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Application News

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Spectrophotometric Analysis

Changes in the Optical Properties of Photochromic Compounds: Use of Lightway™ Photoreaction Evaluation System

Photochromism refers to the phenomenon of reversible change in the optical properties of substances when irradiated by light. Although these photogenerated changes in the optical properties of substances are caused mainly by isomerization of the molecular structure, they may also be caused by dissociation of dimers.

From the viewpoint of thermal stability, photochromic compounds are classified as P-type or T-type. The P-type compounds are thermally-stable compounds which are formed by photoirradiation, and a second irradiation is necessary for reversibility. The T-type compounds are also formed by light irradiation but are thermally reversible. Photochromic compounds are applied as light-modulating materials, photomemory materials, and optical sensors. So-called dimming sunglasses (photochromic sunglasses) are one familiar use of photochromic compounds.

The Lightway [*1] photoreaction evaluation system developed by Shimadzu Corporation measures the absorption spectrum during photoirradiation of a sample, and enables easy observation of the process of change in photochromism. This article introduces observation of the changes in the optical properties of commercially-available photochromic compounds when irradiated with light.

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P-type Photochromic Compounds

Lightway consists of two orthogonally-arranged optical systems (light irradiation system and absorption spectrum measurement system). An LED is used as the light source of the irradiation system, enabling stable measurement in long-term use. A xenon flash lamp is used as the light source for the absorption spectrum measurement system and is capable of measuring the 250 to 800 nm wavelength range at minimum time intervals of 0.1 s by detection with a photodiode array (PDA). A stirrer is installed below the cell holder, making it possible to stir samples during photoreaction measurements.

Diarylethene and fulgide are known as a representative examples of a P-type photochromic compounds. In the case of diarylethene compounds, it is generally thought that the open-ring structure takes a closed ring form under photoirradiation in the ultraviolet (UV) region.

In this experiment, we measured an ethanol solution (concentration: 1×10^{-3} mol/L) of the diarylethene compound 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene. Fig. 1 shows the appearance of the Lightway photoreaction evaluation system used in this measurement, and Table 1 shows the measurement conditions.

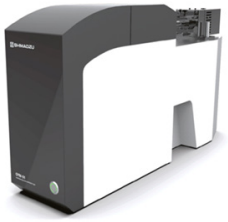

Fig. 1 Appearance of Lightway™ Photoreaction Evaluation System (Appearance of System with Iris-S LED Light Source Manufactured by Cell System Co., Ltd.)

Table 1 Measurement Conditions

Instrument	:	Lightway
Application	:	Photoreaction measurement
Irradiation wavelength	:	365 nm/550 nm
Measurement interval/time	:	1 s/20 min
Measured photon count	:	1.00E16 photon/s (365 nm) 1.00E16 photon/s (550 nm)

Fig. 2 shows the change of the sample color before and after the measurement, Fig. 3 shows the time change in the spectrum under irradiation of 365 nm, and Fig. 4 shows the time change in the spectrum when irradiated with 550 nm after irradiation with 365 nm.

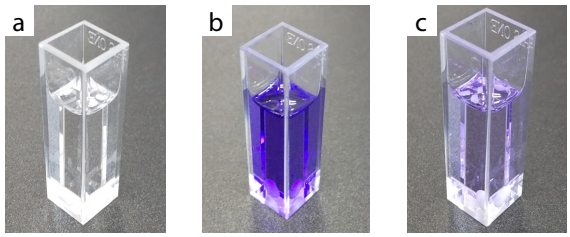

Fig. 2 Change of Sample Color (a: Before Irradiation, b: After Irradiation of 365 nm for 20 min, c: Irradiation of 365 nm for 20 min → Irradiation of 550 nm for 20 min)

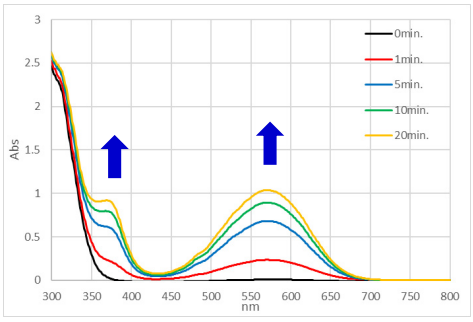

Fig. 3 Time Change of Spectrum Under 365 nm Irradiation

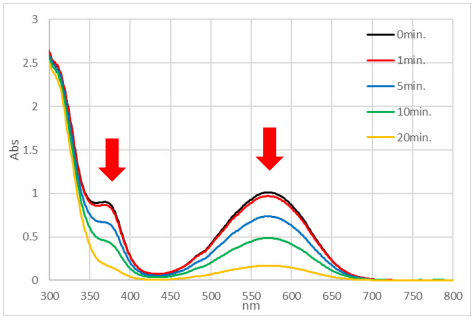

Fig. 4 Time Change of Spectrum Under 550 nm Irradiation After 365 nm Irradiation

From Fig. 3, under irradiation of 365 nm, absorption peaks appear around 375 nm and 580 nm as the irradiation time increases, and because these absorption peaks appear, the sample color changes from colorless to blue, as shown in Fig. 2. Furthermore, from Fig. 4, the absorption peaks that appeared under irradiation with 365 nm decrease under irradiation with 550 nm following 365 nm irradiation. Thus, it is possible to observe the reversible change of the optical properties of this P-type photochromic compound under photoirradiation.

T-type Photochromic Compounds

Among the T-type photochromic compounds, azobenzene and spiropyran are known to be compounds in which photochromism is caused by isomerization of the molecular structure. In the case of spiropyran, it is thought that photoirradiation in the UV region induces photoconversion of the closed-ring structure to an open-ring structure. Here, an ethanol solution (concentration: 5×10^{-4} mol/L) of the spiropyran compound 1,3,3-trimethylindolino-6′-nitrobenzopyrylospiran was measured under the conditions in Table 2.

Fig. 5 shows the change of the sample color before and after the measurement, and Fig. 6 shows the time change of the spectrum under irradiation of 365 nm. Fig. 7 shows the time change of the spectrum when the light source was extinguished after 365 nm irradiation, and the sample was then allowed to stand in a room temperature environment.

Table 2 Measurement Conditions

Application	: Photoreaction measurement/ spectrum measurement
Irradiation wavelength	: 365 nm (photoreaction measurement)
Measurement interval/time	: 1 s/3 min (photoreaction measurement) 30 s/2 h (spectrum measurement)
Irradiation photon count	: 1.00E16 photon/s (365 nm, photoreaction measurement)

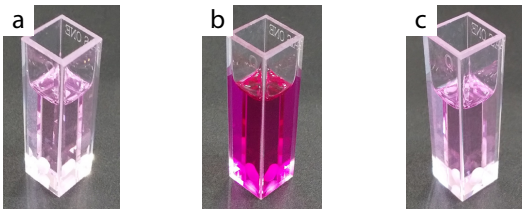

Fig. 5 Change of Sample Color
(a: Before Irradiation, b: After 365 nm Irradiation, c: After Standing 2 h Following 365 nm Irradiation for 3 min)

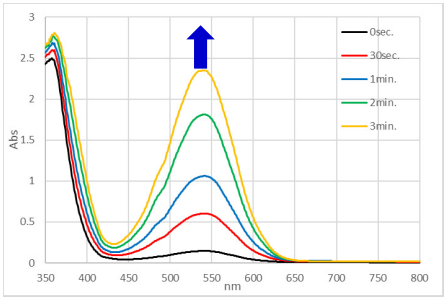

Fig. 6 Time Change of Spectrum Under 365 nm Irradiation

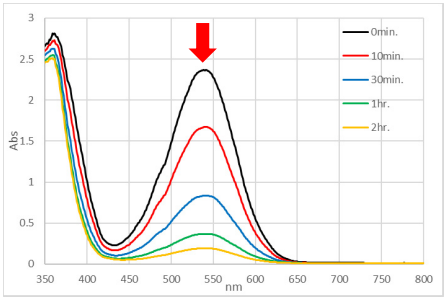

Fig. 7 Time Change of Spectrum While Standing in Room Temperature Environment After 365 nm Irradiation

From Fig. 6, when the sample is irradiated with 365 nm, the absorption peak around 545 nm increases with time, and because this absorption peak increases, the sample color changes to deep red, as shown in Fig. 5. From Fig. 7, when the sample is allowed to stand in a room temperature environment after the light source is extinguished, the absorption peak around 545 nm decreases, and the sample returns to its original color in about 2 h. It was possible to observe the changes in the optical properties of this T-type photochromic compound under photoirradiation, as well as its thermal reversibility.

Hexaarylbiimidazole (2,2′-bis(2-chlorophenyl)-4,4′,5,5′-tetraphenyl-1,2′-biimidazol: HABI) is known as a substance which shows T-type photochromism without isomerization of the molecular structure. In HABI, dimers undergo dissociation upon photoirradiation and form triphenyl imidazolyl radicals (TPIR). These radicals then undergo recombination and the TPIR is reconverted thermally to HABI. This thermal change occurs at higher rate compared with isomerization, An ethanol solution of HABI (concentration: 1×10^{-3} mol/L) was measured under the conditions in Table 3. Fig. 8 shows the measurement results.

Table 3 Measurement Conditions

Application	: Spectrum measurement
Irradiation wavelength	: 365 nm
Measurement interval/time	: 0.2 s/1 min
Irradiation photon count	: 1.00E16 photon/s
Irradiation time	: 30 s

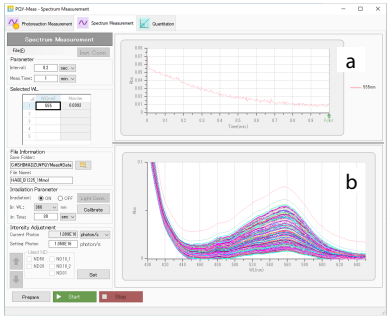

Fig. 8 "PQY-Meas" Screen
(a: Time-Course Graph for 555 nm Irradiation, b: Overwritten Spectra)

When HABI is irradiated with 365 nm, it is known that the absorption peak around 550 nm increases with time. In the spectrum measurement with PQY-Meas, which is the software that controls Lightway, automatic closing of the instrument shutter in front of the LED irradiation light source is possible after light irradiation for the time shown in Table 3, allowing measurement under a light-shielded condition. Fig. 8(a) shows the time-course graph for the period of 1 min after light shielding. It can be understood that the sample returned to its original condition in about 30 s after light shielding.

Conclusion

By using the Shimadzu Lightway photoreaction evaluation system, it was possible to observe the changes in the optical properties of P-type and T-type photochromic compounds when irradiated with light. In the P-type, reversible changes occur upon photoirradiation, while in the T-type, the optical properties initially change under photoirradiation, but then return thermally to the original state. Among T-type photochromic compounds, it was also found that the time required for return to the original state differs depending on the structure after the photogenerated change.

*1 The Lightway photoreaction evaluation system was developed by Shimadzu Corporation under the supervision of Prof. Osamu Ishitani and Associate Prof. Yusuke Tamaki of the Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology.

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