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ARTICLE TYPE

A differentially selective molecular probe for detection of trivalent ions (Al^{3+} , Cr^{3+} and Fe^{3+}) upon single excitation in mixed aqueous medium

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A chemosensor was developed which could selectively detect and differentiate trivalent metal ions (Al^{3+} , Cr^{3+} and Fe^{3+}) upon single excitation at two different wavelengths in aqueous medium. This probe selectively detects trivalent ions in the presence of different metal ions in aqueous medium. It shows an excellent performance in the “dipstick” method.

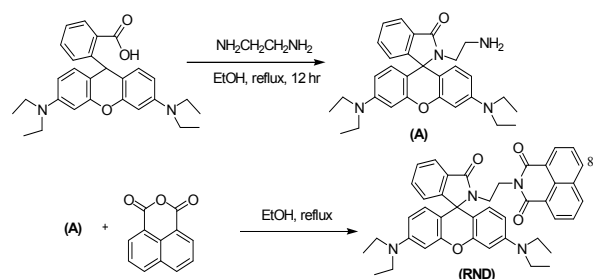
Introduction :

Trivalent cations have important biological properties and are directly involved in the cell function where there is a critical control of M^{3+} levels.¹ On the other hand the development of fluorescent probes for metal ion detection is an attractive field because sensors based on ion-induced changes in fluorescence show simplicity, high sensitivity and instantaneous response.² For example, Al^{3+} is a necessary element in human nutrition. Aluminum is present in its ionic form Al^{3+} in natural waters and biological tissues. The solubility of Al minerals at lower pH increases the amount of available Al^{3+} which is deadly to growing plants and its ultimate effect is the environmental acidification.³ It has been found that Al^{3+} ions exerted several neurotoxic effects in organisms a long time ago.⁴ For example, Al^{3+} has an important role in Alzheimer’s disease, Parkinson’s disease, bone softening, chronic renal failure and smoking-related diseases. According to a WHO report, the average daily intake of aluminum is approximately 3-10 mg per day for human beings as it has been widely used in water treatment, as a food additive, aluminum-based pharmaceuticals, and aluminium containers and cooking utensils. Cr^{3+} has direct impacts on the metabolism of carbohydrates, fats, proteins and nucleic acids by either activating certain enzymes or stabilizing proteins and nucleic acids.⁵ Chromium deficiency can increase the risk factors associated with diabetes and cardiovascular diseases.⁶ Fe^{3+} plays an indispensable role in many biochemical processes at the cellular level,⁷ and in the oxygen transport processes in all tissues in the form of haemoglobin.⁸ And in recent years, it has been recognized that excessive intake of Fe^{3+} leads to a wide range of diseases, such as Alzheimer’s disease, Huntington’s and Parkinson’s diseases.⁹

In the last decade, there are only few chemosensors reported

for detection of trivalent ions and they all reported detection of trivalent ions in a single wavelength.¹⁰ Both trivalent chromium (Cr^{3+}) and iron (Fe^{3+}) are paramagnetic in nature. Thus, in most of the cases they behave as fluorescence quencher¹¹ which makes it difficult to develop a fluorescence turn-on sensor. In contrast, Al^{3+} is diamagnetic, whose binding to sensors often enhances the fluorescence.¹² Recently, Wang et al¹³ reported a chemosensor for trivalent ions at different wavelength. But difference between these two wave length is quite low. It may cause difficulty for detection. Thus, It remains a challenge to design a fluorescent sensor that can recognize and differentiate the trivalent cations (Al^{3+} , Cr^{3+} and Fe^{3+}) in two different wavelengths and the difference between two wavelengths is quite high. Herein, we demonstrated that a dyad containing a rhodamine and a naphthalic anhydride moiety could be used as a fluorescent probe for monitoring trivalent ions at two different wavelengths. Rhodamine has been chosen as an ideal component of a fluorescent chemosensor due to its high quantum yield, photo stability, absorption and emission in the visible region.¹⁴

Hence, considering the above facts, we have designed and synthesized a new rhodamine– naphthalic anhydride based sensor (RDN) for the differentially selective detection of trivalent cations in aqueous media.



Scheme 1: Synthetic scheme of the receptor

The synthesis of the chemosensor RDN is outlined in Scheme 1. Intermediate (A)¹⁶ was synthesized according to the published procedure. The structure of the receptor was confirmed by ^1H NMR, ^{13}C NMR and HR MS spectra (see

ESI).

Experimental section

General :

The chemicals and solvents were purchased from Sigma-Aldrich Chemicals Private Limited and were used without further purification. Melting points were determined on a hot-plate melting point apparatus in an open-mouth capillary and were uncorrected. ¹H-NMR and ¹³C-NMR spectra were recorded on Bruker 400 MHz instruments respectively. For NMR spectra, CDCl₃ was used as solvent with TMS as an internal standard. Chemical shifts are expressed in δ □□units and ¹H–¹H coupling Hz. UV-vis titration experiments were performed on a JASCO UV-V530 spectrophotometer and fluorescence experiment was done using PTI fluorescence spectrophotometer with a fluorescence cell of 10 mm path. IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer, using KBr discs.

Methods for the preparation of receptor :

Synthesis of receptor (RDN): In a 25 mL flask, rhodamine ethylenediamine (1g, 2.06 mmol) and 1,8 naphthalic anhydride (416 mg, 2.1mmol) were suspended in 20mL ethanol. The mixture was refluxed for 12 hr with stirring, during which time an orange precipitate was formed. The precipitate was separated by filtration and washed with 3 x 10 mL ethanol. The crude product was then chromatographed on silica gel using CHCl₃–CH₃OH (95 : 5, v/v) as the eluent, to afford 900 mg (68%) RDN as a orange solid.

¹H NMR (CDCl₃, 400 MHz) δ (ppm): 8.469 (d, 2H, J= 7.6 Hz), 8.148 (d, 2H, J=3.36 Hz), 7.909 (1H, s), 7.687 (t, 2H, J= 7.6 Hz), 7.459 (d, 2H, J= 3.6 Hz), 7.010 (t, 2H, J= 4.2 Hz), 6.832 (d, 3H, J= 9.2 Hz), 6.188 (d, 2H, J= 8.4 Hz), 4.335 (t, 8H, J= 5.6 Hz), 3.688 (t, 4H, J= 4 Hz), 0.868 (t, 12H, J= 6.8 Hz)

¹³C NMR (CDCl₃, 100 MHz): δ (ppm): 177.47, 167.17, 153.77, 148.81, 141.48, 139.41, 137.08, 135.28, 132.44, 131.54, 128.01, 126.25, 123.75, 122.92, 114.05, 107.95, 104.41, 102.46, 97.86, 53.03, 51.43, 44.27, 41.42, 12.53

MS (HR MS): (m/z, %): 665.3931 [(M + H⁺)⁺, 100 %]

Synthesis of the Al³⁺–complex of the sensor RDN: The Al³⁺ complex of the sensor was synthesized by adding the sensor (664 mg, 1 mmole) to a methanolic solution of Al(NO₃)₃·9H₂O (380 mg, 1 mmole) and the whole mixture was refluxed for 5 h to complete the complexation. The solvent was removed under vacuum and the whole mass was washed with diethyl ether several times. Finally a reddish-orange colored solid (510 mg) was obtained (Yield: 74 %).

MS (HR MS): (m/z, %): 710.0076 (RDN + Al³⁺ + H₂O)³⁺, 100 %]

Determination of fluorescence quantum yield:

Here, the quantum yield φ was measured by using the following equation,

$$\phi_x = \phi_s (F_x / F_s)(A_s / A_x)(n_x^2 / n_s^2)$$

Where,

X & S indicate the unknown and standard solution respectively, φ = quantum yield,

F = area under the emission curve, A = absorbance at the excitation wave length,

n = index of refraction of the solvent. Here φ measurements were performed using rhodamine in ethanol as standard [φ = 0.27] (error ~ 10%).

The quantum yield of RDN itself is 0.015 which is remarkably changed into 0.75, an enhancement around 50 fold is observed in presence of Al³⁺.

This quantum yield changed to 0.36 and 0.255 in presence of Cr³⁺ and Fe³⁺.

General method of UV-vis and fluorescence titrations:

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By UV-vis and fluorescence method:

For UV-vis and fluorescence titrations, stock solution of the sensor was prepared (c = 2 x 10⁻⁵ ML⁻¹) in CH₃OH: H₂O (6:4, v/v). The solution of the guest cation was prepared (2 x 10⁻⁴ ML⁻¹) in CH₃OH: H₂O (6:4, v/v) at pH 7.1 by using 10 mM HEPES buffer. The original volume of the receptor solution is 2 ml. Solutions of the sensor of various concentrations and increasing concentrations of cations, anions and amine containing compounds were prepared separately. The spectra of these solutions were recorded by means of UV-vis and fluorescence methods.

Results and discussion

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UV-vis and Fluorescence study :

From the observed change of fluorescence intensity at 582 nm with pH, we found the optimal condition (i.e. pH = 7.1) (near neutral pH) under which the receptor can work as a metal-sensing probe (Figure S4). Now, the behavior of RDN toward a variety of cations was explored with UV-vis absorption spectrometry. The solution of the RDN in HEPES (20 mM, CH₃OH–H₂O, 6 : 4 v/v, pH 7.1) buffer solution was also nearly colorless and did not exhibit apparent absorption above 558 nm, due to the formation of the stable spirolactam ring. Addition of Al³⁺ to a solution of RDN led to an obvious absorption enhancement at 558 nm, along with an obvious color change from colorless to pink (Figure 1a). Thus, this detection behavior could be easily seen with the naked eye. Such absorption change in the UV-vis region may be ascribed to the newly formed complex between the RDN and the metal ion i.e. Al³⁺. In fact, in the presence of 1 equiv. of Al³⁺, a 31 fold enhancement was achieved with respect to the Al³⁺ free solution (Figure 1b).

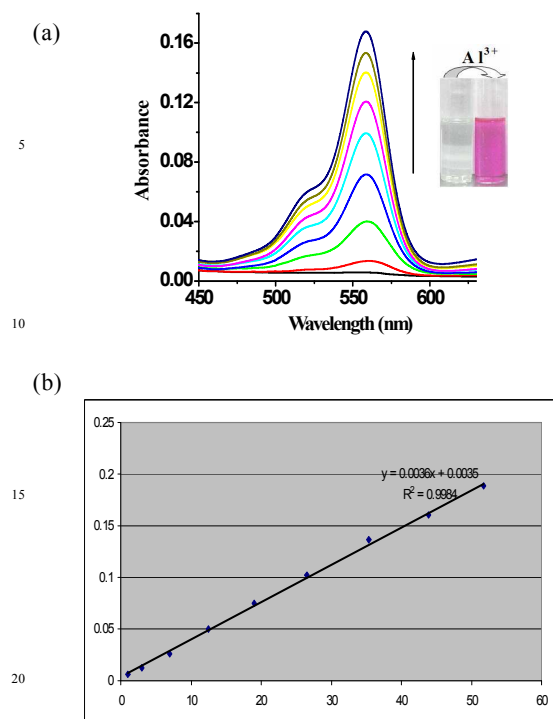


Figure 1 : (a) UV-vis absorption titration spectra of RDN ($c = 2 \times 10^{-5}$ M) in the presence of Al³⁺ ($c = 2 \times 10^{-4}$ M) in MeOH:H₂O (6 : 4, v/v, 25 °C, at pH = 7.1, 20 mM HEPES buffer); (b) Plot of the absorbance vs. the whole range of Al³⁺ concentration tested at 558 nm

The absorption spectra of the RDN probe in the presence of different cations were investigated. As shown in Figure 2 the representative species including Hg²⁺, Cd²⁺, Co²⁺, Ag⁺, Fe³⁺, Cu²⁺, Na⁺, Cr³⁺, Fe²⁺, Ni²⁺, Pb²⁺, Zn²⁺, In³⁺ showed nearly no change in the absorption spectra observed upon the addition of those species at a concentration of 40 mM, indicating that our probe showed a selective response towards Al³⁺ over other cations. Probably, the high positive charge density of Ga³⁺ comparable to Al³⁺ is responsible for this interference.

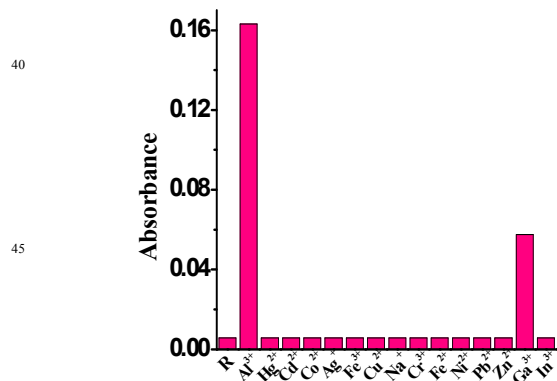


Figure 2 : Comparison of absorption of the RDN probe at pH 7.1 in CH₃OH-H₂O (6 : 4, v/v), in the presence of various cations.

A fluorescence study was carried out in the presence of various cations to determine the selectivity and sensitivity of RDN. The free probe displayed emission peak with maximum intensity at around 375, which are characteristics of the naphthalic moiety. Fascinatingly, treatment of RDN ($\Phi = 0.0015$) with Al³⁺ resulted in a strong increase in the fluorescence intensity in the emission spectrum at 582 nm (red emission) ($\Phi = 0.75$) upon excitation at 330 nm (Fig. 3).

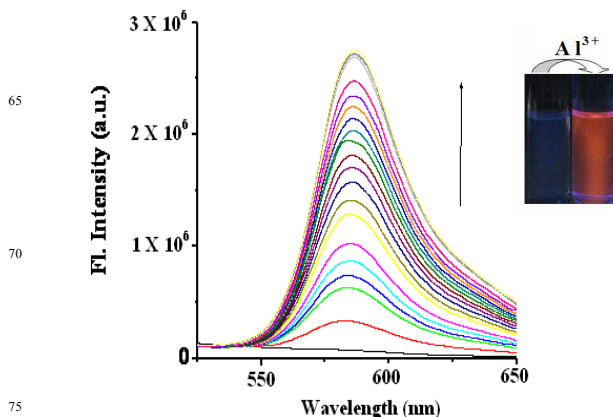
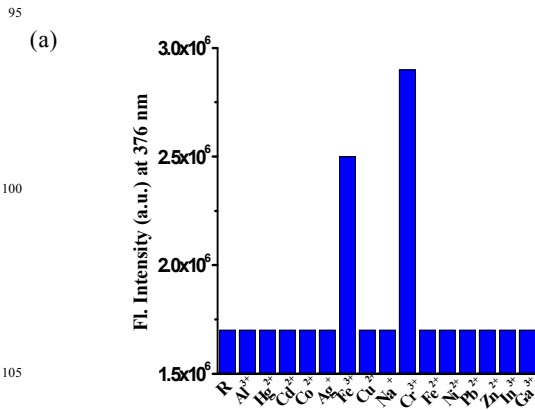


Figure 3 : Fluorescence emission spectra of RDN ($c = 2.0 \times 10^{-5}$ M) with Al³⁺ ($c = 2.0 \times 10^{-5}$ M) at pH 7.1 in CH₃OH:H₂O (6 : 4, v/v) with the naked eye fluorescence change in a UV lamp (inset).

The intensity of the new peak (at 582 nm) increased regularly as the concentration of Al³⁺ was increased. A significant enhancement (62 fold) of emission intensity at 582 nm was observed upon addition of 1 equivalent of Al³⁺ (Figure 3). A further increase in concentration of Al³⁺ (2 equiv.) did not lead to more enhancement of fluorescence intensity at 582 nm. This result indicates that the spirolactam ring (non-fluorescent) of the rhodamine based receptor is opened by complexation with Al³⁺ (Scheme 2). The increased emission intensity was due to the complexation of Al³⁺ and RDN. Due to the oxophilic nature and high charge density of Al³⁺, strong binding happens with RDN and opens the spirolactam ring of rhodamine, followed by a large CHEF effect.¹⁷



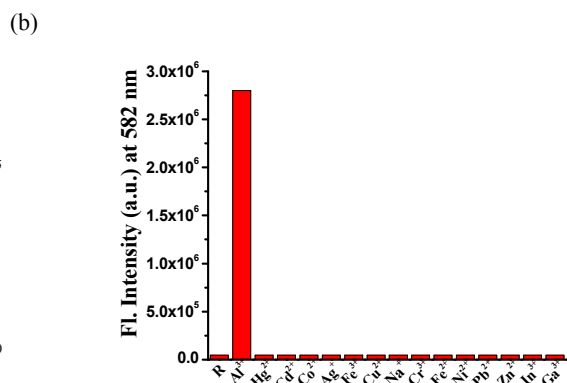
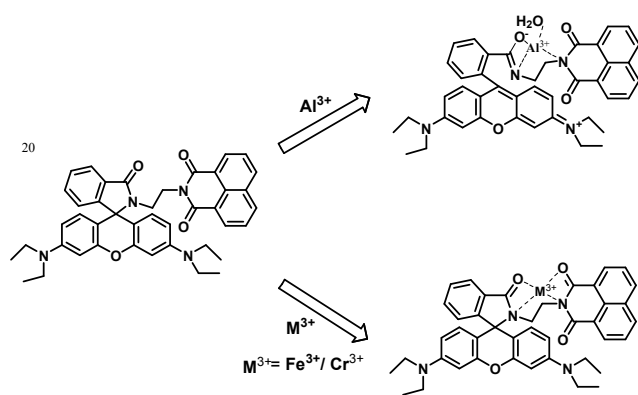


Figure 4: Fluorescence response of RDN (2.0×10^{-5} M) towards cations (1 equiv.) with emission spectroscopy (a) at 376nm and (b) 582 nm



Scheme 2: Probable binding mode of receptor (RDN) with Trivalent (Al^{3+} , Fe^{3+} and Cr^{3+}) ions.

As determined by the fluorescence titration method (Figure S6), the association constant for the sensor RDN with Al^{3+} was estimated to be $1 \times 10^4 \text{ M}^{-1}$ (error < 10%), using the Benesi–Hildebrand equation¹⁸, which indicated that the probe RDN has a higher binding affinity for Al^{3+} . The association constant for the sensor RDN with Cr^{3+} and Fe^{3+} were estimated to be $2.6 \times 10^2 \text{ M}^{-1}$ and $1.2 \times 10^2 \text{ M}^{-1}$ respectively. The calculated detection limits are 1.74 nM (for Al^{3+}), 2.36 μM (for Cr^{3+}) and 2.90 μM (for Fe^{3+}) based on $K \times \text{Sb1}/\text{S}$,¹⁹ where K (a constant) = 2 or 3, Sb1 is the standard deviation of blank measurements and S is the slope of the calibration curve (Figure S1, S2 and S3). The 1 : 1 complex formation between RDN and trivalent ions (Al^{3+} , Cr^{3+} and Fe^{3+}) were established by a Job plot (Figure S5).²⁰

Only the fluorescence of Al^{3+} complexes changed to red (582 nm). The distinctive feature in optical response thus allowed us to distinguish Al^{3+} from Cr^{3+} and Fe^{3+} . These different response to trivalent ions enabled us distinctly detect Cr^{3+} , Fe^{3+} and Al^{3+} cations among all other cations. In the case of Cr^{3+} and Fe^{3+} (1 equiv.) the fluorescence intensity of RDN at 582 nm was increased by 1.7 and 1.47 fold respectively. The

comparison of spectra between these three trivalent metal ions indicates that Al^{3+} can form a tighter complex with RDN may be due to its smaller size than Fe^{3+} and Cr^{3+} (ionic radius 0.50 \AA for Al^{3+} versus 0.69 \AA and 0.64 \AA for Cr^{3+} and Fe^{3+} , respectively). The fluorescence quantum yield of the sensor increased from 0.015 to 0.75, 0.36 and 0.255 respectively, in the presence of 1 equivalent of Al^{3+} , Cr^{3+} and Fe^{3+} (ESI†). The difference in quantum yield is high enough to discriminate between these cations from each other.

A detailed analysis of the emission spectrum of RDN in the presence of other metal cations was carried out. As shown in Figure 4, the addition of 1 equiv. of Hg^{2+} , Cd^{2+} , Co^{2+} , Ag^+ , Cu^{2+} , Na^+ , Fe^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} , In^{3+} and Ga^{3+} had no noticeable effect on the fluorescence emission at 375 nm and 582 nm respectively. Competitive experiments in the presence of the above-mentioned metal cations also demonstrate the selective response of RDN to Al^{3+} or Cr^{3+} or Fe^{3+} (Figure S7). This indicates that the sensor can be used potentially to quantitatively detect Al^{3+} as well as trivalent ions (Cr^{3+} or Fe^{3+}) at low concentration with high selectivity (Figure S8).

Spectral study:

^1H NMR study:

Furthermore, we investigated the ^1H NMR spectra of RDN in presence of trivalent cations (Al^{3+} , Cr^{3+} and Fe^{3+}) and compared with that of the sensor itself. Interestingly, the peak at 4.355 ppm (ethylenic protons of RND) shifted to 4.537 ppm due to binding with Al^{3+} . Moreover, the peak at 6.832 ppm and 6.188 ppm (for rhodamine aromatic protons) shifted to 6.952 ppm and 6.601 ppm respectively after binding with Al^{3+} . From this ^1H NMR titration data we conclude that, rhodamine and naphthalic probe supply a hard base environment towards hard acid Al^{3+} , thus probably both the moieties are involved in binding with Al^{3+} . In case of Cr^{3+} and Fe^{3+} the peak at 4.355 ppm shifted to 4.421 ppm and 4.357 ppm respectively and all aromatic protons very slightly shifted downfield indicating that Fe^{3+} and Cr^{3+} are weakly associated with both rhodamine and naphthalic Moiety.

HRMS study:

The HRMS spectrum of RDN shows a peak at m/z 665.3931 possibly for $[\text{RDN} + \text{H}]^+$ whereas the Al^{3+} complex shows a peak at m/z 710.0076 possibly for $[\text{RDN} + \text{Al}^{3+} + \text{H}_2\text{O}]^{3+}$, which also proves the mononuclear complex of RDN with Al^{3+} (ESI†). For Cr^{3+} , one intense peak appeared at 717.1670, corresponding to $(\text{RDN} + \text{Cr}^{3+})^{3+}$ and for Fe^{3+} at 721.1191 corresponding to $(\text{RDN} + \text{Fe}^{3+})^{3+}$ indicating that $\text{RDN}-\text{Cr}^{3+}$ and $\text{RDN}-\text{Fe}^{3+}$ complexes are also formed.

Applications :

To investigate the practical applications of the chemosensor RDN, test strips were prepared by immersing filter papers into

a CH₃CN solution of RDN (2 X 10⁻⁴ M) and then drying in air. The test strips containing RDN were utilized to sense different cations at naked eye under sunlight. As shown in Fig. 5, when different cation solutions were added to the test kits obvious color changes were observed with Al³⁺ solutions only. Therefore, the test strips could directly detect Al³⁺ compare to other cations including trivalent ions in CH₃CN–H₂O binary solutions. Development of such dipsticks is useful as instant qualitative information is obtained without resorting to instrumental analysis.

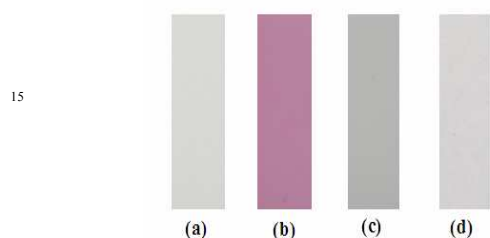


Figure 5 : Color changes of RDN on test paper (a) alone, (b) in the presence of Al³⁺ (c) in the presence of Cr³⁺ and (d) in presence of Fe³⁺ under naked eye.

Conclusions

In conclusion, we have demonstrated a single fluorescent molecular probe that can specifically detect trivalent ions (Al³⁺, Cr³⁺ and Fe³⁺) in aqueous medium at different wavelengths which is the first report to our knowledge. The probe remained silent in the presence of monovalent and divalent cations such as Hg²⁺, Cd²⁺, Co²⁺, Ag⁺, Cu²⁺, Na⁺, Fe²⁺, Ni²⁺, Pb²⁺, Zn²⁺. The acetonitrile solutions of RDN in the presence of Al³⁺ and Fe³⁺, Cr³⁺ resulted in an associated “turn-on” response via the formation of the corresponding metal complexes.

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Notes and references

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