Enhanced Photoluminescence from Micellar Assemblies of Cadmium Sulfide Quantum Dots and Gold Nanoparticles

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Supporting Information

ABSTRACT: We report the preparation and characterization of well-defined hierarchically structured colloidal assemblies, consisting of a block copolymer micelle with a single photoluminescent cadmium sulfide (CdS) quantum dot (QD) in the core and various numbers of gold nanoparticles (GNPs, between 0.001 and 0.077 GNP per micelle) chemically bonded to thiol groups at the terminus of the micelle coronal chains. These assemblies were prepared from tetrablock copolymer chains, poly(acrylic acid)-b-polystyrene-TTC-polystyrene-b-poly(acrylic acid) (PAA-b-PS-TTC-PS-b-PAA), where TTC represents a single trithiocarbonate group, synthesized using reversible addition−fragmentation chain transfer polymerization. The block copolymer chains were first self-assembled in 1,4-dioxane by adding cadmium acetate to form flower-like micelles, followed by templated synthesis of CdS QDs in the micelle cores. Then, the TTC groups in the micelle coronae were reductively transformed into thiol groups, which bonded to added GNPs. In the final structures, each GNP was anchored at a distance of a single solubilized PS block (∼20 nm) away from a CdS QD. This precise spacing between QDs and GNPs prevented any quenching of QD photoluminescence (PL) by the colloidal metal and instead led to an apparent enhancement of QD PL emission relative to QD emission from micelles without GNPs. The observed enhancement increased as the number of GNPs per micelle increased, with a maximum observed emission amplification (EA) of ∼8 times the PL intensity in the absence of GNPs. The EA was also found to increase as the excitation wavelength increased toward the spectral region of the surface plasmon resonance of the GNPs. Lifetime measurements revealed no significant difference between QD emission lifetimes in the absence and presence of GNPs. These results suggest a mechanism of PL enhancement via an excitation antenna effect associated with proximal GNP surface plasmons.

INTRODUCTION

A key goal in nanomaterial research is the incorporation of multiple functionalities within the same structure by the integration and controlled spatial organization of different nanoscale materials. Metal−semiconductor nanostructures are hybrid structures that have attracted increasing attention for many applications such as functional optoelectronic devices,¹ sensors,²,³ imaging probes,⁴,⁵ cancer biomarkers,⁶ and photocatalysts.⁷ Examples of such materials include nanostructured semiconductors and metals incorporated into both thin films⁸,⁹ or composite colloidal particles.²,⁴,⁵,¹⁰−¹⁶ Because of the strong distance dependence of metal−semiconductor interactions, controlling the spatial positioning of metal and semiconductor components within these materials is a critical challenge, which has been addressed using a variety of spacer materials, including DNA,¹³,¹⁷ silica,¹²,¹⁴ polypeptides,¹⁸ and synthetic polymers.²,¹⁹ Because of their unique microphase separation properties both in selective solvents and in bulk films, block copolymers have also been recognized as important materials for controlling the spatial positioning of nanostructures, including metal and semiconductor nanoparticles (NPs).²⁰,²¹ For example, Buriak et al.²⁰ prepared semiconductor surfaces with precise positioning of metallic nanostructures using the chemical reactivity of metal complexes coordinated within diblock copolymers toward semiconductor surfaces. Basu et al.²¹ obtained thin films with hybrid arrays containing semiconductor and metallic NPs using block copolymer templates. The templates offered precise location control of embedded NPs, necessary for varying their optical properties by tuning the exciton-plasmon coupling between the semiconductor and metallic components. Lee et al.²² prepared a system containing nanostructures of gold and CdS NPs embedded in block copolymer micelles, although in that case the spacing between gold and CdS NPs was not precisely controlled and no spectroscopic characterization was presented.

Metallic NPs exhibit a surface plasmon resonance (SPR) due to coherent oscillations of the surface conduction electrons when excited by specific electromagnetic radiation wavelengths.²³ In noble metals, like gold or silver, the SPR presents a strong absorption and scattering cross-section that is sensitive to the
local environment, surrounding solvent, size, shape, and chemical compositions of the nanostructures. \(^{24}\) Metallic NPs, especially gold and silver, have attracted growing interest over the past decade due to their unique optical and electronic properties.\(^{25,26}\) Semiconductor NPs, termed quantum dots (QD), are also intensely studied nanomaterials, due in part to their stable and tunable photoluminescence (PL) emission, which depends on size-dependent electron confinement effects.\(^{27}\) When fluorophores or QDs are in close proximity to metal NPs, QD-metal interactions can result in either enhancement\(^{8\text{-}11,28,29}\) or quenching\(^{13,17,18,30}\) of PL emission. Very short distances (<5 nm) between QDs and metal NPs give rise to PL quenching,\(^{23}\) whereas longer separations (~10–20 nm) give rise to distant-dependent PL enhancement.\(^{31}\) Although the exact conditions under which PL enhancement or quenching will occur in metal-semiconductor nanostructures and the mechanisms for these processes are still under debate, the SPR properties of the metal NPs are believed to be involved in many cases.\(^{8\text{-}11}\)

In this article, we demonstrate the block copolymer-mediated formation of colloidal assemblies of cadmium sulfide (CdS) QDs and gold nanoparticles (GNPs) in which QD-GNP separation distances are precisely defined by the dimension of a single solubilized polystyrene (PS) chain. We obtain these unprecedented structures by the synthesis of a symmetric tetrablock copolymer with two PS inner blocks and two poly(acrylic acid) (PAA) outer blocks, connected to a central trithiocarbonate (TTC) unit by sequential RAFT polymerization (Scheme 1). By adding cadmium acetate to the copolymer chain in organic solvent, flower-like micelles with a cadmium acrylate (PACd) core and a PS shell were formed, followed by templated conversion of Cd\(^{2+}\) ions to a single CdS QD in each micelle core (Scheme 2). Finally, the TTC groups located in the outer shell of the flower-like micelles are reacted with hexylamine to bisect each PS “petal” into two PS chains, each with a terminal SH group, to which various quantities of GNPs were chemically bonded. We show that the resulting assemblies exhibit enhanced PL relative to the QD micelles (QDMs) without bonded GNPs; an SPR-mediated mechanism involving localization of excitation light near the QDs is proposed based on the enhancement data. The resulting GNP-induced enhancement and the precise control of QD-GNP separation distance provided by the present colloidal assemblies provide a proof-of-concept for applications of emission-enhanced materials in functional optoelectronic devices, imaging probes, biomarkers, and sensors.

**EXPERIMENTAL SECTION**

**Materials.** Carbon disulfide, chloroform, and acetone obtained from Riedel-de-Haen; tetrabutylammonium hydrogen sulfate and diethyl ether obtained from Fluka; N,N-dimethylformamide (DMF, PA), tetrahydrofuran (THF, 99%), toluene (99.7%), 1,4-dioxane (99.9%), cadmium acetate dihydrate (CdAc\(_2\), 98%), tetraoctylammoniumbromide, 1-dodecanethiol (>98%), sodium borohydride (NaBH\(_4\), >98.5%), hexylamine (99%), and gold(III) chloride trihydrate (HAuCl\(_4\)•3H\(_2\)O, >99.9% metal basis) obtained from Sigma-Aldrich; trioxane (99%), sodium sulfide (Na\(_2\)S, 90%), and 4,4′-azobis(4-cyanovaleric acid) (ACVA, >98%) obtained from Acros; and methanol, ethanol, and other chemicals obtained from several sources were used without further purification. Acrylic acid (AA) and styrene (Sigma-Aldrich) were distilled under vacuum prior to use. Deionized water from a Millipore system Milli-Q ≥18 MΩcm was used for the preparation of solutions.

**Scheme 1. S,S′-bis(α,α′-dimethyl-α″-acetic acid) trithiocarbonate Chain Transfer Agent (CTA) Was Synthesized to Obtain the Poly(acrylic acid)-trithiocarbonate-poly(acrylic acid) (PAA-TTC-PAA) Chains by RAFT Polymerization**

**Scheme 2. Schematic Representation of the CdS Quantum-Dot Micelle (QDM) Structure**

"PAA-TTC-PAA chains were used in a RAFT polymerization of styrene to form the internal PS blocks of copolymer, giving poly(acrylic acid)-poly(styrene)-trithiocarbonate-poly(styrene)-poly(acrylic acid) (PAA-b-PS-TTC-PS-b-PAA)."
Synthesis of the RAFT Chain-Transfer Agent (CTA) S,S'-bis(α,α'-dimethyl-α'-acetic acid) Trithiocarbonate. In a 500 mL round-bottomed flask with 60 mL of hexane cooled under a gentle flow of argon, we added carbon disulfide (13.77 g, 0.18 mol), chloroform (58.81 g, 0.45 mol), acetone (26.26 g, 0.45 mol), and tetrabutylammonium hydrogen sulfate (1.21 g, 3.6 mmol). To this mixture, we added a 50 wt % sodium hydroxide aqueous solution (100.99 g, 1.26 mol) dropwise over ~90 min. The temperature was kept at ca. 15 °C overnight; afterward, we added 600 mL of water to dissolve the solid and 60 mL of concentrated HCl (37%) to acidify the aqueous layer under an argon atmosphere. The precipitate was filtered, rinsed thoroughly with water, and dried under vacuum to yield 14.14 g of brown-colored solid. The solid was purified by repeated recrystallizations in acetone/hexane mixture (4/1 v/v) to obtain a yellow crystalline solid.

The final S,S'-bis(α,α'-dimethyl-α'-acetic acid) trithiocarbonate solid was characterized by 1H NMR (in DMSO-d6 and CDCl3) and 13C NMR (in CDCl3), recorded on a Bruker Avance II 400 MHz (UltraShield Magnet) spectrometer at 300 K. The resulting peaks were in agreement with those reported by Lai et al. and Gottlieb et al. 1H NMR (DMSO-d6) δ: 1.59 (s, 12H), 12.91 (s, 2H). 1H NMR (CDCl3) δ: 1.69 (s). 13C NMR (CDCl3) δ: 25.31, 55.96, 180.12, 217.38.

Synthesis of the PAA-TTC-PAA Macro-CTA by RAFT Polymerization. AA (previously distilled under vacuum) was polymerized by the RAFT process using S,S'-bis(α,α'-dimethyl-α'-acetic acid) trithiocarbonate as chain transfer agent (CTA) and ACVA initiator in a mixture of water and ethanol (H2O/EtOH 75/25 v/v) at 70 °C. A mixture of AA (9.0 g, 125 mmol), CTA (0.88 g, 3.1 mmol), ACVA (0.029 g, 0.10 mmol), EtOH (6.5 g), H2O (24.8 g, deionized water), and trioxane (0.93 g, 10.3 mmol, internal reference for 1H NMR determination of the monomer conversion) was introduced in a Schlenk tube equipped with a magnetic stirrer. The mixture was deoxygenated by four freeze–pump–thaw cycles and then heated in an oil bath at 70 °C under an argon atmosphere. The polymerization was stopped after 90 min by cooling the Schlenk tube under liquid nitrogen. A final conversion of 97% was determined by 1H NMR using the trioxane protons as an internal reference. Typically, 500 μL of deuterated chloroform, CDCl3, containing tetramethylsilane (TMS), was added to 120 μL of each sample.

The PAA homopolymer was precipitated into ethyl acetate and diethyl ether to remove the unreacted monomers, filtered, and dried under vacuum. The complete elimination of residual monomers was confirmed by 1H NMR. The molecular weight of PAA homopolymer was obtained with MALDI-TOF MS working in linear mode using a Voyager-DE PRO workstation. The matrix used was 2-(4-hydroxyphenyloxazol) benzoic acid (HABA), and it was calibrated with PS (Mn = 2000). The number-average molecular weight obtained for PAA, Mn = 2975 g mol⁻¹ (Mn/Mw = 1.02), is close to the value predicted by mass balance from the synthesis conditions (Mn = 3080 g mol⁻¹). The mean degree of polymerization is calculated as <2n> = 37, and according to the symmetry of the polymer structure, the blocks have an average number of AA units of n = 18.5 (Scheme 1).

Synthesis of the Poly(acrylic acid)-b-poly(styrene)-TTCPoly(styrene)-b-poly(acrylic acid) Block Copolymer (PAA-b-PS-TTC-PS-b-PAA) by RAFT Polymerization. The polymerization of styrene was carried out using the PAA homopolymer previously obtained as a RAFT macro-CTA (Scheme 1): 1.60 g of PAA homopolymer (macro-CTA, 0.54 mmol), 10.1 g of DMF, and 14.0 g of styrene (134 mmol) were introduced in a Schlenk tube equipped with a magnetic stirrer. The mixture was deoxygenated by four freeze–pump–thaw cycles and kept under an argon atmosphere. The Schlenk tube was immersed in an oil bath at 110 °C for 32.5 h. The reaction was stopped by cooling the Schlenk tube in liquid nitrogen. A monomer conversion of 46% was obtained by 1H NMR using the following procedure: the polymerization mixture was diluted in acetone-d6 (typically 100 μL of mixture in 450 μL of acetone-d6), and the ratios of the NMR integrated peaks of the vinyl protons of styrene and the integrated peak of the protons from the methyl group of DMF (used as an internal reference) were compared before and after the polymerization. The 46% monomer conversion corresponds to a degree of polymerization of <2n> = 115, or m = 57.5 (Scheme 1), corresponding to a total molecular weight of Mn = 14 900 g/mol. The final mixture was precipitated in methanol; then, the copolymer was dissolved in THF and reprecipitated three more times in methanol and dried under vacuum for approximately 1 week to guarantee the full elimination of DMF.

To confirm the molecular weight of the copolymer, some of the copolymer was methylated by adding 2.0 M (trimethylsilyl)-diazo methane in hexane solution dropwise to a solution of the copolymer in THF (100 mg/13 mL THF) at room temperature. The addition of the methylation agent was continued until the solution became yellow, after which an excess of methylation agent was further added. The reaction mixture was kept at room temperature for another 3 h before the recovered polymer was injected in the GPC (without purification). To prove the symmetry of the copolymer (see below), we performed aminolysis of 100 mg of the copolymer by dissolving the sample in 13 mL of THF and adding a 50-fold excess of hexylamine. The reaction was left shaking overnight at room temperature and injected in the GPC.

Preparation of CdS Quantum Dot-Containing Block Copolymer Micelles (QDMs). The copolymer PAA-b-PS-TTC-PS-b-PAA was dispersed in (previously filtered) 1,4-dioxane to a concentration of 0.5% w/w. The dispersion was kept at 25 °C overnight with magnetic stirring. Next, a 0.25 M solution of CdAc2 in methanol was added to a stoichiometric ratio of 0.5 mol of CdAc2 per mol of COOH groups to induce formation of micelles with poly(cadmium acrylate) cores. The dispersion was kept at 25 °C overnight with magnetic stirring. Finally, to induce formation of CdS QDs in the micelle cores, 1.9 M Na2S in a mixture of 1:1 methanol:water was added to a ratio of 0.4 mol Na2S per 1 mol of COOH groups and the color of the dispersion immediately changed to yellow. The dispersion was then kept at 25 °C overnight with magnetic stirring. Following Na2S addition, the mixture was protected from light by wrapping the reaction vial in aluminum foil to prevent photobleaching of the QDs. The resulting sample of QD-containing block copolymer micelles was designated QDMs.

Dynamic light scattering (DLS) measurements of QDMs at 20 °C were performed to obtain micelle hydrodynamic diameters (Dh), both in dioxane and in a mixture of 1:1 (v:v) dioxane:toluene. (This solvent mixture corresponded to the mixture of 1:1 (v:v) dioxane:toluene used in the previous paragraph. Then, to yield QDMs in 1:1 (v:v) dioxane:toluene, we added another 2 mL of toluene to 2 mL of diluted QDMs in 1,4-dioxane.)
**Synthesis of Gold Nanoparticles.** GNP s were synthesized in an organic medium using the Brust method. An aqueous solution of HAuCl₄·3H₂O (30 mM, 30 mL) was mixed with a tetracyanomethonium bromide solution in toluene (50 mM, 80 mL) using vigorous stirring over 15 min. Following separation of organic and aqueous phases, 170 mg of dodecanethiol was added to the organic phase, after which the mixture was stirred vigorously for 10 min at room temperature. A freshly prepared aqueous solution of NaBH₄ (0.4 M, 25 mL) was then added slowly to the mixture and the reaction was allowed to proceed for 3 h and 30 min with stirring. Following another separation of organic and aqueous phases, the organic solvent was extracted from the organic phase by evaporation in a rotavap. The black product, consisting of GNP s, was redispersed in 30 mL of ethanol. The particles were filtered with a membrane filter and washed with ethanol and acetone. Finally, the GNP s were dried under vacuum at room temperature. The GNP s were characterized by TEM and absorption measurements.

**Preparation of Gold Nanoparticle-Conjugated Quantum-Dot Micelles (QDM-GNPs).** Dispersions of QDMs with different amounts of GNP s were prepared in a mixture of 1:1 toluene:dioxane (v:v). First, we prepared a more dilute dispersion of QDMs from the original dispersion, mixing 1.5 mL of the original QDM dispersion and 15 mL of 1,4-dioxane. Then, to prepare each sample of GNP-conjugated QD micelles, we used 2 mL of the QDM diluted dispersion, a designated quantity of GNP dispersion in toluene (depending on the desired GNP equivalents), and pure toluene up to a final dispersion volume of 4 mL, so that the final solvent composition was identical for different amounts of GNP s. After the preparation of these samples, we added 1.25 equiv of hexylamine per TTC group to transform TTC groups in the micelle shell to terminal hexylamine, the reactions proceeded with vigorous stirring for 5 h at 25 °C. The various GNP-conjugated QD micelles were designated according to the number of added GNP s per micelle: QDM-GNP(0.001), QDM-GNP(0.007), QDM-GNP(0.011), QDM-GNP(0.015), and QDM-GNP(0.077), where the numbers in brackets indicate the number of GNP s per micelle, which we defined as RₓGNP.

**Characterization.** Static and dynamic light scattering (SLS and DLS) measurements were performed on a Brookhaven instrument (BI-200SM Goniometer and BI-9000AT correlator) using a He–Ne laser (632.8 nm, 35 mW, model 127, Spectra Physics) and an avalanche photodiode detector. The measurements were carried out in glass cylindrical cells to simplify the corrections needed for refractive index variations. The circular vat cell contains decalin to minimize light refraction. The DLS measurements were carried out in glass cylindrical cells to simplify the aggregation of structures that occurs in the process of solvent evaporation in air. First, a block of aluminum (Al) was cooled by immersion in liquid nitrogen. A 300-mesh carbon-coated Cu TEM grid (Electron Microscopy Sciences) was placed on top of the Al block, and one drop of benzene dispersion was placed on the grid resulting in immediate freezing of the drop. The grid was then quickly placed under vacuum to sublimate the frozen solvent.

**RESULTS AND DISCUSSION**

**Synthesis of the PAA-b-PS-TTC-PS-b-PAA Tetrablock Copolymer.** The PAA-b-PS-TTC-PS-b-PAA block copolymer, composed of two identical segments of a PAA-b-PS block copolymer connected via the PS blocks to a central TTC unit, was prepared by sequential RAFT polymerization using a carbosyl-terminated TTC, S,S′-bis(α,α′-dimethyl-α′-acetic acid) trithiocarbonate, as charge transfer agent (CTA) to polymerize the PAA blocks. The polymerization of AA was performed in similar conditions to those reported by Lai et al., but in our case the solvent was a mixture of H₂O/EtOH (75/25 v/v) and the polymerization was carried out at 70 °C with ACVA initiator, using [CTA]/[ACVA] = 30 to minimize the number of chains initiated by ACVA. The number-average molecular weight determined by MALDI-TOF MS for the PAA-TTC-PS homopolymer, Mₓ = 3.0 × 10³ g mol⁻¹, is close to the value predicted by mass balance from the synthesis conditions (Mₓ ≈ 3080 g mol⁻¹). The MALDI-determined polydispersity index (PDI), Mₓ/Mₑ = 1.02, although underestimated due to the slight molar mass dependence of ionizability, clearly corresponds to a low-polydispersity polymer. Because of the reactivity of the CTA, the polymer is expected to have a symmetrical architecture consisting of two PAA blocks joined by the TTC group. This was confirmed by injecting the chains after aminolysis with hexylamine, which yielded a molecular weight of half the initial value. The degree of polymerization calculated from the number-average molecular weight corresponds to two blocks of n = 18.5 AA units each connected by a TTC unit (Scheme 1).

The PAA-TTC-PS homopolymer was used as a macroCTA for the RAFT polymerization of styrene. The solvent used in the
polymerization had to be compatible with both blocks (PS and PAA) as well as with the styrene monomer. Although DMF should have fulfilled these requirements, we obtained a very low yield (under 5%) for the polymerization in DMF at low styrene concentration. We also tried other solvents, as described by Lai under similar conditions but without success, mainly because the PAA was not fully soluble. Thus, we decided to follow the procedure reported by both Postma and Moed for the RAFT polymerization of styrene by thermal initiation at 110 °C in the absence of initiator. In our case, we used a concentrated mixture of styrene in DMF ([Styrene] = 5.2 M) to fully solubilize the PAA-macroCTA. The monomer conversion determined by 1H NMR was 46%, yielding a molecular weight of 3126 g mol⁻¹, corresponding to a degree of polymerization of 2N = 115, which, for symmetric PS blocks, suggests that we have m = 57.5 styrene units in each block (Scheme 1). We note, however, that the molecular weight average determined by 1H NMR for polymers of this dimension can be inaccurate. AlthoughGPC-MALS of amphiphilic copolymers with polyelectrolyte blocks also presents numerous problems, we used this technique to confirm the NMR result. The average molecular weight determined in 1,4-dioxane (Mw = 1.6 × 10⁶ g mol⁻¹), a good solvent for the chain, is very similar to the value obtained by NMR. Furthermore, we converted the AA groups of the PAA blocks into methyl acrylate groups using (trimethylsilyl)-NMR. Furthermore, we converted the AA groups of the PAA polymer in 1,4-dioxane (Mw = 1.04) to the methylated polymer in THF after correction for the extra methyl groups (Mw = 1.5 × 10⁶ g mol⁻¹) confirms the previous results. We use this value throughout our calculations.

The PDI calculated for the methylated copolymer (Mw/Mn = 1.04) is also close to the value obtained for the unmodified polymer in 1,4-dioxane (Mw/Mn = 1.13) and is typical of polymers synthesized by RAFT controlled polymerization, although these values might be slightly underestimated due to some uncertainty in the GPC-MALS detector at large elution volumes (affecting mainly the calculation of Mn). Finally, injection of the polymer chains after aminolysis with hexylamine yielded a molecular weight value decreased to half the initial value, indicating that indeed most of the chains have a power-like structure with a TTC group at the apex.

CdS Quantum Dot Micelle Characterization. The CdS QDs were formed inside the poly(cadmium acrylate) micelle core, following self-assembly of the PAA-b-PS-TTC-PS-b-PAA block copolymers induced by the addition of cadmium acetate in 1,4-dioxane. SLS of these micelles gave a molecular weight of Mw = (2.38 ± 0.02) × 10⁶ g mol⁻¹. A small amount of aggregation forced us to use only low polymer concentrations, and so the error in the Zimm plot slopes was high. However, the error in the determination of the molecular weight is much lower because this value is obtained from the intercepts of both extrapolations. By dividing this value by the mass of the copolymer chain, Mw = 1.5 × 10⁶ g mol⁻¹, we obtain an aggregation number for the micelles of 16, in close agreement with the value estimated from the mass balance (Supporting Information).

The poly(cadmium acrylate) micelle core acts as a nanoreactor in which the cadmium-containing hydrophilic PAA blocks are localized, with the hydrophobic PS blocks surrounding the core in the micelle corona (Scheme 2). The PS external layer imparts organic solvent solubility to the QDs, allowing them to be uniformly dispersed, maintaining their photoluminescence properties. As shown in Scheme 2, the resulting QDM micelles should have a flower-like structure with a TTC group at the apex of each PS “petal”, consisting of the central PS block that folds during self-assembly to allow the outermost PAA blocks in each chain to be incorporated into the core.

Using DLS, we measured the hydrodynamic diameters of the QDMs in dioxane and also in the solvent mixture used to prepare the QDM-GNP assemblies: 1:1 (v:v) toluene:dioxane. The refractive index (nD = 1.460) and viscosity (μ = 0.920 cP) for the solvent mixture, calculated at 20 °C (Supporting Information, S1), were used to obtain hydrodynamic diameters from DLS autocorrelation data via cumulant analysis (Table 1). The QDMs have approximately the same diameter in toluene and in the solvent mixture, with the average hydrodynamic diameter slightly increasing in the solvent mixture (from 45 to 48 nm) over 1 month, possibly due to a slow aggregation process.

In their UV–vis absorption spectra, nanoscale semiconductors exhibit a distinct shoulder due to quantum confinement effects, which in conjunction with the band edge can be used to calculate particle sizes and size distributions. From the shoulder (λsh) and the band edge (λb) positions of the absorption spectrum of QDMs in dioxane (Figure 1), we calculated a QD diameter of (3.2 ± 0.4) nm, corresponding to a radius PDI of 1.03 (Supporting Information, S2). After 1 month in solution, the calculated size increased by only ~8%. This is probably due to Ostwald ripening of the CdS QDs and concomitant decrease in exciton confinement, although we note that size determinations from absorption spectra can also be influenced by the slight increase in light scattering with an increase in micelle size (Table 1). The calculated size dispersity also increased only slightly (Table 2).

We measured the PL spectra of the QDM dispersions in a 1:1 mixture of toluene:dioxane (v:v) for different excitation wavelengths: λex = 350, 370, 390, and 410 nm (Figure 2A). We observed that as the excitation wavelength increases, the PL maximum shifts to slightly higher wavelengths and the PL

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Table 1. Mean Hydrodynamic Diameter (Dh) at 20 °C of QDM in Dioxane and in Dioxane: Toluene 1:1 (v:v) Mixture, Calculated Using Cumulant Analysis of the DLS Measurements

<table>
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<th>Sample Condition</th>
<th>nD</th>
<th>μ (cP)</th>
<th>Dh (nm)</th>
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<tr>
<td>QDM in dioxane</td>
<td>1.422</td>
<td>1.540</td>
<td>45.7 ± 0.3</td>
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<tr>
<td>QDM in a toluene:dioxane 1:1 (v:v) mixture</td>
<td>1.460</td>
<td>0.920</td>
<td>48.0 ± 0.2</td>
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<tr>
<td>QDM in a toluene:dioxane mixture after 1 month</td>
<td>1.460</td>
<td>0.920</td>
<td>48.0 ± 0.2</td>
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Figure 1. Absorption spectra of the QDMs in dioxane (freshly prepared, solid line; stored in the dark for 1 month, dashed line), with the corresponding edge and shoulder features for each case (see Table 2).

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**Figure 1.** Absorption spectra of the QDMs in dioxane (freshly prepared, solid line; stored in the dark for 1 month, dashed line), with the corresponding edge and shoulder features for each case (see Table 2).
intensity decreases. The latter trend is explained by the lower particle absorption at higher excitation wavelengths, as shown in the absorption spectra in Figure 1, whereas the former trend is a function of the particle size distribution, in that larger, lower-energy particles within the distribution will be preferentially excited at higher wavelengths. We also measured the excitation spectra at different emission wavelengths: $\lambda_{em} = 545, 555, 570, \text{and} 580 \text{ nm}$, with all spectra exhibiting nearly identical behavior in terms of intensity and shape; for this reason, only the spectra obtained for $\lambda_{em} = 545 \text{ nm}$ are represented in Figure 2A. As expected, the shape of the excitation spectrum is similar to the shape of the UV-vis absorption spectrum of the QDs.

A representative TEM image of QDs deposited onto a carbon-coated TEM grid is shown in Figure 2B. Because of electron densities, only the CdS QDs in the cores are visible by this technique. From the TEM images and by measuring a total of 390 QDs, we determined a size distribution corresponding to a mean QD diameter of 3.5 nm and a standard deviation of 1.2 nm (Figure 2B).

**GNP Characterization.** GNPs were synthesized according to the Brust method, and their mean diameter was obtained by TEM (Figure 3A). By measuring $\sim 150$ GNPs from TEM images, we determined a GNP size distribution corresponding to an average diameter of 3.3 nm and a standard deviation of 0.7 nm. The absorption spectrum of GNPs dispersed in toluene (Figure 3B) exhibits a relatively broad and weak surface plasmon peak at $\sim 510 \text{ nm}$. The absence of a sharp surface plasmon feature is typical of particles in this size range and has been attributed to the reduced mean free path of the electrons in small metal NPs. A possible contribution from the dispersity of particle size and shape (Figure 3A) is also expected due to the known wavelength dependence of the local surface plasmon resonance (LSPR) band mainly on the shape (aspect ratio) but also on the size of the particles. 23,31,52

<table>
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<tr>
<th>sample</th>
<th>$\lambda_{sh}$ (nm)</th>
<th>$\lambda_{edge}$ (nm)</th>
<th>$D_{CdS}(\lambda_{sh})$ (nm)</th>
<th>$D_{CdS}(\lambda_{edge})$ (nm)</th>
<th>$\sigma$</th>
<th>RPI</th>
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</table>

"Absorption shoulder and edge features ($\lambda_{sh}$ and $\lambda_{edge}$) were obtained, as shown in Figure 1. The calculation of the mean diameters of CdS QDs $D_{CdS}(\lambda_{sh})$ and $D_{CdS}(\lambda_{edge})$, the standard deviation ($\sigma$), and the radius polydispersity index (RPI) is in the Supporting Information, S2.

Figure 2. (A) Emission spectra of QDMs in 1:1 toluene:dioxane (v:v), measured at excitation wavelengths $\lambda_{ex} = 350, 370, 390, \text{and} 410 \text{ nm}$, and the excitation spectrum of the same sample (collected at $\lambda_{em} = 545 \text{ nm}$). (B) TEM image and the corresponding diameter distribution of the QDMs.

Figure 3. TEM image (A) and corresponding diameter distribution of the GNPs. The mean diameter is 3.3 nm (standard deviation = 0.7 nm). (B) Absorption spectrum of the GNPs in toluene showing a broad surface Plasmon feature at $\sim 510 \text{ nm}$.  

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Gold Nanoparticle-Conjugated Quantum Dot Micelles (GNP-QDMs). To assemble the GNP and QDMs, the TTC groups in the PS shell were transformed into thiol (SH) groups using hexylamine as a reducing agent, with each TTC group generating two SH-terminated PS chains (Scheme 3). We prepared different samples using the same molar amount of hexylamine and QDMs, with different amounts of added GNPs, corresponding to relatively small numbers of GNP per QDM (molar ratios of GNP to QDM NPs, \( R_{\text{GNP}} \), 0.001, 0.007, 0.011, 0.015, and 0.077, calculated by mass balance, Supporting Information, S3). We used a small amount of GNPs to avoid the large absorption of light by the GNPs at the excitation and emission wavelengths used for the QDM. No precipitation or increase in turbidity was observed upon the addition of GNPs in any of these samples, indicating that colloidal stability was maintained in all cases.

Comparing DLS of QDMs and various GNP-QDM samples in the same solvent mixture, we observed only a small increase in the average hydrodynamic diameter of the conjugates with the increase in \( R_{\text{GNP}} \) (Table 3). The differences in mean hydrodynamic diameter with and without GNP conjugation (~1 nm for \( R_{\text{GNP}} = 0.001 \) and ~6 nm for \( R_{\text{GNP}} = 0.077 \)) are small and for low GNP loading smaller than the diameter of a single GNP. This is consistent with the observation that even for the case of the low GNP loading smaller than the diameter of a single GNP, an average of only 1 in every 13 QDMs will be conjugated to a GNP.

TEM images of QDM-GNP(0.077) deposited onto carbon-coated grids (Figure 4) show several pairs of proximal light and dark particles, attributed to conjugates of darker, more electron dense GNPs and lighter QDs. The mean distance between QDs and GNPs in these pairs is ~3 nm, slightly below the end-to-end distance of the intervening PS chains in a random coil conformation (~4 nm).

The UV–vis absorption spectra of QDM-GNP samples with different GNP contents in toluene:dioxane 1:1 (v:v) (Figure 5A) are approximately the weighted sum of the absorption spectra of QDM and GNP components (Figure S1A,B), with absorbance at the maximum at 311 nm increasing linearly with the GNP concentration (Figure 5C), consistent with Beer’s law.

Table 3. Mean Hydrodynamic Diameter \( (D_h) \) Determined at 20 °C for QDMs and Two Different QDM-GNP Samples in a Dioxane:Toluene 1:1 Mixture, Measured by DLS

<table>
<thead>
<tr>
<th></th>
<th>GNP equivalents per QDM</th>
<th>( D_h ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QDM</td>
<td>0</td>
<td>45.3 ± 0.2</td>
</tr>
<tr>
<td>QDM-GNP(0.001)</td>
<td>0.001</td>
<td>46.4 ± 0.3</td>
</tr>
<tr>
<td>QDM-GNP(0.077)</td>
<td>0.077</td>
<td>51.3 ± 0.4</td>
</tr>
</tbody>
</table>

The uncorrected emission spectra of QDM-GNP dispersions containing different amounts of GNPs, with excitation at \( \lambda_{ex} = 350 \) nm, are shown in Figure 6. To establish potential QD enhancement due to the excitation of proximal surface plasmons within QDM-GNP conjugates, we first needed to correct these spectra for inner filter effects because, due to spectral overlap, GNPs will absorb some of the excitation light and also reabsorb some of the light emitted by QDs.

Therefore, each spectrum in Figure 6 was corrected for inner filtering of excitation and emission photons using the following equation:

\[
FI_{\text{QDM-GNP}}(\text{corrected}) = FI_{\text{QDM-GNP}} \times \frac{\epsilon_{\text{CdS}}^{\lambda_{ex}}[\text{CdS}] + \epsilon_{\text{Au}}^{\lambda_{ex}}[\text{Au}] + \epsilon_{\text{Au}}^{\lambda_{em}}[\text{Au}]}{\epsilon_{\text{CdS}}^{\lambda_{em}}[\text{CdS}]}
\]

where \( FI_{\text{QDM-GNP}} \) is the measured emission fluorescence, \( \epsilon_{\text{CdS}}^{\lambda_{ex}}[\text{CdS}] \) is the absorbance of QDMs at a specific excitation wavelength \( (\lambda_{ex}) \) for a cadmium sulfide concentration \([\text{CdS}]\), \( \epsilon_{\text{Au}}^{\lambda_{ex}}[\text{Au}] \) is the absorbance of GNPs at the same excitation wavelength \( (\lambda_{ex}) \) at a gold concentration \([\text{Au}]\), and \( \epsilon_{\text{Au}}^{\lambda_{em}}[\text{Au}] \) is the absorbance of the GNP at the emission wavelength \( (\lambda_{em})\).

The inner filter-corrected emission intensities of the QDM-GNP dispersions are shown in Figure 7a \( (\lambda_{ex} = 350 \) nm). A clear increase in the corrected PL intensity is observed as the concentration of added GNPs increases. This strongly suggests an enhancement of QD PL by the added GNPs due to binding of...
the GNP (supported by DLS data, vide supra) to an increasing number of QDMs as the GNP concentration increases. To quantify this apparent emission enhancement, we calculated the average emission amplification (EA), eq 2, by dividing the corrected emission intensity for each QDM-GNP sample by the intensity measured for the QDMs alone at each emission wavelength and averaging for all spectra

$$EA_{\lambda_{exc}} = \frac{\sum_{\lambda_{em}} F1^{QDM-GNP\text{(corrected)}}}{FI_{QDM}}$$

(2)

The PL measurements and calculations described above were repeated for the various QDM-GNP dispersions at a total of four different excitation wavelengths: $\lambda_{exc} = 350, 370, 390$, and $410$ nm. The average EA for the QDM-GNP samples, as a function of $R_{GNP}$ and at different excitation wavelengths, is shown in Figure 8. For each excitation wavelength, we observed a nonlinear increase in the EA with increasing $R_{GNP}$, with the rate of increase in amplification decreasing throughout the GNP addition (Figure 8), characteristic of a surface binding isotherm. Another clear feature of the data in Figure 8 is that for all GNP concentrations, the EA increases with increasing excitation wavelength, showing a maximum amplification of about nine times the QD control when $R_{GNP} = 0.077$ and $\lambda_{exc} = 410$ nm.

To this end, we prepared three dispersions in a 1:1 mixture of toluene:dioxane (v:v): the first containing GNPs alone, the second containing QDMs alone, and the third containing the GNP (supported by DLS data, vide supra) to an increasing number of QDMs as the GNP concentration increases. To quantify this apparent emission enhancement, we calculated the average emission amplification (EA), eq 2, by dividing the corrected emission intensity for each QDM-GNP sample by the intensity measured for the QDMs alone at each emission wavelength and averaging for all spectra

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We ruled out the possibility that the observed enhancement was simply due to increased light scattering by the GNPs, by measuring the scattered light intensity by various QDM-GNP samples as a function of wavelength and comparing these results to the scattering intensities of QDM dispersions without GNPs. To this end, we prepared three dispersions in a 1:1 mixture of toluene:dioxane (v:v): the first containing GNPs alone, the second containing QDMs alone, and the third containing the
conjugates QDM-GNP(0.015). The number concentrations of GNP were identical in the first and third samples, and the number concentrations of QDMs were identical in the second and third samples. To measure scattered intensity from these three different samples over a range of wavelengths, we performed synchronous wavelength scans in the spectral region of Cds emission (Figure 9). The three curves show the expected decrease in intensity with the wavelength, with similar structural features associated with the lamp intensity profile. Comparing the scattering intensities between the curves, we observe similar intensity profiles from the dispersions of QDM-GNP(0.015) and QDMs alone. The dispersion with only GNP showed markedly less scattering than either QDMs alone or QDM-GNP(0.015). This confirms that the effective increase in corrected PL intensity in QDM-GNP conjugates is not due to the simple scattering of emitted photons by the GNP, suggesting that a more subtle enhancement mechanism must be considered.

We also measured the PL lifetimes of QDMs alone and the QDM-GNP conjugates. We used two different excitation wavelengths, $\lambda_{\text{ex}} = 365$ and 410 nm, with corresponding emission decays measured at $\lambda_{\text{em}} = 500$ and 550 nm, respectively (Figure 10). The decays were analyzed with a multieponential decay model, yielding good fitting results with two average decay lifetimes. We observed very similar short and long lifetime components from the QDM control sample and the QDM-GNP samples with different concentrations of GNP, at both excitation wavelengths (Table 4). This indicates that the interaction between the QDMs and GNP does not involve a significant change in the relaxation pathways of the QDs.

**Mechanism of QD Emission Enhancement in QDM-GNP Conjugates.** To summarize the experimental results, we observed PL enhancement factors of up to nine times the PL intensity of unconjugated QDMs upon the addition of GNP. The enhancement increases in a nonlinear manner as the concentration of added GNP increases. DLS results support the conclusion that added GNP bind to terminal thiol groups in the PS chains of the micelle corona. Moreover, the emission enhancement is found to increase as the excitation wavelength increases and approaches the spectral region of the broad SP peak at $\sim 520$ nm. Finally, the emission lifetimes of QDMs with and without GNP indicate that despite the marked enhancement effects the QD decay rates are not strongly influenced by the GNP; therefore, the presence of the metal NPs does not influence significantly the de-excitation pathways of the QDMs. These results are consistent with a mechanism in which the proximal GNP serve as antennae for the incoming excitation light. Plasmon resonant particles become surrounded by an enhanced localized electromagnetic field when excited at their LSPR as a result of the polarization associated with the collective electron oscillation in the particles. In our case, it is reasonable to suggest that when the QDM-GNP conjugates are excited, interaction of light with the GNP SP leads to a local enhancement of the electric field in close proximity to the metal, which in turn leads to more efficient excitation of QDs in the nearby micelle cores. The enhancement increases as the wavelength increases due to improved spectral overlap between the excitation light and the SP resonance at $\sim 520$ nm. Because the effect of the proximal GNP is simply to increase the excitation efficiency of QD excited states, no change in QD lifetimes are expected in this mechanism, consistent with the observed absence of variation in the fluorescence lifetimes. This indicates that whatever the mechanism of enhancement by the GNP it does not involve a change in the excited states or relaxation pathways of the QDs; therefore, it is related to the electric field in close proximity of the metal. Similar enhancement mechanisms have been proposed previously in systems of QD/GNP composite films in which the separation distances between QD and GNP layers were $\sim 10$ nm.

The DLS $z$-average hydrodynamic diameters of the QDMs, $D_h = (45.3 \pm 0.2)$ nm, provide us with an average PS shell thickness of $\sim 20$ nm. We expect the effective distances between Cds QDs in the micelle cores and GNP bonded to the PS coronal chain ends to be lower than this for two reasons: first, the polymer shell is not rigid, and so conformational flexibility will lead to a minimum distance between GNP and QDs that is much smaller than the mean distance (vide infra); second, as a mean value, the $z$-average diameters determined from DLS reflect the higher end of the size distribution. Average QD-GNP spacing values measured from the TEM images are much lower, $\sim 3$ nm; also, it should be noted that the distance determined from TEM will be influenced by solvent evaporation during TEM sample preparation.
CONCLUSIONS

We synthesized for the first time colloidal dimers of QDs and GNPs with well-defined spacings using RAFT-polymerized diblock copolymers. The structure and SH functionality of the resulting block copolymer micelles allowed linking a GNP at the termini of coronal chains at a controlled distance from a QD in the core. We observed an enhancement in the emission of the GNP short lifetime/ns long lifetime/ns short lifetime/ns long lifetime/ns

<table>
<thead>
<tr>
<th>$R_{NP}$</th>
<th>$\lambda_{ex} = 365$ nm</th>
<th>$\lambda_{ex} = 410$ nm</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>32 (23%) 79 (77%)</td>
<td>44 (26%) 112 (77%)</td>
</tr>
<tr>
<td>0.001</td>
<td>33 (23%) 82 (77%)</td>
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Considering $\sim 3$ nm as the mean interparticle spacing, we use the simple model applied recently by El-Sayed et al.\textsuperscript{57} to calculate the expected electric field enhancement for two proximal dipolar NPs, for which the electric field felt by each particle is the sum of the incident light-field and the near-field of the electric dipole on the neighboring particle (Supporting Information, S4). The calculated enhancement using this simple dipole–dipole model is not sufficient large to explain the enhancement observed in our dispersions. A number of considerations may explain the insufficiency of our simple calculations to account for the observed enhancements. First, the calculation assumes a fixed distance between two NP dipoles and thus does not account for the conformational flexibility of the PS spacer bridging the QD and GNP in our case; in fact, the conjugated GNPs will sample many distances about the calculated mean values, including those which result in significant spatial overlap between the near-fields of their excited SPs and the QD emitters. Second, the distribution of GNPs within the QDM population may not be entirely homogeneous but better described by a Poisson distribution, of GNPs within the QDM population may not be entirely homogeneous but better described by a Poisson distribution, and further from the calculated mean values, including those that can be accounted for in the simple calculation involving spherical particles.\textsuperscript{59}

ASSOCIATED CONTENT

Parameters used in DLS, expressions used to analyze the absorption spectra of CdS QDs, calculation of GNP per QDM in QDM-GNP assemblies, and calculation of expected electric field enhancement for two proximal dipolar nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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Table 4. PL Average Decay Lifetimes Obtained for QDMs and QDM-GNP Conjugates with Different Gold Concentrations (Relative Weight of the Decay Components Indicated)

<table>
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References


Enhanced Photoluminescence from Micellar Assemblies of Cadmium Sulfide Quantum Dots and Gold Nanoparticles

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SUPPORTING INFORMATION

S1. Parameters used in dynamic light scattering (DLS)

For QDM in a toluene : dioxane 1:1 (v : v) mixture, we determined the refractive index and the viscosity of the mixture at 20 ºC, in order to obtain the correct hydrodynamic diameter in this mixture. The refractive index of the mixture was determined according to:

\[ n_D = \left[ \phi_{diox}(n_{diox}^*)^2 + \phi_{tol}(n_{tot}^*)^2 \right]^{1/2} \]  

(1)

where \( n_D \) is the refractive index of the mixture, \( \phi_{diox} \) is the weight fraction of 1,4-dioxane in the mixture, \( n_{diox}^* \) is the refractive index of 1,4-dioxane at 20 ºC (1.422), \( \phi_{tol} \) is the weight fraction of toluene in the mixture, and \( n_{tot}^* \) is the refractive index of toluene at 20 ºC (1.496). The viscosity of the mixture at 20 ºC was estimated using the Refutas equation. First, we calculated the viscosity blending number (VBN) at 20 ºC of each component of the mixture using the following expression:
where $\mu$ is the kinematic viscosity in centistokes (cSt) units of each component at 20 ºC. The second step was the calculation of $VBN$ for the mixture ($VBN_{mix}$):

$$VBN_{mix} = [x_{diox} \times VBN_{diox}] + [x_{tol} \times VBN_{tol}]$$

where $x_{diox}$ and $VBN_{diox}$ are the mass fraction and the viscosity blending number for dioxane at 20ºC and $x_{tol}$ and $VBN_{tol}$ are the mass fraction and the viscosity blending number for toluene at 20 ºC, respectively. Finally, we calculated the kinematic viscosity of the mixture by solving equation 2 to viscosity:

$$\mu = \exp \left( \exp \left( \frac{VBN_{mix} - 10.975}{14.534} \right) \right) - 0.8$$

where $VBN_{mix}$ is the viscosity blending number for the mixture at 20 ºC, determined using equation 3. The viscosity obtained in this method is a kinematic viscosity in cSt units. To convert the kinematic viscosity to a dynamic viscosity (used in DLS measurements), we had to multiply the kinematic viscosity by the density in g/mL. In equation 2, we converted the dynamic viscosity of the solvents at 20 ºC, obtained in the literature, to kinematic viscosity, dividing the dynamic viscosity by the density in g/mL at 20 ºC for each component.

We used $n_D = 1.460$ and $\mu = 0.920$ cP for the 1:1 mixture, calculated for 20 ºC.

**S2. Expressions used to analyze the absorption spectra of CdS QDs**

The mean CdS QD diameters ($D_{CdS}$) were calculated using the following empirical expression:\textsuperscript{3-5}

$$D_{CdS}(\lambda_{thresh}) = 1 / (0.1338 - 0.0002345 \lambda_{thresh})$$
where \( \lambda_{\text{thresh}} \) (in Å) is either the shoulder or edge absorption threshold, providing the diameter of the CdS nanoparticles calculated from the shoulder \( D_{\text{CdS}(\lambda_{\text{sh}})} \) or the edge \( D_{\text{CdS}(\lambda_{e})} \), respectively. In order to obtain the size dispersity of the sample, we used the following expression.\(^6\)

\[
d_{1/2} = D_{\text{CdS}(\lambda_{e})} - D_{\text{CdS}(\lambda_{sh})}
\]

where \( d_{1/2} \) can be taken to be twice the standard deviation (2σ), if we assume a Gaussian distribution of particle size, and \( D_{\text{CdS}(\lambda_{sh})} \) will approximate the mean particle diameter. We defined a radius polidispersity index (RPI) for each distribution, according to reference 3, using the following expression:

\[
RPI = \left( \frac{\sigma}{D_{\text{CdS}}} \right)^2 + 1 \leftrightarrow RPI = \left( \frac{d_{1/2}}{2} \right)^2 + 1
\]

The CdS QDs constituting the core of the QDMs have very low size dispersity, with a \( RPI = 1.03 \).

**S3. Calculation of GNP per QDM in QDM-GNP assemblies**

To determine how many gold nanoparticles (GNPs) are present in each assembly, we first calculate the average number of gold atoms in each GNP. The GNPs average diameter is 3.3 nm, obtained from TEM images. Assuming that the particles are all spherical, we can calculate the volume of each particle, \( v_p = 1.88 \times 10^{-20} \text{cm}^3 \). Using the gold density \( (d = 19.7 \text{ g.cm}^{-3}) \), we determine the GNP mass, \( m_p = 3.70 \times 10^{-19} \text{g} \). The number of gold atoms per particle is given by:

\[
N_{Au} = \frac{m_p}{MW_{Au}} \times N_A = \frac{3.70 \times 10^{-19}}{196.97} \times 6.022 \times 10^{23} = 1131
\]

where \( MW_{Au} \) is the molecular weight of gold and \( N_A \) is the Avogadro number.
Next step is to determine how many SH groups do we have in each QDM. We used the diameter of CdS obtained by the threshold of the edge in the absorption spectrum of the QDM (3.2 nm) to calculate the volume of each CdS core, assuming they are spheres, \( v_c = 1.72 \times 10^{-20} \text{cm}^3 \). Using the density of cadmium sulfide, \( d = 4.82 \text{g.cm}^{-3} \), we determined the mass of CdS present in the core, \( m_c = 8.270 \times 10^{-20} \text{g} \). The number of cadmium ions per micelle is given by:

\[
N_{\text{Cd}^{2+}} = \frac{m_c}{MW_{\text{CdS}}} \times N_A = \frac{8.270 \times 10^{-20}}{144.48} \times 6.022 \times 10^{23} = 344
\]

where \( MW_{\text{CdS}} \) is the molecular weight of cadmium sulfide.

Assuming there’s two COO\(^-\) ions for each cadmium ion, we have for each micelle \( 344 \times 2 = 688 \) COO\(^-\) ions. Each polymer chain has 39 COO\(^-\) groups linked, so 688 COO\(^-\) ions correspond to 17 polymer chains. Each polymer chain originates 2 SH groups, so we have 34 SH groups per CdS QD micelle.

We prepared QDM-GNP assemblies with different gold atom moles per SH group: 0.05, 0.25, 0.37, 0.50 and 2.50. We determined the number of gold atoms per micelle multiplying the number of gold atoms per SH group in each case by the number of SH groups present in each micelle, dividing this result by the number of gold atoms present in each GNP to obtain the number of gold nanoparticles per micelle \( (R_{\text{GNP}}) \) in each assembly. In the case of QDM-GNP(0.001), we have an average of 1 GNP per 665 micelles; for QDM-GNP(0.007), 1 GNP per 133 micelles; for QDM-GNP(0.011), 1 GNP per 90 micelles; for QDM-GNP(0.015), 1 GNP per 66 micelles; and for QDM-GNP(0.077), 1 GNPs per 13 micelles. The numbers in brackets correspond to the \( R_{\text{GNP}} \).

**S4. Calculation of expected electric field enhancement for two proximal dipolar nanoparticles**

Based on a dipolar coupling model,\(^7\) the electric dipole moment \( \mu \) of an isolated nanoparticle in an electric field \( E \) is given as


\[ \mu = \alpha \varepsilon_m E \]  

(8)

where \( \alpha \) is the Clausius-Mossotti dipole polarizability for an isolated metal nanoparticle in a quasi-static approximation, which for a sphere is expressed by

\[ \alpha = 3\varepsilon_0 V \left( \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right) \]  

(9)

where \( V \) is the particle volume, \( \varepsilon \) is the wavelength-dependent dielectric constant and \( \varepsilon_0 \) is the vacuum permittivity. If we substitute \( \alpha \) in eq. 8, we obtain

\[ \mu = 3\varepsilon_0 V \varepsilon_m E \left( \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right) \]  

(10)

In the presence of a neighboring particle, the electric field \( (E') \) felt by each particle is the sum of the incident light field \( (E_{inc}) \) and the near-field of the electric dipole on the neighboring particle. In the dipole limit, the near-field decays as the cube of the distance \( (d) \) from the particle. According to ref. 7, when the light is polarized along the interparticle axis, we have

\[ E' = E_{inc} + \frac{\mu'}{2\pi\varepsilon_m \varepsilon_0 d^3} \]  

(10)

The electric field felt by the CdS nanoparticle \( (E_{CdS}) \) and the gold nanoparticle \( (E_{Au}) \) are obtained using the equations 11 and 12 respectively.

\[ E_{CdS} = E_{inc} + \frac{\mu_{Au}}{2\pi\varepsilon_m \varepsilon_0 d^3} \]  

(11)

\[ E_{Au} = E_{inc} + \frac{\mu_{CdS}}{2\pi\varepsilon_m \varepsilon_0 d^3} \]  

(12)

We can determine the electric field felt by the CdS nanoparticle in the presence of a GNP \( \frac{E_{CdS}}{E_{inc}} \) and the electric field felt by the GNP in the presence of a CdS nanoparticle \( \frac{E_{Au}}{E_{inc}} \). The enhancement in the field intensity around each particle was estimated as \( \left( \frac{E_{CdS}}{E_{inc}} \right)^2 \) for the QD and \( \left( \frac{E_{Au}}{E_{inc}} \right)^2 \) for the GNP, using
the following values: $D_{Au}$ (GNP diameter) = 3.3 nm; $D_{CdS}$ (CdS diameter) = 3.2 nm; $\varepsilon_{CdS} = n^2 = 6.4$; $\varepsilon_m = 2.33$; $\varepsilon_{Au}^{real} \approx -2\varepsilon_m \approx 5.722 (\lambda_{ex} = 410\text{nm})$ and $\varepsilon_{Au}^{real} = -1.6906 (\lambda_{ex} = 410\text{nm})$.  

Using the simple model described above, the enhancement in the field intensity is negligible for a separation distance ($d$) between QD and GNP of 10 nm. However, for a separation distance of ~3 nm (determined from TEM), it estimates that the field intensity around the QD is enhanced by a factor of ca. 2 due to the presence of the GNP. This value is still small when compared to the enhancement obtained for the QD photoluminescence in our experiments, but we note that although the model used is very approximate, it still shows that an enhancement is expected.

REFERENCES


