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Novel enantioselective fluorescent sensors for malate anion based on acridine

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ABSTRACT

The compounds **L-1** and **L-2** were synthesized and the interactions of all of the compounds with malate anion were studied by fluorescent titration and ^{1}H NMR experiments. The Sensors **L-1** and **L-2** were found to present good enantioselective fluorescent sensing ability to malate anion. The results indicated that sensors **L-1** and **L-2** were very promising to be used as fluorescent sensors in determining malate anion in CH_3CN.

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1. Introduction

During the past two decades, considerable attention has been focused on the design of chiral substrates that can recognize and sense chiral anions selectively due to the important roles and potential applications anions play in environmental, biological and supramolecular sciences [1–5]. Among these chiral anions, malate anion (MA) plays significant role in pharmaceutics. *D*-Malate can only be found if the synthetic racemate is used as food additive. *L*-Malate is used in the treatment of light-damaged or dry skin, acne, and especially fibromyalgia when combined with magnesium. *L*-Malate is also used to treat atherosclerosis [6,7]. Therefore, the practical, rapid and accurate methods applied in enantioselective recognition of *D*- and *L*-malate are an important analytical agenda.

Up to now, many analytical methods such as nuclear magnetic resonance (NMR), high-performance liquid chromatography, circular dichroism have been developed for chiral anions determination, fluorescent sensors present many appealing advantages, including high sensitivity and selectivity, low cost, easy detection, and especially suitability as a diagnostic tool for biological concern [8–14]. To the best of our knowledge, few chiral fluorescent sensors have been reported up till now for the enantioselective recognition of MA in CH_3CN. In this paper, we reported the synthesis and enantioselective recognition of fluorescent MA sensors developing from acridine.

2. Experimental section

2.1. Materials

The reagents were used of commercial origin and were employed without further purification. Purifications by column chromatography were carried out over silica gel (230–400 mesh). The IR spectra were performed on a Nicolet 670 FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer. Mass spectra were determined by ESI recorded on an Esquire 3000 LC–MS mass instrument. Optical rotations were taken on a Perkin–Elmer Model 341 polarimeter. Elemental analyses were performed by the Vario Elemental CHSN-O microanalyzer. Fluorescence spectra were obtained with an F-7000 FL Spectrophotometer. The anions were used as their tetrabutylammonium salts. 4,5-Bis(bromomethyl)acridine was prepared according to the literature methods [15,16].

2.2. Syntheses

2.2.1. Syntheses of Boc-amino alcohol

$(Boc)_2O$ (2.10 g, 12 mmol) was added to a solution of amino alcohol (10 mmol) and diisopropylethylamine (DIPEA) (1.44 g,

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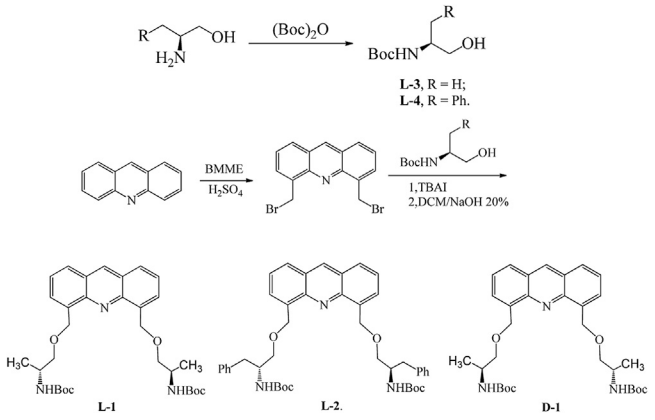

Scheme 1. Synthesis of compounds **L-1**, **D-1** and **L-2**.

12 mmol) in THF(40 mL) under N_2 protection at 0 °C. The mixture was stirred for 6 h at room temperature, then the solvent was removed under reduced pressure and the resulting residue was dissolved in 100 mL ethyl acetate. This solution was washed twice with 100 mL of water, once with 100 mL of saturated aqueous sodium chloride, dried over Na_2SO_4 and concentrated under reduced pressure to give product **L-3** or **L-4** as yellow oil.

L-3: 1.70 g, yield 97%; $[\alpha]_D^{20} = -8.4$ (*c* 0.05, $CHCl_3$); ^1H NMR($CDCl_3$): δ 4.71 (s, 1H), 3.69–3.60 (m, 1H), 3.57–3.42 (m, 2H), 2.21 (s, 1H), 1.36 (s, 9H), 1.12 (d, J = 6.4 Hz, 3H).

L-4: 2.38 g, yield 95%; $[\alpha]_D^{20} = -20.8$ (*c* 0.05, $CHCl_3$); ^1H NMR($CDCl_3$): δ 7.36–7.21 (m, 5H), 4.71 (s, 1H), 3.87 (s, 1H), 3.66–3.55 (m, 2H), 2.84 (d, J = 7.8 Hz, 2H), 2.23 (s, 1H), 1.41 (s, 9H).

2.2.2. *General procedure for the preparation of compounds **L-1**, **D-1** and **L-2***

To a solution of 4,5-bis(bromomethyl)acridine (0.37 g, 1.0 mmol) in dichloromethane (10 mL), 20% NaOH (10 mL), tetrabutylammonium iodide (0.81 g, 2.2 mmol) and *N*-Boc-amino alcohol (2.2 mmol) were added consecutively. The biphasic mixture was then stirred at room temperature for 15 h and monitored via TLC, after which it was poured into a separatory funnel over water and extracted with dichloromethane. The combined organic extracts were rinsed with brine, dried over anhydrous Na_2SO_4 and purified by means of flash chromatography over silica gel using petroleum ether: ethyl acetate (10:1) as eluent to obtain pure product **L-1**, **D-1** and **L-2** as yellow solid, respectively.

L-1: 0.23 g, m.p.: 132–133 °C, yield, 42.2%. $[\alpha]_D^{20} = -12.6$ (c = 0.20, $CHCl_3$); **D-1**: The preparation procedure the same as that of **L-1** with the use of R-N-Boc-amine alcohol as the materials. 0.24 g, m.p.:135–136 °C, yield, 42.4%, $[\alpha]_D^{20} = +12.2$ (c = 0.20, $CHCl_3$); ^1H NMR ($CDCl_3$) : δ 8.75 (s, 1H), 7.93(d, J = 8.4 Hz, 2H), 7.88(d, J = 7.6 Hz, 2H), 7.55(t, J = 7.6 Hz, 2H), 5.38(s, 4H), 4.89(s, 2H), 3.98(s, 2H), 3.76–3.68(m, 4H), 1.43 (s, 18H), 1.29(d, J = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$): 155.49, 145.95, 136.84, 136.03, 127.40, 127.24, 125.56, 74.44, 69.49, 46.53, 28.45, 18.28, IR (KBr):3373, 1691, 1521, 1253, 1128, 758 cm^{-1}; HRMS *m/z*: calculated for $C_{31}H_{43}N_3O_6$, $[M+H]^+$ 554.3225, found 554.3229.

L-2: 0.37 g, m.p.: 141–142 °C, yield, 52.8%. $[\alpha]_D^{20} = -15.6$ (c = 0.20, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.78 (s, 1H), 7.95(d, J = 8.4 Hz, 2H), 7.89(d, J = 6.8 Hz, 2H), 7.57(t, J = 7.6 Hz, 2H), 7.24–7.17(m, 10H), 5.32(d, J = 5.8 Hz, 4H), 5.03(s, 2H), 4.04(s, 2H), 3.66–3.40(m, 4H), 2.98(d, J = 4.0 Hz, 4H), 1.41 (s, 18H); ^{13}C NMR ($CDCl_3$): 155.44, 146.00, 138.35 136.84, 136.09 129.52, 128.39, 127.62, 126.30, 126.23, 125.61, 71.04, 69.46, 52.09, 51.98, 38.12, 38.09, 28.44; IR (KBr): 3365, 1689, 1522, 1390, 1365, 1249, 1170, 757, 700 cm^{-1}; HRMS *m/z*: calculated for $C_{43}H_{51}N_3O_6$, $[M+H]^+$ 706.3851, found 706.3856.

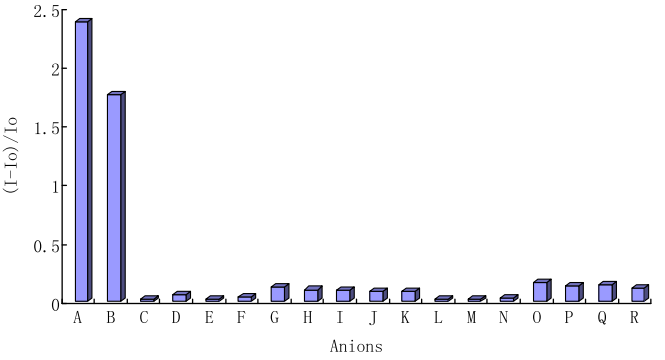

Fig. 1. Fluorescent spectra changes of sensor **L-1** (3.0×10^{-5} M) measured in CH_3CN upon the addition of 100 equivalent of various anions (λ_{ex} = 356 nm, λ_{em} = 423 nm). Fluorescent enhancement ($(I - I_0)/I_0$) of sensor **L-1** (3.0×10^{-5} M) at 423 nm upon the addition of different carboxylate anions (as tetrabutylammonium) in CH_3CN at 25 °C (100 equiv, 3.0×10^{-3} M). A = *D*-MA, B = *L*-MA, C = *L*-mandelic acid anion, D = *D*-mandelic acid anion, E = *L*-phenyl-lactic acid anion, F = *D*-phenyllactic acid anion, G = *L*-methoxyphenylacetic acid anion, H = *D*-methoxyphenylacetic acid anion, I = *L*tartaric acid anion, J = *D*-tartaric acid anion, K = *L*-dibenzoyltartaric acid anion, L = *D*-dibenzoyltartaric acid anion, M = *L*-phenylglycine anion, N = *D*-phenylglycine anion, O = *L*-phenylalanine anion, P = *D*-phenylalanine anion.

3. Results and discussion

3.1. Synthesis

The chiral fluorescence sensors **L-1** and **L-2** were efficiently synthesized by the reaction of intermediate *D*-N-Boc-amino alcohol **L-3** or **L-4** and 4,5-Bis(bromomethyl)acridine (Scheme 1). The preparation procedure of compound **D-1**, the enantiomers of **L-1**, was the same as that of **L-1** by starting with *D*-N-Boc-amino alcohol and 4,5-Bis(bromomethyl)acridine. The ^1H NMR spectra exhibited all the expected signals with the desired integral values and support the molecular structures. The structures of these compounds were characterized by IR, MS, ^1H NMR and ^{13}C NMR spectra. We chose these compounds to undertake the desired fluorescent recognition of MA for the following two reasons: on one hand, the oxygen atoms of the compounds could bind –OH of guest MA well through multiple hydrogen bonds. On the other hand, when the sensors interact with MA, their oxygen atoms were expected to turn on the fluorescence of the sensors by inhibiting the photoinduced-electron-transfer (PET) [17–19] of the oxygen atoms.

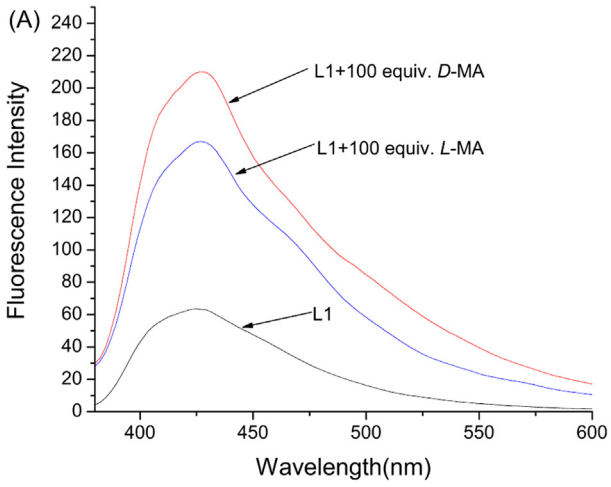

Fig. 2. Fluorescent spectra of **L-1** (3.0×10^{-5} M) with 100 equiv. of *D*- and *L*-MA in CH_3CN.

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