storm activity. We reject this model because (i) mollusks could not reproduce in the salinity of an enclosed lagoon; (ii) Reitz (*18*) has identified estuarine fish species from the Ostra site that spend part of their life cycle in the open ocean; (iii) there is no evidence for a subaerial ridge before 4500 yr B.P., although a beach ridge plain does now separate the stranded embayment from the open ocean (*24*); (iv) faunal data indicating warmer coastal waters are present at the Siches, Quebrada Chorrillos, and Almejas sites in Peru; (v) thermally anomalous molluscan assemblages are present at mid-Holocene sites throughout the world, such as the Atlantic coast of Argentina (*25*), Greenland (*26*), and the Siberian coast of the Sea of Japan (*27*), which suggests that the changes in the paleocirculation we have postulated for the Pacific basin were global in scale; and (vi) independent evidence from northern Australia also suggests that ENSO became active only after 5000 yr B.P. (*28, 29*).

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Organic Optical Limiter with a Strong Nonlinear Absorptive Response

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Molecules with weak ground-state absorption that form strongly absorbing excited states can be used in optical limiters, which can protect sensors or human eyes from optical damage. Phthalocyanine complexes bearing heavy atoms or paramagnetic groups or in solvents containing heavy atoms show optical limiting enhanced by excited triplet-state absorption. A nonhomogeneous distribution of indium tetra(*tert*-butyl)phthalocyanine chloride along the beam path substantially enhances the excited-state absorption, yielding an optical limiter with a linear transmittance of 0.70 that can attenuate 8-nanosecond, 532-nanometer laser pulses by factors of up to 540.

Optical limiters are devices that strongly attenuate intense optical beams while exhibiting high transmittance for low-intensity ambient light levels. These nonlinear optical devices are currently of significant interest (*1–3*) for the protection of human eyes and optical sensors from intense laser pulses, which pose a considerable hazard both in the laboratory and in the field. However, most efforts to develop optical-limiting devices based on various mechanisms including nonlinear absorption and refraction in semiconductors (*4*), optical breakdown–induced scattering in carbon particle suspensions (*5*), thermal refractive beam spreading (*6*), and excited-state absorption (*7–10*) have fallen short of the blocking level needed (attenuation of 10-mJ pulses by a factor of 10^4 or higher) to protect the human eye by two orders of magnitude or more.

Recent work suggests that high levels of blocking at a reasonable linear transmittance, even in highly convergent optical systems, may be possible with high-performance, excited-state absorber materials. Perry *et al.* have shown (*10*) that metallophthalocyanine (M-Pc) complexes containing heavy central metal atoms exhibit enhanced excited-state absorption and optical limiting of nanosecond-duration laser pulses at a wavelength of 532 nm, because of an increased rate of intersystem crossing from the lowest excited singlet state (S_1) to the triplet state (T_1) and the concomitant increase in the population of the strongly absorbing T_1 state during the laser pulse. Moreover, analyses (*11, 12*) of the performance of optical-limiting devices that utilize excited-state absorbers indicate that large enhance-

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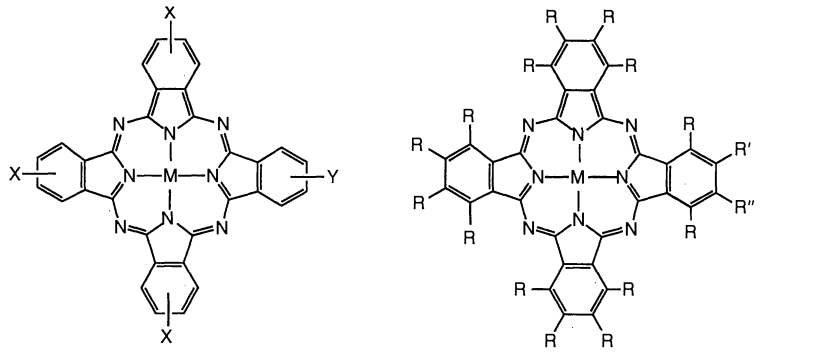
ments are possible in designs where the excited-state absorber is nonhomogenously distributed, so as to achieve the maximal excited-state population along the beam path. We explored the scope of the triplet enhancement mechanism for Pc complexes and report that chromophores with paramagnetic coordinating groups or with heavy atoms covalently attached to the conjugated ring exhibit strong optical-limiting properties. Incorporation of an indium-Pc derivative into a polymeric optical limiter device, comprising a finite-element approximation of the ideal nonhomogeneous concentration distribution, results in an order-of-magnitude improvement in blocking level, which exceeds by a factor of 64 that of a homogeneous solution of C_{60}, a benchmark optical-limiting material (*8*).

The performance of excited-state absorbers can be characterized by the ratio of the excited-state to ground-state absorption cross sections, σ_e^{eff}/σ_g, where σ_e^{eff} includes a weighted average of σ_s and σ_t for S_1 and T_1 states, respectively, and by the saturation intensity or, for excited-state lifetimes longer than the pulse duration, by the saturation fluence, which is given by $F_s = h\nu/\sigma_g$, where h is Planck's constant and ν is the frequency. The ratio σ_e^{eff}/σ_g must be large for effective optical limiting and F_s must be small in order for large excited-state populations to be produced. Time-resolved spectroscopic studies (*13*) of M-Pc complexes have shown that the *T-T* absorption is actually larger by a factor of 2 than the *S-S* excited-state absorption. We have pursued the well-known heavy-atom effect (*14*) as a way of enhancing the triplet population, wherein the large spin-orbit coupling for the metal orbitals and their mixing with the orbitals of the conjugated ring leads to an increased rate of *S* to *T* intersystem crossing and thus to an increased T_1 population during a short laser pulse (*10*).

We investigated a series of molecules (Fig. 1) in which a paramagnetic coordinating group, the vanadyl group, which has an unpaired spin on vanadium, is used [paramagnetic groups can promote intersystem crossing (*14*, *15*)] or in which iodine atoms are attached to the conjugated ring. Attachment of heavy atoms to the conjugated ring provides a synthetically flexible way of maintaining close proximity between the heavy atoms and the ring. This may be important to sustain the *T* enhancement for larger ring molecules, such as naphthalocyanines, where the intersystem crossing rates are lower than for Pc compounds with the same central metal (*16*). A series of iodinated and vanadyl-containing Pc complexes were synthesized and characterized according to methods in (*17*) and (*18*), respectively.

Representative nonlinear transmittance data for $Si(OR)_2PcI_4$ and $Si(OR)_2Pc$ (Fig. 2) show a reduction in transmittance at high fluence for $Si(OR)_2PcI_4$ as compared to $Si(OR)_2Pc$. These data indicate an increase in σ_e^{eff}/σ_g for the iodinated complex. The data for these compounds, as well as the others examined, are well described by a simple fluence-dependent saturation model for the populations, in combination with a numerical solution of the propagation equation for the beam attenuation in the sample (*19*).

The peak wavelength for the lowest energy absorption band (Q band), λ_{max}, the values of σ_g at 532 nm, and the values of σ_e^{eff}/σ_g and F_s, which were obtained from the analysis of the fluence-dependent transmittance data for the series of compounds, are summarized in Table 1. The enhancement of σ_e^{eff}/σ_g on addition of iodines to the ring or of a V=O coordinating group is apparent. The values for the enhanced mol-



$Si(OR)_2Pc$ M = Si[OSi(*n*-hexyl)$_3$]$_2$; X = Y = H

$Si(OR)_2PcI_3$ M = Si[OSi(*n*-hexyl)$_3$]$_2$; X = I; Y = H

$Si(OR)_2PcI_4$ M = Si[OSi(*n*-hexyl)$_3$]$_2$; X = Y = I

$InClPc(t\text{-butyl})_4$ M = InCl; X = Y = *t*-butyl

$VOPc(t\text{-butyl})_4$ M = V=O; X = Y = *t*-butyl

$VOPc(TFE)_{16}$ M = V=O; R = R′ = R″ = $-OCH_2CF_3$

$VOPc(TFE)_{12}$ M = V=O; R = $-OCH_2CF_3$; R′ = R″ = H

$VOPc(TFE)_{12}I$ M = V=O; R = $-OCH_2CF_3$; R′ = H; R″ = I

Fig. 1. Molecular structures of the Pc derivatives examined in this work. TFE, trifluoroethoxy.

Table 1. Optical parameters for a series of M-Pc complexes and C_{60}. All data are for molecules in toluene solution. The values of σ_g, σ_e^{eff}/σ_g, and F_s are for a wavelength λ of 532 nm. We derived the values of σ_e^{eff}/σ_g and F_s using the model described in (*19*), from measurements made with a collimated laser beam geometry, cells with a 1-cm path length, and linear sample transmittances of ~0.95 at 532 nm.

Molecule	λ_{max} (nm)	σ_g (10^{-18} cm^2)	σ_e^{eff}/σ_g	F_s (J cm^{-2})
C_{60}	540	3.1	3.1 ± 0.3	0.27 ± 0.06
$Si(OR)_2Pc$	668	2.8	15 ± 1.5	0.38 ± 0.04
$Si(OR)_2PcI_3$	676	3.0	29 ± 5	0.43 ± 0.13
$Si(OR)_2PcI_4$	678	4.0	28 ± 5	0.34 ± 0.05
$InClPc(t\text{-butyl})_4$	695	1.6	30 ± 6*	0.47 ± 0.05
$VOPc(t\text{-butyl})_4$	697	1.9	28 ± 5	0.83 ± 0.20
$VOPc(TFE)_{16}$	725	1.3	23 ± 3	0.66 ± 0.11
$VOPc(TFE)_{12}$	731	1.2	34 ± 7	1.1 ± 0.2
$VOPc(TFE)_{12}I$	731	1.9	17 ± 2	0.68 ± 0.07

*This value is somewhat greater than the value (25 ± 5) obtained for the $InClPc(t\text{-butyl})_4$-doped PMMA used in the devices.

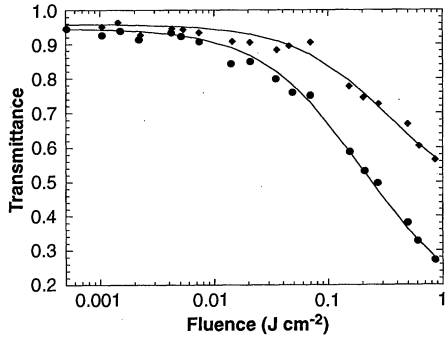


Fig. 2. Nonlinear transmittance response of $Si(OR)_2Pc$ (diamonds) and $Si(OR)_2PcI_4$ (circles) in toluene solution as measured with the use of 8-ns, 532-nm laser pulses. The solution samples were homogeneous solutions, with 95% linear transmittance, in optical cuvettes with a 1-cm path length. A collimated laser beam with a roughly "top-hat" profile and a diameter of about 0.84 mm was used. The curves are best fits of the data to a simple fluence-dependent transmittance model as described in (*19*).

ecules are comparable to those of one of the most active heavy central metal–containing complexes, InClPc(t-butyl)$_4$, for which data are included. Iodine is sufficiently strong in enhancing intersystem crossing that there is no increase in σ_e^{eff}/σ_g on going from the triiodo to the tetraiodo Pc. This is consistent with the $S_1 \rightarrow T_1$ intersystem crossing rate being significantly higher than the reciprocal of the pulse width (8 ns)$^{-1}$ even for the triiodinated complex, such that no greater triplet population can be built up during the pulse. The F_s values for the compounds generally track with the inverse of σ_g but were typically greater by a factor of ~3 than those calculated as $h\nu/\sigma_g$.

An indirect heavy-atom effect resulting from the action of a heavy atom–containing solvent can be effective in the T enhancement of optical limiting for Pc compounds. Dissolution of Si(OR)$_2$Pc in iodobenzene enhanced σ_e^{eff}/σ_g from its value in toluene of 15 ± 1.5 to a value of 22 ± 2, which is 77% of the enhancement obtained by direct attachment of iodines.

The response of InClPc(t-butyl)$_4$, which has a large σ_e^{eff}/σ_g, in an optical-limiting device with a high convergence (f/5 optics), is compared in Fig. 3A with the responses of AlClPc and C_{60}, for which optical limiting has been reported (*7*, *8*). The strong optical-limiting response of the InClPc(t-butyl)$_4$ is apparent, with an increase of the nonlinear attenuation at high energies by a factor of 3 and 7.6 compared to AlClPc and C_{60}, respectively. However, the nonlinear attenuation observed for InClPc(t-butyl)$_4$ is actually much less than one would estimate from σ_e^{eff}, which suggests that the excited-state population is not being efficiently pumped along the beam path.

Maximal attenuation of the optical pulse energy requires strong saturation of the excited-state population along the full beam path in the material. When this condition is achieved across the sample length, optimal use is made of the large excited-state absorption cross section. The fluence along the path must be maintained above (say, 2.5 times) F_s and, at the same time, controlled so that it is below the fluence at which the material damages. Recent device modeling (*12*) suggests that a constant fluence between these limits can be achieved with a hyperbolic concentration profile of the absorber along the beam path. Briefly, in a focusing optical system and well upstream from the focal plane, the beam cross-sectional area varies quadratically with distance $|z|$ from the focus. Therefore, without an absorber, $F(z)$ increases on going toward the focus as $|z|^{-2}$, whereas its fractional rate of change with z, $(1/F)(dF/dz)$, increases as $2|z|^{-1}$. In order to maintain a constant fluence, an attenuation rate that also varies as $2|z|^{-1}$ is needed. This rate can be achieved by using a nonhomogenous concentration profile of absorber, $N(z)$, such that $N(z)\sigma_e = 2|z|^{-1}$ (*12*).

A simple approximation to the ideal hyperbolic concentration profile can be achieved with a geometrically expanding array of uniform concentration plates (Fig. 4). The individual plate thicknesses and locations in this design are chosen so that, when the molecules are driven into saturation, the fluence is kept just below the damage threshold at the front face of each upstream plate and decreases to 2.5 F_s at each plate's exit face. The final plate can be designed to keep the fluence at both entrance and exit faces just below the damage threshold (*12*). To implement the above limiter design, we used a series of molecularly doped InClPc-(t-butyl)$_4$–containing poly(methylmethacrylate) (PMMA) disks that varied appropriately in thickness and spacing. The results of initial experiments on a device composed of three disks in a fast (f/5) optical system are shown in Fig. 3B. The experiment confirmed that nearly an order-of-magnitude enhancement in nonlinear attenuation (corresponding to a maximum attenuation of 540) can be obtained with the use of the three-disk device as compared to a homogeneous concentration, while keeping the linear transmittance constant at 70% (*20*, *21*). The output energy at the maximum input was 12 μJ, greater by a factor of 4 than the performance predicted for the device design, assuming a constant transverse and temporal intensity distribution for the laser pulse. Measurements of the transverse profile and pulse shape of the transmitted beam show that a significant fraction of the excess transmitted energy was due to leakage in the wings of the input pulse. Our results demonstrate that the use of a heavy metal–Pc material together with an appropriate nonhomogeneous concentration profile along the beam path leads to greatly improved optical limiting devices.

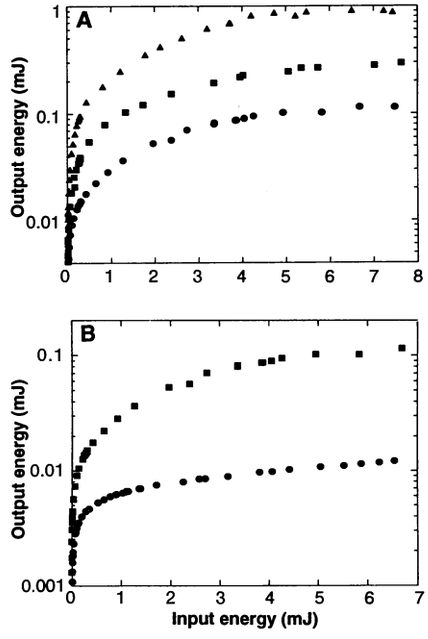


Fig. 3. (**A**) Optical limiting response of C_{60} in toluene (triangles), AlClPc in methanol (squares), and InClPc(t-butyl)$_4$ in toluene (circles) in an f/5 optical system as measured with 8-ns, 532-nm laser pulses. All the solutions had a linear transmittance of 70% in a cell with a path length of 1 cm. The cell was located at the position along the beam that gave the lowest output energy. The initial Gaussian-spatial profile of the laser beam used was expanded to overfill (by five times) the input focusing-lens aperture. The transmitted energy was collected with an f/5 lens 1.5 cm in diameter and then relayed to a spot size 1 mm in diameter on a silicon photodiode detector ~1 cm in diameter. The detector output was calibrated with a volume-absorbing calorimeter (Scientech). We varied the input energy by using a series combination of half-wave plates and polarizers. (**B**) Optical limiting response of a homogeneous solution of InClPc(t-butyl)$_4$ in toluene (squares) and a three-disk InClPc(t-butyl)$_4$–PMMA optical limiter (circles). The concentration of InClPc(t-butyl)$_4$ in the disks (total thickness of 2.1 mm) was ~1.5 × 10^{-3} M, resulting in an internal transmittance of 70% for the set of disks. Other experimental details are as for (A).

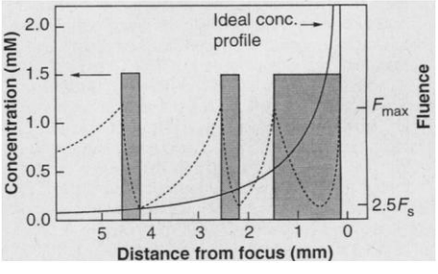


Fig. 4. Schematic illustration of the ideal hyperbolic concentration profile of an excited-state absorber and the geometrically expanding array of uniform concentration disks used as a finite-element approximation. The beam fluence (dashed line) for the case of the three-disk limiter driven to strong saturation and the ideal concentration profile are shown qualitatively. The geometry of the three-disk limiter used in the experiment was, starting with the plate closest to the focal plane (thickness, location of the plate exit plane): first plate (1.39 mm, 0.15 mm from the focal plane), second plate (0.37 mm, 0.75 mm from the first-plate entrance face), and third plate (0.36 mm, 1.58 mm from the second-plate entrance face). We calculated the disk position and spacings as described in (*12*), using the parameters in Table 1 for InClPc(t-butyl)$_4$ and an experimentally determined damage fluence for InClPc(t-butyl)$_4$-doped PMMA of F_{max} = 3 J cm^{-2}.

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18. Although the samples of $Si(OR)_2Pcl_3$ and the tetrasubstituted Pc complexes were mixtures of isomers, the molecular compositions for these and the other compounds were established by elemental analysis and mass spectroscopy, and the compounds were also characterized by ultraviolet-visible absorption spectroscopy and proton nuclear magnetic resonance (NMR) spectroscopy. The NMR spectra suggest that $Si(OR)_2Pcl_4$ was isolated as a single isomer by crystallization from ether-ethanol solution. We measured the fluence-dependent transmittance of the series of compounds by using 8-ns, 532-nm laser pulses from a frequency-doubled Q-switched Nd:yttrium-aluminum-garnet laser.
19. In the simple fluence-dependent model, the cross section is taken as

$$\sigma(F) = (\sigma_g N_g + \sigma_e N_e)/N_0$$
$$= \sigma_g \exp(-F/F_s) + \sigma_e[1 - \exp(-F/F_s)]$$

where N_g, N_e, and N_0 are the ground state, excited state, and total number densities, respectively. The propagation equation is solved numerically by a finite-element approach where each element is chosen to be optically thin such that beam attenuation within the element can be neglected. The attenuation of the beam is calculated as the pulse is passed sequentially through each element, with the output energy of an element used as the input energy for the next element. See, for example, K. Mansour *et al.*, *Proc. SPIE* **1853**, 132 (1993).
20. Use of tandem cells of a Pc excited-state absorber has achieved a comparable blocking level in a slower optical system (*f*/10), but with the chromophore and the tandem cell device design utilized, the linear transmittance was rather low (20%) [D. J. Hagan *et al.*, *Int. J. Nonlinear Opt. Phys.* **2**, 483 (1993)].
21. For comparison, we calculated that a fully saturated C_{60} limiter with the same N_0 and total path length (L), using parameters in Table 1, would give an attenuation [$1/T = \exp(N_0\sigma_e^{eff}L)$] of 6.2. This value is close to that observed for the homogeneous solution (Fig. 3B), indicating that there is no improvement in nonhomogeneously distributing C_{60} for this $N_0\sigma_e^{eff}L$. A much higher (nonhomogeneously distributed) concentration would be needed to achieve an attenuation of 540 and would result in a linear transmission of 0.12.

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Predicting the Occurrence of Endangered Species in Fragmented Landscapes

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Reliable prediction of metapopulation persistence in fragmented landscapes has become a priority in conservation biology, with ongoing destruction of habitat confining increasing numbers of species into networks of small patches. A spatially realistic metapopulation model, which includes the first-order effects of patch area and isolation on extinction and colonization, has been tested. The distribution of an endangered butterfly was successfully predicted on the basis of parameter values estimated for a well-studied congeneric species. This modeling approach can be a practical tool in the study and conservation of species in highly fragmented landscapes.

Habitat destruction around the world (*1*) often leaves the remaining landscape severely fragmented (*2*), a condition that aggravates the threat to the survival of species that originally occupied more extensive and continuous habitats (*3*). Some species may nonetheless persist as metapopulations (*4*), assemblages of local populations inhabiting networks of habitat patches, even in highly fragmented landscapes. The quantitative understanding of metapopulation dynamics has become critical for the successful management and conservation of scores of endangered species (*5*).

Recently, Hanski developed a spatially realistic metapopulation model, called the incidence function model (*6*), which strives to combine generality and realism in a framework that allows parameter estimation and quantitative prediction for real metapopulations (*6*, *7*). In the incidence function model (*8*), the probability of local extinction is determined by the size of the respective habitat patch, which assumes a positive relation between expected population size and patch area. Such a relation is commonly observed for animals (*9*). The probability of colonization of an empty patch is determined by its isolation from the occupied patches and by the sizes of these patches. Our recent studies of the Glanville fritillary butterfly (*Melitaea cinxia*) demonstrated that the effects of patch area and isolation dominate in the dynamics of its metapopulations, with factors that describe the quality of the habitat patches and the surrounding landscape exerting only relatively minor effects (*7*, *10*). Other studies have reached similar conclusions (*11*), although often some attribute of patch quality has also been found to have a significant effect (*12*).

The parameters of the incidence function model can be estimated from a snapshot of patch occupancies (*8*). In making these estimates, we also assumed that the metapopulation from which the snapshot was taken was not far away from a stochastic steady state. This may be a problematic assumption for endangered species, many of which may be declining after recent habitat destruction. Often it is also difficult to collect sufficient data on rare species to estimate the parameters of any model. In this study, we used extensive data on metapopulation dynamics to test whether parameter values estimated for an unendangered butterfly species can be used as surrogates when data are unknown for a rare and endangered congeneric species.

The false heath fritillary butterfly, *Melitaea diamina*, is an endangered species in Finland (*13*) and within much of its range in Europe (*14*). It occurs on moist meadows with the larval host plant *Valeriana sambucifolia*. In spring 1995, we surveyed its only well-known metapopulation in Finland for all suitable habitat patches (*15*). Within an area of 600 km^2 we located 94 suitable patches, of which 35 were found to be occupied (*16*). It is unlikely that there are any other populations outside the study area within several hundred kilometers (*17*). *Melitaea diamina* is ecologically similar to the congeneric *M. cinxia* (*18*), which we have studied intensively in a large network of ~1600 habitat patches (*7*, *19*). We have estimated the parameters of the incidence function model for *M. cinxia* (*7*), and we now use the published parameter val-

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