Synthesis and Characterization of (E)-5-[2-(N-hexylcarbazolyl)vinyl] furan Derivatives with Acceptor Groups

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Abstract: A new series of (E)-5-[2-(N-hexylcarbazolyl)vinyl]furan chromophores with various acceptors have been synthesized by the Knoevenagel condensation of (E)-5-[2-(N-hexylcarbazolyl) vinyl]-2-furaldehydes with malononitrile, 1,3-diethyl-2-thiobarbituric acid, or 3-phenyl-5-isoxazol one, respectively. They are characterized by ^{1}H-NMR, FT-IR, UV-VIS, MS and elemental analysis, and have shown strong solvatochromism and high thermal stability.

Keywords: Chromophores, synthesis, characterization, solvatochromism, thermal-stability.

Organic second-order nonlinear optical (NLO) materials have been extensively studied for their potential application involving telecommunications, optical information process and storage[1]. It has been found that the molecular hyperpolarizability of the NLO chromophores varys dramatically depending upon the donor-acceptor abilities as well as the nature of the conjugated bridge.

Carbazole molecule has an isoelectronic structure of diphenylamine, and thus the introduction of electron acceptor (s) in the 3 and /or 6 position (s) causes intramolecular charge transfer and mesomeric dipole moment, resulting in a strong second-order nonlinear optical response[2]. On the other hand, furan has lower resonance stabilization energy than benzene, and it can provide more effective conjugation between the donor and acceptor. Thus it may enhance the molecular hyperpolarizability[3]. In lights of this, we have recently designed and synthesized some new carbazole chromophores containing furan unit as a part of a conjugating bridge. In this paper we describe the first synthesis, solvatochromism and thermal stability of a new series of (E)-5-[2-(N-hexylcarbazolyl) vinyl]furan chromophores (**IIIa-c**) with various acceptors.

The general process for the synthesis of **IIIa-c** is shown in **Scheme 1**. Compound **I** was synthesized in 83% yield by the Wittig reaction between 2-furyltriphenyl phosphonium bromide and 3-formyl-N-hexylcarbazole. Formylation of **I** with $POCl_3$ and DMF afforded **II** in 87% yield. Various acceptor groups have been introduced based on a formyl group by the Knoevenagel condensation. **IIIa** was obtained in 71% yield from the condensation of **II** with malononitrile in the presence of pyridine as a basic catalyst. Reaction of **II** with 1,3-diethylthiobarbituric acid or 3-phenyl-5-isoxazolone in EtOH gives **IIIb** or **IIIc** in 85%, 78% yields respectively without pyridine. All these condensation reactions yielded preferentially E-geometrical isomer. **IIIa-c** were purified by column chromatography or recrystallization and characterized by ^{1}H-NMR, IR, MS and elemental analysis[4].

Scheme 1

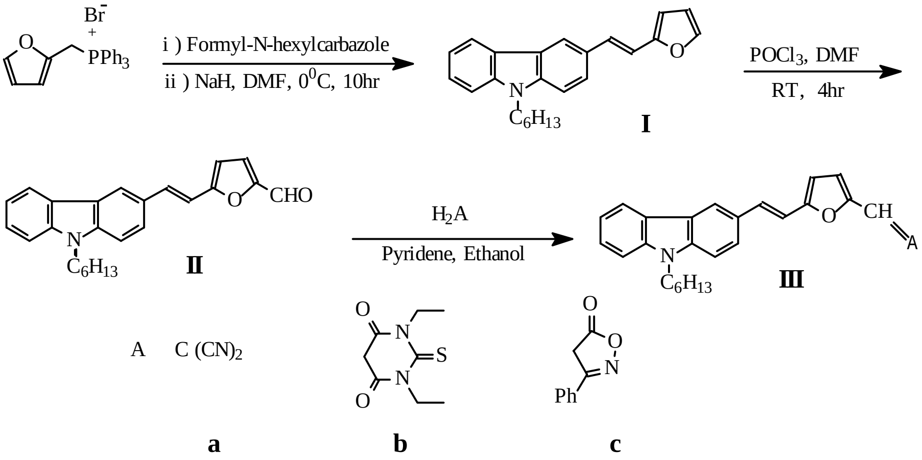

Table 1 UV-Vis absorption, thermal stability data of **IIIa-c**

Compound	λ_{max}/nm				T_d / ℃
	in Dioxane	in AcOEt	in DMF	in DMSO	
IIIa	482	483	495	497	394
IIIb	530	535	554	564	276
IIIc	517	518	535	546	200

IIIa-c exhibit broad and intense absorption bands in the visible region, characteristic of intramolecular charge transfer. The absorption spectra of **IIIa-c** also show strong solvatochromism (**Table 1**), which implies that these compounds exhibit large first molecular hyperpolarizability (β). Their decomposition temperatures (T_d) were measured by thermal analysis at a heating rate of 20 °C min^{-1}. As shown in **Table 1**, carbazolyl-containing chromophores present a high thermal stability which is clearly due to the presence of the carbazole moiety. Experimental measurement of the first molecular hyperpolarizability (β) value is currently in progress.

In conclusion, we have synthesized a new series of chromophores containing both carbazole and furan moieties. These chromophores with good thermal stability and strong solvatochromism are expected to be used in preparing the polymers for nonlinear optical and photorefractive applications.

Acknowledgments

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References and Note

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4. The data are deposited at the Editorial Office of CCL.

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