



Synthesis, characterization, energy transfer and photophysical properties of ethynyl bridge linked porphyrin–naphthalimide pentamer and its metal complexes



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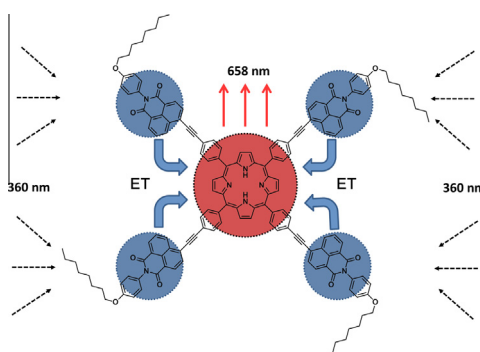
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HIGHLIGHTS

- A novel naphthalimide-functionalized porphyrin **TANPH₂** has been synthesized.
- **TANPH₂** and **TANPZn** can emit intense red light with high fluorescent quantum yields.
- The photo-excitation energy transfer occurred from naphthalimide to porphyrin core.
- **TANPH₂** and **TANPZn** can act as efficient light-harvesting antennae.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel ethynyl bridge linked naphthalimide-functionalized porphyrin **TANPH₂** has been synthesized by a combination of Sonogashira coupling and Gonsalves and Pereira nitrobenzene reaction, and the corresponding metal (Zn^{2+} and Cu^{2+}) complexes **TANPZn** and **TANPCu** were synthesized. The structures of these compounds were characterized by ^1H and ^{13}C NMR spectra, FT-IR, MALDI-TOF-MS and elemental analysis. The photophysical properties have been investigated by UV-Vis absorption and steady-state fluorescence spectroscopy. Energy transfer studies have revealed that the excitation energy transfer occurred from the naphthalimide units to the porphyrin core. By the introduction of ethynyl bridges between the peripheral naphthalimide arms and the porphyrin core, **TANPH₂** and **TANPZn** can emit intense red light with high fluorescent quantum yields.

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Introduction

Porphyrins have been intensively studied as artificial light-harvesting systems over many years [1], because they absorb light energy strongly, have high fluorescence quantum yields and can act as both donor and acceptor. In recent years, porphyrin molecules have attracted considerable attention as useful materials

for organic photo-electronics such as organic light emitting diodes (OLEDs) [2], dye-sensitized solar cells (DSSCs) [3–5], and organic field-effect transistors (OFETs) [6], since they possess large planar π -conjugated structure, unique electronic properties, and good photochemical and thermal stability.

Porphyrins are versatile molecules whose optical, photophysical and electrochemical properties can be systematically tailored by peripheral substitution/or inner metal complexations [7]. In recent years, a wide variety of substituents [8–14] have been introduced to the porphyrin core to form the peripherally functionalized porphyrin molecules, which are good candidates for light-harvesting systems and fluorescence emitting materials. On the other hand, the 1,8-naphthalimide derivatives are a special class of environmentally sensitive chromophores [15]. Because of their strong fluorescence and good photostability, 1,8-naphthalimide derivatives have found extensive application in the field of organic photo-electronics [16–19]. Moreover, a series of light-harvesting systems based on a core as an energy acceptor and functionalized with naphthalimides as donor surface have attracted much attention in the field of chemosensing materials [20–25] and biomedical applications [26,27]. Those molecules, in which naphthalimide unit act as a good energy pump that can absorb light and then efficiently transfer the energy to a single “acceptor”, form a suitable choice for the antenna function. The remarkable properties of both porphyrins and naphthalimides indicate that a naphthalimide–porphyrin system can ensemble as a light-harvesting system with a wider absorption spectrum. However, only a few examples of porphyrin–naphthalimide hybrids have been reported. In our previous paper [28], we have reported the synthesis of a porphyrin–naphthalimide pentamer **TNPPH₂** (Fig. 1) by linking four light-harvesting naphthalimide units to a central porphyrin, via ether bridges, and evidenced that excitation energy transfer occurred from the naphthalimide units to the porphyrin core, and **TNPPH₂** and its Zn porphyrin **TNPPZn** (Fig. 1) can act as efficient light harvesting antennae. In order to receive a clear picture of the influence of different spacers on the energy transfer and fluorescence quantum yields of the naphthalimide functionalized porphyrin molecules. Pursuing our previous work, in this letter, a novel naphthalimide-functionalized porphyrin **TANPH₂** was synthesized, in which four naphthalimide units are attached to the porphyrin core via ethynyl linkers. Furthermore, the corresponding metal (Zn^{2+} and Cu^{2+}) complexes **TANPZn** and **TANPCu** were synthesized. The structures of these compounds were characterized by ^1H and ^{13}C NMR spectra, FT-IR, MALDI-TOF-MS and elemental analysis. The photophysical study revealed that the excitation energy transfer occurred from the naphthalimide units to the porphyrin core. By the introduction of ethynyl bridges between the naphthalimide arms and the porphyrin core, **TANPH₂** and **TANPZn** can emit intense red light with high fluorescent quantum yields of 0.18 and 0.13, respectively, which are higher than previously reported naphthalimide-

functionalized porphyrins with ether bridges. These studies provide wider ground for choice and application of these materials in the field of organic photo-electronics.

Results and discussion

Synthesis

The synthetic routes for all new compounds are shown in Scheme 1. The starting material 4-bromo-N-(4-(octyloxy)phenyl)-1,8-naphthalimide **1** was synthesized following our previously reported synthetic procedure [28]. Trimethylsilyl acetylene reacted with **1** under the standard Sonogashira coupling conditions followed by desilylation of the resultant product with $\text{K}_2\text{CO}_3/\text{MeOH}$ to give 4-ethynyl-N-(4-(octyloxy)phenyl)-1,8-naphthalimide **3**. On the other hand, the key intermediate compound **2** was prepared under the above-mentioned Sonogashira coupling conditions from **1** and 4-ethynylbenzaldehyde, using $\text{Pd}(\text{PPh}_3)_4$ and CuI as the catalysts in the presence of toluene and triethylamine. The new naphthalimide-functionalized porphyrin **TANPH₂** was synthesized from the reaction of pyrrole with **2** by Gonsalves and Pereira nitrobenzene method [29,30], in the mixed solvents of propionic acid and nitrobenzene. Using this synthetic approach, pure porphyrin was obtained by direct crystallization from the reaction medium, and no by-product was observed in the final crystal product. In addition, the complex **TANPZn** was prepared by the reaction of **TANPH₂** with an excess of ZnCl_2 in a mixture of trichloromethane (CHCl_3) and methanol (volume ratio, 3/1) at 70 °C. During the reaction, the UV–Vis absorption spectra of the reaction mixture were monitored by a PerkinElmer Lambda 35 UV–Vis Spectrometer. Completion of the reaction of forming **TANPZn** can be monitored by following the disappearance of Q-bands at 519 and 649 nm, and the growth of a new band at 551 nm. **TANPCu** was prepared under a similar procedure to that for **TANPZn** except for the addition of a suitable amount of KOH to the reaction mixture, and the formation of Cu complex was also monitored by a UV–vis absorption Spectrometer.

Structure characterization

MALDI-TOF-MS and NMR characterization

Matrix-assisted laser desorption/ionization time-of-flight mass spectra (MALDI-TOF-MS) were performed to quantitatively analyze the molecular weights of **TANPH₂** and its complexes **TANPZn** and **TANPCu**. The analysis of date worked well for these compounds, giving a single peak in good agreement with the theoretical value, respectively.

The ^1H NMR signals obtained in CDCl_3 for **TANPH₂** and **TANPZn** are fine and well resolved. **TANPH₂** and **TANPZn** all exhibit both the spectral signatures of the porphyrin core and signals typical of the peripheral naphthalimide units, such as the broad singlet

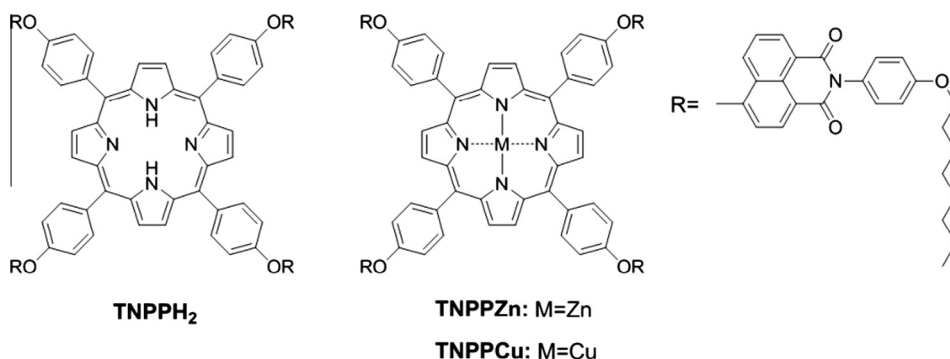


Fig. 1. Structures of compounds **TNPPH₂**, **TNPPZn** and **TNPPCu**.

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