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Synthesis and properties of cyclophosphazenes appended with covalently linked porphyrin–ferrocene conjugates

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ABSTRACT

Cyclotriphosphazene and cyclotetraphosphazene appended with six and eight covalently linked porphyrin–ferrocene conjugates respectively were synthesized by treating $N_3P_3Cl_6$ and $N_4P_4Cl_8$ with appropriate equivalents of ferrocene linked porphyrin containing *meso*-hydroxyphenyl group in THF in the presence of Cs_2CO_3 followed by column chromatographic purification. NMR and absorption studies indicated a weak interaction between adjacent porphyrin–ferrocene conjugates. Electrochemical studies supported electrochemical equivalence of ferrocenyl and porphyrinyl moieties in these multi-porphyrin–ferrocene conjugate assemblies. The fluorescence studies showed significant quenching of porphyrin fluorescence due to photo-induced electron transfer from ferrocene to singlet state of porphyrin unit in these assemblies.

1. Introduction

In recent years there is a considerable amount of interest in the preparation of covalently linked porphyrin–ferrocene conjugates because of their complementary redox properties which can be used to study not only to mimic photo-induced electron-transfer processes of photosynthesis but also for the development of molecular based electronic devices [1]. Compounds possessing electrochemically active groups can be viewed as excellent candidates for multielectron reservoir systems, electron-transfer mediators, redox active materials for the modification of electrodes, ion sensors or materials for electronic devices [2–5]. There are many reports available in literature, where one or more ferrocenyl moieties are linked to porphyrin macrocycle through various spacer groups [6–16]. Bucher et al. [1] recently reviewed all the works on porphyrin–ferrocene conjugates. Furthermore, compounds containing multi-porphyrin–ferrocene conjugates will be potential materials that may possess interesting chemical, optical, redox and magnetic properties. However, to the best of our knowledge, there is no report on multi-porphyrin–ferrocene conjugate assemblies. Recently, we developed simple and short synthetic route for the preparation of hexa porphyrin **1** and octa porphyrin **2** assemblies (Chart 1) in good yields using cyclotriphosphazene and cyclotetraphosphazene respectively as scaffolds [17,18]. Chlorocyclophosphazenes such as $N_3P_3Cl_6$ and $N_4P_4Cl_8$ are small cyclic phosphazenes, renowned for the extreme robustness of their phosphorus–nitrogen backbones, which enables substitution reactions of the chloro groups with retention of the PN structure [19–22]. Furthermore, chlorocyclophosphazenes are closely related to chloropolyphosphazenes, and reactions carried out on chlorocyclophosphazenes to a large extent serve as models for similar reactions on the polymeric analogs. Another advantage of using cyclophosphazenes as supports for multi-redox active assemblies is that the phosphazene rings are extremely stable for redox processes [23]. Thus, cyclophosphazene rings are excellent choice for supporting multi-porphyrin–ferrocene conjugate assemblies. In this paper, we report synthesis and characterization of cyclotriphosphazene and cyclotetraphosphazene containing six and eight covalently linked porphyrin–ferrocene conjugates **3** and **4** respectively (Chart 1). Our synthetic strategy involve the first synthesis of covalently linked porphyrin–ferrocene conjugate containing hydroxyphenyl group at *meso*-position of porphyrin which was further reacted with chlorophosphazenes such as $N_3P_3Cl_6$ and $N_4P_4Cl_8$ in the presence of base under mild reaction conditions to afford multi-porphyrin–ferrocene conjugate assemblies **3** and **4** in decent yields. The spectral and electrochemical properties of these multi-porphyrin–ferrocene conjugate assemblies on cyclophosphazene scaffolds **3** and **4** are also described in this paper.

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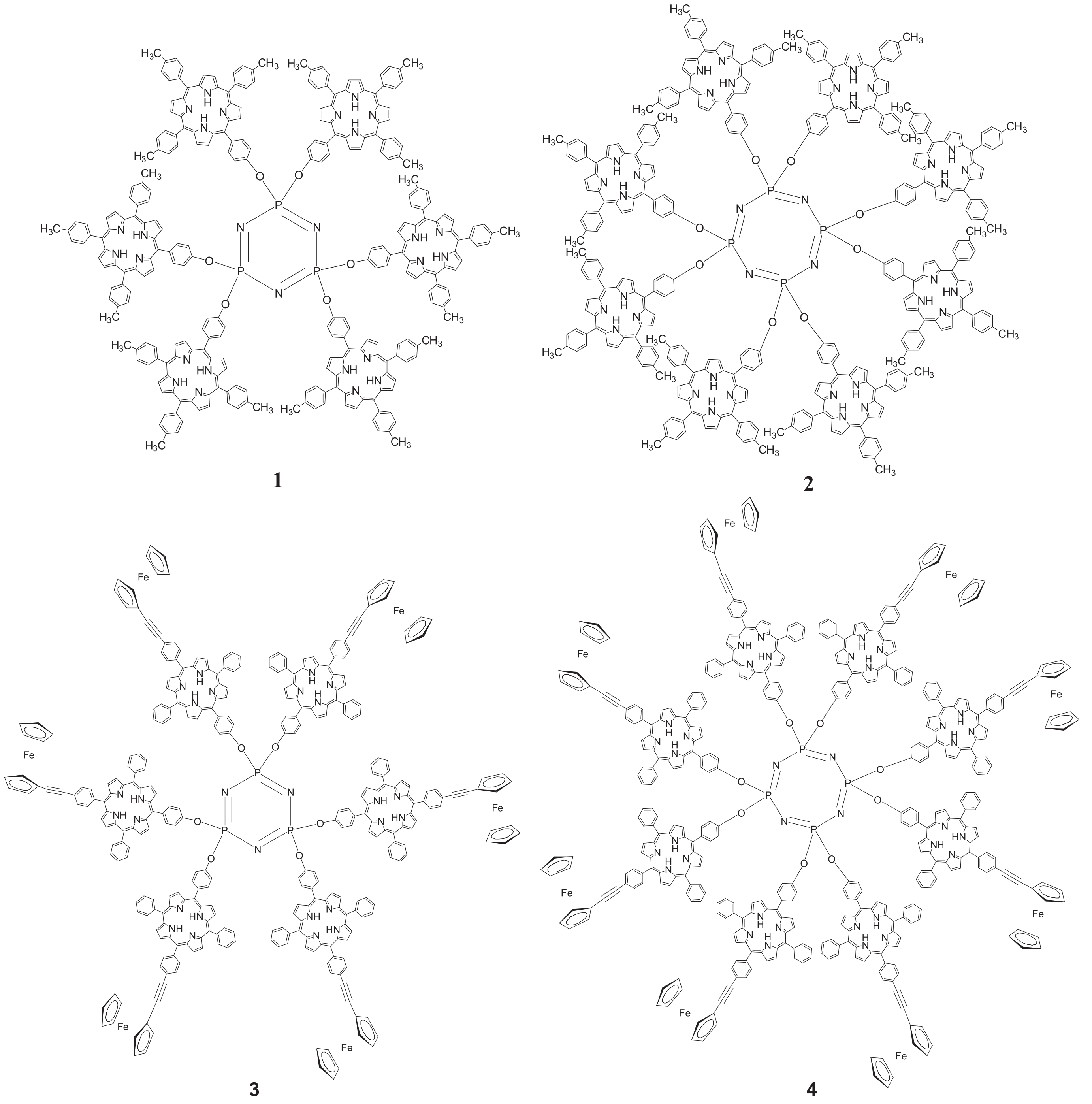

1

2

3

4

Chart 1. Molecular structures of multi-porphyrin assemblies **1** and **2** and multi-porphyrin–ferrocene assemblies **3** and **4** on cyclophosphazene rings.

2. Results and discussion

2.1. Synthesis and characterization

To synthesize the required covalently linked porphyrin–ferrocene conjugate containing one *meso*-hydroxyphenyl group **5**, we need an access to the *trans*-porphyrin building block, 5(4-hydroxyphenyl)-15(4-iodophenyl)-10,20-di(phenyl)porphyrin **6** which was synthesized by condensing two equivalents of *meso*-phenyl dipyrromethane with one equivalent of 4-hydroxybenzaldehyde and one equivalent of 4-iodobenzaldehyde in propionic acid under reflux for 3 h as shown in Scheme 1. The condensation resulted in the formation of the required *trans*-porphyrin building block as major product along with minor amounts of other two to three porphyrins which are formed due to scrambling of *meso*-phenyl dipyrromethane. The crude compound was subjected to silica gel column chromatographic purification and afforded pure *trans*-porphyrin building block in 6% yield. The molecular ion peak in ES-MS mass spectrum at 757.2 as [M$^+$ + H] and at 631.2 [M$^+$ − I] confirmed the identity of the porphyrin **6**. In ^{1}H NMR, the eight β-pyrrole protons appeared as multiplet at 8.87 ppm and the eighteen *meso*-aryl protons appeared as four sets of signals in 7.17–8.22 ppm region indicating