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Synthesis, spectral properties of cyanine dyes-β-cyclodextrin and their application as the supramolecular host with spectroscopic probe

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ABSTRACT

Six new cyanine dye functionalised β-cyclodextrins were designed and synthesized to improve the drawback of the inadequate chromophore in β-cyclodextrin and to be suitable for the study of supramolecular interactions directly by visible spectroscopy. The dye structures were confirmed by ^{1}H NMR, IR, UV–Vis and HRMS. The UV–Vis spectra of the new cyanine dyes in different solvents were investigated. The inclusion behaviour of a quinocyanine derived β-cyclodextrin dye which was used as the supramolecular host with 1-adamantanol or vitamin B_6 was investigated. The results indicated that the stoichiometry for the inclusion complex of the quinocyanine derived β-cyclodextrin dye and both 1-adamantanol and vitamin B_6 was 1:1, and their inclusion constants were 9.39×10^4 L/mol and 6.14×10^2 L/mol, respectively. The quinocyanine derived β-cyclodextrin dye was also used as the supramolecular host for the analysis of vitamin B_6 in tablets with satisfactory results.

1. Introduction

Cyanine dyes present typical optical properties and act as one of the most important organic functional dyes [1,2]. These dyes have tunable wavelengths across the visible spectrum, and exhibit high molar extinction coefficients permitting the use of low concentrations [3]. β-cyclodextrin (β-CD), which has both hydrophobic cavity and hydrophilic surface, is considered as an attractive compound in the field of molecular recognition [4,5], enzyme mimics [6], construction of molecular building blocks with ordered nanostructures [7], commodity [8–11], medicine [12–14] and chemical industry [15–17]. However, β-CD shows poor molecular selectivity in molecular recognition. Therefore, chemically modified β-CD is studied extensively. β-CD was modified with quinoline to obtain the biquinolino-bridged bis-cyclodextrin, which included pyroninophilic dye at different pH to study the protonation and deprotonation of xanthene dyes [18]. Voncina et al. [19], grafted β-CD onto PET textile materials, which could be used as odour carriers or as malodorous absorbers. Suresh and Pitchumani [20], modified β-CD with amino to obtain per-6-amino-β-CD, acting simultaneously as a supramolecular ligand for CuI and host for aryl bromides, which could catalyse *N*-arylation of imidazole with aryl bromides under mild conditions. Yamada and Hashimoto [21], synthesized a water-soluble β-CD-immobilized poly (allylamine), then mixed the water-soluble β-CD derivatives and DNA to form inclusion complexes, which had the potential to absorb harmful compounds. However, there are no reports concerning the use of cyanine dye modified β-CDs as host compounds with spectroscopic probes to recognize colourless guest molecules [22,23].

In this study, six new cyanine dyes-β-CD were synthesized (Fig. 1) and characterized. Their UV–Vis spectra were investigated in different solvents. At the same time, the inclusion interaction of cyanine dye-β-CD (**6**) and 1-adamantanol (Fig. 2(a)) or vitamin B_6 (VB_6) (Fig. 2(b)) was studied by spectroscopic methods. Previously, the molecular recognition study on β-CD and its modified analogues with VB_6 was done using spectrophotometric titration by competitive inclusion method using guest molecules with chromophore or dyes as spectral probes [24,25]. In this work, synthetic dye-β-CD (**6**) had its own chromophore and could be used as a host compound with spectroscopic probe to recognize VB_6 without adding other spectral probes. This study describes the use of dyes-β-CD as host compounds with spectroscopic probes to recognize colourless guest molecules.

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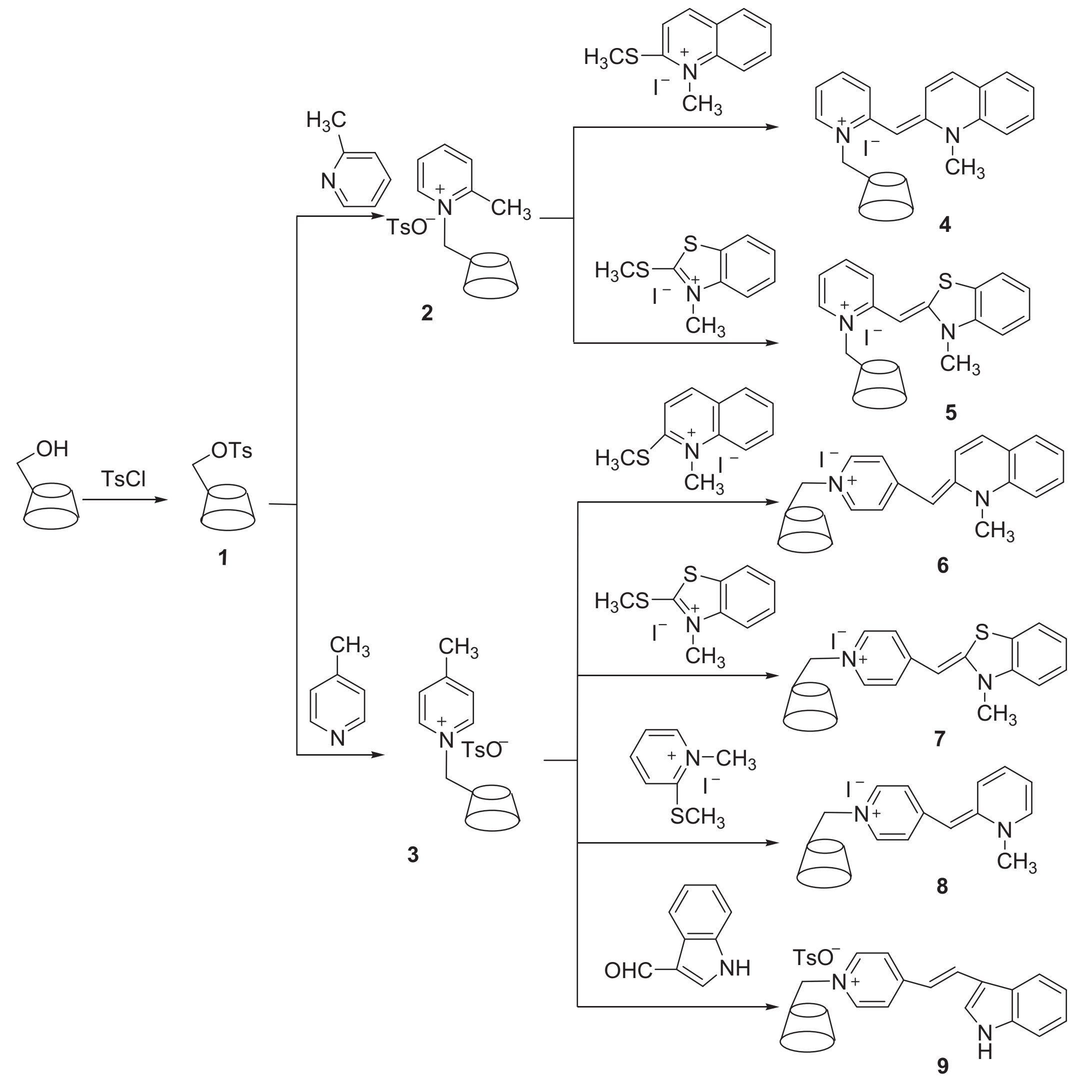

Fig. 1. Synthesis of dyes-β-CD.

2. Experimental

2.1. Chemicals and instruments

2.1.1. Chemicals

Commercially available reagents were used without additional purification. All solvents were of analytical grade.

2.1.2. Instruments

Melting points were taken on an XT-4 micromelting apparatus and uncorrected. IR spectra in cm^{-1} were recorded on a Bruker Equiox-55 spectrometer. The absorption spectra were recorded on a Purkinje General UV-1900 UV–Vis spectrometer. ^{1}H NMR spectra were recorded at 400 MHz on a Varian Inova-400 spectrometer and chemical shifts were reported relative to internal Me_4Si. HRMS was recorded on a microTOFQ II ESI-Q-ToF LC/MS/spectrometer.

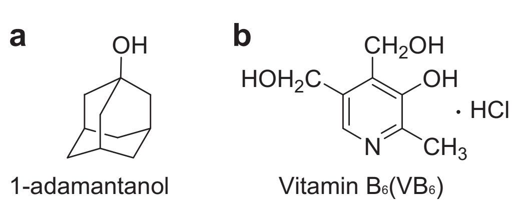

Fig. 2. Structures of 1-adamantanol (a) and VB_6 (b).

2.2. Synthesis of cyanine dyes-β-cyclodextrin

2.2.1. Mono-6-oxygen-tosyl-β-cyclodextrin (1)

Compound (**1**) was prepared according to the literature [26].

2.2.2. Mono-6-deoxy-6-(2-methylpyridinium)-β-cyclodextrin-p-toluenesulfonate (2)

Compound (**2**) was prepared according to the literature [27]. A mixture of compound (**1**) (2.70 g, 2.10 mmol) and 2-methyl pyridine (12.0 mL) was stirred at 85 °C for 12 h. After cooling, the solution was poured into acetone with stirring. The resulting precipitate was collected and purified with water and acetone (yield: 87%, m.p. 267–269 °C).

2.2.3. Mono-6-deoxy-6-(4-methylpyridinium)-β-cyclodextrin-p-toluenesulfonate (3)

Compound (**3**) was prepared according to the literature [27]. The same procedure described above but using 4-methyl pyridine (12.0 mL) (yield: 91%, m.p. 273–275 °C).