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The photophysical behavior of the photochromic naphthopyran derivative having photo-switching ability

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Abstract

The photophysical behavior of the photochromic naphthopyran derivative **9** with photo-switching ability has been investigated in solution phase as well as in crystalline form. The proposed switching motifs might be a versatile framework in the development of photonic devices whose properties can be toggled between two states on exposure to electromagnetic radiations. The closed form of **9** undergoes reversible transformation upon irradiation with light by changing the molecular structure from ring closed conformation **9** to the ring opened form **10**. The compound **9** exhibited first absorption signal at 238 nm with shoulder peak at 261 nm and second absorption signal at 353 nm while on photo-irradiation, the colorless solution of **9** turn to colored and there was ratiometric downfall in the signal intensity for shoulder signal at 261 nm as well as second absorption signal at 353 nm and ultimately results in the disappearance of these both signal after 20 min of irradiations. Meanwhile, the colorimetric change in the reaction solution and considerable shift in the absorption and emission signal intensity as well as position suggest the conformational changes in the molecules from less conjugate conformation **9** to the extended conjugated conformation **10**.

Key words: photochromic; naphthopyran; photo-switching; reversible transformation.

Introduction

Photochromism can be defined as a light induced reversible photoisomerization process in organic molecules between two isomers having different absorption spectra [1,2]. Photochromic molecules undergo a reversible color change, which originates as a results of shift in optical absorption due to changes in molecular structure or conformation in respond to electromagnetic radiation attracts considerable attention from various fields of chemistry, physics and material science as potential candidates for practical applications [3-7]. The photochromism describes a change in the optical properties of a material in response to illumination proclaim growing interest in fundamental academic research as photo-responsive materials with controllable photophysical characteristics by adjusting photoirradiation flux. Alongside the rapid development of modern science and technologies, materials for fast and high density data storage are in high demand. The photochromic compounds exhibits emerging applications as elements of field effect transistors, optical memory devices, light emitting diodes, photovoltaic appliance, smart window, ophthalmic glasses, holographic gratings, logic accessories, drug delivery vesicles, organic semiconductor, high resolution fluorescence imaging and fluorescent sensing materials [8-18]. The photochromic molecules exhibit shape-memory properties through temporary shape change and back recovery to their permanent shape on exposure to the external stimuli [19,20]. The investigation of these molecules may lead to novel photoresponsive materials for photonic applications [21]. The incorporation of photoswitches has been benevolence to researchers in the material and biological sciences offers the conversion of external inputs to useful signals, transistor generation and optoelectronic building blocks in molecular electronics [22-24].

In the past decade, substantial attention in the field of organic photochromic materials has been focused because of their rapid and often instant change of physical and electronic properties such as color, luminescence, conductivity, refractive index which exhibit fascinating applications as rewritable optical memory media, photo-optical switches because of tunable optoelectronic features using external stimuli, such as light, temperature and electricity. Charge transport in organic molecules is actively explored toward the realization of novel electronic circuits and computational devices. Among various types of photochromic dyes, the naphthopyran derivatives are the most promising molecules for electronic circuit applications due to their excellent ring-closing and ring opening isomeric transformation upon light irradiation with adherent superiority of reversibility, fine control over fading kinetics and high fatigue resistance. These switches are particularly valuable due to tunable properties triggered by light, the most widely available, non-invasive, and environmentally benign external stimulus [25-31].

On the basis of these findings, the design and development of new photochromic molecules with photocontrolable fluorescence characteristics in both solution and solid state is demanding in academic, architecture, automotive industries, cosmetics, textiles and decoration. Herein, we report the photophysical behaviors of naphthopyran derivative methyl-9-(dimethylamino)-2,2-bis(4-methoxyphenyl)-2*H*-benzo[*h*]chromene-5-carboxylate **(9)** having photo-switching ability. From single crystal X-ray diffraction analysis, it was confirmed that the compound **9** predominantly exist in ring closed conformation **9** and electromagnetic radiation transform the molecule into ring opened conformation **10** which revert back to the original structure in dark. The interesting photophysical properties both in solid and solutions might be useful for practical application in optoelectronics, photochromic eyeglass lenses, switchable color window glasses, fluorescence sign board material and photonics.

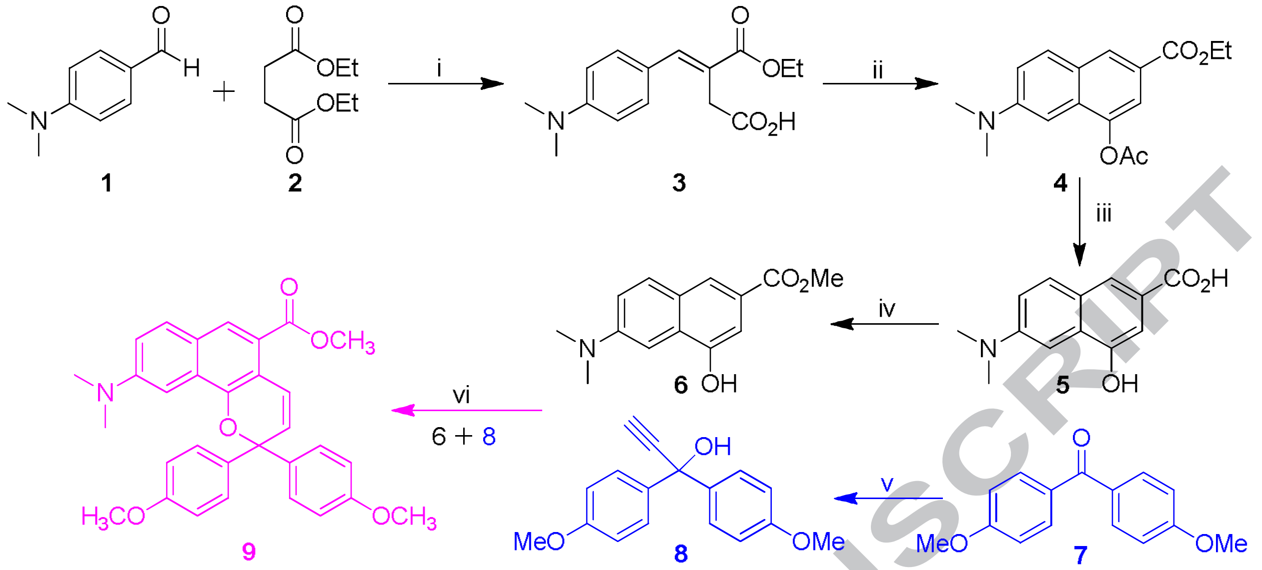
Experimental

Substrate and reagents

All the chemicals and reagents were purchased from Aldrich, Samchun Chemicals and Jin Chemical & Pharmaceutical Company. Briefly, ethanol, methanol, chloroform, water, acetonitrile, dimethyl sulfoxide, diethyl ether, ethyl acetate, *n*-hexane, toluene and 1,4-dioxane (Samchun Chemicals, Korea), H_2SO_4, HCl (Jin Chemical & Pharmaceutical Co. Ltd., Korea) were used in these experiments.

Measurements and instrumentations

The reaction progress was monitored by thin layer chromatographic (TLC) analysis and R_f values were determined by employing pre–coated silica gel aluminium plates, Kieselgel 60 F_{254} from Merck (Germany). Melting points were determined on Fisher scientific (USA) melting point apparatus and are uncorrected. The UV lamp (100 W) was used with photo-intensity 9.0 mW/cm^2 having 360 nm for irradiation. The absorption spectra were measured on a Hitachi U-3300 spectrophotometer. The fluorescence spectra were measured on a SLM8100 spectrofluorometer (Aminco, USA) with a Xe-arc lamp light source using 4 or 8 nm band pass excitation and emission monochromators, in which the rhodamine B solution was used as a reference to correct for variation of the Xe light source with time and wavelength. All spectroscopic measurements were carried out in the presence of 1 x 10^{-5} Mdm^{-3} of **9**. The thermogravimetric analysis (TGA) was performed by using SDT Q600 (V20.9 Build 20) simultaneous TGA/DSC instrument. Proton nuclear magnetic resonance spectra were recorded on a Bruker Avance 400 MHz spectrometer with tetramethylsilane (TMS) as an internal standard. The chemical shifts are reported as sigma values in ppm downfield from TMS of the indicated organic solution. Peak multiplicities are expressed as follows: s, singlet; d, doublet, dd, doublet of doublets; q, quartet and m, multiplet. Single crystal data was obtained by using Bruker SMART APEX II X–ray Diffractometer CCD equipped with MO X–ray tube and graphite monochromator at the ambient temperature. Mass spectra were recorded on the JEOL MStation JMS–700 (USA). The schematic representations of synthetic route adopted to obtain 9 are shown in Scheme 1.



Scheme 1: Synthesis of **9**: Reagents and conditions: (i) Na, EtOH, reflux, N_2 gas; (ii) Anh. Sodium acetate, acetic anhydride; (iii) NaOH, EtOH; (iv) Conc. H_2SO_4, MeOH; (v) 18 W % sodium acetylide/Xylene, anh. THF; (vi) Al_2O_3, toluene, reflux.

Synthesis of (*E*)-4-[4-(dimethylamino)phenyl]-3-(ethoxycarbonyl)but-3-enoic acid (3)

N,*N*-Dimethyl amino benzaldehyde (100 g, 0.67 mL, 1 eq) and diethyl succinate (140 g, 1.2 eq) were completely dissolved in 500 mL anhydrous ethanol at 40-50 °C. Sodium (18.5 g, 1.2 eq) was separately dissolved in anhydrous ethanol and added slowly in the reaction vessel with the help of dropping funnel keeping low temperature. The quick addition may generate solid in the reaction mixture which hinder stirring. The reaction mixture was heated under reflux at 80-90 °C after complete addition into the reaction mixture followed by constant monitoring the reaction progress with the help of TLC. On complete consumption of starting materials, the reaction mixture was cooled, removed ethanol on reduced pressure to left behind high viscous red color fluid. The organic compound was extracted by using solvent extraction (ethyl acetate: H_2O = 1:1, 500 mL). The pH was set at 5.5 using 2 *N* HCl and organic layer was extracted twice and dehydrated by putting $MgSO_4$ followed by evaporation of excess solvent under reduced pressure leave behind **3** with high yield (157 g, 85 %). The structure of **3** was characterized by ^1H NMR analysis and ^1H NMR data are given below

^1H NMR ($CDCl_3$, ppm): δ 1.23 (t, 3H), 2.94 (s, 6H), 3.45 (s, 3H), 4.15 (q, 2H), 6.73 (d, 2H), 7.29 (d, 2H), 7.63 (s, 1H), 12.20 (s, 1H).

Synthesis of ethyl 4-acetoxy-6-(dimethylamino)-2-naphthoate (4)

Compound **3** (100 g, 0.36 mol, 1 eq) and anhydrous sodium acetate (29.5 g, 1 eq) were added in acetic anhydride (500 mL) and heated under reflux for 4 h. On completion, the reaction mixture was cooled to room temperature and poured in 3 L of cold water which afford brown color solid. The solid product was filter and removes the moisture on vacuum dry oven for one day.

^1H NMR ($CDCl_3$, ppm): δ 1.42 (t, 3H), 2.47 (s, 3H), 3.06 (s, 6H), 4.40 (q, 2H), 6.73 (s, 1H), 7.15 (d, 1H), 7.71 (s, 1H), 7.80 (d, 1H), 8.35 (s, 1H).

Synthesis of 6-(dimethylamino)-4-hydroxy-2-naphthoic acid (5)

Compound **4** (100 g, 0.33 mol, 1 eq) was dissolved in 200 mL ethanol and sodium hydroxide (80 g, 6 eq) was separately dissolved in 1 L water. Both solution was mixed and stirred for 2 h. at 80-90 °C. After that ethanol layer was removed on reduced pressure and set the pH 6 of reaction mixture by using 2 N HCl and extracted organic layer using ethyl acetate, dried with $MgSO_4$, finally removed the excess solvent on rotary which left behind deep brown product, yield (70 g, 85 %).

^{1}H NMR ($CDCl_3$, ppm): δ3.32 (s, 6H), 7.07 (s, 1H), 7.23 (s, 1H), 7.87 (s, 1H), 10.00 (s, 1H).

Synthesis of methyl 6-(dimethylamino)-4-hydroxy-2-naphthoate (6)

Compound **5** (100 g, 0.43 mol, 1 eq) dissolved in 2 L methanol and slowly added 25 mL concentrated H_2SO_4 inside the reaction mixture and reflux for 5 h. After that methanol was evaporated on rotary and reaction mixture was neutralized using NaOH, extracted with ethyl acetate and water (due to low solubility product, ethyl acetate and water ratio was kept 1.5:1), dried the ethyl acetate layer with $MgSO_4$ evaporated the excess solvent on rotary left behind solid product of **6**, yield (85 g, 80 %).

^{1}H NMR ($CDCl_3$, ppm): δ3.13 (s, 6H), 3.94 (s, 3H), 6.05 (s, 1H), 7.15 (s, 1H), 7.20 (d, 1H), 7.75 (s, 1H), 7.75 (d, 1H), 8.08 (s, 1H).

Synthesis of 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol (8)

18 W % sodium acetylide in xylene/mineral oil 121.1 mL (0.45 mol, 1 eq) was dissolved in anhydrous THF (1L) saturated with acetylene gas. After that 4,4-dimethoxybenzophenone 100 g (0.41 mol, 1 eq) was put inside the reaction mixture under nitrogen and stirred for 24 h. at room temperature. The product was extracted by solvent extraction using ethyl acetate and water, organic layer was dried with $MgSO_4$ and solid product on vacuum drier. After complete drying, the product again dissolve in ethyl acetate and poured into 1 L hexane slowly under stirring which afford **8** as white color solid, yield (99 g, 90 %).

^{1}H NMR ($CDCl_3$, ppm): δ2.70 (s, 1H), 2.85 (s, 1H), 3.78 (s, 6H), 6.85 (d, 4H), 7.48 (d, 4H).

Synthesis of methyl 9-(dimethylamino)-2,2-bis(4-methoxyphenyl)-2*H*-benzo [*h*] chromene-5-carboxylate (9)

Compound **6** (100 g, 0.41 mol, 1 eq), compound **8** (87 g, 0.8 eq) and Al_2O_3 (415 g, 10 eq) was put inside the reactor (connected with Dean-Stock device) containing toluene (3 L). The reaction mixture was deoxygenized with the stream of nitrogen gas followed by refluxing the reaction mixture. On completion, the reaction mixture was cooled to room temperature, washed with NaOH solution and removed the toluene on rotary. After that solid product was mixed with ethyl acetate: water and organic layer was separated, removed excess solvent on rotary to afford **9** which was purified by column chromatography using hexane: ethyl acetate: toluene (5:1:1) solvent system. Fine yellow crystals of **9** were collected on mixing it with ethyl acetate [32-38].

^{1}H NMR ($CDCl_3$, ppm): δ3.09 (s, 6H), 3.76 (s, 6H), 3.9 (s, 3H), 6.09 (d, 1H), 6.79 (d, 4H), 7.05 (dd, 1H), 7.25 (d, 1H), 7.35 (d, 4H), 7.60 (dd, 2H), 7.95 (s, 1H).

Crystal structure determination of compound 9

In order to get better insight about the predominant conformation of compound **9**, the fine crystal of **9** was grown on ethyl acetate and characterized by single crystal X–ray diffraction analysis. From the single crystal obtained was confirmed that molecule **9** predominantly exist in ring closed conformation (Fig. 1), the closed form shows that both aromatic ring and naphthopyran moieties of the molecule consist of orthogonal nonplanar structure. Thus, the closed form has a stacking rearrangement with the adjacent phenyl rings [39].

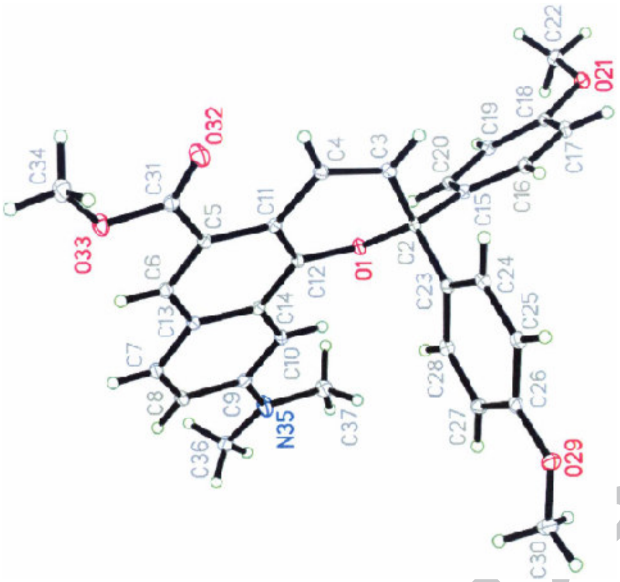


Fig. 1: X–Ray crystal structure of **9**.

Crystal data

The crystallographic data obtained for compound **9** are shown in Table 1

Table 1. Crystallographic data for compound **9**

Description	Experimental values	Description	Experimental values
Empirical formula	$C_{31}H_{29}NO_5$	β	112.334 (1)°
Formula weight	495.55	γ	93.484 (1)°
Temperature	100 K	Volume	1211.85 (3) $Å^3$
Appearance	Pale yellow	z	2
Crystal system	Triclinic	Density (calculated)	1.358 Mg/m^3
Space group	$P\bar{1}$	Absorption coefficient	0.09 mm^{-1}
a	9.8923 (1) Å	F(000)	524
b	10.9535 (1) Å	Crystal size	0.20 x 0.16 x 0.16 mm^3
c	12.1720 (2) Å	Theta range for data collection	2.2–28.4°
α	93.860 (1)°	Refinement method	Full-matrix least-squares on F^2

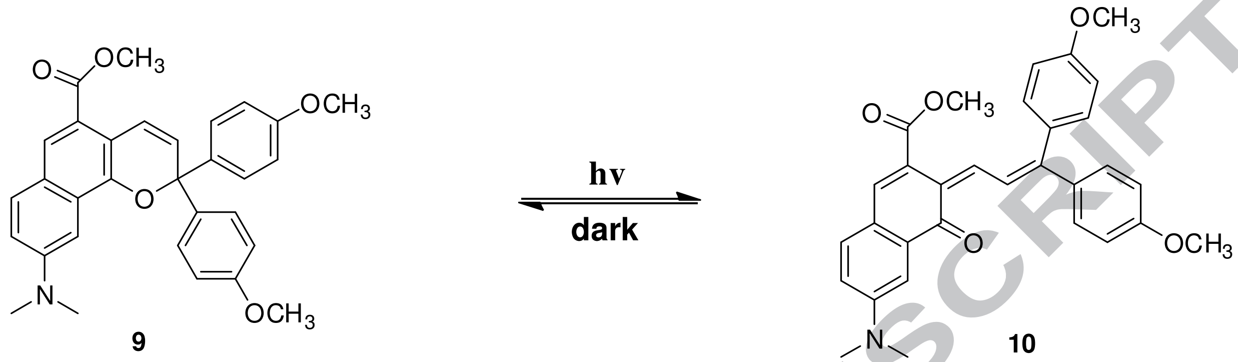
Structure solution and refinement

Data collection: APEX II (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT (Bruker, 2009); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008).

Results and discussions

Photoisomerization mechanism

The schematic representation for the photoisomerization mechanism of **9** are shown in Fig. 2.The compound **9** in solution form was almost colorless in dark while it turns to color on photoirradiation with considerable enhancement in the fluorescence emission intensity suggesting the photoisomerization of less conjugated conformation **9** into extended conjugated conformation **10**. As shown in Fig. 2, there was π electronic delocalization up to higher extent in the ring opened conformation **10** in comparison to the ring closed conformation **9**. Moreover, the electron withdrawing methoxy groups attached to para position of phenyl ring in the core structure of **9** facilitate the photoisomerization from less conjugated conformation **9** into extended conjugated conformation **10**. As soon as molecule was put in dark condition, it reverts back to the more stable ring closed conformation while the ring opening process can only be triggered by external stimuli (light in this case).



9
Ring closed conformation

10
Ring open conformation

Fig. 2: The photoisomerization mechanism of **9**. The left side snapshot of reaction solution was taken in day light while right side image was obtained under UV-lamp by illuminating at 365 nm.

Spectroscopic properties

The spectroscopic properties of **9** were performed in 1,4-dioxane at 25 °C and the corresponding spectra are shown in Fig. 3. The solution of closed form of compound **9** was colorless as shown by inset of Fig. 3 and it exhibited first absorption signal at 238 nm with shoulder peak at 261 nm and second absorption signal at 353 nm with considerable molar absorption coefficient values of 6.3×10^4 $M^{-1}cm^{-1}$, 3.7×10^4 $M^{-1}cm^{-1}$ and 1.3×10^4 $M^{-1}cm^{-1}$, respectively. Interestingly, on photo-irradiation, the solution color of **9** turn to colored and there was ratiometric downfall in the signal intensity for shoulder signal at 261 nm as well as second absorption signal at 353 nm and ultimately results in the disappearance of these both signal after 20 min of irradiations. The change in color of solution from colorless to color is the indication of structural changes in the target molecule **9** from less conjugated conformational structure to the extensive conjugated conformational structural **10** as the compound **9** have fragile carbon to oxygen ether linkage in the core skeleton and photo-irradiation cause breakage of ether linkage with subsequent transformation into new conformation **10** with emergence of carbonyl functionality as well as new double bond which facilitate the delocalization of electronic cloud from one side of the molecule to the other side.

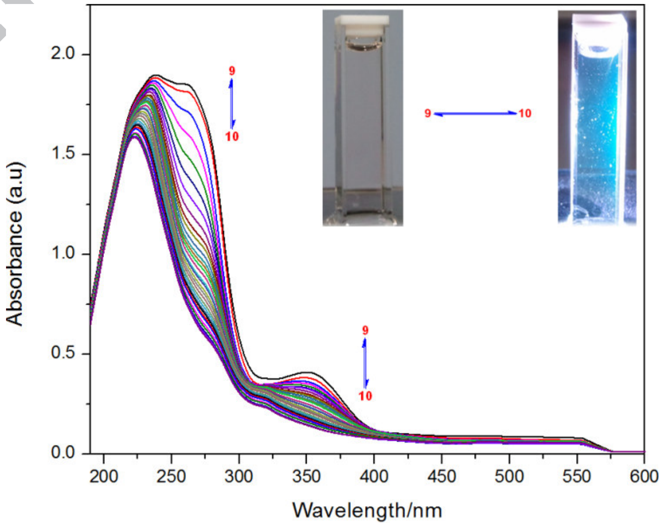


Fig. 3: Electronic absorption spectrum of compound **9** before and after irradiation in 1,4-dioxane at 25 °C on periodic exposure to xenon lamp after regular interval of 1 min; inset snapshot represent the visual color change of compound **9** solution on photo-irradiation with xenon lamp.

When the open form sample put in the dark room, it returned to closed form. In the case of closed form **9**, there was a little emission at 422 nm in 1,4-dioxane at ambient temperature. However, a remarkable emission appeared at 440 nm when the ring closed form **9** changed to the ring open form **10** upon irradiation with ILC PS300-1 Xenon lamp. In particular, there was constant increment in the fluorescence emission intensity with gradual bathochromic shift by increasing the irradiation time from 0 min to 20 min. The bathochromic shift in the fluorescence spectrum of **9** reflect the decrease in energy gape between HOMO to LUMO transition harvesting low energy emission (longer wavelength) spectra due to ring opened conformation **10** triggered by photo irradiation as shown in Fig. 4 while emission intensity was found to decreased gradually by keeping the sample solution in dark room.

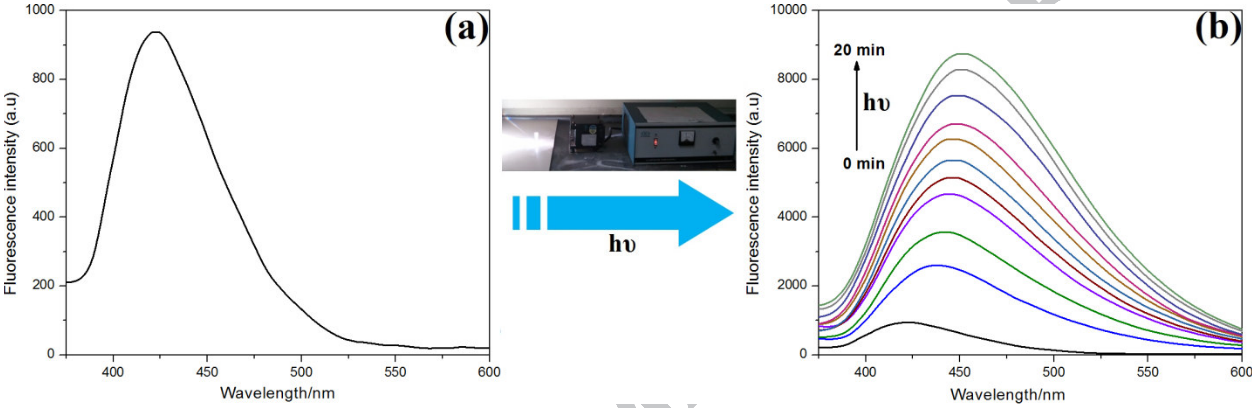


Fig. 4: Fluorescence emission spectra of **9** (1×10^{-5} $molL^{-1}$) in 1,4-dioxane at 25 °C; (a) before irradiation and (b) after irradiation with ILC PS300-1 Xenon lamp on different time interval from 0-20 min.

Solid state photochromism

In the past decade, a number of photochromic molecules have been proposed to improve their photochromic properties such as fatigue resistance, reversibility and stability. Unfortunately, most photochromic dyes do not show photoisomerization in the crystalline state and the photochromic properties have been studied in the solution phase. On this basis, the design and development of photochromic molecules capable of undergoing photochromism in different states of the matter is a wide topic. The present research was conducted to develop molecules with interesting photochromic properties in solution phase and in bulk solid state. From a practical viewpoint, the solid-state photochromism exhibit prospective potential applications, therefore, optical switches based on materials in solid state and even in single crystalline state is indispensable and first important steps for the fundamental studies concerning development of photoelectronic systems for designing high efficient optical memories, solid-state photonic switches, information storage, molecular machines, recording digital information, nonlinear optics and photochromic ophthalmic lenses [40-46]. Keeping in mind the above findings, beside photochromic behavior investigation in solution phase, we have further investigated the photoluminescence measurement of compound **9** in solid state and the results are shown in Fig. 5. The compound **9** showed a characteristic photoluminescence emission band at 467 nm and this photoluminescence emerged by the transformation of ring closed conformation **9** to the ring opened conformation **10** triggered by the light source of the spectrophotometer. The delightful photoluminescence properties of the target compound might be utilized for practical development of photonic materials and photoswitchable accessories.

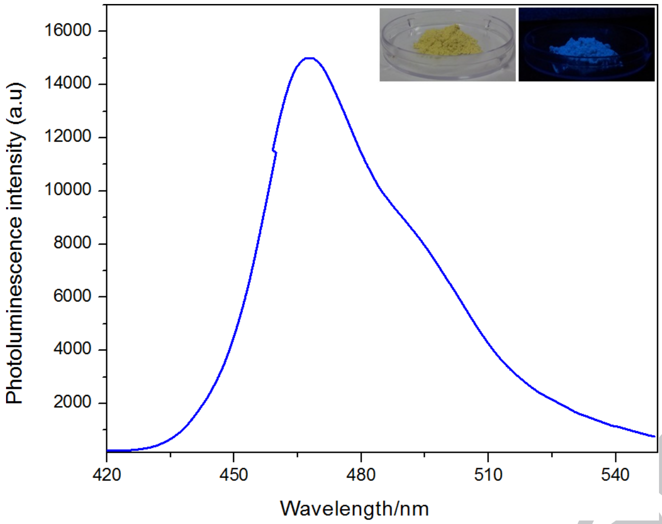


Fig. 5: Solid state photoluminescence emission spectrum of the target compound at 25 °C; Inset photograph showed the visual appearance of **9** in day light (inset, left side photograph) and under UV-lamp by illuminating at longer wavelength of 365 nm (inset, right side photograph).

Fluorescence life time measurement

The measurement of fluorescence life time for the target compound was performed with TRPL method using iHR 320 imaging spectrometer (iHR series spectrometer, Horiba scientific, Japan). The fluorescence decay of open form was found to be practically mono-exponential, which confirmed that this compound possessed only one fluorescent species with a single emission process. As can be seen in Fig. 6, the fluorescence decay curve of open form was clearly mono-exponential with τF value of 0.673 ns. This decay curve was due to open conformation of the target compound and the conformational changes from ring closed conformation **9** to the ring opened conformation **10** was triggered by the light source of the spectrophotometer. Thus, this result showed a clear correlation between the fluorescence lifetime and electronic absorption, demonstrating that there exists only one open form having a very short fluorescence lifetime.

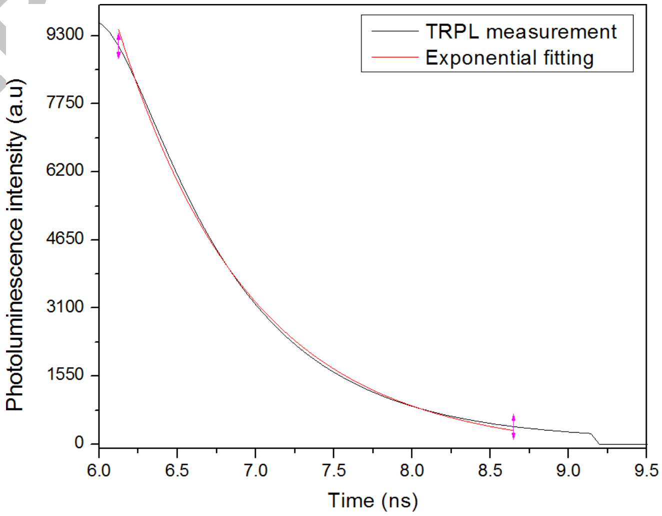


Fig. 6: The photoluminescence decay curve for the compound **10** deduced from the exponential decay of the TRPL signal.

Solvatochromism study

To evaluate the effect of solvent polarities on the photochromic behavior of compound **9**, the fluorescent spectral measurements was carried out in various solvents of different polarities by photoirradiating the sample for 2 min followed by subsequent recording of emission spectra and the results obtained are tabulated in Table 2. Correlation of the fluorescence emission response of compound **9** with different solvents revealed that there was slight bathochromic shift in the emission spectrum by increasing solvent polarity. The solvent with lower values of π* stabilized the energy level of the target molecule, hence their emission spectra appear at shorter wavelength as the stabilized energy level need relatively higher energy for electronic transition. Meanwhile, the fluorescence intensity partially depending on the β values of the indicated solvents. There was successive increment in the fluorescence intensity for the polar aprotic solvent while there was slight downfall in the fluorescence intensity in case of the polar protic solvent due to involvement in the hydrogen bonding.

Table 2: Effect of solvent polarities on the photophysical behavior of compound **9**

S. No.	Solvent	$^{a}\lambda_{max}$ (nm)	$^{b}F/F_o$	$^{c}\pi^*$ [47]	$^{d}\beta$ [47]
1	Diethyl ether	420	2.23	0.27	0.47
2	Cyclohexane	428	2.18	0	0
3	Toluene	434	2.27	0.54	0.11
4	1,4-Dioxane	440	2.71	0.55	0.37
5	Acetonitrile	443	3.02	0.75	0.31
6	Water	453	2.43	1.09	0.18

[a] Fluorescence emission maxima.
[b] F/F_o is determined as a ratio between the maximum fluorescence intensity (F, after 2 min irradiation of sample) and minimum fluorescence intensity (F_o, without photoirradiation).
[c] Index of solvent polarity-polarizability.
[d] Parameter related to the solvent's ability to accept a proton in a solute-solvent hydrogen bonding.

Thermogravimetric analysis

The thermal stability of fluorescent organic materials is prerequisite for the durability, lifetime and efficiency of photochromic materials. Degradation of fluorescent amorphous organic materials may reduce the broad spectrum applications of the photoswitching molecules. To assess the thermal stability of **9**, thermogravimetric analysis (TGA) was performed by flowing dry nitrogen atmosphere at the heating rate of 10 °C/min using 2.4 mg sample in the temperature range of 25–700 °C. The compound **9** shows appreciable thermal stability up to 285 °C without any weight loss, afterward, there was continuous weight loss and molecules loses its 80 % of weight at 400 °C and it was not completely decomposed up to 700 °C (Fig. 7). Due to high thermal stability, the compound **9** can be used as dopant in the manufacturing of photochromic window glasses, photochromic car windows and sign board material where it meet the requirement of sustaining high temperature without thermal decomposition.

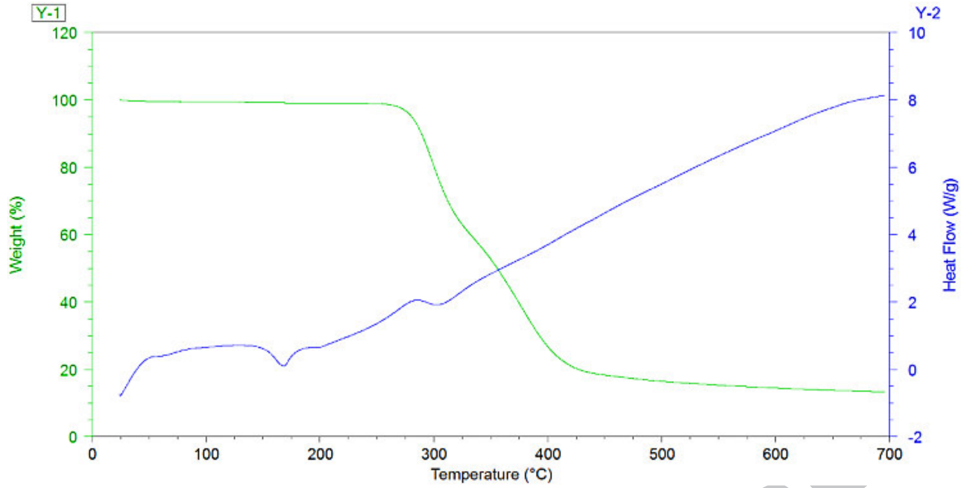


Fig. 7: Thermogravimetric analysis results for compounds **9**.

Conclusion

The photophysical behavior of photochromic naphthopyran derivative **9** with photo-switching ability has been investigated in solution phase as well as in crystalline form. The compound **9** exhibited photoswitching characteristics assessed by spectrophotometric measurement. The target compound exhibited first absorption signal at 238 nm with shoulder peak at 261 nm and second absorption signal at 353 nm with considerable molar absorption coefficient values of 6.3×10^4 $M^{-1}cm^{-1}$, 3.7×10^4 $M^{-1}cm^{-1}$ and 1.3×10^4 $M^{-1}cm^{-1}$, respectively. Interestingly, on photo-irradiation, the colorless solution of **9** turn to colored and there was ratiometric downfall in the signal intensity for shoulder signal at 261 nm as well as second absorption signal at 353 nm and ultimately results in the disappearance of these both signal after 20 min of irradiations. The change in color of solution from colorless to color is the indication of structural changes in the target molecule **9** from less conjugated conformational structure to the extensive conjugated conformational structural **10.** Meanwhile, in the case of fluorescence emission spectral measurement, there was a low intensity signal at 422 nm recorded in 1,4-dioxane. However, a remarkable emission appeared at 440 nm when the ring closed form **9** changed to the ring open form **10** upon irradiation with ILC PS300-1 Xenon lamp by turning the sample solution from colorless to the colored. Concurrently, in the crystalline form, the compound **9** presents an intense and broad emission band at λ_{max} 467 nm. It indicates that open form is linked to the naphthopyran part conjugated with the photochromic skeleton. Therefore, photochromic properties play an important role for the extension of π-conjugation state. The solvatochromism study of the compound **9** in variety of organic solvents with different polarities showed slight bathochromic shift on increasing solvent polarities suggest that the excited state of **9** is more polar than the ground state. The fluorescence decay of open form was found to be practically mono-exponential, which confirmed that this compound possessed only one fluorescent species with a single emission process. The target compound exhibited considerable thermal stability up to 285 °C without any weight loss assessed by thermogravimetric analysis.

Acknowledgments

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Highlights

- The photophysical behavior of the photochromic naphthopyran derivative **9** has been investigated in solution phase as well as in crystalline form.
- The closed form of **9** undergoes reversible transformation upon irradiation with light by changing the molecular structure from ring closed conformation **9** to the ring opened form **10**.
- The compound **9** exhibited an auspicious ratiometric fluorescence response on exposure to white light.
- The bathochromic shift on increasing solvent polarities suggests that the excited state of **9** is more polar than the ground state.

Graphical abstract

The photophysical behavior of the photochromic naphthopyran derivative having photo-switching ability

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The photophysical behavior of the photochromic naphthopyran derivative has been investigated in solution phase as well as in crystalline form.