



Structure-fluorescence relationship of push-pull 2-phenylbenzothiazole derivatives designed based on the firefly light-emitter

Tomoya Fujikawa^a, Takuya Uehara^a, Minoru Yamaji^b, Takuya Kanetomo^{a,c}, Takayuki Ishida^a, Shojiro Maki^a, Takashi Hirano^{a,*}

^a Department of Engineering Science, Graduate School of Informatics and Engineering, The University of Electro-Communications, Chofu, Tokyo 182-8585, Japan

^b Division of Molecular Science, Graduate School of Science and Engineering, Gunma University, Kiryu, Gunma 376-8515, Japan

ARTICLE INFO

Article history:

Received 3 February 2018

Revised 22 February 2018

Accepted 26 February 2018

Available online 27 February 2018

Keywords:

Firefly oxyluciferin

Benzothiazole

Fluorophore

Solvatochromism

Push-pull structure

ABSTRACT

6-Dimethylamino-2-phenylbenzothiazole (**1a**) mimicking the firefly oxyluciferin structure and the derivatives with an electron-withdrawing substituent on the phenyl group were prepared, and their fluorescence properties were investigated in various solvents. **1a** showed solvatochromic fluorescence with good fluorescence quantum yields ($\Phi_f > 0.8$). The introduction of an electron-withdrawing group led to a red-shift of the emission maximum. In particular, the derivatives with the 2,2-dicyanoethenyl and (1,3-dihydro-1,3-dioxo-2H-inden-2-ylidene)methyl groups showed near-infrared fluorescence in chloroform. In addition, the derivative with the phenylimine moiety showed efficient solid-state fluorescence, resulted from a molecular arrangement inhibiting intermolecular interactions for quenching the fluorescence state in crystals.

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Fireflies efficiently produce bioluminescent light with various colors from green to red.¹ The bioluminescence is caused by the enzymatic reaction of firefly luciferin with ATP and O₂ to produce oxyluciferin (OLH) and light. The light emitting center of the reaction is the keto-phenolate anion of OLH (OL⁻) in the excited singlet (S₁) state (Scheme 1).² To confirm the reaction mechanism, the spectroscopic property of OL⁻ were clarified based on that of the phenolate anion of 5,5-dimethyl OLH (Me₂OLH, Scheme 1).³ Because OL⁻ is a solvatochromic fluorophore with relatively high quantum yields, OL⁻ is an attractive prototype for designing new fluorophores. The characteristic fluorescence property of OL⁻ is originated from the molecular structure consisted of the electron-donating and withdrawing moieties (Scheme 1). The significance of the electronically push-pull structure in OL⁻ was supported by the spectroscopic property of 6'-dimethylamino analogue Me₂NMe₂OL (Scheme 1).⁴ We, thus, planned to design benzothiazoles mimicking the push-pull structures of OL⁻ and Me₂NMe₂OL, while the benzothiazole ring has been widely used for various fluorophore designs including solvatochromic fluorophores.⁵ To tune spectroscopic properties of benzothiazole fluorophores for various usages, it is needed to reveal relationship

between structure and fluorescence property of the derivatives. For this purpose, we investigated here the spectroscopic properties of 2-phenylbenzothiazoles **1** (Scheme 1) with push-pull structures. In the course of the study, it was found that one of the derivatives showed a moderate solid-state fluorescence.

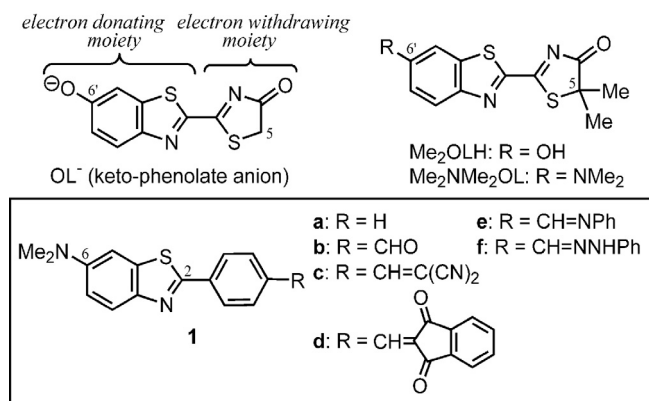
We adopted 6-dimethylamino-2-phenylbenzothiazole **1a** as a basic structure with an electron-donating moiety similar to Me₂NMe₂OL. To introduce various electron-withdrawing substituents to the 2-phenyl group in **1a**, aldehyde **1b** was synthesized as a push-pull derivative. Then, push-pull derivatives **1c–e** were prepared by condensation reactions with **1b**.

Spectroscopic properties of **1a–f** were investigated in solutions of cyclohexane, chloroform, acetonitrile and methanol. Fig. 1 shows the fluorescence spectra while the absorption spectra are deposited in Supplementary data (SD). The numerical data are listed in Tables 1 for the fluorescence and in Table S1 in SD for the absorption. Phenyl derivative **1a** showed a solvent-dependent shift of fluorescence emission maxima (λ_f) with good quantum yields (Φ_f) over 0.8, while electronic absorption maxima (λ_{ab}) of **1a** showed a small solvent-dependency. The λ_f values were red-shifted with an increase in the solvent polarity to show a variation in the range of 393 to 483 nm, indicating that the S₁ state of **1a** has electronically polarized character more than the ground (S₀) state.⁶ Introduction of only the pushing dimethylamino group on the benzothiazole moiety caused push-pull property in the π -electronic structure although **1a** has no pulling substituent on the 2-phenyl

* Corresponding author.

E-mail address: thirano@uec.ac.jp (T. Hirano).

^c Present address: Department of Chemistry, Faculty of Science Division I, Tokyo University of Science, Tokyo 162-8601, Japan.



Scheme 1. Structures of firefly oxyluciferin phenolate anion (OL⁻), 5,5-dimethyl-oxyluciferin analogues (Me₂OLH and Me₂NMe₂OL), and push-pull 2-phenylbenzothiazole derivatives **1a–f**.

group. The λ_{ab} and λ_f values of **1b–f** in cyclohexane are red-shifted compared to those of **1a**. Similar to **1a**, **1b–f** showed solvent-dependent variations of the λ_f values in contrast to a small solvent-dependency of the λ_{ab} values. The substituents on the 2-phenyl group of **1b–f** were expected to affect the spectroscopic properties by their electron withdrawing properties together with expansion of the π -conjugated system. In fact, the electron withdrawing strengths were quantified by using the Hammett σ_p values for the formyl (0.42) in **1b**, 2,2-dicyanoethyl (0.84) in **1c** and (phenylimino)methyl (0.42) in **1e**.⁷ At the same σ_p value for the formyl and (phenylimino)methyl groups, the λ_f values of **1b** and **1e** in cyclohexane, chloroform, and acetonitrile were similar to each other, while the Φ_f values of **1b** were greater than those

Table 1

Fluorescence properties of **1a–f** in various solvents at 298 K.

Compd.	λ_f / nm (Φ_f) ^a			
	C ₆ H ₁₂	CHCl ₃	CH ₃ CN	CH ₃ OH
1a	393, 413 (0.84)	443 (0.84)	475 (0.83)	483 (0.94)
1b	444, 469 (0.80)	550 (0.85)	626 (0.66)	494 (0.10)
1c	526, 562 (0.85)	683 (0.64)	N/A ^b	N/A ^b
1d	535, 572 (0.13)	727 (0.35)	N/A ^b	N/A ^b
1e	445, 469 (0.057)	534 (0.12)	610 (0.72)	639 (0.067)
1f	444, 469 (0.023)	517 (0.057)	541 (0.067)	545 (0.026)

^a Emission maximum (λ_f) and quantum yield (Φ_f) in parenthesis.

^b Not observed.

of **1e**. Aldehyde **1b** showed a blue-shifted fluorescence spectrum in methanol, suggesting that the formyl group of **1b** gave a hemiacetal. Interestingly, **1e** showed a good Φ_f value (0.72) only in acetonitrile. Derivatives **1c** and **1d** showed red-shifted λ_f values upon changing cyclohexane to chloroform, while they showed no fluorescence in acetonitrile and methanol. In particular, the λ_f values in chloroform reached the near-infrared region. The 2,2-dicyanoethyl in **1c** and (1,3-dihydro-1,3-dioxo-2H-inden-2-ylidene) methyl groups in **1d** induce a strongly polarized character of the S₁ states lead to a preferential nonradiative decay in polar solvents. Hydrazone **1f** showed lower Φ_f values than imine **1e**, and a fluorescence spectral change of **1f** depending on the solvents was smaller than that of **1e**.

To understand the photophysical properties of the S₁ states of **1a–f**, fluorescence lifetimes (τ_f) of **1a–f** in cyclohexane were measured (Table 2). The decay profiles of the fluorescence are deposited in Fig. S2 in SD. The estimated rate constants (k_f) of the fluorescence emission processes for **1a–d** were similar among them. Introduction of the (1,3-dihydro-1,3-dioxo-2H-inden-2-ylidene)

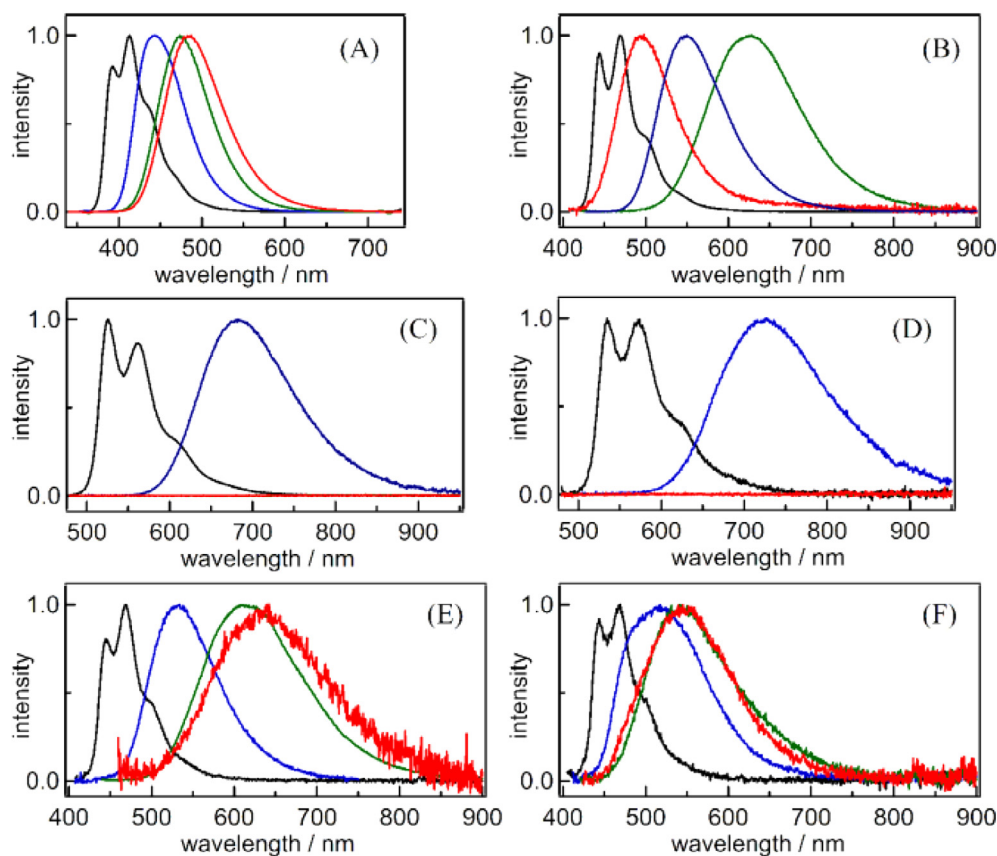


Fig. 1. Fluorescence spectra of **1a** (A), **1b** (B), **1c** (C), **1d** (D), **1e** (E), and **1f** (F) in cyclohexane (black), chloroform (blue), acetonitrile (green), and methanol (red) at 298 K.

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