Photonic Crystals

Advances in Functional Solution Processed Planar 1D Photonic Crystals

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An overview on the properties and applications of polymer and inorganic planar 1D photonic crystals fabricated from solution is provided here. In the last decades, photonic crystals became technologically relevant for light management, photovoltaics, sensing, and lasing. Such structures are traditionally produced by lithographic and vacuum techniques, but the need to reduce costs and to scale-up the fabrication have lead the research toward new materials, simplified structures, and low-cost mass scale growth processes. In this regard, polymer and inorganic mesoporous distributed Bragg reflectors fabricated from solution attracted considerable technological interest. This review focuses on the properties of such structures, concentrating on state-of-the-art fabrication and applications.

1. Introduction

Following the seminal researches by John^[1] and Yablonovitch,^[2] photonic crystals (PhCs) stimulated a wide fundamental interest, which nowadays results in many technological applications.^[3] PhCs are arrays of media having different dielectric function arranged in sub-micrometric lattices.^[4] Such periodic structures affect photons properties as the crystal potential in a semiconductor affects the properties of electrons. Therefore, one can extend to PhCs three basic concepts, among others, from semiconductors: the photonic band structure, which identifies spectral regions forbidden and allowed to photon propagation;^[4b] the photonic band gap (PBG), which is responsible for the PhC chromatic response;^[5] and the density of

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photonic states (PDOS), $^{[2-4]}$ which helps explaining the photoluminescence (PL) changes of materials when embedded in the PhC structure.

Traditionally, PhCs have been made carving bulky inorganic dielectrics or semiconductors. These structures are still a hot topic in photonics for optical fibers, light emitting diodes (LEDs), sensors, photovoltaic devices, lasers, discrete and integrated optical components, lightening, and quantum computing.^[6] However, new solution processable photoactive materials (e.g., organic semiconductors, quantum dots, hybrid perovskites, and self-assembling supramolecular systems) stimulated

the development of PhCs grown with organic and colloidal materials by solution and melt processes. $\ensuremath{^{[7]}}$

Among PhCs, distributed Bragg reflectors (DBRs) are currently the most interesting owing to their planar structure which generates a simple optical response that represents a playground to understand deep physical concepts, as described in Sections 2.4 and 4. DBRs are indeed made of alternated thin films of different dielectric materials. This simplicity makes them the only PhCs that can take advantage of large area growths (see Section 3.1).^[8] Such fabrication methods are unconceivable with bulky inorganic DBRs and might reduce processing costs and enhance customizability, also on industrial scale, thus adding unprecedented market opportunities.

Figure 1 illustrates the evolution and fabrications of solution and melt processed DBRs. The top of the Figure displays three well-known natural DBRs belonging to animal and plant reigns: the mother of pearl,^[9] the Panamanian Tortoise beetle exoskeleton,^[10] and the *Pollia Condensata* skin,^[11] whose growth is driven by the thermodynamics of spinodal phase separation.^[12] The interest in these natural structures leads to their emulation until the development of solution-based fabrication methods for flexible synthetic DBRs made of polymers and inorganic nanoparticles (Figure 1). At the base of Figure 1, we also show some applications arose only in the last decades. From left to right: the use of DBRs in functional architecture, in enhancement of photon absorption for photovoltaic cells and modules, emission control, lasing, and sensing.^[7c,13]

In this paper we will first briefly review the properties of DBRs and then focus on the reasons that guided the research toward new solution-based and large-area fabrications, describing current processes used both at the laboratory and large-area scales. We will then review the main applications of these structures comparing the performances of mesoporous inorganic and polymer devices.



2. Basic Optics of DBRs

This section introduces some basic concepts useful to understand the optical response of DBR structures. Even though the optics of DBRs is well-known,^[4a] their growth, characterization, and applications are nowadays approached by interdisciplinary researchers, then a brief description of their properties should be useful.

As mentioned in Section 1, DBRs are lattices of thin films made of different dielectrics and are considered the simplest PhC structure. As depicted in Figure 2a, for a DBR made of alternated layers of two transparent media with thicknesses $d_{\rm H}$ and $d_{\rm L}$ and real refractive indexes $n_{\rm H}$ and $n_{\rm L}$ ($n_{\rm H} > n_{\rm I}$), light is partially refracted, reflected, and transmitted at each interface. The lattice spacing, and the layer refractive indexes define whether the interference among reflected (transmitted) beams is constructive (disruptive) at a specific wavelength and in turn, this defines the spectral region of the PBG. When nonabsorbing media are used as building blocks, the sum of reflectance and transmittance intensities, neglecting scattering phenomena, is unitary (energy conservation). Then, the photonic structure of a DBR can be easily characterized by mean of simple optical transmittance or reflectance measurements. Figure 2b shows a typical reflectance spectrum of a DBR, where the PBG is detected as a pronounced peak, while the background is dominated by a Fabry-Pérot interference pattern arising from the interference of beams reflected at the external DBR interfaces, i.e., by the overall thickness of the DBR, which can be considered as an effective medium.^[3]

2.1. Photonic Band Gap Properties in DBRs

Intuitively, the spectral position and intensity of the reflectance peak assigned to the PBG depend on the thickness of the DBR layers, on their refractive index and on the internal angles of incidence of light ($\theta_{\rm H}$, $\theta_{\rm L}$), which are connected to the external incidence angle ($\theta_{\rm ext}$) by the Snell's law ($n_{\rm ext} \sin \theta_{\rm ext} = n_{\rm H} \sin \theta_{\rm H} = n_{\rm L} \sin \theta_{\rm L}$). Given the planarity of DBRs, it is easy to model their optical response and extract some simple analytical relations, which correlates the PBG position to the structural parameters and to the incidence angle^[14]

S-polarization
$$\lambda_{PBG} = 4(d_H + d_L) \frac{n_H n_L \cos \theta_H \cos \theta_L}{n_H \cos \theta_H + n_L \cos \theta_L}$$
 (1)

P-polarization
$$\lambda_{\text{PBG}} = 4 \frac{n_{\text{H}} n_{\text{L}} \left(d_{\text{H}} \cos^2 \theta_{\text{H}} + d_{\text{L}} \cos^2 \theta_{\text{L}} \right)}{n_{\text{H}} \cos \theta_{\text{L}} + n_{\text{L}} \cos \theta_{\text{H}}}$$
 (2)

when θ_{ext} increases, the difference between the optical paths of photons reflected at any interface decreases, and the PBG shifts toward short wavelengths. This effect is depicted in **Figure 3a**. The Figure shows the reflectance of a polymer DBR as a function of θ_{ext} calculated by transfer matrix method formalism (see Section 2.4) and plotted as a contour plot.^[15] In the plot, the horizontal axis reports the wavelength scale, while the vertical one displays θ_{ext} . The color scale indicates the reflectance intensity. The top panel of the Figure displays the data for S-polarized





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light, while the bottom one shows those for P-polarized light. As expected, for both polarizations, the PBG shifts toward the short wavelengths increasing θ_{ext} . Moreover, for S-polarization the intensity and the width of the PBG optical signature remain almost unchanged, while for P-polarization, both the PBG reflectance intensity and its spectral width decrease as θ_{ext} approaches the Brewster-angle (θ_{B}) of the structure.^[16] The





Figure 1. Evolution of DBR technologies. From top to bottom: electron microscopy and digital images of natural DBR structures: Mother of pearl (Adapted with permission.^[9] Copyright 2018, American Chemical Society), Panamanian Tortoise beetle (Figure adapted with permission.^[10] Copyright 2007, American Physical Society), and *Pollia Condensata* Berries (Adapted from ref. [11]. Copyright 2012, The Authors, Published by National Academy of Sciences). Photographs and schematic of DBR applications (Adapted from ref. [13a]. Copyright 2018, ChameleonLab; Adapted with permission.^[7c,13b,c] Copyright 2018, 2010, 2014, American Chemical Society).

dispersion of the PBG is described in details by the photonic band structure of the DBR, as reported in Figure 3b.^[16]

Figure 3 displays that light propagation is never completely inhibited for all directions and for all polarizations. In this case the PBG is said to be incomplete,^[4b] and sometime it is called stop-band. The incomplete PBG affects light confinement effects, especially for the photoluminescence from emitters embedded in the structure.^[17] Indeed, photons propagation through leaky modes reduces confinement volume, which is crucial to achieve radiative rate enhancement and Purcell effect (see Section 4.2).^[18] For this reason, new strategies to achieve omnidirectional PBGs including control of the dielectric contrast, development of ternary structures and structures with graded and anisotropic refractive index, are currently highly investigated.^[19] When the high and the low refractive index media allows the same optical path ($n_{\rm L}d_{\rm L} = n_{\rm L}d_{\rm H}$), the lattice is said to fulfil the $\lambda/4$ condition and the DBR can also be called a quarter-wave stack.^[4b] This condition maximizes the reflectance in correspondence of the first order PBG (see Section 2.3) and can be treated analytically.^[4,16] The peak reflectivity then follows

$$R_{\rm PBG} = 1 - 4 \left(\frac{n_{\rm L}}{n_{\rm H}}\right)^N = 1 - 4 \left(1 - \frac{\Delta n}{n_{\rm H}}\right)^N \tag{3}$$

where *N* is the number of periods composing the DBR and $\Delta n = n_{\rm H} - n_{\rm L}$ is the dielectric contrast among the two dielectric materials. Δn also defines the spectral width of the PBG in $\lambda/4$ condition^[4b]





Figure 2. a) Reflection, refraction, and transmission in a DBR with $n_{\rm H} > n_{\rm L}$. b) Reflectance spectrum of a polymer DBR made of 15 periods of transparent layers having $n_{\rm H} = 1.69$ and $n_{\rm L} = 1.46$.

$$\Delta E_{\rm PBG} = \frac{4E_{\rm PBG}}{\pi} \frac{n_{\rm H} - n_{\rm L}}{n_{\rm H} + n_{\rm L}} = \frac{4E_{\rm PBG}}{\pi} \frac{\Delta n}{2n_{\rm L} + \Delta n} \tag{4}$$



Figure 3. a) Calculated angular dispersion reflectance spectra contour plot for a 15-period polymer DBR made of cellulose acetate and poly(*N*-vinylcarbazole) for S-polarized (top panel) and P-polarized (bottom panel) light. b) PBG dispersion of a DBR for S- and P-polarizations; (photonic bands are shaded in red) for $n_L = 1.5$, $n_H = 3.5$, $d_L = d_H$. The dashed lines corresponds to different values of θ_{ext} ; the Brewster' angle is also reported.^[20]

where E_{PBG} is the energy of the PBG peak. Then, reflectivity quickly increases as the number of periods increases. Similarly, large dielectric contrast allows large PBG spectral widths and strong reflectivity.

2.2. The Role of the Dielectric Contrast

Aware of the relations between the PBG properties and the dielectric contrast for quarter wave stacks, it is interesting to compare the response of DBRs made by commodity solution processable polymers with those of bulky inorganic DBRs available on the market. Figure 4a shows the calculated transmittance spectra for a series of DBRs made of 10 periods in $\lambda/4$ condition with PBG centered at 2 eV (\approx 620 nm). The black dotted spectrum represents a bulky DBR made of TiO₂ and SiO₂ ($n_{\rm h} = 2.6$; $n_{\rm l} = 1.46$ at 620 nm, respectively). Such oxides are commercially used for reflectors and optical filters and represent the reference benchmark.^[21] For the comparison, we considered a series of polymer DBRs, where the low refractive index material is a fluorinated polymer $(n_{\rm L} \approx 1.3)$,^[22] which is one of the lowest indexes available on the market.^[22,23] The high index media are instead cellulose acetate (CA, $n \approx 1.46$),^[7b] poly(methyl methacrylate) (PMMA, $n \approx 1.50$,^[24] polyacrylic acid (PAA, $n \approx 1.51$),^[25] polyvinyl alcohol (PVA, $n \approx 1.52$),^[25] polystyrene (PS, $n \approx 1.58$),^[7b] and poly(N-vinylcarbazole) (PVK, $n \approx 1.68$).^[26] Currently, PVK provides one of the highest refractive index available among commodity polymers thanks to the preresonant enhancement from the carbazole group absorption at about 350 nm.^[27] We also calculated the spectra for media with larger indexes (1.8, 1.9, and 2) to consider new polymer-inorganic nanocomposites, hyperbranched polysulphides, and inverse vulcanized systems, which are promising to increase dielectric contrast in polymer DBRs.^[28] In Figure 4a, each spec-

> trum shows the typical low transmittance band assigned to the PBG, which becomes deeper and wider upon the increase of the dielectric contrast. The intensity of the interference fringes also increases with this parameter. In Figure 4b, we highlight the relation between the minimum of transmittance intensity and the number of periods for the different Δn . As expected from Equation (3) and Figure 4a, the relation among the number of periods and the minimum of transmittance is linear on semilogarithmic scale. Indeed, the material pair that shows the deeper PBG (higher reflectance) is SiO₂:TiO₂ (black squares), confirming the efficacy of inorganic dielectrics for filter coatings. However, novel high index polymers with comparable number of layers provide similar PBG transmittance values. As discussed in the next sections, the ability to achieve large reflectance joined to easy processing and large area fabrication methods via solution-based growth motivated the development of new class of polymer and colloidal materials.





Figure 4. a) Calculated transmittance spectra of DBRs made by 10 periods with varying $n_{\rm H}$ and set $n_{\rm L} = 1.3$. The high refractive index increases through the values of commonly used polymers (CA, PMMA, PVA, PAA, PS, PVK, and 1.8, 1.9, and 2). The black dotted spectrum is the transmittance for a TiO₂:SiO₂ DBR. b) Minimum transmittance intensity for the same materials calculated as a function of the number of periods at the PBG peak position (2 eV).

2.3. High Diffraction Orders

The photonic band structure of Figure 3b shows that the DBR lattice generates several PBGs. Such stop-bands remind the higher diffraction order structures (m) predicted by the Bragg's law for crystals, which has been proposed to roughly describe the dispersion for 3D opal PhCs,^[29] and roughly adapted to the case of DBRs

$$m\lambda_{\rm PBG} = 2D_{\rm N} \sqrt{n_{\rm eff}^2 - \sin^2(\theta_{\rm ext})}$$
(5)

where $D = d_{\rm H} + d_{\rm L}$, and $n_{\rm eff}$ is the effective refractive index of the DBR. When considering broad spectral ranges, we need to take into account for the refractive index dispersion to properly describe high diffraction orders. The effect of the dispersion is shown in Figure 5a for a DBR made of CA and PVK (black line) and for the same media neglecting the spectral dependence of n (red line). For nondispersive dielectrics, the higher order PBGs are found exactly at $2E_{PBG}$, $3E_{PBG}$, $4E_{PBG}$, and so on. On the other hand, according to Sellmeir dispersion,^[30] the refractive index increases at larger energies shifting the higher order PBGs to higher values, in agreement with Equation (1) (Figure 5a, black line). Even though CA and PVK are not highly dispersive, especially if compared with inorganic semiconductors and oxides, the effect of the refractive index dispersion must be considered in the structure design, especially when large spectral ranges are investigated.

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Another characteristic of the higher order PBGs is their intensity, which is strongly affected by the optical thickness of the dielectrics. Figure 5b reports as contour plot the calculated reflectance spectra of DBRs having the same total optical path, but layers with different optical thicknesses ratio. The x-axis reports the energy normalized to the first order PBG (E_G). The y-axis instead reports the ratio between the optical thickness of the high index layer $(n_{\rm H}d_{\rm H})$ and the DBR period $(n_{\rm H}d_{\rm H} + n_{\rm I}d_{\rm I})$. This scale goes from 0 (low index medium only) to 1 (high index medium only). The $\lambda/4$ condition is set at $\gamma = 0.5$ and is highlighted with a white line. In this case, the odd orders have maximum intensity (full constructive interference among diffracted beams), while for even orders full destructive interference occurs making their intensity negligible. The $\lambda/4$ condition is exploited to achieve strong light confinement for lasing and strong-coupling applications.^[3,20] Conditions far from the quarter wave stack, which generate both odd and even diffraction orders are however interesting to improve sensitivity and lower detection limit in DBR sensors (see Section 4.3).^[31]

2.4. Modeling the Optical Response of the DBR Structures



Transfer matrix method (TMM) is largely employed to calculate the propagation of photons, or even electrons,^[32] and is the most common approach to simulate the optical response



Figure 5. a) Reflectance spectra for a 30 periods PVK:CA DBR with dispersive (black) and for the same nondispersive (red) dielectric functions. b) Contour plot of calculated DBR reflectance spectra as a function of optical thickness ratio.





Figure 6. a) Schematic of a wave propagating in a DBR period along the *z*-direction with angle of incidence θ_{ext} . b) Electric field components at an interface and c) within a dielectric layer.

of multilayer structures.^[7c,30,33] This method can also be used to calculate energy dispersion relations.^[4a] In the model, a DBR is considered as a series of layers separated by plane and parallel interfaces, while the electric field of the incident radiation is decomposed in a series of waves propagating from one layer to the other through the interfaces, as shown in **Figure 6**a. There, the *z*-axis represents the normal incidence direction to the interfaces separating two adjacent layers, while n_m and d_m are the refractive index and thickness of the *m*th layer.

Within the *m*th subunit, we can focus on two blocks. The first block consists in the interface between the (m-1)th laver and the mth layer (Figure 6b). There, we identify four phasors that indicate the components of the electric field: $E_{i,m-1}$ corresponding to the wave that propagates in negative z-direction and hits the interface from the (m-1)th layer side; E_{rm-1} propagates in positive z-direction and is transmitted at the interface; $E_{t,m}$ propagates in negative z-direction and is transmitted at the interface; $E_{s,m}$ propagates in positive z-direction and hits the interface for the *m*th layer side. The second block instead describes wave propagation in the *m*th dielectric layer alone (Figure 6c), where E_{tm} propagates until the next interface between the mth and (m+1)th layer is reached. At this second interface, we can identify $E_{i,m}$ and $E_{r,m}$, which have the same role of $E_{i,m-1}$ and $E_{r,m-1}$. All the above electric field components are related by simple matrix equations^[34]

$$\begin{pmatrix} E_{t,m} \\ E_{s,m} \end{pmatrix} = D \begin{pmatrix} E_{i,m-1} \\ E_{r,m-1} \end{pmatrix}, \quad \begin{pmatrix} E_{i,m} \\ E_{r,m} \end{pmatrix} = P \begin{pmatrix} E_{t,m} \\ E_{s,m} \end{pmatrix}$$
(6)

where *D* and *P* are respectively the interface and the propagation matrices, which consider the Fresnel reflection (*r*) and transmission (*t*) coefficients at the interface between layers m - 1 and m.

$$D_{m-1,m} = \frac{1}{t_{m-1,m}} \begin{bmatrix} 1 & r_{m-1,m} \\ r_{m-1,m} & 1 \end{bmatrix}$$
(7)

and

$$P_m = \begin{bmatrix} e^{-i2\pi\sigma\tilde{n}_m d_m \cos\theta_m} & 0\\ 0 & e^{i2\pi\sigma\tilde{n}_m d_m \cos\theta_m} \end{bmatrix}$$
(8)

We can now retrieve the reflectance and the transmittance of a DBR placed in air as

$$R = \left| \frac{M_{21}}{M_{11}} \right|^2, \quad T = \left| \frac{1}{M_{11}} \right|^2 \tag{9}$$

where M_{11} and M_{21} are the (1,1) and (2,1) elements of the matrices P or D, depending on the block under consideration, $\sigma = c/\lambda$ are the wavenumbers, $\tilde{n}_m = n_m + ik_m$ is the complex refractive index of the *m*th layer, and θ_m the incidence angle at the *m*, *m*+1 interface.

TMM allows to easily calculate reflectance or transmittance spectra in both coherent or incoherent systems.^[35] Indeed, with respect to the simple and basic formalism here recalled, starting from the late 1990s TMM has been improved to better model real structures and extended to investigate more complex effects than the simple optical response of a DBR. For instance, one of the key issues related to TMM modeling of real systems dwells on coherent light propagation, which usually generates a very dense and intense interference pattern in the simulated spectra. Such pattern owes to the partial reflectance within the thick substrate (e.g., 1 mm thick glass slide or fused silica) and can even hide the optical features related to the DBR. Common approaches to overcome this issue consider light incoherence in real systems, modeling the substrate as an infinitely thick medium, or conversely, assuming it as a nanometric layer to account for the interface with the DBR, only. More rigorous methods introduce phase shifts in the refracted beams, scattering layers, or incoherent propagation media to achieve both incoherent^[34,36] and partially coherent^[34,37] interference.^[34,35,37] Another variant of TMM uses the E and H fields as components of the vector being multiplied.^[4a,33a,38] Moreover, 4D vectors can be used to account for in-plane anisotropies or incoherence of the light traveling through the structure.^[39] The flexibility of the TMM makes it interesting also for the modeling of more complex light-matter interaction effects. For instance, the effect of the modified PDOS on the oscillator strength of emitters embedded into microcavities and distributed feedback structures can be studied including internal sources of spontaneous emission and modeling both photoluminescence^[40] and amplified spontaneous emission.^[41] It has also been shown that TMM can be used to simulate second harmonic generation from multilayered structures^[42] and the optical response of switches^[33b] and sensors.^[43] Investigation of phonon propagation in the multilayers even allows to determine thermal conductivity in multilayered structures.[44]

3. Materials and Fabrication Techniques

Traditionally, DBRs were composed of bulky metal oxides or semiconductors thin films grown by vacuum evaporation technologies.^[45] These state of the art DBRs are widely used for light management purposes including optical filters and mirrors,^[4a,21,46] vertical cavity surface emitting lasers (VCSELs),^[47] and LEDs^[48] are widely available commercially.^[21,46] For instance, VCSEL market is fast growing (estimated up to more than 3 billion of US dollars by 2022)^[49] due to their applications in new devices for sensing, automotive,

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and data communication.^[49] On the other hand, the fabrication of bulky inorganic DBRs is performed by sputtering,^[50] metalorganic chemical vapor deposition,^[51] electron-beam evaporation.^[14] and molecular beam epitaxy.^[14] that all have high cost of installation and maintenance in comparison with solution based methods. Despite bulky inorganic DBRs offer dielectric contrasts as large as $\Delta n = 1$,^[52] these systems are neither flexible, stretchable, nor bendable and their poor mechanical properties, joined to the often-severe deposition conditions, strongly limit their possible application to optoelectronic devices based on organic semiconductors. However, mild vacuum chemical vapor deposition (CVD) has been used for the fabrication of polymer structures using a wide portfolio of monomers. Polymer CVD indeed uses low temperatures, and allows casting of highly reflecting DBRs on flexible substrates such as paper or plastic.^[53] To make a step forward in the simplification of DBR growth, in the last decades important efforts have been devoted to the development of solution-based processing of polymers, inorganic media and even cholesteric liquid crystals^[54] with the aim to further reduce costs and achieve large area fabrications. In this section, we will discuss advantages and drawbacks of both polymer and mesoporous DBRs made by inorganic colloids grown by solution in terms of optical and mechanical properties.

The choice between polymer and mesoporous inorganic building blocks for the fabrication of DBRs is usually mainly driven by the capability of mutually processable dielectrics to offer suitable Δn for the specific goal selected. Once this constraint is addressed, one can focus on active functionalities, such as emission properties for light management applications and lasing, selective interactions with analytes for sensing, and chromic properties for switchers, memories and displays (Section 4). Moreover, mechanical properties might be a significant added value offering flexibility^[7c] and stretchability,^[55] unconceivable with bulky inorganic systems.

With respect to the processability, solutions fabrication of DBRs poses several optical, chemical, and processing constraints. Indeed, large refractive index difference, solubility of the dielectric materials in orthogonal solvents and solvent percolation, thickness and interface roughness control for the entire structure, thermal properties matching, low light scattering, and high transparency must be strictly controlled and steered. Moreover, both polymers and metal oxides building blocks need to be mutually processable, which means that the deposition of any medium must not affect the underlying layers. On the other hand, once cast, the film must provide a wettable surface with respect to its counterpart. Then, the need for mutual processability, in addition to the need for a relatively high Δn strongly limits the number of material pairs suitable for the growth of DBRs via solution-based processes.

Concerning the dielectric contrast, in the transparency spectral region, polymers usually have refractive index ranging from n = 1.3 to n = 1.7 (see Section 2.2).^[56] These relatively low values make them well suitable for sensing,^[25,31,43,53b,57] emission control,^[58] and lasing,^[59] while applications requiring strong light confinement, like radiative rate enhancement and strong coupling, are still challenging (see Section 4).^[33f,g] Indeed, while for applications related to light confinement the large dielectric contrast typical of inorganic media is usually desirable,^[33g,60]

Bragg stacks used for sensing exploit low Δn to detect small spectral variations, to improve the sensor detection limit, and to enhance the sensitivity.^[31] To engineer the refractive index in polymer systems, research is pursuing different strategies. For instance, low index polymers are mainly amorphous per-fluorinated macromolecules where the strong electronegativity of the fluorine atom reduces the molecular polarizability, while the lack of crystallinity provides low density. Such effects reduce the refractive index and push electronic transitions in the deep ultraviolet.^[61] Porous polymer structures are also proposed to lower refractive index.^[22,23,61a,62] In this case, according to the effective medium theory,^[62c] a large volume fraction of nanometer scale voids (n = 1) reduces the refractive index of the composite.^[62a] Unfortunately, solution processing of such polymers to fabricate DBRs where tens of thin films are periodically arranged is still an open issue. Indeed, the lowest refractive index reported in solution processed DBRs is about 1.33, for Hyflon AD family.^[22,23b,28e,63] Concerning high n polymers, materials with refractive index larger than 2 in the near UV have been developed to make lenses for LED with UV emission spectrum,^[64] but extension of such large values to the visible and NIR spectral regions is impossible. Indeed, such large indexes are achieved thanks to a preresonant enhancement, which quickly disappears approaching the visible spectral range. To overcome such limitations, researchers focused on doping with high index inorganic nanoparticles,^[65] metal oxides,^[28e,57a,66] and diamond.^[67] In this case, a large volume fraction of nanosized particles with high refractive index increases the dielectric constant of the composite medium.^[28e,62c] A different approach relies on the covalent addiction of highly polarizable groups or atoms including conjugated moieties, sulphur or selenium in the polymer backbone.^[62a] In these terms, hyperbranched polysulphide and inverse vulcanized polymers^[28a,68] are very promising even though only few reports have been published on DBR preparation so far.^[68a] Mesoporous structures can be similarly doped to modify the effective refractive index of the entire structure.

3.1. Mesoporous Inorganic DBRs

Mesoporous inorganic DBRs are obtained by deposition of metal oxides nanoparticles or their sol-gel precursors to form mesoporous thin films. In this sense, the most employed media are TiO₂,^[69] V₂O₅,⁷⁰ SnO₂,^[71] ZnO,^[72] and SiO₂,^[69] which are coupled in different combinations to obtain the proper Δn . In this case, nanoparticles with the same composition but different size and shape generate film with different void volume fractions and refractive index, which can then be easily engineered. For these systems, Δn is generally lower than for bulky DBRs grown by vacuum technologies because their porosity reduces the $n_{\rm eff}$ of the structure.^[62c] On the other hand, such porosity may favor the intercalation of either high or low index materials to modify $n_{\rm eff}$, allowing easy tunability of the PBG spectral position^[73] or postgrowth intercalation of photoactive materials (see Section 4).^[74]

At the lab scale, mesoporous Bragg stacks can be fabricated by sol–gel deposition methods^[75] or by direct deposition of metal oxide nanoparticles dispersion.^[76] The growth usually

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consists in the deposition of the nanoparticles or their precursors, and the subsequent annealing of the structure at high temperature to sinter the crystals and to provide the film with mechanical stability. The process is then repeated for each layer of the DBR. The deposition can be performed using a variety of methods. Spin coating is the most commonly used at the laboratory scale,^[52d,69,77] and consists in the casting of a solution or of a dispersion on a rotating substrate. The rotation favors the expulsion of the exceeding liquid and the evaporation of the residual solvent to achieve thin films with relative smooth surfaces and controllable thicknesses (Figure 7a).^[78] As depicted in the scanning electron microscopy (SEM) images and in the photographs of Figure 7b,c, spin-coating of inorganic media gathers uniform dielectric layers, whose homogeneity is reflected in the uniformity of the surface color. However, the interlayer roughness is controlled by the size of nanocolloids, which might provide inhomogeneous broadening of the PBG.

Recently, dip-coating allowed to automate the growth process and to produce large area mesoporous DBRs. In this technique, a substrate is dip into a water or alcoholic dispersion of the metal oxide particles or into a solution of their precursors.^[79] The substrate is then lift to allow solvent evaporation (Figure 7d).^[80] Dip-coating also allows layer-bylayer deposition,^[81] where charged particles, polyelectrolytes or ions gather adhesion between the different layers, making the annealing process unnecessary and the growth faster.^[74,92] Recently, the fabrication of mesoporous inorganic DBRs at the square meters scale have been reported for metal oxides casted via spray deposition.^[74,92] Notwithstanding this impressive technological achievement, commercial structures are not yet available for the market.

3.2. Polymer DBRs

The interest in polymer dielectric media comes from their ease of processing, low costs, interesting mechanical properties, high transparency in selected spectral regions, and from the possibility to make nanocomposites with a large variety of organic, inorganic, and hybrid active materials. Amorphous polymers are free from light scattering phenomena that may occur with nanoparticles. Indeed, these structures offer interlayer roughness below 3 nm^[82] providing often nicely squared shaped reflectance bands at the PBG.^[33f] Among commodity



Figure 7. a) Schematic of the spin-coating process, b) SEM images of spun-cast SiO_2 :TiO₂ DBRs, and c) digital photographs of the DBRs. Adapted with permission.^[13b] Copyright 2010, American Chemical Society. d) Schematic of the dip-coating technique.



polymers PVA,^[83] PAA,^[33g] and CA^[7b] are widely used as low index media, while PS^[7c] and PVK^[33f] are common high index ones. Other niche polymers have also been used for applications requiring specific properties. For instance, as mentioned above, fluorinated polymers are difficult to process, but their very low refractive index ensures larger dielectric contrast.^[22,63] Similarly, hyperbranched polymers^[68a] and polymer–inorganic nanocomposites^[28e,57a] provide high refractive indexes. Moreover, semicrystalline polymers can be used as active media in sensing applications to gather selectivity without chemical functionalization (see Section 4.3), when properly processed (see Section 4.3).^[31]

From the fabrication point of view, polymer DBRs are interesting thanks to the variety of techniques available both at the laboratory and at the industrial scale. At the lab scale they are fabricated via spin-coating (Figure 7a),^[7b,33e,68a,84] dip-coating (Figure 7d),^[28e] layer-by-layer deposition,^[85] and by the selfassembling of block copolymers (BCPs, **Figure 8**).^[86] The latter is arising interest^[87] thanks to the possibility to couple polymers pairs otherwise not processable together.^[88] The generation of ordered and periodic lattices by BCPs self-assembling is driven by the blocks chain length (*N*) and the Flory– Huggins parameter (χ), because $\chi \cdot N$ describes the strength of the repulsive interaction between blocks.^[89] The volume ratio



Figure 8. BCP DBR. a) Schematic representation of the mechanism for color change of a copolymer gel in solution. b) Cross-sectional SEM image of the DBR structure. c) Color change of the photonic gel films after intercalation of anions in solution. Adapted with permission.^[86c] Copyright 2012, American Chemical Society.

fraction of the two polymer blocks then defines the morphology of the nanostructures and their characteristics. For instance, a volume fraction of 50% is commonly required to obtain a DBR.^[90] To promote ordered BCP assembly over large areas, external physical templates and electric fields can be used during the assembling process. These techniques gather lattice paths of tens of nanometers, which are intensively investigated for microelectronic lithography masks.^[91] For photonic applications, the need to achieve periodicity above 100 nm (Equation (5)) in the dry state challenges the chemists to achieve highly controlled large polymer chain length. However, lattices with periodicity of tens of nanometers have been demonstrated to be suitable for analyte sensing in the liquid phase. Indeed, the layers composing BCP DBRs can swell to hundredths of nanometers in solution,^[92] allowing colorimetric response to analytes. Conversely, such behavior has not yet been demonstrated for analytes in gas and vapor phases. Notwithstanding BCP large scale self-assembly has not yet been developed, the possibility to overcome the chemical incompatibility among the high and low index polymer chains by the precise control of chain lengths and the fine tuning of chemical physical properties of the blocks make this media extremely interesting for the future of photonic sensors.^[92,93]

Mass scale production of polymer DBRs is instead feasible with well-known techniques used for food packaging manufacturing such as extrusion and coextrusion.^[94] Large area DBRs are indeed commercialized by, among others, 3M,^[95] Toray,^[96] Chameleonlab,^[13a] and Foliophotonics.^[97] Through this technique, two polymer films from two extruders are combined together (Figure 9a). After the formation of the first period, the film is cut, and the two halves are overlapped and pressed together. The process is then repeated, and the number of layers can be increased exponentially through an automated system. Figure 9b,c show two examples of large area products. There, the ease of tunability of the PBG, together with the possibility to couple structures tuned in different region of the sunlight spectrum, makes DBRs coating interesting for their aesthetical properties together with functionalities such as thermal shielding.^[22,98] In Figure 9b an installation by RAW Design, "Prismatica", that made use of 3M's polymer dichroic filters to create a kaleidoscopic effect at the Luminotherapie competition for 2014–2015,^[99] in Montreal. Even more impressive is the "Arc en Ciel" from Chameleonlab, an entire building facade covered with polymer DBRs creating astonishing iridescent colors (Figure 9c).^[100]

4. Applications

In the next sections we will review the technological applications of DBRs fabricated by solution, comparing the performances of polymer and mesoporous inorganic dielectric media.

4.1. Photovoltaics

In the last three decades, fundamental research has played considerable attention to thin film photovoltaic devices based on

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Figure 9. a) Schematic of the coextrusion process. b) *RAW Design* installation with large area polymer DBRs. Reproduced from ref. [99]. Copyright 2018, Convenience Group Inc. c) Arc en Ciel design building in Deventer (NL) from Chameleonlab. Reproduced from ref. [100]. Copyright 2018, ChameleonLab.

solution processable technologies to reduce costs of materials and fabrication with respect to inorganic structures.^[101] These systems use photoactive materials such as semiconducting polymers, organic molecules, and inorganic colloids.^[101a] Notwithstanding such efforts, especially when polymers are used, these devices suffer from drawbacks related to low charge carriers mobility, high charge recombination rates, and limited spectral absorption, that hinder high power conversion efficiencies.^[102] In this sense, PhCs offer new strategies to improve photon collection^[75,87,103] and among these, DBRs represent the most viable approach. Recently, Martorell and co-workers showed that DBRs made of alternated layers of MoO₃ and LiF fabricated by thermal evaporation can be implemented into bulk-heterojunction photovoltaic cells to achieve semitransparent devices with enhanced efficiency. In their design, a DBR with small angular dispersion properties, which were achieved using semiperiodical structures, was inserted in the back of the cell to reflect transmitted light back into the device allowing such photons a second chance to interact with the semiconductor. In this way, enhanced spectral absorption increases the device filling factor, while retaining the transparency of the base cell. The cells are indeed integrable into transparent elements such as building and vehicle windows, and screens.[3,104]

Inorganic mesoporous DBRs possess similar potentiality. These structures are attracting increasing interest to enhance the performance of perovskite solar cells. As an example, Brabec and co-workers implemented inorganic mesoporous DBRs fabricated by doctor blading of commercial refractive inks^[105] as back reflectors in transparent perovskite photovoltaic devices (**Figure 10**a). In addition to the increased absorption cross-section, the color of the device can be tuned according to architectonic needs (Figure 10a').^[105] The implementation of the DBRs as a back reflector provided a significant increase of the short-circuit current with only minor effects on the open-circuit voltage, thus enhancing the power conversion efficiency of about 20% (Figure 10a'').^[105] In another configuration, Miguez and co-workers demonstrated porous TiO₂:SiO₂ DBR integrated as a scaffold into the active layer of a perovskite solar cell, which exhibits well-defined reflectance bands, with the nonreflected light being guided into the perovskite to undergo photovoltaic conversion with high efficiency.^[74]

Moreover, with a suitable design DBRs can enhance power conversion efficiency also when placed in front of a photovoltaic cell. Several photonic structures have been demonstrated as antireflective coatings and smart surface scatterers to increase the optical path of incident light^[86a,106] or to enhance lightmatter interaction via light localization.^[74] This approach has been widely reported for monodisperse polymer microspheres placed on the surface of luminescent solar concentrators (LSCs). These structures exploit a fluorescent slab, usually made of a dve embedded into a polymer matrix.^[107] The dve absorbs the incident sunlight and emits photons that are guided via total internal reflectance to the lateral edges of the polymer slab, where photovoltaic cells are placed.^[107a] This mechanism allows semitransparent devices with reduced angle sensitivity and cell size with respect to systems with comparable power conversion efficiency. The scattering of low energy photons, which are not absorbed by the dye, extends the spectral range that reaches the photovoltaic device providing enhancements of the short current by at least 50% for 1 in. side area device (Figure 10b,b').^[107a,108] On the other hand, the application of front DBRs to LSCs is counter-intuitive because one would expect an increase in reflection losses. However, tuning the PBG on the absorption onset of the photoactive medium, it is possible to guide its PL and gather photon recycling. Moreover, coupling the front DBR with a back reflector, the absorption results further enhanced via constructive interference.^[109] Furthermore, low index DBRs can reduce the dielectric contrast at the air interface, thus realizing dielectric antireflective coatings in the spectral region where the photoactive layer absorbs. As schematized in Figure 10c, a SiO2:TiO2 DBR placed on top of the solar concentrator can indeed enhance waveguiding in the spectral range where the fluorophore emits (Figure 10c'), while transmitting light in the absorbance range of the dye, and acting as antireflective coating in the other spectral







Figure 10. DBRs coupled with thin film solar cells in different configurations: a-a'') Schematic (a), photographs (a'), and current-density curves (a'') for perovskite solar cells using DBRs as back reflectors. Adapted with permission.^[105] Copyright 2016, American Chemical Society. b-b') Effect of a smart polymer colloidal array on the external quantum efficiency of an LSC (b) and SEM image of the colloidal array (b'). Adapted with permission.^[107a] Copyright 2016, Wiley-VCH. c-c'') Schematic of an LSC device coupled with DBRs (c). Absorption (blue line) and emission (red line) of the photoactive organic luminophore (c'). External quantum efficiency for DBR-LSC devices (c''). Adapted with permission.^[107b] Copyright 2016, American Chemical Society.

regions. Figure 10c" shows that the DBRs gathers larger external quantum efficiency to the LSC in an extended spectral range, providing current enhancement up to 23%.^[107b] A similar strategy has also been demonstrated increasing power conversion efficiencies up to 8% and photocurrent enhancement up to 40% in standard photovoltaic devices.^[109]

4.2. Emission Control and Lasing

As depicted in **Figure 11**a, the insertion of a defect layer in the DBR lattice creates a microcavity (MC). The cavity layer, with thickness L_c and refractive index n_c , breaks the DBR periodicity and creates allowed photonic states within the PBG, the

so-called the cavity modes. The MC reflectance spectrum shows indeed a very sharp feature with low reflectance within the PBG band (Figure 11b). The spectral position of the cavity mode is provided by the resonance condition within the optical path of the cavity layer, which generates a standing wave with wavelength λ_c

$$2n_{\rm c}L_{\rm c} = m\lambda_{\rm c} \tag{10}$$

The spectral width of the cavity mode is affected by the reflectivity of the DBRs surrounding the defect, and then by Δn and by the DBR optical quality. The latter is in turn related to the thickness homogeneity among all the layers, their spatial uniformity, and the interfacial roughness.^[4,25,43] Indeed, the





Figure 11. a) SEM image of a mesoporous inorganic MC. Reproduced under the terms of Creative Commons Attribution-NonCommercial-NoDerivs License.^[110] Copyright 2017, The Authors. Published by Wiley-VCH. b) Calculated reflectance spectrum of a polymer planar MC. c) Intensity of electric field inside a planar PVK:CA MC.

cavity mode full width half maximum ($\Delta \lambda_c$) is the Figure of merit for these structures and defines the MC quality factor (*Q*-factor)^[4b,14]

$$Q = \frac{\lambda_{\rm c}}{\Delta\lambda_{\rm c}} = \frac{2\pi n_{\rm c} L_{\rm eff}}{\lambda_{\rm c}} \frac{1}{\alpha L_{\rm eff} - \ln\sqrt{R_{\rm bottom} R_{\rm top}}}$$
(11)

where $L_{\rm eff}$ is the effective cavity length (Equation (13)), α is an average loss factor accounting for common loss mechanisms, and $R_{\rm bottom}$ and $R_{\rm top}$ are the defectivities of the two DBRs. The *Q*-factor is then defined by the total energy stored in the cavity and by the energy dissipation rate. For α constant, higher reflectance DBRs result in a higher *Q*-factor and then, in a sharper cavity mode. High *Q*-factors allow significant threshold reduction in microcavity laser devices and smaller volume of the optical mode (vide infra).^[111] The *Q*-factor is indeed a measure of the light dwelling time within the cavity, that is the photon lifetime in the cavity τ_c

$$Q = 2\pi v_{\rm c} \tau_{\rm c} = \omega_{\rm c} \tau_{\rm c}$$

where $v_c(\omega_c)$ is the oscillation frequency (pulsation) of the cavity mode. Notice that τ_c is much longer than the cavity transit time ($t_{tr} = n_c L_c/c$) because photons dwelling is induced by the multiple light reflections at the interfaces with the DBR mirrors.

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(12)

For polymer microcavities, the Q-factor typically spans in the range of 40-250 depending on materials processability.^[7b,26,33f,g,68a] Higher Q-factor, approaching 10³, are achieved only for MCs fabricated by vacuum technologies with bulky inorganic materials,[112] while those using metallic mirrors, which introduce loss mechanisms, show $Q \approx 10^{[113]}$ Notwithstanding the Q-factor of polymer MCs is not enormous, macromolecular materials show superior mechanical properties, easy processing and economic advantages. These characteristics secure the integration in polymer DBRs of several novel photoactive materials including organic molecules,^[7b,25,26,68a,84a,114] inorganic quantum dots,^[33f] J-aggregates,^[33g] hybrid perovskites,^[7c] as well as photochromic and nonlinear organic materials.^[28e,84a,115] All such materials are hardly compatible with the processing of inorganic DBRs, and in particular with their processing tempe rature.^[7a,33f,g,68a,84a,116] Similarly, mesoporous inorganic systems need high-temperature sintering processes, which would affect organic and polymer emitters, ligands, surface capping layers, unless postgrowth infiltration processes are used. In this case, the porosity of mesoporous DBRs favors the intercalation of small molecules and polymers within the Bragg-stacks, which would be desirable in distributed feedback (DFB) structures, but detrimental in microcavities where the spatial localization of the emitters has a key role.

Conversely to DBRs, MCs allow strong spatial light confinement, that deeply modifies light–matter interaction when fluorophores are embedded within the defect layer^[7b,26] allowing emission intensity enhancement, strong directional control, and spectral redistribution.^[7b,30,114b] Such effects depend on the MCs modal volume, small volume permits tighter light confinement within the resonator and intensifies light–matter interactions.^[4,16,117] In the case of metal mirror MCs, this volume coincides with the geometrical volume of the defect layer, because the electromagnetic field cannot penetrate the metals. Conversely, in the case of dielectric mirrors the field penetrates the DBRs and a lower confinement is achieved.^[118] The modal volume can be easily linked to the microcavity effective length ($L_{\rm eff}$) by simple geometrical considerations

$$L_{\rm eff} = L_{\rm C} + L_{\rm DBR} = L_{\rm C} + \frac{\lambda_{\rm c}}{2n_{\rm c}} \frac{n_{\rm L}}{n_{\rm H}} (n_{\rm H} - n_{\rm L})$$
(13)

where L_{DBR} is sum of the lengths of light penetration within the two DBRs at the cavity mode wavelength. Equation (13) shows that the distribution of the electromagnetic field is centered within the cavity layer and extends into the DBR mirrors depending on their dielectric contrast. This effect is shown in Figure 11c for a PVK:CA microcavity containing a PVK defect layer. For low dielectric contrast media, including polymers and highly porous systems, relatively large L_{DBR} values generate large cavity volumes. Since several light–matter interaction mechanism like strong-coupling and Purcell effect require www.advancedsciencenews.com

small cavity volumes,^[14,18c,117,119] observation of such effects in polymer and mesoporous inorganic systems have not been reported so far. This aspect is stimulating the interest in the synthesis of high refractive index polymers compatible with the DBRs and MCs growth (see Section 3).

The cavity also modifies the fluorescence of fluorophores embedded into the cavity layer. This action is not simply related to the filtering effect on the PL spectrum, but deals with the fundamental light–matter interaction process. We must remind that optical transitions are driven by the Fermi's golden rule

$$W(\boldsymbol{\omega}) = \frac{2\pi}{\hbar} \left| \left\langle \boldsymbol{\mu} \cdot \boldsymbol{E} \right\rangle \right|^2 \rho(\boldsymbol{\omega}) \tag{14}$$

where μ is the transition dipole moment, E is the electric field, and $\rho(\omega)$ is the final electronic density of states. In PhCs, we must consider E related to the allowed optical modes $E_{n,k}(r, \omega)$ of the photonic band structure (ω_n, k) and, introducing the local PDOS $(\rho_l(r, \omega))$, the transition rate becomes^[7b,16,17,29,111b,120]

$$W(\omega) = \frac{2\pi}{\hbar} \rho_l(\mathbf{r}, \omega) = \frac{2\pi}{\hbar} \frac{1}{2\pi^3} \sum_{n} \int d^3 \mathbf{k} \left| \langle \boldsymbol{\mu} \cdot \boldsymbol{E}_{n,k}(\mathbf{r}, \omega) \rangle \right|^2 \delta(\omega - \omega_{n,k})$$
(15)

To understand the role of $(\rho_{l}(\mathbf{r},\omega))$ on the emission, we need to consider that at the cavity mode it is related to the *Q*-factor^[16,111a,121]

 $\rho_{\rm l}(\mathbf{r},\omega) \propto \frac{1}{\Delta\lambda_{\rm c}} \propto Q \tag{16}$

This effect is sketched in **Figure 12**. For a homogeneous medium the PDOS has a parabolic energy dependence (Figure 12a), while in a DBR it is suppressed at the PBG with a slight increase at its edges, where the photonic modes are squeezed (Figure 12b).^[29,120b,122] In an MC, a sharp peak in the PDOS arises at the cavity mode within the PBG (Figure 12c).^[7b,16] Then, when an emitter, whose luminescence spectrum is tuned on the PBG is inserted in the cavity layer and overlapped to the MC standing wave antinodes, the PDOS is suppressed at the PBG frequencies and increased at the cavity mode ones. This results in a drastic spectral redistribution of the emission (Equation (15)), which includes the directionality properties of the photonic band structure (Figure 3) and can be observed in angle resolved fluorescence spectra.^[33fg]

We can distinguish three main effects: when the emitter photo-luminescence is spectrally broader than the PBG, the photons normally emitted at its frequencies are funneled within the cavity mode, accordingly to the PDOS. The overall effect is an intensity enhancement of the light emitted at λ_c and a reduction of intensity at the PBG. Outside the forbidden band, no major effects are observed.^[7b,33f,g,123] Figure 12d,e summarizes such effects for a PVK:PAA microcavity embedding perylene bisimide J-aggregates.^[33g,124] The top panel shows the transmittance spectrum of the sample having a minimum



Figure 12. Schematics of the PDOS a) in free space, b) in a DBR, and c) in an MC. d,f) Experimental (continuous line) and calculated (dashed line) transmission spectra and e,g) emission spectra of the MC (red) and of a reference sample (black): for a PVK:PAA MC containing Perylene Bisimide J-aggregates (d, e) (Adapted under the terms of Creative Commons Attribution-NonCommercial License.^[33g] Copyright 2017, The Authors. Published by Wiley-VCH), and for a PVK:CA MC containing CdS/CdSe core–shell nanocrystals (f, g) (Adapted under the terms of ACS AuthorChoice Licence.^[33f] Copyright 2017, The Authors. Published by American Chemical Society).

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assigned to the PBG, where the cavity mode is visible as a sharp transmittance maximum. The J-aggregate PL spectrum (black line in Figure 12e) is strongly modified. Indeed the signal is enhanced at the cavity mode, suppressed at the PBG frequencies (red line in Figure 12e), and slightly modified outside the PBG range;^[33g] when the emitter spectrum is instead spectrally sharper than the PBG, $\Delta\lambda_c$ plays a leading role in determining the effects of the modified PDOS on the PL. Indeed, in this case a sharpening of the emission and a strong increase of intensity occurs. As an example, Figure 12f shows the transmittance spectrum of a PVK:CA MC embedding a defect layer consisting in dot-in-rods CdS/CdSe nanocrystals loaded into a PS matrix.^[33f] The cavity mode is very sharp and slightly visible at ≈615 nm due to the small Stokes shift, which makes self-absorption effects dominating the transmittance spectrum. Such a sharp cavity has a strong effect on the PL spectrum (black line in Figure 12g), which is sharpened by a factor 10 and whose intensity is strongly enhanced at wavelength corresponding to the cavity mode and suppressed at the PBG wavelength (red line in Figure 12g) giving rise to Q = 255;^[33f] eventually, when the free-space emission spectrum is sharper than both $\Delta \lambda_c$ and the PBG, only an intensity variation occurs joined to a modification of the radiative rate.^[14,119,125] So far, this effect has not been reported for polymer MCs.

As mentioned above, the spectral redistribution of the fluorescence oscillator strength varies strongly also with the collection angle. Indeed, the dot product of the dipole moment vector and the electric field of the cavity standing wave provide an angular dependence, in agreement with the photonic band structure dispersion of Figure 3.^[14,125b]

According to Equation (15), an MC should also modify the emission radiative rate. The total radiative rate in a microcavity can be either enhanced or reduced depending on the spectral overlap between the emitter spectrum and the PDOS. Indeed, Equation (16) considers only one single wavelength while the emission lifetime is linked to the total emission rate

$$W = \int d\omega W(\omega) \tag{17}$$

Therefore, a spectral enhancement in a narrow spectral region does not necessarily imply a change in radiative rate. In fact, if the emitting material spectrum is broader than the cavity mode, the spectrally narrow emission enhancement is usually compensated by the broad suppression in correspondence of the PBG and the result is less effective overall emission, and longer lifetimes.^[4b,17,18,126] When instead the spectrum of the emitting material is sharper than $\Delta \lambda_c$, if strong spatial confinement is also achieved, an increase of the radiative rate can be observed determining the Purcell effect.^[4b,17,18,127] No evidence of Purcell effect has been reported so far for polymer MCs, probably due to the relatively reduced dielectric contrast available. Moreover, careful measurements of PL quantum yields for MCs and the suitable reference are also required to disentangle radiative and nonradiative lifetimes.^[33g] Recently, claim of Purcell effect has been reported for an hybrid system where a fluorescent conjugated polymer has been infiltrated in a monolithic porous silicon MC.^[128]

Concerning inorganic mesoporous structures, the need for severe thermal annealing forbids the introduction of

polymer and organic dyes in the microcavity layers, and only permits their infiltration within the porosity of the entire structure.^[129] As an example, europium emitters have been included into in SiO₂:SnO MCs,^[130] and nanophosphors have been embedded between two ZrO2:SiO2 DBRs.[110] Regarding the implementation of active polymers and organic molecules in mesoporous microcavity, some hybrid structures have been demonstrated to be compatible with temperature sensitive media. For instance, Zhang at al. showed microcavities of alternated layers of TiO₂ sol and a block copolymer requiring thermal annealing at 80 °C, which is compatible with polymer deposition.^[131] In this case, the cavity mode favors local spectral enhancement of the emission intensity of carbon dots embedded into the defect layer. In another work, Miguez and co-workers grew SiO₂:TiO₂ DBRs via dip-coating. This process allowed to spin-cast commercial dye doped nanoparticles within a defect layer.^[132] In this case spectral redistribution and a slight sharpening of the emitted signal with respect to the bare emitter were achieved. No quality factor was reported neither for inorganic nor for hybrid structures, but we can estimate values comparable to those achieved with metallic mirrors.

Microcavities become particularly attractive when the fluorophore shows amplified spontaneous emission (ASE). ASE occurs when the material undergoes population inversion by effect of the external optical pump. When the gain associated to the population inversion exceeds losses due to the microcavity imperfections and material absorption, the lasing action starts. The thresholds ($P_{\rm th}$) of the process is given by^[14,133]

$$P_{\rm th} = \frac{\hbar\omega_{\rm c}^2}{2Q\beta} = \frac{\pi h}{Q\beta} v_{\rm c}^2 \tag{18}$$

where β is the spontaneous emission coupling factor, which provides the fraction of the total spontaneous emission rate emitted into the laser mode (above 10% for inorganic MCs).^[14] Before leaking out, such photons dwell in the cavity for a time τ_c depending on the Q-factor value (Equation (12)). Equation (18) also highlights the importance to increase the Q-factor, to lower the lasing threshold. In solution processed MCs, the O-factor is strictly connected to the material processability and to the dielectric contrast. Since the first demonstration of ASE in conjugated polymers, both in solution and polymer blends,^[134] optically pumped solid state organic laser gained a widespread interest and are still in the spotlight for their potential use in several fields.^[135] Lasing action in microcavities based on a conjugated polymer was first reported in 1996^[136] for a feedback structure consisting in a metal mirror and an inorganic DBR. Following this result, two inorganic DBRs have been employed as feedback structure to gather lasing action by conjugated copolymers.^[137] The first flexible laser was instead demonstrated for distributed feedback cavities where a diffraction grating acting as Bragg reflector was implemented into a planar waveguide. In this case, vertical emission on the second order diffraction occurs (Figure 13a,b).[138] This structures can be easily produced by soft lithography. Sophisticated structures can be even adapted to biochips as membrane lasers (Figure 13f,g).^[103,135,139] After these milestones, lasing action was achieved with several structures including microdisks (Figure 13c),^[140] and whispering gallery fibers (Figure 13d).^[141]



ADVANCED OPTICAL MATERIALS



Figure 13. a–e) Different lasing cavity structures achieved both with organic and inorganic systems. f,g) Example of membrane DBR laser adapter to a biochip. Reproduced under Creative Commons Attribution 4.0 International License.^[135b] Published 2018, Springer Nature.

Infiltrated opaline structures are instead efficiently used to achieve DFB and random lasing.^[142]

Polymer planar microcavity lasers (Figure 13e) have been reported for both the lab scale^[143] and on large area by coextrusion,^[94a,e,144] while only few examples have been shown for inorganic solution processed systems.^[69,145] Indeed, while bulky inorganic DBRs have been widely demonstrated, [136,137,146] due to the issues related to the material confinement previously described, mesoporous inorganic microcavities have not been widely investigated. As discussed before, dye percolation all through the cavity structure can be used to achieve zero-group velocity lasing action in mesoporous DBRs fabricated by spin coating.^[69,114a,145a] Conversely, polymer^[7a,26,116b,e,135b,147] and hybrid^[148] planar MCs have been widely demonstrated. Moreover, they allow to tune the lasing emission exploiting the mechanical properties of elastomeric polymers,^[144a,149] temperature responsive materials^[150] or the ease of modulation in liquid crystals and photochromic media.^[151] Interesting perspectives in the field also concern novel laser feedback cavities made by cholesteric liquid crystals,^[65,151b,152] diatoms,^[153] nanoplasmonic lattices,^[154] and even single cells.^[155]

4.3. Sensing

In the last decade, many PhC structures were demonstrated to be effective transducers for chemical and biological molecules,^[8,156] as well as for physical stimuli like pressure^[157] and temperature.^[158] The sensing process relies on the modification of the PhC optical response triggered by external perturbations affecting the lattice periodicity, its dielectric function or the dielectric environment. In this sense, lacking permeability dense bulky inorganic DBRs are not suitable for sensing, but they can be used to confine the light and achieve surface sensors (vide infra, Bloch surface waves). Conversely, polymer an porous PhCs based on silk,^[159] cellulose and cellulose derivatives,^[25,160] block-copolymers,^[92,93,161] diffraction gratings,^[162] opals, inverse opals,^[160b,163] molecularly imprinted polymer opal-like structures,^[160b,163g,164] colloidal crystals,^[165] porous inorganic^[166] and hybrid^[53d,167] DBRs, are highly sensitive to both liquid and gas analytes, and offer low detection limits and high sensitivity.

In this section, we will focus on the sensing of chemical species based on the variation of the light optical path induced by

analyte intercalation in DBRs made either of dense permeable polymer media or of mesoporous media. Then we will review photonic crystal sensors based on the variation of the dielectric environment at the PhC surface probed by Bloch surface waves.

Inorganic mesoporous DBRs represent the perfect prototype of photonic sensors. They act as efficient membranes, where the permeation of species is ruled by diffusion mechanisms driven by a gradient of chemical potential at the two sides of the membrane. The ease of transport of each species is quantified by the membrane permeability (\wp_i). In the case of photonic sensors, the driving force is provided by the different concentra-

tion at the two sides of the DBR. For ideal gases, the flow (*J*) of a species through a membrane with thickness *L* along the diffusion direction can be related to the pressure difference $(p'_i - p_i'')$ by the Fick's Law

$$J = \frac{\delta \mathcal{P}_i}{L} p'_i - p_i'' \tag{19}$$

Nowadays, DBR sensors rely on two main diffusion mechanisms. The first is typical of mesoporous structures, takes the name of Knudsen diffusion, and rules molecular diffusion through a membrane with pore dimension comparable or larger than the permeating molecules (Figure 14a). In this case, light and smaller molecules diffuse faster than those with larger size and weight. When the pore diameter allows molecular size selection, molecular sieving is achieved, and only small molecules permeate within the porosity while larger molecules are selectively stopped (Figure 14b). In the case of vapor and gas analytes, this process may also allow capillary condensation, which causes strong refractive index changes and then a remarkable variation of the DBR spectral response, that is much larger than the one induced by simple vapor permeation. The second mechanism is instead typical of polymer DBRs, which often behave as dense membranes, where solution-diffusion rules the permeation. In this case, the permeating elements are first dissolved into the membrane and then diffuse through it (Figure 14c).^[168] These elements must have a certain chemicophysical affinity with the dense matrix to be efficiently dissolved. In polymers, such affinity can be described by the Flory-Huggins and Hildebrand parameters, which well describes the ability of an analyte to diffuse and interact with the macromolecules forming the DBR sensors, and in turn the sensitivity to



Figure 14. a) Knudsen diffusion through pores and b) molecular sieving. c) Solution diffusion through dense membranes.

the analyte itself. For this reason these sensors can be called Flory–Huggins photonic sensors. $^{[25,31,43,57a,169]}$

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As mentioned above, thanks to their high permeability, mesoporous DBR sensors always attracted large interest for sensing.^[170] The variation of their optical response is usually driven by vapor–liquid transitions which induce a significative change in the effective refractive index due to the filling of interparticle voids. In this regard, Ozin and co-workers group provided several examples of active mesoporous DBR structures made of silica, titania,^[167] and clay^[171] for the characterization of toluene,^[172] ethanol,^[167] food degradation by-products,^[173] and other organic molecules.^[171] In this case, simple analysis of the PBG spectral shift to investigate the permeation process does not provide qualitative and quantitative information, and multivariate analysis must often be applied.^[17,173] Mesoporous inorganic DBR sensors usually achieve detection of about 10⁻¹ ppm.^[31,174]

Concerning the selectivity of these inorganic sensors, three main mechanisms lead to analyte recognition.^[31] The first uses arrays of chemical targets,^[156g,166a,175] or fluorophores,^[175b,176] also called labels, which selectively interact with the analyte. The optical or colorimetric response of the labeled matrix is then often analyzed via chemiometry. Ozin showed SiO₂:TiO₂ DBRs able to disentangle aliphatic molecules with very similar structure.^[175c,177] To achieve optical selectivity, the DBR was divided into 9 pixels whose surface was functionalized with different silanes to accomplish diverse hydrophobicity. The interaction between the functionalized pixels and the analytes offered a modest optical response, hardly perceived by naked eye. However, when the optical response of each photonic pixel is analyzed via color imagery analysis, which transduces the spectral variation into a Red–Green–Blue pattern, and finally

multivariate analysis is applied, molecular recognition and selectivity can be obtained.

To simplify the signal transduction, one can also employ the DBR spectral variations induced by the analyte intercalati on.^[166b,167,178] This method offers simple data analyses but, in the case of vapor analytes, require their condensation within the DBR porosity, which must be properly tuned to allow both intercalation of large amount of analyte. Moreover, selectivity may be negatively affected by the very similar refractive index shown by different analytes in the liquid phase.^[166b]

The selectivity of mesoporous DBR sensors has been improved including size selective active media. For instance, Lotsch and co-workers used zeolite:TiO2 DBRs fabricated by spin-coating and thermal annealing.^[166b] Figure 15a shows a cross-sectional SEM image of the sensor made of large porosity TiO₂ layers, where Knudsen diffusion occurs, alternated to active layers of zeolite or metal-organic frameworks, which offer selectivity via molecular sieving. The DBR shows spectral shift of the PBG position depending on analyte species and concentration (Figure 15a). A drawback of this method relies on the concentration dependence of the DBR effective refractive index. Low concentrations of analytes with high refractive index may in fact induce the same shift occurring for larger concentrations of another species having smaller molecular polarizability. Figure 15a' shows that for selected concentration ranges the spectral shift versus partial pressure curves for different analytes are overlapped and do not allow their recognition. In spite of that, selectivity can be enhanced combining the response of multilayers with different porosity/periodicity to create matrices of responses,^[179] or exploiting a third variable, beside analyte and concentration, such as temperature.^[180]



Figure 15. a) SEM image of a Zeolite:TiO₂ DBR and a') PBG spectral shift of the same DBR obtained for exposure to different analytes. Adapted with permission.^[166b] Copyright 2012, Royal Society of Chemistry. b) Triple porous silicon DBR stack used to control analyte diffusion dynamic, and b') time resolved PBG spectral shift for different analytes. Adapted with permission.^[179b] Copyright 2011, American Chemical Society.

Discrimination based on the kinetics of the optical response was shown for porous silicon DBRs made of three stacks having different porosity that regulate the analyte diffusion kinetic depending on its molecular size (Figure 15b). The different intercalation kinetic allows time resolved recording of the PGB shift, which are characteristics of the analytes and allow their recognition. As it is shown in Figure 15b' the analysis of the spectral response joined to the kinetics of the process allows to discriminate among organic molecules with very similar properties, such as methanol and ethanol.^[179b]

Recently, polymer DBRs aroused considerable interest due to remarkable spectral response amplified by the ease of swelling of macromolecular media. Moreover, the relatively small PBG spectral width typical of polymer DBRs is advantageous in term of sensitivity and to lower the detection limit. Indeed, block copolymer DBR sensors demonstrated high sensitivity and optical responses easily detectable by the naked eye for the case of analytes in the liquid phase as previously discussed (see Section 3.2).^[92,93,161] Concerning the detection of analytes in the vapor phase, the first report regarding the use of polymer DBRs was by Convertino and co-workers. They reported on the detection of toluene, acetone,[57b] and short chain alcohols[53b] using layers of a pure fluorinated polymer alternated to layers of the same polymer doped with gold nanoparticles fabricated by thermal vapor deposition. Following his work, Zappe and co-workers reported cross-linked PS:PMMA DBRs sensitive to acetone and toluene. In these systems, the Flory-Huggins parameters for polymer-analyte pairs drive the swelling of the cross-linked polymer during analyte intercalation allowing the optical detection.^[181] However, from the fabrication point of view, chemical vapor deposition is costly and time consuming, while cross-linking introduces an additional step in the growth, which can be neglected using amorphous or even semicrystalline polymers. Indeed, DBR vapor sensors fabricated by spin-coating of commodity polymers demonstrated an increased sensitivity to a variety of organic solvents with respect

to that reported for inorganic mesoporous structures.^[7c,31,43] For instance, PS:CA DBRs, where the PS matrix was doped with ZnO nanoparticles to enhance free-volume and then permeability, showed toluene sensitivity below 1 ppm and lower detection limit of 20 ppm.^[43] In the case of polymers, selectivity relies on the different affinity between polymers and analytes. Such affinity, similarly to a chromatographic separation, allows to differentiate the analytes both observing the kinetics of the optical response and the steady state equilibrium response. Indeed, both the optical response and its kinetics are affected by physicochemical parameters which determine the Flory-Huggins and Hildebrand ones, analyte molecular size, and polymer free volume. The mechanism was shown in DBRs made of alternated layers of CA and poly (p-phenylene oxide) (PPO) as active medium for sensing aromatic compounds.^[31] PPO is indeed well-known for its remarkable sorption properties correlated to its crystallinity.^[182] The analytes intercalation in the structure brings to guest induced crystallization of the PPO layers^[182a,d,e] inducing prominent changes in the refractive index and in the response kinetics. These last favor an easy recognition of very similar analytes in term of molecular size and polarity such as benzene and toluene, beside carbon tetrachloride and 1,2-dichlorobenzene (Figure 16).^[31] The first effect of analyte exposure, is a clear DBR color change, which can be perceived by the naked eye providing an easy to read system to monitor pollutants and hazardous compound leakages (Figure 16e).^[31] Moreover, a more detailed analysis of the optical response kinetics of CA:PPO DBRs provides a characteristic fingerprint of the different analytes, as observed in Figure 16 where the kinetics of the evolution of the DBR transflectance spectra upon analyte exposure is reported as a contour plot. The four analytes reported in the Figure clearly give rise to a different response, which allow their discrimination. Very recently, the same mechanism was used to detect fluorinated species using perfluorinated macromolecules as active sensing media within the DBR.^[23b] The choice of the



Figure 16. Contour plots of a PPO:CA DBR transflectance spectra upon 25 min of exposure to a) benzene, b) 1,2-dichlorobenzene, and c) carbon tetrachloride, and d) toluene. e) Digital images of the sensor surface collected before (right) and after (left) exposure to the four vapors. Adapted under the terms of ACS AuthorChoice Licence.^[31] Copyright 2017, The Authors. Published by American Chemical Society.

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proper macromolecule in the DBR sensor is then the key factor to develop colorimetric label-free detectors for environmental monitoring.

Hybrid polymer-inorganic structures were recently reported by Lazarova et al. showing permeable devices made by alternated layers of PMMA and porous V2O5.[70] Sensors were fabricated by alternated spin-coating and thermal annealing of a vanadium sol and a polymer solution. The relatively low dielectric contrast between the polymer and the porous V₂O₅ allows a narrow PBG undergoing significant spectral variation upon chloroform vapor exposure, due to the swelling of the polymer medium. Lazarova also compares the response of DBRs made by porous and compact inorganic layers and demonstrates that the porosity of the thin inorganic layer allows penetration of the analyte within the DBR and thus stronger response induced by a swelling of the polymer films by 5% of their initial volume. Concerning sensitivity and lower detection limit polymer structures show values comparable to those of inorganic systems.^[31]

The examples just mentioned deal with variation of the DBR optical path upon analyte sorption. However, variation in the DBR dielectric environment can also affect its optical response without analyte permeation. To gather high sensitivity and probe the electromagnetic field at the DBR surface, Kretschman configuration has been used to excite Bloch surface waves (BSWs).^[16,121] As depicted in Figure 17, in this configuration the BSW is confined at the outer surface of the DBR structure by two effects: total internal reflection at the prism side, and the PBG at the DBR side (Figure 17a).^[16,183] When the BSW is probed in reflection configuration using white light in the total internal condition, it is observed as a deep minimum (Figure 17b).^[184] Variation in the environmental refractive index (in this case from 1.33 to 1.34) induces a change in the spectral/ angular response of the BSW (Figure 17b). This change can be induced by an analyte flowing in a solution interacting with a receptor anchored on the surface of functionalized DBR. In this case selectivity is guaranteed by the receptor while sensitivity by the tight optical conditions needed to excite the BSW. Beside sensing, BSWs have been extensively used to enhance photoluminescence signal,^[183b] for laser excitation,^[114b,185] to favor surface enhanced Raman scattering^[186] or reflectivity.^[183d,187] and strong-coupling regime.^[183a,c,e,188]

In both cases, thanks to the field localization, BSWs enhance light–matter interaction on the DBR surface facilitating sensing at the molecular level^[183d,189] The efficiency of these systems have been predicted for biomolecules,^[183d,190] and demonstrated for proteins^[187] and small molecules^[191] using bulky inorganic multilayered structures, which provide very sharp BSW fingerprint due to the great control of interfaces roughness and high dielectric contrast available. Currently, polymer DBRs cannot provide similar structural quality, however they have been demonstrated to be suitable to show BSWs with less defined spectral features providing strong modification of fluorescence and its enhancement indicating that all-polymer DBRs can be performant even in this field.^[114b,185b]

4.4. Other Applications

The sensitivity of PhC to electrical, magnetic, chemical, and optical stimuli^[192] makes them very interesting also for a variety of different applications such as displays, optical switchers, and memories. For instance, electrically tunable DBRs are very promising for new generation color e-reader displays.^[193] The electronic-ink displays currently available on the market work without back illumination and are a good replacement for paper books. However, they suffer from low switching velocity due to the electrophoretic generation of the signal and lack of color. The addition of passive filters allowed colored displays, but limits the chromatic rendering.^[194] Pixels based on electrically tunable DBRs might then close the gap between paper and electronic displays.^[195] Indeed, large area commercial polymer DBRs have been demonstrated to be efficient for color tuning in electrically driven devices using emitting conjugated polymers.^[95,196] In this regard, Thomas and co-workers reported on electrochemically tunable block copolymer multilayers^[88] which can change their color from red to green and blue applying low voltages (Figure 18).^[193] The DBRs are made of a PS:(poly 2-vinylpyridine) (P2VP) block copolymer filled with trifluoroethanol, and exploit swelling of the P2VP block achieved through oxidation/reduction processes, which modify the layer thicknesses. This process allows a significant shift of the PBG for increasing voltages (Figure 18a'). Similar effects have been reported by Zhang and co-workers on hybrid TiO2:polydimet



Figure 17. a) Schematic of the DBR-prism geometry for BSWs. b) Reflectance in periodic BSW stacks for two different refractive indexes (n = 1.33 and n = 1.34) of the external medium. Adapted with permission.^[184b] Copyright 2017, Elsevier.







Figure 18. a) Schematic of a tunable block copolymer DBR, a') its transmittance spectra for different applied voltages. The insets show the photographs of the sample surface. Adapted with permission.^[193] Copyright 2009, Wiley-VCH. b) Schematic of the mesoporous SiO₂:ZrO₂ DBRs and b') their transmittance spectra for different applied voltages. The inset shows an SEM image of the DBR section. Adapted with permission.^[198] Copyright 2012, American Chemical Society. c) Right-and left-handed photoswitchable cholesteric LC, c') dynamic photoresponsive flexible display, c'') conventional electrically addressed display (left) and photodisplay carrying the same information (right). Adapted with permission.^[199] Copyright 2008, Society for Information Display.

hylaminoethylmethacrylate DBRs fabricated by spin-coating, whose PBG can be tuned over more than 100 nm using solutions with different pH.^[197]

In 2012, Criante and Scotognella reported on electrical modulation of the optical response of mesoporous inorganic DBRs made of SiO₂ and ZrO₂ heavily doped with a nematic liquid crystal (LC) (Figure 18b). In this device, the electric field aligns the liquid crystals and then the anisotropy of the refractive index steers the optical response of the DBR.^[198] In principle, this system could be adapted to the current LC display technology providing a structural colored pixel and a fast switching operation.

An additional opportunity provided by LC is given by photoaddressable displays.^[156b,199] Indeed, photochromic cholesteric LC allows light driven twisting of the helical pitch (from right handed to left-handed and vice versa, Figure 18c). This mechanism can be used to write the information without electronic devices to drive dynamic responsive displays (Figure 18c').^[156b,199] This kind of displays do not need for patterned electronics, are intrinsically high resolution, can be flexible, and can be self-assembled into highly ordered structures over large areas (Figure 18c''). Moreover, a full color palette is possible via chemical engineering of the molecular structure.^[156b]

An additional proof-of-concept application of polymer and mesoporous DBRs is provided by optical switchers and memories, which exploits active media with different nonlinear optical (NLO) responses. Even though nonlinear media could be adopted in such devices by themselves,^[156b] DBRs possess additional features (e.g., spectral transduction, enhanced light–matter interaction, spatial localization—see Section 4.2) and allow nonlinear behavior at low pumping powers and/or operation in additional spectral ranges. Solution processed MC could then be a viable and low-cost mean for efficient optical switches. For instance, Katouf et al. reported on an ultrafast switcher operating at 1064 nm using PAA:PVK DBRs and MCs doped respectively with second and third order commercial NLO media.^[115b] Zhu et al. showed enhancement of optical nonlinearity of CoO₃ nanoparticles embedded in PVA used as low index medium in PVA:PVK DBRs.^[200] Menon and co-workers showed DBRs made of PMMA and a silver nanoparticle PVA composite as an effective system to induce a three-fold enhancement in the nonlinear absorption coefficient with respect to the bare nanocomposite.^[201] Chandrasekharan and co-workers demonstrated by Z-scan a 3.5-fold enhancement of the nonlinear optical response of a porphyrin layer when embedded as a cavity layer into a CA:PVK MC.^[115a]

Other kind of switchers make use of photo- and thermochromic active media,^[202] as well as of conducting metaloxide heavily doped semiconductors polymer nanocomposite undergoing specific optical variation upon stimulations.^[203] These media are characterized by slow response times, which are not suitable for fast all-optical switching. On the other hand, their modified phases are stable enough to make them interesting for optical memories. Similar effects can be obtained also with photochromic systems. As an example, the azobenzene group, which is also a mesogenic moiety, can be successfully integrated as pendant group into a carrier macromolecule. The efficient photoisomerization process, which converts their rod-like trans form into the cis bent one, allows a substantial change in refractive index ($\Delta n \leq 0.1$).^[204] Moreover, orientation and anisotropy can also be achieved in the nematic liquid crystals phase when polarized light is used to induce the photoisomerization (Figure 19a,b).^[205] Then, embedding a







Figure 19. a) Azobenzene structure, b) sketch of the switching mechanism in DBRs doped with azobenzene. c) Variation of reflectance spectrum of the PMAz6Ac:PVA DBR with thermal annealing. d) Repeatability over several cycle of the photoisomerization process in the DBR. Adapted with permission.^[115c] Copyright 2014, Elsevier. e,f) Transmittance spectra of a CA:PVK MC after irradiation with 405 nm linear polarized writing laser (red) and unpolarized 440 nm erasing laser (blue),^[84a] spectra were collected with white light polarized parallel (e)/orthogonal (f) to the polarization of the writing laser.

photochromic material into a PhC, allows optical response to the photoisomerization in spectral ranges far away from the molecule absorbance, preventing optical losses.^[84a] In this way, only the real part of the refractive index acts on the modulation process. As an example, Kurihara and co-workers reported on DBRs made of 20 periods of azo-functionalized polymer liquid crystal (Figure 19) and PVA to achieve ON/OFF switchers for recording.^[115c] The system is based on the variation of refractive index of the azo-functionalized polymer. Indeed, the randomly oriented liquid crystal polymer shows refractive index n = 1.6. In this configuration, the DBR shows an intense reflectance peak (Figure 19b, ON state). After visible light irradiation and/or thermal annealing, the azo-derivate undergoes isomerization and orientation in the out-of-plane direction. This process decreases its refractive index to n = 1.5, which matches the refractive index of PVA. In this case the dielectric contrast is drastically reduced preventing the PBG formation (Figure 19b, OFF state). As depicted in the inset of Figure 19c, the oriented sample appears indeed transparent, while the randomly oriented one shows a bright orange color. The switching process shows full reversibility through UV-light irradiation and remarkable repeatability (Figure 19c).^[115c]

A similar approach has been used with the azobenzene photochromic in a CA:PVK MCs.^[84a] In this case, the first order cavity mode has been engineered at the telecommunication spectral window, while higher orders appear in the visible spectral range. Blue (unpolarized)-violet (linearly polarized) lasers activates the photoisomerization inducing the anisotropic shift of the cavity mode for both first and second order PBGs. (Figure 19e,f). In this case, the sharp cavity mode can be tuned up to 10 nm by the photoisomerization with an intensity

change of about 20%, which is comparable to that exploited in RW-DVD. $^{\left[84a\right] }$

5. Summary and Perspectives

Since the early 1990s, when the first solution-processes for the fabrication of 1D photonic crystals were reported, many new materials and structures have been investigated. Nowadays, such systems are attracting large attention from both Academia and Industry. As a result, DBRs made of both polymers and inorganic mesoporous materials are the first photonic crystals available on square meter areas. Nowadays, these structures offer low fabrication costs, ease of scale-up, and performances almost comparable to those of inorganic PhCs fabricated via vacuum technologies, with applications including light management, emission control, lasing, optical switches, and sensing. On the other hand, the small dielectric contrast achievable with solution-processed media still forbids strong coupling regime and radiative rate enhancement. In this work, we introduced the basic concepts behind the formation of the photonic band-gap in 1D PhC, its properties and modeling. We also reviewed fabrication processes, and applications in emission control, sensing, and photovoltaics focusing on the figures of merit of polymer and mesoporous inorganic structures. Thanks to the possibility to fabricate large-area structures both with polymers and inorganic dielectric materials by industrial coextrusion and by layer-by-layer deposition, DBRs promise low-cost integrated optoelectronic devices such as large area emitters and lasers, low-cost disposable sensors, and colorimetric safety devices, as well as functional architectural components for SCIENCE NEWS _____ www.advancedsciencenews.com

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thermal shielding in building and transparent photovoltaic modules as well as luminescent solar concentrators.

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Conflict of Interest

The authors declare no conflict of interest.

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