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1 **Direct Laser Writing of Photostable Fluorescent**
2 **Silver Nanoclusters in Polymer Films**

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5 *Juha Toivonen^{†,*}*

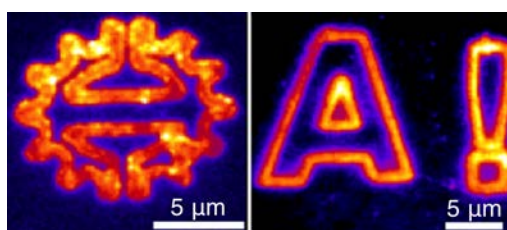
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11 **ABSTRACT**

12 Metal nanoclusters consist of a few to few hundreds of atoms, and exhibit attractive molecular
13 properties such as ultrasmall size, discrete energy levels and strong fluorescence. Although
14 patterning of these clusters down to the microscale or nanoscale could lead to
15 applications such as high-density data storage, it has been reported only for inorganic
16 matrices. Here we demonstrate the first submicron-scale mask-free patterning of fluorescent
17 silver nanoclusters in an organic matrix. The nanoclusters were produced by direct
18 laser writing in poly(methacrylic acid) thin films, and exhibit a broadband emission at visible
19 wavelengths with photostability that is superior to Rhodamine 6G dye. This fabrication
20 method could open new opportunities for applications in nanophotonics like imaging,
21 labeling, and metal ion sensing. We foresee that this method can be further applied to prepare
22 other metal nanoclusters embedded in compositionally different polymer matrices.



24 **KEYWORDS**

25 Optical lithography, metal nanoclusters, photoluminescence, photobleaching, photostability,
26 polymer

27 Metal nanoclusters encompass a new class of luminescent nanomaterials with metal cores
28 consisting of a couple of atoms up to nuclearities of few hundreds, therefore acting as an
29 intermediate state between isolated metal atoms and nanoparticles.^{1,2} They are receiving
30 increasing interest because of their significantly different optical, electrical and chemical
31 properties compared to their larger counterparts.³ For ultrasmall nanoclusters, the continuous
32 density of states breaks up into discrete energy levels leading to molecule-like properties such

33 as strong fluorescence. Due to their intrinsic fluorescence, metal nanoclusters have been
34 proposed for applications such as data storage, biological labeling and detection of metal ions,
35 nucleic acids and proteins.^{4,5} The fluorescence is typically observed as broadband emission
36 in the visible range and often displays characteristics of inhomogeneous broadening.⁶ The
37 presence of strong fluorescence combined with photostability, large Stokes shift and absence
38 of localized surface plasmon resonance peak in their extinction spectrum differentiates such
39 metal nanoclusters from their nanoparticle counterparts.^{2,3}

40 Silver nanoclusters are often difficult to synthesize in aqueous solution, as they tend
41 to aggregate and form larger particles. Generally, the formation of silver nanoclusters can be
42 achieved by reducing silver ions to a zero-valent state and stabilizing the as-generated
43 nanoclusters simultaneously to prevent further growth. Conventionally, reduction of silver
44 ions can be accomplished by using chemical reductants,^{7,8} electrochemistry⁹ or by irradiating
45 Ag^+ solutions with gamma-rays,¹⁰ UV,¹¹ visible light,^{12,13} microwaves¹⁴ or ultrasound.¹⁵
46 Stabilization can be attained by reducing the silver ions in the presence of stabilizer
47 molecules, such as polymers, dendrimers or deoxyribonucleic acid (DNA).^{2,3} Alternatively,
48 photostable silver nanoclusters can be produced in inorganic solids such as glasses^{16,17} and
49 zeolites¹⁸ by using femtosecond direct laser writing (DLW).

50 The development of femtosecond laser has been recognized in 1999 with the Nobel
51 Prize in Chemistry.¹⁹ The key features of the femtosecond laser are its exceptionally high
52 power density and precise delivery of pulse energies in time and space. Because of these
53 salient features, the femtosecond laser is useful in multi-photon DLW, where a tightly focused
54 laser beam is scanned in a photosensitive material to fabricate three-dimensional (3D)
55 structures.^{20,21,22} Such nanofabricated materials have been widely used for many applications
56 such as photonic crystals, metamaterials, microfluidics and biomedical implants.²¹
57 Furthermore, there has been a continuous effort in creating 3D,²³ fluorescent²⁴ and metal²⁵

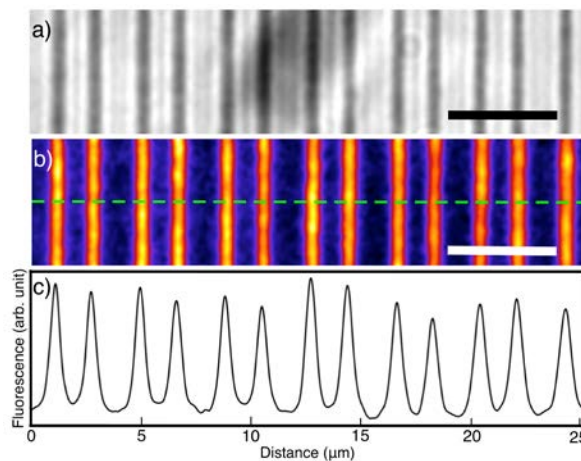
58 microstructures using this technique. Clearly, this two-photon-based absorption technique
59 outperforms other optical lithographic techniques in terms of 3D spatial resolution and
60 flexibility.

61 Poly(methacrylic acid) (PMAA) is an excellent stabilizing agent in generating brightly
62 fluorescent silver nanoclusters.^{12,13} Broadband visible light irradiation of an aqueous solution
63 of PMAA and AgNO₃ has been shown to form (Ag)_n@PMAA nanoclusters that emit red light
64 with a quantum yield of 18.6%.¹² However, this procedure is limited to the formation of
65 nanoclusters in solution. Furthermore, illuminating a solid thin film of PMAA containing
66 silver nitrate with similar broadband visible light leads to the formation of large silver
67 particles that are non-fluorescent. In addition, these nanoclusters generally lose their
68 fluorescence properties when the cluster-containing aqueous solution is dried or spin coated.

69 In this article, we demonstrate the submicron-scale fabrication of fluorescent
70 microstructures by stabilizing silver nanoclusters in a polymer film using DLW. We study the
71 optical properties of the nanoclusters and investigate the DLW-induced structural changes in
72 the polymer films. We found that the nanoclusters possess a broadband emission in the visible
73 range, and show photostability that is superior to the well-known Rhodamine 6G dye.

74 RESULTS AND DISCUSSION

75 **Written structures are fluorescent.** Figure 1a depicts the bright field image of line arrays
76 fabricated by DLW with laser intensity (I_{dlw}) of 80 GW/m², wavelength (λ_{dlw}) of 780 nm and
77 scanning speed of 10 μ m/s in 50% Ag@PMAA samples. The fluorescence images (Figure
78 1b) were acquired by exciting the written structures with an LED light source with wavelength
79 (λ_{exc}) of 473 nm and intensity (I_{exc}) of 2 MW/m² that is very low compared to the I_{dlw} . The
80 fabricated structures exhibit bright fluorescence as compared to the regions that were
81 unexposed to the writing beam (Figure 1b). The large difference in the fluorescence intensities
82 is attributed to the stabilization of fluorescent silver nanoclusters induced by DLW. Figure 1c
83 shows the intensity profile of the fluorescence across the line array (see marked line in Figure
84 1b) with an average line breadth of 540 nm.

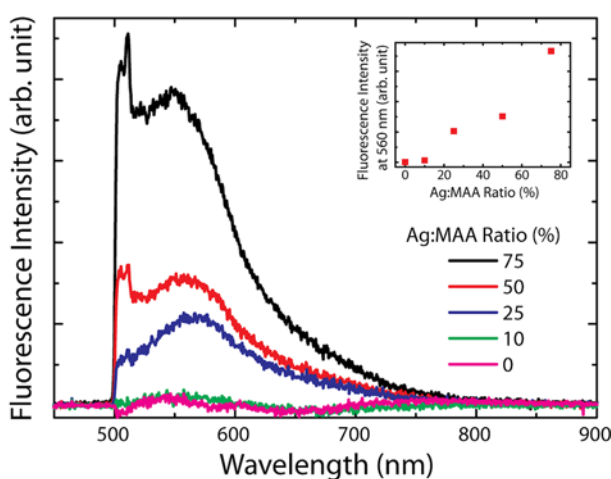


85

86 **Figure 1.** (a) Bright field microscopy image of a fabricated line array in 50% Ag@PMAA
87 samples ($I_{dlw} = 80$ GW/m², $\lambda_{dlw} = 780$ nm). Scale bars = 5 μ m. (b) Corresponding fluorescence
88 images of the same area ($\lambda_{exc} = 473$ nm). (c) Fluorescence intensity profile across the marked
89 line in (b).

90 **Fluorescence obtained from written structures depends on silver concentration.** To
91 investigate the origin of the fluorescence emanating from the fabricated structures in the
92 silver-containing polymers, we performed DLW ($I_{dlw} = 480$ GW/m²) on samples with
93 different Ag:MAA ratios (0 to 600%). For PMAA films without silver, this laser intensity
94 ($I_{dlw} = 480$ GW/m²) did not cause any observable changes to the film, therefore, we used an

95 I_{dlw} of 880 GW/m² to obtain a comparable reference sample (with I_{dlw} of 640 GW/m² as
96 threshold). The fluorescence emission spectra were recorded by exciting the region containing
97 written structures using a laser ($\lambda_{exc} = 473$ nm) operating at I_{exc} of ~ 2 MW/m². In all
98 measurements, the weak fluorescence signal originating from the glass substrate was
99 subtracted. As seen in Figure 2, the fluorescence increases with silver content indicating that
100 the signal is caused by silver nanoclusters in the PMAA matrix. Although structures written
101 on the samples having Ag:MAA ratios of 100%–600% ratios were also fluorescent, these
102 samples were not studied due to unwanted crystallization. Furthermore, addition of silver
103 beyond 75 % Ag:MAA ratio did not further enhance the fluorescence emission intensity
104 (Supporting Information, Figure S1).



105

106 **Figure 2.** Fluorescence emission spectra of laser-written silver nanoclusters in Ag@PMAA
107 films with Ag:MAA ratios ranging from 0 to 75 % ($\lambda_{exc} = 473$ nm). Inset shows the Ag
108 concentration dependence of the fluorescence intensity at 560 nm in Ag@PMAA samples

109 **AFM characterization shows the formation of grooves in the written structures.** We used

110 atomic force microscopy (AFM) to perform detailed analysis of the structures written on

111 Ag@PMAA films. Figure 3 shows the AFM images of the structures formed at different I_{dlw}

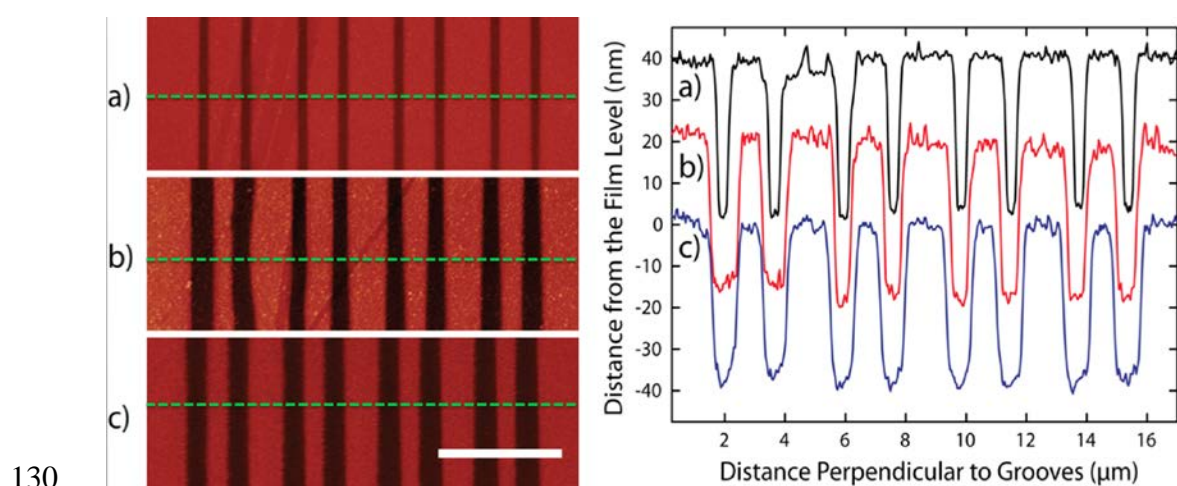
112 and the corresponding line profiles across the marked regions. Surprisingly, the line profiles

113 revealed the formation of 3D grooves at the location of the laser-written structures. The depths

114 and breadths of the grooves were extracted and averaged from 24 line profiles for each laser

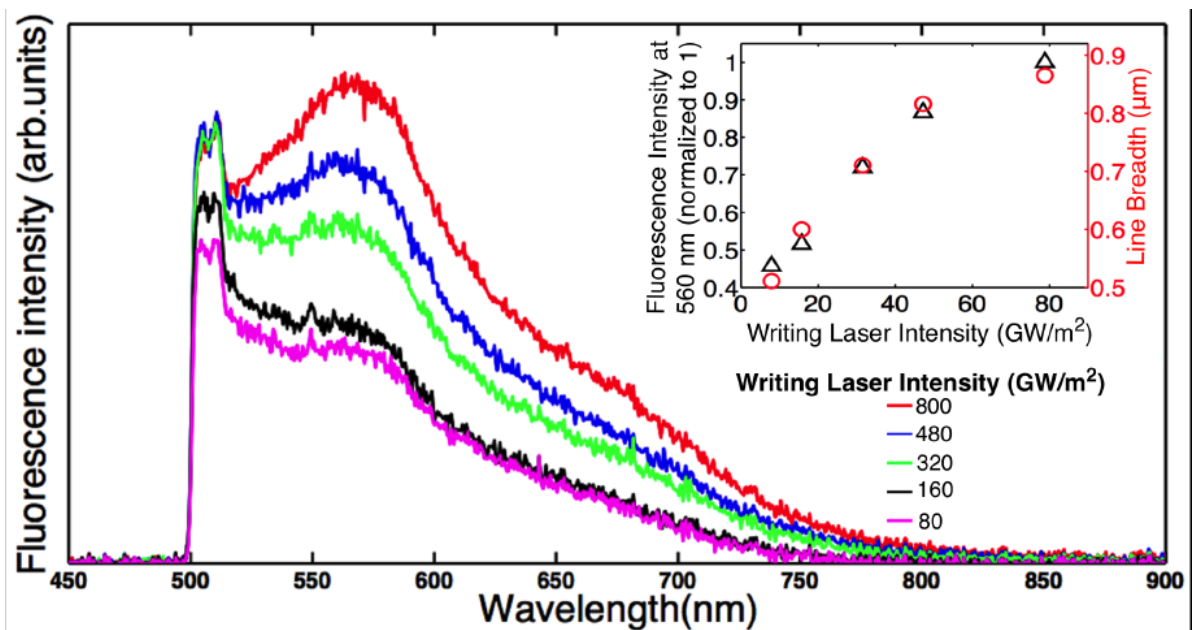
115 intensity. Correspondingly, the breadths of the grooves written at $I_{dlw} = 80, 240, \text{ and } 480$
116 GW/m^2 were found to be $380 \pm 40, 710 \pm 120, \text{ and } 850 \pm 80$ nm, respectively. The depth of
117 the grooves was measured to be 38 ± 1 nm for all cases while the thickness of the Ag@PMAA
118 film was evaluated as 38 ± 3 nm. Thus, the laser beam ablates most of the material at the
119 exposed regions (Figure 3). The line profiles also show sharp edges of the grooves suggesting
120 the absence of material aggregation as reported in DLW of microstructures in silver-
121 containing luminescent glass.^{16,17} Interestingly, despite the fact that most material is ablated
122 under the writing beam, the fluorescence signal is observed precisely at the location of the
123 written structures.

124 We used scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-
125 EDS) to determine the presence of silver at the ablated regions of the Ag@PMAA sample.
126 EDS line profiles perpendicular to the written fluorescent lines show a similar level of Ag at
127 written lines as well as at unexposed areas indicating a constant distribution of Ag in the film
128 (Supporting Information, Figure S2). This confirms that the fluorescence signal originating
129 from the written structures is due to the presence of silver despite the ablation.



131 **Figure 3.** AFM images of structures written with I_{dlw} of (a) 80 GW/m^2 , (b) 240 GW/m^2 and
132 (c) 480 GW/m^2 in 50 % Ag@PMAA samples. Scale bar = $5 \mu\text{m}$. The full width at half maxima
133 (FWHM) of the grooves measured from line-cut topography profiles (right) are (a) 380 ± 40
134 nm, (b) 710 ± 120 nm, and (c) 850 ± 80 nm, respectively. For clarity, the line profiles for (a)
135 and (b) have been vertically shifted for 40 and 20 nm, respectively.

136 **The breadth of lines and fluorescence obtained from the written structures increase with**
 137 **laser power.** By adjusting writing parameters such as laser intensity and exposure time, *i.e.*,
 138 scanning speed, the fluorescence intensity of the fabricated structures can be controlled.
 139 Figure 4 shows the fluorescence emission spectra that are obtained from the structures written
 140 with different I_{dlw} . As expected, the fluorescence is highest in the structure written with the
 141 highest I_{dlw} . Close inspection of the fluorescence images of the written structures further
 142 reveals an increase in the breadth of the lines with I_{dlw} (Figure 4, inset). It is worth noting that
 143 a steady fluorescence signal coming from the entire breadth of the written lines is observed
 144 regardless of the writing laser intensity. Since the transverse spatial resolution of the
 145 microscope (~ 200 nm) is better than the breadths of the written lines (400-900 nm), our
 146 observations suggest that the fluorescence originates from nanoclusters at the bottom of the
 147 grooves where most of the material is removed. This result is consistent with our SEM-EDS
 148 analysis.

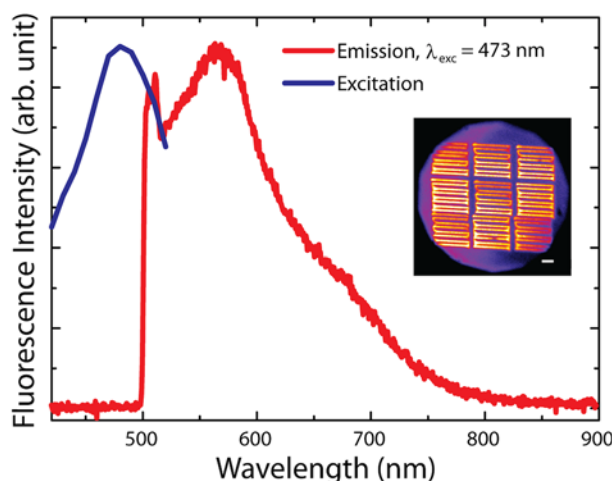


149

150 **Figure 4.** Fluorescence emission spectra ($\lambda_{exc} = 473$ nm) recorded from the structures written
 151 at different I_{dlw} : 80, 160, 320, 480 and 800 GW/m². Inset shows the fluorescence intensity at
 152 560 nm and the corresponding breadth of the fluorescent grooves against writing power.

153 **Optical properties of nanoclusters are similar in character to those observed in solution.**

154 To further investigate the optical properties of nanoclusters, we analyzed the fluorescence
155 excitation and emission spectra of the DLW-fabricated microstructures (Figure 5). The
156 written structures show fluorescence emission when excited with wavelengths ranging from
157 420 nm to 520 nm, with an excitation maximum at 470 nm. Correspondingly, when excited
158 with 473 nm, the written structure shows a broadband fluorescence emission at 500 to 850
159 nm, with a peak at around 560 nm. **Based on the position and the shape of the emission**
160 **spectrum, we consider that the silver nanoclusters** are similar in character to those observed
161 in solution.^{12,13}

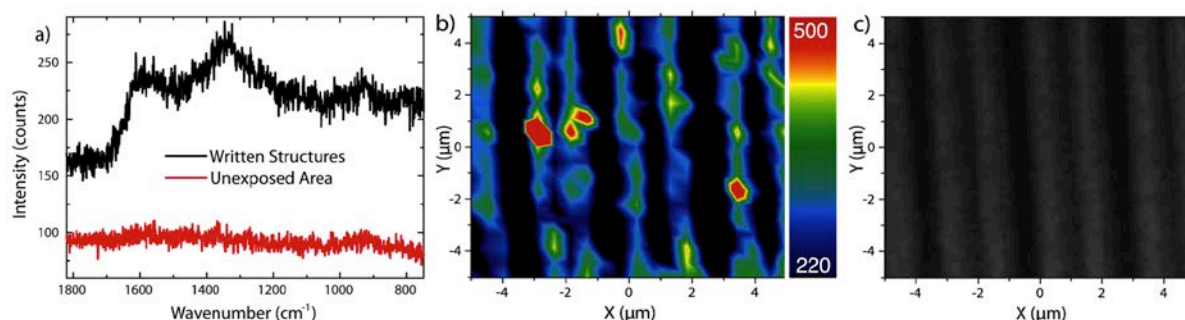


162

163 **Figure 5.** Excitation (blue curve) and emission (red curve) spectra ($\lambda_{exc} = 473$ nm) obtained
164 from fluorescent silver nanoclusters in microstructures (inset). Scale bar = 5 μ m. The
165 excitation spectrum was measured by evaluating the total emission counts between 532 nm
166 and 650 nm. Inset shows the fluorescence image of the investigated microstructures.

167 The emission spectrum from the written structures also exhibits a sharp peak at around 510
168 nm. We suspect that this peak is related to an enhanced Raman scattering effect, whereas the
169 apparent cut-off of the spectrum at shorter wavelengths results from the 500 nm long-pass
170 filter used to avoid unwanted excitation light. To investigate the suspected Raman peak, we
171 measured the Raman spectra from the Ag@PMAA thin films (Figure 6a). The Raman
172 spectrum of the unexposed area does not show any observable signal, whereas the written
173 structures show two broad peaks at 1340 and 1590 cm^{-1} , corresponding to ν_{COO^-} (sym.) and

174 ν_{COO} (asym.) vibrations, respectively.²⁶ The lines observed in the Raman microscopy images
175 of the written structures (Figure 6b) coincide well with the lines in the corresponding
176 brightfield microscopy image (Figure 6c), strongly suggesting that Raman signals are highly
177 localized at the written structures.



178

179 **Figure 6.** Raman spectra (a) detected from the written structures (black curve) and unexposed
180 regions (red curve). (b) Raman microscopy imaging of the written structures at 1340 cm^{-1} .
181 Color scale bar corresponds to the Raman signal counts. (c) Bright field microscopy image of
182 the corresponding area.

183 In addition, we measured the emission spectra of the fluorescent structures with a 473 nm
184 LED (I_{exc} of 1 MW/m^2) and a 473 nm diode laser (I_{exc} of 1 MW/m^2) (Figure S4). The emission
185 spectrum recorded with the 473 nm LED does not show a peak at 510 nm, further supporting
186 our claim of the enhanced Raman signal detection. In addition, we found that the peaks
187 obtained by exciting the written structures with 473 nm laser and 532 nm diode laser overlap
188 at the same Raman shift range (1300–1700 cm^{-1}) from the excitation wavelength, thus
189 coinciding with the observed broad Raman signals (Figure S5). Essentially, our observations
190 suggest that nanoclusters interact with the encapsulating polymer through a charge transfer
191 mechanism to enhance the Raman signal as reported in earlier work.²⁷ Furthermore, as the
192 nanoclusters are too small to support collective electron oscillations, we can disregard
193 plasmonic enhancement effects.

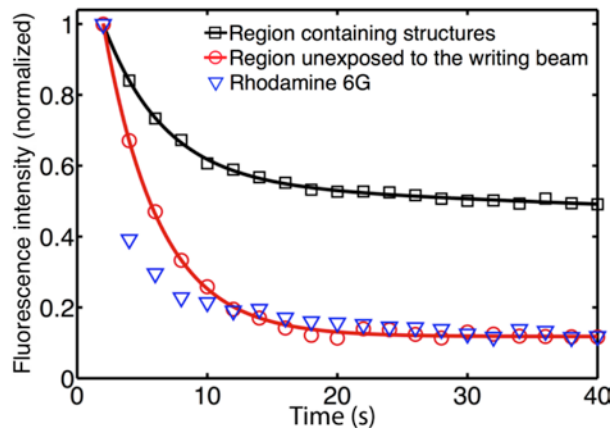
194 **Stabilized nanoclusters show excellent photostability.** We also studied in detail the
195 photobleaching of the silver nanoclusters (Figure 7). In general, fluorescence was detected in
196 three parts of the sample: written structures (or areas which are exposed to the writing beam),

197 unexposed areas of the Ag@PMAA film (background), and glass (substrate). Indeed, in
198 addition to the written structures, fluorescence was also detected in the sample area that was
199 unexposed to the writing beam (Figure 7). The origin of fluorescence in the unexposed area
200 is most likely caused by the generation of nanoclusters in the solution during sample
201 preparation.²⁸ It is possible that such nanoclusters become kinetically trapped in the film
202 during spin coating and are thus not properly protected by the MAA units, and therefore,
203 produce a fluorescence signal that is highly unstable to illumination. The fluorescence from
204 the glass was found to be weak and was subtracted from the emission data.

205 The bleaching data were recorded from two distinct areas: from an area unexposed to
206 the writing beam and from an area containing written structures. The area containing written
207 structures includes area exposed to as well as area unexposed to the writing beam (Figure 5
208 inset). Additionally, bleaching of a Rhodamine 6G reference sample was tested. These data
209 were recorded at two-second intervals for 40 seconds while continuously irradiating the
210 sample with an intensity $\sim 0.3 \text{ MW/m}^2$ ($\lambda_{exc} = 473 \text{ nm}$ laser diode). The total fluorescence
211 intensity is calculated by integrating the area under the emission spectrum. The bleaching data
212 were normalized and plotted as a function of time (Figure 7). Initially, the fluorescence
213 intensities recorded from the area unexposed to the writing beam and from the area containing
214 the written structures are about at the same level, thus no extra fluorescence was induced by
215 DLW. However, under continuous irradiation the area containing written structures bleaches
216 significantly slower than the area unexposed to the writing beam. This suggests that DLW
217 stabilizes the existing nanoclusters rather than that it creates new ones.

218 Furthermore, Figure 7 shows that the fluorescence obtained from the unexposed area
219 bleaches to approximately 10% of its initial value within 20 seconds. The bleaching curve
220 obtained from this unexposed area can be fitted by a single exponential decay equation
221 $y = a \cdot \exp(-t/\tau_1) + c$, with a bleaching time constant (τ_1) of 4.3 s, where a , t , and c are amplitude,

222 time and offset parameters, respectively. On the other hand, the fluorescence bleaching curve
 223 of the area containing written structures can be fitted accurately by a double exponential decay
 224 equation $y=a*\exp(-t/\tau_1)+b*\exp(-t/\tau_2)$ with bleaching time constants τ_1 and τ_2 of 4.7 s and 350
 225 s, respectively. Table 1 summarizes the bleaching time constants resulting from the fitting.
 226 The bleaching time constant τ_1 has almost the same value in both of the fits, and therefore,
 227 the fast-decaying τ_1 is assigned to the bleaching of the area unexposed to the writing beam.
 228 The time constant τ_2 is associated with the bleaching of the fluorescence originating from the
 229 area exposed to the writing beam, *i.e.*, the written structures. The fluorescence from the
 230 written structures is highly photostable having the bleaching time constant of 350 s.



231

232 **Figure 7.** Photobleaching curves of area containing written structures, area unexposed to
 233 writing beam and Rhodamine 6G dye. The microstructures were written with $I_{dlw} = 480$
 234 GW/m^2 ($\lambda_{dlw} = 780 \text{ nm}$) in 50% Ag@MAA film. The bleaching was induced by irradiating
 235 the samples with a laser ($\lambda_{exc} = 473 \text{ nm}$, $I_{exc} = 0.3 \text{ MW}/\text{m}^2$). The solid lines represent single
 236 exponential and biexponential fits to the data points respectively from the area unexposed to
 237 writing beam and from area containing written structures.

238 **Table 1. Comparison of bleaching time constant of written structures and background.**

	bleaching time constant of background (τ_1)	bleaching time constant of written structure (τ_2)
Area Containing Structures	4.7 s	350 s
Area Unexposed to Writing Beam	4.3 s	---

239

240 We also compared the photostability of $(Ag)_n@PMAA$ nanoclusters against the
 241 conventional fluorescent dye, Rhodamine 6G. The fluorescence of the dye bleaches even
 242 faster than the $Ag@PMAA$ film background under identical experimental conditions, thus
 243 showing the high photostability of the written structures (Figure 7). This observation agrees
 244 with earlier studies on the photostability of silver nanoclusters in other scaffolds, such as
 245 glass,^{16,17} zeolites¹⁸ and DNA.⁸ It is worth noting, that the fluorescence images (Figure 1) and
 246 spectra (Figures 2, 4 and 5) were recorded with I_{exc} of 2 MW/m². Already such low laser
 247 intensity bleaches the unexposed $Ag@PMAA$ background within a second, leaving the
 248 written structures as the main source of fluorescence in these experiments.

249 **CONCLUSIONS**

250 We have demonstrated the DLW of fluorescent microstructures by stabilizing silver
 251 nanoclusters in silver-containing PMAA films. Fluorescent structures were written by a
 252 tightly focused near-infrared femtosecond laser beam, thereby reaching line breadths of
 253 submicron scale. To the best of our knowledge, this is the first report about the DLW of
 254 fluorescent silver nanoclusters in an organic matrix. The formed nanoclusters are highly
 255 photostable. This fabrication method could open new opportunities in nanophotonics
 256 applications like imaging, labeling, and metal ion sensing. Furthermore, we anticipate the

257 applicability of our technique in the synthesis of similar metal nanoclusters that are embedded
258 in relevant polymer matrices.

259 METHODS

260 **Sample preparation.** Silver-containing thin films of PMAA (Ag@PMAA) were prepared by
261 spin coating. Aqueous solutions of PMAA (PolySciences, $M_w = 100\,000$ g/mol) and AgNO_3
262 (Sigma-Aldrich, > 99.8 %) were mixed to obtain a PMAA concentration of 1.5 wt% and
263 Ag:MAA ratios ranging from 0 to 600 %, *e.g.*, a ratio of 50 % corresponded to one Ag^+ ion
264 per two MAA units. Before spin coating, the borosilicate glass substrates ($22\text{ mm} \times 22\text{ mm} \times$
265 0.19 mm) were cleaned by rinsing with ethanol and water and dried with nitrogen. The thin
266 films were spin coated on the substrates at 1500 RPM for 120 s. Subsequently, the films were
267 dried in vacuum for 12 h. The water used throughout experiments was Milli-Q grade with a
268 resistivity of $18.2\text{ M}\Omega\cdot\text{cm}$.

269 **Direct laser writing.** The DLW setup (Supporting Information, Figure S7) was employed to
270 fabricate 2D structures in Ag@PMAA samples. A pulsed laser beam (780 nm, 80 MHz, 290
271 fs) was directed and focused by a microscope objective lens (100 \times , NA = 1.4, oil, Leica) onto
272 the sample that is mounted on a 3D nanopositioner. In order to write the structures, the
273 samples were scanned with a speed of $10\text{ }\mu\text{m/s}$ over a fixed laser beam with a regulated input
274 power ($P = 5\text{--}50\text{ mW}$ corresponding to illumination intensities of $80\text{--}800\text{ GW/m}^2$). The
275 focused writing laser spot size was 284 nm in diameter, estimated by the formula, spot size =
276 $0.51 \cdot \lambda_{dlw} / \text{NA}$, where λ_{dlw} is wavelength of laser beam and NA is numerical aperture of
277 objective lens. Samples with Ag:MAA ratio over 75 % were neglected due to severe
278 crystallization observed in those samples (see Supporting Information, Figure S1). An
279 incorporated brightfield microscopy imaging arm was used to monitor the fabrication of the
280 structures.

281 **AFM and SEM characterization.** The thickness of Ag@PMAA films was determined by
282 atomic force microscopy (AFM) in tapping mode (Veeco Dimension 5000 AFM with
283 Nanoscope V controller). The film was scratched with a scalpel and the AFM tip
284 (HQ:NSC15/Al BS, MikroMasch) was scanned perpendicular to the scratch. In addition,
285 AFM was used for detailed characterization of the topographical features of the samples.
286 Field-emission scanning electron microscopy was performed at 1.5 keV electron energy
287 (JEOL JSM-7500FA). The (Ag)_n@PMAA thin film sample was coated with thin layer of
288 carbon prior to measurements (Emitech K950) to promote sample conductivity. Energy-
289 dispersive X-ray analysis was performed with the JSM-7500FA using a Be thin film window
290 and liquid nitrogen cooled detector. Line spectra across DLW written structures were
291 recorded using 10 keV electron energy to analyze the composition of samples.

292 **Optical characterization.** The optical properties of the fabricated structures were
293 characterized using a custom-built fluorescence microscope (Supporting Information, Figure
294 S8). The fluorescence emission spectra were recorded from a set of laser written line array
295 structures using a spectrometer and the excitation spectrum was measured using a
296 photomultiplier tube (see Supporting Information for details). The fluorescence images were
297 colored according to their greyscale values with ImageJ software. Absorption spectra of the
298 thin films were recorded in the UV–visible range with PerkinElmer Lambda 950 UV/Vis/NIR
299 absorption spectrometer. Raman scattering measurements were carried out with a Horiba
300 Jobin-Yvon Labram HR 300 using 785 nm IR diode laser excitation source with 100x air
301 objective (laser spot diameter < 1 μm). Raman mapping was performed by measuring 20x20
302 point spectra from 5x5 μm area. The laser intensity in Raman measurements was kept low
303 compared to DLW writing intensity.

304 ASSOCIATED CONTENT

305 **Supporting Information.** Detailed description of experimental setups, measurements and
306 additional data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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312 P. K. and J. H. contributed equally to this work.

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