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Large Third-Order Optical Nonlinear Effects of Gold Nanoparticles with Unusual Fluorescence Enhancement

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The third-order nonlinear optical properties of two solutions of gold nanoparticles protected by carbazolyldiacetylene derivatives were investigated using the *Z*-scan technique. Both gold nanoparticle colloid solutions in toluene show unusual fluorescent enhancement and large third-order nonlinear optical properties including nonlinear absorption and refractive effects. When extending the π-conjugated length of the ligands, the third-order nonlinear properties of composite materials based on gold nanoparticles were enhanced accordingly.

Introduction

During the past decade, much significant research has been directed toward understanding organic nonlinear optical (NLO) materials and their application in information processing due to their large NLO response and short response time.[1] The motivation is not only to understand the fundamental aggregate structures at different scales but also to explore their potential for futuristic technological applications.[2] The most common approach is to design and synthesize new materials possessing the desirable NLO attributes as inherent properties. For example, polydiacetylene (PDA), due to its delocalized π-electron, has been exploited as a good candidate for organic NLO materials.[3] An alternative approach is to fabricate nanocomposites with well-defined shape holding improved NLO properties. Metallic nanoparticles, therefore, have attracted lots of interest for their fascinating optical and electronic properties.[4] As the particle size reached the nanometer scale not only is the surface-to-

Scheme 1. Chemical Structures of BPCP and DCHD-HS
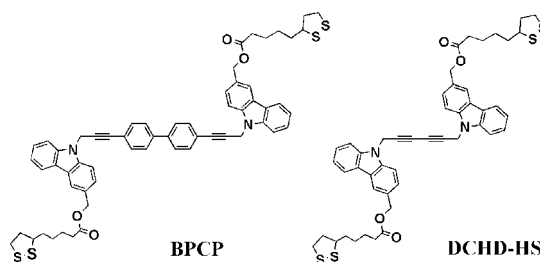
volume ratio drastically changed but a transition from metal to insulator also occurs and effects resulting from quantum confinement may be observed.[5] The surface plasma resonance (SPR), which results from collective electronic excitation at the interface between metal nanoparticles and dielectric matrix, not only is responsible for the linear optical properties but also governs nonlinear optical phenomena.[6]

Many investigations on the potential application of metal nanoparticles in nonlinear optics have been carried out.[7] Combinations of conjugated organic chromophores and gold nanoparticles (AuNPs) are able to produce new classes of organic/inorganic nanomaterials. These materials possess distinct properties which could not be obtained in the individual components.

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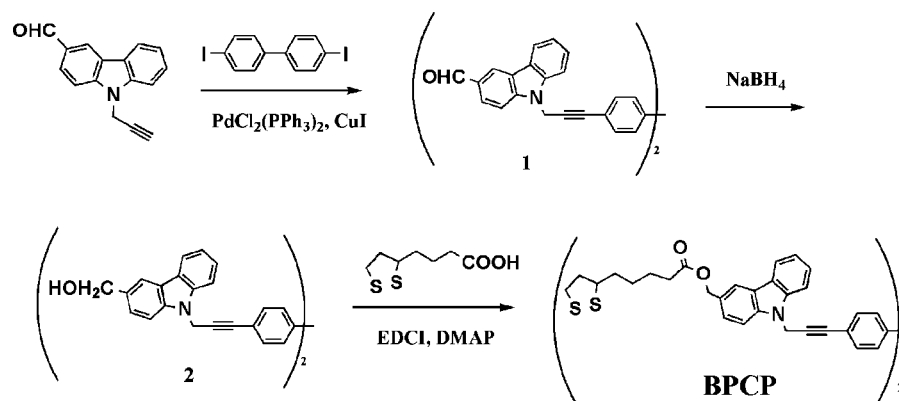§ Suzhou University.
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Scheme 2. Synthetic route of BPCP

Those properties may include either new or improved chemical and physical properties that could be exploited for optical-based devices.[8]

Almost all investigated AuNPs act as photoluminescent quenchers to quench the molecular excitation energy in chromophore−AuNPs composites.[9] Total quenching of the singlet excited states of chromophores limits the applications of chromophore−AuNPs in optoelectronic devices and photonic materials. Thus, as expected, ongoing research in choosing extended π-conjugated molecules to protect AuNPs is able to bring remarkable advances on the properties of the composite materials, including optical and nonlinear optical properties.

Carbazolyldiacetylenes have significantly contributed to the development of materials with implemented nonlinear optical properties.[10] Combinations of carbazolyldiacetylenes and AuNPs are expected to reveal many significant functions. In our previous work, we reported the unusual fluorescence enhancement of 5-[1,2]dithiolan-3-ylpentanoic acid 1,6-bis((*N*-carbazol-3-yl)methyl)-2,4-hexadiyne ester (DCHD-HS) bound to AuNPs.[11] In this successive study, we are devoted to exploiting novel composite materials based on AuNPs with fluorescent enhancement and large nonlinear optical properties for their crucial and multiform applications.[12] Herein, a novel class of AuNPs protected by (9,9′-(3,3′-(biphenyll-4,4′-diyl)bis(prop-2-yne-3,1-diyl))bis(9*H*-carbazole-9,3-diyl))bis(methylene)bis(5-(1,2-dithi-olan-4-yl) pentanoate) (BPCP) was synthesized, and its unusual fluorescence enhancement was studied. In this paper, we investigated the third-order nonlinear optical properties of the colloid solution of BPCP−AuNPs and DCHD−AuNPs using the *Z*-scan technique at a 532 nm wavelength and 4 ns pulse

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width. The chemical structures of BPCP and DCHD-HS are shown in Scheme 1.

Experimental Section

General Information. Reagents were purchased and utilized as received unless indicated otherwise. All solvents were purified using standard procedures. Evaporation and concentration in vacuum were carried out at water aspirator pressure. Column chromatography: SiO$_2$ (200−300 meshes). ^{1}H and ^{13}C NMR spectra were obtained on a Bruker ARX400 spectrometer using tetramethylsilane (TMS) as the internal standard. MALDI-TOF mass spectrometric measurements were performed on a Bruker Biflex MALDI-TOF spectrometer. EI mass spectrometric measurements were performed on a SHZ-MADZU GCMS-QP2010 puls Spectrometer. UV−vis spectra were measured on a Hitachi U-3010 spectrophotometer. The fluorescence spectra were measured on a Hitachi F-4500 fluorimeter. The synthetic route for BPCP is shown in Scheme 2.

Synthesis of 9,9′-(3,3′-(Biphenyl-4,4′-diyl)bis(prop-2-yne-3,1-diyl))bis(9*H*-carbazole-3-carbaldehyde) (1). To a solution of 9-ethynyl-9*H*-carbazole-3-carbaldehyde (112 g, 0.5 mmol) and 4,4′-diiodobiphenyl (80 mg, 0.22 mmol) in tetrahydrofuran (THF)/triethylamine (1:1, v/v) was added the catalyst CuI and PdCl$_2$(PPh$_3$)$_2$ under a nitrogen atmosphere at room temperature (rt). After stirring for 20 h, the resulting mixture was concentrated under reduced pressure. Purification of the crude product by column chromatography (eluent petroleum/chloroform, 1:1) yielded pure **1** (186 mg, 60%) as a yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 10.12 (s, 2H), 8.64 (d, 2H, $J = 0.8$), 8.19 (d, 2H, $J = 7.6$), 8.07 (q, 2H), 7.67 (m, 6H), 7.45 (m, 10H), 5.33 (s, 4H). MS (EI): calcd C$_{42}$H$_{28}$N$_2$O$_2$ 616.7; found 616.

Synthesis of (9,9′-(3,3′-(Biphenyl-4,4′-diyl)bis(prop-2-yne-3,1-diyl))bis(9*H*-carbazole-9,3-diyl))bis(methylene)bis(5-(1,2-dithi-olan-4-yl)pentanoate) (BPCP). To a solution of **1** (80 mg, 0.134 mmol) in THF/methanol (1:1, v/v) was added NaBH$_4$ (200 mg). After stirring for 4 h, the resulting mixture was concentrated under reduced pressure, washed with water, and extracted with dichloromethane (3 × 30 mL). The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The yielded white solid **2** together with 5-(1,2-dithiolan-4-yl)pentanoic acid (70.04 mg, 0.34 mmol) was dissolved in 10 mL of chloroform. To that solution was added EDCI (77 mg, 0.34 mmol) and 4-dimethyl-aminopyridine (DMAP) (43 mg, 0.34 mmol) at 0 °C. After stirring for 1 h, it was allowed to be warmed up to rt, and the mixture was further stirred for another 24 h. The reaction mixture was washed successively with saturated citric acid aqueous solution (3 × 20 mL) and water (2 × 30 mL). The organic phase was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. Purification of the crude product by column chromatography (eluent chloroform) yielded pure BPCP (110 mg, 85%) as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 8.11 (q, 4H), 7.55 (m, 7H), 7.44 (m, 8H), 7.28 (m, 3H), 7.24 (m, 10H), 5.31 (s, 4H). 5.29 (s, 4H), 3.10 (m, 4H), 2.38 (m, 6H), 1.69−1.42 (m, 16H). ^{13}C NMR (400 MHz, CDCl$_3$):
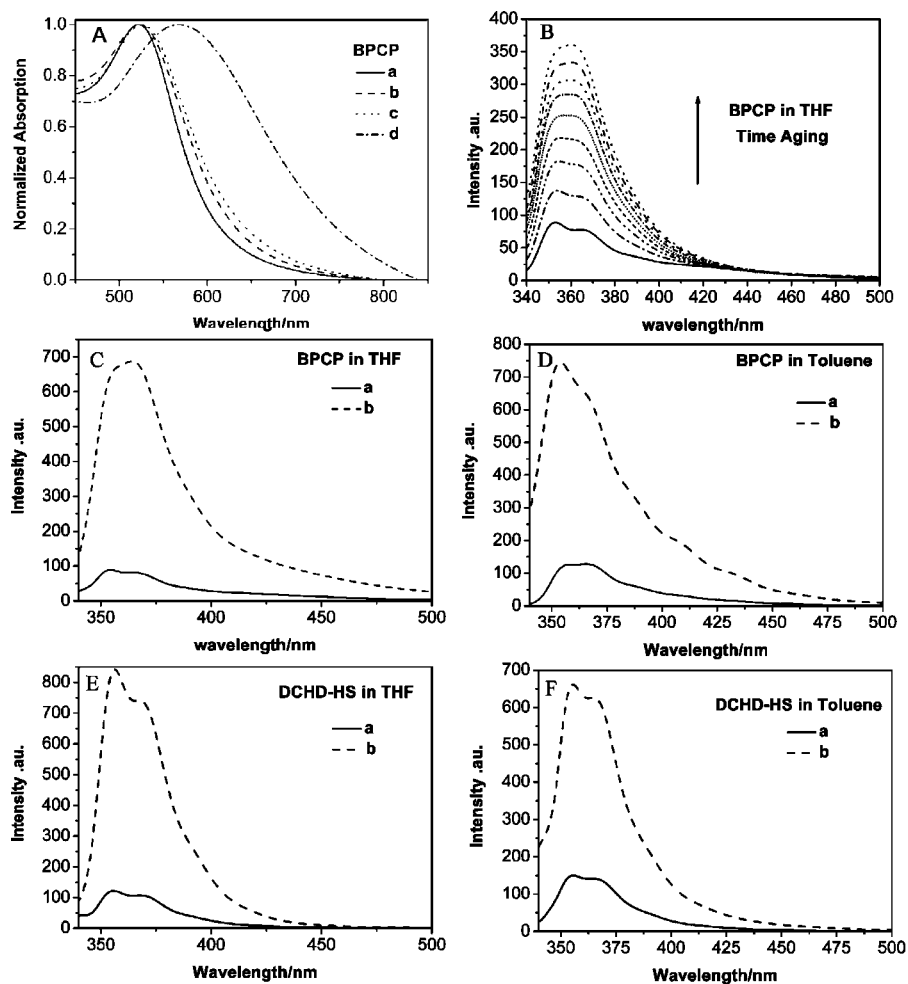
Figure 1. (A) UV−vis absorption spectra of AuNPs in THF solution (a) and toluene solution (b) and BPCP−AuNPs in THF (c) and toluene (d). (B) Time-dependent fluorescence spectra of BPCP−AuNPs in THF (AuNPs, 5×10^{-5} mol/L; BPCP, 2.5×10^{-5} mol/L) every 10 min. Fluorescence spectra of BPCP solution (2.5×10^{-5} mol/L) in THF (C) and toluene (D) before (a) and after (b) addition of AuNPs (5×10^{-5} mol/L), keeping for 24 h. Fluorescence spectra of DHCD-HS (2.5×10^{-5} mol/L) in THF (E) and toluene (F) before (a) and after (b) addition AuNPs (5×10^{-5} mol/L), keeping for 24 h.
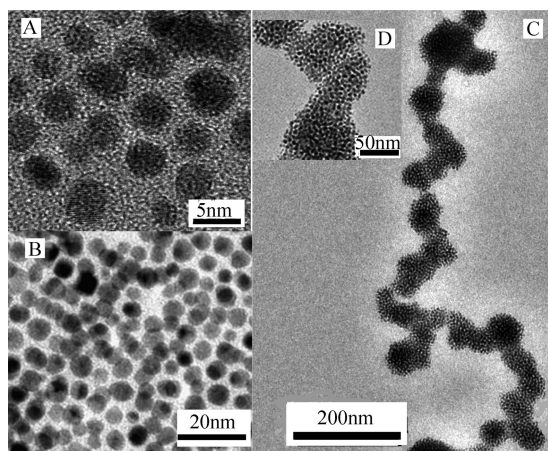

Figure 2. (A) TEM image of TOAB−AuNPs. TEM image of BPCP−AuNPs in (B) THF suspension and (C) toluene suspension. The insert of part C (D) shows the magnified TEM image.

δ (ppm): 173, 140.5, 140, 139, 135.6, 131.6, 129.6, 129.5, 127.8, 127.1, 127, 126.8, 126.7, 126, 123.1, 123.1, 122.8, 121.2, 120.5, 119.3, 108.9, 108.8, 77.4, 77.1, 76.8, 67.1, 56.3, 41.4, 40.2, 38.5, 34.6, 34.2, 28.7, 24.7. MS (MALDI-TOF): calcd for $C_{60}H_{56}N_2O_2S_4$ 996.6, found 996.
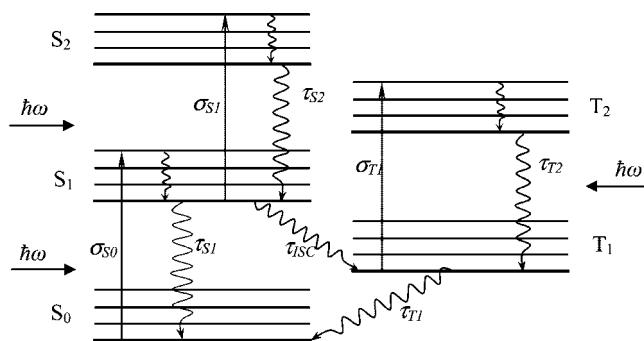

Figure 3. Five-energy-level model.

DCHD-HS was synthesized according to ref 9. Gold nanoparticles protected by tetra-*n*-octylammonium bromide (TOAB−AuNPs) were synthesized according the standard procedure in the literature.[13] The BPCP−AuNPs and DCHD−AuNPs colloid solution was prepared according to the ligand-exchange method[14] by mixing TOAB−AuNPs (1.02×10^{-2} M in toluene) and ligands (BPCP or DCHD-SH) with a specific concentration in toluene or THF.

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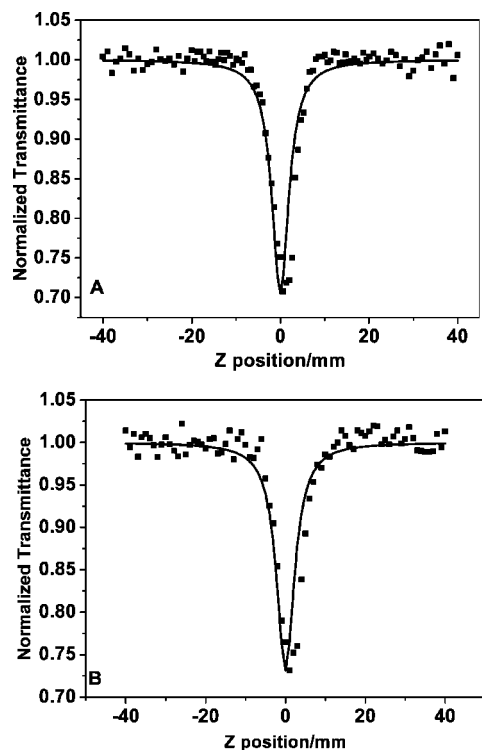
Figure 4. Normailzed transmission data of open-aperture *Z* scan without an aperture for (A) BPCP−AuNPs in toluene with linear transmission of 87% and (B) DHCD−AuNPs in toluene with linear transmission of 87% using 4 ns laser pulses at 532 nm. The solid curves are the best theoretical fitting line.

In nonlinear optical measurements a frequency-double Q-switched laser was used as the light source, which provided linearly polarized 4 ns (fwhm) laser pulses at 532 nm with a repetition rate of 1 Hz. The spatial and temporal profiles of pulses present an approximately Gaussian distribution. The incident single-pulse energy of the source was about 14.9 μJ. The samples were placed in quartz cells with 2 mm thickness, which were placed at the focus of a lens with a focal length of 30 cm. A beam splitter was used to split the laser beam into two parts. One part was measured by a precision laser detector (D1) (818J-09B, Newport Corp.) in order to measure the nonlinear absorption of the samples. The other part was simultaneously measured by another detector (D2), which had a partially closed aperture placed in front of it. The intensity change detected by D2 contains both nonlinear absorption and nonlinear refraction. The sample was mounted on a translation stage (M-531, PI Corp.) that was controlled by the computer to move along the *Z* axis with respected to the focal point.

Results and Discussion

Spectroscopic Properties. Compared with DCHD-HS, BPCP shows a larger π-conjugated length through introducing the biphenyl group. The spectroscopic study of DCHD-HS and BPCP showed homologous results. In the UV−vis absorption spectra of BPCP (2.5×10^{-5} M in THF) the strong absorption band below 300 nm was related to the high-energy transition of the carbazolyldiacetylene chromophore. The double bands centered at 333 and 342 nm showed characteristics of the carbazolyl group.[15] The fluorescence spectra possessed double weak emission bands with maxima at 352 and 369 nm (trace a, Figure 1C).

The position and width of the gold SPR absorption maxima strongly depends on the size and shape of the AuNPs protected by ligands.[16] As exhibited by the UV−vis absorption spectra, solvents affected aggregation of the AuNPs efficiently. In THF solution, the SPR maximum red shifted about 5 nm with addition of BPCP, while in toluene solution the SPR maximum red shifted about 55 nm with addition of BPCP under the same condition, which accounts for assembling of BPCP−AuNPs (Figure 1A). The colloid solutions of BPCP−AuNPs are stable; the center of the absorption bands hardly shifted even when the solution was kept for 24 h. TEM images give direct evidence for the assembling behavior in different solvents (as shown in Figure 2), and the results are in accordance with the UV−vis absorption spectra.

The fluorescence spectra of BPCP−AuNPs colloid solution were studied, and significant fluorescent enhancement was observed. By addition of AuNPs (5×10^{-5} mol/L) into the THF solution of BPCP (2.5×10^{-5} mol/L), an increase in intensity by time aging was observed, as shown in Figure 1B. By keeping for 24 h, the fluorescence intensity was obviously enhanced about 8 times as shown in Figure 1C. Also, we studied the colloid solution of BPCP−AuNPs in toluene (Figure 1D) and DCHD−AuNPs in THF (Figure 1E) and toluene (Figure 1F), all of which showed exceeding enhancement in the fluorescence intensity. Even the enhancement in BPCP−AuNPs colloid solution was stronger (BPCP−AuNPs, 8 times in THF solution and 6.5 times in toluene solution; DCHD−AuNPs, 7 times in THF solution and 4.5 times in toluene solution). All measurements were taken under identical conditions ([ligand] = 2.5×10^{-5} mol/L, [AuNPs] = 5×10^{-5} mol/L, keeping for 24 h). Those results reveal that BPCP, with a larger π-conjugated length through introducing the biphenyl group compared with DHCD-HS, holds the unusual properties of fluorescent enhancement when bound to the AuNPs, which is attributed to the aggregation-enhanced emission by restricted intramolecular rotation in the packed nanoclusters.[9,17]

Nonlinear Optical Properties. The third-order optical non-linearities of the gold nanoparticles with unusual fluorescent enhancement were investigated using the *Z*-scan technique. The *Z*-scan technique is a sensitive single-beam technique for measuring both the nonlinear refractive index and the nonlinear absorption coefficient for a wide variety of materials. It is a method for measuring the optical nonlinearities through detecting the far-field sample transmittance of a focused Gaussian beam as a function of sample position (*z*). This method provides direct measurement of nonlinear absorption and refraction along with the sign of nonlinearity.[18] The experimental setup is similar to that in ref 18. We measured both nonlinear absorption and refractive effects of two gold nanoparticles solutions in toluene at equal concentration ([AuNPs] = 5×10^{-5} mol/L, [ligand] = 2.5×10^{-5} mol/L, keeping for 24 h) by the normalized energy transmission *Z*-scan technique. The nanoparticles colloid solution was placed in a quartz cell with 2 mm thickness. The quartz cell inherently exhibits very weak optical nonlinearities, and its effect on the experimental results can be neglected. The nonlinear

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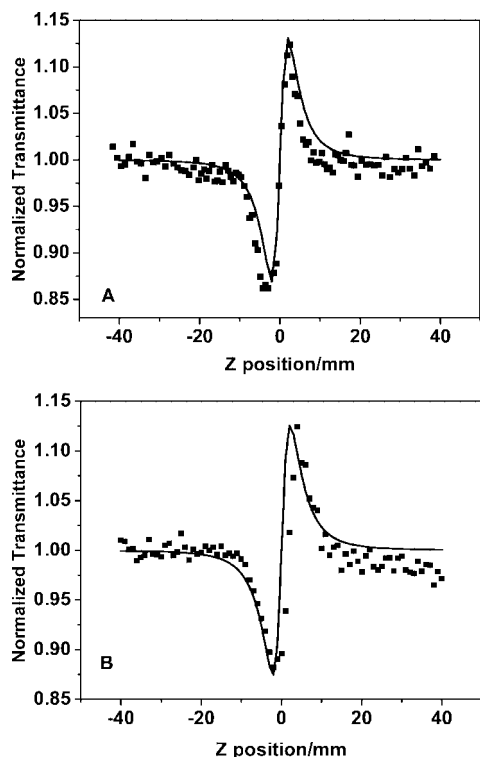
Figure 5. Pure nonlinear refractive Z-scan data of (A) BPCP−AuNPs in toluene with a linear transmission of 87% and (B) DHCD−AuNPs in toluene with a linear transmission of 87% using 4 ns laser pulses at 532 nm. The solid curves are the best theoretical fitting line.

absorption component of the samples can be evaluated under an open-aperture configuration. The nonlinear refraction was measured from the normalized energy transmission of the Z scan with an aperture whose linear transmission, S, is 0.09 under 4 ns laser pulses. The open-aperture Z-scan data are shown in Figure 4, and the pure nonlinear refractive results by Z-scan data with an aperture divided by that without an aperture are shown in Figure 5.

On the basis of the absorption and emission spectra, the five-energy-level model is supposed to be appropriate to interpret the interaction between the incident laser beams and the sample as shown in Figure 3. The transition between the ground state and the excited states has been well illustrated in ref 19. Usually, the complicated five-energy-level system can be simplified for some laser pulse duration. For nanosecond pulses, the assumption that the relaxation times of levels S_2 and T_2 are much shorter than the pulse duration is reasonable (τ_{s2} and τ_{T2} are on the order of a few picoseconds or even less). This assumption could solve the problems of population in S_2 and T_2 when setting the rate equations because the populations remain near zero. In addition, the relaxation time of level T_1 is much longer than the pulse duration, so it can be taken as infinite. The rate equations describing the transitions between the energy levels can be given as follows after the above simplifications.

$$\frac{dN_{S1}}{dt} = \frac{I\sigma_{S0}N_0}{\hbar\omega} - \frac{N_{S1}}{\tau_{S1}} \tag{1}$$

$$\frac{dN_{T1}}{dt} = \frac{N_{S1}}{\tau_{ISC}} \tag{2}$$

$$N_{S0} + N_{S1} + N_{T1} = N_0 \tag{3}$$

Propagation of the incident laser beams in the sample can be described as follows

$$\frac{dI}{dz'} = -\alpha I \tag{4}$$

The total absorption coefficient α can be expressed as $\alpha = \sigma_{S0}N_{S0} + \sigma_{S1}N_{S1} + \sigma_{T1}N_{T1}$, where σ_{S0}, σ_{S1}, and σ_{T1} are the absorption cross section of singlet ground state, singlet excited state, and triplet ground state. The nonlinear phase distortion induced by the population transition between the energy levels is discribed as

$$\frac{d\Delta\varphi(z,t)}{dz} = k\gamma I \tag{5}$$

where γ is the third-order nonlinear refractive index.

The open aperture Z-scan plots of transmittance as a function of sample position Z of BPCP−AuNPs and DHCD−AuNPs are shown in Figure 4A and 4B, respectively. Both nanoparticles solutions in toluene exhibit a significant transmittance drop when the sample moves in the vicinity of the focal plane. In the same experimental conditions the toluene solution of both BPCP and DHCD-HS showed no obvious nonlinear absorption. In addition, the frequency of the incident pulses is within the surface plasmon resonance spectral range of the BPCP−AuNPs and DHCD−AuNPs. Thus, it is believed that the nonlinear optical response of the sample is ascribed to the light-excited surface plasma resonance in the gold nanoparticles which interacted with the designed ligands.[20]

The numerical solution of eqs 3, 4, and 5 can be used to fit the experimental data under open-aperture configuration and the pure refraction data in Figure 4 and Figure 5. An excellent match between the experimental data and the theoretical curves has been achieved. The energy-level parameters used to fit the experimental data are listed in Table 1. The results in Table 1 show that the triplet excited state dominates the nonlinear absorption because of the greater absorption cross section of T_1 and the smaller intersystem crossing time τ_{ISC} compared with the laser pulse time. In BPCP−AuNPs sample, the ratio of σ_{T1} to σ_{s0} is 5, which is larger than that of DHCD−AuNPs. The greater absorption cross-section ratio between the triplet excited state and the ground state undoubtedly results in larger nonlinear absorption in BPCP−AuNPs toluene solution compared with DHCD−AuNPs sample.

The pure nonlinear refractive results by Z-scan data with an aperture divided by that without an aperture are as shown in Figure 5. The peak−valley pattern of the normalized transmittance curve shows that the nonlinear refractive indices of the two kinds of nanoparticles are positive with exhibiting self-focusing behavior. An effective third-order nonlinear refractive index γ can be obtained according to eq 5. For BPCP−AuNPs, γ is 4.2 $\times 10^{-17}$ m²/W; for DHCD−AuNPs, γ is 2.19 × 10⁻¹⁷ m²/W. The results indicate that the nonlinear refractive effect of BPCP−AuNPs is stronger than that of DHCD−AuNPs as well as the nonlinear absorption responses. The stronger nonlinear optical effects, as expected, could be attributed to the larger π-conjugated system in the BPCP ligand through introducing the biphenyl group.

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Table 1. Energy-Level Parameters Fitting the Experimental Data

sample	σ_{s0}, $\times 10^{-21} m^2$	σ_{s1}, $\times 10^{-21} m^2$	σ_{T1}, $\times 10^{-21} m^2$	τ_{s1}, ns	τ_{s2}, ns	τ_{ISC}, ns	γ, $\times 10^{-17} m^2/W$
BPCP−AuNPs	2.5	3	12.5	1	200	0.8	4.2
DHCD−AuNPs	2.5	2.5	7.5	0.9	175	1	2.19

As is well known, the surface plasma resonance can be strengthened as the molecules density and the size of metal nanoparticles increases in the nanocomposites.[22] In this case, the nonlinear scattering can be induced by the light-excited SPR in the gold nanoparticles, which interacted with the designed ligands. Therefore, the nonlinear optic could be highly enhanced. In our previous work, nanocomposite materials based on [60]fullerene derivatives−AuNPs with large third-order nonlinear properties have been designed and studied.[23] In the present study, the colloid solutions of AuNPs protected by the newly designed ligands, BPCP and DHCD-HS, not only exhibit unusual fluorescent enhancements but also show large third-order optical nonlinear properties. It is believed that those results make the nanocomposites a novel kind of nonlinear optical material with multiple potential applications.

Conclusion

We investigated the optical and nonlinear optical properties of the colloid solution of two gold nanoparticles protected by carbazolyldiacetylene derivatives of BPCP and DCHD-HS. Both the toluene solutions of BPCP−AuNPs and DCHD−AuNPs exhibit unusual fluorescent enhancement and large third-order nonlinear optical properties including large nonlinear absorption and refractive effects. With extending the π-conjugated length of the ligands, the third-order nonlinear properties of composite materials based on gold nanoparticles were enhanced accordingly. Those results provide a facile way for rational design of novel nanocomposite materials based on AuNPs for improving optical and nonlinear optical properties. Such novel materials hold potential applications in optoelectronics and integrated optics.

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