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Major Goals: Energetic materials can be initiated through a variety of stimuli, including thermal, mechanical, and electrical means, with the non-thermal stimuli believed to generate heat first which then causes thermally-induced chemical decomposition. Optimizing the performance of energetic materials for specific applications must be balanced against safety and reliability considerations. This process requires an improved fundamental understanding of the chemical reactions inside the material. Our long-term goal is to develop and demonstrate the experimental feasibility to monitor in real-time subsurface chemical reactions in scattering heterogeneous materials. We then plan to use this capability to investigate and characterize subsurface chemical reactions in energetic materials. Our initial focus is on developing and demonstrating the experimental capability to focus a laser beam inside a scattering heterogeneous medium and to perform Raman and LIF measurements at the focal spot.

Accomplishments: We have developed a bidirectional focusing microscope that uses feedback-assisted wavefront shaping to perform subsurface spectroscopy in heterogeneous materials. This microscope is found to have significantly improved signal over a uni-directional design, both due to an expected increase in the number of modes controlled as well as an unexpected boost most likely due to long range mesoscopic correlations in the propagation modes. We characterized the performance of this microscope for different experimental parameters, including: number of SLM bins, number of genetic algorithm generations, sample position (i.e., beam spot size), and the depth of the target particle and find that care must be taken in adjusting the various parameters to optimize the functionality of the microscope.

After characterizing the microscope's performance we then demonstrated its capabilities by measuring subsurface photodegradation of an inert energetic crystal simulant [Eu:Y(acac)₃(DPEPO)] using both fluorescence and Raman spectroscopy. We observe decreasing fluorescence and Raman intensity consistent with air-based measurements, but also observe the formation of new Raman peaks at 1237 cm⁻¹ and 1337 cm⁻¹, which can be assigned to C-N stretch and N-H bend modes, which suggests a subsurface reaction with the IPDI curing agent, which is the only source of nitrogen atoms in the system. These reactions only occur when EYAD is present in the heterogenous sample, so the EYAD is key to the reaction, but it is unclear if the reaction is between the EYAD and the IPDI or if the EYAD is acting as a photocatalyst for a reaction between the IPDI and the HTPB or sugar. Regardless of the mechanism, this demonstration shows the capability of the bidirectional focusing microscope to probe subsurface chemical reactions.

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Training Opportunities: Two postdoctoral research associates, Dr. Benjamin Anderson and Dr. Ray Gunawidjaja, one engineering associate, Ms. Natalie Gese, and four undergraduate students, Rebecca Tucker, Kostiantyn Makrasnov, Jordan Bone, and Andrew O'Kins contributed to this project.

Dr. Anderson learned about wavefront manipulation, microscopy, and Raman spectroscopy.
Dr. Gunawidjaja and Ms. Gese learned about sample preparations, including the synthesis of organic fluorescent guidestar, and the preparation of composites. The students learned about programming to interconnect and control various instruments.

Results Dissemination: Results have been published or submitted for publication in multiple manuscripts.

The PI included results from this project in a presentation at the DOD Basic Research Forum in April 2021.

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Participant: Benjamin Anderson

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Participant: Andrew O'Kins

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Abstract: We characterize the performance of standard and micro genetic algorithms when applied to focusing inside of an opaque media using feedback from a fluorescent guidestar particle. Using this feedback modality we find that the algorithms optimize more quickly (but to a lower enhancement) than when using reflective feedback, with the underlying mechanism being the fluorescence signal's multimodal nature and lower signal-to-noise ratio. We also find that both algorithms' performance decrease at very large numbers of bins due to decoherence effects related to a bin-dependent iteration time. To mitigate this effect we implement multithreaded functionality in the genetic algorithms and find that for our specific computer we obtain a $3.3 \times$ improvement in speed utilizing multithreading. These results demonstrate the usefulness of both algorithms for focusing inside of opaque media, which has applications in biological imaging and the study of subsurface chemical reactions in heterogeneous materi

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Authors: Benjamin R. Anderson, Natalie Gese, Hergen Eilers

Keywords: Lanthanides, Organic Complexes

Abstract: We propose to use the lanthanide complex Eu:Y(acac)₃(DPEPO) as an inert analogue to explosive molecular crystals for subsurface spectroscopy. In this study we perform material and spectroscopic characterization of this complex and consider the effects of thermal and photo degradation on the complex's spectroscopic properties. These measurements will be baseline results for future studies on these reactions when the complex is embedded inside of a heterogeneous material.

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Authors: Benjamin R. Anderson, Natalie Gese, Hergen Eilers

Keywords: Subsurface reactions; Wavefront shaping; Bidirectional Focusing

Abstract: We have developed a bidirectional-focusing microscope that utilizes feedback-assisted wavefront shaping to focus light inside of a heterogenous material in order to monitor sub-surface chemical reactions. The bidirectional geometry is found to provide superior intensity enhancement relative to single-sided focusing due to increased mode control and long range mesoscopic correlations. Also, we demonstrate the microscope's capability to measure sub-surface chemical reactions by optically monitoring the photodegradation of an Eu-doped organic molecular crystal embedded in a heterogeneous material using both fluorescence and Raman spectroscopy as probe techniques.

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Authors: Benjamin R. Anderson, Natalie Gese, Hergen Eilers

Keywords: Wavefront-shaping-assisted bidirectional focusing; Effect of experimental parameters

Abstract: Recently we developed a technique to perform wavefront-shaping-assisted bidirectional focusing in opaque media, which has applications in performing subsurface spectroscopy of heterogeneous materials. In this study we report in detail on the effects of different experimental parameters on the function of this technique. Namely, we consider the effects of: number of bins, target depth, sample positioning, and initial intensity. From these measurements we find that our system functions well for initial SNRs $> 6:7$ (intensities $1.042\times$ larger than the background), that the enhancement depends strongly on the incident beams spot sizes, and that the system operates optimally when the sample is spatially aligned to maximize the flat field intensity and minimize the flat field intensities spot size. We also estimate that the bidirectional focusing microscope can improve focusing on subsurface particles up to a depth of ~ 18 mean free paths (which is $1170\text{ }\mu\text{m}$ for our samples).

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Authors: Benjamin R. Anderson, Natalie Gese, Hergen Eilers

Keywords: Wavefront-shaping-assisted bidirectional focusing; Effect of experimental parameters

Abstract: Recently we developed a technique to perform wavefront-shaping-assisted bidirectional focusing in opaque media, which has applications in performing subsurface spectroscopy of heterogeneous materials. In this study we report in detail on the effects of different experimental parameters on the function of this technique. Namely, we consider the effects of: number of bins, target depth, sample positioning, and initial intensity. From these measurements we find that our system functions well for initial SNRs $> 6:7$ (intensities $1.042 \times$ larger than the background), that the enhancement depends strongly on the incident beams spot sizes, and that the system operates optimally when the sample is spatially aligned to maximize the flat field intensity and minimize the flat field intensities spot size. We also estimate that the bidirectional focusing microscope can improve focusing on subsurface particles up to a depth of ~ 18 mean free paths (which is $1170 \mu\text{m}$ for our samples).

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I certify that the information in the report is complete and accurate:

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1. SUMMARY

One of the main obstacles to better understanding the chemistry of explosive initiation in polymer bonded explosives (PBXs) is optical opacity of PBXs due to their heterogeneous nature. This opacity means that typical optical techniques can only probe near the surface of PBXs, which results in subsurface reactions going unobserved. To address this challenge, we have proposed to use feedback-assisted wavefront shaping (FAWs) to control the propagation of light inside of the heterogeneous PBX such that we can perform subsurface spectroscopy.

To accomplish this goal, we have developed a bidirectional focusing microscope (BFM) that uses two counterpropagating beams which are phase modulated by two independent spatial light modulators (SLMs). Focusing inside of a heterogeneous material is achieved by using fluorescence from an embedded guidestar particle as feedback for a genetic algorithm that controls the SLMs. As the algorithm runs light is modulated such that it couples into propagation modes that allow focusing on the hidden target particle.

We first demonstrate this technique using fluorescent polymer microspheres embedded at different depths in a clear polymer that has dispersed sugar crystals added to cause scattering. These samples were used to characterize the functionality and performance of the BFM for different experimental parameters. We find that several of the parameters have similar effects as when using FAWs for transmission or reflection optimization [1-3], with increasing the number of bins and genetic algorithm generations resulting in greater enhancements, while changing the sample position on the order of microns can have significant effects on the enhancement. We also determined the minimum initial SNR to obtain good optimization to be ≈ 6 , with the obtainable enhancement decreasing below this level.

While the parameters shared between transmission/reflection and fluorescence feedback mechanisms are found to produce similar functional behaviors, we also consider a new parameter (target particle depth) which does not exist for transmission/reflection feedback. For these measurements we prepared three-layer samples with guidestar particles either in the top, middle, or bottom layer and then performed optimization. These samples are found to have scattering mean-free-paths (MFPs) of $l \approx 65 \mu\text{m}$. For the top layer the particles are $\approx 60 \mu\text{m}$ ($0.92 l$) deep, for the middle layer they are $\approx 410 \mu\text{m}$ ($6.31 l$) deep, and for the bottom layer they are $760 \mu\text{m}$ ($11.7 l$) deep. From these measurements we found that the enhancement decreases with particle depth and we estimate that the current version of the BFM has a functional maximum depth of up to 18 mean free paths, which is $1170 \mu\text{m}$ for our samples.

After characterizing the performance of the BFM we next demonstrated its functionality by measuring photodegradation of a guidestar particle embedded in a heterogeneous material. For this purpose we developed a Eu-doped fluorescent organic molecular crystal $[\text{Eu}:\text{Y}(\text{acac})_3(\text{DPEPO})]$ (EYAD), which forms crystallites approximately $10\text{-}50 \mu\text{m}$ in size. These crystals provided both the feedback for the focusing algorithm as well as our particle of interest during photodegradation. Using the BFM we were able to monitor a buried EYAD crystal's photodegradation using both fluorescence and Raman spectroscopy. From these measurements we find that EYAD's photodegradation in a heterogeneous sample differs from its photodegradation in air. Namely, we find new bonds formed with the IPDI curing agent, which do not occur in EYAD in air, nor do they occur in the polymer without EYAD crystals. We also performed subsurface measurements on electrically heated EYAD with the fluorescence results being consistent with the bare wire measurements, while the Raman measurements were overwhelmed by background Raman from the sugar crystals. One possible solution to this issue is spatial filtering of the collected light.

In summary we have successfully demonstrated a bidirectional focusing microscope that uses feedback assisted wavefront shaping to probe subsurface chemical reactions. We have characterized its performance under different experimental conditions to determine its optimal configuration as well as its limitations.

Future work on this technique will involve improving its speed by use of optical phase conjugation, high-speed digital mirror devices, self-healing optical beams, and pulsed laser spectroscopy.

2. INTRODUCTION

Explosives and propellants are heterogeneous materials consisting of energetic molecular crystals (e.g., RDX, HMX, etc.) embedded in polymeric binders (e.g., elastomers, fluoro- polymers, etc.). Figure 1 shows an example of randomly oriented energetic crystals, with sizes ranging from sub-micrometer to hundreds of micrometers, embedded in a polymeric binder. Additional components may include plasticizers, antioxidants, taggants/markers, friction-generating grit, etc. These energetic materials can be initiated through a variety of stimuli, including thermal, mechanical, and electrical means, with the non-thermal stimuli believed to generate heat first which then causes thermally-induced chemical decomposition. For example, as a shock wave travels through such a heterogeneous material, a variety of phenomena such as pore collapse, plastic deformation, micro-fractures, shear banding, binder/crystal and crystal/crystal interface friction, etc. can take place. Each of these mechanisms can lead to localized heating with the temperature rise dependent upon the local rate of inelastic deformation vs. the local heat dissipation. If sufficient heating occurs, these local hot-spots can lead to chemical reactions and energy release in the material.

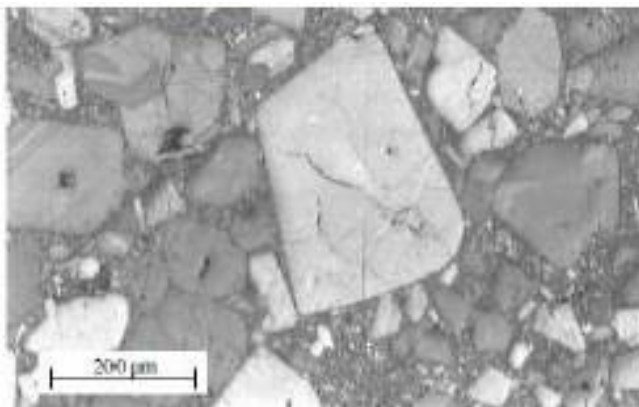


Figure 1. SEM image of PBX (reproduced from Ref. 1).

Optimizing the performance of energetic materials for specific applications must be balanced against safety and reliability considerations. This process requires an improved fundamental understanding of the chemical reactions occurring in the material, and in particular subsurface events (e.g., reactions at interfaces between HE crystal and binders, reactions near pores, etc.). The ability to monitor such subsurface reactions can potentially provide new insights into reaction mechanisms, chemical kinetics, physical and chemical properties, etc. This information could subsequently be used to better understand the various processes occurring in energetic materials and therefore lead to better, safer, and more efficient designs.

Optical techniques such as Raman spectroscopy and Fourier transform infrared (FTIR) spectroscopy, which probe vibrational energy levels, combined with optical emission spectroscopy (OES) and optical absorption spectroscopy, which probe electronic energy levels, are some of the most common approaches to monitor chemical reactions.

However, due to the heterogeneous nature of the materials of interest, a long-standing scientific issue has been how to monitor chemical reactions that occur below the sample surface. The optical opaqueness, caused by optical scattering, makes it very difficult, if not impossible to apply these spectroscopy techniques to optically monitor subsurface chemical reactions in these materials.

To address this challenge we have proposed to use feedback-assisted wavefront shaping (FAWS) [4] to focus probe light inside of a heterogeneous material in order to probe subsurface reactions. FAWS works by modulating the phase of incoming light (using a spatial light modulator) such that when it enters the heterogeneous sample it is coupled into desired propagation modes that optimize the feedback signal. This technique was first demonstrated by Vellekoop and Mosk in 2007 using transmitted light as the feedback signal [5]. Since then many other feedback modalities have been used, including: reflection [1, 6], Raman Scattering [7, 8], fluorescence [9], and nonlinear optical feedback [10-15].

For our technique we have developed a bidirectional focusing microscope (BFM) that uses fluorescence from a guidestar particle to perform FAWS. The BFM is essentially an isotropic focusing microscope (i.e., uses two confocal objectives in a counterpropagating geometry), but with the light being modulated by SLMs before entering the objectives. This design is a modification of Jang *et al.*'s optical phase conjugation (OPC)-assisted isotropic focusing microscope, which uses one SLM to perform OPC [16-19]. Note that we do not use the descriptor "isotropic" for our microscope as we are studying highly scattering samples which makes the focal spot no longer isotropic.

The BFM is designed to function in two modes: (1) use both arms for FAWS in order to obtain focus on the target particle or (2) use one arm to perform FAWS to focus on the target from one direction and then use the other arm to perform DOPC to obtain focus in the opposite direction. The first mode using FAWS alone is significantly easier to implement than the DOPC mode. However, the DOPC mode is almost twice as fast as the dual FAWS mode. For this initial study into this technique, we primarily focus on the dual FAWS modes but did begin investigating the implementation of the DOPC technique (see Appendix B).

3. HETEROGENEOUS SAMPLES

This project requires HE molecular crystal simulants that fluoresce and show chemical reactions that are similar to an HE molecular crystal. We made dysprosium and samarium analogues for a previous project. To make them fluoresce at 532 nm we replace these lanthanides with europium. Additionally, for pure optical focusing, we used fluorescent microspheres.

Figure 2 shows an example SEM micrograph of EYAD crystals, its molecular structure, and an image of EYAD dispersed into a heterogeneous sample, which glows orange under UV illumination. From Figure 2 we find that the crystals tend to come in two forms: a single crystal form that has a well-defined rectangular shape, while the other form is multicrystalline without a well-defined shape. The crystals are also in the 10s of microns range for size.

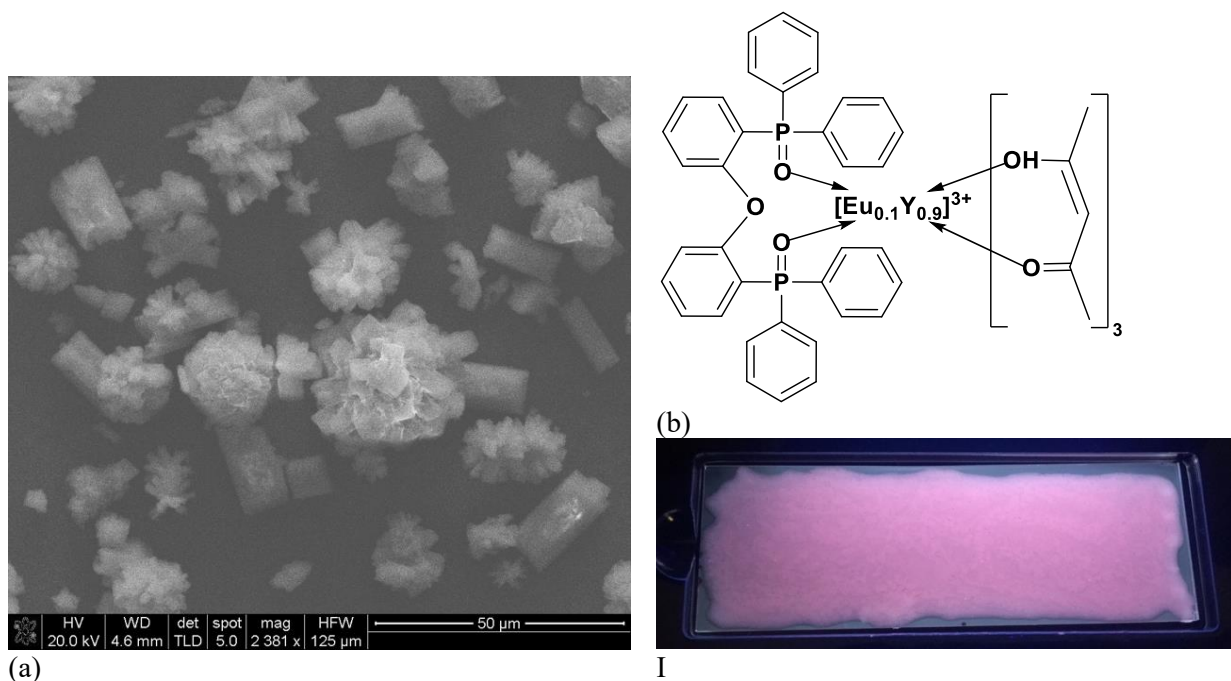


Figure 2. (a) SEM of EYAD particles, (b) diagram of EYAD molecular structure, and (c) image of heterogeneous sample.

In the previous reporting period, we performed spectroscopy on $\text{Eu}:\text{Y}(\text{acac})_3(\text{DPEPO})$ and found decay times on the order of hours. For this reporting period we proposed to demonstrate a faster reaction and hypothesized that switching the acac ligand for hfac would result in a lower degradation temperature and therefore a faster reaction. This hypothesis was based on our previous observations of the $\text{acac} \rightarrow \text{hfac}$ substitution in Sm-doped lanthanide complexes. [2,3]

In summary, we prepared a range of different materials that allowed us to explore the different aspects of this project to monitor chemical reactions and to perform depth-dependent measurements.

Depth Dependent Guidestar Layered Samples

Several polymeric binders were tested for encapsulating scattering and guide star particles: HTPB-based, Epo-Tek 305, and Norland 63. Originally HTPB-based binder was used to prepare these samples, but it was found that more optically transparent binders are preferable and less susceptible to photodegradation and additional fluorescence. Figure 3 shows spectra obtained using a Cary 5000 UV-Vis-NIR spectrophotometer with a DRA 2500 for the three binders. The results indicate less absorbance for the Norland 63 and Epo-Tek 305 compared to HTPB-based binder at the 532 nm laser line. Samples were prepared by curing a 0.5 g of sample onto a glass slide. The background of the glass slide was taken to eliminate its absorbance signal from the spectra.

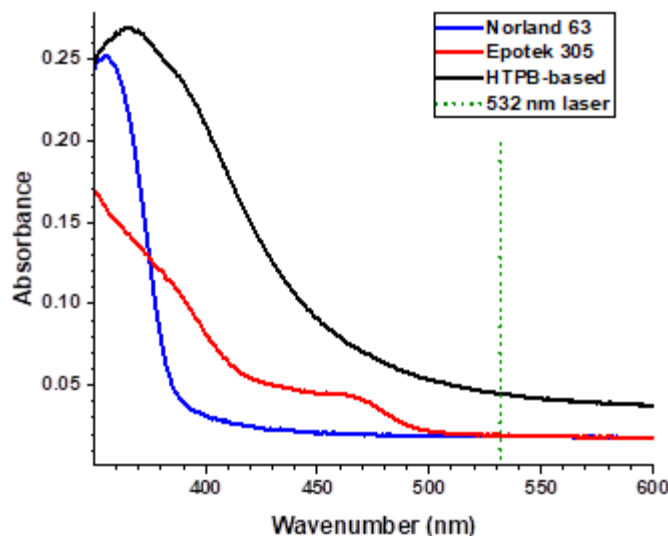


Figure 3. UV-vis absorbance spectra for different binders.

Figure 4 shows a schematic of layered samples with guidestar embedded layers positioned at various depths. Layered samples were prepared on 1 mm thick glass slides. The thin layer containing the guide-star particles is approximately 0.12 mm thick and the remaining thickness is about 0.35 mm for each scattering layer.

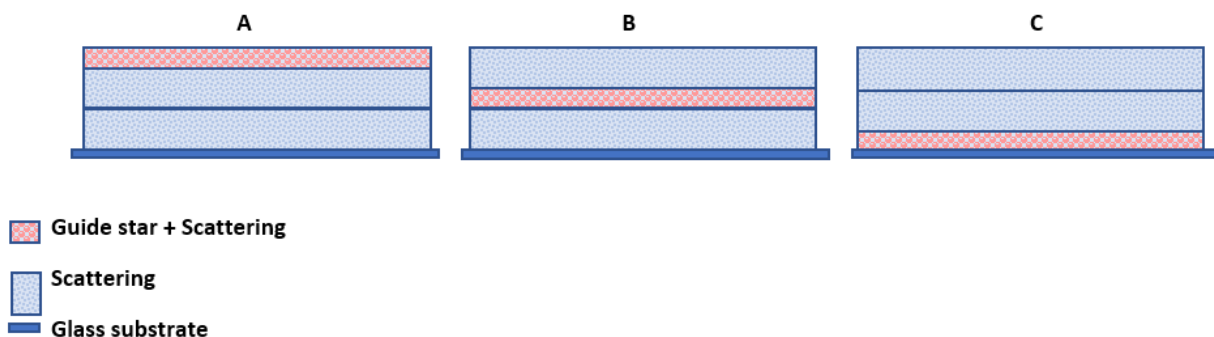


Figure 4. Polymeric binder with depth-dependent guidestar layers.

Scattering particles (Sugar)

Powdered cane sugar was used as a surrogate for energetic molecular crystals. SEM imaging assisted in confirming particle morphology and size distribution as shown in Figure 5. It is well established that the distribution for this sugar classification is typically 98% <75 μm that is set by manufacturers [20]. Additionally, this category of sugar contains 3% starch [20]. The powder morphology indicates the sugar

particles are smaller pulverized fragments of a larger sugar granules plus some starch. The particles observed with SEM in this work were all less than 110 μm .

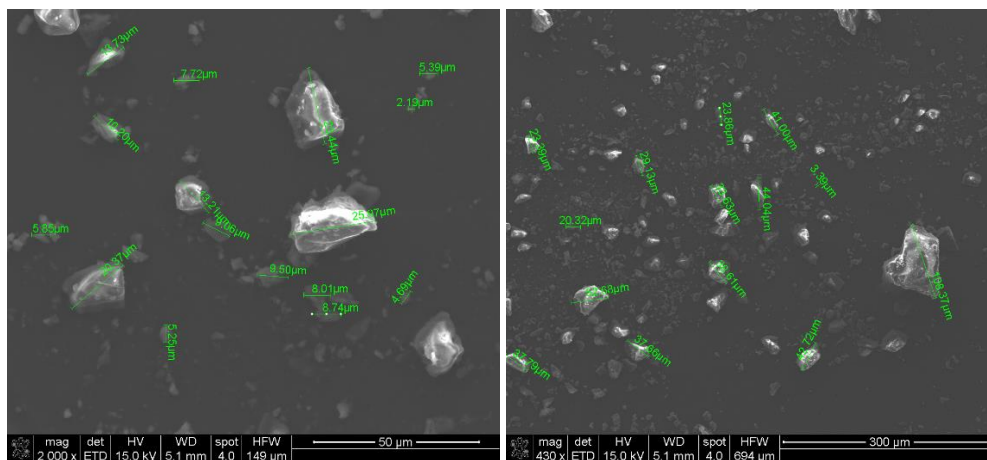


Figure 5. SEM image of sugar crystals used as a scattering surrogate.

Fluorescent particles

Fluorescent orange polymer microspheres (FMO-1.3g/cc, d_{50} =1.5-2.0 μm) were purchased from Cospheric LLC and PS-FluoRed-100 (d_{50} =99.9 μm) fluorescent red microspheres were procured from microParticles GmbH. SEM images are shown in Figure 6.

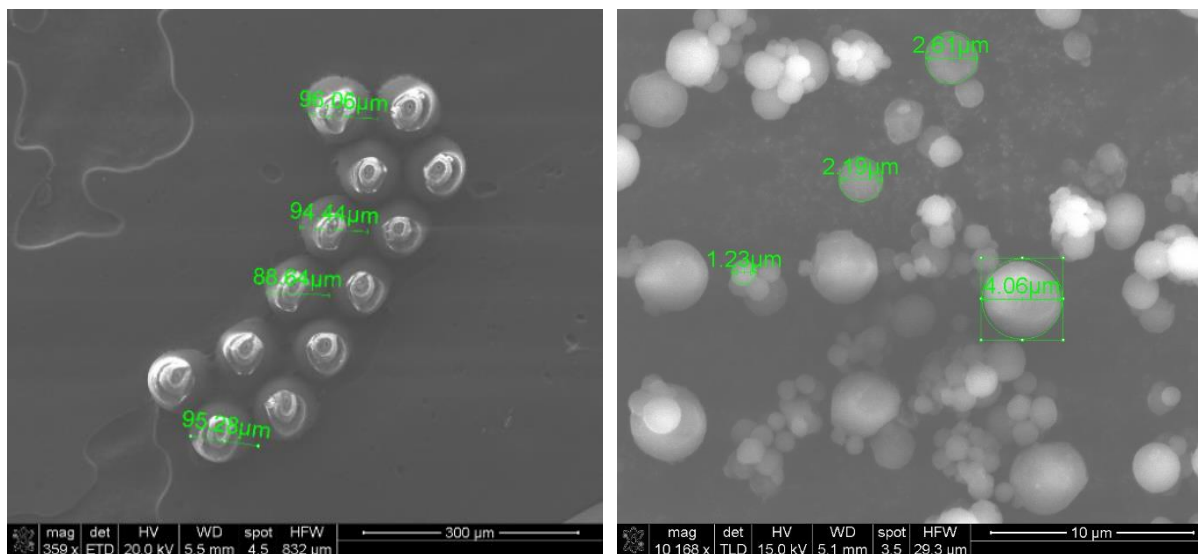


Figure 6. SEM images of PS-Fluo-Red-Fi274 (left) and FMO-1.3 fluorescent orange (right).

EYAD and EYHD were prepared in-house. EYHD synthesis was reported previously and EYAD synthesis is explained in the next section, see Figure 7.

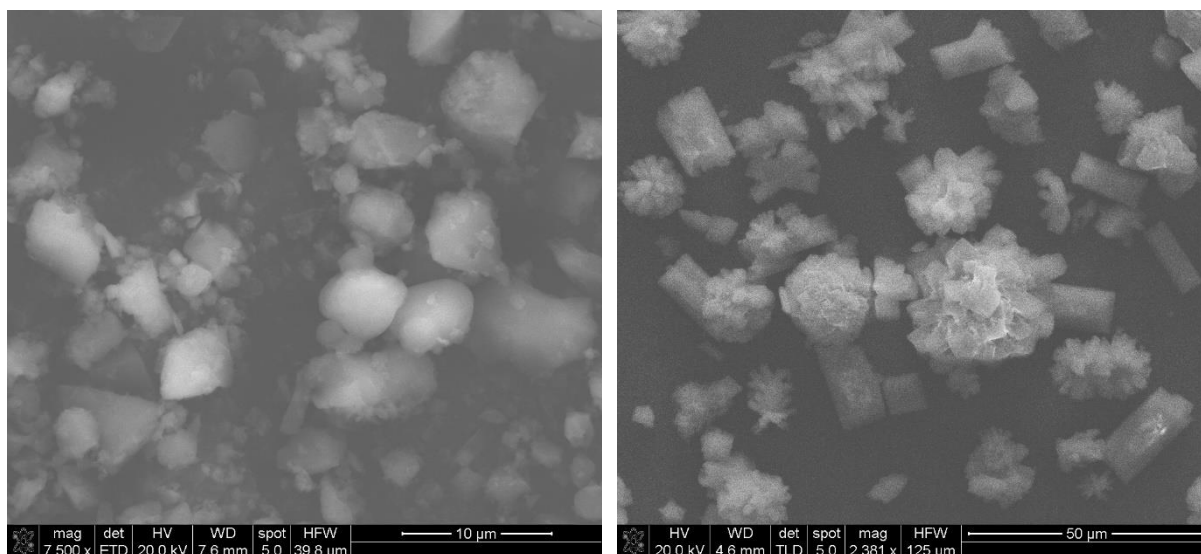
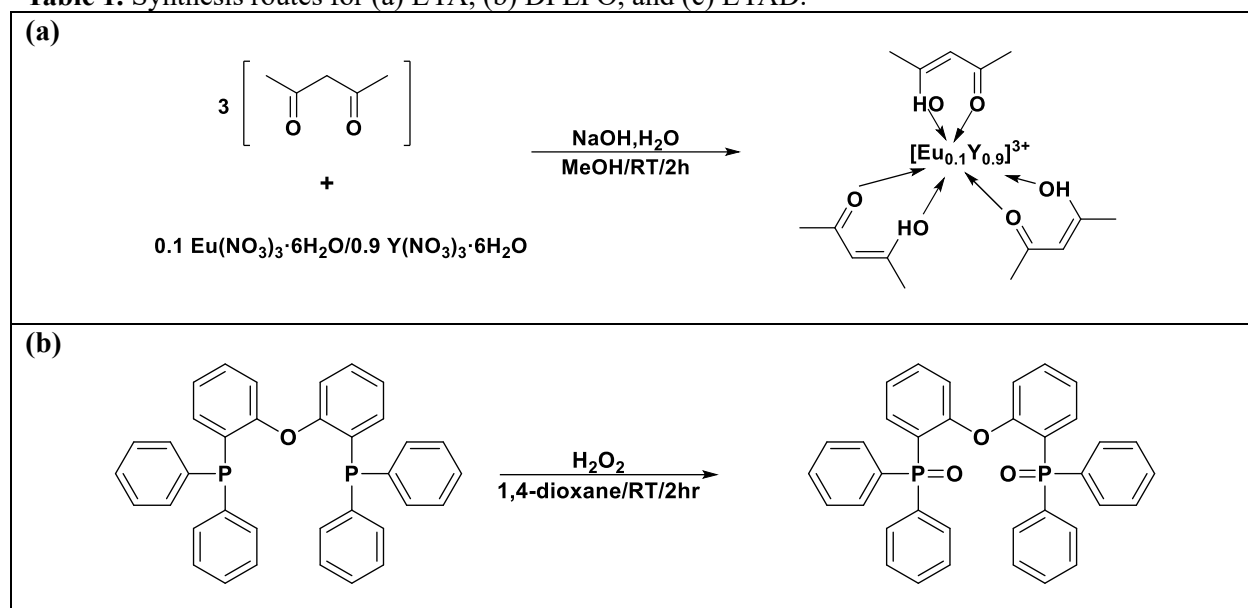


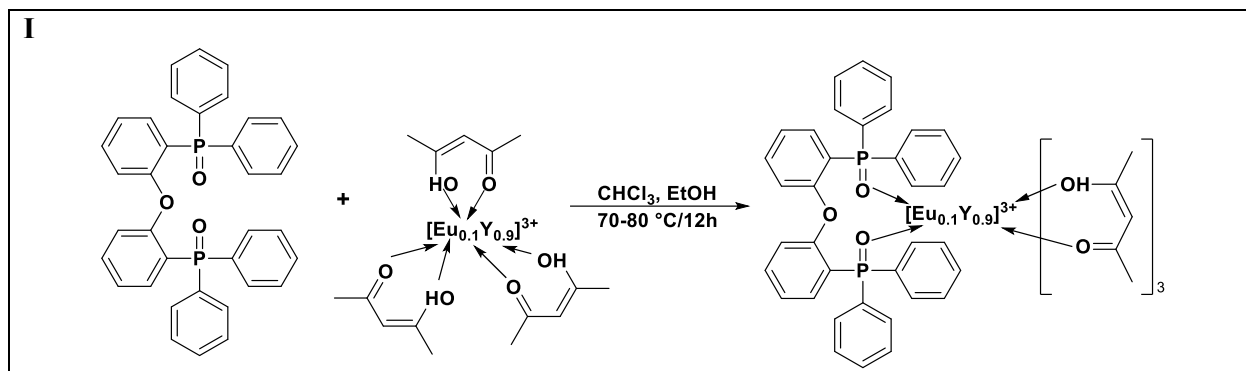
Figure 7. SEM images of EYHD (left) and EYAD (right).

EYAD synthesis

The synthesis of EYAD molecular crystals, $\text{Eu-doped Y}(\text{acac})_3(\text{DPEPO})$, involves the three steps shown in Table 1. EYA (Table 1(a)) and DPEPO (Table 1(b)) are prepared separately, and then EYAD is synthesized by combining EYA and DPEPO using heat and refluxing (Table 1(c)).

Table 1. Synthesis routes for (a) EYA, (b) DPEPO, and (c) EYAD.





Synthesis of $\text{Eu}_{0.1}\text{Y}_{0.9}(\text{acac})_3$ or EYA

For preparation of EYA, an aqueous solution of NaOH (Fisher Chemicals, Bioreagents) is dropwise added to a solution of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, 99.99%), $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, 99.99%), and acetylacetonate (Alfa Aesar 2,4-pentadione, 99%) in methanol, yielding a slightly basic milky white suspension. After aging the suspension for 1-2 h, the white precipitate is washed multiple times with deionized water by centrifuging to isolate the insoluble precipitate, decanting the separated water, then vortexing in DI water to redisperse. This process is repeated 3-5 times. A final washing with a water/methanol mixture (4/1) is repeated and the isolated insoluble product is dried for 12 hours in a vacuum oven at 323.15 K. Finally, the dried insoluble precipitate is crushed into a white powder using a mortar and pestle.

Synthesis of bis(2-diphenylphosphino)phenyl ether oxides) or DPEPO

For preparation of DPEPO, a suspension of bis(2-diphenylphosphino)phenyl ether (Aldrich, 98%) in 1,4-dioxane (Sigma, 99.8%) is prepared. The suspension is cooled in an ice bath. A H_2O_2 solution (30% w/w) is dropwise added to give a transparent solution. After the solution turns turbid (10-15 minutes), let the suspension stir for 2-3 hours. Dissolve the white product in CHCl_3 . Rinse the CHCl_3 solution three times with DI water. Separate the product containing CHCl_3 solution and dry with MgSO_4 (3% w/v). Filter to remove MgSO_4 and evaporate CHCl_3 to yield a white solid product.

Synthesis of $\text{Eu}_{0.1}\text{Y}_{0.9}(\text{acac})_3(\text{DPEPO})$ or EYAD

To prepare EYAD, separate solutions of DPEPO in CHCl_3 and EYA suspension in ethanol are prepared. The DPEPO solution is then dropwise added to the EYA solution. The EYA is not soluble in ethanol, but addition of DPEPO solution in CHCl_3 gradually dissolves EYA. A mortar and pestle are used to suspend the EYA in ethanol. The final mixture is a translucent suspension. The mixture is refluxed in a heated oil bath at 343.15-353.15 K for 12 hours. After 12 hours, the cooled translucent suspension is concentrated using a roto evaporator, precipitated in hexanes and centrifuged to isolate the precipitate. The precipitate is next dried in a vacuum oven at 313.15 K yielding a white powder as shown in Figure 8.

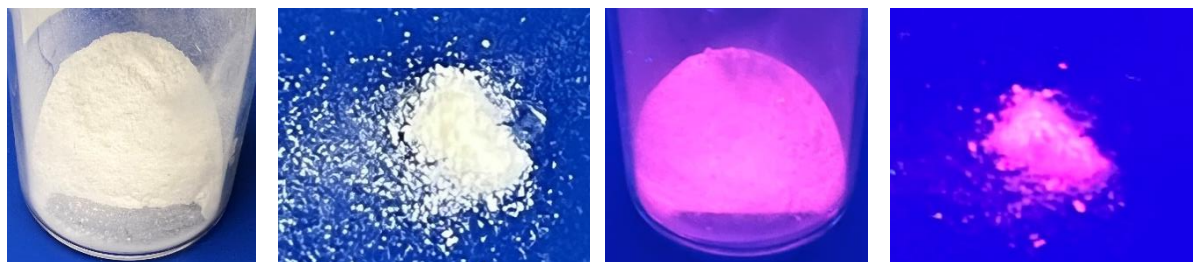


Figure 8. As-prepared EYAD powder under white light (left) and UV light (right).

FTIR of EYAD

The EYAD product was measured using Fourier transform infrared spectroscopy with attenuated total internal reflectance (FTIR-ATR) to verify that the desired material was obtained, see **Error! Reference source not found.**

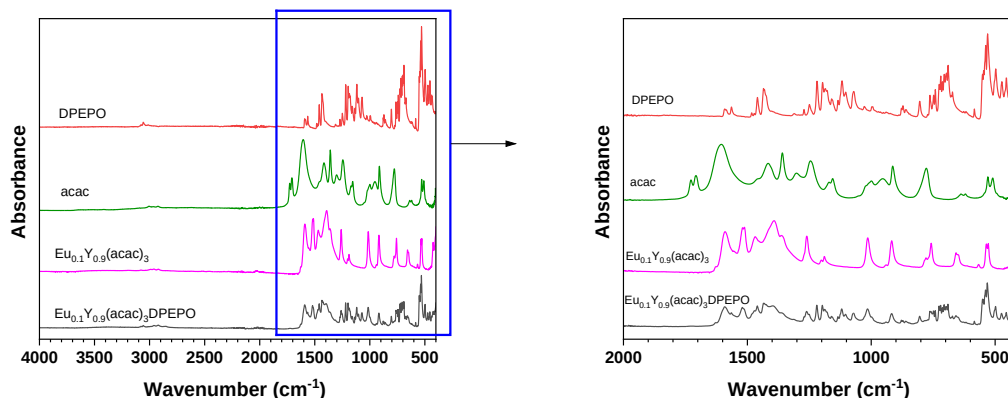


Figure 9. FTIR-ATR spectra of DPEPO, acac, EYA, and EYAD.

HTPB Samples

Hydroxy terminated polybutadiene prepolymer (HTPB, R-45M, $M_n = 2800$, hydroxyl value = 0.72 meq/g) was purchased from CRS Chemicals. Isophorone diisocyanate (IPDI, L13759) curing agent, di-(2-ethylhexyl) adipate (DEHA, L10195) plasticizer, and Di-n-butyltin dilaurate (DBTL, 71130) catalyst were all purchased from Alfa Aesar. Guide star particles were either purchased or prepared in the lab. Tetrahydrofuran (THF, 401757, inhibitor free) was purchased from Sigma-Aldrich.

Polyurethane binder formulations are prepared by the addition 1% (w/w) DBTL catalyst to 10% (w/w) IPDI in HTPB solution. To this solution, 30% (w/w) THF is added. The HTPB/IPDI/DBTL/THF (solution A) is stirred for 15 minutes on a stir plate. DEHA is then added to solution A in a 3:2 ratio (DEHA:A). The particle/DEHA:A solution is mixed with 50 wt% sugar. To prepare scattering layers containing guide star particles are dispersed into THF (0.3 mg/ml) and 30 μ l of this solution is pipetted into the DEHA:A + 50 wt% sugar solution giving a fluorescent particle concentration of 1% (w/w). The final solution is spin coated onto 3"x 1" glass slides at 2500 rpm, for 20 seconds, giving a coating with an estimated thickness of 120-200 μ m. The spin coated films were cured at 313.15 K for 72 hours.

Epo-Tek 305 Samples

Epo-Tek 305 spectrally transparent epoxy was purchased from Epoxy Technology. ACS reagent grade methanol was purchased from Sigma-Aldrich. Epo-Tek 305 epoxy was prepared by mixing 10:2.8 ratio by weight of part A (resin) and part B (hardener). Epo-Tek 305 and sugar scattering particles were mixed in a 1:1 ratio by weight and thinned by adding one part methanol (ACS reagent) per two parts epoxy/sugar mixture to prepare scattering layers. Each scattering layer is approximately 0.5 g and drop cast onto the glass substrate. Epoxy formulations containing scattering particles and guide star fluorescent particle are prepared by dispersing the microparticles into methanol (0.3 mg/ml) and 30 μ l of this solution is pipetted into Epo-Tek 305 epoxy/50 wt % sugar solution giving a fluorescent particle concentration of 0.25-1% (w/w). The final solution is spin coated onto a 3"x 1" glass slide at 2500 rpm for 20 seconds, giving a coating with an estimated thickness of 120 μ m. The epoxy mixtures are cured in an oven at 338.15 K for 1 hour between the application of each layer. Three depth-dependent fluorescent guide star layered samples were prepared as shown in shown in Figure 10. Each scattering layer is approximately 350 μ m giving a

total thickness of approximately 820 μm .

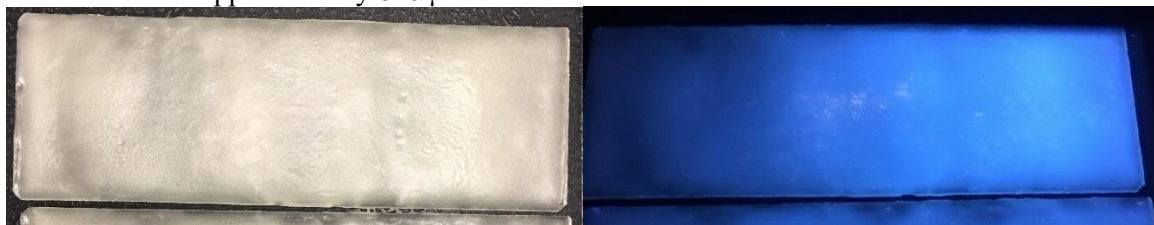


Figure 10. Epo-Tek 305 layered samples illuminated with UV light (right) containing 1wt% PS fluoRed-Fi274.

Norland 63 Samples

Norland 63 ultraviolet cure “photopolymer” (NOA 63) was tested as another potential polymeric binder because of its low fluorescence. NOA 63 was combined with 50 wt% sugar and mixed with a stir rod to prepare the scattering layers. Fluorescent microspheres are added to the NOA 63 and sugar. Each layer is cured using long-wave UV light for 5 minutes. To prepare guide star scattering layers the fluorescent particles are dispersed into THF (0.3 mg/ml) and 30 μl of this solution is pipetted into the Norland 63 + 50 wt% sugar solution giving a fluorescent particle concentration of 1% (w/w).

EYAD Coated Wire Samples

A slurry of EYAD was prepared by suspending in THF (Figure 11) and sonicating. A 2-inch length of 0.076 mm platinum wire (Sigma Chemistry, 357375) was taped to a glass slide and EYAD slurry was applied. The coated wire was verified with optical microscopy (Figure 12) and UV illumination (Figure 13). Additional samples were prepared using the same method with 0.19 mm copper wire (Arcor, 36 gauge) because the thin platinum wires were too delicate. SEM images of EYAD coated wires are shown in Figure 14. Once coated with EYAD, the wires were embedded in Epo-Tek 305 + 50 wt% sugar prepared as described in the previous section.



Figure 11. EYAD coated platinum wire (UV-right).

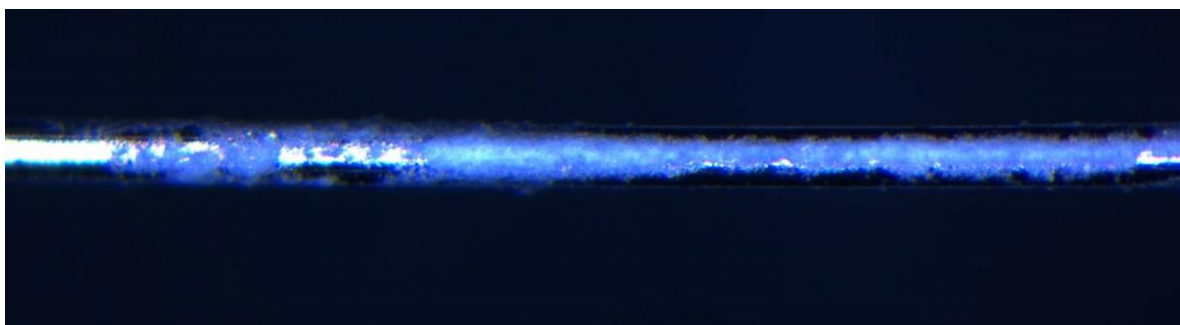


Figure 12. Optical microscopy image of EYAD coated platinum wire, 11.5 X.

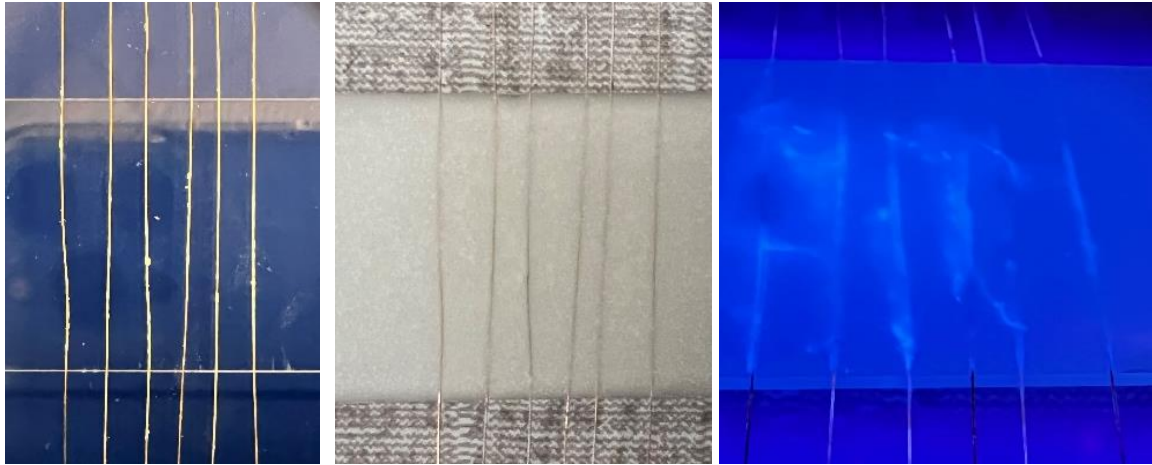


Figure 13. EYAD coated copper wires (left) embedded in Epotek 305 + 50 wt% sugar (center) and under UV illumination (right).

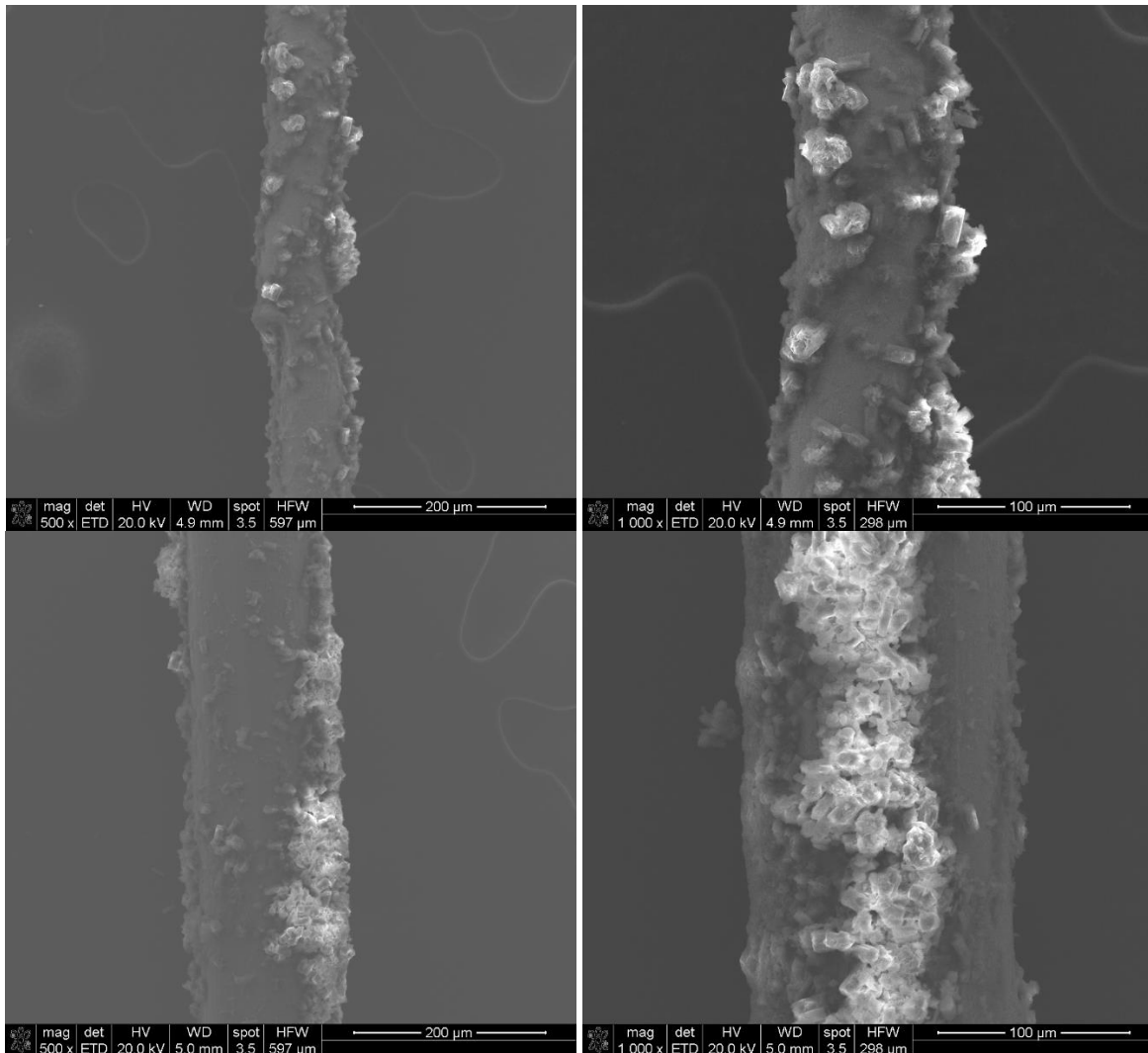


Figure 14. SEM images of EYAD coated platinum wire (top) and copper coated wire (bottom) each at 500X and 1000X.

4. BIDIRECTIONAL FOCUSING MICROSCOPE

Unidirectional Focusing

Initially we set up a unidirectional focusing microscope, which is shown in Figure 15. Note that this is similar to our previous wavefront-shaping controlled reflection system [1, 6], except with the detection using a photodiode and long-pass filter rather than a camera. In this system, the PL from the guidestar is collected by the objective and passed to the photodiode. Using a genetic algorithm, we modulate the incident wavefront such that the light focuses on the guidestar and optimizes the collected PL.

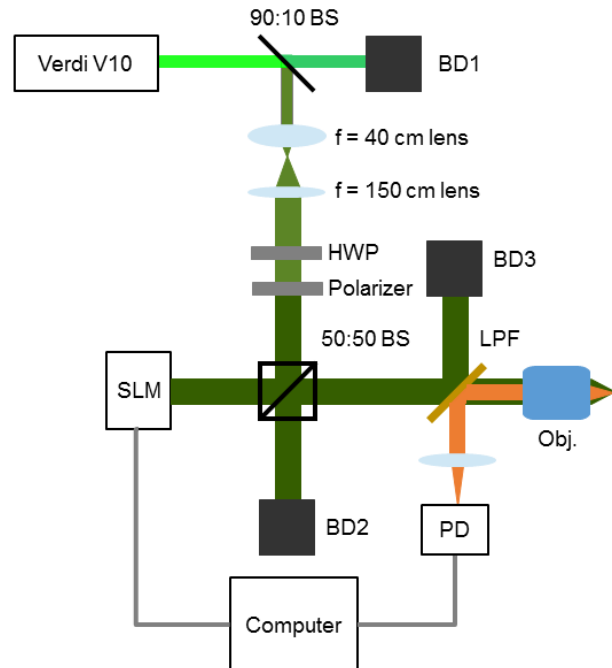


Figure 15. Schematic of optical system for performing subsurface focusing on a guidestar, utilizing wavefront shaping with a single SLM.

Figure 16 shows intensity profiles for feedback assisted focusing using both reflective (a,b) and fluorescence feedback (c,d). In reflection we focus into a single reflection mode making a small spot, whereas fluorescence focusing focuses on a 1-5 μm diameter bead, which results in a significantly larger spot size.

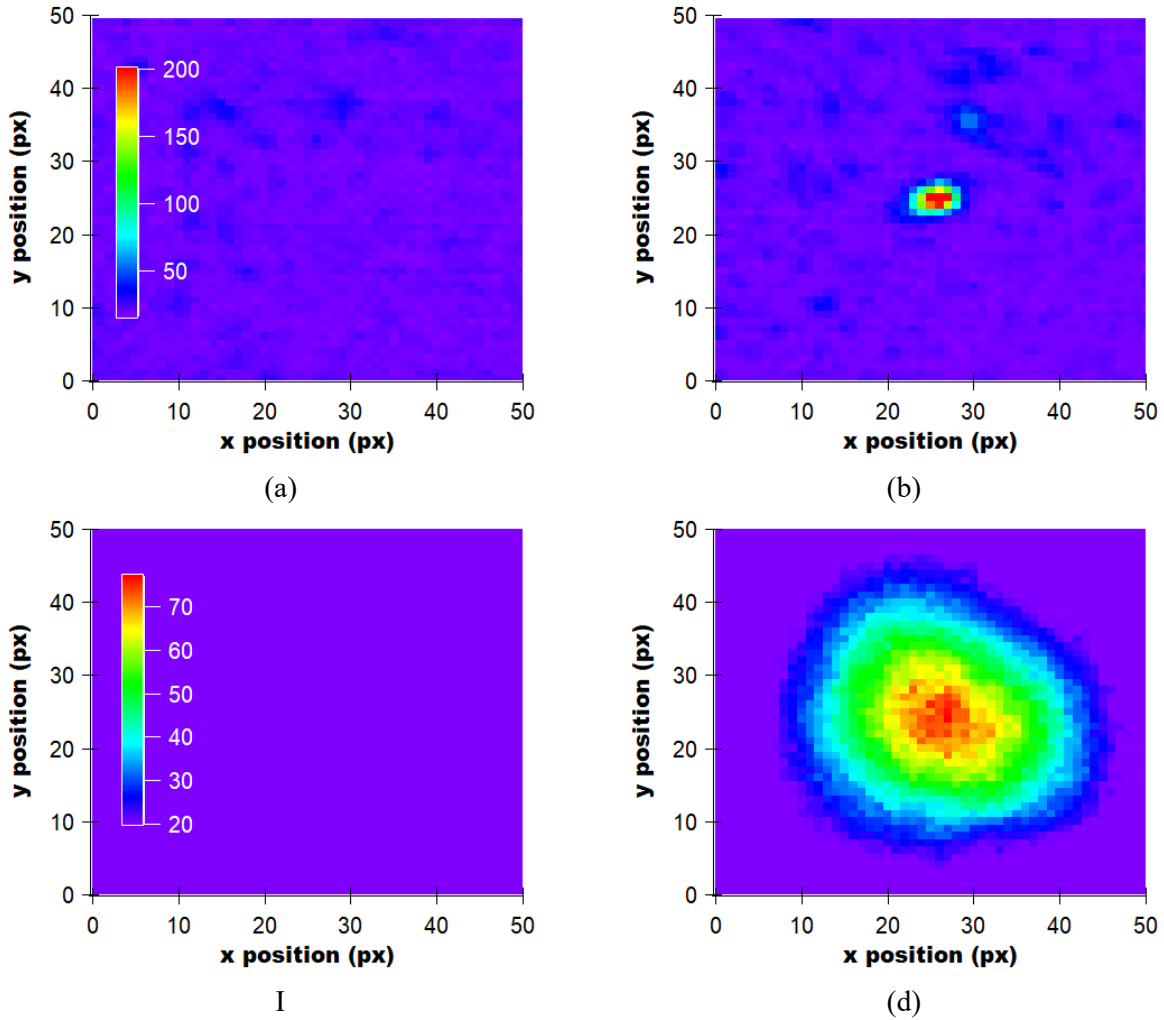


Figure 16. Background (a,c) and optimized (b,d) intensity patterns for reflective (a,b) and fluorescence (c,d) feedback.

Having considered the intensity patterns for the two feedback mechanisms we next compared their enhancement curves as a function of iteration (using a simple genetic algorithm), which are shown in Figure 17. From Figure 17 we find that using reflective feedback we are able to obtain a larger enhancement, but also find that it takes more iterations to reach the final enhancement. Both the lower enhancement and faster convergence in reflection are due to the multi-modal optimization involved with fluorescence feedback. Lower enhancements when performing multi-modal optimization is a well-known phenomenon [21].

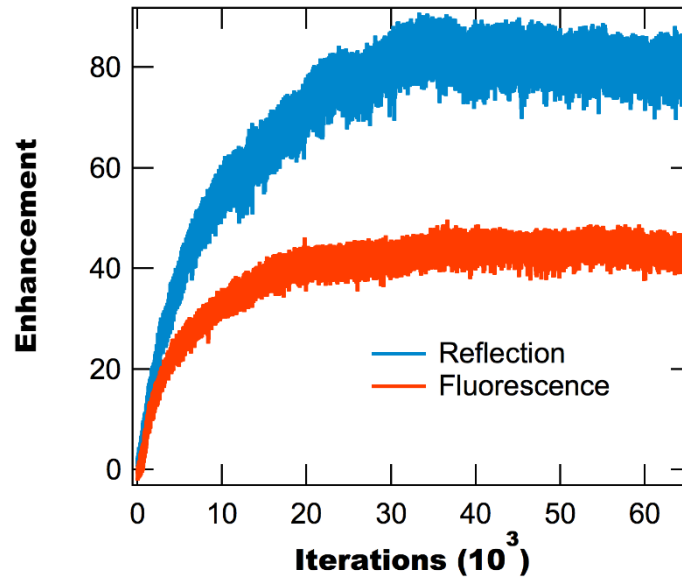


Figure 17. Enhancement as a function of iteration for fluorescence and reflective feedback. Optimization was performed using the SGA with 4096 bins.

After demonstrating single-SLM focusing onto a fluorescent bead embedded in a heterogeneous material, we next tested the performance of three different algorithms used for focusing: the iterative (IA), the simple genetic (SGA), and the microgenetic (μ GA). Figure 18 shows a comparison of enhancement curves for all three algorithms with the μ GA found to be the fastest and the SGA found to reach the largest enhancement. To quantify the speed of each algorithm we consider the number of iterations required to reach 90% of the enhancement curves final value and find the μ GA to take 2990 iterations, while the SGA takes 15907 iterations, and the IA takes 32109. These results translate into the SGA being 2 times faster than the IA, while the μ GA is 5.3 times faster than the SGA and 10.7 times faster than the IA. These results are consistent with our previous algorithm comparisons using reflective feedback [22].

Having considered the relative speed of the three algorithms we next turn to considering the influence of the SLM bin size on the enhancement and calculation time for the two genetic algorithms. Figure 19 shows both the enhancement (a) and iteration time (b) for both genetic algorithms as a function of the number of bin numbers for optimization runs lasting 20000 iterations. From Figure 19a we find that the highest enhancement is obtained using the SGA with bins of size 4 px, which corresponds to 16384 bins. We also find that both Gas have similar performance for bin sizes ≥ 16 px. On the other hand, from Figure 19b we find that while the calculation time for the μ GA doesn't change much with increasing number of bins, the SGA suffers significant speed loss for bins < 4 px.

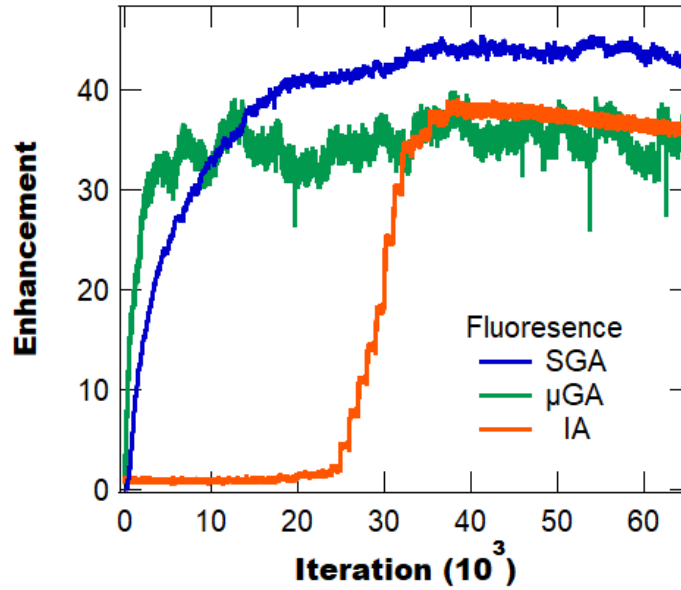


Figure 18. Fluorescence enhancement as a function of iteration for three different optimization algorithms and $N = 4096$ bins.

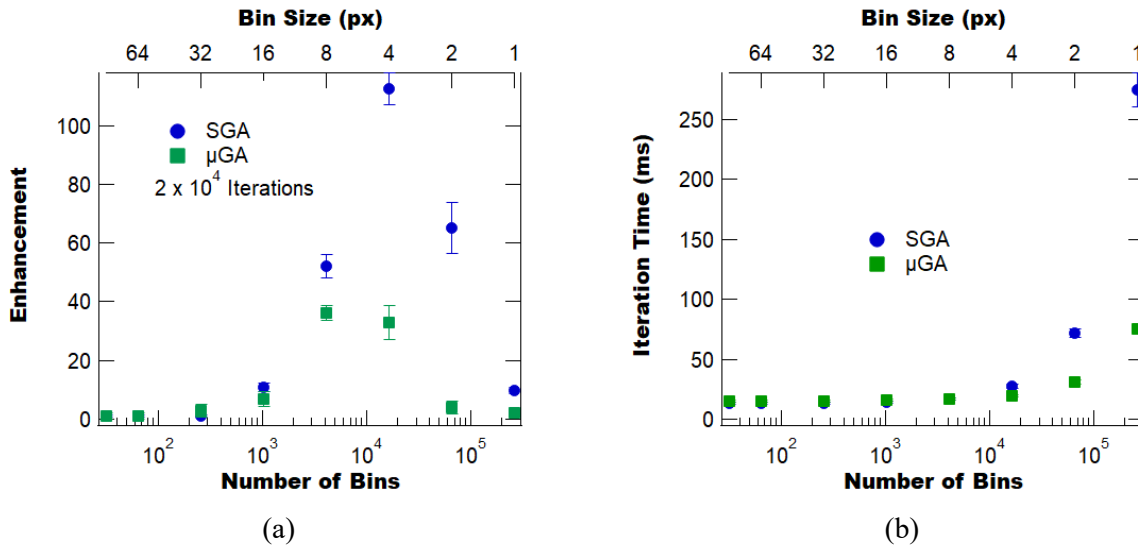


Figure 19. Enhancement (a) and Iteration time (b) as a function of the number of bins for both the SGA and μ GA.

The last algorithm comparison we perform is to consider the effect of noise on the enhancement for each algorithm. For this measurement we perform optimization using all three algorithms with 4096 bins and add noise to the algorithm using a random number generator. Figure 20a shows the average enhancement curves as a function of iteration for 6 different noise levels (quantified by the standard deviation divided by the mean intensity) using the SGA and Figure 20b shows the final enhancement as a function of noise level for the three algorithms. Based on Figure 20 we find that the SGA has the best resilience in the presence of noise, followed by the μ GA and then the IA.

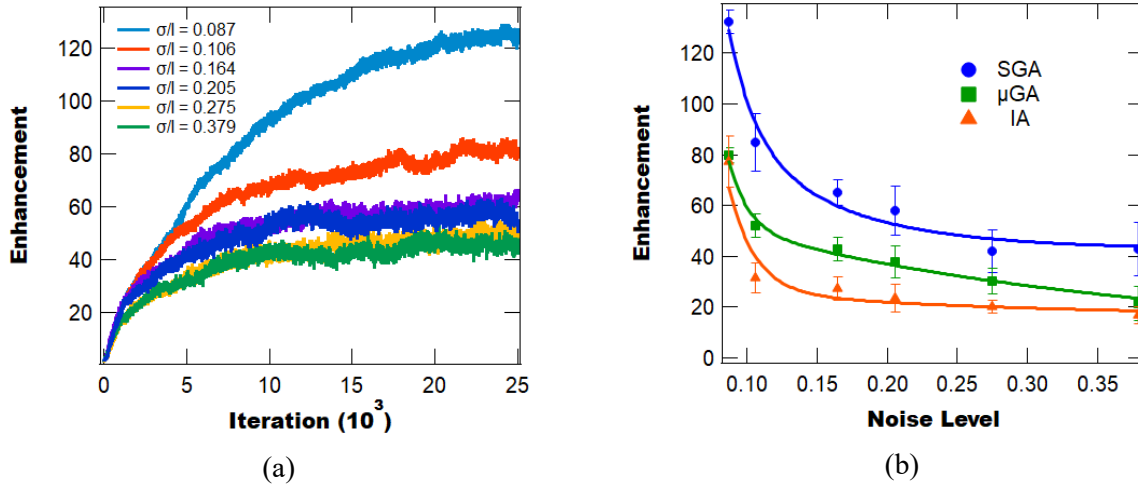


Figure 20. Enhancement as a function of iteration (a) and noise level (b).

Feedback Assisted Bidirectional (Two-SLM) Focusing

Note that portions of this section have been taken verbatim from a pending manuscript.

After demonstrating focusing inside of a heterogeneous sample using a single objective, we next performed focusing using a bidirectional focusing setup using feedback assisted optimization for both directions. Eventually one direction will be replaced by DOPC, but as an example of bidirectional focusing we first use feedback assisted optimization in both directions. For this focusing we use the setup shown schematically in Figure 21.

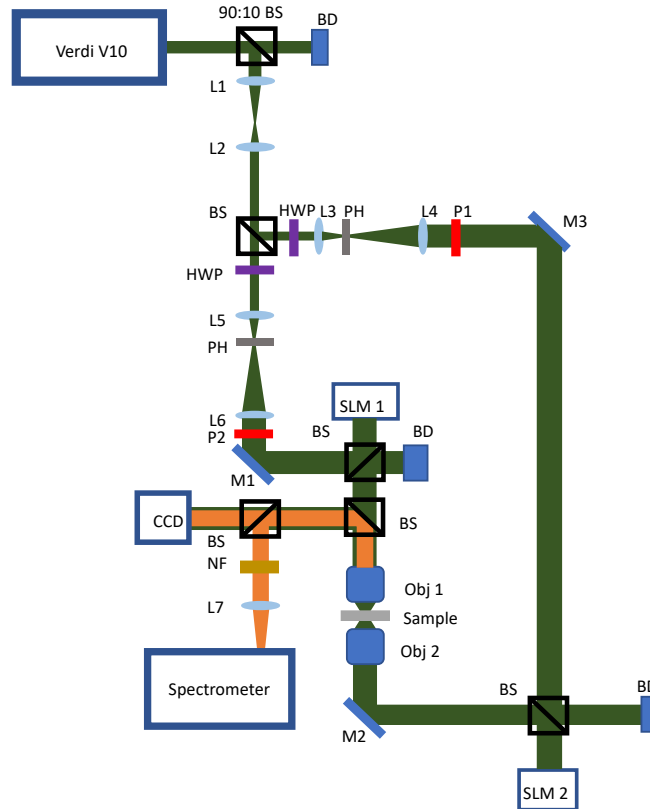


Figure 21. Feedback assisted bidirectional focusing setup schematic.

Before considering the effect of different experimental parameters on the BFM's functionality, we first present the result of an example optimization run using a sample with the fluorescent particle buried at $410 \pm 60 \mu\text{m}$. Figure 22 shows the measured fluorescence image of a buried particle for both SLMs flat, either one of the SLMs optimized and both SLMs optimized. From Figure 22 we find that the SLM in the reflective geometry achieves a greater enhancement than the SLM in the transmissive geometry and that the two SLMs combined provide a greater enhancement than either one by itself. This is to be expected as the use of two SLMs almost doubles the number of controlled propagation modes and therefore improves the possible enhancement [23].

To further characterize the enhancements shown in Figure 22 we take line profiles across the image in the x-direction with the y-direction averaged over a 54 px range, with the resulting line profiles shown in Figure 23 along with the sum of the transmissive and reflective line profiles (corrected for double counting the base intensity). From Figure 23 we find that the reflective-arm SLM obtains a greater enhancement than the transmissive-arm's SLM (3.83 ± 0.65 vs 2.03 ± 0.20) and that when both SLMs are optimized their combined enhancement is greater than summing the individual enhancements. This extra enhancement could be due to long range mesoscopic correlations, which have been previously shown to help improve enhancements [24]. However, confirming this hypothesis will require significant modeling work [25-27].

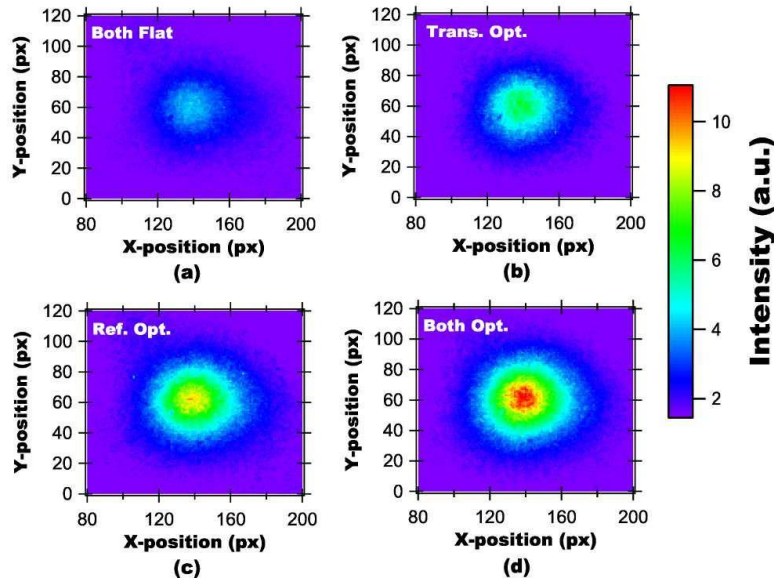


Figure 22. Example fluorescence images of target bead buried $410 \mu\text{m}$ inside of a heterogeneous sample for both SLMs flat, one or the other SLM optimized, and both SLMs optimized.

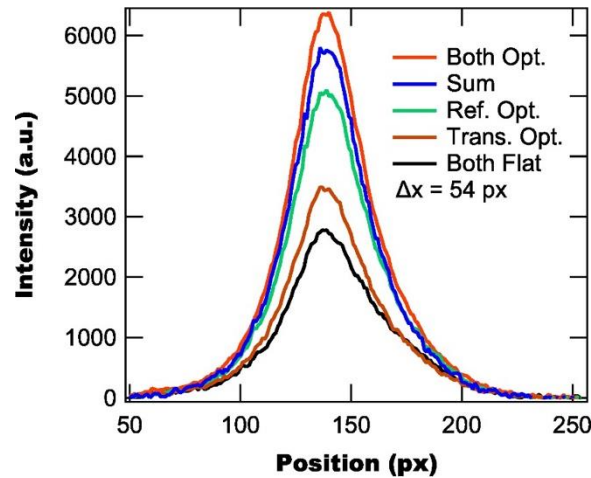


Figure 23. Line profiles across the fluorescence images shown in Figure 2 with the lines averaged in the y-direction using a width of 54 px. Additionally, we include the double-counting-corrected sum of the two SLMs line profiles.

To explain the difference between the transmissive and reflective arm optimization we note that there are two key asymmetries between the two arms of the microscope. First, as the objectives are positioned to be confocal with the sample in focus for the reflective arm, the transmissive arms beam enters the sample almost 820 μm away from its focal point. This leads to significantly different spot sizes between the two arms which impacts the optimization and will be discussed further below. Secondly, our sample is prepared on a glass slide such that one arm of the microscope is incident directly on the polymer while the other arm has to pass through a glass slide first, which introduces wavefront distortions (e.g., spherical aberrations) that reduce the effectiveness of wavefront shaping as well as modifies the pump spot size (see discussion below). To characterize the effect of having the glass slide in the beam path we performed measurements using a sample containing guidestars in the middle layer and we placed the glass slide first in the reflective arm (i.e., the opposite of our initial geometry). Doing so resulted in the reflective arm's enhancement decreasing by $0.54 \pm 0.15 \times$, while the transmissive arms intensity increased by 1.49 ± 0.47 (i.e., the glass reduced the enhancement by $0.67 \pm 0.21 \times$ in the transmissive case). This reduction, caused by the glass slide, can be attributed to both wavefront aberrations and modifications to the beams' spot size due to the beam passing through the glass slide.

Effect of Initial Intensity

Note that portions of this section have been taken verbatim from a pending manuscript.

As the simple genetic algorithm used for optimization requires a nonzero initial intensity to function, we next characterize the minimum intensity (and signal-to-noise ratio) required to perform optimization. To accomplish this we performed single-SLM optimization on a sample containing fluorescent particles in the middle layer using different camera exposures, which allows us to control the initial intensity used by the algorithm. Figure 4 shows the resulting enhancement as a function of camera exposure, with the corresponding SNR shown on the top axis.

From Figure 4 we find that the enhancement behaves approximately as an exponential function with the enhancement becoming essentially constant for exposure times greater than 0.4 ms, which corresponds to an SNR of 6 and an intensity 4.2% larger than the background. This represents the minimum intensity/SNR needed for the algorithm to ideally function. If instead we want to know the minimum value at which the algorithm will produce any enhancement we can extrapolate the fit curve in Figure 4 to shorter exposure times and determine the exposure at which the enhancement = 1 (corresponding to no improvement) and we find the intersection to occur at 0.028 ms, which corresponds to a SNR of 1.78 and an intensity 0.8% larger than the background.

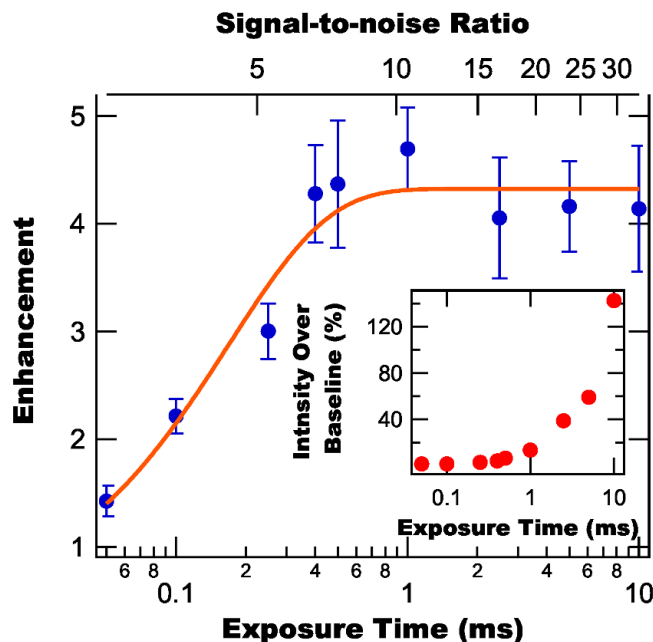


Figure 24. Enhancement as a function of detector gatewidth. The corresponding signal-to-noise ratio is displayed on the top axis.

Effect of Target Depth

Note that portions of this section have been taken verbatim from a pending manuscript.

As the hoped for application of the BFM is monitoring subsurface chemical reactions in heterogeneous materials, it is necessary to consider the impact of target depth on the obtainable enhancement. To this end we performed enhancement measurements on three different samples with guidestar particles at depths of 60 μm , 410 μm , and 760 μm . Figure 25 shows example fluorescence images from each sample for both the flat field and optimized field. Note that while individual particles can be differentiated for the 60 μm and 410 μm depth samples, the 760 μm sample images consisted of broad emission that could well be the superposition of emission from multiple particles.

Interestingly, we find that in order to initially “focus” on the target particle (i.e., minimize the spot size and maximize the intensity) we need to move the sample closer to the imaging objective as the particle depth increases. If we define a focal plane at the surface of the sample to be $z = 0$, we find that the optimal “focal” is $5 \pm 4 \mu\text{m}$ below the surface for the 60 μm sample, $50 \pm 15 \mu\text{m}$ for the 410 μm sample, and $175 \pm 25 \mu\text{m}$ for the 760 μm sample.

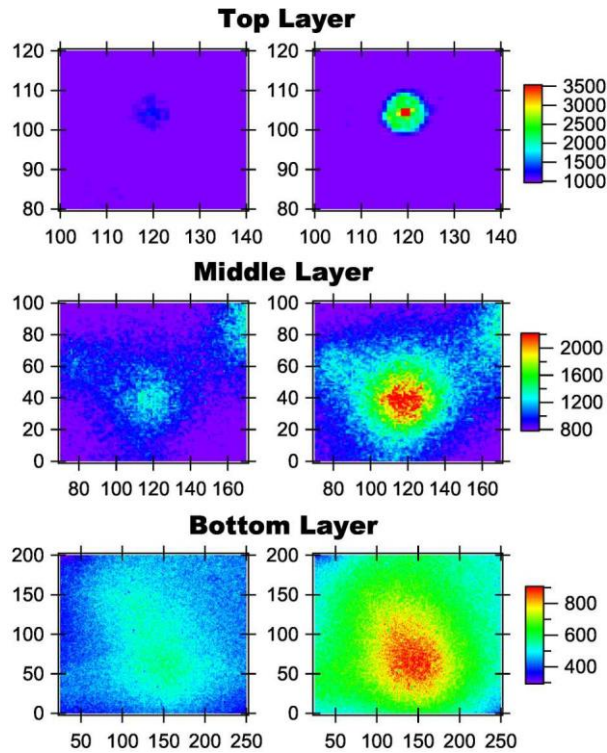


Figure 25. Example fluorescence images of the different depth samples for both flat field and optimized field. As the particle's depth increases the emission intensity decreases and the spot size increases.

We next computed the average flat-field peak intensity, flat-field Gaussian width, and enhancement for each depth with the resulting averages shown in Figure 26, with the top axis giving the depth scaled by the mean free path l . From Figure 26 we find that as the particle depth increases the average peak intensity decreases and the average width increases. These two results are an expected effect due to photon diffusion [28, 29].

However, of more importance, from Figure 26 is the observation that the enhancement decreases with depth. If we assume the enhancement behaves as an exponential function with target depth and we extrapolate the curve to deeper depths, we find that the enhancement will equal unity at a depth of $1170 \mu\text{m}$ (or 18 mean free paths), which corresponds to the BFM not providing any improvement to the particles signal. Note that this estimate is approximate and requires many different assumptions. However, it does allow us to have a rough estimate of the BFM's functional depth.

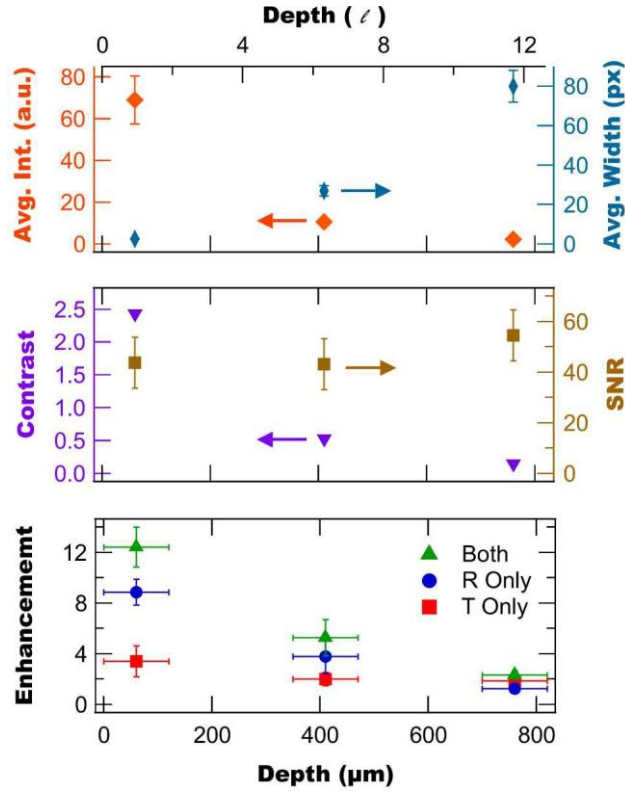


Figure 26. Average target width, intensity, and enhancement as a function of particle depth.

Returning to the issue of the enhancement depending on particle depth: we initially hypothesized that the decreasing target intensity with depth could lead to the SNR impacting the optimization algorithm. However, when we calculated the average SNR for each depth (shown in Figure 26) we found that the SNR is roughly the same at each depth and significantly larger than the minimum SNR determined above. Therefore, it is unlikely that noise factors into this phenomenon.

This decrease in enhancement with particle depth also corresponds with an observation that the SLMs seem to have less impact on the fluorescence image as the particle depth increases (i.e., the fluorescence intensity doesn't change as much when displaying random phase masks on the SLMs as the target depth increases). To quantify this reduction, we define a quantity called the wavefront shaping contrast, which is given by:

$$c = \frac{\sigma}{\langle I \rangle} \quad (1)$$

where $\langle I \rangle$ is the ensemble averaged fluorescence intensity and σ is the standard deviation of the intensity distribution. Both quantities are found by displaying random phase masks on the SLMs and taking fluorescence images to determine the intensity for each image. For our measurements we use 450 random phase masks to produce a set of intensities from which we can determine the wavefront contrast for each target depth, which are shown in Figure 26. From Figure 26 we find that as the target depth increases the contrast decreases, which physically means that changing the phase masks on the SLMs has less of an impact on the fluorescence image. We hypothesize that this reduction in SLM efficacy is the main mechanism behind the reduction in the enhancement.

However, while we can attribute the reduced enhancement to a decrease in wavefront shaping contrast, it begs the question of why the wavefront shaping contrast depends on the target depth at all. Currently this question remains unanswered, but there are several likely mechanisms that factor into this phenomenon:

1. For samples with guidestars in the top layer, the particles are within approximately one mean free path, such that scattering will not play a huge effect yet. This means that the SLM will be controlling both ballistic light and scattered light to obtain focus, which can lead to greater enhancements over the deeper particles which primarily rely on scattered light.
2. For samples with guidestars in the bottom layer, we observe broad emission that may arise from multiple different particles that are nearby. Thus when performing optimization the algorithm will work to optimize focusing on multiple targets, which is well known to reduce the enhancement.
3. For each depth the optimal distance between the imaging objective and the sample changes, with the distance decreasing with increasing depth. This change in distance between the imaging objective and the sample results in different spot sizes on the surface of the sample, which has been previously shown to influence the enhancement when using transmission or reflection as feedback mechanisms [1, 3].

As spot size is likely a key factor in both our depth-dependent observations and our observations for the effect of the glass slide on optimization, we therefore now determine the estimate spot sizes involved for both objectives. To estimate how the spot sizes change with sample positioning we utilize Ray matrix analysis to estimate the spot sizes for both objectives as a function of position. Note that this analysis is approximate as the ray matrix method relies upon the paraxial approximation (e.g., that all rays have shallow angles), while our objectives have NA's of 0.75 which corresponds to exterior rays having significant angles of incidence. To obtain a more exact analysis requires nonparaxial solutions to Maxwell's Equations, which require the use of numerical simulations [30, 31]. However, such analysis is more rigorous than needed for our purposes.

We begin our analysis by considering a Gaussian beam propagating in the reflective arm of the BFM. For this arm we model the objective as a simple lens with a focal length f , equal to the working distance (5.2 mm) and an incident beam diameter $2w_0$, equal to the objectives clear aperture (6 mm). For this system the ray matrix is given by

$$M = \begin{pmatrix} 1 & x \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ -\frac{1}{f} & 1 \end{pmatrix},$$

$$= \begin{pmatrix} 1 - \frac{x}{f} & x \\ -\frac{1}{f} & 1 \end{pmatrix},$$

from which we determine the Gaussian width at a distance x from the objective to be:

$$w = \frac{\sqrt{f^2 \lambda^2 x^2 + \pi^2 w_0^4 (f - x)^2}}{\pi f w_0}. \quad (2)$$

For the case of the transmissive arm objective the situation is more complicated due to the inclusion of the glass slide, which has a nominal thickness $t = 1$ mm, a refractive index of $n_g \approx 1.5$ and an interface with air ($n_a = 1$) and the polymer ($n_p \approx 1.3$). Assuming the incident surface of the slide is a distance d_i away from the objective we write the ray matrix of this system as:

$$M = \begin{pmatrix} 1 & 0 \\ 0 & \frac{n_g}{n_p} \end{pmatrix} \begin{pmatrix} 1 & t \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & \frac{n_a}{n_g} \end{pmatrix} \begin{pmatrix} 1 & d_1 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ -\frac{1}{f} & 1 \end{pmatrix},$$

$$= \begin{pmatrix} 1 - \frac{d_1 + \frac{n_a t}{n_g}}{f} & d_1 + \frac{n_a t}{n_g} \\ -\frac{n_a}{n_p f} & \frac{n_a}{n_p} \end{pmatrix},$$

from which we determine the spot size on the surface of the polymer to be

$$w = \sqrt{\frac{n_p}{f^2 n_a n_g^2 \pi^2 w_0^2}} \times \sqrt{f^2 \lambda^2 (d_1 n_g + n_a t)^2 + \pi^2 w_0^4 (d_1 n_g - f n_g + n_a t)^2}. \quad (3)$$

At this point we know all of the quantities in Equations 2 and 3 except for the distance from the reflective objective to the sample surface and the distance from the transmissive objective to the glass slide. To find these quantities we once again approximate the objectives as a simple lens and are therefore able to determine the distance from the reflective objective to the surface of the sample using the simple lens Equation

$$\frac{1}{f} = \frac{1}{x} + \frac{1}{d_i}, \quad (4)$$

where d_i is the image distance (i.e., the distance from the objective to the camera), which is approximately 260 mm for our system. Solving for x we find that the sample surface is imaged when it is positioned at ≈ 5.306 mm. This distance is past the working distance of the objective (5.2 mm) since we are not using a conjugate lens nor imaging at infinity. Having determined the distance between the sample surface and the reflective objective we now determine the spacing between the transmissive objective and the glass slide as $2f - x - t_s - t = 3.28$ mm, where $2f$ is the inter-objective spacing, x is the sample position relative the reflective objective, t_s is the sample thickness (810 μm) and t is the glass slide thickness. As a check on these estimates, we performed micrometer measurements between the objectives and the sample surface and find a spacing of 5.35 ± 0.10 mm for the reflective objective and 3.30 ± 0.10 mm for the transmissive objective, which are both in agreement with our estimates. Using these distances, Equations 2 and 3, and the measured focal depths for the guidestars in different layers we can calculate the spot sizes at the surface of the sample (when the guidestars are in focus).

We also find that for the top and middle layer the surface of the sample is past the focal point of the lens such that the incident laser first focuses outside of the sample before starting to expand and enter the sample. In the case of the bottom layer sample, the focal point of the lens lies inside of the heterogeneous sample such that the incident light hits the sample before it reaches its absolute focus.

Table 2. Measured focal depth and calculated spot size for reflective arm and transmissive arm.

Target Layer	Focal Depth (μm)	Ref. Spot Size (μm)	Trans Spot Size (μm)
Top	5 ± 4	116.5 ± 4.6	1668.6 ± 5.2
Middle	50 ± 15	65 ± 17	1728 ± 20
Bottom	175 ± 25	80 ± 29	1892 ± 32

Using the estimated objective distances, Equations 2 and 3, and the measured focal depths for the guidestars in different layers we calculated the spot sizes at the surface of the sample (when the guidestars in focus) for both objectives with the spot sizes listed in Table 2. From Table 2 we find that the spot size for the transmissive objective is significantly larger than for the reflective objective, which is expected as the sample surface facing the reflective objective is near the confocal point, which means that the surface facing the transmissive objective is significantly closer to the objective leading to a larger spot size. As the sample is translated closer to the reflective objective the distance on the transmissive side increases, leading to a decrease in the spot size. On the other hand, we find that the reflective objectives spot sizes first decreases and then increases as the particle depth increases. This behavior arises due to the objective's focal point being outside of the sample for the top and middle layer samples, while for the bottom layer sample the focal point lies inside of the sample.

Having discussed the behavior of the spot sizes between samples, we now compare Figure 26 and Table 2 and make the following observations:

1. For the transmissive-arm, the spot size reduction between samples is roughly 10% and we find that the enhancement only varies slightly between all three samples.
2. For the reflective-arm, the spot size is almost cut in half when going from the top layer sample to the middlelayer sample, which corresponds to a significant decrease in enhancement.
3. While the reflective-arm spot size is approximately equal between the middle and bottom layer sample there is a significant difference in enhancement between the two samples.

The first two observations are consistent with previous observations where transmission and reflection were used as feedback mechanisms. In those studies the enhancement changed slowly for large spot sizes, while near the focal point (where spot sizes are smaller) the enhancement changed rapidly [1, 3]. Additionally, the previous study on optimized transmission found that the enhancement peaks at a position offset from the focal point, such that the enhancement started off small near the focal point and increased as the incident objective was defocused. Lastly, the third observation of the enhancement being asymmetric about the focal point is consistent with the previous reflection-based study which found the enhancement was asymmetric about the focal point with the enhancement being larger when the incident beam was allowed to focus before entering the sample [1, 3].

Effect of Sample Position

Note that portions of this section have been taken verbatim from a pending manuscript.

Given our observations above about the enhancement depending significantly on the spot size and the spot sizes' dependence on the sample/objective positioning, we now turn to considering the effect of changing the sample position (while keeping the objectives confocal) and changing the transmissive objectives position (while keeping the sample stationary and “in focus”). For these measurements we use a sample with the particles in the middle layer and measure two different target particles, with five repetitions per target per z position.

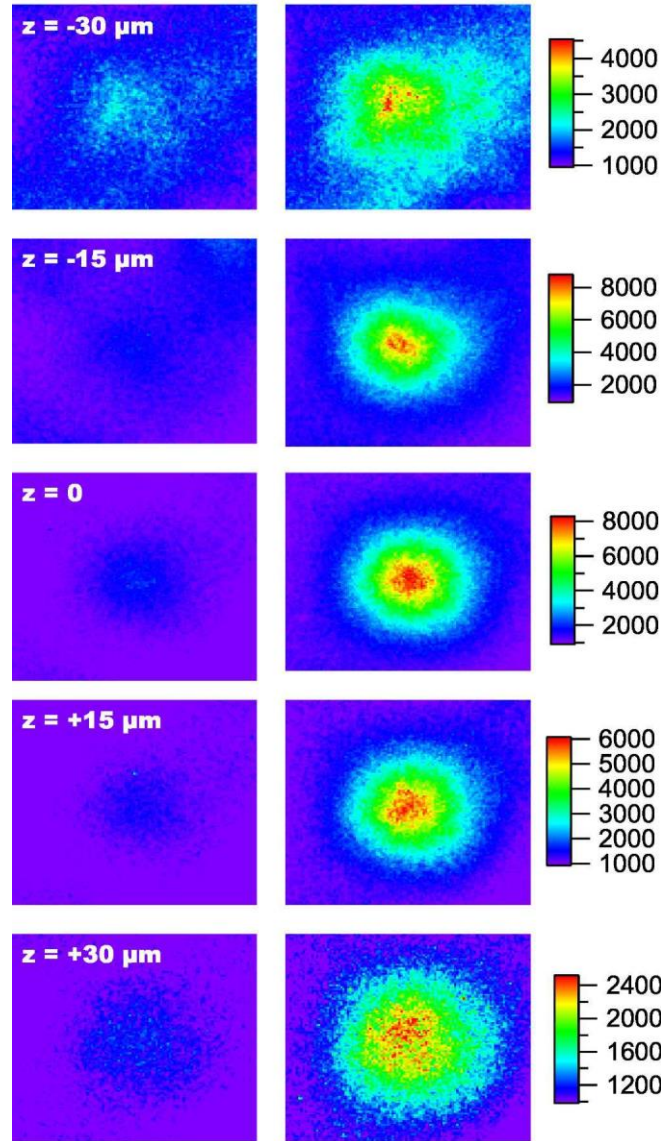


Figure 27. Example fluorescence images of guidestar particle under flat field and optimized field illumination for the sample at different positions along the optical axis with $z = 0$ being the optimal position.

Figure 27 shows example fluorescence images for both the flat-field and optimized-field cases at six different sample positions, with the sample “in-focus” for $z = 0$. Additionally, we also calculate line profiles across each fluorescence spot, which are displayed in Figure 28. From both **Error! Reference source not found.** and Figure 28 we find that as the sample is moved in either direction (away from $z = 0$) the spot size increases and the overall intensity of both the flat-field and optimized-field images decrease. From these figures we also observe that there is an asymmetry between the two directions. For the positive z direction (i.e., towards the imaging objective) we find that the intensity decreases more quickly than in the negative direction, but that the spot shape remains roughly Gaussian, whereas in the negative direction the intensity decays more slowly but the spot shape deforms.

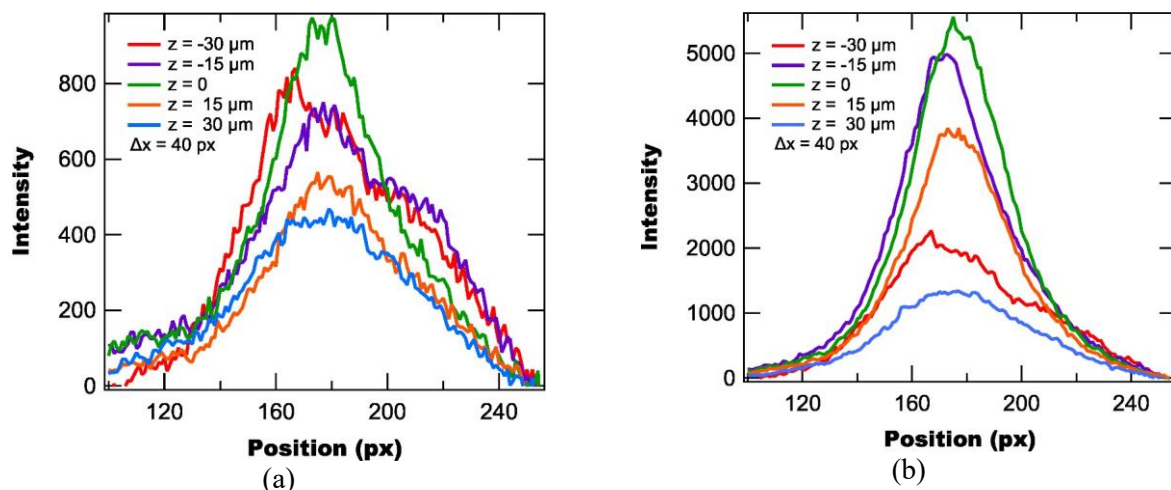


Figure 28. Example line profiles from images in Figure 7 for flat field (a) and optimized (b) illumination.

To compare this behavior to the BFM's imaging response without scattering we prepared a sample consisting of the same fluorescent microspheres dispersed in a clear polymer on a glass slide. We then performed fluorescence imaging of these microspheres using the BFM at different Z positions and performed line profiles across the images (see Figure 28 for example line profiles). From these profiles we computed the peak intensity and FWHM as a function of sample position, with the curves for the no scattering sample shown in Figure 30a and the curves for the heterogeneous sample shown in Figure 30b.

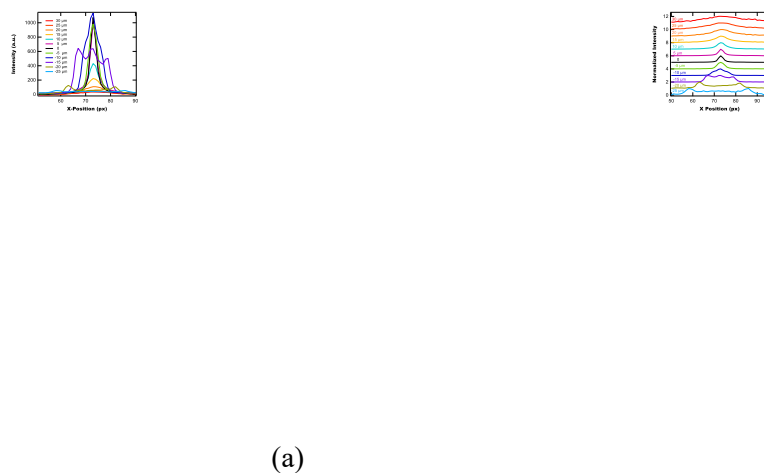
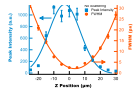
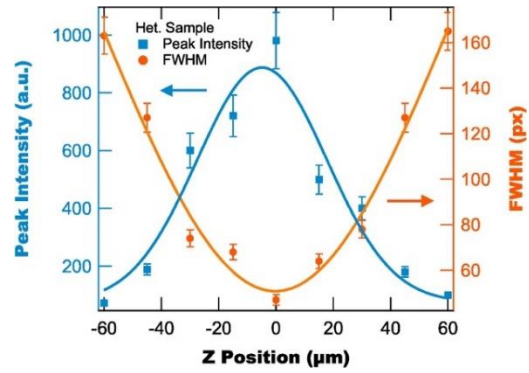


Figure 29. Raw (a) and Normalized (b) line profiles measured from fluorescence images of guidestar particle with noscattering.



(a)



(b)

Figure 30. Peak intensity and FWHM measured from image line profiles for microsphere with no scattering (a) and inside of heterogeneous sample (b).

From Figure 30 we find that in both cases the intensity follows a peaked function that is skewed towards negative z , while the FWHM is roughly parabolic. While the functional form of the imaging responses is consistent between the scattering and no scattering case, we note that for the heterogeneous sample the positional response is slower than for the no scattering case (i.e., the intensity peak FWHM is $57 \mu\text{m}$ for the heterogeneous sample and $24 \mu\text{m}$ for the no scattering case).

Having considered the effect of sample position on the guidestar's fluorescent spot, we now turn to considering how positioning effects the enhancement. Averaging over all the enhancement runs for each position, we compute the average enhancements for each SLM at each sample position with the results shown in Figure 31. From Figure 31 we find that the enhancement as a function of z position follows a peaked curve centered at $z = 0$ (i.e., the particle initially “in focus”) with the reflective arm displaying significant positional dependence while the transmissive arm's enhancement is relatively unchanged over the total $120 \mu\text{m}$ translated. This lack of significant variation in the transmissive-arm's enhancement can be attributed to its largespot size when it is placed in the confocal geometry. On the other hand, in the case of the reflective arm we find there is a negative skew in the enhancement ($-30 \mu\text{m}$ has an enhancement of 4, while $+30 \mu\text{m}$ position has an enhancement of 2.2) similar to the behavior of the peak intensity and that the enhancement's spatial profile is narrower than peak intensity's spatial profile (FWHM of $31 \mu\text{m}$ for the enhancement and $57 \mu\text{m}$ for the intensity).

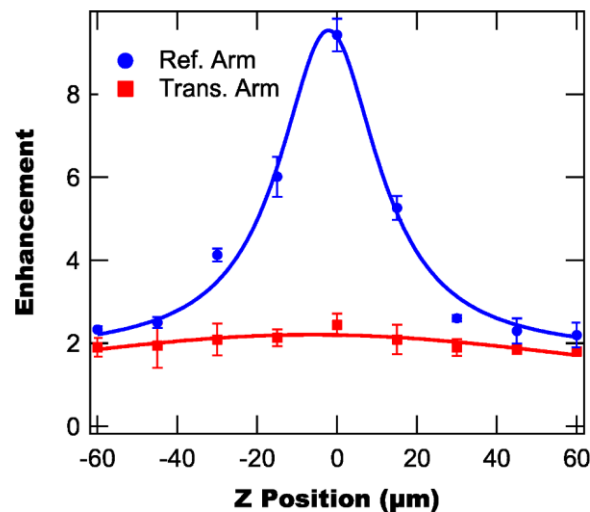


Figure 31. Measured enhancement as a function of sample position along the optical axis (z) along with peak fits (Lorentzian fit for the reflective arm and Gaussian fit for the transmission arm) as a guide for the eye. The transmissive enhancement is found to be roughly the same at all z positions, while the reflective enhancement

The narrowness of the reflective-arm's enhancement, compared to the transmissive-arm's enhancement (and previous measurements on enhancement peaks for transmission [3] and reflection [1] feedback) suggests that the changing enhancement is not only caused by changes in the reflective-arm's spot size, but also the fact that we are using the reflective-arm's objective as the imaging objective. To better understand how the choice of imaging arm affects the enhancement's behavior we are planning on performing future experiments in which the imaging optics and ICCD are placed in the transmissive arm.

Having considered the effect of moving the sample while keeping the objectives stationary we next consider the effect of the transmissive objective's position on the enhancement for the case where the distance between the sample and reflective objective is optimized and held constant. Figure 32 shows the enhancement and initial intensity as a function of the transmissive objective's position with negative z corresponding to the objective being moved away from the sample.

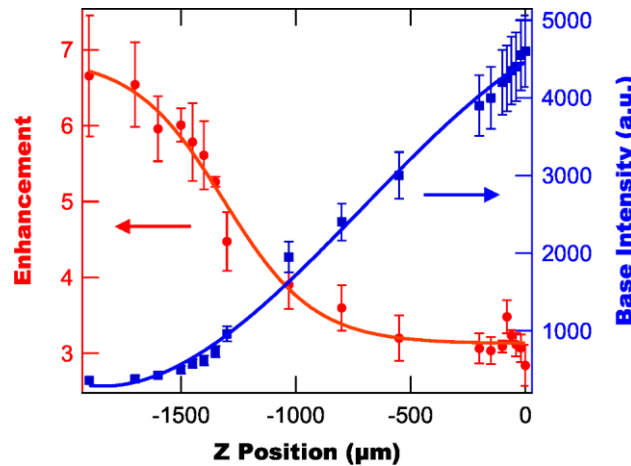


Figure 32. Base intensity and enhancement as a function of transmissive objective's z position.

From Figure 32 we find that as the objective is moved away from the sample the intensity decreases linearly, while the enhancement remains relatively unchanged for almost 1 mm, which is consistent with our observation of the transmissive enhancement being basically flat in Figure 31. However, after moving 1 mm away from the sample the enhancement increases rapidly until about μm at which point the increase begins to slow down. Note that this distance is the estimated distance required for the objective to focus on the surface of the sample. This suggests that when the objective's focal point is on the outside of the sample the enhancement is greater than when the focal point lies inside of the sample. This is consistent with our observations with the reflective objective in the depth dependent samples above as well as consistent with previous work on transmissive and reflective optimization [1, 3]. Based on all of these observations it appears that optimization is more effective when the beam is allowed to focus outside of the sample, rather than entering the sample prior to focus. While the exact reasoning for this is currently unclear, it may have been related to interference effects between the different spatial modes when the beam focuses.

As a final note on Figure 32, we point out that while the enhancement is greater for distances farther from the sample, the initial intensity is also significantly lower. Therefore, while we may get more enhancement at larger distances, the overall optimized intensity may be less, which would make the farther distances less optimal for our application of improving the PL and Raman signal from subsurface particles. Therefore, care must be taken to balance the increases in enhancement with the decrease in initial intensity to obtain the best intensity on target.

5. SUBSURFACE SPECTROSCOPY DEMONSTRATIONS

Photo/thermal-degradation of EYAD in Air

Note that portions of this section have been taken verbatim from a pending manuscript.

Photodegradation

To demonstrate the ARO microscopes capability to measure subsurface chemical reactions we first consider a photodegradation reaction using EYAD. In the section below we will consider measurements on subsurface particles, but at this point we will consider photodegradation measurements of EYAD in pellet form. These measurements will allow us to compare what we observe in both cases to see if being inside of a heterogeneous material changes the reactions. Using a pellet also allows us to consider other characterization techniques, such as FTIR.

To begin we consider the fluorescence spectra at different times during photodegradation, as shown in Figure 33. From Figure 33 we find that the overall intensity decreases during photodegradation, except for in the 615 nm to 630 nm region, which displays an increase in intensity. Most likely this increase is due to spectral broadening, which causes the edges of the peaks to increase.

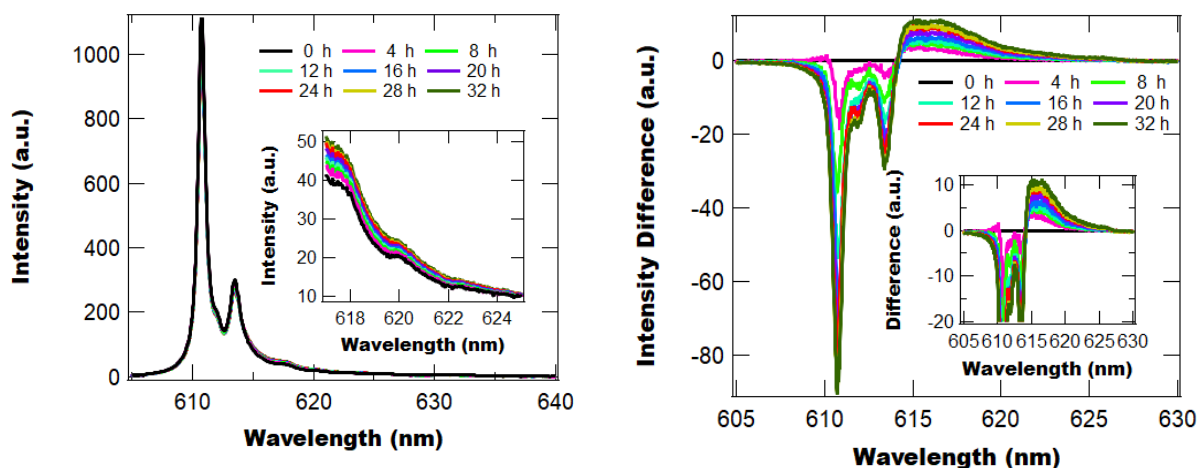


Figure 33. Fluorescence spectra (a) and difference spectra (b) from an EYAD pellet during photodegradation. Insets show zoomed in views of the spectra.

Having considered the main fluorescence peaks of EYAD we next turn to considering EYADs Raman spectra. Figure 34 shows the Raman/fluorescence spectra measured from the EYAD pellet using 532 nm excitation. The green vertical lines mark the location of the Raman peaks, with the remaining peaks being minor fluorescence peaks. To better visualize the effect of photodegradation on the Raman spectra we calculate the difference spectra, which are shown in Figure 35. From Figure 35 we find that photodegradation results in decreasing peak intensity, which is consistent with the breakage of bonds.

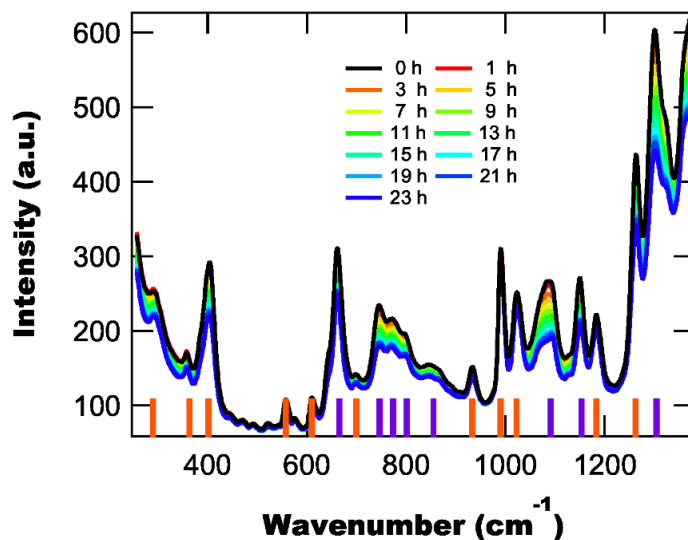


Figure 34. Raman/fluorescence spectra at different times during photodegradation. Orange markers mark Raman peaks and purple markers note PL peaks.

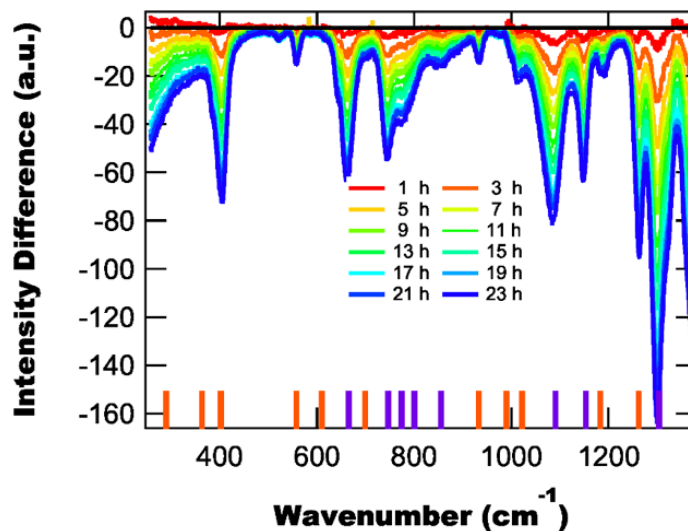


Figure 35. Difference spectra at different times during photodegradation.

To further characterize the effect of photodegradation on EYAD we also measure its FTIR spectra both before and after degradation, which are shown in Figure 36. From Figure 36 we find that the peak structure changes due to photodegradation. While it is hard to discern all the changes due to the complicated peak structure, the one clear difference is the formation of a new peak at 1750 cm^{-1} .

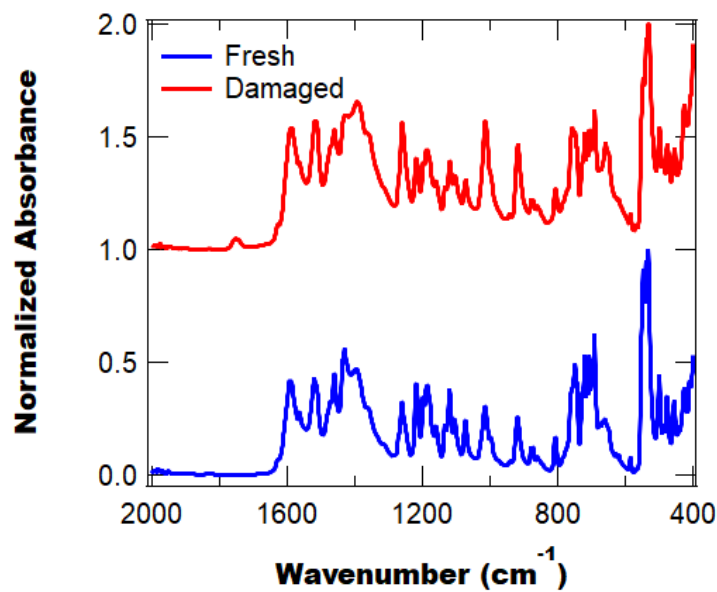


Figure 36. Normalized IR absorbance of EYAD both as prepared and after photodegradation. Note the formation of a new peak at 1750 cm^{-1} due to photodegradation.

Thermal Degradation

Having determined the effect of photodegradation in air on EYAD's spectroscopic properties, we next turn to the effect of "rapid" heating. For this purpose, we deposited EYAD on thin platinum wires which were heated by passing a DC current through the wire. For these measurements we used a modest heating rate of 22 K/s , during which we measured the PL and Raman emission from the EYAD on the wire. Additionally, we also measured the voltage across and current through the wire to determine resistance at each spectral measurement, from which we determine the temperature of the platinum wire.

Figure 37a shows the PL spectra measured at different temperatures, with the inset showing the peak intensity as a function of temperature. From Figure 37a we find that the PL intensity gradually decreases as the temperature increases until a temperature of 400 K is reached, at which point the intensity drastically decreases. This temperature corresponds to the measured melting point of EYAD (see Figure 3). The effect of the phosphor melting on the PL emission can be understood through three mechanisms: 1) melting modifies the crystal sites resulting in a modification of the crystal field, 2) some Eu ions will be ejected from well-defined sites into interstitial sites, and 3) melting increases the number of nonradiative decay channels. All three of these effects will result in decreased emission intensity.

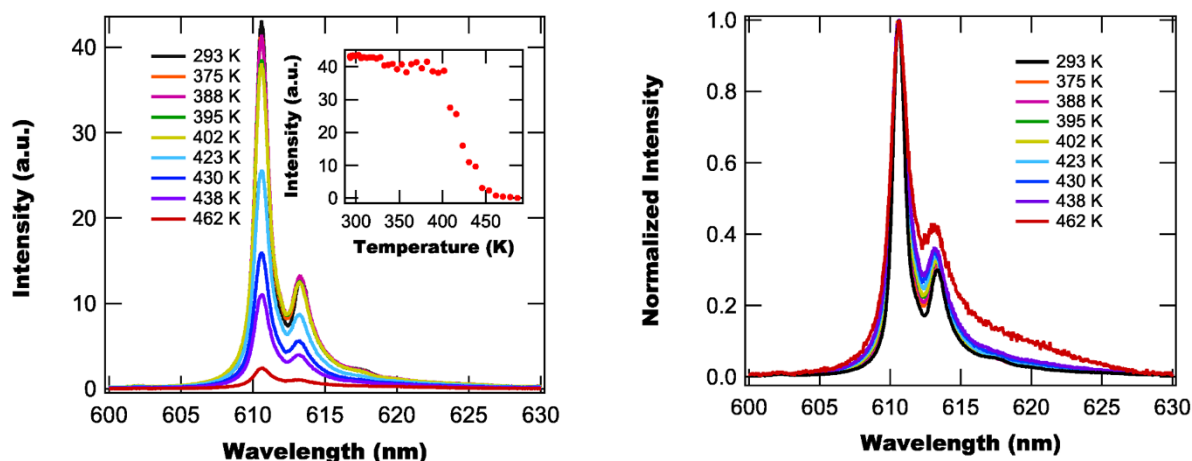


Figure 37. Raw (a) and Normalized (b) PL Spectra of EYAD measured at different temperatures.

Additionally, to better understand how melting affects the PL spectra with increasing temperature we plot the normalized spectra in Figure 37b. From Figure 37b we find that as the temperature increases the peaks broaden resulting in the “wings” of the peaks increasing. This observation is consistent with the dual mechanisms of Eu ions being ejected from crystalline sites and modifications to the crystal field.

Interestingly, when considering the PL spectra during photodegradation and thermal degradation we observe that they behave differently as the reactions continue. In the case of photodegradation we observe an isosbestic point, with part of the spectrum decreasing while another part increases. However, in the case of thermal degradation the entire spectral intensity decreases so quickly that no isosbestic point is formed. This suggests that the underlying mechanisms of the two degradations are different, which is unexpected. Initially, we assumed that 532 nm radiation would have insufficient energy to cause direct photodamage through mechanisms such as photooxidation, bond cleavage, and radical formation [32-37]. We therefore hypothesized that photodegradation involved the Eu ions absorbing light and then nonradiatively relaxing leading to localized heating of the EYAD, which would then undergo thermal degradation. However, our experimental results show that there are different mechanisms underlying the two degradation types.

Having considered the effect of heating on EYAD’s PL spectrum, we next turn to its effect on EYAD’s Raman spectra, which are shown in various forms in Figure 38. Figure 38a shows the raw Raman spectra, Figure 38b shows the normalized spectra, Figure 10 shows the spectra scaled such that the PL peaks above 1300 cm^{-1} are unchanged, and Figure 38d shows the difference spectra obtained by subtracting out the different scaled spectra. Note that we only consider three temperatures above 401 K in Figure 38d as the Raman spectra are relatively unchanged below 401 K. This is anticipated as EYAD is stable below its melting point at 400 K (see Figure 3). Additionally, based on our DSC/TGA measurements we can conclude that the changes in the Raman spectra above 400 K are primarily due to melting as decomposition does not begin until $\approx 500\text{ K}$.

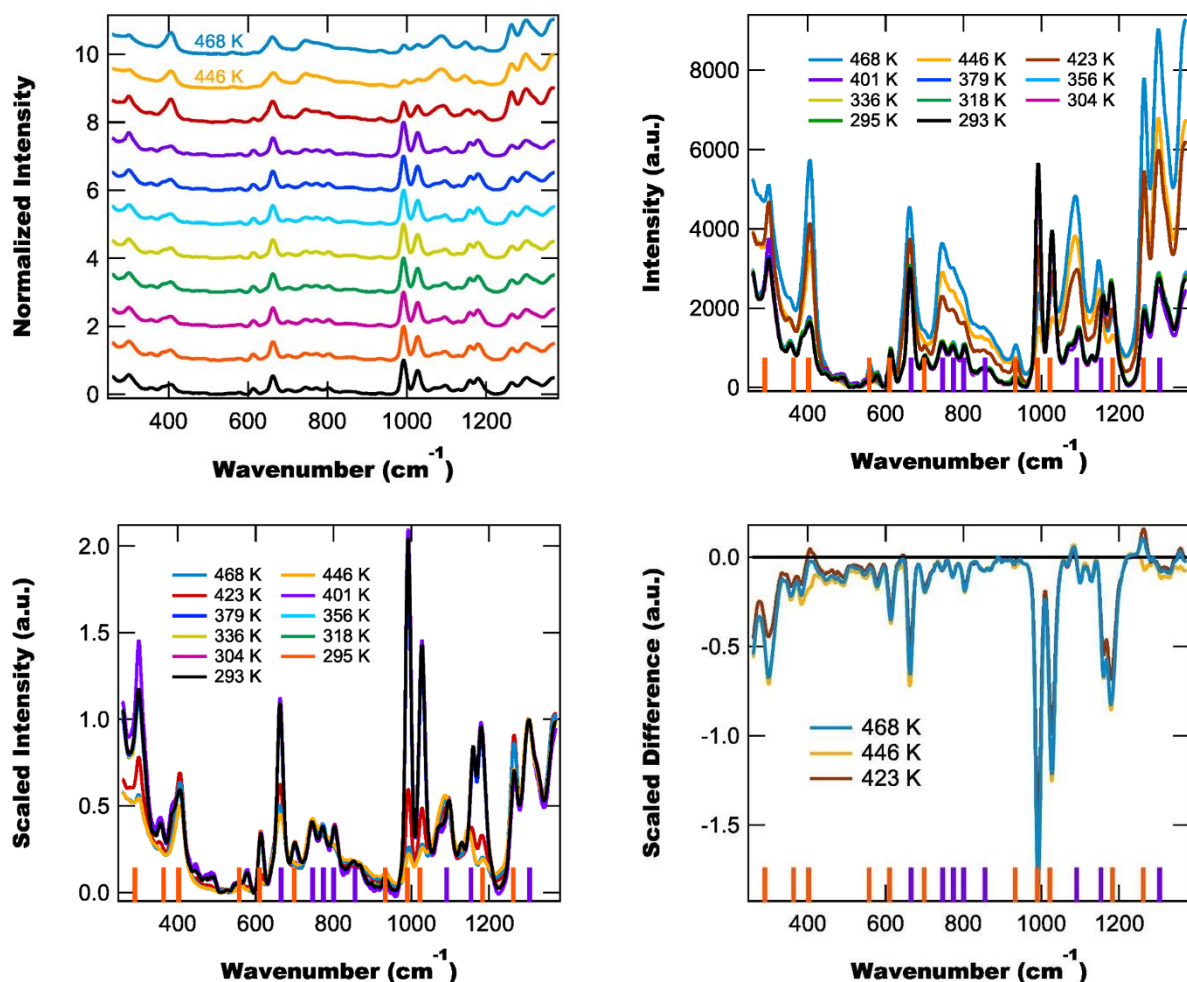


Figure 38. (a) Raw Raman spectra measured at different temperatures. (b) Normalized Raman spectra at different temperatures. (c) Scaled Raman spectra at different temperatures such that most PL peaks remain unchanged. (d) Difference spectra between scaled spectra. Note that only the highest three temperatures show significant differences and so only those are displayed.

Considering the behavior of the Raman peaks in Figure 38, we find that the Raman peaks corresponding to the DPEPO ligand (933 cm⁻¹, 990 cm⁻¹, and 1022 cm⁻¹) undergo the largest changes with temperature, relative to the peaks corresponding to the acac ligand (402 cm⁻¹, 558 cm⁻¹, 1183 cm⁻¹ and 1262 cm⁻¹). This observation is opposite to what we observed for photodegradation, where the acac ligand was the main source of spectral changes, while the DPEPO peaks were relatively unchanged. This provides further evidence that the mechanisms underlying the two degradation pathways are not identical.

Finally, we measure the FTIR spectrum of heated (to 600 K) EYAD with the scaled spectrum shown in Figure 39. From Figure 39 we find that heating EYAD results in the FTIR peaks decreasing and broadening, which is different from the photodegradation case (Figure 36), where the peaks changed in intensity, but continued to have approximately the same spectral width. Additionally, while we observed the formation of a new peak at 1750 cm⁻¹ in the photodegradation case, we do not observe any such peak in the thermal degradation case.

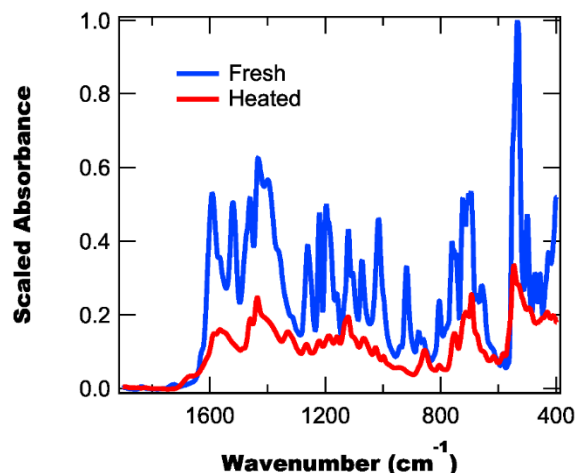


Figure 39. Scaled IR absorbance for fresh EYAD and EYAD heated to 600 K.

Photo/thermal-degradation of EYAD in Heterogeneous Material

Photodegradation

To demonstrate the BFM's ability to monitor subsurface chemical reactions we prepare a sample consisting of EYAD dispersed into HTPB polymer with sugar loaded at 50%. Once prepared, we use the BFM to focus inside of the heterogenous sample onto a target particle. This focus acts as both the probe beam and decay beam.

Figure 40 shows the measured PL spectra at different times during photodegradation, as well as the difference spectra (i.e., spectrum at time t minus the spectrum at time 0). From Figure 40 we find that as the target particle decays the fluorescence peaks at 611 nm and 614 nm decrease, while a broad peak near 618 nm is found to increase. These changes are consistent with those measured in bulk EYAD.

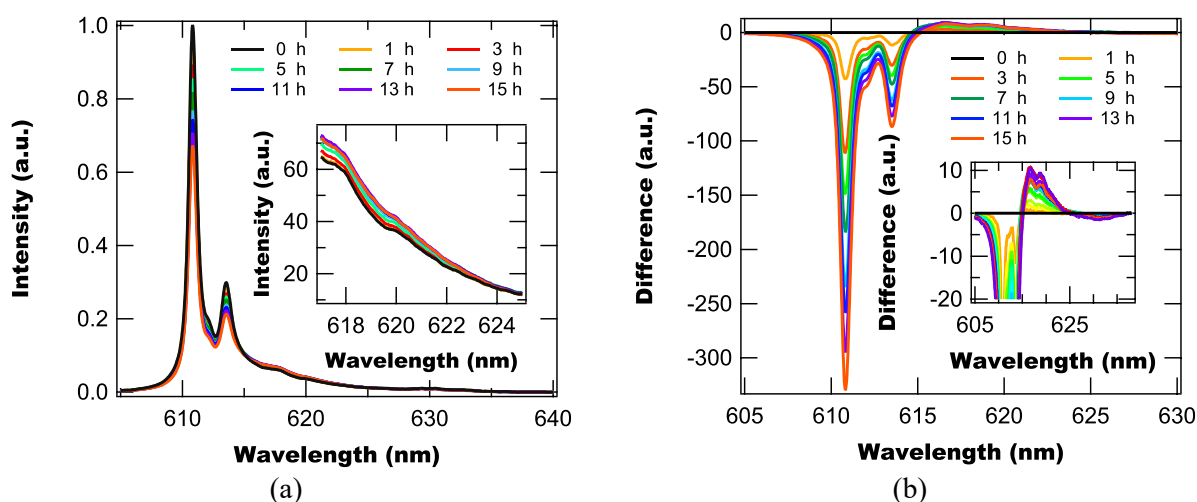


Figure 40. Optimized sub-surface fluorescence spectra (a) and difference spectra (b) during photodegradation. Insets show zoomed in views of the spectra.

After considering the LIF during photodegradation, we next desire to measure the Raman spectra during photodegradation.

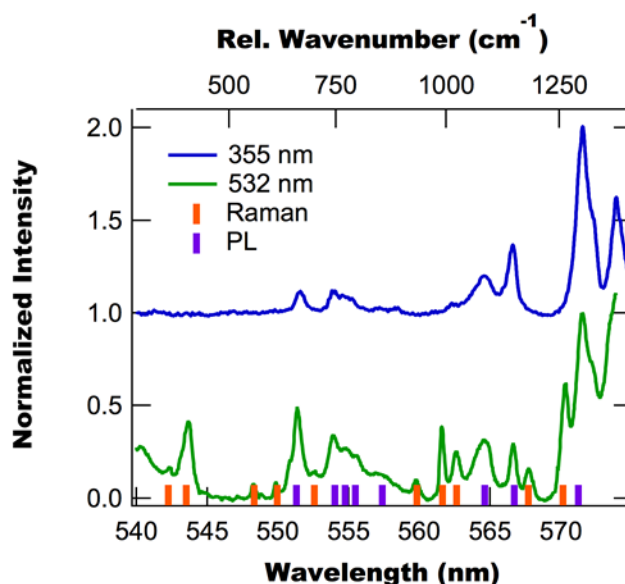


Figure 41. Emission from EYAD excited using both 355 nm and 532 nm light. The peaks common in both spectra are due to PL, while the added peaks in the 532 nm spectrum are due to Raman scattering.

Table 3. Raman peak assignments for EYAD.

Peak / cm^{-1}	Assignment
402	ACAC (in-plane ring deformation)
558	ACAC (out-of-plane deformation)
610	ACAC (C-CH bending)
699	DPEPO
933	DPEPO (C-C stretch)
990	DPEPO
1022	DPEPO (C-H stretch)
1183	ACAC (δ -CH in-plane bending)
1262	ACAC (ν C-C=C + δ O-H)

Figure 42 shows the relevant subsurface Raman data for EYAD during photodegradation in four different forms including: raw spectra (a), background subtracted data (b), Raman difference spectra (c), and zoomed in difference spectra (d). As noted last year we observe a broad baseline photoluminescence (PL), which arises from the polymer (discussed in more detail below). We therefore remove the baseline PL to get the emission from the EYAD, which includes both Raman and PL peaks. Figure 41 shows EYAD's emission under two different excitation wavelengths, which allows us to separate PL peaks from Raman peaks, with the Raman peaks and their assignments tabulated in Table 3.

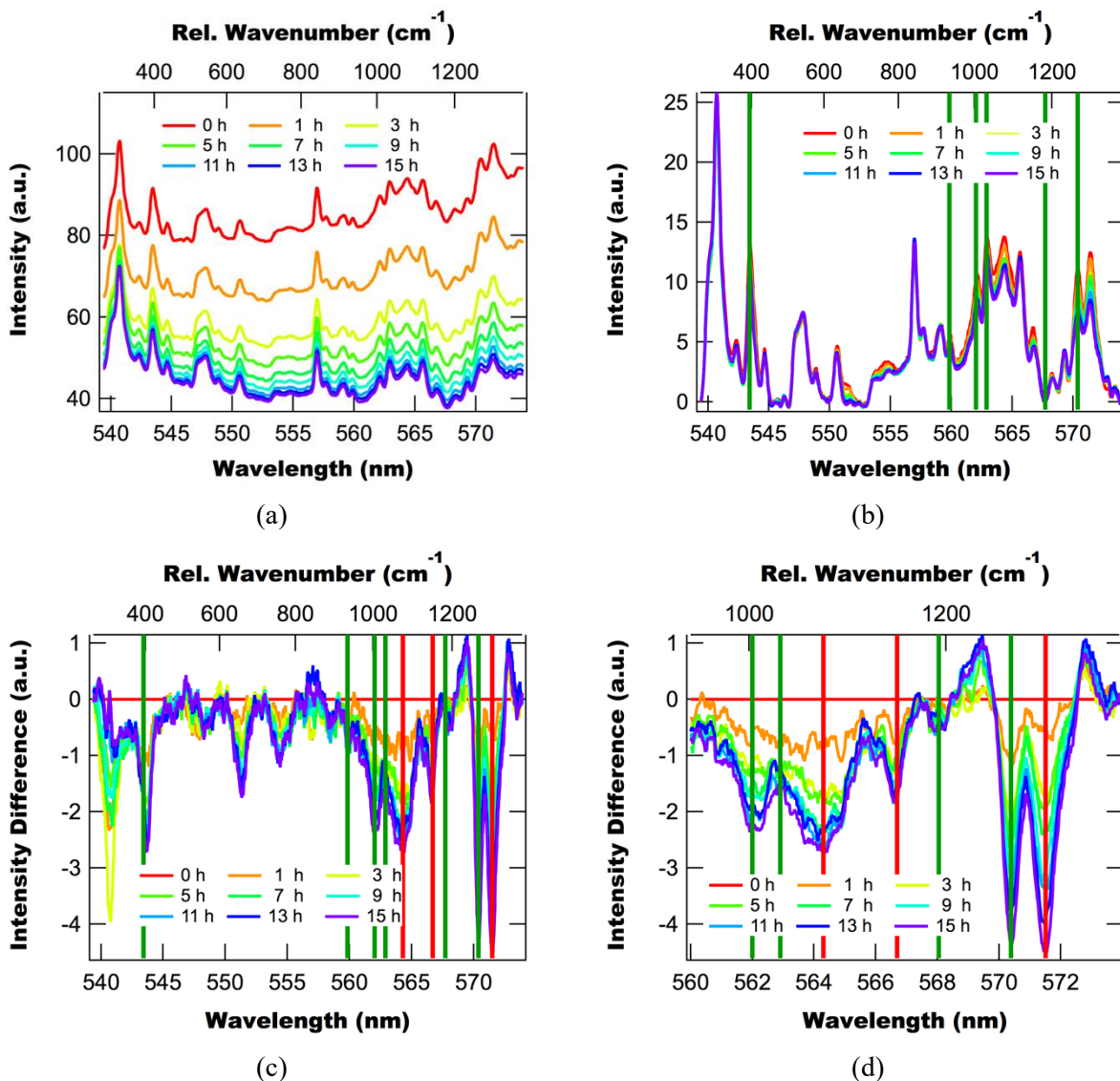


Figure 42. (a) Raw optimized sub-surface emission spectra measured using 532 nm during photodegradation, (b) background subtracted spectra and Raman difference spectra during photodegradation for full spectral range (c) and zoomed in view (d).

Once the polymers background PL was removed, we calculated the difference spectra between time t and the initial spectra, with the results shown in Figure 42c and Figure 42d. From these difference spectra we find that in general the Raman peaks assigned to EYAD decrease over time (suggesting bond breakage), but that there are also increasing peaks at 1237 cm^{-1} and 1337 cm^{-1} , which can be assigned to amide III modes (C-N stretch or N-H bend). [1] As the IPDI additive is the only source of N in the system we can safely assume that the underlying reaction resulting in these new bonds involves IPDI. However, more details of this reaction are difficult to determine given the complexity of the system.

One proposed explanation for these increasing bonds was further curing of the polymer not involving the EYAD molecule at all. To test this hypothesis, we measured the emission from a heterogeneous sample consisting of polymer and sugar (but no EYAD), with the resulting spectra shown in Figure 43. From Figure 43 we observe a broad PL contribution that decays over exposure time leaving only Raman peaks. Once again performing background subtraction we remove the broad PL and find that the Raman peaks remain

essentially unchanged. This contradicts the proposed explanation of further curing (without EYAD) as we would expect to see increasing Raman peaks if new bonds were forming.

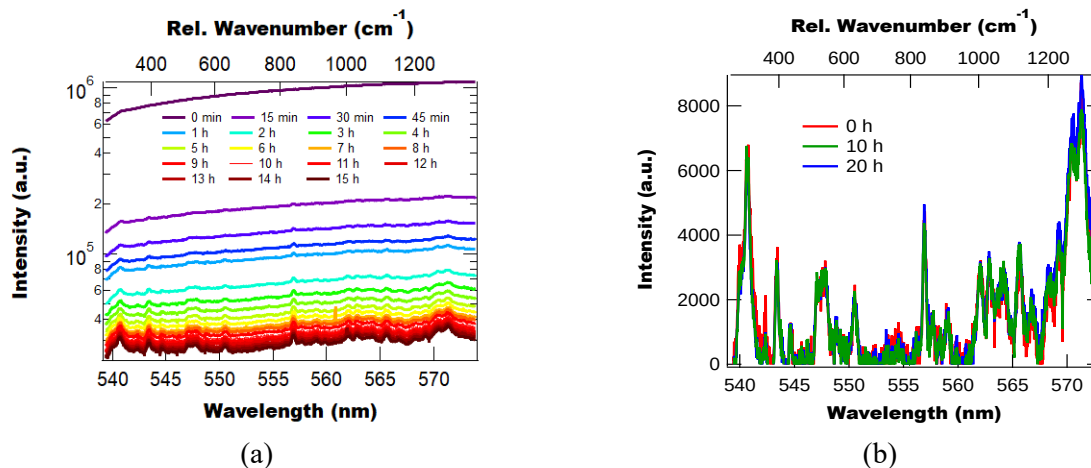


Figure 43. (a) Raw emission spectra from HTPB + sugar sample during continuous 532 nm exposure. (b) Comparison of background subtracted Raman spectra at three times during continuous exposure.

This hypothesis is further disproved by comparing the emission difference spectra for three different samples: EYAD in HTPB/sugar, HTPB/sugar, and EYAD by itself. Figure 45 shows these difference spectra with the HTPB/sugar alone sample having no change due to exposure while both samples containing EYAD display changes. This observation makes sense since absorption measurements of HTPB alone show little absorbance at 532 nm (see Figure 44).

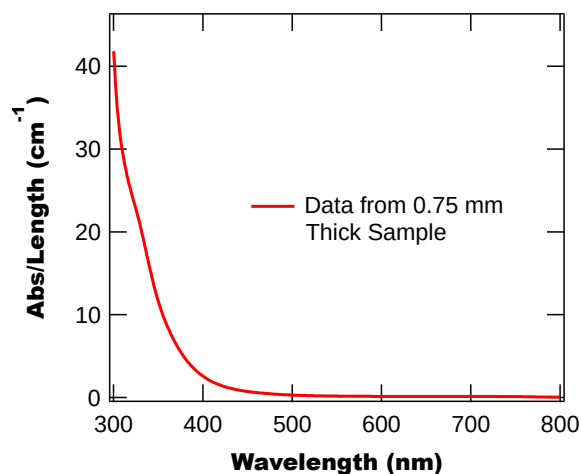


Figure 44. Absorbance per length of HTPB polymer. For 532 nm we find a 1/e absorbance length of 4.9 cm.

A second hypothesis is that the target EYAD molecular crystal acts as a heat source (due to absorption), which leads to further curing. While this hypothesis is more possible, it is not fully supported by the data shown in Figure 45. From a comparison of the EYAD in HTPB/sugar and EYAD by itself, it appears that there are more Raman peaks decreasing in the heterogeneous sample than can be explained by the EYAD. This suggests that there are HTPB/sugar bonds being broken during photodegradation, which is opposite of what would be expected for further curing.

Based on the currently available data the most likely scenario is that under continuous illumination the EYAD guidestar heats up and both the polymer and guidestar undergo thermal degradation into product

molecules, which then react to form new C-N or N-H bonds. The exact nature of these products and reactions is a complex problem, which is beyond the scope of this project.

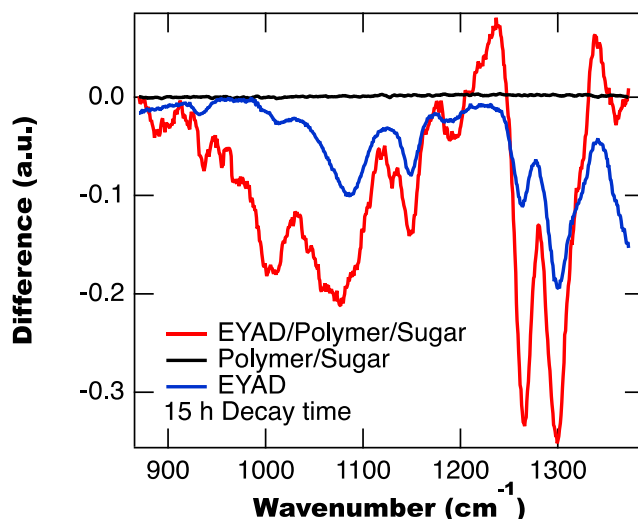


Figure 45. Comparison of Raman difference spectra from different materials after 15 h of exposure to 532 nm light.

HTPB-based Heterogeneous Sample Background

To better understand the source of the background observed in our photodegradation measurements. We perform Raman measurements using 532 nm on a sample consisting of polymer and sugar alone (i.e., no EYAD). The resulting spectra at different times during exposure are shown in Figure 46a, which display a broad background spectrum that decays with time with the Raman peaks remaining fairly stable. To characterize the kinetics of this behavior we consider the intensity at 555 nm as a function of time, which is shown in Figure 46b. From Figure 46b we find that the intensity at 555 nm decays as a double exponential, with one time constant being ≈ 13 min and the other being 321 min.

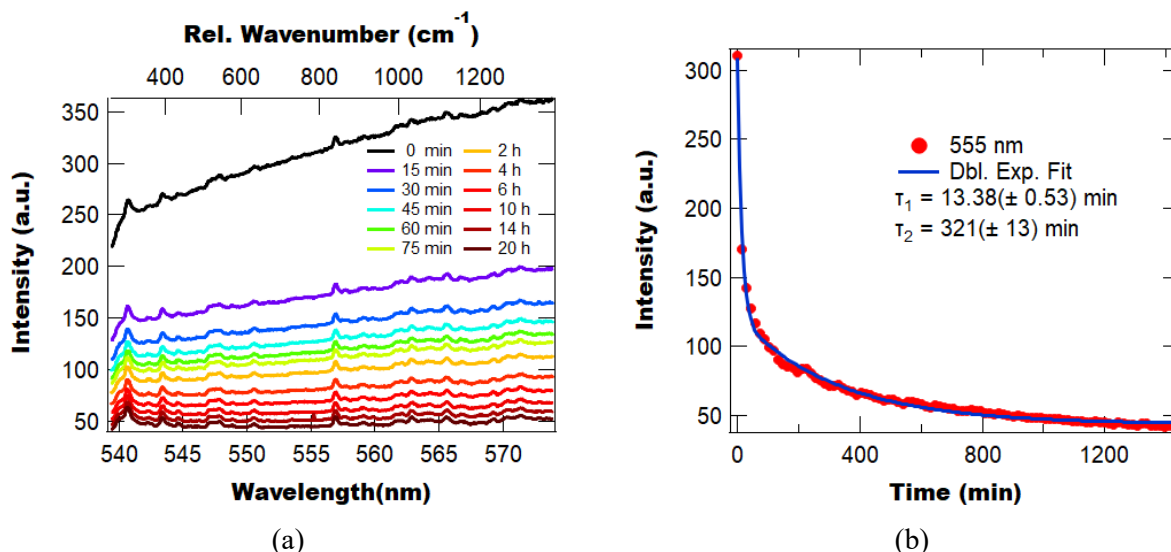


Figure 46. (a) Emission spectra from new heterogeneous sample at different times during laser exposure, and (b) intensity at 555 nm as a function of time during exposure. The spectra are found to decrease in intensity as a double exponential function.

As a different way to visualize this decay we also compare the normalized spectra at $t = 0$ and $t = 20$ h in Figure 47. From Figure 47 we find that the Raman peak locations remain the same at both times, with the primary difference being the addition of a significant broad background at time 0. As the sample is exposed to light the broad background decreases and eventually the Raman peaks become dominate. Given the very broad nature of the background it is most likely due to fluorescence from the polymer. The exact mechanism of this fluorescence is currently unknown.

For reference we also measure the Raman spectra of both a polymer sample and sugar + polymer sample to determine which Raman peaks come from the sugar and which are from the polymer, as shown in Figure 48.

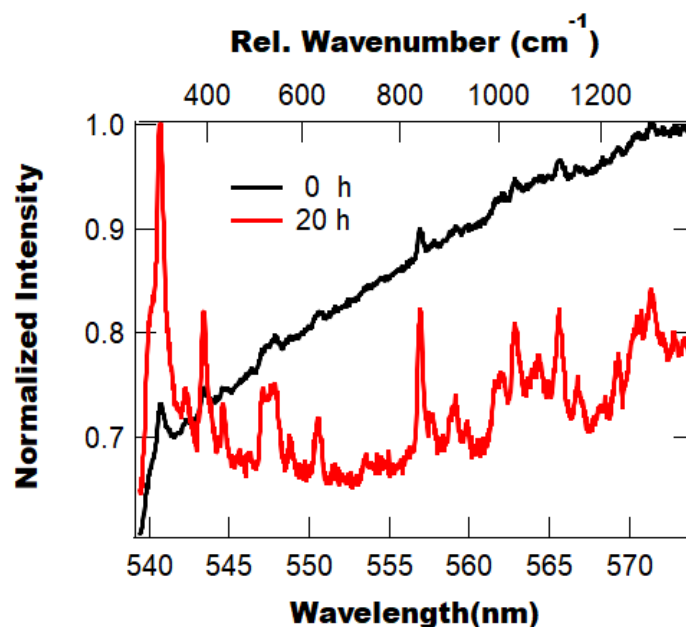


Figure 47. Comparison of normalized spectra at 0 h and 20 h.

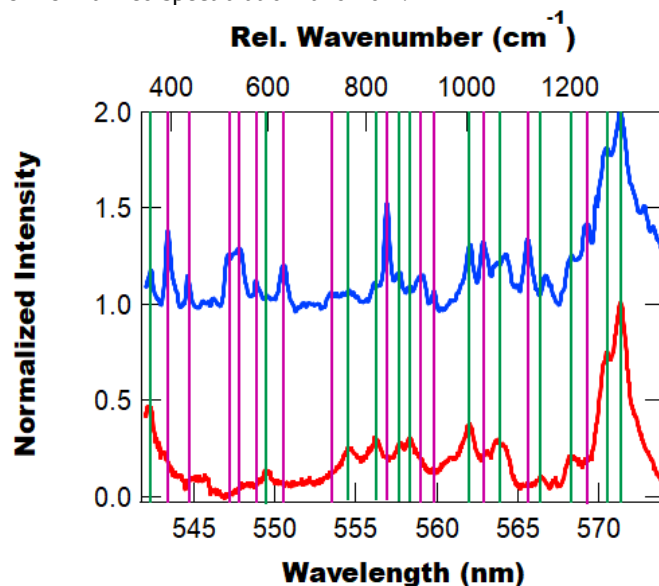


Figure 48. Raman spectra of polymer only (red curve) and polymer + sugar (blue curve). The green vertical lines mark polymer peaks and the purple vertical lines are sugar peaks.

Thermal Degradation

Having demonstrated the BFM's technique to measure subsurface photodegradation (a relatively slow reaction) we next turn to thermal degradation caused by a heated wire, which is significantly faster than photodegradation. Note that while Ohmic heating can produce heating rates on the order of tens of thousands of K/s, we use a modest heating rate of ≈ 3.5 K/s, which is a function of power supply limitations and weak Raman signal from using a CW laser.

Before turning on the power supply and performing thermal degradation on the EYAD coated wire, we first focus onto a guidestar particle located near the wire using the reflective SLM only. Note that we only use the reflective-arm SLM as the transmissive-arm's light is effectively blocked by the wire and does not contribute to the guidestar particle's fluorescence image. Figure 49 shows example fluorescence images for flat field and optimized illumination with the peak optimization found to be approximately 4x.

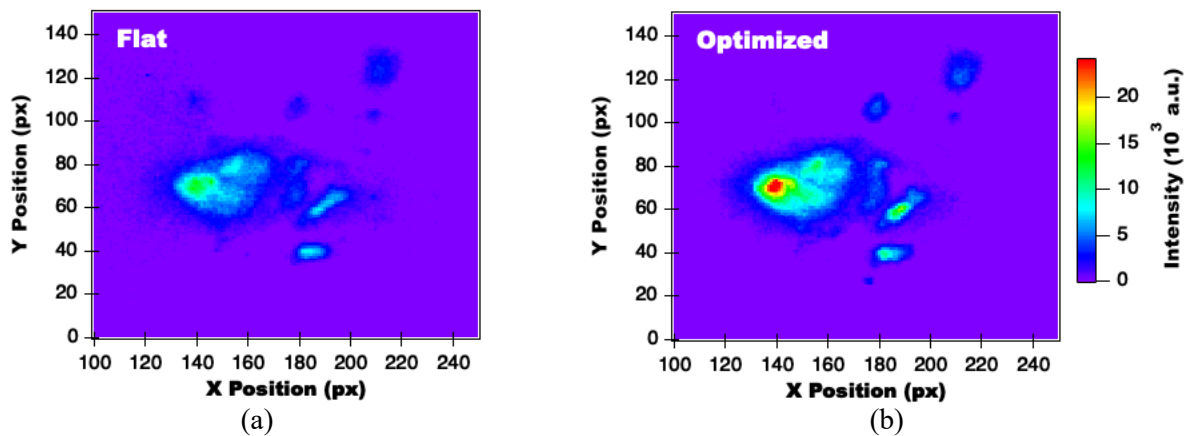


Figure 49. Fluorescence images of EYAD particles on wire embedded in heterogeneous sample for flat (a) and optimized (b) wavefront.

Having considered the effect of optimization on the target's fluorescence image, we next measure its' fluorescence spectrum for both the flat field and optimized field, which are shown in Figure 50. From Figure 50 we find that the fluorescence spectrum displays significantly less enhancement ($\approx 1.3 \times$ vs $\approx 4 \times$) than the images in Figure 49. This reduced enhancement can be attributed to spectral measurements averaging over both the target particle and nearby (unoptimized) particles. Note that this was not an issue in the previous subsurface photodegradation measurements where the guidestars were dispersed throughout the heterogeneous sample rather than being placed on a narrow wire.

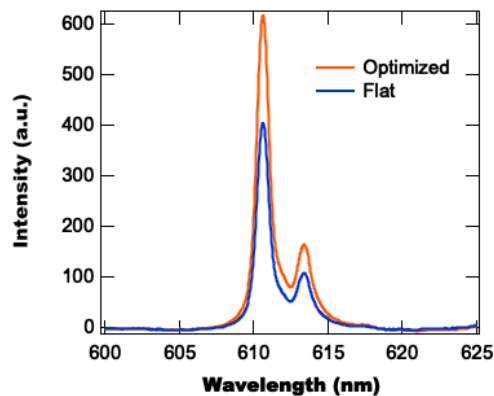


Figure 50. Comparison of measured fluorescence spectrum for flat field and optimized field illumination. Note that the enhancement is less in the spectral response due to the presence of adjacent EYAD particles.

For the heating experiments we continuously run the optimization program throughout the heating run to maintain focus on the target guidestar the entire time. For the heating run we use a heating profile consisting of a linear ramp from 293 K to 612 K with a heating rate of 3.5 K/s followed by the power being cut off. During this time we measure both the fluorescence and Raman spectrum, with **Figure 51** showing the fluorescence spectra and **Figure 52** showing the Raman spectrum.

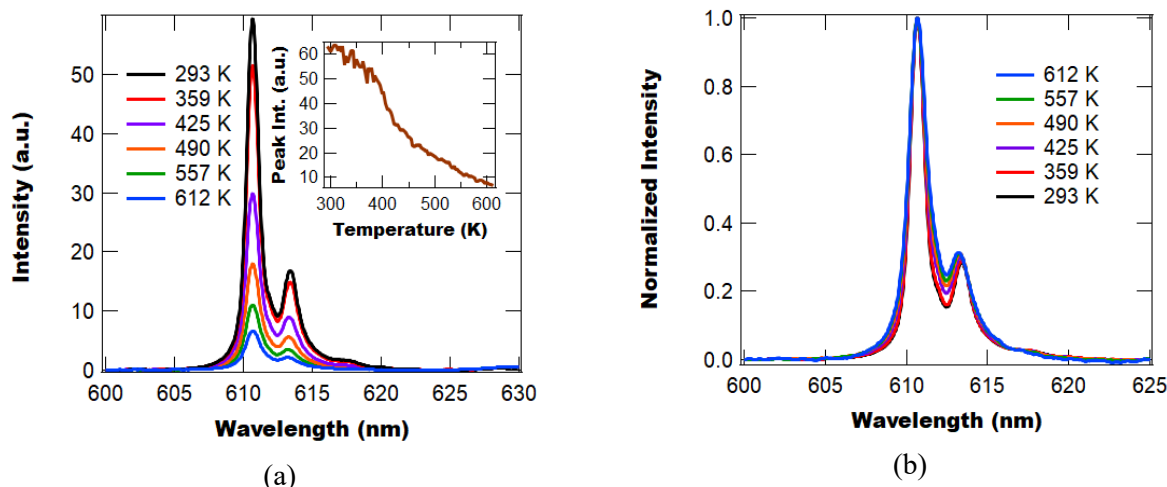


Figure 51. Background subtracted subsurface PL spectra (a) and normalized spectra (b) during heating run.

From Figure 51a we find that the overall fluorescence intensity decreases as the temperature is increased with the rate of change increasing above 400 K, which is consistent with our previous observations of EYAD on a bare wire and is attributed to the EYAD starting to melt. However also note that the fluorescence intensity decays less quickly than observed for the bare wire. This can be explained by noting that this rapid decrease in intensity in the bare wire case is most likely due to the EYAD melting and moving out of focus of the pump laser, but in the heterogenous case the particles are stuck in place by the polymer and therefore the intensity remains higher for longer.

To get a better sense of how the shape of the spectrum changes we also plot the normalized spectra in **Figure 51b**, from which we find that as the temperature increases the spectra broaden as seen in the bare wire case. However, note that the amount of broadening is less in the subsurface case for a higher temperature. While there may be some reaction-based reason for this difference, more likely is that the process of placing the polymer over the wire results in changes to how heat is transferred to the EYAD and thus there may be a larger discrepancy between the temperature of the guidestar particle and the wire's temperature.

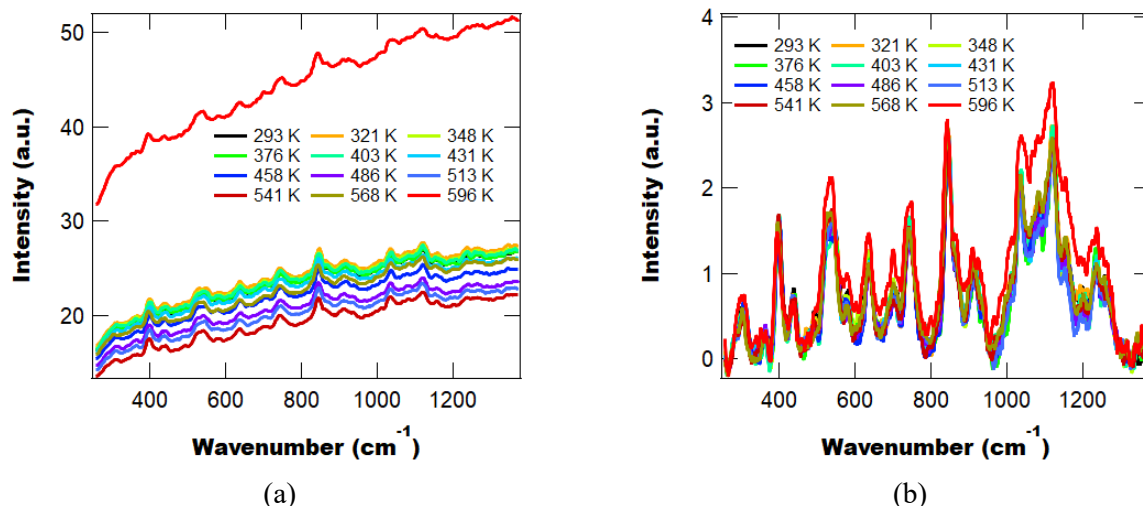


Figure 52. Raw (a) and background subtracted (b) Raman data at different temperatures during heating run.

We next turn to considering the Raman spectra shown in Figure 52, which are shown in both their raw (a) and background subtracted (b) form. From Figure 52a we find that the background changes significantly with temperature, with it first decreasing gradually from 293 K to 541 K after which it quickly increases. We note that this inflection point is near the melting point of Epotek 350 (543 K) and therefore this change in background is most likely due to the wire causing the polymer to start melting. Also, from Figure 52a we find that the Raman peaks observed primarily correspond to sugar's Raman spectra (see Figure 48), with EYAD's Raman peaks drowned out by the sugar signal. This most likely is due to the laser light scattering through the sugar particles to reach the EYAD, which leads to a significant sugar-based signature. This is consistent with our observations with photodegradation. One possible solution to this unwanted signal is to use spatial filtering of the backward collected light such that light from the focal point makes it to the spectrometer, but light from the background is blocked [38].

6. CONCLUSIONS

We have developed a bidirectional focusing microscope that uses feedback-assisted wavefront shaping to perform subsurface spectroscopy in heterogeneous materials. This microscope is found to have significantly improved signal over a uni-directional design, both due to an expected increase in the number of modes controlled as well as an unexpected boost most likely due to long range mesoscopic correlations in the propagation modes [24]. We characterized the performance of this microscope for different experimental parameters, including: number of SLM bins, number of genetic algorithm generations, sample position (i.e., beam spot size), and the depth of the target particle and find that care must be taken in adjusting the various parameters to optimize the functionality of the microscope.

After characterizing the microscope's performance we then demonstrated its capabilities by measuring subsurface photodegradation of an inert energetic crystal simulant [Eu:Y(acac)₃(DPEPO)] using both fluorescence and Raman spectroscopy. We observe decreasing fluorescence and Raman intensity consistent with air-based measurements, but also observe the formation of new Raman peaks at 1237 cm⁻¹ and 1337 cm⁻¹, which can be assigned to C-N stretch and N-H bend modes [39], which suggests a subsurface reaction with the IPDI curing agent, which is the only source of nitrogen atoms in the system. These reactions only occur when EYAD is present in the heterogenous sample, so the EYAD is key to the reaction, but it is unclear if the reaction is between the EYAD and the IPDI or if the EYAD is acting as a photocatalyst for a reaction between the IPDI and the HTPB or sugar. Regardless of the mechanism, this demonstration shows the capability of the bidirectional focusing microscope to probe subsurface chemical reactions.

Having demonstrated the feasibility of using wavefront shaping to probe subsurface chemical reactions in this project, there are two paths forward to further develop this technology towards use in energetic materials, which will require significant improvements in the speed of system. The first path forward is to transition from using LCOS-SLMs (which have refresh rates <1 kHz) to digital mirror devices (that can have refresh rates of almost 40 kHz) and transitioning to using optical phase conjugation in one arm of the microscope. These modifications will allow the microscope to operate at significantly faster rates allowing for probing sub ms phenomenon. Alternatively, we are considering using self-healing beams [40-42] to counteract the scattering of the heterogenous sample to focus onto the target particle and using fast optical phase conjugation via four-wave mixing [43-45], which will allow us to obtain spectroscopic data on a nanosecond time scale.

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8. APPENDIX A: PROGRAM

Early in the reporting period we observed some anomalous behavior when performing focusing inside of heterogeneous materials where the enhancement would decrease as the camera frame rate increased. To better characterize this effect, we performed transmission and reflection optimization with different camera frame rates. The resulting enhancements as a function of frame rate are shown in Figure 53. From the figure we can see clearly that the enhancement decreases as the frame rate increases, which is unexpected.

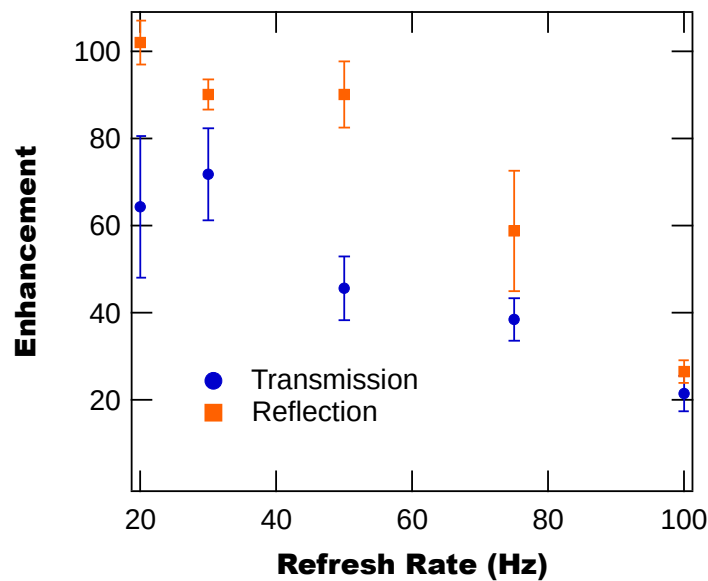


Figure 53. Enhancement as a function of camera refresh rate for reflection and transmission optimization.

Upon further investigation of the underlying programming, we found an issue with how the program handled the camera's buffer. In the original program the camera would send the first buffered frame rather than the last captured image, which meant the camera was using the wrong image for calculations at high frame rates. However, after fixing this error, the program still displayed the anomalous behavior. We then tested an iterative optimization algorithm and found that for the iterative algorithm there is no change in the enhancement with speed, as expected. This suggests that there is a bug somewhere in the genetic algorithm programming that is causing problems when working at higher frame rates. The exact source of this error is currently under investigation.

In the current reporting period, we performed further improvements to our optimization program's interface and began implementing multithreading. Figure 54 shows snapshots of the GUI interface and Figure 55 shows a flowchart of the multithreading process. Figure 56 shows the computation time for SGA as a function of number of bins. Further adjustments to the multithreading process are needed to improve the overall performance.

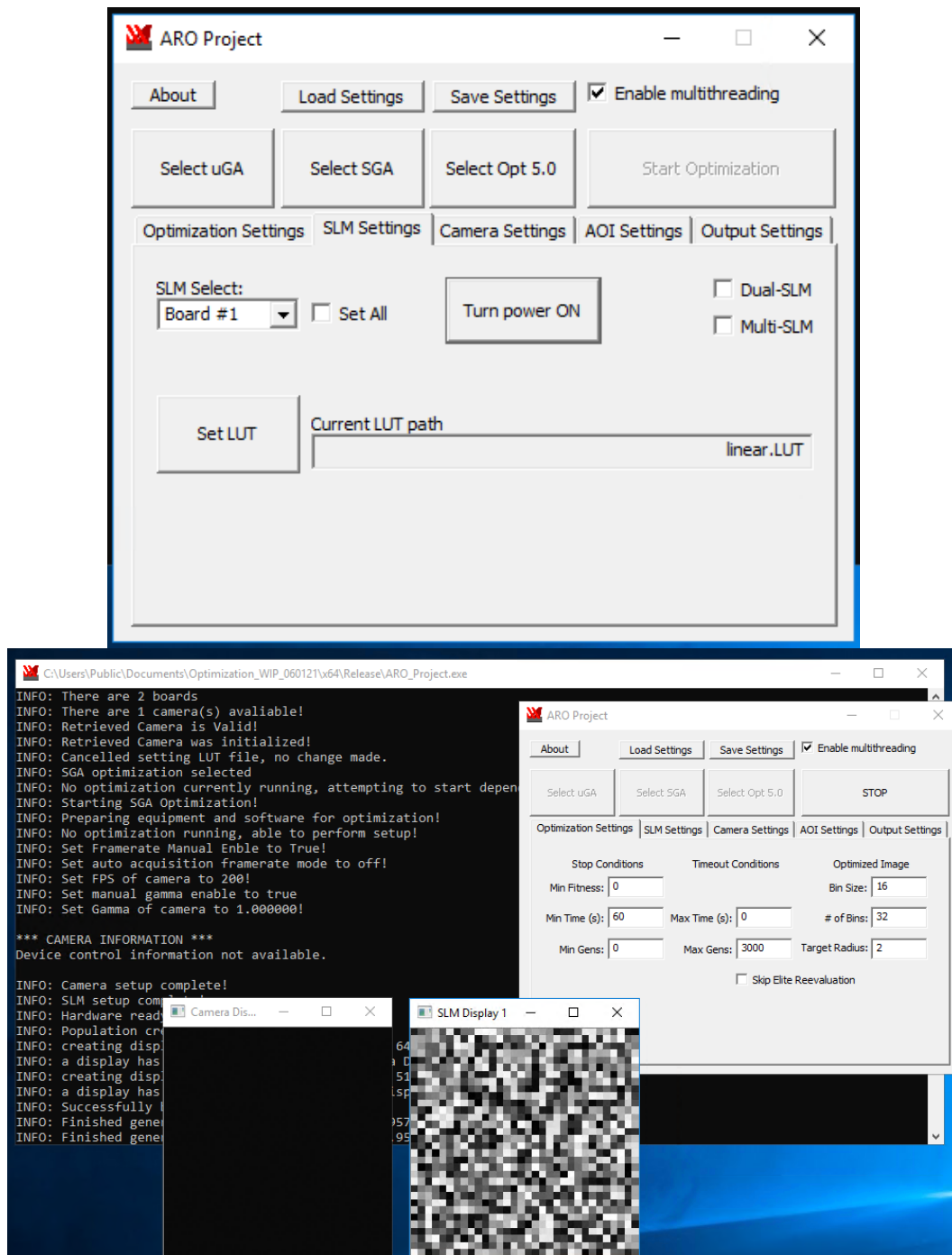


Figure 54. GUI Improvements

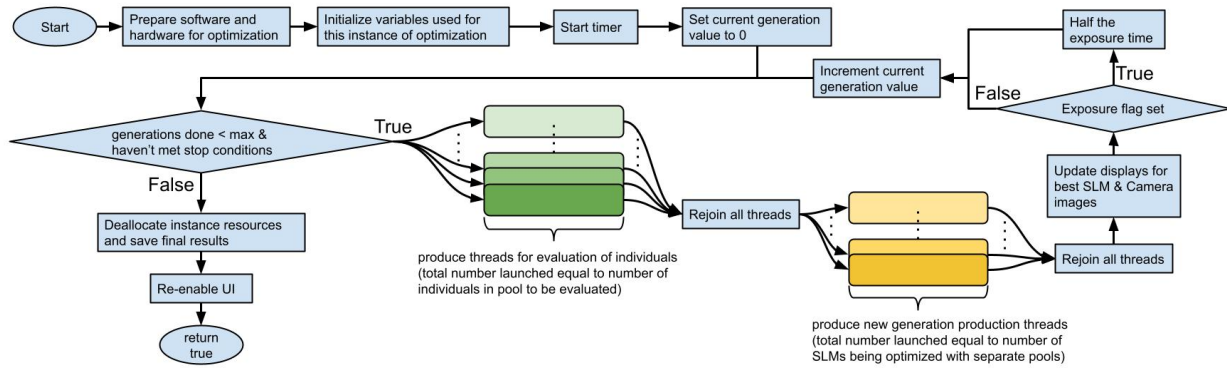


Figure 55. Multithreading flow chart

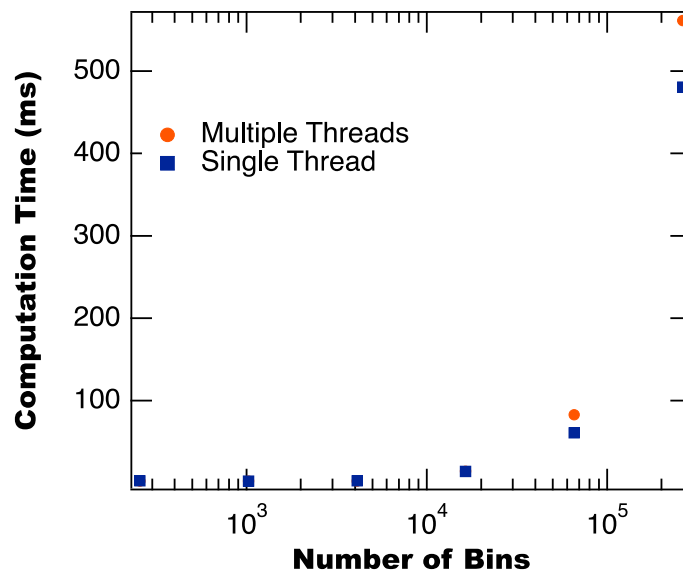


Figure 56. Computation time for SGA as a function of number of bins.

9. APPENDIX B: DIGITAL OPTICAL PHASE CONJUGATION

DOPC Microscope

Setting up the DOPC microscope involves a significant amount of equipment and optics, and care must be taken to ensure compatibility between the various components. Figure 5 shows a schematic of the DOPC microscope with Table 1 tabulating the various components.

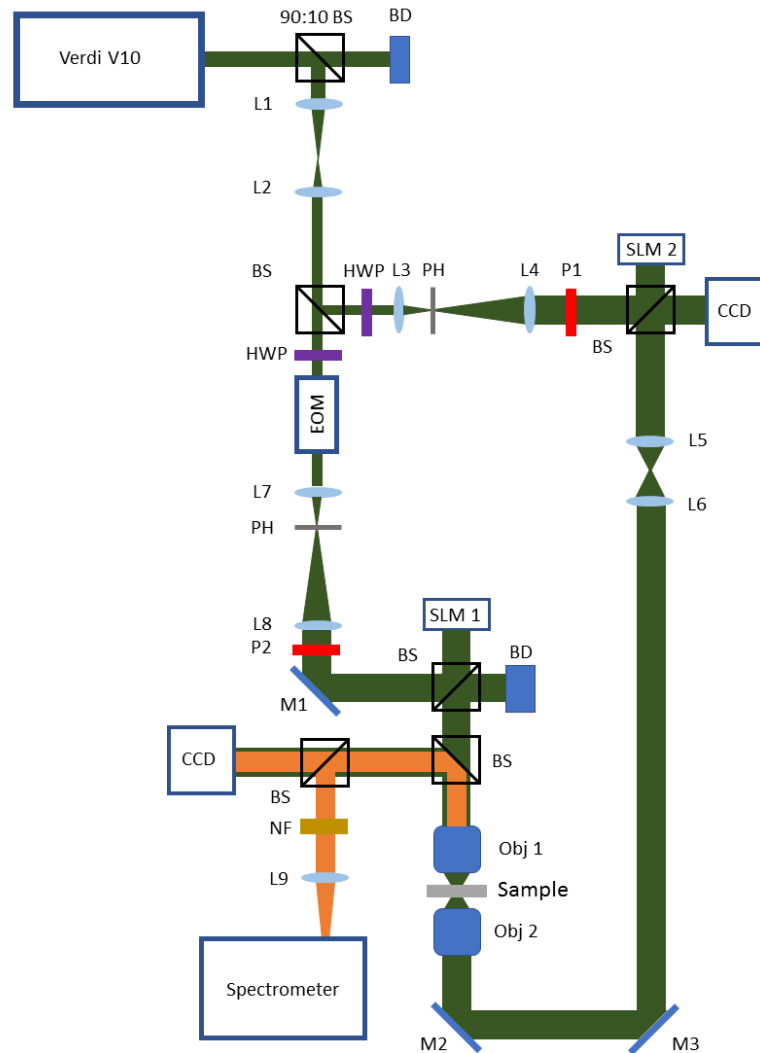


Figure 57. Schematic of DOPC setup. L1-9: lenses, PH: pinhole, BD: beam dump, M1-3: mirrors, BS: Beam splitters, P1-2: polarizers, HWP: half-wave plate, NF: notch filter

We begin with a Verdi V10 laser, whose most stable output is at 10 W with a beam diameter of ≈ 2.2 mm. As we don't need the full 10 W, we pass the beam through a 90:10 beamsplitter which picks off 1 W of the laser. As the EOM has a clear aperture of 2 mm, we need to reduce the beam size, which is accomplished with a 40 mm and 30 mm lens, which gives a reduced beam size of 1.65 mm. This beam is split in two, with one beam going to the probe arm and the other to the reference arm. The reference arm consists of a half-wave plate polarizer combination (for intensity control) and a 5x beam expander/spatial filter. The probe arm passes the narrowed beam through the EOM, followed by the beam expander/spatial filter and

half-wave plate polarizer combination. The expanded beam (now 8.25 mm) is passed through a beam splitter, with one half passed to the first SLM, while the second half is dumped. The SLM modulated beam is then sent through two beam splitters into the microscope objective, which focuses the modulated beam onto the sample. Using wavefront shaping with the first SLM we will focus the beam onto a guidestar particle within the scattering sample. This guidestar is photoluminescent under 532 nm excitation and its PL signal is collected by the first objective and passed to a spectrometer using different beamsplitters and filters.

In addition to focusing with the first objective, we also use the second objective, in conjunction with a DOPC system to perform isotropic focusing. The scattered pump light is collected by the second objective and passed to the DOPC system using two mirrors and a 1x beam expander (which is used for conjugation). The scattered light enters the DOPC system and is interfered with the reference beam onto the CMOS camera. Using the DOPC program described above the computer produces a conjugate phase mask for the second SLM to display. Once the light is modulated by this SLM, it is passed back to the second objective, where it is focused onto the guidestar particle.

Table 4. List of DOPC microscope components

Item	Details	Item	Details
L1	f = 40 mm doublet, Ø1"	BS	50:50 cube beam splitter
L2,L7,L3	f = 30 mm doublet, Ø1"	HWP	Ø1/2" 532 nm Half-waveplate
L4 and L8	f = 150 mm doublet, Ø1"	P1 and P2	Ø1" 480-550 nm Polarizer
L5 and L6	f = 50 mm doublet, low wavefront error, Ø1"	Obj 1 and 2	Mitutoyo 50x M Plan APO HR Objective, 0.75 NA
M1	Standard Ø1" Nd:YAG mirror	SLM1	Boulder Nonlinear Systems P512-0532
M2 and M3	Low wavefront error Ø1" Nd:YAG mirror	SLM 2	Meadowlark ODP512-532

Assembling DOPC System

During the reporting period we purchased and received all of the components necessary to build the full microscope with isotropic focusing and bidirectional phase conjugation. Figure 58 shows a schematic view of the system and a picture of the assembled system. In addition to assembling the hardware for the system we also developed the software necessary to run the system. However, we are still in the process of finalizing alignment of the system, which has proven to be very difficult. We are currently making several modifications to make alignment easier and hope to have the full system operational soon.

$$\phi(x, y) = \arctan \left[\frac{I(x, y; \frac{3\pi}{2}) - I(x, y; \frac{\pi}{2})}{I(x, y; 0) - I(x, y; \pi)} \right] \quad (1)$$

Figure 60 shows example empty microscope interference patterns for the four phase shifts. Plugging these into Equation 1 we then calculate the phase profile shown in Figure 61. This demonstrates the phase retrieval process.

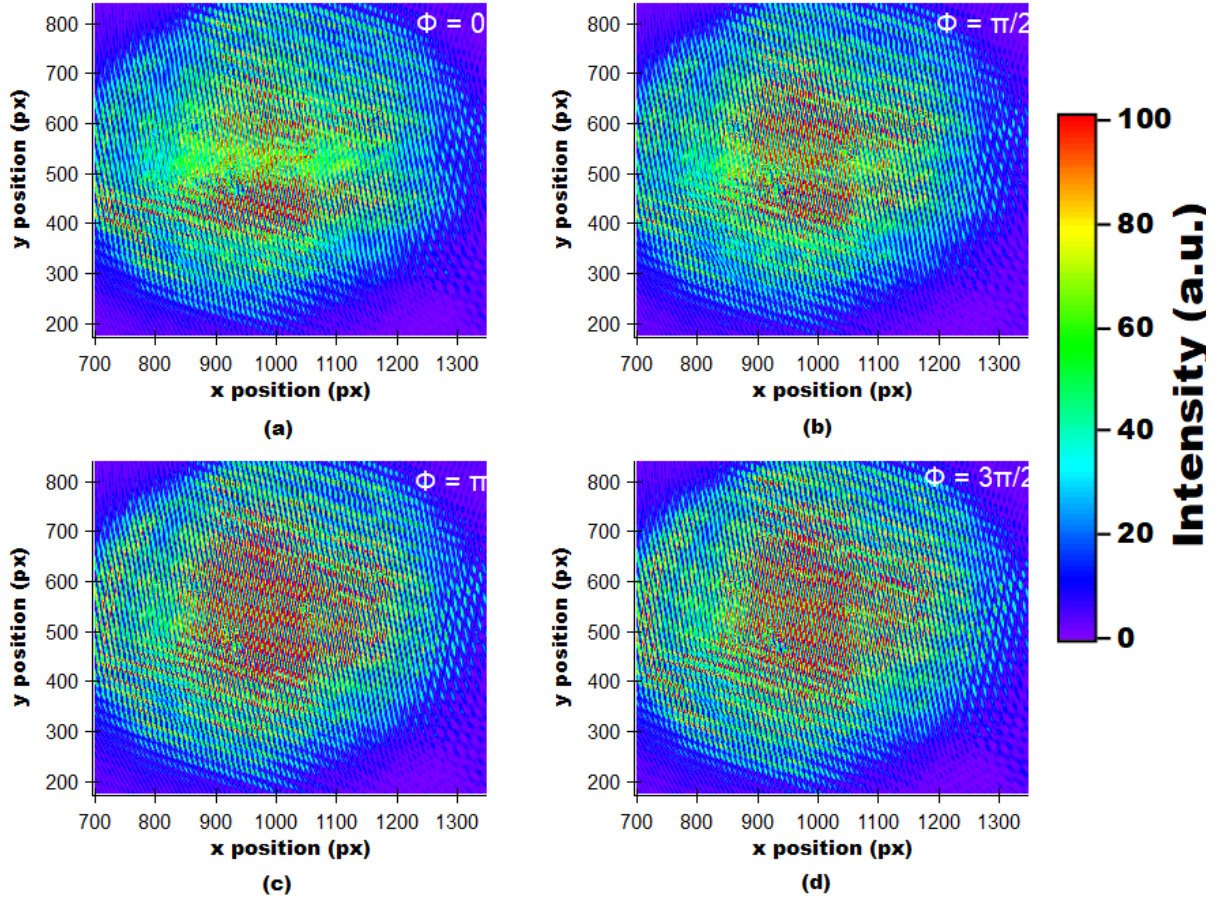


Figure 60. Intensity map image for four different phase shifts.

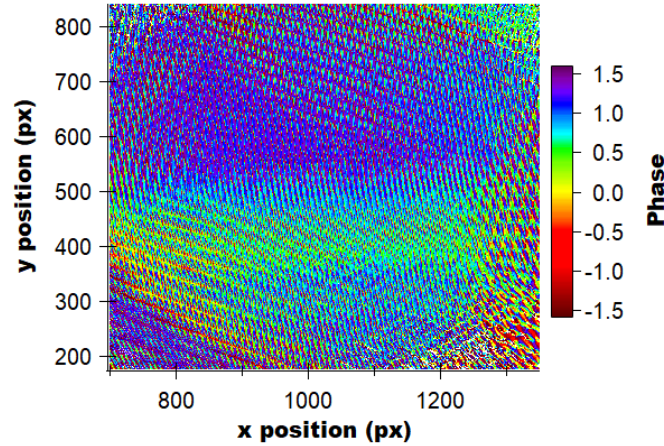


Figure 61. Calculated beam phase found using Equation 1.

Digital Optical Phase Conjugation Program

While we are still waiting for various equipment components to arrive for the DOPC system, we have begun developing the DOPC control program based on Ref's [3-5]. From these references we developed the pseudo-code of the DOPC program as follows:

1. Set electro-optic modulator (EOM) to a phase shift of 0.
2. Take image of interference pattern.
3. Repeat steps 1 and 2 for phase shifts of $\pi/2$, π , and $3\pi/2$.
4. Using the four images (one for each phase shift), calculate the phase profile using the following equation:

$$\phi(x, y) = \arctan \left[\frac{I(x, y; \frac{3\pi}{2}) - I(x, y; \frac{\pi}{2})}{I(x, y; 0) - I(x, y; \pi)} \right] \quad (2)$$

5. Display the phase conjugate $-\phi(x, y)$ on the SLM.

Having developed the pseudo-code, we next set out to write the actual program using C++. This program is still under development and a prototype program has not been completed yet.

10. APPENDIX C: INITIAL GUIDESTAR CANDIDATES

Figure 62 shows images of the Eu-doped BaSO₄ guidestar particles under UV illumination, showing their red photoluminescence. We will use these particles during the initial testing and feasibility demonstration of the proposed microscope.

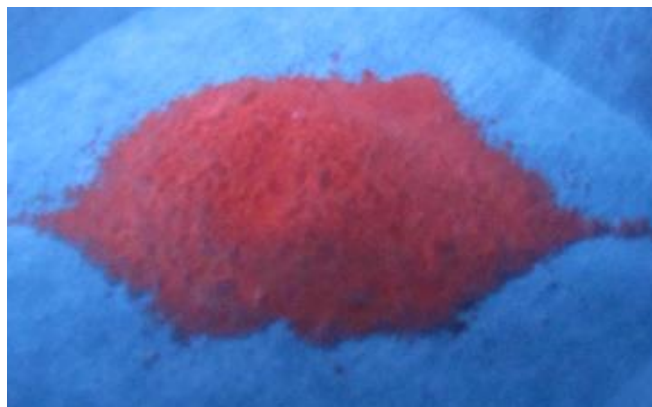


Figure 62. Image of Eu:BaSO₄ guidestar particles under UV light, resulting in red photoluminescence.

Figure 63 shows the photoluminescence and Raman spectra of the Eu:BaSO₄ guidestar particles, outside a scattering sample. These spectra will serve as references for the subsequent subsurface measurements.

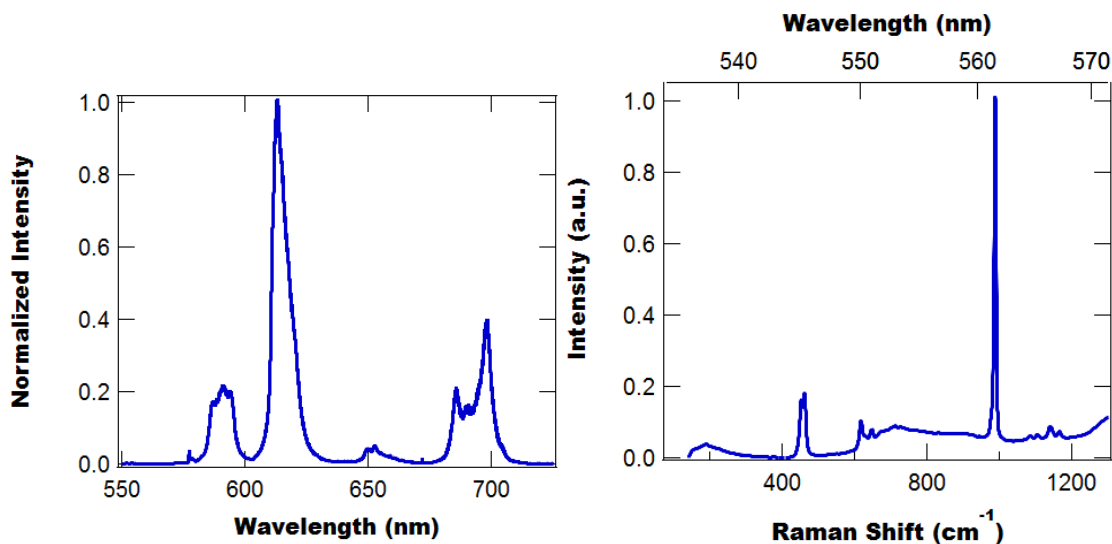


Figure 63. Photoluminescence spectrum (left) and Raman spectrum (right) of Eu:BaSO₄ guidestar particles, acquired using a 532 nm laser.

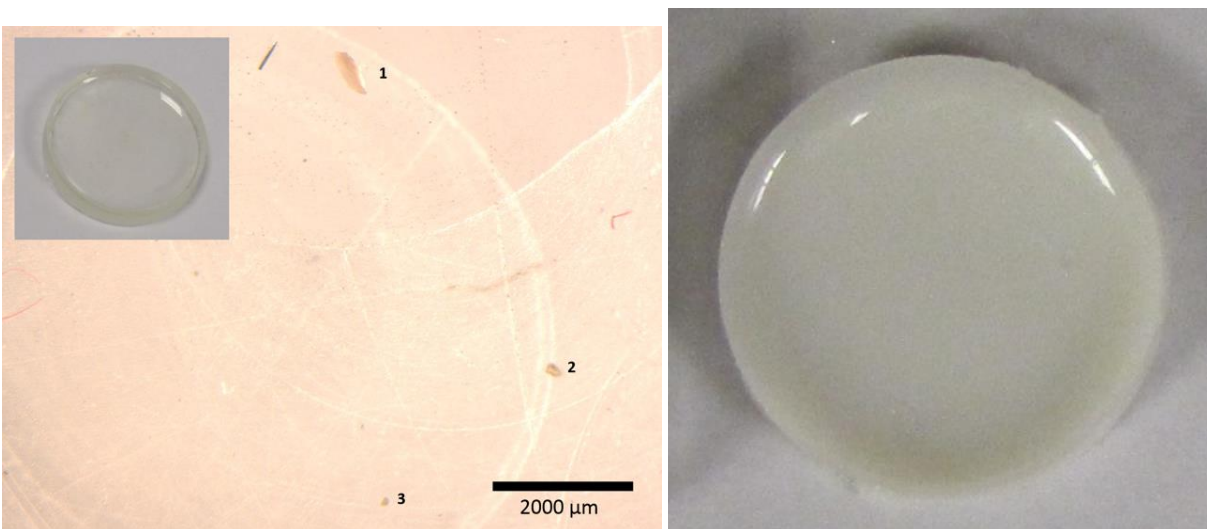


Figure 64. Images of two individual Eu:BaSO₄ guidestar particles (left) and guidestar mixed with scattering particles (right) in an HTPB matrix.

Raman Spectra of Possible Guidestars

To demonstrate subsurface Raman spectroscopy, we need to identify an ideal Guidestar material, which possessed strong Raman scattering with well-defined peaks. Therefore, we measured the Raman spectra of multiple different crystalline materials that are well known hosts for Eu ions (which can act as fluorescent guidestars). Figure 65 shows example spectra from the materials using 532 nm excitation. Based on these measurements and the observed PL intensity of the Eu-doped versions of these materials we determine that Eu:Y(acac)₃(DPEPO) (YAD) is currently the best guidestar material.

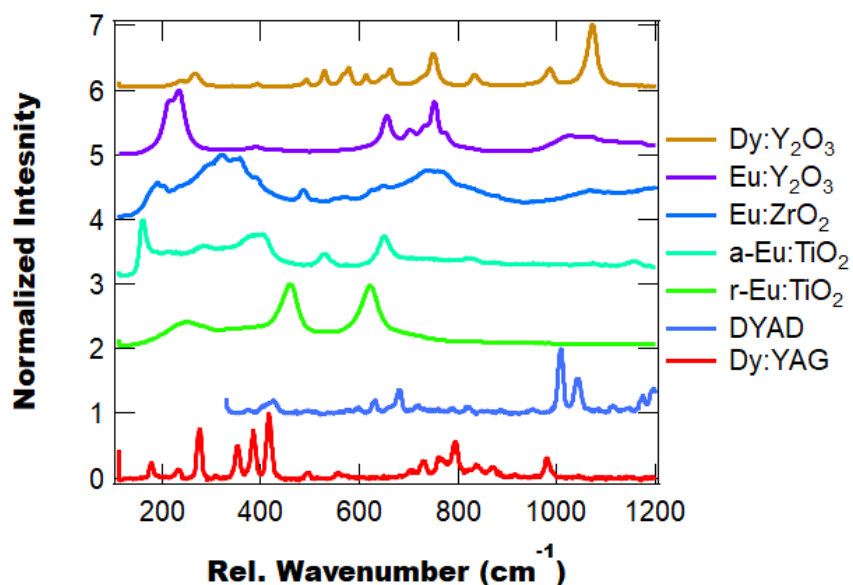


Figure 65. Raman/fluorescence spectra of different particles tested for use as guidestars using 532 nm excitation.

11. APPENDIX D: ALTERNATIVE GUIDESTAR MATERIAL

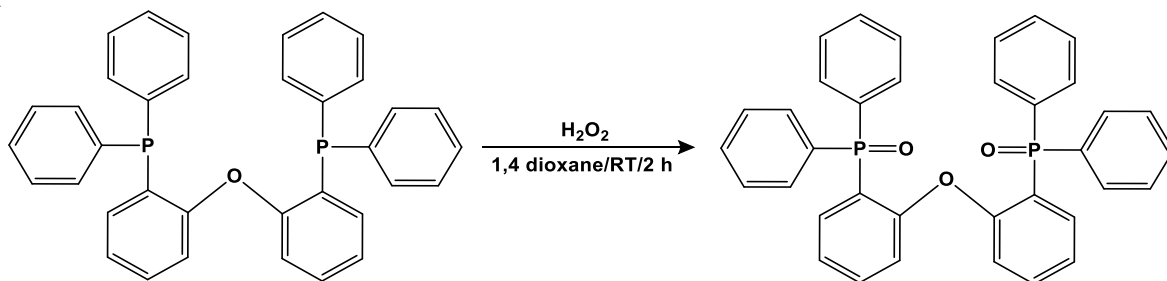
With the objective of finding molecular crystals that would decompose at a lower temperature, we prepared EYHD and performed various characterizations.

Synthesis of EYHD Molecular Crystals

Table 5 shows an overview for the synthesis procedure for EYHD molecular crystals. DPEPO is first prepared as shown in step 1. The DPEPO is then combined with the lanthanide nitrates, hexafluoroacetylacetone (hfa) in step 2.

Table 5. Synthesis routes for (Step 1) DPEPO and (Step 2) EYHD.

Step 1



Step 2

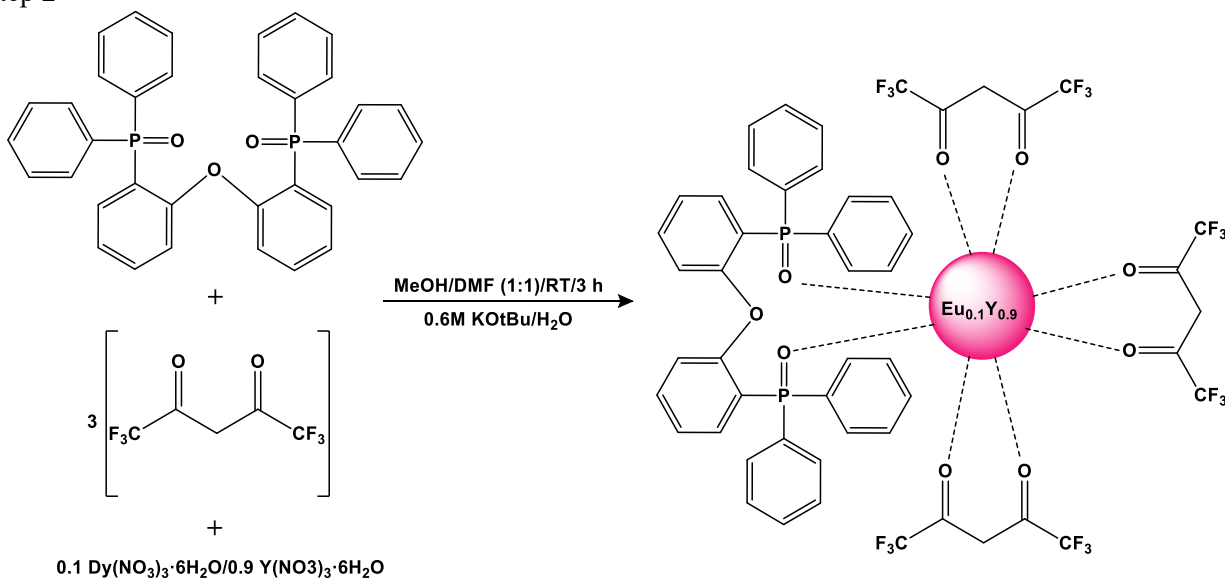


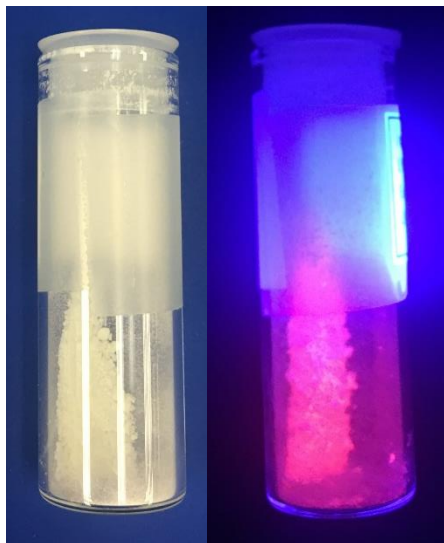
Table **6** indicates chemicals required for the synthesis Bis[2-(diphenylphosphino)phenyl] ether oxide (DPEPO).

Table 6. Chemicals needed for the synthesis of DPEPO.

	30% H ₂ O ₂	bis(2-diphenylphosphino)-phenyl)ether)
<i>Mn</i>	34.01	538.55
<i>moles</i>	0.08925	0.0425
<i>Mole ratio</i>	2.1	1
<i>Concn. (M)</i>	1.05	0.5
<i>Solvent (L)</i>	0.085	
	1,4-dioxane	
<i>Amt.</i>	8.500	22.888
	in mL	in g

To begin the DPEPO synthesis, bis(2-diphenylphosphino)phenyl ether is dissolved in 1,4-dioxane. The stirring solution is cooled down in an ice bath in an oversized flask. Once the solution is fully cooled down 30% hydrogen peroxide solution is added dropwise while stirring until a white suspension is obtained and is stirred for an additional 2-3 hours. Chloroform is added to extract the white product, bis(2-diphenylphosphino)phenyl ether oxide (DPEPO). The DPEPO dissolved in chloroform is washed three times and the aqueous layer is separated from the organic layer using a separatory funnel and then dried with 3% w/v MgSO₄ that is removed by filtration. The chloroform is evaporated to yield white crystals that are then crushed with a mortar and pestle and stored in a vial.

The Eu:Y(hfa)₃(DPEPO), which is called EYHD, is prepared by first dissolving Eu(NO₃)₃·5 H₂O/Y(NO₃)₃·6 H₂O (0.02 M), DPEPO (0.02 M), and hexafluoroacetylacetone, (hfa) (0.06 M) in a dimethylformamide/methanol mixture (1:1 vol/vol ratio). We then add an equi-volume aqueous solution of KO^tBu (0.06 M), which causes the product to precipitate. The suspension is allowed to age for 3 h, after which the precipitates are isolated using centrifugation (6000 rpm for 1 min). With the precipitates isolated we dry them in a vacuum oven at 353.15 K for ≈12 h and stored in a vial (Figure 66).

**Figure 66.** EYHD molecular crystals.

The EYHD product was measured using Fourier transform infrared spectroscopy with attenuated total internal reflectance (FTIR-ATR) to verify that the desired material is obtained (see Figure 67). The IR spectra of the EYHD and DPEPO are almost similar, however, the EYHD displays absorption peaks $\nu(\text{C}=\text{O}) \sim 1629 \text{ cm}^{-1}$. Additionally, the peak at 660 cm^{-1} may indicate an Ln(3+) center. For the EYHD, there are

also additional absorption peaks at $\nu \sim 1525 \text{ cm}^{-1}$ and $\nu \sim 2925 \text{ cm}^{-1}$.

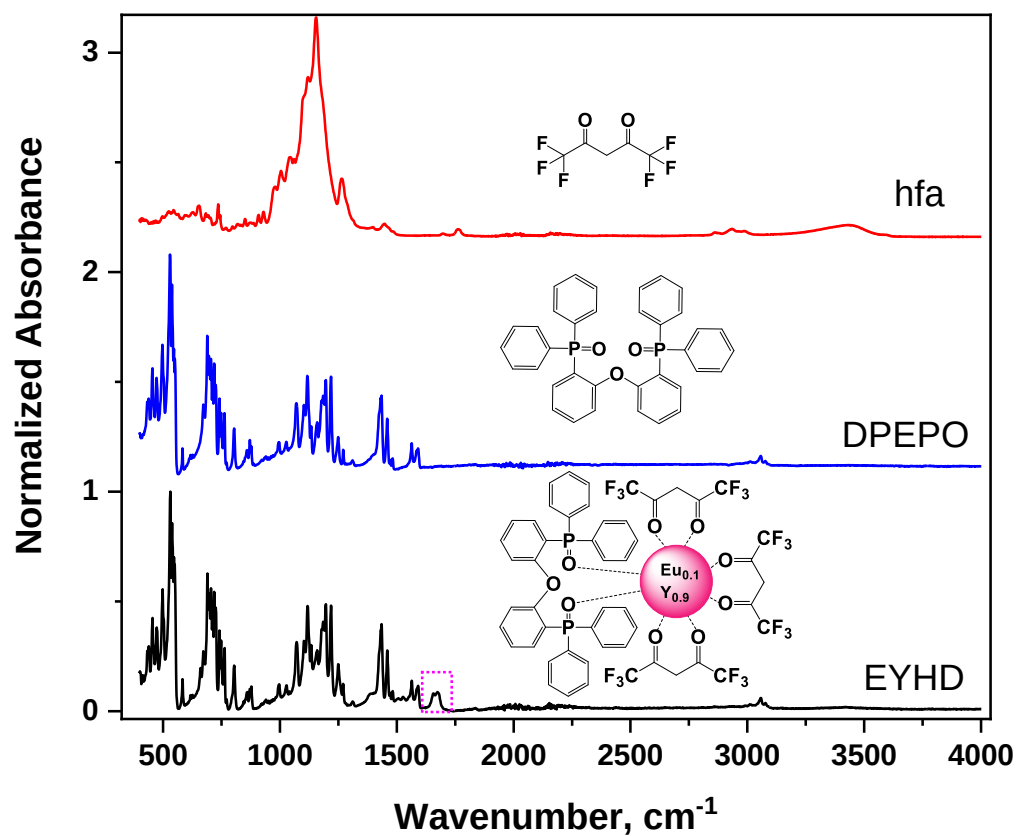


Figure 67. FTIR-ATR spectra of DPEPO, $[\text{Eu}(\text{hfa})_3\text{DPEPO}]$ and hexafluoroacetylacetone between $400\text{-}4000 \text{ cm}^{-1}$.

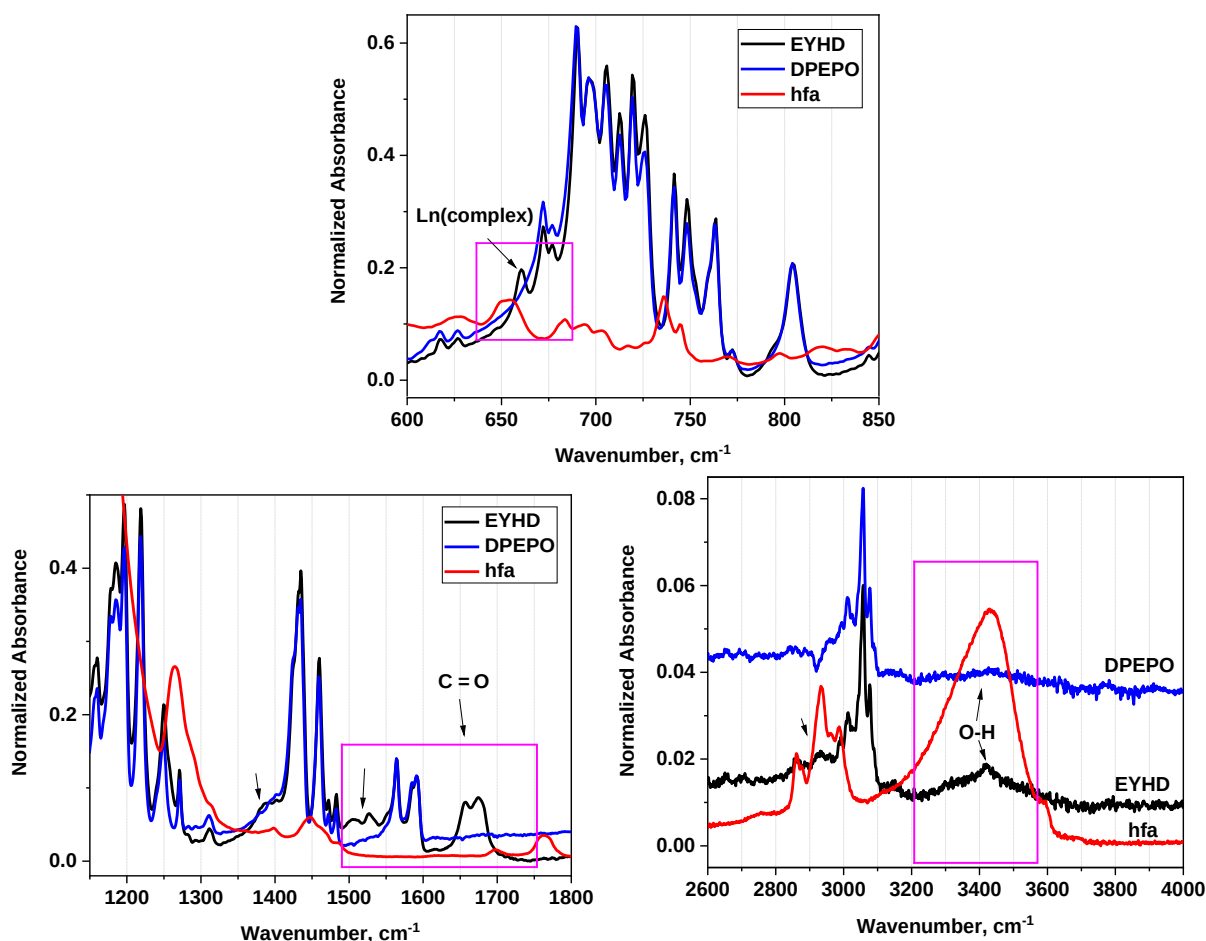


Figure 68. FTIR-ATR spectra of DPEPO, [Eu(hfa)3DPEPO] and hexafluoroacetylacetone magnified views in the ranges between 600-850 cm^{-1} (top), 1150-1800 cm^{-1} (left) and 2600-4000 cm^{-1} (right).

DSC/TGA data for EYAD and EYHD

Simultaneous thermal analysis (STA) or differential scanning calorimetry measured simultaneously with thermal gravimetry (DSC/TG) of EYAD and EYHD was performed. Plots of DSC, TG, and differential thermal gravimetry (DTG) are shown in Figure 69 (synthesis and SEM analysis reported on previously for EYAD). We observe melting (T_m) occurring at approximately 386.15-394.15 K and 527.15-553.15 K and decomposition occurring at 548.15-587.15 K (T_{d1})/588-638.15 K (T_{d2}) and 727.15-773.15 K (T_d), respectively, for EYAD and EYHD, indicating EYHD is more thermally stable than EYAD. There is a two-step decomposition for EYAD and a single-step decomposition for EYHD and the residual masses of 40% and 15%, respectively, for EYAD and EYHD, most likely begin to undergo crystallization which give rise to an exothermic trend in the DSC curves. DSC, TG and DTG obtained for EYHD and EYAD are plotted for comparison in Figure 70.

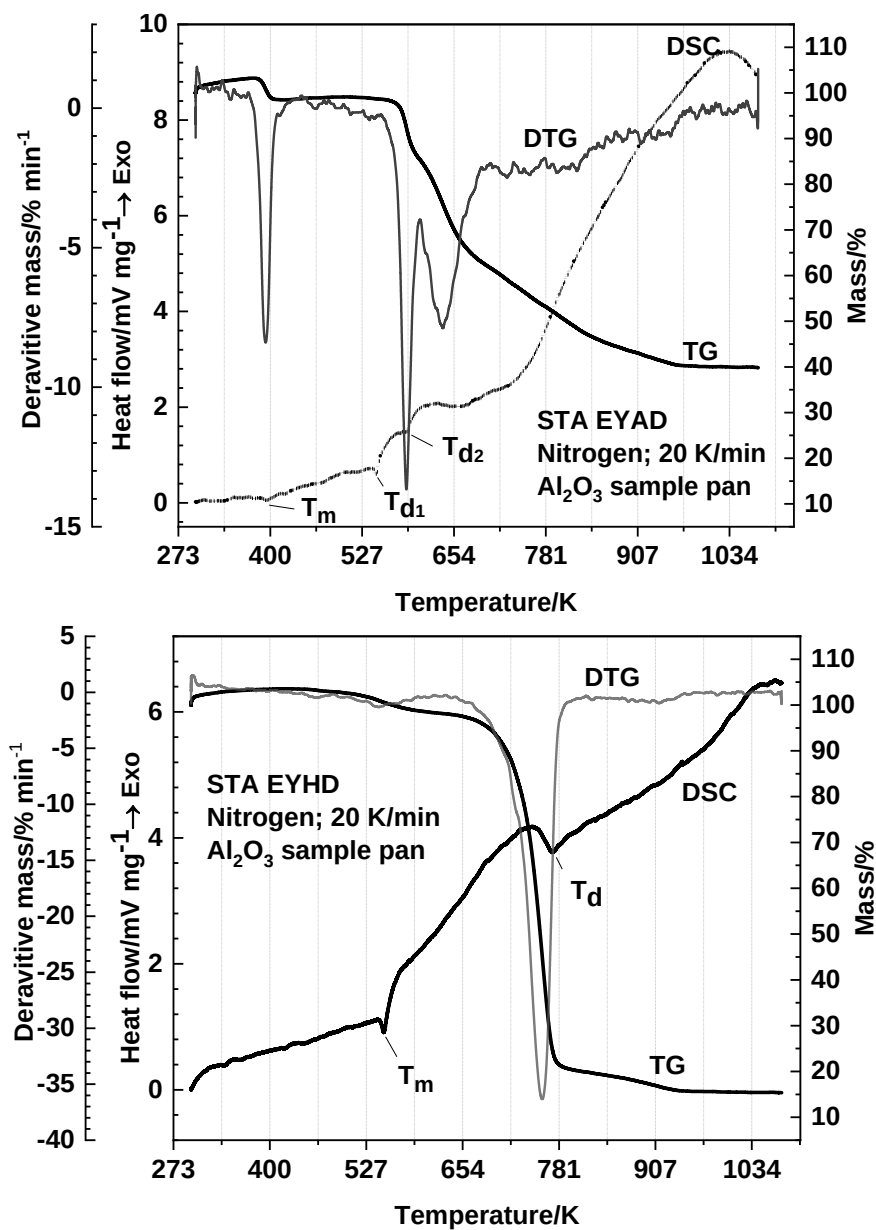


Figure 69. STA of EYAD (top) and EYHD (bottom), 40 ml min⁻¹ nitrogen, 20 K min⁻¹ from 298.15 to 1073.15 K and ~3 mg sample masses.

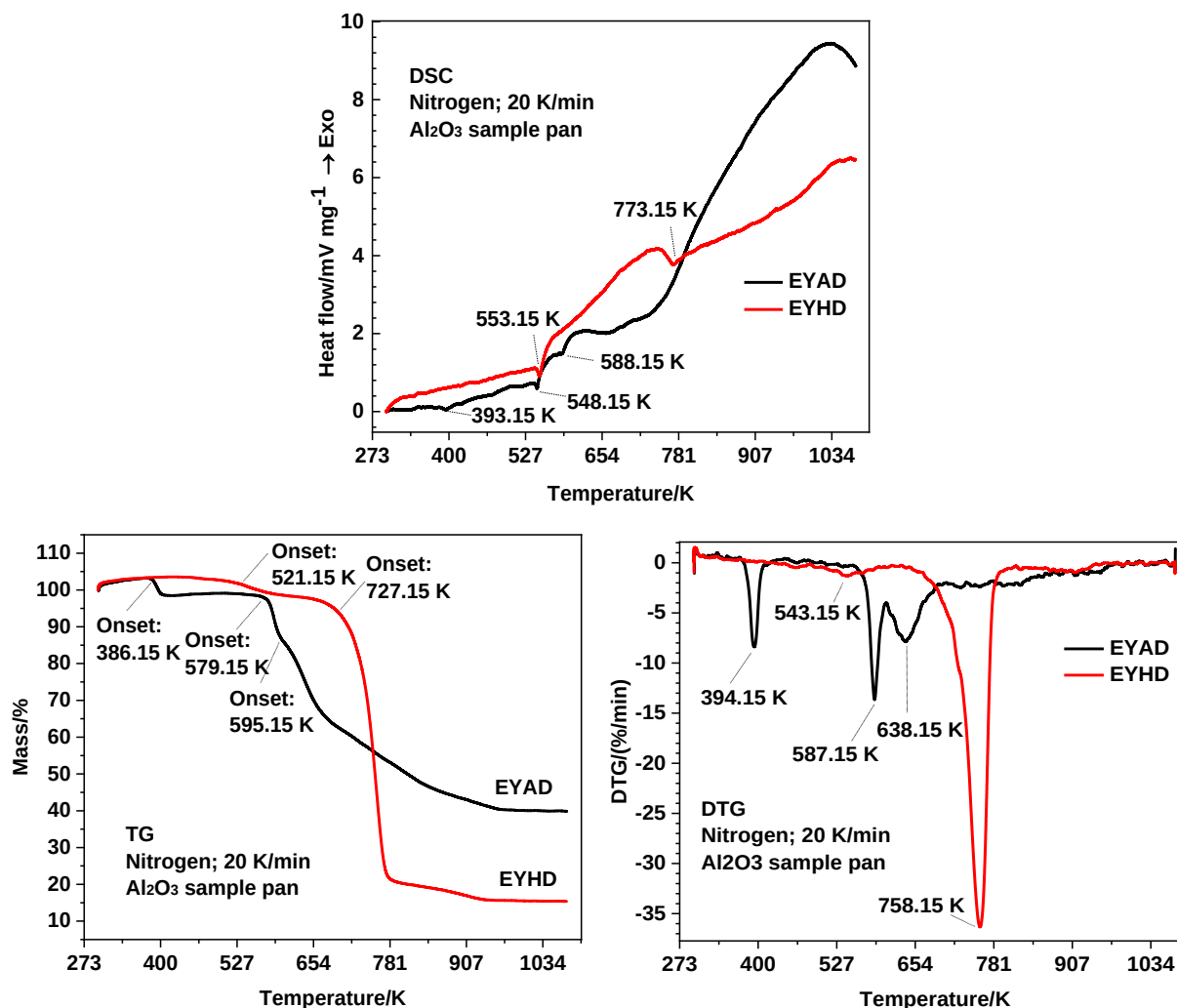


Figure 70. DSC and TG and DTG comparison for EYAD and EYHD (same conditions as above).

SEM-EDX Analysis of EYHD

For a visual understanding of the as-synthesized EYHD, SEM images are shown in Figure 71. Crystals are observed for the as-synthesized EYHD with an average length of 7 μm . EDX analysis was carried out to identify the various elements present in the complex. Figure 72 shows the EDX data in wt% from the indicated sites of interest on the surface of EYHD crystals. The spectra indicate the presence of C, O, F, Eu and P (or Y). Yttria is difficult to observe in low concentration due to overlapping phosphorus. With the presence of these combine elements on the surface of the EYAD crystals, we can use this information to corroborate the successful synthesis of the complex.

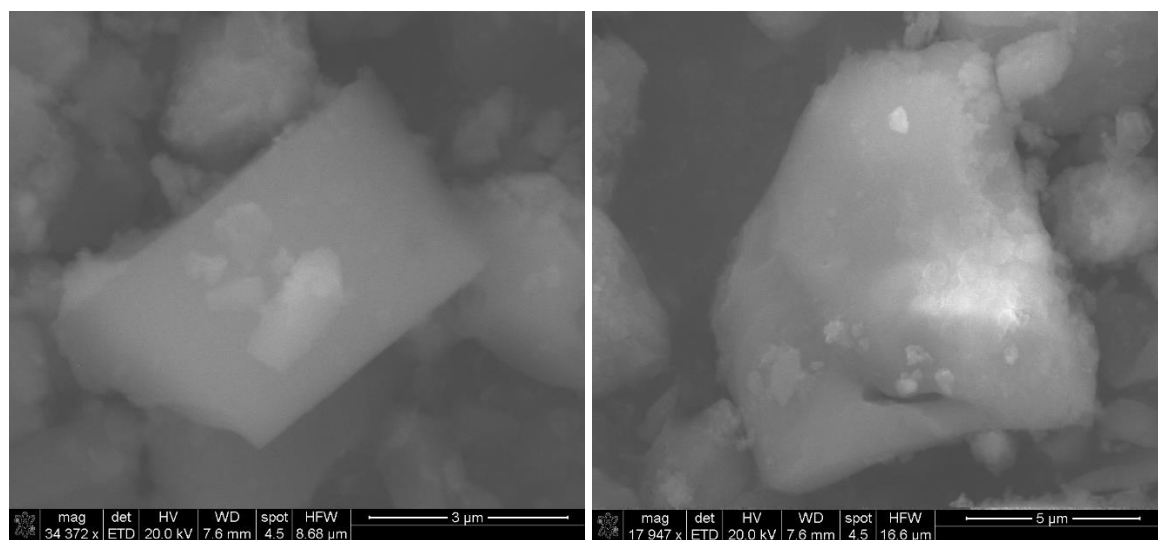
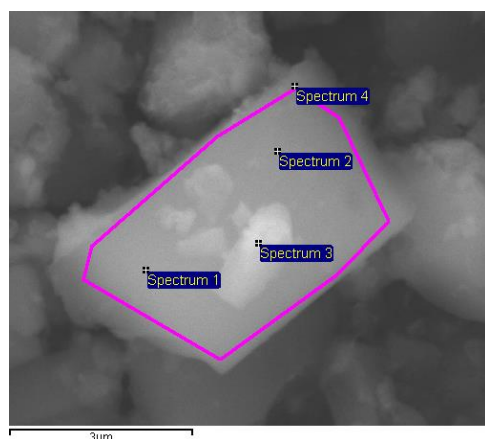
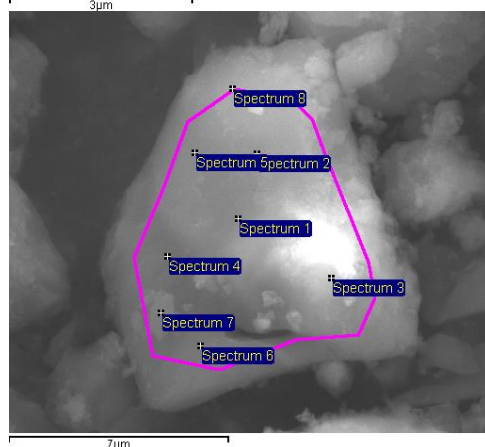


Figure 71. SEM images of as-synthesized EYHD.



Spectrum	In stats.	C	O	F	P	Eu	Total
Spectrum 1	Yes	77.92	14.05	1.85	5.97	0.21	100.00
Spectrum 2	Yes	77.70	15.37	1.82	4.75	0.37	100.00
Spectrum 3	Yes	76.87	15.89	2.31	4.56	0.37	100.00
Spectrum 4	Yes	77.18	14.73	2.49	5.30	0.31	100.00
Mean		77.42	15.01	2.12	5.14	0.31	100.00
Std. deviation		0.48	0.79	0.33	0.63	0.08	
Max.		77.92	15.89	2.49	5.97	0.37	
Min.		76.87	14.05	1.82	4.56	0.21	



Spectrum	In stats.	C	O	F	P	Eu	Total
Spectrum 1	Yes	77.72	8.37	0.91	12.62	0.38	100.00
Spectrum 2	Yes	78.30	9.36	0.89	11.20	0.26	100.00
Spectrum 3	Yes	75.79	12.04	3.32	8.18	0.67	100.00
Spectrum 4	Yes	77.50	7.48	0.51	14.03	0.48	100.00
Spectrum 5	Yes	79.54	7.93	0.88	11.27	0.38	100.00
Spectrum 6	Yes	78.21	12.49	0.69	8.42	0.18	100.00
Spectrum 7	Yes	75.84	9.63	0.74	13.06	0.73	100.00
Spectrum 8	Yes	75.56	11.43	2.86	9.39	0.76	100.00
Mean		77.31	9.84	1.35	11.02	0.48	100.00
Std. deviation		1.44	1.93	1.09	2.18	0.22	
Max.		79.54	12.49	3.32	14.03	0.76	
Min.		75.56	7.48	0.51	8.18	0.18	

Figure 72. EDX spectra of as-synthesized EYHD (all results in wt%).

EYHD PL and Raman Spectra

In addition to FTIR characterization, we also measure EYHD's PL and Raman spectra, which are shown in Figure 73 along with comparison data from EYAD.

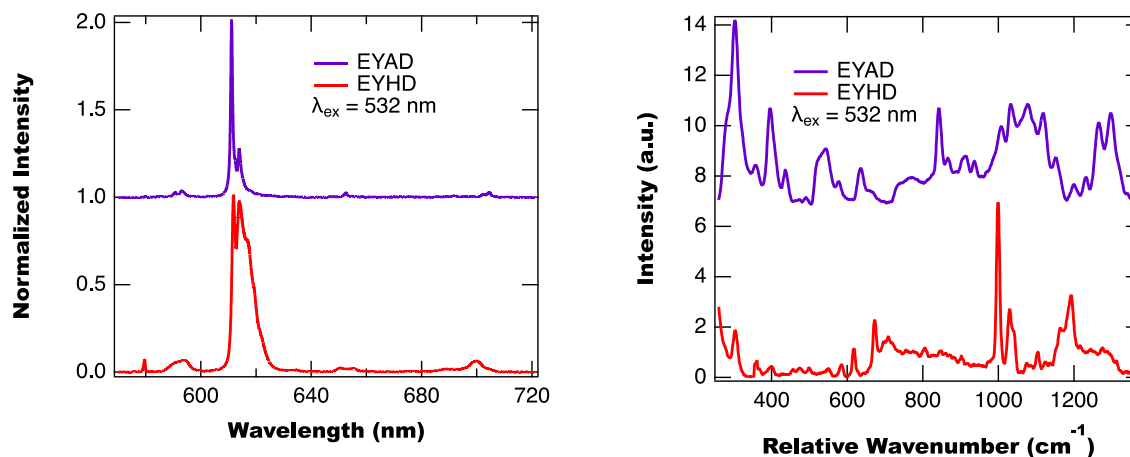


Figure 73. Comparison of PL (a) and Raman/PL (b) spectra for EYAD and EYHD.

EYHD Summary

We synthesized EYHD and characterized the properties of EYHD with FTIR, STA, SEM/EDS and PL. It was found that the EYHD had a higher thermal stability than EYAD and for this reason EYAD was the preferred molecular crystal.