Influence on Fluorescence Properties of Substituents on Benzene Ring of Diimidazo- and Dipyrrolo[1,2-*a*:2*'*,1*'*-*c*]quinoxalines

(*Graduate School of Engineering, Chiba University*) ○ Makoto Takamori, Motohiro Akazome, Shoji Matsumoto

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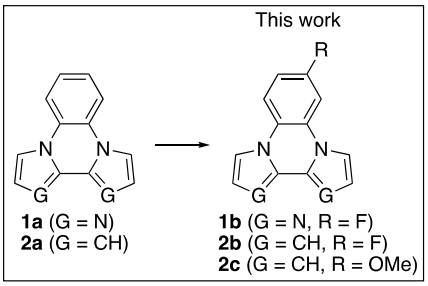

We have reported the fluorescence of diimidazo- and dipyrrolo[1,2-*a*:2*'*,1*'*-*c*]quinoxalines (**1a** and **2a**) in UV and blue region.[1)] To achieve longer fluorescence wavelength using CT transition, we examined the introduction of substituents on their benzene rings.

When fluorine substituent was introduced at 6 position of **1a**, longer fluorescence peaks of **1b** (385 and 396 nm) were obtained compared with **1a** (367 nm) in THF and CH_3CN (Table 1) accompanied with hypsochromic shift of absorption peaks (Table 1). We also found solvent effect in the fluorescence of **1b** although there was no change in **1a**. It would be caused by the CT transition in the excited state of **1b**.

In the case of dipyrrolo[1,2-*a*:2*'*,1*'*-*c*]quinoxalines, similar bathochromic shift of the fluorescence peaks was observed in **2b** against **2a**. Both compounds showed the solvent effect on fluorescence peaks. It would be reason for the electron-rich character of bipyrrole moiety. To compare with **2b**, we investigated methoxy substituted **2c**. Little change of fluorescence peaks was observed with no solvent effect, which means π-π^*transition in the excited state of **2c**. Thus, we revealed that the longer fluorescence was achieved by introducing the electron-withdrawing substituent on benzene rings of **1a** and **2a**.

Table 1. Optical Properties of **1** and **2**

Compound	Solvent	λ_{abs} (nm) [ε($M^{-1}cm^{-1}$)]a)	λ_{em} (nm)b) [Φ_F]c)
1a	CH_3CN	307.5 [12,200]	367 [0.70]
	THF	309 [9,400]	367 [0.72]
1b	CH_3CN	247(sh) [11,900]	396 [0.33]
	THF	249(sh) [12,800]	385 [0.44]
2a	CH_3CN	320 [10,700]	434 [0.17]
	THF	321 [10,600]	416 [0.43]
2b	CH_3CN	322 [15,600]	453 [0.12]
	THF	322 [11,200]	434 [0.22]
2c	CH_3CN	369 [4,900]	434 [0.02]
	THF	367 [4,800]	435 [0.01]

a) Concentration: 3.0×10^{-5} M. b) Concentration: 3.0×10^{-7} M.
c) Determined using *p*-terphenyl (Φ_f=0.87, 265 nm) as a standard.

1) Matsumoto, S.; Sakamoto, K.; Akazome, M. *Heterocycles* **2015**, *91*, 795.