



Light-actuated resorcin[4]arene cavitands

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ABSTRACT

A light-actuated resorcin[4]arene cavitand equipped with two quinone (Q) and two opposite Ru(II)-based photosensitizing walls was synthesized and investigated. The cavitand is capable of switching from an open to a contracted conformation upon reduction of the two Q to the corresponding SQ radical anions by intramolecular photoinduced electron transfer in the presence of a sacrificial donor. The molecular switch was investigated by cyclic and rotating disc voltammetry, UV–Vis–NIR spectroelectrochemistry, transient absorption, NMR, and EPR spectroscopy. This study provides the basis for the development of future light-activated switches and molecular actuating nanodevices.

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1. Introduction

Resorcin[4]arene cavitands [1] are promising systems for the development of the next generation of molecular grippers due to their ability to switch between an *open* and a *closed* conformation [2]. While the *closed* conformation can capture guest molecules in its cavity, the switch to the *open* form could mediate their release. The switching and gripping ability of different resorcin[4]arene cavitands has been previously demonstrated using stimuli such as changes in pH [3], temperature [4,5], metal ion concentration [6], and redox reactions [7–9]. In addition to these methods, light-activated cavitands are highly desired because light allows for switching the molecules with specific spatio-temporal control and

without the need of individual activation [10,11] (e.g. by tunneling electrons from the STM tip) [12], direct contact (e.g. through electrodes in an electrochemical cell) [13], or the need of adding reactants for the operation of the switch.

The latest attempt to develop light-actuated molecular grippers was based on resorcin[4]arene cavitand **1** containing two unreactive quinoxaline (Qx) walls and two redox-active quinone (Q) walls (Fig. 1a) [14,15]. By reducing the quinones (Q) to the semiquinone radical anions (SQ) by means of *intermolecular* photoinduced electron transfer (PET) from [Ru(bpy)₃]²⁺ as a photosensitizer, switching towards the *closed* conformation was achieved. However, this system required the diffusion and contact of the photosensitizer and the cavitand for the photoinduced electron transfer process to take place, as well as the use of triethylamine (Et₃N) as sacrificial electron donor to regenerate the sensitizer and increase the concentration of the SQ radical anions. Although this work was a breakthrough that led to the development of one of the first examples of photoswitchable cavitands, while establishing the

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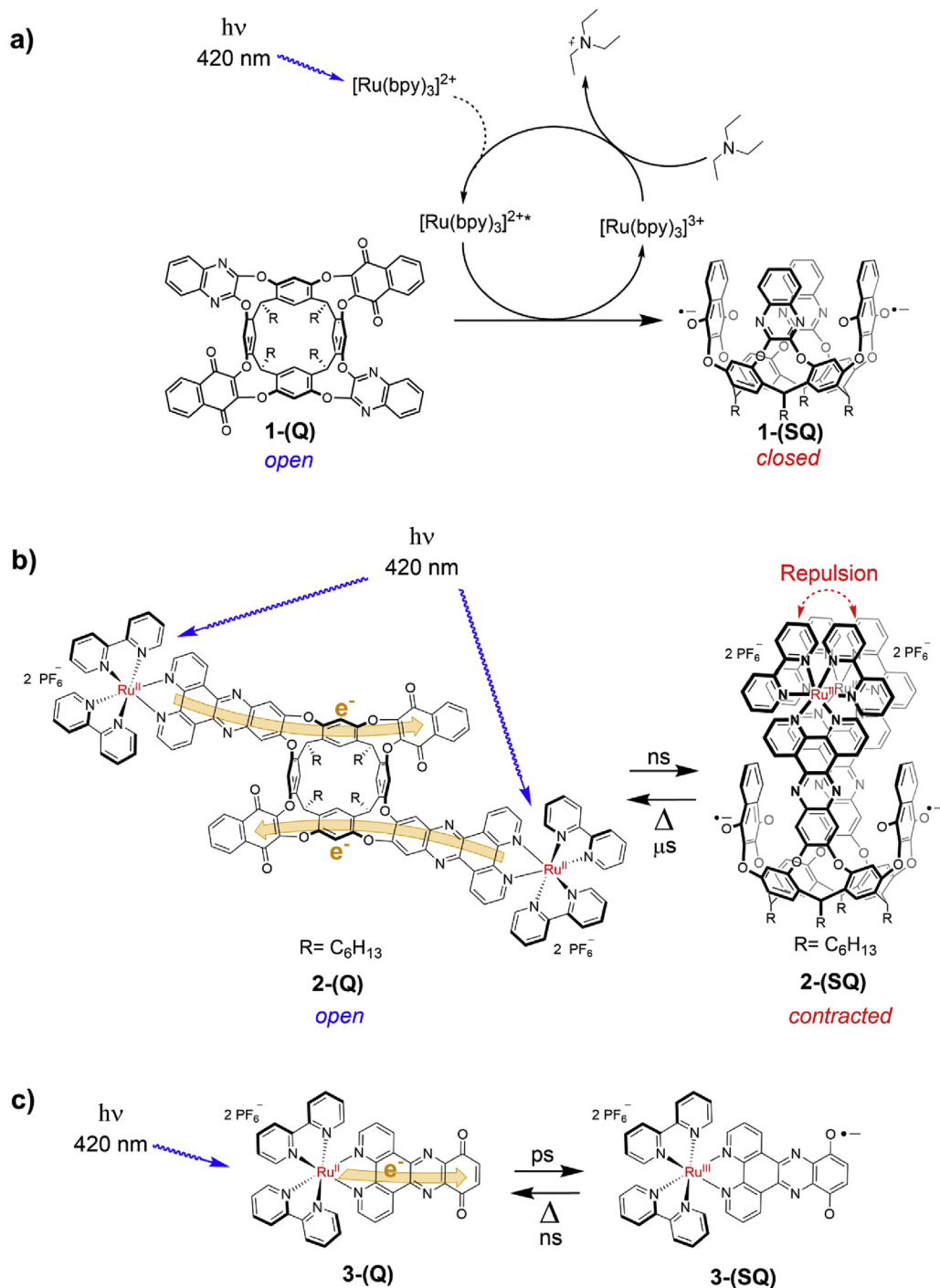


Fig. 1. a) Previously reported cavitant **1** activated by *intermolecular* electron transfer [14,15]. b) Cavitant **2** activated by *intramolecular* electron transfer. The fully *closed* conformation in the **SQ** state cannot be achieved because of strong steric and electrostatic repulsion between the two Ru walls. **SQ** refers to the **SQ** bis(radical anion) unless otherwise specified. c) Alternative model **3** with the Ru^{II} complex installed onto the quinone wall. Faster photoinduced electron transfer and back thermal recombination as compared to cavitant **2** was expected.

methodology for monitoring the switching in the **SQ** state, it does not fulfill the ultimate goal of using light as the only external stimuli without adding external photosensitizers or sacrificial donors.

We envisaged that the switching from the *open* to the *closed* conformation could be achieved by *intramolecular* PET to provide the basis for the development of light-actuated cavitants, which rely on the direct interaction between the cavitant and light as the

only external stimulus. Towards this goal, we herein present the synthesis of the new resorcin[4]arene cavitant **2** with two quinone (**Q**) walls as electron acceptor units and two Ru^{II} -based photosensitizers installed directly within the cavitant backbone (Fig. 1b). We demonstrate the switching from the *open* to a *contracted* conformation upon electrochemical and chemical reduction of the **Q** to the **SQ** radical anion, as well as upon photoexcitation in the presence of a sacrificial donor.

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