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Cyclometalated Complexes: A New Class of Highly Efficient Photorefractive Materials

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The photorefractive effect is of considerable interest in the development of a variety of optical devices.[1] Photorefractivity is a property exhibited by some materials in which the redistribution in space of photogenerated charges will induce a nonuniform electric space-charge field which can, in turn, affect the refractive index of the material. The net effect is a refractive index replica of the illumination pattern. Although photorefractivity was first observed in inorganic salts, in the past decade organic noncrystalline photorefractive materials[2] have been of great interest because of their low cost, chemical structure flexibility, and ease of processing. They usually consist of a host polymer in which the different features required for photorefractive behavior are provided by different guest molecules. We describe here a new material in which a single low-molecular mass entity exhibits all of the functions necessary for photorefractive behavior. The active species is an highly efficient cyclopalladated molecule, and it could be representative of a new class of not yet properly explored photorefractive materials.

The photoconductive[3] and nonlinear optical properties[4] of substances containing a metal complex have recently been described. The investigation reported herein shows that it is possible to combine such features in a single molecule to obtain a photorefractive material. In previous studies we observed that a grating could be written in a polymer containing cyclopalladated azobenzene choromophores using a high-power laser.[5] We decided to extend these preliminary data by using the recently synthesized[6] palladium complex AZPON, whose molecular structure is shown in Figure 1. AZPON is crystalline at room temperature, and to obtain a transparent amorphous sample suitable for optical characterization we mixed the metal complex with an inert polymer like polystyrene (PS) or poly(isobutyl methacrylate) (PIBMA). Phase separation occurred for high complex content, and we limited our optical investigation to homogeneous samples.

As with all organic photorefractive materials, a DC electric field was applied on the samples to obtain better photoconduction. In addition, the electric field is necessary to obtain a macroscopic electrooptic (Pockels) effect by aligning the chromofores, which are initially randomly oriented. To apply the field, samples were prepared by sandwiching our materials between transparent indium−tin oxide-covered glass electrodes. The thickness of the films was controlled by using glass spacers of ∼55 μm.

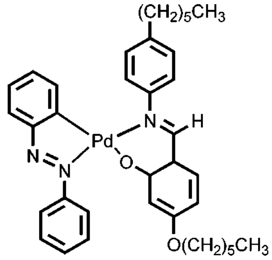

Figure 1. Molecular structure of AZPON. This complex, which contains a palladium(II) center bonded in a square planar geometry, results from the cyclometalation of azobenzene and from the coordination through oxygen and nitrogen atoms to the 2-hydroxy-4-(*n*-hexyloxybenzylidene)-4′-*n*-hexylaniline.

In photorefractive materials the refractive index modulation is induced by a space-charge field which is phase-shifted when compared to the original light pattern. As a consequence, the detection of nonlocality in the index variation is usually taken as a confirmation of its photorefractive nature. This is often done by measuring the energy transfer between two coherent beams which interfere on the material to originate the index grating: only if a phase shift between the interference and the index grating exists, does such energy transfer, usually called two-beam coupling, occur. We performed two-beam coupling experiments by overlapping on our samples two He−Ne laser “writing” beams which were either s or p polarized. To have a component of the applied field along the grating wavevector, we tilted the sample normal away from the bisector of the writing beams. The experiments were performed by using a grating period $\Lambda \approx 3$ μm and by monitoring the intensities of the two beams after they exit from the sample. As shown in Figure 2, the gain coefficient Γ depends on polarization. For p-polarized beams we observed a monotonic increase of the gain up to a value of $\Gamma = 230$ cm^{-1} at $E = 28$ V/μm, which is among the largest measured to date at such low fields in organic materials. The gain then saturates, and it is constant for higher fields. The extinction coefficient in our samples is relatively high ($\alpha = 120$ cm^{-1}), but nonetheless the gain exceedes the absorption by far, and we have a net gain of 110 cm^{-1}. For s-polarized beams the gain is much smaller and of opposite sign. This indicates a substantial orientational contribution to the refractive index grating.[7] From the data of Figure 2, as described in the caption, it is possible to quantitatively estimate the relative contributions of birefringence and nonlinear optical effects to the refractive index grating.[8] We obtain a ratio $A_{\mathrm{BR}}/A_{\mathrm{EO}} = 1.2 \pm 0.2$ which is nearly independent of the applied field and indicates an equivalent contribution of both effects.

To estimate the amplitude of the index grating we also performed degenerate four-wave mixing (DFWM) experiments. In this case, in addition to s-polarized writing beams we used a weak p-polarized “reading” beam which was counterpropagating respect to the writing beam closer to the sample normal. In this geometry, conditions for Bragg diffraction are satisfied. The reading beam originated from the same He−Ne laser as the writing ones. Unlike two-beam coupling gain, diffraction in DFWM experiments is only affected by the amplitude of the index

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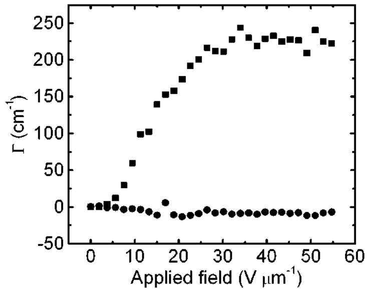

Figure 2. Applied field dependence of the gain coefficient Γ from two-beam coupling in AZPON:PIBMA = 60:40 for s (circles)- and p-polarized (squares) beams. The power density of each writing beam was 0.6 W cm^{-2} and the grating period $\Lambda = 3$ μm. Γ was calculated using $\Gamma d = \cos \alpha \ln[b\gamma/(\mathrm{b} + 1 - \gamma)]$ where $d = 55$ μm is the sample thickness, α is the angle between the sample normal and the probe beam, $b = 1$ is the ratio between the pump and the probe beams before entering the sample and $\gamma = I_{\mathrm{probe}}$ $(I_{\mathrm{pump}} \neq 0)/I_{\mathrm{probe}}$ $(I_{\mathrm{pump}} = 0)$ is the amplification factor. The angle between the sample normal and the bisector of the writing beams was 60° outside the sample. It is possible to estimate the birefringence and electrooptic contributions to the index modulation[8] by using the ratio $A_{\mathrm{BR}}/A_{\mathrm{EO}} = (3 - R)/(R + 2)$. Here $A_{\mathrm{BR(EO)}}$ are empirical constants which take into account both molecular (dipole moment, optical polarizability, hyperpolarizability) and other (temperature, number density of chromophores) parameters. R can be obtained from $\Gamma_{\mathrm{p}}/\Gamma_{\mathrm{s}} = \cos \beta[(R - 1) + (R + 1) \cos \beta]/2$, where β is the angle between the writing beams in the sample.

grating and not by its phase. We measured the intensity of the transmitted and diffracted components of the reading beam as a function of the applied electric field, and results are shown in Figure 3. The diffraction efficiency shows a maximum for an applied field $E \approx 11$ V/μm and it decreases for higher fields, becoming a constant at $E \approx 27$ V/μm, the same field for which the gain saturates. The observed periodic behavior of the diffracted intensity is in accordance with Kogelnik's coupled-wave model.[9] We also measured diffraction efficiencies using s-polarized reading beams. The efficiency in this case is much smaller. In addition, we performed DFWM experiments on a sample prepared by using the two different ligands (azobenzene and 2-hydroxy-4-(*n*-hexyloxybenzylidene)-4′-*n*-hexylaniline) which in AZPON are joined by the palladium atom. The sample contained 60 wt % of an equimolar amount of both species and 40 wt % of PIBMA. No diffraction and no two-beam coupling could be detected in this case in our experimental conditions.

From DFWM experiments it is possible to extract the amplitude of the refractive index modulation Δn. This is done by using Kogelnik's coupled-waves model for slanted dielectric thick transmission gratings.[9] From the model and from the data of Figure 3 we obtain $\Delta n = 4.7 \times 10^{-3}$ at 11 V/μm, where we observe the maximum efficiency. For fields higher than 27 V/μm we reach a constant value of $\Delta n = 9.3 \times 10^{-3}$.

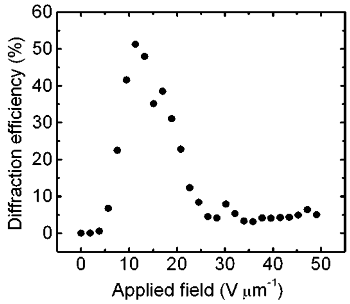

Figure 3. Applied field dependence of the efficiency for DFWM experiments in AZPON:PIBMA = 60:40. Writing beams are s-polarized with a beam ratio $b = 1$ and a power density of 0.6 W cm^{-2} for each beam. The reading beam is p-polarized, and its power density is 5×10^{-4} W cm^{-2}. The grating period is $\Lambda = 3$ μm. Here the efficiency is defined as the ratio between the diffracted intensity and the transmitted intensity without the writing beams, i.e., reflection and absorption losses (~50%) are not taken into account.

As with most photorefractive organic materials, the dynamics of the grating formation are relatively complex and dependent on several factors, including light intensity and applied field. In our experimental conditions and for a field $E = 30$ V/μm the efficiency reaches 90% of its steady-state value after several minutes. Upon the turning off of the writing beams the grating is erased, but we still measure ~2% of the original diffraction intensity after 1 h.

It should be mentioned that the palladium-bonded azobenzene molecule is conformationally blocked, and gratings derived from cis−trans isomerizations can be safely excluded. While our data are consistent with a substantial reorientational contribution to index modulation, the photoconduction properties of AZPON are yet to be understood. However, at this stage, the slight degree of aromaticity displayed by the azobenzene metallocycle[10] could tentatively be invoked to explain the charge-transport properties of AZPON. Our results offer a significant advancement in the search for new photorefractive molecular materials. The excellent performance of AZPON, comparable with that of the most efficient materials known to date, and its simple synthetic route make us foresee a fast optimization of cyclometalated compounds for photorefractive applications.

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