# *Hoplia coerulea*, a porous natural photonic structure as template of optical vapour sensor

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## ABSTRACT

Natural photonic structures found on the cuticle of insects are known to give rise to astonishing structural colours. These ordered porous structures are made of biopolymers, such as chitin, and some of them possess the property to change colour according to the surrounding atmosphere composition. This phenomenon is still not completely understood. We investigated the structure found on the cuticle of the male beetle *Hoplia coerulea* (Scarabaeidae). The structure, in this case, consists in a 1D periodic porous multilayer inside scales, reflecting incident light in the blue. The colour variations were quantified by reflectance spectral measurements using water, ethanol and acetone vapours. A 1D scattering matrix formalism was used for modelling light reflection on the photonic multilayer. The origin of the reported colour changes has to be tracked in variations of the effective refractive index and of the photonic structure dimensions. This remarkable phenomenon observed for a non-open but still porous multilayer could be very interesting for vapour sensing applications and smart glass windows.

**Keywords:** Beetle scale, natural photonic crystals, photonic bandgap materials, structural colour, iridescence, Coleoptera, bioinspiration, selective gas/vapour sensor

## 1. INTRODUCTION

Physical colours in living organisms are known to be produced by various natural photonic structures[1-3]. One of the taxonomic classes presenting the most striking examples is insects: butterflies[3], moths[2], weevils[4-5], longhorns[6-7], etc. The porous structures found on the insect cuticle are ordered at the wavelength scale and made of biopolymers (e.g., chitin). Some of them have the property to change colour when the surrounding atmosphere composition is modified[8-12]. It is also well known that their impregnation with liquid water or ethanol may give rise to colour changes[6,13-15] and is often used in entomology in order to distinguish pigmentary colours from physical colours. The colour change can be very quick and is due to modifications of the photonic structure. The property of changing colour in the presence of water vapour is termed hygrochromism.

One example is the male beetle *Hoplia coerulea* (Fig. 1) also known as the cerulean chafer beetle. It belongs to the Scarabaeidae family and is often found in summer (from May to July) on herbs along watercourses and swamps in South Europe. The male possesses circular scales covering its wings which are mainly made of chitin. Inside the scales, a photonic structure consisting in a periodic porous multilayer gives rise to a blue-violet iridescent coloration[1,15-16]. The structure is enclosed by an envelope whose thickness is about 100 nm. One scale has a diameter of about 80 µm and is 3.5 µm thick. The female displays a pigmentary brownish coloration. In 2009, Rassart *et al.*[15] demonstrated that the blue-violet coloration of the male turns to emerald green when soaked in water.

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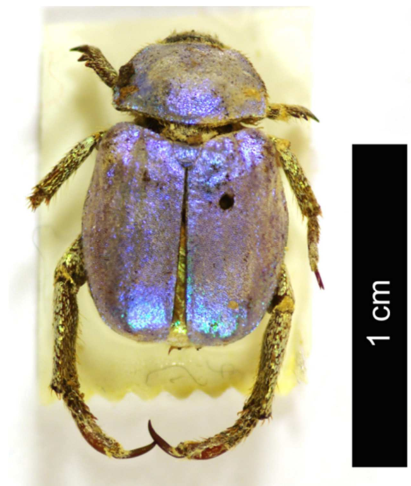



Figure 1. Photograph of the *Hoplia coerulea* male beetle. Its blue-violet coloration has a physical origin. (colours available online)

In this paper, impregnation experiments of *Hoplia coerulea* scales were first performed with liquid water, ethanol, acetone as well as toluene and the colour changes were observed using optical microscopy. The purpose of impregnation experiments was to confirm the sensitivity of the photonic structures to direct contact with liquids, as it was highlighted in previous report[15]. Then, the modifications of the reflectance spectrum induced by the presence of water, ethanol and acetone vapours were investigated using a sealed measurement cell. In spite of the fact of being located inside scales, the non-open but still porous photonic structure is an interesting candidate for the study of colour changes induced by variations in the surrounding atmosphere.

This remarkable effect observed in the *Hoplia coerulea* structure could be very interesting in order to elaborate new sensing concepts and devices through a biomimetic approach. From that approach, a better optimization and emergence of novel bio-inspired optical sensors[8-9,12,15,17] and smart glass windows[18-19] are anticipated. Indeed, the structure could easily be synthesised by nanofabrication methods[17]. However, the origin of the colour changes in such an enclosed porous structure is not understood and has to be tracked in microscopic physicochemical phenomena.

## 2. MATERIALS AND METHODS

### 2.1 Optical characterisation of colour changes

For impregnation experiments, a droplet of liquid (distilled water, absolute ethanol, acetone or toluene) was deposited using a micropipette (0.5 µl) on one single elytron. Microscope observations were performed using an Olympus BX61 optical microscope combined with an Olympus XC50 camera and an Olympus BX-UCB light source.

Variations of reflection factor[†] spectra (often incorrectly called “reflectance spectra”) due to the presence of water, ethanol and acetone vapours in the surrounding atmosphere were investigated using a sealed measurement cell (Fig. 2). In the cell chamber, an insect wing was placed as well as a cup of liquid. Spectra were then measured during the vaporisation of the liquid (right at the placement of the cup, after 20 min, 40 min, 1 h, 3 h and 4 h) with an Avaspec ULS 2048-2 fibre optic spectrometer and an AvaLight Xe xenon lamp. Measurements were performed at 15°-incidence in specular configuration (equal angles of incidence and detection). The spot size of the beam on the sample surface was about several square millimetres, i.e., covering many scales of the elytron. Since measurements were performed during several hours, it was necessary to take the fluctuations of the light source into account. For this purpose, a dual channel spectrometer platform was used. One spectrometer channel measured the reflected light from the sample, while the other one simultaneously measured light reflected on the diffusor.

[†] The reflection factor is the ratio between the intensity reflected by the sample and the intensity reflected by a standard white diffusor with corrections for the noise. This factor can therefore exceed 100% unlike the reflectance.

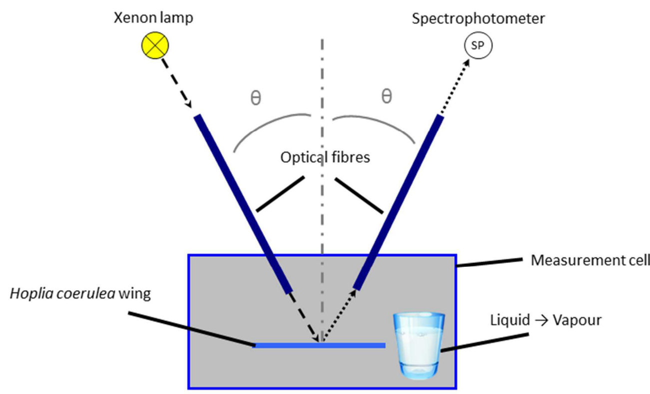



Figure 2. Sealed measurement cell in which the reflection factor variations of *Hoplia coerulea* elytra due to the presence of vapour in the chamber atmosphere were measured.

### 2.2 Optical simulation method

We simulated reflectance spectra of the photonic structure using a thin-film code based on a 1D scattering matrix formalism[20-21]. The code calculates light flow propagation in stratified media made of homogeneous layers. Applying this method for the investigated photonic structure is relevant since, as we will see, the structure does not diffract visible light into diffraction order higher than specular reflection. The reflectance spectra were computed assuming unpolarised visible light at 15°-incident angle.

## 3. RESULTS AND DISCUSSION

The photonic structure at the origin of the blue-violet iridescence of the male beetle scales has already been investigated by Vigneron *et al*.[16] and Rassart *et al*.[15] For the sake of completeness, we remind here the results of structure investigations. The wings and the thorax are covered by small (diameter of about 80 µm), flat (thickness of ca. 3.5 µm) and circular shaped scales (Fig. 3a). The biopolymer forming the structure is chitin whose refractive index is about 1.56[22]. We note that the ventral scales and those on the legs are greenish-white (for both sexes). In the blue scales, the inner structure (Fig. 4), enclosed by a very thin smooth envelope (thickness of ca. 100 nm) is made of a stack of planar layers separated by spacers. The internal photonic structure is approximated by a multilayer consisting in a dozen bilayers with a period of ca. 175 nm, parallel to the outer surface of the scales. Each spacer layer consists in a network of rods which are locally (i.e., for a set of about 10 rods) parallel, very ordered and separated by air voids. The orientations of the rods vary within one layer but also from one layer to another. In the photonic model, the network of spacers is replaced by a homogenised layer with an effective refractive index, mixing air and chitin. The structure is then considered as a 1D photonic crystal film. This approximation is valid because the rods do not lead to high-order diffraction of visible light (except specular reflection). Indeed, the rod interdistance is too small[5] to produce diffraction. Anyway, the rods cannot be reduced to perfect diffraction gratings due to inhomogeneities (never more than 10 rods are parallel). Optical properties were experimentally characterized by Vigneron *et al*.[16] and Rassart *et al*.[15] They measured a reflectance peak located at about 460 nm with a FWHM narrower than 100 nm when the sample was illuminated at normal incidence. When the incidence angle was increased, the reflectance peak was blue-shifted. The colour changes due to interaction with liquids and vapours are described here after.

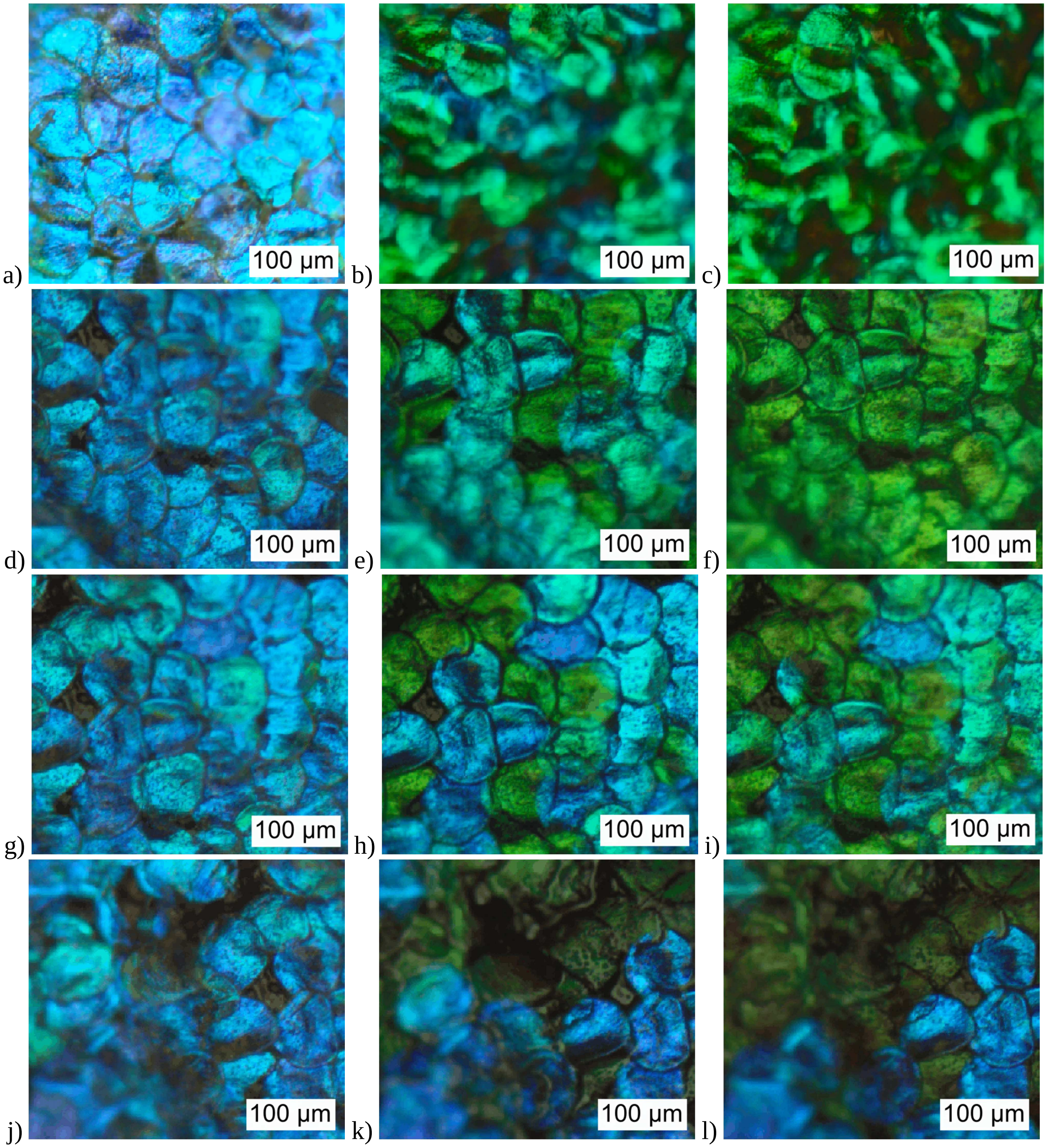



Figure 3. Colour variations of *Hoplia coerulea* scales upon impregnation with water (a-c), ethanol (d-f), acetone (g-i) and toluene (j-l). With these four liquids, the blue-violet scales of the beetle turn to green. a,d,g,j) ambient conditions; b,e,h,k) ongoing colour changes. These micrographs were taken at the mid-time between the ambient conditions and the wet state; c,f,i,l) wet state. The green colour obtained in the case of toluene (l) is different from water (c), ethanol (f) and acetone (i) because its refractive index is quite different. We notice that (i,l) are not totally green is due to acetone and toluene evaporation. (colours available online)

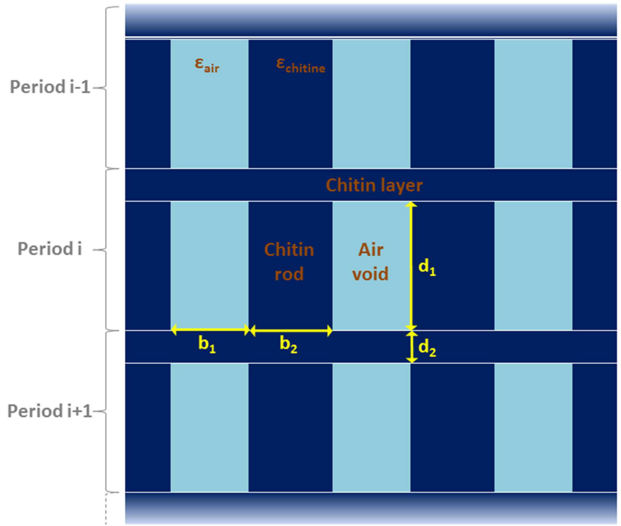



Figure 4. The internal photonic crystal structure at the origin of the blue-violet coloration of *Hoplia coerulea* is made of chitin layers separated by rods and air voids. The thicknesses of the rod layer $d_1$ and the chitin slab $d_2$ are 140 nm and 35 nm, respectively, leading to a Bragg mirror period of $d_1 + d_2 = 175$ nm. The air void $b_1$ and rod $b_2$ widths are equal to 85 and 90 nm, respectively. The refractive indices of air $n_{air}$ and chitin $n_{chitin}$ are taken to be equal to 1 and 1.56[22].

### 3.1 Interaction with liquids

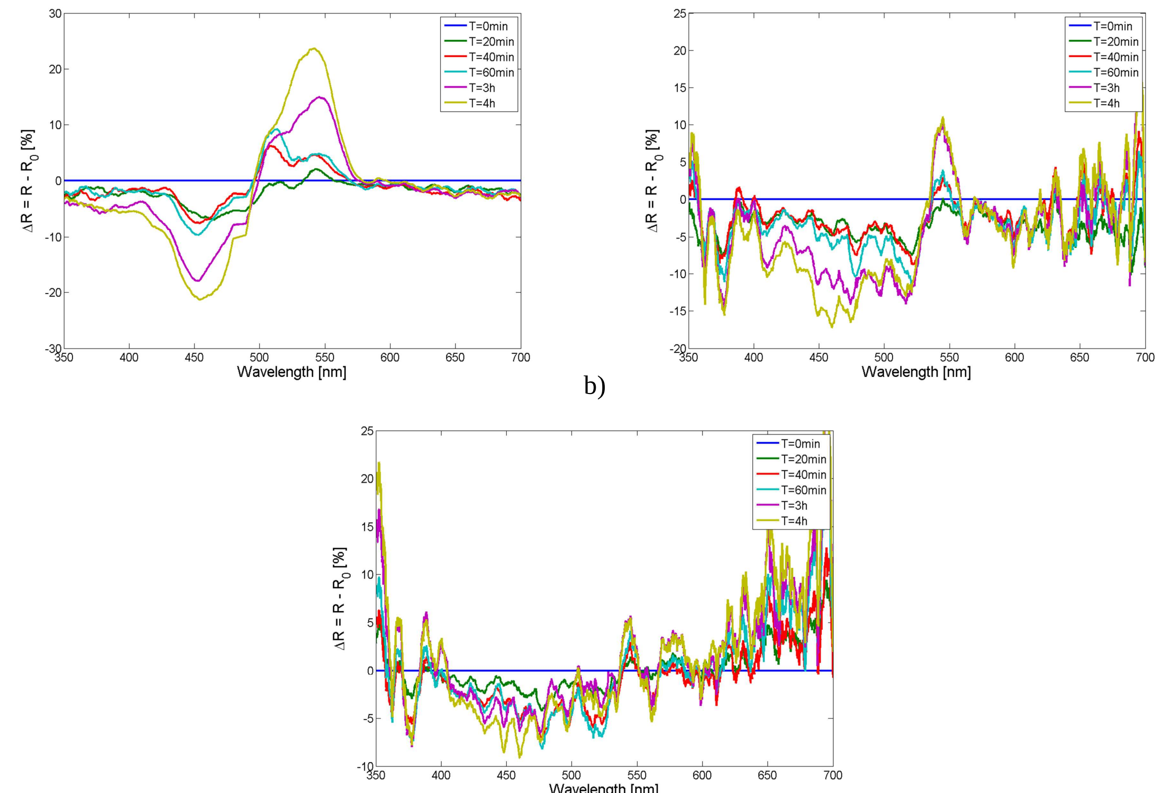
In 2009, Rassart *et al*.[15] highlighted that the colour of *Hoplia coerulea* male beetle turns to green when soaked in water. They measured a shift of reflectance peak position from 450 nm (ambient conditions) to 530 nm (wet state) at an incidence angle equal to 15°. They explained this colour variation by the replacement of air (refractive index equal to 1.00) by liquid water (refractive index equal to 1.33) in the voids of the nanostructure, leading to an increase in the effective refractive index. This phenomenon was demonstrated to be reversible.

Here, impregnation experiments of the beetle scales were performed using droplets of 0.5 µl of distilled water, absolute ethanol, acetone and toluene. The colour changes were observed by optical microscopy (Fig. 3). We notice that the beetle wings are hydrophilic, at the contrary of other insects, especially butterflies[3]. The colour changes take place with all of these four liquids and are similar: just after the droplet is deposited, some scales instantly turn to green. Then, the other scales gradually (i.e., scale by scale) turn to green. Within one minute, the cuticle surface is totally green, except in the cases of acetone and toluene (Fig. 3i). In fact, acetone and toluene evaporate faster than the colour change process. However, some scales can be found to turn to green before acetone and toluene completely evaporate. In the case of toluene, the observed green colour (Fig. 3l) is different from the ones obtained for water (Fig. 3c), ethanol (Fig. 3f) and acetone (Fig. 3i) because the refractive index of liquid toluene ($n_{toluene} = 1.50$) is quite different from those of water ($n_{water} = 1.33$), ethanol ($n_{ethanol} = 1.36$) and acetone ($n_{acetone} = 1.36$).

The key challenge is to explain how liquids infiltrate through the scale envelope and, possibly, replace air in the voids of the structure. We notice that, among the scales whose colour instantly changes, some scales are clearly damaged. We propose that all scales turning instantly to green are damaged. Regarding the gradually changing scales, no porosity could be observed in the scale envelope by SEM analysis. Of course, micropores (i.e., pores with a diameter smaller than 2 nm) could be present. They could allow liquids to fill air voids in the nanostructure, in spite of the fact that they are too small to be observed by SEM. Another possibility is that the chemical composition of the insect cuticle (not only chitin but also other macromolecules like proteins[2]) could lead to permeability of the envelope.

### 3.2 Interaction with vapours

The differential reflection factor spectra $\Delta R$ in the presence of distilled water (Fig. 5a), absolute ethanol (Fig. 5b) and acetone vapours (Fig. 5c) were measured. They are calculated from $\Delta R = R - R_0$, where $R$ is the spectrum measured from scales in contact with vapour during a period of time $T$ (0 min, 20 min, 40 min, 1 h, 3 h and 4 h) and $R_0$ is the spectrum measured just after the placement of the liquid-containing cup in the measurement cell ($T = 0$ min) in ambient conditions (about 45% of relative humidity and 22°C). The temperature was very stable during the experiments (less than 2% variations). Indeed, it was recently demonstrated that the colour of insect wings depended also on temperature[23-24]. The measured colour changes were found to be reversible.

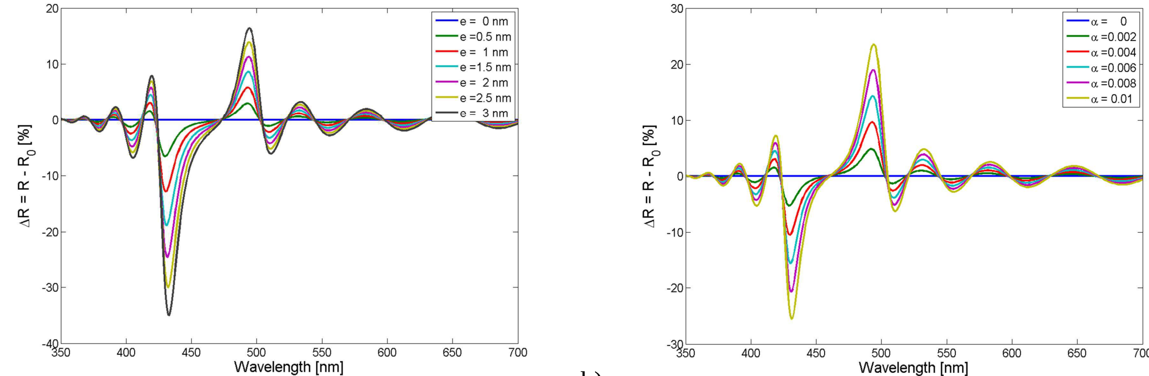



a) b) c)

Figure 5. Differential reflection factor spectra $\Delta R = R - R_0$ collected in the presence of (a) water, (b) ethanol and (c) acetone vapours. R are the spectra measured from scales in contact with vapours during a period of time T and $R_0$ is a spectrum measured just after the placement of the liquid cup in the measurement cell (T = 0 min). (colours available online)

Two phenomena that could explain these observations were investigated[10]: 1) the physical adsorption of vapour in the air voids of the nanostructure and 2) the swelling of the structure.

If a thickness $e$ of water vapour physisorbs on the void surface, the simulated differential reflection factor spectra $\Delta R$ (Fig. 6a) are similar to the experimental ones (Fig. 5). In this case, $\Delta R = R - R_0$ and $R$ is the spectrum simulated for the photonic structure model described by Rassart *et al.*[15] using a physisorbed water vapour thickness $e$ varying from 0 to 3 nm, and $R_0$ is the spectrum simulated without physisorption ($e = 0$ nm). The maximal physisorbed water thickness value we chose ($e = 3$ nm) was experimentally observed on hydrophilic surfaces[25]. Only simulations for water ($n_{water} = 1.33$) are shown. The results for ethanol and acetone ($n_{ethanol} = 1.36$ and $n_{acetone} = 1.36$) are very similar to those for water. A Bruggeman's effective medium approximation was used in order to evaluate the effective refractive index in the spacer layers (mix of air, water and chitin). No capillary condensation was supposed in the modelling because the observed nanostructure pores are too large to be considered as mesopores (i.e., pores giving rise to capillary condensation). Furthermore, capillary condensation within the porous structure would result in modifications of the reflectance spectra which would be too important in comparison with the experimental differential spectra (Fig. 5). Only a few nanometres thickness of physisorbed vapour seems to be enough to explain the colour variations.




a) b)

Figure 6. Differential reflection factor spectra $\Delta R$ simulated for the photonic structure model described by Rassart *et al*.[15] and experiencing (a) physisorption of water vapour and (b) a swelling. R corresponds to the spectra simulated for (a) a thickness of physisorbed vapour $e$ and (b) a swelling factor α. $R_0$ is a spectrum simulated for a structure model without physisorption ($e = 0$ nm) and without swelling ($\alpha = 0$). (colours available online)

The swelling of biopolymers (i.e., an increase of size) due to water contact has already been observed in keratin (bird feathers[26-27]) and in chitin (longhorn beetles[6] and bristle worms[28]). In these cases, hydrogen bonds are disrupted in the polymer due to water infiltration, leading to an increase of the nanostructure size.

A swelling experienced by the *Hoplia coerulea* structure could also explain the measured colour changes since the variations of the reflectance spectra $\Delta R$ are similar (Fig. 6b) to those measured by spectrometry (Fig. 5). In this case, $\Delta R = R - R_0$ and $R$ is the spectrum simulated for Rassart *et al*.'s structure model[15] whose dimensions were multiplied by $1 + \alpha$. $\alpha$ is termed the swelling factor. A value of $\alpha = 0.01$ leads to differential spectra similar to measured ones. This value ($\alpha = 0.01$) is rather low. For instance, swelling factor in the case of the longhorn was estimated to $\alpha = 0.08$[6].

We postulate that the origin of the colour variations is probably a combination of these two phenomena, i.e., physisorption and swelling. Furthermore, in both cases, simulated differential spectra are shifted (of about 25 nm) in comparison with experimental ones. This can be explained by the origin of the insects which is different from the specimens used by Rassart *et al*.[15], leading to slight colour differences due to slight differences in structure dimensions.

## 4. CONCLUSION

The structural blue-violet coloration of the *Hoplia coerulea* was demonstrated to be modified when impregnated by water, ethanol, acetone and toluene liquids or in contact with vapours of these liquids. In spite of being non-open, this porous photonic structure presents this remarkable property of changing colour in the presence of liquid or vapour. The structure at the origin of the colour changes is a 1D periodic porous multilayer (i.e., a repetition of chitin layers and rod-like spacer layers), which is enclosed by a 100 nm-thick envelope.

Two possible origins of the observed effect were investigated: physisorption of vapour on the surface of the nanostructure pores and the swelling of the structure. In both cases, the variations of the spectral reflectance simulated by a thin-film code were similar to measured ones.

This effect is very interesting in order to develop bio-inspired sensors and smart glass devices, as the photonic structure could easily be produced by nanofabrication methods.

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