



Light Responsive Material Based on Schiff Base Zn complexes

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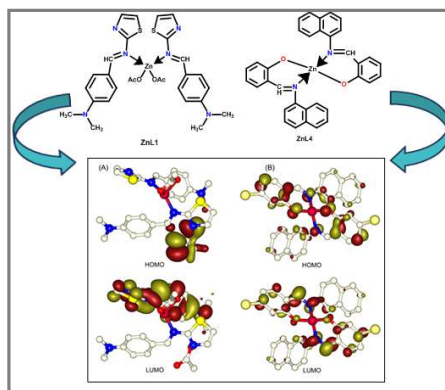
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ABSTRACT

A series of novel Schiff base ligands were systematically synthesized through condensation reactions involving primary amines and benzaldehyde, utilizing molar ratios of 1:1 or 1:1.5. The resulting Schiff base ligands were comprehensively characterized employing various spectroscopic techniques, including ¹H NMR, ¹³C NMR, UV-Vis spectroscopies, and elemental analysis. Subsequently, the coordination behavior of Zn(II) transition metal ions with these newly prepared Schiff base ligands was explored. The study identified imine ligand-containing transition metal complexes, particularly those involving zinc, as highly effective precursors for the synthesis of metal or metal chalcogenide nanoparticles. These synthesized complexes exhibited a versatile range of applications across diverse fields such as medicine, pharmacy, coordination chemistry, biological activities, industries, food packaging, dyes, polymers, and as O₂ detectors. Additionally, the antioxidant activity of the Schiff bases was evaluated using DPPH, revealing a correlation between superior free-radical-scavenging activity and lower absorbance. Notably, one specific ligand, (E)-5-bromo-2-((naphthalen-2-ylimino)methyl) phenol (L4), demonstrated exceptional antioxidant activity with a percentage of 97.14%, as observed in the course of this study.

Graphical abstract:



Selected Kohn-Sham orbitals of optimized geometry of (A) ZnL1 and (B) ZnL4 using UB3LYP/6-31G** level of theory.

Keywords: Schiff base, Condensation, Absorption band, Metal Complex, Antioxidant activity.

INTRODUCTION

Organic reactions that involve the condensation of two or more molecules to generate new compounds are common in the process of drug design as substances with unique biological behaviors [1]. These new compounds can be obtained through the formation of new compounds. Schiff bases are the byproducts of condensation reactions that take place between primary amines and ketones or aldehydes when certain conditions are met during the synthesis process. Schiff bases are significant for a number of reasons, including their capacity to stabilize metal ions in a variety of oxidation states, their involvement in a wide variety of catalytic and industrial applications, and their participation in broad-spectrum biological activities [2, 3]. The azomethine lone pair of electrons (N=CH) is responsible for the creation of stable complexes with metal ions [4, 5]. This is due to the bonding that occurs in the structure of azomethine. These stable complexes have a key role in a wide variety of essential biological activities, as well as in supramolecular chemistry, bioinorganic chemistry, and molecular magnetism [6, 7]. Imine complexes have a wide variety of biological activities, including those that are antibacterial, antifungal, antiviral, and antitumor [8]. In the fight against cancer, they are utilized to overcome medication resistance, and in antimalarial research, they are frequently examined. Additionally, they might be useful for the immobilization of enzymes [9, 10]. A large number of Schiff base ligands and their complexes were investigated for their interesting and important properties. Some of these properties include their photochromic properties, their ability to reversibly bind oxygen, their complexing ability towards some toxic metals, and their catalytic activity in the hydrogenation of olefins. Other complexes of Schiff bases give great applications in biological activity and biological modelling applications [11, 12]. In addition to this, they were crucial in the growth of inorganic biochemistry, the creation of modern coordination chemistry, and the production of optical materials [13]. Salicylaldehyde was utilized in the production of effective herbicides, pesticides, and fungicides [14]. These products possessed properties including anti-inflammatory, antibacterial, sterilization, and antiviral. Because transition metal complexes of Schiff bases play a significant part in the fields of biochemistry, analysis, and antibiotics reagents, they have been the subject of a significant amount of research [15].

Over the past few years, our research has been dedicated to investigating Schiff base metal complexes with biological relevance. Our work encompasses the synthesis of a series of these complexes, their thorough characterization, and exploration of their potential biological applications and light-responsive properties. Notably, all the complexes exhibit remarkable luminescence, both in solid and solution states, with the exciting discovery that we can finely tune their luminescent properties simply by modifying the nitrogen-bound ring, where variations in size and chemical composition significantly impact their behavior. This research holds promise for applications ranging from medicine to materials science, showcasing the versatility and potential of these novel compounds.

MATERIALS AND METHODS

Materials: All chemicals and reagents were purchased from Sigma Aldrich Chemical Company, USA and E. Merck India Ltd, India. All the reactions were performed in oven dried apparatus using dried and distilled solvents. The progress of the reaction was monitored by thin layer chromatography (TLC) using silica gel 60F254 aluminum sheets, and visualized by ultraviolet light at 254 nm.

Instrumentation: Synthesized compounds were purified by column chromatography by using silica gel (100–200 mesh). Melting points recorded on electro thermal apparatus using open capillary tubes are uncorrected. NMR spectra were recorded on BRUKER–AV400 spectrometer (Bruker Co., Faellanden, Switzerland) in DMSO—d₆ (1H at 400 MHz and 13C at 100 MHz). Chemical shifts (δ) are expressed in parts per million (ppm) and J (coupling constant) values in Hz. Multiplicities are

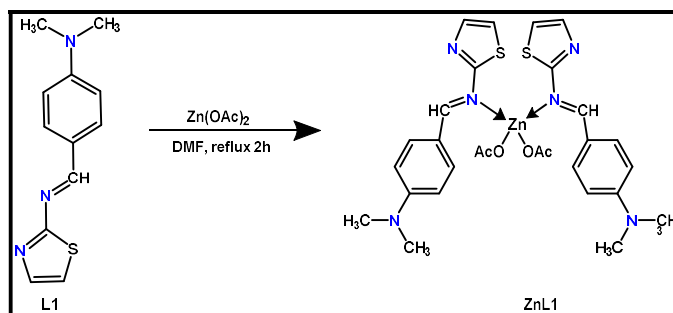
indicated by s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). The elemental analyses were performed on Perkin–Elmer 240–C analysis equipment. UV-Vis-NIR spectra were recorded on a PerkinElmer UV-Vis spectrometer. Steady-state emission measurements were performed on a FluoroMax-4: FM4-3000 spectrofluorometer (Horiba Jobin Yvon Technology) with an accuracy of ± 1 nm. The emission spectra of the solid sample were recorded at 295 K as well as 77 K. The slit widths for both excitation as well as phosphorescence emission were fixed at 1.00 nm.

Experimental Section: Ligand L1, L2, L3, L4, L5 and L6 were prepared using the general procedure; details for one representative case have been described below.

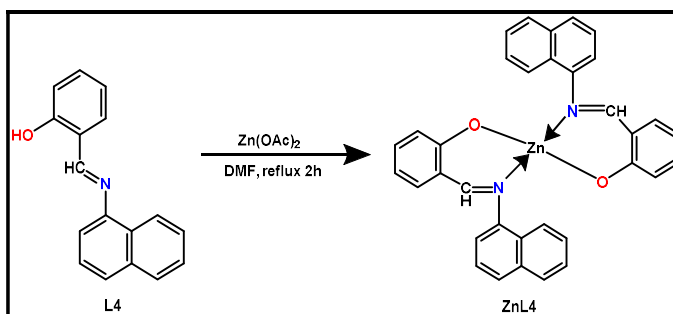
For the synthesis of Schiff base, substituted aromatic aldehyde was treated with commercially available different aromatic amines (1:1) or (1.5:1) in ethanol (30 mL) containing a few drops of glacial acetic acid as a catalyst. The resulting reaction mixture was heated with at 80°-90°C for 6-7 h. The progress of the reaction was checked by TLC. After the completion of the reaction, the reaction mixture was cooled at room temperature, concentrated, poured into ice cold water and basified with 2M NaOH (pH 10) resulting in the formation of a precipitate. The precipitate was filtered, washed with water and dried over CaCl₂ in the vacuum chamber to obtain the crude product. The product was then purified by column chromatography and finally crystallized using ethanol.

RESULTS AND DISCUSSION

Synthesis of metal complexes of Schiff base ligands: The metal complexes were synthesized by introducing a hot solution of the corresponding metal chloride/acetate in ethanol to a heated solution of the ligand in a mixture of ethanol and DMF. The resultant mixture was subjected to reflux for a duration of two hours, leading to the precipitation of the complexes. Subsequent filtration, washing with hot ethanol, and purification through multiple rinses with diethyl ether were employed. The analytical data for carbon (C), hydrogen (H), and nitrogen (N) were obtained through two repetitions.



Scheme 1. Synthesis of Zn (II) Complex of ligand L1.



Scheme 2. Synthesis of Zn (II) Complex of ligand L4.

UV-Visible spectroscopy: Figure 1 displays the absorption spectra of ligands **L1**, **L2** and **L3** when dissolved in dichloromethane (DCM) and measured at room temperature. The initial absorption band detected in the range of 320-340 nm in all these compounds is predominantly attributed to the presence of aromatic rings. In ligand **L1** the absorption maxima were observed at 330 nm while its 350 and 360 nm in **L3** and **L2** respectively. Similar absorption spectrum was observed in case of **L4**, **L5** and **L6** which is given in figure 2. The absorption maxima for **L1**, **L2**, and **L3** were determined to be 350, 370, and 375, respectively, when dissolved in a DCM solution. After metallation, the UV-Vis spectrum undergoes substantial changes. In the case of **ZnL1**, there is an absorption maximum at 380 nm with a shoulder at 400 nm, while in the case of **ZnL4**, the absorption maximum is at 380 nm with a shoulder at 350 nm (Figure 3).

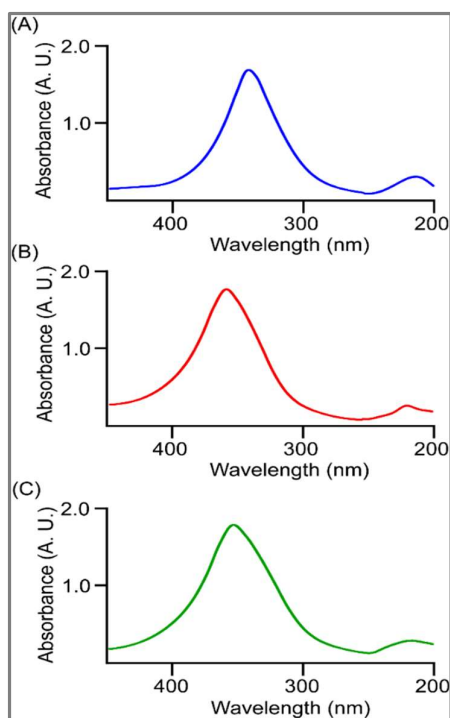


Figure 1. UV-Visible spectra (in dichloromethane at 295 K) of (A) **L1**, (B) **L2** and (C) **L3**.

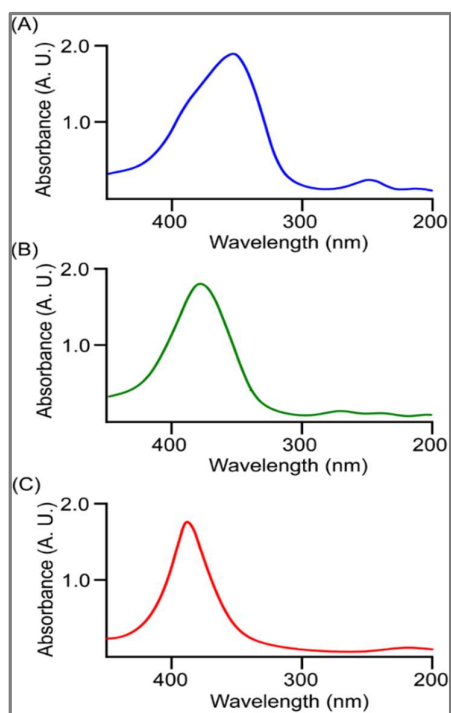


Figure 2. UV-Visible spectra (in dichloromethane at 295 K) of (A) **L4**, (B) **L5** and (C) **L6**.

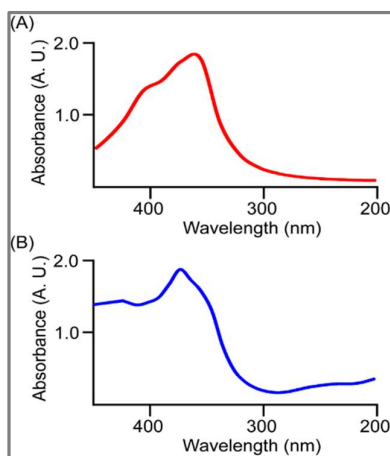


Figure 3. UV-Visible spectra (in dichloromethane at 295 K) of (A) **ZnL1** and (B) **ZnL4**.

Photoluminescence study: The ligands and their Zn complexes, as depicted in figures 4-6, exhibit a color ranging from white to yellow when observed in their solid state. Under the influence of a UV lamp with an excitation wavelength of 320 nm, **L1**, **L2**, **L3**, **L6**, and **ZnL1** display a reddish hue, whereas **L4**, **L5**, and **ZnL4** emit a reddish-yellow luminescence. This luminescent behavior is likely a result of intra ligand charge transfer within the Schiff base ligands.

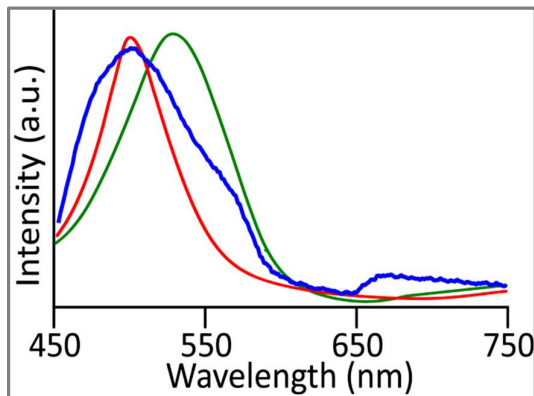


Figure 4. Normalized emission spectra of solid samples of **L1** (blue), **L2** (green) and **L3** (red) at 295 K, excitation wavelength 320 nm.

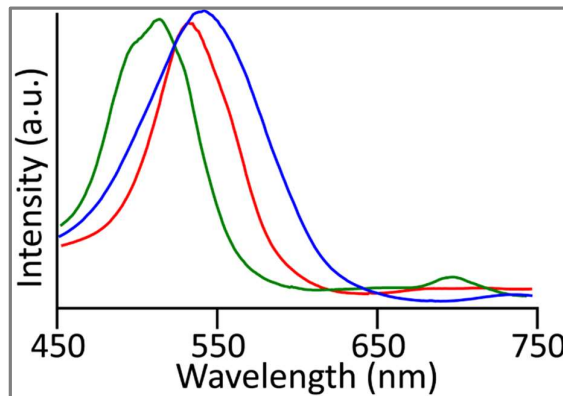


Figure 5. Normalized emission spectra of solid samples of **L4** (blue), **L5** (green) and **L6** (red) at 295 K, excitation wavelength 320 nm.

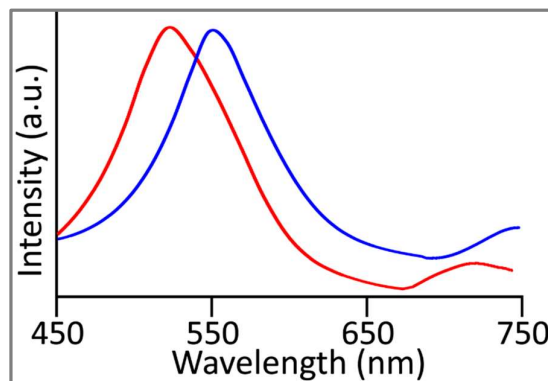


Figure 6. Normalized emission spectra of solid samples of **ZnL1** (blue), and **ZnL4** (red) at 295 K, excitation wavelength 320 nm.

Quantum chemical calculations: To understand the origin of the luminescence spectra, TDDFT method was employed at cam-B3LYP/6-31G**/LANL2DZ level to compute the luminescent spectra on the basis of the lowest singlet state geometry of ligand and their metal complexes. Figures 9 (see in SI) and S1-S2 display frontier molecular orbitals of the ligand and their metal complexes. In ligands **L1**, **L2** **L3** and **L4** HOMOs and LUMOs distributed over entire ligand with significant contribution from C=N bond and aromatic π rings while in **L4** and **L5** HOMOs are confined on naphthalene moiety and LUMOs are located on phenyl ring suggesting charge transfer character in these systems.

In the metal complex **ZnL1** the HOMO is located on ligated acetate and LUMO is present on the thiazole ring, however, in **ZnL4** the HOMO and LUMO are distributed over entire ligand. The UV-Vis spectra of the ligand and its metal complexes has been simulated by employing TD-DFT calculations, which reproduces the major features of the experimental spectrum the calculation shows that absorption maxima appear as a result of the transition between HOMO to LUMO (Figure 7 and Figures 10-12, see in SI). The MO analysis reveals that S1 states of ligand and their metal complexes are ligand to ligand charge transfer (LLCT) [17, 18].

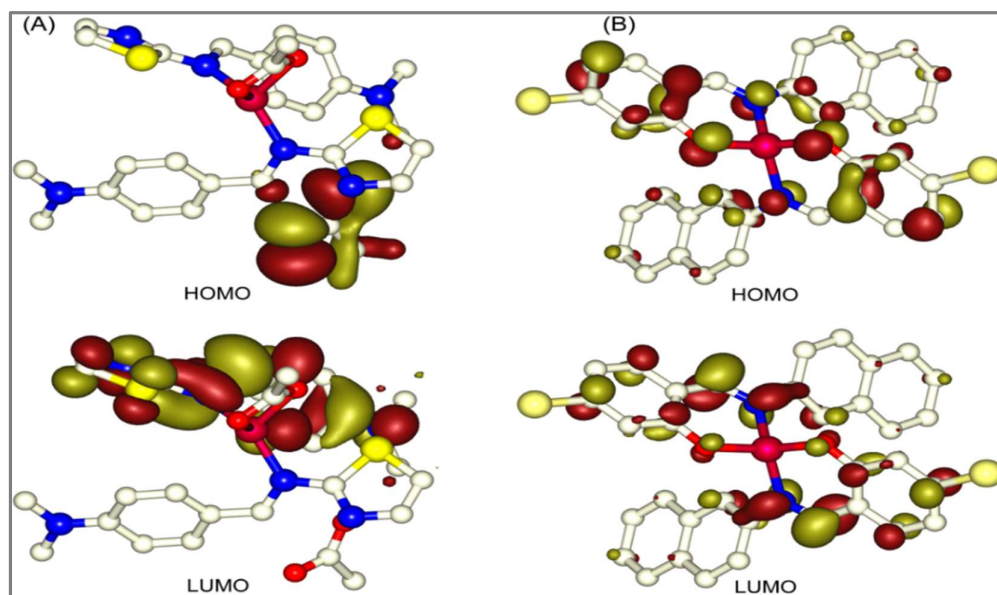


Figure 7. Selected Kohn-Sham orbitals of optimized geometry of (A) **ZnL1** and (B) **ZnL4** using UB3LYP/6-31G** level of theory.

APPLICATION

Antioxidant activity evaluation of Schiff base ligand: The antioxidant activity of the test compounds was evaluated using DPPH (2, 2-diphenyl-2-picrylhydrazyl hydrate) assay. DPPH is a stable free radical, against which the test compounds have spectrophotometrically shown the radical scavenging activity. DPPH reduction occurred by the attack of hydrogen donating antioxidant moiety, which bleached the dark purple color to yellow in methanol [19]. Then UV-Vis spectrophotometer was used for measuring the absorbance at 517 nm. It can be concluded from the present study that the molecules with the greater free-radical-scavenging activity, were associated with lower absorbance. The following equation [20] was used for the calculation of the radical scavenger effect of DPPH*:

Scavenging effect (%)

$$= \frac{\text{Absorbance of control} - \text{Absorbance of sample}}{\text{Absorbance of control}} \times 100$$

Stock solutions (1mg 10 mL⁻¹) of **L1**, **L2**, **L3**, **L4**, **L5** and **L6** (here ‘L’ stands for the ligand or molecule) were prepared in methanol. The stock solution of DPPH* was also prepared at the concentration of 2mg 100 mL⁻¹ in methanol.

Different concentrations such as 2 mL, 1.5 mL, 1 mL, 0.5 mL, 0.25 mL, 0.125 mL of ligands were taken out in the test tube separately and made up the volume up to 2 mL by adding methanol respectively. Now add 2 mL DPPH* solution in each test tube and make the volume up to 4 mL and kept the solutions for 30 minutes in dark. After the incubation, the absorbance of all the samples was recorded by UV- spectrophotometer.

The ligand **L4** showed antioxidant activity with 97.14% while **L1**, **L2**, **L3**, **L5** and **L6** showed 71.92, 60.32, 30.12, 63.12 and 57.78 respectively (from Table 1).

Table 3. Antioxidant activity of Schiff base ligands

S. No.	L1, L2, L3, L4, L5 and L6	% Antioxidant activity (by DPPH* assay)
1	(E)-N,N-dimethyl-4-((thiazo-2-ylimino)methyl)aniline (L1)	71.92
2	(E)-N,N-dimethyl-4-((naphthalen-2-ylimino)methyl) aniline (L2)	60.32
3	(E)-4-((4-(dimethylamino)benzylidene)amino)benzoic acid (L3)	30.12
4	(E)-5-bromo-2-((naphthalen-2-ylimino)methyl)phenol (L4)	97.14
5	(E)-N-(naphthalen-2-yl)-1-(4-nitrophenyl)methanimine(L5)	63.12
6	(E)-4-((naphthalen-1-ylimino)methyl)aniline (L6)	57.78
7	Gallic Acid (Standard)	95.66

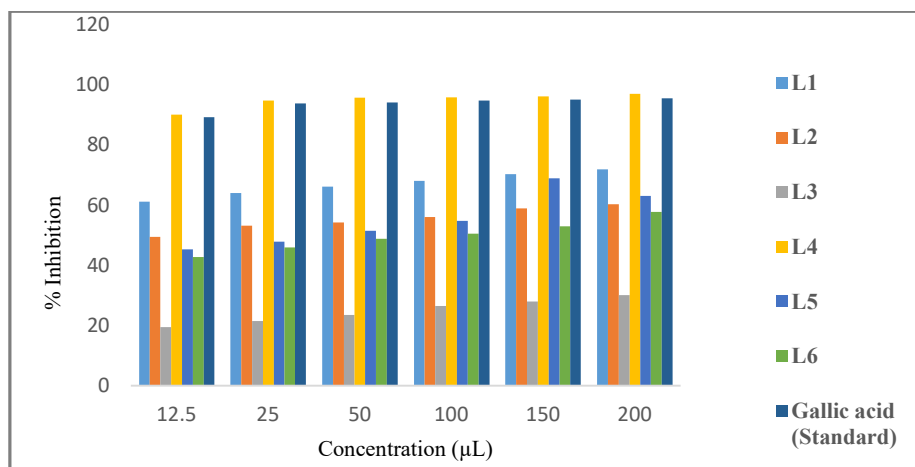


Figure 14. Antioxidant activity of Schiff base ligands.

The ligand L4 showed higher antioxidant activity with 97.14% inhibition in comparison to other Schiff base ligands. The high antioxidant activity of L4 Schiff base ligand is due to the presence of one phenolic -OH group. These phenolic -OH group making the compound highly antioxidant.

CONCLUSION

In this chapter, we have successfully synthesized and thoroughly characterized six distinct Schiff-based ligands along with their corresponding metal complexes using a variety of spectroscopic techniques. This comprehensive analysis enabled us to gain a deep understanding of their molecular structures and properties. Notably, these compounds have been explored for their potential applications as luminescent materials, and the results have been quite remarkable. All of the complexes exhibit a visually captivating reddish fluorescence, which is a highly desirable property for materials used in various applications, including lighting and display technologies.

Furthermore, our theoretical calculations have provided valuable insights into the underlying mechanisms responsible for this striking luminescent behavior. It has been suggested that ligand-to-ligand charge transfer plays a pivotal role in the luminescence of these molecules. This means that electrons within the complex are transferred between the ligands, leading to the emission of light in the visible spectrum. These findings hold significant promise for utilizing these compounds in light-responsive materials, where their unique luminescent properties can be harnessed for applications such as sensors, optical devices, and advanced technologies that rely on controlled light emission and absorption.

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Conflict of interest: The authors declare no competing of interest.

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