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Photoswitching electrospun nanofiber based on a spironaphthoxazine–isophorone-based fluorescent dye system

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ABSTRACT

A bistable photoswitching photochromic spironaphthoxazine/isophorone-based fluorescent dye system was investigated. The photoregulated fluorescence switching behavior of a spironaphthoxazine/isophorone dye loaded poly(methyl methacrylate) nanofiber was also studied. Reversible modulation of fluorescence intensity was achieved using alternating irradiation with UV and visible light. The erasable and rewritable optical storage based on spironaphthoxazine/isophorone dye loaded poly(methyl methacrylate) nanofiber has been developed.

1. Introduction

Recently, photochromic materials have attracted attention because of their importance and potential application in the area of optics which includes optical switching, display, optical memory and non-linear optical devices [1–11]. Spironaphthoxazines (SPO) are photochromic compounds analogous to spiropyrans. These two classes of compounds are similar in many respects. However, the replacement of the benzopyran ring by a naphthoxazine ring results in SPO having the advantage of greatly improved resistance to prolonged UV irradiation, which confers much greater commercial importance upon them [12]. On UV irradiation the C–O bond of the colorless SPO is cleaved and the colored merocyanine form is obtained. Thus, the interconversion of spiro(SP)-merocyanine(MC) systems, SP-MC, has been extensively investigated due to their potential applications in molecular devices and uses in biotechnology [13]. Photochromism studies of SPO in polymer matrices [14], liquid crystal polymers containing SPO as mesophases [15], and SPO grafted poly [2-ethynyl-pyridinum bromide] to form an ionic conjugated polymer [16], poly [*N*, *N*-[(3-dimethylamino) propyl] methacrylamide [17] and other synthetic polymers [18,19] have recently been developed. Our group recently reported the spectral switching properties of SPO derivatives [20–23]. The electrospinning technique allows for rapid and cost-effective fabrication of fibrous polymer membranes with a large surface area [24]. The method can be applied to synthetic and natural polymers, polymer alloys, and polymers loaded with chromophores, nanoparticles, or active agents, as well as to metals and ceramics. The isophorone-based fluorescent dye with an electron donor–π–acceptor (D–π–A) molecular structure showed interesting optical characteristics, which have been intensively developed for applications using as electroluminescent (EL) materials [25,26], dye-sensitized solar cells (DSSCs) [27,28], and chemosensors [29,30]. Herein we report the photostimulated spectral switching properties of an electrospun nanofiber containing both photoswitchable SPO and isophorone-based fluorescent dye in poly(methyl methacrylate) (PMMA).

2. Experimental

SPO and D–π–A type isophorone dye, 2-(3-(4–((2-hydroxyethyl)(methyl)amino)styryl)-5,5-dimethylcyclohex-2-

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enylidene)malononitrile (vinylcyanoacetate)pyran (HDMP) were prepared using previously described procedures [30,31]. Poly (methyl methacrylate) (PMMA, $M_n = 77{,}000$, $M_w/M_n = 1.32$) polymer was purchased from Wako pure chemical industries, Ltd. The 30 wt.% of PMMA solution was prepared in *N*,*N*-Dimethyl formamide (DMF) at room temperature under magnetic stirring for a day. PMMA/SPO/HDMP blend solutions were obtained by dissolving of SPO (2×10^{-5} M) and HDMP (2×10^{-5} M) in the PMMA-DMF solution with gently stirred for 1–2 h. During electrospinning, 30 kV of high voltage power (NANONC Co., Ltd., Seoul, Korea; model NNC-60K-2 mA) was applied to the PMMA/SPO/HDMP blend solutions contained in a syringe via alligator clip attached to the syringe needle. The solution was delivered to the needle tip via syringe pump to control the solution flow rate (0.003 mL/min). Fibers were collected on an electrically grounded aluminum foil placed vertically to the needle tip. The morphology of nanofiber was examined using a JSM-6380LV scanning electron microscope (SEM) and the reflectance changes of nanofiber were investigated by CCM (Computer Color Matching, X-rite Premier 8200). UV–vis spectra were obtained using an Agilent 8457 UV–vis spectrophotometer; fluorescence spectra were measured using a Shimadzu RF-5301PC Fluorescence spectrophotometer. A high pressure mercury lamp (Ushio, SP-3-250D) was used as the UV radiation source and calibrated with a monochromator at 366 nm.

3. Results and discussion

3.1. Spectral properties of SPO and HDMP

Photochromism in SPO generally involves the UV-induced dissociation of the spiro C–O bond from the oxazine ring, to form a planar structure. This is commonly referred to as the photomerocyanine product. The photomerocyanine is usually less stable and returns to the closed form both thermally and photochemically [32]. Electronic absorption spectral changes of SPO upon UV irradiation in DMF are depicted in Fig. 1.

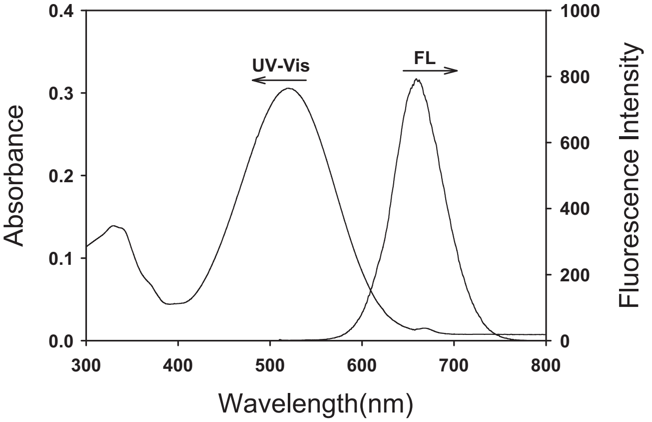

Fig. 2. Absorption and fluorescence spectra of HDMP in DMF at room temperature (2×10^{-5} molL^{-1}, excitation: 500 nm).

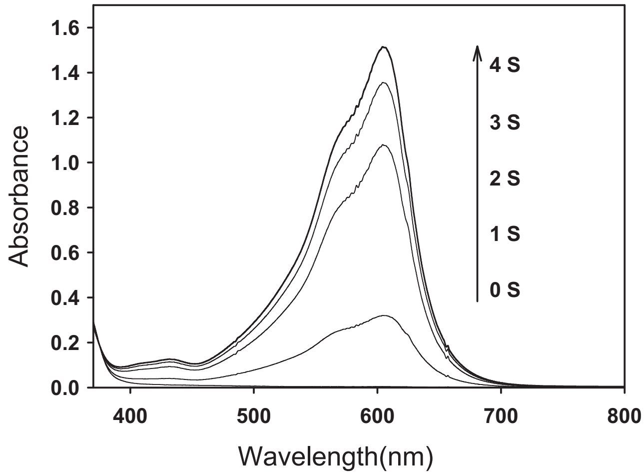

Fig. 1. Absorption spectral changes of SPO in DMF (2×10^{-5} molL^{-1}) under different irradiation time by UV light at room temperature.

The original spectral pattern is reversibly recovered within 1 s. The new band is ascribed to the generation of the open merocyanine form from the closed spiro form. Spectra measured after UV irradiation is at any time proportional to each other in the visible region, indicating that only one species is formed. This allowed the absorption to be monitored at λ_{max} of 605 nm as a function of time to obtain the thermal colour fading rate. Fig. 2 showed the absorption and fluorescence spectra of HDMP in DMF. The intramolecular charge transfer (ICT) interaction, which is from the methylamino-ethanol group to 2-enylidene-malononitrile fragment, is strongly enhanced upon excitation as evidence from the extreme bathochromic shift of the absorption and fluorescence maximum in polar solvents [30]. A large Stokes shift of 140 nm was observed, which may be caused by the strong ICT interaction of this dye molecule.

3.2. Spectral switching of SPO with HDMP

Fig. 3 showed the absorption spectral changes of SPO–HDMP in the ratio of 1:1 equiv by irradiation with UV light. Upon irradiation with UV light, a new band appeared at around 600 nm which continuously increased, depending on the irradiation time.

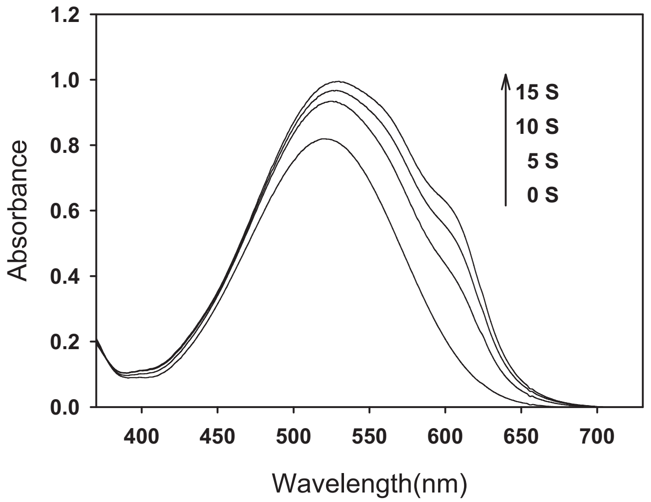

Fig. 3. Absorption changes of SPO/HDMP in DMF solution upon irradiation with UV light at room temperature (SPO: HDMP = 1:1 equiv, 2×10^{-5} molL^{-1}).

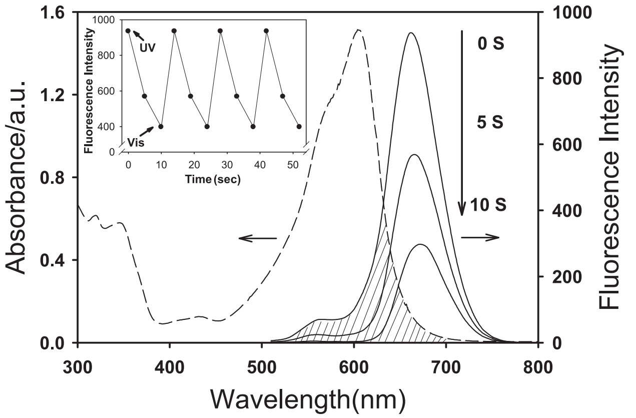

Fig. 4. Fluorescence changes of SPO/HDMP in DMF solution upon irradiation with UV light (SPO (2×10^{-5} molL^{-1}): HDMP = 1:excess equiv, excitation: 500 nm). Inset: Modulation of the HDMP fluorescence with the interconversion of SP and MC induced by alternating irradiation with UV light. UV–vis absorption spectra of open form of SPO (dash line).

This new band was assigned to the formation of the merocyanine form.

Fig. 4 shows the fluorescence spectral change of SPO–HDMP in the ratio of 1:excess equiv with the excitation wavelength at 500 nm at 0 °C. Upon irradiation with UV light, the fluorescent intensity at 660 nm is decreased. UV-induced ring-opening converts the spiro form to the merocyanine form whose visible absorption band partially overlapped with the HDMP emission band. The fluorescence quenching in SPO–HDMP is attributed to the intramolecular energy transfer from the excited HDMP to the SPO photomerocyanine, because the spectral overlap in the range 550–700 nm between the emission band from HDMP and the enhanced absorption band of the opened merocyanine in SPO. Because of the energy transfer, the open merocyanine absorbs the emitted light of HDMP so that the higher fluorescence of HDMP can be quenched by the merocyanine. It is apparent that the fluorescence intensity of the HDMP is efficiently switched by photochromic switching between SPO and HDMP using alternative irradiation with UV/Vis (Fig. 4 inset).

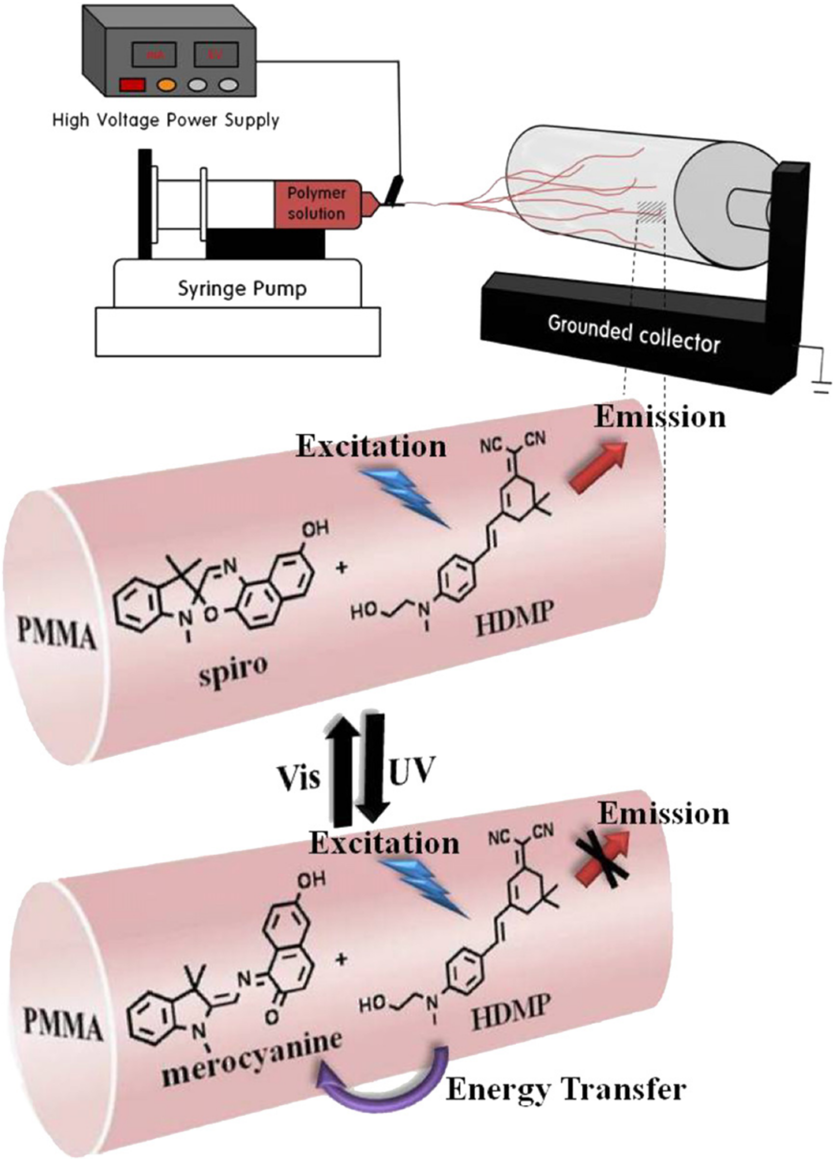

Fig. 5. Schematic representation of the preparation and fluorescence modulation by photochromic switching of SPO/HDMP-loaded PMMA nanofiber.

3.3. Spectral switching of SPO/HDMP-loaded PMMA nanofiber

The photoswitching performance of the SPO/HDMP loaded PMMA nanofiber was next investigated. A typical procedure used for the fabrication of a photoswitching electrospun nanofiber is schematically presented in Fig. 5. A viscous DMF solution containing PMMA, SPO, and HDMP is placed in a syringe. A high voltage (30 kV) is then applied to the syringe needle. The nanofibers are collected on the surface of a grounded aluminum foil. The morphology of the nanofibers, imaged by scanning electron microscopy (SEM), is shown in Fig. 6(a). The nanofibers have a cylindrical structure and a smooth surface. The nanofibers with diameter ranging from 400 nm to 1000 nm are produced (Fig. 6(b).)

Reflection spectra changes of SPO/HDMP-loaded PMMA nanofibers after UV irradiation are depicted in Fig. 7.

Upon UV irradiation, the electrospun nanofiber mats quickly became purple. Besides a small increase in reflection at 500–600 nm, a new broad reflection band around 600–700 nm was observed that corresponds to the ring-opening merocyanine form of SPO produced by ring opening. With subsequent visible light irradiation the reflectance at 600–700 nm was recovered the initial state. At room temperature the efficiency of the decoloration of the SPO/PMMA nanofibers is rather small but it increases with increasing temperature. When the SPO/HDMP-loaded PMMA nanofibers were irradiated with UV light, the emission at 637 nm was remarkably quenched within 10 s (Fig. 8).

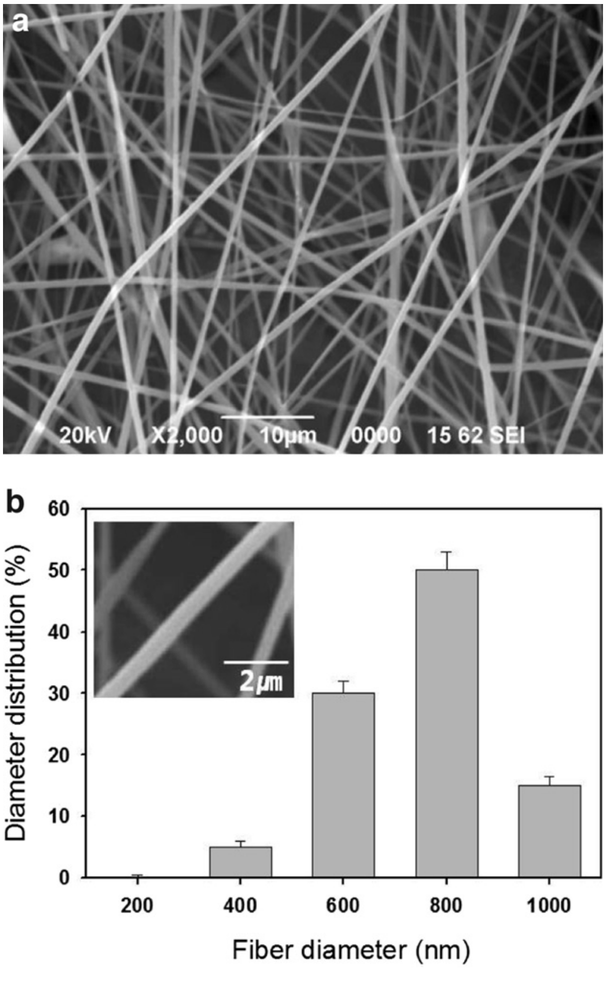

Fig. 6. SEM micrograph (a) and diameter distribution (b) for nanofiber mats spun with applied voltage of 30 kV. Inset of (b): SEM image of single nanofiber. Scale bar in 2 μm ES parameters: needle to collector distance = 17 cm, ϕ = 0.003 mL/min.

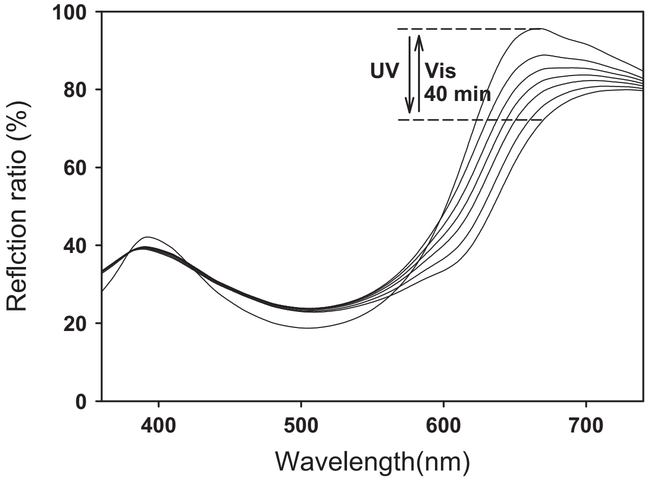

Fig. 7. The reflectance changes of SPO/HDMP-loaded PMMA nanofiber upon irradiation with UV light (SPO: HDMP = 1:1 equiv).

Intramolecular fluorescent energy transfer was responsible for this fluorescence quenching. The SPO/HDMP-loaded PMMA nanofibers are suitable material for optical information recording. We have demonstrated a possible procedure for data recording and erasing in Fig. 9a.

Upon UV-light irradiation through the mask, the optical data were recorded on SPO/HDMP-loaded PMMA nanofiber mats within the mask region. The original pattern was recovered within 30 min. When the nanofiber mats within the mask region were irradiated with visible light, the optical data was erased. Fig. 9b–c shows the practical optical and fluorescent images of erasable and rewritable photoimaging on SPO/HDMP-loaded PMMA nanofiber mats by patterned illumination with a photomask. The abbreviation ‘KNU’ (Kyungpook National University) was recorded as a first image (Fig. 9B), which was subsequently erased and followed by the recording of a second image, LEM (Fig. 9D). The cycles of writing and erasing were repeated more than 20 times.

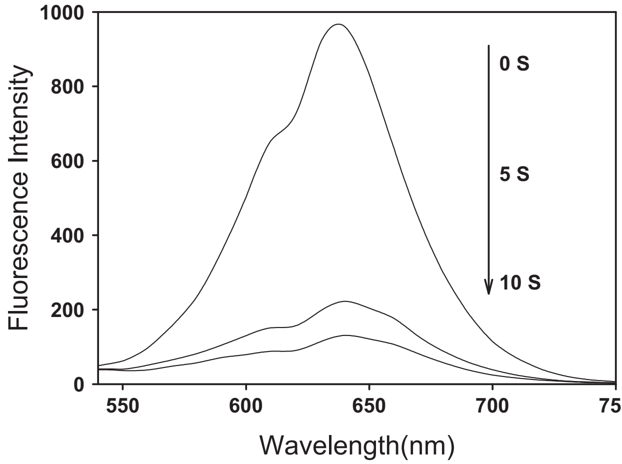

Fig. 8. Fluorescent emission changes of SPO/HDMP-loaded PMMA nanofiber with UV irradiation (SPO: HDMP = 1:1 equiv).

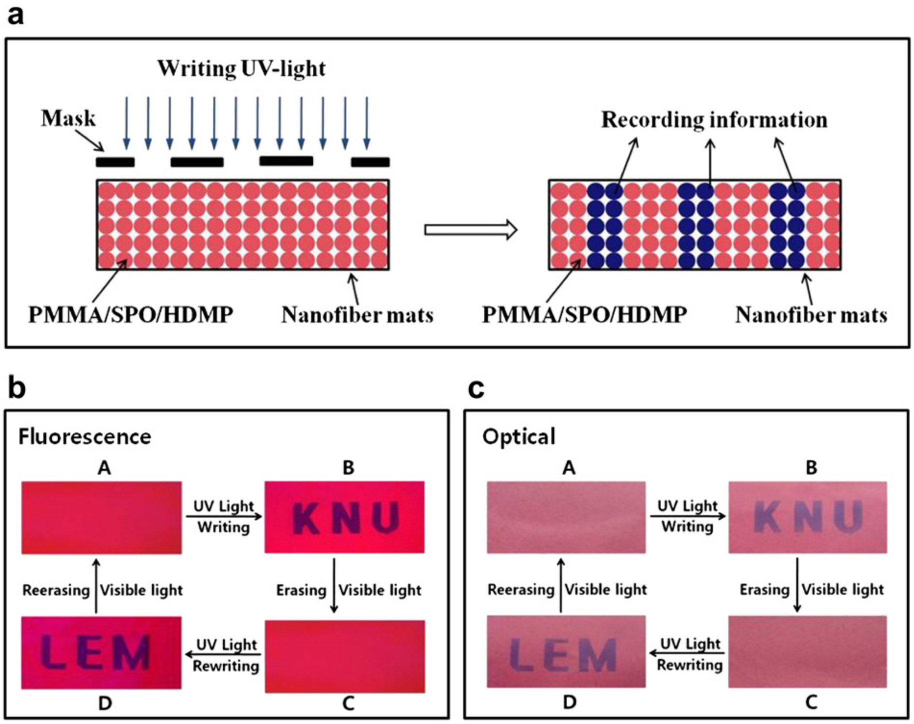

Fig. 9. (a) Principle scheme of the optical data recording on SPO/HDMP-loaded PMMA nanofiber. The (b) fluorescence and (c) optical switching of SPO/HDMP-loaded PMMA nanofiber.

4. Conclusions

In summary, we have constructed a photoresponsive switchable electrospun nanofiber based on an SPO/HDMP-loaded PMMA nanofiber, showing the fluorescence modulation by alternating irradiation with UV light. A facile approach to realizing erasable and rewritable optical storage was successfully demonstrated.

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References

[1] Christie RM, Agyako CK, Mitchell K. An investigation of the electronic spectral properties of the merocyanines derived from photochromic spiroindolinonaphth[2,1-b][1,4]oxazines. Dyes and Pigments 1995;29:241–50.
[2] Mitchell RH, Ward TR, Chen Y, Wang Y, Weerawarna SA, Dibble PW, et al. Synthesis and photochromic properties of molecules containing [e]-annelated dihydropyrenes. Two and three way-switches based on the dimethyldihydropyrene-metacyclophanediene valence isomerization. Journal of the American Chemical Society 2003;125:2974–88.
[3] Berkovic G, Krongauz V, Weiss V. Spiropyrans and spirooxazines for memories and switches. Chemical Reviews 2000;100:1741–53.
[4] Sekkat Z, Wood J, Geerts Y, Knoll W. Surface plasmoni of light-induced modulation in the optical thickness of molecularly thin photochromic layers. Langmuir 1996;12:2976–80.
[5] Evans SD, Johnson SR, Ringsdorf H, Williams LM, Wolf H. Photoswitching of azobenzene derivatives formed on planar and colloidal gold surfaces. Langmuir 1998;14:6436–40.
[6] Biteau J, Chaput F, Boilot JP. Photochromism of spirooxazine-doped gels. Journal of Physical Chemistry 1996;100:9024–31.
[7] di Nunzio MR, Gentili PL, Romani A, Favaro G. Photochromism and thermochromism of some spirooxazines and naphthopyrans in the solid state in polymeric film. Journal of Physical Chemistry C 2010;114:6123–31.
[8] Harada J, Kawazoe Y, Ogawa K. Photochromism of spiropyrans and spirooxazines in the solid state: low temperature enhances photocoloration. Chemical Communications 2010;46:2593–5.
[9] Maurel F, Aubard J, Dognon JP, Rajzmann M, Guglielmetti R, Samat A. Quantum chemical study of photocoloration reaction in the napthoxazine series. Journal of Physical Chemistry A 2006;110:4759–71.
[10] Korolev VV, Vorobyev DY, Glebov EM, Grivin VP, Plyusnin VF, Koshkin AV, et al. Spironaphtoxazines produced from crown-containing dihydroisoquinolines: synthesis and spectroscopic study of cation-dependent photochromism. Journal of Photochemistry and Photobiology A: Chemistry 2007;192:75–83.
[11] Buntinx G, Poizat O, Foley S, Sliwa M, Aloïse S, Lokshin V, et al. Sub-picosecond transient absorption spectroscopy of substituted photochromic spironaphthoxazine compounds. Dyes and Pigments 2011;89:305–12.
[12] Chu NYC, Durr H, Bouas-Laurent H. Photochromism: molecule and systems. Amsterdam: Elsevier; 1990.
[13] Kawata S, Kawata Y. Three-dimensional optical data storage using photochromic materials. Chemical Reviews 2000;100:1777–88.
[14] Suh HJ, Jin SH, Gal YS, Koh K, Kim SH. Synthesis and photochromism of polyacetylene derivatives containing a spiroxazine moiety. Dyes and Pigments 2003;58:127–33.
[15] Hattori H, Uryu T. Photochromic chiral liquid crystalline systems containing spiro-oxazine with a chiral substituent I. Synthesis and characterization of compounds. Liquid Crystals 2001;28:25–34.
[16] Kim SH, Lee SJ, Park SY, Suh HJ, Jin SH, Gal YS. Synthesis and properties of ionic conjugated polymer with spiroxazine moiety. Dyes and Pigments 2005;68:61–7.
[17] Kim SH, Park SY, Shin CJ, Yoon NS. Photochromic behavior of poly[N, N-[(3-dimethylamino)propyl]methacrylamide] having spiroxazine pendant group. Dyes and Pigments 2007;72:299–302.
[18] Kim SH, Ahn CH, Keum SR, Koh K. Synthesis and properties of spiroxazine polymer having photocrosslinkable chalcone moiety. Dyes and Pigments 2004;65:179–82.
[19] Kim SH, Park SY, Yoon NS, Keum SR, Koh K. Synthesis and properties of spiroxazine polymer derived from cyclopolymerization of diallyldimethylammonium chloride and diallylamine. Dyes and Pigments 2005;66:155–60.

[20] Kim SH, Hwang IJ, Gwon SY, Son YA. Photoregulated optical switching of poly(N-isopropylacrylamide) hydrogel in aqueous solution with covalently attached spironaphthoxazine and D-π-A type pyran-based fluorescent dye. Dyes and Pigments 2010;87:158–63.

[21] Kim SH. Molecular switches based on spironaphthoxazine. Journal of the Japan Society of Colour Material 2010;83:129–38.

[22] Wang S, Yu C, Choi MS, Kim SH. Synthesis and switching properties of photochromic carbazole-spironaphthoxazine copolymer. Journal of Photochemistry and Photobiology A: Chemistry 2007;192:17–22.

[23] Wang S, Yu C, Choi MS, Kim SH. A switching fluorescent photochromic carbazole–spironaphthoxazine copolymer. Dyes and Pigments 2008;77:245–8.

[24] (a) Greiner A, Wendorff JH. Electrospinning: a fascinating method for the preparation of ultrathin fibers. Angewandte Chemie International Edition 2007;46:5670–703;
(b) Dzenis Y. Material science: spinning continuous fibers for nanotechnology. Science 2004;304:1917–9;
(c) Teo WE, Ramakrishna S. A review on electrospinning design and nanofibre assemblies. Nanotechnology 2006;17:R89–106.

[25] Sun X, Liu Y, Xu X, Yang C, Yu G, Chen S, et al. Novel electroactive and photoactive molecular materials based on conjugated donor–acceptor structures for optoelectronic device applications. Journal of Physical Chemistry B 2005;109:10786–92.

[26] Fu H, Gao X, Zhong G, Zhong Z, Xiao F, Shao B. Synthesis and electroluminescence properties of benzothiazole derivatives. Journal of Luminescence 2009;129:1207–14.

[27] Ning Z, Zhang Q, Wu W, Pei H, Liu B, Tian H. Starburst triarylamine based dyes for efficient dye-sensitized solar cells. Journal of Organic Chemistry 2008;73:3791–7.

[28] Liu B, Zhu W, Zhang Q, Wu W, Xu M, Ning Z, et al. Conveniently synthesized isophorone dyes for high efficiency dye-sensitized solar cells: tuning photovoltaic performance by structural modification of donor group in donor–π–acceptor system. Chemical Communications; 2009:1766–8.

[29] Kim SH, Gwon SY, Bae JS, Son YA. The synthesis and spectral properties of a stimuli-responsive D–π–A charge transfer dye. Spectrochimica Acta Part A 2011;78:234–7.

[30] Wang S, Kim SH. Photophysical and electrochemical properties of D–π–A type solvatochromic isophorone dye for pH molecular switch. Current Applied Physics 2009;9:783–7.

[31] (a) Kakishita T, Matsumoto K, Kiyotsukuri T, Matsumura K, Hosoda M. Synthesis and NMR study of 9′-substituted spiroindolinonaphthoxazine derivatives. Journal of Heterocyclic Chemistry 1992;29:1709–15;
(b) Durr H, Ma Y, Cortellaro G. Preparation of phtochromic molecules with polymerizable organic functionalities. Synthesis; 1995:294–8.

[32] Durr H, Bouas-Laurent H. Photochromism-molecules and systems. Amsterdam: Elsevier; 1990.