

Highly fluorescent single crystals of a 4-ethoxy-1,3-thiazole

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ARTICLE INFO

Keywords:

4-Hydroxy-1,3-Thiazoles
DFT-calculations
Single crystals
Solid state fluorescence

ABSTRACT

4-Ethoxy-2-(pyridin-2-yl)-5-(3,4,5-trimethoxyphenyl)thiazole (EPTT) was prepared in a four-step synthetic protocol. Column shaped single crystals of EPTT were obtained from a saturated EtOH solution. Both single crystals and a THF solution of EPTT were investigated in terms of their photophysical properties and electronic structure. The crystals showed very intense fluorescence upon photoexcitation as well as a red shifted emission maximum compared to a THF solution of EPTT (single crystals: $\lambda_{em} = 523$ nm, $\Phi_{FL} = 0.82$, THF solution $\lambda_{em} = 477$ nm, $\Phi_{FL} = 0.67$). Quantum chemical methods were then employed to unravel the underlying fundamental transitions and explain the experimental results. Calculations for a small dye cluster modeled after the x-ray crystal structure predicted three dark intermolecular CT states, S_1 - S_3 , below the intramolecular CT state (S_4) for EPTT in the crystalline state. Photoexcitation and subsequent relaxation along the excited states relaxation pathways may populate the low-lying dark intermolecular CT states, which in consequence leads to an exciton moving along the stacked dyes in the crystal. This finding explains the significantly enhanced red-shift of the solid-state fluorescence of EPTT compared to the dissolved dye.

1. Introduction

In recent years, solid-state emissive materials have gained increasing attention due to their potential applications in novel displays [1], lighting [2] and organic lasers [3]. Particular focus was laid to the consequences of molecular packing on the chemical and physical properties of luminescent materials [4–6].

Our group has been investigating the synthesis and optical properties of 4-hydroxythiazole derivatives for over a decade. Since first in-depth investigations on the photophysical properties of 4-hydroxythiazole fluorophores have been reported in 2007 [7], a variety of different derivatives and applications have been developed, including fluoride ion sensors [8], a molecular probe for fluorescence and mass spectrometric detection of biomolecules [9], copolymerizable fluorophores [10] and dyes for dye sensitized solar cells (DSSCs) [11]. Other research groups described several interesting derivatives such as pyrene- and ferrocenyl-substituted hydroxythiazole compounds [12,13].

During our ongoing investigations on this versatile substance class, we prepared 4-ethoxy-2-(pyridin-2-yl)-5-(3,4,5-trimethoxyphenyl)thiazole EPTT as part of a series of 4-ethoxy-substituted donor-acceptor thiazole dyes and found that it readily crystallizes in the form of large

column shaped single crystals that fluoresce intensely upon photoexcitation (Fig. 1). In contrast to tricyclic lactones based on 4-hydroxy-1,3-thiazoles prepared by Calderón Ortiz et al., which feature quantum yields up to 0.40 in the solid state [14], the here reported compound consists of three individual aromatic rings that are not restricted in their intramolecular rotation by fused rings. Yet the quantum yield of the new EPTT is 0.82 in the solid state. This unexpected finding motivated us to investigate this compound thoroughly in order to understand the reasons for its extraordinary photophysical properties.

2. Experimental section

2.1. General procedures and spectroscopic methods

Reagents were purchased from commercial sources and were used directly unless otherwise stated. All solvents were of reagent grade and were dried according to common practice and distilled prior to use. Reactions were monitored by TLC, which was carried out on 0.2 mm Merck silica gel plates (60 F₂₅₄). ¹H and ¹³C NMR spectra were recorded on Bruker Avance 250 and 400 spectrometers, chemical shifts (δ) are given relative to signals arising from the solvent. Mass spectra were recorded on a Finnigan MAT SSQ 710 or MAZ95XL or on a Bruker

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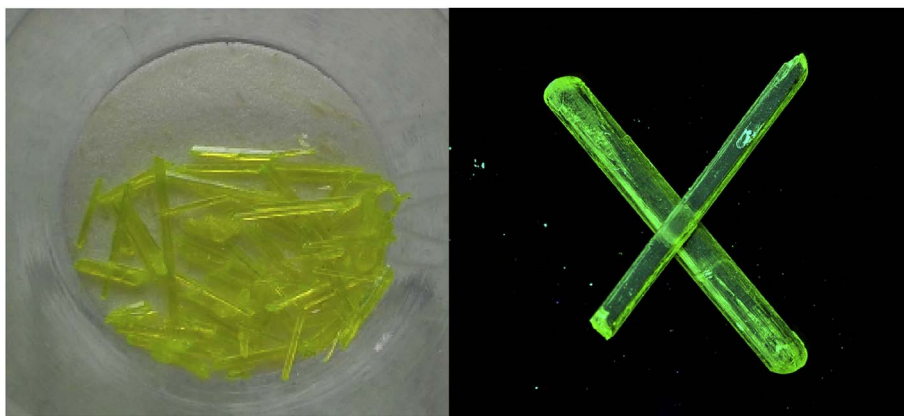


Fig. 1. Left: Single crystals of EPTT on a glass frit, crystallized from EtOH; Right: close-up of two crystals under UV light (365 nm).

maXis impact. Melting points were determined using a Cambridge Instruments Galen III apparatus (Boëtius system) and are uncorrected. UV/vis spectra were recorded with a PerkinElmer LAMBDA 45 UV/vis spectrometer, emission spectra were recorded using a JASCO FP-6500 spectrofluorimeter.

Measurements of the fluorescence intensity were carried out on a PerkinElmer LAMBDA 45 UV/vis spectrometer and JASCO FP-6500 spectrofluorimeter in the perpendicular excitation–emission geometry, while the absorbance at the excitation wavelength used was adjusted to be between 0.04 and 0.05. The calculation of fluorescence quantum yields was done according to the following equation [15].

$$\Phi = \Phi_r \frac{I}{I_r} \frac{A_r}{A} \frac{n^2}{n_r^2},$$

where Φ is the quantum yield, I is the corrected integrated emission intensity, A is the absorbance at the excitation wavelength and n is the refractive index of the solvent. The subscript r refers to a reference fluorophore of known quantum yield; here we used quinine sulfate ($\Phi_r = 0.52$ [16]). All thiazoles were excited as close as possible to their absorption maximum while staying inside the excitation range given in the literature [17].

The quantum yield of EPTT in the solid state was determined using a HAMAMATSU Photonic Multi-Channel-Analyzer C10027 with an integrating sphere (model A10094). The software used is PLQY Measurement-Software-U6039-05 (version 3.7.0).

2.2. Synthesis of the compounds

Ethyl 2-(3,4,5-trimethoxyphenyl)acetate 2: 10.40 g (45.97 mmol) **1** were dissolved in 80 mL of EtOH and treated with 4 mL conc. H_2SO_4 . The resulting mixture was heated to reflux for 3 h and the solvent was subsequently removed *in vacuo*. The residue was then neutralized with saturated NaHCO_3 solution and the resulting suspension was extracted with CHCl_3 (3 \times 30 mL). The combined organic extracts were washed with water and saturated NaCl solution and dried over MgSO_4 . After removing the solvent under reduced pressure, the crude product was dried *in vacuo* to afford the product as a clear, oily liquid (10.99 g, 43.22 mmol, 94%).

^1H NMR (250 MHz, CDCl_3): δ 1.27 (t, $J = 7.1$ Hz, 3H), 3.54 (s, 2H), 3.83 (s, 3H), 3.85 (s, 6H), 4.17 (q, $J = 7.1$ Hz), 6.51 (s, 2H).

^{13}C NMR (63 MHz, CDCl_3): δ 14.18, 41.62, 56.07, 60.79, 60.88, 106.28, 129.64, 137.07, 153.19, 171.51.

MS (EI) m/z (%): 254 (90) $[\text{M}]^{+}$, 239 (22) $[\text{M} - \text{CH}_3]^{+}$, 67 (100) $[\text{M} - \text{C}_3\text{H}_5\text{O}_2]^{+}$, 167 (41) $[\text{M} - \text{C}_4\text{H}_7\text{O}_2]^{+}$.

HRMS calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_5\text{Na}$ $[\text{M} + \text{Na}]^{+}$: 277.10519, found: 277.10498.

Ethyl 2-chloro-2-(3,4,5-trimethoxyphenyl)acetate 3: Under a nitrogen atmosphere, 8 mL (16 mmol, 2 eq.) of LDA (2 M in THF/hexanes) were cooled to -78 °C and a solution of 2.03 g (8.0 mmol,

1 eq.) **2** and 4.6 g (42 mmol, 5.3 eq.) chlorotrimethylsilane in 30 mL dry THF were added dropwise over a period of 15 min. After 1 h, 1.19 g (38 mmol, 4.75 eq.) of *N*-chlorosuccinimide was added in one portion and the mixture was allowed to slowly warm up to room temperature. When the temperature in the flask reached 10 °C, 20 mL of H_2O were added and the cloudy reaction mixture became clear instantaneously. The solvent was then removed *in vacuo*. The crude product was purified by silica gel column chromatography (heptane/EtOAc 2:1). The product was obtained as a colorless oil. Yield: 608 mg (2.11 mmol, 26%).

This reaction was scaled up later on and yielded a mixture of **2** and **3** which was used in the next step without further purification.

^1H NMR (400 MHz, CDCl_3): δ 6.75 (s, 2H), 5.27 (s, 1H), 3.85–3.93 (m, 11H), 1.30 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 168.18, 153.44, 139.24, 131.02, 105.61, 62.39, 60.72, 59.30, 56.28, 13.92.

HRMS (ESI pos.) m/z calcd. for $\text{C}_{13}\text{H}_{17}\text{ClO}_5\text{Na}$ $[\text{M} + \text{Na}]^{+}$: 311.06622. Found: 311.06602.

2-(Pyridin-2-yl)-5-(3,4,5-trimethoxyphenyl)thiazol-4-ol 4: 1.28 g (9.26 mmol) pyridine-2-carbothioamide, 8.08 g of a mixture of **2** and **3** (content of **3** determined from ^1H NMR spectrum, ca. 1.5 eq. of **3** were used) and 1.90 g (23.16 mmol, 2.5 eq.) NaOAc were suspended in 100 mL EtOH and the resulting mixture was heated to reflux for 6 h. After cooling down to r.t. it was poured into 200 mL of H_2O . The precipitate was filtered off and thoroughly washed with water and ethanol. It was then recrystallized from EtOH/DMF to afford the product as a light yellow solid (2.16 g, 6.27 mmol, 68%).

Mp: 263 °C.

^1H NMR (300 MHz, $\text{DMSO}-d_6$): δ 11.57 (s, 1H), 8.59 (d, $J = 4.6$ Hz, 1H), 7.84–8.03 (m, 2H), 7.40–7.49 (m, 1H), 7.05 (s, 2H), 3.81 (s, 6H), 3.67 (s, 3H).

^{13}C NMR (75 MHz, $\text{DMSO}-d_6$): δ 56.31, 60.57, 104.22, 111.08, 118.68, 125.30, 127.85, 136.83, 138.18, 150.15, 150.54, 153.48, 158.80, 160.38.

MS (EI) m/z (%): 344 (100) $[\text{M}]^{+}$, 329 (61) $[\text{M} - \text{CH}_3]^{+}$, 211 (13) $[\text{M} - \text{C}_7\text{H}_5\text{N}_2\text{O}]^{+}$, 197 (22) $[\text{M} - \text{C}_8\text{H}_7\text{N}_2\text{O}]^{+}$, 105 (16) $[\text{M} - \text{C}_{11}\text{H}_{11}\text{O}_4\text{S}]^{+}$.

HRMS (ESI pos.) calcd. for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_4\text{SNa}$ $[\text{M} + \text{Na}]^{+}$: 367.07285. Found: 367.07370.

4-Ethoxy-2-(pyridin-2-yl)-5-(3,4,5-trimethoxyphenyl)thiazole EPTT: 506 mg (1.47 mmol) of the thiazole **4** and 305 mg (2.20 mmol, 1.5 eq.) K_2CO_3 were suspended in 30 mL of acetone and treated with iodoethane (0.13 mL, 1.62 mmol, 1.1 eq.). The resulting mixture was heated to reflux for 4 h and allowed to cool down to r.t. It was then poured into 100 mL of H_2O and extracted with CH_2Cl_2 (3 \times 30 mL). The combined organic extracts were washed with water and saturated NaCl solution and dried over MgSO_4 . After removing the solvent *in vacuo*, the crude product was purified by silica gel column chromatography (CHCl_2 /EtOAc 7:1). The product was obtained as a light yellow solid (501 mg, 1.35 mmol, 92%).

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