

# Quantum interference in organic solid

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**Abstract:** We demonstrate high contrast quantum interference between one-photon and three-photon absorption pathways in an organic solid at room temperature. Illumination of a thin polymer film activated with fluorescing dendrimer chromophores of large three photon absorption cross section with two simultaneous femtosecond pulses at near-IR frequency  $\omega$  and its third harmonic UV frequency  $3\omega$  results in a spatial interference fringe pattern observable by eye.

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**OCIS Codes:** (190.4180) Multiphoton processes; (270.1670) Coherent optical effects

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Quantum interference arises if atom or molecule undergoes a transition from one state to another in more than one way at the same time [1]. In multi-photon absorption, quantum interference can take place if the same optical transition is excited by either one short wavelength photon or three long wavelength photons [2]. An intriguing property of such two-color quantum interference is that it offers a possibility to exert control over the total transition probability via adjusting the relative phase between the two wavelengths. This enables new interesting physical effects and potential applications including suppression of absorption in optically thick medium, coherent control of chemical reactions, precise laser clock synchronization, new type of phase-sensitive detection, and others.

One of the main challenges for implementing these ideas is finding or creating materials where quantum interference is strongly pronounced. Furthermore, to produce practical devices based on the quantum interference effect, the relevant medium needs to be a solid, and should function preferably at room temperature.

Interference between alternative molecular excitation pathways was demonstrated recently by ionizing a gas of small molecules with an intense optical pulses of frequency  $\omega$ , and simultaneously with third harmonic pulse of frequency  $3\omega$ , such that the same molecular transition is excited by absorbing one  $3\omega$ -photon or three  $\omega$ -photons [3-7]. Here we show that by designed a special organic nonlinear-optical solid fluorophore we can increase the efficiency of the three-photon absorption by several orders of magnitude, up to the point where the quantum interference and the associated quantum fringe pattern becomes easily observable, even with an unaided eye. The nonlinear-optical material consists of thin polymer film activated with fluorescing dendrimer molecules [8], which we synthesize to exhibit record large value of three-photon absorption cross-section, owing to cooperative enhancement effect [9-10]. Quantum interference in an organic solid at room temperature may facilitate practical ultrafast quantum molecular switches [11] and quantum memory devices [12].

Consider an IR beam of frequency  $\omega$  crossing at a small angle with a UV beam of frequency  $3\omega$ , as shown in the inset of Fig. 1. A conventional optical sensor or detector, if placed at the intersection of the two beams, is unable to reveal any interference between the UV- and IR wavelengths because the quantum transitions responsible for the absorption of the different frequency photons terminate in different final states (a). The interference can take place if we use, instead, as the detector a nonlinear optical medium, in which the same final state is reached by absorption of one UV photon and three IR photons (b). The population of the final state becomes a coherent superposition of the two excitation amplitudes, and will display a pattern of interference fringes, which are analogous to the classical Young double slit experiment. In principle, one could detect the interference fringes by measuring the fluorescence emitted from the excited state, provided that the efficiency of the excitation is adequate.

Although the principle of the two-color quantum interference is rather straightforward, practical implementation of the above proposed experiment has not been feasible, so far, due to the fact that the efficiency of the multi-photon absorption processes in most known materials is very small. Previous demonstrations of the quantum interference were achieved through indirect highly sensitive detection methods involving either ionization of atomic- and molecular gases [4-7], or by measuring photo-induced current in semiconductors [13,14]. Low probability of simultaneous absorption of three photons in previous experiments implied

tightly focused, very high intensity excitation beams, which also precluded direct observation of the quantum interference fringes.

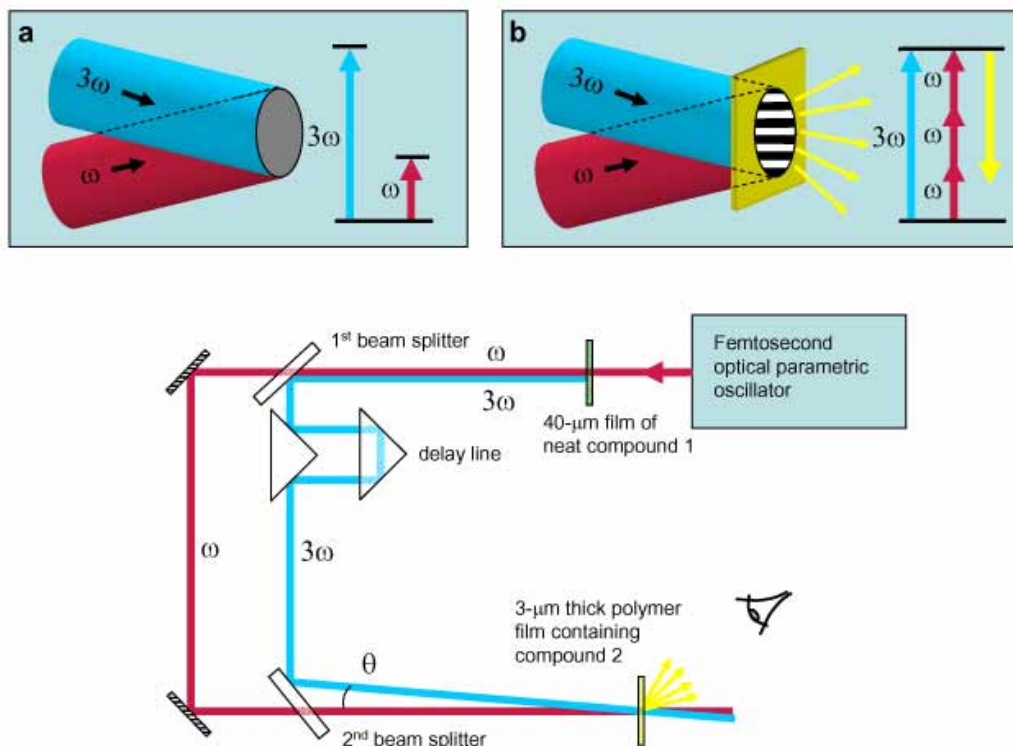


Fig. 1. Main figure: experimental set up. A thin film of compound 1 generates 3rd harmonic at 415 nm with efficiency 1%. Compound 2 absorbs simultaneously UV and IR, and produces visible fluorescence at 560nm wavelength. Inset: a, conventional detector observes no interference between frequency  $\omega$  and  $3\omega$  because these IR and UV wavelengths are absorbed independently from each other. b, Interference appears if a special detector (compound 2) is used, which is capable of absorbing, in the same electronic transition, both UV and IR wavelengths.

In recent years, organic synthesis, assisted by much improved understanding of the underlying structure-property relationships, has enabled a variety of new compounds with enhanced nonlinear-optical properties [15-17]. Here we take advantage of a novel type of branched organic molecules, which we have created to maximize the efficiency of multiphoton absorption [8, 18]. Figure 2 shows two compounds that we have synthesized for the purpose of this experiment: a three-arm G-0 dendrimer based on bis-diphenylamino stilbene (BDPAS) repeat units (compound 1), and four-arm G-0 dendrimer, where four BDPAS arms are attached to bis-diphenylamino di-styryl benzene (BDPADSB) core (compound 2). Figure 2 shows the one-photon- and three-photon absorption spectra of compound 2, where the last has peak value,  $\sigma_3 = 1.5 \cdot 10^{-79} \text{ cm}^6 \text{ s}^2 \text{ photon}^{-2}$ , which is one of the largest values obtained previously for any kind of molecular system. We point out that the maximum transition wavelength of the three-photon absorption coincides with the maximum of the one-photon spectrum, which indicates that both types of transitions take place between the same initial and final states.

The unusually large nonlinear-optical cross section of these molecules derives from two circumstances. First, the particular linear chromophores (BDPAS and BDPADSB) are known as efficient three-photon absorbers [18]. Second, and most important, the molecules with the distinctive two-dimensional dendritic (branched) structure of the type shown in Figure 2,

display strong electron delocalization between the branches, which leads to cooperative enhancement (compared to the sum of the individual chromophores) of electronic transition dipole moments, both in ground state, as well as in excited electronic state [8-9]. By synthesizing such structures, we have recently achieved a profound enhancement of both two- and three-photon absorption cross section for femtosecond pulses in near-infrared range of wavelengths.

Figure 1 shows the scheme of the experimental setup, in which we use the 1245 nm output of a femtosecond optical parametric amplifier (pulse duration 100 fs, pulse energy 0.1 mJ and repetition rate 1 kHz) as the source for the frequency  $\omega$ , whereas the third harmonic at 415 nm serves as the frequency  $3\omega$ . The tripling of the frequency is accomplished by passing the 1245 nm beam through a 40- $\mu\text{m}$  thick film of neat gel of self-soluble three-arm stilbene dendrimer (compound 1 in Fig. 2). The UV pulses are generated collinearly with the IR beam, their energy is about 1%, and their duration is about the same as that of the IR pulses. The first dielectric beam splitter separates the IR from UV by transmitting the IR wavelength and reflecting the UV wavelength. The second beam splitter combines the two beams at a small angle, and brings them to a common 0.4 mm diameter spatial spot on the sample. The exact temporal overlap between the UV- and IR-pulse is achieved by fine adjusting the optical delay in the UV arm of the interferometer (Fig. 1).

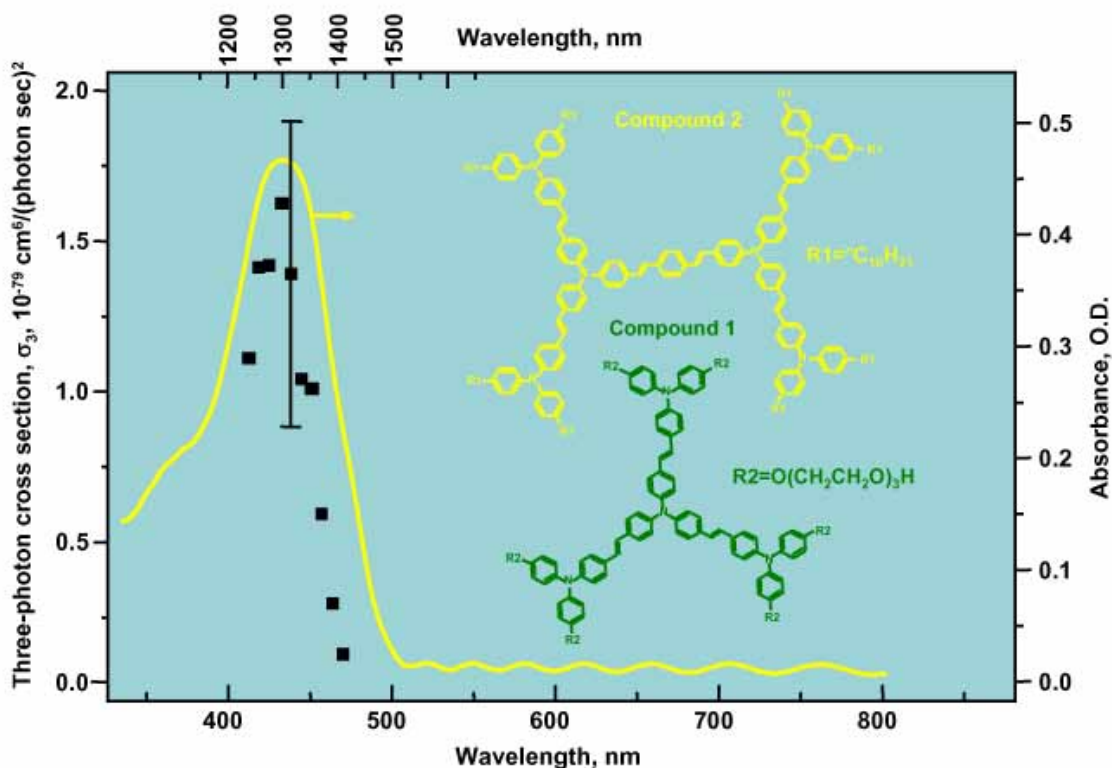


Fig. 2. Absorption spectrum (right vertical scale and lower horizontal scale) and chemical structure of three-arm G-0 dendrimer based on bis-diphenylamino stilbene (BDPAS) repeat units (compound 1), and four-arm hybrid G-0 dendrimer based on bis-diphenylamino di-styryl benzene (BDPADSB) core with attached BDPAS branches (compound 2). Maximum molar extinction is,  $\epsilon(420\text{nm})=1.1 \cdot 10^5 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon(420\text{nm})=2.5 \cdot 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ , for the compound 1 and 2, correspondingly. Black squares present three photon absorption cross section of compound 2 (left vertical scale and upper horizontal scale for laser wavelength).

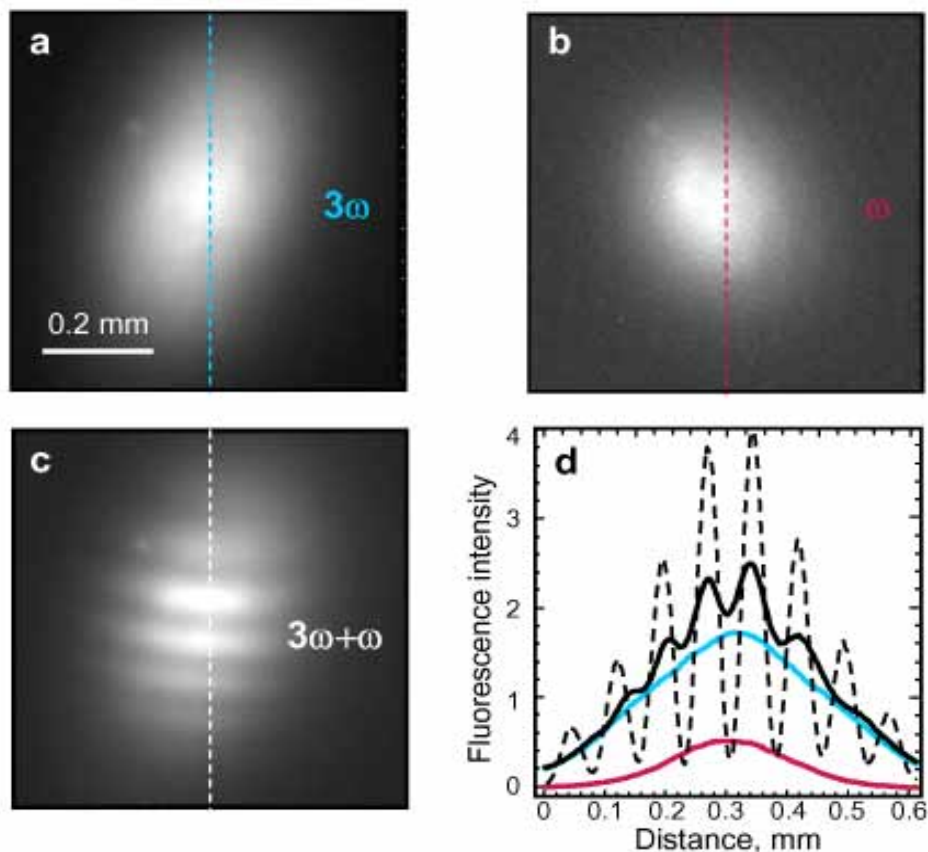


Fig. 3. Image of the fluorescence when UV pulse (a) or IR pulse (b) is applied alone. c, Interference pattern observed when both UV and IR pulses are applied simultaneously. d, Vertical intensity profile of the three images (along dashed lines). Dashed curve, estimated pattern of maximum contrast interference.

Our sample is prepared by spin-coating a 3- $\mu$ m-thick film of polystyrene, activated with the compound 2 at concentration of  $6 \cdot 10^{-3}$  M, on a flat glass substrate. A thermo-electrically cooled digital CCD camera (Xillix) was used to capture and quantify the intensity of the fluorescence signal. Figure 3 shows the spatial pictures of the fluorescence emitted by the sample, when the film is illuminated with UV pulses of incident energy,  $P_{UV} \approx 0.5$ nJ, and IR pulses of energy,  $P_{IR} \approx 8\mu$ J. The intensity of the fluorescence from our chromophore molecules is strong enough to be observed directly by eye through a simple microscope lens used for image magnification.

When the two pulses are applied simultaneously, then the intensity of the fluorescence shows a clear pattern of dark and bright fringes (Fig. 3(c)), which can be seen even with unaided eye. A strong low-pass filter, which cuts off all residual UV light in the IR arm of the interferometer, ascertains that no conventional (optical) interference contributes to this picture. As a further check, we change the angle between the beams, and make sure that the fringe spacing behaves as,

$$D = \frac{c}{3\omega} \frac{1}{2\sin\theta/2}. \quad (1)$$

As expected for quantum interference, in our experiment  $D$  is determined by the frequency of the transition, whereas for conventional (optical) interference  $D$  would be given by the frequency of the illuminating light.

The spectroscopic properties of the fluorescence emission, such as spectrum, quantum yield, etc. are in the current compound, as in most organic solids, largely independent whether the absorption involves one-photon process or three-photon process. Therefore, we can assume that the intensity of the fluorescence signal in our experiment is at all times directly proportional to the population of the excited state. We can make use of this fact to obtain some quantitative insight into the expected contrast of the interference fringes by noting that when the UV pulse alone is applied, then the fluorescence is proportional to the intensity of the UV pulse,  $F_{UV} \propto P_{UV}$  (Fig. 3(a)), while when the sample is illuminated with the IR pulse alone (Fig. 3(b)), then the emission is proportional to the third power of the incident IR intensity,  $F_{IR} \propto P_{IR}^3$ . (Note that, while the physical diameter of the two beams is about the same, the cubic dependence on the intensity makes the IR-excited fluorescence spot in Fig. 3(b) smaller than the corresponding UV-excited spot in Fig. 3(a).). When both the UV pulse and the IR pulse are applied simultaneously, then the emission is proportional to the superposition of the corresponding one- and three-photon excitation probability amplitudes, which can be expressed as,

$$F_{QI} \propto \left| \sqrt{F_{UV}} + e^{i\phi} \sqrt{F_{IR}} \right|^2, \quad (2)$$

where  $\phi$  is the relative phase. Now, by taking the measured ration between the maximum fluorescence signals,  $F_{UV}^{\max} / F_{IR}^{\max} \approx 3$ , we plot the maximum contrast interference (dotted line in Fig. 3(d)), that could be obtained under ideal conditions. Obvious experimental factors that can reduce the contrast of the quantum interference are, for example, large difference of pulse propagation velocity in polymer for two wavelengths, a non-uniform distribution of the pulse amplitude through the sample thickness, random spatial orientation of the molecular dipoles in the polymer material relative to the polarization of the light, etc. It is noteworthy that, even without taking any of these factors into account, the observed fringe contrast is still almost 20% of the absolute maximum value. This finding is even more remarkable because ultrafast sub-picosecond dephasing of electronic coherence, which is very typical to organic solids at room temperature, does not appear to much deteriorate the high contrast of the quantum interference fringes. The fact that the quantum fringes occur with high contrast in a solid at room temperature indicates that the three-photon transition occurs, at least in our material, between the same electronic-vibrational states as the corresponding one-photon transition. In this case the interference is occurring as an instantaneous process, and will not be affected by fast loss of coherence or relaxation of the excited state of the molecule.

A key feature for future applications of the quantum interference effect consists in the possibility of using the relative phase between the alternative excitation paths to switch between different desired outcomes of the processes. This effect was recently exploited to demonstrate active control over the outcome of some elementary chemical reactions in gas phase [19-20]. Our experiment indicates that quantum interference effect could be used to control photochemical reactions in large organic molecules and even in organic solids. The structural advantage offered by the solid medium is an important factor in developing practical quantum interference devices, such as recently proposed ultrafast optical switches [11] and optical quantum memory based on slow light [12].