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ORIGINAL ARTICLE

The synthesis and dyes complexation properties of novel cyclodextrin derivatives with large conjugate acylhydrazone group

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Abstract By reacting β-cyclodextrin with 4-(prop-2-ynyloxy)benzaldehyde, the cyclodextrins (CDs) aromatic aldehyde derivative **6** was prepared in yield of 80 % via click chemistry of the Huisgen [2 + 3] cycloaddition reaction. Further Schiff-base condensation of compound **6** with salicylic hydrazide, nicotinohydrazide, or 2,4-dinitrophenylhydrazine, novel cyclodextrin derivatives with large conjugate acylhydrazone group **7a**, **7b** and **7c** were conveniently obtained in yields of 75–85 %. Their structures were confirmed by elemental analysis, FT-IR, ESI–MS and NMR spectra. Their complexation properties for Orange I and Neutral red were studied by fluorescence titration spectroscopy and complexation MS spectrum. The results suggested that these novel CDs derivatives with large conjugate acylhydrazone group showed excellent complexation abilities for the tested dyes. The association constants were higher than 10^4 and the highest associations constant was 5.85×10^4 for host **7a** with OI. The 1:1 complexes were formed in DMSO solution.

Keywords Cyclodextrin · Acylhydrazone · Synthesis · Complexation · Dye

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Introduction

In recent years, cyclodextrins (CDs) have been extensively used in many research fields such as food chemistry, analytical chemistry, biology, and pharmacy due to their appealing unique binding properties [1–7]. But the complexation properties of native CDs are generally limited and the more elaborated structures are often needed for binding guests effectively. As a result, various functional groups and unique structural units were introduced into CDs to obtain novel CDs derivatives with interesting binding properties up to now [1–7]. However, due to the difficulties of selective modifications of the hydroxyl groups on CDs, the varieties and amounts of CDs derivatives were far fewer than that of other organic supramolecules, such as crown ethers and calixarenes. One pathway to solve this problem is to synthesize efficiently CDs intermediate derivatives containing active-terminal functional groups, which can be used as new synthetic platform to construct novel CDs derivatives by reacting easily with other molecules. For example, the CDs derivatives with terminal amino-group prepared by reacting mono-6-tosyl-β-CD with corresponding amines, were applied to construct some CDs derivatives by addition reaction or ammonolysis reaction, etc. [8–10]. It is well known that the aldehyde group is an important active functional group, which could be easily transformed to other derivatives by reducing, oxidizing, addition or condensation reaction. Thus, the first CD aliphatic aldehyde derivative was reported by oxidation of hydroxyl group as early as in 1994 [11]. Subsequently, several different oxidizing methods for hydroxyl groups of CDs were reported to prepare the CDs aliphatic aldehyde derivatives [12–14]. Also, by the further addition and oxidizing reaction of these aldehyde derivatives, some interesting CDs derivatives with unique

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functional groups were obtained [15–18]. But no condensation reaction, such as Schiff-base condensation, was reported due to the unstably reversible condensation process of aliphatic aldehyde. If the aromatic aldehyde group is introduced into CDs, obviously, the obtained CDs aromatic aldehyde derivative would possess better reaction activities and could be transformed effectively to all kinds of CDs derivatives based on the stable aromatic conjugate structure comparing with the aliphatic aldehyde. Moreover, it is expected that this kind of CDs derivatives with aromatic conjugate group would exhibit better complexation properties for some guests, such as organic dyes, due to the effective π–π stacking action between the aromatic conjugate structure on CDs and the aromatic conjugate structure of organic dyes [19–21]. However, no such CDs derivative was described up to now. On the other hand, it was well-known that the Cu^{I}-catalyzed click chemistry, which react easily azide group with alkynyl group, had been used to prepare CDs derivatives effectively [22–27]. Considering the significance of CDs aromatic aldehyde derivative as the synthetic platform to construct other CDs derivatives, in this paper, we described the first synthesis of CDs aromatic aldehyde derivative via a facile click reaction. Moreover, we prepared novel cyclodextrin derivatives with large conjugate acylhydrazone group for the first time, and their preliminary complexation properties for organic dyes were also investigated.

Experimental

Materials and instruments

All chemicals were purchased from commercial suppliers and used without further purification. The other organic solvents and inorganic reagents were purified according to standard anhydrous methods before use. TLC analysis was performed using pre-coated silica gel glass plates. IR spectra were recorded on a Perkin-Elmer PE-983 infrared spectrometer as KBr pellets with absorption in cm^{-1}.^{1}H NMR spectra was recorded in DMSO-d_6 on a Bruker-ARX 600 instrument at 30 °C. Chemical shifts are reported in ppm, using tetramethylsilane (TMS) as internal standard. ESI–MS spectra were obtained from DECAX-30000 LCQ Deca XP mass spectrometer. Elemental analyses were performed at Vario EL III Elemental Analyzer. 4-(Prop-2-ynyloxy)benzaldehyde **5** were conveniently prepared by reacting 4-hydroxybenzaldehyde, with 3-bromoprop-1-yne under K_2CO_3/MeCN system in yields of 87 % [28].

Fluorescence spectra were measured in a conventional quartz cell (10 × 10 × 45 nm) at 25 °C on a Hitachi F-4500 spectrometer equipped with a constant-temperature water bath, with excitation and emission slits 10 nm wide. The excitation wavelengths were 290 nm. In the fluorescence titration experiments, the concentrations of hosts **7a**,**7b** and **7c** were 1×10^{-4} M and the concentrations of dyes were 0, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0×10^{-6} M, respectively, in the phosphate buffer (pH = 7.20). The stoichiometry of the complexes was determined by the Job method of continuous variations. The association constant was calculated by Benesi–Hilderbrand formula with nonlinear curve fitting procedure [29].

Synthesis of CDs aromatic aldehyde derivative 6

Compound **5** (0.18 g, 1.1 mmol) with compound **3** (1.16 g, 1 mmol) was carried out in DMF (35 mL) in the presence of Cu^{I} generated by the reduction of copper sulfate (0.28 g,1.1 mmol) with sodium ascorbate (0.48 g, 2.4 mmol). The mixture was stirred at room temperature for 15 h. TLC detection indicated the disappearance of materials of compound **3**. After reaction, most of the solvent was evaporated under reduced pressure and 20 mL of distilled water was added with vigorous stirring at room temperature. The mixture was stored in the refrigerator overnight and then the precipitate was collected by filtration. The precipitate was further purified by recrystallization in DMF/acetone for three times. Compound **6** was obtained as grey white solid in yield of 80 %. Compound **6**: IR/cm^{-1}: 3387, 2927, 1679, 1599, 1509, 1157, 1031, 756; ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 2.78–4.10 (m, 40H, CH and CH_2), 4.25–4.68 (8H, OH and NCH_2), 4.69–5.10 (m, 7H, CH), 5.23 (s, 2H, CH_2O), 5.53–5.99 (m, 14H, OH), 7.24 (d, J = 8.0 Hz, 2H, ArH), 7.88 (d, J = 8.0 Hz, 2H, ArH), 8.22 (s, 3H, NCH); 9.87 (s, 1H, CHO). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 191.9, 163.5, 142.4, 132.3, 130.3, 126.2, 115.6, 102.6, 101.7, 83.9, 82.5, 82.1, 81.4, 73.7, 73.6, 73.4, 73.1, 72.9, 72.6, 72.2, 70.5, 61.8, 60.4, 60.0, 59.5, 50.5. MS m/z (%): 1342.3(MNa^{+}, 100). Anal. Calcd. For $C_{52}H_{77}N_3O_{36}$: C47.31, H5.88, N3.18; found C47.38, H5.82, N3.22 %. Mp 288–291 °C (dec).

Synthesis of CDs derivatives 7a, 7b and 7c

Under N_2 atmosphere, a mixture of compound **6** (0.265 g, 0.2 mmol) and corresponding amino-compound (salicyloylhydrazine, nicotinichydrazide or 2,4-dinitrophenylhydrazine) (0.4 mmol) was stirred in 15 mL of DMF solution. The reaction system was heated at 55 °C for 8–18 h. TLC detection indicated the disappearance of compound **6**. Then the solvent was evaporated by reduced pressure. Fifteen milliliter of MeOH was added and the precipitation was formed. The precipitation was recrystallized in MeOH/

$CHCl_3$ and washed by 10 mL of MeOH and 10 mL of acetone subsequently.

Compound **7a** was obtained by refluxing 8 h as brown powder in yield of 84 %. Compound **7a**: IR/cm^{-1}: 3415, 2927, 1605, 1508, 1306, 1079, 1031, 756; ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 2.82–4.11 (m, 40H, CH and CH_2), 4.22–4.70 (8H, OH and NCH_2), 4.71–5.11 (m, 7H, CH), 5.18 (s, 2H, CH_2O), 5.61–5.97 (m, 15H, OH), 6.92 (s, 2H, ArH), 7.18 (s, 2H, ArH), 7.42 (s, 1H, ArH), 7.71 (s, 2H, ArH), 7.92 (s, 1H, ArH), 8.21 (s, 1H, NCH), 8.41 (s, 1, CH), 11.86 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 166.1.9, 162.8, 157.1, 142.8, 141.6, 132.8, 131.6, 129.6, 126.7, 122.4, 115.6 110.6, 101.9, 101.8, 101.7, 101.6, 101.1,83.2, 82.1, 81.8, 81.0, 73.3, 73.1, 72.9, 72.7, 72.5, 72.1, 71.7, 70.1, 61.7, 60.1, 59.8, 59.6, 58.7, 50.2. MS *m/z* (%): 1452.8(M^+, 100). Anal. Calcd. For $C_{59}H_{83}N_5O_{37}$: C48.73, H5.75, N4.82; found C48.69, H5.71, N4.86 %. Mp 276–279 °C (dec).

Compound **7b** was obtained by refluxing 12 h as offwhite powder in yield of 85 %. Compound **7b**: IR/cm^{-1}: 3408, 2923, 1668, 1599, 1508, 1156, 1030, 579; ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 2.81–4.07 (m, 40H, CH and CH_2), 4.21–4.69 (8H, OH and NCH_2), 4.70–5.13 (m, 7H, CH), 5.21 (s, 2H, CH_2O), 5.60–5.94 (m, 14H, OH), 7.22 (s, 2H, ArH), 7.49 (s, 1H, ArH), 7.88 (s, 2H, ArH), 8.21(s, 1H, NCH), 8.32 (s, 1H, ArH), 8.42 (s, 1H, CH), 8.89 (s, 1H, ArH), 9.17 (s, 1H, ArH), 9.89 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 167.4, 162.9, 151.1, 146.5, 141.7, 138.1, 131.7, 129.7, 128.2, 125.5, 123.4, 115.1, 102.1, 101.9, 101.8, 101.7, 83.3, 81.9, 81.5, 81.4, 81.3, 73.1, 73.0, 72.9, 72.8, 72.7, 72.5, 72.3, 72.0, 71.9, 71.8, 71.6, 61.2, 60.0, 59.9, 59.8, 58.7, 59.6, 58.8, 50.3. MS *m/z* (%): 1438.2(M^+, 100). Anal. Calcd. For $C_{58}H_{82}N_6O_{36}$: C48.40, H5.74, N5.84; found C48.47, H5.69, N5.90 %. Mp 278–281 °C (dec).

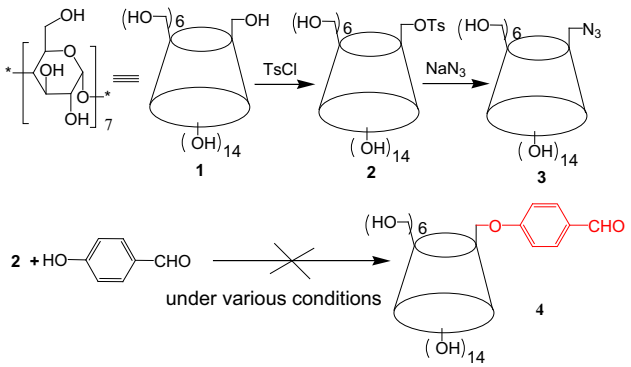
Compound **7c** was obtained by refluxing 18 h as carmine powder in yield of 75 %. Compound **7c**: IR/cm^{-1}: 3418, 2921, 1662, 1614, 1502, 1332, 831; ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 2.84–4.08 (m, 40H, CH and CH_2), 4.23–4.70 (8H, OH and NCH_2), 4.72–5.09 (m, 7H, CH), 5.20 (s, 2H, CH_2O), 5.62–5.93 (m, 14H, OH), 7.18 (d, $J = 8.0$ Hz, 2H, ArH),7.78 (d, $J = 8.0$ Hz, 2H, ArH), 8.11 (d, d, $J = 8.0$ Hz, 1H, ArH), 8.20 (s, 1H, NCH), 8.35 (d, $J = 8.0$ Hz, 1H, ArH), 8.66 (s, 1H, ArH), 8.88 (s, 1H, ArH), 10.05 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 163.0, 158.9, 141.8, 139.8, 134.3, 131.7, 129.7, 125.6, 122.8, 120.7, 118.8, 115.1, 102.1, 102.0, 101.9, 101.8, 101.2, 83.4, 82.0, 81.6, 81.4, 81.3, 80.9, 73.1, 73.0, 72.9, 72.8, 72.5, 72.4, 72.3, 72.1, 72.0, 71.7, 70.0, 61.2, 60.1, 60.0, 59.9, 59.8, 58.9, 50.3. MS *m/z* (%): 1523.1(MNa^+, 100). Anal. Calcd. For $C_{58}H_{81}N_7O_{39}$: C46.43, H5.44, N6.54; found C46.48, H5.48, N6.50 %. Mp 282–285 °C (dec).

Results and discussion

Synthesis and characterization

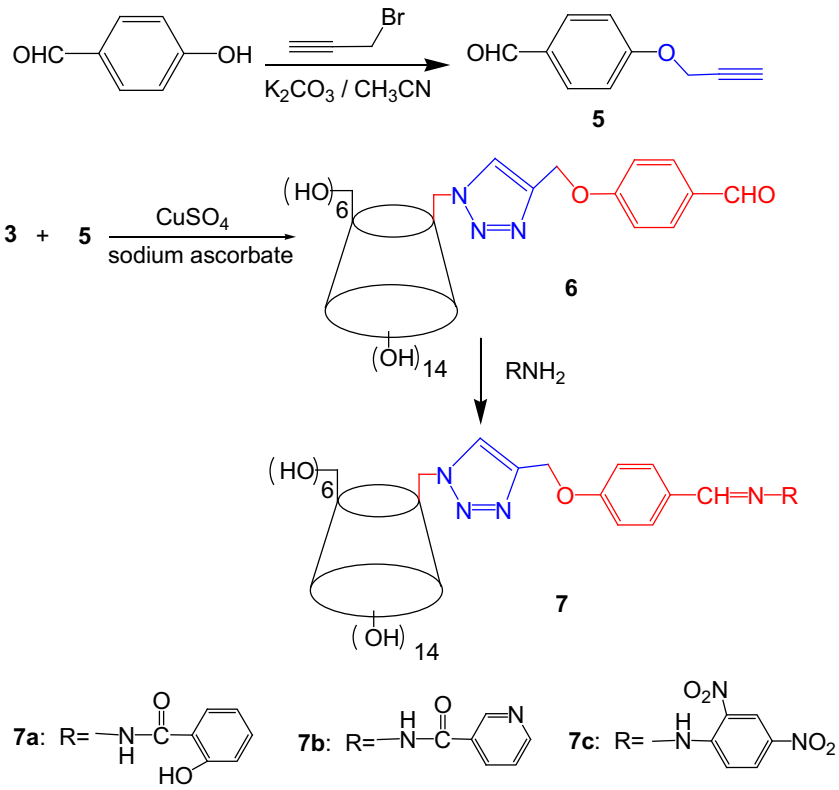
Initially, we tried to prepare the CDs aromatic aldehyde derivative by the nucleophilic substitution reaction of CD derivative **2** with 4-hydroxybenzaldehyde as shown in Scheme 1. However, this reaction failed to afford any product under all kinds of reaction systems, such as K_2CO_3/H_2O, K_2CO_3/DMF, K_2CO_3/MeCN, NaOH/DMF, NaOH/THF, $NaOH/H_2O$, etc. The reason might be attributed to the unfavorable influences of the strong hydrogen bonding between the phenolate and the multiple hydroxyl groups of CD.

Alternately, because the click reaction had been confirmed as a useful reaction mode in introducing other functional groups on CDs [22–27], it was chosen as the linking reaction for aromatic aldehyde with CDs. Scheme 2 showed the synthetic route of cyclodextrin aromatic aldehyde derivative **6** via click chemistry and its acylhydrazone derivatives **7a**, **7b** and **7c**. The mono-6-azido-β-CD **3** was obtained from the readily available mono-6-tosyl-β-CDs according to references [28, 30]. Also, 4-(prop-2-ynyloxy)benzaldehyde **5** was prepared in yield of 87 % by reacting 4-hydroxybenzaldehyde with 3-bromoprop-1-yne under K_2CO_3/MeCN system according to literatures [28, 31]. After the reactants **3** and **5** had been prepared, the coupling reaction of β-CDs azido derivative **3** and compound **5** was carried out by click chemistry of the Huisgen [2 + 3] cycloaddition reaction. The mol ratio of compounds **3** and **5** was 1:1.1, using 1.1 equiv. $CuSO_4{\cdot}5H_2O$ and 2.4 equiv. sodium ascorbate (with respect to the CD) as catalyst. This procedure was accomplished at room temperature in DMF solution in 15 h. The first example of CD aromatic aldehyde derivative **6** was obtained conveniently after simple purifying procedure of recrystallization in DMF/acetone and the yield was as high as 80 %.



Scheme 1 The unsuccessful synthetic route of compound **4**

Scheme 2 The synthetic route of compounds **7a**, **7b** and **7c**



Aromatic aldehyde group is an effective functional group to construct the stable large aromatic conjugate structures by the Schiff-base condensation. By stirring compound **6** with salicylic hydrazide, nicotinohydrazide, or 2,4-dinitrophenylhydrazine in DMF at 55 °C, the corresponding condensation products were obtained. The mol ratios of reactants were 1:2 and no catalyst, such as acetic acid, was needed. The TLC showed that almost all of compound **6** disappeared and only one new dot of product emerged. After distillation of most DMF under vacuum, the residue was recrystallized in MeOH/$CHCl_3$ and the residue of hydrazides was washed by small amount of MeOH and acetone for several times. Then compounds **7a**, **7b** and **7c** were prepared in yields of 84, 85 and 75 %, respectively. Both CDs aromatic aldehyde derivative **6** and its Schiff-base derivatives **7a**, **7b** and **7c** were obtained conveniently by recrystallization to remove some excess of materials, which were seldom applied in the syntheses of CDs derivatives. The yields were as high as 75–85 % and their purifications were confirmed by TLC and spectral characterization. Moreover, it is worthy of noting that compounds **7a**, **7b** and **7c** are novel cyclodextrin derivatives with large conjugate acylhydrazone group, which were not reported before among all kinds of cyclodextrin derivatives [1–7].

The novel CD aromatic aldehyde derivative **6** and its derivatives **7a**, **7b** and **7c** were characterized by elemental analysis, FT-IR, ESI–MS and NMR spectra. The IR spectra of compound **6** exhibited strong absorption peak at 1680 cm^{-1}, indicating the existence of C=O of aromatic aldehyde group. After Schiff-base condensation, the peak at 1680 cm^{-1} disappeared utterly and new peaks for C=N groups were observed in the IR spectra of compounds **7a**, **7b** and **7c**. Their ESI–MS spectra exhibited the corresponding molecular ion peaks at 1342.3 (MNa^+), 1452.8 (M^+), and 1523.1 (MNa^+), respectively (Fig. 1). In their ^1H NMR spectra, the characteristic peaks were assigned well for triazole proton and phenyl proton. For example, in the ^1H NMR spectrum of compound **7a**, all the protons of the functional groups, especially for the aromatic groups, were well assigned as shown in Fig. 2. On the other hand, as generally observed for substituted CDs, the proton signals at sugar units were hardly exploitable due to overlapping and broadening [28, 31]. This phenomenon suggested a modification of the conical CD structures leading to non-equivalent glucopyranose units [28, 31]. As a result, complete signal assignment was therefore difficult for CD units of compounds **6**, **7a**, **7b** and **7c**. By contrast, in their ^{13}C NMR spectra, the characteristic signals were detected distinctly for carbon atoms of aldehyde group, Schiff-base groups, triazole cycle and aromatic groups. For instance, the ^{13}C NMR spectrum of mono CD aromatic aldehyde derivative **6** showed the signals of carbon atoms for aldehyde and triazole cycle at 191, 163 and 142 ppm, respectively. The results of elemental analysis were also in

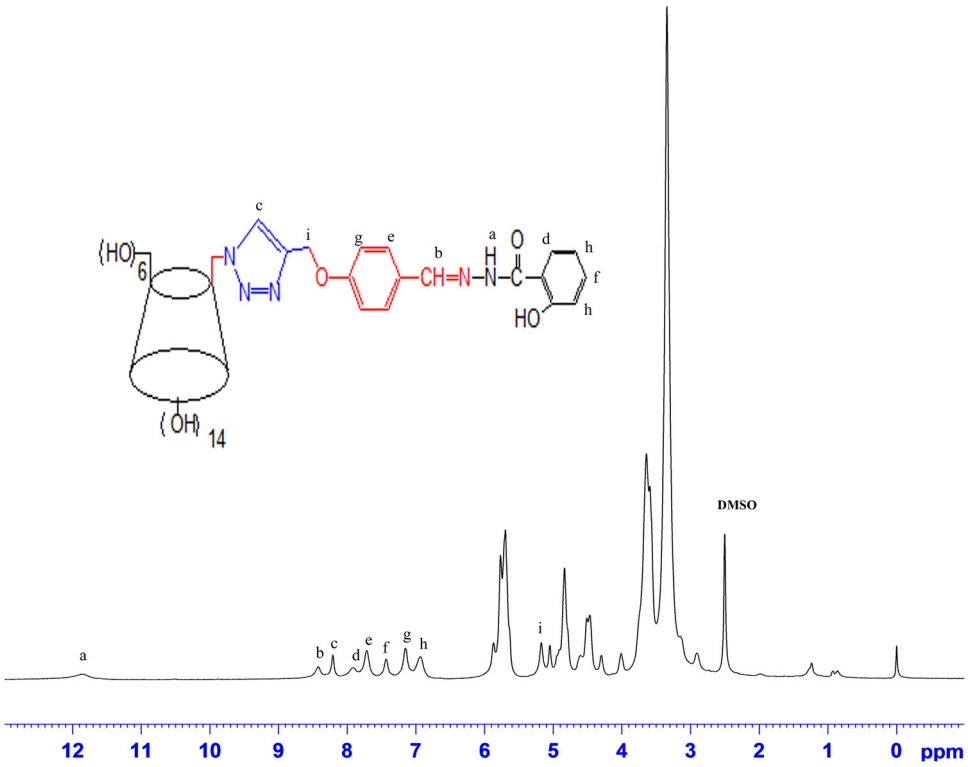
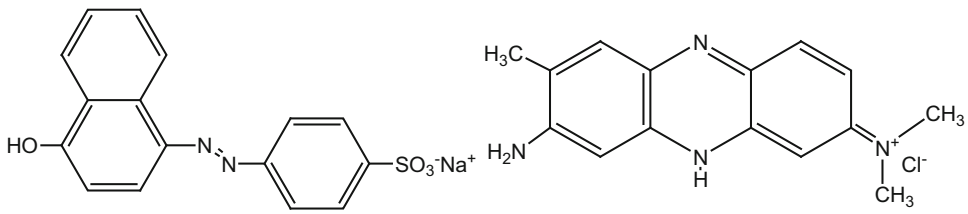


Fig. 1 ^{1}H NMR spectrum of compound **7a**



Orangeɕñ(OI) Neutral red (NR)

Fig. 2 The structures of tested organic dyes

accordance with their structures. As to the cis/trans conformers of C(O)–N bond and *E*/*Z* geometrical isomers respect to the C=N double bonds of compounds **7a**–**7c**, it was reasonable to deduce the existence of isomers by referring to the similar structural analysis in literature [32]. However, it was difficult to determine the percentage of different isomers for compounds **7a**–**7c** due to the overlapped signal of NH and OH in IR spectra and the absence of CH_2 groups beside the C(O)–N bond and C=N double bond which were crucial to study the percentages of different isomers [32]. Based on all these characteristic data of IR, ESI–MS, NMR and elemental analysis, compounds **6**, **7a**, **7b** and **7c** possess the corresponding structures as shown in Scheme 2.

Complexation studies for dyes

The formation of inclusion complexes between cyclodextrin derivatives and guests, such as dyes, were reported

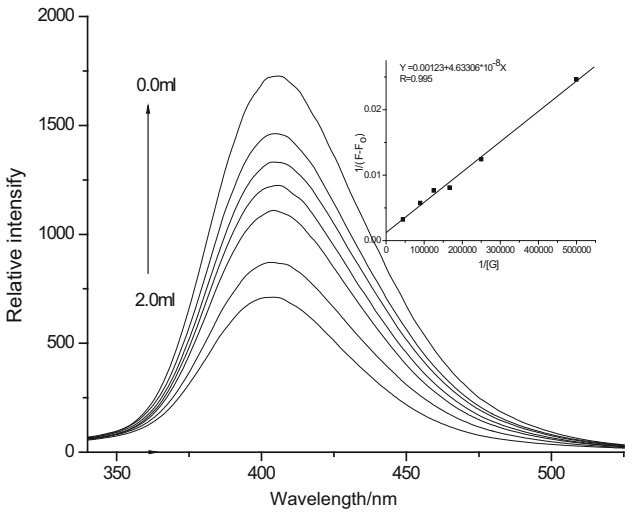


Fig. 3 Fluorescence titration spectra of host **7a** (1×10^{-4} M) with OI (0, 0.2, 0.6, 0.8, 1.0, 2.0×10^{-6} M) in phosphate buffer (pH = 7.20)

Table 1 Association constants (*Ks*) and compexation ratios of compounds **7a–7c** with two dyes

Dyes	**7a**		**7b**		**7c**	
	n	*Ks*	n	*Ks*	n	*Ks*
OI	1	5.85×10^4	1	3.98×10^4	1	5.35×10^4
NR	1	2.65×10^4	1	4.82×10^4	1	4.45×10^4

widely for the potential application on sensors and probes studies [33, 34]. As to novel CDs derivatives **7a**, **7b** and **7c**, it is expected that they showed good binding abilities for dyes based on the cooperation complexation of CDs unit and large conjugate acylhydrazone group with good π–π stacking action for dyes. Thus, the preliminary binding properties of hosts **7a**, **7b** and **7c** for two normal dyes of Orange I and Neutral red were investigated by fluorescence titration spectroscopy. The change of fluorescence spectra of host **7a** for OI was shown as representative ones in Fig. 3. It could be seen that the emission intensity gradually decreased as the concentration of guest increased, indicating a substantial association of these two components. These phenomena might be explained that the fluorescence was quenched directly by the interaction of host and guest, such as π–π stacking action interaction between large conjugate acylhydrazone group and planar aromatic structures of organic dyes. Moreover, based on the changes of emission intensity at maximal wavelength, the association constants and correlation coefficients were calculated by Benesi–Hildebrand equation, which was

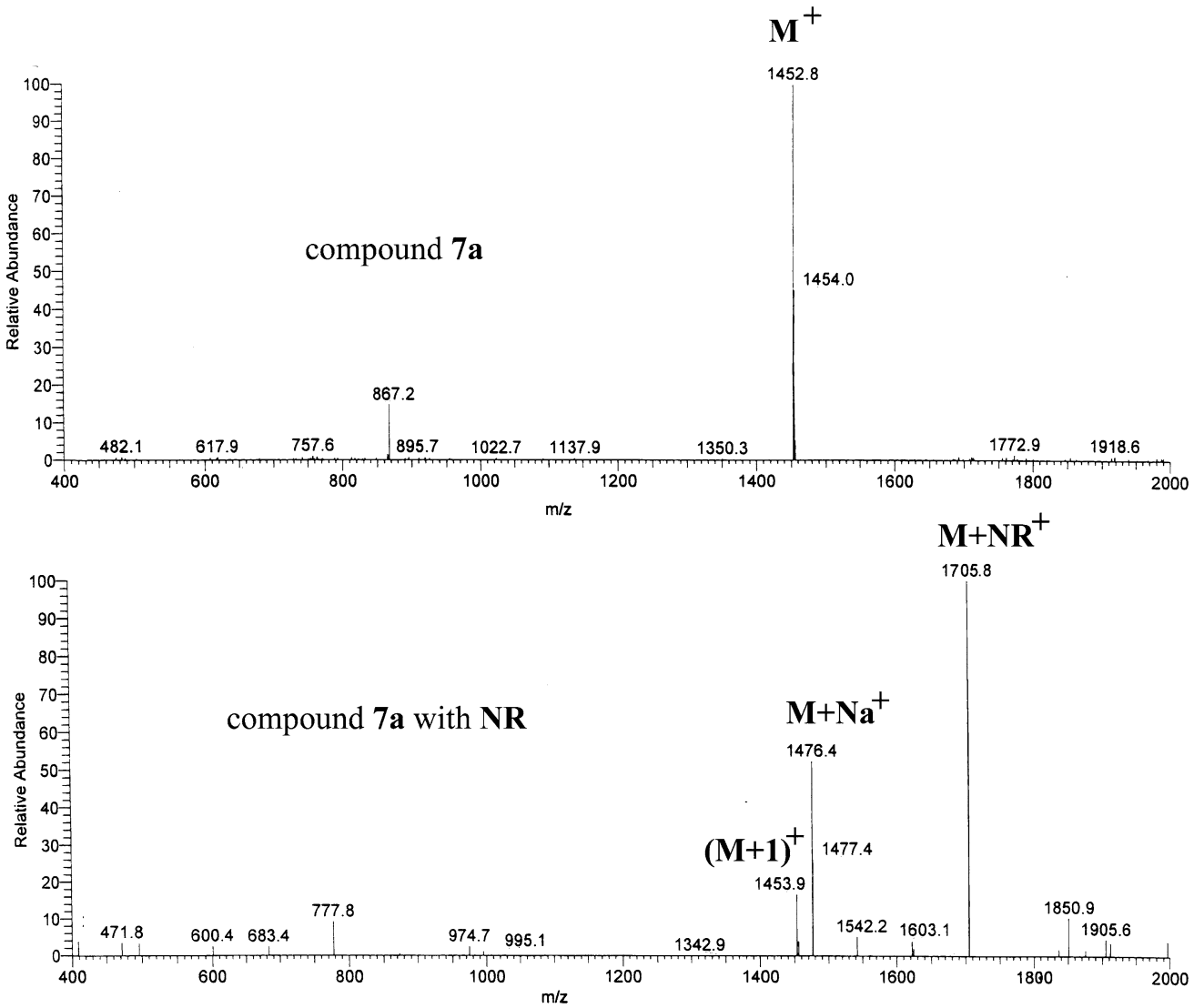


Fig. 4 The ESI–MS spectra of compound **7a** with NR (1:4)

usually used to study the complexation behaviors of host–guest [29]. The calculated formula was as follows:

$$H + nG \rightleftarrows H \times nG$$

$$\frac{1}{\Delta F} = \frac{1}{K_s \Delta f [H][G]^n} + \frac{1}{\Delta f [H]}$$

where H is host; G is guest; n is the ratio of complexation; $[H]$ and $[G]$ are the concentration of host and guest, respectively; K_s is association constant; Δf is the fraction of accessible fluorophore guest to a host; ΔF is the change of emission intensity at maximal wavelength.

The calculated results were summarized in Table 1. These results indicated the formation of 1:1 host–guest complexes for compounds **7a**, **7b** and **7c** with dyes. The association constants were higher than 10^4 and the highest associations constant was 5.85×10^4 for host **7a** with OI. Comparing with the literature reports, the complexation constants of compounds **7a**, **7b** and **7c** were outstanding. For examples, as to the complexation constants of CDs or its derivatives for NR, the associations constants of native CDs, organoselenium-bridged Bis-CDs and triazinylanilino-bridged Bis-CDs were 480, 5090 and 1546, respectively [10, 35], which were far lower than the data in this work. It can be seen that the although the large conjugate acylhydrazone group in compounds **7a**, **7b** and **7c** showed some difference structures, their association constants for dyes were close in the scope of $2.65–5.85 \times 10^4$. These phenomena might indicate that the similar large acylhydrazone conjugate π-electronic systems, resulting in good π–π stacking action with planar organic dyes, play more important roles in binding dyes than the influences of other functional groups such as hydroxyl and nitro group.

Further, the complexation behavior of compound **7a** with NR was studied by ESI–MS spectrum. The complexation of compound **7a** with excess Neutral red (mol ratio = 1:4) was studied in DMSO solution. The result was illustrated in Fig. 4. Before complexation, compound **7a** showed clear molecular ion peak at 1458.2. After complexation with NR, the spectrum exhibited three peaks for host **7a** + H^+ at 1453.9, host **7a** with Na^+ at 1476.4 and host **7a** with NR at 1705.8. The dye complexation peak showed the relative abundance of 100 %, indicating the strong molecular interaction between host and guest. Moreover, it can be seen that although the excess NR was added, only the 1:1 complexation peak was observed. This result was in accordance with the result of 1:1 complexation of fluorescence titration spectra. We also tried to use the ^1H NMR spectrum to investigate the change of proton signal before and after complexation, which might give the valuable located information about complexation of compounds **7a**–**7c** for dyes. But the signals were too complicated to analyze the special binding location. Both the results of complexation fluorescence spectra and complexation ESI–MS spectrum suggested that compounds **7a, 7b** and **7c** possessed excellent complexation abilities for dyes and 1:1 complexes were formed in DMSO solution.

Conclusions

In the paper, we described the facile synthesis of CDs aromatic aldehyde derivative via a facile click reaction. Moreover, the novel cyclodextrin derivatives with large conjugate acylhydrazone group were reported for the first time by Schiff-base condensation of CDs aromatic aldehyde derivative with series phenyl hydrazine or acyl hydrazide derivatives in yields of 75–85 %. Their structures were confirmed by elemental analysis, FT-IR, ESI–MS and NMR spectra. Their complexation properties for two organic dyes were investigated by fluorescence titration spectroscopy and complexation MS spectrum. The results suggested these novel CDs derivatives with large conjugate acylhydrazone group possess excellent complexation abilities comparing with the raw CDs and other CDs derivatives. The associations constants were higher than 10^4 and the highest associations constant was 5.85×10^4 for host **7a** with OI. Both fluorescence titration spectroscopy and complexation MS spectrum indicated that 1:1 complexes were formed in DMSO solution. These dyes complexation results indicated that the large acylhydrazone conjugate π-electronic systems in novel CDs derivatives play important roles in binding dyes based on the π–π stacking action, which extend a new strategy to the design and synthesis of new CDs derivatives with excellent complexation abilities for dyes.

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