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ORGANIC AND HYBRID ORGANIC SOLID-STATE PHOTOVOLTAIC
MATERIALS AND DEVICES

RONALD ZIOLO

CENTRO DE INVESTIGACION EN MATERIALES AVANZADOS, S.C.

02/19/2014

Final Report

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14. ABSTRACT The interface between surface-modified semiconducting nanoparticles and polymers often contributes to the limited efficiency of hybrid photovoltaic cells and luminescent devices. We prepared, characterized and investigated (1) the nanocomposite formed between quantum dot (3 nm) cadmium sulfide capped with 3-mercaptopropyltrimethoxysilane (MPTS) and a copolymer of poly(phenylene ethynylene); (2) nanocomposites of silver nanowires with fluorescent poly(phenyleneethynylene); and (3) fulleropyrrolidine derivatives substituted with oligophenyleneethynylene-ferrocene conjugates. Publication of the results for (1) and (3) are under construction; those for (2) may be found in Nanocomposites of Silver Nanowires with a Fluorescent Poly(phenyleneethynylene): Morphological Implications for Photovoltaic Devices. Reyes Flores, Eduardo Arias, Ivana Moggio, Arturo Ponce, Carlos Gallardo-Vega, Fernando Galembeck, Rubia F. Gouveia, and Ronald F. Ziolo, Journal of Advanced Microscopy Research, 2012, 7, 158-169.					
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FINAL TECHNICAL REPORT

1. General Information:

- Collaborative Program: **CONACYT–CIQA–University of Akron–USAF/AFSOR.**
USAF/AFSOR grant (FA5990-10-1-0236), CONACYT grant (1010/189/10C-286-10)
- Initiative: **ORGANIC AND HYBRID ORGANIC SOLID-STATE PHOTOVOLTAIC MATERIALS AND DEVICES.**
- USA Institution: **University of Akron**
- Mexican Responsible/Institution: **Dr. Ronald Ziolo/ Centro de Investigación en Química Aplicada**
- USA Responsable/Institution: **Dr. Matthew Espe/ University of Akron**
- Report type: **Final**
- Reporting period start-ending date: **December 2010- September 2013**

2. Activities (summary):

- **Scientific Objectives:**

The scientific objectives of the proposed work include several ‘cutting edge’ challenges in synthetic organic and polymer chemistry, optical spectroscopy, solid-state nuclear magnetic resonance spectroscopy, materials science and theory, as elaborated on throughout the proposal. The scientific objectives focus primarily on light acquisition and energy capture, minimal photon loss in the films and devices, carrier extraction with minimization of electron-hole recombination, resistive losses, down conversions and so on and on device processing. Meeting the objectives will be greatly facilitated by the high degree of intra and inter team networking already in place in strategizing for the proposal and through the establishment of multiple feedback loops through Mexico/US video conferencing (including all students) needed to capitalize on the high degree of multidisciplinary correlations that exist in such a scientific study and endeavor.

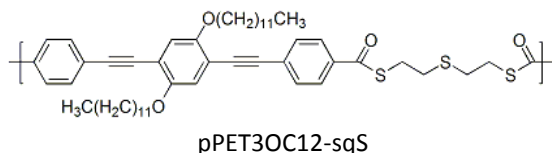
- **Obtained results:**

It was consolidated the inter-institutional and collaborative work by conjoining the diverse expertise of all the involved academic members, in such a way that the continuing research work was/is/will stated as follows: the organic molecular, supramolecular

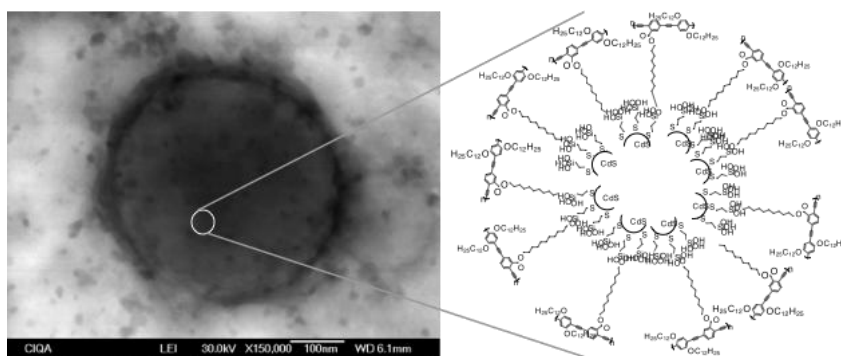
chemistry, electrochemistry, molecular order, photovoltaic devices development are carried out by CIQA research group. The materials are then sending to the University of Akron for the solid state nuclear magnetic resonance study by the proff. Matthew Espe research group. The ultrafast, transient & steady state spectroscopy study by the proff. David Modarelli research group, and the theoretical calculus and photovoltaic devices performance simulation by the Proff. Hendrick Heinz research group.

Materials synthesized and analyzed were divided in three main research lines:

- I. **Nanocomposites of silver nanowires with fluorescent poly(phenyleneethynylene).** Silver nanowires (AgNWs) with diameter of 81 ± 34 nm and length of $7.9 \pm 2.6 \mu\text{m}$ were obtained by the polyol method with co-injection of poly(vinylpyrrolidone) (PVP) and silver nitrate (AgNO_3) in refluxing ethylene glycol (EG) at $250 \mu\text{L}/\text{min}$. After a first survey on the effect of injection rate in the nanowires synthesis, composites were prepared with a conjugated fluorescent poly(phenyleneethynylene), hereafter called pPET3OC12-sqS. A concomitant study by Atomic Force (AFM) and Kelvin force microscopy (KFM) on an individual nanowire visualized in the composite shows that the thickness of the polymer coating varies along different scanning lines, consistently with the self assembly tendency of this polymer that forms, by itself granular type morphology. Heterojunction solar cells were fabricated with the polymer and AgNWs composites and [6,6]-Phenyl-C61-butyric acid methyl ester (PCBM) as electron acceptor material. The cells were not optimized in active layer preparation conditions such as solvent, thickness, annealing, or encapsulation in order to demonstrate the effect of the silver nanowires on the organic solar cells' intrinsic parameters. As a consequence of the self-assembly behavior of pPET3OC12-sqS, the efficiency of the solar cells made with the polymer and AgNWs composites was dependent on relative content of the polymer, PCBM and AgNWs. This study addressed the morphological implications of the incorporation of silver nanowires in active layers prepared with conjugated polymers that present the property to be assembled on the silver nanowires surface.



II. **Functionalization of CdS Quantum dots and nanocomposites with phenyleneethynylene copolymers.** CdS quantum dots of $3.02 \pm 0.46\text{nm}$ were synthesized in presence of 3-mercaptopropyltrimethoxy silane (MPS). This ligand was chosen in order to allow the successive functionalization with phenyleneethynylenes (PEs) through condensation of the methoxy groups of the silane capping agent of the nanoparticles and the OH terminal groups of the lateral chains of the PEs. The functionalization was corroborated by solid state nuclear magnetic resonance as a new peak at -58ppm appears and is ascribed to Si-O-CH₂-bonds. Moreover the peak related to the carbon α to the OH of the PEs at 63 ppm becomes weaker as a consequence of the bonding. XPS Si and C studies confirm also this bond. The hydrolysis of the methoxy groups of the silane and their successive polymerization, induced by the presence of the OH groups of the PE, gives rise to peculiar superstructures of 200-600 nm of diameter. The diameter depends of the pH of the medium being larger at basic pH and consistent with light scattering characterization. STEM analysis shows the presence of CdS clusters inside the larger particles and TEM tomography reveals that these superstructures are not empty. A possible schematic mechanism of formation of the particles is reported in the following:

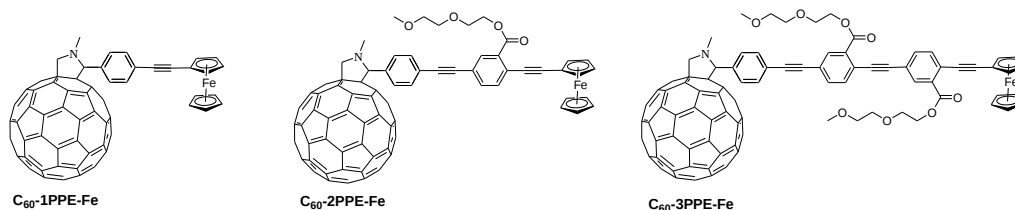


Molecular dynamics study carried out by Dr. Heinz group on CdS composites with oligomeric model systems supports the evidence that hydroxyl group of the phenyleneethynylenes tends to react with the trimethoxysilyl shell of the nanoparticle surface and this causes bending of the conjugated backbone. The photophysical properties of the composite studied at the University of Akron are practically identical to those of the copolymer. Even though electron-transfer upon polymer excitation is energetically feasible, it is not observed probably because of the large average CdS-polymer distance. Energy-transfer is also energetically

possible with CdS excitation, although evidence for it is weak, most likely as a result of the weak absorption of the CdS within the nanocomposites. Solar cells were fabricated with the composite in the ITO/PEDOT/composite/Woods metal configuration and considering that CdS could act as electron withdrawing and the polymer an electron donor material. The efficiency of these devices was very low ($10^{-4}\%$) which can be related to the superstructures formation and its implications in terms of electron transfer process (previously discussed) as well as exciton recombination. In fact even if exciton can be formed in the polymer, the distance from the electron acceptor material is larger than the exciton diffusion length (typical 10-20 nm). Despite the non-promising results in the solar cell application, the formation of the superstructure is an interesting and unexpected result for materials science, yielding several presentations, a PhD thesis and three papers in preparation.

III. *Synthesis of fulleropyrrolidine derivatives substituted with oligophenyleneethynylene-ferrocene conjugates.* A series of fulleropyrrolidine-bridge-ferrocene macromolecules were selectively synthesized by the Sonogashira reaction applying the step-by-step approach. The length of the bridge is constituted by 1, 2 and 3 phenyleneethynylene units (PPE) forming so the C_{60} -1PPE-Fe, C_{60} -2PPE-Fe and C_{60} -3PPE-Fe dyads. DQF-COSY, 1H , APT, DEPT-135 ^{13}C NMR characterization clearly corroborated the expected molecular structure, where the most representative 1H resonant signals correspond to the pyrrolidine heterocycle: N-CH₃ at 2.8 ppm, -CH₂- α -N- at 4.99, 4.95 and 4.34 ppm. Furthermore, negative matrix-assisted laser absorption ionization-time of flight mass spectrometry (MALDI-TOF) confirmed the oligomers' molecular structure by showing their expected molecular ion peak: for C_{60} -2PPE-Fe: m/z 1307.19 (M^- , calcd for $C_{95}H_{33}FeNO_4$: 1307.19); for C_{60} -3PPE-Fe: m/z 1553.30 (M^- , calcd for $C_{109}H_{47}FeNO_8$: 1553.30). The C_{60} -nPPE-Fe tryads present a main absorption peak due to the HOMO-LUMO transition shifting from 304 nm to 355 nm along with the increase of the conjugation length of the phenyleneethynylene chromophore. Additionally the bands due to ferrocene and fullerene could also be visualized. In general, the UV-Vis spectra match well the sum of the spectra of the individual components of the tryads suggesting that no ground state interactions occur. The fluorescence spectra are characterized by an emission at the same wavelength of that of the corresponding benzyl alcohol nPPE precursors but with a strongly reduced quantum yield. The "quenching" with respect to the nPPE emission is increasing with the number of nPPE units yielding a value of 250 for the C_{60} -3PPE-Fc. This behavior has

been previously observed in several fullerene dyads and tryads of conjugated systems and attributed to electron energy transfer from the conjugated backbone to the fullerene moiety, which is the most important requirement for an application in solar cells. Based on the photophysical characterization, C₆₀-oPE3-Fc is the most promising material for a device, study that is currently in progress.



3. Work group:

- **Researchers:**

Dr. Ronald Francis Ziolo
Dr. Eduardo Arias Marín
Dra. Ivana Moggio
Dra. Raquel Ledezma
proff. Matthew Espe
proff. David Modarelli
Proff. Hendrick Heinz

- **Students:**

Gleb Turlakov –PhD at CIQA---thesis defense September 2014
Arxel de León Santillán–PhD at CIQA---thesis defense May 2014
Marcos Joaquín Guillen–PhD at CIQA---thesis defense February 2014
Denisse Sánchez Ramírez–M.C. at CIQA---thesis defense December 2013
Erick Alonso Sánchez–M.C. at CIQA---thesis defense December 2013

- **Post doctoral fellows:**

Rosa Martha Jimenez Barrera-CIQA
Bimala Lama-University of Akron
Natalie Romano-University of Akron
Hua Liu-University of Akron

- **Temporal contracted personal:**

Marlene Rodríguez Rodríguez

Isela Elizabeth Sandoval Herrera

Herlinda Imelda Gallegos Mauricio

Layza Arizmendi Galaviz

María Isabel Martínez Espinoza

Anayantzing Hernández

- **Publications:**

Synthesis, Optical and Structural Properties of Sanidic Liquid Crystal (Cholesteryl)benzoate-ethynylene Oligomers and polymer. Griselda Castruita, Vladimir García, Eduardo Arias, Ivana Moggio, Ronald Ziolo, Arturo Ponce, Virgilio González, Joy E. Haley, Jonathan L. Flikkema and Thomas Cooper. *J. Mater. Chem.* 2012, 22, 3770.

Nanocomposites of Silver Nanowires with a Fluorescent Poly(phenyleneethynylene): Morphological Implications for Photovoltaic Devices. Reyes Flores, Eduardo Arias, Ivana Moggio, Arturo Ponce, Carlos Gallardo-Vega, Fernando Galembeck, Rubia F. Gouveia, and Ronald F. Ziolo, *Journal of Advanced Microscopy Research*, 2012, 7, 158-169.

Direct Synthesis of 2,5-Bis(dodecanoxy)phenyleneethynylene-Butadiynes by Sonogashira Coupling Reaction. Eduardo Arias, Ivana Moggio, Román Torres, Ronald F. Ziolo, José-Luis Maldonado, Kirk Green, Thomas M. Cooper, Geoffrey Wicks, Aleksander Rebane, Mikhail Drobizhev, Nikolay S. Makarov, Massimo Ottonelli, Giovanna Dellepiane, *European Journal of Organic Chemistry*, 2013.24 (2013) 5341-5352.

Celdas Solares Orgánicas con Heterojuntura en Masa Estructuradas con Nanoalambres de Plata. J. R. Flores-Noria, E. Arias, I. Moggio, A. Ponce, M. Lozano, M. L. López. XXXII *Encuentro Nacional y 1^{er} Congreso Internacional AMIDIQ*, ISBN: 978-607-95593-0-4, Vol. CD (2011) 3873-3883.

Synthesis and Optoelectronic Properties of Phenylenevinylenequinoline Macromolecules. Reyes Noria, Rosa Vazquez, Eduardo Arias, Ivana Moggio, Marlene Rodríguez, Ronald F. Ziolo, Oliverio Rodríguez, Dean R. Evans, Carl Liebig, submitted to *New Journal of Chemistry*.

Interaction of Substituted Poly(phenylene ethynylene)s with Core-Shell CdS Nanoparticles. Hua Liu, Matthew Espe, David A. Modarelli, Marcos J. Guillen, Eduardo Arias, Ivana Moggio, Ronald F. Ziolo, Hendrik Heinz. Under construction.

Simulation of Dye Sensitized Solar Cells by a Coarse-Grain Approach. Hua Liu, Miko Cakmak, Eduardo Arias, Ivana Moggio, Matthew Espe, David A. Modarelli, Ronald F. Ziolo, Hendrik Heinz. Under construction.

Facile functionalization of CdS Quantum Dots nanocomposite with a fluorescent Phenyleneethynylene copolymer. M.J. Guillén, E. Arias, I. Moggio, R.F. Ziolo, M. Mata, M. Espe, L. Bimala. Under construction.

Synthesis of fulleropyrrolidine derivatives substituted with oligophenyleneethynylene-ferrocene conjugates. Photophysical properties and photovoltaic devices. R. Flores, E. Arias, I. Moggio, D. Modarelli, N. Romano, H. Heinz, R.F. Ziolo. Under construction.

- **Presentations:**

A Phenyleneethynylene Copolymer CdS QD Nanocomposite - Synthesis, Structure and Properties. M.J. Guillén, E. Arias, I. Moggio, J.M. Mata, M.P. Espe, B. Lama, D.A. Modarelli, N. Romano and R.F. Ziolo, NANOSMAT-USA 2012, Tampa, Florida, USA, March 29, 2012. Oral presentation.

Photophysical Properties of Cadmium Sulfide Nanoparticles and Poly(phenylene-ethynylene) Composites. N. C. Romano, J. Joseph, M. J. Guillén, E. Arias, I. Moggio, J. M. Mata, M. P. Espe, B. Lama, R. F. Ziolo and D. A. Modarelli. University of Akron Student Innovation Symposium, UASIS, Akron, OH, USA, April 12, 2012. Poster.

Photophysical Properties of Cadmium Sulfide Nanoparticles and Poly(phenylene-ethynylene) Composites. N.C. Romano, J. Joseph, M.J. Guillén, E. Arias, I. Moggio, J.M. Mata, M.P. Espe, B. Lama, R.F. Ziolo and D.A. Modarelli, 43rd ACS Central Regional Meeting CeRMACS, Dearborn, MI, USA, June 8, 2012. Oral presentation.

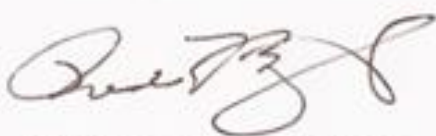
Photophysical Properties of Cadmium Sulfide Nanoparticles and Poly(phenylene-ethynylene) Composites. N. C. Romano, J. Joseph, M. J. Guillén, E. Arias, I. Moggio, J. M. Mata, M. P. Espe, B. Lama, R. F. Ziolo and D.A. Modarelli, University of Akron Student Innovation Symposium, UASIS, Akron, OH, USA, April 11, 2013. Oral presentation.

Interaction of Substituted Poly(phenylene ethynylene)s with Core-Shell CdS Nanoparticles. Hua Liu, Matthew Espe, David A. Modarelli, Marcos J. Guillen, Eduardo Arias, Ivana Moggio, Ronald F. Ziolo and Hendrik Heinz, 24th ACS National Meeting, Philadelphia, PA, USA, Aug. 19–23, 2012. Poster.

Simulation of Dye Sensitized Solar Cells by a Coarse Grain Approach. Hua Liu, Miko Cakmak, Eduardo Arias, Ivana Moggio, Matthew Espe, David A. Modarelli, Ronald F. Ziolo and Hendrik Heinz, 24th ACS National Meeting, Philadelphia, PA, USA, Aug. 19—23, 2012. Poster.

NAME AND SIGNATURE OF THE PRINCIPAL INVESTIGATOR

DATE



15-10-2013

Dr. Ronald Francis Ziolo

15 Octubre del 2012



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October 15, 2013

Final Technical Report for US/Mexican Basic Research Initiative

Award Number: FA9550-10-1-0236 (with CIQA, Saltillo, Mexico)

Title: Organic and Hybrid Organic Solid-State Photovoltaic Materials and Devices

Period of Performance: 05/15/2010 to 10/31/2013

PI: Matthew P. Espe, Department of Chemistry, University of Akron, Akron, Ohio 44325, and Omnova Solutions, Akron, Ohio (since 2012)
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Co-PI (PI for final report): Hendrik Heinz, Department of Polymer Engineering, University of Akron, Akron, Ohio, 44325
Phone: (330) 972 7467, Fax: (330) 972 3406, Email: hendrik.heinz@uakron.edu

CIQA PIs: Ronald F. Ziolo, Eduardo Arias, Ivana Moggio (CIQA's report is separate)

Executive Summary

The team of three PIs from the University of Akron, Ohio, has synthesized and characterized core-shell nanoparticles on the basis of CdS and conductive polyarylene ethynylene polymers for photovoltaic applications. The structure at the molecular scale was characterized using X-ray scattering, NMR spectroscopy, molecular simulation, and absorption-emission spectroscopy. Time-resolved laser studies yielded the relaxation behavior of these and further conductive oligomeric systems containing fullerenes and ferrocenes in collaboration with PIs at CIQA. The new oligomers and nanoparticle hybrids have potential applications in solar cells and may thus provide mobile energy sources for aircraft and soldier technologies. Modeling and simulation with coarse-grain models has been employed to understand transport processes in solar cells on the device scale to compute I/V curves and determine efficiencies for different recombination processes that can be helpful to optimize solar devices in the future. Three PhD theses have been completed as part of this project. Eight manuscripts are in progress, of which four are already published in peer-reviewed journals. In addition, about fifteen conference contributions have been made and the connection between the Mexican and US research laboratories were fostered through numerous joint teleconferences and visits.

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2.2. Photophysical Properties of Nanoparticles, Arylene Ethynylene Polymers, and Nanoparticle-Polymer Composites

2.3. Modeling and Simulation of Nanoparticle Interfaces and Solar Cells at a Device Level

3. Summary and Outlook

1. Project Statistics: Graduate Students, Publications, Impact on DoD Capabilities

1.1. Graduate Students. The project supported 3 PhD theses, 2 MS theses, and contributed to the work of several other graduate students. The PhD students include (1) Dr. Bimala Lama (Espe), “Synthesis and Characterization of CdS Nanoparticle/Polymer Bulk Heterojunction Composites”, defended August 2013, (2) Dr. Hua Liu (Heinz), “Investigation of Transport Mechanisms and Interfacial Properties of Solar Cells by Simulation”, defended June 2013, and (3) Natalie C. Romano (Modarelli), “Photophysical Studies of Oligo(Phenylene Vinylenes), Oligo(Phenylene Ethynyls), and Dyads for Photovoltaic Devices”, defense anticipated in Fall 2014. Supported MS these include (1) Jessi Baughman (Espe), “Solid State NMR Characterization of the Structure and Morphology of Bulk Heterojunction Solar Cells”, defended August 2012, (2) Jojo Joseph (Modarelli), “Time-resolved Photophysical Studies of Polyarenes and Dyads”, in progress, as well as (3) several graduate students in the Heinz lab and in the research group of Dr. Mukerrem Cakmak (University of Akron) working on “Processing of Thin Film Flexible Solar Cells” who exchanged knowledge about device-level questions and capabilities of simulations. The Ohio Department of Development funded these efforts through the Research Commercialization Program (\$8 million).

1.2. Publications and Presentations. Eight manuscripts are in preparation and more than fifteen presentations in the form of talks and posters have been made at international, national, and regional conferences. Seven further related manuscripts have been reported by Eduardo Arias, Ivana Moggio and Ronald Ziolo at CIQA (not mentioned in this report), bringing the total to 15 manuscripts. The manuscripts initiated from U Akron include:

- (1) Lama, B.; Espe, M.P. “Characterization of the Interface of CdS/Polymer Composites: Models for Bulk Heterojunction Materials” (in preparation).
- (2) Lama, B.; Espe, M.P. “Coupling Monomers and Polymers to Water Soluble CdS Nanoparticles” (in preparation).
- (3) Lama, B.; Feng, L.; Cavicchi, K.; Espe, M.P. “Nanocomposites of CdS and RAFT Synthesized Polystyrene” (in preparation).
- (4) Baughman, J.; Bailey, C.; Durstock, M.; Espe, M. P. “Impact of Thermal Annealing on the Structure of the Interface of a Bulk Heterojunction Composite” (in preparation).

- (5) H. Liu, M. P. Espe, D. A. Modarelli, M. J. Guillen, E. Arias, I. Moggio, R. F. Ziolo, H. Heinz "Interaction of Substituted Poly(phenylene ethynylene)s with Core-Shell CdS Nanoparticles" (in preparation).
- (6) H. Liu, M. Cakmak, E. Arias, I. Moggio, M. P. Espe, David A. Modarelli, R. F. Ziolo, H. Heinz "Simulation of Dye Sensitized Solar Cells by a Coarse-Grain Approach" (in preparation).
- (7) M. J. Guillén, E. Arias, I. Moggio, M. Espe, B. Lama, L. Yate, D. Modarelli, N. Romano, H. Heinz, H. Liu, R. F. Ziolo "CdS superstructures for photovoltaic devices" (in preparation).
- (8) R. Flores, E. Arias, I. Moggio, D. Modarelli, N. Romano, H. Heinz, H. Liu, R. F. Ziolo "Synthesis and photophysical properties of fullerene-phenyleneethynylene dyads" (in preparation).

The results from this study have also been presented and discussed at several national, international, and regional meetings in talks and posters. These presentations include:

- (1) "Characterization of the Interface of Polymer-Nanoparticle Composites" Lama, B.; Espe, M. P., Central Regional Meeting of the American Chemical Society, Indianapolis, IN, May, 2011.
- (2) "Hybrid Photovoltaic Materials: Characterization of Polymer-Nanoparticle composites" Lama, B.; Espe, M. P.; Central Regional Meeting of the American Chemical Society, Dayton, Ohio, May 2010.
- (3) "Hybrid Photovoltaic Materials: Characterization of Polymer-Nanoparticle Composites" Lama, B.; Espe, M. P.; CUGSR, The University of Akron, Akron, Ohio, July 2010.
- (4) "Characterization of Conjugated Polymer-Semiconductor Nanoparticles Composites" Lama, B.; Espe, M. P.; Central Regional Meeting of the American Chemical Society, Cleveland, Ohio, May, 2009.
- (5) "Photophysical Properties of Cadmium Sulfide Nanoparticles and Poly(phenylene-ethynylene) Composites." N. C. Romano, J. Joseph, M. J. Guillén, E. Arias, I. Moggio, J. M. Mata, M. P. Espe, B. Lama, R. F. Ziolo and D. A. Modarelli, UASIS, Akron, OH, April 11, 2013. Oral presentation.
- (6) "Photophysical Properties of Cadmium Sulfide Nanoparticles and Poly(phenylene-ethynylene) Composites." N. C. Romano, J. Joseph, M. J. Guillén, E. Arias, I. Moggio, J.

M. Mata, M. P. Espe, B. Lama, R. F. Ziolo and D. A. Modarelli, 43rd CeRMACS, Dearborn, MI, June 8, 2012. Oral presentation.

- (7) “Photophysical Properties of Cadmium Sulfide Nanoparticles and Poly(phenylene-ethynene) Composites.” N. C. Romano, J. Joseph, M. J. Guillén, E. Arias, I. Moggio, J. M. Mata, M. P. Espe, B. Lama, R. F. Ziolo and D. A. Modarelli. UASIS, Akron, OH, April 12, 2012. Poster.
- (8) “Simulation of Dye Sensitized Solar Cells” Hua Liu, Miko Cakmak, Eduardo Arias, Ivana Moggio, Matthew Espe, David A. Modarelli, Ronald F. Ziolo, Hendrik Heinz
Poster at University of Akron Student Innovation Symposium, April, 2012, Akron, Ohio
- (9) “Interaction of Substituted Poly(phenylene ethynylene)s with Core-Shell CdS Nanoparticles” Hua Liu, Matthew Espe, David A. Modarelli, Marcos J. Guillen, Eduardo Arias, Ivana Moggio, Ronald F. Ziolo, Hendrik Heinz.
Poster at ACS Fall National Meeting, Aug 22, 2012, Philadelphia, PA (by Hua Liu)
- (10) “Simulation of Dye Sensitized Solar Cells” Hua Liu, Miko Cakmak, Eduardo Arias, Ivana Moggio, Matthew Espe, David A. Modarelli, Ronald F. Ziolo, Hendrik Heinz
Poster at ACS Fall National Meeting, Aug 21, 2012, Philadelphia, PA (by Hua Liu)
- (11) “Interaction of Substituted Poly(phenylene ethynylene)s with Core-Shell CdS Nanoparticles” Hua Liu, Matthew Espe, David A. Modarelli, Marcos J. Guillen, Eduardo Arias, Ivana Moggio, Ronald F. Ziolo, Hendrik Heinz.
Poster at University of Akron Student Innovation Symposium, April 11, 2013, Akron, Ohio.
- (12-15) Research results were mentioned as part of several invited talks (H. Heinz), including:
UCLA, Materials Science and Engineering, January 25, 2013,
Georgia Tech, School of Chemistry, February 5, 2013,
Auburn University, Chemical Engineering, March 25, 2013,
University of Durham, UK, Chemistry, June 11, 2013,
University of Mainz, Germany, Condensed Matter Physics, July 9, 2013.

1.3. Collaborative and Broader Interactions. The project enabled the integration of research efforts between US investigators, investigators at CIQA in Mexico, and investigators at WPAFB, Ohio. We employed a dropbox folder for real time data exchange and held regular voice

meetings (phone). Ronald Ziolo (CIQA) visited UA and WPAFB several times during the project, and H. Heinz visited AFRL at WPAFB approximately every three months. Valuable input for the project has also been received from members of the dissertation committees at UA. UA investigators have not been able to visit the Mexican laboratories related to budget restraints during the project, and therefore the final workshop in Ensenada (MX) was very helpful. As a follow-up, a visit to Saltillo, MX, is anticipated as well as jointly organized symposia at ACS or MRS National Meetings in the near future.

1.4. Impact on DoD Capabilities. The project generated new insight into photovoltaic systems that may contribute to portable energy generation as needed in aircraft and for soldier technologies. We synthesized and characterized quantum dots with new functional surfactants and conductive polymers, including nanostructured “dyads” with donor and acceptor properties in the same molecule. Specific details of polymer conformations on the surfaces of CdS nanoparticles were investigated by NMR spectroscopy, absorption emission spectroscopy, time resolved laser spectroscopy, as well as modeling and simulation. The dyads and some of the nanoparticle-based composites efficiently absorb light and generate photocurrents. The testing in solar cells at the device scale still requires further efforts. A new molecular dynamics approach to simulate solar cells at the device level has been introduced and shown to yield insight in transport and recombination processes in promising correlation with measurements. The photophysics as well as findings by modeling and simulation developed in this project are encouraging further development.

2. Technical Activities

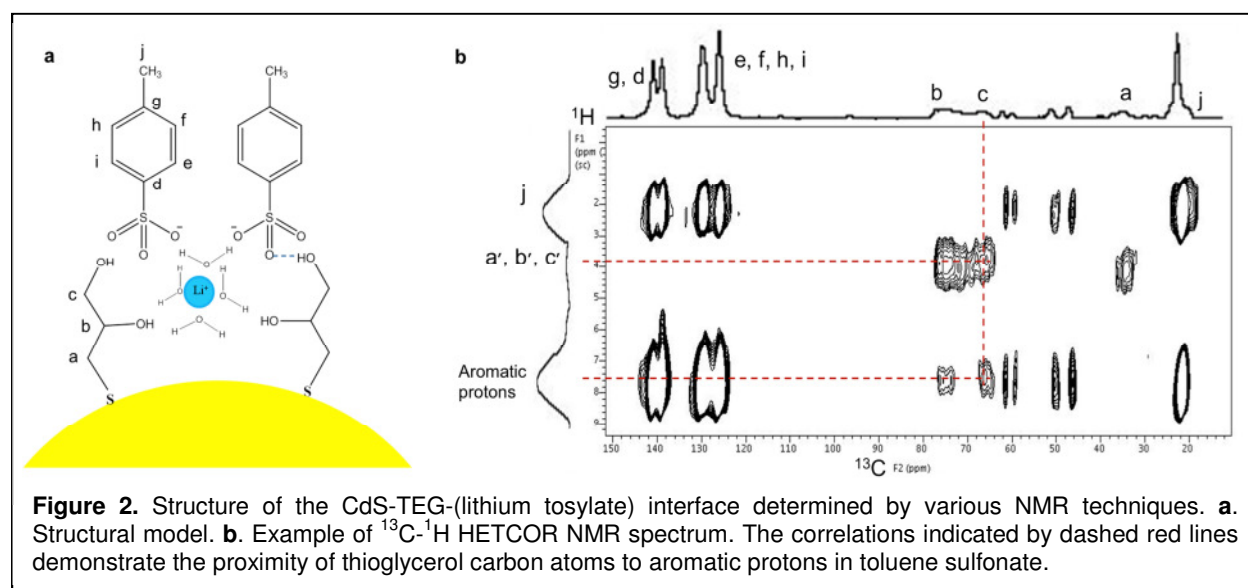
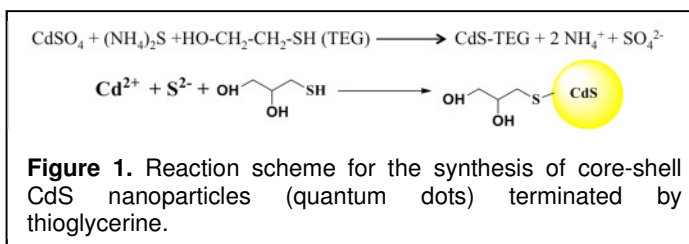
Hybrid organic solar cells are an emerging technology over the last 10 years and have reached comparable performance to dye-sensitized solar cells. While the best efficiencies are still under 12%, which is low in comparison to silicon and multi-junction cells (up to 45%), the cost of hybrid organic PV devices is much lower once in mass production and panels could be made in flexible shapes (see NREL solar cell efficiency roadmap). We have explored new quantum dot/organic materials combinations and introduced modeling approaches that help to understand and overcome current limitations.

2.1. Synthesis and Characterization of CdS Nanoparticle/Surfactant Interfaces (Espe). A number of organically modified cadmium sulfide nanoparticles were synthesized in the presence

of thiol modifiers. The nanoparticles are terminated by short chain thiols and the average nanoparticle size was determined by the UV/Vis absorption spectrum to be 4.6 nm. The method for

determination of nanoparticle size involved a calibration curve with an inverse relationship between the absorption edge and nanoparticle size. The CdS-thioglycerine nanoparticles were subjected to ^{113}Cd solid state NMR that indicate the absence of any Cd species other than sulfide, to ^{13}C NMR that identified the presence of a thioglycerine shell bound to the nanoparticle surface, as well as X-Ray diffraction.

Next, the interface of the nanoparticles with tosylate salts was investigated. This combination is a model for a polymer interface accessible to spectroscopic characterization, whereas the presence of large polymer chains complicates NMR characterization. Various NMR techniques (HETCOR, REDOR) yield a molecular interpretation of the interface (Figure 2). Accordingly, there is an ordered arrangement of toluene sulfonate, hydrogen bonding between the sulfonate group and the thioglycerol group, and Li^+ cations are located in local water pockets, maintaining a sizeable hydration shell. For the measurements, nanoparticles were incubated with lithium tosylate (LiTs) at different concentration. The chosen concentrations corresponded to various molar ratios between superficial thioglycerine and LiTs of about 4:1 to 1:10. Measurements of the tosylate/nanoparticle hybrids involved ^{113}Cd NMR, ^{13}C NMR, ^{13}C - ^1H HETCOR, and $^{13}\text{C}/^7\text{Li}$



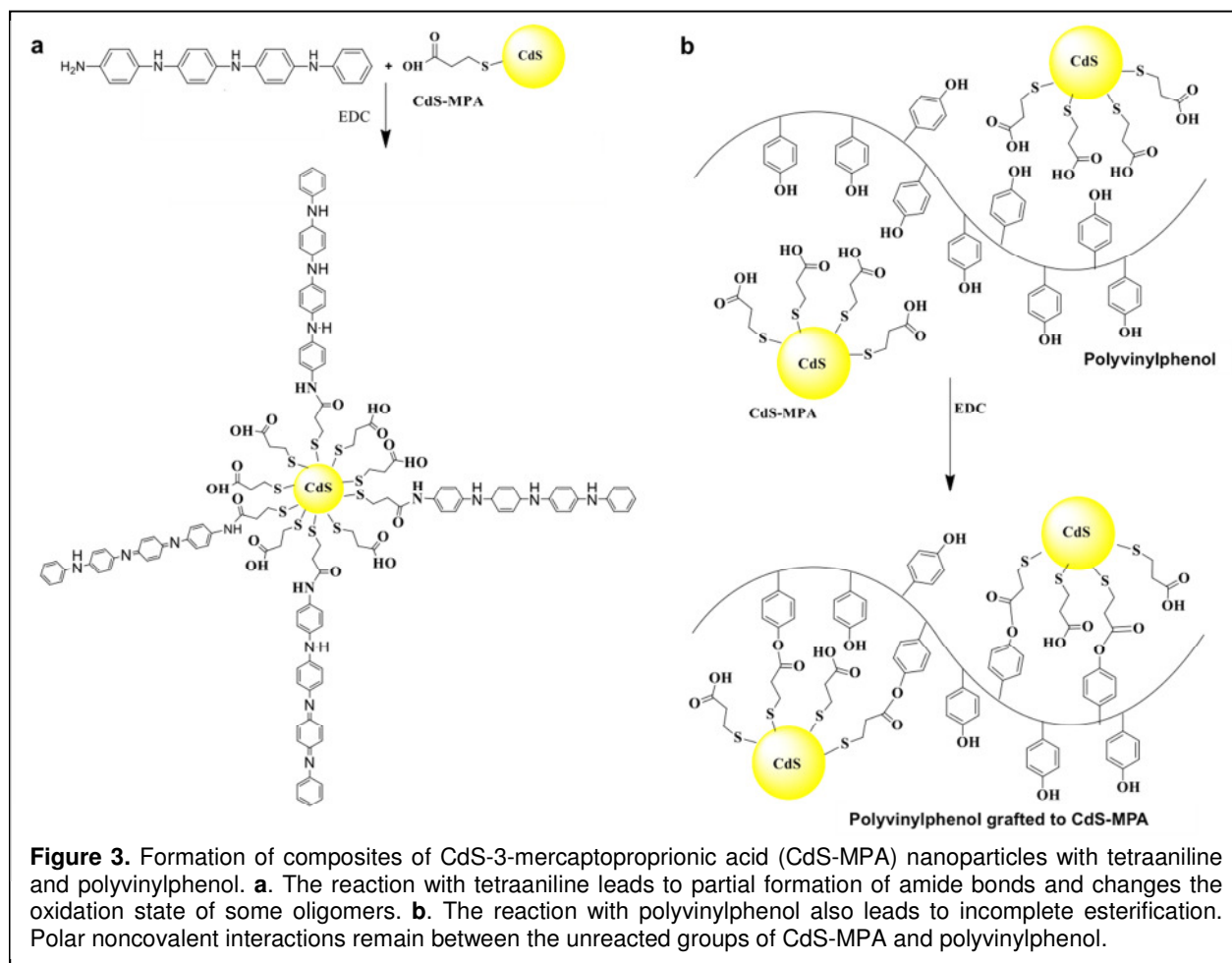
REDOR NMR techniques. The 2D correlation data allowed specific conclusions about the spatial molecular arrangement at the interface as shown in Figure 2. Accordingly, the alcohol groups interact with water molecules trapped in the nanoparticle shell and TsLi is pointing outwards to produce a hydrophobic layer outside the thioglycerol layer on the surface of CdS. This structure is similar to a double shell nanoparticle composed of the CdS core, a hydrophilic thioglycerol layer with entrapped water and cations, and a hydrophobic layer of aromatic rings, which could connect to further hydrophobic polymer chains. Additional measurements were also carried out for sodium tosylate instead of lithium tosylate with similar results. The only difference was a smaller hydration shell of sodium ions versus lithium ions.

Then, CdS-TEG nanoparticles were covalently linked to 2-naphthalenesulfonylchloride (NSC) leading to naphthalene sulfonates. NMR characterization confirmed a core-double shell structure and UV emission near 340 nm of the nanoparticles modified with NSC increased by a factor of about five. The coupling of CdS quantum dots with such molecules could introduce interesting optical properties. The CdS-TEG nanoparticles were also modified with polystyrene to analyze nanocomposite-like structures. A reaction with polystyrene sulfonyl chloride with CdS-TEG nanoparticles in basic medium (NaOH) was employed. Analysis of the reaction products showed that a portion of the sulfonyl chloride reacted with the CdS-TEG nanoparticles and formed covalent linkages while another part of the polystyrene sulfonyl chloride hydrolyzed to polystyrene sulfonic acid. The acidic residues were still found to interact with the CdS-TEG nanoparticles through non-covalent electrostatic interactions, not through covalent bonds.

Finally, surface modification of CdS with a different surfactant, 3-Mercaptopropionic acid (MPA), was tested. The concentration of reagents allowed control over the size of CdS-MPA nanoparticles in the 2 to 4 nm range. Characterization of the core-shell nanoparticles was performed analogously to CdS-TEG nanoparticles using UV, ^{113}Cd NMR, and ^{13}C NMR spectroscopy. The CdS-MPA nanoparticles were further modified with tetraaniline and with poly(4-vinylphenol) (Figure 3). Polyaniline has potential applications in sensors and organic conductors while poly(4-vinylphenol) is a dielectric with applications in organic transistors and TFT LCD displays. In the reaction with tetraaniline, a mixture of different isomers was obtained and less than half of the MPA molecules reacted with aniline tetramers to form amide bonds. In addition, the oxidation state of the aniline tetramer changed when conjugated with CdS-MPA nanoparticles (Figure 3a). The reaction of CdS-MPA with PVP in ethylene dichloride (EDC) and

acetonitrile also lead to partial esterification. The unreacted phenyl groups remained available for electrostatic interactions with the CdS-MPA surface, however (Figure 3b). The influence of covalent versus noncovalent interactions on the structure of the interface and the polymer was analyzed by molecular simulation (see section 2.3). Structural differences were found to be relatively insignificant so that the extent of the reaction may not significantly affect composite properties.

2.2. Photophysical Properties of Nanoparticles, Arylene Ethynylene Polymers, and Nanoparticle-Polymer Composites (Modarelli). Steady-state absorption-emission spectra and time-resolved measurements of absorption, emission, and fluorescence were recorded for a number of different samples. These data explain the light harvesting features of the modified quantum dots and polymer assemblies, as well as the effect of chemical substitution on charge transport properties. The analysis has been carried out for CdS nanoparticles modified with 3-



Mercaptopropyltrimethoxysilane (MPS), CdS-polymer composites, and for ferrocene-oligo(phenylene ethynylene)-buckminsterfullerene molecules (triads).

The CdS-MPS nanoparticles are similar to CdS-MPA (see section 2.1). The difference consists in replacement of the terminal carboxylate group by a trimethylsilyl group that might be more reactive in cross-linking with polymers (Figure 4). The structures of the CdS-MPS nanoparticles and of the two polymers for formation in composites are shown in Figure 4a. Absorption spectra indicate the characteristics of Polymers 1 and 2, as well as the lack of strong absorption by CdS-MPS. The composites after reaction with polymers 1 and 2 show comparable absorption to the neat polymers, except that the intensity is reduced for the NP-Polymer 1 composite at lower wavelengths around 300 nm (Figure 4b). The emission spectra also indicate a high level of similarity between the polymers and the composites (Figure 4c). The emission intensity of the composites is also higher than for the polymers alone, indicating the stimulated emission of the CdS-MPS quantum dots. The absorption-emission data were subsequently used

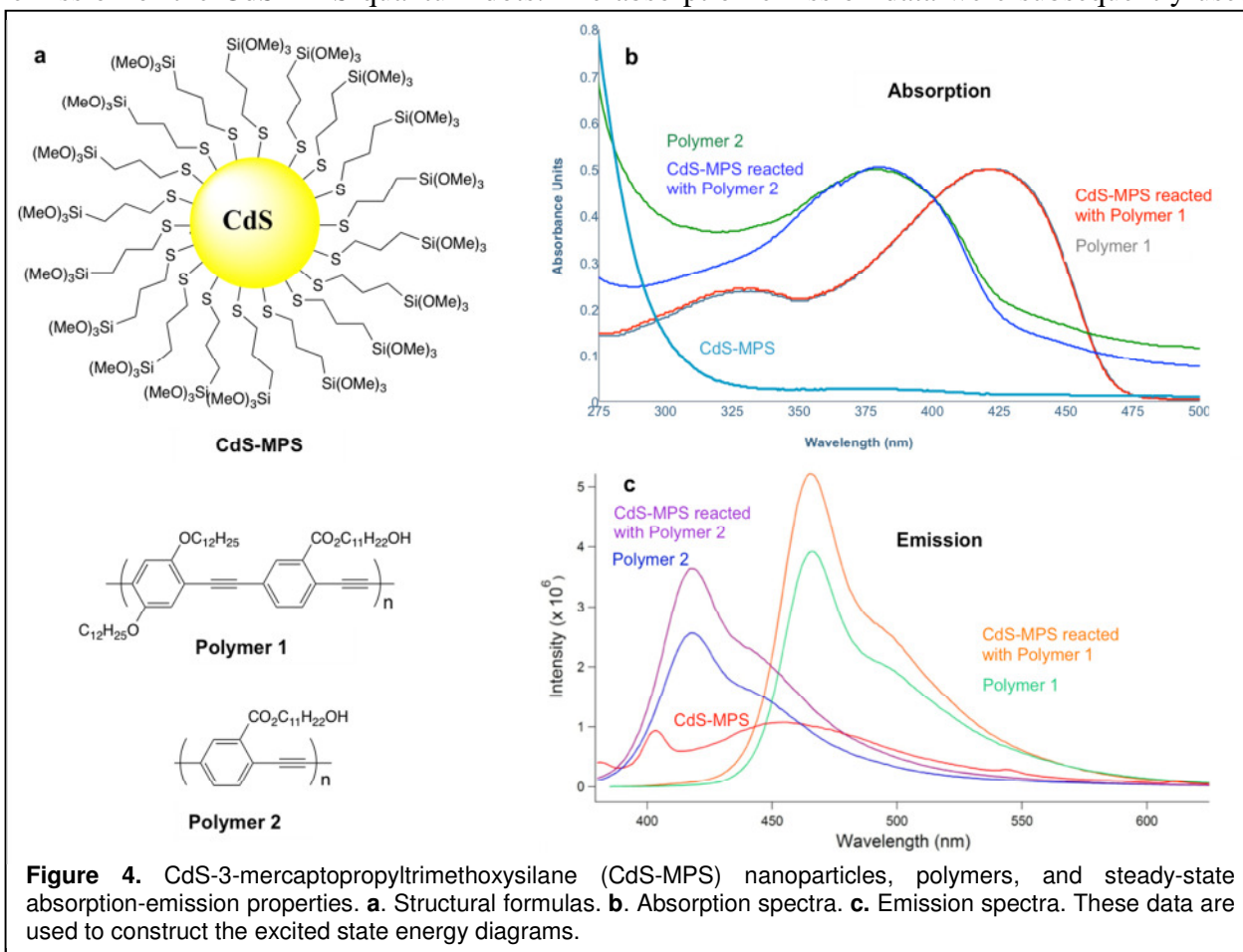
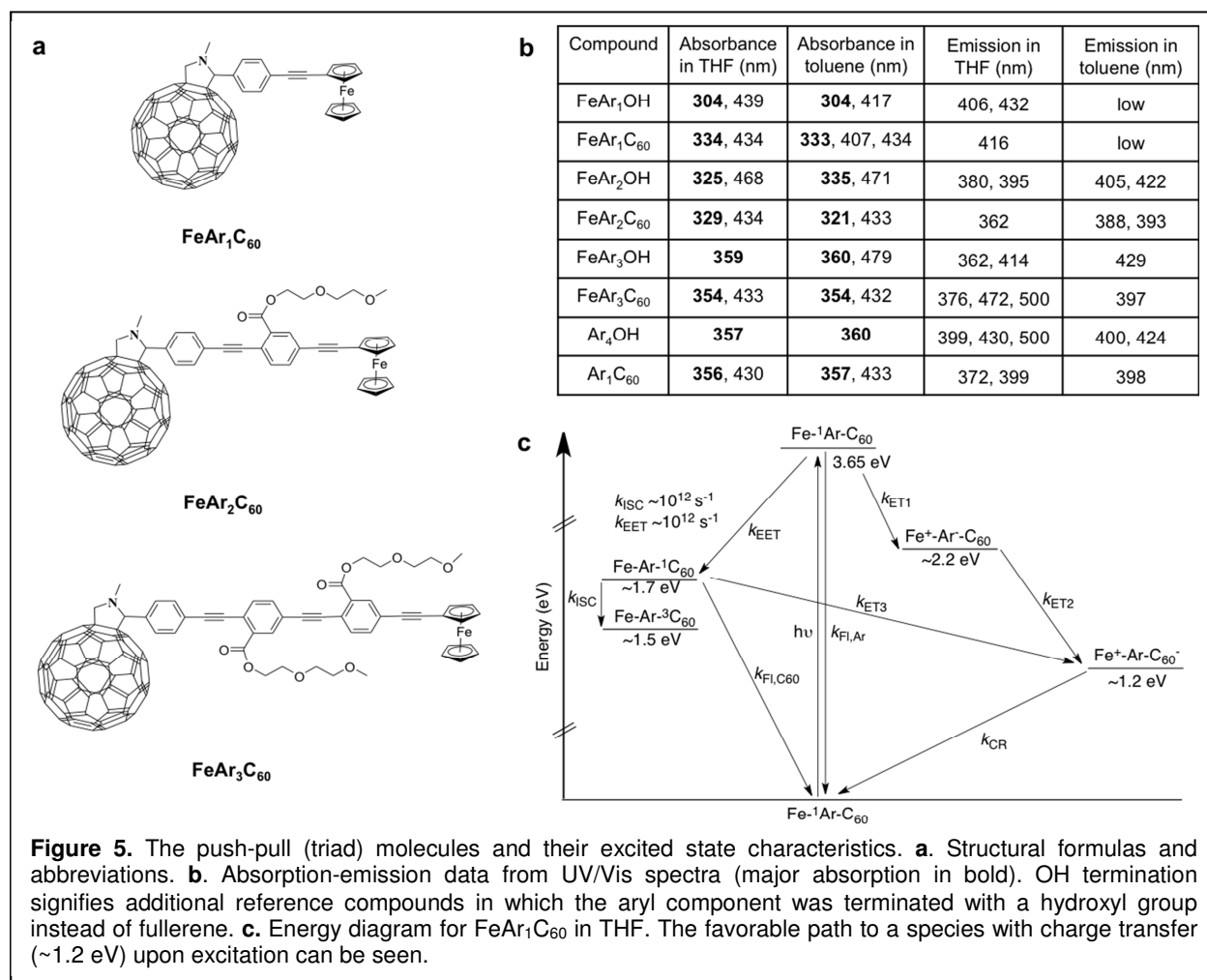


Figure 4. CdS-3-mercaptopropyltrimethoxysilane (CdS-MPS) nanoparticles, polymers, and steady-state absorption-emission properties. **a.** Structural formulas. **b.** Absorption spectra. **c.** Emission spectra. These data are used to construct the excited state energy diagrams.

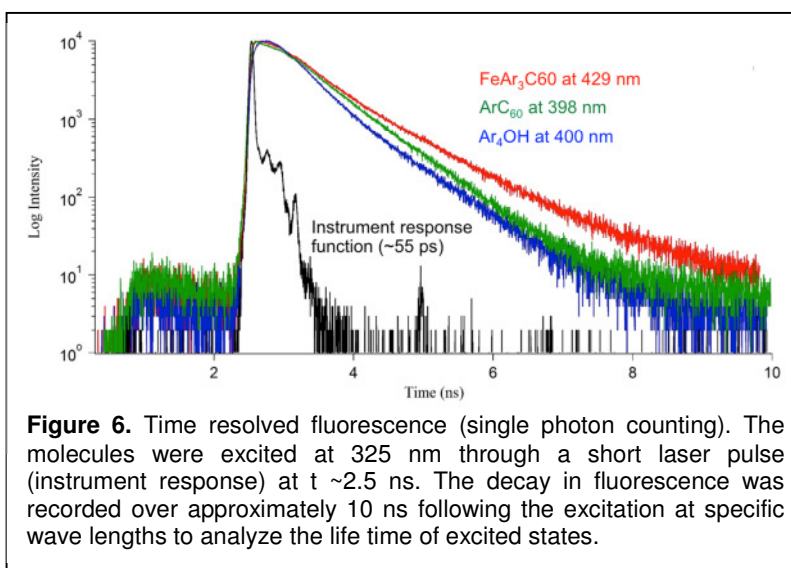
to generate the steady-state energy diagram of excited states under consideration of the contributions of the vibration states to the electronic transitions.

In addition, time-resolved fluorescence spectroscopy was performed using initial laser pulses to stimulate absorption followed by single photon counting. Different excitation wavelengths of 290 nm and 325 nm were employed, and for each excitation the fluorescence response was recorded at higher wavelengths for durations of approximately 10 ns to characterize the emissions. The observed relaxation processes were then modeled as a superposition of three exponential decay processes and the characteristic times τ determined (examples of such data will be illustrated for the triads below). The CdS(MPS) nanoparticles are weakly emissive, with lifetimes in the 700 ps – 2 ns time-scale. The range of lifetimes measured is a function of different trap states generated at different excitation energies. The photophysical properties of the two polymers indicate a longer lifetime for polymer 1, consistent with dialkoxy substitution



on one of the aryl rings that minimizes decay induced by spin-orbit coupling (Figure 4a). Longer lifetimes were observed at longer wavelengths, consistent with energy redistribution. The photophysical properties of the polymer-nanocomposites are similar to the polymer. The emission lifetimes were observed to be longer with an excitation wavelength of 290 nm, consistent with excitation of polymer and of CdS, the latter of which likely transferred energy to the polymer. Even though electron-transfer is energetically feasible, it could not be observed with either CdS or polymer excitation, probably because of the comparatively large average CdS-polymer distance, which amounts to more than seven saturated chemical bonds (a nonbond distance of ~ 1 nm). Energy-transfer may be energetically possible through CdS excitation, although evidence for it is weak and most likely associated with the weak absorption of the CdS within the nanocomposites.

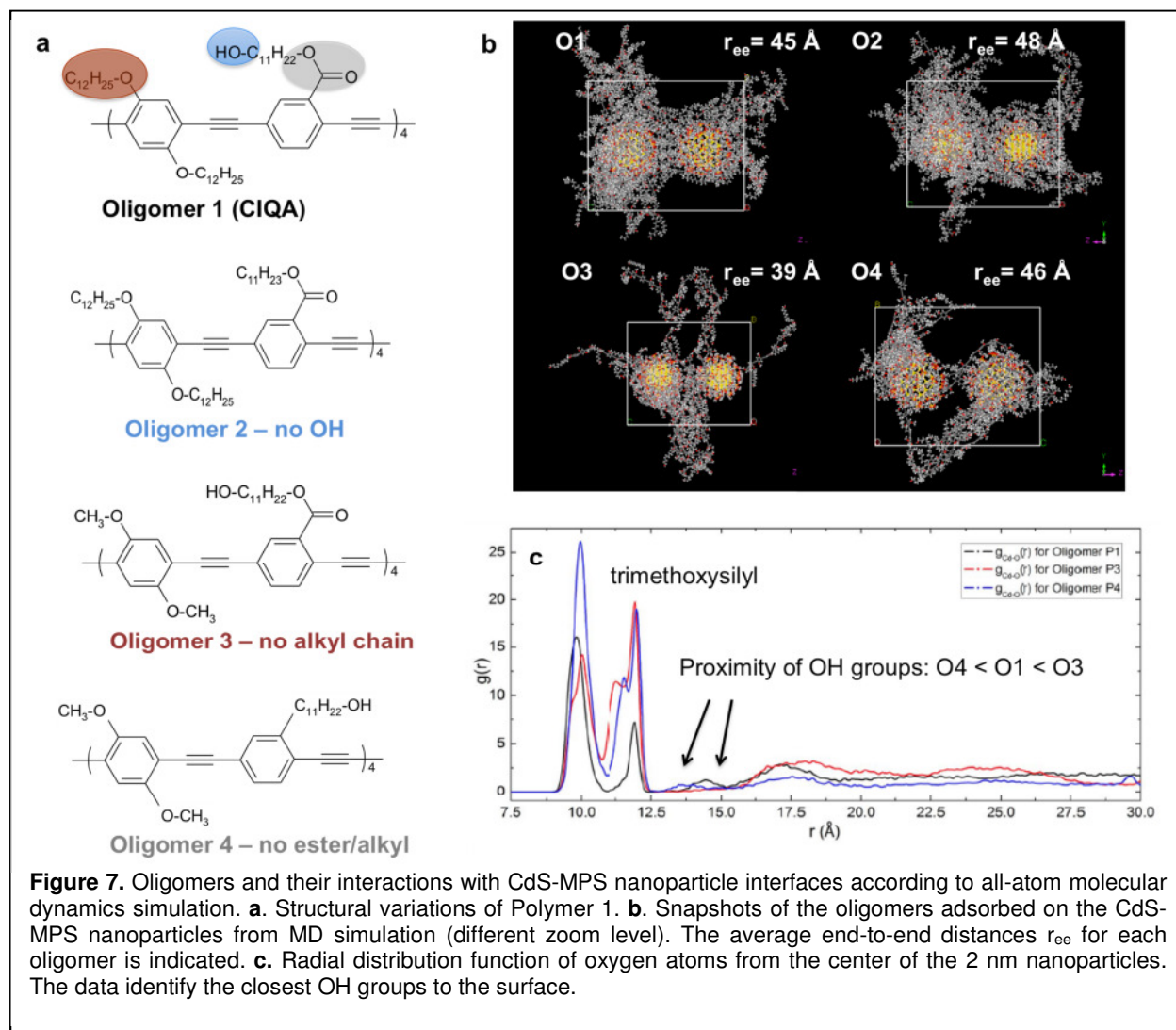
A higher potential for charge transfer was identified for push-pull molecules composed of ferrocene, oligo(phenylene ethynylene), and buckminsterfullerene C_{60} (Figure 5). These compounds were synthesized in Arias and Moggio's lab (CIQA) and characterized for their optical and electronic properties at UA (Figure 5a). The triad molecules, in a simplified notation $Fe-Ar_n-C_{60}$, had three spacer lengths ($n = 1, 2, 3$) and were studied in the two solvents THF and toluene. The absorption spectra show oligomer $\pi-\pi^*$ transitions that undergo a red-shift with increasing spacer length (Figure 5b). Steady-state and time-resolved emission spectra have been collected, although these data remain somewhat inconclusive regarding the nature of the excited state dynamics. The energetics for energy transfer and electron transfer have been elucidated and indicate that energy-transfer from the excited spacer to the C_{60} is quite favorable (Figure 5c). Electron-transfer from both singlet C_{60} and singlet Ar is energetically favorable as well. Since both moieties are likely excited in emission experiments, more work will be necessary to elucidate the contributions of either pathway.



Femtosecond transient absorption experiments are necessary to completely understand the dynamics in these experiments. Further time correlated single photon counting (TCSPC) and quantum yield experiments for the different systems and control systems are in progress to complete all photophysical aspects of this project. An example of the time resolved fluorescence is shown in Figure 6 and lifetimes of excited states over 1 ns have been identified.

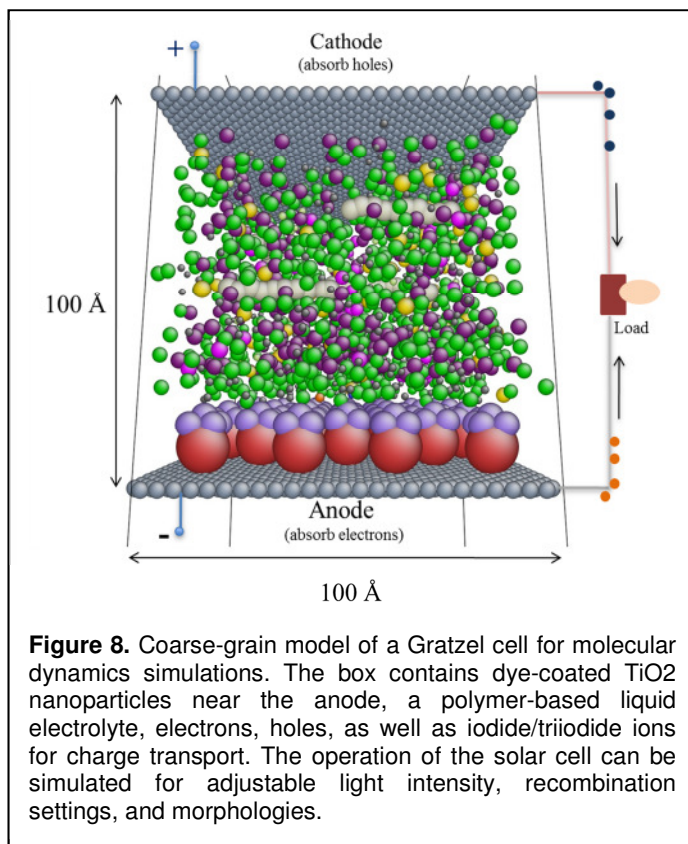
2.3. Modeling and Simulation of Nanoparticle Interfaces and of Solar Cells at Device Level (Heinz). Modeling and simulation has been carried out to understand the orientation of polymers near the nanoparticle surfaces as well as the transport and recombination processes in a solar cell at the device level for payoffs in the longer term. For the analysis of the arrangement of polymers on the nanoparticle surfaces, we prepared models of CdS-MPS core-shell nanoparticles, polymer 1 (Figure 4a) as well as some structurally similar isomers of polymer 1 in the form of 4-mers (Figure 7). We employed all-atom models including new parameters for CdS with atomic charges of +1.0e and -1.0e on S to reflect covalent and ionic bonding contributions according to an Extended Born model. The simulation boxes contained 20 oligomers, one or two nanoparticles in equilibrium, and were subjected to extensive molecular dynamics simulations with an extended PCFF force field (>10 ns), aided by annealing and multiple parallel simulations to sample the conformation space effectively (Figure 7b). We analyzed the equilibrium structures for surface contact of hydroxyl and ester groups, polymer mobility on the surface, end-to-end distance of the adsorbed polymer chains, and the effect of partial covalent bonding of Polymer 1 to the nanoparticle surface. All oligomers containing hydroxyl groups showed close contact of these groups to the surface of CdS-MPS whereby the average closest distance from the nanoparticle center increased from 13.5, 14.5 to 16.5 Å for oligomers O4, O1, and O3 (Figure 7c). Thus, O4 approached the surface most closely and could more easily form covalent bonds with the MPS corona on the nanoparticle. In contrast, ester groups approached the surface less closely. The closest average distance of ester groups from the nanoparticle center was about 16 Å for O3, followed by O2 and O1 in the range 16-17 Å. The location of ester groups between the aromatic ring and the side chain is sterically less accessible, which accounts for the larger distance from the particle surface. Therefore, ester groups are less likely to react with trimethoxysilyl groups on the CdS-MPS surface. The mobility of the polymer chains also showed significant differences. O3 and O4 without long side chains showed significantly faster diffusion compared to O1 and O2 with long side chains (Figure 7b). The side chains wrap around

the nanoparticle and fix the position of the oligomers (polymers) similar to a claw. The end-to-end length was noticeably shorter for O3 than for the other oligomers. Partial covalent bonding of polymer 1 to the surface through esterification on the particle shell had only a small effect on the computed structural properties in comparison to the structures upon noncovalent polar bonding. Therefore, the impact of covalent bonding on optical and excitation properties may also be small.



In addition, we developed a coarse-grain model to simulate transport processes and power conversion efficiencies of an entire solar cell (Figure 8). Suitable models to simulate the mechanisms of operation and performance characteristics of organic/polymer solar cells at the device level have not been previously available. Many simulation techniques such as DFT and quantum mechanics only focus on isolated processes and single molecules or molecular

junctions. In contrast, classical molecular dynamics methods can describe time-resolved processes well and reach realistic length and time scales corresponding to device operation. We made several innovations to enable the simulation of solar cells at the device level (Figure 8): (1) We consider electrons and holes as explicit particles that carry the corresponding elementary charge and a small mass to enable the inclusion in the molecular dynamics algorithm and the observation of a current in the simulation. The electrons and holes are inserted as pairs every given number of time steps in the simulation in agreement with the light intensity. A recombination parameter, currently defined as a spherical cutoff, allows the elimination of electron-hole pairs during the simulation when they reach a short distance. (2) Instead of an atomistic model that requires many specific interactions parameters, we chose a coarse grain model that focuses on the key features of molecular interactions and interactions between the charge carriers and the molecules. At a later

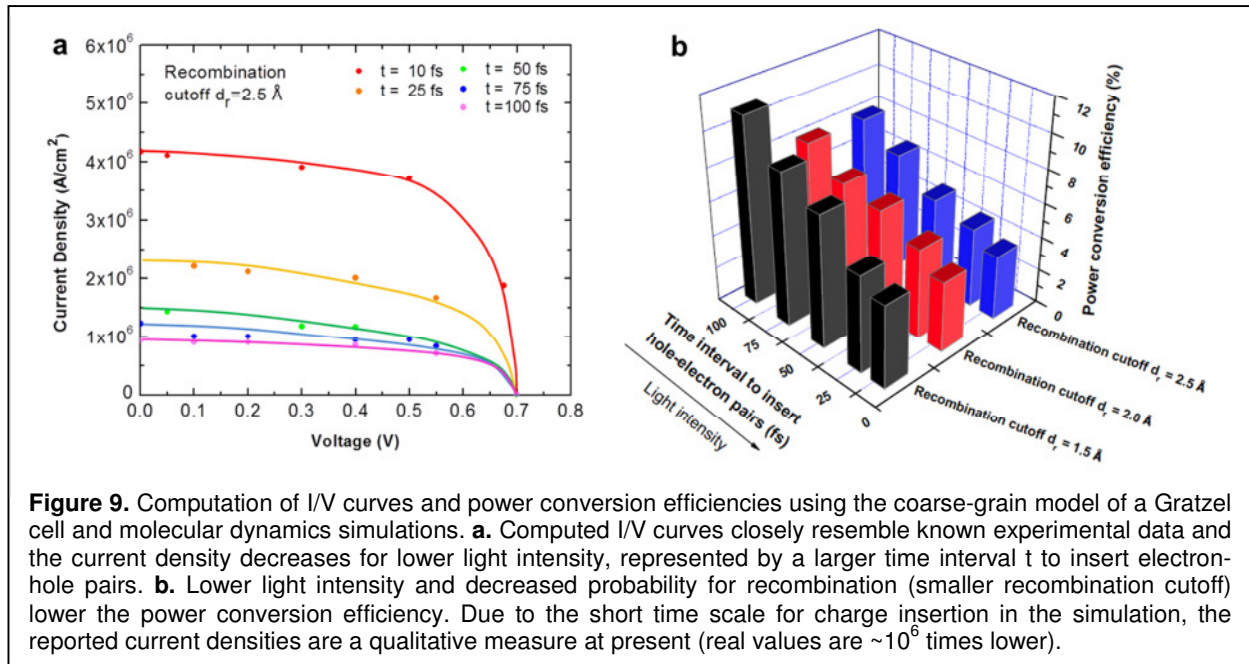


stage, specific chemical information is planned to be added by increasing the resolution to atomistic models and incorporation of further atom-specific interaction parameters. (3) We apply an external electric field in the model that matches the experimentally measured open circuit voltage. This electric field imposes a realistic driving force for the directional motion of the charge carriers and facilitates their collection and measurements of a generated current at the electrodes.

The models, particle insertion and removal routines, were implemented in the Large Scale Atomic and Molecular Massively Parallel Simulator (LAMMPS) code from Sandia National Laboratories for wide utility. We wrote an extension of this code to accommodate the specific operations necessary for the simulation of a solar device. As a model and test system, we chose a

Gratzel cell for simplicity, and the code can be easily modified for other components in the solar cell such as quantum dots and polymer from CIQA once device-scale testing will be performed. The coarse grain parameters for TiO_2 nanoparticles, the Ru dye molecule, and a liquid, polymer-containing electrolyte have the form of a 9-6 Lennard-Jones (LJ) potential as well as harmonic bond stretching parameters for the polymers. The parameters were derived from the molecular geometry and approximate cohesive energy of each component. Parameters for holes and electrons were chosen simply with minimal interaction parameters so that their motion is driven mainly by the electric charge. Tests with larger epsilon and sigma parameters in the LJ potential (up to one order of magnitude) have shown no significant change in performance.

The simulation enables tracking of the path of the charge carriers, the calculation of I/V curves, and estimates of the power conversion efficiency for different light intensity as well as recombination settings (Figure 9). Furthermore, the charge carrier mobility (diffusion constants) has been analyzed as well as the influence of different morphology on current collection. To shorten the simulation time, we used excessive light intensity in the tests here (currently 10^6 times faster), which however has no impact on the simulated device characteristics as an ideal thermostat was applied in the simulation. Simulation times can be expanded by several orders of magnitude in follow-up studies using supercomputing. The shape of the I/V curve is realistic when compared with measurements, and the impact of changes in light intensity and



recombination probability shows physically well supported trends. The relative power conversion efficiency (PCE) was computed based on the I/V curve and the experimentally given open circuit voltage. The results are promising and we think this simulation method lays the foundation for device scale simulation of solar cells. Next steps include incorporation of longer simulation times, adaption of morphologies, implementation of more specific interactions parameters, and application of this model to various types of solar cells. The use in conjunction with laboratory tests will help explain transport mechanisms, predict ideal morphologies, and compositions, and understand limits of the PCE for given designs.

3. Summary and Outlook

We advanced the understanding of nanoparticle-polymer interfaces for photovoltaic applications through synthesis, characterization, and modeling. A variety of CdS nanoparticles with various grafted surfactants and polymers has been characterized, photophysical properties of push-pull molecules with charge generation properties have been analyzed, and new modeling capabilities for solar devices have been developed. Detailed results are described in eight manuscripts for publication as well as in several PhD and Master's theses. The project may benefit from testing and optimization of the new materials as part of photovoltaic and organic electronic devices.

CIQA's report for the project along with their statistics is provided under separate cover to CIMAV, the coordinating institute for the US/Mexican Basic Research Initiative.