

Cucurbit[7]uril limits the binding of coumarin bearing alkyl-acetoacetate with mercury and stimulates the desulphurisation reaction of its sulphur analog

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Abstract

The inclusion of 7-diethylamino-coumarin derivatives, bearing an ethyl acetoacetate (CAM1) and a methyl β -ketodithioester moiety (CAM2) in the cavity of cucurbit[7]uril (CB7), leads to different interaction forms with mercuric ions (Hg^{2+}). The interaction between these ions and CAM1, in the presence of CB7, occurs through the lateral ethyl acetoacetate moiety of the keto form of CAM1, leading to the formation of binary assemblies such as $\text{Hg}^{2+}@CAM1$ and $\text{Hg}^{2+}@CB7$. As a consequence, the metal restricts the insertion of the dye into the CB7 cavity, decreasing the apparent binding constant between them. Interestingly, for the other derivative CAM2, a mercury-induced desulfurisation reaction of its β -ketodithioester moiety is kinetically accelerated by CB7 (by a factor ≈ 25), which subsequently leads to the generation of binary and ternary complexes among the analogue oxygenised from CAM2, metal and CB7. The later effect is a promising strategy that could be considered for the mercury sensing methodology.

Author keywords

CB7-promoted desulfurisation
competitive/cooperative approach
coumarin derivatives
methyl β -ketodithioester framework
Stabilisation keto form