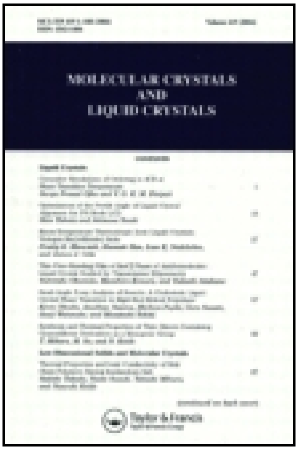

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Low-Tg Photorefractive Materials Based on Bifunctional Molecules

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Low-Tg photorefractive materials based on bifunctional molecules

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The bifunctional molecules presented here, allowed the preparation of photorefractive materials with high optical quality and no aging effect. Because of the low glass transition temperature of the compounds, orientation enhancement of photorefractive properties has been observed. 17 cm^{-1} of net photorefractive gain as been demonstrated at 514 nm.

Keywords : photorefractive, bifunctional, low-Tg, stability, optical quality

INTRODUCTION

Photorefractive (PR) organic compounds are described as one of the most promising class of materials for non linear optical (NLO) application[1],[2]. For this purpose, the materials must exhibit high performances as well as high stability and good optical quality. As doped polymers may reveal segregation and crystallization effects because of the poor solubility of the components, we have designed two new bifunctional molecules. Each of these molecules contains the needed functionalities to ensure both the photoconductive and NLO properties which are required for PR application. In addition, these materials have the characteristic to exhibit a low glass transition temperature (T_g) as well as a low melting point (T_m). Because of these distinctive features, samples of high optical quality could easily be prepared and the photorefractive properties investigated.

MATERIALS

The first bifunctional molecule is constituted by the 9-propylcarbazole moiety and the 9-propyl-3-tricyanoethylene carbazole moiety, connected to each others by a tetramethyldisiloxane spacer Si_2(Cz-Cz/TCNE) as shown in Figure 1a).

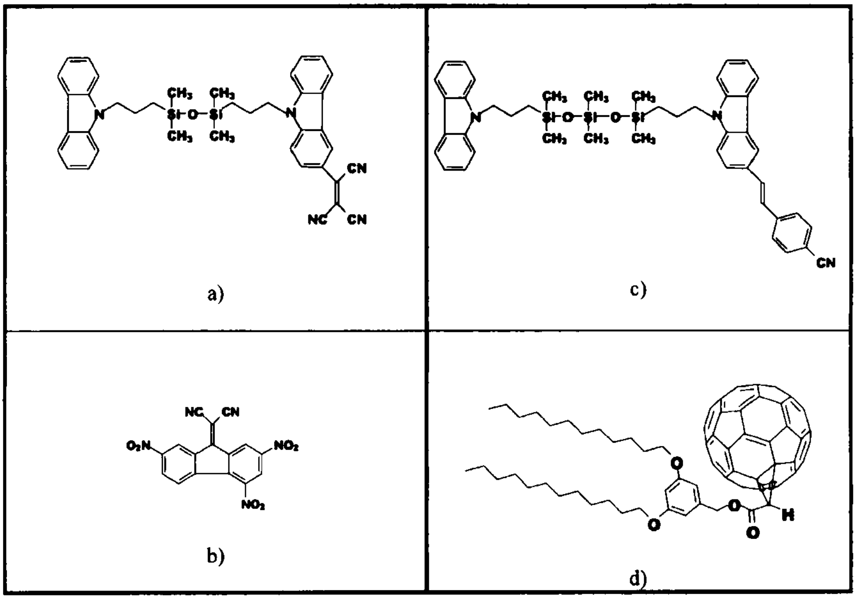

FIGURE 1 Molecules schemes

a) Si_2(Cz-Cz/TCNE)
b) TNFDM
c) Si_3(Cz-Cz/Stilbene)
d) Methanofullerene

In this dimer, the photoconduction is ensured by the carbazole moiety, while the non linear optical properties is obtained from the second carbazole moiety functionalized by the electron acceptor tricyanoethylene group.

The short siloxane spacer linking the two carbazole moieties is used first, for drastically reducing the tendency to crystallization and second, for promoting the emergence of a glassy state. Therefore, the thermal properties and the viscosity of these dimeric materials can easily be tuned by simply modifying the length of the siloxane spacer. As a result, the dimeric material is found to exhibit a low glass transition temperature and melting temperature at T_g=26°C and T_m=46°C, respectively. Once melted, the material does not crystallize -no crystallization was observed on a sample left 14 months at room temperature after melting-. The high stability of the glassy state allows the preparation of materials of high optical quality. In order to sensitize the molecule Si_2(Cz-Cz/TCNE) for photoconduction in the visible range, this dimer was doped with 1% wt. of photosensitizer TNFDM, see Figure 1b). We have prepared sample that does not show any modification after more than one year. This first dimer exhibits an absorption peak at λ_{max}=504 nm with a residual absorption to 625 nm, as shown by Figure 2.

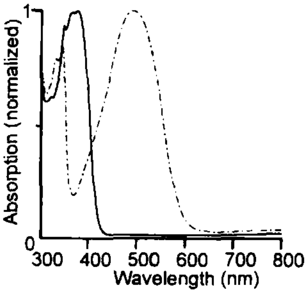

FIGURE 2 Absorption spectra of the dimers.
Dashed Si_2(Cz-Cz/TCNE)
Solid Si_3(Cz-Cz/Stilbene)

As we wanted to lower the absorption and operate in the green region, we have prepared a second dimer Si_3(Cz-Cz/Stilbene), as shown in Figure 1c). The NLO part has been modified by replacing the tricyanoethylene group by the 4-cyano-stilbene group. An increased spacer length composed of a hexamethyltrisiloxane segment has also been introduced. The slight increase of the siloxane spacer led to a pure glassy material with a very low value of Tg of 5°C. No melting temperature was thus observed. As a result, the dimer Si_3(Cz-Cz/Stilbene) was found to be a good candidate for leading to photorefractive materials of high stability and high optical quality. By modifying the NLO part, a much lowered maximum absorption peak at 377 nm (residual absorption until 450 nm) could be obtained. To photosensitize this material in the visible region, a novel fullerene-based sensitizer has been used. A highly soluble methanofullerene[3] derivative, as shown in Figure 1d), has been incorporated at 0.1% wt. in the dimer. The low absorption of the dimer and the use of the methanofullerene sensitizer allowed the investigations of the photorefractive properties at 514 nm.

The preparation of the photorefractive samples was systematically made by mixing the dimer and its photosensitizer in a chloroform solution, followed by a evaporation of the solvent. A drying in a vaccum oven was performed to eliminate any trace of solvent. The doped dimers were then filled into 100 μm thick ITO/glass cells, simply by capillarity. By using such a procedure, we can apply the high electric field needed for photoconduction and molecular orientation in the material maintaining sample's high transmitivity.

MEASUREMENTS

In organic photorefractive materials one can distinguish two different contributions of the NLO molecules on the refractive index variation Δn. The first one is connected to the molecular orientation via the $\mu^2\Delta\alpha$ product, where μ is the molecular dipole and Δα is the linear polarisability anisotropy. The second is the pure electro-optic effect proportional to the μβ product, where β is the molecular quadratic hyperpolarisability. In low T_g materials, Δn variations are, in most cases, dominated by molecular orientation. As we expected this behavior in the two dimers, we have performed frequency dependent ellipsometry[4] measurements which allows the separate quantification of the two contributions : the purely electro-optic and the orientational effects. The results are given in Table 1 for measurements performed at 670 nm. As different wavelengths have been used for the photorefractive investigations (633 nm for Si_2(Cz-Cz/TCNE) and 514 nm for Si_3(Cz-Cz/Stilbene)), we calculated the $\mu^2\Delta\alpha$ and μβ values at these wavelengths according to the two level approximation model[5] for the NLO properties of the molecules.

TABLE 1 Frequency dependent ellipsometry results

		$\mu^2\Delta\alpha$	$\mu\beta$	R
Si_2(Cz-Cz/TCNE)	670 nm	$2.4\ 10^{-57}$ esu	$1.6\ 10^{-45}$ esu	4.8
	633 nm	$3.0\ 10^{-57}$ esu	$2.4\ 10^{-45}$ esu	2.2
Si_3(Cz-Cz/Stilbene)	670 nm	$3.0\ 10^{-57}$ esu	$8.1\ 10^{-46}$ esu	6.7
	514 nm	$4.4\ 10^{-57}$ esu	$1.6\ 10^{-45}$ esu	4.9

The parameter R[6] presented in table 1, corresponds to the ratio of the $\mu^2\Delta\alpha$ and μβ contributions to Δn.

In order to characterize the photorefractive properties in ours materials, two beam coupling experiments have been carried out. At 633 nm for the Si_2(Cz-Cz/TCNE) material, we have measured photorefractive gains up to

180 cm^{-1} for 50 V.µm^{-1} applied electric field as report in Figure 3. However, since the absorption value at this wavelength is 300 cm^{-1} and increases with the applied electric field, no net gain could be obtained. The substitution of the tricyanoethylene group by the 4-cyanostilbene group undergoes a significant shift of the absorption at much lower wavelength. Therefore, Si_2(Cz-Cz/TCNE) has a maximum absorption peak at 377 nm allowing its investigation at 514 nm. At this wavelength, we observed 52 cm^{-1} PR gain under a 60 V.µm^{-1} applied electric field and since the absorption was 38 cm^{-1}, we observed a 14 cm^{-1} net PR gain.

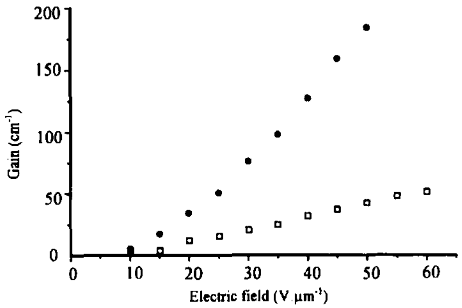

FIGURE 3 PR gain variation with applied electric field
Square : Si_2(Cz-Cz/TCNE)/TNFDM
Circle : Si_3(Cz-Cz/Stilbene)/methanofullerene

Discussion

As seen in Table 1, the fact that the parameter R is always greater than one means that molecular orientation is the predominant phenomena in the Δn variation of the two dimers, as it has been already demonstrated in a number of low T_g organic PR materials[1],[2],[4],[6]. We first obtained this result for the Si_2(Cz-Cz/TCNE) based material. This was the motivation to modified the molecule in order to enhance the molecular orientation effect. We then prepared the Si_3(Cz-Cz/Stilbene) molecule with a longer siloxane chain to lower the T_g and make the molecular orientation easier. We also changed the NLO part in order to increase the $\mu^2\Delta\alpha$ product. Table 1 show that we succeeded in doing this as the parameter R is greater for this last molecule. Finally, we report the increase of the Si_2(Cz-Cz/TCNE) based material absorption at 633 nm with the applied electric field. At this wavelength, absorption measurements on corona poled thin films revealed a red shift of the absorption. The electric field induced absorption and the Δn variations measured by ellipsometry have the same dynamic. As previously demonstrated for the R value, the Δn behavior is dominated by the molecular orientation. This feature let us assure that the electric field induced absorption dependency can be attributed to a dipole-dipole interaction phenomena. Indeed, the dipoles orientation is improved by increasing the electric field thus enhancing the dipole-dipole interaction and leading to the red shift of the absorption.

Conclusion

We have reported two new bifunctional molecules exhibiting high photorefractive performances and no aging effect. These molecules lead to stable PR organic glasses of very good optical quality which is a required characteristic for any kind of application.

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References :

[1.] A. Grunnet-Jepsen, C. L. Thompson, R. J. Twieg, W. E. Moerner, *JOSAB*, **15**, 901 (1998)
[2.] B. Kippelen, S. R. Marder, E. Hendrickx, J. L. Maldonado, G. Guillemet, B. L. Volodin, D. D. Steele, Y. Enami, Sandalphon, Y. J. Yao, J. F. Wang, H. Röckel, L. Erskine, N. Peyghambarian, *Science*, **279**, 54 (1998)
[3.] J.-F. Nierengarten, J.-F. Nicoud, *Tetrahedron Letters*, **38**, 7737 (1997)
[4.]. B. Kippelen, Sandalphon,K. Meerholz, N. Peyghambarian, *Appl. Phys. Lett.*, **68**, 1748 (1996)
[5.] J.L. Oudar, *J. Chem. Phys.*, **67**, 446 (1977)
[6.] L. Mager, C. Melzer, M. Barzoukas, A. Fort, *Appl. Phys. Lett.*, **71**, 2248 (1997)