Chemical Physics Letters 614 (2014) 62–66

Contents lists available at ScienceDirect

Chemical Physics Letters

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

Fabrication of liquid crystal based sensor for detection of hydrazine vapours

Rajib Nandi[a,1], Sachin Kumar Singh[b,1], Hemant Kumar Singh[b],
Bachcha Singh[b,*], Ranjan K. Singh[a,*]

[a] Department of Physics, Banaras Hindu University, Varanasi 221005, India
[b] Department of Chemistry, Banaras Hindu University, Varanasi 221005, India

ARTICLE INFO

Article history:
Received 25 July 2014
In final form 6 September 2014
Available online 16 September 2014

ABSTRACT

A novel liquid crystal (LC) based sensor to detect trace level amount of hydrazine vapour has been developed. The LC 4′-pentyl-4-biphenylcarbonitrile (5CB) doped with 0.5 wt% 4-decyloxy benzaldehyde (DBA) shows dark to bright optical texture upon exposure of hydrazine vapours as revealed by polarizing optical microscopy under crossed polarizers. The hydrazine interacts with the doped DBA and form diimine compound which disrupt the orientation of aligned 5CB. The interaction between DBA and hydrazine has been also studied by Raman spectroscopy.

1. Introduction

Hydrazine ($H_2N—NH_2$) is widely used in many chemical and pharmaceutical industries as rocket propellant, reactant in military fuel cells, polymerization catalyst, blowing agent, reducing agent in organic reaction, oxygen scavenger in boiler feed water to inhibit corrosion and in photography [1,2]. It is a highly toxic and harmful environmental pollutant [3,4]. It is desirable to development a reliable, sensitive, economical and selective analytical method for the determination of trace level of hydrazine especially in environmental samples and industry. There are several effective techniques for the determination of trace level hydrazine such as titrimetric [5], chromatography–mass spectrometric [6], electrochemical methods [7], spectrophotometric methods [8], flow injection analysis [9], high-performance liquid chromatography (HPLC) [10] and potentiometry [11]. However most of these methods involve complex instrumentation, time consuming procedures and high cost.

Liquid crystals (LCs) have numerous potential applications mainly in the field of displays and electro-optics. In last one decade, another important application of LCs is emerging in the field of chemical and biological sensors [12–35]. The main advantage of LC based sensor is that the optical signal produced can be visualized easily with the naked eye without any need of complex instruments and electrical power. It has long been known that LCs can be used for real-time detection of hazard organic vapours [14,27–35]. The basic principle of LC based sensor for organic gas detection with high sensitivity is orientational transitions of LC thin films supported on chemically functionalized surfaces upon exposure of gas. Shah and Abbott et al. [14,27] reported a LC sensor for hexylamine gas by showing homeotropic to planar (tilted) transition of 4′-pentyl-4-biphenylcarbonitrile (5CB) molecules supported on a carboxylic acid decorated surface when it was exposed to hexylamine vapour. In this system, the reaction between hexylamine and carboxylic acid groups breaks the hydrogen bonds between 5CB and carboxylic acid group that results in the in-plane orientational transition of 5CB. Bi et al. [30] developed a LC based sensor for vapourous glutaraldehyde based on orientational transition of 5CB due to the reaction between glutaraldehyde and amine decorated on surface. The same group in another study developed a LC sensor for butylamine gas in air [32]. In this system lauric aldehyde doped 5CB shows bright to dark optical response to butylamine vapour based on reaction between aldehyde and amine. Xu et al. [34] developed a LC sensor for detecting vapour thiols based on the orientational transitions of 5CB driven by the binding of thiol molecules to immobilize copper ion. Optical sensors based on cholesteric LCs for the detection of amines were also reported [36,37].

In this letter we are reporting a novel LC-based sensor to detect hydrazine vapour by studying optical response of 5CB doped with 4-decyloxy benzaldehyde (DBA). The hydrazine vapour interacts with the DBA doped in 5CB to form diimine compound that is observed as change in texture of 5CB from dark to bright by polarizing optical microscopy (POM). We further concentrated to

---

* Corresponding author.
E-mail addresses: bsinghbhu@rediffmail.com (B. Singh), ranjanksingh65@rediffmail.com (R.K. Singh).
[1] Main workers with equal contribution.

http://dx.doi.org/10.1016/j.cplett.2014.09.020
0009-2614/

understand the interaction between DBA and hydrazine by Raman spectroscopy, and how it causes orientational transition in 5CB. This study provides a principle for developing a real-time simple, fast and inexpensive chemical sensor for hazardous chemical vapours like hydrazine.

2. Experimental

2.1. Materials

Glass microslides were obtained from Blue Star, Mumbai, India. Nematic liquid crystal 5CB, dimethyloctadecyl[3-(trimethoxysilyl)-propyl] ammonium chloride (DMOAP), 4-hydroxy benzaldehyde and hydrazine monohydrate were purchased from Sigma–Aldrich (India) and were used as received. Transmission electron microscope grids of copper (100 square mesh) were purchased from Thorlabs GMBH, Munich, Germany. All solvents used in this study were purchased from Merck chemicals and are HPLC grade.

2.2. Synthesis of 4-decyloxy benzaldehyde (DBA)

4-Decyloxy benzaldehyde (DBA) was prepared by reaction of 4-hydroxy benzaldehyde with decyl bromide in the presence of mild base (potassium carbonate) in refluxing 2-butanone for 24 h. The residue was filtered off and the solvent was removed from the filtrate under reduced pressure. The compound was obtained as yellow oil after purification by column chromatography. The compound was fully characterized by various spectroscopic techniques, and satisfactory analytical data were obtained (supplementary information).

2.3. Preparation of DMOAP-coated glass slides

At first, glass slides were immersed in a 5% (v/v) Decon-90 (a commercially available detergent) solution for 2 h. Then, they were rinsed with copious amounts of deionized water and cleaned in an ultrasonic bath twice, each time for 15 min. Subsequently, the slides were etched with a 4.0 M sodium hydroxide solution for 30 min and rinsed thoroughly with deionized water, ethanol and methanol and then dried under a stream of nitrogen. The cleaned substrates were then stored overnight in an oven at 120 °C. The glass slides were functionalized with DMOAP by dipping the cleaned glass slides in 0.5% (v/v) DMOAP solution at room temperature for 20 min, followed by drying in a vacuum chamber according to the reported procedures [23]. Copper grids (100 square meshes, Electron Microscopy Sciences, Hatfield, PA) were cleaned sequentially in ethanol and methanol, dried under nitrogen, and heated at 100 °C for 24 h.

2.4. Preparation of DBA doped 5CB and fabrication of LC sensors

The nematic LC 5CB doped with different concentrations of DBA was prepared by diluting 10 wt% of DBA doped 5CB with pure 5CB at different ratios. Clean glass slide was cut into small squares (1.0 cm × 1.0 cm each). Then, an empty copper grid was placed on the top of the slide and approximately 0.5 μL of DBA doped 5CB was dispensed into the copper grid. The excess mixture was removed by touching the grid surface with a capillary tube. The sensor thus prepared was then placed inside a small laboratory-made chamber linked to the gas generator.

2.5. Preparation of hydrazine vapours from its solutions

To prepare hydrazine vapour, 0.5 μL hydrazine in aqueous solution was taken inside a 100 mL syringe. To avoid leakage the opening of the syringe was sealed with a Teflon® plug. The syringe was kept in an oven at 125 °C to evaporate hydrazine into vapour. The syringe was cooled down to room temperature (28 °C) before exposing to LC sensors. The vapour concentration of hydrazine was controlled by changing the hydrazine concentration in the solution [34].

2.6. Synthesis of diimine product

N,*N*′-bis(4-decyloxybenzylidene)azine: The diimine product was prepared by shaking together absolute ethanolic solution of 4-decyloxy benzaldehyde (DBA) (2 equiv.) and hydrazine monohydrate (1 equiv.) for 10 min and leaving solution for 30 min in a flask closed with guard tube. The microcrystalline pale yellow solid was filtered off by suction, thoroughly washed with cold ethanol and recrystallized from absolute ethanol and dried at room temperature.

A polarized light microscope (HT 30.01 NTT 268 Lomo) was used to capture image of optical textures of nematic 5CB. The LC samples were placed on a circular stage between two crossed polarizers. All images were obtained using a 4× objective lens between crossed polarizers. Images of the optical appearance of each liquid crystal cell were captured with a digital camera (DS-2Mv, Nikon, Tokyo, Japan) that was attached with the polarized light microscope. All images were captured with an exposure time of 40 ms at a resolution of 1600 × 1200 pixels and a shutter speed of 1/10 s. Textures were quantified by interpreting them to a grey scale of intensities, and their luminosities were analyzed using image processing software Adobe Photoshop [38]. Raman spectra of all samples were recorded on a micro-Raman setup from Renishaw, UK equipped with a grating of 2400 lines/mm and a peltier cooled charge coupled device (CCD). The excitation source was 514.5 nm line of Ar^+ laser. The spectral resolution of the spectrometer with 50 μm slit opening was $\sim 1\,cm^{-1}$. Other details of spectrometer were given elsewhere [39].

3. Results and discussions

Copper grids placed on DMOAP coated glass slides were filled with pure 5CB and 0.5 wt% DBA doped 5CB to study optical appearance by POM. The optical micrographs are shown in Fig. 1a–b. Fig. 1(a) shows a dark texture, signifying a homeotropic alignment of 5CB molecules on DMOAP coated glass slide. In this configuration LC has an air–LC interface and a LC–DMOAP coated glass slide interface. The dark appearance of LC is caused due to perpendicular orientation of 5CB molecules at both air and DMOAP coated slide interfaces as well as throughout the LC film due to the hydrophobic interactions between DMOAP and LCs [40]. When the LC film is placed between the crossed polarizer of POM, the director of the LC is parallel to the direction of incident light and therefore incident light experiences only one refractive index. The plane of polarization of the light does not change on passing through the LC. Therefore it appears dark in crossed polarizer [40]. On doping with 0.5 wt% DBA in 5CB there is no effect on the alignment of 5CB molecules as revealed by the dark texture as shown in Fig. 1(b) and also there is no significant change in melting and clearing points. On increasing the doping of DBA in 5CB the LC phase range reduces. We have carried out all experiments with 0.5 wt% DBA doped 5CB.

In the next step we exposed the grid containing 5CB doped with DBA by hydrazine vapour at different concentrations. All textures were taken after exposure of hydrazine vapour after 30 min. Fig. 1(c) shows that upon exposure of 500 ppm of hydrazine vapour on LC grid a fully bright texture is observed. On reducing the concentration of hydrazine vapour to 300 ppm, 200 ppm and 100 ppm, brightness of LC textures are reduced as shown in Fig. 1d–f. On further lowering the concentration of hydrazine vapour to 50 and

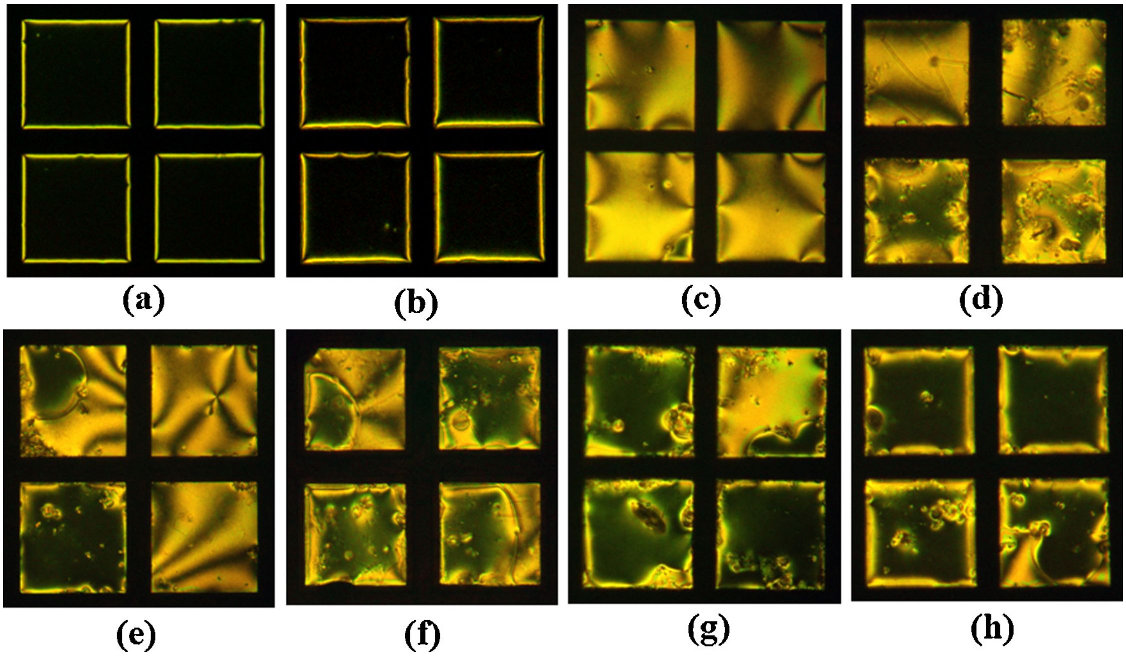

Fig. 1. Polarizing optical images of (a) pure 5CB and (b) 5CB doped with 0.5 wt% DBA. Optical images of 5CB doped with 0.5 wt% DBA when they were exposed to hydrazine vapours at concentrations (c) 500 ppm, (d) 300 ppm, (e) 200 ppm, (f) 100 ppm, (g) 50 ppm and (h) 30 ppm. All images were taken on stabilization after 30 min at temperature 28 °C.

30 ppm, the area and intensity of bright texture are decreased. The luminosity of 5CB doped DBA upon exposure of hydrazine vapour at different concentration has been calculated considering the luminance of the image of the 5CB doped with 0.5 wt% DBA without hydrazine vapour as minimum (0%) and the luminance of the same upon exposure by 500 ppm hydrazine vapours as maximum (100%) as shown in Fig. 2. Based on thrice repeated measurements the mean value of luminosity and standard error at different concentration of hydrazine vapours are reported in Fig. 2. The lowest detected limit of hydrazine concentration for this sensor is 30 ppm. The bright optical appearance of 5CB indicates either planar or tilted orientation of 5CB molecules at LC–air interface. In this condition the tilt angle of 5CB relative to the surface normal varies continuously (through splay and bend deformations) from 0° at the LC–DMOAP interface to 90° at the air–LC interface. The birefringence of liquid crystal rotates the polarization of the incident light and produces in general elliptically polarized light, resulting in a bright optical appearance between two crossed polarizers. Thus, we can conclude that these bright textures in Fig. 1c–h were due to exposure of hydrazine vapour. From these experiments, we can identify the presence of hydrazine.

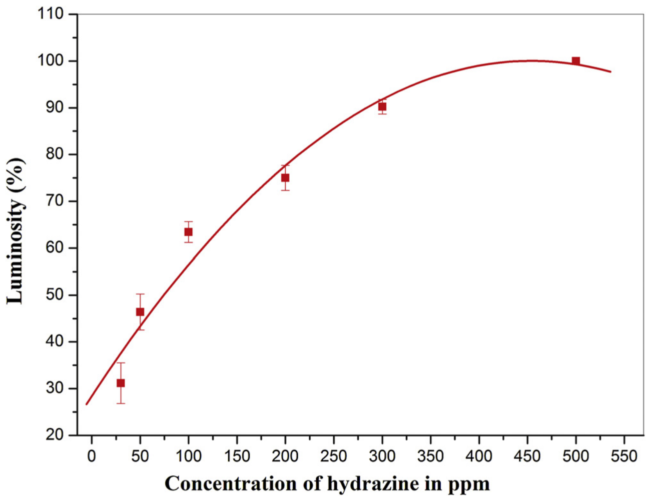

Fig. 2. Luminosity (L) of the optical images of 0.5 wt% DBA doped 5CB upon exposure of hydrazine vapours at different concentrations calculated using the equation $L\,(\%) = (S - S_{\min}/S_{\max} - S_{\min}) \times 100$, where S is the raw luminance of each image, $S_{\min}$ is the luminance of the image of the 5CB doped with 0.5 wt% DBA and $S_{\max}$ is the luminance of images of 5CB doped with 0.5 wt% DBA and exposed to 500 ppm hydrazine vapours. In every set $S_{\max}$ was taken as 100%, therefore we do not report error bar for this data point.

After exposure of hydrazine vapours the bright optical texture of LC cell was caused by the disruption of 5CB due to reaction between DBA and hydrazine. The LC sensor mechanism is illustrated in Fig. 3. The reaction between DBA and hydrazine is very fast and sensitive, which leads to formation of diimine compound (*N*,*N*′-bis(4-decyloxybenzylidene)azine). It is worth noting that hydrazine is a symmetrical molecule with two amine groups. Therefore, both the amine groups have equal reactivity towards aldehydes and the reaction always favours the formation of diimine products at normal condition of temperature. The calculated dipole moment of optimized structure of DBA molecule is 5.00 D and that of diimine molecule is almost zero (supplementary information). The 5CB doped with DBA gives the dark texture because DBA molecule has a significant dipole moment to align it perpendicularly to the surface along with the 5CB molecules. But the diimine molecule having long hydrocarbon chains at both terminals has negligible dipole moment, enough to disrupt the alignment of 5CB molecule at LC/air surface. The change in surface energy after exposure to hydrazine leads to parallel/tilt alignment of 5CB orientation. In this process, the main factors that are responsible to detect the hydrazine vapours are; the reaction kinetics between aldehyde and hydrazine, and the reorientations of 5CB molecules. To understand further details of the reaction between DBA and hydrazine, we have performed Raman spectroscopic measurements. The diimine product was also synthesized separately to identify the Raman marker bands of the product formed due to interaction of hydrazine vapour with doped DBA when exposed to the LC sensors. The Raman spectra of pure 5CB, DBA doped 5CB and DBA doped 5CB after exposure of hydrazine along with the prepared pure diimine doped

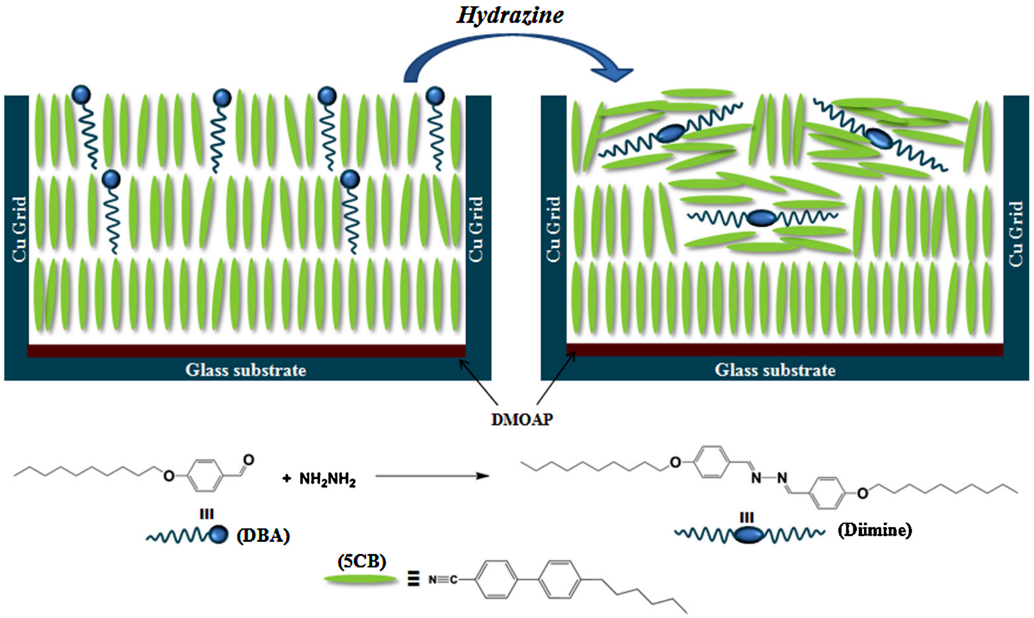

Fig. 3. Schematic illustration of orientational transitions of the 5CB molecules doped with DBA after exposure of hydrazine vapour into the optical cell from homeotropic orientation to planar/tilted orientation.

(0.25 wt%) in 5CB are shown in Fig. 4. In Raman spectrum of DBA doped 5CB the band at 1686 cm^{-1} is due to the stretching vibration of C=O group associated with DBA molecule. Complete disappearance of the 1686 cm^{-1} band and appearance of a new weak band at 1548 cm^{-1} are observed in the DBA doped 5CB on exposure with hydrazine (Fig. 4). The absence of C=O band (~1686 cm^{-1}) in doped 5CB after exposure of hydrazine indicates condensation of aldehyde to hydrazine and therefore diimine product formation (Fig. 3). The Raman spectrum of pure diimine (0.25 wt%) doped in 5CB is similar as the spectrum of the DBA doped 5CB on exposure with hydrazine. In both spectrums a new band at 1548 cm^{-1} is observed which is due the diimine product as a result of reaction between DBA and hydrazine. It is also to be noted that the intensity of the 1548 cm^{-1} band for pure diimine (0.25 wt%) doped in 5CB is greater by a very small amount than the spectrum of the DBA doped 5CB on exposure with hydrazine because the doped percent of DBA is only 0.5% in 5CB and the yield of diimine derivatives are ~70–80% at room temperature conditions. Therefore very low amount (≤0.25%) of diimine product is formed during hydrazine sensing experiments.

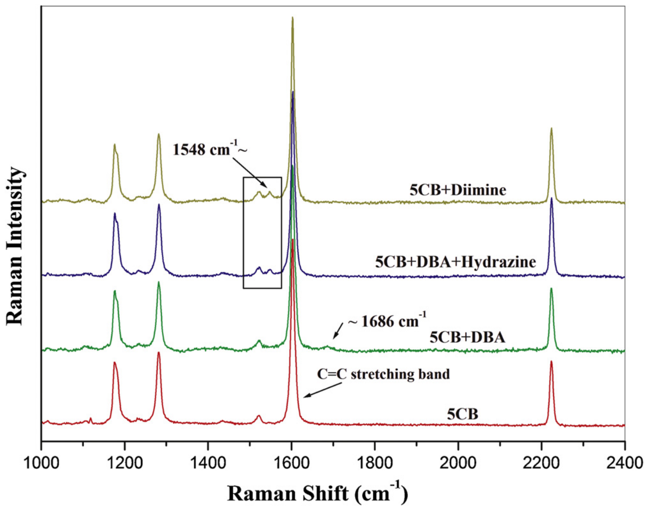

Fig. 4. The Raman spectra of pure 5CB, 5CB doped with DBA, 5CB doped with DBA after exposure of hydrazine vapours (500 ppm) and externally prepared pure diimine product doped (0.25 wt%) in 5CB.

We have exposed decylamine vapours and secondary diethylamine on 5CB doped with 0.5 wt% DBA to study selectiveness of the sensor. From this study we have found no significant optical appearance at concentration 1000 ppm under crossed polarizers as shown in Fig. S2 (supplementary information). Upon exposure of decylamine and diethylamine vapours on LC cell, there is a possibility of formation of imine products with the reaction of DBA doped in 5CB. These imine molecules have a significant dipole moment and therefore have less capability to disturb the alignment of 5CB molecules.

4. Conclusions

First time, a LC based sensor is developed for detecting hydrazine vapours with high specificity. The principle behind the sensor is based on the fact that DBA doping in 5CB react with hydrazine to form diimine compound which disturb the orientation of uniformly aligned 5CB molecules and consequently dark to bright optical response are observed under crossed polarizers in POM. This is a convenient method of detecting hydrazine vapours in air and also distinguishing from other volatile amine compounds and the results can be observed with the naked eye without using additional instrumentation. The lowest detection limit for this sensor is ~30 ppm and further work will be done to achieve more sensitivity.

Acknowledgements

RN is grateful to the University Grants Commission (UGC), New Delhi, India for providing fellowship under Research Fellowship in Sciences for Meritorious Students. SKS, HS and RKS are grateful to Council of Scientific and Industrial Research (CSIR), New Delhi, India, for financial support. SKS and RKS are grateful to DFG, Germany. BS is grateful to DST, India (Project No. SR/S1/IC-08/2012) for providing financial assistance.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2014.09.020.

References

[1] E.W. Schmidt, Hydrazine and Its Derivatives, 2nd ed., John Wiley & Sons, New York, 2001.
[2] J.L. Fan, et al., Chem. Commun. 48 (2012) 8117.
[3] A. Umar, M.M. Rahman, S.H. Kim, Y.B. Hahn, Chem. Commun. 2 (2008) 166.
[4] S. Ameen, M.S. Akhtar, H.S. Shin, Talanta 100 (2012) 377.
[5] Z.K. He, B. Fuhrmann, U. Spohn, Anal. Chim. Acta 83 (2000) 409.
[6] M. Sun, L. Bai, D.Q. Liu, J. Pharm. Biomed. Anal. 49 (2009) 529.
[7] Y.Y. Tang, C.L. Kao, P.Y. Chen, Anal. Chim. Acta 32 (2012) 711.
[8] F. Dias, A.S. Olojola, B. Jaselskis, Talanta 26 (1979) 47.
[9] S. Ikeda, H. Satake, Y. Kohri, Chem. Lett. 13 (1984) 873.
[10] C.M. Morenoa, T. Stadler, A.A. Silva, L.C.A. Barbosa, M.E.L.R. Queiroz, Talanta 89 (2012) 369.
[11] M.A. Koupparis, T.P. Hadjiioannou, Talanta 25 (1978) 477.
[12] V.K. Gupta, J.J. Skaife, T.B. Dubrovsky, N.L. Abbott, Science 279 (1998) 2077.
[13] S.R. Kim, R.R. Shah, N.L. Abbott, Anal. Chem. 72 (2000) 4646.
[14] R.R. Shah, N.L. Abbott, Science 293 (2001) 1296.
[15] J.M. Brake, M.K. Daschner, Y.Y. Luk, N.L. Abbott, Science 302 (2003) 2094.
[16] Y.Y. Luk, N.L. Abbott, Science 301 (2003) 623.
[17] N.A. Lockwood, J.C. Mohr, L. Ji, C.J. Murphy, S.R. Palecek, J.J. de Pablo, N.L. Abbott, Adv. Funct. Mater. 16 (2006) 618.
[18] C.Y. Xue, K.L. Yang, Langmuir 24 (2008) 563.
[19] A.D. Price, D.K. Schwartz, J. Am. Chem. Soc. 130 (2008) 8188;
D. Hartono, W.J. Qin, K.L. Yang, L.Y. Yung, Biomaterials 30 (2009) 843.
[20] D. Hartono, X.Y. Bi, K.L. Yang, L.Y. Yung, Adv. Funct. Mater. 18 (2008) 2938.
[21] X.Y. Bi, D. Hartono, K.L. Yang, Adv. Funct. Mater. 19 (2009) 3760.
[22] Z.Q. Yang, J.K. Gupta, K. Kishimoto, Y. Shoji, T. Kato, N.L. Abbott, Adv. Funct. Mater. 20 (2010) 2098.
[23] V.J. Alin˜o, K.-L. Yang, Analyst 136 (2011) 3307.
[24] Q.-Z. Hu, C.-H. Jang, J. Biotechnol. 157 (2012) 223.
[25] R.J. Carlton, J.T. Hunter, D.S. Miller, R. Abbasi, P.C. Mushenheim, L.N. Tan, N.L. Abbott, Liq. Cryst. Rev. 1 (2013) 29.
[26] M. Tyagi, A. Chandran, T. Joshi, J. Prakash, V.V. Agrawal, A.M. Biradar, Appl. Phys. Lett. 104 (2014) 154104.
[27] R.R. Shah, N.L. Abbott, Langmuir 19 (2003) 275.
[28] K.L. Yang, K. Cadwell, N.L. Abbott, J. Phys. Chem. B 108 (2004) 20180.
[29] K.D. Cadwell, N.A. Lockwood, B.A. Nellis, M.E. Alf, C.R. Willis, N.L. Abbott, Sens. Actuators B 128 (2007) 91.
[30] X. Bi, K.-L. Yang, Sens. Actuators B 134 (2008) 432.
[31] S.S. Sridharamurthy, K.D. Cadwell, N.L. Abbott, H. Jiang, Smart Mater. Struct. 17 (2008) 012001.
[32] X. Ding, K.-L. Yang, Sens. Actuators B 173 (2012) 607.
[33] M.L. Bungabong, P.B. Ong, K.L. Yang, Sens. Actuators B 148 (2010) 420.
[34] H. Xu, X.Y. Bi, X.M. Ngo, K.L. Yang, Analyst 134 (2009) 911.
[35] A. Sen, K.A. Kupcho, B.A. Grinwald, H.J.V. Treeck, B.R. Acharya, Sens. Actuators B 178 (2013) 222.
[36] N. Kirchner, L. Zedler, T.G. Mayerhofer, G.J. Mohr, Chem. Commun. (2006) 1512.
[37] L. Sutarlie, H. Qin, K.L. Yang, Analyst 135 (2010) 1691.
[38] J.J. Skaife, N.L. Abbott, Langmuir 16 (2000) 3529.
[39] R. Nandi, H.K. Singh, S.K. Singh, B. Singh, R.K. Singh, Liq. Cryst. 40 (2013) 884.
[40] D.S. Miller, R.J. Carlton, P.C. Mushenheim, N.L. Abbott, Langmuir 29 (2013) 3154.