



Research paper

Modification of indole by electron-rich atoms and their application in novel electron donor materials



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ABSTRACT

Novel nonlinear optical (NLO) chromophore based on 6-(pyrrolidin-1-yl)-1H-indole as the electron donor group was designed and synthesized. The molecular structure of this chromophore was characterized by ¹H NMR spectra, ¹³C NMR spectra, and MS spectra. The delocalized energy level was estimated by UV–Vis. spectra. The thermal property was studied by thermogravimetric analysis (TGA). The poled films containing chromophores ZML-1 with a loading density of 10 wt% in amorphous polycarbonate (APC) afford an average electro-optic (EO) coefficient (r_{33}) of 19 pm/V at 1310 nm. Compared to the reported aniline-based chromophore ($r_{33} = 12$ pm/V) analogues, chromophore ZML-1 exhibits enhanced electro-optical activity.

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1. Introduction

Due to the potential applications in optical data processing and telecommunication, organic second order NLO materials have attracted much attention recently [1–8]. Most of the researches are focused on improving macro EO coefficients, which can be mainly determined by the first order hyperpolarizability and the ordered arrangement of second order NLO chromophores [9–12]. The first order hyperpolarizability of organic NLO chromophores can be improved by designing and preparing of novel strong electron donor groups, strong electron acceptor groups or electronic bridge with strong electron and charge transfer capacity [13–15]. In addition, the improved ordered arrangement of second order NLO chromophores in EO materials is also a very important factor for large macro EO coefficients. Poor inter-molecular interaction among the chromophores facilitates the improvement of the ordering parameter of EO materials. Fortunately, peripheral modifica-

tion is an efficient method to reduce the inter-molecular interaction [16,17].

Aniline is widely used as the electron donor for fabrication of organic NLO chromophores, because of its mature synthesis route, low price, and proper electron-donating ability [18–20]. Despite the good performance of aniline in NLO field, the further development in NLO filed based on aniline was hindered due to its limited electron donor ability. Moreover, a further modification of aniline group is not so easy. Herein, design and preparation of novel conjugated groups with stronger electron-donating ability, and ability to be modified is desirable.

In this work, 6-(pyrrolidin-1-yl)-1H-indole was introduced as a novel electron donor. Chromophore based on this donor was synthesized and large peripheral modified groups were also introduced to this chromophore to improve its macro EO coefficients.

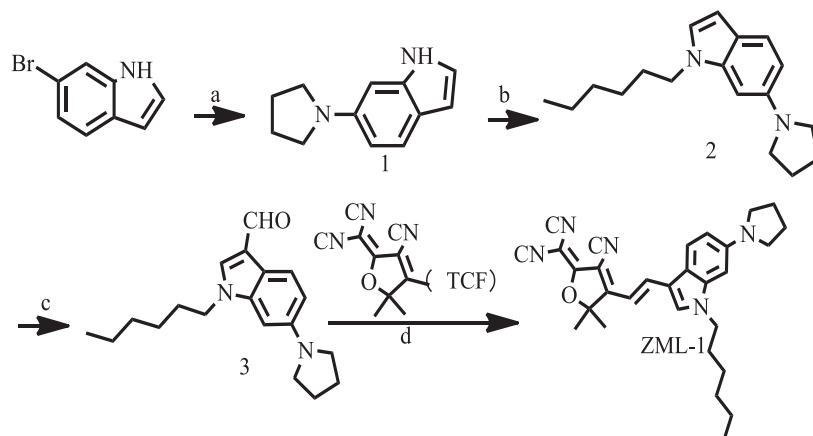
2. Synthesis

2.1. Synthesis of chromophore ZML-1

The structure and synthetic route of chromophore ZML-1 are shown in Scheme 1. Firstly, compound 1 was fabricated by a C–N

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- a. Pyrrolidine, DMPAO, CuI, K_3PO_4 , 110 °C, 20h;
 b. 1-Bromo-hexane, KOH, DMF, 60 °C, 2h;
 c. DMF, $POCl_3$, 0 °C, 2h;
 d. TCF, ethanol, piperidine, 80 °C, 6h.

Scheme 1. Synthesis procedure of chromophore ZML-1.

coupling reaction of commercially obtained pyrrolidine with 6-bromoindole under the catalytic system of CuI/DMPAO. Then, a large flexible chain was introduced to the donor group by the alkylation reaction of the nitrogen atom as the isolated group. Thirdly, compound 3 can be obtained through the Vilsmeier reaction of compound 2 in the presence of $POCl_3$ and DMF. We have done many experiments about the alkylation of nitrogen atoms and Vilsmeier reaction. So, compound 2 and 3 was just characterized by 1H NMR and ^{13}C NMR. Else, the corresponding structures of compound 2 and 3 could also be confirmed by the final compound of chromophore ZML-1. And finally, chromophore ZML-1 was obtained by Knoevenagel condensation between the donor with an aldehyde group and the 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF) acceptor with an active methyl group.

2.2. Experimental

2.2.1. Instruments and materials

1H NMR and ^{13}C NMR spectra were determined by an Advance Bruker 400 M (400 MHz) NMR spectrometer (tetramethylsilane as internal-reference). The MS spectra were obtained on MALDI-TOF (Matrix Assisted Laser Desorption/Ionization of Flight) on BIFLEXIII (Broker Inc.) spectrometer. The UV-Vis. experiments were performed on Cary 5000 photo spectrometer. The TGA was determined by TA5000-2950TGA (TA co.) with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under the protection of nitrogen. All chemicals were used as received without further purification unless stated. 2-dicyanomethylene-3-cyano-4-methyl-2, 5-dihydrofuran (TCF) acceptor was prepared according to the literature [21].

2.2.2. Poling and r_{33} measurements

Guest-host polymers were prepared by formulating chromophores ZML-1 into APC using dibromomethane (CH_2Br_2) as the solvent. The resulting solutions were filtered through a $0.22\text{ }\mu\text{m}$ Teflon membrane filter and spin-coated onto indium tin oxide (ITO) glass substrates. Films of doped polymers were baked in a vacuum oven at 40 °C to remove the residual solvent. The poling process was carried out at a temperature of T_g of the polymer. The r_{33} values were measured using Teng-Man simple reflection technique at the wavelength of 1310 nm [22].

2.2.2.1. Compound 1. An oven-dried two-necked flask was charged with CuI (0.58 g, 3 mmol), DMPAO (1.18 g, 6 mmol), 6-Bromoindole (6 g, 26.5 mmol) and K_3PO_4 (12.98 g, 61 mmol). The flask was evacuated and backfilled with nitrogen. Then pyrrolidine (3.26 g, 48.7 mmol) dissolved in 10 ml n-butanol was added by syringe. The reaction mixture was stirred at 110 °C for 20 h. Then, let the flask cooling to room temperature, water was added and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$, after removal the solvent, the pure product was purified by a silica-gel flash column chromatography (eluent: petroleum ether) to give the white solid (4 g, 21.7 mmol) in 70% yield. 1H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.46 (d, $J = 8.6$ Hz, 1H), 6.97 (s, 1H), 6.57 (d, $J = 8.6$ Hz, 1H), 6.53 (s, 1H), 6.41 (s, 1H), 3.32 (s, 5H), 2.02 (s, 5H); ^{13}C NMR (101 MHz, Acetone): δ 144.85, 138.30, 121.52, 120.49, 119.53, 107.99, 101.03, 93.13, 48.12, 25.20; MS (EI) (M^+ , $C_{12}H_{14}N_2$): calcd:186.253; found: 186.0974.

2.2.2.2. Compound 2. To a solution of potassium hydroxide (1.5 g, 26.8 mmol) in anhydrous DMF (20 ml), compound 1 (1 g, 5.4 mmol) was added and stirred for 1 h at room temperature. Then the corresponding 1-bromohexane and benzyl bromide (0.98 g, 5.9 mmol) were added drop-wise by syringe. The resulting mixture was heated to 60 °C for 3 h. The mixture was cooled and poured into water. The organic phase was extracted with CH_2Cl_2 . The combined organic layers were dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure. The pure product was obtained by a silica-gel flash column chromatography (eluent: petroleum ether) to give a light yellow oil 3a (0.83 g, 3 mmol) in 59% yield. 1H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, $J = 8.5$ Hz, 1H), 6.90 (s, 1H), 6.59 (d, $J = 6.9$ Hz, 1H), 6.39 (d, $J = 16.1$ Hz, 2H), 4.04 (s, 2H), 3.38 (s, 4H), 2.06 (s, 4H), 1.83 (d, $J = 7.0$ Hz, 2H), 1.32 (s, 7H), 0.93–0.87 (m, 3H); MS (EI) (M^+ , $C_{18}H_{26}N_2$): calcd: 270.412; found: 270.1802.

2.2.2.3. Compound 3. Compound 2 (0.83 g, 3.1 mmol) was dissolved in 10 ml DMF in an oven-dried two neck-flask. Then, the mixture was cooled to 0 ~ 5 °C and $POCl_3$ (0.34 ml) was added by drop-wise. After the $POCl_3$ was added, the mixture was stirred at this temperature for another 2 h and heated to 90 °C for 3 h. Then, the solution was poured into saturated $NaHCO_3$ ice-water and

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