Available online at www.sciencedirect.com
ScienceDirect
Chinese Chemical Letters 22 (2011) 647–650
CHINESE CHEMICAL LETTERS
www.elsevier.com/locate/cclet

Off–on–off luminescent switching of a dye containing imidazo[4, 5-f][1, 10]phenanthroline

Hai Guang Zhang [a,b,*], Xu Tang Tao [b], Kao Shan Chen [c], Chun Xue Yuan [b], Shi Na Yan [a], Min Hua Jiang [b]

[a] *College of Chemistry Science, Qufu Normal University, Qufu 273165, China*
[b] *State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China*
[c] *School of Life Science, Shandong University, Jinan 250100, China*

Received 10 September 2010

Abstract

A new acid–base fluorescent switch containing both imidazo[4,5-f][1,10]-phenanthroline and triphenylamine groups has been synthesized. Its fluorescence emissions and absorptions can be reversibly changed through protonation/deprotonation of imidazole and amine moiety by controlling the intramolecular charge transfer (ICT) process, leading to off–on–off fluorescent molecular switching.

Keywords: Fluorescence switch; Imidazo[4,5-f][1,10]phenanthroline; Triphenylamine; Intramolecular charge transfer (ICT)

The design and synthesis of fluorescent molecules exhibiting a switch function is an active area that has been intensively studied, which promises tremendous potential applications in the field of sensor fabrication [1–3]. Imidazo[4,5-f][1,10]phenanthroline (abbreviated as IP) derivatives have shown interesting proton induced on–off emission switching characteristics [4–7]. On the other hand, aromatic amines are typical examples of pH fluorescent switches [8–10]. In this work, we report the synthesis and study of a new proton induced fluorescent molecular switch 2-(4′-di(4-methylphenyl)-aminophenyl)imidazo[4,5-f][1,10]-phenanthroline (**1**).

1. Experimental

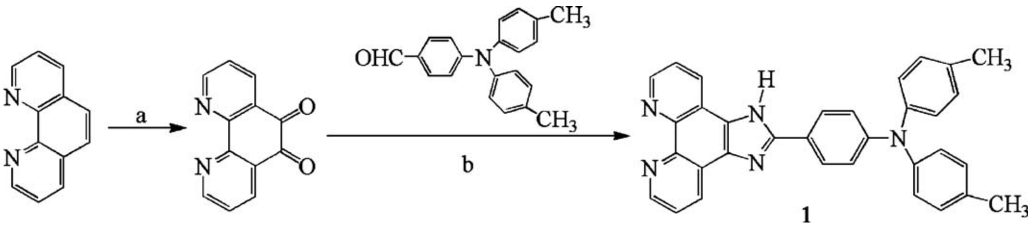
The compound 1,10-phenanthroline-5,6-dione [11] was synthesized according to a method in the literature. The other reagents were obtained commercially and used as supplied. The compound **1** was prepared according to the procedures in the literature [12,13] (Scheme 1).

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker A vance 300 MHz instrument. The electrospray mass spectrum (ES-MS) was determined on an ABI 4000 mass spectrograph. UV–vis absorption spectra were recorded on a

---

* Corresponding author at: College of Chemistry Science, Qufu Normal University, Qufu 273165, China.
E-mail address: haiguangzhang2006@126.com (H.G. Zhang).

1001-8417/$ – see front matter © 2010 Hai Guang Zhang. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.
doi:10.1016/j.cclet.2010.12.005



Scheme 1. Regents and conditions: (a) $H_2SO_4/HNO_3/KBr$, reflux, 2 h, 95%; (b) NH_4Ac/CH_3COOH, reflux, 3 h, 62%.

TU-1800 SPC spectrophotometer. Fluorescence emission spectra were measured using a Hitachi F-4500 fluorescence spectrophotometer.

A mixture of 1,10-phenanthroline-5,6-dione (5 mmol), ammonium acetate (100 mmol), aldehyde (6 mmol) and glacial acetic acid (60 mL) was refluxed for about 2 h, then cooled to room temperature. The yellow precipitate was collected and washed with hot water after the reaction solution being neutralized with concentrated aqueous ammonia. The crude product was purifies by recrystallization from ethanol to obtain compound **1** as yellow needle crystals (yield: 62%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 13.57 (s, 1H), 9.02 (d, 2H), 8.91 (d, 2H), 8.12 (d, 2H), 7.82 (m, 2H), 7.18 (d, 4H), 7.04 (m, 6H), 2.30 (s, 6H). ^{13}C NMR (300 MHz, DMSO-d_6): δ 151.27, 149.37, 148.15, 144.62, 143.75, 136.22, 133.65, 130.72, 130.05, 127.84, 126.57, 125.57, 123.81, 122.81, 119.73, 20.91. ES-MS, $C_{33}H_{25}N_5$ (M^++H) *m/z* (%) Calcd.: 492.6, Found: 492.6 (100%).

2. Results and discussion

The variations in UV–vis spectra during the titration of NaOH aqua to the neutral DMSO solutions are shown in Fig. 1. Specifically, during NaOH titration, the absorptions at 292 nm that can be attributed to local π–π^* electron transition in imidazo[4,5-f][1,10]phenanthroline group progressively decreased until the absorption almost completely disappeared, simultaneously, a new absorption band around 311 nm gradually formed and developed. Particularly, the presence of an isosbestic points at 299 nm indicates that only two species coexisted at the equilibrium. Meanwhile, the absorption band at 366 nm assigned to ICT was strengthened and blue-shifted 5 nm. Particularly, upon the addition of NaOH, the colors of the solutions of the compounds gradually changed from colorless to greenish blue. However, the color as well as the absorption spectra can be recovered after adding appropriate amount of HCl, indicating the occurrence of reversible reactions. On the other hand, during the titration of the neutral solutions with the HCl solution, no appreciable changes in absorption spectra were observed until 20

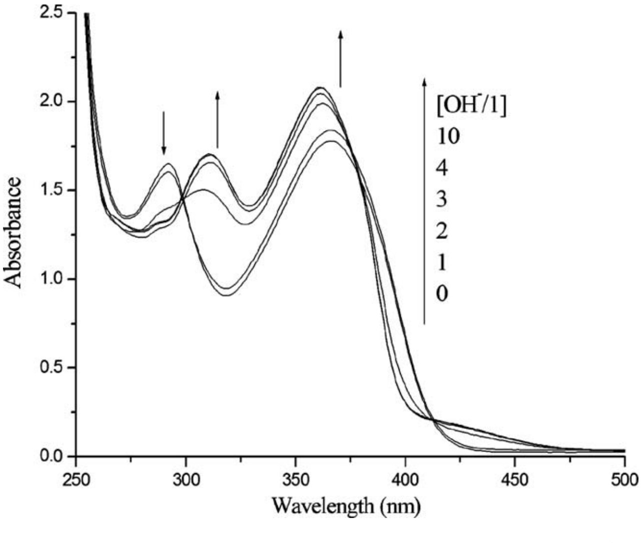


Fig. 1. UV–vis spectra of title compound during the titration of NaOH aqua ($c = 5 \times 10^{-5}$ mol/L).