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Cross-linked C₆₀ Polymer Breaches the Quantum Gap

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Received June 3, 2004; Revised Manuscript Received July 27, 2004

ABSTRACT

Sum rules predict the largest off-resonance electronic nonlinear susceptibility allowed by quantum mechanics. The range between ($10^{-3/2}$ to 1) times the physical limit level has until now not been penetrated experimentally and has become known as the quantum gap. We report the first measured second hyperpolarizability to breach the quantum gap. Through cross-linking, the C₆₀-polymer film reported used delocalized electrons from neighboring three-dimensional C₆₀ molecules and realized significant red shift of its energy levels. An ultrafast second hyperpolarizability of 9.6×10^{-32} esu (55% of the physical limit) has been achieved.

Sum rules predict the largest off-resonance electronic nonlinear susceptibility allowed by quantum mechanics.^{1–5} Comparison with published experimental data⁶ reveals that the very best molecules fall below a factor of $10^{-3/2}$ of the fundamental limit.⁴ The range between the $10^{-3/2}$ level and the fundamental physical limit has become known as the nonlinear molecular susceptibility quantum gap. There is an urgent need to approach this limit as closely as possible to make third-order nonlinear optics of practical utility in ultrafast optical signal processing for fiber-optic communications. Prior to this work, all reported measurements were found to fall well short of the fundamental limit.

The fundamental limit on the diagonal tensor component of the second hyperpolarizability γ satisfies^{1,3}

$$-\frac{e^4 \hbar^4}{m^2} \left(\frac{N^2}{E_{10}^5} \right) \leq \gamma \leq 4 \frac{e^4 \hbar^4}{m^2} \left(\frac{N^2}{E_{10}^5} \right) \quad (1)$$

The negative limit is for a centrosymmetric molecule and the positive limit for an asymmetric molecule. E_{10} , the energy to the first excited state, is determined from the linear absorption spectrum, and the number of electrons, N , is given by twice the number of double or triple bonds.⁵ According to eq 1, to increase the off-resonant hyperpolarizability it is necessary to make a molecule with a single dominant state; λ_{\max} (the wavelength corresponding to the energy to the first excited state) as red shifted as possible and with as many electrons as possible.

We adopted the approach of using the abundant delocalized π electrons available in a three-dimensional fullerene molecule and using cross-linking in the film-forming process to realize significant red shift of λ_{\max} and increase the number of available electrons. As a result, we report herein the first experimentally measured second hyperpolarizability which breaches the nonlinear molecular susceptibility quantum gap and, within experimental uncertainty, approaches the fundamental quantum limit.

A trihydroxyl-containing C₆₀ (3OH–C₆₀) was obtained from the 1,3-dipolar cycloaddition reaction of C₆₀, tricine, and benzaldehyde. The cyclic amine moiety in 3OH–C₆₀ contributed to the required charge transfer, and the hydroxyl groups were used for cross-linking with an isocyanate. Commercially available TMP (a triisocyanate derived from trimethylolpropane and xylylene diisocyanate) was used in the prepolymer formulation with 3OH–C₆₀ (Figure 1).⁷ The cross-linked polyurethane film containing 25 wt % of 3OH–C₆₀ (or 19.1 wt % of C₆₀) was prepared by casting and curing at elevated temperatures.

The spectral dependence of the nonlinear refractive indices (n_2) and the nonlinear absorption coefficient (β) of the film were characterized using the Z-scan technique with a picosecond pulsed laser (pulse width 3.3 ps) tunable across the wavelength range of 1150–1600 nm (Figure 2). The details of the Z-scan technique and the measurement can be found elsewhere.^{8–10} The measurement was performed with a laser intensity of 1.8 GW/cm² within the common laser intensity range used for off-resonant Z-scan measurement, accompanied with the monitoring of the sample morphology by an infrared camera to ensure no heating-resulted degrada-

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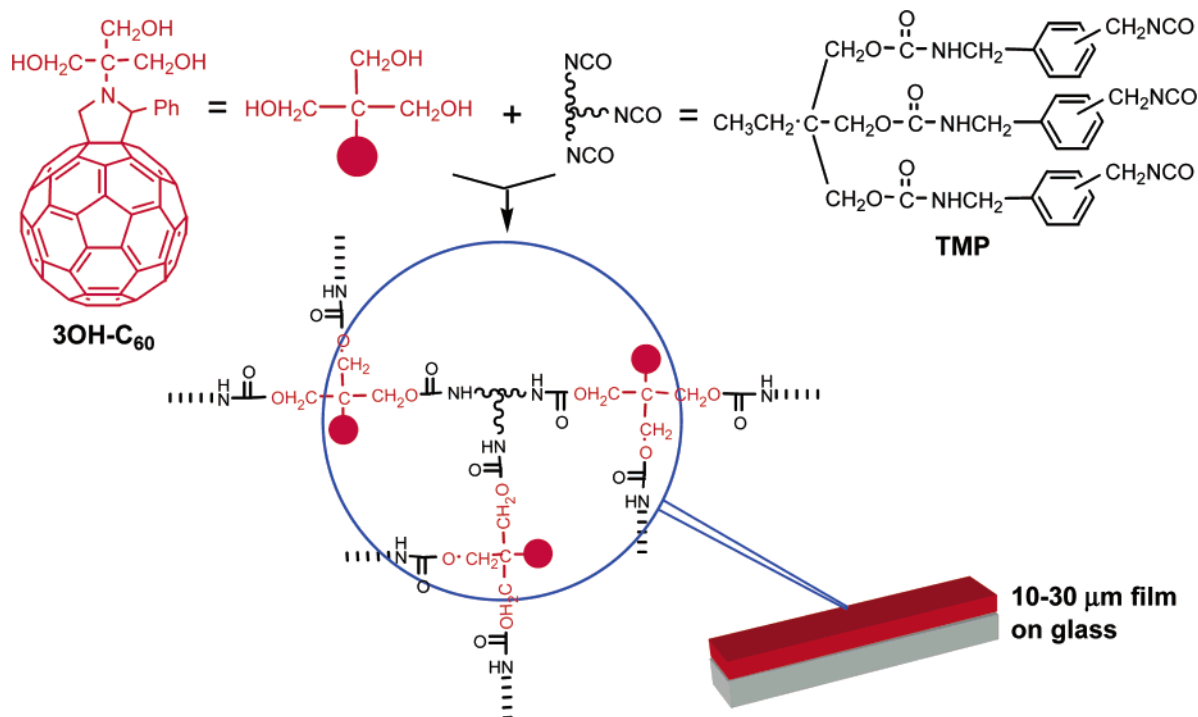


Figure 1. Preparation of cross-linked C₆₀-polyurethane films.

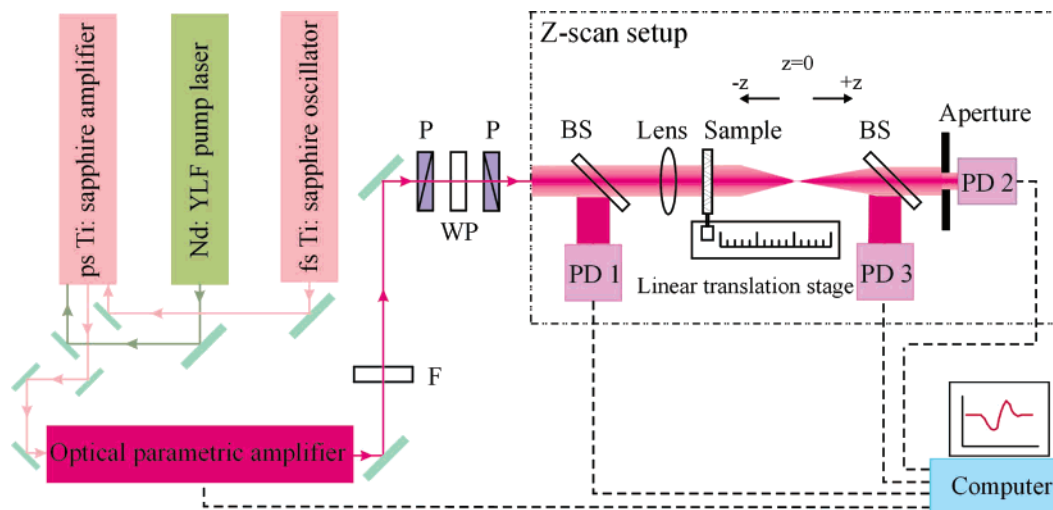


Figure 2. Experimental setup for Z-scan measurement: F, filter; P, polarizer; WP, $\lambda/2$ plate; BS, beam splitter; PD1–PD3, photodetectors.

tion occurred to the film. The off-resonant n_2 at 1550 nm was $2.0(\pm 0.6) \times 10^{-3} \text{ cm}^2/\text{GW}$. The values of the third-order nonlinear optical susceptibility ($\chi^{(3)}$) and molecular second hyperpolarizability (γ) were 9.7×10^{-11} and 9.6×10^{-32} esu, respectively. A comparison of the γ values reported in the literature for pristine and chemically modified C₆₀ in solutions^{11–14} and solid-state^{15–17} with the value reported herein¹⁸ is shown in Figure 3. We show for reference the calculated physical limits for these molecular systems.

For pristine C₆₀, there are 30 double bonds with the corresponding $N_{\text{C}_{60}} = 60$ and $\lambda_{\text{max}} = 330 \text{ nm}$ in the linear absorption spectra. The dressed second hyperpolarizability γ_0 can be calculated as 6020×10^{-36} esu while the $10^{-3/2}$ level is 190×10^{-36} esu. For the C₆₀-polyurethane film we studied, we take one 3OH-C₆₀ together with one TMP as a

molecule for simplified consideration, which gives 45 double bonds ($N = 90$). With $\lambda_{\text{max}} = 550 \text{ nm}$, we can obtain its dressed second hyperpolarizability $\gamma_0 = 174,171 \times 10^{-36}$ esu. The $10^{-3/2}$ level is $5,510 \times 10^{-36}$ esu. The experimental result ($\gamma = 9.6 \times 10^{-32}$ esu) is 17 times the $10^{-3/2}$ level and equal to 55% of the physical limit.

This first breaching of the nonlinear molecular susceptibility quantum gap shows that electrons are efficiently used in our polymer system. The successful enhancement of γ is ascribed to a combination of two strategies. (1) Full utilization of the conjugated double bonds available from the three-dimensional molecule C₆₀. This is done by molecular substitution to break the localization of the double bonds in the poorly delocalized electronic structure of the pristine C₆₀. (2) Increased effective number density. We employed

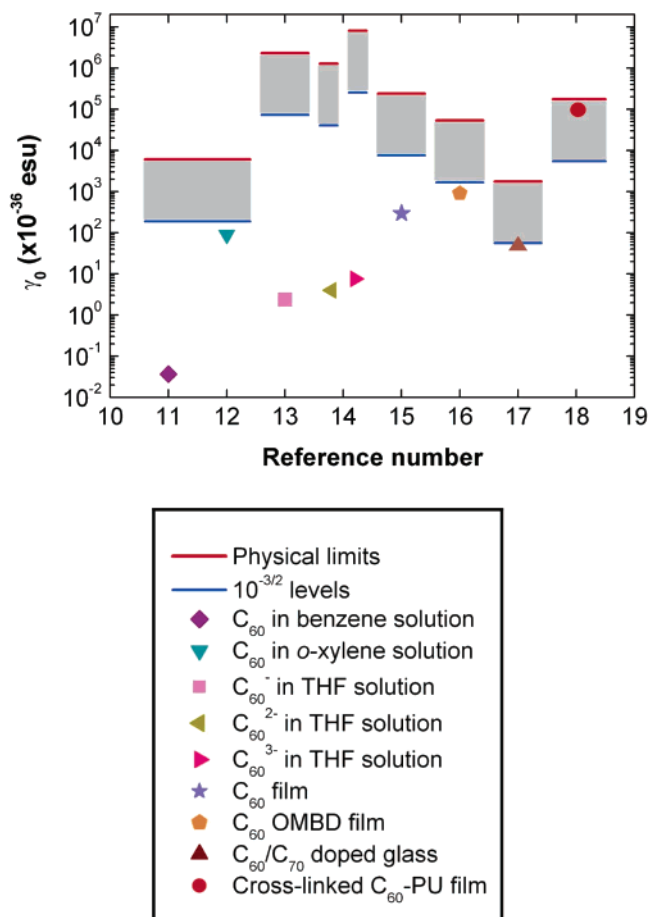


Figure 3. Comparison of the experimental results of the second hyperpolarizability of pristine and chemically modified C_{60} derivatives in solutions and solid-state with their corresponding physical limits and the $10^{-3/2}$ levels. Due to the different substitutions, the linear absorption spectra and the number of electrons are different, resulting in different magnitudes of the physical limits and the $10^{-3/2}$ levels. Shaded areas represent the nonlinear molecular susceptibility quantum gaps.

a high degree of cross-linking, which effectively generated a new chromophore cluster or unit. A unit consisting of N molecules is deemed to have N times as many electrons as the individual C_{60} molecule, leading to a γ value for the unit N^2 times that for the individual molecule. Since the number

of the unit is $1/N$ that of the individual molecules, the bulk value is enhanced by a factor N . In addition, cross-linking allows for a strong molecular interaction between the functionalized C_{60} molecules, as evident by the λ_{\max} red shifted from 330 nm for pristine C_{60} to 550 nm for the C_{60} -polyurethane film.

The results presented herein deploy molecular engineering to achieve nonlinear second hyperpolarizability approaching the physical limit. The large ultrafast second hyperpolarizability of a highly loaded, processible polymer system at telecommunication wavelengths is urgently needed to enable ultrafast all-optical processing of information-bearing signals within the optical domain.

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NL049159Q