

Dependence of the optical absorption and Na⁺ binding energies of coumarin-crown ethers on the size and attachment position of ether ring: density functional investigation

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Abstract The crowned coumarin complexes are well known compounds for their ion recognition abilities. They undergo photophysical changes upon cation binding. On the basis of density functional theory calculations, we examined the sodium cation (Na⁺) binding energies of coumarin-crown ethers based on 15-Crown-5 (15 C5) and 18-Crown-6 (18 C6) as well as the optical absorptions of coumarin-crown ethers based on 12-Crown-4 (12 C4), 15 C5 and 18 C6. We explored why the attachment of crown ether ring to coumarin affects the Na⁺ binding energies of coumarin-crown ethers and also why the optical absorption of coumarin is modified by the crown ethers. Our study reveals that the Na⁺ ion binding energies of coumarin-crown ethers depend strongly on the size of the crown ether ring and also on the attachment position of the ether ring on coumarin. These factors affect the intramolecular charge transfer and overall stability of the complexes. The absorptions of the coumarin and ether ring parts of coumarin-crown ether are red shifted from those of isolated coumarin and crown ether, respectively. The red-shift of the coumarin ester group absorption is much stronger depending on the attachment position of the ether ring to coumarin. The absorption intensity of the coumarin part in coumarin-crown ethers is reduced for the benzene group absorption, but is enhanced for the ester group absorption.

Keywords Coumarin · Crown ethers · DFT · TDDFT · UV

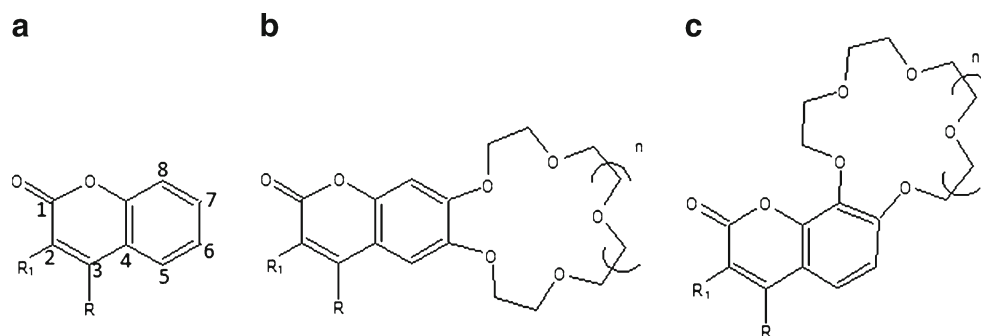
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Introduction

Crown ethers form stable complexes with metal cations in solid state and in solution, and the removal of complexed metal ions occur at temperatures over 200 °C. Crown ethers [1, 2] have received much attention due to their ability to bind metal cations in solution and hence have a very wide range of industrial and biological applications. These include chromatography, isolating radioactive components in nuclear wastes, phase transfer catalysis, solvation of ions in nonpolar solvents, and stabilization of cation action sites in biological molecules, to name a few [3–5]. There are many aspects of crown ethers that determine selectivity, such as the size of the ether ring as well as the nature and arrangement of the groups attached to the ring [6]. Coumarins (Fig. 1a) are important π -conjugated natural products with numerous applications due to their optical properties [7, 8]. Crown ethers fused with coumarins (hereafter, coumarin-crown ethers, see Fig. 1b and c) were synthesized by Erk et al. [9] in an attempt to improve the cation selectivity of crown ethers and modify the optical properties of coumarins. Coumarin-crown ethers are soluble in CHCl₃ and CH₂Cl₂, but their cation-extracting ability is stronger in aqueous media [10, 11]. Due to their ability to dissolve in nonpolar solvents, coumarin-crown ethers can be used as phase transfer carriers. The cation selectivity of crown ethers in solution is generally governed by the size match between the metal cation and the crown cavity, but the size matching is not the only factor affecting the metal-ion binding energies according to gas phase studies [12, 13]. In our previous computational study [14], we examined the optical properties and the alkali ion (Li⁺, Na⁺, K⁺) selectivity of various coumarin-crown ethers in the gas phase and in acetonitrile but did not explore why coumarin affects the alkali ion binding energy of coumarin-crown ethers and also why the optical absorption of coumarin is modified by the

Fig. 1 **a** Coumarin. **b** Coumarin-crown ethers fused at the (6,7) coumarin carbons. **(c)** Coumarin-crown ethers fused at the (7,8) coumarin carbons. The $n=0, 1$ and 2 lead to 12 C4, 15 C5 and 18 C6 frameworks, respectively



crown ethers. In the present study, we investigate these questions on the basis of first-principle density functional calculations by studying the Na^+ ion binding energies of some coumarin-crown ethers (see below). For the purpose of comparison, we also examine the Na^+ ion binding energies of crown ethers (15 C5 and 18 C6), crown ethers fused with benzene ring (hereafter B-15 C5 and B-18 C6) and coumarin-crown ethers. (For the sake of convenience, we represent the coumarin with R_1 and R_2 substituents that has crown ether ring attached at the (6,7) and (7,8) positions will be respectively indicated by adding the terms $\text{C}_{(\text{R}_1, \text{R}_2, 6)}$ and $\text{C}_{(\text{R}_1, \text{R}_2, 7)}$ in front of the ether name. For example, $\text{C}_{(\text{H}, \text{CH}_3, 7)}$ -15 C5 is a coumarin-crown ether in which the coumarin with $\text{R}_1 = \text{H}$ and $\text{R}_2 = \text{CH}_3$ has the 15 C5 crown ether attached at the (7,8) position. In addition, we examine how the Na^+ ion binding energies and the optical absorption of coumarin-crown ethers are affected by the attachment positions of the crown ether ring on the coumarin C atoms.

Methods

The coumarin-crown ethers studied in this work are specified in Table 1, and their IUPAC names are provided in Supplementary information. Geometry optimizations were performed using the DFT method [15–17] with the B3LYP functional [18] and the 6-31 g(d) basis set [19] implemented in Gaussian 2003 software package [20]. The geometries of crown ethers, coumarin-crown ethers and coumarin-crown ethers complexed with metal cations were optimized. The alkali cation binding energies (ΔE) of coumarin-crown ether was calculated as follows:

$$\Delta E = E_{\text{ML}} - E_{\text{M}} - E_{\text{L}}, \quad (1)$$

where M refers to a Na^+ cation, L to a coumarin-crown ether, and ML to the coumarin-crown ether with a bound Na^+ cation (Fig. 2). In calculating ΔE , single-point energy calculations were carried out with the 6-31 + g(d) basis set using the geometries optimized from the 6-31 g(d) basis set calculations. The basis set superposition error (BSSE) was

estimated on the basis of the counterpoise method using the 6-31 + g(d) basis set.

To obtain the UV spectra of coumarin, crown ethers and coumarin-crown ethers, their excited state structures were optimized and the energies of their 20 lowest-lying states were calculated by employing the time-dependent DFT (TDDFT) method [21, 22] with the same basis set used for the geometry optimizations. To plot the theoretical spectra, the oscillator strengths of the electronic transitions were scaled to 1 and to each frequency, a Gaussian curve was fitted and the curves were connected to obtain the final spectra, which were then compared with the available experimental spectra in the literature [9]. The gas phase calculations were repeated in acetonitrile solvent by using the IEF-PCM (integral equation formalism polarized continuum model) solvent method [23].

Binding energy

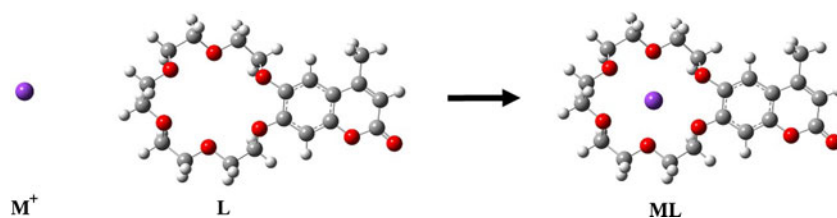
The optimized structures of the crown ethers and their Na^+ ion complexes are depicted in Supplementary information. The Na^+ ion binding energies calculated for some crown ethers are summarized in Table 2, which shows that the Na^+ ion binding energies decrease in the following order:

$$\begin{aligned} 18\text{C6} > \text{B} - 18\text{C6} > \text{C}_{(\text{H}, \text{CH}_3, 7)} - 18\text{C6} \\ > \text{C}_{(\text{H}, \text{CH}_3, 6)} - 18\text{C6} \gg 15\text{C5} > \text{B} - 15\text{C5} \\ > \text{C}_{(\text{H}, \text{CH}_3, 7)} - 15\text{C5} > \text{C}_{(\text{H}, \text{CH}_3, 6)} - 15\text{C5} \end{aligned} \quad (2)$$

Table 1 Oxygen ring sizes of the crown ethers and substituents R_1 and R_2 of the coumarin in various coumarin-crown ethers investigated

	O-ring	R_1	R_2		O-ring	R_1	R_2
5 g	4	H	CH_3	6 g	4	H	CH_3
5 h	5	H	CH_3	6 h	5	H	CH_3
5 i	6	H	CH_3	6 i	6	H	CH_3
5 k	5	H	H	6 k	5	H	H
5 l	6	H	H	6 l	6	H	H

Fig. 2 Schematic representation of the metal-cation (M^+) binding reaction, where L refers to coumarin-crown



This sequence indicates that the 18 C6 crown ring is more flexible than the 15 C5 crown ring in binding a Na^+ ion. When a benzene ring or a coumarin is attached to a crown ring, the flexibility of the crown ring is decreased so that the Na^+ ion binding energy decreases. Since coumarin is larger in size than benzene, the attachment of coumarin reduces the binding energy more than does that of benzene. According to Eq. 2, the flexibility of a crown ether ring is reduced more when the ether ring attached at the (6,7) positions than at the (7,8) positions of coumarin. These observations are also supported in terms of the available experimental binding energies as summarized in Table 2.

We note that there exists an electronic factor reducing the Na^+ ion binding energies in coumarin-crown ethers. As compared in Table 3, the total charge on the oxygen atoms of the ether rings is reduced (by nearly $0.8 e^-$ per ether ring) when the ring has coumarin attached, which reduces the ionic interaction of a Na^+ ion with the ring oxygen atoms and hence reduces the Na^+ ion binding energy. According to Table 3, one might expect that such a decrease in the binding energy will be slightly

larger for the (7,8) than for the (6,7) ring attachment, but the binding energies calculated for the (7,8) and (6,7) attachments exhibit the opposite trends (Eq. 2). This indicates the effect of the flexibility loss is more important than the charge loss from the ether ring.

Absorption spectra

The absorption spectra calculated for $C_{(H,CH_3,7)}$ -12 C4 and $C_{(H,CH_3,6)}$ -12 C4 are presented in Fig. 3a, those for $C_{(H,CH_3,7)}$ -15 C5 and $C_{(H,CH_3,6)}$ -15 C5 in Fig. 3b, and those for $C_{(H,CH_3,7)}$ -18 C6 and $C_{(H,CH_3,6)}$ -18 C6 in Fig. 3c. Crown ethers 12 C4, 15 C5 and 18 C6 show absorption peak below 200 nm. With respect to this peak, the absorption peaks associated with the crown rings of coumarin-crown ethers are red shifted (Fig. 3). Coumarin has strong absorptions centered around ~ 180 and ~ 200 nm (originating essentially from the absorption of the conjugated benzene ring) as well as weaker absorptions centered around ~ 270 and ~ 290 nm (originating essentially from the ester group). With respect to these peaks, the absorption peaks associated with coumarin parts of coumarin-crown ethers are red shifted and the extent of the red shift is larger for the (6,7) attachment than for the (7,8) attachment of the ether ring to coumarin. The attachment of the ether ring at the (6,7) positions of coumarin red shifts more than does that of the ether ring at the (7,8) positions,

Table 2 Calculated and experimental (ref. [9]) Na^+ ion binding energies (in $kcal\ mol^{-1}$) of various crown ethers

Coumarin-crown ^a	$\Delta G_{\text{experimental}}$ (kJ/mol) at 298 K	Binding energy (kcal/mol)
(a) Coumarin-crown ethers		
6 h $\equiv C_{(H, CH_3, 7)}$ -15 C5	-2.69	-84.05
5 h $\equiv C_{(H, CH_3, 6)}$ -15 C5	-2.16	-83.19
6i $\equiv C_{(H, CH_3, 7)}$ -18 C6	-5.55	-98.93
5i $\equiv C_{(H, CH_3, 6)}$ -18 C6	-2.88	-96.24
(b) Crown ethers and benzene-crown ethers		
15 C5	-3.43	-91.52
B-15 C5	-2.88	-86.03
18 C6	-3.43	-103.59
B-18 C6	-2.93	-100.91

^a See Fig. 1b and c for the definition

Table 3 Calculated total charges on the crown ether oxygen atoms

Crown ether	Total charge (esu)
15 C5	-2.45
B-15 C5	-2.38
$C_{(H,CH_3,6)}$ -15 C5	-1.82
$C_{(H,CH_3,7)}$ -15 C5	-1.68
18 C6	-2.87
B-18 C6	-2.78
$C_{(H,CH_3,6)}$ -18 C6	-2.11
$C_{(H,CH_3,7)}$ -18 C6	-2.08

Fig. 3 Calculated absorption spectra (in the 100–400 nm region) of coumarin, crown ethers and coumarin-crown ethers in acetonitrile: **a** Coumarin, 12 C4, $C_{(H,CH_3,7)}$ -12 C4 and $C_{(H,CH_3,6)}$ -12 C4. **b** Coumarin, 15 C5, $C_{(H,CH_3,7)}$ -15 C5 and $C_{(H,CH_3,6)}$ -15 C5. **c** Coumarin, 18 C6, $C_{(H,CH_3,7)}$ -18 C6 and $C_{(H,CH_3,6)}$ -18 C6

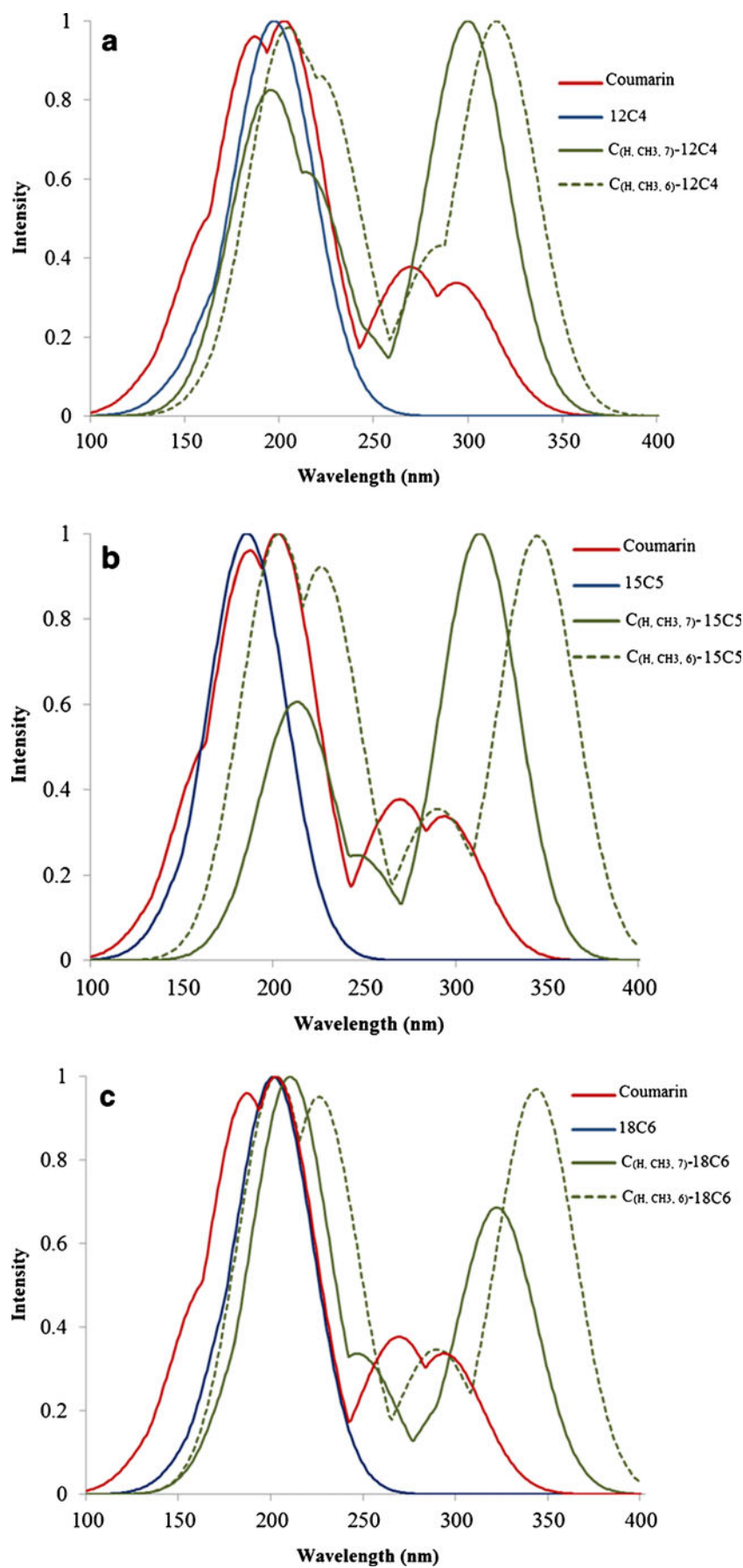


Table 4 The gas phase maximum absorption wavelengths (in nm)

	Experimental ⁹	This work ^a		Experimental ⁹	This work ^a
C _(H,H,7) -15 C5	314	311 (299)	C _(H,H,6) -15 C5	342	347 (334)
C _(H,H,7) -18 C6	313	324 (299)	C _(H,H,6) -18 C6	342	347 (334)
C _(H,CH3,7) -15 C5	313	313 (297)	C _(H,CH3,6) -15 C5	340	344 (329)
C _(H,CH3,7) -18 C6	314	322 (298)	C _(H,CH3,6) -18 C6	323	344 (322)

^a The numbers in the parentheses refer to those calculated for acetonitrile solvent

because the attachment at the (7,8) positions leads to stronger interactions of the coumarin π -orbitals with the lone-pair orbitals of the two O atoms attached to the coumarin benzene ring. We note that the absorption peaks of coumarin-crown ethers associated with the benzene ring absorption show weaker absorption intensity than do those associated with the ester group absorption.

The λ_{\max} values of the ester group absorption peaks in coumarin-crown ethers calculated for the gas phase and acetonitrile solvent are compared with the available experimental values determined in acetonitrile solvent (Table 4). As should be expected, the λ_{\max} values calculated for acetonitrile solvent are in better agreement with experiment. As already pointed out, the coumarin-crown ethers with ether rings attached at the (6,7) positions have substantially larger λ_{\max} values than do those with ether rings attached at the (7,8) positions, because the (6,7) attachment provides a stronger interaction between the coumarin π -orbitals and the lone-pair orbitals of the crown ether O atoms. This is indeed the case as can be seen from Table 2.

Concluding remarks

Our DFT study shows that the Na⁺ ion binding energies of coumarin-crown ethers are significantly affected by the size of the crown ether ring and also by the attachment position of the ether ring on coumarin; the binding energies decrease in the order, 18 C6 > C_(H,CH3,7)-18 C6 > C_(H,CH3,6)-18 C6 > 15 C5 > C_(H,CH3,7)-15 C5 > C_(H,CH3,6)-15 C5. The optical absorptions of a coumarin-crown ethers show that the absorptions of the coumarin and ether ring parts are red shifted from those of isolated coumarin and crown ether, respectively. The absorptions of the coumarin part are affected such that the absorption intensity is reduced for the benzene ring absorption, but is enhanced for the ester group absorption. In addition, the red-shift of the ester group absorption of the coumarin moiety is much larger for the (6,7) than for the (7,8) attachment of the ether ring.

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