Plasmonic Surface of Metallic Gold and Silver Nanoparticles Induced Fluorescence Quenching of Meso-Terakis (4-Sulfonatophenyl) Porphyrin (TPPS) and Theoretical–Experimental Comparable

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Abstract
Colloidal metallic nanoparticles have attracted a lot of interest in the last two decades owing to their simple synthesis and fascinating optical properties. In this manuscript, a study of the effect of both gold nanoparticles (Au NPs) and silver nanoparticles (Ag NPs) on the fluorescence emission (FE) of TPPS has been investigated utilizing steady-state fluorescence spectroscopy and UV–Vis spectrophotometry. From the observed electronic absorption spectra, there is no evidence of the ground state interaction between metallic Au NPs or Ag NPs with TPPS. On the other side, the FE spectra of TPPS have been quenched by both Ag and Au NPs. Via applying quenching calculations, Ag NPs showed only traditional static fluorescence quenching of TPPS with linear Stern–Volmer (SV) plots. On the contrary, quenching of TPPS emission by Au NPs shows composed models. One model is the sphere of action static quenching model that prevails at high quencher concentrations leading to non-linear SV plots with positive deviation. However, at low Au NPs concentrations, traditional dynamic quenching occurs with linear SV plots. The quantum calculations for TPPS structure have been obtained using Gaussian 09 software: in which the TPPS optimized molecular structure was achieved using DFT/B3LYP/6-311G (d) in a gaseous state. Also, the calculated electronic absorption spectra for the same molecule in water as a solvent are obtained using TD/M06/6-311G + + (2d, 2p). Furthermore, the theoretical and experimental results comparable to UV–Vis spectra have been investigated.

Keywords Gold and silver nanoparticles · Porphyrin derivatives · Fluorescence quenching · Non-linear stern–volmer plots · DFT

Introduction
Porphyrins (PPs) are largely colored heterocyclic macrocycle organic compounds with their main absorption bands characterized via very large molar absorptivity. The intense B-band or “Soret band” found around 400 nm is characteristic of macrocyclic conjugation. Additionally, in the Soret band, there are between two and four weaker bands called “Q-bands” situated between 480–700 nm [1].

The number and intensity of those bands can give information on the substitution pattern of the PP and whether it is mutilated or not. Metal-free PPs have a Soret band and four Q-bands, whereas, metal-PPs generally have a Soret band and two Q-bands [2]. The significance in the photophysical characterizations of PP and PP-like geometrical structures has enhanced significantly during the last decades owing to the long-range variety of their applications. For instance, PPs are utilized for the enhancement of nonlinear (NL) photonic devices, like optical limiters [3–5] and optical switches [6, 7]. Their high optical (NL) arise from their geometrical structures existing extended π-conjugated systems [8, 9]. Water-soluble PPs and metalloporphyrin have a lot of potential applications in bioscience [10–13]), and material science [14–16]. Also, in medicine, water-soluble PPs investigated anti-HIV [17] and antibacterial activity [18], and it was utilized as active compounds for singlet oxygen imaging of single cells [19]
and singlet oxygen photosensitization in skin fibroblasts [20]. One of the most significant water-soluble PP derivatives is the synthetic meso-tetrakis (4-sulfonatophenyl) porphyrin (TPPS) [10].

Meso-tetrakis (4-sulfonatophenyl) porphyrin or (5, 10, 15, 20-tetrakis (4-sulfonatophenyl) porphyrin, abbreviated as (H₂TPPS⁻⁴) or (TPPS), is a substituted PP-type molecule with four meso-phenyl rings containing SO₃⁻ groups in the para- positions which make this PP derivative a very good example of anionic water-soluble PP derivatives [21]. TPPS has attracted a lot of researchers’ interests and has been studied as a promising sensitizer for PDT [22]. Besides this TPPS has NL optical absorption [23], which can lead to its application in photonic devices such as optical limiters [24] and switches [25].

Rahman and Harmon investigated absorbance changes and static quenching of fluorescence of TPPS utilizing trinitrotoluene (TNT) [26]. Also, Kathiravan et al. investigated the fluorescence quenching (FQ) of TPPS via certain pyrimidines using steady-state and time-resolved techniques [27]. They found that the Q processes obey the SV equation with linear plots. The FQ of TPPS by applying colloidal nano TiO₂ [28], and colloidal nano CdS [29] was reported. It was found that TPPS was adsorbed on both colloidal semiconducting nanomaterials (TiO₂ and CdS) surfaces through the sulfonate SO₃⁻ group as an anchoring group [29]. Kathiravan et al. reported the FQ of TPPS with colloidal metal-semiconducting (Au/TiO₂, and Ag/TiO₂) core–shell nanomaterials [29]. It was found that TPPS showed higher rates in cases of metal–semiconductor nanomaterials (Au/TiO₂, and Ag/TiO₂) compared with electron transfer to colloidal TiO₂.

The present manuscripts aimed the investigation the interaction of TPPS with Au NPs and Ag NPs using electronic absorption and fluorescence techniques. The second-order rate constants of fluorescence quenching of TPPS in viscous and non-viscous media were also determined. Also, the theoretical–experimental comparable for UV-spectra and the accurate functional and basis set for TPPS geometrical structure have been investigated.

**Experimental Details**

**Materials**

The sodium salt of TPPS, tetrachloroauric acid (99.9%, HAuCl₄.3H₂O), and silver nitrate (AgNO₃) were obtained from Sigma-Aldrich. Citrate trisodium salt (95%, C₆H₅O₇Na₃.2H₂O), hydrochloric and nitric acids were purchased from Fluka.

**Synthesis of Metallic Nanoparticles**

**Synthesis of Gold NPs**

Approximately 13 nm diameter Au NPs were prepared via utilizing the citrate reduction of HAuCl₄.3H₂O [30, 31]. An aqueous solution of HAuCl₄.3H₂O (1 mM, 100 mL) was brought to reflux while stirring, and then 10 mL of a 1% trisodium citrate solution (as nucleating and reducing

![Structure of sodium salt of meso-tetrakis (4-sulfonatophenyl) porphyrin (TPPS)](image_url)
agent) was added quickly, which resulted in a change in solution color from pale yellow to deep red. After the color change, the solution was refluxed for an additional 15 min and allowed to cool to room temperature. A typical solution of 13 nm diameter gold particles exhibited a characteristic surface plasmon band around 520 nm. The size and mono-dispersion of the resulting NPs were well documented for this method of synthesis [32]. The mechanism of the successive reduction of $[AuCl_4]^{-}$ ions into metallic Au NPs is explained in detail in the literature [33]. Form the electronic absorption spectra of the prepared 13-nm diameter of 2.01 nM concentration and 0.3302 optical density (OD) at $\lambda_{\text{max}} = 520$ nm, the extinction coefficient $\varepsilon(\lambda)$ of the prepared Au NPs was calculated as $1.6 \times 10^8$ M$^{-1}$ cm$^{-1}$ comparable literature value of $8 \times 10^8$ M$^{-1}$ cm$^{-1}$ and $2.4 \times 10^8$ M$^{-1}$ cm$^{-1}$ [34].

**Synthesis of Silver NPs**

Ag NPs were prepared by applying the citrate reduction of AgNO3 [32]. An aqueous solution of AgNO3 (1 mM, 125 ml) was heated until it starts to boil, and then 5 ml of a 1% trisodium citrate solution (as nucleating and reducing agent) was added quickly, which resulted in a change in solution color to pale yellow. After the color changed, the solution was removed from the heating element, and allowed to stir until cool to room temperature. A typical solution of silver nanoparticles exhibiting a characteristic surface plasmon around 420 nm was obtained [32]. For 10 nm diameter Ag NPs, the extinction coefficient was calculated as $1.328 \times 10^7$ M$^{-1}$ cm$^{-1}$ compared with the literature value [35]. The prepared Au and Ag NPs were characterized by electronic absorption spectroscopy and by Transmission Electron Microscopy (TEM).

**Spectroscopic Measurements and Nanoparticle Characterizations**

The electronic absorption spectra had been recorded utilizing the Shimadzu UV-3101 PC spectrophotometer. The steady-state fluorescence spectra had been recorded employing the Perkin-Elmer LS-50B scanning Spectrofluorometer, utilizing matched quartz cuvettes. The nanoparticle size changed into characterized with the aid of using a transmission electron microscope (TEM), JEOL JEM-100SX Electron Microscope with a field gun, and an accelerating voltage of 80 kV.

**DFT and TD-DFT Calculations**

The optimized MSs for TPPS in the gaseous state are obtained using the DFT/B3LYP/6-311G (d) method [36–38]. The UV–Vis absorption spectra for TPPS and in H$_2$O are calculated via applying TD/M06-2/311G$^+$ $(2d, 2p)$.

**Results and Discussion**

**Electronic Absorption Spectra**

The electronic absorption spectra of 5.03 and 25.0 nM of Ag NPs and those of 1.14, 2.15, and 4.37 nM of Au NPs were collected in Fig. 1(a and b) with the same spectral features as reports [39]. As presented in Fig. 1a and b), the maximum absorbance of Ag and Au NPs is increased with increasing its concentrations. The object is to display the ELECTRONIC ABSORPTION SPECTRA of different concentrations used in quenching of TPPS geometrical structure (GS). Figure 1 (c and d) show the TEM micrographs of the synthesized Au NPs and Ag NPs. It confirms the nanoscale dimension of the NPs and shows their average diameters of about 13 and 10 nm, respectively.

The electronic absorption spectra of $5 \times 10^{-6}$ M aqueous solution of TPPS GS were recorded in the absence and presence of 2.5 and n M aqueous Ag NPs as shown in Fig. 2a. We noted the shape and band maxima of absorption spectra remain unchanged upon increasing the concentration of Ag NPs. Also, these behaviors are observed with Au NPs as presented in Fig. 2b. Those referring to there is no observable interaction or photochemical reaction between TPPS and Ag or Au NPs in the ground state under the prevailing experimental conditions (see Fig. 2c). reported similar behavior because of Hematite NPs on the spectra of one of the coumarin dyes.

**Fluorescence Quenching**

**Effect of Ag NPs on Fluorescence Emission of TPPS**

The fluorescence emission of TPPS was investigated in the presence of variable concentrations of Ag NPs as a quencher in two different media; one of them contains only pure water and the other contains 40% ethylene glycol (EG) by volume in water at room temperature. Figure 3a shows the fluorescence emission spectra of $1 \times 10^{-5}$ M TPPS in the presence of variable concentrations of Ag NPs in pure water. The fluorescence emission of TPPS exhibits a maximum at 650 nm upon excitation at 414 nm. As the concentration of quencher was increased, $\lambda_{\text{max}}$ of the fluorescence emission bands at 650 nm decreased while the fluorescence emission intensity of the emission band at 760 slightly increases. Under the present experimental conditions, no such quenching of TPPS was seen in the presence of the low concentrations of capping agent indicating that Ag NPs are responsible for...
the fluorescence quenching. The fluorescence emission band appearing beyond 760 nm is assigned to light scattering from colloidal Ag NPs as shown in Fig. 3a. Long-wavelength light scattering from colloidal Ag NPs was reported earlier by Klitgaard et al. [40]. This scattering was explained by a theory based on interference between two surface plasmon resonances of higher concentrations of colloidal nanoparticles [40]. We measured this scattering from the prepared Ag NPs under the prevailing experimental conditions as shown in Fig. 3b.

Figure 3c shows the Stern–Volmer (S-V) plot derived from Eq. (1) of fluorescence emission quenching of TPPS by Ag NPs as a quencher [41].

\[
\frac{I_0}{I} = 1 + K_v[Q]
\]
where $I_o$ and $I$ are the fluorescence emission intensities in the absence and presence of the quencher concentration $[Q]$, respectively. The $K_{sv}$ was calculated as $2.84\times10^7$ M$^{-1}$ and $3.8\times10^7$ M$^{-1}$ in pure water and 40\% EG/water, respectively. The quenching efficiency increases as the medium viscosity increases indicating that the quenching process is not completely diffusion–controlled. This is consistent with a static quenching model in which increasing the medium viscosity leads to a cage effect that enhances the fluorophore uptake on Ag NPs surfaces. Taking the fluorescence lifetime of TPPS in the absence of Ag NPs as 10.4 ns [42], the values of $k_q = K_{sv}/\tau$ are calculated as $2.73\times10^{15}$ M$^{-1}$ s$^{-1}$ in water. This value is much higher than the diffusion rate constant $k_d$ ($k_d = 1.095\times10^9$ M$^{-1}$ s$^{-1}$) for water. This suggests that the static quenching mechanism plays a major role in the quenching of TPPS by Ag NPs.

The Perrin model was valid for the quenching process of TPPS by Ag NPs. The Perrin relationship [43] is given by Eq. (2):

$$\ln\left(\frac{I_o}{I}\right) = VN_o[Q] \quad V = \frac{4}{3}\pi r^3$$

where $I_o$ and $I$ are fluorescence emission intensities in the absence and presence of a quencher, $V$ is the volume of the quenching sphere in cubic centimeters, $N_o$ is the Avogadro’s number, $[Q]$ is the molar concentration of the quencher, and $r$ is the radius of quenching sphere volume. Figure 3d shows a linear plot $\ln(I_o/I)$ versus $[Q]$ with a slope equal to $VN_o$. Accordingly, the volume and radius of the quenching sphere were $3.85\times10^{-14}$ cm$^3$ and 209.5 nm, respectively.

**Effect of Au NPs on Fluorescence Emission of TPPS**

The fluorescence emission of TPPS was studied in the presence of variable concentrations of Au NPs as a quencher in two different media containing 0\% and 40\% EG/water by volume in H$_2$O at room temperature. When the concentration of Au NPs was increased gradually, the fluorescence emission intensity decreased significantly as a consequence of TPPS fluorescence quenching without any appreciable change in position and shape of the emission band, Fig. 4a. This indicates the absence of molecular aggregation under the prevailing experimental conditions.
Upward curvatures were observed, as a result of the quenching process of TPPS by Au NPs in H\textsubscript{2}O and 40\% EG solutions, by applying the traditional SV equation (Eq. 1), Fig. 4b. Each plot shows two trends, namely the linear and nonlinear portions. From the linear portions of the SV plots, the values of $K_{SV}$ in water and 40\% EG solutions were calculated as $1.73 \times 10^8$ and $2.04 \times 10^8$ M\textsuperscript{-1}, respectively. The bimolecular quenching rate constant ($k_q$) has been calculated as $1.663 \times 10^{16}$ M\textsuperscript{-1} s\textsuperscript{-1} (where, $K_{SV} = k_q \tau_o$; taking lifetime of TPPS as $\tau_o = 10.4$ ns in water [43]. This value is much higher than the diffusion rate constant in water ($k_d = 1.095 \times 10^9$ M\textsuperscript{-1} s\textsuperscript{-1}) at room temperature.

The nonlinear plots showed positive deviation and similar behaviors were observed earlier [44]. The positive deviation from linearity suggests that the quenching is not purely static or dynamic and may be due to simultaneous dynamic and static quenching mechanisms as shown in Fig. 5. The analysis of data was carried out by employing the sphere of action static model using the modified form of SV equation [44] given as:

\[
\left( \frac{I_0}{I} \right) = \frac{1}{W} (1 + K_{SV}[Q]) \quad (3)
\]

The additional factor $W$ is expressed as:

\[
W = e^{-\mathcal{V}[Q]} \quad (4)
\]

where ‘$\mathcal{V}$’ is the static quenching constant that represents an active volume element surrounding the fluorophore in its excited state. As $W$ depends on the quencher concentration...
[Q], the SV plots for a quencher with a high quenching ability generally deviate from linearity. Thus, it is worth rewriting Eq. (3) as:

\[ \frac{1 - \left( \frac{I}{I_0} \right)}{[Q]} = K_{SV} \left( \frac{I}{I_0} \right) + \frac{1 - W}{[Q]} \]  

(5)

According to Eq. (5), \( \frac{1 - \left( \frac{I}{I_0} \right)}{[Q]} \) was plotted against \( \left( \frac{I}{I_0} \right) \) as shown in Fig. 4c. The SV dynamic quenching constant \( (K_{SV} = 6.82 \times 10^7) \), was obtained by the least-square fit method determining the slope. The intercept of the plot was used to calculate \( W \) values for each quencher concentration \([Q]\). Plotting of \( \ln W \) against \([Q]\) gave a linear correlation with a negative slope that equals the static quenching constant \( (V = -6.56 \times 10^7) \), as in Eq. (4) as illustrated in Fig. 4d. From the value of \( V \) one can calculate \( r \).

The calculated \( K_{SV}, V, \) and \( r \) values are listed in Table 1. The radii of the fluorophore (R\(_{F}\)) and the quencher (R\(_{Q}\)) molecules were determined by using the additive model [45]. \( R \) is the sum of both molecular radii is named encounter distance \( R \). As seen, the value of kinetic distance \( r \) was greater than the encounter distance \( R \). Therefore, the static effect takes place irrespective of the ground state complex formation provided the reactions are limited by diffusion indicating that the sphere of action model holds well [45]. Further, it may also be noted that a positive deviation in the

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Fig. 4 Emission spectra of \( 1 \times 10^{-5} \) M of (TPPS) in water (\( \lambda_{ex} = 414 \) nm) in the absence and presence of Au NPs (a). Stern–Volmer (S—V) (b) and modified (S – V) (c and d) plots for quenching of \( 1 \times 10^{-5} \) M TPPS by Ag NPs.
SV plot is expected when both static and dynamic quenching occur simultaneously [45].

**Quantum Calculations**

**DFT Calculations**

Utilizing the DFT method, the electronic Geometrical structure (GS) for the ground state of TPPS was computed. The electronic GS optimization was investigated at the DFT/B3LYP/6–311G (d) method in a gaseous state; the result is obtained in Fig. 6. The labeled optimized GS for the TPPS compound is obtained in Fig. 6. The TPPS GS is not planar where the phenyl sodium sulfate rotates out the PP group in TPPS via 71.67° to prevent the steric hindrance as shown in Fig. 6. Selected optimized structural parameters (bond length in Å, bond angle and dihedral angle in degree (°)) computed for TPPS in the ground (S₀) and first excited states (S₁) via applying DFT/B3LYP/6-311G(d) method in the gaseous state are presented in Table 2. DFT was used to get the ground state GS of TPPS in the gaseous state. Also, TD-DFT was applied to get an electronically excited state (S₁) for TPPS in the gaseous phase. Various comments can be concluded from Table 2 for TPPS as follow: (1) Owing 71.67° (C₄₅–C₄₆–C₃₁–C₁) dihedral angle over the entire TPPS backbone of the molecule, the TPPS GS is not planar as shown in Fig. 6 (2) The difference between C–C single bonds and C= C double bonds are very small due to high conjugations. (3) The obtained bond angles refer to the sp² hybridization over the entire TPPS backbone GS. (4) As presented in Table 2 and Fig. 6, the All-bond lengths, bond angles, and dihedral angles for TPPS GS are not affected upon excitation from S₀ to S₁. (5) Upon excitation from S₀ to S₁, the Mulliken charge of all atoms in TPPS GS is decreased except for the charge of C₇₁, C₄₆ and C₂ atoms (See Table 2). (6) It is apparent from Table 2 that the terminal oxygen and sulfur atoms (i.e. (SO₃⁻ group) in the S₀ and S₁ states have a large Mulliken charge compared to the nitrogen atoms in the middle ones. These findings could lead to the binding of the excited state near oxygen atoms in SO₃⁻ to the Au or Ag NPs [46]. This is referring to a good agreement with the experimental results.

The molecular orbitals (MOs) graphical representation of the highest occupied molecular orbital (HOMO (H)), lowest unoccupied molecular orbital (LUMO (L)), HOMO – 1 (H – 1), LUMO + 1 (L + 1), HOMO – 2 (H – 2), LUMO + 2 (L + 2) and energy gaps between the following: H and L (E₂), H -1 and L + 1 (E₁) and H -2 and L + 2 (E₀) for TPPS GS have been calculated: the results are collected in Fig. 7. As shown in Fig. 7, some important comments can be constructed as follow: (1) the H, L, H—1, L + 1 and H—2 MOs are localized over the PP group of TPPS GS. (2) H + 2 MO is localized over the four substituted phenyl groups. (3) The H and L MOs are π-bonding and π*-antibonding anti-bonding characters distributed over the whole target molecule. (4) Orbital energy level analysis and the resultant H – L energy

| Table 1 | Quenching parameters of TPPS—Au NPs system in H₂O |
|---------|-----------------------------------------------|
| Ksv (M⁻¹) | V (M⁻¹) | Ry (Å) | Rq (Å) | R = Ry + Rq (Å) | r (nm) |
| 6.82 × 10⁷ | 6.56 × 10⁷ | 8.2 | 65 | 73.2 | 2962 |
gap ($E_g$) referring to kinetic stability of a molecule [47]. A high $E_g$ indicates high kinetic stability and low chemical reactivity because it is energetically unfavorable to add electrons to a high-lying L or to remove electrons from a low-lying H [47].

TD-DFT Calculations

To achieve the optimum functional and basis set for calculating electronic absorption of the TPPS GS, various functionals, B3LYP [48], CAM-B3LYP [49], M06 [50], and wB97XD [51] were tested using 6-311G(d) basis set in water. The obtained resultant was collected in Fig. 8A in which M06 functionals give the nearest results to the experimental data of compound TPPS (See Fig. 8A). Also, to obtain the best basis set for calculating electronic absorption spectra for target compound, different basis sets, 6-311G(d), 6-311G (d, p), 6-311G+ + (d, p) and 6-311G+ + (2d, 2p) were test using M06 functional. The obtained calculated spectra were collected in Fig. 8B in which the 6-311G+ + (2d, 2p) basis set give the accurate results to the experimental one for target compound. The influence of applying various basis sets indicating calculated electronic absorption spectra of PPO GS is accurate with diffuse functions. Hence, involvement of diffuse functions is essential in obtaining accurate results. Therefore, the M06 functional and 6-311G+ + (2d, 2p) basis set is used to calculate the electronic absorption spectra for TPPS molecule in H$_2$O solvent as presented in Fig. 8B.

The electronic absorption spectra of TPPS GS were obtained experimentally in water; the obtained electronic absorption spectra were presented in Fig. 8A and B.
The experimental electronic absorption spectra of the target compound in an aqueous solution lie in the range (of 325—575 nm). This is owing to the π-π* transition. Also, the calculated electronic absorption spectra of TPPS compound using TD/M06/6-311G+ (2d, 2p) in water lie in the range between (300 – 550 nm). Hence, the results data show that the computational absorption and experimental properties of the studied TPPS compound agree with the experimental data. The calculated excitation state, electronic transition, excitation energy (Eg), oscillator strength (f), coefficient, and calculated maximum absorption wavelength (Th. λmax) parameters are listed in Table 3.

The calculated electronic absorption spectra of TPPS GS in water appear as six transitions. The electronic transitions for TPPS at 591, 559, 411, 405, 362 and 363 nm as shown in Table 3. the third electronic transitions corresponding to the experimental peak at 411 nm (f = 1.571) arises from transition of MO258—>262 (coefficient = 45%).
MO260→263 (coefficient = 56%) and MO261→262 (coefficient = 33%) as presented in Table 3.

**Conclusion**

The behavior of water-soluble TPPS absorption and fluorescence emission spectra has been studied in the presence of aqueous colloidal citrate capped Ag NPs and Au NPs. The observed UV–Vis absorption spectra of TPPS indicate the absence of interaction between TPPS with Ag NPs and Au NPs. But fluorescence quenching studies revealed a positive deviation from SV upon replacing Ag NPs with Au NPs. The latter behavior can be interpreted in terms of action sphere static quenching models. Various rate parameters for the fluorescence quenching process were determined by using a modified SV equation. The optimized TPPS GS using DFT/B3LYP-6-311G(d) was obtained successfully. The calculated electronic absorption spectra of TPPS GS in water appear as six transitions. The electronic transitions for TPPS at 591, 559, 411, 405, 362, and 363 nm. The third electronic transitions corresponding to the experimental peak at 411 nm (f = 1.571) arises from transition of MO258→262 (coefficient = 45%), MO260→263 (coefficient = 56%) and MO261→262 (coefficient = 33%).

### Author Contributions

Ahmed A. AboAlhassan: Experimental examination, Samy A. El-Daly: Visualization and Investigation, El-Zeiny M. Ebeid: Writing-review and editing, Mahmoud A. S. Sakr: Data Curation, Writing-original draft, and Software.

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### Data Availability

All data generated or analyzed during this study are included in this published article.

### Declarations

**Ethical Approval**  This article does not contain any studies involving animals performed by any of the authors.

**Consent to Participate**  This article does not contain any studies involving animals performed by any of the authors.

**Consent to Publish**  All authors mentioned in the manuscript have given consent for submission and subsequent publication of the manuscript.

**Conflict of Interest**  The authors have declared no conflict of interest.

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