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Synthesis, aggregation and photoinduced electron transfer processes of cationic water-soluble 21-thia and 21-oxaporphyrins

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Abstract

The *meso*-pyridyl 21-thia- and 21-oxaporphyrins containing three pyridyl groups at the *meso*-positions have been methylated to obtain water-soluble porphyrins. The porphyrins are highly soluble in water and the water-soluble 21-thiaporphyrins exhibit aggregation behaviour above 10^{-4} M whereas the water-soluble 21-oxaporphyrins strongly aggregate at very low concentrations (10^{-7} M). The interaction of water-soluble ionic porphyrins with ionic surfactant in aqueous solutions has been studied as a function of surfactant concentration by means of absorption, fluorescence and resonance light scattering (RLS) techniques. It has been observed that, at the initial premicellar surfactant concentration, the oppositely charged surfactant induces aggregation and above cmc these aggregates dissociates into monomeric form and gets micellised. The self- and SDS-induced aggregation of these cationic porphyrins is found to depend on the number and position of the positive charge with respect to the porphyrin core. The micellar encapsulation technique is used to promote the photoinduced electron transfer between the porphyrins and neutral aromatic amines and it has been observed that the electron transfer rate becomes slowing down at the micellar surface compared to the bulk acetonitrile solution.

Keywords: Core-modified water-soluble porphyrins; Photoinduced electron transfer; Aggregation; Resonance light scattering (RLS); Micelle; Fluorescence quenching

1. Introduction

Water-soluble porphyrins have generated considerable interest in recent times [1,2], due to their applications as model systems for photosynthesis as well as their potential applications as second and third generation sensitizers for photodynamic therapy [3–6]. Core-modified porphyrins are especially attractive in this respect, as they have been found to be more effective as photosensitizers than the more widely studied sulphonated tetraphenyl porphyrin (TPPS$_4$), which absorb weakly in the therapeutic region (650–700 nm) and exhibit neurotoxicity [7], whereas the substitution of nitrogen with heteroatom such as S, O, Se, Te shifts the absorption bands towards longer wavelength. Furthermore the water-soluble porphyrins exhibit interesting aggregation properties and are likely to find applications in opto-electronic devices and non-linear optics as well [8–10]. Interestingly, except for one report by us, there are no reports on cationic water-soluble heteroporphyrins [11]. In this paper, we report the synthesis, characterization of a series of water-soluble 21-thiaporphyrins **6–8** and 21-oxaporphyrins **9–10** bearing three *N*-methylpyridinium ions at the *meso*-positions (Plate 1).

A second aspect of the present communication is the surfactant-induced aggregation/deaggregation of these porphyrins and Photoinduced Electron Transfer (PET) between selected porphyrins with neutral aromatic amines in bulk acetonitrile and SDS micellar media. The objective behind the study of PET in porphyrinic systems in organized media stems from the urge to develop efficient systems leading to the formation of long-lived ion pairs, so that the energy produced thus can be used fruitfully [12,13]. The first step towards development of such systems is to understand that the rate of electron transfer depends on the distance of donor and accepter moieties. If this distance is too large for the reactants to diffuse to each other during the excited state lifetimes, then PET is suppressed. On the other hand, if the distance is comparable to the van der Waals radius, that the back electron transfer is also ultrafast, leading

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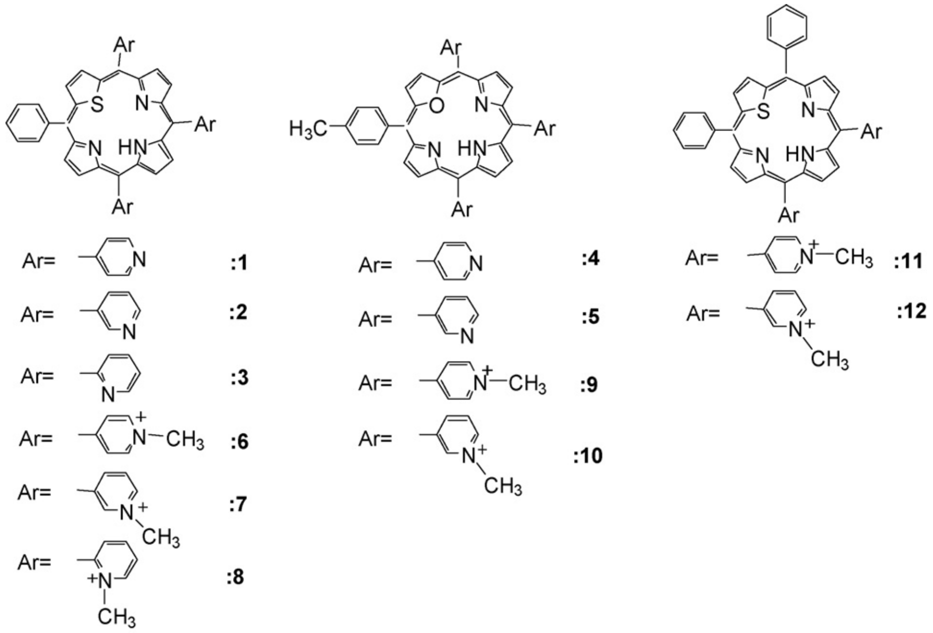


Plate 1.

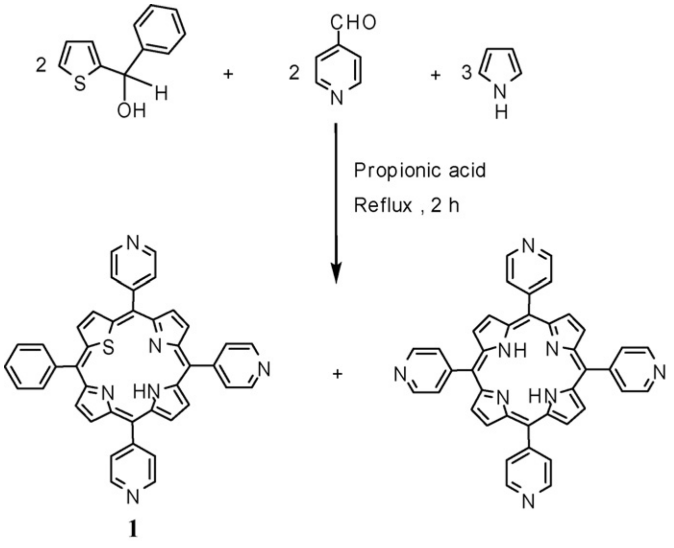
to a very short-lived ion pair. The challenge, therefore, lies in the design of systems where this distance can be controlled in order to have an efficient forward electron transfer and a negligible back electron transfer. This goal can be achieved either by entrapment of the donor or acceptor in organized assemblies like micelles. This has prompted several attempts to develop donor–acceptor systems based on organized assemblies [14–16].

2. Results and discussion

2.1. Synthesis of meso-pyridyl 21-thia and 21-oxaporphyrins

To synthesize the cationic water-soluble porphyrins **6–10**, the 21-thia and 21-oxaporphyrins, having three pyridyl groups at the *meso*-positions **1–5** are required. These pyridyl porphyrins were synthesized by following the mono-ol methodology developed recently in our laboratory [17]. The mono-ols, 2-[α-phenyl-α-hydroxymethyl]thiophene and 2[α-tolyl-α-hydroxymethyl]furan were prepared in 65–70% yields by treating thiophene and furan, respectively, with 1.2 equivalents of *n*-butyl lithium followed by 1.2 equivalents of benzaldehyde or tolyl aldehyde in THF at 0 °C. The 21-thiaporphyrins **1–3** were prepared by condensing the two equivalents of 2-[α-phenyl-α-hydroxymethyl]thiophene with two equivalents pyridine-2, 3 or 4-carboxaldehyde and three equivalents of pyrrole in propionic acid at refluxing temperature for 2 h (Scheme 1). The propionic acid was removed under vacuum and the crude solid after thorough wash with warm water and drying at 100 °C was passed through silica gel column using CH_2Cl_2/CH_3OH to remove the non-porphyrinic impurities. The TLC analysis of the compound showed the formation of two porphyrins with two different porphyrin cores: *meso*-5,10,15,20-tetrapyridyl porphyrin (N_4 core) and the desired *meso*-5,10,15-tris(2, 3 or 4-pyridyl)-20-phenyl-21-thiaporphyrin (N_3S core). The mixture was separated by silica gel column chromatography. The desired 21-thiaporphyrin **1–3** was collected as first band using CH_2Cl_2/CH_3OH and afforded dark purple solids in 2–6% yields. Although the yields were moderate, the compounds could be prepared in sufficient quantity in one pot, the precursors being easily available. Furthermore, there is no other good strategy at present is available to prepare the trifunctionalized heteroporphyrins. The attempts to prepare the 21-thiaporphyrins **1–3** under $BF_3{\cdot}OEt_2$ or TFA conditions did not yield the porphyrin, suggesting the high refluxing conditions in propionic acid were compulsory to prepare these porphyrins.

The 21-monooxaporphyrins **4** and **5** were prepared similarly by condensing two equivalents of 2[α-tolyl-α-hydroxymethyl]furan with two equivalents of pyridine-3 or



Scheme 1. Synthesis of 21-thiaporphyrin having three *meso*-4-pyridyl groups.