Synthesis and Electrochemical and Photorefractive Properties of New Trinitrofluorenone−C_{60} Photosensitizers

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A series of novel trinitrofluorenone−C_{60} acceptors in which the two subunits are placed at different distances have been prepared and their electrochemical and photorefractive properties measured. The photorefractive performance of these compounds as sensitizers in polymer composites based on poly(*N*-vinylcarbazole) is similar to that of C_{60}, but with shorter response times and slightly lower gain coefficients. Since the substitution of C_{60} by these novel trinitrofluorenone−C_{60} systems leads to a reduction of losses due to beam fanning, larger voltages could be applied, resulting in larger gain coefficients.

Introduction

The necessary elements for photorefractivity are photoinduced charge generation, charge transport, trapping, and electrooptical nonlinearity.[1] In particular, for polymers each element can be separately optimized in low-cost samples not requiring careful crystal growth (as contrary to inorganic crystals). One of the drawbacks of photorefractive (PR) materials is their generally low photorefractive speeds.[2] Since the first demonstration in 1991[3] of photorefractivity in polymers, progress in material performance has occurred rapidly.[4] Most of the advances achieved in the first years were related to improvements in gain (Γ) and diffraction efficiency (η), reaching values in the 100−200 cm^{-1} range and 100%, respectively. In contrast, few advances had occurred in the speed of grating formation (τ). In 1998 several high-speed PR polymer composites based on poly(*N*-vinyl carbazole) (PVK), doped with the sensitizer C_{60}, the plasticizer butyl benzyl phthalate (BBP), and a dicyanostyrene (DCST) derivative were reported.[5] They showed growth times less than 10 ms at a writing intensity of 1 W/cm^2, while maintaining high net gain coefficients (>100 cm^{-1}), thus opening new possibilities for video-rate optical processing applications. By investigating the intensity dependence of the response time and the photoconductivity, it was concluded that for these materials speed is limited by photoconductivity (σ_{ph}) rather than by chromophore orientation. In the simplest model

$$\sigma_{ph} = ne\mu = (\phi\alpha I\tau_t/h\nu)e\mu \quad (1)$$

where n is the density of carriers, e is the elementary charge, μ is the mobility, ϕ is the charge generation quantum efficiency, α is the absorption coefficient, I is the optical intensity, τ_t is the time constant for transport, h is Planck's constant, and ν is the frequency of the light. Therefore, one way to enhance the performance of these materials would be to increase the charge generation efficiency, by optimizing the charge-transfer properties between a given sensitizer and the transport molecule. For this reason, the synthesis of new photosensitizers should be pursued.

An important class of sensitizers is the charge-transfer (CT) complexes formed between donor-like and

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acceptor-like molecules or moieties. A new band appears in the UV-vis spectrum of the CT complex giving rise to spectral sensitivity in the visible and the near-infrared part of the spectrum. To date, the most commonly used photosensitizers incorporated into polymers have been 2,4,7-trinitro-9-fluorenone (TNF), perylene dyes, phthalocyanines, and C_{60}.

The strong acceptor C_{60} is known to form CT complexes with donor-like molecules and polymers.[6] Among the sensitizers used as organic photorefractive materials, the highest photogeneration efficiencies are obtained with fullerene-doped phenylmethylpolysilane,[7] fullerene-doped poly(*N*-vinylcarbazole) (PVK),[8] and fullerene doped poly(methyl methacrylate)-*p*-nitroaniline:diethylamino benzaldehydediphenylhydrazone (PMMA-PNA:DEH).[9]

On the other hand, electron acceptors of the fluorene series have attracted tremendous interest as outstanding sensitizers for the photoconductivity of carbazole-containing and related polymeric semiconductors.[10] In particular, polynitrosubstituted 9-fluorenones have been reported as excellent acceptors for CT complex formation, as photosensitizers, and electron transport materials.[11]

For these reasons, C_{60}-bridged-TNF systems should be excellent candidates as sensitizers in photorefractive systems. Surprisingly, despite the high scientific and technological interest of this type of compounds, to date just a couple of nitrofluorene−C_{60} arrays have been synthesized[12] and, to the best of our knowledge, TNF−C_{60} systems have not been described so far.

Herein, we describe for the first time the synthesis, and redox and photorefractive properties of three novel TNF−C_{60} hybrids **1a**−**c** (see Scheme 1), in which the distance between the two subunits is regulated by the position of the phenyl substitution from ortho to meta to para.

Experimental Section

Synthesis. All chemicals were reagent-grade, purchased from commercial sources, and used as received, unless otherwise specified. NMR spectra were measured with a Bruker AC 300 and with a Bruker AVANCE DRX-500. UV−vis spectra were recorded with a Helios Gamma spectrophotometer and IR spectra were recorded with a Nicolet Impact 400D spectrophotometer. Mass spectra were obtained from a Bruker Reflex III matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectrometer.

General synthetic procedures for compounds **3a**−**c** and **1a**−**c** (Scheme 1) follow.

Formylphenyl 2,5,7-trinitrofluorenone-4-carboxylate (3). Solid acid chloride **2** (1.25 g, 3.3 mmol) was added stepwise (over 15 min) to a stirred solution of hydroxybenzaldehyde (3.3 mmol), triethylamine (465 μL, 3.3 mmol), and DMAP (5 mg, 0.04 mmol) in CH_2Cl_2 (17 mL) at room temperature. The mixture was stirred for 3 h at the same temperature and then filtered; the solid was washed with ethyl acetate and CH_2Cl_2 and dried under vacuum at 40 °C overnight.

(3a). 70% yield. $R_f = 0.54$ (toluene/acetic acid: 9/1). ^{1}H NMR (300 MHz, DMSO, 25 °C, TMS) $\delta = 10.16$ (s, 1H, CHO), 9.19, 8.90, 8.74 (3 br s, 1H, 1H, 2H respectively, fluorenone H), 8.10 [d, ^3J(H,H) = 7.3 Hz, 1H, benzaldehyde H], 7.96 [m, 1H, benzaldehyde H], 7.68 [d, ^3J(H,H) = 7.3 Hz, 1H, benzaldehyde H], 7.58 ppm [d, ^3J(H,H) = 8.55 Hz, 1H, benzaldehyde H]. FT-IR (KBr) ν 3084, 2864, 2759, 1742, 1697, 1606, 1536, 1348, 1273, 1233, 1181, 1142 cm^{-1}.

(3b). 89% yield. $R_f = 0.56$ (toluene/acetic acid: 9/1). ^{1}H NMR (300 MHz, DMSO, 25 °C, TMS) $\delta = 10.14$ (s, 1H, CHO), 9.17, 8.97, 8.77 (3 br s, 1H, 1H, 2H respectively, fluorenone H), 8.09 [s, 1H, benzaldehyde H], 8.03 [d, ^3J(H,H) = 6.1 Hz, 1H, benzaldehyde H], 7.96 ppm [m, 2H, benzaldehyde H]. FT-IR (KBr) ν 1749, 1737, 1708, 1534, 1344, 1207 cm^{-1}.

(3c). (89%). $R_f = 0.58$ (toluene/acetic acid: 9/1). ^{1}H NMR (300 MHz, DMSO, 25 °C, TMS) $\delta = 10.07$ (s, 1H, CHO), 9.08, 8.91, 8.71 (3s, 1H, 1H, 2H respectively, fluorenone H), 8.12 [d, ^3J(H,H) = 8.3 Hz, 2H, benzaldehyde H], 7.70 ppm [d, ^3J(H,H) = 8.3 Hz, 2H, benzaldehyde H]. FT-IR (KBr) ν 1749, 1737, 1708, 1534, 1344, 1207 cm^{-1}.

(*N*-Methyl-3,4-fulleropyrrolidinyl)phenyl 2,5,7-trinitrofluorenone-4-carboxylate (1). Through a well stirred mixture of C_{60} (60 mg, 0.083 mmol), formylphenyl 2,5,7-trinitrofluorenone-4-carboxylate (0.45 mmol), and sarcosine (50 mg, 0.56 mmol) in *o*-dichlorobenzene (8.4 mL), a stream of argon was passed for 15 min. Then the purple mixture was heated at 125 °C under argon until it became brown (~2 h). After flash chromatography (SiO_2 hexane/toluene increasing to toluene) the desired products were isolated as brown solids.

(1a). Yield: 14−18%; mp >300 °C. ^{1}H NMR (500 MHz, *o*-DCB-d_4) δ 9.10, 8.74, 8.56, 8.39 (4s, 4 × 1H, 4Harom-fluorenone), 5.64 (s, 1H, CHN), 4.98 (d, 9.4 Hz, 1H, C*H*HN), 4.39 (d, 9.4 Hz, 1H, CH*H*N) and 2.94 ppm (br s, 3H, CH_3N). FT-IR (KBr) ν 3093, 2922, 2851, 1738, 1611, 1539, 1342, 1177, 1142, 730 and 526 cm^{-1}. MALDI-TOF (dithranol) *m/z*: 1210 [M^+], 868 [M − TNFcarbonyl]$^+$.

(1b). Yield: 18−20%; mp >300 °C. ^{1}H NMR (500 MHz, *o*-DCB-d_4) δ 9.08, 8.77, 8.69, 8.58 (4s, 4 × 1H, 4Harom-fluorenone), 5.14 (s, 1H, CHN), 5.02 (d, 9.3 Hz, 1H, C*H*HN), 4.33 (d, 9.3 Hz, 1H, CH*H*N) and 3.02 ppm (br s, 3H, CH_3N). FT-IR (KBr) ν 3085, 2945, 2922, 2849, 2780, 1740, 1611, 1592, 1540, 1342, 1156, 526 cm^{-1}. MALDI-TOF (dithranol) *m/z*: 1210 [M^+], 868 [M − TNFcarbonyl]$^+$. UV−Vis ($CHCl_3$) λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}) 296 (4.7), 324 (sh), 432 (3.6), 470 (sh), 550 (sh), 640 (sh), 705 (2.5) nm.

(1c). Yield: 21−25%; mp >300 °C. ^{1}H NMR (500 MHz, *o*-DCB-d_4) δ 9.04, 8.75, 8.69, 8.59 (4s, 4 × 1H, 4Harom-fluorenone), 5.06 (s, 1H, CHN), 4.99 (d, 9.1 Hz, 1H, C*H*HN), 4.28 (d, 9.1 Hz, 1H, CH*H*N) and 2.86 ppm (br s, 3H, CH_3N). FT-IR (KBr) ν 3084, 2922, 2852, 2785, 1741, 1597, 1537, 1343, 1185, and 527 cm^{-1}. MALDI-TOF (dithranol) *m/z*: 1210 [M^+], 868 [M − TNFcarbonyl]$^+$.

Cyclic Voltammetry. The electrochemical measurements of compounds **1a**−**c**, including the model compounds *N*-methylfulleropyrrolidine (NMF) and methyl-2,5,7-trinitrofluorenone-4-carboxylate (MTNFC), were performed using a BAS 100W electrochemical analyzer (Bioanalytical Systems) in a high vacuum electrochemical cell designed in our laboratory. A glassy carbon (3 mm diameter) was used as the working electrode after being polished with $^1/_4$ mm diamond polishing compound (Metadi II) from Buehler. A silver wire immersed in the solvent mixture with supporting electrolyte and separated from the bulk of the solution by a Vycor glass was used as pseudo-reference electrode. The platinum wire used as the counter electrode was cleaned by heating it in a flame for approximately 30 s. The supporting electrolyte was tetrabutylammonium hexafluorophosphate, $TBAPF_6$. It was pur-

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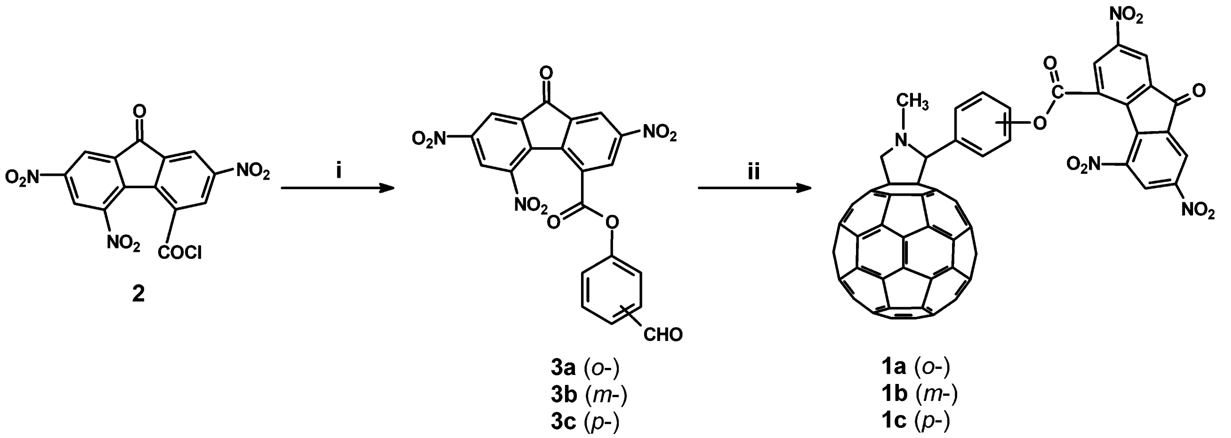
Scheme 1. Synthesis of TNF−C_{60} Dyads 1a−c from the Corresponding Formyl-Substituted TNF 3a−c[a]



[a] Reagents and conditions: (i) *o*-, *m*-, or *p*-hydroxybenzaldehyde, DCM, DMAP, r.t., 70−89%; (ii) C_{60}, sarcosine, ODCB, 125 °C, 14−21%.

chased from Fluka (>99%) and recrystallized twice from an ethanol/water mixture (95:5) and dried in a vacuum oven overnight prior to use.

All electrochemical experiments were carried out under high vacuum conditions. The supporting electrolyte and the compound samples (typically for a solution 0.1 M and 0.2 mM, respectively) were initially placed separately in the electrochemical cell. Ferrocene was also internally added to the cell as a reference (ferrocene/ferrocinium, Fc/Fc^+). The system was then evacuated to approximately 10^{-5} to 10^{-6} mmHg for 1 h, and the solvent, THF−Na−K, was vapor-transferred directly into the electrochemical cell through the vacuum line. After the solvent was transferred (~3 mL) the cell was removed from the vacuum line and the electrochemical experiments were carried out.

Sample Preparation for PR Measurements. The preparation procedure has been described in detail elsewhere.[13] First, a reference solution containing the hole transporting polymer PVK (49.75 wt %), chromophore (PDCST) (35 wt %), the liquid plasticizer BBP (15 wt %), and the sensitizer C_{60} (0.25 wt. %), was prepared in chlorobenzene. The solution was then cast at 45 °C onto indium−tin-oxide (ITO) coated glass plates and dried overnight in an oven at a temperature of 95 °C. Finally, the plates were assembled at 120 °C, yielding films of thickness around 100 μm. Teflon spacers were used to ensure a uniform thickness. A similar procedure was followed to prepare samples containing compounds **1a**−**c** instead of C_{60}. In this case a molar percentage of sensitizer was considered to get samples that could be compared to the reference one.

Optical Experiments. A standard setup for two-wave mixing (TWM) experiments[13] was implemented by using a 633 nm beam from a He−Ne laser. A tilted geometry configuration, consisting of two p-polarized beams of equal intensity intersecting the sample with external angles of 30 and 60° with respect to the sample normal, that generated a grating spacing of 1.6 μm inside the sample, was used. The experiments were performed in the presence of an external electric field that was applied perpendicular to the sample.

First, we checked for the presence of amplified scattering (beam fanning) in each of the interfering beams[14] by turning on one beam and measuring its losses as a function of the applied external field. We chose a configuration with the negative electrode facing the incident beam to reduce beam fanning.[14a] With the same purpose we have reduced the diameter of the beams up to 0.68 mm maintaining the Gaussian profile.

TWM experiments were performed only when total losses due to beam fanning (adding losses for both beams) were less than 5%. A typical TWM run consisted of the following steps. First, in the presence of the 30° beam an electric field was applied to the sample. Then, the pump (60° beam) was turned on and the transmitted output powers of both beams were monitored until steady-state energy transfer was achieved. Gain coefficients (Γ) were determined from the measurement of the multiplicative gain factor (γ_0) at steady state by using the equation

$$\Gamma = \frac{1}{L}\,[\ln(\gamma_0\beta) - \ln(\beta + 1 - \gamma_0)] \tag{2}$$

where β is the ratio between the input intensities ($\beta = I^{30°}(in)/I^{60°}(in)$, γ_0 is the ratio between the output intensity of the 30° beam ($I^{30°}(out)$) with and without the presence of beam 2, and L is the optical path length of the 30° beam inside the sample. Net gain coefficients were calculated by simply subtracting the absorption coefficient (α) of the sample at 633 nm ($\Gamma_{net} = \Gamma - \alpha$). Absorption coefficients were obtained for each sample on a Shimadzu spectrophotometer. Finally, time constants were determined from these transients by using a fitting function as described in detail below.

Results and Discussion

Synthesis. The synthesis of 2,5,7-trinitrofluorenone-4-carboxylic acid chloride **2** was accomplished following the procedure already described.[15] Formyl derivatives **3a**−**c** were synthesized for the first time in high yield by esterification with *o*-, *m*-, or *p*-hydroxybenzaldehyde using 4-(dimethylamino)pyridine (DMAP). TNF−C_{60} derivatives were prepared from the formyl-substituted TNFs **3a**−**c** by an azomethine ylide 1,3-dipolar cycloaddition to C_{60}[16] (Scheme 1). Compounds **1** and **3** were characterized by NMR, FTIR, MALDI-MS, and UV−vis.

Compounds **1a**−**c** are quite insoluble in either polar or nonpolar organic solvents. The products are slightly soluble in chlorinated solvents such as *o*-dichlorobenzene (ODCB) and 1,2-dichloroethane (DCE). The MALDI-TOF spectra of compounds **1** show as base peak a cluster of signals with a maximum at *m/z* 1210, and a cluster with a maximum at 868 corresponding to the loss of the TNF fragment from the parent ion.

UV−Vis Absorption Measurements in Solution. The UV−vis spectra of **1a**−**c** are identical, displaying

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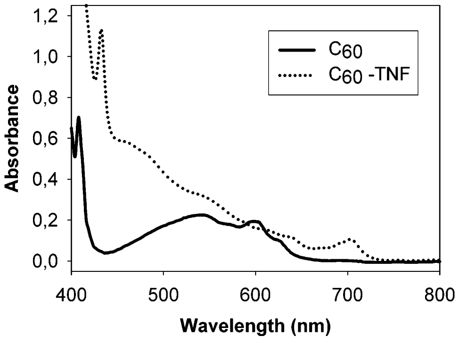


Figure 1. UV-vis spectra of compound **1c** (dashed line) and C_{60} (solid line) in ODCB as solvent.

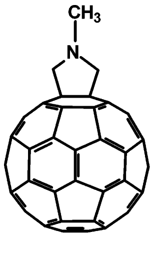
Table 1. Electrochemical Reduction Data for Trinitrofluorenone−C_{60} Derivatives

	reduction (V) vs Fc/Fc$^+$				
	$E_{1/2}$(I)	$E_{1/2}$(II)	$E_{1/2}$(III)	$E_{1/2}$(IV)	$E_{1/2}$(V)
1a	−0.75	−1.09	−1.60	−2.01	−2.31
1b	−0.74	−1.04	−1.53	−1.93	−2.23
1c	−0.78	−1.06	−1.58	−1.99	−2.29
MTNFC	−0.79	−1.07		−1.86	
NMF		−1.00	−1.56		−2.18

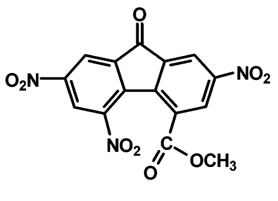
strong absorptions due to both the TNF and the fullerene moieties. Figure 1 shows the UV−vis spectrum of **1a** together with that of C_{60} for comparison in *o*-dichlorobenzene as solvent. The electronic spectra of compounds **1a**−**c** correspond to the superimposition of those of a fluorenone derivative and a typical 1,2-methanofullerene, as indicated by the sharp absorption at 430 nm and a broader band at around 700 nm.[16b] This result shows that both the TNF and the C_{60} moieties have little or no electronic influence on each other in the ground state.

The ability of the acceptors **1a**−**c** to form intermolecular CT complexes with donors was studied in DCE solution using anthracene and *N*-ethylcarbazole as the π-donors. However, the appearance of additional bands in the visible region was not detected, thus indicating the absence of CT complexes in solution.

Cyclic Voltammetry Study. The sample concentration was between 0.5 and 0.1 mM in all cases, including the model compounds (NMF) and (MTNFC). Table 1 shows the compounds studied and their potential values. The two parent compounds, *N*-methylfulleropyrrolidine (NMF) and methyl-2,5,7-trinitrofluorenone-4-carboxylate (MTNFC), were both studied by CV and OSWV. As shown in Table 1, the reduction potentials for these two compounds were used to assign the redox peaks in the CVs for **1a**−**c**.



NMF



MTNFC

The background of the supporting electrolyte was scanned between 0 and −2.5 V before adding the compound to the cell. A cyclic voltammogram of the compound was run using the above potentials at a scan rate of 100 mV/s. Ferrocene was added to the cell and a CV was then recorded to reference the potentials vs $E_{1/2}$ of ferrocene.

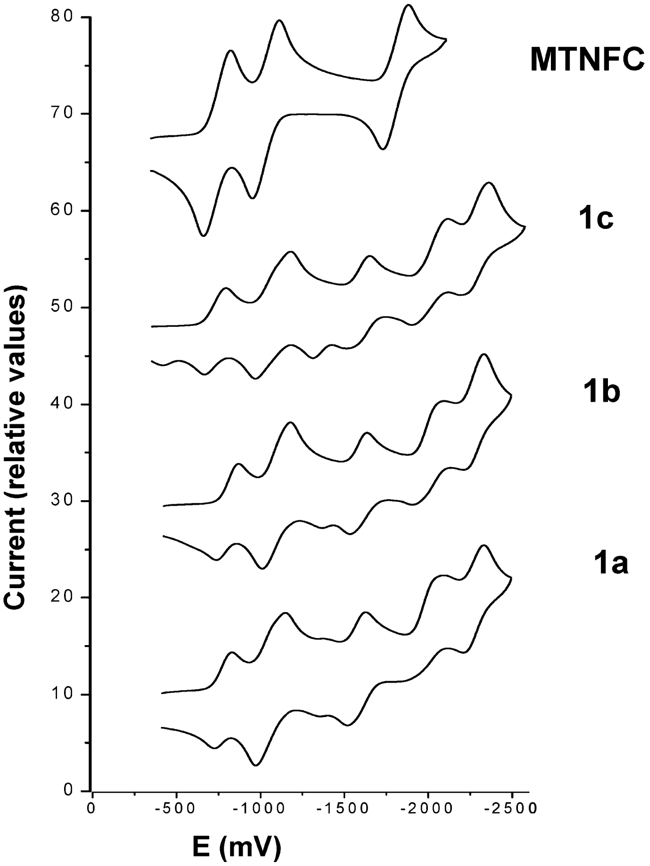


Figure 2. CV of compounds **1a**, **1b**, and **1c**, and MTNFC in THF at GCE vs Fc/Fc+, v = 100 mV/s.

Figure 2 shows the CVs of compounds **1a**−**c** and MTNFC. The first one-electron reduction for **1a**−**c** corresponds to the first reduction of the TNF group. The reduction potentials are essentially similar to those of MTNFC, so electronic effects are not evident in the neutral ground state. The next reduction peak is a two-electron process, with one electron corresponding to a TNF-based reduction (−1.07 V) and the other based on the NMF (−1.00 V). The third reduction must be fullerene-based and its reduction potential is very close to that of the model NMF, although there is a small cathodic shift in the case of **1a** and **c**, and a slight anodic one in the case of **1b**. The fourth reduction must be TNF-based and **1a**−**c** all exhibit cathodic shifts compared with the model TNF. This is an expected result since the attached fulleropyrrolidine moiety is already in its dianionic state at this stage, making it more electron donating. This is also the case for the fifth reduction process, which must be fullerene-based, and must be affected by the presence of the highly charged trianionic TNF group.

Photorefractive Characterization. The photorefractive properties were investigated by standard two-wave-mixing (TWM) experiments to measure the dynamics of the two-beam-coupling gain as described in the Experimental Section.[13] This method has the advantage that the observation of asymmetric two-beam-

Table 2. Photorefractive Properties of Composites of PVK:NLO:BBP:Sensitizer for Different Sensitizers Obtained from TWM Experiments at 633 nm, 60 V/μm, and 1 W/cm²[a]

sensitizer	α (cm^{-1}) ± 2	τ_1 (s) ± 0.01	Γ (cm^{-1}) ± 12	Γ_{net} (cm^{-1}) ± 14
C_{60}	21	0.27	142	121
1a	25	0.06	119	94
1b	22	0.13	111	89
1c	20	0.13	119	99

[a] α (absorption coefficient); τ_1 (response time); Γ (gain coefficient); and Γ_{Net} (net gain coefficient).

coupling in an optically thick sample is an unambiguous signature of photorefractivity and not some local photophysical or photochemical effect producing index modulation. By fitting the two-wave mixing transients with a growth function, the speed of the effect can be quantified. In the simplest single-carrier model of photorefractivity, the gain growth transients are exponential.[1,17] This result is valid under several approximations, including small charge modulation, negligible absorption, weak energy transfer, nondispersive charge mobility, and the slowly varying amplitude approximation. When these assumptions are not valid, deviations from single exponential behavior can be expected. One outcome, if some of these assumptions are violated, is that the recorded grating has a nonsinusoidal shape that distorts the long-time growth transient away from the exponentially growing form.[1a] This problem has been usually circumvented by interpreting only the short-time constant, while the grating is still approximately sinusoidal. In the materials reported in this work, nonexponential behavior of the grating growth has been observed. A detailed study of the cause of the nonexponential transients is out of the scope of this paper. Single exponentials did not provide good fits of the gain growth transients, no matter the length of the transient considered in the analysis. We therefore used an alternate fitting function, the sum of two exponentials:

$$\gamma(t) = 1 + a\{1 - \exp[-(t/\tau_1)]\} + b\{1 - \exp[-(t/\tau_2)]\} \quad (3)$$

and then interpreted only the short time constant τ_1.

Samples of the type PVK:PDCST:BBP:sensitizer were prepared for the various sensitizers previously described (compounds **1a**−**c**), following the method described in the Experimental Section. After preparation, samples showed good optical clarity. In some cases signs of crystallization appear after a few days. Nevertheless, these precipitation problems were overcome by heating the sample up to 120 °C for a few seconds obtaining reproducible performance.

TWM experiments were performed at a laser wavelength of 633 nm as described in the Experimental Section. In Table 2 we report the PR properties of the composites based on sensitizers **1a**−**c** from TWM experiments performed at an applied electric field of 60 V/μm and a writing intensity (sum of the two writing beam intensities) of 1 W/cm².

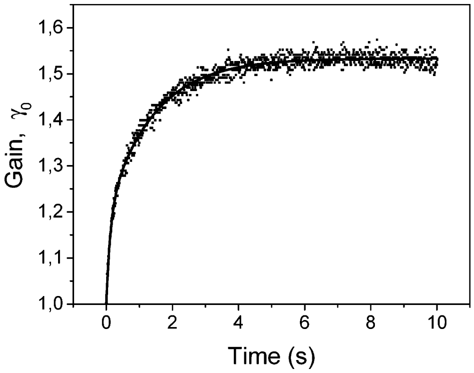


Figure 3. TWM gain vs time in a composite containing sensitizer **1b** (C_{60}−TNF−*meta*) at 60 V/μm and 1 W/cm². Loss curve not shown. The solid curve is the double exponential fit (τ_1 = 125 ms, τ_2 = 1290 ms).

As an illustration of these results we show in Figure 3 the two-beam coupling curve for a composite containing sensitizer **1b**. The solid line corresponds to the fit of the gain growth transient with the double exponential function given by eq 3.

Slightly lower net gain coefficients and rather shorter response times were obtained for sensitizers **1a**−**c** as compared to C_{60}. Also, by comparing the performance of compounds **1a**−**c**, **1a** appears to be faster than **1b** and **1c**. This behavior has been observed also at other voltages (up to 80 V/μm). Since the electrochemical properties do not indicate clear differences from one compound to another, it is difficult to understand the reason for this speed reduction. To clarify this, additional experiments with different conditions (i.e., other nonlinear chromophores, other intensities, etc.) are currently being performed and will be reported elsewhere. In any case, it is important to note that samples containing C_{60} presented a larger amount of beam fanning than samples containing compounds **1a**−**c**. To limit losses due to beam fanning below 5%, the maximum voltage that could be applied in samples containing C_{60} was 60 V/μm. On the other hand, for samples containing compounds **1a**−**c**, losses due to beam-fanning kept below 5% even for applied voltages of 80 V/μm. This constitutes an advantage of sensitizers **1a**−**c** with respect to C_{60}, since one way to increase both the gain coefficient and the response time is to increase the applied voltage. For example, for the composite containing sensitizer **1b**, at 80 V/μm we measured a net gain coefficient of 155 cm^{-1} and a time constant τ_1 of 90 ms.

Conclusions

Compounds **1a**−**c** are the first TNF−C_{60} dyads designed to study the electronic effects between both units. The search for new bridges which permit a better interaction between both moieties is underway in order to enhance the electron acceptor ability of the molecules. The PR performance of compounds **1a**−**c** as sensitizers in PVK-based composite materials is similar to that of C_{60} with shorter response times, but slightly lower gain coefficients. The substitution of C_{60} by compounds **1a**−**c** leads to a reduction of losses due to beam fanning, which could be attributed to the higher solubility in compari-

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(17) Kukhtarev, N. V.; Markov, V. B.; Odulov, S. G.; Soskin, M. S.; Vinetskii, V. L. *Ferroelectrics* **1979**, *22*, 949. Kukhtarev, N. V.; Markov, V. B.; Odulov, S. G.; Soskin, M. S.; Vinetskii, V. L. *Ferroelectrics* **1979**, *22*, 961.

son with C_{60}, thus voltages up to 80 V/mm could be applied, resulting in larger gain coefficients and shorter response times.

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