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# Synthesis and nonlinear optical properties of novel conjugated small molecules based on indole donor

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#### Abstract

Buchwald-Hartwig amination of aryl halides with solvent-free condition was used for the preparation of electron donors with high density of electron cloud. Organic second order nonlinear optical chromophore ZML-c based on this electron donor was designed and synthesized. And chromophore ZML-ref without modified groups was also prepared as the contrast. Their delocalized energy levels were estimated by UV-Vis. spectra. Their thermal properties were studied by thermogravimetric analysis (TGA). Obviously, chromophore ZML-c showed lower delocalized energy levels and lower thermal decomposition temperature (just about 160 °C). The poled films showed the largest electro-optic (EO ) coefficients of 23.5 pm/V and 10.6 pm/V respectively for chromophore ZML-c and ZML-ref. These results indicate that effective modification in indole ring may be a promising way to drastically change the electro-optical features of the titled compounds and show a direction of designing new electron donor in the field of nonlinear optical materials.

Keywords: Chromophore; Indole; Electron donor; Nonlinear optic; Buchwald-Hartwig

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#### 1. Introduction

Due to the special properties of photonics and electronics, organic conjugated small molecules have been widely studied in the recent years. Especially they have widely application in organic photovoltaic, organic light emitting diode, photochromism and so on. [1-5] Nonlinear optical materials are also prepared based on these organic conjugated small molecules. [6-10] Nonlinear optical materials have some special requirements for these organic conjugated small molecules, such as strong electronic mobility, non-central symmetry of the electronic cloud, good thermal and optical stabilities and so on.[11-14] Due to its advantages in bandwidth, response time, machinability and electro-optics coefficients, lots of new chemical reactions and functional groups were used to design and prepare organic conjugated small molecules for nonlinear optical materials application.[15-19] As we know, the introduction of strong electron donors and large conjugated structures can improve the nonlinear optical properties greatly. [20-22] And in the recent years, lots of novel chromophores were reported. [33-36] Indole groups constructed by six-membered conjugated group and five-membered conjugated group, which can improve the conjugated structure greatly. But there is just a nitrogen atom used as the rich electrons atom, which is not enough. If a second atom with rich electron can introduced to indole, the electron donating ability of indole groups can be improved greatly. And the EO coefficients of nonlinear optical materials based on these conjugated small molecules will become larger. [23-25]

To solve this problem, solvent-free Buchwald–Hartwig reaction is used based on the catalytic system of Pd(OAc)<sub>2</sub>/dicyclohexyl(2',6'-diisopropoxy-[1,1'-biphenyl]-2-yl)phosphine. Pyrrolidine is introduced to the conjugated system of indole with high yield, wild chemical reaction conditions. The nitrogen atom of pyrrolidine can be used as the second rich electron centre of such donor groups and the density of electronic cloud of the indole groups is improved greatly. By the introduction of carbon carbon double bonds as electronic bridges and tricyanyl furan as the electronic acceptors, a novel organic conjugated small molecule with D- $\pi$ -A structure is prepared. And its linear optical property, nonlinear optical property, thermal property and solubility are studied in details in this paper.

#### 2. Results and discussion

#### 2.1 synthesis and structure of chromophore ZML-c and ZML-ref

The structure and synthesis of chromophore ZML-c was shown in scheme 1. The

introduction of pyrrolidine to indole was the most important reaction in the synthesis of chromophore ZML-c. And the chemical reaction conditions were studied in details. The reactive temperature, selection of protective gas and catalysts were all optimized. The selection of catalyst influenced the yield of this reaction greatly. The most active catalytic systems were those bearing bulky phosphine ligands. The highest catalytic activity was exhibited by Pd(OAc)<sub>2</sub>/RuPhos, which gave a virtually quantitative yield. Surprisingly, the influence of air to this reaction is very poor, even suffering aerobic conditions, such reaction with the catalyst of Pd(OAc)<sub>2</sub>/RuPhos is still very high.

Vilsmeier reaction was used to introduce aldehyde group to indole, the control of temperature and humidity have great influence on the yield of compound 3. So, the reactants solvents used in this all and step were purified and dried. 2-(3-cyano-4,5,5-trimethylfuran-2(5H)-ylidene)malononitrile (TCF) was prepared according to the literatures. And the coupling between TCF and indole donor was operated by Knoevenagel condensation reaction under the catalyst of piperdinie. The synthesis of chromophore ZML-ref was a little simpler, just including two steps: Vilsmeier reaction and Knoevenagel condensation reaction, which has been reported by Kim S et al in 2011. [37]



Scheme 1. The structure and synthesis of chromophores ZML-c and ZML-ref 2.2. *Linear optical features of chromophore ZML-c* 

The linear optical features of chromophroe ZML-c and ZML-ref were shown in fighre 1. They were measured in the solution of tetrahydrofuran(THF). Chromophore ZML-ref showed us two strong absorption peaks respectively at 309 nm and 489 nm. The absorption peak was stronger at 309 nm than 489 nm. These absorption peaks were attributed to the n- $\pi^*$  and  $\pi$ - $\pi^*$  transition of the electrons in chromophore ZML-ref. Obviously, after the introduction of pyrrolidine group in the donor part, the strong absorption peak at 309 nm disappeared. And the absorption peak at 489 nm was redshifted to 559 nm. After the introduction of piperidine group in the donor part, the n- $\pi^*$  transition was reduced and the $\pi$ - $\pi^*$  transition was enhanced. This was a positive factor for improving the nonlinear optical property of this kind of materials.

Else, chromophores based on traditional aniline electron donors, using the same electron acceptor and bridge with chromophore ZML-c showed the strongest absorption peaks at around 550 nm. As known, absorption peaks have directly relationships with the delocalized energy of this kind of chromophores. Normally, chromophores with lower delocalized energy could show us higher first order hyperpolarizability. The reason for this phenomenon is that the electron mobility of chromophores under external electric fields is decided by their delocalized energy level. As the delocalized energy level is reduced, their electron mobility can be improved greatly. And the improvement of the electron mobility can improve their second nonlinear optical susceptibility at the same time. Comparing the absorption spectrum of chromophore ZML-c and ZML-ref, the advantage for the introduction of piperidine group to the donor part is very obvious.



Fig. 1. UV-Vis. absorption spectrum of chromophores ZML-c and ZML-ref in THF

3.2. Thermal stability of chromophore ZML-1



Fig. 2. TGA profile of chromophores ZML-c and ZML-ref

Thermal stability is an important property for organic second nonlinear optical chromophore, which can decide its applications and test methods in the following steps. The processing of optics-electronic materials and devices is very complicated, mostly including sputtering, plating edible and package process. So the thermal stability can greatly influence the processing. In this paper, the thermal stabilities of chromophore ZML-c and ZML-ref were investigated by thermogravimetric analysis (TGA). The TGA profiles for chromophore ZML-c and ZML-ref were shown in figure 2. The thermal decomposition temperatures were 160 °C and 247 °C respectively for chromophore ZML-c and ZML-ref. Due to the rich electronic property, chromophore ZML-c showed us a lower thermal decomposition temperature, which was just 160 °C. Traditional chromophores based on aniline donors usually showed us thermal decomposition temperatures around 250 °C, which was between chromophore ZML-c and ZML-ref. This result indicated that the thermal stability was influenced by their rich electronic level greatly. Else, the decomposition of chromophore

ZML-c was in one stage. But the decomposition of chromophore ZML-ref was on three stages; in the first stage, the weight loss was about 10wt%; in the second stage the weight loss was about 30wt%. And when the temperature reach 500 °C, the weight loss of chromophroe ZML-c and ZML-ref were about the same (60% wt). Such a phenomenon was hard to explain for us.

Following the previous studies most of the processing (electronic field poling) temperatures were carried out around 100-120 °C. The thermal decomposition temperature was high enough for their application as materials for electro-optic polymer light modulators, even for chromophore ZML-c with a lower thermal decomposition temperature.

3.3. Nonlinear optical property of chromophore ZML-c and ZML-ref

Nonlinear optical property of such kind of materials is the focus of our attention, which can decide the drive voltage and electro-optical conversion efficiency of the devices prepared based on these materials. The nonlinear optical property of chromophore ZML-c and ZML-ref are studied by Teng-Man method at the laser wavelength of 1310 nm. And the results are called electro-optics (EO) coefficients. Before the measurements, such kind of materials should be prepared to optical films on the indium tin oxide (ITO)glass substrate by the method of spin coating and undergo the process of electronic field poling.

		-		
chromophore	10wt%	15wt%	20wt%	25wt% <sup>a</sup>
ZML-c	15.4	18.9	23.5	21.2 <sup>b</sup>
ZML-ref	9.8	10.6	9.3	6.8
	1			

Table. 1. EO coefficients of chromophores ZML-c and ZML-ref

a. Chromophore loading density

b. EO coefficients@1310 nm (pm/V)

The EO coefficients of chromophore ZML-c and ZML-ref were shown in table 1. Chromophore ZML-c showed us the largest EO coefficients at the chromophore loading density of 20wt% about 23.5 pm/V. chromophore ZML-ref showed us the largest EO coefficients at the chromophore loading density of about 15wt% about 10.6 pm/V. the difference between the largest EO coefficients of chromophore ZML-c and ZML-ref was attributed to the electron donating ability of the donors. Else, the five-member cyclic structure of piperidine in the donor of chromophore ZML-c increased the distance between

the chromophore molecules and reduced the intermolecular dipole interaction force. These could improve the poling efficiency and EO coefficients greatly.

Else, we also comparing the EO coefficients of chromophore ZML-c and ZML-ref with the traditional chromophore using aniline as donor, whose largest EO coefficients was about 16.5 pm/V with a loading density of 25 wt% in APC at wavelength 1310 nm. Obviously, the traditional chromophore using aniline as donor showed larger EO coefficients than chromophore ZML-ref and smaller EO coefficients than chromophore ZML-c. This was mainly due to the electron donating ability of the donor and the intermolecular dipole interaction forces. [26]

### 3.4 Theoretical calculation of chromophores ZML-c and ZML-ref

To analyze the origin of the enhanced effect we have performed quantum chemical calculations using Gaussian W09 package [27]. To clarify the role of the particular chromophores, we performed additional quantum chemical simulations particularly for hyperpolarizability at a wavelength of 1310 nm. Molecule models optimization and calculation of first order hyperpolarizabilities such as HOMO and LUMO shape were performed using DFT and B3LYP functional supplemented [28, 29] with the standard 6-31G(d) basis set.

Shapes of HOMO and LUMO orbitals of ZML-c and ZML-ref molecules are presented at Figure 3. Addition of donor pyrrolidine fragment in ZML-c leads to the greater separation of the molecule on two parts – donor and acceptor ones in comparison with ZML-ref. At the case of ZML-c molecule one conclude that we deal with the clear space donor-acceptor space separation defining the principal charge transfer contrary to ZML-ref, where HOMO and LUMO overlap for the most part of molecule. So, including the fact, that D- $\pi$ -A structure is more expressed for ZML-c one can suppose, that NLO properties, namely SHG, likely would be better for the mentioned one. This assumption is also confirmed by the following first order hyperpolarizability ( $\beta$ ) calculations and the experimental measurement of both samples properties.



Fig. 3. HOMO and LUMO shape of chromophores ZML-c and ZML-ref

The hyperpolarizability ( $\beta$ ) is a third order tensor which can be described by a 3 × 3 × 3 matrix with 27 components, which can be reduced to 10 components due to the Kleinman symmetry [30]. Using x, y and z components hyperpolarizability ( $\beta$ ) could be written as follows:

 $\beta = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2}$  $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$  $\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$  $\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$ 

The ( $\beta$ ) components of GAUSSIAN 09 output are reported in atomic units and therefore the calculated values are converted into esu units (1 a.u = 8.6393 × 10<sup>-33</sup> esu). The computed values of the dipole moment  $\mu$  for the ZML-c molecule are equals to 19.7216 Debye, and 15.6567 Debye for ZML-ref, which also confirms more expressed dipole-acceptor structure for the ZML-c. Both static and dynamic (at the 1310 nm) average hyperpolarizabilities ( $\beta$ ) are also greater for ZML-c molecule (1.311·10<sup>-28</sup> and 7.988·10<sup>-28</sup> respectively) then for the ZML-ref one (5.266·10<sup>-29</sup> and 1.064·10<sup>-28</sup> respectively) (Table 2). Thereby, according to the

calculations, ZML-c would possess more effective SHG, what is in good agreement with the experimental measurements.

Tensor component, a.u.	ZI	ML-c	ZML-ref		
	Static	Dynamic 1310 nm	Static	Dynamic 1310 nm	
β <sub>xxx</sub>	<mark>14506.500</mark>	91826.900	<mark>5890.480</mark>	<mark>12118.300</mark>	
<mark>β<sub>xxy</sub></mark>	<mark>-2912.830</mark>	<mark>-13668.500</mark>	<mark>-1520.370</mark>	<mark>-2431.500</mark>	
β <sub>xyy</sub>	<mark>469.183</mark>	<mark>-203.119</mark>	<mark>30.024</mark>	<mark>-20.042</mark>	
<mark>β<sub>xxz</sub></mark>	<mark>24.630</mark>	<mark>37.975</mark>	<mark>0.468</mark>	<mark>1.173</mark>	
<mark>β<sub>xyz</sub></mark>	<mark>11.801</mark>	<mark>13.610</mark>	<mark>-0.029</mark>	<mark>-0.073</mark>	
<mark>β<sub>xzz</sub></mark>	<mark>-82.261</mark>	<mark>-146.513</mark>	<mark>-0.510</mark>	<mark>-6.194</mark>	
<mark>β<sub>yyy</sub></mark>	<mark>-10.269</mark>	<mark>202.032</mark>	<mark>62.841</mark>	<mark>73.542</mark>	
β <sub>yyz</sub>	<mark>3.723</mark>	<mark>3.749</mark>	<mark>-0.031</mark>	<mark>-0.029</mark>	
<mark>β<sub>yzz</sub></mark>	<mark>-6.447</mark>	<mark>-6.546</mark>	<mark>5.242</mark>	<mark>6.026</mark>	
β <sub>zzz</sub>	<mark>-0.851</mark>	<mark>-0.791</mark>	0.001	<mark>0.001</mark>	
β <sub>x</sub>	<mark>14893.422</mark>	<mark>91477.268</mark>	<mark>5919.994</mark>	<mark>12092.064</mark>	
<mark>βy</mark>	<mark>-2929.546</mark>	<mark>-13473.014</mark>	<mark>-1452.287</mark>	<mark>-2351.932</mark>	
β <sub>z</sub>	<mark>27.502</mark>	<mark>40.933</mark>	<mark>0.437</mark>	<mark>1.145</mark>	
β	<mark>15178.835</mark>	<mark>92464.125</mark>	<mark>6095.528</mark>	<mark>12318.668</mark>	
<mark>β, esu</mark>	$1.311 \cdot 10^{-28}$	7.988.10 <sup>-28</sup>	5.266 · 10 <sup>-29</sup>	$1.064 \cdot 10^{-28}$	

Table. 2. Teoretically	/ calculated	hyperpol	arizabilities	of chromo	phore
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ZML-c and ZML-ref

#### **3. Experiments**

#### 3.1 instruments and materials

<sup>1</sup>H NMR spectra were determined by an Advance Bruker 400M (400MHz) 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 °C min<sup>-1</sup> under the protection of nitrogen. All chemicals, commercially available, are used without further purification unless stated. 2-dicyanomethylene-3-cyano-4-methyl-2, 5-dihydrofuran (TCF) acceptor was prepared according to the literature. [31]

3.2 Poling and EO coefficients measurements

Guest-host polymers were prepared by formulating chromophores ZML-c and ZML-ref into APC using dibromomethane (CH<sub>2</sub>Br<sub>2</sub>) as the solvent. The resulting solutions were filtered through a 0.22  $\mu$ 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 45°C to remove the residual solvent. The poling process was carried out at a temperature of T<sub>g</sub> of the polymer. The EO coefficients were measured using Teng-Man simple reflection technique at the wavelength of 1310 nm. [32]

#### 3.3 Synthesis of 6-(pyrrolidin-1-yl)-1H-indole

6-bromo-1*H*-indole (2.05 g, 10.2 mmol), pyrrolidine (0.71 g, 10 mmol), Pd(OAc)2 (0.05 g, 0.02 mmol), RuPhos (0.18 g, 0.04 mmol) and powdered NaOtBu (1.2 g, 1.2 mmol) were dissolved in a screw-cap vial equipped with a magnetic stir bar. The vial was transferred to a preheated oil bath (110 °C). After 12 h, the reaction mixture was cooled and poured into 20 mL water, and then extracted by 10 mL dichloromethane for three times. The organic phase was separated, the solvent was evaporated in vacuo, and the product was isolated by flash chromatography on a silica gel column. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): 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); 13C NMR (101 MHz, Acetone) δ 145.03 (s), 138.30 (s), 121.66 (s), 120.49 (s), 119.74 (s), 107.70 (s), 101.24 (s), 163.03 (s), 93.13 (s), 48.12 (s), 25.20 (s). MS (EI) (M<sup>+</sup>, C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>): calcd: 186.253; found: 186.0974.

#### 3.4 synthesis of chromophore ZML-c

#### Compound 3

6-(pyrrolidin-1-yl)-1*H*-indole (0.56 g, 3.0 mmol) was dissolved in 15 ml DMF in an oven-dried two necked-flask. Then, the mixture was cooled to 0 ~ 5 °C and POCl<sub>3</sub> (0.34 ml) was added by drop-wise. After the POCl<sub>3</sub> 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<sub>3</sub> ice-water and stirred for another 1h. The organic phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> and dried over anhydrous MgSO<sub>4</sub>. After removal of the solvent, the pure product was obtained by a silica-gel flash column chromatography (acetone: petroleum ether=1:15, v/v) to give a bright yellow solid compound 3 (0.39 g, 1.8 mmol) in 61% yield. <sup>1</sup>H NMR (400 MHz, Acetone, ppm):  $\delta$  =10.65 (s, 1H), 9.91 (s, 1H), 7.98 (d, J = 8.6 Hz, 1H), 7.89 (s, 1H), 6.65 (d,

 $J = 8.7 \text{ Hz}, 1\text{H}, 6.59 \text{ (s, 1H)}, 3.29 \text{ (s, 4H)}, 2.02 \text{ (s, 4H)}; \text{MS (EI) (M}^+, C_{13}H_{14}N_2O \text{ ): calcd:} 214.26; found: 214.1053.$ 

#### Chromophore ZML-c

Compound 3 (0.39g, 1.3 mmol) and TCF (0.27 g, 1.4 mmol) were dissolved in 20 ml ethanol. Then, several drops of pyridine was added to the solution. Then the mixture was heated under reflux for 3-4 h. The solution was cooled to room temperature. The resulting product was filtered off washed with cold ethanol and dried as purple solid 5a (0.28 g, 0.6 mmol) in 43% yield. <sup>1</sup>H NMR (400 MHz, DMSO, ppm):  $\delta$ = 12.29 (s, 1H), 8.17 (d, J = 15.7 Hz, 2H), 7.72 (s, 1H), 6.83 (s, 1H), 6.73 (s, 1H), 6.60 (s, 1H), 3.30 (s, 4H), 1.99 (s, 4H), 1.80 (s, 6H); MS(MALDI-TOF), m/z: 395.803(M<sup>+</sup>).

#### 3.5 synthesis of chromophore ZML-ref

The synthesis of chromophore ZML-ref is used the method of synthesis of chromophore ZML-c. Yield 41%1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.96 (d, J = 15.1 Hz, 1H), 7.79 (d, J = 8.7 Hz, 1H), 7.58 (m, 2H), 7.27 (s, 1H), 6.56 (d, J = 8.3 Hz, 1H), 6.30 (d, J=8.3Hz, 1H), 1.78 (s, 6H); MS (MALDI-TOF), m/z: 326.105 (M<sup>+</sup>). Elemental Analysis: C, 73.15; H, 4.35; N, 17.66; O, 4.84(found); C, 73.61; H, 4.32; N, 17.17; O, 4.90 (calculated).

#### 4. Conclusions

Buchwald-Hartwig amination of aryl halides with solvent-free condition was confirmed as a efficient and green reaction for the preparation of novel electron donor. And such kind of reaction may be widely used in the synthesis of novel organic conjugated small molecules. Indole modified by pyrrodine groups showed us excellent electron donating ability. Comparing with chromophroe ZML-ref, after the modification by pyrrodine group, chromophore ZML-c showed us lower delocalized energy levels and larger EO coefficients. These advantages indicated that the effective modification in indole ring may be a potential direction for the design and preparation of electron donor of NLO chromophore. Though the thermal decomposition temperature of chromophore ZML-c reduced to 160 °C; after some other modification for chromophore ZML-c, the thermal stability would be improved in the future. To analyze the origin of the enhanced effect we have performed quantum chemical calculations using Gaussian W09 package. The computed values of the dipole moment  $\mu$  and the average hyperpolarizability ( $\beta$ ) for the ZML-c molecule are equals to 19.7216 Debye,  $2,41\times10-28$  esu and 15.6567 Debye,  $1,89\times10-28$  esu for ZML-ref respectively. At the case of ZML-c molecule one conclude that we deal with the clear space donor-acceptor space separation defining the principal charge transfer contrary to ZML-ref, where HOMO and LUMO overlap for the most part of molecule.

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1. Buchwald-Hartwig amination of aryl halides was used for the preparation of electron donors.

2. Novel chromophore ZML-c based on this electron donor was designed and synthesized.

3. Chromophore ZML-c showed good thermal, optical NLO optical properties.