Investigation of Cobalt Phthalocyanine at the Solid/Liquid Interface by Electrochemical Tip-Enhanced Raman Spectroscopy

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ABSTRACT: Electrochemical tip-enhanced Raman spectroscopy (EC-TERS) with three excitation wavelengths in combination with in situ electrochemical scanning tunneling microscopy (EC-STM) and absorption measurements has been employed to provide comprehensive insights into the electrochemical processes of cobalt phthalocyanine (CoPc) at the solid/liquid interface supported on a Au(111) substrate. As the substrate potential becomes more negative, CoPc molecules form a highly ordered monolayer on the Au(111) surface (>0.1 V) until the ordered-to-diffusing phase transition is triggered (<0.1 V). CoPc molecules in the ordered phase are reduced during cathodic scanning, which leads to a redshift in the resonance condition and gives rise to distinct EC-TERS behaviors which depend on excitation wavelengths. The ordered-to-diffusing phase transition of CoPc molecules results in the disappearance of the EC-TERS signal. The catalytic activity of CoPc for the oxygen reduction reaction (ORR) was not visible in the EC-STM and has negligible effect on the EC-TERS measurements. The comprehensive evidence from EC-TERS, EC-STM, and absorption spectreolectrochemistry clearly demonstrates that partially reduced CoPc molecules are the dominant species under steady state measurements during the oxygen reduction reaction.

INTRODUCTION

Unravelling the electrochemical processes at the solid/ electrolyte interface can greatly improve device efficiency and minimize performance loss in energy conversion and storage technologies such as fuel cells and metal air batteries. In electrochemistry, surface heterogeneity, solvent interactions, and the transport of reactants and products create a dynamic local environment, which presents a significant challenge for understanding the mechanisms of electrochemical processes. The ability to provide accurate and relevant insights into the mechanisms of an electrochemical process can only be achieved through in situ probing of the fundamental interactions under electrochemical (EC) conditions. EC-scanning tunneling microscopy (EC-STM) is a powerful tool to obtain potential-dependent nanoscale topographic information at solid/liquid interfaces. However, topographic images provide only limited chemical information regarding the species undergoing electrochemical reactions at the solid/liquid interface. Surface-enhanced Raman spectroscopy (SERS) can provide characteristic vibrational spectroscopy for the chemical species that are involved in a catalytic process but does not provide topographic information. By integrating Raman spectroscopy with STM, tip-enhanced Raman spectroscopy (TERS) can offer an alternative way to provide local chemical and topographic information with high spatial resolution. In TERS, the highly confined plasmonic field in the tip—sample junction can enhance the detection sensitivity and improve the spatial resolution. These unique features have attracted significant research interest. By exploitation of the fundamental merits of TERS, single-molecule sensitivity and nanometer spatial resolution have been successfully achieved in TERS studies under ultrahigh vacuum (UHV) conditions where low background pressure reduces contamination on the samples and tips and provides great stability of the tip—sample junction. In recent studies, TERS has been used to reveal critical chemical identification under liquid and EC conditions for a number of important reactions. However, molecularly resolved images have not been achieved in these studies, and the lack of clear topographic information could complicate the interpretation of the acquired signal. The combination of EC-TERS and EC-STM has the potential to simultaneously provide molecularly resolved topographic information and chemical identification, which is especially suited for understanding electrocatalysis.

CoCatal-based molecular catalyst is a promising candidate that finds application in electrochemical reactions such as the...
oxygen reduction reaction (ORR),\textsuperscript{23,24} which is an important reaction for fuel cell applications. The state-of-the-art industrial catalysts for proton exchange membrane (PEM) fuel cells\textsuperscript{25} often consist of platinum- (Pt-) based catalysts. Compared to these catalysts, cobalt-based molecular catalysts show advantages in terms of cost and chemical stability. A large body of empirical and theoretical studies have been carried out to examine the catalytic activity of cobalt-based molecular catalysts and their interaction with \textit{O}_2. For example, well-defined monolayers of CoPc molecules supported on Au(111) have been demonstrated by EC-STM.\textsuperscript{26,27} Additionally, chemisorption of \textit{O}_2 on well-ordered CoPc monolayers has provided strong evidence for \textit{O}_2 activation by CoPc when supported on the Ag(111) surface under UHV conditions.\textsuperscript{28} However, simultaneous acquisition of kinetic data, chemical information, and molecular configuration in situ for CoPc has not been accomplished. Herein, we combine EC-TERS and EC-STM to investigate CoPc molecules during the oxygen reduction reaction. Following the onset of ORR, EC-STM results illustrate a rapid consumption of \textit{O}_2 molecules that were initially adsorbed on CoPc, which is consistent with its high activity for hydrogen peroxide production via a two-electron reduction pathway in ORR. As the substrate potential becomes more negative, distinct trends in the EC-TERS measurements with three excitation wavelengths are observed. This phenomenon is explained by the changes in the resonant conditions of CoPc with different excitation wavelengths following a redshift in the absorption band of these molecules upon reduction, which is confirmed by spectroelectrochemical measurements. Our results provide a molecular description of CoPc under steady state conditions during ORR and additional insights of the electrochemical reactions catalyzed by CoPc at the solid/liquid interface.

### EXPERIMENTAL SECTION

#### Sample Preparation.

CoPc (Figure 1a) was purchased from Sigma-Aldrich Co. and used without further purification.

For UHV-STM-TERS studies, the Au(111) single crystals (Princeton Scientific Corporation) were cleaned by multiple sputter–annealing cycles. STM was used to confirm a clean and well-defined Au(111) surface. The adlayer of CoPc was prepared by sublimation of CoPc molecules at ~650 K onto the clean Au(111) surface under UHV conditions.

For EC-STM-TERS studies, the Au(111) single crystal was used as the substrate and chemically cleaned in freshly prepared piranha solution (1:3 mixture of H₂O₂ and H₂SO₄ by volume) for 20 min, followed by thorough rinsing with plenty of Milli-Q water, and immersion in pure ethanol for 10 min to remove the surface oxide. After chemical cleaning, the single crystal was annealed with a butane torch and cooled down to room temperature in air.

The adlayer of CoPc was prepared by immersing a flame-annealed Au(111) crystal in a CoPc saturated solution of N,N-dimethylformamide (DMF) for 5 min. After incubation, the CoPc–Au(111) electrode was rinsed with Milli-Q water, transferred into an electrochemical cell and immersed in electrolyte solution for cyclic voltammetry (CV), EC-STM and EC-TERS measurements. All CV measurements, EC-STM and EC-TERS experiments were carried out in the same cell, except for the spectrotelectrochemical absorption measurements. The supporting electrolyte solution (0.1 M HClO₄) was prepared with HClO₄ (Sigma-Aldrich, 70%) and Milli-Q water (18.2 MΩ·cm, total organic carbon <5 ppb) to minimize the contamination on samples and tips during experiments.

#### Experimental Setups.

The UHV-STM TERS experiments were performed at room temperature in a home-built UHV-STM system under a base pressure of ~2 × 10⁻¹¹ Torr, equipped with side-illumination optical system as detailed in previous studies.\textsuperscript{28,29} A 632.8 nm laser (He–Ne laser, Research Electro-optics) was employed in the UHV-TERS experiments. The EC-STM and EC-TERS experiments were performed using a home-built apparatus, equipped with a side-illumination optical system (see Figure S1 in the Supporting Information for more details). A platinum (Pt) wire was used as the counter electrode. A silver (Ag) wire was used as the quasi-reference electrode (QRE). All electrode potentials discussed are referenced to the reversible hydrogen electrode (RHE) unless noted otherwise. The potential of silver wire vs RHE is 0.5 V. Fluctuations in the silver wire potential before and after experiment was less than 30 mV. Three excitation wavelengths were used in the EC-TERS measurements: 632.8 nm (diode laser, PD-LD), 700 and 720 nm (SolsTiS, M Squared Laser Systems). All Raman spectra presented here were not corrected for the wavelength dependent sensitivity of photon detection systems.

The STM images were obtained with W tips, and the TERS spectra were obtained with Ag tips. For all the UHV-STM and TERS measurements were obtained under constant current mode with the sample biased. For EC-STM and EC-TERS measurements, the tips were insulated with nail polish to...
reduce the faradaic current, and the STM bias is defined as the difference between the sample potential \( (E_{\text{sample}}) \) and the tip potential \( (E_{\text{tip}}) \), i.e., bias = \( E_{\text{sample}} - E_{\text{tip}} \). The sample potential and the STM bias can be controlled independently, in which the former was controlled by a potentiostat (EC301, Stanford Research Systems) and the latter was maintained by the STM electronics controller (R9, RHK Technology). As a result, the tip potential is defined as \( E_{\text{tip}} = E_{\text{sample}} - \text{bias} \). Different tips were used for each excitation wavelength.

**Spectroelectrochemical Absorption Measurements.**
Spectroelectrochemical absorption measurements of CoPc molecules were performed on a double-beam spectrophotometer (Cary 5000, Agilent) with a potentiostat (660D, CH Instruments) in pyridine with 0.3 M tetrabutylammonium perchlorate (TBAP, Sigma, 99%) as the supporting electrolyte. Pyridine used for spectroelectrochemical absorption and cyclic voltammetry measurements was previously dried with NaOH pellets for several hours, followed with nitrogen gas purging for 0.5 h. A quartz cell (10 mm optical length, Starna Cells, Inc.) was used with a Pt mesh (Bioanalytical Systems, Inc.) as working electrode, a Pt wire (Alfa Aesar, 99.99%) as counter electrode, and a leakfree Ag/AgCl unit as reference electrode.

**RESULTS AND DISCUSSION**
UHV provides a highly controlled environment for TERS studies. Prior to EC-TERS studies, UHV-TERS measurements were performed to obtain reference spectra of CoPc adsorbed on Au(111) in a controlled environment. Figure 1b shows a large-scale STM image of a well-ordered monolayer of CoPc formed on a Au(111) surface under UHV conditions. The high-resolution image in the inset shows that the CoPc molecules self-assemble into a square unit cell with a lattice constant of \( \sim 1.4 \) nm, which is in good agreement with previous studies on CoPc molecules.28,30 The ordered adlayer formation is attributed to the competition between the intermolecular interactions and molecule–substrate interactions.

The UHV-TER spectra acquired on this well-ordered molecular sample are shown in Figure 1c. When the tip is engaged, the acquired near-field signal (blue spectrum) shows clear vibrational fingerprints of CoPc molecules. When the tip is retracted from the surface, only a featureless background is observed in the far-field signal (black spectrum), which suggests that the tip is free of contamination. The TERS signal only from CoPc can be obtained by subtracting the far-field signal from the near-field signal, which is shown in red.

After we measured a reference TERS spectrum for CoPc molecules on Au(111), TERS experiments were subsequently performed on CoPc molecules under EC conditions. A typical EC-STM image of the flame-annealed Au(111) in 0.1 M HClO\(_4\) is shown in Figure 2a. When the Au(111) electrode is held at 0.2 V, the electrochemically induced \( (2 \times V/3) \) surface reconstruction can be observed. The inset shows an area larger than \( 300 \times 300 \) nm\(^2\) with a single step edge. Clear herringbone structures and step edges suggest a well-defined Au(111) surface with low density of defects at the nanoscale. Figure 2b shows a typical CV of Au(111) in HClO\(_4\) solution with two oxidation peaks (1.53 and 1.33 V) and one reduction peak (1.13 V) with two small waves as shoulders.31 These features suggest that the Au(111) surface is well-defined over a large scale—an ideal starting substrate for the subsequent EC-TERS experiments. The single electrochemical wave at low potential is assigned as the oxygen reduction reaction catalyzed by Au(111) surface.

**Molecular self-assembly at the solid/liquid interface is guided by intermolecular interactions, molecule–substrate interactions, molecule-solvent interactions, and the solvent–substrate interactions.2,3,5** We successfully obtained a highly ordered monolayer of CoPc molecules on Au(111) under EC conditions as shown in Figure 2c. The detailed structure of the self-assembled adlayer can be observed at higher magnification (Figure 2c, inset). The CoPc molecules form a square unit cell with a lattice constant of \( 1.4 \) nm, in good agreement with the ordered structures obtained under UHV conditions in Figure 1b.

Our EC-TERS study was performed on a well-ordered CoPc–Au(111) sample with Ag tips, which provide a larger field enhancement than the commonly used gold tips.20,21,34,35 On the basis of our EC-TERS experiment of CoPc on Au(111), about 25 out of 120 tips can provide TERS signal with signal-to-noise ratio more than 0.1 ADU/mW/s under EC conditions.

Typical TERS spectra of CoPc at the solid/liquid interface are shown in Figure 2d. With the Ag tips retracted from the surface, only one peak at 931 cm\(^{-1}\) is observed (black spectrum), which is attributed to the symmetric stretching of the ClO\(_4\)\(^-\) in the electrolyte solution. The absence of CoPc Raman bands in the tip-retracted spectrum indicates that the tip is free of contamination. When the tip is engaged, the acquired near-field signal (blue spectrum) shows clear vibrational fingerprints of CoPc and ClO\(_4\)\(^-\). Upon background subtraction, the TERS signal from only CoPc can be obtained,
shown as the red spectrum in Figure 2d. No significant difference can be found between the TER spectra acquired under UHV and EC conditions, as detailed in the Supporting Information, Table S1. We note that two vibrational modes at 1105 and 1305 cm\(^{-1}\) are observed in EC-TER spectra but not in the UHV-TERS results. However, careful examination reveals that these two peaks, which are related to Raman active modes of CoPc molecules, do exist in the UHV-TERS data albeit at a low signal-to-noise ratio. Additionally, small variations in the peak positions (1−3 cm\(^{-1}\)) in UHV- and EC-TERS are within the spectral resolution of our instruments. The discrepancies in the relative intensity of peaks in two TER spectra are attributed to the variation in plasmonic enhancement, which can be different between individual tips and dielectric environments. The direct comparison of the STM and TERS results of CoPc on Au(111) under UHV and EC conditions reveals that the electrochemically controlled environment can provide a sufficiently stable medium for TERS studies.

One major advantage of EC-STM TERS over UHV-STM TERS is that it replicates a realistic reaction environment for \textit{in situ} measurements. In addition, the substrate potential can be adjusted independently of the STM bias, which enables reaction rate control by changing the substrate potential. Figure 3a shows EC-TER spectra of CoPc adsorbed on Au(111) as a function of substrate potential with three excitation wavelengths. Recent research suggests that the huge enhancement in TERS is resulted from the atomic structure of the tip apex.\(^{36,37}\) In order to minimize the possible reactions (e.g., Ag oxidation, surface reconstruction) that would change the atomic structure on the tip apex, the Ag tips were held at 0.5 V vs RHE during the EC-TERS measurement to minimize the faradaic current. TERS conditions: 632.8 nm laser \((E_{\text{tip}} = 0.5 \text{ V}, I = 0.5 \text{ nA}, I_{\text{time}} = 10 \text{ s}, 0.7 \text{ mW})\), 700 nm laser \((E_{\text{tip}} = 0.5 \text{ V}, I = 0.5 \text{ nA}, I_{\text{time}} = 20 \text{ s}, 1.3 \text{ mW})\), 720 nm laser \((E_{\text{tip}} = 0.5 \text{ V}, I = 0.3 \text{ nA}, I_{\text{time}} = 20 \text{ s}, 2 \text{ mW})\). 

The left panel of Figure 3a shows the EC-TER spectra of CoPc at different substrate potentials acquired with 632.8 nm excitation. The TER spectra are observed over a wide range of potentials from 0.45 to 0.2 V. No significant change in peak positions is observed in the EC-TER spectra. However, a decrease in the TERS intensity is observed as the potential becomes more negative. Furthermore, EC-TER spectra excited by 700 and 720 nm lasers show potential-dependent behavior different from the 632.8 nm case. As the substrate potential
becomes increasingly negative, the TERS intensity increases with 700 nm excitation, but remains stable with 720 nm excitation. The different trends in the EC-TERS experiments with three excitation wavelengths also suggest that the bias between the tip and substrate has negligible effects on the observed EC behaviors. Additionally, the TERS signal almost completely disappears when the substrate potential is held at 0.1 V for all three excitation wavelengths.

On the basis of the results from Figure 3a, we summarize two main observations. First, a common characteristic among the EC-TER spectra collected at different excitation wavelengths is the disappearance of EC-TER spectrum at 0.1 V. Second, a potential-dependent change in the EC-TERS intensity was observed and the trend of such potential dependence varies based on the excitation wavelength.

One explanation for these distinct behaviors in the EC-TERS experiments with three excitation wavelengths could be related to the adsorption behavior of CoPc molecules at the solid/liquid interface. In a recent study, the TERS spectral change of adenine molecules due to different applied potentials was attributed to a potential-dependent orientation change of this molecule. In order to examine the possibility of a potential-dependent change in the adsorption configuration of CoPc on Au(111), EC-STM was performed under different substrate potentials. During the EC-STM measurements, W tips were used and held at 0.5 V vs RHE to reproduce the conditions during EC-TERS measurements. A series of STM images in Figure 3b illustrate that a well-ordered CoPc adlayer forms on Au(111) in the potential range from 0.45 to 0.2 V, while a transition from the ordered phase to a disordered phase is observed at 0.1 V. The disordered phase of CoPc molecules at high cathodic potential (<0.1 V) is in good agreement with the absence of EC-TERS signal at 0.1 V in Figure 3a. Under electrochemical conditions, shifting the substrate potential negatively would increase the surface charge density and result in a weaker molecule–substrate interaction, which can cause the ordered-to-disordered phase transition. The ordered-to-disordered phase transition is also dependent on the STM bias. As shown in Figure S4 in the Supporting Information, the ordered-to-disordered phase transition of CoPc occurred at ~0.1 V when the STM bias was fixed at 0.1 V.

The ordered-to-disordered phase transition provides a satisfactory explanation for the disappearance of TERS spectrum at large negative applied potentials (<0.1 V), but it does not explain the three trends in the potential-dependent TERS intensity with different excitations prior to the phase transition (i.e., ordered phase, >0.1 V). We explain this

![Figure 4](image-url)
observation by considering the resonance conditions that are critical to the TERS measurements.

In a TERS measurement, achieving a resonance condition between the excitation wavelength and molecular absorption can lead to a substantial increase in the overall signal intensity. Our previous EC-TERS study on Nile Blue demonstrates that the TERS intensity can appear or disappear entirely depending on the spectral overlap of the excitation wavelength with the molecular resonance. Consequently, we expect that a change in the resonance condition induced by the applied potential would be reflected as a change in the TERS intensity for CoPc as well. To confirm our hypothesis, CV and spectroelectrochemical absorption measurements were performed to offer further insight into the electrochemistry of CoPc molecules at the solid/liquid interface, as shown in Figure 4.

Figure 4a shows the CV of CoPc on Au(111) in 0.1 M HClO4 without oxygen. In the Ar-saturated electrolyte, a redox couple is observed with formal potential $E^0_{\text{CoPc}} = 0.20 \text{ V}$, which is assigned to the transition between the Co$^{2+}$Pc and the Co$^{3+}$Pc anion. The absorbance measurement from the CoPc monolayer adsorbed on metal surface was too weak for making a solid conclusion about the molecular electronic transitions. Instead, Figure 4b illustrates the time evolution of the absorption spectrum of CoPc in pyridine solution when the working electrode potential is $-0.7 \text{ V} \text{ vs } \text{Ag/AgCl}$ (see the CV of CoPc in pyridine in Figure S5 in the Supporting Information). Initially, the CoPc molecules dissolved in pyridine solution are neutral and show a Q-band centered at 657 nm. As the reduction reaction progresses, a clear attenuation in the Q-band intensity is observed due to a decrease in the concentration of neutral Co$^{3+}$Pc molecules and simultaneously a new absorption feature located at 700 nm appears and increases in intensity as the population of reduced Co$^{2+}$Pc anion grows. Such shifting in the Q-band of reduced CoPc is in good agreement with the reported literatures.

Similar to the change in the Q-band of the CoPc molecule dissolved in pyridine, we hypothesis that these molecules adsorbed on Au(111) surface are likely to experience a redshift in the Q-band as the substrate potential becomes more negative. As a result, the red-shifted Q-band leads to a decreased overlap between the molecular electronic transition and the 632.8 nm excitation wavelength, and a subsequent decrease in TERS signal. In contrast, the resonance between the electronic transition of a reduced CoPc and the excitation wavelength increases with 700 nm excitation, which leads to an increase in the TERS intensity. For the 720 nm excitation, the electronic resonance increases but the TERS intensity is unaffected as the substrate potential becomes more negative, which might be related to the interaction between molecules and substrate.

Furthermore, EC tip-SERS experiment with 632.8 nm excitation was performed to study the electrochemical process by modifying the tip with CoPc molecules, as shown in the Figure S6 in the Supporting Information. A decreasing in the intensity is also observed in the tip-SERS signal as the potential becomes more negative. The $E^0_{\text{tip-SERS}}$ acquired from the tip-SERS voltammogram is about 0.23 V, which is in good agreement with the $E^0_{\text{CV}}$ value (0.20 V) as obtained from CV in Figure 4a. Such agreement further suggests that the three trends in the potential-dependent TERS intensity with different excitations are the result of CoPc reduction at more negative applied potential.

In addition to the reduction of CoPc molecules as the substrate potential becomes more negative, the CoPc-catalyzed ORR is also known to occur in the same potential window (0–0.5 V vs RHE). Our current EC-STM TERS setup is opened to the air, which provides a constant supply of oxygen for the ORR. As shown in Figure 4a, the onset for ORR on bare Au(111) surface is observed at 0.3 V, and the onset for ORR on the CoPc–Au(111) surface is observed at 0.45 V during cathodic scanning in the electrolyte exposed to air. A clear electrocatalytic reduction peak of O2 is found at 0.23 V, indicating that the ORR is catalyzed by CoPc. During ORR, a CoPc molecule is first oxidized by adsorbing an O2 to form a CoPc–O2 complex. Following this, the adsorbed O2 receives two electrons and protons to form H2O2, which quickly desorbs and the oxidized CoPc molecule is simultaneously reduced by the substrate. Previous studies have reported TERS signal related to adduct formation between different gas molecules (CO, O2, etc.) and Co-based macrocycles. However, no spectral evidence of CoPc–O2 complex was observed in our EC-TERS experiment, which can be attributed to the combine effect of the low Raman cross section of oxygen related modes and the low population of the CoPc–O2 complex due to the rapid consumption of O2 under ORR potential. With respect to the second hypothesis, molecular-resolution EC-STM images were performed.

On the basis of the studies on CoTPP and FePc by Wan’s group, the CoPc–O2 complex would show a higher contrast in the EC-STM image, as shown in Figure S7 in the Supporting Information. We successfully achieved molecular-resolution EC-STM images at different substrate potentials by tuning the W tip potential, as shown in Figure 4c. The height profiles extracted along the marked lines are presented under the corresponding STM images and shown consistent contrast in all STM images acquired at potentials between 0.45 and 0.2 V (i.e., during ORR). The consistent contrast suggests a rapid consumption of O2 and all observed molecules are CoPc. From the EC-TERS and EC-STM experiments, no evidence about the CoPc–O2 complex was observed under ORR potential. In order to reveal the detailed ORR mechanism using the EC-TERS technique, catalytic systems having stable intermediates with a strong metal–intermediate interaction and a large Raman cross-section that enables facile TERS acquisition are needed.

CONCLUSIONS

To summarize, a systematic study that employs EC-TERS with three excitation wavelengths, in situ EC-STM, and spectroelectrochemistry absorption measurements has been designed and implemented to understand the electrochemical processes on CoPc molecules at the solid/liquid interface. As the substrate potential becomes increasingly negative, the well-ordered adlayer of CoPc is stable on a clean, well-defined Au(111) surface until the ordered-to-disordered phase transition is triggered. Upon reduction, the electronic transition of CoPc redshifts from 657 to 700 nm, changes the resonance conditions at different excitation wavelengths and results in different trends in the EC-TERS measurements with three excitation wavelengths. The ordered-to-disordered phase transition of CoPc results in the disappearance of EC-TERS signal with different excitation wavelengths. The CoPc-catalyzed ORR process has a negligible effect either on the EC-STM or on EC-TERS measurements. Our results contribute new understanding to the electrochemical behavior of the catalytic-
cally active CoPc molecules at the solid/liquid interface under realistic ORR conditions.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b00513.

Experimental setup, peak assignments, SEM images of the silver tips before and after EC experiment, raw data of EC-TERS with three excitation wavelengths, EC-STM on CoPc with constant bias (0.1 V), CV of CoPc in pyridine, EC tip-SERS, and ORR monitored by EC-STM. (PDF)

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**Notes**

The authors declare no competing financial interest.

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