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# 1    **Advanced hybrid plasmonic nano-emitters** 2    **using smart photopolymer**

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10    **Abstract:** The integration of nano-emitters into plasmonic devices with spatial control and  
11    nanometer precision has become a great challenge. In this paper, we report on the use of a smart  
12    polymer for selectively immobilizing nano-emitters on specific preselected sites of gold  
13    nanocubes (GNC). The cunning use of the polymer is twofold. First, it records both the selected  
14    site and the future emitters-GNC distance through plasmon-assisted photopolymerization.  
15    Second, because the polymer is chemically functionalized, it makes it possible to attach the  
16    nano-emitters right at the preselected polymerized sites which subsequently “recognize” the  
17    nano-emitters to get attached. Since the resulting active medium is a spatial memory of specific  
18    plasmonic modes, it is anisotropic, making the hybrid nanosources sensitive to light  
19    polarization. The ability to adjust their statistical average lifetime by controlling the thickness  
20    of the nanopolymer is demonstrated on two kinds of nano-emitters coupled to GNC: doped  
21    polystyrene nanospheres and semiconductor colloidal quantum dots.

22

## 23    **1. INTRODUCTION**

24    Organic and inorganic nano-emitters are used for many topical applications ranging from nano-  
25    optics and nano-photonics to biomedicine and cell biology. [1–3] When weakly or strongly  
26    coupled to metal nanoparticles, their key properties can be controlled: (e. g.) lifetime, [4,5]  
27    quantum yield, [6] fluorescence directivity, [7] emission intensity, [8] and spectral  
28    properties [9]. The integration of these hybrid nano-emitters as optical nanosources into  
29    photonic nanodevices is of interest for research and technological innovation due to their  
30    miniaturization and multi-applications.

31    However, the integration of the emitters near metallic nanostructures with spatial control  
32    and nanometer precision in the three space dimensions remains a challenge. In the simplest  
33    way, the emitters are dispersed randomly on the plasmonic structures, without any position  
34    control. [10,11] By adding a spacer layer, the separation distance between the emitters and  
35    metallic structures can be controlled along one direction. [12–14] To achieve 3D spatial control  
36    of emitters relative to metallic nanostructures, a method based on trapping emitters in an  
37    isotropic silica shell covering the entire metallic nanoparticles has been reported. [15,16]  
38    Scanning-based methods have been reported to study in a controlled way the coupling between  
39    emitters and metallic nanostructures. [17,18] The DNA origami-assisted method, as a powerful  
40    approach, has been used for building special plasmonic nanoantennas and linking together  
41    plasmonic nanostructures and nano-emitters. [19–22] For the structures presenting a gap,  
42    including dimers and particles-film structures, DNA origami has proved to be able to place  
43    emitters, even a single one, within the gap. [23–27]. In other words, DNA is generally used for  
44    both bridging particles together and attaching nano-emitters. In the case of single metal

45 nanoparticles, the whole surface of particles is functionalized. With this approach, it is thus  
46 difficult to control the anisotropy of the emitters distribution around single plasmonic  
47 nanostructures. With the use of a DNA clamp, gold nanoparticles have been placed at three  
48 special positions around a single nanorod, but the DNA clamp and special capture strands on  
49 the clamp limit the shapes and size of the host nanostructures and it is hard to change capture  
50 positions for a defined clamp [28]. Besides, DNA-based hybrid nanosystem are pretty fragile  
51 in the sense that, for the survival of DNA origami, one needs to be in a salty liquid environment,  
52 which limits the types of available metallic nanoparticles, and requires complicated steps. This  
53 environment requirement limits the use of this approach for direct integration into nanophotonic  
54 circuits. Although site-selective coating based on anisotropic chemical growth on metal  
55 nanostructures was reported, [29–32] there are still challenges in achieving anisotropic  
56 distribution of the emitters themselves near metal nanoparticles. As a matter of fact, controlling  
57 in the three space dimensions, the anisotropic spatial distribution of emitters in the vicinity of  
58 single metal nanostructures still constitutes a challenge.

59 Near-field plasmonic photopolymerization has proven to be an effective technique to trap  
60 light-emitting quantum dots and molecules inside polymer volumes that are integrated at  
61 electromagnetic ‘hot-spots’ [33,34]. The anisotropic distribution of emitters can be controlled  
62 by choosing the plasmonic mode used for nanophotopolymerization. However, since the  
63 emitters are initially randomly distributed inside the photopolymerizable formulation, the  
64 spatial distribution of the emitters is still not precise enough. In particular, the distance between  
65 the nano-emitters and the metal nanoparticle in the structures of Ref. 33 is not controlled. In  
66 addition, because the emitter is pre-dispersed within the formulation, it is difficult to consider  
67 the influence of the curing laser on the emitter during the photopolymerization process, such as  
68 the two-photon absorption by the emitters, and the possible light force that may squeeze the  
69 emitters outward.

70 In this letter, we report on the use of a smart nano-polymer that allows us to address the  
71 above issues. The smart nature of the polymer is twofold. First, it is a photopolymer that  
72 reticulates at the plasmonic hot spot of the metal nanoparticle, allowing one to keep the memory  
73 of the selected electromagnetic sites. This “memory” is spatially anisotropic and also decides  
74 the distance between the plasmonic nanostructure and the future nano-emitter to be attached.  
75 Secondly, it is chemically pre-functionalized to electrostatically “recognize” the nano-emitter  
76 that can get selectively attached to the pre-designed sites.

77 Our approach is actually based on the association of three controlled elements: plasmonic  
78 nanostructures, smart photopolymer and nano-emitters.

## 79 **2. EXPERIMENTAL SECTION**

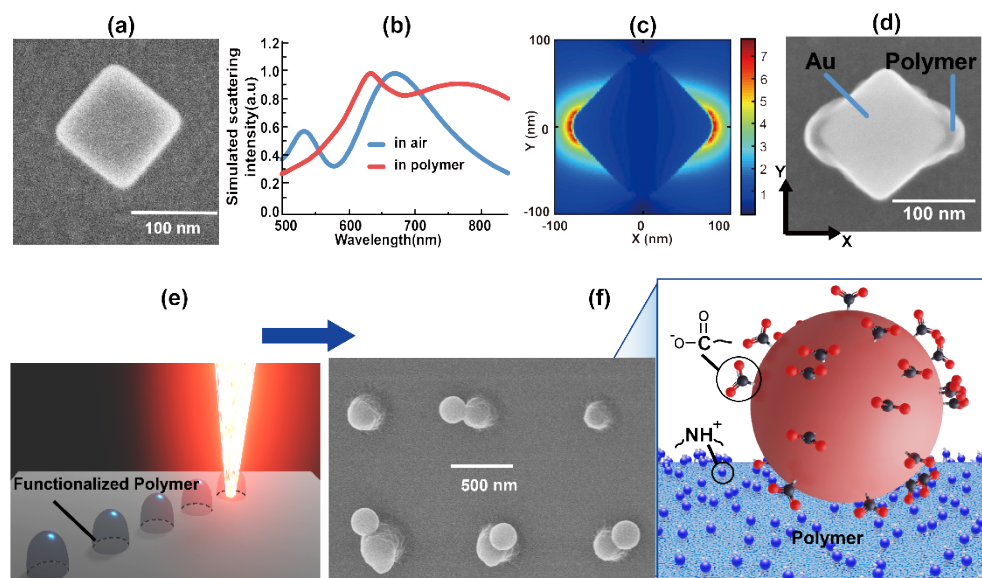
### 80 **A. Plasmonic nanostructures**

81 The plasmonic nanocavities used are 125-nm gold nanocubes (GNC, Fig. 1(a)) made by  
82 chemical synthesis using the method already described in detail in Ref.35. These cubes,  
83 deposited on an ITO-coated glass substrate, present a dipolar plasmon resonance at 670 nm in  
84 air, see blue curve in Fig. 1(b), suitable for resonant near-field two-photon polymerization. [33]

### 85 **B. Smart photopolymer**

86 The photopolymer has been designed for plasmon-induced two-photon nanoscale  
87 polymerization [33, 34] but has been modified: it is also a functionalized polymer that grabs  
88 the emitters to its surface by electrostatic interaction. In that way, we can control both the  
89 number of emitters attached to the polymer surface and the average emitter-metal surface  
90 distance by adjusting the thickness of the polymer on the plasmonic structure. The

91 photosensitive formulation consists of 4.99 mmol of Pentaerythritol triacrylate (PETA)  
 92 monomer functionalized by 2.51 mmol of methyldiethanol amine (MDEA), 0.039 mmol of 2-  
 93 Isopropylthioxanthone (ITX) was added to absorb light and make interaction with MDEA to  
 94 initiate the two-photon polymerization reaction and 1.13 mmol of monomethyl ether of  
 95 hydroquinone (MEHQ) inhibitor was added to control the spatial confinement of the  
 96 polymerization process. After photo reticulation and development, the polymer surface presents  
 97 a high density of amino groups  $10^8$  molecules per  $\mu\text{m}^2$  determined by the orange 2 test.



98

99 **Fig. 1** Gold nanocubes, nanoscale photopolymerization and surface functionalization. (a) SEM image of a  
 100 representative single gold nanocube. (a) Calculated scattering spectrum of a single gold nanocube of 125-nm, in air or  
 101 photopolymer medium (refractive index=1.48), on ITO-coated glass substrate (40 nm thickness of ITO layer with  
 102 refractive index of 2). (b) FDTD map (at the middle sectional plane of the cube,  $\lambda=780$  nm) of the field modulus in  
 103 the vicinity of the gold nanocube illuminated with a X-polarized plane wave. (d) SEM image of the hybrid  
 104 nanostructure resulting from 2-photon polymerization (TPP) triggered by the field shown in (c). (e) Illustration of the  
 105 photopolymerization of mixture of PETA monomer functionalized by amine. (f). Left: SEM image of polymerized  
 106 dots whose surface contains amine group. After immersion in a solution of negatively charged functionalized  
 107 fluorescent doped polystyrene spheres (200-nm diameter), the fluorescent spheres attached on four of the six polymer  
 108 dots by electrostatic interaction. Right: schematic representation of the electrostatic interaction.

109 More information about the smart photopolymer can be found in Ref. 36. The obtained  
 110 polymer nanotemplates are intended to be immersed in acidic medium solution of negatively  
 111 charged nano-emitters, resulting in the specific attachment of these nano-emitters on the  
 112 polymer surface. In other words, during immersion, the negatively charged nano-emitters  
 113 selectively assemble, by electrostatic interaction, on the positively charged functionalized  
 114 polymer surface due to the presence of protonated amine groups [Fig. 1(f)].

### 115 C. Nano-emitters

116 The first considered nano-emitters are fluorescent polystyrene spheres (FPS, from Thermo  
 117 Fisher) doped with light-emitting molecules. They are similar to those introduced in Fig. 1 but  
 118 they are significantly smaller: their average size is 45 nm (see Appendix B). The absorption  
 119 spectrum presents a peak at 580 nm whereas the emission peak is at 620 nm (see Appendix B).  
 120 Such FPSs were used by J. de Torres et al. to demonstrate plasmons-mediated fluorescence  
 121 energy transfer on silver nanowires. [37] The authors deposited the FPSs by spin-coating and  
 122 their spatial distribution was not controlled. The carboxylate-modified FPSs (FluoSpheres,

123 model F8793) used in this letter, are negatively charged and thus able to get selectively  
124 positioned to the functionalized polymer surface by electrostatic force.

125 Based on the three above-described elements, advanced hybrid plasmonic nano-emitters  
126 can be made.

#### 127 **D. Protocol for fabricating the hybrid plasmonic nano-emitters**

128 The protocol for fabricating the hybrid plasmonic nano-emitter consists of two main steps (Fig.  
129 6).

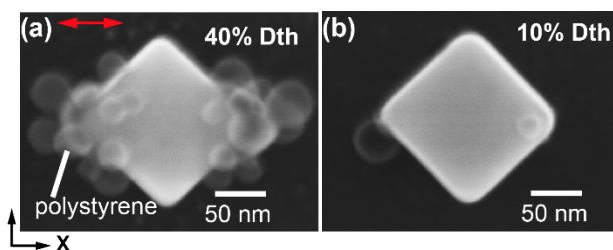
130 Step 1. This step consists of the fabrication of the functionalized nanopolymer on the GNC  
131 surface by plasmon-triggered polymerization at 780 nm. [33,34,38] This wavelength efficiently  
132 excites the GNC plasmon when this later is surrounded by the liquid photopolymer [see red  
133 curve in Fig. 1(b)] and is efficiently absorbed by ITX that is used as a 2-photon absorber. [39]  
134 The photopolymerization occurs specifically at the electromagnetic hot spots, when the near-  
135 field intensity exceeds a certain intensity threshold. During this step, the selected nanoscale  
136 sites are thus recorded by the polymer. After exposure, the deposited polymer volume is  
137 revealed through rinsing with acetone and isopropanol for 10 mins separately. Fig. 1(d)  
138 illustrates a typical hybrid nanocube, revealed after rinsing, that results from nano-  
139 polymerization triggered by the plasmonic dipolar eigenmode excited with a X polarization  
140 parallel to the diagonal of the cube [Fig. 1(c)]. The process relies on the control of the incident  
141 intensity relative to the threshold dose ( $D_{th}$ ) of 2-photon polymerization. For getting the result  
142 shown in Fig. 1(d), the incident laser dose was 40% of the threshold dose, so that no  
143 polymerization occurs, except in the near-field of the GNC [illustrated in Fig. 1(c)] where the  
144 local dose gets higher than  $D_{th}$  through plasmon enhancement.

145 The used experimental configuration for this step is shown in Appendix A, Fig. 7.

146 Step2. Following step 1, the sample is immersed into the FPS solution for 40 min. The FPSs  
147 were stabilized by carboxylic acid and have negative charges on their surface. During  
148 immersion and due to the presence of amine groups on the polymer (positive charges) FPSs get  
149 attracted by the polymer, leading to the selective attachment of FPSs on its surface by  
150 electrostatic interaction. During this step, the pre-recorded smart polymer gets revealed by  
151 selectively attaching nano-emitters.

#### 152 **E. Selective attachment of fluorescent spheres at the nanocube corners**

153 By adjusting the dose used for step 1, we were able to control the nanopolymer's thickness and  
154 thus the average distance between the GNC surface and the nano-emitters to be attached. At  
155 the same time, increased thickness of polymer leads to the increased number of grafted emitters.  
156 Fig. 2 illustrates this point: two different volumes of the polymer lead to a large change in the  
157 number of attached FPSs. The effect of the dose on the volume of polymer is clearly shown in  
158 Appendix C, Fig. 10. The selective immobilization of FPSs at the two corners of GNC is here  
159 successfully demonstrated. The excitation laser used for 2-photon polymerization was X-  
160 polarized, resulting in two lobes of smart polymer that took the shape of the local plasmonic  
161 field [Fig. 1(c) and 1(d)]. In Fig. 2(a) and 2(b), two identical GNC have been polymerized with  
162 two incident doses at 780 nm: 40% and 10% of  $D_{th}$ , respectively (step 1). Step 2 results in  
163 hybrid FPS/GNC with a number of FPS at each cube corner which is strongly dependent on the  
164 dose initially used for step 1: from a tenth of FPSs [Fig. 2(a)] to a few FPSs [Fig. 2(b)]. More  
165 examples can be found in Appendix C, Fig. 9. The Appendix H deals with the control of the  
166 number of emitters that can attach to the polymer lobes. This number depends on the  
167 concentration of emitters in the solution, the size of the emitter, the size of the integrated  
168 polymer area and the immersion time. In particular, Fig. 2, Fig. 9 and Fig. 16 illustrate the  
169 importance of the latter two.



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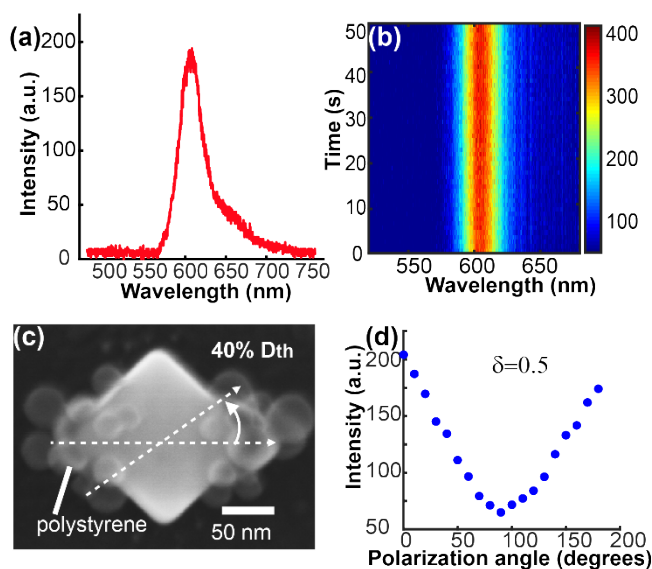
171 **Fig. 2** SEM images of the hybrid FPSs-attached nanostructures fabricated using energy dose of (a) 40% and (b) 10%  
 172 of threshold during step 1. The red arrow in (a) indicates the polarization direction of the excitation laser used for  
 173 polymerization during step 1.

### 174 3. RESULTS AND DISCUSSION

#### 175 **A. Photoluminescence properties of the resulting hybrid nano-emitters**

176 Under 532 nm excitation, the fluorescent signal was collected through a 650/150 nm band-pass  
 177 filter (Semrock FF01-650/150-25). The fluorescence spectrum from the hybrid FPS-GNC  
 178 nano-emitter is shown in Fig. 3(a). In Fig. 3(b), the time trace of fluorescence intensity obtained  
 179 during 50 s shows no blinking and a pretty good stability of the fluorescence intensity. This is  
 180 due to the large number of dyes inside each FPS giving out an ensemble signal and the  
 181 protective environment inside the polystyrene bead isolating the system from the instable  
 182 effects from the external environment.

183 These hybrid nanostructures have an anisotropic nanoscale spatial distribution of FPSs that  
 184 contributes to the polarization sensitivity of their fluorescence intensity. This feature is  
 185 illustrated in Fig. 3(d). The 532-nm excitation light was linearly polarized with a polarization  
 186 angle shown in Fig. 3(c). The considered single hybrid nano-emitter has been fabricated during  
 187 step 1 using 40% of Dth. In Fig. 3(d), the fluorescence intensity decreases when the polarization  
 188 angle of the excitation laser varies from 0° to 90° and increases when the polarization changes  
 189 from 90° to 180°. The fluorescence intensity finally goes back to the same intensity level as the  
 190 intensity of 0°. The switch from high emission signal to weak emission signal is realized by  
 191 rotating the polarization direction, and a signal contrast  $\delta$  of about 0.5 is obtained. In Fig. 3(b),  
 192 the cosine like function, reminding us of the Malus law, is not due to the polarization sensitivity  
 193 of the GNC. Rather, it is due to anisotropic spatial distribution of the active medium permitted  
 194 by the smart polymer. More data on the polarization sensitivity can be found in Appendix D.



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**Fig. 3** (a) Fluorescence spectrum measured from the hybrid FPSs-GNC shown in Fig. 2(a) using polarized green laser of 532 nm wavelength for excitation. A 650/150 nm band-pass filter is used to separate the fluorescent signal from the incident excitation (b) Spectrum time trace, collected for 50s. (c) Definition of the polarization angle for excitation. (d) Fluorescence intensity as a function of the angle of incident polarization defined in (c).

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### **B. Control of the average gap between GNC and nano-emitters and resulting Purcell factor**

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The spatial elongation of the nanopolymer during step 1 can be controlled through incident energy dose. [31, 32] Energy doses ranging from 5% to 70% of  $D_{th}$  were used for fabricating hybrid FPSs-attached hybrid plasmonic nanostructures (step 1). The fluorescence lifetime of the FPSs on the hybrid nanostructures, resulting from step 2, was measured to study the influence of the polymer thickness and thus the mean value of the FPS-GNC distance. Fig. 4(a) shows typical lifetime measurements. When the FPSs are directly attached to pure polymer dots without GNC (red curve), the lifetime is longer than it is when the FPSs are attached on the polymer lobes on GNC, which is in agreement with what is expected, i.e., an increase of the radiative and non-radiative deactivation rates in the presence of the metal nanostructure. The lifetime turns out to decrease as the energy dose used for fabrication decreases: green curve (5%  $D_{th}$ ) demonstrates a much shorter lifetime decay than orange curve (40%  $D_{th}$ ).

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There are hundreds of molecules in each FPS ( $3.5 \times 10^2$  fluorescein equivalents per polystyrene sphere). In general, the overall decay of all the molecules can be fitted by a sum of exponential functions [42], i.e.,

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$$I_{total}(t) = \sum_{i=1}^N A_i \exp(-t / \tau_i), \quad (1)$$

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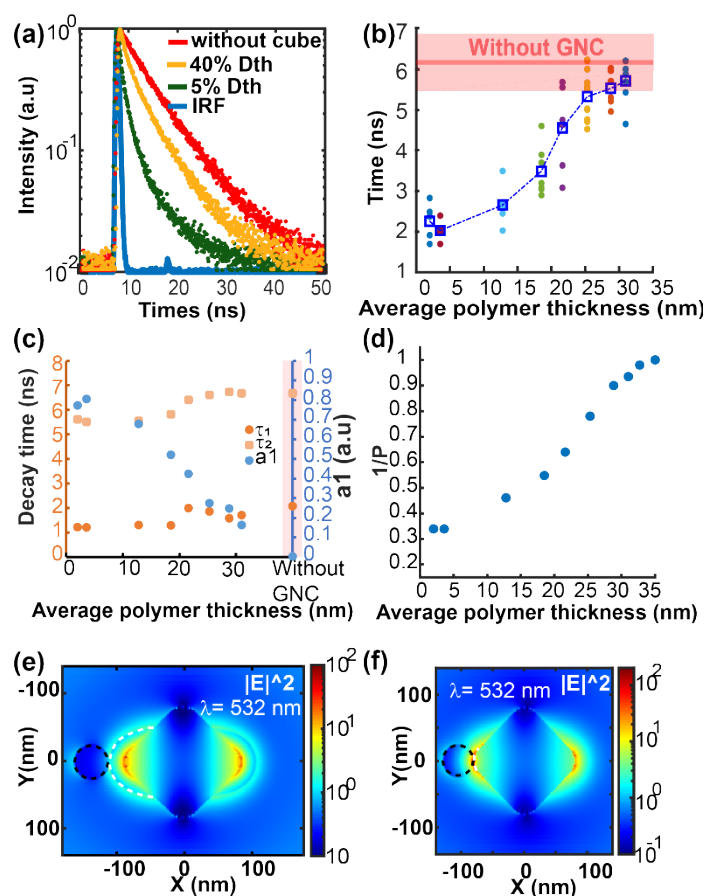
Where  $N$  is the number of dyes,  $I_{total}(t)$  is the normalized fluorescence intensity at time  $t$  from all the FPSs,  $A_i$  is the probability density function, and  $\sum_i^N A_i = 1$ . Parameter  $i$  can be viewed as a specific family of molecules that is characterized by lifetime  $\tau_i$ . The fluorescence lifetime of the FPSs without GNC can be very well fitted using single-exponential function (see Fig.14(a) in Appendix G), suggesting a single family of molecules, with a lifetime in the 6-7 ns range. With the presence of the GNC, the experimental data were fitted by one-exponential, double-exponential and triple-exponential functions. An accurate fit was achieved with double-exponential function, while the third exponential component has near zero probability density (Fig. 14(b)(c), in Appendix G). Hence the whole decay can be expressed as

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$$I(t) = a_1 \exp\left(-\frac{t}{\tau_1}\right) + (1 - a_1) \exp\left(-\frac{t}{\tau_2}\right) \quad (2)$$

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The double-exponential fitting results with different polymer thicknesses are shown in Fig. 4(b). Clearly, we observe a fast decay  $\tau_1$  that is contained in the 1-2 ns range and a slow decay  $\tau_2$  which is roughly stable within the 6-7 ns range. Considering the size of the FPS and keeping in mind that several FPSs are attached, we assign the fast decay  $\tau_1$  to the contribution of the Purcell effect undergone by the dye molecules, while the slow decay  $\tau_2$  is assigned to the emission of unaffected/less affected dye molecules (similar treatment as Ref 43).  $\tau_1$  can be seen as the mean value of the fluorescence lifetimes (Eq. 1) of the molecules that are sensitive to the GNC. Coefficient  $a_1$  stands for the weight of this fast decay component. It is associated with the proportion of molecules which undergo the Purcell effect. As shown in Fig. 4(b),  $a_1$  increases when the average polymer thickness decreases. This indicates an increase of the proportion of the dye molecules which are affected by the presence of the GNC, in terms of the Purcell effect.



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240 **Fig 4** (a) Lifetime measurement of FPSs attached on hybrid polymer-cube fabricated by a dose of 40%  $D_{th}$  (orange)  
 241 and 5%  $D_{th}$  (green). (b) Double-exponential fitting results of the lifetime of FPSs: fast decay component  $\tau_1$ , slow decay  
 242 component  $\tau_2$  and the coefficient  $a_1$  of fast decay component changes as the average polymer thickness varies. (c)  
 243 Weighted average lifetime of FPSs change along the average distance between the metal surface and FPSs increased  
 244 by decreasing the incident dose used for fabricating the hybrid GNC-based nanostructures. Dots of the same color  
 245 represent hybrid nanostructures made with the same excitation energy dose. The pink area represents the variation  
 246 range of the fluorescence lifetime of FPSs attached on polymer dots in the absence of gold particles. (d) The simulated  
 247 average Purcell factor ( $P$ ) of dipoles varies as the nano-polymer distribution changes by considering different incident  
 248 energy dose and resulting average thickness. (e) and (f) are simulated field intensity (at  $Z=25$  nm away from the  
 249 bottom of the cube) of a hybrid FPS-GNC nanostructure fabricated using the energy dose of 40%  $D_{th}$  and 5%  $D_{th}$   
 250 individually. The excitation wavelength is set at 532 nm, and the incident light is polarized along X. The black dotted  
 251 line depicts the FPS, and the white dotted line describes the contour of polymer.

252 The weighted average lifetime ( $a_1\tau_1+(1-a_1)\tau_2$ ) is shown in Fig. 4(c). It is represented as a  
 253 function of the “average polymer thickness” defined in the Appendix E. For statistically  
 254 assessing the influence of the dose, many (from 4 to 8, corresponding to the different dots in  
 255 Fig. 4(c)) hybrid nanostructures have been made for each given dose. Combining the SEM and  
 256 AFM analysis before FPSs attachment (see Appendix E, Fig. 12), estimated polymer 3D  
 257 distribution and the average polymer thickness can be related to the levels of energy dose.  
 258 Consequently, the change in the fluorescence lifetime of FPSs can be presented as a function  
 259 of the average polymer thickness, as shown in Fig. 4(c) that clearly statistically reveals a trend:  
 260 the lifetime decreases as the average polymer thickness decreases and tends to a stable value  $\sim$   
 261 2ns. Fig. 4(d) shows the corresponding simulated results through the inverse of the Purcell  
 262 factor, i.e. the ratio of the de-excitation rate with and without the GNC. The fluorescence



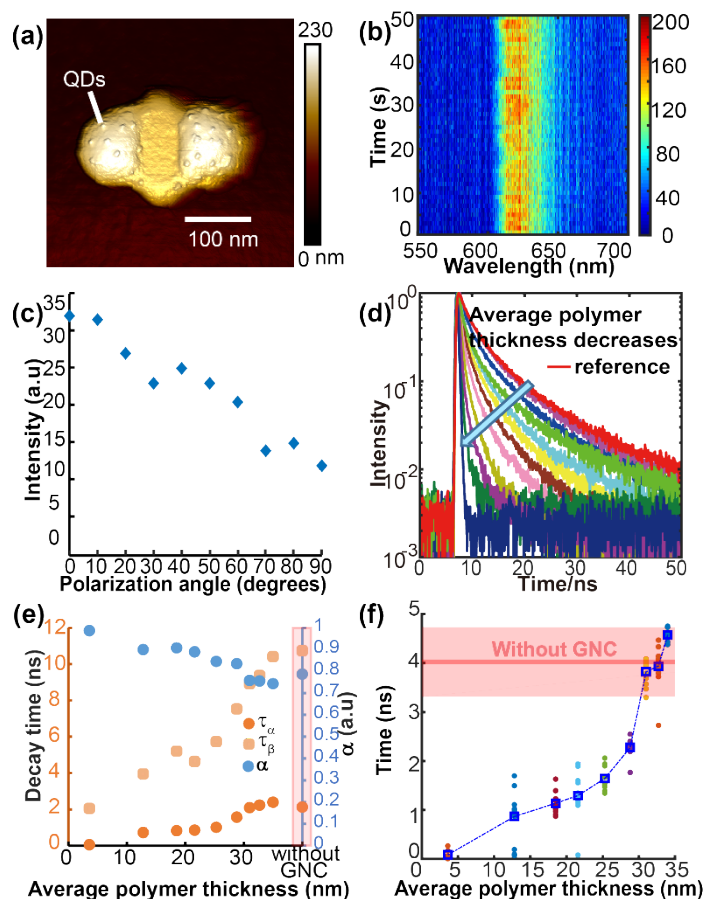
lifetime was calculated by placing dipoles at the center of FPSs at the position corresponding to the polymer distribution, as observed by SEM and AFM (see Appendix E). Fig. 4(c) and 4(d) reveal a consistent lifetime change trend, which confirms that the average polymer thickness is controlled by the incident energy dose used for fabrication of the hybrid nanosource, resulting in the control of the FPS-GNC distance and fluorescence lifetime of FPSs. As a conclusion of this section, through fittings, it turns out that, while  $\tau_1$  and  $\tau_2$  remain relatively stable,  $a_1$  is very sensitive to the polymer thickness, resulting in significant sensitivity of the resulting averaged weighted lifetime ( $a_1\tau_1+(1-a_1)\tau_2$ ) that can be viewed as a « tunable barycenter » in the continuous sum of lifetimes in Eq. 1.

### 272 **C. Further Discussion about the contributing molecules within the FPS**

273 From Fig. 4(c) and 4(d), a maximum Purcell factor can be estimated at 3.1 for smallest polymer  
274 thickness, which is a rather low factor. Because of FPS' size, even is the polymer thickness is  
275 negligible, a large proportion of molecules within the FPS are still too far away from GNC, and  
276 the proportion of the unaffected/less affected molecule cannot go to zero. As a result,  $(1-a_1)$   
277 always  $>0$ . This point is illustrated by Fig. 4(e) and 4(f) in terms of near-field excitation. Two  
278 hybrid nanosources were considered: one fabricated with a 40% Dth dose [Fig. 4(e)], polymer  
279 thickness = 21.6 nm, (see Appendix E, Table 1) and one fabricated with a 5% Dth [Fig. 4(f)],  
280 polymer thickness = 2 nm (see Appendix E Table 1). For simplicity, both hybrid nanosources  
281 present a single FPS. The intensity map at  $Z=25$  nm ( $\lambda=532$  nm) was calculated by FDTD using  
282 an incident X-polarized plane wave propagating along Z. The spatial distribution of the  
283 intensity reveals the two families of molecules in terms of excitation: in Fig. 4(e), there is a  
284 fewer proportion of dyes inside polystyrene sphere that are coupled to the localized field of the  
285 GNC ("close"). Even if this near-field map represents the excitation (rather than the  
286 deexcitation to the LDOS), it illustrates that the contribution of plasmon-coupled molecules to  
287 the average lifetime/Purcell factor of the whole system is weak; most of the molecules whose  
288 lifetime play the main role in the whole system are unaffected from GNC ("far"). In Fig. 4(f),  
289 a bigger proportion of dyes are coupled to the localized plasmonic near-field and their  
290 contribution to lifetime decrease becomes significant. This is consistent with the double  
291 exponential fitting results in Fig. 4(b). The above discussions can also explain why when the  
292 polymer thickness decreases to the smallest, the weighted lifetime/average Purcell factor does  
293 not continue declining but tends to stabilize in Fig. 4(c)/(d).

### 294 **D. Use of semiconductor colloidal quantum dots as nano-emitters**

295 In order to address the above issue, another approach was investigated: semiconductor colloidal  
296 quantum dots were immobilized on a functionalized nanopolymer surface in the close vicinity  
297 of a single gold nanocube. Compared to FPS, they can be considered as point-like emitters.  
298 After step 1 of fabrication (illustrated in Fig. 1(d)) the hybrid GNC was immersed in a colloidal  
299 solution of negatively charged CdSe/ZnS red QDs (with carboxylic acid as reactive group,  
300 bought from Mesolight), with emission wavelength at 623 nm and diameter  $\approx 12$  nm (Fig.  
301 8(c)(d), Appendix B). The obtained results, presented in Fig. 5(a), show a precise and selective  
302 attachment of QDs on the two corners of the gold nanocube where the functionalized polymer  
303 was printed by the plasmon-induced polymerization: Fig. 5(a) is the AFM image of a hybrid  
304 polymer/GNC/QDs obtained with a 40 % Dth energy used for fabrication (step 1). It clearly  
305 shows QDs attached at the surface of the integrated polymer lobes. More data with different  
306 energy doses can be found in Appendix C (Fig. 10).



307

308 **Fig 5.** Use of the smart polymer for coupling spherical CdSe/ZnS quantum dots with gold nanocubes. (a) AFM image of  
 309 a hybrid nanosource made with an energy dose of 40 %  $D_{th}$ . Attached QDs resulting from step 2 of fabrication are  
 310 clearly visible. (b) The spectrum time trace, signal collected during continuous 50s. (c) Polarization sensitivity of the  
 311 hybrid nanosource. (d). Measured lifetime for different hybrid nanosources having different polymer thicknesses. The  
 312 red curve represents a reference lifetime decay of QDs attached on a polymer dot without GNC nearby. (e) Double-  
 313 exponential fitting results: evolution of fast and slow decay components  $\tau_{\alpha}$ ,  $\tau_{\beta}$  and coefficient  $\alpha$  of fast component as  
 314 a function of the average polymer thickness. (f) Weighted lifetime as a function of the average polymer thickness that  
 315 depends on the fabrication condition (%  $D_{th}$  energy used for near-field photo polymerization in step 1).

316 Fig. 5(b) shows a typical PL spectrum centered at  $\lambda=620$  nm collected in the far field for 50 s  
 317 (excitation at 405 nm). As for the FPS-based hybrid sources, the active medium is anisotropic,  
 318 making the sources sensitive to the incident polarization: Fig. 5(c) shows the PL intensity as a  
 319 function of the polarization direction of the excitation at 405 nm (the definition of this direction  
 320 is the same as for Fig. 3(c)).

321 QDs generally have multi-exponential decay dynamics, which are due to their surface  
 322 defects, surface ligands, inhomogeneities of ensemble sample or other characteristics.[44–46]  
 323 Unlike in the situation with FPSs, the reference lifetime from QDs attached on the polymer dot  
 324 without GNC nearby can be fitted well by double-exponential decay (Fig. 15(a), Appendix G).  
 325 The short-time component and long-time component come from two different decay  
 326 pathways [47]. Without QDs, these both lifetime represents a reference that is intrinsic to the  
 327 semiconducting nanocrystal

328 With the presence of GNC, QDs' decay is influenced by the Purcell effect depending on  
329 their relative positions to GNC. The lifetime of QDs can still be fitted by double exponential  
330 functions (Fig. 15(b), Appendix G). Then the normalized intensity can be presented as  
331

$$332 \quad I(t) = \alpha \exp(-t / \tau_{\alpha}) + (1 - \alpha) \exp(-t / \tau_{\beta}), \quad (3)$$

333 where the  $\tau_{\alpha}$  is the fast decay and  $\tau_{\beta}$  is the slow decay.  $\alpha$  describes the contribution of  $\tau_{\alpha}$ .  
334 Fig. 5(d) shows a typical lifetime measurement of different hybrid nanosources fabricated with  
335 different energy doses ranging from 10% to 90% of  $D_{th}$ . From Fig. 5(d), the curves are fitted  
336 by double-exponential decay, using equation (3) and the fitting results are shown in Fig. 5(e).

337 The origin of this double-exponential decay is different from it is in Eq. (2): In Eq. (3), it  
338 results from the intrinsic properties of the QDs [44-47] while it corresponds to two families of  
339 molecules in Eq. (2) ("far" and "close" molecules). Due to the small size of QDs, all the QDs  
340 are affected in the same way by the presence of the GNC (Fig. 13, Appendix E). As the result,  
341 both lifetimes are sensitive to the polymer thickness, as shown in Fig. 5(e).

342 Fig. 5(f) shows the weighted average lifetime ( $\alpha\tau_{\alpha}+(1-\alpha)\tau_{\beta}$ ) for different polymer  
343 thicknesses. Again, for each dose, many similar structures (from 6 to 9) were fabricated to get  
344 a statistical trend. From Fig. 5(d) and 5(f), it turns out that the weighted average lifetime  
345 decreases with the dose, as a result of the decrease of the average distance between quantum  
346 nano-emitters and GNC. Fig. 5(e) shows the fitted values  $\tau_{\alpha}$ ,  $\tau_{\beta}$  and  $\alpha$ , as a function of the  
347 average polymer thickness. Compared to Fig. 4(b), Fig. 5(e) reveals different features of  
348 interest. In Fig. 4(b), we saw that both decay components are almost stable, and  $a_1$  increases  
349 obviously as the polymer thickness decreases, mainly revealing the increase of the proportion  
350 of molecules that are influenced by the GNC and a displacement of the barycenter in Eq. 1. In  
351 Fig. 5(e), the components are both affected:  $\tau_{\alpha}$  and  $\tau_{\beta}$  decrease together as the average polymer  
352 thickness gets smaller. (It is actually impossible to keep  $\tau_{\alpha}$  and  $\tau_{\beta}$  stable, see Fig. 15 (c))  
353 Meantime, coefficient  $\alpha$  presents a weak increase (0.8 to 1), which is still much tiny compared  
354 to the situation of FPS-attached hybrid GNC (in Fig. 4(b),  $a_1$  varies from 0.9 to 0.1). There are  
355 two possible explanations for this. First,  $\alpha$  not only represents the intrinsic ratio between the  
356 two decay pathways but also includes the weak increase of the proportion of QDs influenced  
357 by GNC as the polymer thicknesses decreases. Second, the short-time component of QDs  
358 already plays the major role in free space, the change of it cannot be distinguished as the change  
359 of the long-time component because of the resolution limitation of the set-up. For FPSs, instead,  
360 the variation of weighted average lifetimes is mainly due to  $a_1$ . In addition, according to Fig.  
361 5F, quite different from Fig. 4(c), the maximum Purcell factor in the situation of attached QDs  
362 can get larger than 10. This is because, due to their small size, at a small polymer thickness,  
363 quantum dots may be strongly affected by the Purcell effect, and no quantum dots can escape  
364 from the influence of GNC.  
365

#### 366 4. CONCLUSION

367 The use of a smart photopolymer has been leading to a new kind of plasmonic hybrid  
368 nanosources where different types of nano-emitters can be integrated on demand at predesigned  
369 sites of the metal nanostructures. The cleverness of the polymer makes possible the selection  
370 of the site through local preliminary plasmon excitation resulting in a 3D spatial memory. In  
371 particular, it is possible to control the average distance between the metal nanostructure and the

372 emitter to be attached. This latter is recognized by the polymer through charge affinity, leading  
373 to its selective controlled attachment.

374 Compared to Ref. 33, many advantages can be stressed. First, we can achieve a wider  
375 variety of emitters. While the integration of emitters within the initial acrylate-type liquid  
376 formulation is delicate in terms of phase separation and photochemical effects [48], the new  
377 approach reported here allows any negatively-charged emitters or particles to attach on the  
378 surface of polymer lobes with the help of electrostatic forces. In the future, this approach will  
379 open up many routes. For example, even negatively charged nanodiamonds permitting single  
380 photon emission [49] could be selectively attached. Second, the main novelty lies on the fact  
381 we remain the advantages of our previous method, which can place emitters close to plasmonic  
382 structures with anisotropic distribution and further improve it with more possibilities. By  
383 placing emitters on the surface of the polymer, the thickness of polymer is also the distance  
384 between emitters and plasmonic particles, instead of letting the emitters randomly dispersed  
385 inside the whole volume of the polymer lobes. The control of this distance has been leading to  
386 an actual lifetime engineering. In order to comment further on this point, let us use the spherical  
387 coordinates ( $\phi$ ,  $\theta$ ,  $\rho$ ) of the emitter to be localized. We can control  $\phi$ ,  $\theta$  using the method  
388 introduced in Ref. 33. We now control  $\rho$  with our new approach of functionalized  
389 photopolymer.

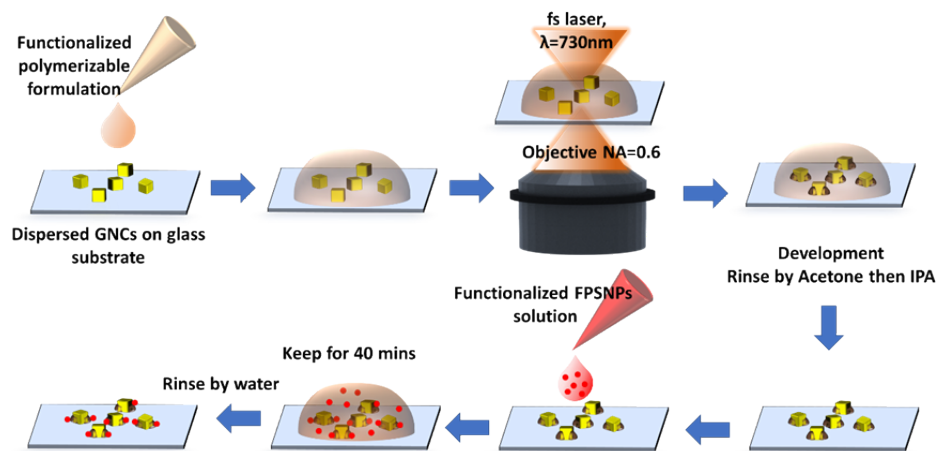
390 Finally, the surface attachment method is likely to avoid bad influence from the laser during  
391 polymerization, which may damage the emitters or introduce other effects such as light force,  
392 and two-photon absorption, etc. These effects are currently being studied by our team.

393 This approach will be used for fabricating single-photon hybrid nanosources [33] and  
394 precisely integrating different kinds of QDs through a multistep process [34], which will be  
395 opening new avenues for advanced integrated nanosources based on weak and strong coupling,  
396 among which multicolor nano lasers [34,50] that may be controlled by light polarization.  
397 Besides, as we demonstrated in Ref. 33, a tunable emitter selection is possible by rotating the  
398 incident polarization, through the concept of polarization-dependent spatial overlap integral  
399 (overlap between the exciting near-field and the emitters). However, in ref. 33, the excitation  
400 was in the blue, which is suitable for emitter excitation but not plasmon excitation. By  
401 integrating emitters that efficiently get excited at 780 nm wavelength through either one or two-  
402 photon absorption, we would take advantage of the plasmonic hot spot for both integrating and  
403 exciting them in the future.

404

#### 405 **APPENDIX A: PROCESS OF FBRICATION**

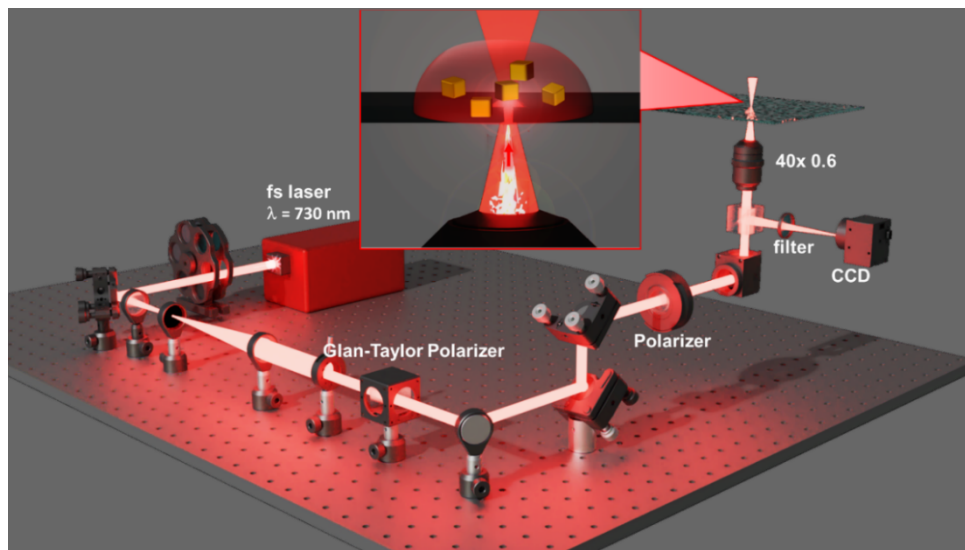
406 The separation distance between each GNC is controlled bigger than 500nm by adjusting the  
407 concentration of GNCs in solution, to avoid the influence from each other in the following  
408 experiments including 2-photon polymerization and emission measurement.



409  
410 **Fig. 6.** The process steps for fabricating hybrid FPSs-attached cubes.

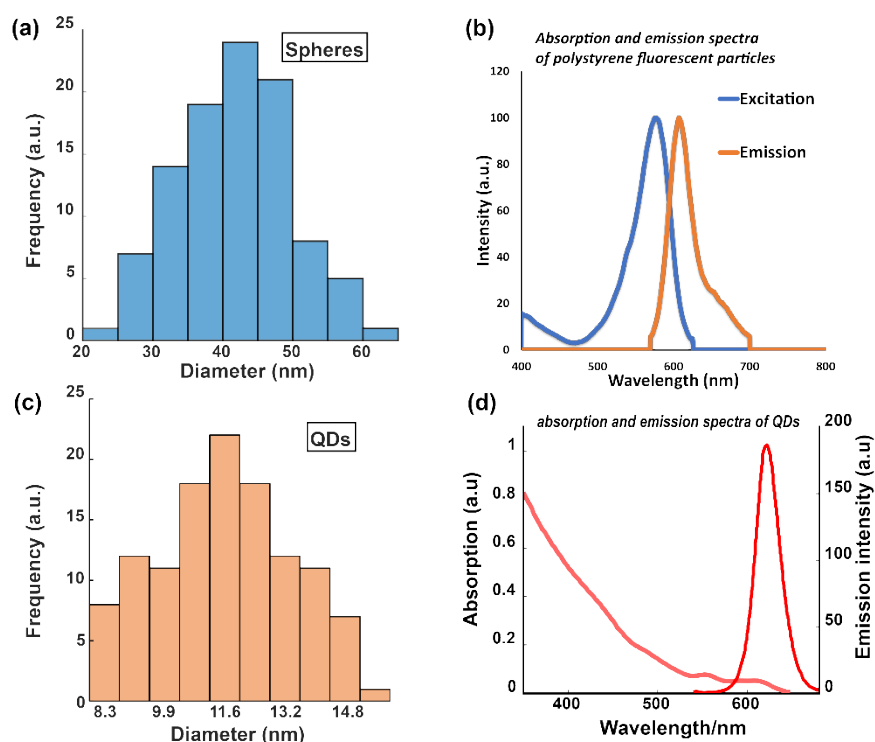
411 **Fig. 6** illustrates the whole steps for preparing hybrid FPSs-attached cubes. And Fig. 7 gives out the optical set-up  
412 used for doing 2-photon polymerization on each single GNC. The position of focused laser spot and GNCs are observed  
413 by a CCD camera and makes it possible to aim the laser spot at each isolated GNC. Plasmon-triggered 2-photon  
414 polymerization process

415 The GNCs are dispersed on a glass substrate with a separation distance between each other  
416 bigger than 500nm. A drop of the functionalized photosensitive formulation is then deposited  
417 on the pre-identified GNCs sample. Each GNC of consistent size and good shape is exposed  
418 one by one using a focused femtosecond laser of 730nm by an objective lens (N. A=0.6) (Fig.  
419 7). During polymerization, the exposure time is kept at 1/15 s. The exposure laser energy dose  
420 is set below than the polymerization threshold and is defined as the percentage of threshold  
421 dose (typical incident dose  $D_{in} = 40\% D_{th}$ ). The polarization direction of curing laser is along  
422 the diagonal of the GNCs.



423  
424 **Fig. 7** Optical configuration to carry out two-photon polymerization.

425 **APPENDIX B: SIZE OF POLYSTYRENE FLUORESCENT PARTICLES AND**  
426 **QUANTUM DOTS**



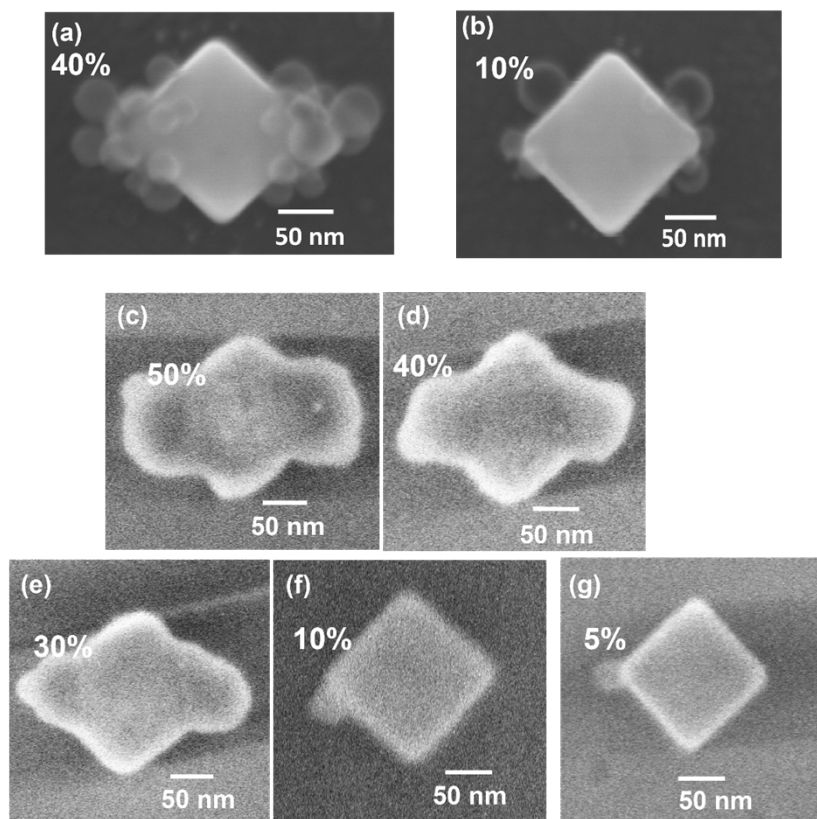
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428 **Fig. 8** (a) Diameter distribution histogram of the polystyrene fluorescent spheres (b) Excitation and emission spectra  
 429 of polystyrene spheres measure by UV-visible Cary 100 spectrometer and Fluorescence Spectrophotometer separately.  
 430 (c) Diameter distribution histogram of the QDs. The QDs are deposited on glass substrate and then after coating of a  
 431 conducting layer, the QDs 'sizes are measured under SEM. Due to the existence of the conducting layer, the size of  
 432 the measured QD is several nanometers larger than the real size of QDs. (d) The absorption and emission spectra of  
 433 the red QDs in toluene.

434 From Fig. 8(a), the average diameter of this kind of polystyrene fluorescent sphere is around  
 435 42.5nm. Different sizes of polystyrene spheres will change the related distance between their  
 436 containing fluorescent dye molecules and the GNC, which will lead to errors in the fluorescence  
 437 lifetime measurement. When the number of attached polystyrene spheres is relatively large,  
 438 since the measured fluorescence lifetime is a statistical average, the influence of the size  
 439 difference of polystyrene spheres on the result can be ignored. However, when the hybrid GNC  
 440 is fabricated by low dose, the number of attached polystyrene spheres is limited, the size  
 441 difference of the fluorescent spheres becomes non-negligible. That can explain why the  
 442 measured lifetime in the situation of smallest average thickness is bigger than the second  
 443 smallest situation in Fig. 4b of the article.

444 These Fluorescent FluoSpheres beads whose average diameter are around 42nm with the  
 445 dyes filling the full volume of the beads and contain 3500 fluorescein equivalents per  
 446 microsphere according to the handbook from Thermofisher.

447 **APPENDIX C: MORE EXAMPLES OF HYBRID NANOCUBES**



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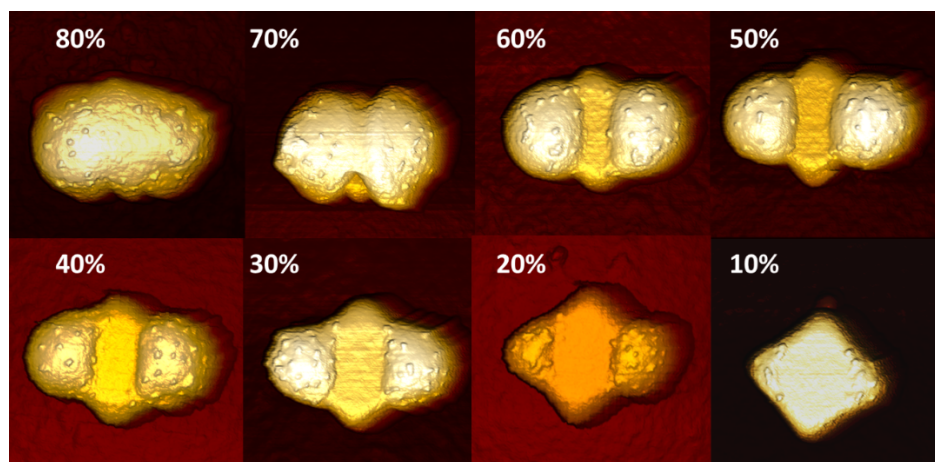
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**Fig. 9** More examples of hybrid FPSs-attached gold nanocubes. (a) and (b) SEM images of the hybrid FPSs-attached nanocubes fabricating using 40%  $D_{th}$  and 10%  $D_{th}$ , and the residence time of FPS solution is 40 mins. 10kV voltage is used for SEM observation. (c) (d) (e) (f) (g) fabricated using 50%  $D_{th}$ , 40%  $D_{th}$ , 30%  $D_{th}$ , 10%  $D_{th}$ , 5% $D_{th}$  separately, and the immersion time of the sample in the FPS solution decreased to 10 mins. 1kV voltage is used for SEM observation



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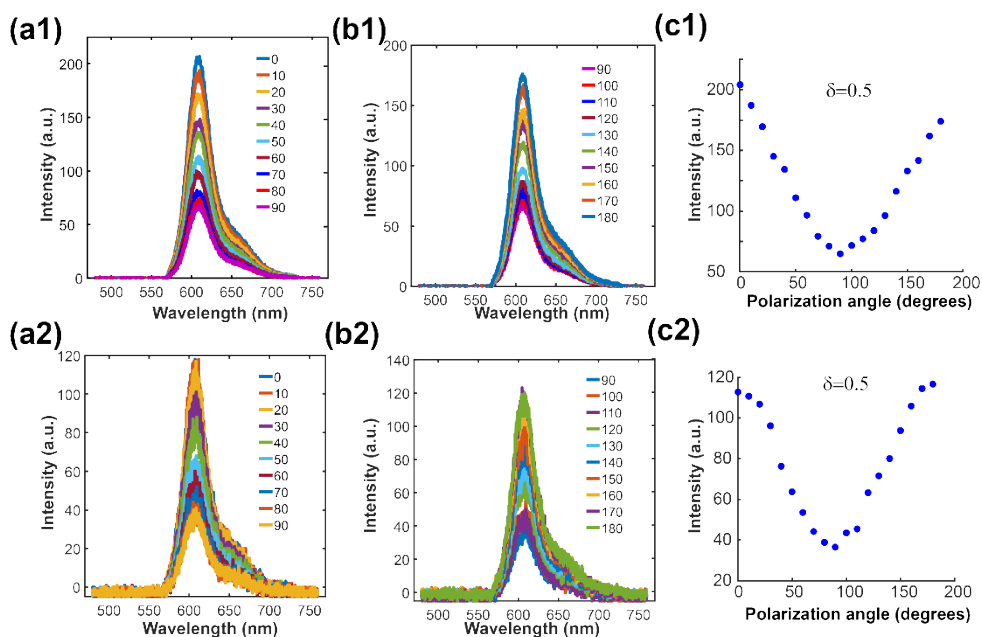
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**Fig. 10** AFM images of some hybrid GNC with attached QDs, fabricated using incident doses from 80% decreasing to 10% of  $D_{th}$  (step 1).

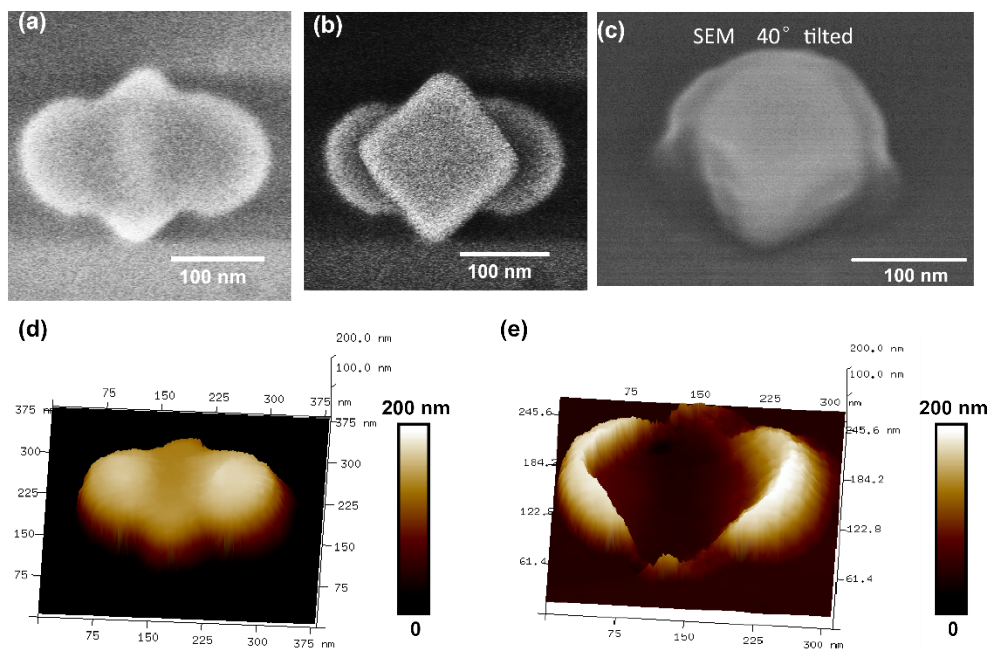
**APPENDIX D: POLARIZATION SENSITIVITY OF THE EMISSION INTENSITY**



459

460 **Fig. 11** Emission spectra from two hybrid FPSs-attached nanocubes fabricated using same parameters, their exposure  
 461 dose is 40%  $D_{th}$ . (a1) and (b1) are the emission spectra from the first hybrid FPSs-attached nanocube when the  
 462 polarization angle of the laser used for exciting varies from 0 degrees to 90 degrees and 90 degrees to 180 degrees  
 463 separately. (c1) is the emission peak intensity changing trend. And (a2) (b2) (c2) are the results from the second hybrid  
 464 FPSs-attached nanocube.

465 **APPENDIX E: 3D POLYMER CHARACTERIZATION AND DEFINITION OF THE**  
 466 **AVERAGE POLYMER THICKNESS**

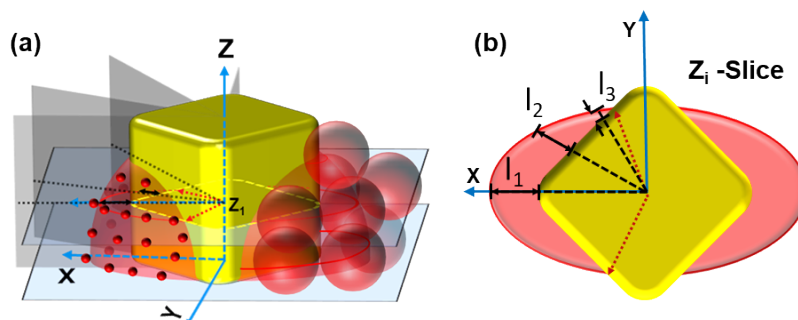


467

468 **Fig. 12** (a) SEM image of a hybrid nanocube without attaching any QDs/polystyrenes (fabricated using 50%  $D_{th}$ ) (b)  
 469 Mixed image, the original SEM image of the cube before exposure is superimposed to (a). (c) 40-degree tilted SEM



470 image. (d) 3D height image measured by AFM of the same hybrid nanocube of (a). (d) 3D height image subtracted by  
 471 the original cube's height profile from (c), demonstrating the 3D polymer distribution.



472

473 **Fig. 13.** Average polymer thickness definition and assessment. (a) The whole hybrid cube-polymer structure is cut in  
 474 the Z direction to get 20 slices of the cross-section. For each z-slice, a quadrant is sliced into n parts on average  
 475 according to angle, and the intersection of the corresponding rays and the polymer profile is averaged to obtain the  
 476 average elongation of the polymer under this Z slice. Finally, the polymer thickness of all slices in the z-direction is  
 477 averaged to get the average polymer thickness. (b) shows the polymer elongations ( $l_1, l_2, l_3$ ) obtained by the three  
 478 tangents when a quadrant is divided into 3 sections in the  $z_i$ -slice, then the average value of the three elongation rates  
 479 of the polymer thickness of this slice.

480 For  $Z_i$ -slice, If the polymer thickness in the third quadrant is sampled at 30-degree intervals  
 481 shown in Fig. 13(b), three polymer thickness  $l_1, l_2, l_3$  are obtained. Then the average polymer  
 482 thickness on  $Z_i$ -slice is  $(l_1+l_2+l_3)/3$ . For each  $Z_i$ -slice, keep sampling at 30-degree intervals, and  
 483 the number of  $l$  obtained will vary with the change of the polymer distribution of each slice.  
 484 Finally, the average of all the obtained  $l$  is taken as the average polymer thickness.

485

Table 1. Calculated average polymer thickness, when using different dose in percentage of Dth

Percentage of Dth (%)	Average polymer thickness (nm)
5	2
10	3.6
20	12.8
30	18.5
40	21.6
50	25.3
60	28.8
70	31.0
80	32.7
90	34

486

## 487 APPENDIX F: FLUORESCENCE SIGNAL AND LIFETIME MEASUREMENT

### 488 A. Optical set-up

489 For fluorescence intensity measurement, every single FPSs-attached hybrid polymer-cube is  
 490 excited using 532nm (CW laser, OBIS 532nm) focused by an objective lens of 40 x 0.6, and its  
 491 fluorescence signal is collected by the same objective, after fitting by a band-pass filter (FF01-  
 492 650/150-25), it is analyzed by a spectrometer. A half-wave plate is used to change the

493 polarization direction of linearly polarized laser and after each polarization rotation, use another  
 494 polarizer to check the polarization direction, and fine-tune the laser output light power to ensure  
 495 that the power reaching the sample surface remains the same (detected before objective lens,  
 496 laser power is set to 10  $\mu$ w). For lifetime measurement, a pulsed laser (Picoquant D-TA-530B)  
 497 connected with an extra driver box (PDL 800-B), whose repetition frequency is set at 10MHz  
 498 is used. The laser beam is focused on the scanning sample hold stage by an objective lens of  
 499 100 x 0.95. The laser power detected before objective lens is about 0.5  $\mu$ w. For each hybrid  
 500 FPSPNs-attached polymer-cube, its fluorescence is collected by reflection, and then after  
 501 passing through a band-pass filter (FF01-650/150-25), the collected light is directed by a fiber  
 502 towards an APD (Picoquant PMA- 182). The signal is sent to the stand-alone TCSPC Module  
 503 (TimeHarp-300), which is linked to the laser driver.

#### 504 **B. Purcell factor simulation**

505 The Purcell factor is calculated by FDTD. For each incident light dose, the corresponding  
 506 3D polymer is constructed as a model with a refractive index of 1.5. And set the diameter of  
 507 the polystyrene sphere to 50nm. For each case, the hybrid polymer cube is cut into N slices in  
 508 the z direction, each  $Z_i$ -slice has a specific polymer contour at the z position, as shown in Fig.  
 509 13. The FPSs are distributed along the contour of the polymer. To calculate, we only chose  
 510 several FPSs along the contour at  $Z_i$ . For each nanosphere, calculate the Purcell factor of the  
 511 ideal dipole at the center of the nanosphere, and finally average these results to obtain the  
 512 average Purcell factor of this z-slice, see Equation (F-1)

$$513 \quad PF_i = \frac{1}{N_i} \sum_{k=1}^{N_i} PF_k \quad (F-1)$$

514 Where  $N_i$  is the sampling number of FPSs on  $Z_i$  slice.

515 The FPSs are assumed uniformly distributed on the surface of polymer, then for each  $Z_i$ -  
 516 slice, the number of attached FPSs depends on the length of the polymer contour line.

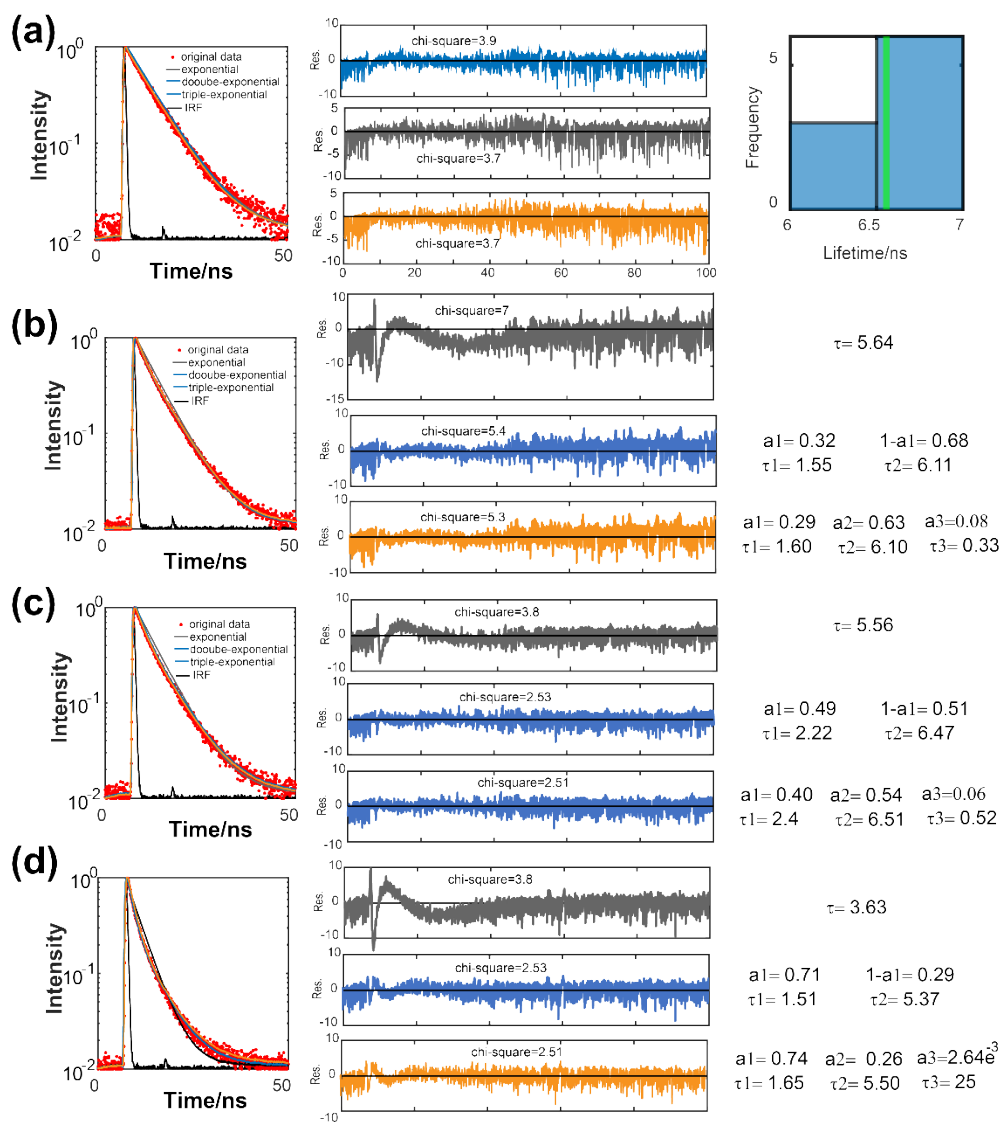
$$517 \quad PF_{total} = (\sum_{i=1}^{i=N} C_i \cdot PF_i) / (\sum_{i=1}^{i=N} C_i) \quad (F-2)$$

518 Where  $C_i$  is the length of polymer contour line of  $Z_i$ -slice, and N is the number of slices in  
 519 z-direction.

520 By this way, the obtained  $PF_{total}$  is worked as the average Purcell factor in the case of a  
 521 hybrid FPSs-attached polymer-cube fabricated by a certain dose.

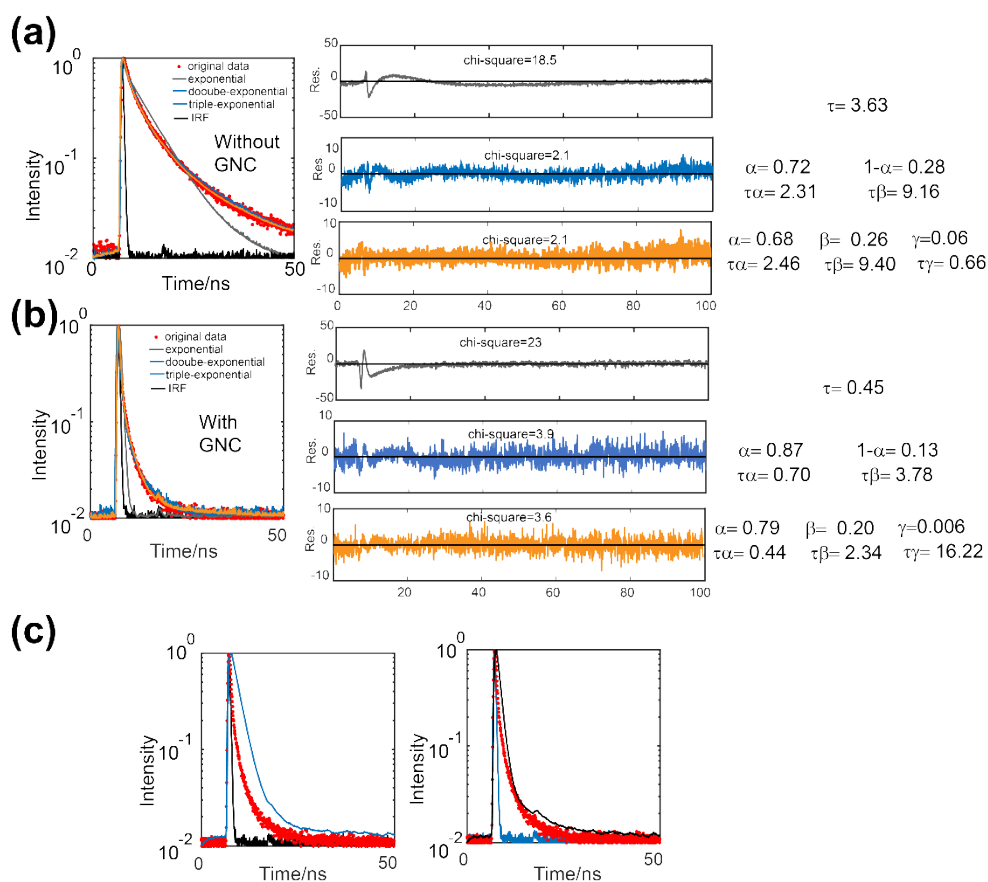
522 For example, of 20% Dth, the polymer volume is cut into 2 slices in the z direction. For  
 523 slice1, 3 positions of fluorescent spheres are calculated. For every position, we calculated the  
 524 Purcell factor of an orientation-averaged dipole placed in the center of sphere. And the  
 525 boundary length of the polymer of this  $Z_1$ -slice is around 48.7nm. For  $Z_2$ -slice, because the  
 526 boundary length of polymer is much smaller than diameter of sphere, we only calculate the  
 527 Purcell factor at one position. Finally, an average Purcell factor  $\sim 2.17$  was obtained according  
 528 to Eq. F-2

#### 529 **APPENDIX G: MULTI-EXPONENTIAL DECAY FITTING OF THE LIFETIME OF** 530 **FPS AND QD IN FREE SPACE**



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**Fig. 14** (a) The first row shows an example of the lifetime from FPSs attached on pure polymer dot without Au nanocube nearby. Two kinds of fitting, single-exponential fitting (grey line) and double-exponential fitting (blue line), triple-exponential fitting (orange line) are used here. From the fitting results, the single exponential function can already achieve good fitting result. The far-right image shows the histogram of FPSs' lifetime under single exponential fitting, and the green line represents the average value. For comparison (b) (c) and (d) show three examples of the lifetime from FPSs attached on polymer lobes of GNC.

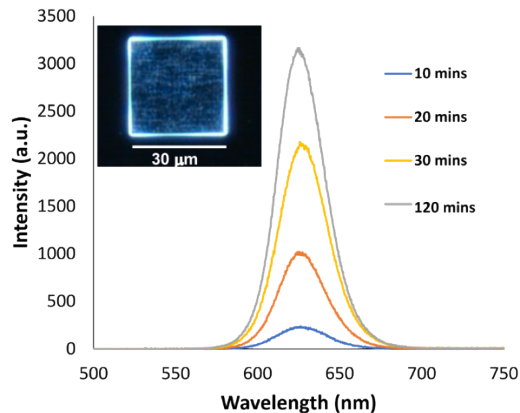


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**Fig. 15** Example of the lifetime from QDs attached on pure polymer dot without Au nanocube nearby (a) and with Au nanocube nearby (b). Single-exponential function is not enough to get a good fitting result while double/triple-exponential function can get a better fit. (c) Two failed attempts. By limiting the value range of  $\tau_a$  (2-3),  $\tau_b$  (9-10), and  $\tau_\alpha$  (1-3),  $\tau_\beta$  (8-10) to attempt to use similar  $\tau_\alpha$ ,  $\tau_\beta$  in (a) to fit the decay curve.

543 **APPENDIX H: NUMBER OF ATTACHED EMITTERS**

544 In Ref. 36, the original principle of this chemically attached method has been described. In this  
545 article, gold nanoparticles (diameter~ 50nm) were attached to the smart photopolymer. The  
546 control of the surface density (and thus the number) of gold nanoparticles has already been  
547 studied. The gold nanoparticles have same size as the fluorescent spheres used in our current  
548 manuscript. We expect that their density changes with the immersion time following the same  
549 law.



550

551 **Fig. 16** Fluorescence intensity from QDs attached on 2D flat functionalized polymer structure (see inset) with respect  
 552 to the immersion time (mins). The excitation laser is 405 nm with a power of 2μm, collection time is kept as 0.1s. The  
 553 left top small image (inset) is the dark-field image of the 2D flat polymer square.

554 As far as the QDs are concerned, Fig.16 shows the fluorescence intensity from QDs attached  
 555 on a micrometer sized functionalized flat polymer structure. Different times of immersion were  
 556 used. Considering the fixed size of the polymer area, this Fig. 16 clearly shows that the intensity  
 557 (and thus the related number of attached QDs) strongly depends on the immersion time.

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 564 (École Universitaire de Recherche, contract ANR-18-EURE-0013). The manuscript was written through contributions  
 565 of all authors. All authors have given approval to the final version of the manuscript.

566 **Disclosures.** The authors declare no conflicts of interest.

567 **Data availability.** Data underlying the results presented in this paper are not publicly available at this time but may  
 568 be obtained from the authors upon reasonable request.

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