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Article

Synthesis, Characterization, and Photophysical Properties of a Free Base and a Biszinc(II) Complex of 1,3-Bisporphyrincalix[4]arene: Evidence for "Tunable Intramolecular Open and Closed Conformations"

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The bismacrocycle 5,17-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrinyl)]-25,26,27,28-tetrapropoxycalix-[4]arene (**4**) was synthesized in three steps from the corresponding bisaldehyde 5,17-diformyl-25,26,27,28-tetrapropoxycalix[4]arene. The biszinc(II) complex (**5**) was prepared as well, and the photophysical properties were measured using 2-MeTHF as solvent at 298 and 77 K. While computer modeling for **5** predicts that both pinched cone conformers, closed (porphyrins near each other) and open (porphyrins away from each other), may exist in the "gas phase", the experimental data indicate clearly that no zinc porphyrin···zinc porphyrin interactions are present in solution at 298 K, favoring the open conformer, where the two macrocycles are placed away from each other. On the other hand, clear evidence for a closed conformer is observed at 77 K. Variable-temperature ^{1}H NMR experiments show that **5** is fluxional between 298 and 183 K, while **4** keeps the open conformation for the whole temperature range. This behavior is unprecedented for calix[4]areneporphyrin compounds, and the relative porphyrin ring rigidity is postulated to explain this difference.

Introduction

Calix[4]arene is a versatile platform molecule capable of multiple functionalizations, at the wide (upper) and narrow (lower) rims and on the side of the macrocycle, promoting ionic pairing assemblies and covalent linkings of redox and photoactive species, luminescent groups, and catalytic metals.[1–6] Among examples of these functionalized species, the chemistry of porphyrin-containing calix[4]arene systems[7–10] and ion pairs[11–13] have been extensively investigated. Indeed, various metalated and free base calix[4]arene–polyporphyrin assemblies have been reported over the past 10 years for applications in the fields of molecular recognition,[9,14–28]

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receptors,[9,14−28] host−guest chemistry,[9,14−28] catalysis,[29] and photoinduced electron transfers.[30−33]

We have recently reported the syntheses, characterization, and photophysical properties of various cofacial bisporphyrins as free bases, mono- and biszinc(II) complexes, rigidly held by anthracene, dimethylxanthene, dibenzofuran, dibenzothiophene, and biphenylene spacers. We evaluate to 5−6 Å the critical inter-chromophore distance where the dominant mechanism for singlet−singlet energy transfer (ET) change from Förster to Dexter.[34] We now report the syntheses, characterization, and photophysical properties of the free base and biszinc(II) complex of 5,17-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin)]-25,26,27,28-tetrapropoxycalix-[4]arene, **4** and **5**, respectively. The photophysical data (2-MeTHF at 77 and 298 K) are consistent with a distal conformation for **4**, where the porphyrin macrocycles are away from each other. On the other hand, both distal and proximal conformations are observed for **5** at 298 and 77 K, respectively. The presence of Zn, which contributes to render the porphyrin macrocycles more rigid, is invoked to explain this difference based on computer modeling.

Experimental Section

Materials. Unless otherwise stated, all reagents and solvents were used as received. DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone) and PTSA (*p*-toluenesulfonic acid) were purchased from Aldrich. 2-MeTHF was purchased from Aldrich (99+%, anhydrous and under inert gas). 3,3′-Diethyl-5,5′-dimethyl-4,4′-dimethyl-2,2′-dipyrrylmethane,[35] 5,17-diformyl-25,26,27,28-tetrapropoxycalix(4)arene (**1**),[36] and 4-ethyl-3-methyl-5-ethoxycarbonyl-2-formylpyrrole[37] were synthesized according to literature methods. Column chromatography was performed with neutral alumina (Merck; usually Brockmann Grade III, i.e., deactivated with 6% water) and silica gel (Merck; 70−120 mm) and were monitored by thin-layer chromatography (Merck 60 F254 silica gel precoated sheets, 0.2 mm thick) and UV−Vis spectroscopy.

5,17-Bis[(2,2′-bis(4-ethyl-3-methyl-5-ethoxycarbonylpyrryl))-methyl]-25,26,27,28-tetrapropoxycalix[4]arene (2). A total of 1.25 g (1.5 mmol) of **1** and 1.44 g (8 mmol) of 4-ethyl-3-methyl-5-ethoxycarbonyl-2-formylpyrrole was dissolved under Ar in the dark in 25 mL of dry ethyl alcohol. Concentrated HCl (0.5 mL) was added, and the mixture was heated under reflux for 3.5 h. The cold red solution was concentrated and filtered. The solid was washed three times with cold methyl alcohol and dried to obtain 1.1 g of a light red solid. Yield 55%. ^{1}H NMR (CDCl$_3$): δ, ppm 8.48 (s, 4H, NH), 6.77 (s, 4H, ArH-calix), 6.25 (t, J = 7.6 Hz, 2H, ArH-calix), 6.05 (d, J = 7.6 Hz, 4H, ArH-calix), 5.44 (s, 2H, meso), 4.39 (d of AB system, ^2J = 13.2 Hz, 4H, ArCH$_2$-calix), 4.27 (q, J = 7.1 Hz, 8H, COOCH$_2$CH$_3$), 4.00−3.67 (m, 8H, O-CH$_2$CH$_2$CH$_3$), 3.04 (d of AB system, ^2J = 13.2 Hz, 4H, ArCH$_2$-calix), 2.44 (q, J = 7.5 Hz, 8H, CH$_2$CH$_3$-pyrrole), 2.03−1.85 (m, 8H, O-CH$_2$CH$_2$-CH$_3$), 1.82 (s, 12H, CH$_3$-pyrrole), 1.31 (t, J = 7.1 Hz, 12H, COOCH$_2$CH$_3$), 1.12 (t, J = 7.5 Hz, 12 H, CH$_2$CH$_3$-pyrrole), 1.06 (t, J = 7.5 Hz, 6H, O-CH$_2$CH$_2$CH$_3$), 0.90 (t, J = 7.5 Hz, 6H, O-CH$_2$CH$_2$CH$_3$).

5,17-Bis[(2,2′-bis(4-ethyl-3-methylpyrryl))methyl]-25,26,27,28-tetrapropoxycalix[4]arene (3). A total of 1.1 g (0.83 mmol) of **2** and 7.4 g (185 mmol) of NaOH in 55 mL of diethylene glycol was heated in the dark under Ar at 140 °C during 1.5 h. The solution was then heated at 160 °C for another 3 h. The hot solution was poured into 250 mL of water and ice. The solid was collected by filtration and washed three times with water. After being dried under vacuum, 0.750 g of a light brown solid was obtained. Yield 85%. ^{1}H NMR (CDCl$_3$): δ, ppm 6.74 (s, 4H, ArH-calix), 6.36−6.25 (m, 10H, H-α-pyrrole and ArH-calix), 5.30 (s, 2H, meso), 4.38 (d of AB system, ^2J = 13.1 Hz, 4H, ArCH$_2$-calix), 3.91 (t, J = 7.1 Hz, 4H, O-CH$_2$CH$_2$CH$_3$), 3.80 (t, J = 7.1 Hz, 4H, O-CH$_2$CH$_2$CH$_3$), 3.05 (d of AB system, ^2J = 13.1 Hz, 4H, ArCH$_2$-calix), 2.44 (q, J = 7.5 Hz, 8H, CH$_2$CH$_3$-pyrrole), 1.98−1.80 (m, 8H, O-CH$_2$CH$_2$-CH$_3$), 1.77 (s, 12H, CH$_3$-pyrrole), 1.19 (t, J = 7.5 Hz, 12 H, CH$_2$-CH$_3$-pyrrole), 1.04 (t, J = 7.5 Hz, 6H, O-CH$_2$CH$_2$CH$_3$), 0.92 (t, J = 7.5 Hz, 6H, O-CH$_2$CH$_2$CH$_3$), NH (4H) not observed. MS (EI): m/z 1048.680 [M$^+$], 1048.6806 g·mol^{-1} calcd for C$_{70}$H$_{88}$N$_4$O$_4$; 939.5914 [M$^+$ − C$_7$H$_{10}$N (pyrrole)], 939.5909 g·mol^{-1} calcd for C$_{63}$H$_{77}$N$_3$O$_4$$^{•+}$.

5,17-Bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrinyl)]-25,26,27,28-tetrapropoxycalix[4]arene (4). A total of 0.750 g (0.72 mmol) of **3** and 0.430 g (1.51 mmol) of 3,3′-diethyl-5,5′-dimethyl-4,4′-dimethyl-2,2′-dipyrrylmethane was stirred under Ar in the dark in 120 mL of anhydrous methyl alcohol. A solution of PTSA (0.155 g, 0.90 mmol) in 20 mL of methyl alcohol was slowly added to the mixture during 3 h. DDQ (0.195 g, 0.72 mmol) was added, and the dark solution was stirred during 1 h. After evaporating the solvent under vacuum, the dark solid was dissolved in CH$_2$Cl$_2$. The solution was poured onto an alumina pad and eluted with CH$_2$Cl$_2$. A second purification on silica gel was performed (CH$_2$Cl$_2$/hexane/NEt$_3$ 80:19:1) to obtain a dark red solid. Recrystallization in heptane/CH$_2$Cl$_2$ gives 0.045 g of the desired compound. Yield 4%. ^{1}H NMR (CDCl$_3$): δ, ppm 10.26 (s, 2H, meso), 10.20 (s, 2H, meso), 9.98 (s, 2H, meso), 7.94 (s, 4H, ArH-calix), 6.91 (d, J = 7.2 Hz, 4H, ArH-calix), 6.82 (t, J = 7.2 Hz, 2H, ArH-calix), 4.88 (d of AB system, ^2J = 13.5 Hz, 4H, ArCH$_2$-calix), 4.56 (t, J = 8.1 Hz, 4H, O-CH$_2$CH$_2$CH$_3$), 4.11 (m, 16H, CH$_2$CH$_3$-pyrrole), 3.84 (t, J = 6.7 Hz, 4H, O-CH$_2$CH$_2$CH$_3$), 3.70 (2s, 12H, CH$_3$-pyrrole), 3.47 (d of AB system, ^2J = 13.5 Hz, 4H, ArCH$_2$-calix), 3.00 (s, 6H, CH$_3$-pyrrole), 2.55 (s, 6H, CH$_3$-pyrrole), 2.45

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(m, 4H, O-CH$_2$CH$_2$CH$_3$), 2.06 (m, 4H, O-CH$_2$CH$_2$CH$_3$), 1.93 (m, 24H, CH$_3$-pyrrole), 1.22 (m, 12H, O-CH$_2$CH$_2$CH$_3$), −3.05 (s, 2H, NH), −3.18 (s, 2H, NH). Anal. Calcd for C$_{104}$H$_{120}$N$_8$O$_4$·MeOH· 3CH$_2$Cl$_2$: C 70.77, H 7.15, N 6.11; found: C 70.30, H 7.60, N 5.84. MS (MALDI-TOF): m/z 1543, 1544 calcd for C$_{104}$H$_{120}$N$_8$O$_4$. UV−Vis: λ_{max}, nm ($\epsilon \times 10^{-3}$ M^{-1} cm^{-1}): Soret 405.1 (529.5), 502.1 (46.9), 537 (21), 571 (20.4), 624.5 (8.3).

5,17-Bis[zinc(II)-5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrinyl)]-25,26,27,28-tetrapropoxycalix[4]arene (5). A saturated solution of Zn(OAc)$_2$·2H$_2$O in methanol (5 mL) was added to 21 mL of a CH$_2$Cl$_2$/NEt$_3$ (20:1) solution of bisporphyrin **4** (0.030 g, 0.02 mmol). The mixture was stirred at room temperature, and the reaction was monitored by UV−Vis. The solvent was removed under vacuum until no starting free base bisphyrin was present in the mixture according to UV−Vis (∼5 min). The solid was dissolved in CH$_2$Cl$_2$ and purified by chromatography (alumina, CH$_2$-Cl$_2$). Recrystallization in CH$_2$Cl$_2$/heptane afforded the pure bis-zinc derivative as a purple solid in quantitative yield (0.033 g). ^{1}H NMR (CDCl$_3$): δ, ppm 10.21 (s, 2H, meso), 9.74 (s, 2H, meso), 9.768 (s, 2H, meso), 8.03 (s, 4H, ArH-calix), 7.03 (d, J = 7.1 Hz, 4H, ArH-calix), 6.89 (t, J = 7.1 Hz, 2H, ArH-calix), 4.94 (d of AB system, ^2J = 13.6 Hz, 4H, ArCH$_2$-calix), 4.63 (t, J = 8.2 Hz, 4H, O-CH$_2$CH$_2$CH$_3$), 4.14 (m, 16H, CH$_2$CH$_3$-pyrrole), 3.87 (t, J = 6.7 Hz, 4H, O-CH$_2$CH$_2$CH$_3$), 3.70 (s, 12H, CH$_3$-pyrrole), 3.52 (d of AB system, ^2J = 13.6 Hz, 4H, ArCH$_2$-calix), 3.00 (s, 6H, CH$_3$-pyrrole), 2.62 (s, 6H, CH$_3$-pyrrole), 2.46 (m, 4H, O-CH$_2$CH$_2$-CH$_3$), 2.09 (m, 4H, O-CH$_2$CH$_2$CH$_3$), 1.91 (m, 24H, CH$_3$-pyrrole), 1.29 (m, 12H, O-CH$_2$CH$_2$CH$_3$). Anal. Calcd for C$_{104}$H$_{116}$N$_8$O$_4$Zn$_2$· 4H$_2$O: C 71.59, H 7.16, N 6.42; found: C 71.59, H 7.18, N 6.28. MS (MALDI-TOF): m/z 1670, 1669 calcd for C$_{104}$H$_{116}$N$_8$O$_4$Zn$_2$. UV−Vis: λ_{max}, nm ($\epsilon \times 10^{-3}$ M^{-1} cm^{-1}): Soret 407.1 (700.1), 533.9 (31.6), 571 (31.1).

Apparatus. The ^{1}H NMR spectra were recorded on a Bruker 300 MHz instrument (300.15 MHz) at the Université de Sherbrooke. Microanalyses were performed at the Université de Bourgogne on a Fisons EA 1108 CHNS instrument. UV−Vis spectra were recorded on a Varian Cary 50 spectrophotometer. Mass spectra were obtained in linear mode with a Bruker Proflex III MALDI-TOF mass spectrometer using dithranol as matrix. Electronic ionization mass spectra for **3** was obtained on a VG Instruments ZAB-IF spectrometer at a potential of 70 eV. Emission and excitation spectra were obtained using a double monochromator Fluorolog 2 instrument from Spex. Fluorescence lifetimes were measured on a Timemaster model TM-3 apparatus from PTI. The source was a nitrogen laser equipped with a high-resolution dye laser (fwhm ∼ 1500 ps), and the fluorescence lifetimes were obtained from deconvolution and distribution lifetime analysis.[38]

Methodology. All studied molecules were oxygen sensitive at 298 K. All samples for photophysical measurements were prepared under inert atmosphere (in a glovebox, P_{O_2} < 1−3 ppm)[38,39] by dissolution of the different compounds in 2-MeTHF using 1 cm^3 quartz cells equipped with septum (298 K) or standard 5 mm NMR tubes (77 K). Three different measurements (i.e., different solutions) were performed for each photophysical data (quantum yields and lifetimes). The sample concentrations were chosen to correspond to absorbance about 0.05. Each absorbance value was measured five times to obtain the measurements of the quantum yields. The reference for quantum yield measurements at 298 K was H$_2$TPP

(Φ = 0.11).[40−42] The reference for the quantum yields at 77 K was H$_2$TPP (Φ = 0.11). The latter value was obtained using (Pd)-TPP (Φ = 0.17; 77 K; MCH: methylcyclohexane) as standard.[43,44]

Computer Modeling. The calculations were performed using the commercially available PC model from Serena Software (version 7.0), which uses the MMX empirical model. No constraint on bond distances and angles was applied to ensure that deviations from normal geometry were depicted.

Results and Discussion

Synthesis. The preparation of the desired bisporphyrin-calix[4]arene assembly is performed with an overall yield of 1.9% starting from the 5,17-diformyl-25,26,27,28-tetrapropoxycalix[4]arene **1** (Scheme 1), using a three-step convergent synthesis, as described in the literature for face-to-face bisporphyrins.[37,45−48] Two pyrroles are condensed with the starting diformyl calix[4]arene spacer (**1**) in acidic solution (HCl in MeOH) to yield the bis(dipyrrole) compound (**2**) as a light pink solid in 55% yield. Subsequently, the ester groups in β-position of the pyrroles are removed by treating **2** at 413 K for 1.5 h in diethylene glycol in the presence of NaOH. Hydrolysis of the ester functions affords carboxylate groups as intermediates, which decompose at 433 K leading to **3**. Reaction between dipyrromethane and the bis(dipyrrole) compound (**3**) in the presence of PTSA, followed by an oxidation with DDQ, provides bisporphyrin **4** as a dark red solid in 4% yield. This low yield is explained by parallel reactions leading to the corresponding undesired monopor-phyrin, 2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin.[49] Several attempts were made to increase the yield but without success. The complexation of zinc(II) proceeds quantitatively using zinc(II) acetate, and the corresponding biszinc(II) complex (**5**) is obtained.

The starting material 5,17-diformyl-25,26,27,28-tetra-benzyloxycalix[4]arene as a potential spacer was also investigated. The benzyl groups are also large enough to prevent any flip of the aryl groups in the calix[4]arene macrocycle and to provide the cone conformer. Again, only the cone conformation of the calix[4]arene is obtained. Unfortunately, this compound is not soluble in MeOH, and the corresponding bis(dipyrrole) could not be obtained. Other solvents and acids (toluene, THF, DMF with PTSA, Lewis acid) were investigated without success.

Computer Modeling. In the absence of X-ray data, computer modeling is used to address qualitatively the two

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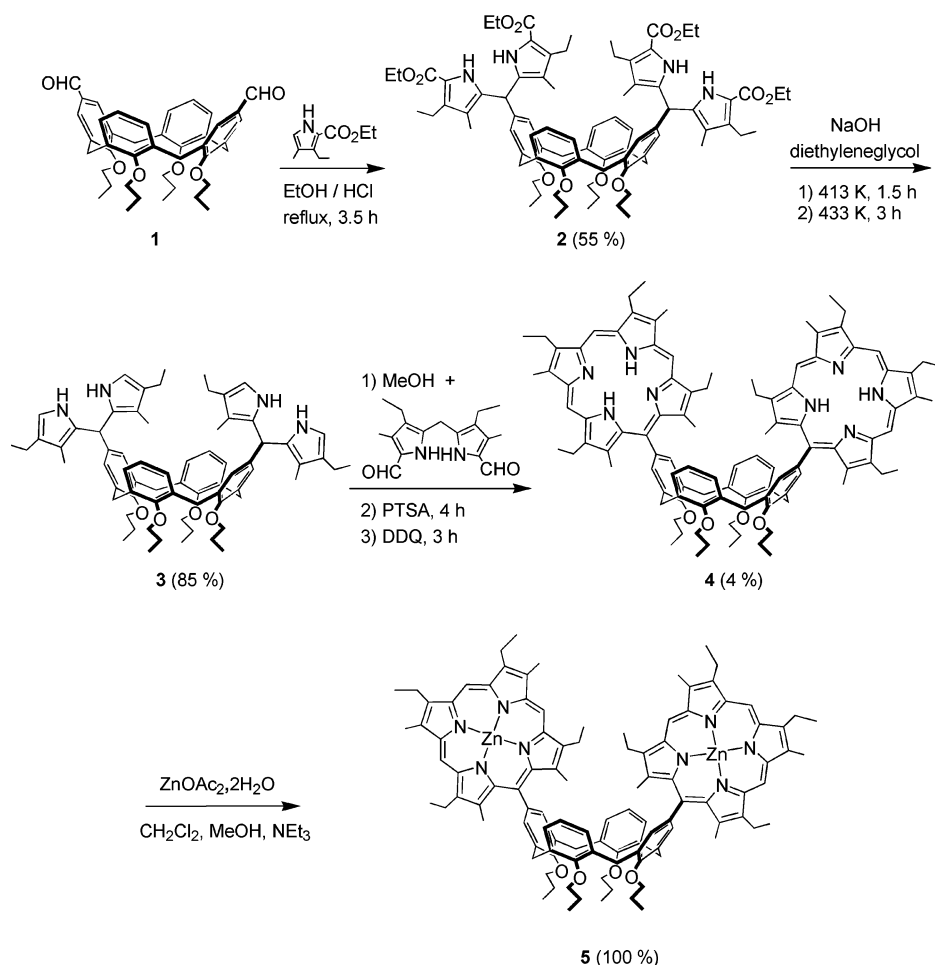(45) Chang, C. K.; Abdalmuhdi, I. *J. Org. Chem.* **1983**, *48*, 5388.

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Scheme 1

1

EtOH / HCl
reflux, 3.5 h

2 (55 %)

NaOH
diethyleneglycol

1) 413 K, 1.5 h
2) 433 K, 3 h

3 (85 %)

1) MeOH +

2) PTSA, 4 h
3) DDQ, 3 h

4 (4 %)

ZnOAc₂,2H₂O

CH₂Cl₂, MeOH, NEt₃

5 (100 %)

possible pinched cone conformers,[1−6,50−52] here denoted as closed and open. The optimized geometry for both "gas phase" conformers for **5** are shown in Figures 1−3. To obtain these final optimized geometries, conformations somewhat close to the final results must be employed as starting points. This behavior is indicating that these belong to a local and true minima which is discussed below.

Some porphyrin···porphyrin contacts are evident in the closed conformation[53] in **5** (Figures 1 and 2), where C···C distances are in the order of 3.60−3.65 Å (the van der Waals radii for the carbon atom is 1.77 Å), but important deviations from planarity of the porphyrin macrocycles are observed. These deviations are caused by steric interactions between the four methyl groups placed inside or near the calix[4]-arene cavity. As the two porphyrin macrocycles are not perfectly cofacial, the term "slipped dimer" would be more appropriate (Figures 1 and 2). The optimized geometry for the corresponding unsubstituted derivative (i.e., no methyl nor ethyl groups) exhibits undistorted porphyrin groups, and the resulting geometry belongs to the C₂ point group. The
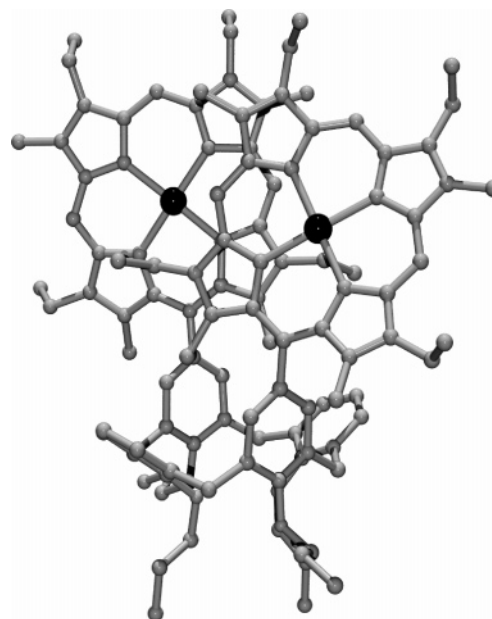
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Figure 1. One view of the optimized geometry for the "closed" conformer of **5**, showing the cofacial nature of the porphyrins orientation. Note that the Zn(II) does not interact with the other porphyrin macrocycle.

open conformer of **5** (Figure 3) exhibits no inter porphyrin contact, and some minor deviations from planarity of the porphyrin planes are also observed. These are also due to the same steric reasons mentioned above.

Table 1. Absorption and Fluorescence Properties of **4**, **5**, H$_2$P, and (Zn)P[a]

compd	λ_{max} (nm) ($\epsilon \times 10^{-3}$ M^{-1} cm^{-1})[b]		emission λ_{max} (nm)[c]		quantum yield Φ_F[d]		lifetime λ_F (ns)	
	Soret region	Q-bands	298 K	77 K	298 K	77 K	298 K	77 K
4	405.1 (529.5)	502.1 (46.9), 537 (21), 571 (20.4), 624.5 (8.3)	630, 661, 691, 700	626, 656, 677, 694	0.087	0.14	17.5	23.2
H$_2$P[e]	402 (154)	502 (15), 532 (8), 578 (6), 626 (4)	629, 696	623, 690	0.089	0.086	17.3	23.3
5	407.1 (700.1)	533.9 (31.6), 571 (31.1)	581, 631	587, 636, 726	0.040	0.018	1.72	1.20
(Zn)P[e]	410 (270)	540 (18), 576 (11)	580, 635	581, 639, 721	0.0214	0.0266	1.7	1.94

[a] In 2-MeTHF, $\lambda_{excitation}$ = 500 nm, the reference for quantum yield was H$_2$TPP 0.11,[40-42] quantum yield for H$_2$TPP (0.11) at 77 K was verified with (Pd)TPP (0.17; 77 K; MCH) as reference (TPP^{2-} = tetraphenylporphyrin dianion).[43,44] [b] In CH$_2$Cl$_2$ at 298 K. [c] The uncertainties of the λ_{max} are ±1 nm. [d] The uncertainties of the quantum yields are ±10%. [e] P^{2-} = 5-phenyl-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin dianion.
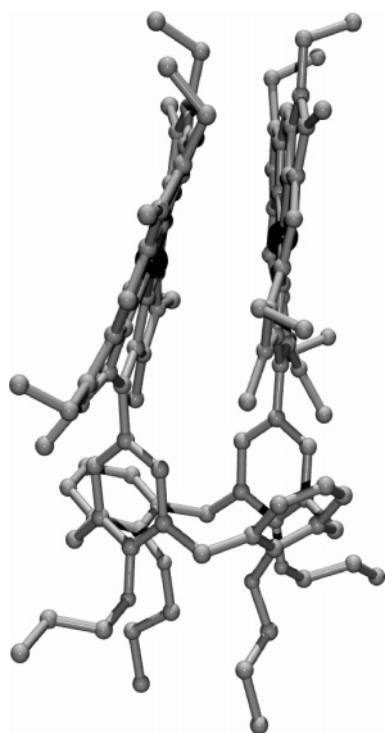
Figure 2. Another view of the optimized geometry for the closed conformer of **5**, showing the distortion of the porphyrin macrocycles.

The total PC model energies for the closed conformers for **5** and its corresponding unsubstituted derivative are found more stable compared to the corresponding open ones (by ~15 (± 2) kJ·mol^{-1}; the uncertainty is related to the relative orientation of the ethyl groups, which may vary). This result is consistent with the presence of favorable π-stacking contributions to the total energy. These computations predict that both conformers are possible. According to the small difference between the total energies computed for these two conformers, both of them should be considered.

Absorption and Photophysical Properties. The UV–Vis data for **4**, **5**, and the corresponding monoporphyrins H$_2$P and (Zn)P (H$_2$P and ZnP, P^{2-} = 5-phenyl-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin dianion) at 298 K, are presented in Table 1 and Figure 4. The absorption bands in the Soret and Q-regions exhibit the expected patterns for these two porphyrin chromophores. The comparison of the λ_{max} and bandwidth of **4** versus H$_2$P and **5** versus (Zn)P shows very little variation. This result indicates that no excitonic interaction is evident.[54,55] At 77 K, the Soret band for **4** does not shift very much (403 nm), but the Soret band

for **5** is red shifted to 421 nm. This ~10 nm shift is also noted in the Q-bands (547 and ~580 nm) for **5**. This behavior ressembles that of *J* aggregates,[54] consistent with the way the two porphyrin macrocycles place themselves as seen in the computer modeling (Figures 1 and 2).

The fluorescence and photophysical data are presented in Table 1 and Figures 5 and 6. The τ_F data for **4** are compared at both 298 and 77 K to the corresponding monoporphyrin (H$_2$P) and exhibit similar values to each other (except for H$_2$P at 77 K, which may need to be revisited). In addition, the lifetime decays are all monoexponential ($\chi \sim 1.0$), indicating that only one species is fluorescing. This similarity indicates that the porphyrin chromophores in **4** do not interact with each other. This result is a clear evidence that only the open conformer is present in solution for **4** and is consistent with most reported 5,17-substituted derivatives of cone-shaped calix[4]arenes.[1-6,56]

Compound **5** behaves differently. While Φ_F expectedly increases from 298 to 77 K for (Zn)P, due to the increase in rigidity of the medium, it decreases for **5**. The Φ_F data change in the same direction. These decreases are associated with additional deactivation pathways that can only occur from close porphyrin···porphyrin interactions. This behavior has been recently observed for cofacial bisporphyrin systems in which the distance between the macrocycles is varied by means of rigid spacers.[34,57] Again, the fluorescence decays are monoexponential. In conclusion, **5** exhibits a closed conformation at 77 K. It is well-known that cooling samples favor aggregation.

The position of the 0–0 peak blue shifts for **4** upon cooling by about 4 nm, while a red shift is observed for **5** (by about 7 nm). This observation supports the hypothesis of the formation of a closed conformer, where the presence of porphyrin···porphyrin interactions are also noted by the presence of a red shift. We have carefully considered the possibility of aggregation of calix–bisporphyrins as well. We find that the absorption and fluorescence maxima, as well as the photophysical data, are independent of the concentration of **4** and **5** at both temperatures (typical 10^{-4}

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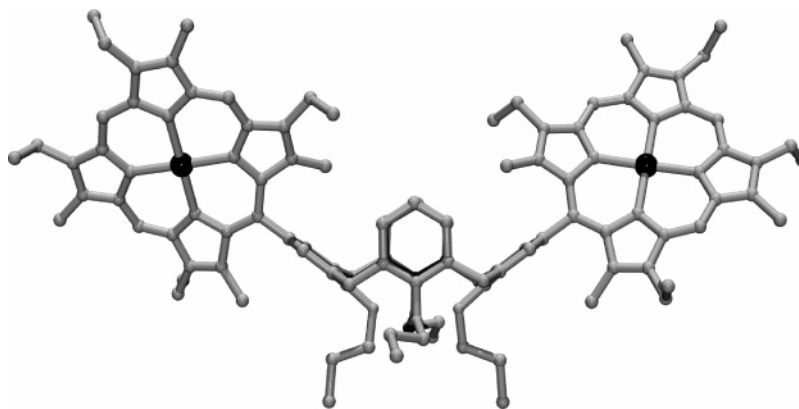
Figure 3. View of the optimized geometry for the open conformer of **5**, showing the distal orientation of the porphyrin macrocycles.
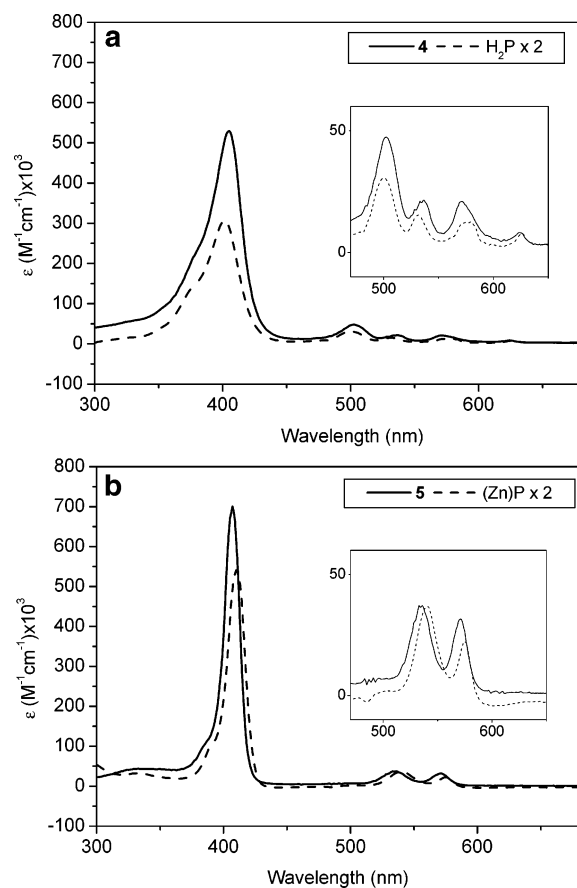

Figure 4. UV−Vis spectra of H$_2$P × 2 as compared to **4**, and (Zn)P × 2 as compared to **5** (298 K, CH$_2$Cl$_2$).

Figure 5. Normalized emission spectra in 2-MeTHF for the free base derivative **4** and the reference, H$_2$P ($\lambda_{excitation}$ = 500 nm).

Figure 6. Emission spectra in 2-MeTHF for the biszinc(II) compound **5** and the reference, (Zn)P ($\lambda_{excitation}$ = 540 nm).

to 10^{-6} M). This observation is perfectly consistent with our previous studies on cofacial bisporphyrin systems where the macrocycles are the same in the series DPS, DPO, DPX, DPA, and DPB (DPS = 4,6-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrinyl)]dibenzothiophene, DPO = 4,6-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrinyl)]dibenzofuran, DPX = 4,5-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrinyl)]-9,9-dimethylxanthene, DPA = 1,8-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrinyl)]anthracene, and DPB = 1,8-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrinyl)]biphenylene, where no anomalous behavior associated to aggregation was noted.[34,39,57]
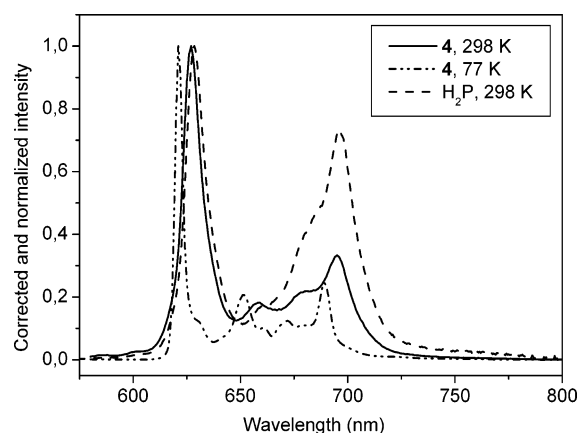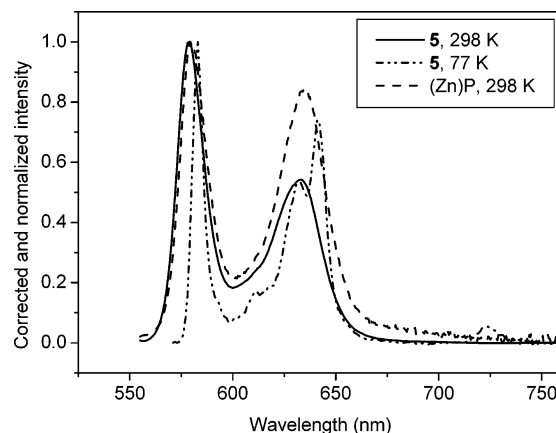
The conversion open to closed in **5** can also be examined by variable-temperature ^{1}H NMR (Supporting Information). **5** exhibits sharp resonances at 298 K in CD$_2$Cl$_2$ as described in the Experimental Section. Upon cooling, these signals gradually become larger, indicating the presence of fluxionality. Some signals remained sharp for the whole temperature range (298−183 K), notably those for the alkyl groups. The temperature of coalescence could not be measured as the solvent freezing point is 176 K. At 183 K, the signals are very broad. The fact that the coalescence temperature is lower than 183 K is consistent with a lower activation energy. The

meso-proton resonances also shift toward the shielding region upon cooling the sample, consistent with the proximity of the meso-proton with the π-system of the neighbor macrocycle in the closed conformation. For comparison purposes, the ^{1}H NMR spectra of **4** have been examined in CD_2Cl_2 at variable temperatures. The free base **4** exhibits no major change going from 298 down to 183 K. The signals become very slightly broader. No evidence for fluxionality was observed. In these experiments, no shift of the meso-proton resonances toward the shielding region is observed, indicating that the open conformation remains, a result in agreement with the photophysical data.

The question arises as why the closed conformation is observed for **5** at low temperature and is never observed for **4**. One possible explanation may be that the presence of the Zn atom increases the rigidity of the porphyrin macrocycle with respect to the free base and movement toward stacking become easier.

Conclusion

Two new bisporphyrin systems have been synthesized and characterized. The photophysical and ^{1}H NMR data indicate the presence of a fluxional process, and a closed conforma-tion is observed for **5** at 77 K. For energy transfer processes, in a donor $((Zn)P)-$acceptor $(H_2P)-$calix[4]arene system, for example, this work suggests that it is possible to modulate the inter-chromophore distance so that small or no energy transfer occurs at high temperature (open) and becomes important at low temperature (closed). In this way, it appears possible to design a "molecular switch" that responds to temperature change. The reported system **5** represents a nice example of that, but the temperature range necessary to see this change is large. The addition of bulky groups at the 11,23-positions of the calix[4]arene macrocycle may favor porphyrin···porphyrin interactions at room temperature and may shift the coalescence temperature.

Supporting Information Available: Variable temperature ^{1}H NMR of **4** and **5** in CD_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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