

Synthesis and Characterizations of Bis-Spiropyran Derivatives

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We synthesized three different derivatives of bis-spiropyran using simple organic reactions with high yields. **BSP1**, a derivative of bis-spiropyran having a connection at the position 6' and **BSP2**, a derivative of bis-spiropyran having a connection at the position 5 and **BSP3**, a derivative of bis-spiropyran containing a dithienylethene group between two spiropyran moieties were synthesized. The optical properties of BSPs were characterized. UV-Vis spectra showed that BSPs exhibit reversible photo-isomerization and the efficiency of photo-isomerization is highly dependent on the position of nitro group. BSPs having nitro group at *para* position of hydroxy group showed the higher efficiency of photo-isomerization than the one having nitro group at *ortho* position. The optical microscope images obtained under ultraviolet or visible light exposure demonstrated that the formation of nanorods can be reversibly controlled by optical signal.

Key Words : Oligo-spiropyran, Photochromic, Photo-induced aggregation, Nanorods

Introduction

Photoresponsive materials exhibiting changes of physical or electrical properties in response to the incident light have been of great interest due to their broad technological applications. For example, photochromic materials show color changes due to reversible photo-isomerization.^{1,2} Among many photochromic materials, spiropyran is one of promising compounds that exhibit reversible structural and optical changes in response to light. Spiropyran converts into colored merocyanine structure by ultraviolet radiation, and which reversibly turns back to the original spiropyran form with exposure of visible light or heating (Scheme 1).³

There have been a few attempts of incorporating spiropyran monomers into the side-chain of polymers for the purpose of investigating their mechanoresponsive properties, photochromism in polymer matrices.⁴⁻¹⁵ However, the synthesis and characterization of oligomers or polymers containing spiropyran moieties in the main backbone have not been well investigated.¹⁶⁻²³ Herein, we report the synthesis and characterization of conjugated bis-spiropyran derivatives. To investigate the effect of connectivity, several bis-spiropyran molecules having connection at different positions were prepared (Scheme 2). **BSP1** is a derivative of bis-spiropyran having a connection at the position 6' and **BSP2** has a connection at the position 5.

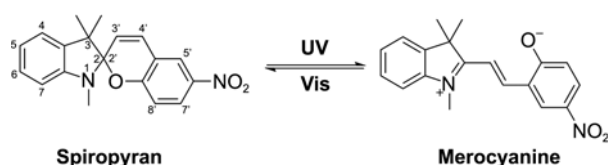
Since two spiropyran monomers are directly connected in both **BSP1** and **BSP2**, merocyanine, a chromophore formed

by the exposure of UV can accordingly be conjugated directly. **BSP3** contains a dithienylethene group between two spiropyran moieties. Similar to spiropyran, dithienylethene also performs photoisomerization. Upon exposure of UV, the open form of dithienylethene converts into the closed form, and reversibly turns back to the open form by visible light radiation. Unlike other photochromic materials, dithienylethene is highly stable to the thermal stimuli and does not isomerize at relatively high temperature. We expect that **BSP3** containing both spiropyran and dithienylethene moieties can be utilized for creating novel *multichromic materials* which exhibits metastable intermediate state other than on/off states when they are carefully combined with photo and thermal stimuli.

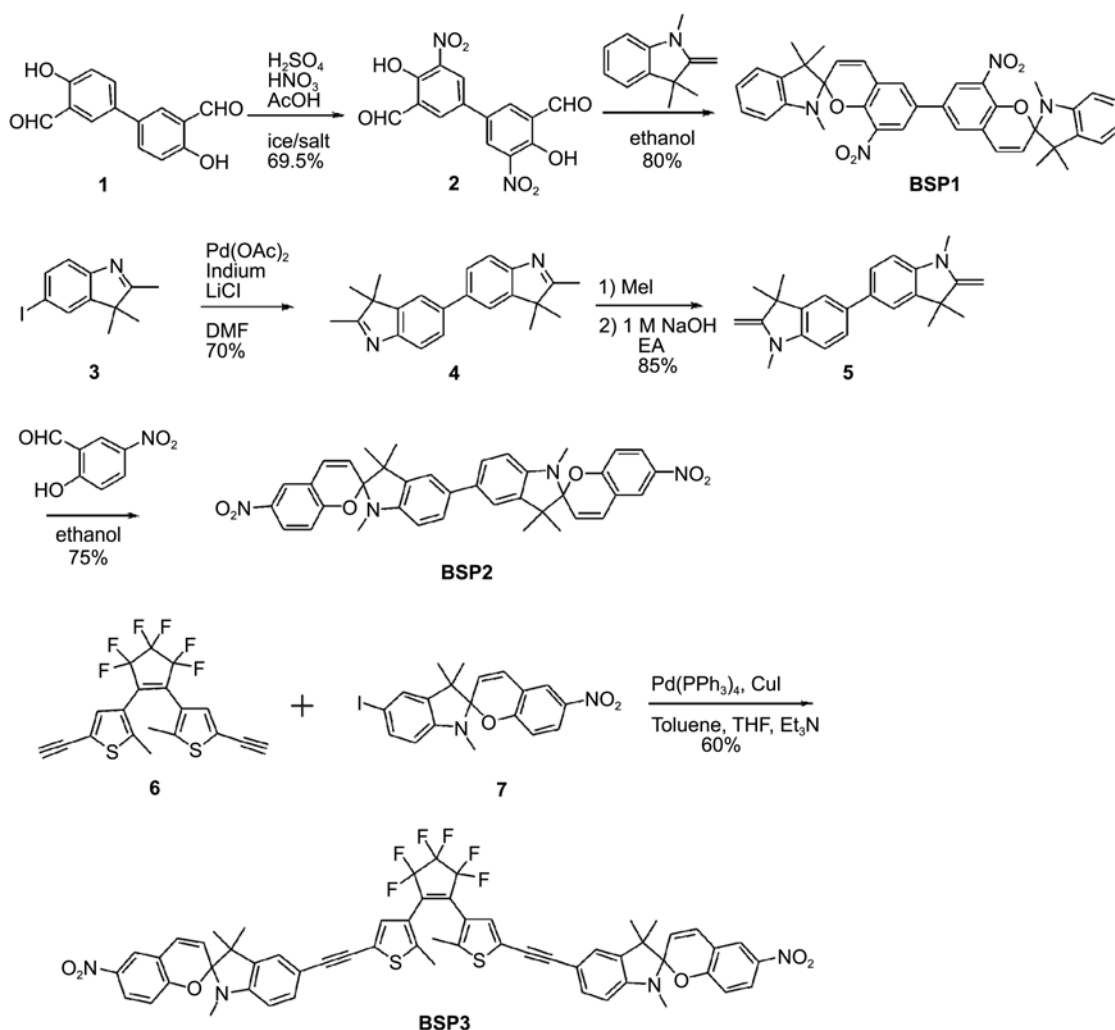
Experimental

Reagents. 4,4'-dihydroxybiphenyl-3,3'-dicarbaldehyde (**1**),²⁴ 5-iodo-2,3,3-trimethyl-3*H*-indole (**3**),²⁵ 3,3'-(perfluorocyclopent-1-ene-1,2-diyl)bis(5-ethynyl-2-methylthiophene) (**6**)²⁶ were obtained by following procedures reported elsewhere. All commercially available materials were used without further purification. All solvents were reagent grade. Reactions were normally carried out under argon atmosphere in flame-dried glasswares. Merck silica gel 60 (partial size 0.04-0.063 mm) was employed for flash chromatography. NMR spectra of samples in CDCl₃ or DMSO-*d*₆ with TMS as the internal standard were recorded on a Varian-400 spectrometer (400 MHz for ¹H; 100 MHz for ¹³C). UV-Vis absorption spectra were recorded on an Agilent Technologies 8453 UV-VIS spectrophotometer.

Synthesis of 4,4'-Dihydroxy-5,5'-dinitrobiphenyl-3,3'-dicarbaldehyde (2). 4,4'-dihydroxybiphenyl-3,3'-dicarbaldehyde (**1**) (0.2 g) in acetic acid (1 mL) was added cautiously with cooling in ice and salt, to a mixture of concent-



Scheme 1



Scheme 2. Synthetic scheme of bis-spiropyran derivatives.

rated sulfuric acid (0.5 mL) and concentrated nitric acid (0.25 mL). After 30 min the nitration mixture was poured on ice water and extracted twice with ethyl acetate washed with brine, dried over anhydrous MgSO_4 , and filtered. Evaporation of the solvent to afford the 4,4'-dihydroxy-5,5'-dinitrobiphenyl-3,3'-dicarbaldehyde (**2**) (0.19 g) in 69.5% yield: IR (NaCl, cm^{-1}) 3420, 2838, 1668, 1535, 1451, 1261, 1108, 1017, 768; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 10.32 (s, 2H), 8.61 (d, $J = 2.4$ Hz, 2H), 8.39 (d, $J = 2.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.60, 153.71, 139.12, 133.78, 129.14, 128.62, 126.26.

Synthesis of Bis-spiropyran 1 (BSP1). An oven-dried round bottom flask was charged with a mixture 4,4'-dihydroxy-5,5'-dinitrobiphenyl-3,3'-dicarbaldehyde (**2**) (0.19 g), 1,3,3-trimethyl-2-methyleneindoline (0.2 g) and absolute ethanol (10 mL). The reaction mixture was heated to reflux for 12 h and cooled to room temperature. After diluted with water, the organic product was extracted three times with ethyl acetate, washed with brine, dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane = 1/7) to afford the **BSP1** (0.29 g) in 80%

yield: IR (NaCl, cm^{-1}) 2962, 2924, 1608, 1528, 1486, 1296, 1266, 1023, 917, 743; ^1H NMR (400 MHz, CDCl_3) δ 7.85 (d, $J = 2.4$ Hz, 2H), 7.43 (d, $J = 2.4$ Hz, 2H), 7.18 (dd, $J = 7.2$, 7.2 Hz, 2H), 7.08 (d, $J = 7.2$ Hz, 2H), 6.98 (d, $J = 10.4$ Hz, 2H), 6.87 (dd, $J = 7.2$, 7.2 Hz, 2H), 6.54 (d, $J = 7.2$ Hz, 2H) 5.93 (d, $J = 10.4$ Hz, 2H), 2.76 (s, 6H), 1.38 (s, 6H), 1.21 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.11, 147.52, 137.43, 136.04, 129.99, 128.97, 128.42, 127.90, 123.10, 122.43, 121.58, 120.09, 107.28, 52.44, 29.03, 26.20, 20.20.

Synthesis of 2,2',3,3',3',3'-Hexamethyl-3H,3'H-5,5'-biindole (4). 2,2',3,3',3',3'-hexamethyl-3H,3'H-5,5'-biindole (**4**) was obtained by palladium-catalyzed intermolecular coupling reactions of aryl halides.^{27,28} A mixture of 5-iodo-2,3,3-trimethyl-3H-indole (**3**) (0.56 g), palladium(II) acetate (0.034 g), indium (0.14 g), lithium chloride (0.13 g) in dry DMF (5 mL) was stirred at 80 °C for 12 h under a argon atmosphere. The reaction mixture was quenched with $\text{Na}_2\text{S}_2\text{O}_3$ (sat. aq.). The aqueous layer was extracted with methylene chloride and the combined organic phase was washed with water and brine, dried with MgSO_4 , filtered and concentrated under a reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1/1) to

afford 2,2',3,3,3',3'-hexamethyl-3*H*,3'*H*-5,5'-biindole (**4**) (0.44 g) in 70% yield: IR (NaCl, cm^{-1}) 2962, 2927, 1723, 1517, 1456, 822, 732; ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, J = 8.0 Hz, 2H), 7.54 (dd, J = 8.0, 1.6 Hz, 2H), 7.49 (d, J = 1.6 Hz, 2H), 2.31 (s, 6H), 1.37 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 188.34, 153.17, 146.45, 138.81, 123.94, 120.44, 120.10, 53.89, 23.34, 15.64.

Synthesis of 1,1',3,3,3',3'-Hexamethyl-2,2'-dimethylene-5,5'-biindoline (5). 2,2',3,3,3',3'-hexamethyl-3*H*,3'*H*-5,5'-biindole (**4**) (0.3 g) was dissolved in methyl iodide (5 mL). The reaction mixture was heated to reflux for 12 h. The resulting pink powder was filtered and washed with ice-cooled methylene chloride and then dried in vacuum. The resulting powder was added into a solution of potassium hydroxide. The suspension stirred for 1 h at room temperature. The reaction mixture was extracted with ethyl acetate, washed with brine, dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane = 1/4) to afford the 1,1',3,3,3',3'-hexamethyl-2,2'-dimethylene-5,5'-biindoline (**5**) (0.28 g) in 85% yield: IR (NaCl, cm^{-1}) 2961, 2921, 1647, 1616, 1492, 1358, 800, 769; ^1H NMR (400 MHz, CDCl_3) δ 7.31 (dd, J = 8.0, 1.6 Hz, 2H), 7.25 (d, J = 1.6 Hz, 2H), 6.57 (d, J = 8.0 Hz, 2H), 3.86 (s, 4H), 3.06 (s, 6H), 1.39 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.18, 145.29, 138.28, 132.63, 125.96, 120.51, 105.12, 73.22, 44.37, 30.15, 29.03.

Synthesis of Bis-spiropyran 2 (BSP2). An oven-dried round bottom flask was charged with a mixture 1,1',3,3,3',3'-hexamethyl-2,2'-dimethylene-5,5'-biindoline (**5**) (0.10 g), 5-nitrosalicylaldehyde (0.12 g) and absolute ethanol (10 mL). The reaction mixture was heated to reflux for 12 h and cooled to room temperature. After diluted with water, the organic product was extracted three times with ethyl acetate, washed with brine, dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane = 1/4) to afford the **BSP2** (0.14 g) in 75% yield: IR (NaCl, cm^{-1}) 2963, 2926, 1614, 1517, 1480, 1336, 1273, 1089, 952, 809, 732; ^1H NMR (400 MHz, CDCl_3) δ 8.03 (m, 4H), 7.41 (dd, J = 8.0, 1.6 Hz, 2H), 7.28 (d, J = 1.6 Hz, 2H), 6.94 (d, J = 10.4 Hz, 2H), 6.80 (d, J = 8.0 Hz, 2H), 6.61 (d, J = 8.0 Hz, 2H), 5.89 (d, J = 10.4 Hz, 2H), 2.78 (s, 6H), 1.36 (s, 6H), 1.25 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.94, 146.70,

141.07, 136.84, 134.03, 128.42, 126.43, 126.01, 122.83, 121.70, 120.16, 118.81, 115.61, 107.36, 106.68, 52.53, 29.12, 26.16, 20.17.

Synthesis of Bis-spiropyran 3 (BSP3). 3,3'-(perfluorocyclopent-1-ene-1,2-diyl)bis(5-ethynyl-2-methylthiophene) (**6**) (0.55 g), 5'-iodo-1,3,3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (1.3 g) were dissolved in toluene (5 mL), THF (10 mL), Et_3N (20 mL). The reaction mixture was cooled to 0 °C and $\text{Pd}(\text{PPh}_3)_4$ (0.03 g), CuI (0.01 g) were added. The resulting mixture was stirred at 60 °C for 5 h and cooled to room temperature. After diluted with water, the organic product was extracted with ethyl acetate, washed with brine, dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane = 1/4) to afford the **BSP3** (0.8 g) in 60% yield: IR (NaCl, cm^{-1}) 2966, 2200, 1612, 1519, 1477, 1339, 1272, 1089, 955, 816, 734; ^1H NMR (400 MHz, CDCl_3) δ 8.03 (m, 4H), 7.39 (dd, J = 8.0, 1.6 Hz, 2H), 7.20 (m, 4H), 6.95 (d, J = 10.4 Hz, 2H), 6.78 (d, J = 8.0 Hz, 2H), 6.52 (d, J = 8.0 Hz, 2H), 5.84 (d, J = 10.4 Hz, 2H), 2.77 (s, 6H), 1.94 (s, 6H), 1.30 (s, 6H), 1.19 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.53, 148.34, 141.30, 136.64, 132.27, 128.70, 126.09, 125.07, 124.91 perfluorocyclopentene (multiplets), 122.70 perfluorocyclopentene (multiplets), 122.87, 121.12, 118.64, 115.60, 113.12, 107.05, 106.18, 95.23, 79.74.

Results and Discussions

The three BSPs were synthesized by using simple reactions with high yield. For the synthesis of **BSP1**, an electron withdrawing nitro group was introduced to 4,4'-dihydroxybiphenyl-3,3'-dicarbaldehyde (**1**) in order to increase the stability of merocyanine structure by stabilizing alkoxy anion. In the IR spectrum, vibrational peaks of hydroxyl and aldehyde functional groups appear at 3240 cm^{-1} and 1668 cm^{-1} respectively. The peak shown at 1535 cm^{-1} is originated by asymmetric stretching of aromatic nitro group (Figure 1(a)). Considering the fact that coupling constant between aromatic protons in ^1H NMR is 2.4 Hz, nitro functional group is believed to be substituted into the *ortho* position of hydroxy functional group. 4,4'-Dihydroxy-5,5'-dinitrophenyl-3,3'-dicarbaldehyde (**2**) and Fischer's base were added at 1:2.5 molar ratio and stirred with refluxing for 12 h

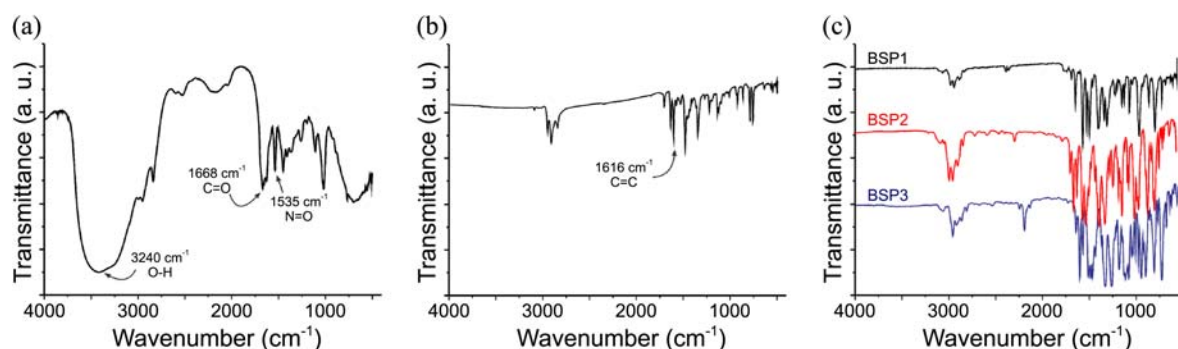


Figure 1. IR spectra of (a) compound **2**, (b) compound **5** and (c) **BSP13**.

in ethanol solution, giving **BSP1** at a high yield of 80%. In the synthesis of **BSP2**, an important step in the overall synthetic process is the synthesis of 2,2',3,3',3',3'-hexamethyl-3*H*,3'*H*-5,5'-biindole (**4**) substance. For the successful reaction, homo-coupling reaction with aryl halides should be carried out at the condition of sufficiently dissolving the reactants prior to elevating temperature. The formation of dimeric Fischer's base (**5**) was verified by appearing of a strong peak at 1616 cm^{-1} which is by terminal double bond (Figure 1(b)). The yield of **BSP2** was 75% when the same method as **BSP1** was used. For **BSP3**, the Sonogashira cross-coupling reaction was used to connect alkyne and aromatic halide with retaining conjugation between dithienylethene and spiropyran. Sharp stretching vibration of internal triple bond can be seen at 2200 cm^{-1} (Figure 1(c)). The as-synthesized BSPs were soluble in many common organic solvents including ethyl acetate, chloroform, THF, toluene *etc.* Upon exposure of UV, the originally clear BSP solutions ($c = 24\text{ }\mu\text{M}$) gradually displayed colors. After 1 min exposure of ultraviolet radiation with energy density = 140 nW/cm^2 ($\lambda_{\text{peak}} = 254\text{ nm}$), **BSP1** became pale bluish green, **BSP2** became blue, and **BSP3** became deep bluish green. The color strength increased in the order of **BSP1** < **BSP2** < **BSP3**. The solutions became clear gain with exposure of visible light ($\lambda_{\text{peak}} = 550\text{ nm}$, energy density = 2.6 mW/cm^2).

Optical properties of the synthesized **BSP13** were further investigated on UV-VIS. As shown in Figure 2, absorption spectra of the as-synthesized BSPs didn't show any significant feature in the visible regime. Upon irradiating UV ($\lambda = 254\text{ nm}$, energy density = 140 nW/cm^2), new peaks appeared at $\sim 600\text{ nm}$, which were attributed to the formation of merocyanine or/and the closed dithienylethene. The peak positions of **BSP1**, **BSP2** and **BSP3** were $\lambda_{\text{peak}} = 628\text{ nm}$, $\lambda_{\text{peak}} = 600\text{ nm}$ and $\lambda_{\text{peak}} = 644\text{ nm}$ respectively. The peak intensity at $\sim 600\text{ nm}$ gradually increased with the exposure time, and reached to the saturation point after 1 min. Comparing with *mono*-spiropyran showing absorption peak at 580 nm , bis-spiropyran derivatives (**BSP1-3**) showed peaks at the longer wavelength, which is possibly due to the extended conjugation length.²⁹ **BSP1** showed a relatively weak optical density than **BSP2** and **BSP3** at the same experi-

mental condition. The major structural difference of **BSP1** from **BSP2** and **BSP3** is the position of nitro group. A strong electron withdrawing nitro group is at *ortho* position of hydroxyl group in **BSP1** while is located at *para* position in **BSP2** and **BSP3**. Since the nitro group at *para* position is more effective for stabilizing hydroxy anion of merocyanine structure, the photo-isomerization of spiropyran form to merocyanine form is expected to be more efficient in **BSP2** and **BSP3** than **BSP1**. The relatively high optical density of **BSP3** is possibly due to combinational effects of *para*-nitro group and an additional chromophor, the closed form of dithienylethene. The retro-isomerization was possible by irradiating visible light. With an exposure (5 min) of visible light with energy density = $2.6\text{ }\mu\text{W/cm}^2$ ($\lambda_{\text{peak}} = 550\text{ nm}$), the colored solution of BSPs became transparent, exhibiting almost identical UV-VIS spectra as those of the unexposed one. These results confirm that bis-spiropyran reversibly isomerizes between spiropyran and merocyanine under UV/Vis irradiation.

Once spiropyran is converted to merocyanine, the interaction between molecules is expected to be increased due to the favorable π - π interaction and the enhanced dipole moments.³⁰ The increased molecular interactions can induce aggregation in solution. To investigate this, **BSP** solutions (10 mM in toluene) were placed on glass slide and their morphology was observed under optical microscope with irradiating UV and visible light. Prior to UV exposure, the solutions were originally transparent and homogeneous. Upon exposure of 254 nm UV for 1 min solution, however rod-like aggregations appeared and their population and

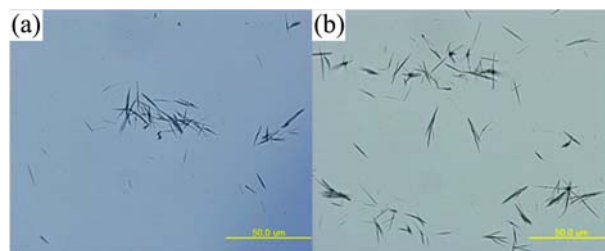


Figure 3. Optical images of (a) **BSP1** and (b) **BSP2** after UV exposure.

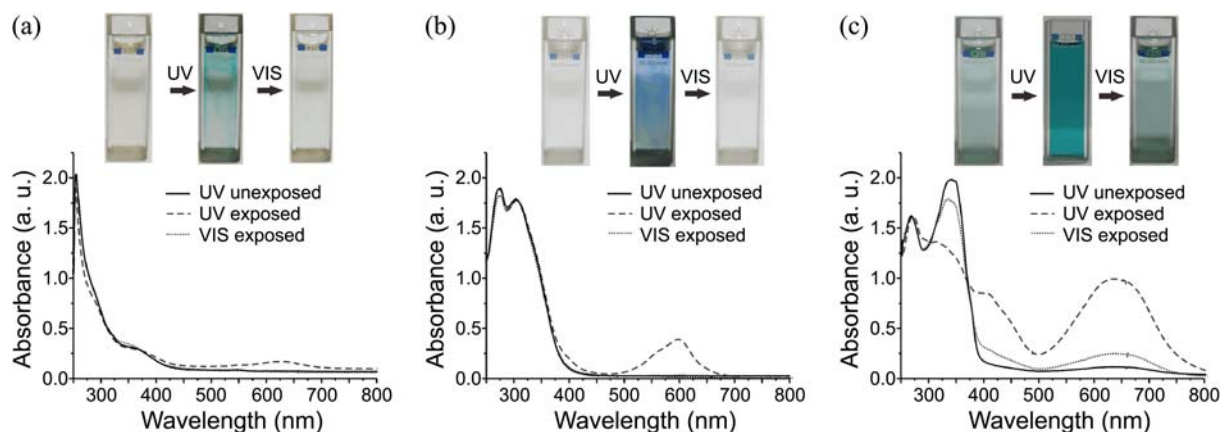


Figure 2. UV-VIS spectra of (a) **BSP1**, (b) **BSP2** and (c) **BSP3** in ethyl acetate ($24\text{ }\mu\text{M}$).

length gradually increased with the exposure time (Figure 3). The length of the nanorods was as long as 20 μm . The relative population of nanorods for the solution of **BSP2** is higher than **BSP1**, which is attributed to the more effective photo-isomerization of **BSP2** than **BSP1**. The nanorods form by UV irradiation were gradually decomposed and eventually disappeared with extended exposure of visible light (30 min).

In conclusion, we synthesized three different derivatives of bis-spiropyran using simple organic reactions with high yields. The optical properties of BSPs were characterized. UV-Vis spectra showed that BSPs exhibit reversible photo-isomerization and the efficiency of photo-isomerization is highly dependent on the position of nitro group. BSPs having nitro group at *para* position of hydroxyl group showed the higher optical density at ~ 600 nm. These results imply that the photo-isomerization of **BSP2** and **BSP3** having nitro group at *para* position is more effective than **BSP1** that has nitro group at *ortho* position. The optical microscope images obtained under ultraviolet or visible light exposure demonstrated that the formation of nanorods can be reversibly controlled by optical signal. We anticipate that such aggregation and disaggregation of photochromic materials controlled by optical signal are very useful for many engineering applications.

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