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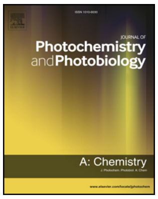

Synthesis of 9,10-distyrylanthracene derivative and its one- and two-photon induced emission in solid state

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ABSTRACT

Solid fluorescence plays an important role in optoelectronic devices. In this paper, 9,10-bis(6-dimethylamino benzoxazole styryl)-anthracene (**1**) was synthesized. **1** displayed a strong emission in solid state (microcrystalline state, amorphous solid state and polymeric thin film) resulted from aggregation-induced emission mechanism, and a large absolute fluorescence quantum yield ($\phi_f = 0.65$) was obtained. **1** also exhibited up-conversion emission in solid state and a strong yellow emission was observed upon excitation with 800–1064 nm, the quadratic dependence of the fluorescence on the excitation laser intensity confirmed that the up-conversion emission resulted from two-photon process.

1. Introduction

Solid fluorescence has played an important role in optoelectronic devices such as display, laser, and biomedicine [1–6]. The molecular systems which exhibit emission in solid are usually from inorganic materials or hybrid materials, and a few examples are based on organic small molecules due to aggregation-induced emission quenching. Fortunately, some molecular systems [7–9] show unique enhanced emission rather than fluorescence quenching upon aggregation in their solid states based on aggregation induced emission or aggregation induced enhanced emission, and the discoveries have promoted research on newly fluorescent materials for their potential applications [10–12].

Up-conversion emission, generating a higher energy light from a lower energy light [13], has attracted a great deal of attention for its potential wide range of applications [14–18]. Recently, up-converted lasing based on two-photon pumped mechanism is of increasing interest since it is a new approach to accomplish frequency up-conversion of coherent light without phase-matching requirements [19,20]. The early reported materials which exhibit up-conversion emission are usually from inorganic rare earth [21–23] or metal oxides semiconductors [24–26], and few are based on organic material due to the quench of emission of organic dye in solid state. Now, more and more organic materials which exhibit up-conversion emission have been reported [27–33]. As compared to inorganic materials, organic materials exhibit more efficient nonlinear optical properties through two or more photon absorption process and tunability within a quite broad spectral range. Moreover, organic materials offer easier processing, faster response time, and lower lasing threshold. The challenge is to develop ideal organic materials with strong two-photon pumped emission in solid states.

9,10-Distyrylanthracene derivatives are a class of promising and attractive aggregation induced emission molecules [34–36], they showed many potential applications including fluorescent probe, sensors, bioimaging, optical waveguide and others [37–41]. Herein, we synthesized a new 9,10-distyrylanthracene-based fluorophore **1** (Scheme 1) and studied its one- and two-photon pumped emission in solid state. It was found that **1** exhibited weak emission in solvents but strong emission in microcrystalline or amorphous solid state, with one- or two-photon excitation, a strong emission was observed.

2. Experimental

2.1. Materials and equipment

^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, with TMS as an internal reference. MS spectra were recorded with TOC-MS spectrometer, respectively. UV absorption spectra and fluorescence spectra in solution were measured with an absorption spectrophotometer (Hitachi U-3010) and a fluorescence spectrophotometer (F-2500), respectively. Fluorescence quantum yields in

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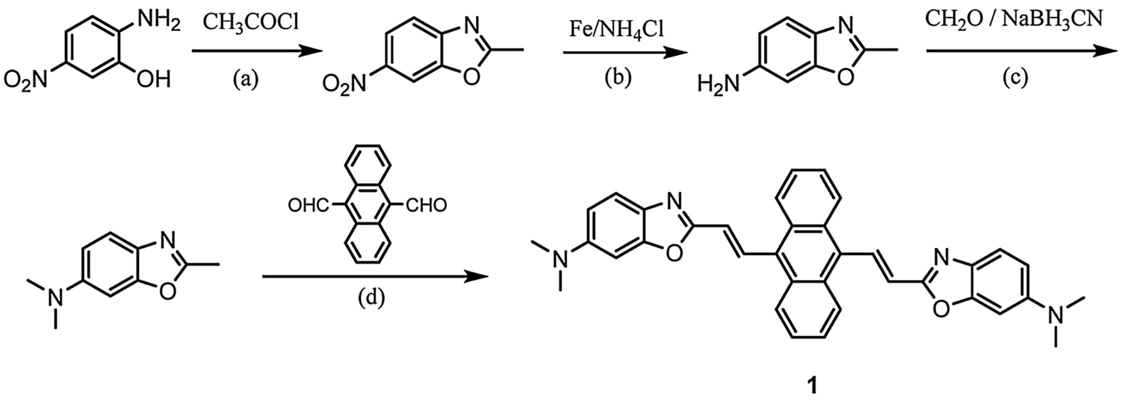

Scheme 1. Chemical structure of **1** and its synthesis.

solid state were measured with a fluorescence spectrophotometer (Edinburgh Instruments FLS-920). Solid absorption spectra were measured with UV–vis-NIR spectrophotometer (Cray 50000, Varian). All chemicals for synthesis were purchased from commercial suppliers, and solvents were purified according to standard procedures. Reaction was monitored by TLC silica gel plates (60 F-254). Column chromatography was performed on silica gel (70–230 mesh).

2.2. *Experiment for two-photon pumped emission*

In two-photon pumped emission experiment, a Ti-sapphire laser system (Mai Tai HP, Spectra-Physics) with a pulse width of 120 fs and a repetition rate of 82 MHz was employed as an excitation light source. The energy of excited pulse can be controlled by neutral density filters, and the beam of exciting laser was focused into the central of the cuvette with a plan-convex lens (focal length = 100 mm) under experiment. The fluorescence emitted from the sample was collected by a fiber spectrometer (SD 2000, Ocean Optics) and the direction of the detection is perpendicular to the laser transmission direction.

2.3. *Molecular orbital calculations*

The optimized structure of the 9,10-bis(6-dimethylamino benzoxazole styryl)-anthracene molecule was calculated at the density functional theory (DFT) level with the hybrid B3LYP functional and the 6–31 G basis set. The electron densities of the HOMO and LUMO were calculated with the Gaussian 03 package.

2.4. *Synthesis of **1***

The synthetic route for **1** was outlined in Scheme 1, and the detailed procedures were presented as follows: (a) To a solution of 2-amino-5-nitrophenol (7.70 g, 50.0 mmol) and pyridine (3.96 g, 50.0 mmol) in dry xylene (150 mL) at 0 °C was added dropwise acetyl chloride (4.32 g, 55.0 mmol). The solution was stirred at ambient temperature for 2 h. To above solution was added *p*-toluenesulfonic acid (1.72 g, 10.0 mmol), the solution was refluxed till no water was discharged. After cooling to room temperature, the solution was washed with water (100 mL × 3) and a saturated solution of NaCl (50.0 mL), respectively. The organic solution was collected and dried over Na_2SO_4, after evaporation of the solvent, the crude 2-methyl-6-nitrobenzoxazole (pale solid, 8.80 g, 95% yield) was obtained for next step without purification. (b) To a solution of 2-methyl-6-nitrobenzoxazole (3.92 g, 22.0 mmol) in methanol (60.0 mL) at 70 °C was added NH_4Cl (11.77 g, 220 mmol) in H_2O (40.0 mL) and Fe (4.48 g, 80.0 mmol). The mixture solution was stirred at 70 °C for 4 h till the starting material disappeared (TLC detection). The mixture solution was cooled to ambient temperature and filtered, the solution was extracted with ethyl acetate (30.0 mL × 3). The combined organic solution was dried over Na_2SO_4, after evaporation of the solvent, the crude 2-methylbenzoxazol-6-amine (2.77 g, 85% yield) was obtained for next step reaction without purification. (c) To a solution of 2-methylbenzoxazol-6-amine (2.66 g, 18.0 mmol) in methanol (30.0 mL) was added formaldehyde (37%, 12 mL, 144 mmol) and $NaBH_3CN$ (2.27 g, 36.0 mmol). The solution was stirred at ambient temperature for 36 h till the starting material disappeared (TLC detection). The solution was poured into H_2O (30.0 mL), and the mixture solution was extracted with ethyl acetate (30.0 mL × 3). The combined organic solution was dried over Na_2SO_4, the solution is concentrated and 2-methyl-6-(*N, N*-dimethylamino) benzoxazole (2.50 g, 79% yield) is obtained by flash column chromatography (elute: petroleum ether / ethyl acetate = 10 / 1, v/v, R_f =0.11). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, J = 8.8 Hz, 1 H), 6.78 (d, J = 2.0 Hz, 1 H), 6.74 (dd, J = 8.8 Hz, J = 2.4 Hz, 1 H), 2.97 (s, 6 H), 2.46 (s, 3 H). (d) To a solution of 2-methyl-6-(*N, N*-dimethylamino) benzoxazole (1.76 g, 10.0 mmol) and anthracene-9,10-dicarbaldehyde (1.18 g, 5.00 mmol) in dry DMF (20 mL) was added KOH (0.56 g, 10.0 mmol). The solution was stirred at 110 °C for 8 h till the starting material disappeared (TLC detection). The solid was filtered and washed with MeOH (30.0 ml), and target compound **1** (1.37 g) is obtained by flash column chromatography (elute: CH_2Cl_2). Yield: 48%. M.p. ≥ 300 °C. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.91 (d, J = 16 Hz, 2 H), 7.52 (d, J = 8.8 Hz, 2 H), 7.23 (d, J = 16 Hz, 1 H), 6.73 (s, 1 H), 6.80 (d, J = 5.2 Hz, 1 H), 6.87 – 6.83 (m, 2 H), 3.05 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.1, 150.4, 142.2, 133.8, 133.1, 129.5, 129.4, 126.2, 125.6, 124.8, 120.1, 100.3, 95.8, 41.9. TOF MS (EI) calcd for $C_{36}H_{30}N_4O_2$ (M^+): 550.2369, found: 550.2372.

3. Results and discussion

3.1. *Synthesis of **1***

The synthetic details for **1** are described in the Experimental. In brief, as depicted in Scheme 1, **1** was obtained in 30% total yield by a 4-step reaction. The key intermediate *N, N*, 2-trimethylbenzoxazol-6-amine was obtained starting from 2-amino-5-nitrophenol, which condensed with acetyl chloride in xylene (98% yield), followed by reduction with NH_4Cl and Fe powder in MeOH-H_2O mixture solution (85% yield). Amino methylation was performed by the reaction of 2-methylbenzoxazol-6-amine with formaldehyde using $NaBH_3CN$ as reduction reagent to afford *N, N*, 2-trimethylbenzoxazol-6-amine in 78% yield. Treatment of *N, N*, 2-trimethylbenzoxazol-6-amine with anthracene-9,10-dicarbaldehyde in dry DMF afforded **1** in 48% yield.

3.2. *Optical properties of **1** in solution*

It has demonstrated [39,42] that centrosymmetric 9,10-distyrylanthracene derivatives usually possess two main absorption bands: one located at ~310 nm corresponded to the absorption of the styryl