Dye giant absorption and light confinement effects in porous Bragg microcavities

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Abstract

This work presents a simple experimental procedure to probe light confinement effects in photonic structures. Two types of porous 1D Bragg microcavities with two resonant peaks in the absorption gap were prepared by physical vapor deposition at oblique angle configurations and then infiltrated with a dye solution of increasing concentrations. The unusual position shift and intensity drop of the transmitted resonant peak observed when it was scanned through the dye absorption band have been accounted for by the effect of the light trapped at their optical defect layer. An experimentally observed giant absorption of the dye molecules and a strong anomalous dispersion in the refractive index of the solution are claimed as the reasons for the observed variations in the Bragg microcavity resonant feature. Determining the giant absorption of infiltrated dye solutions is proposed as a general and simple methodology to experimentally assess light trapping effects in porous photonic structures.

Keywords: Porous Bragg microcavities, light confinement, liquid infiltration, optofluidic analysis, enhanced light absorption, anomalous refraction index,
Introduction

Light trapping in photonic structures (PS) are of paramount importance for a large variety of applications. For example, confinement effects have been used to enhance the quantum efficiencies in dye sensitized, organic, semiconductor or perovskites solar cells when they are coupled with one dimensional photonic crystals (1D-PCs) or themselves manufactured as a 2D-PC. Other reported applications of light confinement in PSs include the enhancement of the photocatalytic activity of TiO$_2$ in the form of inverse opals or similar PC configurations, the preferential capturing of nanoparticles induced by light trapping effects or the increase in the sensing and detection capacity of fluorescent molecules. This variety of applications have fostered the fabrication of PSs according to new configurations (e.g., in the form of wave guides, or honeycomb-like photonic crystal lattice) and the development of fundamental studies about light trapping, photon-phonon coupling and other fundamental issues. Light trapping effects in PSs are generally evidenced in an indirect way (e.g., by the detection of performance enhancements as in photovoltaic solar cells) or just predicted using different theoretical procedures. Herein, we propose a simple experimental method based on the use of dye solutions infiltrated in porous Bragg microcavities (BM) to experimentally determine light trapping effects.

Common 3D and 2D-PS configurations, usually prepared by lithographic techniques or chemical methods, are formed by symmetrical arrangements of holes, nanopillars or by the staking of opal spheres or inverse opals. Recently, we have proposed the use of a multilayer stack of SiO$_2$ and TiO$_2$ porous thin films prepared by electron beam evaporation at oblique angles (oblique angle deposition, OAD) as planar BMs for optofluidic analysis of solutions. In these studies, the investigated liquids were colourless and detection entailed the determination of the solution refractive index following the redshift of the BM resonant peak after liquid infiltration. Herein, the procedure proposed to experimentally determine light confinement effects in porous OAD-BMs involves their infiltration with coloured highly absorbent liquids and the application of geometrical actuation procedures enabling the wavelength scanning of the BM resonant peak through the absorption band. The observed shifts in the position and losses in the intensity of a resonant peak could not be interpreted by a simple interference theory, but accounted for by the existence of an experimentally determined giant absorption and associated strong wavelength dispersion in the refractive index of the dye solution. These experimental findings can be taken as the basis of a general
methodology to probe light trapping phenomena in PS, as well as used for the microfluidic analysis of small amounts of colored liquids and other optofluidic phenomena.

Materials and Methods

Materials preparation and characterization.

A first set of BM samples consisted of uniform, mechanically stable, and highly porous layers made of alternated TiO$_2$ and SiO$_2$ thin films prepared by OAD according to a procedure reported previously $^{21-23}$. A first set of porous BMs with a zig-zag microstructure were e-beam evaporated on glass plates of $1.5 \times 2.5$ cm$^2$ at a zenithal angle of 60° by rotating the substrate 180° from one layer to the next. During the deposition, the substrates were placed at 70 cm from the evaporation source. For electron microscopy characterization, samples were simultaneously deposited on a silicon wafer. Typical thickness of the SiO$_2$ and TiO$_2$ individual thin films was 85nm while the SiO$_2$ central thin film acting as optical defect had a thickness of about 1000nm. To ensure the homogeneity and the absence of roughness and porosity effects inducing light scattering in this thick central SiO$_2$ layer, the substrate was also turned by 180° after each 250nm deposition $^{23}$. Another set of BMs with a slanted microstructure and a thickness varying from 2480nm to 2753nm (~11% of gradient thickness) over a lateral distance of 3.5 cm were prepared at a zenithal angle of 60° by placing a larger substrate (1.5x 3.5 cm$^2$) at 30 cm from the evaporation source. No rotation was applied in this case. For some specific experiments carried out for comparison, SiO$_2$ and TiO$_2$ single layers with a thickness equivalent to that of the whole BM were prepared as described for the zig-zag BMs but using a single source of material for evaporation.

Cross section scanning electron microscopy (SEM) images in Secondary Electrons (SE) and Back-Scattered Electrons (BSE) modes were obtained in a Hitachi S4800 field emission microscope for samples deposited on a silicon wafer that were cleaved for cross-section analysis.

Rhodamine (101) (Rh(101), supplied by Sigma Aldrich) solutions in ethanol, at concentrations between $10^{-3}$ and $10^{-4}$, were used for the optofluidic experiments carried out in this work.
Optofluidic essays

For these essays, the BMs deposited on a glass plate were incorporated in two different cuvettes acting as microfluidic devices as reported in Figure 1. In a cuvette type 1 (c.f., Figure 1a), the glass plate with the BM deposited on its surface was directly sandwiched with another glass plate to minimize the liquid volume outside the BM. In the cuvette type 2 the plate containing the BM was incorporated as one of the walls of a homemade micro-cuvette of 150 μm of path length. A similar device without BM was also used to collect the spectra of Rh101 solutions in ethanol (c.f., Figure 1b). These simple microfluidic arrangements enabled handling the BM devices as flat substrates in front of the light beam while replacing the circulating liquid by simple injection. Measurements were carried out in transmission (type 1 and type 2 cuvette) and reflection (type 2 cuvette) modes. In this latter case the light beam was impinging on the backside of the plate where the BM was deposited, thus ensuring that only the liquid filling the BM was contributing to the observed optical effects.

Figure 1.- Schemes and photographs of the microfluidic cuvettes, type 1 (a) and 2 (b), integrating BMs (dimensions in the schemes are not at real scales).

UV–vis transmission spectra were recorded with the beam impinging either at normal incidence or at different angles with respect to sample normal in a Varian Cary 100 spectrometer. UV-vis reflectance spectra were recorded in normal incidence by means of a home-made set-up consisting of optical fibres with a micrometric movable holder and an Ocean Optics QE65000 Spectrometer. All data acquired either in transmission or reflectance modes were recorded with linearly polarised light along the direction of arrival of evaporated flux during the preparation of the films by OAD.
Simulation analysis

To simulate the reflectance and transmittance spectra we have used the WVASE32 software (J.A. Woollan Co.) to account for the multilayer structure and optical anisotropy of the BM. The optical description of the absorbing solutions was mathematically described through a parameterized GENOSC.MAT formulation. A basis of this method is the self-consistently coupling between the refractive index and extinction coefficient of the medium through Kramers-Kronig relations. The optical properties of the dye solutions within the BMs were described as the superposition of a Cauchy dispersion corresponding to pure ethanol, plus the gaussian-lorentzian absorption bands resulting from the fitting of the experimental transmission and reflection measurements of the BMs.

To evaluate BM in-depth and wavelength electric field strength distribution we used the FILMSTAR Optical Thin Film software. The inputs for this calculation were the optical constants (i.e., refractive index and extinction coefficient of the layers in the BM device) and topology (multilayer structure) as obtained from the WVASE analysis of the measured reflectance and transmittance spectra and the SEM images, respectively.

Results and Discussion

Optofluidic response of BMs.

Figures 2a and 2b show cross section SEM micrographs of the porous BMs utilized in this work. They consist of two symmetrical seven-layer Bragg mirrors (formed by alternated TiO$_2$ and SiO$_2$ films) separated by an intermediate thick layer of SiO$_2$ acting as optical defect. As explained in the Methods section and ref $^{23}$, a first BM type (Figure 2a) presented a zig-zag architecture while the second (i.e., Figure 2b) had a slanted microstructure. While the zig-zag BM was laterally uniform in thickness, thickness increased smoothly in the slanted BM as indicated in the scheme of the Figure 2b. These BMs were incorporated into planar microfluidic devices (i.e., cuvettes) enabling the infiltration of their porous structure with liquids. The UV-vis transmission spectra of these zig-zag and slanted BMs infiltrated with ethanol are reported in Figures 2c and 2d. The presence of two resonant transmission peaks (labelled as P$_1$ and P$_2$) in the gap of the BM was a result of the large thickness of the central SiO$_2$ layer acting as optical defect.
When these porous BMs were infiltrated with non-absorbent liquids their spectra (and resonant peak positions) experienced a *redshift* (with respect to the empty cavities) that varied with the refractive index $n_l$ of the liquid filling the pores.\textsuperscript{22,23} According to the Maxwell–Garnett effective medium approximation theory, these redshifts are due to the variation in the effective refractive index of the individual stacked layers when their pores are filled with the liquid. In agreement with this principle, the higher $n_l$ the larger the magnitude of the spectral *redshifts* (see supporting information Figure S1 showing plots of the difference in the resonant peak positions referred to that of water as a function of $n_l$ of several liquids). This behaviour was reproduced using WVASE simulations and agrees with previous results using single resonant peak BMs.\textsuperscript{22,23}

**Figure 2.** a) and b) BSE and SE cross section SEM micrographs of the *zig-zag* and *slanted* BMs, respectively. The colored scheme at the left of the images highlights the TiO$_2$ (blue) and SiO$_2$ (green) stacked layer structure. c) Series UV-vis transmission spectra recorded with the *zig-zag* BM by polar rotating the sample with respect to the light beam. d) Series UV-vis transmission spectra recorded with the *slanted* BM at different lateral positions $X_i$. The scheme shows how the effective thickness of this BM varies continuously along the observation direction. $P_1$ and $P_2$ denote the resonant peaks used to assess light trapping effects.
The strategy followed in this work to reveal light trapping effects in the porous BMs consisted of scanning one of its resonant peaks through the absorption band of a dye solution. Specifically, using porous BMs with large optical defects and therefore two or more resonant peaks within the reflection band, we could tune one of the peaks with the dye absorption band while taking the other as an internal reference. With the zig-zag BM (Figure 2c) working in transmission mode, this was achieved varying the angle of incidence of the light beam with respect to the sample surface. Polar rotating between $\theta=40^\circ$ and $\theta=55^\circ$, where $\theta$ is the angle formed between the normal to the sample surface and the direction of light, produced a blueshift of the resonant peak position enabling the overlap of the resonant peak $P_1$ and the R101 dye double absorption band at 530-560 nm. For the bare BM without any liquid, the observed blueshift was slightly different for $P_1$ and $P_2$, a difference that smoothly decreased when increasing $\theta$ (see Figure S2 of the supporting information).

In the slanted BM working in transmission mode, tuning $P_1$ with the Rh101 absorption features was achieved by laterally moving the light beam over the layer surface, i.e., by recording spectra at normal incidence at positions where the BM presented a smaller thickness (Figure 2d).

**Optical response of dye infiltrated BMs under polar rotation**

Using the zig-zag BM encapsulated within a microfluidic device (i.e. cuvette type 1), a series of UV-vis transmission spectra were recorded with incident light at several polar angles $\theta$ for $10^{-4}$, $5\cdot10^{-4}$ and $10^{-3}$ M Rh101 ethanol solutions. The spectra recorded in this experiment (c.f., Figure 3) show a net decrease in the intensity of resonant peak $P_1$ in comparison with $P_2$ (Figures 3a and 3b)) and distinct shifts in the positions of the resonant peaks. Thus, while $P_2$ smoothly decreased according to a tendency similar to that found with pure ethanol (see supporting information Figure S2), $P_1$ followed an oscillatory variation that, for the different solutions, is evidenced in Figure 3c by representing the difference in wavelength between $P_2$ and $P_1$ (i.e., $\lambda_{P2}-\lambda_{P1}$) against $\theta$. For the lowest Rh101 concentration, the curve practically coincides with that obtained with pure ethanol. However, for increasingly higher dye concentrations (and therefore increasing values of absorption coefficient) the plot of $\lambda_{P2}-\lambda_{P1}$ vs. $\theta$ depicted an oscillatory behaviour when the resonant peak $P_1$ crossed through the Rh101 absorption band.
Figure 3. a), b) Series of selected transmission spectra recorded for the zig-zag BM encapsulated in a microfluidic device (i.e., type 1 cuvette) for increasingly higher concentrations of Rh101 in ethanol ($5 \times 10^{-4}$ and $10^{-3}$ M). Spectra are recorded for several polar orientations with respect to the light beam. The dashed lines in panel b) correspond to simulated spectra. c) Plot of $\lambda_{P2} - \lambda_{P1}$ vs. polar angle tilt for the different studied solutions. d) Transmission spectra of the Rh101 solutions recorded in a cuvette (i.e., type 2 cuvette) with an approximate optical path of 150 µm.

Tentatively, we attribute this oscillatory behaviour to a wavelength dispersion of the refractive index of the dye solutions around the wavelength interval of the absorption band (for comparison the absorption band of the Rh101 solutions are represented in Figure 3d). A direct application of this effect would be the determination of solution concentrations of highly absorbent dyes by measuring the polar angle dependence of $\lambda_{P2} - \lambda_{P1}$ for infiltrated BMs (see supporting information Figure S3 for an example of this application).

The changes in intensity and position of the resonant peak $P_1$ represented in Figure 3 as a function of polar angle could be reproduced by simulation with a classical interference model and using as inputs effective functions for the wavelength dependent absorption
coefficient (α'(λ)) and refractive index (n'(λ)). These functions, whose exact meaning will be discussed later, are specific for the solutions infiltrated within the BMs and differ from the equivalent α(λ) and n(λ) functions of the same liquid outside the BM. The good match between simulations and experimental results in Figure 3b) confirms the validity of this interference model and effective functions to describe the optofluidic modulation of transmission spectra of BMs infiltrated with highly absorbent liquids.

Optical response of dye infiltrated BMs through thickness variation

In this case, the resonant peak P1 was scanned through the absorption region of the Rh101 dye using the slanted BM incorporated in a 150 nm thick cuvette (i.e. type 2 cuvette, see Methods section) and recording spectra at equally separated lateral positions on the BM. Figure 4 shows transmission and reflection spectra measured for several dye concentrations (note that dye concentrations are different for transmission than reflection) at successive lateral locations separated by 0.15 mm (Figure 4a and b) or 0.30 mm (Figure 4d and e) intervals. In the two cases, the spectra experienced a blueshift, which we attribute to the progressive decrease in total thickness of the BM (a displacement of ca. 0.2 mm corresponds to a difference of 1% in total thickness). In addition, these two series spectra showed a decrease in the intensity of peak P1 that is more intense for high dye concentrations and that proved a net effect of α'(λ) on P1 (as a reference, the absorption coefficient curves of the same dye solutions recorded in a 150µm thick cuvette without BM, α(λ), are superimposed in the figure). The fact that the intensity decrease in P1 occurred for transmission and reflection modes (in transmission, light is absorbed by both the solution filling the 150µm thick cuvette and the BM, while in reflection absorption is restricted to the solution filling the pores of the BM) supports that the dye solution infiltrated in the BM possess an exalted absorption coefficient α'(λ) (i.e., the dye has experienced a giant absorption). In addition, the analysis of the λP2-λP1 vs. λP2 curves in Figure 4c and f for, respectively, the spectra acquired either in transmission or reflection, shows an oscillatory behaviour superimposed on the smooth variation curve of pure ethanol (c.f. Figure 3c)). Similarly to the experiment in Figure 3, this oscillation extends through the wavelength region covered by the dye absorption band.
a) Series of UV-vis transmission spectra recorded through the type 2 cuvette at different positions for the slanted BM infiltrated with ethanol dye solutions of increasing concentrations as indicated.

b) Plots of $\lambda_{P2} - \lambda_{P1}$ vs. $\lambda_{P2}$ derived from the spectra in a) and b).

c) Ibid. for spectra and curves recorded in reflexion mode. The spectra of the Rh101 solution recorded in transmission in the same cuvette without BM are included as dashed lines for comparison.

d) Ibid. for spectra and curves recorded in reflexion mode. The spectra of the Rh101 solution recorded in transmission in the same cuvette without BM are included as dashed lines for comparison.

e) Ibid. for spectra and curves recorded in reflexion mode. The spectra of the Rh101 solution recorded in transmission in the same cuvette without BM are included as dashed lines for comparison.

At this point, it is noteworthy that transmission spectra recorded in a 150 micron thick cuvette with one of its lateral quartz windows covered with porous OAD TiO$_2$ or SiO$_2$ thin films of approximately two micron thickness (i.e. in the range of the total thickness of the investigated BMs) had a similar intensity than the one recorded without thin film (see supporting information Figure S4). This experiment discarded that the enhanced
absorption of the dye solution observed in the BM could be attributed to an enrichment of dye molecules in the film or BM inner space due to their adsorption on the pore surfaces. It also supports that light interference effects within the BMs must be blamed for both the enhanced absorption and the apparently anomalous refractive index dispersion revealed by the odd variation of $\lambda_{P2}-\lambda_{P1}$ vs. $\lambda_{P2}$ curves around the dye absorption band.

Giant absorption and enhanced anomalous dispersion in dye solutions infiltrated in a Bragg microcavity

According to fundamental optical principles, the refractive index of coloured liquids or solutions presents an anomalous wavelength dispersion around the wavelength range of the absorption band. Figure 5a) shows the absorption coefficient ($a(\lambda)$) spectra measured for the utilized Rh101 ethanol solutions in a 150 μm thick cuvette (full lines) and the corresponding refractive index ($n(\lambda)$) functions (in dashed lines) derived through a Kramers-Kronig transformation. It is apparent that around the absorption zone there is an enhancement in the refractive index dispersion that was particularly noticeable at higher dye concentrations. Thus for the $10^{-3}$M Rh101 solution (maximum absorption coefficient of $\sim0.03$ μm$^{-1}$), $n(\lambda)$ varied in the absorption interval by $\sim0.002$ RIU. Surprisingly, when using these $a(\lambda)$ and $n(\lambda)$ functions to simulate the $P_1$ wavelength shifts and the decrease in intensity reported in Figures 3 and 4, we did not obtained a good fitting of the experimental curves. As stated above, a proper reproduction of the experimental spectra was only possible with effective absorption coefficient $a'(\lambda)$ and refractive index $n'(\lambda)$ curves characteristics of the dye solutions infiltrated in the BM. The comparison in Figure 5 of the directly measured and effective curves shows that $a'(\lambda)$ has ca. twenty times higher intensity than $a(\lambda)$ and that this difference entails much higher dispersions in $n'(\lambda)$ as compared with $n(\lambda)$ (i.e., 0.03 vs. 0.009 RIUs for the $10^{-3}$ Rh(101) solutions). The good fitting achieved using these effective functions (c.f. Figure 3b) sustains that the outstanding behaviour of $P_1$ in infiltrated BMs stems from a giant absorption and an enhanced dispersion of refractive index when the dye solutions are infiltrated within the BM.
Figure 5. a) Absorption coefficient $\alpha$ (full lines) and derived refractive index $n$ (dashed lines) spectra of various Rh101 ethanol solutions measured in transmission in a cuvette. b) Effective $n'$ and $\alpha'$ for the same solutions than in a) but obtained for the dye solution infiltrated in the BM. These curves were obtained by fitting analysis of the angle dependent spectra reported in Figures 3 and 4 for an infiltrated zig-zag BM.

Confinement of light electrical field in dye infiltrated BM

According to the effective medium approximation, the refractive index of a porous film infiltrated with a liquid is a weighted average of both, the refractive index of the material (i.e. $n_{TiO2}$ or $n_{SiO2}$ in our case) and that of the liquid $n_L$. For non-absorbing liquids, $n(\lambda)$ depicts a smooth variation with $\lambda$ and there are very little differences between the actual values of this parameter at the wavelengths of the two resonant peaks (for example $n_{ethanol}$ is 1.362 and 1.360 at $\lambda_{P1}=564$ and $\lambda_{P2}=646$ nm, respectively). Accordingly, $P_1$ and $P_2$ positions varied evenly when the BM was infiltrated by a non-absorbent liquid (c.f., Figures 3c and 4c & f).

To reproduce the differential shifts in the position and the substantial decrease in the intensity of $P_1$ (c.f. Figures 3 and 4) we had to assume effective $\alpha'(\lambda)$ and $n'(\lambda)$ functions for the dye solutions that sustain a giant absorption and an enhanced anomalous dispersion of refractive index for the liquid infiltrated in the BM. We relate these functions with the existence of light trapping effects and propose their determination as a procedure to analyse light confinement in PSs.

To prove the link between the determined giant absorption and light trapping effects we calculated, using FILMSTAR software package, the electrical field distribution as a function of the wavelength and the in-depth position ($x$) within the multilayer. A first evidence of this analysis (c.f Figure 6a) was that the averaged amplitude of the electrical field within the BM qualitatively followed the variations in the spectrum of
transmitted light. In addition, the comparison in Figures 6a and c between transmission spectra and calculated electrical field distribution for the infiltrated BM revealed a significant decrease in the electric field amplitude around the resonant peak $P_1$ for the infiltrated BM. This intensity drop must be attributed to the light absorbed by the dye molecules. Meanwhile, the electrical field maps along $\lambda$ and $x$ in Figure 6b reveals a strong localization of electrical field in the central part of the BM multilayer stack (i.e., at around 1200 nm, coinciding with the optical defect region) and a progressive smooth decrease towards the external zones of the BM (for an alternative representation of these variations as a function of $x$ at the $P_1$ wavelength see supporting information, Figure S5). Figure 6d confirms that the field strength around $\lambda_{P_1}$ and the optical defect region (i.e. between 600 and 1800 nm) significantly decreases when the BM becomes infiltrated with the dye solution, clearly proving the effect of the absorbing dye on the electrical field distribution.

**Figure 6.** a) UV-vis transmission spectrum and calculated electrical field strength as a function of the wavelength (blue axis) for a BM infiltrated with ethanol. b) Colour plot of the electrical field intensity as a function of both the wavelength and in-depth position $x$ c) & d) Ditto for a) & b) for the same BM infiltrated with a $10^{-3}$ M Rh 101 solution in ethanol.
A good approximation to estimate the local absorption coefficient of the dye solution in the BM, i.e., $\alpha'(x, \lambda)$, is to take it proportional to $E(x,\lambda)^2 n'(x, \lambda)$, with $E(x, \lambda)$ the local electric field amplitude and $n'(x, \lambda)$ the local effective refractive index within the BM.\textsuperscript{4,5}

Thus, the observed enhancement in absorption coefficient when the absorption band of the dye solution is tuned to $\lambda_{p1}$ can be accounted for by the high amplitude of $E(x, \lambda)$ (c.f., Figures 6b and 6d and S5) and the quadratic dependence of $\alpha'(x, \lambda)$ on $E(x, \lambda)^2$. This enhancement will be further increased by its multiplication by $n'(x, \lambda)$, all together justifying the giant absorption coefficient determined for the dye solution within the BM.

The experimental procedure developed in this work to semi-quantitatively determine the magnitude of light trapping effects implies the polar turning or lateral displacement of BMs with respect to the light beam. However, the principles and strategy could be applied to other PSs where similar enhancements in the absorption coefficient and/or the associated high dispersions in refraction index could be monitored for infiltrated coloured liquids. This technique would also be relevant for analytical purposes as, for example, the determination of the solution concentration of highly absorbent molecules following the position of the resonant peaks, an example of which is reported as supporting information in Figure S3. We envisage that, upon selection of the adequate dye molecule, other applications of this photonic detection could be found for the determination of pH and other liquid properties using dye indicators,\textsuperscript{27,28} the formation of coloured molecular complexes,\textsuperscript{29} molecular recognition\textsuperscript{30–33} or other sensing and biosensing applications where the decoupling between PS resonant features would be used as transduction principle.

**Conclusions**

The previous results and discussion have shown that light confinement effects existing in porous Bragg microcavities can be evidenced by infiltrating a dye solution within their structure. The method consists of following, with respect to an internal reference, the position and intensity of the resonant features of this photonic structure when they overlap with the absorption band of the dye. An adequate analysis of the characteristics of these resonant feature changes has been only possible by assuming a giant absorption and an enhanced refraction index dispersion of the infiltrated dye solutions. It has been proved that these changes in the light absorption phenomenology of dyes are due to
preferential localization of the light electrical field in the optical defect layer of the BM. It is proposed that, going a step forward the current theoretical analysis of light confinement effects, similar experiments carried out with other photonic structures infiltrated with highly absorbent liquids could be carried out to demonstrate and semiquantitatively determine the magnitude of such phenomena. Other applications are also envisaged for the analysis of highly absorbent liquids, sensing and biosensing.

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**Supplementary information**

The Supporting Information is available free of charge on the ACS Publications website.

Effect of the refractive index of infiltrated liquids and of polar rotation in the position of the resonant peaks of the BMs. Correlation between the magnitude of maximum difference between the position of the two resonant peaks and the concentration of dye solution. Effect of single porous and nanostructured OAD thin films on the absorption spectra of infiltrated dye solutions. Alternative representation of light trapping effect calculations.
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Monitoring light confinement effects in porous Bragg microcavities

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Supporting information

Supporting information S1 Effect of the refractive index of infiltrated liquids in the position of the resonant peaks of the BMs

Figure S1. a) UV-vis transmission spectra for the zig-zag BM infiltrated with liquids of different refractive indices. b) Plot of the differences in peak positions according to $\Delta P_i = P_i(\lambda_{\text{liquid}}) - P_i(\lambda_{\text{water}})$ as a function of the refractive index of the infiltrated liquid. Points correspond to ethanol (n = 1.361), cyclohexane (1.426) and toluene (1.497)

The spectra in Figure S1 a) were recorded with the type 1 cuvette and a zig-zag BM infiltrated with a series of liquids of different refraction indices. Figure S1 b) shows that the differences in the positions of the two resonant peaks $P_1$ and $P_2$ (i.e., $\Delta P = P_i(\lambda_{\text{liquid}}) - P_i(\lambda_{\text{water}})$) as a function of $n_i$ follow similar trends. This behavior agrees with WVASE simulations showing a linear shift of the resonant peak position with the refractive index.

Supporting information S2.- Effect of polar rotation on the positions of the resonant peaks of the zig-zag BM

Figure S2. Plot of wavelength peak positions $P_1$, $P_2$ and the difference ($\Delta \lambda = \lambda_{P2} - \lambda_{P1}$) as a function of polar angle of rotation with the zig-zag BM infiltrated with pure ethanol.

$P_1$ and $P_2$ are blue shifted when recording the transmission spectra off normal at increasing angles. The magnitude of this shift was different for $P_1$ and $P_2$ and therefore the difference $\lambda_{P2} - \lambda_{P1}$ depicts a decreasing curve.
Supporting information S3.- Correlation between the magnitude of maximum difference between the position of the two resonant peaks (i.e., \( \text{max. } \lambda P_2 - \lambda P_1 \)) and the concentration of dye solution.

![Graph showing the correlation between concentration and \( \text{max. } \lambda P_2 - \lambda P_1 \)](image)

**Figure S3.-** Plot of the maximum variation in the difference \( \lambda P_2 - \lambda P_1 \) determined from the analysis of the variation of this parameter vs. \( P_2 \) (Figure 3 main text) for the slanted BM infiltrated with dye solutions of different concentrations.

This plot shows that the maximum variation of \( \lambda P_2 - \lambda P_1 \) is a measure of the solution concentration and that its magnitude is directly related with the dispersion of refraction index of the liquid within the BM. A device consisting of a *slanted* BM (Figure 3 main text), or another based on a *zig-zag* BM (Figure 2 of the main text), could be used for this purpose and other analytical applications. It is noteworthy that direct quantitative UV-vis analysis of highly absorbent dye solutions using cuvettes is not straightforward because saturation effects that, to be avoided, would require very little light paths (i.e., special cuvettes with little separation between walls).
Supporting information S4. Effect of single porous and nanostructured OAD thin films on the absorption spectra of infiltrated dye solutions

Figure S4. UV-vis transmission spectra of simple layers of SiO$_2$ and TiO$_2$ in a cuvette type 2 infiltrated with a selected solution of Rh101 and the transmittance spectrum of this solution in a cuvette without deposited thin films (dashed line). Note the oscillations in the spectrum recorded with the TiO2 thin films which are due to interference effects due to the higher refractive index of this layer with respect to that of the glass plate.

The equivalent intensities of the Rh101 absorption bands for the dye solution recorded in a 150 μm cuvette without and with TiO$_2$ or SiO$_2$ porous layers deposited on one of the walls proved that there is not a preferential enrichment of dye molecules within the pores of these films. It also proves that the absorption
contribution of the dye solution within the porous thin films of 2 μm thickness is negligible in comparison to that corresponding the total path length through the cuvette.

**Supporting information S5.** Alternative representation of light trapping effect calculations

![Supporting information S5](image)

**Figure S5.** a) Projected view of Figure 5b). b) Representation of the electric field along in-depth position x for P₁ (λ=580nm) and ethanol (blue line) or dye-ethanol (red line) filling the BM. The thickness variation for a wavelength corresponding to the photonic gap minimum outside the resonant peak is presented for comparison (λ=620nm, black line).

These alternative representations clearly show the existence of light trapping effects at the optical defect layer of the BM, particularly at λP₁.