



Journal of Nanoscience and Nanotechnology Vol. 18, 3299–3305, 2018 www.aspbs.com/jnn

Thermally Reversible Fluorans: Synthesis, Thermochromic Properties and Real Time Application

Ick Jin Kim[†], Ramalingam Manivannan[†], and Young-A Son^{*}

Department of Advanced Organic Materials Engineering, Chungnam National University, 220 Gung-Dong, Yuseong-gu, Daejeon 305-764, South Korea

In the present study, two fluoran molecules (**TH1** and **TH2**) have been synthesized, and their reversible thermochromic properties have been investigated. This work demonstrates the thermochromic reversibility of the fluoran. Furthermore, the three-component mixtures that comprising fluorans (**TH1/TH2**), bisphenol-A (color developer), and methyl stearate a low melting solvent were used to examine the thermochromic behavior with sturdy heating and cooling rates and the thermochromic properties of the fluorans were detailed using UV-Vis, reflectance and FT-IR spectroscopic techniques. Finally, test strip similar to pH paper and acrylic fiber a versatile material used as thermal indicators also been successfully made from these two fluoran derivatives.

Keywords: Fluorans, Thermochromic, Reversible, Thermal Indicator, Acrylic Fiber.

1. INTRODUCTION

IP: 94.45.153.233 On: Thu, 14 Jun 2018 07:01:50

Development of thermochromic materials has attracted much attention in recent years due its significant changes in their optical properties in response to external stimulation, giving them several prospective applications such as sensors, thermal indicators, memory storage devices, security inks, dyes for solar cell application and other luminescent switches.¹⁻⁷ Many leuco dyes (fluorans and crystal violet lactone), spiropyrans, inorganic complexes and conjugated polymers,⁸⁻¹⁴ have been researched. The (thio)xanthene unit¹⁵ forms the core of many functional dyes including rhodamines,¹⁶ rosamines,¹⁷ thiofluoresceins¹⁸ and fluorans¹⁹ were known to act as thermochromic materials. Among these, fluorans have been explored with a greater extent on their commercial applications in recent years. In addition, the dyes, which have been derived from a xanthene core, displays electrochromic property when applied an appropriate potential.^{20, 21}

A large number of fluoran {spiro furan, xanthene-3-one} compounds can act as thermochromic materials through thermochromic formulations incorporate three component systems, includes a fluoran (color former) and a Bronsted acid (color developer) in a low melting solvent, such as methyl stearate.^{19, 22, 23} When the three component mixtures outlined above are heated together in the

Copyright: American scontrolled proportional ratios, the color formers and developers are dissolved in the low melting co-solvent and then the solution changes its color when it is cooled. Thus, the stimulation of the thermochromic effects is mainly dependent on the design of a system with warming and cooling. These types of functional dyes in the solid state undergo a ring-opening reaction and giving rise to a striking color change when it in comes in contact with acid and these changes are reversible with the change in temperature (Scheme 1).^{24–26} Since these systems involve changes in the phase between colored solid and colorless liquid phase, then the thermochromic properties do not affected much when the ratio of the components maintained for microencapsulation.²⁷

Fluorans have wide spread utility as it is used as copying material, in pressure and temperature-sensitive recording materials.^{28–30} In general, fluoran dyes are usually designed in such a way that contains a N,N-dialkylamino group at the meta position of the xanthene ring. Shen Meiqin and coworkers⁸ listed the thermochromic properties of fluoran red and black dyes like the above mentioned frame work. Hojo et al. have developed fluoran moiety and investigated the reversible properties of corresponding fluorans with acid developers together with Mg²⁺ and macrocyclic polyamine.³¹ Intrinsic thermochromic properties, the fluoran itself possess thermochromic characteristics or thermochromic packings added into the polymer matrix.^{32, 33} Bis fluoran derivatives has also been reported where the

^{*}Author to whom correspondence should be addressed.

[†]These two authors contributed equally to this work.

J. Nanosci. Nanotechnol. 2018, Vol. 18, No. 5



Scheme 1. Thermochromic response of fluorans-bisphenol A system.

thermochromic behavior of those fluoran were not discussed in detail.³⁴ In this present study, we synthesized two fluoran moieties with a variation in N,N-dialkylamino (methyl/ethyl) group at the *meta* position of the xanthene oxygen Likewise, we discuss the thermochromic properties of the fluorans (**TH1** and **TH2**) with respect to electronic effects in solid state.

2. EXPERIMENTAL SECTION

2.1. Equipment and Reagents

All reagents were purchased from either Aldrich or TCI chemicals and were used as received. NMR spectra were recorded on a Bruker Avance 300 MHz instrument (¹H NMR 300 MHz, ¹³C NMR 150 MHz) with tetramethylsilane as an internal reference. All new compounds were homogeneous by TLC performed on either Merck TLC aluminum or silica gel 60 F_{254} sheets using a range of eluent systems with differing polarities. Flash column chromatography was performed on chromatography silica gel (230–400 mesh). Solid state UV-Vis and reflectance spectra of the new thermochromic compounds in methyl stearate and bisphenol-A were performed on a Shimadzu Solid Spec-3700. FT-IR spectra were recorded using a Perkin Elmer Spectrum One spectrophotometer equipped

with a diamond probe ATR attachment (neat sample). ESImass spectra were recorded using a Thermo Scientific LTQ Orbitrap XL Fourier transform mass spectrometer. The key intermediates and fluorans (**TH1** and **TH2**) for the present study were prepared according to the literature procedures (Scheme 2).³⁵ For practical application Whatman grade 42 filter paper were used and dip coating method was adopted to apply **TH1/TH2** in filter paper/Acrylic fiber.

2.2. General Method for the Preparation of Intermediates (1,2)

A solution of 3-dimethylamino phenol or 3-diethylamino phenol (1.0 mmol) and phthalic anhydride (1.0 mmol) in toluene was refluxed under N₂ for 5 h and then allowed to stir at 60 °C for 1 h. Then 35% aqueous NaOH was slowly added to the reaction mixture at 60 °C and heated at 90 °C for 12 h. The resulting mixture was poured into distilled water, acidified with conc. HCl at 0 °C, and allowed to stir at room temperature for 2 h. The suspension was then filtered and was then dried to afford a pink solid. The obtained crude material was then purified by column chromatography with gradient enhancement of ethylacetate in petroleum ether. The products 1 and 2 were characterized using ¹H NMR, ¹³C NMR and ESI mass spectral techniques. The results obtained are;

2.2.1. 2-(4-(dimethylamino)-2-hydroxybenzoyl)Benzoic Acid (1)

¹H NMR (CDCl₃, 300 MHz), δ (ppm): 2.94 (*s*, 6H), 5.98 (*m*, 1H), 6.07 (*d*, 1H, J = 1.8 Hz), 6.8 (*d*, 1H, J = 6 Hz), 7.26 (*d*, 1H, J = 7.2 Hz), 7.44 (*t*, 1H, J = 7.2 Hz), 7.53 (*t*, 1H, J = 7.2 Hz), 8.0 (*d*, 1H, J = 7.8 Hz), 12.43 (*s*, 1H) (Fig. S1).

¹³C NMR (CDCl₃, 150 MHz) δ (ppm): 39.95, 97.76, 104.03, 110.34, 127.78, 127.98, 129.20, 131.06, 132.77, 134.32, 141.18, 155.98, 165.13, 170.23, 198.75 (Fig. S2).



Scheme 2. Synthetic route for preparation of fluorans TH1 and TH2.

ESI-MS (m/z) calcd. 285.1, found 283.8 $(M - H^+)$ (Fig. S3).

2.2.2. 2-(4-(diethylamino)-2-hydroxybenzoyl)Benzoic Acid (2)

¹H NMR (CDCl₃, 300 MHz), δ (ppm): 1.09 (t, 6H, J = 14.1 Hz), 3.275 (m, 4H), 5.95 (dd, 1H, J = 9, 9.3 Hz), 6.07 (d, 1H, J = 2.4 Hz), 6.79 (d, 1H, J = 9.3 Hz), 7.28 (d, 1H, J = 7.5 Hz), 7.44 (t, 1H, J = 14.7 Hz), 7.53 (t, 1H, J = 14.7 Hz), 8.02 (d, 1H, J = 7.8 Hz), 12.46 (s, 1H) (Fig. S4).

¹³C NMR (CDCl₃, 150 MHz) δ (ppm): 11.61, 43.69, 96.13, 102.77, 108.93, 127.15, 128.21, 130.11, 131.59, 133.65, 139.99, 153.05, 164.59, 167.22, 197.20 (Fig. S5). ESI-MS (m/z) calcd. 313.1, found 313.9 ($M + H^+$) (Fig. S6).

2.3. General Method for the Preparation of TH1 and TH2

A solution of 2-(4-(dimethylamino)-2-hydroxybenzoyl) benzoic acid (1) or 2-(4-(diethylamino)-2-hydroxybenzoyl)benzoic acid (2) (1 mmol) and 4-bromophenol (1 mmol) in methanesulfonic acid (5 mL) was heated up to 60–90 °C for 2 h. Then the reaction mixture was cooled to room temperature and 25% of NaOH (20 mL) solution was slowly added into the reaction mixture. The resulting alkaline mixture was stirred at room temperature for 1 h. The formed solid was filtered through the filter paper and the obtained crude material was purified by column chromatography with gradient enhancement of ethylacetate in petroleum ether. The products TH1 and TH2 were characterized using ¹H NMR, ¹³C NMR and ESI mass spectral techniques. The results obtained are;

2.3.1. 2'-Bromo-6'-(dimethylamino)-3H-Spiro[isobenzofuran-1,9'-xanthen]-3-One (TH1)

¹H NMR (CDCl₃, 600 MHz), (ppm): 2.90 (*s*, 6H), 6.32 (dd, 1H, J = 8.4, 9 Hz), 6.40 (*d*, 1H, J = 2.4 Hz), 6.51 (*d*, 1H, J = 9 Hz), 6.79 (*d*, 1H, J = 2.4 Hz), 7.06 (*m*, 2H), 7.36 (dd, 1H, J = 9, 9 Hz), 7.53 (*m*, 2H), 7.94 (*d*, 1H, J = 7.8 Hz) (Fig. S7).

¹³C NMR (CDCl₃, 150 MHz) δ (ppm): 39.15, 81.95, 97.38, 104.43, 108.15, 117.94, 120.41, 122.89, 124.11, 125.66, 127.56, 128.83, 129.50, 132.35, 134.09, 149.72, 151.13, 151.21, 151.80, 168.29 (Fig. S8).

ESI-MS (m/z) calcd. 421.03, found 422.1 ($M + H^+$) (Fig. S9).

2.3.2. 2'-Bromo-6'-(diethylamino)-3H-Spiro [isobenzofnnuran-1,9'-xanthen]-3-One (TH2)

¹H NMR (CDCl₃, 600 MHz), (ppm): 1.08 (t, 6H, J = 7.2 Hz), 3.26 (m, 4H), 6.27 (dd, 1H, J = 9, 9 Hz), 6.36 (d, 1H, J = 2.4 Hz), 6.47 (d, 1H, J = 9 Hz), 6.78 (d, 1H, J = 2.4 Hz), 7.06 (d, 1H, J = 8.4 Hz), 7.1 (d, 1H, J = 7.8 Hz), 7.36 (dd, 1H, J = 8.4, 8.4 Hz), 7.53 (t, 1H, J

J. Nanosci. Nanotechnol. 18, 3299-3305, 2018



Figure 1. The color of TH1 and TH2 in (A) acetonitrile and (B) acetic acid.

J = 7.8 Hz), 7.61 (t, 1H, J = 15 Hz), 7.94 (d, 1H, J = 7.8 Hz) (Fig. S10).

¹³C NMR (CDCl₃, 150 MHz) δ (ppm): 11.46, 43.47, 82.18, 96.51, 103.44, 107.64, 114.21, 117.90, 120.49, 122.97, 124.08, 125.85, 127.78, 128.79, 129.52, 132.30, 134.03, 148.73, 149.81, 151.50, 151.67, 168.29 (Fig. S11).

ESI-MS (m/z) calcd. 449.06, found 450.1 $(M + H^+)$ (Fig. S12).

3. RESULTS AND DISCUSSION

3.1. Color Properties in Different Solvents

With the instantaneous addition of fluorans **TH1** and **TH2** in aprotic solvents such as toluene, benzene, tetrahydrofuran, and acetonitrile, no obvious color change has been observed (Figs. 1(A) and S13). This signifies that in aprotic solvents, these compounds substantially can be found to be in colorless lactone form. Meanwhile, in an acetic acid solution, the color of the solution converted to deep orange red color (Fig. 1(B)) is mainly due to the formation of zwitterions of the fluoran moiety.

3.2. UV-Vis Spectral Studies

To determine the electronic change and to confirm the mechanism of the fluoran ring, the UV-Vis spectral study of TH1 and TH2 were recorded in acetonitrile as well as with the addition of small amount of acetic acid to the same. The observed peaks at approximately 300-330 nm in the absorbance spectra of TH1 and TH2 in acetonitrile is due to the colorless ring-closed lactone structure (Fig. 2). In the case of acetic acid medium, these fluorans showed two new broad peaks in the range of 490-530 nm. Thus the addition of acetic acid resulting in the formation of zwitterions of the fluoran moiety makes the $n-\pi^*$ transition relatively easier giving rise to a striking color change from colorless to deep orange red to the ring opened fluoran system. This result reveals that even in the solution state the fluoran has a significant role in both neutral and in acidic medium.

3.3. Thermochromic Properties in the Solid State

In general the thermochromic materials form a composite with three components which includes

(i) fluoron molecules (TH1 and TH2);

3301



Figure 2. (A) UV-vis absorption spectra of (**TH1** and **TH2**) in acetonitrile and in acetic acid, (B) λ_{max} of (**TH1** and **TH2**) in acetic acid.

(ii) acid activator (bisphenol-A) which is capable of reversibly accepting an electron from the electrondonating component; and P: 94.45,153.233 On: T (iii) a low melting solvent such as methyl stearate has a capability to control the temperature and sensitivity of the thermochromic material in its coloration/decoloration phenomenon.

In general these thermochromic mixtures (TH1 and TH2) are deep orange red color when it is cooled, but they become decolorized while warmed (Fig. 3). In the methyl stearate system, both fluorans (TH1 and TH2) demonstrated color reversibility at 40 °C. The ongoing studies indicated that the colorless semisolid (TH1 and TH2) systems turned to a deep orange red color as a result of the ring-opening fluoran system, likely due to the intermolecular association between the electron acceptor phenolic



Figure 3. Solid state color change of fluorans TH1 and TH2 with bisphenol-A and methylsterate.



Figure 4. Changes of orbital hybridization at fluorans spiro ring with proton donors.

moiety and the spirolactone unit. However, in reality, the reason for the color change of **TH1** and **TH2** is due to the fact that: **TH1** and **TH2** are colorless (proton acceptors) because the carbon atom at center of a spiro molecule forms a bond with other carbon atoms through its sp^3 hybrid orbitals, forming the colorless lactone ring. When **TH1** and **TH2** are in contact with a proton donor (bisphenol A), the lactone ring opens, and the sp^3 hybridized orbital of the central carbon atom gets modified to a sp^2 hybrid orbital (Fig. 4). Due to this factor the π -conjugation of the fluoran moiety has been extended and the λ_{max} was moved to higher wavelength.⁸

3.4. Solid State Spectroscopic Studies

To elucidate the electronic properties of these systems in detail, we employed solid state UV-Vis spectroscopic analysis by varying the temperatures (Fig. 5). As shown in the figure the fluoran moiety (**TH1** and **TH2**) showed no peaks around 500 nm at 40 °C, whereas, when cooled to RT, these thermochromic materials exhibited two absorption peaks at approximately 500 to 550 nm. This is normally due to the ring-opening of the fluoran through the intermolecular effect between the electron acceptor phenolic and the spirolactone unit.^{24–26, 36}

The changes in the reflectance of the fluorans (**TH1** and **TH2**) in methyl stearate and bisphenol A at different temperatures are shown by the reflectance spectra (Fig. 6). The spectra showed peaks around 450–600 nm at 24 °C, mainly because of the ring opened form of the fluorans (**TH1** and **TH2**). Whereas, when the temperature is raised up to 40 °C, the color of the mixture was disappeared due to the regeneration of the lactone ring. The role of color developer has been cross verified by carrying out the same experiment in the absence of bisphenol-A, the added **TH1** (5 mg) and methyl stearate (10 mg) without bisphenol-A showed no distinct color change upon heating up to 40 °C due to the lack of proton donor in the combined mixture.

3.5. FT-IR Spectroscopic Studies

FT-IR spectral studies was carried out to confirm the structure of the fluoran molecule, for the above-mentioned thermochromic material (**TH1** and **TH2**) has been recorded at different temperatures (24 °C and 40 °C) (Fig. 7). The results from the FT-IR spectra indicated that the shifts in



Figure 5. Solid state UV-vis spectra of TH1 and TH2 at 24 °C (cool) and 40 °C (heating).

positions of peaks could be endorsed due to the modification in the electronic structure of the thermochromic systems. For both **TH1** and **TH2** system, the peak at the range of 1754 and 1750 cm⁻¹ in the colorless sample (at 40 °C) has been shifted to 1738 cm⁻¹ in the orange red colored sample. The value of 1750 cm⁻¹ is corresponds to the C=O stretching frequency.^{37, 38} This result reveals that the decrease in the frequency of the C=O group in the cooling state is mainly because of the ester ring opening, Th resulting in the formation of a carboxylate group which can be easily protonated.³⁷

3.6. Theoretical Study

To gain further understanding in the mechanism of fluoran moiety **TH1**, molecular modeling was performed using Density Functional Theory calculations at B3LYP/321G level of theory using Gaussian 03 package.³⁹ In the optimized geometry of the lactone **TH1** and the ring opened form **TH1**⁺ are shown in Figure 8. The relevant frontier orbitals and its energy gap ($\Delta E = E_{HOMO} - E_{LUMO}$) for **TH1** and **TH1**⁺ are depicted in Figure 9. In **TH1**, the HOMO is confined on the xanthene unit and the LUMO on the lactone unit while in the case of ring opened form (**TH1**⁺), the LUMO is uniformly distributed throughout the entire molecule when compared to that of the HOMO. This is due to the fact that the ring opened form possesses a larger electronic cloud than the lactone form. The above results indicated that the ΔE value of **TH1**⁺ is relatively lesser when compared to that of the **TH1**. This is in good agreement with the results observed in the electronic spectra of the fluoran moiety.

3.7. Application as Thermal Indicator

Motivated by the favorable fluoran color former **TH1** and **TH2** in which the devising contains **TH1** or **TH2** in low melting solvent methyl stearate containing bisphenol A,



Figure 6. Solid state reflactance spectra of TH1 and TH2 at 24 °C (cool) and 40 °C (heating).



Figure 7. FT-IR spectra of TH1 and TH2 at heat (40 °C) and cool (24 °C).



Figure 8. Optimized geometry of TH1 and TH1 pyright: American Scientific Publishers

and monitored change in the color of the mixture on test strip and in acrylic fiber (as a thermal indicator). In this work, a color former combination of thermal indicator comprising **TH1** or **TH2** (5 wt.%), bisphenol A (2.5 wt.%) and methyl stearate (92.5 wt.%) was prepared. The **TH1**



Figure 9. HOMO–LUMO orbitals of the TH1 and TH1⁺ and their energy level diagram.

or **TH2** and bisphenol-A, which gets dissolved in methyl stearate at about 90 °C. The filter paper/acrylic fiber was dipped into the solution which is colorless and then cooled. During this process, **TH1/TH2** developed an orange red color as a result of ring-opening of the lactone ring through intermolecular association of the phenolic moieties with the spirolactone units (Figs. 10 and S14). The acrylic fiber has also been observed to act as an extreme thermal indicator. As depicted in Figures 10 and S14. Depending on the temperature, the color of the material changed from orange red to colorless and vice-versa.



Figure 10. (A) Color change of TH1 coated thermal indicator paper at 20 °C and 40 °C, (B) color change of TH1 coated acrylic fiber at 20 °C and 40 °C.

Kim et al.

4. CONCLUSION

We have designed and synthesized two new fluoran moiety in which the lactone unit acts as a basic skeleton to produce promising compound for new leuco dyes. The role of the fluoran moiety possessing lactone ring has been effectively verified under acidic conditions. The color change of TH1/TH2, bisphenol-A in methyl stearate (colorless to orange red color) has been tested on both test paper and acrylic fiber, which can act as a potential thermal indicator in real time application.

Acknowledgments: This study was supported by the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (Grant no. NRF-2014M3C1A9060739).

References and Notes

- 1. X. L. Luo, J. N. Li, C. H. Li, L. P. Heng, Y. Q. Dong, Z. P. Liu, Z. Bo, and B. Z. Tang, Adv. Mater. 23, 3261 (2011).
- 2. S. H. Kim, I. J. Hwang, S. Y. Gwon, and Y. A. Son, Dyes Pigm. 87. 158 (2010).
- 3. Y. L. Chen, A. J. H. Spiering, S. Karthikeyan, G. W. M. Peters, E. W. Meijer, and R. P. Sijbesma Nat. Chem. 4, 559 (2012).
- 4. A. Pucci, F. Di Cuia, F. Signori, and G. Ruggeri, J. Mater. Chem. 17, 783 (2007).
- 5. Y. Q. Dong, J. W. Y. Lam, A. J. Qin, J. Z. Liu, Z. Li, and B. Z. Tang, Appl. Phys. Lett. 91, 011111 (2007).
- 6. A. Kishimura, T. Yamashita, K. Yamaguchi, and T. Aida, Nat. Mater. 4, 546 (2005).
- 7. A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, and H. Pettersson Chem. 38. R. M. Silverstein, G. C. Bassler, and T. C. Morrill, Spectromet-Rev. 110, 6595 (2010).
- 8. S. Meiqin, S. Yun, and T. Qiyu, Dyes Pigm. 29, 45 (1995).
- 9. C. F. Zhu and A. B. Wu, Thermochim. Acta 425, 7 (2005).
- 10. N. Carmona, V. Bouzas, F. Jimenez, M. Plaza, L. Perez, M. A. Garcia, M. A. Villegas, and J. Llopis, Sens. Actuators B 145, 139 (2010)
- 11. X. Chen and J. A. Yoon, Dyes Pigm. 89, 194 (2011).
- 12. L. Ying, F. Huang, and G. C. Bazan, Nat. Commun. 8, 14047 (2017).
- 13. S. Sugano and H. Kouzai, Bull. Chem. Soc. Jpn. 89, 27 (2016).
- 14. J. Xie, C. E. Zhao, Z. Q. Lin, P. Y. Gu, and Q. Zhang, Chem. Asian J. 11, 1489 (2016).
- 15. P. Wight, Kirk-Othmer Encyclopaedia of Chemical Technology, New York, Wiley (2000).
- 16. K. Kolmakov, V. N. Belov, J. Bierwagen, C. Ringemann, V. Müller, and C. Eggeling, Chem. Eur. J. 16, 158 (2010).
- 17. L. Wu and K. Burgess, J. Org. Chem. 73, 8711 (2008).
- 18. K. Dahms, A. S. Batsanov, and M. R. Bryce, Tetrahedron Lett. 51, 6605 (2010).
- 19. M. Inouye, K. Tsuchiya, and T. Kitao, Angew. Chem. Int. Ed. 31, 204 (1992).

- 20. W. Weng, T. Higuchi, M. Suzuki, T. Fukuoka, T. Shimomura, M. Ono, L. Radhakrishnan, H. Wang, N. Suzuki, H. Oveisi, and Y. Yamauchi, Angew. Chem. Int. Ed. 49, 3956 (2010).
- 21. K. Kanazawa, K. Nakamura, and N. Kobayashi J. Phys. Chem. A 118, 6026 (2014).
- 22. S. Yamamoto, H. Furuya, K. Tsutsui, S. Ueno, and K. Sato, Cryst. Growth Des. 8, 2256 (2008)
- 23. D. C. Maclaren and M. A. White, J. Mater. Chem. 13, 1701 (2003).
- 24. S. M. Burkinshaw, J. Griffiths, and A. D. Towns J. Mater. Chem. 8, 2677 (1998)
- 25. Y. Sekiguchi, S. Takayama, T. Gotanda, and K. Sano, Chem. Lett. 36, 1010 (2007).
- 26. D. C. Maclaren and M. A. White, J. Mater. Chem. 13, 1695 (2003). 27. G. P. Ritesh, P. P. Manish, and G. P. Ranjan, Dyes Pigm. 66, 7
- (2005)
- 28. R. Zink, United States Patent No. 4,770,904 (1998).
- 29. R. Garner and J. C. Petitpierre, United States Patent No. 4,349,218 (1982)
- 30. R. Garner and J. C. Petitpierre, United States Patent No. 3,929,831 (1975).
- 31. M. Hojo, T. Ueda, A. Inoue, and S. Tokita J. Mol. Liq. 148, 109 (2009).
- 32. F. Azizian, A. J. Field, B. M. Heron, and C. Kilner, Chem. Commun. 48, 750 (2012)
- 33. F. Azizian, A. J. Field, J. Griffiths, and B. M. Heron Dyes Pigm. 92, 524 (2011).
- 34. G. P. Ritesh, V. P. Jignesh, P. P. Manish, and G. P. Ranjan J. Serb. Chem. Soc. 68, 607 (2003).
- 35. Q. H. Liu, X. L. Yan, J. C. Guo, D. H. Wang, L. Li, F. Y. Yan, and L. G. Chen, Spectrochim. Acta A 73, 789 (2009).
- 36. Y. Takahashi, A. Shirai, T. Segawa, T. Takahashi, and K. Sakakibara, Bull. Chem. Soc. Jpn. 75, 2225 (2002).
- K. Costello, K. T. Doan, K. L. Organtini, J. Wilson, M. Boyer, 37. G. Gibbs, and L. J. Tribe, Chem. Educ. 91, 883 (2014).
- ric Identification of Organic Compounds, 5th edn., Weinheim, John Wiley and Sons, Germany (1991).
- 39. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Jr., Montgomerv, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, 03, Revision D.01, Gaussian, Inc., Wallingford, CT (2004).

Received: 1 April 2017. Accepted: 29 April 2017.