

Light-Fueled Transformations of a Dynamic Cage-Based Molecular System

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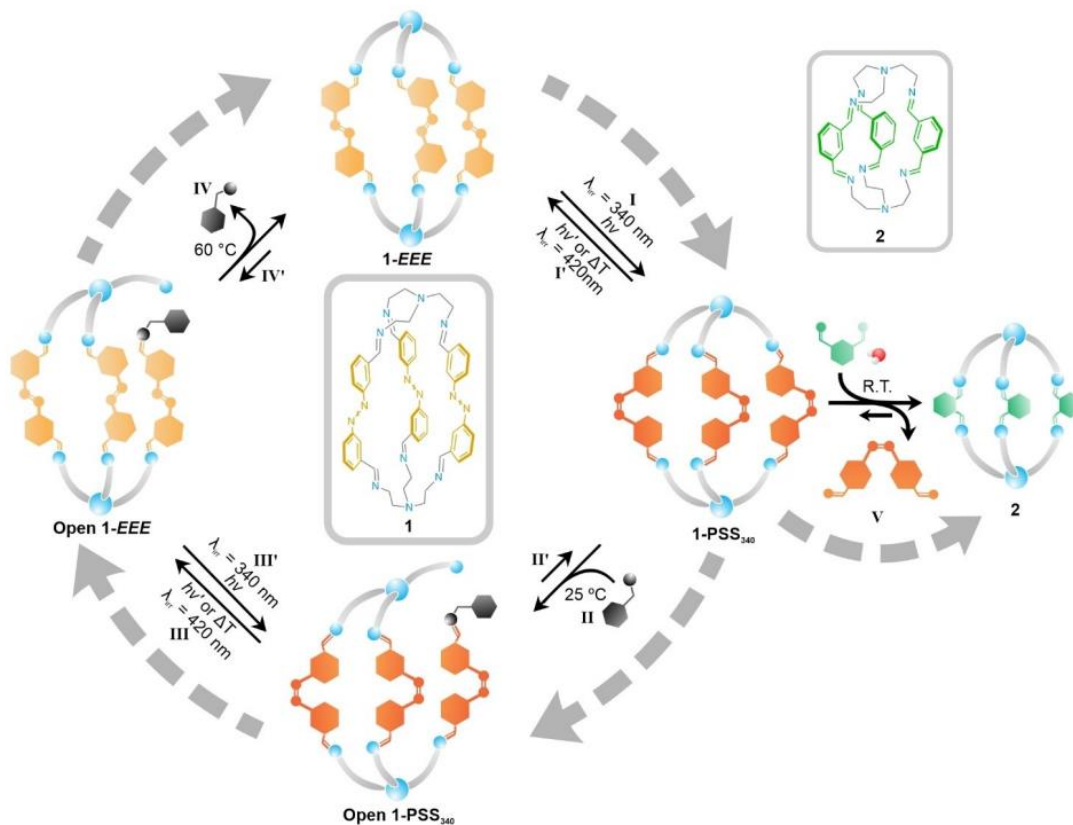


Fig 1: Light-induced transformation of macrobicyclic imine cage

Who are the corresponding authors and what are their research areas?

Ben L. Feringa – Professor of Chemistry at the University of Groningen, Netherland

His research interest is focused on synthetic and physical organic chemistry inspired by nature's principles using the concept of molecular assembly, recognition, transport, motion and catalysis.

What is the main claim of the article?

The studies certainly showed the successful development of the dynamic cage-based molecular system that couples a dynamic equilibrium to a light-induced *E/Z* isomerization of azobenzene imine cage. Upon isomerization their system could shift an amine/imine exchange reaction, according to an energy ratchet mechanism to yield a high-energy, kinetically trapped species as a result of the operation of a 4-step cycle (Fig 1).

How is it demonstrated?

Authors point out two main issues which are the successive transformation of the system to complete opening/closing cycle and the use of energy by the photoresponsive macrobicyclic imine cage. Experimentally, UV-isomerization, time-resolved NMR and kinetic analysis were studied in order to elucidate the mechanism of this 4-step operational system. Authors also used the kinetic analysis to rationalize the fact that *E/Z* isomerization really play a role in the rate acceleration and drive the system out-of-equilibrium (Fig 2).

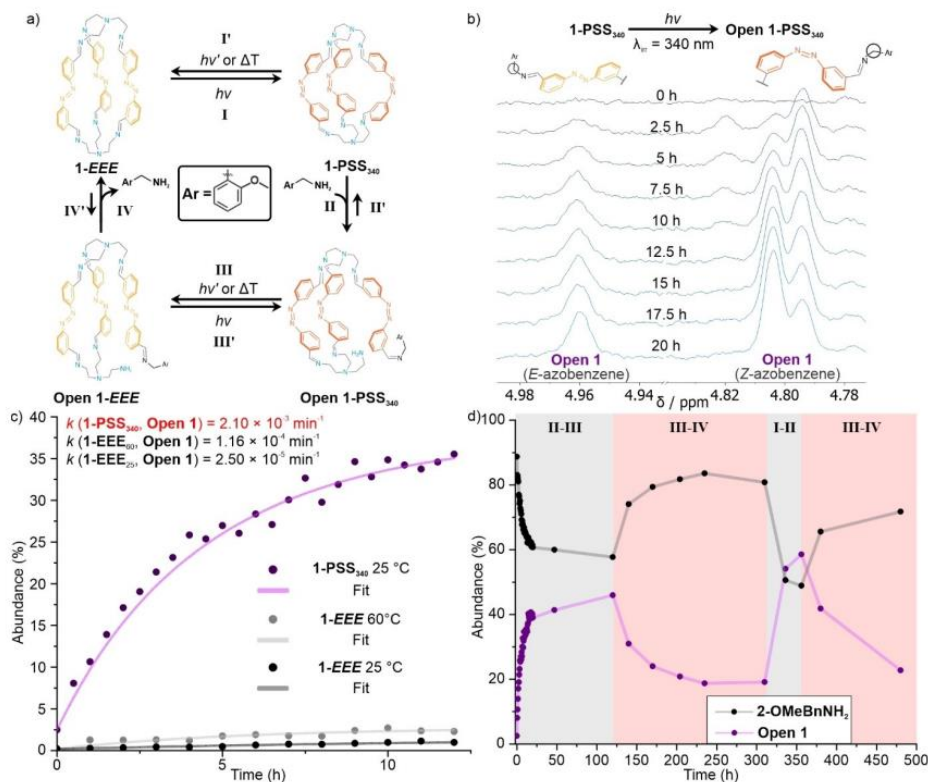


Figure 2. Light-induced cage-opening/closing cycle. a) Opening/closing cycle for 1 in steps I–IV. b) Evolution of a partial ¹H NMR spectrum (from top to bottom) during amine/imine exchange between 1-PSS₃₄₀ and 2-OMeBnNH₂ for 20 h (0.8 mM, 500 MHz, 25 °C in C₆D₆). c) Comparison of the intermolecular amine/imine exchange between 1 and 2-OMeBnNH₂ before switching (black and grey) and after switching (purple). d) Kinetic profiles of the opening/closing cycle of 1 with 2-OMeBnNH₂ (black) as a competing nucleophile.

What are the typical experimental conditions?

UV Vis isomerization studies

Concentration: 10 μ M in benzene. The samples were degassed prior to the measurement. Irradiation to evaluate isomerization by UV Vis spectroscopy was performed with a 340 nm or 420 nm Thorlabs LED model M420F2 (8.9 mW) positioned 1 cm from the samples.

NMR isomerization studies and kinetic analysis

Varian Unity Plus (¹H: 500 MHz, ¹³C: 125 MHz). Irradiation was performed either in-situ with a 340 nm Thorlabs LED model M340F3 (0.85 mW) or 420 nm Thorlabs LED model M420F2 (8.9 mW), via a fiber optic cable from Thorlabs (FT400UMT) modified to fit into the NMR tube or ex-situ with the same LEDs positioned 3 cm from the samples. The concentration of 1-EEE was 1.1 mM in benzene-d₆ for all isomerization experiments in benzene-d₆.

Light-induced amine-imine exchange (cage opening and closing)

1-EEE was irradiated ($\lambda_{\text{irr}} = 340 \text{ nm}$) ex-situ for 11 h. Then a stock solution of the competing amine 2-OMeBnNH₂ was added in a glovebox. Typical concentration 0.8 mM.