Optical and Electrochemical Characteristics of Organic Pigments Derived from Naturally-Occurring Fungi

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ABSTRACT

Organic semiconductors are materials of interest due to their potential for producing lower-cost, flexible, wearable, and sustainable optoelectronic devices. Most of these organics are artificially synthesized, leaving further room for improving sustainability through exploration of materials which can be derived from naturally-sourced products. Our focus is two organic pigments, dramada and xylindein, which can be extracted from fungi native to Oregon, *Scytalidium cuboideum* and *Chlorociboria* spp., respectively. In this multidisciplinary project, we study optical and electrochemical characteristics of these materials, as well as investigate their potential for the formation of microcavity exciton-polaritons. We find that both pigments exhibit signatures of polariton formation. Dramada exhibits pH-dependent optical properties, whereas xylindein shows redox reaction behavior, undergoing a marked reversible shift in its absorbance (color) under different voltage bias. Lastly, we observe that dramada fibers exhibit mechanical flexibility and optical waveguide behavior, which could warrant further study for photonic applications.

Keywords: nature-derived pigments, optical properties, electrochemical properties, strong coupling, waveguiding

1. INTRODUCTION

While much success has been achieved with traditional, inorganic semiconductors, interest in organic semiconductors has offered solutions to some common problems. Organic materials are typically cheaper and more sustainable, solution processability makes organics easier to work with in manufacturing, molecular modification allows for many organics to have tunability in their properties, and some unique properties of organics have opened the door to new potential applications, including their use on devices that would require flexible or wearable substrates. However, there are issues that have hindered their adoption. Organic materials often suffer from low stability with respect to environmental factors, and their (opto)electronic properties have not reached fundamental limits due to detrimental effects of disorder, defects, and trade-offs in structure-property relationships. Moreover, the degree of sustainability of most organic semiconductors is limited due to the synthesis procedures that often require hazardous reactants to create or that produce hazardous biproducts.[1,2] Therefore, the discovery of new sustainable materials and new routes to control optoelectronic phenomena is an important goal for enhancing the functionality and viability of organic materials.

One of the promising routes for enhancing optoelectronic properties utilizes strong light-matter interactions (polariton formation) to enable, for example, polariton-mediated long-range energy transfer.[3] Exciton-polaritons are quasiparticles that inherit attractive properties from their constituent components,[4] such as a low effective mass due to its photonic component while also having the ability to interact with external fields and other quasiparticles due to its excitonic component, which is attractive for applications. Polariton formation can be observed when excitons couple to a strong electric field produced by photons confined in an optical microcavity.

Towards improving sustainability of organic functional materials and exploring polariton-mediated routes of control over their (opto)electronic properties, here we investigate organic pigments–xylindein and dramada (which has also been

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referred to as Draconin Red [5])–derived from Oregon-native spalting fungi *Chlorociboria* spp. and *Scytalidium cuboideum*, respectively. These pigments exhibit extraordinary stability necessitated by their biological functionality, as compared to benchmark synthetic organic semiconductors.[6,7] We report on optical and electrochemical characteristics of the pigments in solutions, evaluate their potential for exciton-polariton formation in films placed in optical microcavities, and investigate optical waveguiding properties in dramada crystals and fibers.

2. METHODS

Pigment preparation

Xylindein extracted from *Chlorociboria* spp. in dichloromethane (DCM) was filtered through VWR 410 filter paper (1 μm particle retention) to remove impurities. Filtered pigment was added to a flat-bottom round flask and attached to a Buchi Rotavapor R-300. 1 L of pigment in solvent was evaporated until between 25-50 mL remained in the flaks. The remainder was transferred to 25 mL vials and evaporated until no solvent remained. This left solid pigment on the side of the glass vials. Dried pigment vials were filled with 20 mL ethanol and ultrasonicated for 100 minutes to create a suspension of solid pigment aggregates in the solvent. Vials were removed from the Ultrasonicator and each shaken by hand for 1 minute or until all aggregates were suspended in ethanol. The mixture was filtered through VWR 415 filter paper (25 μm particle retention) and aggregates rinsed with ethanol 3 times. Aggregates were allowed to dry and then removed from filter paper with forceps.

Dramada pigment extracted from *Scytalidium cuboideum* in acetone was filtered through VWR 410 filter paper (1 μm particle retention) to remove impurities. 500 mL of pigment in solvent was placed into a flat-bottom round flask and evaporated in a Buchi Rotary Evaporator. Once the majority of solvent was evaporated, additional pigment in solvent was added to flask. This process was repeated until crystals began to form and cover the side of the flask. Samples were then filtered in solvent through VWR 415 filter paper to collect crystals. Crystals were allowed to dry and then removed from paper with forceps.

Characterization

Solutions were prepared by dissolving xylindein in chloroform or dramada in acetone and sonicated for 30 minutes. Both pigments have relatively low saturation points in most solvents,[8] with xylindein saturating at concentrations of approximately 3 mM in chloroform and dramada at approximately 5 mM in acetone.

To test the sensitivity of optical absorption spectra of dramada to pH, small quantities of 1M sulfuric acid or 1M potassium hydroxide were added to solutions of dramada to raise or lower the pH, respectively. The solution pH was approximated using VWR pH-test 0-14 strips. For absorption measurements, solutions were diluted with acetone to approximately 50 μM concentration and the pH was retested. All solution and film absorption measurements were conducted following methodology described in our previous work.[9-11]

Electrochemistry

To measure electrochemical characteristics, xylindein solution mixed with N-methyl-2-pyrrolidone (NMP) was drop cast onto an indium tin oxide (ITO) substrate and baked for 30 minutes. Cyclic voltammetry (CV) measurements were conducted in a three-electrode configuration.

Optical Microcavities

The microcavities consisted of five layers deposited on a glass substrate, as shown in Figure 3a. First, 200 nm of silver was thermally evaporated onto a glass substrate to create an opaque bottom mirror. A layer of silicon nitride was then sputtered on top of the bottom mirror to create the lower spacer layer. Next, the organic layer was deposited by static spin casting a pigment/polymethylmethacrylate (PMMA) solution on the lower spacer layer. Another layer of silicon nitride was sputtered on top of the organic layer with equal thickness as the lower spacer layer to create the upper spacer layer. Lastly, a 45 nm of silver was thermally evaporated on the upper spacer layer to form a semi-transparent top mirror which would allow incident light into the microcavity and confining the majority of the photons within the cavity.

We determined the total microcavity thickness such that the resonant photonic fundamental ($\lambda/2$) mode is close to the exciton energy in the organic layer. For angle-resolved reflectance measurements, which were performed following the

methods described by Puro et. al.,[12] cavities were fabricated with the photon resonance energies at normal incidence slightly below the organic exciton energy (i.e., negatively-detuned). Since low saturation points of pigment solutions created an upper limit on the thickness of the organic layer, the two silicon nitride spacer layers of equal thickness above and below the organic layer ensured the appropriate cavity thickness while placing the organic layer in the region where the electric field was maximized (Figure 3a, right). The thickness of each spacer layer was determined such that two of these spacer layers plus the organic layer would have the correct optical path length to create the $\lambda/2$ microcavity, with spacer layers in the range of 10-50 nm per layer tested.

To maximize the organic layer thickness and improve the photon-exciton coupling, we prepared solutions at saturation concentration, 3 mM xylindein in chloroform and 5 mM dramada in acetone. To vary the average intermolecular spacing between organic molecules while having control over the thickness of the organic layer, PMMA was added to organic solutions following the methods detailed by Van Schenck et. al.[10] Average intermolecular spacings between the pigment molecules in the range of 1-2 nm were tested. Solutions were either dynamic- or static-spin cast with speeds ranging between 600-5000 rpm.

The dramada cavity which showed the strongest exciton-photon interaction had silicon nitride spacer layers of 12.2 nm each and featured a dramada/PMMA film with 1.75 nm intermolecular spacing static-spin cast at 1400 rpm. Xylindein cavities generally required thicker spacer layers and lower spin casting speeds due to the longer wavelength exciton (~1.79 eV, or ~690 nm) and slightly lower solution concentration; the best xylindein cavity had silicon nitride spacer layers of 40 nm each and xylindein/PMMA film with 1.9 nm intermolecular spacing static-spin cast at 800 rpm, which was the limit of producing films of mostly-uniform thickness necessary for cavities. While lower intermolecular spacings are generally preferred to increase the molecular density of molecules involved in coupling, these also produced thinner organic layers.

Waveguides

Dramada can crystallize into a variety of crystal types. We used the slow diffusion technique, where the organic dissolved in a strong solvent is placed within a sealed container in open-air contact with a poor solvent as outlined by Torres-Moya et. al. [13] to reliably grow longer one-dimensional (1D) dramada crystals to test as optical waveguides. This method provided better control over the solution evaporation rate, allowing us to more precisely adjust the rate and direction of crystal growth. This allowed us to isolate the crystal growth type, as well as produce higher quality crystals for study. Controlled slow diffusion using 5 mM dramada dissolved in acetone as the stronger solvent and acetonitrile, toluene, or deionized water as the weaker solvent allowed dramada to self-assemble into 1D needle-like crystals up to 8 mm in length.

3. RESULTS AND DISCUSSION

pH-dependent optical properties

Purified dramada solutions, which typically present with a deep orange-red color (Figure 1c, left), have contributions from both the para-symmetric and para-antisymmetric tautomers (Figure 1a,b) to the absorption spectra with about 60:40 ratio [7]. These contributions result in the superposition of two vibronic progressions which comprise the overall solution absorption spectrum (Figure 1e, green). This is similar to xylindein (Figure 2a), which also exhibits contributions of two tautomers (at a ~70:30 ratio) to the absorption spectrum.[6] Dramada solutions with pH < 7 show no observable change either qualitatively in the color or quantitatively in the absorbance spectrum. In contrast, solutions with pH > 7 show a notable shift in color (Figure 1d) from red (pH $\leq$ 7) to magenta (pH 9-10) to purple (pH $\geq$ 12). These correspond to a substantial redshift of up to 50 nm (0.19 eV) in the absorbance spectrum, the degree of which is determined by the pH value (Figure 1e). Also notable is the relative change in the spectral shape (oscillator strengths for various transitions) as the pH increases.

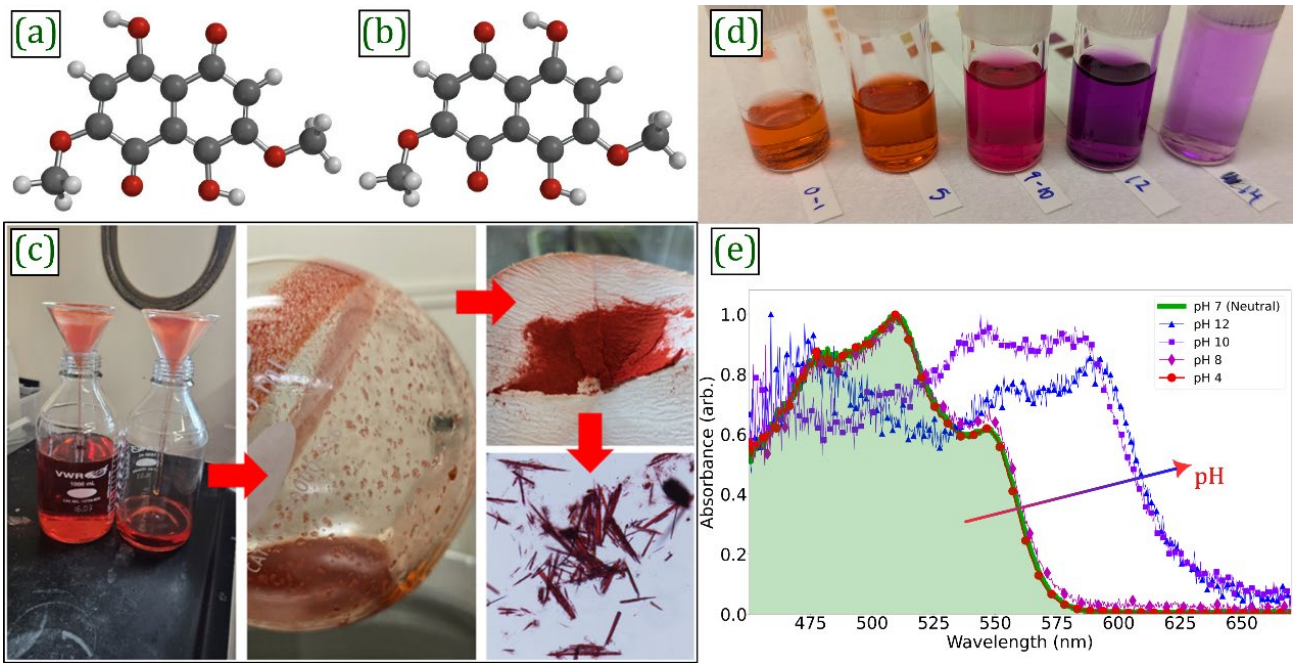

Figure 1. Pigment preparation and characterization. Molecular models of the (a) para-antisymmetric and (b) para-symmetric tautomers of dramada which are both present in solutions. (c) Purification and solidification of extracted pigment for further study. (d) Pigment color changes as pH increases but remains consistent as pH is lowered from neutral. (d) Corresponding absorbance spectrum: the low pH spectrum is similar to the neutral-pH dramada solution spectrum; the pH increase results in a ~50 nm redshift.

This behavior is consistent with previous observations in xylindein:[14] raising the pH of xylindein solutions resulted in a substantial absorbance spectrum redshift. Using DFT calculations, this redshift behavior was found to be in close agreement with a doubly-deprotonated form of xylindein; the presence of a strong base strips off the weakly-bound hydrogens that would produce the two tautomers and allow the pigment to undergo excited-state intramolecular proton transfer (ESIPT). [14] The presence of two co-existing tautomers based on the positioning of the hydrogens and the ability to undergo ESIPT is similar between xylindein and dramada.[7] Additionally, just like in xylindein solutions, absorption redshift was previously observed in dramada in water as compared to that in DCM and attributed to a partial deprotonation of the pigment.[7] Based on these considerations, we attribute the solution absorbance redshift in the presence of a strong base in Figure 1d to deprotonation of dramada.

Electrochemical properties

Electrochemical characterization of xylindein reveals a pronounced and highly responsive redox-dependent optical modulation. When thin xylindein films are deposited on transparent conductive substrates and subjected to bias within a moderate voltage window, they exhibit a fully reversible color evolution from green to yellow and back to green, as evidenced by cyclic voltammetry measurements and in situ optical imaging (Figure 2b). Absorbance spectra for both blue-green and yellow films were measured (Figure 2c), with the recovered blue-green film absorbance being indistinguishable from the original film absorbance aside from a few lingering yellow spots that did not fully revert (Figure 2b, right inset). Absorbance redshift in Figure 2b was also similar to that previously observed for xylindein deprotonation, which may indicate that both proton and electron transfer occur simultaneously or a part of the same process under these conditions.[14] Yellow films were observed to slowly revert to blue-green over a period of hours without external influence. The consistent and repeatable nature of this transition underscores the stability of the underlying redox processes and highlights that optical absorption characteristics of xylindein are highly sensitive to its redox states. Dramada was also tested but did not exhibit the electrochemically induced color changes under the same conditions.

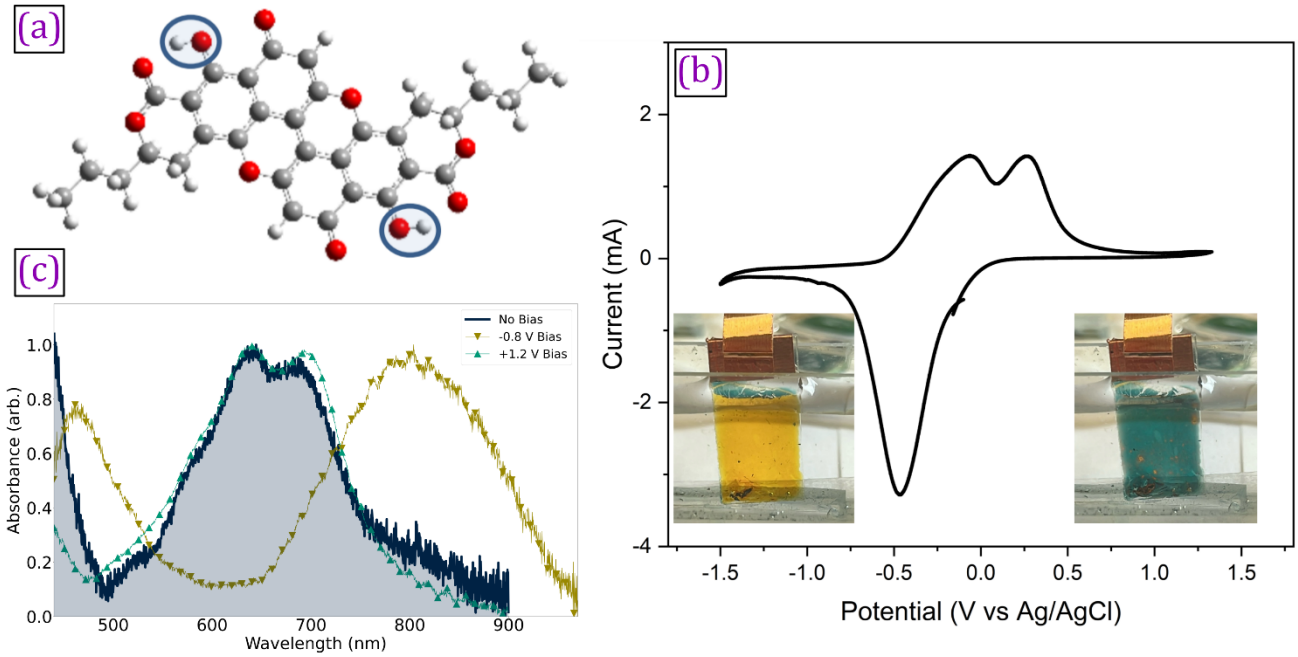

Figure 2. Electrochemical behavior of xylindein. (a) Molecular structure of one tautomer of xylindein; another tautomer is present in solutions and films with the circled hydrogens at different bond angles. (b) Cyclic voltammetry curve for xylindein, which starts as a blue-green film; insets show the transition to a yellow film (bottom left) under negative bias, which reverts to blue-green (bottom right) under positive bias. (c) Film absorbance spectra for xylindein: the original film undergoes a notable redshift under negative voltage bias (yellow film), then blueshifts back to nearly the same absorption spectrum under a positive voltage bias (blue-green film).

Optical Microcavities

Figure 3b shows the angle-resolved reflectance for a negatively detuned dramada cavity. The cavity exhibits three dispersive features due to lower, middle, and upper polariton (LP, MP, and UP, respectively, in Figure 3d). The fit to the coupled oscillator model[10] revealed the coupling of cavity photon to two excitons with energies at 2.41 eV (513 nm) and 2.64 eV (469 nm) with coupling strengths $2V$ of 53 meV and 119 meV (Table 1). The coupling strength did not follow the expected scaling with the oscillator strength ($2V \sim \sqrt{f}$) based on the solution spectra, which could be caused by the preferential cavity photon coupling to particular molecular populations (e.g. fluorescent nanocrystals) as has been observed in organic films with co-existing amorphous and crystalline phases placed in cavities.[10]

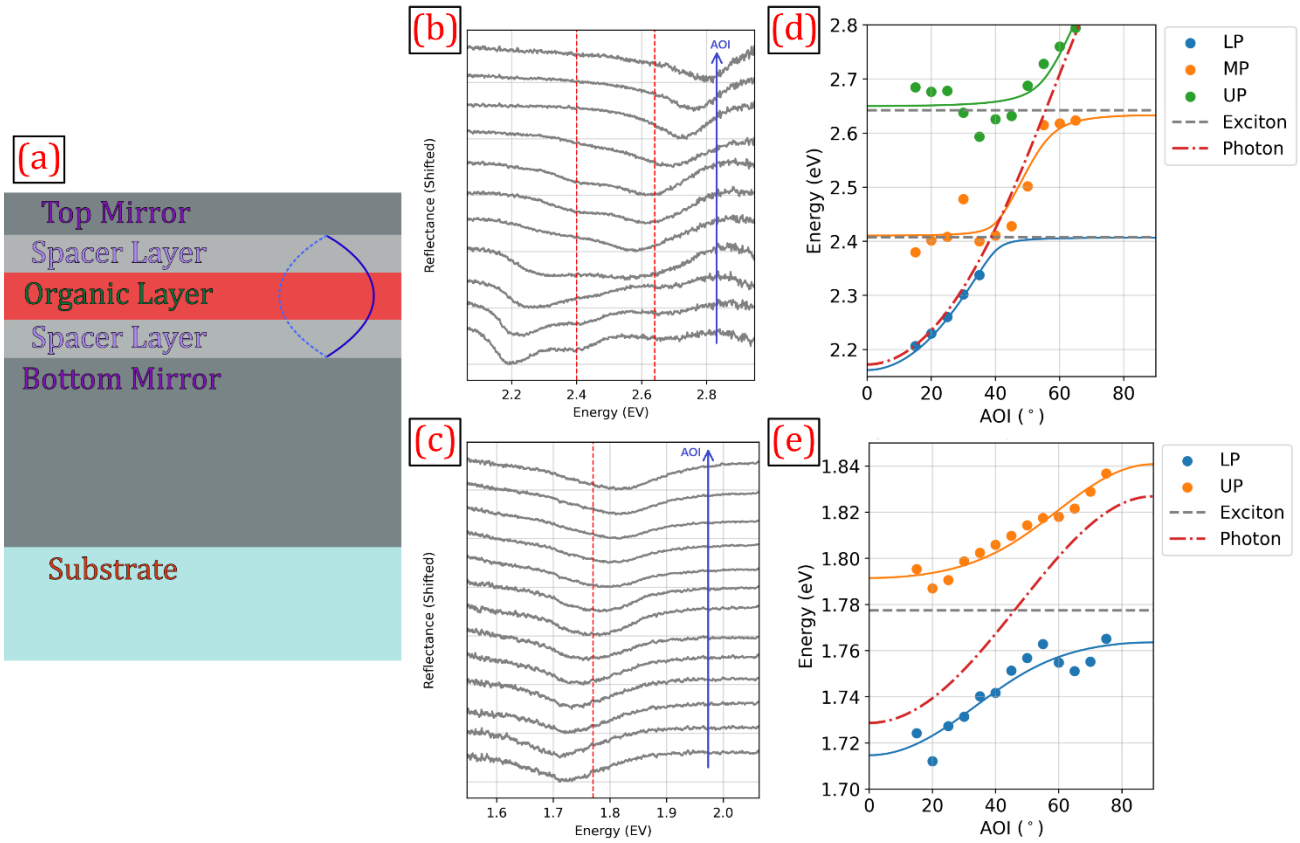

Figure 3. Fungal pigments in optical cavities. (a) Geometry of λ/2 microcavity: light able to pass through the thin silver top mirror is confined within the cavity; the organic layer is placed in the peak of the electric field using silicon nitride spacer layers, allowing the excitons to couple with the photonic cavity mode (fundamental mode shown in blue on right). Shifted reflectance spectra as a function of photon energy are shown for (b) dramada and (c) xylindein, with increasing angle of incidence (AOI) from bottom-to-top; vertical red dashed lines indicate the calculated exciton energies. Reflectance dip energies (points) are plotted as a function of AOI for (d) dramada and (e) xylindein, with fits to the coupled oscillators model shown as lines. Exciton (gray) and photon (red) energies are also included; fit parameters calculated from these data are given in Table 1.

Peak splitting with the coupling strength $2V$ of 59 meV was also observed from xylindein microcavities (Figure 3c), and the measured dispersion for two peaks followed the expected dispersion for an upper and lower polariton (UP and LP in Figure 3d). However, xylindein films feature two transitions with similar oscillator strengths (Figure 2c), and why the coupling occurs only to one exciton (1.78 eV, or 695 nm), why it is considerably weaker than that in, e.g., TIPS-pentacene films in microcavities,[10] and whether the ultrafast ESIPT is responsible for the observed behavior are currently unknown and requires further investigation.

Fit Parameter	Dramada	Xylindein
Exciton Energy (E_x)	2.41 eV, 2.64 eV	1.78 eV
Coupling Strength ($2V$)	53 meV, 119 meV	59 meV
Effective refractive index (n_{eff})	1.45	3.09

Table 1. Coupled oscillators model fit parameters extracted from dispersion data in Figure 3d,e.

Optical Waveguiding

While xylindein preferentially forms porous amorphous structures[15] and does not readily produce crystals, dramada is prone to crystallization and produces a variety of crystal types with absorption edge ranging from 500-575 nm and drastically different photoluminescence (PL) quantum yields, depending on the growth conditions. Most methods of

dramada deposition from solution resulted in a blend of these crystal types, making it difficult to isolate a particular crystal type for individual study. Nevertheless, we identified one particular dramada crystal type, a fluorescent, needle-like crystal, to exhibit the ability to act as a 1D waveguide, which creates opportunities for photonic applications. Under 532 nm excitation, these fluorescent crystals were observed to transmit the excitation light and PL emission along the crystal farther than 3 mm, the maximum distance observable on our current optical microscopy setup (Figure 4a). The absorbance spectrum for this type of crystal (Figure 4b) is remarkably different from the solution absorbance.

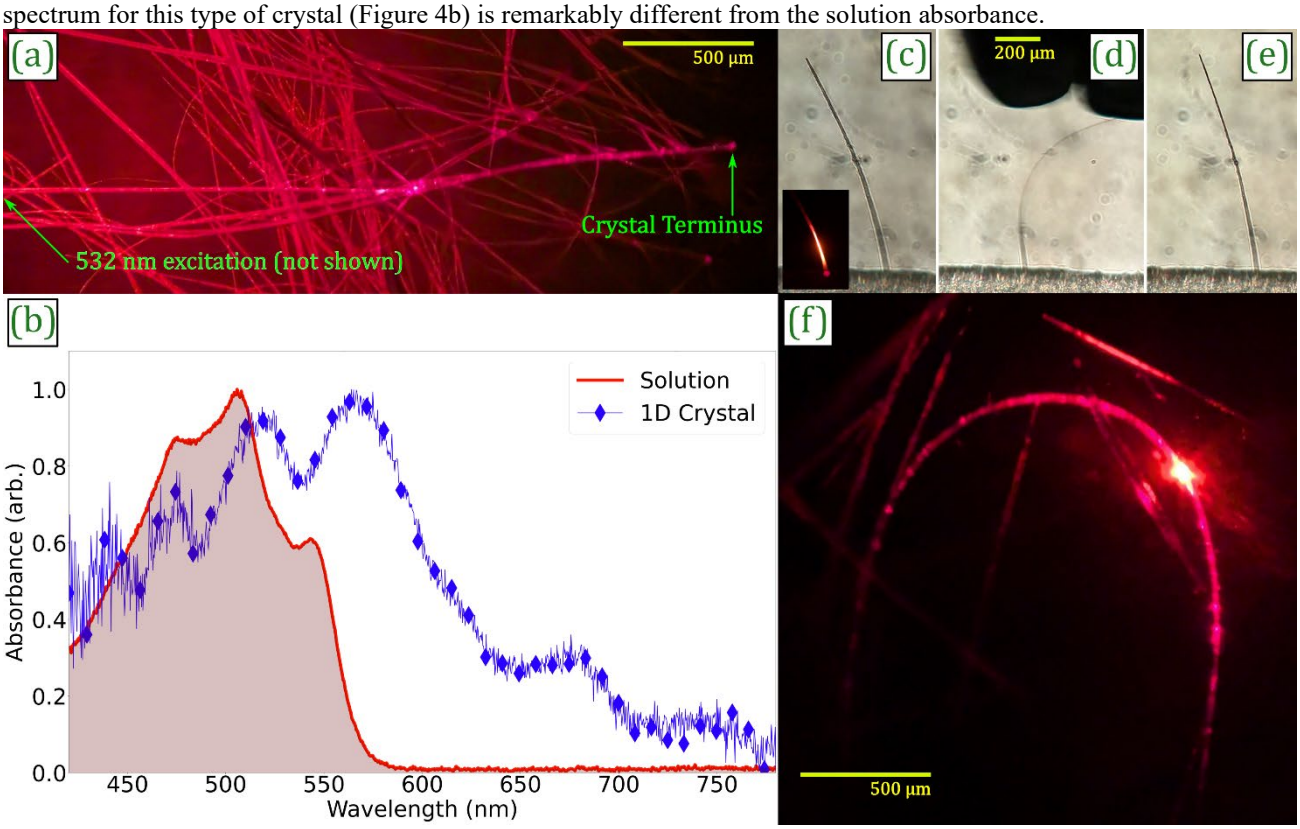

Figure 4. Dramada 1D crystal properties. (a) Optical waveguiding in a dramada fluorescent 1D crystal; excitation source is a 532 nm laser, which was directed onto the crystal outside the viewable area. (b) Absorption spectrum of dramada 1D crystals versus dilute solution absorption. (c) A 1-mm-long dramada fiber on tape; inset shows PL under 532 nm to confirm crystal type. (d) These fluorescent fibers show mechanical flexibility when a force is applied. (e) The fiber returns to its original shape when force is no longer applied. (f) The curved fibers are also able to act as optical waveguides.

While the majority of dramada crystals of this type were straight, some crystals were fiber-like, with a varying degree of curvature (Figure 4f). These fibers exhibited similar waveguiding ability, with excitation and PL directed along the curved fiber. Initial tests have shown that these fibers exhibit some degree of flexibility: a slightly curved 1-mm-long fiber (Figure 4c) has been observed to bend under pressure against the direction of its natural curvature to a radius of curvature less than 400 µm without breaking (Figure 4d). Further, these fibers appear to have some degree of shape memory, as this fiber naturally returned to its original shape once the force was no longer being applied (Figure 4e). Work on quantifying structure-property relationships and waveguiding properties depending on the mechanical deformation of these fluorescent fibers is currently underway.

4. CONCLUSIONS

We identified several properties of fungi-derived pigments xylindein and dramada that are promising for applications. Dramada in solution exhibits strong pH dependence of optical absorption and associated color change. Additionally, dramada crystallizes into fibers that exhibit mechanical flexibility and optical waveguiding, which await quantitative assessment. Xylindein exhibits redox reactions accompanied by a color change, which establishes this pigment as a compelling model platform for exploring charge-induced color tuning in organic semiconductors and naturally derived pigment systems. Continuing efforts aim to quantitatively assess switching kinetics, track detailed spectral evolution, and evaluate long-term cycling behavior, thereby deepening our understanding of xylindein's distinctive redox–optical

response and clarifying its potential for broader technological application. Both pigments exhibit signatures of polariton formation in the microcavities, but more work is necessary to understand the factors limiting the exciton-photon coupling strength.

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REFERENCES

[1] N. Romanova, V. Leont'ev, and A. Khrekin, "Production of commercial naphthalene by coal-tar processing", Coke and Chemistry 61, 453–456 (2018).
[2] Ramesh, A., Archibong, A. E., Hood, D. B., Guo, Z., and Loganathan, B. G., "Global environmental distribution and human health effects of polycyclic aromatic hydrocarbons", Global contamination trends of persistent organic chemicals 63, 97-126 (2011).
[3] O. Ostroverkhova, W. Goldthwaite, and R. Lamug, "Excitons and polaritons in singlet fission materials: photophysics, photochemistry, and optoelectronics", MRS Bulletin 49, 873–884 (2024).
[4] R. Bhuyan, J. Mony, O. Kotov, G. W. Castellanos, J. Gomez Rivas, T. O. Shegai, and K. Borjesson, "The rise and current status of polaritonic photochemistry and photophysics", Chemical Reviews 123, 10877–10919 (2023).
[5] E. M. Hinsch, G. Weber, H.-L. Chen, and S. C. Robinson, "Colorfastness of extracted wood-staining fungal pigments on fabrics: a new potential for textile dyes", Journal of Textile and Apparel, Technology and Management 9 (2015).
[6] G. Giesbers, J. Van Schenck, A. Quinn, R. Van Court, S. V. Gutierrez, S. Robinson, and O. Ostroverkhova, "Xylindein: naturally produced fungal compound for sustainable (opto)electronics", ACS Omega 4, 13309-13318 (2019).
[7] T. Krueger, J. Solaris, L. Tang, L. Zhu, C. Webber, R. Van Court, S. Robinson, O. Ostroverkhova, and C. Fang, "Illuminating excited-state intramolecular proton transfer of a fungi-derived red pigment for sustainable functional materials", Journal of Physical Chemistry C 126, 459-477 (2022).
[8] G. Weber, H.-L. Chen, E. Hinsch, S. Freitas, and S. Robinson, "Pigments extracted from the wood-staining fungi chlorociboria aeruginosa, scytalidium cuboideum, and s. ganodermophthorum show potential for use as textile dyes", Coloration Technology 130, 445–452 (2014).
[9] J. Van Schenck, G. Mayonado, J. Anthony, M. Graham, and O. Ostroverkhova, "Molecular packing-dependent exciton dynamics in functionalized anthradithiophene derivatives: from solutions to crystals", The Journal of Chemical Physics 153, 164715 (2020).
[10] J. Van Schenck, W. Goldthwaite, R. Puro, J. Anthony, and O. Ostroverkhova, "Exciton polaritons reveal "hidden" populations in functionalized pentacene films", Journal of Physical Chemistry C 125, 27381-27393 (2021).
[11] W. Goldthwaite, E. Lambertson, M. Gragg, D. Windemuller, J. E. Anthony, T. Zuehlsdorff, and O. Ostroverkhova, "Morphology and crystal packing-dependent singlet fission and photodegradation in functionalized tetracene crystals and films", Journal of Chemical Physics 161, 194712 (2024).
[12] R. Puro, J. D. Van Schenck, R. Center, E. K. Holland, J. E. Anthony, and O. Ostroverkhova, "Exciton polariton-enhanced photodimerization of functionalized tetracene", Journal of Physical Chemistry C 125, 27072–27083 (2021).
[13] I. Torres-Moya, M. A. Uddin, S. Gamez-Valenzuela, J. Alvarez-Conde, J. Cabanillas-Gonzalez, A. L. Montero-Alejo, A. M. Rodriguez, L. A. Montero-Cabrera, M. C. R. Delgado, B. Gomez-Lor, and P. Prieto, "Experimental and theoretical insights into light confinement within 2d waveguides of alkylphenyl benzothiadiazole crystals", Journal of Materials Chemistry C 13, 17056–17066 (2025).
[14] T. Krueger, G. Giesbers, R. Van Court, L. Zhu, R. Kim, C. Beaudry, S. Robinson, O. Ostroverkhova, and C. Fang, "Ultrafast dynamics and photoresponse of a fungi-derived pigment xylindein from solution to thin films", Chemistry – A European Journal 27, 5627-5631 (2021).
[15] G. Giesbers, J. Van Schenck, S. V. Gutierrez, S. Robinson, and O. Ostroverkhova, "Fungi-derived pigments for sustainable organic (opto)electronics", MRS Advances 3, 3459-3464 (2018).