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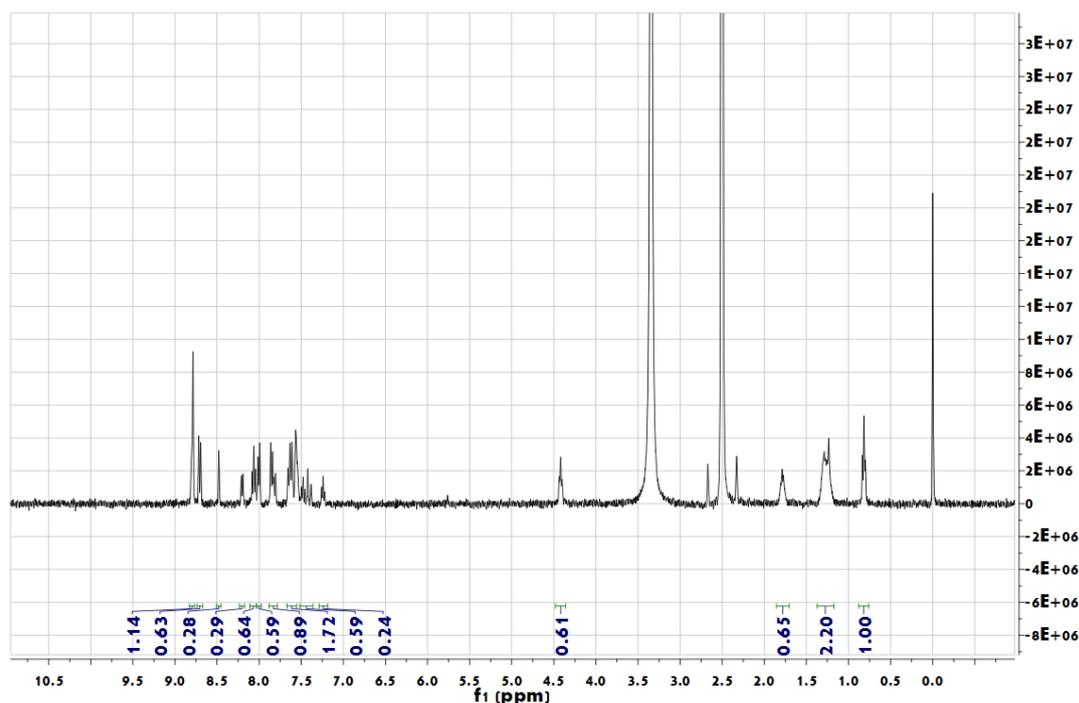
E-mail address: lsl1968@ahu.edu.cn*;* yptian@ahu.edu.cn

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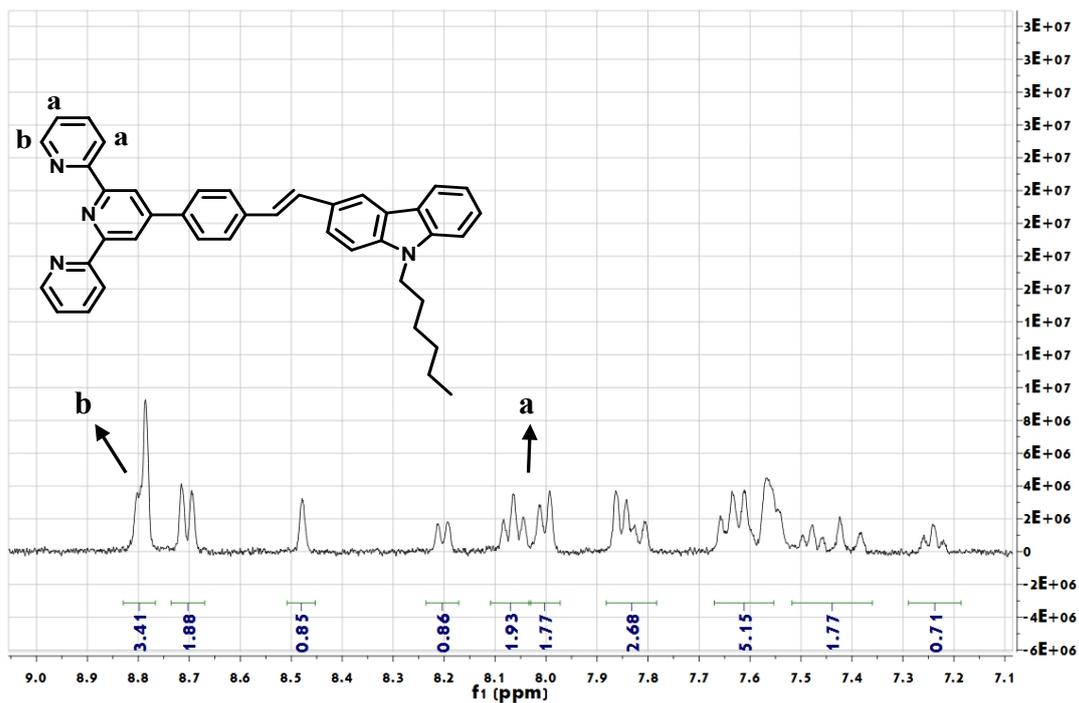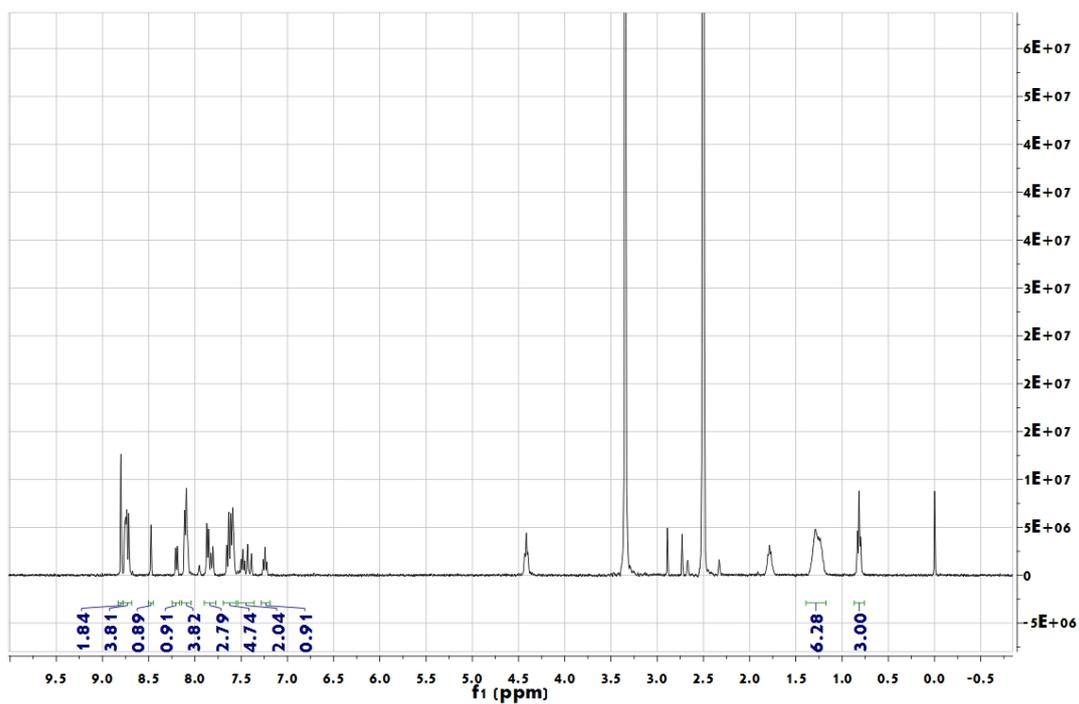
S3 The calculation method:

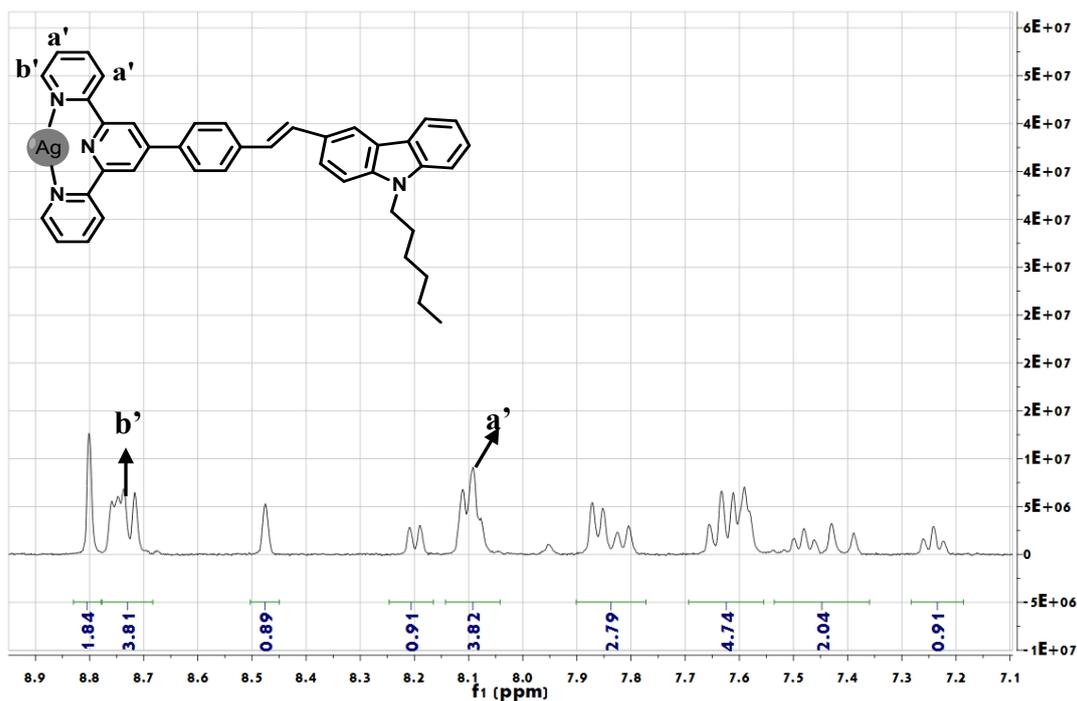**Fig. S1 Relevant peaks in the ^{1}H NMR spectra of pure L in d^6-DMSO**

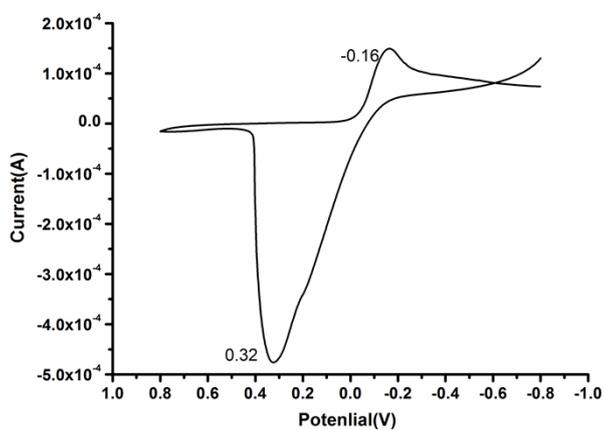**Fig. S2 Relevant peaks in the ^{1}H NMR spectra of L-Ag NCs in d^6-DMSO**

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

S4 The calculation method:

HOMO: Highest Occupied Molecular Orbital

LUMO: Lowest Unoccupied Molecular Orbital

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

A HOMO-LUMO gap: Eopt= hc/λ, ($\lambda=\lambda_{edge}$=589nm. The value of the intersection point of the tangent of the crest

of maximum wavelength and X-axis is λ_{edge}, as shown in Fig. 5, h is Planck constant 4.136×10^{-6}, c is speed of light

3.0×10^8 m/s) so, Eopt is 2.11eV.)

$E_{LUMO} = E_{HOMO} + Eopt = -5.35 + 2.11 = -3.24eV$.

The oxidation potential of L is 0.97 V, which is higher than the electrode potential of Ag^+/Ag (-0.16 V)(shown in Fig. S3). This means that L can exist stably in $AgNO_3$-DMF solution.[25]

E_{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 β and TPA cross-sections (σ) were determined by the OA Z-scan technique. The theoretical data were fitted using the following equations [33]:

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

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

β is the nonlinear absorption (TPA) coefficient of the solution, I_0 is the input intensity of laser beam at focus ($z = 0$) divided by $\pi\omega_0^2$, $L_{eff} = [1-\exp(-\alpha_0 L)]/\alpha_0$ is the effective length with α_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 ω_0 the spot size at focus, λ is the wavelength of the beam and z is the sample position. So the nonlinear TPA coefficient β (in units of cm/GW) can be deduced. Furthermore, the σ could be determined by the following relationship [34]:

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

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

Close-aperture Z-scan:

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

$$\Delta T_{p-v} = 0.406(1 - s)^{0.25} |\Delta\Phi_0| \text{ where } \Delta\Phi_0 = \omega(\Delta n)L = K \gamma I_0 L_{eff} \tag{4}$$

where ΔT_{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, ΔT_{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 ($K=2\pi/\lambda$, λ 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, Re($\chi^{(3)}$), can be calculated by the experimental measurements of g as in Equation (5).

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

where ε_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 Im($\chi^{(3)}$) can be calculated from the value of b as given in Equation (6)

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

[33] Wan Sun, Pingping Sun, Shengli Li, Dyes and Pigments 2015, **115**, 110-119.