

Interactions of heparine with polymethinium salts capped gold nanoparticles in aqueous environment.

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Anions and anionic biopolymers play a fundamental role in a wide range of chemical and biological processes. Development of receptors which are designed for these analytes is an important branch of modern chemistry [1,2]. One of the major challenges in supramolecular chemistry is the design of receptors for selective anion recognition. Nature has developed selective protein receptors even for structurally very similar biologically important anions, e.g., including phosphate and sulfate binding proteins [3]. The design of synthetic receptors for selective sulfate over phosphate recognition in aqueous media has been a significant challenge. In the case of polysulfates, such as heparin, two types of optically-responsive synthetic receptors have been studied. One of these is using cationic boronic sensors [4].

Nowadays, gold nanoparticles are often prepared by chemical reduction of Au(III) [5]. Sodium citrate belongs to the most usable reducing agents [6] to prepare citrate stabilized gold nanoparticles. Mercapto-derivatives have been commonly used as modifiers of gold nanoparticles in recent years. 3-Mercaptopropionic acid (3-MPA) represents such a compound. At basic pH nanoparticles modified by 3-MPA have negative charge on the surface due to carboxylate groups. This allowed immobilization of polymethinium salts (**1**, **2**) which have positive charge due to quaternary nitrogen atoms by ionic bond. It is also possible to immobilized polymethinium salts by direct immobilization to non-modified gold nanoparticles because of their negative surface charge.

The method based on the reduction of $K[AuCl_4]$ by citrate was used to prepare 15 nm average size gold nanoparticles (ref. 5). The immobilization of porphyrin conjugates was carried out by two different ways of ionic interaction. First, direct immobilization of polymethinium salts on nanoparticles, second, immobilization of polymethinium salts on 3-MPA premodified gold nanoparticles. Such prepared nanoparticles were purified by centrifugation and characterized. Interactions of heparine with polymethinium salts in water were studied by UV-Vis spectroscopy.

Immobilization of **1** and **2** on gold nanoparticles (GNP) prevents the polymethinium salts from aggregation in water. Comparative experiments with free **1** and **2** versus GNP-MPA-1, GNP-MPA-2 in water revealed a strong influence of the immobilization of the polymethinium salts on their interactions with heparine. The selectivity of polymethinium salts towards heparine remains the same with comparison to free polymethinium salts in the solution.

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