Organic Electronics 26 (2015) 476–480

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Letter

Photo-induced storage and mask-free arbitrary micro-patterning in solution-processable and simple-structured photochromic organic light-emitting diodes

Yan Qian [a,*], Xiuxia Xu [a], Wenwen Li [a], Jianyun Wang [a], Bingyan Wei [b], Qi Wei [a], Xiaohong Yan [c], Wei Hu [b], Yanqing Lu [b], Linghai Xie [a], Xinwen Zhang [a,*], Wei Huang [a,*]

[a] Key Laboratory for Organic Electronics and Information Displays & Institute of Advanced Materials (IAM), National Jiangsu Synergistic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts & Telecommunications, 9 Wenyuan Road, Nanjing 210023, China
[b] National Laboratory of Solid State Microstructures and College of Engineering and Applied Sciences, Nanjing University, Nanjing 210093, China
[c] School of Opto-Electronic Engineering, Nanjing University of Posts & Telecommunications (NUPT), 9 Wenyuan Road, Nanjing 210046, Jiangsu, China

ARTICLE INFO

Article history:
Received 12 May 2015
Received in revised form 15 July 2015
Accepted 29 July 2015

Keywords:
Photochromophores
Mask-free micro-photopatterning
Rewritable optical storage
Photochromic light-emitting devices

ABSTRACT

A photochromic diarylethene-based compound BMTA, which undergoes a reversible conversion between ring- open and closed isomers by alternating UV and visible light illumination, has been designed and synthesized. By utilizing a mask-free Digital Micro-mirror Device (DMD) micro-lithography system, arbitrary micro-photopatterning in polymer films doped with BMTA can be easily obtained with UV light writing. This recorded photo information can easily be erased by further visible light irradiation. The reversible and rewritable optical storage is based on photo-switched intermolecular energy transfer between the emissive host and the ring-closed isomer *c*-BMTA. Furthermore, the solution-processable organic light-emitting devices (OLEDs) with the single emitting layer doped with BMTA were fabricated, which exhibit rewritable memory behavior with light control. The luminescence and current density decrease significantly upon UV light irradiation, and recover by further visible light illumination. This is because the hole trapping is much facilitated in closed-ring isomer based devices, due to elevated HOMO level of *c*-BMTA. Without incorporating any cross-linking layer, the maximum luminescence and current density on/off ratios of this solution-processable and simple-structured device are 1.9×10^3 and 1.4×10^2, respectively. Arbitrary micro-photolithography of OLEDs by DMD system has also been demonstrated, which shows great prospects in large-scale production of high resolution OLED displays.

1. Introduction

Solution processable organic opto-electronic devices have attracted considerable attention due to their low cost, flexible and large-area production [1,2]. In last decades, remarkable improvements have been obtained in applications of the photochromic materials in opto-electronic devices [3–5], including organic memory diodes [6–8], photochromic light-emitting diodes [9–12], optically switchable multifunctional transistors [13–19], solar cells [20] and electrical circuits [21]. Because these photochromophores undergo a reversible photo-chemical reaction between the open and closed-ring isomers, causing the change of electrical energy levels. Correspondingly, the absorption and/or photoluminescence spectra, oxidation and reduction potentials, dipole moment, ionization potential (I_p) and carrier mobilities, alter and can reversibly switch [3,22–28]. Among these photochromophores, diarylethenes (DAEs), due to their good thermal stability, fatigue resistance, and easy monitoring by using UV–vis spectroscopy [29–33], are intriguing candidates as the stimuli-responsive materials in solution- and vacuum-processable organic opto-electronic devices [4,6–13,15–17,20,21,28,34].

In recent years, there have been attempts to fabricate memorisible organic light emitting diodes (OLEDs) by utilizing photochromic compounds as an independent light-controlled carrier switch, because the photoirradiation-induced change of I_p affects the current injection into the DAE layer [7,8,10–12]. In the open-ring isomer based device, the barrier for charge injection is large and the current injection is difficult, while in the

* Corresponding authors.
E-mail addresses: iamyqian@njupt.edu.cn (Y. Qian), iamxwzhang@njupt.edu.cn (X. Zhang), wei-huang@njupt.edu.cn (W. Huang).

http://dx.doi.org/10.1016/j.orgel.2015.07.059
1566-1199/

closed-ring isomer based device the photochromic layer exhibits an enhanced I_p, which facilities the carrier injection from the photochromophore layer to the emitting layer and enables the devices to be lightened. However, to obtain large current on/off ratio in solution-processable OLEDs, an additional cross-linking overlayer onto the PEDOT: PSS layer is generally required [7,11,12], which results in less photo absorption and thus decreased photo-isomerization efficiency. Besides, these cross-linking materials need numerous synthesis and further comprehensive screening efforts in later practical device performances [34]. Moreover, two additional photochromic layer and cross-linking overlayer further complicate the device structure, leading to increased fabrication cost.

In addition, the photo-reactivity of these incorporated photochromophores in OLEDs make the photo-patterning of the light-emitting devices easily available, which can find good signage applications such as warning signs, indicators, decorative light sources, advertising, and logo displays [35–37]. However, this image procedure generally demands irradiation exposure through a specific shadow mask, one-to-one custom-made according to the required graphic pattern, to illuminate the active area. That is, once a new image graphic is acquired, a new shadow mask should be newly customized accordingly. Previously, a technique for arbitrary mask-free micro-patterning in liquid crystal alignment layer and local polarization control for light wavefront have been proposed and implemented, by utilizing a micro-lithography system with a Digital Micro-mirror Device (DMD) [38]. The DMD, utilized as a dynamic virtual "mask", generates arbitrary patterns by individually tilting angle control of each mirror and thus supplies a low-cost mask-free method for any pattern design.

In this work, without any additional cross-linking layer, solution-processable and simple-structured photochromic OLEDs, with the single emitting layer doped with a DAE-based photochromophore, are easily fabricated and exhibit memory behavior with the maximum on/off ratios of luminescence and current density of 1.9×10^3 and 1.4×10^2, respectively. Arbitrary mask-free micro-pattering of photochromic OLEDs as well as photochromic polymer emitting films are also demonstrated by utilizing the DMD system, indicating great potentials in low-cost and high-resolution optical memory and OLED displays.

2. Experimental section

o-BMTA has been synthesized according to the previously reported method [39]. UV/Vis absorption and fluorescence spectra are performed on Shimadzu UV-3150 and Shimadzu RF-5301 spectrometer, respectively. Optical irradiation was conducted with a CEL-HXF300 xenon lamp by utilizing color filters (UV: $\lambda < 400$ nm; Vis: $\lambda > 450$ nm). The optimum device configuration in our study is indium–tin oxide (ITO)/poly(3,4-ethylenedioxythiophene)-doped poly(styrene sulfonic acid) (PEDOT:PSS)/(2-Methyl-9,10-bis(naphthalen-2-yl)anthracene (MADN): T4TB: BMTA/TPBi/LiF/Al. A thin hole injection layer of PEDOT: PSS (20 nm) was cast onto transparent conductive ITO at a spin speed of 2000 rpm. After baking at 120 °C for 15 min in an oven, a MADN layer (30 nm) doped with T4TB (1 wt%) and BMTA (1 wt‰) was spin-coated on top of the PEDOT:PSS layer from its chloroform solutions. Finally, a 20 nm electron transport layer (TPBi), LiF (0.8 nm) and Al (100 nm) were consecutively deposited by thermal evaporation in vacuum. The luminance–current–voltage characteristics of the devices were recorded using a combination of a source meter (Keithley 2602) and a luminance meter. The EL spectra were determined using a spectrophotometer (Photo ResearchPR655 SpectraScan). All the devices were characterized without encapsulation, and all the measurements were carried out in ambient atmosphere. The emission area of the devices is $4 \times 3 = 12$ mm^2.

3. Results and discussion

The photochromic compound BMTA, phenylbenzothiazole of diarylethene imide derivative, has been synthesized by condensation of 4,4-(cyclopentene-1,2-yl)-bis(5-methyl-thiophene-2-formaldehyde) and 3-(benzo[d]thiazol-2-yl)aniline (see Scheme S1 and the synthetic details in the Supporting Information). BMTA undergoes a reversible photochromic reaction between the ring-open and closed isomers (see the chemical reaction in Fig. 1a), either in solution or film, with a reversible change of their absorption spectra profiles (see Fig. 1a and Fig. S1). By irradiation with UV light (λ_{irr} = 200–400 nm, I_0 = 2.49 mw/cm^2), the open-ring isomer (*o*-BMTA) converts into the closed-ring isomer (*c*-BMTA), with the color changing from transparent into blue, accompanied by a newly emerging broad absorption band around 580–590 nm. Upon further visible light illumination ($\lambda_{irr} > 450$ nm, I_0 = 2.49 mw/cm^2), *c*-BMTA returns to *o*-BMTA, with the gradual decrease of the 580–590 nm absorption band. Meanwhile, the solution becomes transparent again.

Based on this, photo switchable hybrid T4TB/BMTA (wt%: wt% = 10:1) films can be obtained (Fig. 1b). Upon UV light irradiation, *o*-BMTA converts into *c*-BMTA, and the fluorescence of the hybrid film (peaked around 550 nm) is efficiently quenched, with the fluorescence on/off ratio of 8. Subsequently, by visible light illumination, the emission intensity recovers (Fig. S2). This results from the photo-switched intermolecular energy transfer. The yellow emitting material T4TB obtained in our previous work [40] was chosen as the emissive energy donor, due to good spectral overlap between its emission (peaked around 540 nm) and the newly appeared absorption of *c*-BMTA (peaked around 580–590 nm) (see Fig. 1a), which enables efficient energy transfer (only occurring between the T4TB donor and the acceptor of the closed-ring isomer *c*-BMTA) and thus reversible tuning of emission intensity by alternating UV and visible light illumination.

Thus, by using DMD system, mask-free arbitrary high-contrast micro-images and erasable/rewritable optical information storage have been realized in PVK/T4TB (20 wt%)/*o*-BMTA (4 wt%)/B(C_6F_5)$_3$ (46 wt%) hybrid polymer film (see Fig. 2). Here, PVK is applied as the polymer host to improve the solution processability and B(C_6F_5)$_3$ is utilized to cause change of the emission profile with a newly emerging blue fine-structured emission (see Fig. S3a) possibly due to an intermolecular reaction [41] to enhance the imaging contrast (see Fig. S3b). In the DMD computer exposure system [42], the 365 nm UV light can irradiate only through the white regions within the input black-and-white pictures, leading to an emission turn-off in the corresponding area in the film which is caused by the UV-induced energy transfer as discussed above. By utilizing various input electronic pictures in this DMD system, arbitrary complex micro-images can be easily obtained without any shadow mask (Fig. 2). As seen from these images, the resolution can reach 2–3 μm. It is noteworthy that these recorded images can easily be erased upon subsequent visible light irradiation ($\lambda_{irr} > 450$ nm), and a new micro-patterning can be written by UV light irradiation (not shown). The writing and erasing prossesses are reversible and repeatable, indicating that these hybrid films are good candidates for application as rewritable high-density optical information storage.

Enlightened by these results, we further expected that the microlithography can also be applied in date storage of photochromic OLEDs. The solution-processable devices were fabricated with configuration of ITO/PEDOT: PSS/MADN: T4TB (1 wt%): *o*-BMTA (1 wt‰)/TPBi/LiF/Al (Fig. 3a). Here, MADN doped