ORGANIC LETTERS

2007
Vol. 9, No. 8
1557−1560

Synthesis of Novel *N*-Linked Porphyrin–Phthalocyanine Dyads

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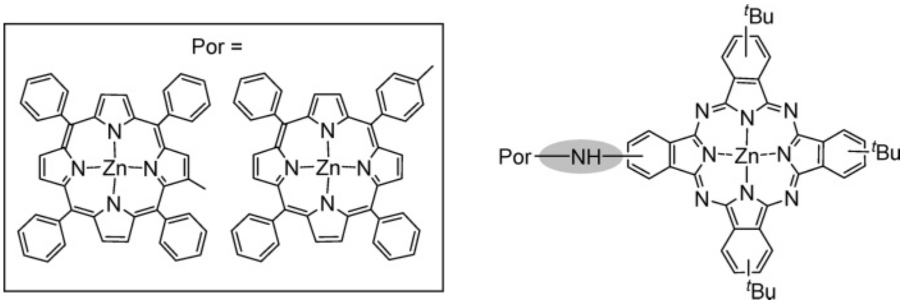
Received February 12, 2007

ABSTRACT



Two types of covalently NH-linked porphyrin–phthalocyanine dyads, connected either through the *meso* phenyl group or the β-pyrrolic position of the porphyrin, have been synthesized following statistical condensation methodologies for phthalocyanine preparation and palladium-catalyzed amination methods. Photophysical studies have revealed that energy transfer from the porphyrin to the phthalocyanine prevails regardless of linkage.

The remarkable properties of both porphyrins (Ps) and phthalocyanines (Pcs) as individual chromophores[1] have given rise in recent years to the synthesis and study of porphyrin−phthalocyanine (P−Pc) ensembles as light-harvesting systems with a wider absorption spectrum. Moreover, since the Q-band absorption of phthalocyanine almost overlaps the fluorescence wavelength of porphyrins, upon excitation, singlet-state intramolecular energy transfer from the porphyrin to the phthalocyanine occurs very efficiently in most P−Pc dyads.

In P−Pc systems previously described, different types of rigid or flexible spacers have been used to connect the two chromophores.[2] Some examples of P−Pc dyads directly connected through the *meso* or the β-pyrrolic position of the

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10.1021/ol0703635 CCC: $37.00

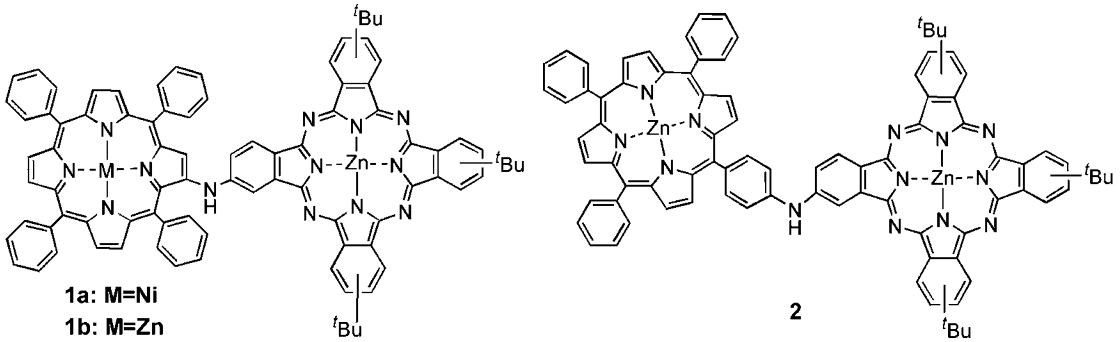

Figure 1. Porphyrin−phthalocyanine dyads **1** and **2**.

porphyrin have also been reported,[3] thus allowing a close proximity of the two units.

We report herein the synthesis of novel P−Pc dyads **1** and **2** (Figure 1) where the two macrocycles are linked through an amino group located either at the β-pyrrolic position or the *meso* phenyl groups of the porphyrin, respectively. The nitrogen atom located between the two macrocycles could play the role of "active" spacer, since it typically behaves as a pH- and redox-sensitive group.

The relevance of phthalocyanines[4] in the field of molecular materials lies not only in their strong optical absorption in the red/near-infrared zone but also in their versatility as molecular building blocks whose properties can be tuned by introduction of different peripheral substituents. Among the wide variety of substituents that have been introduced, the amino group plays an important role regarding its influence in the phthalocyanine properties.[5] In contrast, very few efficient methods for introducing this functional group have been described. In most cases, amino-substituted phthalocyanines are prepared by reduction of a nitro derivative.[6,7] In recent years, palladium-catalyzed coupling reactions have proved an effective method for phthalocyanine functionalization, mainly for attaching alkynyl chains at the peripheral positions.[8] However, a palladium-catalyzed reaction has been applied only once for connecting amino chains onto the Pc macrocycle.[9] This last method would allow the preparation of arylaminophthalocyanines, thus making possible the introduction of relatively elaborate substituents. As far as porphyrins are concerned, palladium-catalyzed amination has emerged as a powerful approach for the formation of carbon−nitrogen bonds.[10]

Herein, we also report on the use of the palladium-catalyzed Buchwald−Hartwig amination reaction[11] as a good method to prepare porphyrinylaminophthalocyanines.

Two different synthetic approaches have been followed for the preparation of dyads **1** and **2**. One of them involves the classical statistical cross-condensation of two differently substituted phthalonitriles, and the other is based on a palladium-catalyzed Buchwald−Hartwig amination reaction of adequately functionalized phthalocyanine and porphyrin fragments. The synthesis of dyad **1a** using a statistical condensation methodology required the preparation of 4-porphyrinylaminophthalonitrile **4** (Scheme 1). This compound was obtained in good yield (ca. 60%) by a Buchwald−Hartwig amination reaction of Ni(II)−2-amino-*meso*-tetraphenylporphyrin (**3**)[12] and 4-iodophthalonitrile. The $Pd(OAc)_2$/*rac*-BINAP catalytic system was employed together with potassium *tert*-butoxide as base. Similar yields were obtained when the reactions were carried out either in toluene or THF at refluxing temperatures. Initially, the NiP−ZnPc dyad **1a** was prepared in 33% yield by statistical condensation of the porphyrinylaminophthalonitrile **4** with an excess of 4-*tert*-butylphthalonitrile in a refluxing mixture of *o*-dichlorobenzene and *N*,*N*-dimethylaminoethanol (DMAE) using zinc chloride as template (Scheme 1). As expected, the reaction afforded a mixture of the desired dyad **1a** and Zn(II) tetra-*tert*-butylphthalocyanine (**Zn^{t}Bu$_4$Pc**) as major

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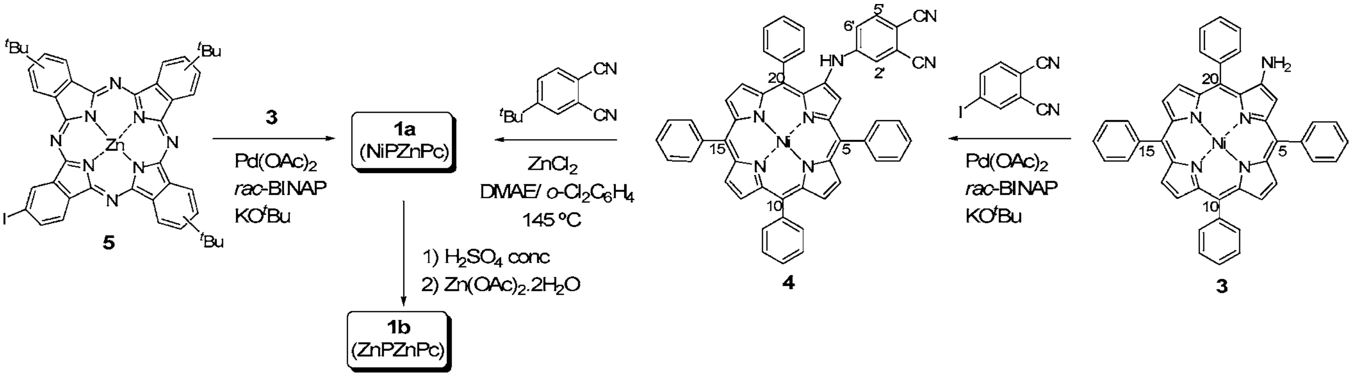
Scheme 1. Synthesis of Porphyrin−Phthalocyanines **1a** and **1b**



products. Additionally, during purification of the reaction mixture by column chromatography, a minor amount of a product identified by HRMS (MALDI-TOF) as a **(NiP)$_2$−ZnPc** triad was obtained. On the other hand, the same dyad **1a** was prepared in 70% yield using the above-mentioned Buchwald−Hartwig reaction conditions from the aminoporphyrin **3** and Zn(II)−2(3),9(10),16(17)-tri-*tert*-butyl-23-iodophthalocyanine (**5**).[13] Finally, in order to obtain the photoactive ZnP−ZnPc dyad **1b**, the porphyrin moiety of the NiP−ZnPc derivative **1a** was demetalated to the corresponding free base, followed by standard metalation using zinc acetate (Scheme 1).

The same strategies were applied to the synthesis of dyad **2**. The required porphyrinylaminophthalonitrile precursor **7** was prepared in four steps from the free-base *meso*-tetraphenylporphyrin (**TPP**). First, selective mononitration with concentrated nitric acid, followed by reduction of the nitro group with SnCl$_2$ in HCl and metalation of the free-base porphyrin with zinc acetate, yielded derivative **6** in 21% global yield.[14,15] This compound was finally subjected to a palladium-catalyzed coupling reaction with 4-iodophthalonitrile (Scheme 2). The amination reaction gave the porphyrinylaminophthalonitrile **7** in low yield (15−20%) whenever refluxing toluene or THF was employed as solvent. When the porphyrinylaminophthalonitrile **7** was subjected to cross-condensation with an excess of 4-*tert*-butylphthalonitrile using the standard conditions, dyad **2** was obtained in 17% yield from the reaction mixture (Scheme 2).

The desired ZnP−ZnPc **2** could also be prepared in 41% yield by coupling Zn(II) 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (**6**) with monoiodoPc **5** in toluene.

Figure 2 shows the UV/vis spectrum of dyad **1b** in THF compared to the spectra of Zn(II)-*meso*-tetraphenylporphyrin (**ZnTPP**) and **Zn^{t}Bu$_4$Pc**. The spectrum of the dyad **1b** shows the characteristic absorptions of the individual macrocyclic components, namely strong absorptions assigned to the porphyrin and phthalocyanine Q and Soret bands. However,

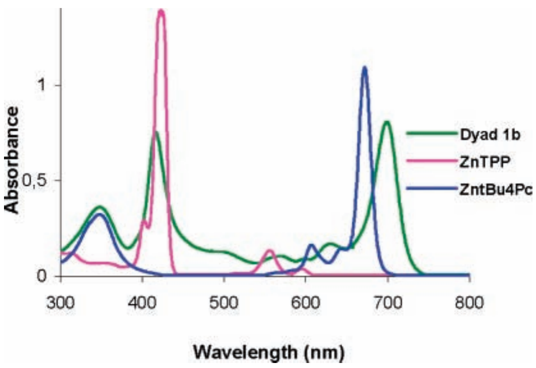
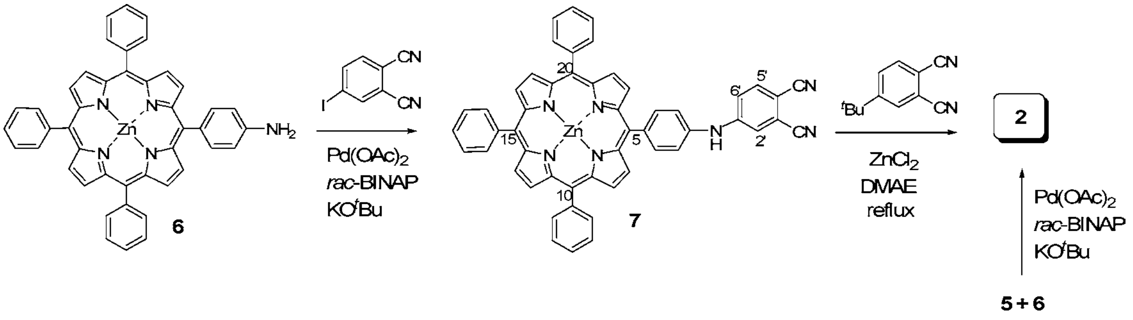


Figure 2. UV/vis spectrum of dyad **1b** in THF, compared to the ones of the **ZnTPP** and **Zn^{t}Bu$_4$Pc** references.

Scheme 2. Synthesis of Porphyrin−Phthalocyanine Dyad **2**



the red shift (ca. 23 nm) experienced by the phthalocyanine Q-band in dyad **1b** is quite remarkable, suggesting a reduction of its HOMO−LUMO gap as a consequence of the electron-donor character of the porphyrinylamino substituent. The same trend was observed in the UV/vis spectrum of dyad **2** (see the Supporting Information).

Excited-state interactions in **1b** and **2** were tested by means of fluorescence and transient absorption spectroscopies. Mirror imaging the absorption spectra, the fluorescence maxima in the dyads shift − relative to the **ZnTPP** (i.e., toluene, 595 nm; THF, 600 nm) and **Zn^{t}Bu$_4$Pc** (i.e., toluene and THF, 680 nm) references—notably to the red. In THF, **1b** exhibits maxima at 605 and 695 nm, whereas those for **2** are at 610 and 710 nm. This trend, which reflects the mutual ZnP/ZnPc electronic coupling, is excitation wavelength independent. More quantitative information was deduced from fluorescence quantum yield determinations. When photoexciting at 425 nm, in the blue part of the spectrum (i.e., 575−675 nm, corresponding to the **ZnTPP** part) fluorescence quantum yields of 0.003 and 0.008 were determined for **1b** and **2**, respectively. **ZnTPP** fluoresces under these conditions with much higher quantum yields of 0.04. In the red part (i.e., 675−800 nm, corresponding to the **Zn^{t}Bu$_4$Pc** part), on the other hand, a fluorescence pattern evolves that is identical to that of **Zn^{t}Bu$_4$Pc** with quantum yields of 0.15 (**1b**) and 0.26 (**2**). Notably, at 425 nm excitation the ZnP/ZnPc absorption ratio in **1b** and **2** exceeds a value of 0.9. In other words, detecting ZnPc fluorescence quantum yields that are nearly quantitative—for **Zn^{t}Bu$_4$Pc** the corresponding value is 0.3—despite its negligible absorption in **1b** and **2** at 425 nm, implies an efficient transduction of singlet excited-state energy. Proof for this hypothesis came from excitation spectra recorded for the 695 and 710 nm fluorescence. They revealed in both cases spectra that are essentially mirror images of the ground-state absorption. Particularly relevant are in this context the ZnTPP contributions.[16]

In time-resolved fluorescence measurements the following lifetimes emerged for the **ZnTPP** and **Zn^{t}Bu$_4$Pc** references: 1.7 ns recorded at ∼600 nm and 3.0 ns recorded at ∼700 nm. In the 600−650 nm range no detectable fluorescence was, however, noted for **1b** and **2** within the 0.1 ns detection range. Turning to the 700−750 nm range for both dyads, lifetimes were noted (2.1 ns (**1b**) and 2.1 ns (**2**)) that are similar and somewhat slower than that of the **Zn^{t}Bu$_4$Pc** reference. Although fluorescence spectroscopy already shed light onto the nature of excited-state interactions we extended our investigation to time-resolved transient absorption spectroscopy. For **ZnTPP** the differential spectrum recorded, for example, right after the conclusion of the laser pulse is characterized by bleaching of the porphyrin *Q*-band at 550 and broad absorption between 570 and 750 nm. These spectral attributes are indicative of the **ZnTPP** singlet excited state ($E_{\text{singlet}} = 2.00$ eV) which decays (i.e., 2.1 ns−4.0×10^8 s^{-1}) to the energetically lower-lying triplet excited state ($E_{\text{triplet}} = 1.53$ eV) predominantly via intersystem crossing. For **Zn^{t}Bu$_4$Pc** we see singlet excited-state features ($E_{\text{singlet}} = 1.80$ eV)—including bleaching of the *Q*-band at 680 and broad absorption between 400 and 600 nm—that decay slightly slower (i.e., 3.0 ns−3.3×10^8 s^{-1}) to the corresponding triplet manifold ($E_{\text{triplet}} = 1.30$ eV). In contrast to the above—when photoexciting at 387 nm or 560 nm—**1b** (i.e., 8.1 ps−1.2×10^{11} s^{-1}) and **2** (i.e., 18.8 ps−5.3×10^{10} s^{-1}) show a rapid transformation of the ZnP singlet excited state. Products of this process are the ZnPc singlet excited-state as evidenced by features that are practically identical to those recorded for the **Zn^{t}Bu$_4$Pc** reference. In **1b** and **2** this state is metastable and decays to the triplet excited state.

This work follows previous investigations, where **ZnTPP** and **Zn^{t}Bu$_4$Pc** building blocks have been covalently linked. Transduction of singlet excited-state energy prevails regardless of linkage to the β-pyrrolic or the *meso* position. Our work further underlines the transduction efficiency of the β-pyrrolic linkage, although different separations (conjugated linkers) between donor and acceptor might also play a role.

Acknowledgment. We are grateful for the financial support of the MEC, Spain, and the Comunidad de Madrid (CTQ-2005-08933-BQU and S-0505/PPQ/000225, respectively). We also thank the EU (RTN network “WONDERFULL”), SFB 583, DFG (GU 517/4-1), FCI, and the Office of Basic Energy Sciences of the U.S. Department of Energy. Thanks are due also to the Fundação para a Ciência e a Tecnologia (FCT, Portugal) and to FEDER for funding this work. A.M.V.M.P., J.P.C.T., and C.M.A.A. are grateful to FCT for doctoral and postdoctoral grants. A.R.M.S. is grateful to the Programa de Mobilidade Leonardo Da Vinci.

Supporting Information Available: Experimental methods and spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Excitation in ZnPc at 685 nm led to quantum yields of 0.12 (**1b**), 0.26 (**2**), and 0.3 (**Zn^{t}Bu$_4$Pc**).