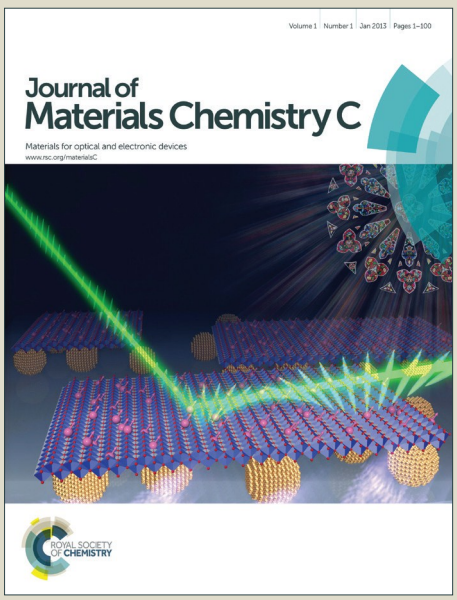
Journal of Materials Chemistry C

Accepted Manuscript



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ARTICLE

Auxiliary donor for tetrahydroquinoline-containing nonlinear optical chromophores: enhanced electro-optical activity and thermal stability

Site this: DOI: 10.1039/x0xx00000x

Received ooth June 2015,
Accepted ooth July 2015

DOI: 10.1039/x0xx00000x

www.rsc.org/

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A series of chromophores FTC, L1 and L2 has been synthesized based on three different types of electron donors, including diethylaminophenyl, tetrahydroquinolinyl and *N*-(4-dimethylaminophenyl) tetrahydroquinolinyl groups respectively, with the same thiophene bridges and strong tricyanovinyldihydrofuran (TCF) acceptors. In particular, the donor part of the chromophore L2 was modified with additional donor *N*-(4-dimethylaminophenyl) substituent, resulting in enhanced thermal stability and electro-optic activity. Cyclic voltammetry measurements showed that chromophore L2 had smaller energy gap than chromophore L1 due to the additional donor. Moreover, Density functional theory calculations suggested that the molecular quadratic hyperpolarizability (μβ) value of chromophore L2 is 29% and 44% larger than that of chromophores L1 and FTC, respectively. The doped film containing the chromophore L2 showed an r_{33} value of 100 pm/V at the concentration of 25 wt% which is much higher than the EO activity of the chromophore L1 (57 pm/V) and two times higher than that of the traditional chromophore FTC (39 pm/V).

1. Introduction

In the past two decades, much research has been focused on the development of Organic electro-optic (OEO) materials due to their great potential applications in optical data processing technologies and photonic application. [1-3] One of the most critical challenges in developing these materials is to design and synthesize second-order nonlinear optical (NLO) chromophores that exhibit good properties such as high thermal and chemical stabilities, large nonlinearity, and good transparency. [4, 5] Organic NLO chromophores, especially those demonstrating high first-order hyperpolarizability (β) values, typically have large ground state dipole moments, tend to lower the NLO response at higher chromophore loading levels due to aggregation effects, so careful design of chromophores and control of the assembly and lattice hardening in a proper polymer matrix is needed to effectively translate these large β values into bulk EO activities (r_{33}). [6, 7]

In general, the second-order NLO chromophore can be divided into three blocks: electro-donor, π-conjugated bridge and strong electro-acceptor, called D-π-A system. [8, 9] In order to search for highly efficient NLO chromophores, rational design and synthesis of dipolar NLO chromophores with high β and robust thermal stability still represents one of the most critical challenges, optimization of the π-conjugated bridge, electron-donor and electron-acceptor characteristics of the substituents are needed [10]. In the past decades, many studies on NLO chromophores have mainly focused on the design of electron bridges and electron acceptors, while the donor units have remained relatively unchanged. [11-14] Among all the materials studied, the NLO chromophores bearing 4-(dialkylamino)phenyl groups or triarylamine groups as a donating group were the most case due to their strong electron-donating ability and ease of synthesis. [12, 15] Many works were focused on the optimization of these two donor groups by different kinds of modification. [16, 17] Some studies have shown

that by introducing additional electron-rich heteroatom group into the donor moiety could effectively enhance nonlinear optical property. [18, 19] However, there are few reports about additional amino groups, which are introduced into chromophore's donor part, how to infect chromophore's NLO activity and thermal stability. [20, 21] Previously, Jen' groups had compared the tetrahydroquinoline-derived donors with a traditional diethylamine donor. [22] The results showed that the tetrahydroquinoline-derived chromophores showed much higher electro-optic (EO) activities. They used a ring-locked tetraene bridge and a CF_3-TCF (tricyanovinyldihydrofuran) acceptor. However, there is no study conducted using a thiophene bridge and a TCF acceptor.

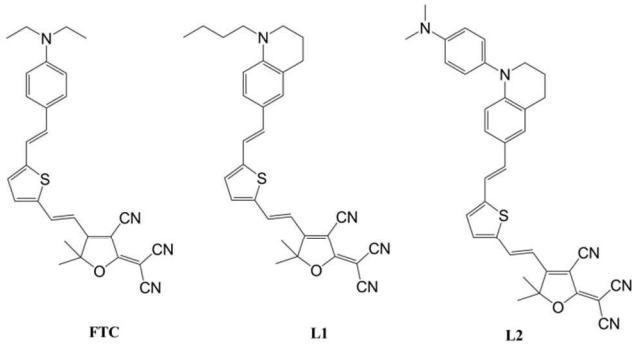


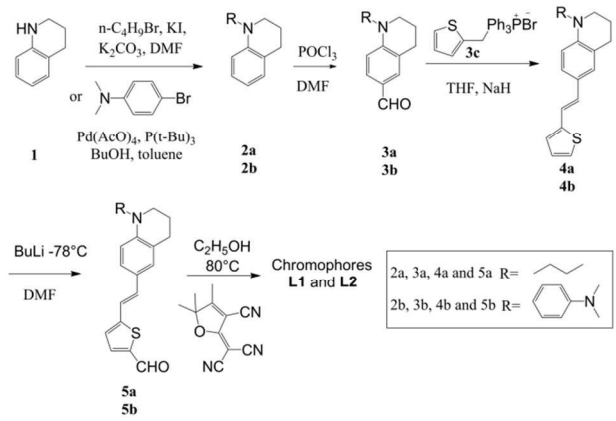
Chart 1 Chemical structure for chromophores FTC, L1 and L2.

So, in this paper, we had designed and synthesized a series of chromophores containing an identical thiophene bridge and TCF acceptor, but with three different electron donors, including diethylaminophenyl, tetrahydroquinolinyl, and *N*-(4-dimethylaminophenyl) tetrahydroquinolinyl groups (Chart 1). The diethylaminophenyl donor-based chromophore FTC was chosen as a reference compound for comparison. The ring-fused aminophenyl structures in tetrahydroquinolinyl facilitate the overlap of the p-orbital of the amino atom with the phenyl ring thus providing a good mechanism to gradually increase the electron-donating strength. [22, 23] In particular, the tetrahydroquinolinyl donor groups of the chromophore L2 was modified with additional donor *N*-(4-dimethylaminophenyl) substituent. This is the first time that the *N*-(4-dimethylaminophenyl) substituent was introduced into donor part of the second-order nonlinear optical (NLO) materials as another donor. The introduction of the *N*-(4-dimethylaminophenyl) groups of chromophore L2 can increase the thermal stability and reduce dipole–dipole interactions so as to translate their hyperpolarizability (β) values into bulk EO performance more effectively than chromophore L1. The synthesis, UV-Vis, solvatochromic behaviour, redox properties, DFT quantum mechanical calculations, thermal stabilities and EO activities of these chromophores were systematically studied and compared to illustrate the influence of electron-donating groups on rational NLO chromophore designs.

2. Results and discussion

2.1 Synthesis and characterization of chromophores

Scheme 1 shows the synthetic approach to the chromophores L1 and L2. Starting from the amine donor intermediates compound **1**, chromophores L1 and L2 were synthesized in good overall yields through simple five step reactions: The free N-H group on the donors was protected by the alkyl or aryl group to improve either the solubility or stability. Treatment of compound **2a-b** with $POCl_3$ and DMF gave an aldehydes **3a-b**. After introduction of the thiophene bridge by a Wittig condensation, compounds **4a-b** were prepared with a high yield. Treatment of compound **4a-b** with n-BuLi and DMF gave aldehyde **5a-b**, the final condensations with the TCF acceptor give chromophores L1 and L2 as green solids. All of the chromophores were fully characterized by ^{1}H-NMR and ^{13}C-NMR spectroscopy and HRMS. These chromophores possess good solubility in common organic solvents, such as dichloromethane, chloromethane and acetone.



Scheme 1 Chemical structures and synthetic routes for chromophores L1 and L2.

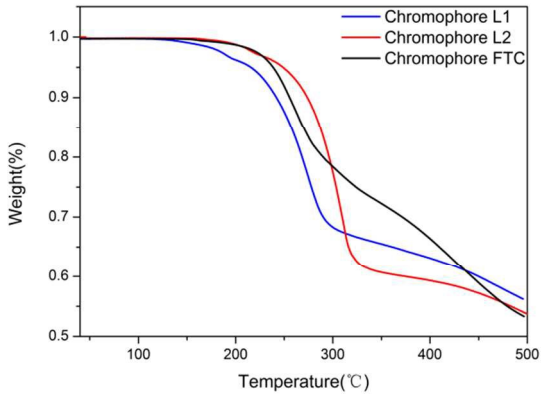


Fig. 1 TGA curves of chromophores FTC, L1 and L2 with a heating rate of 10 °C min^{-1} in nitrogen atmosphere.

2.2 Thermal stability

The thermal properties of the chromophores were investigated using thermogravimetric analysis (TGA) as shown in Figure 1 and Table 1. All the chromophores exhibited good thermal stabilities with the decomposition temperatures (T_d) higher than 210 °C (216 °C-252 °C). Chromophore L2 has the highest decomposition temperature (252°C), followed by chromophore FTC (240 °C) and Chromophore L1 (216 °C). The enhanced thermal stability of the chromophore L2 over chromophores L1 (252 °C over 216 °C) is due to the replacement of alkyl chain to benzene ring on the donor nitrogen. The data indicate that the introduction of *N*-(4-dimethylaminophenyl) substituent to the donor can increase the thermal stability of the chromophore.

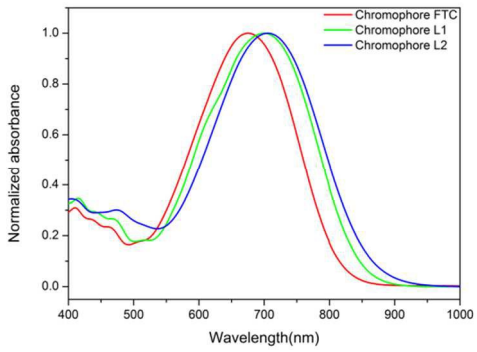


Fig. 2 UV-Vis absorption spectra of chromophores FTC, L1 and L2 in chloroform.

2.3 Optical properties

In order to reveal the effect of different electron donors on the charge-transfer (CT) absorption properties of the chromophores, UV-Vis absorption spectra of the three chromophores were measured in a series solvent with different dielectric constants as shown in Figure 2 and 3. The spectral data are summarized in Table 1. The absorption maxima (λ_{max}) of chromophores FTC, L1 and L2 are 675, 700 and 706 nm, respectively. Chromophores L1 and L2 were red-shifted in their absorption spectra, compared to the traditional chromophore FTC, probably due to the stronger donor tetrahydroquinoline. Compared to chromophore L1, chromophore L2 was red shifted by 6 nm, besides, its charge-transfer band is slightly broader than that of chromophore L1, which extends to about 1000 nm. This could indicate that the CT state is populated over a wide range of energy levels, suggesting energy gaps ΔE (optical) of chromophore L2 is smaller than that of chromophore L1. [24] This result shows that *N*-(4-dimethylaminophenyl) substituent provides extra donating strength to the donor part, shifting the CT absorption band of the chromophore to lower energy.

The solvatochromic behavior was also an important aspect to investigate the polarity of chromophores. It was found that chromophores L1 and L2 showed large bathochromic shifts of 62 nm and 61nm, respectively, on moving from dioxane to chloroform. Chromophore FTC showed slightly smaller bathochromic shift of 55 nm, from dioxane to chloroform. This confirms that chromophores L1 and L2 are more easily polarizable than chromophores FTC. [25]

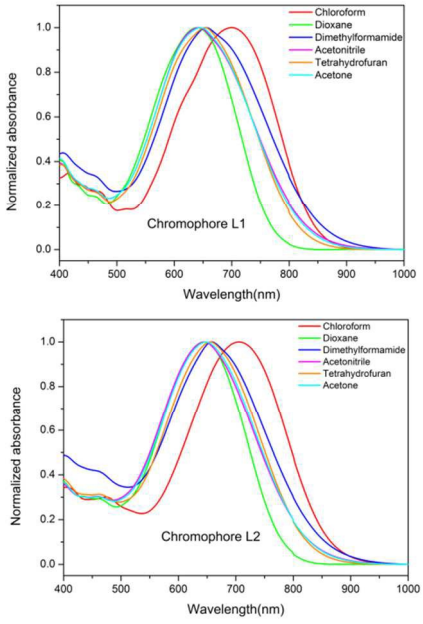


Fig. 3 UV-Vis absorption spectra of chromophores L1 and L2 in six kinds of aprotic solvents with varying dielectric constants.

Table 1 Thermal and Optical Properties data of the Chromophores.

Cmpd	T_d (℃)	λ_{max} [a] (nm)	λ_{max} [b] (nm)	$\Delta\lambda$ [c] (nm)
FTC	240	675	621	54
L1	216	700	638	62
L2	252	706	645	61

[a] λ_{max} was measured in chloroform. [b] λ_{max} was measured in dioxane. [c] $\Delta\lambda$ was the difference between [a] λ_{max} and [b] λ_{max}.

2.4 Redox properties and Theoretical calculations

In order to determine the electrochemical properties of the chromophores, cyclicvoltammetry (CV) measurements were conducted in degassed anhydrous acetonitrile solutions containing 0.1mol/L tetrabutylammonium hexafluorophosphate (TBAPF) as the supporting electrolyte. The relative data of 1×10^{-4} mol/L chromophores were recorded, as shown in Table 2 and Fig. 4. The HOMO and LUMO levels of chromophores L1 and L2 can be calculated from their corresponding oxidation and reduction potentials.[26] The difference between these two values provides the HOMO-LUMO energy difference ΔE (CV). The calculation results are summarized in Table 2. The energy gaps between the HOMO and LUMO energy for chromophores

L1 and L2 were 1.34 and 1.16eV, respectively, while the chromophore FTC exhibited a ΔE (CV) value of 1.529 eV. [27] This comparison demonstrated that the new tetrahydroquinoline-based donor narrowed the energy gap indicating the excellent charge-transfer of the tetrahydroquinoline-based chromophore.

As shown in Fig. 4, it can be concluded that the LUMO energy levels are approximately the same for chromophores L1 and L2. Conversely, chromophores L1 and L2 showed oxidation potential versus ferrocene/ferrocenium at 0.266 V, and 0.099 V, respectively. The gradual decrease of the oxidation potentials were dictated by the progressively increased strength of the donor group. The HOMO energy levels are systematically lowered with an increase in the donor strength which influences the HOMO to a greater extent than the LUMO level. From the λ_{max}, the cutoff wavelength ($\lambda_{cut\text{-}off}$) and the energy gap between the HOMO and LUMO energy of chromophores L1 and L2, we could conclude that the strength of electron donor shows an increase by replacing the alkyl chain group with the electron-rich *N*-(4-dimethylaminophenyl) substituent.

Table 2 Summary of DFT, electro-chemical data and EO coefficients of chromophores

Cmpd	$\Delta E(DFT)^a$ (eV)	$\Delta E(CV)^b$ (eV)	$\beta_{tot}{}^c$ (10^{-30}esu)	μ^d （D）	μβ (10^{-48}esu)	r_{33} (pm/V)
FTC	2.034	1.53	652.08	21.28	13876.2	39
L1	1.976	1.34	722.40	21.47	15509.9	57
L2	1.937	1.16	802.46	24.93	20005.3	100

$\Delta E(DFT)^a$ was calculated from DFT calculations. $\Delta E(CV)^b$ was calculated from their corresponding oxidation and reduction potentials. $\beta_{tot}{}^c$ is the first-order hyperpolarizability, and where calculated from DFT quantum mechanical methods. μ^d is the total dipole moment.

Table 3 The Molecular Orbital Composition (%) in the Ground State for Chromophores FTC, L1 and L2.

Chromophore	L2		L1		FTC	
	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
donor	60.54%	15.07%	58.95%	15.65%	54.88%	14.72%
π bridge	24.56%	39.84%	25.40%	39.82%	27.46%	40.20%
acceptor	14.90%	44.35%	15.66%	44.53%	17.67%	45.08%
D'	8.29%	0.74%				

The molecular orbital composition was calculated using Multiwfn program with Ros-Schuit (SCPA) partition.

To understand the ground-state polarization and microscopic NLO properties of the designed chromophores, the DFT calculations were carried out at the B3LYP level by employing the split valence 6-31G basis set using the Gaussian 09 program package. [28, 29] The first hyperpolarizability (β) were carried out at the cam-B3LYP level by employing the split valence 6-31G basis set using the Gaussian 09 program package. [29] All molecules were assumed to be in trans-configurations.[20, 30] The HOMO-LUMO energy gap, dipole moment (μ), and β of the chromophores obtained from DFT calculations are summarized in Table 2.

The HOMO-LUMO energy gap was used to understand the charge transfer interaction occurring in a chromophore molecule. [20, 31] Fig.6 depicts the electron density distribution of the HOMO and LUMO structures. It can be seen that the density of the ground and excited state electron is asymmetry along the dipolar axis of the chromophores. The HOMO-LUMO energy gaps ΔE (DFT) were also calculated by DFT calculations as shown in Table 2. The energy gaps between the HOMO and LUMO energy for chromophores FTC, L1 and L2 were 2.034, 1.976, and 1.937 eV, respectively. The DFT calculations are corroborated by the electrochemical values. Trends of energy gaps between ΔE (DFT) and ΔE (CV) for the chromophores were found to be consistent. As ΔE is reduced, resulting in a bathochromic shift of λ_{max} within the series of compounds. These results correspond with the conclusion of UV-Vis spectra analysis.

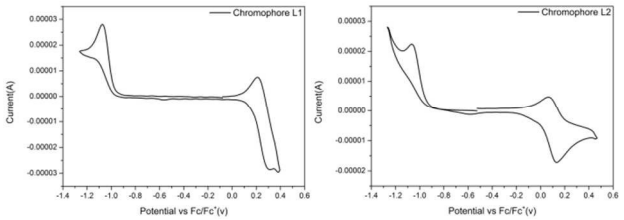


Fig. 4 Cyclic voltammograms of chromophores L1 and L2 recorded in CH_3CN solutions containing 0.1 M Bu_4NPF_6 supporting electrolyte at a scan rate of 100 mV s^{-1}.

The HOMO-LUMO energy gap is used to understand the charge transfer interaction that occurs within a molecular, In

many cases, not only HOMO and LUMO states, the transitions related with HOMO-1, -2 and LUMO+1, +2 states are strongly contributed in such long conjugated materials.[32] So, the combined molecular orbital energy level graph constituted by LUMO+2 to HOMO-2 for all the three chromophores is given in Figure 5. The energy gap of chromophore L2 is smaller than that of the chromophores FTC and L1.

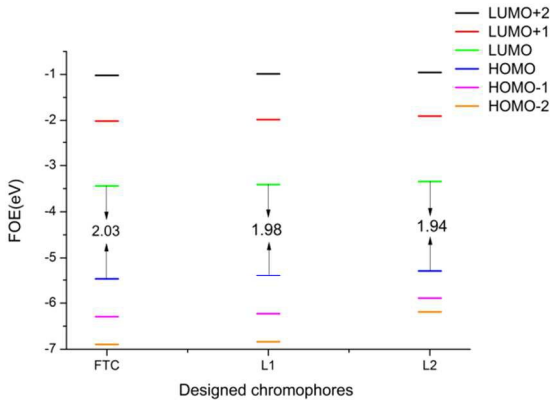


Fig. 5 Molecular orbital energy level diagram of the designed chromophores

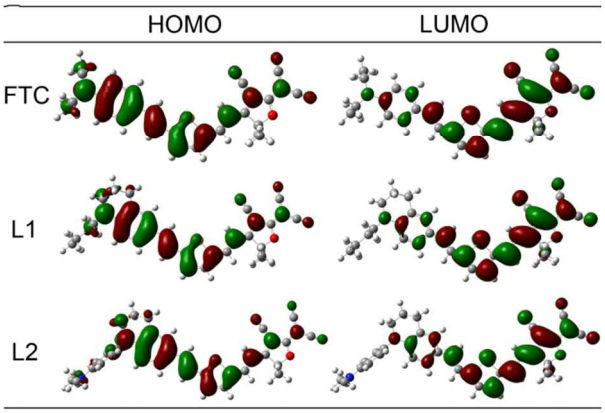


Fig. 6 Frontier molecular orbitals HOMO and LUMO of chromophores FTC, L1 and L2

To get more information from the frontier orbitals, the composition of the HOMOs and LUMOs has been calculated using the Multiwfn program. [32] As shown in Table 3, the whole chromophore molecule was segmented as donor, π-bridge, and acceptor. At the same time, the attribution of the *N*-(4-dimethylaminophenyl) substituent located in donor moiety of chromophore L2 was listed separately. For the three chromophores, the LUMO was largely stabilized by the contributions from acceptor (44.35%-45.08%) and the π-bridge (39.82%-40.20%), while the HOMO was largely stabilized by the contributions from donors (54.88%-60.54%) and π-bridge (24.56%-27.46%). For the chromophore L2, when compare LUMO to HOMO level, the contribution of *N*-(4-dimethylaminophenyl) substituent (D') decreased to 0.74% from 8.29% .The comparison of HOMO and LUMO electron distribution in the *N*-(4-dimethylaminophenyl) substituent indicated the easy delocalization of electrons in the *N*-(4-dimethylaminophenyl) substituent. Consequently, it can be treated as another donor, which efficiently enhances the electron density of the conjugated system and increases the polarizability of chromophore L2. [30]

The dipole moment (μ), and first hyperpolarizability (β) and the molecular quadratic hyperpolarizability (μβ) of the chromophores obtained from DFT calculations are calculate as shown in Table 2. When used carefully and consistently, this method of DFT has been shown to give relatively consistent descriptions of first-order hyperpolarizability for a number of similar chromophores. [33, 34]

Based on the "two level model", [35] β value is associated with the energy gap between HOMO and LUMO. Chromophore with lower energy gap indicates enhanced π-electron delocalization efficiency and may get a larger molecular hyperpolarizability β and μ. As expected, the attachment of stronger donor groups causes an increase of μ, β and μβ as shown in Table 2. The β value of chromophore L1 and L2 were larger than that of chromophore FTC due to narrower energy gap between HOMO and LUMO. With additional electron-rich *N*-(4-dimethylaminophenyl) substituent into the donor moiety, the chromophore L2 show stronger donor strength than chromophore L1 thus results in larger β and μβ. The more powerful the donor, the easier the charge separation, leading to larger β values in these chromophores. The influence of donor groups on the absorption charge-transfer band (λ_{max}: L2> L1) totally reflects the result of β values (β: L2> L1). The trend of increasing λ_{max} is in good agreement with the trend of increasing β value.

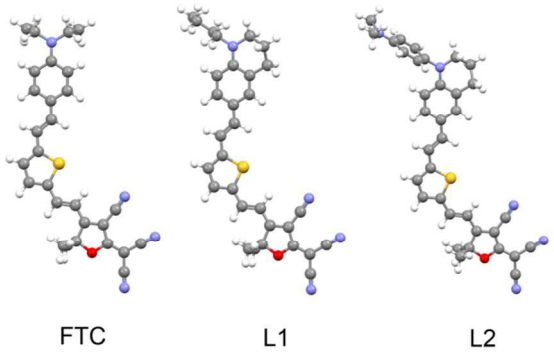


Fig. 7 Optimized structures of chromophores FTC, L1 and L2.

The geometrically optimized structures of the molecules were investigated as shown in Fig. 7. As for chromophore L2, the *N*-(4-dimethylaminophenyl) substituent located on the donor made a large dihedral angle of about 90° with average plane of

the chromophore. This large dihedral angle caused large steric hindrance that suppressed aggregations among molecules.

2.5 Electro-Optic performance

In order to investigate the translation of the microscopic hyperpolarizability into macroscopic EO response, the polymer films doped with 25wt% chromophores into amorphous polycarbonate (APC) were prepared using dibromomethane as solvent. The resulting solutions were filtered through a 0.2-μm PTFE filter and spin-coated onto indium tin oxide (ITO) glass substrates. Films of doped polymers were baked at 80 °C in a vacuum oven overnight. The corona poling process was carried out at a temperature of 10 °C above the glass transition temperature (T_g) of the polymer. The r_{33} values of poled films were measured by Teng–Man simple reflection method at a wavelength of 1310 nm using carefully selected thin ITO electrode with low reflectivity and good transparency in order to minimize the contribution from multiple reflections. [28, 36]

When the intermolecular electrostatic interactions are neglected, the electro-optic coefficient (r_{33}) should increase linearly with chromophore density, dipole moment, first hyperpolarizability and the strength of electric poling field. But chromophores with large dipole moment generate intermolecular static electric field dipole-dipole interaction, which leads to the unfavorable antiparallel packing of chromophores. So the number of truly oriented chromophore is small. In molecular optimization, introducing the huge steric hindrance group to isolate chromophores is the most popular and easy way to attenuate the dipole-dipole interactions of chromophores. [37] To achieve high EO coefficient, the chromophore should have facile intra charge transfer ability. The π-π stacking interactions and inter-molecular charge transport between chromophores should be reduced. In order to balance the steric hindrance and the molecular free mobility for chromophore acentric alignment in guest host EO polymer, the poling condition also should be carefully explored.[38]

The poled films of FTC/APC, L1/APC and L2/APC afforded r_{33} values of 39, 57 and 100 pmV^{-1} at 1310 nm, respectively. In these chromophores, the r_{33} values were gradually improved from 39 pm/V to 100 pm/V, illustrating that the increases donor strength of the chromophores significantly increase their macroscopic EO activities. The stronger the electron-donating power of the donor leads to higher λ_{max}, μβ, and r_{33} value. [18] Besides, solvatochromic behaviour indicated that chromophores L1 and L2 are more easily polarizable than chromophore FTC. Therefore, in corona poling, chromophores L1 and L2 may obtain orientation more easily in contrast with chromophore FTC. The long alkyl chain and the ring-fused alkyl chain structures in chromophore L1 can provides effective site isolation to decrease the strong electrostatic interactions among chromophores.

As reported earlier, 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.[39] As for chromophores L2, the *N*-(4-dimethylaminophenyl) substituent located on the donor which almost perpendicular to the average plane of the chromophore was intended to prevent the strong electrostatic interactions between chromophores. The undesired antiparallel packing between chromophores is expected to decrease during the poling process. [18] The large r_{33} value of chromophores L2 may be attributed to the strong donor ability and the isolated group in the donor moiety. Although the μβ value of chromophore L2 is only 29 % larger than that of chromophore L1, the r_{33} value is almost 73% larger due to a better isolation effect. Moreover, the chromophore L2 showed 44 % larger μβ and more than two times higher r_{33} value than that of traditional chromophore FTC. So the chromophore L2 has not only a larger μβ but also advantages in translating μβ into the macroscopic EO activity due to additional donor nitrogen heteroatom and isolation effect of *N*-(4-methoxyphenyl) substituent.

3. Conclusion

Two novel second-order nonlinear optical chromophores based on modified tetrahydroquinolinyl donor groups have been synthesized and systematically characterized. Theoretical and experimental investigations suggest that donor group's efficacy in chromophores L1 and L2 were higher than that of traditional chromophore FTC. Cyclicvoltammetry (CV) measurements and DFT calculations show that chromophores L1 and L2 have reduced energy gap, much larger β than that of chromophore FTC. In electro-optic activities, the doped film L1/APC containing chromophore L1 displays a maximum r_{33} value of 57 pm/V at the doping concentration of 25 wt%. This value is much higher than the EO activity of the chromophores FTC (39 pm/V). The introduction of the electron-rich *N*-(4-methoxyphenyl) substituent to the donor of chromophore L2 can further increase its r_{33} value to 100 pm/V. Those outcomes indicate that chromophore L2 with additional donor *N*-(4-dimethylaminophenyl) substituent to the donor group could efficiently reduce the interchromophore electrostatic interactions and enhance the macroscopic optical nonlinearity. High r_{33}values, high thermal stability, together with good solubility, showed that the modified tetrahydroquinolinyl donor groups show promising applications in nonlinear optical (NLO) chromophore devices. All these might be useful in designing other new NLO chromophores with modified donor groups to optimize molecular structure for achieving high performance.

4. Experimental

4.1 Materials and instrument

All chemicals are commercially available and are used without further purification unless otherwise stated. *N, N*-dimethylformamide (DMF), Phosphorusoxychloride ($POCl_3$), tetrahydrofuran (THF) and ether were distilled over calcium hydride and stored over molecular sieves (pore size 3Å). 2-Dicyanomethylene-3-cyano-4-methyl-2,5-dihydrofuran(TCF) acceptor was prepared according to the literature. [40] *N,N*-

diethylaniline based chromophore FTC was synthesized according to literature. [27] TLC analyses were carried out on 0.25 mm thick precoated silica plates and spots were visualized under UV light. Chromatography on silica gel was carried out on Kieselgel (200-300 mesh).

^{1}HNMR spectra were determined on an Advance Bruker 400M (400 MHz) NMR spectrometer (tetramethylsilane as internalreference). 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^{-1} under the protection of nitrogen. Cyclic voltammetric data were measured on a BAS CV-50W voltammetric analyzer using a conventional three-electrode cell with Pt metal as the working electrode, Pt gauze as the counter-electrode, and Ag/$AgNO_3$ as the reference electrode at a scan rate of 100 mV s^{-1}. The 0.1 M tetrabutylammonium hexa-fluorophosphate (TBAPF) in acetonitrile is the electrolyte. The melt points were obtained by TA DSC Q10 under N_2 at a heating rate of 10 °C min^{-1}.

4.2 Syntheses

4.2.1 Synthesis of 1-butyl-1,2,3,4-tetrahydroquinoline (Compound 2a)

Under a N_2 atmosphere, anhydrous potassium carbonate (8.29 g, 60 mmol) and Potassium iodide (162 mg, 9.8×10^{-2} mmol) were added to a solution of compound 1 (4.00 g, 30 mmol) and compound n-C_4H_9Br (4.93 g, 36 mmol) in DMF (120 mL). The mixture was allowed to stir at 120 ºC for 12 h and then poured into water. The organic phase was extracted by AcOEt, washed with brine and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography, eluting with (Acetone: Hexane=1:10) to give compound 2a as a yellow oil with 91.3% yield (5.18 g, 27.39 mmol). MS (EI) (M^+, $C_{13}H_{19}N$): calcd: 189.30; found: 189.15. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (t, J = 7.7 Hz, 1H，ArH), 6.97 (d, J = 7.1 Hz, 1H, ArH), 6.59 (m, 2H, ArH), 3.35 – 3.23 (m, 4H, NCH_2), 2.79 (m, 2H, CH_2), 2.04 – 1.90 (m, 2H, CH_2), 1.68 – 1.56 (m, 2H,CH_2), 1.41 (m, 2H, CH_2), 1.01 (t, J = 7.3 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.70, 129.31, 127.24, 122.46, 115.49, 110.78, 51.50, 49.70, 28.80, 28.48, 22.58, 20.69, 14.19.

4.2.2 Synthesis of 4-(3,4-dihydroquinolin-1(2*H*)-yl)-*N*,*N*-dimethylaniline (Compound 2b)

Under a N_2 atmosphere, potassium tert-butylate (3.36 g, 26.00 mmol), palladium acetate(24 mg, 10.8×10^{-2}mmol), tri-tert-butylphosphine (384mg, 2.00mmol) and 4-bromo-*N,N*-dimethylaniline(4.00g, 20.00mmol) was added to a solution of compound 1 （2.67 g，20.00 mmol） in toluene (80ml). The mixture was refluxed for 3 days under N_2 atmosphere. After the reaction was complete, the mixture was filtered and the filtrate washed with saturated aqueous ammonium chloride. After drying the filtrate over anhydrous sodium sulfate, the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography, eluting with (Acetone: Hexane=1:10) to give compound 2b as a white solid in 87.3% yield (4.41g, 17.46mmol). M.p. : 85.9 ºC. MS (EI) (M^+, $C_{17}H_{20}N_2$): calcd: 252.35; found: 252.15. ^{1}H NMR (400 MHz, d_6-acetone) δ 7.09 (d, J = 8.8 Hz, 2H，ArH), 6.94 (d, J = 7.3 Hz, 1H,ArH), 6.83 – 6.79 (m, 3H,ArH), 6.53 (t, J = 7.3 Hz, 1H,ArH), 6.35 (d, J = 8.2 Hz, 1H,ArH), 3.55 – 3.52 (m, 2H,NCH_2), 2.96 (s, 6H,NCH_3), 2.83 (t, J = 6.4 Hz, 2H,CH_2), 2.04 (m, 2H,CH_2). ^{13}C NMR (100 MHz, Acetone) δ 149.83, 147.44, 138.90, 130.23, 128.70, 127.40, 123.55, 117.66, 115.08, 114.82, 52.93, 41.26, 28.74, 23.69.

4.2.3 Synthesis of 1-butyl-1,2,3,4-tetrahydroquinoline-6-carbaldehyde (Compound 3a)

DMF (2.92 g, 40.00 mmol) was added to freshly distilled $POCl_3$ (3.83 g, 25.00 mmol) under an atmosphere of N_2 nitrogen at 0 °C, and the resultant solution was stirred until its complete conversion into a glassy solid. After the addition of 2a (3.79 g, 20.00 mmol) in 1,2-dichloroethane (60 mL) dropwise, the mixture was stirred at room temperature overnight, then poured into a saturation aqueous solution of sodiumacetate (300 mL). After 2 hour stirring at room temperature, the mixture extracted with chloroform (5 × 30 mL), and the organic fractions were collected and dried over anhydrous $MgSO_4$. The crude product was purified through a silica gel chromatography eluting with (Acetone: Hexane = 1:5) to afford a yellow oil 3a in 76.8% yield (3.34 g, 15.36mmol). MS (EI) (M^+, $C_{14}H_{19}NO$): calcd: 217.31; found: 217.15. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (s, 1H，CHO), 7.47 (d, J = 8.7 Hz, 1H,ArH), 7.36 (s, 1H,ArH), 6.51 (d, J = 8.7 Hz, 1H,ArH), 3.32 – 3.28 (m, 2H,NCH_2), 3.27 – 3.23 (m, 2H,NH_2), 2.68 (t, J = 6.2 Hz, 2H,CH_2), 1.86 (dt, J = 11.9, 6.1 Hz, 2H,CH_2), 1.54 (dt, J = 15.1, 7.6 Hz, 2H,CH_2), 1.40 – 1.26 (m, 2H,CH_2), 0.94 (t, J = 7.4 Hz, 3H,CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.51, 150.23, 130.87, 130.21, 124.49, 121.51, 109.19, 51.01, 49.59, 28.26, 27.58, 21.39, 19.97, 13.54.

4.2.4 Synthesis of 1-(4-(dimethylamino)phenyl)-1,2,3,4-tetrahydroquinoline-6-carbaldehyde (Compound 3b)

The procedure for compound 3a was followed to prepare 3b from 2b as orange solid in 79.4% yield (3.34 g, 11.91 mmol). M.p. : 137.5 ºC. MS (EI) (M^+, $C_{18}H_{20}N_2O$): calcd: 280.36; found: 280.16. ^{1}H NMR (400 MHz, CDCl3) δ 9.65 (s, 1H，CHO), 7.51 (s, 1H,ArH), 7.35 (dd, J = 8.6, 1.8 Hz, 1H,ArH), 7.10 (d, J = 8.9 Hz, 2H,ArH), 6.78 (d, J = 8.6 Hz, 2H,ArH), 6.39 (d, J = 8.6 Hz, 1H,ArH), 3.65 – 3.60 (m, 2H,NCH_2), 2.99 (s, 6H,NCH_3), 2.90 (t, J = 6.2 Hz, 2H,CH_2), 2.13 – 1.97 (m, 2H,CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.95, 151.38, 149.18, 135.18, 130.90, 129.96, 127.87, 125.62, 121.41, 113.56, 112.57, 52.14, 40.66, 27.33, 21.70.

4.2.5 Synthesis of (*E*)-1-butyl-6-(2-(thiophen-2-yl)vinyl)-1,2,3,4-tetrahydroquinoline (Compound 4a)

NaH (0.59 g, 25.00 mmol) was added to a stirred solution of compound 3a (1.09 g, 5.00 mmol) and 3c (3.47 g, 6.00 mmol) in THF (100 mL) under nitrogen. The solution was stirred for 24 h and then poured into water. The organic phase was extracted by AcOEt, washed with brine and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography, eluting with (Acetone: Hexane = 1:20) to give compound 4a as yellow oil in 85.2% yield (1.27 g, 4.26 mmol). MS (EI) (M^+, $C_{19}H_{23}NS$): calcd: 297.46; found: 297.16. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.15 (m, 2H，ArH), 7.02 (d, J = 4.3 Hz, 1H,CH), 6.95 (d, J = 3.3 Hz, 1H,CH), 6.92 (s, 1H,ArH), 6.86 – 6.79 (m, 1H), 6.39 (d, J = 11.9 Hz, 1H,CH), 6.33 (d, J = 11.9 Hz, 1H，CH), 3.24 – 3.20 (m, 2H，NH_2), 3.19 – 3.15 (m, 2H，NCH_2), 2.63 (t, J = 6.3 Hz, 2H，CH_2), 1.86 (m, 2H,CH_2), 1.51 (m,2H,CH_2), 1.30 (m, 2H,CH_2), 0.88 (t, J = 7.3 Hz, 3H,CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.82, 133.76, 133.61, 129.79, 128.67, 127.79, 127.10, 126.40, 124.38, 119.65, 110.07, 51.19, 49.42, 30.89, 28.40, 22.16, 20.41, 13.82.

4.2.6 Synthesis of (*E*)-*N*,*N*-dimethyl-4-(6-(2-(thiophen-2-yl)vinyl)-3,4-dihydroquinolin-1(2*H*)-yl)aniline (Compound 4b)

The procedure for compound 4a was followed to prepare 4b from 3b and 3c as orange solid in 83.9% yield (1.51 g, 4.19 mmol). M.p. : 124.2 ºC. MS (EI) (M^+, $C_{23}H_{24}N_2S$): calcd: 360.52; found: 360.18. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (m, 2H,ArH), 7.07 – 7.03 (m, 1H,ArH), 7.01 (d, J = 5.1 Hz, 1H,CH), 6.98 (s, 1H,ArH), 6.96 – 6.93 (m, 1H,CH), 6.89 (d, J = 4.1 Hz, 1H,CH), 6.85 – 6.76 (m, 1H,ArH), 6.70 (d, J = 7.4 Hz, 2H,ArH), 6.43 (d, J = 11.7 Hz, 1H,CH), 6.37 (d, J = 11.7 Hz, 1H,CH), 3.51 (m, 2H,NCH_2), 2.88 (s, 6H,NCH_3), 2.85 – 2.66 (m, 2H,CH_2), 2.01 – 1.97 (t, J=6.3Hz,2H,CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.30, 145.75, 143.99, 140.66, 137.05, 128.90, 127.41, 127.27, 126.29, 125.51, 124.90, 124.11, 122.64, 117.09, 113.99, 113.52, 51.78, 40.62, 27.46, 22.44.

4.2.7 Synthesis of (*E*)-5-(2-(1-butyl-1,2,3,4-tetrahydroquinolin-6-yl)vinyl)thiophene-2-carbaldehyde (Compound 5a)

Under a N_2 atmosphere, 4a (0.59 g, 2.00 mmol) was dissolved in 150 mL freshly distilled THF and cooled to -78 °C. Approximately 2 equivalents of BuLi in hexanes (16 mL, 4 mmol) was added drop wise over 20 min. Reaction continued at -78 °C for 1 h at which time DMF (0.29 g, 4.00 mmol) was added over 1 min. The reaction was allowed to reach RT while the solution stirred for 1h. The organic phase was extracted by AcOEt, washed with brine and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography, eluting with (Acetone: Hexane = 1:5) to give compound 6c as a red oil with 76.9% yield (0.50 g, 1.54 mmol). MS (EI) (M^+, $C_{20}H_{23}NOS$): calcd: 325.47; found: 325.16. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H，CHO), 7.60 (d, J = 3.9 Hz, 1H,CH), 7.19 (dd, J = 8.6, 2.0 Hz, 1H,ArH), 7.11 (s, 1H,ArH), 7.03 (m, 2H,CH), 6.94 (d, J = 15.9 Hz, 1H,CH), 6.53 (d, J = 8.6 Hz, 1H,ArH), 3.34 – 3.30 (m, 2H,NCH_2), 3.30 – 3.25 (m, 2H,NCH_2), 2.75 (t, J = 6.3 Hz, 2H,CH_2), 1.99 – 1.88 (m, 2H,CH_2), 1.59 (m, 2H,CH_2), 1.49 – 1.32 (m, 2H,CH_2), 0.97 (t, J = 7.3 Hz, 3H,CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.12, 154.69, 146.10, 139.76, 137.50, 133.83, 127.62, 126.59, 124.57, 122.79, 122.14, 115.12, 109.98, 51.17, 49.50, 28.44, 28.12, 21.90, 20.25, 13.94.

4.2.8 Synthesis of (*E*)-5-(2-(1-(4-(dimethylamino)phenyl)-1,2,3,4-tetrahydroquinolin-6-yl)vinyl)thiophene-2-carbaldehyde (Compound 5b)

The procedure for compound 5a was followed to prepare 5b from 4b as a red solid in 73.7% yield (0.57 g, 1.47 mmol). M.p. : 151.5 ºC. MS (EI) (M^+, $C_{24}H_{24}N_2OS$): calcd: 388.53; found: 388.16. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H,CHO), 7.61 (d, J = 3.9 Hz, 1H,CH), 7.17 (s, 1H,ArH), 7.12 (d, J = 8.7 Hz, 2H,ArH), 7.07 – 7.05 (m, 1H,ArH),7.04(d, J=16.0Hz, 1H,CH) 7.03 (d, J = 3.9 Hz,1H,CH), 6.95 (d, J = 16.0 Hz, 1H,CH), 6.78 (d, J = 7.1 Hz, 2H,ArH), 6.42 (d, J = 8.4 Hz, 1H,ArH), 3.63 – 3.56 (m, 2H,NCH_2), 2.98 (s, 6H,NCH_3), 2.88 (t, J = 6.3 Hz, 2H,CH_2), 2.11 – 2.01 (m, 2H,CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.25, 154.46, 148.76, 146.99, 139.98, 137.66, 136.37, 133.58, 127.99, 127.72, 125.97, 124.72, 124.16, 122.40, 115.71, 113.76, 113.39, 51.87, 40.77, 27.92, 22.10.

4.2.9 Synthesis of 2-(4-((E)-2-(5-((E)-2-(1-butyl-1,2,3,4-tetrahydroquinolin-6-yl)vinyl)thiophen-2-yl)vinyl)-3-cyano-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (Chromophore L1)

To a solution of 6a (0.16 g, 0.50mmol) and the TCF acceptor (0.12 g, 0.60 mmol) in MeOH (60 mL) was added several drops of triethyl amine. The reaction was allowed to stir at 78 ºC for 5 h. The reaction mixture was cooled and green crystal precipitation was facilitated. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography, eluting with (AcOEt: Hexane = 1:5) to give chromophore A as a green solid in 43.3% yield (0.11 g, 0.22 mmol). M.p. : 192.0 ºC. HRMS (ESI) (M^+, $C_{31}H_{30}N_4OS$): calcd: 507.2219; found:507.2198. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 15.6 Hz, 1H，CH), 7.35 (d, J = 4.0 Hz, 1H, CH), 7.22 (d, J = 8.5 Hz, 1H, ArH), 7.14 (s, 1H, ArH), 7.05 (d, J = 15.8 Hz, 1H, CH), 7.01 (d, J = 4.0 Hz, 1H, CH), 6.97 (d, J = 15.8 Hz, 1H, ArH), 6.61 (d, J = 8.6 Hz, 1H, ArH), 6.54 (d, J = 15.6 Hz, 1H, CH), 3.40 – 3.35 (m, 2H, NCH_2), 3.33 – 3.27 (m, 2H, NCH_2), 2.78 (t, J = 6.2 Hz, 2H, CH_2), 2.02 – 1.92 (m, 2H, CH_2), 1.74 (s, 6H,CH_3), 1.62 (m, 2H,CH_2), 1.43 – 1.32 (m, 2H, CH_2), 0.97 (t, J = 7.3 Hz, 3H, CH_3). ^{13}C NMR (100MHz, $CDCl_3$) δ 181.59, 175.74, 153.93, 144.16, 139.27, 137.55, 137.47, 133.64, 127.07, 126.60, 126.16, 124.26, 117.47, 116.39, 112.05, 111.78, 99.60,

96.97, 52.39, 50.41, 30.86, 28.51, 26.47, 25.12, 24.34, 20.27, 13.90.

4.2.10 Synthesis of 2-(3-cyano-4-((E)-2-(5-((E)-2-(1-(4-(dimethylamino)phenyl)-1,2,3,4-tetrahydroquinolin-6-yl)vinyl)thiophen-2-yl)vinyl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (Chromophore L2)

The procedure for chromophore L1 was followed to prepare chromophore L2 from 5b as a green solid in 41.2% yield (0.12 g, 0.21 mmol). M.p. : 198.2 ºC. HRMS (ESI) (M^+, $C_{31}H_{30}N_4OS$): calcd: 570.2328; found:570.2303. ^{1}H NMR (400 MHz, Acetone) δ 8.11 (d, J = 15.8 Hz, 1H，CH), 7.78 – 7.72 (m, 2H，CH), 7.65 (d, J = 4.0 Hz, 1H，CH), 7.64 (d, J=15.8Hz, 1H, CH), 7.28 (s, 1H, ArH), 7.19 (d, J = 4.0 Hz, 1H, CH), 7.16 (d, J = 7.9 Hz, 1H, ArH), 7.10 (d, J = 8.9 Hz, 2H, ArH), 6.80 (m, 2H, ArH), 6.33 (d, J = 8.6 Hz, 1H, ArH), δ 3.63 – 3.58 (m, 2H，NCH_2), 2.97 (s, 6H，NCH_3), 2.87 (t, J=6.3, 2H，CH_2), 2.21 – 2.11 (m, 2H，CH_2), 1.88 (s, 6H，CH_3). ^{13}C NMR (101 MHz, Acetone) δ 185.96, 177.92, 158.64, 150.29, 141.08, 138.89), 135.60, 132.31, 130.90, 130.55, 128.77, 128.40, 127.73, 125.57, 123.66, 120.46, 116.42, 112.74, 112.22, 110.68, 105.57, 102.07, 57.33), 52.93, 41.13, 26.62, 23.97, 14.33.

Acknowledgments

All calculations were performed on the cluster of Key Laboratory of Theoretical and Computational Photochemistry, Ministry of Education, China. We are grateful to the National Natural Science Foundation of China (No. 11104284, No. 61101054 and No. 21003143) for the financial support.

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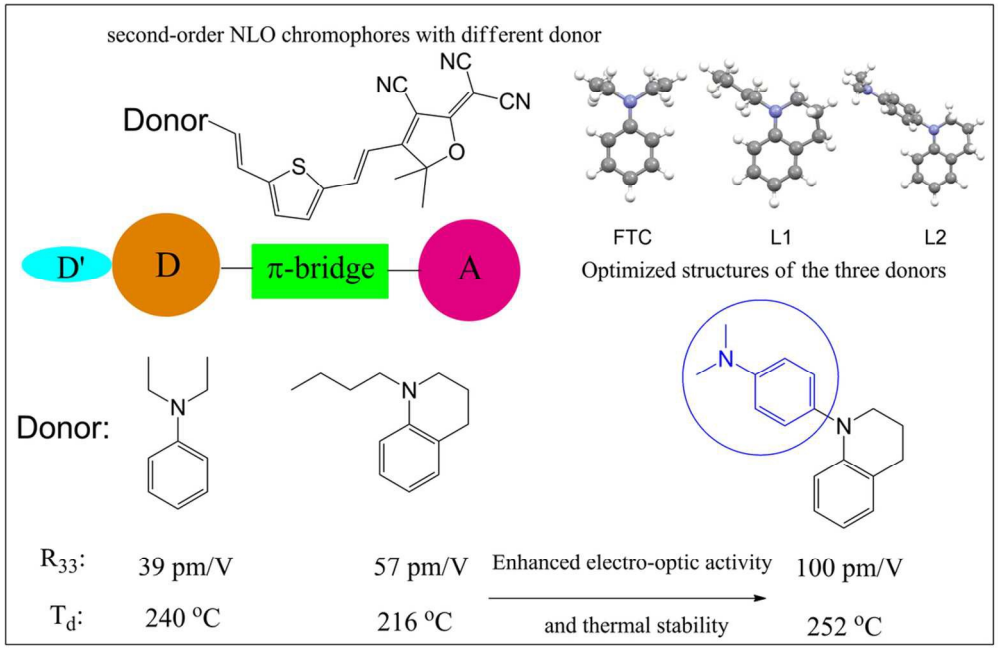

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