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Unsymmetrical Calix[4]arene Bisporphyrin Pacman

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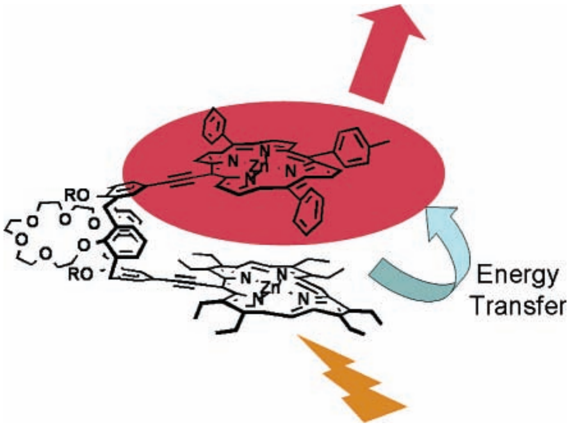
ABSTRACT



The synthesis of a Pacman heterobisporphyrin associating an octaethyl porphyrinatozinc (ZnOEP) energy donor and a triaryl porphyrinatozinc (ZntPP) energy acceptor around a calix[4]arene spacer is described. Contrary to previous symmetrical architectures, correlations between the chromophores in the unsymmetrical calixarene bisporphyrin Pacman scaffold can now be observed in ROESY experiments. Independent of the excitation wavelength, only the luminescence of the ZntPP moiety was observed corresponding to quenching of the OEP moiety's emission.

Over the last 25 years, many structures in which two porphyrins are preorganized in a cofacial geometry have been reported.[1] Although rigid spacers were initially chosen to control the distance separating the tetrapyrrolic macrocycles in the scaffolds, we have recently introduced the concept of flexible Pacman structures by using the upper rim of calix[4]arene spacers as a preorganization platform.[2] Literature reports have shown that the attachment of porphyrins onto the lower rim of calixarenes via ether linkages at the phenol oxygens affords rather flexible hosts whose geometries are controlled by the binding of guests.[3] By functionalizing these calixarene spacers with a rigid and linear acetylenic linker on the upper rim, the cofacial geometry can be controlled, even in the absence of a guest.

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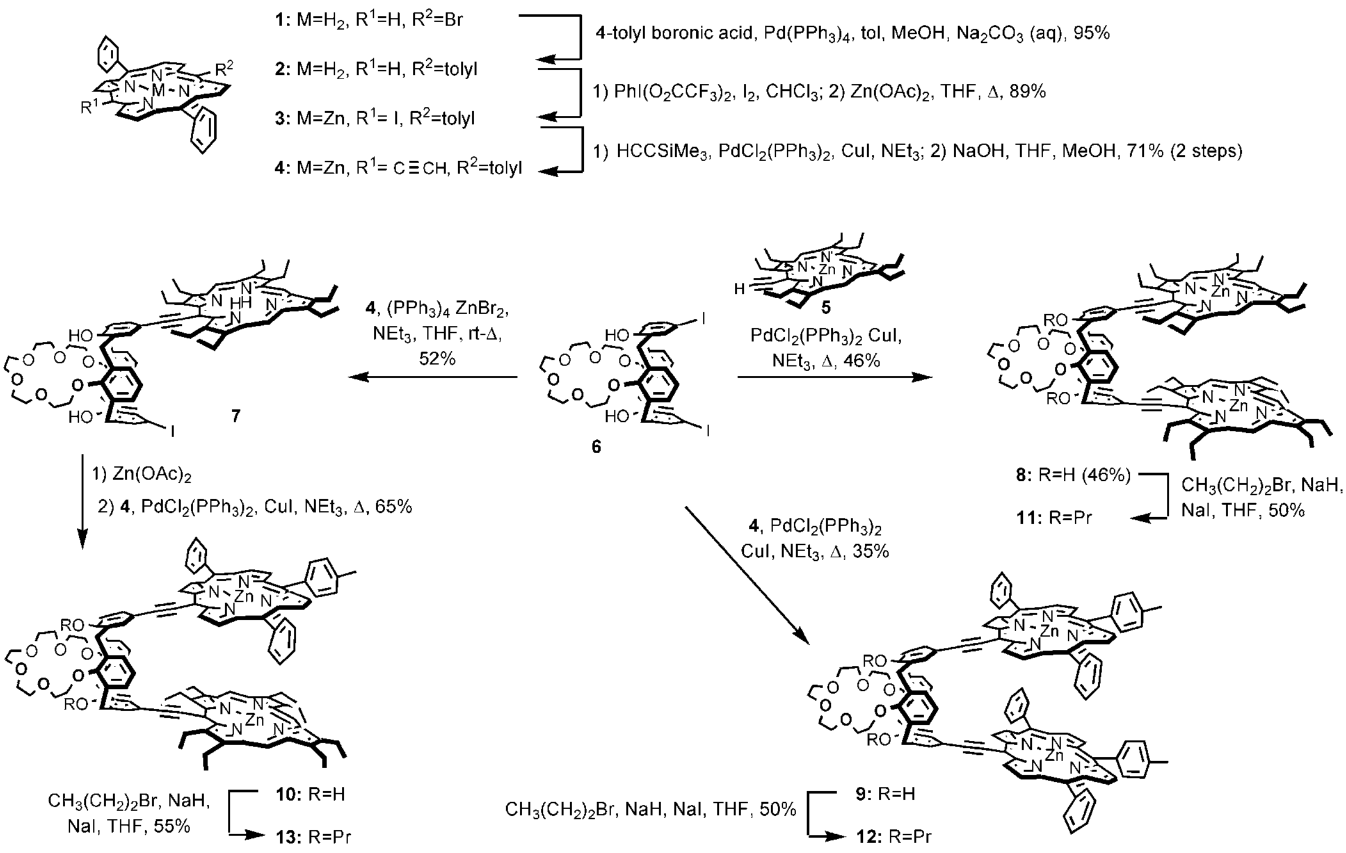
Scheme 1



Over the past 4 years, our synthetic strategy leading to calixarene−porphyrin scaffolds of the Pacman type has been based on a key synthetic step consisting of “one-pot” Sonogashira or Negishi bis-coupling reactions between ethynyl porphyrins and iodo-calixarenes. Although these methods are usually weakly affected by steric constraints, the first coupling occurred much faster than the second. By using stoichiometric amounts of calixarene **6**[4] and zinc 5-ethynyl-octaethylporphyrin[5] **5**, we could isolate the monoporphyrin derivative **7** in decent yields (Scheme 1). This fact represented a unique chance to introduce different chromophores on a calix[4]arene spacer in a controlled cofacial arrangement. Until now, chromophores in this family of Pacman bisporphyrins have been differentiated only by selective metalation of identical porphyrins.[6] It is now possible to selectively combine an octaethyl porphyrin and a triaryl porphyrin substructure within the same scaffold, as reported hereafter. The synthetic possibilities offered by the use of calixarene spacers have been extended by the design and synthesis of the heteroporphyrin dimer **13**. This dimer comprises a zinc octaethyl porphyrin (ZnOEP) and a zinc triphenylporphyrin (ZntPP) and behaves as an energy dyad in which the ZnOEP and ZntPP moieties act, respectively, as an energy donor and as an energy acceptor.

To synthesize the *meso*-ethynyl-triarylporphyrin derivative **3**, 5-bromo-10,20-diphenylporphyrin[7] **1** was coupled with 4-tolylboronic acid[8] under biphasic Suzuki conditions to yield porphyrin **2**. Iodination of the last *meso* position according to the method reported by Dolphin,[9] followed by metalation with $Zn(OAc)_2 \cdot 2H_2O$ in refluxing THF, afforded **3** in 89% yield (two steps). Sonogashira coupling of the latter with trimethylsilyl (TMS) acetylene, followed by removal of the TMS in the presence of NaOH, afforded the *meso*-ethynyl-triarylporphyrin **4** in 71% yield (two steps). Successive or simultaneous Sonogashira couplings of the diiodo-calixarene **6** with ethynyl-porphyrin **4** and/or **5** generated dimers **8**−**10**. Subsequent peralkylation of the calixarene’s lower rim afforded the Pacman heterobisporphyrin **13** and the reference homobisporphyrins **11** and **12**. Only moderate yields were obtained for the coupling, probably due to the binding of solvent molecules to the central zinc core of the porphyrins, which increases the steric bulk within the Pacman structure. Attempts to template the Pacman formation using a bidentate ligand such as diazabicyclo[2,2,2]octane were unsuccessful.

In our previous Pacman porphyrin dimers, 2D NMR studies were precluded due to the symmetrical nature of the

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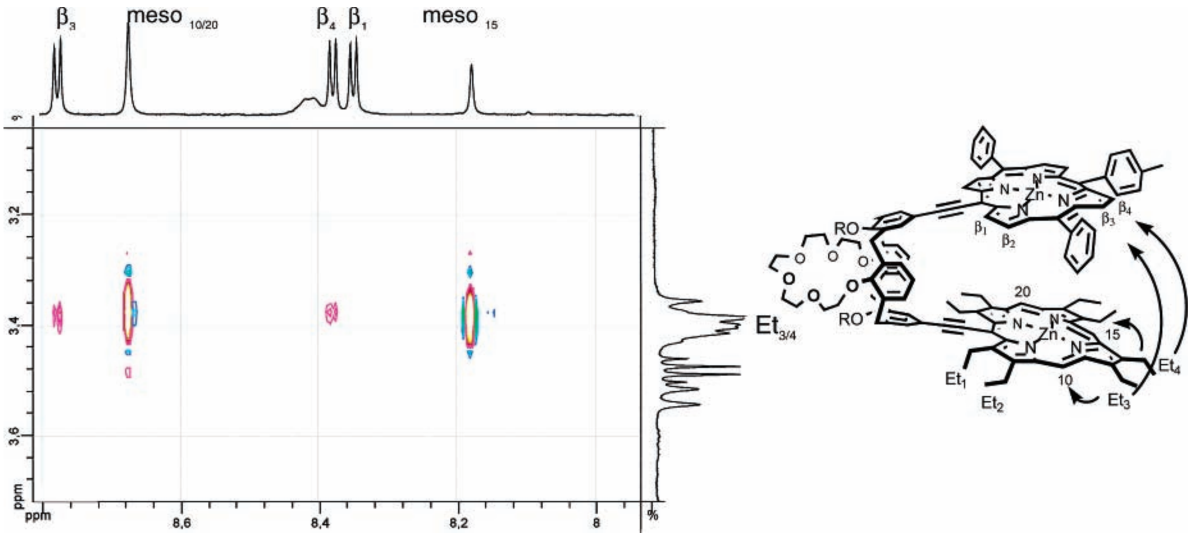

Figure 1. Region of the 500 MHz ROESY plot in $CDCl_3$ for the mixed ZnOEP−ZntPP Pacman **13** showing the correlations at the open end of the molecular scaffold.

scaffolds. Interactions between the two different chromophores have now been probed by ROESY experiments for the ZnOEP−ZntPP dimer **13**.

A full ROESY experiment (see Supporting Information) has been used to assign the porphyrin resonances unequivocally, with the exception of the CH_2 groups of two ethyl substituents of the OEP moiety. The two methylene groups of substituents Et_1 and Et_2 were easily assigned at 4.35 and 3.77 ppm, respectively. On the contrary, the CH_2 groups of Et_3 and Et_4, of the pyrrole between the 10 and 15 *meso* positions, cannot be distinguished due to the very similar chemical shifts of their methylene parts (Figure 1). However, their corresponding methyl groups can be assigned on the basis of their proximity with the tolyl and phenyl substituents of the neighboring tPP moiety (see Supporting Information). The compactness of the scaffold is demonstrated by intense correlations between the protons of the β-pyrrolic ethyl groups Et_3 and Et_4 of the OEP moiety and the β-pyrrolic protons β_3 and β_4 of the tPP moiety as displayed in Figure 1.

As shown in Figure 2, the Soret bands of **11** and **12** are broadened, with a clear split in the case of **12** and a shoulder in the case of **11**. Although the absorption spectrum of **13** is expected to show classical effects of excitonic coupling, such as displacement and hypochroism, it is interesting to note that none are observed. As a result, the UV−visible absorption spectrum of the heterobisporphyrin **13** is essentially the sum of the absorption of the two reference homodimers **11** and **12**. These observations are consistent with excitonic coupling between the two chromophores. The absorption maxima of **13** are close to the original values for the isolated OEP (422 nm) and the tPP (438 nm). This observation may indicate that excitonic interactions in the heterobisporphyrin dyad **13** are weaker than in homochromophoric species due to different orientations of the transition dipole moments in OEP and triaryl porphyrins.[10]

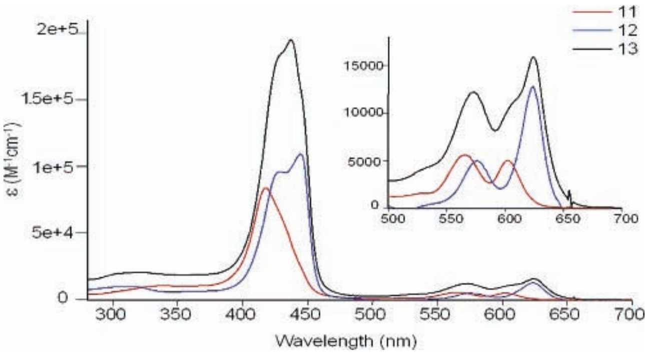

Figure 2. UV−visible absorption of dyad **13** and references **11** and **12** in distilled 2-MeTHF.

Because of their structural differences, the ZnOEP and ZntPP moieties combined in **13** were expected to display distinct photochemical behavior. The absorption bands of the ZnOEP dimer are higher in energy than those of ZntPP. Thus, upon excitation of the heterodimer **13**, energy transfer from the ZnOEP chromophore to the ZntPP moiety would be expected.

Indeed, luminescence spectra of dyad **13** afforded unique emission spectra corresponding to the emission of the ZntPP moiety, regardless of the excitation wavelength.[11] Normalized emission spectra recorded for different excitation wave-

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lengths show emission maxima identical to those of the reference bis(ZntPP) **12**, as depicted in Figure 3.

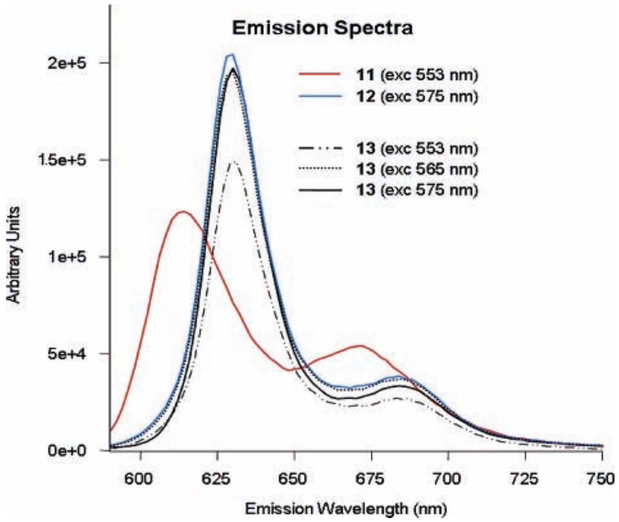

Figure 3. Normalized emission spectra of dyad **13** and reference homodimers **11** and **12** in 2-MeTHF.

Two main emission bands for bis(ZnOEP) **11** are observed and centered at 614 nm for the most intense band and at 672 nm for the weakest one. No contribution from the OEP moiety could be observed in the emission of the heterodyad **13**, suggesting that the excited states of the OEP moiety in **13** are completely quenched by the triaryl porphyrin moiety.

Examination of the excitation spectra (Figure 4) recorded for the dyad **13** and each reference Pacman **11** and **12** confirms the quantitative intramolecular quenching of the ZnOEP S1 excited state by the facing ZntPP chromophore. Indeed, the excitation spectra of the dyad **13** correspond to the superposition of the references bis(ZnOEP) **11** and bis(ZntPP) **12**.

In conclusion, the versatility of our synthetic approach, initially illustrated by variations on the calixarene spacers, has conveniently led to Pacman bisporphyrins incorporating two different porphyrin macrocycles. The presence of two different porphyrin macrocycles provides a tremendous advantage for the preparation of Pacman scaffolds containing various metals.

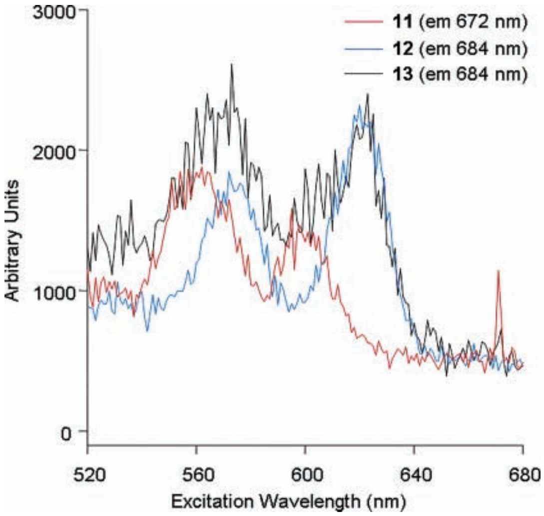

Figure 4. Excitation spectra of dyad **13** and reference Pacman homodimers **11** and **12** in 2-MeTHF.

Preliminary studies suggest an efficient energy transfer from the ZnOEP donor to the ZntPP acceptor. Time-resolved luminescence measurements for singlet energy transfer should be reported shortly. In the future, the photochemical and photophysical properties of these Pacman scaffolds will be tuned by taking advantage of the different metalation rates of *meso*-triaryl and octaethyl porphyrin macrocycles.

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Supporting Information Available: Experimental procedures, ^{1}H NMR spectra of dyads **11**−**13**, and a complete ROESY NMR spectrum for the heterodimer **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Because of the significant overlap of the absorption spectra of **11** and **12**, there is no excitation wavelength at which the donor may be selectively excited. However, at 553 nm, the ϵ of bis(ZnOEP) **11** is 3 times higher than that of bis(ZntPP) **12**.