Supporting Information

Fabrication of Chiral Luminescent Hydrogel from Gold Nanocluster *via* Molecular Recognition

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1. Experiment section

1.1 Experiment section

1.1.1 Materials.

All the solvents and chemicals were of analytical grade and used as received. Hydrogen tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$), NaOH was produced by the Sinopharm Chemical Reagent Co. Thiobarbituric acid (TBA), L-histidine (L-His), R- and S-mandelic acid (S-MA), D/L-tartaric acid (D/L-TA), D-arginine (D-Arg) were purchased from Aladdin Reagent Co. (Shanghai, China), D-histidine (D-His), L-lysine (L-Lys), L-phenylalanine (L-Phe) were obtained from Macklin Reagent Co. (Shanghai, China).

1.1.2 Synthesis of TBA-AuNCs.

In the preparation process, an equal volume of aqueous solution of $HAuCl_4$ (10 mg, 1 mL) was added to the prepared TBA (160 mM, 1mL) in clean glass vial. The mixture was continuously stirred at room temperature until it gradually became opalescent. Then NaOH (1 M, 140 μL) was added into mixed solution (1 mL) to get a clear colorless solution which was used for flowing experiment. The hydrogel was prepared with the following procedure: different volume of chiral molecules solution (c=250 mM) were added into 0.5 mL TBA-AuNCs (c_{HAuCl4}=5 mg mL^{-1}, c_{TBA}=80 mM). Hydrogels were obtained 24 hours later at 20°C.

1.1.3 Methods and characterizations.

High resolution transmission electron microscopy (HR-TEM) was taken by JEOL JEM-2100PLUS. Scanning electron microscopy (SEM) was taken by Sigma

500 (Zeiss, Germany). CD spectra were taken on J-810 Spectra Manager system (Jasco, Japan). Fourier transform infrared (FT-IR) spectrum was recorded from 4000 cm^{-1} to 400 cm^{-1} on a Nicolet iS20 spectrometer. The fluorescence spectra were performed on a F-7000 spectrofluorometer (Hitachi, Japan) with a quartz cell. The photoluminescence lifetime was counted on FLS1000 fluorescence spectrometer (Edinburgh, England). X-ray photoelectron spectroscopy (XPS) measurment was operated on an ESCALAB 250 X-ray photoelectron spectrometer with a monochromatized Al Kα X-ray source (1486.71 eV). Single-crystal X-ray diffraction (XRD, PANalytical X-ray Diffractometer X'pert3) using Cu Kα radiation. Rheology analysis was taken on ARES-G2 system (TA, USA). Amplitude sweep at a fixed frequency of 1 Hz was operated before frequency sweep to ensure that the selected stress was in the linear viscoelastic region. The samples were measured at $20.0\pm0.1^{o}C$ assisted with cyclic water bath. The geometry optimizations were employed by DFT methods with the Gaussian 09 program. The theoretical calculations were carried out at WB97XD levels. The changes in energy (ΔE) of the interactions between TBA and His were also calculated. ΔE is defined as

$$\Delta E\ (\mathrm{TBA\text{-}His}) = E\ (\mathrm{TBA\text{-}His}) - [\ E\ (\mathrm{TBA}) + E\ (\mathrm{His})]$$

where E(TBA) is the energy of TBA, E(His) is the energy of His, and E(TBA-His) is the energy of the optimized geometries of TBA-His complex.

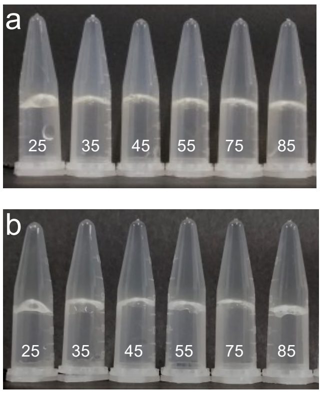

Figure S1. The photos of (a) L- and (b) D- Histidines/TBA-AuNCs hydrogel, respectively (the concentration unit: mM).

Table S1. Transformation temperature of gels with different $c_{L\text{-His}}$.

$C_{L\text{-His}}$ / mM	**15**	**25**	**35**	**45**	**55**	**65**	**75**	**85**	**95**
T / ℃	32.5	37.7	37.7	40.5	46.2	41.7	40.5	35.2	32.5

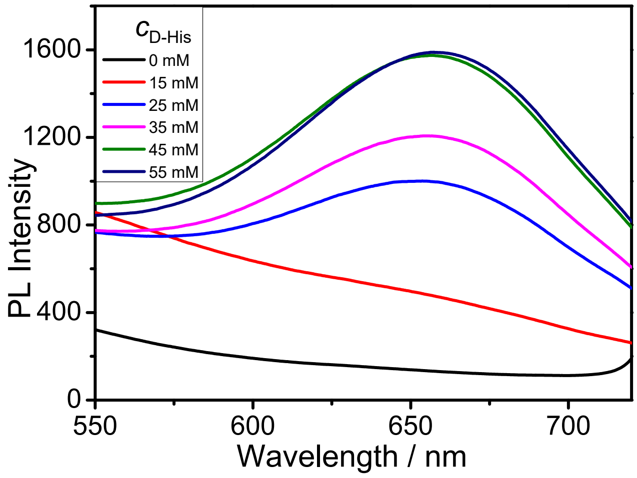

Figure S2. PL spectra of TBA-AuNCs with different concentration of D-His.

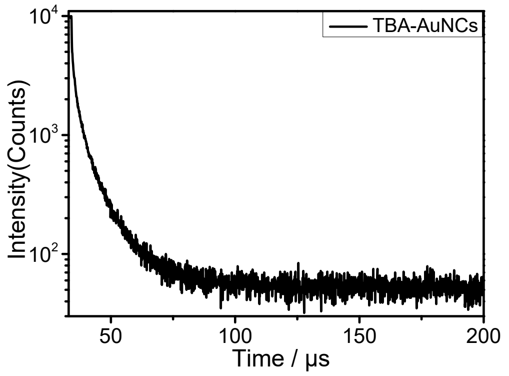

Figure S3. Time-resolved PL decay curves of the TBA-AuNC solution

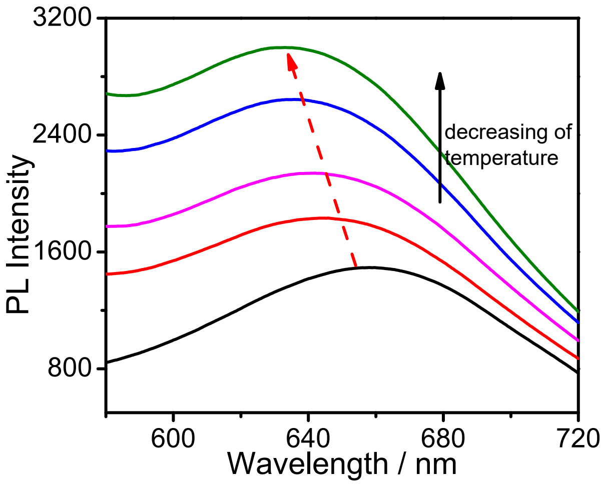

Figure S4. Temperature-dependent PL spectra of **L-gel 1**.

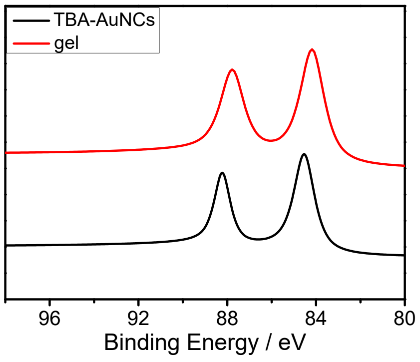

Figure S5. XPS results exhibiting the binding energy of Au(4f) of TBA-AuNCs and **L-gel 1**.

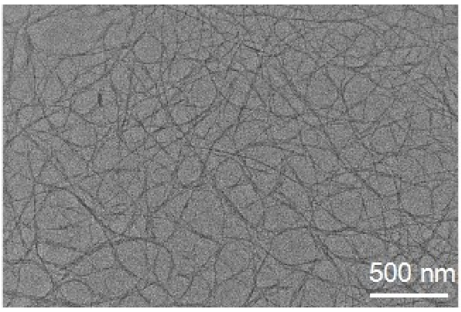

Figure S6. TEM image of the TBA-AuNCs (c_{HAuCl4}=5 mg mL^{-1}).

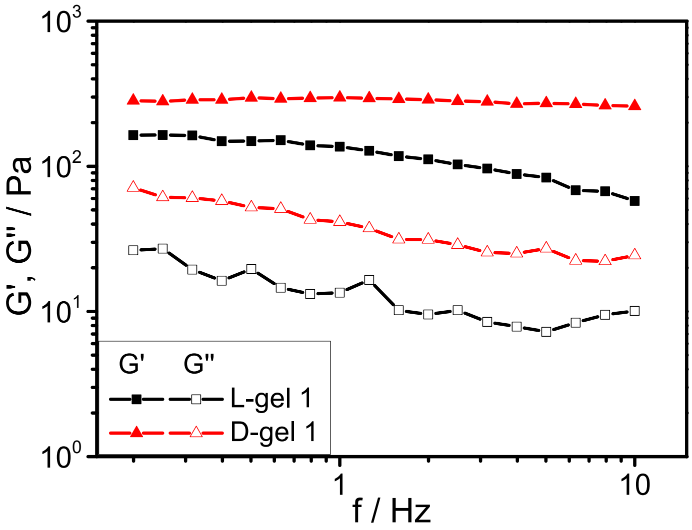

Figure S7. Rheological profiles (G′ and G″ as a function of frequency (τ=1 Pa) of **L-gel 1** and **D-gel 1**.

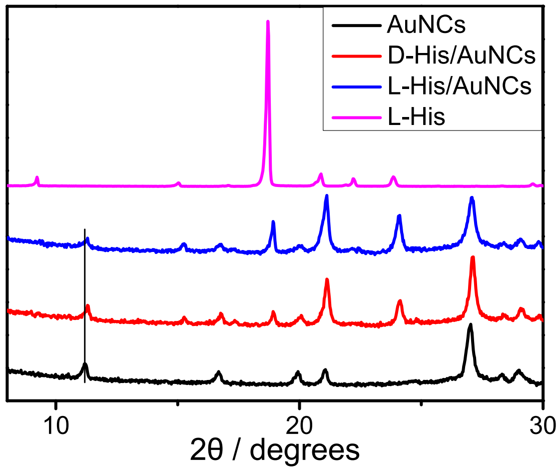

Figure S8. XRD spectra of TBA-AuNCs, L-His and L/D-His/AuNCs

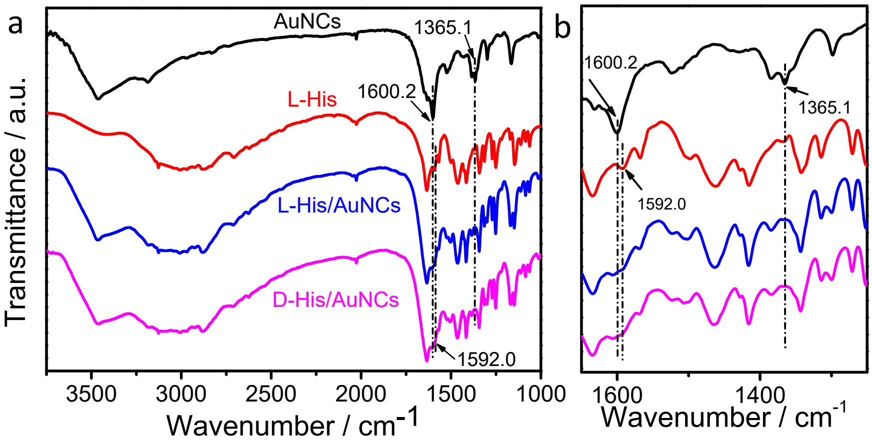

Figure S9. FT-IR spectra of TBA-AuNCs, L-His and L/D-His/ TBA-AuNCs. (a is the entire spectra, b is the amplifying partial spectra)

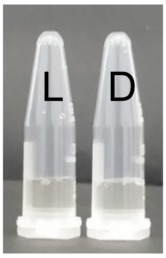

Figure S10. Samples of **L-/D-gel-1** with the addition of urea.

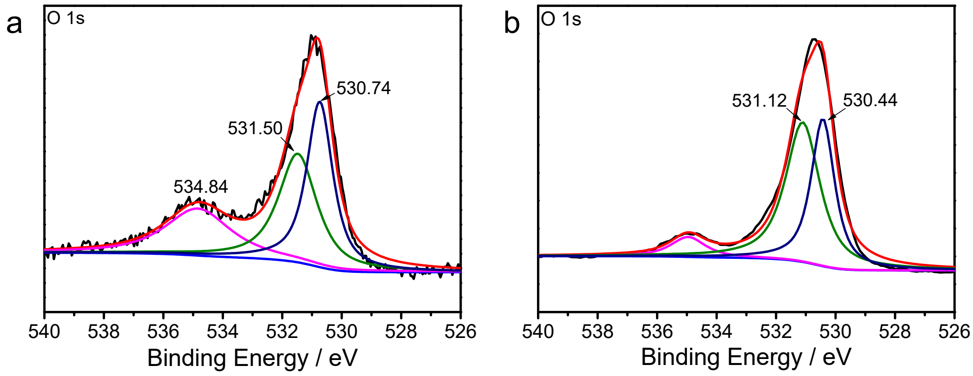

Figure S11. High resolution XPS spectra for O 1s of (a) TBA-AuNCs and (b) **L-gel 1.**

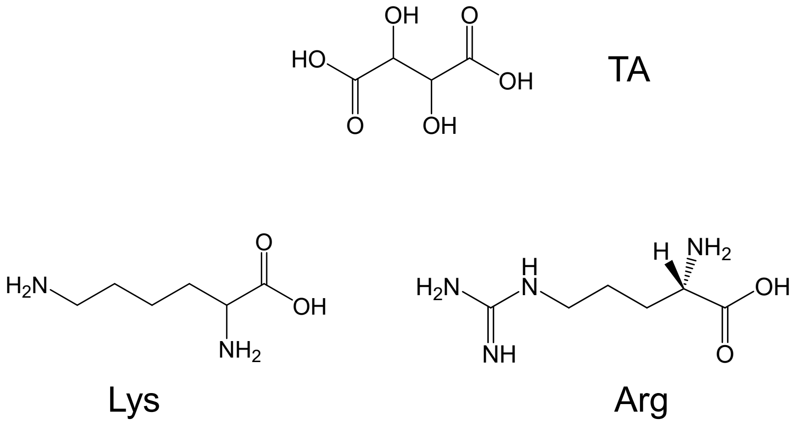

Figure S12. Structure formal of TA, Lys, and Arg.

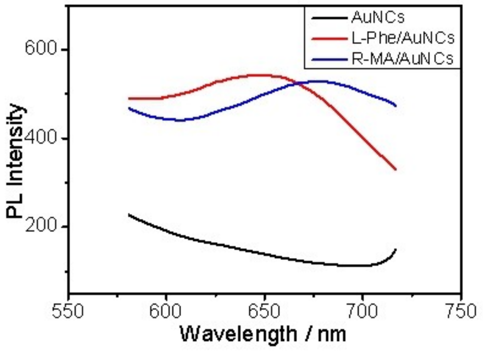

Figure S13. PL spectra of the TBA-AuNCs solution and the AuNCs-based gels with $c_{\text{L-Phe}}$ = 25 mM and $c_{\text{R-MA}}$ = 15 mM, respectively.

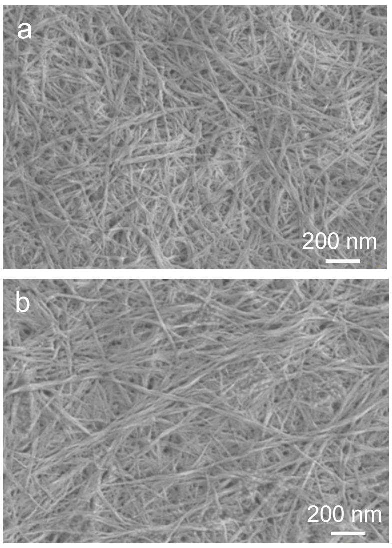

Figure S14. SEM image of (a) S-MA/AuNCs gel and (b) R-MA/ TBA-AuNCs gel at c_{MA} = 30 mM.

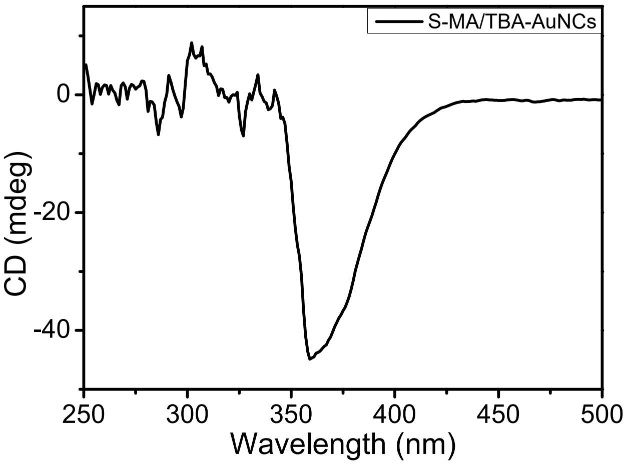

Figure S15. CD spectra of S-MA/ TBA-AuNCs hydrogel.

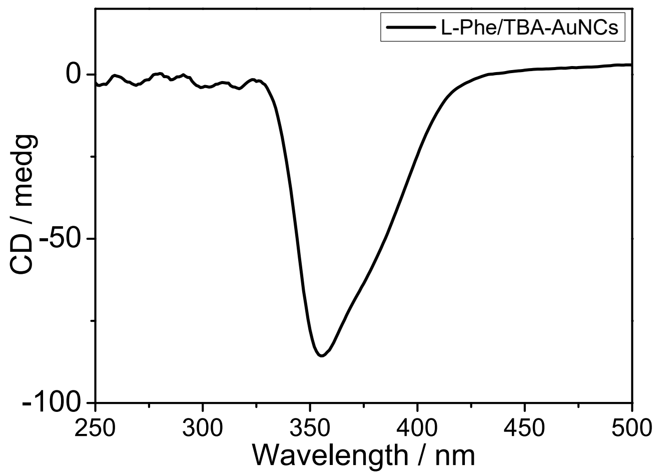

Figure S16. CD spectra of L-Phe/ TBA-AuNCs hydrogel.

As shown in Figure S17, the configuration of the Au(I)-TBA/His complex was optimized. The change in energy (ΔE) of the Au(I)-TBA/His complex with respect to the separated Au(I)-TBA motif and His molecule is -236.83 kJ mol^{-1}, which implies that the Au(I)-TBA also preferentially form a complex with His. This is consistent with the result we displayed in the manuscript and indicate the rationality of calculations.

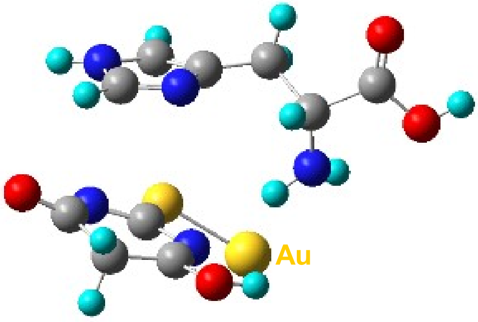

Figure S17. DFT-optimized geometries of Au(I)-TBA/His complex.