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ORIGINAL ARTICLE

Studies on inclusion complexes of 2,4-dinitrophenol, 2,4-dinitroaniline, 2,6-dinitroaniline and 2,4-dinitrobenzoic acid incorporated with β-cyclodextrin used for a novel UV absorber for ballpoint pen ink

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Abstract The inclusion complexes of β-cyclodextrin with different dinitrocompounds like 2,4-dinitrophenol, 2,4-dinitroaniline, 2,6-dinitroaniline and 2,4-dinitrobenzoic acid appears the UV absorption bands in different wavelength region below 400 nm, a combination of these dinitro aromatic compounds of inclusion complexes can improve the UV protection properties of ball point pen ink against photo degradation. The formation of inclusion complexes were characterized by FT-IR, ^{1}H NMR and 2D ROESY NMR spectroscopy. The UV protecting properties of these inclusion complexes were calculated their sun protection factor was discussed. The stability of the ballpoint pen ink has been confirmed by UV–visible spectroscopic method.

Keywords UV absorber · Sun protection factor · Ballpoint pen ink · Inclusion complex · β-cyclodextrin · 2D ROESY NMR

Introduction

Nowadays, everyone using ball point pen to write down a document. Ball point pens containing oil-based inks and whose colorants are based on dyes. If photo unstable compounds presents in the inks composition, such as the methyl violet family, whenever the ink on the paper is exposed to light and it decomposed automatically, while sometimes even appreciating, at first sight, a loss of color [1]. This decomposition even takes place in the dark, ought to the oxidative action of the oxygen in the atmospheric air.

Ink analysis is an important forensic procedure that can reveal useful information about questioned documents [2]. Most of its applications regard the detection and confirmation of alterations to documents with significant financial value [3]. It is therefore evident that there is a great need for improve the stability of the ink. In order to improve the photo stability of the ink by adding UV absorber. For preparation of UV stabilized ball point ink; both organic and inorganic UV absorbers can be used, but unfortunately no single UV absorber exhibits an ideal absorption behavior [4]. Therefore, a remarkable increase in performance can be achieved by the combination of the two or more UV absorbers. This can be achieved by the combination of dinitrophenol, dinitroaniline and dinitrobenzoic acid as UV absorber.

Cyclodextrins are cyclic oligosaccharides comprised (usually) of 6–8 D-glucopyranoside units linked by a 1,4-glycosidic bond [5–10]. The cyclodextrin families are α-cyclodextrin (α-CD), β-cyclodextrin (β-CD) and γ-cyclodextrin (γ-CD), in this three CDs shows an amphiphilic character; due to an apolar cavity and a hydrophilic annulus consisting of a number of hydroxyl groups. Hence, these CDs have attracted considerable interest because of their ability to form a stable inclusion complex with variety of inorganic and organic guest molecules in aqueous solution. Because of their unusual structure, CDs can form inclusion complexes through noncovalent interactions with molecules that fit into the cavity.

Prabhumirashi and Kunte [11] were also studied the dinitrophenol, dinitroaniline and dinitrobenzoic acid are having the intramolecular interactions with $-NO_2$ group. This group is to modify the electronic spectrum of benzene

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in a drastic manner by causing a large red shift of the L_a band to such an extent as to mask almost completely the L_b band. The electronic spectrums indicating that, all the compounds are best charge transfer (CT) character. The other groups, viz. –COOH, –OH and $–NH_2$, in these systems of trisubstituted benzenes are chosen, so as to have a gradation in their electron donating abilities, viz. very weak, mild and strong donors, respectively. The mixture of above compounds will give broad absorption spectra in the range of 210–410 nm. In order to increase the absorption intensities of the above compounds by preparing their inclusion complexes with β-CD. In UV–Vis spectra, the included guest molecules to gives a hypsochromic or bathochromic shift and increases in the absorptivity without change in the λ_{max} have been considered as evidence for interaction between cyclodextrin and the guest molecules in the formation of the inclusion complex processes [12]. Scalia et al. [13, 14] have been studied the inclusion complex of β-CD with sunscreen lotion.

The aim of this work is to study the inclusion complex formation of different dinitro aromatic compounds with β-CD and it was characterized by FT-IR, ^{1}H NMR and 2D ROESY NMR technique and also we have investigated the feasibility of ultraviolet (UV) protection of ball point ink by UV–Vis spectroscopy.

Materials and methods

Instruments

The UV–Vis spectra (absorption and transmittance measurements) were carried out with Shimadzu UV-2401PC double-beam spectrophotometer (range 1,100–200 nm) with scan speed at 400 nm/min, ^{1}H NMR spectra were taken by BRUKER-NMR 500 MHz instrument operating at 300 K using a 5 mm probe. The sample solutions for ^{1}H NMR were prepared by dissolving the dinitro compounds and their complexes in D_2O solvent to obtain the final concentration of 20 mM. Two-dimensional rotating-frame Overhauser effect spectroscopy (ROESY) experiments were performed by BRUKER-NMR 400 MHz instrument operating at 300 K and the standard Bruker program was used, DMSO-d6 was used as a solvent, relaxation delay of 1 s and mixing time 300 ms under the spin lock conditions. FT-IR was recorded using Nicolet 380 Thermo Electron Corporation Spectrophotometer using KBr pellets and scan between 4000 and 400 cm^{-1}.

Materials

β-CD was obtained from Sd fine chemical company, 2,4-DNP was purchased from Loba chemical reagents company, 2,6-DNA, 2,4-DNA and 2,4-DNB were obtained from Alfa Aesar. All the chemicals are used without further purification. Ethylene glycol (SRL chemicals) was used to prepare a gel with mixture of dinitrocompounds of inclusion complex for SPF analysis. Reynolds liquiflo^{TM} ball point pen purchased from local shop, 3 M Micropore^{TM} medical Tape was purchased from local medical shop. The stock solutions were prepared at each of 2,4-DNP, 2,4-DNA, 2,6-DNA and 2,4-DNB is 0.01 mol/L concentration in methanol.

Preparation of inclusion complex of dinitrocompounds with β-CD

Accurately weighed 1 mole equivalent of host (β-CD) was placed into 100 mL conical flask and 30 mL triply distilled water was added and then oscillated this solution up to completely dissolve the β-CD. After that 1 mole equivalent of guest was put into another 10 mL beaker and 5 mL ethanol was added and put over electromagnetic stirrer to stir until it was dissolved [15]. Then guest solution was slowly poured into β-CD solution. The above mixed solution was stirred for 48 h at room temperature. The reaction mixture was kept into the refrigerator for 48 h. At this time, a yellow precipitate (for 2,4-DNP, 2,4-DNA and 2,6-DNA) and a white precipitate (for 2,4-DNB) was formed. The precipitate was filtered by G4 crucible and washed with triply distilled water. The precipitate was taken in a Petri dish and spread over as thin layer and then dried in oven at 50 °C for 12 h. After dried in oven the powder was obtained and it was further analyzed by FT-IR, ^{1}H NMR and 2D ROESY NMR. Our previous work [15] of 2,4-DNP and it inclusion complex studies was published. So that the FT-IR and ^{1}H NMR figures and it related discussions are not shown in this manuscript, even though 2,4-DNP and β-CD inclusion complex was focused for UV absorber studies only in this manuscript.

Measurement of UV protective properties

In vitro SPF analysis; the commercially available 3 M Micropore^{TM} white medical tape (Supplementary Fig. 1). was used as substrate. It is fairly transparent in the ultraviolet and simulates the porosity and texture of human skin. 3 M Micropore^{TM} tape was placed in a single layer on clean 0.2 cm thick quartz slide. The area of the tape was 12.5 cm^2. This layered quartz slide was put over the input optics of the UV–Vis spectrophotometer and the intensity of radiation transmitted through the tape was measured automatically by recording the photocurrent signal at 5 nm steps from 290 to 400 nm. The recommended amount of UV absorber to apply on the tape as per FDA and COLIPA in vivo methodologies is 2 mg/cm^2 or 2 μL/cm^2 [16]. 0.780 g of equal weight of 2,4-DNP, 2,4-DNA, 2,6-DNA

and 2,4-DNB mixture (each of 0.195 g) were taken in a mortar followed by 1 mL of ethylene glycol was added and made it as a cream like consistency. Thirty-two microlitre (25 mg) of cream was applied on the 3 M Micropore tape by "spotting" the sample several sites over the 12.5 cm^2 area. A gloved finger was used to achieve as uniform thickness as possible. The SPF value was predicted from the transmission measurements according to Diffey and Robson [17].

$$SPF = \frac{\int_{290}^{400} E_\lambda S_\lambda d\lambda}{\int_{290}^{400} E_\lambda S_\lambda d\lambda / PF(\lambda)} \quad (1)$$

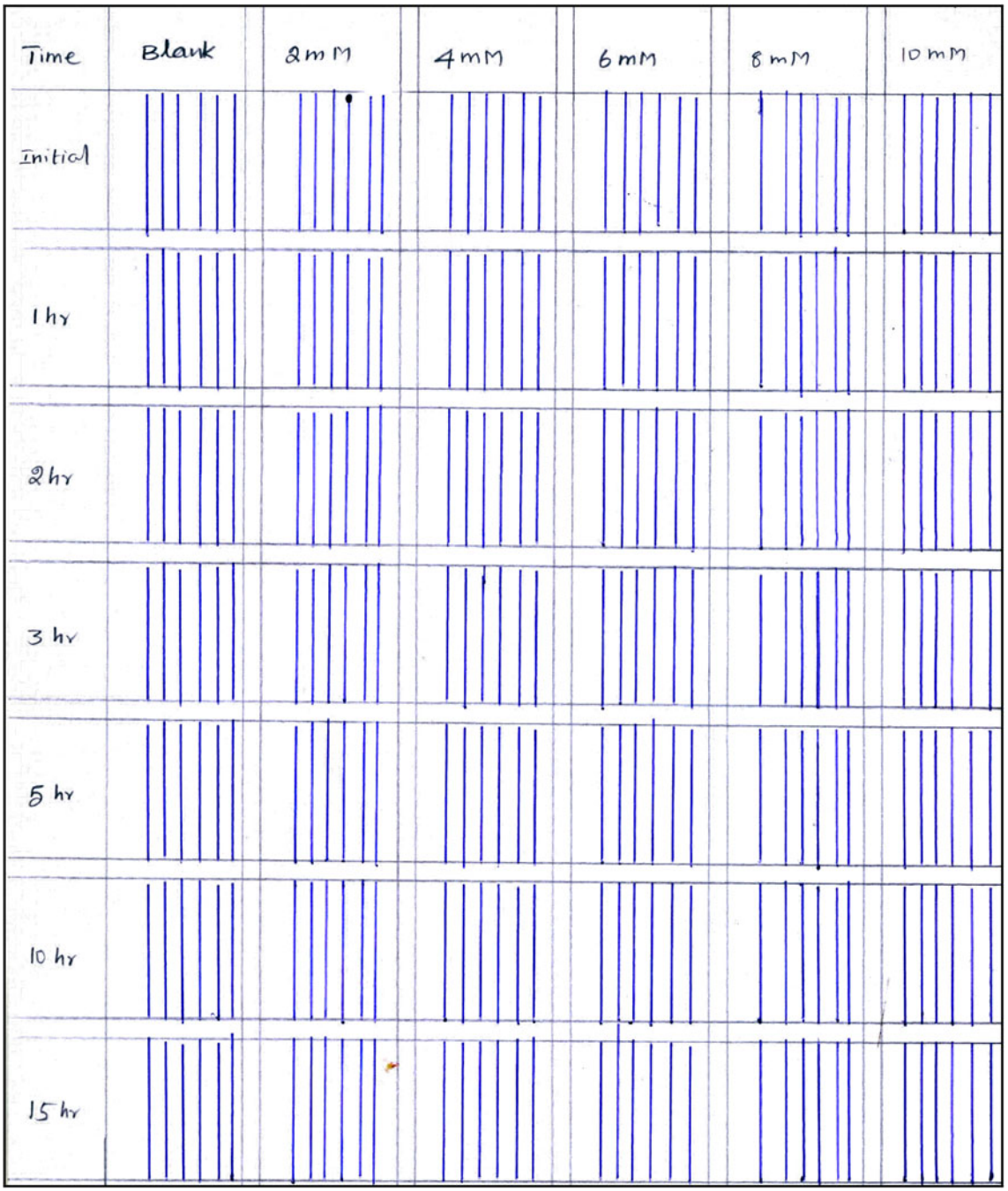

Fig. 1 Line pattern drawn on a white paper using ballpoint pen ink

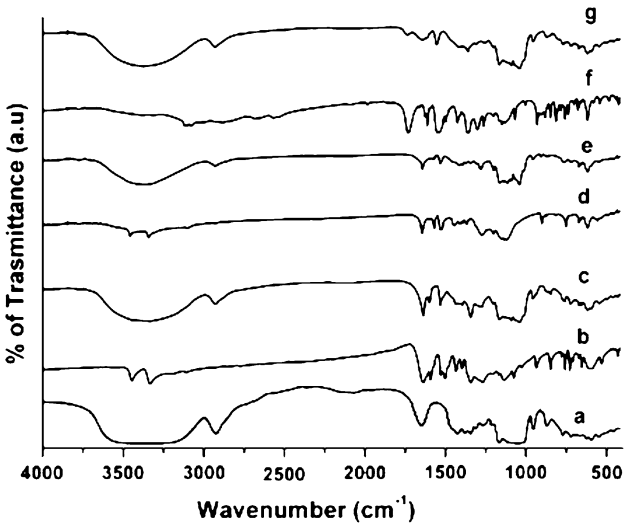

Fig. 2 The FT-IR spectra of **a** β-CD, **b** 2,4-DNA, **c** inclusion complex of 2,4-DNA-β-CD, **d** 2,6-DNA, **e** inclusion complex of 2,6-DNA-β-CD, **f** 2,4- DNB and **g** inclusion complex of 2,4-DNB- β-CD

where E_λ is the erythema action spectrum, S_λ is the spectral irradiance (wm^{-2} nm^{-1}), $PF(\lambda)$ is the mean monochromatic protection factors.

Preparation of UV absorber loaded ballpoint pen

The ball point pen ink was collected from the Reynolds liquiflo^{TM} pen and 1 mL of UV absorber (2 mM in methanol) was added, further it was sonicated for uniform mixing, and then solvent was evaporated up to retain the consistency of ball point ink. Finally the absorber loaded ink was injected into the empty refill tube using 2 mL syringe. Same procedure was followed for loading of UV absorber into four empty refill tubes as following concentration of 4, 6, 8 and 10 mM of solutions were used. The above prepared ballpoint pen ink was tested with write down on a white paper, using these pens drawn an equal lines pattern are shown in Fig. 1. Before and after exposure to the sunlight, the written portions

Table 1 FT-IR absorption bands of 2,4-DNA, 2,6-DNA and 2,4-DNB in free and complexed state determined using KBr pellet

S. no.	Functional group	2,4-DNA		2,6-DNA		2,4-DNB	
		Free (cm^{-1})	Complex (cm^{-1})	Free (cm^{-1})	Complex (cm^{-1})	Free (cm^{-1})	Complex (cm^{-1})
1	NO_2	1,585	1,589	1,562	1,564	1,544	1,531
		1,332	1,332	1,359	1,365	1,350	1,352
2	CN(NO_2)	833	835	889	892	835	858
3	CN(NH)	1,257	1,273	1,266	1,269	–	–
4	–C=C–	1,627	1,629	1,635	1,637	1,618	1,631
5	COOH	–	–	–	–	1,722	1,728

Table 2 ^{1}H NMR chemical shifts of β-CD, 2,4-DNA, 2,6-DNA and 2,4-DNB in free and complexed state determined in D_2O at 300 K

Name of the substance	Protons	Free	Complex					
			2,4-DNA-β-CD		2,6-DNA-β-CD		2,4-DNB- β-CD	
			δ (ppm)	Δδ	δ (ppm)	Δδ	δ (ppm)	Δδ
β-CD	H_1	4.966	4.965	−0.001	4.964	−0.002	4.963	−0.003
	H_2	3.554	3.555	−0.001	3.553	−0.002	3.553	−0.001
	H_3	3.877	3.855	−0.022	3.860	−0.017	3.854	−0.023
	H_4	3.535	3.528	−0.007	3.476	−0.002	3.476	−0.002
	H_5	3.748	3.734	−0.014	3.736	−0.012	3.727	−0.021
	H_6	3.797	3.796	−0.001	3.796	−0.001	3.796	−0.001
2,4-DNA	H_a	8.982	8.908	−0.074	–		–	–
	H_c	8.105	8.086	−0.019				
	H_d	6.982	6.905	−0.077				
2,6-DNA	H_a	8.335	–		8.285	−0.050	–	–
	H_b	7.080			6.996	−0.084		
2,4-DNB	H_b	9.310	–		–		9.265	−0.045
	H_c	8.810					8.786	−0.024
	H_d	8.654					8.585	−0.069

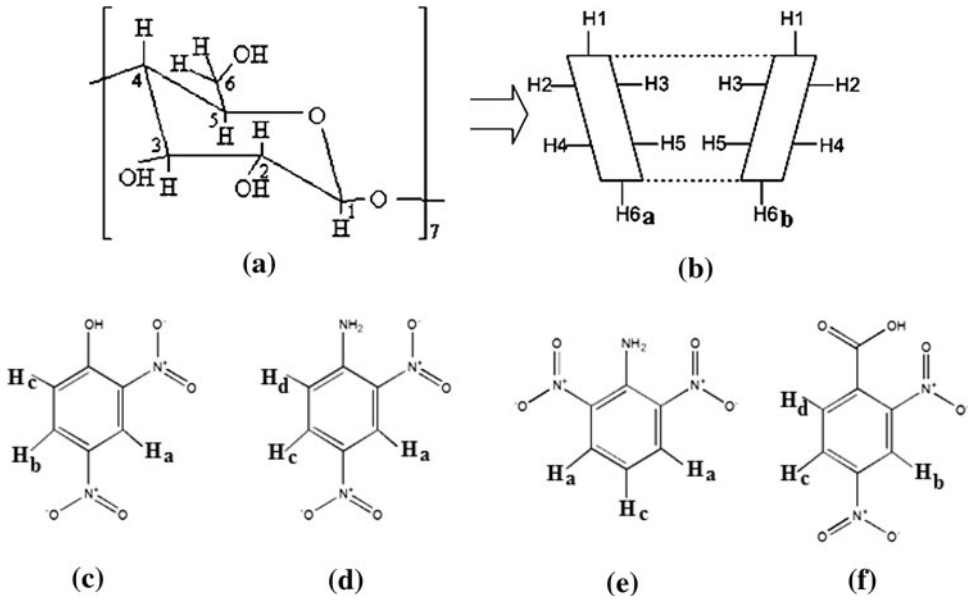

Fig. 3 **a** The stereo-configuration of β-CD **b** truncated-cone of β-CD, **c** 2,4-DNP, **d** 2,4-DNA, **e** 2,6-DNA and **f** 2,4-DNB

of the paper cut off and it was soaked in methanol. Then the absorbance value was measured for initial and same procedure was followed after 1, 2, 3, 5, 10, and 15 h for written portion of the paper. This experiment was carried out on exposure to the sunlight at 10.00 am to 12.00 Noon for 15 h (per day 2 h only) and different temperature was recorded (Supplementary Table 1).

Results and discussion

FT-IR spectral studies

The inclusion complex formation has been analyzed by FT-IR spectroscopy (Fig. 2) because the bands resulting from the included part of the guest molecule are generally shifted or their intensities altered [18]. Figure 2 shows the FT-IR spectra of (a) β-CD, (b) 2,4-DNA, (c) inclusion complex of 2,4-DNA (d) 2,6-DNA (e) inclusion complex of 2,6-DNA, (f) 2,4-DNB and (g) inclusion complex of 2,4-DNB.

The complexation between the dinitro compounds and β-CD can be determined by comparing the FT-IR spectra of free and complexed [19] form of dinitro compounds. The Table 1 and Fig. 2 show the FT-IR bands of free and complexed form of dinitro compounds. The two characteristics stretching of $–NO_2$ peaks of 2,4-DNA (1,585, 1,332 cm^{-1}), 2,6-DNA (1,562, 1,359 cm^{-1}) and 2,4-DNB (1,531, 1,350 cm^{-1}) were observed in free state. These peaks are shifted and the intensities are reduced in the complexed form of 2,4-DNA (1,589, 1,332 cm^{-1}), 2,6-DNA (1,564, 1,365 cm^{-1}) and 2,4-DNB (1,544, 1,352 cm^{-1}). This is due to the nitro groups are included into the β-CD cavity. The characteristics stretching vibration of C–N (–NH) was appeared in 2,4-DNA (1,257 cm^{-1}) and 2,6-DNA (1,265 cm^{-1}) and it was shifted in the complexed form of 2,4-DNA (1,263 cm^{-1}) and 2,6-DNA (1,269 cm^{-1}) and also their intensities are decreased. This is due to the phenyl group of 2,4-DNA and 2,6-DNA was included into the β-CD cavity. In 2,4-DNB the COOH band appeared at 1,722 cm^{-1} and it was shifted in complexed form at 1,726 cm^{-1} and it intensity was decreased. Due to the aromatic COOH group was included into the upper rim of the β-CD. The characteristics stretching vibration of C–N ($–NO_2$) was appeared in 2,4-DNA (833–835 cm^{-1}), 2,6-DNA (889–892 cm^{-1}) and 2,4-DNB (835–858 cm^{-1}) was observed and it was shifted in complexed form, also their intensities are reduced, due to the nitro groups are included into the β-CD cavity. The characteristics stretching of –C=C– peaks of aromatic nuclei of 2,4-DNA (1,627–1,629 cm^{-1}), 2,6-DNA (1,635–1,637cm^{-1}) and 2,4-DNB (1,618–1,631 cm^{-1}) was observed and it was shifted, also their intensities are reduced. Due to the hydrophobic part of benzene ring (2,4-DNA, 2,6-DNA and 2,4-DNB) was included into the β-CD cavity. From the above fact the 2,4-DNA, 2,6-DNA and 2,4-DNB are forms an inclusion complex with β-CD.

^{1}H NMR spectral studies

The formation of inclusion complex can be analyzed by ^{1}H NMR spectroscopy method [20]. The typical ^{1}H NMR spectra of β-CD, 2,4-DNA, 2,6-DNA, 2,4-DNB and their inclusion complexes were studied in D_2O. The chemical shifts (δ) values for different protons of β-CD, dinitro compounds and their inclusion complexes were listed in Table 2.

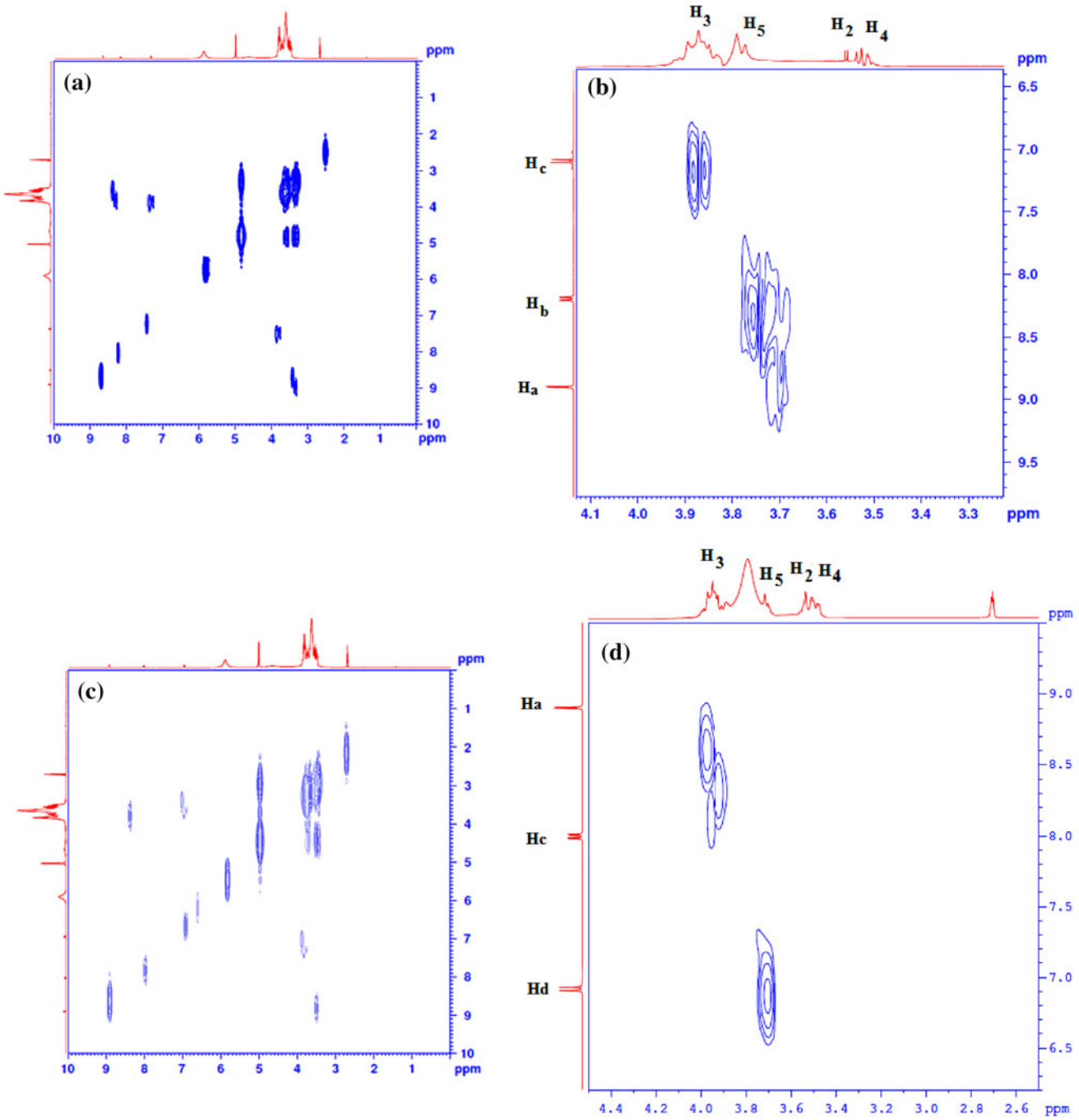

Fig. 4 The 2D ROESY spectrum of inclusion complex of **a** 2,4-DNP:β-CD, **b** partial counter plots of 2,4-DNP:β-CD **c** 2,4-DNA:β-CD, **d** partial counter plots of 2,4- DNA:β- CD, **e** 2,6- DNA:β-CD, **f** partial counter plots of 2,6-DNA:β-CD, **g** 2,4-DNB: β-CD, **h** partial counter plots of 2,4-DNB:β- CD in DMSO-d6 at 300 K

^{1}H NMR spectra of inclusion complex for the H_3 and H_5 protons appears in great upfield region, because the guest molecule located into the nano hydrophobic cavity of β-CD (Fig. 3a, b). The changes of chemical shift (Δδ) of H_3 and H_5 protons (Table 2) of β-CD in 2,4-DNA: β-CD, 2,6-DNA: β-CD, and 2,4-DNB: β-CD are suggested that the 2,4-DNA, 2,6-DNA and 2,4-DNB were present in the nano hydrophobic cavity of β-CD. Similarly, the chemical shifts of 2,4-DNA protons (H_a, H_c and H_d), 2,6-DNA protons (H_a, and H_c) and 2,4-DNB protons (H_b, H_c and H_d), which is located in the nano hydrophobic cavity of β-CD and which was also appeared in upfield (Table 2) region significantly the interaction between 2,4-DNA, 2,6-DNA and 2,4-DNB (Fig. 3d, e, f) with β-CD. The significant

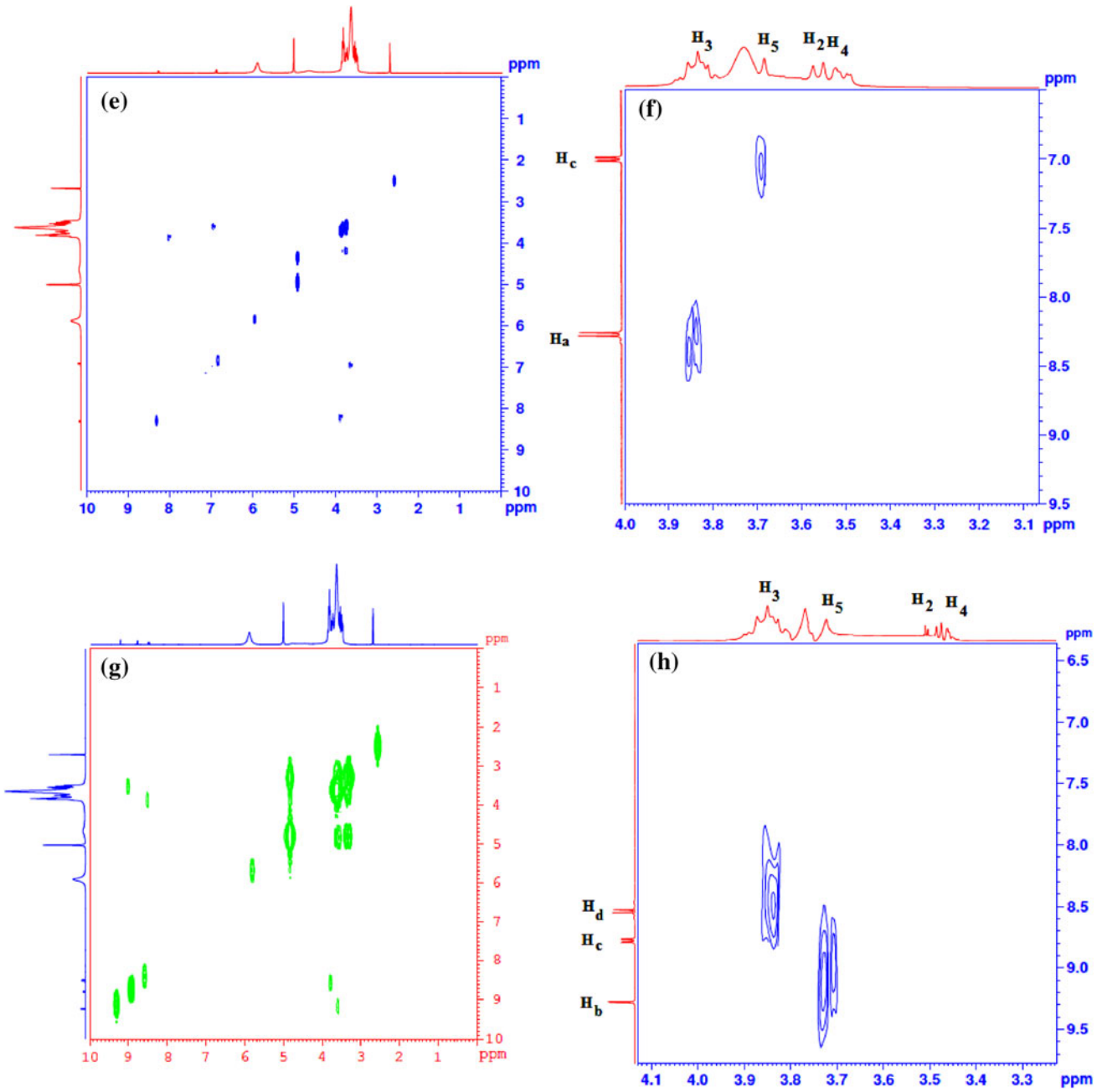

Fig. 4 continued

distinguish for these ^{1}H NMR spectra strongly confirmed that the inclusion complex formation between aromatic dinitro compounds and β-CD.

2D ^{1}H NMR studies (ROESY)

The 2D ROESY NMR is a powerful technique for investigation of inter and intra molecular intractions. The chemical shift changes was shown by H_a, H_b, H_c and H_d protons of aromatic (hydrophobic part) moiety [21] of dinitro compounds may play a major role in the inclusion process. To verify this hypothesis, 2D ROESY NMR spectra were recorded. The presence of NOE cross-peaks between protons of two different species in 2D ROESY spectrum is an indication that they are in spatial contact through space within the cavity of β-CD.

Figure 4 shows the 2D spectrum of (a) 2,4-DNP: β-CD, (b) 2,4-DNA:β-CD, (c) 2,6-DNA:β-CD and (d) 2,4-DNB: β-CD systems, two groups of intermolecular NOE cross-peaks were observed. In the complexes of 2,4-DNP:β-CD,

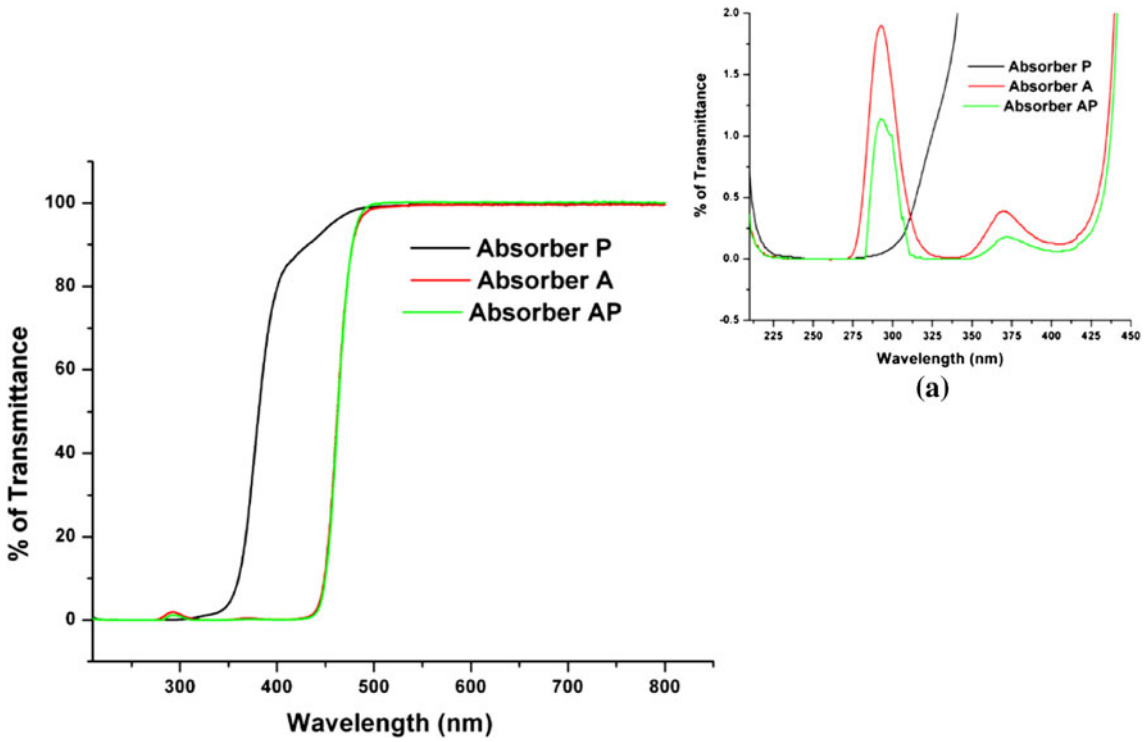

Fig. 5 UV transmittance spectra of absorber P, absorber A and absorber AP in methanol (Conc. 0.01 mol/L). *Inset a* magnification at 200–450 nm

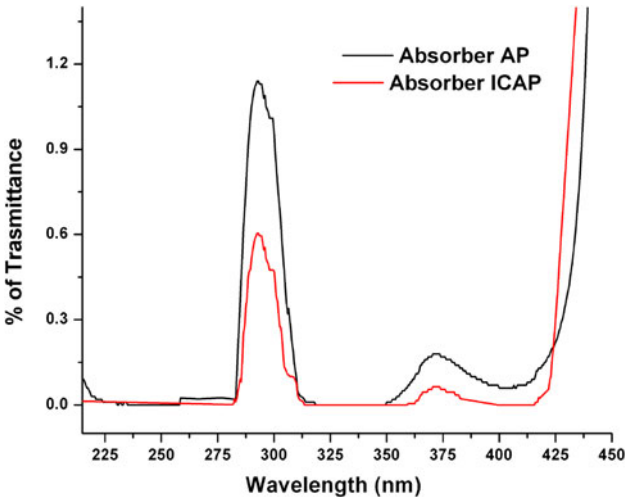

Fig. 6 UV transmittance spectra of absorber AP and absorber ICAP in methanol (Conc. 0.01 mol/L)

2,4-DNA:β-CD, 2,6-DNA:β-CD and 2,4-DNB:β-CD, the first peak was assigned to the interaction between the H_3 protons of β-CD with ortho positioned protons of the 2,4-DNP, 2,4-DNA and 2,4-DNB. The another peak was assigned to the interaction between the H_5 protons of β-CD with meta positioned protons of the 2,4-DNP, 2,4-DNA and 2,4-DNB.

In 2,6-DNA:β-CD complex also two groups of inter molecular NOE cross peaks were observed. The first NOE peak belongs to the interaction between the H_3 proton of β-CD with the meta positioned protons of 2,6-DNA and the another NOE peak was assigned the interaction between the H_5 protons of β-CD with the para positioned proton of 2,6-DNA. In all cases the interaction of dinitro compounds with only internal protons of β-CD were observed. In addition the H_{6ab} protons of β-CD were not affected by the inclusion process. So that we can confirmed that the dinitro compounds are included into the β-CD cavity via wider rim. From the above fact the dinitro compounds are interact with β-CD through space contact, not by bonding.

Ultraviolet transmittance spectra of absorbers

The UV transmittance spectra of the mixture of 2,4-DNP and 2,4-DNB (Absorber P), 2,4-DNA, 2,6-DNA and 2,4-DNB mixture (Absorber A) and 2,4-DNP, 2,4 DNA, 2,6-DNA and 2,4-DNB mixture (Absorber AP) as UV absorber were investigated in methanol (Fig. 5). Absorber AP shows more absorbance in the range 400–290 nm when compared with absorber P and absorber A. The transmittance spectra of absorber P appears in the visible region; it transmits 100 % visible light and it transmits 20–80 % of

Table 3 Sun protection factor for two commercial sunscreen lotions (Melascreen™ and Ayur™), with and without inclusion complex of dinitrocompounds

Wavelength (nm)		Sunscreen lotion		Without inclusion	Inclusion complex
		Melascreen™	Ayur™		
UVA (315–400 nm)	400	16.1968	21.4739	11.5965	14.9616
	395	16.7161	23.7274	11.6519	14.9096
	390	17.0610	25.9198	11.7466	14.8331
	385	17.3237	28.0100	11.8894	14.7621
	380	17.5486	29.8223	12.0731	14.7029
	375	17.7155	30.0899	12.3055	14.6892
	370	17.9412	30.6750	12.5678	14.7398
	365	18.1449	32.3590	12.7897	14.8657
	360	18.2202	31.3761	12.9931	14.9346
	355	18.3956	31.1677	13.2025	15.0616
	350	18.6913	31.2255	13.3495	15.2029
	345	18.9574	31.0623	13.4552	15.2738
	340	18.0783	31.0855	13.5348	15.2611
	335	18.2339	31.0020	13.5985	15.1900
	330	18.4526	31.9259	13.6642	15.0602
	325	18.5335	31.5455	13.7236	14.8582
	320	18.5749	31.7496	13.8128	14.6283
	315	18.5989	30.6587	13.9075	14.3829
UVB (290–315 nm)	310	18.5971	30.5525	14.0221	14.1338
	305	18.6796	32.5121	13.9348	14.1634
	300	18.6195	31.4403	13.8167	14.3306
	295	18.7374	31.3045	13.8537	14.5773
	290	18.7166	31.1653	14.1187	14.9324
SPF		18.1	30.1	13.1	14.8
Labeled SPF		18	30	–	–

UV light in the UVA (315–400 nm) region. The transmittance spectra of absorber A was observed in the visible region; it transmits 100 % visible light, in UVA region it transmits 0.4 % of UV light and it transmits 2 % of UV light in the UVB (290–315 nm) region. The transmittance spectra of absorber AP was observed in the visible region; it transmits 100 % of visible light and it transmits 0.2 % of UV light in the UVA region, in the UVB region it transmits 1 % of UV light. The UVB region is very harmful, so that; in order to increase the absorbance capacity of these compounds by preparation of their inclusion complexes with β-CD. Figure 6 shows the transmittance spectra of inclusion complexes of mixture of dinitro compounds (ICAP). In the UVB region it allows to transmit 0.58 % of UV light only and in the UVA region 0.1 % of UV light was transmitted, most of the UV light absorbed by the absorber ICAP; when compared with absorber AP, it was absorbs the UV light two fold more in the region of UVA and UVB. From the Figs. 5 and 6 the absorber A, absorber P, and absorber AP are less UV absorption behavior, but in the absorber ICAP is a very good UV absorber in this system.

In vitro SPF determination by spectrophotometry

SPF is defined as the increase in exposure time required to induce erythema. Table 3 shows that the SPF values of two commercial sunscreen products (Melascreen™ and Ayur™), with and without inclusion of dinitrocompounds. The two commercial sunscreens are tested by in vitro SPF spectrophotometry method; in that case there was close agreement between the in vitro SPF determined and the labeled SPF value of sunscreen products. So that the present method was calibrated using these sunscreens (Melascreen™ and Ayur™). In this method the SPF value of mixture of dinitrocompounds and inclusion complexes were calculated according to the Eq. (1). The SPF value of inclusion complex was higher than that of without inclusion complex. This is due to the included guests should

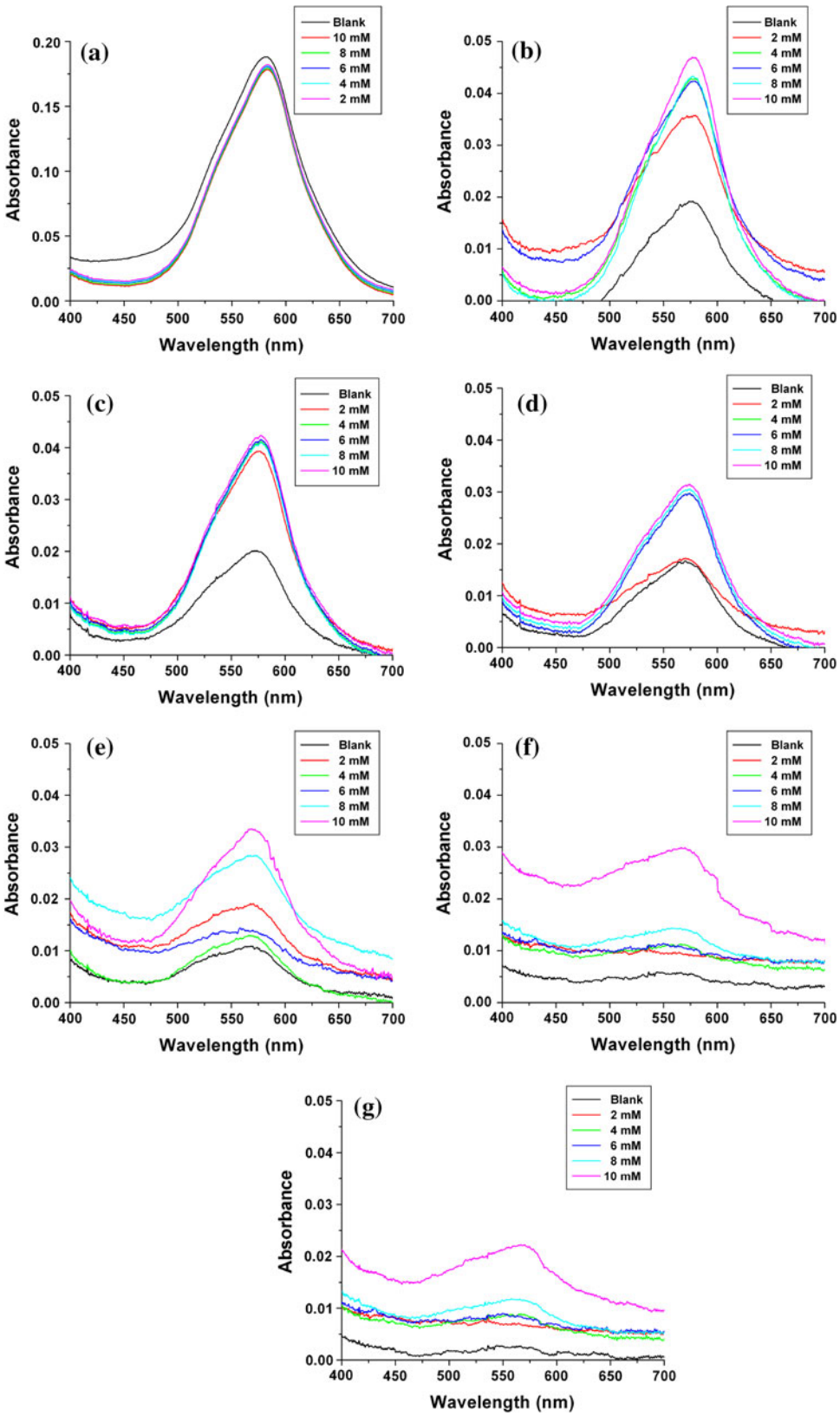

Fig. 7 Absorption spectra of ball point ink in methanol at different time **a** initial (Absence of sunlight), **b** 1 h, **c** 2 h, **d** 3 h, **e** 5 h, **f** 10 h and **g** 15 h exposure on sunlight with and without UV absorber

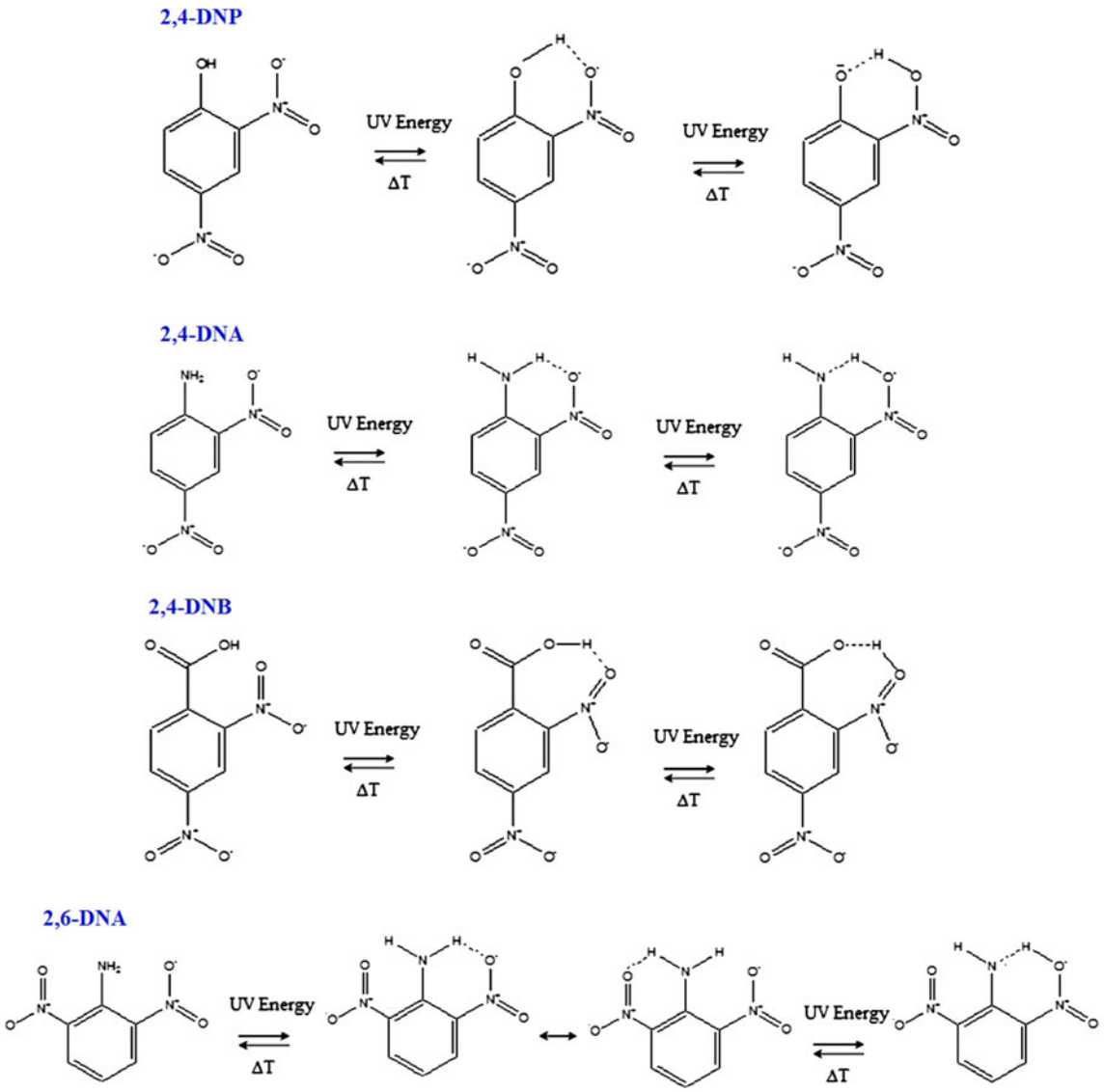

Fig. 8 UV absorption mechanism for 2,4-DNP, 2,4-DNA, 2,6-DNA and 2,4-DNB

Table 4 The stability percentage of ballpoint ink with exposure on sunlight at 0, 1, 2, 3, 5, 10 and 15 h time interval for blank, 2, 4, 6, 8 and 10 mM concentration of UV absorber respectively

Time (h)	Concentration of UV absorber						Sample-blank %
	Blank	2 mM	4 mM	6 mM	8 mM	10 mM	
Percentage of ink retained at the time of exposure on sunlight							
0	100	100	100	100	100	100	–
1	10.1	20.0	23.6	23.7	23.9	25.8	15.7
2	9.0	17.3	18.8	20.2	21.7	24.2	15.2
3	7.4	8.0	9.2	11.0	16.2	22.8	15.4
5	4.3	7.1	7.5	10.2	15.5	20.8	16.6
10	3.1	4.9	5.7	5.2	9.1	17.7	14.7
15	2.9	3.0	3.5	3.9	8.8	15.1	12.2
Average value of sun protection percentage = 15.0							

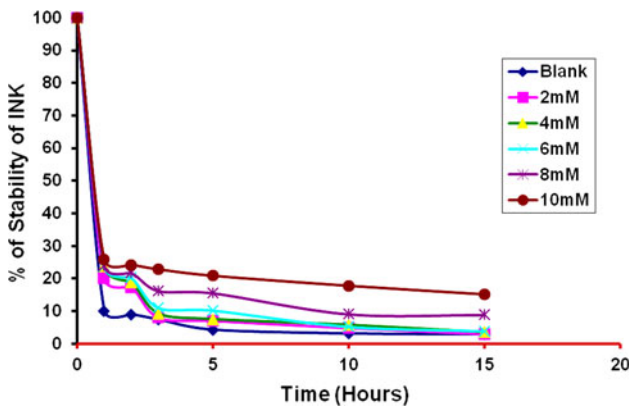

Fig. 9 The stability percentage of ballpoint ink with exposure on sunlight at 0, 1, 2, 3, 5, 10 and 15 h time interval for blank, 2, 4, 6, 8 and 10 mM concentration of UV absorbers respectively

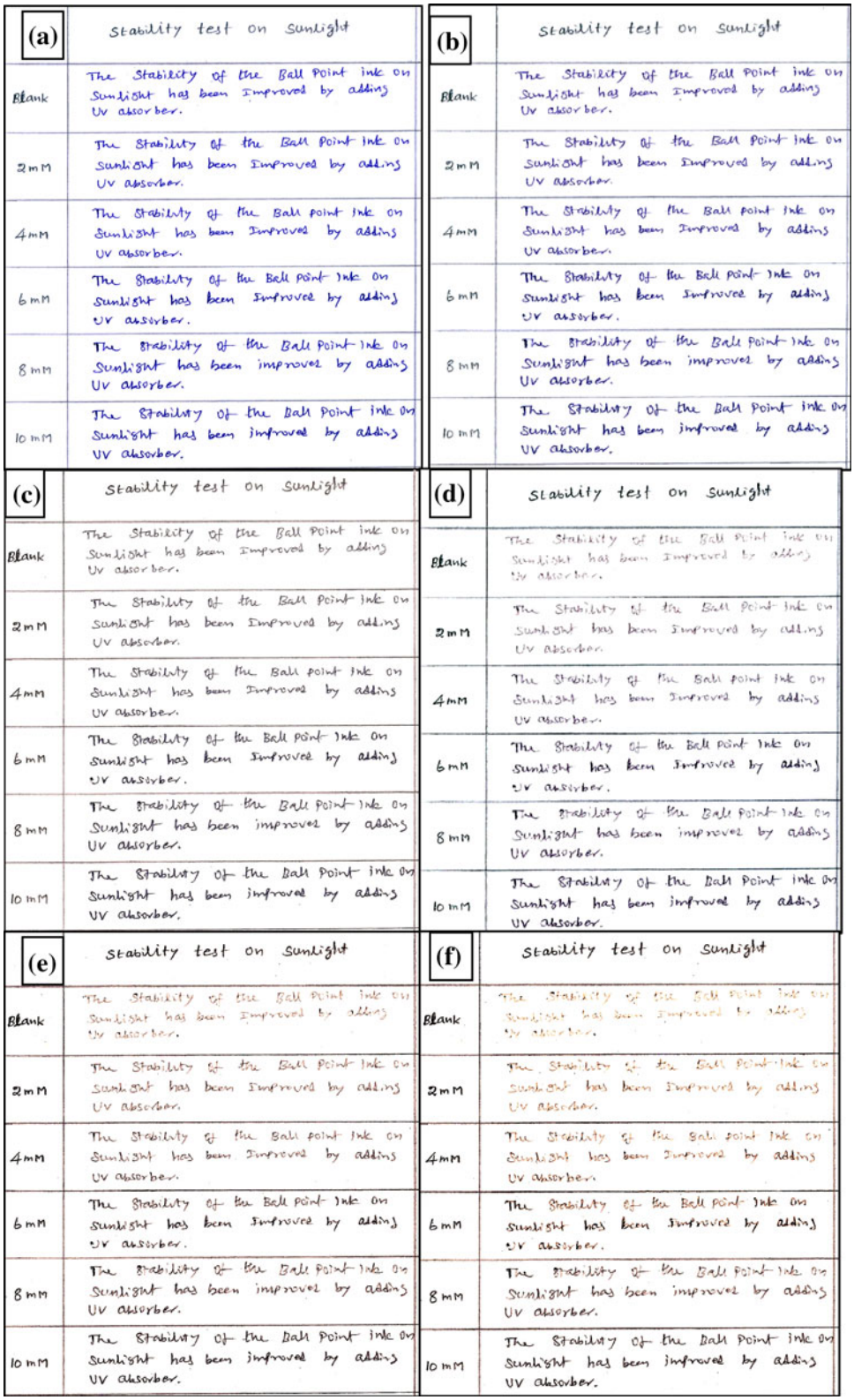

Fig. 10 The stability test of a written document (using ball point ink) on exposure to sunlight **a** initial (without exposure on sunlight) and with exposure on sunlight for **b** 1 h, **c** 3 h, **d** 5 h, **e** 10 h and **f** 15 h with and without UV absorber

increase for the absorptivity without change [12] in the λ_{max} have been considered as evidence for interaction between β-CD and guest in the formation of the inclusion complex. The UV absorption properties increases 1.13 fold than without inclusion complex. The SPF efficiency of included guests can be calculated by the Eq. 2.

$$SPF \text{ efficiency} = \frac{SPF_{(HG)} - SPF_{(G)}}{SPF_{(HG)}} X100 \quad (2)$$

where HG is the Host guest, G is the Guest

The inclusion complex SPF efficiency was increased up to 11.5 % due to higher absorptivity of included guest molecule. The SPF for the inclusion complex was 14.8 and it has better UV protection than without inclusion of dinitrocompounds (SPF 13.1).

Study of UV absorber behavior of dinitro inclusion complexes

Figure 7 shows the absorption spectra of ball point ink in methanol medium at different time interval of exposure on sunlight. Figure 7a shows the absorption spectra of ball point pen ink without exposure on sunlight, and Figs. 7b–g for 1, 2, 3, 5, 10, 15 h exposure respectively. For 1 h exposure of blank sample on sunlight, the absorption intensities are decreased drastically up to 90 % and 80, 76.4, 76.3, 76.1 and 74.2 % for 2, 4, 6, 8 and 10 mM concentration of UV absorber added ball point pen ink respectively. This was indicate that the UV absorber was worked as well, it means the UV absorber absorb the UV energy from sunlight and convert it into heat energy (Fig. 8) instead of allowing the energy to break the ball point pen ink. The UV absorber protects the ball point pen ink against the sunlight up to 25.8 % (For 1 h exposure) when 10 mM concentration of UV absorber was used. Table 4 and Fig. 9 show the percentage (%) of degradation of ink with exposure on sunlight. For 5 h exposure of blank sample, almost of the ink (95.7 %) was lost its blue colour and 4.3 % only with stands on the line pattern (Fig. 1), at the same time the line pattern containing absorber (Conc. 10 mM) was protect the ink up to 20.8 % for 5 h. Up to 15 h exposure 97.1 % of the ink was degraded in the blank sample and 87.8 % of the ink only degraded in 10 mM absorber added sample. The average of UV protecting efficiency of the absorber (10 mM) was 15 % and this efficiency percentage was equivalent with the SPF value (15 %), this indicates the UV absorber was worked as well up to 15 h and protects the ink from sunlight. Figure 10 shows a clear picture of ball point ink decomposition on exposure to sunlight with and without absorber.

Conclusions

The prepared inclusion complex of dinitrocompounds with β-CD was confirmed by FT-IR, ^{1}H NMR and 2D ROESY NMR techniques. UV-Vis transmittance behavior of dinitro compounds with and without inclusion complex were studied by UV transmittance spectra, the inclusion complex absorbs the UV light in the region of UVA and UVB by two fold of without inclusion. The SPF value (14.8) of inclusion complexes of dinitro compounds were increased up to 1.13 fold when compared to without inclusion (SPF 13.1) and also the dinitro inclusion complex SPF efficiency increased up to 11.5 %. The dinitro inclusion complex was used as UV absorber in ballpoint pen ink, the stability of the ink has been improved up to 15 % on exposure to the sunlight.

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References

1. Ezcurra, M., Juan, M., Gongora, G., Maguregui, I., Alonso, R.: Analytical methods for dating modern writing instrument inks on paper. Forensic Sci. Int. **197**, 1–20 (2010)
2. Djozan, D., Baheri, T., Karimian, G., Shahidi, M.: Forensic discrimination of blue ballpoint pen inks based on thin layer chromatography and image analysis. Forensic Sci. Int. **179**, 199–205 (2008)
3. Nicholas, C., Soulias, T., Nikolaos, A., Nicholaos, P., Evmiridis, P.: Multivariate chemometrics for the forensic discrimination of blue ball-point pen inks based on their UV Vis spectra. Forensic Sci. Int. **138**, 75–84 (2003)
4. Mahltig, B., Bottcher, H., Rauch, K., Dieckmann, U., Nitsche, R., Fritz, T.: Optimized UV protecting coatings by combination of organic and inorganic UV absorbers. Thin Solid Films **485**, 108–114 (2005)
5. Zaibunnisa, A.H., Aini Marhanna, M.N.A., Ainun Atirah, M.: Characterisation and solubility study of γ-cyclodextrin and β-carotene complex. Int. Food Res. J. **18**(3), 1061–1065 (2011)
6. Palaniappan, A.L., Francis, X.L., Tay, E.H., Jun, L., Xiaodi, S.: Cyclodextrin functionalized mesoporous silica films on quartz crystal microbalance for enhanced gas sensing. Sens. Actuators B **119**, 220–226 (2006)
7. Yifeng, H., Pei, F., Shen, X., Gao, H.: Cyclodextrin-based aggregates and characterization by microscopy. Micron **39**, 495–516 (2008)
8. Miclea, L.M., Vlaia, L., Vlaia, V., Hadaruga, D.I., Mircioiu, C.: Preparation and characterisation of inclusion complexes of meloxicam and α-cyclodextrin and β- cyclodextrin. Farmacia **58**, 583–593 (2010)
9. Misiuk, W., Zalewska, M.: Investigation of inclusion complex of trazodone hydrochloride with hydroxypropyl-β-cyclodextrin. Carbohydr. Polym. **77**, 482–488 (2009)
10. Bishop, R.: Supramolecular host–guest chemistry of heterocyclic v-shaped molecules. Top Heterocycl. Chem. **18**, 75–102 (2009)
11. Prabhumirashi, L.S., Kunte, S.S.: Solvent effects on electronic absorption spectra of nitrochlorobenzenes, nitrophenols and nitroanilines-l. Studies in nonpolar solvent. Spectrochim Acta Part A **42**, 435–441 (1986)
12. Singh, R., Bharti, N., Madan, J., Hiremath, S.N.: Characterization of cyclodextrin inclusion complexes A review. J. Pharm. Sci. Technol. **2**(3), 171–183 (2010)

13. Scalia, S., Tursilli, R., Iannuccelli, V.: Complexation of the sunscreen agent, 4- methylbenzylidene camphor with cyclodextrins: effect on photostability and human stratum corneum penetration. J. Pharm. Biomed. **44**, 29–34 (2007)
14. Scalia, S., Tursilli, R., Bianchi, A., Nostro, P.L., Bocci, E., Ridi, F., Baglioni, P.: Incorporation of the sunscreen agent, octyl methoxycinnamate in a cellulosic fabric grafted with β-cyclodextrin. Int. J. Pharm. **308**, 155–159 (2006)
15. Stalin, T., Srinivasan, K., Sivakumar, K.: Spectral and electrochemical study of host–guest inclusion complex between 2,4-dinitrophenol and β-cyclodextrin. Spectrochim. Acta Part A **94**, 89–100 (2012)
16. Springsteen, A., Yurek, R., Frazier, M., Carr, K.F.: In vitro measurement of sun protection factor of sunscreens by diffuse transmittance. Anal. Chim. Acta **380**, 155–164 (1999)
17. Diffey, B.L., Robson, J.: A new substrate to measure sunscreen protection factors throughout the ultraviolet spectrum. J. Soc. Cosmet. Chem. **40**, 127–133 (1989)
18. Wang, H.Y., Han, J., Feng, X.G., Pang, Y.L.: Study of inclusion complex Formation between tropaeolin OO and β-cyclodextrin by spectrophotometry and Infrared spectroscopy. Spectrochim. Acta Part A **65**, 100–105 (2006)
19. Boutelliez, C.B., Fontanay, S., Finance, C., Kedzierewicz, F.: Preparation and physicochemical characterization of amoxicillin β-cyclodextrin complexes. AAPS PharmSciTech. **11**, 574–581 (2010)
20. Chen, M., Diao, G., Zhang, E.: Study of inclusion complex of β-cyclodextrin and nitrobenzene. Chemosphere **63**, 522–529 (2006)
21. Sohajda, T., Beni, S., Varga, E., Ivanyi, R., Racz, A., Szente, L., Noszal, B.: Characterization of aspartame–cyclodextrin complexation. J. Pharm. Biomed. **50**, 737–745 (2009)