

Photoresponsive Colorimetric Change of a *t*-BOC-Polyaniline/Spiropyran Film Based on Conducting Pattern

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Among the polymers, polyaniline (PANI) is a unique conjugated polymer in that it can be tailored for specific applications through a non-redox acid/base doping process.¹⁻³ Unfortunately, its poor solubility in most common organic solvents has limited the industrial application of PANI because of its high aromatic nature, strong inter-chain hydrogen bonding, and high charge delocalization. The patterning of conjugated polymers on various substrates was achieved by using a variety of techniques, such as the deposition by scanning electrochemical microscopy,⁴ screen printing,⁵ micro-molding in capillaries (MIMIC),⁶ inkjet printing,⁷ photo-chemical patterning by photolithography,⁸ and microcontact printing through self-assembly monolayer (SAM).⁹ Recently, we reported micro-scale conducting pattern using the organic soluble PANI substituted with acid-labile *tert*-butyloxycarbonyl (*t*-BOC) group on the glass substrate and reversible photochromism between spiropyran (SP) and fluorecein molecules by photolithography.¹⁰⁻¹⁴ If this light-regulated reversible uptake and release of protons to SP is combined with the *t*-BOC-PANI, then the colorimetric change could be controlled by additional stimuli. We report here for the first time the reversible colorimetric change on patterned film of *t*-BOC-PANI/SP by various stimuli such as photo, thermal, acid/base.

Result and Discussion

To develop for producing patterned images, we tested the possibility of generating micro-patterned images based on the photochromism of *t*-BOC-PANI/SP system containing triphenylsulfonium triflate (TPSOTf, 5 wt %) as a photo acid generator.

The solution of SP and *t*-BOC-PANI (1:1 molar ratio) was spin-cast to form 1 μm thick films on a glass plate. The film of dark red color was exposed to UV light with 10 mW/cm² for 1 min through a photomask without PEB (post-exposure bake) process; noted that *t*-BOC group of PANI was not completely removed in this process because the deprotection of *t*-BOC group requires high thermal stress (> 150 °C). Upon additional UV irradiation for one more min, the ME form change into MEH by proton transfer derived from photo acid generator to make an optical microstructure patterning. Thus, the dark red color film before irradiation was changed into bright green color pattern derived from MEH form and *t*-BOC-PANI at UV irradiated portions as

shown in Figure 1 ((a) and (b)). When the film is irradiated with visible light or thermal treatment (50 for 2 min), MEH form completely disappears to SP form switching back to the original color. In this result, this reversible colorimetric change (writing and erasing) is ascribed to sequential chemical reactions of the C-O bond cleavage and C-O bond reformation of SP without deprotecting pathway of *t*-BOC group of PANI. This localized photochromic process was confirmed by changes in the UV spectra. Figure 2 shows them before (black line of left) and after different doses of UV exposure. The unexposed film displays two absorption bands at 320 and 585 nm, characteristic of undoped EB form of PANI. Upon exposure, the exciton band of 585 nm decreases and new peak appearing at 800 nm with increasing exposure dose. This peak is usually assigned to polaron band originated from the conducting, *i.e.*, doped, ES form. Simultaneously, new absorption band of the MEH form appeared around 440 nm (red line of left (Fig. 2)). Thus, colorless SP undergoes the photo-induced ring-opening reaction under UV irradiation to yield its phenoxide of the zwitterionic ME form (around 580 nm) and then ME form can quickly change to MEH form by protonation derived from a photo acid generator. We think that the resulting bright green color was derived from interactions between PANI-ES (dark green) and MEH form (yellow color). To obtain the fully protonated PANI-ES and MEH form, upon additional higher thermal stress (a post-exposure bake at 150 for 2 min) to the patterned film, the bright green color portion of the patterned film was also changed into original color (dark green). In addition, stronger

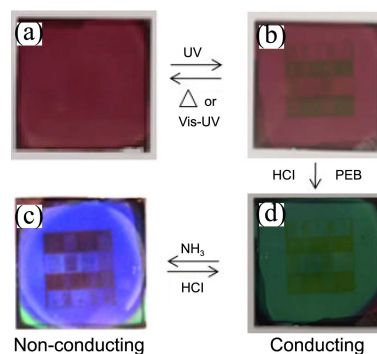


Figure 1. Photographs of SP-embedded *t*-BOC-PANI film before (a), after (b) photomasked UV irradiation, after HCl treatment/PEB of B (c), and after NH₃ treatment of C (d).

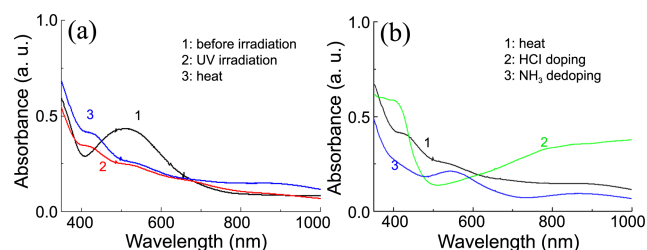


Figure 2. Absorption spectra of the thin film from the mixture of SP/*t*-BOC-PANI containing PAG on quartz after UV irradiation and heat treatment (left), after HCl doping and NH₃ dedoping (right).

and slightly blue shifted absorption bands appear at around 450 and 900 nm as shown in Figure 2 (blue line of left). This is consistent with the increasing absorption bands of MEH form and polaron band of PANI-ES, respectively. Thus, these results indicate that proton transfer takes place from the proton source derived by *t*-BOC to the ME form.

To obtain higher conductive film, the photo-generated film (Fig. 1(b)) was doped with HCl gas for 1 min to give the fully deprotected and doped PANI-ES and MEH. The dark red color at un-irradiated portions and green color at irradiated portions were changed into dark green color of characteristic conducting form by consecutive deprotection and doping process as shown in Figure 1(c). Upon exposure with HCl, the exciton band of 580 nm of PANI was more significantly decreased and new peak appearing at 800 nm strongly increase with exposure time (green line of Fig. 2(right)). As mentioned previously, these peaks are usually assigned to polaron bands originated from the conducting, *i.e.*, doped, emeraldine salts. Thus, more highly doped conducting film can be produced by HCl gas treatment. Upon exposure with NH₃ for regulation of conductivity, the green color of PANI-ES/MEH stage was rapidly changed into blue color of PANI-EB/ME stage (dedoped form). Contrastively, the irradiated portions of green color (PANI-ES/MEH stage) were quickly changed into the characteristic dark pink color due to the formation of the PANI-EB (blue)/ME (pink) in the early stage. This means that selective photoregulation of conductivity of the corresponding film by selective photo-irradiation could be possible. In the corresponding UV spectrum, the absorption band of 580 nm for formation of PANI-EB form was increased and new peak disappearing at around 800 nm slightly decreases with NH₃ exposure time

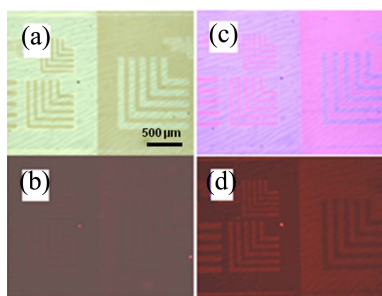


Figure 3. Optical and fluorescence microscope images of the photo-irradiated SP/*t*-BOC-PANI film obtained after HCl treatment ((a) and (b)) and after NH₃ treatment ((c) and (d)).

(blue line of Fig. 2(right)). These absorption bands are usually assigned to the non-conducting, *i.e.*, dedoped, emeraldine base. Consequently, the colorimetric and conducting changes can be controlled by additional stimuli such as acid, base, and photo-irradiation. To investigate the difference of fluorescence properties of PANI-ES/MEH and PANI-EB/ME stage, Figure 3 shows the corresponding optical and fluorescence microscopic images of the PANI-ES/MEH ((c) of Fig. 3) and PANI-EB/ME stage ((d) of Fig. 3), respectively. As an expected, very weak fluorescence intensity of PANI-ES/MEH form can unclearly be seen due to the acidic media (HCl). Contrastively, more strong fluorescence pattern of PANI-EB/ME can clearly be seen due to the basic media (NH₃).

Conclusion

In summary, we report here reversible proton transfer process between a three state (SP, ME, MEH) molecular switch and regulation of conductivity based on photochromic SP and conducting precursor *t*-BOC-PANI film. The colorimetric change of the film can be controlled by selective irradiation. Such conducting mixture, based on organic soluble *t*-BOC-PANI and photochromic material, may find potential application in the field of information recording and processing.

Experimental Section

Materials and Instruments. *t*-BOC-PANI was synthesized according to the procedure in ref. 10. UV-vis spectra were examined on an Agilent 8453 spectrophotometer. Optical images were observed with an Olympus optical and fluorescence microscope (BX51W/DP70).

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References

1. Tasis, D.; Tagmatarchis, N.; Bianco, A.; Prato, M. *Chem. Rev.* **2006**, *106*, 1105.
2. Allen, B. L.; Kichambare, P. D.; Star, A. *Adv. Mater.* **2007**, *19*, 1439.
3. Keren, K.; Berman, R. S.; Buchstab, E.; Sivan, U.; Braun, E. *Science* **2003**, *302*, 1380.
4. Kranz, C.; Ludwig, M.; Gaub, H. E.; Schuhmann, W. *Adv. Mater.* **1995**, *7*, 38.
5. Garnier, F.; Hajlaoui, R.; Yassar, A.; Srivastava, P. *Science* **1994**, *265*, 1684.
6. Beh, W. S.; Kim, I. T.; Qin, D.; Xia, Y. N.; Whitesides, G. M. *Adv. Mater.* **1999**, *11*, 1038.
7. Chang, S. C.; Bharathan, J.; Yang, Y.; Helgeson, R.; Wudl, F.; Ramey, M. B.; Reynolds, J. R. *Appl. Phys. Lett.* **1998**, *73*, 2561.
8. Drury, C. J.; Mutsaers, C. M. J.; Hart, C. M.; Matters, M.; de Leeuw, D. M. *Appl. Phys. Lett.* **1998**, *73*, 108.
9. Bjornholm, T.; Greve, D. R.; Reitzel, N.; Hassenkam, T.; Kjaer, K.; Howes, P. B.; Larsen, N. B.; Bogelund, J.; Jayaraman, M.; Ewbank, P. C.; McCullough, R. D. *J. Am. Chem. Soc.* **1998**, *120*, 7643.
10. Lee, C. W.; Seo, Y. H.; Lee, S. H. *Macromolecules* **2004**, *37*, 4070.
11. Lee, C. W.; Kim, Y. B.; Lee, S. H. *Macromolecules* **2005**, *17*, 366.
12. Lee, C. W.; Song, Y. H.; Ryu, K. S.; Chi, K.-W. *Chem. Commun.* **2009**, 6282.
13. Chi, K.-W.; Hwang, H. Y.; Jin, S. H.; Kim, J.-M.; Lee, C. W. *Chem. Commun.* **2009**, 1647.
14. Chi, K.-W.; Hwang, H. Y.; Kim, J.-M.; Yoon, U. C.; Lee, C. W. *Bull. Korean Chem. Soc.* **2009**, *30*, 1245.