SHORT PAPER

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Synthesis and second-order optical nonlinearity of carbazolyl-substituted furan chromophores with high thermal stability and good transparency†

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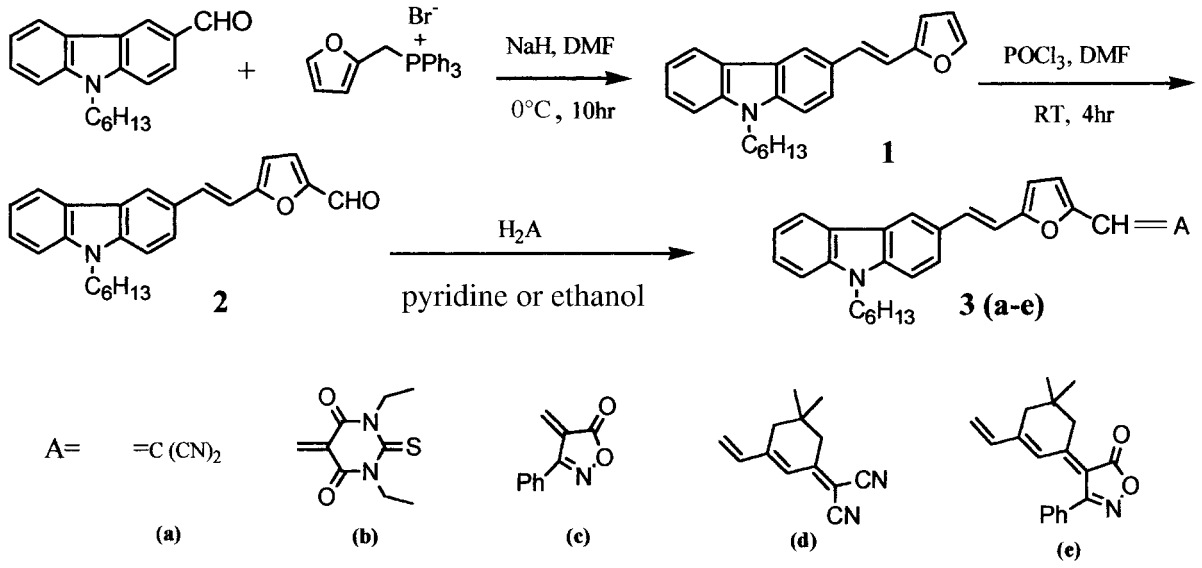
A series of new chromophores, in which *N*-hexylcarbazole acts as an electron donor and a furan ring is part of a conjugation bridge, are synthesised, and exhibit similar values of the first molecular hyperpolarisability, but better transparency compared with their analogues which contain diethylaminophenyl instead of *N*-hexylcarbazole as the donor, in addition to high thermal stability.

Keywords: furans, carbazoles, hyperpolarisability, electronic spectra, nonlinear optical materials

Organic and polymeric second-order nonlinear optical (NLO) materials have attracted much attention for their potential application involving optical modulation, molecular switching, optical memory and information storage.[1] One of the major challenges in this area of research is to design and synthesise second-order NLO chromophores simultaneously achieving large first molecular hyperpolarisability (β), good chemical and thermal stability, and high optical transparency.[2]

Polymers containing a carbazole moiety can be used in many functional materials, such as photoconductors[3] and nonlinear optical[4] and photorefractive[5] materials. The thermally stable carbazole molecule has a structure isoelectronic with diphenylamine, and thus the introduction of electron acceptor(s) in the 3 and /or 6 position(s) causes intramolecular charge transfer and a mesomeric dipole moment, resulting in a strong second-order nonlinear optical response.[6] We have designed and synthesised a series of new carbazole chromophores in which the furan unit is used as one of the conjugation moieties (see Scheme 1, compounds **3a–e**). Furan is used because it has a lower resonance stabilisation energy than benzene; thus chromophores with the furan moiety have proved to display molecular hyperpolarisabilities elevated compared with their benzene analogues.[7] To our knowledge, only three experimental works have been reported for the chromophores containing the furan moiety, in which the electron-donating groups are always alkylamino groups.[8-10] We hope that the new chromophores here may represent new opportunities for the optimisation of all main properties such as nonlinearity, transparency and thermal stability.

The general procedure for the synthesis of **3a–e** is shown in Scheme 1. Compound **1** was synthesised in 83% yield by the Wittig reaction between (2-furylmethyl)triphenylphosphonium bromide and 3-formyl-*N*-hexylcarbazole. Formylation of **1** with $POCl_3$ and DMF afforded **2** in 87% yield. Various acceptor groups were introduced by Knoevenagel condensation with the formyl group. Thus **3a**, **3d** and **3e** were obtained from the condensation of **2** with malononitrile, 3-dicyanomethylene-1,5,5-trimethylcyclohexene and 3-phenyl-4-(3,5,5-trimethyl-2-



Scheme 1

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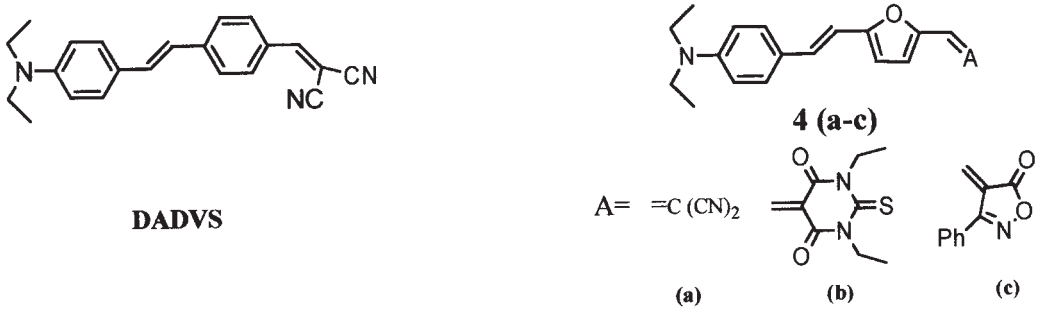
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*



Scheme 2

hexen-1-yliden)isoxazol-5-one in the presence of pyridine as a catalyst, while reaction of **2** with 1,3-diethylthiobarbituric acid and 3-phenyl-5-isoxazolone gave **3b** and **3c** without pyridine catalyst. **3a-e** were purified by column chromatography or recrystallisation and characterised by ^{1}H-NMR, IR, FAB-MS and elemental analysis.

The first molecular hyperpolarisabilities of the chromophores (**3a–e**) were measured by hyper-Rayleigh scattering (HRS) in dimethyl sulfoxide (DMSO) using 1064nm laser light. *p*-Nitroaniline (PNA) was used as the external reference. The technique and the method of analysis for HRS have been described elsewhere.[11] The linear and nonlinear optical properties of various chromophores are summarised in Table 1. Also included in the Table are 5-[2-(*p*-diethylaminophenyl)vinyl]furan analogues (**4a–c**) for the purpose of comparison, and their molecular structures are shown in Scheme 2.

It can be seen that **3a–e** show significant blue shifts in their absorption (λ_{max}) when compared with the 5-[2-(4-diethylaminophenyl)vinyl]furan analogues: 55nm for **3a,** 66nm for **3b,** 58nm for **3c**, 17nm for **3d** (compared with **4a**), and 20nm for **3e** (compared with **4c**) in DMSO, although the length of **3d**, **3e** conjugation bridge is much longer. UV-VIS absorption phenomena of **3a–e** highlight the unusual structure and properties of the carbazole moiety. The replacement of the diethylaminophenyl group by *N*-hexylcarbazolyl reduces slightly the donor strength because of the further delocalisation of the unpaired electron of the nitrogen atom of the carbazole ring with the two benzene rings that connect directly to the nitrogen atom. Hence, a blue-shifted absorption peak can be expected, due to the reduced intramolecular charge transfer (ICT) efficiency.[12]

Although the intramolecular charge transfer (ICT) efficiency of **3a–e** is somewhat reduced, it should be noted that the β_0 values of carbazolyl-substitued furan chromophores are similar to those of diethylaminophenyl analogues from the theoretical investigation and the experimental results. On one hand, the decrease in molecular β_0 value can be compensated in the carbazolyl-substitued chromophores by forming the so-called π'–D–π–A bridge system which extends the effective conjugation length.[12] On the other hand, the two-level model adduces that the β_0 value is also a strong function of the oscillator strengths (f) in addition to $\Delta\mu$, the change of dipole moment between the ground state and the charge-transfer excited state.[11] Thus it can be phenomenologically deduced that the reduction of the ICT efficiency of chromophores **3a–e** does not necessarily accompany a decrease in their *f* and / or $\Delta\mu$ values, and this has been partially verified by the experimental results. As shown in Table 1, the oscillator strengths (*f*)[13] of **3a** are significantly high. Although the full interpretation will required further study, the results suggest that the carbazole chromophores with furan moiety may provide a new possibility for turning the nonlinearity-transparency trade-off.

Comparison of the electronic absorption spectra of **4a** with DADVS (4-diethylamino-4′-dicyanovinylstilbene, see Scheme 2, and its λ_{max} is 506nm in DMSO[14]) reveals that the replacement of benzene with a furan ring causes a 46nm bathochromic shift of the charge transfer absorption band in DMSO. This observation clearly indicates that incorporation of the furan moiety in push–pull compounds enhances their charge transfer properties.

Table 1 Optical properties and thermal stability data

Compound	δ_{max}/nm in DMSO	β_{HRS}	β_0[c]	β_0[d]	*f*	T_d/°C
3a	497	1028[a]	103	52	1.28	394
3b	564	1036[a]	35	48	0.76	276
3c	546	1241[a]	48	49	0.77	200
3d	535	1460[a]	11	59	0.67	360
3e	584	784[a]	114	69	0.74	196
4a	552	77[b]	34	67		
4b	630	254[b]	75	68		
4c	604	300[b]	101	61		

[a]β values of **3a–e** were measured in this work by HRS in dimethyl sulfoxide (DMSO) using the fundamental excitation wavelength of 1064nm. [b]β values of **4a–c** were measured by HRS in DMSO using the fundamental excitation wavelength of 1560 nm.[9] [c]Dispersion-corrected β values of chromophores were calculated by using an approximate two-level model.[11] [d]β_0 values were calculated by MOPAC in Chem3D Pro.

The thermal stability of chromophores (**3a–e)** has also been investigated. Their decomposition temperatures (T_d) were measured by differential thermal analysis (DTA) at a heating rate of 20 deg/min under nitrogen atmosphere. As shown in Table 1, carbazolyl-containing chromophores exhibit relatively high thermal stabilities. Both **3a** and **3d** exhibit a remarkably high decomposition temperature compared with **3b**, **3c** and **3e.** The reason for this difference is unclear but may be attributed to easily thermal decomposition of the thiobarbituric and isoxazolone moieties.[8,15,16] It was found that **3a–e** have good solubility in common organic solvents such as dioxane, $CHCl_3$, AcOEt, DMF, NMP DMSO, *etc*. Grating of the hexyl groups on the donor moiety has proven to be effective in enhancing the solubility of the compounds.

In summary, a series of new chromophores (**3a–e**) containing carbazole as a donor and furan as a part of a conjugating moiety were synthesised, and their β values, UV-VIS absorption and decomposition temperatures were measured. By comparison with the 5-[2-(4-diethylaminophenyl)vinyl]furan analogues (**4a–c**), it can be seen that the *N*-hexylcarbazole group has a significant influence on the UV-VIS absorption and thermal stabilities. These chromophores, achieving relatively high thermal stability, good transparency and high

molecular hyperpolarisability, are expected to have use in the synthesis of polymers for electro-optical and photorefractive applications.

Experimental

Materials: 3-Formyl-*N*-hexylcarbazole was prepared according to the general procedure outlined in the literature.[17] (2-Furylmethyl)triphenylphosphonium bromide was prepared according to the method described.[14] The Wittig reaction between (2-furylmethylene)-triphenylphosphonium bromide and 3-formyl-*N*-hexylcarbazole was performed according to the literature method.[9] 3-Dicyanomethylene-1,5,5-trimethylcyclohexene and 3-phenyl-4-(3,5,5-trimethyl-2-hexen-1-yliden)-2-isoxazol-5-one were prepared following a procedure described in the literature.[16,18] All other reagents and solvents were used as received without further purification.

Characterisation: ^{1}HNMR spectra were obtained using a JEOLFX90Q spectrometer. FT-IR spectra were measured with a Shimadzu FT-IR 8000 series spectrophotometer in the region of 4000–400 cm^{-1} using KBr pellets. UV-Visible spectra were determined with a Shimadzu 160A spectrometer in dimethyl sulfoxide solution. FAB-MS spectra were used with VJ-ZAB-3F Mass spectrometer. Elemental analysis were performed by a Carlo Erba 1106 micro-elemental analyzer. DTA analyses were measured using a Shimadzu DT-40 at a scan rate of 20 °C/min. under nitrogen atmosphere. The second-order nonlinear hyperpolarisability of these compounds were determined by Hyper-Rayleigh Scattering in dimethyl sulfoxide (DMSO) using the fundamental excitation wavelength of 1064 nm, and in the same solvent, the known hyperpolarisability of *p*-nitroanilline (PNA) was used as an external reference.[11] The melting point measurements were made with an uncorrected thermometer.

Preparation of (E)-5-[2-(N-hexylcarbazol-3-yl)vinyl]-2-furaldehyde **(2)**: to DMF (0.21 ml, 2.6 mmol) at 0 °C, phosphorus oxychloride (0.24 ml, 2.6 mmol) was added dropwise. The solution was allowed to warm up to room temperature, and (*E*)-5-[2-(*N*-hexylcarbazol-3-yl)vinyl]-2-furan (0.74 ml, 2.0 mmol) in 1,2-dichloroethane (2 ml) was added. The mixture was stirred at room temperature for 4h, and then poured into ice water. The solution was extracted with chloroform. The organic layer was washed with water and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (100–200m) eluted with petroleum/ethyl acetate (5:1) to obtain a slight yellow liquid. Yield: 0.65 g (87%). IR 1670 (C=O); ^{1}H-NMR ($CDCl_3$) δ 0.84 (t, 3H), 1.30 (m, 6H), 1.85 (t, *J* = 7.0, 2H), 4.28 (t, *J* = 7.0, 2H), 6.42 (d, *J* = 3.6, 1H), 6.85 (d, *J* = 14, 1H), 7.20–7.64 (m, 7H), 8.06 (d, *J* = 14, 1H), 8.24 (d, *J* = 3.6, 1H), 9.48 (s, 1H).

General procedure for the synthesis of derivatives **3a–e***:* (*E*)-5-[2-(*N*-hexylcarbazol-3-yl)vinyl]-2-furaldehyde (182 mg, 0.5 mmol) was dissolved in absoluted ethanol (6ml). An election acceptor (H_2A, see Scheme 1) (0.5 mmol) was added, and the solution was stirred at room temperature and a dark suspension was obtained. The crude condensation products were collected by filtration, followed by rinsing with ethanol, ether, and pentane, then crystallised in a CH_2Cl_2–EtOH mixture.

3a: yield 71%; m.p. 107–108 °C; IR 2216 (C≡N); ^{1}H-NMR ($CDCl_3$) δ 0.84 (t, 3H), 1.32 (m, 6H), 1.86 (t, *J* = 7.0, 2H), 4.26 (t, *J* = 7.0, 2H), 6.52 (d, *J* = 3.6, 1H), 6.88 (d, *J* = 15, 1H), 7.22–7.60 (m, 7H), 7.68 (d, *J* = 3.6, 1H), 8.04 (d, *J* = 15, 1H), 8.18 (s, 1H). MS (FAB), *m/z*: 419, 100%. Anal. Calc. for $C_{28}H_{25}N_3O$: C, 80.19; H, 5.97; N, 10.02. Found: C, 80.35; H, 6.15; N, 9.95.

3b: yield 85%; m.p. 174–175 °C; IR 1662 (C=O); ^{1}H-NMR ($CDCl_3$) δ 0.84 (t, 3H), 1.21 (m, 6H), 1.32 (t, *J* = 6.8, 6H), 1.86 (t, *J* = 7.0, 2H), 4.28 (t, *J* = 7.0, 2H), 4.54 (q, *J* = 6.8, 4H), 6.36 (d, *J* = 15, 1H), 6.68 (d, *J* = 3.6, 1H), 6.80–8.10 (m, 7H), 8.24 (d, *J* = 15, 1H), 8.36 (s, 1H), 8.70 (d, *J* = 3.6, 1H). MS (FAB), *m/z*: 553, 100%. Anal. Calc. for $C_{33}H_{35}N_3O_3S$: C, 71.61; H, 6.33; N, 7.59. Found: C, 71.43; H, 6.55; N, 7.72.

3c: yield 78%; m.p. 153–154 °C; IR 1735 (C=O); ^{1}H-NMR ($CDCl_3$) δ0.84 (t, 3H), 1.32 (m, 6H), 1.84 (t, *J* = 7.0, 2H), 4.24 (t, *J* = 7.0, 2H), 6.68 (d, *J* = 3.6, 1H), 6.90 (d, *J* = 16, 1H), 7.21–7.48 (m, 7H), 7.48-7.68 (m, 5H), 8.04 (d, *J* = 16, 1H), 8.16 (s, 1H), 8.66 (d, *J* = 3.6, 1H). MS (FAB), *m/z*: 514, 100%. Anal. Calc. for $C_{34}H_{30}N_2O_3$: C, 79.38; H, 5.83; N, 5.45. Found: C, 79.14; H, 6.05; N, 5.38

3d: yield 42%; m.p. 139–140 °C; IR 2218 (C≡N); ^{1}H-NMR ($CDCl_3$) δ 0.84 (t, 3H), 1.06 (s, 6H), 1.32 (m, 6H), 1.84 (t, 2H), 2.16 (s, 2H), 2.48 (s, 2H), 4.28 (t, 2H), 6.42 (d, *J* = 3.6, 1H), 6.56 (d, *J* = 15, 1H), 6.80–6.96 (d, 3H), 7.39–7.64 (m, 7H), 8.30 (d, *J* = 15, 1H), 8.40 (d, *J* = 3.6, 1H). MS (FAB), *m/z*: 539, 100%. Anal. Calc. for $C_{37}H_{37}N_3O$: C, 82.37; H, 6.86; N, 7.79. Found: C, 82.15; H, 6.75; N, 7.95.

3e: yield 48%; m.p. 123–124 °C; IR 1728 (C=O); ^{1}H-NMR ($CDCl_3$) δ 0.85 (t, 3H), 1.08 (s, 6H), 1.30 (m, 6H), 1.87 (t, 2H), 2.21 (s, 2H), 2.34 (s, 2H), 4.30 (t, 2H), 6.40 (d, *J* = 3.6, 1H), 6.59 (d, *J* = 3.6, 1H), 6.67 (d, *J* = 16, 1H), 6.83 (d, *J* = 16, 1H), 6.93 (d, *J* = 15, 1H), 7.26–7.65 (t, 7H), 7.68–8.22 (t, 5H), 8.31 (s, 1H). MS (FAB), *m/z*: 633, 100%. Anal. Calcd. for $C_{43}H_{42}N_2O_3$: C, 81.36; H, 6.67; N, 4.41. Found: C, 81.35; H, 6.56; N, 4.57.

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References

1 S.R. Marder, B. Kippelen, A.K-Y. Jen and N. Peyghambarian, *Nature*, 1997, **388**, 845.
2 C.R. Moylan, R.J. Twieg, V.Y. Lee, S.A. Swanson, K.M. Betterton and R.D. Miller, *J. Am. Chem. Soc.*, 1993, **115**,12599.
3 W.E. Moerner and S.M. Silence, *Chem. Rev.*, 1994, **94**, 127.
4 K. Tamura, A.B. Padias, H.K. Hall Jr. and N. Peyghambarian, *Appl. Phys. Lett.*, 1992, **60**, 18.
5 G.E. Johnson, K.M. McGrane and M. Stolka, *Pure Appl. Chem.*, 1995, **67**, 175
6 M.S. Ho, C. Barrett, J. Paterson, M. Esteghamation, A. Natansohnn and P. Rochon, *Macromolecules*, 1996, **29**, 4613.
7 L.T. Cheng, W. Tam, S.H. Stevenson, G.R. Meredith, G. Rikken and S.R. Marder, *J. Phys. Chem.*, 1991, **95**, 10643.
8 A.K-Y. Jen, Y. Cai, P.V. Bedworth and S.R. Marder, *Adv. Mater.*, 1997, **9**, 132.
9 B.R. Cho, K.N. Son, S.J. Lee, T.I. Kang and M.S. Hon, *Tetrahedron Lett.*, 1998, **39**, 3167.
10 S.S.P. Chom and C.H. Shen, *Tetrahedron Lett.*, 1997, **38**, 6407.
11 O.K. Song, J.N. Woodford and C.H. Wang, *J. Phys. Chem. A*, 1997, **101**, 3222.
12 P. Wang, P. Zhu, C. Ye and W. Wei, *Nat. Sci. Progress*, 2000, **10**, 1.
13 Oscillator strengths were calculated from the absorption spectra of chromophores in DMSO as described in reference 2.
14 A.K-Y. Jen, V.P. Rao, K.Y. Wong and K.J. Drost, *J. Chem. Soc., Chem. Commun.*, 1993, 90.
15 O.K. Kim, A. Fort, M. Barzoukas, M. Blanchard-Desce and J.M. Lehn, *J. Mater. Chem*., 1999, **9**, 2227.
16 C. Zhang, A.S. Ren, F. Wang, J. Zhu, L.R. Dalton, J. N. Woodford and C.H. Wang, *Chem.Mater.* 1999, **11**, 1966.
17 D.W. Kim, H. Moon and S.Y. Park, *Reactive and Functional Polymers*, 1999, **42**, 73.
18 R. Lemke, *Synthesis*, 1974, 359.