HYPERBOLIC METAMATERIALS FOR ACTIVE LIGHT MANAGEMENT IN LUMINESCENT SOLAR CONCENTRATORS

I. Introduction

The emergence of metamaterials – sub-wavelength-scale dielectric / metallic composites with exotic electromagnetic properties – is opening new possibilities for light management in a range of optical applications, most of which are just beginning to be explored.\textsuperscript{refs} Solar concentration represents a particularly promising, yet virtually untapped opportunity for metamaterials. Fundamentally, this is because the collection and concentration of sunlight relies on light-matter interactions that are heavily influenced by the photonic density of states (PDOS) of the concentrating medium – a measure of the number of ‘channels’ for storing or routing electromagnetic energy in frequency and momentum space.\textsuperscript{1} Optical-frequency metamaterials support a large number of coupled plasmonic modes, leading to a far greater PDOS whose structure can be more precisely engineered than possible with either conventional isotropic media or traditional plasmonic nanostructures.\textsuperscript{2,3} Consequently, metamaterials are poised to offer greater control over factors such as absorption, radiative emission, spectral shaping, polarization content, and directional guiding of light – the fundamental constitutive processes underlying several types of focusing- and non-focusing solar concentrators.

Aiming to better understand and exploit these properties, here we propose a comprehensive, fundamental research program investigating metamaterial-based solutions for active light management in luminescent solar concentrators (LSCs). We describe a set of new applications, including non-tracking broad-band concentrator sheets and low-loss waveguides. In particular, the research plan centers on the development platform illustrated in Fig. 1, in which a dye-sensitized Type-II hyperbolic metamaterial (HMM) with an integrated sub-wavelength scale grating is imbedded in an LSC. The HMM performs active light management in the LSC by enhancing the sensitizer photoluminescent quantum yield, its Stokes shift, and the light trapping efficiency of the concentrator. This new photonic object – comprising a dye-sensitized HMM with an integrated sub-wavelength scale grating structure – behaves, in effect, like an artificial luminescent species whose optical properties can be engineered in ways not found in the separate components or in any other existing artificial structure, but which can be almost ideally suited for LSC applications. An important aspect of our plan is its comprehensive approach, combining best-in-class nanofabrication capabilities with detailed electromagnetic modeling, optical and spectroscopic characterization. Taken together, the results of this research will be both new concentrator designs with improved performance, as well as a deepened

Figure 1. In a traditional LSC, luminophores imbedded in a planar waveguide absorb sunlight and re-emit Stokes shifted light which travels by total internal reflection to be concentrated at the edges for conversion by bandgap-matched photovoltaics. Active light management using an integrated HMM improves concentrator efficiency by reducing escape-cone losses, increasing photoluminescent quantum yield and Stokes shift. The proposed development platform consists of a dye-sensitized HMM patterned by an integrated diffraction grating imbedded within a transparent polymer waveguide. Optical processing proceeds in four steps: (1) A dye sensitizer located in the HMM near-field absorbs a solar photon (2) transferring its energy to high-k modes in the HMM with a large Purcell efficiency enhancement. (3) Energy from excited plasmonic modes is then scattered out of the HMM as propagating photons at preferential angles lying outside the LSC escape cone using an integrated grating, (4) enabling it to travel with decreased losses over longer distances by total internal reflection.
foundational understanding of light-matter interactions in HMMs at visible and near-IR wavelengths.

Over the last decade plasmonic nanostructures have been investigated for a variety of energy-related applications, ranging from up-conversion efficiency enhancement,\textsuperscript{4} to thermoelectric\textsuperscript{5} and thermophotovoltaic devices,\textsuperscript{6} subcritical boiling,\textsuperscript{7,8} photochemical reaction driving,\textsuperscript{9,10} and localized light trapping.\textsuperscript{11,12} These examples all employ non-metamaterial metallic nanoparticles or films, which although involving plasmonic states, differ from true metamaterials. Indeed, aside from a limited number of investigations using metamaterials for photovoltaic\textsuperscript{13,14} (PV) and thermophotovoltaic\textsuperscript{15,16,17} light trapping, little work has so far been devoted to their application for energy harvesting or conversion, and even less to concentrator applications. Yet, as we argue below, metamaterials may have untapped potential to enable significant performance advantages for some situations. Before this potential can be fully realized however, a number of design, fabrication, and materials selection challenges must first be understood and solved.

In an effort to address these challenges, we propose to create and study a new photonic object--a dye-sensitized HMM with integrated sub-wavelength scale grating--designed to behave, in effect, like an artificial luminescent species for solar concentrator applications. We will study the optical properties of this object, underlying light-matter interaction mechanisms, and materials and methods of fabrication. We seek to understand and optimize its behavior for LSC applications, although it is anticipated the results of this research will provide benefits to a number of related technologies, ranging from visible light communication\textsuperscript{18} to naked-eye 3D displays.\textsuperscript{19}

The system to be studied is shown in Fig. 1, where the flow of electromagnetic energy proceeds in three steps:

1. Absorption of incident sunlight by photoluminescent sensitizer molecules located in the near-field of the HMM. The use of molecular sensitizers as the absorbing species provides three important benefits: (i) since the HMM need not directly absorb far-field light, its design constraints are greatly relaxed and can be focused on optimization of Purcell enhancement, controlled angular emission, and minimization of Ohmic losses, (ii) the spatial orientation of the sensitizer’s absorption and emission transition moments can be independently controlled, facilitating selective mode excitation during energy transfer to the HMM, and (iii) luminophore absorption and emission energies and Stokes shift can be tuned over a wide range of values via molecular design and strategies such as solid-state solvation.\textsuperscript{20}

2. The exciton produced in (1) relaxes, transferring its energy to the HMM. Below we show the efficiency of the energy transfer process is predicted to approach 100\% for some situations, producing a large effective quantum yield enhancement for the sensitizer via a broadband Purcell effect. This enables the use of near-IR and large Stokes shift luminophores whose LQY would otherwise be too low for concentrator applications. Sensitizer position relative to the HMM as well as molecular orientation (vertical, planar, tilted, or isotropic) affect the efficiency and partitioning of energy transfer to the HMM, and these will be controlled using alignable luminophores imbedded in a thin polymerizable liquid crystal layer, along with a dielectric spacer.

3. Electromagnetic energy is scattered from the HMM as freely propagating photons using an integrated, sub-wavelength scale grating patterned atop the HMM. Ohmic losses within the HMM are minimized by rapid extraction, and crucially, the angular and polarization distribution of the resulting propagating field can be engineered via the design of the grating, which as discussed in detail below, is enabled by the fact that the excited HMM modes are tightly bunched in a narrow range of \textit{k}-space.

A final fourth step involves capturing light radiated from the HMM into waveguided modes of the LSC cladding, enabling it to travel by total internal reflection to the concentrator edge for conversion by PV cells. For LSC applications two key properties are afforded by this approach: (i) enhancement of the sensitizer LQY, enabling use of luminophores able to absorb a wider spectral range and with large Stokes
shift reducing self-absorption losses; and (ii) directional emission to avoid escape cone losses. These two loss mechanisms – escape cone losses compounded by self-absorption – are the dominant loss mechanisms in large LSCs and two of the most important factors limiting LSC efficiency.

The research program will focus on a limited set of measurements under highly controlled conditions. Precise control over key experimental parameters including sensitizer molecular orientation and position, HMM layer thickness, composition, and defects is intended to produce benchmark measurements of fundamental phenomena whose interpretation will be guided by a closely integrated program of theory and modeling. To carry out the work, we have assembled an experienced team of senior investigators including experts in liquid crystals, molecular alignment, and LSCs (Patrick, WWU); thin film fabrication and transparent conductors (Kaspar and Chambers, PNNL); fluorophore design and synthesis (Gilbertson, WWU); and electromagnetic and optical modeling (McDowell, WWU).

**HMMs for Active Light Management in Solar Concentrators.** Among all solar concentrator designs, luminescent solar concentrators (Fig. 2) are perhaps the ideal candidate for driving semiconductor-based converters, such as PVs, owing to their ability to deliver high irradiance, narrow bandwidth light by active wavelength shifting. LSCs require no solar tracking, exhibit omnidirectional acceptance producing comparable performance under diffuse and specular illumination, and offer the potential for higher energy concentration ratios (CR) than designs based on mirrors or lenses. They can be transparent or opaque in the visible spectrum, mechanically rigid or flexible, and are damage tolerant, offering the potential for broad deployment scope for both building-integrated and standalone applications, while reducing the cost, of solar power.

The theoretical performance limits of an LSC are established thermodynamically by the optical properties of the luminophore. The upper energy efficiency $E_{\text{lim}}$ obeys the single-bandgap Shockley-Queisser limit, and the limiting energy concentration ratio depends on the Stokes shift. For visible-wavelength luminophores, thermodynamically limited theoretical values of $E_{\text{lim}} \sim 10\% - 20\%$ and $CR_{\text{lim}} \geq 100$ are predicted at room temperature for a Stokes shift of $\sim 0.1$ eV; both limits can be extended using infrared-emitting luminophores. Attached photovoltaics receive high irradiance, narrow bandwidth light, resulting in a power density enhancement, referred to as the flux gain, up to several times larger than $CR_{\text{lim}}$ when the PV’s bandgap is matched to luminophore emission.

Though promising in theory, in practice the performance levels achieved by actual devices fall far below these thermodynamic limits, primarily because of three main factors: (1) only a fraction of incident sunlight is absorbed, determined by the integrated overlap of luminophore absorption and solar spectra; (2) only a fraction of absorbed light is re-emitted, depending on the luminophore’s luminescence quantum yield (LQY); (3) only a fraction of this emitted light is captured in guided modes (~75% in an LSC waveguide with refractive index $n \sim 1.5$), with the remainder (~25%) lost out the top or bottom escape cone defined by Snell’s Law (Fig. 2). Most problematic of all is that losses from mechanisms (2) and (3) occur repetitively, since photons travelling within the waveguide may be re-absorbed and re-emitted by other luminophores multiple times before reaching an edge. Note that in a large LSC the optical pathlength may be a meter or more, so the smallest overlap between absorbance and emission spectra results in catastrophic compounding losses. As a result, concentrator efficiency falls exponentially with the number of re-absorption / re-emission events, which is in turn determined by the overlap of events, wh

![Fig. 2. In a conventional LSC sunlight (blue) is absorbed by luminophores and emitted into a planar waveguide (red), traveling by total internal reflection (TIR) to the edge of the collector to concentrate light for conversion by PV cells. With each such emission a fraction of light is lost to non-unity LQY or out the escape cone defined by Snell’s Law (dashed orange). Self-absorption of emitted photons traveling in the waveguide by subsequent luminophores compounds these losses, causing efficiency to fall rapidly with concentrator size.](image)
luminophore absorption and emission spectra, and the device dimensions.

Over the past 30 years a number of approaches have been investigated to improve LSC performance. Early work focused on luminophore photostability and solar spectrum matching. More recent research has investigated the use of dichroic mirrors and other resonant structures to reduce escape-cone losses, and luminophore orientation to capture a greater proportion of emitted photons in guided modes. Using the latter approach, we recently demonstrated LSCs with the highest optical quantum efficiency reported to date (74%) by aligning organic fluorophores in a polymerizable liquid crystal matrix. However, the greatest share of attention has been given to reducing luminophore reabsorption, since it compounds most other loss mechanisms. Toward this end a wide range of materials and strategies have been investigated, including (i) large Stokes shift organic fluorophores and phosphorescent organometallic complexes; (ii) Stokes shift enhancement by solid-state solvation; and (iii) nanocrystal-sensitized lanthanide phosphors. Unfortunately, it has proven difficult using the first two strategies to produce a sufficiently large Stokes shift without sacrificing LQY, and the third strategy typically involves materials only able to absorb a small portion of the solar spectrum and/or submicron-sized particles that result in catastrophically large scattering losses. Various types of semiconductor nanocrystals (or quantum dots, QDs) have also been investigated, including those with both Type I and II heterojunctions. The Stokes shift of the former is too small, however, and the latter have yet to be demonstrated with the necessary combination of high LQY and low self-absorption. We recently took an important step toward addressing these limitations by preparing LSCs based on phosphor-doped QDs which have virtually zero self-absorption and can exhibit LQYs exceeding 80%. However the emission wavelength of our current best doped-QD materials is limited to $\leq 600$ nm, severely limiting the range of the solar spectrum that can be absorbed, and thus overall device efficiency. Hence, the fundamental limitation hindering development of LSCs since their conception in the 1970’s – and the challenge this proposal aims to try and address – remains the lack of luminescent strategies resulting in high LQY, low self-absorption, and directional emission to avoid escape-cone losses.

**Hyperbolic Metamaterials and Their Optical Properties.** Metamaterials are metal-dielectric nanocomposites in which the sign of the dielectric permittivity $\varepsilon$ differs along orthogonal spatial directions, leading to hyperbolic dispersion relations. The essential criterion leading to meta-behavior is the constraint of free electron motion to one or two dimensions, which can be achieved through a variety of nanostructure geometries, including layered and columnar media. Metamaterials behave toward light like metals for some propagation directions, and dielectrics for other directions. This unique combination of properties has spurred interest in using HMMs for a variety of new applications, including negative refractive index materials, subwavelength imaging, perfect absorbers, and optical cloaking, most of which have just begun to be theoretically and technologically explored. Here, we propose to use HMMs for active light management in LSCs, a new application for these materials which has not, to our knowledge, been previously considered.

In an isotropic optical material, the phase velocity (the magnitude of the wave vector) of light of a fixed frequency is the same in every direction. The resulting isofrequency surface is thus a sphere. (An isofrequency surface, in $k$-space, is the level set $\omega = \text{constant}$, where $\omega$ is the frequency.) More generally, for uniaxial birefringent media, this surface is an ellipsoid. As we describe in more detail below, the term hyperbolic in HMM derives from the fact that for these metamaterials, each isofrequency surface described by the dispersion relation is a hyperboloid. In appropriate coordinates, the dielectric tensor, $\varepsilon$, of an HMM is diagonal and is of the form $\text{diag}(\varepsilon_{||}, \varepsilon_{\perp}, \varepsilon_{\perp})$. Specifically, in HMMs, one of $\varepsilon_{||}$ and $\varepsilon_{\perp}$ is negative. The
To describe electromagnetic wave propagation within a medium, we define the wave vector, \( \mathbf{k} = (k_x, k_y, k_z) \), which gives the direction of propagation of the wave fronts. This does not necessarily coincide with the direction of energy propagation, which is given by the Poynting vector, though in isotropic media the two are indeed parallel. Fixed frequency time-harmonic waves satisfy Maxwell’s equations: \( \text{curl} \mathbf{E} = -i\omega \mathbf{B} \) and \( \text{curl} \mathbf{H} = \frac{i\omega}{c^2} \mathbf{D} \), where we assume the current density \( \mathbf{J} = 0 \) and the medium is nonmagnetic, \( \mu = 1 \) and \( \mathbf{B} = \mathbf{H} \). The displacement vector \( \mathbf{D} \) is related to the electric field vector \( \mathbf{E} \) by the constituent relation \( \mathbf{D} = \varepsilon \mathbf{E} \), where \( \varepsilon \) is the dielectric tensor. In principal coordinates, where \( \varepsilon \) becomes diagonal, we may write \( \varepsilon = \text{diag}(\varepsilon_x, \varepsilon_y, \varepsilon_z) \); in an isotropic medium, \( \varepsilon = \text{diag}(\varepsilon, \varepsilon, \varepsilon) \). Notice that when \( \varepsilon \) is isotropic, \( \mathbf{D} \) and \( \mathbf{E} \) are collinear, but, otherwise, the anisotropy in \( \varepsilon \) describes the divergence of \( \mathbf{D} \) from \( \mathbf{E} \). If we consider plane waves in a homogeneous medium, where the spatial variation is given by \( e^{-ik\mathbf{r}} \), then Maxwell’s equations imply \( \mathbf{k} \times (\mathbf{k} \times \mathbf{E}) = -\frac{\omega^2}{c^2} \varepsilon \mathbf{E} \), which can be rewritten as

\[
(\varepsilon + \varepsilon)\mathbf{E} = \begin{pmatrix}
-k_z^2 - k_x^2 & k_xk_y & k_xk_z \\
k_xk_y & -k_z^2 - k_y^2 & k_yk_z \\
k_xk_z & k_yk_z & -k_z^2 - k_x^2
\end{pmatrix} \mathbf{E} + \frac{\omega^2}{c^2} \varepsilon \mathbf{E} = 0.
\]

For non-trivial solutions, it must therefore hold that \( \text{det} \left( \varepsilon + \frac{\omega^2}{c^2} \varepsilon \right) = 0 \). This equality is called the dispersion relation and describes the geometry of how wave fronts propagate; it describes the \( \mathbf{k} \)-vectors of electromagnetic waves which can be supported by the medium at the given frequency. HMMs are uniaxial, anisotropic media in which, for principal coordinates, the dielectric tensor takes the form \( \text{diag}(\varepsilon_\parallel, \varepsilon_\perp, \varepsilon_\perp) \). We have chosen coordinates so that the axis of anisotropy is in the \( z \)-direction. In this case, a vanishing determinant is achieved by either \( \|\mathbf{k}\|^2 = \frac{\omega^2}{c^2} \varepsilon_\parallel \) (waves which are called ordinary), or, more interestingly, \( \frac{k_x^2}{\varepsilon_\parallel} + \frac{k_y^2}{\varepsilon_\perp} + \frac{k_z^2}{\varepsilon_\perp} = \frac{\omega^2}{c^2} \). Wave vectors for which this holds are called extraordinary. If each of \( \varepsilon_\parallel > 0 \) and \( \varepsilon_\perp > 0 \), then the wave fronts now take the shape of an ellipsoid, thus demonstrating the anisotropy of the medium (in isotropic media the wavefronts are spheres). When one of \( \varepsilon_\parallel \) or \( \varepsilon_\perp \) is negative (that is, \( \varepsilon_\parallel \varepsilon_\perp < 0 \)), the dispersion relation now describes a hyperboloid; in this case that \( \varepsilon_\perp < 0 \), the surface is a two-sheeted hyperboloid (Type I), and when \( \varepsilon_\parallel < 0 \), the surface is one-sheeted (Type II).

Unlike the elliptical dispersion relation, the isofrequency surfaces in (an ideal) HMM are unbounded, and wave vectors of arbitrarily large norm become physically allowable and the electromagnetic waves can now propagate within the medium. For ordinary dielectric materials, when \( \varepsilon_\parallel \varepsilon_\perp > 0 \), the magnitude of \( \mathbf{k} \) has an upper limit beyond which waves are evanescent and simply decay exponentially. Of particular interest here is the further fact that certain regions of \( \mathbf{k} \)-space are now forbidden; waves will not propagate in certain directions, something which is promising for controlling wave propagation within an LSC to be in directions outside of the escape cone of the LSC.

Optical frequency HMMs, or approximate HMMs, have been successfully fabricated by way of multi-layer systems of alternating dielectric-metal layers, and by way of aligned metallic nanowires within a dielectric layer. In the idealized situation where there are infinitely many alternating dielectric-metal layers, it has been shown that waves behave as in a homogeneous medium with effective permittivity parameters:

\[
\varepsilon_\parallel = \frac{\varepsilon_1d_1 + \varepsilon_2d_2}{d_1 + d_2}, \quad \varepsilon_\perp = \left(\frac{\varepsilon_1^{-1}d_1 + \varepsilon_2^{-1}d_2}{d_1 + d_2}\right)^{-1}
\]
where $\varepsilon_1, \varepsilon_2$ are the permittivity constants in the layers of thickness $d_1, d_2$. Since, in the optical range, the permittivity of metals are negative, by varying $d_1$ and $d_2$, it is possible to make $\varepsilon_1$ or $\varepsilon_2$ negative. It is also clear that, since $\varepsilon_j$ depend on wavelength, an HMM can behave differently for different wavelength ranges; by careful optimization over choice of metal and metallic fill fraction one can design an HMM to behave as a Type II HMM over larger optical wavelengths, and effective dielectric over mid-wavelengths, and a Type I HMM over shorter optical wavelengths (Fig. 4).\textsuperscript{52} Treating the layered system as a single homogeneous layer, by way of these expressions for $\varepsilon_1$ and $\varepsilon_2$, has been termed effective medium theory (EMT) in the literature. The validity of EMT relies on the macroscopic field $\mathbf{E}$ being averaged over a scale that includes several layers, but is still smaller than the wavelength.\textsuperscript{53} To accurately model the fields for a finite number of layers requires solving Maxwell’s equations in every layer and including accurate treatment of the boundary conditions at every interface between layers. This results in a considerably more complicated mathematical treatment, but can be achieved by way of transfer matrices.\textsuperscript{54} The agreement between predictions based on EMT and those based on transfer matrix methods is greatest when the layer thicknesses $d_1, d_2$ are small compared to the wavelengths of interest. A similar EMT exists for an HMM consisting of a matrix of metallic nanowires within a dielectric layer, in terms of the volume fraction of the metal.\textsuperscript{55}

The Purcell Effect: The spontaneous radiative emission rate $\Gamma_{rad}$ of an excited luminophore depends on its environment. Plasmonic structures and resonant cavities have long been known to enhance $\Gamma_{rad}$ by providing a larger photonic density of states (PDOS) into which the excited state energy can couple (larger than the PDOS of free space).\textsuperscript{56} The degree of enhancement is measured in terms of the Purcell factor,\textsuperscript{57} which depends upon the energy overlap between luminophore emission and plasmonic or resonant cavity states. However plasmon resonances in metal nanostructures are limited to a few narrow bands, and in high quality optical cavities the resonances are even narrower, resulting in limited overlap with broadband molecular emission spectra, and hence small Purcell enhancements.\textsuperscript{58}

It was recently predicted\textsuperscript{59} and soon thereafter experimentally demonstrated\textsuperscript{60,68,69} that HMMs possess a very large PDOS over a wide and tunable spectrum of energies, leading to a broadband Purcell effect and efficient energy transfer from nearby excited luminophores to modes supported by the HMM. This fast and efficient transfer results in a large reduction in the luminophore’s excited state lifetime,\textsuperscript{61} increasing its LQY, in some cases by nearly two orders of magnitude.\textsuperscript{*ref*}

The Purcell factor, $F$ quantifies the normalized spontaneous emission rates of an emitting dipole in the near-field neighborhood of a particular electromagnetic structure. (The normalization is to that of emission in a vacuum.) $F$ depends on the distance $h$ of the emitting dipole from the HMM, and on the orientation of the dipole; if we decompose the orientation into its parallel $f_\parallel$ and perpendicular $f_\perp$ parts, $f_\parallel^2 + f_\perp^2 = 1$, then we can write $F = F_\parallel + F_\perp$ where $F_\parallel$ is the Purcell factor for a dipole oriented parallel to the plane of the layered HMM and $F_\perp$ is that for a dipole oriented perpendicular to the same plane. These Purcell factors, in turn, depend on the reflection coefficients $r_p$ and $r_s$, for $P$-polarized (transverse magnetic) and $S$-polarized (transverse electric) fields. Specifically,\textsuperscript{62,63,64}

$$F = 1 + \frac{3}{2} \Re \left\{ \int_0^{\infty} \frac{k}{\sqrt{1-k^2}} \left[ f_\parallel^2 k^2 r_p + \frac{1}{2} f_\parallel^2 (r_s - (1-k^2)r_p) \right] e^{2i\frac{\pi}{2} \varepsilon \sqrt{1-k^2} h} dk \right\}, \quad (1)$$

\textbf{MAKE FIGURE}

\textbf{Fig. 4.} Metamaterial phase diagram
Here, $n_c$ is the index of refraction of the cladding material in which the dipole resides. If $k_{\parallel}$ denotes the parallel component of the $k$-vector, $k$, then the variable of integration $k$ above is simply the result of the change of variable $k = k_{\parallel}/(\omega c n_c)$. Thus the above integral naturally decomposes into the sum of an integral $0 \leq k \leq 1$ corresponding to $k$-vectors lying within the escape cone of the cladding, where the square root is real and positive, and the integral $1 \leq k < \infty$, corresponding to evanescent waves, where $\sqrt{1 - k^2} = i\sqrt{k^2 - 1}$ is purely positive imaginary. We naturally define $F_{\|}$ by setting $f_{\perp} = 0$, and similarly for $F_{\perp}$. For an isotropically aligned dipole, $F_{\text{iso}} = \frac{1}{3}(F_{\perp} + 2F_{\|})$.

Figure 5 shows a representative calculation of the Purcell factor for a dipole imbedded in a medium of refractive index 1.5 (representing a polymer cladding such as poly(methylmethacrylate, PMMA) located 10 nm above a Ag/Si HMM composed of 20 nm thick layers. The broadband nature of the enhancement, which exceeds 100 nm FWHM, is evident. The magnitude and wavelength range of the Purcell factor depends on dipole position, orientation, and the composition and structure of the HMM. For example, other realistic configurations predict peak values of $F$ exceeding 100.

Computation of $r_{PS}$ is the same as for the Fresnel coefficients when the HMM is treated as a homogeneous medium via EMT. Otherwise one must use the method of transfer matrices. If the HMM is treated as an infinite half-space (of infinitely many layers), then computation of $r_{PS}$ reduces to an eigenvalue/eigenvector problem for the transfer matrix of a single bi-layer period. It is this treatment we take here in presenting examples of Purcell factor computations. The most precise treatment, however, is to compute the full electric field in every layer, given an incident $P$- or $S$-polarized field, and derive the resulting reflected field. Each treatment has its advantages and disadvantages: EMT has an attractively simply formulation and it is easy to explore the general dependence of $F$ on $h$, on orientation, and on the effective $\varepsilon_{\|}, \varepsilon_{\perp}$. However, EMT overestimates $F$, drastically so as $h \rightarrow 0$; the infinite half-space model is accurate when compared to an HMM with sufficiently many layers, and the added mathematical complexity is not so great that dependence on the material parameters gets lost. This model is the most amenable to accurately exploring performance of various design architectures; the full Maxwell multi-layer treatment for a finite number of layers will most accurately predict performance of an actual fabricated HMM. In computing the Purcell factor, we see from the defining integral that it is the degree of agreement of the computed reflection coefficients that will determine the agreement of each of the models.

**Sensitizer – HMM energy transfer.** The integrand in Eq. 1 represents the normalized dissipated power entering the HMM. Fig. 6 shows this for a dipole oriented perpendicular to the plane of the HMM, the intensity given on a logarithmic scale. The horizontal axis is proportional to $k_{\parallel}$, the parallel component of the $k$-vector, which is the projection of $k$ onto the $xy$-plane. Specifically, the $x$-axis is in units of $k_{\parallel}/k_0(700)$ where $k_0(700)$ is the length of the

![Fig. 5. Computed broadband Purcell factors for a dipole with three orientations (perpendicular, parallel, and isotropic) located $h = 10$ nm above a Ag/Si HMM composed of 20 nm thick metal and dielectric layers.](image)

![Fig. 6. Computed normalized dissipated power spectra for a perpendicular dipole for the same system as in Fig. 5.](image)
wave vector in free-space, at $\lambda = 700$ nm, chosen for illustrative purposes to roughly match the emission wavelength range of the proposed sensitizer luminophores discussed below. The part of the plot corresponding to $\omega(\lambda)/c < n_{cl}$, $n_{cl}$ being the index of refraction of the cladding, has been omitted.

Similar to the computation of $F$, one may compute $F^{clad}$, the normalized radiation rate into the cladding only; this is essentially the part of radiation which lies inside the cladding’s light-cone. The ratio $F/F^{clad}$ therefore quantifies how much of the radiated power gets into the HMM.

STEVE: Can we just compute the percentage into the HMM instead? In Fig. 7 we present the results from computing $F/F^{clad}$ for the same system used in Figs. 5 and 6. We consider a dipole emitting at wavelength $\lambda = 700$ nm inside a cladding with index of refraction $n = 1.5$ and vary the distance $h$ of the dipole from the HMM. Also shown is the height dependence, $h$ of the Purcell factor at $\lambda = 700$ nm. STEVE: Can we add this?

Both quantities are predicted to vary strongly with $h$. For dipoles located within about 25 nm of the HMM, 90% or more of radiated energy is transferred to the HMM, demonstrating the efficiency of the transfer process. The large Purcell factor manifests as a reduction in the excited state lifetime of the sensitizer; this increases the LQY of the luminophore and is the basis for enabling use of longer wavelength, larger Stokes shift sensitizers, which would otherwise have LQYs too low for LSC applications.

Finally, it is important to note that the electromagnetic energy transferred into the HMM is largely confined to the HMM; in the absence of structural defects this energy does not radiate into free space. As a consequence, if the HMM is fabricated using conventional metals such as Ag and Au this energy is rapidly dissipated through resistive losses. Indeed the apparent Purcell factor and external quantum efficiency of luminophore+HMM systems have until very recently been low as a result of this effect. Two goals of the research therefore are to develop scattering gratings for rapidly removing energy from the HMM, and to develop HMMS based on lower loss metal oxides, nitrides, and other transparent conductors, as we discuss in the following.

II. Research Plan

The scientific objectives outlined in the Introduction will be pursued through a systematic research program involving close interconnections between theory and experiment. The program is structured to proceed by first developing a detailed, fundamental understanding of each elemental step in the energy harvesting, transfer, and emission chain shown in Fig. 1, to be followed by fabrication and testing of integrated systems. We seek to elucidate the detailed mechanism(s) and design rules governing system behavior, including those related to LSC performance. Accordingly, many of the experimental measurements proposed below are constructed around simplified model systems in which the important parameters can be carefully controlled and their effects understood and treated theoretically. These include luminophore molecular orientation and position, absorption and emission energies, HMM dielectric tensor properties, and other variables described in the following. Our goal is to assemble the individual conceptual components necessary for producing functional integrated devices by the end of the grant period, including operational LSCs incorporating active light management.

Device Fabrication and Characterization. The experimental system consists of Type II HMM fabricated from alternating metal/dielectric nanolayers, patterned by a sub-wavelength scale diffraction
grating, and coated by a dielectric spacer, thin luminophore-containing polymer film, and multimode polymer slab waveguide (Fig. 8). In the first phase of the project, HMM materials selection will focus on metal/dielectric systems which have been proven in previous work to be successful. This will allow proof-of-principle measurements of luminophore behavior in the vicinity of the HMM. For the metal layer, Ag or Au will be employed. Both are fairly low-loss metals which resist oxidation, facilitating early-stage measurements and convenient shipment of samples between PNNL and WWU. Dielectric layers will be the transparent insulators Al₂O₃ or TiO₂.

TIFFANY/SCOTT: Can we add Si and SiO₂ to this list? Ag/Al₂O₃, Ag/TiO₂, and Au/TiO₂ are all well-established HMM systems.⁷²,⁷³,⁷⁴ HMM stacks will be fabricated in a molecular beam epitaxy (MBE) chamber at PNNL which offers substrate temperature control, and both electron beam evaporators and effusion cells for source evaporation. Examples of epitaxial metal and oxide thin films deposited on single crystal oxide substrates are shown in Fig. 9. For non-epitaxial HMM fabrication, initial stacks will consist of both the metal and the dielectric layer evaporated from electron beam evaporators, with the oxide of interest as the source material (i.e., ceramic TiO₂ or Al₂O₃). This will allow deposition in a high vacuum environment (base pressure 1x10⁻⁸ Torr or better). Atomic absorption spectroscopy will be utilized to monitor the evaporation flux of each source material, ensuring the deposition of well-defined multilayers with precise and uniform layer thicknesses. The slow deposition rate afforded by electron beam evaporators in the MBE chamber is likely to provide sharper, more planar interfaces between the layers compared to equivalent deposition by techniques such as sputter deposition. Interface roughness can be expected to add to the loss mechanisms, particularly in the metal layer, in a manner similar to the surface scattering effects of metal nanoparticles.⁷⁵ HMM optimization will proceed via tuning the metal and dielectric thicknesses, as well as an investigation of the oxygen stoichiometry in the oxide dielectric layer. Particularly for TiO₂, sub-stoichiometric oxygen content leads to n-type doping, which will affect both the dielectric permittivity and the loss mechanisms of the layer. In situ x-ray photoelectron spectroscopy (XPS) will be used to determine the stoichiometry of the oxide layers. The MBE system is equipped with an electron cyclotron resonance (ECR) microwave plasma source, which can provide activated oxygen, or pure O₂, during the oxide deposition process if necessary.

In addition to the MBE chamber, several sophisticated materials characterization techniques are available at PNNL, including x-ray diffraction (XRD) and x-ray reflectivity (XRR), atomic force microscopy.
(AFM), both traditional transmission electron microscopy (TEM) and scanning TEM (STEM) outfitted with electron energy loss spectroscopy (EELS), and variable-angle ellipsometry. XRD will provide information on crystallinity and grain size of the layers. XRR will provide a quantitative measure of layer thicknesses, and qualitative probe of interlayer and surface roughness. AFM will provide complementary, quantitative information on surface morphology and roughness. On selected samples, TEM and STEM will provide detailed information on layer thicknesses, crystallinity, and interface roughness and abruptness. Ellipsometry is a powerful technique to measure the in-plane optical properties ($\varepsilon_{||}$) of the HMM.$^{73}$ The Oxide Epitaxy group at PNNL recently acquired a vertical variable-angle spectroscopic ellipsometer (V-VASE, J.A. Woollam Inc.) which can measure optical properties in the range 190 – 3400 nm (6.53 – 0.37 eV). This non-destructive probe will be extensively utilized to confirm layer thicknesses, and to evaluate the HMM optical properties, providing a metric by which to optimize the HMM stack.

Following fabrication of the inorganic layers at PNNL, samples will be transferred to WWU for further characterization as well as application of sensitizer-containing and cladding layers. Spectroscopic measurements will be performed using a custom fluorometer system$^{76}$ employing fiber optics for small-spot wavelength-, angular-, and polarization-dependent excitation and collection measurements. Funds are requested to add the ability to also perform small-spot confocal nanosecond-scale lifetime measurements using a time-correlated single photon counting setup. Lifetime measurements, combined with measurements of the apparent LQY performed using appropriate thin film reference samples on dielectric and metallic substrates, allows separate estimation of both radiative and non-radiative decay rates, $\Gamma_{\text{rad}}$ and $\Gamma_{\text{nr}}$, which is much more informative than overall lifetime measurements alone.$^3$ The former provides direct connections to electromagnetic modelling,$^{35}$ and together these measurements help to paint a more complete picture of the energy transfer process.

In addition to these measurements, a range of tools will be employed to characterize other 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); sensitizer molecule orientational order parameters (polarized absorption and fluorescence spectroscopy), all of which are available at WWU.

**Sub-Wavelength Scale Gratings for Angular Emission Studies.** THIS SECTION UNDER CONSTRUCTION... An important challenge concerns how to extract electromagnetic energy from bound modes within the HMM as radiative light, and to do so with controlled polar angular intensity distribution. Though many proposed applications involving HMMs call for coupling energy between radiative and nonradiative modes, to date little work has been done on this problem, particularly with respect to outcoupling. Recently Lu and coworkers demonstrated far field emission from Type-II HMMs using a series of parallel grooves, cutting a multilayer HMM into a series of parallel slices.$^{77}$ Using this approach they showed a rhodamine dye located at various distances away from the HMM underwent up to 76-fold Purcell enhancement of the decay rate and 80-fold enhancement of the far-field emission intensity relative to uniform HMMs. They also showed that geometric details of the nanopattern have a pronounced effect on the produced radiation. More generally, this proof-of-principle demonstration suggests an approach which has been widely employed with optical microcavities, organic light-emitting diodes (OLEDs), and planar waveguides, namely, the use of photonic microstructures embedded into or placed on the surface of the device. Such features when incorporated as an integral grating can convert bound light into radiative modes. In OLED applications, for example, appropriately designed microstructures have been demonstrated capable

![Fig. 10. Computed partitioning among HMM modes of energy transferred from a sensitizer molecule located 10 nm above the same system as in Fig. 5. Axis labels](image-url)
of light extraction from substrate modes, bulk waveguide modes, and surface plasmon polariton modes.

A key feature of this approach is the possibility of achieving angular control over emission via a single integrated structure. To see how this may be possible, in Fig. 10 we compute the mode partitioning of energy transferred from a vertical dipole located 10 nm above a Ag/Si HMM. The noteworthy aspect of this result is that the majority of power goes to excite a relatively limited number of modes (in this case, those with $k_\parallel \lesssim 10$). We will calculate the exact nature of the modes excited within the HMM and how these depend on the orientation, position, and emission wavelength range of the emitting dipole. With this understanding, we hope to take advantage of orientational control of the emitting luminophores to selectively excite desired modes within the HMM and to design 2D periodic gratings tailored specifically for these modes, providing preferential emission at the desired polar angles lying outside the escape cone of the LSC cladding.

To test these designs, both focused ion beam (FIB) and a helium ion microscope (HeIM) are available at PNNL for the required nano-scale lithography. FIB utilizes a Ga$^+$ beam for lithography, achieving minimum feature widths of $\sim 30$ nm, with some implanted Ga from the sputtering process. The HeIM, in contrast, can achieve widths $< 10$ nm with a He$^+$ beam, resulting in much sharper features with no sputtering contamination. Post-patterning capping layers of a dielectric such as TiO$_2$ or Al$_2$O$_3$ will be deposited ex situ by pulsed laser deposition (PLD).

**Transparent conductor HMMs.** Efficient solar concentrators require very low photonic losses in all components, including the HMM. Metals such as Au and Ag suffer from relatively large losses, since their very high carrier concentrations result in large plasma frequencies. In fact, resistive losses are typically so large that few applications envisioned for HMMs are likely to ever be realized in practice unless they can be reduced or compensated for. In this part of the research we will explore new materials solutions to this challenge by employing conductors with metallic characteristics but fewer free carriers, such as transparent conductor oxides (TCOs). In the near IR, TCOs exhibit losses nearly five times less than the lowest-loss metal, Ag. In the later stages of the project, Ga-doped ZnO will be explored as the metallic layer in the HMM stack. When deposited in an Ar/H$_2$ environment by pulsed laser deposition, Ga-doped ZnO can achieve carrier concentrations as high as $8.9 \times 10^{20}$ cm$^{-3}$ while still maintaining $>80\%$ transmission in the visible wavelength range (Fig. 11). This opens the possibility of fabricating HMM stacks which are transparent in the visible.

Utilizing a TCO such as Ga:ZnO as the metallic layer in the HMM stack presents several advantages in addition to the potentially superior optical loss characteristics. An all-oxide stack such as Ga:ZnO / Al$_2$O$_3$ is amenable to deposition by PLD, which allows a faster growth rate than is practical with MBE. The low deposition rate per laser pulse (typically $\sim 0.25$ Å/pulse) in the PLD system available at PNNL, combined with the off-axis deposition geometry which minimizes droplet deposition on the film, still achieves high quality oxide films.

Furthermore, the lattice mismatch between ZnO(001) and Al$_2$O$_3$(0001) is favorable for epitaxial deposition. Thus, if the Ga:ZnO / Al$_2$O$_3$ stack were deposited on a single crystal Al$_2$O$_3$(0001) substrate, an epitaxial orientation of each layer can be expected. By eliminating the high-angle grain boundaries found in polycrystalline material, the optical properties will be improved, and in particular the optical loss may be substantially decreased. As an intermediate option, ZnO tends to grow as (001)-oriented columnar grains with random in-plane
orientations on non-lattice-matched substrates, so HMM stack deposition on fused silica or glass which begins with a Ga:ZnO layer may result in a (001)-oriented stack.

TIFFANY/SCOTT: are the carrier concentrations in TCOs high enough to support a plasma frequency in the visible or near-IR, needed to match our dyes? What about some of the newer materials based on intermetallics and ceramics such as transition metal nitrides? Some of these seem to be showing promise at optical wavelengths and may provide further benefits as well, including tunable optical properties, lower cost, compatibility with conventional microelectronic microfabrication processes, and in some cases solution-processability.

Sensitizer Design and Synthesis. The use of molecular sensitizers to perform the initial step of solar photon absorption opens the door to… We will employ molecular sensitizers based on perylenebisimides (PBI s) of the type N,N-bis(2,6-diisopropyl-4-octylaniline)-perylene-3,4,9,10-tetracarboximide, containing pendant orthoalkylated anilines with long alkyl tails (Fig. 12). PBI derivatives have been widely used for LSC applications because they confer intense absorbance, good photostability, and near unity quantum yield, however, \( \pi - \pi \) stacking in unsubstituted PBIs severely limits their solubility. We recently showed the addition of pendant alkylanilines increased both solubility and orientability of the PBIs in a polymerizable liquid crystal matrices, enabling a very high degree of molecular alignment to be achieved (with orientational order parameters up to \( P_2 = 0.8 \)). These design tenets will be extended to other PBI derivatives to generate alignable, soluble sensitizers with tailored absorption, emission, Stokes shifts, and LQY active in the visible/NIR region.

PBI fluorophores that are unsubstituted in the bay position typically have small Stokes shifts, on the order of \( \sim 10 \) nm. To increase this, we will employ a dipolar structure tethering polar groups at the peri-position. This leaves the opposing anhydride free to form the imide with orthoalkylated anilines containing long alkyl tails, increasing the aspect ratio of the molecule for alignment purposes. Recent work has shown that this type of dipolar structure in PBIs can result in a Stokes shift up to \( \sim 300 \) nm. This approach can also be used for shifting the absorption and emission properties of the PBIs deeper into the red. However, the LQY diminishes rapidly upon substitution at the bay or peri-positions. In this work, the LQY Purcell effect enhancement will allow us to utilize PBI fluorophores that have been overlooked for LSC applications in the past (due to their low LQYs).

As shown in Fig. 13, attachment of the proposed polar groups to the peri-position shifts the absorption from \( \lambda_{abs} = 526 \) nm in Lumogen Orange (E, Fig. 12) to \( \lambda_{abs} = 668 \) nm in the (dimethylamino(diphenylamine)) analog (4). These molecules will be synthesized via standard Buchwald-Hartwig cross coupling reactions of the 9-brominated perylenemonoimide in the case of 1 and 4 and nucleophilic substitution of the 9, 10 – dibromonated perylenemonoimide for 2 and 3. We will examine the tails A-E in Fig. 12 to optimize the pendant imide for alignment in polymerizable liquid crystal matrices. It should be noted that substitution of the bay positions of the PBI core can also be used to tune
the solubility, but that typically leads to a decrease in the aspect ratio causing very poor alignment characteristics. Note that, a solid film of PBI luminophores (which have extinction coefficients $\varepsilon \sim 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) would achieve optical density of 1 at a thickness around 10 nm, enabling absorption of 90% or more of incident sunlight in a narrow layer within the near-field of the HMM.

**Sensitizer orientation and proximity to the HMM.** As discussed above, the sensitizer luminophore position and orientation influence the strength of absorption of incident sunlight, the efficiency of energy transfer to the HMM, and partitioning of energy among the subpopulation of excited HMM states. Absorption is affected both by the orientation of the absorption dipole moment with respect to the direction of travel of incident solar photons, and by the position of the absorber because the electric energy density above an HMM varies periodically with distance due to constructive and destructive interference of reflected waves.$^{61,103}$ The distance between dye molecules and the HMM will therefore be controlled by a variable thickness dielectric spacer layer. Using the PBI family of luminophores described in the preceding section, molecular orientation is controlled by dispersing the dye in a photopolymerizable liquid crystal solvent, a representative example of which is shown in Fig. 14), which can be spin-coated onto a range of different substrates.$^{104,105,106,107}$ Subsequent photopolymerization “locks in” molecular orientational order (Fig. 15). We have significant prior experience with this method, which allows for vertical, in-plane, tilted or random molecular orientation, with orientational order parameters up to $P2 \approx 0.80$. $^{*}$refs$*$ The polymerized LC is birefringent, an effect which will be incorporated into our optical models.

![Fig. 14. LC diacylate monomers. RM257 (n=3), RM82 (n=6) - Image 391x365 to 539x429](image1.png)

**Modeling and Theory.** The behavior of electromagnetic waves in a neighborhood of, and within, an HMM requires a complete mathematical treatment of the Maxwell system. The simplest treatment is by way of effective medium theory, where the HMM is treated as a homogeneous medium with averaged effective permittivity tensor. This provides a concise and powerful setting in which to study the principal properties of electromagnetic field propagation.$^{108}$ It is, however, an idealized and unrealizable theory since it considers the limit as the number of layers goes to infinity, while the thicknesses go to zero. In practice only a finite number of alternating dielectric-metal layers, or a finite density of nanowires, can be fabricated. For the layered system, the exact finite system can be analyzed by taking into account the boundary conditions which must be satisfied at each interface, together with the boundary condition at the outer surfaces of the HMM.$^{109}$ These boundary conditions are all coupled together, and can result in a complicated, and arguably untenable, system of equation. However the use of transfer matrices, as presented by Mills and Maradudin$^{110,111}$ and applied extensively in the literature to layered systems, allows for a concise and rigorous treatment of the full EM field theory in such structures. We will compute theoretical emission patterns from emitting dipoles: in both idealized HMM using EMT and in finite systems using transfer matrices; aligned both perpendicular to, and parallel to, the axis of anisotropy, and with arbitrary alignment by way of superposition of the fields for perpendicular and parallel orientations; both embedded in the HMM, and embedded in a dielectric layer adjacent to the HMM. We will also compute the net emission patterns for emission dipoles stochastically aligned with the anisotropy axis, taking into account the probability distribution for the angle of alignment. Such theoretical treatment allows for exploration of the parameter space of varying thicknesses of the layers, the number of layers, the permittivity constants in the layers, and the degree of alignment of the emitting molecules. Discoveries
from this work will guide the fabrication of prototypes; measurements from such prototypes will provide verification of the accuracy of the theoretical modeling and calculation.

Understanding how a grating placed on, or etched into, one face of the HMM interacts with the modes within the HMM presents a new challenge. We will develop first-principle models for this architecture and will use them to determine what patterning best couples HMM modes with propagating modes in the adjacent waveguide. We hope to take advantage of the fact that HMMs support large numbers of $k$-vectors, the family of which are somewhat controllable by the orientation of the emitting dipoles and the architecture of the HMM itself. With predictions based on these computations, we will then compare the theory with measurements made on fabricated structures.

Ultimately, modeling the proposed HMM-Waveguide systems will require a successful combination of electromagnetic field theory at two very different length-scales. HMMs require consideration at the sub-wavelength length scale, whereas energy extracted out from the HMM will propagate within the waveguide, which is orders of magnitude thicker than the wavelength of the propagating fields. We must therefore also model transport of photons within the optically transparent waveguide containing the luminophores. Due to the significant Stoke's shift of the proposed dyes, re-absorption of emitted photons by luminophores is not a principal loss mechanism, though must still be taken into account. What remains to be understood, therefore, is the efficiency of total internal reflection. This is a product of the transparency, or lack thereof, of the host medium in which the luminophores are embedded, and of the physics of the interaction of a propagating photon with the boundary of the HMM. We will understand this interaction from first principles and incorporate this into our model for simulation of photon transport within a waveguide.

Isotropic models which account for extinction, absorption and re-emission probabilities, and escape-cone losses have appeared in the literature with varying degrees of sophistication.\textsuperscript{112,113,114,115,116,117,118,119,120} We have gone beyond these considerations in developing highly sophisticated models and code to predict performance of a conventional waveguide by way of Monte-Carlo simulations of photon transport. This code takes into account: the energy and polarization of the propagating photon; the stochastic distribution of absorption and emission dipoles of embedded luminophores; the potential birefringence of the host matrix (especially in the case of aligned luminophores); the precise shapes of the absorption and emission profiles of the luminophore, specifically where they overlap; any scattering due to less than perfect transparency of the waveguide; and the Fresnel relations at every interaction with a boundary between regions of differing indices of refraction. We will adapt this code to incorporate the adjacency of an HMM, and by simulating the propagation of large numbers of photons, perform Monte-Carlo simulations to predict performance of the proposed composite systems. These results will provide invaluable guidance in the design and fabrication of prototypes.

Indeed, the number of parameters over which we have control in device design is very large. These include the thicknesses and permittivities of the material used in the HMM, the number of layers, the thickness of the dielectric spacer between the dye layer and the HMM, the luminophore used, together with its absorption and emission profiles, the material used for the host matrix, the nano-structuring, or grating used to achieve out-coupling, the degree of orientation of the luminophores, and more. Such a huge parameter space cannot be explored without efficient and accurate modeling and simulation. Such theoretical treatment will enable an exploration of design parameters which lead to the most advantageous properties and optimal performance.

III. Organization and Deliverables

The proposed research involves concepts from several disciplines and an experienced team of researchers has been assembled to provide expertise in each area. \textbf{Dr. David Patrick (WWU)} is a materials chemist with expertise in liquid crystals, LSCs and optical spectroscopy. He will lead the experimental work on composite device characterization and will provide overall direction to the research program as Principle Investigator. \textbf{Dr. Scott Chambers (PNNL)} is a terrific person and will lead the work on... \textbf{Dr. Tiffany Kaspar (PNNL)} is an equally terrific person and will be responsible for... \textbf{Dr. John Gilbertson}
(WWU), a synthetic chemist, will lead the effort to prepare new fluorophores. Modeling of optical properties will be performed by mathematician Dr. Stephen McDowall (WWU) a specialist in the study of photon transport and light-matter interactions within scattering and absorbing media. He also has experience working with the full Maxwell system of equations applied to complex geometries.

As discussed throughout, the proposed research is highly synergistic, with iterative connections between theory and modeling, materials selection/synthesis, and device fabrication and characterization. WWU and PNNL are about a six hour drive apart. The PIs and their students will hold monthly joint group meetings by video conference to share results and ideas, and discuss progress.

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### IV. Broader Scientific Impacts.
The development of highly concentrating, high efficiency LSCs would represent a major advance in solar energy technology, potentially bringing about a transformative reduction in the cost of PV generated electricity. This research will develop new concepts in LSC design based on active light management we believe have the potential to reach this goal. Some of the anticipated broader scientific impacts are:

- HMM-based active light management offers the potential to qualitatively advance LSC performance by reducing or eliminating escape-cone losses, increasing while providing broadband solar absorption and high luminescent quantum yield.
- which have already been demonstrated on flexible, transparent polymeric substrates over areas exceeding 8”x8”.ref*
- The research explores several basic aspects of light-matter interactions involving metamaterials, many of which are relevant to other technologies beyond solar concentration while also being of fundamental interest. As such, the proposed research also paves the way for the better understanding of optical wavelength metamaterials and their use in a wide range of tangential applications, including information processing,ref* communications, ref* and chemical sensing, ref*.
- Many important links in the infrastructure needed for eventual implementation of LSC technology are already in place: Approximately $1B has been invested in mirror and lens-based concentrators since the 1970’s, and although electricity generation from solar concentration currently represents less than 1% of total solar generation capacity worldwide, there is a growing acceptance of concentrating technologies in the industry. For example, several megawatt-scale concentrating PV installations are now operating, and more than a dozen companies produce or are developing concentrator PV cells designed for long term use at over 500 suns. This infrastructure, along with current trends in PV cost and efficiency improvements, suggest that if the performance benchmarks outlined in the proposal can be
met, there should be reasonable prospects for eventual commercialization of resulting technologies.

V. Summary.

Exploiting the potential for active light management, we will develop and study LSC architectures tailored for two main goals:

1. Increasing the effective LQY of the dye, thereby allowing use of longer wavelength, larger Stokes shift luminophores whose LQYs would otherwise be inadequate for LSC applications. This will result in reduced self-absorption losses while enabling better matching with the solar spectrum.
2. Engineering directional emission from the coupled luminophore/HMM system, thereby reducing or potentially even eliminating escape cone losses, the main loss mechanism in LSCs.

- An increase in the LQY of the luminophore via Purcell effect enhancement. Enhancements up to 80× have been reported for luminophores with small intrinsic LQY.*ref* Reduced excited state lifetime should also increase photostability, a concern for some classes of candidate LSC luminophores.*ref*
- The enhanced LQY enables use of larger Stokes shift, long wavelength luminophores whose LQYs would otherwise be too low for LSC applications. This reduces self-absorption, and enables incorporation of luminophores into LSCs able to harvest a larger portion of the solar spectrum by, for example, use of near-IR dyes.
- Electromagnetic energy in the HMM is concentrated in narrow range of high-\(k\) modes, facilitating the design of sub-wavelength scale diffraction gratings for directional emission, thereby reducing and possibly eliminating escape-cone losses – the dominant loss mechanism in traditional LSCs.
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