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The synthesis and spectral properties of an encapsulated aminoazobenzene dye

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ABSTRACT

An aminoazobenzene dye rotaxane containing *N*,*N*-dimethylamino end groups in the presence of α-cyclodextrins was synthesized and its UV–visible spectral properties investigated as a function of pH. The rotaxane structure was characterized using ^{1}H NMR and 2D COSY NMR. The azo dye rotaxane exhibited enhanced polarity and was soluble only in polar solvents, displaying good solubility in water. The formation of the rotaxane structure did not interfere with the protonation of the threaded aminoazobenzene dye. In a sol–gel film coating the azo dye rotaxane exhibited pH sensitivity under neutral to acidic conditions in a reversible and reproducible manner.

1. Introduction

A rotaxane is a dumbbell-like shaped, supramolecular assembly which has a macrocycle around the molecular axis. It is commonly formed when rod-like molecules thread the cavities of macrocycles and bulky terminal groups on both sides prevent the threaded molecule from escaping [1,2]. Cyclodextrins (CDs) are cyclic oligosaccharides consisting of 6-(α-CD), 7-(β-CD) or 8-(γ-CD) glucose units, and have been studied extensively as a host molecule in supramolecular chemistry [3]. CDs have a conical shape with the primary hydroxyl groups on the narrow side of the torus glucose residues and the secondary hydroxyl groups on the wider side. They have a hydrophobic interior and a hydrophilic exterior, and are widely used as hosts for various organic molecules including polymers [1,4]. Several azo dye rotaxanes have been synthesized using hydrophobicity to direct rotaxane formation [5], in which cyclophane and α- and β-CD were used as macrocycles. In these crystal structures, the macrocycle was found to embrace the center of the azo dye [6]. CD can act as a protective sheath for an azo dye by including its chromophore inside the cavity. An azo dye rotaxane has been synthesized as a single stereoisomer, with the 2,3-rims of both CDs pointing outwards [7]. It was also reported that rotaxane-encapsulation enhances the stability of an azo dye without preventing the dye from binding to the surface of textile fibers [8]. When cellulosic fibers were dyed using a chlorotriazine-functionalized azo dye rotaxane, the stability of the ensuing dyeing to bleach was dramatically increased.

However, despite earlier studies [5–8], there have been no reports on the effect of CD macrocycle on the color of threaded azo dyes. In the present study, an azo dye rotaxane having *N*,*N*-dimethylamino end groups in the presence of α-cyclodextrin (Fig. 1) was synthesized and its spectral properties with a view to pH indicating behavior were investigated. The structure was characterized using ^{1}H NMR and 2D COSY NMR techniques and the changes in spectroscopic properties of the aminoazobenzene dye with the rotaxane formation were examined by UV–visible spectroscopy under different pH conditions. Also, the sol–gel film coating doped with **3** was prepared, and its sensitivity to various pH values was measured at room temperature.

2. Experimental

2.1. Materials

The chemicals used in the synthesis and purification of azo dye rotaxane were *N*,*N*-dimethyl-1-naphthylamine, α-cyclodextrin, sodiumsulfidenonahydrate, sodium(anilinomethane)sulfonate, ethanol, HCl (37%), $NaNO_2$, sodium acetate, toluene, hexane,

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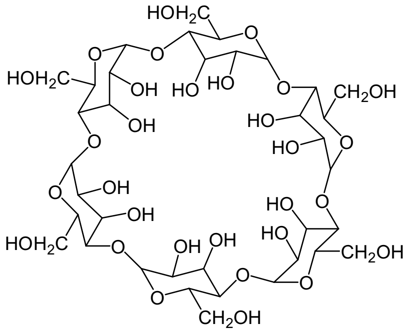


Fig. 1. Chemical structure of α-cyclodextrin.

chloroform, silica, methylethylketone, ammonium hydroxide, 1-propanol, ethylacetate, $CDCl_3$ and DMSO-d_6. All chemicals used in the syntheses were of laboratory reagent grade.

2.2. Azo dye rotaxane synthesis

The rotaxanated azo dye was synthesized by following previous reports [5,7,8] and using *N*,*N*-dimethyl-1-naphthylamine as the coupling components (Scheme 1).

2.2.1. Sodium (4-((4-nitrophenyl)diazenyl)phenylamino)-methanesulfonate (**1**)

p-Nitroaniline (2.76 g, 0.02 mol) was suspended in water (10 ml) at 0–5 °C. HCl (35%, 4.4 ml, 0.05 mol) and $NaNO_2$ (1.38 g, 0.02 mol) were added slowly, and then the mixture was stirred for 1 h to complete diazotization. In order to prevent the triazine structure, sodium(anilinomethane)sulfonate was used as a coupling component [9] and then hydrolyzed under aqueous alkaline solution to form 4-((4-nitrophenyl)diazenyl)benzenamine.

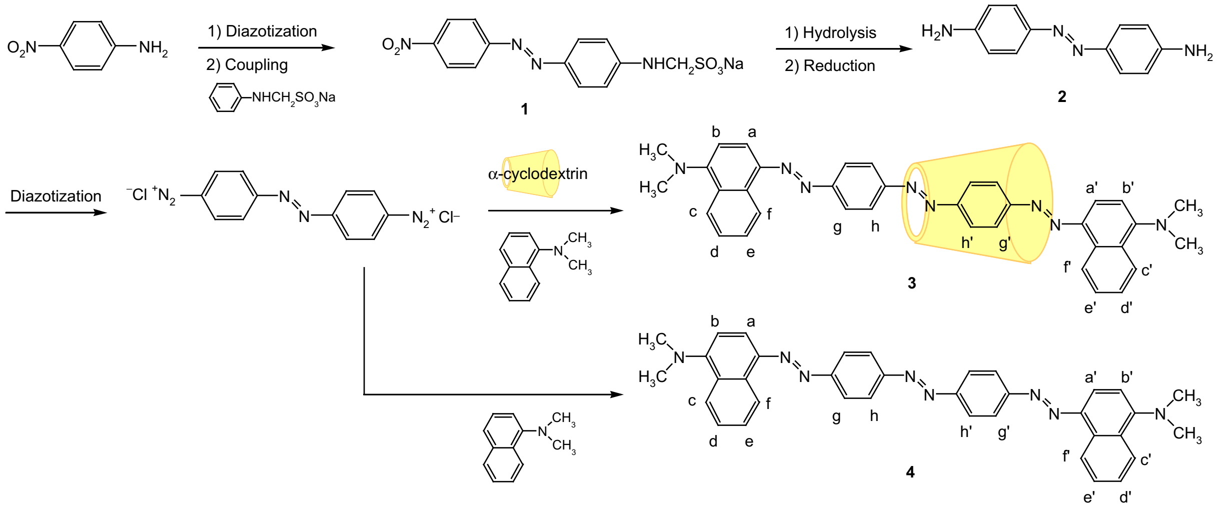
$NaHSO_3$ (2.08 g, 0.02 mol) was added to the solution of water (40 ml) and ethanol (50 ml), and then heated to 60 °C. After cooling the reaction mixture to room temperature, aniline (1.86 g, 1.82 ml, 0.02 mol) and HCHO (1.6 ml, 0.02 mol) were added to the solution, followed by stirring for 1 h. Then, the coupling solution was slowly added to the diazotization solution, and stirred at room temperature overnight. After reaction, the pH of the solution was adjusted to 5.0 by adding CH_3COONa, and the crude product was collected by filtration. The intermediate **1** was purified by recrystallization in ethanol (3.6 g, yield 50%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta_H = 8.4$ (d, 2H), 8.2 (d, 2H), 7.8 (d, 2H), 6.6 (d, 2H), and 5.2 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta_C = 158.5$, 150.6, 145.8, 141.0, and 75.0.

2.2.2. 4,4′-(Diazene-1,2-diyl)dibenzenamine (**2**)

The intermediate **1** was dissolved in 1% NaOH aqueous solution, which was then heated under reflux for 4 h. The solution was cooled to room temperature, and 4-((4-nitrophenyl)diazenyl)benzenamine was collected by filtration. The terminal nitro group was reduced using equivalent sodiumsulfidenonahydrate to have amino end groups at both ends [10]. 4-((4-Nitrophenyl)diazenyl)benzenamine (0.23 g, 1 mmol) was dissolved in ethanol (20 ml). $Na_2S \cdot 9H_2O$ (0.48 g, 2 mmol) in water (20 ml) was added dropwise, and then the combined solution was refluxed for 3 h. On completion of the reaction, the mixture was poured into cold water (100 ml). Precipitate 4,4′-(diazene-1,2-diyl)dibenzenamine (**2**), was filtered off, washed with water, and dried *in vacuo* (0.15 g, yield 65%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta_H = 7.7$ (d, 2H), 6.7 (d, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta_C = 148.0$, 140.5, 124.9, and 116.2.

2.2.3. Azo dye rotaxane (**3**)

The intermediate **2** (60 mg, 0.28 mmol) is suspended in ethanol and water at 0–5 °C. Dilute HCl (37%, 1.2 ml, 1.1 mmol) and $NaNO_2$ (41 mg, 0.59 mmol) solutions are added successively, and then the solution is stirred for 1 h to complete diazotization. α-CD (780 mg, 0.80 mmol) in water is added to above reaction mixture and stirred for 1 h at 0–5 °C. *N*,*N*-dimethyl-1-naphthylamine (96 mg, 0.56 mmol) is added dropwise and the mixture is stirred for 4 h at room temperature (Scheme 1). Dilute sodium acetate is added to increase pH up to 6.5, and dye precipitate is collected by filtering the solution. The rotaxanated dye (**3**) was purified by soxhlet extraction using hexane and chloroform, and then isolated by column chromatography on silica using methylethylketone/ammonium hydroxide/1-propanol (1/1/1 vol. %) as an eluent. The total yield was 30%. The ^{1}H NMR and 2D COSY NMR spectra are measured in solvents of $CDCl_3$ and DMSO-d_6 using Mercury Vx 300 (Varian, 300 MHz). ^{1}H NMR (300 MHz, DMSO-d_6): $\delta_H = 9.1$ (d, 1H), 9.0 (d, 1H), 8.5 (d, 2H), 8.2–8.1 (m, 6H), 8.0–7.9 (m, 4H), 7.6–7.7 (m, 4H), 7.2–7.1 (q, 2H), 5.3 (s, 6H), 5.2 (s, 6H), 4.7 (d, 6H), 4.3 (s, 6H), and 3.7–3.1 (m, 36H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta_C = 191.9$, 155.8, 152.7, 145.3, 142.3, 128.3, 126.5, 124.6, 124.0, 113.8, 102.8, 82.6, 73.8, 72.7, 72.1, 60.3, and 45.1; MALDI–TOF MS: m/z 1548.6, M^+.



Scheme 1. Synthesis of azo dye rotaxane (**3**) and free azo dye (**4**).

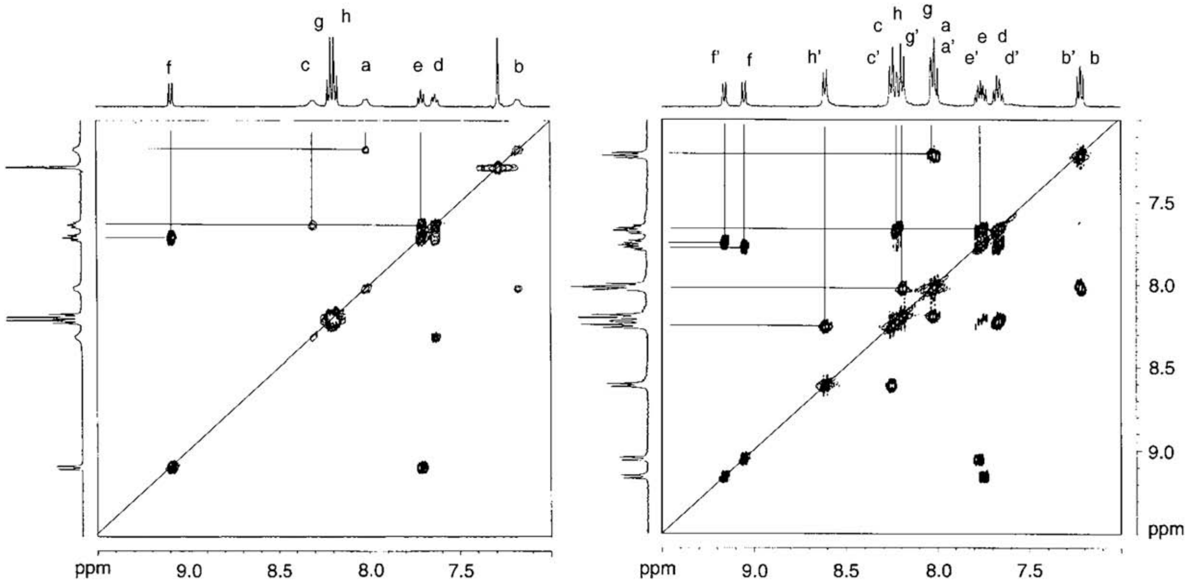


Fig. 2. 2D COSY ^{1}H NMR of **4** (free dye, left, $CDCl_3$) and **3** (rotaxanated dye, right, DMSO).

The free dye (**4**) was synthesized following the same routes, but without the addition of α-CD with an eluent of ethylacetate–toluene (1:6 v/v). The total yield was 70%. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta_H = 9.07$ (d, 2H), 8.2 (d, 2H), 8.1 (q, 8H), 7.9 (d, 2H), 7.6–7.5 (m, 4H), and 7.1 (d, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta_C = 154.2$, 147.5, 125.6, 123.5, 120.3, 115.3, and 44.0; MALDI–TOF MS: *m*/*z* 577.3 $(M+H)^+$.

2.3. Spectral properties measurement

In order to check the solubility changes, DMSO was used as solvent with the addition of different amount of water. The absorption spectra of each dye in DMSO/water mixed solvents were obtained at room temperature on a Lambda 7 (Perkin Elmer) UV–visible spectrophotometer in 1 cm cuvette. Absorbance at various pH values was measured in ethanol/water mixed solvent. The temperature of 298 K was maintained by a thermostatted cell holder.

2.4. Sol–gel film preparation

In a typical preparation of sol–gel coating film [11,12], 20 mg of the rotaxanated dye (**3**) in 2.75 ml tetraethylorthosilicate, 4.5 ml ethyl alcohol and 3 ml water was sonicated for 30 min. To the above solution, 0.15 ml of 0.5 M HCl was added as acidic catalyst. The mixture was allowed to sit for two days. About 0.5 ml sol was put on a pre-cleaned glass slide for 1 min and then spin-coated at 1500 rpm for 50 s to cast transparent and uniform silicate film. The film was dried under ambient conditions for a day and then baked at 100 °C for 2 h. In comparison, as for the free dye (**2**), it had limited solubility in given sol mixtures, and thus the cast film showed very uneven and irregular surface. The sol–gel glass was dipped in given pH solutions for about 10 min, and then pH solutions were adjusted by adding dilute HCl. The absorption spectra were measured by putting the prepared sol–gel glass in the optical path of UV spectrophotometer.

Table 1
Spectral properties of the synthesized dyes.

Dye	Solvent	λ_{max}	ε_{max}
3	DMSO (Dimethylsulfoxide)	550 nm	44,384
4		545 nm	40,980
3	Ethanol	524 nm	42,800
4		510 nm	20,910

3. Results and discussion

3.1. Characterization

The formation of dye rotaxane (**3**) was characterized by ^{1}H NMR spectroscopy. When ^{1}H NMR spectra were recorded in DMSO-d_6, all the signals for hydroxyl groups were sharp and easily-identified, showing two primary hydroxyls at $\delta = 5.5$–5.7 ppm and one secondary hydroxyl at $\delta = 4.5$ ppm. From the relative integrals, the ratio between chromophore and CD in the rotaxanated dye (**3**) is found to be 1:1 [2]. The 20 aromatic protons appear as complex and split peaks in the proton NMR spectra at $\delta = 9.1$–7.1 ppm, but can be readily assigned by comparison of all peaks in the rotaxanated dye (**3**) and the free dye (**4**). Aromatic protons from uncovered part of the rotaxanated dye show their peaks at the same positions as those of the free dye. COSY experiments are carried out to confirm the assigned peaks to their corresponding protons. In the plot of the COSY plot (Fig. 2), the rotaxanated dye clearly shows non-equivalent environment of aromatic protons at both ends making proton peaks of aromatic more split, which results from the threading of azo chromophore within the conical structure of α-CD.

3.2. Spectral properties of solution

Compared to the free dye, the rotaxanated dye exhibits its maximum absorption at longer wavelength, coupled with higher color strength (Table 1). This result is more obvious in ethanol. Azo dyes with hydrophobic substituents on terminal phenyl rings are readily subject to intermolecular interactions, especially face-to-face arrangement of dye molecules (H-aggregates) [13], which is thought to be responsible for blue shift of the free dye in absorption band. As for the rotaxanated dye, CD macrocycle around azo linkage can hinder dyes' aggregation, and it promotes the dominant existence of monomeric state of dye molecule. This leads to an increase in color strength, with a higher ε_{max} value.

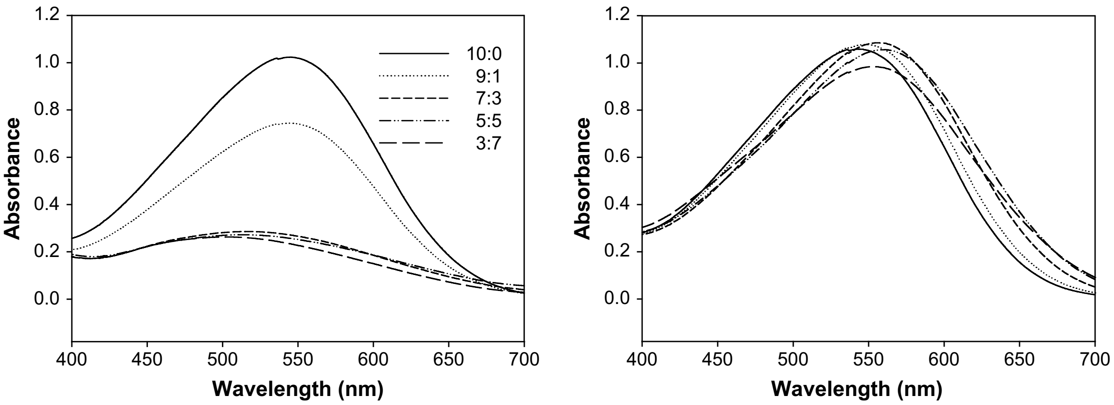


Fig. 3. UV–visible spectra of **4** (free dye, left) and **3** (rotaxanated dye, right) in mixed solvents (2.5×10^{-5} M DMSO:water, v/v) at 298 K.

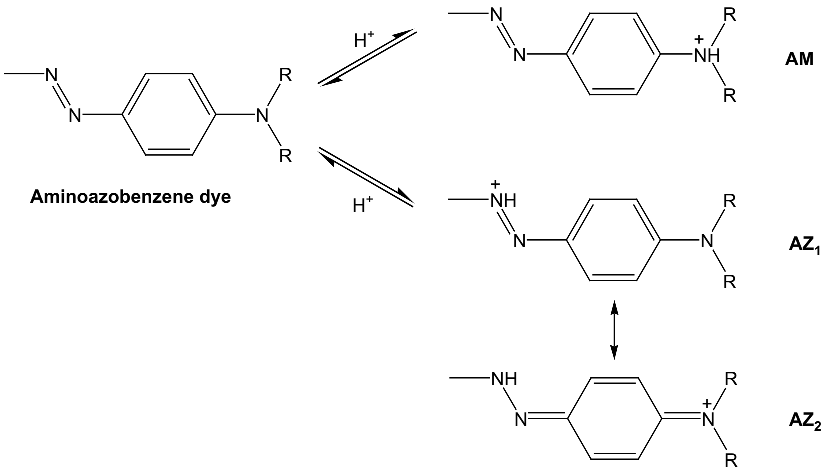
The UV–visible spectra of two dyes in DMSO/water mixed solvents are shown in Fig. 3. As is evident, the two dyes show different behavior with increasing amounts of water. As for the free dye, its absorbance quickly decreases, which is mainly due to the formation of precipitate and settling out of the solution. The chemical structure of the free dye containing no solubilizing group is similar to that of disperse dye. Thus, with increasing water content, it begins to precipitate out of the solution. Also, the addition of α-CD into the free dye in mixed solvent of high water content does not improve the solubility due to the limited water-solubility of hydrophobic free dye. Therefore, we infer that the size of end-capper, *N*,*N*-dimethyl-1-naphthylamin, is sufficient to prevent the formation of inclusion complex between the free dye and the α-CD.

However, once rotaxanated, the rotaxanated dye shows increased hydrophilicity due to hydroxyl groups on the CDs. The rotaxanated dye remains soluble even in water-rich condition, showing a slight increase and then decrease in absorbance. Therefore, the rotaxane structure makes threaded chromophore more stable in aqueous condition. From this result, we see that rotaxane formation can be an efficient way to increase aqueous solubility of azo dyes without the necessity of the introduction of solubilizing groups.

The effect of CD macrocycle on the absorption spectra of aminoazobenzene dye under different pH conditions was also investigated. *N*,*N*-dialkylaminoazo dyes are well-known to undergo a sharp color change in acid solution [14–16]. This phenomenon, so-called halochromism, is based on tautomeric equilibrium between the ammonium and azonium tautomers [17]. Protonation of a 4-aminoazobenzene derivative can occur either at the terminal amino group to give ammonium tautomer (AM), or at the β-nitrogen atom of the azo group to give the azonium tautomer (AZ) (Scheme 2).

The ammonium tautomer, in which its amino end groups no longer possess a lone pair of electrons, resembles azo benzene substituted in *para* position with an electron-withdrawing group [18]. Thus, it generally exhibits a blue shifted absorption band along with weaker color strength. In contrast, the azonium tautomer contains a delocalized positive charge ($AZ_1 \leftrightarrow AZ_2$), and its chemical structure resembles that of cyanine dyes [19]. Its absorption band is more red-shifted and tinctorially stronger. It is known that acidity results in an increase in the proportion of azonium tautomer, which is attributed to the red shift of aminoazobenzene dye in acidic medium [20].

According to the measurements in ethanol/water mixed solvents, both dyes, the free dye and the rotaxanated dye, showed similar behaviors of red shift and hyperchromic effect under acidic conditions (Fig. 4 and Table 2). Therefore, it seems that the presence of CD does not interfere with the protonation of aminoazobenzene dye. In Fig. 5, the corresponding titration curves are shown. However, their pKa values, obtained from the pH values at the inflection point in both titration curves, reveal some difference, with the rotaxanated dye having higher pKa value by difference of 0.57. We obviously see that CD induces fine-tuning of the pKa value of threaded azo dye, thereby changing its acidity. This phenomenon is attributed to the different microenvironments provided in the cavity of the CD. At the acidic condition, *N*,*N*-dimethylamino azo



Scheme 2. Tautomeric equilibrium between ammonium (AM) and azonium (AZ_1 and AZ_2) tautomers.

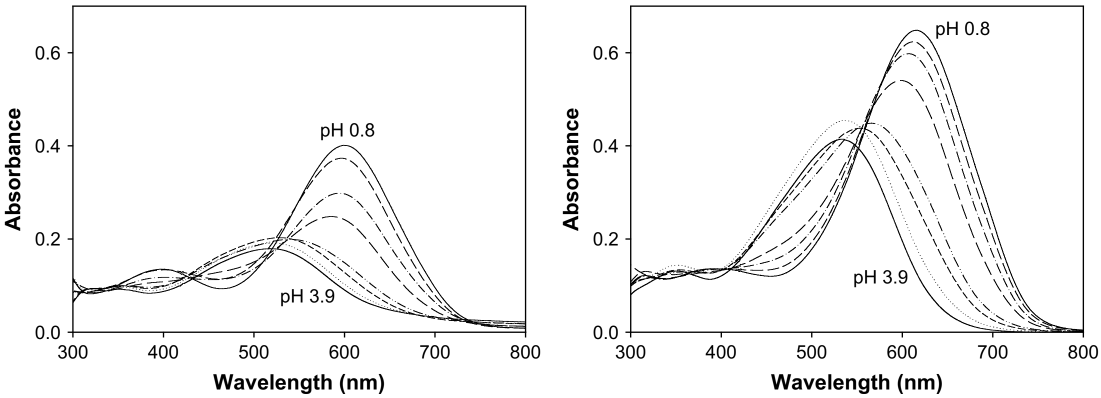


Fig. 4. Absorption spectra variation of **4** (free dye, left) and **3** (rotaxanated dye, right) with pH in mixed solvents (1.0×10^{-5} M, ethanol:water = 9:1, v/v) at 298 K.

Table 2
Absorption bands in different pHs (ethanol:water = 5:1, vol).

pH	3		4	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}
3.94	534 nm	41,430	521 nm	17,910
2.79	553 nm	43,790	521 nm	19,140
2.51	566 nm	44,870	536 nm	19,920
2.08	599 nm	54,050	584 nm	24,820
1.77	607 nm	59,790	594 nm	29,850
1.44	612 nm	62,340	597 nm	37,330
0.82	617 nm	64,820	599 nm	40,090

dye undergoes protonation. Within CD cavity, dye experiences more hydrophilic environment with a number of hydroxyl groups in CD around dye axis. It enables the rotaxanated dye to get readily protonated with greater access and affinity toward the proton, compared to the free dye.

3.3. *Spectral properties of sol–gel film*

In order to investigate the use of rotaxane structure as a pH indicator, the rotaxanated dye was entrapped in sol–gel film on a glass slide. Since Avnir and co-workers first reported the use of sol–gel glasses doped with dyes and pH sensors [21], the sol–gel process has been a very useful method to prepare a solid matrix with entrapment of organic molecules for chemical sensory applications [22–24]. Generally, host materials, tetramethoxysilane or tetraethoxysilane depending on the solvent system, can be polymerized in the presence of water with catalytic amounts of acid or alkali. When the polymerization is complete, the dopants, dye molecules are entrapped in the inorganic polymeric network.

The absorption spectra of the rotaxanated dye sol–gel film under different pH are shown (Fig. 6). Even in the solid matrix, the rotaxanated dye was observed to be highly pH sensitive, exhibiting a similar red shift in pH ranging from neutral to acidic conditions. This behavior is similar to that in aqueous solution. However, its sensitivity, in terms of changes in intensity and λ_{max}, is not as big as in aqueous solution. Also, this pH sensitivity was found to be reversible and reproducible, and no damage of the sol–gel film was observed during repeated measurements. From this, it can be seen that the current sol–gel film with the rotaxanated dye is suitable as a pH indicator in the range of acid and neutral conditions. However, in alkaline solutions, slow leaching was observed. This is due to the ionization of hydroxyl groups in α-CDs, leading to an increase in dye solubility. In comparison, as for the free dye, it has limited solubility in a given sol mixture, and thus the cast film showed an uneven and irregular surface. This clearly shows the limitation of water insoluble free dye for this application [23–25]. Generally, entrapment may cause some changes in spectroscopic properties due to restricted degree of freedom of the dyes [20]. Methyl Red, when trapped in sol–gel glass using acid–catalyst, shows its pH sensitivity in the ranges of neutral to alkaline condition, while Methyl Red is normally sensitive to acidic condition [25]. However, when the absorption spectra of the rotaxanated dye were compared in the solution state (Fig. 4 right) and sol–gel coating film (Fig. 6), no such difference was observed in terms of λ_{max}. It is attributed to the fact that, as for rotaxane structure, dye molecules are already trapped within the cavity of CD, thus no additional restriction is applied for the movements of these dyes in sol–gel matrix.

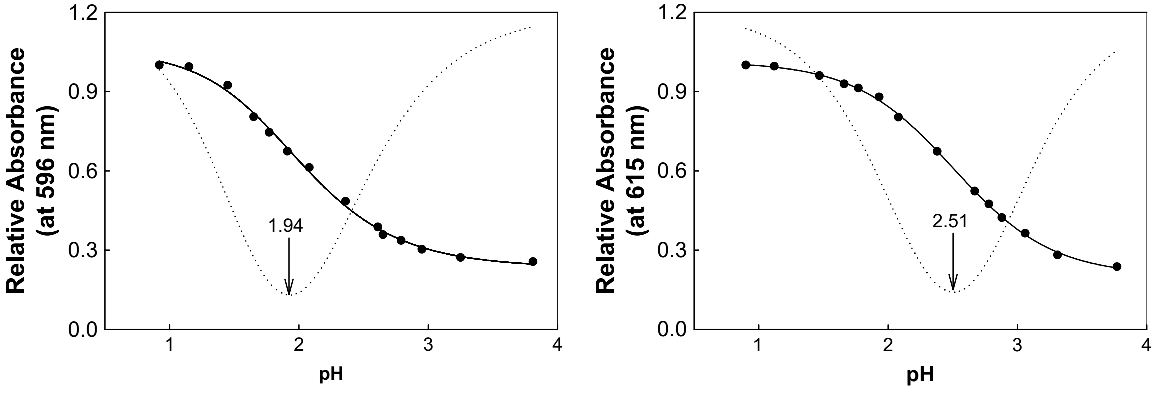


Fig. 5. pH titration curves for the absorbance changes at 596 nm (**4**, free dye, left) and 615 nm (**3**, rotaxanated dye, right) in mixed solvents (1.0×10^{-5} M, ethanol:water = 9:1, v/v, dotted lines are 1st-order differentiation curves).

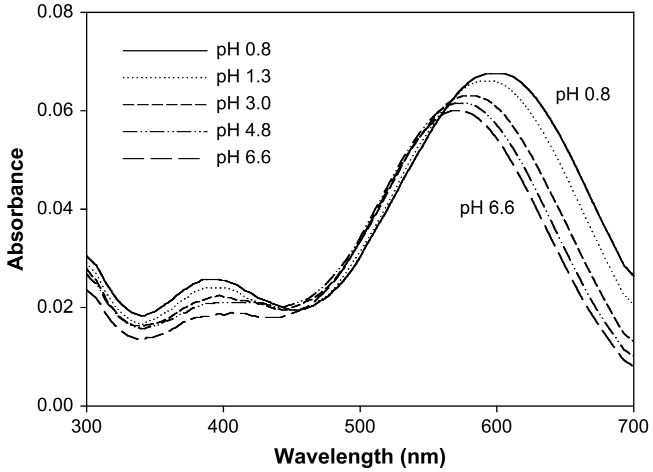


Fig. 6. Absorption spectra variation of **3** (rotaxanated dye) sol–gel film with pH.

4. Conclusions

Azo dye rotaxane with α-cyclodextrin was successfully synthesized and characterized. Azo dye rotaxane exhibited higher polarity, soluble only in polar solvents and showing good solubility in water. It was found that the formation of rotaxane structure did not interfere with the protonation of the threaded aminoazobenzene dye. However, the presence of α-cyclodextrins caused the fine-tuning of the pKa value of threaded azo dye, changing its acidity. In sol–gel coating film, azo dye rotaxane still exhibited pH sensitivity in the ranges from neutral to acidic conditions in a reversible and reproducible way.

Therefore, the introduction of α-cyclodextrins around a dye chromophore to form dye rotaxane would be a simple way to achieve the properties of azo dye as desired; improved aqueous solubility, enhanced dye stability, fine-tuning of pKa value, and high pH sensitivity in sol–gel coating film. All these changes in physical properties could be accomplished without synthesizing a different set of dyes.

Acknowledgements

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