

Development of a Portable Petroleum By-Products Chemical Sensor

NYS-DOT
RF CUNY Subcontract: 55657-06-15
Phase 1&2 Report
07/31/2006

Professor Michael A. Carpenter, College of NanoScale Science and Engineering
Professor Marina A. Petrukhina, Department of Chemistry
University at Albany, SUNY
Albany, NY 12203

Glossary:

PCB's	Polychlorinated Biphenyls
BTEX	Benzene, Toluene, Ethyl Benzene, Xylene
OMM	Operation, Maintenance, Monitoring
QD's	Quantum Dots
TEM	Transmission Electron Microscopy
NMR	Nuclear Magnetic Resonance
HC's	Hydrocarbons
TDPA	Tetradecylphosphonic Acid
HDA	Hexadecylamine
TOPO	Trioctylphosphine Oxide
TOP	Trioctylphosphine
PL	Photoluminescence
PFSA	Perfluorosulfonic Acid
PBA	Pyrenebutyric Acid
H¹NMR	Proton (Hydrogen) NMR
BBA	Benzylbutyric Acid
BA	Benzoic Acid
FBA	Perfluorobenzoic Acid
FNMR	Fluorine NMR
NA	Naphthylamine
FNA	Heptafluoronaphthylamine
HRTEM	High Resolution TEM
SA	Stearic Acid
PMMA	Polymethylmethacrylate
AIBN	Azobisisobutyronitrile
PLMA	Polylaurylmethacrylate
NYS -DOT	New York State Department of Transportation
RF-CUNY	Research Foundation of The City University of New York
SUNY	State University of New York
US – EPA	United States Environmental Protection Agency
NYSERDA	New York State Energy Research and Development Authority
NYSTAR	New York State Office of Science, Technology and Academic Research

Research Summary

We have proposed to tailor design nanoparticle based chemical sensors for the sensitive, selective and field portable analyses of soil samples for petroleum spill indicating hydrocarbons (such as benzene, toluene, ethyl-benzenes, xylenes, PCBs, trichloroethylene). The broader impacts of the hydrocarbon sensor research program lies in the future target applications of nanoparticle based chemical sensors. NYS-DOT spends approximately \$10-12M/yr on the testing of soil and groundwater samples, which does not include the NYC-DOT.¹ By moving the majority of these tests from an off-site analytical lab, to a field portable device the overall cost of construction budgets will be significantly lower and construction projects will experience fewer delays due to untimely analytical lab reports. Another example leading to a broader impact of the program is for monitoring benzene, toluene, ethyl benzene, and xylenes (BTEX) for applications in groundwater well networks or soil sample analysis. BTEX compounds are indicative of petroleum by-product contamination and currently the US-EPA has regulations for performing a standardized test of groundwater and soil samples using modern analytical laboratory equipment. Off-site analytical lab testing of both groundwater and soil samples are a significant expense of environmental monitoring and cleanup operations throughout the federal and state level Superfund program. Since its inception in 1986, the New York State Superfund program alone has identified, characterized and placed a total of 1,714 sites on the Registry of inactive hazardous waste disposal sites. Details of these sites are as follows:²

1. A total of 934 sites have been identified that require remediation; growth is approximately 30 sites/yr
2. 215 of these sites require long-term operation, maintenance, and monitoring (OMM) to ensure that remediated sites continue to protect the public health (growth of OMM sites is approximately 30/yr)
3. In the 1999/2000 fiscal year approximately \$9 million were spent on site investigation, remediation investigation and OMM, all of which required extensive sampling, monitoring and analysis of soil and groundwater samples
4. To date funds spent or obligated to be spent total approximately \$4.61 billion: \$3.01 billion by responsible parties, \$1.05 billion by New York State and \$554 million by the federal government

It is clear that significant cost savings at both the state and federal levels would occur if chemical sensors integrated with pattern recognition techniques were developed for continuous on-site environmental monitoring, specifically for analyzing groundwater well and soil samples. Future advances and phases of the proposed research program would likewise integrate in-situ remediation processes in the event of a detected pollution plume and lead to far less expensive cleanup procedures.

During the first year of the program we have adapted colloidal synthetic chemistry procedures to attach a combination of stabilizing and sensing ligands to the surface of semiconducting quantum dots (QDs). The sensing ligands are designed and utilized to achieve the first level of selective detection of the target hydrocarbons. These tailored QDs have been incorporated into a polymer matrix, which is chosen to achieve a second level of selectivity in the detection the target hydrocarbons. Testing of these tailored QD

films has required the development and integration of a reliable sensor testing station so that ppm to % level hydrocarbon concentrations can be delivered and detected using fluorescence spectroscopy techniques. Currently, we have been able to achieve a **15 ppm** detection limit for **xylenes** in an ambient air mixture, which is approximately **3 times** the **50 ppm** detection limit for **toluene**. This increased sensitivity with the development of selective films for the detection of aromatic hydrocarbons, which only differ by a single methyl group, is justification that our proposed program, which entails the development of tailored QD-polymer films, is a promising technology for the development of a portable petroleum by-products chemical sensor.

During the second year of the program we continued the optimization of the tailored sensing ligands and likewise performed further studies to select an optimal polymer host for the QDs, thereby achieving an increase in sensitivity to ppb levels while enhancing the degree of selectivity we achieved in year 1. These goals were achieved in part by developing nearly parallel analysis techniques which leverage equipment purchased with the infrastructure funds obtained in year one. Libraries of films have been deposited in a nearly parallel fashion and subsequent testing against hydrocarbon exposure events using fluorescence techniques. A series of experiments on film libraries have been used to optimize the sensing ligand, sensing ligand loading, QD density, and polymer hosts. It is expected that during phases III and IV that we will continue with these parallel deposition and develop parallel analysis techniques so that arrays of films will be interrogated against hydrocarbon exposure events. These parallel techniques were expected to enhance the throughput by at least an order of magnitude thus allowing for the rapid development of hydrocarbon sensing films.

Staffing

Key to the overall success of this program is the research efforts led by two postdoctoral associates. Dr. Oxana Vassiltsova, in Professor Petrukhina's research group has developed and extended QD synthetic procedures to include the use of stabilizing and sensing ligands, which are required for the first level of hydrocarbon selectivity. Furthermore, Dr. Vassiltsova has led the efforts in analyzing the tailored QDs using a variety of analytical techniques that include transmission electron microscopy (TEM), NMR, Uv-vis absorption spectroscopy and fluorescence spectroscopy. During Phase 2 of this program Dr. Vassiltsova also designed and tested several new polymeric host materials using *in situ* polymerization approach. Starting from January 2005, Dr. Vassiltsova supervised an undergraduate student, David Jayez, who worked on the project for several semesters and graduated with a B.S. in Chemistry in May 2006. Dr. Zhouying Zhao, in Professor Carpenter's research group has developed methods for the incorporation of the tailored QDs into polymer matrices thereby achieving the sensor detection limit for HCs down to 15ppm, which is much lower than what is reported in literature so far for QD based sensors. Likewise Dr. Zhao designed, implemented and optimized the sensor testing station that was used for the detailed exposure tests performed in year 1. Moreover, Dr. Zhao has also characterized the QD-polymer films using Uv-vis absorption spectroscopy and fluorescence spectroscopy. As part of the education program we have had 2 high school research interns as well as 1 undergraduate research intern and 1 undergraduate student participate in research activities during year

one. As part of our growth, during year 2 of the program we hired a graduate student, Ms. Mayrita Arrandale, who has been assisting with the sensor testing work being performed by Dr. Zhao. The internship program for both undergraduates and high school students was continued during year 2.

Funding

During year one, we leveraged the investment made by the Department of Transportation by almost an order of magnitude. Specifically, the hydrocarbon sensor program successfully received one year of funding from NYSERDA, \$33,000, to develop tailored nanoparticles for the detection of hydrocarbons in aerosol particles. As both the NYS-DOT and NYSERDA programs are related, they will be leveraged to help provide overall support of research staff and supplies for the programs. Furthermore, \$1,200,000 in infrastructure funding was raised by Professor Carpenter, through his participation and collaboration in the Syracuse University Environmental Quality Systems New York State STAR Center program. These funds have been used for the purchase of analytical instrumentation and equipment for support of the NYS-DOT program.

Proposals are currently pending and will be submitted to both state and federal agencies during phase 3 & 4 to promote programmatic growth of the hydrocarbon sensing research initiative, thereby providing continued leverage of the investment made by the Department of Transportation. Hydrocarbon sensors are being sought for use in environmental, indoor air, agricultural, homeland security, the food industry, pharmaceutical and industrial applications, therefore we envision expanding this program into a high technology research center that provides the rapid development of sensors tailored for targeted applications.

Outreach

Presentations on our progress to date have been given at the 2003 National American Chemical Society, 2004 National American Chemical Society, 2003 Northeast regional American Chemical Society, the 2004 regional AMSE meetings, NY Nanotech 2004 and 2nd Joint Quebec-New York Workshop on Nanotechnology, Albany, NY, 2004; Fall 2005 National American Chemical Society Meeting, Fall 2005 Materials Research Society Meeting, Spring 2006 National American Chemical Society Meeting, Spring 2006 Materials Research Society Meeting. The results have been very well received and both Dr. Oxana Vassiltsova and Dr. Zhouying Zhao were very busy presenting our results at each of these meetings. The results generated during phase 1 and 2 are currently under further analysis. One paper was submitted to *Sensors and Actuators B*, and we have 2 other papers that are currently in preparation. We now envision that several other manuscripts will be drafted and submitted to peer reviewed scientific journals at the next stage.

Results to Date

QD Synthesis and Characterization

QDs such as CdSe are ideal candidates for sensing applications due to their extremely high surface/volume ratio and sensitivity of their optical properties to the changes in their

chemical environment. Surface modification of CdSe nanocrystals by the appropriate anchoring molecules are being explored. This approach tests the ability of donor-substituted aromatic compounds to form π -complexes with electrophilic functionalities of molecules grafted to the surface of QDs by chemisorption or self-assembly. Consequently, any changes in the surface environment of QDs significantly should affect their photophysical and photochemical properties, which will be exploited for the development of sensing technologies.

During the first and second years of the NYS-DOT program, several methods of QDs synthesis have been tested. The known literature procedures have been adapted to allow both stabilizing and sensing ligands to be attached to the QD surface. Specifically, the known literature procedures have been adapted (1, 2, 3, and 9). Attempts also have been made to adjust the literature methods to our research goals by introducing potential sensor groups on the QDs surfaces (4, 5, 6, 7, and 8). $^1\text{H-NMR}$ analysis was used to analyze the degree of ligand attachment.

1) CdSe QDs with tetradecylphosphonic acid (TDPA)³

This method of synthesis was tested to produce QDs ranging in size from 1.8 to 3nm, since TDPA and HDA are known as strong ligands, thus limiting the particle growth. CdO (64.2 mg, 0.5 mmol) was placed into a three-neck flask containing 4 ml of TOPO and 3 ml of HDA. The mixture is heated to ca. 270° C under a nitrogen flow. Upon addition of 0.227 g (2.1 mmol) of TDPA a colorless solution was formed. At 250° C, 7.5 ml of a 0.3 M solution (2.25 mmol) of Se powder in TOP was swiftly injected. At the desired nanocrystal size, the reaction was stopped by removal of the heating bath. Purification was carried out by two cycles of precipitation with methanol and redispersion of the nanocrystals in toluene.

This synthetic method with TDPA and HDA was successful and afforded very small QDs ranging in size from 1.8 to 3 nm (Figure 1). The size of CdSe particle synthesized was determined based on analysis of the Uv-Vis absorption properties according to Yu et al..⁴

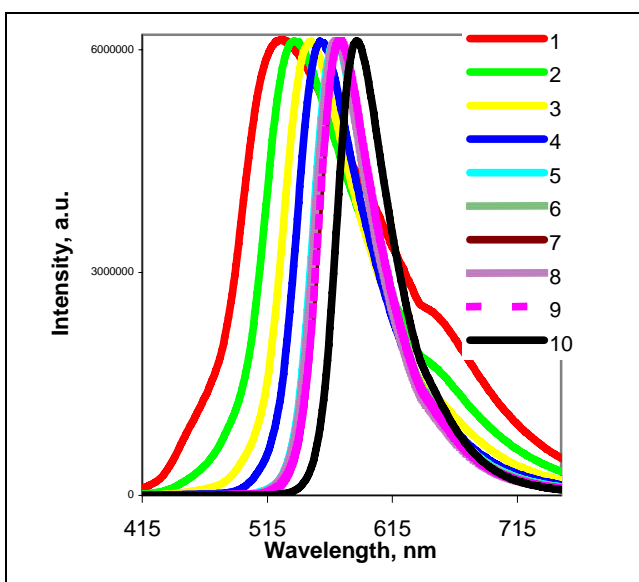
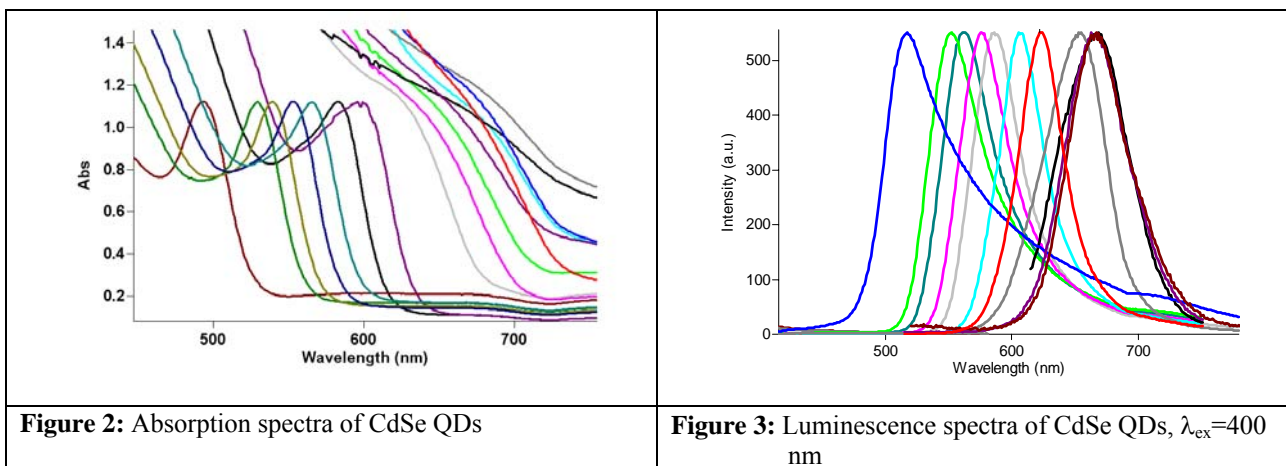


Figure 1: Photoluminescence (PL) spectra of set of CdSe QDs. Sizes ranges from 1.8 nm up to 3 nm

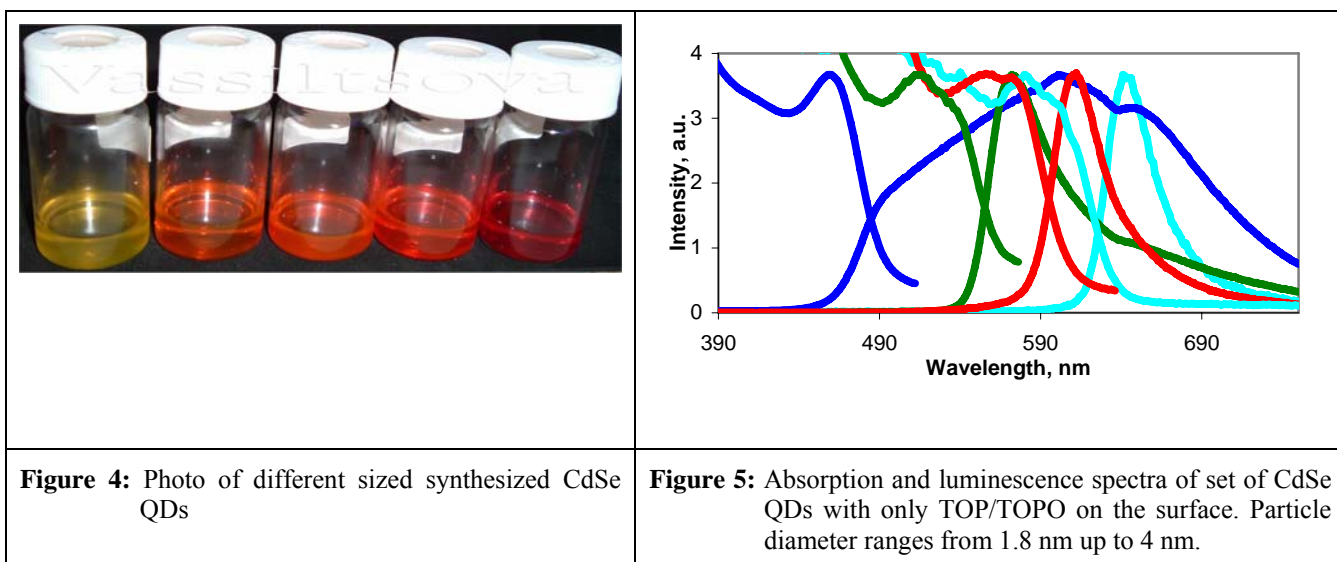
2) Set of CdSe QDs from 2.3 up to ~ 10.4 nm in diameter

To produce a wider size range of QDs we performed the synthesis of CdSe QDs as described above, but only with TOPO and HDA as the protecting ligands. We produced the smaller sized particles, however the luminescence of larger particles was less efficient and the absorption maxima for these large particles were also not very pronounced. Luminescence maxima for those QDs were in a range from 517 nm up to 667 nm (Figure 2&3).



3) CdSe QDs with TOP/TOPO

This method was tested to get CdSe QDs containing only TOP/TOPO surface-bound ligands and were used both as our reference QDs (to compare it with CdSe QDs with grafted sensing ligands) and for ligand exchange reactions (to attach sensing ligands).



A selenium stock solution was prepared by mixing 0.178 g of Se in 7.5 ml of TOP. 10 g of TOPO and 0.064 g of CdO were placed under nitrogen flow and heated to 350° C. At this temperature the Se stock solution was swiftly injected into the reaction vessel in a single step. The reaction temperature was adjusted to 250° C immediately after the

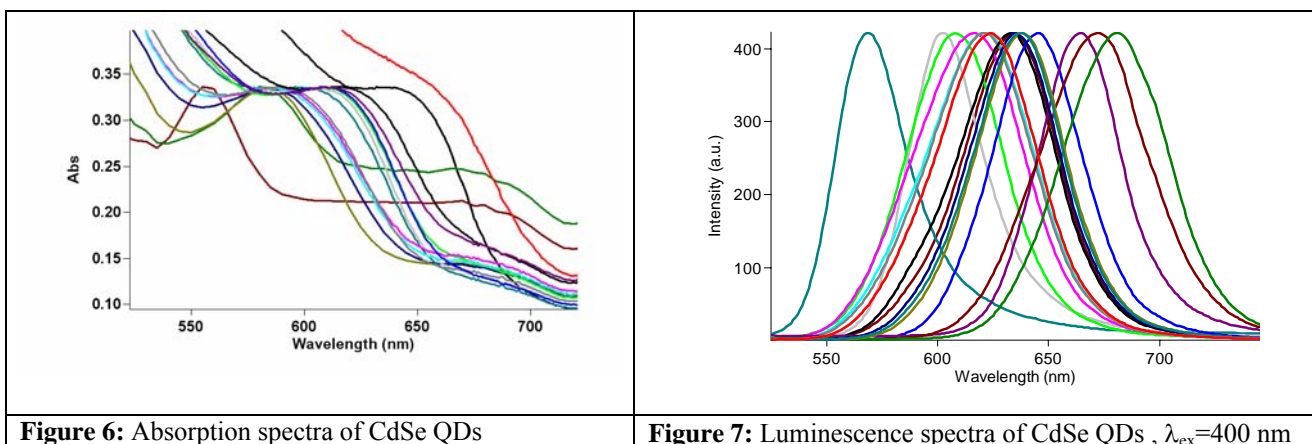
injection. The reaction was stopped 5 min after the injection, and heat was immediately removed. The reaction mixture was allowed to cool to $\sim 30\text{-}50^\circ\text{C}$, and methanol was added to precipitate the nanocrystals. As a result of the above synthetic procedure, a set of QDs ranging in size from 1.8 to 4nm was produced with the optical properties displayed in Figures 4 and 5.

4) CdSe with stearic acid⁵ or perfluorostearic acid (PFSA)

As our goal was to modify the surface of CdSe QDs by perfluorinated and nonfluorinated carboxo-bound agents, we chose this synthetic method which used stearic acid as a surface bound ligand, and later substituted it with PFSA. With this procedure we were able to synthesize both small and large QDs with high PL yield and good stability. QDs emitting well separated wavelengths were chosen for incorporation into polymer films as described later.

The synthesis of CdSe was performed in the mixture of TOPO, HDA and stearic acid (or PFSA). In a typical reaction procedure CdO (0.0127 g, 0.1 mmol) and stearic acid (0.1140 g, 0.4 mmol) were loaded into a 25 mL three-neck flask and heated to 150°C under a nitrogen flow. After CdO was completely dissolved, the mixture was allowed to cool to room temperature. TOPO and hexadecylamine (HDA), 3.44 g for each, were added to the flask, and the mixture was heated to 280°C to form an optically clear solution. At this temperature, the Se solution containing 0.079 g (1 mmol) of Se dissolved in 2.920 g of TOP was swiftly injected into the reaction flask. After the injection, the temperature was set at 250°C . For all reactions, the total mass of the reaction mixture was fixed as 10 g, and 10 times the amount of the selenium precursor was used in comparison to the cadmium precursor.

This procedure resulted in stable QDs ranging in size from 3.2 up to ~ 9.2 nm in diameter with emission maxima from 569 nm up to 681 nm (Figures 6&7). We have chosen 3 different types of QDs and incorporated them in polymer films.



The low sublimation temperature of a new potential surface-bound molecule, PFSA (135°C), its limited thermal stability and low solubility in organic solvents all have affected the reaction pathway to achieve PFSA substituted QDs and did not result in the preparation

of stable QDs. We therefore concluded that PFSA should be added to the pre-formed QD system through ligand exchange procedures and not during the direct high temperature CdSe synthesis.

5) CdSe QDs with pyrenebutyric acid (PBA)

The method of synthesis of QDs was developed in order to place sensing ligand PBA on the surface of CdSe QDs. CdO (51.4 mg, 0.4 mmol), 227.6 mg (0.8 mmol) of stearic acid and 230.7 mg of PBA were placed into a three-neck flask and heated to 150°C under nitrogen flow. After CdO was completely dissolved, the mixture was allowed to cool to room temperature. 3 g of TOPO and 1.5 g of HDA were added to the flask and the mixture was heated to ca. 300° C under nitrogen flow. At this temperature Se solution containing 316 mg of Se powder in 2.1 mL of TOP was swiftly injected. At the desired nanocrystal size, the reaction is stopped by removal of the heating bath. Aliquots were mixed with methanol and the precipitated QDs were separated by centrifugation. The process of dispersion in methanol and centrifugation was repeated several times. This method of synthesis was also used for the subsequent acids described later.

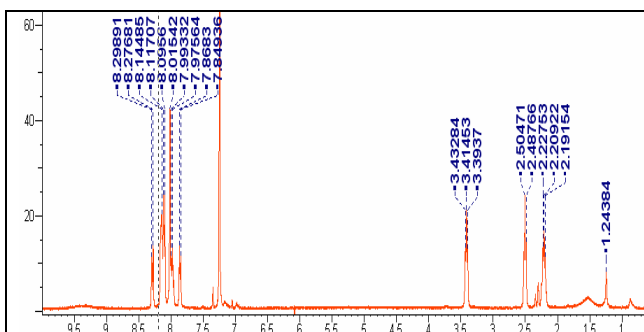


Figure 8: ^1H NMR of PBA in CDCl_3

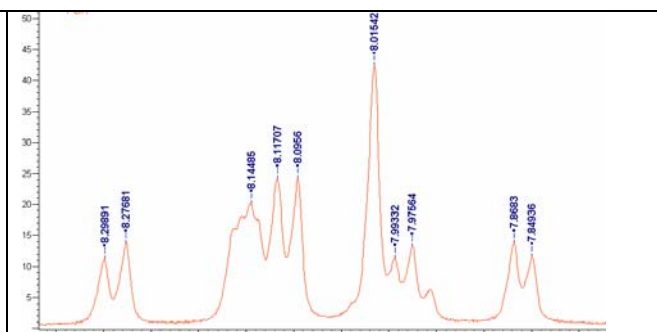


Figure 9: ^1H NMR of PBA in CDCl_3

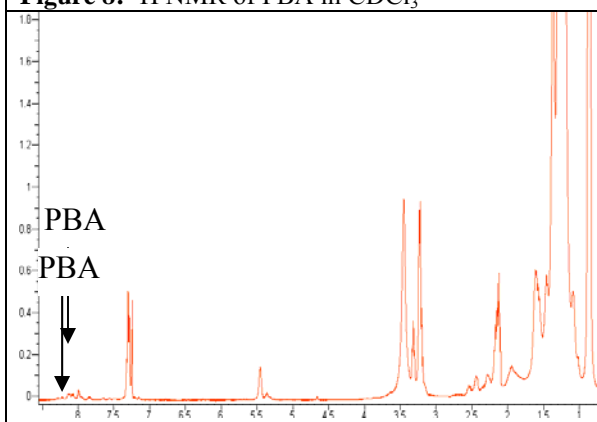


Figure 10: ^1H NMR of CdSe QDs washed 1 time, in CDCl_3

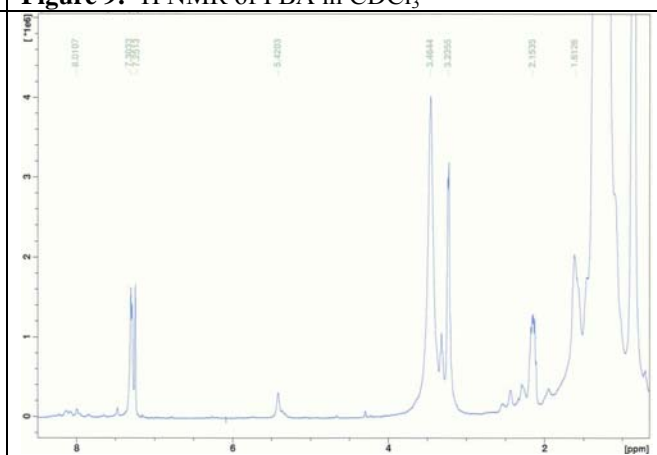


Figure 11: ^1H NMR of CdSe QDs washed 6 times, in CDCl_3

Comparison of ^1H -NMR spectra of PBA and CdSe QDs allowed us to conclude that PBA was present in CdSe QDs solution even after washing excess of ligands by methanol 6 times (Figure 8-11). With each of these subsequent washings the QDs luminescence

became less intense, see Figure 12, due to a reduction in the QD concentration within the remaining solution. In Figure 12 the peak at 475nm is due to PBA excimer formation, and as can be seen the excimers are not washed away. We have synthesized QDs of sizes from 2.5 nm up to 10 nm. But for large particles (bigger than 4 nm) luminescence from QDs disappears, and only luminescence from PBA excimer remains. By modifying the synthetic procedure we were able to produce QDs with concentrations of bound PBA, see NMR spectra in Figure 16, that did not form excimers, as indicated in the lack of a peak at 475nm in the luminescence spectra shown in Figure 17. We have also been able to correlated high concentrations of PBA with a reduction in the QD luminescence.

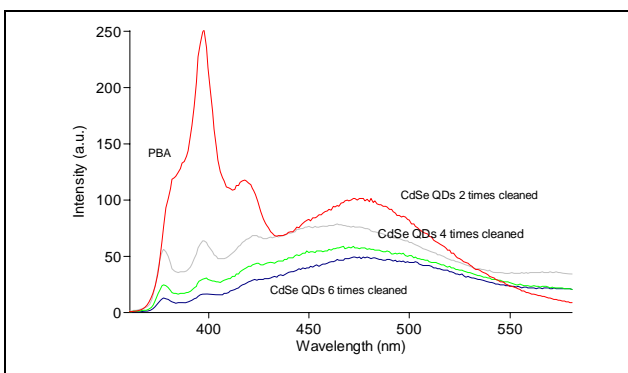


Figure 12: Luminescence spectra of several times washed CdSe QDs and PBA, $\lambda_{ex}=300$ nm

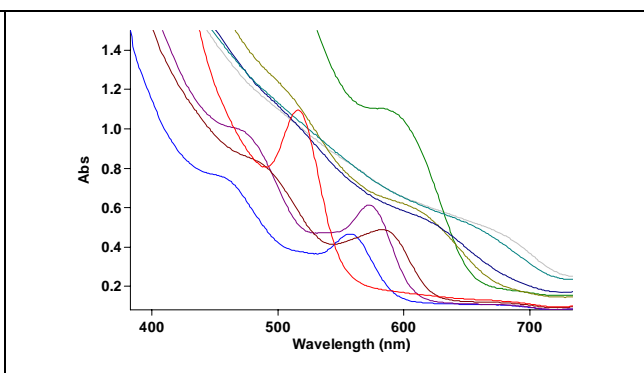


Figure 13: Absorption spectra of CdSe QDs (with PBA) of different sizes: from 2.5 nm up to 10 nm

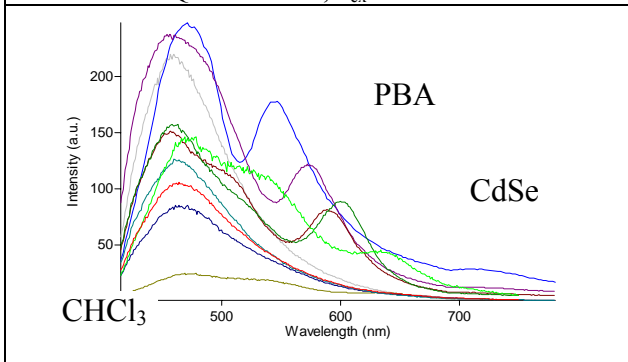


Figure 14: Luminescence spectra of CdSe QDs (with PBA) of different sizes: from 2.5 nm up to 10 nm, $\lambda_{ex}=400$ nm.

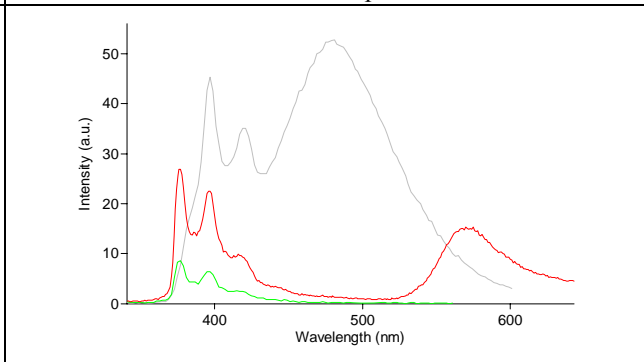


Figure 15: Luminescence spectra of CHCl₃, CdSe, PBA, $\lambda_{ex}=330$ nm

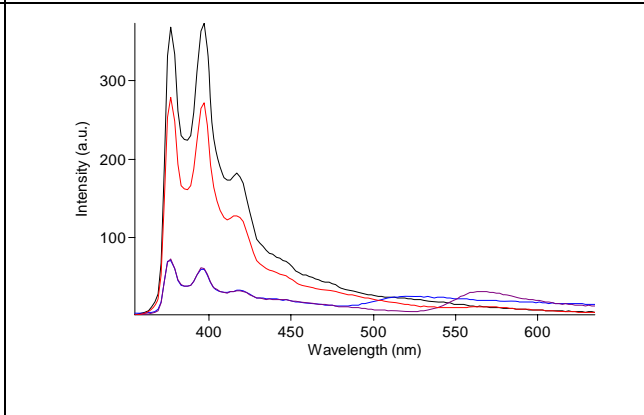
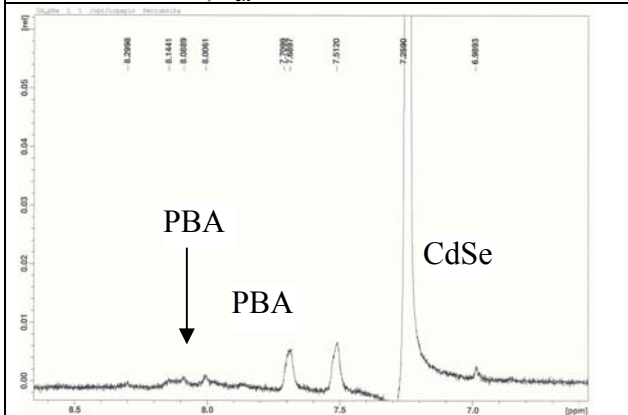
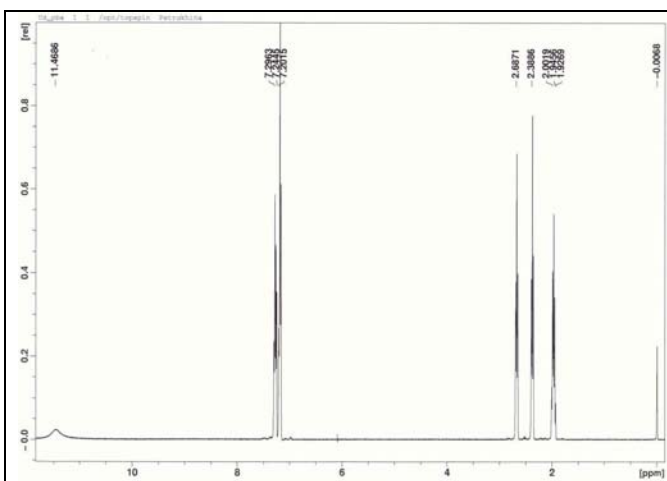
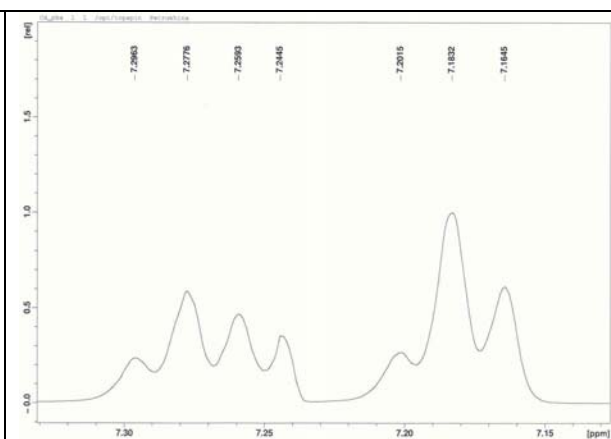
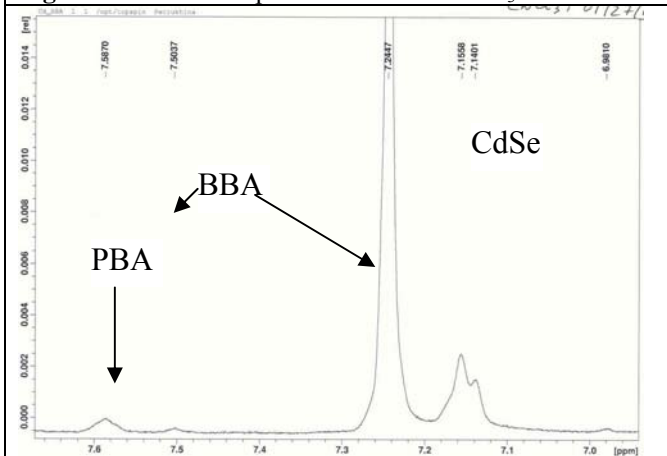
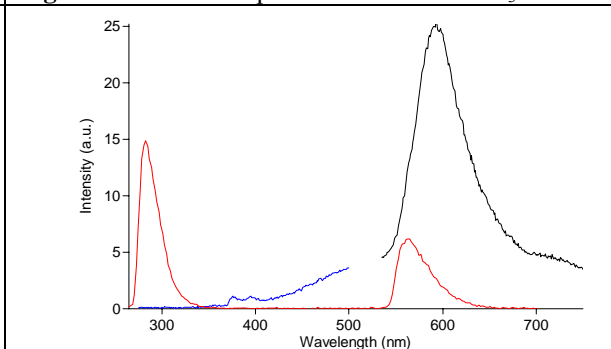
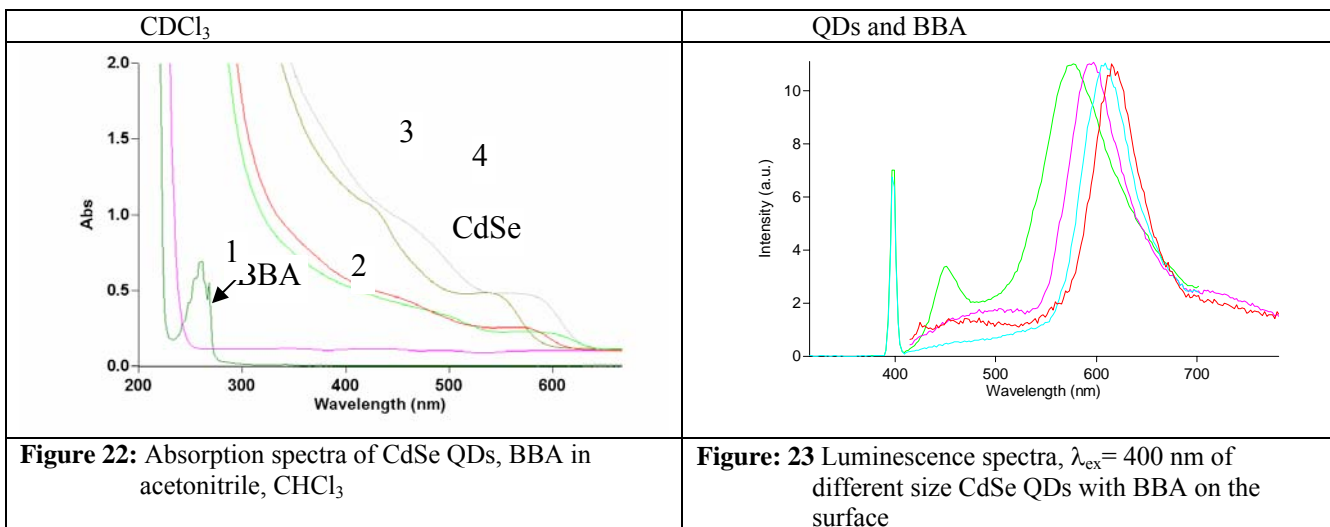


Figure 16: ^1H NMR spectra of CdSe QDs with PBA on the surface**Figure 17:** Luminescence spectra of CdSe QDs $\lambda_{\text{ex}} = 340$ nm**6) CdSe QDs with Benzylbutyric acid (BBA)**

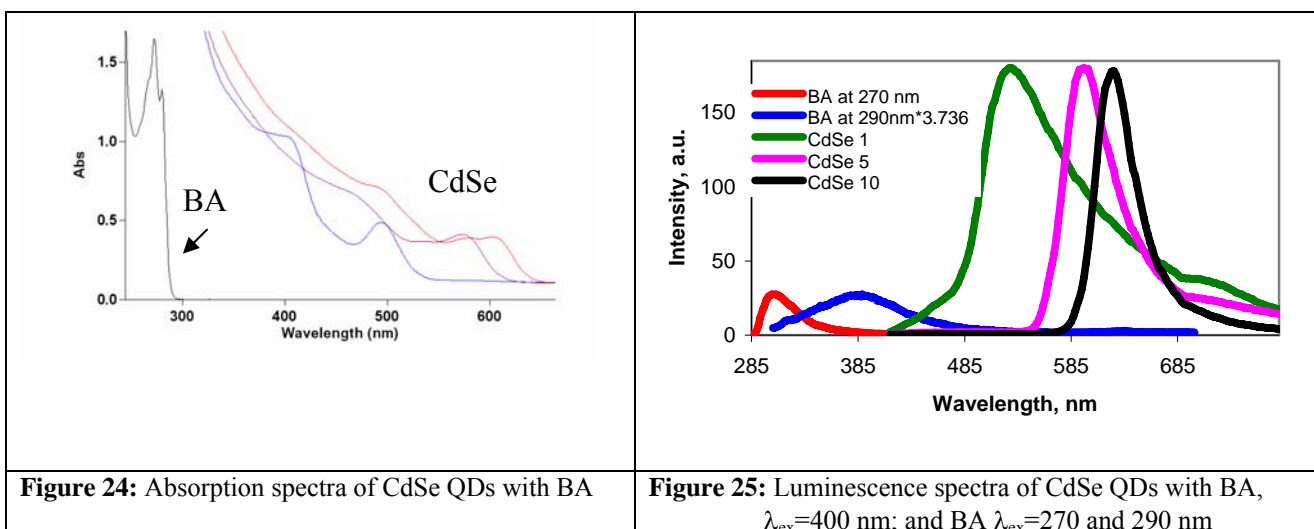
As our goal was to modify the surface of CdSe QDs by perfluorinated and nonfluorinated arene carboxo-bound ligands, we chose this method using benzylbutyric, benzoic, pentafluorobenzoic acids as surface bound ligands. It is necessary to mention in the synthesis of CdSe with BBA even during the heating of CdO with BBA it is possible to observe fast dissolution of CdO even at 150°C that means that BBA interacts with CdO. BBA is adsorbed on the surface of CdSe QDs, since it is possible to observe it in ^1H NMR spectra of CdSe QDs solutions (Figure 18-20). In luminescence spectra of BBA it is possible to observe 2 maxima (Figure 21) at 280 and 560 nm. The peak at 280nm corresponds to known peaks observed for BBA. The maximum at 560 nm was not observed in the literature for BBA and cannot be attributed to excimer formation, since excimer emission is usually in the range 430-480 nm. In luminescence spectra of CdSe QDs of different sizes it is possible to observe emission maximum in the case of small particles at 460 nm, which could be attributed to BBA excimer (Figure 23). In other cases no excimer maxima was observed.

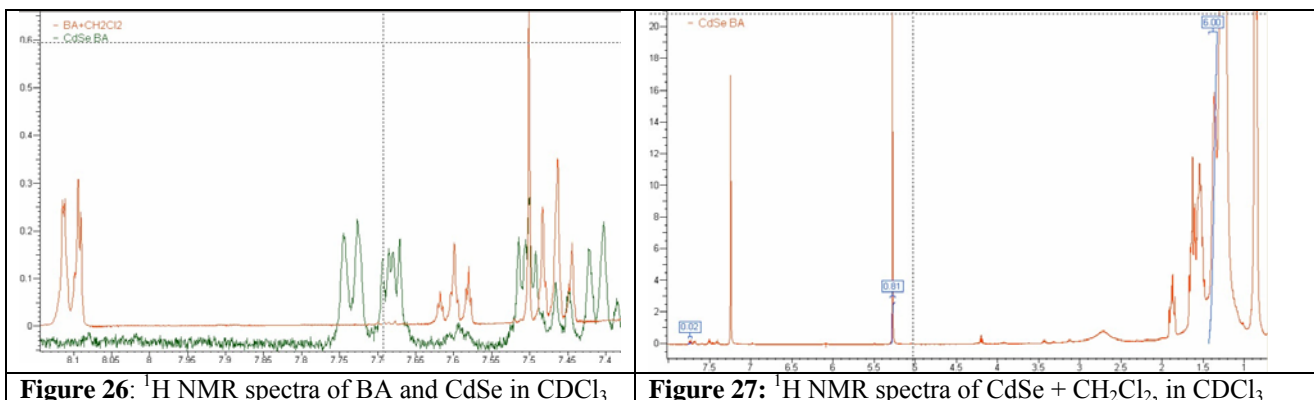
**Figure 18:** ^1H NMR spectra of BBA in CDCl_3 **Figure 19:** ^1H NMR spectra of BBA in CDCl_3 **Figure 20:** ^1H NMR spectra of CdSe QDs with BBA in**Figure 21:** Luminescence spectra, $\lambda_{\text{ex}} = 260$ nm of CdSe



7) CdSe QDs with Benzoic acid (BA)

Another sensing ligand we used was BA. As with BBA, BA easily react with CdO during synthesis. In luminescence spectra we did not detect formation of BA excimer (Figure 25). In ¹H NMR spectra of BA and CdSe in CDCl₃ (Figure 26) it is possible to observe chemical shift of BA signals, indicative of BA attachment to CdSe QDs. Also one can conclude that there is equilibrium between BA on the surface and in solution (Figure 26). Addition of known amount of CH₂Cl₂ to CdSe QDs sample allows the determination of the bound BA with respect to bound TOPO. (Figure 27) Integration of CH₂Cl₂ let roughly estimate amount of BA and TOPO on the surface. According to this estimation there are about 1 molecule of BA and 12 molecules of TOPO. This corresponds to ~50% TOPO surface coverage for ~3 nm diameter QDs and is in accordance with data published by Becerra⁶.





8) CdSe QDs with Perfluorobenzoic acid (FBA)

Using FBA instead of BA should provide better sensing properties of CdSe QDs. Intensity of luminescence excitation spectrum of CdSe QDs with FBA is very high and covers emission spectrum of FBA. In luminescence emission spectra of CdSe QDs with FBA on the surface one can observe high intensity of FBA excimer. It is necessary to note, that while increasing the QD size, the excimer emission (at 470 nm) decreases (Figure 29). Depending on the excitation wavelength intensity ratio of FBA excimer and CdSe QDs luminescence can vary.

Measuring the ^{19}F -NMR spectrum of QDs with FBA on the surface (Fig. 30) we can see two sets of signals. Comparing this spectrum with the ^{19}F -NMR spectrum of only FBA (Fig. 31) and known data⁷, we can conclude, that since signals in F-NMR of QD-FNA are shifted and split, FBA is attached to the CdSe QDs surface.

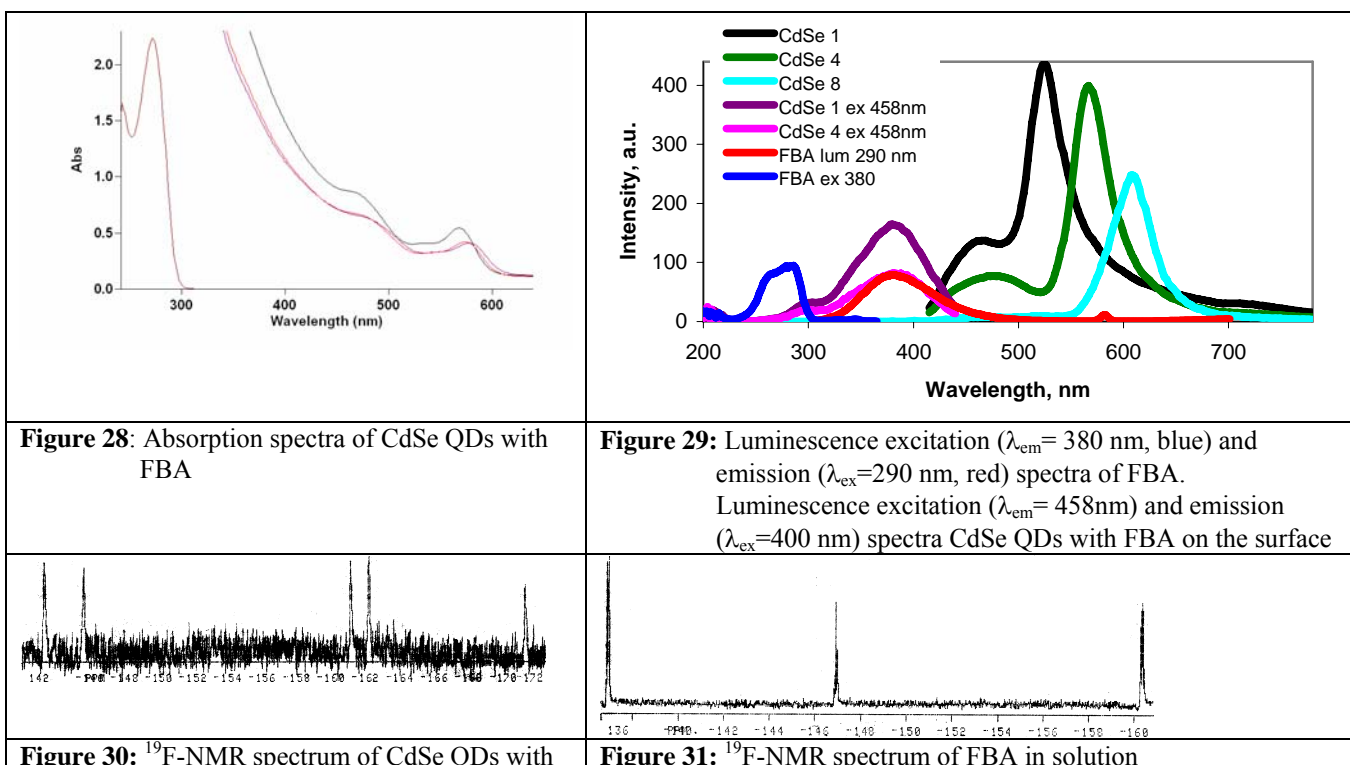


Figure 30: ^{19}F -NMR spectrum of CdSe QDs with

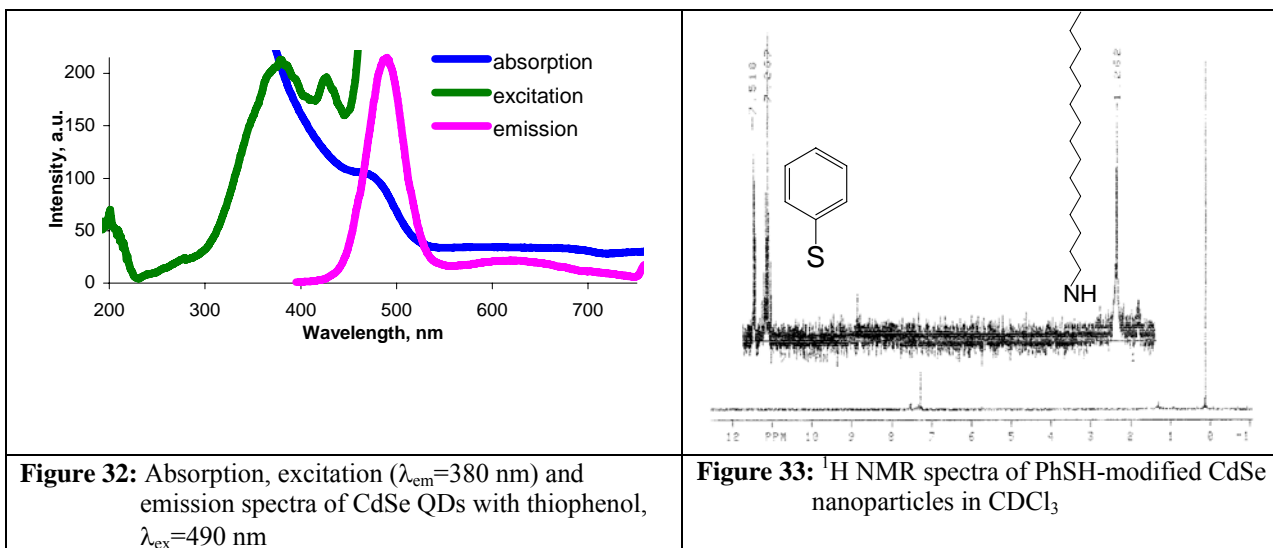
Figure 31: ^{19}F -NMR spectrum of FBA in solution

9) CdSe QDs synthesized from preorganized clusters $\text{Li}_4[\text{Cd}_{10}\text{Se}_4(\text{SPh})_{16}]$

Thiophenol (PhSH) was chosen as another type of sensing ligand, which has strong binding to CdSe surface. Synthesis of CdSe QDs from preorganized complex $\text{Li}_4[\text{Cd}_{10}\text{Se}_4(\text{SPh})_{16}]$ was used to bind PhSH on the QDs surface.

Approximately 55 g of HDA (hexadecylamine) was degassed under vacuum at 120°C. To the stirred solution of HDA under N_2 was added 1.0 g (0.28 mmol) of previously synthesized $(\text{Li})_4[\text{Cd}_{10}\text{Se}_4(\text{SPh})_{16}]^8$ using standard airless techniques, and the solution temperature was raised to 220-240°C (1°C/min). Growth rates depend on the initial reactant concentration and can be followed by absorption spectroscopy. At the desired crystal size, the reaction mixture was cooled by 20°C and left overnight to narrow the size distribution by annealing the nanocrystals. The CdSe was isolated by selective precipitation by addition of 100 mL of anhydrous MeOH and centrifugation. Excess HDA was removed by subsequent resuspension in MeOH and isolation by centrifugation.

This method of QDs synthesis also allows narrowing CdSe QDs size distribution (Figure 32). NMR spectroscopy proves presence of thiophenol and hexadecylamine on the surface of CdSe QDs (Figure 33).

**10) CdSe QDs with Naphthylamine (NA) or Heptafluoronaphthylamine (FNA)**

This method of synthesis of QDs was developed in order to place new sensing ligands, NA or FNA, on the surface of CdSe QDs. In a typical reaction procedure, CdO (0.103 g, 0.8 mmol) and stearic acid (0.911 g, 3 mmol) were placed into a three-neck flask and heated to 150°C under a dinitrogen flow for the synthesis of unmodified QDs, while the respective addition of NA (0.4 mmol) or FNA (0.4 mmol) to this mixture was utilized for the synthesis of the surface modified QDs. After CdO was completely dissolved, the mixture was allowed to cool to room temperature and 6 g of TOPO and 3 g of HDA were

added to the flask. The mixture was then heated to *ca.* 300°C under a dinitrogen flow. At this temperature a Se solution containing 0.632 g of Se powder in 4.2 mL of TOP was swiftly injected. After the injection, the temperature was reduced to 250°C. At the desired QD size, the reaction was stopped by removal of the heating bath. Aliquots were mixed with methanol and the precipitated QDs were separated by centrifugation. In order to remove unbound reagents, the process of dispersion in methanol and centrifugation was repeated several times.

To reduce intensity of emission of excimers, and to investigate influence of concentration of NA (or FNA) on the surface of QDs, we varied NA (FNA) concentration from 0.4 mmol (“0 times reduced”) to 0.02 mmol (“20 times reduced”), keeping all the other parameters the same. As can be seen from Fig. 34, reduction of the concentration of NA from 0.4 mmol to 0.06 mmol (“7 times reduced”) results in diminishing of the emission maximum at 395 nm that belongs to excimer. It was found that sensing properties of surface-modified QDs also depend on the NA (FNA) concentration.

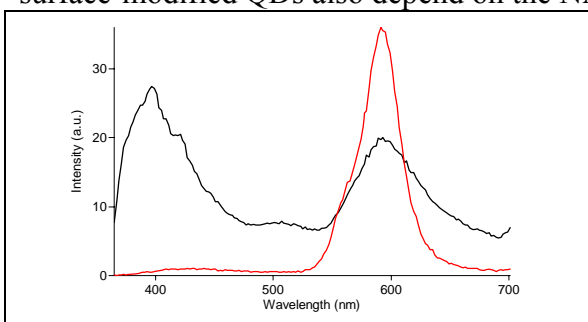


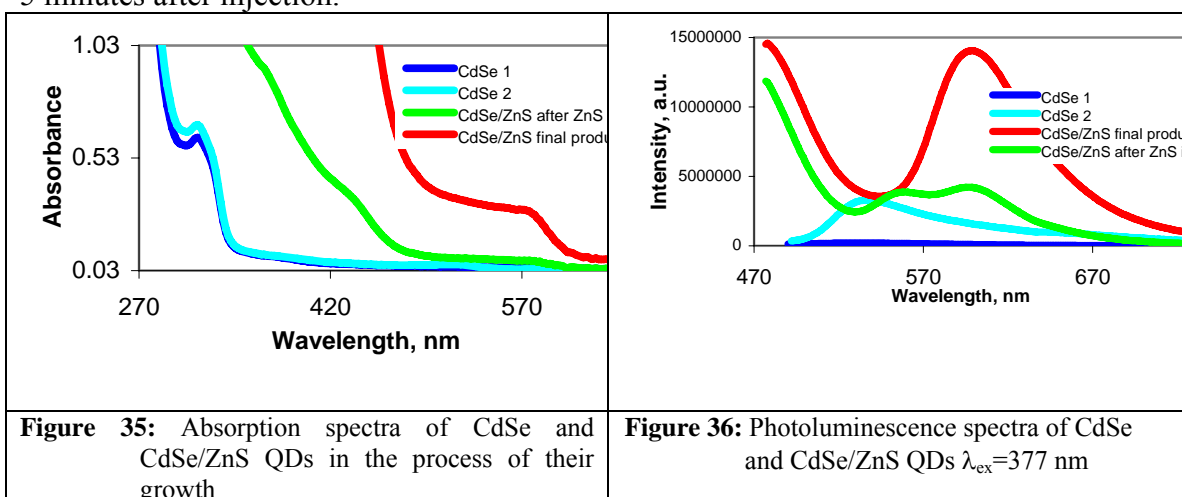
Figure 34: Emission spectra of CdSe QDs with NA, $\lambda_{\text{ex}}=350$ nm. Black – 0.4 mmol NA (not reduced), red – 0.06 mmol (7 times reduced).

11) CdSe/ZnS⁹ QDs

In order to improve stability and PL properties of CdSe QDs, a shell protected QDs were synthesized. A mixture of CdO 0.05 g (0.39 mmol), HDA 7.09 g (30 mmol) and TOPO 7.09 g (18 mmol) was heated up to ~340° C under N₂ flow on a Schlenk line. After the formation of a CdO–HDA complex, the system was allowed to cool to 260° C. As the temperature stabilized at 260° C for around 3–5 h, Se/TOP Se 0.0375 g (0.475 mmol) in 13.43 ml (50 mmol) TOP was quickly injected (<2 s) into the hot CdO/HDA/TOPO solution to proceed with the nucleation and the growth of CdSe nanocrystals. Subsequently, the Zn/S/TOP shell stock solution was injected to the core solution via the syringe, while the temperature remained at 230° C for the growth of CdSe/ZnS quantum dots. The injection of shell stock solution was divided into five portions at ~20 s intervals to minimize the nucleation of shell particles¹⁰. Upon injecting all the Zn/S/TOP shell stock solution, the reaction mixture was allowed to cool and stir at 110° C for a period of 1–2 h. The final molar ratio between Cd/Se (core) and Zn/S (shell) was kept constant, typically ~1:4.

ZnS/TOP shell stock solution was prepared by dissolving $\text{Zn}(\text{CH}_3)_2$ ~156 μl (0.312 mmol) and hexamethylsilathiane $(\text{TMS})_2\text{S}$ ~162 μl (0.137 mmol) in TOP 12 ml (48 mmol) at room temperature. The use of very volatile and reactive $(\text{TMS})_2\text{S}$ as a sulfur precursor requires a separated glove box that is currently unavailable. Other sulfur-containing sources should be considered and tested.

For the above-described core/shell formation, the precursor concentrations were largely diluted by TOP and HDA, resulting in a significant reduction of the particle growth rate. The resulting nanocrystals with selected diameters and shell thickness could thus be extracted at different aging times. Isolation and purification of crystallites was made in $\text{CHCl}_3/\text{CH}_3\text{OH}$ system. For characterization purposes, several aliquots of 100 μl of reaction mixture were taken by syringe and diluted by 2 ml of CHCl_3 . First few of them are of the CdSe particle solution, next – right after the injection of ZnS precursors, last – 5 minutes after injection.



Based on the data obtained we can conclude that initially formed CdSe nanoparticles are about of 1 nm in diameter (absorption band at 316 nm, Figure 32). Importantly, photoluminescence emission of QDs covered by ZnS is increased compared to the unprotected CdSe particles as shown in Figure 33.

12). TEM Analysis

The QDs have been analyzed using transmission electron microscopy, for investigation of the size distribution and corresponding crystallinity. As is shown in Figure 37 the QD are nominally 2 nm in diameter and as detailed in the HRTEM shown in the inset the QDs have a high degree of crystallinity. Dr. Oxana Vassiltsova received training on TEM instrumentation during the 2nd stage of the program and performed these measurements to confirm the size distribution calculated from the optical analysis.

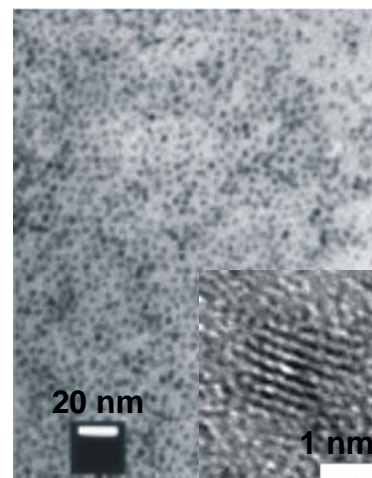


Figure 37: TEM micrograph of CdSe QDs, HRTEM of single QD shown in inset

Sensor Testing Station Setup

A micro-testing chamber has been installed and is shown in Figure 38. The test chamber has an internal volume of 20ml. The nanocomposite films are mounted in the chamber and gases of various compositions can be passed over the samples. A Varian Eclipse spectrofluorometer with a fiber coupling attachment is used for the fluorescence analysis of single nanocomposite films. In order to perform hydrocarbon (HC) exposure tests, a reliable HC vapor source is required. In this test, a vapor producing system via a Kontes bubbler and Environics gas mixing system was designed and integrated to deliver HC vapor to a 20cc stainless test cell with the vapor concentration adjustable from several ppm to several percent by changing of the gas flow rate. Both pressure and temperature of the bubbler is monitored to ensure a reliable vapor concentration delivered.

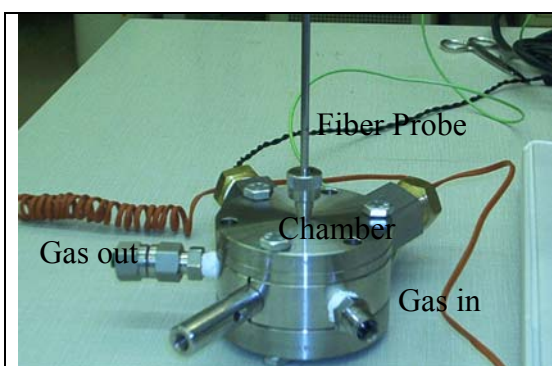


Figure 38: Test chamber used for QD exposure experiments

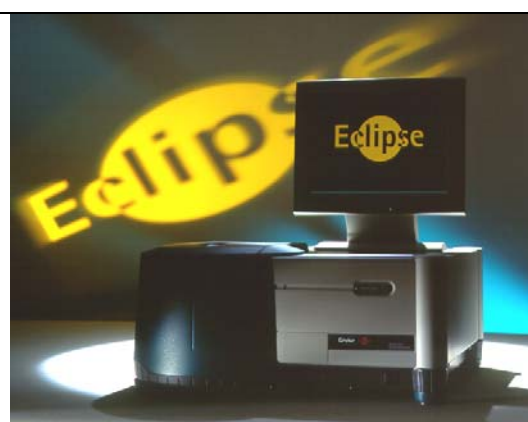


Figure 39: Varian spectrofluorometer to be used for parallel testing of QD film libraries

The HC response properties of the films were characterized by monitoring peak fluorescence intensity change of the QDs while the gas environment of the test cell was varied from pure N₂ to a HC vapor in N₂ through the computer controlled vapor producing system and an Environics gas mixing system. The total test gas flow, pressure and temperature were maintained at 1200 sccm, 760 Torr and ~ 25 °C, respectively. A Varian Eclipse Spectrofluorometer, Figure 39, was employed to record the fluorescence intensity via an optical fiber assembled accessory, which utilizes a bifurcated optical fiber bundle to direct a single (choosing 350nm in this test) excitation wavelength from a Xenon light source to the sample and collect emitted fluorescence light from the QDs for detection by a monochromator and a photomultiplier tube detector.

The initial testing chamber, Figure 38, only allows for one sample at a time to be investigated. **During year 2** of the program we increased our efficiency by depositing an array of films with QDs of varied composition and mass loading, different polymer hosts and polymer viscosities. This **library** of films, deposited in a **parallel** fashion could then be tested in a **parallel fashion** and **speed** the testing and analysis by **orders of magnitude**, as only films that tested with positive sensing attributes for the chemicals of interest would be processed for a detailed materials analysis. The Varian Eclipse system allows for the optical fluorescence testing of a library of films, up to 12 elements in the

deposited array, as a function of a change in the gaseous hydrocarbon environment. A miniature testing chamber has been designed, that has been placed in a standard micro-well plate holder accessory for analysis with the Varian Eclipse system. While this attachment was useful, it did not reduce the testing time as it is still a sequential measurement. We have recently been investigating a cost effective array imaging apparatus which will monitor the photoluminescence properties of 6 films simultaneously using a cost effective assembly of test equipment. This device assembly will be further investigated during phase III and IV with support from a pending proposal from a 2006-07 Region II UTRC Research Initiative.

Fabrication and Characterization of QDs/Polymer Nanocomposite Thin Film Sensors

Incorporation of the tailored QDs into a polymer matrix is a key step towards developing a quantum dot based chemical sensor. The polymer matrix not only serves as protection against oxidation of the semiconductor quantum dot but also used for a level of selectivity in the sensing process. During phase 2 we tested two different approaches to incorporate CdSe QDs in polymer films: first by drop coating of CdSe/PMMA solutions (in chloroform) on Si substrates and second - via *in situ* polymerization in four different monomers such as hexyl methacrylate, lauryl methacrylate, stearyl methacrylate and behenyl methacrylate that have been chosen to encapsulate QDs.

Drop-coated Nanocomposite Films and Sensing Performances

Semiconductor quantum dots/ polymer sensing films of micron-range thickness were prepared by drop coating of CdSe/PMMA solutions (in chloroform) on Si substrates. The QD concentration in the polymer matrix was designed to achieve a strong fluorescence output and an enhanced surface passivation for the dots at the same time. The detailed dot size and mole concentration in the polymer matrix are listed in Table 1, where the dots were covered with four respective surfaces groups in additional to TOPO ligand.

Table 1

	CdSe-SA/PMMA	CdSe-BA/PMMA	CdSe-FBA/PMMA	CdSe-NA/PMMA
QD Size (nm)	2.8	4.0	3.6	3.6
QD/Polymer ($\mu\text{mol/g}$)	0.25	0.2	0.44	0.18

Figure 40 displays the fluorescence spectrum of a CdSe-SA/PMMA film before and after HC exposure, where SA serves as a surface-stabilizing group. The spectra show good repeatability, indicating the efficient reversibility from the HC exposure.

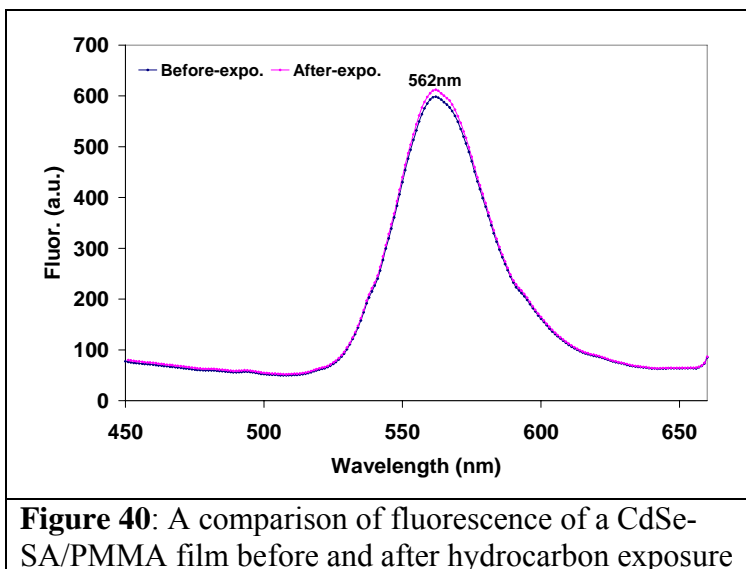


Figure 40: A comparison of fluorescence of a CdSe-SA/PMMA film before and after hydrocarbon exposure

The peak (562nm) fluorescence intensity resulting from excitation at 350 nm, was monitored in the exposure test with toluene and xylenes. Figure 41 shows that the fluorescence intensity reversibly increases upon exposure to toluene at concentration levels from ~ a thousand down to hundreds of ppm. The sensitivity to toluene is approximately 250 ppm. When exposed to xylenes, the fluorescence reversibly increases over a similar ppm concentration range (Figure 42), while the sensitivity of the film for xylenes is increased to approximately 100 ppm (estimated), a factor of 2.5 higher than that for toluene.

In contrast to the above response, when exposed to high concentrations, i.e. percent level concentrations of HCs, the fluorescence intensity displays a significant decrease rather than an increase in fluorescence intensity for both toluene and xylenes vapors, as shown in Figure 43. The decrease in fluorescence results from an interaction of the PMMA matrix with the absorbed hydrocarbon chemicals, which results in a wetting of the QDs/polymer film, and in turn light/matter interaction change. This effect became noticeable at levels as low as ~1250 ppm for xylenes, as indicated in Figure 42 by the decrease in signal change at the higher xylene concentrations.

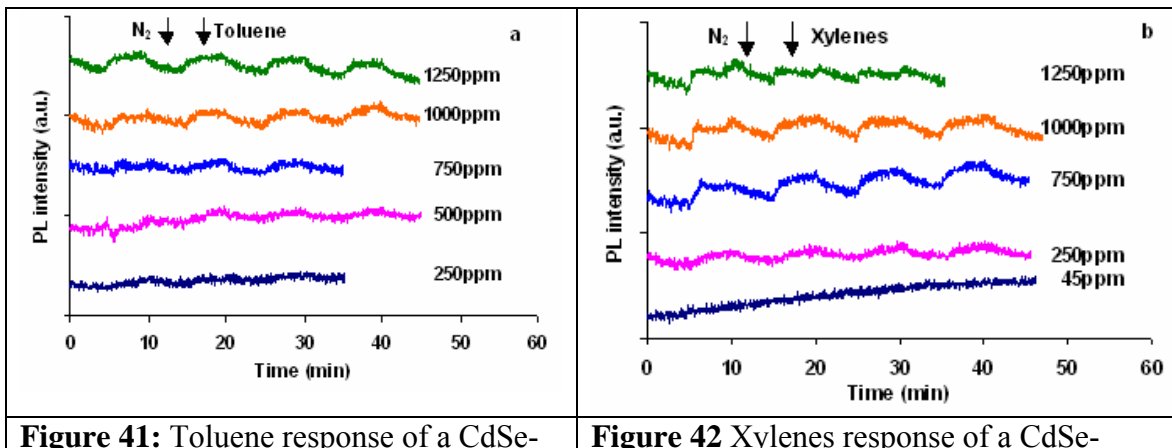


Figure 41: Toluene response of a CdSe-

Figure 42 Xylenes response of a CdSe-

SA/PMMA film as a function of time	SA/PMMA film as a function of time
------------------------------------	------------------------------------

In order to improve the sensitivity of the QDs towards the targeted HCs, aromatic sensing groups of fluorobenzoic acid (FBA), benzoic acid (BA), and naphthylamine (NA) were grafted to the QD surface, respectively, with an expectation of increasing the sensitivity towards the detection of the HCs. The fluorescence spectra of the QDs/surface group systems are presented in Figure 44, where for each of the curves the peak appearing at longer wavelength comes from the QDs emission while that at shorter wavelength is from the emission of the excimers of the bond surface groups. The presence of the excimer emission indicates competing photon absorption by the surface groups, which should be suppressed or reduced for enhanced photon absorption by QDs. The dependence of the sensing signal on the surface group coverage will be discussed later. The QD fluorescence peak of the each film was monitored under the excitation of the same 350nm light for the exposure experiments.

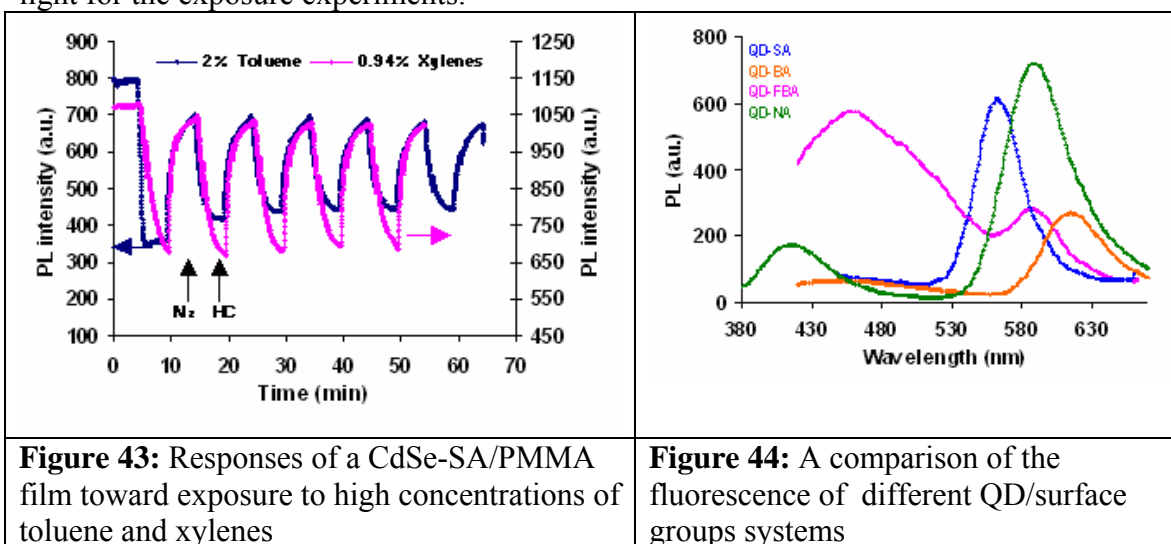


Figure 45 & 46 representatively displays the sensing performance of the QD-FBA/PMMA system. What is particularly promising is that these tailored QD-polymer films demonstrate an increased sensitivity to less than 15 ppm for xylenes (Figure 45) and less than 50 ppm for toluene (Figure 46), a factor of more than five enhancement in the sensitivity compared to the above SA-grafted QDs. This film also presents an improved selectivity for xylenes over toluene, as shown along with that of the QD-NA/PMMA film, in Figure 47, for 50 ppm concentrations.

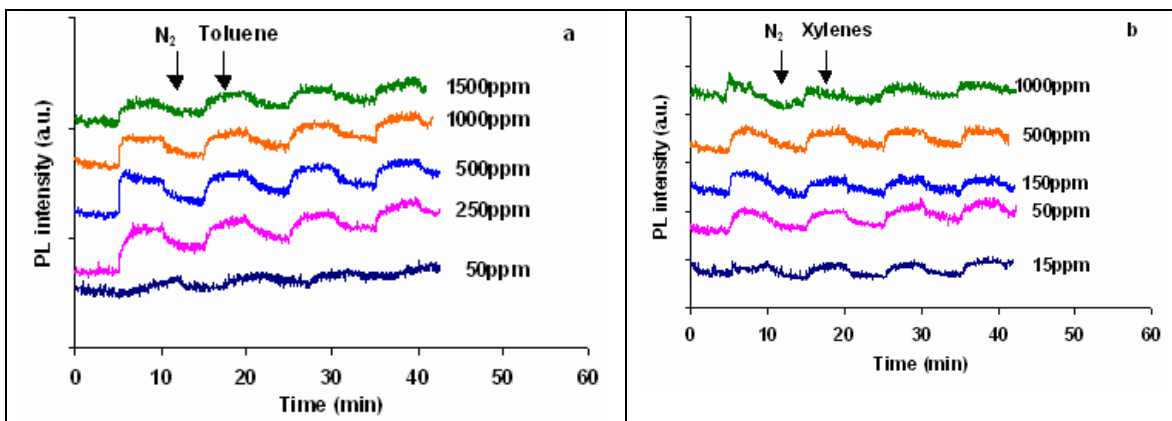


Figure 45: Xylenes response of a CdSe-FBA/PMMA film as a function of time

Figure 46: Toluene response of a CdSe-FBA/PMMA film as a function of time

Figure 48 compares the sensing capability of the QD sensors with different sensing enhancing groups attached to the QD surface towards 50 ppm of xylenes. It is clear that the aromatic group modified QDs have a higher sensitivity to xylenes compared to that of the stearic acid ligands. Furthermore, there is a slight increase in sensitivity for the fluorinated benzoic acid sensing ligand over the non-fluorinated benzoic acid and naphthylamine surface groups.

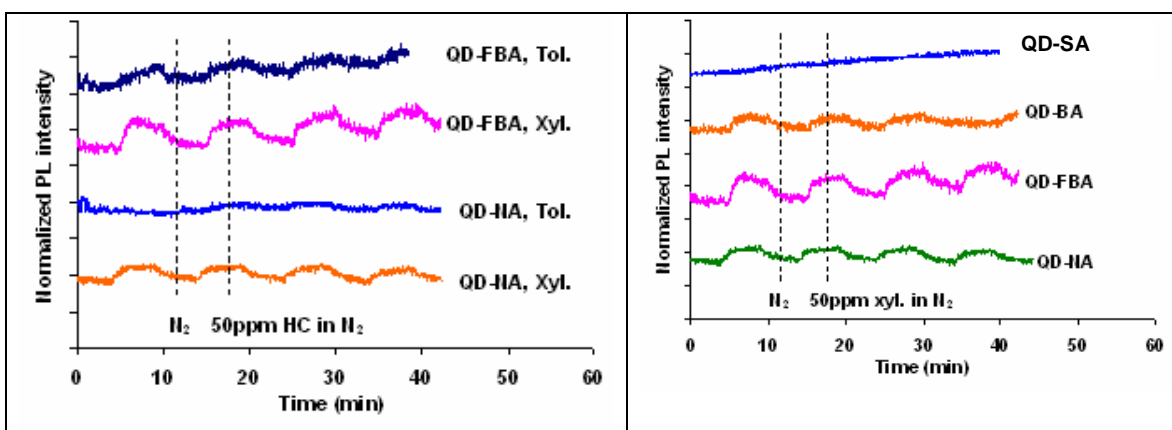


Figure 47: A comparison of sensitivities of a CdSe-FBA/PMMA film toward 50 ppm xylenes and toluene

Figure 48: A comparison of sensing capabilities of aromatic group tailored and non-tailored QDs films toward exposure to 50 ppm xylenes

The described sensor and performances has been repeatedly obtained through the reliable and reproducible sensor fabrication using the developed drop-coating method as illustrated in Figure 49 & 50 for the QD-FBA system.

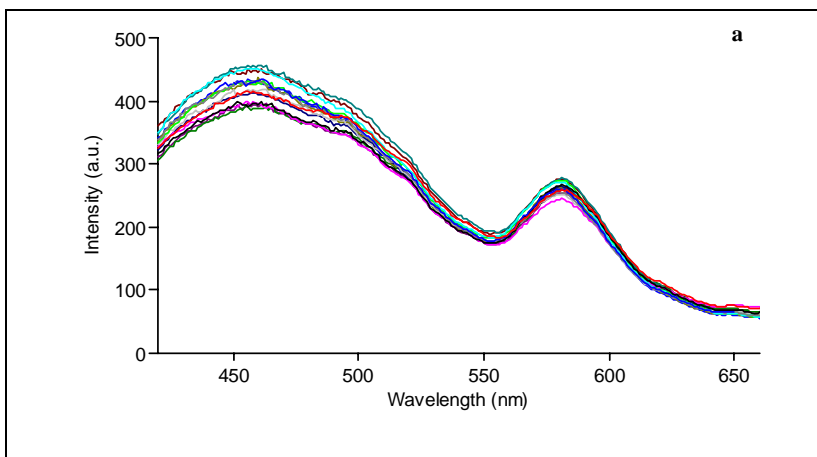


Figure 49: Fluorescence spectra of 15 drop coated QD-FBA films

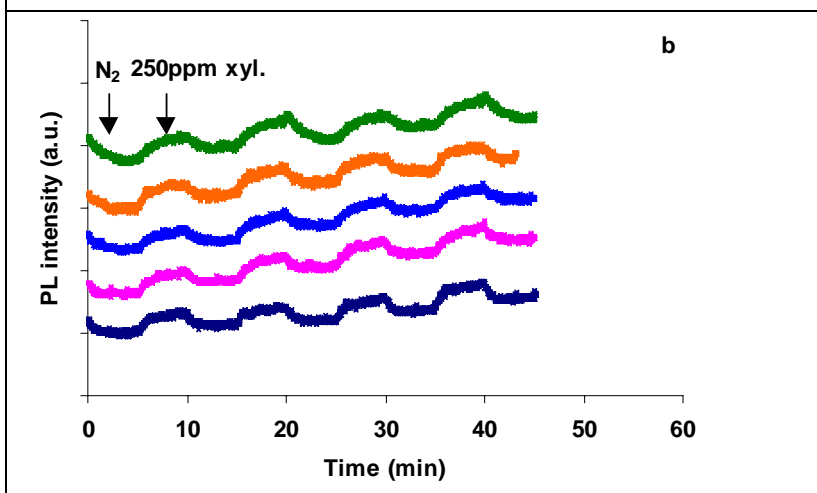
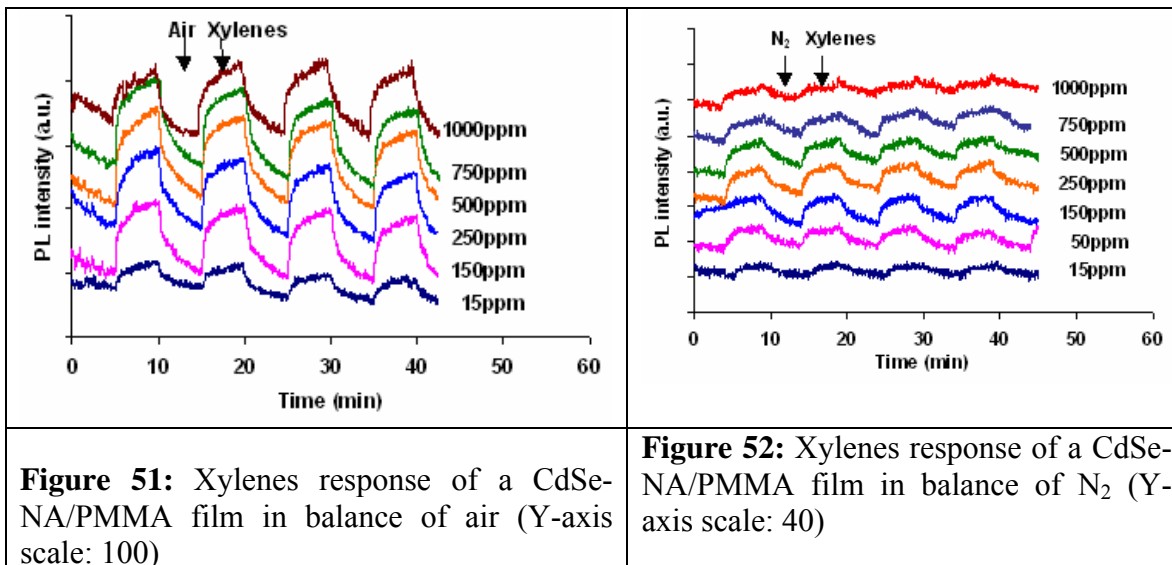


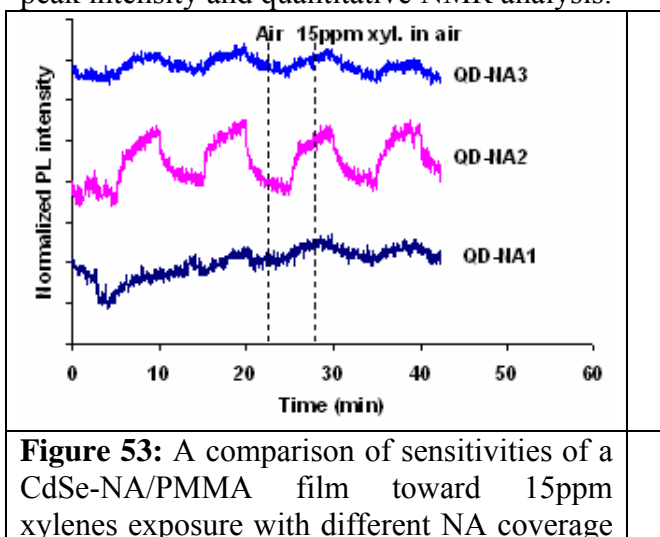
Figure 50: Peak fluorescence intensity responses of five of these QD-FBA films towards a 250 ppm xylenes exposure

All the above sensing results were collected for the sensor in N_2 as carrier gas. It is necessary to examine the sensing performance in air for practical applications, thus in phase II, the sensing characterization was carried out for HCs exposure in a balance of air. What is shown in Figure 51 is a representation of the PL responses to cyclic HC exposures from the QD-NA/PMMA film in dry air compared to that in N_2 (Figure 52). Although it is well known that any QDs will suffer from photooxidation/oxidation induced instability in air, the presented data demonstrate a remarkably stable performance of the QD sensing film in air. This stability is attributed to a combined stabilization from the QD surface bond protective groups and polymer host as an additional protective layer while retaining the QD's intrinsic environmental sensitivity. In particular, the signal change is large for all the tested concentrations of HC in air even at 15ppm xylenes.

These data indicate the potential application of our developed QD based sensor in real word.



As presented above, the QD sensitivity can be significantly improved by modification of the QDs with surface sensing enhancing groups. The degree of such surface group coverage has also shown a profound influence on the sensing ability as shown in Figure 53 and Table 2 for QD-NA system that was tested in air. There is trend showing a maximum signal change at a medium surface coverage, while the reduced signal change observed at a high surface coverage is due to the competing photon absorption by the surface bond group excimers as mentioned previously. The large signal change at 15ppm xylenes from the moderate NA covered QD sensor suggests that the detection limit at ppb level is achievable. Therefore, control of the surface coverage is also a key step to optimize the sensor performance via monitoring the surface-group excimer fluorescence peak intensity and quantitative NMR analysis.



(see table 2)	
---------------	--

Table 2 NA Coverage on CdSe Quantum Dots

Sample	QD-NA1	QD-NA2	QD-NA3
Moles of NA*	4.9×10^{-5}	4.0×10^{-5}	1.6×10^{-5}

*Moles of NA used for quantum dot synthesis

It has been seen that the fabricated QD sensors possess a certain degree of selectivity with the surface bound group providing the first level selectivity and the polymer host for the second level selectivity. Further improvement in selectivity for fingerprinting targeted chemical species can be accomplished by a smart sensor design using QD/polymer optical arrays that consist of either different QD sizes or the same QD size attached with different surface sensing enhancing groups or different polymer hosts or a combination of all of them. Figure 54 & 55 show some preliminary results on the sensor arrays made manually and a blend (two size QDs) fluorescence spectrum behavior compared to that of individual QDs. It is interesting to see (Figure 55) that in the blend of the two sizes of QDs, the fluorescence peak intensity from the smaller QDs (the peak at shorter wavelength) is reduced while that from bigger QDs (the peak at longer wavelength) is enhanced, due to fluorescence energy transfer through a reabsorption process. This means that it is possible to design a QD optical array pattern for chemical detection in speciation manner, while a well-controlled array fabrication can be realized via matured commercial tools like dip pen and ink jet printing. Much more about it will be performed in phase III and IV of this research program.



Figure 54: Optical microscope image of an QD array of different sizes or colors

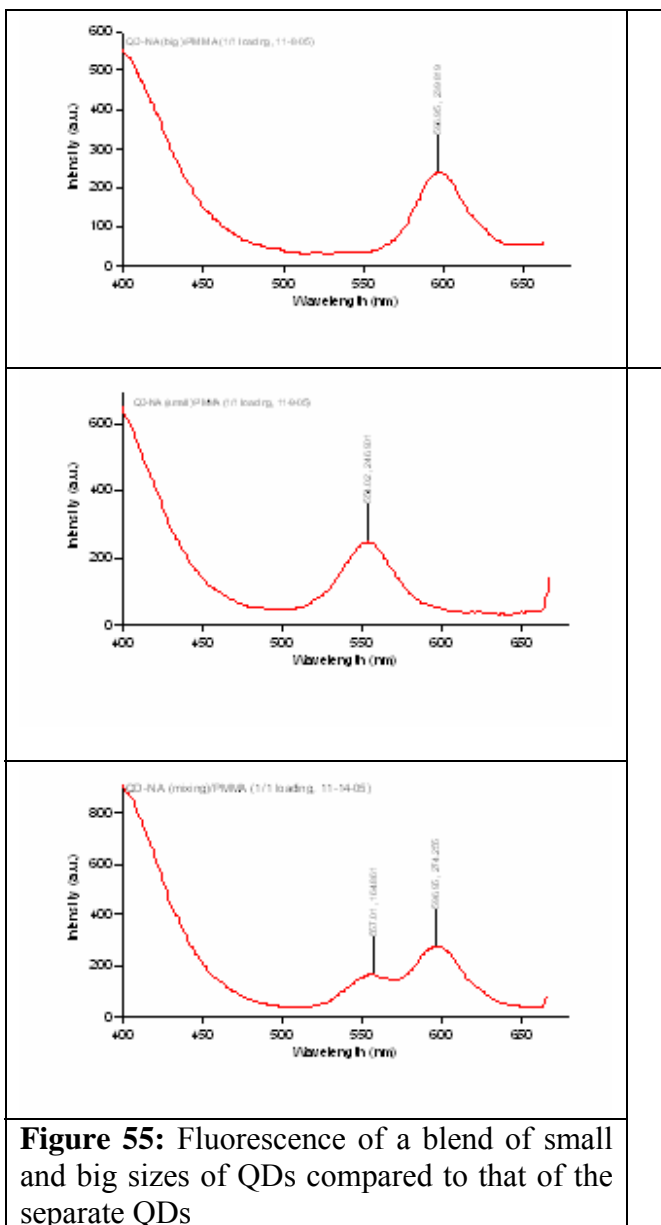


Figure 55: Fluorescence of a blend of small and big sizes of QDs compared to that of the separate QDs

Incorporation of QDs into Composite Films During *in situ* Polymerization

Long hydrocarbon chains of monomers (hexyl methacrylate, lauryl methacrylate, stearyl methacrylate and behenyl methacrylate) prevent aggregation and subsequent luminescence quenching of the QDs in polymer matrix, and allow better dispersion of QDs in polymer. CdSe QDs were mixed with monomer and TOP, while stirring. Then, ethyleneglycol dimethacrylate crosslinker was added to the QD-monomer solution with a 1:4 volume ratio of cross-linker to monomer and stirred. After azobisisobutyronitrile (AIBN) radical initiator was added and stirred. Then the mixture was polymerized in oven at 70 °C.

We tested polymer encapsulated QDs sensitivity towards exposure to hydrocarbons (toluene and xylenes) by monitoring QDs photoluminescence intensity changes relative to drop casted composite films of poly(methyl methacrylate) with QDs.

No matter what sensing groups were on the surface of QDs, better dispersion of QDs in methacrylate polymer matrixes with long hydrocarbon chains were less sensitive towards hydrocarbons when compared to the drop-coated mixture of poly(methyl methacrylate) with QDs, as shown in Figure 56. The detection limit to xylenes for the polymer-encapsulated QDs was 1200 ppm, that is about 80 times less sensitive than for the drop-coated QDs. Thus good dispersion of CdSe QDs in a polymer matrix appears to reduce the sensing properties of QDs/polymer composites.

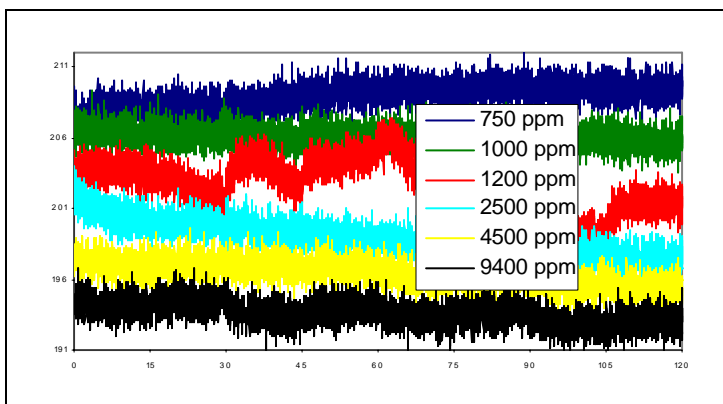


Figure 56: PL intensity changes of QDs-FBA 10wt% in PLMA while exposure to xylenes.

Conclusions

In summary, we have completed phases I and II of the research program for the development of a portable petroleum by-products chemical sensor. QDs of sizes ranging from 1.8 nm up to 10.4 nm in diameter have been synthesized. Emission wavelengths are in the range from 517 to 681 nm. CdSe QDs covered by ZnS surface were synthesized as well. Synthesized nanoparticles are stable, uniform and have good crystallinity (as proven by TEM) and have bright emission. We adapted several techniques of QDs synthesis with grafting of several new surface modifying ligands on the QDs surface. Attachment of these ligands to the surface of QDs was confirmed using ^1H and ^{19}F -NMR analysis. QDs with grafted groups on the surface were incorporated into various polymer matrices to form QDs-based composite films by drop coating and using *in situ* polymerization. We performed exposure tests of these films that have shown a high degree of selectivity and sensitivity to xylenes and toluene at ppm concentrations. What is particularly promising is that by tailoring the sensing ligands attached to the QD surface we are able to achieve a factor of 5 enhancement in the sensitivity of the QD-polymer film. For example, for perfluorinated benzoic acid ligand modified QDs display fluorescence intensity changes which are more pronounced than for nonfluorinated benzoic acid, which has different electrophilic properties. Selected systems have been tested in high hydrocarbon concentration range (up to 1%) and low concentration range (up to 15 ppm). At high

hydrocarbon concentrations changes in the polymer matrix are attributed to the fluorescence intensity changes observed. At low hydrocarbon concentrations the main contribution in fluorescence intensity changes is due to formation of π -complexes of aromatic hydrocarbons with sensing ligand on QDs surface, which result in the luminescence changes of the QDs. Better dispersion and incorporation of QDs into polymer during *in situ* polymerization decreases sensing abilities of QDs. The results obtained during phases 1 and 2 strongly support the proposed concept and show the potential of surface modified QDs for sensing applications.

References

- ¹ J. Hewitt, NYS-DOT, Private Communication
- ² New York State Department of Environmental Conservation, “New York State Inactive Hazardous Waste Disposal Site Remedial Plan: 2000 Report”, www.dec.state.ny.us.
- ³ P. Reiss, S. Carayon, J. Bleuse and A. Pron. Synthetic Metals (2003), 139, 3, 649
- ⁴ W. W. Yu, L. Qu, W. Guo, and X. Peng. Chem. Mater. (2003), 15, 2854
- ⁵ L. Qu, W. Yu, X. Peng. Nano Lett. (2004), 4, 3, 465
- ⁶ L. R. Becerra, C. B. Murray, R. G. Griffin, M. G. Bawendi, Investigation of the surface morphology of capped CdSe nanocrystallites by ³¹P nuclear magnetic resonance, J. Chem. Phys. 100 (1994) 3297-3300.
- ⁷ B. Gierczyk, G. Wojciechowski, B. Brzezinski, E. Grech, G. Schroeder, J. Phys. Org. Chem. 14 (2001) 691-696
- ⁸ Cumberland S., Hanif K., Javier A., Khitrov G., Strouse G., Woessner S., and Yun C. Chem. Mater. **2002**, 14, 1576
- ⁹ G-W Huang; Ch-Y Chen; K-Ch Wu; M. Ahmed; P-T Chou, Journal of Crystal Growth (2004), 265(1-2), 250.
- ¹⁰ M.A. Hines and P. Guyot-Sionnest. J. Phys. Chem. (1996), 100, 468