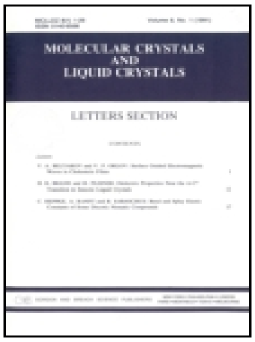


Taylor & Francis
Taylor & Francis Group

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Properties of liquid crystals and Cu^{2+} recognition based on Schiff bases

Zhilian Liu, Zhenning Yu, Jian Zhang & Shuxiang Zhang

To cite this article: Zhilian Liu, Zhenning Yu, Jian Zhang & Shuxiang Zhang (2016) Properties of liquid crystals and Cu^{2+} recognition based on Schiff bases, Molecular Crystals and Liquid Crystals, 624:1, 11-19, DOI: 10.1080/15421406.2015.1017310

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1017310

MOL. CRYST. LIQ. CRYST.
2016, VOL. 624, NO. 1, 11–19
http://dx.doi.org/10.1080/15421406.2015.1017310

Taylor & Francis
Taylor & Francis Group

Properties of liquid crystals and Cu^{2+} recognition based on Schiff bases

Zhilian Liu[a,b], Zhenning Yu[a], Jian Zhang[a], and Shuxiang Zhang[a,b]

[a]School of Chemistry and Chemical Engineering, University of Jinan, Jinan, China; [b]Shandong Key Laboratory of Fluorine Chemistry and Chemical Engineering Materials, Jinan, China

ABSTRACT

Two series of new Schiff base compounds were synthesized. For Schiff base compounds with a pyridine nitrogen atom in 4-position (**7a–e**), their supramolecular hydrogen bonding complexes show good liquid crystal properties. However, no liquid crystal property is observed for **8a–e**. Results of theoretical calculations demonstrate that it is the intermolecular hydrogen bond of Schiff base compounds (**8a–e**) that prevents the formation of supramolecular hydrogen bonding. The Schiff base compounds, with terminal alkoxy chains, can recognize Cu^{2+} selectively with a color change. Nevertheless, others cannot recognize Cu^{2+}.

KEYWORDS
Fluorine; Schiff base; liquid crystals; recognition; Cu^{2+}

1. Introduction

Schiff bases are condensation products of primary amines with carbonyl compounds and they were first reported by Schiff [1] in 1864. Schiff bases are some of the most widely used organic compounds in catalytic chemistry [2], organometallic chemistry [3], biochemistry [4], photochemistry [5], and liquid crystal chemistry [6–15]. Several studies [16–22] showed that the presence of a lone pair of electrons in a sp^2 hybridized orbital of nitrogen atom of the azomethine group is of considerable chemical and biological importance. Nowadays, the research field dealing with Schiff base and its coordination chemistry [23] has expanded enormously. Versatility of Schiff base ligands and biological, analytical, and industrial applications of their complexes make further investigations in this area highly desirable.

However, Schiff bases, bearing fluorine substitutions, have not been studied extensively. In our previous work [24, 25], we synthesized Schiff base compounds with terminal fluoroalkoxy chains and studied the effect of the fluoroalkoxy on their liquid crystalline properties. Herein we present mesomophic properties of Schiff base (**7a**) hydrogen bonding liquid crystals. Nevertheless, under the same conditions, another series of Schiff base compounds (**8a–e**), with different position of pyridine nitrogen atom, show no liquid crystalline properties for their intermolecular hydrogen bond interaction. It is interesting that **8a–c** with terminal alkoxy chains can recognize Cu^{2+} with a noticeable color change while **8d–e** cannot for the electron withdrawing effect of the terminal fluoroalkoxy chains.

CONTACT Zhilian Liu and Shuxiang Zhang ✉ chm_liuzl@ujn.edu.cn; zhilianliu@163.com School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China

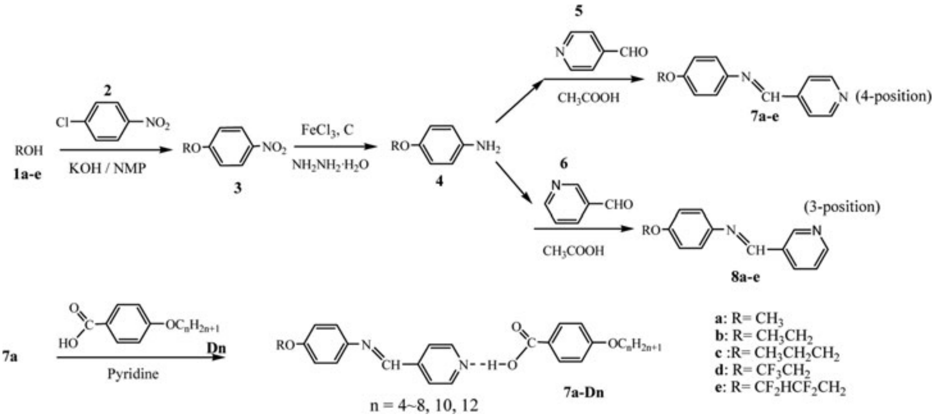
Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

2. Results and discussion

2.1. *Synthesis*

In our previous work, we have synthesized **7c–e** [24] and **7b** [25]. In this paper, we synthesized the Schiff base **7a** using the same method. Schiff bases **8a–e** were prepared with **4** and 3-pyridinecarboxaldehyde (**6**) in ethanol at 85°C for 12 h by the similar method.

4-n-alkoxybenzoic acids (**Dn**) were synthesized as the literature [26]. The supramolecular hydrogen bonding liquid crystal complexes (**7a–Dn**) were prepared with equimolar Schiff base **7a** and one of 4-*n*-alkoxybenzoic acids in pyridine. After slow evaporation of pyridine, the mixture was dried in vacuo at 65°C for 24 h. Supramolecular hydrogen-bonded liquid crystals complexes were obtained as yellow or brown solid (Scheme 1).



Scheme 1. Synthesis of Schiff bases and supramolecular liquid crystal complexes.

2.2. *Liquid crystalline properties*

The structures of new Schiff bases **7a** and **8a–e** were identified by IR, ^{1}H NMR, ^{19}F NMR, mass spectra and elemental analyses. The hydrogen bonds in the supramolecular complexes (**7a–Dn**) were identified by infrared spectra for the two new peaks centered at 2426 and 1924 cm^{-1} compared with Schiff bases **7a** and 4-*n*-alkoxybenzoic acids (Fig. 1, **7a–D5** for example) [27–29].

The thermal behavior of supramolecular liquid crystals **7a–Dn** was studied using differential scanning calorimeter (DSC) and polarizing optical microscope (POM). The transition temperatures for all the new supramolecular liquid crystal complexes are shown in Table 1. All supramolecular complexes exhibit good liquid crystal properties with wide mesomorphic phase ranges.

The POM pictures reveal that all supramolecular complexes have nametic phases (Fig. 2). Our previous work [24, 25] demonstrated that all of supramolecular hydrogen bonding liquid crystal complexes, formed by Schiff bases **7b–e** and 4-n-alkoxybenzoic acids (**Dn**), had good liquid crystalline properties. Investigation of the optical textures by polarizing microscopy revealed that **7d–Dn** and **7e–Dn**, tailed by the fluoroalkoxy, showed smectic A phase instead of nematic phase of **7b–Dn** and **7c–Dn** with terminal alkoxy chains. Supramolecular hydrogen bonding liquid crystal complexes **7a–Dn**, with terminal alkoxy chains, also show nematic phase (N phase). This result is in accordance with our previous studies.

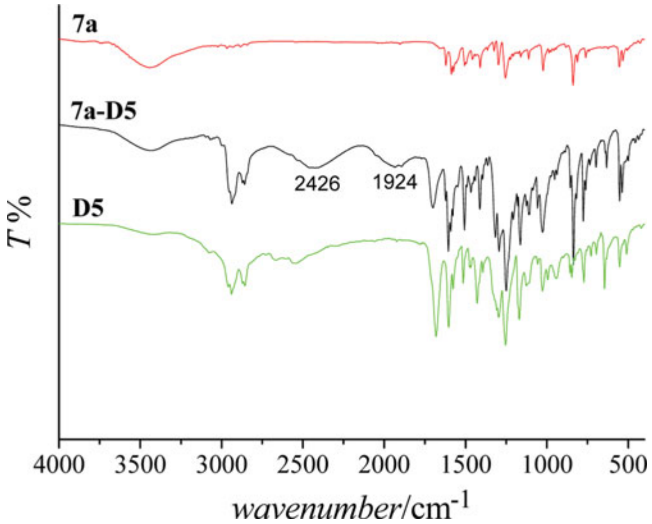


Figure 1. Infrared spectra of Schiff base (**7a**) and 4-n-pentyloxybenzoic acid (**D5**) and their supramolecular liquid crystal complex (**7a–D5**).

However, no new peak was found in the infrared spectra for the mixture of Schiff bases **8a–e** and 4-n-alkoxybenzoic acids (**Dn**). Meanwhile, no color pictures were found under crossed polarizers. It was all dark. Two independent melting processes were observed without crossed polarizers during heating from room temperature to 250°C. one melting point is correspond to Schiff bases **8a–e**, and the other is correspond to 4-n-alkoxybenzoic acids (**Dn**). These phenomena suggest that Schiff bases **8a–e** and 4-n-alkoxybenzoic acids (**Dn**) are independent of each other and no supramolecular hydrogen bonding forms between N atom of the pyridines and H atom of the benzoic acids.

The only difference between **7** and **8** is the position of the N atom in the pyridine ring. Why does no supramolecular hydrogen bonding form when N atom is in 3-position? We get a stable structure (**8a**) with the lowest energy through theoretical calculations (Fig. 3). In this simulant structure, the C-H distance (a) and the N-H distance (b) is 1.087 Å and 2.699 Å respectively. The N···H-C angle is 176.10° which is almost in a straight line. Therefore, it can be deduced that a N···H-C hydrogen-bond formed between two **8a** molecules. The existence of intermolecular hydrogen bond hinders the N atoms in the pyridine rings to form hydrogen-bonds with H atoms of the benzoic acids. No supramolecular hydrogen bonding liquid crystal complex forms in the mixture of **8** and **Dn** although it was prepared with the same method as **7** and **Dn**.

Table 1. Transition temperatures (°C) of new supramolecular liquid crystal complexes.

Compound	transition temperature[a]	Compound	transition temperature[a]	Compound	transition temperature[a]
7a–D4	Cr107 N 137 I	**7a–D5**	Cr 82 N 133 I	**7a–D6**	Cr 88 N 124 I
7a–D7	Cr 89 N 128 I	**7a–D8**	Cr 87 N 128 I	**7a–D10**	Cr 80 N 125 I
7a–D12	Cr 87 N 124 I				

[a] Cr: crystal state; I: isotropic liquid; N: nematic phase; the onset temperature of the phase transition from DSC of the second heating.

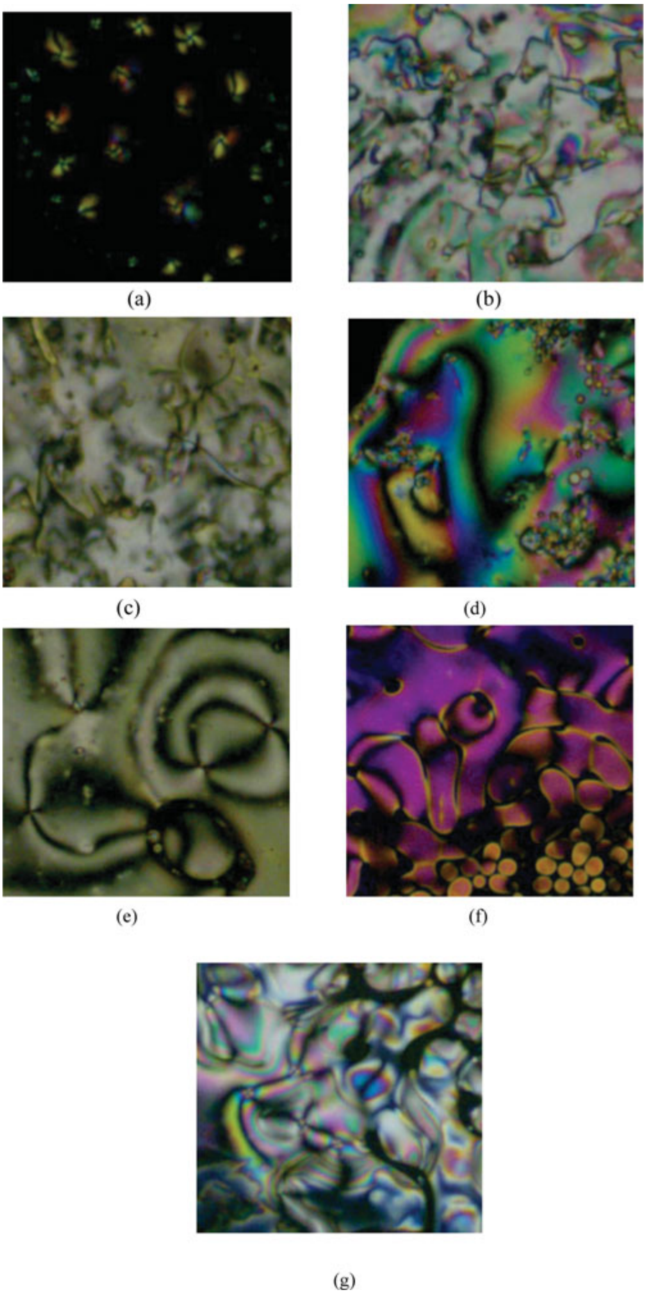


Figure 2. liquid crystal textures of **7a–Dn**.(a): **7a–D4**, heating to 130°C, N phase; (b): **7a–D5**, heating to 123°C, N phase; (c): **7a–D6**, heating to 100°C, N phase; (d): **7a–D7**, heating to 126°C, N phase; (e): **7a–D8**, cooling to 110°C, N phase; (f): **7a–D10**, cooling to 112°C, N phase; (g): **7a–D12**, cooling to 108°C, N phase. (crossed polarizers, magnification 20 ×).

2.3. *Cu^{2+} recognition properties*

In consideration of good complexation ability of Schiff base compounds, we studied metal cation recognition properties of **8** and get interesting results. Among ten kinds of metal cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Mn^{2+}, Pb^{2+}), **8a-c**, tailed by the alkoxy, can

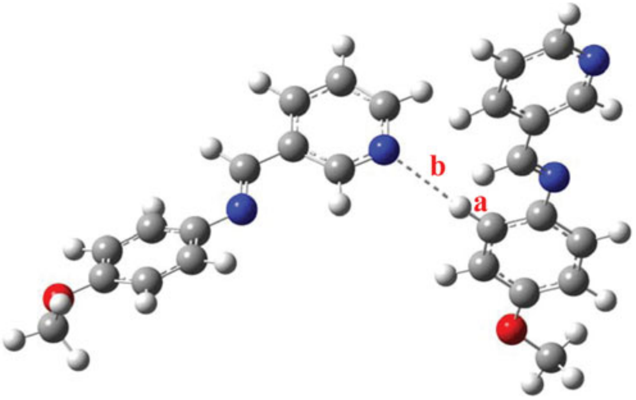


Figure 3. Simulant structure of Schiff base (**8a**). the C–H distance (a) : 1.087 Å; the N–H distance (b): 2.699 Å; the N···H–C angle: 176.10 °.

selectively recognize Cu^{2+} with a new peak centered at 507 nm in UV-Vis absorption spectra (Fig. 4).

The new peak is different from the maximum absorption wavelength of the solution of Cu^{2+} in acetonitrile which is at 462 nm (Fig. 5, dash). There is a red shift of 45 nm. It is also different from that of **8b** (Fig. 5, dot) because there is no absorption for **8b** in the visible region. After the addition of equal molar Cu^{2+}, the solution of **8b** in acetonitrile changes its color from colorless to brown (Fig. 5, inset). The mixed solution's color is darker and the absorbance at 507 nm is higher when the Cu^{2+} concentration is increased. It can be inferred that there is interactions between **8b** and Cu^{2+}. These results suggest that **8a–c** can be used as colorimetric chemosensors for Cu^{2+} with a noticeable color change.

Nevertheless, **8d–e**, tailed by the fluoroalkoxy, cannot recognize any one kind in these ten metal cations. No new peak is observed in the absorption spectra of the mixture of **8d** and different concentration of Cu^{2+} (Fig. 6). In the visible region, there is only one peak centered at 462 nm which is the same as the copper ion's (Cu^{2+}) absorption. It is obvious that the

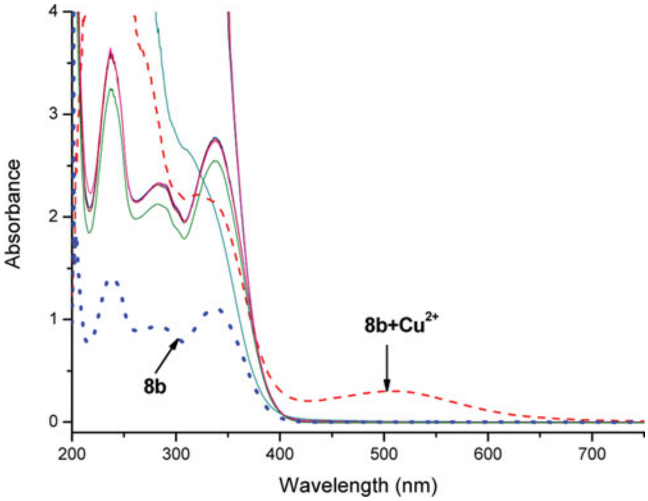


Figure 4. Absorption spectra of **8b** (5×10^{-4} mol/L) before (blue dot···) and after the addition of equal molar metal cations (red dash—: Cu^{2+}; solid line: Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, Mn^{2+}, Zn^{2+}, Pb^{2+}) in acetonitrile.

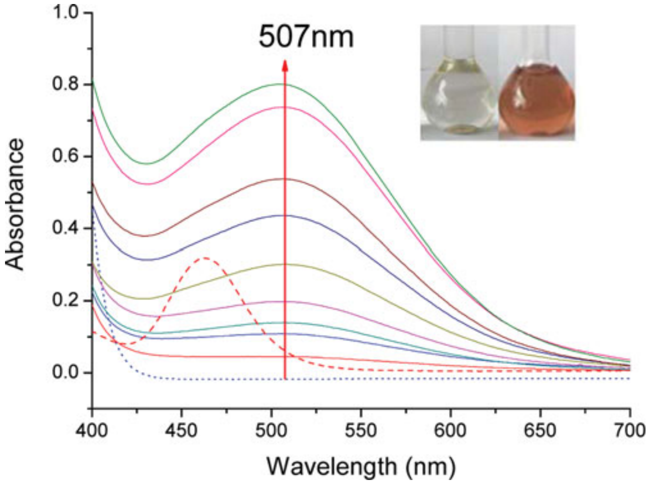


Figure 5. Absorption spectra of **8b** (5×10^{-4} mol/L, blue dot···), Cu^{2+} (5×10^{-4} mol/L, red dash—), and **8b** with different concentrate of Cu^{2+} (from bottom to top $[Cu^{2+}] = 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 2.5, 3.0$ folds of the concentration of **8b**)in acetonitrile.

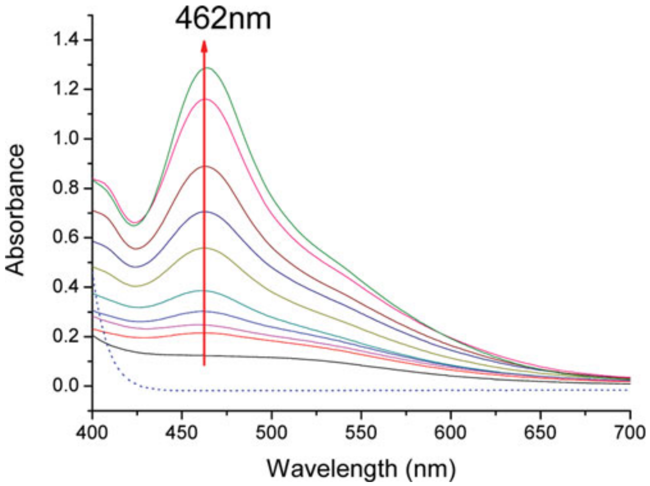


Figure 6. Absorption spectra of **8d** before (5×10^{-4} mol/L, blue dot···) and after the addition of different concentrate of Cu^{2+} (from bottom to top $[Cu^{2+}] = 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 2.5, 3.0$ folds of the concentration of **8d**)in acetonitrile.

different recognition ability between **8a–c** and **8d–e** is due to fluorine atoms. They, with strong electronegativity, pull partial electron from the whole conjugated system of the benzene ring and the pyridine ring linked by an imine bond. Then, there are no enough electrons for **8d–e** to interact with Cu^{2+}. As a result, no new peak appears in the absorption spectra of the mixture of **8d-e** and Cu^{2+}. Further studies on the mechanism are under way in our laboratory.

3. Conclusion

We have synthesized and characterized two series of new Schiff base compounds containing alkoxy or fluoroalkoxy as the terminal chains. Schiff bases **7**, with a pyridine nitrogen atom in 4-position, can form supramolecular liquid crystals with 4-n-alkoxybenzoic acids. However, Schiff bases **8**, with a pyridine nitrogen atom in 3-position, cannot form supramolecular liquid crystals for their intermolecular hydrogen bonds N···H-C. It is interesting that **8a–c**, tailed by the alkoxy, can recognize Cu^{2+} with a new absorption peak and a noticeable color change while **8d–e**, tailed by the fluoroalkoxy, cannot for the strong electron withdrawing effect of fluorine atoms in the terminal chains.

4. Experimental

4.1. *General considerations*

All the reagents were analytical grade, purchased from commercial sources and used as received. ^1H and ^{19}F NMR spectra were recorded on a 400 MHz nuclear magnetic resonance spectrometer. Chemical shifts were reported relative to Me_4Si for ^1H and ^{19}F NMR spectra (Avance III, 400 MHz NMR spectrometer, Bruker, Faellanden, Switzerland). The solvent was $CDCl_3$ unless otherwise specified. The DSC was recorded on a differential scanning calorimeter at a scan rate of 10°C min^{-1}. Optical micrographs were observed with a polarizing optical microscope (POM) (Nikon LINKAM-THMSE600). Elemental analyses were performed on an EXETER CE-440 Elemental Analyzer.

4.2. *General procedure for the preparation of 7a and 8a-e*

7a was synthesized by the same method as **7c–e** in our previous paper [24].

The synthetic method of ***8a–e*** *is also similar to that of* ***7a–e****.*

3-Pyridinecarboxaldehyde ***6*** *(1.9 mL, 0.02 mol) and acetic acid (2 mL) were added to a solution of* ***4*** *(0.02 mol) in ethanol (60 mL). The mixture was stirred at 85°C for about 12 h until no reactant appeared in the silicon TLC plate. After evaporation and dry in vacuo, pale-brown solid was obtained.*

4-methoxy-N-(pyridin-4-ylmethylene)benzenamine (7a): Yield 51.6%, mp 58–59°C. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 3.85 (s, 3H, $-OCH_3$), 6.95 (d, 2H, Ar-H), 7.30 (d, 2H, Ar-H), 7.78 (d, 2H, Pyridine-H), 8.49 (s, H, -CH=N), 8.74(d, 2H, Pyridine-H). HRMS ESI (*m/z*) Obsd 212.2510 Calcd 212.2510 ($C_{13}H_{12}N_2O$). Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20. Found C, 73.70; H, 5.45; N, 13.33%.

4-methoxy-N-(pyridin-3-ylmethylene)benzenamine (8a): Yield 50.3%, mp 61–62°C. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 3.73 (s, 3H, $-OCH_3$), 6.81 (d, 2H, Ar-H), 7.12 (d, 2H, Ar-H), 7.32 (q, 1H, Pyridine-H), 8.21 (d, 1H, Pyridine-H), 8.33 (s, H, -CH=N), 8.48 (d, 1H, Pyridine-H), 8.82(s, 1H, Pyridine-H). HRMS ESI (m/z) Obsd 212.2510 Calcd 212.2510 ($C_{13}H_{12}N_2O$). Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20. Found C, 73.49; H, 5.66; N, 13.41%.

4-ethoxy-*N*-(pyridin-3-ylmethylene)benzenamine (8b): Yield 48.7%, mp 65–66°C. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 1.23 (q, 3H, $-OCH_2\underline{CH_3}$), 3.87 (t, 2H, $-O\underline{CH_2}CH_3$), 6.74 (d, 2H, Ar-H), 7.08 (d, 2H, Ar-H), 7.34 (q, 1H, Pyridine-H), 8.23 (d, 1H, Pyridine-H), 8.36 (s, H, -CH=N), 8.50 (d, 1H, Pyridine-H), 8.85(s, 1H, Pyridine-H). HRMS ESI (*m/z*) Obsd 226.2780 Calcd 226.2780 ($C_{14}H_{14}N_2O$). Anal. Calcd for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38. Found C, 74.16; H, 6.20; N, 12.49%.

4-propoxy-*N*-(pyridin-3-ylmethylene)benzenamine (8c): Yield 45.6%, mp 55–56°C. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 1.05 (q, 3H, $-OCH_2CH_2\underline{CH_3}$), 1.82 (m, 2H, $-OCH_2\underline{CH_2}CH_3$), 3.96 (t, 2H, $-O\underline{CH_2}CH_2CH_3$), 6.96 (d, 2H, Ar-H), 7.29 (d, 2H, Ar-H), 7.58 (q, 1H, Pyridine-H), 8.48 (d, 1H, Pyridine-H), 8.57 (s, H, -CH=N), 8.70 (d, 1H, Pyridine-H), 9.07 (s, 1H, Pyridine-H). HRMS ESI (*m/z*) Obsd 240.3050 Calcd 240.3050 ($C_{15}H_{16}N_2O$). Anal. Calcd for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66 Found C, 75.11; H, 6.58; N, 11.61%.

***N*-(pyridin-3-ylmethylene)-4-(2,2,2-trifluoroethoxy)benzenamine (8d)**: Yield 49.6%, mp 93–94°C.^{1} H NMR (400 MHz, $CDCl_3$, δ ppm): 4.41 (q, 2H, -OC$\underline{H_2}$CF$_3$), 7.02 (d, 2H, Ar-H), 7.30 (d, 2H, Ar-H), 7.66 (q, 1H, Pyridine-H), 8.55 (d, 1H, Pyridine-H), 8.58 (s, H, -CH=N), 8.76 (d, 1H, Pyridine-H), 9.13(s, 1H, Pyridine-H). ^{19} F NMR ($CDCl_3$, δ ppm): −174.13 (s, 3F, –CH$_2$C$\underline{F_3}$). HRMS ESI (*m/z*) Obsd 280.2490 Calcd 280.2490 ($C_{14}H_{11}F_3N_2O$). Anal. Calcd for $C_{14}H_{11}F_3N_2O$: C, 60.00; H, 3.96; N, 10.00. Found C, 60.13; H, 3.85; N, 10.09%.

***N*-(pyridin-3-ylmethylene)-4-(2,2,3,3-tetrafluoropropoxy)benzenamine(8e)**: Yield 43.9%, mp 56–57°C.^{1} H NMR (400 MHz, $CDCl_3$, δ ppm): 4.38 (t, 2H, —-OC$\underline{H_2}$CF$_2$CF$_2$H), 6.09 (t, 1H, -OCH$_2$CF$_2$CF$_2$$\underline{H}$) 6.99 (d, 2H, Ar-H), 7.29 (d, 2H, Ar-H), 7.45 (q, 1H, Pyridine-H), 8.33 (d, 1H, Pyridine-H), 8.70 (s, H, -CH=N), 8.71 (d, 1H, Pyridine-H), 9.02(s, 1H, Pyridine-H). ^{19} F NMR ($CDCl_3$, δ ppm): −139.45 (d, 2F, -CH$_2$CF$_2$C$\underline{F_2}$H), −124.95 (t, 2F, -CH$_2$C$\underline{F_2}$CF$_2$H). HRMS ESI (*m/z*) Obsd 312.2670 Calcd 312.2670 ($C_{15}H_{12}F_4N_2O$). Anal. Calcd for $C_{15}H_{12}F_4N_2O$: C, 57.70; H, 3.87; N, 8.97. Found C, 57.85; H, 3.93; N, 8.79%.

Acknowledgments

The authors gratefully acknowledge the support of the Shandong excellent Young Scientist Research Award Fund (Project No. BS2011CL007).

References

[1] Da Silva, C. M., Da Silva, D. L., & Modolo, L. V. (2011). *J. Adv. Res.*, *2*, 1–8.
[2] Isse, A. A., Gennaro, A., & Vianello, E. (1997). *Electrochim. Acta.*, *13–14*, 2065–2071.
[3] Liu, X. H., Abser, M., Nurul, B., & Duncan, W. (1999). *J. Organomet. Chem.*, *577*, 150–152.
[4] Desai, S. B., Desai, P. B., & Desai, K. R. (2001). *Heterocycl. Commun.*, *7*, 83–90.
[5] Zhao, J. Z., Zhao, B., Xu, W. Q., Liu, J. Z., Wang, Z. M., *et al.* (2001). *Chem. J. Chin. Univ.*, *22*, 971–975 (in Chinese).
[6] Matsunaga, Y., Hikosaka, L., Hosono, K., Ikeda, N., Saka-Tani, T. K., *et al.* (2001). *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect.*, *A 369*, 103–116.
[7] Yeap, G. Y., Ha, S. T., Lim, P. L., Boey, P. L., Ito, M. M. *et al.* (2006). *Liq. Cryst.*, *33*, 205–211.
[8] Campillos, E., Marcos, M., Oriol, L. T., & Serrano, J. L. (1992). *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect.*, *A 215*, 127–135.
[9] Hu, P., Zhao, K. Q., Zhang, L. F., Lin, Z. R. & Xu, H. B. (1999). *Acta Chim. Sin.*, *57*, 931–936 (in Chinese).
[10] Shin, S. T., Choi, H., Lee, C. K., Kwon, S. S., Kim, T. S. *et al.* (2004). *Liq. Cryst.*, *31*, 935–940.
[11] Umadevi, S., & Sadashiva, B. K. (2005). *Liq. Cryst.*, *32*, 1233–1241.
[12] Richard, J. B., & Ken, K. (2011). *Liq. Cryst.*, *38*, 1415–1426.
[13] Ian, S. (2011). *Liq. Cryst.*, *38*, 1551–1561.
[14] Achalkumar, A. S., & Yelamaggad, C. V. (2012). *Tetrahedron Lett.*, *53*, 7108–7112.
[15] Shilpa, S., Sumyra, S., & Santanu, K. P. (2012). *Tetrahedron Lett.*, *53*, 6446–6450.
[16] Singh, P., Goel, R. L., & Singh, B. P. (1975). *J. Indian Chem. Soc.*, *52*, 958.
[17] Perry, B. F., Beezer, A. E., Miles, R. J., Smith, B. W., Miller, J. *et al.* (1988). *Microbois.*, *45*, 181.
[18] Elmali, A., Kabak, M., & Elerman, Y. (1999). *J. Mol. Struct.*, *477*, 151–158.
[19] Patel, P. R., Thaker, B. T., & Zele, S. (1999). *Indian J. Chem.*, *A38*, 563.
[20] Valcarcel, M., & Laque de Castro, M. D. (1994). *Flow-Throgh Biochemical Sensors*, Elsevier: Amsterdam.
[21] Spichiger-Keller, U. (1998). *Chemical Sesors and Biosensors for Medical and Biological Applications*, Wiley-VCH: Weinheim.
[22] Lawrence, J. F., & Frei, R. W. (1976). *Chemical Derivatization in Chromatography*, Elsevier: Amsterdam.
[23] Vigato, P. A., & Tamburini, S. (2004). *Coord. Chem. Rev.*, *248*, 1717–2128.
[24] Liu, Z. L., Zhang, J., Li, T. F., Yu, Z. N. & Zhang, S. X. (2013). *J. Fluorine Chem.*, *147*, 36–39.

[25] Liu, Z. L., Han, J. Z., Zhang, J., Yu, Z. N., Li, T. F. *et al.* (2013). *Monatshefte für Chemie – Chemical Monthly*, DOI:10.1007/s00706-013-1021-8.
[26] Fornasieri, G., Guittard, F., & Geribaldi, S. (2003). *Liq. Cryst.*, *30*, 663–669.
[27] Kato, T., Kihara, H., Uryu, T., Fujishima, A., & Frechet, J. M. (1992). *Macromolecules*, *25*, 6836–6841.
[28] Jariwala, C. P., & Griffin, A. C. (1994). *Polymer*, *35*, 4550–4554.
[29] Pourcain, C. B., & Griffin, A. C. (1995). *Macromolecules*, *28*, 4116–4121.