

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/252132198>

Realization of submicrometer structures by a confocal system on azopolymer films containing photoluminescent chromophores

ARTICLE *in* JOURNAL OF APPLIED PHYSICS · APRIL 2010

Impact Factor: 2.18 · DOI: 10.1063/1.3382945

CITATIONS

9

READS

22

7 AUTHORS, INCLUDING:



A. Ambrosio

Università di Pisa

25 PUBLICATIONS 99 CITATIONS

SEE PROFILE



Antonio Carella

University of Naples Federico II

47 PUBLICATIONS 430 CITATIONS

SEE PROFILE



Fabio Borbone

University of Naples Federico II

38 PUBLICATIONS 277 CITATIONS

SEE PROFILE



Antonio Roviello

University of Naples Federico II

140 PUBLICATIONS 1,779 CITATIONS

SEE PROFILE

Realization of submicrometer structures by a confocal system on azopolymer films containing photoluminescent chromophores

A. Ambrosio,^{1,a)} A. Camposeo,² A. Carella,³ F. Borbone,³ D. Pisignano,^{2,4} A. Roviello,³ and P. Maddalena¹

¹CNR-SPIN Napoli and Dipartimento di Scienze Fisiche, Università degli Studi Federico II, Complesso Universitario di Monte Sant'Angelo, Via Cintia, I-80126, Napoli, Italy

²NNL, CNR-Istituto Nanoscienze, Università del Salento, via Arnesano, I-73100, Lecce, Italy

³Dipartimento di Chimica, Università degli Studi Federico II, Complesso Universitario di Monte Sant'Angelo, Via Cintia, I-80126, Napoli, Italy

⁴Scuola Superiore ISUFI, Università del Salento, via Arnesano, I-73100, Lecce, Italy

(Received 27 July 2009; accepted 8 March 2010; published online 29 April 2010)

The mass migration phenomenon occurring on the free surface of azobenzene-containing polymers illuminated by light of appropriate wavelength is employed to pattern polymeric films constituted by an azopolymer doped with photoluminescent chromophore. Different topographical features are obtained by adjusting the laser scanning parameters, in particular the laser polarization direction. A detailed microscopic analysis of the patterned samples, based on atomic force microscopy and spectral confocal imaging, evidences the photobleaching of the emitting chromophore in the exposed regions, whereas the emitting features of the chromophore are preserved by the mass migration process. Our results are important for the design of nanostructured light emitting photonic devices based on azopolymers. © 2010 American Institute of Physics. [doi:10.1063/1.3382945]

I. INTRODUCTION

In 1995 Kim *et al.*^{1,2} first observed the change in the morphology of the surface of an azobenzene-containing polymer film under illumination. They were able to draw a topographical grating on the film surface by exposure to the interference pattern of two laser beams. Trenches were formed in the light intensity maxima whereas protrusions appeared at the edges due to material displacement. The phenomenon of mass migration (material displacement) observed on the free surface of azopolymers films has its origin in the trans-cis-trans isomerisation of the azobenzene moieties, induced by light absorption, and subsequent molecular orientation perpendicularly to the light polarization direction. The latter effect leads also to the local variation in the refractive index of the polymer within the illuminated region.³ After these first reports, mass migration has been exploited to draw topographical gratings on the free surface of azobenzene-containing polymers with diffraction efficiencies up to 40%.^{4,5} Topographical structures have been drawn involving up to 50% of the film thickness.⁶ After writing, light-induced structures are stable for months and can be erased either by heating the sample above the glass transition temperature or by exposure to a circularly polarized laser beam that alters any preconstituted orientation. The possibility of using circularly polarized light to erase previously drawn structures shows that the appearance of trenches under illumination is not due to light-induced permanent modifications, whose structures should be not light-erasable.⁷ Furthermore, the sample volume has been shown to remain unaltered during the lithography process.⁸ In the most recent demonstrated applications, the length variation in azomoi-

eties in turning from trans-to cis-forms has been even exploited in some configurations to apply mechanical forces in light-switched devices.^{9,10} In the experiments, the light used to induce mass migration in azopolymers is typically in the UV-visible spectral region although, very recently, two-photon activated mass migration has been achieved by means of near-IR femtosecond laser pulses.^{11,12}

The possibility of fully-optical structuring of azopolymer films surface has recently attracted further interest for its potential application in optoelectronics. For instance, Ubukata *et al.*¹³ have reported on the fabrication of a double-layered distributed feedback (DFB) laser based on a diffractive element constituted by a one-dimensionally structured azopolymer, obtained by exposing to the interference pattern of two visible laser beams from an Argon ions laser. The authors have observed lasing emission by optically pumping the devices.¹³ Furthermore, they have shown that the DFB structure can be erased by illuminating the sample with a circularly polarized light beam. Reinke *et al.*,¹⁴ have reported on a DFB-based organic light emitting diode (OLED) with improved light out-coupling. In their device the emitting layer, 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (Alq3:DCM), was evaporated on a prepatterned layer of a low molecular weight azoglass.

In fact, mixing active compounds with azobenzene molecules or polymers can represent a strategic way for obtaining systems that combine patterning capability (through the azobenzene photoisomerization) with light emission. In general, blending different organic molecules, polymers or inorganic particles can lead to improve the performance of resulting materials and devices, such as for broadly tunable films¹⁵ and OLEDs,¹⁶ solar cells with enhanced power conversion efficiencies,¹⁷ low threshold organic-based

^{a)}Electronic mail: antonio.ambrosio@na.infn.it.

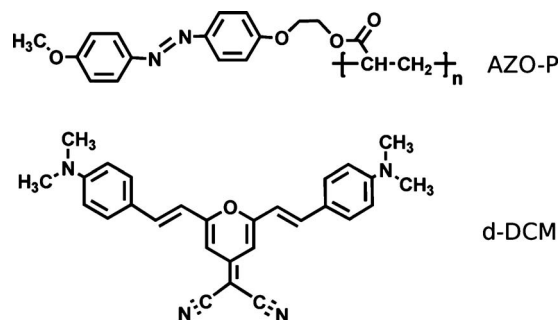


FIG. 1. Molecular structure of the azopolymer and of the photoluminescent d-DCM chromophore.

lasers,^{18,19} and low loss waveguides.²⁰ In this framework, the exploitation of azo-based light emitting blends for the fabrication of optoelectronic devices needs first an in-depth investigation of the microscopic properties of the mixed compounds and of the effects of the photoisomerization and, consequently, mass-migration on the emission. In fact, the latter can be in principle significantly influenced by the presence of a guest molecule. In this paper we report on the optical patterning of an azopolymer containing a photoluminescent chromophore and the investigation of the photoluminescence (PL) of the structured regions by means of confocal spectral imaging. Our results show the possibility to pattern the blends by means of a laser scanning technique, thus realizing photoluminescent features whose shapes and spatial distribution can be arranged by exploiting the light-polarization dependence of the mass migration process.

II. EXPERIMENTAL

The structure of the azopolymer used for this investigation is shown in Fig. 1. The azomolecule is synthesized following a method reported in literature.²¹ Namely, 4-hydroxyethoxy-4'-methoxyphenylazobenzene is reacted with acryloyl chloride to obtain the corresponding 4-acryloyloxyethoxy-4'-methoxyphenylazobenzene (AZO-A). Afterwards, the homopolymer of AZO-A (AZO-P) is synthesized as follows: 1.00 g of AZO-A was dissolved in 4 ml dry N,N-dimethylformamide and 2 wt % AIBN was added as initiator. The solution was degassed by 3 freeze-thaw cycles and the polymerization was carried out at 70 °C for 48 h under vacuum. The polymer was precipitated in 200 ml of methanol, filtered and purified by dissolving in chloroform and reprecipitating in hexane several times. The samples were prepared as thin films on glass slides by spin coating a solution obtained by dissolving 70 mg of the polymer AZO-P and 30 mg of 4-(dicyanomethylene)-2,6-bis-(p-dimethylamino-styryl)-4H-pyran (d-DCM) (Ref. 22) chromophore (molecular structure in Fig. 1) in 1 ml of 1,1,2,2-tetrachloroethane. The resulting films contain 30 wt % of the chromophore with respect to the polymer matrix. The typical resulting thickness of the azopolymer films is of a few hundreds of nanometers.

The absorption spectrum of the samples, shown in Fig. 2, is obtained by an UV-Visible Near-IR spectrometer. The peak around 348 nm is attributed to the azomoiety, that have a wide absorption spectrum in the UV/visible region

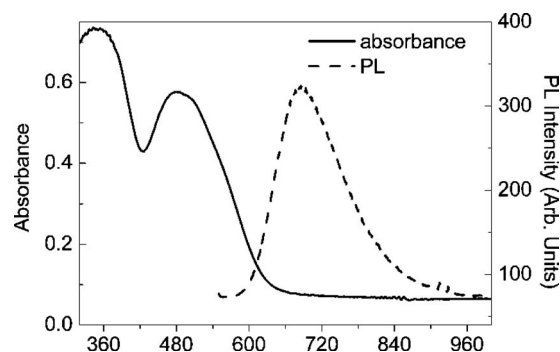


FIG. 2. Absorbance (continuous line and left vertical scale) and PL (dashed line and right vertical scale) spectra of the chromophore-polymer films.

due to π - π^* and n - π^* transitions related to the molecules isomerization. In the case of our polymer, the spectrum due to azomoiety isomerization overlaps with the absorption band of the d-DCM chromophore, peaked at around 483 nm. The emission lines of an Argon ions laser peaked at 488 nm (writing wavelength) and 514.5 nm (reading wavelength) are exploited to drive the mass migration in the azopolymer and to excite the d-DCM emission, respectively. The PL spectrum of our blends is shown in Fig. 2, exhibiting a maximum around 685 nm with a full width at half maximum of about 125 nm.

The experimental setup used for our investigation is constituted by an inverted optical microscope equipped with a 1.3 numerical aperture (NA) 100 \times microscope objective, oil immersed, and infinite corrected. The light beam from the Argon laser, both at 488 and at 514.5 nm, is coupled to the objective and focused into a diffraction-limited spot (linear dimensions of about half the laser wavelength). The sample is hosted on a piezoelectric scanner capable of nanometric movements within a full-scan range area of 30 \times 30 μ m². Both surface patterning and spectral imaging are obtained by scanning the sample while retaining the laser beam focus fixed.

The same setup is used for confocal imaging of the sample PL, excited by a wavelength of 514.5 nm. The light from the sample (emitted and/or scattered) is collected by means of the same objective and sent to a spectrograph equipped with a cooled charge coupled device camera for spectral analysis. The sample light hence results into a collimated weak beam that is coupled to the entrance slit of the spectrograph by means of a 19 mm focal-length lens. This allows us to reduce the monochromator slit aperture to a few tens of micrometers, resulting into a twofold effect. On one hand, this configuration allows to properly exploit the spectral resolution of the spectrograph (a fraction of nanometers). On the other hand, the entrance aperture, operating as the pinhole of a confocal system, enables the spatial filtering of the collected light, thus contributing to decrease the collection sample volume. The possibility, during confocal imaging, of collecting the whole spectrum in correspondence of each of the points of the scanned area on the sample, constitutes a characteristic feature of our setup. By this way it is possible to avoid inserting band-pass optical filters into the collected light path in order to select the spectral range to

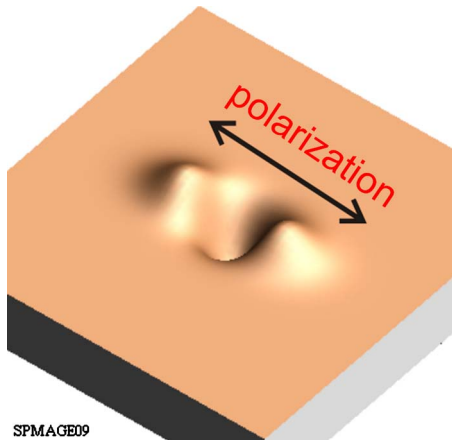


FIG. 3. (Color online) Sketch of the feature obtained illuminating an azopolymer by a focused, linearly polarized laser beam. The mass displacement occurs along the polarization direction of the injected light (double-headed arrow).

analyze. The collected spectrum includes both light scattered from the sample at the laser excitation wavelength and the PL light due to chromophore emission. Images of the scanned sample area in specific wavelengths ranges are then obtained by means of proper data processing.

The topographical investigation of the exposed structures is performed by an atomic force microscope (AFM, Multimode Veeco) operating in tapping-mode. Both confocal and AFM images are then analyzed using a free software provided by Nanotec Electrónica S.L.²³

III. RESULTS AND DISCUSSION

According to the models describing the mass migration phenomenon as due to a light gradient force moving material from a small polymer volume, for a cylindrical symmetry light distribution around the propagation axis, like that of our focused Gaussian laser beam, the mass migration occurs in the direction of the light polarization.⁷ In this case, the dependence of the driving force \vec{f} from the illuminating electromagnetic field can be, in fact, synthesized in the relation:

$$\vec{f} \propto [\vec{P} \cdot \vec{\nabla}] \vec{E}, \quad (1)$$

where \vec{E} is the electric field and \vec{P} is the local polarizability of the sample. The mass migration occurs along those directions where the light polarization has a nonzero component along the illuminating light gradient. Although this is not the only proposed model (for a review see for example, Ref. 24), its main features well apply to our experimental results. Upon illuminating the polymer surface by a focused light spot, the material displacement occurs in the direction of the linear polarization of the light injected into the microscope objective. The result is thus a track with two lateral bumps along the light polarization direction, as sketched in Fig. 3.

The light polarization dependence of mass migration can be exploited to accomplish different distributions of surface features while keeping unaltered the experimental configuration. An example is shown in Figs. 4 and 5. Figure 4 displays the topography and the cross-section profile, respectively, of five adjacent lines, spaced by 1 μm , written by moving the

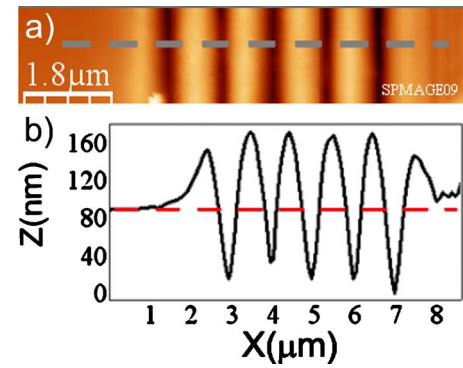


FIG. 4. (Color online) (a) AFM image of trenches obtained moving the sample orthogonally to the light polarization direction, and corresponding profile (b) along the gray dotted line in (a). The light power of the 488 nm writing beam is of 26 μW at the plane of the microscope objective aperture.

sample perpendicularly to the light polarization direction. Each line is a trench, about 480 nm wide, characterized by the accumulation of material at the edges. It is worth noting the overall volume conservation in the written area, a fingerprint of mass migration phenomenon that is clearly appreciable by comparing the profile above and below the red dotted line representing the level of the unaltered polymer surface in Fig. 4.

Moving the sample along the polarization direction, without changing other exposure parameter, results in different structures, such as the four lines spaced by 1 μm shown in Fig. 5. For this configuration of the scanning direction with respect to the laser polarization, the features are bumps whose lateral size is comparable to the linear dimensions of the diffraction-limited focused laser spot (about 200 nm). These results evidence that the light-driven mass migration process is not remarkably affected by the dispersed emitting chromophore, allowing photopatterning of the light emitting samples with submicrometer resolution.

Figure 6 shows a small grating constituted by 7 lines (28 μm long and spaced by 2 μm), realized by moving the sample perpendicularly to the light polarization direction. These features exhibit a larger width than those in Figs. 4 and 5, since a 40 \times objective (NA=0.5) is used for this experiment. The cross-sectional profile evidences the accumulation of material between adjacent trenches [Fig. 6(c)]. The

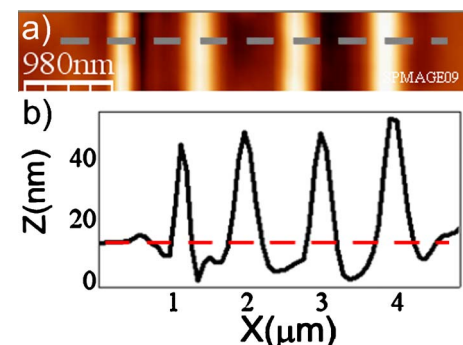


FIG. 5. (Color online) (a) AFM image of lines obtained by moving the sample along the light polarization direction, and corresponding profile (b) along the gray dotted line in (a). The light power of the 488 nm writing beam is of 26 μW at the plane of the microscope objective aperture.

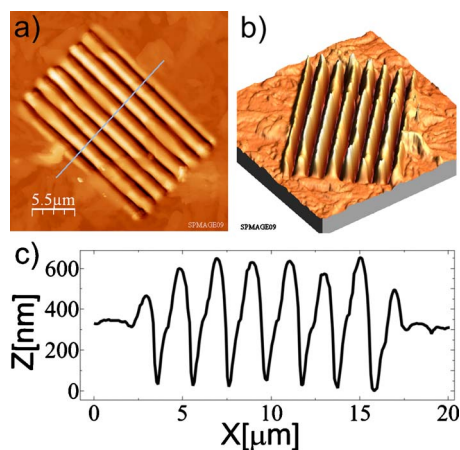


FIG. 6. (Color online) Two- (a) and three-dimensional (b) topographical images of a patterned micrograting and corresponding profile (c) along the line in (a).

central lines, in fact, are characterized by a height almost double with respect to the lateral ones, an effect that can be easily reduced by exposure time scaling. Recently, we demonstrated the possibility to pattern areas as large as $1.2 \times 0.5 \text{ cm}^2$ by a similar laser scanning technique.¹²

Concomitantly to mass migration, the high photon fluxes (of the order of hundreds of W/cm^2), needed to spatially drive the azocomponent, lead to PL photobleaching due to damages occurring into the chromophore molecules. This effect is shown in Fig. 7, where we display PL spectra of the d-DCM chromophore collected at fixed time intervals (75 s), while keeping the irradiation parameters constant. The PL peak value decreases by about 60% after 75 s and by more than 80% after 150 s.

The photobleaching, together with the local change of the dielectric properties within the exposed areas due to azobenzene molecular orientation, allows the confocal optical imaging of the patterned features with submicrometer resolution. Figures 8(a) and 8(b) show two confocal micrographs of 26 μm long lines, spaced by 13 μm (the moving direction during the writing process has been parallel to the light polarization direction). Figure 8(a) obtained by integrating the collected signal with wavelength from 480 to 550 nm, shows the intensity of the light back-scattered by the sample. The written lines appear brighter than the unexposed polymer. The contrast mechanism that permits to visualize

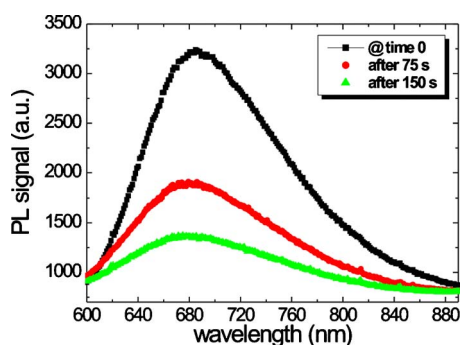


FIG. 7. (Color online) Decrease in the PL emission of the d-DCM during irradiation by the writing laser beam. The excitation is at 514.5 nm and the value of the power at the objective aperture plane is of 6 μW .

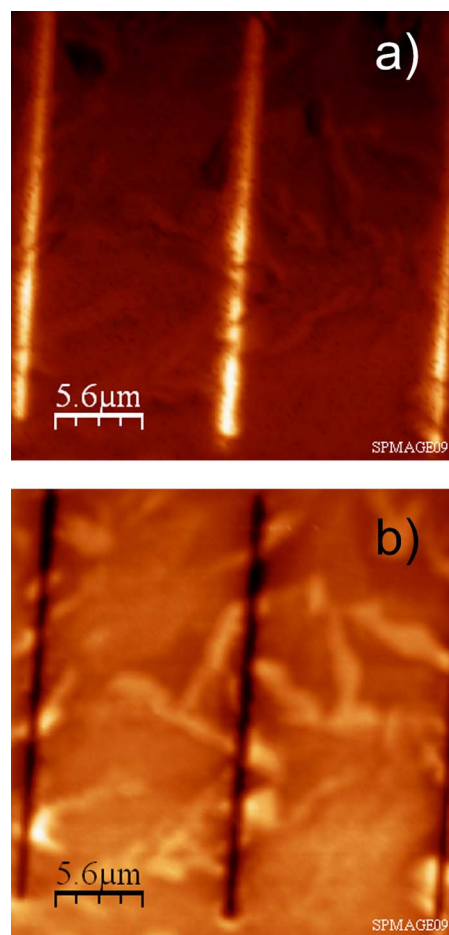


FIG. 8. (Color online) Spectral confocal images of lines obtained moving the sample along the light polarization direction. (a): spectral image obtained by integrating the PL signal from 480 to 550 nm, thus including the wavelength of the excitation beam. (b): spectral image of the same lines obtained by integrating from 670 to 730 nm.

the pattern is twofold, since on one hand the surface topographical modification results into a different optical coupling of scattered light into the collection light path. This can then result in higher signal values corresponding to the written features. Furthermore, the isomerization cycles originating mass migration lead also to the local change of the refractive index of the material. This phenomenon may affect the signal collection from exposed features by locally changing the sample reflectivity and/or absorption, thus, contributing to enhance the imaging contrast at the wavelength of illuminating light.

Figure 8(b) is instead, obtained by integrating signal from 670–730 nm, a spectral range overlapping with the PL emission from d-DCM. The PL intensity is weaker in the exposed regions, where photobleaching of the emissive chromophore occurs. This effect has to be taken carefully into account for the design of a photonic structure. For instance, it can be exploited for achieving concomitant refractive index and gain modulation upon embedding suitable active molecules in azopolymers, thus realizing DFB laser devices with sharp emission linewidth. Finally, it is worth noting that, although the writing/reading wavelengths are quite close each other, the reading process by means of PL excitation with light at 514.5 nm does not modify the sample mor-

phology, allowing the exploitation of the emission of the dispersed emitting chromophore as reading mechanism of previously written features in azopolymers.

IV. CONCLUSION

In this work we demonstrate the patterning of an azopolymer containing a dispersed chromophore by exploiting mass migration originated by azomoieties photoisomerization. The PL properties of the textured samples are analyzed by a setup allowing confocal spectral imaging of the polymeric films. The polarization dependence of the mass migration is exploited to realize different extended structures, trenches or bumps, by changing the mutual orientation of the light polarization direction with respect to the sample scanning direction. This permits to keep the light beam always in axis and to fix the alignment of the optical elements of the setup, which is strategic for consecutive writing-imaging.

We point out that, while azopolymers have been, so far, mainly textured by holographic techniques, leading to the fabrication of periodic structures, patterning by polarized laser scanning allows the realization of arbitrary shapes, with submicrometer resolution. The confocal spectral analysis evidences that during the writing process only the exposed areas are photobleached. This result can be applied in designing plastic optoelectronic devices containing light emitting and/or gain molecules. The advantage of this approach stands in the possibility of realizing devices, based on a single polymeric layer, by a one-step, purely-optical lithographic process, instead of using sacrificial layers and/or adding further photoluminescent layers.

ACKNOWLEDGMENTS

A.A. is grateful to the European Collaborative Project “S-five” for financial support. A.C. and D.P. acknowledge the support from the Italian Minister of University and Research through the FIRB Contract No. RBIP06SH3W and from the Apulia Strategic Project PS_144.

- ¹D. Y. Kim, S. K. Tripathy, L. Li, and J. Kumar, *Appl. Phys. Lett.* **66**, 1166 (1995).
- ²D. Y. Kim, L. Li, X. L. Jiang, V. Shivshankar, J. Kumar, and S. K. Tripathy, *Macromolecules* **28**, 8835 (1995).
- ³V. Cimrová, D. Neher, R. Hildebrandt, M. Hegelich, A. von der Lieth, G. Marowsky, R. Hagen, S. Kostromine, and T. Bieringer, *Appl. Phys. Lett.* **81**, 1228 (2002).
- ⁴X. Jiang, L. Li, J. Kumar, D. Y. Kim, V. Shivshankar, and S. K. Tripathy, *Appl. Phys. Lett.* **68**, 2618 (1996).
- ⁵C. J. Barrett, A. L. Natansohn, and P. L. Rochon, *J. Phys. Chem.* **100**, 8836 (1996).
- ⁶N. C. R. Holme, L. Nikolova, S. Hvilsted, P. H. Rasmussen, R. H. Berg, and P. S. Ramanujam, *Appl. Phys. Lett.* **74**, 519 (1999).
- ⁷P. Rochon, E. Batalla, and A. L. Natansohn, *Appl. Phys. Lett.* **66**, 136 (1995).
- ⁸S. Bian, J. M. Williams, D. Y. Kim, L. Li, S. Balasubramanian, J. Kumar, and S. K. Tripathy, *J. Appl. Phys.* **86**, 4498 (1999).
- ⁹L. V. Schäfer, E. M. Müller, H. E. Gaub, and H. Grubmüller, *Angew. Chem.* **119**, 2282 (2007).
- ¹⁰V. Ferri, M. Elbing, G. Pace, M. D. Dickey, M. Zharnikov, P. Samorì, M. Mayor, and M. A. Rampi, *Angew. Chem., Int. Ed.* **47**, 3407 (2008).
- ¹¹S. Bian, H. Ishitobi, S. Shoji, T. Hiramatsu, H.-B. Sun, Z. Sekkat, and S. Kawata, *Opt. Express* **16**, 14106 (2008).
- ¹²A. Ambrosio, E. Orabona, P. Maddalena, A. Camposeo, M. Polo, A. A. R. Neves, D. Pisignano, A. Carella, F. Borbone, and A. Roviello, *Appl. Phys. Lett.* **94**, 011115 (2009).
- ¹³T. Ubukata, T. Isoshime, and M. Hara, *Adv. Mater.* **17**, 1630 (2005).
- ¹⁴N. Reinke, T. Fuhrmann, A. Perschke, and H. Franke, *J. Lumin.* **110**, 413 (2004).
- ¹⁵A. A. R. Neves, A. Camposeo, R. Cingolani, and D. Pisignano, *Adv. Funct. Mater.* **18**, 751 (2008).
- ¹⁶G. Heliotis, P. N. Stavrinou, D. D. C. Bradley, E. Gu, C. Griffin, C. W. Jeon, and M. D. Dawson, *Appl. Phys. Lett.* **87**, 103505 (2005).
- ¹⁷S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz, and J. C. Hummelen, *Appl. Phys. Lett.* **78**, 841 (2001).
- ¹⁸V. G. Kozlov, V. Bulović, P. E. Burrows, and S. R. Forrest, *Nature (London)* **389**, 362 (1997).
- ¹⁹R. Gupta, M. Stevenson, A. Dogariu, M. D. McGehee, J. Y. Park, V. Sdranov, A. J. Heeger, and H. Wang, *Appl. Phys. Lett.* **73**, 3492 (1998).
- ²⁰A. Camposeo, E. Mele, L. Persano, D. Pisignano, and R. Cingolani, *Opt. Lett.* **31**, 1429 (2006).
- ²¹K. Sadagopan, A. S. Rekha, D. Ratna, and A. B. Samui, *J. Appl. Polym. Sci.* **104**, 3497 (2007).
- ²²L. Yang, M. Guan, Z. Bian, J. Xie, T. Chen, and C. Huang, *Thin Solid Films* **500**, 224 (2006).
- ²³I. Horcas, R. Fernández, J. M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero, and A. M. Baro, *Rev. Sci. Instrum.* **78**, 013705 (2007).
- ²⁴A. Natansohn and P. Rochon, *Chem. Rev.* **102**, 4139 (2002).