Transparent nanometric organic luminescent films as UV active components in photonic structures.

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The flavonoids, natural compounds in diverse plants, have been extensively studied due to their anti-oxidant properties in biological systems.[1] Within this family, 3-Hydroxyflavone (3HF) is one of the most interesting derivatives because their singular luminescent properties. In solution under ultraviolet illumination (UV) this molecule shows two types of fluorescence emission: a normal deep-violet emission and a yellow-green emission assigned to an excited proton-transfer tautomer of the normal molecule with a large Stokes' shift of ~180 nm. This excited state intermolecular proton transfer mechanism (ESIPT) of 3HF in solution was initially described by Sengupta and Kasha and further studied by many authors in the last decades.[2-4] This process involves a very efficient non-radiative energy dissipating mechanism whereby the 3HF molecule absorbs one photon while, in the excited state, one hydroxyl proton is transferred to a neighbouring carbonyl group.[5] The

ESIPT mechanism in 3HF is very sensitive to the chemical environment. Thus, emission of the tautomer form with a very low contribution of the normal emission has been observed in non-polar media.[4,6,7]

The molecule in solution has been extensively utilized as colorimetric reagent, polarity probe, probe in biological microenvironments or lasing mediums.[1,3,8] Hydroxyflavone doped polymeric thin films prepared by solution polymerization and sol-gel hybrid films have been utilized as scintillator and wavelength shifters.[6,9] Films prepared by vacuum deposition, magnetron sputtering and other methods have been used in OLEDs and in commercial Si photodiodes.[9,10]

In this article, we present an alternative approach to the fabrication of 3HF containing thin films and their unprecedented implementation as active components in photonic structures that can be useful for the fabrication of devices such as UV-sensors, UV-to-visible wavelength shifters and UV-filters. In our preparation procedure, the films are deposited in vacuum at room temperature by sublimating the dye in the downstream region of a low power microwave plasma. The main difference from a standard vacuum deposition or a plasma polymerization process is that the interaction with the plasma produces the fragmentation of only a fraction of the dye molecules in the gas phase creating highly reactive molecular moieties that form a polymeric-like film onto the substrate surface.[11] In this plasma assisted vacuum deposition process, the working conditions and reactor geometry are finely controlled to avoid a complete fragmentation of the dye molecules. The resulting material is a polymeric film with a given percentage of integer 3HF molecules embedded in it that depicts quite different properties than those of layers obtained by the direct sublimation of molecules. Although some examples of a similar synthetic methodology have been very recently reported for other functional molecules, this is the first time that such deposition process is applied to the growth of 3HF films.[11–13] The composition of the films as determined by XPS analysis was 78 %C, 22 %O. This composition is close to that corresponding to the molecular

formula of the dye (i.e., 83 %C and 17%O). The oxygen enrichment found on these polymeric films is a general characteristic of any deposition process involving plasmas.[11-13, 15]

To characterize the films and further confirm the incorporation of integer dye molecules into the polymeric matrix we used the ToF-SIMS technique. Among the very numerous peaks of the spectrum shown in **Figure 1**a) the most intense ones appearing in the region m/z 40–120 are associated to the cross linked polymeric matrix. The spectrum also clearly depicts the peaks corresponding to the 3HF M+ (m/z ~238) and MH+ (m/z ~239) molecular ions indicating a high percentage of integer 3HF molecules embedded in the film. This spectrum is very different to the 3HF reference spectrum (see Figure S1 in the Supporting Information) composed by the molecular ions peaks and a few low intense peaks at lower m/z.[14]

A high transmittance in the visible and a low roughness are critical requisites for the integration of the dye thin films together with photonic structures. For this application, mechanical stability and insolubility in water or alcohol are other required conditions that are fulfilled by our films. The AFM micrograph of a 3HF thin film in Figure 1b) confirms that these films surface are very homogeneous, crack free and smooth with a RMS roughness of ~0.4 nm. Such a low surface roughness assures that there will be no significant light scattering at the surface of the films incorporated onto the photonic structures. The absence of any light dispersing crystalline aggregates, typically found in other dye sublimated films is another remarkable feature of the 3HF films evident by optical characterization.[13, 17]

Figure 1c) shows the UV-VIS transmission spectra of a set of 3HF thin films with different thicknesses. All the films absorb in the UV region and are transparent in the visible region (i.e., $\lambda > 390$ nm), a significant property for many final applications of these films.[18] The absorption features at ~310 and ~345 nm are similar to those reported for dilute alcoholic solutions of the dye.[1,4] The intense and continuous light absorption at wavelengths lower than 390 nm can be attributed to both the dye molecules and the unsaturated bonds in the

polymeric matrix. It is also worth noting the high UV absorption capacity of films with a thickness as low as ~50 nm and the fact that for ~300 nm films UV absorption is nearly complete. Saturation of absorption and sharpness of the absorption edge are requirements for the fabrication of UV-filters, an application where our films can compete in performance with thin film materials prepared by other methods.[19] At wavelengths higher than ~390 nm, already in the visible and near infrared regions, the films are visible blind (i.e., transparent) showing the typical interference patterns due to a different refractive index than the substrate (cf. Figure 1c). The high transparency of these films in the whole visible range is confirmed by the very low value of its extinction coefficient function determined by ellipsometry (cf. Figure 1d). The refractive index value of the 3HF thin films is 1.62 at 630 nm.

The fluorescence behavior of the 3HF polymeric films is analyzed in **Figure 2**. The shape of the excitation spectrum in Figure 2a, characterized by a maximum at ~345 nm and a shoulder at ~310 nm, is very similar to that of the dye molecule in solution.[1,4] Information about the corresponding fluorescence intensity decay can be found in the Supporting Information (see Fig. S2). The emission spectrum is formed by a single and intense feature at ~535 nm corresponding to the tautomer emission of the 3HF molecule. Meanwhile, the emission of the normal form at ~425 nm is negligible. This result suggests that the non-polar character of the cross-linked 3HF polymeric matrix quenches the hydrogen bond donating ability of the molecule.[4,9] From the point of view of their applications, it also sustains the use of these materials as selective emitters of green light or as UV detectors since, contrary to the molecule in solution or other media, only one emission channel remains in the films. To prove the feasibility of this latter application, Figure 2b) shows that the fluorescence emission varies almost linearly with the UV light ($\lambda=360$ nm) for a large range of intensities (i.e. $0.01-1.5$ mW/cm^2). No departures from this linear behavior are observed after several cycles of increasing and decreasing the UV irradiation, thus supporting the high UV stability of the films. The emission process has to be very intense for this application and for its potential use

as green light emitter. This is actually shown in Figure 2c) where it can be easily observed with the naked eye the green light emitted by films illuminated with a low intensity UV lamp (see the illuminated walls of the container). The experiments in this figure corresponds to a ~100 nm thick film deposited on glass, polyethylene, PMMA and polycarbonate both before and during UV illumination. Two additional examples of the deposition on Euro bank notes and a flexible polymer are included (Figure 2d)-e)) to demonstrate the fully compatibility of the deposition process with any kind of sensitive substrate. These examples also prove the high efficiency for green light emission clearly appreciable even under daylight conditions. Another advantage of our methodology is the straightforward lithographic deposition of the thin films in one step. The fluorescence micrographs reported in Figure 2f) show a micrometric pattern and a planar waveguide-like pattern obtained by the deposition of a ~100 nm film through a shadow mask. The possibility of depositing optical structures by using masks, together with the mechanical, optical and luminescent properties of the 3HF polymeric films make them ideal for their incorporation as active materials in photonic structures (i.e., interferometric and resonant structures) used for the fabrication of photonic devices. Furthermore, the 3HF polymeric films can be selectively removed from the surface by plasma etching which assures that the photonic structures, the most expensive part of the final devices, can be reused for the preparation of new devices.

Three different photonic structures incorporating the fluorescent films will be presented here to demonstrate the feasibility of this concept: a vertical and a planar Fabry-Perot (F-P) resonator and a disk resonator. The vertical Fabry-Perot resonator structure is relatively simple and consists of a periodic 1-D photonic crystal with a central planar defect. The 3HF dye thin film is the active component and is deposited as the upper cladding of the multilayered structure (see the scheme of the device Figure S3 A1−2). The periodic distribution of thin layers forming a Bragg reflector consists of 18 pairs of nine SiO_2 (100 nm) and Si_3N_4 (65 nm) layers while the defect or cavity is a Si_3N_4 thin film of 190 nm. The

structure is designed to have a wide photonic band gap extending from 460 to 625 nm with a sharp transmission peak with a FWHM of ~2.5 nm located at ~535 nm within the spectral position of the 3HF polymer fluorescence maximum (see structureVC18 in **Figure 3** A1). Figure 3 A2) shows the emission spectrum of a 3HF thin film deposited on quartz and the same spectrum measured through the vertical structure where the 3HF thin film is deposited as a cladding. The plot shows that the fluorescence light of the dye layer is converted from a relatively broad band with a FWHM of ~65.8 nm to a peak with a FWHM of ~3.5 nm when transmitted through a structure whose surface is illuminated with UV light. A picture of the transmitted fluorescence light is shown in the inset of the Figure 3 A2).

The second photonic structure is based on a silicon nitride multimode strip waveguide with a width of 10 µm and a height of 300 nm. The lower cladding is a 5 µm thick SiO_2 layer grown on Si. The planar F-P resonator consists of Si_3N_4/air pairs separated 90 nm with a cavity height of 140 nm (see Figure S3 B2). The dye layer is selectively deposited through a mask just on the resonant micro-cavities (see Figure S3 B1). The waveguide and resonator structure are designed to transmit the 3HF emission up to the output, even if there are several transmission modes. Figure 3 B1) shows a fluorescence micrograph image of the 3HF active area covering the resonator structure, while Figure 3 B2) shows a fluorescence confocal image taken in cross section to prove that the fluorescence light is selectively transmitted through the wave guide. In the inset of this figure it can be observed the transmission modes obtained of the fluoresce emission modulated by the Fabry-Perot resonant cavity at the edge of the output waveguide.

The third photonic structure consisted of a disk resonator and a Si_3N_4 strip forming a high refractive index waveguide (Figure S3 C1−C2). The waveguide cross section is 600 nm and its height around 80 nm, a topology that only permits the propagation of the fundamental TE mode. The lower cladding is a layer of SiO_2 with a thickness of 5 µm on a Si substrate. The upper cladding is also SiO_2. A window through this SiO_2 upper cladding was open over

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the resonant disk and nearby waveguide to enable that the active 3HF film is selectively deposited onto this zone (see Figure 3 C1). This process was carried out at wafer scale covering trough masks a large number of ring resonators. The design and dimension of this photonic structure is such that the waveguide can couple the green fluorescence emitted by the active 3HF film. The disk is an optical resonator coupled by evanescent field to the waveguide. To get an effective coupling, the distance between the ring and the waveguide was between 100 and 150 nm and various disks with different diameters ranging from 50 to 200 µm were fabricated onto a wafer. Figure S3 C2) shows a SEM image of one of these disk resonators/waveguide ensembles and Figure 3 C1) a fluorescence micrograph showing a device illuminated with λ~365 nm. It must be noted that the central region including part of the strip waveguide and the whole resonant disk is brighter than the rest of the chip. The good performance of this photonic device can be seen in Figure 3 C2) showing that the green light is collected and transmitted up to the waveguide output in the chip edge. This preferential distribution of the fluorescence light supports that, as predicted by electric field simulations (data not shown), the field intensity is higher in the disk and becomes transmitted through the waveguide out of the 3HF coated region up to the border of the structure.

In this work we have presented a new kind of photonic organic thin film material prepared by a novel plasma assisted vacuum deposition procedure. The films consist of a polymeric matrix with a high concentration of free 3HF molecules absorbing in the UV and emitting in the visible. Besides its extraordinary good performance as UV-filter, UV-sensor and green emitter, the deposition of these films through masks on the surface of different photonic structures has proved their suitability as photonic active components for the fabrication of reusable photonic chips. These concepts have been proved by monitoring the spectral response of a chip consisting of a vertical and planar Fabry-Perot structure and by direct observation of the fluorescence light paths in planar photonic structures (horizontal Fabry-Perot and ring resonators). In these latter cases, the selective deposition through masks

is another key characteristic enabling the wafer scale fabrication of complex photonic chips. Furthermore, the deposition process allows the fabrication of the luminescent films onto sensitive substrates. An outstanding achievement of the process is the direct deposition of luminescent nanometric films/patterns on flexible polymers and paper. Such advantages will be determinant for the integration of this new material as active component in organic optical and microelectronic devices.

Experimental

Plasma procedure. The polymerized thin films were prepared by sublimation of the 3-HF dye molecules (Aldrich) in the downstream region of the Ar microwave ECR plasma working at 150 W and the argon pressure $1x10^{-2}$ mbar. Film thickness (in the range 30–300 nm) and evaporation rate were monitored by using a quartz crystal monitor placed besides the sample holder in the deposition region (see also refs. 11 and 12). Adjusting the plasma condition and geometry of the deposition process was possible to reproducibly control the concentration of integer 3-HF molecules in the films.

Thin film and photonic structures characterization. The mass spectra of the samples were recorded on a TOF-SIMS IV instrument from Ion-ToF GmbH Germany. UV-Vis transmission spectra were recorded in a Perkin-Elmer λ12 spectrophotometer. Fluorescence spectra were measured in a Jobin-Yvon Fluorolog3 spectrofluorometer. Fluorescence microscopy images were obtained with a Leica TCS SP2 confocal fluorescence microscope. For the cross-sectional images the samples were illuminated with a 365 nm 3mW LED source.

Optical characterization of the thin films has been carried out with a variable angle spectroscopic ellipsometer (VASE) from J.A. Woollam Co., Inc. The spectral range was 200-2000 nm and the measurements were performed at 60º, 65º and 70º angles of incidence. Non-contact AFM measurements were carried out with a Cervantes AFM system from NANOTEC.

Field Emission Scanning Electron Microscopy (FESEM) micrographs were obtained with a

Hitachi Field Emission S-5200.

Supporting Information
Supporting Information is available online from Wiley InterScience or from the author)).

Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

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Figure Captions

Figure 1. a) ToF-SIMS spectrum of a 3HF 120 nm film, b) AFM micrograph of a 150 nm thin film, c) UV-vis transmission spectra of films with different thickness and d) refraction index and extinction coefficient as a function of the wavelength of a ~100 nm thin film.

Figure 2. a) Excitation and emission spectra of a ~100 nm thick thin film, b) evolution of the intensity of the emission spectrum as a function of the UV intensity used for excitation; c-e) photographs of a series of transparent luminescent thin films deposited onto several sensitive substrates as labeled, f) fluorescence micrographs taken for 3HF films deposited through masks designing an squared pattern and two lines of a waveguide structure.

Figure 3. Responses of the 3HF thin film deposited onto photonic structures. A1) Transmission spectrum trough a vertical cavity and A2) comparison of the fluorescent spectra recorded for a 3HF film deposited on a quartz slice and onto the vertical cavity as indicated in the insets. B1) Normal fluorescence micrographs taken for a Fabry-Perot structure with the 3HF film deposited on the resonator zone. B2) Idem taken in cross section at the edge of the output waveguide. In the inset is shown the experimental and fitted (red line) transmission modes obtained of the fluoresce emission modulated by the Fabry-Perot resonant cavity. C1) Normal fluorescence micrographs taken for a ring resonator structure with the 3HF film deposited on the resonator zone and from a boundary zone showing the fluorescence light carried by two wave guides. C2) Picture of the end part of the waveguide at the wafer edge.
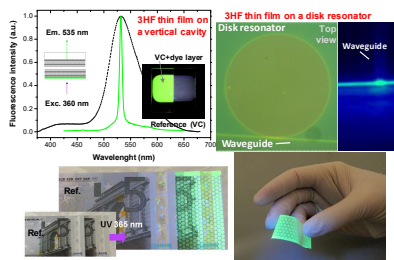
Table of Content

We present a new kind of *visible blind* organic thin film material consisting of a polymeric matrix with a high concentration of embedded 3HF dye molecules absorbing in the UV and emitting in the center of the visible spectra. The thin films can be grown in sensitive substrates including flexible polymers and paper. Their suitability as photonic active components is demonstrated for the fabrication of different types of photonic devices.
Functional Coatings; Optically Active Materials; Photonics; Nanodevices; Sensors/Biosensors; Thin Films, Photoluminescence

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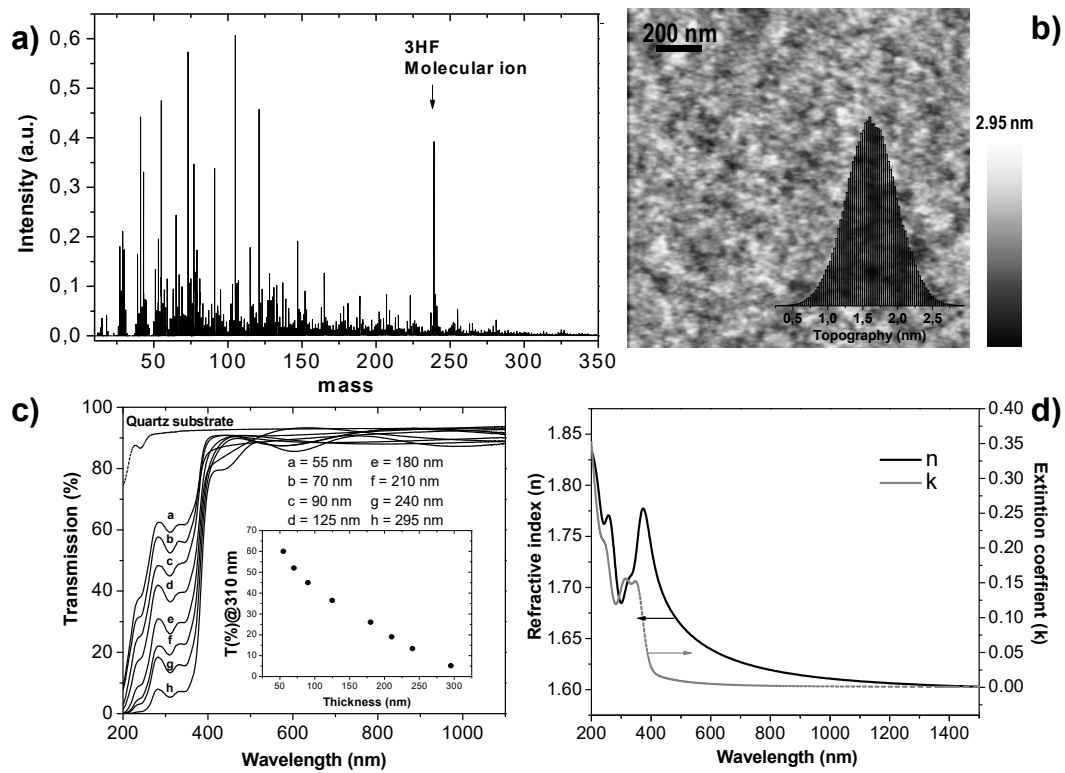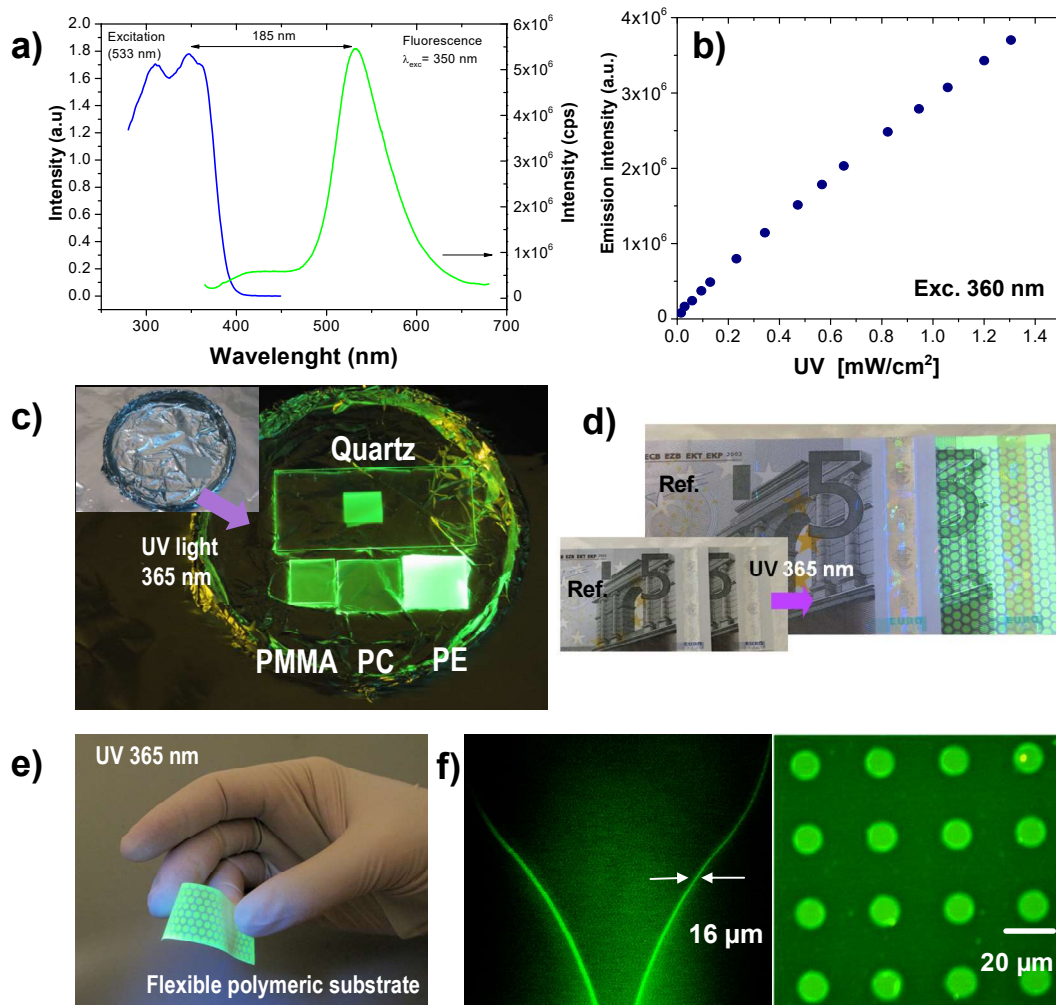Transparent nanometric organic luminescent films as UV active components in photonic structures.

a)

b)

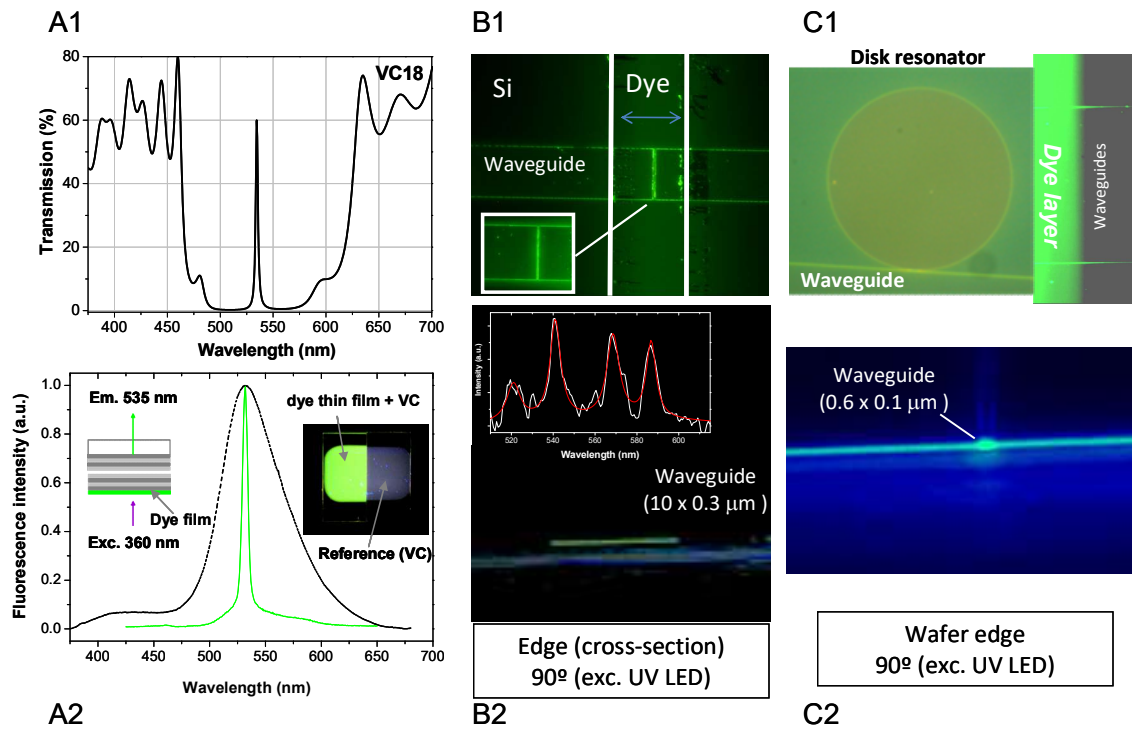**c)**

a = 55 nm   e = 180 nm
b = 70 nm   f = 210 nm
c = 90 nm   g = 240 nm
d = 125 nm h = 295 nm

d)

Figure 1.

Figure 2.

A1

A2

B1

B2

Edge (cross-section)
90º (exc. UV LED)

C1

C2

Wafer edge
90º (exc. UV LED)

Figure 3.