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3,6-Disubtituted fluorans containing 4(3*H*)-quinazolinon-3-yl, diethyl amino groups and their application in reversible thermochromic materials

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Abstract

3,6-Disubstituted fluorans containing 4(3*H*)-quinazolinone-3-yl and diethylamino groups were synthesized by reacting 4-diethylamino-2-hydroxy-2′-carboxybenzophenone with various 4(3*H*)-quinazolinones in the presence of dehydration condensing agent. These 4(3*H*)-quinazolinones were derived by reacting various substituted benzoxazine-4-ones with 3-aminophenol. All the fluorans have been identified by conventional methods (IR, ^{1}H NMR), elemental analysis, and UV–visible spectroscopy in organic solvent and 95% acetic acid. These fluorans have been applied in reversible thermochromic materials.

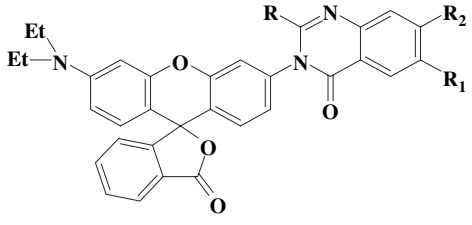
Keywords: 3,6-Disubstituted fluoran; 4(3*H*)-quinazolinone; Reversible thermochromic materials

1. Introduction

Among various classes of leuco dyes, fluoran compound (Spiro[*iso*-benzofuran-1,9′-xanthene]-3-one) [1] has been used in a variety of fields such as thermo-indicator [2], printed circuits (thermal recording cards) [3], writing materials (non-reversible [4] and reversible [5]), medical applications [6,7], thermal printing materials [8], multicolour thermal recording [9], prepaid card [10], thermally reversible recording materials [11], carbonless copying paper [12] and thermosensitive recording paper [13].

A number of heterocyclic compounds such as quinolines [14], indole [15], benzthiazole [16], triazine [17], pyridine [18], pyrimidine [19], pyrryl [20] and morpholine [21] containing fluorans are colourless or nearly colourless chromogenic compounds which are converted to a colouration upon contact with an acidic colour-activating substance such as organic acid, acid clay, activated clay, phenol formalin resin, metal salts of aromatic carboxylic acids and bisphenol-A. This colour formation reaction is reversible. Thus, the coloured form can easily reproduce the colourless form by treating with base.

The first aspect of the investigation, synthesis of nearly colourless chromogenic fluoran compounds containing 4(3*H*)-quinazolinone have the following structural formula.



($C_{1\text{-}6}$)

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wherein

Comp. no.	R	R_1	R_2
C_1	CH_3	H	H
C_2	Ph	H	H
C_3	CH_2Cl	H	H
C_4	CH_2Ph	H	H
C_5	CH_3	NO_2	H
C_6	CH_3	NO_2	Cl

The second aspect of the investigation relates to thermochromic materials exhibiting a sharp and reversible metachromathem. Reversible thermochromic material has been achieved by the combined use of three components: (a) an electron-donating chromatic organic compound, i.e., a colour former; (b) a compound capable of reversibly accepting an electron or electrons, i.e., a colour developer; and (c) a compound controlling the temperature and sensitivity of colouration/decolouration of the thermochromic materials, non-polar co-solvents (long-chain alkyl compounds). Pigmentation of these reversible thermal sensitive materials was obtained by microencapsulation [1] of these compositions.

2. Experimental

2.1. General

All melting points (m.p.) are uncorrected and expressed in °C. IR spectra of all the compounds were recorded on a Nicolet Impact-400D FT-IR spectrophotometer using KBr pellets. The ^{1}H NMR spectra were recorded on Hitachi R-1500 instrument, using TMS as internal standard. Chemical shifts are given in δ (ppm). ^{13}C NMR were recorded on DPX 200 Brucker FT-NMR spectrometer using $CDCl_3$ as solvent and TMS as internal standard. Absorption spectra of the compounds in toluene and 95% acetic acid were recorded on Shimadzu UV-240 instrument.

2.2. Synthesis of disubstituted fluorans

2.2.1. Synthesis of various substituted benzoxazine-4-ones ($I_{a–f}$)

The various substituted benzoxazine-4-ones **I**, were synthesized according to the method reported in the literature [22–27]. The benzoxazine-4-ones synthesized were 2-methyl-4*H*-3,1-benzoxazine-4-one $\mathbf{I_a}$ (R = CH_3, R_1, R_2 = H) [22], 2-phenyl-4*H*-3,1-benzoxazine-4-one $\mathbf{I_b}$ (R = Ph, R_1, R_2 = H) [23], 2-chloro-methyl-4*H*-3,1-benzoxazine-4-one $\mathbf{I_c}$ (R = CH_2Cl, R_1, R_2 = H) [24], 2-benzyl-4*H*-3,1-benzoxazine-4-one $\mathbf{I_d}$ (R = CH_2Ph, R_1, R_2 = H) [25], 2-methyl-6-nitro-4*H*-3,1-benzoxazine-4-one $\mathbf{I_e}$ (R = CH_3, R_1 = NO_2, R_2 = H) [26], and 7-chloro-2-methyl-6-nitro-4*H*-3,1-benzoxazine-4-one $\mathbf{I_f}$ (R = CH_3, R_1 = NO_2, R_2 = Cl) [27].

2.2.2. General synthetic procedure for quinazolinone ($A_{1–6}$)

A mixture of each compound **($I_{a–f}$)** (0.01 mol) and 3-aminophenol (0.01 mol) was heated at a specified temperature for 3 h. The reaction mixture was cooled to 30 °C and absolute alcohol (20 ml) was added to it. The separated solid was collected by filtration and crystallized from absolute alcohol. The reaction temperature, melting point and percentage yields of each compound are presented in Table 1.

2.2.2.1. IR and ^{1}H NMR data for compounds ($A_{1–6}$). 3-(3-Hydroxyphenyl)-2-methyl-4(3H)-quinazolinone (A_1): IR (KBr): 3200–3400 cm^{-1} (OH); 1696 cm^{-1} (C=O); 1595 cm^{-1} (C=N); 3066, 1474, 1320 cm^{-1}(Ar–Me); and 810–750 cm^{-1} and 710–690 cm^{-1} for the *m*-substituted benzene. ^{1}H NMR (DMSO-d_6): 9.81 (H, s, OH); 7.10–8.35 (8H, m, Ar–H); 2.27 (3H, s, Ar–CH_3).

3-(3-Hydroxyphenyl)-2-phenyl-4(3H)-quinazolinone (A_2): IR (KBr): 3200–3400 cm^{-1} (OH); 1682 cm^{-1} (C=O); 1608 cm^{-1} (C=N); and 810–750 cm^{-1}, 710–690 cm^{-1} for the *m*-substituted benzene. ^{1}H NMR (DMSO-d_6): 9.80 (1H, s, OH); 6.90–8.37 (13H, m, Ar–H).

2-Benzyl-3-(3-hydroxyphenyl)-4(3H)-quinazolinone (A_3): IR (KBr): 3200–3400 cm^{-1} (OH); 3080, 1335 cm^{-1} (CH_2Cl); 2982, 2949, 2883 cm^{-1} (N–Et); 1696 cm^{-1} (C=O); 1595 cm^{-1} (C=N); and 810–750 cm^{-1} and 710–690 cm^{-1} for the *m*-substituted benzene. ^{1}H NMR (DMSO-d_6): 9.82 (1H, s, OH); 6.90–8.36 (13H, m, Ar–H); 4.08 (2H, s, Ar–CH_2Ph).

2-(Chloromethyl)-3-(3-hydroxyphenyl)-4(3H)-quinazolinone (A_4): IR (KBr): 3200–3400 cm^{-1} (OH); 3086,

Table 1
Physical properties for compounds ($A_{1–6}$)

Compound number	Compound **A**			Molecular weight	Reaction temperature (°C)	Yield (%)	m.p. (°C)
	R	R_1	R_2				
A_1	CH_3	H	H	252.27	125–130	80	140–145
A_2	Ph	H	H	314.34	165–170	81	202–204
A_3	CH_2Ph	H	H	286.71	170–175	80	136–140
A_4	CH_2Cl	H	H	328.39	150–155	79	150–152
A_5	CH_3	NO_2	H	297.27	150–155	80	175–180
A_6	CH_3	NO_2	Cl	331.71	160–165	81	198–199

1340 cm^{-1} (CH_2Cl); 1693 cm^{-1} (C=O); 1609 cm^{-1} (C=N); and 810–750 cm^{-1}, 710–690 cm^{-1} for the *m*-substituted benzene. ^1H NMR (DMSO-d_6): 9.80 (1H, s, OH); 6.99–8.35 (8H, m, Ar–H); 4.23 (2H, s, Ar–CH_2Cl).

*3-(3-Hydroxyphenyl)-2-methyl-6-nitro-4(3H)-quinazolinone (**A5**)*: IR (KBr): 3200–3400 cm^{-1} (OH); 3164, 1340 cm^{-1} (CH_3); 2962, 2933, 2860 cm^{-1} (N–Et); 1696 cm^{-1} (C=O); 1602 cm^{-1} (C=N); 1521 cm^{-1} and 1353 cm^{-1} (NO_2); 1321 cm^{-1} (CH_3); 810–750 cm^{-1} and 710–690 cm^{-1} for the *m*-substituted benzene. ^1H NMR (DMSO-d_6): 9.83 (1H, s, OH); 7.10–8.84 (7H, m, Ar–H); 2.26 (3H, s, Ar–CH_3).

*7-Chloro-3-(3-hydroxyphenyl)-2-methyl-6-nitro-4(3H)-quinazolinone (**A6**)*: IR (KBr): 3200–3400 cm^{-1} (OH); 3193, 1427, 1342 cm^{-1} (CH_3); 2980, 2951, 2881 cm^{-1} (N–Et); 1694 cm^{-1} (C=O); 1608 cm^{-1} (C=N); 1520 cm^{-1} and 1354 cm^{-1} (NO_2); 1323 cm^{-1} (CH_3); 823 cm^{-1} (Cl); and 810–750 cm^{-1} and 710–690 cm^{-1} for the *m*-substituted benzene. ^1H NMR (DMSO-d_6): 9.84 (1H, s, OH); 6.90–8.76 (6H, m, Ar–H); 2.25 (3H, s, Ar–CH_3).

2.2.3. Synthesis of 4-diethylamino-2-hydroxy-2′-carboxybenzophenone (**B**)

4-Diethylamino-2-hydroxy-2′-carboxybenzophenone was synthesized by refluxing equimolar proportion of 3-diethylaminophenol and phthalic anhydride in toluene as reported in literature [28]; m.p. 205–207 °C. IR (KBr): 3294 cm^{-1} (–OH); 2992, 2856, 2891, 1488 cm^{-1} (N–Et); 1702 cm^{-1} (CO; Ar–COOH); 1669 cm^{-1} (–CO–); 1608, 1427, 1320, 1300, 1055, 1011, 944, 809, 802, 708, 541 cm^{-1}. ^1H NMR (DMSO-d_6): 12.59 (2H, s, –COOH, OH); 6.77–7.97 (7H, m, Ar–H); 3.16–3.55 (4H, q, N–(CH_2–CH_3)$_2$); 1.06–1.28 (6H, t, N–(CH_2–CH_3)$_2$).

2.2.4. General synthetic procedure for fluoran compounds (**C1–6**)

In 10 ml of concentrated sulfuric acid, each compound (**A1–6**) (0.01 mol) and **(B)** (0.01 mol) was dissolved at 40 °C and thereafter stirred at room temperature for 48 h. After the reaction was completed, the reaction mixture was poured into 100 g of ice-cold water and the solid substance consequently precipitated was collected by filtration. The solid substance was dispersed in water, and the pH was adjusted to 10 by adding an aqueous solution of 10% sodium hydroxide, filtered and dried. The dried substance was then recrystallized from *n*-butyl alcohol.

The solution of this compound in toluene is almost colourless while in contact with silica gel instantaneously formed a colour as shown in Table 2.

*2.2.4.1. Elemental analysis, IR and ^1H NMR data for compounds (**C1–6**). 6-Diethylamino-3-(2′-methyl-4′-oxo-(3′-hydroquinazolin-3′-yl)) fluoran (**C1**)*: Calculated for $C_{33}H_{27}N_3O_4$: C, 74.84; H, 5.14; N, 7.93%. Found: C, 73.94; H, 5.21; N, 7.96%. IR (KBr): 3086, 1467, 1345 cm^{-1} (–CH_3); 2965, 2938, 2863 cm^{-1} (N–Et); 1783 cm^{-1} (C=O group of lactone ring); 1696 cm^{-1} (C=O group of quinazolinone); 1595 cm^{-1} (C=N). ^1H NMR (CD_3COCD_3): 6.46–8.32 (14H, m, Ar–H); 3.20–3.53 (4H, q, N–CH_2–CH_3); 2.31 (3H, s, Ar–CH_3); 1.06–1.28 (6H, t, N–CH_2–CH_3). ^{13}C NMR ($CDCl_3$): 12.9, 24.7, 44.9, 83.8, 98.0, 99.4, 105.1, 109.3, 117.5, 121.0, 121.3, 123.2, 123.3, 124.3, 124.9, 125.4, 127.2, 127.4, 127.6, 129.3, 130.2, 135.2, 135.3, 139.6, 147.9, 150.3, 153.2, 153.4, 154.2, 162.5, 169.8.

*6-Diethylamino-3-(2′-phenyl-4′-oxo-(3′-hydroquinazolin-3′-yl)) fluoran (**C2**)*: Calculated for $C_{38}H_{29}N_4O_6$: C, 77.14; H, 4.94; N, 7.10%. Found: C, 76.28; H, 4.90; N, 7.01%. IR (KBr): 2979, 2945, 2879, 1420, 1353 cm^{-1} (N–Et); 1783 cm^{-1} (C=O group of lactone ring); 1695 cm^{-1} (C=O group of quinazolinone); 1597 cm^{-1} (C=N). ^1H NMR (CD_3COCD_3): 6.47–8.37 (19H, m, Ar–H); 3.20–3.42 (4H, q, N–CH_2–CH_3); 1.06–1.28 (6H, t, N–CH_2–CH_3). ^{13}C NMR ($CDCl_3$): 12.9, 44.8, 83.8, 98.0, 109.1, 118.5, 121.0, 121.3, 123.2, 123.3, 124.4, 124.5, 125.3, 127.1, 127.6, 127.8, 129.1, 129.3, 129.7, 130.0, 130.3, 132.4, 135.0, 135.3, 139.6, 147.8, 150.1, 152.2, 153.5, 154.2, 162.5, 169.7.

*6-Diethylamino-3-(2′-benzyl-4′-oxo-(3′-hydroquinazolin-3′-yl)) fluoran (**C3**)*: Calculated for $C_{39}H_{31}N_3O_4$: C, 77.34; H, 5.16; N, 6.93%. Found: C, 76.10; H, 5.05; N, 7.03%. IR (KBr): 2985, 2952, 2885, 1447, 1342 cm^{-1} (N–Et); 1770 cm^{-1} (C=O group of lactone ring); 1696 cm^{-1} (C=O group of quinazolinone); 1597 cm^{-1} (C=N). ^1H NMR (CD_3COCD_3): 6.42–8.35 (19H, m, Ar–H); 4.08 (2H, s, –CH_2Ph); 3.22–3.45 (4H, q,

Table 2
Physical data for compounds (**C1–6**)

Compound number	Compound **C**			Yield (%)	m.p. (°C)	λ_{max} in 95% acetic acid	λ_{max} in Toluene	Colour on silica gel
	R	R_1	R_2					
C1	CH_3	H	H	74	147–150	496, 370, 255	290	Red
C2	Ph	H	H	68	109–111	532, 346, 278	289	Purple
C3	CH_2Ph	H	H	71	143–145	533, 356, 278	291	Purple
C4	CH_2Cl	H	H	66	125–128	532, 373, 277	290	Purple
C5	CH_3	NO_2	H	73	161–163	532, 343, 278	323	Purple
C6	CH_3	NO_2	Cl	72	180–182	554, 347, 283	346	Purple

N–CH_2–CH_3); 1.07–1.29 (6H, t, N–CH_2–CH_3). ^{13}C NMR ($CDCl_3$): 12.9, 30.1, 44.9, 83.9, 98.1, 105.1, 109.2, 112.0, 118.1, 121.1, 123.9, 124.2, 124.8, 125.6, 127.2, 127.5, 128.8, 129.0, 129.1, 129.3, 129.4, 130.2, 135.2, 135.4, 138.7, 147.8, 150.3, 152.9, 153.1, 155.1, 162.5, 169.4.

*6-Diethylamino-3-(2′-chloromethyl-4′-oxo-(3′-hydroquinazolin-3′-yl)) fluoran (**C₄**)*: Calculated for $C_{33}H_{26}ClN_3O_4$: C, 70.27; H, 4.64; N, 7.45%. Found: C, 70.79; H, 4.46; N, 7.52%. IR (KBr): 3086, 1340 cm^{-1} (CH_2Cl); 2987, 2952, 2887 cm^{-1} (N–Et); 1763 cm^{-1} (C=O group of lactone ring); 1693 cm^{-1} (C=O group of quinazolinone); 1598 cm^{-1} (C=N). ^{1}H NMR (CD_3COCD_3): 6.41–8.38 (14H, m, Ar–H); 4.22 (2H, s, CH_2Cl); 3.22–3.44 (4H, q, N–CH_2–CH_3); 1.08–1.27 (6H, t, N–CH_2–CH_3). ^{13}C NMR ($CDCl_3$): 12.9, 44.9, 51.2, 83.8, 98.1, 99.4, 105.1, 109.3, 117.5, 121.0, 121.3, 123.2, 123.3, 124.3, 124.9, 125.4, 127.2, 127.4, 127.6, 129.3, 130.2, 130.2, 135.2, 139.6, 147.9, 150.3, 153.2, 153.4, 154.2, 162.5, 169.8.

*6-Diethylamino-3-(2′-methyl-6′-nitro-4′-oxo-(3′-hydroquinazolin-3′-yl)) fluoran (**C₅**)*: Calculated for $C_{33}H_{26}N_4O_6$: C, 68.98; H, 4.56; N, 9.75%. Found: C, 69.58; H, 4.67; N, 9.65%. IR (KBr): 3167, 1347 cm^{-1} (CH_3); 2965, 2939, 2865 cm^{-1} (N–Et); 1756 cm^{-1} (C=O group of lactone ring); 1696 cm^{-1} (C=O group of quinazolinone); 1595 cm^{-1} (C=N); 1520 cm^{-1}, 1353 cm^{-1} (NO_2). ^{1}H NMR (CD_3COCD_3): 6.4–8.83 (13H, m, Ar–H); 3.20–3.44 (4H, q, N–CH_2–CH_3); 2.21 (3H, s, Ar–CH_3); 1.06–1.29 (6H, t, N–CH_2–CH_3). ^{13}C NMR ($CDCl_3$): 12.9,17.9, 45.0, 83.6, 97.9, 101.5, 106.7, 109.0, 110.1, 112.2, 120.9, 123.6, 124.5, 125.0, 127.7, 128.9, 129.5, 129.7, 129.8, 134.6, 136.4, 142.7, 150.0, 150.4, 151.8, 153.9, 154.3, 162.6, 169.8.

*6-Diethylamino-3-(7′-chloro-2′-methyl-6′-nitro-4′-oxo-(3′-hydroquinazolin-3′-yl)) fluoran (**C₆**)*: Calculated for $C_{33}H_{25}ClN_4O_6$: C, 65.08; H, 4.14; N, 9.20%. Found: C, 69.45; H, 4.01; N, 9.31%. IR (KBr): 3198, 1432, 1347 cm^{-1} (CH_3); 2982, 2954, 2882 cm^{-1} (N–Et); 1756 cm^{-1} (C=O group of lactone ring); 1693 cm^{-1} (C=O group of quinazolinone); 1595 cm^{-1} (C=N); 1520, 1353 cm^{-1} (NO_2). ^{1}H NMR (CD_3COCD_3): 6.48–8.73 (12H, m, Ar–H); 3.22–3.53 (4H, q, N–CH_2–CH_3); 2.19 (3H, s, Ar–CH_3); 1.08–1.28 (6H, t, N–CH_2–CH_3). ^{13}C NMR ($CDCl_3$) 12.9, 17.6, 45.1, 83.6, 97.9, 101.5, 105.7, 109.2, 110.1, 112.0, 120.7, 123.4, 125.0, 127.7, 128.9, 129.5, 129.7, 129.8, 134.6, 136.4, 142.7, 150.0, 150.4, 151.8, 153.9, 154.3, 162.6, 169.8.

2.3. Reversible thermal sensitive materials

Thermochromic materials described here comprise (a) an electron-donating chromatic organic compound; (b) a compound capable of reversibly accepting an electron or electrons from the electron-donating, one or more phenolic hydroxy group-containing compounds and derivatives thereof and carboxyl group-containing compounds and derivatives thereof; (c) a compound controlling the temperature and sensitivity of colouration/decolouration of the thermochromic material, such as one or more alcohols, esters, ketones, ethers, acid amides, and carboxylic acids. The compositions and the characteristics of the thermochromic materials are shown in Table 3.

2.3.1. Microencapsulation of reversible thermochromic materials

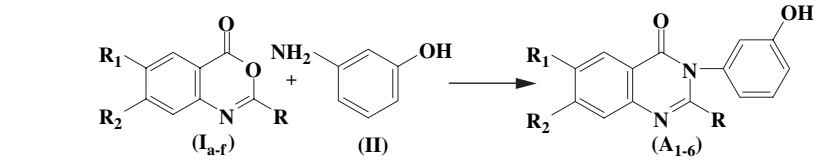
One gram of an epoxy resin (bisphenol-A diglycidyl polyether, average molecular weight: 378) was dissolved in 6 g of the thermochromic material prepared as mentioned above by heating at 80 °C. The solution was added dropwise to 30 g of aqueous solution of gelatin and stirred to yield fine droplets at 70 °C. Subsequently, a solution of 0.6 g of a hardener (amine adduct of epoxy resin) in 5 g of water was gradually added to the above solution, which was still being stirred at 70 °C. The resulting solution was further stirred for 4 h while maintaining the solution temperature at 80 °C. The epoxy resin reacts with the hardener at the interface between the droplet of the thermochromic materials and water, forming fine microencapsulated thermochromic solid materials. The solid polymeric materials (5–10 μm) were separated as a fine dry powder.

3. Results and discussion

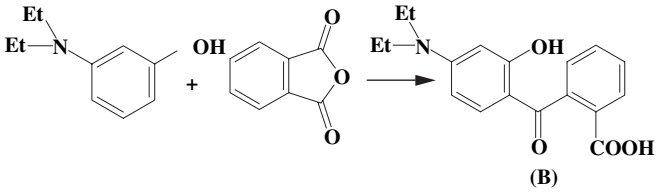
Reaction Scheme 1 outlines the synthesis of fluoran compounds (**C_{1-6}**). All the fluoran compounds have

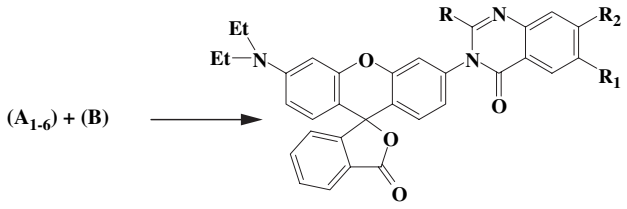
Table 3
Composition and colouration/decolouration of thermal sensitive materials

Thermochromic material			Temperature of colouration/decolouration (°C)
Component (a) (1 g)	Component (b), (2 g)	Component (c), (25 g)	
C_1	Bisphenol-A	Diphenyl ether	red $\overset{4-5}{\underset{12}{\rightleftharpoons}}$ colourless
C_1	Bisphenol-A	Lauryl alcohol	red $\overset{}{\underset{16}{\rightleftharpoons}}$ colourless
C_1	Bisphenol-A	Butyl stearate	red $\overset{}{\underset{40}{\rightleftharpoons}}$ colourless
C_1	Bisphenol-A	Lauric acid	red $\overset{}{\underset{44}{\rightleftharpoons}}$ colourless
C_1	Bisphenol-A	Benzophenone	red $\overset{}{\underset{48}{\rightleftharpoons}}$ colourless
C_1	Bisphenol-A	Cetyl alcohol	red $\overset{}{\underset{52}{\rightleftharpoons}}$ colourless
C_1	Bisphenol-A	Stearyl alcohol	red $\overset{}{\underset{70}{\rightleftharpoons}}$ colourless
C_1	Bisphenol-A	Stearic acid	red $\overset{}{\underset{80}{\rightleftharpoons}}$ colourless
C_1	Bisphenol-A	Acetamide	red $\overset{}{\underset{80}{\rightleftharpoons}}$ colourless
C_1	Bisphenol-A	Acetoacetanilide	red $\overset{}{\underset{120}{\rightleftharpoons}}$ colourless
C_1	Bisphenol-A	Benzamide	red $\overset{}{\underset{131}{\rightleftharpoons}}$ colourless
C_1	Bisphenol-A	Sebacic acid	red $\overset{}{\underset{149}{\rightleftharpoons}}$ colourless
C_1	Bisphenol-A	Adipic acid	red $\rightleftharpoons$ colourless
C_2	Bisphenol-A	Cetyl alcohol	purple $\overset{48}{\underset{48}{\rightleftharpoons}}$ colourless
C_3	Bisphenol-A	Cetyl alcohol	purple $\overset{48}{\underset{48}{\rightleftharpoons}}$ colourless
C_4	Bisphenol-A	Cetyl alcohol	purple $\overset{48}{\underset{48}{\rightleftharpoons}}$ colourless
C_5	Bisphenol-A	Cetyl alcohol	purple $\overset{48}{\underset{48}{\rightleftharpoons}}$ colourless
C_6	Bisphenol-A	Cetyl alcohol	purple $\overset{}{\underset{48}{\rightleftharpoons}}$ colourless



Where in
R = CH_3, Ph, CH_2Cl or CH_2Ph
R_1=H, NO_2 when R = CH_3
R_2 = H, Cl when R = -CH_3 and R_1 = NO_2





Wherein R, R_1, R_2, as above

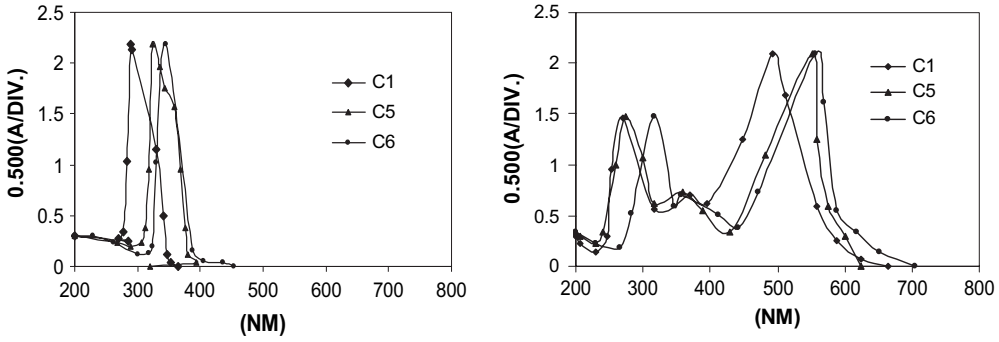
Reaction Scheme 1

been characterized by elemental analysis, UV, IR and ^{1}H NMR spectroscopy.

The IR spectra of all fluorans ($\mathbf{C_{1-6}}$) showed the disappearance of characteristic absorption band of the OH group and the appearance of the C=O group of the lactone ring at 1745–1790 cm^{-1} and at 1680–1700 cm^{-1} for the C=O group of 4(3*H*)-quinazolinone and other characteristic absorption bands for the rest of the molecules.

The absorption maxima in toluene and 95% acetic acid of all these fluoran compounds ($\mathbf{C_{1-6}}$) are shown in Fig. 1 and Table 2. The appearance of one peak in the spectrum of fluoran compounds in toluene is due to the lactone form while various peaks in the 95% acetic acid are due to quinone, zwitterions and lactone form as reported previously [29,30]. The solution of these compounds in toluene was free of colour and in contact with silica gel instantaneously forms a red to purple colour due to the acidic nature of silica gel.

Reversible thermal sensitive materials are themselves thermochromic, and they are also sensitive to some variables other than temperature, for example, a pH sensitive colourants. Functional dyes of this type tend to undergo a ring-opening reaction and change from a colourless to



λmax of $\mathbf{C_1}$, $\mathbf{C_5}$, $\mathbf{C_6}$ in toluene

λmax of $\mathbf{C_1}$, $\mathbf{C_5}$, $\mathbf{C_6}$ in 95% Acetic acid

Fig. 1. λ_{max} of $\mathbf{C_1}$, $\mathbf{C_5}$, and $\mathbf{C_6}$ in toluene and 95% acetic acid.

a coloured state when placed in contact with acid. The trick of inducing thermochromic effects into a colour former is to design a system in which the acidity experienced by the colourant varies with heating and cooling, and such a variation in turn leads to the colour of the system changing in response to differences in temperature. One means of achieving this requires the combined use of three components: (a) colour former; (b) colour developer; and (c) non-polar co-solvent (that controls the interaction between (a) and (b)). When three components (a), (b) and (c) are heated and mixed together in the correct proportions so that the colour former and developer are dissolved in the co-solvent and the solution then cooled, the solid composite formed is intensely coloured. Heating the composition above its melting points (determined largely by that of the co-solvent) results in complete colour loss. The colour change is reversible; the point at which it occurs corresponds closely to the range of temperature at which the formulation melts. Since these systems involve changes in the phase between coloured solid and colourless liquid states, the necessity for microencapsulation stems from the need to maintain the ratio of the components in the formulation so that the thermochromic properties do not suffer [1].

The compositions and characteristics of the thermochromic materials are shown in Table 3. Component (a), $\mathbf{C_1}$ and component (b), bisphenol-A were kept fixed and varying the third component various thermochromic compositions have been prepared which shows colouration/decolouration range from temperature 5 to 149 °C. When thermochromic composition is prepared from component (b), bisphenol-A and component (c), cetyl alcohol was kept fixed and varying the component (a), $\mathbf{C_2}$–$\mathbf{C_6}$ observed that a change in the colour is purple to colourless at temperature 48 °C. The development of colour in this colour formation reaction depends on the substitution on the fluoran compounds; the substitution on the 4(3*H*)-quinazolinone moieties also effects the development of colour formation reaction, such as $\mathbf{C_1}$ is a red while $\mathbf{C_2}$–$\mathbf{C_6}$ is purple.

4. Conclusion

The 3,6-disubstituted chromogenic fluoran compounds of the present investigation are highly soluble in organic solvent without producing a colour and show spontaneous colour-forming property in aqueous acid solution and acidic colour-activating substance such as silica gel. The reversible thermochromic material was colourless in a disordered state and coloured in an ordered state. The development of colour in this colour formation reaction depends on the substitution on the fluoran compounds; the substitution on the 4(3*H*)-quinazolinone moieties also effects the development of colour formation reaction, such as $\mathbf{C_1}$ is red while $\mathbf{C_2}$–$\mathbf{C_6}$ is purple.

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