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Synthesis and characterizations of novel spindle-like terphenyl-type chromophores for non-linear optical materials

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ABSTRACT

A series of novel spindle-like terphenyl-type chromophores, based on 2,5-diphenyl-1,4-distyrylbenzene π-conjugating bridge, *N*,*N*-dimethyl and triphenyl amino donors, and Tricyanovinyldihydrofuran(TCF), 1,3,3-trimethyl-5-dicyanovinyl-1-cyclohexene (TDC) acceptors, have been synthesized successfully for the first time. And the non-linear optical properties were evaluated by using the finite-field (FF) method. The results show that, the first-order hyperpolarizability of the chromophores increase with the increase of the withdraw ability of the substituent group on the π-conjugating bridge.

1. Introduction

During the past decade, organic molecules for non-linear optical materials were deeply researched, because of their potential applications in ultrafast electro-optic modulations.[1–3] A lot of molecules with large hyperpolarizabilities and excellent thermal and chemical stabilities were synthesized.[4–6]

Most of those types of chromophores have the traditional one dimension D–π-A structures, the design and synthesis of donor–acceptor substituted hetero aromatic compounds have attracted widespread interest because it was experimentally and theoretically demonstrated that these structures could effectively improve the second-order non-linear optical (NLO) properties of the chromophores. The $\mu\beta$ values of these chromophores developed by Alex etc.[1c,3a] are even larger than $18\,000\times10^{-48}$ esu. At the same time, tetrapolar and octupolar[1d–h] molecules were researched widely, some interesting molecules, such as Λ, X, Y, and H, etc. types[7,8] were also developed and indicated good second-order linear optical properties. For the practical application of second-order NLO materials, the chromophores need to have a large hyperpolarizability, good thermal stability and low optical loss. In the recent years, terphenyl compounds have been deeply studied because of their excellent electro-optic properties in application of organic light-emitting diodes (OLED) and lasers.[9] In our view, these types of molecules have never been used in non-linear optical materials, and their unique structure could effectively prevent the aggregation of the chromophores in the poled films and greatly improve the temporal and long term stability.[10]

In pursuit of chromophores with large optical nonlinearity, thermal stability, and high optical transparency, many rules and principles have been proposed by Dewar, Dalton, Alex, etc.[11] By following Dalton's principles, the shape of the chromophores may play an important role in determining NLO response of the material, and spherical chromophores may be the ideal shape for NLO materials. Through this designation, Dalton found the spectra shift[1c] of intramolecule charge-transfer transition of chromophore when changing the molecule shapes.

Therefore, to achieve the major challenging topic of the nonlinearity-transparency trade-off, in this paper, we synthesized a series of novel chromophores (Chart 1) with terphenyl moiety as the conjugating bridge, tripenylamino and alkyl amino as the donor groups, Tricyanovinyldihydrofuran(TCF), 1,3,3-trimethyl-5-dicyanovinyl-1-cyclohexene (TDC) as accepters by a Suzuki coupling reaction and Wittig reaction, their structures were fully characterized by NMR, FTIR, elemental analysis, and differential scanning calorimeter (DSC) methods. Moreover, we explored the structure–property relationship by changing the substituent groups on the π-conjugating bridge from electron-donating group to electron-drawing group, which shows that the stronger of the electron-drawing ability, the larger of the first-order hyperpolarizability.

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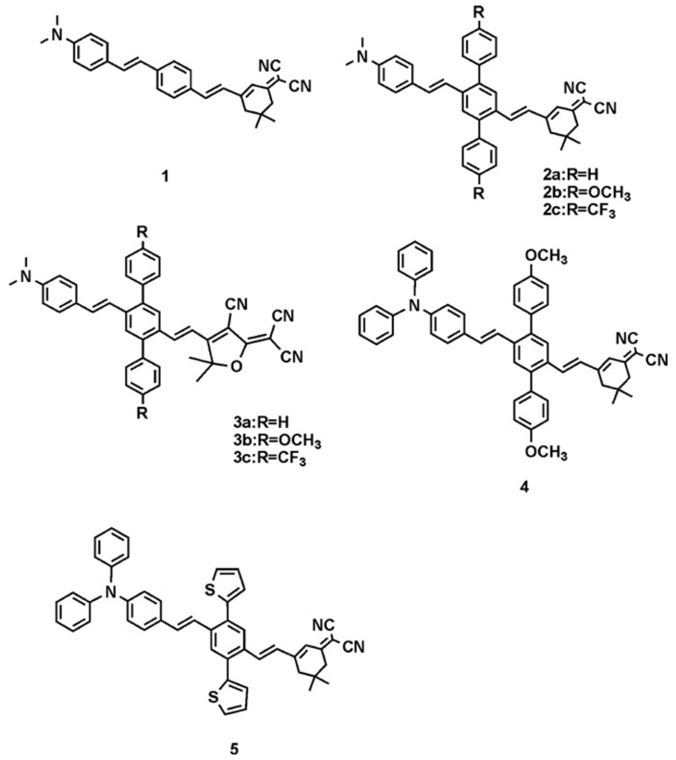


Chart 1. Structures of the chromophores.

2. Results and discussion

2.1. Synthesis and characterization

Scheme 1 shows the synthesis of the two electro-donor groups, *N*,*N*-dimethyl-phenylamino-triphenylphosphorus methyl bromide was directly synthesized according to Raimundo's report[12a] and synthesis of Triphenyl amino(TPA)-triphenylphosphorus methyl bromide(**6**) need three steps, first, single-aldehyde was prepared via Vilsmeier formylation in the presence of $POCl_3$ and *N*,*N*-dimethyl formylation(DMF); then it was reduced by sodium boron tetrahydride; Compound **6** was finally obtained by further reaction with triphenyl phosphorus bromide in high yields.

2,5-dibromo-1,4-dialdehyde-benzene (**7**) was prepared by the method similar with its isomer 1,2-dibromo-4,5-dialdehyde-benzene, which has been reported before.[9,12d]

The key intermediates terphenyl-1,4-dialdehydes compounds (**8a**–**c**) and 2,5-dithienyl-1,4-dialdehyde-benzene(**8d**) were readily prepared by a Pd(0)-catalyzed Suzuki cross-coupling reaction of 4-methoxyphenylboronic acid, 4-phenylboronic acid, 4-(trifluoromethyl) phenylboronic acid and thiophene-2-boronic acid with Compound **7**.

Synthesis of NLO chromophores containing diphenylphenyl and dithinylphenyl as the conjugating bridges is shown in Scheme 1. The compound **6** and two different acceptors, 1,3,3-trimethyl-5-dicyanovinyl-1-cyclohexene(TDC) and Tricyanovinyldihydrofuran (TCF) were used for the chromophore synthesis by the Knoevenagel condensation reactions.

To clarify the influence of the group substituted on the conjugating bridge, a series of aromatic groups, with electro-donor group or electro-acceptor group, were synthesized to systematically compare their electronic effect. Fig. 1 shows the ^1H NMR spectra of compound **8a**–**d**, and terephthalaldehyde served as a reference value. The reference value is located at 8.05 ppm, and any electron-withdrawing group introduced neighboring H_a, resulting in a downfield shift of H_a relative to 8.05 ppm. If the substitute is an electron-donating group, an upfield shift of H_a will be obtained.[13,14] From the Fig. 1 we can see that all of the aromatic substituted groups act as electro-drawing groups to make downfield chemical shift of H_a. Compared with compound **8a**, the chemical shift of H_a in compound **8b** and **8c** located at 8.06 ppm and 8.12 ppm, respectively. The chemical shift of H_a in compound **8d** is at 8.16 ppm suggesting that the thiophene group acts as a strong electron-withdrawing group. Compared to the unsubstituted compound **1**(reported by Qin[12c]), the electronic effect of aromatic groups at the conjugating bridge play great role, two aromatic H_b and H_c neighboring the aromatic substitutes in all chromophores experience significant deshielding of chemical shifts compared to the corresponding protons in compound **1** (7.45–7.48 ppm), which implies that the aromatic groups result in decreased electron density at the phenyl ring and cause the attached protons resonate at a lower field. While from ^1H NMR data, which are listed in Table 1, both of the chemical shift of H_b and H_c indicated the same trends. The 4-trifluoromethylphenyl and thienyl substituted chromophores exhibit electron-drawing effect to make the chemical shift move to a lower field, while 4-methoxyphenyl substituted chromophore exhibit electron-donating effect to make the chemical shift move to a higher field.

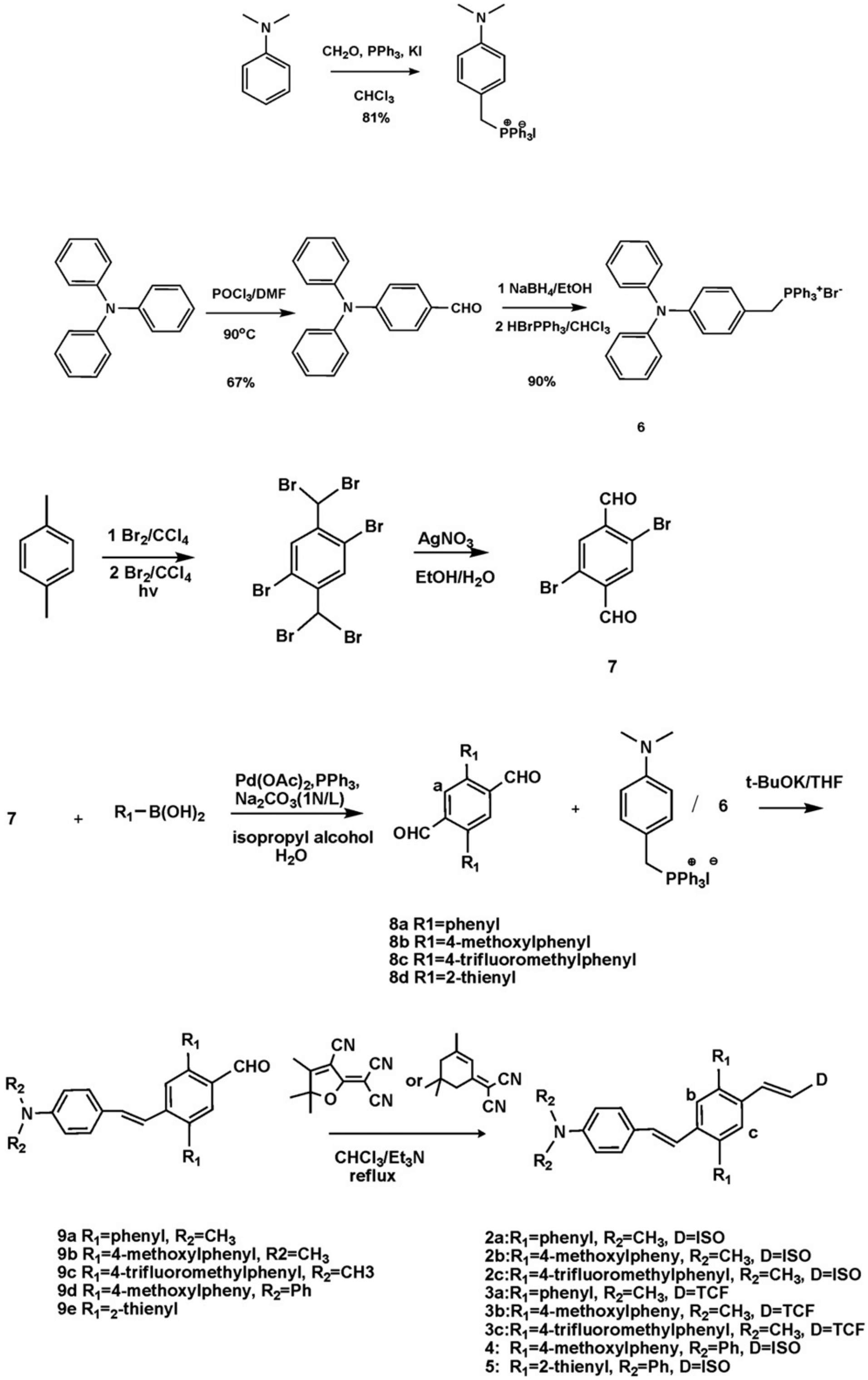
The UV–vis absorption spectra are employed to explore the differing π-conjugating bridge properties of the modified conjugating bridges. The UV–vis absorption spectra of compounds **1**, **2a**, **2b**, **4**, and **5** in dichloromethane are displayed in Fig. 2(a) and all of the photophysical data are listed in Table 2.

Compared to chromophore **1**, these spectra show multiple absorption peaks, and the lower-lying peaks are relatively strong. This relatively strong low-lying absorption in these chromophores maybe due to the $\pi-\pi^*$ transition of the aromatic ring substituted in the π-conjugating bridge. Replacing the π-conjugating bridge with the substituted phenyl group, has a profound effect on the charge-transfer bands resulting in 64 nm, and 43 nm, respectively, blue-shifted values for chromophores **2c** and **2b** (Fig. 2a). And it means that groups substituted in the π-conjugating bridge can greatly affect the transition states of these chromophores, and this variation maybe potentially influence their NLO properties.[15]

It should be noted that the λ_{max} of the compound **2a**–**c** are all red-shifted (35–62 nm), while compound **3a**–**c**, **4** and **5** are blue shifted (7–26 nm) upon increasing the solvent dielectric constant from CH_2Cl_2 to DMF (see Table 2). An extended solvatochromic study was attempted for Compound **5**; the spectra are overlain in Fig. 2b. While the charge-transfer band showed decent solvatochromic red-shift upon increasing the solvent dielectric constant, there appears to be a threshold for this behavior for compound **5** that there occurs a reversal of the λ_{max} upon increasing the dielectric constant to beyond 9.8 [CH_2Cl_2 and DMF (37.6) appear to favor excessive charge transfer in this compound] leading to back electron donation causing blue-shift from the absorption in chloroform. This confirms the concept that chromophores **5** are more strongly polarizable than **2a**–**c**.[14] The optimized structures of some of the chromophores are shown in Fig. 3.

2.2. Thermal stability

Thermal properties of these chromophores were explored by differential scanning calorimetry and are shown in Fig. 4. All of the compounds have a range of melting point (mp) of 200–300 °C, except chromophore **4** at about 165 °C. As shown in Table 2, all chromophores exhibit good thermal stability with onset decomposition temperatures over 200 °C. Substitutes on the terphenyl groups cause a significant decrease of decomposition temperatures (Td). An acceptor dependence of thermal stability was observed for the resulting NLO chromophores. **2a**–**c**, **4**, and **5** containing TDC group as electro-acceptor exhibited the highest



Scheme 1. Synthetic route of the terphenyl-type chromophores.

stability at up to 386 °C compared to corresponding chromophores with TCF as electro-acceptor (Fig. 5).

2.3. Non-linear optical properties

The static hyperpolarizability reflect the intrinsic polarization of the molecules at zero frequency, generally there are several method to measure the β values of chromophores, such as EFISH method based on the SHG signal and a solution-based hyper-Rayleigh scattering measurements for the important term $\beta_{HRS}(-2\omega;\omega,\omega)$.[7a,14,16–18] Theoretical calculation can help to rationalize the experimental results and rank the existing molecular structures according to their linear and non-linear susceptibilities prior to experiment and thus to propose new promising compounds to chemists.[19] In the past decade, advances in computer technology and methodology of molecular orbital calculation make it possible to calculate response properties

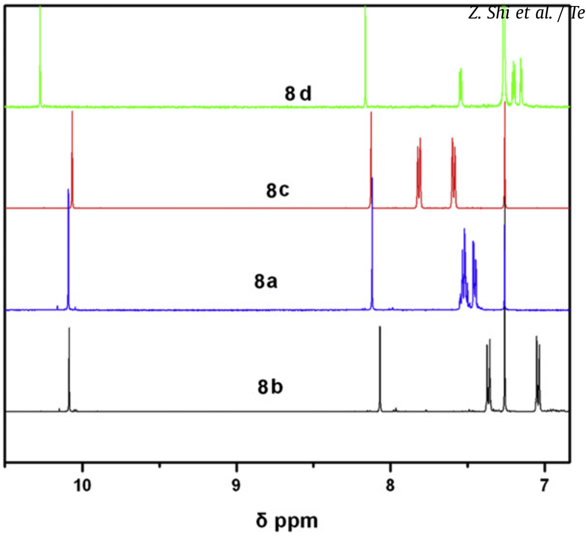


Fig. 1. ^1H NMR spectra of the compound **8a–d**.

Table 1
Chemical shift of the H_b and H_c in chromophores **2a–c** and **5**

	1	2a	2b	2c	4	5
H_b	7.45	7.68	7.68	7.77	7.66	7.72
H_c	7.45	7.73	7.69	7.79	7.69	7.91

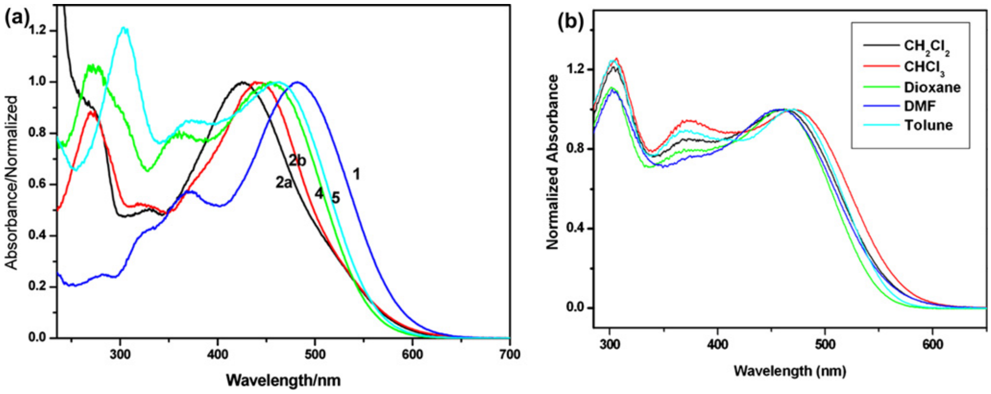


Fig. 2. (a) UV–vis spectra of the chromophores in CH_2Cl_2; (b) UV–vis spectra of chromophore **5** in different solvents varying dielectric constants (dioxane: 2.25; toluene: 2.38; $CHCl_3$: 4.81; CH_2Cl_2: 9.8; DMF: 37.6).

due to higher-order perturbation in molecular systems within a realistic computation time.[20] Moreover, the prediction values of new chromophores based on theoretical calculation, and often give very close results to experimental values.[18] Thus density functional theory (DFT) quantum mechanical methods were employed to determine theoretical β (0; 0,0) values for the chromophores.

Table 2
Summary of optical absorption data

Compd	λ_{max}(nm) CH_2Cl_2	λ_{max}(nm) DMF	ε($10^4M^{-1}cm^{-1}$)	ΔE(UV)[a](eV)	Td[b](°C)
1	482	486	4.8	2.10	250
2a	425	460	1.6	2.28	375
2b	439	481	3.03	2.29	350
2c	417.5	479	6.9	2.49	300
3a	473.5	447	1.2	2.09	297
3b	482	470.5	1.6	2.09	290
3c	498	474.5	2.1	2.05	290
4	453	446	4.2	2.23	386
5	464	457	3.33	2.20	350

[a] Estimated from the onset of the absorption at the low-energy edge in dichloromethane.

[b] Onset temperature for weight loss determined from TGA in nitrogen at a heating rate of 20 °C min^{-1}.

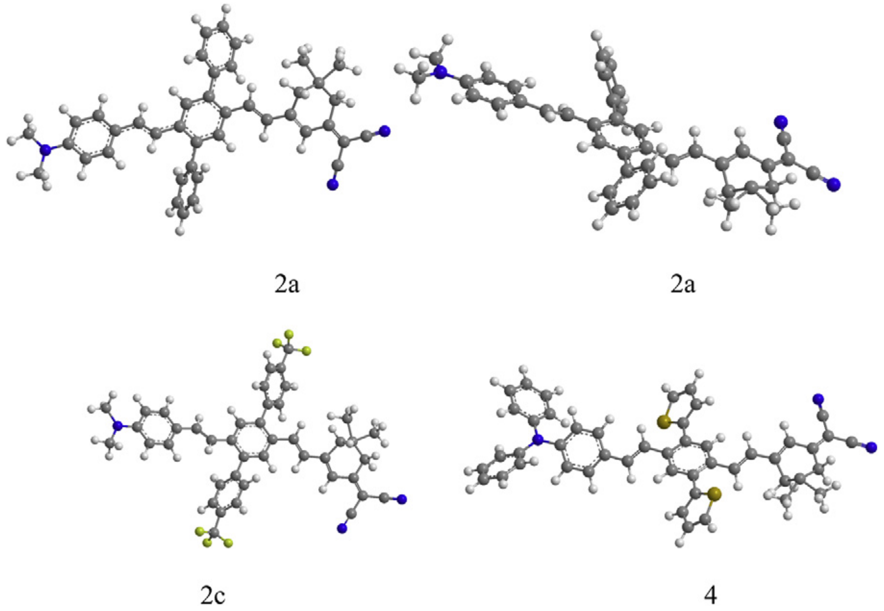
Properly selective method and basis set are the premise of accurate predication NLO response. The structures of our studied compounds are similar to that of *para*-nitroaniline (PNA). First PNA was taken as an example to test the reliability of our adopted method. The first-order hyperpolarizablity values of PNA using the B3LYP/6-31G* and B3LYP/6-311++G** are 6.62 and 7.99, respectively, which are very close to the experimental value (9.2).[20a] To save the computational time, the B3LYP/6-31G* was used in the following calculation.

The first-order hyperpolarizablity of all compounds were calculated by the FF and method at the B3LYP/6-31G* level. Due to the lack of experimental value, three kind of first-order hyperpolarizabilities value are calculated and given in Table 3. The results show that the β values of **2a–c** decreased in comparison with reference compound **1** when the π-conjugating bridge changed from phenyl to terphenyl-type groups. It may be caused by the bad delocalization of the intramolecular charge transparency, which was demonstrated by the UV study. Moreover, the first-order hyperpolarizabilities of these compounds (**2a–c**, **3a–c**) are related to the substituted group on the phenyl group of π-conjugating bridge. A substitution with an electro-drawing group CF_3 (**2c**) improves the NLO property, an electro-donating group OCH_3 (**2b**) displays a little decrease referenced with nonsubstituted compound **2a**. Compounds with TCF as the electro-acceptor group display larger β values than chromophores with TDC as the electro-acceptor. Introduction of TPA group in compound **4** and **5** enhanced second-order NLO properties. Finally we can conclude that the matching of suitable electro-donor and acceptor and a suitable electro-drawing substituted group on the π-conjugating bridge could play a great role in designing NLO chromophores with large β values.

2.4. Orientation stabilities of chromophores in poled films

Fig. 6 shows the UV–vis absorption spectrum of the poled films, from which we observe a decrease in absorption after poling. Furthermore, according to the absorbance change, we also estimated the order parameter ($\Phi=1-A_p/A_0$) of the two kinds of poled films (0.19 and 0.38, respectively, for polymers 1/PMMA and 2a/PMMA), which is related to the poling efficiency.[21] The result indicated that 2a/PMMA was poled more effectively than 1/PMMA in the same poling conditions, and it maybe due to the unique shape of the chromophores, which could decrease the intermolecular dipole–dipole interactions and chromophore aggregation.

Orientation stability of the poled film was also investigated by the depoling experiments, in which the UV–vis spectra of the poled films are monitored as the films stayed at room temperature in air


2a

2a

2c

4

Fig. 3. Some optimized molecular structures with AM1 method.

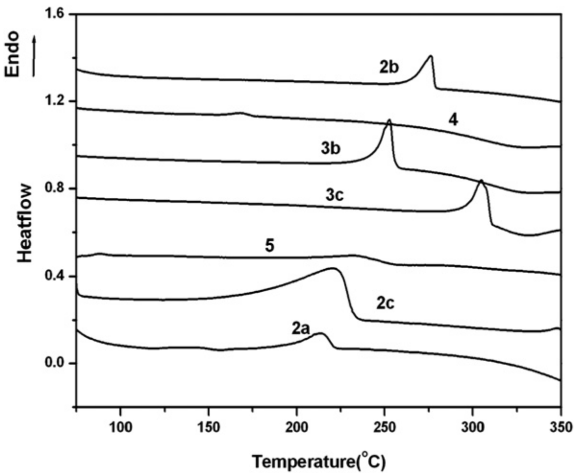


Fig. 4. DSC thermograms of chromophores **2a**–**c**, **3b**–**c**, **4**, and **5**.

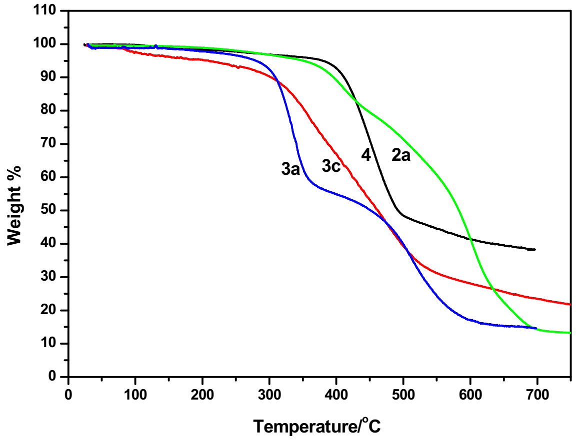


Fig. 5. TGA curves of chromophore **2a**, **3a**, **3c**, **4** in nitrogen with a heating rate of 20 °C min^{-1}.

with the time. After aging for 4 days, the order parameter (Φ) of the poled films decreased by 26%, 19%, respectively, for polymers 1/PMMA and 2a/PMMA (Fig. 6). The result suggests that the side groups could efficiently block the relaxation of the chromophores and keep good orientation stability.

3. Conclusions

In this paper, a shape controlling strategy for non-linear optical chromophores, with terphenyl π-conjugating bridge, was developed. On this shape-considering designation, a series of spindle-like chromophores based on terphenyl group were synthesized. The measurement results of UV–vis spectra demonstrated that the chromophores are remarkably different from the traditional one dimensional molecule as the reference compound, which cause a large blue-shift of the absorption band, and furthermore theoretical calculation demonstrated that the β values of these chromophores increased with the electro-drawing ability of the substituted group on the π-conjugating bridge. Thermal analysis also indicated that these chromophores exhibit very good thermal stabilities, the decomposition temperature even up to 386 °C. Therefore, this strategy could give a new way to solve the trade-off between nonlinearity and transparency in designing NLO chromophores.

4. Experimental

4.1. Materials

Tetrahydrofuran (THF) and 1,4-dioxane were purified by fractional distillation over sodium, Potassium *tert*-butoxide(Acros Organics), Tricyanovinyldihydrofuran(TCF), malononitrile, 1,3,3-trimethyl-5-dicyanovinyl-1-cyclohexene (TDC), and thiophene-2-boronic acid was prepared according to previous literatures.[6,12b] All other solvents and chemical reagents were used as received, without further purification.

4.2. Measurements

Nuclear magnetic resonance (NMR) spectra were measured on a Bruker AVANCE NMR spectrometer at a resonance frequency of

Table 3
Shows the molecular hyperpolarizabilities (β) of the resulting NLO chromophores calculated using the DFT method

	1	2a	2b	2c	3a	3b	3c	4	5
β_0/B3LYP	531.63	434.22	429.15	438.88	544.35	536.11	562.29	524.54	552.76
β_{vec}/B3LYP	−493.84	−386.02	−383.59	−388.50	−511.03	−501.43	−527.81	−432.29	−433.17
β_{HRS}/B3LYP	439.58	278.17	276.97	281.35	376.24	370.22	388.75	344.77	378.71

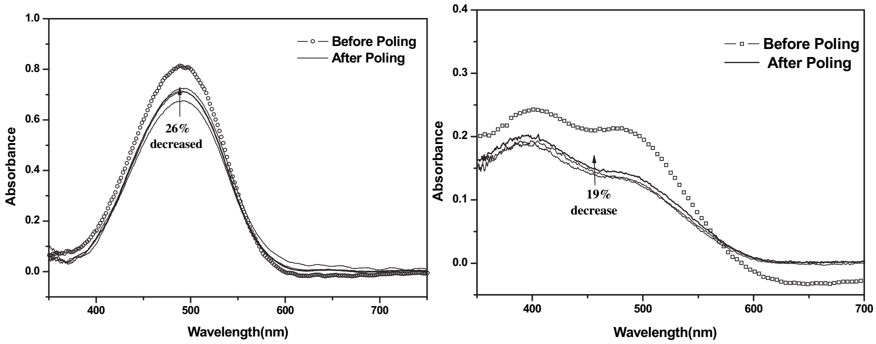


Fig. 6. UV–vis spectra of poled films (1/PMMA, left) compared to the poled films 2a/PMMA (right) varied with time in room temperature. Changes of the order parameter ($\Phi=1-A_p/A_0$) were monitored every 10 h for 4 days.

500 MHz for ^{1}H in CDCl$_3$, and TMS was used as internal standard. IR spectra were taken on an AVATAR 360 FTIR spectrometer. Elemental analysis was carried out with a FLASH EA 1112 SERIES elemental analyzer. The molecular weights were determined by high performance liquid chromatography-mass spectrometry (HPLC–MS) on an ANGILENT 1100 LC/MS. Differential scanning calorimeter (DSC) was performed with NETZSCH 4 at a scan rate of 10 °C/min under nitrogen. The software of DSC 204 on 18 TASC 414-4 was used to analyze the DSC curves. The decomposition temperature of the chromophore samples was analyzed using Perkin–Elmer TGA 7 thermogravimetric analyzer (TGA) at a heating rate of 10 °C/min in nitrogen. Thermal degradation temperatures were measured in the range 50–400 °C. Ultraviolet–visible (UV–vis) absorption spectra were measured on an SHIMADZUUV-3100 spectrophotometer.

4.3. Poling conditions

For studying the properties of chromophores in polymer materials, guest–host polymers were generated by mixing compounds **1** or **2a** (25 wt %) with poly(methylmethacrylate) (PMMA) using 1,1,2,2-tetrachloroethane as the solvent, the resulting solutions were filtered through 0.2 μm Teflon syringe filters and were spin coated onto precleaned indium tin oxide (ITO) glass substrates. A film thickness of 2.0±0.5 μm was obtained by using a spin rate in the range 850–1000 rpm. After baking at 60 °C under vacuum for 6–12 h in order to remove the solvent, the films were wire poled using a tungsten wire held parallel to and above the films (at a distance of 1 cm) under a poling field of 3.0 kV at 80 °C.

4.4. Synthesis

*4.4.1. (4-Diphenylamino)triphenylphosphorusbromide (**6**).* To a solution of triphenylamine(4.9 g, 20 mmol) in *N*,*N*-dimethyl formamide (DMF) (50 ml) was added POCl$_3$ (1.2 mL), the solution was stirred under ice-bath condition for 10 min. The reaction mixture was heated to 90 °C and stirred for 4 h. After cooling down to room temperature, the mixture was extracted with ethyl acetate three times. After evaporating the solvent, the mixture was added sodium borohydride in absolute ethanol (50 mL) and reacted for 2 h. After removing the solvent, the residue was added triphenyl phosphorus hydrobromide (6.86 g, 20 mmol) in CHCl$_3$. The solution was heated to reflux for 2 h. After removing the solvent, the residual solid was recrystallized in anhydrous ethyl ether to give the light green solid (7.2 g, 60% yield). Mp=249 °C. ^{1}H NMR (CDCl$_3$) *δ*: 5.36–5.38(d, *J*=14 Hz, 2H, CH$_2$), 6.79–6.81(d, *J*=8 Hz, 2H, Ph), 6.90–6.93(m, *J*=8.5 Hz, 2H, Ph), 6.99–7.03(m, *J*=8.5 Hz, 6H, Ph), 7.21–7.24(t, 4H, *J*=8.5, 7.5 Hz, Ph), 7.62–7.66(t, *J*=7.5 Hz, 6H, Ph), 7.75–7.79(t, 9H, *J*=7.5 Hz, Ph). ^{13}C NMR (125 MHz, CDCl$_3$, TMS): *δ* (ppm) 149.75, 145.91, 137.43, 136.26, 129.94, 129.65, 128.88, 128.71, 127.93, 126.98, 125.74, 50.14.

*4.4.2. 2,5-Dibromobenzene-1,4-dicarbaldehyde (**7**).* The reference method[12a] was modified using the *p*-xylene as starting material, resulted white solid (7.53 g, 96%). Mp=192–193 °C. ^{1}H NMR(CDCl$_3$): δ10.35 (s, 2H), 8.16 (s, 2H). MS (ESI), *m*/*z*: 291.0 $[M+H]^+$. ^{13}C NMR (125 MHz, CDCl$_3$, TMS): *δ* (ppm) 189.81, 137.27, 134.94, 125.47.

*4.4.3. 2,5-Terphenyl-dicarbaldehyde (**8a**).* Triphenyl phosphine (0.015 g, 0.06 mmol), palladium acetate (0.002 g, 0.01 mol), phenylboronic acid (0.24 g, 2 mmol), and **7** (0.29 g, 1 mmol) were added into a flask. A degassed mixture of isopropyl alcohol (10 ml), sodium carbonate (aq) (2 N/L, 3 ml), and water (1 ml) was transferred onto the solids, and the resulting solution was stirred under reflux at 70 °C for 4 h. The crude product was extracted with dichloromethane and washed with aq NaHCO$_3$. The organic layer was concentrated under vacuum and purified by column chromatography on silica gel eluting with petroleum/ethyl acetate (30:1) to give white crystals (0.27 g, 95%). ^{1}H NMR (500 MHz, CDCl$_3$, TMS): *δ* (ppm) 7.44–7.46(d, 4H, *J*=9.5 Hz, Ar), 7.50–7.53 (t, 6H, *J*=9.5 Hz, Ar), 8.11(s, 2H, Ar), 10.09(s, 2H, C*H*O). IR (KBr, cm^{-1}): 1665 (–CHO). ^{13}C NMR (125 MHz, CDCl$_3$, TMS): *δ* (ppm) 189.42, 150.17, 131.59, 130.47, 124.05, 123.91, 123.52, 121.74.

*4.4.4. 2,5-(4′,4″-Dimethoxy)-terphenyl-dicarbaldehyde (**8b**).* The procedure for **8a** was repeated with 4-methoxyphenylboronic acid (0.3 g, 2 mmol) and a reaction time of 12 h resulting a yellow crystal (0.29 g, 85%). ^{1}H NMR (500 MHz, CDCl$_3$, TMS): *δ* (ppm) 7.03–7.05(d, 4H, *J*=8.5 Hz, Ar), 7.35–7.37 (t, 4H, *J*=8.5 Hz, Ar), 8.06(s, 2H, Ar), 10.08(s, 2H, CHO). IR (KBr, cm^{-1}): 1660 (–CHO). ^{13}C NMR (125 MHz, CDCl$_3$, TMS): *δ* (ppm) 191.06, 159.05, 142.74, 135.47, 130.27, 129.10, 127.70, 113.21, 54.39.

*4.4.5. 2,5-(4′,4″-Ditrifluoromethyl)-terphenyl-dicarbaldehyde (**8c**).* The procedure for **8a** was repeated with 4-(trifluoromethyl) phenylboronic acid (0.38 g, 2 mmol) and a reaction time of 12 h. Resulting a yellow crystal (0.34 g, 80%). ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ (ppm) 7.58–7.59(d, 4H, *J*=8 Hz, Ar), 7.80–7.82 (t, 4H, *J*=8 Hz, Ar), 8.12(s, 2H, Ar), 10.06(s, 2H, CHO). IR (KBr, cm^{-1}): 1677 (−CHO). ^{13}C NMR (125 MHz, CDCl$_3$, TMS): δ (ppm) 189.50, 142.55, 138.89, 135.53, 130.24, 129.55, 129.29, 124.80, 123.92.

*4.4.6. 2,5-Di(thiophen-2-yl)-terphenyl-dicarbaldehyde (**8d**).* The procedure for **8a** was repeated with thiophene-2-boronic acid (0.25 g, 2 mmol) and a reaction time of 5 h. Resulting a yellow crystal (0.27 g, 90%). ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ (ppm) 7.14–7.15(d, 2H, *J*=5 Hz, thienyl), 7.19–7.21 (t, 2H, *J*=5, *J*=4 Hz, thienyl), 7.54–7.55(d, 2H, *J*=5 Hz, thienyl), 8.16(s, 2H, Ar), 10.27(s, 2H, CHO). IR (KBr, cm^{-1}): 1680(−CHO). ^{13}C NMR (125 MHz, CDCl$_3$, TMS): δ (ppm) 191.54, 137.76, 137.37, 128.52, 128.73, 130.49, 131.26, 137.17.

*4.4.7. 2-[4-(N,N-dimethylamino)styryl]-1,4-diphenylbenzaldehyde (**9a**).* Terphenyl-1,4-dicarbaldehyde **8a** (0.60 g, 2 mmol) and 4-(*N,N*-dimethylamino)benzyltriphenyl phosphonium iodide (1.05 g, 2 mmol) were dissolved in anhydrous dichloromethane (50 ml), a solution of potassium *tert*-butoxide (0.34 g, 3 mmol) in anhydrous dichloromethane (10 ml) were added, and the mixture was then allowed to stir for 2 h at room temperature. After filtration, the filtrate was evaporated then purified by column chromatography on silica gel eluting with petroleum/ethyl acetate (15:1). An orange crystalline compound was then obtained by recrystallization in aq ethanol (0.52 g, 64%). Mp=173–174 °C. IR (KBr, cm^{-1}): 1668 (−CHO). ^{1}H NMR (CDCl$_3$, 500 MHz) δ 2.98 (s, 6H), 6.68 (d, *J*=9.0 Hz, 2H), 6.96 (d, *J*=16 Hz, 1H), 7.20 (d, *J*=16 Hz, 1H), 7.34 (d, *J*=9.0 Hz, 2H), 7.40(d, *J*=9.5 Hz, 2H), 7.46(d, *J*=8 Hz, 4H), 7.52 (t, *J*=8 Hz, 6H), 7.79 (s, 1H), 7.99(s, 1H), 9.99 (s, 1H). ^{13}C NMR (125 MHz, CDCl$_3$, TMS): δ (ppm) 191.69, 149.76, 134.98, 134.64, 134.01, 133.77, 133.65, 131.46, 131.39, 130.12, 129.95, 129.80, 129.64, 117.61, 116.48, 111.74, 111.55, 39.72. MS (ESI), *m/z*: 404.1 [M+H]$^{+}$. Anal. Calcd for C$_{29}$H$_{25}$NO: C, 86.32; H, 6.24; N, 3.47. Found: C, 86.45; H, 6.33; N, 3.55.

4.5. General procedure for the synthesis of compound 2–5

Compound **9** (1 equiv) was dissolved in THF, 3-dicyanomethylene-1,5,5-trimethylcyclohexene or Tricyanovinyldihydrofuran (1.1 equiv) and piperidine (cat. amount) were added, and the stirred mixture was then heated to reflux for 2 h. A purple solution was obtained. It was then poured into water. The crude dark precipitate was collected by filtration. The product was purified by column chromatography on silica gel eluting with petroleum/ethyl acetate.

*4.5.1. 2-(3-(4-(4-(Dimethylamino)styryl)-2,5-diphenylstyryl)-5,5-dimethylcyclohex-2-enylidene)malononitrile (**2a**).* Red powder (0.30 g, 53%). Mp=221–224 °C. IR (KBr, cm^{-1}): 2219 (−CN). ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ(ppm) 0.98 (s, 6H), 2.19 (s, 2H), 2.51 (s, 2H), 2.93(s, 6H), 6.64–6.66(d, 2H, *J*=7 Hz), 6.78(s, 1H, C*H*=C(CN)$_2$), 6.94–6.98(m, 2H, Ar), 7.06–7.13(dd, 2H, *J*=16 Hz), 7.27–7.28(d, 1H, C*H*=CH), 7.36–7.37 (d, 1H, CH=C*H*), 7.44–7.52(m, 10H, Ar), 7.68 (s, 1H, Ar), 7.73(s, 1H, Ar). ^{13}C NMR (125 MHz, CDCl$_3$, TMS): δ (ppm) 169.05, 154.25, 150.17, 141.49, 140.13, 137.37, 135.76, 131.71, 130.84, 129.78, 128.24, 128.10, 128.04, 127.80, 127.61, 127.49, 127.04, 126.93, 125.43, 123.18, 121.98, 113.58, 112.19, 77.95, 42.83, 40.35, 38.90, 31.85, 27.86. MS (ESI), *m/z*: 572.3 [M+H]$^{+}$. Anal. Calcd for C$_{41}$H$_{37}$N$_3$: C, 86.13; H, 6.52; N, 7.35. Found: C, 86.06; H, 6.61; N, 7.43.

*4.5.2. 2-(3-(4-(4-(Dimethylamino)styryl)-2,5-(4′,4″-dimethoxyphenyl)styryl)-5,5-dimethyl cyclohex-2-enylidene)malononitrile (**2b**).* Yield (0.51 g, 81%). Mp=271–273 °C; IR (KBr, cm^{-1}): 2218 (−CN). ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ (ppm) 1.02 (s, 6H), 2.25(s, 2H), 2.56 (s, 2H), 3.12(s, 6H), 3.91(s, 6H, OC*H*$_3$), 6.81(s, 1H, C*H*=C(CN)$_2$), 6.97–6.99(d, 2H, *J*=8 Hz, Ar), 7.00–7.05(m, 2H, C*H*=C), 7.06–7.09(d, 1H, *J*=16 Hz, C*H*=C), 7.12–7.15(d, 1H, *J*=16 Hz, C*H*=C), 7.35–7.38(dd, 6H, *J*=8 Hz, Ar), 7.45–7.46(d, 4H, *J*=8 Hz, Ar), 7.68(s, 1H, Ar), 7.69(s, 1H, Ar). ^{13}C NMR (125 MHz, CDCl$_3$, TMS): δ (ppm) 159.25, 154.32, 140.91, 139.83, 137.35, 135.99, 132.40, 131.35, 131.26, 131.18, 130.97, 130.91, 130.09, 130.01, 129.44, 128.19, 127.91, 127.34, 126.30, 123.29, 113.75, 90.34, 55.42, 42.92, 39.01, 31.98, 29.68, 27.97. MS (ESI), *m/z*: 632.3 [M+H]$^{+}$. Anal. Calcd for C$_{43}$H$_{41}$N$_3$O$_2$: C, 81.74; H, 6.54; N, 6.65. Found: C, 81.65; H, 6.41; N, 6.77.

*4.5.3. 2-(3-(4-(4-(Dimethylamino)styryl)-2,5-(4′,4″-ditrifluoromethylphenyl)styryl)-5,5-dimethylcyclohex-2-enylidene)malononitrile (**2c**).* Yield (0.56 g, 79%). Mp=221–225 °C; IR (KBr, cm^{-1}): 2220 (−CN). ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ (ppm) 1.02 (s, 6H), 2.21 (s, 2H), 2.56 (s, 2H), 3.11(s, 6H), 6.84(s, 1H, C*H*=C (CN)$_2$), 6.99–7.0(d, 2H, *J*=5.5 Hz, Ar), 7.01–7.05(d, 1H, *J*=16 Hz, C*H*=CH), 7.09–7.13(d, 1H, *J*=16 Hz, CH=C*H*), 7.42–7.46(m, 2H, *J*=16 Hz, C*H*] C*H*), 7.56–7.59 (m, 6H, Ar), 7.71 (s, 1H, Ar), 7.72(s, 1H, Ar), 7.77–7.79(dd, 4H, *J*=8 Hz, Ar). ^{13}C NMR (125 MHz, CDCl$_3$, TMS): δ (ppm) 170.36, 168.95, 159.75, 143.60, 137.36, 134.15, 130.60, 130.08, 128.25, 128.04, 127.38, 125.39, 125.34, 124.04, 120.52, 113.34, 113.15, 112.59, 112.37, 78.16, 42.85, 38.92, 32.32, 29.66, 27.92. MS (ESI), *m/z*: 708.2 [M+H]$^{+}$. Anal. Calcd for C$_{43}$H$_{35}$F$_6$N$_3$: C, 72.97; H, 4.98; N, 5.94. Found: C, 72.78; H, 4.76; N, 6.06.

*4.5.4. 2-(3-Cyano-(4-(4-(dimethylamino)styryl)-2,5-diphenylstyryl) 5,5-dimethylfuran-2(5H)-ylidene)malononitrile (**3a**).* Deep red powder(0.46 g, 78%). IR (KBr, cm^{-1}): 2226 (−CN). ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ(ppm) 1.25 (s, 6H), 3.02 (s, 6H), 6.67–6.68 (d, 2H, *J*=8 Hz), 6.98–7.01 (d, 1H, *J*=16 Hz, C*H*=CH), 7.18 (d, 1H, *J*=16 Hz, CH=C*H*), 7.29–7.31 (d, 2H, Ar, *J*=8 Hz), 7.36–7.37 (d, 2H, *J*=8 Hz), 7.43–7.46 (d, 1H, *J*=16 Hz, C*H*=CH), 7.45–7.48 (m, 3H, CH=C*H*, Ar), 7.49–7.55 (m, 6H, Ar), 7.75 (s, 1H, Ar), 7.83 (s, 1H, Ar). ^{13}C NMR (125 MHz, CDCl$_3$, TMS): δ (ppm) 158.51, 150.60, 144.08, 141.98, 140.16, 138.99, 138.38, 133.53, 132.97, 132.45, 131.44, 130.31, 130.16, 129.97, 129.72, 128.78, 128.62, 128.48, 128.38, 127.77, 127.00, 121.07, 112.20, 111.93, 80.97, 48.99, 40.17, 29.64. MS (ESI), *m/z*: 585.2 [M+H]$^{+}$. Anal. Calcd for C$_{40}$H$_{32}$N$_4$O: C, 82.17; H, 5.52; N, 9.58. Found: C, 82.05; H, 5.65; N, 9.63.

*4.5.5. 2-(3-Cyano-(4-(4-(dimethylamino)styryl)-2,5-(4′,4″-dimethoxyphenyl)styryl)5,5-dimethylfuran-2(5H)-ylidene)malononitrile (**3b**).* Red powder (0.42 g, 65%). IR (KBr, cm^{-1}): 2227 (−CN). ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ(ppm) 1.25 (s, 6H), 3.01 (s, 6H), 3.90 (s, 6H), 6.77–6.78 (d, 2H, *J*=8 Hz), 7.01–7.06 (m, 5H, *J*=8.5 Hz, Ar, C*H*=CH), 7.16–7.19 (d, 1H, *J*=16 Hz, CH=C*H*), 7.26–7.29 (m, 3H, *J*=16 Hz, Ar, C*H*=CH), 7.32–7.35 (m, 3H, Ar, CH=C*H*), 7.38–7.40 (d, 2H, *J*=8.5 Hz, Ar), 7.77 (s, 1H, Ar), 7.78 (s, 1H, Ar). ^{13}C NMR (125 MHz, CDCl$_3$, TMS): δ (ppm) 160.02, 159.26, 158.91, 143.57, 142.06, 139.61, 133.19, 131.43, 131.17, 130.96, 130.69, 130.28, 128.32, 127.07, 121.57, 114.42, 113.95, 113.23, 112.16, 80.62, 55.46, 55.34, 40.29, 29.69. MS (ESI), *m/z*: 645.2 [M+H]$^{+}$. Anal. Calcd for C$_{42}$H$_{36}$N$_4$O$_3$: C, 78.24; H, 5.63; N, 8.69. Found: C, 77.96; H, 5.72; N, 8.81.

*4.5.6. 2-(3-Cyano-(4-(4-(dimethylamino)styryl)-2,5-(4′,4″-di-trifluoromethyl)phenylstyryl) 5,5-dimethylfuran-2(5H)-ylidene)malononitrile (**3c**).* Deep red powder (0.59 g, 82%). IR (KBr, cm^{-1}): 2220 (−CN). ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ(ppm) 1.25 (s, 6H), 3.00 (s, 6H), 6.77 (m, 2H, Ar), 6.86–6.89 (d, 1H, C*H*=CH, *J*=16 Hz), 7.19–7.23 (dd, 2H, *J*=16 Hz, C*H*=C*H*), 7.28–7.30 (m, 3H, Ar, CH=C*H*), 7.50–7.51 (d, 2H, *J*=7.5 Hz, Ar), 7.58–7.60 (d, 2H, *J*=8 Hz, Ar), 7.66 (s, 1H, Ar), 7.76–7.77 (d, 2H, Ar, *J*=8.5 Hz), 7.81–7.83 (m, 3H, Ar). ^{13}C NMR (125 MHz, CDCl$_3$, TMS): δ (ppm) 157.33, 143.09, 142.55, 142.23, 141.88, 139.21, 138.07, 134.79, 130.47, 130.18, 130.07, 128.58, 127.34, 127.17, 126.79, 126.00, 125.95, 125.90, 125.67, 125.62, 119.90, 113.82, 112.88, 112.16, 90.37, 82.30, 40.23, 29.69. MS (ESI), *m/z*: 721.2

$[M+H]^+$. Anal. Calcd For $C_{42}H_{30}F_6N_4O$: C, 69.99; H, 4.20; N, 7.77. Found: C, 69.86; H, 4.32; N, 7.87.

*4.5.7. 2-(3-(4-(4-(Diphenylamino)styryl)-2,5-(4′,4″-dimethoxyphenyl) styryl)-5,5-dimethyl cyclohex-2-enylidene)malononitrile (**4**).* Yield (0.57 g, 76%). Mp=170–172 °C. IR (KBr, cm^{-1}): 2219 (–CN). ^1H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) 1.01 (s, 6H), 2.22 (s, 2H), 2.54 (s, 2H), 3.89(s, 6H), 6.81 (s, 1H, C*H*=C(CN)$_2$), 6.93–7.11(m, 15H, C*H*=CH, Ar), 7.13–7.16 (d, 1H, *J*=15 Hz, CH=C*H*), 7.19–7.25 (m, 6H, *J*=8.5 Hz, Ar), 7.35–7.37(d, 2H, *J*=8.5 Hz), 7.38–7.39 (d, 2H, *J*=8.5 Hz, Ar), 7.45–7.46 (d, 1H, *J*=9 Hz, Ar), 7.66 (s, 1H, Ar), 7.69(s, 1H, Ar). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ (ppm) 169.11, 159.04, 154.17, 147.38, 146.78, 140.80, 139.83, 137.14, 136.00, 132.32, 132.12, 130.78, 130.44, 129.80, 129.56, 129.16, 128.41, 128.10, 127.74, 127.40, 124.94, 124.49, 124.25, 123.24, 122.87, 113.65, 112.68, 55.22, 42.79, 38.89, 31.86, 29.51, 27.83. MS (ESI), *m*/*z*: 756.3 $[M+H]^+$. Anal. Calcd for $C_{53}H_{45}N_3O_2$: C, 84.21; H, 6.00; N, 5.56. Found: C, 84.17; H, 5.86; N, 5.69.

*4.5.8. 2-(3-(4-(4-(Diphenylamino)styryl)-2,5-di(thiophen-2-yl) styryl)-5,5-dimethylcyclo hex-2-enylidene)malononitrile (**5**).* Yield (0.58 g, 82%). Mp=226–229 °C. IR (KBr, cm^{-1}): 2219 (–CN). ^1H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) 1.02 (s, 6H), 2.16 (s, 2H), 2.50 (s, 2H), 6.86(s, 1H, C*H*=C(CN)$_2$), 6.92–6.95 (d, 1H, *J*=16 Hz, CH=C*H*), 7.04–7.13 (m, 14H, C*H*=CH, Ar), 7.16–7.18 (t, 2H, *J*=3.5 Hz, thienyl), 7.23–7.25(d, 2H, *J*=8.5 Hz, Ar), 7.27–7.29 (d, *J*=8.5 Hz, 2H, Ar), 7.32–7.35(d, 1H, *J*=16 Hz, CH]CH), 7.41–7.43(d, 2H, *J*=8.5 Hz, Ar), 7.46–7.47(d, 2H, *J*=8.5 Hz, Ar), 7.72 (s, 1H, Ar), 7.91(s, 1H, Ar). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ (ppm) 168.95, 153.52, 147.25, 140.56, 138.07, 133.94, 132.2, 130.92, 129.34, 128.21, 128.02, 127.92, 127.7, 127.62, 126.88, 124.82, 124.68, 124.19, 124.1, 123.4, 123.32, 123.25, 123.08, 122.87, 113.4, 79.13, 45.64, 39.14, 31.99, 29.68, 27.98. MS (ESI), *m*/*z*: 708.2 $[M+H]^+$. Anal. Calcd for $C_{47}H_{37}N_3S_2$: C, 79.74; H, 5.27; N, 5.94. Found: C, 79.87; H, 5.35; N, 6.03.

4.6. Computational details

Geometrical optimization of our studied compound without any symmetry constraint was carried out with the B3LYP combinations of density functional theory (DFT) in the Gaussian 03 computational chemistry program.[22] The B3LYP functional is a combination of Becke's three-parameter hybrid exchange functional[23] and the Lee–Yang–Parr[24] correlation functional. Basis sets of 6-31G* were applied to our studied compounds. The first-order hyperpolarizabilities were calculated by using the finite-field (FF) method.[25]

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2011.03.108.

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