Surface Functionalization of Cadmium Sulfide Quantum Confined Semiconductor Nanoclusters. 2. Formation of a "Quantum Dot" Condensation Polymer

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Pyridine-functionalized nanoclusters, recently reported in our laboratories, can undergo condensation polymerization with α,α′-dibromo-*p*-xylene and other organic dihalides to form novel semiconductor "quantum dot" containing polymeric materials. These polymers are air and water stable and thermally stable and appear to form discrete spherical clusters of approximately 800–1000 Å diameter, and linear assemblies several micrometers long. The polymers can be suspended in many organic solvents, swell dramatically in water, and are miscible with a variety of other polymers, such as polystyrene, casting processable films. The polymer films are both photoluminescent and electroluminescent. Electronic absorption, fluorescence, and ^{1}H NMR spectra along with transmission electron microscopy of the new polymeric materials are reported.

Semiconductor clusters of nanometer dimensionality, frequently referred to as "quantum dots", have received much recent attention.[1] This intriguing class of inorganic clusters may lead to the development of new electronic materials possessing single-electron transistor properties,[2] enhanced nonlinear optical activities,[3] and controllable band parameters. Indeed, the bandgaps of these nanoclusters are affected widely and predictably by altering the cluster size. Nanometer-sized metal clusters have already demonstrated practical utility in the area of chemical catalysis.[4] Numerous preparative pathways to quantum dots of prespecified sizes have appeared in the recent literature and include molecular beam epitaxy (MBE), metal organic chemical vapor deposition (MOCVD), microlithography, chemical precipitation in inverted micelles or zeolite matrices, and kinetic trapping.[5–7] Quantum dots have been prepared from a variety of semiconductors including cadmium sulfide, cadmium selenide, and lead sulfide, as well as from numerous transition metals.[8]

It is generally accepted that the main luminescence of semiconductor nanoclusters in the visible region is related to the surface states.[9,10] We attempt here to modify these states as a first step toward potentially useful optical materials with strongly enhanced luminescence properties. A feasible route toward enhancement of emission is the concentration of large numbers of nanometer-sized clusters into larger "superarrays". Such arrays will have an immense surface area and hence a large concentration of surface states, while the individual clusters are still smaller than the excitation wavelength.[9,11] In addition, by linking the clusters, one may couple them electronically, as has previously been observed with quantum dot superlattices.[12–14] Recently, we reported a convenient approach by which a variety of chemical functionalities may be tethered to the surface of CdS quantum confined nanoclusters[15] and demonstrated the activity of the surface functionalities by further ligation of electroactive or photoactive transition-metal complexes and covalently linked organic

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(15) (a) Noglik, H.; Pietro, W. J. *Chem. Mater.* **1994**, *6*, 1593. (b) Thiophenols, CdS, DMF, DMSO, and halogenated organic compounds are toxic and should be handled with the appropriate precautions. DMSO may be absorbed directly through the skin carrying dissolved solutes with it. Latex gloves are also permeable to DMSO. The MSDS sheets should be consulted before handling DMSO solutions. The reactions mixtures for the polymer formation have a strong nauseating odor. Synthesis and purification procedures should be carried out in a fume hood.

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Scheme 1

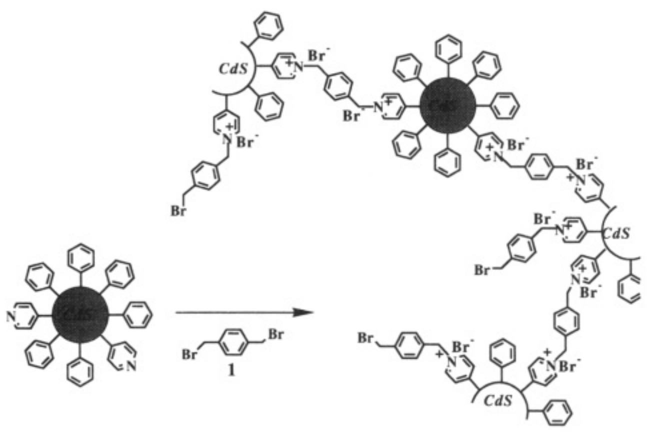


Table 1. Observed Photoluminescence Wavelengths for Alkyl- and Aryl-Bridged Pyridine Functionalized CdS Quantum Dot Polymers

bridge	MM2 length (Å)	λ_{max} (nm)
ethyl	2.3	NA
octyl	6−8	540
tert-butenyl	5	545
tert-xylenyl	6	555

moieties. In this contribution we report the polymerization of a surface-functionalized CdS nanocluster with dihalide bridges to form a new class of polymeric electronic materials with unusual fluorescent and electroluminescent properties.

Thiophenol-capped CdS nanoclusters (20 Å) containing 8% surface pyridine functionality, [CdS_x (sϕ, 8% Spy)$_y$] (hereafter denoted as Qdpy), were synthesized by a kinetic trapping procedure previously described.[15] Qdpy (1.0 g) was added to 20 mL of a 40 mM solution of α,α′-dibromo-*p*-xylene (recrystallized from chloroform), **1**, in distilled acetone containing 10% (v/v) THF under dry argon. After a brief sonication, the suspension was stirred at room temperature for 24 h. The resulting pale yellow pasty reaction mixture was then diluted with 100 mL of acetone, resuspended, and stirred under argon for and additional 6 h. The solid was then separated by centrifugation, repeatedly washed alternately in water, methanol, and dimethyl ether via sonication/centrifugation, and finally dried in vacuo (10^{-4} Torr) at room temperature for 24 h.

The polymerization follows from a common difunctional amine quaternarizaion reaction as shown in Scheme 1. The polymer is highly ionic and likely highly cross-linked. The solubility/suspendability properties of the resulting material, $\{CdS_x\,[s\phi, 8\%\ Spy(CH_2\phi CH_2)_z]_y\}_n$ (hereafter referred to as QPX) are quite different from those of pristine thiophenol-capped ($[CdS_x(s\phi)_y]$) or pyridine functionalized thiophenol-capped Qdpy CdS nanoclusters. The polymer is rather soluble in methanol and acetonitrile forming relatively nonturbid suspensions which exhibit a marked Tyndall effect. Contrary to the monomeric quantum dots, the polymer is much less suspendable in dimethyl sulfoxide (DMSO) and dimethylformamide (DMF), in which highly turbid suspensions form. QPX also swells dramatically in water and can be heated to 140 °C in air with no apparent degradation. The elemental analysis of QPX gives an empirical formula of $[CdS_{0.56}(SPh)_{0.89}(Spy)_{0.33}(xyl)_{0.37}Br_{0.74}\cdot(H_2O)_{0.26}]$ (SPh = thiophenol, Spy = thiopyridyl, and xyl = xylyl).[16] This formula indicates some reaction of the halide functionalities with sulfur, resulting in an excess of xylyl moieties. This is not unexpected under these reaction conditions but is unavoidable as lower concentrations of bridging dihalide do not lead to polymeric assemblies. The content of mercaptopyridine is 37% (of total thiol) which further supports the argument of side reactions to form thioethers which are washed out during workup. Polymers prepared using three other bridging dihalide moieties (see Table 1) also gave similar results.

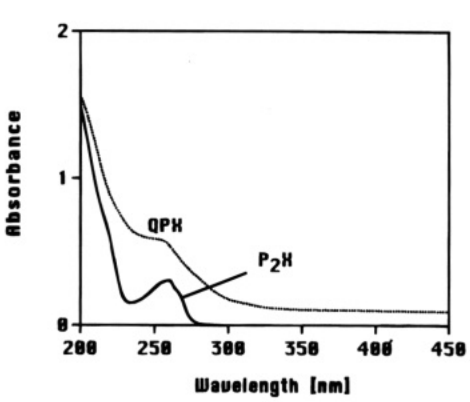
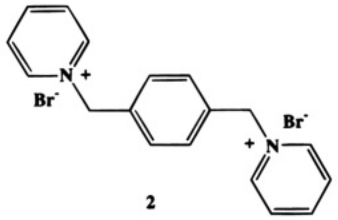


Figure 1. Electronic absorption spectra of QPX and P_2X in acetonitrile.

The electronic absorption spectra of all synthesized polymers are dominated by the pyridinium $\pi-\pi^*$ transition at 260 nm (Figure 1). For comparison, the spectrum of a quaternary pyridinium model monomeric unit, P_2X, **2**, is also presented. Figure 2 compares the fluorescence spectra of QPX and unpolymerized Qdpy in acetonitrile. As reported previously, Qdpy shows an excitonic emission at 470 nm, while the characteristic 557 nm emission due to trap-induced electron−hole recombination is fully quenched.[15] The fluorescence spectrum of QPX, on the other hand, exhibits a reappearance of the surface state carrier recombination emission at 557 nm with an intensity some 2 orders of magnitude higher than in the unfunctionalized clusters, whereas the excitonic fluorescence is now quenched. Similar observations have been made by Bahnemann and co-workers, who found that the green emission of ZnO clusters increases with increasing concentration of



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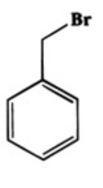

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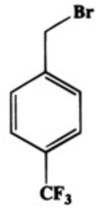

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[16] Elemental analysis was performed by Microanalytical Systems, Inc., Vancouver, B.C. Found: C: 31.2%; H: 2.39%; N: 1.28%; S: 15.4%; Cd: 30.6%; Br: 15.99%; O: 1.12%.

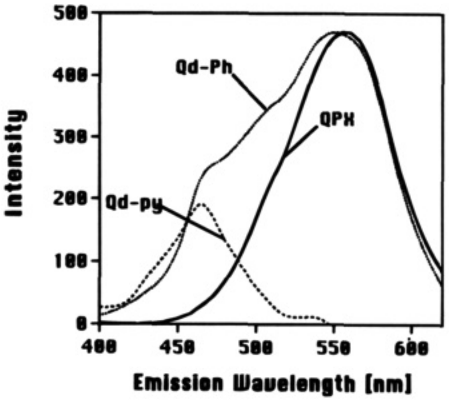

Figure 2. Emission spectra (baseline corrected) of 1 mg/mL QdPh and Qdpy and 0.01 mg/mL QPX in acetonitrile. Excitation wavelength was 330 nm.

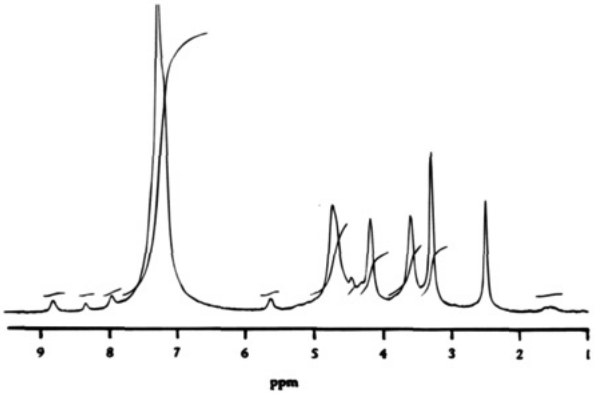

Figure 3. Proton NMR spectrum of QPX in DMSO-d_6 with TMS as an internal standard.

Table 2. ^{1}H NMR Resonance Assignments for CdS Quantum Dot Polymer QPX

	observed resonance (ppm/TMS)		
assignment	QPX	P_2X	lit.[18]
$[\text{py-R}]^+$	7.9, 8.3, 8.8	8.0, 8.6, 9.4	7.8–9.5
aromatic	7.3	7.5	7.2–7.5
$-CH_2Br$	4.4	NA	4.5
$[\text{py}-CH_2R]^+$	4.8, 5.6	6.0	4.9, 6.0
$-SCH_2R$	1.5, 4.1	NA	1.7, 3.8–4.5
$-SH$	3.4	NA	3.4

oxygen as an electron acceptor.[10c] Control experiments where Qdpy was reacted with α-bromotoluene, **3**, and 1-(bromomethyl)-4-trifluoromethylbenzene, **4**, show only the luminescence due to excitonic states at about 380 nm, with the fluorescence in the visible range completely quenched.[17] Prolonged extraction with boiling water results in quenching of the strong emission and formation of the typical 470 nm fluorescence with a shoulder at 570 nm, while the water picks up a small fraction of pyridinium bridges. No indications for electronic coupling due to tunnelling or subband formation by UV/vis/NIR have been observed as was found for zeolite entrapped CdS superlattice arrays;[14] however, the dependence of the strong emission on the presence of bridges and formation of grains may indicate Coulombic interactions between the clusters.[12,13] Further investigations are needed to address this problem. The position of the intense polymer emission shifts only weakly as a function of the bridging molecule, as summarized in Table 1.

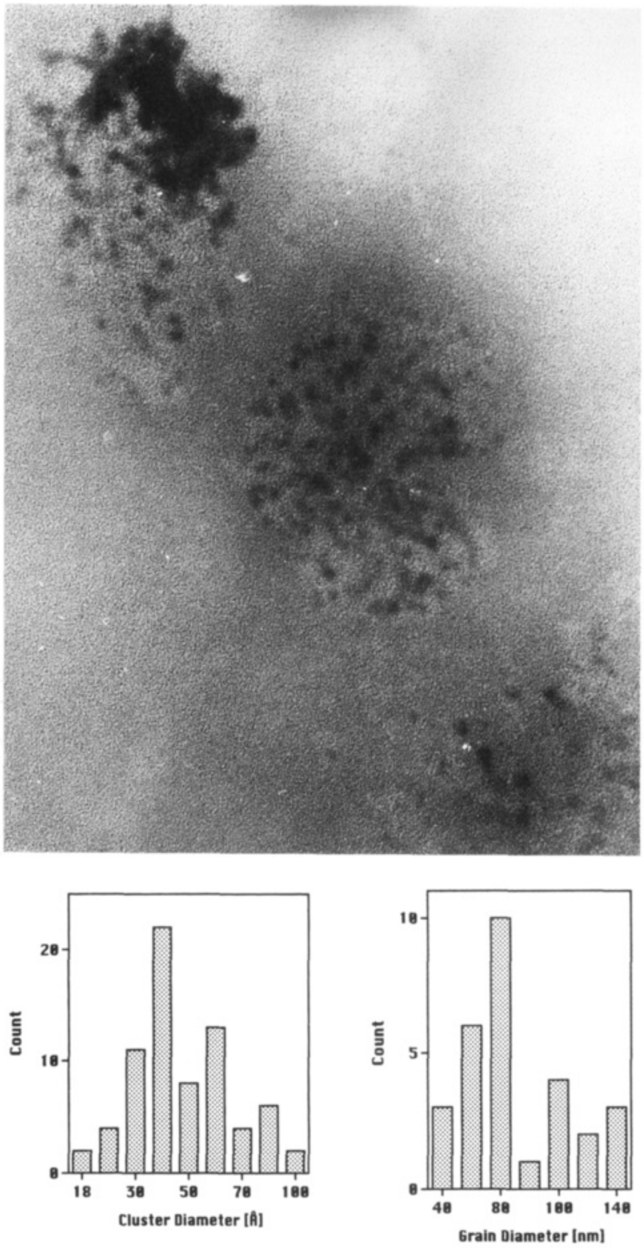

Figure 4. Transmission electron micrograph and corresponding histograms of QPX macroclusters on carbon coated Cu grid. Print magnification is 495 000 (5 mm = 100 Å).

The ^{1}H NMR of QPX was recorded in DMSO-d_6 using TMS as an internal standard and appears in Figure 3. The signals are dramatically broadened relative to the unpolymerized Qdpy, and new peaks are observed. The assignments of the resonances are summarized in Table 2. For comparison, these data are listed along with P_2X resonances and appropriate systems taken from the literature.[18] Soxhlet extraction with water and repeated sonication/centrifugation cycles in various solvents do not affect the positions or intensity ratios of the signals.

The transmission electron micrographs of QPX are most interesting and are presented in Figure 4, along with corresponding histograms for the cluster and grain diameters. Whereas TEM pictures of unpolymerized

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Qdpy show the individual quantum dots to be separated and randomly distributed,[15] QPX quantum dots appear to cluster into discrete spherical units of approximately 800–1000 Å diameter and linear assemblies several micrometers long. As presented in the histograms, cluster and grain size varies widely. Individual cluster diameters range from 18 to 100 Å with an average diameter of 48 Å. It is, however, difficult to obtain very accurate images, as the large concentration of charges and organic groups gives rise to shadowing in the image.[19]

The polymeric QPX is miscible with other polymers, and as a demonstration of potential processability, a QPX/polystyrene composite film was cast as follows. A sonicated suspension of QPX in CH_3CN (1 mL) was added to 2 mL of a saturated toluene solution of polystyrene and sonicated to a transparent suspension. A few drops of this mixture was placed on a glass microscope slide and left to harden overnight. The resulting film is optically transparent between 280 and 800 nm. The luminescence spectrum of the QPX/polystyrene composite film was measured at an angle of 45° to an incident excitation beam and is presented in Figure 5. The spectrum is broadened and the emission maximum is shifted to higher energy, further suggesting that the observed emission is strongly related to the surface states. In addition to the photoluminescence, QPX powders and films also exhibit a bright yellow-green electroluminescence when immersed in the electric field of a Tesla coil under vacuum ($<10^{-6}$ Torr). We are currently in the process of investigating the electroluminescence in more detail.

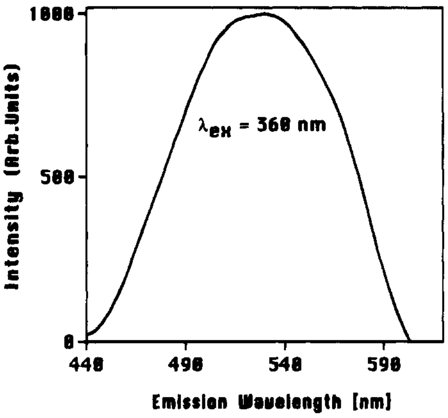

Figure 5. Luminescence spectrum (baseline corrected) of a QPX/polystyrene composite film, excited at 360 nm.

Conclusions

Pyridine-functionalized CdS nanoclusters can undergo condensation polymerization with α,α′-dibromo-*p*-xylene and similar dihalide bridging linkages to form novel "quantum dot polymers". The polymers are air and water stable, thermally stable, and form aggregates of about 800–1000 Å in diameter and linear assemblies several micrometers in length. The polymers are may be suspended in a number of organic solvents and are miscible with other polymers forming castable, processable films. The polymers exhibit 2 orders of magnitude more intense luminescence than their monomeric counterparts and are also electroluminescent. Further investigation into the nature of these systems may lead to novel optical and optoelectronic materials.

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