How cucurbit[7]urils allow the formation of a highly stable and stimuli responsive hexacationic flavylium-based quaternary rotaxane

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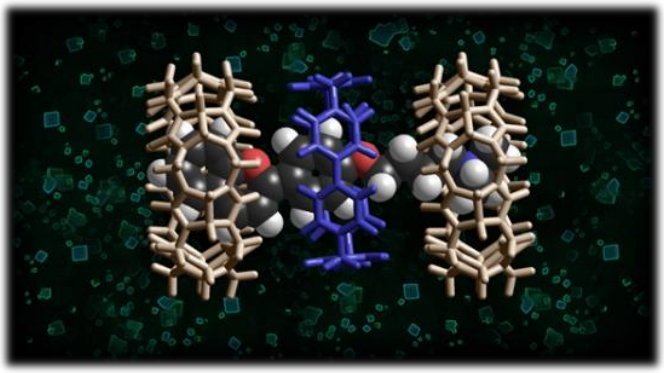
Rotaxanes are among the most well-known families of host-guest systems. Simply put, they consist of an axle to which a macrocycle binds and the presence of stoppers in the axle mechanically prevents the dissociation of the complex. In this work we present a rather novel rotaxane, assembled in aqueous solution, in which the tetracationic blue box binds to a dicationic flavylium guest having two cucurbit[7]urils acting as supramolecular stoppers. The flavylium/chalcone photoswitch is explored and when in chalcone form, the axle binds one macrocycle of each type. Upon irradiation and formation of the flavylium cation, a second CB7 binds the axle, locking the blue box in place with a very high binding constant (>1x10^{7} M^{-1}) accompanied by a drastic increase in fluorescence quantum yield (12x, QY=0.78). In the absence of cucurbiturils no interactions between the flavylium axle and blue box are observed. Furthermore, in the axle, we explored two different tail groups appended to the flavylium/chalcone moiety. One has a cationic trimethylammonium, another has an anionic sulfonate and we found that only the one with the cationic tail forms this hetero[4]rotaxane since it provides a binding site for the second CB7.



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