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# In-plane anisotropic photoresponse in all-polymer planar microcavities

Robert J. Knarr III <sup>a, 1</sup>, Giovanni Manfredi <sup>a</sup>, Elisa Martinelli <sup>b</sup>, Matteo Pannocchia <sup>b</sup>, Diego Repetto <sup>c</sup>, Carlo Mennucci <sup>c</sup>, Ilaria Solano <sup>c</sup>, Maurizio Canepa <sup>c</sup>, Francesco Buatier de Mongeot <sup>c</sup>, Giancarlo Galli <sup>b</sup>, Davide Comoretto <sup>a, \*</sup>

<sup>a</sup> Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, via Dodecaneso 31, 16146 Genova, Italy
<sup>b</sup> Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Pisa, via Moruzzi 13, 56124 Pisa Italy

<sup>c</sup> Dipartimento di Fisica, Università degli Studi di Genova, via Dodecaneso 33, 16146 Genova Italy

#### A R T I C L E I N F O

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#### ABSTRACT

We report on the optical photomodulation properties of all-polymer planar microcavities in which the photochromic poly((4-pentyloxy-3'-methyl-4'-(6-methacryloxyhexyloxy))azobenzene) (PMA4) acts as photoresponsive cavity layer. We induce the trans-cis isomerization process of the azobenzene group by polarized 405 nm CW-laser irradiation, while the backward process is driven by unpolarized CW-laser irradiation at 442 nm. The all-optical photoisomerization process induces a remarkable in-plane anisotropic spectral shift of the cavity modes for the first and second order photonic band gaps. The spectral and intensity modulation effects for these flexible all-polymer microcavities are discussed with respect to those so far reported in literature for analogous systems.

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#### 1. Introduction

Polymers containing azobenzene pendant groups are suitable materials for many applications including photo-actuators [1,2], molecular motors [3], photoswitching systems [4], conductance switches [5,6], and optical memories [7]. The *trans-cis* isomerization (and vice-versa) may occur following irradiation with UV–visible light, mechanical stress, or electrostatic stimulation [8]. Transto-cis photoisomerization of the azo group occurs rapidly while the lifetime of the thermodynamically less stable *cis* form can be very long depending on the chemically tailored polymer structure [9,10].

It is interesting to remind that the azobenzene groups in their *trans* form are mesogenic and favor formation of a liquid crystal mesophase, typically nematic, whereas they are disorderly arranged in an isotropic phase when in their *cis* form [10,11]. Moreover, the photoisomerization process is accompanied by a rearrangement in the spatial configuration of the compound [12,13], and when polarized light is used, alignment of azobenzene

moieties induces anisotropies that modify the optical response of the material [10,11,13]. The absorption spectra of azo-derivatives show mainly two peaks assigned to the  $\pi \rightarrow \pi^*$  transition (about 350 nm) and to the symmetry forbidden  $n \rightarrow \pi^*$  transition (about 450 nm). The  $\pi \rightarrow \pi^*$  transition is more intense for the *trans* azo-benzene while the  $n \rightarrow \pi^*$  peak possesses a higher oscillator strength for the *cis* form [10]. The absorption of photons with such energies allows reversible photo-isomerization, even though the quantum efficiencies of the back and forth processes are not equal [4,8,9,14,15].

From the photonic point of view, the photoisomerization process is appealing since inducing a modification of the real part of the refractive index ( $\Delta$ n), which can be used for different devices [16–25]. Novel opportunities are provided by exploiting such  $\Delta$ n to tune the optical response of photonic crystals (PhC), i.e. periodical arrays of materials possessing different refractive index on a submicrometer scale. In PhC the coherent diffraction of light by the dielectric lattice planes generates a photonic band gap (PBG), i.e. a spectral region where photons cannot propagate into the structure thus being backward diffracted giving rise to a strong chromatic response. The spectral fingerprint of the PBG is a peak (minimum) in the reflectance (transmittance) spectrum of the PhC. The spectral position of the PBG is dictated only by the periodicity of the





polymer

<sup>\*</sup> Corresponding author.

E-mail address: davide.comoretto@unige.it (D. Comoretto).

<sup>&</sup>lt;sup>1</sup> Present address: Department of Chemistry, University of Basel, St. Johanns-Ring 19, CH-4056 Basel, Switzerland.

dielectric lattice and by the difference in the refractive index of the composing materials (dielectric contrast) [26,27]. When one of them is a photochromic material, the  $\Delta n$  associated with the photoisomerization process is expected to modify the PBG properties since affecting the dielectric contrast. In this way, innovative alloptical switching, modulation or limiting devices can be envisaged [28]. In this respect, the PhC behaves as a transducer of the photoisomerization process (detected in the absorption spectra at the blue-UV wavelengths) into a "chromatic" effect occurring in any desired spectral range of interest (for instance in the near infrared at telecommunication windows). Even though different organic and hybrid photonic crystal structures have been already tested in the field [29–37], recently the use of all-polymer planar structures like multilayers (i.e. Distributed Bragg Reflectors, DBR) or planar microcavities (i.e. multilayers where the periodicity along one direction is broken by a structural defect) gained an increasing interest [27]. Indeed, such structures have been shown to be efficient for vapor sensing [38], fluorescence enhancement [39,40] and lasing [41–44]. When photochromic azo-polymers are embedded into DBRs, very strong and efficient intensity photomodulation of the reflectance spectrum has been demonstrated making the system interesting for display applications as demonstrated by the Kurihara' group [45,46]. Additional opportunities are provided by using more refined structures such as the planar microcavity since the engineered periodicity defect there inserted generates an allowed state (the cavity mode) within the forbidden PBG. Due to the stronger spatial localization of light provided by microcavities with respect to DBR, light-matter interaction is there deeply modified [27].

For this reason, we have prepared all-polymer microcavities where the defect layer is made by poly((4-pentyloxy-3'-methyl-4'-(6-methacryloxyhexyloxy))azobenzene) (PMA4, Fig. 1a), a photochromic polymer carrying one azobenzene pendant groups for each monomer unit. CW polarized/unpolarized photomodulation of the microcavities gives rise to large and in-plane anisotropic spectral shifts as well as to intensity modulation of cavity modes. The photomodulation is also observed for multiple diffraction PBG orders at different spectral ranges.

#### 2. Experimental

PMA4 was synthesized according to a literature procedure [23]. Weight and number average molar masses ( $M_w = 181500 \text{ g mol}^{-1}$  and  $M_n = 47500 \text{ g mol}^{-1}$ ) were determined by size exclusion chromatography. Glass transition and nematic-isotropic (NI)



Fig. 1. a) Chemical structure of PMA4. b) Sketch of the microcavity's structure.

transition temperatures,  $T_g = 35$  °C and  $T_{NI} = 85$  °C, were measured by differential scanning calorimetry. PMA4 films were prepared by spin-coating its toluene (Sigma–Aldrich, 99.8%) solutions with concentrations of 30 or 60 mg mL<sup>-1</sup> at a spinning rate in the range 10–100 rps. Films are quite uniform on an area of about 24 × 24 mm<sup>2</sup> and have thicknesses varying from tens of nanometers to about 1 µm PMA4 solutions at the higher concentrations are very viscous, thus reducing film uniformity at the lowest spinning velocities.

The microcavities are composed of two Distributed Bragg Reflectors (DBRs) that encapsulate the engineered defect. The two DBRs are prepared by spin coating, a reliable technique already tested for the preparation of multilayered structures [39,44,47-49]: they are made by 15 alternating layers of poly(Nvinylcarbazole) (PVK) and Cellulose Acetate (CA) (concentration, about 30 mg mL<sup>-1</sup>; spin velocity, 55 rps, thickness  $d_{CA} = 272$  nm,  $d_{PVK} = 156 \text{ nm}, d_{PVA} = 100 \text{ nm}$ ). PVK was supplied by Acros Organics and is used as high refractive index material (n~1.69), while CA is supplied by Sigma–Aldrich and is used as low refractive index material (n~1.46). Since toluene (the solvent for PMA4) and diacetone alcohol (the solvent for CA) are not perfectly orthogonal solvents in our conditions, PMA4 cavity is sandwiched between two polyvinyl alcohol (PVA) layers. The PVA (supplied by Sigma--Aldrich) is dissolved in a mixture of equal parts of water and ethanol. This mixture dissolves neither CA nor PVK and is immiscible with toluene. In this way, the defect surrounded by the two DBRs is composed not of a single layer but of three layers: the external PVA ones and the internal one made by PMA4 (about 928 nm thick, see Fig. SI3 in Supplementary Information). The structure of the entire system is sketched in Fig. 1b. The microcavity can be peeled-off from the substrate where is grown and then bent or folded.

The back and forth photochromic transition is driven by a polarized continuous-wave (CW) laser at 405 nm Oxxius SN LAS-00676, 50 mW sample spot ~4 mm diameter ("writing" laser) and by an unpolarized 40 mW CW laser at 442 nm CNI MDL–III–442, sample spot 3 mm diameter ("erasing" laser). In order to prevent possible thermal induced effects, particular care was used to limit the exposure time of the cavity to the writing/erasing beam. According to the data reported in Fig. SI1c, we notice that the writing process is very fast, while the erasing one presents a long time (several minutes) tail. Then, the writing process usually lasts for a few seconds (depending also on the laser power and PMA4 film thickness), while the erasing one lasts for about a couple of minutes.

The optical spectra (transmittance and near-normal incidence reflectance spectra) were collected using setups based on optical fiber coupled with an Avantes 2048 XL spectrometer (200–1100 nm, resolution 1.4 nm), an Ocean Optics Jazz compact modular spectrometer (350–550 nm and 530–880 nm, 0.5 nm resolution) or with an Arcoptics FT-interferometer (900–2600 nm, resolution 8 cm<sup>-1</sup>). For the photomodulation measurements the highest resolution spectrometer was used. The light source was a combined deuterium—halogen lamp Micropak DH2000BAL. A Glan-Taylor polarizer was used to polarize light either parallel (LP, like polarized) or perpendicular (ULP, un-like polarized) to the one of the writing laser.

The morphological characterization of PMA4 thin films was performed by a commercial Nanosurf Atomic Force Microscope (AFM). Surface polymer images have been acquired in three different states: on the as-spun film, after writing and after erasing. The thickness of PMA4 film was measured by AFM in the three different states. The film was mechanically scratched to remove the polymer from the underlying fused silica substrate (see for instance Figure SI3a). Afterwards, AFM images were acquired along the step. Download English Version:

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