



Synthesis, characterization and properties of covalently linked porphyrin–naphthalimide pentamer and its metal complexes



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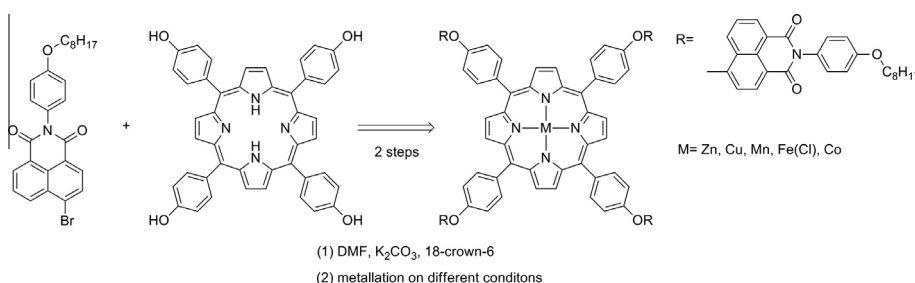
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HIGHLIGHTS

- A novel porphyrin–naphthalimide pentamer was synthesized and the corresponding metal complexes were obtained.
- The porphyrin–naphthalimide pentamer **5** and its Zn complexes **6a** emit intense red light.
- The fluorescence quantum yields were 0.14 and 0.08 respectively.
- Due to the efficient energy transfer, the compound **5** and **6a** can act as efficient light-harvesting antennae.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel porphyrin–naphthalimide pentamer **5** was synthesized by linking four light-harvesting naphthalimide units to a central porphyrin, via ether bridges. The corresponding metal (Zn²⁺, Cu²⁺, Mn²⁺, Fe³⁺, Co²⁺) complexes **6a–6e** were obtained under different reaction conditions. The structures of these compounds were characterized by ¹H and ¹³C 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. It is found that the excitation energy transfer occurs from the naphthalimide units to the porphyrin core, and that the free base porphyrin **5** and Zn porphyrin **6a** can emit intense red light. Additionally, the electrochemical properties of compounds **5** and **6a–6e** were also investigated by cyclic voltammetry.

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Introduction

Porphyrins, a class of macrocycle compounds with interesting spectroscopic and chemical properties, have attracted considerable attention for many decades due to their comprehensive applications

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in a number of rapidly growing research fields, such as organic light emitting diodes (OLEDs) [1], organic photovoltaic (OPV) [2,3], and photocatalytic degradation [4,5].

Porphyrins are versatile molecules whose physicochemical properties can be readily adjusted by modification of the electronic distribution on the aromatic ring via peripheral substitution [6]. Furthermore, the porphyrin skeleton permits to be functionalized by attaching four photo-harvesting units at the porphyrin macrocycle periphery, to form light-harvesting system. This kind of molecular system, in which a porphyrin acceptor is covalently linked to four donor chromophores, forms a suitable choice for

the antenna function. In recent years, a wide variety of substituents [7–12] 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.

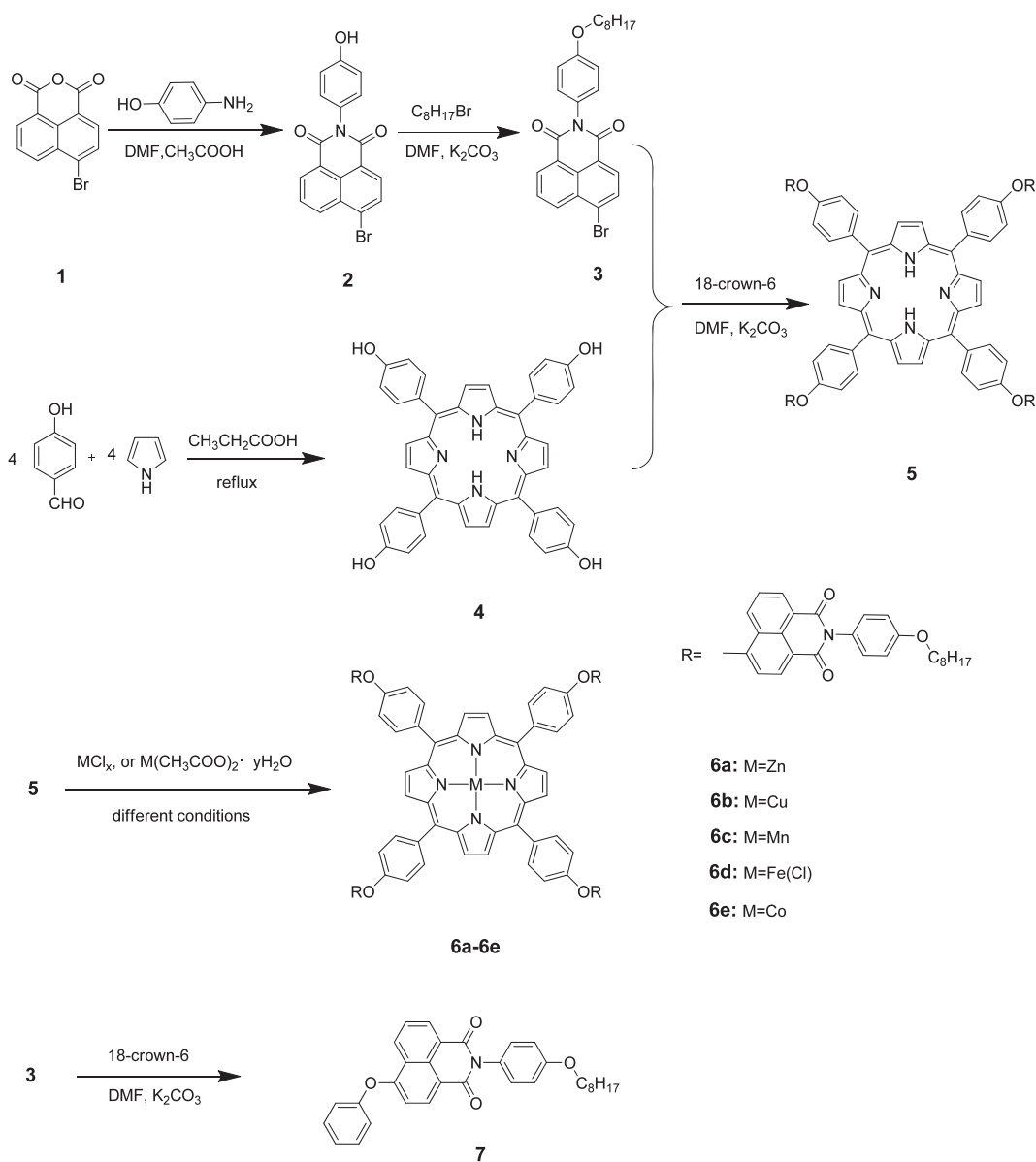
On the other hand, the 1,8-naphthalimide derivatives are a special class of environmentally sensitive chromophores [13]. Because of their strong fluorescence and good photostability, 1,8-naphthalimide derivatives have found extensive application in the field of organic photo-electronics [13,14,16]. In recent years, a series of light-harvesting molecules based on a core as an energy acceptor and peripherally functionalized with naphthalimide as a donor surface have attracted much attention in biomedical applications [13–23]. In those molecules, naphthalimide moiety exhibits a good energy pumping antenna function. If naphthalimide is introduced to the porphyrin skeleton, its excitation energy may transfer to porphyrin fragment, showing interesting photophysical properties. Moreover, the naphthalimide structure with strong absorption in the UV region will also help improve the light harvesting ability of the functionalized porphyrin molecules. To the best of our

knowledge, there is no report on the synthesis of the naphthalimide functionalized porphyrin. Herein, we report the design and synthesis of a novel porphyrin–naphthalimide light-harvesting system **5** (TNPPH₂) where the four naphthalimide units are linked via ether bridges to the meso-phenyl groups of the porphyrin (Scheme 1). Moreover, the metal complexation reactions of **5** and metal ions (Zn²⁺, Cu²⁺, Mn²⁺, Fe³⁺, Co²⁺) were also performed on different reaction conditions to finally obtain metal complexes **6a–6e**. Additionally, the structure characterization, photophysical, photo-induced energy transfer and electrochemical results are also reported. These studies provide wider ground for choice and application of the materials in the field of organic photo-electronics.

Results and discussion

Synthesis

The synthetic routes for compounds **5**, **7** and **6a–6e** are shown in Scheme 1. 4-Bromo-1,8-naphthalic anhydride **1** as the starting material was reacted with 4-aminophenol in a mixture of N,



Scheme 1. Synthesis of compounds **5**, **7** and **6a–6e**.

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