

Short note

Enhanced brightness of 2,6-diphenylthiazolo[4,5-*b*]pyrazines by introducing double electron donating groupsYoshihisa Suzuki^a, Minoru Yamaji^b, 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

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ABSTRACT

Thiazolo[4,5-*b*]pyrazine (TPy) derivatives with enhanced fluorescence brightness were developed by tuning the double substituents. The spectroscopic and photophysical properties were investigated by measurements of absorption and fluorescence spectra, fluorescence yields and lifetimes. Based on the DFT calculations, the increased brightness was rationalized by the enhanced electronic absorptivity and fluorescence yields. The developed methodology provides the guide to design high-performance TPy fluorophores.

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1. Introduction

Organic fluorophores are essential compounds for analytical and imaging techniques in the field of life sciences [1–5]. Researching and developing novel fluorophores, therefore, become one of important tasks for organic chemists. On designing a new fluorophore, it is crucial to clarify the relationship between the structures and the physical properties including absorption wavelength (λ_{ab}), extinction coefficient (ϵ), fluorescence emission wavelength (λ_{fl}), lifetime (τ_f), and quantum yield (Φ_f) for a specific class of fluorophores. Fluorescence brightness defined as the product ($\epsilon\Phi_f$) of the extinction coefficient and the fluorescence quantum yield is also a key index for determining the detection limit of the lowest quantity of a fluorophore under a particular excitation light intensity [2–5]. Thus, enhancement of fluorescence brightness is one of the aims in a fluorophore design.

We have been paying attention to bioluminescence emitting compounds such as Cypridina oxyluciferin as prototypes for developing and designing new fluorophores [6–8]. Accordingly, we have investigated the spectroscopic properties of thiazolo[4,5-*b*]pyrazine (TPy) derivatives prepared from amidopyrazine derivatives that share the common core structure with Cypridina oxyluciferin [9,10]. In the previous studies, it was found that TPy

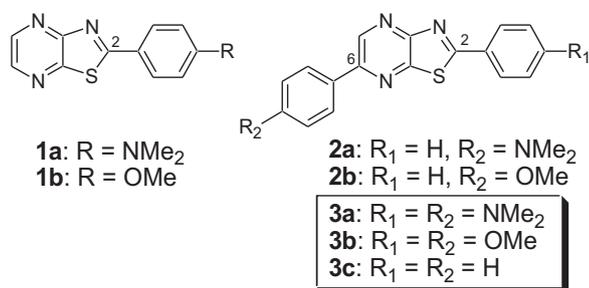
derivatives **1** and **2** with a phenyl group having an electron-donating substituent such as the dimethylamino and methoxy groups show solvatochromic fluorescence with moderate quantum yields (Scheme 1). In particular, the 2,6-diphenyl derivatives **2** show fluorescence performance better than the 2-phenyl derivatives **1**. To improve the fluorophore brightness of these TPy derivatives, we have investigated the effects of introducing two electron-donating groups on the two phenyl rings in the 2,6-diphenyl TPy structure. In this research note, we report that introducing the double electron-donating group efficiently increases the fluorescence brightness in the 2,6-diphenyl TPy derivatives **3**.

2. Experimental

General methods for characterizing the new compounds, spectroscopic and photophysical measurements, and DFT calculations were described in Supplementary data. TPys **3** were prepared from the corresponding amidopyrazine derivatives with Lawesson's reagent according to the preparation method for **1** and **2** (Scheme S1) [9–11]. Experimental details of the synthesis are described in Supplementary data.

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Scheme 1. The TPy derivatives 1–3.

3. Results and discussion

3.1. Spectroscopic and photophysical properties of TPy derivatives 3

UV/vis absorption and fluorescence spectra of TPy derivatives **3** in various solvents are illustrated in Fig. 1. Their absorption and fluorescence spectroscopic data are summarized in Tables S1 and S2, respectively, in Supplementary data together with those of **2** for comparison [9,10]. The λ_{ab} values of **3** are red-shifted with increasing the electron donating ability of the substituent on going from R=H (Hammett constant $\sigma_p=0$) to OMe ($\sigma_p=-0.27$) and NMe₂ (Hammett $\sigma_p=-0.83$) [12], and slightly red-shifted compared to those of the corresponding NMe₂ and OMe derivatives **2a** and **2b**. Interestingly, the extinction coefficients (ϵ) of **3** significantly increase with increasing the electron donating ability of the substituent, and greater than those of the corresponding derivatives **2**. The compounds **3a** and **3b** showed intense fluorescence with the exception of the fluorescence of **3a** in methanol and **3b** in cyclohexane, while **3c** showed weak fluorescence. The fluorescence quantum yields (Φ_f) of **3a** and **3b** are similar to or slightly larger than those of the corresponding

derivatives **2a** and **2b** in all the used solvents. The λ_{ab} values of the lowest energy absorption bands of **3** showed a small variation depending on the solvents. Conversely, the fluorescence spectra of **3a** and **3b** showed solvatochromism similar to those of **2a** and **2b**, while **3c** showed a negligible fluorescence solvatochromism.

As **3a** and **3b** have relatively large ϵ values in the lowest energy absorption bands and Φ_f values compared to those of the corresponding derivatives **2a** and **2b**, they have fluorescence brightness ($\epsilon\Phi_f$) greater than those of **2a** and **2b**. In fact, the $\epsilon\Phi_f$ values of **3a** and **3b** in cyclohexane are estimated to be 46,000 and 19,000 M⁻¹ cm⁻¹, respectively, whereas those of **2a** and **2b** are 36,000 and 10,000 M⁻¹ cm⁻¹, respectively (Table 1). The maximum $\epsilon\Phi_f$ values of **3a** and **3b** are 62,000 M⁻¹ cm⁻¹ in benzene and 43,000 M⁻¹ cm⁻¹ in methanol, respectively. Thus, **3a** with the double dimethylamino groups shows the best performance for fluorescence brightness among the TPy derivatives.

The photophysical data including the τ_f values of **3** in cyclohexane are summarized in Table 1 together with those of **2** for comparison [9,10]. The rates of the fluorescence (k_f) of **3a** and **3b** estimated with the τ_f and Φ_f values are slightly greater than those of the corresponding derivatives **2a** and **2b**. This result

Table 1
Photophysical properties of **2** and **3** in cyclohexane at 295 K.

Compounds	Φ_f	τ_f/ns	$k_f^a/10^8 \text{ s}^{-1}$	$\epsilon\Phi_f/10^4 \text{ M}^{-1} \text{ cm}^{-1}$
2a ^b	0.89	2.3	3.9	3.6
2b ^b	0.24	0.56	4.2	1.0
3a	0.80	1.5	5.3	4.6
3b	0.38	0.63	6.0	1.9
3c	0.03	<0.3	>1.0	0.10

^a Determined by $k_f = \Phi_f \tau_f^{-1}$.

^b Refs. [9] and [10].

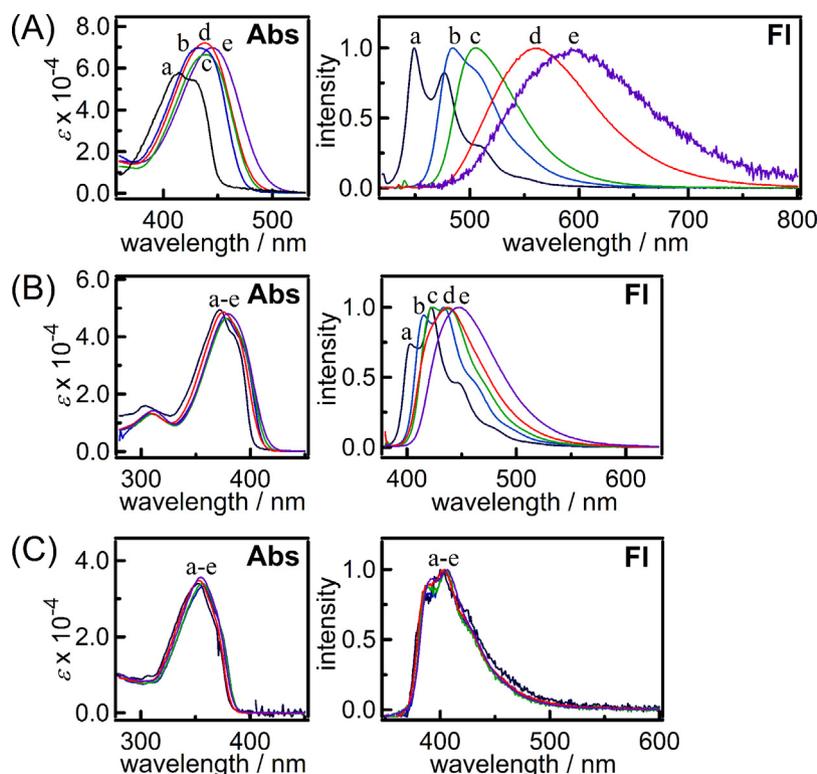


Fig. 1. UV/vis absorption (Abs) and fluorescence (Fl) spectra of **3a** (A), **3b** (B), and **3c** (C) in cyclohexane (a), benzene (b), chloroform (c), acetonitrile (d), and methanol (e) at 298 K.

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