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Synthesis and Characterization of a New Asymmetric Bis-Porphyrinato Lanthanide Complex Presenting Mixed Hydrophilic–Hydrophobic Properties and Its Precursor Form

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The synthesis and spectroscopic characterization of a new family of heteroleptic porphyrinate double-deckers are reported. The investigated compounds are represented by the formulae $La^{III}H(TPyP)(TPP)$ and $[La^{III}(TMePyP)(TPP)]I_3$. UV–vis spectroscopy of the title complexes confirms the presence of a strong π–π interaction between the macrocycles in each derivative. With ^1H and 2-D NMR data, we were able to distinguish two major NMR regions: the *endo*, between the bonded macrocycles, and the *exo*, outside the macrocycles, which are characteristic features of porphyrinic double-deckers. Finally, the electrochemical study confirms the strong π–π interaction for $La^{III}H(TPyP)(TPP)$ and completes this first approach for the investigation of this new family of derivatives.

Introduction

Complexes that contain two porphyrin macrocycles bound to a single metal center are proven to be useful as structural and spectroscopic models of the reaction center of bacteriochlorophyll *b*, the so-called "special pair" in photosynthesis.[1] Most of the lanthanide and actinide sandwich porphyrins that have been synthesized thus far are symmetrical (the two porphyrin rings are identical).[2] Only a few reports on the synthesis of some heteroleptic porphyrin complexes have been reported.[3] For all, so far reported, metalloporphyrinic derivatives of this type with rare earth elements, the two porphyrinic units possess the same form, cationic or neutral. This contribution concerns a new family of asymmetric derivatives presenting biphasic properties and describes the synthesis, and some physicochemical data, of the asymmetrical double-decker, $La^{III}H(TPyP)(TPP)$, as well the $[La^{III}(TMePyP)(TPP)]I_3$, which possesses only one neutral porphyrin ring (TPP^{-2}) and the other porphyrin ring ($TPyP^{-2}$) or the cationic form ($TMePyP^{+2}$), respectively.

Experimental Section

General Information. All solvents, reagents, and supporting electrolytes were purchased commercially and used as supplied except for tetrahydrofuran (THF), which was distilled under an argon atmosphere over a mixture of sodium/benzophenone before use. The $H_2(TPP)$ and $H_2(TPyP)$ free bases were synthesized according to a reported method,[4] and the metalation reactions were performed by the acetylacetonate method.[5] All syntheses were performed under an argon stream atmosphere using Schlenk-tube techniques.

Experimental Procedures. Absorption spectra were collected on a Perkin-Elmer Lambda 6 grating spectrophotometer (ϵ, log ϵ $dm^3\ mol^{-1}\ cm^{-1}$ measurements were performed in DMF and $CHCl_3$ solutions of 0.05×10^{-3} M). IR spectra were recorded on a Perkin-Elmer FT series 1760 spectrophotometer in KBr pellets, while for

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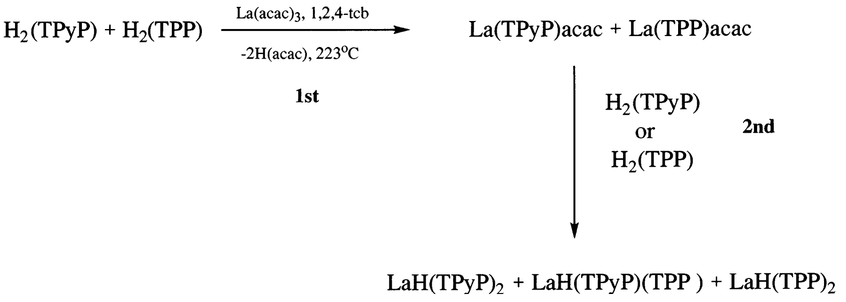

Figure 1. Reaction scheme for the synthesis of symmetric and asymmetric double-deckers.

NMR spectra an AMX 500-MHz or an MSL 300-MHz Bruker spectrometer was used. Electrochemical experiments were performed in an airtight three-electrode cell connected to vacuum/argon line. The cell was degassed and filled according to standard vacuum techniques. The reference electrode consisted of SCE separated from the solution by a bridge compartment filled with the same solvent and supporting electrolyte solution as used in the cell. The counter electrode was a spiral one of ca. 1 cm^2 apparent surface area, made from ca. 8 cm of a 0.5 mm diameter platinum wire. The working electrode was a 1 mm diameter Pt disk, and RDE (rotating disk electrode) was a 2 mm diameter Pt disk (Tacussel EDI). With this reference and bridge system, $E° = 0.54$ V was obtained for 2 mM ferrocene solutions in 0.1 M THF/n-Bu_4NBF_4. The synthetic routes that have been used to synthesize the lipophilic compound are similar with those used for the synthesis of $La^{III}H(OEP)(TPP)$.[3d] The essential steps 1 and 2 to create lanthanum porphyrin double deckers are depicted in Figure 1. The monoporphyrins $La^{III}(TPP)acac$ and $La^{III}(TPyP)acac$, which presumably are formed according to step 1, have never been obtained (only observed in traces by UV−vis) because double decker formation is rather rapid for lanthanum(III). The methylation reaction occurs in the presence of CH_3I in $CHCl_3$.

Synthesis of the Neutral Complex $La^{III}H(TPyP)(TPP)$. To a solution of 175 mg (0.282 mmol) of $H_2(TPyP)$ and 174 mg (0.282 mmol) of $H_2(TPP)$ in 40 mL of 1,2,4-tcb was added 1000 mg of $La^{III}(acac)_3 \cdot xH_2O$, and the mixture was brought to reflux for 5−7 h. The reaction mixture was then allowed to cool at room temperature and, then, was passed through a column of Al_2O_3 (5 cm × 10 cm basic, grade I), activated at 150 °C overnight, using hexane as elution solvent. The first fraction contained the unreacted free base $H_2(TPP)$. At this stage, all traces of 1,2,4-tcb (the solvent used) were also eliminated. By using CH_2Cl_2 as the elution solvent, a second fraction containing $La^{III}H(TPP)_2$ was eluted. Using a mixture of solvents CH_2Cl_2/MeOH (99:1), again a portion of the unreacted free base $H_2(TPyP)$ was eluted. Then, by increasing the molar ratio of MeOH in the solvent mixture CH_2Cl_2/MeOH (97:3), the heteroleptic porphyrin double-decker, $La^{III}H$ (TPyP)(TPP), was eluted in a pure form. At the end, the elution of $La^{III}H$ $(TPyP)_2$ was accelerated by using a mixture of solvents CH_2Cl_2/MeOH, (90:10) as the eluant. The fraction containing $La^{III}H$ (TPyP)(TPP) was evaporated to dryness. The dark blue solid was filtered and washed with hexane and diethyl ether. The solid was dried overnight in a vacuum oven at 50 °C (yield 48%). Anal. Calcd for $C_{84}H_{53}N_{12}La$ (mol wt 1369.34): C, 73.70; H, 3.90; N, 12.27. Found: C, 73.22; H, 3.72; N, 12.47%.

Synthesis of the Cationic Complex $[La^{III}$ (TMePyP)(TPP)]I_3. To a solution of 60 mg (6.3 × 10−5mol) of the double-decker $La^{III}H$ (TPyP)(TPP) in 30 mL of $CHCl_3$, 2 mL (32.1 mmol) portion of methyl iodide was added dropwise. The mixture was stirred at ambient temperature for up to 6 h. The reaction mixture was heated to 38 °C for 0.5−1 h in order to complete the methylation process.

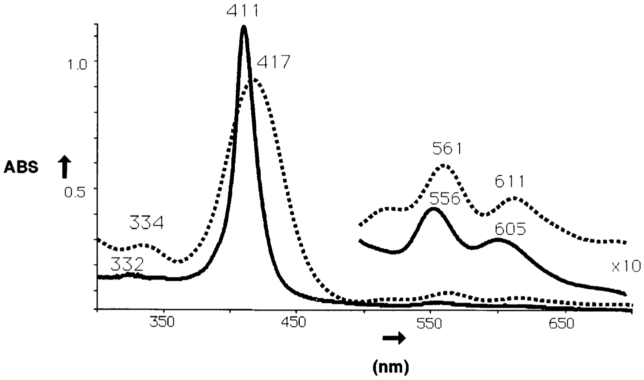

Figure 2. UV−vis spectra of (a) $La^{III}H(TPyP)(TPP)$ in $CHCl_3$ (—) and (b) $[La^{III}(TMePyP)(TPP)]I_3$ in DMF (···).

Once the reaction had been completed, the solvent was removed under reduced pressure, and the dark blue solid was filtered and washed with hexane and diethyl ether. The solid (yield 92%) was dried overnight in a vacuum oven at 50 °C. Anal. Calcd for $C_{88}H_{64}N_{12}LaI_3$ (mol wt 1809.17): C, 58.42; H, 3.57; N, 9.29; I, 21.04. Found: C, 58.03; H, 3.32; N, 9.41; I, 21.28%.

Results and Discussion

At first glance, the double-deckers present a “normal” UV−vis spectrum of a metalloporphyrin derivative with strong $\pi-\pi$ interaction between the macrocycles, as would be expected for a lanthanoid porphyrin.[6,7] UV−vis data are recorded in $CHCl_3$ for the non-methylated derivative and in DMF for the methylated one. The last complex shows a medium solubility in H_2O (10 mg/lt), because only one of the two porphyrin rings is found in the cationic form. This property classifies that complex in a new category of double-deckers. All the cationic double-deckers which were synthesized in the past possess great solubility in water, as both the porphyrin rings are charged.[2h,8] In $CHCl_3$, there appears a strong B (“Soret”), followed by the characteristic Q(0,1) and Q(0,0) bands (in parentheses, log ϵ) at 411 (5.46), 556 (3.47), and 605 (3.34) nm for $La^{III}H(TPyP)(TPP)$, and 417 (5.13), 561 (3.62), and 611 (3.51) nm, for $[La^{III}(TMePyP)(TPP)]^{3+}$ in DMF (Figure 2). The UV−vis spectrum of $[La^{III}(TMePyP)(TPP)]^{3+}$ in DMF exhibits intermediate features of the two symmetrical double-deckers with TMePyP and

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TPP rings with the Soret band at 417 nm. So, in the same solvent this band is blue shifted (10 nm) compared to the corresponding $[La^{III}(TMePyP)_2]^{7+}$ double-decker[8] (427 nm) and red shifted (6 nm) compared to the $[La^{III}(TPP)_2]^-$ (411 nm). The same is also observed for $La^{III}H(TPyP)(TPP)$ in $CHCl_3$.

FT-IR data for the asymmetric derivatives $La^{III}H(TPyP)(TPP)$ and $[La^{III}(TMePyP)(TPP)]I_3$ present the characteristic pattern of bands of both components (TPP, TPyP, and TMePyP for each case, see also Supporting Information). The disappearance of the N−H frequency was the first indication concerning the metal insertion to the porphyrin ring. The C=N ring stretch of the pyridyl group was detected at 1653 cm^{-1}, while for $[La^{III}(TMePyP)(TPP)]I_3$ the corresponding stretch is shifted to 1593 cm^{-1}. This is of course due to the partial ionization of the C=N bond following methylation of the pyridyl group in the latter complex.

The ^1H NMR data confirm the proposed molecular formula for the titled complexes. These complexes give broad, structureless ^1H NMR signals due to the flipping motion of the rings, as previously reported, or to the equal contribution of the different positional isomers.[2c,9−10] For $La^{III}H(TPyP)(TPP)$[11] and $[La^{III}(TMePyP)(TPP)]^{3+}$, signals are indicative of the two different porphyrin rings and clearly assigned with regard to their position. From the ^1H NMR data, one can distinguish two sets of peaks, one for the *ortho* and one for the *meta* protons of the peripheral phenyl or pyridyl group for both complexes (depending on the case, Figure 3a). A demonstration of the full methylation process is given by ^1H NMR spectroscopy on the $[La^{III}(TMePyP)(TPP)]^{3+}$ complex. The integration of the methyl groups at 4.70 ppm (Figure 3b) proves the existence of 12 protons, as expected. An unambiguous assignment of the $La^{III}H(TPyP)(TPP)$ and $[La^{III}(TMePyP)(TPP)]^{3+}$ spectra was obtained with the use of COSY and NOESY experiments. From COSY experiments, connectivities have been observed between protons of phenyl groups, but not of pyridyl groups (Figure 4). The COSY spectrum of $La^{III}H(TPyP)(TPP)$ showed connectivities between *o*- and *m*-protons, which clearly indicate the two different *endo*- and *exo*-protons (*o-endo* at 9.02 ppm with *m-endo* at 8.14 ppm and *o-exo* 7.19 ppm with *m-exo* at 7.53 ppm, respectively). The two *m*-protons at 8.14 and 7.53 ppm (*endo* and *exo*) correlate with the *p*-proton at 7.85 ppm. The ^1H NMR assignment of the pyridyl protons is achieved through a 2D NOESY experiment, and connectivities between protons of the phenyl group are shown. The NOESY map displays a strong exchange of cross-peaks between diastereotopic *ortho* and *meta* pairs. So, one can observe that the signal from *o-endo* at 8.95 ppm correlates with the signal from *o-exo* at 6.89 ppm, and *m-endo* protons at 9.20 ppm correlate with the diasterotopic *m-exo* proton at 8.74 ppm, (Figure 5). There are two possible formulae describing the protonated complexes in the asymmetric (as well as the corresponding symmetric with the TPP ring) double-decker: $Ln^{III}(PorH)(Por')$ or $Ln^{III}(Por)(Por'H)$. The equilibrium between the protonated and deprotonated form of the complexes is well-known.[12] The protonated process is solvent-dependent. In $CHCl_3$, the protonated form is present, while in basic solvents the non-protonated form becomes dominant.[9] For diamagnetic $La^{III}H(TPyP)(TPP)$ only one peak has been observed at −4.29 ppm for the protonated forms. We claim that this proton peak belongs to the more basic ring (TPyP), and the reason is described in the

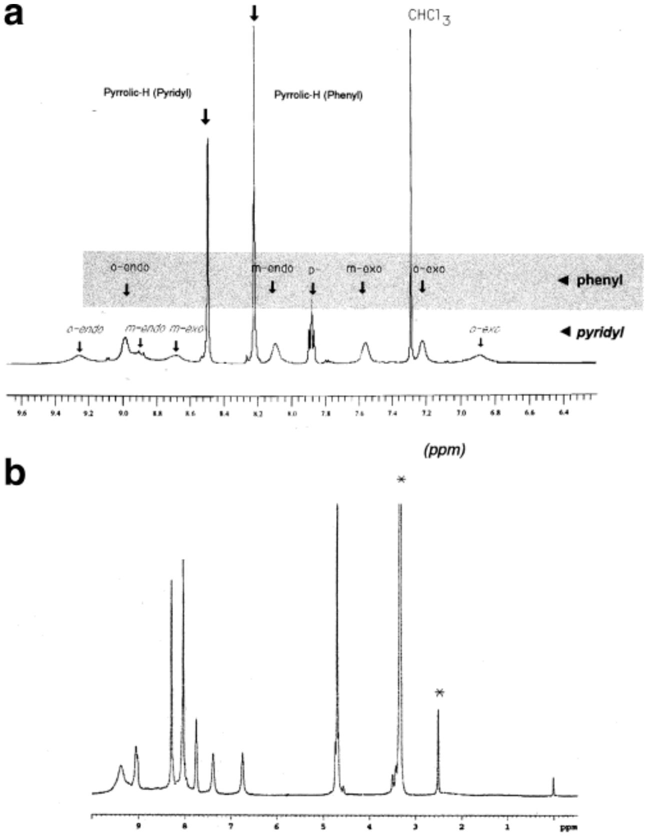

Figure 3. ^1H NMR of (a) $La^{III}H(TPyP)(TPP)$ in $CDCl_3$ and (b) $[La^{III}(TMePyP)(TPP)]I_3$ in DMSO-d_6.

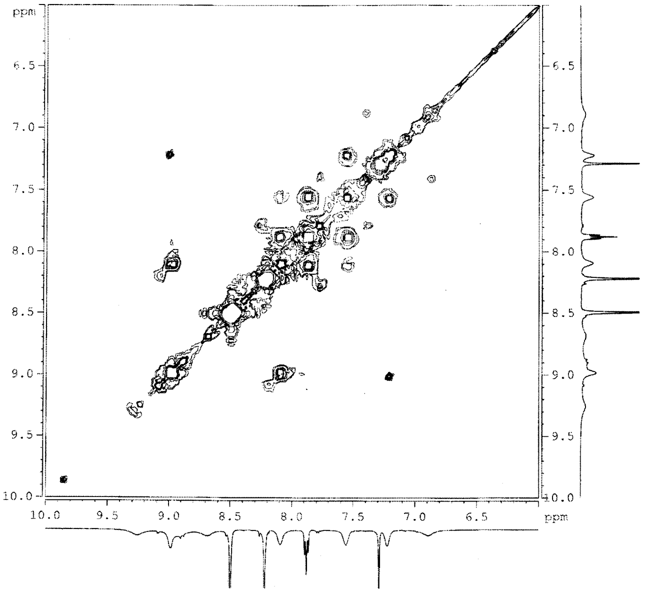

Figure 4. 2D-COSY spectrum of $La^{III}H(TPyP)(TPP)$ in $CDCl_3$.

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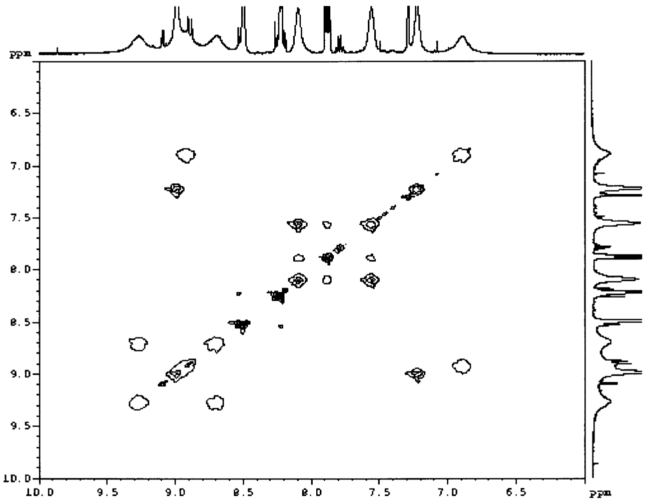

Figure 5. 2D-NOESY spectrum of $La^{III}H$ (TPyP)(TPP)in $CDCl_3$.

following text. In the case of $La^{III}H(TPP)_2$, the nitrogen proton is shown at −3.73 ppm. We did not see the analogous peak for $La^{III}H$ $(TPyP)_2$. The last complex exists only in the deprotonated form in solution, because it is soluble only in basic solvents, like DMF or pyridine. Nevertheless, taking into consideration the chemical shifts of the nitrogen protons of the corresponding free bases (−2.94 ppm for H_2(TPyP), and −2.07 ppm for H_2(TPP)), the chemical shift of the nitrogen proton in the $La^{III}H(TPP)_2$ complex (at −3.73 ppm) and the observed chemical shift at −4.29 ppm of the $La^{III}H$(TPyP)(TPP) complex, we deduce that the last peak belongs to the TPyP ring.

The electrochemical data for the neutral asymmetric double-decker obtained by cyclic voltammetry are comparable to those published for the symmetric species.[2b,3f] The potentials of the first oxidation of the lipophilic compound lie between the corresponding values for the symmetric ($La^{III}H(TPP)_2$ and $La^{III}H(TPyP)_2$[8,13]) analogues, also indicating the strong $\pi-\pi$ interaction for these complexes. The cyclic voltammogram of $La^{III}H$(TPyP)(TPP) in THF (Figure 6) exhibits two oxidation potentials, $E_{1/2}$ values at +0.52 and +0.96 V, and two reduction $E_{1/2}$ potentials at −1.36 and −1.70 V versus SCE, assignable to the two oxidation and two reduction processes attributable to a ligand-based oxidation or reduction, respectively. The first oxidation process lies slightly closer to the potential value of $La^{III}H(TPyP)_2$ than that of $La^{III}H(TPP)_2$. In this case, the TPP ring is reduced first. Adsorption phenomena during the described investigation of the cationic complex were observed, and for this reason, it was difficult to extract direct information on the electrochemical processes involved. The electrochemical studies of these complexes are extremely complicated in comparison to the symmetric or asymmetric similar derivatives. Our efforts are directed to the extension of this new family[14] to include all of the lanthanide ions, and their complete physicochemical study is still under investigation.

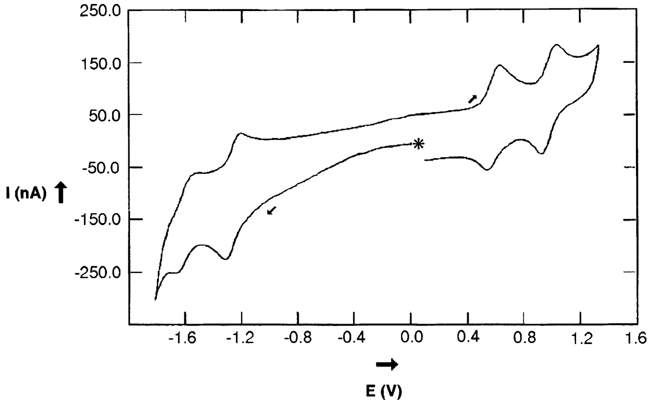

Figure 6. Cyclic voltammogram of $La^{III}H$(TPyP)(TPP) in THF/*n*-Bu_4NF_4, 0.1 M.

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Supporting Information Available: FT-IR spectra of $La^{III}H$ $(TPP)_2$, $La^{III}H$ (TPyP)(TPP), and $La^{III}H$ $(TPyP)_2$; FT-IR spectra of $La^{III}H$ (TPyP)(TPP) and $[La^{III}$ $(TMePyP)(TPP)]I_3$; ^1H NMR spectrum of $La^{III}H$ (TPyP)(TPP) in $CDCl_3$; 2D-COSY spectrum of [LaIII $(TMePyP)(TPP)]I_3$ in DMSO-d_6; 2D-NOESY spectrum of $[La^{III}$ $(TMePyP)(TPP)]I_3$ in DMSO-d_6. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) $La^{III}H$(TPyP)(TPP): for pyridyl group, *o-endo* (8.95), pyrrolic-H (8.47), *m-endo* (9.20), *m-exo* (8.74), *o-exo* (6.89); for phenyl group, *o-endo* (9.02), pyrrolic-H (8.18), *m-endo* (8.14), *p*- (7.85), *m-exo* (7.53), *o-exo* (7.19), and N−H (−4.29) in $CDCl_3$. $[La^{III}$ $(TMePyP)(TPP)]I_3$: for pyridyl group, *o-endo* (9.37), pyrrolic-H (8.27), *m-endo* (9.37), *m-exo* (9.37), *o-exo* (9.37), CH_3-N^+ (4.70); for phenyl group, *o-endo* (9.03), pyrrolic-H (8.04), *m-endo* (8.05), *p*- (7.76), *m-exo* (7.37), *o-exo* (6.74) in d_6-DMSO.

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(14) Abbreviations of the dications: $(TPyP)^{2-}$ = 5,10,15,20-tetrapyridylporphyrinate, $(TMePyP)^{2-}$ = 5,10,15,20-tetra(methylpyridyl)-porphyrinate, $(TPP)^{2-}$ = 5,10,15,20-tetraphenylporphyrinate.