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Xinzhen Du[a]; Weihua Lu[a]; Yarong Wang[a]; Yanchun Sun[a]; Hualin Deng[a]; Jinguo Hou[a]
[a] Department of Chemistry, Northwest Normal University, Lanzhou, P. R. China

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Steric Considerations in Supramolecular Inclusion of Modified β-cyclodextrins with Triton X-100 and α-bromonaphthalene

XINZHEN DU*, WEIHUA LU, YARONG WANG, YANCHUN SUN, HUALIN DENG and JINGUO HOU

Department of Chemistry, Northwest Normal University, Lanzhou 730070, P. R. China

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Supramolecular inclusion of modified β-cyclodextrin (β-CD) with Triton X-100 (TX) and α-bromonaphthalene (BN) was studied by fluorescence and phosphorescence measurements. Major differences were observed in the magnitude of the apparent stability constants and quenching constants of the inclusion complexes. Methyl substitution on the rims of β-CD increased the binding of TX with β-CD but was unfavorable to the protection of the phenyl group of TX from fluorescence quenching and further accommodation of BN for steric considerations. According to the overall molecular size of β-CD, TX and BN, further inclusion of BN in the cavity of β-CD occupied by TX may force the flexible *tert*-octyl chain of TX to deform to a greater extent and close packing complexes were obtained. Phosphorescence of BN arising from intermolecular energy transfer between BN and the phenyl group of TX was observed when the phenyl group of TX was irradiated. In the case of heptakis(2,6-di-*O*-methyl)-β-CD, BN failed to penetrate into the cavity because of the steric hindrance of the methyl substituents at the rim of the β-CD cavity.

Keywords: β-Cyclodextrin; Triton X-100; Surfactant; Supramolecular inclusion; Fluorescence and phosphorescence

INTRODUCTION

Cyclodextrins (CDs) are cyclic oligosaccharides linked by α-1,4 bonds from the glucopyranose units in a classical C1 chair conformation. This geometry gives CDs the overall shape of torus-like macro-rings with the wider side formed by the secondary 2- and 3-hydroxyl groups and the narrower side formed by the primary hydroxyl groups. As a result of this arrangement of functional groups in CDs, the cavity is relatively hydrophobic compared to the water phase while the external faces are hydrophilic. CDs have been extensively studied for their ability to modify the photophysical properties of included molecules [1–3], and to improve the solubility and bioavailability of drugs [4,5] and the stability of flavors and fragrances [6]. Of three well-known industrially produced CDs, low-cost β-CD has been further chemically modified. Much attention has been paid to improve its solubility for the purpose of studying the physical properties of inclusion complexes of β-CD with functionalized compounds [7–10] or to synthesize functionalized β-CD for the purpose of molecular recognition [11–14]. However, substitution of hydroxyl groups at the rim of β-CD may affect the inclusion of the β-CD host with guests in the above-mentioned areas to a significant extent on the basis of dimensional and hydrophobic considerations. A few groups have reported that modified β-CD shows different hydrogen bonding interactions and thermodynamic parameters [8,9,12]. Little description was presented on steric considerations during the course of inclusion of guests, especially the second guest in the CD cavity. Hence, in this investigation, the β-CD derivatives include those without wide rim substitution and those with substitution on both the wide and narrow rims of β-CD. Triton X-100 (TX), a nonionic detergent with a built-in aromatic chromophore, was used as a fluorescent probe to study the inclusion of modified β-CD with a guest. TX included by CDs exhibits different fluorescence compared to TX alone. In the presence of CD and TX, the changes in spectral characteristics of the probe α-bromonaphthalene (BN) allow for direct investigation of the microenvironmental difference in the cavity of CDs. This

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*Corresponding author. E-mail: duxz@nwnu.edu.cn

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provides further information about the steric considerations in inclusion of modified CD with a rod-shaped amphiphile and a pie-like polyaromatic hydrocarbon probe as the phosphorescence of the probe is extremely sensitive to its surrounding microenvironment affecting its excited triplet state.

EXPERIMENTAL

α-Bromonaphthalene (BN) was obtained from Beijing Zhonglian Fine Chemicals and distilled under reduced pressure. β-Cyclodextrin (β-CD) was purchased from Sigma. Mono(6-*O*-methyl)-β-CD (M-β-CD) and mono(2,6-di-*O*-methyl)-β-CD (DM-β-CD) were obtained from Shangdong Huantai Fine Chemicals and recrystallized two times prior to use. Heptakis(2,6-di-*O*-methyl)-β-CD (HDM-β-CD) was supplied by Beckman and used as received. Triton X-100 (TX) was obtained from Merck and used as received. Concentrations of BN of 5.0×10^{-5} M, CDs of 2.5×10^{-3} M and TX of 2.0×10^{-3} M were used throughout the experiments, unless stated otherwise.

All steady-state fluorescence and phosphorescence spectra were obtained on a Shimazhu RF-540 recording fluorescence spectrophotometer equipped with a 150-W xenon lamp as an excitation light source and a thermostated cell holder. Excitation and emission bandpasses of 5 nm were used. Absorption measurements were obtained with Hitachi U-3400 spectrophotometer. A Barnstead(Thermolyne EASYpure UV/UF compact reagent water system was used to further purify distilled water. Surface tension measurements were performed by the maximum bubble pressure method at 25 ± 1°C. Molecular dimensions were estimated by CambridgeSoft Chem3D Pro 5.0 on a personal computer.

RESULTS AND DISCUSSION

Influence of Steric Hindrance on the Fluorescence of TX and Phosphorescence of BN

TX exhibits intrinsic fluorescence at 305 nm with an excitation wavelength maximum of 279 nm at 5.0×10^{-5} M due to its built-in aromatic chromophore. In the presence of β-CD and its derivatives, TX shows enhanced fluorescence accompanied by a bathochromic shift of the excitation wavelength maximum and a hypsochromic shift of the emission wavelength maximum. The spectral behavior was similar to that of phenolic derivatives in water and dioxane, respectively [15]. This result reveals that the phenyl group between the *tert*-octyl chain and the polyethylene glycol moiety was located in the less-polar CD cavity rather than the more-polar water phase. Figure 1 shows a fluorescence plot for TX at 2.0×10^{-3} M in the presence of excess β-CD. Addition of β-CD to the solution of TX micelles also results in fluorescence enhancement of TX. Figure 2 shows the effect of β-CD on the surface tension of TX solutions. The presence of β-CD results in an increase in surface tension indicating that the hydrophobic *tert*-octyl chain tethered with the phenyl group was entrapped in the cavity forming an inclusion complex. This is in agreement with the general conclusion that the hydrophobic moiety of the surfactant is encapsulated in the CD cavity, which has been supported by conductance and surface tension experiments [16]. In the presence of 1.0×10^{-3} M TX, the surface tension maximum around 1.0×10^{-3} M β-CD also reveals that the inclusion complex was formed with a stoichiometry of 1:1.

BN shows weaker fluorescence than native naphthalene due to the internal heavy-atom effect. The fluorescence of an aqueous solution of BN was

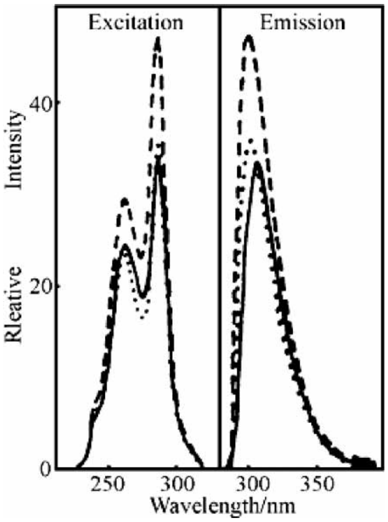

FIGURE 1 Fluorescence of TX in the presence of β-CD and BN. TX (...), β-CD:TX (–) and β-CD:TX:BN (—).

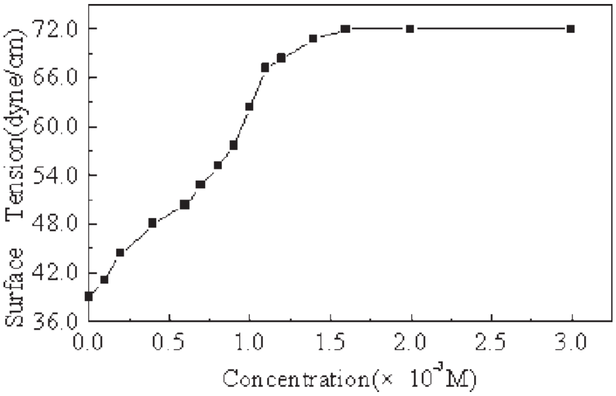

FIGURE 2 Effect of β-CD on surface tension of 1.0×10^{-3} M TX.

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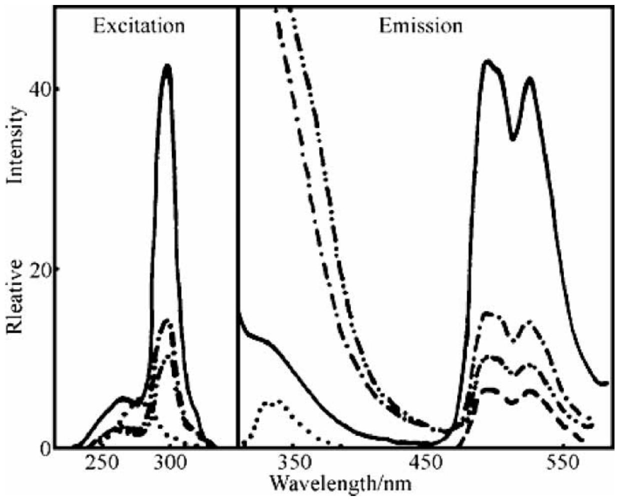

FIGURE 3 Phosphorescence of ternary inclusion complexes. β-CD:BN (. . .), DM-β-CD:TX:BN (-··-), M-β-CD:TX:BN (-··-) and β-CD:TX:BN (— at $\lambda_{ex} = 298\,nm$ and - - - at $\lambda_{ex} = 264\,nm$).

slightly influenced by the addition of β-CD. Hence the fluorescence of TX and the phosphorescence of BN were used to monitor the inclusion of β-CD with TX and BN. Phosphorescence from BN was observed when it was added to an aqueous solution of the β-CD:TX complex [17]. Figure 3 shows the excitation and typical phosphorescence of BN in the presence of modified β-CD:TX complexes. The intense phosphorescence from BN indicates that the excited BN is located in a very favorable microenvironment, shielding it from dissolved oxygen in the aqueous solution. The large bathochromic shift of the excitation maximum also reflects the fact that BN is situated in a significantly less polar environment. These results directly demonstrate that BN was included in the cavity of β-CD occupied by TX, and a ternary inclusion complex was formed in aqueous solution. Figure 3 shows the appearance of phosphorescence accompanied by significant fluorescence quenching of TX. It clearly indicates that the phenyl group of TX is located in the proximity of BN in the supramolecular complex because fluorescence quenching by BN is an intermolecular process and is dependent on the distance between the phenyl group and BN. Thus both the *tert*-octylphenyl groups of TX and BN are included in the cavity of β-CD. In the presence of the β-CD:TX complex, however, the phosphorescence of BN is nine times greater than that in the presence of the M-β-CD:TX complex and even 15 times greater than that in the presence of DM-β-CD:TX complex. In the ternary inclusion complexes, the fluorescence quenching of TX by BN was also found to decrease in the order β-CD > M-β-CD > DM-β-CD. This demonstrates that the methyl substitution at the rim of the β-CD cavity affects the inclusion of BN and accordingly results in the greater distance between the phenyl group of TX and the bromine atom of BN. Consequently, both decreased phosphorescence of BN and decreased fluorescence quenching of TX were observed. In the case of HDM-β-CD, no phosphorescence of BN was detected.

In addition, it is noteworthy from Fig. 3 that the sharp 298 nm excitation band from the β-CD:TX:BN complex is accompanied by a shoulder at 264 nm that corresponds to the shorter excitation wavelength of TX in Fig. 1. When TX was irradiated at 264 nm, excitation energy is transferred from the phenyl group of TX to BN residing in the single cavity and the phosphorescence of BN was also obtained. Energy transfer clearly shows us that the close distance needed for efficient energy transfer is greatly influenced by the spatial constraints of the supramolecular inclusion complexation, which places BN near to the phenyl group of TX because the rate constant for energy transfer exhibits a $1/r^6$ (Forster) distance dependence [18].

Inclusion of Modified β-CDs with TX and BN

The stoichiometry of the binary inclusion complexes was determined by the difference in fluorescence in the presence and absence of excess CD. For 1:1 inclusion complexes, all plots are linear according to the Benesi–Hildebrand expression [19]:

$$1/\Delta I_F = 1/a + 1/aK[\mathrm{CD}]$$

where ΔI_F is the difference in fluorescence intensity of TX in the presence and absence of modified β-CD, K the apparent stability constant, a the combined instrumental constant and [CD] the equilibrium concentration of modified β-CD. Figure 4 shows the double reciprocal plot of $1/\Delta I_F$ versus 1/[β-CD] for the β-CD:TX complex. Apparent stability constants obtained by the ratio of intercept to slope are summarized in Table I.

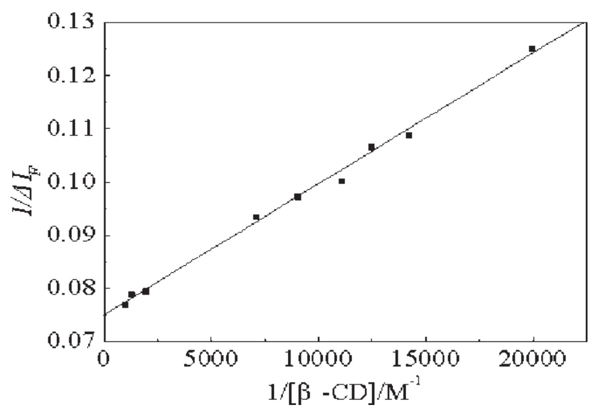

FIGURE 4 A Benesi–Hildebrand plot of $1/\Delta I_F$ vs 1/[β-CD] for the β-CD:TX complex. 5.0×10^{-5} M TX.

TABLE I Apparent stability constants for the binary inclusion complexes at 25°C

Complex	K/M^{-1}
β-CD:TX	$(3.0 \pm 0.2) \times 10^4$
M-β-CD:TX	$(3.2 \pm 0.3) \times 10^4$
DM-β-CD:TX	$(3.3 \pm 0.2) \times 10^4$
HDM-β-CD:TX	$(6.0 \pm 0.9) \times 10^4$

TABLE II Stern–Volmer quenching constants for the binary inclusion complexes

Complex	K_{SV}/M^{-1}
Free TX	11.5 ± 0.1
β-CD:TX	0.8 ± 0.1
M-β-CD:TX	4.1 ± 0.4
DM-β-CD:TX	3.7 ± 0.4
HDM-β-CD:TX	4.0 ± 0.2

Compared with those of β-CD with simple benzene derivatives [20], much larger *K*-values of the β-CD complex with TX reveal that the hydrophobic *tert*-octyl chain was included in the cavity of β-CD. These experimental data indicate that the methylation at the rim of the β-CD cavity is favorable to the binding of the long flexible hydrophobic hydrocarbon chain of TX to the modified β-CD from the thermodynamic point of view.

Fluorescence Quenching of TX and Phosphorescence Quenching of BN in the Presence of Modified β-CDs

Quenching measurements were used to prove that the phenyl group of TX was included in the cavity of β-CD. In homogeneous solution, dynamic fluorescence quenching is described by the Stern–Volmer equation:

$$I_0/I = 1 + K_{SV}[\mathrm{Q}]$$

where I_0 and I are the fluorescence intensity in the absence and presence of quencher, respectively, K_{SV} is the quenching constant and [Q] the concentration of quencher. In the absence of β-CD, the fluorescence of TX was significantly quenched by iodide. Figure 5 presents the fluorescence quenching of TX by potassium iodide in the presence of β-CD. A summary of the K_{SV} values extracted from the slopes of Stern–Volmer plots is presented in Table II. Modified β-CDs cause shielding of the phenyl group of TX from iodide ions in aqueous solution relative to free TX. These data provide direct evidence that the phenyl group of TX was included in the cavity of β-CD together with its octyl chain. Furthermore, β-CD provides the best protection against fluorescence quenching of TX compared to M-β-CD, DM-β-CD and HDM-β-CD. The methyl substituents at the rim of β-CD seem to be unfavorable to shield the phenyl group of TX from the quencher. However, it does not correlate with the apparent stability constants. This clearly indicates that steric considerations are decisive factors in determining the fluorescence quenching of TX by iodide.

Phosphorescence quenching measurements were also used to provide further information about supramolecular inclusion complexation because the triplet state is extremely sensitive to quenching by iodide dissolved in aqueous solution. Figure 6 depicts phosphorescence quenching by the iodide ion for the β-CD:TX:BN system. The data in the plots exhibit normal Stern–Volmer quenching behavior in aqueous solution. The Stern–Volmer quenching constants estimated by linear regression of experimental data are summarized in Table III. They dramatically increase from the β-CD:TX:BN complex to the DM-β-CD:TX:BN complex. The phosphorescence quenching effect exhibits a marked dependence on the methyl substitution of hydroxyl at the rim of the β-CD cavity. This reveals that the β-CD cavity can shield BN effectively from the iodide ion

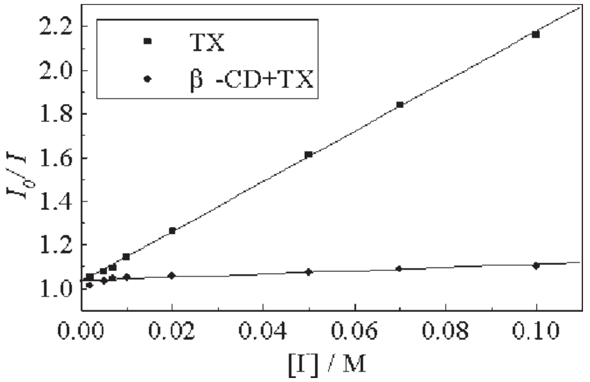

FIGURE 5 Stern–Volmer plots of I_0/I vs $[\mathrm{I}^-]$ for the β-CD:TX complex. 5.0×10^{-5} M TX and 5.0×10^{-3} M β-CD.

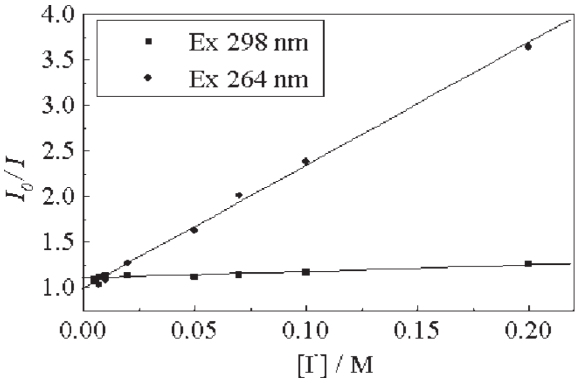

FIGURE 6 Stern–Volmer plots of I_0/I vs $[\mathrm{I}^-]$ for the β-CD:TX:BN complex.

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TABLE III Stern–Volmer quenching constants for the ternary inclusion complexes

Complex	K_{SV}/M^{-1}	λ_{ex}/nm
β-CD:TX:BN	0.69 ± 0.09	298
	13.5 ± 0.5	264
M-β-CD:TX:BN	40.5 ± 2.5	298
DM-β-CD:TX:BN	71.5 ± 1.6	298

in the ternary β-CD:TX:BN complex, whereas BN is more significantly exposed to the water phase to some extent in the ternary inclusion complexes of M-β-CD:TX:BN and DM-β-CD:TX:BN. For the β-CD:TX:BN complex, the Stern–Volmer quenching constant was further evaluated to be $13.5 \pm 0.5\,M^{-1}$ for phosphorescence arising from energy transfer between BN and the phenyl group of TX when the phenyl group of TX was irradiated at 264 nm. This parameter is much larger than the K_{SV} value for phosphorescence arising from BN when BN was irradiated at 298 nm. It reveals that the phenyl group of TX is exposed to the bulk phase to a greater extent compared to BN in the ternary inclusion complex.

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Effect of BN on the Fluorescence of TX in Ternary Inclusion Complexes

Phenolic derivatives are also indicators used to monitor changes in the microenvironment [15]. This was indeed the case here, as described previously. In ternary inclusion complexes, the bromine substituent of BN induces the fluorescence quenching of TX by introduction of BN into the same cavity of β-CD. Higher concentrations of BN result in more significant fluorescence quenching of TX included. In contrast to that of corresponding binary inclusion complexes in the absence of BN, as noted in Table IV, the emission maximum of the phenyl group of TX was red-shifted with increasing concentration of BN at the same time. Based on the solvent effect on the spectra of TX as mentioned earlier, the phenyl group of TX was located in a more polar microenvironment instead of the less polar cavity of β-CD. A bathochromic shift of the emission maximum of the phenyl group of TX was also observed in the presence of M-β-CD and DM-β-CD. This result may originate from the exposure of the phenyl group of TX to the water phase in the ternary inclusion complexes to a greater extent.

TABLE IV Emission wavelength of TX from the β-CD:TX:BN complex at different concentrations of BN

Concentration/M^{-1}	λ_{em}/nm
–	303.0
5.0×10^{-6}	303.5
1.0×10^{-5}	303.8
2.5×10^{-5}	304.8
5.0×10^{-5}	306.0

Steric Considerations in Supramolecular Inclusion of TX and BN by Modified β-CDs

An analysis of molecular dimensions permits an approximate evaluation of steric considerations in supramolecular inclusion of modified β-CD with TX and BN. TX is a rod-like amphiphilic molecule. The cylindrical diameter (*D*), length (*L*) and volume (*V*) of its fully extended *tert*-octyl chain with the phenyl group approximately correspond to 5.79 Å, 8.80 Å and 201.72 $Å^3$, respectively. According to the diameter (*D*), height (*H*) and approximate volume (*V*) of the β-CD cavity (6.5 Å, 7.9 Å and 262 $Å^3$, respectively) [21], the channeled cavity of β-CD is wide enough to almost completely include the *tert*-octyl chain with the phenyl group of TX for the formation of stable binary inclusion complexes with a 1:1 stoichiometry. Surface tension measurements show that TX micelles were destroyed due to the encapsulation of the *tert*-octyl chain responsible for aggregation. The changes in the microenvironment surrounding the phenyl group of TX result in the enhanced fluorescence of TX and its wavelength shift. For this reason, the fluorescence quenching of TX by the iodide ion was greatly attenuated. Generally, inclusion complexation induces the release of water molecules from the CD cavity [21]. Strong hydrophobic interactions cause BN to penetrate into the cavity of β-CD to form ternary inclusion complexes with a 1:1:1 stoichiometry [17]. According to the overall molecular size of BN ($V = 171.55\,Å^3$) and the *tert*-octyl moiety with the phenyl group of TX and the space-filling model of Chem3D, rigid BN may squeeze into the hydrophobic cavity occupied by the flexible octyl chain of TX and force it to deform to some extent. Consequently, the crowded packing of BN and the hydrophobic tail of TX in the constrained cavity of β-CD leads to an increased phosphorescence of BN in aerated aqueous solutions, due to better rigidity and shielding from dissolved oxygen, and the significant quenching effect of BN on the fluorescence of neighboring TX, due to the heavy-atom effect. The experimental data demonstrate that the phosphorescence of BN was slightly affected by iodide. Intermolecular energy transfer from the phenyl group of TX to BN was also observed for the tightly compact β-CD:TX:BN complex because of close contact between the phenyl group of TX and BN in the crowded cavity. Considering the relative binding strength [20] and the limited space in the cavity of β-CD, the phenyl group of TX in the β-CD:TX:BN complex

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was displaced from the cavity to some extent compared to that in the β-CD:TX complex. The bathochromic shift of the emission wavelength of TX was observed with increasing concentrations of BN because the phenyl group was exposed to the polar bulky phase.

In the case of M-β-CD, DM-β-CD and HDM-β-CD, the values of the apparent stability constants support the idea that methyl substitution on the rims of β-CD increases the lipophilicity at the opening end and offers some assistance toward accommodation of TX. Simple extension of the length of the cone with methyl groups affords a stronger complex of TX with modified β-CDs than with natural β-CD. As the methyl group is directed toward the cavity and results in self-inclusion, methyl substituents at the 6-position or the 2- and 6-positions on the rims of β-CD may decrease the volume and the diameter of the cavity for steric considerations [22,23]. As a result, the phenyl group of TX included by M-β-CD, DM-β-CD and HDM-β-CD exposes to the bulk phase to a greater extent with respect to that included by β-CD and exhibits a greater fluorescence quenching by iodide. M-β-CD and DM-β-CD further accommodate BN into the cavity occupied by the hydrophobic moiety of TX to a lesser extent due to the steric hindrance of methyl groups at the opening of the β-CD cavity. For this reason, BN is exposed to the bulk water and shows a decreased phosphorescence. As for HDM-β-CD, the permethylated substitution at the 2- and 6-positions on the rims of β-CD retards further inclusion of BN, which is responsible for the lack of phosphorescence.

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