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Thermochromic Properties of Fluorans in Solid State and Application in Acrylic Fiber as Thermal Indicator

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This work demonstrates the study on the thermochromic property of the synthesized fluoran molecules (TC1 and TC2) and their reversible color changing behavior through heating and cooling process. Three-component mixtures containing TC1/TC2, color developer and low melting solvent were used in this study to describe the thermochromic behavior of fluorans with significant heating and cooling and the chromic behavior of the fluorans were confirmed by various spectral techniques such as Ultraviolet-visible spectroscopy (UV-Vis), reflectance and Fourier-transform infrared spectroscopy (FT-IR). For the real time examination, three component mixtures were applied to filter paper and to acrylic fiber which serves as a thermal indicator. Also the material tends to show reversible color change on heating and cooling process.

Keywords: Fluorans, Thermochromic, Reversible, Heating-Cooling, Thermal Indicator.

1. INTRODUCTION

Stimuli-responsive materials have been involving a considerable attention in recent years due to its significant changes in their optical properties, change in color of the molecule repeatedly between different temperature or dark and bright state. In solid state, these materials have considerable utility in the area of sensors, thermal displays, device for memory storing, security inks, dye material for solar light harvesting and luminescent materials [1–7]. Thermochromic property in the materials was achieved using fluorans and crystal violet lactone, spiropyrans, metal complexes and polymers [8–14]. Most of the functional dyes such as like rhodamines [15], rosamines [16], thiofluoresceins [17] and fluorans [18] xanthene unit, forms the core to act as thermochromic materials. Thermochromic materials attained using fluorans were studied in recent years in a view to commercialize the material towards thermal indicators and also they have wide spread utility, it is used as copying material, in pressure and temperature-sensitive recording materials and as electrochromic material [19, 20]. In addition, the dyes which are designed to possess xanthene core can be used as a probe for sensor material in biological system, used as an electrochromic material with an appropriate potential [21, 22]. Thermochromic behavior in fluorans can be achieved through proper formulation which is obtained by incorporating color developer and low melting solvent to it based on temperature requirement, the low melting solvent can be selected. Thus three component system is the basic requisite to obtain thermochromic property (1) fluoran (color former), (2) bronsted acid (color developer) and (3) low melting solvent (methyl stearate) [18, 23, 24]. The ratio of these three component mixture where heated to form homogeneous mixture so that the material gets the color changing property under heating and cooling condition. Thus, the designed system under thermal stimulation giving rise to reversible thermochromic effects with warming and cooling. Fluoran based functional dyes in solid state undergo a ring-opening reaction and resulting in a noticeable color change, these changes are reversible when varied the temperature (Scheme 1) [25–27]. Since these systems involve phase change, in solid state it is colored and in liquid phase colorless, the thermochromic properties not affected much when the ratio of the components maintained for microencapsulation so as to achieve a durable thermochromic material [28].

In this work, we report here two new fluoran moiety with *N*,*N*-dimethylamino functionality at *meta* position to the xanthene oxygen and a detailed investigation

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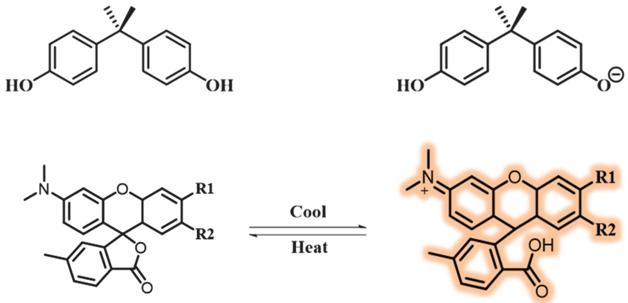


Scheme 1. Thermochromic response of fluorans-bisphenol A system.

of thermochromic properties of these fluorans (TC1 and TC2) with respect to electronic effects in solid state was described in detail.

2. EXPERIMENTAL DETAILS

2.1. Equipment and Reagents

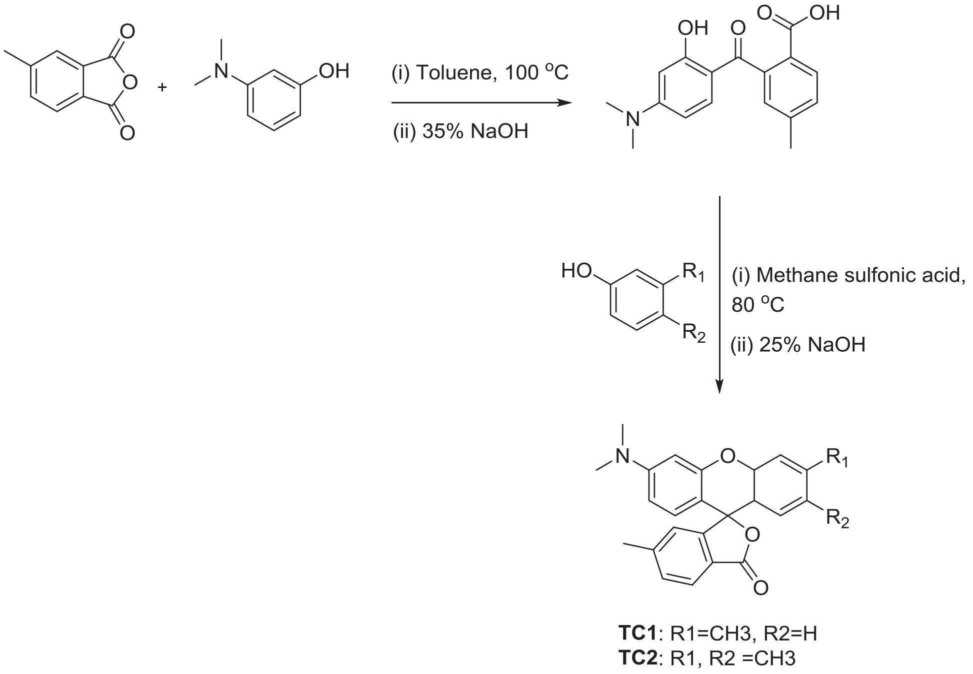
Reagents and solvents used in this work were purchased from Aldrich/TCI chemicals. ^{1}H-NMR spectra recorded on a Bruker Avance 300 MHz instrument with TMS as an internal reference. Column chromatography was done to purify all the compounds. Solid state UV-Vis and reflectance spectra of the new thermochromic compounds in methyl stearate and bisphenol-A, were performed on a Shimadzu Solid Spec-2700 instrument. UV-Visible absorption spectra were recorded using an Agilent 8453 instrument. FT-IR spectra were recorded using a Perkin Elmer Spectrum One spectrophotometer equipped with a diamond probe ATR attachment (neat sample). ESI-mass spectra were recorded using a Thermo Scientific LTQ Orbitrap XL mass spectrometer. The intermediate 2-(4-(dimethylamino)-2-hydroxybenzoyl)-4-methylbenzoic acid for the synthesis of TC1, TC2 was prepared following reported literature (Scheme 2) [29].

2.2. General Method for the Preparation of TC1 and TC2

The reaction mixture consisting of 2-(4-(dimethylamino)-2-hydroxybenzoyl)-4-methylbenzoic acid (1.0 equiv) and m-cresol (1.0 equiv) or 3,4-dimethylphenol (1.0 equiv) in methanesulfonic acid and stirred the reaction mixture at 80 °C for 2 h and cooled to room temperature and added 25% aq · NaOH (20 mL) to the reaction mixture, the resulting solution was stirred at room temperature for 1 h, slowly the solid precipitated out which is filtered and the obtained solid was column purified. The products TC1 and TC2 were characterized using ^{1}H NMR and ESI mass spectral techniques and the results are given below;

6′-(dimethylamino)-3′,6-Dimethyl-4a′,9a′-Dihydro-3H-Spiro[isobenzofuran-1,9′-xanthen]-3-One (TC1)

^{1}H NMR ($CDCl_3$, 300 MHz), (ppm): 2.30 (*d*, 6H), 2.91 (*s*, 6H), 6.31 (*m*, 1H), 6.42 (*d*, 1H, $J = 2.4$ Hz), 6.54 (*m*, 2H), 6.72 (*m*, 1H), 6.86 (*m*, 2H), 7.29 (*dd*, 1H, $J =$ 8.1 Hz), 7.72 (*m*, 1H). ^{13}C-NMR ($CDCl_3$, 600 MHz), δ (ppm): 20.27, 21.00, 39.20, 82.31, 82.73, 97.50, 97.54, 105.39, 105.43, 107.77, 115.62, 115.65, 116.05, 122.59, 123.07, 123.35, 123.38, 123.58, 123.74, 126.27, 126.81, 126.87, 127.69, 127.73, 129.58, 134.91, 138.69, 139.72, 145.04, 149.86, 150.44, 150.55, 151.03, 151.06, 151.43, 151.55, 153.21, 168.77, 168.81. ESI-MS (m/z) calcd. 373.1, found 374.3 ($M+H^+$).



Scheme 2. Synthetic route for preparation of fluorans TC1 and TC2.

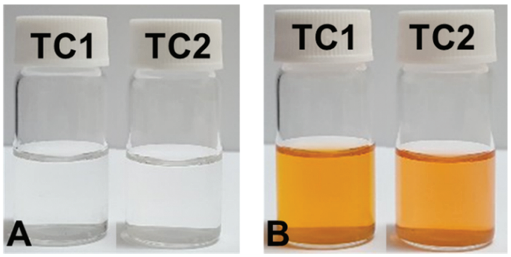
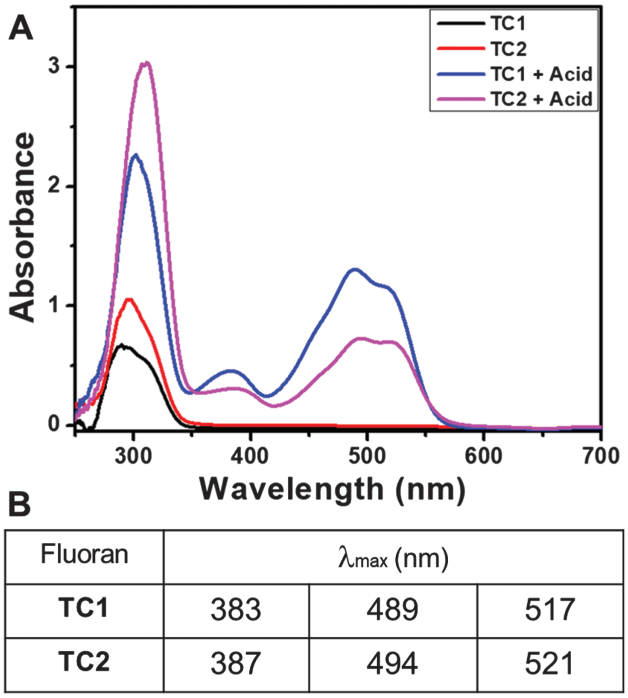


Figure 1. The color of TC1 and TC2 in acetonitrile (A) without acetic acid (B) with acetic acid.



Fluoran	λmax (nm)		
TC1	383	489	517
TC2	387	494	521

Figure 2. (A) UV-Vis absorption spectra of (TC1 and TC2) in acetonitrile and in acetic acid, (B) $\lambda_{\max}$ of (TC1 and TC2) in acetic acid.

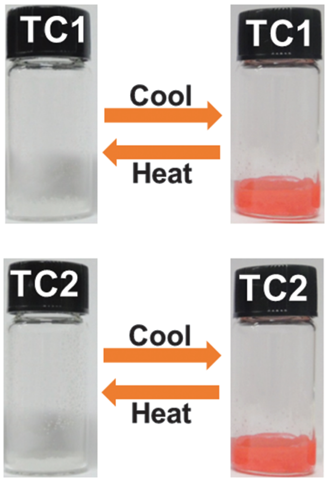


Figure 3. Solid state color change of fluorans TC1 and TC2 with bisphenol-A and methyl stearate.

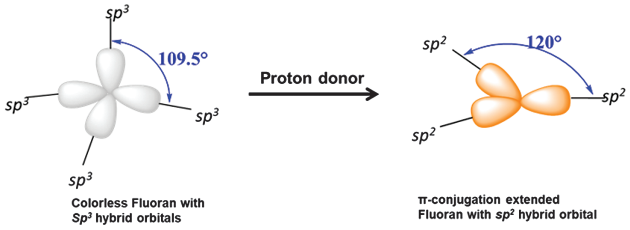


Figure 4. Changes of orbital hybridization at fluoran spiro ring with proton donors.

6′-(dimethylamino)-2′,3′,6-Trimethyl-4a′,9a′-Dihydro-3H-Spiro[isobenzofuran-1,9′-xanthen]-3-One (TC2)

^{1}H NMR (CDCl$_3$, 300 MHz), (ppm): 2.00 (*s*, 3H, $J=3$ Hz), 2.19 (*s*, 3H), 2.29 (*d*, 3H), 2.90 (*s*, 6H), 6.29 (*m*, 1H), 6.39 (*m*, 2H), 6.52 (*m*, 1H), 6.84 (*m*, 2H), 7.29 (*dd*, 1H, $J=7.8$ Hz), 7.72 (*m*, 1H). ^{13}C-NMR (CDCl$_3$, 600 MHz), δ (ppm): 17.99, 18.01, 18.80, 20.30, 21.02, 28.67, 39.20, 82.44, 82.87, 97.47, 97.51, 105.41, 105.45, 107.65, 115.38, 115.41, 116.45, 122.59, 123.07, 123.30, 123.55, 123.72, 126.19, 127.13, 127.19, 127.70, 127.75,

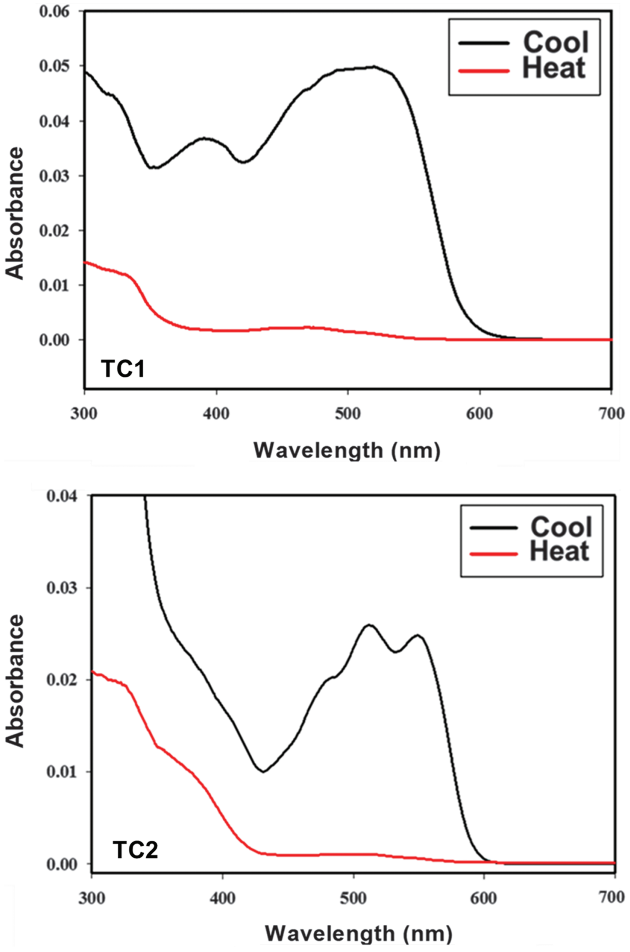


Figure 5. Solid state UV-Vis spectra of TC1 and TC2 at 20 °C (cool) and 40 °C (heating).

129.54, 130.72, 130.75, 134.92, 138.51, 138.60, 145.02, 148.59, 148.71, 150.05, 150.97, 151.00, 151.43, 151.56, 153.39, 168.90, 168.93. ESI-MS (*m*/*z*) calcd. 387.1, found 388.2 ($M+H^+$).

3. RESULTS AND DISCUSSION

3.1. Color Properties in Solvents

The color properties of fluorans TC1 and TC2 determined by dissolving them in different solvents and the results indicated that the fluorans dissolved in aprotic solvents such as toluene, benzene, tetrahydrofuran, and acetonitrile, is colorless and no noticeable change in color has been detected. This result indicated that, in aprotic solvents, TC1 and TC2 were found to be ring closed colorless lactone form. While, an addition of few drops of acetic acid to the dissolved fluoran the color of the solution changes to orange color (Fig. 1), this intense color change happened due to ring opening of lactone ring in the fluoran moiety.

3.2. UV-Vis Spectral Studies

UV-Vis spectral studies were done to identify the electronic change in the fluoran moiety in solution state. As discussed above, the color properties in solvents, TC1 and TC2 showed no color in acetonitrile solvent and when added acetic acid dramatic color change has been observed which is confirmed by recording UV-Vis spectra. The spectra of TC1 and TC2 showed peaks in the region of 300 nm in acetonitrile medium and no obvious peak observed beyond that region this indicating TC1 and TC2 existing in ring closed lactone form and the solution is colorless upon adding acetic acid to it turns solution to orange color, UV-Vis spectra recorded for the sample showed broad peaks in the range of 480–520 nm (Fig. 2). The appearance of absorbance peak at 480–520 nm region attributes to the zwitterion formation in TC1 and TC2 after adding acetic acid which makes the n–π^* transition in fluoran relatively easier resulting in noticeable color change in the molecule. Also the result obtained indicating that even in solution

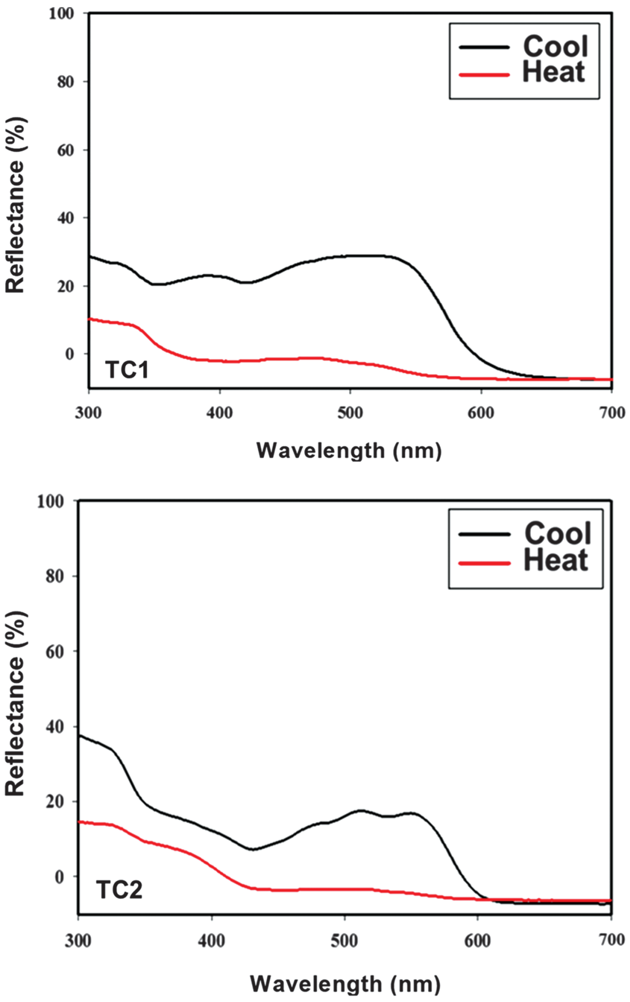


Figure 6. Solid state reflectance spectra of TC1 and TC2 at 20 °C (cool) and 40 °C (heating).

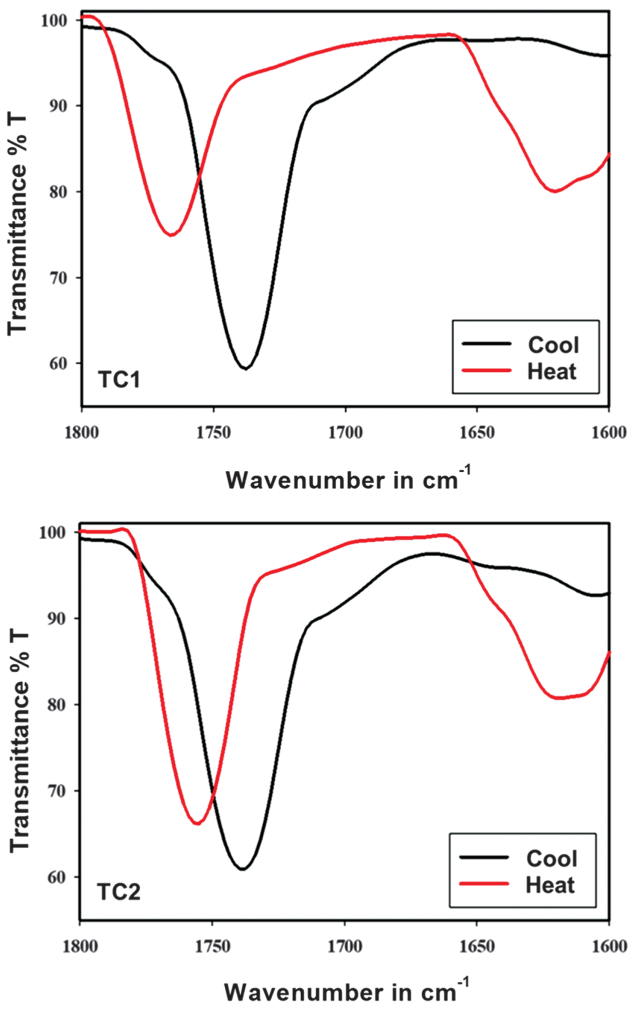


Figure 7. FT-IR spectra of TC1 and TC2 at heat (40 °C) and cool (20 °C).

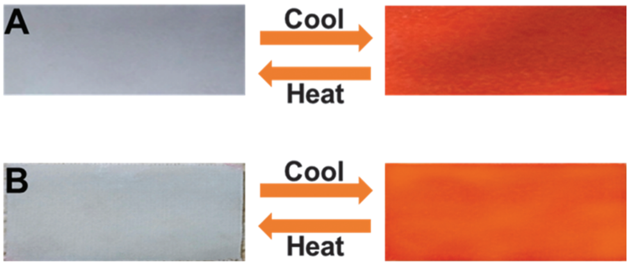


Figure 8. (A) Color change of TC1 coated filter paper at 20 °C and 40 °C, (B) color change of TC1 coated acrylic fiber at 20 °C (cool) and 40 °C (heat).

state, this fluoran moiety has significant role in neutral and acidic solution.

3.3. Thermochromic Properties in the Solid State

Thermochromic properties of TC1 and TC2 in solid state was examined by preparing a composite with bisphenol-A, an acid activator and methyl stearate a low melting solvent. Bisphenol-A has the ability to accept electron from electron donating component and the process tend to be reversible whereas methyl stearate controls the temperature in the thermochromic material resulting in coloration and discoloration in cooling and heating process. In general, these thermochromic blended material (TC1 and TC2) are orange color in cooled condition and becomes colorless when heated to 40 °C (Fig. 3). In low melting solvent system, these fluorans (TC1 and TC2) showed color reversibility between 20 and 40 °C. The obtained result in this current study reveals that the colorless form of TC1 and TC2 is due to ring closed lactone ring in the system which gets converted to orange color due to ring-opening of lactone ring in fluoran moiety, this may be due to the fact that there exhibited an intermolecular interaction between the electron acceptor phenolic group and the spirolactone unit. The actual reason behind the color change of these fluoran moiety is due to the change of hybridization in the carbon atom centered at spiro molecule, TC1 and TC2 are proton acceptor, when it is a closed ring system they are colorless this is because the carbon atom at center of a spiro molecule forms a bond with other carbon atoms through its sp^3 hybrid orbitals and these fluorans when it comes in contact with proton donor that is with bisphenol-A, the lactone ring opens which converts the sp^3 hybridized orbital of the carbon atom to sp^2 hybrid orbital (Fig. 4). This is the reason, π-conjugation in fluoran moiety gets extended and the absorbance peak of ring opened lactone ring in fluoran moiety appeared with a bathochromic shift [8].

3.4. Solid State Spectroscopic Studies

To explain the electronic behavior of fluoran composite (TC1 and TC2) in detail, we carried out solid state UV-Vis spectral study in heating and cooling state (Fig. 5). As shown in the Figure 5, no absorbance peak was observed in the range of 480–500 nm when heated the sample at 40 °C, whereas the temperature was brought to 20 °C for the fluoran molecule, broad peak in the region of 480–500 nm was appeared, the appearance of peak in the region for these fluoran attributed to the transformation of closed lactone ring to open form. This effect normally happens because of the intermolecular effect between the electron acceptor phenolic and the spirolactone unit in the fluoran moiety [25–27, 30].

Further to confirm the electronic effect of fluoran moiety with bisphenol-A and methyl stearate in heating and cooling state, reflectance was measured and is shown in Figure 6. The reflectance spectra showed broad peaks in the range of 500–600 nm at 20 °C, and no peaks when heated the sample to 40 °C. The fluoran moiety gives rise an intense orange color at 20 °C due to ring opening in the fluoran moiety, while discoloration in the molecule at 40 °C resulting in no peaks in the reflectance spectra due to ring closing process in the fluoran molecule. The thermochromic effect of TC1 and TC2 in the absence of color developer also examined, which showed no effect in the thermochromic property in the fluoran molecule and the observation of no color change confirms the significant role of bisphenol-A inclusion in the fluoran composite preparation.

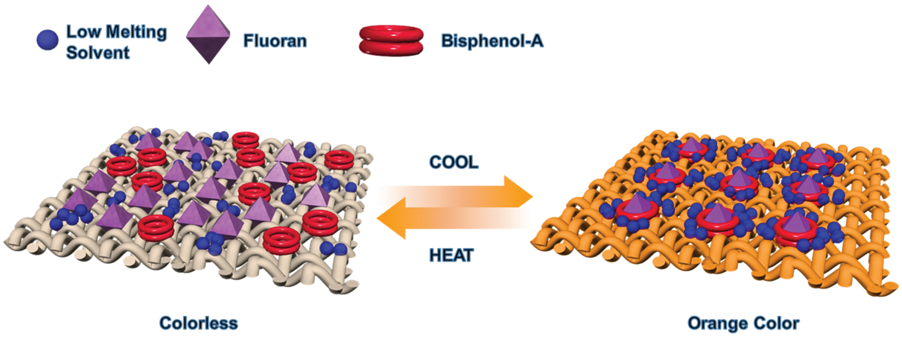


Figure 9. Plausible mechanism of three component mixture in thermal indicator.

3.5. FT-IR Spectroscopic Studies

FT-IR was recorded to confirm the structural changes in TC1 and TC2, the spectra was measured at different temperatures (20 and 40 °C) (Fig. 7). The measured FT-IR spectra showed a peak in the range of 1760 cm^{-1} for TC1 and TC2 which agrees with $C=O$ stretching frequency [31, 32] for the fluoran molecule (colorless) in the heating state at 40 °C, and for the sample in cooled state at 20 °C of fluoran moiety (orange color) the peak appeared at 1738 cm^{-1}. The results obtained from the spectra reveals that the shift in the peak position validate to the transformation of structure in the thermochromic material both in heating and cooling condition, the frequency shift towards lower region for the $C=O$ group for the orange colored sample due to ring opening of lactone ring results in carboxylate group formation which further gets protonation easier [31].

3.6. Application as Thermal Indicator

Inspired by the thermal color changes of the synthesized fluoran moiety TC1 and TC2, we prepared a thermal indicator for the real time application using TC1. TC1 composite was applied to filter paper as well as in acrylic fiber, for this purpose the composite was prepared by mixing 5 wt.% of TC1, 2.5 wt.% bisphenol-A and 92.5 wt.% low melting solvent methyl stearate were mixed homogenously, and applied to filter paper and acrylic fiber and color change on heating and cooling was checked thoroughly in repeated manner to confirm the reversibility in color change. In this process, TC1 generates orange color at 20 °C and becomes colorless when heated to 40 °C (Fig. 8) and Plausible mechanism of three component mixture in thermal indicator upon heating and cooling process has been shown in Figure 9.

4. CONCLUSION

In summary, fluoran based thermochromic material was synthesized, and its color changing property in solid as well as liquid state was successfully demonstrated. These fluoran moieties TC1 and TC2 have the lactone unit in the structure tend to show a promising material for leuco dyes. A reversible color change from colorless to orange was obtained when controlled the temperature between heating and cooling process. The composite prepared using TC1, bisphenol-A and methyl stearate has been successfully applied in filter paper as well as acrylic fiber showed reversible color change between 20 and 40 °C which can be used in real time as a thermal indicator.

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