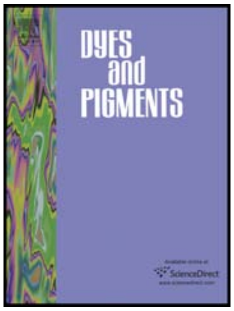

A Nunchaku-like Nonlinear Optical Chromophore for improved temporal stability of Guest-Host Electro-Optic materials

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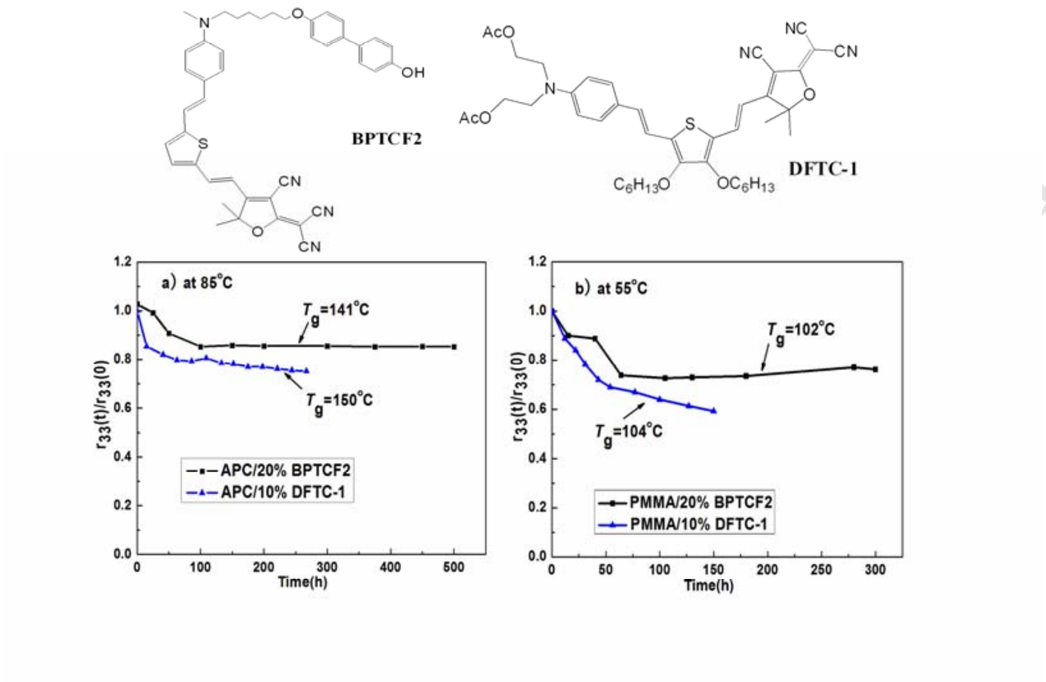

BPTCF2
DFTC-1
N
O
OH
S
CN
AcO
NC
$C_6H_{13}O$
OC_6H_{13}
a) at 85°C
T_g=141°C
T_g=150°C
$r_{33}(t)/r_{33}(0)$
Time(h)
APC/20% BPTCF2
APC/10% DFTC-1
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0
100
200
300
400
500
b) at 55°C
T_g=102°C
T_g=104°C
PMMA/20% BPTCF2
PMMA/10% DFTC-1
50
150
250

1. A novel nunchaku-like organic second order NLO chromophore containing a D-π-A backbone and a rigid biphenylene unit was prepared.
2. The chromophore demonstrates good thermal stability, solubility, weak intermolecular interactions and a large electro-optic effect.
3. The influence of the rigid biphenylene group on the temporal stability of poled electro-optic films was also investigated.

A Nunchaku-like Nonlinear Optical Chromophore for improved temporal stability of Guest-Host Electro-Optic materials

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Abstract

A novel nunchaku-like organic second order nonlinear optical chromophore containing a D-π-A backbone and a rigid biphenylene unit was prepared. The UV-vis absorption spectra studies demonstrated that the large rigid structure could suppress dipole-dipole interactions effectively. The electro-optic coefficient of a poled film containing 20% wt of the new dye doped in amorphous polycarbonate afforded a value of 39 pm/V at 1310 nm. Compared with results obtained from a similar D-π-A chromophore without the rigid isolated group, the new dye gave better performance. Moreover, the electro-optic film prepared with the new dye gave greater temporal stability, compared to a similar D-π-A doped poled film that was reported previously. These results indicated that the introduction of a biphenylene group could effectively reduce the intermolecular electrostatic interactions and aid the alignment of the chromophores.

Keywords: nonlinear optical materials; chromophore; biphenylene; electro-optic; temporal stability; poled film

1. Introduction

Organic electro-optic (EO) materials have drawn a great deal of attention in recent decades due to their attractive potential applications in telecommunications such as phased array radar, optical gyroscopes and modulators [1-6]. Organic and polymeric nonlinear optical (NLO) materials have many advantages over conventional inorganic/semi-conductor EO materials, such as large nonlinear optical coefficient, ease of synthetic design, simple preparation and low cost. To realize application of devices, organic EO materials are required to fulfill several requirements: large optical nonlinearity, minimal optical loss at operation wavelength, good mechanical strength and processability for multilayer fabrication, thermal stability in the device processing and long-term stability of polar order [7]. The long-term temporal stability is the indispensable requirement for organic EO materials, and also the challenge for the practical application.

Guest-host EO polymers are composite materials which contain nonlinear optical chromophores as a dissolved guest and a polymer host. Such guest-host types were believed to be advantageous systems for the research of structure-property relationships and prototype proof-of-concept EO devices due to their facile preparation [8]. However, for practical application, some problems such as macro-phase separation, lower loading density, should be solved. More importantly, the thermal relaxation of the poling-induced order offered unsatisfactory temporal stability. Although using high T_g polymers as the host could enhance the stability of guest-host materials to some extent [8, 9], some excellent NLO chromophores could not tolerate the stringent condition of such high poling temperatures. Several approaches, including the covalent incorporation of NLO chromophores into the structures of main-chain polymers [10-13] and side-chain polymers [14, 15], the self-assembly or the layer-by-layer deposition processes [16-18], and a variety of cross-linkable EO polymers [19-22], have been proposed to resolve these problems. Nevertheless, these systems require more complex synthetic effort compared to simple guest-host polymers, although they could effectively address the stability issues of EO polymers.

Designing new chromophores which can reduce favorable intermolecular interactions has been proposed to be a novel approach to improve the temporal stability of guest-host polymers [23-26]. The rigid rod-like structures of biphenyl or biphenylene units potentially take preferential orientation induced by intermolecular interaction or an external field [27-30]. If these units are introduced into the NLO chromophores, the temporal stability of the poling-induced alignment of chromophores may be enhanced. The introduction of the biphenyl or biphenylene units onto chromophore units has scarcely been investigated [31, 32] and no research on the influence of the units on the temporal stability has been reported. In this article, a new molecular design route is reported to develop the new nonlinear chromophore. Owing to the molecular shape, it is referred to as “nunchaku-like” molecule [29]. We designed a new nunchaku-like NLO chromophore constructed by connecting a rigid biphenylene unit and a D-π-A conjugated structure via a flexible spacer. The solubility of the chromophore will decrease due to the introduction of a rigid biphenylene unit, conversely the flexible spacer can improve the solubility. The influence of the biphenylene unit on the aggregation of chromophores was studied, guest-host EO polymers based on amorphous polycarbonate (APC) and polymethylmethacrylate (PMMA) as the hosts were prepared. The EO activities of these materials, especially the long-term temporal stability were investigated in detail.

2. Experimental

2.1 Materials and instrument

Biphenyl-4,4'-diol was purchased from Beijing Ouhe Technology Co.Ltd. All other solvents and chemicals were purchased from Beijing Chemical Reagents Company. All the reagents were used as received unless otherwise stated. Compound **A** was synthesized by our group, 4-((6-chlorohexyl)(methyl)amino)benzaldehyde and TCF acceptor were prepared according to the literature [31, 33].

^{1}HNMR spectra were determined using a Varian Gemini (400 MHZ) NMR spectrometer (tetramethylsilane as internal reference). The Mass spectra were obtained on MALDI-TOF (Matrix Assisted Laser Desorption/Ionization of Flight) on BIFLEXIII(Broker Inc.) spectrometer. Elemental analyses were taken from a Thermo Finnigan Flash EA1112 microelemental analyzer. The UV-vis spectra were performed on Hitachi U2001 photo spectrometer. FT-IR spectra were recorded on BIO-RAD FTS-165 spectrometer. The melt points were obtained by TA DSC Q10 under N_2 at a heating rate of 10 °C/min. The TGA was determined by TA TGA Q50 with a heating rate of 10 ℃/ min under the protection of nitrogen.

2.2 Syntheses

2.2.1 Synthesis of Compound 1

A diethyl ether solution (50 mL) of 4-((6-chlorohexyl)(methyl)amino)benzaldehyde (1.76 g, 4.0 mmol), NaH (1.20 g, 50 mmol), and compound **A** (1.76 g, 4.0 mmol) was stirred at room temperature for 24 h, then poured into ice water (200 mL). The mixture was extracted with dichloromethane (3×50 mL), and dried over magnesium sulfate. The extract was concentrated by rotary evaporation, the resulting product was purified by silica-gel column chromatography with a mixture of ethyl acetate and petroleum ether (v/v =1/9) as the eluent. The viscous reddish-brown liquid was obtained (1.12 g, yield: 84%). IR(KBr), υmax/cm^{-1}: 2932, 2858 (C−H), 1604, 1524 (benzene ring), 1274, 1184, 956, 818, 698. ^{1}H NMR (400 MHz, Acetone) δ 7.46 (dd, J = 8.9 Hz,1.5Hz, 2H), 7.38 (d, *J* = 4.0 Hz, 1H),7.17 (dd, 1H), 6.95 (s, 2H), 6.74 (dd, J = 8.9 Hz, 1.5Hz, 2H), 6.49 (d, *J* = 4.0 Hz, 1H),3.60 (t, *J* = 6.7 Hz, 2H), 3.42–3.36 (m, 2H), 2.97 (s, 3H), 1.83–1.74 (m, 2H), 1.62 (dt, *J* = 15.0, 7.5 Hz, 2H), 1.50 (dt, *J* = 14.3, 7.0 Hz, 2H), 1.43–1.35 (m, 2H). MS, m/z: 333.13(M$^+$).

2.2.2 Synthesis of Compound 2

A solution of compound **1** (1.00 g, 3.0 mmol) in anhydrous THF (10 mL) was prepared, purged with nitrogen, and cooled to −78 °C. Then the solution was added dropwise n-BuLi (2.32 mL, 2.5 M in hexanes), and the resulting mixture was stirred for 1 h. Anhydrous N,N-dimethylformamide (DMF) (0.28 mL) was added, and the mixture was stirred for one additional hour. Saturated NH_4Cl solution was added to quench the reaction, and the mixture was then warmed to room temperature. The mixture was poured into water and the organic layer was extracted with dichloromethane (3×50 mL). The combined organic layers were washed with water and dried over anhydrous $MgSO_4$.The extract was concentrated by rotary evaporation, the resulting product was purified by silica-gel column chromatography with a mixture of ethyl acetate and petroleum ether (v/v =1/6) as the eluent. Yield: red solid (0.98 g, 91%). m.p.: 64.54 °C. IR(KBr), υmax/cm^{-1}: 2932, 2858 (C−H), 1658 (−CHO), 1597, 1516 (benzene ring), 1381, 1184, 1045, 956, 810. ^{1}H NMR (400 MHz, Acetone) δ 9.86 (s, 1H), 7.82 (d, J = 4.0 Hz, 1H), 7.46 (d, J = 8.9 Hz, 2H), 7.22 (d, J = 4.0 Hz, 1H), 7.18 (s, 2H), 6.74 (d, J = 8.9 Hz, 2H), 3.60 (t, J = 6.7 Hz, 2H), 3.46 – 3.39 (m, 2H), 3.00 (s, 3H), 1.83 – 1.74 (m, 2H), 1.63 (dt, J = 15.0, 7.5 Hz, 2H), 1.50 (dt, J = 14.3, 7.0 Hz, 2H), 1.38 (dt, J = 7.3, 4.5 Hz, 2H). MS, m/z: 361.13(M^+).

2.2.3 Synthesis of Compound 3

Biphenyl-4,4'-diol (0.66 g, 3.5 mmol) and compound **2** (1.27 g, 3.5 mmol) were added into a mixture of anhydrous K_2CO_3(6.90 g, 50 mmol) and KI (0.913 g, 5 mmol) in anhydrous DMF (100 mL) with stirring. After reaction at 80 °C for 12 h, the mixture was poured into an excess of NaOH aqueous solution (0.1 mol/ L) and was extracted with dichloromethane (3×50 mL). The combined organic layers were washed with saturated salt water and dried over anhydrous $MgSO_4$. After removal of the solvent, the crude product was purified by silica-gel column chromatography with a mixture of acetone and petroleum ether (v/v =1/3) as the eluent. Yield: orange-red solid (0.93 g, 52%). m.p. (with decomposition): 201 °C . IR(KBr), υmax/cm^{-1}: 3410 (Ph-OH), 2935, 2858 (C−H), 1658 (−CHO), 1593, 1500 (benzene ring), 1250 (C−O−Ph), 1177, 1134, 1115, 821. ^{1}H NMR (400 MHz, Acetone) δ 9.85 (s, 1H), 8.31 (s, 1H), 7.80 (d, J = 4.0 Hz, 1H), 7.56–7.38 (m, 5H), 7.29–7.15 (m, 3H), 7.01–6.86 (m, 4H), 6.79–6.58 (m, 3H), 4.03 (t, J = 6.4 Hz, 2H), 3.44 (m, 2H), 3.00 (s, 3H), 1.86–1.75 (m, 2H), 1.66 (dt, J = 15.0, 7.5 Hz, 2H), 1.56 (dt, J = 14.4, 7.0 Hz, 2H), 1.46 (dd, J = 15.0, 8.1 Hz, 2H). MS, m/z: 511.68(M^+).

2.2.4 Synthesis of Chromophore BPTCF2

TCF (0.29 g, 1.5 mmol) and compound **3** (0.25 g, 0.5 mmol) were dissolved in anhydrous methanol (30 mL) under stirring. After heating under reflux for 4 h the mixture was concentrated by rotary evaporation, the crude product was purified by silica-gel column chromatography with a mixture of ethyl acetate and petroleum ether (v/v =1/2) as the eluent. Yield: green powder (0.25 g, 74%). m.p. : 137.41 °C. IR(KBr), υmax/cm^{-1}: 2932, 2860 (C−H), 2226 (C≡N), 1593, 1523 (benzene ring), 1276 (C−O−Ph), 1049, 949. ^{1}H NMR (400 MHz, Acetone) δ 8.29 (s, 1H), 8.13 (d, *J* = 4.0 Hz, 1H), 7.65 (d, *J* = 4.0 Hz, 1H), 7.52–7.39 (m, 5H), 7.24–7.16 (m, 3H), 6.95 (dd, *J* = 8.8 Hz,1.5Hz, 2H), 6.88 (dd, *J* = 8.6 Hz, 1.4Hz, 2H), 6.82 (s, 1H), 6.79–6.65 (m, 3H), 4.01 (t, *J* = 6.4 Hz, 2H), 3.50–3.41 (m, 2H), 3.03 (s, 3H), 1.85 (s, 6H), 1.79 (dd, *J* = 14.4, 6.8 Hz, 2H), 1.67 (dd, *J* = 14.5, 7.4 Hz, 2H), 1.60–1.51 (m, 2H), 1.50–1.40 (m, 2H). ^{13}C NMR (101 MHz, Acetone) δ 177.60, 175.34, 159.32, 157.67, 154.69, 151.30, 140.94, 139.01, 135.35, 133.25, 129.95, 128.41, 124.68, 116.95, 116.72, 115.87, 113.41, 112.96, 99.18, 68.70, 52.97, 38.73, 27.68, 26.90, 26.51. MS, m/z: 692.53(M^+). Anal. Calcd. for $C_{43}H_{40}N_4O_3S$: C,74.54; H, 5.82; N, 8.09. Foud: C, 74.40; H, 5.86; N, 8.03.

2.3 Film preparation

For the UV–vis analysis and r_{33} measurements, guest–host polymers films were prepared by formulating chromophore **BPTCF2** into **APC** (T_g = 190 °C) and **PMMA** (T_g = 128 °C). The **BPTCF2** (15 mg) were mixed with **APC** (75 mg) in dibromomethane(0.65 mL) as the solvent. After stirring for 12 h, the solutions were filtered through a 0.22 μm Teflon membrane filter and spin-coated onto indium tin oxide (ITO) glass substrates at room temperature with the spinning rate of 700 rpm to give the films and then baked overnight at the room temperature under vacuum, yielding optical quality thin films with thickness of around 3 μm. The other films were obtained using the same process. The poling process was carried out at a temperature of about 10°C above the T_g of the polymers.

Scheme 1

3. Results and discussion

3.1 Synthesis and characterization

The synthetic route towards the nunchaku-like NLO chromophore **BPTCF2** containing a rigid biphenylene unit and the D-π-A conjugated structure is depicted in Scheme 1. Treatment of the 4-((6-chlorohexyl)(methyl)amino) benzaldehyde with Wittig salt **A** and NaH afforded compound **1** in a reasonable yield, followed by a Vilsmeier reaction to yield the corresponding aldehyde **2**. Compound **3** was obtained through an S_N2 reaction between compound **2** and biphenyl-4,4'-diol. Finally the **TCF** acceptor unit was introduced into the chromophore using a known condensation reaction [34-37]. The structure of **BPTCF2** was confirmed by IR spectroscopic analysis, ^{1}HNMR, ^{13}CNMR , CHN elemental analyses and mass spectroscopy.

3.2 Thermal property of the chromophore

Chromophores must be thermally robust enough to withstand encountered temperatures in electric field poling and subsequent processing of chromophore/polymer materials. The decomposition temperatures of the chromophore can be assessed by techniques such as thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The thermal property of **BPTCF2** was investigated by TA TGA Q50 under N_2 at a heating rate of 10 °C/min. **BPTCF2** displayed high thermal stability with 5% loss temperature (T_d) higher than 235 °C, which was high enough for the application in EO device preparation [38].

3.3 UV-Vis spectra

It has been suggested that the solvatochromic effects are related with the molecular nonlinearity of NLO chromophores [39-42]. In order to reveal the effect of electron donor with a rigid isolated group on the electronic structures of dipolar chromophore **BPTCF2**, UV-vis absorption spectra were measured quantitatively in a series of solvents with different polarity so that the solvatochromic behavior could be investigated. As shown in Fig. 1 a), in non-polar solvents such as 1,4-dioxane and toluene, **BPTCF2** exhibited a progressive red-shift of the maximum absorption (λ_{max}) and a saturation behavior was found in chloroform. With a further increase of solvent polarity, it reversed to a hypsochromic shift in chloroform, dichloromethane (**DCM**), acetone and acetonitrile, namely negative solvatochromism [41]. This interesting solvent-dependent spectral behavior suggested that the structure of **BPTCF2** can be easily influenced on the basis of the dipole formed by charge migration from the donor to the acceptor in the most polar solvents. Notably, similar solvent-dependent changes of absorption spectra could also be found for many merocyanine dyes. Therefore, the solvatochromism has been commonly regarded as an indication of molecular nonlinearity of NLO chromophores [40].

Fig.1

The UV–vis spectra of **BPTCF2** was also determined in chloroform with different concentrations (from 0.4×

10^{-5} to 10×10^{-5}mol·L^{-1}), which was shown in Fig. 1 b). The shape of the absorption band has not changed apparently as the concentration increased even the maximum concentration increased to 10^{-4} order of magnitude. Inspection of Fig. 1 c) clearly shows the relationship of the concentration and absorbance. It was not difficult to find that the absorbance was increasing linearly as the concentration increased, which showed that the interval of absorbance change was highly uniform. These results indicated that there are only weak dipole-dipole interactions among the chromophores. The strong dipole–dipole interaction could easily induce the aggregation of chromophores, and even nano-crystal generation (self-assembly) via a solvent exchange method [40]. Unlike other chromophores we studied, no crystallization behavior was observed for chromophore **BPTCF2**. These results confirmed that the introduction of a rigid isolated group on electron donor could widen the distance between chromophores and weaken the dipole–dipole interactions between dipolar molecules, which benefit the macroscopic electro-optic efficiency.

3.4 Nonlinear optical property

In order to investigate the NLO property of chromophore **BPTCF2**, a guest-host EO polymer system was explored. The poling process was carried out at a temperature of about 10°C above the T_g of the polymer. The EO coefficients of the poled films were determined by the simple reflection technique initially proposed by Teng and Man [43, 44]. The r_{33} values were calculated by the following equation:

$$r_{33}=\frac{3\lambda I_m}{4\pi V_m I_c n^2}\frac{(n^2-\sin^2\theta)^{3/2}}{(n^2-2\sin^2\theta)}\frac{1}{\sin^2\theta} \qquad (1)$$

where r_{33} is the EO coefficient of the poled polymer, λ is the optical wavelength, h is the incidence angle, I_c is the output beam intensity, I_m is the amplitude of the modulation, V_m is the modulating voltage, and n is the refractive indices of the polymer films.

The r_{33} values of poled **APC**/10%**BPTCF2**, **APC**/20%**BPTCF2** and **APC**/30%**BPTCF2** were 19 pm/V, 39 pm/V, and 24 pm/V, respectively. The maximum r_{33} value of 39 pm/V was obtained when the loading density reached 20%wt. This result is much better than that for **DFTC-1** which was 30 pm/V [45]. The enhancement of the EO activity further demonstrated that the rigid isolated group on electron donor effectively suppressed the dipole-dipole interaction and assisted the orientation of chromophores during poling process.

Moreover, the order parameter changes of the poled EO films were studied through measuring the UV-Vis absorption spectra of EO films before and after poling [46]. After the corona poling, the chromophores in the polymer were aligned, and the absorption intensity decreased due to birefringence. From the absorption changes, the order parameter (Φ) can be described according to the following equation: $\Phi = 1-A_1/A_0$, where A_0 and A_1 are the absorbance of the un-poled and poled EO polymer films at normal incidence. The Φ values of poled **APC**/20%**BPTCF2** film and **PMMA**/10%**BPTCF2** film were about 27.7% and 23.9% (Fig. 2), which showed that the Φ values had reached the average values and that the poling process was typically efficient. The Φ values are related to the chromophores' orientation，and more effective chromophore orientation would provide larger Φ values . The obtained higher Φ values indicated that **BPTCF2** could effectively orientate in the poled films, which was caused by the introduction of rigid isolated group.

Fig.2

3.5 The temporal stability

The long-term stability of the poled EO films was investigated. As shown in Fig. 3 a), after annealing at 85°C for 500 h, the poled film of **APC**/20%**BPTCF2** can retain more than 85% of its initial r_{33} value, and this percentage was considerably higher than those of **APC**/10%**DFTC-1** investigated previously, where only 75% of the initial r_{33} value was kept after 300 h [47]. In the common guest-host organic EO materials, the T_g greatly influenced the temporal stability of the EO activity, and the EO material that has a higher T_g usually has a better temporal stability [8]. In this work, the T_g of **APC**/20%**BPTCF2** and the benchmark **APC**/10%**DFTC-1**were 141 °C and 150 °C, respectively, **APC**/20%**BPTCF2** exhibited more promising long-term temporal alignment stability, although it has the lower T_g. The improvement of temporal stability for **APC**/20%**BPTCF2** provided direct evidence that the relaxation of chromophores in the poled films had been restricted through introducing the biphenylene unit. The improved temporal stability was probably contributed to by two aspects. On the one hand there were the weak non-covalent interactions such as π-π stacking between chromophores (mainly biphenylene groups) and polymer backbones (phenyl groups). On the other hand, due to the biphenylene units potentially taking preferential orientation induced by intermolecular interaction, such kind of non-covalent interaction assisted the alignment of chromophores during poling and restricted the movement of chromophores after poling.

To further investigate the influence of biphenylene unit on the temporal stability and determine which factors play the major role. Two kinds of guest-host polymers using **PMMA** as host were investigated. Fig. 3 b) showed the decay of the poled films of **PMMA**/10%**BPTCF2** and **PMMA**/10%**DFTC-1** at 55 °C. After a fast decay at the initial 50 h, 74% of the initial r_{33} value was retained over 300 h for **PMMA**/10%/**BPTCF2**, the **PMMA**/10%**DFTC-1** decayed below 60% only after 150 h although both systems had a similar T_g. **PMMA**/10%**BPTCF2** also exhibited more promising long-term temporal alignment stability. These results indicated that the main reason of the guest-host EO polymers containing chromophore **BPTCF2** exhibited good temporal stabilities was the weak intermolecular non-covalent interactions, it was also confirmed that the rigid isolated group in electron donor enhanced the temporal stability of the guest-host EO material.

Fig.3

4. Conclusion

In summary, a new NLO chromophore **BPTCF2** with a large rigid isolated group was successfully synthesized and characterized by ^{1}HNMR, ^{13}CNMR, CHN elemental analyses and MS. The intermolecular interactions and molecular nonlinearity were studied by UV-vis absorption spectroscopy and these results confirmed that the isolated group could greatly reduce intermolecular interactions. EO films were prepared by doping chromophore **BPTCF2** in **APC** or **PMMA** with different loading densities, and they showed high EO activity (39 pm/V). Moreover, the temporal stability of poled **APC**/20%**BPTCF2** film and **PMMA**/10%**BPTCF2** film could retain 85% (500 h) and 74% (300 h) of the initial values at evaluated temperature (85 °C and 55 °C) respectively, which were much better than films prepared by traditional FTC chromophores.

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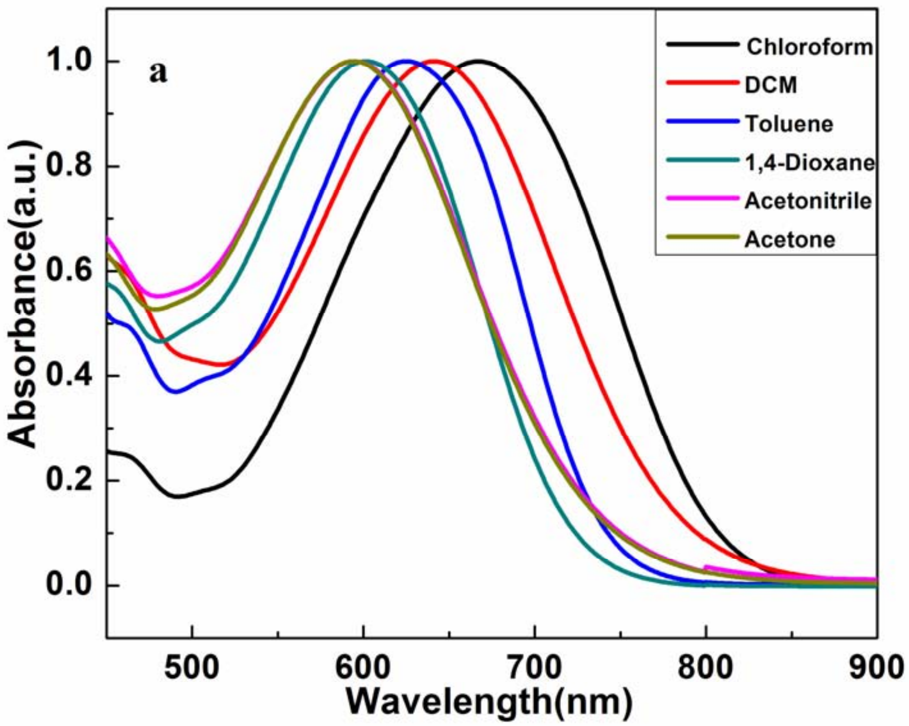
Figure Captions

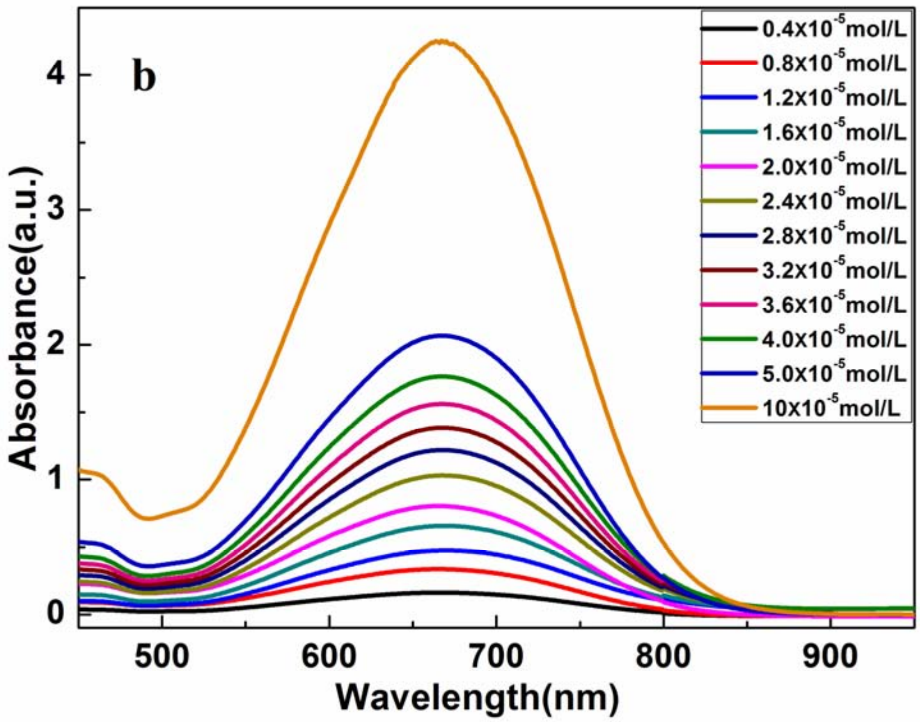
Fig. 1 a) Solvatochromic behavior of **BPTCF2** recorded in different solvents (2×10^{-5} M) of varying dielectric constants (1,4-dixoane:2.25; toluene: 2.38; chloroform: 4.81; dichloromethane: 8.93; acetone:20.7; acetonitrile: 37.5). b) UV-vis absorption spectra of **BPTCF2** in chloroform with different concentrations. c) Linear plot of the concentration and absorbance.

Fig. 2 UV-Vis absorption spectra of E-O polymers **BPTCF2** doped in a) **APC**; b) **PMMA** before and after poling.

Fig. 3 Temporal stabilities of the poled films. a) **APC**/20% **BPTCF2** and **APC**/10% **DFTC-1**. at 85^{o}C. b) **PMMA**/20% **BPTCF2** and **PMMA**/10% **DFTC-1** at 55^{o}C.

Scheme 1 Chemical structures and synthetic scheme for chromophore **BPTCF2**


a
Chloroform
DCM
Toluene
1,4-Dioxane
Acetonitrile
Acetone
Absorbance(a.u.)
0.0
0.2
0.4
0.6
0.8
1.0
500
600
700
800
900
Wavelength(nm)


b
0.4X10^{-5}mol/L
0.8X10^{-5}mol/L
1.2X10^{-5}mol/L
1.6X10^{-5}mol/L
2.0X10^{-5}mol/L
2.4X10^{-5}mol/L
2.8X10^{-5}mol/L
3.2X10^{-5}mol/L
3.6X10^{-5}mol/L
4.0X10^{-5}mol/L
5.0X10^{-5}mol/L
10X10^{-5}mol/L
Absorbance(a.u.)
0
1
2
3
4
500
600
700
800
900
Wavelength(nm)

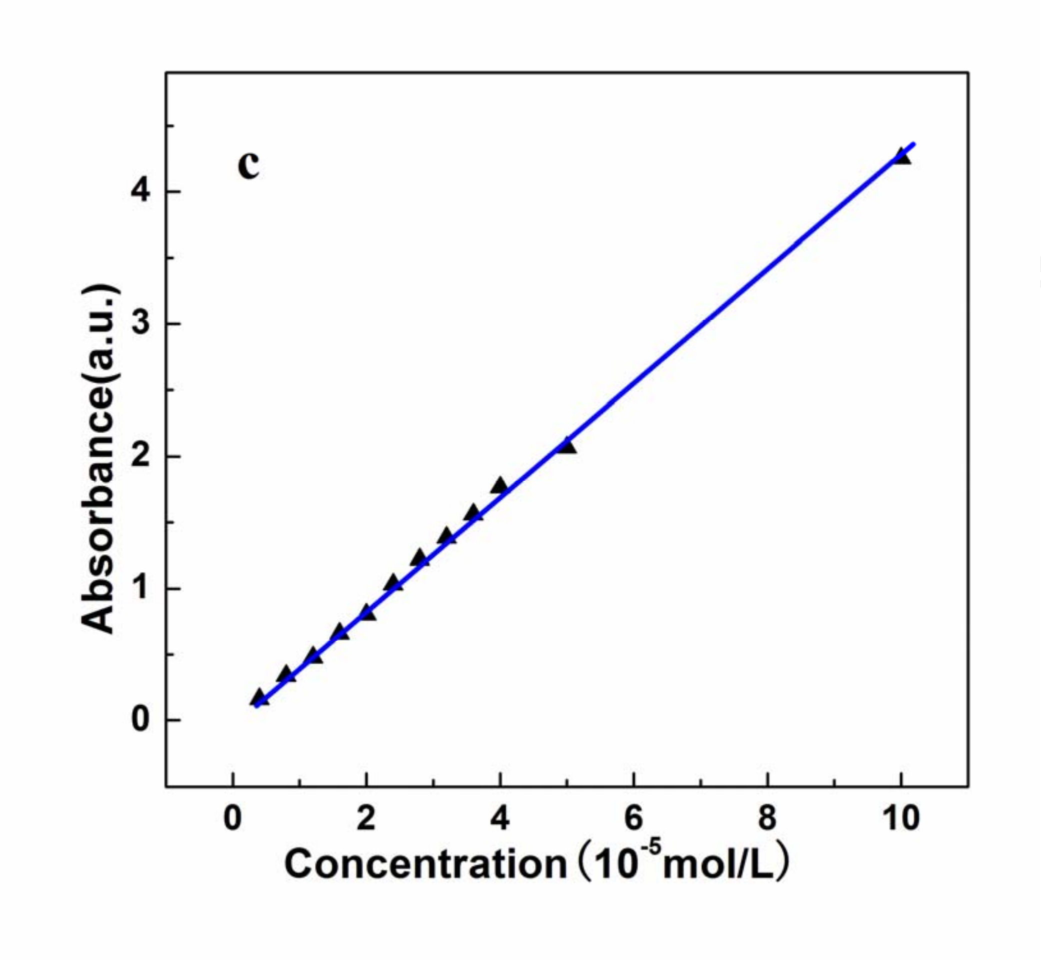
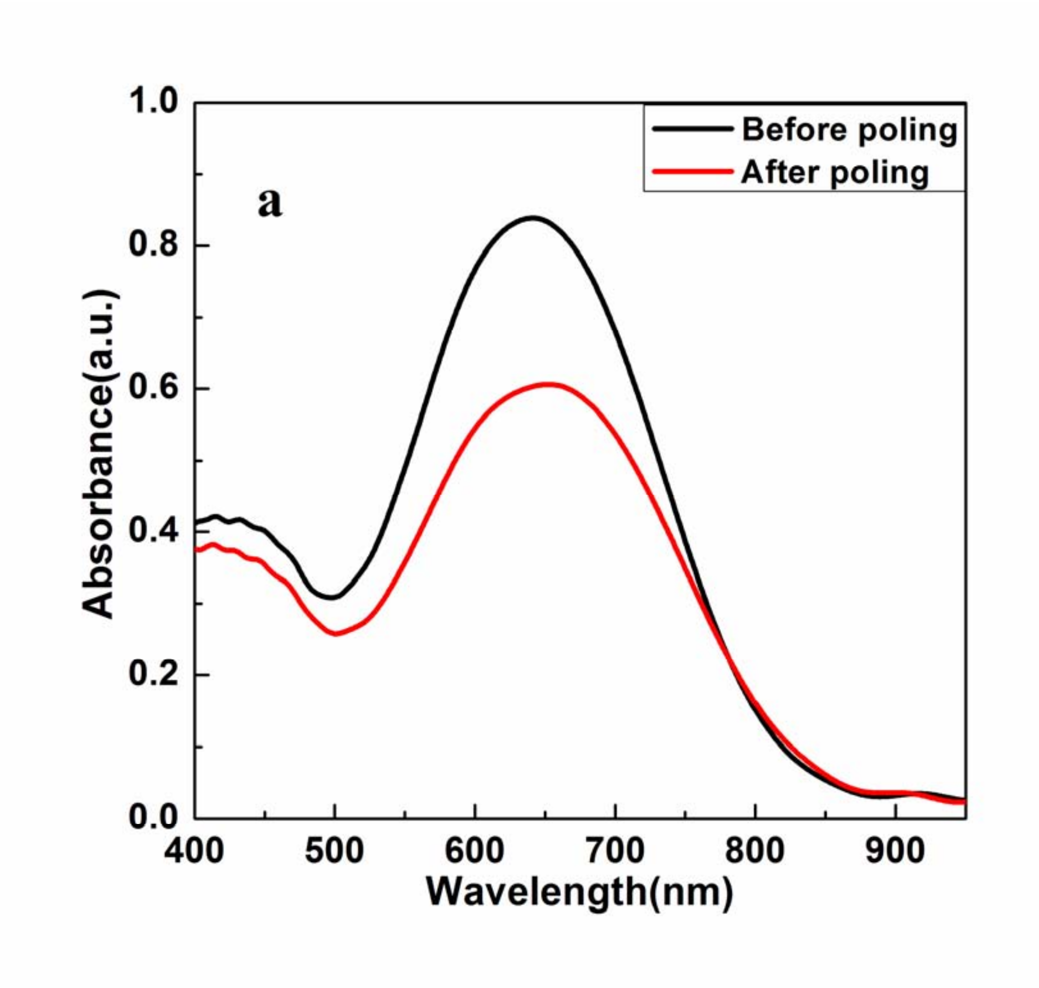


Fig. 1


a
Before poling
After poling
Absorbance(a.u.)
1.0
0.8
0.6
0.4
0.2
0.0
400
500
600
700
800
900
Wavelength(nm)

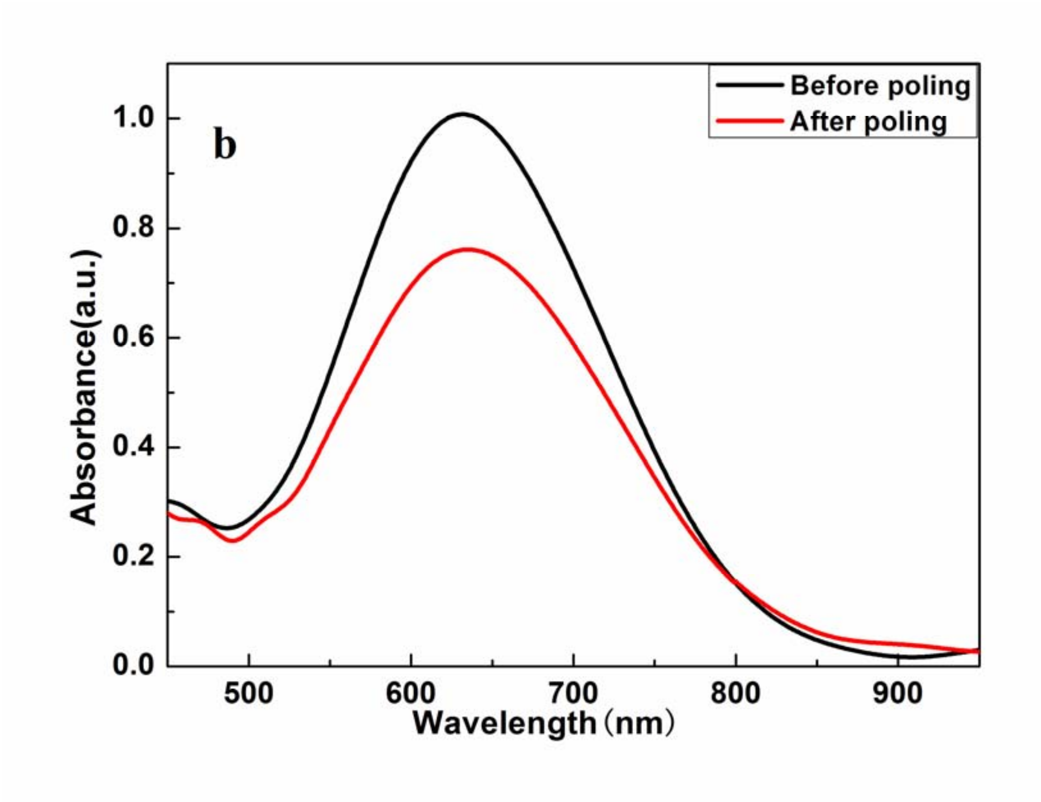
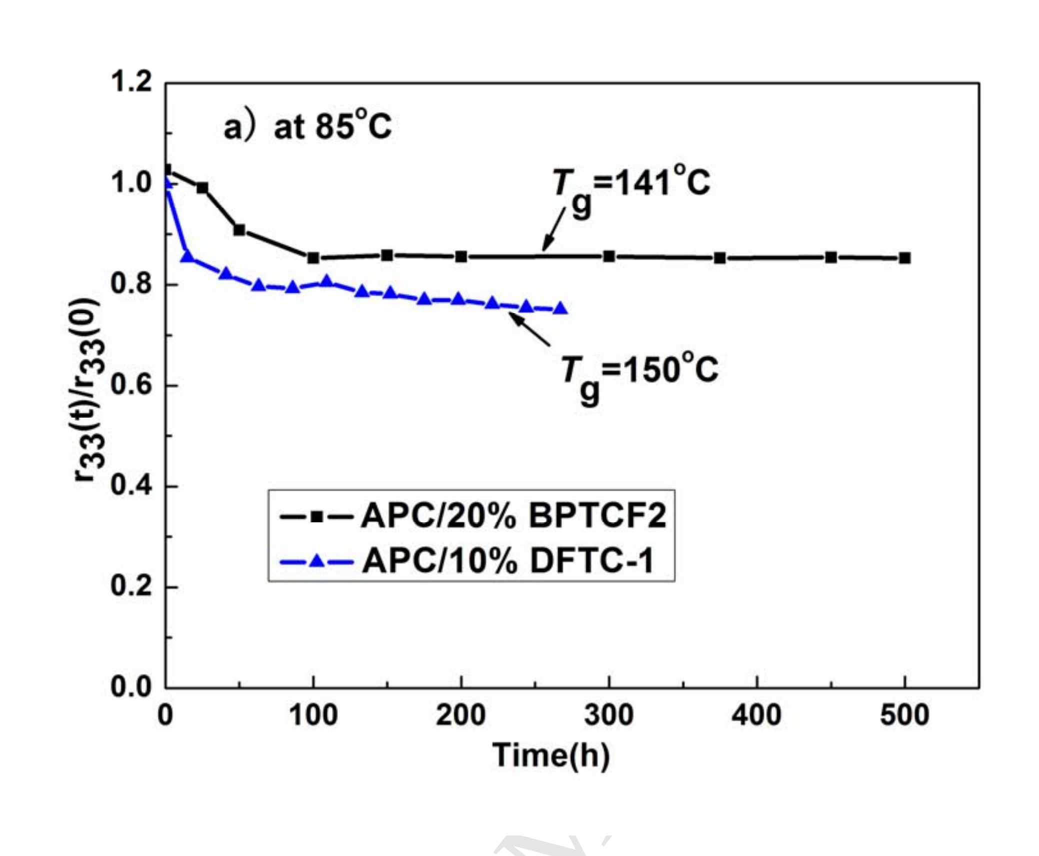

b
Before poling
After poling
Absorbance(a.u.)
0.0
0.2
0.4
0.6
0.8
1.0
500
600
700
800
900
Wavelength（nm）

Fig. 2


a) at 85°C
T_g=141°C
T_g=150°C
$r_{33}(t)/r_{33}(0)$
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
100
200
300
400
500
Time(h)
APC/20% BPTCF2
APC/10% DFTC-1

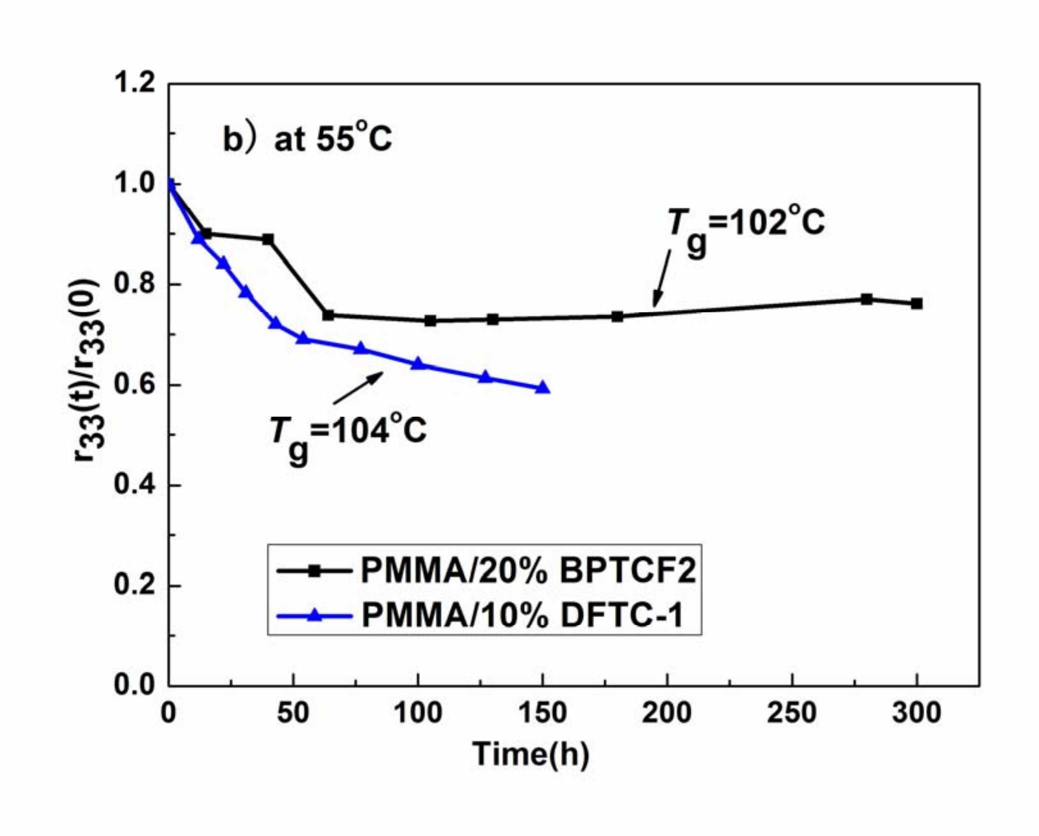
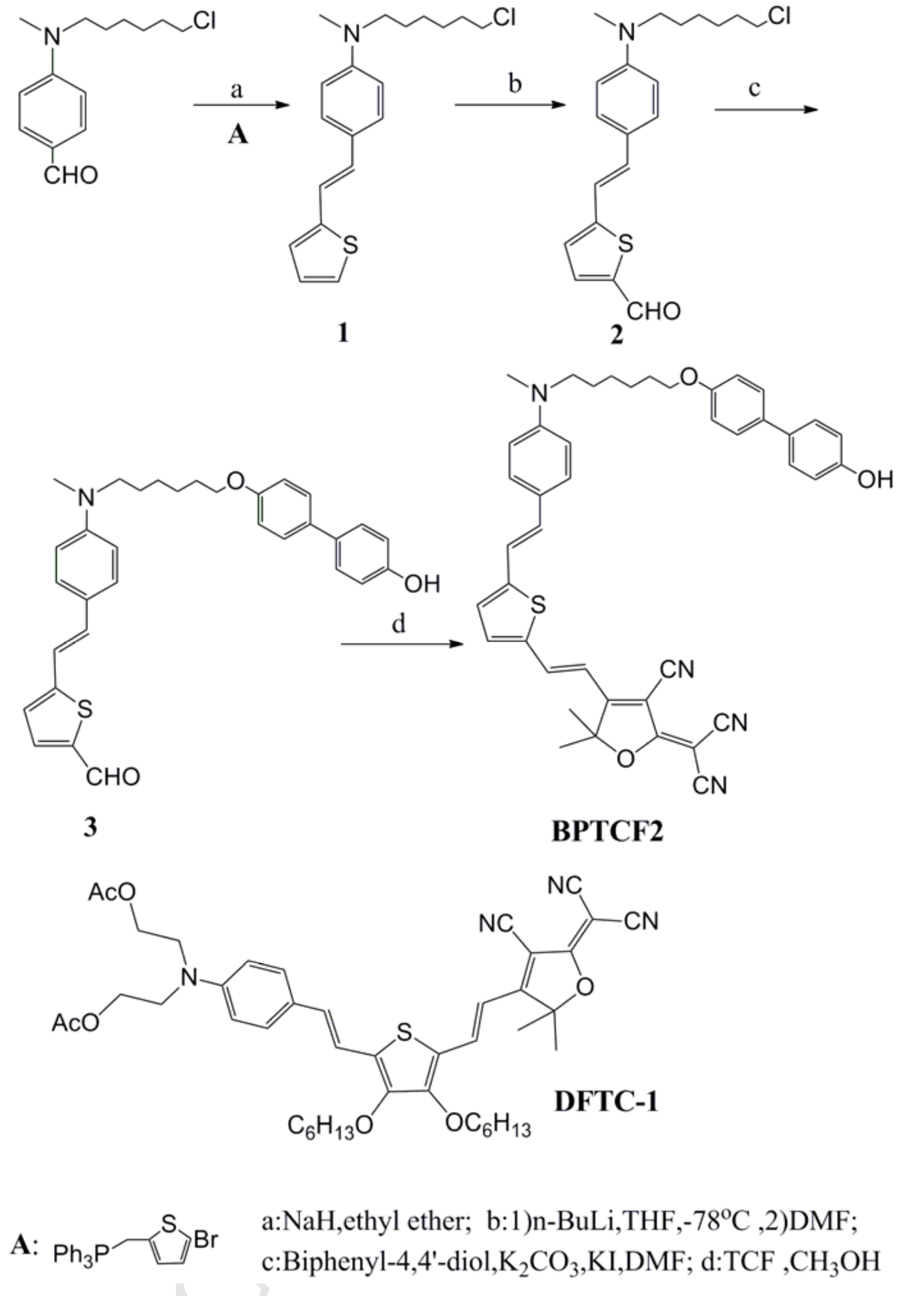

b) at 55°C
T_g=102°C
T_g=104°C
$r_{33}(t)/r_{33}(0)$
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
250
300
Time(h)
PMMA/20% BPTCF2
PMMA/10% DFTC-1

Fig.3



a:NaH,ethyl ether; b:1)n-BuLi,THF,-78^{o}C ,2)DMF;
c:Biphenyl-4,4'-diol,K_2CO_3,KI,DMF; d:TCF ,CH_3OH

Scheme 1