Organic materials for all-optical signal processing and optical limiting

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Newly developed, conjugated organic materials exhibit large refractive or absorptive nonlinearities that are promising for optical-signal handling at telecommunications wavelengths.

Materials with large third-order nonlinear optical responses are of great interest for ultrahigh-bandwidth optical-signal processing and also for selective attenuation of strong laser pulses (referred to as ‘optical limiting,’ OL) For optical-signal processing, most schemes attempt to use the refractive-index change of a nonlinear material in the presence of a strong control beam to switch a signal beam. However, nonlinear absorption (such as two-photon absorption, 2PA) must be minimized to achieve effective switching. On the other hand, strong nonlinear absorption facilitates OL of intense laser pulses, but materials with suitably high nonlinear suppression over a wide bandwidth and a range of pulse widths in the near-IR spectrum are lacking.

Conjugated organic materials with high electron delocalization exhibit large third-order optical nonlinearities, \( \chi^{(3)} \), whose real (Re) and imaginary (Im) parts are related to nonlinear refraction and 2PA, respectively. For all-optical signal processing, a large magnitude of \( \chi^{(3)} \) and a \( \text{Re}(\chi^{(3)})/\text{Im}(\chi^{(3)}) \) ratio greater than \( \sim 10 \) are needed for effective optical switching. For OL, a large \( \text{Im}(\chi^{(3)}) \) or higher-order nonlinear absorption coefficient is of particular interest.

Conjugated molecules called cyanines have extremely high, essentially 1D, electron delocalization and exhibit optimized molecular third-order nonlinearity, \( \gamma \), per molecular length. Cyanines show a high-order, power-law dependence of the nonlinearity on length, suggesting that extended cyanines may provide a route to extremely large nonlinearities. However, cyanines undergo symmetry breaking at long lengths, which localizes electrons and greatly diminishes the molecular nonlinearity. Extended cyanines with dioxaborine terminal groups (see Figure 1) retain high electron delocalization at large lengths, where other systems succumb to symmetry breaking. We
observed a very large, negative nonlinearity with $\text{Re}(\chi^{(3)}) \approx -5 \times 10^{-3}$ esu for this substance at 1300nm. The $\text{Re}(\chi^{(3)})$ of a thin film of dioxaborine cyanine molecular salt was $-3.6 \times 10^{-10}$ esu, with $\text{Re}(\chi^{(3)})/\text{Im}(\chi^{(3)}) \approx 10^3$. Moreover, we realized $\text{Re}(\gamma)/\text{Im}(\gamma) > 100$ over telecommunications bands with selenopyrylium cyanines of different lengths. Understanding the energy-level structure of the one- and two-photon states of cyanines was crucial to identify a region of low 2PA in the near-IR regime between two low-energy 2PA bands. This allows a rational choice of laser wavelengths for pre-resonance enhancement through a small detuning from the one-photon band while avoiding significant 2PA to realize an exceptionally large $\text{Re}(\gamma)/\text{Im}(\gamma)$ ratio.

In contrast, we observed strong nonlinear optical absorption for a lead porphyrin diacetylide polymer with $\sim$13 repeat units. The porphyrin-ring electronic states are strongly coupled through diacetylene linkages, resulting in a strong, sharp excitonic band at 858nm, as well as large 2PA cross sections in the near-IR spectral regime, ranging from $\sim$1200GM (1GM, or Goeppert-Mayer, unit equals $10^{-50}$ cm$^4$ s/photon) at 1450nm to $\sim$6000GM at 1064nm. Femtosecond transient spectroscopy revealed strong excited-state absorption (ESA) bands caused by short-timescale singlet-singlet and long-lived triplet-triplet absorption, possessing broad bandwidths of $\sim$600nm. Each band plays a critical role in OL on different timescales (see Figure 2). Rapid intersystem crossing results in a large triplet yield and the corresponding triplet ESA leads to effective nanosecond-OL. We performed OL studies at 1064, 1300, and 1550nm for both femto- and nanosecond ($\sim$7ns) pulses (see Figure 2). The optical suppression, defined as the inverse of the sample transmittance prior to damage, was substantial throughout the near-IR range. It exceeded 18dB (60×) in the femtosecond regime and 14dB (25×) in the nanosecond regime. Incorporation of lead porphyrin polymer solutions into a hollow-core optical fiber allowed an increase of the effective interaction length from 1mm to 1.8cm through wave-guiding, while maintaining a linear transmittance of 80%. In this geometry, we demonstrated optical suppression of nearly 100× for nanosecond pulses at 1300nm.

In summary, we have demonstrated the feasibility of developing conjugated organic molecules with large refractive nonlinearities and low nonlinear loss. Our next step is to translate these exceptional molecular nonlinearities into processable, low-linear-loss materials that may be integrated with silicon photonic-waveguide structures. The latter provide a powerful platform for high-bandwidth, low-power all-optical signal processing. We also showed the effectiveness of conjugated polymers as broadband, wide-temporal-range, nonlinear absorbers that strongly suppress near-IR pulses for OL applications.

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Continued on next page
References


