



Design of pyridyl-modified amphiphilic polymeric ligands: Towards better passivation of water-soluble colloidal quantum dots for improved optical performance



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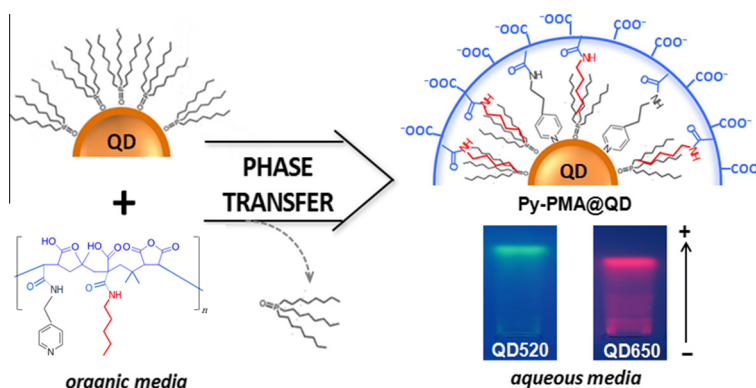
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HIGHLIGHTS

- Colloidal quantum dots in aqueous medium by means of pyridyl-modified amphiphilic polymeric ligands.
- Combination of two different anchoring groups in the polymer for its stable interaction with the quantum dot surface.
- The photoluminescence quantum yield of the quantum dots is preserved after transferring to aqueous phase.
- Good colloidal stability under relevant biological conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: An effective surface passivation is crucial to obtain quantum dots (QDs) with good photoluminescence response. Whereas the encapsulation of QDs inside amphiphilic polymers provides colloidal stability, a decrease in the quantum yield (QY) is observed. Pyridyl motifs are known to bind strongly to the ZnS on core/shell QD and increase the structure rigidity. Hence, the incorporation of pyridyl groups into the polymer could make it more compact in order to improve the optical behavior of the QDs.

Experiments: Pyridyl-modified amphiphilic polymeric ligands were synthesized based on a poly(isobutylene-*alt*-maleic anhydride) backbone with pyridyl and alkyl end-groups as anchoring groups. The proportion of both ligands was optimized. The resulting QDs were characterized using complementary techniques such as absorption spectroscopy, static and time-resolved photoluminescence spectroscopy, transmission electron microscopy, and dynamic light scattering.

Findings: Coating with the designed polymer maintains the high QY of the QDs after being transferred to water and provides them colloidal stability under relevant biological conditions (*i.e.* wide range of pH and ionic strength, biological buffers and stability over time). The significant improvements of such ligand may be attributed to the synergistic effect of two anchoring groups (pyridyl and alkyl groups) which establish different types of interaction with the QD.

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1. Introduction

The surface chemistry of water-soluble colloidal quantum dots (QDs) remains still a topic of continuous investigation [1,2]. The surface chemistry should warrant for colloidal stability in aqueous solution, while maintaining a high photoluminescence quantum yield (PL QY) [3–6]. Both properties may be in conflict. Ligands used for water-solubilization may create surface defects. The presence of surface defects tends to deteriorate the optical properties of QDs, as they act as temporary traps for the electrons, holes, or excitons, introducing effective nonradiative decay pathways, and thus, reducing the QY [7–10]. Thus, an effective passivation of the surface is crucial to obtain QDs with a good PL behavior regardless of the surrounding medium. In contrast with the conventional picture wherein traps are viewed as stable electronic states that can be filled or emptied, recent results point to a new scenario, in which surface traps are dynamic, *i.e.* they can be created or destroyed [11]. Therefore, the passivation strategy should not only remove the existing traps, which are usually achieved by the formation of an inorganic shell around the core in the organic phase, but also avoid the creation of new ones when the nanoparticles are transferred to water. This latter requirement has not been taken into account until recently, and it is highly important in order to preserve the QY in aqueous medium. The first type of passivation by means of a shell of a larger bandgap semiconductor is known since long ago. Core-shell structures (e.g. CdS/ZnS, CdSe/ZnS) and even core-shell-shell QDs (e.g. CdSe/CdS/ZnS, CdTe/CdS/ZnS) are nowadays commonly used to reduce the probability of light-generated charge carriers to reach the surface and help to confine them to the core. This shell also helps to block the leaching out of potentially toxic metal ions from the core materials such as CdS and CdSe [12–14]. However, this passivation strategy does not avoid the large reduction in PL QY which typically is observed when QDs are transferred from organic solvents to aqueous media [15–17], e.g. a loss of 40–60% in case of mercaptocarboxylic acid functionalization [18]. Other approaches to manipulate the PL QY by playing with the surface nature of the QDs have also been explored, such as passivation by judicious selection of capping ligands [19–21], by means of light (“photoactivation”) [22,23], photoinduced annealing [24,25], thermal annealing [26], or by using photo-redox chemistry [27].

Concerning the passivation by using capping ligands, encapsulation of the native hydrophobic QDs inside amphiphilic polymers is a versatile and effective method to provide water-solubility and colloidal stability [28–31], with several advantages over ligand-exchange methods, in particular concerning colloidal stability [17,32]. Still, the polymer shell is not tight, but allows for diffusion of small molecules. This can be seen by the fact that small molecules such as H^+ and Cl^- can reach ion-sensitive fluorophores [33,34] that are located inside the polymer shell [35]. Diffusion of oxygen to the QD surface will result in oxidation of the QDs and the creation of trap states. In fact, most of the amphiphilic polymers reported so far lead to a considerable decrease in the PL QY of the resulting polymer-coated water-soluble QDs. Some authors have reported ~25–35% loss of the QY upon the water-solubilizing process [36,37]. Consequently, the design of new amphiphilic polymers able to overcome this critical drawback is demanded.

Considering that most of the group II–VI based QD core-shell structures have ZnS as outer shell, the search of chemical groups able to coordinate Zn in the QD surface, and thus provide passivation, is a first step in designing new surface chemistries for those QDs. In this context, pyridine has the potential to replace the original hydrophobic ligands on the QD surfaces. Pyridine has already been extensively utilized to fabricate QD-based solar cells [38–40]. In comparison to the common used thiolated-ligands which have issues of long-term stability owing to their susceptibility to

photooxidation in air [41], pyridyl-ligands are not sensitive to degradation by air and light. Skaff and Emrick [42] reported the use of para-substituted pyridines for QD passivation by synthesizing poly(ethylene glycol) (PEG) with attached pyridine monomers, in which the pyridine and PEG units worked as surface anchoring and water solubilizing groups, respectively. Surprisingly, as far as our knowledge, this interesting fact has been left aside and rarely exploited for further polymer modifications [43], pointing out clearly the necessity for a deeper exploration.

Here, the potential of the pyridyl as anchoring groups in a polymer is examined in greater depth. We present the design and synthesis of pyridyl-modified amphiphilic polymeric ligands (referred to as Py-PMA), which provides a simple and effective approach to obtain water-soluble polymer-coated QDs with a high PL QY and good colloidal stability over a broad range of conditions. The polymeric ligand design relies on the introduction of a controlled proportion of pyridyl and alkyl anchoring groups onto a poly(isobutylene-*alt*-maleic anhydride) backbone *via* a one-step nucleophilic addition reaction. The polymer modification is optimized in terms of maximum QY, and the characterization of the resulting polymer-coated QDs is reported. The relevance of the work relies mainly on studying the ability of the pyridyl groups in improving the optical performance of QDs. Moreover, the straightforward one-step synthesis of target polymers grafted with different anchoring groups would be attractive for other scientists to pursue further studies on design and synthesis of similar surface ligands.

2. Materials and methods

The synthesis of the amphiphilic polymeric ligands was carried out according to previously published protocols [30,48], but with significant modifications by using different ligands in order to get specific functionalities. They consisted of a linear backbone of poly(isobutylene-*alt*-maleic anhydride) (PMA, average molecular weight $M_w \sim 6000$ g/mol) with pyridyl and alkyl end-groups as anchoring groups. The proportion of these two types of side chains was modified to synthesize a set of different polymers (Fig. 1). Two-sized hydrophobic CdSe/ZnS core/shell QDs (with core sizes of 2.9 nm and 6.2 nm) were synthesized following reported protocols (see Supporting Information). The QDs were then overcoated with the different pyridyl-modified amphiphilic polymers obtaining water-soluble Py-PMA@QDs. Details of the polymer synthesis, polymer coating process, and the purification procedure are available in the Supporting Information.

UV/Vis absorption measurements of the Py-PMA@QDs samples in water were carried out with an Agilent Technologies 8453 UV/Vis spectrometer. Photoluminescence (PL) measurements were performed on a Fluorolog-3 (model FL3-22, Horiba Jobin Yvon) fluorescence spectrometer. For the PL lifetime measurements, a Fluorolog-TCSPC (Horiba Jobin Yvon) spectrometer was used. TEM pictures of QDs were taken on a JEOL JEM-1400PLUS. FTIR were recorded with a Tensor 27 FT-MIR spectrophotometer equipped with a Hyperion 2000 microscope, using KBr pellets prepared from the samples. A Malvern Zetasizer, equipped with a 10 mW He–Ne laser operating at a wavelength of 633 nm, was used to measure the hydrodynamic diameter d_h (with dynamic light scattering, DLS) and the zeta-potential (with laser Doppler anemometry, LDA).

3. Results and discussion

3.1. Design and synthesis of pyridyl-modified amphiphilic polymers (Py-PMA)

There were two important design criteria for the pyridyl-modified polymers: (1) to enhance the PL QY by means of an

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