Chapter 11

Novel Two-Photon Absorbing Polymers

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1. INTRODUCTION

Multiphoton absorption has a number of inherent characteristics that make it attractive for use in a number of fast emerging technologies, including multiphoton fluorescence imaging, microfabrication, and optical power limiting to name but a few. To meet the needs of these, and other, applications, the design and synthesis of polymeric materials that exhibit high multi- or two-photon absorption is critical.

Two-photon absorption (TPA) is the nonlinear process in which two photons can be simultaneously absorbed in the material at high input irradiance. Although multiphoton absorption processes have been known since 1931, through the theory of simultaneous absorption of two-photons developed by Goeppert-Mayer (1), this field remained undeveloped until the advent of the pulsed laser providing very high-intensity light. It was not until the early 1960s that the two-photon absorption process was experimentally verified by Kaiser and Garrett (2), using pulsed lasers that provided very high intensity. In the presence of intense laser pulses, molecules can simultaneously absorb two or more photons mediated by a so-called ‘virtual state,’ a state of the molecule that has no classical analogue (3). The transition probability for absorption of two identical photons is proportional to $I^2$, where $I$ is the intensity of the laser pulse. The combined energy of the two photons accesses a stable excited state of the molecule. If the two photons are of the same energy (wavelength), the process is referred
to as degenerate TPA. On the other hand, if the two photons are of different energy (wavelength), the process is non-degenerate TPA.

As light passes through a molecule, the virtual state may form, persisting for a very short duration (of the order of a few femtoseconds). TPA can result if a second photon arrives before decay of this virtual state, and for this reason, the probability of TPA is proportional to the square of the light intensity. Thus, TPA involves the concerted interaction of both photons that combine their energies to produce an electronic excitation analogous to that conventionality caused by a single photon of a correspondingly shorter wavelength. Unlike single-photon absorption, whose probability is linearly proportional to the incident intensity, the TPA process depends on both a spatial and temporal overlap of the incident photons and takes on a quadratic (nonlinear) dependence on the incident intensity. The linear absorption of material may be very weak in the wavelength range where the TPA occurs, facilitating the potential to excite materials at greater depth than might be possible via one-photon excitation.

Two-photon transitions can be described by two different mechanistic types. In non-polar molecules with a low-lying strongly absorbing state \( |g\rangle \) near the virtual level, only excited states that are optically forbidden by single photon selection dipole rules can be populated via two photon absorption (type 1) (3). The probability that this low-lying state can contribute to the virtual state is predicted by Heisenberg’s uncertainty principle, with a virtual state lifetime approximated as \( \hbar / (4\pi \Delta E) \), where \( \hbar \) is Planck’s constant and \( \Delta E \) is the energy difference between the virtual and actual states. Using this equation, it is predicted that an allowed state can contribute to formation of the virtual state for time \( t_{\text{virtual}} \) which is equal to about \( \hbar / (4\pi \Delta E) \) with the transition probability proportional to \( \Delta \mu^2 \). In polar molecules, strong TPA can occur by a different mechanism (type 2) in which a large change in dipole moment \( (\Delta \mu > 10 \text{D}) \) occurs upon excitation of the ground to an excited state (3), in this case the lifetime of virtual state is proportional to \( \Delta \mu^2 \). An allowed two-photon transition can be viewed as a sequence of two one-photon allowed transitions \( |g\rangle \rightarrow |u\rangle \rightarrow |g\rangle \) (4). Two-photon absorptivity, \( \delta_i \), is expressed in Goeppert-Mayer units (GM), with \( 1 \text{GM} = 1 \times 10^{-50} \text{ cm}^4 \text{ s molecule}^{-1} \text{ photon}^{-1} \).

Particular organic molecules can undergo upconverted fluorescence through non-resonant two-photon absorption using near-IR radiation, resulting in an energy emission greater than that of the individual photons involved (up-conversion). The use of a longer wavelength excitation source for fluorescence emission affords advantages not feasible using conventional UV or visible fluorescence techniques, e.g. deeper penetration of the excitation beam and reduction of photobleaching. The wavelength used for two-photon excitation is roughly twice that for one-photon excitation.