

# Supporting Information

## Photochemistry of Bismuth and Silver Containing Glasses under Femtosecond Laser Irradiation: Energy Transfers and 3D-localized Background-Free Near-Infrared Fluorescence Emission

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(A) Luminescence properties of PZn0.17Bi glass showing the characteristic excitation band of Bi<sup>3+</sup> for 440 nm emission and its corresponding emission band for the 257 nm excitation.

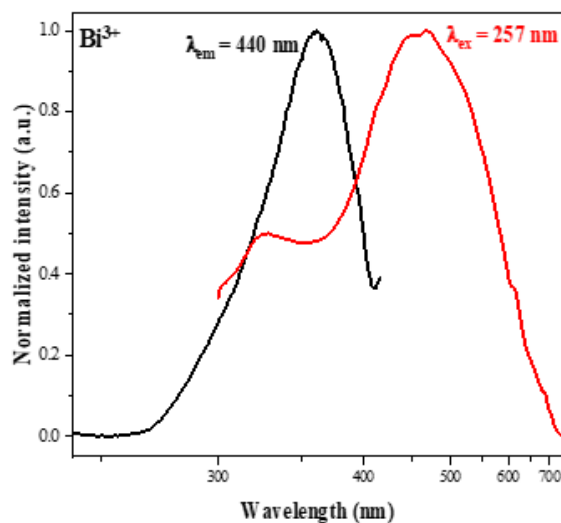


Figure S 1 : Excitation and Emission spectroscopy of Bi<sup>3+</sup>

(B) Wide field fluorescence microscopy image of the Fs DLW induce structural matrix in PZn:Ag(S2.a) and PZn:Ag0.17Bi (S2.b) glasses respectively when excited with 375 nm laser diode has been performed on PZn:Ag and PZn:Ag0.17Bi using similar irradiation parameters. Matrix correspond to an identical square patterns of 50  $\mu\text{m}$  X 50  $\mu\text{m}$  structure with interline of 10  $\mu\text{m}$  resulting from different laser irradiances and sample displacement velocities under 160  $\mu\text{m}$  of the glass surface. The patterns were induced by linear translation of the glass sample with a control motion of speed from 10 to 100  $\mu\text{m}\cdot\text{s}^{-1}$  and different laser irradiance range from 3.70  $\text{TW}\cdot\text{cm}^{-2}$  to 5.74  $\text{TW}\cdot\text{cm}^{-2}$ . This range of laser irradiance has been chosen as standard to triggers

both silver and the bismuth photochemistry without damaging the glass sample. The pattern was inscribed with an increase sample displacement velocity corresponding to the decrease of the accumulation dose, and an increase of the laser pulse irradiance.

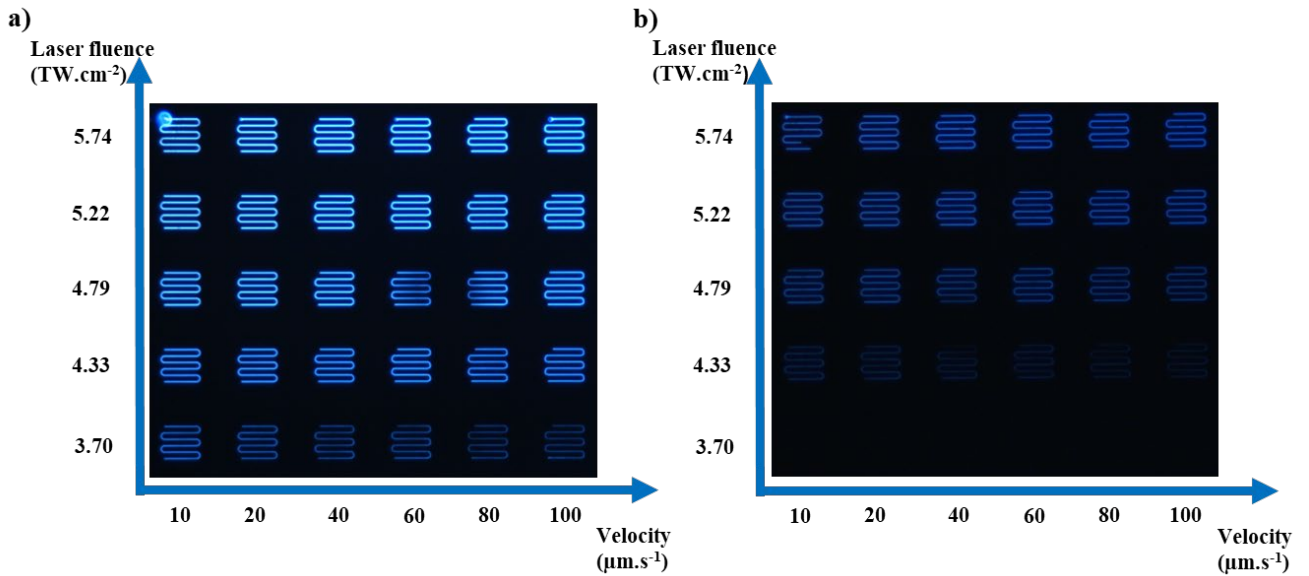


Figure S 2: Wide field fluorescence images of DLW induced pattern with different laser intensity and sample displacement velocity in (a) PZn:Ag glass and (b) PZn:Ag<sub>0.17</sub>Bi glass

(C) Confocal wide field fluorescent images of  $\text{Ag}_m^{x+}$  (S3.a) and  $\text{Bi}^{2+}$  (S3.b) fluorescence of the laser inscribed patterns for different laser intensity and sample displacement velocities similar to what was reported S2.b. Fluorescence from  $\text{Ag}_m^{x+}$  can only be observed for the patterns inscribed with laser irradiance above  $3.70 \text{ TW.cm}^{-2}$ . While a red fluorescence, originating from  $\text{Bi}^{2+}$  is seen whatever the laser irradiance used in this study. S3.c combines the fluorescence image from S3.a and S3.b with similar fluorescence magnitude to illustrate the spatial distribution and interplay between  $\text{Ag}_m^{x+}$ , and  $\text{Bi}^{2+}$  fluorescence. As result, the  $\text{Bi}^{2+}$  fluorescence dominate at lower laser irradiance and cumulating dose, while the  $\text{Ag}_m^{x+}$  fluorescence become more prominent at higher irradiance and cumulating dose. The inset shows the magnified image of a given pattern, highlighting double-track fluorescence for both  $\text{Ag}_m^{x+}$  and  $\text{Bi}^{2+}$  that might preferentially formed at the edge of the voxel of laser/matter interaction upon the laser passes.

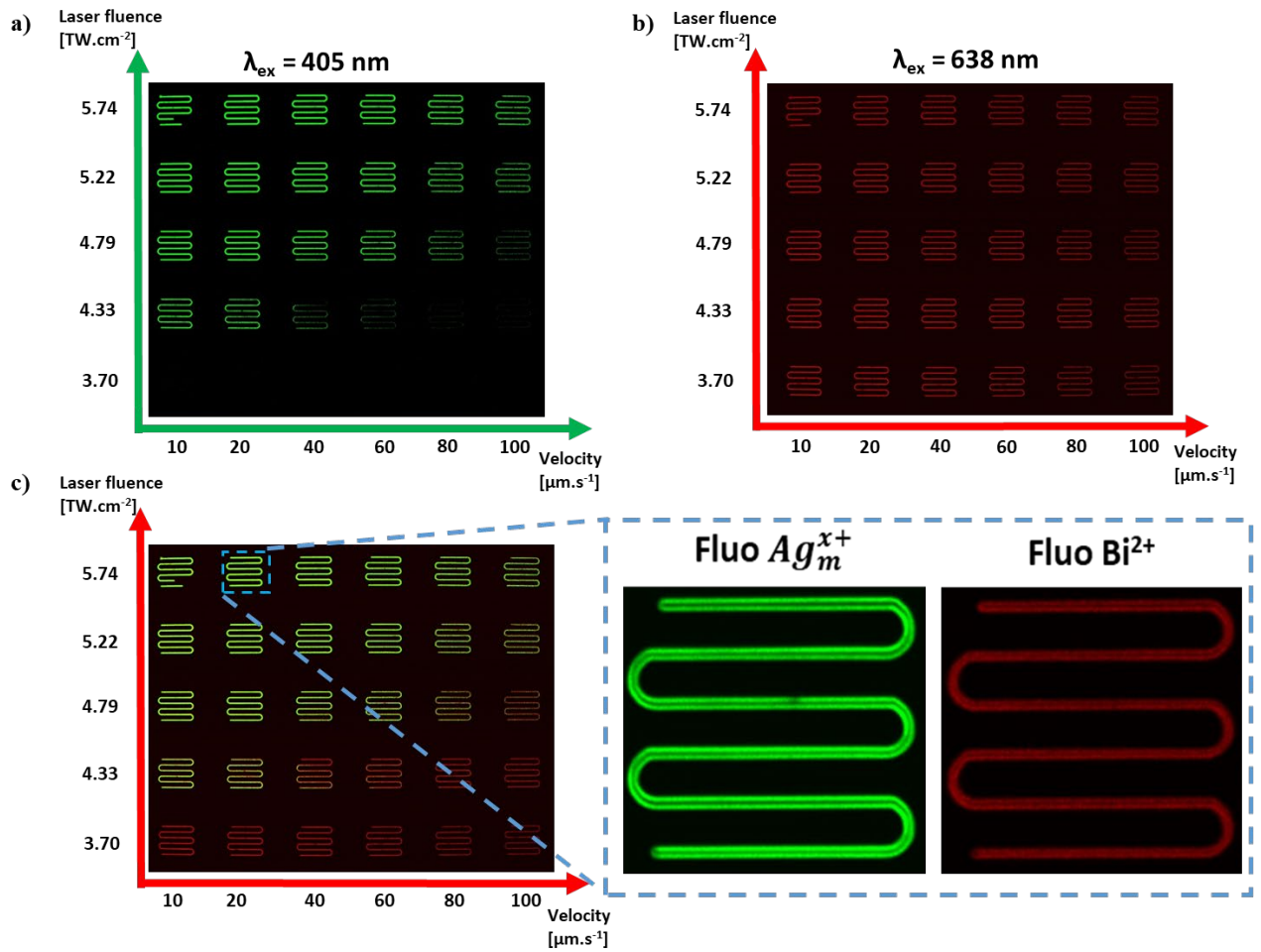


Figure S 3: Wide field confocal fluorescence images of laser inscribed patterns for (a) 405 nm excitation and fluorescence in 480 nm - 580 nm range, (b) excitation at 638nm and fluorescence in 680 nm -750 nm range, (c) fusion of both images a and b.

(D) Emission spectroscopy of Bi<sup>2+</sup> (S4.a) and Bi<sup>+</sup> (S4.b) of a pattern inscribed with the same laser parameter (5.74 TW.cm<sup>-2</sup> and 20 μm.s<sup>-1</sup>) in PZnAg:0.17Bi and PZn0.17Bi glasses for the 532 nm excitation. An enhancement of about 10 times of both Bi<sup>2+</sup> and Bi<sup>+</sup> emissions intensity is observed in presence of silver. The intensity of both Bi<sup>2+</sup> and Bi<sup>+</sup> emissions enhances about 10 times in the presence of silver (PZn:Ag0.17Bi glass).

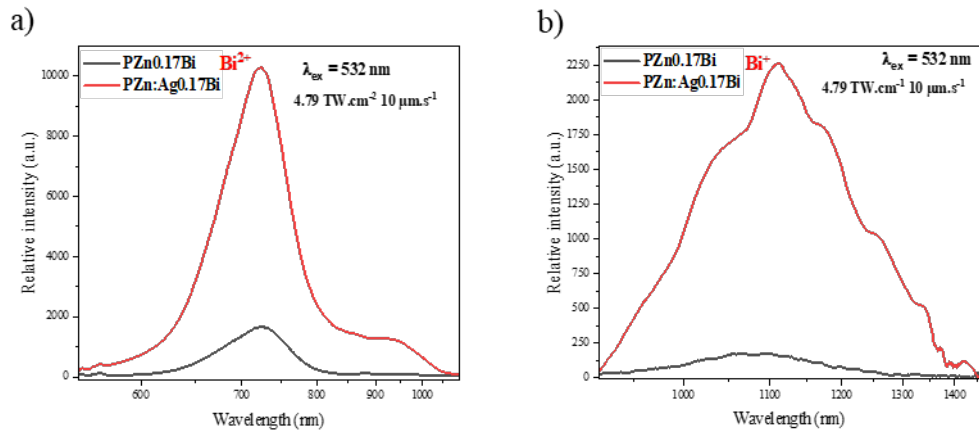


Figure S 4: (a, b) Bi<sup>2+</sup> ions and Bi<sup>+</sup> ions emission respectively of a DLW pattern in both PZn0.17Bi and PZn:Ag0.17Bi glasses for 532 nm excitation.