Flavylium Compounds Meet Cucurbiturils:

A Multi-Responsive Pseudo-Rotaxane

André Seco[1]*, Nathan Mcclenaghan[2], A. Jorge Parola[1], Nuno Basílio[1]

[1] Associated Laboratory for Green Chemistry - LAQV, REQUIMTE, Chemistry Department - NOVA School of Science and Technology, 2829-516 Monte de Caparica, Portugal

[2] CNRS/Univ. Bordeaux, Institut des Sciences Moléculaires, Talence, France

* *am.seco@campus.fct.unl.pt*

Rotaxanes and pseudo-rotaxanes are among the most well studied types of supramolecular devices and cucurbiturils have proven over the last two decades that they are an ideal macrocycle to build this kind of devices in aqueous media, something that still presents a challenge in the field. In this work will be presented a pseudo-rotaxane assembled from a cucurbit[7]uril, CB7, wheel and a 2-hydroxychalcone based axle.

This 2-hydroxychalcone based axle was designed to take advantage of the pH dependence and light sensitivity that are characteristics of these compounds, related to the anthocyanin's family multistate [1]. Indeed, while the chalcone is stable at neutral pH and has a measured affinity constant towards CB7 of K_{11}=1.2x10^5 M^{-1}, at acidic pH (< pH 2) it undergoes a series of (reversible) reactions that culminate in the cationic flavylium form that has an even larger affinity constant towards CB7 (K_{11}=1.5x10^8 M^{-1}). This flavylium form is also highly fluorescent on its own (QY = 0.29) and upon 1:1 complexation the quantum yield increases drastically to an almost unitarian quantum yield (QY_{11} = 0.97) [2].

Considering these stark differences in affinity, we can work at an intermediate pH where we start with the chalcone form and use light to promote the formation of the flavylium in a metastable equilibrium that eventually reverts to the chalcone form. That causes the CB7 wheel to switch from a loose binding on the chalcone, to a locked conformation on the flavylium and back to a loose binding on the chalcone again, and so on, as shown by the cycling experiment in the picture bellow.

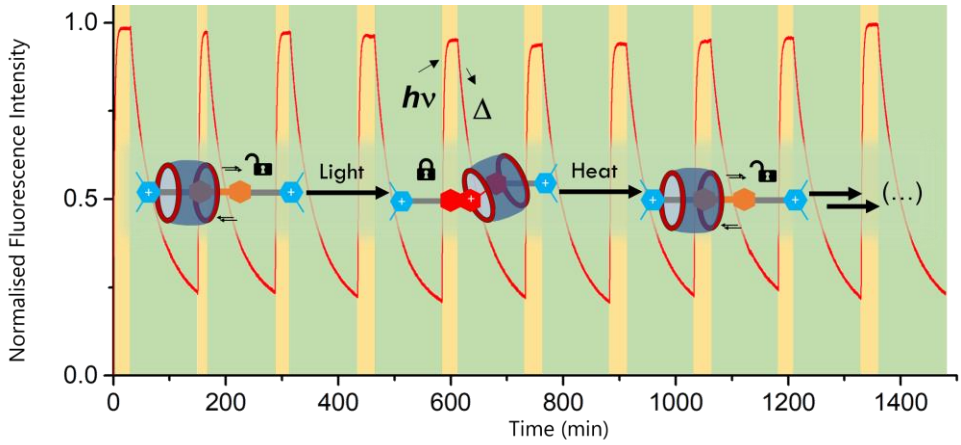

Figure. *Shuttling of the cucurbit[7]uril along the pseudo-rotaxane axle in response to light and thermal stimuli, for a fixed pH. The fluorescence signal was used to follow the changes in binding.*

References

[1] L. Cruz, et al, Chem. Rev., **2022**, 122, 1, 1416–1481.

[2] A. Seco, *et al, Chem. Eur. J.*, **2021**, 27, 16512.