

Synthesis of a coumarin/phenanthridine-fused heterocycle as a lockable colorimetric fluorescence molecular switch

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Abstract

A coumarin/phenanthridine-fused heterocycle was synthesized via base-mediated annulation of *N*-alkylquinolinium salt and coumarin. Its potential to function as a lockable molecular switch by use of pH and redox chemistry as external stimuli was evaluated. When treated with an acid, the light yellow, fluorescent ring-closed heterocycle is instantly switched to the red, non-fluorescent ring-opened iminium salt, and this process is reverted by adding a base. The acidichromism can be selectively "locked" by converting the ring-closed and -opened compounds to their "pH-inert" forms via NBS oxidation and NaBH₄ reduction, respectively. A lockable colorimetric fluorescence molecular switch is introduced.

Keywords: Coumarin, phenanthridine, annulation, acidichromism, fluorescence molecular switch

Introduction

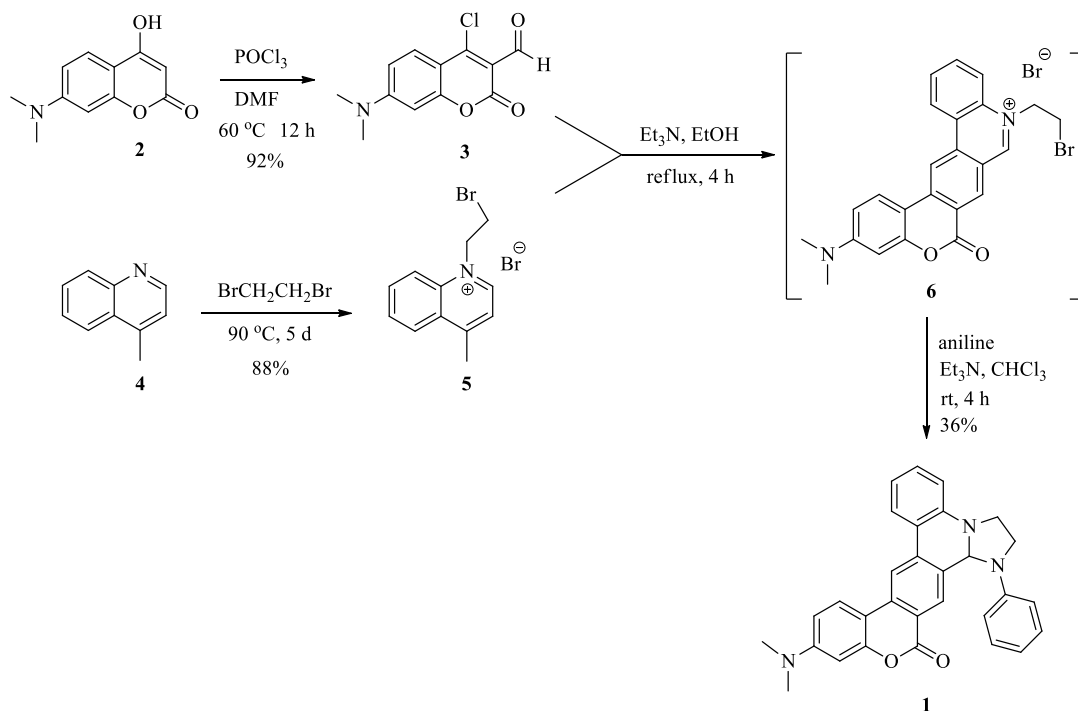
Molecules or ions which can be switched from one configuration to another by an external perturbation continue to receive considerable attention, partly due to their potential applications in molecular information processing and storage.¹ Most examples of molecular switches typically consist of two stable states distinguishable by physical or chemical properties, which are interchangeable through the alteration of controllable parameters such as pH, temperature, light, redox potential, and metal ions.² Recently, Cronin and coworkers³ reported the use of a pH-modulated cyclization of a phenanthridine derivative to switch between two states with complementary redox activities that can then be selectively "locked" by oxidation or reduction. In this system, the phenanthridine and its corresponding phenanthridinium derivative are interchangeable via pH control and can also be further converted to their "pH-inert" forms by chemical oxidation and reduction, respectively. This combination of two separate control

parameters creates a switchable system with a gated response where one parameter controls the other, thus allowing for read-write and read-only behavior.⁴ The four compounds were found to possess similar emission spectra, therefore the switching between the two states can only be monitored by use of UV-vis and proton NMR spectrometry. Since fluorescence emission is considered to be one of the most attractive signal outputs of switching materials owing to its high sensitivity, easy detection and low-cost procedure,⁵ we believe the fluorescence detection of the output properties of this switching system can be realized by incorporation of a fluorophore such as coumarin to the phenanthridine moiety. Here, we report the synthesis of a new fluorescent coumarin/phenanthridine-fused heterocycle and subsequent evaluation of its potential to function as a lockable molecular switch by use of pH and redox chemistry as external stimuli.

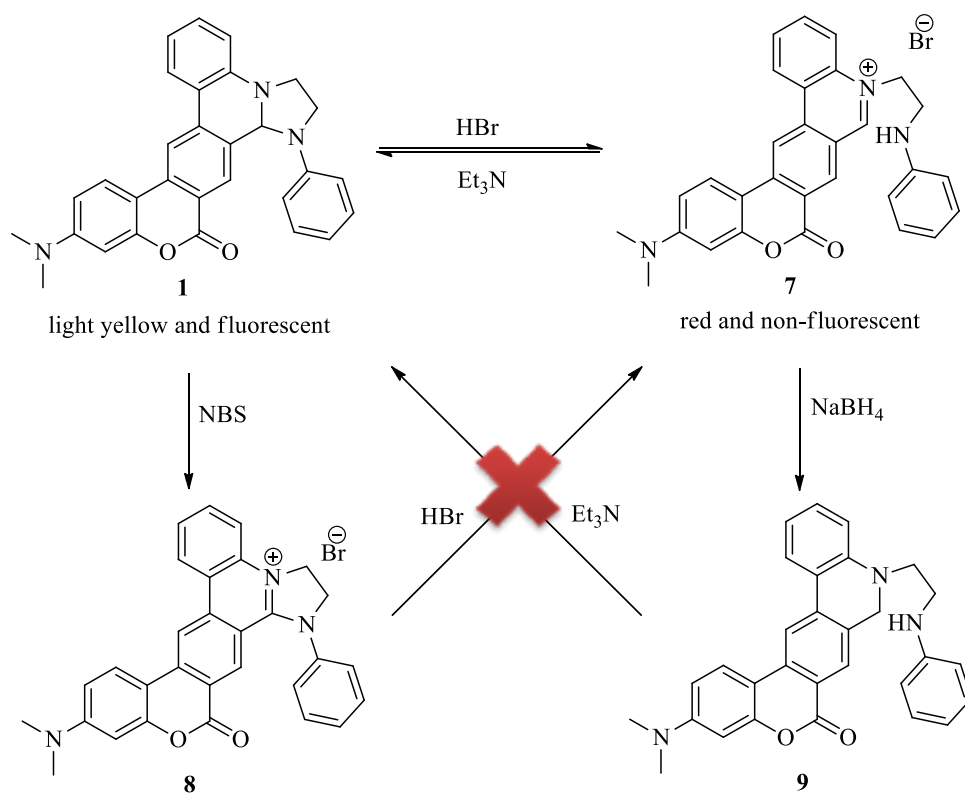
Results and Discussion

Scheme 1 shows the preparation of the coumarin and phenanthridine-fused heterocycle **1**. It started with first converting 7-dimethylamino-4-hydroxycoumarin (**2**)⁶ to 4-chloro-7-dimethylamino-2-oxo-2*H*-chromene-3-carbaldehyde (**3**) by treating it with phosphorus oxychloride in DMF. The subsequent condensation of **3** and *N*-(2-bromoethyl)-4-methylquinolinium bromide (**5**) in the presence of triethylamine as a base in ethanol under reflux conditions gave the intermediate iminium bromide **6**,⁷ which was further reacted with aniline in chloroform at room temperature to afford the target compound **1**. Compound **5** was prepared by refluxing the commercially available 4-methylquinoline (**4**) with 1,2-dibromoethane as literature described.⁸ The molecular structure of **1** was confirmed by the observation of two characteristic singlet aromatic hydrogen absorption peaks at 8.24 and 8.05 ppm as well as the singlet imidazolidinyl hydrogen absorption peak at 5.37 ppm on the proton NMR spectra. Similar mechanisms for the formation of intermediate **6**⁷ and compound **1**^{3b} have been previously investigated.

With the heterocycle **1** in hand, its acidichromic properties were then explored. When treated with an acid (HBr), the light yellow, fluorescent ring-closed **1** is converted to the corresponding red, non-emissive ring-opened iminium salt **7** (Scheme 2). This process can be reverted by adding a base (Et₃N). Figures 1 and 2 show the UV-vis and emission spectra of compounds **1**, **7-9** in acetonitrile, respectively. Interestingly, the UV-vis spectra of **1** exhibit multiple absorption patterns. By comparison with the absorption spectra of the phenanthridine derivative reported by Cronin,³ the peaks at 250 and 340 nm were unambiguously identified to be the absorption of phenanthridine chromophore. The other absorption bands around 300 and 375 nm were attributed to the intrinsic benzene/coumarin-fused chromophore. Also, compound **1** is fluorescent due to the presence of the dimethylaminocoumarin fluorophore. Conversely, compound **7** is red ($\lambda_{\text{max}}=494$ nm) owing to the highly conjugated coumarin/phenanthridinium-fused chromophore, but is practically not fluorescent since the fluorescence is presumably quenched by the electron-deficient, positively charged phenanthridinium moiety.



Scheme 1. Synthetic route for the title compound **1**.



Scheme 2. A lockable colorimetric fluorescence molecular switch.

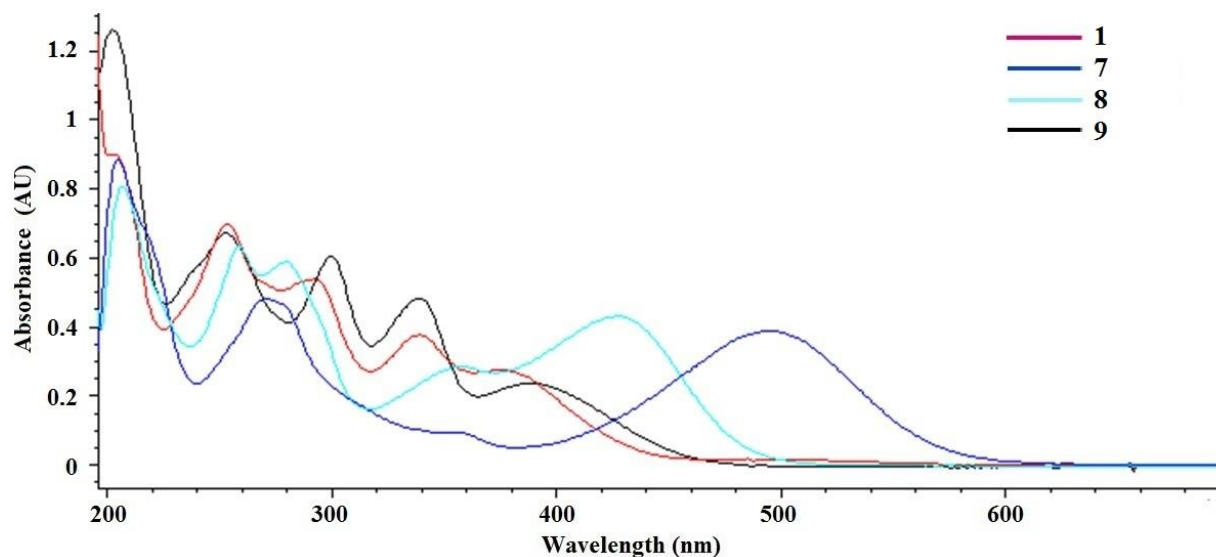


Figure 1. UV-vis spectra of **1** and **7-9** (1.0×10^{-5} M in CH_3CN) at room temperature.

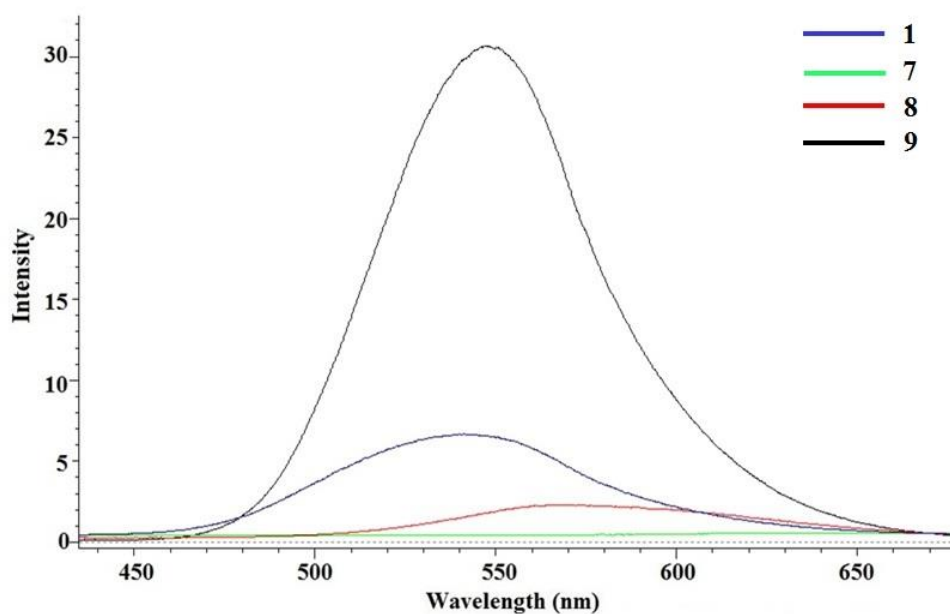


Figure 2. Emission spectra of **1** and **7-9** (3.0×10^{-6} M in CH_3CN) at room temperature.

Table 1 summarizes the fluorescence parameters of compounds **1**, **7-9** in acetonitrile. Among them, compound **9** has the highest fluorescence quantum yield with the Φ_f value of 0.133, follows by compound **1** ($\Phi_f = 0.035$). The Φ_f difference between **1** ($\lambda_{em} = 541$ nm) and **7** ($\lambda_{em} = 646$ nm) is determined to be more than 35-fold. Figure 3 shows the fluorescence spectra of **1** in the absence and presence of excess triethylamine, indicating that the added base triethylamine does not cause any increase or decrease in fluorescence intensity of **1**.

Table 1. Fluorescence parameters for compounds **1**, **7-9** in acetonitrile

Compound	λ_{ex} (nm)	λ_{em} (nm)	Φ_f
1	375	539	0.035
7	494	646	< 0.001
8	426	569	< 0.001
9	387	547	0.133

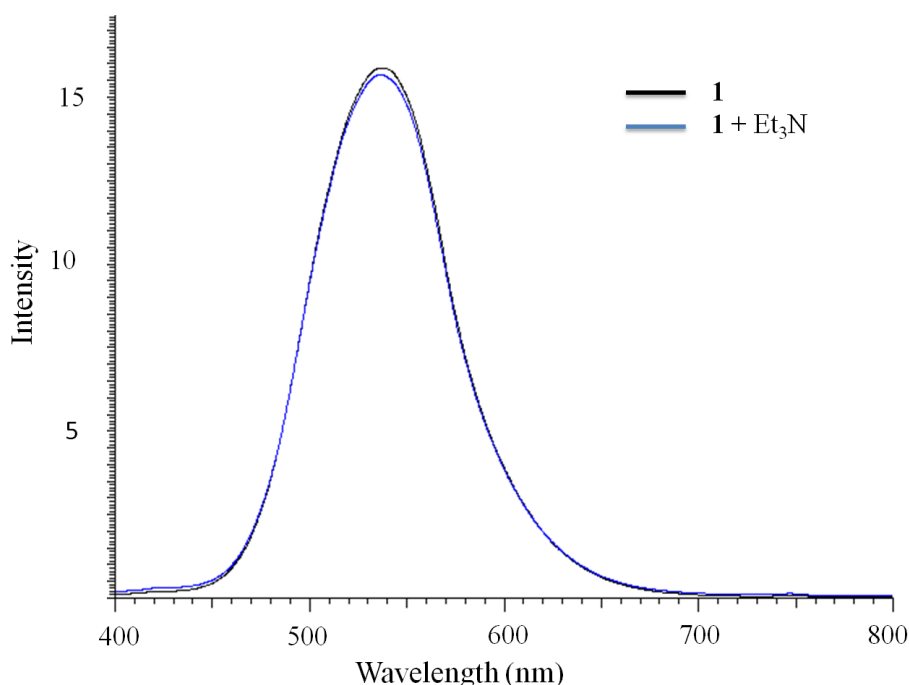
**Figure 3.** Fluorescence spectra of **1** in the absence and presence of excess triethylamine.

Figure 4 shows the reversible acidichromic behaviors of **1** during sequentially exposing it with an acid–base sequence. The results indicate that the reversible switching process between **1** and **7** can be repeated at least eight times without significant changes in the UV–vis spectra.

In addition to be interchangeable from one to the other via pH control, the two molecules **1** and **7** can also be further manipulated through exploitation of their redox potentials to convert them to their "pH-inert" forms. For instance, the acid-sensitive **1** can be oxidized by *N*-bromosuccinimide (NBS) to the acid-insensitive iminium bromide **8**, whereas the base-sensitive **7** can be reduced by NaBH_4 to the base-insensitive amine **9** (Scheme 2). Figure 5 shows the UV-vis spectra of **8** and **9** prior to and after addition of HBr and Et_3N . No major spectral variation between 350–500 nm was observed after the acid or base was added (the drastic absorbance increase of **9** between 230–350 nm under the basic conditions is due to the added triethylamine), implying that both **8** and **9** are now "pH-inert". The fact that alternation of the pH after oxidation

or reduction does not yield UV absorption bands correlating either **1** or **7**, indicating that the reversible cyclization process indeed had been inhibited. Our studies have demonstrated that this lockable molecular switch system (Scheme 2) not only maintains the read-write and read-only behavior, but also provides color and emission variations to the on/off responses as easily detectable dual output properties. We believe the current switching system may find useful applications in future development of molecular devices that combine write-read-erase and write-read-lock mechanisms.

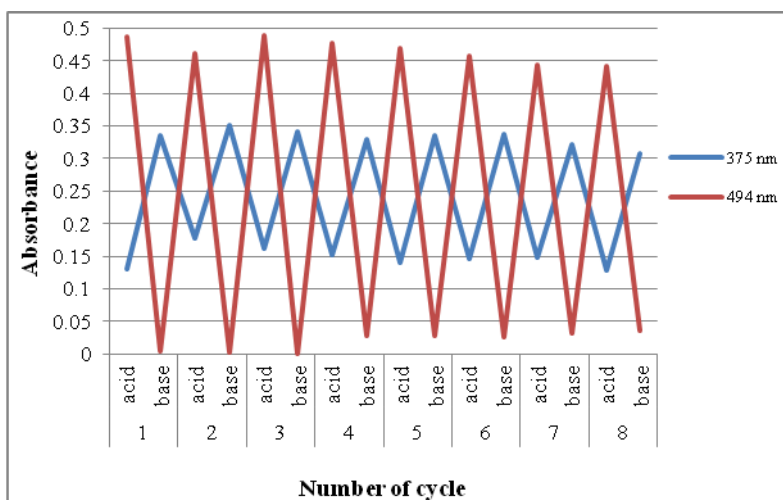


Figure 4. Reversible acidichromic behaviors of **1**. Optical density variations at acidic (375 nm) and basic (494 nm) conditions during sequentially exposing **1** with an acid–base sequence in CH₃CN/H₂O for eight cycles.

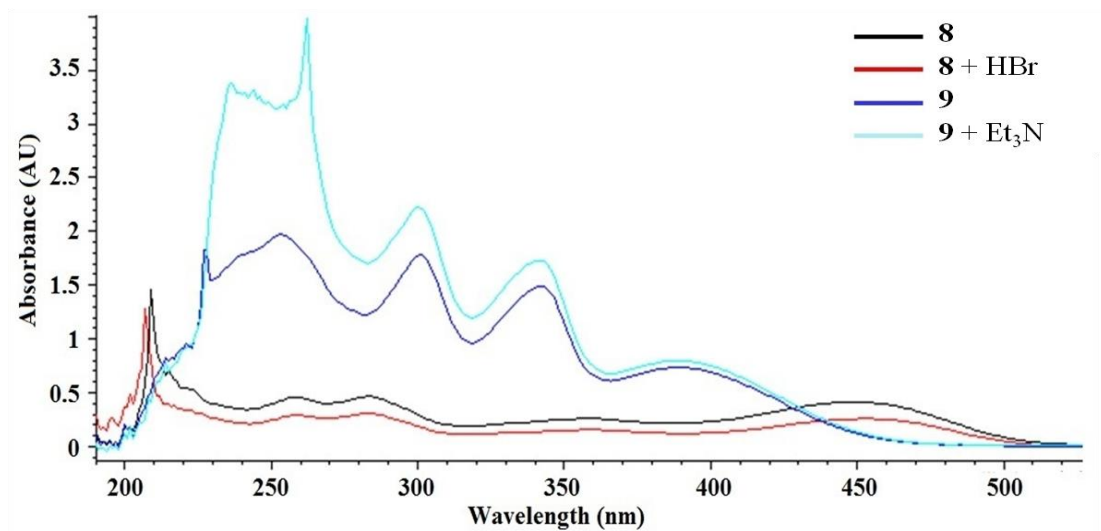


Figure 5. UV-vis spectra of **8** and **9** (1.0×10^{-5} M in CH₂Cl₂/H₂O) prior to and after addition of an acid (HBr) or a base (Et₃N).

Conclusions

In summary, the coumarin and phenanthridine-fused heterocycle **1** was efficiently synthesized using a base-mediated annulation of *N*-alkylquinolinium salt and coumarin as a key step. The prepared compound can function as an acidichromic colorant using an acid or a base as an external stimulus, along with easily detectable color and fluorescence variation as dual output properties. Moreover, the molecular switching between **1** and **7** is lockable via redox chemistry. They can be converted to their “pH-inert” forms by NBS oxidation and NaBH₄ reduction. Further anchoring the amino group on the coumarin moiety of **1** onto a solid support to enhance its performance is currently underway.

Experimental Section

General. Melting points were determined on a Mel-Temp melting point apparatus in open capillaries and are uncorrected. MS were performed with a JEOL JMS-SX/SX 102A spectrometer. Absorption spectra were recorded using a HP8453 spectrophotometer. Fluorescence spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. 7-Diethylamino-4-methylcoumarin ($\Phi_f = 1.00$ in acetonitrile) was used as an external standard for the measurement of fluorescence quantum yields of **1** and **7-9**. Fluorescence quantum yields were measured by comparing the integrated area under the fluorescence curve for **1** and **7-9** and 7-diethylamino-4-methylcoumarin at equal absorbance at the same excitation wavelength. The quantum yields were corrected for the refractive index of the solvent. ¹H and ¹³C NMR spectra were recorded at 300 and 75 MHz on a Varian VXR300 spectrometer or at 600 and 150 MHz on a Varian VXR600 spectrometer. Chemical shifts were reported in parts per million on the δ scale relative to an internal standard (tetramethylsilane, or appropriate solvent peaks) with coupling constants given in hertz. ¹H NMR multiplicity data are denoted by s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Analytical thin-layer chromatography (TLC) was carried out on Merck silica gel 60G-254 plates (25 mm) and developed with the solvents mentioned. Flash chromatography was performed in columns of various diameters with Merck silica gel (230-400 mesh ASTM 9385 kieselgel 60H) by elution with the solvent systems. 4-Methylquinoline, 1,2-dibromoethane, aniline and triethylamine were commercially available. The commercial chemicals were used as received. Solvents, unless otherwise specified, were reagent grade and distilled once prior to use. All new compounds exhibited satisfactory spectroscopic and analytical data. 7-Dimethylaminocoumarin was prepared according to the reported procedure.⁶

Synthetic procedure for 4-chloro-7-dimethylamino-2-oxo-2*H*-chromene-3-carbaldehyde (**3**).

To a solution of DMF (2 mL) was added POCl₃ (2 mL) in one portion at 0 °C. The resulting solution was heated at 50 °C for 0.5 h. A solution of 7-dimethylaminocoumarin (**2**, 1.42 g, 6.71

mmol, dissolved in 10 mL DMF) was then added to the mixture at that temperature. The mixture was further heated at 60 °C for 12 h. After cooled to room temperature, the mixture was poured into ice-water and the precipitate was filtered. The cake was extracted with methylene chloride twice. The combined organic extracts were dried over MgSO₄, filtered, and concentrated to obtain an orange solid; yield 92%; R_f = 0.45 (40% EtOAc/hexanes); mp 185–187 °C; ¹H NMR (CDCl₃, 300 MHz) δ 10.30 (s, 1H), 7.86 (d, J = 9.3 Hz, 1H), 6.71 (dd, J = 9.3, 2.7 Hz, 1H), 6.44 (d, J = 2.7 Hz, 1H), 3.17 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 187.1, 159.9, 156.1, 155.6, 154.4, 129.1, 111.3, 110.9, 107.9, 97.0, 40.6; IR ν (KBr) 1718, 1681, 1615, 1555, 1504, 1384, 1146, 822 cm⁻¹; HRMS (EI) calcd for C₁₂H₁₀ClNO₃ [M⁺] 251.0349, found 251.0350.

2-Bromo-ethyl-4-methyl-quinolinium bromide (5). To a solution of 4-methylquinoline (**4**, 4.3 g; 30 mmol) in 1,2-dibromoethane (50 mL) was heated at 90 °C for five days. Any precipitate formed during the reaction was recovered by filtration daily. After each filtration, the precipitate was rinsed with an additional 5 mL of 1,2-dibromoethane and the mother liquor stirred at 90 °C until the next filtration. The reaction was complete when no more precipitate formed. The precipitates were combined and washed thoroughly with acetone to give a beige solid; yield 88%; mp 198–200 °C (lit.^{8a} 271–272 °C); ¹H NMR (DMSO-*d*₆, 300 MHz) δ 9.45 (d, J = 6.0 Hz, 1H), 8.64 (d, J = 5.7 Hz, 1H), 8.57 (dd, J = 5.7, 1.2 Hz, 1H), 8.26 (ddd, J = 8.4, 7.2, 1.5 Hz, 1H), 8.14 (d, J = 6.0 Hz, 1H), 8.06 (td, J = 7.5, 0.9 Hz, 1H), 5.49 (t, J = 6.0 Hz, 2H), 4.13 (t, J = 6.0 Hz, 2H), 3.03 (s, 3H).

12-(Dimethylamino)-1-phenyl-2,3-dihydro-1*H*-chromeno[3,4-*j*]imidazo[1,2-

***f*]phenanthridin-15(16*bH*)-one (1).** To a solution of **3** (205 mg, 0.81 mmol) in ethanol (12 mL) was added 2-bromoethyl-4-methylquinolinium bromide (**5**, 268 mg, 0.81 mmol) and triethylamine (169 μL, 1.21 mmol) at room temperature. The resulting solution was refluxed for 4 h. After cooled to room temperature, the precipitate was filtered to give a red solid **6**. To this red compound **6** (200 mg, 0.38 mmol) in CHCl₃ (10 mL) was added aniline (34 μL, 0.38 mmol) and triethylamine (160 μL, 1.14 mmol) at room temperature. The resulting solution was stirred at that temperature for 4 h. After the reaction was complete, the mixture was transferred to a separating funnel and washed with water (15 mL) and brine (5 mL). The organic phase was then dried over MgSO₄ and concentrated. The crude product was purified by column chromatography to give a light yellow solid; yield 36% (from **3** and **5**); R_f = 0.22 (50% EtOAc/hexanes); mp 238–240 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.24 (s, 1H), 8.05 (s, 1H), 8.03 (d, J = 6.3 Hz, 1H), 7.97 (d, J = 9.3 Hz, 1H), 7.41 (td, J = 7.5, 1.2 Hz, 1H), 7.31–7.25 (m, 2H), 7.08 (td, J = 7.2, 1.2 Hz, 1H), 6.86 (td, J = 6.3, 0.9 Hz, 2H), 6.75–6.73 (m, 3H), 6.59 (d, J = 2.4 Hz, 1H), 5.37 (s, 1H), 4.12–4.04 (m, 1H), 3.97–3.92 (m, 1H), 3.70–3.65 (m, 1H), 3.40–3.36 (m, 1H), 3.60 (s, 6H); ¹³C NMR (CDCl₃, 150 MHz) δ 161.7, 153.1, 151.9, 148.3, 144.4, 138.2, 135.5, 132.9, 130.9, 129.3, 126.4, 124.6, 123.5, 123.0, 120.0, 118.6, 115.0, 113.8, 113.4, 112.6, 109.1, 106.8, 99.3, 75.1, 50.8, 44.8, 40.2; IR ν (KBr) 2924, 2853, 1721, 1617, 1362, 1244, 1133, 750 cm⁻¹; HRMS (EI) m/z calcd for C₃₀H₂₅N₃O₂ [M⁺] 459.1947, found 459.1936.

3-(Dimethylamino)-6-oxo-9-(2-(phenylamino)ethyl)-6*H*-chromeno[3,4-*j*]phenanthridin-9-ium bromide (7). To a solution of **5** (100 mg, 0.22 mmol) in methylene chloride (5 mL) was

added water (5 mL). Phases were separated and then extracted into excess 47% HBr (1 mL). The acidic extract was concentrated under vacuum and the residue was triturated with acetone to afford a red solid as the product; yield 82%; mp 230 °C (dec.); ¹H NMR (DMSO-*d*₆, 600 MHz) δ 10.01 (s, 1H), 9.43 (d, *J* = 8.4 Hz, 1H), 9.39 (s, 1H), 9.17 (s, 1H), 8.60 (d, *J* = 9.6 Hz, 1H), 8.57 (d, *J* = 7.8 Hz, 1H), 8.14 (t, *J* = 7.2 Hz, 1H), 8.09 (t, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 7.8 Hz, 2H), 6.83 (dd, *J* = 9.6, 1.8 Hz, 1H), 6.59–6.54 (m, 4H), 5.86 (s, 1H), 5.10–5.09 (m, 2H), 3.83–3.70 (m, 2H), 3.09 (s, 6H); ¹³C NMR (DMSO-*d*₆, 150 MHz) δ 159.6, 155.4, 153.9, 153.8, 147.4, 141.9, 137.2, 137.1, 133.9, 132.9, 130.0, 129.1, 127.1, 126.4, 125.2, 120.8, 120.3, 119.7, 116.7, 114.0, 112.3, 109.8, 104.9, 98.2, 56.7, 41.6, 39.6; IR ν (KBr) 3391, 3016, 2566, 1744, 1598, 1377, 1119, 761, 616 cm⁻¹; HRMS (EI) *m/z* calcd for C₃₀H₂₆BrN₃O₂ [M⁺] 539.1208, found 539.1205.

12-(Dimethylamino)-15-oxo-1-phenyl-1,2,3,15-tetrahydrochromeno[3,4-*j*]imidazo[1,2-*f*]phenanthridin-4-ium bromide (8). To a solution of **1** (70 mg, 0.15 mmol) in ethyl acetate (12 mL) was added *N*-bromosuccinimide (30 mg, 0.17 mmol) at room temperature for 3 h in the dark. The precipitate was filtered and washed with ethyl acetate to give a brown solid; yield 88%; mp 330 °C (dec.); ¹H NMR (CD₃OD, 300 MHz) δ 8.91 (s, 1H), 8.78 (d, *J* = 8.1 Hz, 1H), 8.19 (d, *J* = 9.0 Hz, 1H), 8.06 (s, 1H), 7.89 (t, *J* = 8.1 Hz, 1H), 7.76–7.62 (m, 7H), 6.73 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.36 (d, *J* = 2.7 Hz, 1H), 4.98–4.80 (m, 2H), 4.70–4.60 (m, 2H), 3.05 (s, 6H); ¹³C NMR (CD₃OD, 150 MHz) δ 160.9, 155.0, 154.9, 153.7, 141.2, 140.2, 139.9, 134.8, 133.8, 132.8, 132.6, 132.0, 127.9, 127.1, 126.8, 126.4, 121.3, 119.2, 117.0, 115.8, 113.1, 110.9, 105.4, 99.0, 55.7, 48.0, 40.2; IR ν (KBr) 3403, 1733, 1610, 1570, 1545, 1388, 1269, 1131, 775 cm⁻¹; HRMS (FAB) *m/z* calcd for C₃₀H₂₄BrN₃O₂ [M + H⁺] 538.1130, found 538.1131.

3-(Dimethylamino)-9-(2-(phenylamino)ethyl)-8,9-dihydro-6*H*-chromeno[3,4-*j*]phenanthridin-6-one (9). To a solution of **7** (100 mg, 0.19 mmol) in methanol (25 mL) was added sodium borohydride (21 mg, 0.56 mmol) in one portion at room temperature. The red solution turned yellow instantly. After completion of the reaction within 5 min, and the crude product was purified by column chromatography to give an orange solid; yield 83%; *R*_f = 0.23 (20% EtOAc/hexanes); mp 185–187 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.18 (s, 1H), 8.03 (s, 1H), 7.95 (d, *J* = 9.0 Hz, 1H), 7.91 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.31 (td, *J* = 8.4, 1.5 Hz, 1H), 7.19 (td, *J* = 7.5, 1.2 Hz, 2H), 6.93 (t, *J* = 6.9 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.73 (t, *J* = 7.5 Hz, 1H), 6.72 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.63 (dd, *J* = 8.7, 1.2 Hz, 2H), 6.60 (d, *J* = 2.4 Hz, 1H), 4.38 (s, 2H), 3.86 (s, 1H), 3.47 (t, *J* = 5.7 Hz, 2H), 3.06 (t, *J* = 5.7 Hz, 2H), 3.07 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 161.8, 152.8, 151.7, 147.7, 146.9, 138.2, 135.3, 131.1, 130.8, 129.3, 127.0, 125.0, 123.2, 121.9, 118.5, 117.8, 117.4, 113.5, 113.0, 112.9, 109.1, 106.8, 99.2, 52.4, 49.7, 40.4, 40.1; IR ν (KBr) 3371, 1706, 1620, 1604, 1496, 1282, 1131 cm⁻¹; HRMS (EI) *m/z* calcd for C₃₀H₂₇N₃O₂ [M⁺] 461.2103, found 461.2115.

Reversible acidichromic behaviors of 1. The initial sample was prepared as a 9.8 × 10⁻⁵ M solution of compound **1** (1.35 mg, 2.94 × 10⁻³ mmol) in 15 mL of CH₃CN and 15 mL of H₂O. With a drop of 47% HBr_(aq) to reduce the pH of the mixture to ~3 and the UV-vis spectra of the

solution (at 494 nm) was measured. The resulting solution was then basified to ~pH 9 by drop-wise addition of triethylamine and its UV-vis spectra (at 375 nm) was measured. This cycle was repeated eight times.

UV-vis spectra of 8 and 9 prior to and after addition of an acid or a base. For compound **8**, the initial sample was prepared as a solution of compound **8** (1.35 mg, 2.51×10^{-3} mmol) in 10 mL of CH_2Cl_2 and 10 mL of H_2O . The UV-vis spectra were obtained for the organic layer. The biphasic solution was then acidified by drop-wise addition of 47% $\text{HBr}_{(\text{aq})}$ to reduce the pH to ~3, and the UV-vis spectra were obtained again for the organic layer. For compound **9**, the initial sample was prepared as a solution of compound **9** (0.63 mg, 1.36×10^{-3} mmol) in 10 mL of CH_2Cl_2 and 10 mL of H_2O . The UV-vis spectra were obtained for the organic layer. Triethylamine was then added drop-wise to the biphasic solution to basify the aqueous layer to the pH ~9, and the UV-vis spectra were obtained again for the organic layer.

Acknowledgements

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