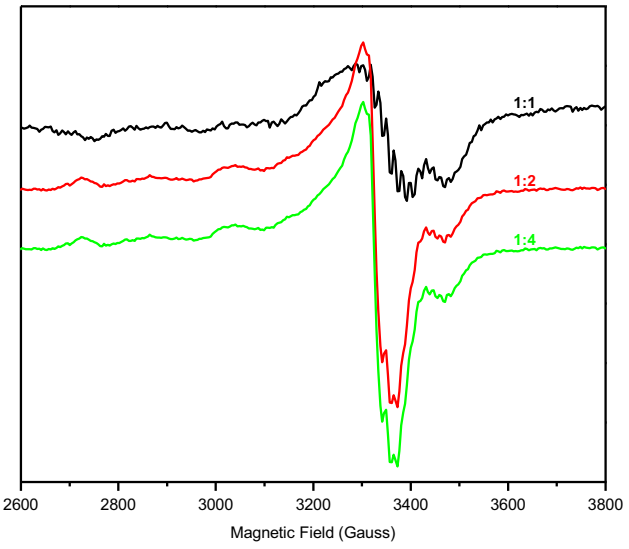


Fig. 7. Frozen solution EPR spectra of porphyrin **P4** upon addition of copper(II) in 1:1 (black line), 1:2 (red line), and 1:4 (green line) obtained in DMSO at 20K.

clearly indicates the coordination of the metal ion to the porphyrin nitrogen atoms as can be seen by comparison with Fig. 5 and demonstrates the preference of the metal ion for the N_4 coordination sphere. The signal obtained upon addition of copper(II) in a 1:2 molar ratio (red line) shows the presence of a new signal superimposed with the previous one and, which exhibits features recognizable in Fig. 6. This observation provides evidence for chelation of copper(II) by the two 3,4-HPO arms. The EPR spectrum obtained after addition of the metal ion in a 1:4 molar ratio (green line) is identical to the one previously observed (red line) thus signifying that the fulfillment of both coordination sites is achieved upon addition of copper(II) in a 1:2 molar ratio.

Taking into account the structure of porphyrin **P4** we believe that both structures presented in Fig. 8 are possible for the complexes formed although at present we cannot rule out one of them. EPR signals characteristic of the existence of a magnetic interaction between two paramagnetic centers were not observed, in any of the spectra, thus indicating that the two copper centers they must be far apart. These results confirm those we have previously found for other tetradentate 3,4-HPO ligands in which a relatively rigid and planar platform does not provide sufficient proximity between the copper centers to allow magnetic interaction while for a more flexible platform such interaction is observed.[13]

Considering the previously observed preference of copper for the porphyrin ring we monitored by EPR the species formed by porphyrin **P3** upon addition of copper(II) in 1:1, 1:2, and 1:4 molar ratios and the spectra obtained are shown in Fig. 9.

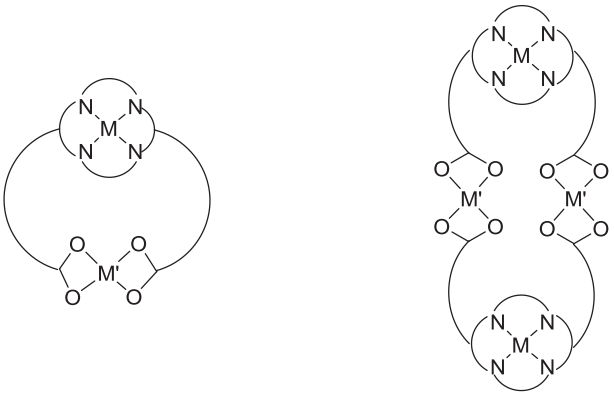


Fig. 8. Possible structures of the binuclear species formed by the di-substituted porphyrins.

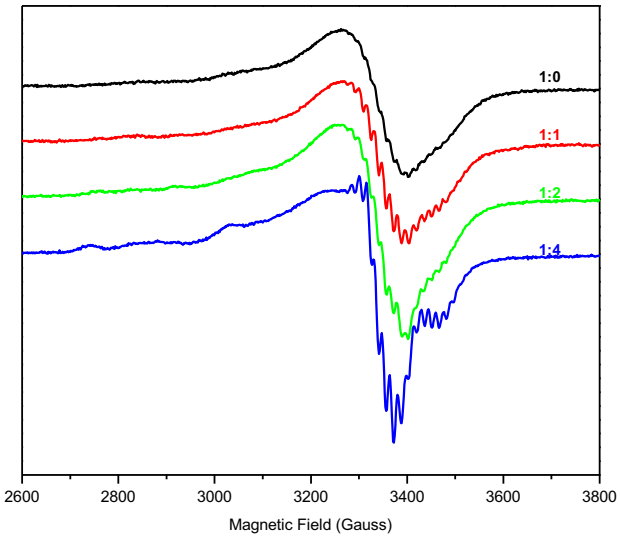


Fig. 9. Frozen solution EPR spectra of porphyrin **P3** (black line), and upon addition of copper(II) in 1:1 (red line), 1:2 (green line), and 1:4 (blue line) obtained in DMSO at 20 K.

In this case the signal of the copper on the porphyrin site is predominant at 1:1 and 1:2 molar ratios and at 1:4 the signal characteristic of copper in the 3,4-HPO coordination environment, although clearly visible seems to reflect a smaller number of paramagnetic centers. The results illustrate the fact that porphyrin **P3** is a bidentate ligand while porphyrin **P6** is a tetradentate one. A tentative structure of the trinuclear species formed is presented in Fig. 10.

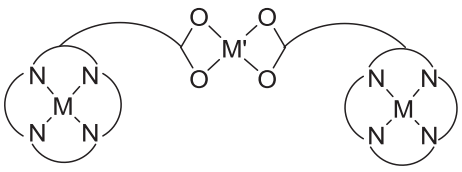


Fig. 10. Possible structure of the trinuclear species formed by the mono-substituted porphyrins.

3. Conclusions

Metal free, zinc(II) and copper(II) porphyrins were successfully functionalized with one and two 3,4-HPO bidentate ligands. In the latter case a ligand with separate binding sites that provides two types of coordination spheres (N_4 and O_4) was produced. EPR

spectra obtained upon addition of copper(II) to the di-substituted porphyrin allowed us to monitor the coordination of copper to the available binding sites and demonstrated that the porphyrin core is preferred by the copper ion. The set of porphyrins synthesized permit the formation of both homo- and hetero- binuclear complexes in which the metal centers do not interact magnetically has shown by the absence of EPR features at g=4. These results also confirm that the flexibility of the anchor platform is crucial to design polidentate ligands that allow the formation of binuclear metal complexes as has been observed for other tetradentate 3,4-HPO ligands. It is important to mention that, once again, EPR spectroscopy proved to be of value to monitor and characterize the paramagnetic species formed by the new ligands.

The new set of bifunctional porphyrin ligands also has characteristics that allow the use of the pyridinone arms as anchoring tools that permit the immobilization of the metal free porphyrin core in surfaces of several types of materials. Such a possibility is important as the porphyrin ligand may be used to trap metal ions that can be further removed in acid conditions[9c] thus allowing its recycle. Moreover, the detection of metal ion binding to the porphyrin core may be easily monitored by absorption or fluorescence electronic spectroscopy. More detailed information can be gathered by EPR.

4. Experimental section

4.1. General information

Reagents and solvents were purchased as reagent-grade and used without further purification unless otherwise stated. NMR spectra were recorded with Bruker Avance III 400 spectrometer (400.15 MHz for ^{1}H and 100.63 MHz for ^{13}C). Chemical shifts (δ) are reported in parts per million and coupling constants (J) in hertz; internal standard was TMS. Unequivocal ^{1}H assignments were made with aid of 2D gCOSY (^{1}H/^{1}H), while ^{13}C assignments were made on the basis of 2D gHSQC (^{1}H/^{13}C) and gHMBC experiments (delay for long range J C/H couplings were optimized for 7 Hz). The electrospray mass spectra (ESI-MS and ESI-MS/MS) were acquired using an electrospray Q-ToF2 (Micromass, Manchester) operating in the positive ion mode and using a MassLynx software system (version 4.0). The needle voltage was set at 3000 V, the cone voltage at 35 V and the ion source at 80 °C. Tandem mass spectra (MS/MS) of $[M+H]^+$ ions produced under ESI conditions were obtained by collision induced decomposition and varying the collision energy between 40 and 50 eV. Microanalyses were carried out by Unidad De Análisis Elemental of Santiago de Compostela.

5-(4-Aminophenyl)-10,15,20-triphenylporphyrin **7a** and 5,10-bis(4-aminophenyl)-15,20-diphenylporphyrin **7b** were prepared according to the literature method.[23] Porphyrin **7b** was further converted into porphyrin **7c** by metalation with copper acetate hydrate as described in general procedure. The 3-benzyloxy-1-(3′-carboxypropyl)-2-methyl-4-pyridinone was synthesized from the initial benzylation of OH group of maltol (3-hydroxy-2-methyl-4-pyrone), followed by reaction with 4-amino-butyric acid, using a similar procedure to the one described in the literature.[24]

*4.1.1. Synthesis of porphyrin (**8a**).* A mixture of 3-benzyloxy-1-(3′-carboxypropyl)-2-methyl-4-pyridinone (82.0 mg, 0.29 mmol, 1.2 equiv), DCC (64.0 mg, 0.31 mmol, 1.3 equiv), HOBt (42.0 mg, 0.31 mmol, 1.3 equiv), and DMF (2 mL) was stirred at room temperature under argon atmosphere during 30 min. After that time, porphyrin **7a** (0.15 g, 0.24 mmol) was added. The resulting reaction mixture was protected from light mixture and it was allowed to stir at room temperature under argon atmosphere for 24 h. Upon filtration and removal of the solvent under reduced pressure, the residue was purified by flash chromatography using firstly dichloromethane as eluent in order to remove reaction side-products and then a mixture of dichloromethane/methanol (95:5) to give the porphyrin **8a** (145 mg, 68%) as purple solid. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): δ −2.92 (s, 2H, NH), 2.36 (s, 3H, CH_3), 2.94 (t, J=6.8 Hz, 2H, 3″-H), 4.34 (t, J=6.8 Hz, 2H, 2″-H), 5.07 (s, 2H, $CH_2C_6H_5$), 6.24 (d, J=7.6 Hz, 1H, H-5′), 7.34–7.41 and 7.45–7.48 (2 m, 5H, $CH_2C_6H_5$), 7.74 (d, J=7.6 Hz, 1H, 6′-H), 7.81–7.88 (m, 9H, 10,15,20-Ph−H_{m+p}), 8.02 (d, J=8.6 Hz, 2H, 5-Ar−H_m), 8.16 (d, J=8.6 Hz, 2H, 5-Ar−H_o), 8.21–8.24 (m, 6H, 10,15,20-Ph−H_o), 8.81–8.88 (m, 8H, H-β), 10.49 (s, 1H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm) δ: 13.4 (CH_3), 38.6 (3″-C), 50.4 (2″-C), 73.3 ($CH_2C_6H_5$), 117.5 (5′-C), 118.9, 121.4, 128.4, 129.2, 129.5, 129.6, 129.7, 135.6, 136.1, 137.5, 139.2, 140.2 (6′-C), 141.0 (2′-C), 142.0, 142.6, 143.1, 146.8 (3′-C), 169.9 (1″-C), 173.3 (4′-C). ESI-MS/MS m/z: 899 $[M+H]^+$.

*4.1.2. Synthesis of porphyrin (**8b**).* A mixture of 3-benzyloxy-1-(3′-carboxypropyl)-2-methyl-4-pyridinone (87.0 mg, 0.30 mmol, 2.3 equiv), DCC (65.0 mg, 0.32 mmol, 2.4 equiv), HOBt (43.0 mg, 0.32 mmol, 2.4 equiv), and DMF (2 mL) was stirred at room temperature under argon atmosphere during 30 min. After that time, porphyrin **7b** (85 mg, 0.13 mmol) was added. The resulting reaction mixture was protected from light and it was allowed to stir at room temperature under argon atmosphere for 2 days. Upon filtration and removal of the solvent under reduced pressure, the residue was purified by flash chromatography using firstly dichloromethane as eluent in order to remove reaction side-products and then a mixture of dichloromethane/methanol (9:1) to give the porphyrin **8b** (109 mg, 70% yield). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm) δ: −2.92 (s, 2H, NH), 2.36 (s, 6H, 2× CH_3), 2.94 (t, J=6.8 Hz, 4H, 2×3″-H), 4.33 (t, J=6.8 Hz, 4H, 2×2″-H), 5.06 (s, 4H, 2× $CH_2C_6H_5$), 6.24 (d, J=7.6 Hz, 2H, 2× H-5′), 7.37–7.41 and 7.45–7.48 (2 m, 10H, 2× $CH_2C_6H_5$), 7.74 (d, J=7.6 Hz, 2H, 2×6′-H), 7.81–7.86 (m, 6H, 15,20-Ph−H_{m+p}), 8.02 (d, J=8.6 Hz, 4H, 5,10-Ar−H_m), 8.16 (d, J=8.6 Hz, 4H, 5,10-Ar−H_o), 8.21–8.23 (m, 4H, 15,20-Ph−H_o), 8.80–8.87 (m, 8H, H-β), 10.50 (s, 2H, 2× NH). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm) δ: 12.0 (CH_3), 37.2 (C-3″), 49.0 (C-2″), 71.9 ($CH_2C_6H_5$), 116.2, 117.5, 119.80, 119.85, 127.0, 127.8, 128.1, 128.2, 128.3, 134.2, 134.7, 136.1, 137.8, 138.8, 139.6, 140.6, 141.2 (C-2′), 145.4 (C-3′), 168.5 (C-1″), 171.9 (C-4′).

4.2. General metalation procedure

Metalation of porphyrins with Zn(II) or Cu(II) was accomplished by refluxing zinc acetate hydrate or copper acetate hydrate (2 equiv) in a mixture of chloroform/methanol (5:2). The solutions were heated under reflux for 2 h (until UV–vis indicated completion of the reactions). After evaporation of the solvent, the resulting residues were dissolved in chloroform and washed with deionized water several times to remove excess metal salt. The organic phase was dried over anhydrous Na_2SO_4 and reduced to dryness.

*4.2.1. Synthesis of zinc(II) complex (**9a**).* Metalation of porphyrin **8a** (70.0 mg, 78.0 μmol) with Zn(II) was accomplished by refluxing zinc acetate hydrate (34.2 mg, 0.16 mmol, 2 equiv) in 40 mL of a mixture of chloroform/methanol (5:2), using the general protocol. The zinc(II) complex **9a** (66.9 mg, 89%) was crystallized from chloroform/methanol. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm) δ: 2.36 (s, 3H, CH_3), 2.93 (t, J=6.8 Hz, 2H, 3″-H), 4.34 (t, J=6.8 Hz, 2H, 2″-H), 5.06 (s, 2H, $CH_2C_6H_5$), 6.23 (d, J=7.6 Hz, 1H, 5′-H), 7.34–7.41 and 7.45–7.47 (2 m, 5H, $CH_2C_6H_5$), 7.74 (d, J=7.6 Hz, 1H, 6′-H), 7.78–7.81 (m, 9H, 10,15,20-Ph−H_{m+p}), 7.98 (d, J=8.8 Hz, 2H, 5-Ar−H_m), 8.11 (d, J=8.8 Hz, 2H, 5-Ar−H_o), 8.17–8.19 (m, 6H, 10,15,20-Ph−H_o), 8.75–8.81 (m, 8H, H-β), 10.46 (s, 1H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm) δ: 11.9 (CH_3), 37.1 (3″-C), 48.9 (2″-C), 71.8 ($CH_2C_6H_5$), 116.1 (5′-C), 117.1, 120.0, 120.2, 126.5, 127.4, 127.7, 128.1, 128.3, 131.5, 134.0, 134.5, 139.5 (6′-C), 140.6 (2′-C), 142.6, 145.3 (3′-

C), 149.1, 149.2, 149.3, 168.3 (1″-C), 171.8 (4′-C). ESI-MS/MS *m*/*z*: 961 $[M+H]^+$.

*4.2.2. Synthesis of copper(II) complex (**10a**).* Metalation of porphyrin **8a** (70.0 mg, 78.0 μmol) with Cu(II) was accomplished by refluxing copper acetate hydrate (31.2 mg, 0.156 mmol, 2 equiv) in 40 mL of a mixture of chloroform/methanol (5:2), using the general protocol. Cu(II) complex **10a** (64.3 mg) was obtained in 86% yield. ESI-MS/MS *m*/*z*: 960 $[M+H]^+$.

*4.2.3. Synthesis of zinc(II) complex (**9b**).* Metalation of porphyrin **8b** (35.0 mg, 30 μmol) with Zn(II) was accomplished by refluxing zinc acetate hydrate (13.0 mg, 60 μmol, 2 equiv) in 20 mL of a mixture of chloroform/methanol (5:2), using the general protocol. The Zn(II) complex **9b** (36.0 mg 98% yield) was crystallized from chloroform/methanol. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm) δ: 2.43 (s, 6H, 2× CH_3), 2.98 (t, *J*=6.8 Hz, 4H, 2×3″-H), 4.44 (t, *J*=6.8 Hz, 4H, 2×2″-H), 5.08 (s, 4H, 2× $CH_2C_6H_5$), 6.48 (d, *J*=7.0 Hz, 2H, 2× H-5′), 7.35–7.43 and 7.47–7.49 (2 m, 10H, 2× $CH_2C_6H_5$), 7.79–7.81 (m, 6H, 15,20-Ph–H_{m+p}), 7.93 (d, *J*=7.0 Hz, 2H, 2×6′-H), 7.98 (d, *J*=8.4 Hz, 4H, 5,10-Ar–H_m), 8.11 (d, *J*=8.4 Hz, 4H, 5,10-Ar–H_o), 8.16–8.19 (m, 4H, 15,20-Ph–H_o), 8.74–8.80 (m, 8H, H-β), 10.48 (s, 2H, 2× NH). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm) δ: 12.3 (CH_3), 36.9 (C-3″) 49.7 (C-2″), 72.4 ($CH_2C_6H_5$), 115.4, 117.2, 120.0, 120.2, 126.6, 128.0, 128.3, 128.4, 131.6, 134.1, 134.5, 137.5, 137.7, 138.2, 140.4, 142.7 (C-2′), 144.9 (C-3′), 149.24, 149.42, 168.3 (C-1″), 171.0 (C-4′).

*4.2.4. Synthesis of copper(II) complex (**10b**).* Metalation of porphyrin **8b** (35.0 mg, 0.30 μmol) with Cu(II) was accomplished by refluxing copper acetate hydrate (11.8 mg, 0.60 μmol, 2 equiv) in 20 mL of a mixture of chloroform/methanol (5:2), using the general procedure. Cu(II) complex **10b** (36.0 mg) was obtained in 98% yield.

4.3. General hydrogenolysis procedure

Pd/C (10%) (catalytic amount) was added to a solution of porphyrin in DMF (minimal volume) and the resulting mixture was subjected to hydrogenolysis (H_2, 5 bar) until hydrogen uptake ceased. The resulting solution was filtered to remove the catalyst (in case of hydrogenolysis with porphyrins **1** and **4**, a few drops of HCl were added in order to solubilize the porphyrins in DMF). The solvent was removed under reduced pressure and the resulting residue was crystallized.

*4.3.1. Synthesis of porphyrin (**P1**).* Pd/C (10%) (catalytic amount) was added to a solution of porphyrin **8a** (8.5 mg, 9.46 μmol) in DMF (3 mL) and the resulting mixture was subjected to hydrogenolysis, following general procedure. The resulting residue was crystallized from chloroform/methanol to give **P1** (6.3 mg, 83%). [Found: C 71.55; H, 5.62; N, 9.56. $C_{53}H_{40}N_6O_3\cdot 9/2H_2O$ requires: C, 71.53; H, 5.55; N, 9.44%]; UV–vis (DMSO), λ_{max} nm (log ε) 421 (5.42), 516 (4.01), 554 (3.88) 596 (3.62) and 648 (3.51). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm) δ: −2.92 (s, 2H, NH), 2.53 (s, 3H, CH_3), 3.00 (t, *J*=6.8 Hz, 2H, 3″-H), 4.47 (t, *J*=6.8 Hz, 2H, 3″-H), 6.34 (d, *J*=6.4 Hz, 1H, 5′-H), 7.54 (d, *J*=6.4 Hz, 1H, 6′-H), 7.79–7.85 (m, 9H, 10,15,20-Ph–H_{m+p}), 8.03 (d, *J*=8.4 Hz, 2H, 5-Ar–H_m), 8.17 (d, *J*=8.4 Hz, 2H, 5-Ar–H_o), 8.20–8.23 (m, 6H, 10,15,20-Ph–H_o), 8.76–8.82 (m, 8H, H-β), 10.50 (s, 1H, NH). ESI-MS/MS *m*/*z*: 809 $[M+H]^+$.

*4.3.2. Synthesis of zinc(II) complex (**P2**).* Pd/C (10%) (catalytic amount) was added to a solution of porphyrin **9a** (63.6 mg, 66.3 μmol) in DMF (20 mL) and the resulting mixture was subjected to hydrogenolysis, following general procedure. The resulting obtained residue was recrystallized from chloroform/methanol to give **P2** (40.3 mg, 70%). [Found: C, 68.01; H, 4.57; N, 8.65. $C_{53}H_{38}N_6O_3Zn$. CH_2Cl_2 requires: C, 67.75; H, 4.21; N, 8.78%]; UV–vis (DMSO), λ_{max} nm (log ε): 429 (5.77), 561 (4.29) and 601 (4.05). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm) δ: 2.45 (s, 3H, CH_3), 2.97 (t, *J*=6.8 Hz, 2H, 3″-H), 4.40 (t, *J*=6.8 Hz, 2H, 3″-H), 6.22 (d, *J*=7.2 Hz, 1H, 5′-H), 7.71 (d, *J*=7.2 Hz, 1H, 6′-H), 7.79–7.80 (m, 9H, 10,15,20-Ph–H_{m+p}), 7.98 (d, *J*=8.4 Hz, 2H, 5-Ar–H_m), 8.11 (d, *J*=8.4 Hz, 2H, 5-Ar–H_o), 8.17–8.19 (m, 6H, 10,15,20-Ph–H_o), 8.76–8.82 (m, 8H, H-β), 10.47 (s, 1H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm) δ: 11.4 (CH_3), 37.2 (3″-C), 49.1 (2″-C), 110.7 (5′-C), 117.2, 120.0, 120.1, 120.2, 126.5, 127.4, 128.8 (2′-C), 131.5, 131.6, 134.1, 134.5, 137.6, 137.8 (6′-C), 138.1, 142.6, 145.4 (3′-C), 149.12, 149.16, 149.4, 168.3 (1″C), 168.7 (4′-C). ESI-MS/MS *m*/*z*: 871 $[M+H]^+$.

*4.3.3. Synthesis of copper(II) complex (**P3**).* Pd/C (10%) (catalytic amount) was added to a solution of porphyrin **10a** (63.2 mg, 65.9 μmol) in DMF (20 mL) and the resulting mixture was subjected to hydrogenolysis, following general procedure. The resulting residue was recrystallized from chloroform/methanol to give **P3** (40.3 mg, 70%). [Found: C, 71.38; H, 4.07; N, 9.41. $C_{53}H_{38}CuN_6O_3\cdot H_2O$ requires C, 71.65; H, 4.54; N, 9.46%]; UV–vis (DMSO), λ_{max} nm (log ε): 419 (5.59) and 542 (4.28). ESI-MS/MS *m*/*z*: 870 $[M+H]^+$.

*4.3.4. Synthesis of porphyrin (**P4**).* Pd/C (10%) (catalytic amount) was added to a solution of porphyrin **8b** (30 mg, 25.4 μmol) in DMF (20 mL) and the resulting mixture was subjected to hydrogenolysis, following general procedure. The resulting residue was recrystallized from chloroform/methanol to give **P4** (19 mg, 75%). [Found: C, 56.69; H, 4.60; N, 8.83. $C_{62}H_{50}N_8O_6\cdot 4H_2O\cdot 4HCl$ $CHCl_3$ requires C, 56.45; H, 4.74; N, 8.36; UV–vis (DMSO), λ_{max} nm (log ε): 422 (5.52), 516 (4.15), 554 (3.95), 592 (3.69) and 648 (3.73). ^{1}H NMR (DMSO-d_6+TFA, 400 MHz, ppm) δ: 2.71 (s, 6H, 2× CH_3), 3.19–3.22 (m, 4H, 2×3″-H), 4.79–4.82 (m, 4H, 2×3″-H), 7.25 (d, *J*=7.0 Hz, 2H, 2× H-5′), 8.03–8.08 (m, 6H, 15,20-Ph–H_{m+p}), 8.33 (d, *J*=8.4 Hz, 4H, 5,10-Ar–H_m), 8.36 (d, *J*=7.0 Hz, 2H, 2× H-6′), 8.62–8.71 (m, 16H, 5,10-Ar–H_o and 15,20-Ph–H_o and H-β), 10.85 (s, 2H, 2× NH). ESI-MS/MS *m*/*z*: 1003 $[M+H]^+$.

*4.3.5. Synthesis of zinc(II) complex (**P5**).* Pd/C (10%) (catalytic amount) was added to a solution of porphyrin **9b** (35.0 mg, 28 μmol) in DMF (20 mL) and the resulting mixture was subjected to hydrogenolysis, following general procedure. The resulting residue was recrystallized from chloroform/methanol to give **P5** (14.6 mg, 49%). [Found: C, 62.59; H, 3.81; N, 9.19. $C_{62}H_{48}N_8O_6Zn\cdot CHCl_3\cdot H_2O$ requires C, 62.85; H, 4.27; N, 9.31%]; UV–vis (DMSO), λ_{max} nm (log ε): 430 (5.72), 562 (4.25) and 602 (4.04). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm) δ: 2.45 (s, 6H, 2× CH_3), 2.94–3.01 (m, 4H, 2×3″-H), 4.36–4.43 (m, 4H, 2×3″-H), 6.21 (d, *J*=7.2 Hz, 2H, 2× H-5′), 7.69 (d, *J*=7.2 Hz, 2H, 2× H-6′), 7.77–7.84 (m, 6H, 15,20-Ph–H_{m+p}), 7.98 (d, *J*=8.0 Hz, 4H, 5,10-Ar–H_m), 8.11 (d, *J*=8.0 Hz, 4H, 5,10-Ar–H_o), 8.17–8.18 (m, 4H, 15,20-Ph–H_o), 8.75–8.82 (m, 8H, H-β), 10.47 (s, 2H, 2× NH). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm) δ: 11.4 (CH_3), 37.3 (C-3″), 49.2 (C-2″), 110.5 (C-5′), 117.2, 120.0, 120.1, 120.6, 126.5, 127.4, 128.6 (C-2′), 131.4, 131.6, 134.1, 134.5, 137.6 (C-6′), 138.1, 142.6, 145.4 (C-3′), 149.10, 149.14, 149.29, 149.33, 168.3 (C-1″), 169.0 (C-4′). ESI-MS/MS *m*/*z*: 1065 $[M+H]^+$.

*4.3.6. Synthesis of copper(II) complex (**P6**).* Pd/C (10%) (catalytic amount) was added to a solution of porphyrin **10b** (34.7 mg, 0.28 μmol) in DMF (20 mL) and the resulting mixture was subjected to hydrogenolysis, following general procedure. **P6** (18.8 mg) was obtained in 63% of yield. [Found: C, 64.07; H, 4.25; N, 9.58. $C_{62}H_{48}CuN_8O_6$. $CHCl_3$ requires C, 63.91; H, 4.17; N, 9.46%]; UV–vis (DMSO), λ_{max} nm (log ε): 421 (5.53), 543 (4.23). ESI-MS/MS *m*/*z*: 1064 $[M+H]^+$.

*4.3.7. Synthesis of copper(II) complex (**11**).* Complexation of metalloporphyrin **P5** was accomplished by refluxing a mixture of **P5**:

copper acetate hydrate (1:1) in chloroform/methanol (5:2), following the general procedure. The resulting complex **11** was filtered, dried and characterized by EPR spectroscopy.

4.4. Spectroscopic studies

UV–vis measurements: Electronic absorption spectra were recorded with a Varian Cary bio50 spectrophotometer, equipped with a Varian Cary single cell Peltier accessory. Spectra were recorded at 25 °C in 1 cm path length quartz cells with a slit width of 1 nm, in the range 350–750 nm. Spectra were record in dried DMSO and acetonitrile. Stock solutions of the compounds were obtained by dissolution in DMSO. Samples were prepared by dissolving of a known volume of the DMSO stock solution (the percentage of the DMSO in the final volume in case of the acetonitrile solutions was always less than 1% in the final volume). Typical solution concentrations for the determination of the molar extinction coefficient were 8×10^{-5}–2×10^{-6} M.

Fluorescence measurements: Fluorescence measurements were carried out in a Varian spectrofluorometer, model Cary Eclipse, equipped with a constant-temperature cell holder (Peltier single cell holder). Stock solutions of the compounds were obtained by dissolution in DMSO. All solutions were prepared by dilution of the right amount of the stock solution in the solvent (% DMSO less than 1% when the solvent was acetonitrile). The spectra in DMSO and acetonitrile were obtained using λ_{exc} in the range 421 nm–430 nm and emission between 550 and 800 nm. The slit width values used for excitation end emission processes were 5 for porphyrins **P1**, **P2**, **P3**, **P4**, and **P5** and 10 for porphyrin **P3** and **P6** in DMSO and acetonitrile.

Electron paramagnetic resonance: EPR spectra were recorded in frozen solution in the temperature range 20–77 K using an X-band (9 GHz) Bruker EMX spectrometer equipped with a variable temperature unit (Oxford ESR900) and a frequency meter. The samples were prepared by dissolution of compound in dried toluene or DMSO, placed in quartz tubes and frozen. Regarding the samples for the titration of porphyrin **P4** with copper (II), different solutions were prepared by mixing the right amounts of porphyrin and copper (II) solution in the ratios 1:0.5, 1:1, 1:2, and 1:4. The copper (II) solution was prepared by dissolution of its acetate salt in methanol, while the porphyrin was dissolved in DMSO. A concentration range of $1–5\times10^{-3}$ M was used. The Spin-Hamiltonian parameters were determined by simulation of the experimental spectra using the computer suite Bruker WinEPR/SimFonia.

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Supplementary data

The supplementary data contains selected NMR spectra (^{1}H, ^{13}C, COSY, HMBC, and HSQC) and mass spectra of compounds. Fluorescence spectra in acetonitrile are also available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.07.063.

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