行政院國家科學委員會補助專題研究計畫 X 成果報告 □期中進度報告

設計及合成光致變色材料及其光化學反應機構研究

Design and synthesis of photochromic colorants and their photochemical mechanism studies

計畫類別：X 個別型計畫　□ 整合型計畫

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執行單位：東海大學化學系

中　華　民　國　100　年　9　月　25　日

目 錄

一、中文摘要

本報告為執行國科會專題研究計畫「設計及合成光致變色材料及其光化學反應機構研究」之成果報告，此計劃為期兩年，第一年計劃研究內容分為四小項，分別為：(I) 新型氧氮雙環光致變色物之合成；(II) 香豆素及耦合衍生物之合成及其光化學性質測試；(III) 新型π–π stacking 控制之潛在光致變色物之設計與合成；(IV) 5-氮香豆素衍生物之合成及其性質測試。其中第 I 項，亦即：「新型氧氮雙環光致變色物之合成」，在進行目標物之合成時，我們碰到一些困難，因此改變研究方向。我們發現此類衍生物有可能充作化學感測器，用以偵測 cyanide ion，又這類化合物對光非常敏感，照 UV 光後可生成 indazole 衍生物。第 II 項，亦即：「香豆素及耦合衍生物之合成及其光化學性質測試」，我們已成功地合成出目標物，並發現此類化合物不但對光敏感且具熱致變色性質，結果已發表於今年(2011)之 Organic Letters 期刊。第 III 項，亦即：「新型π-π stacking 控制之潛在光致變色物之設計與合成」，我們已完成目標物之合成，並成功地取得其 X-ray 晶體結構，可惜此香豆素衍生物並無預期之光致變色性質。第 IV 項，亦即：「5-氮香豆素衍生物之合成及其性質測試」，我們已成功地合成出目標物，性質測試結果顯示目標物的確對光敏感並可進行重排反應，但可惜不可逆，無預期之光致變色性質。

第二年計劃研究內容分為三小項，分別為：(I) 氧氮雙環類光致變色材料之光化學反應機構研究；(II)螺吡喃類光致變色材料之光化學反應機構研究；(III) oxazine 類光致變色材料之光化學反應機構研究。在第 I 項氧氮雙環類光致變色材料之光化學反應機構研究中，我們蒐集了目標物之各種光譜資料，包括 EPR、CV 及 spectroelectrochemistry 等，結果顯示目標物光致變色性質極可能涉及「自由基」反應機構。在第 II 項螺吡喃類光致變色材料之光化學反應機構研究中，重新測量目標物 EPR 光譜顯示其為 EPR silence，估計原先觀察到之 EPR 光譜吸收峰有可能是 EPR tube 遭到污染所致，目前我們認為其光致變色性質應無涉及「自由基」反應機構。在第 III 項 oxazine 光致變色材料之光化學反應機構研究中，目標物之合成尚在進行當中，完成後將立即進行性質測試，另外我們合成數個含有 *o*-nitrobenzylamine 之 perimidine 衍生物並取得其晶體結構，後續之 EPR 光譜及照光顯示 *o*-nitrobenzylamine 化合物為 EPR-silent 且對光極為敏感，此結果提供「自由基」反應機構之另一佐證。

關鍵詞：香豆素，光致變色，熱致變色，光化學性質，反應機構。

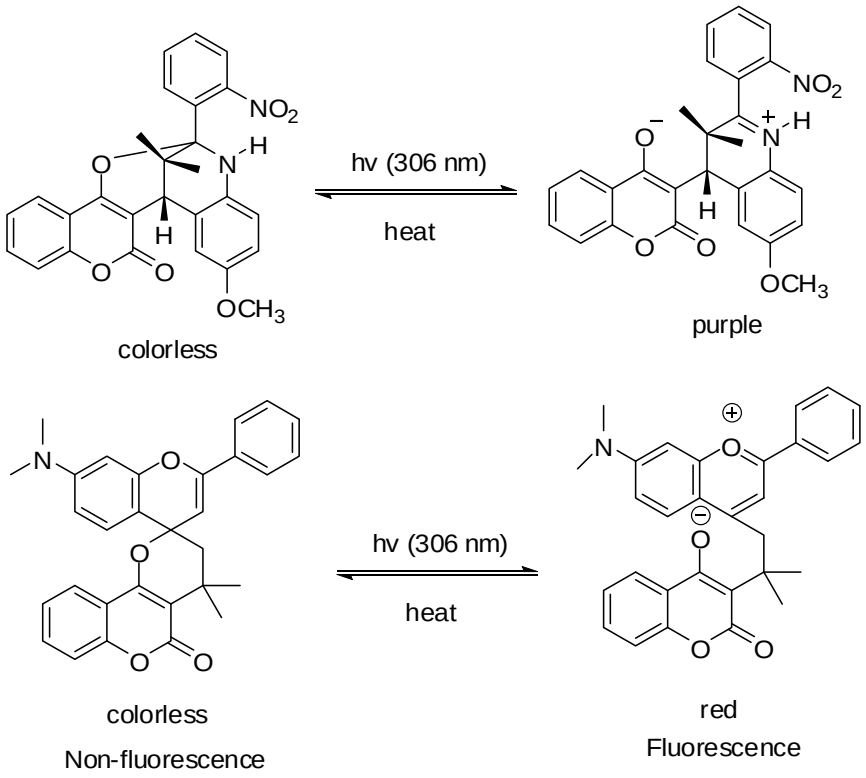
二、英文摘要

This reports contains the results of our studies of the two year grants "Design and synthesis of photochromic colorants and their photochemical mechanism studies". In the first year of the grant, we have focused our studies on the following four separate topics: (I) Design and synthesis of a potential oxazabicycle photochromic colorant. (II) Synthesis of coumarin/phenanthridine-fused heterocycles and their photochemical property studies. (III) Design and synthesis of π–π stacking-controlled photochromic colorant. (IV) Design and synthesis of a 5-azacoumarin derivative and its photochemical property studies. In Part I, although we encountered some difficulties while pursuing the target compound synthesis, we discovered that the *o*-nitrophenyl iminium ion is sensitive to cyanide ion. It turned from red to light yellow or colorless after being attacked by cyanide ion. Thus, the *o*-nitrophenyl iminium ion may have the potential to functional as an organic chemosensor specific for cyanide ion. This *o*-nitrophenyl benzyl derivative is also sensitive to light, and can be converted to the corresponding indazole upon UV irradiation. In Part II, we have successfully synthesized the target coumarin/phenanthridine-fused heterocycles. Some were found to be sensitive to light, some are sensitive to heat. In this particular study, we have revealed a new class of thermochromic colorants. The results of our studies have been published on the journal Organic Letters (2011). In Part III, we also have successfully synthesized the target π–π stacking-controlled photochromic colorant. Unfortunately, it does not possess the proposed photochromism. In Part IV, we have finished the synthesis of the target molecule. Although the compound is sensitive to light and undergoes aryl migration as expected, the photogenerated product cannot be reverted to the starting material. Therefore, it does not exhibit photochromic properties. In the second year of the grant, we have focused our studies on the following three separate topics: (I) Mechanistic studies of photochromism of the oxazabicycle; (II) Mechanistic studies of photochromism of the spiropyran; (III) Mechanistic studies of photochromism of the oxazine. In Part I, we have collected various spectroscopic data of the target compound oxazabicycle, which included EPR, CV, and spectroelectrochemistry. The discernible EPR signals strongly suggest that the photochromic mechanism involves a diradical intermediate. In Part II, we remeasured the EPR spectra of the spiropyran in a very careful way. The results indicate that this spiropyran is EPR-silent. The discrepancy between our previous and current studies may be caused by the contamination of the EPR tube used in the previous measurement. The EPR-silent observation along with our futile attempts to isolate and characterize the possible radical mechanism by-product upon UV irradiation of the spiropyran compound prompted us to believe that the photochromism of the spiropyran does not involve radical mechanism. In Part III, the synthesis of the target compound is still underway. Several *o*- and *p*-nitrobenzylamine-containing perimidine derivatives were also prepared and characterized to provide the mechanistic ring opening details of the oxazine. Our studies suggest *o*-nitrobenzylamine-containing perimidines are EPR-active and are light-sensitive, whereas *p*-nitrobenzylamine-containing perimidines are EPR-silent and are insensitive to light. Apparently, the *o*-nitro group plays a vital role in the photochromism and presumably a radical mechanism is involved.

Keywords**:** coumarin, photochromism, thermochromism, photochemical property, mechanism.

三、緣由與目的

Owing to their practical applications in ophthalmic lenses and glasses, etc., organic photochromic dyes have long attracted great attention.[1,2] Extensive investigations have been carried out on bisdiarylethenes,[3] bispyrans,[4] bisbenzodihydropyrenes[5] and bishydroindolizines[6]. While modifications of the existing photochromes may still generate compounds with unprecedented properties, new classes of organic photochromic dyes with novel molecular scaffolds should be developed for use as suitable materials for optical memory media, photooptical switch components, and other applications. During the past few years, our research group has developed two new organic photochromic dyes with novel molecular structures, as shown below. The discovery of the aforementioned two organic photochromic dyes prompts us to design of other novel 7-dimethylamino-4-hydroxycoumarin-based photochromic colorants.[7,8] Therefore, in this proposal, we will continue our studies in design, synthesis and characterization of 7-dimethylamino-4-hydroxycoumarin-based derivatives and subsequently explore their photochemical properties. Moreover, their photochromism will also be investigated by various spectroscopy.

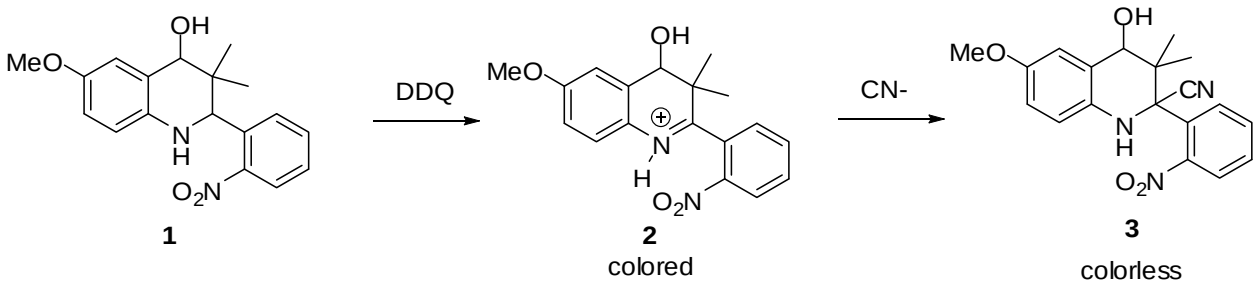


The results of our studies may not only provide practical applications of organic photochromes in photonic devices such as erasable memory media and optical switching but also valuable information regarding the ring-opening and ring-closing mechanism of oxazabicyclic, spiropyran, and oxazine photochromic colorants, which may serve as a solid background for future development of the photochromic dyes with novel molecular structures.

四、報告內容

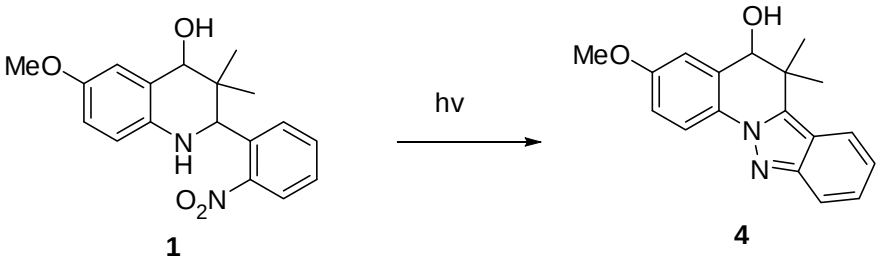
The first year report

In the proposed studies of Part I, that is, design and synthesis of a potential oxazabicycle photochromic colorant, we encountered some difficulties while pursuing the target compound synthesis, but we discovered an interesting observation. The colored *o*-nitrophenyl iminium ion **2**, which can be prepared by in situ DDQ oxidation of **1**, is cyanide-sensitive (Scheme 1). The oxidized red iminium ion **2** turned colorless after being attacked by cyanide ion to give compound **3**. Thus, we speculate that compound **1** may have the potential to functional as an organic chemosensor specific for cyanide ion. No similar observation was made by the *p*-nitrophenyl substituted derivative. This result suggests that the *o*-nitro group plays an important role in this cyanide ion detection process.



Scheme 1. A potential chemsensor for cyanide ion.

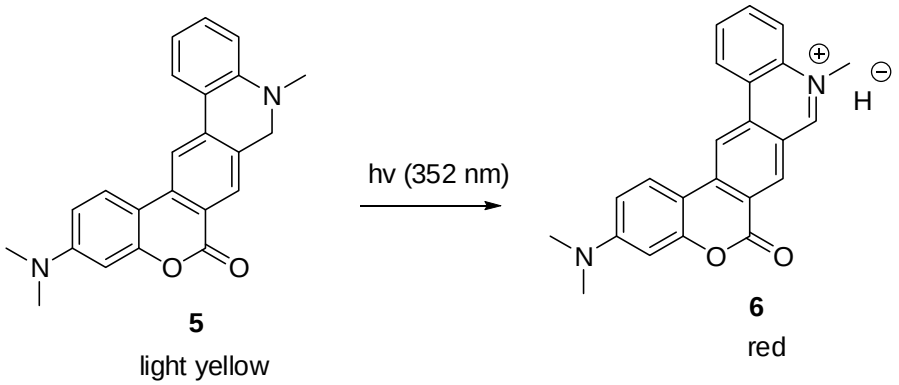
Further, we found that compound **1** is also sensitive to UV light. Upon UV irradiation, it can be converted to the corresponding indazole derivative **4** in relatively good yield (Scheme 2). The detailed mechanism for this transformation is currently under investigation.



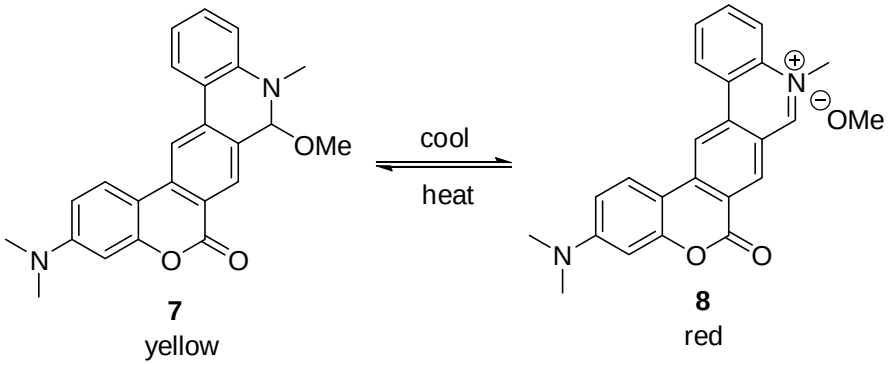
Scheme 2. Formation of indazole **4** from **1**.

In the proposed studies of Part II, that is, synthesis of coumarin/phenanthridine-fused heterocycles and their photochemical property studies, we have successfully prepared and characterized serveral coumarin/phenanthridine-fused heterocycles. Some were found to be sensitive to light; some sensitive to heat. For instance, the light yellow compound **5** turned red instantly upon UV irradiation to afford the ion pair **6** (Scheme 3). Conversely, compound **7** was found to possess thermochromic properties (Scheme 4). It is light yellow in methanol at +50 ^{o}C and turns red as temperature is decreased. The color reverts swiftly to yellow when temperature is increased. Figure 1 shows the UV-vis absorption spectra of **7** in methanol under temperature

between +50 to 0 °C. With the decrease of the temperature, the absorption band with the peak wavelength around 485 nm gradually increases, along with four isosbestic points at 226, 253, 290, and 412 nm. In other words, we have discovered a new class of negative thermochromic colorants. The results of our studies have been recently published on the international journal *Organic Letters* (2011, the paper is attached in the end of this report).[9, 10]



Scheme 3. Proposed photochemical product **6**.



Scheme 4. Proposed thermochromic switch between **7** and **8** in MeOH.

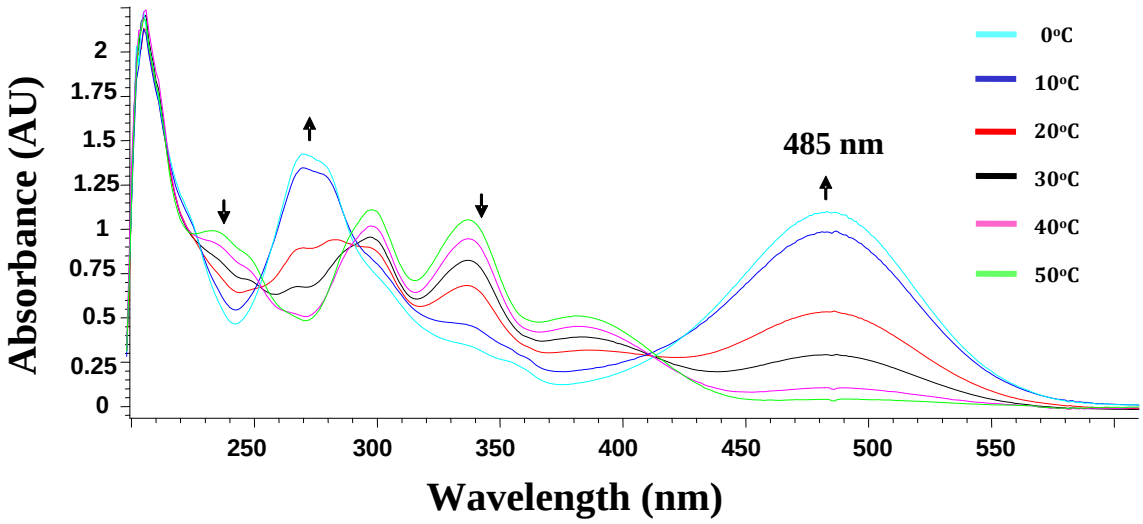
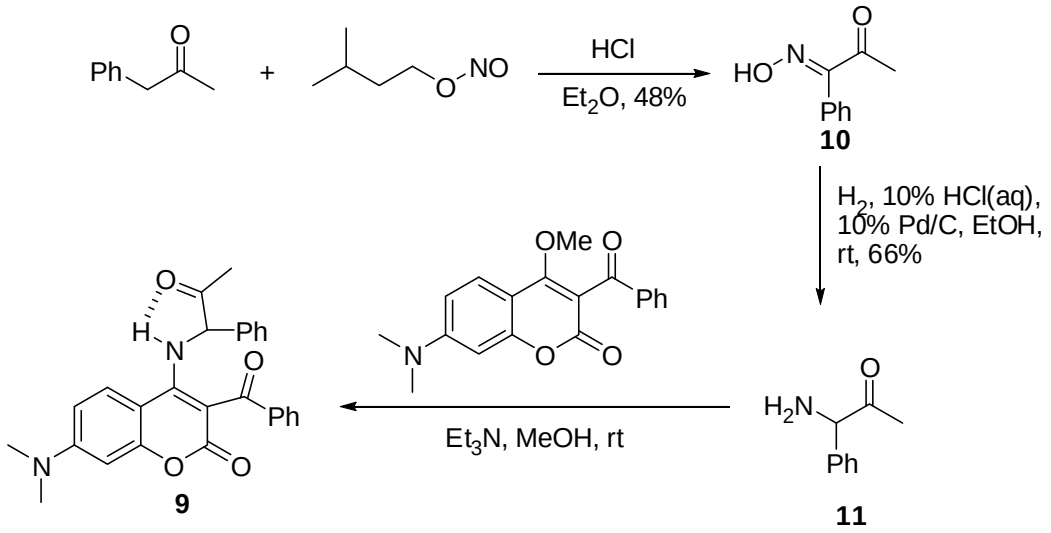


Figure 1. UV–vis spectra of **7** (1.5×10^{-5} M in MeOH) at temperature between +50 to 0 °C, with decrements of 10 °C.

In the proposed studies of Part III, we also have successfully synthesized (Scheme 5) and characterized (Figure 2) the target π–π stacking-controlled compound **9**. Unfortunately, compound **9** does not possess the proposed photochromism, presumably due to the fact that the intramolecular hydrogen bonding disrupts the π–π stacking interaction between the two benzene moieties.



Scheme 5. Preparation of compound **9**.

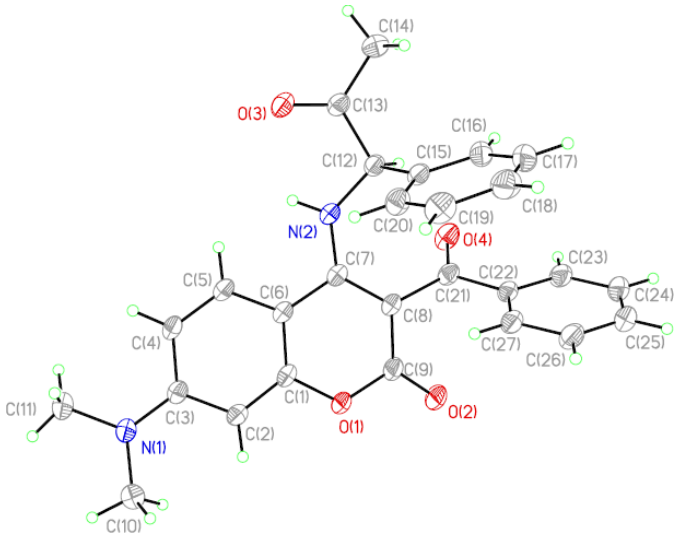
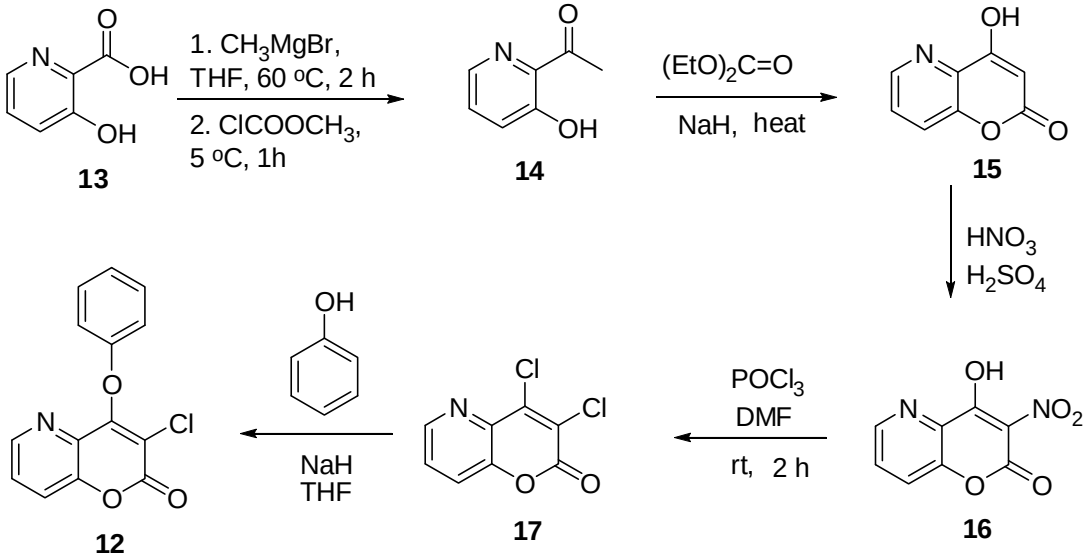


Figure 2. ORTEP crystal structure of **9**.

In Part IV, we encountered some difficulties at the beginning of the synthesis of the target 5-azacoumarin derivative **12**. Luckily, the problems have been solved and now we have finished the synthesis, as shown in Scheme 6. The X-ray crystal structure of **12** is shown in Figure 3.



Scheme 6. The synthesis of 5-azacoumarin **12**.

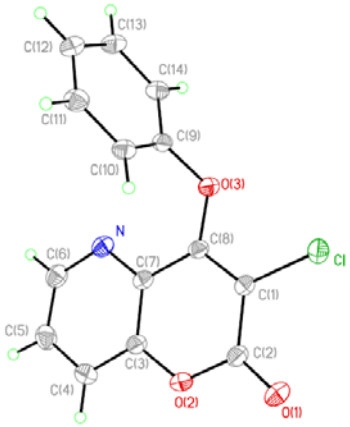
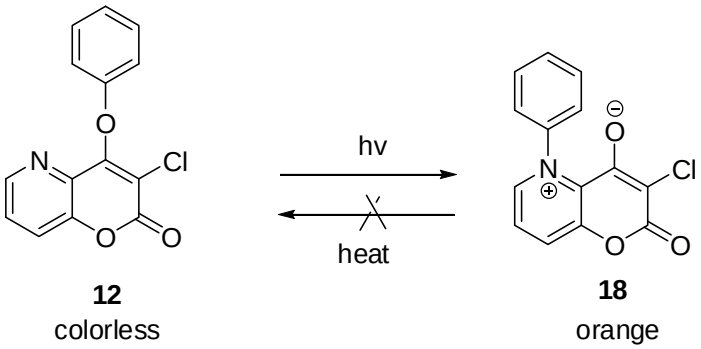


Figure 3. ORTEP crystal structure of **9**.

With this compound **12** in hand, we then went ahead to investigate its photochemical and photochromic properties. Although compound **12** is light-sensitive and can be converted to the colored zwitterion **18** (Scheme 7). Figure 4 shows the X-ray crystal structure of **18**. Unfortunately, compound **18** cannot be reverted to the starting material **12** when being heated. Therefore, compound **12** does not exhibit the expected photochromic properties.[11]



Scheme 7. The photogenerated product **18**.

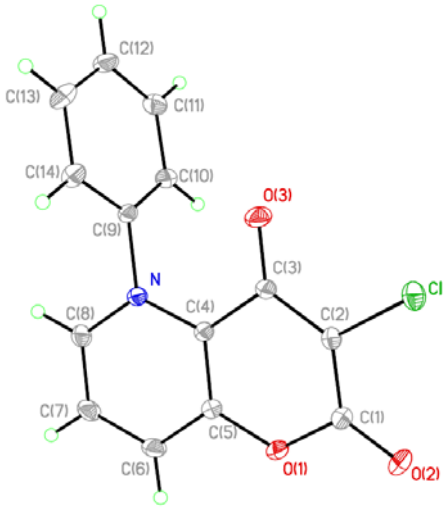


Figure 4. ORTEP crystal structure of **18**.

The second year report

In the proposed studies of Part I, that is, mechanistic studies of photochromism of the oxazabicycle, we first managed to obtain the X-ray crystal structure of the oxazbicycle **19**, as shown in Figure 5.

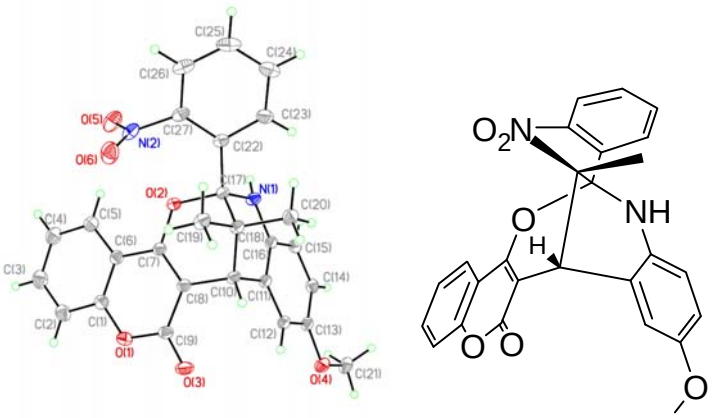


Figure 5. ORTEP crystal structure of **19**.

Subsequently, we focused our attentions to a deeper analysis of the photo-induced ring opening mechanism of the oxazabicycle by ESR spectroscopy. Figure 7 shows EPR spectra of **19** under various UV irradiation time and temperature. The discernable splitting pattern at different irradiation time strongly suggest that the photochromism involved a diradical intermediate. The next question will be what the structure of this intermediate is. We speculate that the diradical intermediate is likely come from the *o*-nitrophenyl group and the adjacent amine moieties. To test this hypothesis, we measured the EPR and spectroelectrochemical spectra of compound **20** (the structure shown in Figure 8). As expected, the compound **20** is EPR-active (Figure 7). It turned red when subjected to a +0.95 v and the process is reversible, as shown in Figure 8.

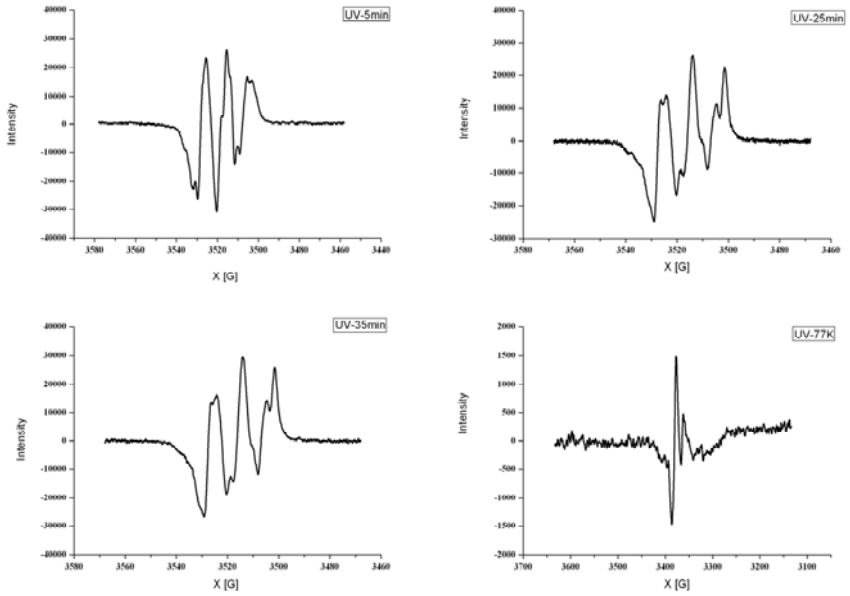


Figure 6. EPR spectra of **19** under various conditions.

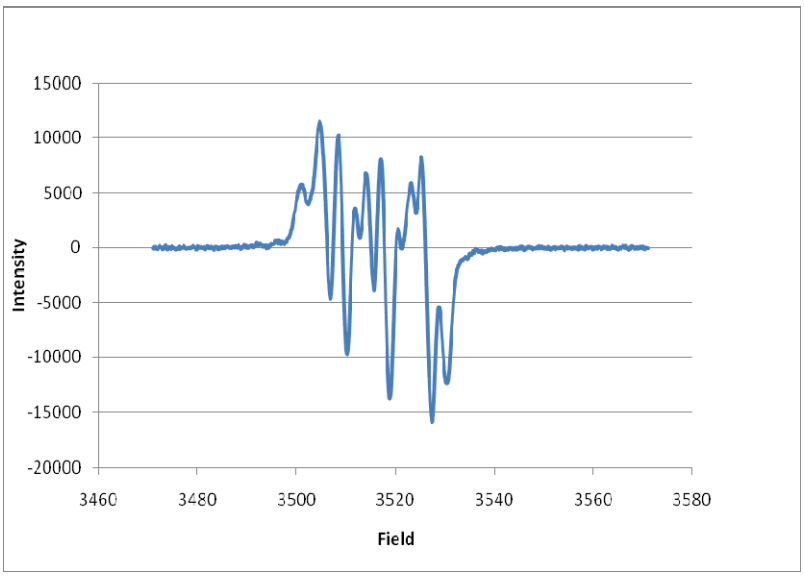


Figure 7. EPR spectra of **20** at room temperature.

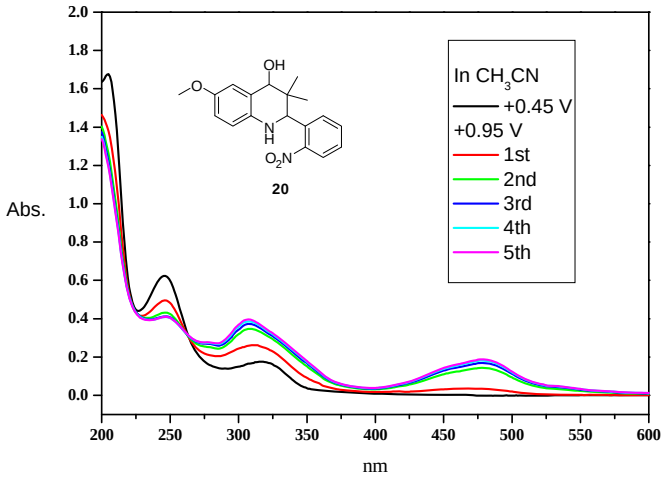
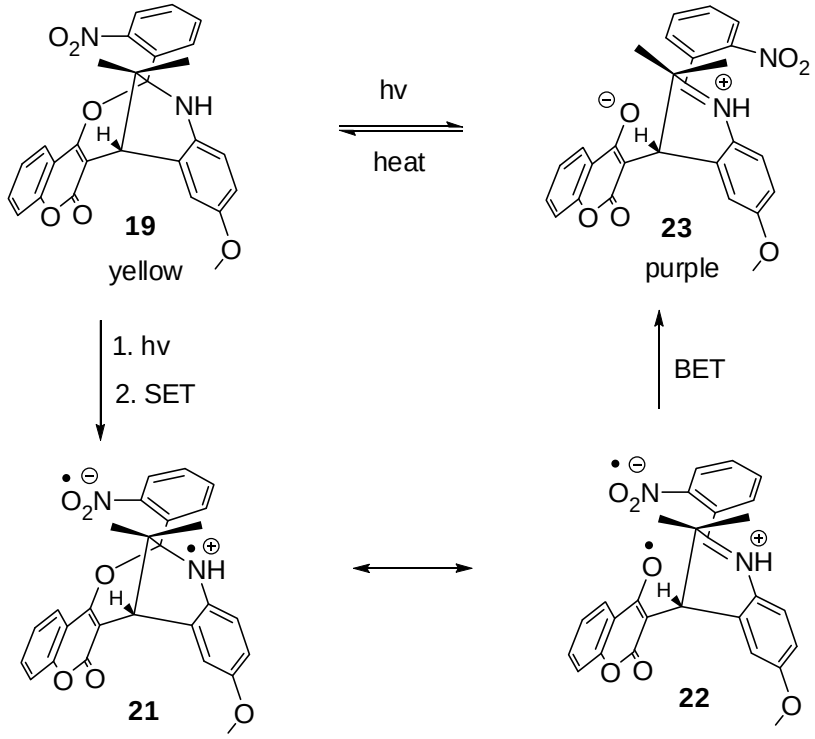


Figure 8. Spectroelectrochemistry of **20**.

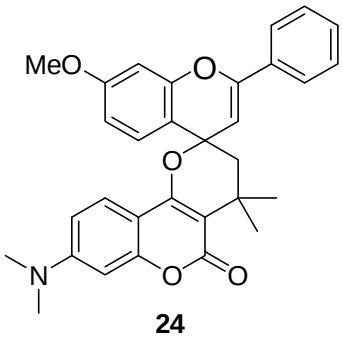
Combination the above information, a plausible photochromic mechanism of the oxazobiycle is then proposed in Scheme 8. Upon UV irradiation, an intramolecular single-electron transfer (SET) from amine to nitrobenzene occurs to give the diradical intermediate **21**. The subsequent C-O bond breaking results the ring-opening product **22**. The final back-electron transfer (BET) from nitrobenzene group to the oxygen radical affords the final photogenerated product **23**.



SET: single-electron transfer; BET: back electron transfer

Scheme 8. Proposed photochromic mechanism.

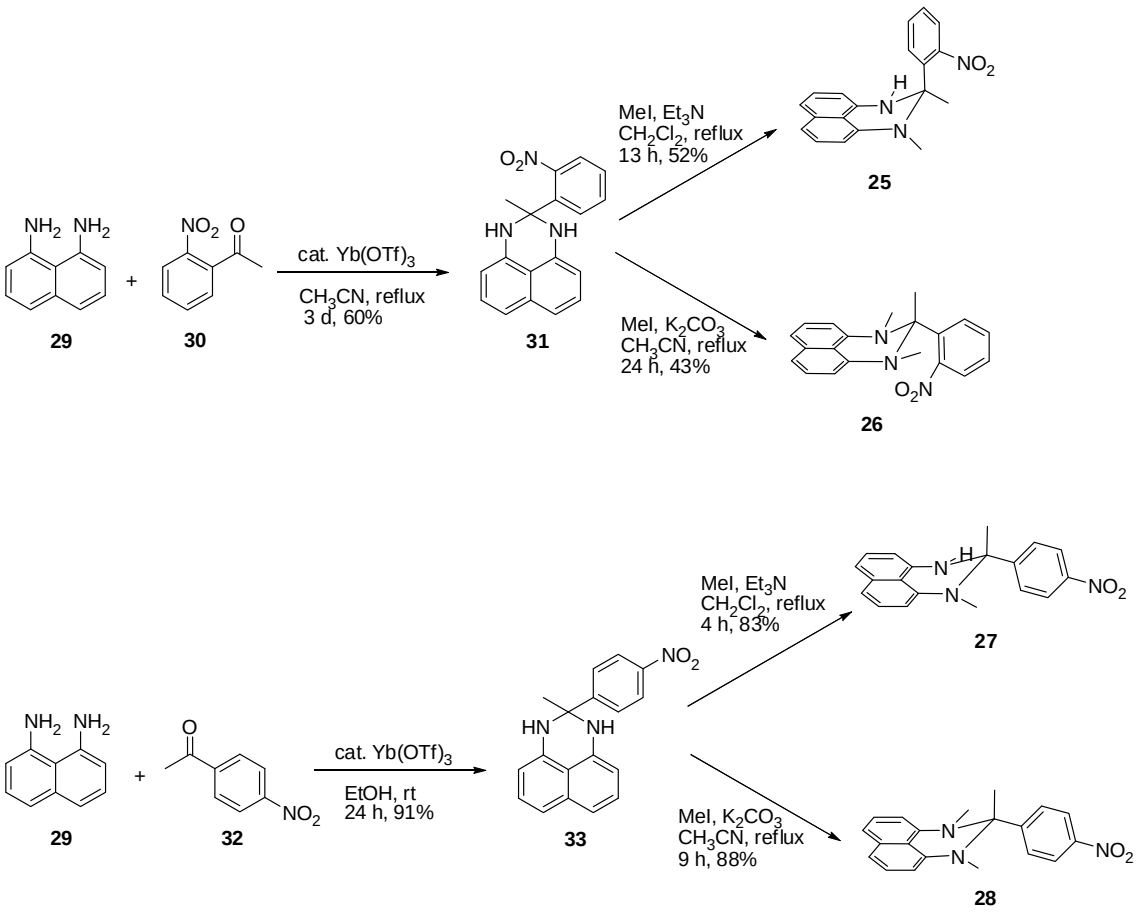
In the proposed studies of Part II, that is, mechanistic studies of photochromism of the spiropyran, we remeasured the EPR spectra of the spiropyran **24** (Figure 9) in a very careful way. The results indicate that this spiropyran is EPR-silent. The discrepancy between our previous and current studies may be caused by the contamination of the EPR tube used in the previous measurement. The EPR-silent observation along with our futile attempts to isolate and characterize the possible radical mechanism by-product upon UV irradiation of the spiropyran compound prompted us to believe that the photochromism of the spiropyran does not involve a radical mechanism.



24

Figure 9. Structure of the spiropyran **24**.

In the proposed studies of Part III, that is, mechanistic studies of photochromism of the oxazine, we aim to extend our mechanistic investigation to a photochromic switch based on the opening and closing of an oxazine ring. At the beginning, we encountered some difficulties in the preparation of the model compound. Nevertheless, the synthesis of the target compound is still ongoing and should be finished shortly. On the other hand, four *o*- and *p*-nitrobenzylamine-containing perimidine derivatives were also prepared and characterized to investigate the structure and photochemical properties relationship and to provide the additional mechanistic ring-opening details of the oxazine (Scheme 9). The X-ray crystal structures suggest the conformation of these perimidine derivatives is greatly influenced by the *ortho* substituent on the benzene moiety as well as the substituents on the two amine groups (Figure 10). Further, only **25** with the *o*-nitrophenyl group adopting the axial position on C-2 was found to be EPR-active (Figure 11) and light-sensitive, and its photogenerated products were characterized to be the perimidinone **34** and 2*H*-indazole **35** (Scheme 10).[12]



Scheme 9. Preparation of compounds **25**-**28**.

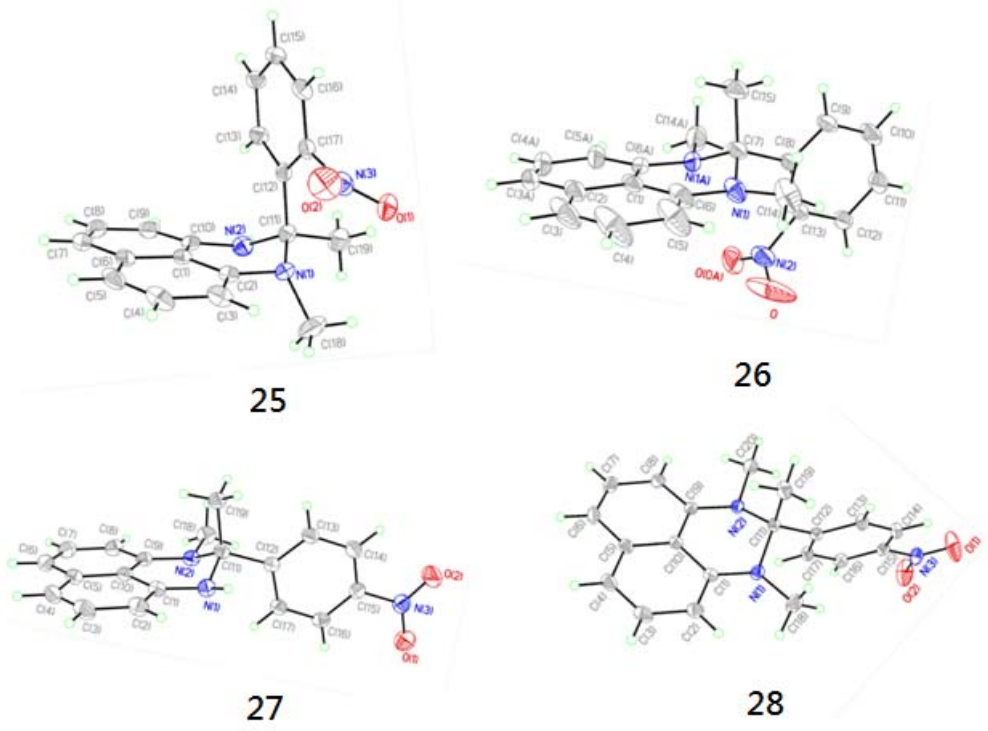


Figure 10. ORTEP crystal structures of **25**-**28**.

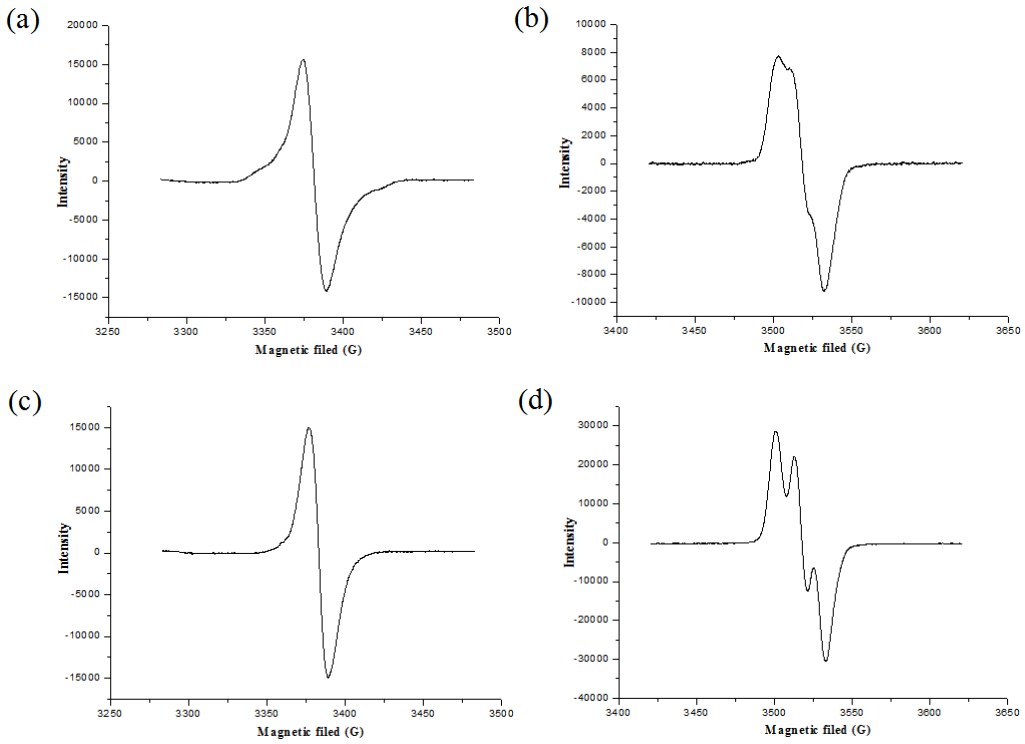
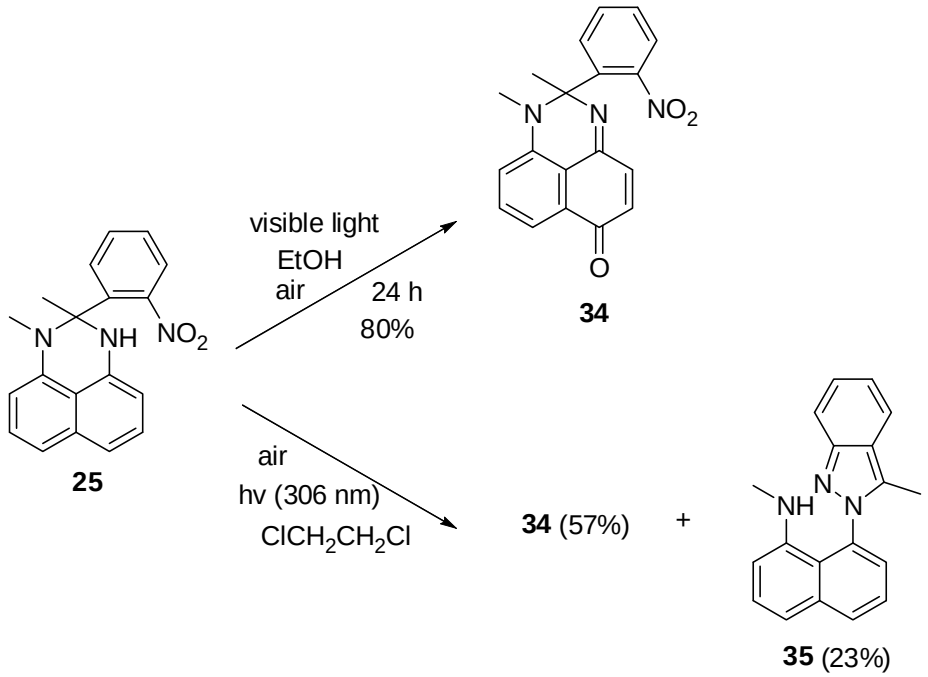
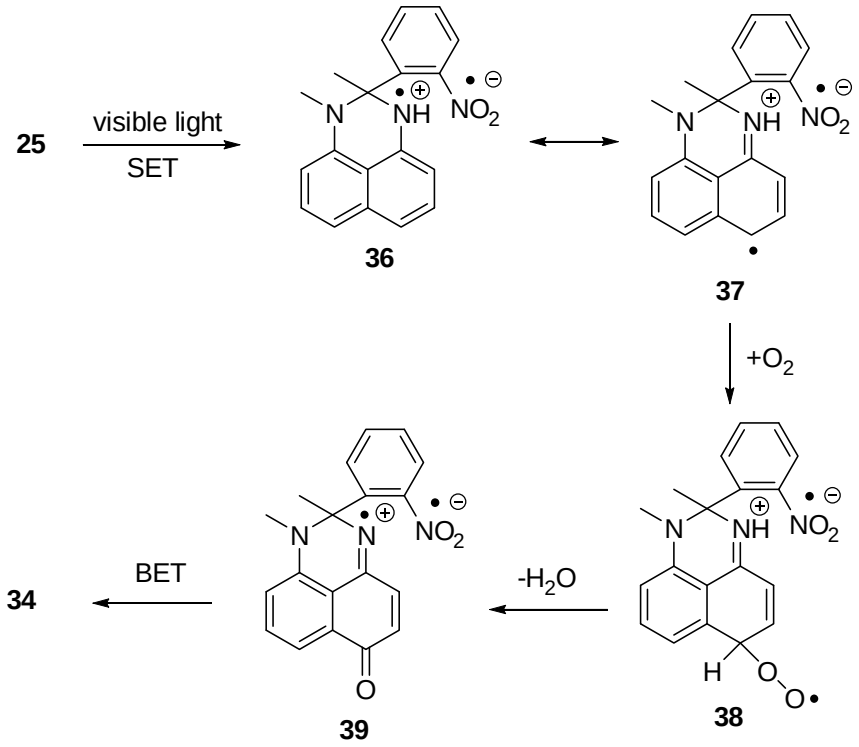


Figure 11. EPR spectra of **25** recorded in degassed CH_2Cl_2 solution (a) at 77 K; (b) at room temperature; (c) immediately after irradiation with a 360 nm laser source at room temperature; (d) after irradiation with a 360 nm laser source for 5 min at room temperature.



Scheme 10. The structures of photogenerated products perimidinone **34** and 2*H*-indazole **35**.

The mechanism for the formation of the perimidinone **34** from **25** is proposed in Scheme 11. Since it is well-known that the amine is a good electron donor and the nitrobenzene is a good electron acceptor, we speculate that the mechanism involves a light-mediated single-electron transfer (SET) from the amine to the nitrophenyl group of **25** to generate the biradical species **36**. The *para* radical of the contributing structure **37** then reacts with O_2 to form the peroxide **38**. The subsequent loss of one molecule of water from **38** affords the perimidinone radical cation **39**. Final charge neutralization by transferring one electron from the nitro radical anion back to the iminium radical cation furnishes the product **34**. Essentially, the key step of this mechanism is the formation of the radical cation/anion species **36**, which can only occur when the amine and nitro groups are in close proximity and suitable conformation to affect the intramolecular electron transfer process upon irradiation. This proposed mechanism also explains why only **25** is sensitive to visible light and others are not, since compounds **26**–**28** lack the well-positioned *o*-nitrobenzylamino scaffold for SET to occur. Apparently, the *o*-nitro group plays a vital role in the photochromism and presumably a radical mechanism is involved.



Scheme 11. Proposed mechanism for the formation of perimidinone **34** from **25**.

五、結論

In summary, we have almost completed the proposed two-year studies. In the first year study, some target compounds exhibit the expected properties, some do not. In this study, we have developed an efficient route for the construction of a novel coumarin and phenanthridine-fused molecular skeleton via a base-catalyzed condensation of 4-methylquinolium salt and 7-dimethylamino-2-formyl-4-hydroxycoumarin. Moreover, a potential organic chemosensor for cyanide ion and a novel thermochromic colorant with negative thermochromism were discovered. In the second year, our studies suggest that the photochromism of the oxazabicycle and the oxazine is likely to involve a diradical intermediate, whereas the spiropyran is not. The results of these studies will be published shortly.

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Synthesis of Coumarin/Phenanthridine-Fused Heterocycles and Their Photochemical and Thermochromic Properties

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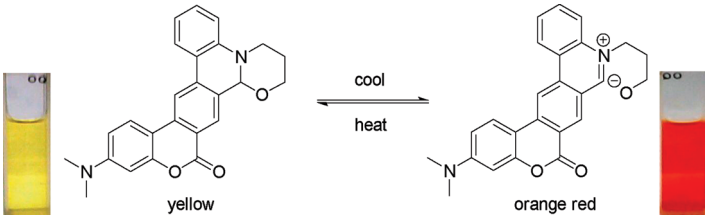
ABSTRACT



Four coumarin and phenanthridine-fused heterocycles were efficiently synthesized using base-mediated annulation of *N*-alkylquinolinium iodide and coumarin as a key step. One compound is found to be sensitive to light and changes color upon UV irradiation; the others are sensitive to heat and possess negative thermochromic properties. A novel light- and heat-sensitive molecular skeleton is introduced.

Heterocyclic rings are one of the fundamental components in the skeleton of the biologically active compounds produced by nature.[1] A facile synthetic route to a new family of heterocycles may not only open the possibility of finding further types of biologically active units for therapeutics but also generate potential functional materials to construct molecular devices. Perhaps because of this, great efforts have been focused on developing new methodologies that increase the structural complexity while decreasing the number of synthetic steps to facilitate the construction of new heterocycles.[2]

In this respect, coumarins and phenanthridines represent two important subsets of heterocycles that have wide applications in various aspects such as drugs,[3] DNA targeting agents,[4] and dyes.[5] While numerous methods for preparations of coumarin[6] and phenanthridine[7] derivatives were developed in the past, the synthesis of compounds with a coumarin and phenanthridine-fused molecular skeleton has never been reported. In light of their potential biological activities and functional properties associated with the coumarin and phenanthridine

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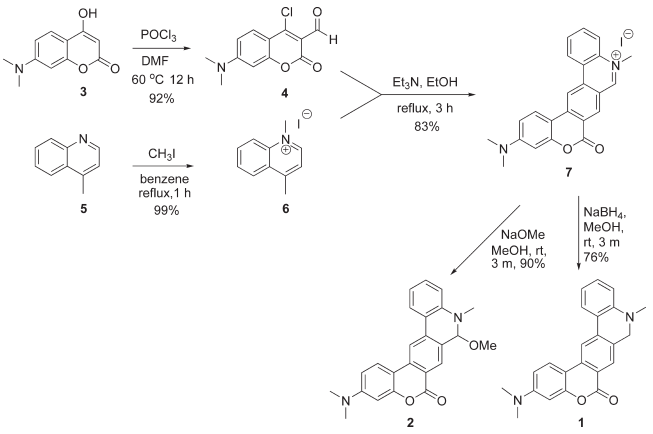
moieties, we envisioned that an efficient preparation of the novel coumarin and phenanthridine-fused heterocycles may generate compounds with unprecedented properties. Here we report our efforts toward the development of a facile scaffold using base-mediated annulation of *N*-alkylquinolinium salt and coumarin. The photochemical behaviors and the thermochromic properties of the synthesized compounds were explored by UV−vis, EPR, and variable temperature proton NMR spectroscopy.

Scheme 1



Scheme 1 shows the preparation of the coumarin and phenanthridine-fused heterocycles **1** and **2**. The starting material 7-dimethylamino-4-hydroxycoumarin (**3**)[8] was first converted to 4-chloro-7-dimethylamino-2-oxo-2*H*-chromene-3-carbaldehyde (**4**) by treating it with phosphorus oxychloride in DMF. The condensation of **4** and *N*-methyl 4-methylquinolinium iodide (**6**) in the presence of triethylamine as a base in ethanol under reflux conditions gave the intermediate iminium iodide **7**, which can be trapped by sodium borohydride or sodium methoxide in methanol to afford the target compounds **1** and **2**, respectively. Compound **6** was prepared by refluxing the commercially available 4-methylquinoline (**5**) with methyl iodide in benzene. The molecular structures of **7**, **1**, and **2** were elucidated by X-ray crystallography as shown in Figure 1,[9] which all reveal a coumarin and phenanthridine-fused skeleton. The proposed mechanism for the annulation is depicted in Scheme 2. It starts with a triethylamine-mediated deprotonation of the 4-methyl hydrogen on **6** to yield 1,4-dihydro-1-methyl-4-methylenequinoline (**8**). The condensation of **8** and **4** affords the intermediate **9**, which then undergoes intramolecular cyclization to give the alcohol **10**. The final dehydration of **10**

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(9) Crystallographic data (excluding structure factors) for **1**, **2**, **7**, **13**, and **17** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-778474, -778475, -791032, -786005, and -786004, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

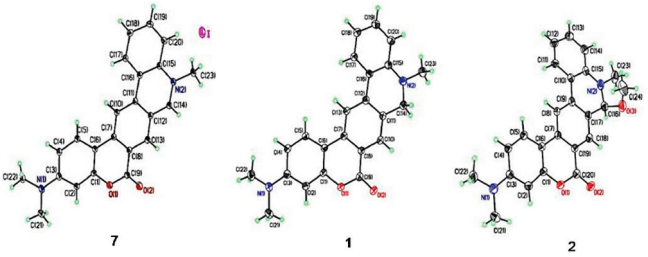
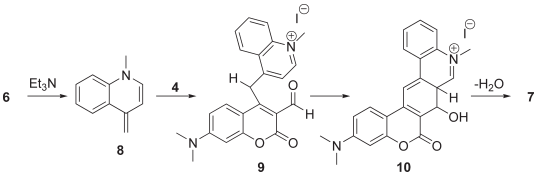


Figure 1. ORTEP crystal structures of heterocycles **7**, **1**, and **2**.

Scheme 2



generates the aromatized iminium iodide **7**. This base-mediated annulation not only provides a quick access to a coumarin and phenanthridine-fused skeleton but also offers the possibility of synthesizing a library of potentially bioactive compounds. Presumably, this annulation methodology can also be extended to the synthesis of other *N*-heterocycles such as naphthalene and phenanthridine-fused derivatives.

Having characterized the structures of heterocycles **1** and **2**, we turned our attention toward their photochemical and thermochromic properties. Compound **1** was found to be highly sensitive to light. Upon UV irradiation (352 nm), the light yellow **1** in methylene chloride turns red within seconds. This light-induced color variation is irreversible even when the photogenerated product is heated. Figure 2 shows the UV−vis absorbance changes of **1** before and after irradiation. With the increase of exposure time, a new absorption band with the peak

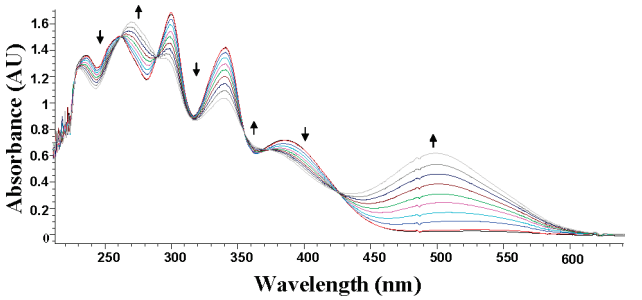
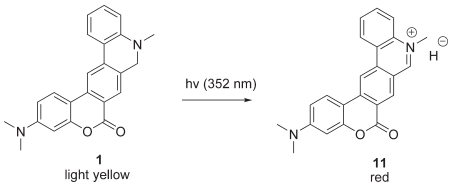


Figure 2. UV−vis spectra of **1** (1.0×10^{-4} M in CH_2Cl_2) obtained with different exposure time (352 nm), 0−4 min with 30 s increments.

wavelength around 499 nm gradually increases, along with the appearance of five isosbestic points at 262, 289, 355, 369, and 425 nm.

Scheme 3



Although the proposed photogenerated product **11** (Scheme 3) is not stable enough to be isolated and characterized, its formation is confirmed by the ^{1}H NMR spectra of compound **1** in deuterated DMSO after irradiation, which clearly indicate the appearance of the characteristic iminium carbon hydrogen, *N*-methyl, and hydride ion absorption signals of the iminium hydride **11** at 10.10, 4.48, and −35.33 ppm, respectively (Supporting Information (SI), Figure S1).[10] The photoreaction presumably involves first a light-induced homolytic C−H bond cleavage to generate a benzylic radical and a hydrogen radical and is followed by an electron transfer from the former to the latter to afford the ion pair **11**. Evidence for the presence of radical species is furnished by EPR-spectral studies. The irradiated solution of **1** in degassed methylene chloride at room temperature exhibits EPR signals around 3500−3550 G (Figure 3), revealing a typical EPR absorption pattern of diradical species.

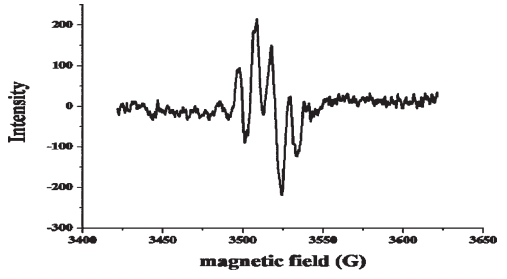


Figure 3. EPR spectra of **1** in degassed CH_2Cl_2 solution at 25 °C, recorded after irradiation with a 360 nm laser source.

Theoretically, this iminium hydride **11** may function as a light-induced hydride source in organocatalytic hydride reductions.[11]

Interestingly, compound **2** was found to exhibit negative thermochromic properties in protic solvents. It is light yellow in methanol at +50 °C and turns orange red as the temperature is decreased. The color reverts swiftly back to yellow when the temperature is increased. Figure 4 shows the UV−vis absorption spectra of **2** in methanol under temperatures between +50 to 0 °C. When the temperature is decreased, the absorption band with the peak wavelength around 485 nm gradually increases, along with the appearance of four isosbestic points at 226, 253, 290, and 412 nm. When the temperature is increased, the red species in methanol quickly decays away with the disappearance, i.e., turning yellow, of the 485 nm band.

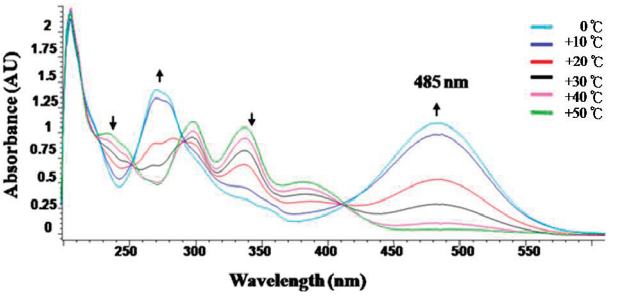
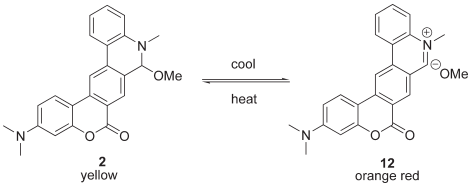


Figure 4. UV−vis spectra of **2** (2.0×10^{-5} M in MeOH) at temperatures between +50 to 0 °C, with decrements of 10 °C.

This reversible thermochromic process is repeated ten times without significant changes in the UV−vis spectra (SI, Figure S3). Scheme 4 shows the proposed negative thermochromic switch between **2** and **12**. While various attempts to isolate the iminium methoxide **12** proved to be futile, variable temperature NMR experiments of **2** in CD_3OD did provide evidence for its emergence, that is, the appearance of three new discernible singlets at around 9.63, 5.19, and 4.36 ppm (with the integration ratio close to 1:3:3), which were assigned to the absorptions of the iminium carbon hydrogen, methoxide hydrogens, and *N*-methyl hydrogens of **12**, respectively (SI, Figure S2).[10]

Scheme 4



The switching between **12** and **2** probably involves a thermally induced nucleophilic attack of the methoxide ion to the iminium carbon of the highly conjugated orange red ion pair **12** to give the less conjugated yellow neutral species **2**. When the temperature is decreased, **2** reverts to **12** via the elimination of the methoxide ion to regain the aromaticity. Although the methoxide ion is far from a good leaving group, we speculate that its elimination from the coumarin/phenanthridine-fused skeleton at lower temperature is

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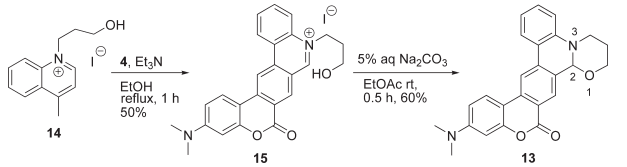
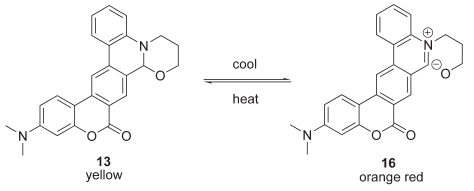
substantially facilitated by adopting an *antiperiplanar* conformation relative to the lone pair electrons on the adjacent nitrogen atom, as indicated in the X-ray crystal structure of **2** (Figure 1). Furthermore, the fact that the OMe group is nearly orthogonal to the coumarin/phenanthridine-fused plane also leads to a decrease of the C−OMe bond strength (the C−OMe bond length reads 1.436 Å, which indeed is longer than the average C−O bond length). To the best of our knowledge, the thermal equilibrium between **2** and **12** represents the first example of organic negative thermochromism that involves the dissociation of an alkoxide (methoxide) ion as a leaving group rather than the commonly seen neutral amines.[12]

Scheme 5



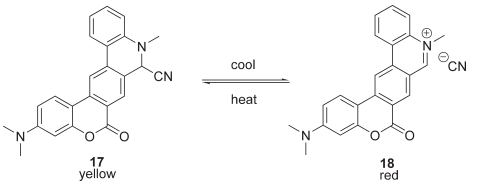
In an effort to alter the thermochromic switch between **2** and **12** from an intermolecular to an intramolecular reaction, the oxazine **13** was designed and prepared by a similar method as described in Scheme 5. The 4-methylquinoline (**5**) was first *N*-alkylated by reacting with 3-iodopropan-1-ol in benzene to give the imminium iodide **14**, which was followed by condensation with **4** in the presence of triethylamine in ethanol under reflux conditions to give the iminium iodide **15**. Final cyclization was realized by treating **15** with aqueous sodium carbonate in ethyl acetate at room temperature to afford **13**. Indeed, **13** was found to exhibit negative thermochromic properties (SI, Figures S5−S7). It is light yellow in methanol at room temperature and turns orange red (zwitterion **16**) as the temperature is decreased (Scheme 6).

Scheme 6



Since cyanide is a better leaving group than methoxide, carbonitrile **17** was also prepared by treating iminium iodide **7** with potassium cyanide in methanol to further explore the scope of this new type of thermochromic reactions. As expected, the carbonitrile **17** was found to possess the negative thermochromic properties similar to that of **2** and **13** (Supporting Information, Figures S9−S11). It is light yellow in methanol at +60 °C and turns red (iminium cyanide **18**) as the temperature is decreased (Scheme 7).

Scheme 7



The observation of light-sensitive and thermochromic properties of these coumarin/phenanthridine-fused heterocycles suggests that light or heat can conceivably serve as a third controllable parameter (stimulus) in addition to pH jump and redox potential for the newly developed phenanthridine-based lockable molecular switch.[13] Moreover, this coumarin and phenanthridine-fused molecular skeleton may also function as a potential photoresponsive chromophore in the design of new photochromic colorants, if an appropriate functional group is introduced onto the phenanthridine moiety. Considering the redox- and light-sensitive properties associated with phenanthridine derivatives along with the intrinsic fluorescence properties of coumarins, we believe that this readily available coumarin and phenanthridine-fused scaffold may have a major influence on the future development of novel coumarin/phenanthridine-based organic functional materials.

In summary, we have developed an efficient route for the construction of a novel coumarin and phenanthridine-fused molecular skeleton via an Et_3N-mediated condensation of *N*-alkylquinolinium salt and coumarin. Four compounds were synthesized as examples for illustration, and their photochemical and thermochromic properties were investigated. Our studies indicate that **1** is sensitive to light, and **2**, **13**, and **17** possess negative thermochromic properties. Further development of related photochromic colorants based on this coumarin and phenanthridine-fused skeleton is currently underway.

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Supporting Information Available. Synthesis of **1**, **2**, **4**, **6**, **7**, **13**−**15**, and **17**; experimental details; and additional spectra. X-ray structure details for **1**, **2**, **7**, **13**, and **17** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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