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## COLLABORATORS AND OTHER AFFILIATIONS

**David L. Patrick**

<table>
<thead>
<tr>
<th>Name</th>
<th>Affiliation</th>
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<tr>
<td>Dr. Mark Bussell</td>
<td>National University of Singapore</td>
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<td>Dr. Amy Spivey</td>
<td>University of Puget Sound</td>
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<td>Dr. Andrea Munro</td>
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<td>Dr. Carlisle Chambers</td>
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<tr>
<td>Dr. Stuart Clarke</td>
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<tr>
<td>Dr. Daniel Gamelin</td>
<td>University of Washington</td>
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<td>Dr. Hunter McDaniel</td>
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<td>Dr. John Gilbertson</td>
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<td>Dr. Brad Johnson</td>
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<td>Dr. Janelle Leger</td>
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<td>Dr. Stephen McDowall</td>
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<tr>
<td>Dr. David Rider</td>
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</tbody>
</table>
COLLABORATORS

John D. Gilbertson

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  Kelsey Scharnhorst, University of California Los Angeles
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Graduate and Postdoctoral Advisors (2):
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Graduate Students (3):
  William Benjamin (2012)
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Collaborators and Affiliations for Co-PI Stephen McDowall

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Prof. David Isaacson</td>
<td>Rensellaer Polytechnic Institute</td>
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<tr>
<td>Prof. Plamen Stefanov</td>
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<td>University of California, Santa Cruz</td>
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<td>Prof. Alex Tamasan</td>
<td>University of Central Florida</td>
</tr>
<tr>
<td>Profs. Brad Johnson, David Patrick, Jenelle Leger, John Gilbertson</td>
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<tr>
<td>Prof. Daniel Gamelin</td>
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Graduate and Postdoctoral Advisors:

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<tr>
<td>Prof. Gunther Uhlmann</td>
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<td>Prof. Adrian Nachman</td>
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</table>
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Prof. Stephen McDowall (Western Washington University, Mathematics Department)
Prof. Byron D. Gates (Simon Fraser University, Department of Chemistry)
Dr. Mark Engelhard (Pacific Northwest National Laboratories, EMSL)
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Mr. Kevin Bussard (Zodiac Aerospace Materials and Processing Engineer)
Mr. Jordan Kiesser (PACCAR Technical Center)
RUI: Suschem: Engineering Nanoscale Disorder in Polymer-Semiconductor Nanocrystal Composites for Minimized Optical Losses

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Not a collaborative proposal

CO-PD NAME

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Certification for Authorized Organizational Representative (or Equivalent) or Individual Applicant

By electronically signing and submitting this proposal, the Authorized Organizational Representative (AOR) or Individual Applicant is: (1) certifying that statements made herein are true and complete to the best of his/her knowledge; and (2) agreeing to accept the obligation to comply with NSF award terms and conditions if an award is made as a result of this application. Further, the applicant is hereby providing certifications regarding conflict of interest (when applicable), drug-free workplace, debarment and suspension, lobbying activities (see below), nondiscrimination, flood hazard insurance (when applicable), responsible conduct of research, organizational support, Federal tax obligations, unpaid Federal tax liability, and criminal convictions as set forth in the NSF Proposal & Award Policies & Procedures Guide, Part I: the Grant Proposal Guide (GPG). Willful provision of false information in this application and its supporting documents or in reports required under an ensuing award is a criminal offense (U.S. Code, Title 18, Section 1001).

Certification Regarding Conflict of Interest

The AOR is required to complete certifications stating that the organization has implemented and is enforcing a written policy on conflicts of interest (COI), consistent with the provisions of AAG Chapter IV.A.; that, to the best of his/her knowledge, all financial disclosures required by the conflict of interest policy were made; and that conflicts of interest, if any, were, or prior to the organization’s expenditure of any funds under the award, will be, satisfactorily managed, reduced or eliminated in accordance with the organization’s conflict of interest policy. Conflicts that cannot be satisfactorily managed, reduced or eliminated and research that proceeds without the imposition of conditions or restrictions when a conflict of interest exists, must be disclosed to NSF via use of the Notifications and Requests Module in FastLane.

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By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent), is providing the Drug Free Work Place Certification contained in Exhibit II-3 of the Grant Proposal Guide.

Debarment and Suspension Certification

(If answer “yes”, please provide explanation.)

Is the organization or its principals presently debarred, suspended, proposed for debarment, declared ineligible, or voluntarily excluded from covered transactions by any Federal department or agency? Yes ☐ No ☒

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The undersigned certifies, to the best of his or her knowledge and belief, that:
(1) No Federal appropriated funds have been paid or will be paid, by or on behalf of the undersigned, to any person for influencing or attempting to influence an officer or employee of any agency, a Member of Congress, an officer or employee of Congress, or an employee of a Member of Congress in connection with the awarding of any Federal contract, the making of any Federal grant, the making of any Federal loan, the entering into of any cooperative agreement, and the extension, continuation, renewal, amendment, or modification of any Federal contract, grant, loan, or cooperative agreement.
(2) If any funds other than Federal appropriated funds have been paid or will be paid to any person for influencing or attempting to influence an officer or employee of any agency, a Member of Congress, an officer or employee of Congress, or an employee of a Member of Congress in connection with this Federal contract, grant, loan, or cooperative agreement, the undersigned shall complete and submit Standard Form-LLL, “Disclosure of Lobbying Activities,” in accordance with its instructions.
(3) The undersigned shall require that the language of this certification be included in the award documents for all subawards at all tiers including subcontracts, subgrants, and contracts under grants, loans, and cooperative agreements and that all subrecipients shall certify and disclose accordingly.

This certification is a material representation of fact upon which reliance was placed when this transaction was made or entered into. Submission of this certification is a prerequisite for making or entering into this transaction imposed by section 1392, Title 31, U.S. Code. Any person who fails to file the required certification shall be subject to a civil penalty of not less than $10,000 and not more than $100,000 for each such failure.

Certification Regarding Nondiscrimination

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) is providing the Certification Regarding Nondiscrimination contained in Exhibit II-6 of the Grant Proposal Guide.

Certification Regarding Flood Hazard Insurance

Two sections of the National Flood Insurance Act of 1968 (42 USC §4012a and §4106) bar Federal agencies from giving financial assistance for acquisition or construction purposes in any area identified by the Federal Emergency Management Agency (FEMA) as having special flood hazards unless the:
(1) community in which that area is located participates in the national flood insurance program; and
(2) building (and any related equipment) is covered by adequate flood insurance.

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) or Individual Applicant located in FEMA-designated special flood hazard areas is certifying that adequate flood insurance has been or will be obtained in the following situations:
(1) for NSF grants for the construction of a building or facility, regardless of the dollar amount of the grant; and
(2) for other NSF grants when more than $25,000 has been budgeted in the proposal for repair, alteration or improvement (construction) of a building or facility.

Certification Regarding Responsible Conduct of Research (RCR)

(This certification is not applicable to proposals for conferences, symposia, and workshops.)

By electronically signing the Certification Pages, the Authorized Organizational Representative is certifying that, in accordance with the NSF Proposal & Award Policies & Procedures Guide, Part II, Award & Administration Guide (AAG) Chapter IV.B., the institution has a plan in place to provide appropriate training and oversight in the responsible and ethical conduct of research to undergraduates, graduate students and postdoctoral researchers who will be supported by NSF to conduct research. The AOR shall require that the language of this certification be included in any award documents for all subawards at all tiers.
**Certification Regarding Organizational Support**

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) is certifying that there is organizational support for the proposal as required by Section 526 of the America COMPETES Reauthorization Act of 2010. This support extends to the portion of the proposal developed to satisfy the Broader Impacts Review Criterion as well as the Intellectual Merit Review Criterion, and any additional review criteria specified in the solicitation. Organizational support will be made available, as described in the proposal, in order to address the broader impacts and intellectual merit activities to be undertaken.

**Certification Regarding Federal Tax Obligations**

When the proposal exceeds $5,000,000, the Authorized Organizational Representative (or equivalent) is required to complete the following certification regarding Federal tax obligations. By electronically signing the Certification pages, the Authorized Organizational Representative is certifying that, to the best of their knowledge and belief, the proposing organization:

1. has filed all Federal tax returns required during the three years preceding this certification;
2. has not been convicted of a criminal offense under the Internal Revenue Code of 1986; and
3. has not, more than 90 days prior to this certification, been notified of any unpaid Federal tax assessment for which the liability remains unsatisfied, unless the assessment is the subject of an installment agreement or offer in compromise that has been approved by the Internal Revenue Service and is not in default, or the assessment is the subject of a non-frivolous administrative or judicial proceeding.

**Certification Regarding Unpaid Federal Tax Liability**

When the proposing organization is a corporation, the Authorized Organizational Representative (or equivalent) is required to complete the following certification regarding Federal Tax Liability:

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) is certifying that the corporation has no unpaid Federal tax liability that has been assessed, for which all judicial and administrative remedies have been exhausted or lapsed, and that is not being paid in a timely manner pursuant to an agreement with the authority responsible for collecting the tax liability.

**Certification Regarding Criminal Convictions**

When the proposing organization is a corporation, the Authorized Organizational Representative (or equivalent) is required to complete the following certification regarding Criminal Convictions:

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) is certifying that the corporation has not been convicted of a felony criminal violation under any Federal law within the 24 months preceding the date on which the certification is signed.

**Certification Dual Use Research of Concern**

By electronically signing the certification pages, the Authorized Organizational Representative is certifying that the organization will be or is in compliance with all aspects of the United States Government Policy for Institutional Oversight of Life Sciences Dual Use Research of Concern.

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Overview. This research will develop new approaches for the design and preparation of densely-packed, high performance polymer-luminescent semiconductor nanocrystal (NC) composites engineered to minimize optical losses through nanometer- to micron-scale control of interparticle spacing distributions. Polymer-NC composites are employed as optically-active elements in a wide range of applications, such as downshifting layers for lighting and displays, as scintillation detectors, hybrid organic/inorganic light-emitting diodes, and luminescent solar concentrators. These and related applications often require a higher volumetric density of NCs, along with better nanoparticle dispersion, than is currently achievable, in order to minimize aggregation-induced optical losses from light scattering and interparticle energy- and charge-transfer. Purely random dispersions fail to minimize optical losses from several important mechanisms characterized by a non-linear dependence on particle spacing, including elastic light-scattering, and quenching caused by near-field interparticle energy- and charge-transfer, because these processes are dominated not by the mean interparticle separation, but instead by fluctuations around the mean. The development of high performance polymer-NC composites for the most demanding optical applications necessitates a careful balance of order and disorder, managed over nanometer- to micron-length scales, requiring more careful design and control over interparticle spacing statistics than has generally been recognized or pursued.

Scientific Merit. We propose an integrated program of theory, synthesis, and materials characterization, aimed at identifying, measuring, and controlling the key statistical properties of NC spatial distributions which govern non-linear distance-dependent loss mechanisms. We focus in particular on elastic light-scattering and applications of these new materials as high performance, large area luminescent solar concentrators (LSCs) for solar energy harvesting. The principles developed here, however, will be broadly applicable to a range of important technologies.

We will study solid, filler-free assemblies of CuIn(S,Se)2/ZnS/silica core/shell/shell NCs, capped with polyalkylmethacrylate brush ligands, fabricated into planar waveguides. CuIn(S,Se)2/ZnS nanophosphors are among the best performing luminophores identified so far for LSC applications, combining broadband absorption well-matched to the solar spectrum with an extremely large effective Stokes shift that results in a small Förster radius and minimal self-absorption. By combining polymer brush ligands with silica shelling, a high degree of control over NC spacing will be achieved via tuning of the silica shell thickness, brush molecular weight, and grafting density, which together will allow precise programming of the effective interparticle interaction potential, and hence short- and long-range structure in composite materials. The optical and nanostructural properties of composite thin-film waveguides will be characterized in detail, and the results fed back to a closely integrated program of theory and modeling informing ligand and silica shell design. The overall result will be new concepts and new materials for high performance polymer-NC composites needed for LSC and other demanding optical applications.

Broader Impacts. WWU is a primarily undergraduate institution where undergraduates comprise the majority of the scientific workforce and will be involved in every phase of the research. Six undergraduates per year (total 12-18 over the grant period) will participate year-round on the project, receiving a strong foundation in materials and synthetic chemistry, optics, and mathematics, as well as the chance to experience the excitement of independent, creative scientific investigation. The PIs encourage students to explore and understand implications of their work beyond science by participating in regional business plan contests with product concepts derived from this undergraduate research. Over the last five years teams of Chemistry, Engineering, Industrial Design, and MBA students have won approximately $100,000 in prize money at several competitions based on commercial products they proposed derived from the topic of this proposal, and we will continue our mentorship of such teams.

The PIs are also committed to supporting students of all ages in their pursuit of education and training in the STEM fields, and they and their students will be involved in a wide range of outreach efforts, particularly to traditionally underrepresented groups. Related activities include laboratory tours and hands-on activities with 5th and 6th graders through WWU’s Compass-to-Campus program; direct involvement of high school students in the research; and outreach to local high schools, especially those serving large populations of Hispanic students. The PIs will also continue to produce a video series called ‘Scientist Citizen,’ discussing contemporary societal issues informed by science.
**TABLE OF CONTENTS**

For font size and page formatting specifications, see GPG section II.B.2.

<table>
<thead>
<tr>
<th>Section</th>
<th>Total No. of Pages</th>
<th>Page No.* (Optional)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cover Sheet for Proposal to the National Science Foundation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Project Summary (not to exceed 1 page)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Table of Contents</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Project Description (Including Results from Prior NSF Support) (not to exceed 15 pages) <em>(Exceed only if allowed by a specific program announcement/solicitation or if approved in advance by the appropriate NSF Assistant Director or designee)</em></td>
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<td>References Cited</td>
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<tr>
<td>Biographical Sketches (Not to exceed 2 pages each)</td>
<td>8</td>
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</tr>
<tr>
<td>Budget (Plus up to 3 pages of budget justification)</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Current and Pending Support</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Facilities, Equipment and Other Resources</td>
<td>3</td>
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<td>Special Information/Supplementary Documents (Data Management Plan, Mentoring Plan and Other Supplementary Documents)</td>
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<td>Appendix (List below.) <em>(Include only if allowed by a specific program announcement/solicitation or if approved in advance by the appropriate NSF Assistant Director or designee)</em></td>
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<td>Appendix Items:</td>
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*Proposers may select any numbering mechanism for the proposal. The entire proposal however, must be paginated. Complete both columns only if the proposal is numbered consecutively.
I. Overview and rationale.
Polymer-semiconductor nanocrystal (NC) composites are employed as optically-active elements in a wide range of applications, such as downshifting layers for lighting and displays,\textsuperscript{1-3} as scintillation detectors,\textsuperscript{4,5} fiber lasers,\textsuperscript{6-8} amplified spontaneous emission sources,\textsuperscript{9,10} hybrid organic/inorganic light-emitting diodes,\textsuperscript{11-15} luminescent solar concentrators,\textsuperscript{14,16} and other optical devices.\textsuperscript{17} These and related applications often require a high volumetric density of NCs along with good nanoparticle dispersion in order to minimize aggregation-induced optical losses from light scattering and interparticle energy- and charge-transfer. The most common method for preparing such composites is to use capping ligands or host polymer chemistries designed to minimize NC aggregation by steric stabilization or immobilization at polymer binding sites, aimed at producing uniform nanoparticle dispersions, i.e. a spatially random three-dimensional distribution of NCs within a polymer solvent. However, completely random dispersions do not actually minimize optical losses from several important mechanisms characterized by a non-linear dependence on particle spacing, including elastic light-scattering, and quenching caused by near-field interparticle energy- and charge-transfer. This is because the rates of such processes are dominated not by the mean interparticle separation, but instead by fluctuations around the mean, i.e. by a small subset of NCs with the smallest nearest-neighbor separations, and follows directly from the statistics of random distributions, as discussed below. The opposite approach – arrangement of NCs on an ordered crystalline lattice – could in principle prevent such losses, but stacking faults would almost certainly behave as strong scattering centers. Consequently, the development of high performance, concentrated polymer-nanoparticle composites for the most demanding optical applications – such as those mentioned above – necessitates a careful balance of order and disorder, managed over nanometer- to micron-length scales. This will require more careful design and control over interparticle spacing statistics than has generally been recognized or pursued.

The objective of this research is to develop and demonstrate new concepts for densely-packed, high performance polymer-luminescent NC composites engineered to minimize light-scattering and other nonlinear losses via nanometer- to micron-scale control of interparticle spacing statistics. To do this, we propose an integrated program of theory, synthesis, and materials characterization, aimed at identifying, measuring, and controlling the key statistical properties of NC spatial distributions which govern non-linear distance-dependent loss mechanisms, focusing in particular on elastic light-scattering. Our immediate motivation is to employ these new materials as high performance, large area luminescent solar concentrators (LSCs), although the underlying principles developed here will have broad applicability to many related technologies.

We will study solid, filler-free assemblies of CuIn(S,Se)\textsubscript{2}/ZnS/silica core/shell/shell NCs, capped with polyalkylmethacrylate brush ligands, fabricated into planar waveguides (Fig. 1). Neat, solid samples of these so-called “hairy” nanoparticles can be prepared via a number of routes,\textsuperscript{18-20} resulting in

![Fig. 1. We will prepare and study thin film polymer-NC composite waveguides based on filler-free assemblies of CuIn(S,Se)\textsubscript{2}/ZnS/silica core/shell/shell NCs, capped with polyalkylmethacrylate brush ligands. Elastic light-scattering and other non-linear losses will be reduced through careful control over interparticle spacing statistics on nanometer- to micron-length scales, guided by a closely integrated program of theory and modeling. Particle packing will be tuned through a combination of (i) silica shell thickness, (ii) brush graft density and molecular weight, and (iii) mixing ratios of nanoparticles having different overall diameters.](image)
composites spanning a wide range of structures, from fully amorphous, to locally ordered, to long-range polycrystalline organization.\textsuperscript{21,22} By combining polymer brush ligands with silica shelling, a high degree of control over NC spacing will be achieved via tuning of the silica shell thickness, brush molecular weight, and grafting density, which together will allow precise programming of the effective interparticle interaction potential, and hence short- and long-range structure in composite materials.

As discussed below, CuIn(S,Se)\textsubscript{2}/ZnS nanophosphors are among the best performing luminophores identified so far for LSC applications. They combine broadband absorption well-matched to the solar spectrum with an extremely large effective Stokes shift (\( \geq 500 \) meV, Fig. 2), resulting in small Förster radii \( r_0 \) and minimal self-absorption. For the CuInS\textsubscript{2} sample in Fig. 2 for example, we estimate \( r_0 = 4 \) – 5 nm in a medium having a refractive index equal to 1.5 based on the overlap integral computed from the measured extinction and emission spectra. This is about equal to the NC diameter even in the absence of ligands. Consequently, colloidal suspensions taken to dryness and stabilized only by short C12 ligands remain highly luminescent (Fig. 2). Because of this, elastic light-scattering is expected to be the most important loss mechanism in these composite waveguides with dense packings. The polymer-brush NCs will be solvent cast into planar waveguides containing no additional polymer filler, and their optical and nanostructural properties characterized in detail, with a focus on understanding and controlling light-scattering. The experimental work will be guided by a closely integrated program of theory and modeling using a multi-scale treatment to describe light-scattering in which the scattering cross section at small scales is computed exactly using the \( T \)-matrix approach, and at larger scales by an effective medium theory. The overall approach will follow an integrated “model-make-measure” cycle of optimization, theory, and materials development aimed at elucidating nanoscale design principles for luminescent semiconductor NC-polymer composites with ultralow optical losses. The above goals will be pursued through four main activities:

- **Preparation of CuIn(S,Se)\textsubscript{2}/ZnS/silica polymer brush NCs** (Leads: Gilbertson & Rider): Ternary colloidal semiconductor CuInSe\textsubscript{2}/ZnS and CuInS\textsubscript{2}/ZnS NCs will be prepared, shelled with silica, and capped with layers of polyalkylmethacrylate brush ligands to allow precise programming of the effective interparticle interaction in composite materials.

- **Waveguide fabrication and characterization** (Lead: Patrick): Conduct systematic studies on the effects of silica shell thickness, brush grafting density and molecular weight on the nanostructural and optical properties of thin film polymer-NC composite waveguides. Large samples will also be studied as luminescent solar concentrators.

- **Optical Modeling** (Lead: McDowall): Formulation and application of a model to predict nanoscale composite structure-dependent light-scattering losses, including model validation and refinement informed using experimental data.

- **Student involvement**: Western Washington University (WWU) is a primarily undergraduate institution with a very strong tradition of student involvement in research. The proposed work will be conducted primarily by undergraduate researchers, with a total of 12 – 18 students receiving interdisciplinary scientific and professional training over the course of the project.

![Fig. 2. Absorption and photoluminescence of CuInS\textsubscript{2} and CuInSe\textsubscript{2} NCs.](image)

(Left) Spectra of CuInS/CdS measured in the PLMA-NC composite LSC waveguide shown in Fig. 3. (Right) photoluminescence from a dry powder of CuInSe\textsubscript{2}/ZnS NCs under 405 nm excitation. Their large Stokes shift reduces self-absorption and results in a small Förster radius, making these phosphors less prone to concentration quenching than most other colloidal semiconductor NCs.
Application to Luminescent Solar Concentrators (LSCs)

Luminescent solar concentrators (LSCs) use down-converting phosphors embedded in a dielectric waveguide to absorb sunlight, trap luminescent photons by total internal reflection, and deliver high irradiance, narrowband output light for driving photovoltaic, photochemical, and other solar energy conversion devices. LSCs have emerged as one of the most promising approaches for practical building-integrated solar energy harvesting because they can concentrate diffuse as well as direct sunlight, are tolerant to partial shading, are semi-transparent, and can be architecturally integrated into building facades or windows (Fig. 3).23-25 LSCs theoretically enable conversion efficiencies superior to other concentrator designs,26-28 but to achieve a high level of gain requires a thin (~1 mm), large area (~1 m²) form factor, demanding a high concentration of luminophores and extremely small optical propagation losses (< 0.01 dB cm⁻¹). These requirements make LSCs a very good target application for this proposed research.

All LSCs are affected by four principle optical loss mechanisms (Fig. 3):29-32 (1) only a fraction of incident sunlight is absorbed, determined by the luminophore absorption spectrum; (2) only a fraction of absorbed sunlight is re-emitted, depending on luminophore photoluminescence (PL) quantum yield (Φ); (3) only a fraction of this emitted light is captured in guided modes (e.g. ~75% in a planar waveguide with refractive index n ~ 1.5),33 with the remainder lost to escape cones defined by Snell’s Law; and (4) a fraction of guided light is lost during transport to the concentrator edges by parasitic waveguide losses, which are primarily caused by scattering from luminophore aggregates. Typically, losses (2) and (3) are most problematic because they occur repetitively, since waveguided photons may be reabsorbed/re-emitted by subsequent luminophores repeatedly before reaching an edge. Long optical pathlengths in a high-gain LSC cause even the smallest overlap between absorption and emission spectra to result in compounding self-absorption losses and place stringent demands on waveguide transparency.34 Designs incorporating advanced light management strategies such as wavelength-selective mirrors35-37,55 or luminophore alignment38-43 can mitigate only a portion of these losses, and come at the expense of increased complexity, cost, and/or transparency. Fundamentally, the success of LSC technologies depends on the development of improved luminophores combining high brightness and large Stokes shift with broadband absorbance and their incorporation into low-loss waveguides.

The search for LSC phosphors able to meet these requirements has proven to be a challenging one.21,31 Over the last 40 years a wide variety of candidate dyes have been investigated, including small molecule and polymer fluorophores,45-49 lanthanide-doped glasses,50-55 as well as various types of semiconductor nanocrystals (Types I and II,56-62 “giant shell”63-65 and “dot-in-rod”66). Among these, semiconductor NCs such as Mn²⁺:ZnSe, Mn²⁺:Cd,Zn₁₋ₓSe, CuInSe₂, and Cu⁺:CdSe currently appear most promising.67-73 These nanophosphors combine good photostability, high PL quantum yield (Φ ≥ 50-90%), and intense, broadband absorbance well-matched to the solar spectrum (300 ~ 1000 nm with absorptivity 10⁴ – 10⁵ M⁻¹cm⁻¹ at the
first maximum) with lower scattering than larger heterostructure NCs. PL is associated with localized midgap states arising from impurities, native defects, or exciton self-trapping. Carrier or energy localization from the photoexcited host NC results in emission with a giant effective Stokes shift, suppressing self-absorption. In addition, these NCs possess other properties required for high-performance LSCs, including minimal concentration quenching, higher resistance to photo-oxidation than most organic dyes or Type I/II semiconductor NCs as a result of excited-state energy localization within the NC interior, compatibility with solution processing, and the potential to be made from low-cost and low-toxicity elements.

Two years ago we were the first to introduce this family of phosphors for LSCs, studying devices based on Mn\textsuperscript{2+}:ZnSe/ZnS core/shell NCs incorporated into poly(laurylmethacrylate) (PLMA) waveguides. Compared to previous generations of LSC luminophores, these and related giant effective Stokes shift NC phosphors demonstrate greatly reduced self-absorption losses, enabling large area devices to achieve optical power efficiencies now approaching 5% based on smaller bandgap, large Stokes shift NC phosphors such as CuInS\textsubscript{2} and CuInSe\textsubscript{2}.

**Optical loss mechanisms in semiconductor NC / polymer composite LSCs.**

Recent work in the groups of two of the PIs has shown that significant further improvements in efficiency and optical gain should be possible in large LSC devices if light-scattering losses can be reduced. Detailed analysis of optical loss mechanisms in PLMA – CuInS\textsubscript{2} LSCs shows that for concentrators with a large geometric gain \( G \geq \sim 10 \) (where \( G \) is the ratio of facial to edge areas), efficiency is limited by propagation losses caused primarily by scattering from NC aggregates. This is illustrated in Fig. 4 based on measurements of an LSC containing 2 wt% NCs.

Figure 5 shows how these losses depend on NC loading, where the loss rate is expressed in terms of the attenuation coefficient \( \alpha \) (dB cm\(^{-1}\)), which determines the rate of loss of optical power as a function of pathlength \( r \) in the waveguide: \( P = P_0 e^{-\alpha r/4} \). The quantity \( \alpha \) is sometimes referred to as the turbidity, and the factor 4.34 arises from converting dB cm\(^{-1}\) to Naperian units (cm\(^{-1}\)). For reference, an attenuation coefficient of \( \alpha = 0.1 \) dB cm\(^{-1}\) results in a loss of \( \sim 2\% \) of guided photons per centimeter pathlength.

Referring to Fig. 5, there is a small, nearly concentration-independent attenuation coefficient up to an optical density of \( \sim 0.25 \), beyond which attenuation increases rapidly. The data in Fig. 5 are fit using the attenuation function

\[
\alpha = \alpha_o + \beta c_o + \gamma c_o^3 \left(1 + \delta c_o^{2/D}\right)^{-D/2}
\]  

(1)

derived assuming particle aggregation produces clusters with fractal geometries and with a size distribution related to NC concentration. Here, \( c_o \) represents NC concentration, \( D \) is the fractal dimension of NC aggregates, and \( \alpha_o, \beta, \gamma, \delta \) are constants. The first term in Eq. 1 accounts for intrinsic propagation losses in the absence of NCs, and arises from absorption and scattering by the polymer, impurities, and at interfaces and
imperfections. The second and third terms describe scattering from single NCs and aggregates, respectively. For \( D = 1.8 \), a typical fractal dimension for such aggregates,\(^7\) we find an intrinsic attenuation rate \( \alpha_g = 0.16 \text{ dB cm}^{-1} \) and negligible single-particle scattering losses (\( \beta = 0.02 \text{ dB cm}^{-1} \text{ wt}%^{-1} \)). The latter is consistent with an estimate of the Rayleigh scattering cross section, which indicates that scattering from individual NCs is 1-2 orders of magnitude too small to account for the observed attenuation, and also with the observations of Knowles et al. who found no significant scattering for similar CuInS\(_2\) NCs in toluene at even greater volume fractions and over a pathlength of 1.2 m.\(^7\) At low NC loadings, \( \alpha \) is dominated by intrinsic waveguide losses. The intrinsic attenuation of optical-grade methacrylate polymers in this wavelength range is\(^7\) \( \sim 1 \times 10^{-3} \text{ dB cm}^{-1} \), and that of the glass cladding is even lower.\(^10\) At high NC concentrations \( c_o \geq \sim 2 \text{ wt} \%), the analysis indicates that scattering losses begin to dominate, as evidenced by the signature cubic scaling of attenuation rate with NC concentration.

Absorption by the polymer matrix is another challenge for long pathlength device applications such as LSCs. In particular, the transparency window for commodity optical polymers such as PMMA is mostly limited to the visible region, with the wavelength window between 800 – 1100 nm, important for c-Si photovoltaics, rendered essentially opaque by absorption from the 3rd and 4th harmonics of the stretching vibrations of the C-H bonds, with smaller contributions from the bending vibrations (Fig. 6).\(^77\) This is another reason for including a silica overcoating in this work: in addition to providing an extra means for tuning the diameter and effective modulus of the nanoparticles as discussed below, the silica overcoating also replaces a substantial volume of C-H–rich polymer, reducing absorption in a key wavelength window for LSC applications, and also around 1500 – 1600 nm, relevant for optical telecommunications applications.

Nonlinear loss mechanisms in random NC dispersions.

The results discussed above are for a polymer-NC composite in which CuInS\(_2\) NCs were dispersed approximately uniformly, in which a degree of aggregation is possible. Such a distribution may be approximated as a Poisson point process, which has the following statistical properties: If there exists a NC at position \( x \), then we denote by \( P(N(r) = 1 \mid x) \) the probability that there is a NC at distance \( r \) from \( x \), conditional on the fact that there is a NC at \( x \). The distribution depends on the macroscopic density of NCs, \( \rho \) NCs per unit volume. The resulting nearest neighbor function, \( D_x(r) \), is the probability distribution function of the distance from a given NC to the nearest neighboring point. It is defined to be \( D_x(r) = 1 - P(N(r) = 1 \mid x) \), and, for a Poisson point process, takes the form

\[
D_x(r) = 1 - e^{-\rho \frac{4}{3} \pi r^3}.
\]

The associated probability density function for a NC being at distance \( r \) of a given NC at \( x \) is

\[
f_x(r)dr = 4\pi r^2 \rho e^{-\rho \frac{4}{3} \pi r^3} dr.
\]

From the point of view of aggregation, we are most interested in the probability that there are (at least) \( n \) NCs within a critical distance \( r^* \) of \( x \), where \( r^* \approx \lambda/4\pi \) is the separation at which a pair of subwavelength-sized scattering objects begin to behave as a single scatterer for light of wavelength \( \lambda \), i.e. undergo coherent scattering.\(^10\) This is given by

\[
P(\# \text{ neighbors within distance } r^* \geq n) = 1 - e^{-\rho \frac{4}{3} \pi r^3} \sum_{j=0}^{n-1} \left( \rho \frac{4}{3} \pi r^3 \right)^j / j!.
\]

When the NC concentration is low (< ~1 wt%), very little scattering occurs, as has been demonstrated in the literature for LSCs with low concentrations where essentially zero scattering losses are observed. For such densities, the above formula yields negligibly small probabilities for aggregates to form and so there

![Fig. 6. Near IR spectrum of a 2 cm thick sample of PMMA.](image-url)
is little-to-no coherent scattering. As we demonstrate below, when the NC concentration is increased – as is required for many practical applications including LSCs – the probabilities of aggregation of multiple NCs become significant, even for uniform random dispersions. The challenge we face, and will overcome by way of spatial control of the NC centers, is to increase NC loading without causing refractive index fluctuations which will lead to light-scattering.

When there is variation in the density of NCs, the main contribution to scattering comes from groups of NCs in closer proximity to one another than those in the surrounding volume. This is because, for a group of $n$ scatterers separated by a distance less than $r^*$, scattering is coherent and the total scattered intensity increases in proportion to $n^2$, whereas for widely separated objects scattering is incoherent and the total scattered intensity increases as $n$. Consequently, for high nanoparticle loadings, local fluctuations in NC concentration become the dominate cause of scattering. For example, if we use a density of $\rho = 10^{21}$ NCs per m$^3$ and take $\lambda = 1000$ nm, we compute the probability of a cluster forming with $n$ NCs; weighting this by the factor $n^2$ for small separations, Fig. 7 demonstrates the relative scattering effects due to fluctuations in local NC concentration.

### Summary

We propose an integrated program of experiment and theory using CuIn(S,Se)$_2$/ZnS/silica polymer brush nanoparticles to produce ultra-low loss, high NC-loading waveguides for LSC and related applications by engineering nanoscale structural disorder. We will prepare and study thin film composite waveguides with particle packing tuned through a combination of (i) silica shell thickness, (ii) brush graft density and molecular weight, and (iii) mixing ratios of nanoparticles having different overall diameters. The optical and nanostructural properties of composite thin film waveguides will be characterized in detail, and the results fed back to a closely integrated program of theory and modeling informing polymer brush and silica shell design, and nanoparticle size mixing ratios. The overall result will be new concepts and new materials for high performance polymer-NC composites serving the most demanding optical applications.

### II. Results from Prior NSF Support

“SOLAR: Tandem Waveguide Solar Luminescent Concentrators.” CHE-DMR-DMS SOLAR-1035512 (PI D. Patrick, Co-PIs: J. Gilbertson, S. McDowall, J. Leger, B. Johnson, WWU. 8/10/10-8/30/15, $969,501). This research investigated molecular orientational control and tandem plasmonic waveguides for increasing LSC efficiency. Intellectual Merit: Major accomplishments include development of highly luminescent, alignable perylene luminophores and their incorporation into LSC devices with the highest optical quantum efficiencies reported to date (74%); development of new photon transport models incorporating photon polarization, birefringence, luminophore absorption and emission spectra, for accurate predictive modeling of LSC performance. This work produced five publications, seven presentations, four MS theses, and two patent applications. Broader Impact: Over 20 undergraduate and five M.S. researchers worked on this project. Students supported by the project entered a series of business plan competitions based on technology developed under this grant, winning several first-place competitions. Concepts from this research have been incorporated in WWU’s College Quest “Renewable Energy” summer class for high school students and a new senior-level undergraduate course co-taught by PI Patrick. An outreach video was produced and disseminated to the public outlining the project and undergraduate student involvement.
III. Research Plan
The research plan is divided into six main activities:

III.A CuInSe$_2$/ZnS and CuInS$_2$/ZnS Nanocrystal synthesis
Ternary colloidal semiconductor CuInSe$_2$/ZnS and CuInS$_2$/ZnS NCs will be prepared following the procedures in Refs. 88 and 89, respectively. Briefly, the synthesis begins with preparation of 2 – 4 nm diameter CuIn(S,Se)$_2$ cores by a hot injection technique using ionic indium and copper sources, and 1-dodecanethiol or trioctylphosphine selenide as S or Se sources, with oleylamine. Subsequent overgrowth of a few monolayers of ZnS using zinc stearate and elemental sulfur dissolved in trioctylphosphine increases the photoluminescence quantum yield from ~10% to over 80%.$^{90}$ Silica and polymer shells will be added as described in the next section. Typical NCs prepared by this method are pseudo-spherical with overall diameters of 3 – 6 nm. The groups of the PIs (Patrick and Gilbertson) are experienced in both syntheses. NCs will be characterized using X-ray diffraction, scanning/transmission electron microscopy, absorbance and photoluminescence spectroscopy, and elemental analysis by inductively-coupled plasma mass spectrometry, energy-dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy, all of which are available at WWU.

III.B Preparation of Silica & Polymer Shells
As stated above, we plan to investigate filler-free nanocomposites in order to minimize the optical losses described. Ultimately, the outer most layer of NCs will require some amount of polymer to eliminate void space, provide more uniformity in the refractive index of the solid, permit solution processability of films, and reduce scattering losses of bulk NC solids (Figure 8). A polymer brush layer will also act to manage aggregation by tailoring interparticle interaction potential, and hence short- and long-range structure in composite materials.$^{91}$ The chemistry for installing a polymer brush of tailored molecular weight (N, number of repeat units) and tunable grafting density (σ) is therefore necessary.

We will investigate two different approaches: the “grafting to” and the “grafting from” approaches. When σ is low, the polymer chains assume a ‘mushroom’ configuration with minimal side-to-side interactions. When σ is high, the polymer chains are in a ‘concentrated polymer brush’ (CPB) regime where polymer chains extend away from the surface and are forced to adopt a highly extended conformation.$^{92,93}$ In this configuration, the brush layer is highly impenetrable by solvent or other polymer chains. Since the volume per chain increases radially from the NC surface, the conformation of the chain can transition from highly extended to one with more free volume available for entanglement (leading to a semidilute polymer brush, SDPB).$^{94,95,96}$ A brush layer with a mushroom-type σ provides the minimum amount of material for absorbance due to CH overtones but weak entanglement between brush layers on adjacent NCs and poor space filling properties. In contrast, a SDPB will increase CH-overtone absorbance but will allow for beneficial entanglement, space filling, melt flow and lubricity will program for reduced optical losses and increased stability. We will investigate both regimes in order to optimize the systems.

NCs with a polymer brush molecular weight (N) that exceeds the transition molecular weight for the SDPB regime (Nc) can be viewed as a core/shell$_1$/shell$_2$ system where shell$_1$ represents the portion of the brush that contains highly stretched polymer chains and corresponding stiffness and shell$_2$ represents the portion of the brush that adopts a more random coil conformation and is more disordered and soft (Figure 9). The thickness of shell$_1$ scales as $\sim N^{0.5}$ whereas the thickness of shell$_2$ scales as $N^{0.5}$. $N_c$ also
increases with particle size. As an example, the $N_c$ for polystyrene brushes on 15.4 nm diameter silica nanospheres is 250. Nanomaterials functionalized with a SDPB capable of entanglement will largely adopt melt, flow and order/disorder transition characteristics similar to bulk analogs. It is known that the critical degree of polymerization required to decrease structural regularity of NC arrays can be estimated from the volume fraction of segments in the SDPB portion of the NC ($\phi_{SDPB}$) and the available void space created by packing the NCs into a solid (Figure 8). In the limiting condition where face-centered cubic packing leads to an interstitial void volume fraction minimum of 0.26, the threshold $\phi_{SDPB}$ value that must be exceeded to disorder this system is estimated from:

$$\phi_{VOID} = 0.26 < \phi_{SDPB} = C \cdot 4\pi \cdot (R_{NC} + h_{SiO2})^2 \cdot \sigma_{PMMA} \cdot N_{SDPB} \cdot \alpha^3$$

here, $C$ is a constant that accounts for the number of particles per cubic unit cell volume, $R_{NC}$ is the radius of the NC (including any inorganic QD shell, if present), $h_{SiO2}$ is the thickness of a NC silica shell, $\sigma_{PMMA}$ is the graft density at the SiO$_2$ surface, $N_{SDPB}$ is the degree of polymerization in the semidilute polymer brush shell and $\alpha$ is the segment length of the polymer. Since the optical requirements of the LSC are highly specific for small values of $R_{NC}$ (i.e. < 5 nm), adding silica to the NC structure is the most effective way to increase the volume fraction of the SDPB. For this reason, we are interested in the encapsulation of NCs with silica shells rather than the analogue where silica is omitted and the brush extends directly from the NC surface.

**Silica & Polymer Shells for CuIn(S,Se)$_2$/ZnS NCs.**

In order to evaluate the scope for brushing silica-capped NCs with PMMA, several “grafting to” steps will be surveyed for high $\sigma$ using end-functionalized PMMA. This effort will be complemented by a “grafting from” strategy (see below). For both approaches, we aim to apply CuIn(S,Se)$_2$/ZnS NCs (core diameter = 4 nm, shell thickness = 1 nm) capped with silica. For a 5 nm silica shell, the molecular weight of PMMA required to transition the brush into the SDPB regime will be ~25 kDa. Under the condition of a $\sigma = 0.6$ chains/nm$^2$, the corresponding order-to-disorder (OTD) brush molecular weight is therefore 300 kDa. Since the OTD decreases with $\sigma$ (see Figure 9) we anticipate that the “grafting to” approach, that typically has decreasing $\sigma$ with molecular weight, will provide sufficient molecular weight and $\sigma$. The overall synthetic goal of this “grafting to” approach will be to understand a two-channel mode for fine tuning of $\sigma$ of PMMA – one based on molecular weight and another based on diluents in the shell. The overall synthetic goal of the “grafting from” approach will generally provide higher $\sigma$ that is largely independent of brush molecular weight and tunable based on a diluents in the shell.

We will synthesize the silica shells on CuIn(S,Se)$_2$/ZnS NCs via a microemulsion reaction according to Scheme 1. The silica shell thickness can be specified by the stoichiometry of the base catalyst (NH$_4$+) and/or the nonionic surfactant IGEPAL CO-520. The initial target thickness for the silica shell is 5 nm. The outer silylol residues of the TEOS silica shell will be reacted with the various chlorosilanes for functionalization. Direct reaction with chlorosilane terminated PMMA is the most direct brushing strategy. Entries 4-6 from Table 1 will be used to install surface coupling groups for “grafting to.” We intend to apply the silanes listed in Table 1, entries 7 and 8 in order to install graft initiation sites for polymerization. Entries 2 and 3 are capping groups for the silica interior and exterior, respectively, and will act as diluents for any surface functional groups in order to decrease $\sigma$. The degree of polymerization of the TEOS in the shell (and any relevant copolymers) will be determined by thermogravimetric analysis (TGA). The combination of dynamic light scattering (DLS) and scanning transmission electron microscopy (STEM) will be used to determine the dimensions of the inorganic NC core and silica shell.
The preparation of a chlorosilane terminated PMMA (P2) appropriate for grafting to surface hydroxyl residues is outlined atop in Scheme 2. The initial target molecular weight of for all end-functionalized PMMA samples is 50 kDa. Thiol-terminated PMMA (P1) will be isolated from the reversible addition–fragmentation chain transfer (RAFT) polymerization of MMA followed by hydrolysis of the phenylthiocarbonylester. A thiol-ene conversion of the thiol-terminus to a dimethylchlorosilane-capped PMMA is the second and final step to synthesize P2. Gel permeation chromatography (GPC) and/or matrix assisted laser desorption ionization time of flight (MALDI–TOF) chromatography will be used for characterization of all polymers (reactive end groups will be quenched before analysis). A condensation “grafting to” reaction of P2 with the TEOS silica-capped NCs will be conducted characterized where any unreacted surface hydroxyl groups can be quenched with a capping agent (entry 2, Table 1). The resulting PMMA-SiO2-shelled NC will be characterized for size and σ using DLS, STEM and TGA. Should σ be found to be too large (greater than ~0.4), sub-stoichiometric amounts of trimethylchlorosilane (Table 1, entry 3) can be reacted with the shell or a copolymerization of TEOS with ethyltriethoxysilane (Table 1, entry 2) can be conducted.

The preparation of alternative end-group functionalized PMMAs that are in-line for grafting to the complementary functional groups on the alternative silica shell surfaces is also outlined in Scheme 2 (middle and bottom panels). An α-carboxy-ω-thio-polymethylmethacrylate (P3) will be used as a common starting material for all required polymers. In brief, the thiol terminus of polymer P3 will be capped by a thiol-ene reaction with butene (P4) followed by conversion of its carboxy terminus to an amidoimidazolyl that primes this P5 polymer end group for esterification. Polymer P5 is transformed into an alkyne terminated analogue (P6) by displacement of the imidazole group with 3-bromopropyne. Similarly, P5 can be converted into an azido-terminated analogue (P7) by reaction with azidoethylamine. Many of these polymers are also commercially available and can be purchased with the required molecular weights listed herein.

Similarly, CuIn(S,Se)2/ZnS NCs, capped with 5 nm of silica and decorated with various reactive surface groups will be used to evaluate other polymer “grafting to” chemistries using the complementary library of polymers listed above. In brief, the shell surface thiols will be reacted with the alkyn group from P6. Shell surface vinyl groups will be reacted with the thiol group from P1. Similarly, shell surface alkyn groups will be reacted with the thiol group from P1. Lastly, shell surface alkyn groups will be reacted with the azido terminus of polymer P7. These “grafting to” reactions will be characterized for size and graft density using DLS, STEM and TGA. This survey of grafting to reactivity will allow us to select the approach

### Table 1. Summary of silica shell precursors and their purpose.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Purpose</th>
<th>X– linker</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dense x-linking of SiO_x</td>
<td>OEt</td>
<td>none</td>
<td>OEt</td>
</tr>
<tr>
<td>2</td>
<td>Diluent for surface OH groups</td>
<td>CH_3</td>
<td>CH_2</td>
<td>OEt</td>
</tr>
<tr>
<td>3</td>
<td>Inert cap for surface OH</td>
<td>CH_3</td>
<td>none</td>
<td>CH_3</td>
</tr>
<tr>
<td>4</td>
<td>Graft to via thiol-yne reaction</td>
<td>SH</td>
<td>(CH_3)_2</td>
<td>CH_3</td>
</tr>
<tr>
<td>5</td>
<td>Graft to via thiol-yne reaction</td>
<td>CH_2=CH</td>
<td>(CH_3)_2</td>
<td>CH_3</td>
</tr>
<tr>
<td>6</td>
<td>Graft to via click reaction</td>
<td>HC=CH</td>
<td>(CH_3)_2</td>
<td>CH_3</td>
</tr>
<tr>
<td>7</td>
<td>Graft from via RAFT</td>
<td></td>
<td>(CH_3)_2</td>
<td>CH_3</td>
</tr>
<tr>
<td>8</td>
<td>Graft from via ATRP</td>
<td></td>
<td>(CH_3)_2</td>
<td>CH_3</td>
</tr>
</tbody>
</table>
with the highest $\sigma$. The scope of the most ideal grafting reaction will then be studied with molecular weight ranged polymers that are easily synthesized by tailoring the stoichiometry of the RAFT polymerization for (P1). Through the linkers outlined in Table 1, and the PMMA grafting groups in Scheme 2, we will be able to synthesize composites spanning a wide range of structures, from fully amorphous, to locally ordered, to long-range polycrystalline organization (see Figure 9).

Surface initiated polymerization of MMA by ATRP and RAFT has been applied to many different inorganic substrates. We intend to apply the silanes listed in Table 1, entries 7 and 8 in order to install graft initiation sites for PMMA chains. The area density of these initiators can also be decreased for reasons listed above (see Figure 9) using the inert capping group, chlorotrimethylsilane. Again, we aim to apply CuIn(S,Se)$_2$/ZnS NCs, capped with 5 nm of silica bearing a surface with the appropriate functionality for initiation and polymerization of MMA. The ATRP and RAFT polymerization of MMA from silica surface has been described and will guide the grafting from approach. $\sigma$ values are typically the range of ~0.02-2 chains/nm$^2$ are easily afforded with controlled polymerization conditions. Typically, small amounts of untethered initiators are often added during the surface initiated polymerization of MMA and the resulting untethered polymer chains will be used to provide approximation for the molecular weight and distribution of polymer brush chains and, hence, graft density for a specific polymer layer. Our target molecular weights for triggering disorder in the bulk solids of the brushed NCs is dependent on $\sigma$, but we expect a need to exceed ~25 kDa ($\sigma$ of 0.6 chains/nm$^2$) and in the range of 100kDa.

The above proposed grafting methods are expected to be highly flexible and would easily lend themselves to contingency plans should particle-particle attractive forces be too high. Recently, Benicewicz, Schadler et al. found that TiO$_2$ NPs could be grafted with both short and long brushes of PDMS. The short chains enhanced core-core screening to reduce the particle-particle attraction while long chains were sufficient for entanglement and dispersing the NPs. We anticipate that the research plan could be easily modified to afford silica shells with a surface that could be functionalized with two or more functional groups for polymer grafts (P2, P6 and/or P7) with differing molecular weights.

WWU’s new STEM instrument (JEOL 7200F; 0.8 nm resolution) and RMC microtome with an advanced substrate holder will permit the acquisition of micrographs of films of serially microtomed samples. The advanced substrate holder also allows for tomographic investigations where a 3-D reconstruction of serially sectioned samples can be conducted. IMOD software (freeware) can be used to assign the spatial coordinates of any resolved NCs and to render various projections of a representative bulk samples. High-resolution TEM images will be acquired from the facilities at UW-Seattle. Plane view STEM images (DF and/or BF) and 3D tomographic micrograph projections will be transformed into Fast-Fourier Transform renditions in order to confirm SAXS assignments for structure and order. Both SAXS and STEM data will be used to characterize particle packing statistics used in light scattering calculations described below.

**Scheme 2.** Summary of synthesis of end-group functionalized PMMA polymers (P1-P7) that will be used for “grafting to” approach. CDI – carbonyldiimidazole.
III.C Composite Waveguide Fabrication and Characterization

Polymer-brush NCs developed in section III B will be solvent-cast into planar waveguides 1 – 100 μm thick, supported on a substrate of thin B270 glass (Fig. 10). The glass substrate provides a low autofluorescence, low roughness and low loss support (α_{B270\text{glass}} = 1.8×10^{-4} \text{ dB cm}^{-1} \text{ at } 400 \text{ nm}).^{106} Due to the high density of NCs within the composite, a 100 μm-thick waveguide provides an absorbance exceeding 90% at the wavelength of the first absorbance peak, enabling efficient solar absorption for LSC applications. Because the waveguides are so thin, a large geometric gain (G > 50) can be achieved with a square waveguide measuring only a few cm on each side. The PIs’ groups are experienced in fabricating and characterizing NC-doped polymer waveguides for LSC applications up to 400 × 400 mm in size.

Composite waveguide optical properties will be measured with a custom spectrometer employing fiber optic bundle excitation and collection sources allowing output to be measured as a function of position in order to separately determine reflection, transmission, absorption, scattering, and transport properties (Fig. 11). Samples can be illuminated uniformly, or over regions of varying size by means of a movable aperture. Edge-emitted light is collected either using an integrating sphere, or for angular emission measurements, an index matching hemispherical lens. The setup allows characterization of waveguides approaching 1 m in length. Three types of illumination sources will be employed: (i) a monochromator for spectral measurements; (ii) a small-spot solar simulator; and (iii) a large area (up to 2” diameter) solar simulator. Spot size and beam characteristics can be selected to provide diffuse or specular illumination and varying intensity. These measurements are in models developed by the PIs to extract optical loss rates by each mechanism described on p. 3,43,67,69,70 In addition to optical properties, a range of tools will be employed to characterize other critical waveguide properties, including surface roughness (atomic force microscopy), refractive indices and film thicknesses (ellipsometry), polymer transition temperatures and completeness of polymerization (differential scanning calorimetry and FTIR spectroscopy) and NC loading (thermal gravimetric analysis). Transmission electron microscopy and small-angle x-ray scattering will also be used, as described above.

III.D Predictive modeling and simulation for guiding materials development

At each stage of the research, theory and modeling will be used to predict expected performance metrics for a given design architecture and used to guide optimal choices of materials and designs. The spatial distribution of NCs within the waveguide, and the resulting loss mechanisms due to light-scattering and non-radiative relaxation, among others, remains the limiting factor for achieving large scale, low-loss transport of photons. The relationship between NC packing density and loss mechanisms such as light-scattering is a highly non-linear one. We will study and model the statistics of inter-NC separation distances.

Fig. 10. Thin film planar waveguides prepared at WWU from colloidal semiconductor NCs in PLMA. Scale bar is 1 inch.

Fig. 11. Apparatus for measuring waveguide optical properties. Point or area illumination of devices up to 1 m in length is performed using a rail-mounted mask. Edge-emitted light is collected by an integrating sphere, or for angular emission measurements, by a hemispherical lens system (not shown). LS=light source, IS=integrating sphere, L=Xe lamp, M1-3=monochrometers, D=photomultiplier detector. The light source can be exchanged for a solar simulator. Waveguide in upper right panel measures 4”x4”.
and the effects these have on light-scattering. These statistics can range from a fully ordered crystalline structure with a single separation distance, to various perturbations of a crystalline structure, to a random arrangement in which the density of NCs is modeled by a Poisson distribution. Apart from the theoretically optimal arrangements, we also consider the practically realizable distributions, and the expected spatial variances of these. As well as minimizing the associated loss mechanisms, at the same time, we are seeking to maximize the density of NCs per unit volume, thus maximizing the light absorbed over a minimal thickness of the waveguide. We will also model light propagation within the various spatial distributions to understand their light-scattering properties. We can control the degree of minimal separation of the NCs by way of the size of polymer coatings; from a modeling standpoint, we will treat the resulting structures as soft spheres, the softness characterized by a parameter we may understand as a spring constant. We can, to some degree, control this softness. Within the space of these models, we will also consider situations in which there is a mixture of more than one sized sphere. Initial computations and simulations will inform the choices made in ligand and silica shell synthesis, as well as the relative ratios and sizes of mixtures of nanoparticles in polydisperse composites. This will then feed back to the modeling, giving important insights as to what type of distribution results from the prescribed sizes, softness and concentration, and verifying, or correcting the models used.

The limiting, ideal, configuration of NC centers would be a regularly spaced, tightly packed, crystalline structure. This follows from the Ewald-Oseen extinction theorem\textsuperscript{108} which can be understood as stating that the closely spaced regular system behaves like a uniform medium with a new index of refraction. It is not the density itself, but fluctuation in the density of point scatterers that results in a non-zero contribution to the total scattering at non-zero scattering angles.\textsuperscript{109} Thus we are led to consider an architecture in which we seek to control the inter-particle spacing as rigidly as possible, for, if achievable, this would lead to a maximal concentration with little-to-no light-scattering. In considering how closely packed the spheres can be, we will constrain the NCs from being so close to one another that concentration quenching occurs.

It is unlikely that a perfect crystalline structure will be achievable in practice. Combining TEM and SAX measurements with simulations, we will study the statistics of the packing distributions achieved in fabricated waveguides. Understanding light propagation and scattering in such complex systems of a very large number of scatterers can be difficult and computationally expensive. We propose two (similar and complementary) approaches to compute scattering cross-sections for ensembles of tightly packed scatterers.

The first approach is begins with computation of the radial distance function $g_x(r)$ centered on $S_x$, a given NC. This is given by $g(r) = n(r)/\rho 4\pi r^2 \Delta r$, where $n(r)$ is the number of centers lying within the shell of radii $r$ to $r + \Delta r$ centered at $S_x$. The typical shape of $g(r)$ is one that oscillates to some degree up until a critical value $r = L_x$ beyond which it is approximately constant. For $r > L_x$, the arrangement of spheres cannot be distinguished from a random distribution, from the point of view from $S_x$; for $r < L_x$ this is not the case and the actual distribution of centers needs to be considered for scattering computations. We repeat this over all centers $S_x$ and average $g_x(r)$ over $x$ to define a single radial distance function $g(r)$, and, correspondingly, an average critical value $r = L^*$. We propose to understand scattering from the full collection of spheres by separating local behavior, in a neighborhood $r < L^*$ of a center, from the surrounding volume which we will treat as an effective medium with averaged scattering properties. In the following discussion, we refer to a local collection of NCs in an $(r < L^*)$-neighborhood as a \textit{cluster}. Restricted to this local cluster, the number of scatterers involved is small enough that there are exact computational approaches one can take to compute the scattering cross-section of the cluster. This hybrid treatment of exact local scattering computation and global effective medium field propagation will result in computationally feasible problems that retain an accuracy that goes beyond a single global effective medium treatment.

Particles in a cluster are electromagnetically coupled: each particle is excited by the external field and the resultant field scattered by all the other particles in the cluster. But the field scattered by a particle depends on the total field to which it is exposed. Thus an approach which treats the full cluster of particles as an intertwined system is necessary. To achieve this computation of the scattering cross sections for clusters, we propose to use the so-called $T$-matrix method\textsuperscript{110,111} in which solutions to Maxwell’s equations

\begin{equation}
\begin{aligned}
\text{clusters, we propose to use the so-called T-matrix method} \text{ which solutions to Maxwell’s equations}
\end{aligned}
\end{equation}
are computed, satisfying appropriate boundary conditions; the incident and scattered electric fields are then expanded into norm-convergent series of spherical vector wave functions (SVWF). As described below, SVWFs together with appropriate addition theorems\textsuperscript{113,114} facilitate treatment of intertwined scattering systems.

SVWFs arise from expressing solutions to Maxwell’s equations in spherical coordinates. Assuming time-harmonic waves as fixed frequency, the electric field $\mathbf{E}$ satisfies the vector Helmholtz equation $\nabla \times (\nabla \times \mathbf{E}(r)) - k^2 \mathbf{E}(r) = 0$. The spherical harmonics $Y_{lm}(\theta, \phi)$ are special functions defined in spherical coordinates which form a complete set of orthonormal functions with respect to the $L^2$ inner product with the area measure on the sphere. They are eigenfunctions of the spherical Laplacian. Thus, any square-integrable function on the sphere is uniquely expressible as an infinite linear combination of the spherical harmonics. Restricting a vector field $\mathbf{E}$ to a sphere, $\mathbf{E}$ can be expressed in terms of the spherical harmonics with vector-valued coefficients. The purpose of introducing SVWFs is to provide a complete vector-valued basis so that expansions of vector fields in terms of this basis have scalar coefficients. Briefly, from each $Y_{lm}(\theta, \phi)$ we define three vector-valued basis elements $A_{jlm}$, $j = 1, 2, 3$, in terms of (appropriate weighted) $Y_{lm}(\theta, \phi)$ together with its gradient and its curl. Defining the natural $L^2$ inner product and norm for vector fields on the sphere, the $A_{jlm}$ again satisfy orthogonality conditions on the sphere, for each fixed $j$. This orthogonality property facilitates straightforward computation of the generalized Fourier coefficients in the series expansion of a field in terms of the $A_{jlm}$. To compute scattering from a collection of spheres we must formulate an intertwined system of equations for the coefficients of the series expansion of the field. For this we need to be able to describe the fields scattered from different origins of coordinate systems, but in terms of a single set of basis functions (SVWFs). What facilitates this is the ability to express the basis elements of one representation in terms of those of another. This is done by way of addition theorems for SVWFs obtained by Stein and Cruzan,\textsuperscript{112-115} With this machinery, we are able to compute the scattered field resulting from a given geometry of scattering centers.\textsuperscript{116-121} Such computations have been verified experimentally,\textsuperscript{122-124} have been used to study the dependence on the cluster arrangement,\textsuperscript{125,126} and have been extended to include anisotropic scatterers.\textsuperscript{127,128}

A similar approach was taken in Borghese et. Al.\textsuperscript{118,119} using vector Helmholtz harmonics (VHH) which, similarly, expresses a VHH in a coordinate system centered on one scatterer in terms of the VHH’s centered on other scatterers and permits computation of the terms representing interaction between the spheres within the cluster. This is achieved by analogous addition theorems for VHH.\textsuperscript{129} We will consider both formulations.

The second approach is a far-field approach which develops generalized multiparticle Mie solutions (GMM).\textsuperscript{130-133} If the number of scatterers treated by the $T$-matrix method gets too large, truncations necessary in series expansions of fields can lead to inaccuracy, and so the $T$-matrix method is limited in the overall size of the system that can be treated successfully. In far-field GMM computations, however, truncation is determined by the size of the scatterers involved, and potentially allows for treatment of a larger number of scattering centers. As in the $T$-matrix approach, incident and scattered waves are expanded in terms of SVWFs; for each individual scatterer the incident and partial scattered waves are similarly expanded in terms of SVWFs in a reference frame centered on the scatterer (and consequently the addition formulae of the $T$-matrix method are unnecessary). In an architecture with spheres of only one size, these expansions will all be identical; in a system comprising two or three sized spheres, there will only be two or three such expansions. This reduces one part of the computational complexity. Computation of the individual expansions involves matching of boundary conditions at interfaces where the index of refraction changes. The resulting systems are themselves $T$-matrix formulations, and it is in this sense that the two approaches are complimentary.

IV. The Scientific Team & Project Management

Modeling and theory-driven design will be led by mathematician Dr. Stephen McDowall, who has expertise in the study of photon transport within scattering and absorbing media as well as experience working with the full Maxwell system of equations applied to complex geometries. Dr. David Rider, a
polymer chemist, will lead the development of polymer brushes. Dr. John Gilbertson, an inorganic chemist, will lead the work on silica shelling. Dr. David Patrick, a materials chemist with expertise in LSC fabrication and characterization, will provide overall direction to the research as Principle Investigator and lead the experimental work on waveguide development and device testing. As discussed throughout, the proposed research is highly synergistic, with iterative connections between theory and modeling, materials selection/synthesis, and device fabrication and characterization. Although the collaboration among the PIs is new, several of them have already jointly supervised students, and jointly published several manuscripts and filed one patent application, providing a strong indication of future success.

V. Broader Impacts.

Undergraduate Students. The research will involve 6 undergraduates per year (total 12-18 over the grant period) working year-round on the project. WWU is a primarily undergraduate institution where undergraduates comprise the majority of the scientific workforce. Between them the PIs have mentored over 100 undergraduate researchers, and undergraduates are included nearly 50 times as co-authors on published papers from their groups. These students are involved in every phase of the research. Participating students will receive a strong foundation in materials and synthetic chemistry, optics, and mathematics, as well as having the chance to experience the excitement of independent, creative scientific investigation. Further details concerning undergraduate student involvement are provided in the RUI impact statement.

High school students. The PIs regularly involve high school students in their research. These students integrate into the environment and eventually participate at a level close to the undergraduates. As evidence of the success of this outreach effort, two high school students working in the PIs’ groups have been finalists in the Intel Science Talent Search, the oldest and most prestigious high school science competition in the nation, and others have done very well in regional and state science fairs. We anticipate 1 high school student per year will participate in this research.

Interdisciplinary Student Preparation. The proposed research involves participants in several subdisciplines, who therefore will benefit from working closely with colleagues from different academic and preparatory backgrounds. The PIs encourage students to explore and understand implications of their work beyond science. For example, we have mentored a series of student teams in regional business plan contests with product concepts derived from their undergraduate research. Over the last five years teams of Chemistry, Engineering, Industrial Design, and MBA students have won approximately $100,000 in prize money at several competitions based on commercial products they proposed derived from the topic of this proposal (Fig. 12). We will continue our mentorship of such teams, involving 2-3 researchers directly involved in the work and 4-6 additional students from other disciplines.

Additional Outreach Activities. The PIs are committed to supporting students of all ages in their pursuit of education and training in the STEM fields, and they and their students are involved in a wide range of related outreach efforts. Patrick teaches a one-week summer course to high school students on the science of renewable energy incorporating laboratory activities with solar concentrators. Three of the PIs participate in WWU’s compass-to-campus program, which brings approximately 1000 5th and 6th graders to campus every year for laboratory tours and hands-on science activities. The PIs are devoted to broaden participation by under-represented groups in their research programs. Rider, who speaks Spanish,
participates in an annual Science Night at nearby Mount Vernon High school (since 2012), which is in a district with an especially high concentration of Hispanic students. One of his native Spanish-speaking undergraduate research students, Diane Perez, was featured in a local media campaign highlighting the importance of scientific research opportunities for students from traditionally underrepresented groups (Fig. 13). The PIs are also actively involved in outreach to the local community through the production of a video series titled “Scientist Citizen”. Scientist Citizen is a program that aims to introduce chemistry into the local media by training a generation of scientist citizens to communicate their ideas and engage the public outside the classroom setting. Even with the advent of social media via the internet, television continues to be the main source of news for Americans. Therefore, there is real opportunity for our undergraduate students to become "scientist citizens" thereby engaging the local public and improving general chemical literacy by utilizing both classical and social media outlets. Links to the video series can be found at https://cse.wwu.edu/chemistry/scientist-citizen.

**Broader Scientific Impacts.** The successful development of densely-packed, high performance polymer-luminescent NC composites engineered to minimize light-scattering and other nonlinear losses will impact a wide range of technological applications. The resulting new materials and design principles, along with deepened fundamental understanding of the optical and structural properties of these composites, will also have broader scientific impacts:

- Development of high transparency polymer-NC composites would improve performance in NC-based electroluminescent devices, color conversion films, and scintillation detectors and many other current and emerging applications.
- Successful development of high performance LSCs would enable more widespread deployment of solar energy applications in the built environment.
- Development of new methods for preparing nanocrystals with functional silica shells and polymer brushes. Silica shelled NCs with functional groups are promising candidate materials for bioimaging and biosensing. The functional groups that will be used for grafting may also be used for the attachment of other biomarkers and targeting groups. Polymer brushed, silica shelled NCs will also show interesting mechanical properties owing to the possibility as physical crosslinks in polymer blends or, as reporters for mechanical stress if self-quenching NC are used instead of those described above.
- Multiscale modeling of light-scattering for densely packed scatterers will lead to new computational approaches which bridge the gap between exact, full Maxwell-equation solutions for small numbers of scatterers, and averaged, effective medium treatments for large numbers of statistically described scatterers. Accurate computation of scattering mechanisms will have applications in many photon transport applications at a wide range of scales.

**Fig. 13.** WWU’s full page ad in Nov. issue of Alaska Airline's in-flight magazine (inset is Cover).
References.


98 Li, C.; Benicewicz, B. C., Synthesis of well-defined polymer brushes grafted onto silica nanoparticles via surface reversible addition-fragmentation chain transfer polymerization, Macromolecules 2005, 38, 5929.


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BIOGRAPHICAL SKETCH

David L. Patrick

Department of Chemistry, Western Washington University, 519 High St., Bellingham, WA 98225
https://cse.wwu.edu/chemistry/dpatrick

Professional Preparation
Univ. of California (Davis, CA) Chemistry B.S. 1990
Univ. of Utah (Salt Lake City, UT) Physical Chemistry Ph.D. 1995

Appointments
Director, Advanced Materials Science Center 2007 – 2010, 2016 – present Western Washington Univ.
EPSRC Visiting Fellow July 2010 – Aug 2011 University of Cambridge
Professor of Chemistry Sept. 2005 – present Western Washington Univ.
Associate Professor of Chemistry Sept. 2001 – Sept. 2004 Western Washington Univ.
Visiting Fellow June 2002 – Aug 2003 University of Oxford
Assistant Professor of Chemistry Sept. 1996 – Sept. 2001 Western Washington Univ.

Products
Most closely related to the proposed project (* = WWU undergraduate, # = WWU M.S.-level graduate student)

Other significant products (* = undergraduate, # = M.S.-level graduate student)
Synergistic Activities

1. Director, Advanced Materials Science Engineering Center (AMSEC), Western Washington University, 2007-present. The PI is the founding Director of AMSEC, an interdisciplinary institute promoting research, undergraduate education, and industry collaboration in materials science and engineering. As Director the PI oversees the creation of the program including establishing $1.2M in permanent funding, development of new curricula, faculty and staff hiring, and creation of a materials research and instrumentation laboratory.

2. Member, Institute for Energy Studies, Western Washington University, 2013-present, and Snohomish PUD Professor of Energy Studies. The PI is a member of the executive committee of a new institute working to develop energy-related curricula, outreach and research programs. Supported by $1.3M in state funding and over $1M in private gifts, the institute has hired six faculty and two staff and is introducing two new majors, one minor and an engineering concentration. The PI has been particularly active in the design of a new energy science degree, to be introduced Fall, 2015.

3. The PI is involved in outreach efforts with local high schools and a frequent speaker at public events. His recent activities include public lectures on nanotechnology; working with teachers in local schools to introduce laboratory experiments involving WWU instrumentation; advising two local elementary schools on how to start and sustain annual science fairs; and testimony before the WA State Legislature on the role of research at predominately undergraduate institutions. The PI also typically includes one high school student in his research group, two of which have been finalists in the Intel Science Talent Search.

4. The PI is active in service to his profession, including: serving as program committee member for the AVS Surface Analysis 2012 Conference; chair of the Pacific Northwest Chapter of American Vacuum Society (2005); Chair of the Linus Pauling Award (2006 & 2014); organizing committee member of the U.S. National Academy of Sciences / Alexander von Humboldt Foundation German-American Frontiers in Science Symposium Series; as a consultant to other primarily undergraduate chemistry departments with active research programs; and as an invited participant/panelist at various professional workshops and symposia.
BIOGRAPHICAL SKETCH

John D. Gilbertson
Department of Chemistry, Western Washington University, 516 High St., Bellingham, WA 98225
https://cse.wwu.edu/chemistry/gilberj4

Academic Rank: Associate Professor                       Field: Inorganic Chemistry

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Research and Professional Experience
Associate Professor, Western Washington University, 2014 -
Assistant Professor, Western Washington University, 2008 - 2014
Visiting Assistant Professor, Augustana College, SD, 2007-2008
University of Oregon Doctoral Research Fellowship (awarded but declined), 2005
National Science Foundation IGERT Fellowship, 2002 - 2005
Graduate Assistant, University of Oregon, 2001 - 2005

Products  (* =WWU undergraduate, # = WWU graduate co-author)

Most Relevant to proposed project:


Other Significant Products


**Synergistic Activities**

- Mentored 25 undergraduate student researchers (seven of these students are women, one is African-American, one is Laotian, two are Asian, two are Hispanic, and one is Native American). 24 students have graduated with B.S. degrees; most graduates from the group have been accepted to either graduate (21) or professional school (1).
- My publications describing work done at WWU have undergraduate and M.S. student co-authors from WWU who are responsible for a majority of the work reported. We have published nine manuscripts with 15 different undergraduate (chemistry and physics) or graduate (MS) coauthors (18 total authorships).
- Nine students have presented their research results in six different posters at regional or national meetings of the American Chemical Society, in addition to numerous presentations at local meetings and symposia.
- Developing a video series entitled “Scientist Citizen” to increase local science literacy. https://cse.wwu.edu/chemistry/scientist-citizen
BIOGRAPHICAL SKETCH

Stephen R. McDowall

Department of Mathematics, Western Washington University, 519 High St., Bellingham, WA 98225-9063
myweb.facstaff.wwu.edu/mcdowas/

Professional Preparation
University of Canterbury (New Zealand)  Mathematics  B.Sc. (Hons.) 1992
University of Canterbury (New Zealand)  Mathematics  M.Sc. (Dist.), 1993
University of Washington (Seattle, WA)  Partial Differential Equations  Ph.D., 1998

Appointments
Professor  Western Washington University, WA  2012—present
Associate Professor  Western Washington University, WA  2006—2012
Assistant Professor  Western Washington University, WA  2002—2006
Visiting Assistant Professor  University of Rochester, NY  1998—2001

Products
Most closely related to the proposed project (* = undergraduate, # = M.S.-level graduate student)

Other significant products (* = undergraduate, # = M.S.-level graduate student)

**Synergistic Activities**

1. **Advisor for Master’s students at Western Washington University (mathematics):**
   a. Brandon Culley – “Calculus of variations” (2003);
   b. Brandon Peden – “The Gale transform and infinite dimensional polytopes” (2004);
   c. Mark DeSmet – “The Fourier transform and its properties” (2005);
   d. Will Freeman – “X-ray tomography and the Radon transform and its inversion” (2005);
   e. Nicola Parker – “Wavelets: theory and applications” (2006);
   f. Dan Fortin – “Optical tomography in two dimensions” (2007);
   g. Dale Trockel – “Boundary rigidity in Riemannian geometry” (2008);
   h. Amber Goodrich – “The Study of Traffic Flow” (2011);
   i. Tony Marzetta – “Layer potentials and solutions to Dirichlet and Neumann problems” (2014);
   j. Gage Cosgrove – “The Quotient Manifold Theorem” (2015);

2. **Advisor of Senior Theses (mathematics)**
   a. Timothy Mesikepp – “The Mathematics of Magnetic Resonance Imaging” (2011);

3. **Presentation of lectures on “optical tomography in media with varying index of refraction” for graduate students and recent Ph.D.’s at annual meetings organized by members of “Focused Research Group” NSF grant.**

4. **Co-organizer of 2009 American Mathematical Society “Mathematics Research Communities” meeting on “Inverse Problems” designed to facilitate research collaborations among new PhDs.**

5. Gave general audience lecture at the Bellingham City Chambers entitled “The x-ray vision of mathematics” as part of WWU’s series of science-based outreach talks to the Bellingham community.
BIOGRAPHICAL SKETCH

David A. Rider
Department of Chemistry, Western Washington University, 519 High St., Bellingham, WA 98225
https://cse.wwu.edu/chemistry/riderd

Professional Preparation
Simon Fraser Univ. (Burnaby, Canada) Chemistry B.S. 2002
Univ. of Toronto (Toronto, Canada) Chemistry Ph.D. 2007
Univ. of Alberta (Edmonton, Canada) Nanotechn./Chemistry Postdoc. 2007-2010

Appointments
Associate Professor of Chemistry Sept. 2016 – present Western Washington Univ.
Assistant Professor of Chemistry Sept. 2010 – June 2016 Western Washington Univ.
NSERC Postdoctoral Fellow Sep 2009 – Jun. 2010 Univ. of Alberta

Products
Most closely related to the proposed project (*undergraduate and θgraduate chemistry student; #undergraduate engineering student)

Other significant products (* = undergraduate, # = M.S.-level graduate student)
**Synergistic Activities**

(i) Advanced Materials Science Engineering Center (AMSEC), Western Washington University, 2010-present. The CoPI is one of 2.5 AMSEC faculty, an interdisciplinary institute promoting research, undergraduate education, and industry collaboration in materials science and engineering.

(ii) Migrant Youth Conference for middle- and high-school students whose families work in local county agricultural jobs (2012-present). The CoPI also typically includes one high school student each summer in his research group.

(iii) Chair for Committee for WWU’s “Research and Creative Opportunities Grant for Undergraduates (2012-present).

(iv) Organizer of several public seminar series in WWU Chemistry and AMSEC.

(v) “SACNAS-Applying to Grad School” Discussion Panelist (2012).

(vi) Organizer and participant for WWU-AMSEC’s role in Compass-to-Campus (2013-present).

(vii) WWU Organizer and participant in Mount Vernon High School’s Science Night (2012-present)

(viii) Five invited lectures in U.S.A. and Canada

(ix) Symposium Chair for Linus Pauling Medal Award 2014
### SUMMARY PROPOSAL BUDGET

**ORGANIZATION**
Western Washington University

**PRINCIPAL INVESTIGATOR / PROJECT DIRECTOR**
David L. Patrick

#### A. SENIOR PERSONNEL: PI/PD, Co-PI's, Faculty and Other Senior Associates
(List each separately with title, A.7. show number in brackets)

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#### B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)

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**TOTAL SALARIES AND WAGES (A + B)**

59,661

#### C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS)

**TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C)**

71,799

#### D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING $5,000.)

**TOTAL EQUIPMENT**

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<tr>
<td>4. OTHER</td>
<td>0</td>
<td>0</td>
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</tbody>
</table>

**TOTAL NUMBER OF PARTICIPANTS**

0

**TOTAL PARTICIPANT COSTS**

0

#### G. OTHER DIRECT COSTS

<table>
<thead>
<tr>
<th>Category</th>
<th>Number</th>
<th>Rate</th>
<th>Base</th>
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<tbody>
<tr>
<td>1. MATERIALS AND SUPPLIES</td>
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<tr>
<td>2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION</td>
<td>0</td>
<td>0</td>
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<tr>
<td>3. CONSULTANT SERVICES</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4. COMPUTER SERVICES</td>
<td>0</td>
<td>0</td>
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<tr>
<td>5. SUBAWARDS</td>
<td>0</td>
<td>0</td>
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<tr>
<td>6. OTHER</td>
<td>4,000</td>
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**TOTAL OTHER DIRECT COSTS**

42,202

**TOTAL DIRECT COSTS (A THROUGH G)**

122,001

#### I. INDIRECT COSTS (F&A)(SPECIFY RATE AND BASE)

**Salaries and wages (Rate: 52.2000, Base: 59661)**

**TOTAL INDIRECT COSTS (F&A)**

31,143

**J. TOTAL DIRECT AND INDIRECT COSTS (H + I)**

153,144

**K. SMALL BUSINESS FEE**

0

**L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)**

153,144

**M. COST SHARING PROPOSED LEVEL**

0

**AGREED LEVEL IF DIFFERENT**

0

**PI/PD NAME**
David L. Patrick

**FOR NSF USE ONLY**

**INDIRECT COST RATE VERIFICATION**

**ORG. REP. NAME**
Kathleen Kitto

1 *ELECTRONIC SIGNATURES REQUIRED FOR REVISED BUDGET*
<table>
<thead>
<tr>
<th>ORGANIZATION</th>
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<th>DURATION (months)</th>
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<tbody>
<tr>
<td>Western Washington University</td>
<td></td>
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</table>

**PRINCIPAL INVESTIGATOR / PROJECT DIRECTOR**

David L. Patrick

### A. SENIOR PERSONNEL: PI/PD, Co-PI's, Faculty and Other Senior Associates

<table>
<thead>
<tr>
<th>Name</th>
<th>PI/PD</th>
<th>Co-PI</th>
<th>Faculty</th>
<th>Other Senior Associates</th>
</tr>
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<tbody>
<tr>
<td>John DGilbertson</td>
<td>0.00</td>
<td>0.00</td>
<td>0.50</td>
<td>6,877</td>
</tr>
<tr>
<td>Stephen R McDowall</td>
<td>0.00</td>
<td>0.00</td>
<td>1.00</td>
<td>11,258</td>
</tr>
<tr>
<td>David A Rider</td>
<td>0.00</td>
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<td>1.00</td>
<td>9,092</td>
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<td>David L Patrick</td>
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<td>6,877</td>
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**B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)**

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<th>Category</th>
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</tr>
<tr>
<td>Other Professionals</td>
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<td>Graduate Students</td>
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<td>Undergraduate Students</td>
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<tr>
<td>Secretarial - Clerical</td>
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<td>Other</td>
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**C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS)**

<table>
<thead>
<tr>
<th>Rate</th>
<th>Amount</th>
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<tbody>
<tr>
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**D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING $5,000.)**

<table>
<thead>
<tr>
<th>Item</th>
<th>Amount</th>
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<tbody>
<tr>
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**E. TRAVEL**

<table>
<thead>
<tr>
<th>Type</th>
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</thead>
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<td>Foreign</td>
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**F. PARTICIPANT SUPPORT COSTS**

<table>
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</thead>
<tbody>
<tr>
<td>Stipends</td>
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<td>Travel</td>
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<tr>
<td>Subsistence</td>
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<td>Other</td>
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**G. OTHER DIRECT COSTS**

<table>
<thead>
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<th>Amount</th>
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<tr>
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<td>Subawards</td>
<td>0</td>
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<tr>
<td>Other</td>
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**H. TOTAL DIRECT COSTS (A THROUGH G)**

<table>
<thead>
<tr>
<th>Amount</th>
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<tbody>
<tr>
<td>111,822</td>
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**I. INDIRECT COSTS (F&A)(SPECIFY RATE AND BASE)**

<table>
<thead>
<tr>
<th>Salaries and wages (Rate: 52.2000, Base: 61261)</th>
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<tr>
<td></td>
<td>31,978</td>
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**J. TOTAL DIRECT AND INDIRECT COSTS (H + I)**

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<tr>
<th>Amount</th>
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<tr>
<td>143,800</td>
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**K. SMALL BUSINESS FEE**

<table>
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<th>Amount</th>
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</thead>
<tbody>
<tr>
<td>0</td>
</tr>
</tbody>
</table>

**L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)**

<table>
<thead>
<tr>
<th>Amount</th>
</tr>
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<tbody>
<tr>
<td>143,800</td>
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**M. COST SHARING PROPOSED LEVEL**

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<tr>
<th>Proposed Level</th>
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<tbody>
<tr>
<td>0</td>
<td>0</td>
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</table>

**PI/PD NAME**

David L. Patrick

**FOR NSF USE ONLY**

<table>
<thead>
<tr>
<th>ORG. REP. NAME*</th>
<th>Date Checked</th>
<th>Date Of Rate Sheet</th>
<th>Initials - ORG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kathleen Kitto</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2 **ELECTRONIC SIGNATURES REQUIRED FOR REVISED BUDGET**
## SUMMARY PROPOSAL BUDGET

### FOR NSF USE ONLY

**ORGANIZATION**
Western Washington University

**PRINCIPAL INVESTIGATOR / PROJECT DIRECTOR**
David L. Patrick

<table>
<thead>
<tr>
<th>A. SENIOR PERSONNEL: PI/PD, Co-PI's, Faculty and Other Senior Associates (List each separately with title, A.7. show number in brackets)</th>
<th>NSF Funded Person-months</th>
<th>Funds Requested by proposer</th>
<th>Funds granted by NSF (if different)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. David L Patrick - PI</td>
<td>0.00</td>
<td>0.00</td>
<td>0.50</td>
</tr>
<tr>
<td>2. John D Gilberston - Co-PI</td>
<td>0.00</td>
<td>0.00</td>
<td>0.50</td>
</tr>
<tr>
<td>3. Stephen R Mc Dowall - Co-PI</td>
<td>0.00</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>4. David A Rider - Co-PI</td>
<td>0.00</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>5.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. (0) OTHERS (LIST INDIVIDUALLY ON BUDGET JUSTIFICATION PAGE)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>7. (4) TOTAL SENIOR PERSONNEL (1 - 6)</td>
<td>0.00</td>
<td>0.00</td>
<td>3.00</td>
</tr>
</tbody>
</table>

### B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)

| 1. (0) POST DOCTORAL SCHOLARS | 0.00 | 0.00 | 0.00 | 0 |
| 2. (0) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.) | 0.00 | 0.00 | 0.00 | 0 |
| 3. (0) GRADUATE STUDENTS | 0 |
| 4. (6) UNDERGRADUATE STUDENTS | 0 |
| 5. (0) SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY) | 0 |
| 6. (0) OTHER | 0 |

**TOTAL SALARIES AND WAGES (A + B)**

62,918

### C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS)

13,000

**TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C)**

75,918

### D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING $5,000.)

TOTAL EQUIPMENT

0

### E. TRAVEL

1. DOMESTIC (INCL. U.S. POSSESSIONS)

8,000

2. FOREIGN

0

### F. PARTICIPANT SUPPORT COSTS

1. STIPENDS
2. TRAVEL
3. SUBSISTENCE
4. OTHER

TOTAL NUMBER OF PARTICIPANTS (0)

TOTAL PARTICIPANT COSTS

0

### G. OTHER DIRECT COSTS

1. MATERIALS AND SUPPLIES

25,000

2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION

1,000

3. CONSULTANT SERVICES

0

4. COMPUTER SERVICES

0

5. SUBAWARDS

0

6. OTHER

4,000

**TOTAL OTHER DIRECT COSTS**

30,000

**TOTAL DIRECT COSTS (A THROUGH G)**

113,918

### I. INDIRECT COSTS (F&A)(SPECIFY RATE AND BASE)

**Salaries and wages (Rate: 52.2000, Base: 62918)**

**TOTAL INDIRECT COSTS (F&A)**

32,843

### J. TOTAL DIRECT AND INDIRECT COSTS (H + I)

146,761

### K. SMALL BUSINESS FEE

0

### L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)

146,761

**M. COST SHARING**

PROPOSED LEVEL $0

AGREED LEVEL IF DIFFERENT $0

**PI/PD NAME**
David L. Patrick

**FOR NSF USE ONLY**

**INDIRECT COST RATE VERIFICATION**

**ORG. REP. NAME**
Kathleen Kitto

---

3 *ELECTRONIC SIGNATURES REQUIRED FOR REVISED BUDGET*
<table>
<thead>
<tr>
<th>ORGANIZATION</th>
<th>Western Washington University</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRINCIPAL INVESTIGATOR / PROJECT DIRECTOR</td>
<td>David L Patrick</td>
</tr>
</tbody>
</table>

A. SENIOR PERSONNEL: PI/PD, Co-PI's, Faculty and Other Senior Associates (List each separately with title, A.7. show number in brackets)

<table>
<thead>
<tr>
<th>Name</th>
<th>CAL</th>
<th>ACAD</th>
<th>SUMR</th>
<th>Funds Requested By Proposer</th>
<th>Funds Granted by NSF</th>
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</thead>
<tbody>
<tr>
<td>David L Patrick - PI</td>
<td>0.00</td>
<td>0.00</td>
<td>1.50</td>
<td>20,643</td>
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<tr>
<td>John D Gilbertson - Co-PI</td>
<td>0.00</td>
<td>0.00</td>
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<td>14,846</td>
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<tr>
<td>Stephen R McDowall - Co-PI</td>
<td>0.00</td>
<td>0.00</td>
<td>3.00</td>
<td>33,793</td>
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<tr>
<td>David A Rider - Co-PI</td>
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<td>0.00</td>
<td>3.00</td>
<td>27,291</td>
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5. ( ) OTHERS (LIST INDIVIDUALLY ON BUDGET JUSTIFICATION PAGE) 0.00 0.00 0.00 0

7. ( 4 ) TOTAL SENIOR PERSONNEL (1 - 6) 0.00 0.00 9.00 96,573

B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)

<table>
<thead>
<tr>
<th>Category</th>
<th>Number</th>
<th>Funds Requested By Proposer</th>
<th>Funds Granted by NSF</th>
</tr>
</thead>
<tbody>
<tr>
<td>POST DOCTORAL SCHOLARS</td>
<td>( )</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.)</td>
<td>( )</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>GRADUATE STUDENTS</td>
<td>(0)</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>UNDERGRADUATE STUDENTS</td>
<td>(18)</td>
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<tr>
<td>SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY)</td>
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<td>0</td>
<td></td>
</tr>
<tr>
<td>OTHER</td>
<td>( )</td>
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</tr>
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</table>

TOTAL SALARIES AND WAGES (A + B) 183,840

C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS) 37,699

TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C) 221,539

D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING $5,000.)

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<thead>
<tr>
<th>Item Description</th>
<th>Amount</th>
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<tbody>
<tr>
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<tr>
<td>E. TRAVEL</td>
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</tr>
<tr>
<td>1. DOMESTIC (INCL. U.S. POSSESSIONS)</td>
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</tr>
<tr>
<td>2. FOREIGN</td>
<td>0</td>
</tr>
<tr>
<td>F. PARTICIPANT SUPPORT COSTS</td>
<td></td>
</tr>
<tr>
<td>1. STIPENDS</td>
<td>$0</td>
</tr>
<tr>
<td>2. TRAVEL</td>
<td>0</td>
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<tr>
<td>3. SUBSISTENCE</td>
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<tr>
<td>4. OTHER</td>
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<tr>
<td>TOTAL NUMBER OF PARTICIPANTS</td>
<td>( )</td>
</tr>
<tr>
<td>TOTAL PARTICIPANT COSTS</td>
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<tr>
<td>G. OTHER DIRECT COSTS</td>
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</tr>
<tr>
<td>1. MATERIALS AND SUPPLIES</td>
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<td>2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION</td>
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<td>4. COMPUTER SERVICES</td>
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<td>5. SUBAWARDS</td>
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<td>6. OTHER</td>
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<td>TOTAL OTHER DIRECT COSTS</td>
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<td>H. TOTAL DIRECT COSTS (A THROUGH G)</td>
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<td>I. INDIRECT COSTS (F&amp;A) (SPECIFY RATE AND BASE)</td>
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<tr>
<td>TOTAL INDIRECT COSTS (F&amp;A)</td>
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<tr>
<td>J. TOTAL DIRECT AND INDIRECT COSTS (H + I)</td>
<td>443,705</td>
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<td>K. SMALL BUSINESS FEE</td>
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</tr>
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<td>L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)</td>
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M. COST SHARING PROPOSED LEVEL $ 0 AGREED LEVEL IF DIFFERENT $ 0

PI/PD NAME | David L Patrick

FOR NSF USE ONLY

INDIRECT COST RATE VERIFICATION

ORG. REP. NAME* Kathleen Kitto

Date Checked Date Of Rate Sheet Initials - ORG

C *ELECTRONIC SIGNATURES REQUIRED FOR REVISED BUDGET
A. Senior Personnel
Salary is requested for 0.5 summer person month per year for the duration of the grant for the PIs (Patrick and Gilbertson). Salary is requested for 1.0 summer person month per year for the duration of the grant for McDowall and Rider. McDowall will be developing new models to accurately computing scattering profiles for densely packed small scattering centers. He will write and implement computer code to facilitate numerical realizations of developed models. He will also mentor and advise students who will learn the mathematics involved and will learn to write code to perform relevant numerical computations. Rider/Patrick/Gilbertson will oversee the synthetic/characterization aspects of this project, including supervision and mentoring of undergraduate student research assistants, and dissemination of results. During the academic year, the PIs will train and recruit research students. Summer months will focus full-time on the activities in this proposal. Faculty members at Western Washington University are paid on a nine-month contract. Each person month of summer support is calculated as one-ninth of the faculty’s contracted salary. Annual increases of 4.25% in year two and year three of this grant are requested.

B. Other Personnel
Undergraduate research assistants: Undergraduate research assistants will be the primary contributors to this research program described throughout the proposal. Undergraduate research assistants at Western Washington University receive course credit during the academic year. Summer months provide the most productive research opportunity, and therefore, funds are requested to support students during the summer quarter (40 hours/week, 10 weeks). The PIs are requesting funds for six undergraduate student stipends ($4800 each) per summer for a total of 18 undergraduate student stipends over the lifetime of the grant. The PIs will actively recruit students as necessary to maintain a consistent level of undergraduate students for this project.

C. Equipment
None

D. Travel
Funds are requested ($8000 per year) for the travel of the PIs (and undergraduate researchers when results dictate) to national scientific meeting per year such as the national meeting of the American Chemical Society. Conference attendance is essential for the dissemination of results from this proposal, and to allow the PIs to stay current with developments in related areas of research. It will also assist the PIs in establishing collaborative interactions with other investigators. The opportunity for students to travel and present their work is a critical portion of their experience at WWU. Conference attendance also provides an ideal venue for students to network with professionals in the field, and to learn about career opportunities following completion of their degree. Travel funds will also be used for TEM analysis (see below).

E. Other Direct Costs
E.1. Materials and Supplies: We are requesting $32,800 in the first year and $25,000 per year for years two and three for Materials and Supplies costs. These costs are an estimate based on the last three years of research in the PIs lab. Funds for four computers are requested in year one (one PC for McDowall for modeling, theory, etc.; and one PC for each of the other three PIs for student data workup, analysis, etc.)

The PIs have access to most of the major instrumentation required for the successful completion of this proposal. Funds are requested for the following items to be purchased in year 1:
Panalytical: Molybdenum window "SAXS Slit"; "Easy SAXS" software.

Funds ($4402) are requested for the purchase of a small angle scatter slit for the incident beam in order to limit the size of the incident beam for small angle scattering experiments. This additional hardware for the diffractometer will reduce specular scattering and allow for larger particles and aggregates to be studied. The interpretation of SAXS data will require the purchase of “Easy SAXS,” a program that upgrades the existing diffractometer software. This software will allow for basic fitting and analysis of reflectance scattering data by undergraduates and novice users which will allow for higher throughput and characterization of samples. Advanced modeling and fitting will be conducted outside of the software package using Origin Pro, Excel or Mathematica.

The bulk structure of the NC materials will be probed with small-angle X-ray scattering (SAXS), using free-standing disks or supported films (0.1 mm to 3 mm thick and ~1 cm² in area). SAXS will be carried out with a PANalytical X’PertPro Materials Research Diffractometer (MRD) configured for SAXS, using Cu Kα radiation (λ = 1.54 Å) and a SAXS slit (1/32°) also equipped with small angle scatter slit for the incident beam and automatic beam attenuator for the diffracted beam. Samples will be held with custom made Mylar sheet holders. The scattering intensity data will be measured with a detector in a reflectance geometry typically programmed to scan from ~ −0.1 to 5°. SAXS data will be reported in arbitrary intensity units as a function of Q, the momentum transferred during a scattering event.

E.2. TEM Funds: Funds ($4000) are also requested for TEM user fees. WWU has encumbered funds for the purchase and installation of a JEOL 7200F STEM and RMC ultracryomicrotome. These instruments will be operational by the Spring term of 2017. When possible, STEM investigations will be carried out using this WWU equipment which entails no costs to the PIs or their students. If necessary, samples or sections of samples can be pre-assessed in-house, and then, if high resolution micrographs are necessary or automated stage-tilt TEM-tomography is needed, samples can be studied at the nearby University of Washington for fees ~$100/hr. The main users will be the undergraduate students associated with this aspect of the project. Rider has experience operating TEM instruments and will be involved providing the undergraduate researchers hands-on training and experience in TEM.

E.3. Publication: Funds are requested ($1000/yr) to support publication of research related to the proposed work.
Support: Current Pending Submission Planned in Near Future
Project/Proposal Title: RUI: Organic Molecular Crystal Formation in Complex Solution Environments
Source of Support: NSF
Total Award Amount: $320,000
Total Award Period Covered: 7/15 – 8/18
Location of Project: Western Washington University
Person-Months Per Year Committed to the Project. Cal: 0.00 Acad: 0.0 Sumr: 2.0

Support: Current Pending Submission Planned in Near Future
Project/Proposal Title: Transmission Electron Microscope
Source of Support: Murdock Charitable Trust
Total Award Amount: $272,000
Total Award Period Covered: 11/15 – 11/18
Location of Project: Western Washington University
Person-Months Per Year Committed to the Project. Cal: 0.00 Acad: 0.0 Sumr: 0.0

Support: Current Pending Submission Planned in Near Future
Project/Proposal Title: Smart Solar Windows
Source of Support: EPA
Total Award Amount: $75,000
Total Award Period Covered: 8/15 – 9/17
Location of Project: Western Washington University
Person-Months Per Year Committed to the Project. Cal: 0.00 Acad: 0.0 Sumr: 0.0

Support: Current Pending Submission Planned in Near Future
Project/Proposal Title: Demonstrating Activated Nanocrystals for Practical Luminescent Solar Concentrators
Source of Support: Washington Research Foundation
Total Award Amount: $27,000
Total Award Period Covered: 8/15 – 3/18
Location of Project: Western Washington University
Person-Months Per Year Committed to the Project. Cal: 0.00 Acad: 0.0 Sumr: 0.0

Support: Current Pending Submission Planned in Near Future
Project/Proposal Title: RUI: Suschem: Engineering Nanoscale Disorder in Polymer-Semiconductor Nanocrystal Composites for Minimized Optical Losses (This Proposal)
Source of Support: NSF
Total Award Amount: $443,712
Total Award Period Covered: 7/1/17 – 6/31/20
Location of Project: Western Washington University
Person-Months Per Year Committed to the Project. Cal: 0.00 Acad: 0.0 Sumr: 0.5

Support: Current Pending Submission Planned in Near Future
Project/Proposal Title: Highly Luminescent Organic Dyes with Giant Fundamental Anisotropy
Source of Support: NSF
Total Award Amount: $500,000 (approx.)
Total Award Period Covered:
Location of Project: Western Washington University
Person-Months Per Year Committed to the Project. Cal: 0.00 Acad: 0.0 Sumr: 0.0
CURRENT AND PENDING SUPPORT

October, 2016  Investigator: **John D. Gilbertson**

**Support: Current Pending Submission Planned in Near Future**

Project/Proposal Title: **CAREER/SusChEM: Understanding and Utilization of the Secondary Coordination Sphere of Novel Biomimetic Catalysts for Small Molecule Activation**
Source of Support: **NSF**
Total Award Amount: **$470,000**
Total Award Period Covered: **3/13 – 3/18**
Location of Project: **Western Washington University**
Person-Months Per Year Committed to the Project. Cal: **0.00** Acad: **0.0** Sumr: **1.0**

**Support: Current Pending Submission Planned in Near Future**

Project/Proposal Title: **MRI: Acquisition of a 500 MHz NMR for Faculty Research and Undergraduate Training at Western Washington University**
Source of Support: **NSF**
Total Award Amount: **$529,900**
Total Award Period Covered: **3/13 – 3/18**
Location of Project: **Western Washington University**
Person-Months Per Year Committed to the Project. Cal: **0.00** Acad: **0.0** Sumr: **0.0**

**Support: Current Pending Submission Planned in Near Future**

Project/Proposal Title: **Integrating Visible-Light Photocatalysts and Redox-Active Ligands for the Photoreduction of CO₂**
Source of Support: **ACS Petroleum Research Fund**
Total Award Amount: **$70,000**
Total Award Period Covered: **7/17 – 8/20**
Location of Project: **Western Washington University**
Person-Months Per Year Committed to the Project. Cal: **0.00** Acad: **0.0** Sumr: **0.5**

**Support: Current Pending Submission Planned in Near Future**

Project/Proposal Title: **Bioinspired Structure/Function Studies that Leverage Proton-Responsive Secondary Coordination Spheres and Ligand-Based Redox Sites**
Source of Support: **NIH**
Total Award Amount: **$300,000**
Total Award Period Covered: **7/17 – 7/20**
Location of Project: **Western Washington University**
Person-Months Per Year Committed to the Project. Cal: **0.00** Acad: **0.0** Sumr: **1.0**

**Support: Current Pending Submission Planned in Near Future**

Project/Proposal Title: **RUI: SusChem: Engineering Nanoscale Disorder in Polymer-Semiconductor Nanocrystal Composites for Minimized Optical Losses (This Proposal)**
Source of Support: **NSF**
Total Award Amount: **$443,712**
Total Award Period Covered: **7/1/17 – 6/31/20**
Location of Project: **Western Washington University**
Person-Months Per Year Committed to the Project. Cal: **0.00** Acad: **0.0** Sumr: **0.5**
Support: Current Pending Submission Planned in Near Future
Project/Proposal Title: **Highly Luminescent Organic Dyes with Giant Fundamental Anisotropy**
Source of Support: NSF
Total Award Amount: $500,000 (approx.)
Total Award Period Covered:
Location of Project: **Western Washington University**
Person-Months Per Year Committed to the Project. Cal: 0.00 Acad: 0.0 Sumr: 0.0
CURRENT AND PENDING SUPPORT

October, 2016  Investigator: Stephen McDowall

Support: Current Pending Submission Planned in Near Future
Project/Proposal Title: Demonstrating Activated Nanocrystals for Practical Luminescent Solar Concentrators
Source of Support: Washington Research Foundation
Total Award Amount: $27,000
Total Award Period Covered: 8/15 – 3/18
Location of Project: Western Washington University
Person-Months Per Year Committed to the Project. Cal: 0.00 Acad: 0.0 Sumr: 0.0

Support: Current Pending Submission Planned in Near Future
Project/Proposal Title: RUI: Suschem: Engineering Nanoscale Disorder in Polymer-Semiconductor Nanocrystal Composites for Minimized Optical Losses (This Proposal)
Source of Support: NSF
Total Award Amount: $443,712
Total Award Period Covered: 7/1/17 – 6/31/20
Location of Project: Western Washington University
Person-Months Per Year Committed to the Project. Cal: 0.00 Acad: 0.0 Sumr: 1.5
CURRENT AND PENDING SUPPORT

October, 2016  Investigator: David Rider

Support: Current Pending Submission  Planned in Near Future
Project/Proposal Title: RUI: Suschem: Engineering Nanoscale Disorder in Polymer-Semiconductor Nanocrystal Composites for Minimized Optical Losses (This Proposal)
Source of Support: NSF
Total Award Amount: $443,712
Total Award Period Covered: 7/1/17 – 6/31/20
Location of Project: Western Washington University
Person-Months Per Year Committed to the Project. Cal: 0.00  Acad: 0.0  Sumr: 1.0

Support: Current Pending Submission  Planned in Near Future
Project/Proposal Title: Transmission Electron Microscope
Source of Support: Murdock Charitable Trust
Total Award Amount: $272,000
Total Award Period Covered: 11/15 – 11/18
Location of Project: Western Washington University
Person-Months Per Year Committed to the Project. Cal: 0.00  Acad: 0.0  Sumr: 0.0

Support: Current Pending Submission  Planned in Near Future
Project/Proposal Title: Understanding and Utilizing Block Copolymer Templates for the Preparation of Bimetallic Catalysts for Fuel Cell Applications
Source of Support: ACS PRF
Total Award Amount: $70,000
Total Award Period Covered: 8/14 – 8/17
Location of Project: Western Washington University
Person-Months Per Year Committed to the Project. Cal: 0.00  Acad: 0.0  Sumr: 1.25

Support: Current Pending Submission  Planned in Near Future
Project/Proposal Title: Transitioning new and re-invented thermoset resins from the lab into aerospace composites
Source of Support: Joint Center for Aerospace Technology Innovation
Total Award Amount: $99,500
Total Award Period Covered: 8/16 – 6/17
Location of Project: Western Washington University
Person-Months Per Year Committed to the Project. Cal: 0.00  Acad: 0.0  Sumr: 0.5
FACILITIES, EQUIPMENT, & OTHER RESOURCES

FACILITIES

John Gilbertson’s Laboratory: Approximately 900 sq. ft. of dedicated laboratory space housed in the Chemistry Department (five hoods and bench space) plus desk space for undergraduate and M.S.-level graduate students.

David Patrick’s laboratory: Approximately 900 sq. ft. of dedicated laboratory space, plus separate desk space for M.S.-level graduate and undergraduate students, and a semi-private office for postdoctoral fellows. In addition, there is an adjacent 1800 sq. ft. physical chemistry teaching laboratory available during summer months, when it is not used for instruction.

David Rider’s laboratory: Approximately 700 sq. ft. of dedicated laboratory space, plus separate desk space for M.S.-level graduate and undergraduate students. In addition, there is an adjacent 1800 sq. ft. physical chemistry teaching laboratory available during summer months, when it is not used for instruction.

Advanced Materials Science Engineering Center (AMSEC): AMSEC occupies a 2000 sq. ft. laboratory located in the same building as the Physics Department. AMSEC equipment used in the research program is available at no cost.

WWU Scientific and Technical Services (SciTech) provides technical support to faculty, staff, and students for a wide variety of teaching and research activities. SciTech operates the University Instrument Center, a multi-user facility equipped with advanced analytical instrumentation. SciTech also operates machine, electronics, and woodworking shops for the design, manufacture, and repair of academic, scientific, and supporting equipment at no cost except for materials.

MAJOR EQUIPMENT (relevant to the proposed research)

Equipment in Gilbertson’s laboratory:
- Synthetic setup with four vacuum/Schlenk manifolds
- One MBraun dual port glovebox
- Jasco V670 UV-Vis/NIR spectrometer (3200 nm) with integrating sphere and polarizing/depolarizing capability
- 375 mL Parr high pressure batch reactor with dip probe capability
- ReactIR Spectrometer

Equipment in Patrick’s laboratory:
- Two scanning tunneling microscopes (RHK Inc. electronics and software with home-built scanners)
- Atomic force microscope (Digital Instruments Nanoscope III)
- High resolution FT-IR spectrometer (Therm-Nicolet Nexus 470)
- FT-IR microscope (Thermo-Nicolet Continuum)
- Custom-built fluorescence system using fiber optic cables for remote excitation and collection, including polarizing optics and an integrating sphere, all connected to a Horiba Fluorlog modular spectrometer.
- Olympus BX-51 polarizing microscope with digital camera
- Horiba Auto SE LT Ex-situ ellipsometer
- Laurell WS-400B vacuum chuck spin coater
- Two 1.2 T variable field electromagnets
- Several custom deposition chambers for organic thin film growth
- An assortment of electronic test equipment including two HP 4145B semiconductor parameter analyzers and an electrical characterization probe station with micromanipulators and integrated digital microscope
Equipment in Rider’s laboratory:

- Harrick PDC-32G power and pressure controlled reactive ion etch instrument
- CV 50W Bioanalytical Systems Potentiostat
- EG&G 273 Potentiostat with Oscillator
- Princeton Applied Research Potentiostat PARSTAT 2273
- Pine bipotentiostat (Wave Driver10) equipped with a Rotating Ring Disk Electrode accessory
- Nicolet iS50 FTIR spectrometers enabled with two specular reflectance accessories from Pike Techn. and Harrick Sci. (atmospheric conditions and elevated temperature and pressure reactor)
- Coupled TGA-FTIR spectrometer (TA instruments Q50 - Nicolet iS10 FTIR)
- Coupled TGA-Mass spectrometer (Perkin Elmer TGA4000 – Hiden QGA)
- SAGE 100 X-ray Photoelectron Spectrometer System (includes automated sample changer)
- Micrometrics Pulse Chemisorb 2700 system
- Micrometrics ASAP2020 Surface Analyzer System
- VAC Atmospheres Inert atmosphere glove box with spin coater (Laurell)
- Schlenk lines with dedicated hoods (4)
- Muffle Furnace
- Vacuum Ovens (2; one 27 step-programmable)
- Laurell Spin Coater in Dust Free Hoods
- Karl Fisher Titrator
- Rayonet photochemical reactor (RPR-600)

Computing equipment: McDowall

- Dell Precision Tower (8 Core Intel Xeon, 2.4 GHz; 12 GB RAM, purchased October 2010)
- MacPro Tower (12 Core Intel Xeon, 2.4 GHz; 32 GB Ram, purchased April 2013)

Equipment located in AMSEC Materials Characterization Laboratory:

- Scanning electron microscope (Vega 5136MM SEM) with EDS system (EDAX Genesis 2000)
- Powder X-ray diffractometer (Rigaku DMX)
- Grazing incidence X-ray diffractometer (PANalytical)
- Vacuum coater system (Denton Vacuum Systems)
- DSC/TGA analyzer (TA Instruments)
- Agilent 7500 Series Inductively Couple Plasma – Mass Spectrometer (with New Wave Research UP213 Laser Ablation Accessory)
- Surface Science Instruments X-ray Photoelectron Spectrometer (includes sample pretreatment chamber)

Other significant equipment, all available free of charge:

- Numerous modern chromatographic instruments (HPLC, HPLC-MS, GC, GC-MS)
- Numerous modern spectrometers (500 & 300 MHz NMR, FT-IR, fluoroimeter, polarimeter, Conversion Electron Mössbauer Spectrometer capable in the temperature range 5-1200 K
- Viscotek Gel Permeation Chromatography with RI, UV and RALS and LALS detectors
- JEOL 7200F STEM with retractable backscatter, STEM and EDX detectors (150 mm²)
- RMS Ultramicrotome with cryosectioning system and an ASH-100 advanced substrate holder for serial sectioning for tomography
- Beckman Dynamic Light Scattering Particle Sizer NanoS
- Beckman ZetaPotential / Dynamic Light Scattering Particle Sizer NanoHC
- TA instruments Q800 Dynamic Mechanical Analysis Instrument
- TA instruments DHR-2 Rheometer
OTHER RESOURCES

Instrument Support:
Together the Chemistry and Physics departments employ three full-time instrument technicians that assist in trouble-shooting and instrument repair of departmental and research equipment. The Advanced Materials Science and Engineering Center (AMSEC), of which the PIs are members, also employs a full-time instrument technician and WWU’s Scientific Technical Services (SciTech) provides two full-time instrument technicians. All services are available at no cost.

Computer Support:
The College of Sciences and Technology provides a computer support group that is responsible for the maintenance of the College’s computers and networks. All services are available at no cost.

Machine Shop:
WWU’s SciTech provides two full-time professional machinists. All services are available at no cost, except for materials.

Electronics Shop:
WWU’s SciTech provides one full-time electronics technician. All services are available at no cost, except for materials.
DATA MANAGEMENT PLAN

**Products of the Research**
This research will generate numerical data on the chemical systems studied such as FTIR spectra of the starting materials and products (solution and solid state), NMR spectra on the starting materials and products, GC-MS of the starting materials and products, as well as UV-Vis and fluorescence spectral data. TEM, TGA, DSC, and SAXS data will also be collected. Monte Carlo simulations and numerical computation is performed using Wolfram’s *Mathematica* (version 9).

**Data Format**
UV-Vis, fluorescence, and FTIR data are stored as electronic files readable by the respective software utilized to generate them and can be easily converted to .csv format (text output). NMR data are stored as fid files readable by Bruker/Varian software and also can be easily converted to .pdf format. GC-MS data and UV-Vis data are stored as instrument output files and can be readily converted to .csv files. TEM (image files) and SAXS data (.csv) will be output as well. Computational results are stored within Mathematica notebooks, and data generated from simulations are stored as .csv or .tsv files.

**Access to Data/Data Sharing Practices and Policies**
All primary data from this work that are publishable will be published in the respective chemical literature and can be accessed through the websites of the respective journal(s) (including the supporting information of the journal) or by contacting the corresponding author. Primary data posted on group websites will mostly consist of previous data generated from this work already available in the chemical literature, or possibly small, unpublished nuggets of information. Requests for access to unpublished data will be granted at the discretion of the P.I. and when appropriate, WWU’s nondisclosure policies will be enacted. This will include the signing of a nondisclosure form. The P.I.s anticipate the inclusion of data generated by this project into data bases that mine the chemical literature only after the data are published in the chemical literature.

**Policies for Re-Use, Re-Distribution, and Production of Derivatives**
For data published in the chemical literature, those subsequent policies outlined by the respective journals for re-use, etc. will be obeyed. For data posted on the P.I.’s website the website will contain disclaimers, when appropriate, regarding the re-use and re-distribution of the data. Such disclaimer would read “The publication of data obtained from this website is prohibited without the author’s written consent.” However, it is assumed by the P.I. that data posted to the P.I.’s (or group) website is likely appropriate for re-use/re-distribution, etc.

**Archiving Data**
Data in the P.I.’s lab are collected in laboratory notebooks and also in electronic form as stated above. These notebooks are kept by the P.I. after the data generators leave the group and are stored when not in use by the P.I. (office cabinet). When in use, these notebooks are stored in the P.I.’s laboratory on shelves away from the sprinkler system. All electronic data are stored on a computer located in the P.I.s’ laboratories. The computers are backed up to a network server located in the chemistry building weekly. The electronic data are stored and archived/indexed in said computers according to project. Data are also stored on the P.I.s’ office computers which are also backed up to a network server. Recent materials will be in the care of a current researcher of the laboratory. The data will be preserved for at least three years beyond the award period, as required by NSF guidelines.
**Western Washington University (WWU).** Western Washington University (WWU) is a primarily undergraduate institution and ranks among the largest universities in the state of Washington. Of the approximately 15,000 students enrolled, 96% are pursuing undergraduate degrees and the remainder are Master’s students. WWU’s commitment to high quality education has consistently resulted in being ranked as a top regional public university and a “best value” public university by sources such as *U.S News and World Report*, *Kiplinger’s Magazine*, and *Forbes Magazine*. WWU is also committed to promoting diversity in its students, faculty, and staff. As of 2015, statistics from the WWU admissions office indicate that 55.6% of enrolled students were women, and 23.6% represent ethnic minorities. The incoming 2015 freshman class consisted of 28.5% students that self-identified as ethnic minorities, and WWU has an established taskforce to continually support initiatives aimed at expanding equity, inclusion, and diversity.

**WWU Chemistry Department.** The department has sixteen faculty members and offers B.A. and B.S. degrees in chemistry, the latter being certified by the American Chemical Society, as well as a B.S. degree in biochemistry and a M.S. degree in chemistry. The department is conducting two faculty searches in fall 2013, one of which is in the area of organic/inorganic chemistry with a preferred focus in organometallic catalysis. Over the past ten years, the department has graduated an average of 47 students each year at the bachelor’s level (60% male, 40% female) as well as about five students per year at the Master’s level. In 2008-09, the most recent year for which the ACS has published statistics, the WWU Chemistry Department graduated 38 ACS-certified B.S. degree students (of 59 total bachelors graduates), which ranked 12th nationally for colleges and universities [1]. The chemistry department has a thriving undergraduate research program; ~45 undergraduates received stipends to participate in summer research in 2016.

Approximately 45% of graduating seniors have continued their studies at either graduate or professional schools; among the graduate schools attended in recent years include MIT, Cornell University, Stanford University, Caltech, the University of California (Berkeley, Los Angeles, Santa Barbara, Davis, and Irvine campuses), Scripps Research Institute, Penn State University, and the Universities of Washington, Wisconsin, Michigan, and Colorado (Boulder). Graduates who choose to enter directly into the job market typically find employment within the state in the traditional fields of the forest products, oil refining and aerospace industries, but also in newer industries such as biotechnology, high-tech materials and renewable energy.

The WWU Chemistry Department is housed in a 70,000 sq. ft. building devoted entirely to chemistry, which includes approximately 5,000 sq. ft. of new laboratory space opened in fall 2010. Most of the newly added laboratory space is being used for programs in materials chemistry and biochemistry. WWU’s science and technology research programs rank in the top 3% of all non-Ph.D. granting colleges and universities in the country based on extramural funding (ranking 30th among 1430 Carnegie Master’s and Baccalaureate colleges and universities in the U.S.) [2,3]. In addition to receiving a substantial number of individual and collaborative research grants, the chemistry faculty has received numerous National Science Foundation equipment grants in support of its instructional and research programs, helping to augment a substantial portfolio of state-of-the-art instrumentation.

In recent years, the chemistry department has placed increased emphasis upon providing meaningful research opportunities for its majors. *More than two-thirds of WWU chemistry graduates have research experiences during the course of their studies, even though it is not a degree requirement. This high level of undergraduate research participation is a testament to the value placed on research by the faculty and students alike. This vibrant undergraduate research culture spins off benefits to other parts of the chemistry program. Students spend long hours in the department working together on homework and studying for exams. The department also has a vital ACS Student Chapter that was selected for an ‘Outstanding Chapter Award’ by the ACS in both 2010-11 and 2011-12 [4].*

The academic year is capped at WWU by the university-wide “Scholars Week”, in which undergraduate and M.S. students from across campus give oral and poster presentations on their research
and students in the arts participate in concerts, plays, and exhibits. During Scholars Week, the chemistry department hosts a distinguished chemist to campus where he/she interacts with students during the oral and poster sessions and gives a keynote lecture. Chemistry Scholars Week speakers over the last twelve years have included Bill Tolman (2001), Carolyn Bertozzi (2003), Harry Gray (2006), Elsa Reichmanis (2007), Charles Casey (2008) and Gerard Parkin (2011) and Joseph Francisco (2013). In 2011 (and renewed in 2015), the WWU chemistry department received an NSF Research Experiences for Undergraduates (REU) grant to bring two- and four-year college students to campus to participate in summer research. Of the 70 NSF-REU Chemistry sites less than 20% are at PUIs [5], providing an indicator of the strength of the WWU undergraduate research program in chemistry.

**WWU Mathematics Department:** The Math department graduates ~60 students per year. As of a conglomeration of annual math student exit surveys, 51% found employment in jobs related to their field of study. 19% of math graduates went on to employment in jobs not related to their field of study. 22% continued their education in professional and graduate schools. The mathematics department also has a Master's program usually comprising at least 20 students. The majority of these (17 or 18) are funded as teaching assistants. Throughout their two years study they teach one pre-calculus level class each quarter under the mentorship of a faculty member. The program has a history of producing a large number of graduates who go on to be very successful teachers at community colleges. Most years also produce two or three students who go on to PhD programs at well reputed universities throughout the country. They are typically well prepared in terms of exposure to subject matter, and in terms of teaching experience making them attractive candidates as TA's. The Master's students' study consists predominantly of class work, but also includes a final project.

**Advanced Materials Science and Engineering Center (AMSEC):** Formed in 2007, AMSEC is an interdisciplinary center that includes faculty and students from the biology, chemistry, engineering, geology, mathematics, and physics departments. AMSEC offers a minor degree in materials science that includes coursework and an interdisciplinary research experience for enrolled undergraduates. Materials Science at WWU is one the most research-active predominately undergraduate programs of its kind in the nation, with dozens of students conducting research year around. AMSEC faculty have received over $3.5M in competitive external support for their research over the past five years. The environment is fast-paced, stimulating, and encourages hard work and commitment among undergraduate students.

**Patrick:** As a scientist and educator Patrick is committed to training students to become critical thinkers, problem solvers, and scientifically literate members of society. Some of the most effective teaching – and student learning – takes place in the research lab, and extensive participation of undergraduate researchers is therefore a central part of his program. His group normally consists of 5 – 6 undergraduates working full-time during the summer and part-time for academic credit during the school year, along with 1 – 2 M.S.-level graduate students. Undergraduates make a minimum one-year commitment and are involved in every phase of the research. They are included as co-authors on any publication, and encouraged to present their work at regional and national symposia. Patrick has also been extremely successful including high school students in his research program. These students integrate into the environment and participate at a level comparable to the undergraduates. As evidence of the success of this outreach effort, two high school students working with the PI have been finalists in the Intel Science Talent Search, the oldest and most prestigious high school science competition in the country, and another was the state-wide winner of the WA science fair. Upon graduation these high school students have gone on to attend very good universities, most recently Harvey Mudd College, Caltech, and Stanford University. Since joining the faculty at WWU in 1996, in total Patrick has mentored over 50 students in research who combined have made more than 40 presentations at regional and national meetings and received over two dozen awards related their research. About 25 students of his students (nearly half) are listed as co-authors (often first-authors) on peer-reviewed scientific publications resulting from work in his group, including reports in high-impact journals such as *J. Am. Chem. Soc.*, *Angew. Chemie*, and *Phys. Rev. Lett.*
Since 2000 his program has been supported by over $2.5M in external research funding, excluding equipment grants.

**Gilbertson:** Helping WWU to achieve its goal of integrating research experiences into its undergraduate science and technology programs, the PI has been committed to involving undergraduate students in his research program since joining the chemistry department in 2008. The PI’s research program typically operates with one M.S. level and 4-5 B.S. level students working with the PI in the laboratory. Each fall, the PI solicits applications from undergraduate students interested in participating in his research program. Students are asked to commit to one calendar year of research and many undergraduates participate in the PI’s research program for two years. During the academic year, students receive academic credit for their efforts and typically commit to at least 10 hours per week. Students write research reports at the end of each quarter and give oral or poster presentations during WWU’s “Scholars Week”. During summers, students receive stipends during a ten week summer research program to support full-time research. In addition to being included as co-authors on publications when appropriate, students working in the PI's laboratory give oral or poster presentations within the university and/or at the American Chemical Society (Puget Sound Section) Undergraduate Research Symposium that is held annually in the spring. Undergraduate students from the PI’s research group also give poster presentations at a variety of regional and national meetings. The PI will continue efforts to broaden the participation of under-represented groups in his research program (Fig. 1). 19 of the undergraduate students mentored are women (40%) and eight are minority (32%), with six being underrepresented minorities (24%). All five of the MS students mentored are minority students, with three being underrepresented. The PI strives to foster a safe, inclusive research environment in order to attract and retain students that might otherwise fall through the cracks. Since 2008 his program has been supported by over $2.5M in external research funding, including equipment grants.

**Rider:** The Rider research group typically conducts its research with 4-7 undergraduates at a time. Each student is asked to commit to his or her project for ~1.5 years and to work 10+ hours per week during the academic year and full-time during the summer. Sophomores or juniors declared as a majors in either Chemistry, Engineering Technology, Mathematics and Physics have conducted research in the Rider group. Approximately half of the group members thus far have also minored in Materials Science through WWU’s AMSEC. To date, Dr. Rider has mentored four graduate students in Chemistry, twenty-six Chemistry students, four Engineering students, three Physics/Math students, and four NSF-REU students. Since joining both departments in 2010, the PI has encouraged undergraduate students from Chemistry and Engineering Technology to participate in his research program. The PI’s current research program has one M.S. level and 6 B.S. level students who work with the PI in the laboratory. Engineering majors are included in the work through a series of senior level research courses that encompass the student’s senior project. The PI is devoted to broaden participation by under-represented groups in his research program, which currently operates with 4 female students, one of which self-identifies as Hispanic in origin. Of the 37 undergraduate students who participated in the PI’s most recent research projects 15 were women and seven self-identified as non-white in origin. Co-PI Rider’s
commitment to supporting students of all ages in their pursuit of education and training in the STEM fields is reflected in his outreach activities which includes annual participation a Mount Vernon High school’s Science Night (since 2012), WWU’s compass to campus (since 2012) and participate in WWU’s advertisements and recruitment efforts of students of all backgrounds from the northwest (see Figure 2). Since 2010 Prof. Rider’s research program has been supported by over $1.2M in external research funding, excluding equipment grants.

**McDowall:** As a mathematician and an educator McDowall has advised 11 master’s students since he began his position at WWU in 2002. Topics studied have ranged from the study of traffic flow, to applications such as X-ray tomography, optical tomography and wavelets, to theoretical areas related to Riemannian geometry, such as boundary rigidity, the Quotient Manifold theorem and the study of Jacobi fields and conjugate points. His research in inverse problems and in applications such as photon transport within waveguides has attracted master’s students due to the fact that the research is motivated from practical questions from physics and solar power generation. Several students have gone on to earn PhDs in Mathematics at highly respected universities, and others have established successful careers teaching at community colleges. McDowall has also supervised undergraduate theses, including a study of the mathematics behind magnetic resonance imaging, and a study of chaos as demonstrated by the Lorenzian wheel.

**References**

1. American Chemical Society: Annual Reports of Earned Bachelor’s Degrees in Chemistry. [http://portal.acs.org/portal/acs/corg/content?_nfpb=true&_pageLabel=PP_SUPERARTICLE
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CERTIFICATION OF RUI/ROA ELIGIBILITY

By submission of this proposal, the institution hereby certifies that the originating and managing institution is an accredited college or university that awards Associate's degrees, Bachelor's degrees, and/or Master's degrees in NSF-supported fields, but has awarded 20 or fewer PhD/DSci degrees in all NSF-supported fields during the combined previous two academic years.

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