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Investigation on photophysical properties of a substituted 3H-indole-modified β-cyclodextrin
I. Conformation in water and recognition mechanism as a chemosensor

Aihua Wu [a], Qi Chen [a], Ke Xia [a], Tingjun Hou [b], Xinghai Shen [a,*], Hongcheng Gao [a], Xiaojie Xu [b]

[a] *Department of Applied Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China*
[b] *Institute of Physical Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China*

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Abstract

A substituted 3*H*-indole-modified β-cyclodextrin (β-CD), mono-6-deoxy-(2-[(*p*-amino) phenyl]-3,3-dimethyl-5-carboxyl-3*H*-indole)-β-CD (compound A) has been synthesized and characterized by elemental analysis, mass spectrum (MS) and ^{1}H NMR. Induced circular dichroism (ICD), time-resolved fluorescence and computational analysis yield information on the molecular structure that compound A adopts rim-covering conformation in aqueous solution. It forms the 1:1 (guest:host) inclusion complex by addition of native β-CD. Novel recognition behavior of compound A is investigated by means of ICD, time-resolved and steady-state fluorescence. In contrast to the behavior of most conventional CD-based chemosensors with self-inclusion conformation, the fluorescence intensity of this new kind chemosensor is increased upon addition of guest molecules. This new chemosensor exhibits high sensitivity to acyclic and adamantine molecules, but not to the bile acids.

Keywords: Molecular recognition; Chemosensor; Steady-state fluorescence; Molecular dynamics

1. Introduction

Cyclodextrin, containing 6 (α-CD), 7 (β-CD), or 8 (γ-CD) D-glucose units, is one of the most popular host molecules to construct various molecular assemblies [1]. Modification of native cyclodextrins by introducing nucleophilic or electrophilic substituents can affect not only the original molecular binding ability but also the relative molecular selectivity [2,3]. Substituted 3*H*-indole molecules as sensitive fluorescence probes have been widely used in reversed micelles, aqueous micelles, surfactant vesicles and cyclodextrins [4]. Very recently, we studied the locations of different groups of a cationic surface-active 3*H*-indole probe molecule in the AOT (sodium bis-(2-ethylhexyl) sulfosuccinate)-based w/o microemulsion and the physicochemical properties of Triton X-100 micelles [5]. In addition, we have studied the interactions of substituted 3*H*-indoles with bovine serum albumin (BSA) and human serum albumin (HSA). Some preliminary results concerning the energy transfer phenomenon in these systems have been obtained [6]. Rotaxane-like 1:3 (guest:host) inclusion complex formed by a substituted 3*H*-indole and β-CD has also been reported [7]. In this article, we choose a substituted 3*H*-indole molecule as the chromophore moiety in our designed new compound A (see Scheme 1). Considering the high sensitivity of the substituted 3*H*-indole moiety as well as the good molecular binding ability and solubility of β-CD, we believe this new compound will exhibit some interesting properties. Besides the experimental methods, the computational methods, i.e., molecular mechanics and dynamics, were used to ascertain the conformation of compound A.

It is well known that molecular recognition by modified CD-based chemosensors is currently a significant topic in host–guest chemistry [8]. As contributing to advances in enzyme mimics, chiral selectors in separation science, pharmaceutical and analytical chemistry, a wide variety of cyclodextrin derivatives have been designed and synthesized to investigate the recognition mechanism that controlled by simultaneous cooperation of weak non-covalent interactions [9]. As to chemosensors of chromophore-modified cyclodextrin derivatives, a self-inclusion conformation other than out-stretching or rim-covering ones is usually observed [10]. The recognition mechanism concerning

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* Corresponding author. Tel.: +86 10 62765915; fax: +86 10 62759191.
E-mail address: xshen@pku.edu.cn (X. Shen).

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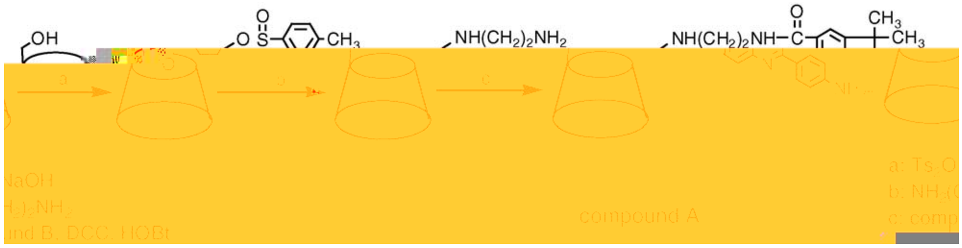
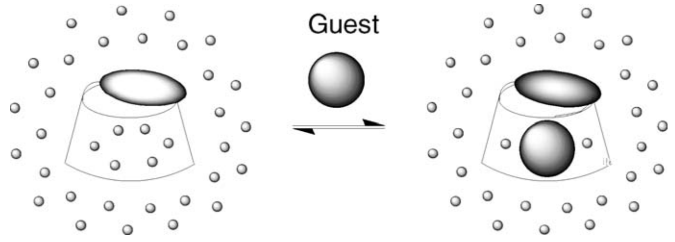


Scheme 1. Synthesis route of compound A.



Scheme 2. Novel recognition mechanism of CD-based chemosensor that adopts rim-covering conformation.

these conventional CD-based chemosensors has been investigated extensively [11]. Most of them show a decrease in fluorescence intensity upon addition of guest molecules resulting from the fact that the location of the chromophore is transferred from inside to outside of the cavity of CD. Some chromophore-modified γ-CDs are found to show an increase in fluorescence intensity in contrast to the behaviors of the most cases. This phenomenon may be due to the large cavity of γ-CD that possesses enough space to accommodate the modified chromophore and the guest together [12]. More recently, a novel recognition mechanism was proposed for the β-CD-based chemosensors adopting rim-covering conformation. The modified chromophore of these chemosensors is located at the rim of the cavity of CD, surrounded by water molecules both inside and outside of the cavity (see Scheme 2) [13]. In contrast to the behavior of most conventional CD-based chemosensors, the fluorescence intensity of this new kind chemosensor is increased upon addition of guest molecules. This new recognition phenomenon has ever been observed in the chemosensors synthesized by Inoue et al. [14]. In our work, the molecular recognition behavior of compound A is investigated by means of ICD spectra, time-resolved fluorescence and steady-state fluorescence. Interestingly, compound A shows high sensitivity to acyclic and adamantine molecules, but not to the bile acids. Therefore, the recognition mechanism for compound A has been discussed.

2. Experimental part

2.1. Materials

β-CD (Beijing Shuanghuan, China) was recrystallized three times from tridistilled water. Iso-butyraldehyde (Shanghai Medicine, China, 99%), Morpholine (Tianjing Tiantai, China, 99%), *p*-nitrobenzoly chloride (Beijing Xizhong, China, 99%), 4-hydrazinobenzoic acid (Acros, 98%), ethylenediamine (Beijing, China, 99%), dicyclohexycarbodiimide (DCC) (Acros, 99%), 1-hydroxybenzotriazole (HOBt) (Sigma, 98%), 1-adamantanecarboxylic acid (Fluka, 99%), 1-adamantanol (Acros, 99%), (−)-borneol (Fluka, 99%), cholic acid (Fluka, 99%), (−)-camphor (Fluka, 99%), cyclohexanol (Alfa Aesar, 99%), cyclooctanol (Alfa Aesar, 99%), deoxycholic acid (Alfa Aesar, 99%), (−)-menthol (Fluka, 99%), nerol (Alfa Aesar, 97%) were used as received. All other chemical reagents used in this study were of analytical grade.

2.2. Instrumentations

^{1}H NMR spectra were recorded with a Bruker ARX-400 NMR spectrometer. Induced circular dichroism spectra were recorded on a Jobin Yvon CD 6 spectropolarimeter. Steady-state fluorescence measurements were performed on F-4500 (Hitachi) spectrofluorimeter. The excitation and emission band-passes were 10 and 5 nm, respectively. Each solution was excited near its maximum absorption wavelength using 1 cm quartz cells. Fluorescence lifetime measurements were made on a multiplexed time-correlated single-photon counting fluorimeter FLS920 (EDINBURGH). The fluorescence lifetime was determined from data on the fluorescence transient waveform of the material to be tested and the lamp waveform data using the least-squares iterative deconvolution method [15]. Three thousand counts were collected for each sample.

2.3. Synthesis of compound A

The substituted 3*H*-indole, 2-[(*p*-amino)phenyl]-3,3-dimethyl-5-carboxyl-3*H*-indole (compound B), 6-deoxy-6-(*p*-tolylsulfonyl)-β-cyclodextrin (Ts-CD) and 6-deoxy-6-[(2-aminoethyl) amino]-β-CD (CDen) were prepared according to desired product as a pale yellow solid (100 mg, 33%). Anal. calcd for $C_{61}H_{90}N_4O_{35}\cdot8H_2O$: C, 46.27; H, 6.70; N, 3.54. Found: C, 46.26; H, 6.43; N, 3.52. MS (MALDI TOF): *m/z* calcd for $(M+H^+)$ 1439, found, 1439. ^1H NMR (400 MHz, DMSO-d_6, δ_{ppm}): 1.52):s,): $_3$),):3.20–3.80m,): $_{2-6}$H),):4.49 (s,)334.31$_6$**H),)334.31**0.83)334H),(s,)334.315.60–5.90)334C$_{2,3}$(m,)334.3114H,)334.31O $_2$),)20016.60–6.70d,)20012H,)2001Ph–H),)20017.45–7.50d,]TJ-8.9181 -1.2 TD[(1H,)226.11Ph–H),)226.117.80–7.85)2

2.4.

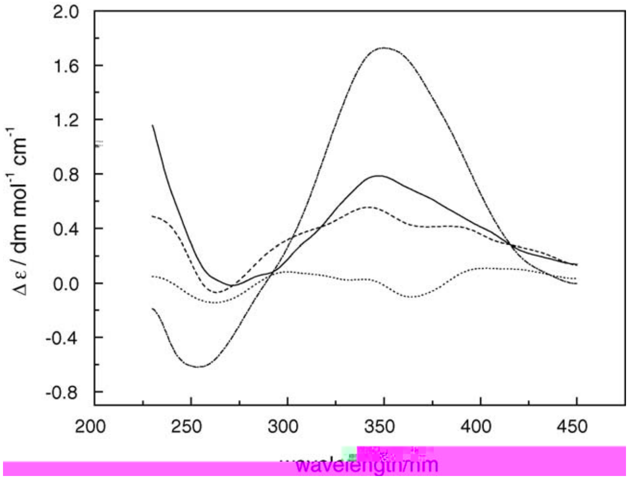


Fig. 1. Induced circular dichroism spectra of compound A in water (solid line) and presence of β-CD (dash-dot line), cyclohexanol (dash line) and cyclooctanol (dot line). [compound A] = 1×10^{-4} M, [β-CD] = 1×10^{-2} M, [guest] = 1×10^{-3} M.

valence force field (CVFF) [21]. The initial conformers were subjected to energy minimization until the maximum derivative became less than 0.1 kcal/mol Å. Then the minimized conformers were brought into contact with water by forming a water shell [22]. The water was divided into two layers: water molecules in the outer 6 Å thick layer are fixed while others in the inner 8 Å thick layer can move freely. Starting with the minimized conformer of complexes, molecular dynamics (MD) at 300 K was carried out for 100 ps after an initial 10 ps equilibration. An integration step of 1 fs was used. During the calculation, a structure is stored every 1 ps and after the MD the energy is minimized until the maximum derivative became less than 0.1 kcal/mol.

4. Results and discussion

4.1. ICD spectra

As can be seen from Fig. 1, ICD spectrum of compound A in water shows a peak of minute negative Cotton effect and that of weak positive cotton effect, corresponding to the ^1L_a band at 271 nm ($\Delta\varepsilon = -0.02$) and the ^1L_b band at 346 nm ($\Delta\varepsilon = 0.77$), respectively. According to the sector rule proposed by Kajtar et al. [23], the occurrence of above weak cotton effects indicates that the substituted 3*H*-indole moiety of compound A is located at the rim of the hydrophobic cavity of β-CD itself. It is noted that the ICD spectrum of compound A in the presence of native β-CD exhibits much stronger negative and positive cotton effects at 254 nm ($\Delta\varepsilon = -0.62$) and 350 nm ($\Delta\varepsilon = 1.73$), respectively. This suggests that the substituted 3*H*-indole moiety of compound A has been transferred into the chiral cavity of native β-CD, no longer at the rim of the cavity of β-CD itself.

4.2. Time-resolved fluorescence

It is reported that the fluorescence lifetime of a substituted 3*H*-indole probe molecule increases when it transfers from polar to apolar solvent [4–7]. As can be seen from Table 1, both compound A and B show short lifetimes in water, i.e., 0.89 and 0.95 ns, respectively. It can be inferred from the literature that the substituted 3*H*-indole moiety of compound A and the whole compound B are not rigid and that the phenyl ring can liberate within the *k*T energy barrier [24]. This torsional movement is responsible for the geometric changes taking place in the ground and excited states and provides an important deactivation pathway for the S_1 state. For compound B in water, the main nonradiative decay pathway has been ascribed to the formation of a nonemissive twisted intramolecular charge transfer (TICT) state originating in the amino group [25], and thus the short lifetime suggests that the TICT state is formed. As the structure of the substituted 3*H*-indole moiety of compound A is similar to the structure of compound B, the short lifetime of compound A in water also indicates the formation of a nonemissive TICT state. When adding excessive β-CD, longer lifetimes of 2.63 and 2.50 ns were obtained for compound A and B. These results show that in the mentioned two media the substituted 3*H*-indole moiety of compound A is located in similar environments to those of compound B. The shorter lifetime of compound A reflects that its substituted 3*H*-indole moiety is exposed to bulk water without self-inclusion. The longer lifetimes indicate that both the substituted 3*H*-indole moiety of compound A and the whole compound B move to less aqueous sites that avoid the intramolecular twisting responsible for the stabilization of the TICT state [7b], and form inclusion complexes with the adding β-CD. This provides further information with respect to the conformational feature that the substituted 3*H*-indole moiety of compound A is not self-included. Otherwise, two lifetimes in

Table 1
Fluorescence lifetimes of compound A, B in different media

Compound	$c/10^{-6}$ M	Medium	τ_1 (ns)	B_1	τ_2 (ns)	B_2	χ^2
A	2.0	Water	0.89	1.00	–	–	1.24
		β-CD (1 mM)	0.96	0.51	2.63	0.49	1.19
B	2.0	Water	0.95	1.00	–	–	1.13
		β-CD (1 mM)	1.03	0.25	2.50	0.75	0.91
A	5.0	Cyclohexanol	0.81	0.69	1.72	0.31	0.92
		Cyclooctanol	0.85	0.50	1.75	0.50	0.97
		β-CD (10 mM)	1.12	0.47	2.89	0.53	1.28

[cyclohexanol] = [cyclooctanol] = 5×10^{-5} M. B_i is a pre-exponential factor representing the fractional contribution to the time-resolved decay of the component with a lifetime τ_i, $I(t) = \sum_i B_i e^{-t/\tau_i}$.

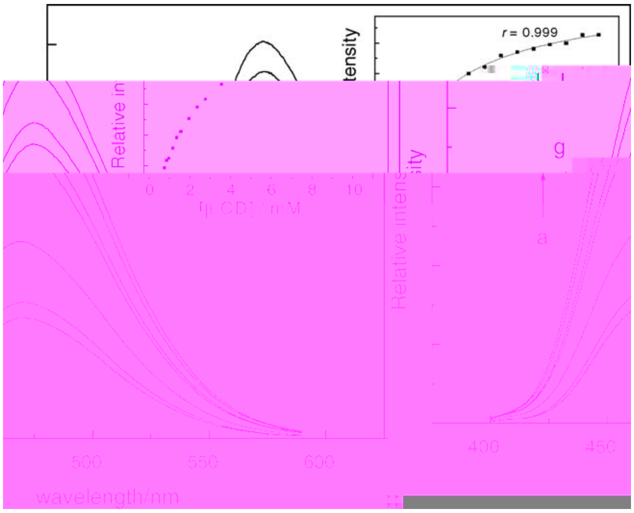


Fig. 2. Fluorescence spectra of compound A (2 μM) in aqueous solutions of β-CD at various concentrations (from a to g: 0, 0.1, 0.8, 2.8, 3.6, 6.8, 10 mM). The inset shows NLR result of the 1:1 inclusion complex.

water would be expected, a shorter one showing that the substituted 3*H*-indole moiety is exposed to the bulk water and a longer one showing that the substituted 3*H*-indole moiety is located inside the cavity of the β-CD itself.

4.3. Interaction of compound A with β-CD

As reported, compound B can form 1:1 and 1:2 mixed inclusion complexes with β-CD in aqueous solutions [4–7]. Consequently, the interaction of compound A with β-CD has also been investigated. It is noted from Fig. 2 that the fluorescence intensity of compound A is increased with increasing β-CD concentration. This suggests that the substituted 3*H*-indole moiety of compound A transfers from water to a less aqueous site and an inclusion complex might be formed. To estimate the association constants and the stoichiometries of the inclusion complexes, we consider the following situations [26]:

- Case 1: only the 1:1 complex is formed:

$$I=\frac{I_0+I_1K_1[\mathrm{CD}]}{1+K_1[\mathrm{CD}]} \qquad (1)$$

- Case 2: 1:1 and 1:2 complexes coexisting:

$$I=\frac{I_0+I_1K_1[\mathrm{CD}]+I_2K_1K_2[\mathrm{CD}]^2}{1+K_1[\mathrm{CD}]+K_1K_2[\mathrm{CD}]^2} \qquad (2)$$

- Case 3: only the 1:2 inclusion complex is formed:

$$I=\frac{I_0+I_2K_1K_2[\mathrm{CD}]^2}{1+K_1K_2[\mathrm{CD}]^2} \qquad (3)$$

where I_0, I_1 and I_2 are fluorescence intensities of a fluorescent probe in pure water, in 1:1 and 1:2 inclusion complexes, respectively, while K_1 and K_2 denote the association constants of 1:1 and 1:2 inclusion complexes. [CD] is the equilibrium concentration of β-CD, which can be replaced by $[\mathrm{CD}]_0$, the initial concentration, since it is much larger than the concentration of compound A. From the none-linear regression (NLR) analysis, reasonable results (values of the variables, standard errors, 95% confidence intervals, correlation coefficient, and absolute sum of squares) can be obtained only when case 1 applies. The fit based on Eq. (1) with the intensity at a fixed wavelength (λ = 467 nm) near the maximum emission converges well with a correlation coefficient $r = 0.999$ (see the insert plot of Fig. 2). The value of K_1 is estimated to be $(354 \pm 12)\,\mathrm{M}^{-1}$. The result of double-reciprocal plot (the figure not shown) further confirmed the formation of only 1:1 inclusion complex, and the r and K_1 values are estimated to be 0.998, $(329 \pm 11)\,\mathrm{M}^{-1}$, respectively. This means that compound A associates only one added β-CD molecule. When the substituted 3*H*-indole moiety of compound A is included in the cavity of the added native β-CD, the other part, the bonding β-CD group itself acts as a stopper to prevent the native β-CD from slipping. Interestingly, this 1:1 inclusion complex can be regarded as a kind of semi-rotaxane.

4.4. Computational analysis

In order to compare the stabilities of forms A–C (see Scheme 3) more precisely, besides the conformal energy, the solvation energy calculated by Dephi was also considered. Thus the total energy change ΔG can be demonstrated by

$$\Delta G = \Delta E_{\mathrm{conform}} + \Delta E_{\mathrm{solv}} \qquad (4)$$

where $\Delta E_{\mathrm{conform}}$ and ΔE_{solv} are the conformational energy and the solvation energy, respectively.

Comparing the different energies of the three forms listed in Table 2, it is obvious that the rim-covering conformer (form C) is most stable. Thus, the self-inclusion phenomenon does not occur in compound A, which is in good agreement with the experimental observations.

In order to ascertain whether compound A can form inclusion complex with β-CD in water environment and what shape of this complex will present, we define $\Delta(\Delta G)$ as

$$\Delta(\Delta G) = (\Delta E_{\mathrm{conformN}} - \Delta E_{\mathrm{conformLOW}} - \Delta E_{\mathrm{conformCD}}) + (\Delta E_{\mathrm{solvN}} - \Delta E_{\mathrm{solvLOW}} - \Delta E_{\mathrm{solvCD}}) \qquad (5)$$

where the subscript conformN represents one form among forms I, II, III, IV (see Scheme 4); the subscript conformLOW represents the lowest energy conformer of compound A; the subscript conformCD represents the optimized conformer of β-CD; the subscript solvN represents solvation of one form among forms I–IV; the subscript solvLOW represents the lowest energy solvation of compound A; the subscript solvCD represents the optimized solvation of β-CD. Comparing $\Delta(\Delta G)$ values listed

Table 2
The conformer potentials and solvation energies of three possible structures of compound A

Conformer	E_{conform}/kcal mol^{-1}	ΔE_{sol}/kcal mol^{-1}	ΔG /kcal mol^{-1}
Form A	296.80	−183.07	113.73
Form B	329.90	−189.18	140.72
Form C	303.51	−200.95	102.56

Table 3
The conformer potentials and solvation energies of four possible structures of inclusion complexes between compound A and β-CD

Conformer	$\Delta E_{\mathrm{conform}}$/kcal mol^{-1}	ΔE_{solv}/kcal mol^{-1}	ΔG/kcal mol^{-1}	$\Delta(\Delta G)$/kcal mol^{-1}
Form I	519.68	−306.30	213.38	51.09
Form II	516.55	−308.22	208.33	43.04
Form III	474.42	−338.37	136.05	−20.24
Form IV	554.51	−369.57	184.94	19.65

in Table 3, we can draw a conclusion that compound A can form 1:1 inclusion complex with added native β-CD in water and form III is the most possible conformer.

4.5. Molecular recognition

Fig. 3 shows that the fluorescence intensity of compound A increases upon addition of various guests. This indicates that the substituted 3*H*-indole moiety of compound A is transferred from a hydrophilic microenvironment to a less hydrophilic one, supporting the proposed novel recognition mechanism as illustrated in Scheme 2 [13]. A guest-induced ICD enhancement means that the fluorophore moiety moves towards the cavity of CD [12,14]. For compound A, a slight enhancement of negative cotton effect corresponding to the ^1L_a band around 260 nm upon addition of cyclohexanol and cyclooctanol (see Fig. 1) indicates that the substituted 3*H*-indole moiety of compound A, initially locating on the rim of the cyclodextrin cavity, may suffer slight conformational changes, and moves towards the chiral hydrophobic cavity of β-CD to some extent. The change of the positive cotton effect corresponding to the ^1L_b band around 350 nm is complicated which suggests that the change of the microenvironment of the substituted 3*H*-indole moiety of compound A is much different in these cases [12,14]. Time-resolved fluorescence is used to investigate further the microenvironment of the substituted 3*H*-indole moiety of compound A upon addition of cyclohexanol, cyclooctanol and native β-CD. Double-exponential decay is observed (see Table 1). The long lifetime corresponds to the substituted 3*H*-indole moiety of compound A locating in a less hydrophilic microenvironment. These results strongly support the validity of the novel recognition mechanism.

The sensing ability of compound A during host–guest recognition is studied by steady-state fluorescence. The extent of fluorescence intensity variation is evaluated by a sensitivity parameter defined as $\Delta I/I_0$ ($\Delta I = I - I_0$), where I and I_0 denote the fluorescence intensity of compound A in the presence and absence of guest molecule, respectively. The sensitivity parameters of all guests we studied are illustrated in Fig. 4. Both the novel chemosensor reported [13] and the conventional ones [12a] show high sensitivity to adamantine group. Similar phenomenon is exhibited in compound A. The order of the sensitivity of compound A to the terpenes is acyclic (nerol) > monocyclic ((−)-menthol) > bicyclic ((−)-borneol) terpenes, which is opposite to that of the conventional chemosensor [12a]. (−)-Borneol and (−)-camphor have the same framework but different functional group, a hydroxyl group for the former and a ketone group for the latter. The sensitivity of compound A to (−)-borneol doubles that to (−)-camphor. Compared with cyclohexanol, cyclooctanol with a ring of larger size shows larger sensitivity of being recognized. Both cholic acid and deoxycholic acid with the same steroidal framework have low sensitivity values. This is much different from the situation using the conventional

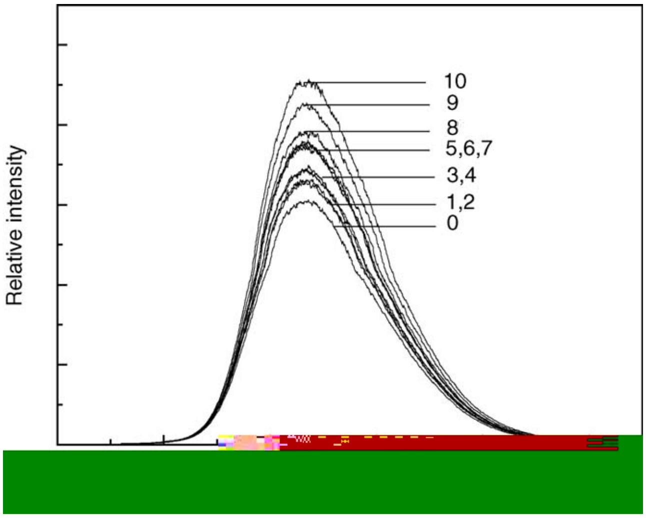


Fig. 3. Fluorescence emission spectra of compound A in water in the absence (0) and presence of guests: cholic acid (1), (−)-camphor (2), deoxycholic acid (3), cyclohexanol (4), (−)-borneol (5), 1-adamantanol (6), (−)-menthol (7), 1-adamantanecarboxylic acid (8), cyclooctanol (9) and nerol (10). [Compound A] = 5 × 10^{-6} M, [guest] = 5 × 10^{-5} M.

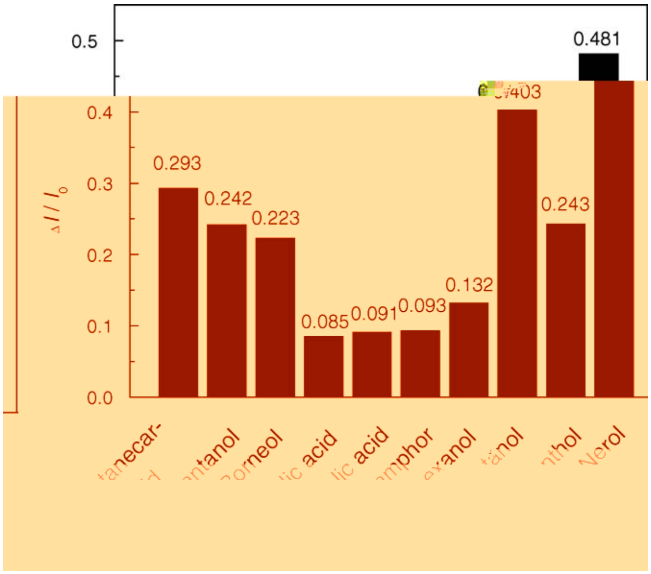


Fig. 4. Sensitivity parameters ($\Delta I/I_0$) of compound A for various guests. [Compound A] = 5 × 10^{-6} M, [guest] = 5 × 10^{-5} M.

chemosensor [12a], but agrees well with the recent work of Ikeda group [13]. The new recognition characteristics and the high sensitivity exhibited by the new kind CD-based chemosensors further broaden the application of CD-based chemosensor in molecular recognition.

5. Conclusion

In the present study, we synthesize a new compound A and characterize it by elemental analysis, MS and ^{1}H NMR. Both experimental and computational analyses indicate that the substituted 3*H*-indole moiety of compound A adopts rim-covering conformation in aqueous solution and 1:1 (guest:host) inclusion complex is formed by addition of native β-CD. The recognition behavior of compound A is investigated by means of ICD spectra, time-resolved and steady-state fluorescence spectra. In contrast to the behavior of most conventional CD-based chemosensors with self-inclusion conformation, the fluorescence intensity of this compound A is increased upon addition of guest molecules, showing novel recognition mechanism. It shows high sensitivity to acyclic and adamantine molecules, but not to the bile acids.

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References

[1] (a) M.L. Bender, M. Komiyama, Cyclodextrin Chemistry, Springer, New York, 1978;
(b) J.-M. Lehn, Supramolecular Chemistry, VCH, Weinheim, 1995.
[2] (a) S.A. Nepogodiev, J.F. Stoddart, Chem. Rev. 98 (1998) 1959;
(b) R. Breslow, S.D. Dong, Chem. Rev. 98 (1998) 1997;
(c) E. Engeldinger, D. Armspach, D. Matt, Chem. Rev. 103 (2003) 4147.
[3] (a) H. Ikada, A. Matsuhisa, A. Ueno, Chem. Eur. J. 9 (2003) 4907;
(b) T. Aoyagi, H. Ikada, A. Ueno, Bull. Chem. Soc. Jpn. 74 (2001) 157;
(c) Y. Liu, B. Li, B.H. Han, T. Wada, Y. Inoue, J. Chem. Soc., Perkin Trans. 2 (1999) 563;
(d) A.D. Qi, L. Li, Y. Liu, J. Inclusion Phenom. Macrocycl. Chem. 45 (2003) 69;
(e) S.R. McAlpine, M.A. Garcia-Garibay, J. Am. Chem. Soc. 120 (1998) 4269.
[4] (a) M. Belletête, M. Lachapelle, G. Durocher, J. Phys. Chem. 94 (1990) 7642;
(b) S. Nigam, R.S. Sarpal, M. Belletête, G. Durocher, J. Colloid Interface Sci. 177 (1996) 143;
(c) R.S. Sarpal, G. Durocher, J. Photochem. Photobiol. A: Chem. 80 (1994) 307;
(d) X. Shen, M. Belletête, G. Durocher, J. Phys. Chem. B 101 (1997) 8212.
[5] (a) Y. Chen, T. Xu, X. Shen, H. Gao, J. Photochem. Photobiol. A: Chem. 169 (2005) 123;
(b) J. Li, X. Shen, H. Gao, Chem. Phys. Lett. 342 (2001) 529;
(c) J. Li, X. Shen, H. Gao, Spectrosc. Spectr. Anal. 21 (2001) 508.
[6] (a) T. Xu, X. Shen, H. Gao, Spectrosc. Spectr. Anal. 25 (2005) 857;
(b) T. Xu, X. Shen, N. Li, H. Gao, Chin. Chem. Lett. 16 (2005) 943;
(c) T. Xu, Ph.D. Thesis, Peking University, Beijing, 2003.
[7] (a) Y. Chen, T. Xu, X. Shen, H. Gao, J. Photochem. Photobiol. A: Chem. 173 (2005) 42;
(b) X. Shen, M. Belletête, G. Durocher, J. Phys. Chem. B 102 (1998) 1877;
(b) X. Shen, M. Belletête, G. Durocher, Chem. Phys. Lett. 301 (1999) 193.
[8] M.V. Rekharsky, Y. Inoue, Chem. Rev. 98 (1998) 1875;
(b) T. Aoyagi, A. Nakamura, H. Ikeda, T. Ikeda, H. Mihara, A. Ueno, Anal. Chem. 69 (1997) 659.
[9] (a) J.M. Haider, Z. Pikramenou, Chem. Soc. Rev. 34 (2005) 120;
(b) D. Yana, T. Takahashi, H. Mihara, A. Ueno, Macromol. Rapid Commun. 25 (2004) 577;
(c) A.G. Fang, J.V. Mello, N.S. Finnev, Tetrahedron 60 (2004) 11075.
[10] (a) A. Ueno, A. Ikeda, H. Ikeda, T. Ikeda, F. Toda, J. Org. Chem. 64 (1999) 382;
(b) A. Ueno, M. Takahashi, Y. Nagano, H. Shibano, T. Aoyagi, H. Ikeda, Macromol. Rapid Commun. 19 (1998) 315.
[11] (a) N. Dorjpalam, M. Toda, H. Itoh, F. Hamada, J. Inclusion Phenom. Macrocycl. Chem. 50 (2004) 79;
(b) C.M. Rudzinski, A.M. Young, D.G. Nocera, J. Am. Chem. Soc. 124 (2002) 1723;
(c) T. Toyoda, H. Mihara, A. Ueno, Macromol. Rapid Commun. 23 (2002) 905;
(d) T. Tanabe, K. Touma, K. Hamasaki, A. Ueno, Anal. Chem. 73 (2001) 3126.
[12] (a) H. Ikeda, M. Nakamura, N. Ise, N. Oguma, A. Nakamura, T. Ikeda, F. Toda, A. Ueno, J. Am. Chem. Soc. 118 (1996) 10980;
(b) M. Narita, F. Hamada, I. Suzuki, T. Osa, J. Chem. Soc., Perkin Trans. 2 (1998) 2751;
(c) M. Narita, F. Hamada, J. Chem. Soc., Perkin Trans. 2 (2000) 823.
[13] H. Ikeda, The 3rd Asian Cyclodextrin Conference, Tianjin, China, 2005, pp. 30–31.
[14] Y. Inoue, K. Yamamoto, T. Wada, S. Everitt, X.-M. Gao, Z.-J. Hou, L.-H. Tong, S.-K. Jiang, H.-M. Wu, J. Chem. Soc., Perkin Trans. 2 (1998) 1807.
[15] A.M. Song, J.H. Zhang, M.H. Zhang, T. Shen, J.A. Tang, Colloids Surf. A 167 (2000) 253.
[16] (a) P. Skrabal, J. Steiger, H. Zellinger, Helv. Chim. Acta. 58 (1975) 800;
(b) A. Popowycz, M. Sc. Thesis, University of Montreal, Canada, 1991.
[17] N. Zhong, H.S. Byun, R. Bittman, Tetrahedron Lett. 39 (1998) 2919.
[18] S.E. Brown, J.H. Coates, D.R. Coghlan, C.J. Easton, Aust. J. Chem. 46 (1993) 953.
[19] Q. Chen, X. Shen, H. Gao, Chin. Chem. Lett. 15 (2004) 179.
[20] S. Diego, InsightII User Guide, Accelrys Inc., USA, 2002.
[21] P. Dauber-Osguthorpe, V.A. Roberts, D.J. Osguthorpe, J. Wolff, M. Genest, A.T. Hagler, Proteins: structure, Funct. Genet. 4 (1988) 31.
[22] Minimization algorithms are packaged into a "smart" minimizer, which uses a robust but less accurate algorithm in the first stage of the calculation such as steepest descent, followed by the more accurate but less robust one such as conjugate gradient method. In this method, Polak-Ribiere algorithm, a highly accurate but less robust one near the end of the run such as BFGS in Newton method, is used. The ensemble chose in molecular dynamics is NVT, the dynamics is modified to allow the system to exchange heat with the environment at a controlled temperature. The temperature controlling method used in molecular dynamics is velocity scale method, which is used to control the kinetic temperature of a system and leads it to equilibrium quickly. This method involves maintaining the temperature within a given range of a target temperature.
[23] (a) M. Kajtar, C. Horvath-Toro, E. Kuthi, Acta Chim. Acad. Sci. Hung. 110 (1982) 327;
(b) K. Harata, H. Uedaira, Bull. Chem. Soc. Jpn. 48 (1975) 375.
[24] (a) M. Belletête, G. Durocher, J. Phys. Chem. 93 (1989) 1793;
(b) M. Belletête, M. Lachapelle, G. Durocher, J. Phys. Chem. 94 (1990) 5337.
[25] M. Belletête, S. Nigam, G. Durocher, J. Phys. Chem. 99 (1995) 4015.
[26] C. Zhang, X. Shen, H. Gao, Chem. Phys. Lett. 363 (2002) 515.