Development of real time experimental system for investigating photochromic response to UV irradiation

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Abstract. Photochemistry is a field of chemistry that deals with the chemical effects of light such as ultraviolet (UV), visible (Vis) or infrared (IR) radiation. Among many types of photochromic molecules, particular attentions have been given on spiropyrans because of their potential applications in industrial fields. Spiropyrans have the ability to change their chemical structure after exposed to a certain appropriate wavelength of light. However, spiropyrans are very sensitive dyes. For these reasons, an UV irradiation chamber was developed to control the surrounding environment which governs the external light intervention during photochromic work and when direct absorption measurement was performed. The chamber was then exploited to investigate the substituent effect on the absorption spectra of Benzo Indolino Pyrano Spiran (BIPS) dyes, 6-nitro BIPS and 8-ethoxy-6-nitro BIPS. Thus, our results suggest that the developed chamber was successfully utilized for photochromic system since it can protect the dyes from environmental intervention.

1. Introduction
Photochromism is a branch of photochemistry, which deals with photochemical or thermal reversible photochemical reactions [1]. Since the photochromic dyes are sensitive to light [2], the existence of any external light before the initial absorption measurement may change the actual behavior. Moreover, the irradiation and absorption measurement should be done simultaneously to avoid time gap which can cause error. Besides, prolong exposure to UV radiation can lead to adverse effects to human health such as cataract formation and retinal degeneration [3, 4]. For these reasons, it is essential to establish a closed system for the photochromic work in order to control the surrounding environment, which governs the external light intervention and perform simultaneous irradiation and absorption measurement. Therefore, there is a need to design an UV irradiation chamber to provide shielding against UV radiation and thus improving the efficiency of the absorption measurement method. This strategy will minimize error during data collection.

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Previous studies, irradiation as well as characterization processes were conducted in dark condition due to the fact that the photochromic dyes can be easily affected by external light [5, 6]. However, there were researchers who had done the processes separately [7, 8]. They irradiated the samples, followed with manual transfer of the sample inside the measurement chamber for characterization. The time delay, were around 2 s between the two processes [7] and 60 s [8]. However, during a trial experiment in this research, the absorption value decreased rapidly in less than 2 s once the radiation is terminated. None of the previous studies had discussed about the chamber design in detail. Thus, this paper will focus on the designing of the UV irradiation chamber and investigation of the substituent effect on the absorption spectra of Benzo Indolino Pyrano Spiran (BIPS) dyes, 6-nitro BIPS and 8-ethoxy-6-nitro BIPS.

2. Design and specifications

Figure 1 illustrates the schematic diagram of the real time photochromic measurement. The main objective of the design is to irradiate the samples and record the absorption measurement at the same time. Two light sources are utilized for this purpose. The UV serves as to change the color of the dye whereas xenon is to emit the light signal. The xenon light source is directed to pass through the dyes and trigger the built-in detector inside the spectrometer, which is used to measure the absorption spectra of the dyes.

![Diagram of UV irradiation chamber](image)

**Figure 1.** Schematic diagram of the real time photochromic measurement.

In this design, both light sources were coupled by Y-shaped input fiber cable connection. The UV lamp was connected to foot switch, which acts as step-on button. The light is transmitted through input fiber into a cuvette placed in a dark chamber. The light passed through the sample, went through output fiber and directly to the spectrometer connected to the computer which has been installed with SpectraSuite software.

For the SpectraSuite software, the ‘Integration Time’ was set at 100 ms, ‘Scans to Average’ at 1, and ‘Boxcar Width’ at 5. The sample was left inside the chamber for a while. After about one minute, the initial absorption spectrum was recorded and the absorption spectrum was recorded after irradiation stopped. Figure 2 provides real view of the chamber as well as the experimental setup with the spectrometer is connected to the computer.
Figure 2. Complete images of (a) UV irradiation chamber, and (b) experimental setup for the real time photochromic measurement.

2.1. Light sources
The UV lamp (Efos Acticure A4000, currently known as Exfo Acticure A4000) uses a high pressure 100 W mercury vapor short arc type of lamp. The xenon lamp (Ocean Optics PX-2 Pulsed Xenon Light Source) is a high flash rate, short-arc xenon lamp for a variety of applications including absorbance, reflection, fluorescence and phosphorescence measurements, and particularly for optically or thermally unstable samples. When it is coupled to the spectrometer, the operation of both the light and detector can be easily synchronized. However, this PX-2 emits ultraviolet radiation. Thus, safety eyewear is needed and direct eye contact with the light source must be avoided to prevent from permanent eye damage. The technical specifications of the xenon lamp were listed in table 1.
Table 1. Technical specifications of the xenon lamp.

| Specifications      | Details                                      |
|---------------------|----------------------------------------------|
| Power consumption   | 1.5 A @ 12 VDC                               |
| Power output        | 45 µJ per pulse maximum                      |
|                     | 9.9 W average power                          |
|                     | 220 Hz pulse rate maximum                    |
| Spectral range      | 220-750 nm                                   |
| Pulse duration      | 5 µs (at 1/3 height of pulse)                |
| Aperture            | 3 mm                                         |
| Connector           | SMA 905                                      |

2.2. Input and output fibers (Ocean Optics Optical Fiber Assemblies)
Both types of input (Y-shaped) and output fibers can be connected easily to light sources, sensors, and spectrometers via an SMA 905 Connector. Table 2 shows the characteristics of the input and output fibers.

Table 2. Characteristics of the fibers.

| Part                      | Item code   | Wavelength range | Core diameter | Buffer / coating | Length |
|---------------------------|-------------|------------------|---------------|------------------|--------|
| Laboratory-grade          | BIF600-UV-VIS | 300-1100 nm      | 600 µm ± 10 µm | Polyimide        | 2 m    |
| Bifurcated Optical Fiber  |             |                  |               |                  |        |
| (Y-shaped input fiber)    |             |                  |               |                  |        |
| Laboratory-grade Optical  | P600-1-UV-VIS | 300-1100 nm      | 600 µm ± 10 µm | Polyimide        | 1 m    |
| Fiber (output fiber)      |             |                  |               |                  |        |

2.3. UV irradiation chamber
In the chamber, a 1-cm path length cuvette is fitted in the cuvette holder (Ocean Optics CUV-ALL 4-way cuvette holder) which has an opening diameter of 5 mm as the light passage. Meanwhile, the neutral density filter (Newport FSQ-OD100) is placed behind the cuvette to attenuate the amplitude signal for avoiding signal saturation at CCD array detector. It is made of neutral density colored glass (BK 7 or equivalent for 0.04 OD) with dimension of 50.8 x 50.8 x 1.57 mm. The optical density is 1.0 at 546.1 nm.

2.4. Spectrometer (Ocean Optics USB4000-VIS-NIR Fiber Optic Spectrometer)
The spectrometer is a high-performance, miniature fiber-optic spectrometer that can measure bandwidth in the range of 348-1043 nm. It is connected to a computer via the USB port or serial port. The USB4000 spectrometer is a great equipment as it can be utilized for various applications of basic absorbance, reflectance and emission measurements. It can be operated by the SpectraSuite software. The important descriptions of the spectrometer were documented in table 3.

Table 3. Descriptions of the spectrometer.

| Specifications        | Details                                    |
|-----------------------|-------------------------------------------|
| Power consumption     | 250 mA @ 5 VDC                            |
| Detector              | 3648-element Toshiba TCD1304AP Linear CCD array |
| Fiber optic connector | SMA 905 to single-strand optical fiber (0.22 NA) |

2.5. SpectraSuite software
SpectraSuite is a complete modular, Java-based spectroscopy software which can control any Ocean Optics USB spectrometer and device. The software supports a real-time interface to a variety of
signal-processing functions. Hence, the spectroscopic measurements (such as absorbance, reflectance, and emission) can be performed, all system parameters can be manipulated, data can be collected and presented in real time, and also reference monitoring and time acquisition tests can be done.

Absorbance spectra are a measure of how much light a sample absorbs. For most samples, it is linearly proportional to the sample concentration. SpectraSuite software determines the absorbance at wavelength $\lambda$ ($A_\lambda$) by using the following equation:

$$A_{\lambda 10} = \frac{S_{\lambda} - D_{\lambda}}{R_{\lambda} - D_{\lambda}}$$

where at wavelength $\lambda$, $S_{\lambda}$ is the sample intensity, $D_{\lambda}$ is the dark intensity, and $R_{\lambda}$ is the reference intensity.

3. Example of application in photochromic study

Photochromism is defined as a reversible transformation of a chemical species induced in one or both directions by the absorption of electromagnetic radiation between two forms having different absorption spectra [9, 10]. From scheme 1, molecule A is transformed into molecule B by irradiation. The back reaction of B into A can either occur thermally or photochemically. Mostly but not all of the spectral change is observed by visible color, together with differences in other physical properties [11].

Scheme 1. Photochromism of molecule A to molecule B.

Cleavage of the central C-O bond in ring-closed isomer (spiropyran form, SP) of 1',3',3'-trimethyl spiro[2H-1-benzopyran-2,2'-indoline] (BIPS) leads to the formation of ring-opened isomer (merocyanine form, MC) as depicted in scheme 2. In organic solvents, the ring-opening reaction is stimulated by UV irradiation and cause an intense absorption in the range 500-600nm, which gradually returns to the original closed form thermally or upon visible light irradiation [12-14].

Scheme 2. Spiropyran and merocyanine photoisomers of 1',3',3'-trimethyl spiro[2H-1-benzopyran-2,2'-indoline] (BIPS).

3.1. Chemicals

There are two types of spiropyrans used in this study, which are 6-nitro BIPS ($R_6=NO_2$, $R_8=H$) and 8-ethoxy-6-nitro BIPS ($R_6=NO_2$, $R_8=OC_2H_5$) as can be seen in scheme 2. The photochromic dyes were purchased from Sigma-Aldrich and absolute ethanol from RCI Labscan.
3.2. Sample preparation, UV irradiation and absorption measurements
In photolithography room, the dyes were dissolved individually in a polar solvent, absolute ethanol, at a concentration of 10^{-5} M. The samples were then transferred into 10 mm plastic cuvette. The cuvette was placed inside the chamber. After about one minute, the sample was irradiated with absolute ethanol as blank. The absorption spectra were measured prior to and after five seconds of UV irradiation.

3.3. Results and discussion
Both of 6-nitro BIPS and 8-ethoxy-6-nitro BIPS showed a color change upon UV irradiation. The very light pink of 6-nitro BIPS became brighter while the slightly purplish 8-ethoxy-6-nitro BIPS became darker, reflecting that both dyes undergo photoisomerization in the solvent. Different colors of the photoinduced form were obtained when the molecule structure of spiropyrans is varied [15], because of the presence of 8-ethoxy group attached to 6-nitro BIPS molecules in this study. Generally, nonpolar solvents favor the spiropyran form, while polar solvents produce the merocyanine structure [16].

Figure 3 illustrates the absorption spectra of 6-nitro BIPS and 8-ethoxy-6-nitro BIPS in ethanol at a concentration of 10^{-5} M for before and after five seconds of UV irradiation. Initially, 6-nitro BIPS is in very light pink color, thus gives zero absorption value. The absorption value increased to 0.172% after five seconds of irradiation. The maximum absorption wavelength was detected at 540nm with absorption peak covered the wavelength ranging from 650 to 430nm. On the other hand, the color of prepared 8-ethoxy-6-nitro BIPS is slightly purplish, which gives an absorption value of 0.029%. The value then increased to 0.124% with five seconds of UV exposure. The absorption value began to increase at wavelength of 680nm and ended at 450nm with absorption maximum at 570nm.

![Figure 3. Absorption spectra of 6-nitro BIPS and 8-ethoxy-6-nitro BIPS in ethanol.](image)

The absorption results for both BIPS photochromic dyes were presented in figure 4 while the wavelengths were tabulated in table 4. Although the initial absorption value for 6-nitro BIPS is lower than 8-ethoxy-6-nitro BIPS, the value became higher upon UV irradiation. Apart from that, the wavelength peak is slightly narrow compared to 8-ethoxy-6-nitro BIPS, 220nm to 230nm, respectively. The maximum wavelength (λ_{max}) for 6-nitro BIPS was observed at 540nm while 8-ethoxy-6-nitro BIPS at 570nm, which indicates that the peak shift towards longer wavelengths (bathochromic or red shift).
Figure 4. The absorption values of 6-nitro BIPS and 8-ethoxy-6-nitro BIPS.

Table 4. The wavelength peaks of 6-nitro BIPS and 8-ethoxy-6-nitro BIPS.

| Wavelength   | 6-nitro BIPS | 8-ethoxy-6-nitro BIPS |
|--------------|--------------|-----------------------|
| $\lambda_{\text{start}}$ (nm) | 650          | 680                   |
| $\lambda_{\text{max}}$ (nm)    | 540          | 570                   |
| $\lambda_{\text{end}}$ (nm)    | 430          | 450                   |

The presence of ethoxy group attached at $R_8$ position in 6-nitro BIPS molecule introduced another charge influential site within the 6-nitro BIPS molecule. Oxygen ions in ethoxy group act as electron-donating groups contributed as another resonation atom binds together with benzopyran and the electronegativity of the oxygen atom contributed as charge resonation and repulsion site. This repulsive force influence the magnitude of stabilization in benzopyran cyclic within 6-nitro BIPS and eventually allowed the photoisomerization of open structure at C-O bond in benzopyran at lower energy and longer wavelength as observed in 8-ethoxy-6-nitro BIPS. In addition, the position of ethoxy groups at $R_8$ also reduced the photochromism activation upon UV responsive light by contributing steric factor as observed by the broader absorption peak for 6-nitro BIPS with ethoxy functional group compared to 6-nitro BIPS without such substituent group.

4. Conclusion
Given that zero initial absorption value of 6-nitro BIPS was recorded and the maximum absorption wavelength of 6-nitro BIPS at 540nm while 8-ethoxy-6-nitro BIPS at 570nm, with the difference of 30nm only was detected, the UV irradiation chamber certainly provides absolute dark condition in this study. Thus, the developed chamber was successfully utilized for photochromic system since it can protect the dyes from environmental intervention.

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