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ORIGINAL ARTICLE

Studies on Absorption and Emission Characteristics of Inclusion Complexes of Some 4-Arylidenamino-5-phenyl-4H-1, 2, 4-triazole-3-thiols

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Abstract The inclusion complexes of a series of 4-arylidenamino-5-phenyl-4H-1, 2, 4-triazole-3-thiols have been prepared with β-cyclodextrin. The compounds and their inclusion complexes have been characterized by studying their physical and spectral properties. The thermodynamic stability constant and free energy of activation have been determined to know the stability of inclusion complexes and type of host-guest relation. Finally, absorption, excitation and emission spectra of the compounds (4-arylidenamino-5-phenyl-4H-1, 2, 4-triazole-3-thiols) and their inclusion complexes have been taken. It is found that inclusion complex formation brings about a drastic change in absorption and fluorescence characteristic (both excitation and emission spectra) of newly synthesized compounds.

Keywords Triazole-3-thiol · Inclusion complex · Absorption spectra · Excitation spectra · Emission spectra

Introduction

Fluorescence characteristics of fluorophores depend upon a number of environmental factors including interactions between the fluorophore and surrounding solvent molecules (dictated by solvent polarity), other dissolved inorganic and organic compounds, temperature, pH, and the localized concentration of the fluorescent species. The effects of these parameters vary widely from one fluorophore to another. The exitation and emission spectra as well as quantum yields, can be heavily influenced by environmental variables. In fact, the high degree of sensitivity in fluorescence is primarily due to interactions that occur in the local environment during the excited state life time [1–7].

The drugs containing 1, 2, 4-triazole nucleus are reported to exhibit a wide spectrum of pharmacological activities like antimicrobial [8–12], anticancer [13, 14], antiviral [15], anti-inflammatory [16], analgesic [17], anticonvulsant [18] etc. It is known that the formation of inclusion complex of drug molecules with β –cyclodextrin improves their solubility, stability as well as bioavailability [19–24]. But transference of drug molecules which are usually nonpolar in nature, in to hydrophobic core of β –cyclodextrin causes a drastic change in its microenvironment. Since the spectral chacteristics of molecules depend upon the molecular structure and its microenvironment [6, 7] such a transference will definitely have some impact on fluorescence characteristics of the molecules.

In view of these facts, an attempt has been made to synthesize some 4-arylidenamino −5-phenyl-4 H-1,2,4-triazole-3-thiol (Schiff bases) in their purest forms and prepare their inclusion complexes with β-cyclodextrin. The absorption, excitation and emission spectra of the compounds and their inclusion complexes are taken to examine whether the inclusion complex formation has any impact on absoption and emission characteristics of 4-arylidenamino-5-phenyl-4H-1, 2, 4-triazole-3-thiols.

Experimental

Materials and Methods

All the chemicals used in the present work were procured from local market. Double distilled water was used as solvent.

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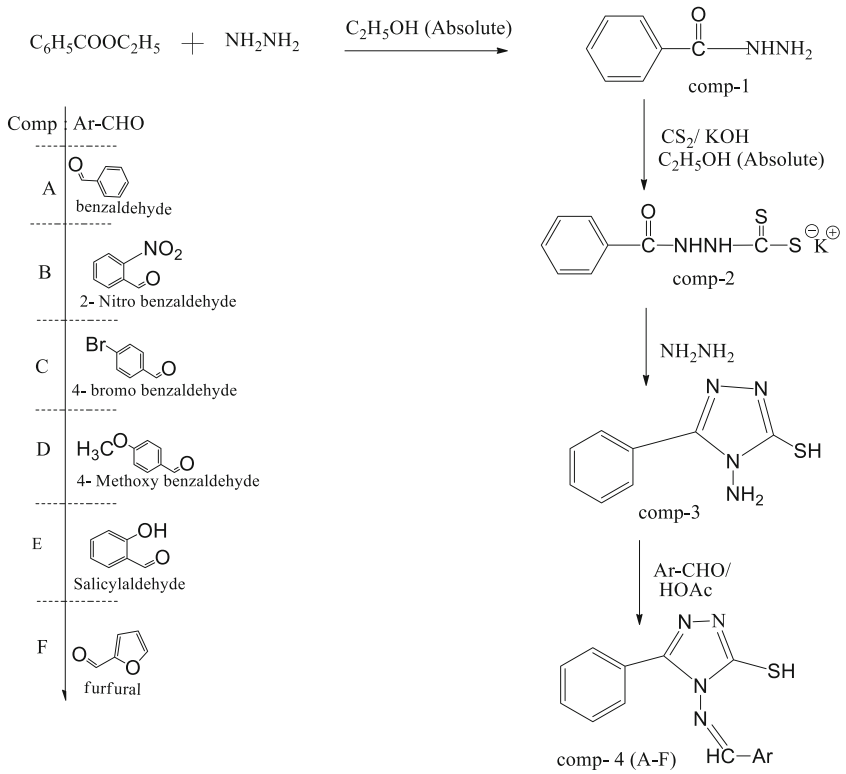

Scheme 1 A**:** 4-Benzilidenamino −5-phenyl-4H-1, 2, 4-triazole-3-thiol. B**:** 4-[2-Nitrobenzilidenamino] -5-phenyl-4 H-1,2,4-triazole-3-thiol. C**:** 4-[4-Bromobenylideneamino] -5-phenyl-4*H*-1, 2, 4-triazole-3-thiol. D: 4-[4-Methoxybenylideneamino] -5-phenyl-4*H*-1, 2, 4-triazole-3-thiol. E**:** 4-[2-Hydroxybenzylideneamino] -5-phenyl-4*H*-1, 2, 4-triazole-3-thiol. F**:** 4-[(furan-2-yl)methyleneamino] -5-phenyl-4*H*-1, 2, 4-triazole-3-thiol

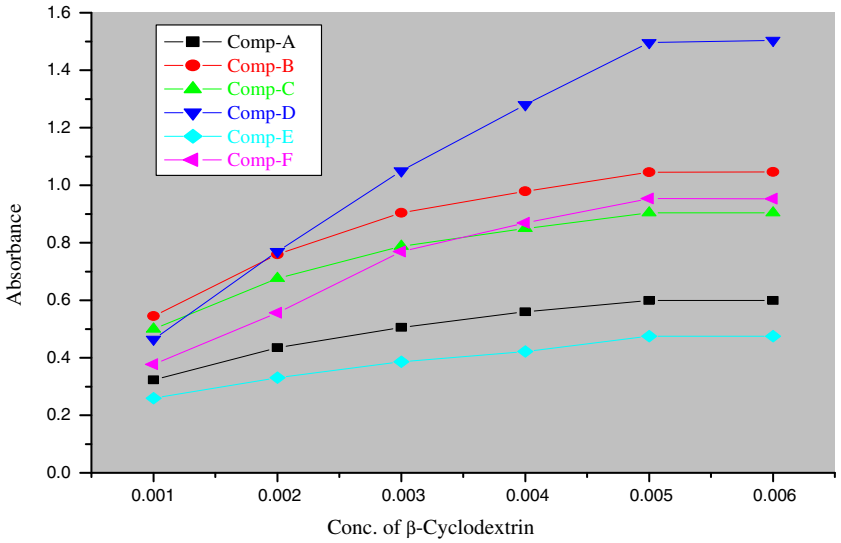

Fig. 1 Phase solubility study of the synthesized compounds in aqueous solution of β-cyclodextrin

The elemental analysis was performed in a CHN analyzer. Melting points were recorded by open capillary method. Absorption spectra were recorded in Shimadzu UV-1800 spectrophotometer and IR spectra were recorded in KBr pellets in Shimadzu 8400 FT-IR spectrophotometer. ^{1}HNMR spectra were obtained with Brukers spectrophotometer model ultra-shield at 300 MHz in DMSO- d_6 solution with TMS as internal standard. The purity of the newly synthesized compounds were checked by TLC. Fluorescence emission and excitation spectra were recordedy in a Shimadzu RF-1501 spectrofluorimeter equipped with a150W xenon lamp. The synthesis of the titled compounds A, B, C, D, E and F were carried out as per Panda et al. 2015 [24] as shown in Scheme 1.

Phase Solubility Measurements

The aqueous phase solubility of the compounds at various concentrations of β –cyclodextrin (0-10 mM) was studied by Higuchi-Conner method [25].

Synthesis of Inclusion Complexes

Co-precipitation method was used for the preparation of inclusion complexes of the compounds with β-cyclodextrin [22, 26].

Study of Thermodynamic Properties

The thermodynamic stability constants of the complexes were calculated from plot of inverse of change in absorbance versus inverse concentration of β-cyclodextrin using Benesi-Hilderband relation [27].

$$1/\Delta A = 1/\Delta\varepsilon + 1/K'.\Delta\varepsilon[\text{Guest}]_o.[\beta - CD]$$

where ΔA is change in absorbance, Δε is change in absorption coefficient, K is stability constant, $[\text{Guest}]_o$ is the concentration of compound and [β-CD] is the concentration of β-cyclodextrin. The values of K for all the complexes are calculated using the relation

$$K = \text{Intercept}/\text{Slope}$$

The value of ΔG at 298 K was calculated using the equation:

$$\Delta G = -RT\ln K$$

Results and Discussion

Six different 4-arylidenamino −5-phenyl-4 H-1, 2, 4-triazole-3-thiols (A, B, C, D, E and F) have been synthesized (as shown in scheme 1) in their purest forms. The inclusion complexes of A, B, C, D, E and F have been prepared with β-cyclodextrin (β-CD) after determining the optimum concentration of host and guest through aqueous phase solubility study (Fig. 1). The structures of the compounds (A, B, C, D, E and F) have been confirmed from the study of their physical properties, elemental composition, FT-IR and ^{1}HNMR data (Tables 1 and 2). The elemental

Table 1 Some physical properties of the synthesized compounds and their inclusion complexes

Sl No.	Compound/Complex	Molecular formula	Molecular weight	Colour	M.P. (°C)	Yield(%)
1	Compound- A	$C_{15}H_{12}N_4S$	280. 35	Light brown	180–185	73
	I.C.A			white	272–274	75
2	Compound- B	$C_{15}H_{11}N_5O_2S$	325.35	Pale yellow	170–172	72
	I.C.B			Dull white	282–285	74
3	Compound- C	$C_{15}H_{11}$ BrN_4S	359.24	Light yelllow	178–180	77
	I.C.C			white	275–280	77
4	Compound- D	$C_{16}H_{14}N_4OS$	310. 37	Dull White	160–162	71
	I.C.D			white	280–285	77
5	Compound- E	$C_{15}H_{12}ON_4S$	296.35	Dull white	145–148	71
	I.C.E			white	278–280	75
6	Compound- F	$C_{13}H_{10}N_4OS$	270. 31	Dark gray	170–175	73
	I.C.F			white	281–283	77

Table 2 Spectral data and elemental composition of the compounds and their inclusion complexes

Sl No. name	Compound/ Complexcase	IR (KBr) cm^{-1}rcase	NMR(DMSO-d_6)	Elemental Analysis Calculated (Found)		
				C	H	N
1	A	968.27 (N-C-S str), 3034.03, 3099.61, (Ar-H str),1498.69(C = C_{str})696.38 (C-S str), 1350.17 (C-N str)0.1610.56 (C = N_{str})	7.52–7.90 (m, 10 H, Ar-H),14.25(s, 1 H, SH), 9.70(s, 1 H, N = CH).	64.26 (64.46)	4.31 (4.02)	19.98 (19.92)
	I.C.A	937.4 (N-C-S str), 2931.80 (Ar-H str), 1409.96(C = C_{str})756.10 (C-S str), 1332.81 (C-N str)0.1656.85(C = N_{str}), 3398.57(OHstr, β-CD),2931.80 (C-Hstr, β-CD)	7.32–7.91 (m, 10 H, Ar-H),3.35(s,1 H,β-CD), 3.43(s,1 H,β-CD), 3.45(s,1 H,β-CD), 3.57(s,1 H,β-CD), 3.59(s,1 H,β-CD)			
2	B	943.27 (N-C-S str), 3115.04 (Ar-H str), 696.30(C-S str), 1498.69(C = C_{str}) 1342.46 (C-N str). 1529.55,1342.46 (NO_2), 1610(C = N_{str})	7.53–8.34(m, 9 H, ArH), 14.304 (s, 1 H, SH),10.499 (s, 1 H, N = CH).)	55.37 (55.27)	3.41 (3.32)	21.53 (21.50)
	I.C.B	937.40(N-C-S str), 2933.80(Ar-H str), 1409.96(C = C_{str})704.02(C-S str), 1361.74 (C-N str)0.1409.96 (NO_2), 1658.78(C = N_{str}), 3367.71(OHstr, β-CD),2931.80(C-Hstr, β-CD)	7.92–8.13 (m, 9 H, Ar-H),3.37(s,1 H,β-CD), 3.61(s,1 H,β-CD), 3.63(s,1 H,β-CD), 3.64(s,1 H,β-CD), 3.66(s,1 H,β-CD),			
3	C	968.27 (N-C-S str), 2941.44, 3113.11 (Ar-H str),1500.62 (C = C_{str})684.73 (C-S str), 1355.96 (C-N str)0.1510.56 (C = N_{str})609.51(C-Br)	7.54–7.89 (m, 9 H, Ar-H),	50.15 (50.19)	03.09 (3.14)	15.60 (15.51)
	I.C.C	937.40 (N-C-S str), 2931.80 (Ar-H str), 1409.96(C = C_{str})756.10 (C-S str), 1332.81 (C-N str)0.1658.78(C = N_{str}), 3385.07(OHstr, β-CD), 2931.80 (C-Hstr, β-CD), 613.36(C-Br)	7.36–7.96 (m, 9 H, Ar-H),3.35(s,1 H,β-CD), 3.42(s,1 H,β-CD), 3.46(s,1 H,β-CD), 3.54(s,1 H,β-CD), 3.58(s,1 H,β-CD)			
4	D	943.19(N-C-S str), 3076.46,3115.04 (Ar-H str), 1500.62(C = C_{str})696.30 (C-S str), 1352.10(C-N str), 1598.99 (C = N_{str})	7.04–8.62 (m, 9 H, Ar-H), 3.82–3.85(s, 3 H, OCH_3)	61.92 (61.95)	04.55 (4.52)	18.05 (18.01)
	I.C.D	937.40(N-C-S str), 2931.80, (Ar-H str), 1409.96(C = C_{str}) 1658.78(C = N_{str}), 756.10 (C-S str), 1332.81,(C-N str) 0.3371.57(OHstr, β-CD),2912.51 (C-Hstr, β-CD)	7.94–8.78(m, 9 H, Ar-H), 3.32(s,1 H,β-CD), 3.34(s,1 H,β-CD), 3.37(s,1 H,β-CD), 3.61(s,1 H,β-CD), 3.64(s,1 H,β-CD), 2.73–2.89 (s, 3 H, OCH_3			
5	E	941.26 (N-C-S str), 2951.09, 2993.52 (Ar-H str), 1446.61(C = C_{str}), 696.30 (C-S str), 1350.17 (C-N str), 3134.33 (ArOH), 1610.56(C = N_{str})	7.49–7.88 (m, 9 H, Ar-H), 8.98 (s, 1 H, OH)	60.79 (60.84)	4.08 (4.12)	18.91 (18.93)
	I.C.E	937.40 (N-C-S str), 2931.80 (Ar-H str), 1409.96(C = C_{str})756.10(C-S str), 1361.74 (C-N str),1658.78(C = N_{str}) 3365.78(OHstr, β-CD), 3226.91(Ar-OH), 3236.55, 3294.42(C-Hstr, β-CD)	7.94–8.28 (m, 9 H, Ar-H),3.34(s,1 H,β-CD), 3.54(s,1 H,β-CD), 3.57(s,1 H,β-CD), 3.62(s,1 H,β-CD), 4.46(s,1 H,β-CD)			
6	F	941.26 (N-C-S str), 3099.61, 3134.33 (Ar-H str), 1571.99, (C = C_{str}) 696.30(C-S str), 1350.17 (C-N str). 1610.56 (C = N_{str})	6.78–8.06(m, 8 H, ArH),	57.76 (57.64)	03.73 (3.76)	20.73 (20.70)
	I.C.F	937.40(N-C-S str), 2931.80, (Ar-H str), 1656.85(C = C_{str})705.95 (C-S str), 1361.74 (C-N str). 1653.00 (C = N_{str}), 3290.56.71(OHstr, β-CD),3167.12 (C-Hstr, β-CD)	7.95–8.23 (m, 8 H, Ar-H),3.31(s,1 H,β-CD), 3.35(s,1 H,β-CD), 3.55(s,1 H,β-CD), 3.63(s,1 H,β-CD), 3.66(s,1 H,β-CD)			

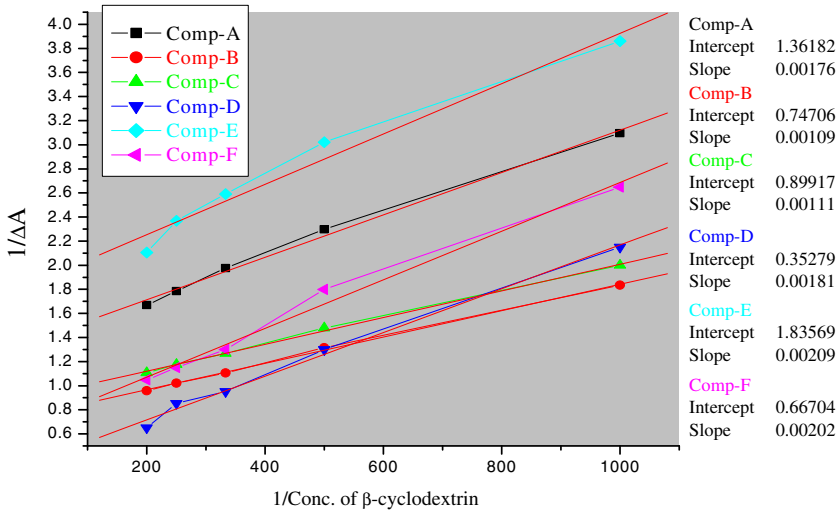

Fig. 2 Plot of inverse absorbance against inverse concentration of β-cyclodextrin

composition of the compounds matches with theoretical data (Table 2). The FT-IR and ^{1}H NMR data of the compounds confirm the expected structures. The preparation of inclusion complexes of the compounds have been confirmed from the changes in melting point, colour and FT-IR and ^{1}H NMR spectral characteristics (Tables 1 and 2). The IR- stretching frequencies due to different bonds undergo downward shift towards lower energy and the peaks become broader, weaker and smoother. The ^{1}H NMR signals due to different protons undergo smaller shifts (small shift towards down field in case of all the compounds) after their inclusion complex formations. The changes in IR spectral characteristics may be attributed to the restriction on the compounds for undergoing vibration within the cavity of β-CD due to the development of weak interaction like H-bonding, vander-Waal forces and hydrophobic interactions etc. [22]. This observation clearly demonstrates transference of the compound from a more protic environment (aqueous media) to a less protic environment (cavity of β-CD). The compound and β-CD interaction leading to inclusion complex formation is further supported by ^{1}H NMR data (Table 2). The changes in the microenvironment of the compound after encapsulation may cause a small shift in ^{1}H NMR signals.

Table 3 Thermodynamic stability constant and free energy change of inclusion complexes

Sl.No.	Inclusion complex	Thermodynamic stability Constant (M^{-1})	ΔG (kJ/mol)
1	I.C.A	773.76	−16.478
2	I.C.B	685.37	−16.178
3	I.C.C	810.06	−16.592
4	I.C.D	194.91	−13.063
5	I.C.E	878.32	−16.793
6	I.C.F	330.21	−14.369

The aqueous phase-solubility diagrams of the compounds with β-cyclodextrin are shown in Fig. 1. It is seen that aqueous solubility of the compounds increases linearly as a function of the concentration of β-cyclodextrin up to 5th point followed by a decline. This clearly indicates that the concentration at 5th point is the optimum concentration for inclusion complex formation. The plot of inverse change in absorbance against inverse concentration of β-cyclodextrin gives straight lines with definite slope and intercept for different compounds (Fig. 2). The thermodynamic stability constants (K) have been calculated from the slope and intercept [27] and are found to be in the range of 194.91 to 878.32 (Table 3). Since all the values are remaining within ideal range [28] all the inclusion complexes formed are quite stable. Further, it is found that the values of all the slopes are less than one indicating the inclusion complexes to have 1:1 stoichiometry [21–23]. Negative

Table 4 Absorption, exitation and emission peak positon of the compounds and their inclusion complexes

Sl. No.	Compound/ Complex	Absorption maximum λ_{Max}(nm)	Exitation peak position λ (nm)	Emission peak position λ (nm)
1	Compound- A	294	299	448
	I.C.A	270	295	445
2	Compound- B	295	313	451
	I.C.B	275	286	437
3	Compound- C	295	326	453
	I.C.C	270	307	433
4	Compound- D	294	307	451
	I.C.D	278	294	445
5	Compound- E	294	294	449
	I.C.E	265	283	439
6	Compound- F	292	316	452
	I.C.F	287	303	439

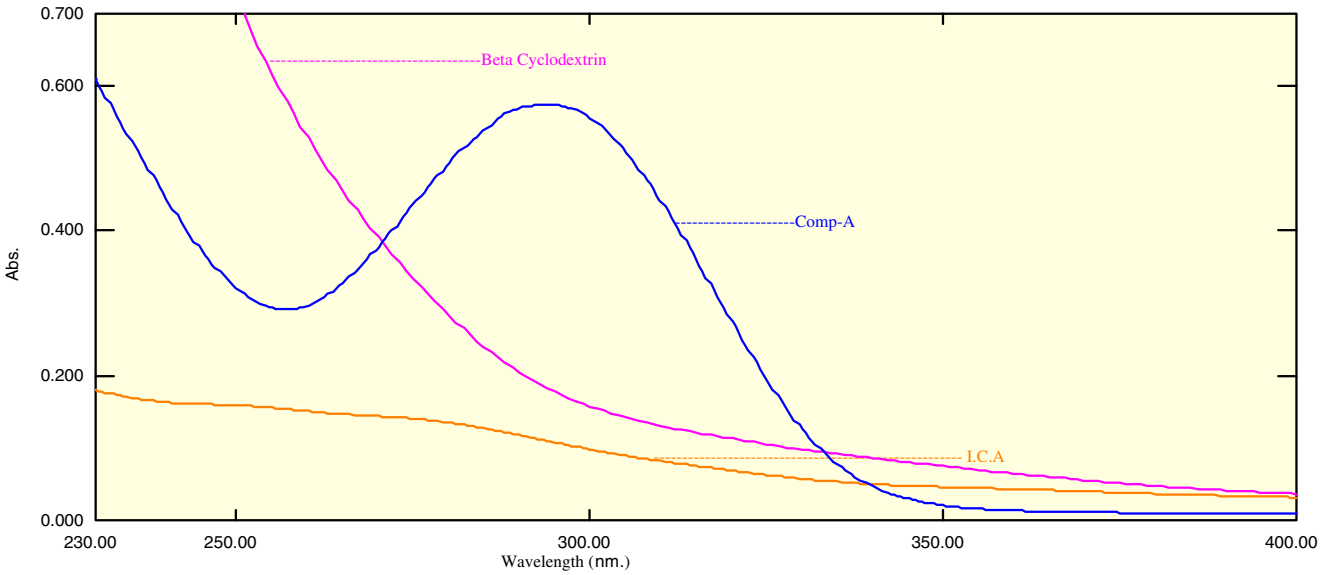

Fig. 3 UV spectrum of β- cyclodextrin, compound A and its inclusion compex

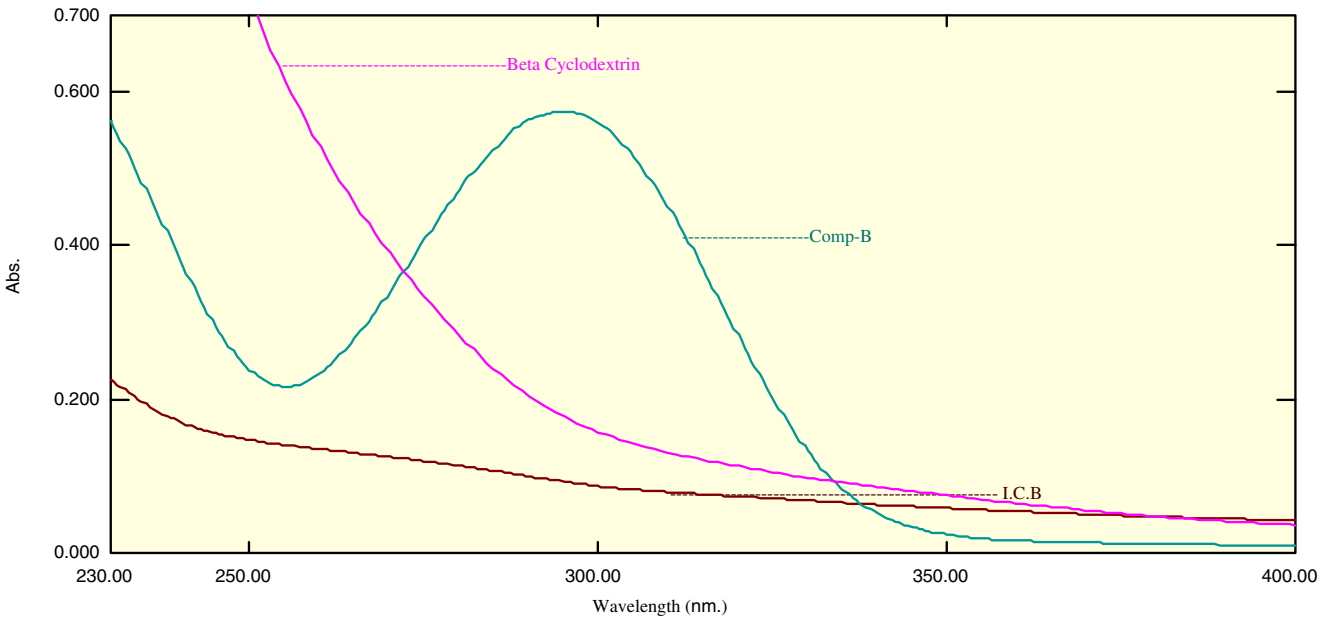

Fig. 4 UV spectrum of β- cyclodextrin, compound B and its inclusion compex

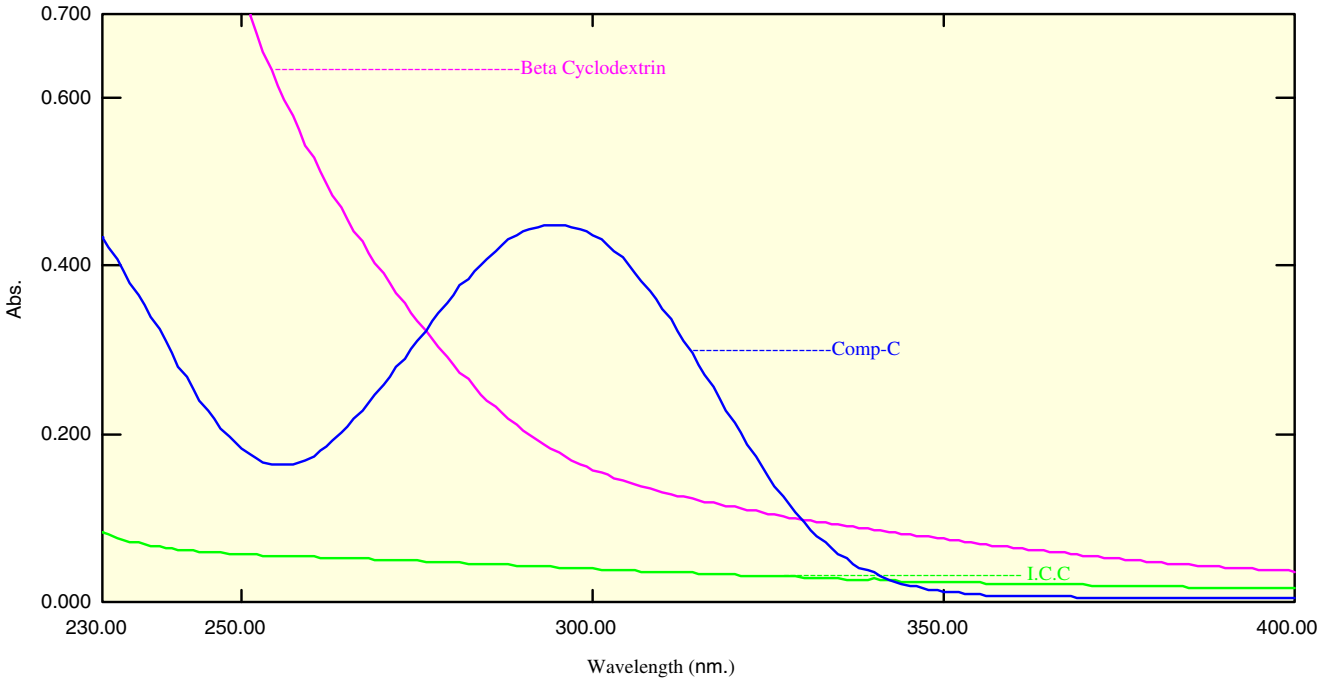

Fig. 5 UV spectrum of β- cyclodextrin, compound C and its inclusion compex

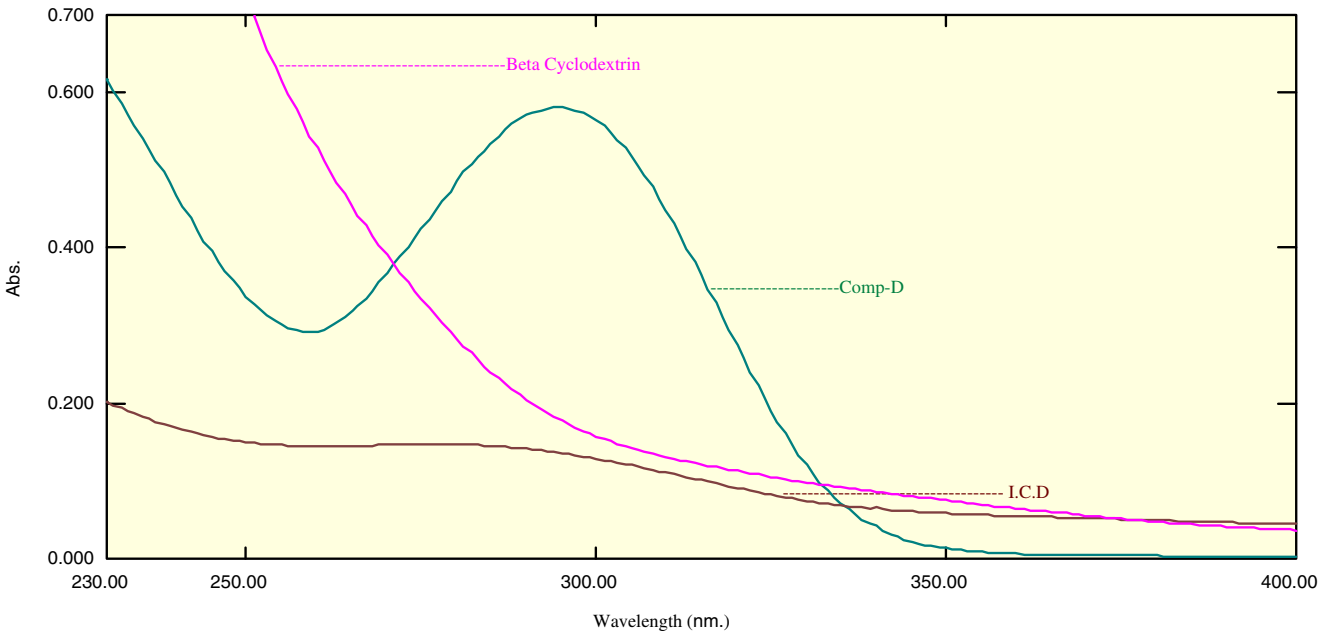

Fig. 6 UV spectrum of β- cyclodextrin, compound D and its inclusion compex

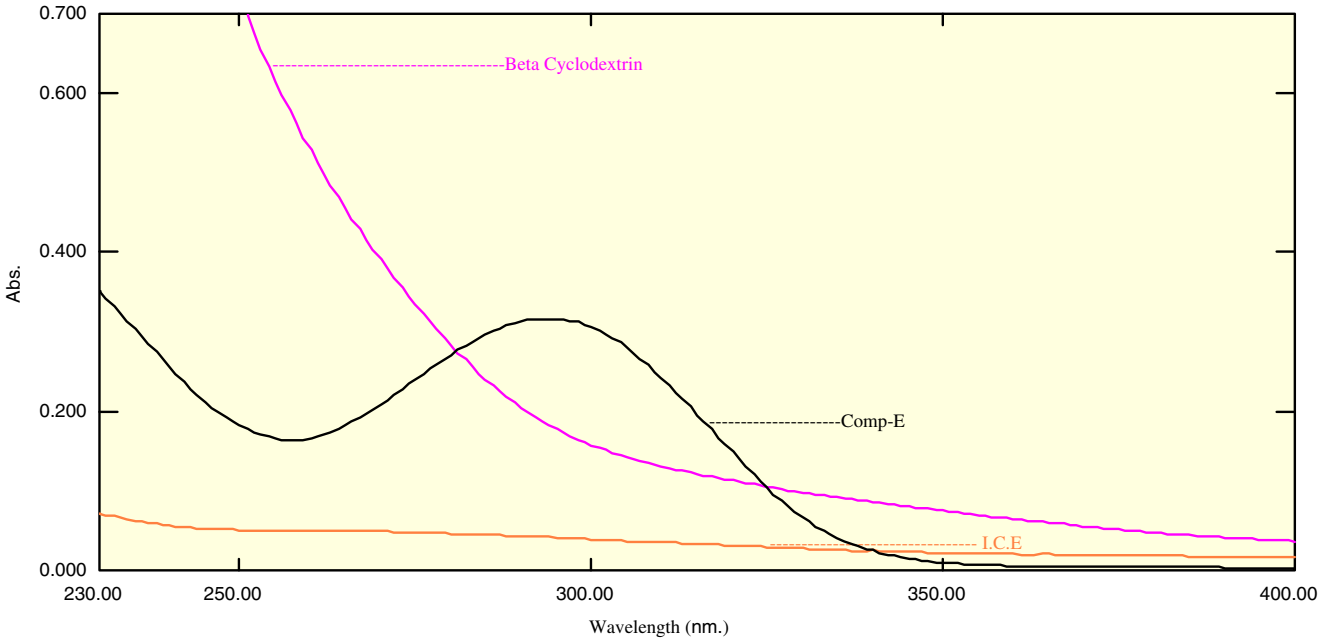

Fig. 7 UV spectrum of β- cyclodextrin, compound E and its inclusion compex

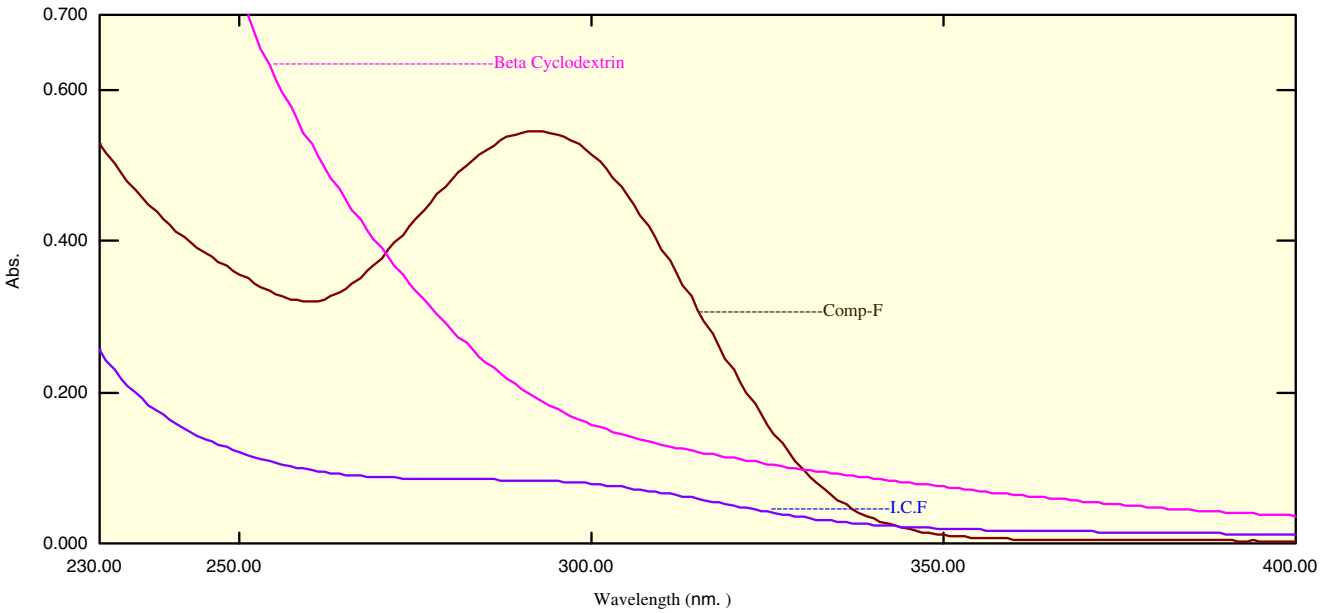

Fig. 8 UV spectrum of β- cyclodextrin, compound F and its inclusion compex

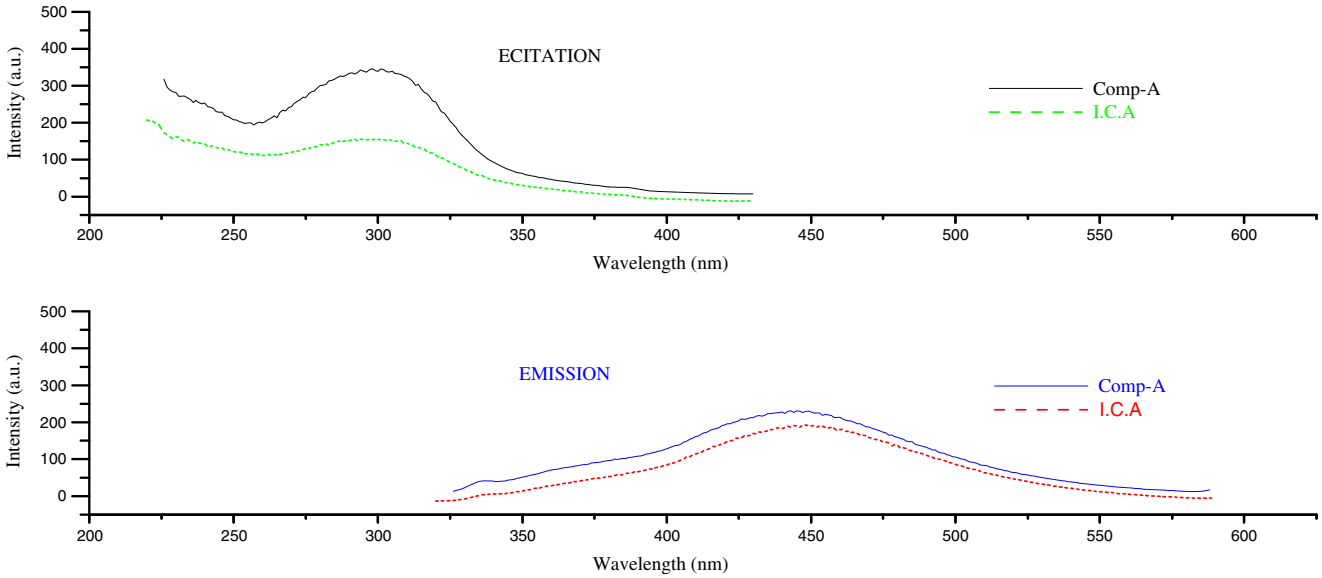

Fig. 9 Excitation and emission spectra of compound A and its inclusion comlex

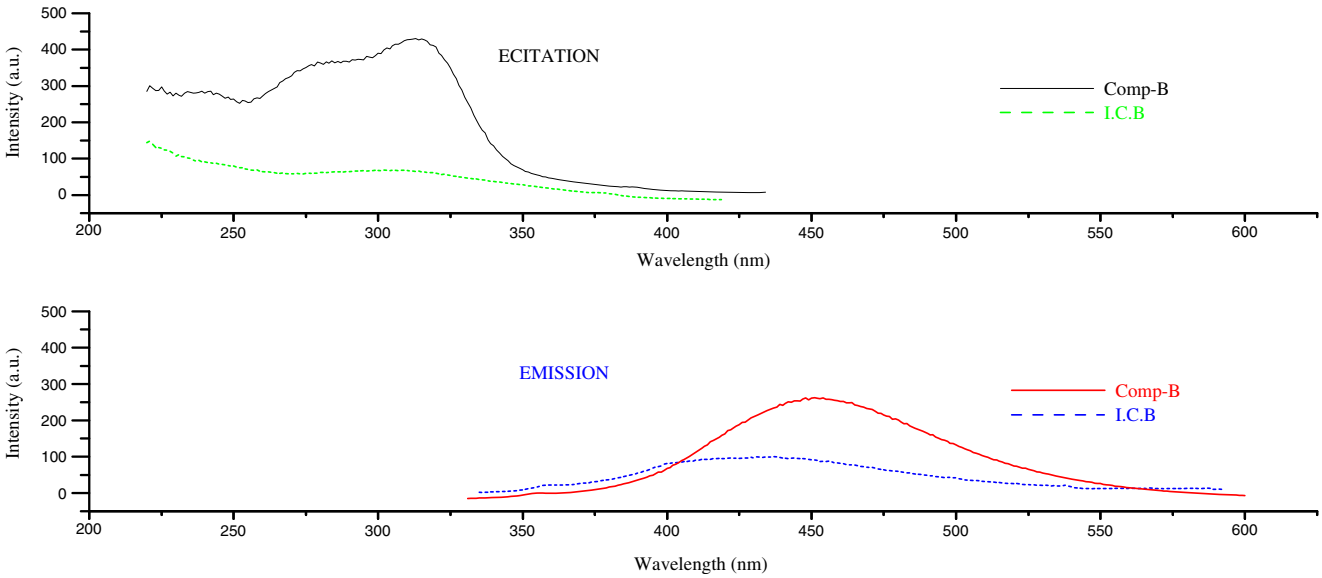

Fig. 10 Excitation and emission spectra of compound B and its inclusion comlex

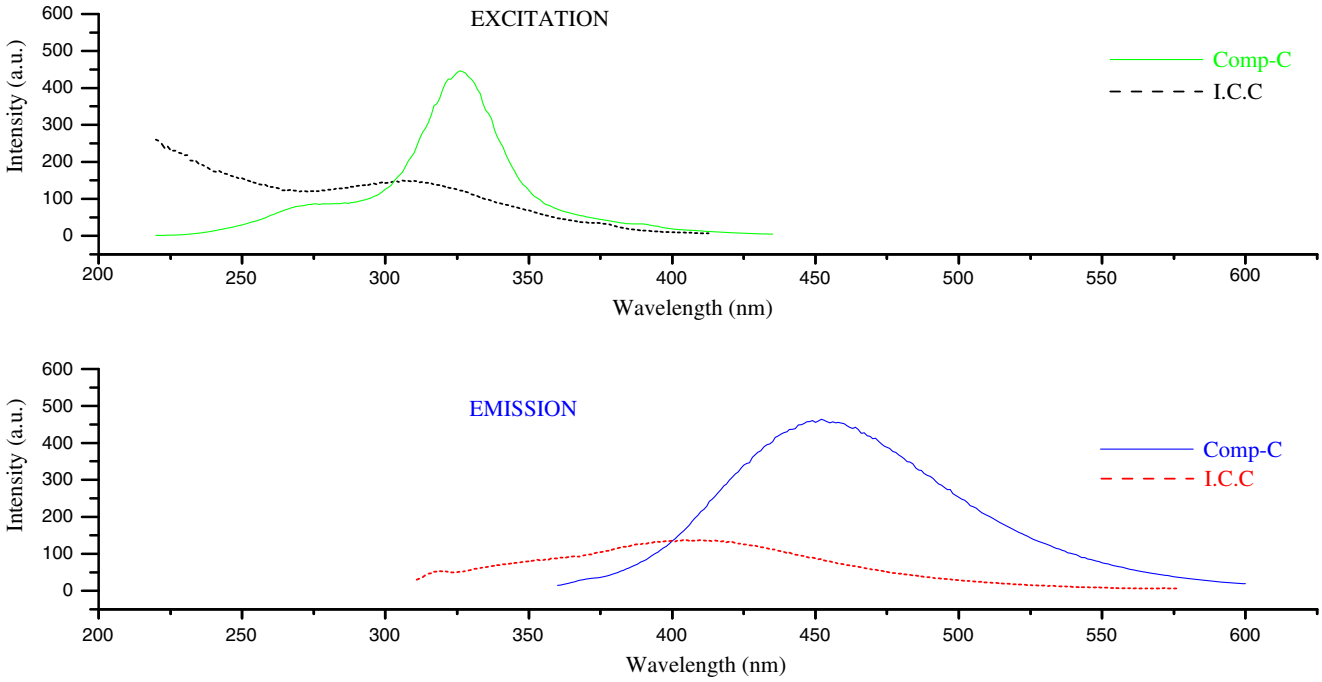

Fig. 11 Excitation and emission spectra of compound C and its inclusion comlex

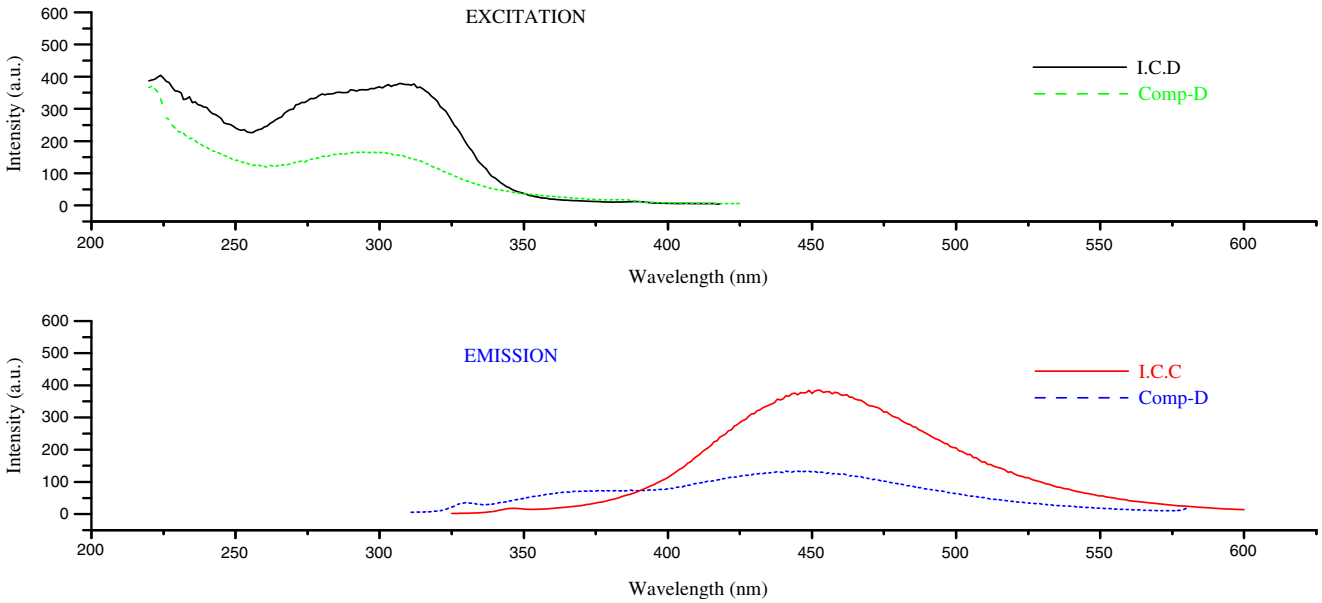

Fig. 12 Excitation and emission spectra of compound D and its inclusion comlex

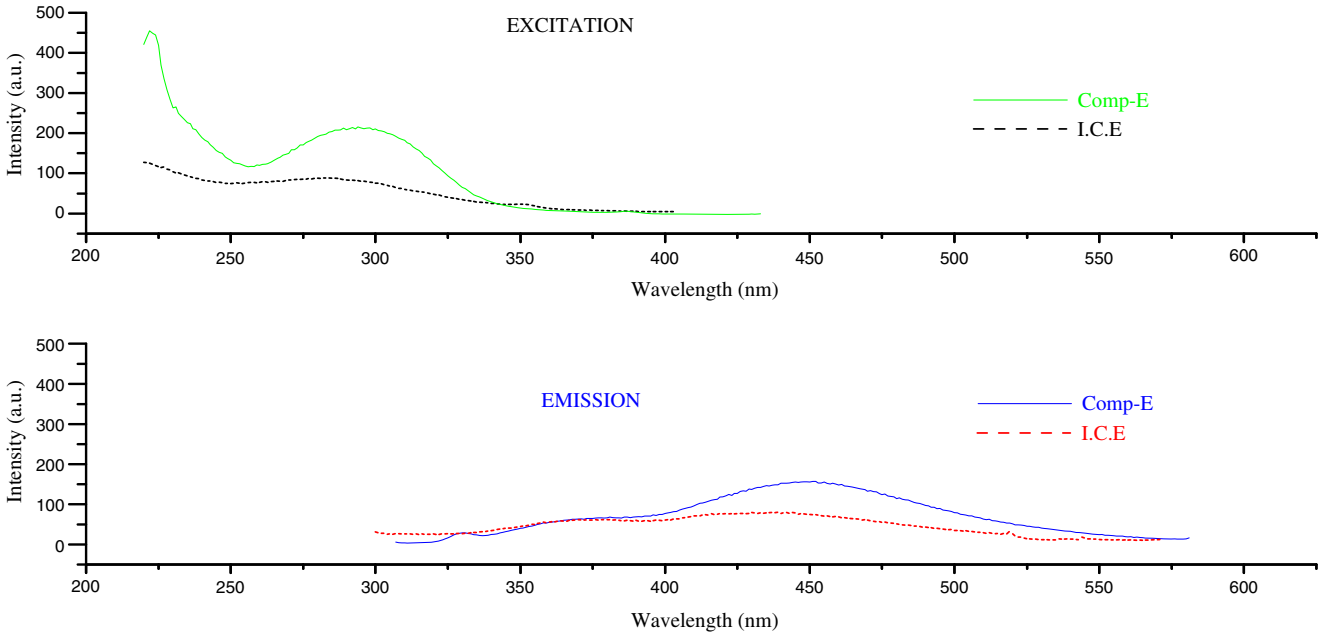

Fig. 13 Excitation and emission spectra of compound E and its inclusion comlex

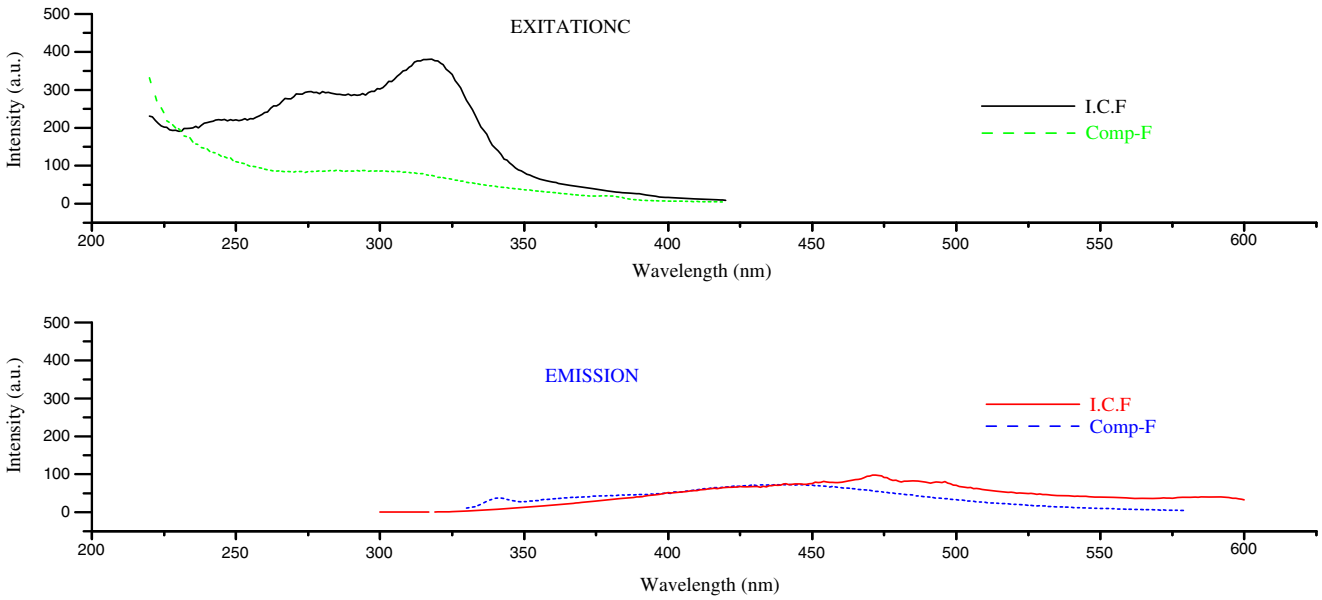

Fig. 14 Excitation and emission spectra of compound F and its inclusion comlex

values of free energy changes for all the inclusion complexes (Table 3) further suggest that the process of inclusion complex formation is spontaneous and thermodynamically allowed.

It is interesting to note that the absorption and emission characterestics of all the compounds (A, B, C, D, E and F) undergo drastic changes after their inclusion complex formation. The absorption maxima shifts towards lower wavelength (Table 4)and the intensity of the peaks becomes higher after their inclusion complex formation (Figs. 3, 4, 5, 6, 7, and 8). However, although the excitation and emission peaks shift towards lower wavelength, the intensity of the peaks becomes lower after their inclusion complex formation (Figs. 9, 10, 11, 12, 13, and 14). The shifting of absorption and excitation peak positions may be due to the fact that more amount of energy is required for the compounds for their excitation after encapsulation because the molecules get stabilized within the cavity of β-cyclodextrin through some weak intermolecular forces. The lowering of fluorescence intensity may be due to lesser population of molecules in the excited state than ground state.

Conclusion

The above results established the fact that the inclusion complexes of the synthesized compounds alter the absorption and emission characteristics of the molecules.

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