



Tautomeric chromoionophores derived from 1-aryloxyanthraquinones and 4'-aminobenzo-15-crown-5 ether: Sandwich complex formation enhanced by interchromophoric interactions



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ABSTRACT

A series of tautomeric chromoionophores were prepared photochemically from 1-aryloxyanthraquinones and 4'-aminobenzo-15-crown-5 ether. All the synthesized dyes can bind strontium and barium cations as sandwich-type 2:1 ligand–metal complexes that show higher stability constants ($K_{2:1}$) than the corresponding 1:1 complexes ($K_{1:1}$), the $K_{2:1}/K_{1:1}$ ratio reaching a value of 10 (in MeCN). The inverse relation, i.e. $K_{2:1} < K_{1:1}$, is observed for the related complexes of unsubstituted benzo-15-crown-5 ether. The sandwich complexes were studied by spectrophotometry, ¹H NMR spectroscopy, mass spectrometry, and density functional theory calculations. A correlation was found between the $K_{2:1}/K_{1:1}$ ratio and the number of short stacking contacts in the sandwich complex.

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1. Introduction

The optical properties of tautomeric dyes, dependent on the ratio of tautomeric forms, can be affected by various factors, such as solvent polarity, pH, aggregative state, and photoexcitation.¹ Rational integration of an ionophore into a tautomeric dye can lead to a compound with ion-controllable optical characteristics. Crown ethers are well known as selective ligands for alkali and alkaline-earth metal cations.² They are widely used as building blocks in the design and synthesis of various functionalized compounds, such as photocontrolled molecular receptors^{3–5} and optical molecular sensors (chromo- and fluoroionophores).^{4,6,7} Among the variety of chromogenic crown compounds reported in the literature, there are very few examples of tautomeric dyes that can operate as optical sensors for metal ions.^{8–12}

Imine derivatives of 1-hydroxyanthraquinone are known to undergo prototropic tautomerization to exist as an equilibrated mixture of the imine and enamine isomers both in solution and in

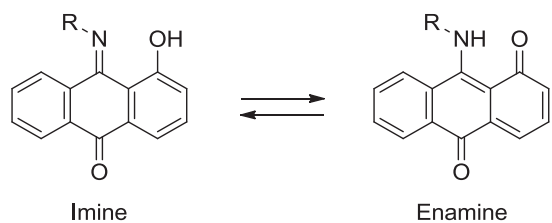
the solid state (Scheme 1).^{13,14} Recently, we reported the synthesis of a 1-hydroxyanthraquinone-9-imine derivative containing a benzo-18-crown-6 ether moiety.¹⁵ The tautomeric equilibrium of this dye was found to shift toward the imine form in the presence of alkaline-earth metal cations.

It is well known that 15-crown-5 ethers are able to form sandwich-type 2:1 complexes with relatively large metal ions, such as K⁺, Sr²⁺, and Ba²⁺.^{16,17} This feature has been utilized in the design of various ion-selective molecular devices.¹⁸ The sandwich complexes of aromatic crown ethers can have an enhanced stability owing to weak stacking interactions.^{19,20} For crown ether dyes possessing extended π -systems, the effect of stacking interactions on the sandwich complex formation has been little-studied quantitatively.

Here we report on the synthesis of a series of five 1-hydroxyanthraquinone-9-imine dyes containing a benzo-15-crown-5 ether moiety. The complexation of these chromoionophores with alkali and alkaline-earth metal cations was comprehensively studied by spectrophotometry, ¹H NMR spectroscopy, mass spectrometry, and quantum chemical calculations. Particular attention was paid to the effect of interchromophoric interactions

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Scheme 1. Tautomerism of 1-hydroxyanthraquinone-9-imines.

on the thermodynamic stability of the 2:1 complexes of the dyes with Sr^{2+} and Ba^{2+} .

2. Results and discussion

2.1. Synthesis

Crown-containing 1-hydroxyanthraquinone-9-imine dyes **1** (Scheme 2) were synthesized photochemically according to the general procedure published previously.²¹ A benzene solution of photochromic 1-aryloxyanthraquinone **2** with aminobenzo-15-crown-5 ether **3** was exposed to sunlight for 6–8 h. The photoinduced migration of the aryl group in **2** resulted in the *ana*-quinoid isomer **4** possessing a high reactivity toward nucleophilic agents.¹³ The subsequent nucleophilic substitution of the aryloxy group in **4** by the arylamino group of **3** gave the desired products in 58–75% yields. The synthesis of dyes **1a**, **1d**, and **1e** is reported for the first time. Dyes **1b** and **1c**, as obtained by solid-state synthesis, have been described previously.²²

2.2. Spectrophotometric study

The complexation of dyes **1a–e** with alkali and alkaline-earth metal cations in MeCN was studied by spectrophotometric titration (SPT, see the Experimental). Fig. 1 shows the SPT data for **1a** and **1c** with $\text{Ca}(\text{ClO}_4)_2$ (similar data for dyes **1b**, **1d**, and **1e** are presented in Fig. S1).

Dye **1a** exhibits two broad absorption bands between 350 and 600 nm, assignable to the imine (416 nm) and enamine (464 nm)

tautomeric forms (Scheme 1).¹³ The absorption spectral changes observed on the addition of $\text{Ca}(\text{ClO}_4)_2$ suggest that the tautomeric equilibrium of **1a** shifts toward the imine isomer. This shift is attributable to the electron-withdrawal effect of the crowned metal ion on the amine nitrogen atom.¹⁵ The same conclusions about the coexistence of two prototropic tautomers and the nature of cation-induced spectral changes hold also for dyes **1b**, **1d**, and **1e**.

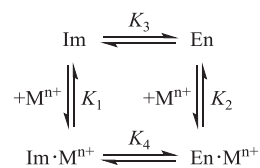
Dye **1c** unlike the others shows a single absorption band peaked at 497 nm, which implies that in MeCN this dye exists almost completely as a single tautomer, presumably, as the imine one. The binding of Ca^{2+} to the crown ether moiety of **1c** induces a hypsochromic shift of the absorption band, indicating a charge-transfer character of the lowest-energy excited state.

The complexation stoichiometry, the complex stability constants, and the absorption spectra of pure complexes for dyes **1** with metal cations were derived from SPT data using the global analysis methods described previously.²³ In most cases, the SPT data were well fitted to one equilibrium:

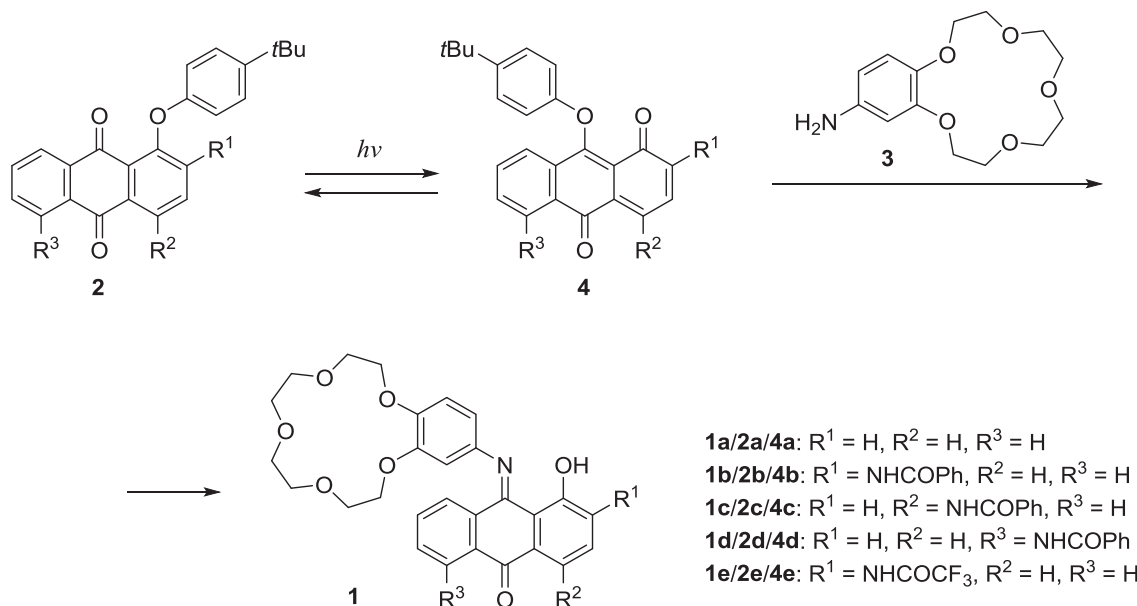


where L is the dye, M^{n+} is the metal ion, and $K_{1:1} = [\text{L} \cdot \text{M}^{n+}] / ([\text{L}][\text{M}^{n+}])$ is the stability constant of the 1:1 complex.

More rigorously, the 1:1 complexation of the tautomeric dyes should be described by a model involving four light absorbing components, the concentrations of which are determined by the following thermodynamic cycle:



where Im and En are the imine and enamine isomers of the dye, respectively, and K_1 – K_4 are the equilibrium constants. It is obvious that the concentration ratios $[\text{Im}]/[\text{En}]$ and $[\text{Im} \cdot \text{M}^{n+}]/[\text{En} \cdot \text{M}^{n+}]$ do not depend on the metal cation concentration; therefore, the system can be formally described by the equilibrium of Equation (1)



- 1a/2a/4a:** $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{H}$
1b/2b/4b: $\text{R}^1 = \text{NHCOPh}$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{H}$
1c/2c/4c: $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{NHCOPh}$, $\text{R}^3 = \text{H}$
1d/2d/4d: $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{NHCOPh}$
1e/2e/4e: $\text{R}^1 = \text{NHCOCF}_3$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{H}$

Scheme 2. Synthesis of dyes **1a–e**.

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