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Supramolecular Assembly Based on 9,10-bis(3,5-dihydroxy-1-phenyl)Anthracene-tetrakis β-cyclodextrin with Guest Molecule

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The synthesis of 9,10-bis(3,5-dihydroxy-1-phenyl)anthracene-tetrakis β-cyclodextrin was synthesized from DCC coupling between anthacene-tetracarboxylic acid and amino β-cyclodextrin in a high yield. ^{1}H-NMR, IR and TOF-mass spectroscopy carried out the identification of the titled compound. TOF-mass spectroscopy shows a molecular weight peak at 4970.40, which means $(M+Na)^+$ peak. In this study, we investigated to form supramolecular assembly mediated by guest molecule.

Key Words : Cyclodextrin, Supramolecular assembly, Chemical sensor, Anthracene

1. Introduction

Recently, the research on porous organic materials with a zeolitic capability have developed in host-guest chemistry. As previously reported, 9,10-bis(3,5-dihydroxy-1-phenyl)anthracene (**1**)[1] can set up a second order network by hydrogen bond to yield a huge molecule as shown in Figure 1. For further extension of this work, anthracene-tetrakis β-cyclodextrin (**3**) have been synthesized to investigate the capability of a formation of supramolecular assembly, which could be applied for sensing system such as a chemical sensor. We have synthesized absorbent such as 9,10-bis (3,5-dihydroxy-1-phenyl)anthracene (**1**), in which nearly perpendicular resorcinol moieties forms an extensive hydrogen-bonded network that results in enforced formation of anthracene columns. We have further demonstrated to synthesize 9,10-bis(3,5-dicarboxy-1-phenyl) anthracene (**2**), in which intermolecular hydrogen bond was recognized and resulted in the porous crystal structure was constructed. In an addition of hydrogen and coordination bond, we tried to construct zeolitic structure based on intermolecular hydrophobic interaction. For this target, we designed molecular structure in application of cyclodextrins (CyDs). CyDs are composed of six, seven or eight units of D-glucopyranose linked in the manner of α-1,4 combination. They are usually called as α-, β- and γ-CyD, respectively. Most of interested ability of CyDs is to exhibit inclusion with a variety of organic compounds into the hydrophobic cavity of the CyDs in aqueous media and have been widely used as functional units of supramolecules and molecular recognition systems[2-5]. CyDs form inclusion complexes with various organic guests in an aqueous solution. Recently, chromophore-modified CyDs have been shown to exhibit remarkable variations in circular dichroism, absorption and fluorescence spectra, depending on the formation of host-guest complexation. Therefore, the appended chromophores can be used as a probe to detect guest molecules. Previously, we have discussed fluorescence molecular sensing systems of CyDs modified with fluorescent active units at the upper rim. In those systems, it was found that the fluorescence spectra are most sensitively observed in spectrophotometry, in which variations of guest-induced fluorescence intensities effectively work as a sensing probe, showing much more complete and accurate sensing patterns. In this study, we tried to make supramolecular assembly based on anthracene-tetrakis β-cyclodextrin (**3**) in the presence of guest molecule.

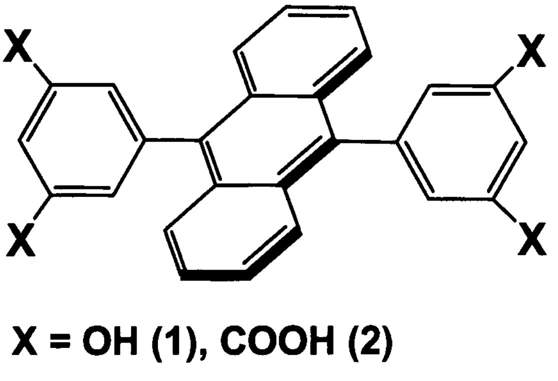


Figure 1 Structures of 1 and 2

2. Experimental

2.1 Synthesis of anthracene-tetrakis CyD (3)

9,10-bis(3,5-dicarboxy-1-phenyl)anthracene (50 mg, 0.098 mmol) and 1-hydroxy benzotriazole 74.0 mg (0.549 mmol) were resolved in 5 mL of DMF, the reaction mixture was stirred at −10℃ for 30 minutes. After that, 113 mg (0.549 mmol) of *N,N*-dicyclohexyl carbodiimide (DCC) was added, and the reaction mixture was stirred at -10 °C for another 30 minutes. To a reaction mixture, DMF solution of amino β-CyD (622 mg, 0.549 mmol) was added, and the reaction mixture was stirred for 48 hours at ambient temperature. After the reaction was completed down, the obtained powder was washed enough with chloroform and concentrated. The obtained crude fraction containing **3** was applied to a reversed-column (Lobar column LiChroprep RP-18, Merck Ltd., 310 mm × 10 mm). Stepwise elution with 1000 mL of MeOH and then 500 mL of a mixture solvent consisted with MeOH, H_2O and acetonitrile by same volume gave the pure product of anthracene-tetrakis β-cyclodextrin (**3**) (211.8 mg, 41.7%). ^{1}H-NMR (300 MHz, DMSO-d_6, 25 °C, TMS): δ = 7.46 (m, 8H, aromatic-H of anthracene), 8.09 (d, 4H, J = 7.58 Hz, aromatic-H), 8.35 (t, 2H, aromatic-H), 4.25-5.05 (m, 15H, O^{6}H, C^{1}H of CD), 5.58-5.98 (m, 16H, O^{2}H, O^{3}H of CD), R_f 0.48 (ethyl acetate:2-propanol:ammonium hydroxide:water 1:1:1:1 by volume; TLC; silica gel 60F$_{254}$), TOF-Mass m/z 4993.23 [M+Na]$^+$, calcd. for $C_{198}H_{294}N_4O_{140}$, 4993.39.

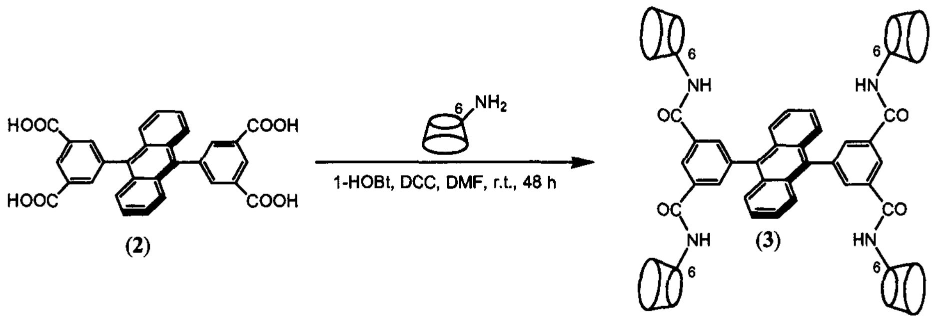
2.2 Preparation of adamantane dimer

1,2-bis(2-aminoethoxy)ethane (68 μL, 0.46 mmol) and tetraethyleneamine (100 μL, 0.99 mmol) were added in 5 mL benzene. To a reaction mixture, benzene solution (5 mL) of 1-adamantanecarbonyl chloride (197 mg, 0.99 mmol) was added, and the reaction mixture was stirred for 2 hours at ambient temperature under a nitrogen atmosphere. After the reaction was completed down, the obtained powder was washed enough with benzene and filtered and dried in vacuo to give a pure adamantane dimer (118.5 mg, 25.4%).

^{1}H-NMR (300 MHz, DMSO-d_6, 25 °C, TMS): δ = 1.12-1.98 (m, 30H, adamatane), 2.92-3.63 (m, 12H), IR (KBr) ν 1638 cm^{-1} (amide bond), R_f 0.10 (MeOH; TLC; silica gel 60F$_{254}$)

2.3 Measurements

Fluorescence and induced circular dichroism (ICD) were measured at 25 °C using a Perkin-Elmer LS 40B fluorescence spectrophotometer, JASCO J-700 spectropolarimeter, respectively. For the fluorescence measurements, the excitation wavelength of the fluorescence spectra was 375 nm and excitation and emission slits were 5 nm. Dimethyl sulfoxide (DMSO) aqueous solution (10 vol.%) was used as a solvent for the host for the spectroscopic measurements because the solubility of titled compound in pure water is poor. Bisphenol A of 5.0×10^{-2} M in MeOH and adamantane dimer of 5.0×10^{-3} M in MeOH were injected into a 10 vol.% DMSO aqueous solution of the host (2.5 mL) to make a sample solution with a host concentration of 1.0×10^{-7} M. ICD



Scheme 1 Synthesis of **3**

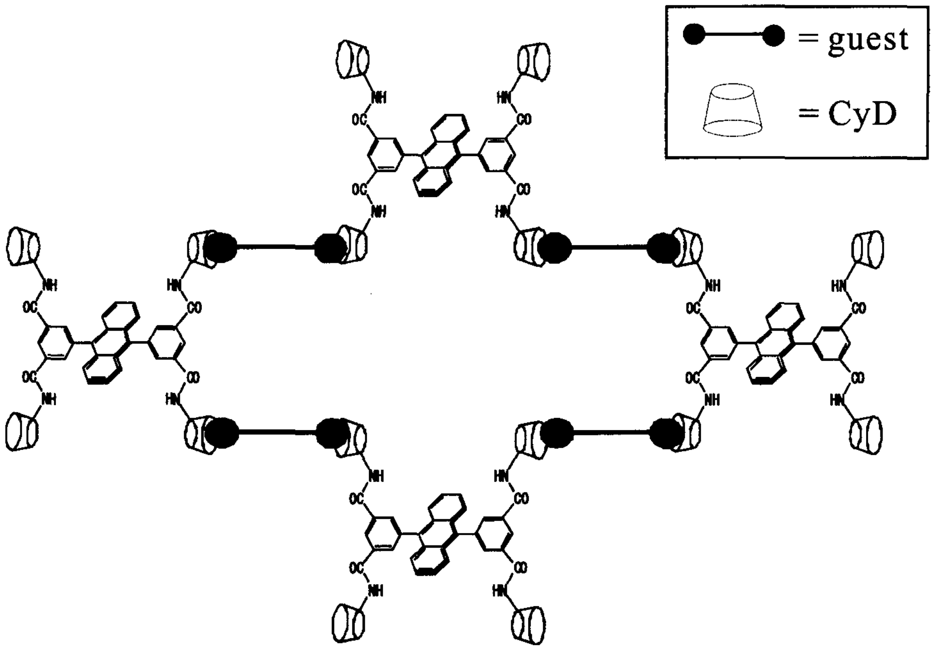


Figure 2 Image of supramolecular network of **3** with guests

spectra were measured at 1.0×10^{-5} M of **3** in a 10 vol.% DMSO aqueous solution.

3. Results and discussion

3.1 The preparation of anthracene-tetrakis β-CyD (3)

The synthesis of **3** has done by DCC coupling with amino β-CyD and **2** as shown in scheme 1. The purification of **3** was achieved using reverse phase RP-18 column chromatography.

3.2 Fluorescence spectra

Figure 3 shows the fluorescent spectra of **3** in a 10 vol.% DMSO aqueous solution. The fluorescent spectrum of the host is composed of almost pure monomer emission with a peak around 411 nm and 430 nm. The fluorescent intensity of **3** was decreased upon addition of bisphenol A, which is indicating that one phenol unit of bisphenol A was included in the host as shown in Figure 3 (a). The environment surrounded for host-guest complexation could become hydrophilic when bisphenol A was included in the host and the other part of phenolic unit was exposed in an aqueous area because it was reported that the fluorescent intensity was decreased when fluorescent unit existed in hydrophilic environment[6]. On the other hand, adamantane dimer was added to the solution of **3**, the fluorescence intensities of the host were increased as shown in Figure 3 (b). It might be supposed that adamantane dimers were included in both host and resulted in the formation of supramolecular assembly. It is suggested that surrounding area of anthracene moiety would be hydrophobic environments as a whole.

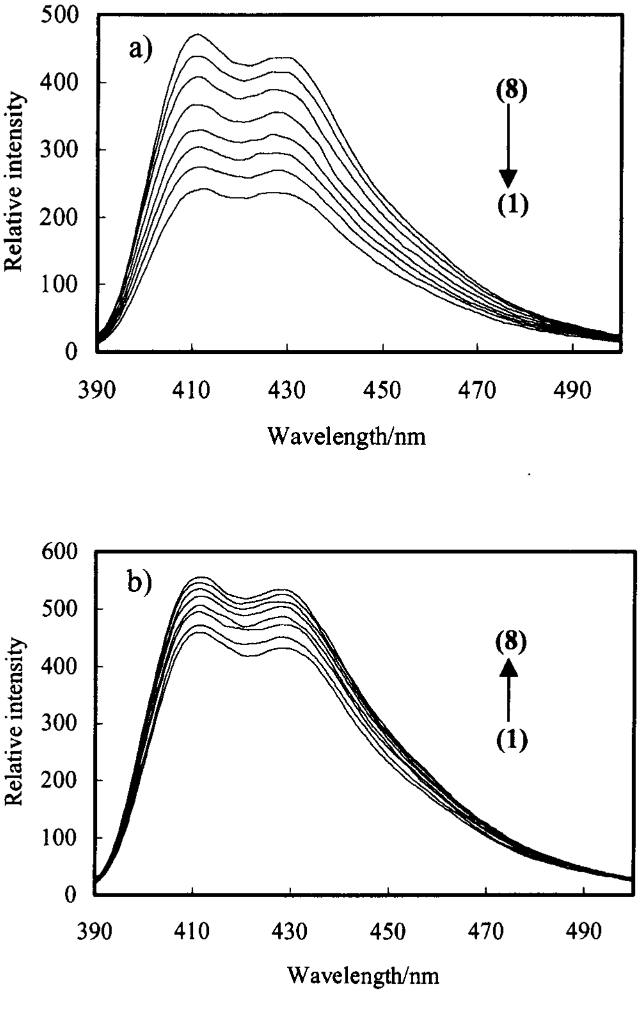


Figure 3 (a) Fluorescent spectra of **3** in a 10 vol.% DMSO aqueous solution (1.0×10^{-7} M, 25℃ at various concentrations of bisphenol A examined (guest concentration is 5.0×10^{-2} M, host : guest concentration ratio=(1)1:0, (2)1:200, (3)1:600, (4)1:1200, (5)1:2000, (6)1:3000, (7)1:5000, (8)1:10000) Ex=375 nm. (b) Fluorescent spectra of **3** in a 10 vol.% DMSO aqueous solution (1.0×10^{-7} M, 25℃ at various concentrations of adamantane dimer examined (guest concentration is 5.0×10^{-3} M, host : guest concentration ratio=(1)1:0, (2)1:20, (3)1:60, (4)1:120, (5)1:200, (6)1:300, (7)1:500, (8)1:1000) Ex=375 nm.

3.3 Induced circular dichroism (ICD) spectra

The ICD spectra of **3** alone or with adamantane dimer in 10 vol.% DMSO aqueous solution was taken to investigate how supramolecular assembly formation was going on. In Figure 4 the ICD signs around 260 nm and around 390 nm change from a positive to a negative and from a negative to a positive a Cotton paeak, respectively, when a guest was added to **3**. It is indicating that the environment for surrounding area of anthracene moiety should be changed. This result suggested that the conformation of **3** was changed to aggregate to make a supramolecular assembly when adamantane dimer was included into the CyD cavity.

3.4 TOF-Mass spectra

Figure 5 shows the MS spectra of the precipitates obtained from a mixture of **3** and adamantane dimer in a 10 vol.% DMSO aqueous solution. The molecular weight peaks apperead at 15884.8165, 20451.0548, 23814.6796, 31411.8811. This result shows molecular assembly, as shown in Figure 6, was formed. On the other hand, MS peaks of the supernatant appeared at less than 10,000 molecular weight. When a bisphenol A was used as a guest, less than thousand molecular peaks were recognized. Therefore, it is probable that supramolecular assembly might not be formed in the presence of bisphenol A.

3.5 Chemo-sensor ability of 3 for organic compounds

Figure 7 shows the fluorescent spectra of **3** in 10 vol.% DMSO

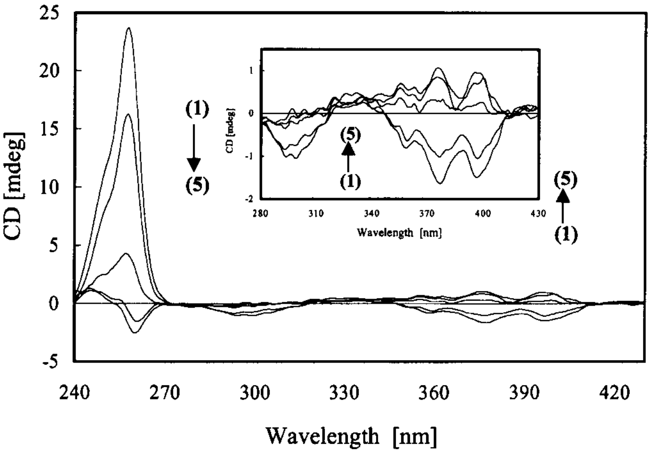


Figure 4 Induced circular dichroism spectra of **3** in a 10 vol.% DMSO aqueous solution (1.0×10^{-5} M, 25℃ at various concentrations of adamantane dimer examined (guest concentration is 5.0×10^{-2} M, host : guest concentration ratio=(1)1:0, (2)1:2, (3)1:6, (4)1:12, (5)1:20)

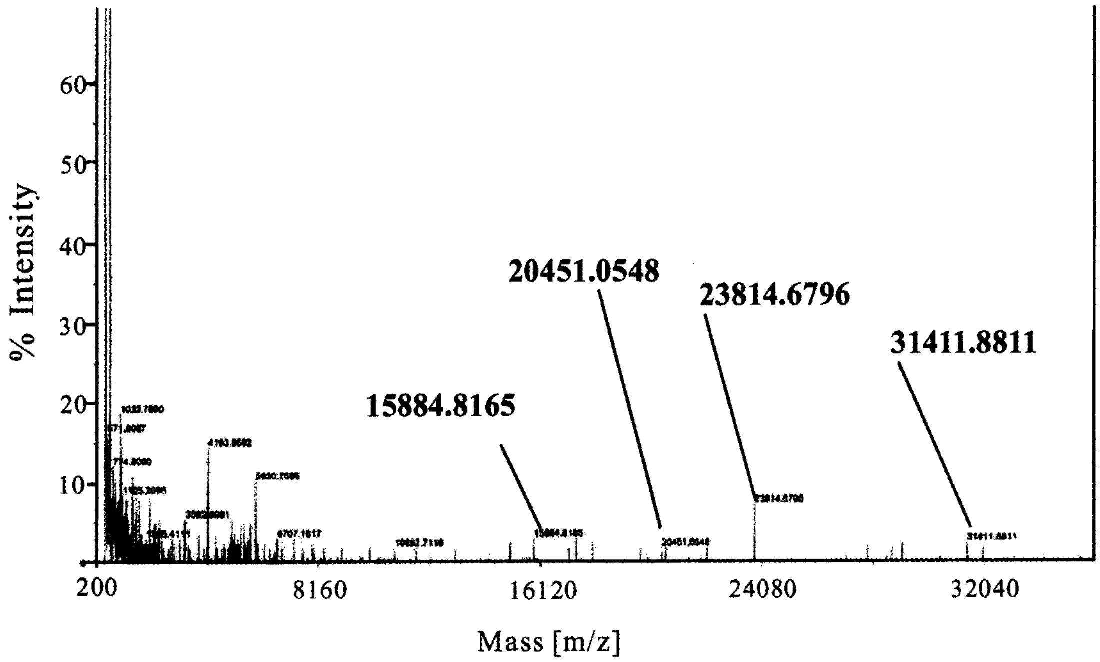


Figure 5 TOF-Mass spectra of **3** in a 10 vol.% DMSO aqueous solution (1.0×10^{-6} M, 25℃ at 0.05 M adamantane dimer examined (host : guest concentration ratio = 1:15)

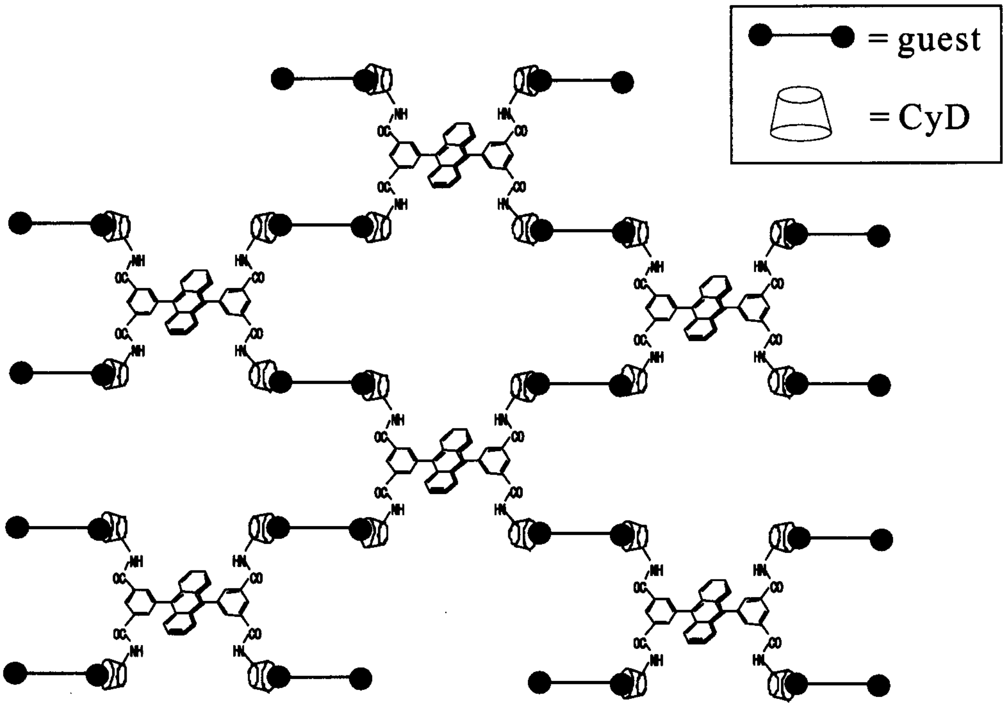
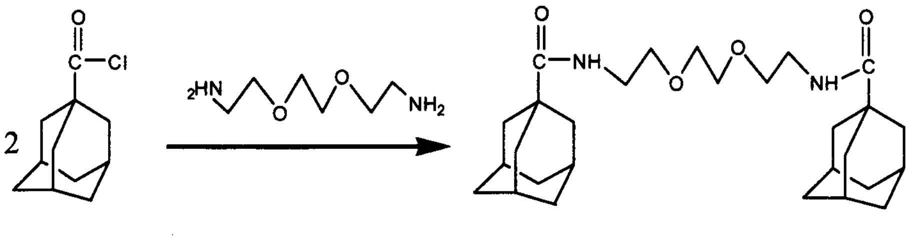


Figure 6 Image of supramolecular network of **3** with adamantane dimer



Scheme 2 Preparation of adamantane dimer

aqueous solution in the absence and presence of adamantanol. It is shown that the different extent of variation on the fluorescence intensity of **3** was seen by the different guest molecules. It might be used as a fluorescent sensor of molecule. A couple of organic guest molecules as shown in scheme 3, were used to evaluate the capability of **3** as the devices of chemo-sensor. Five microlitres of guest species of 5.0×10^{-2} M in DMSO or MeOH were injected into a 10 vol.% DMSO aqueous solution of **3** with a concentration of 1.0×10^{-7} M and guest concentration of 1.0×10^{-4} M. In order to display the sensing ability of **3**, the $\Delta I_{411}/I^0_{411}$ and $\Delta I_{430}/I^0_{430}$ were used as sensitivity parameters. Here, ΔI_{411} and ΔI_{430} are I_{411}-I^0_{411} and I_{430}-I^0_{430}, respectively, where I^0_{411} is the intensity in emission at 411 nm and I^0_{430} is the intensity in emission at 430 nm for host alone and I_{411} and I_{430} are those for a complex. Figure 8 shows the parameter sensitivity values of **3** with 1-adamantanol (*g-1*), 1-adamantoic acid (*g-2*), (-)-borneol (*g-3*), bisphenolA (*g-4*), ursodeoxycholic acid (*g-5*), chenodeoxycholic acid (*g-6*), cholic acid (*g-7*), and deoxycholic acid (*g-8*) at 0.1 mM. Among *g-1* and *g-2*, their parameter values are opposite, which means **3** can detect the differ-

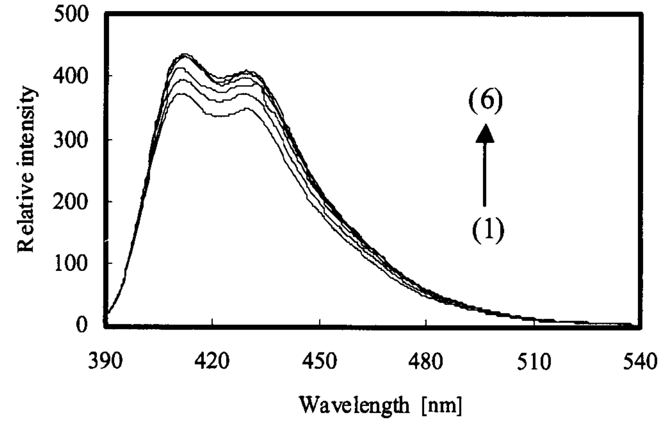
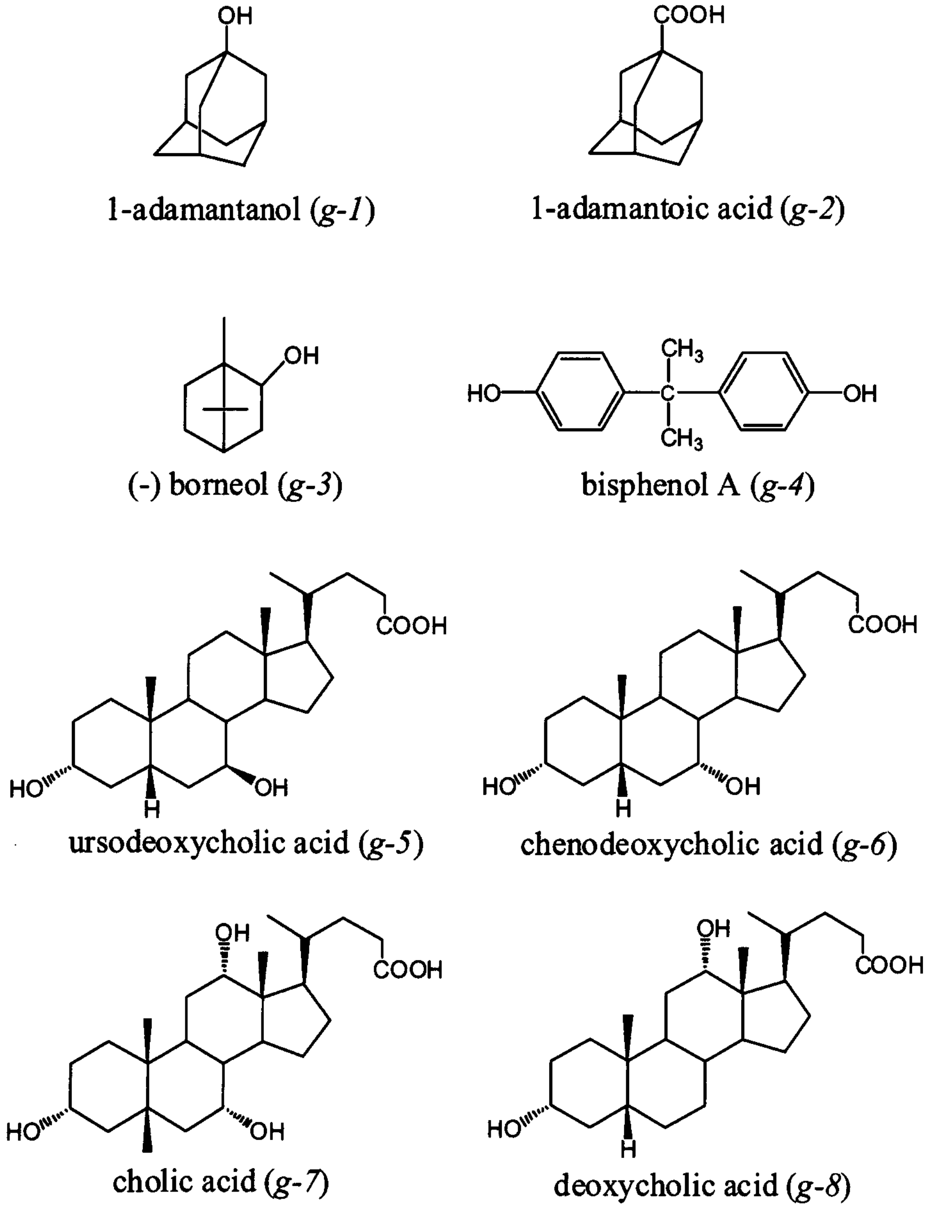


Figure 7 Fluorescent spectra of **3** in a 10 vol.% DMSO aqueous solution (1.0×10^{-7} M, 25℃ at various concentrations of adamantanol examined (guest concentrations = (1) 0, (2) 2.0×10^{-5}, (3) 4.0×10^{-5}, (4) 6.0×10^{-5}, (5) 8.0×10^{-5}, (6) 1.0×10^{-4} M) Ex = 375 nm.



Scheme 3 Guest molecules

ence of functional groups such as hydroxyl and carboxylic acid. Among steroidal guest molecules such as from *g-5* to *g-8*, *g-5* was detected by **3** with the most high sensitivity of which the parameter value is -0.4 and -0.37 for $\Delta I_{411}/I^0_{411}$ and $\Delta I_{430}/I^0_{430}$, and next one is *g-6*. The *g-7* and *g-8* were hardly detected by **3**. These results suggested that **3** could recognize the number and regio of hydroxyl groups on the steroidal framework. Bisphenol A (*g-4*) was detected with medium size of sensitivity. It seems that only a phenol part of *g-4* would be included in the cavity of **3**, because parameter value is negative.

4. conclusion

Anthracene-tetrakis β-CyD (**3**) was prepared as molecular device to be supramolecular assembly based on hydrophobic interaction in the presence of guest molecule and as fluorescence active chemo-sensor system for organic compounds. When adamantane dimer was used as a guest, the supramolecular assembly formation was occurred. Although, bisphenol A showed no capability to make a molecular assembly.

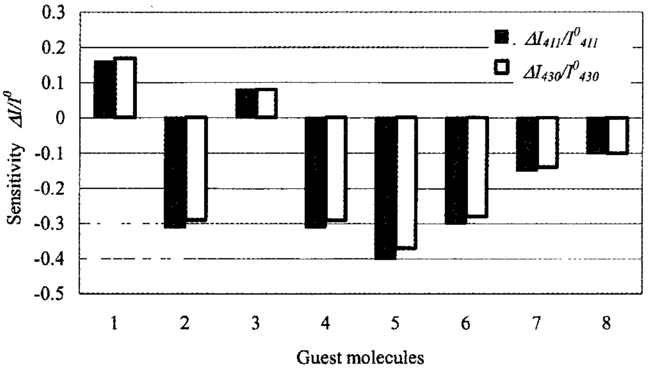


Figure 8 Parameter values of **3** in 10vol.% DMSO aqueous solution (1.0×10^{-7}M) with added guests (1.0×10^{-4}M) examined.

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