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Effect of *L*–tryptophan and *L*–phenylalanine residues in the pillar[5]arene structure for the formation of fluorescein containing nanoparticles and imparting fluorescence properties

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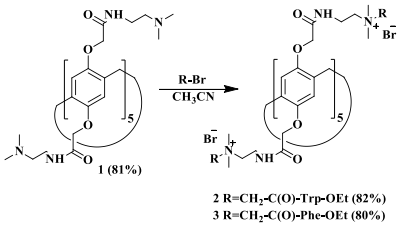
Introduction

Fluorescein nanoparticles are often covalently bonded to the substrate, which limits the biomedical applications of these systems. In this regard, the creation of nanoparticles based on biomimetic macrocyclic derivatives, in which fluorescein would be non-covalently bound to the platform, turns out to be of current interest. Pillar[5]arenes are a relatively new class of molecular receptors that have a number of attractive properties (cylindrical structure, accessibility of starting regents for precursor synthesis, ease of functionalization, structure-property control that allows manage supramolecular self-assembly processes, and etc.)



In this work, we synthesize decasubstituted pillar[5]arene derivatives with *L*–tryptophan (Trp) and *L*–phenylalanine (Phe) amino acids fragments, and studied physicochemical properties of binary (macrocycle-fluorescein) systems

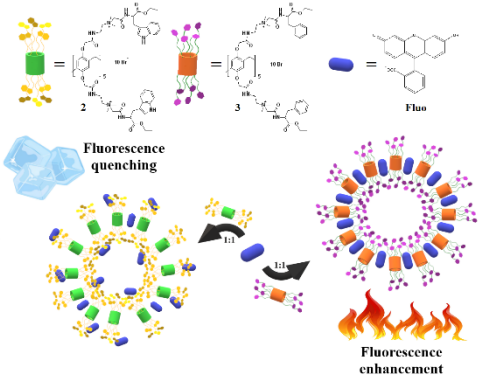


Fig. 1. Schematic representation of the formation of various associates based on synthesized macrocycles **2, 3** and **Fluo**, exhibiting different fluorescence mechanisms.

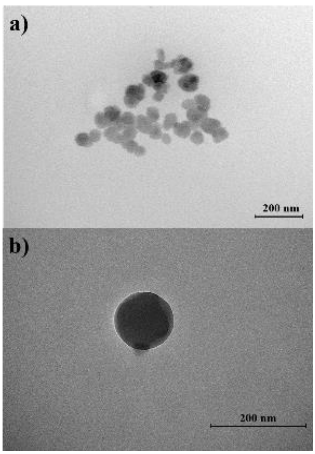


Fig. 3. TEM image of aggregates formed by macrocycle (a) **2+Fluo**; (b) **3+Fluo** at 1:1 ratio (EtOH–H_2O, 1×10^{-4} M).

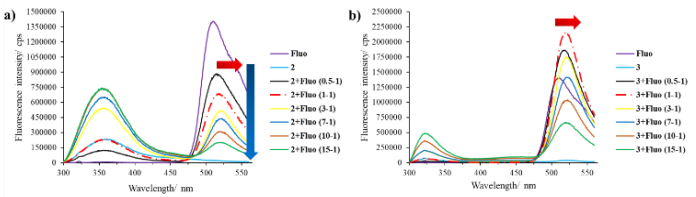


Fig. 2. (a) Fluorescence spectra of **Fluo** (1×10^{-5} M) at different pillar[5]arene **2** concentrations (0.05–1.5×10^{-4} M); (b) fluorescence spectra of **Fluo** (1×10^{-5} M) at different pillar[5]arene **3** concentrations (0.05–1.5×10^{-4} M).

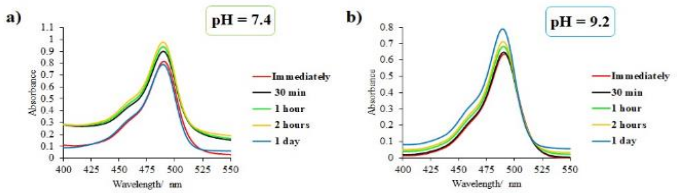


Fig. 4. Electronic absorption spectra of the system **2+Fluo** in a) phosphate buffer solution (pH=7.4); (b) sodium tetraborate buffer (pH=9.2) ($C_2=1\times10^{-5}$ M, $C_{Fluo}=1\times10^{-5}$ M).

Conclusions

Thus, for the first time, decasubstituted pillar[5]arenes with the amino acids fragments of *L*–tryptophan **2** and *L*–phenylalanine **3** were synthesized. The association of macrocycles 2, 3 with Fluo into nanoparticles was confirmed by DLS and TEM methods (92÷1 and 79÷1 nm respectively). The ability to form complexes and associates with fluorescein by synthesized macrocycles was studied by electron UV–vis and fluorescence spectroscopy, two–dimensional ^{1}H–^{1}H NOESY NMR spectroscopy. Pillar[5]arene with *L*–phenylalanine moieties more efficiently binds fluorescein (lgK_a = 3.92) comparing with pillar[5]arene with *L*– tryptophan moieties (lgK_a = 2.94). The two systems exhibited different fluorescence mechanisms aggregation–induced emission (AIE) for the mixed particles based on pillar[5]arene with *L*– phenylalanine fragments and aggregation–caused quenching (ACQ) – for pillar[5]arene with *L*– tryptophan moieties. It was found that the fluorescein release was observed only from the associates based on pillar[5]arene with *L*–tryptophan residues in the neutral (pH = 7.4) and alkaline (pH = 9.2) solutions. The results of this work may be useful for further research to create targeted drug or fluorescent marker delivery systems with pH–controlled release.

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