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A Novel Approach to the Synthesis of Conjugated Carbazole Trimers as Multifunctional Chromophores for Photorefractive Materials

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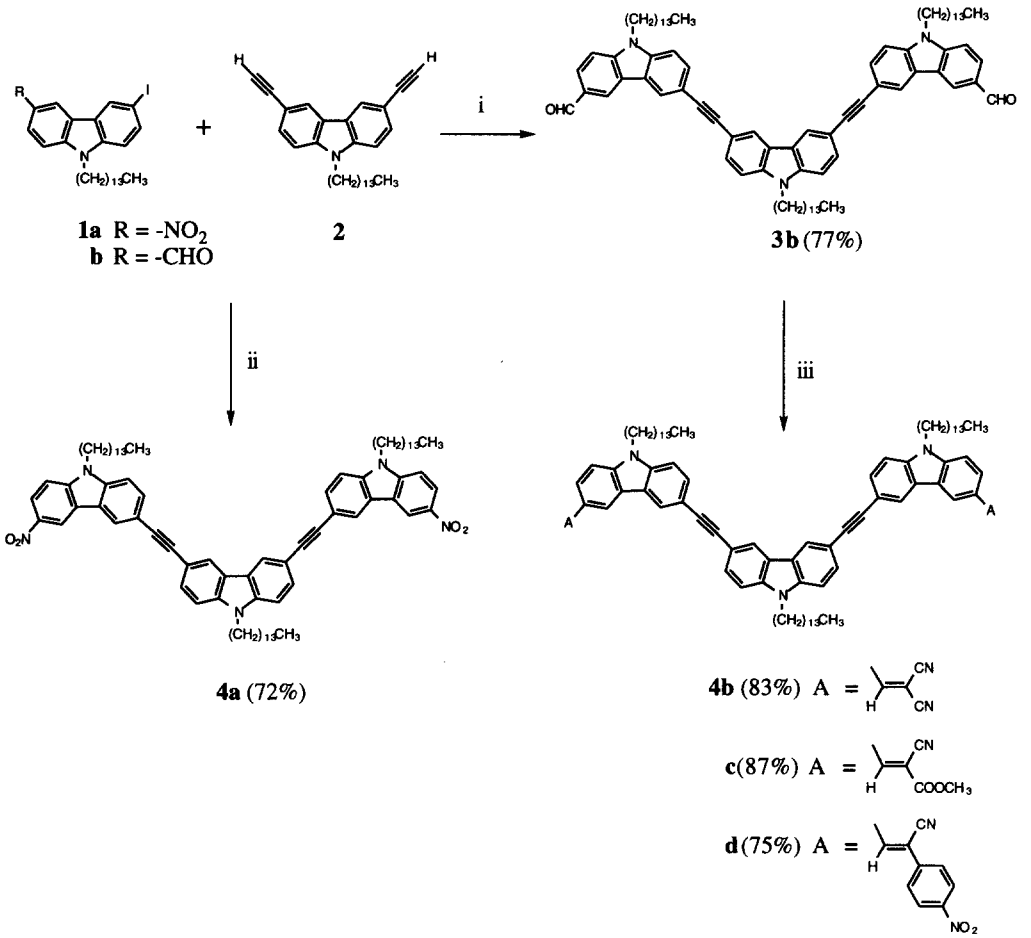
ABSTRACT: A new series of amorphous conjugated carbazole trimers have been synthesized for photorefractive applications. It was found that these trimers possess large photorefractive optical net gain and high photorefractive diffraction efficiency.

Recently increasing research interest has been on the optimization of amorphous photorefractive materials due to the need of new advanced materials for dynamic holographic storage and image processing applications.[1] To be photorefractive, materials must show multifunctional properties, second-order optical nonliearity and photoconductivity. This multifunctionality can be achieved by two design approaches, guest-host approach and fully-functional approach. Most of the reported amorphous photorefractive materials are obtained based on guest-host systems using a nonlinear optical polymer, a charge-transporting polymer or an inert polymer as a host doped with other corresponding necessary components.[2] Fully-functional polymers have all necessary functional groups either in the polymeric main-chain or in the side-chain.[3] Photorefractivity have been demonstrated in both types of systems and the high photorefractive performances were obtained from guest-host systems.[4] Bifunctional chromophores for photorefraction have been reported which function as charge-transporting agents as well as second-order nonlinear optical compounds.[5] It is well known that many types of second-order nonlinear chromophores have been designed and synthesized based on the aromatic systems with donors and acceptors.[6] However, the systematic design and synthesis for photorefractive chromophores have not been reported due to the multifunctional requirements of the photorefractive chromophores.

In our laboratory, the new molecular design approach to the synthesis of photorefractive materials have been developed based on carbazole building blocks which show both photoconductive and second-order nonlinear optical properties.[7] Our target is development of the multifunctional photorefractive chromophores. In this communication, we report the synthesis and photorefractive effects of a series of new multifunctional chromophores, conjugated carbazole trimers. In this design approach, conjugated structure was used to design the photorefractive chromophores owing to relatively high photogenerated carrier mobility of the conjugated carbazole polymers and oligomers.[8] In this trimers, carbazole rings are linked each other by ethynyl group and both side carbazoles substituted with acceptor groups. These structures should exhibit both photoconductive

and second-order nonlinear optical properties. In order to obtain amorphous carbazole trimer with a low glass transition temperature to form the thickness films in which the orientation of the chromophores can be achieved at room temperature by applying an electric field, the three long aliphatic groups are introduced to such kind of trimers on 9-position of each carbazole ring.



Scheme 1 Reagents and conditions: i, $Pd(PPh_3)_2Cl_2$/CuI, Et_3N, r.t., 8 h; ii, $Pd(PPh_3)_2Cl_2$/CuI, Et_3N, r.t., 12 h; iii, malononitrile, cyanoacetic acid methyl ester or 4-nitrophenylacetonitrile/4-dimethylaminopyridine (DMAP)/THF, r.t., 3 h.

The general methodology for the synthesis of conjugated carbazole trimers **4a-4d** is show in Scheme 1. 3,6-Diiodo-9-tetradecylcarbazole and 3-iodo-9-tetradecylcarbazole were synthesized by nucleophilic substitution reaction of 1-bromotetradecane with 3,6-diiodocarbazole and 3-iodocarbazole, respectively. 3-Iodocarbazole and 3,6-diiodocarbazole were synthesized according to the synthetic method reported by Tucker.[9] 3,6-Diethynyl-9-tetradecylcarbazole was prepared from 3,6-diiodo-9-tetracylcarbazole and trimethylsilylacetylene by Pd-catalytic coupling reaction and followed by the removal of trimethylsilyl group. 3-Iodo-6-formyl-9-

tetradecylcarbazole and 3-iodo-6-nitro-9-tetraecylcarbazole were yielded by a formylation reaction and a normal nitration reaction, respectively. Carbazole trimers with two nitro groups **4a** and two formyl groups **3b** could be synthesized from compounds **1** and **2** by Pd-catalytic coupling reaction. Carbazole trimers **4b-4d** with other acceptor groups could be obtained by Knoevenagel condensation starting from **3b**. All trimers were purified by silica gel column. All compounds and carbazole trimers have been characterized by ^{1}H NMR, IR, UV-Visible and elemental analysis. It was found that carbazole trimers **4a** and **4b** are amorphous and exhibit the glass transition temperatures (as shown in Table 1) at about room temperature.

Carbazole trimer **4a** and carbazole trimer **4b** doped with 0.06 wt% of 2,4,7-trinitro-9-fluorenone (**4b/TNF**) as a sensitizer were sandwiched between two indium tin oxide (ITO) covered glass substrates. The films with thickness about 150 μm guaranteed by a Teflon film spacer could be obtained at 60°C. The absorption coefficients (α) at a wavelength of 532 nm for trimer **4a** and at a wavelength of 633 nm for trimer **4b/TNF** are shown in Table 1.

Trimer samples **4a** and **4b/TNF** have been determined to be both photoconductive and second-order nonlinear optically active. Second harmonic generation (SHG) experiments were carried out in order to probe the orientation of chromophores in films at room temperature. Infrared light (1064 nm) from a Q-switched Nd:YAG laser was incident on the sample and the intensity of the second harmonic (SH) signal was monitored. With no electric field applied, the SH intensity was zero, as a result of the centrosymmetric random arrangement of the chromophores. After switching on the electric field, orientation of the chromophores was achieved, reaching a stable value within a few seconds. This orientation of the chromophores at room temperature came as the result of the low T_g and chromophore dipoles of trimers **4a** and **4b**. The detail research work on the electrooptic (EO) measurements of these trimer materials will be reported separately. The photoconductivities were studied at a wavelength of 532 nm for **4a** and at a wavelength of 633 nm for **4b/TNF** using a photocurrent method.[10] The photoconductive sensitivities (σ/I) for **4a** and **4b/TNF** are shown in Table 1.

Table 1. Glass transition temperature (T_g), photoconductive sensitivity (σ/I), absorption coefficient (α), applied electric field (E_a), photorefractive optical gain (Γ), photorefractive net optical gain (Γ_n), and diffraction efficiency (η) for conjugated carbazole trimers **4a** and **4b/TNF**.

Trimer	T_g[a] (°C)	σ/I (cm/ΩW)	α[b] (cm^{-1})	E_a (V/μm)	Γ (cm^{-1})	Γ_n (cm^{-1})	η (%)
4a[c]	19	1.20×10^{-11}	8.2	33	35.0	26.8	13
4b/TNF[d]	29	1.22×10^{-10}	5.8	30	81.8	76.0	18

[a] Measured by a PERKIN ELMER DSC-7. [b] Measured by a SHIMADZU UV-3100PC. [c] Monolithic chromophore **4a** without dopants. [d] Trimer **4b** doped with 0.06 wt% of TNF.

The photorefractive properties of carbazole trimers **4a** and **4b/TNF** were studied on about 150 μm films by the two-beam coupling (TBC) and four-wave mixing (FWM) techniques.[2] In the TBC experiment, holographic gratings were written by two p-polarized laser beams. Two writing beams with a wavelength at 633

nm and with a wavelength at 532 nm were used for **4a** and **4b/TNF**, respectively. An asymmetric optical energy exchange between the two beams were observed when the applied electric field was switched on. The photorefractive optical gains and net gains obtained from TBC measurements are shown in Table 1. The diffraction efficiency (as shown in Table 1) could also be obtained from these material films by FWM measurements. The preliminary results indicated that the optical gain and the diffraction efficiency were strongly electric field dependent. The application of this new photorefractive oligomer system in information storage and image processing has been explored with demonstrations of holographic image recording and retrieving.

In conclusion, we have synthesized a series of multifunctional chromophores, conjugated carbazole trimers which show large photorefractive optical net gain and high diffraction efficiency. We have developed, for the first time to our knowledge, the new design approach to the multifunctional chromophores as photorefractive chromphores. We have obtained the good reasonable photorefractive effects from both monolithic trimer **4a** and sensitizer doped trimer **4b/TNF**. These trimers should be quite useful for photorefractive applications and this chromophore design approach should be useful enlightenment for development and optimization selection of new photorefractive materials. The synthetic flexibility of this carbazole oligomers allows modification of the oligomer structure to further improve the photorefractive properties.

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