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Cu^{2+} induced charge transfer switch by choosing the right cyclodextrin environment

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ABSTRACT

Compounds like *trans*-2-[4-(dimethylamino)styryl]benzothiazole (DMASBT) take part in compound induced cyclodextrin (CD) nanotubular suprastructure formation. The molecule undergoes differential encapsulation inside the CD cavities of different sizes and hence experience restricted freedom in its movement. DMASBT is capable of undergoing intramolecular charge transfer in the excited state in polar media. This physical phenomenon has been exploited to study the Cu^{2+} sensing capability of encapsulated DMASBT. The intramolecular charge transfer is found to get switched on employment of Cu^{2+} ions with the proper choice of cyclodextrin molecules for encapsulation. The differential encapsulation of the compound inside the CD cavities is held to be responsible for this behavior. The complexation takes place in the ground state and because of the difference in charge density on the ligating centers; the system is capable to show a switching behavior in the twisted intramolecular charge transfer (TICT) emission of the guest molecule inside the various cyclodextrin moieties.

1. Introduction

The development of fluorescent-based molecular devices for probing and characterizing chemical events is of huge significance for both chemistry and biology [1–3]. Copper is a significant metal pollutant due to its widespread use, but it is also an essential trace element in biological systems. Copper(II) ion is known to be able to quench the fluorescence via a photoinduced electron transfer (PET) process, which includes the transfer of an electron from the fluorophore in the excited state to the metal ion [4]. Because of its biological and environmental importance, detection and monitoring of Cu^{2+} are highly demanding. Fluorescence signaling is one important technique in this context due to its high detection sensitivity and intrinsic operation simplicity. Considerable efforts have been made to synthesize fluorescent chemosensors that are selective, sensitive, and suited to highly resolved imaging for monitoring biological processes [5–7].

A new coumarin-derived Cu^{2+}-selective fluorescent sensor has been synthesized by Jung et al. [8] to study the fluorescence quenching mechanism by femtosecond time-resolved fluorescence spectroscopy and quantum calculations. They found that the derivative appending 2-picolylamide enables efficient tridentate complexation for Cu^{2+} in preference to a variety of other common heavy and toxic metal ions. In another work, fluorescent dinuclear chiral zinc complexes were synthesized in a "one-pot" method in which the lysine-based Schiff base ligand was generated in situ [9]. They were found to act as a highly sensitive and selective fluorescent ON–OFF probe for Cu^{2+} in water at physiological pH. Other metal ions such as Hg^{2+}, Cd^{2+}, and Pb^{2+} gave little fluorescence change. Some intramolecular charge transfer (CT) fluoroionophores for Cu^{2+} are known that show an enhancement in the short wavelength emission of the locally excited state (LE state), at the expense of the long-wavelength CT emission [10–12]. Wen et al. [13] designed a fluoroionophore on the basis of the dual fluorescent CT fluorophore 4-(N,N-dimethylamino)benzamide [14] whose electron acceptor is derived into 2-methoxybenzaldehyde hydrazone, the metal ionophore. According to the authors, their results provide a new strategy for constructing turn-on CT fluorophores for transition metal ions [13].

An interesting work has been reported by Santra et al. [15] where they have describe a new photochemical mechanism to restore the fluorescence of a Cu^{2+} ion–cyclodextrin–pyrene complex upon interaction with glutamate. Upon inclusion of a fluorophore, cyclodextrins (CDs) offer a more protective microenvironment and generally enhance the luminescence of the guest molecule by shielding the excited species from quenching and non-radiative decay processes that occur in bulk solution. In general, the guest molecule loses its solvation sphere upon entering the cyclodextrin cavity, and solvent molecules are simultaneously expelled out from the cavity. Cu^{2+} ions are known to quench the fluorescence via a photoinduced electron transfer process which involves a transfer of electron from the fluorophore in the excited state to the metal ion [4]. A new fluorescence-quenched ternary complex, Cu^{2+}/DMABN/β-CD, was prepared by Santra et al. [16] using

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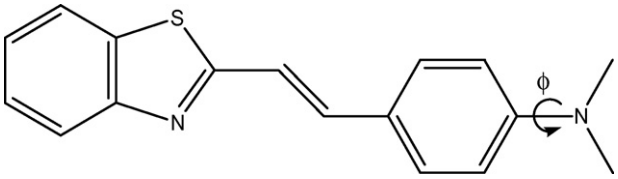


Scheme 1. Representative structure of DMASBT. ϕ indicates the twist angle of the $-N(CH_3)_2$ moiety with respect to the rest of the molecule.

β-CD, Cu^{2+} ions, and 4-(dimethylamino)benzonitrile (DMABN). The compound DMABN is known to exhibit dual fluorescence, namely fluorescence from the locally excited (LE) state in non-polar medium and from the twisted intramolecular charge transfer (TICT) state in solvents with higher polarity [17]. This property of DMABN has been very effectively exploited by Santra et al. in their synthesis of the ternary complex [17].

In the present report, we have used a similar compound, *trans*-2-[4-(dimethylamino)styryl] benzothiazole (DMASBT) (Scheme 1), that shows TICT in solvents with high polarity [18,19]. This compound can also induce cyclodextrin nanotube formation very effectively in aqueous medium [20–22]. The process has been proved to be guest concentration dependent and undergo fragmentation at higher guest concentration, especially in the cases of α-, and γ-CDs. The cyclodextrin nanotubes are best formed when the DMASBT concentration is kept at ~2 μM and the formation gets completed when the concentrations of the cyclodextrins (α, β, and γ) reach around 6–7 mM [20–22]. In this report we have kept the α-CD concentration fixed at 10 mM, whereas, the concentrations of β-, and γ-CDs are kept at 6 mM. It is also noted that the encapsulation of DMASBT inside the different CDs is not of the same motif because of the different cavity size of hosts (inner cavity diameters of α-, β-, and γ-CDs are 5.7, 7.8 and 9.5 Å, respectively) [23]. They undergo differential encapsulation as has been proved elsewhere by Purkayastha et al. [23]. The present work defines a novel way to switch the intramolecular charge transfer by employing Cu^{2+} ion with the proper choice of cyclodextrin encapsulation. The restricted molecular motion inside the formed nanotubular suprastructures seems to influence the process of complexation and hence the switching behavior.

2. Experimental

2.1. Materials and preparations

DMASBT was procured from Aldrich Chemical Company, WI, USA and was recrystallized from a mixture of ethanol and small percentage (~10%) of n-hexane. Triple distilled water was used for the preparation of aqueous solution. Stock solution of DMASBT (1.001×10^{-3} M) was prepared in pure methanol, 0.1 mL of which was poured in a 10 mL volumetric flask and left for a few hours for complete evaporation of methanol before dissolving in water containing appropriate concentration of the CDs. The final volume of solution was 10 mL and the final concentration of DMASBT was 1×10^{-5} M. CDs were procured from Sigma–Aldrich, WI, USA, and was used as obtained. Copper sulfate pentahydrate ($CuSO_4$, $5H_2O$) was procured from Merck, India.

2.2. Instruments and methods

The absorption spectra were recorded using a Jasco V570 UV–vis spectrophotometer. Fluorescence measurements were performed using a Shimadzu RF-5301PC scanning spectrofluorimeter. The fluorescence lifetimes were measured by the method of time-correlated single-photon counting and a nanosecond spectrofluorimeter (Edinburgh Instrument, 199) was used for the purpose. A nano-LED pulsed diode powered by a pulsed diode controller (IBH) was used as the excitation light source. The excitation wavelength was 407 nm. The typical response time of this laser system was 70 ps. To calculate the lifetime, the fluorescence decay curves were analyzed by an iterative fitting program provided by IBH.

3. Results and discussion

3.1. Fluorescence decay of DMASBT in different cyclodextrins

We worked on the Cu^{2+} ion sensing capability of DMASBT molecules when they are suitably encapsulated inside the cyclodextrin nanotubular suprastructures. It can be noted from the structure of the molecule that it has two N groups, one at the donor part, i.e., the $-N(CH_3)_2$ moiety and another at the acceptor part, i.e., the benzothiazole moiety. These two N-atoms are supposed to be capable of donating the lone pair of electrons to the available Cu^{2+} ions to form coordinate bonds. There is also an S atom in the acceptor part that is capable of complexation with Cu^{2+} ions, but it is supposed to form weak complex compared to the N-centers [24]. Hence, we put our attention more toward the N-centers. Among the two N-centers, the one in the donor part again is supposed to have lower electron density compared to that at the acceptor part because of the inductive effect (+I) of the two $-CH_3$ groups attached to it and the resonance effect (+R). This difference in charge distribution is inherent to DMASBT in the ground state. Charge transfer is favored in the molecule in the excited state. The absorption spectra show an increase in absorbance at 400 nm for DMASBT in α-CD without any shift in the absorption maxima indicating that the complexation process, most probably, does not vary the molecular stabilization. However, in the case of β-CD encapsulation there is a small increase in the absorption maximum along with a concomitant blue shift. This indicates a destabilization in the DMASBT molecule probably because of the arresting of the resonance. Encapsulation inside γ-CD shows a moderate increase in the absorption maximum with a mild red shift which is in contrast to the α-CD case. This provides some hint of stabilization of the system in the ground state. As has been mentioned elsewhere [21] that there is multiple guest encapsulation inside the γ-CD nanochannels, so we cannot ignore any sort of chelate formation in the presence of the Cu^{2+} ions.

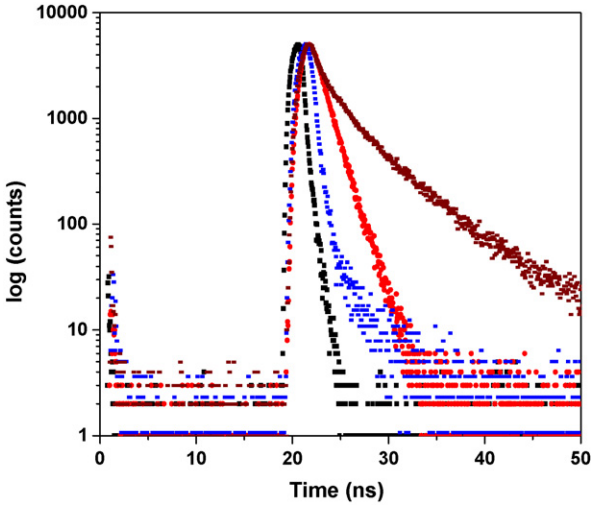


Fig. 1. Fluorescence decay profiles for DMASBT (2 μM) in different CDs ((■) 10 mM α-CD; (■) 6 mM β-CD; (■) 6 mM γ-CD; (■) probe lamp profile). λ_{ex} = 370 nm; λ_{em} = 500 nm.

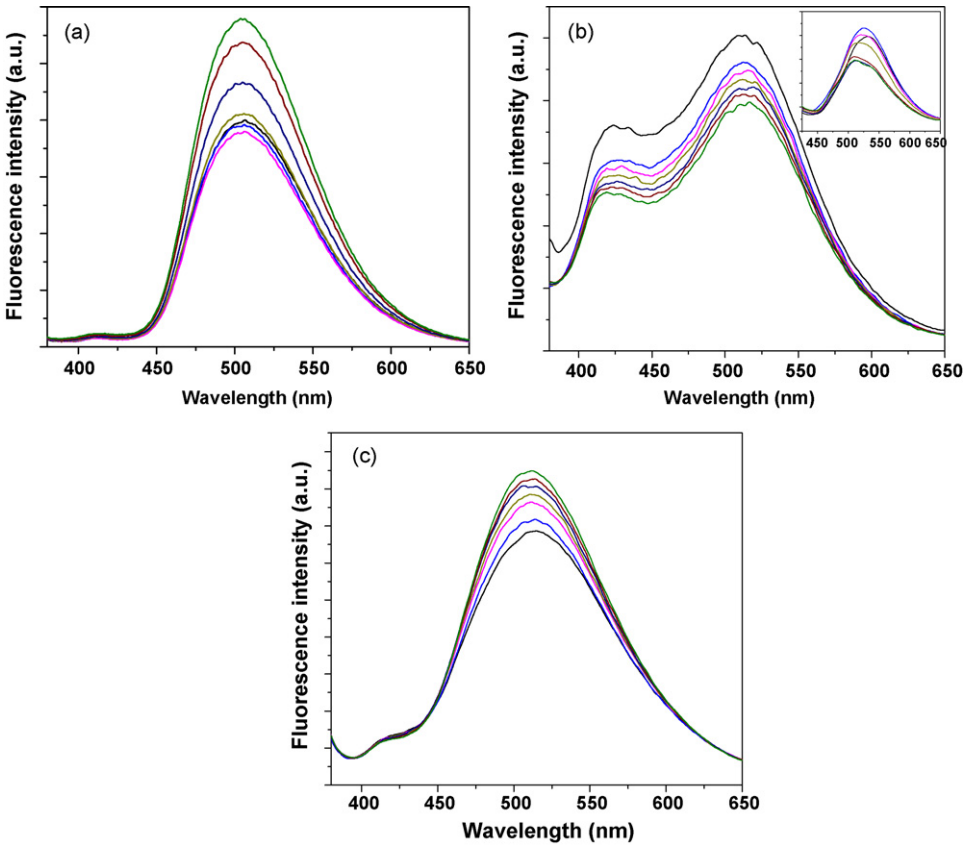


Fig. 2. Fluorescence spectra of DMASBT in (a) 10 mM α-CD, (b) 6 mM β-CD, and (c) 6 mM γ-CD. The inset of (b) shows the fluorescence spectra of free DMASBT with added Cu^{2+} ion. The Cu^{2+} ion concentrations are (—) 0 mM, ( ) 1 mM, ( ) 3 mM, ( ) 6 mM, ( ) 10 mM, ( ) 15 mM, and ( ) 21 mM. The excitation wavelength is 360 nm.

Fig. 1 shows the fluorescence decay profiles of DMASBT in the three CDs used wherefrom we see that the order of the decay rate is β-CD > α-CD > γ-CD. The respective mean fluorescence lifetimes are ~158, ~2000 and ~2200–4000 ps [20–22]. This indicates that the guest molecule may be much more mobile (translational motion) in β-CD compared to the other CDs. DMASBT has a very short excited state lifetime in free state in solvents of less viscosity [25]. The scheme for the TICT formation states that in the excited conditions the locally excited (LE) state gets converted to the TICT state and thus the LE emission becomes very low compared to the TICT emission. Since, DMASBT gets some space to move inside the β-CD cavity, the TICT lifetime gets lowered, as is obvious from Fig. 1 and one of our previous reports [22]. Thus, the LE emission is not as low as expected from the simple TICT scheme. The scarcity of space inside the α-CD cavity does not permit the molecule to move freely [20], whereas, ample space in γ-CD allows multiple molecules inside the nanochannel thereby resisting the free motion of the molecules [21]. On the other hand, in β-CD the space is not as much as that in γ-CD that it could accommodate multiple molecules inside, but the molecule is also not as tight as in α-CD [21]. This variance in molecular motion was used in the present work where we observed a switch in the intramolecular charge transfer process in DMASBT induced by the addition of Cu^{2+} ions to the encapsulated guests.

3.2. Steady state fluorescence of DMASBT in different CDs and added Cu^{2+} ion concentration

Fig. 2(a–c) represents the fluorescence spectra for DMASBT in α-, β-, and γ-CD, respectively, with increasing concentration of Cu^{2+} ion. The TICT fluorescence of DMASBT is observed to enhance in α-, and γ-CD with increasing Cu^{2+} ion concentration in the solution whereas, in β-CD TICT fluorescence decreases similar to that for free DMASBT with Cu^{2+} ions (inset of Fig. 2(b)). The real picture of the process can be perceived when we look at Fig. 3. The TICT fluorescence of free DMASBT initially increases at low concentrations of Cu^{2+} and then decreases progressively with added Cu^{2+} ion.

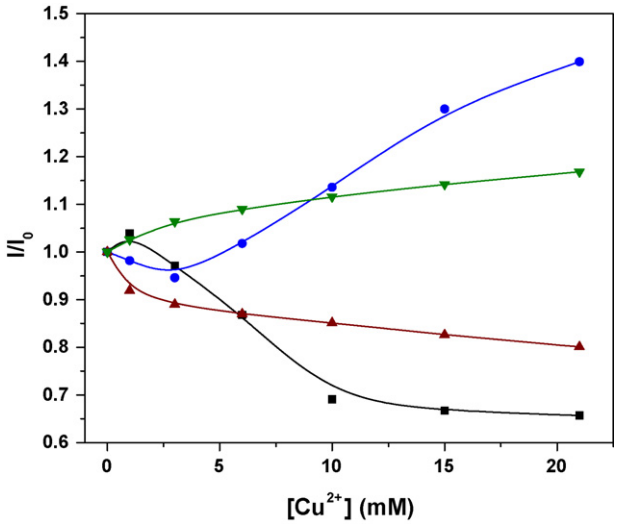


Fig. 3. Titration plot of DMASBT in 10 mM α-CD (blue), 6 mM β-CD (brown), and 6 mM γ-CD (green). The black curve is for the titration of free DMASBT with Cu^{2+}. The fluorescence intensity at 550 nm has been taken for the calculation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

As per the discussions before about the behavior of DMASBT in the ground state we can presume that at low concentration of Cu^{2+}, the tendency of the complexation should be with the more potent ligating center, i.e., the N-atom of the benzothiazole or the acceptor moiety. This phenomenon is supposed to increase the amount of charge transfer in the molecule in the excited state. The sensibility of DMASBT lets us to perceive this process even with the Cu^{2+} concentration in the range of 1–2 mM. The subsequent decrease in the TICT emission can be attributed to the attachment of Cu^{2+} to both the N-centers of the molecule as there is supposed to be maximum tumbling motion in the free condition. The choice of the more convenient center for the binding of the Cu^{2+} ion does not seem to be too applicable in this case. Similar decrease in TICT fluorescence of DMASBT is observed in the case of β-CD encapsulation. As has been mentioned previously that the molecule can move more freely inside the β-CD nanochannel due to more available space [22], the Cu^{2+} ion probably looses the proper choice of bond formation with the ligand. As a consequence, unlike the behavior in the case of free DMASBT, the TICT fluorescence decreases progressively from the beginning. In the β-CD nanochannel the molecular motion is restricted to some degree than that for the free molecule [22]. Once the lone pair of the N-center at the $-N(CH_3)_2$ group gets engaged the TICT process gets hindered. However, when DMASBT is encapsulated inside α- and γ-CD nanochannels, the TICT fluorescence is observed to get enhanced with addition of Cu^{2+} ions. Fig. 1 should be emphasized here to explain this phenomenon. It is seen that inside of either α- or γ-CD, DMASBT moves much slower than that in β-CD. The slow movement of the molecule probably increases the selectivity of the Cu^{2+} ion and it finds the better center for attachment, i.e., the N-center with the benzothiazole moiety. As has been discussed earlier that the N-atom in the $-N(CH_3)_2$ moiety will have less electron density, it can be considered therefore that a more thermodynamically stable complex may form with the N-atom in the benzothiazole ring. The latter N-atom is able to donate more electron density to the metal ion in forming the coordination bond and thus involving a higher decrease in the value of the enthalpy of bond formation. A more precise description may point out the initial decrease in the TICT fluorescence of DMASBT encapsulated inside the α-CD nanochannels. This may give an idea about the much slower movement of the compound in case of the γ-CD cavity compared to that in α-CD. Initially the Cu^{2+} ions, present in low concentration, presumably get attached either to the N-centers or facing a competition in binding to the specific sites inside the α-CD nanochannel. This behavior vanishes once there is sufficient number of Cu^{2+} ions. All these things may have happened in the ground state and are reflected in the excited state through the switching of the TICT emission of DMASBT.

The fast motion of DMASBT inside the β-CD nanochannel diminishes the excited state lifetime of DMASBT thereby making the LE emission prominent (Fig. 2(b)). A closer look at the fluorescence spectra of free DMASBT in presence of Cu^{2+} ion shows that the reduction in the TICT fluorescence brings the structured LE fluorescence band back. The initial increase in the TICT fluorescence in case of free DMASBT may be due to the fact that Cu^{2+} initially starts with binding to the better site but soon looses the resolution. The initial decrease in the TICT fluorescence in case of α-CD can also be explained in a similar way. In this case, the complexation of DMASBT with Cu^{2+} ions probably started without a choice because of the tightly bound DMASBT but later move toward the better N-center. This has correlation to the kinetic and thermodynamic stability of the complexes. Due to the restricted motion of the molecules and less tumbling in the solution, the Cu^{2+} ions may form complexes initially at both the probable centers and the system gets stabilized on addition of more reactants to the medium. The change in the heat of reaction and the activation energy for the reaction are supposed to deviate the complex formation toward the more favorable direction. However, binding of Cu^{2+} to the encapsulated DMASBT molecules does not have appreciable stability in any of the cases and thus the excited state lifetimes of these complexes are not supposed to change remarkably.

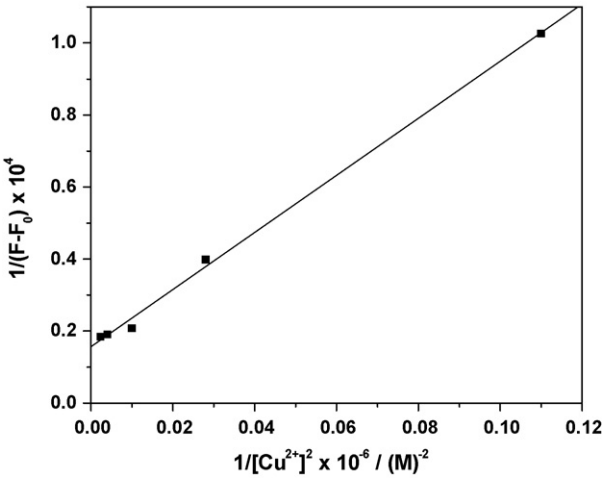


Fig. 4. Plot of $1/(F-F_0)$ vs. $1/[Cu^{2+}]^2$ to determine the binding constant and the stoichiometry for Cu^{2+} ions binding to free DMASBT in aqueous environment. The fluorescence intensities have been measured at 550 nm.

3.3. Determination of binding constant and stoichiometry of Cu^{2+}

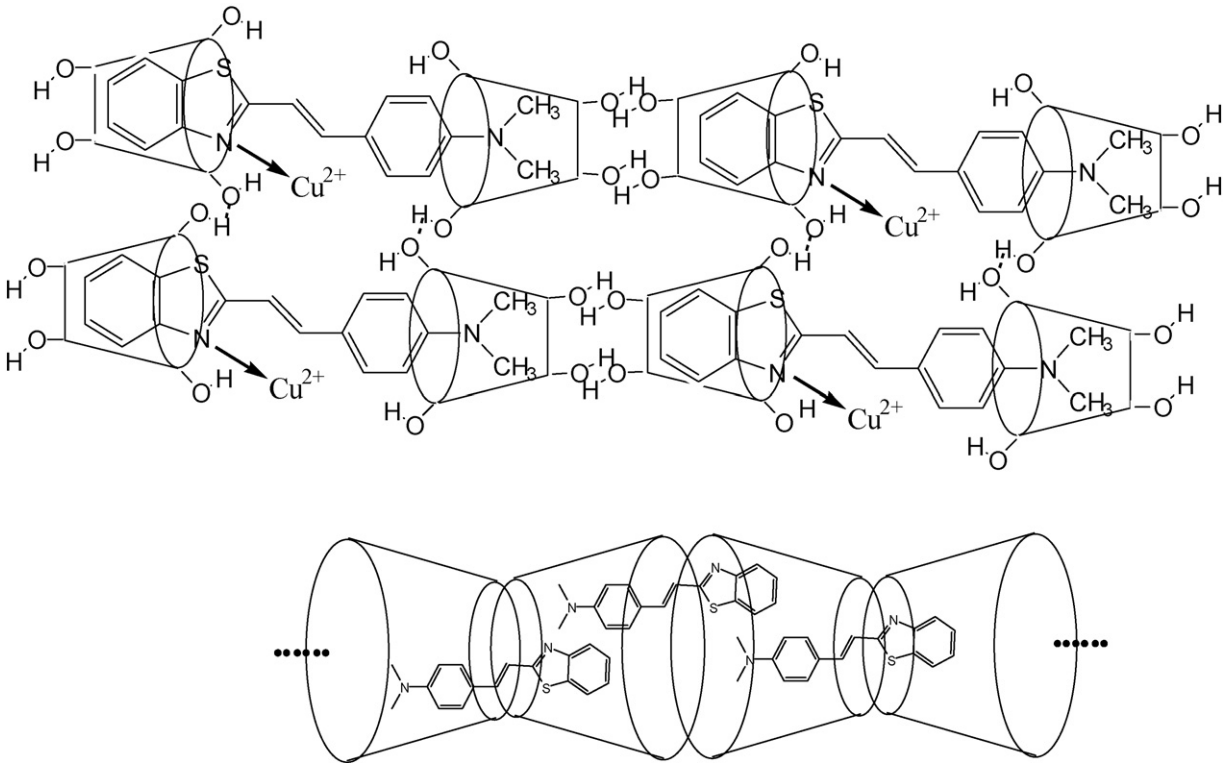
Determination of the binding constant and the stoichiometry for the Cu^{2+} ions binding to the freely tumbling DMASBT molecules in aqueous solution will provide information about the complex formation. For this purpose we adopted the Benesi–Hildebrand double reciprocal method following the equations [26,27]:

$$\frac{1}{F-F_0} = \frac{1}{F_m-F_0} + \frac{1}{K[Cu^{2+}](F_m-F_0)} \quad (1)$$

$$\frac{1}{F-F_0} = \frac{1}{F_m-F_0} + \frac{1}{K'[Cu^{2+}]^2(F_m-F_0)} \quad (2)$$

Here F_0 and F_m are the fluorescence intensities at zero and the maximum concentrations of Cu^{2+} ions, $[Cu^{2+}]$ is the total Cu^{2+} concentration in the respective solutions and K and K' are the binding constants. The slope of the linear fit to $1/(F-F_0)$ vs. $1/[Cu^{2+}]$ or $1/[Cu^{2+}]^2$ with a positive intercept gives the stoichiometry and the slope of the line gives the binding constant. Eq. (1) does not give a linear fit to the calculated data and rules out the formation of any 1:1 complex. Fig. 4 shows that Eq. (2) provides a good linear fit to the data ($R = 0.999$) and the intercept and slope of the straight line curve yield the binding constant for the free DMASBT–Cu^{2+} complex, which is 19813.96 M^{-2}. This confirms that the complex formation is through 1:2 binding of the DMASBT and the Cu^{2+} ion. This also proves that there is nearly no selectivity in the binding process and the Cu^{2+} ions choose the two most potent centers for binding. Same practice does not provide any linear fit in either of α-, β- and γ-CD cases as is obviously because of the nanotubular suprastructure formation [20–22].

The differential encapsulation of DMASBT in the different CDs also appears to play some role here [23]. This point will be clear from the Scheme 2 that illustrates the different motifs of encapsulation of DMASBT within α- and γ-CDs. The limited space in α-CD makes the N-center in the benzothiazole moiety more accessible to the Cu^{2+} ions. The coordinate bond formation between the two species makes the acceptor part thirstier for electrons and thus enhances the charge transfer in the molecule. γ-CD nanochannel has more interior space and hence can accommodate multiple



Scheme 2. Schematics of differential encapsulation of DMASBT in α-CD (top) and γ-CD nanochannels.

DMASBT molecules thus restricting the molecular motion and the fluorescence decay. The slow movement of the molecule facilitates the attack of the N-center of the benzothiazole moiety with the Cu^{2+} ion, thus increasing the TICT. The tighter encapsulation by α-CD enhances the TICT more than the γ-CD.

4. Conclusion

Through the present work we have been able to define a novel way to switch the intramolecular charge transfer by employing Cu^{2+} ion with the proper choice of cyclodextrin encapsulation. Mainly the restricted molecular motion inside the formed nanotubular suprastructures influences the process of complexation. The minute change in the fluorescence intensity of the TICT form of the encapsulated DMASBT due to the application of the Cu^{2+} ions proves it to be a sensible candidate for the observation of the switching of the discussed photophysical property. Since Cu^{2+} ion is known to be an essential species in biological systems, this sort of impact on biologically potent drugs will be very helpful in controlling the properties of the molecules in aqueous medium. The cyclodextrin encapsulation serves a dual purpose of giving shelter to the drug molecules and controlling the accessibility of the essential elementary ions to undergo complexation to switch the properties of the drugs.

Acknowledgments

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