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Discrimination of homologous and isomeric dicarboxylic acids by gold nanoparticlepillar[n]pyridinium ensembles

Abstract

Dicarboxylic acids are one of the most important and well-known chemical compounds. They are used in the fabrication of dyes, perfumes, pharmaceuticals, and many other products. On the other hand, diacids play a crucial role in many biochemical processes such as energy production and storage. However, their omnipresence not only improves the quality of the life but also creates serious environmental problems and increases the risk of various diseases in humans. Therefore, their detection is of a paramount significance.

Dicarboxylic acids are colorless crystals with similar physicochemical properties. Therefore, their discrimination is extremely difficult. The methods of their detection developed so far recognize only selected diacids and often require specialized equipment. To address this issue, we have decided to develop a general and simple strategy for the recognition of dicarboxylic diacids. To this end, we have developed a supramolecular nanosensor made of gold nanoparticles coated by pillar[n]pyridinium (PnP) macrocycles.

The first part of the PhD thesis focuses on the visual discrimination of phthalic acids, which are positional isomers. Compared to previous studies, the developed by us sensor recognizes all three isomers. In the presence of the nanoparticles, these acids produce a multilevel response, including the color change observed with the naked eye. The desired optical response is attained through specific non-covalent interactions between the diacids and the NPs coated with cationic pillar[n]pyridinium hosts, resulting in the formation of NP aggregates with different interparticle gaps.

The second part of the thesis describes the recognition of aliphatic dicarboxylic acids, which are chemical homologs. The principle of the operation of the sensor, in this case, is the same and consists in cross-linking the NPs with the diacids. The obtained plasmonic coupling depends on the length, flexibility, and odd-even character of the aliphatic chain of each diacid.

The third part of the thesis concentrates on differentiating geometric isomers. Specifically, we used the dicarboxylic derivatives of ethylene, stilbene and azobenzene. As in the previous cases, the recognition of each diacid depends preliminary on the spatial position and relative distance between carboxylic groups. For short diacids, a more pronounced plasmonic response is obtained for *trans* isomer, while for long diacids for *cis* isomers. Importantly, the nanoparticles not only discriminate between *trans*- and *cis*-forms but also undergo reversible self-assembly which is controlled remotely by light.

The nanosensor we have developed stands out from other similar platforms which are more complex and are able to discriminate only selected isomers. In the future, this sensor can be also utilized for recognizing other chemically similar compounds containing anionic groups.

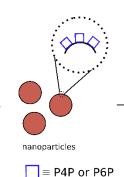
phthalic acid isomers

α,ω-alkanedicarboxylic acids

n=0-8

E/Z isomeric dicarboxylic acids

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