

Supramolecular Self-Assembly of 5,10,15,20-Tetrakis-(3-hydroxyphenyl)porphyrinatozinc with Some Transition Metals and Bidentate Ligands

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Abstract—Coordination interactions between 5,10,15,20-tetrakis(3-hydroxyphenyl)porphyrinatozinc(II) and transition metal chlorides [La(III), Mn(II), Cr(III), Sn(II)], 1,4-diazabicyclo[2.2.2]octane, and 4,4'-bipyridine were studied. Self-assembly of supramolecular bis-porphyrin structures was developed.

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Studies on porphyrin-based supramolecular structures are important due to unique optical and electrochemical properties and high thermal and chemical stability of such systems, which make them promising from the viewpoint of design of new materials for photoconductors, nonlinear optics, catalysis, membrane technology, and medicine [1–3]. Self-assembly involves selective binding of a substrate (guest molecule) by receptor (host) via molecular recognition [4]. The rigid porphyrin skeleton makes cyclic tetrapyrroles ideal structural units of a supramolecular associate (host molecule) where substituents capable of interacting in different ways with guest molecules are arranged in a definite order.

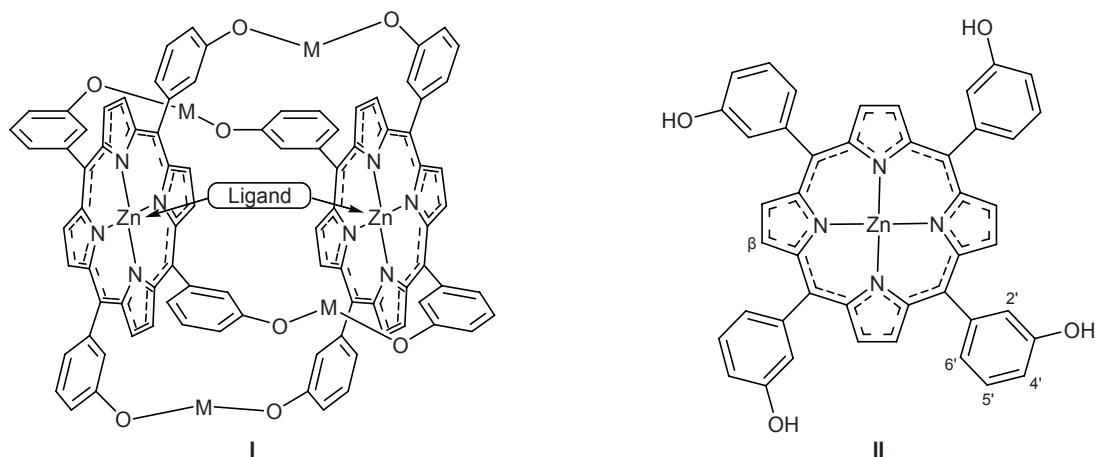
Metal porphyrin receptors are capable of recognizing various species via axial (extra) coordination of ligands at the central metal ion [5]. Coordination structures containing metalloporphyrins belong to a specific group of structurally organized systems whose molecular components possess unique selectivity; the conditions of their formation and stability depend on the metal nature and properties of the metalloporphyrin which constitutes the base of supramolecule [6].

The goal of the present study was to build up bis-porphyrin structures formed as a result of self-association of molecular components via coordination interactions. The target structure was supramolecular dimer **I** consisting of two metalloporphyrin fragments

which are held together through axial coordination of a bidentate ligand and possessing additional peripheral centers for binding metal cations. As base structural component we selected 5,10,15,20-tetrakis(3-hydroxyphenyl)porphyrinatozinc(II) (**II**, ZnTHPP) having several potential reaction centers and therefore capable of forming numerous bonds. The central Zn(II) ion in **II** is coordinately unsaturated, so that extra coordination is possible. Peripheral hydroxy group can also be involved in donor–acceptor interactions with metal cations.

Self-assembly processes imply that the components be complementary, i.e., the ratio between information provided by receptor and information that can be perceived by substrate should be optimal. Such information may be encoded in the receptor architecture and its binding sites [4]. Thus, “instruction” for assembly of a supramolecular system is put into the structure of its low-molecular components.

Structural specificity of metalloporphyrin receptor **II** imply assembly of just dimeric supramolecular associates so that axial ligand be oriented orthogonally to the plane of the porphyrin macroring. If a bidentate ligand is coordinated through both coordination centers, two porphyrin fragments are arranged in parallel planes. Zinc porphyrins are capable of accepting only one axial ligand to give five-coordinate central metal ion [7]), which prevents formation of polymeric structures.



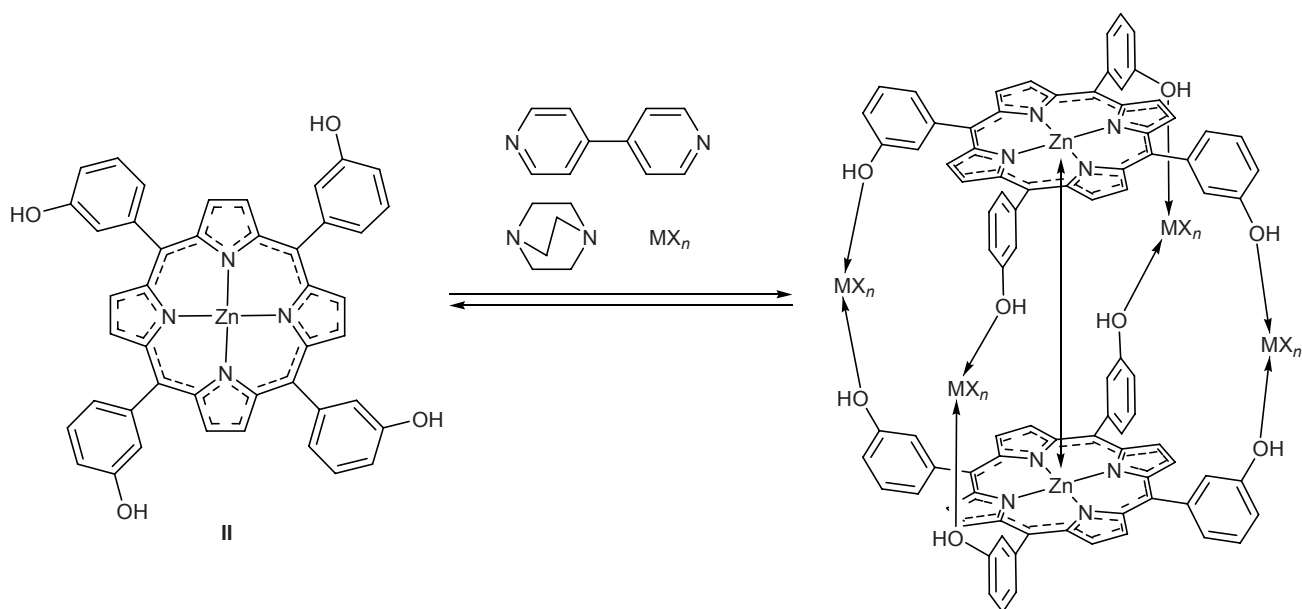
Peripheral hydroxy groups in the *meta* positions of the α^4 -atropisomer are oriented in accordance with the axial ligand position (Scheme 1), whereas *para* position of the self-complementary hydroxy groups favors formation of netlike polymeric structures [8, 9]. Two zinc porphyrin fragments may be linked via coordination with a bidentate ligand which plays the role of intermolecular spacer. Taking into account the nature of the central metal ion, we examined nitrogen-containing bidentate ligands, 1,4-diazabicyclo[2.2.2]octane (**III**, DABCO) and 4,4'-bipyridine (**IV**, 4,4'-bpy).

Porphyrinatozinc **II** can react with a bidentate ligand to give 1:1 and 2:1 complexes (Scheme 2) whose composition will depend on the reactant ratio and ligand nature [10, 11]. Extra coordination is readily reversible, and the stability of the resulting com-

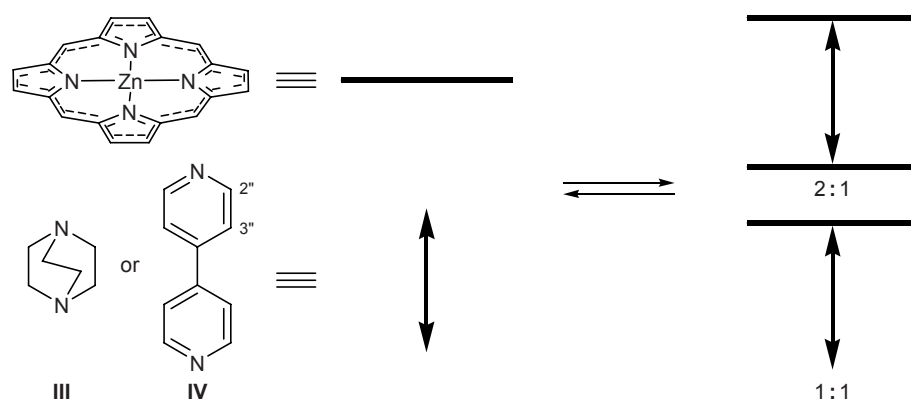
plexes should be determined by the reaction medium. The largest association constants (K_a) are usually observed in inert aromatic solvents (benzene, toluene), while polar solvents favor displacement of the complex formation equilibrium toward initial metalloporphyrin [5, 6]. 5,10,15,20-Tetrakis(3-hydroxyphenyl)-porphyrinatozinc is soluble only in polar medium, which considerably hinders the extra coordination process.

The reaction of ZnTHPP with 0.5 equiv of DABCO was accompanied by upfield shift of signals from the β -protons and ($\Delta\delta = -0.33$ ppm) and protons in the benzene rings ($\Delta\delta \approx -0.2$ ppm) in the ^1H NMR spectrum; the signal from protons in DABCO was also displaced upfield ($\delta -4$ to -5 ppm; $\Delta\delta \approx -7$ ppm). In keeping with published data [10–13], we presumed

Scheme 1.



Scheme 2.



formation of a 2:1 complex in which two ZnTHPP molecules are linked through DABCO molecule. Mutual influence of the two porphyrin fragments leads to additional shielding of protons therein. The coordinated ligand is weakly held in the cavity formed by the porphyrin macrocycles; free and coordinated ligands are readily exchanged in solution at room temperature, thus leading to considerable broadening of the ligand signals in the ^1H NMR spectrum [14, 15]. In the presence of more than 1 equiv of DABCO, the upfield shift of the ZnTHPP proton signals is insignificant; presumably, in this case ZnTHPP–DABCO complex with a composition of 1:1 is formed. Upfield shift of signals from protons in the guest molecule results from strong shielding by the ring current in the porphyrin macrocycle [10, 11]. The upfield shift attains its maximal value when 2:1 complex is formed, for the shielding produced by two porphyrin macrocycles is twice as strong.

In the reaction of ZnTHPP with 0.5 equiv of 4,4'-bpy and more, the chemical shifts of protons in the former change insignificantly ($\Delta\delta \approx -0.05$ ppm). By contrast, the signals from 4,4'-bpy are displaced considerably upfield, the 3''-H signal being displaced to a lesser extent ($\Delta\delta \approx -1.3$ ppm) than that of 2''-H ($\Delta\delta \approx -3.3$ ppm). This is readily understood, for the 3''-H protons are more distant from the porphyrin macrocycles. As with DABCO, the signals from protons (especially from 2''-H) in the 4,4'-bpy ligand are broadened. Probably, in this case 1:1 complex is formed. According to published data [16], the upfield shift of 4,4'-bpy signals upon formation of 2:1 complex should be greater ($\Delta\delta \approx -3$ and -7 ppm for 3''-H and 2''-H, respectively).

Thus ZnTHPP with the above ligands in polar medium forms preferentially 1:1 complexes, though the formation of labile 2:1 complexes is also possible.

Obviously, additional binding centers are necessary to ensure stability of structure I.

Bidentate coordination of a ligand by two metalloporphyrin macrocycles makes the latter spatially closer, so that the peripheral hydroxy groups adopt appropriate orientation for donor–acceptor interaction with external metal ions (Scheme 1). Just the presence of a bidentate ligand should favor assembly of the desired structure from monomeric species present in solution [17].

We used anhydrous oxophilic metal salts MX_n ($\text{M} = \text{Mn}^{2+}$, Cr^{3+} , Sn^{2+} , La^{3+}) to ensure binding at the hydroxy groups and avoid competition between the latter and electron-donating nitrogen atoms in the ligand. The reactions were carried out at low reactant concentrations ($\sim 10^{-3}$ M) to prevent formation of various oligomers. In the reaction of ZnTHPP with MnCl_2 in the presence of DABCO or 4,4'-bpy, signals in the ^1H NMR spectrum of the reaction mixture were strongly broadened and were difficult to interpret; a probable reason is paramagnetic effect of manganese cation. The reactions of ZnTHPP with SnCl_2 and CrCl_3 in the presence of 0.5 equiv of DABCO or 4,4'-bpy were accompanied by protonation of the porphyrin macrocycle, presumably due to liberation of hydrogen chloride.

The best results were obtained in the reaction of ZnTHPP with 2 equiv of anhydrous lanthanum(III) chloride. The resulting complexes were soluble only in strongly coordinating solvents like $\text{DMSO}-d_6$ that are capable of destroying coordination dimers; in this case ^1H NMR spectroscopy becomes noninformative. Therefore, the self-assembly processes were studied by MALDI TOF mass spectrometry. The energy of intermolecular interactions is much smaller than the energy of covalent bonds, so that weak coordination bonds are partially disrupted as a result of ionization, and the

intensity of ion peaks corresponding to supramolecular associates is much lesser than the intensity of those corresponding to molecular fragments.

In the reaction with 4,4'-bpy as ligand, the mass spectrum of the reaction mixture contained three groups of signals (isotope multiplets) corresponding to three dimeric structures **V–VII**. Presumably, lanthanum cations coordinate water molecules on exposure to air during application of a sample onto the target. Thus two modes of association of ZnTHPP are possible: self-complementary via hydrogen bonding with formation of simple (ZnTHPP)₂ dimer **VII** and hetero-complementary through coordination to Ln(III) with formation of structure **VI** which can accommodate 4,4'-bpy molecule.

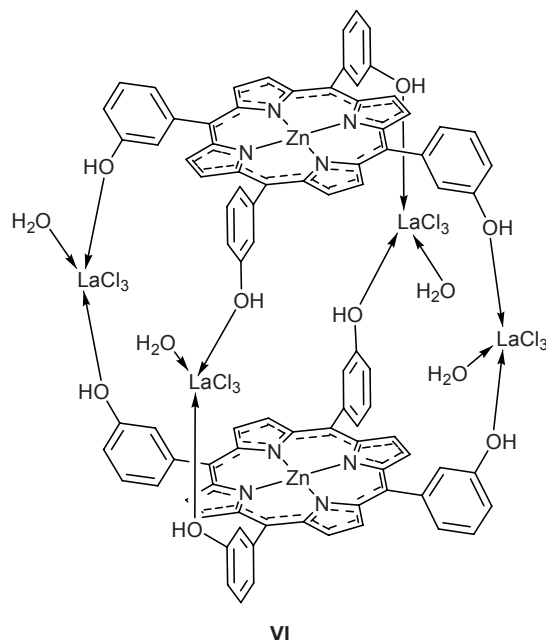
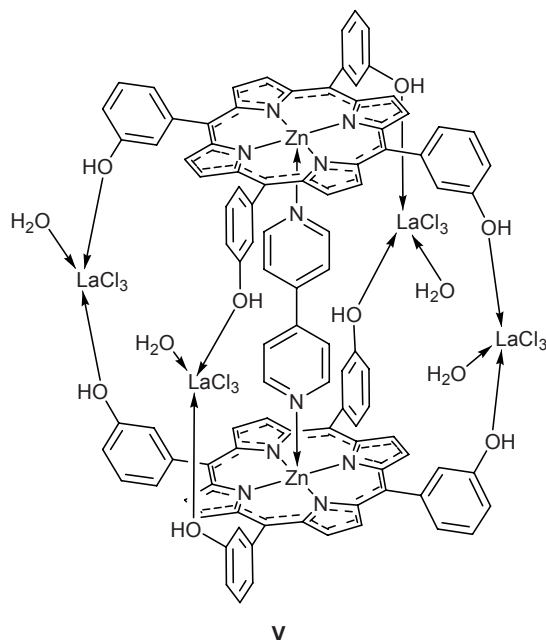
According to the mass spectra, only dimers **VI** and **VII** are formed in the presence of DABCO. A probable reason is that the size of the DABCO molecule (3.75 Å; cf. 7 Å for 4,4'-bpy) does not fit the dimer cavity, so that coordination bonds with the ligand are weak, and complex like **V** is not formed.

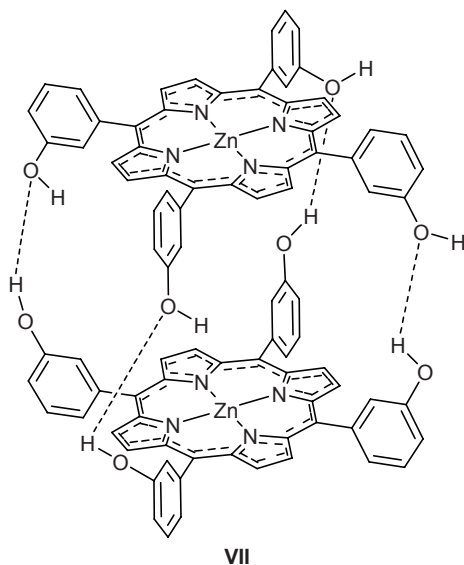
Dimer **VII** was detected in the mass spectra of all reaction mixtures containing ZnTHPP. It is readily formed in solution via hydrogen bonding between the peripheral hydroxy groups. Similar orientations of the phenyl rings in **II** with respect to the porphyrin macro-ring (α^4 -atropoisomer) give rise to four binding centers which ensure stability of that dimeric structure in solution.

The electronic absorption spectra of the complexes are characterized by blue shift of the lanthanum ab-

sorption maximum ($\Delta\lambda = 23$ nm). Analogous shift is observed in the absence of ligand (DABCO or 4,4'-bpy), indicating selective coordination of LaCl₃ at the hydroxy groups of ZnTHPP. The position of the Soret band in the spectrum of complex **VII** remains unchanged; it also does not change in the presence of various amounts of lanthanum(III) chloride and 4,4'-bipyridine. In keeping with published data, coordination of 4,4'-bipyridine inside the porphyrin dimer cavity should be accompanied by a 1–2-nm red shift of the Soret band, but such shift is often not observed in the spectra [10]. The formation of “face-to-face” dimer should lead to a blue shift of the Soret band as a result of interactions between electrons in the two porphyrin systems [18]; presumably, these opposite effects compensate each other.

To conclude, we have studied self-assembly of coordination dimers from 5,10,15,20-tetrakis(3-hydroxyphenyl)porphyrinatozinc(II) and a number of metal cations and exobidentate ligands. The formation of supramolecular dimers with different structures was detected by MALDI TOF mass spectrometry. In particular, coordination dimer with lanthanum(III) chloride possesses a cavity where reversible coordination of 4,4'-bipyridine is possible. Stable supramolecular bis-porphyrin structures can be formed via coordination of four peripheral centers to external metal ions. These structures give rise to labile complexes with exobidentate ligands. The stability of such complexes could be enhanced by introducing stronger peripheral ligand centers with a view to isolate them as individual substances.





EXPERIMENTAL

The progress of reactions and the purity of products were monitored by thin-layer chromatography on Merck 60 F₂₅₄ silica gel plates. Column chromatography was performed on silica gel 60 (Alfa Aesar, 70–230 mesh).

The electronic absorption spectra in the visible and UV regions were measured on a Varian Cary-100 spectrophotometer using rectangular quartz cells (cell path length 10 mm). The ¹H NMR spectra were recorded at room temperature on a Bruker AM-400 spectrometer (400 MHz); the chemical shifts were determined relative to the residual proton signals of deuterated solvents (acetone-*d*₆, δ 2.06 ppm; DMSO-*d*₆, δ 2.50 ppm). The mass spectra (MALDI TOF) were obtained on a Bruker Daltonics Ultraflex mass spectrometer (positive ion registration, target voltage 20 mV, no matrix).

Anhydrous lanthanum(III) chloride was prepared by reaction of 0.63 g (3.07 mmol) of La₂O₃ with 2 ml of 37% hydrochloric acid. Excess HCl and water were removed on a rotary evaporator, and the residue was dried with SOCl₂. 5,10,15,20-Tetrakis(3-hydroxyphenyl)porphyrin (THPP) was synthesized in 20% yield according to the procedure described in [19]; its NMR, UV, and mass spectra were consistent with published data.

5,10,15,20-Tetrakis(3-hydroxyphenyl)porphyrinatozinc(II) (II). Zinc(II) acetate dihydrate, 1676 mg (7.6 mmol), was dissolved in ~100 ml of acetonitrile on heating under stirring, 260 mg (0.383 mmol) of THPP was added, and the mixture was stirred for 4 h,

the progress of the reaction being monitored by TLC. The mixture was filtered through a layer of silica gel (~30 g) to collect the main purple fraction. Removal of the solvent on a rotary evaporator gave 257 mg (98%) of complex **II** as a dark red amorphous substance. ¹H NMR spectrum (acetone-*d*₆), δ, ppm: 7.31 d.d (4H, 4'-H, ³*J* = 8.3, 1.5 Hz), 7.61 t (4H, 5'-H, ³*J* = 7.8 Hz), 7.71 d (4H, 6'-H, ³*J* = 7.8 Hz), 7.73 s (4H, 2'-H), 8.73 s (4H, OH), 8.96 s (8H, β-H). Electronic absorption spectrum (THF), λ_{max}, nm (ε × 10⁻³, 1 mol⁻¹ cm⁻¹): 555 (10), 595 (2.7), 422 (164) (Soret band). Mass spectrum: *m/z* 740 (*I*_{rel} 100%) [*M*]⁺.

Reaction of ZnTHPP with 1,4-diazabicyclo[2.2.2]octane (III). *a.* A 0.061 M solution of DABCO (**III**) in carbon tetrachloride, 80 μl (0.005 mmol), was added to a solution of 7.7 mg (0.01 mmol) of ZnTHPP (**II**) in 0.5 ml of acetone-*d*₆. ¹H NMR spectrum (acetone-*d*₆), δ, ppm: -5 to -4 br.s (6H, C₆H₁₂N₂), 7.19 d (4H, 4'-H, ³*J* = 7.5 Hz), 7.38 br.s (4H, 5'-H), 7.43–7.47 m (8H, 6'-H, 2'-H), 8.21–8.25 br.s (4H, OH), 8.63 s (8H, β-H).

b. A 0.061 M solution of DABCO (**III**) in carbon tetrachloride, 165 μl (0.01 mmol), was added to a solution of 7.7 mg (0.01 mmol) of ZnTHPP (**II**) in 0.5 ml of acetone-*d*₆. ¹H NMR spectrum (acetone-*d*₆), δ, ppm: 0.07 br.s (12H, C₆H₁₂N₂), 7.28 m (4H, 4'-H), 7.55 m (8H, 5'-H, 6'-H), 7.62 s (4H, 2'-H), 8.53 s (4H, OH), 8.81 s (8H, β-H).

c. A 0.061 M solution of DABCO (**III**) in carbon tetrachloride, 1 ml (0.06 mmol), was added to a solution of 7.7 mg (0.01 mmol) of ZnTHPP (**II**) in 0.5 ml of acetone-*d*₆. ¹H NMR spectrum (acetone-*d*₆), δ, ppm: 2.23 s (72H, C₆H₁₂N₂), 7.17 d.d (4H, 4'-H, ³*J* = 8.3, 1.5 Hz), 7.50 t (4H, 5'-H, ³*J* = 7.8 Hz), 7.60 m (8H, 6'-H, 2'-H), 8.87 s (8H, β-H). ¹H NMR spectrum of pure DABCO (acetone-*d*₆): δ 2.67 ppm, s.

Reaction of ZnTHPP with 4,4'-bipyridine (IV). *a.* A 0.013 M solution of 4,4'-bipyridine (**IV**) in acetonitrile, 420 μl (0.006 mmol), was added to a solution of 8 mg (0.011 mmol) of ZnTHPP (**II**) in 6 ml of acetonitrile, and the mixture was stirred for 1 h. ¹H NMR spectrum (acetone-*d*₆), δ, ppm: 5.43 br.s (2H, 2''-H), 6.45 br.s (2H, 3''-H), 7.26 m (4H, 4'-H), 7.54 t (4H, 5'-H, ³*J* = 7.8 Hz), 7.62 m (4H, 6'-H), 7.65 m (4H, 2'-H), 8.68 s (4H, OH), 8.89 s (8H, β-H).

b. A 0.013 M solution of 4,4'-bipyridine (**IV**) in acetonitrile, 1.7 ml (0.022 mmol), was added to a solution of 8 mg (0.011 mmol) of ZnTHPP (**II**) in 6 ml of acetonitrile, and the mixture was stirred for 1 h. ¹H NMR spectrum (acetone-*d*₆), δ, ppm: 6.84 br.s (8H,

2''-H), 7.00 br.s (8H, 3''-H), 7.28 m (4H, 4'-H), 7.56 t (4H, 5'-H, $^3J = 7.8$ Hz), 7.65 m (4H, 6'-H), 7.68 m (4H, 2'-H), 8.69 s (4H, OH), 8.92 m (8H, β -H). ^1H NMR spectrum of pure 4,4'-bipyridine (IV) (acetone- d_6), δ , ppm: 7.76 m (3-H), 8.74 m (2-H).

Reaction of ZnTHPP (II) with LaCl_3 in the presence of 4,4'-bipyridine (IV). A 0.008 M solution of 4,4'-bipyridine (IV) in anhydrous tetrahydrofuran, 810 μl (0.0068 mmol), was added under stirring to a solution of 10 mg (0.0135 mmol) of ZnTHPP (II) in 15 ml of anhydrous THF, 1.125 ml of a 0.024 M solution of LaCl_3 in anhydrous DMF was then added, and the mixture was stirred for 2 h. ^1H NMR spectrum (DMSO- d_6 -acetone- d_6), δ , ppm: 7.27 d (4H, 4'-H, $^3J = 8.1$ Hz), 7.54 t (4H, 5'-H, $^3J = 7.8$ Hz), 7.62 (4H, 6'-H), 7.74 m (4H, 2'-H), 7.78 d (2H, 3''-H), $^3J = 5.8$ Hz), 8.65 d (2H, 2''-H, $^3J = 5.8$ Hz), 8.87 s (8H, β -H), 10.03 s (4H, OH). Mass spectrum, m/z (I_{rel} , %): 740.4 (100) (ZnTHPP), 810 (40), 1483.3 (12.7) (VII), 2533.6 (2) (VI), 2684.7 (10) (V).

Reaction of ZnTHPP (II) with LaCl_3 in the presence of DABCO (III). A 0.085 M solution of DABCO (III) in anhydrous THF, 80 μl (0.0068 mmol), was added under stirring to a solution of 10 mg (0.0135 mmol) of ZnTHPP (II) in 15 ml of anhydrous THF, 1.125 ml of a 0.024 M solution of LaCl_3 in anhydrous DMF was then added, and the mixture was stirred for 2 h. ^1H NMR spectrum (DMSO- d_6 -acetone- d_6), δ , ppm: 1.7–2.0 br.s (6H, $\text{C}_6\text{H}_{12}\text{N}_2$), 7.27 d (4H, 4'-H, $^3J = 8.1$ Hz), 7.54 t (4H, 5'-H, $^3J = 7.8$ Hz), 7.62 m (4H, 6'-H), 7.75 m (4H, 2'-H), 8.89 s (8H, β -H), 9.94 s (4H, OH). Mass spectrum, m/z (I_{rel} , %): 739.6 (100) (ZnTHPP), 812.3 (41), 1482.0 (13.6) (VII), 2533.5 (3) (VI).

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