

# Nanostructuring of Azomolecules in Silica Artificial Opals for Enhanced Photoalignment

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Many modern systems are based on photoresponsive materials, in which properties such as the refractive index need to be effectively controlled. An extensively used means of achieving this is to photoinduce birefringence by alignment of anisotropic azochromophores via light-induced isomerization. However, the refractive index changes are typically small ( $<10^{-2}$ ), slow (seconds or minutes) and not spontaneously reversible, which excludes use of this approach in a variety of optical systems. The drawbacks are generally attributed to hindered photoalignment due to the molecular environment, which suggests that optimizing the arrangement of the functional moieties to minimize the mobility restrictions could decisively improve the photoresponse. Here, a simple solution-processing approach is reported for favorable distribution at the molecular level of neat azochromophore into a three-dimensionally nanostructured hybrid system exhibiting an extremely enhanced photoresponse. The standard azoderivative Disperse Red 1 is adsorbed on silica colloidal crystals that are chosen as 3D-templates because their photonic bandgap, which is sensitive to refractive index changes, provides a direct tool to study photostimulated processes in the chromophore. The system is thoroughly investigated with different techniques to identify molecular out-of-plane photoalignment as the main phenomenon responsible for the optical response, and to discern the key factors leading to improved performance. It is found that the dye molecules are spontaneously adsorbed on the silica spheres, building a highly photoreactive surface multilayer. A low amount of azochromophore allows for outstanding material response upon cw-irradiation, as a result of very large and fast refractive index changes in the chromophore ensemble (up to 0.36 – birefringence of 1.1 – in 15 ms at  $0.09 \text{ J cm}^{-2}$ ) that, in addition, is fully reversible by thermalization. Finally, as proof-of-principle for real applications, long-duty cycle photoswitching at 100 Hz (for over 2 million cycles) is demonstrated in this system.

## 1. Introduction

Photochromic materials are of great interest for many optical applications that are based on changes of the refractive index.<sup>[1,2]</sup> Systems exhibiting reversible, large and fast

photoinduced effects are needed in most cases. Photoisomerization (PI) in azobenzenes (anisotropic, cigar-like molecules with the optical transition dipole moment approximately lying along the long axis) has attracted a great research effort over recent decades as a versatile process to photoinduce changes in the material refractive index. Thereby, light irradiation induces selective depletion of the *trans* molecules parallel to the light polarization to the *cis* state (*angular hole burning*), and successive *trans-cis-trans* cycles lead to gradual photoalignment of the molecules perpendicular to light polarization, so they absorb less light (*angular redistribution*).<sup>[3]</sup> The material becomes *birefringent* as light perceives different refractive indices depending on its direction of propagation, i.e., an extraordinary index  $n_e$  (along the axis of anisotropy) and an ordinary index  $n_o$  (perpendicular to it). The degree of anisotropy is given by the *birefringence* (BR)  $|n_e - n_o|$ . In thin films it is usual to distinguish between *in-plane* and *out-of-plane* BR, depending whether the anisotropy is induced parallel or perpendicularly to the film plane, respectively.<sup>[4]</sup>

In general, azo-based systems (azo-dispersed polymers, deposition films) exhibit small macroscopic effects ( $\Delta n$  of about  $10^{-3}$ ), slow response (seconds or even minutes) or incomplete reversibility (which leads to an effective loss of performance, thus needing additional excitation or heating for complete erasure).<sup>[1,2]</sup>

Since photoalignment necessarily involves spatial rearrangement of the azomolecules as well as of their surroundings,<sup>[5]</sup> macroscopic changes are assumed to happen in an intrinsically slow fashion, especially in condensed phases. PI may be drastically handicapped not only by the environment but also by aggregation phenomena due to the polar character of azo-dyes or  $\pi$ - $\pi$  stacking (H-aggregates).<sup>[6–8]</sup> Thus, the optimization of the organizational characteristics of isomerizable moieties and their environment will decisively improve the efficiency of the PI process. However, this straightforward strategy has barely been explored so far.<sup>[9]</sup> The largest photoanisotropies to date are exhibited by azobenzene-side-chain polymers<sup>[10–12]</sup> and liquid crystalline azopolymers.<sup>[13,14]</sup> They generally consist of large

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molecules comprising photoresponsive and mesogen units, in which very large BR (as high as 0.76) can be photoinduced. The large response is due to cooperative rearrangements of microdomains, at the expense, however, of difficult erasure (unwanted for many applications) and slower rates (of several hundreds of milliseconds in the best cases<sup>[15,16]</sup> but, in general, of many seconds). Sub-millisecond response is only achieved in pulse laser experiments using very high light doses.<sup>[17,18]</sup> Further, these systems are costly and require important synthetic efforts associated with covalent reactions, purification difficulties, and poor solubilities.<sup>[2,4]</sup> Thus, easy-to-fabricate azo-containing systems exhibiting large, fast and spontaneously reversible photoalignment are demanded, preferably involving small azomolecules and solution-processable techniques, as reported in this work. Besides, the results offer relevant insights into the intrinsic limits of PI-induced processes and open new applications in optical systems.

## 2. Strategy

Our aim is to obtain simple azomolecular ensembles with enhanced photoalignment performance through improved arrangement of the active molecules in a favorable environment. Other criteria like the non-necessity of synthesis and low-cost fabrication (i.e., solution processability) are of great importance as well. Recently, improved PI-induced anisotropy through favorable distribution of azomolecules was demonstrated,<sup>[9]</sup> in which Disperse Red 1 (DR1) molecules were covalent bonded to an amorphous silica backbone by a sol–gel process. The covalent bond of the dye to the backbone prevented the formation of chromophore aggregates. Further, additional organic groups were incorporated to the silica to provide more internal free volume and flexibility to the matrix, which improved the spatial motion of the chromophore and diminished dye–dye interactions. DR1 isomerization was found to induce large refractive index modulation in the medium ( $\Delta n = 0.04$ ) with subsecond response, which meant a clear enhancement compared to previous DR1-containing materials. However, two important restrictions still remained: i) the highly amorphous silica matrix of the sol–gel most likely led to rather inhomogeneous dye distribution with subsequent electrostatic constraints or partial aggregation, and, ii) the strong covalent bond to the silica probably limited the dye mobility in the matrix.

In this work, we present a much more direct approach for chromophore structuring, in which, firstly, we employ the *neat* chromophore to avoid matrix constraints and synthesis. Secondly, the chromophore molecules are weakly (but stably) attached at hydrophilic silica by physical adsorption rather than by chemical bond. Thus, we intend to minimize aggregation while keeping freedom of motion. Thirdly, in order to obtain a highly regular allocation of the dye in the bulk, we use a well-defined 3D nanostructure as a *template*. All goals are easily achieved by infiltrating an artificial silica opal with neat azo-chromophore by simple casting. Artificial opals, formed by self-assembled colloidal spheres, constitute easy-to-fabricate, 3D-organized nano/microstructures widely employed as inexpensive and adaptable photonic crystals.<sup>[19]</sup> Thus, the use of opals as template provided us with a versatile nanostructured

matrix. Further, they exhibit photonic bandgaps (PBG) that strongly depend on the refractive index of the medium filling the interstitial voids. This property offers a straightforward tool for measuring, on the one hand, the amount of chromophore infiltrated and, on the other hand, the refractive index changes induced by PI.

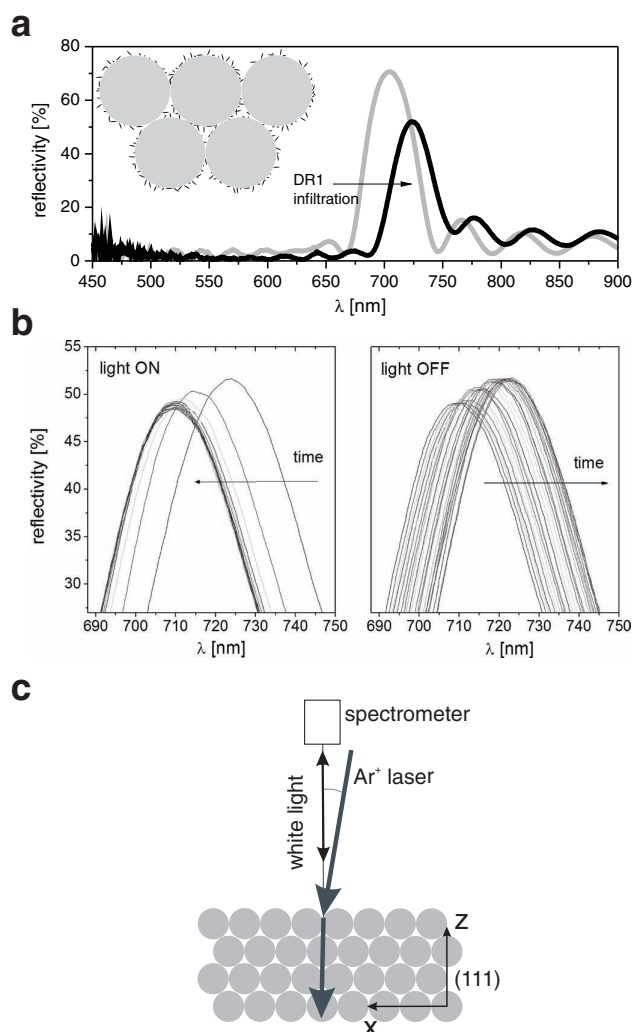
This strategy provides a very simple solution-processed way to prepare versatile 3D-distributed isomerizable systems without synthesis. Note that our approach essentially differs from other studies in which opals are infiltrated with a photoactive medium for optical tuning of their photonic properties.<sup>[20–22]</sup> Besides, in these studies azo units were either embedded in or bonded to a polymer matrix. In our approach, opals are just used for 3D nanostructuring of the photoactive medium, aiming for improved photoresponse independently of the opal properties. Furthermore, we avoid using any polymeric matrix in order to prevent, as much as possible, constraints to the dye motion due to the environment.

## 3. Results and Discussion

### 3.1. Opal Infiltration with Chromophore

To prove the validity of this approach we chose the standard azochromophore DR1, which exhibits efficient performance and well-known dynamics in conventional films. Further, DR1 is a pseudo-stilbene-type (*push–pull*) molecule, characterized by strong overlapped  $\pi$ – $\pi^*$  and  $n$ – $\pi^*$  absorption bands and a metastable *cis* state.<sup>[1,3,23]</sup> Thus, the photoinduced BR is predominantly due to angular redistribution (photoalignment). Moreover, pseudo-stilbene azo derivatives are particularly sensitive to the local environment.<sup>[3]</sup> DR1 also possess an –OH end group, which should facilitate the adsorption of the chromophore by the silanol groups at the silica surface. Silica opals were directly infiltrated with pure DR1 by simple casting. The Bragg peak (see the Experimental Section) shifted to longer wavelengths after infiltration, which evidenced that the voids were partially filled with chromophore after solvent evaporation (Figure 1a): the voids filling led to the increase of  $n_v$  and the subsequent increase of the peak position  $\lambda_{\text{Bragg}}$  (Equations 1 and 2). The reflectance decreased due to the lowering of the dielectric contrast between spheres and voids. Scanning electron microscopy (SEM) showed that the dye molecules formed no macroscopic conglomerates on or between the opal spheres (Figure 1b).

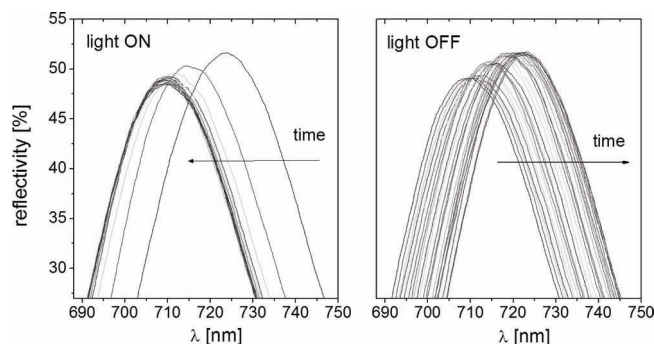
The bandgap redshift after infiltration gives a direct measurement of the amount of chromophore kept attached at the opal, if the refractive index of neat (condensed-phase) DR1 in the opal,  $n_{\text{DR1}}$ , is known. The latter, although not straightforwardly, can be estimated with sufficient accuracy, as described in the Experimental Section. By measuring the absorbance  $A$  of the infiltrated opal we obtain, using Equations 3–5,  $n_{\text{DR1}} = 1.56$  (at 720 nm) and the DR1 density  $\rho_{\text{DR1}} = 0.1 \text{ g cm}^{-3}$ . The redshift of 20 nm measured in Figure 1a corresponds to  $n_v = 1.14$  (Equation 1), which yields a relatively high filling of the void volume,  $g$ , of 0.25 (Equation 2). This corresponds to a DR1 filling of 6.5 vol-% of the total opal volume or, substituting  $\rho_{\text{DR1}}$  in Equation 6, to a DR1 weight content of 0.4 wt-%. The latter value agrees



**Figure 1.** a) Reflection spectra of an as-grown silica opal, before and after infiltration with DR1 (grey and black lines, respectively). Inset: scheme of the DR1 distribution on the spheres surface, partially filling the opal voids. b) SEM image of the DR1-infiltrated opal (the scale bar is 500 nm). c) Experimental setup for opal characterization and in situ Ar<sup>+</sup> laser photoirradiation.

with rougher estimations obtained by elemental analysis,  $(0.3 \pm 0.2)$  wt-%, and thermogravimetry,  $(0.4 \pm 0.2)$  wt-%. Note that  $\rho_{\text{DR1}}$  in our system is about one order of magnitude smaller than the values of most polymers and chromophores, close to  $1.2 \text{ g cm}^{-3}$ .<sup>[24]</sup> Such a low density is consistent with the rather high volume filling (causing the large redshift of 20 nm) and the small amount of DR1 molecules in the opal (low weight content). The latter fact agrees with the relatively low absorbance measured.

The opal was irradiated with a linearly polarized 488 nm Argon line while measuring in situ the opal reflection spectrum (Figure 1c). This procedure gave straightforward information about the changes photoinduced in the system, in particular in  $n_{\text{DR1}}$ . With the choice of the sphere size, the opal PBG appeared far enough from the chromophore absorption band, ensuring



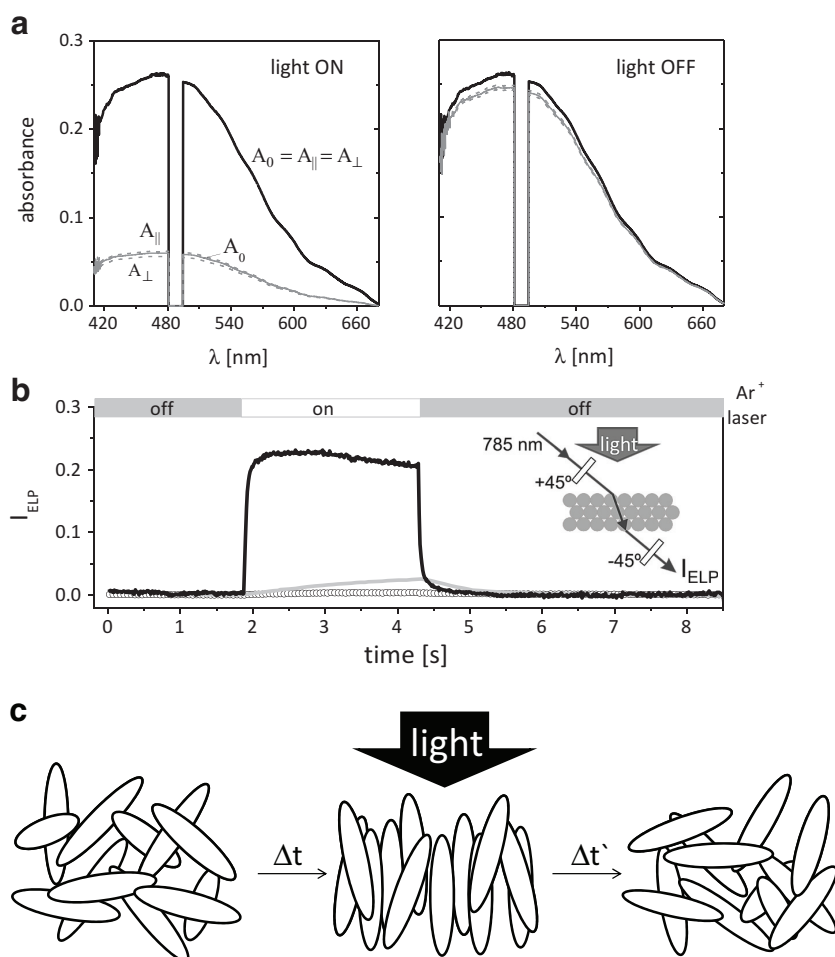
**Figure 2.** Time-dependent response of the Bragg peak of a DR1-infiltrated as-grown silica opal under 488 nm photoirradiation ( $6 \text{ W cm}^{-2}$ ) and following relaxation under dark conditions. Reflection spectra were measured every 5 ms.

weak absorption and negligible resonance. The PBG was also far from the excitation wavelength, which excluded *slow photon* phenomena increasing the PI response.<sup>[25]</sup> Thus, opals were used in this work just as templates for the structuring of the azochromophore, allowing us to delimit our study to the influence of the bulk distribution independently of the opal photonic properties.

### 3.2. Photoinduced Bragg Peak Changes and Chromophore Photoalignment

488 nm light is not absorbed by the silica matrix but by the chromophore, causing PI. Photoexcitation induced no spectral changes in the bare opal, while it significantly affected the Bragg peak of the DR1-infiltrated opal. The bandgap showed, for a broad range of light intensity  $I$ , a pronounced shift ( $\Delta\lambda_{\text{Bragg}}$ ) to shorter wavelengths on the ms scale and spontaneously recovered its original position rapidly after switching the light off (Figure 2). Blueshifts ranged from about 1.5 nm in 900 ms at  $I = 60 \text{ mW cm}^{-2}$  to 16 nm in 15 ms at  $I = 6 \text{ W cm}^{-2}$ . The PBG behavior indicates that light may induce a fast and reversible decrease of  $n_v$  (Equation 1). This is compatible, according to Equation 9, with the decrease of the *in-plane* refractive index of the azochromophore ( $n_{\text{DR1}}^{\text{in-plane}}$ ) as a result of PI-induced photoalignment. Note that, although relatively high light intensities for cw photoexcitation were used, the light doses ( $I \times \text{irradiation time}$ ) were significantly low in all cases (between 0.05 and  $0.09 \text{ J cm}^{-2}$ ), which are some orders of magnitude lower than those typically used in cw studies ( $1\text{--}50 \text{ J cm}^{-2}$ ) or pulse experiments ( $20\text{--}200 \text{ J cm}^{-2}$ ).

The photoresponse of DR1 in the opal was verified by two independent techniques. First, polarization-dependent absorbance was investigated. Hereby, the photoalignment of DR1 molecules perpendicularly to the polarization of the probe light leads to absorbance decrease. Given the fast response of the system,  $A$  was measured *in situ* during irradiation (Figure 3a). Before excitation, both perpendicular ( $A_{\perp}$ ) and parallel ( $A_{\parallel}$ ) absorbances were identical to that measured with unpolarized probe light ( $A_0$ ), demonstrating isotropic orientation of the DR1 molecules after the opal infiltration. Under linear polarized photoexcitation, the chromophore absorbance significantly



**Figure 3.** a) UV-vis absorbance of a DR1-infiltrated as-grown opal before irradiation (black lines), and during and after irradiation (gray lines in left and right panels, respectively). b) Transmission signal ( $I_{ELP}$ ) in null-transmission ellipsometry experiment (sketch in inset) performed on as-grown and 450 °C annealed opals infiltrated with DR1 (black and gray lines), and on as-grown opal infiltrated with a non-isomerizable chromophore (symbols). c) Scheme of reversible out-of-plane photoalignment of DR1 molecules, predominantly along the direction of propagation of the pump  $Ar^+$  beam. Experiments were performed by in situ photoexcitation with linearly polarized 488 nm light ( $600 \text{ mW cm}^{-2}$ ). In absorbance measurements; scattering from  $Ar^+$  laser was blocked with a 488-nm notch filter.

reduced, independently of the probe light polarization, which suggests an overall photoalignment of the azomolecules along the propagating direction of the pump light (out-of-plane orientation, sketched in Figure 3c). This holds because the *cis* population of pseudo-stilbene type azomolecules is low, even under light exposure (i.e., the contribution to the photoresponse of the angular hole burning can be ignored). This is further justified by the high *cis*-to-*trans* quantum yield of DR1.<sup>[23,26]</sup> Figure 3a (left) shows a slight anisotropy between  $A_{||}$  and  $A_{\perp}$  under irradiation, which is indicative of low but nonvanishing in-plane orientation. After irradiation (Figure 3a, right), the initial isotropy is virtually recovered as the original absorbance is recuperated. The reversibility in the absorption changes rules out dye photobleaching.

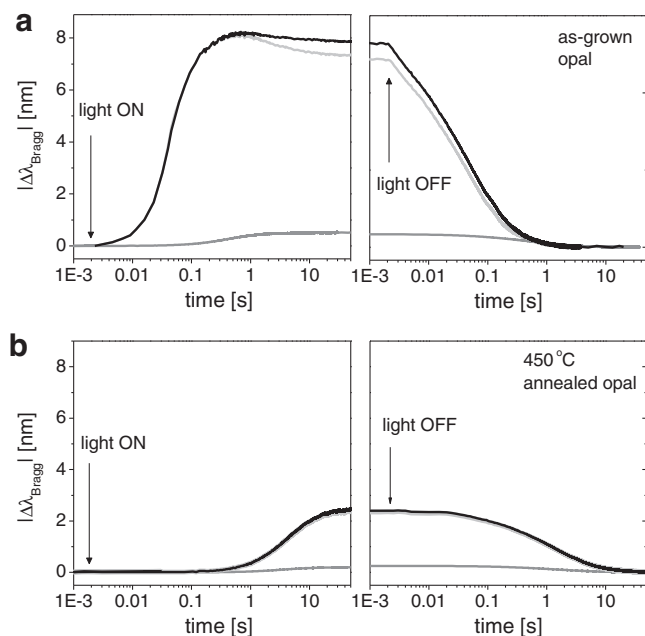
Second, photoalignment was further confirmed by null-transmission ellipsometry (Figure 3b, inset). Here, anisotropic

DR1 orientation alters the polarization of the NIR probe light propagating non-parallel to the anisotropy axis. Probe light transmission is only allowed if the sample is birefringent. Figure 3b shows that the transmission rapidly increased under light exposure, indicating photoinduced anisotropy. Once more, the light-induced changes were spontaneously reversed under dark conditions. The vanishing transmission before irradiation confirms the initial system isotropy. The dynamics were comparable to that observed in the Bragg peak changes (Figure 4). Note that the measured birefringence under irradiation can also arise from in-plane azo orientation (perpendicularly to the pump polarization). However, the small difference between  $A_{||}$  and  $A_{\perp}$  (Figure 3a) rather suggests out-of-plane BR, which corroborates the preferential homeotropic distribution of the DR1 molecules (sketched in Figure 3c). PI-induced out-of-plane orientation, already reported in a number of azo-containing systems,<sup>[4,9,21]</sup> implies both the increase of the refractive index along the z-axis ( $n_{DR1}^z$ ) and the decrease of  $n_{DR1}^{\text{in-plane}}$ . This fully agrees with the photoinduced Bragg peak blueshift (Equation 9).

### 3.3. Photoinduced Refractive Index Changes: General Features

Thus, DR1 photoalignment is responsible for the outstanding photoresponse of the azo-infiltrated opal showed in Figure 2, even enclosing low chromophore content. The fast and reversible performance validates the strategy followed for efficient PI response. In particular, after irradiation, the spontaneous and rapid recovery of the initial random orientation by thermalization drastically differs from the typical behavior in azo-

containing materials, where active erasure is needed. This imposes small hindrance to the molecular motion, as intended. Among other aspects, the efficient adsorption of the DR1 molecules by the silica surface revealed to be of paramount importance. This was verified as the silanol density was varied, prior to dye infiltration, by opal annealing to progressively remove the -OH groups from silica.<sup>[27]</sup> Although having the same degree of DR1 infiltration, the photoresponse of the annealed opals drastically changed (Figure 4). While the hydrophilic as-grown opals exhibited ms-scale response with large photoinduced  $\Delta\lambda_{\text{Bragg}}$ , 450 °C-annealed opals showed, at same  $I$ , strongly reduced Bragg peak blueshifts and response times of several seconds. By increasing the annealing temperature and, then, decreasing the silica hydrophilicity, the response further deteriorated until being completely inhibited in 600 °C-annealed opals (not shown). Identical behavior was observed with null-transmission



**Figure 4.** Temporal evolution of the Bragg peak position of infiltrated as-grown (a) and 450 °C-annealed (b) silica opals under photoexcitation with 488 nm light (600 mW cm<sup>-2</sup>) and the following relaxation under dark conditions. Both types of opals were infiltrated, either with the isomerizable DR1 chromophore to measure the PI-induced changes (black lines) or with non-isomerizable chromophores (dark gray lines). Light gray curves represent the “net” PI effect, calculated by subtracting dark gray curves from black ones.

ellipsometry, i.e., less and much slower anisotropy was photo-induced in the 450 °C-annealed opal (Figure 3b) while no response was observed in 600 °C-annealed opals (not shown). This confirms the degradation of the azo photoalignment in hydrophobic silica opals.

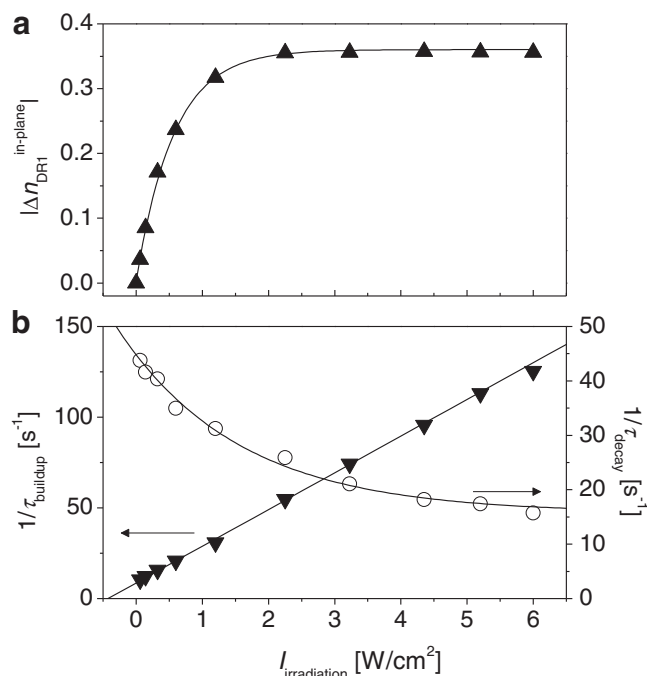
The necessary presence of silanol groups is accompanied by the existence of adsorbed water in the opal voids and between adjacent spheres.<sup>[28,29]</sup> The high absorption of DR1 in the UV-vis region leads to local heating upon 488 nm irradiation and, thus, to water evaporation. Loss of water diminishes  $n_v$  and the spacing between planes  $d_{111}$ , leading in both cases to additional bandgap blueshift (Equation 1). Nevertheless, this *thermal* contribution was confirmed to be substantially smaller than that due to the DR1 response. Therefore, photoexperiments were repeated in opals infiltrated with a non-isomerizable chromophore, instead of the azoderivative DR1. The infiltration was adjusted to achieve identical absorbance at 488 nm, ensuring comparable local heating. Indeed, some contribution to  $\Delta\lambda_{\text{Bragg}}$  due to water evaporation occurred but it was essentially different to that due to the azo photo-response: the shift was much lower and its dynamics slower (Figure 4). For example, the thermal PBG shift in as-grown opals at  $I = 600 \text{ mW cm}^{-2}$  was less than 0.5 nm in 2 s, which is negligible as compared to the 4 nm shift in 40 ms achieved by PI of the azochromophore (Figure 4a). As expected, the thermal contribution was even smaller in annealed opals (Figure 4b), in which the amount of adsorbed water was lower. It is important to remark that some photoinduced anisotropy

in the non-azo chromophore can be safely disregarded as vanishing ellipsometric transmission was measured under photoexcitation (Figure 3b). Note that almost identical behavior was obtained using different non-isomerizable chromophores (see the Experimental Section), which is consistent with heat-induced phenomena.

The thermal effect increased linearly with  $I$ , becoming non-negligible at higher irradiances, although it remained small over the whole measurement range. On this account, we considered the *net* effect on the PBG due to azochromophore PI by subtracting the thermal part from each measurement (Figure 4). From the net shift, we calculated the change in  $n_{\text{DR1}}^{\text{in-plane}}$  induced by photoalignment (Equation 9) and analyzed its dynamics, both of which clearly depended on  $I$  (Figure 5). As expected, the higher the irradiation intensity, the larger  $|\Delta n_{\text{DR1}}^{\text{in-plane}}|$ , according to a higher degree of photoalignment caused by the increasing number of absorbed photons. The increase was linear at low  $I$  but saturated above  $1 \text{ W cm}^{-2}$  (Figure 5a), indicating that the maximum degree of alignment was nearly achieved. An enormous refractive index change was obtained, up to  $\Delta n_{\text{DR1}}^{\text{in-plane}} = -0.36$  at  $2 \text{ W cm}^{-2}$  (which corresponded to a PI-induced  $\Delta\lambda_{\text{Bragg}}$  of  $-12 \text{ nm}$ ). Before saturation, the index change was also very high at low  $I$ , e.g.,  $\Delta n_{\text{DR1}}^{\text{in-plane}} = -0.24$  at  $600 \text{ mW cm}^{-2}$  ( $\Delta\lambda_{\text{Bragg}} = 8.2 \text{ nm}$ ). Regarding the kinetics, the photoalignment became faster with rising  $I$ . For sake of comparison we consider  $\tau_{\text{buildup}}$  as the irradiation time needed to reach half the maximum value of  $\Delta n_{\text{dye}}$ . The buildup rate  $1/\tau_{\text{buildup}}$  increased linearly with  $I$  (Figure 5b, left axis). This linearity, typical of PI processes,<sup>[3,23,30]</sup> confirms that no significant additional effects were involved up to  $I = 6 \text{ W cm}^{-2}$ . Contrary to the buildup, the relaxation back to random orientation became slower at increasing  $I$ . Thus, the decay rate ( $1/\tau_{\text{decay}}$ , where  $\tau_{\text{decay}}$  is the time required to drop half the value of  $\Delta n_{\text{dye}}$ ) decreased monoexponentially with  $I$  (Figure 5b, right axis). In general, the fast response of the system was remarkable: buildup half-times were as fast as 8 ms (at  $6 \text{ W cm}^{-2}$ ) and decay times faster than 60 ms. Furthermore, the consistent behavior over the whole measurement range strongly supports the same origin of the net photoresponse in all cases.

### 3.4. Out-of-Plane Birefringence

It is useful to express the change in the in-plane refractive index in terms of the more common concept of birefringence. As mentioned above, the decrease of  $n_{\text{DR1}}^{\text{in-plane}}$  straightforwardly leads to the increase of  $n_{\text{DR1}}^z$ , which implies the occurrence of out-of-plane BR ( $BR_{\text{DR1}}^z$ , Equation 10). From Equation 13, the values of  $\Delta n_{\text{DR1}}^{\text{in-plane}}$  denote that huge and fast BR was photo-induced in the dye ensemble. For example,  $BR_{\text{DR1}}^z = 0.71$  was achieved in about 100 ms at  $I = 600 \text{ mW cm}^{-2}$ ; at  $I = 6 \text{ W cm}^{-2}$  only 15 ms were needed to achieve  $BR_{\text{DR1}}^z = 1.06$ . Such BR values exceed by several orders of magnitude those reported on conventional films (like azo-dispersed polymers or vapor deposited azo layers). They are also larger than those achieved in the best photoresponsive liquid crystalline polymers.<sup>[12,13]</sup> Further, the response time of few milliseconds in our system clearly surpasses even those of the fastest azo-based systems (cw



**Figure 5.** Light intensity dependence of the refractive index change photo-induced in a DR1-infiltrated as-grown opal. a) maximum  $\Delta n_{\text{DR1}}^{\text{in-plane}}$  (absolute value), b) buildup rate ( $1/\tau_{\text{buildup}}$ ) under irradiation, and decay rate ( $1/\tau_{\text{decay}}$ ) under dark conditions (left and right axes, respectively). Symbols are the experimental data while lines are mono-exponential ( $\Delta n_{\text{dye}}$ ,  $1/\tau_{\text{decay}}$ ) and linear ( $1/\tau_{\text{buildup}}$ ) fitting curves.

experiments).<sup>[9,15,16]</sup> These results are more impressive given the fairly low light doses needed (less than 0.09 J cm<sup>-2</sup> in all cases).

Such outstanding performance proves the validity of our strategy for high molecular photoalignment. However, it must be kept in mind that these BR values are referred to only the photoisomerizable dye ensemble within the opal. Nevertheless, even the BR exhibited by the whole system (i.e., including the inert silica substrate) was as high as 0.069 (Equation 14) while the fast response and reversibility remained identical. The values we estimate for the whole system agree well with those obtained from ellipsometry: e.g., at 600 mW cm<sup>-2</sup>,  $BR_{\text{opal}}^z = 0.046$  as calculated from  $\Delta \lambda_{\text{Bragg}}$ , while  $BR_{\text{opal}}^z = 0.043$  from ellipsometry (Equation 15, data from Figure 3b). This confirms again that the photoresponse was mainly due to dye out-of-plane photoalignment. Obviously, a next step towards increasing the overall system BR will be to reduce the inert component and/or to increment the photoresponsive one without losing efficiency in the response per photoactive unit.

### 3.5. Arrangement of DR1 Molecules in the Silica Opal

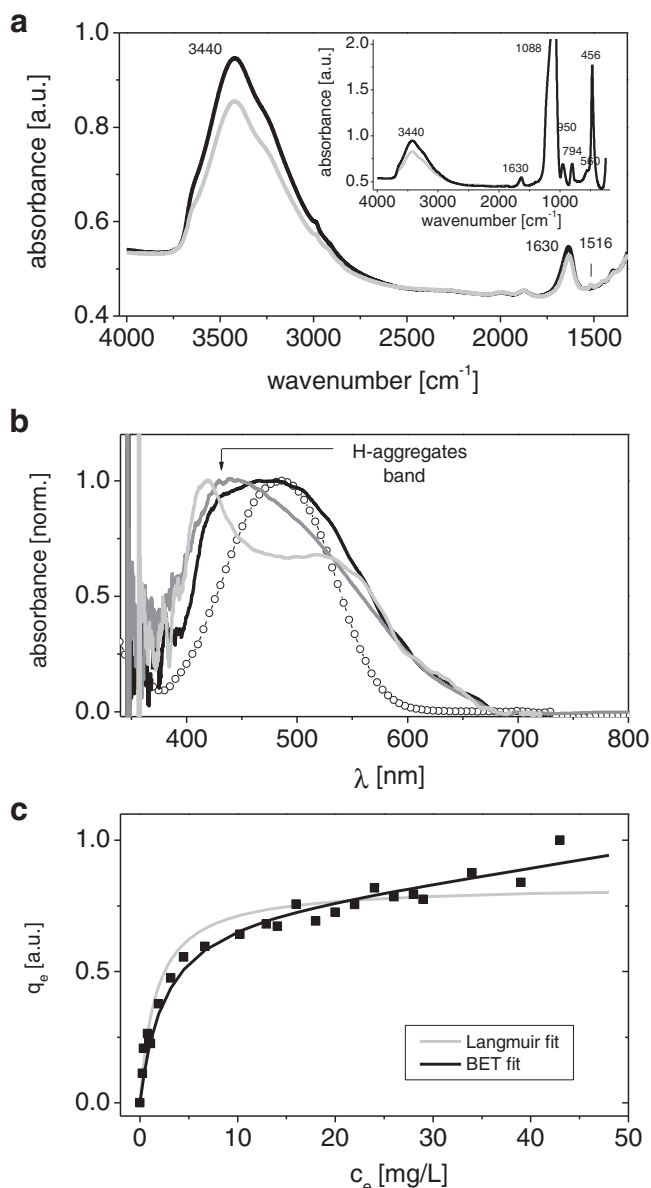
It is important to gain a general picture of the arrangement adopted by the DR1 molecules within the opal that allows such efficient photoresponse. Therefore, we performed a number of specific experiments in order to discern the improving aspects

present in our system. The most decisive factor appeared to be the hydrophilic character of the opal (Figure 4). The presence of silanol groups on the silica surface allowed physisorption of the DR1 molecules via hydrogen bond, preferentially through the -OH groups of DR1 rather than the nitro groups.<sup>[31–33]</sup> On the one hand, FTIR spectroscopy absorption measurements on as-grown silica opals showed, after DR1 infiltration, a decrease in the absorbance of bands assigned to adsorbed water. Thus, the peaks centered at around 3440 cm<sup>-1</sup> (O–H stretching of adsorbed water and SiO–H stretching of surface silanols hydrogen-bonded to water) and 1630 cm<sup>-1</sup> (O–H bending of adsorbed water)<sup>[34,35]</sup> decreased in 14% and 11% of their respective areas (Figure 6a). This indicated a clear reduction of the ability of dye-infiltrated opals to take up ambient moisture, which can be assigned to the partial occupation of silanol groups by bonded DR1 molecules.

On the other hand, UV-vis spectroscopy gave direct information about the aggregation states of the DR1 molecules (Figure 6b). The absorption spectrum of the infiltrated as-grown opal mimicked that of DR1 in solution: the H-aggregates band of dye barely appeared, evidencing the dominant presence of non-aggregated species, highly favorable for photoresponse. By contrast, DR1 absorption spectra in annealed opals showed a marked shoulder at around 420 nm and a clear blueshift (hypsochromic shift). Both effects (the higher the annealing temperature, the more pronounced they were) are the signature of H-aggregates.<sup>[6,7,9,33]</sup> Thus, the progressive removal of silanol groups by annealing hindered DR1 adsorption, which led to precipitation of the unbonded molecules after solvent evaporation and to subsequent aggregation. As a result, the azo photoresponse progressively degraded until complete inhibition, as discussed in Figure 4.

From the chromophore density  $\rho_{\text{DR1}}$  we calculate a surface density of adsorbed DR1 of 0.2 molecules per nm<sup>2</sup> (Equation 7), i.e.,  $2 \times 10^{13}$  cm<sup>-2</sup>. Thereby, we have assumed that the molecules lie almost perpendicular to the surface, as previously observed in DR1-deposited systems,<sup>[32,33]</sup> so that the average thickness of the first DR1 layer on the surface is approximately 1 nm, which is the length of the DR1 *trans* state.<sup>[36]</sup> This is also supported by the appearance of an absorption peak at 1516 cm<sup>-1</sup> (Figure 6a), which corresponds to the asymmetric stretching of NO<sub>2</sub>, while the out-of-plane bending of aromatic C–H at 860 and 829 cm<sup>-1</sup> was not observable.<sup>[33]</sup> The chromophore surface density in our system is about one order of magnitude smaller than those usually reported in related systems,<sup>[8,31,32,37]</sup> and low enough to avoid significant adsorbate–adsorbate interactions.<sup>[38]</sup> Considering a silanol density in colloidal silica of approximately 5 nm<sup>-2</sup>,<sup>[27]</sup> the surface density corresponds to a 1:25 DR1/silanol ratio, so that about 4% of the silanol groups have adsorbed a DR1 molecule. The fact that moisture uptake of infiltrated opals reduced in around 12% suggests that water molecules find steric hindrances to reach the silica surface, due to the presence of bonded DR1, so less free silanol groups were able to adsorb moisture.

According to the filling fraction of chromophore in the opal (6.5 vol-%), DR1 builds up a film of thickness  $d = 4.7$  nm on the spheres surface (Equation 8). This would correspond to a multilayer dye ensemble formed by 4–5 DR1 layers. The tendency to spontaneous multilayer formation was confirmed by adsorption isotherm experiments (Figure 6c), in which the DR1 uptake



**Figure 6.** a) FTIR absorption spectra of as-grown silica opals, bare (black line) and infiltrated with DR1 (gray line). b) Normalized (unpolarized) UV-vis absorption spectra of three different DR1-infiltrated opals (lines): as-grown, 450 °C and 600 °C annealed silica opals (black, dark gray and light gray lines, respectively). The absorption band around 420 nm corresponds to DR1 H-aggregates. For reference, spectrum of DR1 in THF solution is also shown (open circles). c) Adsorption isotherm measured in an as-grown opal and fitting by Langmuir and BET equations.

from solution obeyed the BET equation, which models multilayer adsorption, rather than a Langmuir isotherm describing monolayers (Equations 16 and 17). Such an arrangement probably occurs by head-to-tail organization of the dipolar DR1 molecules (through donor–acceptor attractive interactions between –OH and –NO<sub>2</sub> groups), as reported in other studies.<sup>[32,33]</sup> Note that this chromophore distribution is compatible with the initial isotropy of the dye-infiltrated opal given the spherical symmetry of the silica beads.

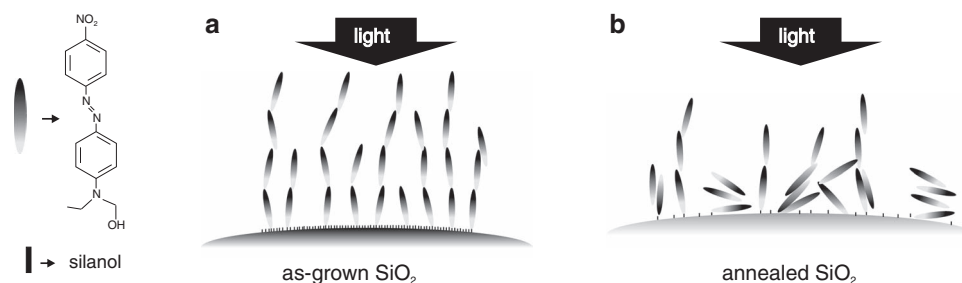
With the insights gained by the different experiments and calculations, we propose the following scheme describing the arrangement of the DR1 molecules on the opal spheres (Figure 7). On the one hand, a high density of silanol groups on the surface (as in the case of as-grown opals) allows for efficient adsorption of the DR1 molecules through their –OH group although keeping low surface density. The attachment of the first layer facilitates the subsequent multilayer formation by head-to-tail organization of the dipoles with ordered, loose dye distribution and low aggregation, so the response to irradiation is highly improved (Figure 7a). On the other hand, a low silanol density (as a result of, for example, annealing) implies a reduced dye adsorption, leading to more aggregation and less organized ensemble (Figure 7b), and, ultimately, to a diminished photoresponsivity.

It must be noted that partial aggregation was measured in as-grown opals after a few days, probably due to thermal rupture of some DR1-silanol bonds. As a consequence, the photoalignment exhibited some loss of efficiency but it stabilized after about two weeks:  $\Delta n_{\text{DR1}}^{\text{in-plane}}$  reduced by approximately 30% with a four-fold slower response. Regarding annealed opals, the photoresponse could be recovered by growing a new silica layer on the spheres surface by chemical vapor deposition<sup>[39]</sup> prior to dye infiltration. This interesting feature provides a direct way to control the density of silanol groups in the matrix, even in a reversible manner, which boosts the versatility of our system. It must be pointed out that DR1 infiltration of opals not having silanol groups, *e.g.*, polystyrene or aluminium oxide opals, exhibited pronounced dye aggregation and, as expected, no photoresponse was observed.

### 3.6. Distinctive Features

A number of factors must be considered in order to explain the high, fast and reversible refractive index change reported. Our results indicate that the mobility of the azochromophores has been strongly enhanced because: i) no matrix is surrounding the azo units as the neat chromophore is used, ii) the weak but stable hydrogen bond of the chromophore to the silica, rather than a covalent bond, ensures more rotational freedom, and, iii) the low density of the chromophore packing provides free internal volume and minimizes electrostatic interactions. Moreover, the efficient dye adsorption by the uniformly distributed silanol groups helps the homogeneous arrangement without aggregated species, and the formation of azo multilayers further enhances the response. On the other hand, the well-ordered 3D distribution provided by the opal reduces overlapping, aggregation and steric hindrance. The fixed backbone (*i.e.*, the spheres) ensures that the arrangement was maintained. The absence of mobile structures allows ruling out the formation of domain motions, which are slow and hinder back orientation. The fast reversibility of the photoalignment just by thermal relaxation is in accordance with both the high degree of molecular mobility and the absence of mesogens.

Large, fast, and fully reversible response to light is the premise of a system for real applications regarding photoswitching. As



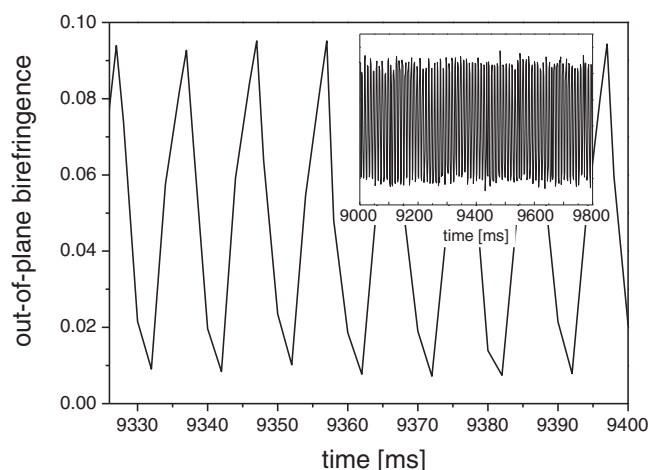
**Figure 7.** Proposed scheme for distribution of the adsorbed DR1 molecules in as-grown and 450 °C-annealed silica opals. The high density of silanol groups in the as-grown opal helps chromophore structuration on the sphere surface by adsorption, minimizing precipitation and formation of aggregates. The multilayer arrangement further improves the photoresponse. By contrast, the removal of silanols in the annealed opal reduces the chromophore adsorption, which provokes aggregation and hindrance of the photoresponse. In a 600 °C-annealed opal (not shown), only a few silanol groups remain in the silica so DR1 molecules predominantly precipitate, exhibiting even higher aggregation and completely hindered photoalignment.

a proof-of-principle, **Figure 8** shows the modulation of  $BR_{DR1}^z$  (obtained from  $\Delta\lambda_{Bragg}$ ) in a switching experiment at a high rate of 100 Hz and  $I = 600 \text{ mW cm}^{-2}$  (light dose of  $0.003 \text{ J cm}^{-2}$ ). The experiment was carried out over 5 h – i.e., 2 million cycles – with remarkable reproducibility (fluctuations were less than 5%) and no signs of fatigue. This further demonstrates the very high recycling ability of our system, in contrast to the clear fatigue typically observed in PI-based systems proposed for switching.

#### 4. Conclusions

We have demonstrated a novel, direct solution-processed approach to prepare extremely efficient photoisomerizable systems, in which neat azochromophore is directly infiltrated in conventional silica colloidal crystals by simple casting. Enhanced photoalignment is obtained upon cw-irradiation enabling huge and fast refractive index changes in the chromophore ensemble at low light doses (as large as 0.36, i.e., birefringence of 1.1, in 15 ms at  $0.09 \text{ J cm}^{-2}$ ). A comprehensive study is implemented to discern the nature of the photoresponse and the features explaining the performance. The chromophore is found to be well-distributed in multilayers on the silica surface, weakly anchored to the silanol groups, resulting in a low-density arrangement with reduced aggregation and strongly improved mobility. The absence of a surrounding matrix further avoids steric hindrance and allows complete and spontaneous reversibility of the photoalignment. The findings obtained from the different experimental methods are consistent and confirm the proposed scenario. Additionally, excellent reliability for high-rate photoswitching is proved and makes this system promising for applications like switches and modulators.

Although other nanostructures having suitable groups for dye adsorption may be employed as 3D-templates, here we choose artificial silica opals providing a straightforward tool to measure the chromophore photoresponse profiting from the sensitivity of their photonic bandgap. Thus, using a novel procedure, the birefringence is directly obtained from the PBG spectral change, with good agreement with ellipsometric measurements. The results reported in this work offer relevant



**Figure 8.** Modulation of the out-of-plane birefringence induced in the chromophore ensemble ( $BR_{DR1}^z$ ) by photoswitching ( $\text{Ar}^+$ -laser on/off) at a frequency of 100 Hz ( $I = 600 \text{ mW cm}^{-2}$ , light dose of  $0.003 \text{ J cm}^{-2}$ ). Inset: performance over 800 ms (80 cycles). The entire experiment (not shown) was carried out over 5 h (2 million cycles) with identical reproducibility.

insights into the intrinsic limits of PI-induced processes like photoalignment as much as molecular nanostructuring and surface behavior. Finally, our simple approach, based on efficient dye adsorption, is demonstrated using commercial or easy-to-fabricate components and eludes the necessity of substituents (as molecular spacers) and synthetic procedures, which may enable large-scale production of inexpensive nano-sensors and photonic devices.

#### 5. Experimental Section

**Opals Fabrication:** Artificial opal templates were prepared from approximately 330 nm silica spheres (polydispersity below 3%) synthesized by the Stöber-Fink-Bohn procedure,<sup>[40]</sup> following the vertical deposition method.<sup>[41]</sup> The resulting opals were formed by around 15 spheres layers, as calculated from Fabry-Perot oscillations and SEM. Eventually, opals were annealed at 450 or 600 °C for 5 h in a conventional oven for controlled removal of silanol groups from the spheres surface. Silica treatment at temperatures above 400 °C completely eliminated

vicinal silanols and progressively geminal and isolated silanols. The silanol density reduced from 5 nm<sup>-2</sup> in as-grown opals to about 2.5 and 1 nm<sup>-2</sup> after annealing at 450 and 600 °C, respectively.<sup>[27]</sup>

**Chromophore Infiltration:** Two different chromophore types were used to dope the opal: on the one hand, an isomerizable chromophore (the azobenzene Disperse Red 1, DR1 (*N*-ethyl-*N*-(2-hydroxyethyl)-4-(4-nitrophenylazo)aniline, pursued by Aldrich, 95%) and, on the other hand, a set of non-isomerizable molecules: i) methylene blue hydrate (Fluka, ≥95%), ii) Remazol Brilliant Blue R (Sigma, recrystallized), iii) protoporphyrin IX (Sigma, ≥95%), iv) protoporphyrin IX disodium salt (Sigma, approximately 95%), v) hemin chloride (Sigma, ≥90%), vi and vii) amino-thienyldioxycyano-pyridines ATOP-4 and ATOP-7 (synthesized as reported elsewhere,<sup>[42]</sup> around 95%). Note that protoporphyrin IX and hemin chloride contain hydroxyl groups, like DR1, in order to reproduce analog adsorption conditions. All chromophores exhibit significant absorption at the excitation wavelength (488 nm).

In all cases, the chromophore was dissolved in anhydrous, inhibitor-free tetrahydrofuran (THF, Sigma-Aldrich) and the infiltration was accomplished by casting the solution onto the opal template placed on a hot plate at 110 °C in order to partially remove adsorbed moisture. The solvent rapidly evaporated while a portion of dye remained in the interstitial voids. Following this procedure, the opal was infiltrated only by neat chromophore being neither embedded in a matrix nor chemically attached to the opal spheres. This further made the infiltration process basically reversible by simple washing of the template with THF. Nevertheless, a rest of dye remained in the opal since some PBG redshift (around 2 nm) and a small photoresponse persisted. Complete chromophore removal was achieved with O<sub>2</sub>-plasma etching for 2 h at 30 °C (Diener Electronic). Such reversible dye infiltration was efficient over at least 20 cycles.

In order to compare the optical response using the isomerizable DR1 and non-isomerizable compounds, we carefully ensured the same absorbance at 488 nm after infiltration of the opals (as-grown and annealed). Therefore, we adjusted in each case the amount of chromophore to be dissolved in THF (1.5 mg of DR1 and amounts between 0.9 and 2.6 mg of the non-isomerizable molecules were dissolved in 5 mL of THF). For better reproducibility, we further select under the microscope an opal area with the exact absorbance.

**Spectral Characterization:** Opals were characterized by reflection spectroscopy performed on a small area (around 20 μm<sup>2</sup>) with a diode array spectrometer (Ocean Optics 2000+) using unpolarized white light from a halogen lamp (Osram HLX 64623). The position of the Bragg peak, the bandgap associated to the diffraction at the (111) family planes (Figure 1c), can be described with sufficient accuracy by Bragg's law, where the maximum reflectance wavelength λ<sub>Bragg</sub> at normal light incidence is given by

$$\lambda_{\text{Bragg}} = 2d_{111} n_{\text{eff}} \quad (1)$$

$$n_{\text{eff}} = f n_{\text{silica}} + (1 - f) n_v$$

where  $d_{111} = (2/3)^{1/2} D$  is the spacing of the (111) planes in the fcc package ( $D$  is the spheres diameter) and  $n_{\text{eff}}$  is the effective refractive index, which depends on  $n_{\text{silica}}$  and  $n_v$ , the refractive indices of the silica spheres and the interstitial void region, respectively, and on the filling fraction of the opal,  $f$ . We assume  $n_{\text{silica}} = 1.43$  (refractive index of silica at approximately 700 nm) and  $f = 0.74$  (ideal fcc structure). For simplicity, we also assumed that voids of bare opals were filled only by air ( $n_v = n_{\text{air}} = 1$ ). In as-grown opals, λ<sub>Bragg</sub> = 704 nm, which corresponds to spheres of  $D = 327$  nm, according to Equation 1. In 450 and 600 °C-annealed opals, having reduced silanol densities, λ<sub>Bragg</sub> shifted to 693 and 678 nm, respectively, due to the less amount of adsorbed water. The opal thickness ( $t$ ) was about 4 μm, which is in agreement with 15  $d_{111}$ .

The opal infiltration with chromophore leads to partial void filling, so that  $n_v$  increased and the Bragg peak shifted to longer wavelengths. In the case of DR1 infiltration, the resulting Bragg peaks were at 724, 713 and 697 nm in as-grown, 450 and 600 °C-annealed opals, respectively.  $n_v$  increased according to

$$n_v = g n_{\text{DR1}} + (1 - g) n_{\text{air}} \quad (2)$$

which depends on the DR1 refractive index,  $n_{\text{DR1}}$ , and the filling fraction of the void by DR1,  $g$ .

**Characterization of the DR1 Ensemble within the Opal:** Equations 1 and 2 give a direct estimate of the chromophore content in the opal if  $n_{\text{DR1}}$  is known.  $n_{\text{DR1}}$  refers to the refractive index of the neat solid DR1, which strongly depends on the condensed phase of the chromophore in each particular case, and, especially, on its density. Further, the characteristics of our system make difficult to measure the refractive index with techniques typically used in thin films or composites. Alternatively we proceed to calculate  $n_{\text{DR1}}$  using the approach described in the literature.<sup>[24,43]</sup> We consider the Lorentz equation to obtain the dispersion in the refractive index:

$$\varepsilon(\omega) = \varepsilon_b + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\omega\gamma} = (n_{\text{DR1}}(\omega) + i\kappa_{\text{DR1}}(\omega))^2 \quad (3)$$

where  $n_{\text{DR1}}$  and  $\kappa_{\text{DR1}}$  are the real and imaginary parts of the complex refractive index,  $\varepsilon_b$  is the background dielectric function,  $\omega$  is the angular frequency of observation,  $\omega_0$  is the angular frequency at the absorption maximum (λ<sub>max</sub>), and  $\gamma$  is the full width at half maximum (FWHM) of the absorption band fitted to a single Lorentzian (in inverse time units). At last,  $\omega_p$  is the plasma frequency, given by

$$\omega_p^2 = \omega_0 \varepsilon_b \gamma \sqrt{\eta + \frac{\eta^2}{4}} \quad (4)$$

$$\eta = \left( \frac{\varepsilon_{\text{max}} \rho_{\text{DR1}} / M n_{\text{DR1}}}{2\pi \sqrt{\varepsilon_b / \lambda_{\text{max}}}} \right)^2$$

where  $\varepsilon_{\text{max}}$  is the extinction coefficient at λ<sub>max</sub>,  $\rho_{\text{DR1}}$  is the chromophore density and  $M = 314.34$  g mol<sup>-1</sup> is the DR1 molecular weight. From absorption spectra of DR1 solutions or from the literature one can directly obtain λ<sub>max</sub> = 478 nm,  $\varepsilon_{\text{max}} = 31000$  L mol<sup>-1</sup> cm<sup>-1</sup> and  $\gamma/(2\pi c) = 4790$  cm<sup>-1</sup>.<sup>[24]</sup>  $\varepsilon_b = 1.53^2$ , based on the dispersion curves for organic NLO crystals.<sup>[24]</sup> For a given  $\rho_{\text{DR1}}$ , Equation 4 yields  $\omega_p$ , and Equation 3 gives the corresponding  $n_{\text{DR1}}$ . Substituting these values in Equations 1 and 2 we get the filling fraction  $g$  from λ<sub>Bragg</sub> after DR1 infiltration. Finally, knowing  $g$  (and the input value  $\rho_{\text{DR1}}$ ) allows the calculation of the absorbance  $A$  of the infiltrated opal according to

$$A = \varepsilon_{\text{max}}(\rho_{\text{DR1}}/M) t_{\text{DR1}} = \varepsilon_{\text{max}}(\rho_{\text{DR1}}/M) (1 - f) g t \quad (5)$$

where  $t_{\text{DR1}} = (1 - f) \times g \times t$  is the thickness of absorbing medium in an opal of thickness  $t$  (given by the volume fraction of DR1,  $(1 - f) \times g$ , since silica does not absorb in the visible range).  $A$  from Equation 5 must agree with the experimental value, easily obtained from absorbance measurements ( $A = 0.26$  at the absorption maximum; see Figure 3a, before irradiation). In a simple iterative process, we adjust  $\rho_{\text{DR1}}$  in Equation 4 and obtain, subsequently,  $g$ .

From these values the calculation of other relevant parameters of DR1 in the opal is straightforward. The weight fraction (in wt-%) is given by

$$100 \times \frac{\text{DR1 mass}}{\text{total mass}} = 100 \times \frac{(1 - f) g \rho_{\text{DR1}}}{(1 - f) g \rho_{\text{DR1}} + f \rho_{\text{silica}}} \quad (6)$$

where  $\rho_{\text{silica}} = 2.2$  g cm<sup>-3</sup>. Considering homogeneous chromophore deposition on the silica beads, the number of DR1 molecules (adsorbed on the silica spheres) per surface unit,  $N$ , is given by

$$N = \rho_{\text{DR1}} h / (M / N_A) \quad (7)$$

where  $h$  is the average height of a DR1 monolayer and  $N_A$  is the Avogadro number. The thickness ( $d$ ) of the film formed by the DR1 molecules on the spheres surface can be estimated by assuming the ratio between the volumes of spheres of radii  $(D/2 + d)$  and  $D/2$  to be equal to the ratio between the filling fractions of "silica + DR1" and silica. Thus,

$$\left(\frac{D/2 + d}{D/2}\right)^3 = \frac{f + (1-f)g}{f} \quad (8)$$

**Photoexcitation:** Dye-infiltrated opals were irradiated with a linearly polarized 488 nm Ar<sup>+</sup> laser line while reflection spectra were simultaneously recorded (Figure 1c). The acquisition time, as short as 2 ms, allowed the monitoring of the fast kinetics. In order to avoid the reflected laser light reaching the spectrometer, the beam impinged with a small external incidence angle of 10° (internal angle of approximately 5°) with respect to the normal of the opal. A holographic notch filter (Semrock 488 nm, Δλ = 14 nm) was placed in front of the spectrometer to eliminate scattered laser light. The laser beam FWHM was 380 μm and its intensity ranged from 0.06 to 6 W cm<sup>-2</sup>. The laser wavelength nearly coincides with λ<sub>max</sub> of DR1 (Figure 6b), so efficient light absorption was ensured. However, the absorbance of the chromophore ensemble (Figure 3a) was low enough to guarantee sufficient light transmission throughout the sample.

**Photoinduced Changes in DR1 Refractive Index:** Reflection spectra were taken normally to the (111) opal planes, i.e., the optical electric field of the probe white light lies on the XY plane. Thus, the Bragg peak is actually sensitive only to the in-plane refractive indices in the opal. In particular, silica and air are optically nonactive, so photoinduced PBG shifts were exclusively caused by changes in the in-plane DR1 refractive index Δn<sub>DR1</sub><sup>in-plane</sup> = n<sub>DR1</sub><sup>in-plane</sup> - n<sub>DR1</sub><sup>in-plane</sup>(0) (where "0" refers to values before irradiation). Rewriting Equations 1 and 2, the shift Δλ<sub>Bragg</sub> is given by

$$\Delta\lambda_{\text{Bragg}} = 2d_{111}(1-f)g\Delta n_{\text{DR1}}^{\text{in-plane}} \quad (9)$$

Thus, PBG blueshift (negative Δλ<sub>Bragg</sub>) implies that n<sub>DR1</sub><sup>in-plane</sup> has decreased under irradiation (negative Δn<sub>DR1</sub><sup>in-plane</sup>).

**Birefringence:** The photoalignment of DR1 molecules primarily along the z-axis implies that BR is induced out of plane (in-plane BR is negligible, see Figure 3a), and n<sub>DR1</sub><sup>in-plane</sup> and n<sub>DR1</sub><sup>z</sup> correspond to the ordinary and extraordinary indices, respectively. Thus, the out-of-plane birefringence (BR<sub>DR1</sub><sup>z</sup>) is given by:

$$BR_{\text{DR1}}^z = |n_{\text{DR1}}^z - n_{\text{DR1}}^{\text{in-plane}}| \quad (10)$$

Since the DR1 ensemble become uniaxial with rotational symmetry about the z-axis, the average refractive index is given by:

$$n_{\text{DR1}} = (n_{\text{DR1}} + 2n_{\text{DR1}}^{\text{in-plane}})/3 \quad (11)$$

Initially, DR1 molecules are isotropically oriented, so that,

$$n_{\text{DR1}}^z(0) = n_{\text{DR1}}^{\text{in-plane}}(0) = n_{\text{DR1}} \quad (12)$$

and BR<sub>DR1</sub><sup>z</sup> = 0 (Equation 10). Upon light exposure, the photoinduced out-of-plane BR is directly related to the measured Δn<sub>DR1</sub><sup>in-plane</sup> by substituting Equations 11 and 12 in Equation 10:

$$BR_{\text{DR1}}^z = 3|\Delta n_{\text{DR1}}^{\text{in-plane}}| \quad (13)$$

Here it has been assumed that the average n<sub>DR1</sub> did not change under irradiation, which holds for same *trans* DR1 population (that is, neglecting photobleaching and the stable *cis* population).

Regarding the whole sample, the birefringence (BR<sub>opal</sub><sup>z</sup>) is given by the difference between the z- and in-plane components of n<sub>eff</sub> in analogy to Equation 10. Since n<sub>silica</sub> and n<sub>air</sub> are isotropic, the total BR is given by the fraction of DR1 in the opal:

$$BR_{\text{opal}}^z = (1-f)g|n_{\text{DR1}}^z - n_{\text{DR1}}^{\text{in-plane}}| = (1-f)gBR_{\text{DR1}}^z \quad (14)$$

**Null-Transmission Ellipsometry:** This technique<sup>[44]</sup> was performed with a weak NIR probe beam (λ = 785 nm, 10 mW cm<sup>-2</sup>) impinging with

external angle of 50° at the dye-infiltrated opal, which was placed between two crossed polarizers set at ±45° with respect to the plane of incidence (inset in Figure 3b). The (normalized) transmitted intensity I<sub>ELP</sub> across a uniaxial medium of thickness t, average index n and birefringence |n<sub>e</sub> - n<sub>o</sub>| is given by I<sub>ELP</sub> = sin<sup>2</sup>(2πt|n<sub>e</sub> - n<sub>o</sub>|/(λG)), where G = n(n<sup>2</sup> - sin<sup>2</sup>θ)<sup>1/2</sup>/sin<sup>2</sup>θ is a geometric factor (θ is the external incidence angle of the probe beam with respect to the anisotropy axis).<sup>[44]</sup> In our system (taking n<sub>eff</sub>(0) as n to obtain G = 2.58) this corresponds to:

$$I_{\text{ELP}} = \sin^2\left(\frac{2\pi t BR_{\text{opal}}^z}{\lambda G}\right) \quad (15)$$

Equivalently, the same I<sub>ELP</sub> is obtained by considering just the DR1 ensemble (the only photoactive medium) with effective thickness t<sub>DR1</sub> = (1-f) × g × t (already used in Equation 5). Thus, Equations 14 and 15 are fully consistent.

**Absorbance Measurements:** Transmission spectra of opals were taken in the experimental arrangement depicted in Figure 1c but placing the spectrometer below the sample. The setup allowed simultaneous photoirradiation of the opal by the 488 nm Ar<sup>+</sup> laser (pump light). Spectra were recorded using unpolarized probe white light to obtain A<sub>0</sub>, or linearly polarized, perpendicular and parallel to the Ar<sup>+</sup> laser polarization to obtain A<sub>⊥</sub> and A<sub>||</sub>, respectively. The strong light scattering produced by the opal spheres in the UV-vis range drastically increased the measurement noise below 450 nm. In order to obtain the whole DR1 absorption band (Figure 6b), an integrating sphere (Mikropack 50 mm) was coupled to the spectrometer. The absorbances A were obtained from A = -log (transmitted I)/(incident I) after subtracting reflection and scattering losses.

**FTIR Absorbance Spectra:** As-grown opals (bare or DR1-infiltrated) were separated from the glass substrate, pulverized and mixed with KBr, and pressed to a pellet. Spectra were taken in transmission mode with a Nicolet Magna 750 Fourier FTIR spectrometer by averaging 128 scans at a resolution of 1 cm<sup>-1</sup>.

**Adsorption Study:** Equilibrium adsorption isotherms were measured by submerging fixed amounts of pulverized bare opal (m = 40 mg) in DR1 solutions (in THF, V = 2 mL) at different concentrations. The opal was left to adsorb at 20 °C for 24 h to ensure full chromophore adsorption. The remaining DR1 concentration in the supernatant was determined from the absorbance at 489 nm with a Cary Variant 4000 spectrometer. The DR1 uptake, q<sub>e</sub>, was calculated by q<sub>e</sub> = (c<sub>0</sub> - c<sub>e</sub>) V/m, where c<sub>0</sub> and c<sub>e</sub> are the initial and equilibrium concentrations of the DR1 solution. In order to discern whether the adsorbed DR1 molecules form monolayers or multilayers, we fitted the q<sub>e</sub> data to both Langmuir and Brunauer-Emmett-Teller (BET) isotherms. The first, which describes monolayer adsorption, is given by:<sup>[45]</sup>

$$q_e \propto \frac{K_L c_e}{1 + K_L c_e} \quad (16)$$

where K<sub>L</sub> is the equilibrium adsorption constant. The second, commonly used to describe multilayer adsorption, can be formulated as:<sup>[46]</sup>

$$q_e \propto \frac{K_1 c_e}{(1 - K_2 c_e)(1 + (K_1 - K_2) c_e)} \quad (17)$$

where K<sub>1</sub> is the equilibrium constant for the molecule/surface interaction (first layer) and K<sub>2</sub> is the equilibrium constant for the molecule/molecule interactions (all subsequent layers). Data regressions in Figure 6c yielded K<sub>L</sub> = 0.6 L mg<sup>-1</sup>, K<sub>1</sub> = 0.4 L mg<sup>-1</sup> and K<sub>2</sub> = 0.0045 L mg<sup>-1</sup>.

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