

Available online at www.sciencedirect.com



CHINESE CHEMICAL LETTERS

Chinese Chemical Letters 22 (2011) 647-650

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.

© 2010 Hai Guang Zhang. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

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).

¹H NMR and ¹³C 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) H₂SO₄/HNO₃/KBr, reflux, 2 h, 95%; (b) NH₄Ac/CH₃COOH, 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%). ¹H 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). ¹³C 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, C₃₃H₂₅N₅ (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).



Fig. 2. The emission fluorescent spectra of compound 1 during the titration of NaOH (a) or HCl aqua (b) (excitation at 366 nm) ($c = 5 \times 10^{-5}$ mol/L).

times mole amount of HCl relative to the titrand has been added, indicating a negligible effect of protonation on the ground states of **1**.

The variations in fluorescent spectra of compound 1 responding to the addition of the NaOH or HCl solutions are shown in Fig. 2. Specifically, at room temperature, the compound 1 at concentration $c = 5 \times 10^{-5}$ mol/L exhibited strong fluorescence emissions at 500 nm (excitation at 366 nm). However, upon the addition of NaOH, its emissions decreased significantly while the maximum emission wavelength was red-shifted about 36 nm. The emission spectra of 1 no longer changed remarkably after more than 3 times mole amount NaOH were added, indicating almost complete deprotonation of imidazole. The fluorescence quantum yields Φ_F was determined by the method in Ref. [14] with Cormarin 307 in methanol ($\Phi_F = 0.57$) was adopted as a reference. The Φ_F of 1 was calculated as 0.63, while the Φ_F of deprotonated 1 was calculated as 0.14, which was only 22% of that of 1, it can be attributed to the quenching of fluorescence emissions caused by the photo-induced electron transfer (PET) from IP to phenylamine group that was induced by enhanced electron density in IP group as a result of the deprotonation of imidazolyl group. On the other hand, as Fig. 2(b) shown, the fluorescent emissions of 1 decreased accompanying the addition of HCl into the neutral solutions until their emissions have been completely quenched, the shift of the maximum emission wavelength cannot be observed. When the HCl or NaOH solution was added into the above basic or acid solutions, the fluorescent



Fig. 3. Electron distributions as well as HOMO and LUMO energy levels of 1, 1-OH (deprotonated) and 1-H (protonated).

emission gradually increased until the initial intensity was completely recovered. In short, the compound **1** behaved as an excellent off–on–off emission switch via deprotonation/protonation by adding base/acid.

To be able to gain a deeper insight into the ICT process of 1 and its (de)protonated state, the theoretical calculations have been conducted based on Gauss03 program in which the compounds were perfectly optimized at the B3LYP/6-31G(d) level. The electron distribution in HOMO and LUMO energy states of 1, 1-OH (deprotonated) and 1-H (protonated) are shown in Fig. 3. As shown in Fig. 3, the electron distribution in the frontier MOs of 1 revealed a HOMO–LUMO excitation in which the electron distribution extended from TPA moiety to the IP moiety, exhibiting strong ICT migration characteristics. Meanwhile, the electron distribution in the frontier MOs of deprotonated 1 revealed a HOMO–LUMO excitation in which the electron migrated from IP to TPA moiety, indicating the occurrence of an efficient PET process. It was well consistent with the PET quenching observed in the base solutions in the experiments. For protonated 1, we calculated the molecule that the H⁺ was connected with the N atom of phenylamine group but not imidazolyl group because of the more basic of phenylamine group than imidazolyl group. As shown in Fig. 3, an electron migration from the IP moiety to the phenyl ring of TPA moiety has been observed in protonated 1 by the electron distribution in HOMO–LUMO excitation. However, the ICT migration from TPA to IP cannot be found here, which is consistent with the observed fluorescent quenching in the acid solutions during the experiments.

3. Conclusion

To conclude, we designed and synthesized a new dye containing both imidazo[4,5-f][1,10]phenanthroline and triphenylamine groups. Particularly, an acid/base induced absorption and fluorescent molecular switch has been demonstrated by modulating the ICT process from phenylamine group to the IP group via protonation/deprotonation. Meanwhile, the electron distributions of HOMO–LUMO excitation in compound 1 have been obtained via theoretical calculations, which were well consistent with the results of the fluorescence emission changes observed during the experiments.

Acknowledgments

The authors greatly acknowledge the financial support of the State National Natural Science Foundation of China (No. 50325311) and National 863 Project Foundation of China (No. 2007AA10Z334).

References

- [1] B.L. Feringa, Molecular Switches, Wiley-VCH, Weinheim, Germany, 2001.
- [2] M. Zhang, M. Yu, F. Li, M. Zhu, et al. J. Am. Chem. Soc. 129 (2007) 10322.
- [3] K. Kinbara, T. Aida, Chem. Rev. 105 (2005) 1377.
- [4] F. Gao, X. Chen, F. Zhou, et al. Inorg. Chim. Acta 362 (10) (2009) 4960.
- [5] Y. Pellegrin, R.J. Forster, T.E. Keyes, Inorg. Chim. Acta 362 (2009) 1715.
- [6] F. Gao, H. Chao, F. Zhou, et al. Inorg. Chem. Commun. 10 (2007) 170.
- [7] F.R. Liu, K.Z. Wang, G.Y. Bai, et al. Inorg. Chem. 43 (2004) 1799.
- [8] P. Passaniti, P. Ceroni, V. Balzani, et al. Chem. Eur. J. 12 (2006) 5685.
- [9] Z.X. Wang, G.R. Zheng, P. Lu, Org. Lett. 5 (2005) 3669.
- [10] S. Wang, S.H. Kim, Spectrochim. Acta Part A 72 (2009) 677.
- [11] C. Hiort, P. Lincoln, B. Norden, J. Am. Chem. Soc. 115 (1993) 3448.
- [12] Z.Q. Bian, K.Z. Wang, L.P. Jin, Polyhedron 21 (2002) 313.
- [13] M. Sun, H. Xin, K.Z. Wang, et al. Chem. Commun. (2003) 702.
- [14] J.N. Demas, G.A. Crosby, J. Phys. Chem. 75 (1971) 991.