Supplementary material

Formation and nonlinear optical properties of Ag nanocrystals capped with the conjugated ligand carbazolyl styryl terpyridine

Wan Sun a, Yingzhong Zhu a, Anran Wang a, Lin Kong a, Shengli Li a*, Jieying Wu a, Yupeng Tian a,b,c*  

a (Department of Chemistry, Anhui Province Key Laboratory of Functional Inorganic Materials, Anhui University, Hefei 230039, China)  
b (State Key Laboratory of Crystal Materials, Shangdong University, Jinan 250100, China)  
c (State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China)  

*Corresponding author. Fax: +86-551-65107342; Tel: +86-551-65108151  

E-mail address: lsl1968@ahu.edu.cn; yptian@ahu.edu.cn  

Contents  
Fig. S1 Relevant peaks in the 1H NMR spectra of pure L in d6-DMSO  
Fig. S2 Relevant peaks in the 1H NMR spectra of L-Ag NCs in d6-DMSO  
S3 The calculation method:

![NMR spectra](image-url)
Fig. S1 Relevant peaks in the $^1$H NMR spectra of pure L in d$_6$-DMSO
Fig. S2 Relevant peaks in the $^1$H NMR spectra of L-Ag NCs in d$_6$-DMSO

Fig. S3 The cyclic voltammetry curve of AgNO$_3$

S4 The calculation method:

HOMO: Highest Occupied Molecular Orbital

LUMO: Lowest Unoccupied Molecular Orbital

$$E_{\text{HOMO}} = - e (E_{\text{onset}} + 4.38) \text{ eV}, \quad (E_{\text{onset}}: \text{the first onset oxidation potential, } E_{\text{onset}}=0.97 \text{V}).$$

A HOMO-LUMO gap: $E_{\text{opt}} = \frac{hc}{\lambda}, \quad (\lambda=\lambda_{\text{edge}}=589 \text{nm}. \text{The value of the intersection point of the tangent of the crest of maximum wavelength and X-axis is } \lambda_{\text{edge}}, \text{as shown in Fig. 5, } h \text{ is Planck constant } 4.136 \times 10^{-34}, \text{c is speed of light } 3.0 \times 10^8 \text{ m/s}) \text{ so, } E_{\text{opt}} \text{ is } 2.11 \text{eV}.)$
$E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{opt}} = -5.35 + 2.11 = -3.24 \text{eV}$.

The oxidation potential of L is 0.97 V, which is higher than the electrode potential of $\text{Ag}^+/\text{Ag}$ (-0.16 V) (shown in Fig. S3). This means that L can exist stably in AgNO$_3$-DMF solution.$^{[25]}$

$E_{\text{HOMO}}$ was close to the Fermi level of Ag (-4.26 eV). The result indicates that the L combining with Ag nanoparticle is accompanied by electron redistribution, which probably leads to the optical property change.$^{[26]}$

**Open-aperture Z-scan:**

The NLO absorption components were evaluated by Z-scan experiment under an open aperture configuration. The TPA coefficient $\beta$ and TPA cross-sections ($\sigma$) were determined by the OA Z-scan technique. The theoretical data were fitted using the following equations $^{[33]}$:

$$T(z,s = 1) = \sum_{m=0}^{\infty} \left[ -q_0(z) \right]^m (m + 1)^{3/2} \text{ for } |q_0| < 1$$

$$q_0(z) = \frac{\beta I_0 L_{\text{eff}}}{1 + \chi^2}$$

$\beta$ is the nonlinear absorption (TPA) coefficient of the solution, $I_0$ is the input intensity of laser beam at focus ($z = 0$) divided by $\pi\omega_0^2$, $L_{\text{eff}} = [1 - \exp(-\alpha_0 L)]/\alpha_0$ is the effective length with $\alpha_0$ the linear absorption coefficient and $L$ the sample length. $\chi = z/z_0$, $z_0 = \pi\omega_0^2/\lambda$ is the diffraction length of the beam with $\omega_0$ the spot size at focus, $\lambda$ is the wavelength of the beam and $z$ is the sample position. So the nonlinear TPA coefficient $\beta$ (in units of cm/GW) can be deduced. Furthermore, the $\sigma$ could be determined by the following relationship $^{[34]}$:

$$\sigma = \frac{h \gamma \beta}{N_A d} \times 10^{-3}$$

Here, $h$ is the Planck constant, $\gamma$ is the frequency of incident laser, $\sigma$ is molecular TPA cross-section, $N_A$ is the Avogadro number, and $d$ is the concentration (in units of mol·L$^{-1}$). Based on equation(3), the molecular TPA cross-section $\sigma$ can be calculated.

**Close-aperture Z-scan:**

For the closed aperture, the calculation of the nonlinear refractive index $\gamma$ fitting can be done as in Equation (4).

$$\Delta T_{P-V} = 0.406 (1 - s) \gamma \Delta \Phi_0$$

where $\Delta \Phi_0 = \omega_0 (\Delta n) L = K \gamma I_0 L_{\text{eff}}$ (4)

where $\Delta T_{P-V}$ is the peak-valley transmittance difference from the closed-aperture scan. It can be seen that the difference between normalized transmittance values at valley and peak positions, $\Delta T_{P-V}$, was 0.73 for R and 1.49
for the nanohybrid. $s$ is the fraction of the transmitted beam through the aperture (0.20 in our experiment). $\Delta \Phi_0$ is the on-axis nonlinear phase shift and $K$ is the wave vector ($K=2\pi/\lambda$, $\lambda$ was 790 nm for R and the nanohybrid).

The third-order nonlinear susceptibility ($\chi^{(3)}$) was also determined through the closed-aperture Z-scan method. The value of the real part of the third-order nonlinear susceptibility, $\text{Re}(\chi^{(3)})$, can be calculated by the experimental measurements of $g$ as in Equation (5).

$$\text{Re}\chi^{(3)}(\text{esu}) = n_0^2\varepsilon_0 c^3 \gamma / \pi$$ (5)

where $\varepsilon_0$ is the vacuum permittivity, $c$ is the velocity of light in a vacuum, $n_0$ is the linear refractive index.

The value of the imaginary part of the third-order nonlinear susceptibility $\text{Im}(\chi^{(3)})$ can be calculated from the value of $b$ as given in Equation (6)

$$\text{Im}\chi^{(3)} = n_0^2\varepsilon_0 c^3 \lambda \beta / 4\pi^2$$ (6)