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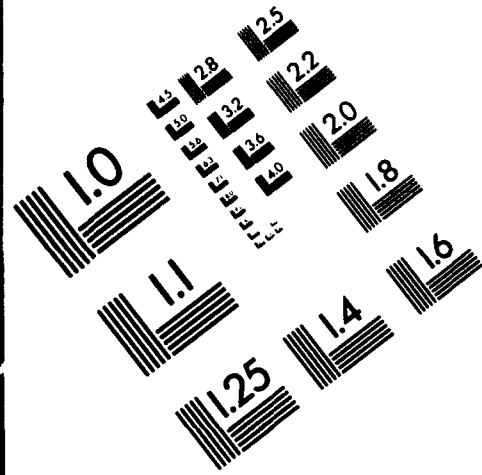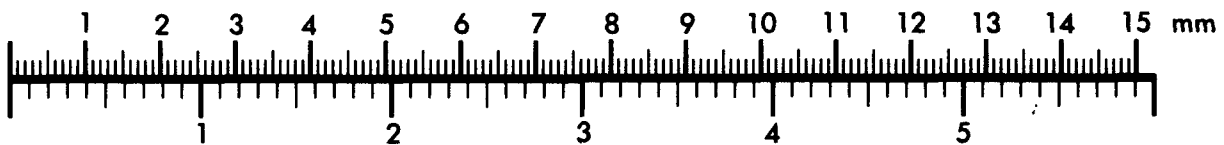
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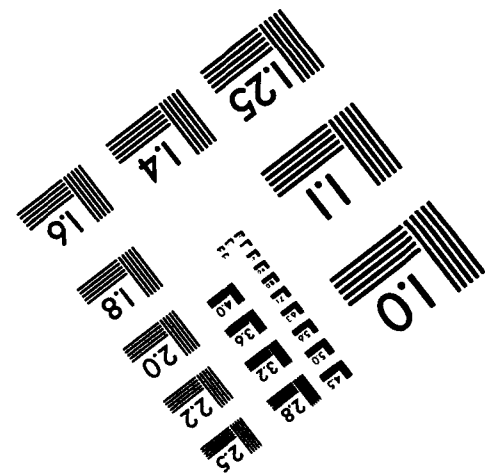1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 mm

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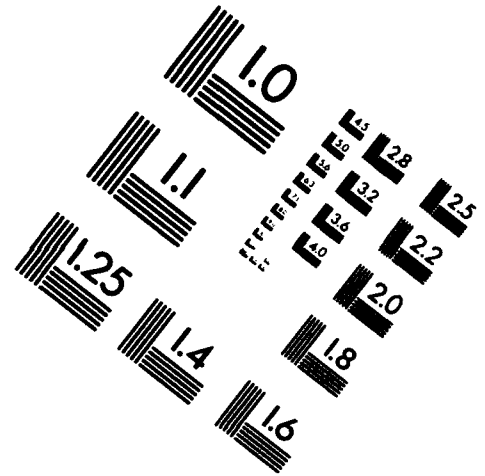
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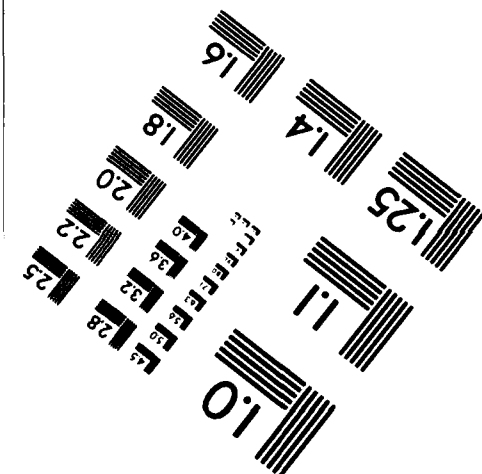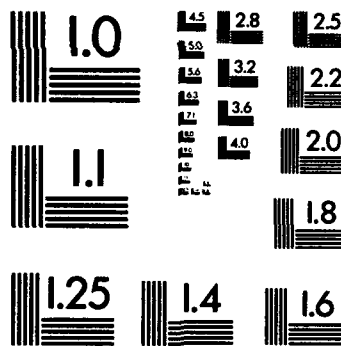
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New Mechanisms and New Materials for Organic Optical Nonlinearity

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Photorefractive Polymers[1,2]

In order to be photorefractive, a material has to combine photogeneration, photoconductivity, trapping and electro-optic (EO) properties. For our work we have developed a guest/host polymer composite based on the photoconducting polymer poly(N-vinylcarbazole) (PVK). Photosensitivity in the visible was provided by the charge transfer (CT) complex that PVK forms with 2,4,7-trinitro-9-fluorenone (TNF). The azo dye 2,5-dimethyl-4-(p-nitrophenylazo) anisole (DMNPAA) was used as the EO active chromophore. We added N-ethylcarbazole (ECZ) as an additional plasticizer to further decrease the glass transition temperature of the material. This guarantees good alignment of the nonlinear optical chromophores in an externally applied electric field, necessary to obtain a macroscopic EO effect in the material.

By improving the preparation procedure of the films, the concentration of the EO chromophore could be increased by 10 %wt in comparison with earlier work of our group,[1] up to 50 %wt without observation of crystallization. The composition of the material is DMNPAA:PVK:ECZ:TNF 50:33:16:1 %wt. As an additional result of the improved preparation technique, external fields up to 100 V/μm can be applied to the 105-μm thin samples without risking dielectric breakdown.

The high dye concentration and the dielectric strength of the material allowed us to observe, for the first time, nearly complete diffraction of a light beam in a four-wave-mixing geometry.[2] The maximum diffraction efficiency for the p-polarized readout of holograms stored in our material was 85% at an external applied field of 60 V/μm. For even higher fields, energy is pumped back and forth between the diffracted beam and the original probe beam. This oscillatory behavior is in agreement with theoretical predictions by Kogelnik's coupled-waves model.[3] Furthermore, in two-beam-coupling experiments, which represent the unambiguous proof of the PR nature of the gratings generated in the material, we observed a high *net* gain coefficient of more than 200 cm^{-1}.

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We performed model calculations on the basis of the coupled waves model[3] and the oriented gas model.[4] They provide evidence that the periodic orientation of the chromophores by the internal space-charge field is largely responsible for the excellent PR properties of our material. This leads to refractive index changes due to different order phenomena such as the linear birefringence and the (second-order) EO effect. Our calculations reveal that the linear birefringence is the dominant contribution to the total refractive index modulation rather than the EO effect.

The results offer a significant breakthrough in the field of PR polymers. The values for the diffraction efficiency and the gain coefficient found in our composite represent, by far, the highest reported in organic materials. They originate from refractive index modulations as large as $\Delta n_p \simeq 6 \times 10^{-3}$, which can be reversibly generated in the material. High performance of our polymer composite has been demonstrated in 105-μm thin films using low-power laser diodes. These considerations, together with the low cost, make this material promising for many practical applications.

Optical Nonlinearities in Organic Materials

A. Instrumentation

To fulfill the proposed project of studying mechanisms of optical nonlinearity in organic systems (polydiacetylenes and phthalocyanines in particular), we have designed and constructed a versatile, tunable wavelength source to study the spectra of nonlinear optical response in organic materials. Preliminary measurements of various organic compounds have been taken.

The tunable wavelength source mentioned above is an optical parametric generator - optical parametric amplifier (OPG-OPA). In this device two BBO crystals are placed in tandem and pumped by the third harmonic output (355 nm) of a picosecond Nd:YAG laser, where the first crystal generates various wavelengths and its output is selectively amplified by the second one. The OPG-OPA device has a wavelength tuning range from 410 nm to 2100 nm. It is an ideal device for nonlinear spectroscopy because of its wide tuning range and high peak power.

Using OPG-OPA we have made measurements of third-order nonlinear coefficient $\chi^{(3)}$ by means of a conventional third harmonic generation setup. Output from OPG-OPA is focused on the sample, and a SPEX monochromator is used to distinguish the third harmonic signal. We have made preliminary measurements of $\chi^{(3)}$ in a poly(1,6-di(N-carbazole)-2,4-hexadyne) polydiacetylene (DCH-PDA) sample; 50 nm of DCH-PDA was deposited on a mica substrate. The nonlinear response measured in the 1.0 - 1.1 micron region is consistent with published results, and the experiment farther into the infrared region (up to 1.8 microns) is currently underway. We are also doing a general survey of suitable substrates for

third harmonic measurements in phthalocyanine, which is another organic compound listed in the original proposal.

Our tunable wavelength source will enable us to learn the spectral features in nonlinear response of organic systems, knowledge which is indispensable in verifying numerous theories concerning the underlying mechanisms of optical nonlinearity in organic compounds and will give us insight in finding ways to improve the performance of organic nonlinear optical materials.

B. Electroabsorption in DCH-Polydiacetylene, Experiment and Theory[5]

We conducted a combined experimental and theoretical investigation to characterize the optoelectronic properties of a DCH-PDA thin film and to understand the nature of band and excitonic states. Our measured differential absorption spectra showed a Stark shift of the lowest energy exciton, accompanied by a large high-energy oscillatory signal [see Fig. 1(a) and (b)], whose origin has been a subject of controversy. Comparisons of our experimental results and exact numerical calculations [see Fig. 1(c) and (d)] indicate that the high-energy signal is due to transitions to the conduction band. This work led to our determination of the precise mechanism of third-order optical nonlinearity. It was shown that the high-energy band states play a strong role not only in electroabsorption, but in other nonlinear optical measurements as well.
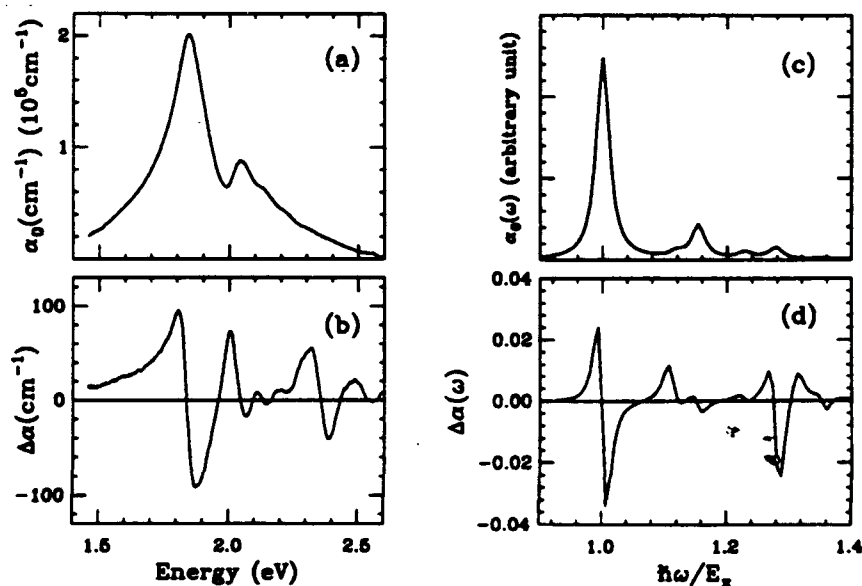

Figure 1. (a) The measured linear absorption coefficient, $\alpha_0(\omega)$, of our DCH-PDA sample. The large excitonic peak is shown with higher-energy vibronic sidebands; (b) absorption changes, $\Delta\alpha = \alpha - \alpha_0$, for a 120-kV/cm field applied to the sample with coplanar electrodes separated by 50 μm. A Stark shift of the exciton and its vibronics is clearly seen with an additional higher-energy feature beginning at 2.35 eV. (c) Calculated linear absorption in arbitrary units for the extended Hubbard Hamiltonian. (d) Calculated field-induced $\Delta\alpha$. The new feature at high energy is due to the conduction band.

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C. Biexcitons and Mechanism of Third-Order Optical Nonlinearity[6]

Theoretical work on third-order optical nonlinearity has focused entirely on the relatively low-energy excited states (see above), i.e., the lowest optically allowed one-photon exciton, an optically forbidden two-photon exciton, and the lower threshold of the conduction band. Two-electron, two-hole excitations were not previously taken into account. In collaboration with Z. V. Vardeny of the University of Utah, Mazumdar has recently shown that π-conjugated polymers like polyparaphenylenevinylene (PPV) possess bound states of two excitons or a biexciton. Photo-induced absorption from the one-photon exciton occurs to the biexciton in the picosecond time domain, as shown in Fig. 2. This experiment puts the biexciton at an energy 1.7 eV above the exciton at 2.4 eV, implying a very large biexciton binding energy (0.7 eV). It has been shown that this picosecond photo-induced absorption is distinct from the induced absorptions due to triplets and bipolarons, seen under cw excitation (see Fig. 2). Theoretical work not only confirmed stable biexcitons, but also predicted a second low-energy photo-induced absorption in the i.r. This induced absorption has been seen subsequently.
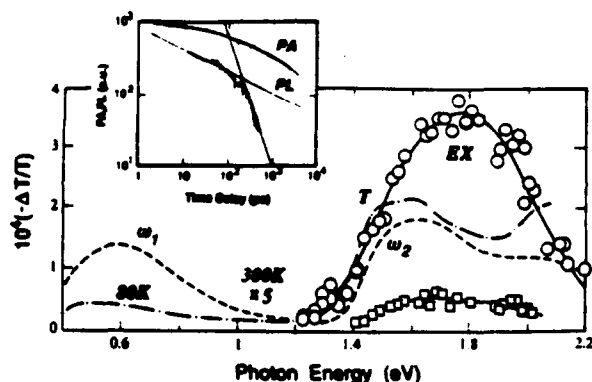

Figure 2. PM spectra of PPV in the picosecond time domain (open circles for t = 0, open squares for t = 1 ns) and cw at 80 K (dot-dashed line) and 300 K (broken line). The full lines through the picosecond data points are guides to the eye. The PA band denoted by EX corresponds to biexcitons. The PA band T is due to triplet absorption, and ω_1 and ω_2 correspond to bipolarons. Various PA bands (EX, T, ω_1, and ω_2) are assigned. The inset shows the PA (at 1.7 eV) and photoluminescence (PL) decays.

The occurrence of stable biexcitons with large binding energies indicates that in addition to the nonlinear optical channels involving the one electron-hole states described in subsection B, new channels involving two electrons and two holes will become important at high frequencies. Whether or not operation at such high frequencies should be of interest in device applications is currently being investigated.

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D. Metal Phthalocyanines

1. *Molecular Second Hyperpolarizibilities*

There are many phthalocyanines and naphthalocyanines whose third-order optical nonlinearities are nearly as large as those of conjugated polymers. Theoretical evaluations of the second hyperpolarizibilities of the actual molecular systems do not exist. This is primarily because of the very large sizes of the molecules, which make calculations including configuration interactions difficult. Existing theoretical work has therefore been limited to the much simpler annulenes. We believe that it is important to perform molecular calculations for the real molecular systems. We have initiated a configuration interaction calculation for metal-phthalocyanines. Currently, we are able to calculate the linear absorptions within the CI scheme. Calculated absorption spectra show remarkable similarities with experimental spectra. Calculations of third-order optical nonlinearities are in progress.

Initial calculations suggest that the optical nonlinearities of phthalocyanines should be at least as large as β-carotene. More detailed calculations, which can also be extended to naphthalocyanines, are in progress. In particular, we are interested in theoretically evaluating the role of two-photon absorption in the nonlinearities of these molecules. In the case of conjugated polymers, it has become clear that the applicability of these systems becomes severely limited by two-photon absorption in the phthalocyanines, and the naphthalocyanines should be weaker, due to the presence of heteroatoms, which should raise the energies of the two photon states.

2. *Optical Nonlinearities of Metal-Pthalocyanine Thin Films[7]*

The research described above focuses only on molecular hyperpolarizibilities. In addition, our interest lies in evaluating and characterizing the nonlinear optical properties of thin film metallophthalocyanines and naphthalocyanines that are being made by an organic/inorganic epitaxial technique. This particular process gives high-quality samples with linear absorptions that are extremely narrow compared to polycrystalline materials. We have applied molecular exciton theory to describe the optical properties of these layered materials. Depending on the relative orientations of the dipole moments within the individual molecular components, linear absorption can be red or blue-shifted within the theory. This is also found in experiments and is due to the formation of an exciton-band. Even when the dipole-dipole coupling extends between a relatively small number of layers, the one-exciton bandwidth approaches the infinite-layer bandwidth. The theory is then extended to include multiple excitations on neighboring molecules. For noninteracting excitons on neighboring molecules, it is shown that the two-exciton bandwidth converges to the infinite-layer bandwidth much more slowly than the one-exciton

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bandwidth, which implies that the energy to create two neighboring excitons is different from twice the energy required to create a single exciton. Photo-induced absorption from the one-exciton state to the two-exciton state is then expected. Selection rules that have been derived predict that in the epitaxial samples in which the linear absorption is red- (blue) shifted with respect to the monomer, photo-induced absorption should occur to the blue (red) of the bleaching. This prediction has now been experimentally confirmed in two different epitaxial materials: chloroindium-phthalocyanine (InPc-Cl) and fluoroaluminum-phthalocyanine (AlPc-F). The linear absorption in the former is red-shifted with respect to the monomer, and a photo-induced absorption on the high-energy side of the bleaching signal has been observed in pump-probe experiments. Similarly, in AlPc-F, linear absorption is blue-shifted with respect to the monomer; a photo-induced absorption on the low-energy side of the bleaching has been found. Figure 3 shows the experimental result of a femtosecond pump probe measurement in an epitaxially grown AlPc-F film or tindisulfide. Note the photo-induced absorption at 550 and 690 nm.
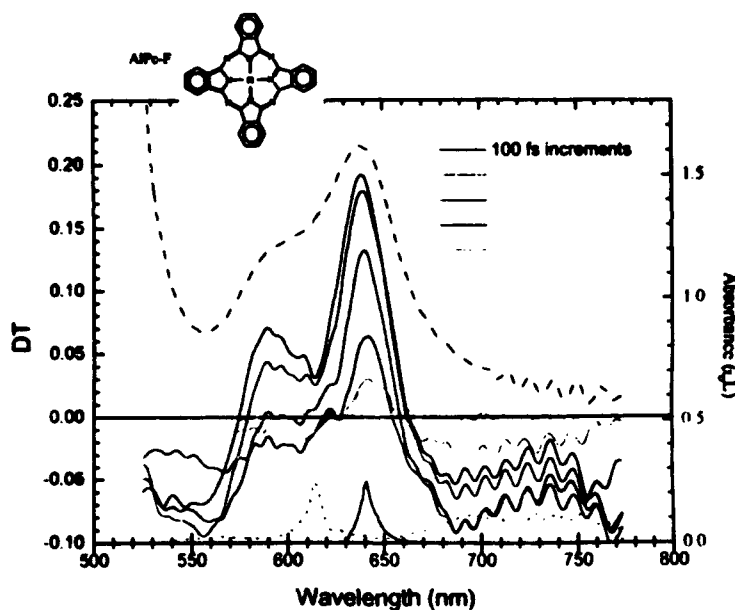
Figure 3. Differential transmission of an epitaxial grown AlPc-F film as a function of time after pumping at 640 nm. The decays at four different wavelengths are shown.

The evaluation of the third-order nonlinear optical properties of epitaxial metallo-phthalocyanines would require a synthesis of our calculations of molecular hyperpolarizibilities and the molecular exciton theory which approximates each molecule as a two-level system. Such an effort is currently in progress.

6

E. String-Excitons in a Charge-Transfer Solid[6]

We have proposed that metal-halide (M-X) chains are potentially good candidates for third-order nonlinear optical materials. There are two reasons for this. First, these materials are charge-density wave systems, as opposed to the π-conjugated polymers which are spin density wave. This implies that two-photon excitations are relatively high in energy. Secondly, both the metal and the halogen atoms are heavier than carbon, and as such, i.r. vibrations should occur at much lower energies than in carbon-based systems, thereby providing a wider frequency window for device applications.

Samples of M-X chains are currently being synthesized. Meanwhile, we have investigated the optical nonlinearity mechanism of a different charge density wave system which can be considered a strongly correlated model for the M-X chains. We have made the first observation and provided a theoretical description of multiexciton states in an organic CT solid. Binding of more than two excitons is not possible with conventional semiconductors. This is not true in one-dimensional strongly correlated materials, where the CT excitons are bound due to the combined effects of strong Coulomb interaction and one-dimensional confinement.

In order to verify the occurrence of the multiexciton states, we have carried out differential transmission measurements on Anthracene-PMDA. At low pump photon intensities, photo-induced absorption to only the 2-exciton (biexciton) is observed. At higher intensities a new photo-induced absorption develops at even lower energy. This has been explained as absorption from the 2-exciton to a stable 3-exciton within our theoretical calculation. The experimental and theoretical results are compared in Fig. 4.
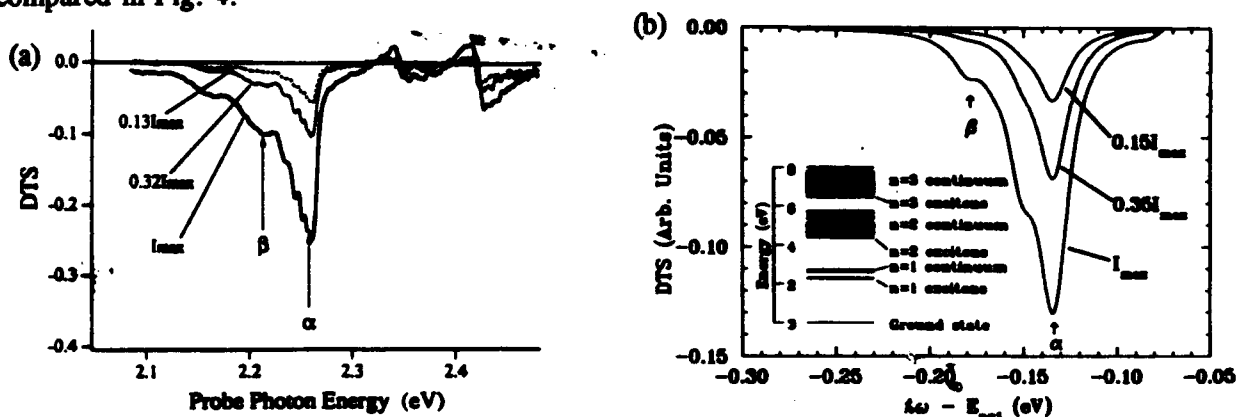
Figure 4. (a) The differential transmission spectrum (DTS) at three different pump intensities; I_{max} corresponds to the maximum pump fluence of 1 mJ cm^{-2}. Note that the induced absorption α appears at all pump intensities, while a second induced absorption β appears only at strong intensities. (b) Calculated DTS in a strongly neutral CT solid for different pump intensities I. The inset shows the energy spectrum. The calculations were done for a periodic ring of 14 sites, with t = -0.1 eV, V_I = 0.5 eV, $V_{|m|}$ = V_I/m, and ε = 1.38 eV. The above magnitudes of t and V_I are typical for CT solids, whereas ε was chosen to fit the experimental energy of the 1-exciton. Note that the calculation reproduces the induced absorptions α and β seen in the experiment. The larger energy shifts in the calculated DTS compared to the experiment are finite-size effects.

Similar multiexcitons may also be stable in the M-X chains, in which case they will strongly influence the nonlinear optical behavior of these materials. Theoretical and experimental work on M-X chains is currently in progress.

F. Organic Superlattices of PTCDA and InPc-Cl - 'Exciton Confinement'? and Charge/Energy Transfer

In order to elucidate the excitonic dynamics in organic superlattices of PTCDA and InPc-Cl, we prepared periodic multilayers of these materials on epitaxial sapphire substrates. Figure 5 shows the result of the linear absorbance measurements for four samples where the monolayers (MLs) were changed from one to four.
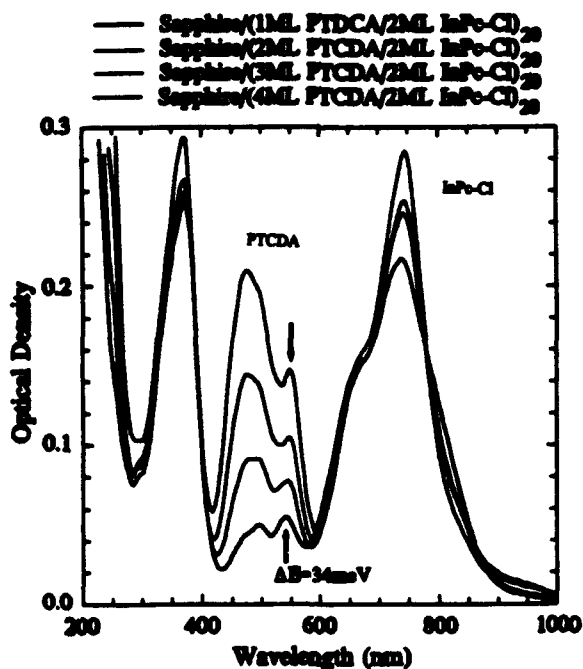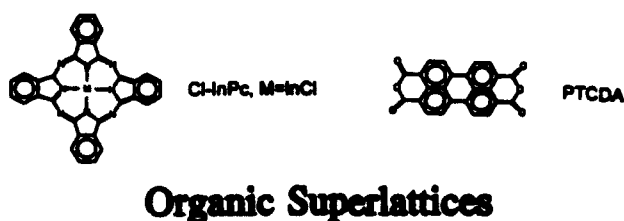

Figure 5. Chemical structure of InPc-Cl and PTCDA and linear absorbance of different periodic multilayers of the type sapphire/ (x ML PTCDA / y ML InPc-Cl)$_{20}$. Note the blue shift in the exciton position (arrows) for decreasing PTCDA thickness.

The molecular excitonic feature of the PTCDA spectra (marked by arrows in Fig. 4) is shifted to higher energies with decreasing PTCDA thickness (blue-shift). This result is important because similar findings of an increase in energy with decreasing width in a quantum well are discussed as "exciton confinement."[9] Whether our multilayer thin films show the same ordering as previous PTCDA/NTCDA[8] is not clear. However, the fact that we see a blue-shift in the PTCDA spectrum comparable to these earlier results is a strong hint that the explanation of this result by quantum confinement of the PTCDA excitons is not necessary. We believe that the blue-shift is caused by the changing polarization environment that the PTCDA molecules experience with decreasing layer thickness (Frenkel exciton model). We have recently been able to calculate such peak shifts in films of phthalocyanines from the measured architecture of the film[10] and expect a similar relationship in perylene dye films.

The dynamics of the exciton in the periodic multilayers was investigated with the help of femtosecond pump probe spectroscopy. It was shown that when pumped at the wavelength of the PTCDA exciton, energy or charge is transferred to the phthalocyanine layers. This is visible in the experiments as a delayed bleaching at the InPc-Cl absorbance maximum. Further experiments of this nature are underway to explore the effect of the changing PtCDA (and related perylene spacers) thickness on the rate and extent of energy and/or CT to the phthalocyanine layer. Optical nonlinearities of these materials (off resonance) will also be explored in the next funding period.

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