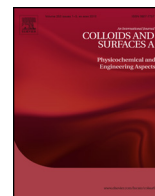




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Aggregation-free DNA nanocage/Quantum Dot complexes based on electrostatic adsorption



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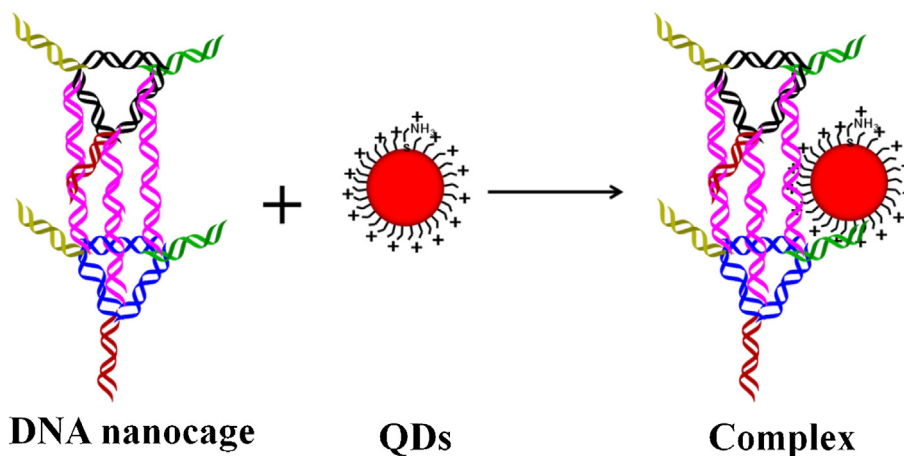
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HIGHLIGHTS

- DNA nanocage/Quantum Dot complexes are constructed using electrostatic adsorption.
- The complexes are in an aggregation-free state.
- The aggregation-free nature relates to the 3D rigid structure of the DNA nanocage.

GRAPHICAL ABSTRACT



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ABSTRACT

Fabrication of DNA/Quantum Dot (QD) complexes making use of electrostatic adsorption forces has advantages of the cost-efficiency and simplicity. To obtain aggregation-free complexes, high molecular weight polymers or the purposefully designed ligands are commonly employed as a bridge between DNA and QDs, which limits their applications in practice. In this work, DNA/QDs complexes were obtained using electrostatic adsorption between cysteamine stabilized CdTe QDs and self-assembled DNA nanocages. Zeta potential, dynamic light scattering and gel electrophoresis measurements demonstrated their aggregation-free state, different from the cases where single-stranded and double-stranded DNAs were used. The appearance of aggregation-free complexes in the case of DNA nanocages was ascribed to their 3D rigid structure. Förster resonance energy transfer (FRET) was demonstrated for the complexes of Cy3 labeled DNA nanocages and QDs, pointing out on the close proximity of these building blocks.

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1. Introduction

Owing to their molecular recognition properties and the nucleobase sequence controllability, DNAs are emerging as powerful

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and versatile building blocks for the construction of nanostructures [1,2]. Both two- and three-dimensional DNA nanostructures can be precisely designed [2–7]. An elegant strategy was developed to assemble DNA strands into well-defined DNA nanocage structures, with a high yield and stability [8–10]. Much attention has been focused on construction of DNA/ Quantum Dots (QDs) complexes [11–14]. Such complexes combine the unique optical properties of QDs with the molecular recognition ability of DNA, which has broad implications in the fields of material science [15–18] and biosensing [19–21]. The most important step in the construction of DNA/QDs complexes is the attachment of DNA to the QD surface. Depending on the surface characteristics of QDs and DNA, several attachment methods have been developed, including streptavidin–biotin linking methods [22,23], covalent bonding methods using –COOH, –NH₂ or –SH groups [24–26], and electrostatic adsorption methods [20,27,28]. DNA based nanostructures have a negative charge in solutions with neutral pH. In order to construct DNA/QDs complexes making use of electrostatic adsorption forces, QDs should be either positively charged by employing appropriate ligands at the synthesis stage, or a positively charged layer has to be applied onto QD surface post-preparatively. During the electrostatic adsorption process, the positive charge of the QDs will be (partially) neutralized by the negative charge of the DNA, which may adversely influence their colloidal stability [14]. To prevent QDs from aggregation, positively charged polymers were often employed as a bridge between QDs and DNA [20,28,29]. However, polymers have high molecular weight, leading to a large distance between DNA and QDs. Several groups used positively charged ligands on the QDs for the construction of DNA/QDs complexes [30,31]. Lee et al. designed positively charged QDs using DHLA-2,2'-(ethylenedioxy) bis(ethylamine) trifluoroacetate [30], while Yeh et al. developed a two-step ligand exchange process [32]. Such approaches require complicated ligand synthesis and design, which limits their applications in practice. Therefore, it is highly desirable to fabricate aggregation-free DNA/QDs complexes using electrostatic adsorption, while avoiding large molecular weight polymers and complicated ligand design.

In this work, DNA/QD complexes were obtained by using electrostatic adsorption between positively charged cysteamine stabilized CdTe QDs and self-assembled DNA nanocages. Zeta potential measurements, dynamic light scattering, gel electrophoresis, and optical spectroscopy were applied to confirm the aggregation-free nature of the DNA nanocage/QD complexes, which was different for the cases when single-stranded DNAs (ssDNA) and double stranded DNAs (dsDNA) were employed. Förster resonance energy transfer (FRET) was demonstrated for the complex of Cy3 labeled DNA nanocages and QDs, pointing out on the close proximity of these building blocks.

2. Materials and methods

2.1. Materials

All chemicals including cadmium acetate di-hydrate, tellurium powder, sodium borohydride, cysteamine hydrochloride, acetic acid, *N,N,N'*-tetramethylethylenediamine, glycerol, and acrylamide were purchased from Sigma–Aldrich. *N,N'*-Methylenebis (acrylamide), urea, boric acid, formamide, magnesium chloride, EDTA, tris (hydroxymethyl) aminomethane (Tris), (3-aminopropyl) trimethoxysilane, ammonium persulfate were purchased from J&K. Agarose was purchased from Vivantis. HydraGreen™ Safe DNA Dye was purchased from ACTGene. DNA sequences were purchased from IDT. TAMg buffer (1×) is consisted of 45 mM Tris, 7.6 mM MgCl₂, with pH adjusted to 7.8 using glacial acid. PBS Buffer (1×) is consisted of 137 mM NaCl, 2.7 mM KCl, 10 mM Na₂HPO₄, 2 mM

KH₂PO₄, with pH adjusted to 7.4 using HCl. TA buffer (1×) is consisted of 40 mM Tris with pH adjusted to pH 8.0 using Glacial acetic acid. All other chemicals were used as received. The DNA sequences and the related information are presented in Table S1.

2.2. Assembly of DNA nanocages and Cy3 labeled DNA nanocages

The methods to assemble DNA nanocages and Cy3 labeled DNA nanocages together with their characterization data are presented in SI.

2.3. Synthesis of cysteamine stabilized CdTe QDs

Cysteamine stabilized CdTe QDs were prepared according to the previous report [33]. The concentration of QDs was determined according to Ref. [34]. The emission quantum yield of QDs was in the range of 5–18%, estimated using Rhodamine 6G in ethanol as a standard.

2.4. Assembly of DNA/QDs complexes

Before use, cysteamine stabilized QDs were precipitated by 2-propanol, and re-dissolved in a DI-water to achieve the concentration of 2.5 μM. Typically, 5.4×10^{-11} mol of ssDNA or dsDNA was mixed with 1.8×10^{-11} mol of QDs, respectively. The ratio of ssDNA and dsDNA to QDs was 3:1. For assembly of DNA nanocage/QD complexes, 1.8×10^{-11} mol of DNA nanocages was mixed with 1.8×10^{-11} mol of QDs. The ratio of DNA nanocages to QDs was 1:1. DI water was used to adjust the volume into 80 μL. All the measurements were conducted after incubation of solutions for 30 min under room temperature.

2.5. Characterization

Absorption and photoluminescence (PL) spectra of samples were measured directly on Varian Cary 50 UV–vis spectrophotometer and Cary Eclipse fluorescence spectrometer, respectively. The hydrodynamic diameter (number-weighted mean diameter) and zeta potentials of QDs and DNA/QDs complexes were measured by dynamic light scattering (DLS) on a Zeta Sizer Nano. Before measurements, the ssDNA/QDs, dsDNA/QDs and DNA nanocage/QD complexes were mixed with 1 mL of PBS buffer (1×). The final concentrations of QDs, ssDNA, dsDNA and DNA nanocages were 18 nM, 54 nM, 54 nM and 18 nM, respectively. UV/vis measurements of DNA were conducted on NanoDrop spectrophotometer (ND-1000). Gel electrophoresis experiments regarding native or denaturing gel were carried out on an acrylamide 20 × 20 cm Maxi Vertical electrophoresis apparatus (MV-20DSYS), in TAMg buffer (1×). Agarose gel electrophoresis was conducted on Midi plus-2Horizontal Electrophoresis System (ME15-7-10-15), in TA buffer (1×). Gel scanning was performed by Fujifilm ImageQuant LAS 4000.

3. Results and discussion

3.1. Construction of DNA nanocage/QD complexes

Cysteamine stabilized CdTe QDs synthesized at a neutral pH show a positive charge (zeta-potential: +32.6 mV), which makes them suitable for fabrication of DNA/QDs complexes. They possess a continuous broad absorption stretching from 400 to 600 nm and a PL emission maximum at 625 nm.

Scheme 1 illustrates 3 different types of DNA/QDs complexes created by electrostatic adsorption between cysteamine stabilized QDs and DNA nanocages, ssDNA and dsDNA. Zeta potential changed from +32.6 mV for the bare QDs to –32.9 mV for the DNA

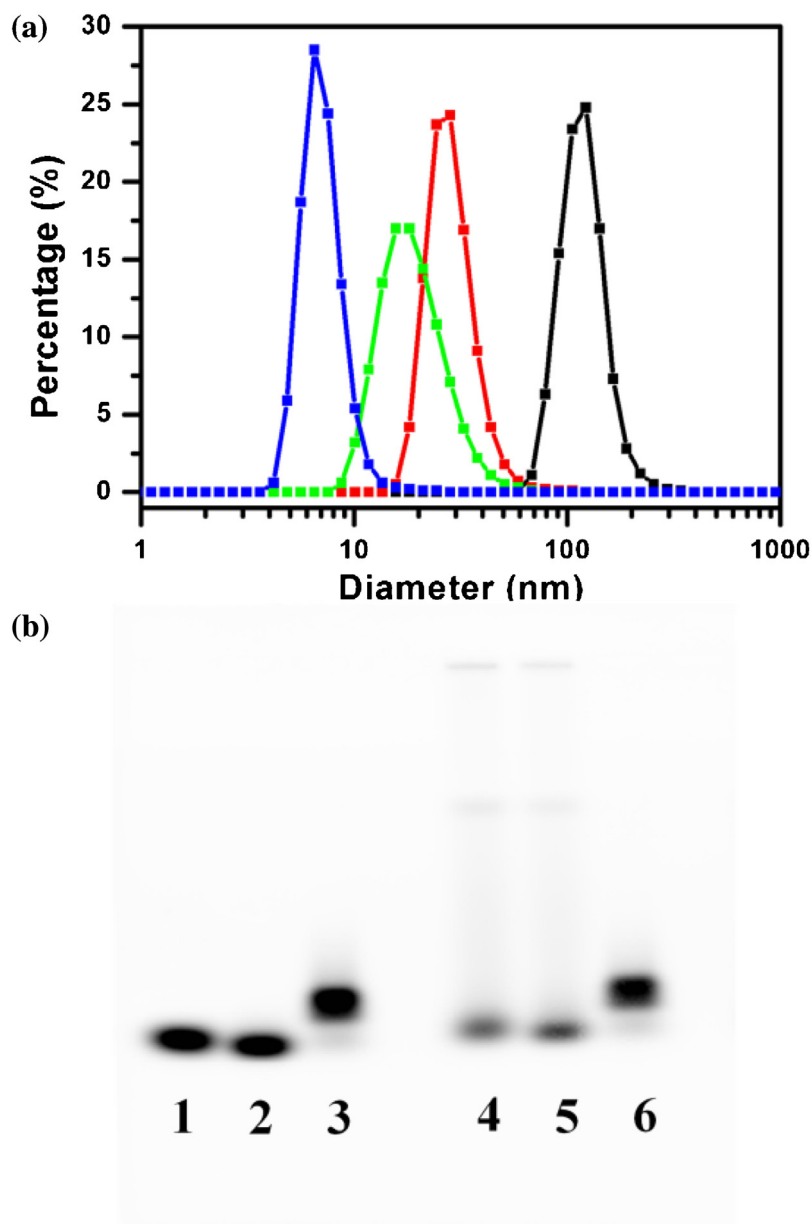


Fig. 1. (a) Size distribution of bare QDs (blue line), ssDNA/QDs complex (black line), dsDNA/QDs complex (red line) and DNA nanocage/QD complex (green line). (b) 3% agarose gel electrophoresis of ssDNA (line 1), dsDNA (line 2), DNA nanocages (line 3), ssDNA/QDs complex (line 4), dsDNA/QDs complex (line 5), and DNA nanocage/QD complex (line 6). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

nanocage/QD complex. For the ssDNA and dsDNA, zeta potential changed to -37.8 and -39.3 mV, respectively.

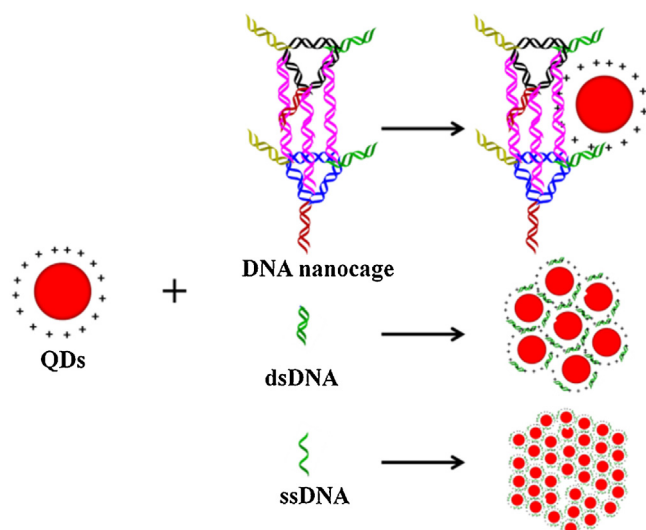
3.2. Dynamic light scattering

The hydrodynamic diameter of DNA/QDs complexes is a critical parameter allowing us to estimate their aggregation degree in solution. A common standard for the aggregation-free bare QDs is that their hydrodynamic diameter should be less than double of the TEM-estimated core size [35,36]. As shown in Fig. 1a, the hydrodynamic diameter of bare QDs and the DNA nanocage/QD complex is 6.5 and 16.9 nm, respectively. Estimated from the DLS, the hydrodynamic diameter of the bare DNA nanocages is about 7.6 nm [10]. The smallest DNA nanocage/QDs complex is one DNA nanocage coupled with one QD and the hydrodynamic diameter of such a

complex can be estimated as ~ 14 nm. From the experimental data of Fig. 1a, we conclude that the DNA nanocage/QD complex forms preferably in such a monomeric state. In comparison, the hydrodynamic diameter of ssDNA/QD and dsDNA/QDs complexes were estimated as 122 nm and 28 nm, respectively, being much larger. Even so the aggregation of the dsDNA/QD complex appears to be less severe than for ssDNA/QD complex, both of them are strongly affected by agglomeration.

3.3. Agarose gel electrophoresis

Aggregation states of DNA/QD complexes were further studied by the agarose gel electrophoresis. As shown in Fig. 1b, two DNA bands with lower mobility and reduced DNA band intensity of free ssDNA or dsDNA were observed after adding the QD to the ssDNA or



Scheme 1. Schematic illustration of 3 different kinds of DNA/QDs complexes, depending on the structure of the DNA building blocks used.

dsDNA (lane 4 and 5), as compared with only ssDNA or dsDNA (lane 1 and 2). This indicated that the aggregation took place and some higher molecular weight products/complexes were formed. In contrast, a slightly slower mobility DNA band is observed and no high molecular weight product is formed after adding QDs to the self-assembled DNA nanocages (lane 6) as compared to the free DNA nanocages (lane 3). These results revealed an absence of aggregation in the latter case, being consistent with observations related to hydrodynamic diameters.

The difference of the aggregation degree among DNA nanocage/QD, ssDNA/QD and dsDNA/QD complexes most probably originates from the different rigidity of these three DNA structures. ssDNA is flexible and dsDNA is more rigid, while the DNA nanocages have most rigid 3D structure. The formation of aggregation-free DNA nanocage/QD complexes is thus attributed to the 3D rigid structure of the DNA nanocages, which different to dsDNA and in particular to ssDNA provides a strong steric repulsion preventing the complexes formed from aggregation (see Scheme 1 for illustration).

3.4. Optical spectroscopy and FRET study

FRET is a classical tool to study molecular conformational changes and intermolecular distances between chromophores [37–40]. A typical FRET system consists of a donor and an acceptor. The energy of a donor, initially in its electronic excited state, transfers to an acceptor through nonradiative dipole–dipole coupling, when the distance between donor and acceptor is small enough, as determined by the Förster radius. In order to confirm the close proximity of chromophores within the DNA nanocage/QD complex, FRET process between Cy3 dye (donor) labeled DNA nanocages and QDs (acceptor) was studied. Each DNA nanocage was labeled by three Cy3 dye molecules, and after mixing Cy3 labeled DNA nanocages with QDs, Cy3 DNA nanocage/QD complexes have been constructed. Owing to the continuous and broad absorption of QDs (from 400 to 600 nm), there is an overlap between the absorption of QDs and the emission of Cy3 dye (maximum at 564 nm). Thus, a FRET pair is formed with a Cy3 as a donor and QDs as acceptor. The absorption spectra of the equal concentrations of QDs, Cy3 DNA nanocages and of Cy3 DNA nanocage/QD complex are shown in Fig. 2a. For wavelengths above 580 nm, the absorption of Cy3 is negligible, whereas the absorption spectrum of QDs is almost the same as that of the Cy3 DNA nanocage/QD complex. This demon-

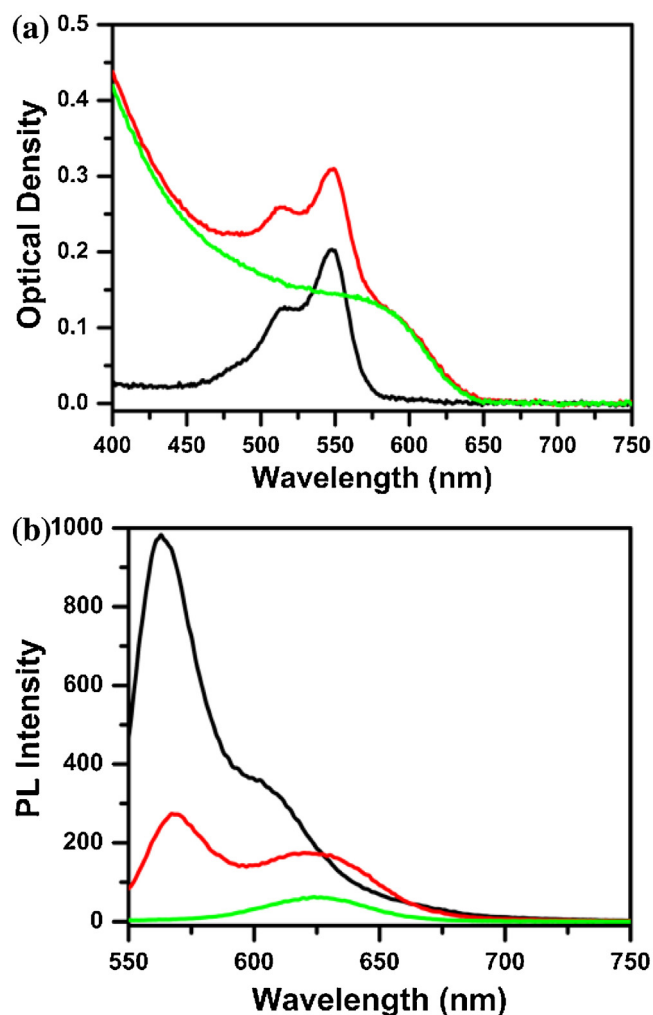


Fig. 2. (a) Absorption and (b) emission spectra of QDs (green line), Cy3 labeled DNA nanocages (black line) and Cy3 DNA nanocage/QD complex (red line). All samples were excited at 540 nm, the optimal excitation wavelength for Cy3. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

strates that the band gap of QDs is not affected during the formation of DNA nanocages/QDs complex. The occurrence of FRET is obvious in the PL spectra excited at the wavelength of 540 nm, as shown in Fig. 2b. Upon formation of the Cy3 DNA nanocage/QD complex, the PL intensity of Cy3 on DNA nanocages is quenched by 3.6-fold and the PL intensity of QDs is almost doubled. Noticing that, there is a slight red shift on the PL spectrum after forming Cy3 DNA nanocage/QD complex, which may be caused by the change of zeta potentials. This demonstrates the close proximity between the DNA nanocage and the QDs, and further confirms the formation of the DNA nanocage/QD complex.

The FRET efficiency can be calculated based on the absorption and emission spectra. However, in our case there is an overlap between the emission spectra of Cy3 and QDs, which is hard to separate from. In order to calculate the FRET efficiency, the spectra of QDs and Cy3 in DNA cage have been fitted to Gaussian functions (as shown in Fig. S5). Above Gaussians are further used to fit PL spectrum of Cy3 DNA nanocage/QD complex. After adding a red shift parameter (20 meV), a good fitting to the PL spectrum of Cy3 DNA nanocage/QD complex was obtained, as shown in Fig. 3. Fitting formulae

$$F_{\text{complex}}(E) = 0.269 \times F_{\text{Cy3}}(E) + 1.886 \times F_{\text{QDs}}(E) \quad (1)$$

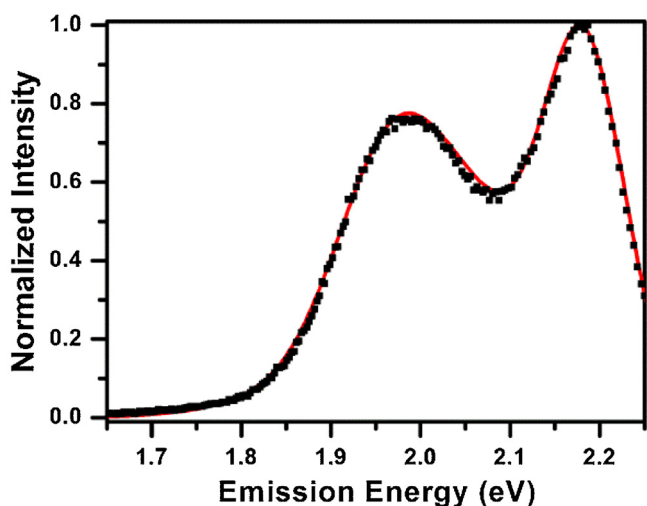


Fig. 3. PL spectrum of the Cy3 DNA nanocage/QD complex (dotted line) estimated by a fitting function (1), solid red line. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

can be used, where $F_{\text{complex}}(E)$, $F_{\text{Cy3}}(E)$ and $F_{\text{QDs}}(E)$ are the best fitting functions for the PL spectra of the Cy3 DNA nanocage/QD complex, Cy3 DNA nanocage and QDs, respectively. The FRET efficiency can be calculated as $E = 1 - (\Phi_{D-A}/\Phi_D)$, where Φ_{D-A} and Φ_D are the quantum efficiencies of the Cy3 DNA nanocage/QD complex and the Cy3 DNA nanocage [41]. In our case, it can be rewritten as $E = 1 - 0.269 \times A_D/A_{D-A}$, where A_{D-A} and A_D are the absorption of Cy3 DNA nanocage/QD complex and Cy3 DNA nanocage at the excitation wavelength (540 nm). Applying above equation to the absorption spectra, E equals to 84%.

4. Conclusions

In summary, aggregation-free DNA nanocage/QD complexes have been constructed using electrostatic adsorption between positively charged, cysteamine stabilized CdTe QDs and negatively charged, self-assembled DNA nanocages, without the need for molecular binders such as polymers or specially designed QD ligands. The formation of DNA nanocage/QD complexes was confirmed by zeta potential measurements, DLS and gel electrophoresis, which also points out that the complexes obtained is in an individual monomeric state. ssDNAs and dsDNAs were also able to form complexes with QDs, but with a high degree of aggregation, which is related to the different rigidity of these three DNA structures. The occurrence of FRET, with a efficiency of 84%, in a system of Cy3-labeled DNA nanocage/QD complexes further confirms the close proximity between the DNA and QDs. Stable, aggregation-free DNA nanocage/QD complexes presented here may found applications in biosensing.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2016.02.002>.

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