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Enlarged ultrafast optical Kerr response of C_{60} with attached multielectron donors

Shufeng Wang, Wentao Huang, Ruisheng Liang, and Qihuang Gong*
National Laboratory for Mesoscopic Physics and Department of Physics, Peking University, Beijing, 100871, China

Hongbo Li, Huiying Chen, and Di Qiang
College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China

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We measured the ultrafast third-order optical nonlinearity of C_{60} derivatives with multigroups of electron donor, —NH_2CN and —$(NH_2)_2CNCN$ attached to the C_{60} framework. The magnitudes of second-order hyperpolarizability for these two derivatives were estimated at 1.0×10^{-32} esu and 3.5×10^{-32} esu. The values are several times larger than that for C_{60} poly-aminonitrile, which is a monoadduct of C_{60} and —(—NH_2CN—$)_6$ group, and two orders larger than that for the C_{60} molecule.

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INTRODUCTION

π-conjugated organic materials were believed to exhibit a large nonlinear optical response and to increase with conjugation length.[1,2] For years, the investigations on third-order nonlinearity, or the second-order hyperpolarizability γ, of C_{60} and its derivatives with large conjugation, were carried out using different methods.[3–15] The third-order nonlinearity of the C_{60} molecule has recently been proved to be very small both from experiments[16,17] and from theory[18] for nonresonant cases. However, chemical modified fullerene derivatives[19] of charge transfer complexes (CTC's) (Ref. 17) or anions showed extremely large optical nonlinearity. This is due to the break of the highly symmetric electronic structure of C_{60} by the introducing electrons. Also, the C_{60} shows some electron deficient character, which makes it easy to be an electron acceptor while interacting with electron-rich groups (donors). These specialities indicate a new way to synthesize optical materials with large optical nonlinearity. Previous works on nonlinearity of modified C_{60} were focused mostly on extending molecule size along a single dimension. Long groups were chemically attached to the cagelike framework of the fullerene molecules.[17,20] It was proved efficient for increasing the NLO response of fullerene materials. The γ for C_{60} poly-aminonitrile and for C_{70} poly-aminonitrile were 3.2×10^{-33} esu (Ref. 17) and 1.6×10^{-32} esu (Ref. 20) at a nonresonant wavelength of 820 nm. These values were more than 30 times larger than the upper limits of the C_{60} and C_{70} molecules, respectively. Recently, theoretical calculation and femtosecond optical nonlinearity measurement on third-order nonlinearity of the C_{60} derivative of carbon nanotubes were reported.[21–24] The extremely large γ for the single wall carbon nanotubes (SWCN's) shows another way to increase the third-order nonlinearity of fullerene materials.

The third-order nonlinear response of a one-dimension donor-acceptor (D/A) molecule system, such as C_{60} poly-aminonitrile, had been regarded to grow up with the increase of electron delocalization length. However, will the single-dimension charge transfer fully develop the electronic structure of the C_{60} system for the largest optical nonlinearity? In a previous report, Wang *et al.*[25] tested C_{60} attached with seven —NH_2CN groups. Only two times enhancement of γ was found when comparing it to C_{60}. In their measurement, a femtosecond visible laser at 647 nm was used. Extremely large nonlinearity for C_{60} itself was obtained. Their results conflicted with the most recently experimental and theoretical conclusions that C_{60} exhibited poor third-order optical nonlinearity. This might be the result of resonant enhancement. In this paper, a similar complex of C_{60} attached by five —NH_2CN groups was synthesized. The optical nonlinearity was measured by a femtosecond optical Kerr gate technique at 830 nm. Its γ was obtained as 1.0×10^{-32} esu. Compared with that for C_{60}, which is less than 9×10^{-35} esu by our former report,[17] enhancement of more than two orders on γ is proved. Meanwhile, we also tested another similar multigroups attached C_{60} derivative, $C_{60}[(NH_2)_2CNCN]_5$. The γ was obtained as 3.5×10^{-32} esu. This result is accordant with the delocalization length dependence of third-order optical nonlinearity. We noticed that this type of chemical modification can provide a potential benefit for nonlinear optical application.

MATERIALS AND METHOD

Materials synthesis

The two C_{60} derivatives were synthesized using a two-phase reaction method. For $C_{60}(NH_2CN)_5$, 350 mg NH_2CN was dissolved in 10 ml 1.5 M sodium dydroxide. 20 mg C_{60} was dissolved in 20 ml toluene. Then the two solutions were mixed in a round-bottomed flash with phase transfer catalyst and tetrabutyl ammonium iodide. The mixture was stirred at room temperature until the purple color of the toluene layer disappeared and the water phase became turbid brown. The water phase was separated and centrifuged to obtain the brown precipitate. The precipitate was washed by toluene, acetone, and methanol for several times, then dried in vacuum. According to the elemental analysis result, the average number of NH_2CN molecules added to C_{60} was five. The illustrative formula of the adduct may be represented as $C_{60}(NH_2CN)_5$. The $C_{60}[(NH_2)_2CNCN]_5$ was synthesized with the same method.

The absorption spectra for the solutions of these two derivatives are shown in Fig. 1. They indicate no absorption at a laser wavelength of 830 nm. In the experiment, $C_{60}(NH_2CN)_5$ was dissolved in the mixture of water and dimethyl sulphoxide (DMSO, 1:3 for volume ratio) at 3×10^{-3} M. $C_{60}[(NH_2)_2CNCN]_5$ was dissolved in the mixture of water and DMSO (1:9 for volume ratio) at 1×10^{-3} M.

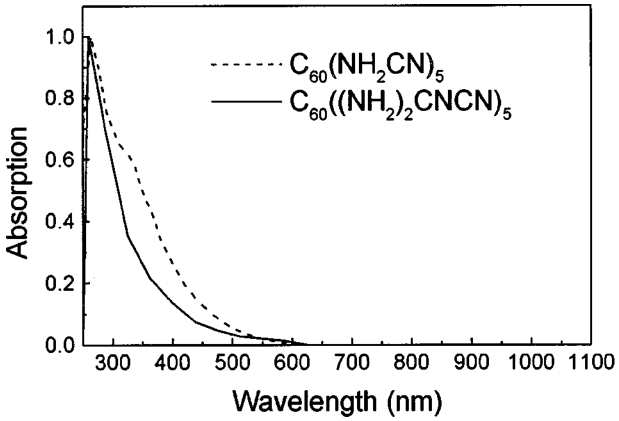

FIG. 1. Absorption spectra of $C_{60}(NH_2CN)_5$ and $C_{60}[(NH_2)_2CNCN]_5$.

Measurement method

The femtosecond optical Kerr gate technique was applied in this experiment.[17,20,26] The femtosecond laser, centered at 830 nm, delivered from a Ti:sapphire laser system (Mira 900F, Coherent, USA), which was pumped by a multiline Ar^+ laser system (Innova 400, Coherent, USA) at 11 W. The repetition rate was 76 MHz. The average power was about 1.5 W. This femtosecond laser beam was split into a probe beam and a pump beam by a beam splitter. The intensity ratio for the probe beam and pump beam was 1:10. The polarization of the probe beam was carefully adjusted at 45° to the linear polarized pump beam. The pump beam passed through a delay line driven by a step motor. Then it was carefully reflected parallel to the probe beam at an adjacent configuration. The two beams were focused by a convex lens. At the focus of the lens, the two beams overlapped each other. This focus would be enclosed within the sample cell of 1 mm in thickness during the measurement. The sample cell also could be replaced by a BBO crystal to determine the pulse width *in situ* with the autocorrelation technique. By this measurement, we determined the pulse width as 120 fs. After transmitting through the sample cell, the pump beam was blocked, while the probe one passed an analyzer, of which the transmission axis was strictly perpendicular to that of the probe beam. Finally, the generated optical Kerr effect (OKE) signal entered the photodiode detector. The signal collected by the detector was transmitted to a lock-in amplifier (SR830, Stanford, USA), then to a personal computer, which acted as controller for the whole system.

Results and discussion

Our synthesis productions were proved as five groups attached C_{60}. The structure for multiadduct cyclopentadiene mode is shown in Fig. 2 with top view and side view. It is well known that isomeric compounds of multiadducted C_{60} show only a small energy difference. Therefore, different conformations may be mixed together in the final production. These conformations include a vinylamine mode and a cyclopentadiene mode *et al.*[27] In this experiment, while excessive radical groups were added, the five-adducted C_{60} of cyclopentadiene mode shown in Fig. 2 was almost exclusive.

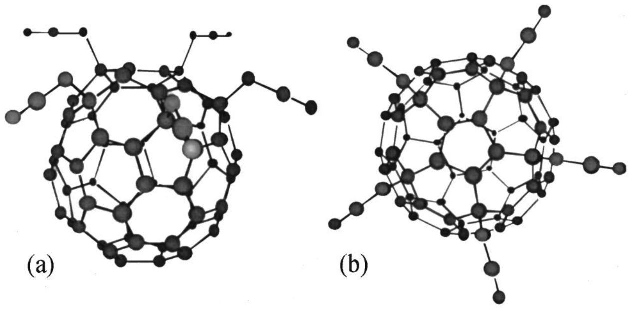

FIG. 2. Possible structure of five adduct derivative of $C_{60}(NH_2CN)_5$. Side view (a) and top view (b).

The samples were measured in a series of concentrations to verify the square dependence of signal to concentration. This series for $C_{60}(NH_2CN)_5$ were 3×10^{-3} M, 2×10^{-3} M, and 1×10^{-3} M. The OKE signals for the three concentrations are shown in Fig. 3, together with solvent response. Very good signal-to-noise ratio shown in the figure means that under our condition control, laser scattering and heating effects of solutions were ruled out. The signals were ultrafast and symmetric. This indicates the electronic contribution was the main mechanism for third-order optical nonlinearity. Therefore, the conclusion that the optical nonlinearity came mainly from electronic contributions of π conjugation and charge transfer could be made. In the experiment, we used CS_2 as reference sample. The following equation was employed to calculate the third-order nonlinearity of sample solutions at different concentrations:[17,20]

$$\chi_S^{(3)}=\chi_R^{(3)}\left(\frac{I_S}{I_R}\right)^{1/2}\left(\frac{n_S}{n_R}\right)^2. \tag{1}$$

In this equation, the subscripts of S and R, stand for sample and reference sample of CS_2. I is the OKE signal intensity, while n is the refractive index. The $\chi^{(3)}$ for $C_{60}(NH_2CN)_5$ was 5.8×10^{-14} esu at 3×10^{-3} M. The γ for CS_2 was 1×10^{-13} esu. This value for CS_2 was reported by K. Minoshima, Taiji, and Kobayashi previously[28] at a femtosecond

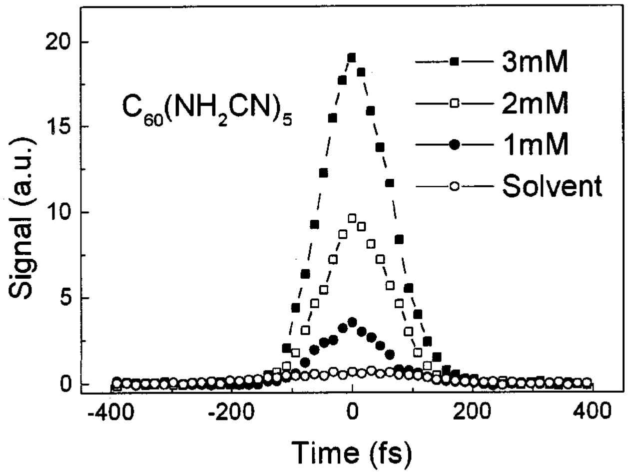

FIG. 3. Nonlinear response of $C_{60}(NH_2CN)_5$ at different concentrations, including solvent response.

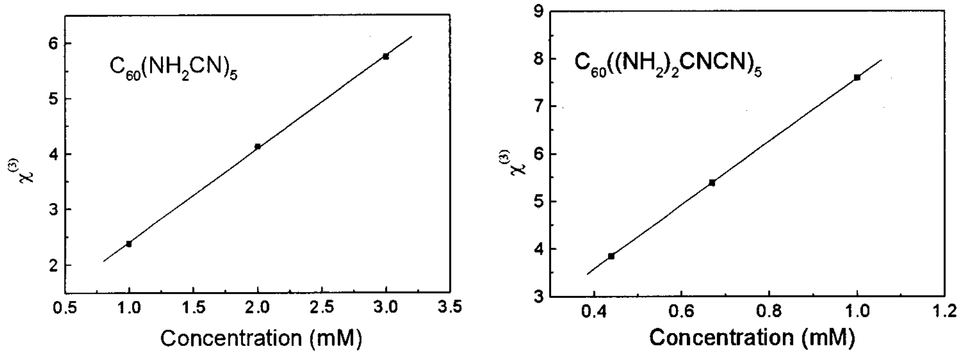

FIG. 4. The linear relationship between third-order NLO susceptibility, $\chi^{(3)}$ and concentration of $C_{60}(NH_2CN)_5$ and $C_{60}[(NH_2)_2CNCN]_5$.

time scale. As shown in Fig. 4, the $\chi^{(3)}$ increased linearly to the sample concentration. This proves the third-order NLO response of solutions came from sample molecules instead of the nonmolecule response such as aggregation effect, which would show very poor square dependence. The γ could be calculated as

$$\gamma=\chi^{(3)}/(NL), \tag{2}$$

where N is the molecule concentration of sample solution and L is local field correction factor, which is defined as $[(n^2+2)/3]^4$. By Eq. (2), we may calculate γ of $C_{60}(NH_2CN)_5$ molecule as 1.0×10^{-32} esu. This γ is among the largest nonresonant second-order hyperpolarizability of organic NLO molecules. The same measurement and calculation were also performed to $C_{60}[(NH_2)_2CNCN]_5$. The concentration series used was 1×10^{-3} M, 6.7×10^{-4} M, and 4.4×10^{-4} M. The result clearly showed stronger signals when comparing to the former one. The γ was 3.5×10^{-32} esu for $C_{60}[(NH_2)_2CNCN]_5$. Though different concentrations, 3×10^{-3} M and 1×10^{-3} M, were used for the two derivatives, the incident laser intensity was kept through the whole experiment. (The change of laser intensity would alternate the reference signal of CS_2, in addition, it might damage the sample at high power.) The square dependencies of the signal to concentration were independent to any specific concentration. This independence proved that the signals came from the uniformly distributed molecule system. If any other effect existed, such as aggregation, irregular dependence would appear at high concentration instead of square one.

Comparing to our previous work,[17] we add five small chemical groups of —NH_2CN and —$(NH_2)_2CNCN$ to C_{60} framework, other than single poly-aminonitrile group. The nonlinearity of these molecules were more than three times larger than that for C_{60} poly-aminonitrile, which attached only one ‘‘long tail’’ to C_{60} molecules. In addition, the optical nonlinearity of $C_{60}(NH_2CN)_5$ and $C_{60}[(NH_2)_2CNCN]_5$ increased according to the length of the group from —NH_2CN to —$(NH_2)_2CNCN$. The reason for the improvement on nonlinear response of C_{60} while forming a charge transfer complex is that the introduced electrons alternate the electronic symmetry of C_{60} molecule. C_{60} was formerly recognized as an excellent third-order NLO material for its double bonds rich electronic structure. However, with the regular presence of alternated hexagon and pentagon, the double bonds are localized and a poorly delocalized electronic structure was formed. The highly symmetric structure of C_{60} block most of transition pathway from ground state, which is of A_g symmetric, to excited states. This view was proved true by testing the anions of C_{60} (Refs. 29 and 30) from C_{60}^{-} to C_{60}^{3-}. These anions showed γ increased significantly with the increase of a negative charge. The system suggested further modification and utilization. By breaking double bonds and attaching electron donor groups, the C_{60} derivatives showed prominent enhancement on third-order NLO response comparing to the C_{60} molecule. For multiadducted C_{60} derivatives and former reported materials, the significant increment on NLO response was obvious. The reason for this phenomenon is the formation of strong charge transfer complex in which the fullerene acts as an electron acceptor and the attached groups are electron donors. The multidonor structures can induce more charge transfer process than the single donor. Therefore, they exhibit larger nonlinearity. This is reasonable for the proposed molecular structure and consistent with the conclusion of Lascola and Wright.[29,30] As suggested in Fig. 2, the radicals both attached to the upper hemisphere of the C_{60} molecule. Comparing with other multiadduct production, a more prominent spatial charge separation and asymmetry occurred along the axis of molecule, which may also help to enhance the optical nonlinearity.[31]

CONCLUSION

We measured the ultrafast third-order optical nonlinearity of C_{60} derivatives of $C_{60}(NH_2CN)_5$ and $C_{60}[(NH_2)_2CNCN]_5$, which multielectron donors were attached. Femtosecond OKE experiment at 830 nm wavelength was carried out. The two derivatives show a more enhanced off-resonant NLO response than that for single polymer group attached C_{60}. This new way of molecule design is of potential effectiveness on increasing γ of C_{60} derivatives. The study on samples with different charge transfer donors and metal ions is in progress.

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[*] Corresponding author. Email: qhgong@ibm320h.phy.pku.edu.cn

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