SUPPORTING INFORMATION

COLORIMETRIC DETECTION OF PERFLUORINATED COMPOUNDS BY ALL-POLYMER PHOTONIC TRANSDUCERS

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S1: Contact Angle

To assess the water contact angle on HY films, 9 different samples were fabricated using solution of HY in Galden HT100® with different concentration and casted by spin-coating at different rotation speeds. For all the samples the contact angle ranges between 118° and 120°. These data confirm the high reproducibility of the deposition condition.

![Figure S1: Contact angle as retrieved for HY films with different thicknesses on glass substrates.](image)

S2: DBR exposure to PFC GaldenHT55®: Reflectance contour plot

Supporting Information Figure S2 shows the spectra collected during the exposure to Galden HT55® of a DBR where the capping layer is HY instead of PVK. In this case, we notice that the response of the sensor is instantaneous without any induction time (compare with Figure 3, main text). Indeed, the PBG, which is visible in the contour plot in red-tones and is initially positioned at ~630 nm, undergoes a sudden and monotone blue-shift to ~550 nm within the first 15 mins of exposure. Then the PBG fades, while other two peaks appear at ~950 nm and ~450 nm. These signals are compatible with the first and second diffraction order of a swollen DBR, where the HY layers absorbed the analyte.

The blue-shift of the PBG can be easily explained considering that, when the lower refractive index medium is the capping layer of a DBR, the PBG results affected by the interference pattern as describe in details in our previous work.¹ Consequently, the interference between the Fabry-Pérot pattern and the PBG may result in an apparent shift of the PBG to the blue-part of the spectrum even during the swelling of the polymer media.²
**Figure S2:** Contour plot spectrum collected during the exposure of a HY-PVK having HY as upper layer DBR to GaldenHT50®.

**S3: DBR exposure to PFC GaldenHT55®: Reflectance spectra**

Supporting Information Figure S3 shows the spectra of the HY-PVK DBR collected every 20 minutes during the exposure to GaldenHT55®. The spectrum initially shows a first order PBG at 900 nm and a second order replica peaked at 450 nm (black line). After 20 min of exposure the intensity of these two features decreases, while a further signal appears at ~1150 nm. After 40 min of exposure, the first order PBG is broad and ranges between 800 nm and 1600 nm, while the second order appears still at about 450 nm. This behavior can be assigned to the swelling of the HY layers closer to the air environment enriched with GaldenHT55®. This behavior was already observed in previous works.\(^1\)\(^-\)\(^2\) The second order replica of the PBG does not reflect with the same efficiency the formation of a photonic structure assigned to the swollen DBR. This behavior may arise from the inhomogeneous swelling of the HY layers. After 60 mins of exposure the PBG keep broadening. Indeed, a large structure ranging from 800 to 2000 nm is detected. So far, the signal was more intense on the short wavelength side of this spectral feature, while it now appears more intense on the long-wavelength side. This phenomenon confirms the formation of a PBG assigned to a swollen disordered structure, which increases in intensity as the deeper layers swells. Indeed, the intensity of the long wavelength structure is even higher at 80 min of exposure. After this time, the spectrum show some structures at 420 nm, 900 nm, and 1500 nm, but the features assigned to the PBGs faded. Such characteristics suggest that despite the strong swelling of the polymer layers, some order...
is still present in the DBR, but the perfect periodicity allowing the formation of a clear PBG was destroyed.

This hypothesis was tested performing a simulation of the optical response of the swollen structure at 80 min of exposure via transfer matrix method. The resulting spectrum (dashed black line in Figure S3) was calculated for a multilayer made of 15 alternated films of PVK and HY. The PVK thickness was set at 196 nm (as retrieved from calculations, see Figure 1) and kept constant (see Supporting Information Figure S5 for details regarding PVK behavior during the exposure). To calculate the response, we considered a progressive intercalation of the analyte in the DBR through the surface closer to the enriched environment and thus a progressive swelling of the HY layers starting from the one on top of the DBR, which is closer to the analyte environment, to the bottom one, which is closer to the glass substrate. Under this assumption we set the thickness of the two bottom HY layers (closer to the substrate) equal to the value calculated for the unexposed sample, which is \( d_{HY} = 102 \) nm. The thicknesses of the other layers were instead retrieved averaging the response of 1500 different random combination of normal distributed layers thicknesses retrieving the spectrum reported in the dashed line in Figure S3, which correspond to an average PVK thickness of \( d_{HY}=295 \pm 133 \) nm. The good agreement between the calculated spectrum and the spectrum of the sample exposed for 80 min (brown line) confirm the inhomogeneity of the exposed sample and the swelling mechanism.

**Figure S3:** Experimental evolution of the reflectance spectrum upon exposition to GaldenHT55® for HY:PVK DBR (colored continuous line) and calculated optical response of after 80 mins of exposure (black dashed line)
S4: CA:PVK DBR

To confirm that HY plays as the active sensing medium, a DBR similar to the one analyzed so far was fabricated replacing HY with cellulose acetate (CA). Supporting Figure S4 shows the reflectance spectra of the sample collected over 8 different spots of the surface. Such spectra are almost superimposed, testifying the homogeneity of the sample. All the spectra show a first order PBG tuned at 907 nm, followed by a second order replica at 456 nm, and a third order at 321 nm. The spectrum background is dominated by an interference pattern. It is worth to notice the large differences in term of PBG spectral width and intensity between of the sample grown using CA with those of the sample grown using HY (Figure 2c). Indeed, notwithstanding both the samples have the same number of periods and were fabricated using similar conditions, the large dielectric contrast of the HY-PVK DBRs allows much larger and more intense spectral features. The optical response of the PVK:CA sample to GaldenHT55® is reported in Figure 3b.

![Experimental and calculated spectra CA-PVK DBR.](image)

**Figure S4.** Experimental and calculated spectra CA-PVK DBR.

**Supporting Information References**

(1) Lova, P.; Bastianini, C.; Giusto, P.; Patrini, M.; Rizzo, P.; Guerra, G.; Iodice, M.; Soci, C.; Comoretto, D., Label-free vapor selectivity in poly(p-phenylene oxide) photonic crystal sensors. *ACS Appl. Mater. Interfaces*, 2016, 8, 31941–31950.

(2) Lova, P.; Manfredi, G.; Boarino, L.; Comite, A.; Laus, M.; Patrini, M.; Marabelli, F.; Soci, C.; Comoretto, D., Polymer distributed Bragg reflectors for vapor sensing. *ACS Photonics*, 2015, 2, 537-543.