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Note

An effective mutli-wavelength emissive aluminum ion fluorescence chemosensor based on 3-[1′-(2′-hydroxy-α-methylbenzylidene-imino)]-2-(*p*-*N*,*N*-dimethylaminophenyl)-1,2-dihydroquinazolin-4-(3H)-one

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ABSTRACT

In the paper, a novel mutli-wavelength emissive aluminium ion chemosensor based on 3-[1′-(2′-hydroxy-α-methylbenzylidene-imino)]-2-(*p*-*N*,*N*-dimethyl aminophenyl)-1,2-dihydroquinazolin-4-(3H)-one is designed and synthesized. According to the fluorescence behavior toward several metal ions, it shows high selectivity to Al^{3+} over other commonly coexistent metal ions (Na^{+}, Mg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Fe^{3+}, Cr^{3+}, Hg^{2+}, Zn^{2+}, Cd^{2+}) in aqueous environment (pH 7.40). Meanwhile the binding constant between Al^{3+} and chemosensor achieves 3.92×10^{6} M^{-1} in aqueous media. Moreover, according to the Job plot, 1:1 stoichiometry between Al^{3+} and the sensor was deduced in aqueous media (pH 7.4). The good selectivity and sensitivity in aqueous media effectively enhance the application value of the chemosensor for Al^{3+}.

1. Introduction

The highly selective and sensitive chemosensors of metal ions in aqueous environment are of great importance for studying and tracking the chemical and physiological functions in the wide range of chemical and biological processes [1–5]. Recently, considerable efforts have been devoted to developing fluorescence chemosensors based on nitrogen atom heterocyclic derivates due to their simplicity, high selectivity and sensitivity toward corresponding metal ions [6–10]. Aluminium is not a biologically essential element and exhibits considerable cytoxicity in living organism. Recent study advances have some light on the biological roles of aluminium, particularly on its functions related to neurobiology. Moreover, in the physiological processes such as brain, prostate and intestine locations, abnormal level of Al^{3+} even can cause some relevant diseases like Parkinson's disease. Additionally, high Al^{3+} content in drinking water is very bad for human health [11–16]. The incomplete understanding of the biological effects of Al^{3+} remains active topics of research. Thus, there is a considerable need to design highly selective chemosensors, which are capable of detecting the presence of Al^{3+} in environmental and biological system in aqueous media at a physiological pH value. To date, some Al^{3+} selective chemosensors have been achieved [17,18]. However, to the best of our knowledge very few fluorescent sensors for Al^{3+} in aqueous media have been designed.

When aiming at the rational development of specific fluorescence chemosensors for targeting Al^{3+}, the choice of binding motif is a critical factor. Because in the cellar level, many transition metal ions such as Hg^{2+} and Cd^{2+} can interfere with Al^{3+} binding. It is well known that the chelating groups such as C=N, C–O and C=O exhibit high affinity to such metal cations, but less binding affinity toward alkali and alkaline earth metal cations [19,20]. Thus, in the present investigation, novel heterocycle compound 3-[1′-(2′-hydroxy-α-methylbenzylidene-imino)]-2-(*p*-*N*,*N*-dimethylaminophenyl)-1,2-dihydroquinazolin-4-(3H)-one architecture is designed to increase the selectivity and sensitivity for detecting Al^{3+}. According to the spectra analysis, the fluorescence sensor exhibits high selectivity toward Al^{3+} over other metal ions in aqueous buffer media (pH 7.4).

2. Experimental

2.1. Characterization and materials

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian 400-MHz spectrometer with TMS as an internal standard. The melting point of the compounds were determined on a Beijing XT4-100X microscopic melting point apparatus. ESI-MS was recorded on the Esquire 6000 instrument. The UV–Vis spectra were recorded on a Perkin-Elmer Lambda-35 UV–Vis spectrophotometer. Fluorescence spectra were obtained on a Shimadzu RF-5301 spectrophotometer at room temperature. Elemental analysis was tested on a Elementar Vario EL Elemental Analyzers instrument.

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Stock solutions (1.0×10^{-3} M) of metal ions (metal nitrate) were prepared using in two-distilled water. The stock solution of L (5.0×10^{-3} M) was prepared in CH_3CN–HEPES (9:1). In titration experiments, each time a 20 μL solution of L (5.0×10^{-3} M) was filled in a quartz optical cell of 1 cm optical path length. Then equal amount of Al^{3+} stock solution (10 μL) was added to the compound solution with micro-pippet. Spectral data was recorded at 1 min after the addition. In selectivity experiment, the test samples were prepared by placing appropriate amounts of metal ion stock into 2 mL aqueous solution of L (5.0×10^{-5} M). For fluorescence measurements, excitation wavelength is at 345 nm.

Compound 1 was prepared by the reported methods [21]. The synthesis routine of 3-[1'-(2'-hydroxy-α-methylbenzylidene-imino)]-2-(*p*-*N*,*N*-dimethylaminophenyl)-1,2-dihydroquinazolin-4-(3H)-one (L) were shown in Scheme 1. All the chemicals were of reagent grade and were used without further purification. All spectroscopic measurements were performed in CH_3CN-HEPES (9:1) buffer solution (pH 7.4).

2.2. Synthesis of 3-[1′-(2′-hydroxy-α-methylbenzylidene-imino)]-2-(p-N,N-dimethylaminophenyl)-1,2-dihydroquinazolin-4-(3H)-one (L)

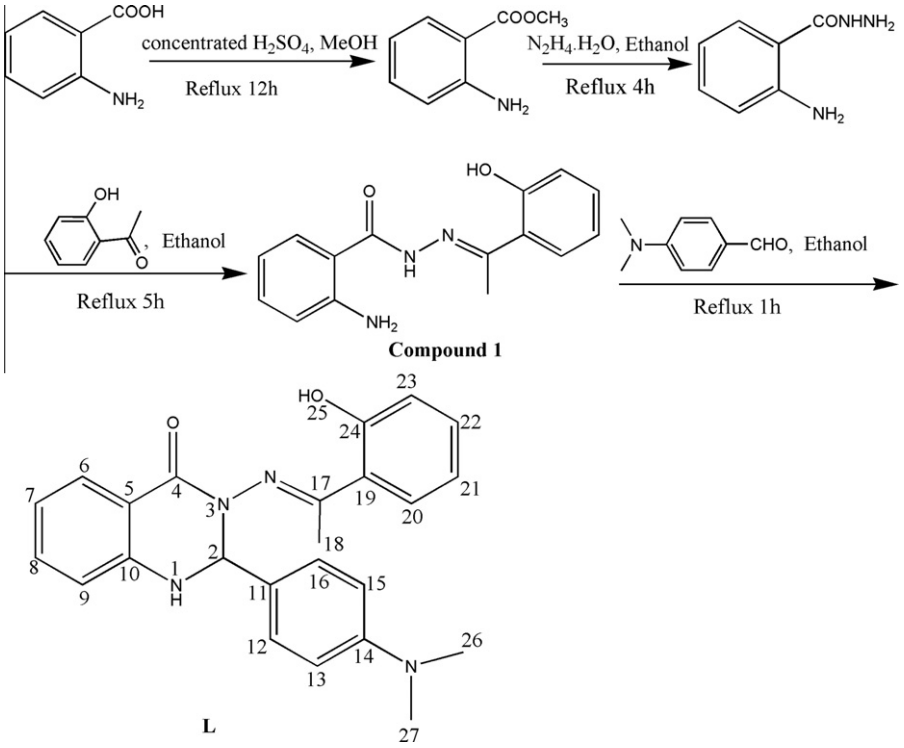
An ethanol solution (20 mL) of compound 1 (1 mmol, 0.269 g) was added to another ethanol (20 mL) containing 4-dimethylamino benzaldehyde (1 mmol, 0.149 g), Then the solution was reflux for 1 h under stirring and some white precipitant appeared. The mixture was filtered and dried under vacuum. Recrystallization from DMF H_2O (V:V = 1:1) gave 3-[1′-(2′-hydroxy-α-methylbenzylidene-imino)]-2-(*p*-*N*,*N*-dimethylaminophenyl)-1,2-dihydroquinazolin-4-(3H)-one (L), which was dried under vacuum. Yield, 75%. m.p: 283–285 °C. ^{1}H NMR (Fig. S1), ^{13}C NMR (Fig. S2) and ESI-MS (Fig. S3) were listed in Supplementary materials. ^{1}H NMR (DMSO-d_6 400 MHz): δ 12.26 (1H, s, –C^{25}–H), δ 7.73–7.75 (1H, d, –C^6–H), δ 7.59–7.61 (1H, d, –C^9–H), δ 7.43 (1H, s, –N^1–H), δ 7.29–7.43 (4H, m, –$C^{12,13,15,16}$–H), δ 6.85–6.89 (2H, m, –C^7–H), δ 6.80–6.84 (2H, m, –$C^{21,22}$–H), δ 6.74–6.77 (1H, m, –C^8–H), δ 6.66–6.68 (1H, d, –C^8–H), δ 6.14 (1H, s, –C^2–H), δ 2.85 (6H, s, –$C^{26,27}$–H). δ 2.27 (3H, s, –C^{18}–H). ^{13}C NMR (DMSO–d_6 400 MHz): δ 17.04. δ 75.14. δ 111.72. δ 113.30. δ 114.49. δ 117.11. δ 117.47. δ 118.39. δ 118.62. δ 126.07. δ 127.99. δ 128.25. δ 129.60. δ 132.42. δ 133.88. δ 147.49. δ 150.66. δ 159.25. δ 160.52. δ 173.24. ESI-MS Calc. for $C_{24}H_{24}N_4O_2$ ([L]+H^+): 401.19; Found for 401.3. The elemental analysis data *Anal.* Calc. for C, 71.98; H, 6.04; N, 13.99. Found: C, 71.55; H, 5.96; N, 14.06%.

3. Results and discussion

3.1. The fluorescence emission spectroscopy of L to Al^{3+}

To investigate the fluorescence selectivity toward special metal ions, the fluorescence selectivity experiments of various metal (Al^{3+}, Na^+, Mg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Fe^{3+}, Cr^{3+}, Hg^{2+}, Zn^{2+}, Cd^{2+}) were carried out in CH_3CN–HEPES (9:1) buffer solution at pH 7.4. As Shown in Fig. 1a, in the absence of metal ions, the ligand exhibited a single fluorescence signal peak in the range from 400 to 500 nm in CH_3CN-HEPES media (pH 7.4). However, with addition of equivalent various metal ions, only the addition of Al^{3+} lead to interesting multi-wavelength emssive fluorescence enhancement. Clearly, the addition of Al^{3+} lead to the formation of Al^{3+}–L with enhanced fluorescence intensity, which indicated 3-[1′-(2′-hydroxy-α-methylbenzylidene-imino)]-2-(*p*-*N*,*N*-dimethylaminophenyl)-1,2-dihydroquinazolin-4-(3H)-one could act as an highly selective fluorescence probe for Al^{3+} under physiological pH conditions. In addition, according to the histogram (Fig. 1b), the high selectivity of L for Al^{3+} over other metal ions were indicated obviously.

Fluorescence titration experiment (Fig. 2a) using L and Al^{3+} was performed in aqueous buffer media (pH 7.4) at room temperature. Upon addition of Al^{3+}, A new fluorescence signal at 500 nm significantly appeared. It was explicit that the binding between L and Al^{3+} induced the tranger of electron from L, which was responsible



Scheme 1. The sysnthesis line of fluoresence sensor L (3-[1′-(2′-hydroxy-α-methylbenzylidene-imino)]-2-(*p*-*N*,*N*-dimethylaminophenyl)-1,2-dihydroquinazolin-4-(3H)-one).

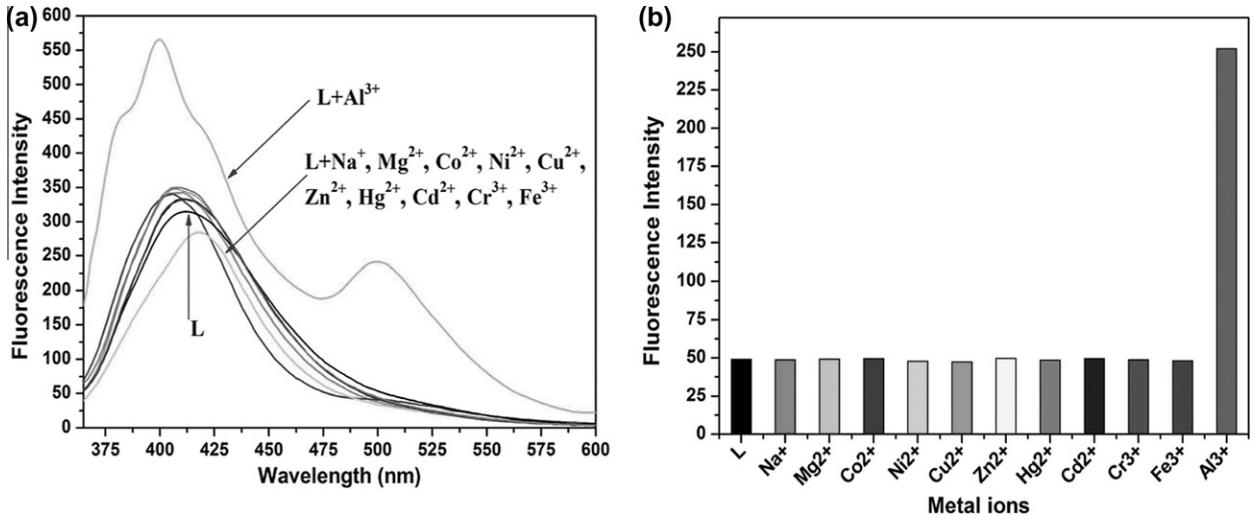


Fig. 1. (a) The changes in the fluorescence spectra (excitation at 345 nm) of L (5.0×10^{-5} M) in the presence of different metal ions (5.0×10^{-5} M) in CH_3CN–HEPES buffer solution (9:1, pH 7.4). (b) The histogram of selectivity for various metal ions.

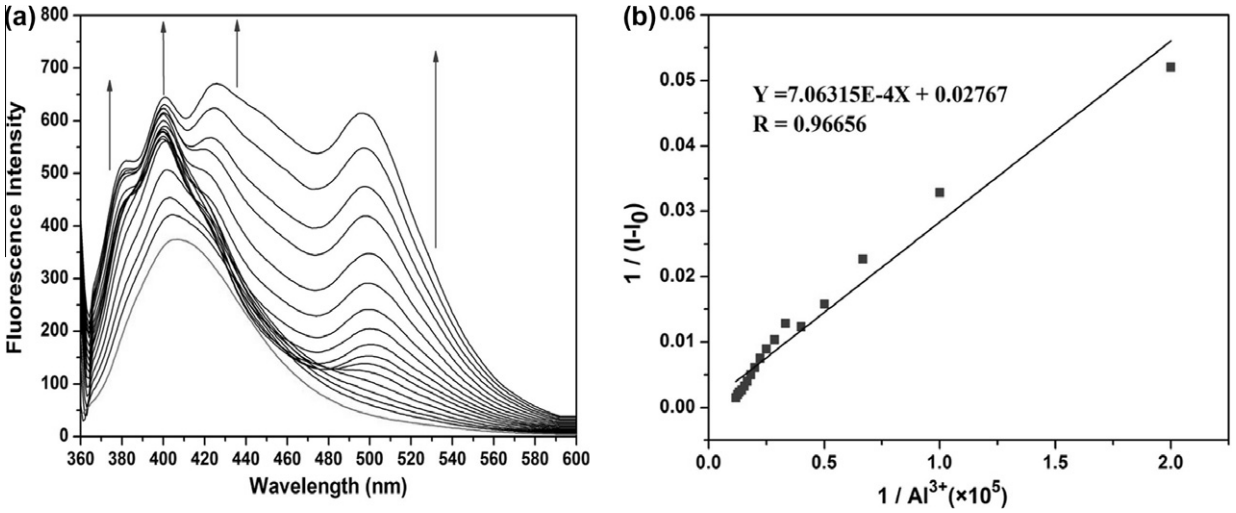


Fig. 2. (a) Fluorescence spectrum of L (5.0×10^{-5} M) upon addition of Al^{3+} in CH_3CN–HEPES solution (pH 7.4). Excitation at 345 nm, Red represents the ligand without the addition of Al^{3+}. (b) The association constant between L and Al^{3+} from Benesi–Hildebrand expression.

for the fluorescence change. It was also clear that the PET process, which was switched on by Al^{3+} as the excitation at 345 nm, resulted in the emission of L–Al^{3+} with a maximum wavelength at 500 nm. As shown in Fig. 2b, the association constant for Al^{3+} was estimated to be 3.92×10^6 M^{-1} in aqueous media (pH 7.4) by fitting the data to the Benesi–Hildebrand expression ($I_0/(I–I_0) = I_0/[L] + I_0/[L]{\cdot}K_s{\cdot}[M]$) with a good linear relationship [22,23]. I is the change in the fluorescence intensity at 500 nm, K_s is the stability constant, [L] and [M] are the concentration of L and Al^{3+}, respectively. I_0 is the fluorescence intensity of L in the absence of Al^{3+}. On the basis of the plot of $1/[I]$ versus $1/Al^{3+}$, the binding constant can be obtained. It demonstrated the there was a high binding tendency between L and Al^{3+}.

Additionally, by the Job plot shown in Fig. 3, the binding mode between L and Al^{3+} was investigated systemically. We could deduce that there was a 1:1 stoichiometry between them. Moreover, in accordance with the 1:1 stoichiometry, the fluorescent turn-on chemosenor was most likely to chelate with Al^{3+} via its carbonyl O, imino N and 2′-hydroxyacetophenone O atoms. And the coordination stoichiometry between L and Al^{3+} is in accordance with the data from ESI-MS (Fig. S4).

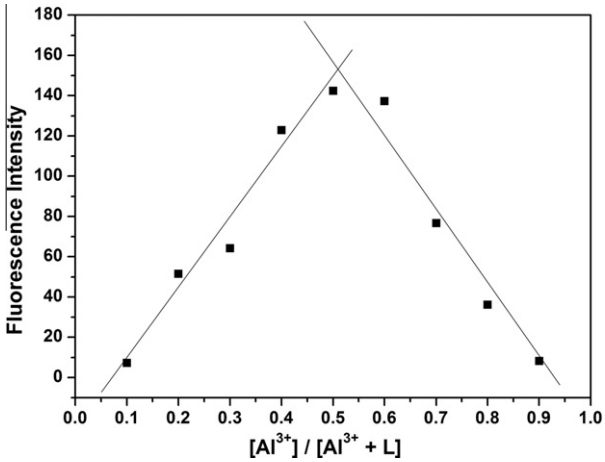


Fig. 3. Job's plot according to the method for continuous variations, indicating the 1:1 stoichiometry for L–Al^{3+} (the total concentration of L and Al^{3+} is 2.0×10^{-5} M) (λ_{ex} = 345 nm).

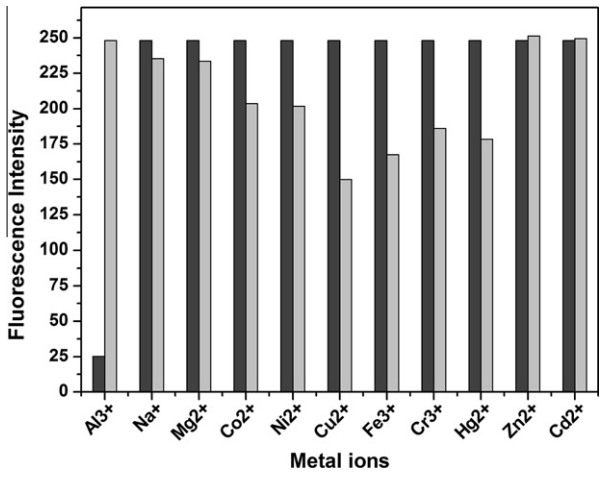


Fig. 4. The selectivity of **L** for **Al^{3+}** in the presence of other metal ions (Na^+, Mg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Fe^{3+}, Cr^{3+}, Hg^{2+}, Zn^{2+}, Cd^{2+}) in CH_3CN–HEPES (pH 7.4). Excitation at 345 nm. The response is normalized with respect to background fluorescence of the free L (5.0×10^{-5} M). Al^{3+} (5.0×10^{-5} M) is added at first. Then other metal ions were added (5.0×10^{-5} M).

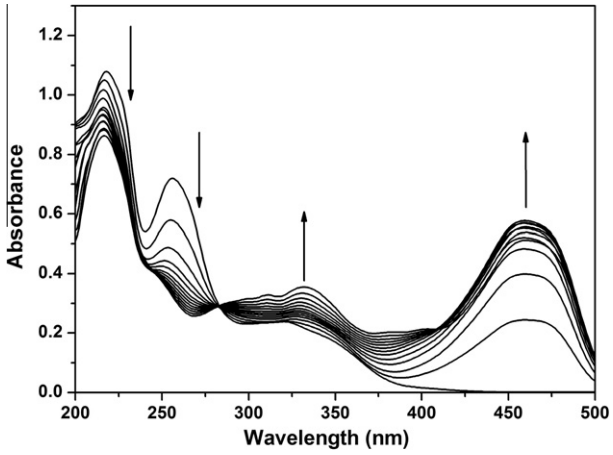


Fig. 5. The absorption spectra of L (5.0×10^{-5} M) in CH_3CN–HEPES media in the presence of different amounts of Al^{3+} (0–2 equiv).

Furthermore, to validate the higher selectivity of L for Al^{3+} relative to other metal ions, the fluorescence competitive experiments of Al^{3+} with other cations were also investigated. Equivalent Al^{3+} was added to the aqueous solution of L (5.0×10^{-5} M), then equivalent amount of other metal ions (Na^+, Mg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Fe^{3+}, Cr^{3+}, Hg^{2+}, Zn^{2+}, Cd^{2+}) were also added into the solution. Their fluorescence intensities were recorded, respectively. The histogram of fluorescence changes were listed in Fig. 4. As shown in Fig. 4, no significant variation in the fluorescence emission was observed by comparison with that without the other metal ions. All the results indicated that the high selectivity of L toward Al^{3+} over other co-existent metal ions in aqueous media (pH 7.4).

3.2. The UV–Vis absorption spectroscopy response of L to Al^{3+}

As shown in Fig. 5, the absorption spectrum of L (5.0×10^{-5} M) in aqueous media (pH 7.4) exhibited a strong peak at 260 nm, which was ascribed to the characteristic band of sensor molecule L. With addition of Al^{3+}, the absorption spectrum changed significantly with the solution turning from colorness to yellow, clearly indicating the interaction of L with Al^{3+}. A new absorption bands appeared obviously at 450 nm upon addition of Al^{3+}, which also indicated the coordination between L and Al^{3+} lead to the mutli-wavelength emissive fluorescence emission.

4. Conclusions

In summary, we have developed 3-[1′-(2′-hydroxy-α-methylbenzylidene-imino)]-2-(*p*-*N*,*N*-dimethylaminophenyl)-1,2-dihydroquinazolin-4-(3H)-one based multi-wavelength emissive fluorescent chemosensor for Al^{3+}. It exhibits high selectivity toward Al^{3+} over other metal ions in aqueous media (pH 7.4). Moreover, according to the investigation, 1:1 stiochiometry between L and Al^{3+} is formed. The excellent selectivity of chemosensor for Al^{3+} in aqueous media (pH 7.4) indicates its potential application value in the biological monitoring and tracking of Al^{3+}.

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Appendix A. Supplementary material

The ^1H NMR, ^{13}C NMR, ESI-MS of 3-[1′-(2′-hydroxy-α-methylbenzylidene-imino)]-2-(*p*-*N*,*N*-dimethylaminophenyl)-1,2-dihydroquinazolin-4-(3H)-one and ESI-MS of 3-[1'-(2'-hydroxy-α-methylbenzylidene-imino)]-2-(*p*-*N*,*N*-dimethylaminophenyl)-1,2-dihydroquinazolin-4-(3H)-one with Al^{3+} in aqueous media were listed in supplementary materials. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.10.009.

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