Tetrahedron 66 (2010) 5549–5565

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis of oligo(*p*-phenylene)-linked dyads containing free base, zinc(II) or thallium(III) porphyrins for studies in artificial photosynthesis

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ARTICLE INFO

Article history:
Received 13 April 2010
Received in revised form 13 May 2010
Accepted 14 May 2010
Available online 17 June 2010

Keywords:
Artificial photosynthesis
Porphyrin
Building block
Array
Electron transfer
Energy transfer
Hole transfer
Thallium
Zinc
Free base
Suzuki
Sonogashira

ABSTRACT

A series of (p-phenylene)$_n$-linked *meso*-mesityl-substituted porphyrin dyads (n=2–4) was prepared via Suzuki coupling of zinc(II) and free base porphyrin building blocks. The resulting zinc(II)/free base porphyrin dyads were demetalated. The series of free base porphyrin dimers (n=1–4), four other porphyrin dimers (with *p*-phenylene, diphenylethyne or diphenylbutadiyne linkers; and aryl or tridec-7-yl *meso* substituents), and several benchmark monomers were converted to the thallium(III)chloride complexes under mild conditions. The collection of eight Tl(III)Cl/Tl(III)Cl dimers is designed for studies of ground-state hole-transfer processes and comparison with the excited-state energy- and hole-transfer processes of the corresponding Zn(II)/free base dyads. Altogether, 18 new porphyrin arrays and benchmark monomers have been prepared.

1. Introduction

One of the key objectives in artificial photosynthesis is to gain a deep understanding of the physical principles that underlie light-harvesting and energy-transduction processes. The processes of interest include excited-state energy-transfer (as occurs in the photosynthetic antenna complexes), excited-state electron-transfer (as occurs in the reaction center), and subsequent ground-state hole- and electron-transfer reactions that give rise to a spatially separated hole and electron of sufficient lifetime for ultimate storage of energy in the form of chemical fuels.

Studies to examine electronic communication among interacting constituents have focused on multiporphyrin arrays wherein the porphyrins serve as surrogates for the naturally occurring (bacterio)chlorophylls, and the linker that joins the porphyrins provides for architectural control in lieu of a protein matrix. A vast number of synthetic arrays have been prepared to date.[1–14] Still, there remains a need for arrays with systematic variation of the parameter under investigation, such as distance, orientation, energetics, frontier-orbital composition, excited-state lifetime, π-framework (e.g., hydroporphyrin vs porphyrin), etc. Our goal was to create a set of arrays to enable direct comparison of processes of (1) excited-state energy transfer in neutral complexes, (2) excited-state hole transfer in singly oxidized complexes, and (3) ground-state hole-transfer in singly oxidized complexes, all as a function of increasing linker length between two interacting porphyrins. The collective studies were aimed to deepen our understanding of electronic communication between the porphyrins, largely mediated by the intervening linker that supports such processes.

To achieve this goal we sought a specific set of compounds wherein two porphyrins of distinct or identical metalation states were joined at the *meso*-positions via a relatively rigid linker of defined distance (Chart 1). The metalation states included zinc(II)/free base ('ZnFb') for excited-state energy-transfer and hole-transfer studies, and thallium(III)/thallium(III) ('TlTl') for ground-state hole-transfer studies. Diverse ZnFb porphyrin dyads have been prepared with linkers of a range of lengths,[6] but to our knowledge, no Tl(III)-containing porphyrin arrays of any type have heretofore been prepared. For our studies, the primary linker of choice was an oligo(*p*-phenylene) unit to achieve a high degree of

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0040-4020/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2010.05.059

molecular rigidity and substantial increments of distance (phenyl—quaterphenyl) within a given molecular composition. Two other linkers (diphenylethyne, diphenylbutadiyne) were employed for comparison with the large body of available data concerning multiporphyrin arrays of these types.[7]

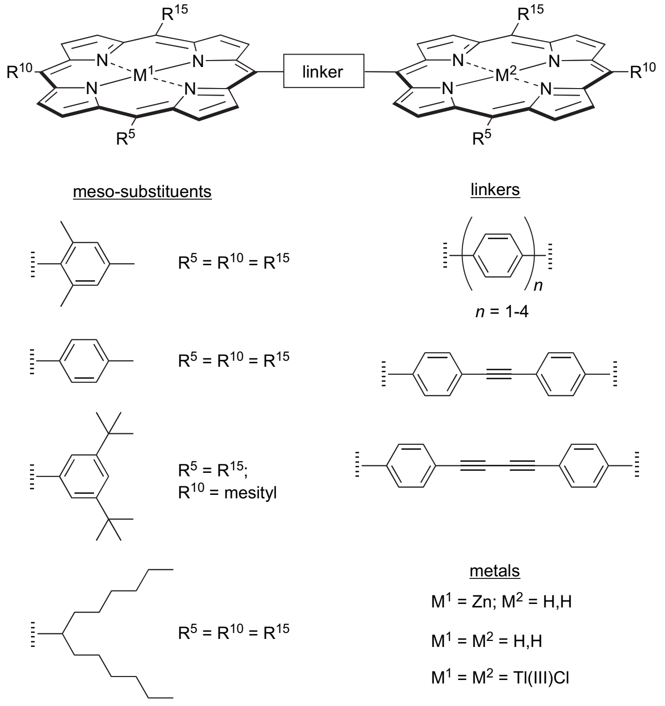

Chart 1.

Key molecular design issues in addition to the linker included the following: (i) pattern of substitution of the non-linking substituents, (ii) electronic features of the non-linking substituents, and (iii) solubilizing features of the non-linking substituents.[7] Porphyrins bearing electron-releasing aryl groups (e.g., phenyl) or alkyl groups located at the *meso*-positions typically exhibit the a_{2u} HOMO (vs a_{1u} HOMO with β-alkyl or *meso*-pentafluorophenyl-substituted porphyrins). The a_{2u} orbital is desired owing to the large electron density at the *meso*-position, the site where the oligo(*p*-phenylene) linker is positioned. Accordingly, a bulky, electron-rich group was located at each of the non-linking *meso*-positions to achieve the desired frontier-orbital composition and a high degree of solubilization in organic solvents.

In this paper we report the synthesis of 18 new porphyrin arrays and benchmark compounds. The primary targets included the arrays containing two porphyrins linked by oligo-*p*-phenylene units (spanning phenyl—quaterphenyl), mesityl groups at the non-linking *meso* sites, and several distinct metalation states (FbFb, ZnFb, and TlTl). Four TlTl dimers equipped with various non-linking substituents (mesityl, 3,5-di-*tert*-butylphenyl, tridec-7-yl) and linkers (*p*-phenylene, diphenylethyne, diphenylbutadiyne) also were prepared. Of this latter set, three of the constructs were previously known as the FbFb species and were subjected here to metalation, whereas the swallowtail-substituted diphenylethyne-linked FbFb dimer was prepared herein from the corresponding building blocks. Altogether, three new ZnFb porphyrin dyads, three new FbFb porphyrin dimers, eight new TlTl porphyrin dimers, and four thallium-containing porphyrin monomers are described herein. The photochemical features of the ZnFb porphyrin dyads were recently described,[15,16] whereas the ground-state hole-transfer properties of the TlTl porphyrin dimers will be described elsewhere.

2. Routes to oligo(*p*-phenylene)-linked porphyrin dyads

Synthetic oligo(*p*-phenylene)-linked porphyrin dyads have been prepared via a wide variety of chemistries. The various approaches can be assessed on the basis of (i) whether the route provides rational access to (symmetric) dimers or (unsymmetric) dyads, and (ii) at what stage in the synthesis the porphyrin macrocycle is constructed. In this regard, the oligo(*p*-phenylene) linker can be pre-installed on an acyclic precursor to the porphyrin followed by a cyclization reaction to create the porphyrin macrocycle, or intact porphyrin building blocks can be joined via Suzuki coupling to form the oligo(*p*-phenylene) linker. The Suzuki coupling can entail a single joining (mono-coupling) to create dyads or a double joining (bis-coupling) to create dimers. In general, any route to dyads can be employed to access dimers. Representative routes are displayed in Table 1.

Synthesis of a biphenyl-linked porphyrin dimer was first reported by McLendon and co-workers, via condensation of a 4,4′-biphenyl-linked bis(dipyrromethane) and a 1,9-diformyldipyrromethane followed by oxidation (entry 1).[17,18] Extension of this method with a 4,4″-terphenyl- or 4,4‴-quaterphenyl-linked bis(dipyrromethane) afforded terphenyl- or quaterphenyl-linked porphyrin dimers.[19] Alternatively, the reaction of biphenyl-4,4′-dicarboxaldehyde, a dipyrromethane and an aldehyde gave a symmetric biphenyl-linked porphyrin dimer (entry 2).[20–22] Similar reaction of terephthalaldehyde, benzaldehyde, and pyrrole afforded the *p*-phenylene-linked dimer (entry 3).[23,24] This reaction is statistical in that multiple porphyrin products can form, and is undirected in that no control is provided over the individual metalation state of each porphyrin.

The Suzuki coupling reaction enables C—C bond formation to create the oligo(*p*-phenylene) linkers, which gives strategic flexibility in the preparation of oligo(*p*-phenylene)-linked porphyrin arrays. Biphenyl- and terphenyl-linked porphyrin dimers were prepared by Suzuki coupling of a halophenylporphyrin and a linker bearing a bis(boronic acid) unit (entry 4).[25,26] Similar Suzuki coupling was employed with a *meso*-substituted dioxaborolanylporphyrin and a dihalo-substituted phenylene linker (entry 5).[27] Both examples provide rational access to dimers yet were undirected with respect to the metalation states and substituents of the respective porphyrins.

The synthesis of dyads requires a directed route wherein the two porphyrins are created sequentially, or two porphyrin building blocks are joined in an unsymmetric fashion. The condensation of a porphyrin bearing a *p*-biphenylcarboxaldehyde unit with a dipyrromethane and an aldehyde gave the biphenyl-linked porphyrin dyad (entry 6).[28,29] This approach was statistical in that a porphyrin triad and a porphyrin monomer also could form. We reported the Suzuki mono-coupling of a dioxaborolanylphenylporphyrin and a *meso*-haloporphyrin; although the synthesis was rational and entailed a directed coupling, the product was a *p*-phenylene-linked porphyrin dimer rather than a dyad given that both porphyrins contained the same substituents and were free base species (entry 7).[30] Nocera and co-workers recently reported the Suzuki mono-coupling of a dioxaborolanylbiphenylporphyrin and a *meso*-haloporphyrin to give a biphenyl-linked porphyrin dyad (entry 7).[31] Following these approaches, porphyrin dyads bearing linkers as long as the quaterphenyl unit have been reported so far.[18]

The reaction of a porphyrin bearing a dipyrromethane with a dipyrromethane/dicarbinol (or vice versa) afforded the corresponding *p*-phenylene-linked porphyrin dyad (entry 8).[32] The porphyrin-forming conditions were sufficiently mild to accommodate metalation states such as Zn/Fb, Mg/Fb, and Zn/Mg. Porphyrin dyads in distinct metalation states (e.g., ZnFb) in principle can be prepared by statistical metalation or demetalation of porphyrin dimers. In practice, however, separation of zinc/zinc, zinc/free base, and free base/free base arrays typically entails elaborate chromatography.