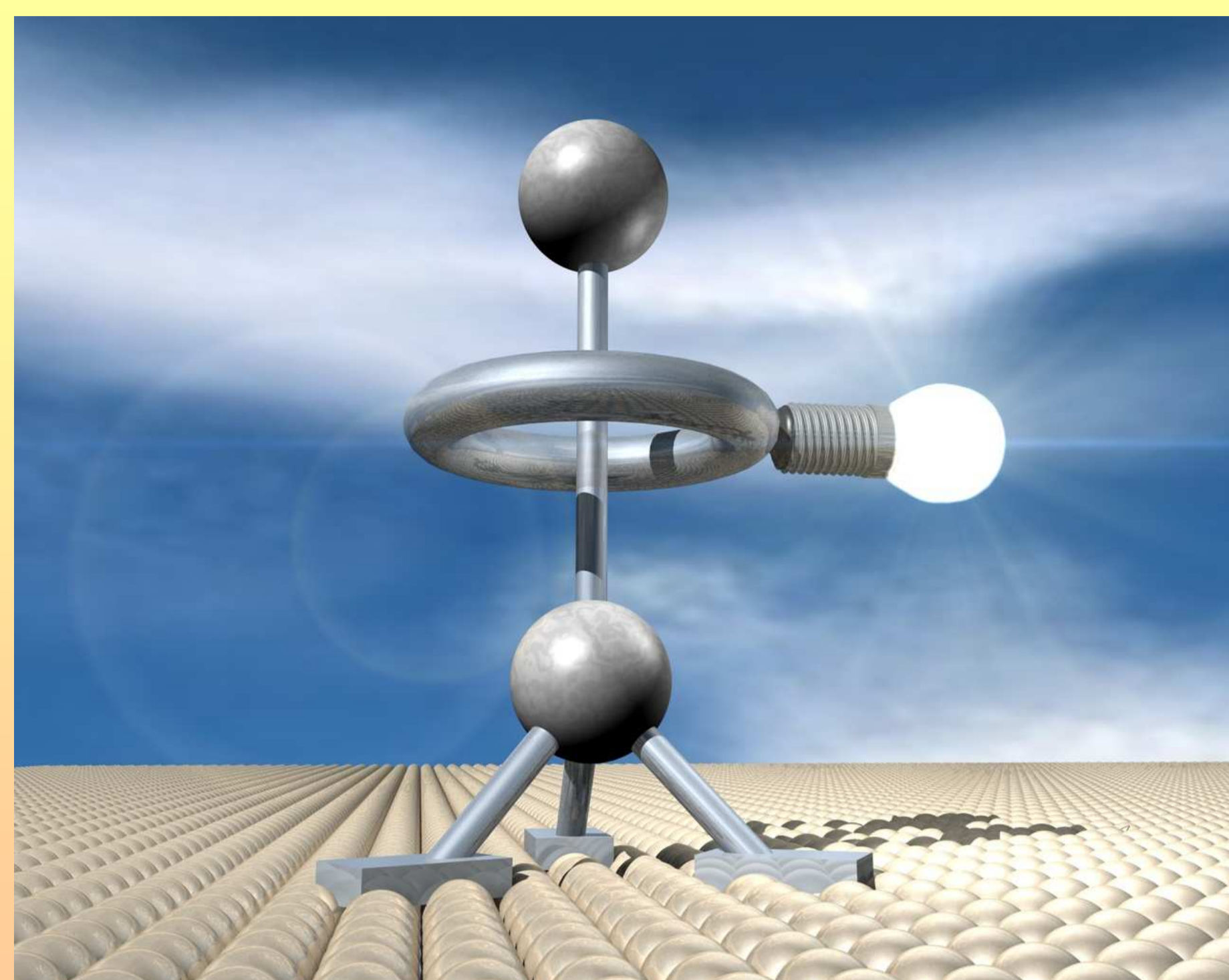


# Design and Synthesis of a Rotaxane for Observation via Single Molecule Spectroscopy

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## I. Introduction

For the development of molecular machines, the understanding of inter- and intra-molecular interactions is essential. The investigations of the bacterial flagellar motor and the F1-ATP synthase are still in progress, even if recent single molecule spectroscopy reveals much about how they work.<sup>1</sup> Both molecular motors use a rotor and stator system. As an interlocked molecule a rotaxane could also be described as a very abstract and simplified motor. But even for this basic system, kinetic, thermodynamic, structural and functional data still have to be gathered for the development of a molecular motor. To acquire this information, a rotaxane with a fluorescence wheel for single molecule spectroscopy was designed and synthesised as described here.

Necessary conditions:

To observe the rotation of the wheel around the axle of the rotaxane a fluorescent molecule has to be attached to the wheel.

The fluorescent dye should not disturb the free rotation.

The fluorescent molecule should be rigidly attached, so that every fluorescence movement can be correlated with a movement of the wheel.

To ensure that the rotaxane does not move during the observation and measurements it should be attached to a solid surface like glass.

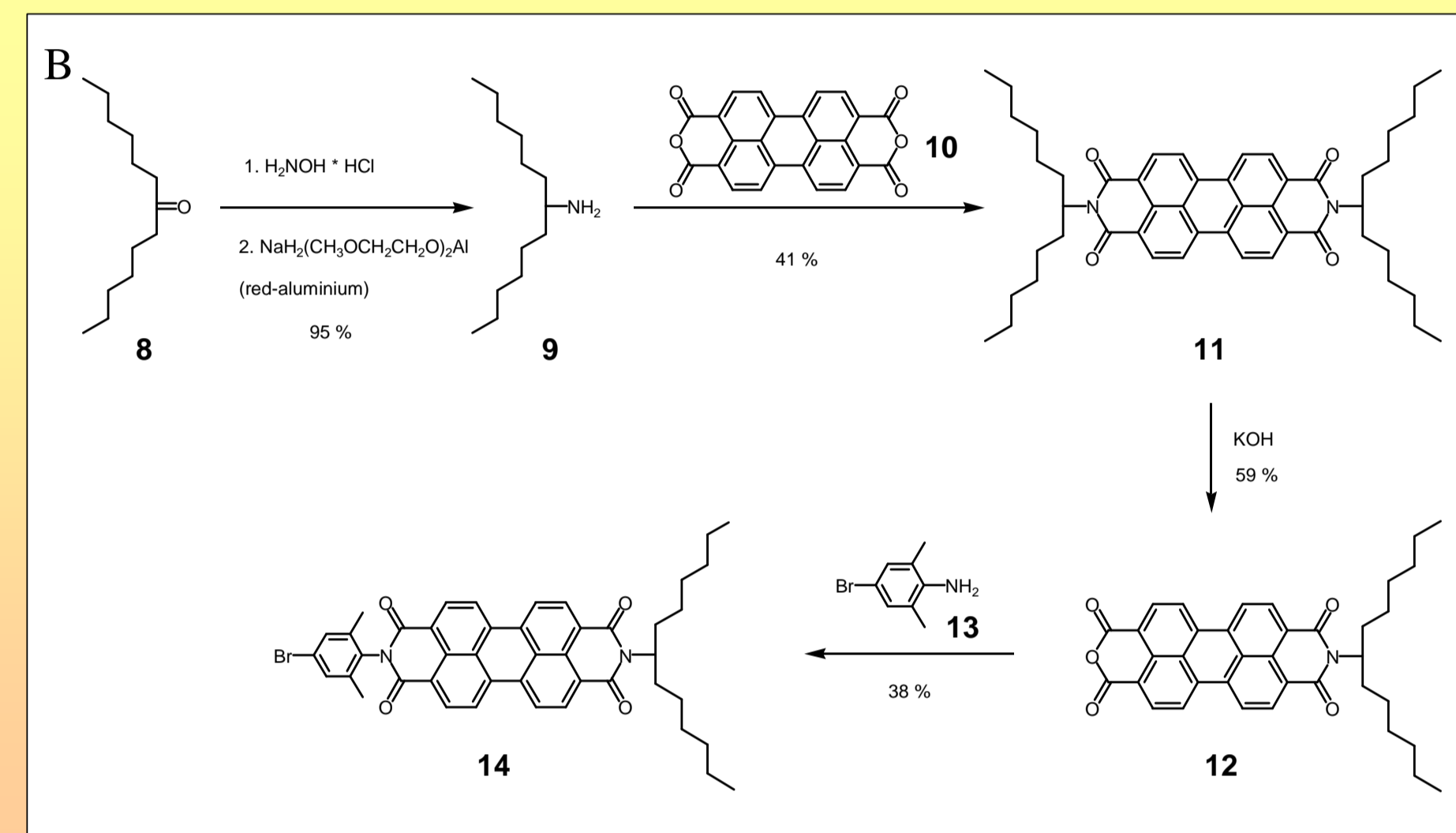
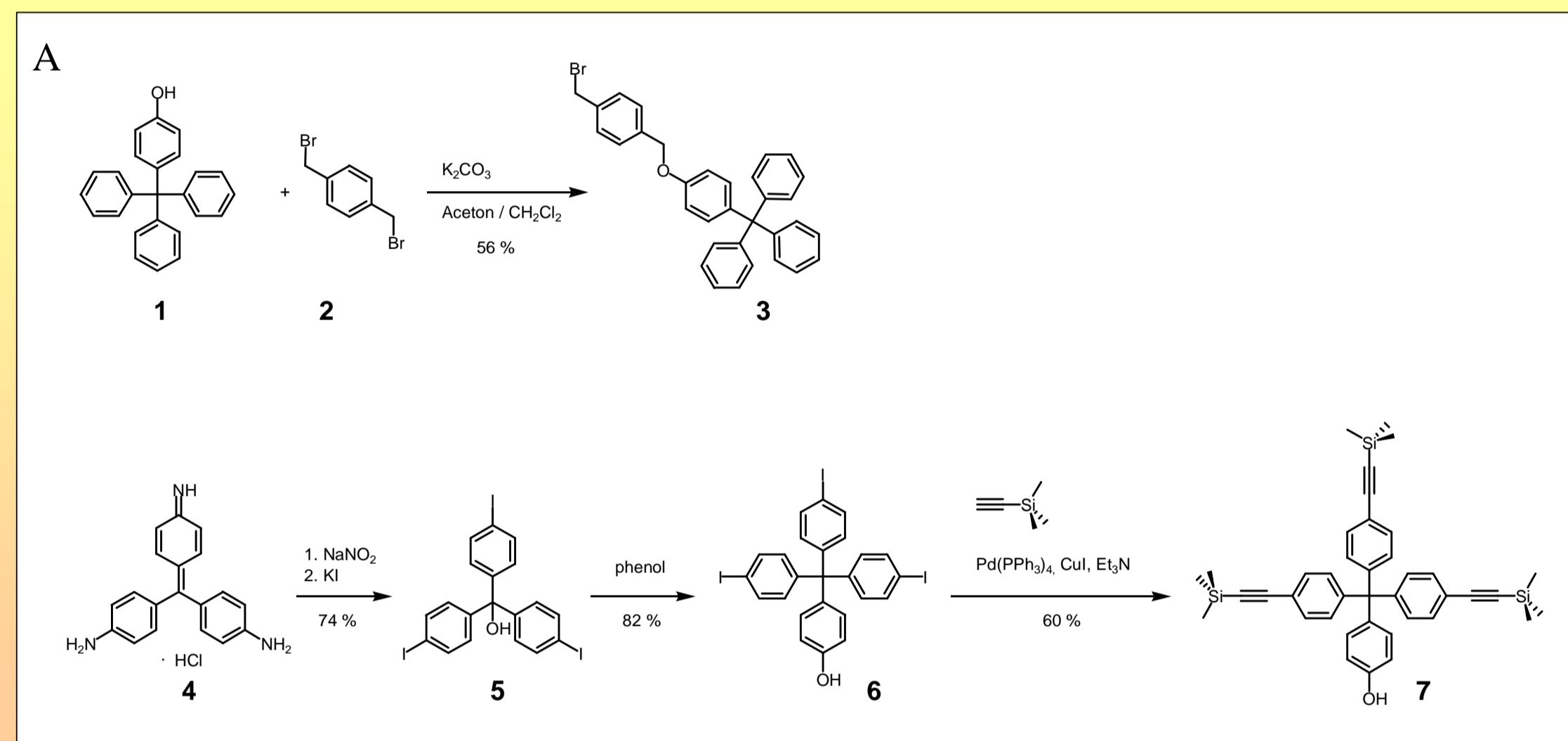
The rotaxane should not be able to fall over onto the surface which would interfere with the free rotation of the wheel.

The general structure should be similar to other rotaxanes so that known information and measurements of other rotaxanes can be compared.

## II. Stopper and Dye

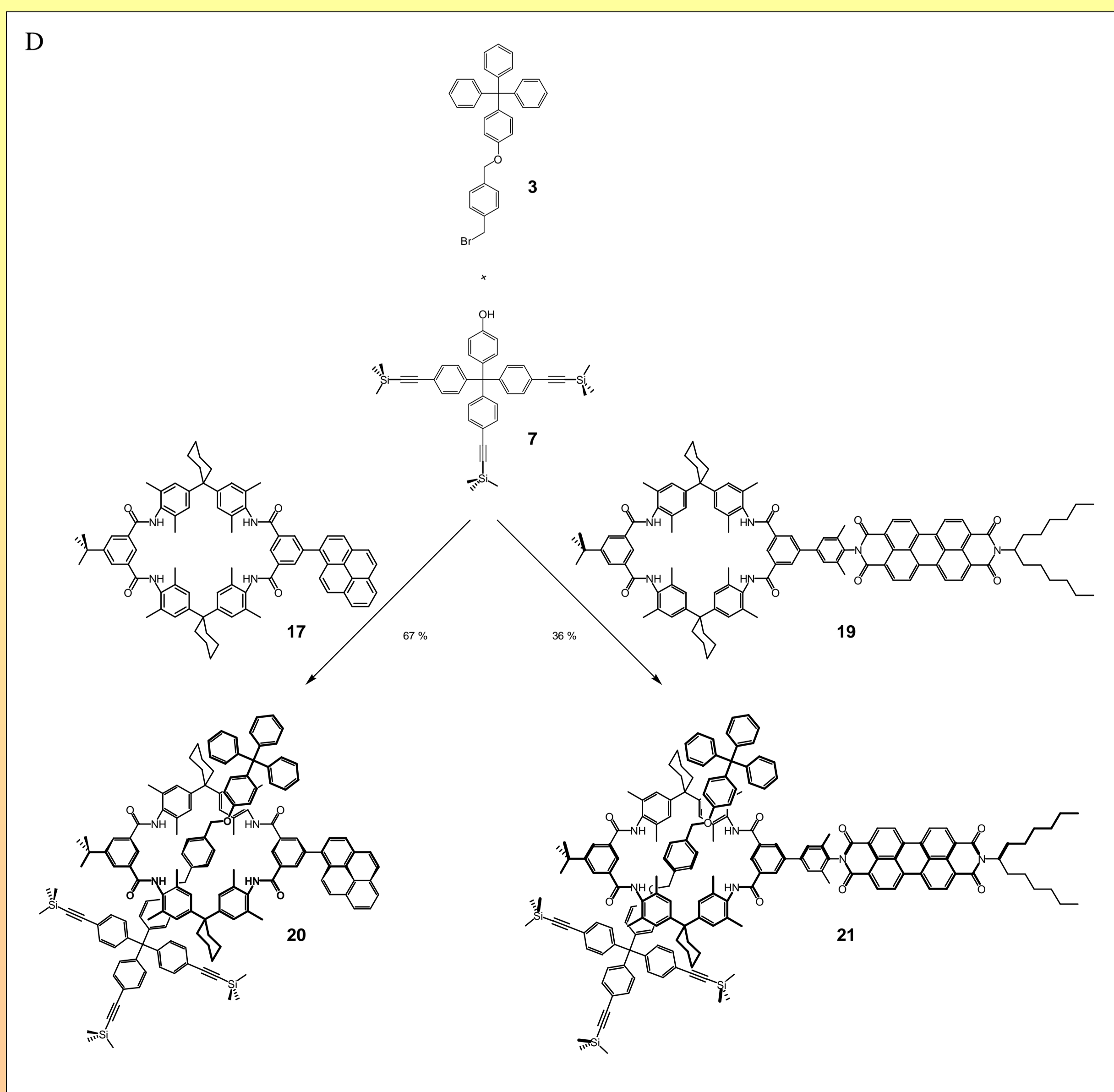
For the stopper, a tripod based on parafuchsin 4 was chosen. This provides a stable connection with the surface and the tetrahedral geometry restricts the axle of the rotaxane to a vertical position. Analogous to a synthesis of Sengupta *et al.*,<sup>2</sup> a threefold Sonogashira reaction leads to the acetylene functionalised stopper 7.

A perylene molecule is used as the fluorescent dye. These dyes have a high quantum yield and are very photostable. Because of their low solubility they are converted into a more soluble derivative<sup>3</sup> and then functionalised with a bromo group (14).



## III. Fluorescent Wheel

For the wheel, the tetralactam macrocycle of Hunter<sup>4</sup> is used and substituted during its synthesis with a triflate group (15). With pyrene boronic acid 16 it is possible to obtain the pyrene wheel 17 in a Suzuki reaction. Alternatively, a borylation of the wheel provides the opportunity for cross-coupling with the perylene dye 14.



## IV. Rotaxanes

For the formation of the rotaxanes, the anion template effect of Vögtle *et al.* was used.<sup>5</sup> The phenolate of the stopper 7 is strongly hydrogen-bonded to two amide hydrogens of the wheel. This supramolecular nucleophile then reacts with the half axle 3 to form a non-symmetrical axle. After this S<sub>N</sub>-reaction, the wheel is trapped on the axle yielding a stable rotaxane (20 and 21).

In figure E, MM2-forcefield-generated structures of the perylen rotaxane are shown. Figure F shows the excitation (300-570 nm, emission at 576 nm) and emission (460-700 nm, excitation at 458 nm) fluorescence spectra. Figure G shows a FT-ICR mass spectrum. The insets represent the isotope patterns obtained by experiment (top) and calculation (bottom).

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