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Synthesis and Characterization of Novel Second-Order Nonlinear Optical Chromophore Based on New Julolidine Donor

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Abstract

New chromophore HK containing cis,cis-1,7-diethoxy-3-isopropyljulolidine group as a novel electron-donor, thiophene as π-conjugated bridge and tricyanofuran (TCF) acceptor have been synthesized and systematically investigated in this paper. Its corresponding chromophore FTC using 4-(diethyl amino)benzyl as electron donor group was also prepared for comparison. It is the first time that cis,cis-1,7-diethoxy-3-isopropyljulolidine group was introduced into NLO materials. Density functional theory (DFT) was used to calculate the HOMO-LUMO energy gap and first-order hyperpolarizability (β) of the new chromophore. The HOMO–LUMO gap was also investigated by cyclic voltammetry (CV). Upon using the cis,cis-1,7-diethoxy-3-isopropyljulolidine group as the donor, a reduced energy gap of 1.007 eV was obtained compared with chromophore FTC ($\Delta E = 1.529$ eV). The high molecular hyperpolarizability of the new chromophore can be effectively translated into large electro-optic (EO) coefficients (r_{33}) in poled polymers. The doped films containing the new chromophore HK showed a value of 72 pm /V at the concentration of 25 wt % at 1310 nm. This value is almost two times higher than the EO activity of usually reported traditional (*N, N*-diethyl) aniline nonlinear optical (NLO) chromophore FTC. High r_{33} values indicated that the new julolidine donor can efficiently improve the electron-donating ability and reduce intermolecular electrostatic interactions thus enhance the macroscopic EO activity. These properties, together with the good solubility, suggest the potential use of the new chromophore as advanced materials devices.

1. Introduction.

Organic electro-optic (EO) materials have attracted considerable attention over the past two decades due to their potential applications in high-speed and broadband information technology. [1-5] These potential applications have stimulated a research boom for materials with large EO activities, both at molecular level (β) and as processed materials (r_{33}). However, for practical applications, one of the challenges in preparing excellent EO materials is to develop nonlinear optical (NLO) chromophores with large hyperpolarizability (β) and to reduce adverse strong inter-molecular electrostatic interaction among the chromophores molecules. [6,7] Thus, optimizing chromophores with large β and weak inter-molecular electrostatic interaction has become the focus of the researchers.

Generally, the NLO chromophores have the structures of a donor-π-acceptor which usually possess a rod-like structure. So the strong intermolecular dipole-dipole interactions will develop in the polymeric system and further make the poling-induced noncentrosymmetric alignment of chromophores a daunting task. [8] Furthermore, accompanying with the increased concentration of chromophore moieties in the materials, these intermolecular dipole-dipole interactions would become stronger, which would finally lead to a decreased EO activity. [9] Thus, how to decrease these interactions, and efficiently translate the large β values of the organic chromophores into high macroscopic EO activity of polymers, has become one of the major problems in optimizing organic NLO materials. [10-12] To achieve higher EO activity and suppress the dipole interaction among chromophores, rational molecular designs of

dipole chromophores have been made from the conjugated push–pull molecules. Many efforts have been carried out to design and synthesize novel NLO chromohores, seeking to engineer NLO molecules both microscopically (β) and macroscopically (r_{33}).[5, 10 13] However, the electron acceptor groups and π-conjuncted bridges are widely studied to optimize the comprehensive properties of chromophores,[14-21] the electron donors have not received much attention, though they are important blocks for the construction of NLO chromophores just as the other two.

This paper describes our experimental approach to the design and synthesis of the new NLO chromophore HK (Chart 1). Chromophore HK has the cis,cis-1,7-diethoxy-3-isopropyljulolidine group as the donor. Besides, chromophore FTC, which has 4-(diethyl amino)benzyl group as the donor, and has been synthesized as a benchmark chromophore for comparison. As reporped,[22] Jen groups have compared two different kinds of julolidene donors with a diethylamine donor. They use a CLD bridge and CF_3, Ph-TCF acceptor and the results is better. While there was no paper using a thiophene bridge and dimethyl TCF acceptor for comparison. So this paper may present some new results. Chromophore HK with a 12-atom 3-fused ring donor has large three-dimensional steric hindrances. Thermal stability, photophysical properties, DFT calculation results and nonlinear optical properties of the chromophores were systematically compared to prove the benefits of the julolidinyl-based donor in applications of nonlinear optical chromophores design and synthesis.
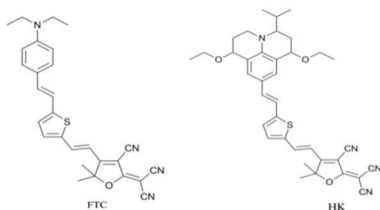

Chart1: the structure of the chromophore of FTC and HK

2. Results and discussion.

2.1 synthesis and characterization of chromophores

The synthesis of HK chromophore is depicted in Schemes 1. This novel chromophore HK was prepared by the stepwise synthetic protocol illustrated in Scheme 1. New chromophore HK was conveniently synthesized in five steps from the cis,cis-1,7-diethoxy-3-isopropyljulolidine 1. The new julolidine donor was synthesized according to the report [23]. The bromojulolidine 2 was synthesized by bromination with NBS in $CHCl_3$ as reported in the literature. [24] Treatment of compound 2 with n-BuLi and DMF gave an aldehyde 3. Aldehyde 3 was condensed with 2-thienyltriphenylphosphonate bromide by Wittig condensation to gain 4. As expected, after introduction of the thiophene bridge by Wittig condensation, treatment of compound 4 with n-BuLi and DMF gave an aldehyde 5. The target chromophore HK was obtained via the Knoevenagel reaction of aldehyde 5 with acceptor TCF in the presence of a catalytic amount of piperidine. The traditional FTC

chromophore was synthesized according to our previous work.[25]

2.2 Thermal analysis

The thermal stabilities of chromophores were evaluated by thermal gravimetric analysis (TGA) under nitrogen, with a heating rate of 10 ℃/min. The temperature for 5% weight loss of the chromophore is summarized in table 1. The chromophore HK is 202℃. The NLO chromophores must be thermally stable enough to withstand encountered high temperatures in electric field poling and subsequent processing of chromophore/polymer materials. The temperature in practical materials processing was generally below 200 ℃. Therefore, although the T_d of the HK chromophor was lower than FTC chromophore, it was high enough for the practical application in EO device preparation.
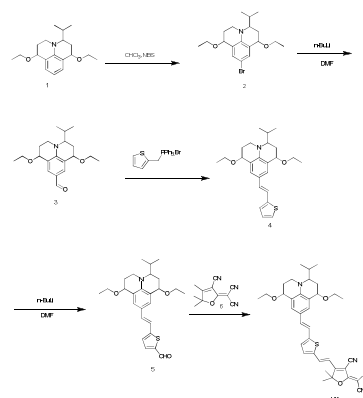
Scheme1 Chemical structures and synthetic scheme for chromophore HK

2.3 Optical properties

In order to reveal the effect of new julolidine donor on the intromolecular charge transfer (ICT) of dipolar chromophores, UV-Vis absorption spectra of these chromophores (c=1×10^{-5} mol/L) were measured in a series of aprotic solvents with different polarity so that the solvatochromic behavior of these chromophores could be investigated to explore the polarity of chromphores in a wide range of dielectric environments (Figures 1). The spectrum data are summarized in Table 1. The synthesised chromophore and FTC chromophore exhibited a similar $\pi \rightarrow \pi^*$ intramolecular charge-transfer (ICT) absorption band in the visible region. HK showed the maximum absorption (λ_{max}) of 702 nm in $CHCl_3$. This value is larger compared to the traditional FTC (λ_{max} of 676 nm in $CHCl_3$) with aniline donor and the same π-conjugated bridge and acceptor. The new julolidine donor shifted the ICT absorption band of the chromophore to the lower energy. As shown in Fig. 1, the peak wavelength of HK chromophore showed a bathochromic shift of 61 nm from dioxane to chloroform, displaying the larger solvatochromism compared with the FTC chromophore (55 nm in Table 1). The resulting spectrum data confirmed that the chromophore with the new julolidine donor was more easily polarizable than the traditional FTC chromophore. These analysis implied that the new julolidine donor improved the

electron-donating capability and increased the polarizability of the chromophore HK.
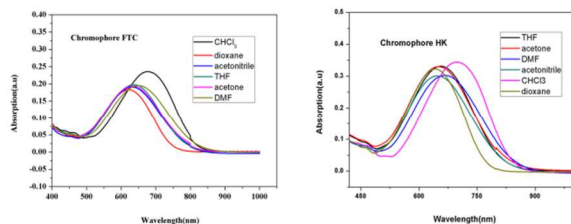

Fig. 1 UV-Vis absorption spectra in different solvents of chromophore FTC and HK. (c=1×10⁻⁵mol/L)

Traditional chromophores were easy to aggregate, which were beneficial for self-assembly. But it was unfavorable for NLO application, because the chromophores were easy to form the antiparallel aggregation.This phenomenon can be demonstrated by absorption intensity, wavelength and shape of absorption band in UV-vis spectra. To study the effect of new donor on attenuating chromophore aggregation, the absorption of the chromophore was measured in $CHCl_3$ at different concentration (range from 0.005 mM to 0.1 mM). As Fig. 2 showed, the λ_{max} of the chromophore at different concentration. As the concentration rose, no obvious blue-shift or red-shift was found. Even at high concentration, no obvious characteristic absorption band of aggregation was observed.
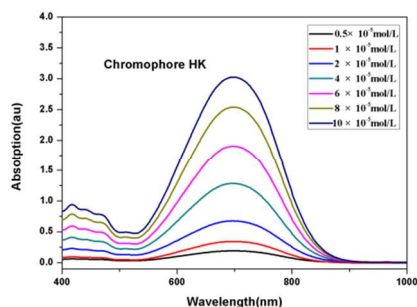

Fig.2 UV-Vis absorption spectra of different concentrations of chromophore HK at $CHCl_3$

2.4 Theoretical calculations

In order to model the ground state molecular geometries, the HOMO-LUMO energy gaps and β values of these chromophores were calculated. The DFT calculations were carried out at the hybrid B3LYP level by employing the split valence 6-31 g (d, p) basis set. [26-28] The data obtained from DFT calculations are summarized in Table 2.

The frontier molecular orbitals are often used to characterize the chemical reactivity and kinetic stability of a molecule and to obtain qualitative information about the optical and electrical properties of molecules.[28, 29, 30] Besides, the HOMO-LUMO Energy gap is also used to understand the charge transfer interaction occurring in a chromophore molecule. [30-32] In the case of these chromophores, Fig.3 represents the frontier molecular orbitals of chromophores FTC and HK. According to

Table1. Summary of Thermal and Optical Properties and EO Coefficients of Chromophores FTC and HK

	$T_d{}^a$	$\lambda_{max}{}^b$	$\lambda_{max}{}^c$	$\Delta\lambda^d$	$r_{33}{}^e$
	(℃)	(nm)	(nm)	(nm)	(pm/V)
FTC	242	676	621	55	39
HK	202	702	641	61	72

[a]T_d was determined by an onset point, and measured by TGA under nitrogen at a heating rate of 10 ℃ /min.

[b] λ_{max} was measured in $CHCl_3$.

[c]λ_{max} was measured in dioxane.

[d]$\Delta\lambda=\lambda_{max}{}^b - \lambda_{max}{}^c$

[e] r_{33} values were measured at the wavelength of 1310nm.

the Fig.3, it is clear that the electronic distribution of the HOMO is delocalized over the thiophene linkage and benzene ring, whereas the LUMO is mainly constituted by the acceptor moieties.[30]

The HOMO and LUMO energy were calculated by DFT calculations as shown in Figure 3 and Table 2. For the new HK chromophore, the new julolidine donor structure narrows the energy gap between the HOMO and LUMO energy with DE values of 2.009 eV. By contrast, the DE value of FTC is 2.032 eV. It can be concluded that the LUMO energy of chromophore FTC is 0.128 eV larger than that of HK (−3.320 eV vs. −3.192 eV), while the HOMO energy of FTC is 0.105 eV larger than that of HK (−5.329 eV vs. −5.224 eV). This may result from the fact that the julolidine donor structure influences the HOMO energy to a greater extent than the LUMO energy. The HOMO–LUMO gaps of HK (2.009 eV) is lower than FTC (2.032 eV), and this indicates that HK should exhibit better ICT and NLO property than FTC. As repoted[30], the optical gap is lower, the of the charge-transfer (ICT) ability is greater and thus improve the nonlinearity. Chromophore HK showed a lower optical gap, so it may indicate that HK should exhibit better ICT and NLO property than FTC.
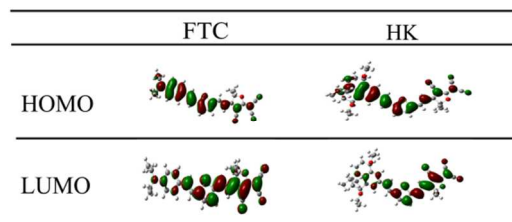
Fig. 3 The frontier molecular orbitals of chromophores FTC and HK

The HOMO–LUMO gap was also investigated by cyclic voltammetry (CV). As shown in Fig. 4, The new chromophore HK exhibited one reversible oxidative wave with a half-wave potential, $E_{1/2}$=0.5(E_{ox} + E_{red}), versus Ag/AgCl at about 0.54 V corresponding to the cis,cis-1,7-diethoxy-3-isopropyljulolidine donor group and had an irreversible reduction wave corresponding to the acceptor moieties at E_{red} = -0.53 V (vs Ag/AgCl). It showed an energy gap (ΔE) value of 1.007 eV for

HK, While the chromophore FTC exhibited a ΔE value of 1.529 eV. [33] The HOMO and LUMO levels of the new chromophore was calculated from their corresponding oxidation and reduction potentials. The HOMO levels of chromophore HK was estimated to be -4.940 eV and the chromophore FTC is -5.027 eV, [33] showing a noticeable increase by replacing the diethylaminophenyl group with the stronger julolidine donors. In the meantime, the corresponding LUMO level of chomophore was -3.870 eV, and the chromophore FTC is -3.498eV[33], also showed a noticeable changes. This comparison demonstrated that the new julolidine donor narrowed the energy gap indicating the excellent ICT of the julolidine chromophore. This result corresponded with the conclusion of UV-Vis spectra analysis and the DFT results.
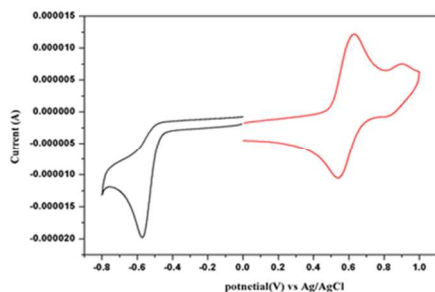

Fig.4 Cyclic voltammograms of chromophore HK

Further, the theoretical microscopic Zero-frequency (static) molecular first hyperpolarizability β was calculated by Gaussian 03. As the reference reported earlier, the β has been calculated at the 6-31 g (d, p) level in vacuum. [34] From this, the scalar quantity of β can be computed from the x, y, and z components according to the following equation:

$$\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad\quad (1)$$

Where $\beta_i = \beta_{iii} + \frac{1}{3}\sum_{i \neq j}(\beta_{ijj} + \beta_{jij} + \beta_{jji}),\ i, j \in (x, y, z)$

As shown in table 2, chromophore HK possessed a little smaller β (870×10^{-30}esu) value than the FTC (883×10^{-30}esu), However, as reported, the β value of julolidine group with a CLD bridge and CF_3, Ph-TCF acceptor is larger than the diethylamine donor with the CLD bridge and CF_3, Ph-TCF acceptor. This can be explained as follows: the β value is related to the substituent, steric hindrance, and intramolecular charge-transfer. As shown in the fig. 5, it may be attributed to
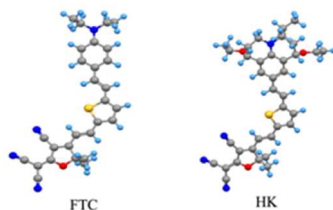

Fig.5 The optimized structure of chromophore FTC and HK

the big torsion between thiophene ring and benzene ring of the chromophore HK hindered the effective π conjugation between donor and acceptor and resulted in a lower β value. Although it showed a little β value, it showed a larger r_{33} value in the next section. Many factors can affect the r_{33} value. One important factor may be the less electrostatic interaction for HK between the chromophore molecules.

2.5 Electric field poling and EO property measurements

For studying EO property derived from these chromophores, a series of guest-host polymers were generated by formulating the chromophores into amorphous polycarbonate (APC) using dibromomethane as solvent. The resulting solutions were filtered through a 0.2μm PTFE filter and spin-coated onto indium tin oxide (ITO) glass substrates. Films of doped polymers were baked in a vacuum oven at 80 ℃ overnight to ensure the removal of the residual solvent. The corona poling process was carried out at a temperature of 10 ℃ above the glass transition temperature (T_g) of the polymer. The r_{33} values were measured using the Teng-Man simple reflection technique at the wavelength of 1310 nm using a carefully selected thin ITO electrode with low reflectivity and good transparency in order to minimize the contribution from multiple reflections. [35]

The r_{33} values of films containing chromophores FTC (fillm-A) and HK (film-B), were measured in different loading densities, as shown in Fig. 6. Traditional chromophore FTC with the *N,N*-diethylaniline benzyl donor gained the r_{33} value from 12 pm V^{-1} (10 wt%) to 39 pm V^{-1} (25 wt%), while the r_{33} values of chromophore HK was gradually improved from 26 pm V^{-1} (10 wt%) to 72 pm V^{-1} (25 wt%). This may be attributed to the strong donor ability and the isolated group in the julolidine donor moiety. As reported earlier, [36] the introduction of some isolation groups into the chromophore moieties to further control the shape of the chromophore could be an efficient approach to minimize interactions between the chromophores. So the double donor chromophores have an obvious advantage in translating β into r_{33} and thus increased the macroscopic EO activity. So by introducing the isolated groups of isopropyl and the two ethyoxyl to the donor, it control the shape of the chromophore and decreased the interaction between the chromophore thus increased the r_{33} value. Besides, as reported [37], due to the electron–vibration interactions, there was contributions to the final EO coefficient. This may be the other factor for the larger r_{33} value.

Table 2 Data from DFT calculations

Chromophores	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE^a (eV)	ΔE^b (eV)	β_{max}^c (10^{-30}esu)
FTC	-5.224	-3.192	2.032	1.529.	883
HK	-5.329	-3.320	2.009	1.007	870

$\Delta E = E_{LUMO} - E_{HOMO}$,

[a]Results was calculated by DFT

[b]Results was from cyclic voltammetry experiment

[c]β values were calculated using gussian03at B3LYP/6-31 g(d) level and the direction of the maximum value is directed along the charge transfer axis of the chromophores.

3. Experimental

3.1. Materials and instrumentation

^{1}H NMR spectra were determined by an Advance Bruker 400(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 spectra were performed on Cary 5000 photo spectrometer. The TGA was determined by TA5000-2950TGA (TA Co) with a heating rate of $10\,°C\,/\,min$ under the protection of nitrogen. Cyclic voltammetry (CV) experiments were performed on a CHI660D electrochemical workstation by a cyclic voltammetry (CV) technique in CH_3CN solution, using Pt disk electrode and a platinum wire as the working and counter electrodes, respectively, and a saturated Ag/AgCl electrode as the reference electrode in the presence of 0.1 M n-tetrabutylammoniumperchlorate as the supporting electrolyte. The ferrocene/ferrocenium (Fc/Fc+) couple was used as an internal reference. All chemicals, commercially available, are used without further purification unless stated. The DMF, $POCl_3$ and THF were freshly distilled prior to its use. The 2-dicyanomethylene-3-cyano-4-methyl-2,5-dihydrofuran (TCF) acceptor was prepared according to the literature.[38]
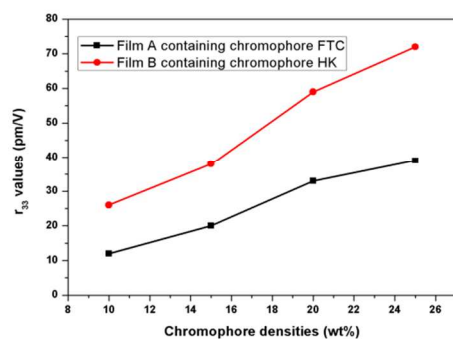

Fig. 6 EO coefficients of NLO thin films as a function of chromophore loading densities.

3.2. Synthesis

3.2.1 Synthesis of compound 1

Compound 1 was synthesized according to literature.
^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.19 (d, J = 7.4 Hz, 1H), 7.08 (d, J = 7.4Hz, 1H), 6.63 (t, J = 7.4Hz, 1H), 4.46 (t, J = 5.7Hz, 1H), 4.25 (t, J = 3.6Hz, 1H), 3.78 – 3.66 (m, 2H), 3.65 – 3.55 (m, 2H), 3.28 – 3.16 (m, 2H), 3.05 – 2.97 (m, 1H), 2.45 – 2.33 (m, 1H), 2.07 – 1.91 (m, 4H), 1.30 – 1.21 (m, 6H), 0.99 (d, J = 7.5Hz, 3H), 0.88 (d, J = 8.0 Hz, 3H).
^{13}C-NMR (100 MHz, CDCl$_3$) δ 142.35, 129.45, 128.07, 122.42, 121.63, 114.62, 73.93, 73.11, 63.78, 63.33, 62.11, 42.71, 29.04, 27.55, 26.94, 20.58, 17.31, 15.75, 15.66.
MALDI-TOF: m/z calcd for : $C_{19}H_{29}NO_2$:303.22 [M]$^+$; found: 303.18.

3.2.2 Synthesis of compound 2

Compound 2 was synthesized according to literature.[24]

^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.19 (d, J = 2.3 Hz, 1H), 7.09 (d, J = 2.3 Hz, 1H), 4.25 (t, J = 6.1 Hz, 1H), 4.10 (t, J = 4.1 Hz, 1H), 3.69 – 3.58 (m, 2H), 3.53 – 3.44 (m, 2H), 3.18 – 3.01 (m, 2H), 2.94 m, 1H), 2.34 – 2.23 (m, 1H), 1.91 – 1.82 (m, 4H), 1.21 – 1.13 (m, 6H), 0.91 – 0.87 (m, 3H), 0.76 (t, J = 6.0 Hz, 3H).
MALDI-TOF: m/z calcd for : $C_{19}H_{28}BrNO_2$:381.13 [M]$^+$; found: 381.22.

3.2.3 Synthesis of compound 3

To a solution of compound 2 (2.28 g, 6.00 mmol) in dry THF (20 mL) was added a 2.4 M solution of n-BuLi in hexane (4.0 mL, 9.00 mmol) dropwise at -78 ℃ under N$_2$. After this mixture was stirred at this temperature for 1 h, and the dry DMF (0.56 mL, 7.20 mmol) was introduced. The resulting solution was stirred for another 1h at -78 °C and then allowed to warm up to room temperature. The reaction was quenched by water. THF was removed by evaporation. The residue was extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was dried by $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/acetone, v/v, 10/1) to obtain a red solid (1.68 g, 84%).
^{1}H-NMR (400 MHz, CDCl$_3$) δ 9.69 (s, 1H), 7.67 (d, J = 1.8 Hz, 1H), 7.60 (d, J = 1.8 Hz, 1H), 4.35 (t, J =6.0 Hz, 1H), 4.32 (t, J = 3.9 Hz, 1H), 3.78 – 3.64 (m, 2H), 3.64 – 3.55 (m, 2H), 3.50 – 3.29 (m, 2H), 3.11 (m, 1H), 2.45 (m , 1H), 1.98 (m, 4H), 1.31 – 1.21 (m, 6H), 0.99 (d, J = 6.5 Hz, 3H), 0.89 (d, J = 6.5 Hz, 3H).
^{13}C-NMR (100 MHz, CDCl$_3$) δ 188.88, 145.85, 130.43, 130.26, 123.07, 121.09, 120.52, 72.08, 71.77, 63.31, 62.50, 43.32, 28.49, 26.36, 25.79, 19.61, 17.19, 14.56, 14.49.
MALDI-TOF: m/z calcd for $C_{20}H_{29}NO_3$:331.21 [M]$^+$; found: 331.22.

3.2.4 Synthesis of compound 4

Under N$_2$, a mixture of compound 3 (1.66 g, 5 mmol) and 2-thienyl triphenylphosphonate bromide (2.64 g, 6 mmol) in dry THF (20 mL) at room temperature, NaH (1.20 g, 0.05 mol) was added. The mixture turned yellow and was stirred at room temperature for 24 h. Saturated NH$_4$Cl was added and the resulting mixture was extracted with EtOAc (20 × 3 mL). The combined extracts were washed with water and dried over MgSO$_4$. After filtration and removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel (hexane/acetone, v/v, 10/1) to obtain a yellow liquid (1.29 g, 63%).m
^{1}H-NMR (400 MHz, Acetone) δ 7.31 (d, J = 2.1 Hz, 1H), 7.24 (d, J = 2.1 Hz, 1H), 7.17 (d, J = 5.1 Hz, 1H), 7.09 (d, J=16.1Hz, 1H), 6.99 (d, J = 3.6 Hz, 1H), 6.93 (dd, J = 5.1, 3.6 Hz, 1H), 6.84 (d, J = 16.1 Hz, 1H), 4.33 (t, J = 5.4 Hz, 1H), 4.23 (t, J = 4.1 Hz, 1H), 3.75 – 3.61 (m, 2H), 3.59 – 3.45 (m, 2H), 3.25 – 3.18 (m, 2H), 3.00 (m, 1H), 2.44 – 2.32 (m, 1H), 1.94 – 1.88 (m,4H), 1.23 – 1.12 (m, 6H), 0.93 (d, J = 6.5 Hz,3H), 0.84 (d, J = 6.7 Hz, 3H).
^{13}C-NMR (100 MHz, CDCl$_3$) δ 143.28, 140.89, 140.73, 139.95, 129.60, 129.40, 128.36, 128.21, 126.61, 126.38, 125.78, 125.52, 125.44, 123.34, 123.09, 122.93, 122.27, 121.78, 121.67, 121.31, 120.95, 120.33, 118.25, 72.76, 71.99, 62.96, 62.39, 61.30, 41.90, 28.18, 28.11, 26.51, 26.28, 19.48, 16.41, 14.70, 14.62, 14.54.
MALDI-TOF: m/z calcd for $C_{25}H_{33}NO_2S$: 411.22 [M]$^+$; found: 411.09.

3.2.5 Synthesis of compound 5

To a solution of compound 4 (1.23 g, 3.00 mmol) in dry THF (20 mL) was added a 2.4 M solution of n-BuLi in hexane (1.9 mL, 4.50 mmol) dropwise at -78 ℃ under N_2. After this mixture was stirred at this temperature for 1 h, and the dry DMF (0.28 mL, 3.60 mmol) was introduced. The resulting solution was stirred for another 1h at -78 °C and then allowed to warm up to room temperature. The reaction was quenched by water. THF was removed by evaporation. The residue was extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was dried by $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/acetone, v/v, 10/1) to obtain a red solid (1.13 g, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.62 (d, J = 3.9 Hz, 1H), 7.35 (d, J = 1.8 Hz, 1H), 7.24 (d, J = 1.8 Hz, 1H), 7.09 (d, J = 15.9 Hz, 1H), 7.04 (d, J = 3.9 Hz, 1H), 6.97 (d, J = 15.9 Hz, 1H), 4.40 − 4.36 (m, 1H), 4.29 (t, J = 3.8 Hz, 1H), 3.81 − 3.55 (m, 4H), 3.34 − 3.25 (m, 2H), 3.07 (m, 1H), 2.41 (m, 1H), 2.12 − 1.93 (m, 4H), 1.35 − 1.23 (m, 6H), 0.98 (d, J = 6.8 Hz, 3H), 0.89 (d, J = 6.9 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 182.26, 154.68, 142.83, 139.84, 137.65, 134.17, 128.45, 127.36, 124.65, 122.79, 122.61, 121.93, 73.50, 73.01, 64.09, 63.47, 62.39, 43.26, 30.92, 29.10, 27.14, 27.09, 20.55, 17.50, 15.70, 15.63.

MALDI-TOF: m/z calcd for $C_{26}H_{33}NO_3S$: 439.22 $[M]^+$; found: 439.13.

3.2.6 Synthesis of chromophore HK

A mixture of aldehydic bridge 5 (0.44 g, 1.00 mmol) and acceptor 6 (0.22 g, 1.10 mmol) in ethanol (30 mL) was stirred at 75 ℃ for 4 h in the presence of a catalytic amount of piperidine. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 4:1). A dark solid was obtained (0.22 g, 35%).

^{1}H-NMR (400 MHz, Acetone) δ 8.00 (d, J = 15.8 Hz, 1H), 7.53 (d, J = 4.0 Hz, 1H), 7.32 (d, J = 3.6Hz, 1H), 7.28 (d, J = 3.6 Hz, 1H), 7.10 − 7.06 (m, 3H), 6.66 (d, J = 15.8 Hz, 1H), 4.26 (t, J = 6.1 Hz, 1H), 4.19 (t, J = 4.2 Hz, 1H), 3.62 (m, 2H), 3.55 − 3.44 (m, 2H), 3.28 − 3.20 (m, 2H), 3.03 (m, 1H), 2.42 − 2.24 (m, 1H), 1.97(m, 4H), 1.75 (s, 6H), 1.14 − 1.04 (m, 6H), 0.87 (d, J = 6.7 Hz, 3H), 0.77 (d, J = 6.9 Hz, 3H).

^{13}C-NMR (100 MHz, Acetone) δ 177.42, 175.17, 154.85, 144.03, 140.77, 138.90, 138.69, 135.85, 129.11, 128.76, 127.93, 124.06, 123.71, 123.34, 116.41, 113.34, 113.01, 112.68, 111.85, 98.95, 97.80, 74.19, 73.82, 64.71, 63.97, 63.42, 44.68, 28.27, 28.20, 26.39, 20.81, 18.16, 16.04, 16.00.

MALDI-TOF: m/z calcd for $C_{37}H_{40}NO_3S$: 620.28 $[M]^+$; found: 620.29.

3.2.7 Synthesis of chromophore FTC

Chromophore FTC was synthesized according to literature.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 7.77 (d, J = 15.7 Hz, 1 H, CH), 7.38 (d, J = 8.6 Hz, 2 H, Ar-H), 7.37 (d, J = 3.9 Hz, 1 H, CH), 7.09 (d, J = 15.7 Hz, 1H, CH), 7.01 (d, J = 3.9 Hz, 1 H, CH), 6.68 (d, J = 8.6 Hz, 2 H, Ar-H), 6.57 (d, J = 15.2 Hz, 1 H, CH), 3.52 − 3.29 (m, 4 H), 1.73 (s, 6 H), 1.28 − 1.14 (m, 6 H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 182.03, 172.86, 153.58，148.02, 142.13, 140.08, 139.33, 137.39, 129.07, 111.61, 110.91, 110.21, 108.85, 104.96, 99.53, 96.90, 44.81, 44.55, 24.42, 12.58.

MALDI-TOF: m/z calcd for $C_{28}H_{28}N_4OS$: 468.20 $[M]^+$; found: 468.33.

4. Conclusions

In summary, a new nonlinear optical (NLO) chromophore with new donor have been synthesized and systematically investigated to explore the effects of donors on the macroscopic optical nonlinearity. Theoretical and experimental investigations suggest that the new donor group play a critical role in affecting the linear and nonlinear properties of dipolar chromophores. In general, the energy gap of chromophore HK is 1.007 eV, which is 0.522 eV lower than the traditional FTC chromophore. From linear properties of chromophores HK and FTC determined in different polarity solvents, it is evident that chromophore HK can be polarized more efficiently than chromophore FTC. The effects of bathochromic and solvatochromoic behavior on the UV-vis absorption were also investigated to prove the stronger electron donating ability and weaker intermolecular interactions of chromophore HK than FTC. The DFT calculation corresponds to the conclusions we made. In electro-optic activities, the doped film-B containing chromophore HK displays a maximum r_{33} value of 72 pm/V at the doping concentration of 25 wt%, while film-A containing chromophore FTC shows a maximum r_{33} value of 39 pm/V at 25 wt%. Those outcomes indicate that the chromophore HK with the julolidinyl-based donor could efficiently reduce the interchromophore electrostatic interactions and enhance the macroscopic optical nonlinearity. This novel donor shows promising applications in nonlinear optical (NLO) chromophore synthesis.

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Notes and references

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