Inorganic Chemistry
Article

Inorg. Chem. **2009**, *48*, 8263–8270 **8263**
DOI: 10.1021/ic900887q

Three-Component Noncovalent Assembly Consisting of a Central Tetrakis-4-pyridyl Porphyrin and Two Lateral Gable-Like Bis-Zn Porphyrins

Maryline Beyler,† Valérie Heitz,*,† Jean-Pierre Sauvage,*,† Barbara Ventura,‡ Lucia Flamigni,*,‡ and Kari Rissanen§

†Laboratoire de Chimie Organo-Minérale, Institut de Chimie, Université de Strasbourg-CNRS/UMR 7177, 4, rue Blaise Pascal, 67070 Strasbourg-Cedex, France, ‡Istituto per la Sintesi Organica e la Fotoreattività (ISOF), CNR, Via P. Gobetti 101, 40129 Bologna, Italy, and §NanoScience Center, Department of Chemistry, University of Jyväskylä, FIN-40014 Finland

Received May 7, 2009

A pentaporphyrinic assembly was formed in one step, quantitatively, from a gable like zinc(II) bis-porphyrin and a free-base *meso*-tetrakis(4-pyridyl)porphyrin, because of the formation of four zinc−nitrogen coordination bonds. The X-ray crystal structure obtained shows a symmetrical structure, the free-base porphyrin being located at the center of a square formed by the four zinc atoms of the two zinc(II) bis-porphyrins. The two phenanthrolines connecting the zinc porphyrins are respectively above and below the plane of the central free-base porphyrin because of favorable CH-π interactions between several porphyrinic assemblies within the crystal. Spectrophotometric and spectrofluorimetric titrations and studies reveal a high association constant for the porphyrinic assembly in the order of 10^{14} M^{-2}. As expected, energy transfer from the zinc porphyrin component to the central free-base porphyrin quenches the fluorescence of the zinc porphyrin components whereas no sensitization of the emission of the free-base porphyrin was observed. Hypotheses on this unusual behavior are discussed.

Introduction

Coordination bonds such as those formed between the nitrogen atom of a pyridinic compound or a related Lewis base and the central metal atom of a porphyrin such as zinc(II), playing the role of a Lewis acid, have been abundantly exploited to construct a large variety of fascinating multiporphyrinic assemblies,[1−17] including catenanes and rotaxanes.[18−22] The preparation of complex edifices of this type represents a synthetic challenge. It is also important in relation to electron and energy transfer processes able to

---

*To whom correspondence should be addressed. E-mail: heitz@chimie.u-strasbg.fr (V.H.),.sauvage@chimie.u-strasbg.fr (J.-P.S.), flamigni@isof.cnr.it (L.F.).

(1) Chambron, J.-C.; Heitz, V.; Sauvage, J.-P. Noncovalent Multiporphyrin Assemblies. In *Handbook of Porphyrins*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, **1999**; Vol. *6*, p 1 and references therein.

(2) Fabrizi de Biani, F.; Grigiotti, E.; Laschi, F.; Zanello, P.; Juris, A.; Prodi, L.; Chichak, K. S.; Branda, N. R. *Inorg. Chem.* **2008**, *47*, 5425–5440.

(3) Aimi, J.; Nagamine, Y.; Tsuda, A.; Muranaka, A.; Uchiyama, M.; Aida, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 5153–5156.

(4) Flamigni, L.; Ventura, B.; Oliva, A. I.; Ballester, P. *Chem.—Eur. J.* **2008**, *14*, 4214–4224.

(5) Jensen, R. A.; Kelley, R. F.; Joong Lee, S.; Wasielewski, M. R.; Hupp, J. T.; Tiede, D. M. *Chem. Commun.* **2008**, 1886–1888.

(6) Bernad, P. L., Jr.; Guerin, A. J.; Haycock, R. A.; Heath, S. L.; Hunter, C. A.; Raposo, C.; Rotger, C.; Sarson, L. D.; Sutton, L. R. *New J. Chem.* **2008**, *32*, 525–532.

(7) Iengo, E.; Zangrando, E.; Alessio, E. *Acc. Chem. Res.* **2006**, *39*, 841–851.

(8) Hajjaj, F.; Yoon, Z. S.; Yoon, M.-C.; Park, J.; Satake, A.; Kim, D.; Kobuke, Y. *J. Am. Chem. Soc.* **2006**, *128*, 4612–4623.

(9) Ballester, P.; Oliva, A. I.; Costa, A.; Deyà, P. M.; Frontera, A.; Gomila, R. M.; Hunter, C. A. *J. Am. Chem. Soc.* **2006**, *128*, 5560–5569.

(10) Flamigni, L.; Talarico, A. M.; Ventura, B.; Rein, R.; Solladié, N. *Chem.—Eur. J.* **2006**, *12*, 701–712.

(11) Tsuda, A.; Hu, H.; Tanaka, R.; Aida, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 4884–4888.

(12) Ballester, P.; Costa, A.; Deyà, P. M.; Frontera, A.; Gomila, R. M.; Oliva, A. I.; Sanders, J. K. M.; Hunter, C. A. *J. Org. Chem.* **2005**, *70*, 6616–6622.

(13) Hwang, I.-W.; Park, M.; Ahn, T. K.; Yoon, Z. S.; Ko, D. M.; Kim, D.; Ito, F.; Ishibashi, Y.; Khan, S. R.; Nagasawa, Y.; Miyasaka, H.; Ikeda, C.; Takahashi, R.; Ogawa, K.; Satake, A.; Kobuke, Y. *Chem.—Eur. J.* **2005**, *11*, 3753–3761.

(14) Baldini, L.; Ballester, P.; Casnati, A.; Gomila, R. M.; Hunter, C. A.; Sansone, F.; Ungaro, R. *J. Am. Chem. Soc.* **2003**, *125*, 14181–14189.

(15) Haycock, R. A.; Hunter, C. A.; James, D. A.; Michelsen, U.; Sutton, L. R. *Org. Lett.* **2000**, *2*, 2435–2438.

(16) Cheng, K. F.; Drain, C. M.; Grohmann, K. *Inorg. Chem.* **2003**, *42*, 2075–2083.

(17) Paul, D.; Wytko, J. A.; Koepf, M.; Weiss, J. *Inorg. Chem.* **2002**, *41*, 3699–3704.

(18) Gunter, M. J.; Bampos, N.; Johnstone, K. D.; Sanders, J. K. M. *New J. Chem.* **2001**, *25*, 166–173.

(19) Mullen, K. M.; Johnstone, K. D.; Webb, M.; Bampos, N.; Sanders, J. K. M.; Gunter, M. J. *Org. Biomol. Chem.* **2008**, *6*, 278–286.

(20) Chichak, K.; Walsh, M. C.; Branda, N. R. *Chem. Commun.* **2000**, 847–848.

(21) Wu, J.; Fang, F.; Lu, W.-Y.; Hou, J.-L.; Li, C.; Jiang, X.-K.; Li, Z.-T.; Yu, Y.-H. *J. Org. Chem.* **2007**, *72*, 2897–2905.

(22) Hunter, C. A.; Low, C. M. R.; Packer, M. J.; Spey, S. E.; Vinter, J. G.; Vysotsky, M. O.; Zonta, C. *Angew. Chem., Int. Ed.* **2001**, *40*, 2678–2682.

mimic the natural photosynthetic reaction centers.[23–25] To study electron and/or energy transfer processes within multiporphyrin assemblies, an important prerequisite is that differently metalated porphyrins be incorporated in the same species. In such a way, a given component will act as energy or electron donor (often, a zinc porphyrin) and another porphyrinic component will be an acceptor (usually a free-base porphyrin for energy transfer and a metalated species for electron transfer). We would now like to report that an oblique bis-porphyrin, extensively used in the past for constructing various rotaxanes and catenanes in the presence of copper(I),[26–30] leads quantitatively to a five-porphyrin assembly in the presence of 5,10,15,20-tetra(4-pyridyl)-porphyrin (TPyP: **3**). The two porphyrin units of the oblique bis-porphyrin are complexed to zinc, which allows TPyP to interact with the bis-porphyrins in a well-defined fashion.[31] The noncovalent assembly obtained has been characterized by spectroscopic techniques, and an X-ray structure of it could be obtained.[32] The multicomponent species displays novel energy and electron transfer properties as demonstrated by a detailed photochemical study.

Results and Discussion

1. Synthesis of the Pentaporphyrinic Assembly. The synthesis principle is indicated in Scheme 1 as well as the chemical structure of the various fragments used and the final multiporphyrin complex **1**. As pointed out, the synthesis of bis-porphyrin **2** has already been reported long ago using a low-yielding procedure.[33] Recently developed methods based on C–C coupling reactions are much more efficient and were reported recently.[34] **3** is commercially available.

Compound **1** was prepared in a very simple way by adding a solution of **3** (1.9 mmol) in degassed $CHCl_3$ (5 mL) to a solution of **2** (3.7 mmol) in the same solvent (1 mL) at room temperature under argon. After a few hours of stirring followed by solvent evaporation under vacuum, **1** was obtained as a purple greenish solid in quantitative yield.

The multiporphyrin assembly **1** was characterized by ^{1}H NMR, including COSY and ROESY. A DOSY experiment confirmed that **1** was the sole product obtained in the complexation reaction. The NMR spectra of **1** and of its components are shown in Figure 1. In the assembly, the pyridine protons of TPyP undergo an expected strong upfield shift. Their signals are also broad because of restricted motions of the pyridine nuclei, as already observed in related cases.[31,35]

2. X-ray Structure Analysis. X-ray quality single crystals of **1** were obtained by slow diffusion of toluene into a solution of **1** in chloroform. X-ray structure analysis[32] of the assembly **1** reveals a highly symmetrical structure (Figure 2). The bond distances between the porphyrinic Zn-atoms and the nitrogen atoms of the pyridyl groups borne by the tetrapyridyl porphyrin are normal, and the Zn atoms have a slightly distorted pyramidal 5-coordination. The central tetrapyridyl porphyrin **3** retains its perfect 4-fold structure, and no alterations in its geometry are observed. The assembly **1** is planar through the Zn atoms, and the central tetrapyridyl porphyrin **3** also lies on the same plane. Because of the sterical repulsion of the six methyl groups in the both ends of the gable-like bis-porphyrin **2**, the Zn-porphyrin moieties are twisted (11.42° between the two halves of the Zn-porphyrin moiety). In spite of the 4-fold symmetry, the Zn···Zn distances do not form a regular square. The Zn···Zn distances are 13.78 Å within the bis-porphyrin **2** moiety whereas the Zn···Zn distances between the bis-porphyrin halves are 14.23 Å, also reflecting the sterical repulsions between the bulky *tert*-butyl groups. The two non-disordered chloroform molecules are hydrogen bonded to the phenantroline moiety of the bis-porphyrin **2**. The assemblies **1** pack sideways via CH-π stacking from the phenanthroline moiety and from the *tert*-butyl methyls to the aromatic rings of the adjacent molecules and on top of each other by van der Waals (vdW) contacts between the *tert*-butyl groups (Figure 3).

3. Absorption and Luminescence Studies. 3.1. Assembly in Solution. The X-ray data provided evidence for the structure of the assembly **1** in the solid state; to characterize the complex in solution, a series of spectrophotometric and spectrofluorimetric titrations were performed to derive information on the thermodynamics and the stoichiometry of the complex in toluene at room temperature.

The absorption and emission spectra of the components **2** and **3** are reported in the Supporting Information Figure S1, together with their fluorescence spectra and are in agreement with former reports.[36–38,31] Increasing amounts of **2** were added to a constant concentration of **3** (1.9×10^{-7} M) in toluene. Spectral absorption changes not consistent with the simple superposition of the spectra

---

(23) Kobuke, Y. *Eur. J. Inorg. Chem.* **2006**, 2333–2351.

(24) Nakamura, Y.; Aratani, N.; Osuka, A. *Chem. Soc. Rev.* **2007**, *36*, 831–845.

(25) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40–48.

(26) Chambron, J.-C.; Harriman, A.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1993**, *115*, 6109–6114.

(27) Blanco-Pillado, M.-J.; Jiménez, M. C.; Chambron, J.-C.; Heitz, V.; Linke, M.; Sauvage, J.-P. *Chem. Soc. Rev.* **1999**, *28*, 293–305.

(28) Andersson, M.; Linke, M.; Chambron, J.-C.; Davidsson, J.; Heitz, V.; Sauvage, J.-P.; Hammarström, L. *J. Am. Chem. Soc.* **2000**, *122*, 3526–3527.

(29) Flamigni, L.; Talarico, A. M.; Chambron, J.-C.; Heitz, V.; Linke, M.; Fujita, N.; Sauvage, J.-P. *Chem.—Eur. J.* **2004**, *10*, 2689–2699.

(30) Flamigni, L.; Heitz, V.; Sauvage, J.-P. *Struct. Bonding* (*Berlin*) **2006**, *121*, 217–261.

(31) Iengo, E.; Zangrando, E.; Alessio, E.; Chambron, J.-C.; Heitz, V.; Flamigni, L.; Sauvage, J.-P. *Chem.—Eur. J.* **2003**, *9*, 5879–5887.

(32) Crystal Data for **1**. Formula $Zn_4C_{382}H_{386}N_{28}O_2Cl_{24}$, crystal size $0.30 \times 0.30 \times 0.40$ mm, monoclinic, space group $C2/c$, $a = 43.4560(8)$ Å, $b = 32.7340(6)$ Å, $c = 16.2330(5)$ Å, $\beta = 74.644(3)°$, $V = 23058.6(9)$ Å^3, $Z = 2$, $D_{calc} = 0.938$ g/cm^{-3}, $\mu = 0.39$ mm^{-1}, 52057 reflections measured ($2\theta_{max} = 25°$), 20180 independent, 12587 with $I > (2I)$, number of parameters 971, $R_{int} = 0.0695$, $R = 0.1257$ [$I > (2I)$], $wR^2 = 0.3632$ [all data], GOF = 1.266. Maximum and minimum peaks in the difference map, 3.276/1.730 (near Zn) and −0.587 e Å^{-3}.

(33) Noblat, S.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Tetrahedron Lett.* **1987**, *28*, 5829–5832.

(34) Beyler, M.; Heitz, V.; Sauvage, J.-P. *Eur. J. Org. Chem.* **2009**, 2801–2805.

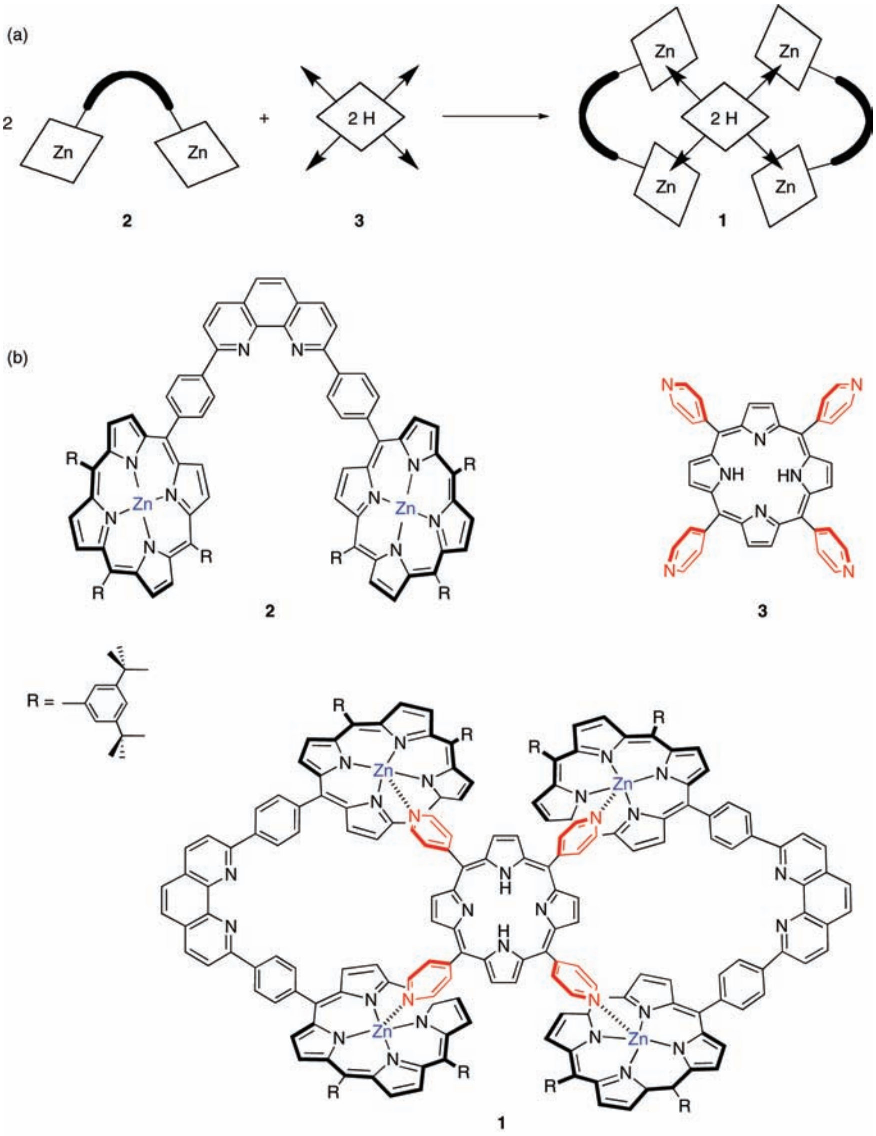
(35) Beyler, M.; Heitz, V.; Sauvage, J.-P. *Chem. Commun.* **2008**, 5396–5398.

(36) Prodi, A.; Indelli, M. T.; Kleverlaan, C. J.; Scandola, F.; Alessio, E.; Gianferrara, T.; Marzilli, L. G. *Chem.—Eur. J.* **1999**, *5*, 2668–2679.

(37) Chernook, A. V.; Rempel, U.; vonBorczyskowski, C.; Shulga, A. M.; Zenkevich, E. I. *Chem. Phys. Lett.* **1996**, *254*, 229–241.

(38) Formiga, A. L. B.; Nogueira, A. F.; Araki, K.; Toma, H. E. *New J. Chem.* **2008**, *32*, 1167–1174.

Scheme 1. (a) Schematic Representation of the Assembly Process,[a] and (b) Chemical Structure of the Two Components and the Final Assembly



Scheme 1

[a] The porphyrin units are represented as lozenges. The 2,9-diphenyl-1,10-phenanthroline connectors are indicated by bold U-shaped symbols. Each coordination bond between a pyridine nitrogen atom (Lewis base) and a zinc(II) atom (Lewis acid) is represented by an arrow.

of the two fragments are detected. It is in fact well-known that upon axial coordination of pyridyl residues, the absorption bands of zinc porphyrins display a bathochromic shift of a few nanometers.[4,31] A derived spectral profile $\Delta A(\lambda)$, defined as the difference between the experimental absorbance detected for the mixture and the cumulative absorbance of the individual components is reported in Figure 4 where a plot of the change in absorbance at two significant wavelengths is also reported.

The inset shows that a plateau is reached at about 4×10^{-7} M of **2**, indicating formation of a complex with a **2** to **3** stoichiometry of 2:1 and a high association constant. Likewise, also the luminescence of a solution of **3** is modified by addition of increasing concentrations of **2** in a way that is not consistent with the simple addition of the fluorescence from the individual components. $\Delta I(\lambda)$, defined as the difference between the experimental emission detected for the mixture and the cumulative fluorescence of the individual components, upon excitation at the isosbestic point between complexed and uncomplexed forms for a series of increasing concentrations of **2** added to **3** (1.9×10^{-7} M) in toluene, is reported in the Supporting Information, Figure S2. A plot of the trend of the emission at selected wavelengths as a function of increasing **2** concentration is displayed in Figure 5.

Increasing the concentration of **2** leads to a progressive decrease in its fluorescence (596 nm) until a plateau is reached at about 4×10^{-7} M. On the other hand, the emission of **3** (712 nm) is approximately constant upon addition of increasing amounts of **2**. Quenching of the short-lived singlet excited state of **2** (lifetime 2 ns) can occur only within the complex, and not by diffusive reactions, so fluorescence quenching is strictly related to the formation of the assembly. The concentration of **2** at the plateau is identical to the one found by spectrophotometric titration experiments and confirms a strong association with formation of a 2:1 assembly, that is, **1**.

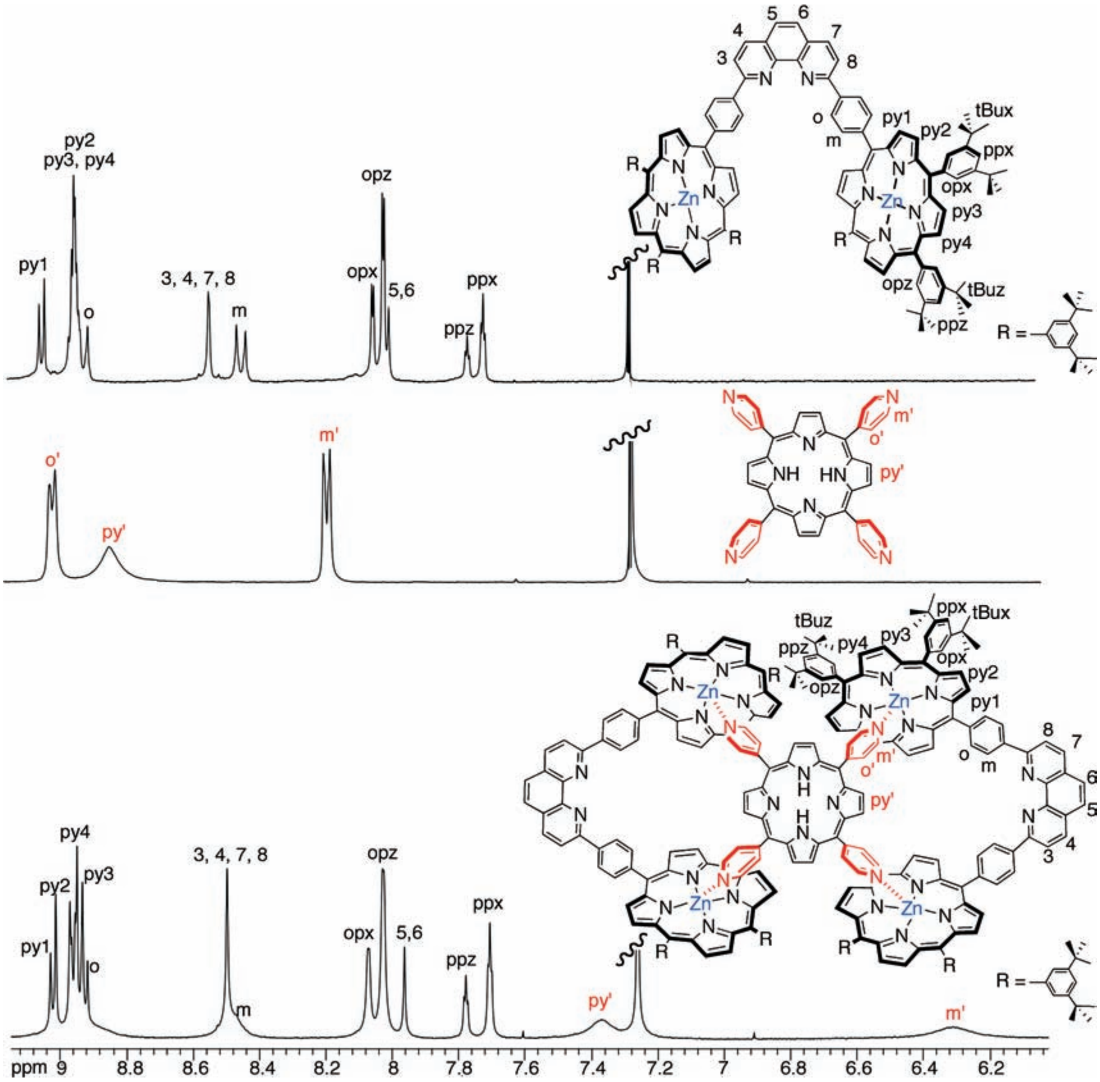


Figure 1. Proton NMR spectra of zinc(II) porphyrin **2**, TpyP: **3**, and of the multiporphyrin assembly **1**.

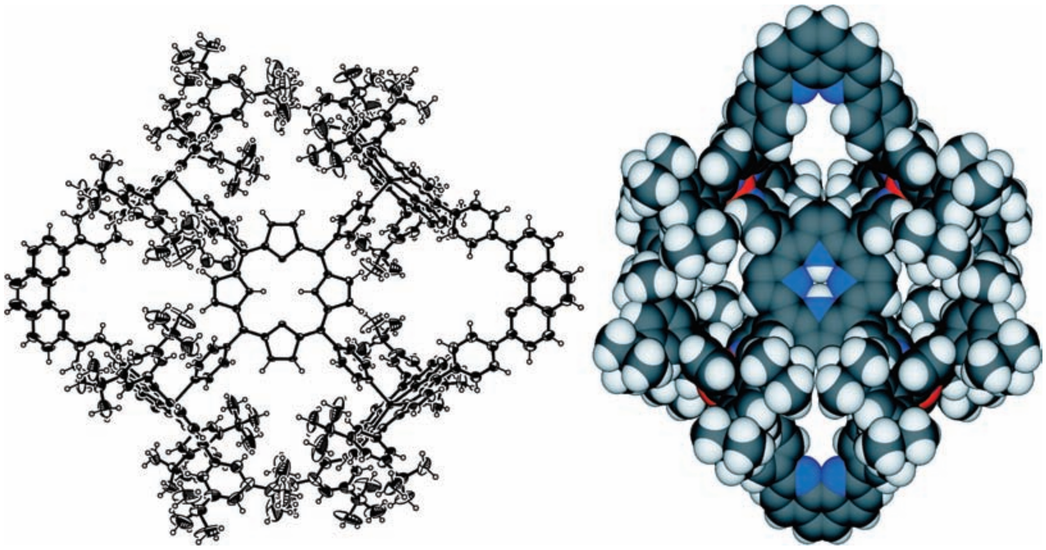


Figure 2. View with thermal ellipsoids at 50% propability level (left) and the CPK presentation (right) of assembly **1**. The solvent molecules and the disorder of the two tetrapyridyl porphyrins are omitted for clarity.

Similarly to the absorption titration data reported above, there is no evidence of a biphasic behavior in the trend, which would indicate subsequent complexation steps ($\mathbf{2} + \mathbf{3} \rightarrow \mathbf{2}\cdot\mathbf{3}$, $\mathbf{2}\cdot\mathbf{3} + \mathbf{2} \rightarrow \mathbf{2}_2\cdot\mathbf{3}$) with quite different

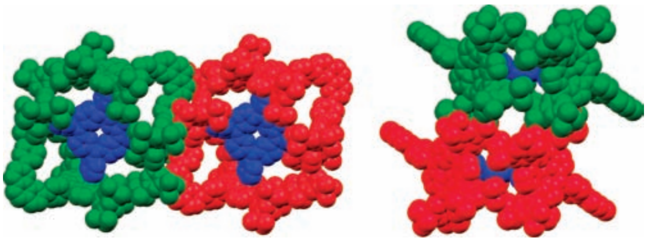


Figure 3. Packing of the assembly **1**, sideways (left) and on top each other (right). The central porphyrin is shown in blue. The hydrogen atoms, the solvent molecules, and the disorder of the two tetrapyridyl porphyrins are omitted for clarity.

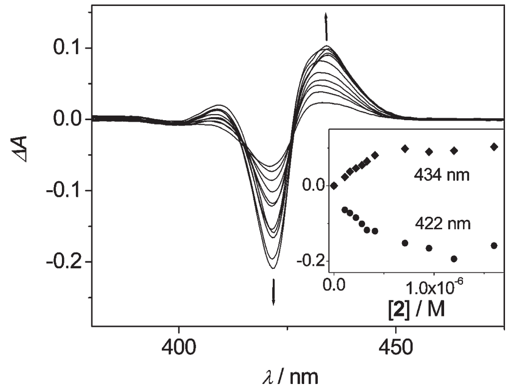


Figure 4. ΔA (see text for definition) of mixtures in toluene containing [**3**] = 1.9 × 10^{-7} M and increasing concentrations of **2** (from 1.1 × 10^{-7} M to 2.1 × 10^{-6} M). The change in ΔA at 434 and 422 nm is reported in the inset.

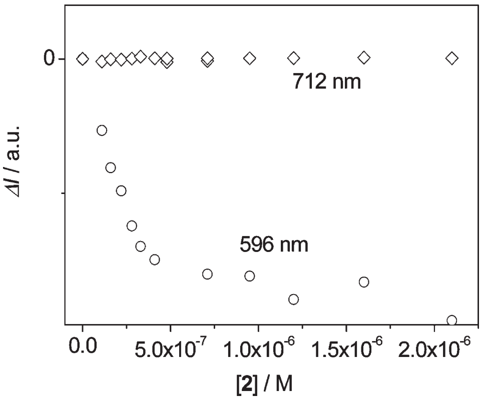


Figure 5. ΔI, see text for definition, at 596 nm (emission of **2**) and at 712 nm (emission of **3**) from Supporting Information, Figure S2 after normalization. Excitation is at 428 nm, see Supporting Information for details.

association constants. This suggests that the association processes corresponding to the two steps are similar, and both lead to thermodynamically highly stable complexes. In practice, the two double-binding *cis* positions of **3** behave independently. This implies a geometry of **1** in solution similar to the solid state (see Figure 3 right panel) where the plane containing **3** is tilted with respect to the planes containing the two coordinating **2** to prevent steric congestion by the *tert*-butyl substituents.

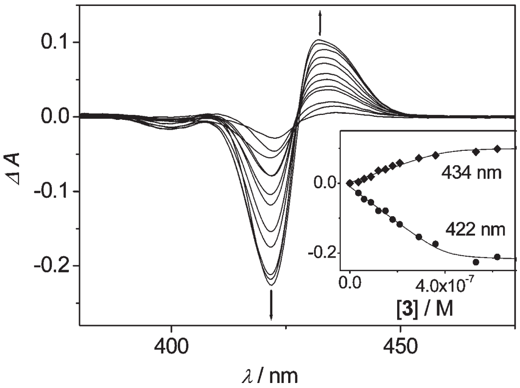


Figure 6. ΔA of mixtures in toluene containing [**2**] = 4.0 × 10^{-7} M and increasing concentrations of **3** (from 3.6 × 10^{-8} M to 7.1 × 10^{-7} M). The change in ΔA at 434 and 422 nm are shown in the inset with a fitting according to the formation of a 1:1 complex.

Experiments according to the continuous variation method (Job's plot) were run to have further confirmation on the stoichiometry of the complex, see Supporting Information, Figure S3.[39] The theoretical maximum for a 1:1 complex is 0.5 and for a 2:1 complex is 0.66. The experiments indicate an intermediate value, 0.6, and this intermediate value might be interpreted as an indication that both complexes can be formed and are equally stable, depending on the concentration ratio of the components in the specific experiment. We decided to confirm this hypothesis by titrating a constant concentration of **2** by increasing amounts of **3**; the results for absorption are reported in Figure 6. The inset displays the variation of absorption at 422 and 434 nm; the trend is still monotonic, but the plateau is now reached at a concentration of **3** of about 4 × 10^{-7} M, indicating that the 1:1 complex is formed. Fitting of the data according to a 1:1 complex formation leads to an association constant K_a of about 5 × 10^7 M^{-1}.[40] In the reasonable assumption, as discussed above, that the second association leading to **1** has a similar K_a as the first one, the overall association constant K_a for the reaction leading to the formation of **1** would be of the order of 10^{14} M^{-2}. The results of a fluorimetric titration for the same system can be seen in the Supporting Information, Figure S4.

3.2. Photoinduced Processes within the Complex. Spectrofluorimetric titrations discussed above show that upon addition of either **2** to a constant concentration of **3** or of **3** to a constant concentration of **2**, formation of the complexes causes a dramatic quenching of the zinc porphyrin fluorescence, whereas the fluorescence of **3** is unaffected, if not slightly reduced (see Figure 5 and Supporting Information, Figure S4). This behavior is in striking contrast with the results obtained in a 1:1 complex between the same **2** and a *meso*-5,10-bis(4′-pyridyl)-15,20-diphenylporphyrin (**4′-*cis*DPyP**), where the strong quenching of the fluorescence of **2** (λ = 597 nm) was accompanied by a sensitization of the **4′-*cis*DPyP** (λ = 714 nm).[31] In that case, in addition to fluorimetric steady state evidence, time-resolved experiments supported energy transfer: decay of the singlet excited state ^{1}**2** (2.06 eV) and rise of the lower singlet excited state of **4′-*cis*DPyP** (1.94 eV) with the same lifetime (τ = 50 ps at RT) were indisputable evidence. After sensitization, the singlet

---

(39) Beck, M. T. In *Chemistry of Complex Equilibria*; Van Nostrand Reinhold Company: London, 1970; pp. 85−89.

(40) Flamigni, L.; Talarico, A. M.; Ventura, B. *J. Porphyrines Phthalocyanines* **2003**, *7*, 318–327.

Table 1. Luminescence Properties of Components **2**, **3**, and Assembly **1** in Toluene; the Properties of **4′-*cis*DPyP** Are Also Reported for Comparison

	295 K			77 K		
	λ_{max}/nm	ϕ_{fl}	τ/ns	λ_{max}/nm	τ/ns	E/eV[d]
2[a]	597, 648	0.065	2.0	602, 658	2.8	2.06
				788[b]		1.57[b]
4′-*cis* DPyP [a]	648, 714	0.11	9.3	640, 710	14.8	1.94
3	645, 712	0.085	9.4	637, 697, 706	10.6	1.95
1	616, 650, 712	0.019[c]	0.18, 5.0	618, 643, 708		2.01, 1.93

[a] From reference 31. [b] Phosphorescence. [c] Fluorescence yield upon selective excitation of **3** at 646 nm. [d] From the fluorescence maxima, see Supporting Information, Figures S1 and S5.

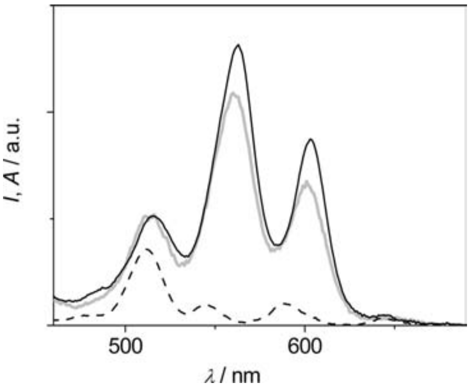


Figure 7. Corrected excitation spectrum of the complex recorded at 730 nm from a toluene solution with $[\mathbf{3}] = 1 \times 10^{-6}$ M and $[\mathbf{2}] = 2 \times 10^{-6}$ M, (gray), and arbitrarily scaled absorption spectra of the same solution (black) and of **3** (dash).

excited state localized on **4′-*cis*DPyP** decayed with the same lifetime as the uncomplexed model, 9.3 ns (Table 1). It should be pointed out that the photophysical properties of **3** are essentially identical to those of the formerly studied **4′-*cis*DPyP** (Table 1). Complexation alters the spectroscopic levels of the excited states of **2** as formerly observed for other zinc porphyrins complexed at the Zn, lowering by about 0.05 eV the ^{1}**2** level but leaves unaltered the ^{1}**3** level, Supporting Information, Figure S5.[41,10] There is therefore no evident reason for not having an efficient energy transfer also in the present case. To check this, we performed an excitation spectrum of the complex in dilute conditions with detection of the fluorescence at 730 nm, where only **3** emits, and the results are illustrated in Figure 7.

It is quite evident that the excitation spectrum overlaps reasonably well the absorption spectrum of **1**, indicating that excitation of **2** is about 80% efficient (see bands at 563 and 603 nm) in promoting the luminescence of **3**. These results prove that an energy transfer takes place from the zinc porphyrin component to the free-base component and, given the short lifetime of the excited state of **2**, this can only occur within the complex. However, a determination of the fluorescence yield of **3** in the complex upon its selective excitation at 646 nm indicates a value of 0.019, about 20% of the yield in free **3**, see Table 1. The lack of sensitization of the luminescence of **3** in the complex in spite of energy transfer from the zinc porphyrin unit, might therefore be assigned to a decrease of its own fluorescence yield, presumably the consequence of new competitive processes depleting ^{1}**3** in the complex.

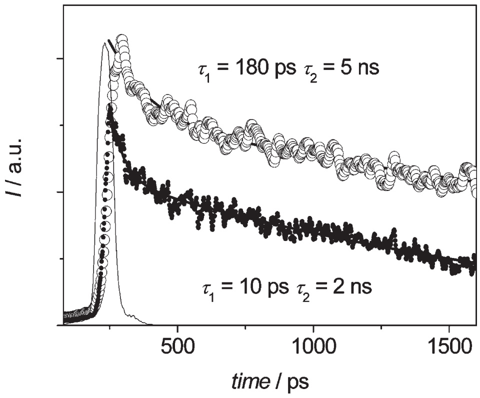


Figure 8. Room temperature luminescence profiles for complex **1** in toluene at 600 nm (dots) and 715 nm (open circles).

Time resolved luminescence experiments with nano second resolution on **1** were performed. A very weak emission with a lifetime of about 2 ns around 600 nm, ascribable to traces of uncomplexed **2**, could be detected and a lifetime of 5 ns around 720 nm, where the emission is due essentially to **3** was identified. It should be noticed that the lifetime of complexed **3** is about half the lifetime of free **3**, 9.4 ns. Picosecond time-resolved experiments on **1** gave us further information. The typical traces registered at the wavelengths for **2** luminescence (λ = 600 ± 10 nm) and **3** luminescence (λ = 715 ± 10 nm) are reported in Figure 8. It is evident that, in addition to a fast quenching (τ = 10 ps, 85% of the total decay) of the zinc component, there is a fast quenching (τ = 180 ps, 24% of the total decay) also on the free-base component. This reduced lifetime, together with the one registered on the nanosecond time scale, 5 ns, can explain the lack of sensitization of **3** fluorescence at 712 nm in the steady state experiments, in spite of energy transfer.

In general, the photophysical properties of pyridyl free-base porphyrins within self-assembled porphyrinic arrays are little altered; following an energy transfer from the zinc porphyrin component to the free-base unit, the latter retains the usual properties of the model. This has been repeatedly observed before in *cis* or *trans* dipyridyl porphyrins complexed with Zn bisporphyrinic tweezers[10,31,41] and in other porphyrinic assemblies.[4] Only in a few cases involving the tetrapyridyl derivative **3** was a decrease of the luminescence of the latter noticed. In one of these cases, a three-component (pentameric) porphyrin array similar to the present one, a decrease in the fluorescence quantum yield of **3** was detected from comparison of excitation spectra, but no in depth investigation was performed and no hypothesis was put forward.[37] In another case, where a cyclic Zn tetraporphyrin host was complexed to a central **3**, a strong fluorescence quenching of both zinc porphyrin and free-base porphyrin was noticed by steady state spectroscopy and assigned to intramolecular electron transfer. However, also in this case no further support was provided.[42]

---

(41) Flamigni, L.; Talarico, A. M.; Barigelletti, F.; Johnston, M. R. *Photochem. Photobiol. Sci.* **2002**, *1*, 190–197.

(42) Anderson, S.; Anderson, H. L.; Bashall, A.; McPartlin, M.; Sanders, J. K. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1096–1099.

The anomalous behavior following energy transfer from the zinc porphyrin component, consisting in the absence of sensitization and, as demonstrated by our determinations, in a quenching, seems therefore peculiar to the tetrapyridyl porphyrin derivative **3**. The bi-exponential behavior of the quenching might indicate reactivity of two independent populations non equilibrating within the lifetime of the excited state. A possible interpretation for the quenching of fluorescence of **3** might be an electron transfer process, as formerly postulated,[42] from one of the zinc porphyrins of **2** to the central **3** occurring via a HOMO−HOMO process from ^{1}**3**. The same electron transfer, but occurring via a LUMO−LUMO process might take place also from ^{1}**2**, which has a slightly higher energy than the free-base porphyrin excited state, and should therefore be more favored. However deactivation of the latter state occurs mainly by energy transfer, as demonstrated by the excitation spectrum, and the electron transfer might be only a secondary reaction.

Though this explanation might be reasonable, a different explanation based on a simple perturbation on the electronic states of **3** cannot be excluded. In fact, the close packing and the possible distortion and constraint experienced by **3** within the complex might introduce changes in the photophysical parameters as internal conversion, intersystem crossing, or radiative decays, affecting the luminescence properties of complexed **3**. We are presently exploring the different possibilities, either an electron transfer within the complex or an alteration of the intrinsic photophysical parameters of **3**, to explain the observations of the unexpected quenching, occurring with two independent rates corresponding to two independent populations, of the sensitized free-base **3**.

Experimental Section

Materials and Reagents. Chloroform ($CHCl_3$) was distilled from calcium hydride under argon. 5,10,15,20-Tetra(4-pyridyl)porphyrin was purchased from Aldrich and purified by column chromatography over silica gel eluted with $CHCl_3$/MeOH (100/0 to 95/5) before used. Bisporphyrin **2** was prepared as described in the literature.[34]

Nuclear Magnetic Resonance (NMR) spectra for ^{1}H were acquired on Bruker AVANCE 300 spectrometers. The spectra were referenced to residual proton-solvent references (^{1}H: $CDCl_3$ at 7.26 ppm). In the assignments, the chemical shift (in ppm) is given first, followed, in brackets, by the multiplicity of the signal (s: singlet, d: doublet, t: triplet, m: multiplet, bd: broad doublet), the number of protons implied, the value of the coupling constants in hertz if applicable, and finally the assignment.

Mass spectra were obtained by using a Bruker MicroTOF spectrometer (ES-MS).

Synthesis of the Pentaporphyrinic Assembly 1. In a round-bottom flask, **2** (8.2 mg, 0.0037 mmol) was dissolved in 1 mL of freshly distilled and degassed $CHCl_3$. In another round-bottom flask, **3** (3 mg) was dissolved in 5 mL of freshly distilled and degassed $CHCl_3$ and 0.1 mL of degassed MeOH. Two milliliters (0.0019 mmol) of this solution were added dropwise to the solution of **2** in $CHCl_3$. The solution turned immediately purple-green. The mixture was allowed to react for 3 h at room temperature under argon. The solvents were removed under reduced pressure to yield quantitatively the desired complex **1** as a purple greenish solid (9.35 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K). δ (ppm) 9.03 (d, 8 H, ^3J = 4.8 Hz, py$_1$), 8.97 (d, 8 H, ^3J = 4.8 Hz, py$_4$), 8.96 (d, 8 H, ^3J = 4.6 Hz, py$_3$), 8.93 (d, 8 H, ^3J = 4.8 Hz, py$_2$), 8.90 (vbs, 8 H, o), 8.50 (bs, 8 H, 3, 8 + 4, 7), 8.50 (vbs, 8 H, m), 8.07 (d, 8 H, ^4J= 1.6 Hz, op$_z$), 8.03 (d, 16 H, ^4J= 1.6 Hz, op$_x$), 7.96 (s, 4 H, 5, 6), 7.78 (t, 4 H, ^4J= 1.8 Hz, pp$_z$), 7.71 (t, 8 H, ^3J= 1.8 Hz, pp$_x$), 7.37 (bs, 8 H, py′), 6.32 (bs, 8 H, o′), 3.50 (vbs, 8 H, m′), 1.50 (s, 72 H, tBu$_z$), 1.40 (s, 144 H, tBu$_x$).

ES/MS. m/z 2526.73 ((**1** + H^+ + Na^+)/2) calcd. 5054.12 for $C_{336}H_{338}N_{28}Zn_4NaH$.

Crystallography. Data were recorded with a Bruker-Nonius Kappa APEX II diffractometer using graphite-monochromatized Mo Kα radiation [λ = 0.71073 Å)] and at 123.0(1) K. The data were processed with Denzo-SMN v0.95.373,[43] and the structure was solved by direct methods.[44] Refinements based on F^2 were made by full-matrix least-squares techniques.[45] No absorption correction was applied. The hydrogen atoms were calculated to their idealized positions with isotropic temperature factors (1.2 or 1.5 times the C temperature factor) and refined as riding atoms. Because of the moderate crystal quality and the severe disorder of the solvent molecules, the final electron density map shows two high peaks which could not be removed (close to the Zn atoms). The solvent toluene molecules were badly disordered so that in only one toluene the methyl carbon could be located. Also most of the solvent chloroforms were disordered. Two moderate electron density peaks were found close to one disordered (population parameter 0.5) toluene molecule and were treated as fractional water molecules. The crystal lattice contains large voids, and the electron density belonging to severely disordered solvent molecules within the voids was treated with the SQUEEZE-program.[46]

Spectroscopic Measurements. Spectroscopic grade toluene, dichloromethane, and methanol (Carlo Erba) were used as received. Absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer in 10 mm optical path cells. The molar absorption coefficient of **3** in toluene was determined by preparing diluted toluene solutions ($2-5 \times 10^{-7}$ M) with the addition of small fractions of methanol (less than 5%) and extrapolating the absorption coefficient value to infinite dilution. Toluene solutions with concentrations of **3** higher than 5×10^{-7} M were obtained preparing a stock solution of **3** in dichloromethane ($1-2 \times 10^{-5}$ M), vacuum drying aliquots of it, and adding the desired **2** solution. The mixtures were left in the dark at room temperature overnight, and **3** resulted perfectly dissolved in toluene in the presence of **2.** For the titrations, increasing amounts of **2** (or **3**) were added to a constant concentration of **3** (or **2**) and to avoid dilution of the guest, solutions of **2** (or **3**) at the desired concentrations were vacuum-dried and the solution of **3** (or **2**) was added. For each mixture the corresponding solution of **2** (or **3**) alone was also monitored, as well as the constant concentration of **3** (or **2**). The properties of the complex were studied in toluene solutions with a concentration of **2** twice the concentration of **3** to favor the formation of the three-component array **1**.

Emission spectra, uncorrected if not otherwise specified, were detected by a Spex Fluorolog II spectrofluorimeter equipped with a Hamamatsu R928 photomultiplier. Fluorescence quantum yields were evaluated from the area of the luminescence spectra corrected for the photomultiplier response, with reference to TPP (tetra-phenyl-porhyrin) in aerated toluene (Φ_{fl} = 0.11).[47] Relative emission yields in the mixtures were determined versus the model compounds. Experiments at 77 K made use of quartz capillary tubes immersed in liquid nitrogen contained in a homemade quartz Dewar flask. Fluorescence lifetimes in the nanosecond range were detected by an IBH Time Correlated

---

[43] Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307–326.
[44] Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
[45] Sheldrick, G. M *Acta Crystallogr.* **2008**, *A64*, 112–122.
[46] Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.
[47] Seybold, P. G.; Gouterman, M. *J. Mol. Spectrosc.* **1969**, *31*, 1–13.

Single Photon Counting apparatus with excitation at 373 or 560 nm (resolution 0.3 ns). Time resolved luminescence experiments in the picosecond range made use of a Nd:YAG laser (Continuum PY62−10) with a 35 ps pulse duration, 532 nm, 1.6 mJ/pulse and a Streak Camera (Hamamtsu C1587 equipped with M1952). The luminescence signals from 5000 laser shots were averaged, and the time profile was derived from the streak image in a wavelength range of about 20 nm around the selected wavelength. The overall time resolution of the system after the deconvolution procedure is 10 ps.[4,48] Estimated errors are 10% on lifetimes for single exponentials, 20% on more complex kinetics, 20% on quantum yields, 20% on molar absorption coefficients, and 3 nm on emission and absorption peaks. Working temperature, if not otherwise specified, was 295 ± 2 K.

Conclusions

Two gable-like bis- zinc(II)porphyrins were assembled quantitatively with a *meso*-tetrakis(4-pyridyl)porphyrin ligand. The assembly **1** is highly symmetrical as shown by the NMR spectra and the solid state X-ray crystal structure. The central tetrapyridyl porphyrin is coordinated to the Zn atoms of the bis-porphyrin **2** with normal bond distances and angles, yet the bulky *tert*-butyl groups induce a slight twisting of the Zn-porphyrins.

Assembly **1** is very stable in solution (K_a of the order of 10^{14} M^{-2}) and displays unusual photoinduced processes. Whereas the higher energetic singlet excited state of **2** is quenched by energy transfer to the free-base component **3** within the assembly, as demonstrated by excitation spectra, the fluorescence yield of the latter is not enhanced. On the contrary, a quenching of the fluorescence of **3** in the self-assembly is detected. This might be due to a competing process depleting the excited state of **3**, for example electron transfer, or alternatively to a perturbation of the intrinsic photophysical parameters of the tetrapyridyl porphyrin engaged in the complex. Both hypothesis are reasonable, and we are presently working to elucidate this point.

The formation of Zn-pyridine coordination bonds is a very efficient tool in the construction of large multicomponent assemblies as illustrated by the present work and by many contributions from other groups.[1−22] Assembly **1** displays unique properties in the sense that the spacers used are 1,10-phenanthroline nuclei, which will allow coordination of transition metals and extension of the present system toward more complex molecular assemblies and unusual topologies.

Acknowledgment. The authors gratefully acknowledge CNRS, COST D31, the Academy of Finland (K.R., proj. no. 212588), CNR of Italy (PM.04.010 MACOL) for financial support. We acknowledge the French Ministry of Education for a fellowship (M.B.).

Supporting Information Available: Crystallographic data for complex **1** (CIF) and supplementary spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(48) Flamigni, L. *J. Phys. Chem.* **1993**, *97*, 9566–9572.