Self-Assembly of Europium-Containing Polyoxometalates/Tetra-\(n\)-alkyl Ammonium with Enhanced Emission for Cu\(^{2+}\) Detection

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Supporting Information

ABSTRACT: Lanthanide-containing polyoxometalates (POMs) can be used to detect various materials, but their luminescence in water has suffered enormous limitations due to the strong fluorescence quenching. Herein, to resolve this problem, three-dimensional nanoparticles built by mixed Weakley-type europium-containing POMs (Na\(_9\)[EuW\(_{10}\)O\(_{36}\)]·32H\(_2\)O, abbreviated to EuW\(_{10}\)) and tetra-\(n\)-alkyl ammonium (TA) with enhanced fluorescent properties have been designed in aqueous solution using an ionic self-assembly (ISA) technique, which is mainly driven by the electrostatic interaction between EuW\(_{10}\) and TA. The morphology and fluorescent properties of the system as well as some influencing factors (alkyl chain length, amino group, and inorganic salt concentration) were systematically investigated. The results indicated that the fluorescent intensity of EuW\(_{10}\)/tetramethylammonium bromide (TMAB) composite increased about 14 times, whereas the extent of increase of fluorescence for EuW\(_{10}\)/tetraethylammonium bromide (TEAB) and EuW\(_{10}\)/tetrabutylammonium bromide (TMAB) composites gradually decrease due to the bulkier steric hindrance of the longer alkyl chain. Besides, the luminescence of EuW\(_{10}\)/TMAB nanoparticles is pH responsive, and the reversibility of their structures and luminescence can be realized upon the addition of NaOH/HCl. Moreover, the EuW\(_{10}\)/TMAB system also shows great fluorescence-sensing behavior, which could detect Cu\(^{2+}\) with a detection limit of 0.15 \(\mu\)M. Our work provides a facile construction strategy for a functional fluorescent complex via POMs-based supramolecular self-assembly in aqueous solution, which will be further used in biomarkers and sensors.

INTRODUCTION

The detection of biologically and environmentally related heavy metal ions (Cd\(^{2+}\), Hg\(^{2+}\), Cu\(^{2+}\), etc.) is crucial due to their important roles in biological processes and hazard to the environment.\(^1\) Among various heavy metals, copper is an essential trace element for living systems. The excess of unbound Cu\(^{2+}\), the natural form of free copper in biological media, is quite harmful and can even cause various neurodegenerative diseases. Meanwhile, Cu\(^{2+}\) may be a common pollutant of drinking water that affects water quality and leads to multifarious infections.\(^2,3\) Until now, the approaches for Cu\(^{2+}\) ion detection reported are inductively coupled plasma atomic emission spectroscopy (ICP-AES), atomic absorption spectroscopy, inductively coupled plasma mass spectroscopy (ICP-MS), and voltammetry. However, these approaches are time consuming, expensive, and quantitative; thus, it is necessary to develop a new method for the detection of Cu\(^{2+}\) ions.

For the past few years, the development of a range of smart fluorescence materials including transition-metal complexes,\(^4,5\) organic dyes,\(^6\) inorganic semiconductor nanocrystals,\(^7,8\) carbon dots,\(^9,10\) and lanthanide-doped upconverting nanoparticles\(^11,12\) have attracted particular attention. These fluorescent compounds have great demand in optoelectronics, lighting, and so forth;\(^13,14\) especially, fluorescent probing or sensing is now becoming an effective detection modality. Fluorescence detection is a highly versatile spectroscopic method with a short response period, high sensitivity, technical simplicity, and extensive applicability, which can be widely used at real time and in situ.\(^15\) Therefore, it is a vital challenge to explore a robust fluorescent material with excellent sensitivity, selectivity, and a rapid response time for Cu\(^{2+}\) ions.

Polyoxometalates (POMs) are a well-known class of environment friendly and structurally well-defined nanosized metal-oxide clusters with significant applications in optics, catalysis, electronics, magnets, and biomedicine.\(^16–23\) Espe-
cally, lanthanide (Ln) group element-doped polyoxometalates are of great importance in the fluorescence field because of their excellent photoluminescence properties, such as narrow emission bands, long lifetime, large Stokes shift, tunable emission, and abundant valence electrons in f orbitals.24,25 Thus, Ln3+-doped nanoscale POM composite materials are suitable as fluorescent sensors to detect heavy metal ions.26

Although lanthanide-containing POMs (such as Na₆[EuW₁₀O₃₈]·32H₂O abbreviated to EuW₁₀) have excellent fluorescent properties,27 the biggest problem is the quenched emission in water solution due to the ubiquitous O–H vibrations.28,29 To solve this problem, using the concept of self-assembly to suppress such quenching is a powerful methodology. Self-assembly is one of the advanced nanotechnologies used to design novel nanostructures, which is driven by noncovalent interactions such as hydrogen bonding, electrostatic interaction, hydrophobic interaction, steric effect, van der Waals force, and π–π stacking30–33 and can efficiently enhance the fluorescence property. Thus, it is attractive to improve the fluorescent properties and construct novel supramolecular nanostructures of lanthanide-containing POMs through the self-assembly of POMs with other components.

With these issues in mind, we reported a new aggregate that comprises Weakley-type lanthanide-containing POMs (EuW₁₀) and tetra-n-alkylammonium (TA), which form well-defined hybrid nanoparticles with enhanced emission. Moreover, our results further demonstrate that the fluorescent nanoparticles showed a pH-responsive behavior and can selectively detect Cu²⁺ in water with the detection limit of 0.15 μM, suggesting the potential of the fluorescence materials for optoelectronic applications and sensing device fabrication.

**RESULTS AND DISCUSSION**

**Phase Behavior of the EuW₁₀/TA System.** First, the complexes of EuW₁₀ with four different chain lengths of tetra-n-alkyl ammonium (TA) (n = 1, 2, 4, 6) were constructed. The concentration of EuW₁₀ is maintained at 0.6 mM, whereas that of TA is gradually increased. Figure 1f displayed the phase behavior of EuW₁₀/TA systems as a function of c_TA. It can be observed that all of them share the same phase behaviors in that the solution phase gradually turned to the precipitate phase with increasing c_TA which may be induced by the electrostatic interaction of the oppositely charged EuW₁₀ and TA. Nevertheless, the difference between them was that the concentration of TA, the inflection point from solution to precipitate, was going down with the increase of chain lengths. It could be explained by the reason that TA with a longer alkyl chain owns poor flexibility and higher hydrophobicity, which induced the faster appearance of the precipitate.

**Characterization and Analysis of EuW₁₀/TA Nanostructures.** For the pellucid EuW₁₀/TA solution, there was a typical Tyndall phenomenon when a laser goes through the solution, indicating the existence of aggregates. Hence, taking the sample of 0.6 mM EuW₁₀/30 mM TMAB as an example, we carried out electron microscopic research to study the morphology of the aggregates in the EuW₁₀/TMAB system. Nanoparticles with diameters varying from 90 to 300 nm were clearly detected in the transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images of Figure 2a,b. The structure of the nanoparticles was clearer with atomic force microscopy (AFM) analyses (Figure 2c), which implied that their corresponding diameters are larger than their vertical heights (20–150 nm) by three to five times, indicating an oblate sphere structure. Besides, the Fourier transform infrared (FT-IR) spectra of EuW₁₀, EuW₁₀/TMAB, and TMAB were analyzed to explain the atomic interaction vibration, and the results are shown in Figure 2d. The bands at around 2960, 2914, and 1486 cm⁻¹ are assigned to asymmetric stretching vibrations, symmetric stretching vibrations, and C–H bending vibrations of the methyl groups in TMAB, respectively.34,35 The bands in the low-frequency region are attributed to the vibrations of EuW₁₀ (Figure 2e); to be specific, the characteristic vibration bands are listed as follows: ν (W = O₉, 943 cm⁻¹), ν (W=O₉–W, 844 cm⁻¹), and ν (W=O₉–W, 784/703 cm⁻¹), where O₉ represents the bridged oxygen of two octahedra with a shared corner, O₉ is the bridged oxygen of two octahedra with an edge shared, whereas O₉ is the terminal oxygen.36 These peaks moved to 921, 833, 789, and 671 cm⁻¹ for the complex after the assembly with TMAB, confirming that electrostatic interaction and hydrogen bonding may be the main driving forces for successful hybridation.37

To further verify the existence of electrostatic interaction, the ζ-potential of the EuW₁₀/TMAB system was measured to further study the evolution of the assembly behavior. The results in Figure 2f revealed that the ζ-potential values of EuW₁₀/TMAB system increased from −35.6 to −11.2 mV when the concentration of TMAB increased. The increasing trend of the ζ-potential confirmed that electrostatic interaction between EuW₁₀ and TMAB was the dominant interaction of self-assembly. Moreover, the negative value of ζ indicated that the interaction of POMs and TA is weaker than that with other surfactants, and thus the cationic TA did not displace all surfactants, and thus the cationic TA did not displace all surfactants, and thus the cationic TA did not displace all surfactants, and thus the cationic TA did not displace all surfactants, and thus the cationic TA did not displace all surfactants.

**Fluorescence Behavior of the EuW₁₀/TMAB System.** POMs with rare earth elements doped have more prominent photoluminescent advantages than other inorganic fluorescent nanomaterials.41 In our system, although EuW₁₀ powder has

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Structures of (a) EuW₁₀, (b) tetramethylammonium bromide (TMAB), (c) tetraethylammonium bromide (TEAB), (d) tetrabutylammonium bromide (TBAB), and (e) tetrahexylammonium bromide (THAB). (f) Phase behaviors of EuW₁₀/TA system as a function of c_TA at 0.6 mM EuW₁₀ for different chain lengths of tetra-n-alkyl ammonium.
excellent fluorescence property in the solid state, the emission of EuW10 in aqueous solution is quite weak. Hence, it would be significant if the fluorescence of the EuW10/TMAB system can be improved compared with pure EuW10 aqueous solution. Then, taking the EuW10/TMAB system as an example, we conducted a series of measurements to study its fluorescence performance. The photographs of 0.6 mM EuW10 aqueous solution and EuW10/TMAB with varied c_{TMAB} under 254 nm UV light are shown in Figure 3A; it can be found by the naked eye that the luminescence of EuW10/TMAB enhanced obviously as c_{TMAB} increased gradually, and the confocal laser scanning microscopy (CLSM) image (Figure 3B) exhibiting...
shown in Figure 3D, the ratio of calculated to be 0.87, whereas for the EuW10/TMAB mixed system, it improved to 1.62 at 30 mM TMAB, suggesting that EuW10 to take the place of water ligands by electrostatic interaction, and thus enhanced the energy of the LMCT to induce more, the time-resolved fluorescence decay curves of EuW10 composite observed under UV lamp. It is worth noting that the maximal luminescence of the EuW10 composite increased by about 14 times compared with the discrete EuW10 solution. Hence, the remarkably enhanced photoluminescence decay of compact self-assemblies because of strong electrostatic interactions between TMAB and EuW10, and replacing the water ligands of Eu3+ by TMAB is the main contributor to the emission enhancement of EuW10.

**Figure 4.** (A) Photographs under 254 nm UV irradiation, (B) fluorescence spectra, (C) the corresponding intensity ratios of 594→621 nm (I594/I621), and (D) time-resolved fluorescence decay curves of EuW10 (0.6 mM) with 30 mM TA of different chain lengths. (E) Fluorescence spectra of 0.6 mM EuW10/30 mM TMAB and 0.6 mM EuW10/30 mM TMPB. (F) Fluorescence spectra of EuW10 (0.6 mM), 0.6 mM EuW10/30 mM TMAB before and after binding with NaBr.

In addition, to the best of our knowledge, the relative intensity ratio of 3D0→5F1 transition to 3D0→5F2 transition is often applied to assay the symmetry variation degree of the Eu3+ coordination microenvironment of different systems. As shown in Figure 3D, the ratio of I594/I621 for EuW10 alone was calculated to be 0.87, whereas for the EuW10/TMAB mixed system, it improved to 1.62 at 30 mM TMAB, suggesting that the Eu3+ in complexes is located at a higher symmetry microenvironment. What’s more, the time-resolved fluorescence spectra of EuW10 before and after binding with TMAB were analyzed to gain an in-depth insight into the mechanism of fluorescence enhancement. Figure 3E illustrates the luminescence decay curves of the fluorescence intensity monitored at 594 nm, which was a biexponential decay and showed two different lifetimes and proportions as summarized in Table S1. As can be found that the measured lifetime was gradually longer in the wake of the increase of the TMAB proportion. Compared with pure EuW10 (τave = 2.051 ms), the longest average lifetime of EuW10/TMAB (1:50) reached 2.582 ms, and these observed results confirmed the formation of compact self-assemblies because of strong electrostatic interactions between TMAB and EuW10, and replacing the water ligands of Eu3+ by TMAB is the main contributor to the emission enhancement of EuW10.

**Influencing Factors for the Fluorescence Behavior of the EuW10/TA System.** The factors of alkyl chain lengths, amino group, and inorganic salt have a certain effect on the fluorescence behavior. Replace TMAB to TEAB and TBAB with longer alkyl chain lengths, the emission intensity decreased gradually as shown in Figure 4A,B. The lower luminescence enhancement for longer alkyl chains suggested weaker electrostatic interaction and looser aggregation of the EuW10/TA system. The corresponding ratio of I594/I621 for EuW10/TA also decreased and the measured lifetime became shorter as the alkyl chain lengths increased (Figure 4C,D). In addition, the relevant electrical conductivity and ζ-potential values in Figure S2 decreased clearly. All of these demonstrated that the Eu3+ in a longer alkyl chain system was located in a lower-symmetry microenvironment. This may be because the steric hindrance effect as well as nonpolarity of alkyl chains increase as the cationic alkyl chain length increases, which hinders the electrostatic interaction between EuW10 and TA and induces less fluorescence enhancement consequently. Above all, the formation mechanism of EuW10/TA nano-
particles in the presence of different alkyl chain lengths of TA are summarized in Scheme 1.

What’s more, the effects of the amino group and inorganic salt on the fluorescence behavior were also studied. As shown in Figure 4E, the luminescence of EuW10/TMPB had increased in comparison with pure EuW10 solution, but the intensity was much lower than that of EuW10/TMAB. It illustrated the existence of the more ordered arrangement between N+ and EuW10 than P+ and EuW10 in the self-assembly atop the active layer.51 As for the sensitiveness of EuW10/TMAB system to ionic strength, it can be seen that for the same ratio of EuW10/TMAB and EuW10/NaBr solution, the latter emission intensity is lower, but is higher than that of pure EuW10 solution (Figure S3A,B). However, when NaBr was added to the EuW10/TMAB system, the fluorescence intensity became weaker than that of EuW10/TMAB (Figure 4F), which proved that the increase of ionic strength destroyed the original assemblies. This is because the added salt might compress or shield the electrical double layer and weaken the electrostatic interaction of EuW10 and TMAB.24

Response to pH of the EuW10/TMAB System. Stimuli-responsive POM-based supramolecular materials with multiple functions like reversible photoluminescence and self-assembly behavior in aqueous solution will broaden the potential applications of these materials. In case of the 0.6 mM EuW10/30 mM TMAB system (pH = 6.3), the fluorescence property at different pH adjusted by HCl or NaOH was also analyzed. The fluorescence of the system could be completely quenched at pH 7.4 and then recovered at pH 6.3 (Figure 5a); in the meantime, the phase behavior transfers from clear solution to precipitate with pH from 6.3 to 7.4 and this procedure can reverse over four cycles with only little loss of fluorescence intensity (Figure 5b). The morphological evolution by alternating the pH was also investigated in detail. When the pH increased to 7.4, the nanoparticles disassembled into a disordered network structure (Figure S4a,b), whereas the nanoparticles rebuilt when the pH of the system recovered to 6.3. It has been proved previously that TMAB acts as the cation and can interact with the EuW10 cluster through electrostatic interaction; thus, upon treatment with NaOH, the deprotonated amino group weakened the electrostatic interaction between EuW10 and TMAB and induced the breakout of nanoparticles.52

Fluorescent Detection of Cu2+. Lanthanide-containing polyoxometalates are sensitive to ambient chemical environments and widely used in luminescent sensing or probing.53 In our work, the strong fluorescence intensity of the Eu3+ ions is hypersensitive to the microenvironment. Thereby, a series of metal ions (Ca2+, Mg2+, Ba2+, Al3+, Pb2+, Cd2+, Zn2+, Fe3+, Cu2+) were added to the EuW10/TMAB aqueous solution to explore the possibility of fluorescence detection. It is obvious from the fluorescence spectra (Figure 6A) that only Cu2+ led to drastic quenching of the fluorescence (95%), which suggested that the nanoparticles can selectively detect Cu2+.
ions. Aiming to assess the performance of the sensor, the selectivity for Cu$^{2+}$ over other metal ions was also studied by competition experiments in the presence of 30 μM Cu$^{2+}$ mixed with other equimolar interfering metal ions (Figure 6B). The results indicated that Cu$^{2+}$ still induced strong quenching of EuW$_{10}$/TMAB in the presence of other tested metal ions.

To further study the sensitivity of the fluorescence sensor for Cu$^{2+}$ ions, the fluorescence spectra as a function of Cu$^{2+}$ ion concentration were measured. In Figure 6C, the fluorescence intensity of Eu$^{3+}$ ions gradually decreases with the increase of c$_{Cu^{2+}}$, which can be found by the naked eye under UV light (inset of Figure 6C). An approximately linear relationship between fluorescence intensity ($I_{ex} = 265 \text{ nm}$, $I_{em} = 594 \text{ nm}$) and c$_{Cu^{2+}}$ can be obtained when c$_{Cu^{2+}}$ is in the range of 0.2−1.0 μM (Figure 6D). Thus, the detection limit was calculated to be ca. 0.15 μM for Cu$^{2+}$ through the 3σ method, which was much lower than the EPA-defined safety level of Cu$^{2+}$ in drinking water (20 μM). Moreover, the 1/(I$_0$ − I) value as a function of 1/[Cu$^{2+}$] displayed a wonderful linear fit (R = 0.998) based on the emission intensity changes, and the binding constant (K$_{SV}$) calculated according to the Benesi–Hildebrand equation was close to 4.65 × 10$^6$ M$^{-1}$ (Figure S5).

To explore the nature (static or dynamic) of the fluorescence quenching of Cu$^{2+}$, the relationship of the plot of I$_0$/$I_0$ (I$_0$ and I$_o$ fluorescence intensity of EuW$_{10}$/TMAB with and without Cu$^{2+}$) with Cu$^{2+}$ concentration was studied and it showed a good linear relationship ($R^2 = 0.9815$) (Figure S6). Based on the modified Stern–Volmer relationship ($I_0/I = K_{SV}$ [Cu$^{2+}$] + C) in which K$_{SV}$ is the Stern–Volmer’s constant and [Cu$^{2+}$] is the concentration of Cu$^{2+}$, the dynamic nature of the fluorescence quenching in our system can be proved. Hence, the mechanism of the fluorescence quenching was speculated to be energy transfer. Then, the reversibility of the quenching upon addition of ethylenediaminetetraacetic acid (EDTA) solution (2 mM, 30 μL) to the Cu$^{2+}$-quenched EuW$_{10}$/TMAB solution was checked. The initial fluorescence can recover in the presence of EDTA solution, suggesting the formation of a strong complex of Cu$^{2+}$ with EDTA. Besides, TEM and FT-IR of EuW$_{10}$/TMAB before and after the addition of Cu$^{2+}$ were further compared to investigate the mechanism of the fluorescence detection of Cu$^{2+}$ ions (Figure S7). The results showed that both the morphology and structure were barely affected by Cu$^{2+}$, indicating that the energy release from the O → W LMCT excited state transferred to Cu$^{2+}$ rather than the $^5D_0$ emitting state of Eu$^{3+}$ is the possible reason for the fluorescence quenching. Specifically, as Cu$^{2+}$ diffused into the solution and came close to the Eu$^{3+}$ ion surface, the energy transfer was more efficient for the smaller sized nanoparticles and externally distributed EuW$_{10}$.

**CONCLUSIONS**

In our work, the design of notably fluorescence-enhanced solutions by a cationic component (TMAB) and an anionic cluster POMs (EuW$_{10}$) by the ionic self-assembly strategy was presented. The fluorescent emission of the EuW$_{10}$/TA system revealed a downward trend as the alkyl chain length of TA increased, which can be attributed to electrostatic interaction and steric hindrance effect. What’s more, the EuW$_{10}$/TMAB complex showed excellent responsiveness to pH and, most importantly, EuW$_{10}$/TMAB composites can act as sensitive fluorescence sensors for Cu$^{2+}$ in water, providing an environmentally friendly and real-time rapid detection method. Our results further proved that the fluorescent functional materials...
have unlimited potential in optoelectronic applications and sensing.

**EXPERIMENTAL SECTION**

**Materials.** EuW₁₀ was synthesized according to the description of Sugeta and Yamase.³⁴ Tetramethylammonium bromide (TMAB), tetraethylammonium bromide (TEAB), tetrabutylammonium bromide (TBAB), tetracycloexylammonium bromide (THAB), and tetramethylphosphonium bromide (TMPB) were all obtained from Macklin Biochemical Co. Ltd (Shanghai). The structures of EuW₁₀, TMAB, TEAB, (TMPB) were all obtained from Macklin Biochemical Co. Ltd (Shanghai). In this experiment, 3 mM of the 0.2 mL EuW₁₀ aqueous solution was added to 0.8 mL TMAB aqueous solution under stirring. The solution incubated for 1 day in a thermostat was obtained from Tianjin Baishi Chemical Industry Co. Ltd. and used directly. Ethylenediaminetetraacetic acid (EDTA) nitrates were acquired from Sinopharm Chemical Reagent Co. Ltd (Shanghai). The structures of EuW₁₀, TMAB, TEAB, TBAB, and THAB are shown in Figure 1a-c.

**Instruments.** Transmission electron microscopy (TEM) was carried out on a JEM-1011 (JEOL) instrument. Field-emission scanning electron microscopy was carried out on Hitachi SU8010 at 5.0 kV. Transmission electron microscopy (TEM) was carried out on a JEM-1011 (JEOL) instrument. The sample was excited at 488 nm. Atomic force microscopy (AFM) results were acquired from a Dimension Icon (American) with a ScanAsyst. Fourier transform infrared (FT-IR) spectra were observed from an α-T spectrometer of Germany Bruker Optics. The values of ζ-potential were acquired from Malvern Zetasizer Nano ZS ZEN3600. The fluorescence spectra were collected on a UV−vis spectrophotometer (Hitachi, U4100). A Lumina Fluorescence Spectrometer (Thermo Fisher) of the model Thermo Scientific Lumina was applied to observe the fluorescence spectra. The fluorescence lifetimes were determined using a spectrofluorometer (FLSP920, Edinburgh Instruments Ltd) with a time-correlated single-photon-containing method.

**Sample Preparation of the EuW₁₀/TMAB Composite.** In this experiment, 3 mM of the 0.2 mL EuW₁₀ aqueous solution was added to 0.8 mL TMAB aqueous solution under stirring. The solution was incubated for 1 day in a thermostat at 20.0 ± 0.1 °C, after which the sample was used for other characterizations.

**Detection of Cu²⁺.** Metal salts (30 μL; c⁻metal = 2 mM) were put into 2 mL of the hybrid nanostructure system (c⁻EuW₁₀/c⁻TMAB = 0.6/30 mM) for the detection of metal ions. Cu²⁺ salts (30 μL; c⁻metal = 2 mM) were put into 2 mL of the hybrid nanostructure system (c⁻EuW₁₀/c⁻TMAB = 0.6/30 mM) including other kinds of metal ions (V = 30 μL, c⁻metal = 2 mM) to investigate the selectivity of nanostructures for Cu²⁺.

**ASSOCIATED CONTENT**

*Supporting Information*  
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01636.

Lifetimes and ratios, UV−vis spectra, electrical conductivity of the EuW₁₀/TMAB, electrical conductivity and ζ-potential of the EuW₁₀/TA, fluorescence spectra of 0.6 mM EuW₁₀ with different ratios of NaBr, TEM images of 0.6 mM EuW₁₀/30 mM TMAB for different pH, the linear relationship of 1/(I₀ − I) vs 1/[Cu²⁺] as well as I₀/I vs [Cu²⁺] for 0.6 mM EuW₁₀/30 mM TMAB, TEM images and FT-IR spectra of 0.6 mM EuW₁₀/30 mM TMAB before and after adding 30 μM Cu²⁺.

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**Notes**

The authors declare no competing financial interest.

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