



Synthesis and physical properties of various organic dyes derived from a single core skeleton, 1,2-dihydroindol-3-one

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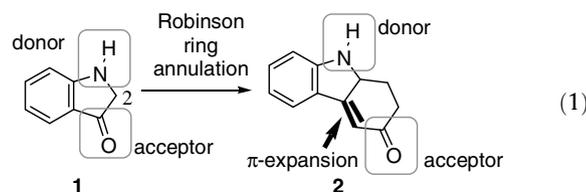
ABSTRACT

Various organic dyes were synthesized from 1,2-dihydroindol-3-one analogue via Robinson ring annulation, which proceeded efficiently using DBU as a base to give the π -expanded compounds. These compounds exhibited longer Stokes shifts (over 100 nm) than the 1,2-dihydroindol-3-ones (50–80 nm). Emission peaks of the obtained materials covered the 440–640 nm range.

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The importance of organic light-emitting materials has increased greatly in recent years. They can be used in electroluminescent¹ and electrogenerated chemiluminescent² materials, chemosensors,³ environmental sensors (temperature,⁴ pH,⁵ solvent,⁶ and viscosity⁷), metal ion sensors,⁸ etc.⁹ Recently, these types of materials have received much attention for potential biological applications in fluorescence imaging and bio-labeling.^{10–16} We are interested in compact structures with luminescence properties that can be introduced into various compounds causing little structural change.¹⁶ Efficient fluorophores require the following characteristics: (1) a good donor–acceptor relationship and (2) a rigid structure to prevent nonradiative decay. In this context, coumarin derivatives bearing a donor–acceptor system are thought to have an enhanced fluorescence quantum yield by introducing a donating amino moiety into the cyclic system.¹⁷ Consequently, we focused on a 1,2-dihydroindol-3-one structure (1). It consists of the donor (amino group) and acceptor (carbonyl group) parts connected by a π -system (benzene ring); it also has a ring structure that will enhance the fluorescence quantum yield. Structure (1) possesses an α -proton activated by a carbonyl group, which can facilitate the expansion of the π -system via a Robinson ring annulation at the 2-position of 1 (Eq. 1). The synthesis of 1,2-dihydroindol-3-one derivatives has been examined for use as intermediates in the synthesis of alkaloids, pharmaceutical agents, and insecticides.¹⁸ Surprisingly, however, few reports describe the optical properties of derivatives of 1.^{18d,19} Herein, we report the synthesis and optical properties of 1,2-dihydroindol-3-one derivatives with

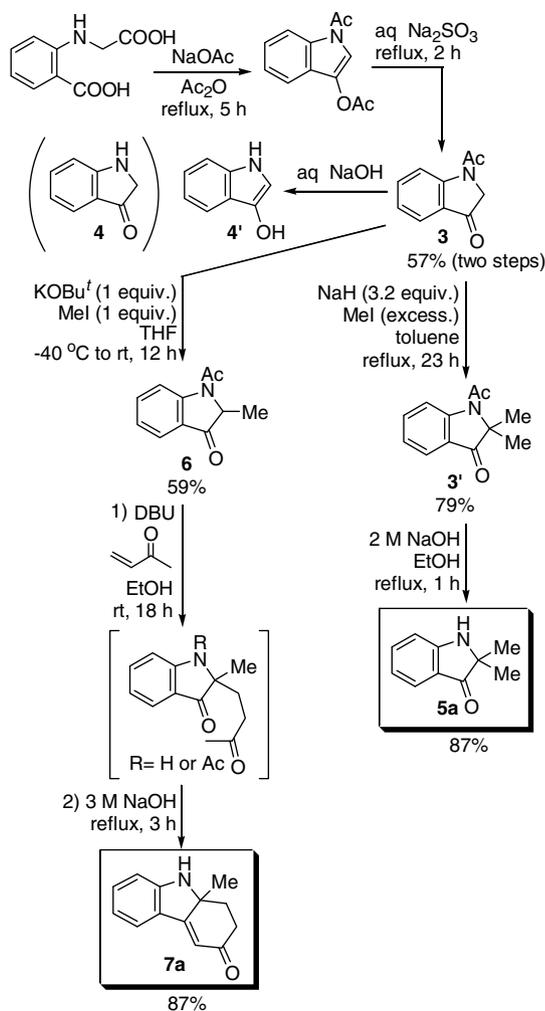
various ranges of emission peaks by a simple reaction of the original 1,2-dihydroindol-3-one structure.



Synthesis of the basic compound, *N*-acetyl-1,2-dihydroindol-3-one (3), was based on a procedure reported in a related patent²⁰ (Scheme 1). The reaction of 3 with NaOH was examined to remove the acetyl group, but the desired compound (4) was not obtained. However, the enol form (4') was observed in the ¹H NMR spectrum (solvent: CDCl₃). Therefore, we protected the 2-position using a methyl group. The dimethylated derivative (5a) was obtained by the reaction of 3 with methyl iodide, with subsequent removal of the acetyl group. The monomethylated compound (6) was also formed by the reaction with methyl iodide by judicious choice of a base (KOBU^t) and its equivalent (1.05 equiv) in comparable yield. After the investigation of various bases for the Robinson ring annulation, we found that DBU was the best base for the reaction of 6 with methyl vinyl ketone to give 7a. The one-pot synthesis of 7a could be achieved by the reaction of 6 with DBU, followed by reaction with aq NaOH under reflux in EtOH.²¹

To investigate comprehensive changes by an expansion of the π -system, methyl and phenyl substituents on nitrogen atoms as well as a dicyanomethylene group at the carbonyl moiety were introduced into 5a and 7a (Scheme 2).

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The UV–vis absorption and fluorescence spectra of the obtained compounds were measured in CH₃CN (Fig. 1). The optical data are presented in Table 1. The compounds bearing methyl (**5b** and **7b**) and phenyl (**5c** and **7c**) substituents on the nitrogen atom showed longer absorption and emission peaks than **5a** and **7a**, indicating that these groups enhanced the electron-donating ability of the amino group. To obtain longer absorption and emission peaks, it was efficient to change the carbonyl group to the stronger electron-withdrawing dicyanomethylene moiety. Large bathochromic shifts were obtained in the absorption and emission spectra of **5a** versus **8a** and **5b** versus **8b**. Enhancement of the molecular absorption coefficients (ϵ_{max}) was also observed.

Regarding UV–vis absorption spectra, a bathochromic shift between **5a** and **7a** was observed. This result is consistent with those of various substituted compounds (**5b** vs **7b**, **5c** vs **7c**, **8a** vs **9a**, and **8b** vs **9b**) accompanied by ca. 14–30 nm change. The red shift of 30 nm in the absorption peaks by the introduction of another C–C double bond is well known in the estimation of α,β -unsaturated ketones.²² Khodorkovsky and co-workers reported the introduction of two vinyl tethers in their donor–acceptor system in which a bathochromic shift of ca. 80 nm (40 nm/one vinyl component) was observed.²³ Therefore, our system is slightly defective in the π -expansion in relation to absorption, possibly a result from the torsion of the fused π -conjugated ring system.

Specific changes of the emission characters were observed. The emission peak shifted to longer wavelength (about 49–70 nm) be-

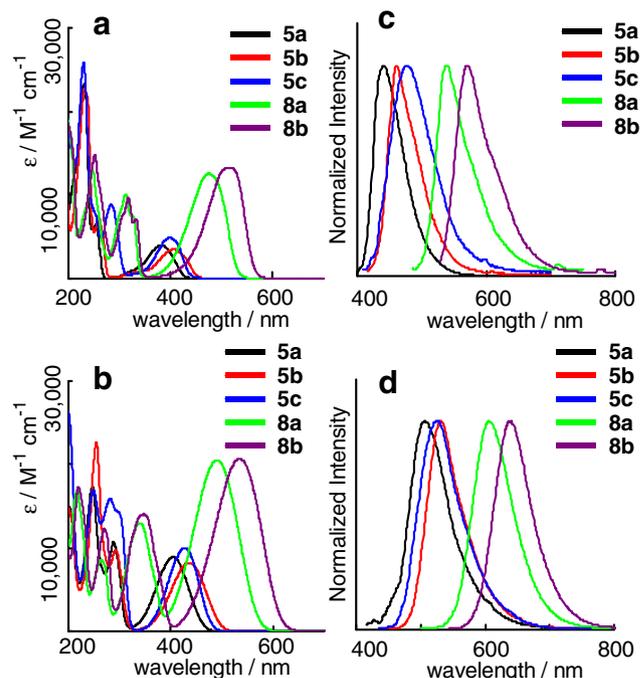
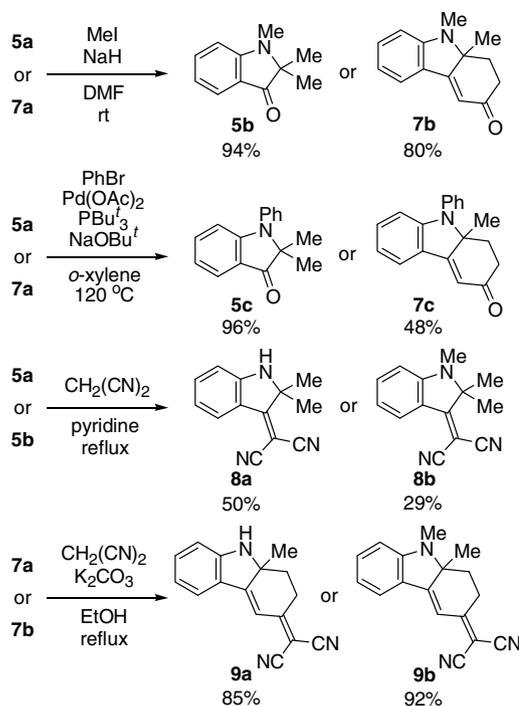


Figure 1. UV–vis absorption spectra of (a) **5** and **8**, (b) **7** and **9** in CH₃CN (3.0×10^{-5} M), and FL spectra of (c) **5** and **8**, (d) **7** and **9** in CH₃CN (3.0×10^{-7} M) excited at λ_{max} . Black line, **5a** and **7a**; red line, **5b** and **7b**; blue line, **5c** and **7c**; green line, **8a** and **9a**; purple line, **8b** and **9b**.

tween **5** and **7** or **8** and **9**. It is noteworthy to maintain the full width at half maximum (fwhm) in a range of 55–80 nm even in the bathochromic shift of the emission peaks.^{16c,24} Quantum yields (Φ_{F}) of the carbonyl derivatives were maintained or decreased by the change in the π -system (**5** vs **7**). Interestingly, the quantum yield increased in compounds having a dicyanomethylene moiety

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