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ORIGINAL ARTICLE

Characterization of group-inclusion complexations of rhodamine derivatives with native and 2,6-*di*-*O*-methylated β-cyclodextrins

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Abstract

The inclusion complexations of rhodamine derivatives with native and 2,6-*di*-*O*-methylated β-cyclodextrins (β-CD and DM-β-CD) were studied spectrophotometrically. Rhodamine derivatives were shown to form 1:1 inclusion complexes with β-CDs by the continuous variation method. The structures of the inclusion complexes were characterized by ^{1}H-^{1}H rotating frame nuclear Overhauser effect spectroscopy (ROESY) NMR measurements. It was found that native β-CD encapsulates the xanthenyl ring of rhodamines into the cyclodextrin cavity, while DM-β-CD forms two group-in complexes (phenyl-in and xanthenyl-in (bidirectional (bimodal) inclusion complexes)) with rhodamines bearing moderately bulky functional groups. Furthermore, we demonstrated the unique thermodynamics for the group-inclusion complex formation by DM-β-CD. The quantum yields for the inclusion complexes of rhodamines were determined using a quantum measurement apparatus equipped with a half-moon unit. The results indicated that the cyclodextrin inclusion of rhodamines with the bulky amino substituents on the xanthenyl ring largely decreases the quantum yield values. Based on these results, the substituent effects on the fluorescence process for the cyclodextrin inclusion complexes of rhodamines were discussed. This study provides useful insights for the functional group recognition of native and modified β-CDs.

Keywords Rhodamine dye · β-Cyclodextrins · Group-inclusion complex · Quantum yield · Substituent effect

Introduction

Fluorescent molecules have attracted much attention for use in the development of sensors, switches, and high-density optical data storage units [1–3]. Rhodamine dyes are useful fluorescence probes and find widespread application in the fields of chemistry and biology [4, 5]. Among the many reported fluorophores, rhodamines have excellent optical-physical properties such as long-wavelength absorption and emission, high fluorescence quantum yield, and high stability [6, 7]. The optical properties of rhodamines are sensitive to the polarity and hydrogen donating ability of the medium and can be tuned by incorporating suitable electron-donating and/or electron-accepting groups [6, 7]. Therefore, it is beneficial to clarify the photochemical processes and solvatochromic behaviour of rhodamines.

Several limitations of organic dyes, including undesirable aggregation, photo-bleaching, and surface adsorption, have hampered their application as molecular biological probes and sensors [8, 9]. These disadvantages can be addressed by the inclusion of supermolecules, which minimizes aggregation and surface adsorption [9–11]. Nau and co-workers reported that the addition of the cucurbit[7]uril host molecule to rhodamine 6G solution resulted in several advantageous effects such as enhanced brightness and aggregation reduction [9, 12].

Cyclodextrins have been used extensively as host molecules [13]. β-Cyclodextrin (β-CD) has an appropriate cavity that can accommodate many aromatic compounds and it has received much more attention than other cyclodextrin analogues. Therefore, numerous chemically

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modified β-CDs have been designed and synthesized in order to enhance the solubility and cavity hydrophobicity. The fundamental properties of functional molecules are improved by CD inclusion [14]. However, the effects of such inclusion on the fundamental properties of rhodamine derivatives are not well established.

In this study, using five rhodamine derivatives as guest molecules, we have examined the inclusion complexation of native and modified β-CDs. We have unveiled the characteristic inclusion behaviour of rhodamines with the β-CD modified by methylation of the hydroxy groups on the rim. Based on these results, we have demonstrated the functional group recognition ability of β-CDs. Furthermore, using a fluorescence quantum efficiency analysis system equipped with a half-moon unit, we examined the effects of various substituents on the quantum yields for inclusion complexes of rhodamines with β-CDs; further, we discussed fluorescence processes of rhodamines.

Experimental

Materials

The structures of the rhodamine derivatives are shown in Fig. 1. The rhodamines were obtained commercially and used as received (purity > 98%): RB (Tokyo Chemical Industry Co.); TMRM (Thermo Fisher Scientific K. K.); R110 (Sigma-Aldrich Chemical Company, Inc.); R123 and R101 (Santa Cruz Biotechnology, Inc.). Two kinds of β-CDs (β-cyclodextrin (β-CD) and 2,6-di-*O*-methylated β-CD (DM-β-CD)) were purchased from Nacalai Tesque and were used without further purification. Water was purified by distillation and used as the solvent.

Absorption, fluorescence, and NMR measurements

The absorption spectra of rhodamines were measured on a Shimadzu UV-1850 spectrometer. The solution temperature

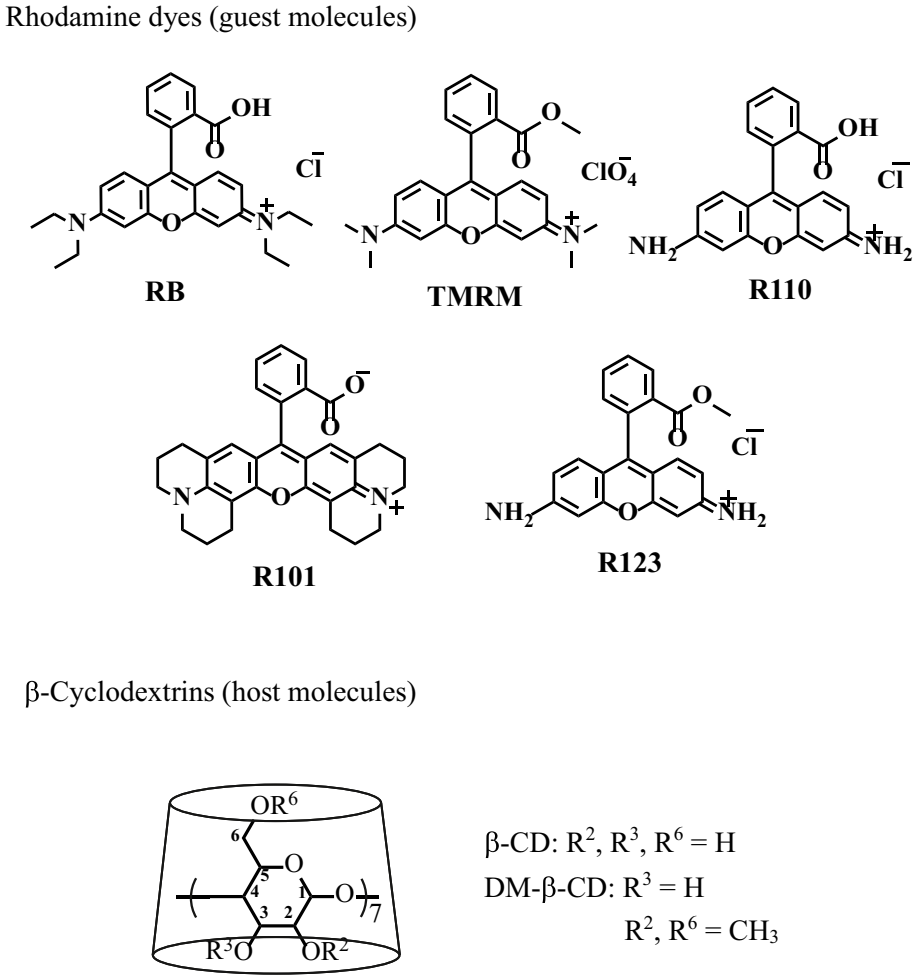

Fig. 1 Structures of rhodamine dyes and β-cyclodextrins (native and 2,6-methylated β-CDs)

was maintained at 298.0 ± 0.2 K by means of an external circulating water bath. The ϕ values of the inclusion complexes of rhodamines were determined on an Otsuka Electronics Quantum Efficiency Analysis System (QE 1000) equipped with a half-moon unit (Otsuka, Japan) at 298.0 ± 0.5 K. The quantum yield was calibrated using quinine bisulfate solution in sulfuric acid (0.05 M (1 M = 1 mol dm^{-3})) as a standard: excitation wavelength = 347.5 nm and ϕ = 0.51 ± 0.02 [15].

^{1}H-NMR spectra of the β-CD inclusion complexes with rhodamines were recorded on a Varian 400-MR ASW spectrometer (400 MHz) at room temperature. Chemical shifts are given as δ values relative to HOD (δ 4.79) as the internal standard. 2D ROESY-NMR measurements were carried out on a Varian VNS600 spectrometer (600 MHz) at 303 K. The mixing time for each ROESY-NMR measurement was 200 ms.

Results and discussion

Evaluation of complexation constants of inclusion complexes

The typical absorption spectra for the complexation of RB with native β-CD and modified DM-β-CDs in the visible region are shown in Fig. 2. The absorption intensities of RB decreased upon the addition of β-CDs. To confirm the stoichiometry for the complexation of RB with β- and DM-β-CDs, NMR spectral shift measurements were conducted by varying the mole fraction of RB and β-CDs (continuous variation method, Job's method) [16]. The Job plots ($\Delta\delta(1-x_H)$ vs x_H: $x_H = [\beta\text{-CD}]_0/([\beta\text{-CD}]_0 + [\text{RB}]_0)$) for the complexation of RB with β-CDs showed a maximum at $x_H = 0.5$ (Fig. 2), suggesting a 1:1 complex formation. Similar results were obtained for the complexation of other rhodamine derivatives with native and modified β-CDs. The equilibrium for the 1:1 complexation can be expressed as

Guest + Host ⇌ Comp

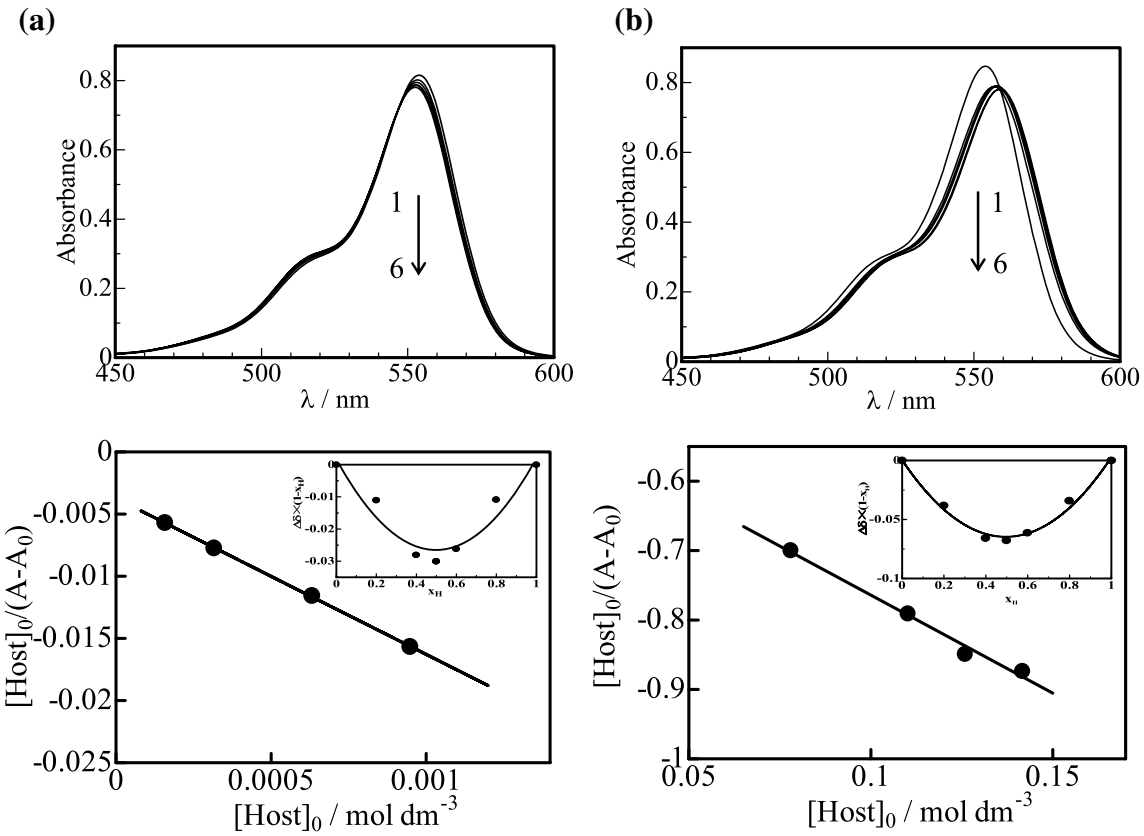

Fig. 2 Absorption spectra of RB in aqueous solution containing *a* β-CD and *b* DM-β-CD at 298 K: *a* $[\text{RB}]_0 = 7.8 \times 10^{-3}$ mM, $[\beta\text{-CD}]_0$ = (1) 0, (2) 0.16, (3) 0.32, (4) 0.63, (5) 0.95, and (6) 1.3 mM; *b* $[\text{RB}]_0 = 7.8 \times 10^{-3}$ mM, $[\text{DM-}\beta\text{-CD}]_0$ = (1) 0, (2) 0.79, (3) 0.94, (4) 1.1, (5) 1.4, and (6) 1.6 mM. *Down* Determination of inclusion complexation constants of RB with native and 2,6-methylated β-CDs. *Inset* Job's plots for the inclusion complexation of RB with β-CDs

$$K = \frac{[\text{Comp}]}{[\text{Guest}][\text{Host}]} \quad (1)$$

where Guest and Host denote rhodamines and β-CDs, respectively. Comp denotes the complex of rhodamines with β-CDs. Under the condition [Host] > > [Guest], the absorption spectral data in Fig. 2 were analysed according to the Benesi–Hildebrand equation for the 1:1 complex formation [17]:

$$\frac{[\text{Host}]_0}{(\text{A} - \text{A}_0)} = \frac{1}{\text{A}_\infty - \text{A}_0}[\text{Host}]_0 + \frac{1}{K[\text{A}_\infty - \text{A}_0]} \quad (2)$$

where A and A_0 are the absorption intensities. As shown in Fig. 2, a good linear relationship between $[Host]_0/(A - A_0)$ and $[Host]_0$ was obtained and the complexation constant K of inclusion complex could be determined from the slope and intercept in Eq. 2.

The K values obtained for the complexation of rhodamines with β-CDs at various temperatures are listed in Table 1. The K values for DM-β-CD are larger than those for native β-CD, except for the inclusion of RB. In DM-β-CD, methylation of the OH groups on the CD rim widens the hydrophobic environment around the cavity. An enhancement of the inclusion ability is responsible for larger K values in the case of DM-β-CD inclusion. In the case of the complexation of RB, the K values for native β-CD are larger than those for DM-β-CD, which is attributable to the difference in the inclusion complex structures, as explained in the next section.

Structures of inclusion complexes with β-CDs

ROESY-NMR experiments provide information on the position of the guest molecules in the CD cavity. Figure 3 shows the representative ROESY-NMR spectra of the inclusion complexes of rhodamine R110 with β- and DM-β-CDs. The ROESY-NMR spectra for the inclusion complexes of other rhodamines are shown in Figs. S2–S7 in the Supplementary Data. In R110/β-CD, cross peaks were detected between the inner C(3,5)-protons of the β-CD cavity and the C(1,4,5,8)-protons in the xanthenyl group: specifically, interactions between C(3)-H of β-CD and C(1,8)-H in the xanthenyl group, and between C(5)-H of β-CD and C(2,7)-H in the xanthenyl group were seen. Furthermore, there was no correlation with the protons of the phenyl group. These observations indicated that the xanthenyl group of R110 is encapsulated from the wide end of β-CD. In R110/DM-β-CD, the inner protons of DM-β-CD interacted with the C(3′,4′,5′,6′)-protons of the phenyl ring in R110, and cross peaks arising from the C(3,5)-protons of DM-β-CD and C(1,4,5,8)-protons of the xanthenyl group in R110 were also observed. As suggested above, the continuous variation method for the complexation of rhodamines with β- and DM-β-CDs suggests a 1:1 complex formation. Therefore, it is noteworthy that R110, which has two bulky functional groups, forms two group-in inclusion complexes, where either a phenyl or xanthenyl group is included in the DM-β-CD cavity (phenyl-in and xanthenyl-in complexes). On the basis of ESR experiments, Kotake and Janzen reported that a nitroxide radical having more than one bulky functional group forms two group-in inclusion complexes (bidirectional inclusion complexes) [18]. Furthermore, a few NMR and theoretical calculation studies on inclusion complexation with CDs assumed the presence of bidirectional inclusion complexes [19, 20], which is in agreement with our observations.

The relative intensities of the cross peaks for the inclusion complexes of rhodamines with β- and DM-β-CDs are listed in Table S1 (Supplementary Data). In the inclusion of TMRM and R123 by β-CD, cross peaks of the C(1,2,4,5,7,8)-protons of rhodamines with the inner C(3,5)-protons of β-CD were observed, while no interaction between the protons of the phenyl group in the rhodamines and the C(3,5)-protons of β-CD was detected, indicating that the xanthenyl moiety of

Table 1 The complexation constants and thermodynamic parameters for inclusion complex formation of rhodamines with β-CDs

Guest	Host	10^{-2} K/M^{-1}			ΔH/kJ mol^{-1}	ΔS/kJ mol^{-1} K^{-1}
		288 K	298 K	308 K		
RB	β-CD	48.1 ± 1.0	33.6 ± 0.4	23.7 ± 0.5	− 26.2 ± 0.2	− 20.5 ± 0.7
RB	DM-β-CD	8.14 ± 0.04	5.83 ± 0.14	4.51 ± 0.04	− 21.8 ± 0.8	− 20.1 ± 2.7
TMRM	β-CD	13.9 ± 0.2	10.3 ± 0.2	7.93 ± 0.07	− 20.6 ± 0.1	− 11.5 ± 0.4
TMRM	DM-β-CD	55.5 ± 0.9	41.5 ± 0.6	31.2 ± 0.8	− 21.3 ± 0.2	− 2.23 ± 0.66
R110a	β-CD	1.40 ± 0.01	1.21 ± 0.03	–	− 10.6 ± 0.5	4.27 ± 1.61
R110	DM-β-CD	2.36 ± 0.05	2.06 ± 0.04	1.74 ± 0.05	− 11.3 ± 0.6	6.40 ± 2.11
R123	β-CD	2.46 ± 0.03	2.06 ± 0.02	1.78 ± 0.03	− 11.9 ± 0.4	4.50 ± 1.27
R123	DM-β-CD	12.1 ± 0.1	9.91 ± 0.07	8.05 ± 0.16	− 15.1 ± 0.3	6.50 ± 0.96
R101	DM-β-CD	7.66 ± 0.15	6.85 ± 0.09	6.36 ± 0.05	− 6.88 ± 0.45	31.3 ± 1.5

[a]The K values for the inclusion complexation of R110 with β-CD were determined at 288, 293, and 298 K because the complexation constants with CDs decreases with increasing temperature: K (293 K) = 1.29 ± 0.03 M^{-1} for the complexation of R110 with β-CD

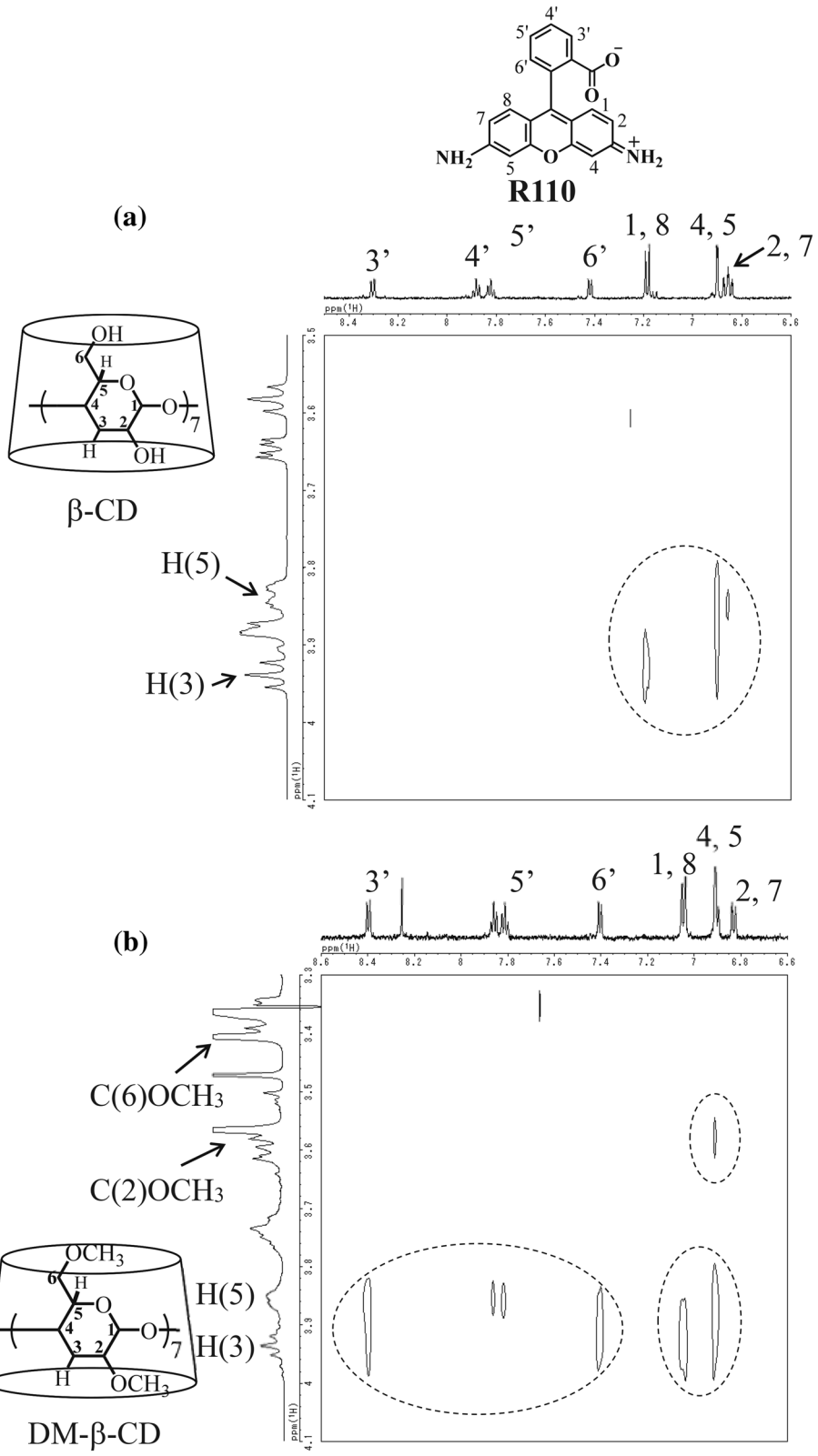

Fig. 3 The fragments of ROESY-NMR spectra for the inclusion complexes of R110 with *a* β-CD and *b* DM-β-CD in D_2O-CD_3CD (9:1, v/v) mixture: $[R110]_0 = 1.0$ mM, $[\beta\text{-CD}]_0 = 3.0$ mM, and $[\text{DM-}\beta\text{-CD}]_0 = 2.9$ mM

the rhodamines is encapsulated in the β-CD cavity (Figs. S3 and S5). In the inclusion of TMRM and R123 by DM-β-CDs, the inner protons of DM-β-CD interacted with the protons of both the phenyl and xanthenyl groups in the rhodamines (Figs. S4 and S6). These observations indicated that the inclusion modes of TMRM and R123 are similar to that of R110.

In RB/β-CD, cross peaks between the C(5)-proton of β-CD and C(1,4,5,8)-protons of RB were detected, and the interaction of the C(3,5)-proton of β-CD with the -$N(CH_2CH_3)_2$ protons of RB was observed (Fig. S1). These observations indicated that the -$N(CH_2CH_3)_2$ group of RB is included from the narrow end of β-CD. In RB/DM-β-CD, cross peaks corresponding to the protons of bidirectional complexes were observed, in analogy with the R110/DM-β-CD complex. Furthermore, the -$N(CH_2CH_3)_2$ protons strongly interacted with the C(2)OCH_3 protons on the DM-β-CD rim (Fig. S2), indicating that the -$N(CH_2CH_3)_2$ group of RB is located at the narrow end of the DM-β-CD.

In the inclusion of R101 by β- and DM-β-CDs, cross peaks arising from the protons of R101 and the inner protons of β-CD were not observed, and the C(1,8)- and $N(CH_2CH_3)_2$-protons of R101 strongly interacted with the inner C(3)-proton of DM-β-CD (Fig. S7 and S8, Table S1 in Supplementary Data). These observations revealed that a part of the xanthenyl ring in R101 is encapsulated into the DM-β-CD cavity. Based on the NMR results, the plausible structures for the inclusion complexes of RB, R110, and R101 with β- and DM-β-CDs are proposed, as depicted in Fig. 4.

Thermodynamic parameters for inclusion

To obtain additional information on the inclusion of rhodamines with β-CDs, the thermodynamic parameters (enthalpy and entropy changes (ΔH and ΔS)) for the inclusion process were determined from van't Hoff plots by using the complexation constants K of inclusion complexes. The obtained values are listed in Table 1. A linear relationship between the ΔH and ΔS values is obtained for the inclusion complexation of rhodamines with native β-CD (Fig. 5), suggesting that a single mechanism operates in the inclusion process [21]. In the R101 inclusion by DM-β-CD, a large shift from the above linear relationship is obtained, which is ascribed to the difference in the free-energy changes for inclusion processes, as expected from the difference in the structures of the inclusion complexes (Fig. 4). In the inclusions of RB, TMRM, R123, and R110 by DM-β-CD, the ΔH-ΔS plot is considerably scattered (Fig. 5).

As suggested above, the four rhodamines form bidirectional inclusion complexes with DM-β-CD. The equilibria for the group-in inclusion complex formation are expressed as follows:

$$\text{Guest} + \text{DM-}\beta\text{-CD} \rightleftharpoons \text{xanthenyl-in, complexation constant } K_1$$

$$\text{Guest} + \text{DM-}\beta\text{-CD} \rightleftharpoons \text{phenyl-in, complexation constant } K_2$$

$$K = \frac{[\text{group-in}]}{[\text{Guest}][\text{DM-}\beta\text{-CD}]} = \frac{[\text{xanthenyl-in}] + [\text{phenyl-in}]}{[\text{Guest}][\text{DM-}\beta\text{-CD}]} = K_1 + K_2 \quad (3)$$

The formation of bidirectional inclusion complexes suggests that the apparent complexation constant K is composed of two group-in inclusion equilibria, which would be responsible for scattering in the ΔH–ΔS competitive relationship.

Fluorescence quantum yields of rhodamine complexes

Rhodamines have a fluorescence efficiency close to 100%, but the fluorescence is strongly quenched in polar solvents such as water [22, 23]. Measurement of the quantum yield (ϕ) of inclusion complexes is useful for understanding the inclusion behaviour. The ϕ values of the inclusion complexes are determined on an Otsuka fluorescence spectrometer and are expressed by the following equation:

$$\phi = \frac{\text{FP}_{\text{complex}}}{\text{AP}_{\text{complex}}} = \frac{\text{FP} - \text{FP}_{\text{guest}}}{\text{AP} - \text{AP}_{\text{guest}}} \quad (4)$$

where FP and AP denote the fluorescence and excitation photon numbers of the inclusion complexes, free rhodamines (guest) and apparent solutions, respectively. The FP and AP values of the apparent and guest solutions were measured, and the concentration of the free guest rhodamine was estimated using the complexation constants K of inclusion complexes in Table 1. The obtained ϕ values are listed in Table 2 and can be summarized as follows: the ϕ values decrease in the order of $\phi_{\text{free}}(\text{R110}) \approx \phi_{\text{free}}(\text{R123}) > \phi_{\text{free}}(\text{TMRM}) > \phi_{\text{free}}(\text{RB})$. The electron donor capability of the amino groups in the xanthenyl ring increases in the order of $NH_2 < N(CH_3)_2 < N(C_2H_5)_2$, as can be seen from the decrease of the ionization potential (IP) values ($NH_2 > N(CH_3)_2 > N(C_2H_5)_2$) [24]. Electron transfer from the amino groups plays an important role for the determination of ϕ values. In RB and TMRM, ϕ values are decreased by inclusion of β- and DM-β-CDs and the effects of CD inclusion on ϕ values become large as the donor capability of amino groups increases. In the R101/DM-β-CD inclusion, the effect of inclusion on ϕ value is not observed, which is attributable to the difference in binding modes of inclusion complexes (inclusion of the rigid amino group by DM-β-CD). The ϕ values of R110 with –COOH in the phenyl group is comparable to that of R123 with –COOMe, suggesting that the inductive effect of –COOMe through the phenyl group is insensitive to the radiative process.

Albeloa et al. suggested that the fluorescence quantum yield of rhodamines is strongly reduced by the formation of a twisted conformation in the excited state (non-radiative deactivation process) [23]. Our observations indicate that the inclusion of RB and TMRM having bulky

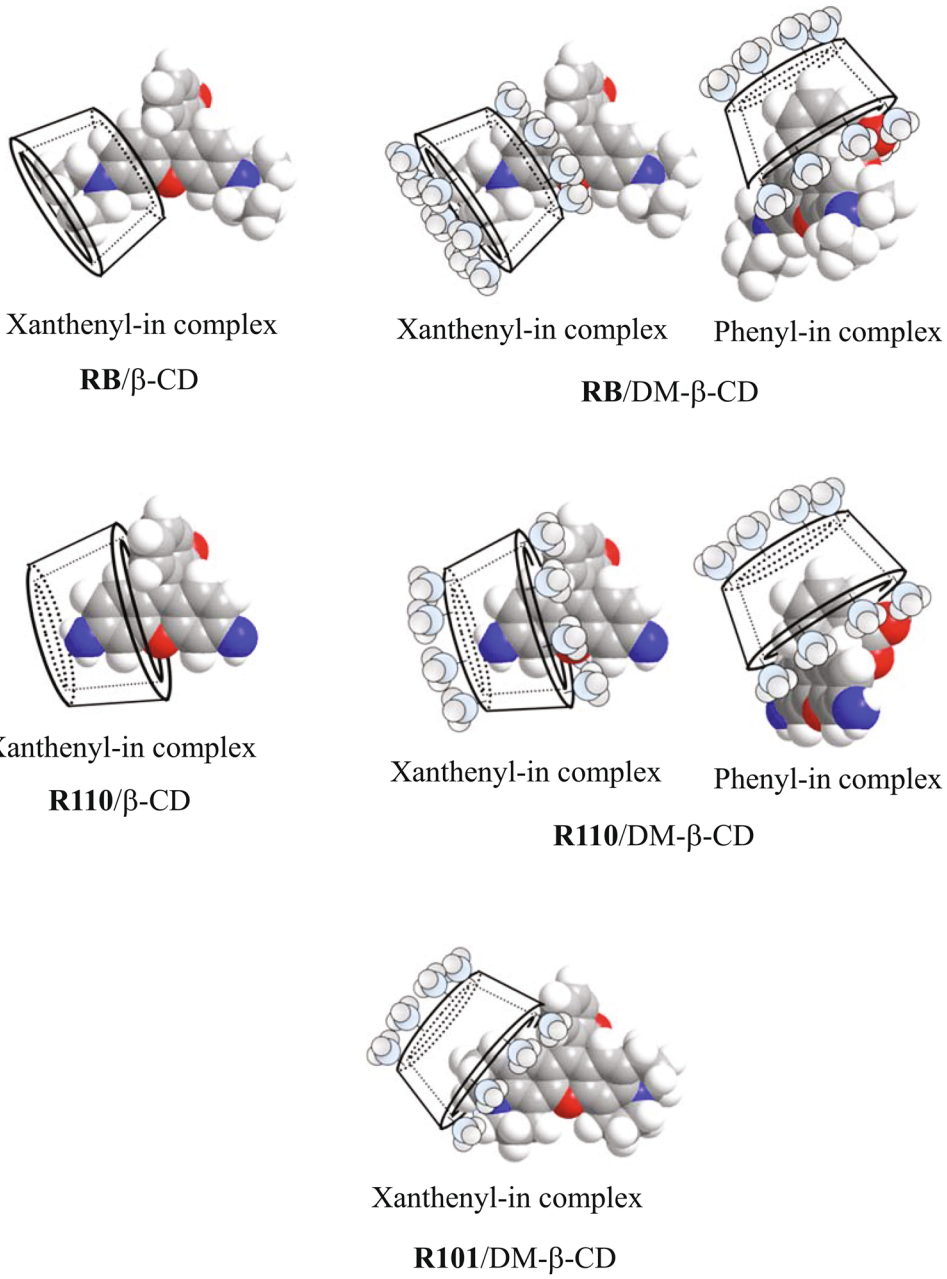

Fig. 4 Plausible structures of the inclusion complexes of RB, R110, and R101 with β- and DM-β-CDs

amino-substituents favours the formation of twisted non-radiative structure, resulting in decrease of ϕ values.

In summary, the complexation constants and fluorescence quantum yields of inclusion complexes were determined for the inclusion complexes of substituted rhodamines with native and 2,6-methylated β-CDs. The thermodynamic parameters and ROESY-NMR spectra of the inclusion complexes of rhodamines with DM-β-CD showed the formation of bidirectional inclusion complexes. It was found that the inclusion of rhodamines having bulky amino-substituents on the xanthenyl ring favours the formation of the twisted excited state, resulting in a decrease in ϕ values. These results provide useful insights for functional group recognition of native and 2,6-methylated β-CDs.

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Table 2 Quantum yields $\phi_{complex}$ of inclusion complexes between rhodamines and β-CDs in aqueous solution at 298 K

Guest	Host	$\phi_{free\ and\ complex}$	$\phi_{complex}/\phi_{free}$
RB	–	0.200 ± 0.003	
RB	β-CD	0.0976 ± 0.0013	0.49
RB	DM-β-CD	0.142 ± 0.001	0.71
TMRM	–	0.260 ± 0.003	
TMRM	β-CD	0.188 ± 0.003	0.72
TMRM	DM-β-CD	0.176 ± 0.005	0.68
R110	–	0.626 ± 0.007	
R110	β-CD	0.628 ± 0.006	1.0
R110	DM-β-CD	0.569 ± 0.007	0.91
R123	–	0.614 ± 0.005	
R123	β-CD	0.608 ± 0.009	0.99
R123	DM-β-CD	0.595 ± 0.008	0.97
R101	–	0.495 ± 0.006	
R101	β-CD	–	–
R101	DM-β-CD	0.508 ± 0.004	1.03

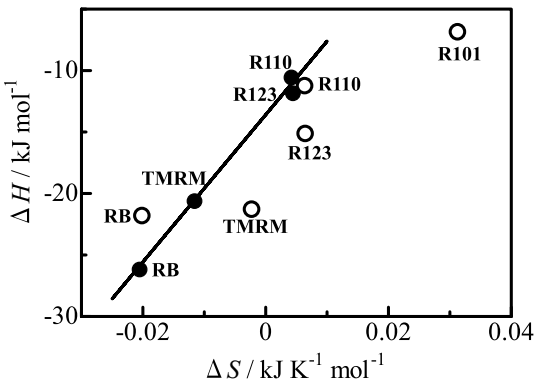

Fig. 5 Relationship between ΔH and ΔS for the inclusion complexation of rhodamines in aqueous solution. Filled circle: β-CD and open circle: DM-β-CD

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