A new family of amorphous molecular materials showing large photorefractive effect

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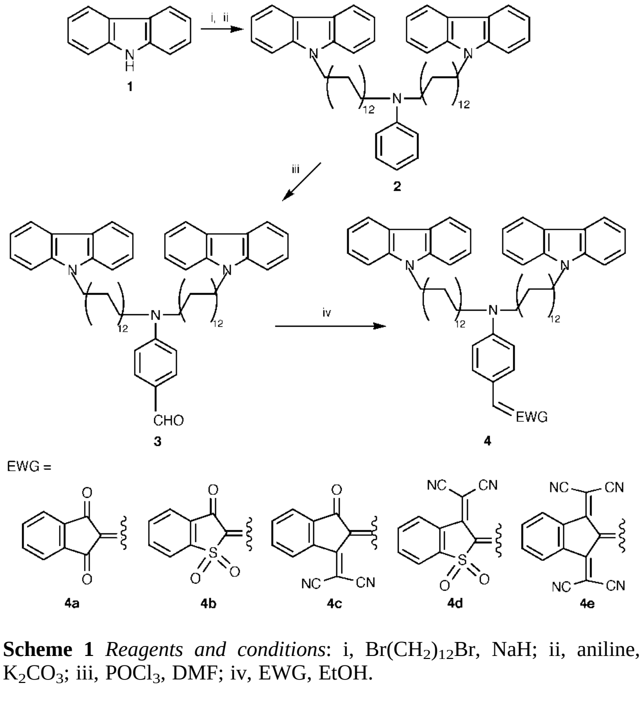
A novel series of amorphous molecular materials containing carbazole and methine dyes have been synthesized and characterized for photorefractive applications.

In recent years, functional molecular materials exhibiting nonlinear optical, electroluminescent, ferromagnetic and photoconducting properties have been sought for practical applications.[1–4] These materials possess excellent processibility, transparency and can be efficiently purified by many well-known techniques such as chromatography. The versatility of structural modification offers a unique opportunity to meet additional challenges, for example, designing multifunctional materials that could simultaneously possess several properties. Photorefractive (PR) materials are such multifunctional materials that combine photoconductivity and nonlinear optical (NLO) response to modulate the refractive index of the medium.[5] Due to their potential applications in holographic optical data storage and real-time optical processing, various classes of organic PR materials including polymers,[6–8] liquid crystals[9] and organic glasses[10,11] have been explored. Herein, we report a novel series of amorphous molecular materials based on carbazole and methine dyes, which exhibit very interesting charge-transfer complex formation and large PR responses.

The synthetic route is shown in Scheme 1, where carbazole was chosen as the photoconductive component for hole transport. Condensation of aldehyde **3** with electron withdrawing groups yielded methine dye as the NLO chromophores. The molecules synthesized (compound **4**) thus possess dual functions: photoconductivity and second-order NLO activity. The long aliphatic chain was introduced to prevent the materials from crystallization and help resulting compounds remain amorphous at room temperature. The structures of the compounds were confirmed by microanalysis and by spectroscopic methods.[12] The thermal properties of the compounds are summarized in Table 1, which indicated the low T_g nature of the materials. These compounds were found to readily form amorphous films, as evidenced by differential scanning calorimetry (DSC), polarizing microscopy and X-ray diffraction. The amorphous films made from these compounds are very stable in an ambient atmosphere for over a year up to the present time and no crystallization phenomenon was observed even on further heating. The UV/vis spectra of compound **4** in CH_2Cl_2 display two intense bands. The one at around 347 nm can be attributed to the carbazole moiety, while the other is due to the NLO chromophore. As also shown in Table 1**,** increasing acceptor strength by replacing carbonyl groups with sulfonyl and dicyanovinyl groups results in a bathochromic shift in the corresponding chromophores. It is interesting to note that in solid UV/vis spectra, new long-wavelength absorption bands were observed in addition to the peaks from chromophore and carbazole. The intensity of these new peaks varies as a function of temperature. As the temperature increases, the absorbance decreases and finally becomes zero at around 75 °C. These new bands were assigned to the formation of charge-transfer complexes (CTC) between the carbazole and electron withdrawing groups because it was observed that when compound **2** was mixed with electron acceptors in CH_2Cl_2 solution, an intense coloration with new long-wavelength absorption peaks developed immediately. For example, CTC bands at 492 and 690 nm were observed for compounds **4b** and **4c** respectively. These new absorption bands enable us to photoexcite the materials mainly through the charge-transfer complex at a longer wavelength. It is worth mentioning that additional photosensitizers, such as 2,4,7-trinitrofluoren-9-one (TNF), are needed in most reported composite PR materials containing a carbazole moiety.[13] The system reported here shows all necessary functions for PR response in single molecules.

Photocurrent measurements indicated these materials are photoconductive and a second harmonic generation signal was observed as a function of an external field. The PR nature of these molecular materials was verified in two-beam coupling measurements. In this experiment, two coherent laser beams (*p*-polarized) intersect inside the sample to write a holographic



Scheme 1 *Reagents and conditions*: i, $Br(CH_2)_{12}Br$, NaH; ii, aniline, K_2CO_3; iii, $POCl_3$, DMF; iv, EWG, EtOH.

Table 1 The properties of carbazole containing amorphous molecules

Compound	T_g/°C[a]	T_d/°C[a]	λ_{max}/nm[b]	ε_{max}/l mol^{-1} cm^{-1}[b]
4a	9	292	491	48 900
4b	10	282	492	59 100
4c	13	211	570	49 000
4d	7	228	602	59 300
4e	6	205	628	18 300

[a] The glass transition temperature (T_g) and the decomposition temperature (T_d) were determined by DSC, 10 °C min^{-1}. [b] Measured in CH_2Cl_2.

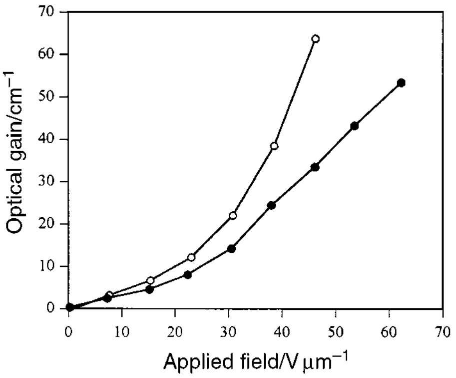


Fig. 1 Photorefractive optical gain of compound **4b** (○) and compound **4c** (●) as a function of the applied field.

grating. It is known that this grating has a non-zero phase shift with respect to the light intensity pattern. An asymmetric energy exchange between the two beams, characterized by the two-beam coupling gain coefficient Γ, can be observed.[5] A further note is that in this experiment, the normal of the sample surface needs to be tilted 52 °C to yield a projection of the grating wave vector along the poling axis. The films for PR characterization were prepared by sandwiching the melt of compounds between two glass substrates coated with indium-tin oxide. The thickness of films is about 128 µm, maintained by a polyimide spacer. Some preliminary results performed on compound **4b** and **4c** are presented in Fig. 1. Compound **4b** was measured with a He-Ne laser (632.8 nm), while compound **4c** was excited by a diode laser with a wavelength of 780 nm. As the applied field increased, the intensity of one beam increased, while that of the second beam decreased. When the electric field was turned off, the intensities returned to their original levels and no energy exchange was observed. The strong field dependence of the optical gain reflects the field dependence of both the quantum yield of photogeneration of charge carriers and the second-order NLO response. For compound **4b**, at a field of 46 V µm^{-1}, an optical gain value of 65.4 cm^{-1} was achieved. The absorption coefficient of the material was only 1.4 cm^{-1}, thus giving us a net optical gain of 64 cm^{-1}. For compound **4c,** we have obtained a PR gain of 53 cm^{-1} by applying a field of 62 V µm^{-1}, whereas the absorption coefficient was 4.3 cm^{-1}. The index grating recorded in the material was further tested by a weaker, counter-propagating probe beam (*p*-polarized) in the four wave mixing experiments. The diffraction efficiency η is calculated as the intensity ratio of the diffracted signal to the probe beam. It was observed that the diffraction efficiency also had a strong dependence on the applied field and reached 17% for compound **4b** and 9% for compound **4c** at E = 42 V µm^{-1}.

In summary, a new series of multifunctional amorphous molecules has been synthesized and characterized for photorefractive applications. Selecting different electron acceptor groups affords control not only of electrooptic effects but also of charge generating characteristics of the resulting materials. This approach opens the way for an extension of PR sensitivity to near-IR or even IR regions, which is very interesting for applications in telecommunication. Moreover, the synthetic flexibility and simplicity of this molecular system offer great possibilities for structural modifications to further improve performance or match the laser wavelength for the application desired. Extensive work based on this system is now under way.

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Notes and references

1 T. Noda and Y. Shirota, *J. Am. Chem. Soc.*, 1998, **120**, 9714.
2 M. Thelakkat and H. Schmidt, *Adv. Mater.*, 1998, **10**, 219.
3 K. Naito and A. Miura, *J. Phys. Chem.*, 1993, **97**, 6240.
4 Y. Shirota, K. Moriwaki, S. Yoshikawa, T. Ujike and H. Nakano, *J. Mater. Chem.*, 1998, **8**, 2579.
5 *Photorefractive Materials and Their Applications*, ed. P. Gunter and J. P. Huignard, Springer-Verlag, Berlin, 1988, vol. I and II.
6 W. E. Moerner and S. M. Silence, *Chem. Rev.*, 1994, **94**, 127.
7 L. P. Yu, W. K. Chan, Z. H. Peng and A. Gharavi, *Acc. Chem. Res.*, 1996, **29**, 13.
8 W. Li, A. Gharavi, Q. Wang and L. P. Yu, *Adv. Mater.*, 1998, **10**, 927.
9 G. P. Wiederrecht, B. A. Yoon and M. R. Wasielewski, *Adv. Mater.*, 1996, **8**, 535.
10 P. M. Lundquist, R. Wortmann, C. Geletneky, R. J. Twieg, M. Jurich, V. Y. Lee, C. R. Moylan and D. M. Burland, *Science*, 1996, **29**, 13.
11 Q. Wang, A. Gharavi, W. Li and L. P. Yu, *Polym. Prepr.*, 1997, **38**(2), 508.
12 *Selected data* for **4b**: δ_H($CDCl_3$) 1.24–1.37 (m, 36H, alkyl), 1.55 (m, 4H, alkyl protons), 1.85 (t, *J* 7.32, 4H, arom), 3.36 (t, *J* 7.74, 4H, CH_2N), 4.28 (t, *J* 7.19, 4H, CH_2Ar), 6.69 (d, *J* 8.97, 2H, arom), 7.23 (t, *J* 7.31, 4H, arom), 7.38 (d, *J* 8.08, 4H, arom), 7.45 (m, 5H, arom), 7.75 (t, *J* 7.89, 1H, arom), 7.81 (t, *J* 7.85, 1H, arom), 7.91 (s, 1H, vinyl), 7.98 (d, *J* 8.05, 2H, arom), 8.03 (d, *J* 8.10, 1H, arom), 8.09 (d, *J* 7.79, 4H, arom) (Calcd. for $C_{63}H_{74}N_3O_3S_1$: C, 79.42; H, 7.77; N, 4.41. Found: C, 79.34; H, 7.79; N, 4.34%).
13 Y. Zhang, R. Burzynski, S. Ghosal and M. K. Casstevens, *Adv. Mater.*, 1996, **8**, 111.

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