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Synthesis and Characterization of Hydroxypropyl α-Cyclodextrin Inclusion Complexes with Azo Dyes

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ABSTRACT

Azo dyes have got innumerous applications in various industries and there is a great demand to improve the solubility and stability of the dyes. Molecular encapsulation technique is one such strategy used in enhancing the desirable properties in the dye. In this investigation, inclusion complexes of azo dyes like 4-(Phenylhydrazo)benzoic acid (PABA) and 2-(4-Hydroxyphenylazo)benzoic acid (HABA) are synthesized with hydroxypropyl α-Cyclodextrin(HPα-CD) and their spectral characteristics are studied.The liquid inclusion complexes are characterized using UV-Visble spectroscopy and spectrofluorimetry. Solid inclusion complexes are characterized by Fourier Transform Infra Red (FTIR) spectroscopy. The binding constant values and ΔG are calculated and the stoichiometry of the inclusion complexes are found to be 1:1. Hydroxypropylα-Cyclodextrin complexation serves as a good supramolecular strategy for the enhancement of solubility and stability of the dyes.

Keywords: 4-(Phenylhydrazo)benzoic acid, 2-(4-Hydroxyphenylazo) benzoic acid, hydroxypropyl α-Cyclodextrin, inclusion complex, binding constants.

INTRODUCTION

Azo compounds play an important role not only in analytical chemistry as metal chrome agents but also find application as dyes, acid-base indicators as well as histological stains[1,2]. Azo molecules are characterized by a high photoinduced anisotropy[3] being excellent photo aligning substrates for liquid crystals[4] and highly efficient photorefractive media[5]. Their photosensitivity and the superior structuring properties are mainly due to the lability of substituents binding to the N=N groups. Cyclodextrins are well known as forming host- guest inclusion complexes which have the remarkable property of including organic, inorganic and

biological molecules in their cavities[6-8]. So long as the guest molecules have suitable polarity and dimension, when a fluorophore gets included into the cavity, the fluorescence and selectivity increased obviously. This led to the wide application of cyclodextrins in the field of medicine, food, organic synthesis, environmental protection and analytical chemistry[9]. 4-(Phenylazo)benzoic acid (PABA) is used a test kit for rapid screening of functional group affinity to metal oxides in the preparation of a novel photochromic ZrO_2 precursor solution. 2-(4-Hydroxyphenylazo)benzoic acid (HABA) has been found to be very advantageous for matrix-assisted ultraviolet laser desorption ionisation mass spectrometry. The aim of this investigation is to study the effect of HPα-CD on both the compounds ie.4-(phenylazo)benzoic acid and 2-(4- Hydroxyphenylazo) benzoic acid.

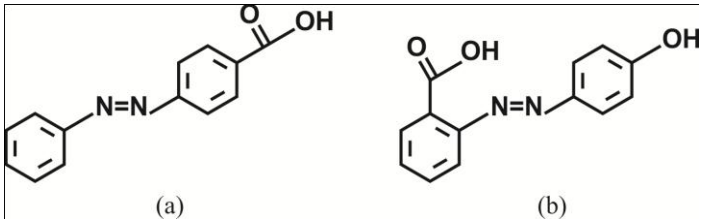

Fig.1 Chemical Structure of (a) 4-(Phenylazo) benzoic acid and (b) 2-(Hydroxy phenylazo)benzoic acid

MATERIALS AND METHODS

An analytical grade of 4-(phenylazo)benzoic acid, 2-(4-Hydroxyphenylazo) benzoic acid, Hydroxypropyl α-cyclodextrin purchased from sigma Aldrich were used for the investigation. The solvents used were of analytical grade and purchased from Merck. Triple distilled water was used for the preparation of stock solutions. UV-VIS spectra arerecorded using Systronics Smart Double beam Spectrophotometer-2203.Fluorescent spectra are recorded using JASCO Spectrofluorometer FP-8200. IR spectra are recorded using Shimadzu FTIR Spectrophotometer,

Preparation of liquid inclusion complex of PABA:HPα-CD and HABA:HPα-CD

About 0.0045 g of PABA and 0.0048 g of HABA was accurately weighed and dissolved separately in 10 ml methanol. About 0.354 g of HPα-CD was dissolved in 30 ml distilled water in a 250 ml beaker. Inclusion complexes of PABA:HPα-CD and HABA:HPα-CD were prepared by varying the concentration of HPα-CD from $2x10^{-3}$ M to $1x\ 10^{-2}$ M with PABA and HABA.

Preparation of solid inclusion complex of PABA: HPα-CD and HABA:HPα-CD

Solid inclusion complex of PABA: HPα-CD and HABA:HPα-CD are prepared by co evaporation method. The precipitate obtained after evaporation was dried and used for characterization.

RESULTS AND DISCUSSION

Effect of HPα-CD

The absorption and fluorescent maxima of both PABA and HABA in varying concentration of HPα-CD are depicted in Table 1. Upon increasing the concentration of HPα-CD in both the compounds the absorption maxima showed the bathochromic shift. A spectral shift of 329 nm to 339.7 nm is observed for longer wavelength and 237.2 nm to 246.0 nm is observed for shorter wavelength in the case of PABA indicated in Fig.2 (a)

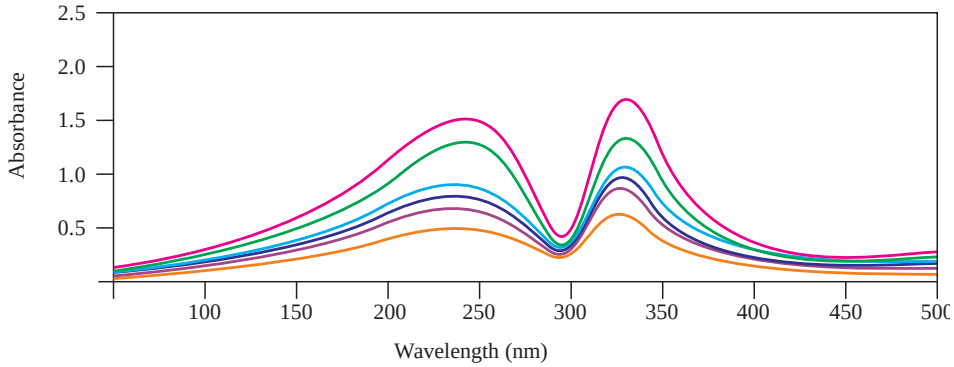

Fig.2 (a) Absorption Spectra of 4-(Phenylazo)benzoic acid

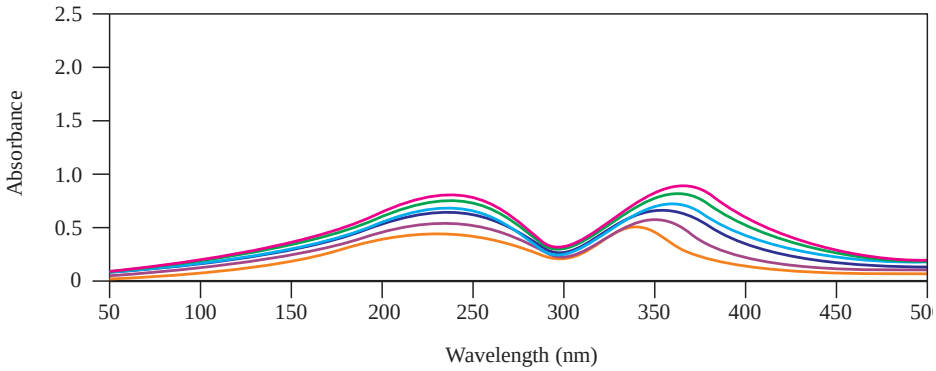

Fig.2 (b) Absorption Spectra of 2-(Hydroxy phenylazo)benzoic acid

But in the case of HABA shown in Fig 2(b), a red shift of 343.4 nm to 361.3nm is observed for longer wavelength. And a spectral shift of 236.3 nm to 246.2nm is observed for shorter wavelength. An isosbestic point is obtained in the case of both PABA and HABA indicating the possibility of a single equilibrium involving 1:1 complexation between PABA vs HPα-CD, and HABA vs HPα-CD. The spectral shifts are attributed to the entrapment of both the compounds PABA and HABA into the HPα-CD cavity[10-13]. In order to determine the stoichiometry of the inclusion complexes the dependence of HPα-CD on absorbance and

fluorescence of both PABA and HABA were analysed using the Benesi- Hildebrand equation[14] for 1:1 complexes for absorption.

$$\frac{1}{A-A_0} = \frac{1}{A'-A_0} + \frac{1}{(A-A_0)\,[HP\propto-CD]} \quad (1)$$

Where A_0- initial absorbance, A- observed absorbance, A' is the absorbance of the HPα-CD inclusion complexes.

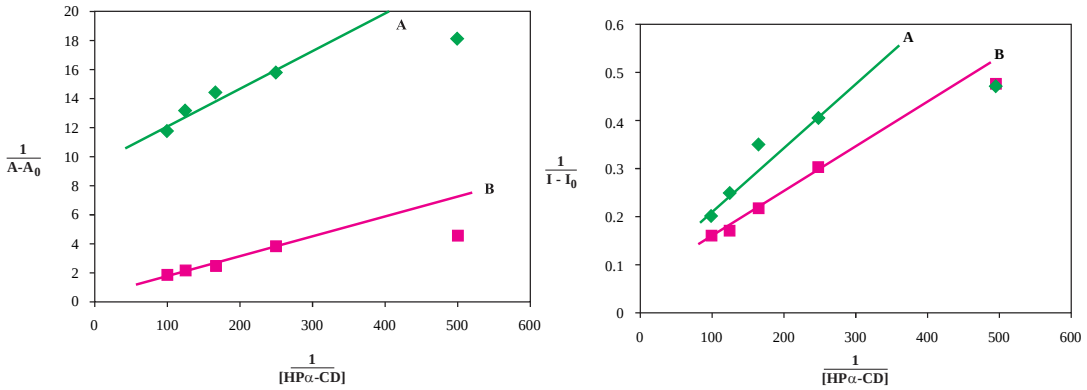

Fig.3 Benesi Hildebrand plot of (A) 4-(Phenylazo)benzoic acid and (B) 2-(Hydroxy phenylazo)benzoic acid

From Table.2 and Fig. 4, the fluorescent characteristics of both the compounds showed an increase in fluorescent intensity and suggest the formation of the inclusion complex between the compounds and HPα- CD. For Fluorescence.

$$\frac{1}{I-I_{0'}} = \frac{1}{I'-I_0} + \frac{1}{K(\mathrm{I}-\mathrm{I}_0)\,[HP\alpha-CD]} \quad (2)$$

Where I_0 is the initial fluorescence intensity, I- observed intensity and I' is the intensity of HPα-CD inclusion complexes. From the Benesi-Hildebrand plot shown in Fig.3 it was observed that a linear relation is obtained for both the compounds which indicates that the stoichiometry of the inclusion complexes formed for both the compounds is 1:1.

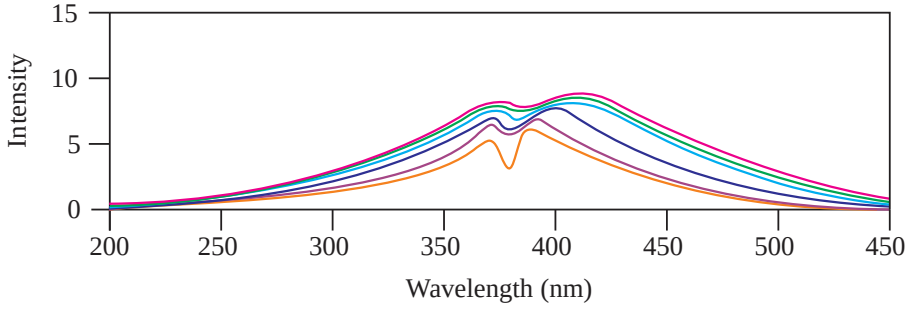

Fig. 4 (a) Fluorescent Spectra of 4-(Phenylazo)benzoic acid

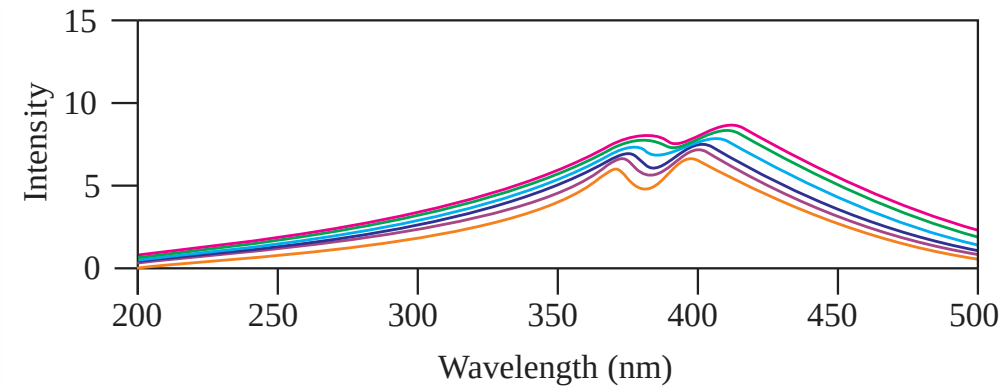

Fig. 4 (b) Fluorescent Spectra of 2-(Hydroxy phenylazo)benzoic acid

The fluorescent maxima of both PABA and HABA are regularly red shifted. For PABA, the spectral shift is from λ_{flu} 389 nm to 417 nm for longer wavelengths and 369 nm to 380 nm for shorter wavelength. The fluorescent spectra of HABA depicts a spectral shift of 398 nm to 411 nm for longer wavelength and 371 nm to 382 nm for shorter wavelengths. The spectral shifts are highly shifted bathochromically for PABA when compared to HABA. The fluorescent intensity increases with increase in HPα-CD concentration for both the compounds. Such changes in both compounds caused by the introduction of HPα-CD are indicative of the formation of an inclusion complex. The binding constant K and the stoichiometric ratios of the compounds can be determined according to the Benesi-Hildebrand relationship assuming the formation of a 1:1 host-guest complex.

A good linear correlation is obtained between a plot of $\frac{1}{A-A_0}$ vs $\frac{1}{[HP\alpha\text{-}CD]}$ and $\frac{1}{I-I_0}$ vs $\frac{1}{[HP\alpha\text{-}CD]}$ confirming the formation of 1:1 inclusion complex. $\Delta G = - RTlnK$ (3)

The ΔG values for PABA S_0= - 16.029 kJ/mol S_1 = - 14.54 kJ/ mol and

HABA S_0 = - 14.56 kJ/mol and S1 = - 18.84 kJ/ mol.

The K values obtained are 320.8 M^{-1} for PABA and 1768 M^{-1} for HABA. The K value is higher for HABA which can be attributed to the hydrophobic interaction between the phenyl ring with the internal wall of the HPα-CD. Also, in hydrophilic environment the – OH group is located outside the HPα-CD cavity. The free energy was calculated from the formation constant (K).

Table. 1 Absorption and fluorescence maxima of 4-(Phenylazo)benzoic and 2-(4-Hydroxyphenylazo)benzoic acid at different concentrations of HPα-CD

No	Concentration of HPα-CD	4-(Phenylazo)benzoic acid			2-(4-Hydroxyphenylazo)benzoic acid		
		λ_{max}	log ε	λ_{flu}	λ_{max}	log ε	λ_{flu}
1	Water	329	4.03	389	343.4	3.74	398
		237.2	3.82	369	236.3	3.24	371
2	0.002	332	3.96	393	350.6	3.74	401
		239.2	3.67	370	238.2	3.24	373
3	0.004	335.4	3.97	400	353.0	3.88	403
		240.7	3.68	372	240.7	3.54	375
4	0.006	336.7	3.95	411	356.4	3.70	407
		242.1	3.62	375	241.3	3.26	378
5	0.008	338.5	3.97	414	358.0	3.74	409
		244.8	3.75	377	243.7	3.36	381
6	0.010	339.7	3.96	417	361.5	3.71	411
		246.0	3.79	380	246.2	3.38	382
7	Excitation wave length	320			340		
8	Binding constant (1:1)	644		320.8	323.9		1768
9	ΔG(1:1) (Kcal / mol)	-16.029		-14.540	-14.56		-18.84

The negative values of ΔG suggest that the inclusion proceeds spontaneously at 303 k. The negative ΔG values under the experimental conditions indicate that the inclusion controlled process. The hydrophobic interaction between the internal wall of HPα-CD and the compounds is an important factor for the stability of inclusion complexes. The difference in magnitude of the hydrophobic interaction is related to the contact area of the compounds and the internal wall of HPα-CD.

FTIR Spectra of PABA and HABA

The FTIR spectra of PABA, HPα-CD, and the solid inclusion complexes with HPα-CD are studied PABA examined in KBr pelleting shown in Fig.5 (a), (b) and (c) displays one absorption band at 3410.15 cm^{-1} due to O-H stretching is shifted to lower wavelength at 3398.57 cm^{-1} of higher energy in the inclusion complex of PABA:HPα-CD because of intermolecular H- bonding. The aromatic C-H stretching of PABA appears around 3039.81 cm^{-1} and 2981.95 cm^{-1}, 2819 cm^{-1} is shifted to higher energy lower wavelength at 2927.24 cm^{-1} some frequencies are lost in the inclusion complex. The N=N stretching frequency at 1500.62 cm^{-1}in PABA is lost in the inclusion complex which implies that N=N group is encapsulated in the HPα-CD cavity. The C=O stretching band (1678.07 cm^{-1}) in the PABA remains as such as in the inclusion complex of PABA:HPα-CD This indicates that C=O group lies outside the HPα-CD cavity. The C=C stretching frequency in PABA corresponding to 1600.92 cm^{-1} is shifted to higher wavelength 1604.77 cm^{-1}in the complex. The frequency corresponding to the carboxylic acid group appears at 1219.01 cm^{-1} is present as such in both the compound and the inclusion complex. This shows one benzene ring with the carboxyl groups lies outside the cavity of HPα-CD. And one of the aromatic ring with the azo group lies inside the HPα-CD cavity.

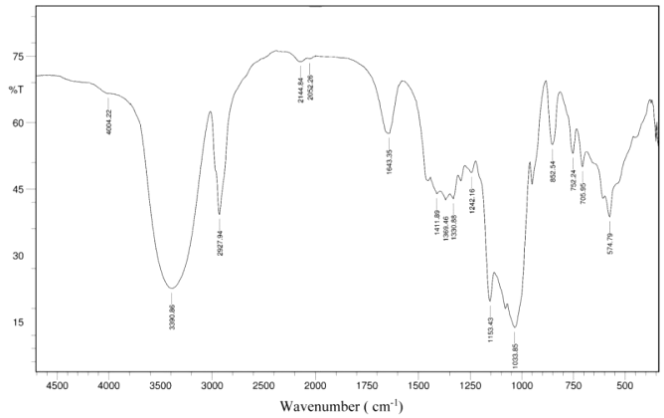

Fig. 5 (a) FTIR spectra of HPα-CD

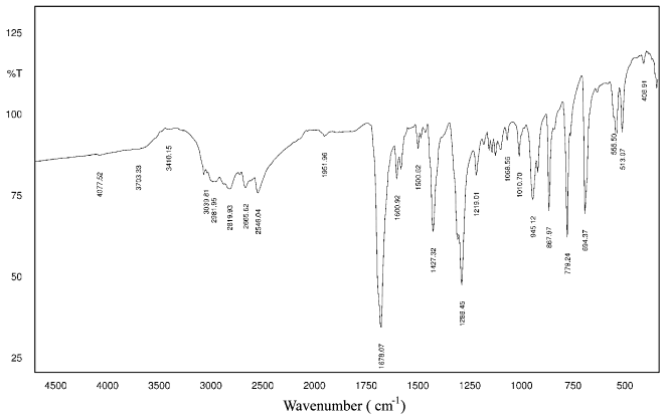

Fig. 5 (b) FTIR spectra of PABA

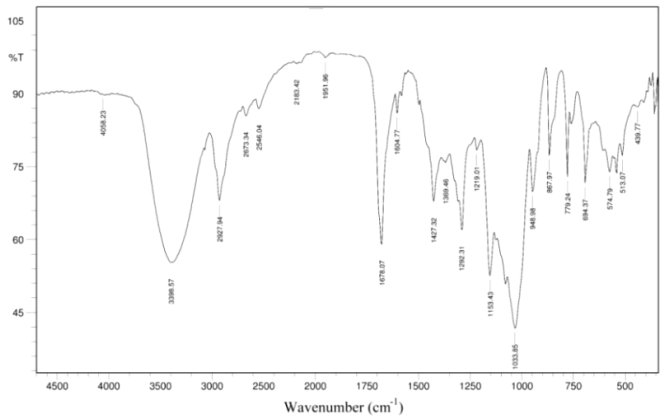

Fig. 5 (c) FTIR spectra of PABA:HPα-CD

The FTIR spectra of HABA, HPα-CD and the solid inclusion complexes with HPα-CD are shown in Fig. 5(a), 6(a) and (6b). Pure HABA exhibits bands at 2619cm^{-1} and 2555.75 cm^{-1} corresponding to aromatic C-H stretching frequencies. These bands are lost in the inclusion complex. The aromatic ring stretching frequency appears around 1697.36 cm^{-1},1589 cm^{-1} in pure HABA. These frequencies are very weak ie.1705.07 cm^{-1} and 1593.20 cm^{-1} in the inclusion complex.

The frequency1504.48 cm^{-1} corresponding to N=N group is lost in the inclusion complex. The frequency corresponding to C-OH bending at 1415.75 cm^{-1} remains unalte red in the inclusion complex. The frequency corresponding to the C-N stretching band 1284.59 cm^{-1} is shifted to 1288.43 cm^{-1} in the complex. The C-H out of plane bending appears around 999.13 cm^{-1}-686.66 cm^{-1}. Further the absorption bands of HPα-CD corresponding to O-H stretching at 3390.86 cm^{-1}, frequency corresponding to C-H asymmetric stretching at 2931.94 cm^{-1} and C=C stretching at 1644 cm^{-1} also appears in the inclusion complex. From these information it is implied that an aromatic ring with azo group is included in the HPα-CD cavity and the phenolic O-H projects outside the cavity. The presence of carboxylic acid group at 1242.16 cm^{-1} in the compound is present as such in the inclusion complex. The other aromatic ring with carboxylic group lies outside the cavity of HPα-CD.

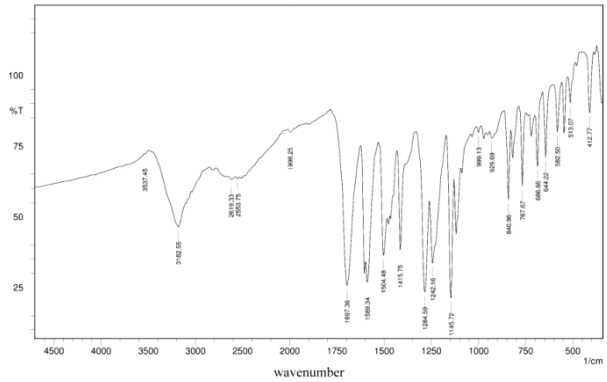

Fig. 6 (a) FTIR spectra of HABA

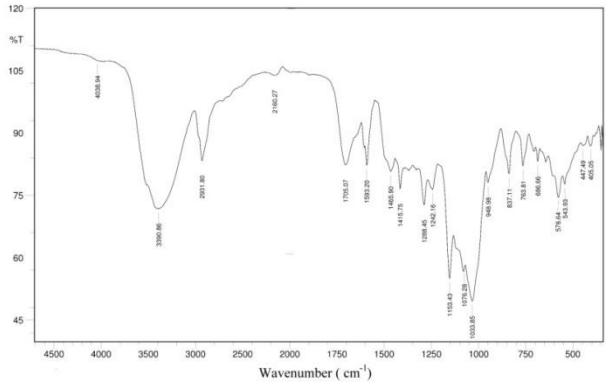

Fig.6 (b) FTIR spectra of HABA:HPα-CD

These occurrences suggest a weakening of the interatomic bonds as a consequence of an altered environment around these bonds upon complexation.1The disappearances of several guest signals can be considered as a confirmation of the formations of the inclusion complexes[15-18].

CONCLUSION

The effect of HPα-CD studies showed that both 4-(phenylazo)benzoic acid and 2-(4-Hydroxy phenylazo)benzoic acid are red shifted indicating the encapsulation of both the compounds inside the HPα-CD cavity. The stoichiometric ratio of the inclusion complexes is found to be 1:1. The binding constant values calculated indicate that PABA is tightly included into the HPα-CD cavity than HABA and inturn it is understood PABA formed more stable complexes than HABA. The negative values of ΔG indicate that the inclusion process takes place simultaneously and the reaction is exothermic. Hydroxypropylα-Cyclodextrin complexation serves as a good supramolecular strategy for enhancement of solubility and stability of the dyes.

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