

# Plasmon-triggered living photopolymerization for elaboration of hybrid polymer/metal nanoparticles

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#### Graphical abstract

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# Plasmon-triggered living photopolymerization for elaboration of hybrid polymer/metal nanoparticles

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Surface plasmon resonance can be used to manipulate light at the nanoscale. It was used here to trigger 20 photopolymerization of an atom transfer radical polymerization (ATRP) molecular system, leading to a 21 thin polymer shell at the surface of the metal nanostructure. The polymerization can be reactivated 22 from the first polymer shell to covalently graft a second monomer layer with precise control over the 23 thickness at the nanometric scale, depending on the photonic parameters. This route can be applied to 24 different nanoobjects and allows an anisotropic surface modification in agreement with the spatial 25 localization of the enhanced electromagnetic field near the nanostructure. This new route opens the 26 door towards the preparation of multifunctional hybrid metal/polymer nanostructures. 27

#### 29 Introduction

Reversible deactivation radical polymerization (RDRP) has 30 proved to be a powerful tool for preparing polymers, with high 31 control over the structure at the molecular scale. Using RDRP, 32 it is possible to precisely control the architecture of polymers 33 34 and their average molar masses with narrow molecular weight distributions. Several strategies for RDRP have been developed, 35 such as nitroxide mediated polymerization (NMP) [1-3], reversi-36 37 ble addition-fragmentation chain transfer polymerization (RAFT) [4,5] or atom transfer radical polymerization (ATRP) [6-38 11], which can be applied to many different families of mono-39 mers. Recently, new approaches have been developed to trigger 40 RDRP reactions by light to achieve photoinduced polymerization 41 42 [12,13]. Main attainments were reported in review papers [12–

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<sup>16].</sup> In this case, a light source (LED, laser, lamp, etc.) is used 43 to provide the energy to excite the photoactive catalyst to the 44 state necessary to start the polymerization process. Most RDRP 45 techniques have been adapted to photoactivation; examples 46 such as PhotoATRP [6,8,11,17], PhotoNMP (NMP2) [1,18,19], 47 and PhotoRAFT [5] can be found in recent literature. These reac-48 tions usually rely on organometallic catalysts or metal ions where 49 the metal can be copper [6,20–22], zirconium [7], ruthenium 50 [23], iron [8,24], cobalt [25], gold [9], manganese [10,26] or irid-51 ium [11,27-30]. One of the interests of this photoactivation 52 pathway is linked to the possibility of spatially and temporally 53 controlling the polymerization reaction. The polymerization 54 starts upon irradiation in irradiated areas, stops when irradiation 55 is stopped and can be reactivated to start the cycle many times. 56 In addition, phototriggered RDRP has opened new possibilities 57 in the field of micro- and nanofabrication, using the spatial con-58 trol of a photoactivated reaction. Several examples have shown 59

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the possibility of restarting the polymerization from a first polymer surface [19,20,28,31-33], leading to the *in situ* synthesis of a copolymer structure on the first polymer surface. For example, Wang et al. [33] demonstrated the grafting of copolymer brushes on silicon. They photopolymerized a first layer of a methylmethacrylate polymer brush on the substrate in the presence of an initiator and a catalyst. Then, using a mask, a second photopolymerization of a hydrophobic fluorinated monomer was triggered onto the previously generated polymer brushes. Using an iridium complex as a photoinitiator catalyst, Telitel et al. [28] polymerized via ATRP a photopolymer film on a substrate followed by a local polymerization of a monomer onto the film using direct laser writing. By adding a drop of a monomer and using a light source, the polymerization was easily triggered because of the presence of the iridium complex, which is regenerated through a catalytic cycle.

In both cases, control of the polymer thickness was achieved by tuning the photonic parameters, such as light power or irradiation time, but high-resolution patterning has not yet been explored. One of the fundamental interests of the work presented in this paper is to investigate the possibility of using PhotoRDRP to reach nanoscale resolution.

For this purpose, we used an optical near-field (ONF) photopolymerization approach. ONF is intrinsically а nondiffraction-limited technique and is thus compatible with nanoscale photofabrication. The idea behind ONF is to benefit from the local enhancement of the electromagnetic field in the vicinity of metal nanostructures excited by light. Indeed, upon plasmonic excitation, metal nanostructures exhibit highly con-88 89 fined near-fields close to their surfaces. In this context, the use 90 of a suitable photopolymer in well-controlled conditions opens 91 the way to confine the polymerization to this nanoscale volume under the condition that the diffusion of reactive species is 92 controlled. 93

The proof of concept was proposed by several teams, includ-94 ing our consortium [34-38]. Using atomic force microscopy 95 (AFM), the photopolymerization of a triacrylate monomer 96 around silver nanoparticles (NPs) was demonstrated. Ueno 97 et al. used gold nanoblocks to trigger photopolymerization 98 between them according to a certain polarization direction 99 [39]. In all those cases, the formed photopolymer had a nanome-100 ter volume. One of the practical motivations of this approach is 101 to provide access to a convenient process to produce hybrid poly-102 103 mer-metal nanostructures with original optical properties. From a more fundamental point of view, this configuration is also a 104 unique method for investigating photoinduced polymerization 105 at the nanoscale, which brings information on specific 106 physico-chemical phenomena occurring with extreme confine-107 ment [37]. 108

Although the feasibility has been proved, the application of 109 110 this concept has been limited to only a few photopolymer sys-111 tems. Coupling ONF photopolymerization and PhotoRDRP 112 opens new perspectives, which motivated us to carry out this 113 work.

We first demonstrate that PhotoATRP can be used in the ONF 114 configuration, leading to nanoscale photopolymerization. Com-115 pared to previous works, we have used an iridium complex 116 117 (namely, Ir(piq)<sub>2</sub>(tmd)) [28,29,40] that is interesting for its absorbance band, which is extended towards high wavelengths. This condition is important since an overlap between the extinction spectrum of the metal NP and the absorption spectrum of the photopolymer is required.

Due to the high confinement of the photopolymerization observed in this configuration, a new experimental strategy was developed to characterize the polymerization process at the nanoscale: the complete process was conducted on Si<sub>3</sub>N<sub>4</sub> membranes of transmission electron microscopy (TEM) grids. This allows the following individual NPs to be characterized after each step of the process with nanoscale resolution. The main advantages over previous studies based on scanning electron microscopy (SEM) and/or AFM are a better resolution and a fast view over a large number of NPs that allows one to carry out a statistical analysis. Moreover, TEM allows a precise characterization of the NPs, such as their crystallinity, their shape, the presence of residual surfactant and the possibility to observe it in 3D thanks to a tomographic mode.

The impact of the main parameters on the efficiency of the photopolymerization is studied to investigate the principal physico-chemical parameters driving the process. Then, we show that the polymerization can be reactivated from the nanoscale first layer. The 3D spatial extent of the polymer is compared to the spatial distribution of the electromagnetic near-field. Moreover, the confinement mechanism is also discussed. Herein, we thus explore the limits of PhotoATRP in terms of resolution thanks to ONF photopolymerization. In addition to the fundamental science, an illustration of the interest of this nanofabrication toolbox for complex metal nanostructures and multichemistry is given in the last part. The objective is to open new opportunities to build complex hybrid metal-polymer nanosystems with tunable compositions in shape and chemistry. One original feature of this NP preparation pathway is the possibility of obtaining anisotropic functionalized NPs with control over the surface chemistry and position of the polymer at the nanoscale.

This process makes it possible to prepare metal/polymer hybrid nanoparticles with a complex polymer structure (multichemical and anisotropic), while remaining relatively simple to implement. It is therefore useful for any application for which such objects are indispensable: for biomedical applications, such nanoparticles are very interesting for synthesizing injectable nanomaterials for the transport and delivery of drugs. Nanosensor applications can be envisaged, where the covalent grafting of the sensitive layer onto the metal structure would be very precise, controlled and facilitated. Applications in nanophotonics in which the grafting of photoactivatable molecules (fluorophores, photochromes...) could be placed very precisely on the metal surface are possible. Also, the grafting of multilayer polymers onto metallic objects allows the preparation of nanoobjects that couple optical and mechanical responses (for thermoresponsive hybrid metasurfaces for example).

#### **Experimental methods**

#### Preparation of the formulation.

The iridium complex is (bis(1-phenylisoquinolinato-N,C2')iri 172 dium(2,2,6,6-tetramethyl-3,5-heptanedionate), denoted as Ir 173

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#### FIGURE 1

(a) Chemical structure of the the  $lr(piq)_2(tmd)$  complex, PETA and TMPTA acrylate monomers. (b) Schematic of the hybrid nanoparticle preparation process by PhotoATRP. (i): 43 nm-diameter gold NPs are deposited onto the TEM grid. (ii): The TEM grid is covered with a drop of the photopolymerizable formulation, and the irradiation is performed at 90% of the threshold dose. (iii): The sample is developed with ethanol and characterized by TEM. (iv): A second irradiation is performed in the presence of a second monomer, without a photoinitiator. (v): The sample is developed, revealing the second polymer layer covalently bounded to the first layer. (c) Photoinduced molecular mechanism of PhotoATRP. (d) Schematic of the nanoparticle surface after (i) the first photopolymerization and (ii) the second photopolymerization.

(piq)<sub>2</sub>(tmd) (Fig. 1a). Its synthesis is described in the paper of 174 Tian et al. [40]. The photopolymerizable formulation was pre-175 176 pared by mixing Ir(piq)<sub>2</sub>(tmd), 2-bromoacetophenone (denoted 177 as PBr), and N-methyldiethanolamine (MDEA) in pentaerythritol 178 triacrylate (PETA), without the use of a solvent. These products were obtained from Sigma-Aldrich and were used as received. 179 The composition was set to 1 wt. % Ir(piq)<sub>2</sub>(tmd), 3 wt. % PBr 180 and 4 wt. % MDEA. Trimethylolpropane triacrylate (TMPTA) 181 and 2,2,3,4,4,4-hexafluorobutyl acrylate (HFBA) were purchased 182 from Sigma-Aldrich. The formulas of acrylate monomers can be 183 found in Fig. 1a. Other compounds are depicted in Fig. S1 in 184 185 the supporting information (SI).

Spherical (43 nm diameter) and cubic (57 nm edge) gold NPs 186 were prepared by colloidal chemistry using cetyltrimethylammo-187 nium bromide (CTAB) as the capping agent [41-44]. The cubes 188 were obtained, in a first step, according to an already published 189 protocol [41,42]. They were converted to highly spherical nano-190 spheres in a second step by chemical etching in the presence of 191 HAuCl<sub>4</sub> and CTAB. The oxidation of Au nanocrystals with Au 192 (III)-CTAB complexes was indeed shown to occur preferentially 193 at surface sites with high curvatures [43,44]. The surfactant was 194 removed from the surfaces of the NP by centrifugation in an 195 aqueous solution and UV-ozone treatment after drop deposition 196

onto the substrate. TEM was used to characterize the NP size distribution and confirm the elimination of the surfactant (Fig. S2).

#### Characterization of samples

TEM characterization was conducted on 2 microscopes. A PHI-200 LIPS CM200 TEM was used to characterize NPs after each step 201 of the near-field photopolymerization process. An ARM200F 202 JEOL High-Resolution transmission electron microscope 203 equipped with a double tilt sample holder (tilting angle tunable 204 from  $+60^{\circ}$  to  $-60^{\circ}$ ) was used to perform tilt experiments. In all 205 cases, silicon TEM grids with two rectangular slits 206  $(1500\,\mu m \times 100\,\mu m)$  covered on one face with a 50 nm-thick 207 Si<sub>3</sub>N<sub>4</sub> membrane were used (TEDPELLA). ImageJ v.1.8 software 208 was used to adjust the brightness and contrast levels of the 209 TEM images and evaluate the thickness of the polymer shell from 210 the TEM images. 211

#### Simulations

The experiment is complemented by numerical simulations213based on the boundary element method (BEM) via its implemen-<br/>tation in the multiple nanoparticles BEM MNPBEM toolbox214[45,46]. The BEM approach provides solutions of Maxwell's equa-<br/>tions in the case of arbitrarily shaped dielectric interfaces. The<br/>solutions are expressed in terms of surface charges and currents,218

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so that only surfaces between the different materials have to be discretized providing fast simulations. For more details, see [47,48]. A Au sphere 43 nm in diameter is modeled on an infinite Si<sub>3</sub>N<sub>4</sub> substrate. The distance between the Au NP and the substrate is fixed at 1 nm. The NP is covered by a monomer formulation with a refractive index n = 1.48. The refractive index of Au is taken from Johnson and Christy [49], that of the Si<sub>3</sub>N<sub>4</sub> substrate is fixed  $atn_{Si_3N_4} = 2.056$  [50]. Illumination is carried out from the wide band gap semiconductor substrate side under normal incidence with a circular polarized 532 nm light source. Simulations carried out in quasistatic and retarded field approximations give similar results. Maps of the squared modulus of the optical near electric field  $|E_{nf}|^2$  around one Au NP are determined. Note that incident field amplitude is normalized to unity within the substrate. Equivalent numerical simulations have been conducted on 57 nm edge Au cubes. In addition to field maps, extinction spectra have also been calculated.

#### Optical near-field photopolymerization process

Before the deposition of NPs onto the TEM grids, the TEM grids 237 238 were functionalized by a self-assembled APTS monolayer ((3-Ami 239 nopropyl)triethoxysilane from Sigma-Aldrich) to promote the anchoring of the NPs onto the substrate surface. UV-ozone treat-240 ment was then used to remove the surfactant at the surface of the 241 NP. The TEM grid with gold NPs deposited on its surface (Fig. 1b-242 i) was put in the pathway of a frequency-doubled Nd-YAG laser 243 (532 nm, 6 W, VERDI model from Coherent). The details of the 244 optical setup are given in Fig. S3. The setup was designed to gen-245 erate a collimated illumination, with a homogeneous power den-246 247 sity over the area of interest (typ. a few  $mW/cm^2$  on 1  $cm^2$ ) and with circular polarization. Once properly placed, a drop of the 248 formulation (4 µL) was deposited onto the TEM grid. The laser 249 beam irradiated the photopolymer through the Si<sub>3</sub>N<sub>4</sub> substrate 250 251 (wide band gap semiconductor) so that there was no attenuation 252 of the laser beam by the photopolymer on the plane of the NPs. The polymerization threshold time  $(t_{\rm T})$  was determined in a sep-253 arate experiment. This corresponds to the minimum time needed 254 to start the polymerization at the substrate surface for a given 255 light power density [37]. To determine it experimentally, the liq-256 uid photopolymer was deposited onto the TEM membrane (with-257 258 out NPs), irradiated, rinsed in ethanol and observed by optical microscopy. When polymer parts are observed on the TEM grid, 259 the threshold time of polymerization is reached. In the presence 260 of the NPs, the sample was typically irradiated at 90%  $t_{\rm T}$  (Fig. 1b-261

ii). Under such conditions, far-field photopolymerization is 262 avoided, while plasmonic intensity enhancement in the near-263 field of NPs (typically by a factor of 28, see below) provokes the 264 265 start of photopolymerization in this nanovolume. After irradia-266 tion, the sample was rinsed by immersion for 10 min in an etha-267 nol bath. Then, the sample was dried in air and characterized by 268 TEM (Fig. 1b-iii). The entire process was carried out under inac-269 tinic red light to avoid any degradation of the photocatalyst. In 270 a second step, repolymerization from the surface was tested by placing the grid in the same optical setup. It was irradiated after 271 being covered by a monomer (generally TMPTA). For this step, 272 no photoinitiator was added to the monomer (Fig. 1b-iv). The 273 274 development step was performed in exactly the same way as for the first step, and the NPs studied after the first exposure were 275 characterized once again (Fig. 1b-v). Several examples are given 276 in the SI to show that the same NPs could be found after different 277 steps of the process. 278

#### **Results and discussion**

#### Photopolymerizable formulation

The molecular process for light-induced controlled photopoly-281 merization can be described as proposed by Hawker et al. 282 (Fig. 1c) [31]. At the molecular scale, the scheme is basically an 283 oxidative catalytic cycle involving the iridium complex. After 284 light absorption, the complex in its excited state reduces an alkyl 285 bromide to generate the alkyl radical that initiates the polymer-286 ization of the acrylate monomers. The oxidizing state (Ir<sup>IV</sup>Br) 287 can then react with a propagating radical, which regenerates 288 the initial Ir<sup>III</sup> in its ground state and a dormant polymer chain 289 with a bromo end group. Photopolymerization triggered by the 290 Ir(piq)<sub>2</sub>(tmd) complex was confirmed in previous studies [27-291 29]. The behavior of Ir complexes in oxidative catalytic cycles 292 has been established by Telitel et al. [51] It has also been shown 293 that additional amines can be used as reductive agents to regen-294 erate Ir<sup>III</sup> from Ir<sup>IV</sup>, significantly improving the polymerization 295 kinetics. Therefore, the three-component Ir<sup>III</sup>/PBr/amine system 296 combines fast initiation and polymerization rates with good con-297 trol of the chain end. Due to this livingness property, we expect 298 that the first polymer shell on gold NPs contains reactivable Ir 299 complexes (Fig. 1d-i) that can start a second photopolymeriza-300 tion (Fig. 1d-ii). The presence of metal could be problematic for 301 certain applications, especially in biology. However, the presence 302 of Ir complex in the final material does not appear as central as 303 the concentration of the Ir complex is only 1 wt %, which means 304 that the amount of Ir in the nano-sized polymer lobes is very 305 low. Additionally the second polymer layer grafted onto the first 306 acts as a barrier masking the Ir complexes from the external envi-307 ronment. Moreover, it is likely that some of the Ir complexes are 308 removed during the development step by immersion of the sam-309 ple in ethanol. This removal is more likely when the thickness of 310 the polymer is very small. 311

#### Photopolymerization initiated by the Ir complex in the far-field configuration

The photopolymerization at 532 nm in the far-field configura-314 tion (e.g., via irradiation by a propagative plane wave in a thin 315 film, without the presence of the NP) was first checked to con-316 firm the negative tone behavior of the photopolymer. In partic-317 ular, we characterized the polymerization threshold energy for 318 several light power densities. This value is not only important 319 from a practical point of view to determine the exposure condi-320 tions but also brings additional information on the photochem-321 ical phenomena involved in the material. The  $t_{\rm T}$  irradiation time 322 was determined for different power densities (0.8 mW/cm<sup>2</sup>, 323 2.5 mW/cm<sup>2</sup>, 4.8 mW/cm<sup>2</sup>, 7.2 mW/cm<sup>2</sup> and 9.9 mW/cm<sup>2</sup>) and 324 plotted in Fig. 2a (black segments). For each power density, the 325 times above and below the threshold dose are represented by 326 blue and red crosses, respectively. These values give good preci-327 sion regarding the  $t_{\rm T}$  values. As expected, the higher the power 328 density is, the lower the threshold time. The threshold energy 329  $(E_{\rm T})$  was then calculated by multiplying  $t_{\rm T}$  by the power density 330

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#### FIGURE 2

(a) Threshold time ( $t_T$ , black segments) and threshold energy density ( $E_T$ , green triangles) determined for different power densities. The blue and red crosses represent the doses for which the photopolymerizations occur or not, respectively, at the considered power density. (b) UV–Visible extinction spectra of the photopolymerizable formulation, the gold NPs dispersed in water (Au NP (1)) and the Au NPs deposited on the Si<sub>3</sub>N<sub>4</sub> substrate and covered by the photopolymer (simulated BEM extinction spectrum \_ Au NP (2)). (c and d) Calculated distribution of the square modulus of the optical near electric field enhancement  $|E_{nf}/E_{incident}|^2$  around one Au NP evaluated by BEM with irradiation at 532 nm (circularly polarized light propagating along the *z* direction). (c) top and (d) side views, respectively. Incident field amplitude is normalized to unity within the substrate. (e) TEM images of NPs after a first irradiation at 90% of the threshold dose for a density power of (i) 2.5 mW/cm<sup>2</sup>, (ii) 4.8 mW/cm<sup>2</sup>, (iii) 7.2 mW/cm<sup>2</sup> and (iv) 9.9 mW/cm<sup>2</sup>.

and plotted on the same figure (green triangles). Interestingly, 331 332 the threshold energy for this system decreases when the power 333 density increases. This effect is significant within the narrow 334 range of laser power used, which means that this system is sensitive to a side reaction. This behavior is characteristic of a pho-335 topolymerizable formulation sensitive to oxygen quenching. 336 Indeed, for this system, when the power is decreased, the contin-337 uous replenishment of oxygen by diffusion from the nonirradi-338 ated area and surrounding area increasingly affects the 339 polymerization. This behavior was frequently observed in free 340 radical polymerization [52,53]. Here, it is more pronounced due 341 to the relatively low photoreactivity of the initiating system. 342 However, the polymerization is achievable in the entire range 343 of tested powers. 344

#### 345 Optical near-field photopolymerization

346 The objective of this section is to demonstrate that this pho-347 topolymer is compatible with near-field photopolymerization. 348 Fig. 2b shows the experimental extinction spectrum of the gold NPs in a solution (water n = 1.33) and the corresponding calcu-349 lated spectrum of particles with the same size (43 nm) deposited 350 on a Si<sub>3</sub>N<sub>4</sub> substrate and surrounded by PETA (dielectric medium 351 with a refractive index equal to 1.48). The extinction spectrum of 352 the photoinitiating system, given by the iridium complex, is also 353 354 plotted. It can be observed that there is an overlap of the NPs and the iridium complex spectra at 532 nm (emission wavelength of the laser).

The enhancement and spatial extend distribution of the opti-357 cal near field around one Au NP are determined from BEM simu-358 lations. In more details, maps of the squared modulus of the 359 optical near electric field enhancement  $|E_{nf}/E_{incident}|^2$  around 360 one Au NP are determined. Incident field amplitude is normal-361 ized to unity within the substrate. Two views are considered, 362 an equatorial top view (Fig. 2c) and a polar side view (Fig. 2d). 363 In the equatorial plane (xy) of the NP, the electromagnetic field 364 shows a circular symmetry in agreement with the circular charac-365 ter of the light excitation. At a distance r = R + 0.5 nm where 366 2R = 43 nm, the square of the enhancement factor EF amounts 367 to 28.3 (e.g. EF = 5.3). Field map in the polar plane (*xz*) exhibits 368 maxima close to the equatorial plane of the NP and minima 369 along its polar axis. Field enhancement is minimal (EF = 2.8) at 370 the top of the particle. The presence of a high refractive index 371 substrate (Si<sub>3</sub>N<sub>4</sub>) results in an additional field enhancement 372 below the NP (asymmetric distribution). Within these near-373 field volumes with enhanced optical intensities, an acceleration 374 of the polymerization kinetics is expected, and thus, gelification 375 should be reached at lower doses. A dose close to the threshold 376 (90%) was chosen in the following near-field photopolymeriza-377 tion experiments by adjusting the irradiation time according to 378 the light power used. 379

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#### FIGURE 3

(a-b, q-e, g-h) TEM images of two 43 nm gold NPs after (i) the first irradiation at 7.2 mW/cm<sup>2</sup> and at 90% of the threshold dose (irradiation time: 0.9 s) and after the second irradiation at (ii) 7.2 mW/cm<sup>2</sup> for 3000 s, (ijii) 7.2 mW/cm<sup>2</sup> for 600 s and (iv) 35 mW/cm<sup>2</sup> for 600 s. (c, f, i) Histogram and Gaussian fit of the photopolymer thickness distribution after (c) irradiation (i) and (ii) (statistics realized on 85 NPs), (f) irradiation (i) and (iii) (statistics realized on 63 NPs) and (i) irradiation (i) and (iv) (statistics realized on 40 NPs). The diameters of the NPs with ( $A_{NP}$ ) and without the photopolymer ( $A_N$ ) were measured. Afterwards, the thicknesses were calculated by subtracting  $A_N$  from  $A_{NP}$  and dividing the result by two.

380 The effect of power density on the polymerized volume during the first irradiation was studied to define the most suitable 381 condition for near-field photopolymerization (Fig. 2e). Indeed, 382 the intensity of the laser is known to be an important parameter 383 for controlling the shell thickness [37]. Powers were chosen 384 according to Fig. 2a. For each power density, irradiation of the 385 gold NPs with the photopolymerizable formulation at 90% of 386 the threshold dose was performed, and samples were character-387 ized by TEM (Fig. 2ei-eiv). These images are typical images 388 389 shown in Figs. S4–S6. In each case, the images reveal a thin shell 390 of polymer surrounding the NPs. It turns out that the impact of the power density on the polymer shell thickness is weak. The 391 limited polymer thickness is in agreement with the low photore-392 393 activity of the system, the high sensitivity to the inhibitor, the limited number of photoinitiator molecules in the near-field vol-394 ume (ca. 80 molecules) and the high confinement of the electro-395 magnetic field around the NPs. In the TEM images (top view), the 396 397 repartition of the polymer follows the expected circular intensity distribution around the equator of the particle, in agreement 398 with the numerical simulations (Fig. 2c). 399

Considering the very low thickness of the polymer layer, control experiments were conducted to exclude any misinterpretation of these results. In the first control experiment, we verified
that the polymer shell is indeed related to the polymer and not
to the monomer adsorbed at the surface of the NP, without polymerization. To do so, a drop of the formulation was deposited

onto a TEM grid with gold NPs and was not irradiated. The sam-406 ple was developed in the same way as described above in the 407 experimental part. TEM images were taken before and after the 408 drop deposition and revealed that no formulation remained on 409 the surface of the NPs (see Fig. S2B in the SI). This experiment 410 validates the development process. We also excluded, in our 411 experimental conditions, a direct polymerization of the acrylic 412 monomer as described by Wang et al. [54,55]. In their study, 413 the authors explained that the polymerization on the NP surface 414 is triggered by the ejection of hot electrons, without the need of a 415 photoinitiator. In this case, the control experiment consisted of 416 covering the NP with the raw monomer (without the photoiniti-417 ating system) and carrying the irradiation under the conditions 418 described before. The TEM analysis after irradiation did not show 419 any polymer at the surface of the NP, which is consistent with a 420 photoinduced polymerization process following the pathway 421 described in Fig. 1c. In our model, the NP contribution enables 422 modification of the spatial distribution of the electromagnetic 423 near-field, accelerating the photopolymerization in the near-424 field region. 425

#### Repolymerization from the polymer surface

The main objective of this work is to demonstrate the living char-<br/>acter of the polymer chains grafted in the first step, *i.e.*, that these<br/>chains can be reactivated by irradiation, without an initiator, at<br/>the same wavelength to covalently attach another polymer chain427<br/>428

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at the surface. Here, the power density for the first irradiation was 431 chosen to be  $7.2 \text{ mW/cm}^2$ . The corresponding irradiation time to 432 433 reach 90% of the threshold dose is 0.9 s. After the first step described above, different areas on the sample were characterized 434 by TEM, and representative NPs are shown in Fig. 3ai and bi. A 435 thin polymer shell is visible around the NPs, which indicates that 436 photopolymerization was triggered, confirming the results 437 shown in Fig. 2c. 438

To start the second polymerization, the NPs were covered 439 440 with pure TMPTA monomer and irradiated with the same configuration, with the same power density as for the first step. The 441 irradiation time was set to 3000 s. For this step, a long irradiation 442 time can be used without far-field polymerization since there is 443 no photoinitiating system in the TMPTA monomer. After irradi-444 ation, the sample was rinsed by immersion in ethanol, under 445 conditions identical to those used after the first irradiation. Sam-446 ples were then characterized by TEM. TEM imaging was carried 447 out on the same NPs that can be found on the TEM grid after 448 each step (Fig. 3aii-bii; see Fig. S7 for TEM images at lower 449 magnifications). 450

Images aii and bii in Fig. 3 clearly show an increase in the 451 452 polymerized shell thickness. Fig. 3c presents the statistical analysis of the thickness of the polymer layer around the NPs deter-453 mined by TEM. Since the thickness is not always homogeneous 454 around the NP, we evaluated the mean thickness as follows: 455 the diameters of the NPs with and without the photopolymer 456 were measured for 85 NPs to evaluate the polymer thickness after 457 the different steps. It appeared that the mean NP shell thick-458 nesses resulting from the first and the second irradiation were 459 460  $1.24 \text{ nm} \pm 0.55 \text{ nm}$  and  $2.16 \text{ nm} \pm 0.70 \text{ nm}$ , respectively. The 461 increase in thickness after the second irradiation is confirmed by the histogram, where a global shift to higher thicknesses is 462 observed. 463

To verify that the increase in the polymer layer was indeed 464 465 induced by laser irradiation, the following control experiment was conducted: after the first step, a drop of TMPTA was depos-466 ited onto the sample, and development was done without any 467 irradiation using our standard procedure (Fig. S8). The character-468 ization of the control sample by TEM did not reveal any change 469 in the polymer thickness, demonstrating that the increase in the 470 diameter of the hybrid NP does not result from the adsorption of 471 a thin monomer layer. 472

#### 473 Effect of the irradiation conditions on the second

#### 474 polymerization

In the previous experiment, the same power density as for the 475 first polymerization was used, and repolymerization is shown 476 after 3000 s of irradiation. Higher energy is thus required for a 477 478 second photopolymerization, which we confirmed by using dif-479 ferent conditions, as shown in Fig. 3d-i. Previous works on 480 repolymerization at micro- or millimeter scales indeed showed 481 a direct dependence of the polymer layer on the photonic parameters (power density and time) [19,28]. For completeness, addi-482 tional samples were prepared by performing the first irradiation 483 at 7.2 mW/cm<sup>2</sup> at 90% of the threshold dose and by changing 484 the photonic parameters of the second irradiation. 485

As observed in the former experiment, a thin polymer shell was observed after the first irradiation (Fig. 3di-ei). In Fig. 3di-

ii-eiii, the second irradiation time was 600 s, and the power density was maintained at 7.2 mW/cm<sup>2</sup>. For the second irradiation, there is no clear evidence of a second polymerization. The histogram shown in Fig. 3f confirms this trend for a large number of NPs (63 NPs). We investigated whether the second irradiation efficiency can be improved with higher laser power. In another experiment, the second irradiation was carried out for 600 s with a power density of 35 mW/cm<sup>2</sup>, *i.e.*, the total energy was the same as that in the first experiment (cf. Fig. 3aii and bii) but with a higher power density. TEM images of the gold NPs are shown after the first irradiation (Fig. 3gi and hi) and the second irradiation (Fig. 3giv and hiv; see supporting information, Fig. S9). As depicted in the polymer thickness histogram shown in Fig.  $3i_t$ these irradiation conditions significantly favor the growth of the second polymer layer since a clear increase in the polymer thickness can be observed. For a given energy, a higher power density favors the growth of the second polymer layer. We conclude from this set of experiments that although the first irradiation is not very efficient, with suitable irradiation conditions, most of the NPs can be functionalized with a polymer shell (at least 90%). We show in these experiments that this thin layer contains enough reactivable species to restart the photopolymerization. In particular, the photosensitive compounds are not washed out during the development steps, and despite the loss of mobility expected in the polymer matrix compared to the photopolymerizable solution in the first step, they are accessible to the second monomer and can still be activated when embedded in the polymer layer.

Moreover, despite the low reactivity of the nanohybrid system during the second irradiation, we demonstrate that the polymerization can be started again as long as the energy delivered is high enough. A low yield can be explained by the inhibition quenching of radical species in the presence of oxygen in the surrounding medium. The impact of the power confirms this assumption since higher power provides a higher rate of radical production and a more efficient competitive pathway against oxygen inhibition. Quenching of the excited states of the iridium complex by the metal nanostructure could also be involved, as it is well known that non-radiative de-excitation occurs in the vicinity of metal NPs [56]. Although this effect may be present, it does not completely inhibit the polymerization in both steps.

#### 3D repartition of the photopolymer

The question of the spatial distribution of the photopolymer around the NPs has been scarcely discussed in previous studies dealing with ONF photopolymerization. The discussion has been indeed limited to observation in 2D due to the limits of the employed imaging techniques (AFM and SEM).

Here, we propose using the tomographic mode of TEM to investigate the spatial distribution of the polymer layer around the NPs. Indeed, the transmission electron microscope used in this study is equipped with a rotation sample holder that makes it possible to record images of the NPs with tilt angles ranging from  $+60^{\circ}$  to  $-60^{\circ}$ .

As shown in the simulations (Fig. 2c and d), the field distribution is not spatially homogeneous around the NP. In the circular polarization and normal irradiation configuration, the near-field enhancement is indeed higher (i) at the equator of the NP and (ii)

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in the interstice between the NP and the substrate. Case (i) is related to the boundary condition of the field component perpendicular to the metal/dielectric interface: this component is not continuous through the interface and leads to an important polarization charge density at the metal surface. Since the incident field is an in-plane field, this perpendicular component, and the resulting charge density, is maximum along the equator and decreases at locations closer to the poles along the vertical direction. Field enhancement in case (ii) is due to the high refractive index of the substrate (Si<sub>3</sub>N<sub>4</sub> membrane) used in these experiments. On the other hand, the near-field is almost null at the other pole of the particle. Based on this last analysis, a representation of a hybrid NP was considered (Fig. 4a), and a tilt experiment was performed to validate it.

After the second polymerization (under the same conditions described in Fig. 3giv and hiv), hybrid NPs were observed along several angles. TEM images for one NP are shown in Fig. 4bihi. To acquire an easier view of the results obtained from this experiment, the polymer sections are highlighted in blue (Fig. 4bii\_hii). Below, for every angle, a representation of the hybrid NP is shown in Fig. 4biii-hiii and compared to the TEM images. The observation normal to the substrate plane (0°) shows the typical polymer layer around the NP (Fig. 4b). From this image, it is deduced that the polymer shell is present at the equator of the NP, but the electron absorption cross section of the metal being much higher than that of the polymer, it is not possible to confirm the presence of the polymer in other areas of the NP. When the particle is tilted, it is observed that the polymer thickness decreases on one side (top left in Fig. 4ci-hi). The polymer layer disappears after a tilt angle of 30°. The 3D representation in Fig. 4a confirms the absence of polymer at the top (Fig. 4eiii, north pole). On the opposite side (bottom right), the polymer is still visible at 30°, which means that there is polymer below the particle. However, the polymer layer thickness decreases, indicating that the quantity of the polymer below the NP is less than at the equator. These results confirm that the polymer is not distributed homogeneously around the particle but follows the spatial distribution of the calculated electromagnetic field in 3D. From this observation, several 583 conclusions can be made. We first confirm the photochemical 584 nature of the polymerization. Indeed, thermal polymerization 585 would result in a loss of spatial control, leading to a homoge-586 neous polymer layer all over the NP. The second polymerization 587 preserves the spatial distribution, which means that the spatial 588 extent of the repolymerization is well controlled at the nanos-589 cale. Remarkably, this result was obtained despite a small volume 590 corresponding to a very limited number of photoinitiator mole-591 cules. Considering a homogeneous distribution of the photoini-592 tiator within the photopolymer, we can indeed estimate an 593 average concentration of one molecule of Ir(piq)2(tmd) per 594 100 nm<sup>3</sup>, which corresponds roughly to 80 Ir complex molecules 595 in a 2 nm-thick polymer shell. As a consequence, this basic calcu-596 lation illustrates the small number of reactivable functions 597 within the polymer shell. However, we prove that polymeriza-598 tion can be reactivated, and this is also consistent with the rela-599 tively high irradiation conditions needed to obtain a significant 600 repolymerization. 601

Effect of the shape of NPs on near-field photopolymerization PhotoATRP can be applied to several nanoobject topologies different from the sphere. In practice, we used dimers, trimers and nanocubes and demonstrated that the ONF photopolymerization principle also applies to these objects. It should be stressed that such nanostructures permit a spatial symmetry breaking of the problem: despite the circular incident polarization, local field enhancement presenting azimuthal anisotropy can be achieved.

PhotoATRP was first applied to dimers. The results are shown in Fig. 5a. In the case of dimers, we expect a maximum enhanced field in the gap between both NPs [57]. Fig. 5ai shows the polymer repartition around the dimer after the first polymerization. Polymer can be distinguished all around the dimer, with a thicker layer at the gap position, as expected. The increase in the polymer shell layer is the most important in the gap, in agreement with a higher field intensity in this region (Fig. 5aii). These observations confirm the photoinduced character of the repolymerization step.



#### FIGURE 4

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(a) Schematic representation of an NP with the second photopolymer shell; the blue arrow represents the rotation axis, and the red arrow indicates the tilt direction: (i) TEM images of the same gold NP (two irradiations under standard conditions) after tilting by (b)  $0^{\circ}$ , (c)  $10^{\circ}$ , (d)  $20^{\circ}$ , (e)  $30^{\circ}$ , (f)  $40^{\circ}$ , (g)  $50^{\circ}$  and (h)  $60^{\circ}$ . The scale bar represents a length of 15 nm. (ii) TEM images, with the polymer highlighted in blue. (iii) Schematic representation of the tilted NP for the corresponding tilt angle.

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#### FIGURE 5

TEM images of (a) a dimer and (b and c) trimers of 43 nm gold nanospheres. TEM images of a (d) 57 nm-edge gold nanocube. (e and f) TEM images of 43 nm gold nanospheres. The images were obtained after (i) the first irradiation at 7.2 mW/cm<sup>2</sup> and after the second irradiation, with a circular polarization at 35 mW/cm<sup>2</sup> for 600 s with (ii) TMPTA or (iii) a fluorinated monomer HFBA. (g) Chemical structure of the HFBA fluorinated acrylate monomer. (h) Representation of the double shell system after irradiation under condition (i) and then condition (iii).

The same trend was observed with trimers (Fig. 5b and c). In 620 621 this case, as expected, the high-field regions are located at the contact positions of the metal NPs. Concerning a closed trimer 622 structure (Fig. 5c), it remains difficult to conclude from the single 623 TEM image regarding the presence or absence of polymer at the 624 center of the trimer, but polymer is very present at the periphery 625 of the object assembly, although the polymer thickness turns out 626 to be clearly larger in regions close to the gaps. 627

628 Gold nanocubes with a 57 nm edge length were synthesized according to the procedure described in the literature [41,42] 629 and used here. This size was chosen to obtain a nanocube plas-630 mon resonance that fits with the laser wavelength. A near-field 631 photopolymerization was performed on gold nanocubes depos-632 ited onto TEM grids via the same protocol as previously used 633 (Fig. 1b) and under the same conditions as those employed in 634 635 Fig. 3g and h. Herein (Fig. 5d), the polymer can be grafted onto the lateral sides of the nanocube. The second polymerization 636 was proved to be effective, leading to a relatively thicker shell 637 (Fig. 5dii; see Fig. S10). TEM in tomographic mode (Fig. S11) 638 639 allowed further investigation of the 3D repartition of the polymer on the cube surface. We demonstrate that there is no poly-640 mer on top of the cube, meaning that it is possible to 641 functionalize only the lateral sides of the cube, which is a unique 642 feature of this process. 643

#### Tuning the surface chemistry through the choice of the second 644 monomer 645

Finally, we would like to show the great versatility of the process 646 for tuning the surface chemistry of metal nanoobjects. Indeed, so 647 648 far, the two polymerizations were performed with two different monomers but with similar structures and properties. Therefore, the second polymerization allowed for the modification of the thickness of the locally grafted polymer but with similar chemical properties. This is interesting, as it demonstrates that the extension was confined to the enhanced field area. Here, we show that other acrylate monomers with very different properties can be used.

HFBA monomer was employed as a substitute for TMPTA in the second polymerization. The objective here is to show that our process can be used to graft a hydrophobic monomer at the surface of the NP and thus change its surface property. Indeed, the contact angles with water of polymer films prepared with PETA, TMPTA or HFBA are quite different (Fig. S12). For the polymer prepared with PETA or TMPTA, the contact angle was found to be close to 55°, but it drastically increased to 106° when it was prepared with HFBA.

The objective here is to show that HFBA can be grafted in the second step. TEM images of NPs after the first irradiation at 7.2 mW/cm<sup>2</sup> at 90% of the threshold dose are shown in Fig. 5ei and fi (see Fig. S13 for more examples of the NPs studied). A thin polymer layer of poly-PETA was obtained, as described in the previous section. For the second polymerization, the irradiation conditions used were  $35 \text{ mW/cm}^2$  for 600 s in the presence of HFBA (Fig. 5eiii and fiii). We observe a thicker polymer layer and conclude that repolymerization from the first polymer is possible with a fluorinated monomer (HFBA, Fig. 5g), as schematically depicted in Fig. 5h. A copolymer is created since the development step performed after irradiation would easily remove the second polymer layer if no covalent bound was created. Interestingly, we noticed that the second polymerization was less efficient than that for TMPTA, as revealed by a thinner polymer layer. A possible reason may be the higher diffusion rate of the oxygen in the low-viscosity fluorinated monomer. Inhibition by oxygen may thus be more pronounced under these conditions [58].

#### Conclusions

We have demonstrated that PhotoATRP can be triggered by plasmon resonance excitation to generate multilayer covalent polymer parts with spatial control at the nanoscale. From a fundamental point of view this shows that PhotoATRP systems can be used with nanometer-scale spatial resolution. Despite the very limited number of photoactivable molecules embedded in the polymer shell, these species are accessible for further reaction and still reactivable to graft a second layer. This route provides a new degree of freedom for the fine tuning of the geometry and surface chemistry of nanoobjects, with the unique feature to realize this in a nonisotropic way. It also shows that fine surface functionalization of metal nanostructures can be realized with very precise control over the spatial distribution of the functional material. The achievements described in this work thus represent a major milestone in the development of advanced functional hybrid nanoparticles.

#### **CRediT** authorship contribution statement

Farid Kameche: Investigation, Methodology, Formal analysis, Visualization, Writing - original draft, Writing - review & editing.

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Wajdi Heni: Investigation, Methodology. Siham Telitel: Investigation, Methodology. Dandan Ge: Resources, Software. Loïc Vidal: Resources. Fréderic Dumur: Resources, Writing - review & editing. Didier Gigmes: Writing - review & editing. Jacques Lalevée: Writing - review & editing. Sylvie Marguet: Resources, Writing - review & editing. Ludovic Douillard: Resources, Software, Writing - review & editing. Céline Fiorini-Debuisschert: Writing - review & editing. Renaud Bachelot: Conceptualization, Writing - review & editing. Olivier Soppera: Conceptualization, Methodology, Visualization, Writing - original draft, Writing - review & editing, Supervision.

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#### 720 Data availability

The raw/processed data required to reproduce these findings can-not be shared at this time due to technical limitations.

#### 723 Appendix A. Supplementary data

Supplementary data to this article can be found online at
 https://doi.org/10.1016/j.mattod.2020.03.023.

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