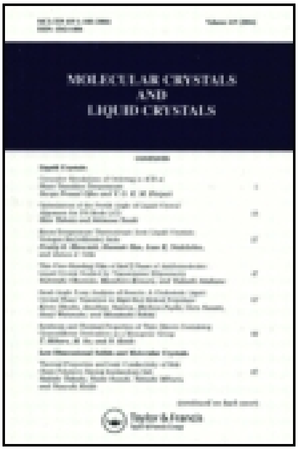

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Bis(2-hydroxyphenyl)-1,3,4-oxadiazole Derivative for Anion Sensing and Fluorescent Patterning

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Version of record first published: 12 Mar 2007

To cite this article: Tae Hoon Kim, Chi-Han Lee, Chan Gyu Kwak, Moon Soo Choi, Won Ho Park & Taek Seung Lee (2007): Bis(2-hydroxyphenyl)-1,3,4-oxadiazole Derivative for Anion Sensing and Fluorescent Patterning, Molecular Crystals and Liquid Crystals, 463:1, 255/[537]-261/[543]

To link to this article: http://dx.doi.org/10.1080/15421400601028054

Mol. Cryst. Liq. Cryst., Vol. 463, pp. 255/[537]–261/[543], 2007
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400601028054

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We have attempted to synthesize an oxadiazole compound which has ability of anion sensing and of fluorescent pattern construction. Organic soluble oxadiazole molecule with adjacent hydroxyphenyl groups for excited-state intramolecular proton transfer (ESIPT) was synthesized. Significant UV-vis absorption and fluorescence changes were observed upon addition of F^-. UV-irradiation on the poly (methyl methacrylate) (PMMA) film doped with oxadiazole compound in the presence of photoacid generator (PAG) induced novel fluorescence quenching-induced patterning.

Keywords: anion sensor; bishydroxyphenyloxadiazole; ESIPT; fluorescence patterning

INTRODUCTION

As the fluorescence is one of the most sensitive signals for the environmental changes, a great deal of attention have been focused on the fluorometric sensing of inorganic anions because of their importance in numerous biological and chemical processes for past decades [1,2]. Among these chemosensors for anions, phosphate and fluoride ion

Financial support from the Korea Research Foundation is gratefully acknowledged (Grant No. 2005-005-J00402).

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sensing are of special interest due to their importance in a number of disease states and environmental pollutions [3]. However, simple and easily prepared anion optical sensors are rather rare because optical signal transduction might be limited by many factors, and thus there is still a need for good anion sensors with a high sensitivity and selectivity [4].

The oxadiazoles with *ortho*-hydroxyphenyl group have been studied in their abnormally red-shifted fluorescence due to excited-state intramolecular proton transfer (ESIPT) [5]. Main advantage of this large Stokes shift is the increase in emission output as a result of low self-absorption of emitted light. The ESIPT plays an important role within the limited quantity of known primary photochemical and photophysical processes. The product of the ESIPT reaction, excited phototautomer form (keto form), emits light in a longer wavelength region than the emission of the initial 'normal' form (enol form) [6,7]. Among variety types of compounds with ESIPT, oxadiazole compounds with ESIPT have been widely studied from the view point of photophysics [8].

Herein, we are reporting a new chemosensor for phosphate and fluoride anions containing *ortho*-hydroxyphenyl oxadiazole with large Stokes shift. Besides, fluorescence quenching-based patterning system by addition of an acid was examined for the application of optical data storage. It is thought that the patterned image without lithography process has an advantage in the cost and production time.

EXPERIMENTAL

Reagents and Measurements

5-Bromosalicylic acid and semicarbazide hydrochloride was purchased from Acros and Aldrich, respectively. PMMA and triphenylsulfonium triflate as a PAG were purchased from Aldrich. ^{1}H-NMR spectrum was obtained with a Bruker DRX-300 spectrometer (Korea Basic Science Institute). Elemental analysis was performed with CE Instruments EA-1110 Elemental Analyzer. All UV-vis spectra were measured with a Perkin Elmer Lambda 35 spectrometer. Steady-stated fluorescence was taken from a Perkin Elmer LS 45 spectrofluorometer. Chloride, fluoride and phosphate anions were purchased from Aldrich as their tetrabutylammonium salt forms. Photographs of fluorescence image were taken from Cannon A80 digital camera.

Synthesis of 2,5-Bis(5-bromo-2-hydroxyphenyl)-1,3,4-oxadiazole 2

To polyphosphoric acid solution 5-bromo-2-salicylic acid **1** (5 g, 23.03 mmol) and semicarbazide hydrochloride (2.54 g, 23.03 mmol) were added. The resulting mixture was stirred at 150–160°C for 3 hr and then was poured into ice water [9]. The residual solid was filtered and washed with water, and then crystallized with acetic acid to give white crystals (2.41 g, 51%).

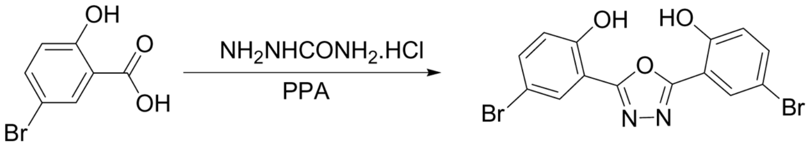
^{1}H-NMR ($CDCl_3$): δ 9.88 (s, 2H), 8.03 (d, 2H), 7.6 (q, 2H), 7.1 (d, 2H) ppm; $C_{12}H_8\,Br_2N_2O$ Found: C, 40.33; H, 1.83; N, 6.60. Calculated C, 40.80; H, 1.96; N, 6.80%.

Measurement of Sensing Ability and Fluorescent Image Fabrication

UV-vis absorption and emission changes of **2** solution [5×10^{-5} M in *N,N*-dimethylformamide (DMF)] were measured upon exposure to anions. The anions used in the ion-responsive property measurements were $H_2PO_4^-$, F^- and Cl^- in water and methanol solution. The PMMA film was obtained from the THF solution composed of 1 wt% of **2** with PAG on a silicon wafer after filtration with a 0.25 μm syringe filter. The cast film was thoroughly dried in a vacuum oven at 40°C for 12 hr and exposed under UV light of 254 nm for 2 hr to investigate the construction of fluorescence pattern.

RESULTS AND DISCUSSION

2,5-Bis(5-bromo-2-hydroxyphenyl)-1,3,4-oxadiazole **2** was obtained from the simple condensation reaction with **1** and semicarbazide hydrochloride by an one-step reaction as shown in Scheme 1. The chemical structure of **2** was confirmed with ^{1}H-NMR in $CDCl_3$ and FT-IR, which showed the presence of phenolic hydrogen at 9.88 ppm and 3400 cm^{-1}, respectively. Compound **2** was a off-white needle-shaped crystal and was easily soluble in common organic solvents such as THF, chloroform, and DMF. The DMF solution of **2** showed strong absorption at 330 nm and weak one at 420 nm, and emission at 380 nm (from enol form) and around 500 nm (from keto form). The film exhibited a similar behavior to that in the solution, however, the weak



1 **2**

SCHEME 1 Synthesis scheme of 2,5-bis(5-bromo-2-hydroxyphenyl)-1,3,4-oxadiazole.

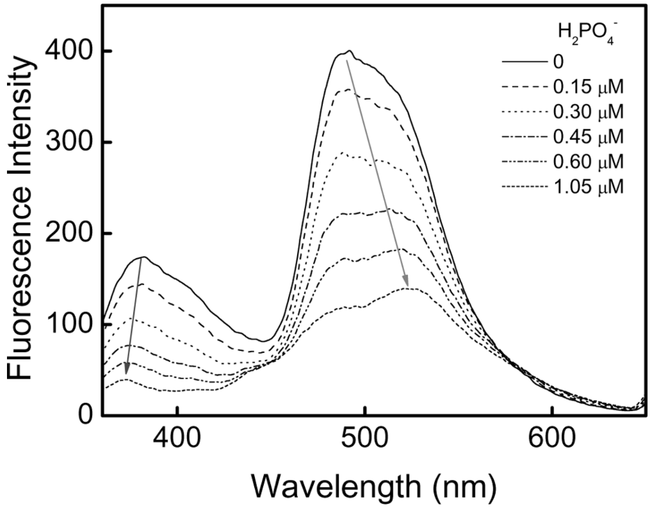


FIGURE 1 Fluorescence changes of **2** in DMF (25.0 μM) upon addition of $H_2PO_4^-$ (0, 0.15, 0.30, 0.45, 0.60, 1.05 μM) excitation wavelength 333 nm.

absorption at 420 nm and weak emission at 380 nm were not observed mainly due to energetically preferred keto-form freezing in solid state [10,11]. The emission spectrum of the film was centered at 500 nm which corresponded to green fluorescence at excitation wavelength 365 nm. The absence of emission band at short wavelength indicated the compound **2** formed keto form easily in the film.

Figure 1 shows the fluorescence spectra of **2** in the presence of various amounts of $H_2PO_4^-$ in DMF solution. The addition of $H_2PO_4^-$ leads to strong quenching and slight red-shift of the emission to around 520 nm indicating that the possible formation of intermolecular hydrogen bond between $H_2PO_4^-$ and hydroxyl group in **2**. In the case of F^-, decrease in emission intensity observed under 0.3 μM of fluoride ion, however, above this concentration, the formation of new intermediate band between original emission bands of enol and keto forms was observed around at 450 nm (Fig. 2). The new emission was the result of a new species generated under basic condition, anionic form of **2** in DMF solution. In contrast, the addition of Cl^- showed almost unchanged fluorescence spectra. It is presumed that the difference in emission changes between fluoride anion and other anions lies in the difference in the anion size as well as anionic nucleophilicity.

As shown in Figure 3, in the presence of $H_2PO_4^-$ or F^- (3 μM), the original absorption band at 330 nm decreased with increase in

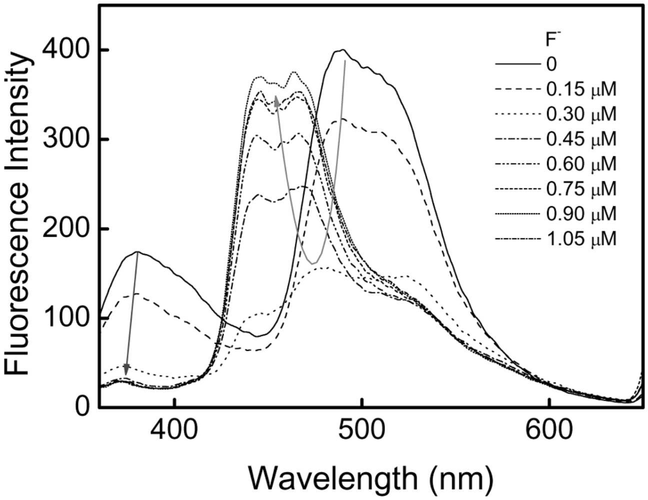


FIGURE 2 Fluorescence changes of **2** in DMF (25.0 μM) upon addition of F^- (0, 0.15, 0.30, 0.45, 0.60, 0.75, 0.90, 1.05 μM) excitation wavelength 333 nm.

long-wavelength absorption around 420 nm. The maximum intensity of this new absorption peak was largest for the F^- ion. Accordingly the color of DMF solution changed from colorless to yellow upon exposure to F^-.

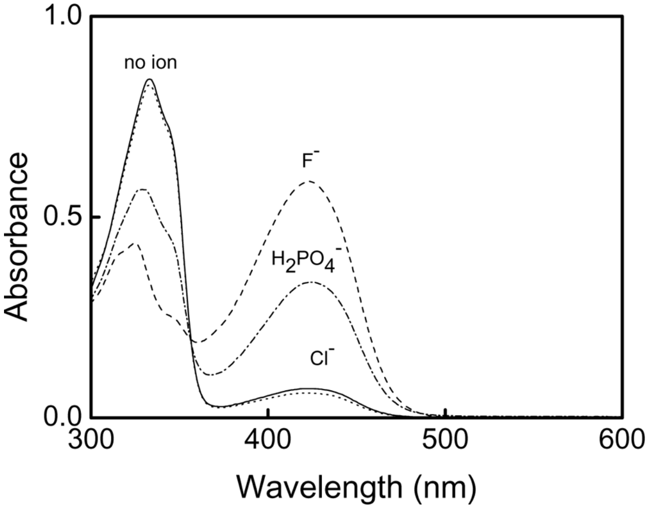


FIGURE 3 Absorption spectra of **2** in DMF (50.0 μM) after addition of 3.0 μM of anions.

FIGURE 4 Fluorescence pattern produced with a 1 wt% of **2**/PMMA blend film with photoacid generator upon irradiation of a wavelength of 254 nm through a photomask; (a) under sunlight and (b) under UV light. The area of green fluorescence was an unexposed portion (Film size 1.5 cm × 5 cm).

Fluorescence quenching of **2** by addition of an acid was investigated. It can be expected that fluorescence quenching was facilitated by addition of acid due to the blocking of keto formation. 1 wt% of **2**/PMMA solution with PAG (10 wt% of **2**) was spin-coated on a silicon wafer (1.5 cm × 5 cm). Monochromatic UV light of 254 nm was irradiated on the film through photomask and well-patterned fluorescence image was obtained after baking at 100°C for 60 sec. In the exposed area, it is presumed that the proton from reductive PAG interrupts the ESIPT of **2**, resulting in fluorescence quenching as shown in Figure 4. It is expected that this oxadiazole compound can be used as a potential candidate for the optical data storage.

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