



Conformational restriction of flexible molecules in solution by a semirigid bis-porphyrin molecular tweezer



Sara Norrehed, Prasad Polavarapu, Wenzhi Yang, Adolf Gogoll*, Helena Grennberg*

Department of Chemistry-BMC, Uppsala University, Uppsala S-75123, Sweden

ARTICLE INFO

Article history:

Received 18 March 2013
Received in revised form 22 May 2013
Accepted 3 June 2013
Available online 12 June 2013

Keywords:

Conformational analysis
NMR spectroscopy
Host–guest systems
Supramolecular chemistry
Porphyrinoids

ABSTRACT

A semirigid bis-porphyrin molecular clip with a glycoluril backbone has been synthesized. The clip provides an adaptable molecular cavity for binding of diamines. Binding constants for diamines of 10^4 – 10^7 M^{-1} are orders of magnitude higher than those for monoamines of 10^3 M^{-1} , indicating a preference to bidentate binding. NMR studies confirmed that binding of bidentate guests occurs inside the clip. Short- and medium-size acyclic molecular guests are locked into a single, extended conformation, and also guests with longer flexible chains exhibit considerably less conformational mobility than when free in solution. The size of the cavity adapts to the guest size, as indicated by modelling studies and self diffusion constants of the complexes.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Metallated bis-porphyrins are regarded as interesting hosts for the ditopic binding of organic guest molecules. A variety of spacers have been used to connect two porphyrin units, providing molecular clips of varying conformational flexibility¹. This has been exploited, e.g., for the size-selective complexation of guest molecules in bis-porphyrins with rigid spacers², or for the determination of absolute stereochemistry using bis-porphyrins with flexible spacers.³ Dimeric porphyrins with various topologies have been reported as model systems for enzymes⁴ and the photosynthetic reaction centre. The guest molecule requires the presence of preferably two Lewis-basic functional groups to interact with the bis-porphyrin metal ions, with ditopic binding providing stronger interaction as well as conformational restriction^{5,6}.

In this context, we found it interesting to address the effect of binding between acyclic diamines of varying chain length and semirigid bis-porphyrin clips, regarding both conformational restriction of the guest, and adaptation of clip size (i.e., the volume of the molecular cleft) to the guest volume. For the spacer of such a semirigid bis-porphyrin clip we chose the glycoluril backbone^{7,8}.

In this paper, we present the synthesis of a new symmetric zinc(II)porphyrin-terminated glycoluril clip **1** (Scheme 1), and a survey of its host–guest interaction with a series of diamino compounds.

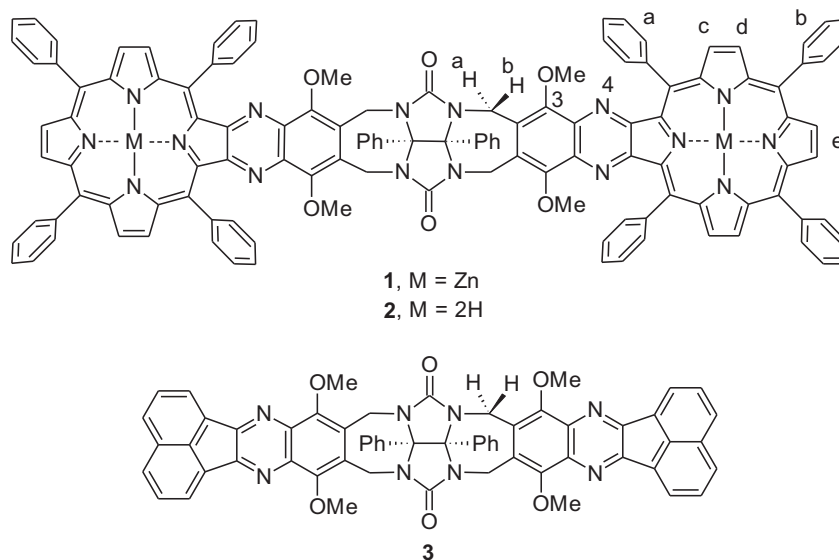
2. Results and discussion

2.1. Synthesis and characterization of bis-porphyrin glycoluril clips

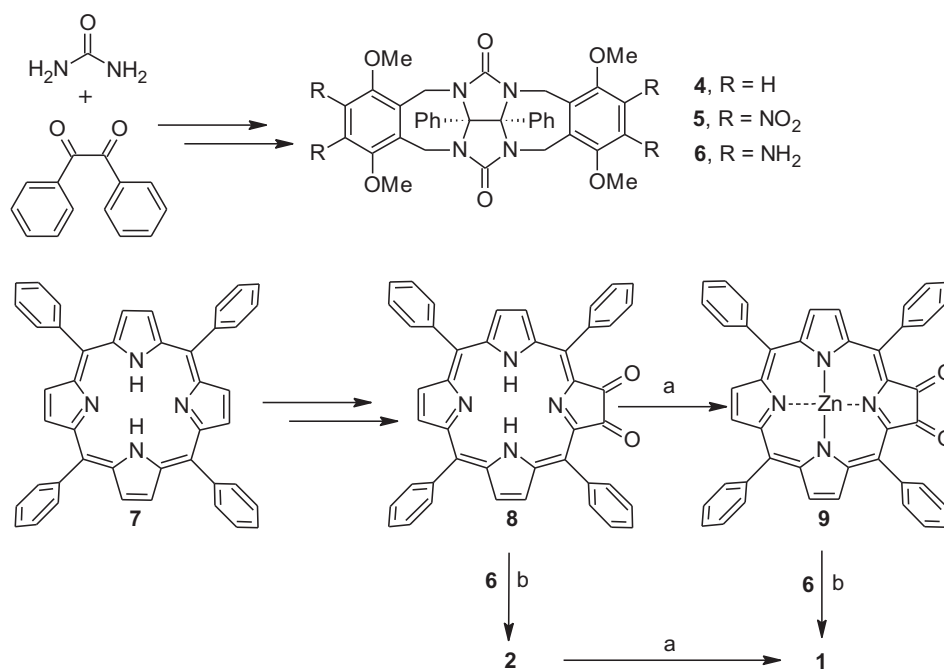
Using the same strategy as for our recently reported glycoluril-based clip **3** (Scheme 1),⁸ Zn-porphyrin clip **1** and free-base porphyrin clip **2** were prepared from the corresponding porphyrin dione (**8** or **9**) and the air-sensitive tetraamino backbone component **6** (Scheme 2). Compound **6** was synthesized in two steps from the glycoluril derivative **4**,⁹ prepared by condensation of urea and benzil^{7c}. Zinc-porphyrin dione **9** was obtained by metallation of its free-base dione **8**, which was prepared in several steps starting from porphyrin **7**. Alternative literature procedures towards synthesizing the porphyrin dione, e.g., hydroxylation of β -nitroporphyrin using sodium benzaldoximate,¹⁰ or dihydroxylation using OsO_4 ¹¹ did not work in our hands. Likewise, dihydroxylation attempts of Zn(II):**7** using RuO_4 , produced in situ from $RuCl_3$ and $NaIO_4$,¹² did not yield any dioxo compound.

Purification of **1** and **2** was challenging. Clip **1** was subjected to several flash chromatographic separations with a consecutive series of eluents ($CHCl_3$, a mixture of CH_2Cl_2 and MeOH at different ratios, and toluene). Inclusion of solvent molecules contributes to

* Corresponding authors. Tel.: +46 018 471 3822 (A.G.); tel.: +46 018 471 3821 (H.G.); e-mail addresses: adolfg.gogoll@kemi.uu.se (A. Gogoll), helena.grennberg@kemi.uu.se (H. Grennberg).



Scheme 1. Molecular structure of clips **1**, **2** and previously reported clip **3**.⁸



Scheme 2. Reagents and conditions: a: Zn(OAc)₂·2H₂O, MeOH/CHCl₃, reflux, 3 h; b: THF/MeOH 1:1, reflux, 16 h.

purification difficulties, a common problem not only in porphyrin synthesis but also encountered for some glycoluril compounds ^{7c,13–15}. In particular, removal of traces of toluene was very difficult, indicating the formation of inclusion compounds. The purification of free-base clip **2** was even more challenging as several ¹H NMR signals for the porphyrin NH protons at negative chemical shifts were always observed, indicating a mixture of porphyrin tautomers that could not be resolved even by HPLC. Considering that the clip possesses two porphyrin units with no through-bond conjugation, the observation is not unexpected but still potentially problematic in our intended NMR application that benefits from a high degree of symmetry in the host. Metallation of the mixture of clip **2** tautomers with Zn(II) resulted in clean formation of clip **1** as a single compound.

Glycoluril-based clips may exist in three conformational isomers, interchanged by rotation of the single bonds of the elbow CH₂ (marked as H_a and H_b in **Scheme 1**), with substantial differences in the cavity opening, the closed (aa or *anti-anti*) is the desired one and also the most commonly observed in this class of molecular hosts (**Fig. 1**).¹³ The conformational isomers are easily assigned by analysis of coupling constants and NOE effects in the elbow region.⁸ ¹H NMR analysis of **1** confirmed that the closed form was the only isomer present. However, the elbow region is still conformationally dynamic: at rt, the proton signals for the methoxy group and elbow CH₂ are broad, whereas the signals for the porphyrin units and the backbone phenyls are sharp. At lower temperatures the signals of the porphyrin units become broader. At higher temperatures, the elbow signals are significantly sharper, whereas some of the signals

Download English Version:

<https://daneshyari.com/en/article/5218655>

Download Persian Version:

<https://daneshyari.com/article/5218655>

[Daneshyari.com](https://daneshyari.com)