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SYNTHESIS AND PROPERTIES OF PYRAZINO[2,3-*g*]QUINOXALINE DERIVATIVES: BLUE AND GREEN FLUORESCENT MATERIALS WITH ELECTRON AFFINITY

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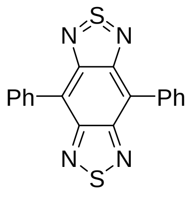
Abstract – The title compounds have been synthesized and their optical and electronic properties were surveyed in comparison to those of [1,2,5]thiadiazolo[3,4-*g*]quinoxaline and benzo[1,2-*c*:4,5-*c*']bis([1,2,5]thiadiazole) derivatives. They are blue or green fluorophores with electron affinity due to the fused pyrazine rings. Substitution of the fused pyrazine ring for the fused 1,2,5-thiadiazole one led to red shifts of *ca.* 50 nm in the fluorescence spectra. The substitution also resulted in an increase of electron affinity in the 14π-electron systems. Using a series of these compounds, red-green-blue (RGB) fluorescent emission was achieved.

Introduction of fused heterocycles is a useful method for modification of π-conjugation systems together with functional groups. Fused pyrazine and 1,2,5-thiadiazole rings, which are electron-accepting units, have been utilized for organic functional materials.[1] Especially, molecules containing fused thiadiazole rings have been studied as electrical conductors[2] and magnetic materials.[3] Polymers with fused thiadiazole rings were also reported as emission materials in organic electroluminescent (EL) devices.[4] 4,8-Diphenylbenzo[1,2-*c*:4,5-*c*']bis([1,2,5]thiadiazole) (**1**), which is a hetero analog of 9,10-diphenylanthracene containing two fused thiadiazole units, showed its absorption maximum at a much longer wavelength and has a high electron affinity comparable to benzoquinone due to the extended 14π-electron system.[5] Furthermore, compound (**1**) showed a strong red fluorescence with a long lifetime.[6] In this context, interest in fused pyrazine rings has been, recently, enlarged in materials science.[7] Therefore, we have prepared pyrazino[2,3-*g*]quinoxaline (**2a**) and its 9,10-diaryl derivatives (**2c**,**d**). Their electronic and optical properties were investigated in comparison to those of compound (**1**) and 4,9-diphenyl[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (**3**) in order to survey the functional effects between fused pyrazine and 1,2,5-thiadiazole rings. We report herein the preparation and properties of **2** and the substitution effect of the fused heterocycles.



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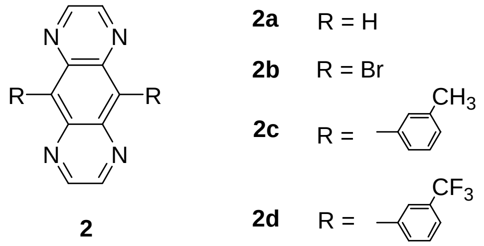

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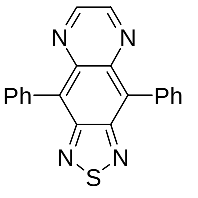

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Pyrazino[2,3-*g*]quinoxaline (**2a**) was obtained by oxidation of 1,2,3,4-tetrahydropyrazino[2,3-*g*]-quinoxaline with active MnO_2 in refluxing toluene as a modification of the reported method.[8] Bromination of **2a** with two equimolar amounts of NBS in DMF afforded dibromide (**2b**) in 76% yield. Compounds (**2c**) and (**2d**) were prepared in 60% and 8% yields by the Suzuki coupling reaction of **2b** with the corresponding boronic acids (1 mol % $Pd(PPh_3)_4$, 1.0 M Na_2CO_3(aq.)/THF, 48 h), respectively. These compounds were isolated as colorless crystals for **2a** (mp 216-218 ºC; lit.,[8] mp 215-216 ºC) and yellow crystals for **2b** (mp > 300 ºC), **2c** (mp > 300 ºC), and **2d** (290 ºC decomp). The absorption maxima of **2a**,**c**,**d** are listed in Table 1 and are compared with those of compounds (**1**) and (**3**). The maxima of **2c**,**d** were red-shifted by *ca*. 40 nm from that of **2a** due to the π-conjugation with the aromatic rings at the 9,10-positions. There is no difference between methyl and trifluoromethyl groups as *meta*-functional groups of the aromatic rings. The absorption maxima of **3** and **1** are moved to longer wavelength of *ca*. 80 nm from those of **2c** and **3**, respectively, by substitution of the pyrazine moiety for the 1,2,5-thiadiazole one (**2c**→**3**→**1**). These red shifts are ascribable to a lowering of the LUMO energies in the 14π-electron systems.

Table 1. Absorption maxima and emission maxima in dichloromethane

Compound	$\lambda_{\mathrm{abs,\ max}}$/nm (log ε)	$\lambda_{\mathrm{em,\ max}}$/nm
2a	356 (4.08)	466
2c	398 (3.91), 364 (4.04)	509
2d	394 (3.84), 361 (4.01)	493
3[a]	471 (3.99), 363 (4.26)	561
1[a]	558 (3.99), 359 (4.33)	624

[a] Reference 5.

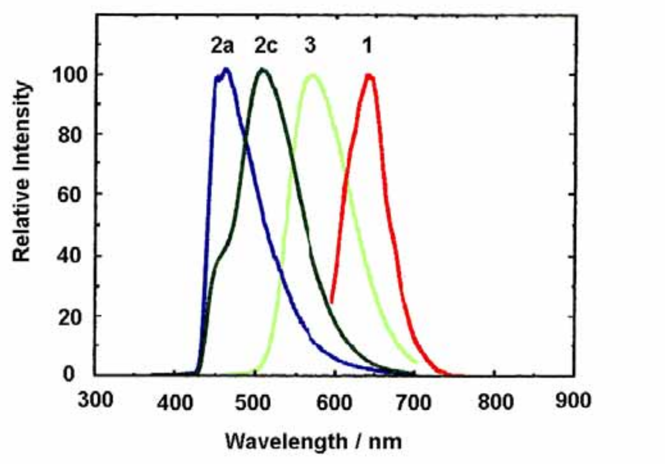

Figure 1. Fluorescence spectra of **1**, **2a**, **2c**, and **3** in CH_2Cl_2.

Figure 1 shows fluorescence spectra of **2a**,**c** in dichloromethane together with those of compounds (**1**) and (**3**). Four spectra were observed at the extended wavelength region from 420 to 730 nm (Table 1). The emission maximum of **2c** was observed at the longer wavelength of *ca*. 40 nm than that of **2a**. Furthermore, the emission maxima of **3** and **1** are shifted to longer wavelengths of *ca*. 50 nm from those of **2c** and **3**, respectively, by exchanging the pyrazine ring for the 1,2,5-thiadiazole one (**2c**→**3**→**1**). The fluorescent color is, depending on the shift of the spectra, blue for **2a**, blue green for **2d**, green for **2c**, yellow green for **3**, and red for **1**. This result indicates that the fluorescent properties are determined by fused heterocycles; pyrazine and 1,2,5-thiadiazole. In addition, RGB fluorescent emission was achieved by a set of these compounds (**1**, **2c**, and **2a**).

The cyclic voltammograms (CV) of **2a**,**c**,**d** in dichloromethane showed two reversible one-electron redox waves. The half-wave reduction potentials are given in Table 2. Since the reduction potentials of **2c**,**d** are similar to that of **2a**, the aromatic rings have little influence on the electron affinity of the 14π-electron systems. The electron affinity increases by exchanging the pyrazine ring for the 1,2,5-thiadiazole one (**2**→**3**→**1**). Their electron-accepting properties are also determined by selection of the fused heterocycles.

Table 2. Half-wave reduction potentials in the cyclic voltammetry[a]

Compound	E_1^{red}/V	E_2^{red}/V	ΔE/V
2a	−0.95	−1.48	0.52
2c	−0.97	−1.48	0.50
2d	−0.91	−1.48	0.57
3[b]	−0.82	−1.46[c]	0.64
1[b]	−0.61	−1.30	0.69

[a] 0.1 M *n*-Bu_4NClO_4 in CH_2Cl_2, Pt electrode, scan rate 100 mV s^{-1}, V vs SCE.
[b] Reference 5. [c] E_{pc} + 0.03 V.

In summary, we have prepared pyrazino[2,3-*g*]quinoxaline derivatives (**2**), which are blue or green fluorophores with electron affinity. Their optical and electronic properties were discussed together with those of compounds (**1**) and (**3**). The fluorescent color and electron affinity can be controlled by selection of the fused heterocycles; pyrazine and 1,2,5-thiadiazole. RGB fluorescent emission was achieved by a series of the fluorophores with high electron affinity.

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