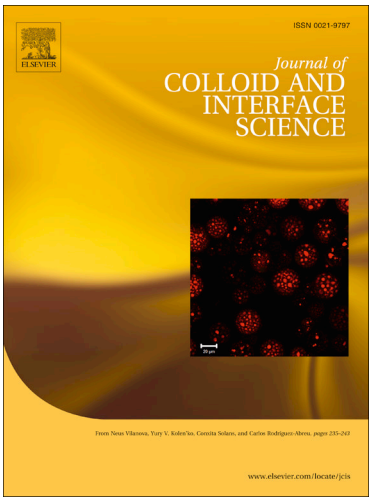

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Hybrid supramolecular materials constructed from pillar[5]arene based host–guest interactions with photo and redox tunable properties

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ABSTRACT

Monocarboxylate functionalized pillar[5]arene **1** with excellent solubility in organic solvent was prepared. It could be abosorpted on the surface of gold nanorod spontaneously. Then, hybrid supramolecular materials were constructed from **1** stabilized gold nanorods and a linear dinitriles **2** driven by host–guest interaction. Interestingly, the hybrid supramolecular materials show dynamic near-infrared (NIR) and redox dual-responsive reversible properties. ^{1}H nuclear magnetic resonance (NMR) spectra, transmission electron microscopy (TEM), scanning electron microscopy (SEM), optical microscopy, and specific viscosity were used to characterize the obtained materials and the reversible behavior under external stimuli. We suggest that this NIR and redox dual-responsiveness properties would be useful in preparation other smart materials and have potential *in vivo* applications.

1. Introduction

Pillar[*n*]arenes, which were first reported by Ogoshi in 2008,[1] are a new type of macrocyclic hosts after crown ethers,[2] cyclodextrins,[3] calixarenes[4] and cucurbiturils.[5] The frame works of pillar[*n*]arenes are made up of hydroquinone units or their derivatives linked by methylene (-CH_2-) bridges at their *2* and *5* positions.[6] Compared with crown ethers and calixarenes, pillar[*n*]arenes have more rigid structures; on the other hand, compared with cyclodextrins and cucurbiturils, pillar[*n*]arenes can be modified more easily. So, over the past several years, the syntheses,[7] conformational mobility,[8] derivatization,[9] host–guest complexation,[10] self-assembly[11] and applications[12] of pillar[*n*]arenes have been widely investigated.

Recently, the fabrication of noble metal nanoparticle doped organic materials has attracted tremendous interests due to their advanced electronic, optical and biological properties than the individual nanoparticles.[13] For example, Jang and *co*-workers found that hybrid nano-fibers assembled from PMMA and Ag nanoparticles had the antimicrobial ability against both Gram-negative and Gram-positive bacteria.[13c] Up to now, different strategies have been developed to prepare metal nanoparticle doped hybrid materials through H-bonding, π-π stacking, host-guest interactions and CH-π interactions.[14] However, the reverse process, disassembly of the materials is difficult to realize due to the linkages between the particles could not be broken and recovered repeatedly.[15] So it is a major challenge in materials chemistry to construct reversible hybrid materials, which is very important for the repeated application of them in various areas.