



Investigation by Fluorescence Technique of the Quenching Effect of Co^{2+} and Mn^{2+} Transition Metals, on Naphthalene-Methyl-Beta-Cyclodextrin Host-Guest Inclusion Complex

Umit Ay¹ · Sinem Ezgi Sarlı¹

Received: 7 August 2018 / Accepted: 12 September 2018 / Published online: 2 October 2018
© Springer Science+Business Media, LLC, part of Springer Nature 2018

Abstract

Inclusion complex of naphthalene with methyl-beta-cyclodextrin in water has been formed. The aqueous solutions of the various amounts of Co^{2+} and Mn^{2+} salts have been added to naphthalene-methyl-beta-cyclodextrin (NAP-Me- β -CD) inclusion complexes. Fluorescence properties of the naphthalene (NAP) compound have been utilized to observe the changes in fluorescence intensities. Stern-Volmer quenching constants and fluorescence quantum yields have been calculated. Characterization of the resulting complex by FT-IR and ¹H NMR technique has been determined. Fluorescence lifetime measurements have been made in the presence and absence of the quenching reagent and Gibbs free energy change has been calculated.

Keywords Inclusion complex · Heavy metal ions · Fluorescence · Quenching · Methylated- β -cyclodextrin · Fluorescence lifetime

Introduction

Cyclodextrin molecules are cyclic oligosaccharides consisting of six to twelve α -D-glucopyranose monomers attached to 1 and 4 carbon atoms. Six to eight cyclodextrins with α -D-glucopyranose units are categorized as α -, β - and γ -cyclodextrins, respectively. Among these types of cyclodextrins of varying type, α -cyclodextrin is less preferred and γ -cyclodextrin is expensive. β -cyclodextrin is widely used because its cavity size is suitable for a wide range of various guest molecules and is readily available. Addition of a hydrophobic guest to aqueous cyclodextrin solutions leads to the formation of a new complex without breaking the covalent bonds. In general, the most specific characteristic of cyclodextrins is the ability to form inclusion complexes with different organic molecules that are host-guest interaction efficient with the internal cavity providing a hydrophobic environment to

capture a polar molecule [1]. Here, the most critical parameters in complex formation depend not only on the size, shape and polarity of the guest molecule, but also on the low polarity that the inner cavity of the cyclodextrin has. Perhaps the best known smallest natural organic host molecule in the cyclodextrin family is beta-cyclodextrin. The internal cavity, which provides a hydrophobic chiral environment for small organic guest molecules, is about 0.8 nm deep and 0.7 nm in diameter [2]. The inclusion complex formation with cyclodextrin usually results in a highly fluorescent fluorescence quantum yield [3]. Van der Waals interactions or hydrophobic interactions between the cyclodextrin cavity and the hydrophobic part of the guest molecule, hydrogen bonds between the hydroxyl groups of the cyclodextrin and the polar functional groups of the guest molecule, highly energetic water molecules that are released from the cavities in the complex formation process, and the tensile energy that is activated in the cyclic cyclodextrin system are generally accepted as forces associated with complex formation. Due to the inclusion complex forming ability of cyclodextrins and their derivatives, many hydrophobic organic contaminants (such as polyaromatic hydrocarbons (PAHs), dioxins, and furans) are suitable guests to form complexes with cyclodextrins [4]. Organic and inorganic pollutants, even in very small amounts, are a very important threat to human health. Organic pollutants can be absorbed by plants, poisoning living organisms in the food chain.

✉ Umit Ay
umurege@kocaeli.edu.tr; umitay36@hotmail.com

Sinem Ezgi Sarlı
sinamezgisarli@gmail.com

¹ Department of Chemistry, Kocaeli University,
41380 Kocaeli, Turkey

Inorganic pollutants, heavy metals such as cobalt and manganese are toxic substances that affect human health and the central nervous system at a fatal level. The quantities of these heavy metals must continuously be determined in environment related samplings. Polycyclic aromatic hydrocarbons (PAH_s) are hydrophobic organic compounds which are poorly soluble and are abundantly found in the environment. They can be found in the air, water and soil. It is obviously undesirable for many types of them to be in the environment because of their carcinogenicity [5].

In this study, the effect of Co²⁺ and Mn²⁺ metals on the fluorescence emission intensity of naphthalene-methyl-beta-cyclodextrin (NAP-Me-β-CD) inclusion complex formed in water has been observed. The Benesi-Hildebrand method has been used to obtain information about the stoichiometry of the resulting complex. Varying amounts of heavy metals have been incorporated in the inclusion complex solution and the changes in the intensity of fluorescence emission have been recorded. Stern-Volmer quenching constants have been calculated from the slope of the Stern-Volmer plots (I_0 / I vs [Me-β-CD] graphs). The Gibbs free energy value of the formed inclusion complex has also been calculated and the fluorescence lifetime values have been measured in the presence and absence of the quenching reagent.

Experimental

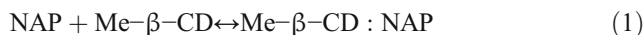
Materials and Apparatus

Me-β-CD (average molecular weight = 1310 g mol⁻¹, Aldrich, Steinheim, Germany), naphthalene (Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany), 9,10-Diphenyl anthracene (Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany), ethanol (EtOH) (Merck, Darmstadt, Germany) have been used in the study, and fluorescence lifetime (prompt) chemicals from Ludox-AS-30 colloidal silica (Sigma-Aldrich Chemie GmbH) have been used as reference solution. All solutions containing metal ions have been prepared in ultra pure water. All chemicals used are of analytical purity. Varian Agilent Cary Eclipse instrument has been used as the fluorescence spectrophotometer. Bruker-Alpha model device was used for FT-IR measurements.

The fluorescence lifetimes have been obtained using Horiba-Jobin-Yvon-SPEX Fluorolog 3-2iHR instrument with Fluoro Hub-B Single Photon Counting Controller at an excitation wavelength of 470 nm. Signal acquisition has been performed using a TCSPC module (NanoLED -390 emitting 390 nm).

Preparation of NAP-Me-β-CD Inclusion Complexes

Host-guest inclusion complexes have been prepared by dissolving 10⁻³ M Me-β-CD and 10⁻³ M to 10⁻⁵ M naphthalene concentrations in 100 mL of purified water. The solutions have been stirred in a magnetic stirrer for 24 h. Finally, they have been transferred to volumetric containers. Complex formation in the solution is a dynamic equilibrium process. Reaction is shown below in Eq. 1.



The stability of the inclusion complex is defined in Eqs. 2 and 3 in terms of formation constant (K_f) or dissociation constant (K_d). The inclusion complex formation is shown in Scheme 1.

$$K_f = [\text{Me-}\beta\text{-CD} : \text{NAP}] / ([\text{Me-}\beta\text{-CD}][\text{NAP}]) \quad (2)$$

$$K_d = 1/K_f = ([\text{Me-}\beta\text{-CD}][\text{NAP}]) / [\text{Me-}\beta\text{-CD} : \text{NAP}] \quad (3)$$

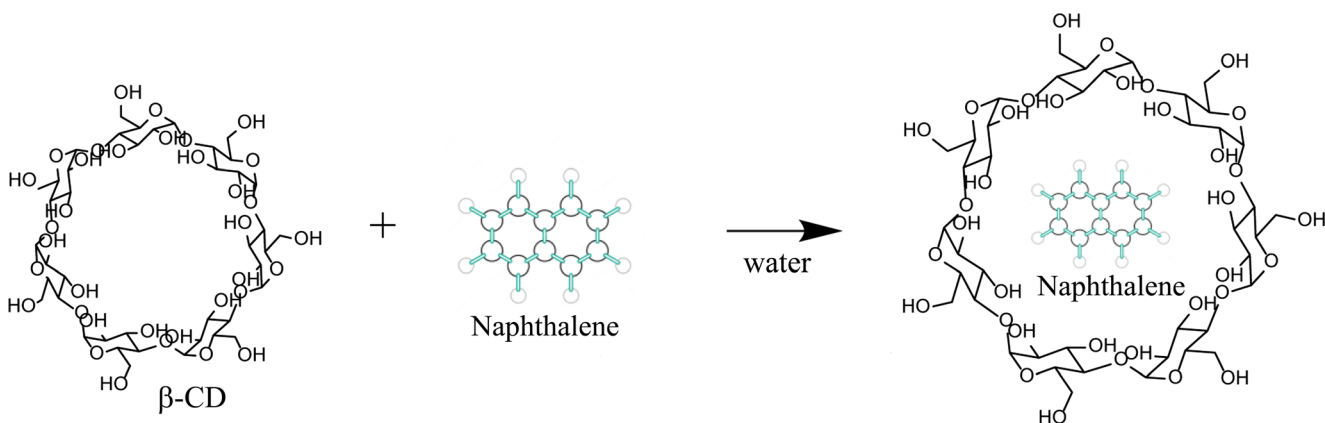
Quenching of NAP-Me-β-CD Inclusion Complexes with Co²⁺ and Mn²⁺ Salts

Firstly, fluorescence measurements of prepared inclusion complexes have been performed in a quartz cell with a size of 1.0 × 1.0 cm². Second, the effect of metal ions on fluorescence spectra has been investigated by directly adding metal ions from the stock solutions into the known volumes (1.5 mL) of inclusion complexes at μL level by micropipette. Finally, the emission spectra have been recorded at 258 nm excitation wavelength (Figs. 1, 2, and 3).

Results and Discussion

Emission Spectral Characteristic of NAP in Me-β-CD

The aim of this work is to prepare a probe molecule and investigate the fluorescence quantum efficiency and fluorescence quenching in the interaction of the probe molecule with heavy metal ions. Many heavy metals do not show fluorescence properties. For this reason, naphthalene, which is a polyaromatic hydrocarbon showing fluorescence properties, has been selected as a probe. Naphthalene is a suitable fluorophore for PAH studies [6]. Inclusion complexes have been prepared with Me-β-CD and different concentrations of naphthalene. The Benesi-Hildebrand method has been used to obtain data about the stoichiometry of the resulting host-guest complexes [7–9]. The increase in fluorescence intensity has been measured as a function of the host concentration while the total naphthalene concentration is constant. It is interesting to note that the increase in the Me-β-CD



Scheme 1 Formation of inclusion complex

concentration and the increase in the fluorescence intensity of naphthalene depend on the incorporation of naphthalene into the non-polar cavity. An increase in fluorescence intensity has been observed at certain concentrations of Me-β-CD. The data in Fig. 1 have been obtained using Benesi-Hildebrand equation. There are two types of binding patterns: (1:1) and (1:2). Equations (4 and 5) for these models are given below.

$$\frac{1}{I-I_0} = \frac{1}{I-I_0} + \frac{1}{(I_1-I_0)K[\beta-CD]} \tag{4}$$

$$\frac{1}{I-I_0} = \frac{1}{I-I_0} + \frac{1}{(I_1-I_0)K[\beta-CD]^2} \tag{5}$$

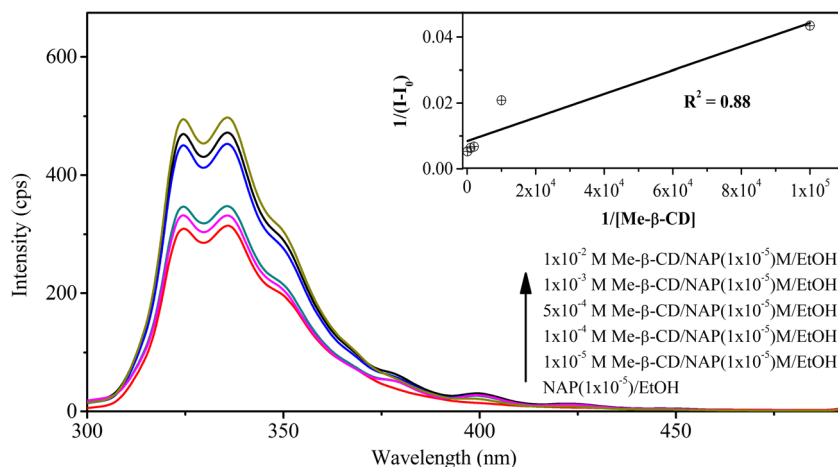
Here, I and I₀ show initial fluorescence intensities of naphthalene in the presence and absence of Me-β-CD dissolved in ethanol, for naphthalene does not dissolve in water. I₁ is the estimated fluorescence intensity of all guest molecules in the complex. When all the guest molecules enter the complex, the best linear line is obtained at 1/I-I₀ vs. 1/[Me-β-CD] graph according to Eq. 4 (see Fig. 1). The K value has been calculated (11 × 10⁴ M⁻¹). The size of this value indicates that inclusion complex formation is strong. With the use of this value

and of Eq. 6, a value of -28.8 kJ/mol was calculated for the standard Gibbs energy change (ΔG⁰) at 298 K.

$$\Delta G^0 = -2,303 RT \log_{10} K \tag{6}$$

Where R is the gas constant, T is the temperature, and K is the coupling constant. K has been obtained from the change in fluorescence intensities of naphthalene with Me-β-CD (Fig. 1). The linearity of the graph obtained in Fig. 1 (R² = 0.88) reflects the 1:1 pattern for the complex formed between Me-β-CD and naphthalene. The linearity of the graph obtained from Eq. 5 is not sufficient. Thus, it has been observed that 2:1 complex formation is not possible. NAP-Me-β-CD inclusion complex formation has been studied at various concentrations of naphthalene in order to see the effect of heavy metals. From the wavelength at the point where the naphthalene excitation and emission spectra overlap, the excited singlet state energy is calculated as 378.7 kJ/mol. This value usually ranges from 200 to 600 kJ/mol. It has been observed that the addition of heavy metal solutions reduces the fluorescence intensity of the NAP-Me-β-CD inclusion complex. The results of each experiment are shown in Figs. 2a–c and 3a–

Fig. 1 Effect of increasing methyl-beta-cyclodextrin concentration on the fluorescence spectrum of naphthalene dissolved in 1 × 10⁻⁵ M chloroform. The Benesi-Hildebrand graph (1/[I-I₀] vs. 1/[Me-β-CD])



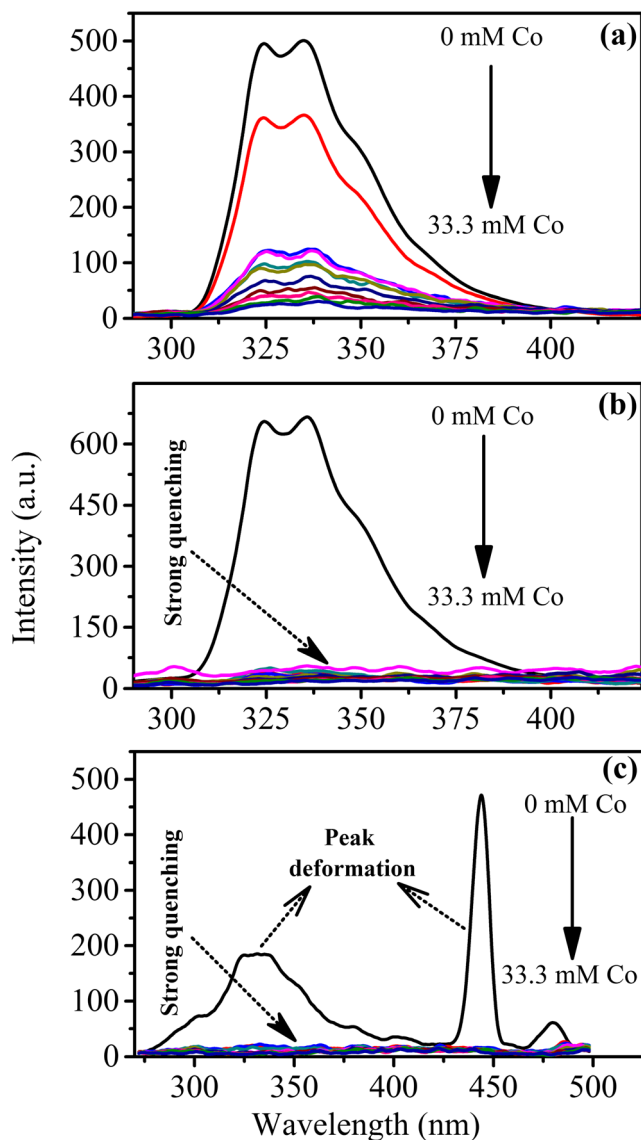


Fig. 2 (a) Quench effect on 10^{-3} M naphthalene of 0.1 M Cobalt (b) Quench effect on 10^{-4} M naphthalene of 0.1 M Cobalt (c) Quench effect on 10^{-5} M naphthalene of 0.1 M Cobalt

c. Graphs of Co^{2+} and Mn^{2+} containing 10^{-4} and 10^{-5} M naphthalene show a similar quenching effect, but the emission intensity decreases down to zero. In addition, at these concentrations, the characteristic emission spectrum of naphthalene in the graph of Mn^{2+} has also been observed to deteriorate. For this reason, it is difficult to calculate a statistically valid K_{sv} value for these concentrations. This is because the resulting graphs are far from being linear (R^2 values range from 0.50 to 0.57). All Figs. 2 and 3 show that heavy metal ions effectively quench the fluorescence emission of the formed inclusion complex. It is thought that the quenching here is a dynamic one. The Stern-Volmer quenching constants are calculated from the slope of the Stern-Volmer graphs (Fig. 4) drawn against the K_{sv} values I_0/I on $[Q]$. As can be seen in Fig. 4, the most suitable linear graph is obtained for 10^{-3} M Co^{2+} and

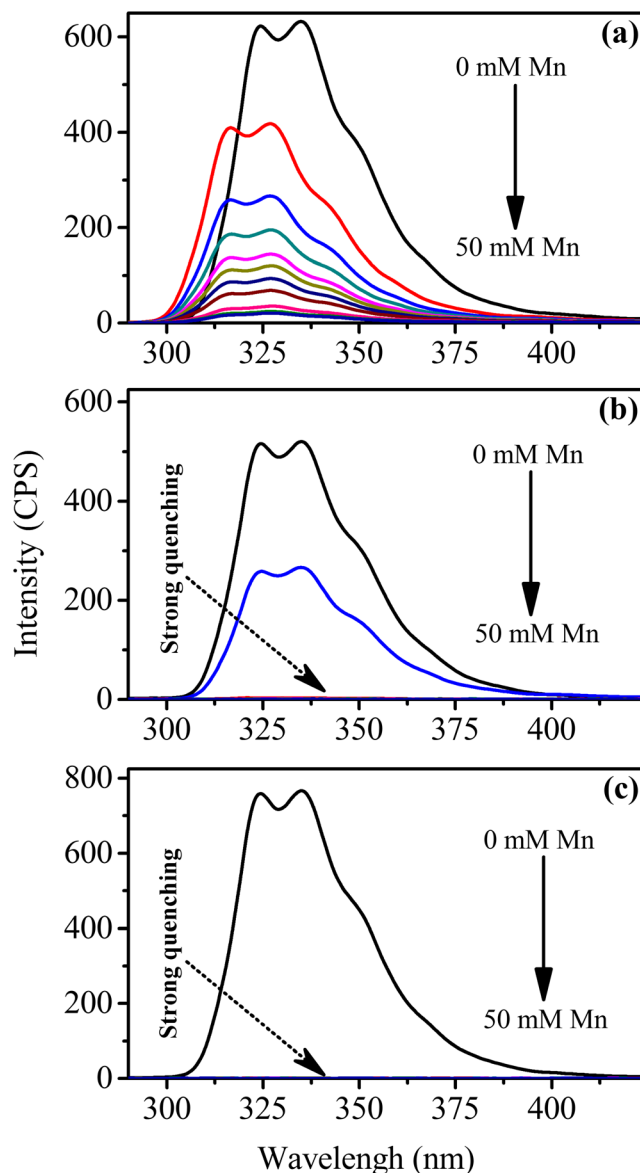


Fig. 3 (a) Quench effect on 10^{-3} M naphthalene of 0.1 M of Manganese (b) Quench effect on 10^{-4} M naphthalene of 0.1 M Manganese (c) Quench effect on 10^{-5} M naphthalene of 0.1 M Manganese

Mn^{2+} , and R^2 values are 0.96 and 0.97, respectively. The K_{sv} values for these values are 5520 and 612, respectively. As mentioned above, it is difficult to work on solutions diluted at levels more than 10^{-3} M. The linearity of the graph in Fig. 4 suggests that dynamic and static quenchings are not realized simultaneously. Otherwise, if dynamic and static quenchings were simultaneous, non-linear graphs would be obtained and the event would take place according to the following mechanism (Scheme 2) [10]. Note that the I_0/I on $[Q]$ is linear, which is identical to dynamic quenching. Hence, the measurement of fluorescence lifetimes is the most ultimate method to distinguish static and dynamic quenching [11]. If the fluorescence lifetime value of the excited material does not change in the presence of a quenching reagent, then static quenching

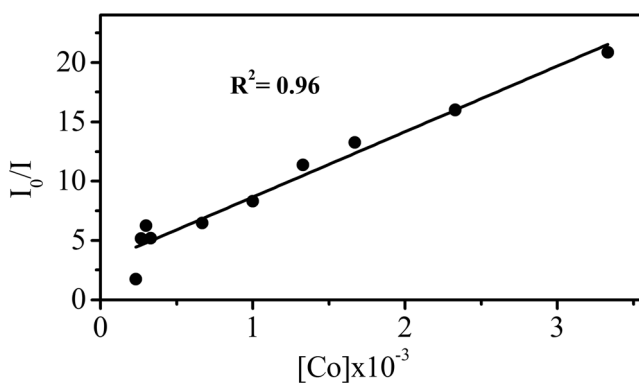


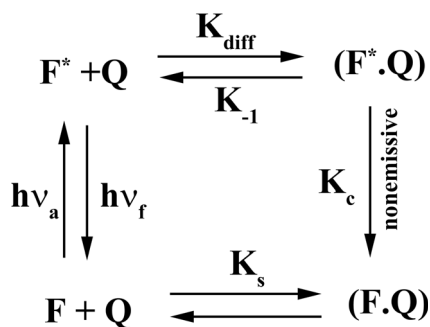
Fig. 4 Stern-Volmer graph for Co²⁺

would be the case ($\tau_0 / \tau = 1$) [12]. Here, on the contrary, the shorter fluorescence life time value is observed in the presence of the quenching reagent.

The fluorescence quantum yields of the NAP-Me- β -CD complexes are calculated as a result of the changes in the emission spectrum after each addition of the quencher reagent. 9,10-Diphenyl anthracene ($\Phi_f = 0.95$) has been used as a standard to calculate the fluorescence quantum yield (Φ_f) according to Eq. 7 below.

$$\phi_{f(sample)} = \phi_{f(std)} \times \frac{(Area_{(sample)})}{(Area_{(std)})} \quad (7)$$

Here, Area (std) and Area (sample) are areas below the fluorescence emission spectra of the standard and samples. The quantum yield values which are found to be smaller than 1 indicate that other reactions are in competition with the main reaction in the process. Both the samples and the standard are excited at the same wavelength. Two effects can be considered in the binding of the fluorescent ligand (L) to the metal (M) in quenching of fluorescence by heavy metals. The metal may partially or completely suppress the fluorescence of the ligand, or the new species (ML) itself may exhibit fluorescence quality. Diamagnetic and paramagnetic species also quench fluorescence. When fluorescence quenching is observed, the metal ion is seen to be inhibiting or terminating the radiative transition leading to fluorescence emission. Hence, decreases have been observed in the intensity of the first spectrum [13].



Scheme 2 Realization of dynamic and static quenching simultaneously

The magnitude of the transition between systems is the most important factor in determining the emission of fluorescence and phosphorescence of the metal chelate compound. If excited species contain paramagnetic ions, fluorescence may not occur due to the increased transit speed between paramagnetic species and systems. In a fluorophore solution, the presence of foreign paramagnetic ions may also have the same effect. The quenching effect of heavy metals on the fluorescence intensity of Me- β -CD can be explained in this way. Many transition metal ion complexes, which contain partially filled d orbitals, exhibit fluorescence in the fluid solution. Many coordinated transition metal ions are paramagnetic. The quantum yield (Φ_f) of NAP-Me- β -CD was calculated to be 0.7612 in the absence of Co²⁺ and Mn²⁺ heavy metal ions. By varying the amount of heavy metal salts, that is to say by varying the amount of the quencher, the figure varied from 0.7612 to 0.0012. Low fluorescence quantum yield causes the guest molecule within the CD cavity to transform into the triplet between the systems. The triplet quantum yields can also be calculated using Eq. 8. It is known by us that heavy metal ions reduce the emission of fluorescence of the inclusion complex by increasing the inter-system transmission.

$$\Phi_T = (1 - \Phi_f) \quad (8)$$

Where, Φ_T is the triplet quantum yield and Φ_f is the fluorescence quantum yield. After Singlet is quenched, a lot of triplets of naphthalene have been obtained. Heavy metal salts similarly quench the inclusion complex. The quenching of the fluorescence of the inclusion complex of heavy metals is perhaps due to the π interaction between naphthalene having electron rich aromatic ring and the heavy metal. The quenching of the naphthalene-Me- β -CD inclusion complex results in the transfer of an electron into the quencher from the fluorophore group. Which of these two ions have more quenching effect depends perhaps on their electronegativity values or on their paramagnetic / diamagnetic properties. It is seen here that, of the 2 paramagnetic metal cations, Mn²⁺ (d⁵) and Co²⁺ (d⁷): Mn²⁺ is a weaker quencher as compared to Co²⁺ due to the stability of Mn²⁺ with half-packed shell. Stemming from their electronegativity values, it is also possible to say for heavy metals that the higher their electronegativity value is the more they quench fluorescence.

Interaction of NAP with Me- β -CD

FT-IR Spectral Analysis

The FT-IR technique is one of the most important and powerful techniques to confirm inclusion complex formation between naphthalene (NAP) and Me- β -CD. Stanculescu et al. [14] studied the interaction of β -CD with polychlorophenol

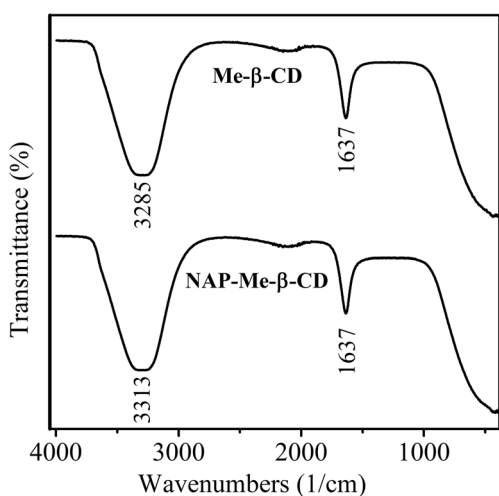


Fig. 5 FT-IR spectra of (a) Me- β -CD and (b) NAP-Me- β -CD

compounds in aqueous media using FT-IR and molecular modeling techniques. This study, too, displays the interaction of Me- β -CD with naphthalene by employing the FT-IR technique. The FT-IR spectra of 10^{-3} M Me- β -CD and

10^{-3} M NAP-Me- β -CD inclusion complex are shown in Fig. 5. In the aqueous solution, the strong O-H tensile band at 3300 cm^{-1} of water has been reported in the literature to reduce the spectral contrast of the aromatic C-H stretching bands between 3150 and 2900 cm^{-1} (<http://www.astrochem.org/data/napH2O.php>). In this study, despite the influence of the O-H band, a significant shift of about 30 cm^{-1} in the C-H stretching vibration confirms the formation of inclusion complex.

^1H NMR Spectral Analysis

^1H NMR spectra of Me- β -CD, Naphthalene (NAP) and NAP-Me- β -CD have been obtained as additional evidence for inclusion complex formation between naphthalene and Me- β -CD (Fig. 6). All NMR experiments were performed at 298.15 K on a Varian VNMRs 600 spectrometer (Varian, San Francisco, CA, USA) operating at 599.747 MHz for proton (^1H) resonance frequency equipped with a 5 mm One NMR probe using 5 mm sample tubes (5 mm diameter, 178 mm length, Duran Group, Mainz, Germany). The

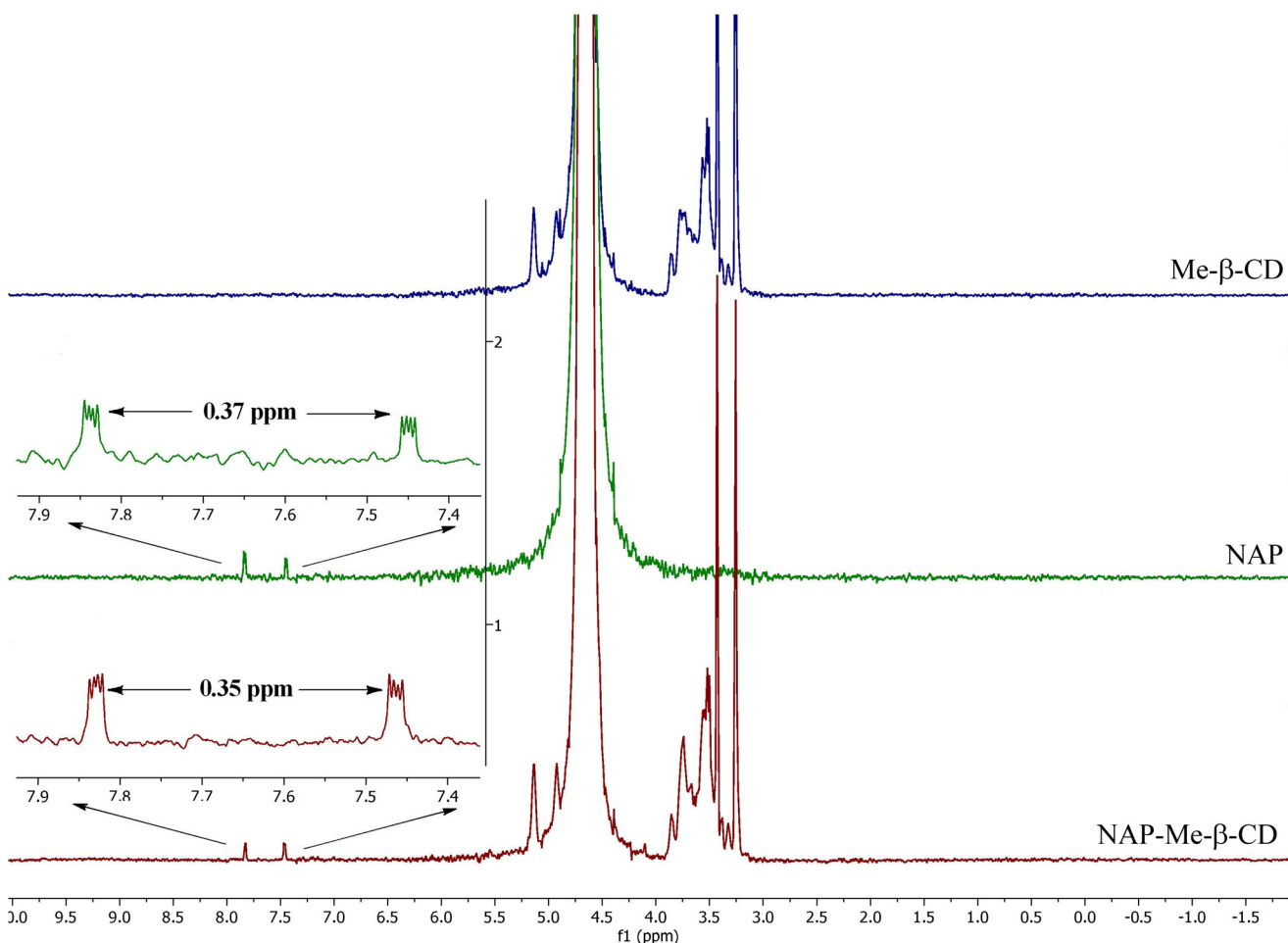


Fig. 6 ^1H NMR spectra of Me- β -CD, Naphthalene and Inclusion complex of naphthalene with Me- β -CD

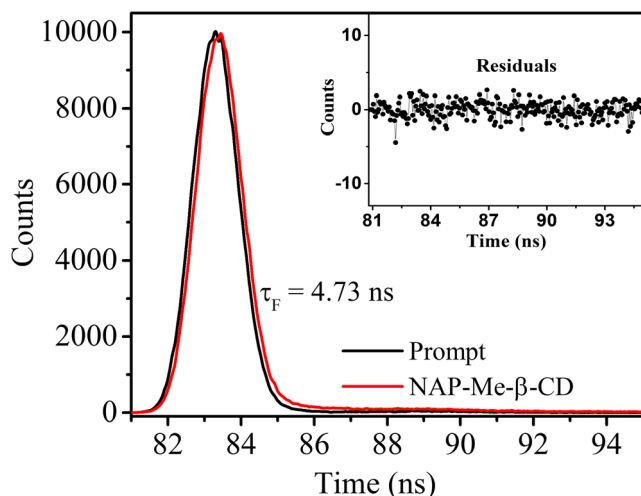


Fig. 7 Fluorescence lifetime measurement of naphthalene-Me-β-CD inclusion complex (without Quencher)

softwares VnmrJ 4.2 (Agilent Technologies, Santa Clara, CA, USA) and MestReNova 11.0.0 (Mestrelab Research S.L. Santiago de Compostela, Spain) were used for data acquisition and data processing, respectively.

Water suppression using presaturation (presat) experiments was recorded with 32 scans without sample spinning. Samples dissolved in Deuterium Oxide. The measurements were conducted with the following parameters optimized for ^1H -Presat: pulse angles of 90° , 64 k data points, acquisition time of 3.4 s, relaxation delay 2 s, offset 4.64 ppm, spectral width 9615.4 Hz and auto gain function. Chemical shift was referenced to the TSP- d_4 signal at 0.00 ppm in D_2O . Chemical shift values of samples: Naphthalene (NAP) (^1H -Presat NMR (600 MHz, Deuterium Oxide) δ 7.84 (dd, $J=6.2$, 3.4 Hz, 4H), 7.45 (dd, $J=6.4$, 3.2 Hz, 4H). NAP-Me-β-CD (^1H -Presat NMR (600 MHz, Deuterium Oxide) δ 7.83 (dd, $J=6.2$, 3.3 Hz, 4H), 7.46 (dd, $J=6.3$, 3.2 Hz, 4H). Looking at the spectrum, spectra of Me-β-CD, naphthalene and inclusion complex can be observed. It is seen that, inclusion complex formation changes the chemical shift value of naphthalene in the spectrum. We can think of this as evidence that the chemical environment of the naphthalene changes and that it enters the Me-β-CD. Here, the induced chemical shifts of the guest molecule protons show that the proton moiety is included in the CD cavity. At the same time, it reveals the newly formed molecular structure.

Lifetime

The fluorescence lifetimes have been obtained using Horiba-Jobin-Yvon-SPEX Fluorolog 3-2iHR instrument with Fluoro Hub-B Single Photon Counting Controller at an excitation wavelength of 470 nm. Signal acquisition has been performed using a TCSPC module (NanoLED-390 emitting 390 nm). Here; we have read the lifetime values in the

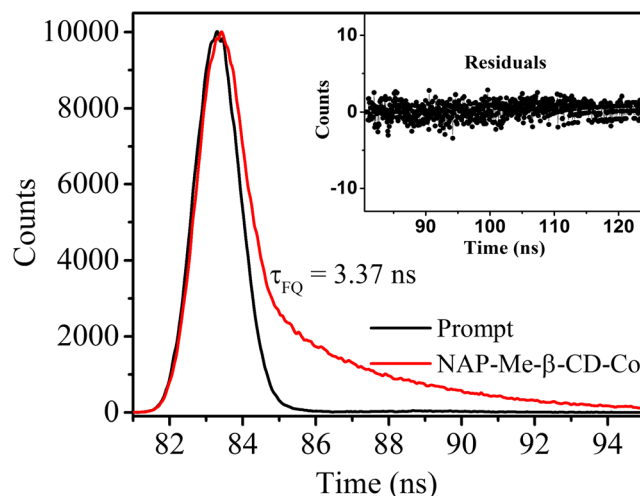


Fig. 8 Fluorescence lifetime measurement of naphthalene-Me-β-CD inclusion complex (in the presence of Quencher)

presence of quencher (Fig. 7) and absence of it (Fig. 8). A shorter lifetime value has been detected in the presence of quencher or of heavy metals. This shows that the phenomenon here is a dynamic quenching, as mentioned earlier.

Assuming that the phenomenon in this study is diffusion controlled, the bimolecular quenching rate constant can be calculated theoretically (Eq. 9).

$$k_{\text{diff}} = 8RT/3\eta = 6.6 \times 10^9 \text{ M}^{-1}\text{S}^{-1} \quad (9)$$

In this formula, $R = 8.314 \text{ J / Kmol}$. T is the temperature in kelvin, and η is the viscosity in kg / m.s . When quenching is diffusion controlled, it can be considered that the bimolecular quenching rate constant can be approximately equal to the diffusion rate constant ($k_q \approx k_{\text{diff}}$) and inversely proportional to the viscosity of the solution (<https://www.chem.uzh.ch/de/study/download/year2/che211.html>). This value can be compared with the stern-volmer value (K_{sv}) obtained from the stern-volmer graphs and thus can be used at the same time to theoretically calculate the fluorescence lifetime value (Eq. 10) [15].

$$\frac{\tau_{\text{FQ}}}{\tau_{\text{F}}} = 1 + K_{\text{sv}}[Q] = 1 + k_q\tau_{\text{FQ}}[Q] \quad (10)$$

At the same time, using the measured fluorescence lifetime value, a bimolecular quenching rate constant can also be found. Using the fluorescence lifetime value measured in the absence of the quencher reagent, the bimolecular quenching rate constants for Co^{2+} and Mn^{2+} i.e., k_q values, have been calculated to be $11.69 \times 10^{11} \text{ M}^{-1}\text{s}^{-1}$ and $1.30 \times 10^{11} \text{ M}^{-1}\text{s}^{-1}$, respectively. These values are greater than the diffusion rate constant. That they are greater indicates that the mechanism of the quenching phenomenon is not solely dependent on molecular dynamic diffusion. According to the literature, the bimolecular quenching phenomenon associated with singlet

state of an organic molecule is mainly based on long-range Förster energy transfer or electron transfer [16]. Approximate quenching activation energy can also be calculated using Eq. 11 [17].

$$k_q = Z_{12} \exp(-\Delta E/RT) \quad (11)$$

Here, k_q represents the bimolecular quenching rate constant, Z_{12} is the number of collisions for a solution of about $10^{11} \text{ M}^{-1} \text{ s}^{-1}$, $R = 8.314 \text{ J / Kmol}$ and T is the temperature value in kelvin.

Conclusion

The NAP-Me- β -CD inclusion complex was successfully formed and characterized. The quenching effect of heavy metals added to the inclusion complexes was studied by fluorescence spectroscopy. Co^{2+} showed more quenching effect than Mn^{2+} . Many transition metal ions are not fluorescent. However, thanks to the probe molecule prepared in this study, the photophysical properties of the metal and the probe molecule at the excitation level can be easily monitored. Although the fluorescence lifetime values of the inclusion complex point to the dynamic quenching in the presence and absence of a quencher, the bimolecular quenching and diffusion rate constants show that molecular dynamic diffusion alone is not effective in quenching. Förster energy transfer or electron transfer may also be effective in quenching.

Acknowledgements As the authors, we would like to thank to Scientific Research Coordinaton Unit (BAP) of Kocaeli University (Project No: 2017/010) for their contribution to this study, and to the Department of Chemistry of Gebze Technical University for their assistance in measurements of the fluorescence lifetime. We thank TUBITAK (UME) for their assistance in measurements of ^1H NMR.

References

- Murugan M, Anitha A, Sivakumar K, Rajamohan R (2018) Supramolecular interaction of primaquine with native β -cyclodextrin. *J Solut Chem* 47:906–929
- Norkus E (2009) Metal ion complexes with native cyclodextrins, an overview. *J Incl Phenom Macrocytl Chem* 65:237–248
- Li S, Purdy WC (1992) Cyclodextrins and their applications in analytical chemistry. *Chem Rev* 92:1457–1470
- Ehsan S, Prasher SO, Marshall WD (2007) Simultaneous mobilization of heavy metals and polychlorinated biphenyl (PCB) compounds from soil with cyclodextrin and EDTA in admixture. *Chemosphere* 68:150–158
- Ay U, Dogruyol Z, Arsu N (2014) The effect of heavy metals on the anthracene-me- β -cyclodextrin host-guest inclusion complexes. *Supramol Chem* 26:66–70
- Evans CH, Partyka M, Van Stam J (2000) Naphthene complexation by β -Cyclodextrin: influence of added short chain branched and linear alcohols. *J Incl Phenom Macrocytl Chem* 38: 381–396
- Abdel-Shafi AA (2007) Spectroscopic studies on the inclusion complex of 2-naphthol-6-sulfonate with β -Cyclodextrin. *Spectrochim Acta A* 66:732–738
- Mukhopadhyay M, Banerjee D, Koll A, Mandal A, Filarowski A, Fitzmaurice D, Das R, Mukherje SJ (2005) Excited state intermolecular proton transfer and gaging of salicylidine-3,4,7-methyl amine in cyclodextrins. *Photochem Photobiol A Chem* 175:94–99
- Balta DK, Arsu N (2008) Host/guest complex of β -cyclodextrin/5-thia pentacene-14-one for photoinitiated polymerization of acrylamide in water. *J Photochem Photobiol A Chem* 200:377–380
- López-de-Luzuriaga n JM, Monge M, Elena Olmos M, Pascual D (2014) Analysis of fluorescence quenching of naphthalene by two mercury containing organometallic complexes. *J Lumin* 154:322–327
- Nouhi A, Hajjoul H, Redon R, Gagne JP, Mounier S (2018) Time resolved laser fluorescence spectroscopy of organic ligands by europium: fluorescence quenching and lifetime properties. *Spectrochim Acta A* 193:219–225
- Yang H, Ran G, Yan J, Zhang H, Hu X (2018) A sensitive fluorescence quenching method for the detection of tartrazine with acriflavine in soft drinks. *Luminescence* 33:349–355
- Jenne EA (1998) Adsorption of metals by geomeia variables, mechanisms, and model applications. Academic press (<http://www.apnet.com>)
- Stanculescu I, Dobrica I, Mandravel C, Mindrila G (2010) FTIR and molecular modeling study of the interaction between β -Cyclodextrin and polychlorobiphenyls. *Analele Universității din București – Chimie (serienouă)* 19:47–52
- Drössler P, Holzer W, Penzkofer A, Hegemannb P (2003) Fluorescence quenching of riboflavin in aqueous solution by methionin and cystein. *Chem Phys* 286:409–420
- Wu A, Shen X, Gao HJ (2007) Investigation on photophysical properties of a substituted 3H-indole- modified β -cyclodextrin-II, efficient photoinduced energy transfer with naphthalene and its derivatives. *Photochem Photobiol A Chem* 185:144–149
- Baggott JE, Pilling MJ (1980) Temperature dependence of excited-state-electron-transfer reactions, quenching of RuL_3^{2+} emission copper (II) and euripum (III) in aqueous solution. *J Phys Chem* 84:3012–3019