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Paramagnetic Nitronyl Nitroxide Radicals on $Al_2O_3(11-20)$ Single Crystals: Nanoscale Assembly, Morphology, Electronic Structure, And Paramagnetic Character toward Future Applications

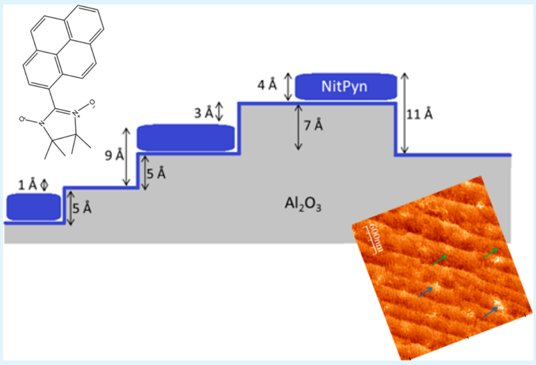
Sabine Abb,[†] Sabine-A. Savu,[†] Andrea Caneschi,[‡] Thomas Chassé,[†] and M. Benedetta Casu*,[†]

[†]Institute of Physical and Theoretical Chemistry, University of Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

[‡]Department of Chemistry and RU INSTM, University of Florence, Via della Lastruccia 3, I-50019 Sesto Fiorentino

Supporting Information

ABSTRACT: Aiming at future technological applications, we describe the interface and the thin film processes of a pyrene-substituted nitronyl nitroxide radical deposited on $Al_2O_3(11-20)$ single crystals. Electronic properties, chemical environment at the interface, and morphology of the thin films have been investigated by a multitechnique approach. Spectroscopic and morphologic analyses indicate a Stranski−Krastanov growth mode and weak physisorption of the molecules on the surface. The deposition does not affect the paramagnetic character of the molecules. The results presented in this paper show not only that the investigated system is a promising candidate as a model for understanding thin film processes in purely organic-based magnets, but its characteristics are worth its future use in electronics, because the radical character of the molecules is completely preserved in the thin films.



KEYWORDS: *nitronyl nitroxides, X-ray photoelectron spectroscopy, XPS, magnetism, thin film growth, organic paramagnets on surfaces*

INTRODUCTION

Electronics is a world of interfaces: a working device is based on specific properties of the active layer, together with a good matching of the interfaces that play a role; for example, between the active layers (e.g., light-emitting materials, hole blocking materials, electron blocking materials) and the contacts/substrates (e.g., metals, metal oxides, conductive polymers, etc.). Thus, understanding and controlling the growth and the interface between two materials is the essential step toward technological applications of thin films. Small organic molecules such as organic semiconductors attract broad attention for their use in electronic devices.[1−7] At the same time, intensive investigations focused on organic thin films demonstrate that their growth and their properties are determined by intermolecular interactions and molecule-surface interactions as well as by substrate morphology, preparation parameters, and postgrowth treatments.[8−13] The knowledge that has been gained during the last decades on nucleation and growth processes in organic thin films can be readily adapted for thin films of molecular magnets such as nitronyl nitroxide radicals.[14−17]

For this class of radicals, the stability of the unpaired electron, due to its complete delocalization over both NO groups, is an important characteristic, coupled with its redox richness that has been proposed to be adaptable in devices.[18] It has been shown in previous investigations that this class of molecules can be evaporated in thin films[14,15] while their magnetic properties are preserved.[14,15] However, applications such as spintronic devices, sensor materials, or memory devices cannot be accomplished without the knowledge of the organic thin film processes at the interface with technologically relevant materials like organics, metals, or metal oxides.[6,7,14]

Aiming at suitable strategies for layer growth and characterization of molecular magnetic systems, we focus on the thin film deposition of nitronyl nitroxide radicals on oxidic substrates. Here, we report on the successful growth on $Al_2O_3(11-20)$ single crystals of thin films of a nitronyl nitroxide derivative with a pyrene moiety, namely 4,4,5,5,-tetramethyl-2-(pyrenyl)-imidazoline-1-oxy-3-oxide (NitPyn, Figure 1), by organic molecular beam deposition (OMBD) in ultra high vacuum (UHV). We choose this specific substrate due to its exceptional properties, which are the reason for its wide use in electronic devices such as in laser optics,[19] in magnetic tunneling junctions (TMR,)[20] and as gate insulator in organic field-effect transistors (OFETs).[21] Moreover, previous studies have revealed that very smooth, atomically flat surfaces can be prepared by appropriate annealing of the crystals.[22−24]

Thickness-dependent X-ray photoelectron spectroscopy (XPS) gives insight into the molecule−substrate interactions. It also reveals the electronic structure and, indirectly, the

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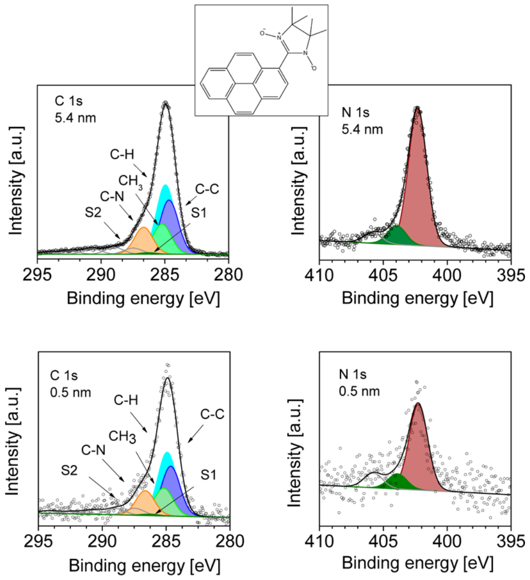

Figure 1. Thickness-dependent C1s and N1s core level spectra together with their peak-fit analysis for NitPyn thin films deposited on $Al_2O_3(11-20)$ single crystals. Upper panel: a 5.4 nm nominally thick film. Lower panel: a 0.5 nm nominally thick film. The molecular structure of NitPyn is also shown.

paramagnetic character of the thin film. The morphology is investigated by atomic force microscopy (AFM). Additional precise information about film characteristics, thin film stoichiometry,[25,26] and growth mode[27] can be gained by XPS investigations. To the best of our knowledge, only few attempts have been made to investigate by XPS the electronic structure of an organic thin film deposited on a large gap insulator like sapphire.[12,28,29] This is very challenging due to the charging effects induced by the insulating substrate upon the emission of photoelectrons. The presence of a core-hole that cannot be readily screened (being the material an insulator) causes shifts and distortions of the XPS peaks.[28] On the one hand, charge compensation/neutralization is needed, but on the other this procedure may damage the organic adsorbate. To overcome these obstacles, we measured all spectra with a non-monochromatic, dual anode source, establishing a stable and reproducible experiment. For comparison of the XPS signals obtained with a monochromatic and a nonmonochromatic X-ray source, see Figure 1S in the Supporting Information.

■ RESULTS AND DISCUSSION

Figure 1 shows the C1s and N1s core level spectra of a thin and a thick NitPyn film deposited on $Al_2O_3(11-20)$ together with their fitting curves. The ratio of the integrated signal intensities of the XPS lines meets the expected stoichiometric ratio: this clearly demonstrates a deposition without degradation (see Table 1S in the Supporting Information). The C1s core level spectra are fitted according to a best fit procedure of the XPS lines on the basis of the fit analysis discussed for NitPyn on Au(111)[14] (for fit parameters, see Table 2S in the Supporting Information). In detail, four main components are used for the fit: the aromatic carbon sites with a differentiation into C−C and C−H bounded carbons, the carbons of the methyl group (CH_3), and the carbons bound to nitrogen (C−N). Because of the electronegativity of the substituents on the carbon sites, the aromatic components together with the methyl groups contribute to the main line at lower binding energies, whereas the carbons bound to nitrogen atoms result in a second feature observed as a shoulder at higher binding energies. For the aromatic components, the C−H carbons are assigned to higher binding energies than the C−C carbons indicating a more efficient screening of the core hole for internal C−C ring bonds.[30]

In addition to these components, assigned as discussed in ref 14, we introduce further components to account for the rich satellite structure at higher binding energies: The shakeup satellites are characteristic in photoemission core level spectra of aromatic hydrocarbon ring molecules.[31] They are due to electronic relaxation effects. Different contributions to the satellite spectrum are given by the large number of non-equivalent carbon sites originating by the symmetry reduction due to the core-hole formation. The satellite S1 can be assigned to the first HOMO−LUMO shakeup. Its energy position with respect to the main line is at 1.6 eV, which is lower than the corresponding HOMO−LUMO gap characterized by optical means (2.3 eV[32]). This effect is typical for polyaromatic systems such as polyacenes[31] or perylene-based molecules.[33] This is explained with the enhanced screening of the core-hole because of its delocalization over the aromatic system. The value of 1.6 eV is in good agreement with the value obtained for tetracene (1.48 eV).[31] The satellite signals are included in the stoichiometric constraints for the fit analysis with all but S2 accounted for the aromatic carbons. We assume that S2 counts for the CH_3 species because of the stoichiometric argument and its binding energy distance from the spectral line.

The atomic species carrying paramagnetic character are nitrogen and oxygen; therefore, the analysis of the N1s and O1s core level spectra is relevant to explore the intactness of the molecule and its mesomeric character in the films. In our previous investigations, we have not only demonstrated that we are able to achieve evaporation without NitPyn degradation, but we have also established a robust correlation between XPS and electron spin resonance (ESR) measurements.[14] We take advantage of this correlation to identify if the magnetic properties of organic-based magnets are preserved in thin films. If the molecule is intact and therefore still a nitronyl nitroxide radical, we expect only a single XPS peak for both species, nitrogen and oxygen, because of the mesomeric structure of the molecule. As the substrate already contains oxygen, we concentrate on the nitrogen species. It is known that the first change upon degradation is recognizable in the N1s photoemission line because the degradation products (imino-nitroxide or diimino derivatives) give contributions to spectroscopic lines in the lower binding energy range with respect to the main line.[14] The N1s main line (see Figure 1, right panel) is at 402.3 eV which correlates very closely with the binding energy observed for the N1s main line in films of intact NitPyn deposited on Au(111).[14] Similarly to the C1s core level spectra, a satellite structure is evident at higher binding energies for the N1s spectra, also including the first HOMO−LUMO shakeup satellite that is 1.6 eV higher in binding energy, and the second HOMO−LUMO shakeup satellite at 405.9 eV. Note that there is a broad feature at lower binding energy (around 400 eV) that we have not considered in the present fit. This is because it may be due to structural differences in the film caused, for example, by different adsorption sites. On the other hand, we cannot exclude that it may also be due to degradation products of a relatively small amount of molecules (around 7%, as determined by a XPS line analysis).

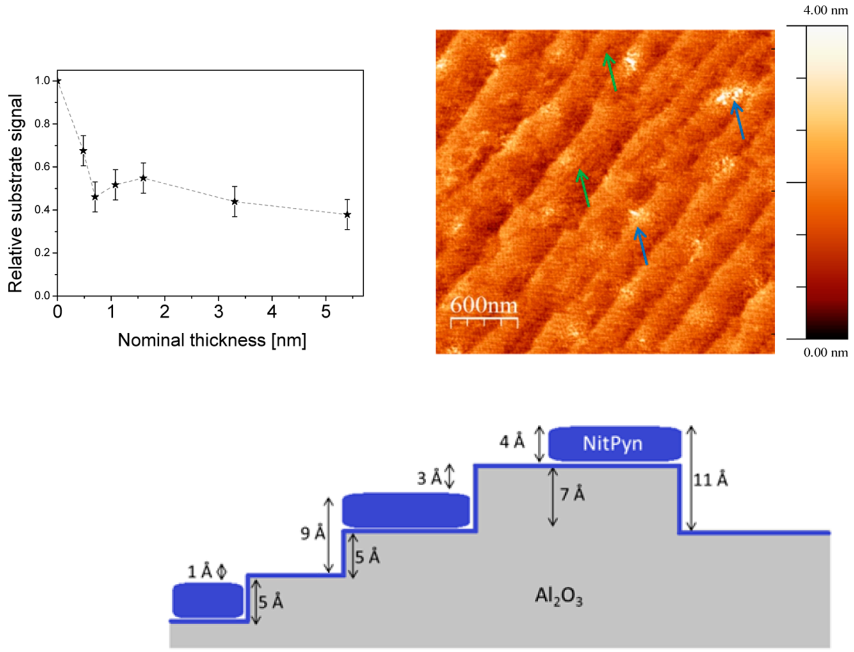

Figure 2. Upper panel left: Attenuation of the Al2s XPS signal, normalized to the corresponding saturation signal, as a function of the nominal thickness.. The gray dotted curve represents a guide to the eye. Upper panel right: A typical 3 μm × 3 μm AFM image of a 2.85 nm nominally thick NitPyn film. The blue arrows indicate islands, the green arrows indicate indentations. Lower panel: Sketch of the proposed growth model.

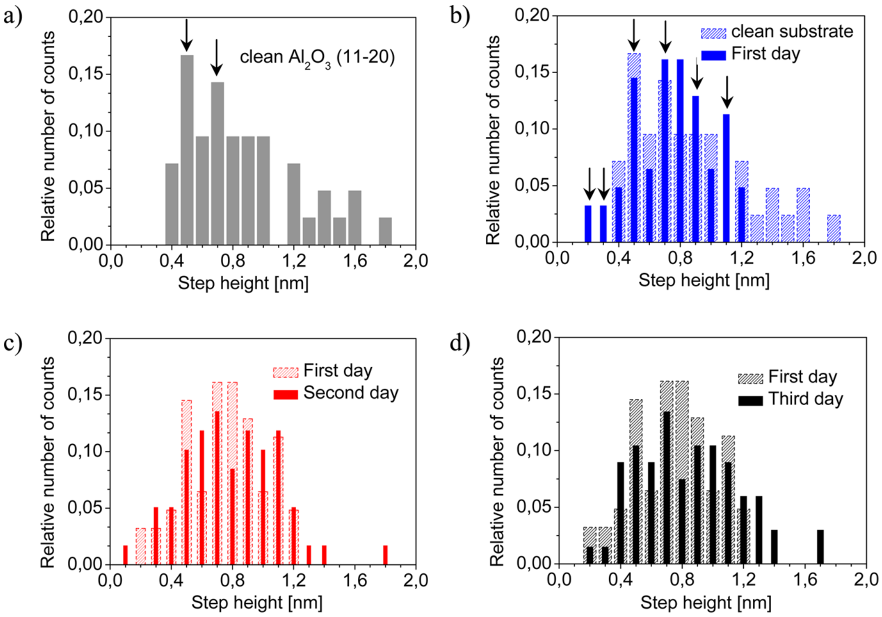

Figure 3. Time evolution over three consecutive days of the step height distribution of a 2.85 nm nominally thick NitPyn film. The corresponding AFM images are shown in Figure 3S in Supporting Information. (a) Clean substrate; (b) 2.85 nm nominally thick NitPyn film, first day. In the background, the step heights of the clean substrate are given as a reference. (c, d) A 2.85 nm nominally thick NitPyn film, (c) second day and (d) third day. In the background, the step heights of the film as measured the first day are given as a reference. The arrows indicate the relevant step heights, as discussed in the text.

As mentioned, the nature of the interaction of the first layer of molecules with the substrate (mode of adsorption and screening mechanisms[10,26]) can be addressed by thickness-dependent XPS. A comparison of the C1s and N1s core level spectra of the thin (0.5 nm) film in the monolayer regime and the thick (5.4 nm) film (see Figure 1 and Table 2S in Supporting Information) shows that there is no difference in the peak shape. The binding energies of the components and their relative intensity do not change with film thickness. This demonstrates a very weak interaction of the molecules with the substrate and a weak influence of sapphire on the electronic structure of the molecule indicating that NitPyn molecules are weakly physisorbed on Al_2O_3(11−20). The absence of relevant changes in the binding energy peaks in the two cases demonstrates that the screening of the core-hole is not assisted by the substrate, even for the first monolayer. This is not surprising given the insulating nature of the substrate. However, a similar observation also holds for NitPyn deposited on

Au(111). This behavior suggests that the molecules are rather distant from the surface which has only little influence on electronic and paramagnetic properties of the molecules in the thin films. The NitPyn molecular orbitals stay unperturbed at the interface. Systematic annealing experiments reveal that the complete desorption of the molecules occurs in the range 510−580 K (the exact temperature is not determined because of a limitation of the experimental setup) further supporting the conclusion of a weak interaction of the molecules with the sapphire substrate.

We also investigated the growth mode of NitPyn on $Al_2O_3(11-20)$ under the present preparation conditions by monitoring the attenuation of the Al2s XPS substrate signal versus the nominal thickness (Figure 2). The attenuation curve consists of two regimes with a clear break at a nominal thickness of 0.8 nm. This behavior strongly suggests Stranski−Krastanov growth mode (i.e, first one or more layers grow on the substrate and afterward island nucleation occurs) which is also in good agreement with the AFM images (Figure 2) and the discussed weak interaction of the molecules with the substrates.[34]

The AFM image of a 2.85 nm nominally thick film is shown in Figure 2. The step structure of the substrate is still clearly visible underneath the organic film that shows island formations (see blue arrow in Figure 3). A peculiar feature of AFM images obtained for the thin films (i.e., not seen in the clean substrate) is the presence of indentations (see green arrow in Figure 3). They show the existence of an organic layer on top of the substrate, giving further evidence for a Stranski−Krastanov growth mode, as found with XPS.

The indentations may be due to grain boundaries formed during the growth of the layers or dislocations occurring at the surface of the film because of pressure variation or air exposure (the AFM measurements are performed ex situ). Although the techniques used in the present work do not allow us to unequivocally determine their origin, we can infer useful information on the film morphology and structure from their presence. A distribution of the indentation depth (see Figure 2S in Supporting Information) reveals that the indentations are around 4 Å in depth. Note that the pyrene moiety of this molecule is 11.66 Å large, 9.28 Å wide, and 3.89 Å thick.[35] Therefore, the extracted depth of the indentations suggests flat lying molecules in the layers of the film. This finding is quite surprising: pyrene and acene derivatives are known to mostly adopt a stand-up geometry on oxide substrates at room temperature.[36,37] However, few examples of flat lying molecules on oxidized substrates are also reported in literature.[38−40] Other investigations are certainly necessary in order to identify the film structure (e.g., Raman spectroscopy, neutron scattering, near edge X-ray absorption fine structure spectroscopy on Al_2O_3 thin films) and further clarify this point. The distribution of the step height reveals substrate steps of mainly 5, 7, 9, and 11 Å for the film (Figure 3). The steps of 5 and 7 Å are in good agreement with the step height found on the clean substrate (see Figure 3a, b) and also consistent with literature (multiples of 2.4 Å for steps on $Al_2O_3(11-20)$[23,24]), whereas the larger step heights are related to the deposited film. Note that some step heights lower than 5 Å are also observed for the film in contrast to the clean substrate surface.

The observed step heights can be explained as follows: If the layer is only on top of the upper terrace of a step edge, the observed step height will increase by the height of the layer, yielding a height of 9 Å or 11 Å. However, it is possible that the lower terrace is also covered, resulting in a decrease of the step height to 1 Å or 3 Å, respectively. If both terraces are covered equally, the step height is the same as for the substrate steps. The different coverage on different terraces separated by a step edge suggests that the diffusion over the step edges is restrained. This characteristic may hint to the presence of an additional barrier required by the molecules to surmount a downward step to give rise to a smooth surface. In the direction normal to the surface, the film morphology is in general controlled by the mass transport depending on the energetic barriers to diffusion and to transverse step-edges, as for example the Ehrlich−Schwoebel barrier.[41,42] Analogously to what is seen for NitPyn on $SiO_2/Si(111)$ where closed layers are observed,[43] we may assume that at least the first layer of the layer-and-island growth is also closed on $Al_2O_3(11-20)$ and the surface is completely covered by the molecules. For the molecules landing on top of the first layers, the effect of the interaction with the substrate decreases, whereas the additional barrier seen by the molecules (Ehrlich−Schwoebel barrier) may increase until the molecules cannot overcome the step edge anymore. As a result, the coverage on each terrace may differ.

As discussed for NitPyn deposited on Au(111), NitPyn molecules are characterized by a high mobility on the surface because of NitPyn vapor pressure. We monitor the film surface by AFM for three consecutive days to get additional information about its evolution in time. We do not find a change of the distribution of the indentation depth. However, the step height distributions per day (Figure 3) indicate that the surface slightly changes with time: the distribution gets wider and the step heights at around 11 Å increase in number. This behavior hints at a ripening process in which the molecules agglomerate at the upper terraces of a step edge resulting in the observation of larger step heights. This is also mirrored by the increase in the root-mean-squared (RMS) roughness with time from 0.48 nm (0.38 nm) on the first day to 0.54 nm (0.44 nm) on the third day of AFM measurements, measured on the $10 \times 10\ \mu m$ ($3 \times 3\ \mu m$) images. Also this behavior can be explained by the NitPyn high vapour pressure at room temperature.[14] To obtain deposition from the vapor phase, it is necessary to work in nonequilibrium conditions. This is achieved by OMBD working in supersaturation. However, after growth, the adsorbed islands relax toward an equilibrium configuration to minimize their free energy. The step edges may consequently act as molecules/island traps upon reorganization.

We also note that the RMS roughness of the freshly deposited film (0.38 nm) does not change relevantly with respect with the RMS roughness of the substrate (0.37 nm for a $3 \times 3\ \mu m^2$ image) meaning that the films follow smoothly the substrate topography, confirming our previous assumption that at least one closed monolayer covers the substrate, as observed in NitPyn on $SiO_2/Si(111)$. Note that the value of the RMS roughness in this system, because of the stepped surface, has a purely statistical meaning.

■ CONCLUSIONS

In conclusion, we have performed a comprehensive investigation of the electronic structure and morphology of NitPyn thin films deposited on the technologically relevant $Al_2O_3(11-20)$ substrate, showing that NitPyn/$Al_2O_3(11-20)$ is certainly a promising candidate as a model system for understanding thin film processes in purely organic-based magnets. The XPS investigations allow us (1) to prove from the XPS stoichiometry and line shape analysis the intactness of the molecules in the films; (2) to show the preserved mesomery of the N atoms in the films from the singly peaked N1s core level spectra. The characteristics of this system are worth its future use in electronics, because the radical character of the molecules is completely preserved in the thin films and their morphology can be appropriately tuned by using different preparation conditions favoring two-dimensional film growth against island nucleation.[8,9,12,44] The behavior of NitPyn on Al_2O_3(11−20) single crystals, a stepped surface, may open the way to use patterned surfaces to further influence the thin film processes in purely organic magnets.

■ EXPERIMENTAL SECTION

Sample preparation and XPS measurements were performed in an UHV system consisting of two preparation chambers, one dedicated to the substrate preparation and one for OMBD, and an analyzing chamber (2×10^{-9} mbar) equipped with a SPECS Phoibos 150 hemisperical electron analyzer, a monochromatic Al Kα source (SPECS Focus 500) and a dual Mg/Al anode source. A clean sapphire single crystal (MaTeck GmbH) was used as a substrate and prepared following a well-established procedure.[22−24] After a one-time ambient annealing at 1600 K for 1 h, the sample was introduced into the UHV system and cleaned by several cycles of argon ion sputtering (1000 V, 3.5 h) and subsequent annealing at 1073 K for 30 min. The cleanness and structural properties were checked by XPS and low energy electron diffraction (LEED). NitPyn thin films were evaporated on the substrate in situ by OMBD (0.8−1.4 Å/ min, substrate at RT). The evaporation rate was measured with a quartz crystal microbalance. We have taken all precautions necessary to avoid radiation damage (i.e., short beam exposure, a freshly prepared film for each spectrum), thus, no beam-induced degradation of the samples was observed on the time scale of the presented experiments, unless differently discussed in the text. Atomic force microscopy was performed under ambient condition in tapping mode using a Digital Instruments Nanoscope III Mutimode AFM.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Further experimental details. Table 1S with all fit parameters. Table 2S containing the NitPyn stoichiometry and integrated XPS experimental signal intensities for the films. The XPS spectra comparing the line shape obtained with and without monochromatic X-ray radiation. Distribution of the indentation depth of a 2.85 nm NitPyn film monitored over three consecutive days. AFM images a 2.85 nm NitPyn film monitored over three consecutive days. XPS time-dependent investigations. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: benedetta.casu@uni-tuebingen.de. Tel. +49 7071 29 76252. Fax: +49 7071 29 5490 (M.B.C.).

Notes

The authors declare no competing financial interest.

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