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Phthalocyanines as Efficient Sensitizers in Low-T_g Hole-Conducting Photorefractive Polymer Composites

Francisco Gallego-Gómez,[†,§] José A. Quintana,[†] José M. Villalvilla,[†]
María A. Díaz-García,*[,†] Luis Martín-Gomis,[‡] Fernando Fernández-Lázaro,[‡] and
Ángela Sastre-Santos*[,‡]

[†]*Instituto Universitario de Materiales de Alicante, Universidad de Alicante, 03080 Alicante, Spain, and* [‡]*División de Química Orgánica, Instituto de Bioingeniería, Universidad Miguel Hernández, Elche, 03202 Alicante, Spain.* [§]*Current address: Instituto de Ciencia de Materiales de Madrid (CSIC), c/ Sor Juana Inés de la Cruz 3, 28049 Madrid, Spain*

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The capability of phthalocyanines (Pc's) to efficiently sensitize low glass transition temperature (T_g) poly(*N*-vinylcarbazole)-based composites for high-performance photorefractivity (PR) is reported for the first time. Gratings exhibiting total diffraction and two-beam-coupling coefficients as large as 350 cm^{-1} are recorded in the millisecond range. The performance is compared to that of standard composites sensitized with C_{60} showing advantages like much larger phase-shifts, highly convenient for applications based on optical gain. The dependence of the PR performance on the Pc concentration is studied in detail, revealing that only a very small amount of Pc is needed to obtain high efficiency, which allows us to minimize absorption losses and aggregation. The investigation of two different Pc derivatives provides relevant knowledge to design phthalocyanines with improved sensitization properties.

1. Introduction

Photorefractive (PR) materials are promising candidates for a number of holographic applications like high-density optical data storage, image processing, phase conjugated mirrors and lasers, and real-time imaging.[1] Among them, organic PR polymers have the advantage over inorganic crystals of possessing low dielectric constants (allowing for stronger internal fields), large nonlinearities, versatile composition, and low cost. For the occurrence of photorefractivity, a number of requirements must be fulfilled: optical nonlinearity, photogeneration and photoconductivity.[2] The most direct approach in organic PR systems is the synthesis of fully functionalized (FF) polymers satisfying all conditions. However, composites consisting of a mixture of several molecules that accomplish the various required functions have been by far the most successful. This approach allows us to optimize the PR performance by adjusting separately the individual components. Small amounts of sensitizers are usually incorporated to the composite in order to provide enough photogeneration of charge carriers. The interaction between the sensitizer and the photoconducting agent has a crucial repercussion in the material properties. Particularly, it directly determines − mostly through the PR phase-shift− the magnitude of the two-beam coupling, i.e., the energy exchange between the beams writing the hologram, which is of great interest in conjugate optics and image amplification.[1] However, sensitizing properties have been studied only in a few molecular systems. Moreover, charge-involving processes in PR polymers still need a better understanding.

The widest used composite type consists of a hole-conducting polymer, such as poly(*N*-vinylcarbazole) (PVK), photosensitized with small electron-acceptor molecules that form charge-transfer complexes with the electron-donor moieties of the polymer (e.g., carbazole units in PVK).[2] Mainly fullerene-type molecules [C_{60}[3,4] or [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM)[5]] and fluorene-type molecules [2,4,7-trinitro-9-fluorenone (TNF) or 2,4,7-trinitro-9-dicyanomethylenfluorene (TNDCF)] have been employed.[6] Moreover, TNF-C_{60} and TNDCF-C_{60} dyads[7] have shown interesting PR performances.[8] CdSe/CdS core-shell quantum dots have

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*Tel: 34 96 590 3543 (M.A.D.-G.); 34 96 665 8408 (A.S-S.). Fax: 34 96 590 9726 (M.A.D.-G.); 34 96 665 8351 (A.S.-S.). E-mail:maria.diaz@ua.es (M.A.D.-G.); asastre@umh.es (A.S-S.).

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also been successfully used in PVK-based materials.[9] Only a few attempts have been performed using electron-conducting polymers, sensitized, for example, by Ru(II)-tri(bipyridyl) complexes or metalloporphyrins, but with clearly inferior PR performances.[10]

Phthalocyanines (Pc's)[11] are outstanding light harvesting molecules used as photosensitizers[12] mainly in photoinduced charge-transfer processes and in photodynamic cancer therapy. The merits of Pc's as photosensitizers include among others (i) high thermal- and photostability, (ii) large absorption cross-sections in the visible−near-infrared region with a molar extinction coefficient in the range of 1×10^5 M^{-1} cm^{-1}, and (iii) tuneability of the oxidation and reduction potentials by changing the central atom as well as the peripheral substituents. As a result of these properties, Pc's are promising candidates for efficient sensitization of PR polymers. However, only a few studies toward doping polymers with Pc's have been reported to date. Transition metal Pc's were used as macrocyclic complexes, looking for efficient electron transfer from Pc's via metal-to-ligand charge transfer from the metal atom into PPV-based backbones.[13] Low-glass-transition-temperature (T_g) FF polymers including Pc moieties in the polymer body were synthesized, but with only moderate PR performance, i.e. internal diffraction efficiencies (η) under 20% and gain coefficients (Γ) under 100 cm^{-1}. Besides, further improvement would require a huge synthetic effort, as typical in FF systems. Recently, crown-ether-substituted RuPc's have been incorporated into high-T_g polymer matrixes for IR-range photorefractivity.[14] Although the use of a polyimide as conducting polymer yielded a reasonable optical gain ($\Gamma \approx 140$ cm^{-1}) only in the presence of a 20% of ferrocene (as additional charge transporter) and under the application of a high external electric field (110 Vμm^{-1}), the utilization of PVK as matrix led to a very slow PR performance (seconds) and a small optical gain ($\Gamma < 100$ cm^{-1}) even in the presence of ferrocene and under a high electric field (160 Vμm^{-1}).

In this paper, the capability of Pc's in very low concentrations to efficiently sensitize low-T_g hole-conducting polymers for PR purposes is demonstrated. In fact, very effective sensitization in the visible range with very small amounts of different Pc's is revealed by writing high-performance gratings in low-T_g PVK-based blends, which exhibit total diffraction, very high optical net gain coefficients, and fast (millisecond) response.

2. Experimental Section

2.1. Composites and Sample Fabrication. Two different Pc-derivatives were successfully incorporated in a standard low-T_g composite consisting of a hole-conducting PVK matrix (about 50 wt %), plasticized with butyl benzylphthalate (BBP (Aldrich, purity 98%), 15 wt %) and heavily doped with the nonlinear optical chromophore 4-pyperidindicyanostyrene (PDCST, 35 wt %). Composites with different Pc concentrations were prepared, as described in detail below. PVK (Aldrich, secondary standard) was purified prior to use by dissolving the polymer in boiling absolute ethanol and precipitating with toluene twice, while the chromophore PDCST was synthesized by methods previously described.[15] This type of composite has been widely studied using C_{60} as sensitizer (usually at a concentration of 0.5 wt %).[2,4] Thus, composites sensitized with 0.5 wt % of C_{60} (Aldrich, purity 99.9%) were also studied in order to evaluate the potential of Pc's as sensitizers by direct comparison. The materials were made by solving separately every component in dry dichloromethane and mixing them with the corresponding concentrations. Pc-solutions were diluted at least twice in order to minimize errors. Solvent was evaporated by slowly dropping on two glass plates heated at 50 °C. After complete solvent evaporation, composites were homogenized by mechanical pressing between the two plates at 110 °C. Finally, 105 μm thick and 12 μm thick samples were fabricated for holographic and photoconductivity experiments respectively, by placing the material between two ITO electrodes. The thickness was controlled by using fiber-glass spacers.

2.2. Differential Scanning Calorimetry. Glass transition temperatures (T_g values) were measured by means of differential scanning calorimetry with a TA Instruments apparatus. T_g values were determined during the heating (at 10 K min^{-1}) of the second cycle. Because of the broadness and weakness of the transitions, T_g values were obtained from the derivatives of those curves, in order to have a better precision.

2.3. Absorption Measurements. Absorption coefficients α were calculated from $\alpha = \ln 10\ A/d$ where the absorbances A were measured on 105-μm-thick samples with a Helios Gamma UV−vis spectrophotometer; d is the sample thickness.

2.4. Holographic Characterization. The composites were characterized by standard degenerate four-wave-mixing (DFWM) and two-beam coupling (TBC) experiments for various Pc contents and applied fields. For that, gratings were written by p-polarized 633 nm write beams (WBs) in 105-μm-thick samples. A typical tilted recording geometry was used, with internal WB angles $\theta_1 = 26.7°$ and $\theta_2 = 33.3°$ (see sketch in Figure 2), yielding a grating tilt angle $\Psi = 30°$ and a grating spacing $\Lambda = 3.2$ μm. Both internal WB intensities were 160 mW cm^{-2}. Gratings were read out by a weak p-polarized 633 nm read beam (RB), counterpropagating WB_1. RB Gaussian full-width at half-maximum (FWHM) was 0.3 mm compared with 2.0 mm for the WBs. Time-resolved measurements were carried out after uniformly preilluminating the sample by WB_1 under a poling field during 15 min, and switching WB_2 on at $t = 0$. Electric-field dependence was studied by measuring at different poling fields

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and taking the values reached after 20 s. (quasi steady-state). The PR performance is characterized by the internal diffraction efficiency η (ratio of the diffracted RB intensity to the sum of the diffracted and the transmitted RB intensities) and the two-beam coupling (TBC) gain coefficient (Γ), calculated according to[1]

$$\Gamma = \frac{1}{d}\left[\cos\theta_1 \ln\left(\frac{I_1}{I_1(0)}\right) - \cos\theta_2 \ln\left(\frac{I_2}{I_2(0)}\right)\right] \qquad (1)$$

where d is again the sample thickness, and $I_{1(2)}(0)$ and $I_{1(2)}$ are the $\mathrm{WB}_{1(2)}$ intensities after the sample when no gratings is present and when the grating is being recorded, respectively. Γ will be positive when the beam 2 transfers energy to beam 1. The diffraction efficiency η is related to the index modulation of the grating, Δn, by [16]

$$\eta = \sin^2\left(\frac{\pi d \Delta n}{\lambda(\cos\theta_1 \cos\theta_2)^{1/2}}\right) \qquad (2)$$

where λ is the RB wavelength. Besides, the PR phase-shift Θ (i.e., the phase difference between the index grating and the light interference pattern) can be calculated from Γ and Δn, from[1]

$$\Gamma = \frac{2\pi}{m\lambda}\Delta n \sin\Theta \qquad (3)$$

where m is the holographic contrast. The phase-shift, for a given field E, is related to the number of PR traps (N_{eff}) according to[1]

$$\tan\Theta \approx \frac{2\pi\varepsilon\varepsilon_0}{e}\frac{\sin\Psi}{\Lambda}\frac{E}{N_{\mathrm{eff}}} \qquad (4)$$

where ε is the dc dielectric constant of the medium, ε_0 the permittivity (MKS units). Finally, we consider the parameter τ_{50} (of η or Γ) for direct comparison of the build-up speed of the gratings, defined as the time required to reach half of the steady-state value.

2.5. Photoconductivity Measurements. Measurements were carried out on 12-μm-thick samples by a simple dc technique. A voltage $V = 260$ V (22 Vμm^{-1}) was applied to the samples in the dark and under illumination at the 633 nm light provided by a He−Ne laser (fwhm = 10 mm) with an intensity of 50 mW cm^{-2}. Current i after 10 s was measured with a Keithley 600B electrometer. Conductivity in the dark (σ_{dark}) and in the presence of light (σ_{light}) were calculated from $\sigma = id/VS$, where $S = 4.2$ mm^2 is the electrode area. Photoconductivity σ_{ph} was calculated as the difference between σ_{light} and σ_{dark}.

3. Results and Discussion

3.1. Composites. (2,9,16,23-Tetra-*tert*-butyl-phthalocyaninato) zinc (ZnPc) and bis(*p*-methylbenzoate) (2,9,16,23-tetra-*tert*-butyl-phthalocyaninato) silicon (SiPc)[17] (Figure 1) were chosen to be incorporated to the standard composite. The selection of these particular systems is justified by the fact that ZnPc's and SiPc's are the most studied Pc's as photosensitizers because of their interesting photophysical properties. ZnPc's are closed-shell diamagnetic metal substituted rings with both high triplet yields ($\phi_\tau > 0.4$) and long lifetimes.[18] On the other hand, SiPc's prevents the formation of photoinactive aggregates because of the possibility of covalent linking of different ligands in the Si axial positions. Moreover, the presence of the peripheral tertbutyl substituents increases the solubility of the compounds in organic solvents and prevents aggregation by sterical hindrance. Different concentrations of Pc's were tested in order to find the optimal one for PR performance, as well as to learn relevant features of their behavior. Two main factors limit the highest amount to be used: the typically high absorption of Pc's at 633 nm and the tendency to form aggregates at high concentrations. Here, ZnPc concentrations ranged between 0.0020 and 0.40 wt %, corresponding to (0.025−5) × 10^{-6} mmol of sensitizer per mg of composite. The same molar concentrations were taken for SiPc that correspond to 0.0026−0.52 wt % because of its different molecular weight. For sake of comparison, composites sensitized by the standard C_{60} concentration 0.5 wt % (6.25 × 10^{-6} mmol mg^{-1}) were also prepared.[4]

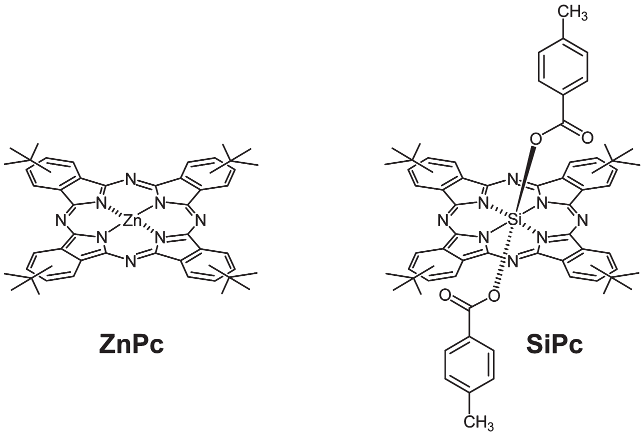

Figure 1. Chemical structures of the ZnPc and SiPc derivatives used in this work.

The materials were easy to work with, exhibited high resistivity toward dielectric breakdown (about 100 Vμm^{-1}) and showed very good optical quality for several months under normal laboratory conditions. Some light scattering was observed for high Pc concentrations (>2.5 × 10^{-6} mmol mg^{-1}), probably due to Pc-induced organization of the molecules in microcrystalline domains. The materials' T_g was 23 °C (as measured by differential scanning calorimetry) and was not influenced by the small amount of sensitizer. The absorption coefficients α at 633 nm were nearly proportional to the Pc content, varying from 3 to 180 cm^{-1} (for ZnPc) and from 6 to 380 cm^{-1} (for SiPc) for concentrations ranging between 0.025 × 10^{-6} and 5 × 10^{-6} mmol mg^{-1}.

3.2. Photorefractive Characterization. The sensitization of the composites by both Pc's was verified by an efficient recording of gratings. Large η and Γ values were achieved at moderate applied fields by using Pc concentrations as small as 0.0020 wt % (0.025 × 10^{-6} mmol mg^{-1}). No holograms could be recorded in the absence of sensitizer. Typical grating buildups plotted in Figure 2 show essential differences of the material behavior

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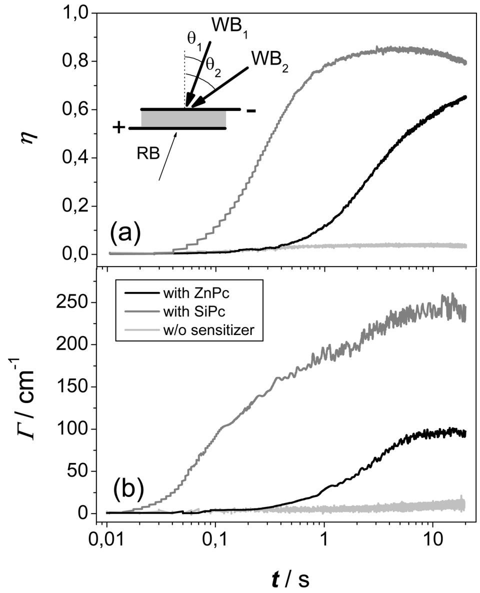

Figure 2. Temporal evolution of the (a) diffraction efficiencies and (b) gain coefficients of PVK/PDCST/BBP composites sensitized by 1.25×10^{-6} mmol of ZnPc (black line) or SiPc (gray line) per mg of composite, and without sensitizer (light gray). The gratings were recorded at 57 V μm^{-1}. Inset: sketch of the recording geometry, where WB_1 and WB_2 are the write beams and RB the read beam. Internal angles θ_1 and θ_2 are depicted outside the sample for clarity.

depending on the type of Pc used. First, composites based on SiPc are much faster (millisecond range) than those containing ZnPc (seconds). Second, the steady-state values of η are similar in both cases (somewhat smaller using ZnPc), whereas Γ is clearly larger for the composite sensitized with SiPc. This is general for all concentrations used, as described in detail below and indicates a more efficient hole generation and faster transfer to the polymer backbone using SiPc than ZnPc.

3.2.1. Dependence on the Phthalocyanine Content. The PR behavior as a function of the Pc content gives valuable information. Data measured at a field of 57 V μm^{-1} are shown in Figure 3. Particularly remarkable is the high performance achieved at very low concentrations of sensitizer. For instance, diffraction of 76% and $\Gamma = 230$ cm^{-1} are obtained at 57 V μm^{-1} by sensitizing with only 0.06×10^{-6} mmol mg^{-1} of SiPc (100 times less than the C_{60} density in a standard PR material). As observed, η grows when the Pc concentration increases, until around 2×10^{-6} mmol mg^{-1} for which η reaches values of 75 and 86% for ZnPc and SiPc respectively. Gain coefficients also increase with the Pc content, although the maximal values (149 and 253 cm^{-1} for ZnPc and SiPc, respectively) are reached at a lower Pc concentration (around 0.1×10^{-6} mmol mg^{-1}). The observed improvement of η and Γ when the Pc concentration increases is expected because the higher density of sensitizing units increases the charge photogeneration, which leads to stronger space-charge fields. This enables larger Δn and, thus, larger η and Γ.[19] Nevertheless, because the absorption coefficients also

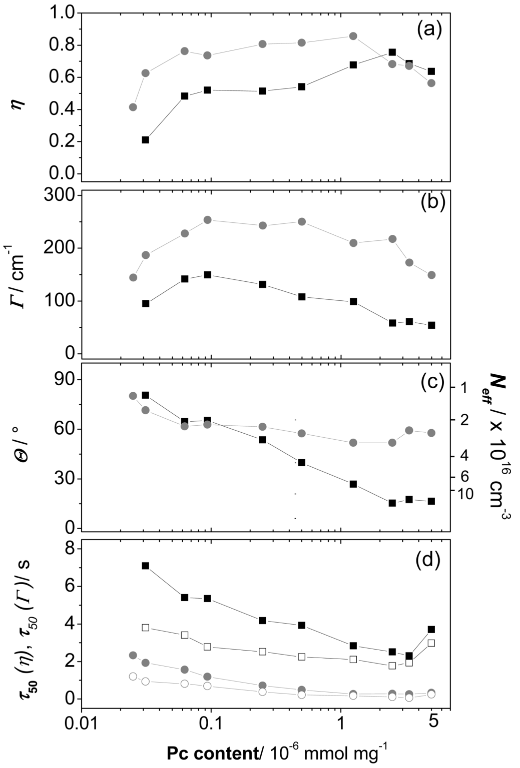

Figure 3. PR performance of composites containing different concentrations of ZnPc (squares) or SiPc (circles). (a) Internal diffraction efficiency; (b) gain coefficient; (c) phase-shift (Θ) and trap density (N_{eff}), calculated from eqs 3 and 4; (d) response times τ_{50} of η (full symbols) and τ_{50} of Γ (open symbols). Gratings were recorded at 57 V μm^{-1} for 20 s.

increase with the Pc content, this leads to a considerable decrease of the net gain coefficients ($\Gamma_{\mathrm{net}} = \Gamma - \alpha$). In this respect, the advantage of getting good PR performances with low Pc contents is that the absorption coefficients are very low. It should be noted that the sign of Γ indicates the nature of the free charge carriers (holes or electrons):[1] because Γ is in all cases positive for the configuration sketched in Figure 2 (negative if the field polarity is inverted), we unambiguously deal with hole gratings. We also calculate explicitly the PR phase-shift Θ and the trap density N_{eff} from the measured η and Γ values, according to eqs 2 and 3 (Figure 3c). The steady-state Θ decreases (i.e., N_{eff} increases) with increasing Pc contents, more clearly in the case of ZnPc. Because the density of ionized Pc molecules should also increase with higher Pc contents, this behavior indicates that Pc ions act as charge traps, similarly to C_{60} or fluorenes.[20] Regarding the speed of the PR response (Figure 3d), given by τ_{50} (as described in the Experimental Section), the grating buildup becomes faster for higher Pc concentrations as expected from the higher charge density, especially in the low-content region. On the other hand, a slight degradation of the performance is observed for sensitizer contents higher than approximately 1×10^{-6} mmol mg^{-1}: η and Γ decrease and speeds do not further improve or even get worse. This suggests a less effective charge generation,

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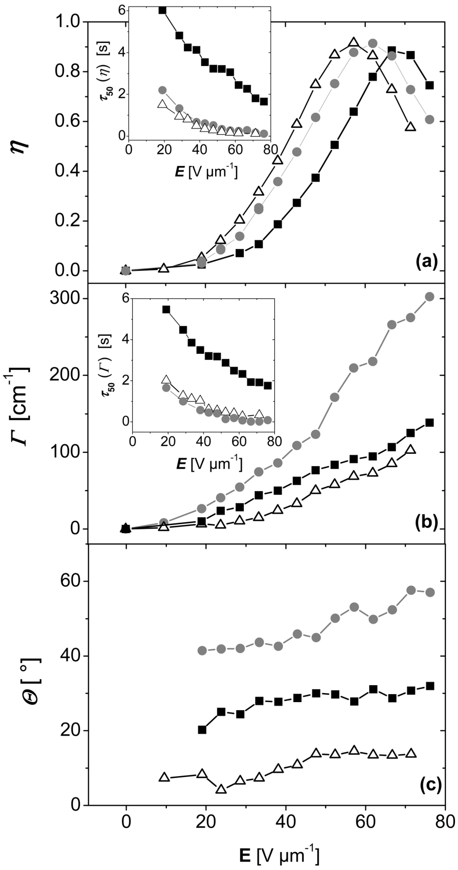


Figure 4. PR performance as a function of the applied electric field for composites sensitized with 1.25 × 10^{-6} mmol mg^{-1} of ZnPc (black squares) or SiPc (gray circles), compared with the composite standarly sensitized with 0.5 wt % (i.e, 6.25 × 10^{-6} mmol mg^{-1}) of C_{60} (open triangles). (a) Internal diffraction efficiency; (b) gain coefficient; (c) phase-shift; Insets: response times τ_{50} of (a) η and (b) Γ.

which agrees with the lowering of N_{eff} (less traps) at high contents (Figure 3c). It should be noted that the PR performance can be further improved by applying higher fields. For instance, near total diffraction is achieved in composites doped with 2.5 × 10^{-6} mmol mg^{-1} of ZnPc (η = 89% at 66 Vμm^{-1}) or when doped with 1.25 × 10^{-6} mmol mg^{-1} of SiPc (η = 91% at 62 V μm^{-1}). This demonstrates the large PR index modulation (Δn) induced in the materials, as large as 0.004 (ZnPc) and 0.005 (SiPc) at 76 Vμm^{-1}, as calculated according to eq 2. The application of high electric fields also leads to larger gain coefficients, reaching values of 210 cm^{-1} and 350 cm^{-1} at 76 V μm^{-1} in composites doped with 0.094 × 10^{-6} mmol mg^{-1} of ZnPc and SiPc, respectively.

3.2.2. Electric-Field Dependence and Comparison with a C_{60}-Sensitized Material. Figure 4 shows the PR performance as a function of the external applied electric field for composites sensitized with SiPc and ZnPc. Data shown correspond to composites with 1.25 × 10^{-6} mmol mg^{-1} of ZnPc or SiPc, as a trade-off between high diffraction or gain and fast response, according to Figure 3. For sake of comparison, we repeated the PR experiments with a composite sensitized with the standard C_{60} (0.5 wt %, 6.25 × 10^{-6} mmol mg^{-1}) and the results have also been included in the figure. The absorption coefficients at 633 nm for these composites were 38, 62, and 33 cm $^{-1}$ for PcZn, PcSi, and C_{60}, respectively. Composites sensitized with Pc's show somewhat lower diffraction than that of the C_{60}-blend, but clearly higher gain coefficients, which implies that the phase-shift of the recorded gratings is larger for both Pc-based materials (eq 3). SiPc exhibits the largest Θ (e.g., 58° at 71 V μm^{-1}, compared to 31 and 14° using ZnPc and C_{60}, respectively), which enables very large optical gains up to ~300 cm^{-1}. The lower phase-shift (i.e., higher N_{eff}) of C_{60}-based materials is expected from the energy levels of the fullerene (as discussed in detail below): its more effective charge generation leads to a higher trap density (more ionized sensitizer molecules) and thus to lower phase-shifts. Concerning PR speed, it is remarkable the good performance of composites sensitized with SiPc, which show response times as low as τ_{50} (Γ) = 105 ms at 71 V μm^{-1}, comparable to that of the composite containing C_{60} and clearly better than the one with ZnPc (see inset of Figure 4b). This is of great interest for fast imaging applications or phase conjugation. The faster TBC response of the SiPc indicates a faster displacement of the charges in the grating, probably due to a lower trap density. The ZnPc-material is much slower in any case, as expected from the less-favorable energy diagram (see discussion below). Note, that the comparison between the sensitizing effect of Pc's and that of C_{60} is only qualitative because they are different systems and a number of other parameters not considered here may be relevant.

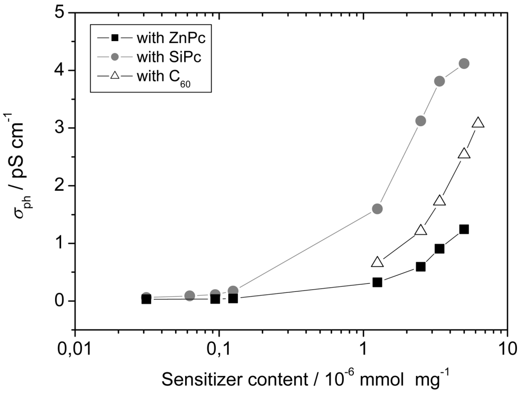
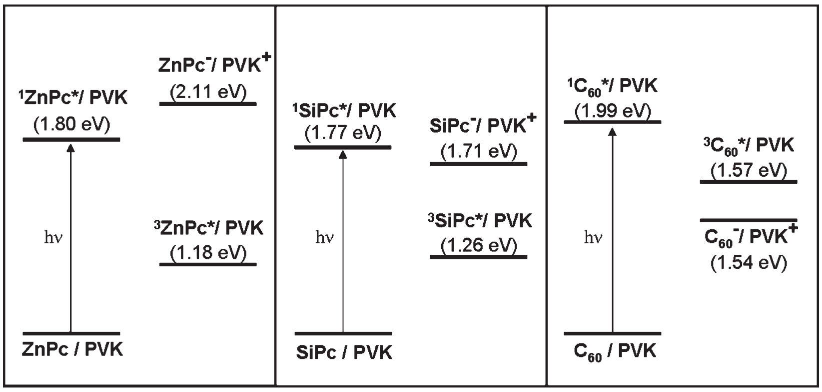


Figure 5. Photoconductivity, measured at 22 V μm^{-1}, of composites containing different concentrations of ZnPc (black squares), SiPc (gray circles), or C_{60} (open triangles).

3.3. Photoconductivity Measurements. To gain further insight, we performed photoconductivity (σ_{ph}) measurements as a function of the sensitizer content (Figure 5) for composites based on the Pc's under study, as well as for C_{60}. As observed, for similar sensitizer concentrations, σ_{ph} for the SiPc blends is significantly larger than that of composites based on both ZnPc and C_{60}. This demonstrates that certain Pc's (i.e., SiPc) can sensitize a PVK matrix even more effectively than standard fullerenes and explains the fast material speed, as shown in Figure 4. Figure 5 also indicates that in all cases σ_{ph} increases approximately linearly with the content of sensitizer, although some saturation is observed in SiPc-composites for contents higher than 2.5 × 10^{-6} mmol mg^{-1}. Note that the high absorption of SiPc blends (in particular, at

Scheme 1. Energy Diagrams of the Photodynamics of ZnPc, SiPc, and C_{60} with PVK[a]



[a] ^{1}ZnPc*, ^{1}SiPc*, and $^1C_{60}$Pc* represent the energy of the singlet excited states; ^{3}ZnPc*, ^{3}SiPc*, and $^3C_{60}$Pc* represent the energy of the triplet excited states; and ZnPc$^-$/PVK$^+$, SiPc$^-$/PVK$^+$, and $C_{60}{}^-$/PVK$^+$ represent the energy of the charge-separated states between the photosensitizer and the PVK.

high contents of sensitizer) could lead to a deviation of the measured photoconductivities from the real (intrinsic) values because of the attenuation of the light intensity through the medium.[21] Thus, we calculated the photoconductivity by taking into account the absorption corrections described in detail in the ref 21. We checked that for 12 μm samples these corrections are negligible and the saturation in σ_{ph} persists. This behavior might indicate that the number density of free charge carriers saturates (eq 4), i.e., the charge photogeneration per sensitizer unit is less efficient at high contents. A possible reason for this is the above-mentioned formation of microcrystalline domains. In any case, the high absorbance of the 105 μm Pc-containing samples and the large TBC coefficients might originate a significant beam depletion within the sample, leading to a worse performance at high sensitizer contents.

3.4. Photophysical Discussion. The main differences in the sensitizing performance of both Pc's in this type of composites might be roughly explained in terms of the energies of the singlet, triplet and charge-separated (CS) states of a system composed of the photosensitizer and PVK. This way, assuming previous reported energies for singlet and triplet excited state and electrochemical data for the ZnPc,[22] SiPc[17] and C_{60}[23] derivatives [reduction potentials vs SCE (standard callomel electrode) of -1.01, -0.61, and -0.44 V respectively] and taking into account the oxidation potential of PVK (1.1 V vs. SCE)[15] we propose the energy diagrams depicted in Scheme 1.

For all systems under study, photoexcitation of the composite will yield the singlet excited state of the photosensitizer. In the case of SiPc-containing composites, this singlet excited state ^{1}SiPc* may generate either the CS state SiPc$^-$/PVK$^+$ (which is 0.06 eV lower in energy) or the triplet excited state ^{3}SiPc* by intersystem crossing. In the first case, because of the external electric field and the existence of a hole transporting network (PVK), holes will migrate and the system will never deactivate to the ground state. For ZnPc-containing composites the situation is very different, as the CS state ZnPc$^-$/PVK$^+$ is even more energetic than the singlet excited state ^{1}ZnPc*. The external electric field probably can help some molecules to undergo charge separation and the subsequent hole migration. However, the percentage of molecules evolving to the triplet excited state will be higher than in the case of the SiPc systems, and a larger number of activation−deactivation cycles will be required to achieve the space charge distribution required for photorefractivity. This is in accordance with the observed higher speed of SiPc composites when compared to the ZnPc ones. According to this analysis, the fast PR response of C_{60}-based materials (as seen in Figure 5) is a consequence of its low-lying CS state $C_{60}{}^-$/PVK$^+$, which can be reached from both the singlet and the triplet excited states.

On the basis of this discussion, it seems that a lower reduction potential of the photosensitizer would diminish the energy of the CS state of the photosensitizer$^-$/PVK$^+$ complex, thus improving the PR performance of its corresponding composite. Thus, a clear strategy for the enhancement of the PR material response would be the usage of Pc's with higher electron affinity by, for example, introducing acceptor groups as substituents in the isoindole rings. Studies in this direction are currently in progress.

To check the possible existence of a charge-transfer (CT) complex in the ground state between the Pcs and PVK, similar to those of C_{60} with either PVK[24] or arylamines,[25] we have performed UV−vis measurements of ZnPc and SiPc compounds upon addition of *N*-ethylcarbazole (ECZ), used as reference compound for PVK. Contrary to the case of C_{60} and ECZ, where a CT complex with a binding constant of 1.5 M^{-1} was found by UV−vis measurements,[24] no changes either in extinction coefficients or in the absorption maxima are observed in the UV−vis spectra of the Pc's, showing that both the PVK and the Pc moieties have very weak or no electronic influence on each other in the ground state.

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4. Conclusions

The capability of phthalocyanines to act as sensitizers in low-T_g hole-conducting polymers for photorefractivity is demonstrated. Two types of Pc's have been incorporated in low-T_g PVK-based composites. The achievement of near total diffraction efficiency (91%), optical gain as large as 350 cm^{-1} as well as response times as low as 100 ms (at fields of 76 V μm^{-1} or less) demonstrates the efficient charge-transfer process with the hole-conducting PVK. Most remarkable is that only a very small amount of Pc (i.e., 0.06×10^{-6} mmol mg^{-1}) is needed to obtain high performance, which minimizes absorption losses and aggregation. Thus, the content of Pc can be adjusted in order to match the material properties required for a given application. The general PR performance of composites sensitized with Pc's is comparable to that of the standard composite (sensitized with C_{60}), even using much lower concentrations (i.e., two orders of magnitude). In particular, two-beam coupling in SiPc-sensitized materials is significantly larger than that in the standard C_{60}-containing blend, while showing similar PR speeds. This is explained by the marked phase-shifted nature of their gratings together with the efficient charge photogeneration of SiPc, and opens the possibility to use them in applications based on optical gain. Results also show that ionized Pc molecules act as PR traps. A further, crucial advantage of using Pc's as sensitizers is their chemical versatility, which allows further design of the molecular structure for particular applications.

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