# Two Photon Induced Pulsed Laser Polymerization with Near Infrared Light

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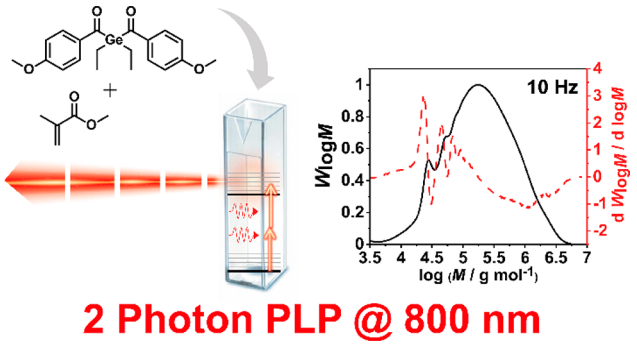
**ABSTRACT:** We introduce two-photon (2P) pulsed laser polymerization (PLP) at 800 nm, demonstrating its working principle even through b iological tissue. We show that 2P PLP is reliab le in determining propagation rate coefficients on the example of the free radical polymerization of methyl methacrylate (MMA) at frequencies ranging from 10 to 100 Hz.




The determination of kinetic rate coefficients in free radical polymerization is a challenging task as, mathematically, the polymerization evolves according to a system of coupled differential equations, making the determination of individual coefficients complex. This complexity stems from the fact that the rate coefficients of propagation, $k_p$, and termination, $k_t$, could for a long time only be determined in a coupled fashion as $k_t/k_p$. In addition, some of the rate coefficients critically depend on the state of the polymerization and the macromolecules within it. For example, the termination rate coefficient—a diffusion-controlled entity—is dependent on the chain length of the terminating macromolecules, the viscosity (and thus the conversion of the reaction mixture), the pressure, and the reaction temperature.[1] Determination of the propagation rate coefficient is, however, somewhat simpler, largely due to the pioneering work of Olaj and colleagues,[2] who in 1987 reported a laser-based method for determining propagation rate coefficients with unprecedented accuracy, building on the theoretical work of Alexandrov et al.[3] The method relies on consecutive pulses of a nanosecond (ns) laser system dictating the start and end of macromolecular growth. During the brief illumination periods, initiating radicals are generated through the decomposition of a photoinitiator, commencing a new generation of chains to grow, while simultaneously terminating the existing generation of growing macroradicals. The period between the ns laser pulses thus determines the length to which a polymer chain is (ideally) able to grow. In other words, the frequency domain of the pulsing action is translated into a length domain of polymer chains, which can be read out by size exclusion chromatography (SEC). Most notably, the pulsing action of the laser generates structured molecular weight distributions, with different lengths of polymer chains clearly distinguishable, formed by propagating chains that are able to propagate beyond a single dark time. Ideally, the molecular weight of these different generations of terminated polymer chains are multiples of each other, determined from the inflection points ($M_i$) before the individual peak maxima ($i$), which are best determined by the first derivative of the molecular weight distribution. Jointly with the knowledge of the dark time between laser pulses ($\nu$) and the monomer concentration ($c_M$), the propagation rate coefficient can be deduced for a wide array of reaction conditions as shown in eq 1. The method has been developed into an IUPAC standard tool, termed Pulsed Laser Polymerization−Size Exclusion Chromatography (PLP-SEC), and so-called benchmark publications report the propagation rate coefficients for a wide variety of monomer systems.[4−10]

$$M_i = k_p c_M i \nu^{-1} \quad (1)$$

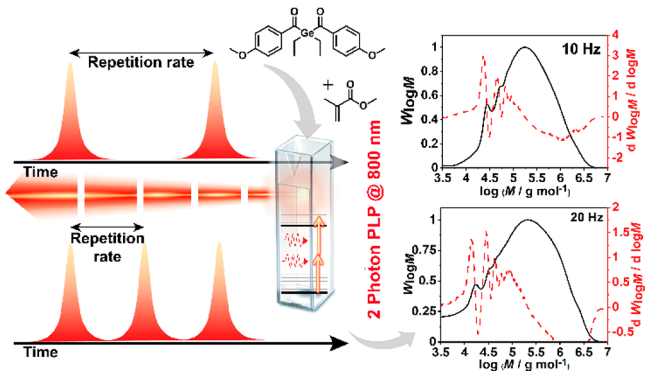
Typically, laser wavelengths in the UV regime are utilized to fragment the photoinitiator into primary radicals, with some limited reports on using UV or visible laser pulses to conduct PLP-SEC.[11−13] While these systems have found many

applications in fields such as photolithography, adhesives, dentistry, and manufacturing, short wavelength irradiation is not suitable for biological applications, where the light has low penetration depth and can have harmful consequences.

A way to circumvent the challenges associated with short wavelength light is to employ two-photon (2P) absorption. Originally predicted by Nobel Laureate Maria Goeppert-Mayer in 1931,[14] 2P absorption occurs when a chromophore simultaneously absorbs two low-energy photons, collectively providing sufficient energy to elevate an electron into an excited singlet state. 2P absorption is a statistically unlikely process that depends quadratically on the incident light intensity. By employing pulsed laser sources with high photon flux, the required light intensities to generate practical levels of 2P absorption can be achieved, such as for 2P-induced polymerization (2PP) reactions. 2PP is a fundamental technique for well-known applications in direct laser writing and microfabrication.[15−21] Traditionally, 2PP reactions are performed with repetition rates in the MHz regime.[15,18−21] However, 2P pulsed laser polymerization with low repetition rates facilitates heightened control over the polymer molecular weight and dispersity, and hence 2P-PLP-SEC is an outstanding advance that we address herein.

In the following we pioneer PLP-SEC triggered by a 2P process using a femtosecond (fs) laser operating within the biological benign window at 800 nm. We unambiguously demonstrate the functionality and operating principle of 2P-PLP-SEC at various repetition rates (refer to Scheme 1), in

**Scheme 1. Concept of Two-Photon Pulsed Laser Polymerization (2P-PLP)**




direct comparison with 1P-PLP-SEC. Critically, we demonstrate that 2P-PLP-SEC can be employed to conduct experiments through considerable tissue barriers due to the high penetration ability of near-infrared (NIR) light.

To initiate a 2P-induced polymerization, we selected Ivocerin (bis-4-(methoxybenzoyl)diethylgermanium) as a blue light photoinitiator. Previous studies have successfully shown that polymerization can be initiated by acylgermanes as photoinitiators by visible-light PLP.[22] With an extinction maximum at 410 nm and no extinction in the near-infrared (NIR) region (refer to the Supporting Information, Figure S1), Ivocerin is ideal as a 2P initiator at 800 nm.

To demonstrate that 2P-PLP-SEC is indeed functional and laser-controlled, polymers were synthesized with various laser repetition rates, analyzed via SEC, and compared to polymer distributions generated under classical 1P-PLP-SEC conditions. The SEC traces of the generated poly(methyl methacrylate) (PMMA) when solutions of methyl methacrylate (MMA) (bulk) and Ivocerin (12 mmol $L^{-1}$) were irradiated under both conditions (400 nm: 295 $\mu$J $cm^{-2}$; 800 nm: 5.5 mJ $cm^{-2}$) at repetition rates ranging from 10 to 100 Hz are presented in Figure 1a−c (frequencies 10, 20, and 50 Hz shown; 100 Hz data are close to the edge of the resolution of the experiment and can be found in the Supporting Information Section 3.1). With increasing pulse frequency, the maxima within the distribution generated through the pulsing action of the laser are expected to shift to lower molecular weights. For both conditions, it is evident from Figure 1a−c that the maxima shift as a function of molecular weight, and we will discuss their analysis below. A striking observation is that the molecular weight patterning is less pronounced in the 2P than in the 1P case, which is most likely due to a lower overall radical concentration generated in the 2P case.

According to Olaj et al.,[2] a clear indicator of PLP structure and, thus, of a laser-controlled reaction, is given by the analysis of the derivative of the SEC trace. Using such an analytical approach (refer to Figure 1d−f), displaying the first derivatives of the SEC distributions generated under 1P and 2P conditions, respectively, the laser pulse frequency can be directly assigned to the molecular weight $M_i$ of the polymer chain length, and thus the propagation rate coefficient can be determined (refer to the Supporting Information Section 3.1 for more details). Not surprisingly, in the case of the 1P pulse-initiated polymerizations (400 nm)—for each repetition rate—the calculated propagation rate coefficient is consistent with the IUPAC accepted literature value (267 L $mol^{-1}$ $s^{-1}$) as evident from Table 1.[5] Confident that our 1P setup functions well, we transfer the experiment to the NIR region (800 nm) and compare the obtained results to the visible-light-triggered experiments (Figure 1). For each repetition rate, the NIR-light-generated polymer SEC distributions and their respective derivatives (red curves) are superimposed with the previously conducted visible-light-triggered experiments, indicating excellent agreement, noting the somewhat less-pronounced structuring of the 2P experiments due to the lower primary radical concentrations. The superposition of the peak positions of both the red and the black curves as well as the agreement of the propagation rate coefficients (refer to Table 1) that are derived from the NIR−light-induced experiments clearly evidence laser control during NIR light-induced polymerization.

Batchelor et al.[23] have previously reported using Ivocerin as a suitable 2P NIR-triggered photoinitiator in three-dimensional (3D) laser lithography, indicating that it can be fragmented via two-photon processes. While the above data is strong evidence that PLP is initiated by a 2P process, we sought to further underpin this notion by measuring the initiator conversion as a function of the incident beam fluence (refer to Figure 2) using UV−vis−NIR analysis (refer to the Supporting Information Section 3.2 for more details). To confirm that the photo-induced decomposition of Ivocerin is critical to initiating polymer growth, we initially irradiated the monomer methyl methacrylate (MMA) in the absence of the initiator with 800 nm fs laser pulses (35 fs, 100 Hz, 5.5 mJ $cm^{-2}$) and, as expected, observed no polymer formation, serving as first indication that we observe a 2P-induced polymerization. Two-photon absorption (2PA) is a second-order nonlinear optical process, and as such we expect a quadratic dependence of the initiator decay on the variation of the laser fluence. For each sample, 250 $\mu$L was taken from a stock solution (12 mmol $L^{-1}$)

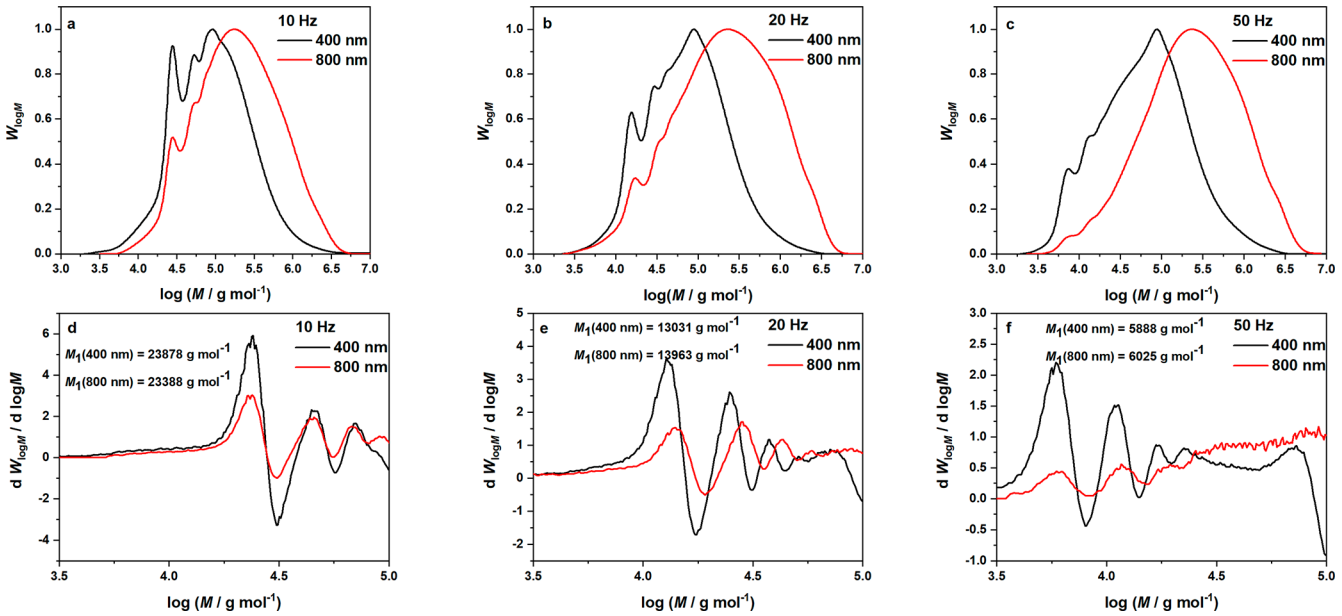



**Figure 1.** (top row) Molecular weight distribution of PMMA generated by 400 nm (black) and 800 nm (red) pulsed-laser-triggered Ivocerin fragmentation ($c$ = 12 mmol L$^{-1}$ in bulk MMA) at (a) 10 Hz, (b) 20 Hz, and (c) 50 Hz. (bottom row) First derivatives of SEC traces shown in the top row with (d) a repetition rate of 10 Hz, resulting in inflection points of the distribution close to $M_1$ = 23 900 g mol$^{-1}$, $M_2$ = 45 700 g mol$^{-1}$, and $M_3$ = 69 180 g mol$^{-1}$, (e) a repetition rate of 20 Hz where the inflection points of the distribution are close to $M_1$ = 13 000 g mol$^{-1}$, $M_2$ = 26 300 g mol$^{-1}$, and $M_3$ = 40 000 g mol$^{-1}$, and (f) a repetition rate of 50 Hz where the inflection points of the distribution are close to $M_1$ = 6000 g mol$^{-1}$, $M_2$ = 11 000 g mol$^{-1}$, and $M_3$ = 17 400 g mol$^{-1}$. Refer to the Supporting Information for the SEC trace and first derivative for PMMA generated by 400 and 800 nm triggered Ivocerin at 100 Hz.

**Table 1**

PLP-SEC distribution derived propagation rate coefficients of MMA with various repetition rates under 1P (400 nm) and 2P (800 nm) conditions.

| $\lambda$/nm | *Frequency*/ Hz | $k_p$ ($M_1$)/L mol$^{-1}$ s$^{-1}$ | $k_p$ ($M_2$)/L mol$^{-1}$ s$^{-1}$ | $k_p$ ($M_3$)/L mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|
| 400 | 10 | 242 | 247 | 244 |
| | 20 | 239 | 222 | 224 |
| | 50 | 267 | 254 | 257 |
| | 100 | 300 | 286 | 269 |
| 800 | 10 | 242 | 247 | 248 |
| | 20 | 256 | 255 | 258 |
| | 50 | 267 | 266 | 288 |
| | 100 | 280 | 293 | |

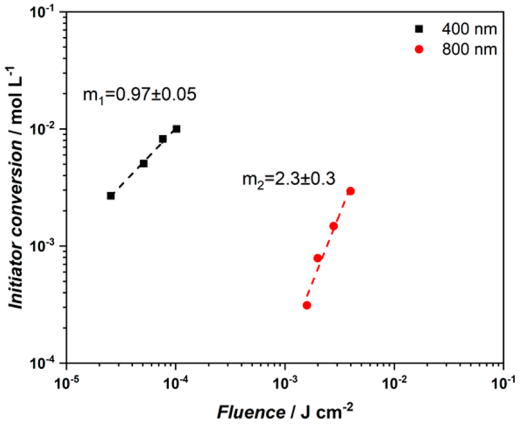



**Figure 2.** Initiator conversion of a solution containing Ivocerin in bulk MMA ($c$ = 12 mmol L$^{-1}$) after 90 s irradiation with 25, 50, 76, and 102 $\mu$J cm$^{-2}$ at 400 nm (black data points) with a slope of $m_1$ = 0.97; initiator conversion of a solution containing Ivocerin in bulk MMA ($c$ = 12 mmol L$^{-1}$) and after 1 h irradiation with 1.6, 2, 2.8, and 4 mJ cm$^{-2}$ at 800 nm (red data points) with a slope of $m_2$ = 2.3.

and transferred into a vial to be irradiated from below, with the aim of illuminating the highest possible proportion of the solution. The irradiated solutions were subsequently transferred into a 1 mm cuvette and placed into a UV–vis–NIR spectrometer. After recording the UV/vis spectrum of a non-irradiated sample, we determined the monomer conversion after the irradiation for 1 h as a function of increasing fluences (for details refer to the Supporting Information Section 3.2). We further followed the initiator conversion at 400 nm as a comparison experiment. The fluence was increased from 25 to 102 $\mu$J cm$^{-2}$ in steps of 25 $\mu$J cm$^{-2}$ for the 400 nm experiment, while fluences between 1.6 and 4 mJ cm$^{-2}$ were employed for the 800 nm experiment. The data in Figure 2 demonstrates that the conversion of Ivocerin is based on a 2P absorption process, when irradiated with high-intensity 800 nm light. While the data points obtained for 400 nm follow a linear trend (black dashed line), the data points of the 800 nm experiment closely follow a quadratic trend (red dashed line), as suggested by the slopes $m_1$ and $m_2$ of the linear fitted data points plotted on a double logarithmic scale. Combined with the control experiment without initiator, we thus conclude that the photoinduced decay of Ivocerin at 800 nm is predominantly based on a 2P excitation process.

It is mandatory at this point to explore whether the 800 nm-induced 2P PLP mechanism leads to a different polymer (end-group) product spectrum, compared to 1P-initiated polymerization. We explored this using high-resolution electrospray ionization mass spectrometry (ESI-MS), comparing 800 and 400 nm triggered polymerization products. Figure 3 depicts an

enlarged region of the mass spectrum of one polymer repeat unit (for the full spectrum refer to the Supporting Information Section 3.3).

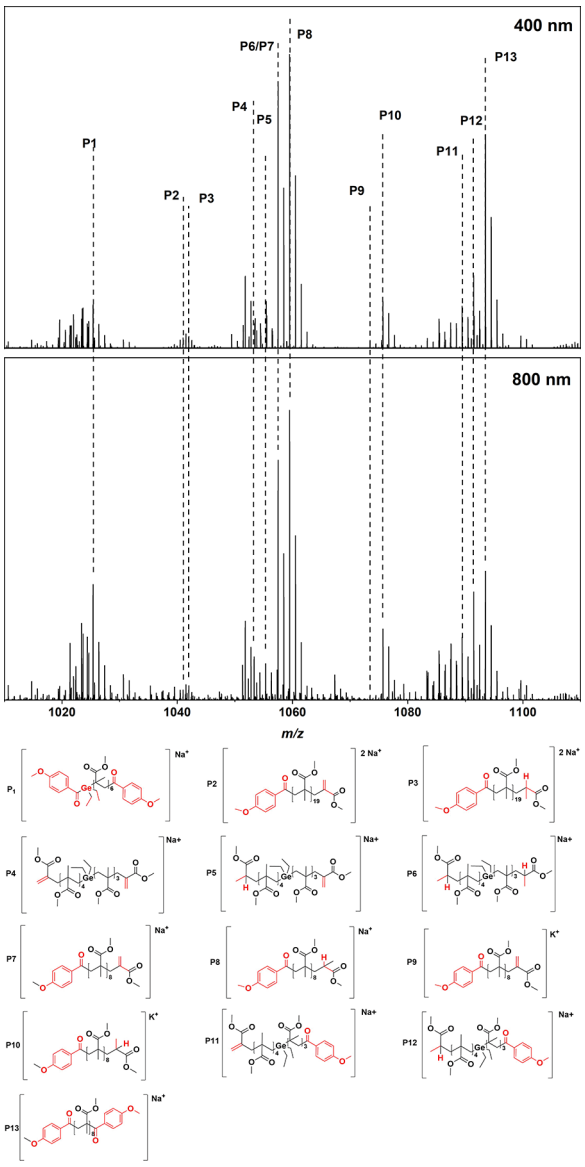
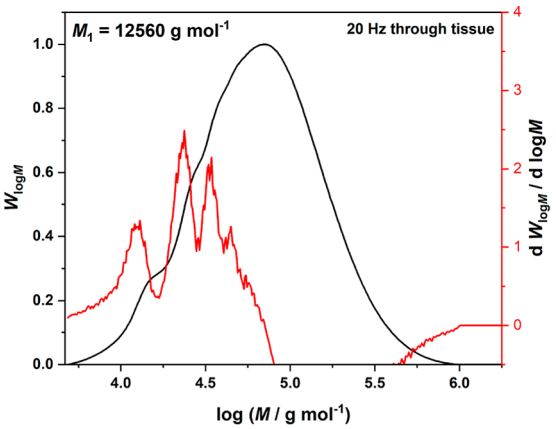



**Figure 3.** ESI-MS spectra of PMMA after photoinitiation with 12 mmol $L^{-1}$ Ivocerin in bulk MMA after 15 min irradiation with 102 $\mu$J $cm^{-2}$ at 400 nm (1P) and 1 h with 1.3 mJ $cm^{-2}$ at 800 nm (2P). Zoom into the repeat unit between 1010 and 1110 $m/z$ and assignment of the main species **P1–P13**. The full mass spectrum is depicted in the Supporting Information, which also contains detailed isotopic pattern simulations.

As expected, the assigned species are combination as well as disproportionation products dominated by Ivocerin fragment end groups. The detailed assignments by comparison with a simulation of the isotopic pattern can be found in the Supporting Information Section 3.3. Both the 1PP and the 2PP result in an identical end-group distribution pattern. Setting the abundance of the product with the highest peak intensity within one repeat unit to unity, the abundance of the other products was determined relative to the initially defined product. Interestingly, however, the end-group abundances appear to be somewhat different for the two cases, yet overall it is reasonable to deduce that the in-principle initiation mechanism for both cases is identical. An overview of the relative abundance X of the most dominant species is provided in Table S7 jointly with all relative species' abundances in the Supporting Information Section 3.3.

Finally, we explore 2P-PLP-SEC through biological tissue. Specifically, a thin slice of bacon was placed into the path of the laser beam. To minimize the decrease of the laser beam fluence caused by scattering effects due to the natural structure of the tissue, the bacon was placed directly in front of a 1 cm cuvette, which contained the sample solution. We successfully generated polymer after the irradiation of Ivocerin in MMA ($c$ = 12 mmol $L^{-1}$) with a fluence of 5.5 mJ $cm^{-2}$ (reduced to close to 1 mJ $cm^{-2}$ by the tissue) and a repetition rate of 20 Hz. The resulting molecular weight distribution of the generated polymer is depicted in Figure 4.




| Frequency / Hz | $k_p$ ($M_1$) / L $mol^{-1}$ $s^{-1}$ | $k_p$ ($M_2$) / L $mol^{-1}$ $s^{-1}$ | $k_p$ ($M_3$) / L $mol^{-1}$ $s^{-1}$ |
|---|---|---|---|
| 20 | 228 | 214 | 216 |

**Figure 4.** Molecular weight distribution of PMMA generated by 800 nm pulsed laser triggered Ivocerin fragmentation ($c$ = 12 mmol $L^{-1}$ in bulk MMA) through tissue (<1 mm) at 20 Hz (black) and first derivative of SEC trace with repetition rate of 20 Hz, resulting in inflection points of the distribution at $M_1$ = 12 560 g $mol^{-1}$, $M_2$ = 23 713 g $mol^{-1}$, and $M_3$ = 35 809 g $mol^{-1}$ for irradiation at 800 nm (red). The tissue showed no visible damage after irradiation. The SEC distribution-derived propagation rate coefficients of MMA with 20 Hz at 800 nm under 2P conditions through tissue are provided in the table below Figure 4.

For all inflection points $M_i$ (refer to Supporting Information Section 4 for the detailed assignment), the calculated $k_p$ values are in good agreement with the $k_p$ values of the experiment without tissue and thus with the literature value of $k_p$.

In conclusion, we introduce two-photon (2P) activated pulsed laser polymerization, demonstrate its reliability, and show that it can be conducted through tissue. Our innovation allows one for the first time to conduct PLP with NIR light, opening the in-principle possibility of interrogating the propagation rate of polymerizing systems in biological systems, possibly even in the confined environments of living cells.[24]

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CRediT: **Philipp Neidinger** data curation (lead), formal analysis (lead), investigation (lead), writing-original draft (equal); **Dominik Voll** formal analysis (equal), visualization (equal), writing-review & editing (equal); **Sarah L Walden** conceptualization (equal), formal analysis (equal), supervision (equal), writing-review & editing (equal); **Andreas-Neil Unterreiner** conceptualization (equal), funding acquisition (supporting), methodology (equal), supervision (equal), project administration (equal), writing-review & editing (equal); **Christopher Barner-Kowollik** conceptualization (equal), funding acquisition (lead), project administration (equal), supervision (equal), writing-original draft (equal).

### Notes

The authors declare no competing financial interest.

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