Supramolecular self-assembly and photophysical properties of pillar[5]arene-stabilized CdTe quantum dots mediated by viologens†

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Colloidal semiconductor quantum dots (QDs) represent one of the fastest and attractive developing research fields of science and nanotechnology, owing to their unique size-tunable optical, electronic, and physicochemical properties superior to conventional fluorescent dyes, such as high fluorescence, long fluorescence lifetimes, broad excitation, precise tunability of symmetric and narrow emissions, negligible photobleaching and excellent chemical and photostabilities.1 QDs have been successfully used in biological sensing,2 immunoassays,3 and biomacromolecular fluorescence labeling and biological imaging4 in the past decade. Recently, hybrid materials composed of QDs and organic molecules, e.g., π-conjugated dyes and macrocyclic receptors, have been increasingly considered for optoelectronics, sensing, nanoparticle assembly, and superlattice construction.5

On the other hand, pillar[5]arene (P[5]A) and its derivatives, as a new class of macrocyclic, $D_5$-symmetric cylindrical or pillar-shaped supramolecular host molecule, was firstly reported by Ogoshi and Cao et al.6 Recently, we developed a highly-efficient TfOH-catalyzed synthetic method for P[5]A and its derivatives, and ruled out a solution-phase catalytic mechanism.7 P[5]A and its derivatives have been shown to act as excellent host compounds for different guest molecules, especially viologen and pyridinium compounds,8 attributed to the charge-transfer interactions between their electron-rich cavities and the encircled electron-poor guests.9 Very recently, we reported the successful modification of P[5]As on the surfaces of Au nanoparticles to form a novel nanomaterial, which was then used for herbicide detection.10 However, using P[5]A or its derivatives to fine-tune the surface chemistry of QDs, and control the self-assembly and photophysical properties of QDs through pillararene-based host–guest chemistry, still remains an unexplored research field.

In general, water-soluble QDs are synthesized in the presence of various thiol-ligands,11 and the surface modification of QDs with synthetic macrocyclic compounds has received extensive attention.12-17 For example, derivatives of cyclodextrins and calixarenes have been used to hybridize with QDs to obtain composite materials as sensors for ions,12 organic molecules,13 and chiral compounds.14 It is worth noting that not only have mono-thiolated compounds been successfully used to stabilize nanoparticles, but also multi-thiolated (or multi-carboxylated and multi-carbonyl) compounds have been employed as better stabilizers to modify the surfaces of nanoparticles. For example, strong multivalent interactions between metal nanoparticles and cucurbit[n]urils, which contain 2n carbonyl groups on their portals, can make cucurbit[n]urils sit right on gold/silver nanoparticle surfaces.15,16 Meanwhile, QDs have been made stable in aqueous solutions at room temperature upon coating the surfaces with multi-carboxylated calixarenes.17 Moreover, dimeric and trimeric oligomers of QDs have been successfully assembled through rigid multi-carboxylated terylene diimide dyads as bridges.18 Therefore, the above-mentioned methods pave a new way for a wide range of ligands to be modified on the surfaces of colloidal nanoparticles as suitable stabilizers. P[5]A, with five hydroxyl groups distributed on both rims,19 was chosen to be further derivatized with carboxylate groups for this purpose.

Herein, carboxylatopillar[5]arene (CP[5]A),10 containing five carboxyl anions on each rim of the cavity, was synthesized from P[5]A and functionalized onto the surfaces of CdTe QDs via a ligand-exchange method to obtain a new composite nanomaterial (CP[5]A@QD) (Scheme 1). TEM experiments showed that these nanocomposites were stable in water (Fig. 1a, S1 and S2, ESI†).
The successful modification of CP[5]As on QD surfaces via a ligand-exchange method was identified by ultraviolet-visible (UV-vis) spectroscopy and Fourier transform infrared (FT-IR) spectroscopy. The UV-vis spectrum of CP[5]A@QD shows a shoulder peak at 293 nm, corresponding to CP[5]A absorption and indicating the presence of CP[5]A on the QD surfaces (Fig. 2).

Meanwhile, FT-IR spectra provided additional evidence (Fig. 3). For example, the strong transmission peak at 1205 cm\(^{-1}\) corresponds to the asymmetric telescopic vibration \(\nu_{\text{a(C-O-C)}}\) from CP[5]A. The transmission peak at 1500 cm\(^{-1}\) (Fig. 3, curves a and b) is attributed to the bend vibration \(\delta(\text{Ar-H})\) of the benzene of CP[5]A. The strong transmission band between 3000 cm\(^{-1}\) and 3500 cm\(^{-1}\) is credited to the stretching vibration \(\nu(\text{Ar-H})\) of water (Fig. 3, curves a and b). However, different from the FT-IR peaks of free carbonyl groups, the transmission peak of the stretching vibration \(\nu(\text{C=O})\) of CP[5]A@QDs appears at a low wavenumber, owing to the interaction of the carbonyl groups of CP[5]A with the surface atoms of CdTe QDs.\(^{17}\) As shown in the spectrum b of Fig. 3, the transmission peak of the stretching vibration \(\nu(\text{C=O})\) of CP[5]A@QDs appeared at 1600 cm\(^{-1}\), overlapping with the transmission peak of the stretching vibration \(\nu(\text{C=C})\) of benzene. In addition, the inset UV-vis spectra b of Fig. 2 show that the absorption peak at 530 nm was red-shifted and became broader, which further indicated that...
CP[5]A was coated on the surfaces of QDs due to the size changes of QDs.15

QDs are known to serve as electron donors.1 When an electron-deficient guest, i.e., methyl viologen (MV) or bridged bis(MV),10,20 was added into an aqueous solution of CdTe QDs stabilized with 3-mercaptopropionic acid (MPA@QDs), the chemical stability and photophysical properties of MPA@CdTe QDs were severely influenced via electron transfers from MPA@QDs to bridged bis(MV). The zeta potentials of MPA@QDs indicated them to be very stable in aqueous solutions at room temperature (Table S1, ESI†). But, their stability was dramatically decreased upon the addition of even a trace amount of MV or bridged bis(MV), and MPA@QDs decomposed with continuous addition of MV or bridged bis(MV). However, CP[5]A@QDs showed remarkable chemical stability, and negligible influence was found upon the addition of a certain amount of MV or bridged bis(MV) owing to the successful capture of electron-deficient guest molecules by the surface bonded macrocyclic host, CP[5]As, and thus the inhibition of the electron transfer between QDs and electron-deficient guest molecules. With the continuous addition of excess bridged bis(MV), the stability of CP[5]A@QD decreased due to the saturation of host–guest complexation between QD surface-bound CP[5]As and electron-deficient guest molecules (Fig. S5, ESI†).

Besides the chemical stability, the photophysical properties of MPA@QDs, i.e., fluorescence, were also severely influenced by the addition of various viologens20–30 (MV and bridged bis(MV)). As shown in the fluorescence spectra (Fig. 4), the fluorescence intensity of MPA@QDs was dramatically decreased upon the addition of a small amount of MV or bridged bis(MV) (Fig. 4). However, the fluorescence intensity of CP[5]A@QDs was slightly influenced by the addition of MV or a small amount of bridged bis(MV). These observations were rationalized considering that CP[5]As could efficiently trap MV or bridged bis(MV) inside the cavities through host–guest binding interactions,8,56 and thus efficiently prevent the direct interaction or electron transfer from CdTe QDs to MV or bridged bis(MV).21 In addition, QD fluorescence was quenched by the addition of an excess of electron-deficient guest compounds after reaching the maximum loading capacity of QD-surface bonded CP[5]As (Fig. 4).

On the other hand, the monodisperse hybrid nanocomposite CP[5]A@QDs (Fig. 1a, S1 and S2, ESI†) were induced to form an aggregated supramolecular network upon the addition of bridged bis(MV) (Fig. 1b, S3 and S4, ESI†). Host–guest interactions between CP[5]As on different QDs and bridged bis(MV) provided the main driving force to induce the nanocomposites to form an aggregated 3D network structure, where bridged bis(MV) served as bridges to cross-link different CP[5]A@QDs.

In conclusion, CP[5]As were modified on the surfaces of QDs via a ligand-exchange method, paving a new way for the stabilization of nanocrystals with multi-carboxylated group functionalized organic compounds. The newly synthesized organic-inorganic nanocomposite was stable in aqueous media at room temperature, and showed potential as a candidate for the detection of herbicide, i.e., paraquat, based on its special photophysical properties. Meanwhile, the nanocomposite could form an aggregated supramolecular network upon the addition of bridged bis(MV) via supramolecular host–guest interactions. This hybrid material, combining the properties of QDs and pillararanes, is expected to serve as an efficient chemical sensor or detector for various analytes in the future.

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Notes and references


