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NMR and fluorescence enhancement effect studies of ternary inclusion complexes among naphthalenediamines-triethylene tetramine modified β -cyclodextrin-lanthanide metal ions

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The 6-OH group of β -cyclodextrin (β -CD) was modified by triethylene tetramine. The modified host molecule successfully complexes 1,5-naphthalenediamine and 1,8-naphthalenediamine, respectively, in the presence of lanthanide metal ions (Y^{3+} , Yb^{3+} , Nd^{3+} , Sm^{3+}). As a result, eight ternary inclusion complexes (host-guest-metal) were formed, which were characterized via 1H nuclear magnetic resonance (NMR) technique. The chemical shift variations of host and guest molecules were studied. The stoichiometric proportion of host and guest molecules is 2:1 for all the eight complexes. Signal degeneration still exists for the guest molecules after the inclusion, which verifies the symmetrical conformation of the guest molecules inside the cavities of the two host molecules. After the inclusion process, we found that the fluorescent strength of guest molecules was increased in a remarkable degree in this series, meanwhile, the fluorescent strength of 1,5-naphthalenediamine was higher than that of 1,8-naphthalenediamine by 3 to 4 times, which verifies that 1,8-naphthalenediamine coordinates with lanthanide metal ions, however, similar coordination does not occur in the case of 1,5-naphthalenediamine.

Key words: β -Cyclodextrin (β -CD), modification, naphthalenediamine, lanthanide metal, nuclear magnetic resonance (NMR), fluorescence, complexation.

INTRODUCTION

Cyclodextrins (CD) are cyclic organic compounds obtained by enzymatic transformation of starch. Among the class of "host" molecules, the β -CD is one of the most abundant natural oligomers and corresponds to the association of seven glucose units (Bender and Komiyama, 1978; Saenger, 1980; Szejtli, 1988), of which the cavity exhibits a hydrophobic character whereas the exterior is strongly hydrophilic. This peculiar structure allows various

substrates to be included in the cavity via non covalent bonds to form what is called inclusion complexes.

In the field of environmental research, the inclusion ability of CDs has attracted considerable attention for the merit of stabilizing and increasing the solubility of labile xenobiotics (Yamamoto and Katsuda, 1980; Szejtli, 1985; Cieslak, 1991; Szenté and Szejtli, 1996; Ishiwata and Kamiya, 1999). β -CD molecules are notably well-known to greatly affect the chemical behavior of many pesticides absorption (Watanabe et al., 1992), solubility, stability (Djedainipilard et al., 1993) and decomposition rate (Pranker et al., 1992).

Supramolecular fluorescence sensor (Yuan and Bo, 2008) based on host-guest chemistry is a hot investigation field recently. Its advantages (Hayashita et al., 2004) includes: controlled dynamic molecular recognition;

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Abbreviations: CD, Cyclodextrin; NMR, nuclear magnetic resonance; TSPP, tetrasodium pyrophosphate; DMSO, dimethyl sulfoxide.

the efficiency and selectivity of combination is increased by means of individual interaction; and the multiplicity of combination between individual components can recognize variant ions and molecules. Cyclodextrin is a main important host compound based on the advantages.

Liu et al. (2001a, 2000, 2001b, 2003) synthesized a series of β -CD dimmers linked via polyethylenediamine. The synergistic coordination of the bridged CD dimmers could change the fluorescence effect of guest molecules. Natural β -CD could quench rhodamine B, however, bipyridine-bridged β -CD has a great effect in increasing its fluorescence strength (Liu et al., 2001c). Hu et al. (2007) synthesized a series of light-controlled β -CD dimmers, which forms 1:1 host-guest inclusion complex with tetrasodium pyrophosphate (TSPP), which results in the fluorescence quenching of TSPP. Wang et al. (1992, 1994) investigated the modification of β -CD by dansyl group and its fluorescence effect in aqueous media. They found that different modification sites of β -CD, 2-OH, 3-OH or 6-OH would exhibit different fluorescence effect in aqueous media. Corradini et al. (1996, 1997) synthesized a series of ethylenediamine-bridged dansyl group modified β -CD host molecules, which coordinated with copper ions and resulted in the fluorescence quenching of dansyl group. Pagliari et al. (2000) investigated dansyl group modified β -CD fluorescent molecules based on phenylalanine, which coordinated with copper ion and quenched the fluorescence of dansyl group.

In aqueous media, triethylene tetramine modified β -CD (TTCD) is able to complex lanthanide metal ions via coordinate linkage. The lanthanide metal ions can also complex naphthalenediamine inside the cavity. The stoichiometric proportion between β -CD and guest molecules is 2:1. The ternary complexes were investigated by means of ^1H nuclear magnetic resonance (NMR) and fluorescence spectra. Studies showed that, the fluorescence effects of the guest molecules are greatly enhanced by means of inclusion with TTCD. The possible conformations of the ternary complexes are still investigated herein.

MATERIALS AND METHODS

Reagents

β -Cyclodextrins, 1,5-naphthalenediamine, 1,8-naphthalenediamine, TsCl (paratoluenesulfonyl chloride), triethylene tetramine were purchased from Aldrich and used without any further purification.

NMR experiments

NMR spectra were obtained with a Varian Mercury AS400 instrument. All the experiments of the inclusion complexes were recorded using $\text{DMSO-}d_6$ as solvent. The solutions were transferred in 5 mm NMR tubes, giving a sample total volume of 600 μl . The probe temperature was regulated to 300 K. The resonance at 2.48 ppm (^1H NMR) due to residual solvents, present as impurities

(dimethyl sulfoxide (DMSO)), was used as internal reference.

Fluorescence spectroscopy experiments

Fluorescence spectra were obtained with a RF-5301PC fluorescence spectrometry. The samples were grounded into homogeneous powder, which was scanned via the fluorescence spectrometry directly. Operation conditions are as follows: Optical grating slit width, 5 nm or 1.5 nm; excitation wavelength, 280 nm; temperature, 25°C.

General preparation method of ternary inclusion complexes

Triethylene tetramine modified β -CD (TTCD) was prepared according to the previously reported methods (Liu et al., 1995; Tabushi and Shimizu, 1978). Their inclusion complexes with 1,5/1,8-naphthalenediamine; lanthanide metal ions were prepared as follows: 0.1 g TTCD, 0.02 g MCl_3 (SmCl_3 , YCl_3 , YbCl_3 , NdCl_3) was dissolved in 30 ml of sodium bicarbonate buffered deionized water, 0.01 g naphthalenediamine was dissolved in 1 ml of DMSO and added to the above aqueous solution by dropwise. The mixture was kept stirring at room temperature for 3 to 4 h. The mixture was centrifuged to collect the precipitate and dry in vacuo.

RESULTS AND DISCUSSION

Reaction scheme

Figure 1 illustrates the modification of β -CD by triethylene tetramine and complexation with naphthalenediamine and lanthanide ions.

NMR spectra results and discussion

Figure 2 lists the hydrogen labeling of host and guest molecules. For each molecule, we observed the difference in the chemical shifts between TTCD, naphthalenediamines, and their inclusion complexes. ^1H NMR chemical shifts provided unambiguous evidence on the formation of the complexes. The effects were qualitatively used.

Tables 1 to 16 lists the ^1H NMR chemical shift difference of host and guest molecules upon complexation with lanthanide metal ions. After the complexation, host and guest molecules did not show pronounced chemical shift variations, since the main interaction forces between host and guest molecules are weak Van der Waals forces, for example, dipole-dipole force, dispersion force, etc. Although, amino groups are good coordination groups, however, no coordination process occurred between lanthanide metal ions and the amino group in 1,5-naphthalenediamine, which was verified by minute chemical shift variation of the corresponding amino groups. Lanthanide metal ions only coordinate with the amino groups from triethylene tetramine, which is verified from the NMR signals of hydroxyl groups in TTCD. Before the complexation process, the hydrogen signals of the

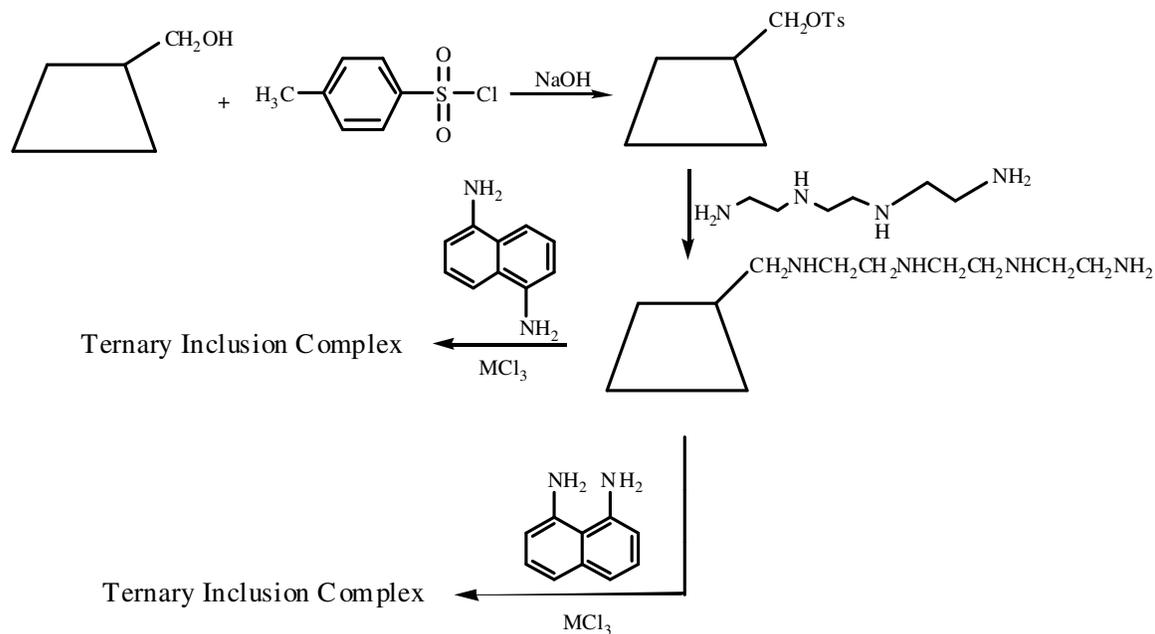


Figure 1. Reaction scheme of modification and complexation (M=Y, Yb, Sm, Nd).

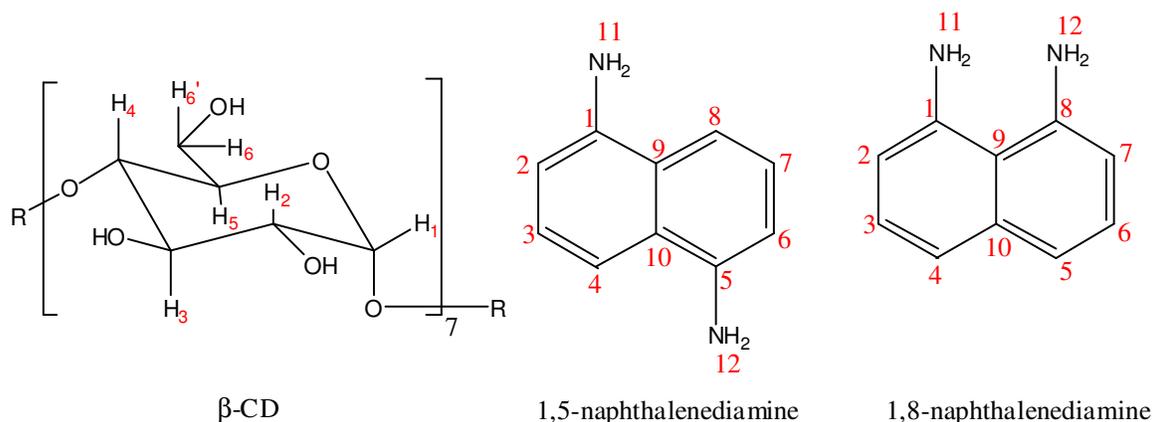


Figure 2. Structure and hydrogen labeling of host and guest molecules.

Table 1. ^1H NMR chemical shift of 1,5-naphthalenediamine in the presence and absence of TTCD/ YCl_3 .

1,5-Naphthalenediamine	δ (ppm) (free)	Complex δ (ppm)	$\Delta\delta$ (ppm)
H-2, 6	6.62(d)	6.60(d)	-0.02
H-3,7	7.07(t)	7.05(t)	-0.02
H-4,8	7.23(d)	7.21(d)	-0.02
H-11,12	5.41(s)	5.41(s)	0

hydroxyl groups almost disappeared; however, they reappeared as sharp peaks after the complexation process. It is the hydrogen bonding that affects the signal configuration. Before the complexation process, strong hydrogen bonding exists between the amino groups from

the branched triethylene tetramine, which resulted in the hydroxyl signals almost disappearing. After the process, the amino groups in the branched chain formed strong coordinated bond with lanthanide metal ions, which set hydroxyl groups free; consequently, their NMR signals

Table 2. ^1H NMR chemical shift of TTCD in the presence and absence of 1,5-naphthalenediamine and YCl_3 .

TTCD	δ (ppm) (free)	Complex δ (ppm)	$\Delta\delta$ (ppm)
H-1	4.83(d)	4.83(d)	0
H-3	3.64(t)	3.61(t)	-0.03
H-6,6'	3.67(t)	3.66(t)	-0.01
H-5	3.57(d)	3.56(d)	-0.01
H-4	3.34(t)	3.34(t)	0
H-2	3.29(d)	3.29(d)	0

Table 3. ^1H NMR chemical shift of 1,5-naphthalenediamine in the presence and absence of TTCD/ YbCl_3 .

1,5-Naphthalenediamine	δ (ppm) (free)	Complex δ (ppm)	$\Delta\delta$ (ppm)
H-2, 6	6.62(d)	6.58(d)	-0.04
H-3,7	7.07(t)	7.05(t)	-0.02
H-4,8	7.23(d)	7.20(d)	-0.03
H-11,12	5.41(s)	5.42(s)	0.01

Table 4. ^1H NMR chemical shift of TTCD in the presence and absence of 1,5-naphthalenediamine and YbCl_3 .

TTCD	δ (ppm) (free)	Complex δ (ppm)	$\Delta\delta$ (ppm)
H-1	4.83(d)	4.83(d)	0
H-3	3.64(t)		
H-6,6'	3.67(t)		
H-5	3.57(d)	3.28-3.62	—
H-4	3.34(t)		
H-2	3.29(d)		

Table 5. ^1H NMR chemical shift of 1,5-naphthalenediamine in the presence and absence of TTCD/ SmCl_3 .

1,5-Naphthalenediamine	δ (ppm) (free)	Complex δ (ppm)	$\Delta\delta$ (ppm)
H-2, 6	6.62(d)	6.60(d)	-0.02
H-3,7	7.07(t)	7.05(t)	-0.02
H-4,8	7.23(d)	7.19(d)	-0.04
H-11,12	5.41(s)	5.41(s)	0

reappeared as sharp peaks. Probably due to the spatial restrictions, the amino group from 1,5-naphthalenediamine was unable to coordinate lanthanide metal ions. According to the integration result of the above four complexes, it was found that the stoichiometric proportion between host and guest molecules is 2:1, which is different to our reported result (Jiang et al., 2007). Signal degeneration of the guest molecule still exists upon complexation with TTCD and lanthanide metal ion, which provides some information of

possible conformation of the guest molecule inside the cavities of host molecules.

After the complexation, the chemical shifts of 1,8-naphthalenediamine showed pronounced variations, which clearly proves the formation of the inclusion complexes. The hydrogen atoms in the naphthalene ring showed a variation between $-0.2\sim 0.03$, bigger than the magnitude of 1,5-naphthalenediamine. The shift of amino groups reaches up to 1.03 ppm, on the average, which can elucidate the coordination between lanthanide metal

Table 6. ^1H NMR chemical shift of TTCD in the presence and absence of 1,5-naphthalenediamine and SmCl_3 .

TTCD	δ (ppm) (free)	Complex δ (ppm)	$\Delta\delta$ (ppm)
H-1	4.83(d)	4.83(d)	0
H-3	3.64(t)		
H-6,6'	3.67(t)		
H-5	3.57(d)	3.20-3.64	—
H-4	3.34(t)		
H-2	3.29(d)		

Table 7. ^1H NMR chemical shift of 1,5-naphthalenediamine in the presence and absence of TTCD/ NdCl_3 .

1,5-Naphthalenediamine	δ (ppm) (free)	Complex δ (ppm)	$\Delta\delta$ (ppm)
H-2, 6	6.62(d)	6.60(d)	-0.02
H-3,7	7.07(t)	7.05(t)	-0.02
H-4,8	7.23(d)	7.20(d)	-0.03
H-11,12	5.41(s)	5.42(s)	0.01

Table 8. ^1H NMR chemical shift of TTCD in the presence and absence of 1,5-naphthalenediamine and NdCl_3 .

TTCD	δ (ppm) (free)	Complex δ (ppm)	$\Delta\delta$ (ppm)
H-1	4.83(d)	4.83(d)	0
H-3	3.64(t)		
H-6,6'	3.67(t)		
H-5	3.57(d)	3.20-3.60	—
H-4	3.34(t)		
H-2	3.29(d)		

Table 9. ^1H NMR chemical shift of 1,8-naphthalenediamine in the presence and absence of TTCD/ YCl_3 .

1,8-Naphthalenediamine	δ (ppm) (free)	Complex δ (ppm)	$\Delta\delta$ (ppm)
H-2, 7	6.53(d)	6.55(d)	0.02
H-3,6	7.15(t)	7.04(t)	-0.11
H-4,5	7.15(d)	6.96(d)	-0.19
H-11,12	4.40(s)	5.44(s)	1.04

metal ion and amino groups, occurs. Similar phenomena also exist for the NMR signal configuration changes of hydroxyl group in TTCD before and after the complexation. Lanthanide metal ions will coordinate with the amino groups from the branched triethylene tetramine and the amino groups from 1,8-naphthalenediamine. In the case of 1,5-naphthalenediamine, only minute shift occurs in the amino group, which means no coordination bonds form between the amino group and lanthanide metal ion. According to the integration result, the

stoichiometric proportion between TTCD and 1,8-naphthalenediamine is also 2:1, similar to the case of 1,5-naphthalenediamine, different to our reported result (Jiang et al., 2007). The signal degeneration of guest molecule still exists upon complexation, showing symmetrical conformation of the guest molecules inside the cavity of host molecules after forming the ternary inclusion complexes. NMR results provide important evidence to elucidate the possible conformation of the guest molecule inside the cavity of host molecules.

Table 10. ^1H NMR chemical shift of TTCD in the presence and absence of 1,8-naphthalenediamine and YCl_3 .

TTCD	δ (ppm) (free)	Complex δ (ppm)	$\Delta\delta$ (ppm)
H-1	4.83(d)	4.83(d)	0
H-3	3.64(t)	3.61(t)	-0.03
H-6,6'	3.67(t)	3.66(t)	-0.01
H-5	3.57(d)	3.56(d)	-0.01
H-4	3.34(t)	3.36(t)	0.02
H-2	3.29(d)	3.28(d)	-0.01

Table 11. ^1H NMR chemical shift of 1,8-naphthalenediamine in the presence and absence of TTCD/ YbCl_3 .

1,8-Naphthalenediamine	δ (ppm) (free)	Complex δ (ppm)	$\Delta\delta$ (ppm)
H-2, 7	6.53(d)	6.56(d)	0.03
H-3,6	7.15(t)	7.01(t)	-0.14
H-4,5	7.15(d)	6.95(d)	-0.20
H-11,12	4.40(s)	5.43(s)	1.03

Table 12. ^1H NMR chemical shift of TTCD in the presence and absence of 1,8-naphthalenediamine and YbCl_3 .

TTCD	δ (ppm) (free)	Complex δ (ppm)	$\Delta\delta$ (ppm)
H-1	4.83(d)	4.81(d)	-0.02
H-3	3.64(t)		
H-6,6'	3.67(t)		
H-5	3.57(d)	3.28-3.66	-
H-4	3.34(t)		
H-2	3.29(d)		

Table 13. ^1H NMR chemical shift of 1,8-naphthalenediamine in the presence and absence of TTCD/ SmCl_3 .

1,8-Naphthalenediamine	δ (ppm) (free)	Complex δ (ppm)	$\Delta\delta$ (ppm)
H-2, 7	6.53(d)	6.53(d)	0
H-3,6	7.15(t)	7.01(t)	-0.14
H-4,5	7.15(d)	6.94(d)	-0.19
H-11,12	4.40(s)	5.41(s)	1.01

Fluorescence spectra

Figures 3 and 4 illustrate the fluorescence spectra of the guest molecules in the ternary inclusion complexes in comparison with the corresponding free guest molecules. All the fluorescence spectra were obtained by measuring the solid samples directly, thus solvent effect will be ignored. According to Figures 3 and 4, free 1,5-naphthalenediamine and 1,8-naphthalenediamine exhibit weak fluorescence yield, however, after forming ternary inclusion complexes, their fluorescence yields were increased by a remarkable extent. The highest absorption

peak in the spectra is assigned to $\pi \rightarrow \pi^*$ of the naphthalene. The great fluorescence yield enhancement can be explained by the following reasons: Enhanced molecular rigidity. After forming ternary inclusion complexes, naphthalenediamine enters the hydrophobic cavity of CD through Van der Waals forces; for example, dipole-dipole interaction, dispersion force, hydrogen bonding, naphthalenediamine is bounded inside the cavity firmly, the molecular rigidity is increased greatly as a result. The guest molecular vibrations decrease, the mutual interactions between naphthalenediamine molecules also diminishes, relaxation phenomena will be

Table 14. ^1H NMR chemical shift of TTCD in the presence and absence of 1,8-naphthalenediamine and SmCl_3 .

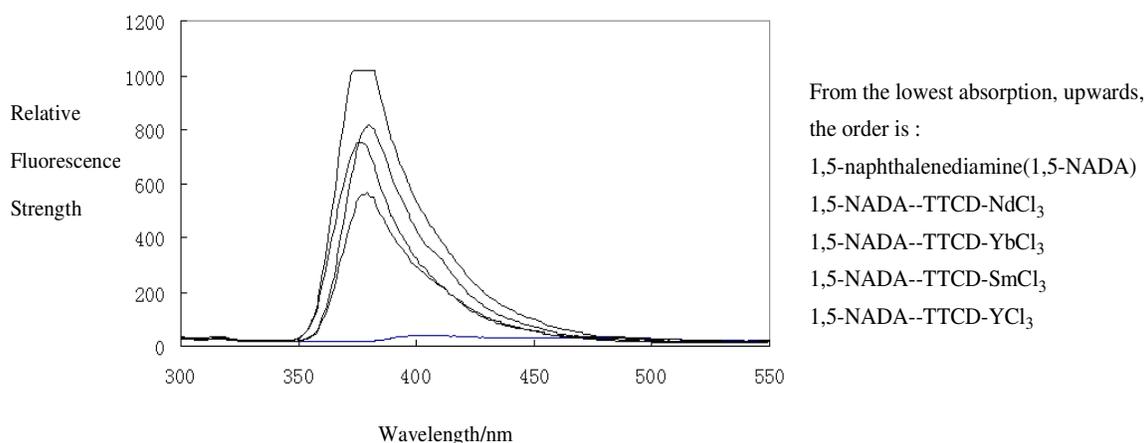
TTCD	δ (ppm) (free)	Complex δ (ppm)	$\Delta\delta$ (ppm)
H-1	4.83(d)	4.83(d)	0
H-3	3.64(t)		
H-6,6'	3.67(t)		
H-5	3.57(d)	3.28-3.66	-
H-4	3.34(t)		
H-2	3.29(d)		

Table 15. ^1H NMR chemical shift of 1,8-naphthalenediamine in the presence and absence of TTCD/ NdCl_3 .

1,8-Naphthalenediamine	δ (ppm) (free)	Complex δ (ppm)	$\Delta\delta$ (ppm)
H-2, 7	6.53(d)	6.55(d)	0.02
H-3,6	7.15(t)	7.04(t)	-0.11
H-4,5	7.15(d)	6.96(d)	-0.19
H-11,12	4.40(s)	5.45(s)	1.05

Table 16. ^1H NMR chemical shift of TTCD in the presence and absence of 1,8-naphthalenediamine and NdCl_3 .

TTCD	δ (ppm) (free)	Complex δ (ppm)	$\Delta\delta$ (ppm)
H-1	4.83(d)	4.83(d)	0
H-3	3.64(t)		
H-6,6'	3.67(t)		
H-5	3.57(d)	3.30-3.63	-
H-4	3.34(t)		
H-2	3.29(d)		

**Figure3:** Fluorescence spectra of 1,5-naphthalenediamine in free and inclusive state.

decreased in a remarkable extent, which will result in enhanced fluorescence yield.

The cavity of CD is an electron rich system, resulting in

the enhanced conjugate degree of the guest molecules; consequently, the molar absorptivity of the guest molecules is increased.

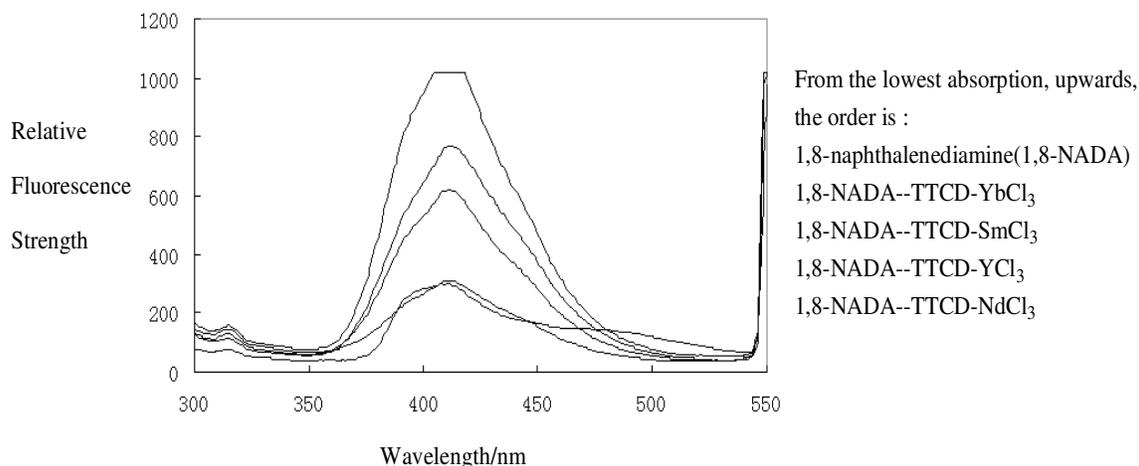


Figure4: Fluorescence spectra of 1,8-naphthalenediamine in free and inclusive state (Grating width: 5nm).

In comparison with the fluorescence spectra of 1,5-naphthalenediamine and 1,8-naphthalenediamine (Figures 3 and 4), we found that, after forming ternary complexes, the fluorescence enhancement magnitudes of 1,5-naphthalenediamine are much higher than those of 1,8-naphthalenediamine. It is probably due to the following fact that, the two amino groups of 1,8-naphthalenediamine form a forcipate structure, which can easily form coordination bonds with lanthanide metal ions; however, similar coordination process does not occur in the case of 1,5-naphthalenediamine. Different guest molecules will form different spatial arrangements, resulting in different conformations, which can also result in no coordination formation between lanthanide metal ion and 1,5-naphthalenediamine. Similar results can also be deduced from NMR results. After forming complexes, the hydrogen atom in the amino group of 1,8-naphthalenediamine showed a significant downfield shift (up to 1.05 ppm); however, negligible shift occurred in the case of 1,5-naphthalenediamine. The coordination between 1,8-naphthalenediamine and lanthanide metal ions resulted in fluorescence quenching of the guest molecules. The analysis of fluorescence spectra also provides important information to elucidate possible conformation of the guest molecules inside the ternary inclusion complexes. The conformations of the ternary complexes are still investigated herein.

Conclusion

β -Cyclodextrins (CD) was modified by triethylene tetramine in its 6-OH position. The modified β -CD can easily include hydrophobic guest molecules, for example, naphthalenediamines, inside its cavity. Due to the existence of three amino groups which are good ligands in the side chain of β -CD, the complex will coordinate with lanthanide metal ions (Y^{3+} , Yb^{3+} , Nd^{3+} , Sm^{3+}) to form

ternary complexes. In the ternary complexes, the chemical shifts of host and guest molecules showed diverse variations, which clearly prove the formation of complexes. The stoichiometric proportions between host and guest molecules both are 2:1, in the case of 1,5-naphthalenediamine and 1,8-naphthalenediamine, different to our reported result (Jiang et al., 2007). Naphthalenediamine does not show strong fluorescence effect in their free states, however, after being included inside the cavity of TTCD, it showed pronounced fluorescence effects. The main reason is the enhancement of the rigidity of the guest molecules inside the cavity. These reports will be beneficial in the design of fluorescent dye molecules and can be applied in the fluorescent dyes industry.

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