

Photorefractive triphenylamine-based glass: a multifunctional low molecular weight compound with fast holographic response

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A novel organic photorefractive composite system is presented consisting of the amorphous multifunctional low-molar mass compound DR1-DCTA, doped with C₆₀ as sensitizer and diisooctyl phthalate (DOP) as plasticizer. DR1-DCTA, a carbazole substituted triphenylamine with a covalently attached nonlinear optical azo chromophore unit has been synthesized in a 4 step reaction. The compound forms a stable glass. Its thermal, optical and electrochemical properties are discussed. Holographic experiments (2BC, DFWM) of the photorefractive composite exhibit a fast response time in the range of only 30 ms and a maximum gain coefficient of 90 cm⁻¹.

Introduction

Organic photorefractive (PR) materials which combine two well known properties, photoconductivity and optical nonlinearity, have attracted much attention because of their possible application in optical computing, optical switching and holographic data storage. The PR-effect is defined as a light-induced modulation of the refractive index involving the generation of space charges.^{1,2} Since the first observation of this unique electro-optic effect in organic crystals in 1990³ and in polymers in 1992,⁴ it became obvious that these materials are able to compete with commonly used inorganic crystals such as LiNbO₃.⁵ Since then, several organic systems have been found which show higher refractive index modulations (Δn) and two-beam-coupling gain coefficients (Γ) than their inorganic counterparts.⁶⁻⁸

Photorefractivity in an organic material can be achieved by incorporating a nonlinear optical (NLO) chromophore into a photoconducting matrix. Small amounts of sensitizing agents such as 2,4,7-trinitrofluorene-9-one (TNF) or fullerene C₆₀ have to be added to form charge-transfer complexes sensitive to the wavelength of the laser irradiation. Many of these so-called guest-host systems based on molecularly doped polymers (e.g. polyvinylcarbazole (PVK)⁹ or carbazole-substituted polysiloxanes¹⁰) have been described in the past. However, the maximum dye concentration in such materials is usually limited by the onset of crystallization.

A possible solution of this problem is the design of a multifunctional low-molecular weight system consisting of an amorphous hole transporting molecule covalently bound to an NLO-moiety.¹¹⁻¹⁴

A morphologically stable amorphous state in a low molar mass compound can be achieved by a structurally rigid and bulky substitution of a non-planar core, e.g. triphenylamine. If such a material is heated to the melt followed by quick cooling (quenching), a homogeneous amorphous glass is obtained. Several glass forming hole transport materials based on substituted triphenylamines such as *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)biphenyl-4,4'-diamine (TPD),¹⁵ tris(4-carbazol-9-ylphenyl)amine (TCTA)¹⁶ and tris[4-(diphenylamino)phenyl]amine (TDATA)¹⁷ have been designed within the last few years. Because of their excellent hole transport properties they are commonly used in xerography and in organic electroluminescent (EL) devices.¹⁸

Our aim was to combine the well known properties of such a material with those of an NLO-chromophore *via* chemical bonding. The current contribution focuses on the chemistry

and characterization of one representative of a group of multifunctional low-molecular weight glasses¹¹ which combines shelf lifetimes of more than one year with an excellent photorefractive performance.

Experimental

Instrumentation

NMR-spectra were measured with a Bruker AC 250 (250 MHz), UV-VIS spectra with a Perkin Elmer Lambda 19, and FTIR spectra with a Bio-Rad Digilab FTS-40 spectrometer. DSC measurements were performed with a Perkin Elmer DSC-7 and cyclic voltammetry (CV) measurements with a three electrode and potentiostat configuration from EG&G Princeton Applied Research.

Photorefractive measurements were performed with a holographic setup. We determined the gain coefficient Γ from two-beam coupling measurements (2BC) and the refractive index modulation Δn from degenerate four-wave mixing experiments (DFWM). The experiment is based on a diode laser operating at 670 nm, which is split into two writing beams of equal intensity (1.2 W cm⁻²). They overlap in the sample at an angle of 17°; the sample is tilted by 60° with respect to the bisector of the writing beams. This results in a grating period of 4.0 μ m. 2BC experiments are performed by a rapid sample translation using a piezoelectric element. Meanwhile, the intensities of both writing beams are monitored with photodiodes. In the case of DFWM experiments, a weak beam from a second diode laser (670 nm) counterpropagates one of the writing beams. Its transmitted and diffracted part are detected by photodiodes.

Synthesis

All reagents and solvents were of commercial quality and were purified or dried and stored under argon using standard procedures. All reactions were performed in argon atmosphere. 4-Methoxytriphenylamine **1** was synthesized as described by Gauthier and Fréchet.¹⁹

4,4'-Diiodo-4"-methoxytriphenylamine, 2. 8.77 g (32 mmol) of 4-methoxytriphenylamine **1** and 7.05 g (43 mmol) of potassium iodide in 130 ml of acetic acid and 13 ml of water were heated to 80 °C. 6.83 g (32 mmol) of potassium iodate were added and the mixture was reacted for 3 h, allowed to cool overnight and neutralized with aqueous sodium hydrogen

carbonate. The black residue was filtered off, dissolved in toluene, washed with aqueous sodium hydrogen carbonate and dried. Further purification by column chromatography using silica gel with toluene as eluent gave 13.71 g (yield: 82%) of a transparent glass ($C_{19}H_{15}I_2NO/527.14$). IR (ν/cm^{-1}): 2821, 1573, 1507, 1483 (C=C ar.), 1315, 1287 (C-N), 1242 (C-O-C), 817. 1H -NMR ($CDCl_3$) δ (ppm): 3.78 (3H, methoxy), 6.76, 6.83, 7.01, 7.46 (6 \times 2H, ar.). ^{13}C -NMR ($CDCl_3$) δ (ppm): 55.4, 84.7, 115.0, 124.6, 127.5, 138.0, 139.4, 147.3, 156.8. MS [m/z]: 527, 512, 400, 273, 229.

4,4'-Di(carbazol-9-yl)-4"-methoxytriphenylamine, 3. 12.60 g (75 mmol) of carbazole, 6.38 g (0.1 mol) of copper powder, 27.75 g (0.2 mol) of potassium carbonate and 1.33 g (5 mmol) of 18-crown-6 in 150 ml of 1,2-dichlorobenzene were heated to reflux. 13.24 g (25 mmol) of **2** in 20 ml of 1,2-dichlorobenzene were added slowly and the mixture was reacted at 190 °C for 24 h. After the inorganic components were filtered off while hot, the product was precipitated into methanol and further purified by column chromatography with silica gel using toluene as eluent to yield 14.32 g (yield: 94%) of a colorless solid ($C_{43}H_{31}N_3O/605.74$). IR (ν/cm^{-1}): 3043, 1625, 1599, 1507, 1480 (C=C ar.), 1452, 1318, 1288 (C-N), 1242 (C-O-C), 1231, 830. 1H -NMR ($CDCl_3$) δ (ppm): 3.78 (3H, methoxy), 6.93 (2H, ar.), 7.25–7.45 (22H, ar.), 8.11 (4H, ar.). ^{13}C -NMR ($CDCl_3$) δ (ppm): 55.5 (O-CH₃), 109.8, 115.2, 119.7, 120.3, 123.2, 123.5, 125.8, 127.9, 128.1, 131.4, 139.9, 141.0, 147.0, 157.0. MS [m/z]: 605, 590, 303, 302, 281, 241.

4,4'-Di(carbazol-9-yl)-4"-hydroxytriphenylamine, 4. A solution of BBr_3 (14 mmol) in 14 ml of dry CH_2Cl_2 was added dropwise to a solution of 6.0 g (10 mmol) of **3** in 50 ml of CH_2Cl_2 at -78 °C. The mixture was stirred and allowed to warm up to room temperature overnight. 60 ml of H_2O were added and the phenolic product was collected by extraction with CH_2Cl_2 . Column chromatography using silica gel and toluene-ethyl acetate (15:1) as eluent afforded 4.97 g (yield: 85%) of a colorless solid ($C_{42}H_{29}N_3O/591.71$). IR (ν/cm^{-1}): 3600–3400 (O-H), 3042, 1622, 1597, 1506, 1469, 1446, 1312, 1270, 1230, 1134, 1056, 834, 798. 1H -NMR ($CDCl_3$) δ (ppm): 4.58 (OH), 6.9 (2H, ar.), 7.2–7.5 (22H, ar.), 8.15 (4H, ar.). ^{13}C -NMR ($CDCl_3$) δ (ppm): 109.8, 116.7, 119.8, 120.3, 123.2, 123.5, 125.9, 128.3, 128.5, 131.5, 140.4, 141.1, 147.0, 153.0. MS [m/z]: 591, 504, 332, 295, 241, 166.

4-[N-(2-Tosyloxyethyl)-N-ethylamino]-4'-nitroazobenzene, 5. 8.0 g (25 mmol) of 4-[N-(2-hydroxyethyl)-N-ethylamino]-4'-nitroazobenzene (Disperse Red 1) were dissolved in 40 ml of pyridine, cooled to 0 °C and subsequently reacted with 5.98 g (31 mmol) of toluene-4-sulfonyl chloride for 16 h at that temperature. The product was isolated by adding water, extraction with CH_2Cl_2 , washing with diluted HCl, aqueous Na_2CO_3 and H_2O . Red crystals of **5** (5.55 g, 47%) were obtained by recrystallization from isopropyl alcohol. ($C_{23}H_{24}N_4O_5S/468.54$). IR (ν/cm^{-1}): 2921, 2850, 1600 (C=C, ar.), 1517 (N=O), 1391 (S=O), 1337 (N=O), 1135, 1001, 858. 1H -NMR ($CDCl_3$) δ (ppm): 1.18 (3H, CH₃), 2.38 (3H, CH₃), 3.42, 3.69, 4.29 (3 \times 2H, CH₂), 6.61, 7.25, 7.71, 7.82, 7.9, 8.31 (6 \times 2H, ar.).

4,4'-Di(carbazol-9-yl)-4"-(2-{N-ethyl-N-[4-(4-nitrophenylazo)phenyl]amino}ethoxy)triphenylamine, DR1-DCTA, 6. To a solution of 2.55 g (4.3 mmol) of **4** in 75 ml of dry THF, 4.7 mmol of KO^tBu (1 M solution in THF) were added and heated to reflux for 30 min. Afterwards, 2.06 g (4.4 mmol) of **5** in 60 ml of dry THF were added dropwise and reacted for 19 h at 60 °C. After evaporation of the solvent crude **6** was redissolved in CH_2Cl_2 washed with H_2O and purified by column chromatography using silica gel and CH_2Cl_2 as eluent. Freeze drying from benzene gave 2.6 g (yield: 68%) of a red powder

($C_{58}H_{45}N_7O_3/888.04$). Found C: 77.9; H: 5.06; N: 10.3%. Requires C: 78.45; H: 5.11; N: 11.04%. IR (ν/cm^{-1}): 3046, 2921, 2850, 1600 (C=C, ar.), 1507 (N=O), 1452, 1337 (N=O), 1231 (C-O-C), 1134, 750. 1H -NMR ($CDCl_3$) δ (ppm): 1.31 (3H, CH₃), 3.63, 3.87, 4.22 (3 \times 2H, CH₂), 6.81, 6.95 (2 \times 2H, ar.), 7.2–7.5 (22H, ar.), 7.87, 7.9 (2 \times 2H, ar.), 8.13 (4H, ar.), 8.27 (2H, ar.). ^{13}C -NMR ($CDCl_3$) δ (ppm): 12.3 (CH₃), 46.1, 49.8, 65.6 (3 \times CH₂), 109.7, 111.4, 115.7, 119.8, 120.3, 122.5, 123.3, 123.8, 124.6, 125.8, 126.2, 127.9, 131.5, 140.4, 141.0, 143.7, 146.8, 147.3, 151.2, 155.7, 156.6. MS [m/z]: 887, 671, 591, 296, 241, 146, 92, 57, 44.

Sample preparation

Samples of the photorefractive composite of DR1-DCTA **6**, diisooctyl phthalate (DOP) and C_{60} (71:28:1 wt%) were obtained by filling commercial ITO cells (10–100 μm , obtained from E.H.C. Co. Ltd., Tokyo) with the melted material at 180 °C. The mixture was previously dissolved in benzene, filtered (0.2 μm) and freeze-dried over night to remove residual solvent.

Results and discussion

Synthetic approach

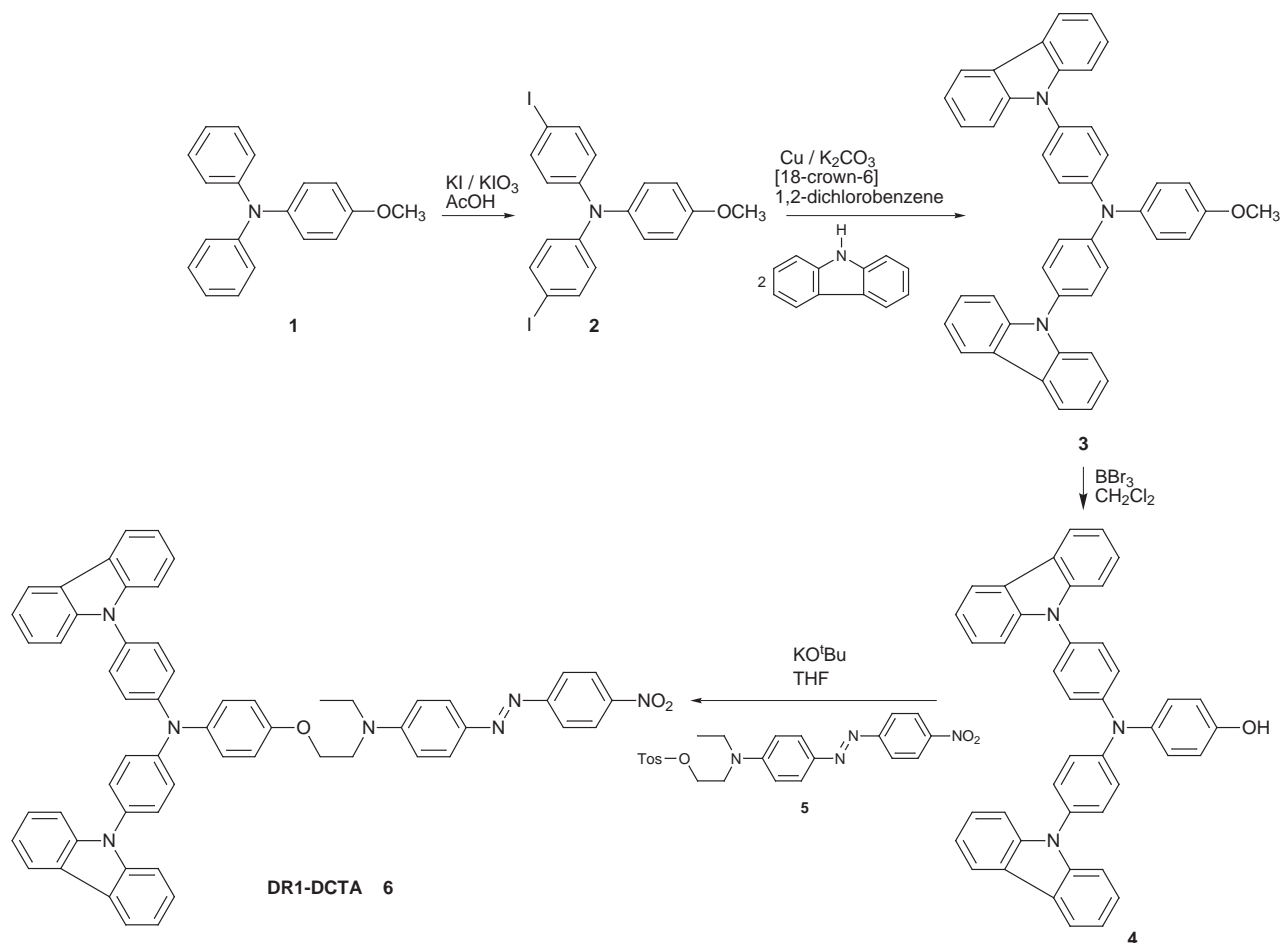
DR1-DCTA **6** was synthesized as described in Scheme 1 in a four-step reaction. We started from the monoprotected triphenylamine core, 4-methoxytriphenylamine **1**,¹⁹ which was iodinated in the two remaining *para*-positions with potassium iodide–potassium iodate in acetic acid. The resulting compound **2** was coupled with carbazole in an Ullman reaction to yield 4,4'-dicarbazol-9-yl-4"-methoxytriphenylamine **3**. Subsequently the methyl ether was cleaved with BBr_3 in CH_2Cl_2 and thus the phenol **4** was obtained. In the last step, compound **4** was converted to the phenolate by KO^tBu in THF and reacted with the tosylated NLO-dye Disperse Red 1 **5** to give the final glass DR1-DCTA **6**. Purification of this compound as well as some of the intermediates cannot be achieved by recrystallization as these materials are obtained as glasses. Column chromatography using silica gel and toluene or methylene chloride as eluents is the best method to obtain pure and well defined compounds.

Thermal characterization

The DSC-traces of DR1-DCTA **6** are depicted in Fig. 1. Only a glass transition is found at 120 °C within the first heating cycle. Upon cooling with 10 K min⁻¹, no recrystallization occurs. In order to check the stability of the glass, we carried out annealing experiments, but we never found evidence for recrystallization. After annealing at 160 °C for 24 h, DR1-DCTA is still fully amorphous.

To prove the fully amorphous character of **6**, its WAXS spectrum²⁰ is displayed in Fig. 2. No crystalline peak is visible but only a broad amorphous halo.

Transparent films of high optical quality with a thickness up to 1 μm can be obtained by spin-coating from solution. Thicker films, which are necessary for photorefractive measurements, are extremely brittle, making device preparation rather difficult. In addition, to obtain a net electrooptic gain, a certain orientational mobility of the multifunctional compounds has to be guaranteed to allow for an alignment of the polar chromophores under the influence of the space-charge field. Moerner *et al.*²¹ have shown that this orientational enhancement of the chromophores increases the photorefractive performance drastically. Thus, we lowered the glass transition temperature of our material to room temperature where sufficient flexibility and orientational freedom is guaranteed. For this we used 28 wt% of diisooctyl phthalate (DOP) as plasticizer, lowering the T_g of the composite to 21 °C (Fig. 1)



Scheme 1 Synthesis of DR1-DCTA **6**.

without causing any phase separation or crystallinity. A simple method to obtain thick and homogeneous samples free of solvent or gas cavities is to fill commercial ITO-cells with the melted composite by means of capillary forces. The photorefractive mixture of **6**, DOP (71:28 wt%) as well as 1 wt% of fullerene C_{60} (allowing for a more efficient photogeneration at the laser wavelength of 670 nm) is shown in Fig. 3. Due to its low melt viscosity, this low molar mass composite is easily drawn between the glass layers of the ITO-cell yielding homogeneous films of defined thickness.

The thermal stability of our composite has been checked by TGA measurements. The TG-traces of pure DR1-DCTA and the photorefractive mixture are depicted in Fig. 4. Compared to **6**, which is characterized by a high thermal stability of up

to 300 °C in air, weight loss starts at 195 °C within the composite material which is caused by evaporation of the plasticizer DOP. In spite of its high boiling temperature of 384 °C, the liquid plasticizer is volatile above 195 °C. Nevertheless, decomposition of the composite under the conditions applied for device preparation (180 °C) can be excluded.

Fig. 5 shows the absorption spectrum of **6** in dioxane solution. The bands at $\lambda = 310$ nm and 340 nm belong to the absorption of the aromatic triphenylamine core. The maximum absorption of the azo chromophore is at 465 nm. The insert shows the tail of the absorption coefficient α of a 25 μm film of the composite. Only a small absorption of approximately 30 cm^{-1} is found at the laser wavelength of 670 nm.

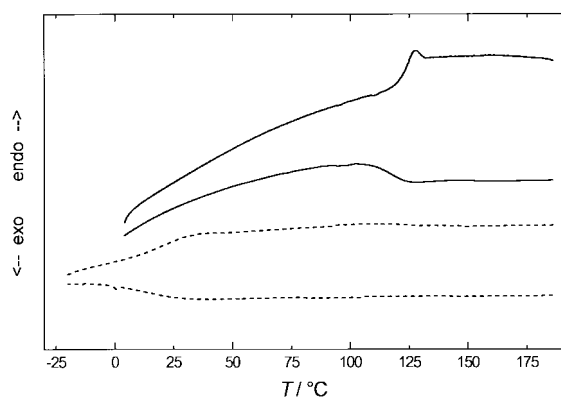


Fig. 1 DSC-traces of DR1-DCTA **6** (—), and the mixture of **6**/DOP/ C_{60} (71:28:1 wt%), (---), 1st heating (above) and cooling (below) at a rate of 10 K min^{-1} .

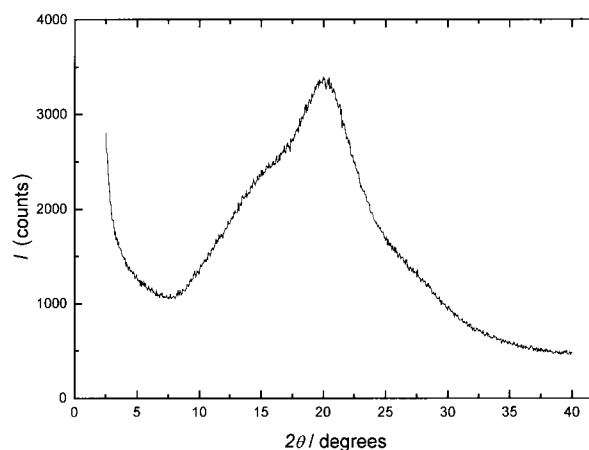


Fig. 2 WAXS-spectrum of DR1-DCTA **6**.

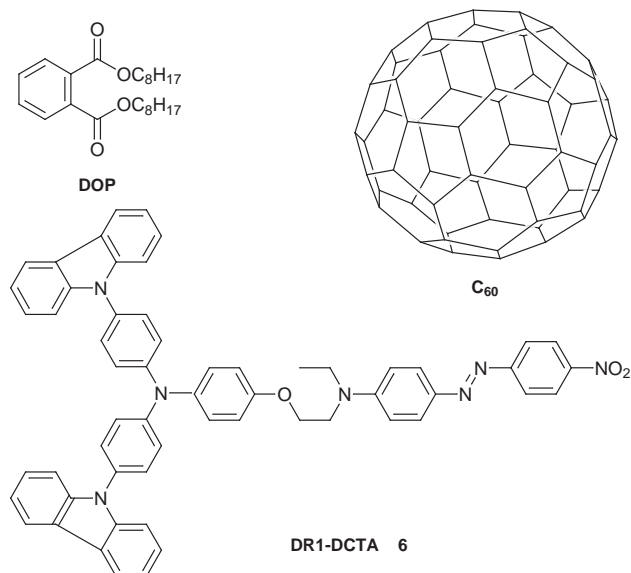


Fig. 3 Components of the photorefractive composite material.

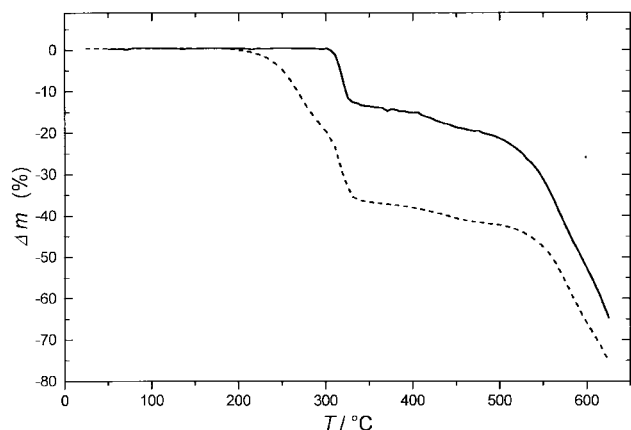


Fig. 4 TGA-measurements of DR1-DCTA 6 (—) and the mixture of 6/DOP/C₆₀ (71:28:1 wt%) (---), heating rates: 10 K min⁻¹ (air).

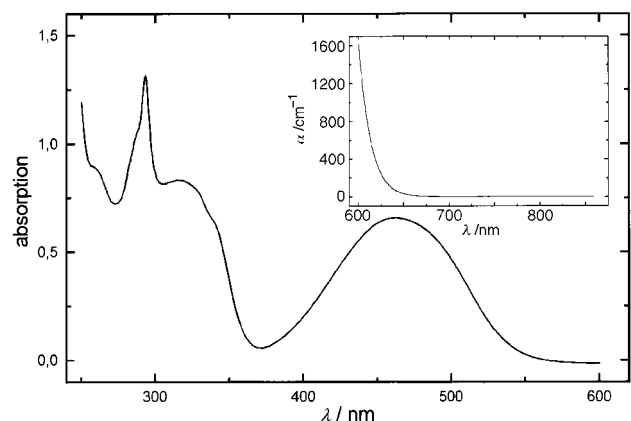


Fig. 5 UV-VIS-spectrum of DR1-DCTA 6 (10^{-4} mol l⁻¹ dioxane solution). The insert shows the absorption coefficient α of a 25 μ m film of 6/DOP/C₆₀.

Cyclic voltammetry

The electrochemical stability and the reversibility of the redox process of DR1-DCTA 6 was studied using cyclic voltammetry (CV). The measurements were carried out at a glassy carbon electrode in a solution of carefully dried acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) at room temperature. The potentials were measured against

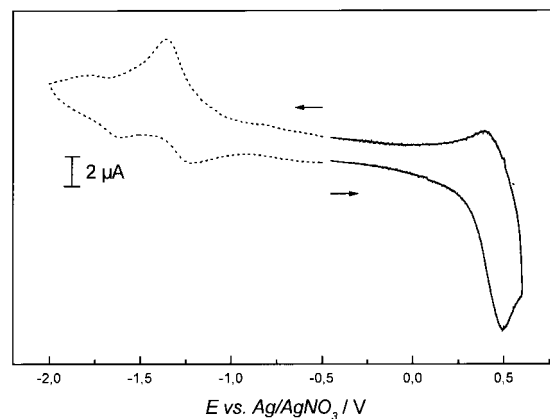


Fig. 6 Cyclic voltammograms of DR1-DCTA 6 for the first oxidation step (—) and the reduction steps (---) measured in acetonitrile-TBAPF₆ at a scan rate of 200 mV s⁻¹.

Ag/AgNO₃ as reference electrode and each measurement was calibrated as usual with the standard ferrocene/ferrocenium (Fc) redox system.²² The HOMO and LUMO energy values of the compound were determined from the oxidation and reduction potentials respectively by taking the value of -4.8 eV as HOMO energy level for Fc with respect to zero vacuum level as described by Daub *et al.* in the literature.²³ The compound is electrochemically stable, for the same redox potentials are observed for repeated cycles of redox processes. As expected, DR1-DCTA exhibits multi-oxidation steps corresponding to mono-, di-, and tri-cation radicals similar to its parent photoconductor, TCTA.¹⁶ The first oxidation stage and the reduction curves obtained at a scan rate of 200 mV s⁻¹ are given in Fig. 6. The average of the peak potentials is 0.45 V *vs.* Ag/AgNO₃ which corresponds to 0.40 V *vs.* Fc. The HOMO energy value determined from the first oxidation potential is -5.20 eV. The first oxidation step is completely reversible for the entire scan rate of 50 mV s⁻¹ to 500 mV s⁻¹. The anodic and cathodic peak currents are 11.3 μ A and 11.6 μ A respectively and the peak separation potential approaches 60 mV (at a scan rate of 50 mV s⁻¹) as expected for a fast reversible single electron transfer. The compound shows two reduction steps, at -1.35 V and -1.79 V, respectively. The reversibility of the reduction processes could not be confirmed under the experimental conditions used. The LUMO energy value which results from the first reduction potential is -3.40 eV.

Holographic characterization

With DFWM experiments, we determined the absolute value and the dynamics of the diffraction efficiency η . At an applied electric field of 80 V μ m⁻¹, diffraction efficiencies for p-polarized reading of up to 27% are reached in samples of 40 μ m thickness. This corresponds to refractive index modulations (see Fig. 7) of about 3.5×10^{-3} .

The response time of the material was determined from the decay of the diffraction efficiency after one writing beam was blocked. The decay was fitted with a biexponential function²⁴⁻²⁷ [eqn. (1)].

$$\eta(t) = \eta_0 (a \exp[-t/\tau_1] + (1-a) \exp[-t/\tau_2])^2 \quad (1)$$

The latter is motivated by the occurrence of two processes. First, homogeneous light-induced generation of charges will erase the internal space charge field (first decay constant τ_1), then the chromophores—which perform an orientation during writing—will subsequently exhibit orientational relaxation (second time constant τ_2). Fig. 8 shows the fitted first time constants which describe the decay of the space charge field. The material reaches response times down to 30 ms, which is

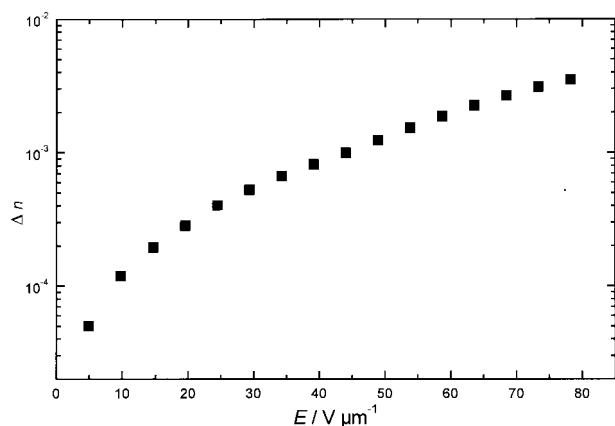


Fig. 7 Refractive index modulation Δn for a p-polarized reading beam as a function of the applied electric field E .

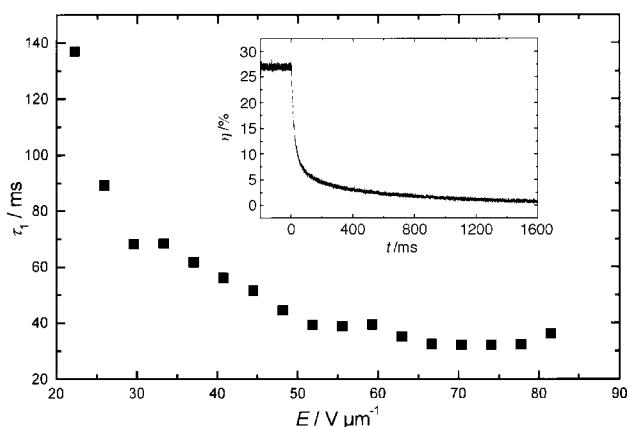


Fig. 8 Fast time constant τ_1 of the holographic grating decay as determined by a fit with eqn. (1). Inset: Erasure dynamics of the diffraction efficiency at an applied electric field of $80 \text{ V } \mu\text{m}^{-1}$.

among the best systems published so far. The inset of Fig. 8 depicts a close-up of the grating decay at $80 \text{ V } \mu\text{m}^{-1}$.

Characteristic for the photorefractive effect is the nonlocal nature of the grating, *i.e.* the phase shift between the light intensity and the refractive index grating. This gives rise to the two-beam coupling (2BC) effect, an energy exchange between the two writing beams. The latter is characterized by the gain constant Γ [see eqn. (2)].

$$\Gamma = 1/(d \cos\theta) [\ln(\gamma_0\beta) - \ln(\beta + 1 - \gamma_0)]. \quad (2)$$

Here, β is the ratio of the power of the writing beams in front of the sample, and γ_0 is given by the ratio of [power of beam 1 while beam 2 is on]/[power of beam 1 while beam 2 is off] behind the sample. Fig. 9 shows the results for s- and p-polarized writing beams. Due to the orientational enhancement effect, the sign of Γ is opposite for the two polarizations. The maximum gain coefficient is about 90 cm^{-1} .

In our opinion, photorefractive low molar-mass glasses have potential for still further optimization. Up to now, only standard NLO chromophores have been incorporated. Tailormade chromophores such as recently introduced by Würthner *et al.*²⁷ which are optimized for high orientational enhancement may provide even higher gain and diffraction efficiencies.

Conclusion

We have shown the synthesis and chemical properties of a novel organic photorefractive material in which a nonlinear optical chromophore is covalently bound to hole transporting triphenylamine and carbazole moieties. With suitable plasticizer and sensitizer, a stable photorefractive composite which

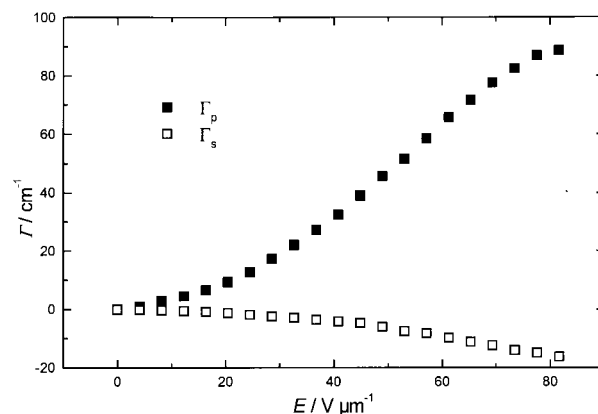


Fig. 9 Two-beam coupling gain Γ for s-polarized (\square) and p-polarized (\blacksquare) beams as a function of the electric field.

is amorphous and exhibits a shelf lifetime of more than a year is obtained. The photorefractive properties were characterized by 2BC and DFWM experiments. The material shows a fast holographic response of 30 ms and a gain coefficient of 90 cm^{-1} . High refractive index modulations are readily obtained.

The flexibility of the synthetic concept allows for further optimization, *e.g.* by incorporating sophisticated NLO chromophores.

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