ORGANIC
LETTERS

2010
Vol. 12, No. 18
4046−4049

N-Annulated Perylene Fused Porphyrins with Enhanced Near-IR Absorption and Emission

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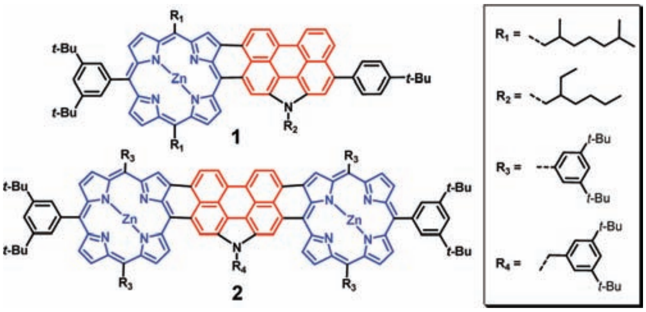
Received July 15, 2010

ABSTRACT



***N*-Annulated perylene fused porphyrins 1 and 2 were synthesized by oxidative dehydrogenation using a $Sc(OTf)_3$/DDQ system. These newly synthesized hybrid molecules are highly soluble in organic solvents and exhibit remarkably intense near-IR absorption, as well as detectable photoluminescence quantum yields, all of which are comparable to or even exceed those of either *meso-β* doubly linked porphyrin dimer/trimer or bis/tri-*N*-annulated rylenes.**

Large π-systems with near-infrared (NIR) absorption/emission[1] have attracted considerable attention in light of their increasing applications in the fields of solar cells,[2] nonlinear optics,[3] and bioimaging.[4] Stimulated by the promising potential, scientists have been devoted to developing facile methods for the preparation of polycyclic aromatics that do function in the NIR spectral region. Porphyrins and metalloporphyrins generally possess an intense absorption in the 400−450 nm region called the Soret band and relative weak absorptions in comparison to the Soret band in the 500−700 nm region named Q bands. In order to achieve NIR absorption and simultaneously enhance the Q-band absorption, numerous efforts have been made toward the design and synthesis of π-extended porphyrins with low symmetry, which include fused porphyrin arrays[5] and aromatic ring-fused porphyrins.[6] On the other hand, perylene and its derivatives,[7] key chromophores in dye chemistry, have been intensively studied not only owing to their remarkable physical properties (large extinction coefficients and high fluorescence quantum yields), outstanding chemical, thermal, and photochemical inertness, nontoxicity, and low cost but

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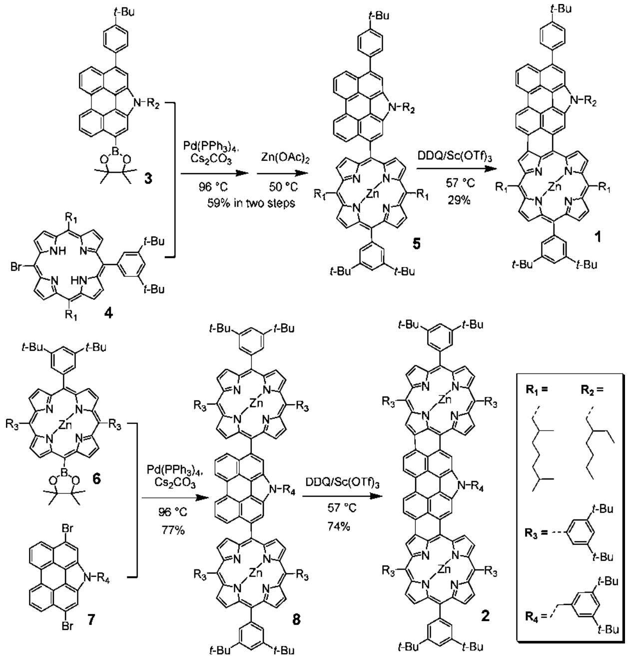
10.1021/ol1016383

also due to the availability of their active sites (*peri-* or *bay-*positions) that allow further chemical modifications. A recent rising interest is to synthesize rylene bisimides, namely, terrylene,[8] quaterrylene,[9] pentarylene,[10] and hexarylene bisimides,[10] or to construct push–pull structures[11] based on the perylene core, both of which can shift the absorption into the NIR spectral region.

Since both the perylene unit and the porphyrin core are attractive and intriguing, we envisaged that incorporation of perylene to the porphyrin skeleton could lead to a NIR absorption with unusual properties including high molar extinction coefficient and desirable quantum yield as a result of the outstanding physical properties of perylene itself and loss of symmetry of the porphyrin core. Although the perylene unit had been covalently attached to the porphyrin core through a single C–C bond,[12] the fusion of perylene moiety to the porphyrin core, to the best of our knowledge, has never been reported, presumably because of the lack of appropriate active building blocks and the difficulty in the ring-closure reaction. Herein, we report the first class of perylene-fused porphyrins **1** and **2** (Scheme 1) with varied optical and electronic properties.

Scheme 1



The major challenge for the synthesis of perylene-fused porphyrins is the intramolecular ring cyclization of the singly linked porphyrin-perylene dyads, which usually can be prepared by Pd-catalyzed coupling reactions between appropriate perylene and porphyrin building blocks. It has been demonstrated that the ring fusion of electron-rich metalloporphyrins (e.g., Zn porphyrin) requires the second component to be also electron-rich, and $Sc(OTf)_3$-DDQ system is usually used as the oxidant.[5,6] We therefore chose electron-rich *N*-annulated perylene as one of the building blocks in compounds **1** and **2** because it has been proven that *N*-annulated perylenes can undergo self-fusion reactions to give higher order quaterrylene and hexarylene derivatives upon treatment of $Sc(OTf)_3$/DDQ.[13]

Bulky 4-*tert*-butylphenyl, 3,5-di-*tert*-butylphenyl, 3,5-di-*tert*-butylbenzyl, 2,6-diisopropylphenyl, and branched aliphatic chains were introduced to these molecules to surmount the solubility problem and to suppress the aggregation of the chromophores in solution. Scheme 1 outlines the synthetic route for compounds **1** and **2**. The monobrominated porphyrin **4** was first synthesized as the key porphyrin building block (see Supporting Information for details). Suzuki coupling between **4** and *N*-annulated perylene boronic ester **3** (see Supporting Information) and subsequent Zn-metalation

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of the as-formed porphyrin-perylene dyad gave the key intermediate **5**. The combination of Sc(OTf)$_3$ and DDQ was then applied to promote the ring closure of **5** and eventually led to the desired compound **1**. Extension of π-conjugation length of **1** along the long molecular axis by fusion two porphyrin units with one *N*-annulated perylene is supposed to lead to a more red-shifted and intense NIR absorption. Thus a precursor such as **8** was prepared by Suzuki coupling reaction between porphyrin boronic ester **6** and dibrominated *N*-annulated perylene **7** (see Supporting Information), and this was followed by oxidative dehydrogenation by Sc(OTf)$_3$/DDQ. However, when the branched alkyl chains (i.e., R$_1$ and R$_2$) were used as the substituents, a complicated mixture was obtained after cyclodehydrogenation and the separation of this mixture and characterization of final product turned out to be very difficult because of the strong aggregation tendency of the obtained perylene-fused porphyrins. Therefore, bulky 3,5-di-*tert*-butylphenyl (R$_3$) and 3,5-di-*tert*-butylbenzyl (R$_4$) groups were used, and pure hybrid molecule **2** was successfully obtained in 74% yield. The final compound **2** did not show obvious aggregation in solution and allowed us to separate and characterize it more conveniently.

Compounds **1** and **2** appear as carmine and brown waxy solids, respectively, and are highly soluble in common organic solvents. The absorption spectra of the *N*-annulated perylene-fused porphyrin **1** and bis-porphyrin fused *N*-annulated perylene **2** in toluene demonstrate a significant bathochromic shift of the absorption maximum with respect to those of their precursors **5** and **8** (Figure 1 and the data are collected in Table S1 in Supporting Information). The absorption maximum of **1** was found at 775 nm, and extension of π-conjugation length along the long molecular axis in **2** apparently leads to a bathochromic shift with absorption maximum at 952 nm. Addition of a small amount of pyridine to the toluene solution of **2** further promotes the absorption maximum to 981 nm, probably due to the coordination of pyridine to Zn(II), which is effective to suppress the aggregation of perylene-fused porphyrins.

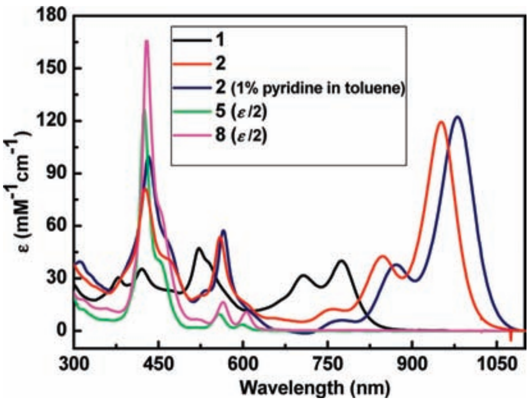

Figure 1. UV−vis−NIR absorption spectra of **1**, **2**, **5**, and **8** in toluene (1.0 × 10^{-5} M). The molar extinction coefficients of **5** and **8** were divided by 2 because of their strong absorption around 450 nm.

Perylene-fused porphyrins **1** and **2** exhibit remarkably intense NIR absorptions in toluene with molar extinction coefficients ε = 39,980 and 119,380 M^{-1} cm^{-1} at long wavelength maximum, respectively. Such intense NIR absorptions, especially the molar extinction coefficient of **2**, have seldom been reported among aromatic compound-fused porphyrin analogues.[6] Also noteworthy is that compound **1** shows NIR photoluminescence with emission maximum at 800 nm (Figure S1 in Supporting Information), and the photoluminescence quantum yield was measured as 5.6%. Considering the relatively low photoluminescence quantum yield of porphyrin tapes[5g,14] in NIR region, this value is acceptable. In addition, the absorption maximum of **2** is comparable to that of *meso*-β doubly linked Zn(II) porphyrin trimers[5g] but much longer than that of tri-*N*-annulated hexarylene. [13d] Different from porphyrin trimers,[5g] the bis-porphyrin fused *N*-annulated perylene **2** shows detectable fluorescence with emission maximum at 982 nm in toluene containing 1% pyridine, and a photoluminescent quantum yield of 0.8% was determined (Figure S2 in Supporting Information). Such an enhancement in the NIR absorption/emission of **1** and **2** is remarkable, and the reason is still under investigation in our laboratory. Because of their low emission quantum yields and expected short excited state lifetimes, their excited state lifetimes were measured by using femtosecond pump probe experiments (Figure S3 in Supporting Information). Their average excited state lifetimes were determined to be 245 and 221 ps for **1** and **2**, respectively, which is consistent with their emission quantum yield data.

Time-dependent density function theory (TDDFT at B3LYP/6-31G**) calculations were conducted for **1** and **2** to further understand their geometric and electronic structures. Their optimized molecular structures, dipole moments, and frontier molecular orbital profiles are shown in Figure 2. The perylene moieties in **1** and **2** slightly deviate from

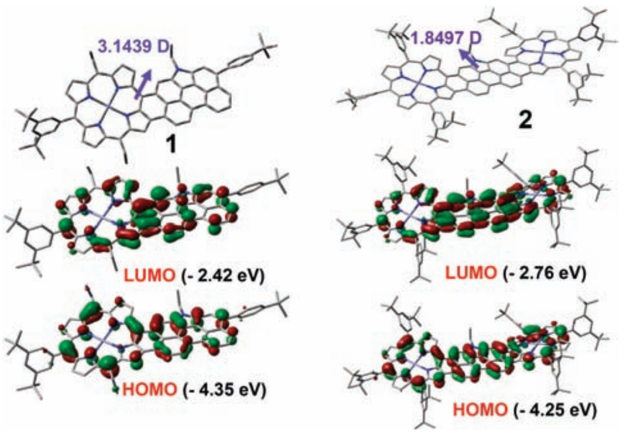

Figure 2. Optimized molecular structures, dipole moments (indicated by arrow), and frontier molecular orbital profiles of molecules **1** and **2** (only branched aliphatic chains are replaced by ethyl during the TDDFT calculations).

the porphyrin plane due to the steric hindrance between the β-proton of porphyrin and the *meta*-proton of the perylene core. The asymmetry in **1** and **2** obviously gives rise to different dipole moments, which are calculated as 3.1439 and 1.8457 D, respectively. TDDFT calculations predict that each compound exhibits three major absorption bands (see Supporting Information), which were also observed in Figure 1. The longest absorption maxima for **1** and **2** are calculated to be 706.6 and 895.4 nm, respectively, and such tendency also agrees well with our experimental results.

The electrochemical properties of compounds **1** and **2** were investigated by cyclic voltammetry (CV) in dry DCM (Figure 3 and Table S1 in Supporting Information). The cyclic voltammogram of **1** exhibits two reversible oxidation waves with half-wave potentials ($E_{ox}{}^{n}$) at 0.12 and 0.47 V (vs Fc^+/Fc), whereas four reversible oxidative waves with $E_{ox}{}^{n}$ at −0.08, 0.40, 0.65, 0.81 V were measured for **2**. It is obvious that the perylene-fused porphyrin tape **2** has a larger extended π-system and can stabilize multiple charges. The lower first oxidation potential observed for **2** can be explained by the extended π-conjugation between the three fused electron-rich units. Furthermore, both compounds show one quasi-reversible reduction wave, with E_{red} at −1.42 and −1.31 V for **1** and **2**, respectively. Chemical oxidation titrations of compounds **1** and **2** were conducted in DCM by using $SbCl_5$ as oxidant and the process was followed by UV−vis−NIR absorption spectroscopy (Figure S11 in Supporting Information). Both compounds can be oxidized by $SbCl_5$ into stable radical cation with appearance of new characteristic absorption bands in the shorter and longer wavelengths around the original NIR absorption band. It is worth noting that despite extremely narrow band gaps and the high electron density, solutions of **1** and **2** are stable upon exposure to visible light, whereas the bis-*N*-annulated quarterrylene can be readily oxdized by singlet oxygen in the air.[13c] This observation clearly demonstrates that the porphyrin unit is able to stabilize the highly conjugated system with an electron-rich character.

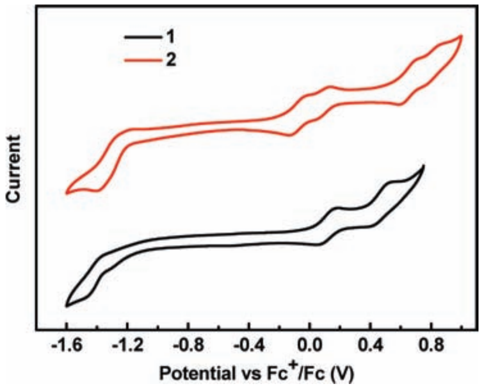

Figure 3. Cyclic voltammograms of compounds **1** and **2** in dichloromethane with 0.1 M Bu_4NPF_6 as supporting electrolyte, AgCl/Ag as reference electrode, Au disk as working electrode, Pt wire as counter electrode, and scan rate at 20 mV/s. Fc/Fc^+ was used as internal reference.

In summary, the electron-rich *N*-annulated perylene was successfully fused to the porphyrin core for the first time to form compounds **1** and **2** with an intense NIR absorption/emission and different electrochemical behavior. The porphyrin unit turns out be effective to stabilize a highly electron-rich π-system. In particular, dye **1** shows an acceptable fluorescence quantum yield, which is typically difficult to achieve for porphyrin-based materials. Further extension of the conjugation from **1** to **2** results in intense NIR absorption that is comparable to that of a porphyrin trimer. However, *N*-annulated perylene fused porphyrin **2** has the advantages of high solubility, ease of preparation, and detectable photoluminescence quantum yield. Further studies on the nonlinear optical properties (e.g., two-photon absorption) of these dyes for potential optical limiting applications as well as the synthesis of their higher homologues with more extended conjugation are currently underway in our laboratories.

Acknowledgment. This work was financially supported by Singapore DSTA DIRP Project (DSTA-NUS-DIRP/2008/03), the NRF Competitive Research Program (R-143-000-360-281), and NUS Young Investigator Award (R-143-000-356-101) to J.W. and a KAUST baseline funding to K.-W.H.

Supporting Information Available: Experimental details and characterization data of all new compounds, theoretical calculation data, and chemical oxidation titration details. This material is available free of charge via the Internet at http://pubs.acs.org.

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