Available online at www.sciencedirect.com
ScienceDirect
Dyes and Pigments 76 (2008) 310−314
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Synthesis and properties of novel Y-shaped NLO molecules containing thiazole and imidazole chromophores

Jun Ren, Shi-Min Wang*, Li-Fang Wu, Zu-Xun Xu, Bing-Hai Dong

Ministry-of-Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, Hubei University, Wuhan 430062, PR China

Available online 6 April 2007

Abstract

Two new second-order NLO molecules, derived from a five-membered heterocyclic ring (thiazole and imidazole), were synthesized. The thermal stability, optical transparency and second-order nonlinear optical (NLO) properties were investigated. As a result, good nonlinearity-transparency-thermal stability trade-off was achieved.

© 2006 Published by Elsevier Ltd.

Keywords: Second-order nonlinear optical; Thiazole; Imidazole

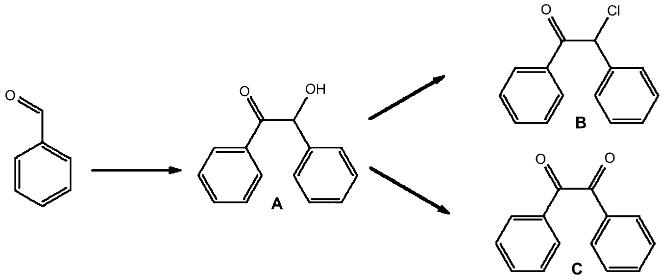
1. Introduction

Second-order nonlinear optical (NLO) materials have been advancing for a few decades as a promising field with important applications in the domain of opto-electronics and photonics [1−5]. Organic NLO molecules have proven to be of great interest in recent years due to their extremely large optical nonlinearities as compared to most of the inorganic crystals that are transparent in the visible region [6−8]. One of the major challenges in the area of organic NLO molecules is to design and synthesize second-order NLO chromophores which, simultaneously, exhibit large hyperpolarizability (β), good optical transparency and high thermal stability.

Most attempts to design molecules with large β have relied upon endcapping an optimal π-conjugated bridge with different donors and acceptors [9]. However, this enhancement of β is always accompanied with a red-shift in the λ_{max} peak, which is a so-called nonlinearity-transparency trade-off. Y-shaped chromophores show improved trade-off compared to classical one-dimensional dipolar chromophores, due to the contribution of the large, off-diagonal β tensorial components.

Utilising a multiple substitution strategy, we designed and synthesized two Y-shaped molecules containing the thermally stable thiazole and imidazole chromophores. As a result, good nonlinearity-transparency-thermal stability trade-off was achieved for the two novel NLO molecules.

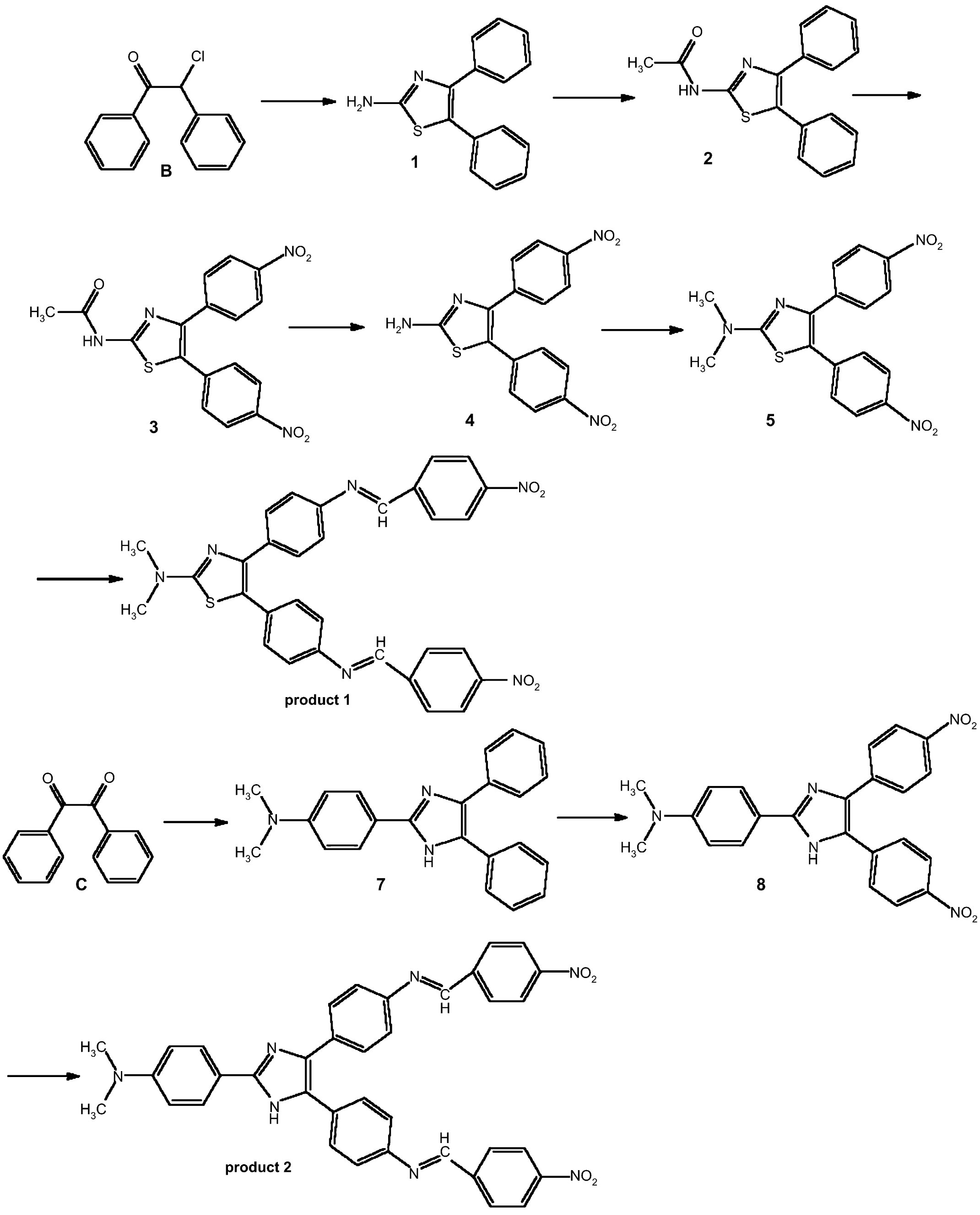
2. Experimental



---

* Corresponding author. Tel.: +86 27 50865319; fax: +86 27 88663043.
E-mail address: wangshimin@hubu.edu.cn (S.-M. Wang).

0143-7208/$ - see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.dyepig.2006.09.003



2.1. Chemicals and instruments

^{1}H NMR spectra were obtained using an Inova 600 MHz spectrometer using TMS as an internal standard. Infrared spectra were recorded on a spectrum one FT-IR spectrometer. The UV absorption spectra of dilute solutions were recorded on a TU-1800 SPC spectrophotometer using a 1 cm path length quartz cuvette. The one-photon fluorescence spectra were obtained on an RF-450 spectrofluorometer. Compounds **A**, **B** and **C** were synthesized according to the literature [10].

2.2. Synthesis

2.2.1. 4,5-Diphenylthiazol-2-amine (*1*)

2-Chloro-1,2-diphenylethanone **B** (20 g, 83 mmol) and thiourea (7 g, 90 mmol) in 80 mL ethyl alcohol were refluxed for 2 h. The solvent was removed under vacuum and the solid product was soaked in 100 mL of 30% NaOH at 50 °C for 7 h. The crude product was filtered and washed with water to neutrality and then was recrystallized from 95% alcohol to obtain a grey, needle-shaped solid (15.7 g, 72% yield). M.p.: 188–189 °C. IR: $\nu_{\max}/\mathrm{cm}^{-1}$: 3400, 3250 (–NH$_2$), 1620 (C=N), 1590, 1490, 1440 (−C_6H_4−), 590 (C−S); ^{1}H NMR (DMSO-d_6) δ (ppm): 5.11 (2H, s, N−H), 7.23−7.27 (8H, m, Ph-H), 7.45−7.46 (2H, m, Ph-H). Anal. Calcd for $C_{15}H_{12}N_2S$: C, 71.42; H, 4.79; N, 11.10; found: C, 71.05; H, 4.62; N, 11.35%.

2.2.2. *N-(4,5-Diphenylthiazol-2-yl)acetamide (**2**)*

Compound **1** (10 g, 40 mmol), 2 drops H_2SO_4 and 6 mL acetic anhydride were added to glacial acetic acid (100 mL). The mixture was refluxed for 1 h and poured into 1000 mL ice-water to give a white precipitate. The solid was filtered and washed with water to the neutrality to obtain **2** (11.4 g, 97.5% yield). M.p.: 260−261 °C. IR: ν_{max}/cm^{-1}: 3270 (−NH−), 2960 (−CH_3), 1690 (−CO−), 1620 (C=N), 1590, 1490 (−C_6H_4−), 1320 (−NO_2), 620 (C−S) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ (ppm): 2.32 (s, 3H, −CH_3), 7.6−7.8 (8H, m, Ph-H), 8.1−8.4 (2H, m, Ph-H). Anal. Calcd for $C_{17}H_{14}N_2OS$: C, 69.36; H, 4.79; N, 9.52; found: C, 69.41; H, 4.82; N, 9.47%.

2.2.3. *N-(4,5-Bis(4-nitrophenyl)thiazol-2-yl)acetamide (**3**)*

To 35 mL of fuming nitric acid cooled to <0 °C in an ice−salt mixture, compound **2** [*N*-(4,5-diphenylthiazol-2-yl)-acetamide] (8 g, 27 mmol) was added gradually with vigorous stirring. The mixture was stirred for 30 min and then poured into 1000 mL ice-water and neutralized (pH 7) with aqueous sodium hydroxide. Product **3** was filtered and recrystallized from chloroform (6 g, 57.4% yield). M.p.: 213−214 °C. IR: ν_{max}/cm^{-1}: 3350 (−NH−), 2980 (−CH_3), 1690 (−CO−), 1620 (C=N), 1590, 1490, 1440 (−C_6H_4−), 1540, 1320 (−NO_2), 590 (C−S); ^{1}H NMR (DMSO-d_6) δ (ppm): 2.32 (3H, s, −CH_3), 7.6−7.8 (4H, m, Ph-H), 8.1−8.4 (4H, m, Ph-H). Anal. Calcd for $C_{17}H_{12}N_4O_5S$: C, 53.12; H, 3.15; N, 14.58; found: C, 52.98; H, 3.22; N, 14.47%.

2.2.4. *4,5-Bis(4-nitrophenyl)thiazol-2-amine (**4**)*

Compound **3** [*N*-(4,5-bis(4-nitrophenyl)thiazol-2-yl)acetamide] (2.5 g, 6.5 mmol), KOH (4 g, 71 mmol), H_2O (5 mL), CH_3OH (25 mL) and tetrahydrofuran (40 mL) were added to 10 mL tetrahydrofuran. The mixture was heated under reflux for 10 min and then hot water (100 mL) was added and heating was continued for a further 20 min. After neutralization with 6 M HCl, the crude product was collected and recrystallized from chloroform (1.8 g, 81% yield). IR: ν_{max}/cm^{-1}: 3350, 3100 (−NH_2), 1620 (−C=N−), 1590, 1560, 1520, 1420 (−C_6H_4−), 1340 (−NO_2); ^{1}H NMR (DMSO-d_6) δ (ppm): 8.2−8.5 (4H, m, Ph-H), 7.65−7.67 (2H, m, Ph-H), 7.45−7.47 (m, 2H, Ph-H), 3.7 (2H, s, NH_2). Anal. Calcd for $C_{15}H_{10}N_4O_4S$: C, 52.63; H, 2.94; N, 16.37; found: C, 52.55; H, 2.89; N, 16.50%.

2.2.5. *N,N-Dimethyl-4,5-bis(4-nitrophenyl)-thiazol-2-amine (**5**)*

To a solution of compound **4** [4,5-bis(4-nitrophenyl)thiazol-2-amine] (2 g, 5.8 mol) 1.5 mL 30% NaOH and tetrahydrofuran (30 mL), CH_3I (1.5 mL, 24 mmol) in 30 mL THF was added dropwise. The mixture was heated at 50 °C for 10 h and the solvent was then removed in vacuum and the residual solid was washed with water (10 mL × 3) and hot ethanol (10 mL × 3) to give a red solid (2 g, 92.5% yield). IR: ν_{max}/cm^{-1}: 2940 (−CH_3), 1600 (−C=N−), 1560, 1520, 1500, 1440 (−C_6H_4−), 1340 (−NO_2); ^{1}H NMR (DMSO-d_6) δ (ppm): 8.2−8.5 (4H, m, Ph-H), 7.67 (2H, d, $J = 9$ Hz, Ph-H), 7.37 (2H, d, $J = 9$ Hz, Ph-H), 3.2 (6H, s, −CH_3). Anal. Calcd for $C_{17}H_{14}N_4O_4S$: C, 55.13; H, 3.81; N, 15.13; found: C, 55.27; H, 3.77; N, 15.09%.

2.2.6. *4,4′-(2-(Dimethylamino)thiazole-4,5-diyl)bis-(N-(4-nitrobenzylidene)benzenamine) (product **1**)*

A mixture of compound **5** (2 g, 5.4 mmol) and iron powder (1.5 g, 27 mmol), 20 mL ethanol and 10 mL water were heated to reflux. HCl (10% aq., 3 mL) was added under N_2 and the mixture was refluxed for another 3 h. The ensuing mixture was filtered while hot and the filtrate was dried by removing the solvent under vacuum to give a red solid. This solid (0.8 g, 2.6 mmol) and 1-nitro-4-vinylbenzene (1.5 g, 10 mmol) were dissolved in 50 mL ethanol and refluxed for 3 h with efficient stirring. The red precipitate was filtered and washed with hot ethyl alcohol (15 mL × 3) to obtain compound **1** (1.16 g, 78.6% yield). IR: ν_{max}/cm^{-1}: 3290 (−CH_3), 1620 (−C=N−), 1590, 1510 (−C_6H_4−), 1340 (−NO_2), 1110 (C=N); ^{1}H NMR (DMSO-d_6) δ (ppm): 8.58 (2H, s, =CH), 8.40 (4H, m, Ph-H), 8.33 (4H, m, Ph-H), 7.63 (2H, m, Ph-H), 7.36 (2H, m, Ph-H), 7.20 (4H, m, Ph-H), 3.2 (6H, s, −CH_3). Anal. Calcd for $C_{31}H_{24}N_6O_4S$: C, 64.57; H, 4.20; N, 14.57; found: C, 64.29; H, 4.05; N, 14.86%.

2.2.7. *4-(4,5-Diphenyl-1H-imidazol-2-yl)-N,N-dimethylbenzenamine (**7**)*

N,N′-Dimethyl-4-vinylbenzenamine (2.8 g, 18 mmol), benzoin (4 g, 18 mmol) and ammonium acetate (25 g, 320 mmol) were added to glacial acetic acid (100 mL) and the mixture was refluxed for 2 h, poured into ice-water and neutralized with aqueous ammonia. The ensuing red solid was washed with water, and recrystallized from ethanol to obtain **7** (4.7 g, 73.4% yield). M.p.:182−184 °C. IR: ν_{max}/cm^{-1}: 3020 (−CH_3), 1620 (−C=N), 1550, 1510, 1490, 1440 (−C_6H_4−), 690 (C−N); ^{1}H NMR (DMSO-d_6) δ (ppm): 7.9 (2H, m, Ph-H), 7.51 (4H, m, Ph-H), 7.27−7.35 (6H, m, Ph-H), 6.79 (m, 2H, Ph-H), 3.2 (6H, s, −CH_3). Anal. Calcd for $C_{25}H_{21}N_3$: C, 81.38; H, 6.24; N, 12.38; found: C, 81.21; H, 6.42; N, 12.57%.

2.2.8. *4-(4,5-Bis(4-nitrophenyl)-1H-imidazol-2-yl)-N,N-dimethylbenzenamine (**8**)*

To 24 mL of concentrated sulfuric acid cooled to <0 °C in an ice−salt mixture, compound **7** (2 g, 6 mmol) was added gradually with vigorous stirring. Eight milliliters of well-cooled, fuming nitric acid was added gradually with stirring. The mixture was stirred for 20 min and then poured into ice-water and neutralized with aqueous sodium hydroxide. The product **8** was filtered and recrystallized from ethanol (1.9 g, 75% yield). IR: ν_{max}/cm^{-1}: 3080 (−CH_3), 1620 (−C=N), 1600, 1520, 1480, 1440 (−C_6H_4−), 1340 (−NO_2), 690 (C−N); ^{1}H NMR (DMSO-d_6) δ (ppm): 7.85 (2H, m, Ph-H), 7.40 (4H, m, Ph-H), 7.30 (4H, m, Ph-H), 6.73 (2H, m, Ph-H), 3.0

Table 1
Properties of chromophores

Compounds	λ_{max} (nm)	β^a (10^{-30} esu)	$T_d{}^b$ (°C)
1	417.0	17.31	289.2
2	358.1	40.66	226.7

[a] Measured by solvatochromic method at 1.907 μm.
[b] Determined by TGA at a rate of 10 °C min.

(6H, s, $-CH_3$). Anal. Calcd for $C_{25}H_{19}N_5O_4$: C, 64.33; H, 4.46; N, 16.31; found: C, 64.57; H, 4.48; N, 16.29%.

*2.2.9. 4,4′-(2-(4-(Dimethylamino)phenyl)-1H-imidazol-4,5-diyl)bis(N-(4-nitro benzylidene) benzenamine) (product **2**)*

A procedure similar to that carried out in Section 2.2.6 was carried out using compound **8** (2.0 g, 4.7 mmol) instead of compound **5** to yield **2** (0.93 g, 73.6%). IR: ν_{max}/cm^{-1}: 2930 ($-CH_3$), 1700 ($-C{=}N-$), 1610, 1590, 1510, 1440 ($-C_6H_4-$), 1360 ($-NO_2$), 1070 (C=N); ^{1}H NMR (DMSO-d_6) δ (ppm): 8.32 (2H, s, =CH), 8.18 (8H, m, Ph-H), 7.66 (8H, m, Ph-H), 7.45 (4H, m, Ph-H), 3.3 (6H, s, $-CH_3$). Anal. Calcd for $C_{37}H_{29}N_7O_4$: C, 69.91; H, 4.60; N, 15.42; found: C, 69.78; H, 4.65; N, 15.56%.

3. Results and discussion

We have synthesized and characterized two new second-order NLO molecules, which contain multiple donor or acceptor substituents and thermally stable imidazole or thiazole ring, as “Y shaped” molecules [11]. The UV–vis absorption maximum (λ_{max}), first hyperpolarizabilities (β) and decomposition temperatures (T_d) of the NLO-phores are presented in Table 1. Both compounds show good nonlinearity-transparency trade-off compared with classical one-dimensional dipolar chromophores.

The UV–vis spectra of NLO-phores at 10^{-5} mol/L at 20 °C in CH_3OH are shown in Fig. 1. Usually, the molecules which have the largest second NLO coefficient are mostly benzene ring conjugate systems, which have poor transparency and largest multi-wavelength ultraviolet absorption in the 400–600 nm range.

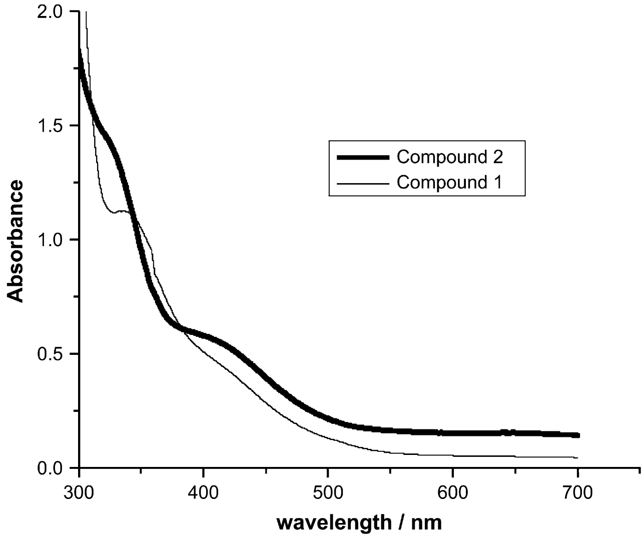


Fig. 1. UV–vis spectra of NLO-phores.

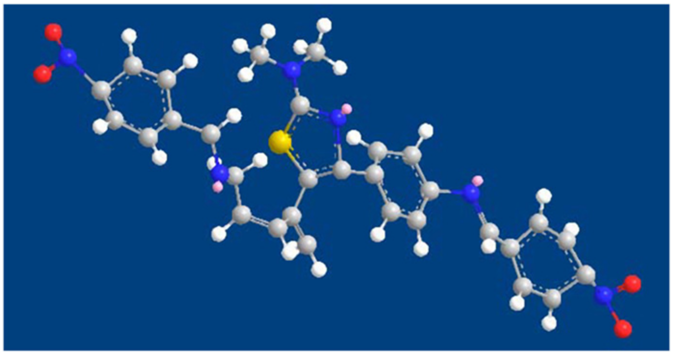


Fig. 2. Energy-minimized molecular modeling of compound **1**.

However, the largest ultraviolet absorption wavelengths of the thiazole and imidazole derivatives, compounds **1** and **2**, are 419.0 nm and 358.1 nm, respectively, which show good transparency. The blue-shift of the maximum absorption may be attributed to the poor coplanarity of the benzene ring and the thiazole and imidazole rings. Using MM2 calculation, it was found that the benzene ring of the Schiff base was not coplanar with the thiazole and imidazole rings, as shown in Figs. 2 and 3. This non-coplanarity could improve the transparency and prevent intermolecular electrostatic interaction among the chromophores, which in turn may enhance the poling efficiency and decrease scattering-induced optical loss. At the same time, the electron donation of the electron-donating center was strengthened, thereby increasing molecular polarity.

Fig. 4 shows the thermal gravimetric analysis (TGA) of two NLO molecules, which showed that they were thermally stable (>200 °C).

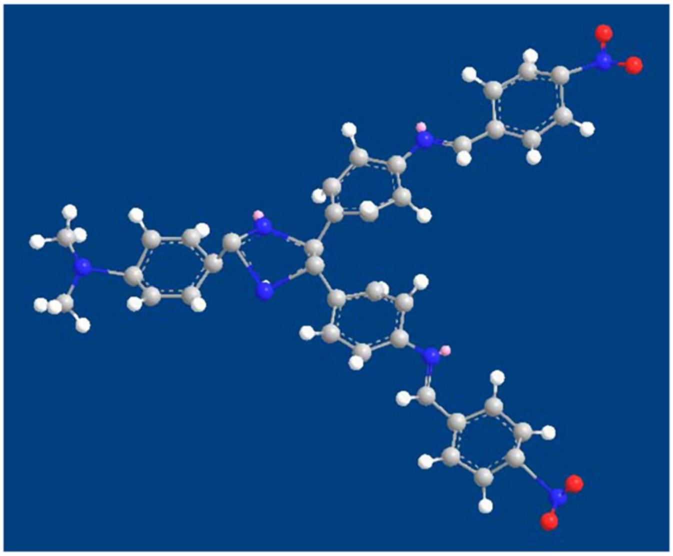


Fig. 3. Energy-minimized molecular modeling of compound **2**.

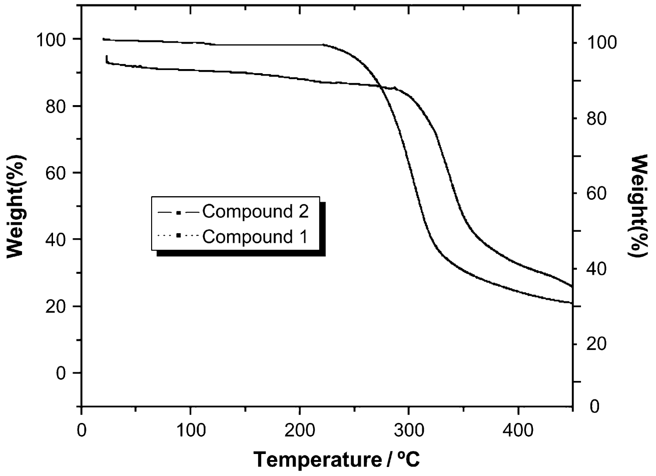


Fig. 4. TGA of NLO-phores.

The hyperpolarizabilities (β) of these NLO-phores were 17.31×10^{-30} esu and 40.66×10^{-30} esu, as determined by using the solvatochromic method [12]. Although, the β values are lower than those of some heterocyclic molecules [13], such as thiophene and substituted quinopyran, they may have better physical properties for application due to their improved nonlinear-transparency trade-off.

Acknowledgements

This research was supported by National Natural Science Foundation of China (no. 20472017).

References

[1] Wang ZS, Li FY, Huang CH. Phys Chem B 2001;105:9210.
[2] Kim M, Ju JJ, Park SK, Do JY, Lee M-H. Chem Phys Lett 2006;417:277.
[3] So BK, Lee KS, Lee SM, Lee MK, Lim TK. Opt Mater 2003;21:87.
[4] Guy K, Sonja S, Thierry V, Andere P, Celest S. Polymer 2003;44:3785.
[5] Heck J, Dabek S, Meyer-Friedrichsen T, Wong H. Coord Chem Rev 1999;190:1217.
[6] Marder SR, Sohn JE, Stucky GD. Materials for nonlinear optics: chemical perspectives. In: ACS symposium series, vol. 455. Washington, DC: ACS; 1991.
[7] Xie HQ, Huang XD. Eur Polym J 2001;37:497.
[8] Gudbjartson H, Biradha K, Poirier KM. J Chem Soc 1999;121:2599.
[9] Jen AK-Y, Cai Y, Bedworth PV, Mader SR. Adv Mater 1997;9:132.
[10] Blatt AH. Org Synth Colloid 1995;2:159.
[11] Ermer S, Girton DG, Leung DS, Lovejoy SM, Valley JF, Van Eck TE, et al. Nonlinear Opt 1995;9:259.
[12] Zhang GB, Wang SM, Zhao L, Cheng SY. Chin J Appl Chem (Yingyong Huaxue) 2000;17:507.
[13] Albert IDL, Marks TJ, Ratner MA. J Am Chem Soc 1998;120:11174.