



Strong fluorescence following two-photon excitation in fully conjugated oxadiazole-based oligoaryl



Chih-Hsien Chen*, Yen-Ting Cao, Tse-Sheng Wang, Zi-Huan Luo

Department of Chemical Engineering, Feng Chia University, Taichung 407, Taiwan

ARTICLE INFO

Keywords:

Highly fluorescent
Two photon absorption
Oxadiazole
Thiophene
Olefination

ABSTRACT

Highly fluorescent oxadiazole-based chromophore with alternating alkoxy benzene and thiophene moieties has been designed and synthesized, and large two-photon absorption (TPA) cross section in near infrared (NIR) region was performed. DFT calculation predicted fully π -conjugation among molecular skeleton and minor behavior of intra-molecular charge transfer (ICT). The solvent dependent emission spectra also suggested the occurrence of ICT was trivial, although oxadiazole was electron deficient and alkoxy benzene was electron rich. On the other hand, the resulting chromophore exhibited fluorescence quantum yield up to 75% because of the incorporation of oxadiazole. The quadratic dependence of emission intensity on input excitation power indicated TPA mechanism under irradiation of NIR laser. Based on two-photon excited fluorescence method, the designed fluorophore exhibited the largest TPA cross section (620 GM) at 850 nm. The cooperative phenomena of large TPA response and strong fluorescence output in this designed molecule might ensure a potential use for application of two-photon excited light-emitting materials.

1. Introduction

The diazole derivative is one of interesting heterocyclic five-member rings, and has been widely employed in material chemistry and pharmaceutical applications [1,2]. Due to the electron withdrawing effect of two nitrogen atoms, the ring is very electron deficient, and thus, certain nucleophilic reactions can take place. The presence of azole group increases the lipophilicity that affects the transmembrane diffusion of drug [3], and influences relative bioactivity [4–7]. Among those diazole derivatives, 1,3,4-oxadiazole is easy to be synthesized by dehydration cyclization, and the 2' and 5' positions can be modified with numerous aryl groups. Besides small molecules, this heteroaromatic has also been incorporated into polymers and served as an electron acceptor [8]. The 2,5-disubstituted 1,3,4-oxadiazoles exhibit stable thermal property [9] and highly luminescent behavior [10]. Thus, this kind of derivatives owns potential applications in optoelectronics and biochemistry.

Highly fluorescent materials have been of interest to light emitting diode and sensor [11,12]. Especially, in cell imaging, the fluorescence quantum yield and penetration of light dominated the performance of dye [13]. Therefore, various strategies were utilized to design a fluorophore to get better sensitivity. Two-photon excitation is one method to achieve this purpose. The model of this nonlinear optical response was proposed by M. Goeppert-Mayer in 1931, in which a virtual state was

introduced between molecular ground and excited states [14]. The simultaneous absorption of two photons with less frequency can complete the excitation of molecule via this virtual state. The sum of the energy of these two photons is equal to the energy difference between ground and excited state. Through this mechanism, the incident light with longer wavelength, such as near infrared (NIR), is selected to excite the fluorophores in deep layer tissue due to relatively better penetration within organism and reduced autofluorescence [15]. Structurally, the incorporation of alternating electron donating and withdrawing groups into molecule and extension of π -conjugation length could enhance the ability of two-photon absorption (TPA) [16–22]. Recently, numerous D- π -A chromophores including benzodiazole [23,24], fluorene [25–31], and diketopyrrolopyrrole [32,33] were synthesized and provided great performance in cell imaging and photodynamic therapy. The major strategy of molecular design of above chromophores was increasing the effect of intra-molecular charge transfer (ICT), and thus, aryl amine [22,25,26,32] and cyano group [28,34] were widely used. However, amine group is easy to be oxidized and the cyano-substituted olefin in molecules might reduce luminescence [35]. It is envisaged that replacement of amine and cyano group with alkoxy benzene and oxadiazole might benefit the development of TPA dye. Especially, there are several studies that utilized oxadiazole as a key role in TPA [36–39]. We herein describe the work toward the design, synthesis, and characterization of a novel

* Corresponding author.

E-mail address: chschen@fcu.edu.tw (C.-H. Chen).

chromophore, **BOTB**, containing electron donating and withdrawing parts in molecule. The arrangement of alkoxybenzene and oxadiazole moieties in **BOTB** formed an A- π -D- π -A structure that benefited TPA characteristics, and the bromo-substituted phenyl-oxadiazole might further improve electron withdrawing effect. It is expected that not only large cross section of TPA but also highly fluorescent property might be achieved.

2. Material and methods

2.1. General

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded using a Varian 400 Unity plus (400 MHz) at ambient temperature. Chemical shift (δ) and coupling constant (J) were expressed in unit of ppm and Hz, respectively. Samples for ^1H and ^{13}C NMR measurement were dissolved in CDCl_3 or d-DMSO, and the CHCl_3 or DMSO residues in the corresponding deuterated solvents were used as the internal standard. The chemical shift of CHCl_3 and DMSO were calibrated at δ 7.26 and 2.50 ppm in ^1H NMR spectra and δ 77.0 and 39.5 ppm in ^{13}C NMR spectra, respectively. All ^{13}C NMR spectra were recorded with the proton completely decoupled. High-resolution mass spectrometric measurements were obtained from a Jeol-JMS-700 mass spectrometer using the FAB method in 3-nitrobenzyl alcohol matrix. A CHI potentiostat/galvanostat is used for electrochemical experiments where Pt electrodes were used as working and counter electrodes, Ag/Ag^+ electrode was used as reference electrode, and 0.1 M $^t\text{Bu}_4\text{NPF}_6$ in THF was used as electrolyte.

2.2. Synthesis

The starting materials **1**, **5** and reagents were purchased from Acros Organics. Compounds **2**, **3**, and **6** were prepared according to published literatures [8,40]. The target **BOTB** was synthesized by Wittig reaction with **4** and **9**, and then, after column chromatography, single isomer was obtained in which the configurations of both double bonds are *E* form (Fig. S6). The synthesis route of **BOTB** is illustrated in Scheme 1, and the details of unknown compounds are described as following.

2.2.1. The synthesis of 5,5'-(2,5-bis(octyloxy)-1,4-phenylene)bis(thiophene-2-carbaldehyde) (**4**)

A solution of **3** (1.0 g, 2.0 mmol) in THF (20 mL) at -78°C was added dropwise with a hexane solution of *n*-BuLi (1.2 mL, 2.5 M, 3.0 mmol) under N_2 . After 1 h, *N,N*-dimethylformamide (0.22 g, 3.0 mmol) was introduced and the mixture was gradually warmed to rt. After further stirring for 3 h, the reaction mixture was quenched with sat. NaHCO_3 . The organic layer was washed with brine, water and dried (MgSO_4). After evaporation of the solvent in vacuo, the residue was chromatographed on silica gel ($\text{CH}_2\text{Cl}_2/\text{hexane} = 1/3$) to give **4** as a yellow solid (1.24 g, 56%): mp: 121–122 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 0.90 (t, $J = 7.2$ Hz, 6H), 1.20–1.60 (m, 20H), 1.95 (quintet, $J = 6.8$ Hz, 4H), 4.19 (t, $J = 6.6$ Hz, 4H), 7.30 (s, 2H), 7.65 (d, $J = 4.2$ Hz, 2H), 7.75 (d, $J = 4.2$ Hz, 2H), 9.93 (s, 2H); ^{13}C NMR (CDCl_3 , 400 MHz): δ 14.3, 22.8, 26.3, 29.30, 29.32, 29.4, 31.9, 69.8, 112.4, 123.1, 126.3, 135.8, 142.8, 148.4, 149.7, 182.9; HRMS (FAB+) (M^+) calcd for $\text{C}_{32}\text{H}_{42}\text{O}_4\text{S}_2$: 554.2525 found: 554.2521.

2.2.2. The synthesis of 4-bromo-*N'*-(2-bromoacetyl)benzohydrazide (**7**)

A mixture of **6** (0.65 g, 3 mmol), 2-bromoacetyl chloride (0.53 g, 3.3 mmol), and K_2CO_3 (0.48 g, 3.5 mmol) in THF (30 mL) was stirred for 18 h under N_2 . The organic layer was washed with brine, water and dried (MgSO_4). After evaporation of the solvent in vacuo, the residue was chromatographed on silica gel ($\text{CH}_2\text{Cl}_2/\text{hexane} = 1/3$) to give **7** as a white solid (0.86 g, 85%): mp: 93–94 $^\circ\text{C}$; ^1H NMR (d-DMSO, 400 MHz): δ 3.98 (s, 2H), 7.72 (d, $J = 8.4$ Hz, 2H), 7.80 (d, $J = 8.4$ Hz, 2H), 10.44 (s, 1H), 10.63 (s, 1H); ^{13}C NMR (d-DMSO, 400 MHz): δ 27.1,

125.7, 129.5, 131.3, 131.6, 164.4, 165.3; HRMS (FAB+) (M^+) calcd for $\text{C}_9\text{H}_8\text{Br}_2\text{N}_2\text{O}_2$: 333.8953 found: 333.8959.

2.2.3. The synthesis of 2-(4-bromophenyl)-5-(chloromethyl)-1,3,4-oxadiazole (**8**)

A solution of **7** (0.67 g, 2.0 mmol) in POCl_3 (5 mL) was refluxed for 18 h under N_2 . After cooling to rt, POCl_3 was distilled and the residue was re-dissolved in CH_2Cl_2 . The organic layer was washed with brine, water and dried (MgSO_4). After evaporation of the solvent in vacuo, the residue was chromatographed on silica gel (hexane) to give **8** as a white solid (0.49 g, 90%): mp: 115–116 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 4.78 (s, 2H), 7.67 (d, $J = 8.8$ Hz, 2H), 7.94 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR (CDCl_3 , 400 MHz): δ 32.9, 122.2, 127.0, 128.5, 132.5, 162.3, 165.3; HRMS (FAB+) (M^+) calcd for $\text{C}_9\text{H}_6\text{BrClN}_2\text{O}$: 271.9352 found: 271.9355.

2.2.4. The synthesis of **BOTB**

A mixture of **8** (0.54 g, 2.0 mmol), triphenyl phosphine (0.58 g, 2.2 mmol) in toluene (20 mL) was stirred at 80 $^\circ\text{C}$ for 18 h under N_2 . After cooling to rt, toluene was distilled and the residue was poured into water. The solid was filtered and washed with ethanol to give **9** without further purification. Following previous step, a mixture of **4** (0.55 g, 1.0 mmol), **9** (1.07 g, 2.0 mmol) and potassium *tert*-butoxide (0.25 g, 2.2 mmol) in THF (20 mL) was refluxed for 24 h. After cooling to rt, the organic layer was washed with brine, water and dried (MgSO_4). After evaporation of the solvent in vacuo, the residue was chromatographed on silica gel (hexane) to give **BOTB** as an orange solid (0.45 g, 45%): mp: 151–152 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 0.91 (t, $J = 7.2$ Hz, 6H), 1.22–1.62 (m, 20H), 1.99 (quintet, $J = 7.4$ Hz, 4H), 4.15 (t, $J = 6.6$ Hz, 4H), 6.88 (d, $J = 16.2$ Hz, 2H), 7.28 (m, 4H), 7.54 (d, $J = 4.0$ Hz, 2H), 7.67 (d, $J = 8.8$ Hz, 4H), 7.72 (d, $J = 16.2$ Hz, 2H), 7.98 (d, $J = 8.8$ Hz, 4H); ^{13}C NMR (CDCl_3 , 400 MHz): δ 14.1, 22.7, 26.3, 29.36, 29.37, 29.4, 31.8, 69.8, 107.7, 112.0, 122.8, 122.9, 126.3, 126.4, 128.3, 130.2, 132.0, 132.4, 139.8, 142.0, 149.5, 163.2, 164.4; HRMS (FAB+) (M^+) calcd for $\text{C}_{50}\text{H}_{52}\text{Br}_2\text{N}_4\text{O}_4\text{S}_2$: 994.1797 found: 994.1789.

2.3. Optical measurements

The single-photon absorption spectra were recorded on a Hitachi U-3900 spectrophotometer and emission spectra on a Hitachi F-7000 fluorescence spectrophotometer. TPA cross-section (σ_2) of sample was obtained by two-photon excited fluorescence method [41–43] with a mode-locked Ti:Sapphire laser (repetition rate: 76 MHz; pulse width: ~ 150 fs) passed through an optical parametric amplifier to produce desired wavelength of pulse laser. The fluorescence of samples were reflected by a grating (150 g/mm; BLZ: 500 nm) and detected by an optically triggered streak camera (Hamamatsu C5680). The σ_2 value of sample was estimated in comparison with that of fluorescein based on the following equation: $\sigma_2 = \sigma_{ref} \times (\Phi_{ref}/\Phi) \times (C_{ref}/C) \times (n_{ref}/n) \times (F/F_{ref})$, where the subscripts *ref* denotes the reference dye, fluorescein. Φ and C are the fluorescence quantum yield and concentration, respectively, and n is refractive index of solution. F is the integrated signal of the detected two-photon excited fluorescence. In time-resolved fluorescence experiments, a mode-locked Ti:sapphire laser (repetition rate: 76 MHz; pulse width: < 200 fs) passed through an optical parametric amplifier. The fluorescence of sample was reflected by a grating (150 g/mm; BLZ: 500 nm) and detected by an optically triggered streak camera (Hamamatsu C5680). The sample was prepared with 1.0×10^{-5} M concentration, and using ultra-micro cuvet with 1 mm pathlength to maintain the excitation at the same time.

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