CHAPTER VI

Enhancement of Fire Resistivity & Conversion into Bio-Degradable Pollutant to Minimize Environmental Pollution Explored by Physicochemical Contrivance

Abstract: Inclusion complexation of a non-biodegradable pollutant in hydrophobic cavity of β-cyclodextrin and hydroxypropyl-β-cyclodextrin were synthesized and characterized to retain its fire resistance property and converted it into bio-degradable molecule. ^{1}H NMR, 2D ROESY, HRMS, SEM, surface tension, etc. studies have been executed to establish this fact. The stoichiometry of the two complexes has been obtained as 1:1. The inclusion has been established by ^{1}H-NMR and 2D ROESY spectroscopic analysis. Substantial shifts in IR stretching frequency support the inclusion process. HRMS measurement gives the molecular ion peaks corresponding to the inclusion complex of 1:1 molar ratio of host and guest molecules. Surface texture properties of the inclusion complexes were studied by SEM and the presence of bromine were proved by EDXS. Thermal stabilities of the inclusion complexes were illustrated by DSC and melting point analysis. The aqueous solubility of the inclusion complexes demonstrate that these are more bio-available to the microorganism making them biodegradable in nature. The biodegradability study confirms the conversion of non-biodegradable HBCDD into biodegradable material by encapsulating in the two cyclodextrins.

1. Introduction

1,2,5,6,9,10-hexabromocyclododecane(HBCDD) is mainly globally used as fire retardant additives for producing extruded or expanded polystyrene foam materials in bulk amount and has been widely manufactured from 1960[1](Figure 1). Moreover, it is used as an additive to manufacture various things such as upholstered furniture, automobile interior textiles, car cushions, electric and electronic equipment etc[2-5]. In recent past decades it is one of the major environmental concern pollutant due to its persistent, toxic, bio-accumulative and biomagnifying or bio-transformative nature in environment[4,6,7]. For these reasons this cyclic aliphatic brominated compound is very harmful to aquatic life. Global market demand of HBCDD was 22000 tons per year in 2003[8].The major portion of HBCDD was used in Europe which was estimated at

11,000 tons in 2006,of which about 96% were used in expanded and extruded polymer[9]. Recently, it is included in Annex A of the Stockholm Convention on Persistent Organic Pollutants (POP),2009 and in 2013 for elimination with restricted uses[5,8,10]. Due to all of the adverse effects on environment it is restricted in Japan in2014 and in Republic of Korea(South Korea) in 2015 permanently till the advanced substituted one upto 2020[11,12].In recent years, the bromine industry has taken important steps to reduce discharges from manufacture and use of HBCDD and other fire retardants, notably its production is closed in HBCDD manufacturing site Newton Aycliffenearly NE coast of England. According to Newton EU risk assessment, "it was the largest single source of emissions of HBCDD to the environment"[13]. But unfortunately brominated compounds are still manufactured in huge extent and used in customer's product in both developed and developing countries resulting environmental contamination and highly exposure to wildlife and human beings to a great extent[11,12]. HBCDD has been found in different environment samples for example residential dust, pooled milk, human breast milk, geographic polar areas, sediments and marine food, marine animals i.e. Harbor porpoises and Fishes, Birds, Bird eggs, water, mounting and sealant foam, oriented strand board and other composite woods, etc.[6,8,14-16]. Among different adverse toxicological and environmental effects on biota, the most crucial effect is on the mammalian nervous system. Lowest observable effects at very low μM concentrations about 1000-20,000 ng g^{-1} of HBCDD are observed in vitro exposures and in vivo exposures[1].

Because of its dramatically negative environmental impact, the development of efficient HBCDD removal technologies has increasingly become a significant environmental concern. The bio-accumulative and biomagnifying nature of HBCDD is critically threaten to the sustainable development of our planet as influence of HBCDD on the environment is long-term and difficult to repair. Some traditional methods had applied to remove this HBCDD from water for example, debromination technique, UV-irradiation technique, adsorption technique etc. and also some micro biodegradation technique etc. had applied to degrade it[17-21]. Here we approach a new novel way to remove this POP via making an encapsulation complex with β-cyclodextrin (β-CD) and hydroxypropyl-β-cyclodextrin (HP-β-CD) respectively. These supramolecular cyclodextrin compounds have been chosen as host moiety due to

their unique bi-phasic catalytic structural features i.e. hydrophobic interior and hydrophilic exterior and having an interesting internal capacity for undergoing reversible capture and release of molecular guest species[22,23]. Cyclodextrins are well established oligosaccharide of glucose units in multiple area of science for last few decades. As HBCDD is a hydrophobic molecule,it may be inserted into the hydrophobic cavity of cyclodextrin giant molecule. Cyclodextrin molecules have wide range of applications in different area of science for example trapping of different chemicals, chemo-sensors solubility enhancement, molecular switches, selective transport of compounds, molecule-based logic gates, controlled drug delivery, perfume release,chromatography, molecular machines,transmembrane channels, supramolecular polymers, transmembrane channels etc.[24-28].

Here, we have attempted to make inclusion complexes of HBCDD within the apolar cavity of β-CD and HP-β-CD respectively. The structure of inclusion complexes has been characterized by several reliable spectroscopic techniques such as ^{1}H NMR,2D ROESY,HRMS, SEM, DSC and FTIR spectra.This novel work moves toward the removal of HBCDD organic pollutant from environment via formation of inclusion complexes with water soluble cyclodextrin supra-molecules. The aim of this novel work is to enhance the water solubility and bioavailability of HBCDD towards microorganisms for its faster biodegradability.

2. Experimental

2.1. Materials

1,2,5,6,9,10-hexabromocyclododecane and β-CD of purity grade were bought from Sigma-Aldrich and Hydroxypropyl-β cyclodextrin was purchased from Tokyo Chemical Industry and also used as received.The purity of all these compounds were ≥95%,97% and98% respectively.

2.2. Apparatus

^{1}H NMR spectroscopy were done in DMSO-d^{6} at 300 MHz in Bruker Avance 300 MHz apparatus at 298 K and 2DROESY experiment was performed in Bruker Avance 400 MHz apparatus at 298 K.Theelaborated ^{1}H NMR and 2D ROESY spectra have been shown in Figure 2 and S1-S5.All the data are represented in terms of

chemical shift andthe signals were taken as δ values in ppm byDMSO-d^6 atδ = 2.50 ppm as internal standard.

Fourier transform infrared spectra were done in a Perkin Elmer FT-IR spectrometer as per KBr disk technique. KBr disks were prepared in 1:100 ratio of sample to KBr.At room temperature 4000-400 cm^{-1} scanning range had taken during the FTIR studying.

Mass spectrometry was performed by Q-TOF apparatus with positive mode ionization using methanol solution of the inclusion compounds.

Surface tension data were obtained by platinum ring detachment method using digital tensiometer K9, KRÜSS. Temperature was kept at 298.15 K by circulating thermostatic water through a double walled glass vessel holding the solution.

The surface morphology of HBCDD, β-CD, HP-β-CD and their inclusion complexes was studied by JEOL JSM IT 100 Scanning Electron Microscope (SEM) using different accelerating voltage. Dry samples were spread onto carbon tapes (double adhesive carbon-coated tape) adhered to aluminum stubs which were then coated with a thin layer of gold ions in gold -ionization chamber. Then samples were scanned by SEM and images were taken under different resolutions.

Melting points of HBCDD and the two inclusion complexes were determined with the help of capillary tube by Thiele tube method.

2.3. Procedure of formation of solid inclusion complexes

All the experimental samples were accurately weighed in desired proper quantities with the help of METTLER TOLEDO AG-285 analytical balance having uncertainty of ±0.1 mg at 298.15K. Adequateprotectionwas taken to reduce the loss of solvent caused by evaporation throughout working with the solutions. The solid inclusion complexes have been prepared with 0.3mM of β-CD and HP-β-CD separately in two clean and dried beakers with triply distilled and deionized water which were allowed to stir for 6 hours on a magnetic stirrer at room temperature. Then 0.3 mM solution of HBCDD was prepared in a beaker with HPLC grade absolute ethanol and allowed to stir for 6 hours. After that, the prepared HBCDD solution was added

dropwise to those respective host solutionsseparately making the ultimate equimolar solutions. After completion of 48 hours stirringmaintaining the temperature at 50-55°C, the solutions were taken off from the hot-top (Tarsons Digital Spinot) in order to cool down at room temperature. Suspensions appeared after cooling were filtered off and stored in vacuum desiccator after drying in air.[29]

2.4. Procedure for biodegradation study

10 mM solution of the two inclusion complexes and pure HBCDD in DMSO were separately incubated at 37^{o}C in a medium of 1.0 g of glucose, 5.0 g of polypeptone, 5.0 g of yeast extract, and 10 g of NaCl per liter, pH 7.0 with and without Pseudomonas sp. bacteria in 100 ml conical flask for 7 days. 2 mL solution was taken out from each incubated media and subjected to centrifuge in orbital incubator at 10,000 rpm speed for 10 minutes. Then the soup was extracted after being thoroughly mixed with equal volume of ethyl acetate (EAA) for each case and with the solution in EAA, TLC was performed with 10% EAAin n-hexane solution media. The respective TLC spots were observed in a closed glass chamber which was completely saturated with iodine vapour.

3. Result and discussion

3.1. ^{1}H NMR and 2D ROESY spectra analysis of the inclusion complexes

Encapsulation of any molecule inside the hydrophobic cavity of β and HP-β-CD results the change in the chemical shift of the interacting protons of the guest along with CD in ^{1}H NMR spectrabecause of the mutual shielding via space.CD has H3 and H5 hydrogenatoms inside the torus cavity, specially, the H3 protons are located near the wider rim while H5 protons are positioned close to the narrower rim while the other H1, H2 and H4 protons are located at the outer surface of the CD molecule[22,29-31]. The ^{1}H NMR spectra ofHBCDD,β-CD, HP-β-CD and their two ICs areshown in FigureS1-S5, where the hydrogens of HBCDD as well as signals for H3 and H5 hydrogens of cyclodextrin is appeared with shifted chemical shift (δ) values. The ^{1}H NMR spectra for all of these newly formed complexes reveal considerable upfield shift confirming the construction of inclusion complexes.[32-34]

2D ROESY NMR spectroscopy offersconvincingsupport about the spatial close proximity of the interacting atoms of the guest with the host molecules by detecting the off-diagonal cross-correlations[35,36].The hydrogens which are placed within 0.4 nm in gap may generate a rotating-frame NOE spectroscopy (ROESY)[37].2D ROESY spectra of HBCDD with β and HP-β-CDwere recordedin DMSO-d^6which show noteworthy correlation of the hydrogens of HBCDD with the respective H3 and H5 protons of both CD molecules establishing that the HBCDD molecule was encapsulated into the both cyclodextrin cavities (Figure2)[38,39]. It may be noticed that the H-6 protons of cyclodextrins did not interact with the protons of HBCDD by the inclusion processes, suggesting that the pollutant molecule was inserted into the cyclodextrin cavity via the wider rim and not from the side of the narrower rim otherwise off-diagonal cross-peaks could be observed for the interaction of H6 with the guest molecule in the respective ROESY spectra[40,41].

3.2. FTIR spectra of solid inclusion complexes

Infra-red spectroscopic analysis of IC's along with the pure host and guest molecules also unveils the reliability about the way by which the IC's are formed and found to mimic the mode of host – guest interaction as obtained from the 2D ROESY NMR spectroscopic study[42-44]. KBr disk of the samples were prepared separately and the spectra obtained are reported in Figure 3, 4. The significant peaks of corresponding chemical bonds that undergo shift by wavelength while complexations are listed in table 1 and S1.

The following spectral changes (Table 1), taking place in the (HBCDD+β-CD) system may enable us to recognize it as an inclusion complex. (i) The signal for (C^{sp3}-Br) stretching of HBCDD usually appears in the range between 718.02-538.17 cm^{-1}, but most of the signals in this span of wavelength were found to be masked leaving a broad signal at 604.28 cm^{-1} while complexed with β-CD. (ii) The peak at 1442.06 cm^{-1} responsible for ($C^{sp3}H_2$) bending of HBCDD is now shifted to 1380.34 cm^{-1} making a large wavenumber shift of 61.72 cm^{-1}. (iii) (C^{sp3}-H) stretching frequency of HBCDD appearing at 2930.25 cm^{-1}, shifted to 2915.05 cm^{-1} during its complexation with β-CD. (iv) A frequency shift of 13.25 cm^{-1} is also observed for (O-H) stretching of β-CD for

which, signal of (O-H) stretching at free and complexed state were noted as 3436.28 and 3423.03 cm^{-1} respectively.

The formation of (HBCDD + HP β-CD) inclusion complex and various interactions developed thereby were analyzed by the following spectral changes – (i) The peaks for (C^{sp3}-Br) stretching of HBCDD were observed in the range of 718.02-538.17cm^{-1}, shifted to the wavelength range of 701.15-529.11 cm^{-1} in case of inclusion complex. Beside shifting (12.955 cm^{-1}) masking of various significant is also observed in this region. (ii) The signal responsible for ($C^{sp3}H_2$) bending mode of HBCDD appearing at 1442.06 cm^{-1}, shifted to 1419.23 cm^{-1} while formation of inclusion complex with HP β-CD. (iii) The (C^{sp3}-H) stretching frequency of HBCDD was observed at 2930.25 cm^{-1}, in case of inclusion complex it was found to appear in the range 2940.07-2895.12 cm^{-1} making a significant shift of 15.155 cm^{-1}. (iv) The (O-H) stretching frequency of HP β-CD also made to be shifted from 3419.25 to 3405.05 cm^{-1} owing to the supramolecular host – guest interaction.

This is hardly to detect the appearance of additional signals in the infra-red spectrum of studied ICs suggests there is no sign of chemical reaction which may be taken place during complexation. Now, it is easy to say that, the spectral changes, observed in case of inclusion complexes responsible for supramolecular interaction.

3.3. High resolution mass spectrometric (HRMS) analysis of inclusion complexes

The formation of two inclusion complexes i.e., IC-1 and IC-2 may be confirmed with the help of ESI-MS study. Figure 5 shows mass spectra of two ICs, which show the intense peaks at m/z 1798.27 and 2183.88 respectivelyindicating the formation of $[HBCDD+\beta\text{-}CD+Na]^+$and $[HBCDD+HP\text{-}\beta\text{-}CD+H]^+$inclusion complexes and their corresponding host-guest stoichiometric ratio is 1:1 (Table 2). It is noted that no other peaks around those values are observed in mass-spectrometry[45,46].

3.4 Surface tension and stoichiometry in the inclusion complex

Surface tension (ST) data provides the stoichiometry of the host-guest inclusion complex. The ST is plotted against the mole ratio of β-CD and HP-β-CD respectively with HBCDD. Figure 6 explains the variation of ST, where in both cases

there were progressively rising trend of ST with increasing concentration of cyclodextrins as a result of encapsulation of the HBCDD molecule from the surface of the solution into the hydrophobic cavity of cyclodextrins forming host-guest inclusion complexes. Most importantly both the plots demonstrate that there are single clear breaks in each curve (figure 6), which not only reveal the formation but also specify the 1:1 stoichiometric ratio for each of the inclusion complexes formed [47] [48] [29] [49].

3.5. Scanning electron microscopic (SEM) analysis of the inclusion complexes

Scanning electron microscopy is a qualitative method to determine surface topographical aspect of the raw materials and corresponding products formed by complexation with cyclodextrins[50]. Figure 7 shows the micro-photographs of HBCDD, β-CD, HP-β-CD, IC-1 and IC-2 respectively. From these images it is cleared to see that the original individual characteristic morphology of each raw materialwas completely lost in their respective products i.e. IC-1 and IC-2. The irregular characteristic amorphous natured HBCDD, irregular and parallelogram shaped β-CD and cavity with spherical shaped HP-β-CDwere completely changed in their respective ICs[51]. Here,IC-1 showed more compactness from its individual raw materials but still some amorphous character was present in it and IC-2 appeared as smooth, homogeneous, even, regular and plate-like shape. But it is clear that it was not possible to differentiate between two individual components in their respective binary systems(IC-1 and IC-2).

Thus, the reason behind the formation of these new surfaced products (IC-1 and IC-2) is possibly due to the strong complexing interaction of HBCDD with β-CD and HP β-CD accordingly, which is further supported by Energy-Dispersive X-ray Spectroscopy (EDXS) analysis[52].

EDXS is an analytic technique used for elemental analysis of a sample. From Figure 8 it is shown that, in pure β-CD and HP-β-CD there is no Br atoms at all but in their ICs with guest HBCDD, we can see the appearance of Br atoms which also supported the fact drawn from the SEM studies.

3.5. DSC thermogram

The differential scanning calorimetry (DSC) is a suitable method for the investigation of thermal properties of CD based inclusion complexes as both the qualitative and quantitative insights about the physicochemical state of the drug can be gathered while encapsulated into the cavity of CDs. Normally, the shifting of an endothermic peak in DSC thermogram indicates a change in melting point, crystal lattice or sublimation point due to inclusion complexation[53,54]. DSC thermograms of inclusion complexes, pure host and pure HBCDD have been depicted in figure 9, which is evident that the peak at 139^0C of pure HBCDD is absent in the HBCDD-β-CD and HBCDD-HP-β-CD inclusion complexes respectively. This indicates the higher stability and more fire resistivity of the inclusion complexes than the pure HBCDD.

3.7. Melting point and aqueous solubility of the solid inclusion complexes

Melting points for both the ICs including pure HBCDD were determined with the help of capillary method. From Table 3,it can be seen that the melting points of HBCDD, IC-1 and IC-2 differ significantly from each other[55]. The melting point for HBCDD is 195.0^0C, for IC-1 209.5^0C and for IC-2 210.5^0C. The higher melting point of the inclusion complexes compare to its parent compound, namely, HBCDD are because of the fact that extra amount of heat is required for that compound to come out from the corresponding cyclodextrins (β-CD and HP-β-CD respectively) cavity and also these higher values of melting point i.e. 209.5^0C and 210.5^0C clearly indicate the formation of two new inclusion complexes i.e. IC-1 and IC-2 respectively[55].

The aqueous solubility of HBCDD is very low in a wide range of temperature. But, the inclusion complexes were found to be fairly soluble in water at room temperature (Figure 10 and Table 4)[56-58]. This is the indication of a molecule to be bio-available and also bio-degradable by the microorganisms. Thus the pollutant HBCDD which was a non-bio-degradable in nature, now has been converted into a bio-degradable material through the newly formed inclusion complexes with β and HP-β-CD respectively**.**

3.8. Bio-degradability study of the inclusion complexes

The two inclusion complexes and pure HBCDD were exposed to Pseudomonas sp. bacteria in a medium (1.0 g of glucose, 5.0 g of polypeptone,5.0 g of yeast extract,

and 10 g of NaCl per liter, pH 7.0) in 100 ml conical flask for 7 days to explore the degradation of HBCDD in the IC-1 and IC-2.[59,60,61]Interesting results were found after incubation at 37^{o}C. The IC-2 was found to be fully degraded at this condition and IC-1 was found partially degraded by the Pseudomonas sp. bacteria, while incubation of pure HBCDD with Pseudomonas sp. bacteria under identical condition causes no degradation of the pollutant as found from the spots in TLC plates.

TLC of the incubated inclusion complexes are shown in figure 11, which confirm the use of HP-β-CD andβ-CD as the encapsulating agent for HBCDD to make the pollutant bio-available and bio-degradable.

The TLC plates I and II show the degradation study of IC-1 and IC-2 respectively. Spot I-a is for the incubated solution of IC-1 with bacteria, I-b for incubated solution of IC-1 without bacteria, I-c for IC-1 and I-d for HBCDD. Similarly for the second TLC Spot II-a is for the incubated solution of IC-2 with bacteria, II-b for incubated solution of IC-2 without bacteria, II-c for IC-2 and II-d for HBCDD. After incubation no spot was found for IC-2, clearly indicating the decomposition of HBCDD while encapsulated byHP-β-CD. The HBCDD was decomposed partially while encapsulated by β-CD as found from the faint spot on TLC plate. This study evidently reveals that the non-biodegradable pollutant HBCDD has been converted to biodegradable by making inclusion complexes with HP-β-CD and β-CD.

4. Conclusion

In this novel study the inclusion complexation of a non-biodegradable pollutant (HBCDD) with β-CD and HP-β-CD were synthesized and characterized to retain its fire resistance property and to convert it into bio-degradable molecule. Various spectroscopic studieshave been performed to establish this fact. The stoichiometry of the two complexes has been foundas 1:1 molar ratio of host and guest molecules. Surface texture properties of the inclusion complexes were studied by SEM and the presence of bromine in the complexes were evidenced by EDXS. The melting point analysis indicates that the inclusion complexes are more stable than HBCDD and hence ICs are preferred to HBCDD. The aqueous solubility of the inclusion complexes demonstrates that the inclusion complexes are more bio-available to the microorganism and thus evidently inclusion complexation of HBCDD converts it into

bio-degradable material making them eco-friendly in nature and minimizes the environmental pollution.

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Author contribution

BM, SS and BR: designed, performed the experiments and wrote the article, DR: performed the experiments, RG: designed the experiments, SB provided the theme of the work, designed and assisted to write the article and MNR: corresponding author, supervised the entire work.

Additional Information

The authors do not have any competing financial and non-financial interests.

TABLES

Table 1. FTIR frequency of some significant groups of β-CD, HP β-CD, HBCDD observed at free and complexed state showing corresponding shift

Group	Free state/cm^{-1}	Complexed state/cm^{-1}	Shift/cm^{-1}
HBCDD + β-CD			
$(O\text{-}H)_{str}$ of β-CD	3436.28	3423.03	13.25
$(C^{sp3}\text{-}H)_{str}$ of HBCDD	2930.25	2915.05	15.20
$(C^{sp3}H_2)_{bend}$ of	1442.06	1380.34	61.72

HBCDD			
$(C^{sp3}\text{-}Br)_{str}$ of HBCDD	718.02-538.17	604.28	23.815
HBCDD + HPβ-CD			
$(O\text{-}H)_{str}$ of HP β-CD	3419.25	3405.05	14.20
$(C^{sp3}\text{-}H)_{str}$ of HBCDD	2930.25	2940.07-2895.12	15.155
$(C^{sp3}H_2)_{bend}$ of HBCDD	1442.06	1419.23	22.83
$(C^{sp3}\text{-}Br)_{str}$ of HBCDD	718.02-538.17	701.15-529.11	12.955

Table 2. Exact mass and the observed m/z values of the two inclusion complexes

Inclusion complex	Exact mass	m/z
IC-1	1799.00	1798.27
IC-2	2184.25	2183.88

Table 3. Melting points of HBCDD, IC-1 and IC-2

	Melting point /^{0}C
HBCDD	**195.0**
IC-1	**209.5**
IC-2	**210.5**

Table 4. Aqueous solubility of HBCDD, IC-1 and IC-2 at 298 K

	Solubility /mM mL^{-1}
HBCDD	5.3×10^{-9}
IC-1	2.9×10^{-3}
IC-2	3.7×10^{-3}

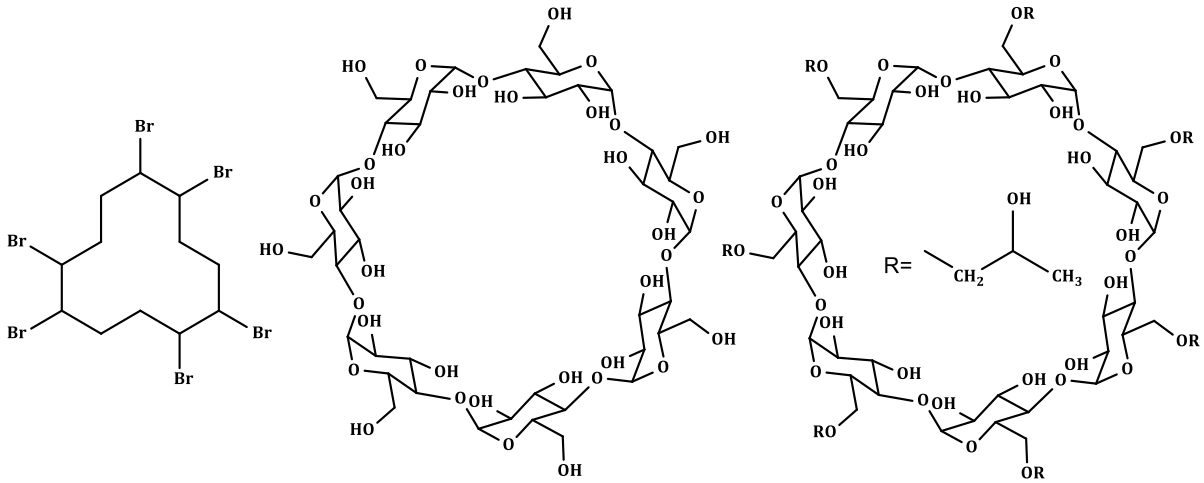
Table S1. Frequencies of FTIR spectra ofβ-CD, HP-β-CD, HBCDDand two solid inclusion complexes

β-cyclodextrin (β-CD)		**Hydroxy-propyl β-cyclodextrin (HP β-CD)**	
Wavenumber (cm^{-1})	**Group**	**Wavenumber (cm^{-1})**	**Group**
3436.28	-O-H stretching	3419.25	-O-H stretching
2923.07	-C-H stretching	2917.19	-C-H stretching
1377.14	-C-H and -O-H bending	1369.19	-C-H and -O-H bending
1157.11	C-O-C bending	1157.16	C-O-C bending
1029.13	C-C-O stretching	1028.27	C-C-O stretching
940.12	skeletal vibration involving α-1,4linkage	951.25	skeletal vibration involving α-1,4linkage
Hexabromocyclododecane (HBCDD)			
Wavenumber (cm^{-1})		**Group**	
2930.25		-C-H stretching	
1442.06		$-CH_2$ out of plane bending	
718.02-538.17		C-Br stretching	

HBCDD + β-CD		**HBCDD + HP-β-CD**	
Wavenumber (cm^{-1})	**Group**	**Wavenumber (cm^{-1})**	**Group**
3423.03	-O-H stretching	3405.05	-O-H stretching
2915.05	-C-H stretching	2940.07-2895.12	-C-H stretching
1380.34	$-CH_2$ bending	1419.23	$-CH_2$ bending

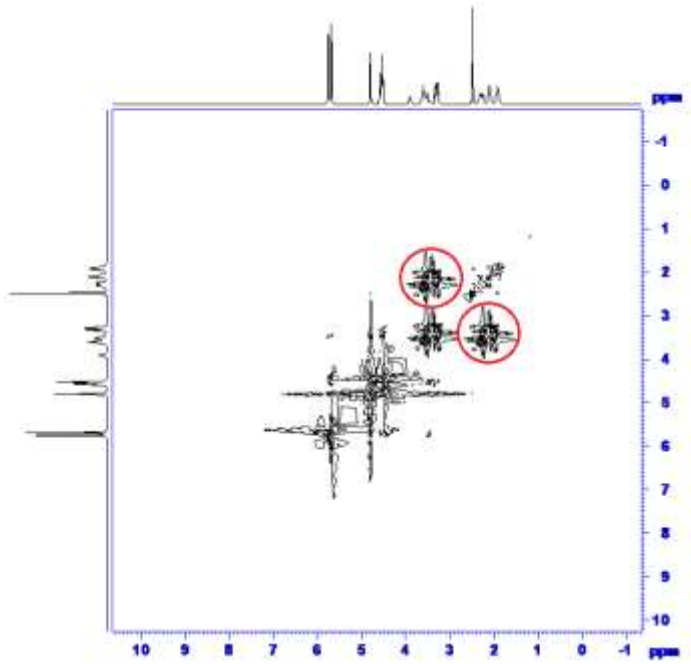
1156.01	C-O-C bending	1157.18	C-O-C bending
1029.01	C-C-O stretching	1033.31	C-C-O stretching
604.28	C-Br stretching	720.15-583.11	C-Br stretching

FIGURES

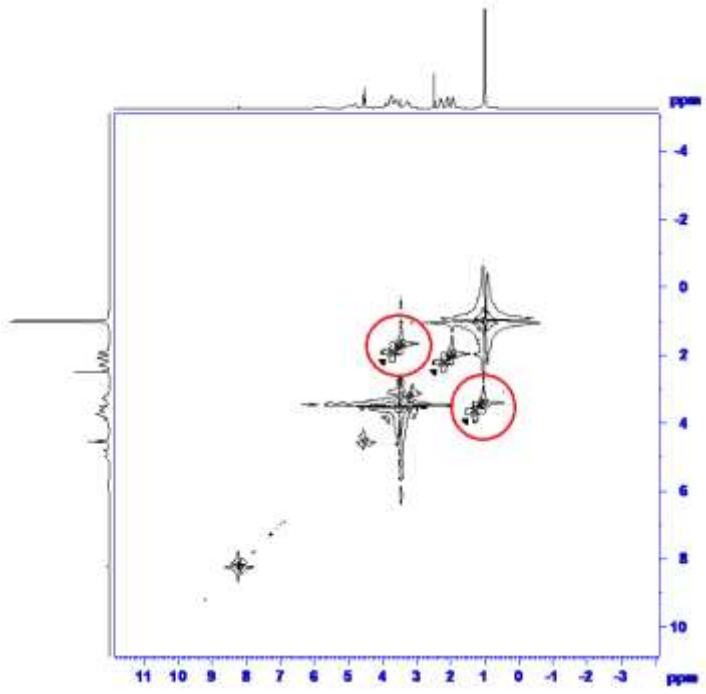


(a) **(b)** **(c)**

Figure 1. Molecular structures of (a) 1,2,5,6,9,10-hexabromocyclododecane (b) β-cyclodextrin and (c) hydroxypropyl-β-cyclodextrin.



(a)



(b)

Figure 2. (a) 2D ROESY spectra of inclusion complex of HBCDD and β-CD in DMSO-d^6(correlation signals are marked by red circles) (b) 2D ROESY spectra of inclusion complex of HBCDD and HP-β-CD in DMSO-d^6(correlation signals are marked by red circles).

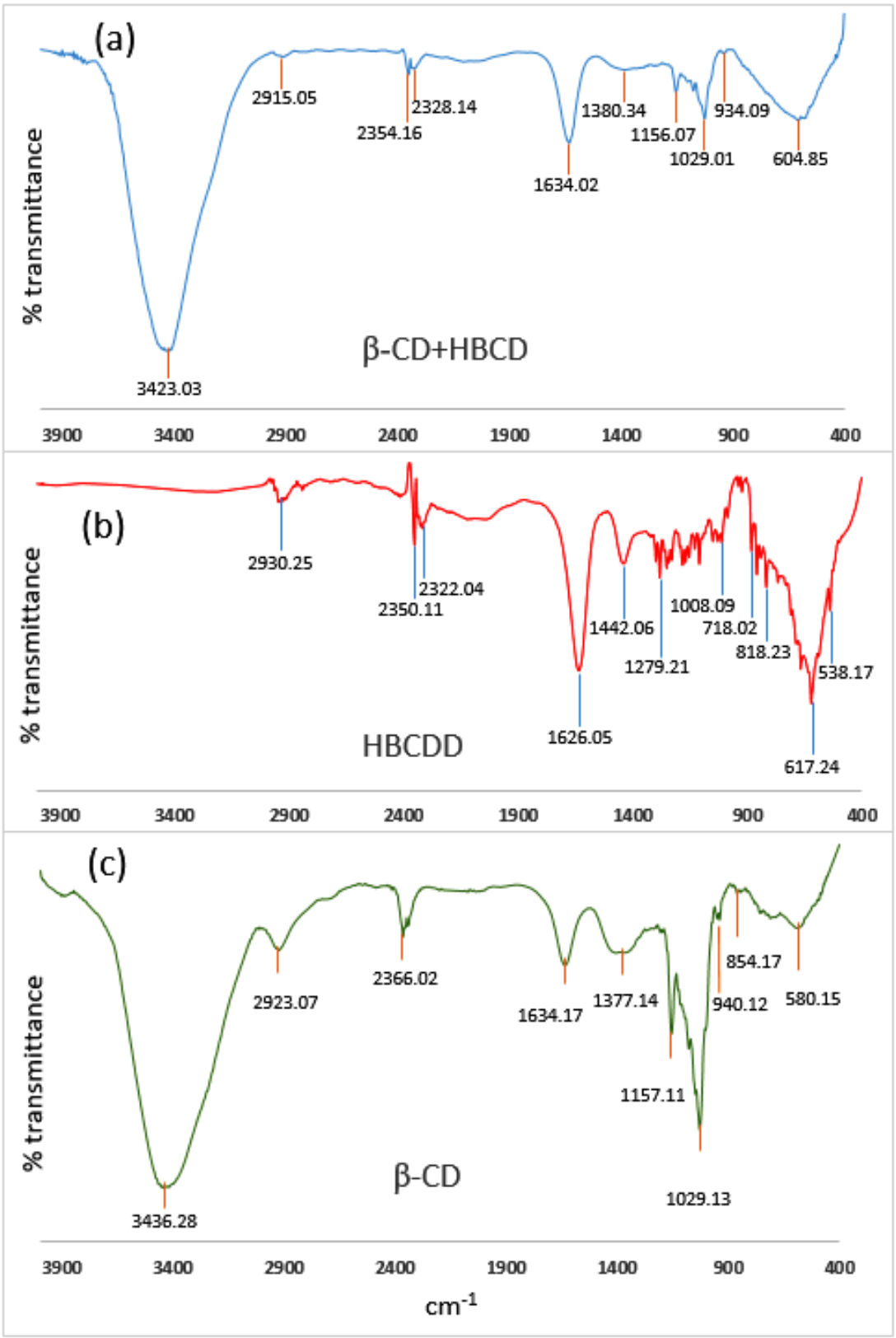


Figure 3(a, b, c): FTIR spectra of (a) (HBCDD+β-CD) inclusion complex, (b) HBCDD, (c) β-CD.

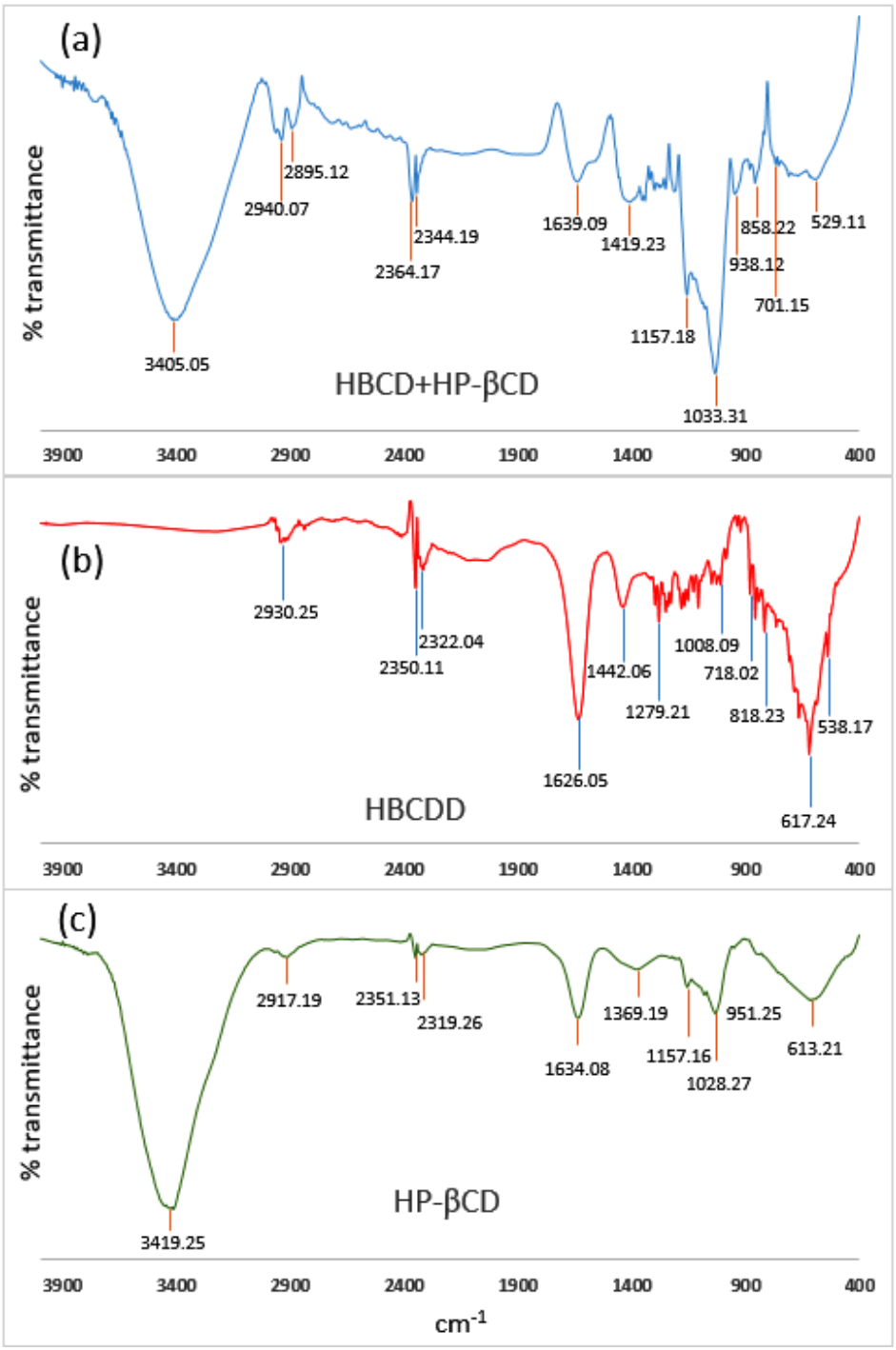


Figure 4(a, b, c): FTIR spectra of (a) (HBCDD+HP β-CD) inclusion complex, (b) HBCDD, (c) HP β-CD

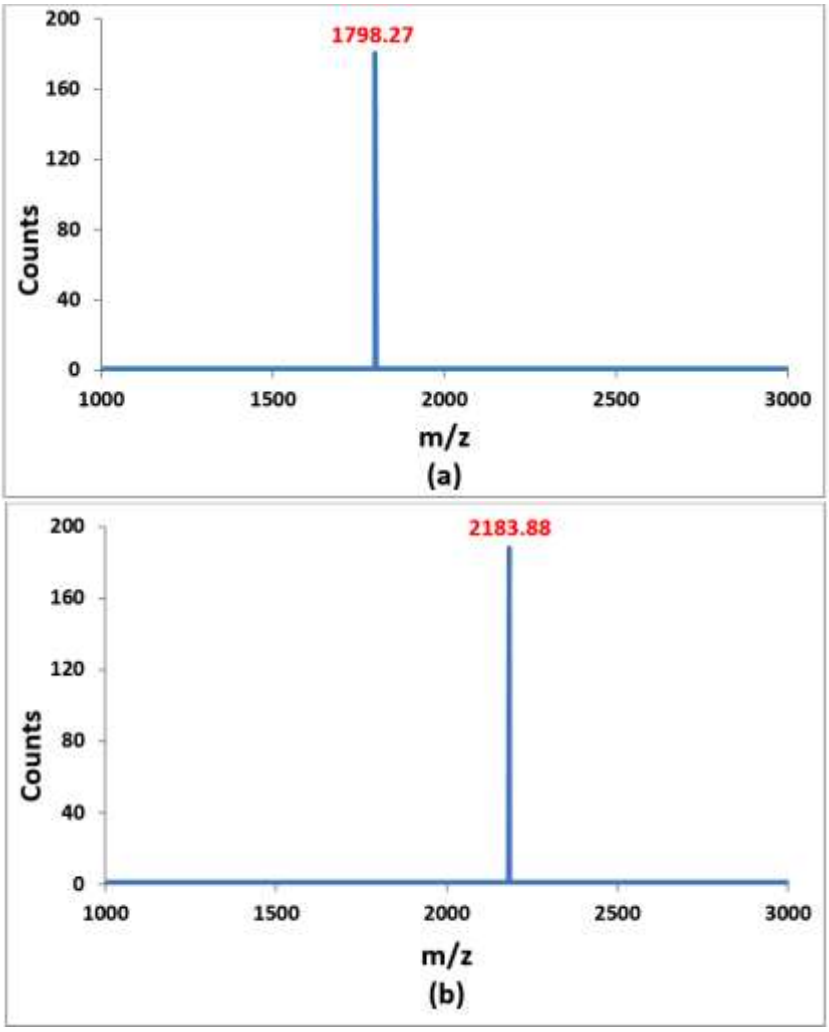


Figure 5. HRMS spectra of (a) HBCDD-β-CD inclusion complex and (b) HBCDD-HP-β-CD inclusion complex.

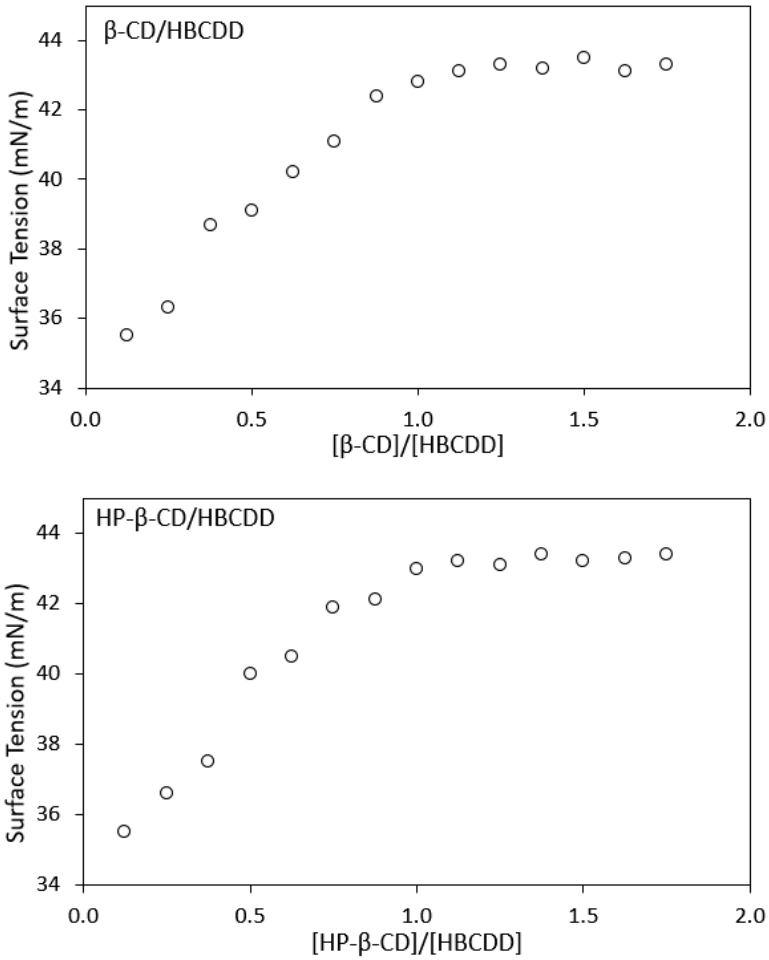


Figure 6. Variation of surface tension with mole ratio of β-CD and HP-β-CD respectively.

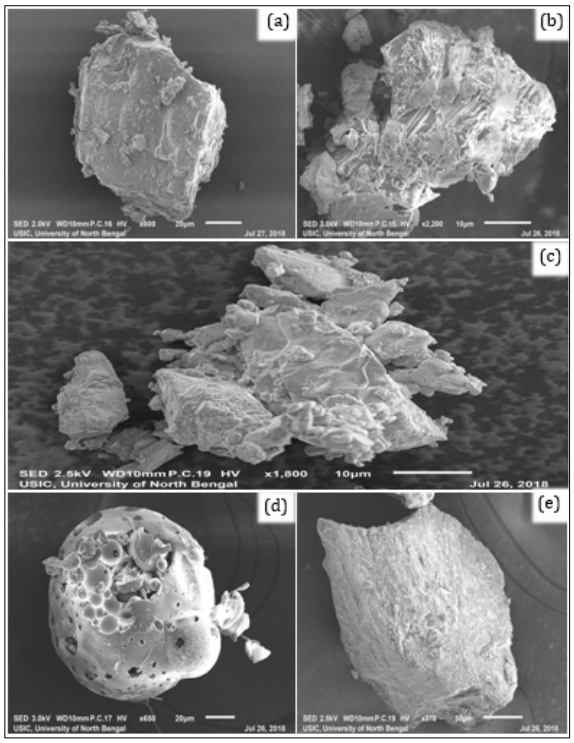


Figure 7. SEM images of (a) β-CD, (b) IC-1, (c) HBCDD, (d) HP-β-CD and (e) IC-2.

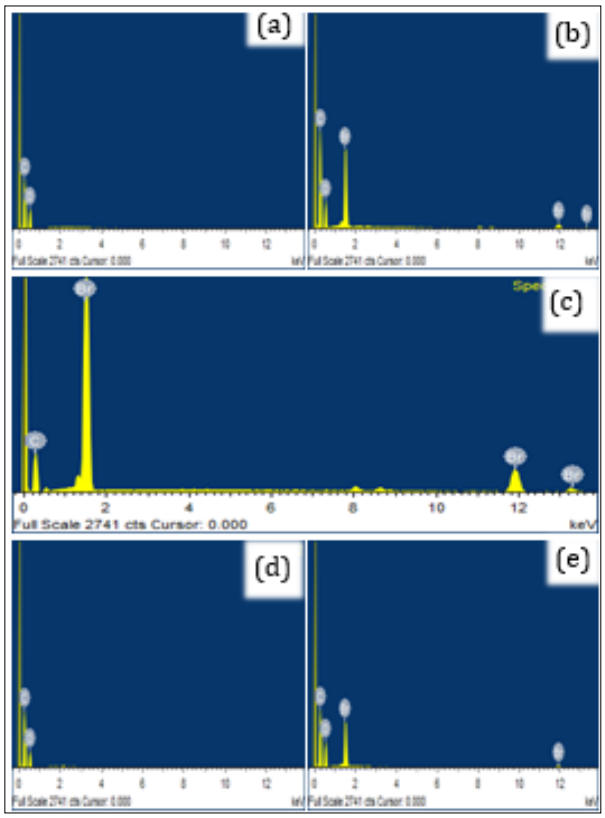


Figure 8. EDX images of (a) β-CD, (b) IC-1, (c)HBCDD, (d) HP-β-CD and (e) IC-2

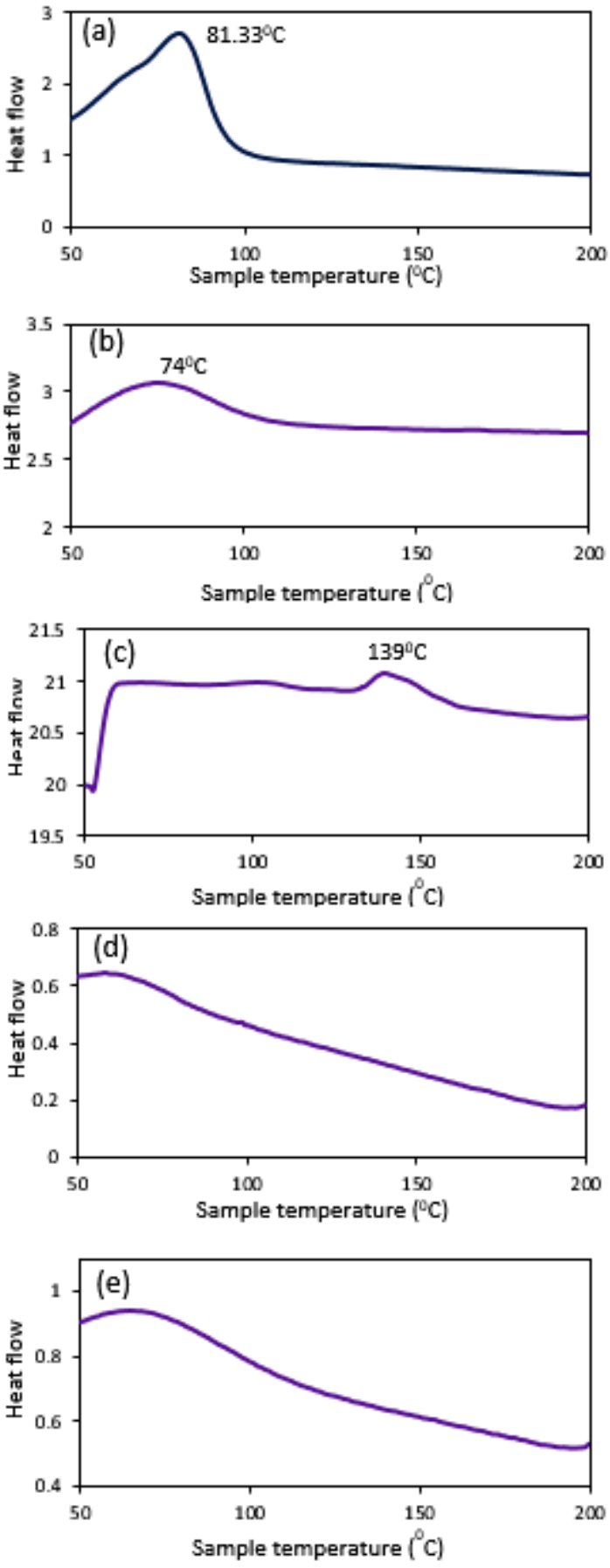


Figure 9: DSC thermograms of (a) β-CD, (b) HP-β-CD, (c) HBCDD, (e) IC-1, (d) IC-2.

Figure 10. Solubility of (a) HBCDD, (b) HBCDD-β-CD inclusion complex and (c) HBCDD-HP-β-CD inclusion complex in water.

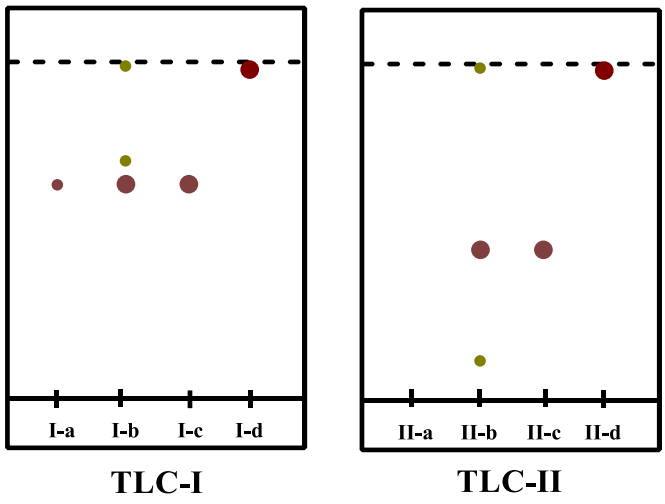


Figure 11. Representative TLC plats for degradation studies of IC-1 and IC-2.

TLC-I: R_f (I-a): 0.77; R_f (I-b): 0.77, 0.86, 0.96; R_f (I-c): 0.77; R_f (I-d): 0.98.

TLC-II: R_f (II-b): 0.21, 0.60, 0.96; R_f (II-c): 0.60; R_f (II-d): 0.98.

Figure S1. ^{1}H NMR spectra of HBCD in DMSO-d^{6} at 298.15 K

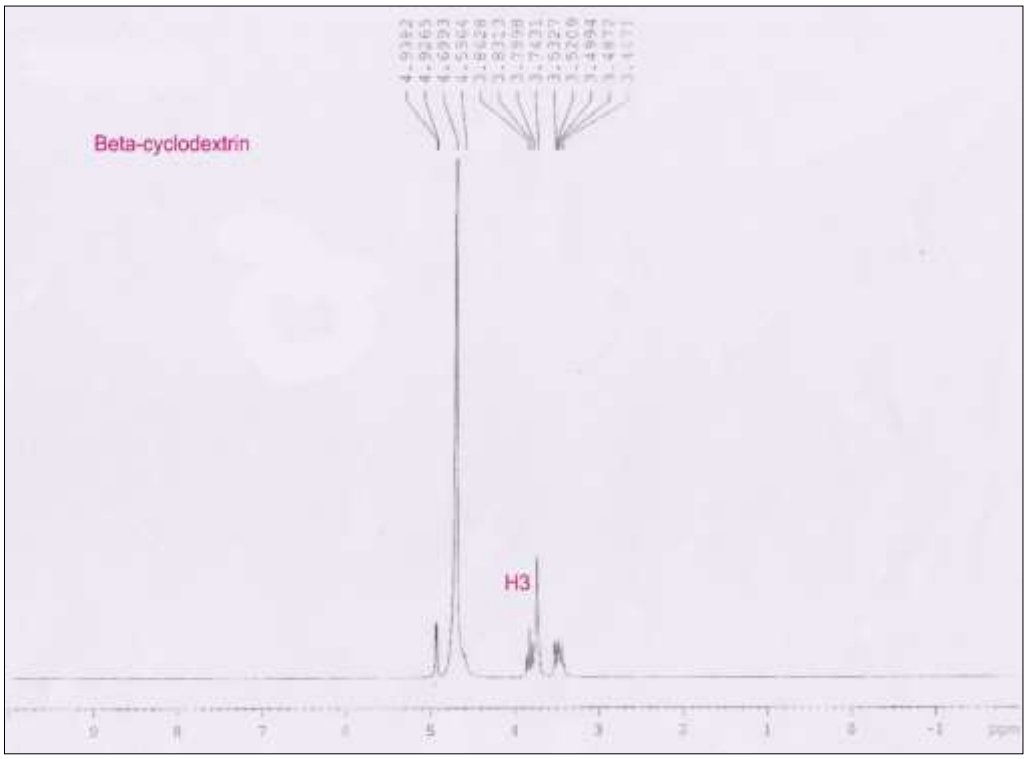


Figure S2. ^{1}H NMR spectra of β-cyclodextrin in DMSO-d^{6} at 298.15 K

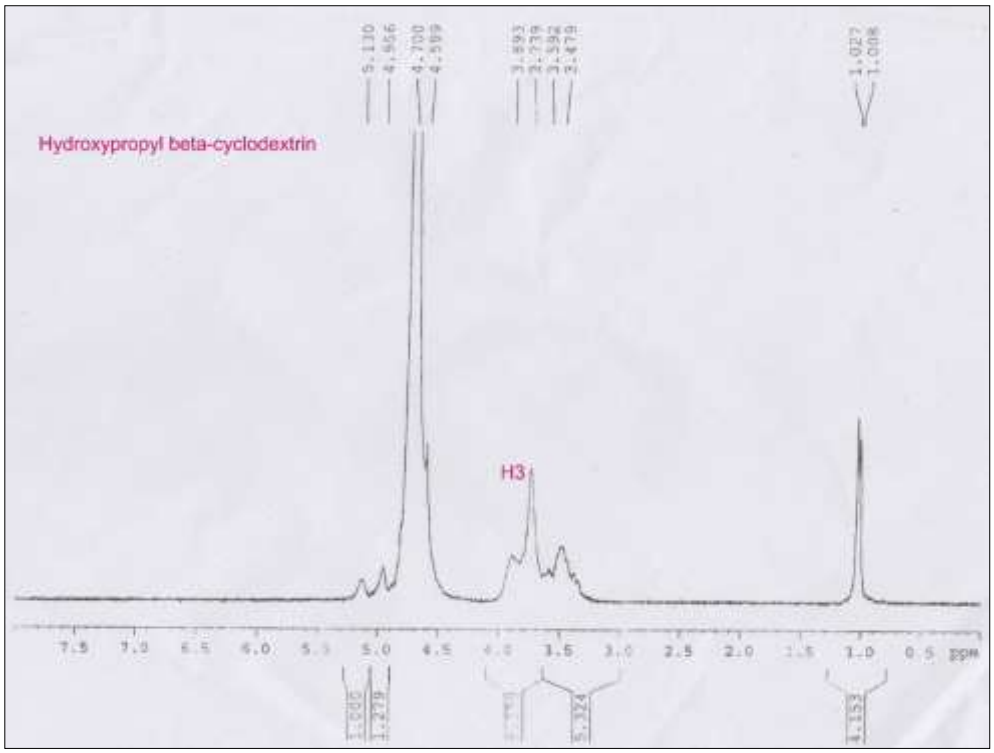


Figure S3. ^{1}H NMR spectra of HP-β-cyclodextrin in DMSO-d^{6} at 298.15 K

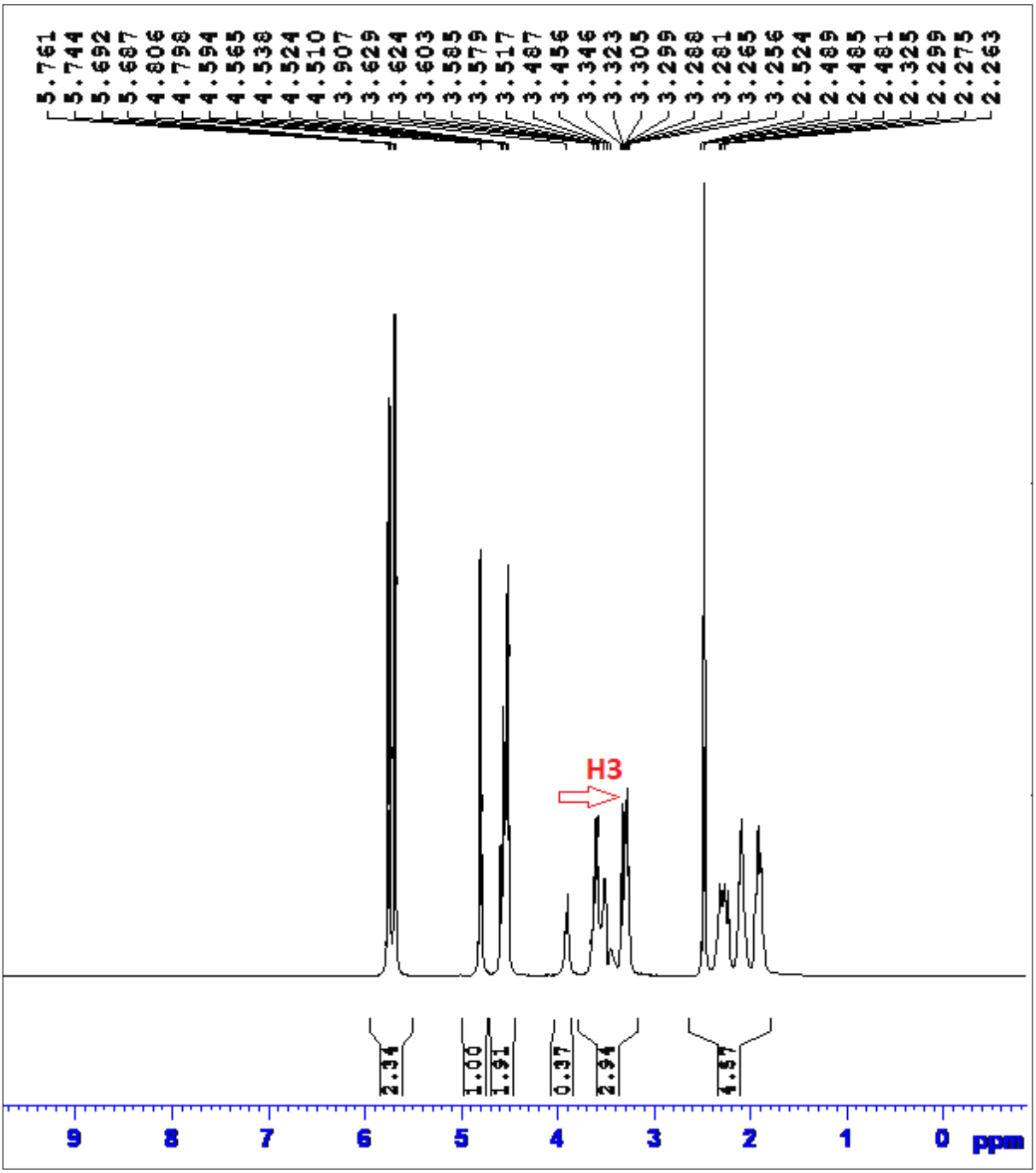


Figure S4. ^{1}H NMR spectra of IC-1 in DMSO-d^{6} at 298.15 K

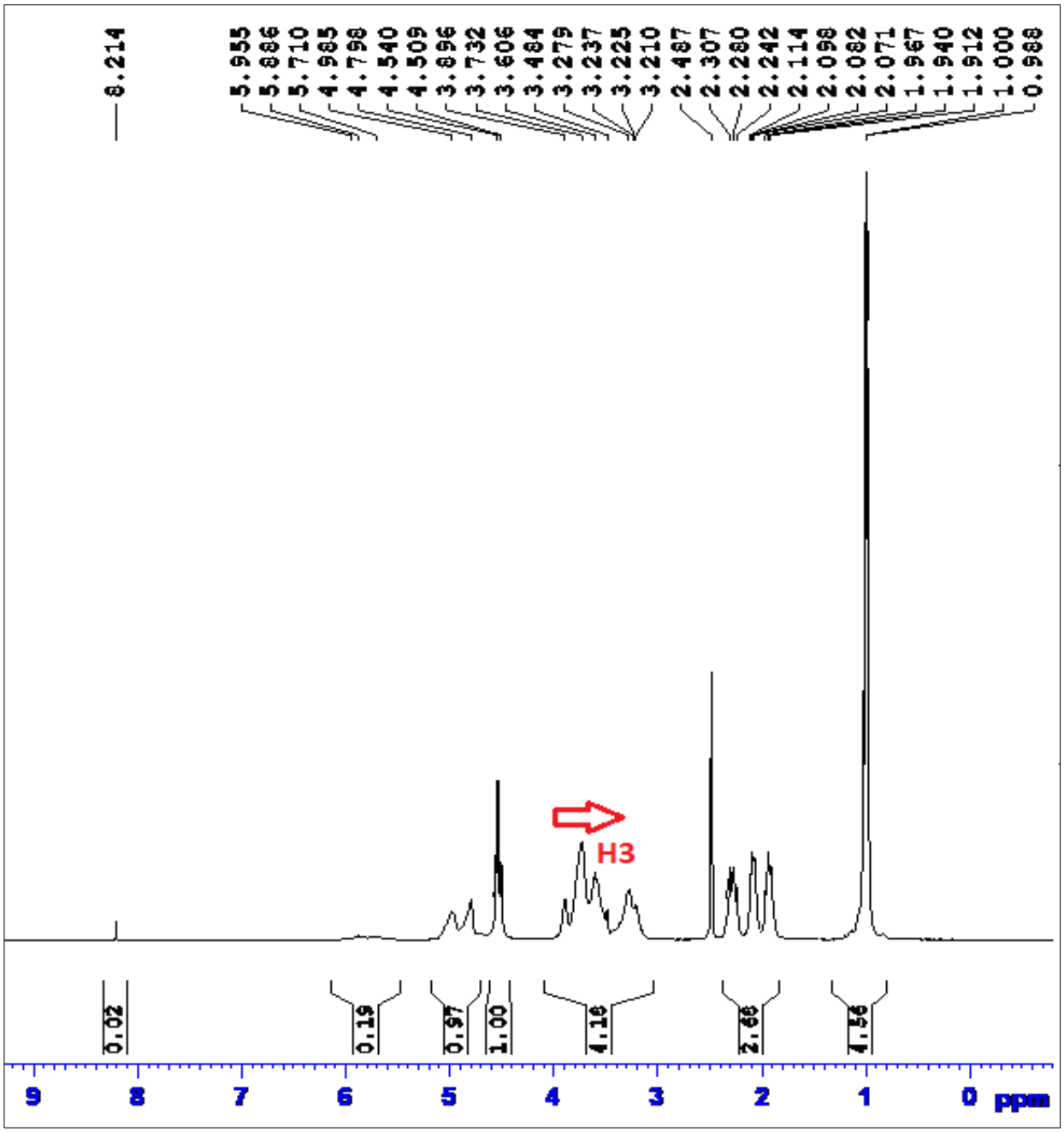


Figure S5. ^{1}H NMR spectra of IC-2 in DMSO-d^{6} at 298.15 K.