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Introduction of N atom into the conjunction system of organic second order nonlinear optical chromophores: An effective method for improving the photochemistry stability

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ABSTRACT

Organic nonlinear optical chromophores with different number of N atoms were prepared and characterized. Their nonlinear optical character was studied both by theoretical calculation and second harmonic generation experiment. Chromophore ZJ1 showed us the largest d_{33} value of 87.5 pm/V. More importantly, the photochemistry stability of the chromophores was also studied in details. Chromophores with N atoms in the conjugated system showed us better photochemistry stability than the traditional chromophores.

1. Introduction

Organic electro-optic (EO) material becomes a research focus in the recent years for varies properties and potential applications in photonic fields (such as optical information processing, optical sensing, data storage, and telecommunications) [1–3]. Organic second order nonlinear optical chromophores as the core of organic EO materials have been developed rapidly and lots of novel organic second order nonlinear optical chromophores with different structures have been prepared and reported [4–6].

The photochemistry stability of organic second nonlinear optical materials is an obvious defect that should be improved. In the early days, most of researchers paid their attentions to find the second order nonlinear optical materials with large EO coefficients; as the rapid improvement in EO coefficients, more and more researchers paid their attentions to the long-term thermal stability of this kind of materials [7–10]. As the solution of the long-term thermal stability and the application in the preparation in devices, photochemistry stability would be the next key problem should be solved. If this problem of organic second order nonlinear optical materials could be solved, the stability and service life could be improved greatly of optoelectronic devices prepared by this kind of materials [1,11].

In this work, in order to obtain the practical organic second order nonlinear optical materials with both high EO coefficient and good photochemistry stability, we introduced the N atom into the conjunction system of organic second order nonlinear optical chromophores. Carbon-nitrogen double bond and nitrogen-nitrogen double bond were introduced as the conjugate bridges in different chromophores. By the comparison with traditional chromophore with the similar conjugate structure, both of the EO coefficients and photochemistry stability were improved greatly. All of the structures of the chromophores studied in this paper have been shown in Scheme 1.

2. Experimental

2.1. Materials and instrumentation

All reagents were used as received unless stated. TCF acceptor was prepared according to a method described in the Ref. [12]. 5-nitro-2-thiophene carboxyaldehyde were prepared according to the Ref. [11]. ^{1}H NMR spectra were measured on an Avance 400 (Bruker) spectrometer using tetramethylsilane as the internal standard. The MS spectra were obtained on MALDI-TOF-(Matrix Assisted Laser Desorption/Ionization of Flight) on BIFLEXIII (Broker

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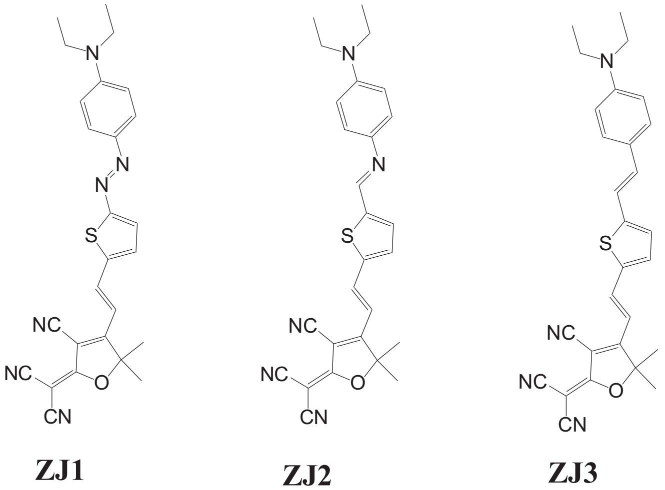


Scheme 1. Structures of the chromophores used in this work.

Inc.) spectrometer. UV–vis spectra were obtained using a Hitachi U-2001 spectrometer.

2.2. Synthesis of chromophore ZJ1

To a solution of 10 ml concentrated hydrochloric acid and 10 ml THF, 6.8 g stannous chloride (30 mmol) was added. The mixture was stirred, and a solution of 5-nitro-2-thiophene carboxyaldehyde (1.6 g, 10 mmol) was added in one portion. The temperature of the reaction rose to 50 °C and was maintained at the same temperature for 1 h, then gradually cooled to room temperature. A mixture of glacial acetic acid (20 ml) and propionic acid (10 ml) was added and cooled to −5 to 0 °C. A solution of sodium nitrite (0.69 g, 10 mmol) in minimum amount of water was added cautiously. The reaction mixture was allowed to stir at −5 °C for 2 h to form the diazonium salt, which was used directly in the next step.

The diazonium salt solution was slowly added to the solution of N, N-diethylaniline (1.49 g, 10 mmol) in the mixture of glacial acetic acid (40 ml), propionic acid (20 ml) and sulfamic acid (1.0 g, 10 mmol) at −5 to 0 °C. After the addition, the red solution was stirred at −5 °C for 12 h and overnight at room temperature. The mixture was poured into a large amount of water and filtrated. The solid was collected and purified by chromatography, affording us compound 3 as a dark solid, 2.07 g, 72%. MS, m/z: 287.063 (M^+). ^1H NMR (400 MHz, $CDCl_3$) δ: 10.02 (s, 1 H), 6.75 (d, 1 H), 6.49(d, 1 H), 5.98(d, 2 H), 5.82 (d, 2 H), 3.83 (t, 4 H), 3.68 (m, 4 H), 1.84 (t, 6 H).

2.2.1. Chromophore Z1

A catalytic amount of triethylamine was added to the solution of compound 3 (2.07 g, 7.2 mmol) and TCF acceptor (1.99 g, 10 mmol) in 5 ml dichloromethane. The temperature was kept at 70 °C for 5 h. After removing of the solvent, the crude product was purified with short column chromatography using petroleum ether as eluent to afford chromophore ZJ1 as a green solid (1.51 g, 3.24 mmol), 45%. MS (MALDI-TOF), m/z: 468.213 (M^+), ^1H NMR (400 MHz, CD_3COCD_3), δ: 7.43 (d, 1 H), 7.35 (d, 1 H), 7.03 (d, 2 H), 6.89 (d, 2 H), 6.72 (d, 1 H), 6.68 (d, 1 H), 3.96 (m, 4 H), 2.85 (s, 6 H), 1.79 (t, 6 H).

3. Results and discussion

3.1. Synthesis of the chromophores

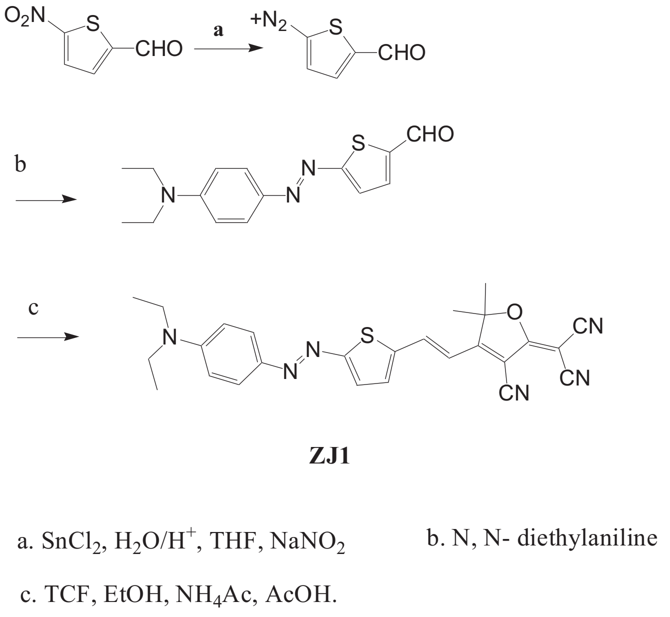
Chromophore ZJ2 and Zj3 were prepared according to the Refs. [13,14]. Chromophore Zj1 was firstly reported in this paper. As shown in Scheme 2, Chromophore ZJ1 was prepared according to the synthetic methodology as follows: 1) the preparation of 5-nitro-2-thiophenecarboxyaldehydes followed by reduction of nitro groups to yield the amino compounds; 2) the introduction of the donor group by diazo coupling reaction; (3) Knoevenagel condensation between the diazo-based thiophenealdehyde and TCF acceptor.

3.2. Thermal stability of the chromophores

Thermal stability is an important requirement for the incorporation of new chromophores in poled polymer structures and the preparation process of electro optic devices [15,16]. The thermal decomposition curves were investigated by thermo gravimetric analyzer (TGA) under the nitrogen atmosphere. Due to the similar conjugated structures, all of the chromophores started to decompose around the temperature of 200 °C. But the decomposition speeds were very different. Chromophore ZJ3 showed us the fastest decomposition speed. At the temperature of 300 °C, 40% weight of chromophore ZJ3 has been reduced. At this time, the weight loss for chromophore ZJ1 and ZJ2 were just 5% and 8% respectively. This result indicated that the conjugated double bonds were the weaknesses of the chromophores and the introduction of nitrogen atoms could improve the stability of these weaknesses. Else, chromophore ZJ2 showed us faster decomposition speed than chromophore ZJ1 around 250 °C. But when the temperature rose to above 330 °C, the decomposition speed of chromophore ZJ1 became faster. This is a strange phenomenon and hard to be explained (Fig. 1).

3.3. Nonlinear optical characters of the chromophores

To evaluate the s second harmonic generation characters of chromophore ZJ1, ZJ2, ZJ3, guest–host polymers were prepared by formulating the chromophores into polymethyl methacrylate



a. $SnCl_2$, H_2O/H^+, THF, $NaNO_2$ b. N, N- diethylaniline

c. TCF, EtOH, NH_4Ac, AcOH.

Scheme 2. Synthesis of the chromophore ZJ1.