



Short communication

Tetrahydro[5]helicene-based dye with remarkable and reversible acid/base stimulated fluorescence switching properties in solution and solid state



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ABSTRACT

A new organic imide dye based on tetrahydro[5]helicene skeleton was synthesized, and its helical structural feature was confirmed by the crystal structure. It was found that the dye exhibited remarkable and reversible acid/base stimulated fluorescence switching properties in both solution and solid state, in which the dye was changed from “D–A type” to “A–A type” in the presence of TFA, and returned to its original form upon the addition of TEA. This switchable behavior was also evidenced by the ¹H NMR experiments and theoretical calculations.

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1. Introduction

Organic dyes with stimulated fluorescence switching properties have attracted increasing interest in recent years for their wide potential applications in luminescence sensors [1–3], logic gates [4–7], optoelectronic and storage materials [8–11]. Although various of organic fluorescence dyes in solution were reported [12,13], most of them showed quenched fluorescence in solid state, and also could not realize intense fluorescence in two different states, mainly owing to the aggregation and intramolecular charge transfer. Consequently, two main aspects were considered to obtain switchable fluorescence materials in solid state. One strategy is to obtain new skeleton of solid-state fluorescence dyes by introduction of bulky substituents [14–18], J-aggregated formation [19,20] and aggregation-induce emission [21–23]. Changing the packing mode [24–29] and intramolecular charge transfer of dyes molecules [30–33] and even altering the molecular skeletons [34] provided another way to obtain multiply stimulated switching

fluorescence [35–38]. Since most of the switchable fluorescence materials are “ON–OFF” types, they could not form multiple fluorescent signals. Although several successful examples have been reported [39–44]. The organic dyes with intense reversible fluorescence under the external stimuli in solution, especially in solid state are still limited. Thus, the development of new switchable fluorescent dyes especially in solid-state is very attractive and important.

Recently, we reported a new kind of organic imide dyes based on tetrahydro[5]helicene skeleton [45–47]. By the combination of the π conjugated skeleton, intense intramolecular charge transfer, and non-planar structure, the dyes exhibit intense emission and large Stokes shifts in both solution and solid state. It can be envisaged that since typical “D–A type” dye **1** containing dimethylamino groups could be easily transformed into “A–A type” dye **1**–2H⁺ after the protonation, and vice versa (Fig. 1), the reversible fluorescence property between dye **1** and its protonated species could be conveniently achieved, which would provide us an opportunity to develop new switchable fluorescent materials. Herein, we report a new dye **1**, which shows remarkable acid/base stimulated fluorescence switching properties in not only solution but also solid state.

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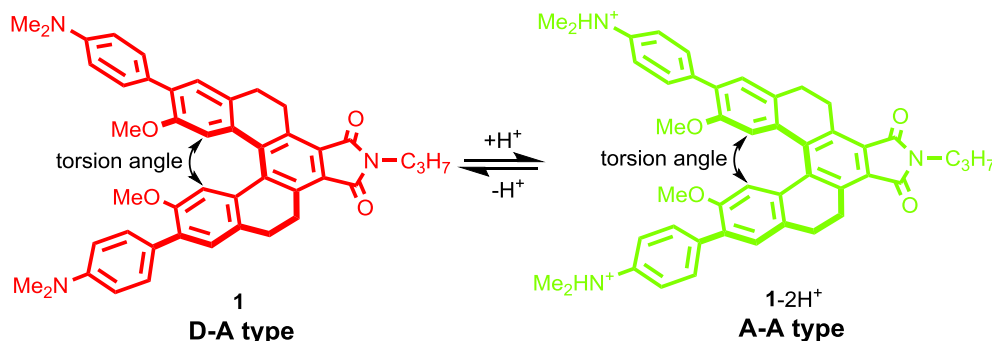


Fig. 1. Tetrahydro[5]helicene-based dye **1** with reversible acid/base stimulated fluorescence switching properties.

2. Experimental

2.1. General

All reactants were commercial and used without further purification excepted as noted. ^1H NMR and ^{13}C NMR spectra were recorded with DMX300/400/500 NMR at 298 K. MALDI-TOF mass spectra were determined with a BIFLEXIII mass spectrometer. HRMS mass spectra were measured in the ESI mode. Single crystal data of **1** were collected on Rigaku Saturn diffractometer with CCD area detector. All calculations were performed using the SHELXL97 and crystal structure crystallographic software packages. Absolute fluorescence quantum yields were measured by Hamamatsu Photonics Quantaury QY at room temperature. Fluorescence lifetimes were measured based on the time resolved PL experiments. Photographs of emissions were recorded with a Cannon digital camera.

2.2. Synthesis of dye **1**

To a mixture of compound **2** (600 mg, 0.99 mmol), K_2CO_3 (1.36 g, 9.9 mmol), and 4-(dimethylamino)phenylboronic acid (2.97 mmol) in DMF (30 mL) and toluene (20 mL) under argon atmosphere was added catalytic amount of $\text{Pd}(\text{PPh}_3)_4$ (5% mol). The resulting mixture was stirred for 12 h at 90°C under argon atmosphere, cooled to room temperature and then poured into ethyl acetate (100 mL). The organic layer was washed with saturated brine (3×100 mL), dried over anhydrous MgSO_4 , and then concentrated *in vacuo*. The residue was purified by column chromatography with ethyl acetate and petroleum ether (1:5, v/v) as eluant to give **1** (547 mg, 80%) as red solid. M. p.: $>300^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ 7.47–7.44 (m, 4H), 7.26 (s, 2H), 6.84 (s, 2H), 6.79–6.76 (m, 4H), 4.17–4.12 (m, 2H), 3.68–3.64 (m, 2H), 3.31 (s, 6H), 2.99 (s, 12H), 2.92–2.80 (m, 4H), 2.63–2.49 (m, 2H), 1.79–1.67 (m, 2H), 0.98 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 169.3, 154.3, 149.9, 138.6, 138.5, 132.1, 132.0, 131.1, 130.1, 129.4, 126.0, 125.9, 114.0, 112.3, 55.3, 40.7, 38.0, 32.1, 29.78, 29.77, 29.74, 29.65, 29.5, 29.4, 28.8, 27.8, 27.1, 24.5, 22.8, 14.3. MALDI-TOF MS: m/z 691.4 $[\text{M}]^+$. HRMS (ESI): m/z calcd for $\text{C}_{45}\text{H}_{46}\text{N}_3\text{O}_4$ $[\text{M} + \text{H}]^+$ 692.3483, found 692.3478.

2.3. X-ray crystallography

X-ray crystallographic data were collected by using a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite-monochromated $\text{Mo-K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. The data were corrected for Lorentzian, polarization, and absorption effects. Structures were solved by direct methods and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and refined by using a riding model. CCDC 915890 for dye **1** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Results and discussion

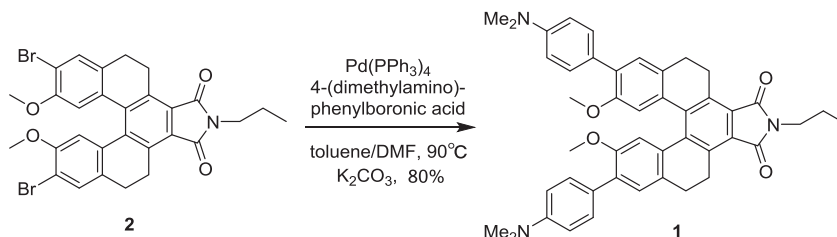
3.1. Synthesis and structural characterization of dye **1**

As shown in Scheme 1, dye **1** was conveniently synthesized in 80% yield by the Suzuki coupling reaction of the dibromide precursor and 4-(dimethylamino)phenylboronic acid in DMF and toluene in the presence of K_2CO_3 and catalytic amount of $\text{Pd}(\text{PPh}_3)_4$. The new compound was characterized by ^1H NMR, ^{13}C NMR, mass spectra and single crystal structure.

Single crystal of dye **1** suitable for X-ray analysis was obtained by its slow evaporation in CH_2Cl_2 and petroleum ether solution. As shown in Fig. 2, molecule **1** exhibited a significantly twisted structure with the torsion angle of 44.18° . There existed multiple C–H π interactions between the adjacent molecules, which resulted in a herringbone-like packing (Fig. S2). It could be expected that the structural feature of **1** could effectively prevent the intermolecular π – π stacking, and fluorescent quenching in solid state.

3.2. Photophysical properties of dye **1** in various solvents and film state

The photophysical properties of **1** were firstly tested in CH_2Cl_2 . As shown in Fig. 3, it was found that its absorption bands were



Scheme 1. Synthesis of dye **1**.

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