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# New Fullerene-Based Mixed Materials: Synthesis and Characterization

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## Abstract

This is the final report of a three-year, Laboratory Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). We present results of broadband femtosecond transient absorption and broadband nanosecond optical limiting studies of $C_{60}$ and derivatized $C_{60}$. We have investigated both solutions and solid-state mixed materials (sol-gel glass hosts doped with fullerene guests). We show that derivatized fullerenes provide enhanced solubility and processability, with a ground-state absorption extended into the infrared compared with $C_{60}$. We have extensively studied both the dynamic optical response and the excited-state absorption cross sections of solutions and solids for multiple wavelengths in the visible to near infrared. Wavelength-dependent studies show that the optical limiting response improves monotonically at longer wavelengths, demonstrating broadband limiting in all 6,6 mono-adducts and neat $C_{60}$. We report new approaches to processing sol-gel glass/fullerene composites to improve the optical limiting performance of solid-state materials to approach the response of solution limiters.

## Background and Research Objectives

Since the first isolation of Buckminsterfullerene ($C_{60}$) in appreciable quantities [Ref. 1], there has been an explosion of research into the unique properties of this new form of carbon [Ref. 2]. The geometry of $C_{60}$ resembles a soccer ball, with truncated icosohedral ($I_h$) symmetry. The unique nonlinear optical properties of the fullerenes are due to the highly polarizable conjugated $\pi$-electrons, which are delocalized over the surface of the sphere. $C_{60}$ can be modified by synthetic chemical techniques (including those developed as part of this project). We have studied the effects of these modifications on the optical and electronic properties of the fullerenes (Publications 1-3). We have explored the

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fundamental chemical and physical properties of pristine and modified fullerenes, and incorporated them within silica glass hosts using sol-gel methods to form new composite materials for nonlinear optical applications (Publications 1-12).

In developing fullerene/glass composites, we invented techniques to form optimized solid-state materials for optical limiting (OL) (Publication 4). Fullerenes have the property that they absorb light much more strongly under intense laser excitation than for low intensities [Ref. 3]. This OL behavior is desirable for protection of eyes and sensors from harmful pulsed lasers. Fullerene/sol-gel glasses are one of the most promising solid-state optical limiters in the near-infrared spectral range.

## Importance to LANL's Science and Technology Base and National R&D Needs

This project has contributed to the basic understanding of the physics of organic $\pi$-conjugated molecules, and their interactions with inorganic host matrices. We have systematically explored the effects of chemical substitution on the electronic states and relaxation dynamics in fullerenes. We have developed significant new experimental resources for both femtosecond time-resolved spectroscopy and for nanosecond nonlinear optical spectroscopy. We have patented several new materials for optical limiting, and have begun to commercialize this technology under ongoing CRADA partnerships. We have successfully made the transition from a basic science research program funded under LDRD, to an externally funded program to develop critical technology for national defense needs. In particular, the need is acute for viable materials that provide passive protection for eyes and sensors from damaging pulsed laser radiation . Our research has led to new solid-state materials for optical limiting, and new promise for field-testable devices.

## Scientific Approach and Accomplishments

### *Ultrafast Optical Studies of Fullerenes and Fullerene Derivatives*

The linear absorption spectra are shown for $C_{60}$ and two soluble derivatives in Figure 1. The structures of the derivatives are shown in Figure 2. We have performed extensive studies of broadband femtosecond (fs) transient absorption (TA) of these compounds. We have developed an improved measurement technique for fs TA spectra that allows sensitivity to $10^{-5}$ in differential transmission (Publication 13). This improved instrumentation has allowed us to make a detailed comparison of excited-state spectra with established energy level diagrams for $C_{60}$ deduced from linear absorption measurements [Ref. 4]. This is the first direct mapping of excited-state transitions and their oscillator strengths to the ground-state transitions (Publications 1,2). This data is illustrated in Figures 3 and 4.

In $C_{60}$, the early-time excited-state absorption spectrum is dominated by transitions for the initially excited singlet states (spins of the excited-states aligned anti-parallel). Within 1 nanosecond (ns), the singlets convert to triplet states (spins aligned parallel) due to 96% efficient intersystem crossing. Thus, the excited-state absorption spectrum at long delays is dominated by the long-lived triplet excited-state transitions. In $C_{60}$, the triplet excited-state absorption is much larger than the ground-state absorption over much of the visible to near-infrared spectral range, leading to reverse saturable absorption (RSA) and the desirable optical limiting effect. By fitting the relaxation dynamics of the transient absorption spectra, it is possible to deduce both the intersystem crossing time, and the relative magnitudes of singlet-singlet and triplet-triplet excited-state cross sections (Publications 1-3). This information is critical for understanding the optical limiting behavior.

***Synthesis of Fullerene/Glass Composites***

We have formed glass composites containing $C_{60}$ and soluble derivatives using sol-gel chemistry techniques. We have demonstrated that the fullerene concentration in these glasses can be controlled over a wide range and that the resulting materials can be polished to high-quality surfaces and have optical damage thresholds much higher than plastic host materials. Our synthetic methods for preparing sol-gel composites have been published and patented (Publications 2,3,4,8-11). A series of glasses doped with variable fullerene concentrations is shown in Figure 5. Fullerene/sol-gel glasses are one of the most promising solid-state optical limiters in the near-infrared spectral range.

***Optical Limiting in Fullerene/Sol-gels***

We have observed enhanced optical limiting behavior in solutions of derivatized fullerenes, including PCBM (Publication 9) and CPB (Publications 1,2), from 532 nm to 700 nm. As described above, our transient absorption measurements determined the spectral and temporal regions of interest for optical limiting in $C_{60}$ and $C_{60}$ derivatives, and predicted enhanced limiting at longer wavelengths (Publications 1-3,9). Intensity-dependent transmission measurements made at several wavelengths confirmed these results (Publications 1-3,9). We find that the increased solubility and broadened ground state absorption of the functionalized $C_{60}$ (Fig. 6, solid circles) make it a more effective optical limiter in the red and near-infrared than the pure $C_{60}$ (Fig. 6, solid squares).

We also used transient absorption to demonstrate that the morphology of the fullerene molecules in the solid state is a crucial parameter in the optical-limiting effectiveness for nanosecond pulses (Publications 1-3). Figure 7a shows the normalized

relaxation dynamics for the desirable triplet-triplet excited-state transition for $C_{60}$ in solution, thin films, and a sol-gel glass (Publication 1). The glass allows isolation of the fullerenes relative to the film, for which the relaxation of the excited states is so rapid that no significant optical limiting effect is observed for thin films (Publications 1-3). The solvent used can also influence the relaxation kinetics, with dichloro-benzene (DCB) solutions decaying much faster than toluene solutions as seen in Figure 7b (Publication 1).

The optical limiting of the pre-doped sol-gels is lower than that in solution. However, by appropriate treatment of the sol-gel glass, the optical limiting can be improved to approach the performance seen in solution (Figure 8) (Publications 1,2). The optimized sol-gel glass composites have excellent durability, optical damage thresholds higher by a factor of 10-20 than for solutions or solid-state devices using plastic (PMMA) hosts, and optical limiting behavior nearly identical to that of the same molecules in solution. Under the United States Army STTR Program, we are now participating in a CRADA with GELTECH, Inc. (a manufacturer of optical components using sol-gel methods) to commercialize these materials.

## Publications


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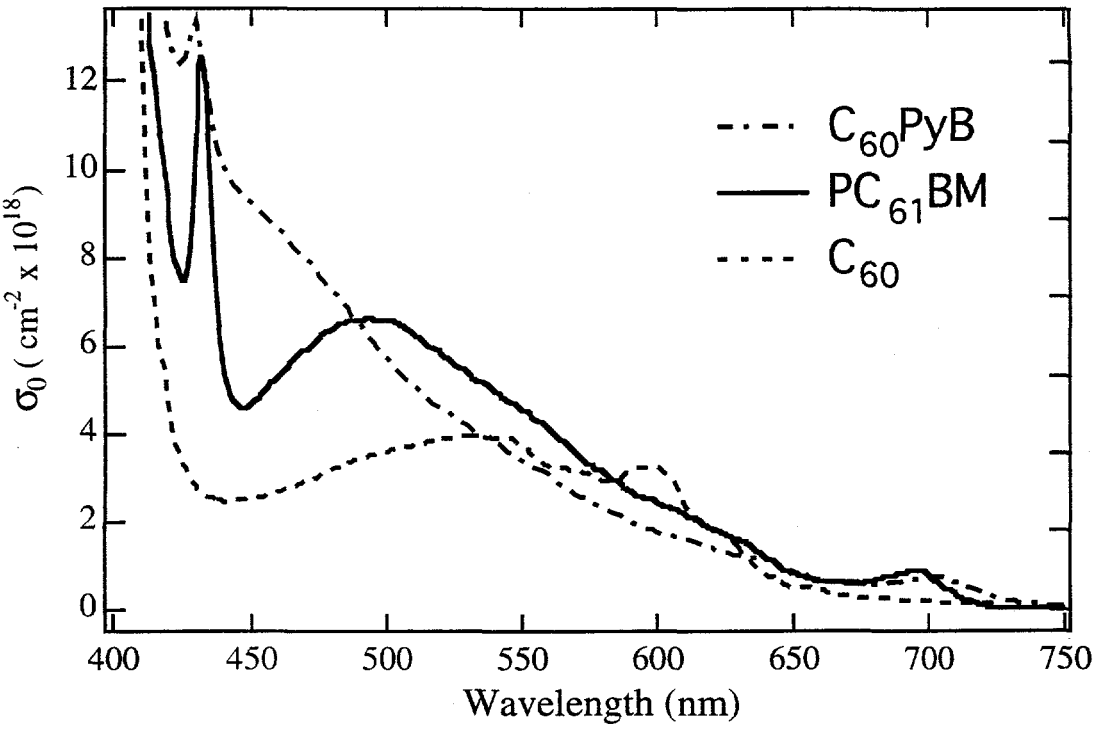
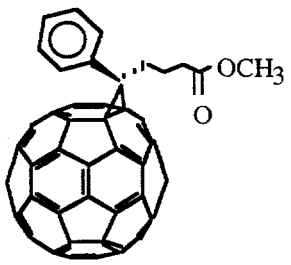
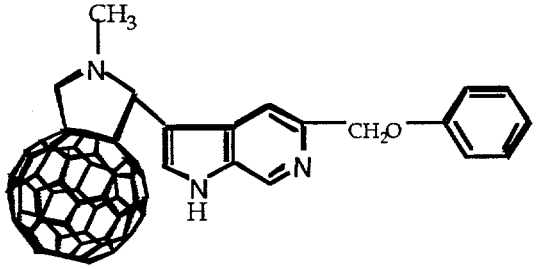



Figure 1. Ground state absorption for solutions of $C_{60}$ (dashed), PCBM (solid), and CPB (dot-dash).




6,6 Phenyl-$C_{61}$ butylmethoxy (PCBM)




$C_{60}$-pyrrolidine(3)-5-benzyloxy-1H-pyrrolo[2,3-C]-pyridine (CPB)

Figure 2. Structures for fullerene derivatives PCBM and CPB.

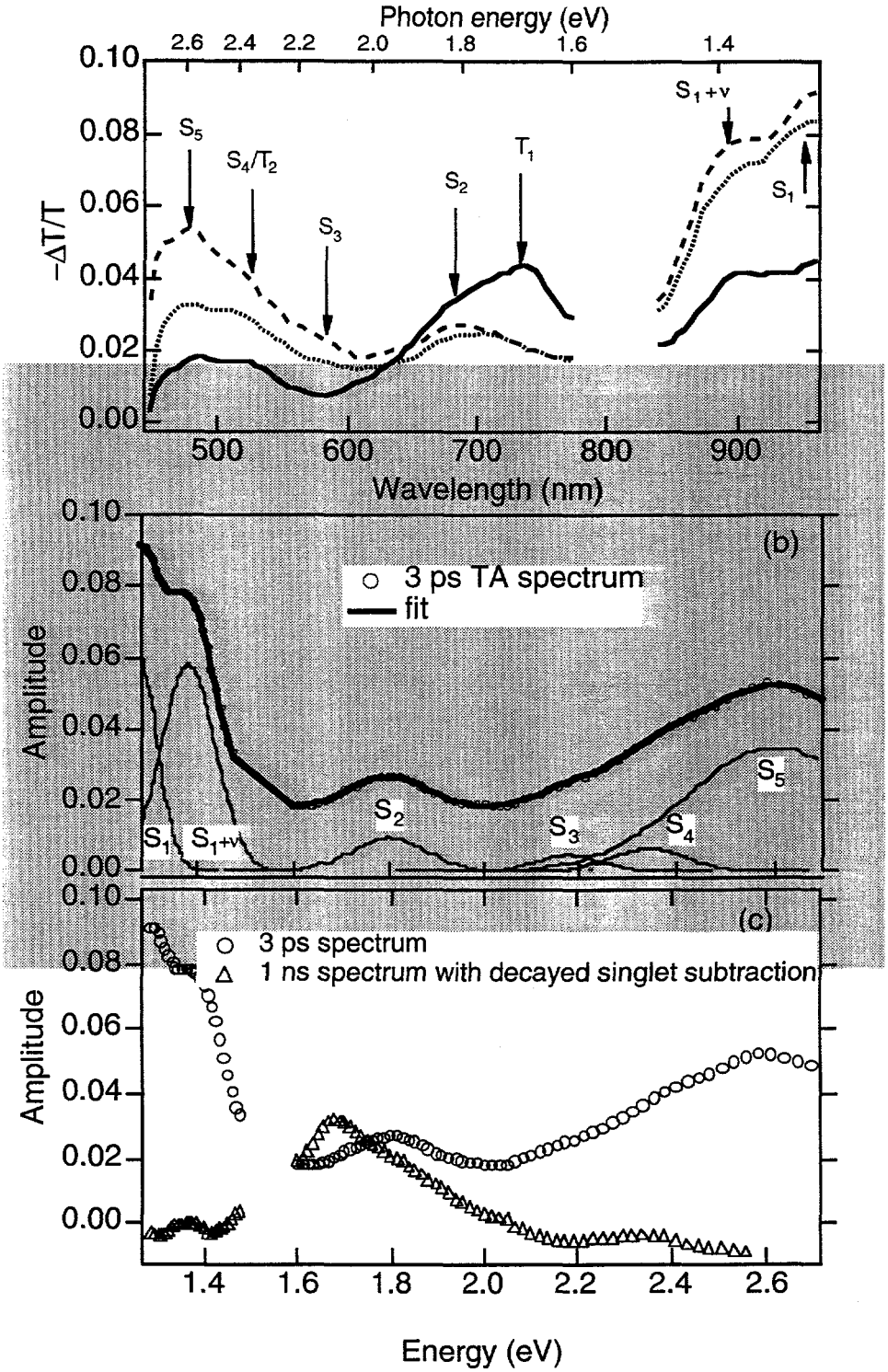



Figure 3. (a) Differential transmission (-ΔT/T )for \cs\ in toluene solution taken at three delay times: 3 ps (solid line, singlet excited-state absorption), 100 ps (dashed line), and 1 ns (dot-dashed line, triplet excited state absorption). (b) Nonlinear least quares fit of 3 ps transient absorption spectrum for $C_{60}$ using six gaussian peaks. (c) Spectrum for the triplet at 1 ns obtained by subtracting the time-decayed singlet spectrum.

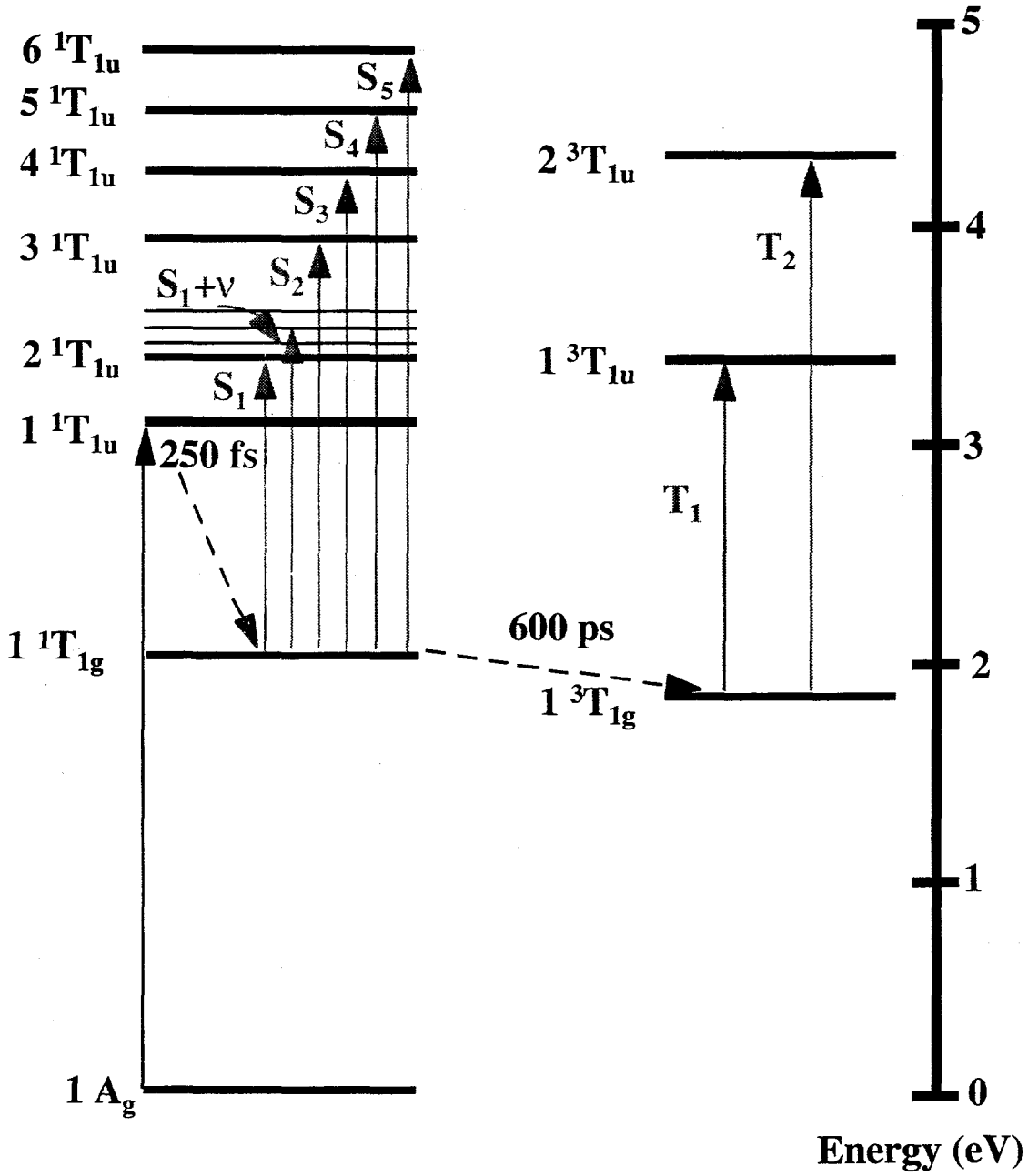



Figure 4. Energy level diagram for $C_{60}$, adapted from Ref. 4, showing excited-state transitions as labelled in Fig. 1.

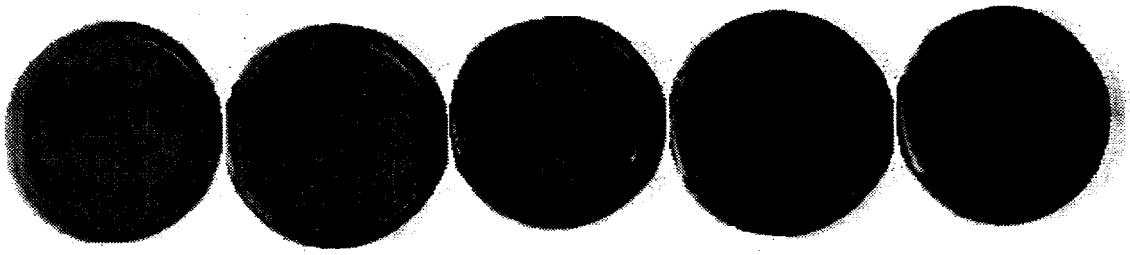


Figure 5. Composite silica glasses containing variable concentration of the chemically modified fullerene derivative PCBM.

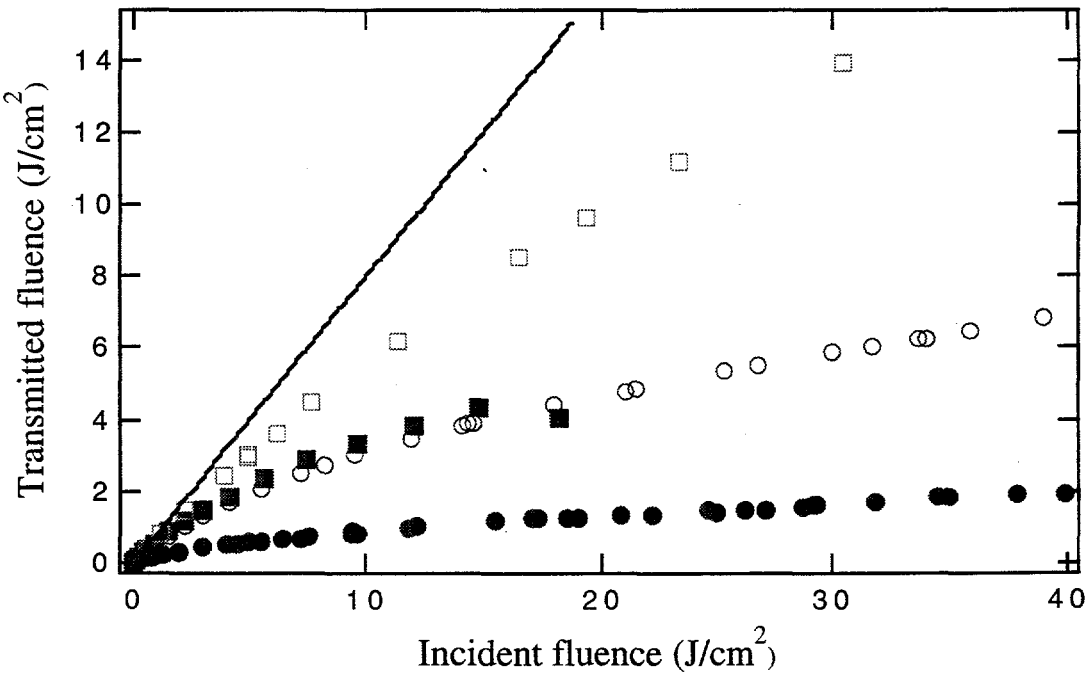



Figure 6. Intensity-dependent transmission for $C_{60}$ at 532 nm (open squares, low intensity transmission T=80%) and 700 nm (solid squares, T=80%) and for 6,6 PCBCR at 700 nm (open circles, T=80%; solid circles, T=50%).

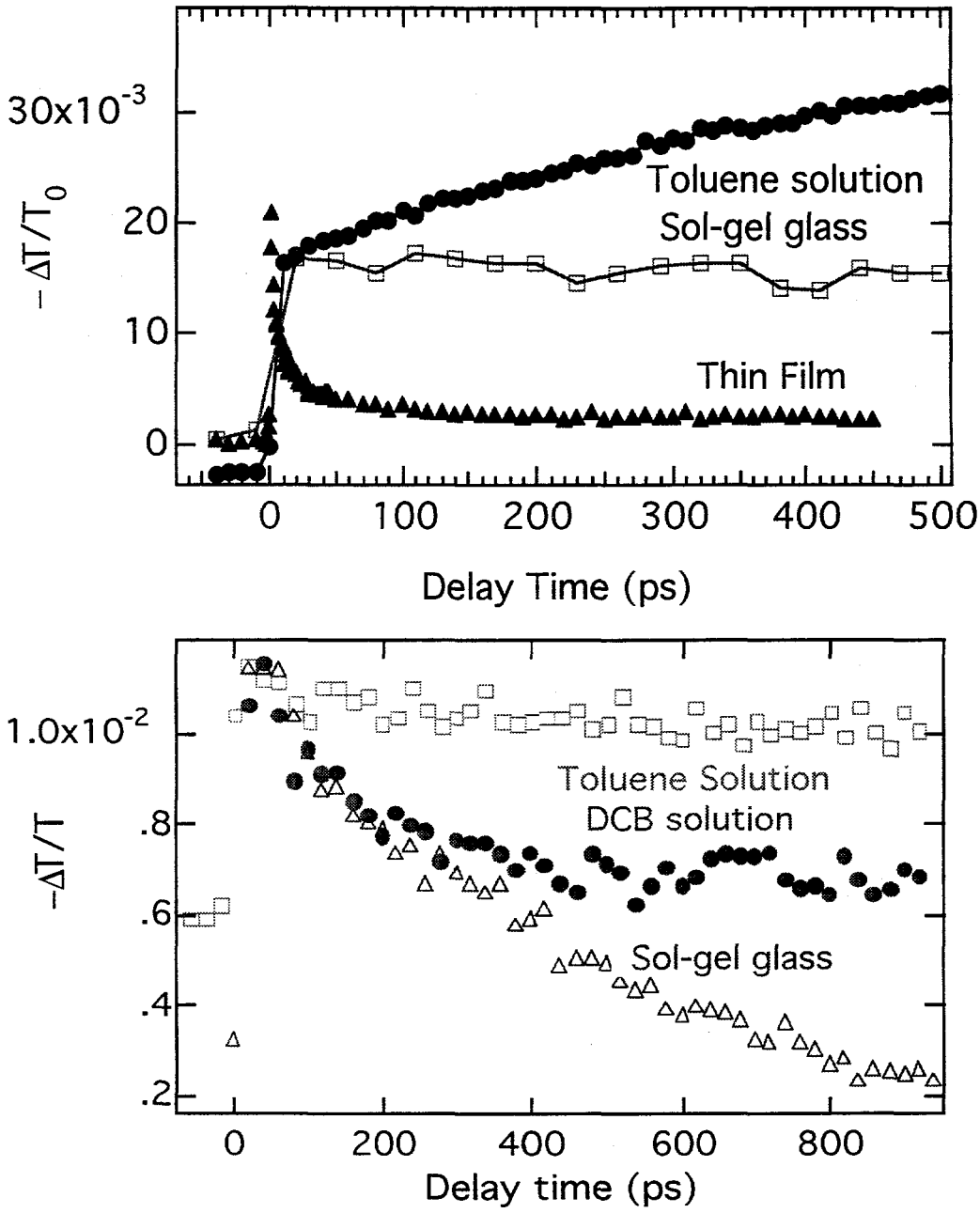



Figure 7. (a) Dynamics at 750 nm of \cs\ in toluene compared with thin film and pre-doped sol-gel glass. (b) Dynamics at 600 nm of PCBM in toluene and DCB compared with pre-doped sol-gel.

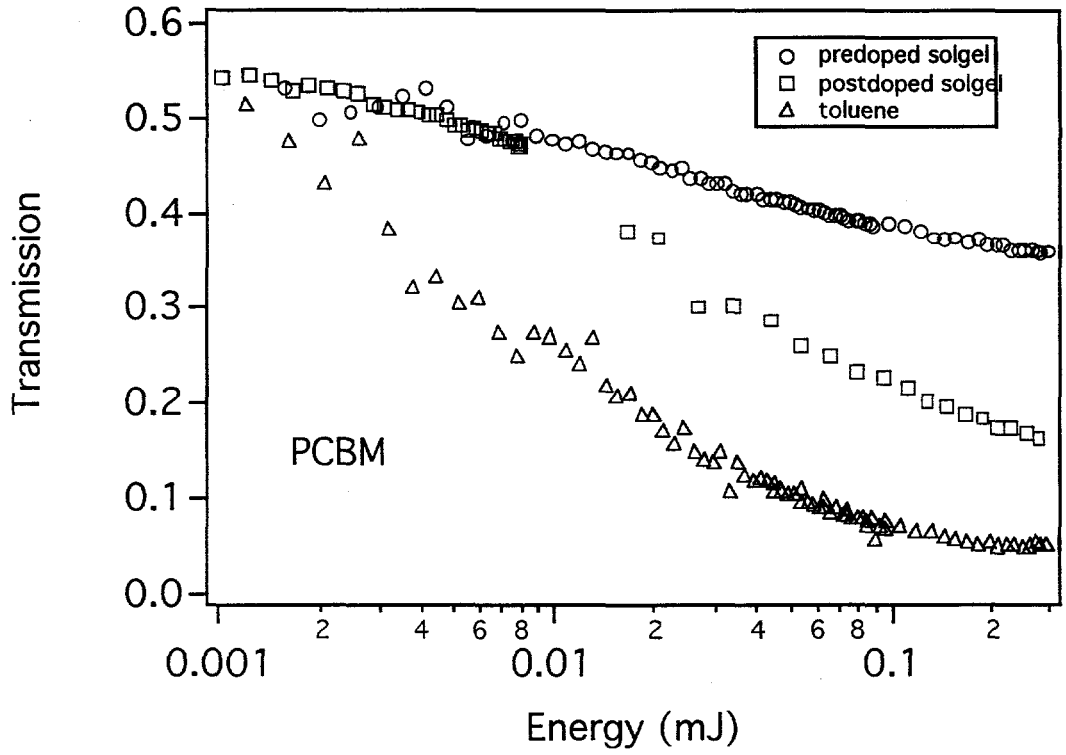



Figure 8. Optical limiting at 650 nm for PCBM in toluene, pre-doped sol-gel, and post-doped sol-gel.