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THE DESIGN OF FUNCTIONAL SUPRAMOLECULAR CRYSTALS VIA COMPETITION-DRIVEN DIFFUSION CONTROL IN AQUEOUS SOLUTIONS

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Nowadays supramolecular functional materials are being applied in various fields, such as biomedicine, sensing and electronics [1]. The majority of functional properties of these materials depend on their shape and morphology [2]. Thus, the tunability of the properties can be achieved by controlling the morphology. One of the possible ways to control the growth of supramolecular crystals is to apply a reaction diffusion approach to self-assembly [3].

Here, on the example of supramolecular self-assembly of small organic molecules, melamine and barbituric acid, we demonstrate the possibility of transferring the reaction diffusion approach from media with high viscosity, as it was described previously, into the aqueous solutions. In order to do so, we introduced an intermediate stage – the complexation of barbituric acid with transition metal ions [4]. The process of complex formation allows slow diffusion of barbituric acid to the solution containing melamine and leads to delayed nucleation of melamine barbiturate. The complexation was approved by potentiometric titration, where the second equivalence point occurred. For each of used metal ions the stability constants of obtained complexes with barbituric acid were evaluated from the potentiometric titration data. The evaluated constants also as DFT calculations results indicate the formation of complexes with four barbiturate ions per one cation – $[Me(BA)_4(H_2O)_2]^{2-}$ as the most possible product.

As a result, the above-described approach leads to the formation of pure crystalline melamine-barbiturate with larger size of crystals and less defects on their surface compared to the products of convenient growth of melamine barbiturate.

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