Electronic Supplementary Information (ESI):

Flexible Au Nanoparticles Arrays induced Metal-Enhanced Fluorescence toward Pressure Sensor

Changqing Ye,[a,b] Mingzhu Li,[*a] Mianqi Xue,[c] Weizhi Shen,[a,b] Tingbing Cao,[c] Yanlin Song[*a] and Lei Jiang[a]

[a]*Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Organic Solids, Laboratory of New Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, P. R. China E-mail: ylsong@iccas.ac.cn; mingzhu@iccas.ac.cn; Fax: (+86) 10- 6252 9284.*

[b]*Graduate University of Chinese Academy of Science, Beijing, 100049, P. R. China*

[c]*Department of Chemistry, Renmin University of China, Beijing, 100872, P. R. China*

Fabrication of the Au nanoparticles arrays on PDMS

Thin metal films were first evaporated onto poly-di-methyl-siloxane (PDMS) stamps that were generated by replica molding from photo-lithographically fabricated masters. These metal-coated stamps, when brought into contact with a second substrate having appropriate surface chemistry, selectively transferred the metal film from the raised features of the PDMS to the substrate.

Soft lithography and rapid prototyping were used to fabricate features in SU-8 (Micro-Chem Corp.), which were subsequently replica-molded using a PDMS prepolymer to fabricate the flexible stamps. The obtained stamps were first plasma-treated for 10 min to be hydrophilic and then immediately immersed into 20 nm Au nanoparticle colloid (Sigma-Aldrich®) for 24 h, which was repeated for 3 times. A second piece of fresh PDMS was also plasma-treated for 10 min, and then coated with (3-mercaptopropyl)-trimethoxysilane (Sigma-Aldrich®) in 10 mM ethanol solution at 60^{o}C for less than 30 min. The Au nanoparticles-coated PDMS stamp and self-assembled monolayer (SAM)-coated PDMS were put in contact with each other without additional pressure, and separated to achieve the gold wire arrays on the self-assembled monolayer (SAM)-coated PDMS substrate.

Fluorescence imaging measurement

The confocal mode of Witec-Alpha scanning near-field optical microscope was used for fluorescence imaging with 532 nm excitation. The fluorescence was separated from the excitation light by an optical long pass filter (OG570, Schott). A

20X/0.40 LWD objective len was used to collect the fluorescence. The scanning area was 12 μm×12 μm. The image sampled 12 pixels of points per line, 12 pixels of lines per image. For each sample point, the fluorescence intensity was integrated in the range from 540 nm to 780 nm to obtain the integrated fluorescence intensity. The spectra integration time was 1 s. A two-dimension contour map of the integrated fluorescence intensity of the whole scanning area was plotted.

The fluorescence intensity variation in nine steps with the external pressure fluctuation:

An image sequence change of the integrated fluorescence intensity was directly monitored in the Fig. S1. Correspond to the strain value variation from 0 to 0.23%, the area of higher fluorescence intensity on the contour map increased near the Au nanoparticles arrays as the force was pressed on the sample in the direction parallel to the line (Fig. S1, step 1-5). In reverse process, the images returned to the original pattern (Fig. S1, step 6-9).

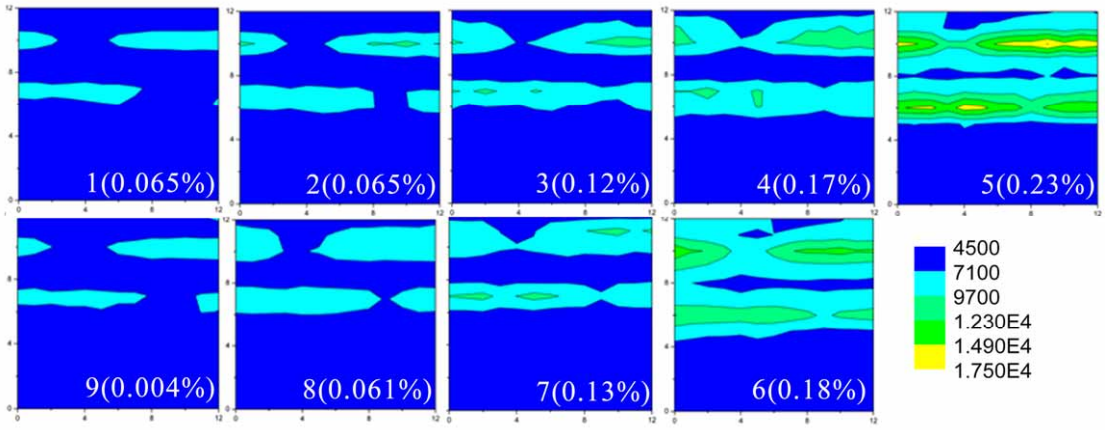

Fig. S1 The contour maps of the integrated fluorescence intensity as the strain value increases from 0 to 0.23% (step 1-5) and then reverts (step 6-9).

Detailed derivation of the Fluorescence-Pressure equation

Lakowicz and coworkers have proved that the distance between the metal and fluorophores (d) and the enhanced factor of the fluorescence emission intensity (N) obeys the exponential function as such[1]:

$$N(d) = N^{(d=0)} \exp(-\frac{d}{R_r}) + 1 \qquad (S-1),$$

where Rr is the characteristics distances over which these effects decrease to 1/e exponentially. In Fig. 2c, the fluorescence intensity of Zone F, D (I_F, I_D) and the strain value (γ) was perfectly fitted this exponential relationship:

$$I_F = 891\exp(\frac{\gamma}{0.12}) + 6363 \qquad (S-2);$$
$$I_D = 388\exp(\frac{\gamma}{0.092}) + 5877 \qquad (S-3),$$

which can be generalized into one equation:

$$I = A\exp(\frac{\gamma}{B}) + C \qquad (S-4),$$

where A,B,C are three constant. The strain value (γ) increases, the intervals of Au nanoparticles are narrowed correspondingly. The collective enhanced fluorescence is strengthened owing to the strain-dependent manner of MEF.

According to Hooke's law, the pressure (P) exerted on the PDMS obeys the function:

$$P = G \cdot \gamma \qquad (S-5),$$

where G (ca. 400 KPa) is the elastic modulus of the elastomer. The strain value (γ) can be transformed into the pressure (P) which is exerted on the sample. The function relationship of the pressure (P) and the fluorescence emission intensity (I) is:

$$I = A\exp(\frac{P}{B \cdot G}) + C \qquad (S-5)$$

Thus by monitoring the fluorescence intensity, the pressure exerted on the substrate can be measured.

The fluorescence intensity of control area (zone B) obeys linear relationship with the strain value: $I = 3209 \cdot \gamma + 4991 \qquad (S-6)$.

Reference

1. K. Ray, R. Badugu and J. R. Lakowicz, *Langmuir*, 2006, 22, 8374-8378.