Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 117 (2014) 397–401

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Fluorescent 1:2 demultiplexer and half-subtractor based on the hydrolysis of N-salicylidene-3-aminopyridine

Liyan Zhao, Wujiong Xia *, Chao Yang

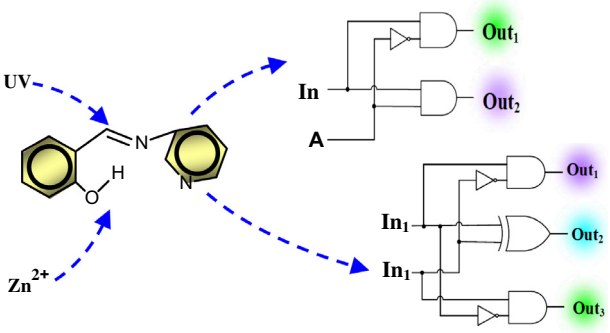
The State Key Lab of Urban Water Resource and Environment & Academy of Fundamental and Interdisciplinary Science, Harbin Institute of Technology, P.O. Box 3026, 2 Yikuang Street, Harbin, Heilongjiang 150080, PR China

HIGHLIGHTS

- A fluorescent 1:2 demultiplexer was expressed.
- A fluorescent half-subtractor were expressed.
- The spectrum changes were originated from the photoinduced electron transfer.

GRAPHICAL ABSTRACT

Based on the hydrolysis, a simple molecule has implemented the important demultiplexer and half-subtractor.



ARTICLE INFO

Article history:
Received 4 April 2013
Received in revised form 21 July 2013
Accepted 2 August 2013
Available online 13 August 2013

Keywords:
Schiff bases
Fluorescent devices
Logic gate
Half-subtractor
Demultiplexer

ABSTRACT

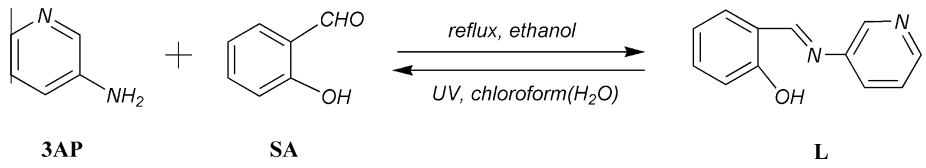
In moist chloroform solution, the ultraviolet light irradiation would cause N-salicylidene-3-aminopyridine (**L**) to hydrolyze into salicylaldehyde and 3-aminopyridine. To consider an optical signal (UV light) and a chemical signal (Zn^{2+}) as inputs, the luminescence signals as outputs, the logic behavior of compound **L** was investigated. Interestingly, excited by two different wavelengths lights, two sharp distinct fluorescent spectra were collected. Consequently, a fluorescent 1:2 demultiplexer and a fluorescent half-subtractor were respectively expressed.

Introduction

Following the concept of molecular logic proposed by Aviram in 1988 [1], de Silva firstly contributed an AND logic gate at molecular level [2]. Since then, a large number of significant logic functions were exploited [3–11]. Among the logic gates reported, the ones using fluorescence as outputs are ideal because of its ease of detection. Salicylidene Schiff base is a kind of active material for its excellent luminescence and remarkable coordination properties [12,13]. Therefore, salicylidene Schiff base is very suitable to develop the fluorescent logic operations. In our previous work, we have reported several logic functions of salicylidene Schiff base [14–19]. Herein, we will present what we have achieved on developing fluorescent logic function based on salicylidene Schiff base.

* Corresponding author. Tel./fax: +86 451 86403193.
E-mail address: xiawj@hit.edu.cn (W. Xia).

1386-1425/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.saa.2013.08.009



Scheme 1. The structure, preparation and hydrolysis of compound **L**.

Recently, we found that, in moist chloroform solution, UV light irradiation could lead salicylidene Schiff bases to hydrolyze into the corresponding salicylaldehyde and amine [20]. This result aroused our interest. It can be envisioned that, in moist chloroform solution, UV light and transition metal ion would likely stimulate salicylidene Schiff base to act some interesting logic functions. In order to efficiently utilize the fluorescence signals as outputs, we introduced pyridine group on salicylidene Schiff base to increase the coordination ability. Hereby, one salicylidene Schiff base **L** was prepared (shown in Scheme 1). We tracked the irradiation experiment of **L** by time-dependent absorption spectroscopy and time-dependent NMR. The results demonstrated that, upon the irradiation of UV light, **L** was hydrolyzed into salicylaldehyde (**SA**) and 3-aminopyridine (**3AP**). The structure, preparation and hydrolysis of **L** are shown in Scheme 1.

UV light and Zn^{2+} were selected as inputs to stimulate the response molecule **L**. The fluorescence spectroscopy was employed to investigate the response process. The actions of inputs had induced dramatic fluorescence changes. Interestingly, when different excitation lights were used (370 nm and 320 nm), two widely distinct fluorescent spectra were obtained. Consequentially, fluorescent 1:2 demultiplexer and fluorescent half-subtractor were expressed. Demultiplexer [21–26] and half-subtractor [27–33] are essential logic operations in the information processing and calculation field respectively.

Experimental

Material

Salicylaldehyde and 3-aminopyridine were purchased from Aldrich. Compound **L** was synthesized by the condensation of the 3-aminopyridine with salicylaldehyde according to the previous procedures [34]. Pure **L** was obtained after recrystallization twice from absolute ethanol. The ^{1}H NMR (DMSO, 25 °C, TMS): δ 12.58 (s, 1H), 9.02 (s, 1H), 8.64 (s, 1H), 8.63 (s, 1H), 8.50 (d, 1H), 7.86 (d, 1H), 7.70–7.43 (2H), 7.00 (t, 2H). ^{13}C NMR ($CDCl_3$): δ 164.54, 161.13, 148.00, 144.68, 143.10, 133.88, 132.65, 127.98, 123.88, 119.36, 118.94, 117.42. GC–MS (EI): 198 (M^+), 181, 165, 147, 120, 104, 78, 51. HRMS (ESI) $[M+H]^+$, 199.0876, calcd for: 199.0866.

Experimental details for spectral studies

All of the spectral analysis were accomplished in chloroform. The concentration of **L** solution for spectral analysis was 6.06×10^{-5} mol/L. A low-pressure mercury (16 W) lamp was used as light source for irradiation stimulations in the spectral measurement. The interval irradiation time was 1 min. Solutions for spectrophotometric titration were titrated directly in 1 cm absorption cells by successive additions of corresponding chemical reagent using a microliter syringe. After addition of each aliquot, the cell was capped and mixed by inversion. And then, the spectrum was retaken. The time-dependent ^{1}H NMR experiments were accomplished in deuterochloroform. The concentration of **L** solution for spectral analysis was 2.02×10^{-2} mol/L. A high-pressure mercury lamp (500 W) was used as light source for irradiation reaction in NMR measurement. The interval time was 1 h.

Instrumentation

The UV–Vis absorption spectra were recorded in a Hitachi (Model U-4100) UV–Vis–NIR spectrophotometer. The fluorescence spectra were determined with a FluoroMax-4 (JobinYvon) fluorimeter. ^{1}H NMR spectra were recorded at 400 MHz on a Bruker AV-400 instrument. ^{13}C NMR spectra were recorded at 100 MHz. Low-resolution mass spectra were measured on an Agilent 7890A-5975C GC–MS using electron impact (EI) ionization at 70 eV. High-resolution mass spectra were taken on an Agilent 1200–6520 Q-TOF electro spray mass spectrometer.

Results and discussion

Photochemical experiments

First of all, we studied the photochemical behavior of compound **L** by the time-dependent absorption spectra as shown in Fig. 1. With irradiation, the original absorption band at 370 nm gradually decreased; meanwhile, a new absorption at 252 nm appeared and intensified. In addition, the absorption at 295 nm gradually decreased and simultaneously red-shifted to 320 nm. Above spectral changes were similar to the experimental result reported in our previous work [20]. Such changes have been testified to be due to the hydrolysis reaction of salicylidene Schiff bases [20]. Therefore, it was speculated that compound **L** might have been hydrolyzed into **SA** and **3AP** as shown in Scheme 1.

And then, we employed the time-dependent ^{1}H NMR to verify this hypothesis. Considering that the concentration for NMR measurement must be higher, we increased the concentration of **L** from 6.06×10^{-5} mol/L to 2.02×10^{-2} mol/L. Consequently, the irradiation time in time-dependent ^{1}H NMR spectra was longer. The

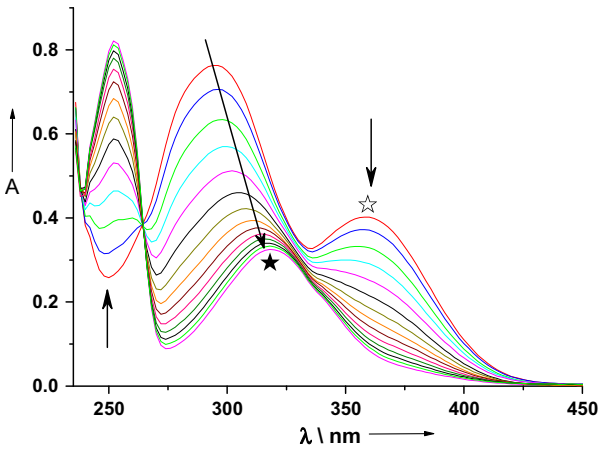


Fig. 1. UV–Vis absorption spectral changes of **L** with 254 nm UV light irradiation. Interval irradiation time is 1 min. ☆ is the original state, ★ is the final state. Conditions: 6.06×10^{-5} mol/L of chloroform solution.

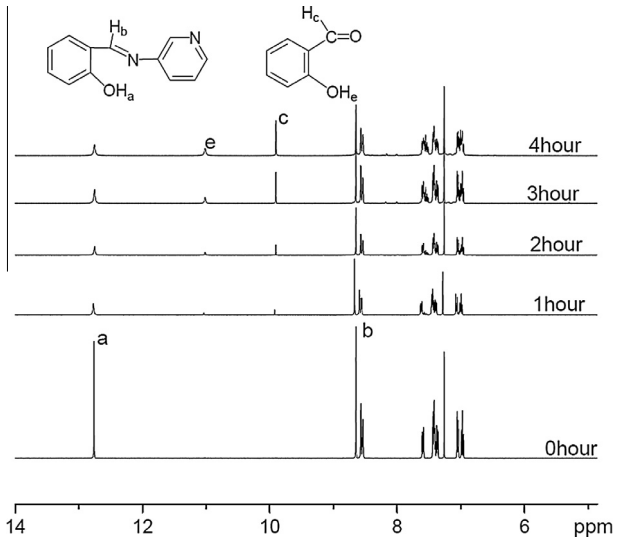


Fig. 2. Partial ^{1}H NMR (400 MHz) spectral changes of compound **L** in CD_3Cl upon irradiation of high-pressure UV light. Interval time is 1 h. Concentration: 2.02×10^{-2} mol/L.

experimental result of time-dependent ^{1}H NMR spectra was shown in Fig. 2. It could be observed that the primary proton H_a and H_b gradually decreased. Meanwhile, two new chemical shifts (around 11 ppm and 10 ppm) appeared and intensified with the irradiation. These two new chemical shifts belonged to the characteristic ^{1}H NMR signals of reactant **SA** (H_c and H_e, the ^{1}H NMR of **SA** can be seen in the Electronic Supplementary Information file). Above ^{1}H NMR spectral changes were consistent with the experimental results reported in our previous work [20]. Thus, it could be concluded that compounds **L** had been hydrolyzed into **SA** and **3AP** as shown in Scheme 1.

Moist chloroform was dried with anhydrous $CaCl_2$. And then, the filtrate was distilled from P_2O_5. Consequently, dried chloroform was obtained. When the photochemical behavior of compound **L** was studied in dried chloroform, no hydrolysis reaction was observed. In addition, the hydrolysis reaction did not occur in other solvents such as benzene, acetonitrile, cyclohexane. Moreover, in deuterated benzene or deuterated acetonitrile, the irradiation of UV light had not caused any changes within the ^{1}H NMR spectra. Above results suggested that the hydrolysis might be relevant to the moist chloroform.

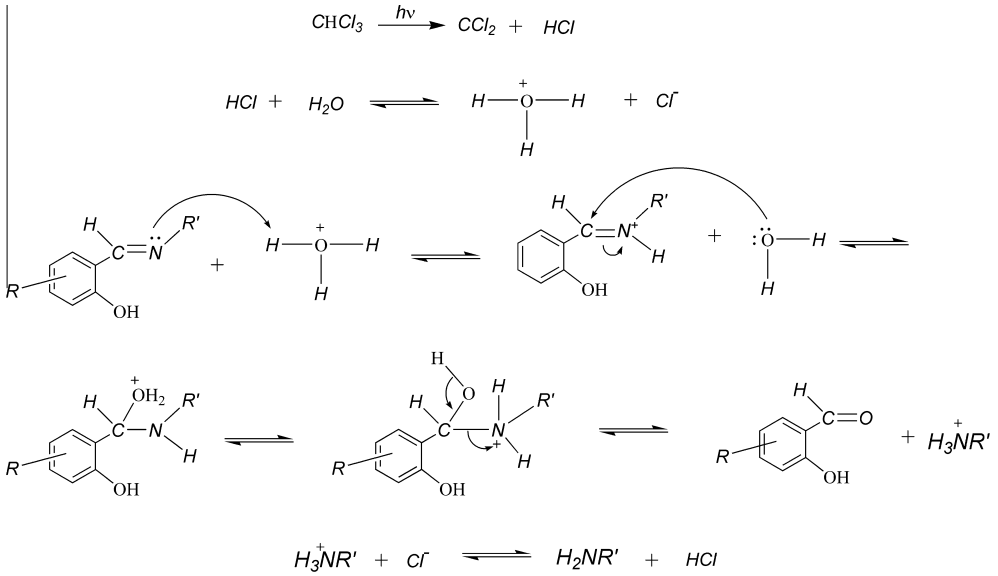
According to literature retrieval, it has been confirmed that chloroform is photolabile. Irradiated by UV light, chloroform will produce HCl [35,36]. It is well known that HCl can catalyze the hydrolysis process of Schiff bases. The possible hydrolysis mechanism of N-salicylidenaniline Schiff bases was proposed in the Scheme 2 [20]. Furthermore, we investigated the hydrolysis in chloroform solution containing different amount of water. When the sample **L** and water were in proportion of 1:1, the hydrolysis reaction could be carried out completely. When the amount of water was continuously increased, the velocity of hydrolysis reaction would speed up.

The fluorescent spectral analysis

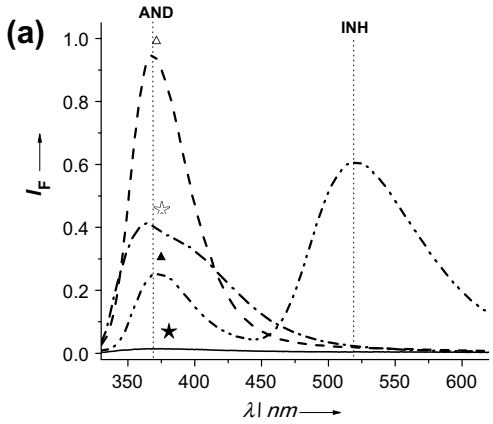
Fluorescence spectroscopy was employed to investigate the processes of irradiation and coordination with Zn^{2+}. The concentration of **L** was 6.06×10^{-5} mol/L and the total irradiation time was 13 min. The characteristic absorptions before and after irradiation (370 nm and 320 nm shown in Fig. 1) were respectively selected as the excitation light to investigate the fluorescent properties. Interestingly, two different excitation lights had induced two widely distinct fluorescent spectra as shown in Figs. 3a and 4a, which would be particularly discussed in the following sections.

Excited with 320 nm light

When 320 nm light was used as the excitation light, the actions of UV light and Zn^{2+} had led to sharp changes in the fluorescence spectra (Fig. 3a) The detailed irradiation and titration spectra are shown in Supplementary data file: Figs. S1–S3. As seen in Scheme 1, the hydrolysis product was a mixture of **SA** and**3AP**. Which component would be responsible for the emissions related to the actions of irradiation? We tried our best to grow crystals, but failed. Using 320 nm light as excitation light, we measured the fluorescent spectra of **SA**, **3AP** and their complexes. The fluorescence spectra were collected in Fig. 5. Comparing Fig. 3a with Fig. 5, it can be found that the shapes, positions and relative intensities of the fluorescent spectra labeled with ☆ and △ (Fig. 3a) are consistent with the ones labeled with 3-aminopyridine and 3-aminopyridine + Zn^{2+} respectively (Fig. 5). Therefore, **3AP** is responsible for the emission



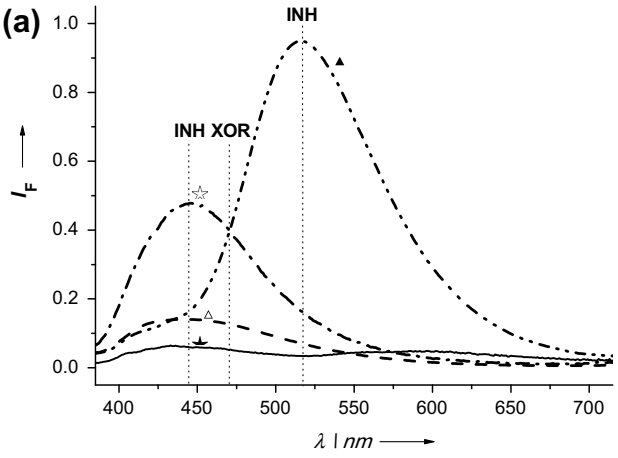
Scheme 2. The hydrolysis mechanisms for salicylidene Schiff bases.

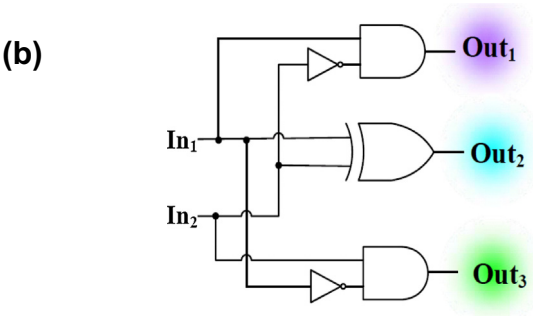


(c)

Inputs		Outputs	
Zn^{2+}(In_2) Data input	UV (In_1) Adress input	INH Out_1 520 nm	AND Out_2 368 nm
0	0	0	0
1	0	1	0
0	1	0	0
1	1	0	1

Fig. 3. (a): Fluorescence spectra of **L** (6.06×10^{-5} mol/L of chloroform solution, λ_{ex} = 320 nm) upon the actions of inputs: ★ **L** alone; ☆ after irradiation by UV light (total irradiation time is 13 min); ▲ with 5 equiv of Zn^{2+}; △ irradiation by UV light + Zn^{2+}. (b): The logic diagram and (c): The truth table for the 1:2 demultiplexer.





(c)

Inputs		Outputs			Half-substractor	
UV In_1	Zn^{2+} In_2	INH Out_1 445 nm	XOR Out_2 470 nm	INH Out_3 520 nm	a-b 520/470 nm	b-a 445/470 nm
0	0	0	0	0	00	00
1	0	1	1	0	01	11
0	1	0	1	1	11	01
1	1	0	0	0	00	00

Fig. 4. (a): Fluorescence spectra of **L** (6.06×10^{-5} mol/L of chloroform solution, λ_{ex} = 370 nm) upon the actions of inputs: ★ **L** alone; ☆ after irradiation by UV light (total irradiation time is 13 min); ▲ with 5 equiv of Zn^{2+}; △ irradiation by UV light + Zn^{2+}. (b): The logic diagram and (c): The truth table for the half-subtractors.

of irradiation products and the complex of **3AP** with Zn^{2+} is responsible for the emission after the actions of UV light plus Zn^{2+}. It must be noted that there is some slight difference in above two pairs of fluorescent spectra respectively. The difference may be due to the fact that hydrolysis products is a mixture, consequently, another component **SA** will affect the correlative fluorescent spectra to some extent. In addition, ^{1}H NMR titration experiments for the irradiation sample had provided further evidence. As can be seen from Fig. S8 (shown in the Electronic Supplementary Information file), after titration with Zn^{2+}, the signals around 8.60 ppm and 7.10 assigned to the H atoms of **3AP**, were shifted upfield. These differences in the ^{1}H NMR indicated that the change of the electron density owning to the through-bond electronic effects, in other words, **3AP** had coordinated with Zn^{2+}.

Coordination will reduce the photoinduced electron transfer (PET). Therefore, the complexes before and after irradiation all presented higher emission than the ones of ligands **L** and **3AP** [37]. Since 320 nm was not the optimal excitation wavelength for both **L** and **L**Zn^{2+}, they showed relatively weaker fluorescence (Fig. 3a) than the case of 370 nm light as excitation light (Fig. 4a). It could be observed that only complex **L**Zn^{2+} exhibited emission at longer wavelength region. This red-shifted emission probably due to the charge transfer transition (CT) presenting in the process of co-ordination [38,39].

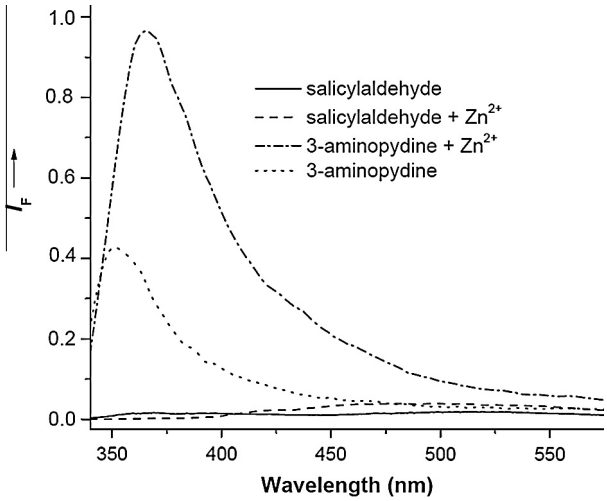


Fig. 5. Fluorescence spectra of salicyladehyde (solid), salicyladehyde + Zn^{2+} (dash), 3-aminopydine (dash dot) and 3-aminopydine + Zn^{2+} (dot). Chloroform solution, λ_{ex} = 320 nm.

Excited with 370 nm light

In sharp contrast, when the 370 nm light was employed to excite the response system, considerable different spectra were obtained (Fig. 4a) The detailed irradiation and titration spectra are shown in Supplementary data file: Figs. S4–S6. In this case, a more significant emission at λ_{max} = 520 nm was observed. This emission also was original from the PET and CT processes of **L**Zn^{2+} mentioned in Section 3.2.1. According to the literature, pyridine ring in molecule **L** would undergo a complete rotation after coordination with metal ion [40]. Consequently, the molecular packing showed a "close" structure with short distances between ligands. Therefore, the π–π stacking between salicyl rings and imine double bonds was formatted, which would induce enhanced fluorescence and red-shift. We tried our best to grow crystal of **L**Zn^{2+}, but failed. Since 370 nm was not the optimal excitation wavelength, complex of **3AP** with Zn^{2+} showed a relatively weaker emission than **L**Zn^{2+}.

The logic analysis under actions of UV light and Zn^{2+}

The logic nature derived from Fig. 3a was collected in the truth table as shown in Fig. 3c. As it could be seen, the fluorescence intensity at 520 nm (Out_1) was high only in the absence of UV light, but in the presence of Zn^{2+}. This truth table justly expressed an INHIBIT logic gate. The intensity of another fluorescence channel at 368 nm (Out_2) was high only in the presence of both UV light and Zn^{2+}, which worked as an AND logic gate. Therefore, using UV light as the address input, Zn^{2+} as the data input, and the fluorescence emission at 368 nm and 520 nm as the dual data outputs, compound **L** could act as 1:2 digital demultiplexer. The logic diagram was shown in Fig. 3b.

Now we turned to the discussion of the logic operations as shown in Fig. 4a. When the emissions were followed at three different channels, 445 nm (Out_1), 470 nm (Out_2) and 520 nm (Out_3), the clear digital nature of the inputs and outputs became legible as described in Fig. 4c. In the channels of Out_1 and Out_3, compound **L** could act as two INHIBIT gates. In addition, the channel of Out_2 could express a XOR gate. Therefore, concatenation half-subtractors were obtained (Fig. 4b). It should be pointed out that when the Out_3 combined with Out_2, the *a*–*b* numeration was operated. However, the Out_1 and Out_2 would perform the *b*–*a* logic function.

Conclusions

In summary, we further developed the salicylidene Schiff base as both a fluorescent 1:2 demultiplexer and a fluorescent half-subtractor based on a hydrolysis reaction. The arithmetic and demultiplexer functions constructed in this work may be helpful to future application of salicylidene Schiff bases in the molecular devices. Furthermore, it is of interest to point out that two different logic functions presented here mainly depend on two different wavelength of excitation lights. Work on the crystal growth and exploring detailed photoinduced proton transfer is underway.

Acknowledgements

This work is supported by the China NSFC (Nos. 20802013 and 21072038), the New Century Excellent Talent Program of Chinese Ministry of Education (No. NCET-07-0242), the Fundamental Research Funds for the Central Universities (Grant No. HIT. NSRIF. 2012043), SKLUWR of HIT (No. ES201010), Project Supported by Development Program for Outstanding Young Teachers of HIT (HITQNJS 2009.068), program of excellent Team in HIT, China Postdoctoral Science Foundation (20080440867), and Heilongjiang Postdoctoral Fund (LBH-Z08199).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.08.009.

References

[1] A. Aviram, J. Am. Chem. Soc. 110 (1988) 5687–5692.
[2] A.P. de Silva, N.H.Q. Gunaratne, C.P. McCoy, Nature 364 (1993) 42–44.
[3] K. Szaciłowski, Chem. Rev. 108 (2008) 3481–3548.
[4] E. Katz, V. Privman, Chem. Soc. Rev. 39 (2010) 1835–1857.
[5] J. Andréasson, U. Pischel, Chem. Soc. Rev. 39 (2010) 174–188.
[6] M. Amelia, L. Zou, A. Credi, Coord. Chem. Rev. 254 (2010) 2267–2280.
[7] G. Bergamini, E. Marchi, P. Ceroni, Coord. Chem. Rev. 255 (2011) 2458–2468.
[8] J. Wang, C.S. Ha, Sens. Actuators B 146 (2010) 373–380.
[9] P. Singh, J. Kaur, W. Holzer, Sens. Actuators B 150 (2010) 50–56.
[10] S. Kou, H.N. Lee, D. Van Noort, K.M.K. Swamy, S.H. Kim, J.H. Soh, K.-M. Lee, S.-W. Nam, J. Yoon, S. Park, Angew. Chem. Int. Ed. 47 (2008) 872–876.
[11] N. Kaur, N. Singh, B. McCaughan, J.F. Callan, Sens. Actuators B 144 (2010) 88–91.
[12] K.C. Gupta, A.K. Sutar, Coord. Chem. Rev. 252 (2008) 1420–1450.
[13] J.A. Riddle, S.P. Lathrop, J.C. Bollinger, D. Lee, J. Am. Chem. Soc. 128 (2006) 10986–10987.
[14] L. Zhao, S. Wang, Y. Wu, Q. Hou, Y. Wang, S. Jiang, J. Phys. Chem. C. 111 (2007) 18387–18391.
[15] L. Zhao, D. Sui, J. Chai, Y. Wang, S. Jiang, J. Phys. Chem. B. 110 (2006) 24299–24304.
[16] S. Wang, L. Zang, L. Zhao, X. Wang, Q. Hou, S. Jiang, Spectrochim. Acta A 77 (2010) 226–231.
[17] S. Wang, G. Men, L. Zhao, Y. Wu, Y. Wang, S. Jiang, IEEE Sens. J. 1–3 (2009) 277–280.
[18] S. Wang, G. Men, L. Zhao, Q. Hou, S. Jiang, Sens. Actuators B 145 (2010) 826–831.
[19] S. Wang, G. Men, Y. Wang, L. Zhao, Q. Hou, S. Jiang, IEEE Sens. J. 11 (2011) 137–141.
[20] L. Zhao, W. Xia, B. Gou, Y. Lu, C. Yang, D. Li, Spectrochim. Acta A 95 (2012) 199–203.
[21] M. Amelia, M. Baroncini, A. Credi, Angew. Chem. Int. Ed. 47 (2008) 6240–6243.
[22] E. Perez-Inestrosa, J.M. Montenegro, D. Collado, R. Suau, Chem. Commun. (2008) 1085–1087.
[23] J. Andréasson, S.D. Straight, S. Bandyopadhyay, R.H. Mitchell, T.A. Moore, A.L. Moore, D. Gust, J. Phys. Chem. C 111 (2007) 14274–14278.
[24] S. Gaweda, G. Stochel, K. Szacilowski, Chem. Asian J. 2 (2007) 580–590.
[25] M.F. Budyka, N.I. Potashova, T.N. Gavrishova, V.M. Lee, J. Mater. Chem. 19 (2009) 7721–7724.
[26] M.A. Arugula, V. Bocharova, J. Halamek, M. Pita, E. Katz, J. Phys. Chem. B 114 (2010) 5222–5226.
[27] Y. Liu, W. Jiang, H. Zhang, C. Li, J. Phys. Chem. B 110 (2006) 14231–14235.
[28] Z. Guo, P. Zhao, W. Zhu, X. Huang, Y. Xie, H. Tian, J. Phys. Chem. C 112 (2008) 7047–7053.
[29] V. Luxami, S. Kumar, New J. Chem. 32 (2008) 2074–2079.
[30] S.J. Langford, T. Yann, J. Am. Chem. Soc. 125 (2003) 11198–11199.
[31] A. Coskun, E. Deniz, E.U. Akkaya, Org. Lett. 7 (2005) 5187–5189.
[32] R. Baron, O. Lioubashevski, E. Katz, T. Niazov, I. Willner, Angew. Chem. Int. Ed. 45 (2006) 1572–1576.
[33] M. Suresh, D.A. Jose, A. Das, Org. Lett. 9 (2007) 441–444.
[34] H.E. Smith, S.L. Cook, M.E. Warren, J. Org. Chem. 29 (1964) 2265–2267.
[35] K.S. Georgiou, Appl. Phys. A 92 (2008) 1013–1017.
[36] C. Romanzin, B. Gans, S. Douin, S. Boyé-Péronne, D. Gauyacq, Chem. Phys. 351 (2008) 77–82.
[37] L. Gao, Y. Wang, J.Q. Wang, L. Huang, L.Y. Shi, X.X. Fan, Z.G. Zou, T. Yu, M. Zhu, Z.S. Li, Inorg. Chem. 45 (2006) 6844–6850.
[38] P.F. Wang, Z. Hong, Z.Y. Xie, S.W. Tong, O.Y. Wong, C.S. Lee, N.B. Wong, L.S. Hung, S.T. Lee, Chem. Commun. (2003) 1664–1665.
[39] P.G. Lacroix, S.D. Bella, I. Ledoux, Chem. Mater. 8 (1996) 541–549.
[40] F. Robert, A.D. Naik, B. Tinant, R. Robiette, Y. Garcia, Chem. Euro. J. 15 (2009) 4327–4342.