Enhanced Light Absorption in All-Polymer Biomimetic Photonic Structures by Near-Zero-Index Organic Matter

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Natural photosynthetic photonic nanostructures can show sophisticated light–matter interactions including enhanced light absorption by slow light even for highly pigmented systems. Beyond fundamental biology aspects, these natural nanostructures are very attractive as blueprints for advanced photonic devices. But the soft-matter biomimetic implementations of such nanostructures is challenging due to the low refractive index contrast of most organic photonic structures. Excitonic organic materials with near-zero index (NZI) optical properties allow overcoming these bottlenecks. Here, it is demonstrated that the combination of NZI thin films with photonic multilayers like the ones found in nature enables broadband tunable strong reflectance as well as slow light absorption enhancement and tailored photoluminescence properties in the full VIS spectrum. Moreover, it is shown that this complex optical response is tunable, paving the way toward the development of active devices based on all-polymer and near-zero index materials photonic structures.

1. Introduction

The control of light absorption is crucial for photosynthesis, the process by which light energy is transformed into chemical energy by phototrophic organisms. However, the lack of detailed optical descriptions for such complex natural photonic systems has made it difficult to address the photonic phenomena in photosynthetic membranes.[1] Natural photonic structures provide a mechanism by which higher plants and other living organisms are able to manipulate light at the nanoscale beyond the intrinsic properties of the organic compounds. It was recently discovered that some higher plants present sophisticated hierarchical photonic multilayer structures in their photosynthetic membranes (thylakoids), known as iridoplasts, that can serve to adapt light absorption capabilities to the spectral distribution available in their environment.[2] Recent developments have demonstrated that the narrowband absorption spectrum of the pigments in photosynthetic membranes is key to achieving the near unity light-harvesting quantum efficiency[3] of photosynthesis. In addition, iridoplasts present a photonic crystal with a hierarchical distribution of thylakoids, providing photonic modes and narrow absorption bands simultaneously and in the same photosynthetic system.

In natural systems, the narrow absorption bands of thylakoids are provided by molecular aggregates embedded within the photosynthetic light harvesting apparatus.[4] In order to mimic the excitonic and photonic properties of photosynthetic membranes, it is necessary to realize hierarchical photonic structures with similar strong narrow absorption bands. Replicating these structures with soft matter materials with similar optical properties has not yet been achieved. In this context, J-aggregates have recently attracted much attention[5] due to their narrow absorption and emission properties being much closer to the natural counterpart in photosynthesis than other non-aggregating dyes. It was recently demonstrated that, with high levels of aggregation, certain J-aggregates present narrow absorption and emission bands[6,7] that, as we show in this work, correspond to refractive indices that are close to zero. Interestingly, the refractive index properties shown by thin films of J-aggregates embedded in polymeric matrices can approach values suitable for near-zero index materials (NZI).[8–12]
Epsilon-near-zero (ENZ) media are those that present a spectral region in which the real part of the dielectric function may cross zero (\(\text{Re}(\varepsilon)\)) ≈ 1. Interestingly, under certain conditions, not only can the permittivity achieve vanishing values but also the refractive index can be reduced to near zero (\(n = 0\)) given that \(n = \sqrt{\varepsilon \mu}\) and \(\mu = 1\) for homogenous materials in the optical regime. These NZI materials\[^{[13]}\] have to present finite losses to maintain causality.\[^{[12]}\] Interestingly, NZI conditions can be realized in many different systems, including metals, doped semiconductors, photonic materials, or structured materials.\[^{[13,14]}\] These materials present a refractive index (\(n\)) close to zero with characteristic values in the order of \(n = 0.5 + 2i\) for metals.\[^{[13]}\] For materials which the optical properties can be described by a Lorentz model\[^{[9,14]}\] like the ones used in this work, the NZI spectral region will occur close to the anomalous dispersion region and the narrowband absorption of the material.

Their inherent strong dispersion in a narrow spectral range provides these materials with unique features such as strong phase velocity divergences or large electric field enhancements\[^{[15,16]}\] making them attractive in a wide range of applications\[^{[13]}\] particularly as emission control and extreme nonlinear interactions.\[^{[18]}\] Most realizations of NZI materials make use of metal nanostructures showing strong optical resonances to electric field oscillations through engineered plasmonic properties.\[^{[14]}\] These building blocks can be integrated in more complex structures such as to form an effective medium with tunable NZI properties in the visible to infrared range.\[^{[13]}\] Mixing NZI materials with a positive permittivity material (e.g., a dielectric) in a periodic arrangement has been used to form a photonic structure with enhanced NZI properties. This approach has recently been proposed to be capable of providing a superabsorbing close-to-darkest material in simple multilayer structures formed by ITO/TIO pairs.\[^{[19]}\] However, NZI implementations with highly processable, low-loss, or loss-free and largely tunable materials are still to be developed.

Here, we propose and show experimentally that iridoplasts can work as a blueprint for the implementation of a photonic structure in which NZI properties are enhanced by the photonic multilayer designed to tailor absorption at wavelengths well off the narrow absorption maximum. We do this by doping polymer layers with J-aggregates and forming a Bragg stack similar to the distribution of photosynthetic pigments in iridoplasts. We demonstrate that the combination of the NZI properties of the J-aggregate layers with the biomimetic photonic structuring allows for enhanced absorption at particular wavelengths. These wavelengths can be selected by choosing the appropriate multilayer periodicity, allowing tunability, while the NZI material provides photonic bandgap splitting close to the resonance. We also demonstrate that the slow light effects\[^{[20]}\] described for iridoplasts in the natural system can be engineered in an all-polymeric NZI system to obtain strong tunable off-resonance absorption which opens the way for the use of all organic NZI materials in several fields. Finally, we show that photoemission of the biomimetic iridoplast is tailored by the photonic dispersion bands of the heterostructure. This is, to the best of our knowledge, the first all-organic structure fabricated to demonstrate light absorption enhancement by slow light, induced by near-zero index organic materials.

2. Results and Discussion

2.1. Theoretical Description

Iridoplasts are natural Distributed Bragg Reflectors (DBR) where the thylakoid membranes containing photosynthetic chromophores are evenly separated by the stroma, a homogeneous nonabsorbing protein-rich aqueous medium.\[^{[21]}\] The distance between thylakoids is appropriate to create a photonic stopband in the visible range. To mimic the iridoplasm we consider here a 1D photonic crystal composed of 16 unit cells, each formed by a pair of polymer thin films (i.e., 32 layers in total), as shown in Figure 1a. One of the polymer thin films is nondoped polystyrene (PS), which will play the role of the stroma, the homogeneous layers of the natural system. PS was selected due to its ease of processing and well established optical properties as a dielectric (Figure 1b). The second constituent of the unit cell is an organic excitonic dye-doped polymer film. We selected the cyanine dye known as TDBC that can be assembled into a J-aggregate form in which the exciton delocalization makes them the most suitable candidates as biomimetic photosynthetic chromophores.\[^{[22]}\] Moreover, since TDBC is stable in aqueous solutions, polyvinyl alcohol (PVA) is used as a polymer host-matrix.

J-aggregates are supramolecular structures with a narrow absorption band of around 10 nm in width. We can therefore consider a generic description of a material doped with J-aggregates as a highly dispersive material modeled by a Lorentz oscillator with a strong exciton transition at the central vacuum frequency \(\omega_0\).

\[
\varepsilon_r(\omega) = \varepsilon_* + \frac{\varepsilon_0 \omega_0^2}{\omega_i^2 - \omega^2 - i\gamma_0 \omega}
\]

where \(\omega\) is the working frequency, \(\omega_0\) is the Lorentz oscillator strength, \(\gamma_0\) is the damping rate, and \(\varepsilon_*\) is the permittivity at high energy, a term that considers the dielectric constant of the material hosting the excitonic species. Therefore, for off-resonance frequencies, the dielectric constant tends towards the constant value \(\varepsilon_*\) and it is strongly dispersive near the resonance. J-aggregates have been used in photonic structures, for example, to present strong coupling with inorganic multilayers\[^{[24]}\] and to create all-polymer photonic cavities.\[^{[24]}\] Interestingly, the optical properties of films resulting from embedding TDBC into PVA can be modified as a function of the J-aggregate concentration on the final films obtaining films whose permittivity can reach ENZ values which correspond to a real part of the refractive index close to zero (below 0.5) in a bandwidth of tens of nanometers,\[^{[7,13]}\] hence making them suitable as NZI materials. These NZI optical properties are obtained in the case of highly doped films with very large oscillator strengths, as high as \(f = 0.4\), which provides a strong dispersive material.

Figure 1b shows the characteristic complex refractive index \((n = \sqrt{\varepsilon(\omega)}\) for highly concentrated TDBC-PVA according to literature, where the central wavelength is \(\lambda_c = 590\) nm (\(\omega_0 = 2.1\) eV) with an oscillator strength of \(f = 0.4\) and a damping rate of \(\gamma = 0.0658\) eV.\[^{[7]}\] For simulation purposes, we have considered \(\varepsilon_* = 2.25\) (equivalently \(n = 1.5\)) to represent the dielectric constant of PVA at high energies. Interestingly, in the anomalous
dispersion region, between 550 and 600 nm, the refractive index reaches very low \((n < 0.5)\) and very high \((n > 3)\) values below and above the excitonic resonance, respectively. Because of the very low refractive index, between \(\lambda = 550\) and 585 \(\text{nm}\), with values \(\approx 0.5\), we consider TDBC-PVA as a NZI \([8]\) in this range. Moreover, within this range, TDBC-PVA presents a negative dielectric constant, yielding metal-like optical properties (see Figure S1, Supporting Information, for reflection of TDBC-PVA slab).

In this work, we study how the photonic structure modifies the absorption of TDBC-PVA films when they are structured as a DBR, similarly to the natural system \([25]\). The main parameter determining the photonic properties of the biomimetic iridoplast is the period of the DBR structure. The thicknesses of PS and TDBC-PVA thin film are, respectively, called as \(d_{\text{PS}}\) and \(d_{\text{TDBC-PVA}}\); therefore, the period of the DBR is then \(\Delta = d_{\text{TDBC-PVA}} + d_{\text{PS}}\) (see Figure 1a). Importantly, any increase in \(d_{\text{TDBC-PVA}}\) will modify the absolute absorptance of each single TDBC-PVA layer by effectively introducing more absorbing materials into the final DBR and making the comparison between structures with different periods not straightforward. For this reason, we will vary the period \(\Delta\) of the structure (hence the position of the bandgap of the DBR) solely by varying the thickness \(d_{\text{PS}}\) of the nonabsorptive homogeneous material, while we maintain constant \(d_{\text{TDBC}}\) and hence the volume of absorptive material present in the dye doped layers (TDBC-PVA).

Using a transfer matrix method \([26]\) simulation (see the Experimental Section for more detail), we calculated the reflectance at normal incidence for a fully undoped DBR (16 pairs of PVA and PS, thickness 53 and 90 \(\text{nm}\), respectively) and a doped DBR with the same structure but using TDBC-PVA with oscillator strength \(f_0 = 0.4\) (Figure 1c). The reflectance of the undoped structure shows a strong reflectance peak that marks the spectral position of the photonic stopband \([26]\) given by the phase-matching condition (Note SII, Supporting Information). However, in the case of the doped DBR, two high reflectance bands are seen which can be associated with two different stopbands. We coin the terms \(\lambda^+\) and \(\lambda^-\) to identify the central wavelength of the stopband depending on whether it is in the spectral range below or above respectively of the anomalous dispersion region (550 < \(\lambda\) < 600 \(\text{nm}\)). These regions are represented in Figure 1c by the red and blue colors, respectively. Moreover, it is also remarkable that, for the \(\lambda^-\) region, the refractive index of TDBC-PVA film is below that one of the PS while, for the \(\lambda^+\) region, the opposite is true. In this example, for the doped DBR, the \(\lambda^-\) stopband is far from the anomalous dispersion region and, due to the increase in refractive index contrast \(\Delta n = n_{\text{PS}} - n_{\text{TDBC-PVA}}\), the absolute reflectance gets enhanced when compared to the undoped case, achieving over 80% reflectance. However, for the doped DBR in the \(\lambda^+\) stopband, the Bragg reflection is close to the excitonic resonance where absorptance is high which reduces the reflectance peak through damping.

Figure 1. Description and optical properties of the bioinspired DBR. a) Schematic of the Bragg mirrors composed by 16 pairs of two different materials: Polystyrene (PS) and TDBC-PVA. The TDBC-PVA thickness \(d_{\text{TDBC-PVA}}\) is kept constant at 53 \(\text{nm}\) while the PS thickness \(d_{\text{PS}}\) is varied. b) Complex refractive index \((n + ik)\) of TDBC-PVA and PS. Dashed gray line is the real part of PS (no imaginary component) obtained by ellipsometry. Black and blue lines represent the real and imaginary component of TDBC-PVA and the solid and dashed lines represent the theoretical [using Equation (1)] and experimentally measured using ellipsometry refractive index (see the Experimental Section). c) TMM calculated reflectance at normal incidence for undoped (red line) and doped (black line) DBR with \(d_{\text{PS}} = 90\) \(\text{nm}\). d) Normal incidence reflection of DBRs as a function of PS layer thickness. Red and black dashed lines represent photonic stopband central wavelength of un-doped and doped DBRs respectively obtained from dispersion equation solution (Note SII, Supporting Information). The white dashed horizontal line represents the cross-section plotted in (c) for \(d_{\text{PS}} = 90\) \(\text{nm}\).
By tuning the thickness of the PS layer (hence modifying period Δ), it is possible to shift the λs stopband of the DBR away from the anomalous dispersion band while pushing the λa stopband across the excitonic wavelength λexc = 590 nm.

Figure 1d shows a contour plot of the reflectance at normal incidence for a DBR with 16 layers of 53 nm of TDBC-PVA while the PS thickness is varied from 60 to 200 nm. We observe a clear dependence of the reflectance on the periodicity of the structure, with an anomalous reflection region near the resonance. Interestingly, for periods with 80 nm < dPS < 180 nm, the photonic stopband is strongly modified by the highly anomalous dispersion. Under these conditions, the highly dispersive nature of TDBC creates a narrow band of strong refractive index contrast on both sides of the exciton band, allowing therefore simultaneously existence of λa and λs. This phenomenon is corroborated by solving the dispersion equation (Note SII, Supporting Information) for dPS = 90 nm show the two stopbands centered at λa = 436 nm and λs = 604 nm. It can be observed that, at normal incidence, the electric field intensity distribution at the blue edge of the λa stopband (λ = 416 nm) shows a pseudostanding wave distribution which maximum field intensity is concentrated in the TDBC-PVA film (Figure 2b). On the other hand, for the red-edge of the λs stopband (λ = 467 nm) the maximum field intensity concentrates at the PS thin film. This is in agreement with slow-light properties for wavelengths at photonic stopband edges.[27] The strong reduction of group velocity at those spectral ranges produces a standing wave field intensity distribution within the photonic crystal, hence increasing light-matter interactions between those wavelengths. The electric field intensity concentrates in the higher refractive index regions for the low energy band edge of the photonic stopband while it concentrates in the lower refractive index regions for the high energy band edge.[27] If the standing wave concentrates in the absorptive material, light absorption will be enhanced as demonstrated with broad absorbers to increase the efficiency of solar cells[29] and sensors.[28] Figure 2 demonstrates that in the case of a very narrow absorption band (i.e., strong anomalous dispersion of the refractive) the absorption enhancement by slow light could also be fulfilled for wavelengths far from resonance. These properties are studied in detail in the last section of this paper. It is also noteworthy that, for a DBR with a long enough period, the stopband shifts toward wavelengths longer than the resonance (λa > λexc) making the refractive index contrast (Δn) change from positive to negative sign.
In that case, the maximum electric field intensity concentration at the lower energy stopband ($\lambda_\text{c}$) will occur within the PS thin layer instead of the TDBC-PVA as shown in the Figure S2 (Supporting Information). At the excitonic resonance ($\lambda_\text{exc} = 590$ nm), the electric field intensity distribution shows the characteristic exponential decay of a homogeneous absorbing medium.

Interestingly, it was recently proposed that natural iridoplasts might undergo self-tuning of the photonic properties to avoid photodamage. In this process, the period of the 1D photonic structures is modified to de-tune the photonic stopband from the absorption band of photosynthetic pigments.[25] The artificial iridoplast described above could be considered as a simplified scenario of the natural system where the use of an NZI building block is enabling to i) experimentally tune the photonic properties, ii) study light–matter interaction enhancement at different layers of the material, and iii) shift two stopbands simultaneously by simply varying the period of the system. Moreover, it is remarkable the higher refractive index contrast caused by the doping ($\Delta n_{\text{TDBC-PVA-PVA}} > 1.8$ for every wavelength except at the resonance) allows for a stronger reflection (~90%) than in the non-doped system (30%, Figure 1c) providing a strong advantage for applications where large photonic strength is required. These properties open endless technological possibilities for this type of structure making it possible to obtain strong narrow band reflectance at specific wavelengths with all polymer structures and only few layers.[29]

2.2. Experimental

To demonstrate the feasibility of the NZI biomimetic iridoplast described above, a methodology was developed for the fabrication of excitonic all-organic multilayers at different periods (see the Experimental Section). Each sample is formed by 32 layers (N) with 16 of PS and 16 of TDBC doped PVA. All samples were done starting (on glass) with PS and alternating with TDBC-PVA doped layers. The thickness of the TDBC-PVA layer is maintained constant for all layers and samples at 53 nm. Therefore, the period and bandgap of the DBR structure changed as a function of the PS thickness (see Figure S3, Supporting Information). However, as the number of layers of TDBC-PVA and their thickness is the same between samples, the total concentration of absorptive molecules is also the same between samples independently of the period. The thickness of the PS layer is varied from 88 to 154 nm: 88 ($\Delta_0 = 141$ nm), 100 ($\Delta_0 = 153$ nm), 105 ($\Delta_0 = 158$ nm), 129 ($\Delta_0 = 182$ nm), 147 ($\Delta_0 = 200$ nm), and 154 nm ($\Delta_0 = 207$ nm). The reference sample is a TDBC-PVA pseudo-slab structure ($\Delta_0 = 0$) formed by 16 layers of TDBC-PVA of 53 nm, each separated by just $\approx 23$ nm of PS layer, thin enough to produce negligible photonic effects outside the resonance. The structure is therefore optically equivalent to a TDBC-PVA only slab with the same total concentration of absorptive molecules that are the same that in the DBR structures.

Figure 1b shows the TDBC-PVA and PS thin film optical properties obtained by ellipsometry (Woollam VASE Model, see the Experimental Section for more information). The experimental data obtained are in outstanding agreement with the theoretically calculated ones using Equation (1). While TDBC-PVA films show strong dispersive optical properties, PS films show a near-constant refractive index of value $\approx 1.6$. The refractive index of PS was also measured by ellipsometry and we always use this refractive index in the simulations. In contrast, we have used the theoretical TDBC-PVA refractive index on the previous simulations; however, from here onwards, we will always use the experimentally measured refractive indices for TDBC-PVA on all our simulations.

To analyze the absorptance of the biomimetic iridoplast, we measured reflectance ($R$) and transmission ($T$) over the same area of the samples. The absorptance at normal incidence can be calculated by $A = 1 - R - T$ assuming that scattering in other directions is negligible. To compare the absorptance quantitatively, we use the wavelength-dependent absorptance enhancement coefficient ($\gamma(\lambda)$) used in other studies[2,25] and obtained by

$$\gamma(\lambda)_{1,2,3} = \frac{A(\lambda)_{1,2,3}}{A_0(\lambda)}$$

where $A$ is the absorptance at normal incidence and the subcript numbers represent the samples with periods $\Delta_0$, $\Delta$, $\Delta_0$, etc. As a control for the absorptance of effective NZI material without photonic stopband ($A_0$), we consider the reference sample ($\Delta_0$). The $\gamma$ parameter is a powerful tool to understand the modifications that a particular photonic environment might induce over absorptance properties of the bulk materials. In the case of the NZI biomimetic iridoplast analyzed here, it allows for the comparison between the absorptance of a nonstructured TDVC-PVA thin film with a DBR containing exactly the same material thickness but distributed within the photonic DBR structure. Under this definition, one could find that a given DBR can present $\gamma > 1$ (enhanced absorptance) at a particular wavelength or $\gamma < 1$ (reduced absorptance).

By the naked eye, the samples fabricated present high uniformity as shown in Figure 3 and Figure S3 (Supporting Information). A change in color with the period between samples is visible not only to the naked eye but also in high-magnification images (Figure 3 and Figure S4, Supporting Information). Reflectance measurements at normal incidence corroborate the differences in the reflectivity color between samples. The theoretical reflectivity corresponds well to the experiments but with a wider bandwidth for $\lambda_c$, explaining why the photonic bandgap center in this range is slightly redder. The analysis of the reflectance over four points on the samples (see Figure S5, Supporting Information) showed minimal variation in the central wavelength of the photonic bandgap and absolute reflectance. This result highlights the robustness to disorder and homogeneity of the all-polymer excitonic DBRs. Moreover, as the period increases, the $\lambda_c$ stopband shifts away from the excitonic resonance. When the $\lambda_c$ stopband is outside the absorption region, the maximum absolute reflectance is achieved, with values close to 90%. In the case of the $\lambda_c$ stopband, when the period decreases, it shifts away from the excitonic resonance in the region where the absorptance is low; therefore the absolute reflectance also reaches values close to 100%. However, as $\lambda_c$ and $\lambda_e$ get closer to $\lambda_{\text{exc}}$, there is a damping on the absolute reflection associated to the absorptance peak of TDBC. The DBR with an intermediate
value for the DBR period, i.e., $\Delta_4$, shows the convergence of both stopbands around the exciton band with some features resembling those of a strong coupling regime under a classical description.\[^{[40]}\] The coupling regime achieved by the structures is out of the scope of this paper as we focus on how the strong dispersive optical properties of the TDBC-PVA plays a role in defining two high reflectance bands ($\lambda_+$ and $\lambda_-$) with enhanced absorption due to the inverse contrast of index of the pair of layers due to the increase of the refractive index contrast. When the period of the DBR is large enough ($\Delta_4$), a third stopband appears with central wavelength $\lambda_*$. Interestingly this new stopband only appears for samples with periods where the stopband of the undoped DBR cross the excitonic resonance. For small period samples, both $\lambda_*$ and $\lambda_*$ stopbands are degenerate, making them indistinguishable. However, as the period increases and the $\lambda_*$ stopband gets closer to the excitonic resonance, $\lambda_*$ and $\lambda_*$ split and the two stopbands become evident as in $\Delta_4$ (Figure 4). When the period of the DBR is large enough ($\Delta_4$), $\lambda_*$ and $\lambda_*$ start merging, particularly at small angles. For $\Delta_4$, at angles $\theta > 40^\circ$, the blueshift of $\lambda_*$ causes a split between this stopband and $\lambda_*$. Moreover, because p-polarized reflection is more sensitive to angle and has a smaller full width at half maximum, this split becomes evident at lower angles (see also Figure S6, Supporting Information). The reflectance of $\lambda_*$ is barely visible in the experimental reflectance due to the strong narrow band absorption of the TDBC-PVA layers. However, we would like to remark that the third stopband condition is only reached in a narrow wavelength window, where large values of the refractive index of TDBC-PVA are achieved ($n = 3$, see Figure 1). That wavelength restriction affects to the angular response of the dispersion curve of this third band with i) modes only supported at small angles (case $\Delta_4$) or ii) modes

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**Figure 3.** Optical characterization of biomimetic iridoplast of different periods. Left: Reflection at normal incidence for samples with period $\Delta_2$, $\Delta_4$, and $\Delta_5$ (see Figure S4, Supporting Information, for all samples). Black lines and blue lines represent experimental and theoretical fit, respectively. Gray vertical line marks the TDBC excitonic resonance ($\lambda_{exc} = 590$ nm). The green lines are the central wavelengths for high ($\lambda_+$) and low ($\lambda_-$) energy stopbands calculated using the dispersion relation for the corresponding period. Right: Epi-illumination (reflectance) optical microscope images of the measured areas for each sample.

**Figure 4.** Angle-resolved reflectance of biomimetic iridoplast. Contour plots show the angle-resolved measured reflectance for the same samples as in Figure 3 (periods $\Delta_2$, $\Delta_4$, $\Delta_5$) under s-polarized illumination. Dashed white lines highlight the exciton band spectral position. The red dotted line shows the calculated dispersion of the stopband for PS-PVA undoped DBR with the same period. The black solid lines show the numerical calculation of the dispersion relation of the three photonic stopbands for TDBC-PVA/PS DBRs of different periods.
only supported at larger angles ($\Delta_3$ and $\Delta_4$). The experimental data is corroborated by the theoretical dispersion lines calculated numerically according to ref. [26] for each of the stopbands (black lines, Figure 4).

We have shown that the strong dispersive optical properties of the excitonic molecular material can strongly modify the photonic crystal properties when the biomimetic iridoplast morphologies are considered. Moreover, these strong dispersive materials can achieve NZI properties acting as candidates for the fabrication of exotic absorbing materials with superabsorbing capabilities.[13] For example, Figure 2 shows that, for a DBR with a response on the NZI wavelength region, the field can be strongly localized in the active TDBC-PVA layers at the edges of the stopband. On the other hand, it has been proposed that iridoplasts in high plants can present photosynthetic tissue structured as DBRs to induce slow light phenomena[2] and produce absorptance enhancements at wavelengths of light available in their environment. It is predicted that slow light is actively tailored within these organelles by modifying the period of the natural DBRs hence allowing for their photonic stopband to be tuned depending on the plant needs.[24] Given the optical properties of the biomimetic NZI iridoplast presented above, it is worth investigating whether we can observe similar phenomena in the artificial counterparts.

**Figure 5a** shows theoretical and experimental data evidence for $\Delta_1 = 158$ nm. Two well-defined spectral ranges are obtained where $\gamma > 1$, demonstrating that the presence of the photonic bandgap can enhance the absorptance of the structure. In particular, the enhancement occurs at the short- and long-wavelength band edges of the $\lambda_-$ and $\lambda_+$ stopband, respectively. The enhanced absorptance is due to the slow light effect at those particular band-edges which creates a quasi-standing wave with maximum field intensity at TDBC-PVA positions (as shown in Figure 2 and Figure S2, Supporting Information, for the theoretical analysis) thus enhancing light absorptance, i.e., $\gamma > 1$. Interestingly, $\gamma > 1$ takes place at opposite photonic stopband edges as a result of the change in the sign of the refractive index contrast ($\Delta n = n_{\text{DBR}} - n_{\text{PS}}$) as described above.

To further explore the slow light effects over the NZI organic material, we performed reflection and absorptance analysis for the different DBR periods. The experimental reflectance (absorptance) measurements are represented on the upper (bottom) panels of Figure 5b,c as PS thickness variation, $d_{\text{PS}}$. On the blue edge of the high energy photonic bandgap ($\lambda_+$), we observe a pronounced absorptance enhancement for all $d_{\text{PS}}$, reaching values as high as $\gamma = 1.6$. In contrast, on the low energy gap ($\lambda_-$) this enhancement occurs on the red edge, reaching values of $\gamma > 2$. Absorptance enhancement ($\gamma > 1$) occurs at these edges as this is where light is concentrated in the absorptive material. The reverse happens at the red edge of $\lambda_-$ and the blue edge of $\lambda_+$ where light concentrates in the homogeneous material, reducing light absorptance ($\gamma < 1$). Figure 2 and Figure S2 (Supporting Information) show two structures, each having the most pronounced photonic bandgap on opposing sides of the excitation wavelength and hence the sign of the refractive index contrast is also different ($\Delta n = n_{\text{PS}} - n_{\text{TDBC-PVA}} > 0$ for $\lambda < \lambda_{\text{exc}}$ and $\Delta n < 0$ for $\lambda > \lambda_{\text{exc}}$). This means the high index material is different (PS for $\lambda < \lambda_{\text{exc}}$ and TDBC-PVA for $\lambda > \lambda_{\text{exc}}$) and hence the edge of the photonic bandgap where the wave concentrates in this high index material.

![Figure 5](image-url)
Figure 5b shows the simulated reflectance ($R$) and absorptance enhancement coefficient ($\gamma$) at normal incidence for the polystyrene thicknesses ($d_{PS}$) range under consideration from the fabricated samples. Note that the reflectance plot is distinct from Figure 1c as the refractive index used here was the one obtained from ellipsometry measurements, while in Figure 1c the refractive index from Equation (1) was used. Figure 5c shows the reflectance and absorptance enhancement coefficient experimentally measured (Figure S8, Supporting Information, shows the same but in 2D line plots). The photonic bandgaps observed in reflection (Figure 5b,c top ($\lambda_c$ and $\lambda_\gamma$) are very clearly seen translated in the areas where $\gamma < 1$ (Figure 5b,c bottom) and which redshift with an increase in period ($\Delta$). A region with ($\gamma > 1$) is observed at $\lambda = \lambda_{exc} = 590$ nm and for $d_{PS} < 130$ nm but only for the theoretical case. This enhanced absorptance region presents almost no spectral shift upon period variation. Similarly, our calculations for the spectral position of the third stopband $\lambda_{2}$ (as an almost-vertical dotted black line in Figure 1c) show the same behavior in this region. This, therefore, reinforces our hypothesis that the absorptance enhancement close to resonance is correlated to the presence of the third stopband of the DBR due to the strong anomalous dispersion of the NZI material. In addition, we have demonstrated that the closer the photonic bandgap is to the excitonic band, the higher the effect of the damping of the dipole oscillator which eventually reduces the photonic strength of the structure. Therefore, it is expected that a redshift of the stopband $\lambda_c$ toward the exciton maximum absorptance will reduce $\gamma$. The opposite happens when $\gamma$ increases in the long wavelength band-edge of $\lambda_{25}$, as the stopband is redshifted by the period increase, it departs from the molecular absorption band.

Despite differences in absolute values, the agreement between theoretical and experimental data is outstanding, validating the results. In $\gamma$ we again see that the photonic bandgap in the longer wavelengths ($\lambda_{123}$) has a wider bandwidth in the theory than in the experiments. At $\lambda_{123}$, the absolute values of $\gamma$ are very similar even at infra-red wavelengths ($\lambda > 700$ nm). It is worth mentioning that the theoretical narrowband absorptance enhancement shows values of $\gamma = 1.2$ at $\lambda = 580$ nm. This absorptance enhancement region is related to the third stopband $\lambda_{25}$ not being visible in reflectance due to strong narrowband absorption. Also, this spectral region corresponds to the lowest refractive index values of the TDBC-PVA, that is, is the region where the material presents a larger NZI character and therefore the interaction with the third possible stopband becomes more intense. We do not experimentally observe $\gamma > 1$ at those wavelengths. Yet, an increase in $\gamma$ is observed compared to the bandgap region. The reason for this mismatch is most likely related to the fact that is not possible to produce a perfect slab with the same number of molecules as a reference. In this range, $\Delta n = 1.5$ which would induce enhanced absorption even for short periods like the pseudo-slab with $d_{PS} = 25$ nm used as reference in the experiments (see Figure S7, Supporting Information).

J-aggregate supramolecular dyes are fluorescent, therefore we can use their fluorescence to understand how light is absorbed and emitted by the photonic structures. Photoemission is intrinsically correlated to absorptance and, as a consequence, the photoluminescence of thin-film J-aggregate molecular assemblies present a narrowband emission with a small Stokes shift of a few nm to the narrow absorptance peak in most cases.[23] Interestingly, the high degrees of aggregation required to obtain NZI properties will have a dramatic effect on emission. The photoluminescence of DBRs and reference samples were measured in a Fluoro-MAX 3 spectrofluorometer (Horiba Scientific), seen in Figure S9 (Supporting Information). To measure the thin films, we placed them at 45° to the incident light source. The incident wavelength selected for the photoluminescence (PL) measurements is 550 nm for all the samples. We also performed photoluminescence excitation (PLE) where the emission wavelength is fixed at the maximum wavelength peak of the emission for each sample while the excitation wavelength ($\lambda_{exc}$) is scanned in the range $\lambda_{exc} = 400–630$ nm. By tuning the excitation source it was possible to obtain intensity and spectral measurements of the photoemission for the same sample and measurement area for excitation at different wavelengths. We note that the light intensity required to be able to excite photoluminescence is much higher than the intensity used to perform the reflection measurements. Therefore, photoluminescence has no impact on the reflectance measurements.

Figure 6a shows the emission spectra for the TDBC-PVA pseudo slab ($\Delta_0 = 0$) and the different biomimetic iridoplast fabricated under excitation at $\lambda_{exc} = 550$ nm. The emission of the TDBC-PVA pseudo slab shows an asymmetric spectrum with maximum emission at $\lambda = 620$ nm which is consistent with emission properties of few-molecules layers of TDBC-PVA reported in the literature.[31] The slightly stronger asymmetry towards longer wavelengths is most likely due to weak Fabry–Perot optical modes supported by the thick structure. Interestingly, for increasing periods of the Bragg reflector, a continuous reduction of intensity takes place. Such intensity reduction is consistent with the position of the photonic stopbands for each period. As can be observed in the reflectance measurements shown in Figure 6a, the stopbands redshift as period increases also at 45° of incidence as already shown in Figure 4. For short periods ($\Delta_{1,2,3}$), the bandgap $\lambda_{25}$ is located at shorter wavelengths than emission band of the TDBC as well as to the excitation wavelength of the PL measurements ($\lambda_{exc} = 550$ nm). Similarly, the condition for $\lambda_{25}$ is not totally fulfilled (see Figure 4). As a result, no strong change in spectral shape or intensity of the PL is observed but for a small reduction of the intensity of the PL of $\Delta_0$ attributed to the sample defects. Hence, the PL spectra of the DBR samples are similar to a TDBC slab (Figure 6a,b).

However, when the period is long enough ($\Delta_{5,6}$) the $\lambda_{25}$ bandgap is redshifted and crosses both excitation wavelength and emission wavelength of the TDBC as seen by the evolution of the left grey line marking the stopband in Figure 6a. Moreover, the stopband $\lambda_{25}$ is also visible. Therefore, two mechanisms affecting PL are in place for the longer periods. Because the $\lambda_{25}$ stopband is redshifted at increasing periods, we will expect that samples $\Delta_{5,6}$ will show $\lambda_{25}$ stopband close to the excitation wavelength, producing a strong reflectance at $\lambda_{exc} = 550$ nm and preventing excitation illumination from reaching the inner TDBC-PVA layers of the structure which reduces the overall intensity of the emission. Second, the $\lambda_{25}$ stopband will induce a suppression of PL on the DBR samples. The combination of these two mechanisms results in a reduction of the PL intensity for the three longer periods as seen in Figure 6a. Moreover,
it can also be appreciated a spectral shift of ≈15 nm to longer wavelengths. Both changes in intensity and spectral shift of PL are compatible with a modification of the emission rates due to the modifications of the local density of states induced by the photonic crystal structure, in particular for those cases where the emission band matches the band-edge of the photonic stop-band. However, the study of these properties would include time resolved fluorescence studies to quantify how local density of states affect the emission of the TDBC embedded within the structure which is out of the scope of this work.

It is also worth analyzing the evolution of the emission maximum intensity upon excitation with different wavelengths. The contour plot in Figure 6b shows the PLE for all the periods, while Figure S10 (Supporting Information) shows these results as 2D plots next to the reflection of the corresponding sample at 45°. These spectra were obtained by fixing the collection at maximum emission for each period and varying the excitation wavelength between 400 and 600 nm. The reference (Δ0 ≈ 0 nm) emission shows a uniform increase of the intensity for excitation wavelengths < 520 nm while it decreases for longer excitation wavelengths, as expected from the increased reflectance of the pseudo slab due to the NZI dispersive region of the TDBC-PVA (see Figure 1b). Overall, the biomimetic iridoplasts show a reduction of the emission intensity in agreement with Figure 6a.

It is worth noting that the periodic structures (Δ1-6) also show a narrowband spectral region where emission intensity is highly reduced. This reduction in emission matches the position of the photonic stopband for each period (Δ2 = 473 nm and Δ6 = 575 nm in Figure S10, Supporting Information). Figure 6b shows that the central wavelength of the high energy stopband λ at 45° follows the same pattern as the absorptance dip for an incident angle of 45° as shown in Figure 6c. The reason for this decrease in PLE signal is the match between stopband and excitation wavelength which prevents excitation of inner TDBC-PVA molecules and hence reduces absorptance. Note that, at 45°, the photonic bandgaps of the structure are redshifted, in particular, λ, is pushed for wavelengths longer than 600 nm and it is therefore not observed here. These measurements corroborate the measurements in Figure 5 for the modification of the absorptance by the stopbands and open the door to the study of excitonic photonic materials where absorptance and emission properties are tailored by a complex photonic environment. We observed an outstanding agreement between the calculation of the central wavelength for the stopband for each period and the drop of photoluminescence upon excitation at the same wavelength. Nevertheless, the simultaneous existence of several stopbands in the emission band of the TDBC-PVA requires further analysis that will consider not only the enhanced/prevented absorption of the excitation source demonstrated here, but also the enhancement/inhibition of emission determined by long-wavelength photonic band-edge. This analysis is out of the scope of this work and will be analyzed elsewhere.

3. Conclusions
In conclusion, our work demonstrates that by using photosynthetic photonic systems as inspiration it is possible to tailor...
light–matter interactions in soft excitonic materials beyond their intrinsic properties. Our work also shows that J-aggregates are a suitable building block for NZI nanophotonics; these properties can be used to generate new phenomena in photonic structures such as multistopband photonic crystals or slow-light-based multiwavelength absorptive materials with broad spectral separation. Our implementation also supports the hypothesis that the photonic structure of the natural photosynthetic photonic iridoplast uses the phenomena of slow light to enhance light absorptance at suitable wavelengths for photosynthesis. Despite the complexity of the photosynthetic natural systems, our results show the path to the demonstration of slow light phenomena in living organisms.

From a technological perspective, this work opens the door for a new set of building blocks for bioinspired NZI materials. The properties demonstrated on this work for TDBC-PVA can be expanded to the whole family of J-aggregate molecules covering the whole UV–VIS–NIR spectral range. Furthermore, the fact that this structure is fully organic provides material advantages such as low cost of fabrication and low environmental impact. Moreover, more elaborate nanostructuring could add further control over light-matter interaction within the structure, providing therefore a highly processable and low contaminant method for the production of NZI excitonic metamaterials.

4. Experimental Section

Numerical Calculations: Reflectance, transmission, and absorptance for all structures were obtained using an in-house implementation of the transfer matrix method (TMM) developed in Python programming language. Data are available upon request to M.C. Photonic bandgaps and band edge calculation was obtained from the same TMM implementation. The central wavelength of the stopband was also obtained in some cases using the phase matching condition as detailed in Note SII (Supporting Information).

Ellipsometry Measurements: For the characterization of optical properties of the TDBC-PVA film a single layer of was deposited on a glass substrate. Spectroscopic ellipsometry characterization was carried out from the near-IR-to-near-UV 0.70 to 4.5 eV (1770 to 275 nm) using a VASE capable Woollam (WVASE) ellipsometer. The source light is a Xenon lamp, the wavelength is selected with a single monochromator, and a polarizer-retarder-sample-rotating analyzer configuration is used for the measurements (Woollam Co. Inc.). The ellipsometry data Psi and Delta data were acquired at angles of incidence (AOI) of 60°, 70°, and 75°. Additionally, the transmission of the film was measured at normal incidence (AOI 0°). For the analysis, a model including the glass substrate and the film was used. The film optical constants were modeled with a Lorentz oscillator. The transmission and ellipsometric parameters Psi and Delta were analyzed simultaneously using the WVASE32 software (Woollam Co. Inc.) that allows multilayer fitting of the spectra using the transfer matrix (Abelès) formalism.

For the optical characterization of PS, a single layer of the homogeneous polymer was deposited on top of a glass substrate. The ellipsometer used was the J.A. Woollam M-2000 with a wavelength range from the UV to the near IR: 371 to 1000 nm. The source light is a 50 W QTH lamp. Again, Psi and Delta data were acquired at angles of incidence (AOI) of 55°, 65°, and 75°. The model to analyze the data included the glass substrate and the film used. The film optical constants were modeled using the Cauchy's equation. The results were in agreement with previously published data.

Sample Preparation: The biomimetic iridoplast structures were fabricated on a coverslip (170 µm thickness) by sequential deposition of PS and TDBC-PVA layers by spin-coating. In the case of TDBC-PVA films, TOBC water solution was mixed with PVA by using a 3:1 mixture of 6.0% wt poly(vinyl alcohol) (PVA: Aldrich PVA Mw = 85 000–124 000) and 2% wt of J-aggregate molecules (TDBC: 5,6-dichloro-2-[5,6-dichloro-1-ethyl-3-(4-sulphophthyal)-benzimida-zol-2-ylidene]-propeny]-1-ethyl-3-(4-sulphophthyal)-benzimida-zoliu hydroxide, sodium salt, inner salt) both in water following an already published protocol.[1] Further stirring of a mix of both solutions was performed. This solution was then diluted further with water in a 3:1 ratio (3 parts solution and 1 part water). For the deposition of PS thin films a solution of polystyrene (Aldrich, Mw = 192 000) diluted 2.9% wt in toluene was used. The sequential deposition of each solvent on a polymer diluted on a non-polar solvent (or vice versa) ensured minimal damage to the underlying layer, thus enabling processability and flexibility to the fabrication.[3] The thickness of the PS layer is different for each of the doped DBRs, something controlled solely by the rpm speed during the spin coating process from 2000 to 6000 rpm (Figure S3, Supporting Information). TDBC-PVA is deposited at 4500 rpm to yield the same 53 nm thick layer of TDBC-PVA, for both doped DBRs and pseudo-slab. This makes the tuning of the photonic bandgap by PS deposition simpler as only one solution concentration is needed. To fabricate a 25 nm layer of PS for the pseudo-slab, a 1% wt PS solution at 6000 rpm was used.

Reflectance and Transmission Measurements: Samples were characterized using a Fourier image spectroscopy setup coupled to a high-magnification optical microscope.[4] No sample preparation was required for the measurements. For reflection, samples were inspected with a tungsten-halogen white light lamp covering UV–vis–NIR spectral range. Samples were procured focusing and collecting through either a numerical aperture (NA) lens (Olympus Plan N 4×, NA = 0.10) for normal incidence measurements or a high numerical aperture (Nikon Plan Fluor 40×, NA = 0.75 OFN25 DIC M/N2) in case of angle-dependent reflection. Under these conditions, the measurement spot diameter was reduced, respectively, to 360 and 40 µm. Normal incidence transmission measurements were performed using the same light source. Both reflection and transmission at normal incidence were collected in Fourier plane using a fiber-coupled 2000+ Ocean Optics (Dunedin, USA) spectrometer. The angle-dependent reflection measurements were measured using a spectrograph (Princeton Instruments, Acton SpectraPro SP-2150) and a CCD camera (QImaging Retiga R6 USB3.0 Color). Each reflection measurement was normalized against the reflection of an optically thick silver mirror and each transmission measurement to a bare substrate which was measured under the same conditions as the DBRs.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.
Author Contributions

M.C., W.P.W., S.N.-S. and M.L.-G. conceived the work and analyzed the optical data. M.C. fabricated the samples and performed the optical measurements of the samples and designed and ran the optical models. C.E.-V., I.P.-S. and S.N.-S. performed and analyzed the photoluminescence measurements. R.S. performed and analyzed the ellipsometry data. All authors contributed to the writing.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

Biomimetics, excitonics, J-aggregates, photonic crystals, photosynthesis, slow light

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