Supplementary Information

Improved Charge Transport across Bovine Serum Albumin – Au Nanoclusters Hybrid Molecular Junction

*Ashwini Nawade*<sup>a,‡</sup>, *Kumar Babu Busi*<sup>b,‡</sup>, *Kunchanapalli Ramya*<sup>a</sup>, *Goutam Kumar Dalapati*<sup>a</sup>, *Sabyasachi Mukhopadhyay*<sup>a,*</sup>, *Sabyasachi Chakrabortty*<sup>b,*</sup>

<sup>a</sup>Department of Physics, SRM University, AP- Andhra Pradesh, Andhra Pradesh, 522 240, India

<sup>b</sup>Department of Chemistry, SRM University, AP- Andhra Pradesh, Andhra Pradesh, 522 240, India

‡ These authors contributed equally.

Email - sabyasachi.c@srmap.edu.in; sabyasachi.m@srmap.edu.in
Contents

Experimental section

S1. Materials

S2. Sample nomenclatures

S3. X-ray photoelectron spectroscopy (XPS) characterization

S4. Electrical Characterization of protein films

S5. Electrical conductance data analysis method

Additional Results

S6. UV-Visible absorbance and PL characteristics of control samples

S7. Temperature-dependent PL emission spectrum of different BSA-Au samples

S8. I-V data of films prepared with various concentrations

S9. Summary of Electrical conductance data analysis for films prepared with various concentrations
**S1. Materials**: Tetrachloroauric (III) acid trihydrate (HAuCl₃·3H₂O), Bovine Serum Albumin (BSA), procured from Himedia, sodium hydroxide pellets (NaOH) purchased from Finar. Fluorine-doped Tin Oxide (FTO) glass substrates were supplied by Global Nanotech, Mumbai. Alfa Aesar supplied indium Gallium Eutectic. All materials were used without purification.

**S2. Sample nomenclature**: BSA protein with “BSA” represents unmodified BSA protein, whereas “Control” represents BSA protein after adding gold salt, without letting them react to get Au NCs. Different amounts of Au on each BSA molecule (i.e., six different loading morphology) were carried out by altering their effective concentrations during preparation, shown in Table S1.

| Sample Name | Synthetic Condition Employed | Effective mole ratio (BSA : Au) | PL QY (%) |
|-------------|------------------------------|--------------------------------|-----------|
| Au 1        | While 40 mg/mL was used during Au NC synthesis | 1 : 1398                      | 5.1       |
| Au 2        | While 25 mg/mL was used during Au NC synthesis | 1 : 2243                      | 6.8       |
| Au 3        | While 18 mg/mL was used during Au NC synthesis | 1 : 3115                      | 3.5       |
| Au 4        | While 12.5 mg/mL was used during Au NC synthesis | 1 : 4546                      | 1.6       |
| Au 5        | While 9 mg/mL was used during Au NC synthesis | 1 : 6214                      | 0.8       |
| Au 6        | While 6.25 mg/mL was used during Au NC synthesis | 1 : 8947                      | 0.03      |

**Table S1a**: Synthetic conditions of various Au samples where the red color arrow indicates the effective increase of Au atoms per BSA and PL QY measurements from Au 1 to Au 6.

We have used Au 1, Au 2, Au 4, and Au 6 for subsequent measurements to obtain their trends in electrical conduction. Similar small fluorescent Au NCs reported in the literature are listed in Table S2.
Table S1b: TRPL decay analysis of various BSA-Au NCs hybrid. Three exponential fittings were employed to obtain relative amplitude and corresponding lifetime values.

| Sample name | Relative Amplitude | PL decay (sec) | Average Lifetime |
|-------------|--------------------|---------------|-----------------|
|             | $A_1$     | $A_2$     | $A_3$     | $\tau_1$   | $\tau_2$   | $\tau_3$   |               |
| Au 1        | 1.95      | 1.41      | 96.65     | 3.55E-08   | 1.81E-09   | 1.00E-06   | 9.67E-07      |
| Au 2        | 1.84      | 1.39      | 96.77     | 3.02E-08   | 1.38E-09   | 9.89E-07   | 9.58E-07      |
| Au 3        | 3.7       | 95.4      | 0.9       | 9.20E-08   | 9.57E-07   | 2.74E-09   | 9.16E-07      |
| Au 4        | 2.45      | 4.31      | 93.24     | 3.18E-09   | 8.09E-08   | 9.97E-07   | 9.33E-07      |
| Au 5        | 4.75      | 2.88      | 92.37     | 7.50E-08   | 1.81E-09   | 9.65E-07   | 8.95E-07      |
| Au 6        | 1.68      | 19.11     | 79.21     | 2.06E-07   | 7.92E-09   | **9.45E-10**| 5.72E-09      |

Table S2: Fluorescent Au NCs size from HRTEM analysis reported in the literature
S3. X-ray photoelectron spectroscopy (XPS) characterization:

The surface elemental analysis of the sample was determined by X-ray photon spectroscopy (XPS) measurements were conducted using Al Kα (1486.6 eV) radiation (PHI VersaProbe III). The measure was carried out with a detection angle of 45 °C, using pass energies at the analyzer for survey spectra as 6.5 eV and detailed spectra as 280 eV, respectively. The x-ray power provided was 24.17 Watt, and the beam diameter (x-ray spot size) was 100 µm. The exact surface spot size of the sample (5 × 5 µm) was selected for the XPS analysis, which took 20 minutes to complete the survey. The samples were neutralized with electrons from a flood gun (current 20 µA) to compensate for the charging effects of the surface. The energy resolution is ≤0.5eV for our well-tuned instrument. We obtained it by measuring the FWHM of the Ag3d Peak, with data collected by using the least pass energy. For calibrating the binding energy scale, Au and Cu peaks are used at 83.96eV and 932.62eV, respectively, after the sample is sputter cleaned. PHI VersaProbe III typically calibrates the instrument to within 0.1eV on those peaks. Therefore, we get the calibration peak for Au at 83.95 eV. The instrument was recalibrated before almost all-new samples. OriginPro 2016 software was used to analyze data. The data points plotted were Fitted using the Non-linear curve fit Gaussian function and Levenberg Marquardt iteration algorithm. This algorithm provided the best fit for almost all the data collected.
Figure S1: XPS spectra: (a) C$_{1s}$ of BSA-Au 6 show three peaks, the first peak attributed to C=C or C-C (red curve), the second peak (green curve) attributed to C-C/COOH/ C-N, and the last peak (blue curve) attributes to C=O/ C=N respectively. (b) N$_{1s}$ peaks confirm the presence of CH$_3$CN (Red curve) and NH$_3$ (Blue curve) (c) O$_{1s}$ show three peaks attributing O**=C-OH (red curve), O=C-O**H (blue curve), and O$_2$/C (green curve) all the three elements contributing to the presence of protein.$^{12,13}$ (d) S$_{2p}$ shows two peaks attributing to sulfur gold (Au-S) (red curve) and oxidized sulfur (SO$_2$)(blue curve) $^{14,15}$The black line represents experimental data in all the figures. The bonds for various BE values were confirmed by using the NIST-XPS database.
| Protein Constructs | BE (eV) (Au 0) | Percentage (%) | BE (eV) (Au +1) | Percentage (%) | Conductivity (S/cm) |
|--------------------|----------------|----------------|-----------------|----------------|-------------------|
| BSA + Au salt      | 84.6           | 55.2           | 88.3            | 44.7           | 4.2E-5            |
| BSA + Au1          | 83.8           | 50.6           | 87.4            | 49.3           | 4.5E-4            |
| BSA + Au4          | 83.6           | 52.9           | 87.3            | 47.1           | 1.7E-3            |
| BSA + Au6          | 83.3           | 55.1           | 86.9            | 44.8           | 8.1E-3            |

**Table S3:** Binding energy (BE) and percentage of the various oxidation state of Au4f for different protein constructs and their Conductivity.

| Element | Binding energy | Bonds | R² square |
|---------|----------------|-------|-----------|
| C       | 284.55 ± 0.5   | C- C or C= C | 0.99      |
|         | 285.74 ± 0.04  | C- C or COOH or C-N |       |
|         | 287.46 ± 0.04  | C=O/ C=N |           |
| N       | 399.11 ± 0.18  | CH₃-C-N | 0.97      |
|         | 399.68 ± 0.02  | NH₃ |                   |
| O       | 531.34 ± 0.07  | O**=C-OH | 0.98      |
|         | 532.74 ± 0.26  | O=C-O**H |           |
|         | 536.98 ± 0.07  | O₂/C |             |
| S       | 161.74 ± 0.02  | Au S bond | 0.91      |
|         | 167.85 ± 0.15  | SO₂ |               |

**Table S4:** Binding energies of various functional groups present in the protein and their corresponding bonds.
S4. Electrical Characterization of protein films:

The globular BSA protein has been studied widely by various researchers for numerous years, using varied techniques to illustrate multiple biophysical and biochemical systems. The studies indicate a prolate ellipsoidal shape for defatted BSA molecules having a molecular weight of 66700 ±400 Da. The primary structure of BSA protein comprises 585 amino acid residues, while its secondary structure contains 67% of alpha-helix and 17 disulfide bridges that validate its noteworthy stability. To measure the electrical data from BSA protein film, the Keithley Source-Measurement Unit (2636B SYSTEM Source Meter) instrument was used to measure the electrical characteristics between the two electrodes. One of the two electrodes was the cleaned FTO glass substrate.

In contrast, the second electrode was attached to the protein film with a hanging drop of Eutectic Indium Gallium (EGaIn) to avoid damage to the film, which is only a thickness of about a few μm. KickStart 1.98 software was used to take readings of I-V characteristics for each particular protein concentration in films. The current was recorded for +1V to -1V and -1V to +1V for each set of I-V data. The current had to be converted into current per unit area per unit thickness (normalized current density) of the protein films to normalize the effect of contact area and the thickness variation of the protein films. We have estimated the contact area of the EGaIn droplet from optical images, and the thickness of each film prepared with various protein concentrations was obtained from optical Profilometer measurements. ImageJ software measured the contact area using ImageJ software, from where the radius and contact angle were measured, and the contact area was calculated. One of the examples is explained in detail; other contact areas were also measured in the same way (Figure S2).
Figure S2: (a) Digital image of Eutectic Indium-Gallium drop electrode (b) Estimation of electrical contact area with Eutectic Indium-Gallium drop electrode and BSA protein films utilizing optical images.

Contact area Calculations:

\[ \theta_1 = 90 - 42 = 48^\circ \]

\[ \theta_2 = 90 - 43 = 47^\circ \]

BOC = 180 - (47 + 48) = 85 ° ~ 1.48 Radian

Radius = r = average of diameter = (180+160)/2 = 85 μm

BC = \((2\pi r/2\pi) \times \text{(BOC in radian unit)}\) = 85 \times 1.48 = 125.8 μm

Circular contact area = \(\pi \times (\text{BC}/2)^2\) = 3.14 \times (125.8/2)^2 = 12,423 μm²

S5. Electrical conductance data analysis method:

The current density is the current divided by the contact area of the material. The calculated current density was further used for the calculations of Conductivity \(\frac{G \times L}{A_{\text{measured}}}\) by MATLAB programing for each current density-voltage profile at a low applied bias regime (-0.2V to +0.2V) where L is the thickness over the protein films, the individual thin films of different concentrations, which were subjected to an optical profilometer to measure the film.
thickness and $A$ measured is the contact area. Thickness measurement was done under INUP at CeNSE, IISc Bangalore. The resultant was used to measure Conductivity (S/cm) for each concentration of BSA protein. The average thickness of protein films prepared with different concentrations is tabulated in Table S5 –

| Sr no. | BSA solution Concentration (mg/ml) | Mean Film thickness (µm) |
|--------|-----------------------------------|--------------------------|
| 1      | 12.5                              | 4.0                      |
| 2      | 6.3                               | 2.3                      |
| 3      | 2.5                               | 0.9                      |

**Table S5:** Average thickness of different BSA films with variable concentration

Statistical analysis of conductance variations for each specific protein concentration was carried out with Origin Pro 2016 software using the descriptive statistics algorithm where frequency counts for specific conductance bins were obtained. The Frequency count method was used for the calculations where bin centers were considered for further classification. The Bin size considered was 0.1nS, 1nS, 10nS, and 100nS, which allowed us to include maximum data points. The Bin centers were plotted against frequency counts of that protein. The plotted data points were fitted using the Non-linear curve fit sing Log-Normal function and Levenberg Marquardt iteration algorithm. This algorithm provided the best fit for almost all the data collected. Around 90-100 junctions were analyzed for each set of concentrations.

The formula for log-normal fit where $y_0$ is $y$ at maximum, $xc$ is center, $w$ is the full-width half maxima (Log standard deviation), and $A$ is the area of the fitted curve.

$$y = y_0 + \frac{A}{\sqrt{2\pi w} x} e^{-\left[\ln\frac{x}{xc}\right]^2}$$
Conductivity for the highest 12.5 mg/ml was obtained at $1.64 \times 10^{-5}$ S/cm, whereas, for 6.25 mg/ml, it showed a decrease as it was recorded as $6.37 \times 10^{-5}$ S/cm and $6.55 \times 10^{-5}$ S/cm for 2.5 mg/ml of BSA protein concentrations.

In the graphs reported in the main text (Figure 4), the vertical axis represents Conductivity (S/cm), and the horizontal axis illustrates the Au cluster dopant concentrations variance.

There is a reduction in the Conductivity for films prepared with higher protein concentration following larger film thicknesses with more Au clusters in the transport path, which may constrict the charge migration through the thin films.

In our experiments, we have utilized five films for each concentration, and we have prepared around 20-30 different junctions for each film by approaching and retracting the upper electrode.
Additional Results

S6. UV-Visible absorbance and PL characteristics of control samples

Figure S3: (a-b) Comparison of absorbance and PL characteristics of various control samples such as
Au salt (10 mM), Bovine Serum Albumin (25 mg/mL), Sodium Hydroxide (1 M) with Au NCs.

**S7. Temperature-dependent PL emission spectrum of different BSA-Au samples**

Temperature-dependent PL characteristics of Au 2 to Au 6 samples were shown in Figure S3, where the temperature varied from 10°C to 60°C. In all the cases, better PL intensity was observed in lower temperatures.

*Figure S4:* (a-e) Temperature-dependent PL spectrum of representative BSA-Au 2 to BSA-Au 6
S8. I-V data of films prepared with various concentrations

**Figure S5:** Average Current Density-Voltage plot as obtained from films prepared with BSA solution

**Figure S6:** Average Current Density-Voltage plot as obtained from films prepared with BSA-Au 1 NCs solution
Figure S7: Average Current Density-Voltage plot as obtained from films prepared with BSA-Au 2 NCs solution.

Figure S8: Average Current Density-Voltage plot as obtained from films prepared with BSA-Au 4 NCs solution.
**Figure S9:** Average Current Density-Voltage plot as obtained from films prepared with BSA-Au 6 NCs solution
S9. Summary of Electrical conductivity data analysis for films prepared with various concentrations:

The total junctions measured, the peak of log-normal fitting obtained along with Conductivity which has maximum occurrences, the width of the fitting curve, and the ratio of the most occurring junction to total junction are given in the table below with the individual graph for each concentration.

| Graph 1: BSA- Au1 NCs : 2.5 mg/ml | Total junction examined = 97 |
|----------------------------------|-------------------------------|
|                                  | Peak of the Log-normal fitting = 4.87E-04 S/cm |
|                                  | FWHM = 1.43E-4 |
|                                  | Conductivity with maximum occurrences = 8.28E-4 S/cm |
|                                  | Count of most occurring junction/ Total junction Measured = 21/97 |

| Graph 2: BSA- Au1 NCs: 6.25 mg/ml | Total junction examined = 97 |
|-----------------------------------|-------------------------------|
|                                   | The peak of the Log-normal fitting = 6.3E-4 S/cm |
|                                   | FWHM = 1.54E-4 |
|                                   | Conductivity with maximum occurrences = 8.1E-4 S/cm |
|                                   | Count of most occurring junction/ Total junction Measured = 26/97 |
| Graph 3: BSA- Au1 NCs :12.5 mg/ml | Total junction examined = 99 |
|----------------------------------|------------------------------|
|                                  | Peak of the Log-normal fitting = 1.43E-4 S/cm |
|                                  | FWHM = 4.003E-5 |
|                                  | Conductivity with maximum occurrences=2.33E-4 S/cm |
|                                  | Count of most occurring junction/ Total junction measured= 12/99 |

| Graph 4: BSA- Au2 NCs: 2.5 mg/ml | Total junction examined = 101 |
|----------------------------------|------------------------------|
|                                  | The peak of the Log-normal fitting = 6.2E-4 S/cm |
|                                  | FWHM=1.96E-4 |
|                                  | Conductivity with maximum occurrences=8.11E-4 S/cm |
|                                  | Count of most occurring junction/ Total junction measured= 44/101 |

| Graph 5: BSA- Au2 NCs : 6.25 mg/ml | Total junction examined = 93 |
|-----------------------------------|------------------------------|
|                                   | The peak of the Log-normal fitting = 6.1E-4 S/cm |
|                                   | FWHM=1.5E-4 |
| Conductivity with maximum occurrences = 3.6E-4 S/cm |
| Count of most occurring junction/ Total junction |
| Measured = 40/93 |

Graph 6: BSA- Au2 NCs :12.5 mg/ml

Total junction examined = 92

The peak of the Log-normal fitting = 2.4E-4 S/cm

FWHM= 1.223E-4

Conductivity with maximum occurrences = 2.13E-4 S/cm

Count of most occurring junction/ Total junction

Measured = 26/92

---

Graph 7: BSA- Au4 NCs :2.5mg/ml

Total junction examined = 98

The peak of the Log-normal fitting = 1.8E-3 S/cm

FWHM= 6E-4

Conductivity with maximum occurrences = 1.68E-3 S/cm

Count of most occurring junction/ Total junction

measured= 28/98
| Graph 8: BSA- Au4 NCs: 6.25 mg/ml | Total junction examined = 90 |
|---------------------------------|-----------------------------|
| | The peak of the Log-normal fitting = 7.1E-4 S/cm |
| | FWHM = 1.48E-4 |
| | Conductivity with maximum occurrences = 3.34E-4 S/cm |
| | Count of most occurring junction/ Total junction |
| | Measured = 27/90 |

| Graph 9: BSA- Au4 NCs: 12.5 mg/ml | Total junction examined = 87 |
|---------------------------------|-----------------------------|
| | The peak of the Log-normal fitting = 601E-4 S/cm |
| | FWHM = 1.37E-4 |
| | Conductivity with maximum occurrences = 2.03E-4 S/cm |
| | Count of most occurring junction/ Total junction |
| | Measured = 24/87 |

| Graph 10: BSA- Au6 NCs: 2.5 mg/ml | Total junction examined = 90 |
|---------------------------------|-----------------------------|
| | The peak of the Log-normal fitting = 8.4E-3 S/cm |
| | FWHM = 0.004 |
| Graph 11: BSA- Au6 NCs: 6.25 mg/ml | Graph 12: BSA - HAuCl₄: 2.5 mg/ml (Control) |
|---------------------------------|---------------------------------|
| Conductivity with maximum occurrences = 8.5E-3 S/cm | Conductivity with maximum occurrences = 1.69E-5 S/cm |
| Count of most occurring junction/ Total junction Measured = 66/90 | Count of most occurring junction/ Total junction Measured = 20/97 |
| Total junction examined = 91 | Total junction examined = 97 |
| Peak of the Log-normal fitting = 8.6E-3 S/cm | The peak of the Log-normal fitting = 4.5E-5 S/cm |
| FWHM= 0.00316 | FWHM = 7.39E-5 |
| Conductivity with maximum occurrences = 3.6E-3 S/cm | Conductivity with maximum occurrences = 1.69E-5 S/cm |
| Graph 13: BSA - HAuCl4: 6.25 mg/ml (Control)          |                          |
|------------------------------------------------------|--------------------------|
| Total junction examined = 91                         |                          |
| The peak of the Log-normal fitting = 6.3E-4 S/cm    |                          |
| FWHM = 8.31E-4                                       |                          |
| Conductivity with maximum occurrences = 3.43E-4 S/cm |                          |
| Count of most occurring junction/ Total junction     |                          |
| Measured = 26/91                                     |                          |

| Graph 14: BSA - HAuCl4: 12.5mg/ml (Control)          |                          |
|------------------------------------------------------|--------------------------|
| Total junction examined = 69                         |                          |
| Peak of the Log-normal fitting = 1.2E-3 S/cm        |                          |
| FWHM= 1.66E-3                                        |                          |
| Conductivity with maximum occurrences = 8.3E-3 S/cm  |                          |
| Count of most occurring junction/ Total junction     |                          |
| measured= 18/69                                     |                          |

| Graph 15: BSA :2.5mg/ml                              |                          |
|------------------------------------------------------|--------------------------|
| Total junction examined = 98                         |                          |
| Peak of the Log-normal fitting = 6.2E-5 S/cm        |                          |
| FWHM= 2.38E-5                                        |                          |
| Conductivity with maximum occurrences = 2.14E-4 S/cm |                          |
| Count of most occurring junction/ Total junction | Measured |
|-------------------------------------------------|----------|
| Graph 16: BSA: 6.25mg/ml                        | 30/98    |
| Total junction examined = 97                     |          |
| The peak of the Log-normal fitting = 6.3E-5 S/cm|          |
| FWHM= 1.36E-5                                   |          |
| Conductivity with maximum occurrences = 3.48E-5 S/cm |        |
| Count of most occurring junction/ Total junction | 26/97    |
| Measured = 26/97                                |          |

Graph 17: BSA: 12.5mg/ml

| Count of most occurring junction/ Total junction | Measured |
|-------------------------------------------------|----------|
| Total junction examined = 91                     |          |
| The peak of the Log-normal fitting = 1.7E-4 S/cm|          |
| FWHM= 4.633E-5                                  |          |
| Conductivity with maximum occurrences = 4.47E-5 S/cm |        |
| Count of most occurring junction/ Total junction | 20/91    |
| Measured = 20/91                                |          |
References:

(1) Pramanik, G.; Humpolickova, J.; Valenta, J.; Kundu, P.; Bals, S.; Bour, P.; Dracinsky, M.; Cigler, P. Gold Nanoclusters with Bright Near-Infrared Photoluminescence. *Nanoscale* **2018**, *10* (8), 3792–3798. https://doi.org/10.1039/c7nr06050e.

(2) Cui, M. L.; Liu, J. M.; Wang, X. X.; Lin, L. P.; Jiao, L.; Zhang, L. H.; Zheng, Z. Y.; Lin, S. Q. Selective Determination of Cysteine Using BSA-Stabilized Gold Nanoclusters with Red Emission. *Analyst* **2012**, *137* (22), 5346–5351. https://doi.org/10.1039/c2an36284h.

(3) Yarramala, D. S.; Baksi, A.; Pradeep, T.; Rao, C. P. Green Synthesis of Protein-Protected Fluorescent Gold Nanoclusters (AuNCs): Reducing the Size of AuNCs by Partially Occupying the Ca2+ Site by La3+ in Apo-α-Lactalbumin. *ACS Sustainable Chemistry and Engineering* **2017**, *5* (7), 6064–6069. https://doi.org/10.1021/acssuschemeng.7b00958.

(4) Qiao, J.; Mu, X.; Qi, L.; Deng, J.; Mao, L. Folic Acid-Functionalized Fluorescent Gold Nanoclusters with Polymers as Linkers for Cancer Cell Imaging. *Chemical Communications* **2013**, *49* (73), 8030–8032. https://doi.org/10.1039/c3cc44256j.

(5) Li, H. W.; Yue, Y.; Liu, T. Y.; Li, D.; Wu, Y. Fluorescence-Enhanced Sensing Mechanism of BSA-Protected Small Gold-Nanoclusters to Silver(I) Ions in Aqueous Solutions. *Journal of Physical Chemistry C* **2013**, *117* (31), 16159–16165. https://doi.org/10.1021/jp403466b.

(6) Halawa, M. I.; Wu, F.; Nsabimana, A.; Lou, B.; Xu, G. Inositol Directed Facile “Green” Synthesis of Fluorescent Gold Nanoclusters as Selective and Sensitive Detecting Probes of Ferric Ions. *Sensors and Actuators, B: Chemical* **2018**, *257*, 980–987. https://doi.org/10.1016/j.snb.2017.11.046.
(7) Liu, J. M.; Cui, M. L.; Jiang, S. L.; Wang, X. X.; Lin, L. P.; Jiao, L.; Zhang, L. H.; Zheng, Z. Y. BSA-Protected Gold Nanoclusters as Fluorescent Sensor for Selective and Sensitive Detection of Pyrophosphate. *Analytical Methods* **2013**, *5* (16), 3942–3947. https://doi.org/10.1039/c3ay00054k.

(8) Sun, J.; Yang, F.; Zhao, D.; Yang, X. Highly Sensitive Real-Time Assay of Inorganic Pyrophosphatase Activity Based on the Fluorescent Gold Nanoclusters. *Analytical Chemistry* **2014**, *86* (15), 7883–7889. https://doi.org/10.1021/ac501814u.

(9) Sun, J.; Zhang, J.; Jin, Y. 11-Mercaptoundecanoic Acid Directed One-Pot Synthesis of Water-Soluble Fluorescent Gold Nanoclusters and Their Use as Probes for Sensitive and Selective Detection of Cr$^{3+}$ and Cr$^{6+}$. *Journal of Materials Chemistry C* **2013**, *1* (1), 138–143. https://doi.org/10.1039/c2tc00021k.

(10) Xu, S.; Gao, T.; Feng, X.; Mao, Y.; Liu, P.; Yu, X.; Luo, X. Dual Ligand Co-Functionalized Fluorescent Gold Nanoclusters for the “Turn on” Sensing of Glutathione in Tumor Cells. *Journal of Materials Chemistry B* **2016**, *4* (7), 1270–1275. https://doi.org/10.1039/c5tb02195b.

(11) Annie Ho, J. A.; Chang, H. C.; Su, W. T. DOPA-Mediated Reduction Allows the Facile Synthesis of Fluorescent Gold Nanoclusters for Use as Sensing Probes for Ferric Ions. *Analytical Chemistry* **2012**, *84* (7), 3246–3253. https://doi.org/10.1021/ac203362g.

(12) Sai, L.; Chen, J.; Chang, Q.; Shi, W.; Chen, Q.; Huang, L. Protein-Derived Carbon Nanodots with an Ethylenediamine-Modulated Structure as Sensitive Fluorescent Probes for Cu$^{2+}$ Detection. *RSC Adv.* **2017**, *7* (27), 16608–16615. https://doi.org/10.1039/C7RA01441D.
(13) Artemenko, A.; Shchukarev, A.; Štenclová, P.; Wågberg, T.; Segervald, J.; Jia, X.; Kromka, A. Reference XPS Spectra of Amino Acids. *IOP Conf. Ser.: Mater. Sci. Eng.* **2021**, *1050* (1), 012001. https://doi.org/10.1088/1757-899X/1050/1/012001.

(14) Tanaka, A.; Takeda, Y.; Imamura, M.; Sato, S. Dynamic Final-State Effect on the Au 4 f Core-Level Photoemission of Dodecanethiolate-Passivated Au Nanoparticles on Graphite Substrates. *Phys. Rev. B* **2003**, *68* (19), 195415. https://doi.org/10.1103/PhysRevB.68.195415.

(15) Le Guével, X.; Hötzer, B.; Jung, G.; Hollemeyer, K.; Trouillet, V.; Schneider, M. Formation of Fluorescent Metal (Au, Ag) Nanoclusters Capped in Bovine Serum Albumin Followed by Fluorescence and Spectroscopy. *J. Phys. Chem. C* **2011**, *115* (22), 10955–10963. https://doi.org/10.1021/jp111820b.