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Chromium-doped zinc gallate: Impact of Sn⁴⁺ co-doping on the persistent luminescence properties at the nanoscale applied to bio-imaging

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1 **Chromium-doped zinc gallate: impact of Sn⁴⁺ co-doping on the persistent luminescence**
2 **properties at the nanoscale applied to bio-imaging**

3

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18

19 **Abstract**

20 Persistent luminescence (PersL) nanoparticles emit a signal that lasts long after the excitation has
21 ended, enabling highly sensitive bioimaging without background noise. When using UV light as
22 excitation source before the injection, a strong PersL signal can be detected *in vivo* before
23 disappearing within a few hours. For long-term imaging, we have shown in the past that visible
24 LED can be used to re-excite $\text{ZnGa}_{1.995}\text{Cr}_{0.005}\text{O}_4$ (ZGO:Cr³⁺) nanoparticles *in vivo*, producing a
25 signal intensity that is, however, much lower compared to the signal obtained after the UV pre-
26 excitation method. This lower signal intensity of the nanoprobe when using visible LED may
27 prevent its detection in some cases. Herein, we report an improvement in the excitation efficiency
28 of visible LED using $\text{Zn}_{1.33}\text{Ga}_{1.335}\text{Cr}_{0.005}\text{Sn}_{0.33}\text{O}_4$ (ZGSO:Cr³⁺) PersL nanoparticles. We fully
29 compared ZGSO:Cr³⁺ and original ZGO:Cr in term of structure, optical properties and bio-imaging
30 potential. The co-doping with tin strongly enhances the persistent luminescence, even at the
31 nanoscale. *In vivo* imaging results showed that ZGSO:Cr³⁺ exhibits an approximately 3-fold signal
32 enhancement compared to ZGO:Cr³⁺ using UV pre-excitation. Even more interestingly, when
33 using LED excitation, the signal intensity of ZGSO:Cr³⁺ is more than 10-fold higher than the one
34 of ZGO:Cr³⁺, making ZGSO nanoparticles much easier to detect. ZGSO:Cr nanoparticles can be
35 surface-modified with PEG to get nanoprobes with a much longer residence time in blood. This
36 unique comparison between both compositions makes ZGSO:Cr³⁺ a more effective imaging
37 diagnostic probe than the original ZGO:Cr³⁺ nanoparticles, opening up new applications for *in vivo*
38 diagnostics.

39 **Highlights:**

40

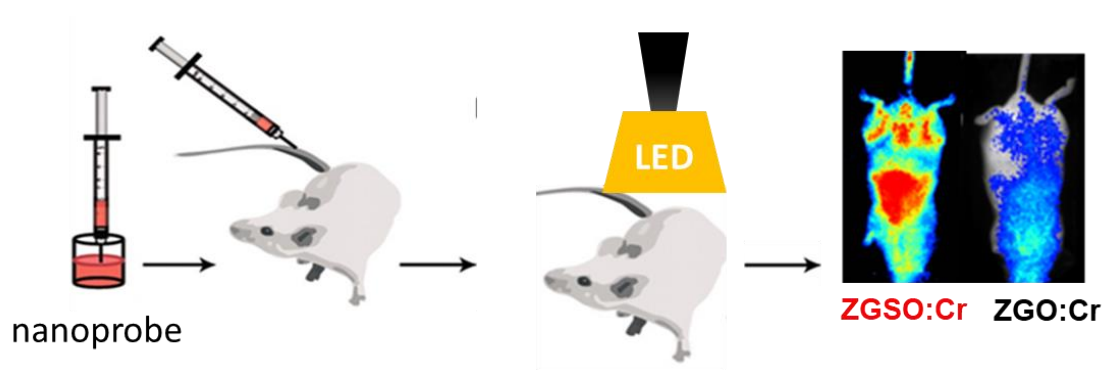
41 ● ZGSO:Cr³⁺ NPs emit 10-fold enhanced PersL compared to original ZGO:Cr³⁺

42 ● Improvement of PersL imaging *in vivo*;

43 ● High efficacy of *in situ* excitation using visible light (LED).

44

45 **Graphical Abstract**



46

47

48 1. Introduction

49 Persistent luminescence (PersL) materials can absorb and store the photoexcitation energy into
50 traps, before slowly releasing it in the form of a PersL signal that lasts for a relatively long duration
51 (minutes to hours) after the excitation has been stopped [1-6]. This intriguing optical feature has
52 attracted extensive attention in various fields such as imaging [7] and lighting [8-10]. Recently,
53 near-infrared (NIR) PersL nanoparticles (NPs), as a new type of luminescent probes, have been
54 widely applied in biology when prepared at the nanoscale for imaging [7, 11-16] diagnosis [17-20]
55 and therapies [21-28], and even in other broader fields [29-32]. Compared to traditional
56 fluorescence imaging, bioimaging using NIR PersL NPs exhibits a higher signal-to-noise ratio
57 (SNR) due to less background noise [33]. For such application, the PersL nanoprobe can be pre-
58 excited before their injection with ultraviolet (UV) light, for example when using silicate NPs
59 doped with Eu, Dy, Mn [12], phosphate NPs doped with Eu, Dy, Mn or nitridosilicate NPs doped
60 with Eu, and Tm [34]. Although various PersL NPs compositions and other excitation sources
61 varying from X-rays to visible light [35-40] have been widely used, the re-excitation efficiency *in*
62 *vivo* is still an issue due to the limited tissue penetration of the excitation light, particularly when
63 using UV or visible light sources [41].

64 In the past, we have shown that $\text{ZnGa}_{1.995}\text{Cr}_{0.005}\text{O}_4$ (ZGO:Cr) is a safe and very effective
65 nanoprobe for bioimaging [41-43]. However, a limit of this probe is the limited efficiency
66 of the *in vivo* LED excitation [41], meaning that the signal obtained after LED excitation,
67 either to (i) photostimulate and release already filled deep traps [44] or (ii) favor the creation
68 of traps, is much lower than after UV pre-excitation, differing by about one log in intensity
69 [41, 43]. This may prevent the detection of the nanoprobe, especially if present in small
70 amount [43]. It has been demonstrated that enhancement of the LED excitation of ZGO:Cr^{3+}
71 can be obtained by co-doping the zinc-gallate host with various tetravalent cations such as
72 Ge^{4+} [45] or Sn^{4+} [46, 47] increasing defect formation. Pan *et al* [46] for instance reported
73 an enhancement in the first minutes of the persistent decay. However, such observation was
74 reported at the bulk scale with materials prepared using a solid state method, preventing
75 their administration as a suspension *in vivo*.

76 In the present study, we report the synthesis of $\text{Zn}_{1.33}\text{Ga}_{1.335}\text{Cr}_{0.005}\text{Sn}_{0.33}\text{O}_4$ (ZGSO:Cr) at
77 the nanoscale, using a hydrothermal method followed by an annealing at 750°C and a ball
78 milling process. After the extraction of 90-nm size nanoparticles, the signal intensity of

79 ZGSO after UV or visible LED light excitation was compared to the original ZGO:Cr NPs,
80 strictly prepared under the same conditions. Thus, it has been proved that a better efficiency
81 is always obtained for ZGSO:Cr NPs, both in dry form and in suspension, underling the
82 environmental impact on luminescence efficiency. More importantly, it was possible to get
83 a 10-fold signal intensity improvement with ZGSO vs ZGO using LED as the excitation
84 source. To evaluate the efficiency of ZGSO:Cr NPs in regards to ZGO:Cr NPs, signals
85 emitted by both NPs through different layers of tissues, as well as *in vivo* using mice were
86 performed. Compared to what was observed in the bulk [46], our results demonstrate that
87 even at the nanoscale, visible LED can efficiently excite ZGSO:Cr NPs to produce a NIR
88 PersL signal, up to 10-fold higher, offering an alternative of interest to ZGO:Cr NPs. These
89 point by point comparison between ZGSO and ZGO, such as structure, optical properties,
90 as well as the evaluation of the effect on bio-imaging in deep tissue and *in vivo*, makes
91 $\text{Zn}_{1.33}\text{Ga}_{1.335}\text{Cr}_{0.005}\text{Sn}_{0.33}\text{O}_4$ (ZGSO:Cr) a superior nanoprobe to visible LED light
92 excitation, highly promising for further *in vivo* imaging, after an appropriate surface
93 functionalization.

94 **2. Materials and methods**

95 **Chemicals**

96 3-Aminopropyl-triethoxysilane (APTES) was obtained from Sigma-Aldrich. Zinc nitrate
97 hexahydrate (>99%) was purchased from Fluka. Tin chloride (>99.9%), gallium oxide
98 (99.999%), chromium (III) nitrate nonahydrate (99.99%), and dimethylformamide
99 (>99.9%) were purchased from Alfa Aesar. Alpha-methoxy-omega-N-hydroxysuccinimide
100 poly(ethylene glycol) PEG MW 5000 Dalton was bought from Iris Biotech GmbH.

101

102 **2.1 Preparation of ZGO:Cr³⁺ and ZGSO:Cr³⁺ NPs**

103 ZGO:Cr NPs were synthesized by the hydrothermal method as already published by our
104 laboratory. First, gallium nitrate was formed by reacting 8.94 mmol of gallium oxide with
105 20 mL of nitric acid (35 wt.%) under hydrothermal conditions at 150 °C for 24 hours. Then,
106 a mixture containing 0.045 mmol of chromium nitrate and 8.97 mmol of zinc nitrate in 10
107 mL of water was added to the previous solution of gallium nitrate under vigorous stirring.
108 The resulting solution was adjusted to pH 7.5 with an ammonia solution (30 wt.%), stirred

109 for 3 hours at room temperature, and transferred into a 45 mL Teflon-lined stainless-steel
110 autoclave for 24 h at 120 °C. The resulting solid was washed several times with water and
111 ethanol before being dried at 60 °C for 2 hours. The dry white powder was finally sintered
112 in air at 750 °C for 5 hours. Hydroxylation was performed by acid wet grinding of the
113 powder (500 mg) for 15 minutes, with a mortar and pestle in 2 mL of 5 mM HCl solution,
114 and vigorously stirred overnight at room temperature at 10 mg.mL⁻¹ in 5 mM HCl. The
115 hydroxylated ZGO (ZGO-OH) NPs with a diameter ~ 90 nm were selected from the whole
116 polydisperse colloidal suspension by centrifugation on a SANYO MSE Mistral 1000 at
117 4500 rpm for 10 minutes. ZGO NPs present in the supernatant were gathered and
118 concentrated.

119 The synthesis of Zn_{1.33}Ga_{1.335}Cr_{0.005}Sn_{0.33}O₄ (ZGSO:Cr) was adapted from the synthesis of
120 ZGO:Cr nanoparticles by a hydrothermal method with a subsequent calcination process
121 [44]. In this method, 8.94 mmol of gallium oxide were dissolved in 10 mL of nitric acid
122 (35 wt%) under hydrothermal conditions for 48 h at 150 °C. Then 10 mL of an aqueous
123 solution containing 17.82 mmol of zinc nitrate hexahydrate, 4.42 mmol tin (IV) chloride
124 pentahydrate, and 0.07 mmol chromium (III) nitrate nonahydrate were added to the vessel
125 under vigorous stirring. The pH of the solution was adjusted to 7.5 using ammonia solution
126 (30 wt%). The mixture was stirred for 3 h at room temperature, and then transferred into a
127 stainless-steel autoclave before heated at 120 °C for 24 h in an oven. The resulting solid
128 was washed several times with water and ethanol, dried at 60 °C for 2 h, and then sintered
129 in air at 750 °C for 5 h. The obtained white powder was then ground in hydrochloric acid
130 (5 mmol.L⁻¹), stirred overnight in HCl 5 mM, and centrifuged at 4500 rpm for 10 min,
131 selecting the supernatant that had an average size of ~ 90 nm, following the same method
132 as for ZGO:Cr NPs.

133

134 **2.2 Functionalization of ZGO:Cr³⁺ and ZGSO:Cr³⁺ NPs**

135 The surface of ZGO:Cr³⁺ NP and ZGSO:Cr³⁺ NPs was functionalized using the same
136 method and parameters, using a slightly modified protocol we previously reported [41].
137 Following is an example using the ZGSO NPs. Briefly, ZGSO-NH₂ nanoparticles were
138 prepared by adding 20 µL of 3-aminopropyl-triethoxysilane (APTES) to a suspension of 5
139 mg ZGSO-OH in 2 mL DMF. The reaction mixture was sonicated for the first 2 minutes

140 using a Branson Ultrasonic Cleaner 1210 and kept under vigorous stirring for 5 hours at
141 room temperature. Then, the nanoparticles were washed from the unreacted APTES by three
142 centrifugation and redispersion steps in DMF. ZGSO-PEG nanoparticles were prepared by
143 reacting 10 μmol of MeO-PEG_{5kDa}-NHS (50 mg) with 5 mg of ZGSO-NH₂ nanoparticles in
144 2 mL DMF. To ensure a maximum PEG density, this functionalization step was achieved
145 overnight, under vigorous stirring at 90°C.

146

147 **2.3 Characterizations**

148 *2.3.1. X-ray Diffraction (XRD)*

149 X-ray diffraction (XRD) patterns were obtained with an X-ray diffractometer (XPert PRO,
150 Malvern Panalytical Ltd.,) equipped with a Ge111 single-crystal monochromator and by
151 selecting the K α 1 radiation wavelength of the Cu X-ray tube (0.15405 nm). The two
152 materials showed crystalline phases with cubic spinel structures.

153

154 *2.3.2. Dynamic Light Scattering (DLS)*

155 The hydrodynamic diameter of ZGO and ZGSO NPs was characterized by dynamic light
156 scattering (DLS) performed with a Zetasizer Nano ZS (Malvern Instruments, Southborough,
157 MA, USA) equipped with a 632.8 nm helium–neon laser and 5 mW power, with a detection
158 angle of 173° (non-invasive backscattering). Zeta potentials were characterized using the
159 same equipment and measurements were done in NaCl 20 mM.

160

161 *2.3.3. Optical Spectroscopy*

162 Absorption measurements of the dry ZGO:Cr and ZGSO:Cr NPs were carried out in a
163 UV/Vis/NIR spectrophotometer (Varian Cary 6000i, Agilent). The resolution was 0.1 nm
164 for the Cr bands. Visible and deep-red (or NIR-I) photoluminescence (PL) measurements
165 of dry ZGO:Cr and ZGSO:Cr NPs were performed using an ICCD camera (Roper Pixis
166 100, Teledyne Princeton Instruments) cooled at -65 °C and coupled to a monochromator,
167 with 300 grooves per mm and centered at 500 nm.

168

169 *2.3.4. Persistent Luminescence and Thermoluminescence*

170 The dry ZGO:Cr and ZGSO:Cr powder samples were thermally detrapped before each
171 experiment by increasing the temperature up to 90 °C and then kept in the dark.
172 Thermoluminescence (TL) measurements were performed using a closed-cycle Heflow
173 cryostat (Sumitomo Cryogenics HC-4E) attached to a temperature controller (Lakeshore
174 340). The samples were firstly excited with a 365 nm lamp for 5 min at 10 K, and after
175 excitation removal, the TL curves were recorded at a 10 K/min incline while heating up to
176 470 K. The signal was recorded using an ICCD camera (Roper Pixis 100, Teledyne
177 Princeton Instruments) coupled to a visible monochromator (Acton Spectra Pro, Princeton
178 Instruments), at 300 grooves per mm, centered at 500 nm. Typically, a measurement time
179 of 1 hour was needed for the temperature-dependent luminescence intensity shown in this
180 work.

181
182 *2.3.5 Transmission electron microscopy (TEM) and Thermogravimetric analysis (TGA)*
183 Transmission electron microscopy (TEM) images were obtained using a TecnaiSpiritG2
184 microscope operating at 120 kV. 5 µL of each suspension at 1 mg/mL) have been dropped
185 for 1 min and the grids have been wiped. TGA was performed by using a TGA/DSC 1 from
186 Mettler-Toledo (Greifensee, Switzerland) sensitive to 1 µg and calibrated beforehand with
187 internal standard weights. Dry samples of approximately 2 mg were analyzed in alumina
188 pans with a central hole of 1 mm diameter. The experiments were performed at a heating
189 rate of 5 K min⁻¹, under a dry air flow of 70 mL min⁻¹.

190
191 *2.4 Deep tissue imaging*
192 Two different procedures have been used: 1) pre-excitation and 2) *in situ* activation method.
193 For the first procedure (Fig 4a and 5a), UV excited NPs (suspension at 2 mg/mL) were
194 covered by 1-3 pieces of tissue (pork pieces with thickness ~ 2 mm / piece) and transferred
195 into an Optima camera (Biospace Lab) for a PersL signal detection for 5 minutes. For the
196 *in situ* excitation procedure (Fig 4c and 5c), PersL NPs covered by tissues (1-3 pieces were
197 used) are excited using visible LED source (Philips Lumiled 70W 5700 lm equipped with
198 515 nm cut-off filter) for a 2 minutes charging time. Then, the Optima camera (Biospace
199 Lab) camera is used for 5 min PersL signal acquisition.

200

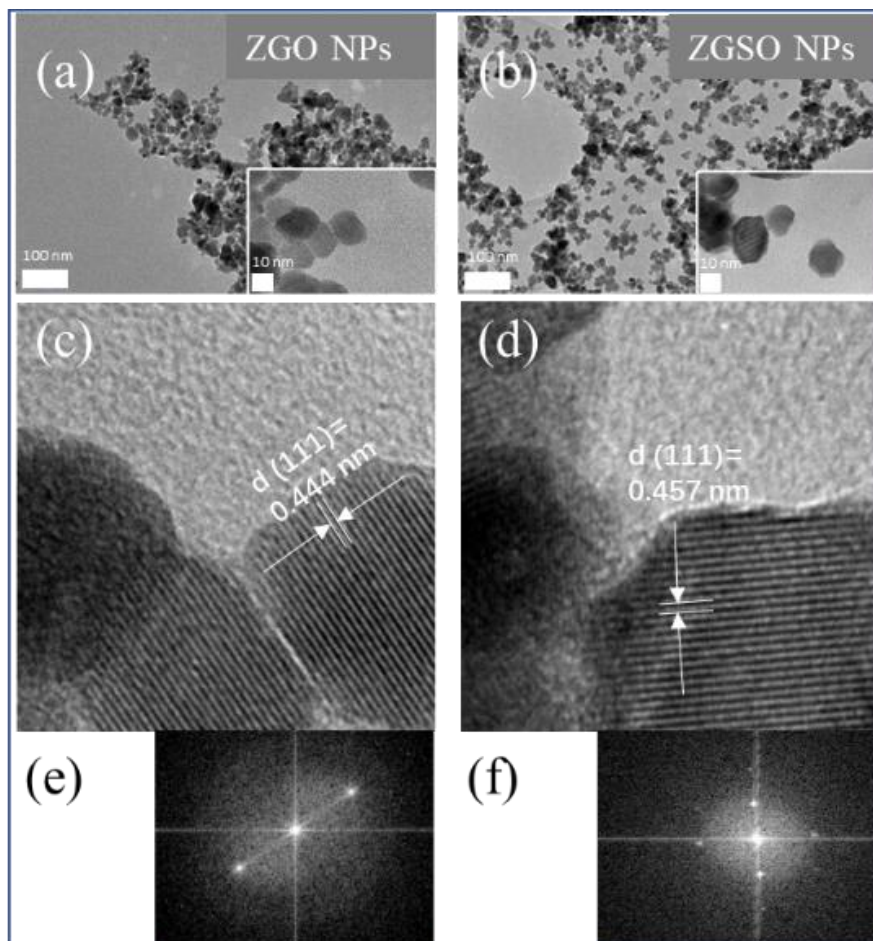
201 2.5 *In vivo* imaging

202 Balb/cJRj female mice, eight weeks of age (18 ~ 22 g), were purchased from Janvier labs.
203 *In vivo* experiments were approved by French National Ethics Reflection Committee on
204 Animal Experimentation (Comité national de réflexion éthique sur l'expérimentation
205 animale, CNREEA). UV pre-excited NPs were injected in retroorbital way by using insulin
206 syringes (0.2 mL volume containing 10 mg/mL NP suspension in 5% glucose solution). At
207 different time points after injection (~1 h, ~4 h), mice were irradiated for 2 min with visible
208 LED light and then imaged for 5 min with the Optima camera (Biospace Lab). 4 hours after
209 injection, animals were anesthetized with gaseous isoflurane and sacrificed by cervical
210 dislocation. Liver, spleen, lungs, heart and kidneys were collected and placed on a black
211 plate and irradiated with LED. Persistent luminescence decay curves were obtained with an
212 Optima camera (Biospace Lab, France). The LED emission is covering the range from 515
213 to 700 nm, centered at ~600 nm, as shown in Fig. S2.

214 3. Results and discussion

215 3.1 Microscopic morphology of ZGO:Cr and ZGSO:Cr NPs

216 Transmission electron microscopy (TEM) was used to determine the morphology and
217 microstructure of pristine ZGO:Cr NPs (Fig. 1a) and ZGSO:Cr NPs (Fig. 1b) and coated
218 NPs (Fig 7g-h). These images show that particle sizes of both PersL NPs are similar, around
219 20 nm. Note that the interplanar spacing of the ZGSO:Cr [$d(111) = 0.457$ nm] (Fig. 1 c) is
220 larger than for ZGO:Cr [$d(111) = 0.444$ nm] (Fig. 1 d), as Sn atoms, with larger radius than
221 Ga atoms, may strongly enlarge neighboring atoms or ions, resulting in an increase
222 interplanar spacing [46]. Indeed this leads to an expansion of the crystal lattice. The regular
223 shape observed is due to a slow growth of nanocrystals in the hydrothermal reaction, and a
224 high crystallinity of the compounds, as observed in the electron diffraction (ED) results of
225 the single crystals (Fig. 1 e – f).



226
 227 Fig. 1. TEM images of (a) ZGO:Cr³⁺ NPs and (b) ZGSO:Cr³⁺ NPs with size diameter ~ 20
 228 nm; (c, d) lattice fringes of ZGO:Cr³⁺ NPs and ZGSO:Cr³⁺ NPs under the HRTEM; (e, f)
 229 the electron diffraction of ZGO:Cr³⁺ NPs and ZGSO:Cr³⁺ NPs. All illustrations are partial
 230 enlargement of the TEM images.

231
 232 *3.2 Physical properties of pristine NPs*

233 The PL Excitation spectra of the ZGO:Cr³⁺ and ZGSO:Cr³⁺ spinel NPs are shown in Fig. 2
 234 a. They show two broad excitation bands centered at ~ 550 nm and ~ 420 nm for the
 235 ZGO:Cr³⁺ and at ~ 580 nm and ~ 440 nm for the ZGSO:Cr³⁺, which originate from the well-
 236 known ⁴A₂(4F)→⁴T₂(4F) and ⁴A₂(4F)→⁴T₁(4F) Cr³⁺ absorption transitions. The observed
 237 shoulders at ~ 300 nm are due to the ⁴A₂(4F)→⁴T₁(4P) spin-allowed absorption band of
 238 Cr³⁺, partially overlapping the band gap edge of the ZGO and ZGSO matrices [46, 48, 49].
 239 Bandgap absorption edge originates from the O²⁻-Ga³⁺ charge-transfer transition [46, 48].
 240 Compared to ZGO:Cr³⁺, the three mentioned absorption peaks are localized at longer

241 wavelengths in the ZGSO:Cr³⁺, due to a decrease of the crystal field strength induced by tin
242 insertion in the matrix. This will be favorable in the case of ZGSO:Cr³⁺ to longer
243 wavelengths UV excitation but also to an orange excitation (coming from LED in the
244 present work) as seen in the following part of the paper (Fig. 3a, c). With the presence of
245 Sn⁴⁺ in the material, band gap absorption edge is red-shifted towards longer wavelengths.
246 The evolution of the PersL properties is presented in Fig. 2 b). Compared to ZGO:Cr³⁺,
247 ZGSO:Cr³⁺ presents a PersL spectrum with a red shifted emission (from 695 nm to 705 nm)
248 and a broadening of the peak. The shifted emission towards the near infrared range is due
249 to the Crystal Field variation to lower value. The broadening of the peak (FWHM is
250 increasing from ~ 44 nm (ZGO:Cr emission) to ~ 61 nm (ZGSO:Cr emission)) is related to
251 the enhanced contribution for the highest wavelengths of the Cr³⁺ ⁴T₂→⁴A₂ transition, as
252 the Sn⁴⁺ content increases. In addition, low temperature PL spectra (shown in Fig. S1 b) are
253 well structured and composed of several sharp lines including R2 and N2 lines characteristic
254 of chromium on the gallium octahedral site as reported in the literature [44, 48, 50]. When
255 Sn⁴⁺ substitutes Ga³⁺, several modifications of the PL spectra are observed. At first, Cr³⁺
256 emission lines strongly broaden with Sn⁴⁺ doping. This can be explained by the increased
257 of the Cr³⁺ nearest-neighbors disorder as the Sn⁴⁺ content increases [46]. In parallel, a large
258 contribution appears in the NIR range between 700 nm and 900 nm. The broadening of the
259 emission band toward longer wavelengths attributed to the ⁴T₂→⁴A₂ (Cr³⁺) emission [51],
260 is well supported by low temperature spectra (seen in Fig. S1 b). Furthermore, we noticed
261 that N2 line is enhanced in ZGSO:Cr³⁺ as a consequence of Sn⁴⁺ doping in regard to the
262 ZGO spinel matrix. Notice that the enhancement of the N2/R1 ratio is favorable to the PersL
263 properties [44]. In addition, when the dry NPs are dispersed into water, the emission and
264 excitation wavelength do not vary (as shown in Fig S1 a).

265 The optical properties of the NPs are dependent on their crystalline structure. XRD patterns
266 of ZGO:Cr³⁺ and ZGSO:Cr³⁺ presented in Fig. 2 c) measured after calcination, before ball
267 milling, suggest that both synthesized PersL NPs have a normal spinel structure,
268 corresponding to the standard pattern of ZnGa₂O₄ (PDF No. 01-086-0413). Nevertheless,
269 the diffraction peaks of ZGSO slightly shift to a lower angle for the
270 Zn_{1.33}Ga_{1.335}Cr_{0.005}Sn_{0.33}O₄ NPs becoming closer to the diffraction peaks of Zn₂SnO₄ (PDF
271 No. 01-073-1725), indicating that the unit cell parameters are intermediate to those of

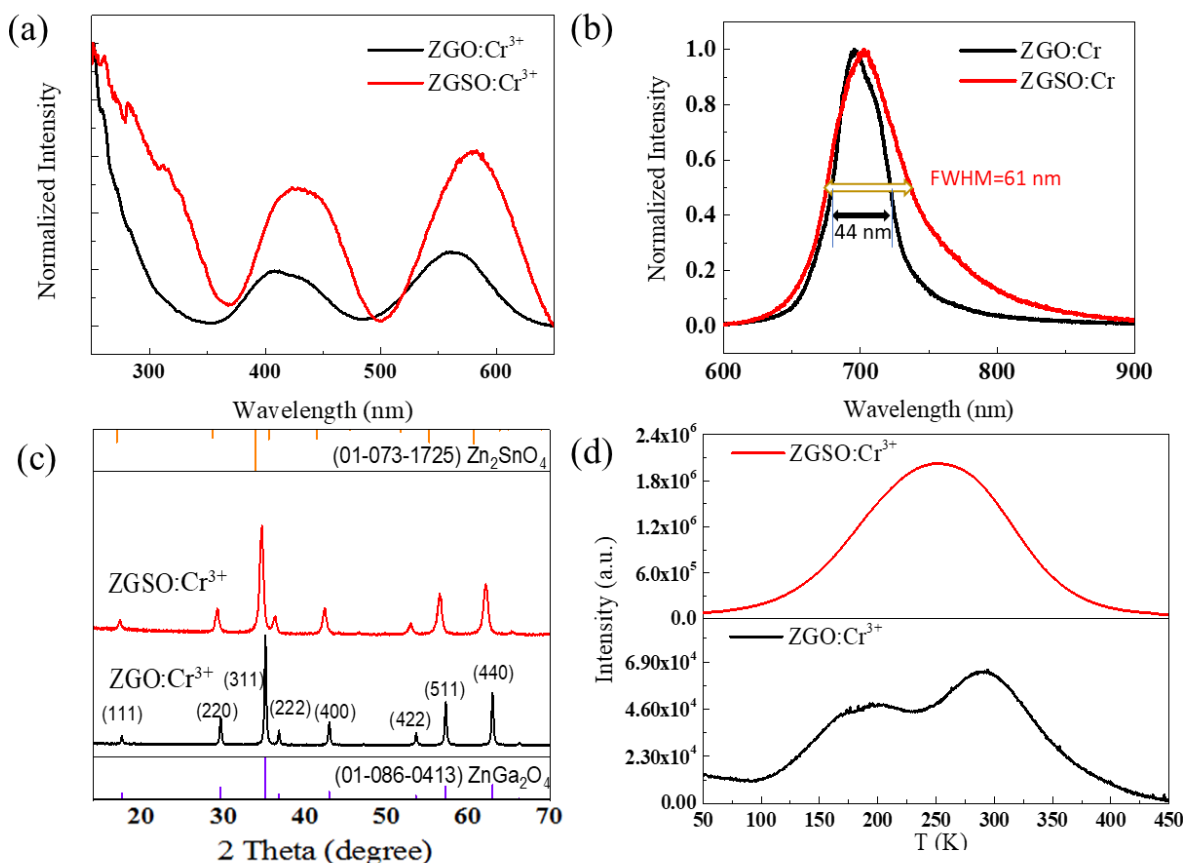
272 ZnGa₂O₄ and Zn₂SnO₄ spinel materials. This corroborates the good tin insertion into the
273 spinel host.

274 The difference of the optical properties between ZGO:Cr³⁺ and ZGSO:Cr³⁺ can explain the
275 different thermoluminescence (TL) glow curves shapes as well. From the TL curves in Fig. 2 d, we
276 observe for the TL peak responsible to the PersL (closer to room temperature) a less structured
277 shape, coming with a decrease in temperature peak (*T_m*) of the ZGSO:Cr³⁺, compared to the
278 ZGO:Cr³⁺ with a broadening of the glow curve due to the disorder since Sn⁴⁺ substitutes Ga³⁺ in
279 ZGSO:Cr³⁺ nanocrystals. The shift in *T_m* value from about 300 K to 260 K is in agreement with
280 the smaller band gap of the ZGSO:Cr³⁺ as already reported in the bulk system [46]. This is also in
281 agreement with the red shift of the absorption wavelength in the UV range [46, 48]. This can be
282 related to the increasing number of Zn_{Ga}' defects. Namely additional defects such as Sn_{Ga}^o appear.
283 These defects can act as hole traps and electron traps respectively. In that case, an enhancement of
284 PersL is expected due to the increased total traps capacity. This is indeed seen in Fig. 2 d (from the
285 background level and the intensity axis scales). The total charging capability of the ZGSO:Cr³⁺
286 materials have been enhanced, as compared to the ZGO:Cr³⁺. Trap depths can be calculated, using
287 the following expression reported long time ago by Urbach and still widely used for the persistent
288 phosphor [52-54]:

$$289 \quad E_T = \frac{T_m}{500} \quad \text{formula (1)}$$

290 The shift in *T_m* values (Fig. 2d) from about 300 K to 260 K is in agreement with the smaller band
291 gap energy for ZGSO:Cr in regards to ZGO:Cr. With formula (1), trap depth value is decreasing
292 from 0.6 eV to 0.52 eV.

293



294
 295 Fig. 2. (a) PL excitation spectra and (b) PersL spectra of ZGSO:Cr³⁺ NPs and ZGO:Cr³⁺
 296 NPs. (c) X-ray diffraction pattern of ZGSO:Cr³⁺ (red curve) and ZGO:Cr³⁺ (black curve)
 297 and the two standard JCPDS cards of ZnGa₂O₄ and Zn₂SnO₄ materials. (d)
 298 Thermoluminescence (TL) glow curves of ZGSO:Cr³⁺ NPs (red curve) and ZGO:Cr³⁺ NPs
 299 (black curve). Notice the strong variation in the intensity scales.

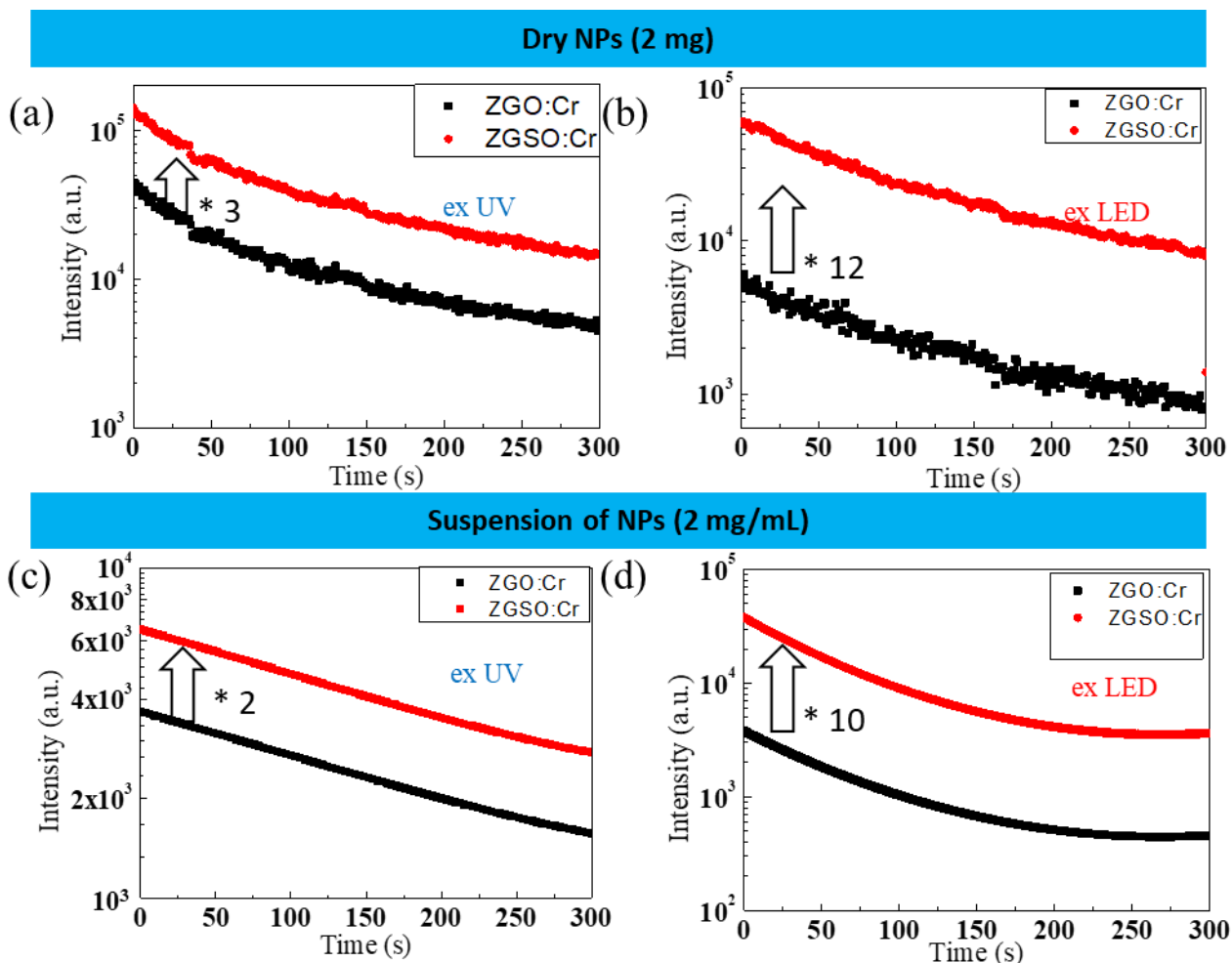
300
 301 *3.3 Persistent luminescence properties of pristine NPs*
 302 To compare the PersL properties of ZGO:Cr NPs and ZGSO:Cr NPs, the first 5 min of
 303 PersL signal of both samples was collected as seen in Fig. 3, by monitoring Cr³⁺ emission
 304 at ~700 nm (²E → ⁴A₂ emission) after 2 min of photo excitation and waiting one minute
 305 before recording the PersL for each sample. When comparing the PersL after UV excitation
 306 of the two samples in dry NPs form in Fig. 3 a, the initial PersL signals in the same
 307 experimental conditions are about 1.4×10⁵ counts for ZGSO:Cr NPs and about 4×10⁴ counts
 308 for ZGO:Cr NPs. ZGSO:Cr NPs show ~ 3 times stronger NIR PersL signal. This result is

309 well supported by the TL results presented in the previous figure. As there are much more
310 traps and released charges in ZGSO:Cr NPs, this causes stronger PersL, compared to
311 ZGO:Cr NPs [46].

312 Not only UV but also visible orange LED light can be used as an excitation source for both
313 dry NPs and dispersed NPs into water, both are presented in Fig. 2 and Fig. S1 a as well as
314 in Fig. S2 for the PersL spectra. Orange LED source provides a broad emission peak
315 centered at ~600 nm, as proposed in the illustration of Fig. S2 suggesting a better excitation
316 of ZGSO sample due to its red shift of the $^4A_2(4F) \rightarrow ^4T_2(4F)$ excitation band. This highlights
317 the importance of matching excitation wavelengths with material properties especially using
318 the low energy excitation towards localized antisite traps. Indeed, we can find that the initial
319 PersL signals are $\sim 5 \times 10^3$ counts for ZGO:Cr NPs and $\sim 6 \times 10^4$ counts for ZGSO:Cr NPs in
320 Fig. 3 b within the same experimental conditions. Thus, using visible LED excitation
321 source, there is a ~ 12 times stronger PersL signal emitted by ZGSO:Cr NPs compared to
322 ZGO:Cr NPs.

323 To further investigate the effect of solvent on the NIR PersL, the PersL signals of
324 ZGSO:Cr³⁺ NPs and ZGO:Cr³⁺ NPs in water were collected at a concentration of 2 mg/mL.
325 Interestingly, when dispersed into suspension, the presence of water leads to a significant
326 decrease in PersL signal intensity for both ZGO and ZGSO under UV excitation due to
327 water's strong UV absorption [55]. This underlines the environmental impact on
328 luminescence efficiency. Fig. 3 c shows the NIR PersL (at ~ 700 nm) signal of both
329 suspensions with respect to the decay time after irradiation/charging with UV light.
330 Anyway, the larger amount of traps suggest about a 2-times stronger PersL signal emitted
331 by ZGSO:Cr suspension compared to ZGO:Cr one.

332 Unlike UV, LED excitation in the orange/red range shows improved efficiency in water
333 suspension, thanks to lower absorption by water[55]. This suggests visible LED excitation
334 as a more effective approach for PersL applications in aqueous environments. With orange
335 LED light excitation, much stronger NIR PersL can be detected during the first 5 min, which
336 is a ~ 10 times stronger (around 5×10^4 counts) for the ZGSO:Cr suspension. These results
337 suggest that the ZGSO:Cr NPs exhibit better PersL performance in suspension, which is
338 particularly interesting for further *in vivo* imaging experiments that will use visible/orange
339 LED light excitation.



341
 342 Fig. 3. (a-b) PersL decay of ZGO:Cr (black curve) and ZGSO:Cr NPs (red curve) in dry
 343 NPs form (2 mg) after removal of UV (a) and LED (b) excitation. (c-d) PersL decay of
 344 ZGO:Cr (black curve) and ZGSO:Cr NPs (red curve) in suspension at 2 mg/mL after
 345 removal of UV (c) and LED (d) excitation. For all samples, the acquisition starts 1 min after
 346 removal of excitation by UV or visible orange LED light. (The LED emission is shown by
 347 Fig. S2 in supplementary information.)

348

349 3.4 Deep tissue imaging

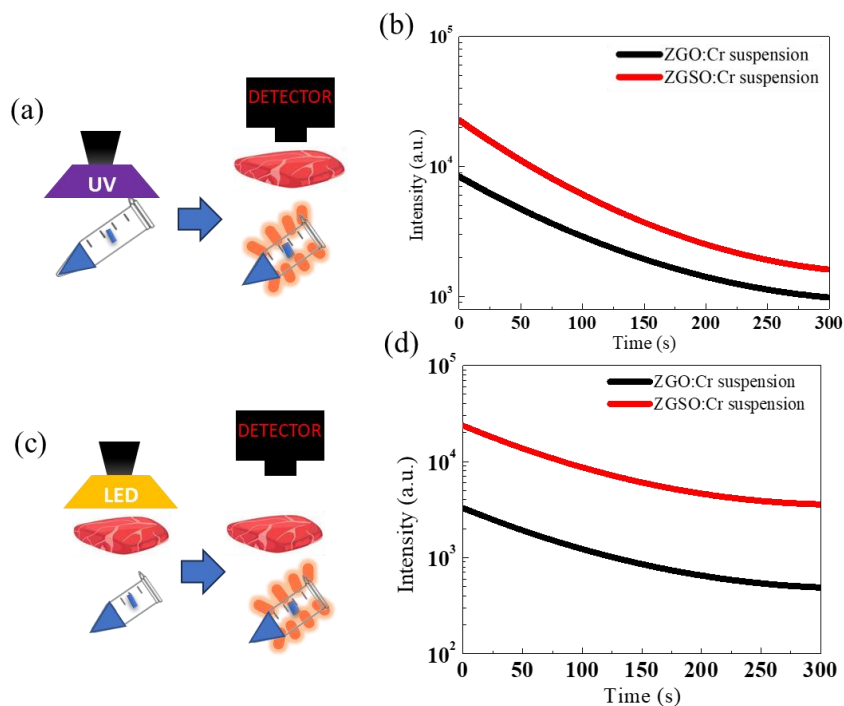
350 In the previous section, we have studied the PersL properties of the two kinds of NPs namely
 351 ZGSO:Cr and ZGO:Cr either in dry powders form or dispersed into water suspension. In
 352 the following, we will first model bio-imaging by covering the PersL NPs suspension by
 353 one piece of pork tissue with a thickness of ~ 2 mm. As before, herein, we tested two

354 different ways of imaging tissue. At first with pre-excitation for charging the PersL
355 materials, as it can provide an efficient and direct photo excitation of NPs by UV light (see
356 Fig. 4 a). PersL NPs in suspension with UV pre-excitation or LED excitation show
357 afterglow decay curves (with 5 min time collection, Cr³⁺ emission at ~700 nm for the ²E →
358 ⁴A₂ emission) as presented in in Fig. 4 b. As expected, the initial PersL signals of ZGSO:Cr
359 NPs are stronger than for ZGO:Cr NPs. The *in situ* re-excitation way, using relatively
360 orange LED light (see insert Fig. S2) is shown in Fig. 4 c-d. As a result, when comparing
361 the PersL of the two PersL suspensions for *in situ* excited tissue imaging, the detectable
362 PersL signal for ZGSO:Cr NPs is ~7 times stronger than ZGO:Cr NPs. Second, in an
363 additional way, the visible orange LED light can be used as pre-excitation source as well,
364 as shown in Fig. S7, producing also a stronger PersL signal for ZGSO:Cr NPs suspension
365 compared to the ZGO:Cr NPs.

366 To sum up, both excitation methods presented in Fig. 4 can be successfully used for PersL
367 bioimaging. Generally, with the UV pre-charging strategy several minutes are required
368 before starting acquisition and the initial PersL signal is lost and unavailable. The *in situ*
369 excitation method is beneficial for repeatability and suitable for the long-term monitoring
370 and imaging using excitation light with good penetration in tissues.

371

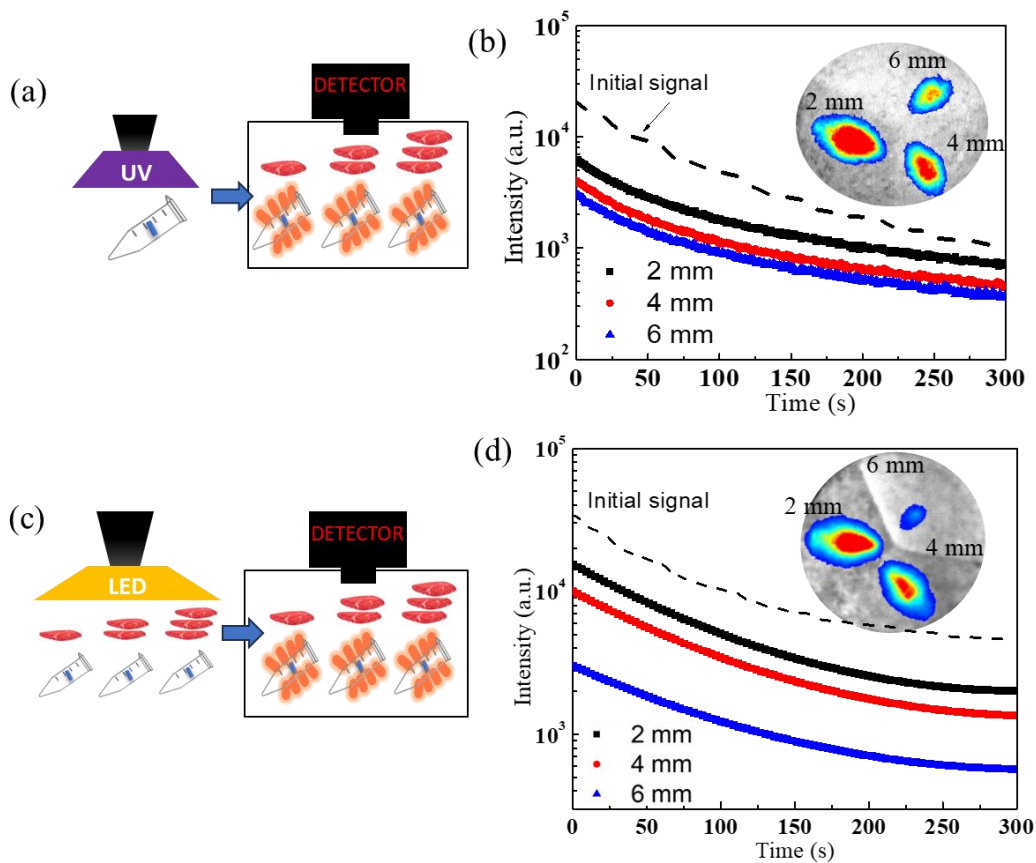
372



373
 374 Fig. 4. (a) Schematic of pork tissue imaging based on PersL NPs *via* UV pre-excitation of
 375 NPs, and (b) the decay curve of ZGO:Cr³⁺ and ZGSO:Cr³⁺ NPs suspension after covering
 376 with tissue; (c) Schematic of pork tissue imaging based on PersL NPs *via in situ* excitation
 377 with visible orange LED light through one piece of tissue. (d) Decay curves of ZGO:Cr³⁺
 378 and ZGSO:Cr³⁺ NPs in suspension at 700 nm through one piece of tissue.

379
 380 Furthermore, to mimic a little more animal experiments, we have investigated the impact of
 381 the tissue thickness on the PersL signal (Fig. S3). Noticed that several tissue slices, each of
 382 them with a thickness of 2 mm, were used in the study. Here, only ZGSO:Cr³⁺ NPs have
 383 been used, due to their better efficiency and the measurements were done using either the
 384 UV pre-excitation strategy (Fig. 5 a-b) or *in situ* through tissue LED excitation (Fig. 5 c-d).
 385 The observations revealed that, as expected, the PersL intensity decreased as the number of
 386 tissue layers covering the PersL probes increases (from 1 to 3 pieces of tissues). In the case
 387 of UV pre-excitation (Fig. 5a-b), even with approximately 6 mm of tissue (3 pieces)
 388 covering the probes, the NIR PersL signal remained clearly detectable during the 5-minutes
 389 acquisition. For thicker tissues, Fig. S5 represents the PersL decay curves of ZGSO:Cr³⁺
 390 NPs in suspension at different depth (even 16 mm and 32 mm) covered by tissues after UV
 391 pre-excitation. Additionally, tissue imaging after *in situ* visible/orange LED light excitation

392 are demonstrated in Fig. 5 c-d. As before, the study evaluates the PersL intensity by varying
 393 the tissue thicknesses, ranging from 2 mm to 32 mm (see more information in Fig. S3 and
 394 S4 in supplementary). As expected, the intensity decreases when increasing the thickness
 395 of the covering tissue. This attenuation is well attributed to the tissue's absorption and
 396 scattering properties, which limit the PersL signal propagation through thicker layers (Fig.
 397 S3). Fig. S4 shows the PersL decay curves of ZGSO:Cr³⁺ NPs and ZGO:Cr³⁺ NPs in
 398 suspension with different penetration depths and limitation of tissue imaging *via* visible
 399 orange LED light *in situ* excitation. A detection of the signal through about 20 mm of tissue
 400 thickness is possible using ZGO:Cr³⁺ NPs. The signal detection increases up to 32 mm with
 401 the ZGSO:Cr³⁺ NPs suspension. These depth limitations are measured using suspension
 402 with NPs concentration of 2 mg/mL in 1mL volume. Note that this depth limitation is also
 403 controlled by the sensitivity of the detection devices. However for all cases, ZGSO:Cr³⁺ is
 404 more appropriate than ZGO:Cr³⁺ for deep tissue imaging.



405

406

407 Fig. 5. (a) Principle of PersL excitation of ZGSO:Cr³⁺ NPs *via* (a) UV pre-excitation then
408 tissue covering or (c) *in situ* excitation with visible orange LED light through tissue. (b, d)
409 PersL signal detection through different tissue thickness, using UV pre-excitation (b) or
410 visible/orange LED light *in situ* excitation method (d), respectively (drops at about 20s is
411 due to experimental apparatus).

412

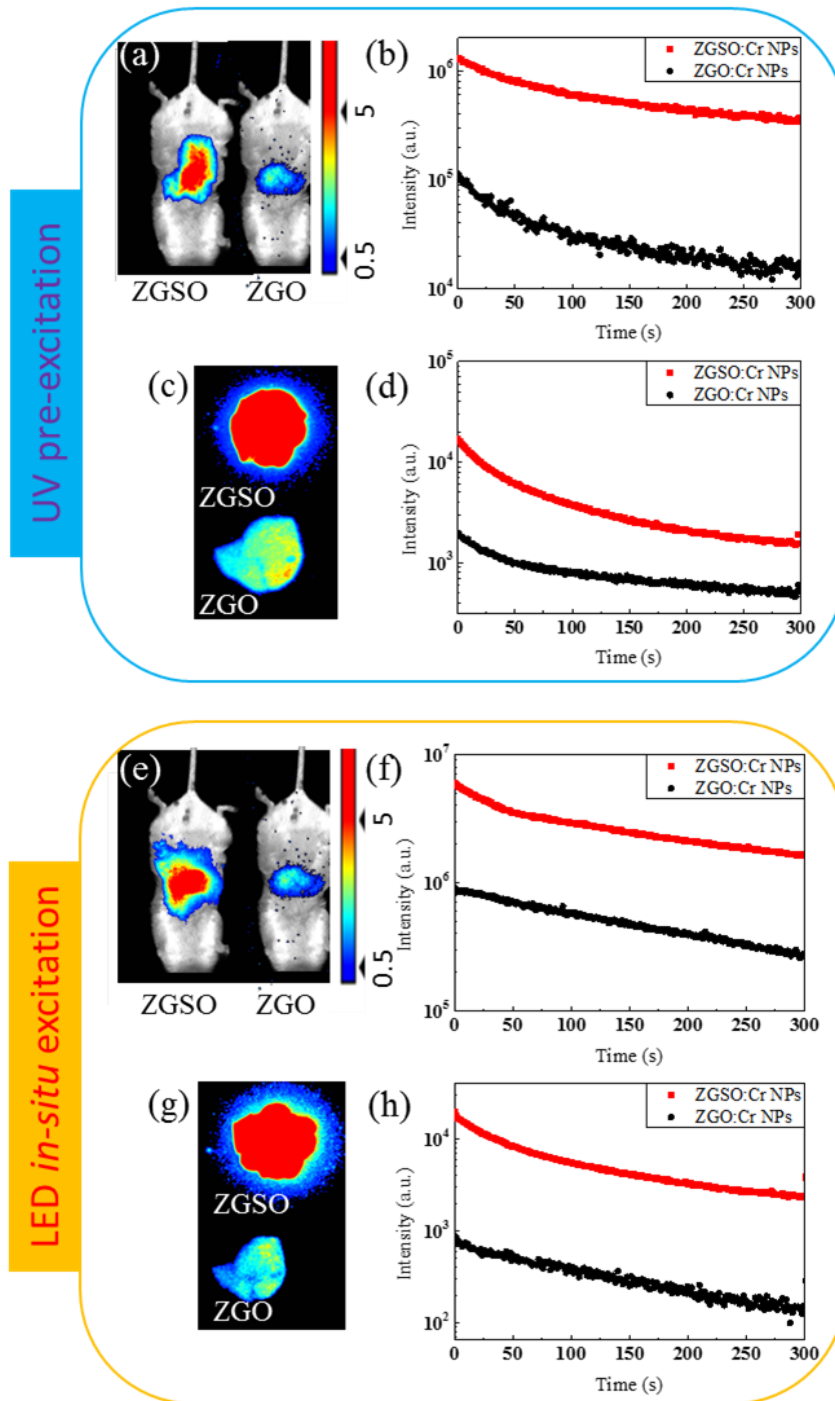
413 3.5 *In vivo* imaging with mice using pristine particles

414 In the following part, we have performed *in vivo* imaging experiments to further explore the
415 performances of both PersL NPs. In a first experiment, mice were injected with 200 μ L of
416 10 mg/mL ZGO:Cr³⁺ NPs or ZGSO:Cr³⁺ NPs pre-excited with UV. Both NPs have a
417 hydrodynamic diameter of approximately 90 nm and exhibited slightly positive surface
418 charge (15 ± 2 mV for ZGO and 5 ± 1 mV for ZGSO NPs). Images presented in Fig. 6 a and
419 data analysis based on UV pre-excitation revealed that mice injected with ZGSO:Cr NPs
420 produce stronger PersL signal in comparison to those injected with ZGO:Cr NPs, as shown
421 in Fig. 6 b. *Ex vivo* imaging was performed 4 hours after injection, and as expected with
422 non-functionalized NPs, most of the PersL signal was detected in the liver (Fig. 6 c). A
423 PersL signal about 7 times stronger from the liver containing ZGSO:Cr NPs is obtained,
424 emphasizing their superior PersL properties and detectability, compared to ZGO:Cr NPs, as
425 shown in Fig. 6 d.

426 To demonstrate the advantage of ZGSO:Cr NPs using *in situ* excitation for *in vivo* imaging,
427 a second group of mice was injected with ZGSO:Cr NPs and ZGO:Cr NPs and then excited
428 with the visible orange LED light source. Resulting images (Fig. 6 e) and data analysis (Fig.
429 6 f) show again a stronger PersL signal in mice injected with ZGSO:Cr NPs, with an initial
430 intensity of $\sim 6 \times 10^6$ counts, compared to those injected with ZGO:Cr NPs (initial intensity
431 $\sim 8 \times 10^5$ counts). Again, *ex vivo* images show that most of the PersL signal after 4 hours was
432 detected in the liver (Fig. 6 g), with approximately 10 times stronger PersL for ZGSO:Cr
433 NPs in comparison to ZGO:Cr NPs (Fig. 6 h).

434

435



436

437 Fig. 6. (a) *In vivo* PersL decays of ZGO:Cr NPs and ZGSO:Cr NPs. (b) PersL decays of
 438 ZGO:Cr NPs and ZGSO:Cr NPs. (c) *Ex vivo* imaging results and (d) PersL decay based on
 439 ZGO:Cr NPs and ZGSO:Cr NPs. (e) *in vivo* imaging results, using in situ LED excitation,
 440 and (f) PersL decays, (g-h) *Ex vivo* imaging results based on ZGO:Cr NPs and ZGSO:Cr

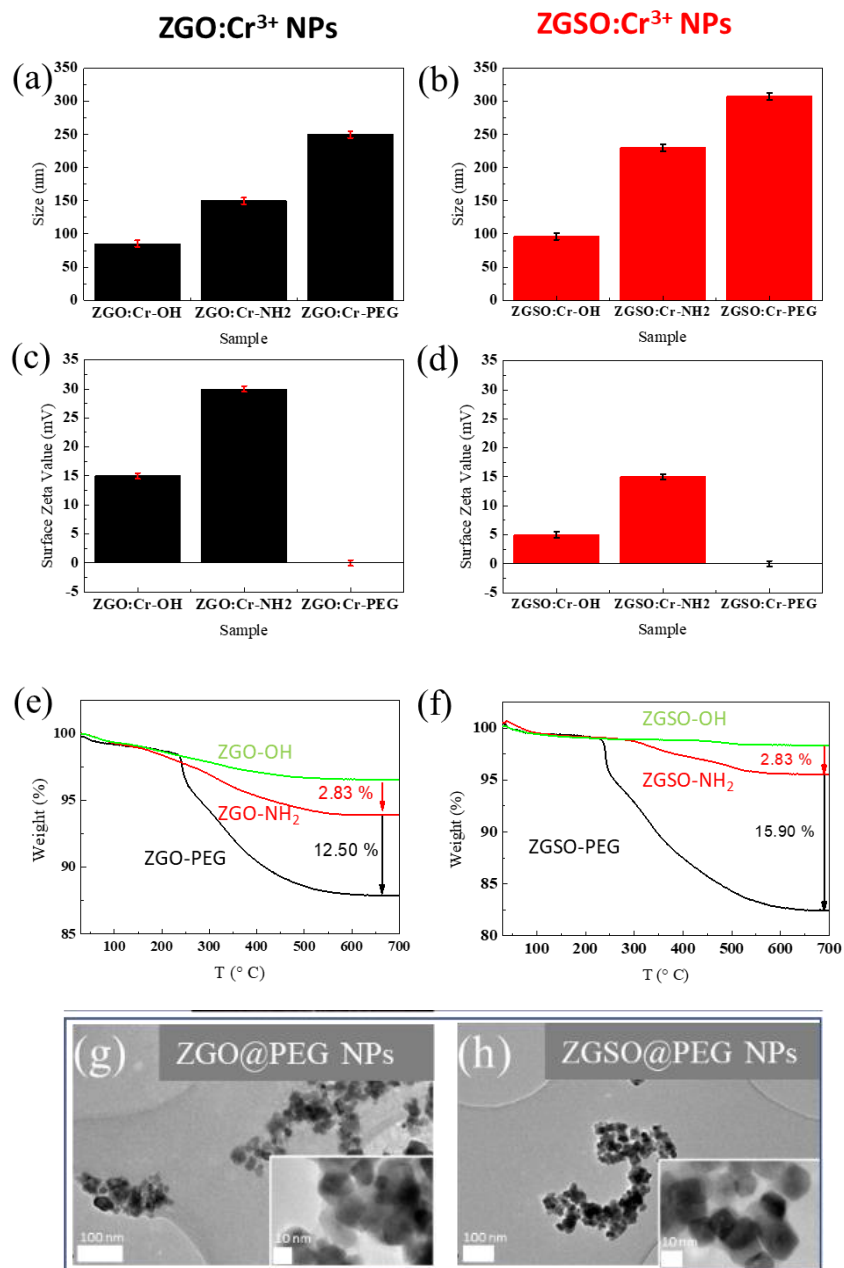
441 NPs and PersL decay. Notice that the LED excitation is 70 W versus 6 W for the UV lamp
442 (see Figure S2).

443

444 *3.5 In vivo imaging using PEGylated particles and biodistribution study.*

445 It's well known that surface functionalization of NPs can prolong their residence time in the
446 bloodstream [56-61]. In this study, we used an already established method for obtaining
447 PEG-coated PersL NPs, as described in our previous works [41, 62]. The surface
448 modification involved a two steps process, resulting in the preparation of first NPs-NH₂ and
449 then NPs-PEG. We assessed the size and surface charge of both functionalized NPs (ZGSO
450 and ZGO) using Dynamic Light Scattering (DLS). The results showed a size increase at
451 each step of the synthesis: from 80 (\pm 5) nm for ZGO:Cr³⁺ to 150 (\pm 5) nm for ZGO:Cr-
452 NH₂, and further to 250 (\pm 5) nm for ZGO:Cr-PEG. Similarly, the size of ZGSO:Cr³⁺ NPs
453 increased from 90 (\pm 5) nm for ZGSO:Cr to 170 (\pm 5) nm for ZGSO:Cr-NH₂, and finally to
454 290 (\pm 5) nm for ZGSO:Cr-PEG (Fig. 7 a-b). These size variations indicate successful
455 chemical surface modification at each step. Additionally, the zeta potential of the PersL NPs
456 evolved from +15 (\pm 1) mV for ZGO:Cr³⁺ to +30 (\pm 1) mV for ZGO:Cr-NH₂ and ~ 0 mV
457 for ZGO:Cr-PEG (Fig. 7 c). The same trend was observed for ZGSO:Cr³⁺ NPs, with a
458 change from +5 (\pm 1) mV to +15 (\pm 1) mV for ZGSO:Cr-NH₂ and finally ~ 0 mV for
459 ZGSO:Cr-PEG (Fig. 7 d). To further confirm the success of the coating and to quantify the
460 amount of PEG grafted onto PersL NPs, we have used thermogravimetric analysis (TGA).
461 The results, shown in Fig. 7 (e-f), indicate a weight loss of approximately 3% for both
462 ZGO:Cr-NH₂ NPs and ZGSO:Cr-NH₂ NPs. For the second step, ZGO:Cr-PEG NPs
463 exhibited a weight loss of approximately 12.5%, and ZGSO:Cr-PEG NPs showed a weight
464 loss of approximately 16%. Finally, TEM images reveal, with the PEG coating, a ~ 5 nm
465 thickness of "shell" on the NPs of both ZGO:Cr-PEG (ZGO:Cr@PEG) NPs (Fig. 7 g) and
466 ZGSO:Cr-PEG (ZGSO:Cr@PEG) NPs (Fig. 7 h). These findings collectively demonstrate
467 successful functionalization of both types of PersL NPs.

468



469

470

471

472 Fig. 7 (a,b) Size (DLS), (c,d) surface zeta potential and (e,f) thermogravimetric results of
 473 ZGO:Cr and ZGSO:Cr NPs after each functionalization steps. TEM images of (g) ZGO:Cr-
 474 PEG NPs and (h) ZGSO:Cr-PEG NPs with size diameter 30 nm (including ~ 20 nm of
 475 ZGO:Cr / ZGSO:Cr core and ~ 5 nm thickness of PEG coating shell, respectively). The
 476 illustrations are partial enlargement of the TEM images.

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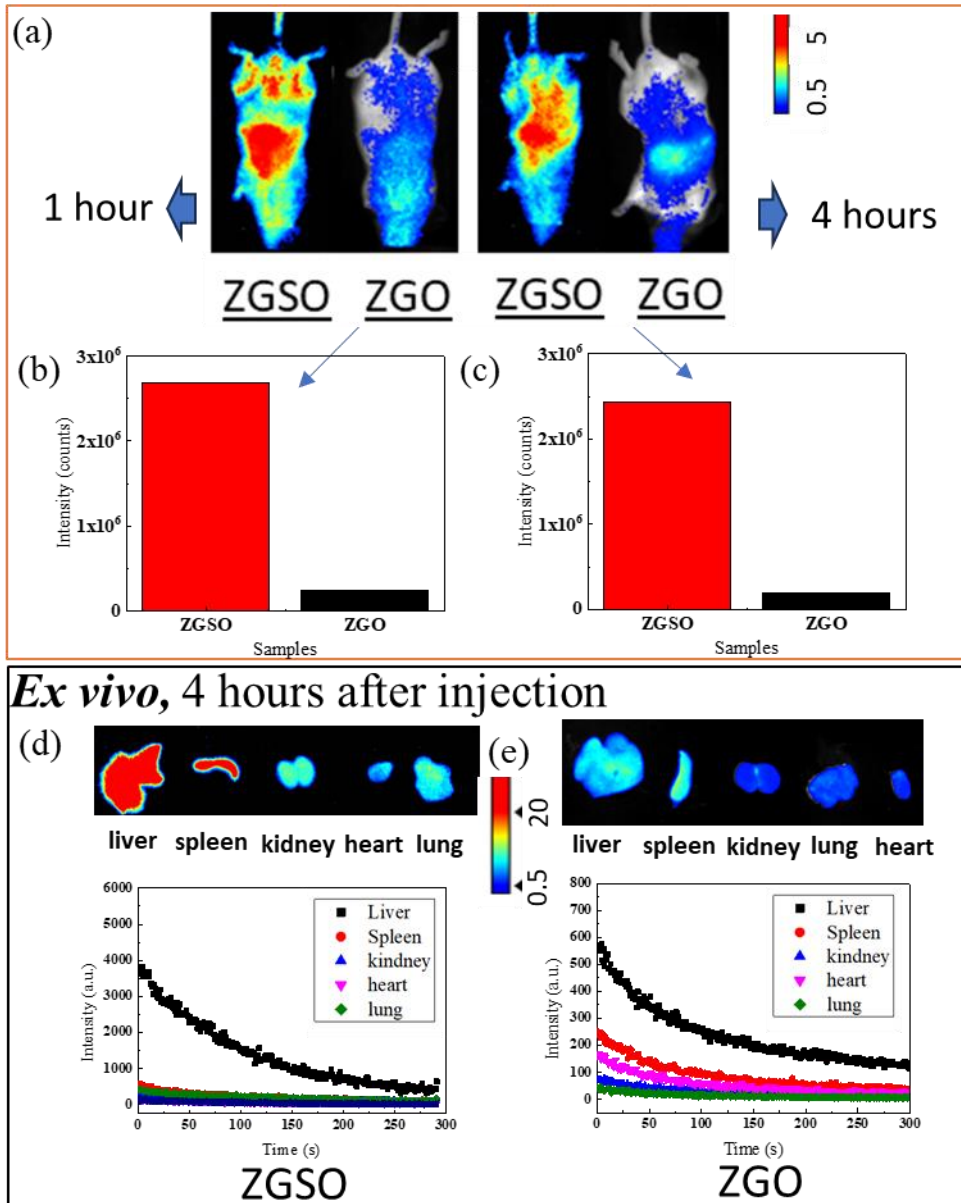
478 When comparing the two types of suspensions, each containing PersL NPs coated with PEG
 479 at a concentration of 10 mg/mL, we observed a noteworthy difference in the PersL signal

480 strength. Specifically, after UV pre-excitation, the ZGSO:Cr@PEG suspension exhibited a
481 PersL signal that was ~6 times more robust than the ZGO@PEG suspension, as depicted in
482 Fig. S6 (a). Additionally, the use of visible orange LED light excitation provides compelling
483 evidence for the superior PersL properties of ZGSO:Cr@PEG PersL NPs. Fig. S6 (b)
484 displays the NIR PersL decay of ZGO:Cr@PEG and ZGSO:Cr@PEG PersL NPs in
485 suspension, demonstrating a PersL signal strength more than 10 times stronger for the
486 ZGSO:Cr@PEG suspension compared to the ZGO:Cr@PEG suspension. These findings
487 are attributed to the enhanced performance of ZGSO:Cr@PEG NPs, further underlined by
488 the use of a potent visible/orange LED light excitation source. Considering that ZGSO:Cr³⁺
489 NPs present improved PersL performances and good sensitivity to visible orange LED light
490 excitation, which are two significant advantages, we finally confirmed their superiority for
491 *in vivo* use by conducting further *in vivo* imaging experiments with a detailed comparison
492 of both PEGylated ZGSO:Cr³⁺ and ZGO:Cr³⁺ NPs (10 mg/mL × 200 μL). We found that
493 coated NPs are well circulating into the mice body 1 hour after *in vivo* injection (Fig 8 a),
494 which is a good improvement, compared to the uncoated NPs, rapidly captured by liver
495 (Fig. 6 a and e). Even 4 hours after injection, a strong PersL signal can be detected in all the
496 mice body after a visible orange LED light *in situ* excitation. Remarkably, the decay curve
497 shows that ZGSO:Cr³⁺@PEG emits a consistently higher initial PersL signal 1 hour (Fig. 8
498 b) and 4 hours (Fig. 8 c) after *in vivo* injection, compared to the ZGO:Cr³⁺@PEG. This
499 simple illumination with orange light, even across living tissues, is sufficient to efficiently
500 activate ZGSO:Cr³⁺-PEG NPs.

501 The red-shifted excitation spectrum of ZGSO:Cr³⁺ NPs (seen in Fig. 2 a) covers well the
502 orange range which leads to a better efficiency of this excitation. As a result, this PersL
503 imaging probes show advantages for *in vivo* imaging properties not only with *in situ* re-
504 excitation, but also using visible orange LED light as a pre-excitation source (Figs. S7 – S8
505 in supplementary). The mice injected with ZGSO:Cr³⁺ NPs exhibited over 5 times higher
506 signal intensity, underscoring the advantageous sensitivity of these NPs to visible orange
507 LED light sources.

508 Importantly, the *in situ* triggering of PersL also enabled *ex vivo* absolute optical
509 quantification. This work revealed a predominant localization of both ZGSO:Cr³⁺-PEG NPs
510 (Fig. 8 d) and ZGO:Cr³⁺-PEG NPs (Fig. 8 e) in the liver (left part of the images), with

511 limited uptake by the spleen. For example, see the ~ 6 times stronger PersL from the liver
 512 with ZGSO:Cr³⁺ NPs. This factor is in good agreement with the PersL intensity difference
 513 between the equivalent ZGSO: Cr³⁺-PEG and ZGO: Cr³⁺-PEG PersL NPs as seen in Fig.
 514 S6 (a).



515
 516 Fig.8. (a) Biodistribution of ZGSO:Cr@PEG NPs and ZGO:Cr@PEG NPs 1h and 4h after
 517 injection using the *in situ* LED light excitation. (b-c) PersL *in vivo* imaging based on
 518 ZGSO:Cr@PEG NPs and ZGO:Cr@PEG NPs at 1h (b) or 4h (c) after injection, with *in situ*

519 re-excitation. (d-e) *ex vivo* imaging measurements in the different organs, 4h after injection
520 of ZGSO:Cr@PEG NPs (d) and ZGO:Cr@PEG NPs (e).

521 4. Conclusions

522 Nanoscale $\text{Zn}_{1.33}\text{Ga}_{1.335}\text{Cr}_{0.005}\text{Sn}_{0.33}\text{O}_4$ (ZGSO:Cr³⁺) material was successfully
523 synthesized by hydrothermal method with subsequent annealing and milling process
524 allowing getting 20 nm nanoparticles (measured by TEM). The optical performances of
525 such NPs have been compared to the original ZGO:Cr³⁺ NPs prepared using the same
526 procedure. Both ZGSO:Cr³⁺ and ZGO:Cr³⁺ NPs exhibit PersL emission, stemming from the
527 $^2\text{E} \rightarrow ^4\text{A}_2$ (Cr³⁺) transition, around 700 nm in the deep red/near-infrared (NIR) range.
528 Notably, ZGSO:Cr³⁺ NPs feature a red-shifted excitation spectrum that aligns well with the
529 prominent emission wavelength of visible orange LED lights. This advantageous spectral
530 overlap enhances the *in situ* excitability of PersL, particularly when illuminated with a
531 visible orange LED light, which boasts good tissue penetration capabilities. Consequently,
532 ZGSO:Cr³⁺ NPs demonstrate a more robust PersL emission due to their adept
533 responsiveness to the powerful LED excitation source, showcasing superior sensitivity to
534 orange LED light irradiation, and harboring a higher concentration of traps compared to
535 ZGO:Cr³⁺ NPs.

536 Deep tissues imaging and *in vivo* imaging results show that ZGSO:Cr³⁺ exhibit slightly
537 enhanced (factor ~ 3) NIR emission intensity after UV excitation compared to ZGO:Cr³⁺.
538 More interestingly, when using visible orange LED light excitation, the signal intensity of
539 ZGSO:Cr³⁺ is much higher (factor > 10) than ZGO:Cr³⁺. Thus, within the same situation,
540 ZGSO:Cr³⁺ is a better choice for deeper tissue *in vivo* imaging than original ZGO:Cr³⁺. The
541 depth limitation of the *in situ* excited deep tissue imaging reaches 32 mm for ZGSO:Cr³⁺
542 NPs suspension, with a worthily notable improvement, compared to 20 mm for ZGO:Cr³⁺
543 NPs suspension. Using PEG surface-functionalized NPs, a good distribution of ZGSO:Cr³⁺
544 NPs exhibiting in all animals bodies over at least 4 hours, which indicates a good circulation
545 time in the blood.

546 Facing that X-rays excitation sources for recently proposed PersL nanomaterials [35],
547 such as NaLnF₄ [63] ZGGO:Cr³⁺,Mn²⁺ [64] and LiGa₅O₈:Cr³⁺, are limited due to potential
548 health risks, visible orange LED light *in situ* excitation offers a safe and efficient method

549 for *in situ* & *in vivo* imaging. Therefore, we believe that visible orange LED light *in situ*
550 excitation of ZGSO:Cr³⁺ NPs have great potential in bioimaging, and should overcome
551 pioneer work using the original ZGO:Cr³⁺ for improved *in vivo* diagnosis.

552 **Author Contributions**

553 G.C., B.V. and C.R. conceived and designed the research. G.C., J.S., T.N. carried out the
554 experiments. J.S. was responsible for biological characterization and small animal *in vivo* imaging.
555 G.C. responsible for optical and TL characterization and mechanism. All of the authors analyzed
556 the data and discussed the results. G.C., C.C., B.V., and C.R. wrote the manuscript. The authors
557 declare no conflict of interest.

558 **Conflicts of interest**

559 There are no conflicts to declare.

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