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Study on two thermostable NLO chromophores with different π -electron bridges using fluorene as donor

Haoran Wang ^{ab}, Fenggang Liu ^{ab}, Yuhui Yang ^{ab}, Maolin Zhang ^{ab}, Chengcheng Peng ^{ab}, Shuhui Bo ^{a*}, Xinhou Liu ^a, Ling Qiu ^a Zhen Zhen ^{a*}

Two chromophores C1 and C2 based on fluorene electron donor with different π -electron bridges and same electron acceptor have been synthesized and systematically characterized by NMR, MS and UV-vis absorption spectra. The energy gap between ground state and excited state and molecular nonlinearity were studied by UV-vis absorption spectroscopy, Density Functional Theory calculations and cyclic voltammetry measurements. The different properties between C1 and C2 were systematically compared. The results showed C2 had better performance than C1. The electro-optic coefficient of a poled film containing 25 wt% of C2 doped in amorphous polycarbonate afforded a value of 40 pm/V at 1310 nm. In addition, the excellent thermostability of C2 made itself a favourable candidate for practical application.

Introduction

The development of the highly efficient organic electro-optic (EO) materials has been the focus of recent research for many organic materials groups because of their attractive potential in such applications as optical data transmission and optical information processing.¹⁻³ The organic and polymeric nonlinear optical (NLO) materials have many advantages over traditional inorganic and semiconductor materials such as large nonlinear optical coefficients, simple process and low cost.⁴⁻⁸ Generally, the NLO chromophore molecules possessing a dipolar D- π -A type structure is the core component in such materials, which turned the design and preparation of NLO chromophores into a research hotspot in the area of organic EO materials.⁹⁻¹² To increase the possibility of the application of chromophores in the devices, the dipole chromophores should have not only high first-order hyperpolarizability (B) but also good thermal and photochemical stabilities as well as good solubility and compatibility with polymer matrix.

It is a well-established fact that the conjugation length and donor/acceptor strength of such D- π -A type push-pull chromophore molecules can cause dramatic shifts to their second-order nonlinear responses.^{5,7-8,11} In order to search for highly efficient NLO chromophores, finding an optimal combination of donor and acceptor remains one a critical challenge.¹³⁻¹⁵ In the past decade, the researches on NLO chromophores have mainly focused on the design of electron bridges and electron acceptors.¹⁶⁻²² However, the electron donors, which are important components of NLO

chromophores, have received much less attention since the traditional alkyl and aryl anilines were considered to be the ideal electron donors and as such were consistently utilized.^{23,24}

To the best of our knowledge, most constantly-used donors contained heteroatoms such as alkyl and aryl anilines, and the chromophores including these donors, thiophene bridge and TCF acceptor, however, in some cases, had low decomposition temperature and poor thermostability, so they couldn't tolerate the stringent condition during the poling process.²⁵⁻²⁸ In this article, a new type of chromophores with excellent thermostability and good solubility in common organic solvents was designed using fluorene as donor. The significant difference between this type of chromophores and the traditional ones was that the donor didn't contain heteroatoms. The donor was composed of two resonance benzene rings and a five-membered carbon-ring, and the rigid structure might contribute to the thermostability of chromophores. The two synthesized chromophores (C1 and C2) with the different π electron bridges (one was thiophene bridge, the other was isophorone bridge) had the same tricyanofuran acceptor (TCF) for comparison. The thermal, electrochemical, linear and nonlinear optical properties of C1 and C2 were thoroughly investigated, and the differences between them were systematically compared. The excellent thermostability made itself a favourable candidate for practical application.

Results and discussion

Synthesis of chromophores

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Scheme 1 Chemical structures and synthetic scheme for chromophores C1 and C2 and TCF acceptor.

Scheme 1 showed the synthetic routes for the chromophores C1, C2 and TCF acceptor. Fluorene, as the donor of the chromophores, reacted with 1-Bromobutane to produce compound 2. Compound 3 was obtained by the introduction of bromine using N-bromosuccinimide (NBS) as bromide reagent. Compound 3 was then formylated to give compound 4. The synthetic routes were divided into two different ones Route A and Route B from compound 4 to obtain the chromophore C1 and C2 respectively. On the one hand, by the introduction of the thiophene bridge using Witting condensation reaction, compound 5a was attained. Then a formylation reaction was carried out to afford compound 6a. After the Knoevenagel condensation of 6a with TCF, chromophore C1 was obtained as purple solid. On the other hand, compound **5b** was produced under alkaline condition using compound 4 as reactant, then it reacted with diethyl cyanomethylphosphonate under alkaline condition for extending the conjugated carbon chain to produce compound **6b**. The cyano group of **6b** was reduced to aldehyde group using DIBAH as reductant to produce compound 7b. Then another Knoevenagel condensation of 7b with TCF was conducted, high yield of 67.9 % of chromophore C2 was obtained as blue solids. Both the prepared chromophores were fully characterized by ¹H NMR, ¹³C NMR, and mass spectroscopy. They also possess good solubility in common organic solvents, such as chloroform, acetone and N,Ndimethyl formamide.

In order to reveal the solvatochromic behavior of chromophores C1 and C2, UV-vis absorption spectra were measured quantitatively in a series of aprotic solvents with different polarity. In other words, the solvatochromic behavior could be investigated for the polarity of two chromophores in a wide range of dielectric environments. As shown in Fig. 1, the molar absorptivity (ɛ) of C2 was larger than C1 in the same solvents. The ε values for C1 were only 19674 L/(mol cm) and 17400 L/(mol cm) in dioxane and chloroform respectively compared to the relative ϵ values of 56560 L/(mol cm) and 57073 L/(mol cm) for C2 (Table 1). Theoretically, each



Fig. 1 UV-vis absorption spectra of chromophores C1 and C2 in six kinds of aprotic solvents (0.02 mM) with different dielectric constants (dioxane: 2.25; chloroform: 4.81; THF: 7.58; acetone: 20.7; acetonitrile: 37.5; DMF: 38.3) at room temperature.

chromophore absorbed an excitation photon to undergo intramolecular charge-transfer (ICT), but in fact, not each molecular in solution underwent $\pi \rightarrow \pi^*$ charge-transfer due to the fact that they were too close to each other or formed π - π packing.^{29,30} Therefore the larger ε value meant that C2 was much easier to undergo ICT at the same concentration and had stronger ICT ability. In addition, the polyene structure of C2 was more easily polarized compared to the thiophene bridge of C1.^{8,31} Furthermore, C2 reached up to λ_{max} of 589 nm in chloroform, while C1 only afforded a value of 563 nm correspondingly, and the λ_{max} of C2 showed a bathochromic shift of 35 nm from dioxane to chloroform, displaying better solvatochromism than C1 (29 nm). This also illustrated that C2 was more polarized than C1.

To reveal the difference of the chromophores on the configurations, the energy gap of the ground state and excited state and first-order hyperpolarizability of the chromophores, Density Functional Theory (DFT) calculations were carried out at the hybrid B3LYP level by employing the split valence 6-31 g (d, p) basis set.³²⁻³⁴ It was reinforced by theoretical calculations and optical characterizations that the β value has a close relationship with the substituents, molecular configuration and intramolecular charge-transfer. As reported earlier,³⁵ the β has been calculated at 6-31g (d, p) level. From this, the scalar quantity of β can be computed from the x, y and z components according following equation:

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

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

Firstly, we optimized the configurations of the chromophores to keep them in the most stable state. The optimized configurations of the chromophores showed good coplane along the π -electron bridge (Fig. 2). Moreover, the large angle (95 °) of the two alkoxy chains put the chromophores in a state

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Table 1 UV-vis data and DFT calculations of chromophores C1 and C2									
UV-vis data	DFT calculations								
Chromophore	$\lambda_{max}\!/\!(nm)^a$	ε	$\lambda_{max}/(nm)^b$	ε ^b	$\Delta\lambda/(nm)^{ab}$	E _{HOMO} /(eV) ^c	E _{LUMO} /(eV) ^d	$\Delta E/(eV)^e$	$\beta/(10^{-30} \operatorname{esu})^{\mathrm{f}}$
C1	534	1967	563	1740	29	-5.82	-3.57	2.25	606
C2	554	5656	589	5707	35	-5.67	-3.50	2.17	683

^a λ_{max} was measured in dioxane, ^b λ_{max} was measured in chloroform, $\Delta\lambda/(nm)^{ab}$ was the difference between $\lambda_{max}/(nm)^{a}$ and $\lambda_{max}/(nm)^{b}$. The values of ^c E_{HOMO} , ^d E_{LUMO} and ^f β were calculated using Gaussian 03 at B3LYP/6-31g (d,p) level. $\Delta E = E_{LUMO} - E_{HOMO}$.



Fig. 2 Optimized configurations of C1 and C2.

of stretch, and this optimized state could keep the adjacent chromophores away and prevent the aggregation of the chromophores, in addition, the two methyl groups linked at the cyclohexene of C2 might behave in the same way. Fig. $S1^{\dagger}$ depicted the electron density distribution of the HOMO and LUMO structures. It could be seen that the density of the ground and excited state electron was asymmetry along the dipolar axis of the chromophores. To get more insight from the frontier orbitals, the composition of the HOMOs and LUMOs had been calculated using the Multiwfn program with Ros-Schuit (SCPA) partition.³⁶ As shown in Table S1^{\dagger}, the whole chromophore molecule was segmented as donor, π -bridge and acceptor. The orbitals of HOMO of C1 and C2 were almost uniformly distributed along the dipolar axis of the chromophores, while orbitals of LUMO distributed mainly in the acceptor.

The data obtained from DFT calculations were summarized in Table 1. It could be seen that the β values of **C1** and **C2** were 606×10^{-30} esu and 683×10^{-30} esu respectively, and the energy gap of the ground state and excited state of **C2** (2.17 eV) was smaller than that of **C1** (2.25 eV). The larger β value and smaller energy gap of **C2** illustrated that it had greater potential of translating molecular microscopic hyperpolarizability into macroscopic EO activity than **C1**.

To determine the redox properties of **C1** and **C2**, cyclic voltammetry (CV) measurements were conducted in degassed anhydrous acetonitrile solutions containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF) as the



Fig. 3 Cyclic voltammograms of C1 and C2 recorded in solutions containing 0.1 M Bu_4NPF_6 supporting electrolyte at a scan rate of 100 mV/s.

Table 2 Data of o	oxidation and	reduction	potentials
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	E _{red} ((V)	$E_{ox}(V)$	E _{LUMO} (eV)	E _{HOMO} (eV)) $E_{eg}(eV)$
C1	-0.9	25	0.910	-3.87	'5	-5.710	1.835
C2	-0.7	43	0.881	-4.05	57	-5.681	1.624
The	values	of	E _{LUMO} and	E _{HOMO}	were	calculated	using their
corre	espondin	ng o	xidation and	reductio	n pote	ntials. E _{eg} (e	$eV) = E_{LUMO}$ -
E _{HON}	40.					-	

supporting electrolyte. The potentials were measured against Ag/AgCl as reference electrode and each measurement was calibrated with an internal standard, ferrocene/ferrocenium (Fc) redox system.³⁷ As shown in Fig. 3, **C1** and **C2** all exhibited irreversible oxidative and reductive waves, and the data obtained from CV measurements was summarized in Table 2. The HOMO and LUMO energy values for **C1** and **C2** were calculated based on the value of -4.8 eV for Fc with respect to zero vacuum level.³⁸ The energy gap of the ground state and excited state of **C1** and **C2** were 1.835 and 1.624 eV respectively, and these values were consistent well with the UV-vis data and DFT calculation.

NLO chromophores must be thermally stable enough to withstand encountered high temperatures (>100 °C) in electric field poling and subsequent processing of chromophore/polymer materials. Fig. S2[†] showed the thermogravimetric analysis of C1 and C2. We could see that both the decomposition temperatures (T_d) of C1 (243 °C) and C2 (294 °C) were above 200 °C, which were high enough for

Table 3 Optical poling parameters and EO co	coefficients (r_{33})
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	20 wt% C1- APC	25 wt% C1- APC	30 wt% C1- APC	20 wt% C2- APC	25 wt% C2- APC	30 wt% C2- APC
T _g (°C) ^a	128	130	115	147	147	140
$T_p(^{\circ}C)^b$	128	130	120	150	150	140
$V_p^r (kV)^c$	11	11.5	11.5	11	11	11
Time(min) ^d	10	15	12	10	12	12
r ₃₃ ^e	19	22	20	26	40	32
^a Glass transition temperature (T _g) was measured by DSC with a heating rate of 10 °C /min in nitrogen, ^b Poling temperature, ^c Poling						
voltage, ^d Poling time, ^e pm/V, electro-optic coefficients, measured by simple-reflection technique at 1310 nm.						

the application in EO device preparation.²⁸ As we know, T_d for most of chromophores was around or below 250 °C,²⁵⁻²⁸ for example, T_d of the **FTC**, **FTC-yh1** and **FTC-yh2** of ref. 22 were 242 °C, 249 °C and 247 °C respectively. The T_d for **C2** reached up to 294 °C, which meant **C2** could be used under the stringent condition in the devices.

From the above discussion, C2 had larger β value and smaller energy gap. Hence, it was expected that EO films containing C2 would show higher efficiency of translating molecular microscopic hyperpolarizability into macroscopic EO activity. To evaluate the EO activities of C1 and C2 in polymers, 20 wt%, 25 wt% and 30 wt% of chromophores were formulated into amorphous polycarbonate (APC) to prepare the guest-host films C1-APC and C2-APC for EO measurements. Corona poling was applied to induce the acentric ordering of chromophores. The optimal poling parameters were listed in Table 3. All the poling temperature of the films were equal or above the T_g . It could be seen that r_{33} value of 22 pm/V for 25 wt% C1-APC was obtained at 1310 nm after 15 mins' poling under the applied voltage of 11.5 kV. However, no bigger value was obtained when we changed either the poling parameters or the concentration of C1 in APC. All the optimized applied voltages of C2-APC were 11 kV, and the r₃₃ values of 26 pm/V and 32 pm/V were achieved for 20 wt% C2-APC and 30 wt% C2-APC respectively, which were higher than C1-APC. After 12 mins' poling, 25 wt% C2-APC afforded the highest r₃₃ value of 40 pm/V.

Conclusions

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Two chromophores C1 and C2 based on fluorene electron donor with different π -electron bridges and same electron have synthesized and acceptor been systematically characterized by NMR, MS and UV-vis absorption spectra. The energy gap between ground state and excited state and molecular nonlinearity were studied by UV-vis absorption spectroscopy, DFT calculations and CV measurements. The results showed that C2 had lower energy gap between ground state and excited state, according to which we speculated that C2 had better electro-optic performance than C1 when they were doped into polymer. The electro-optic coefficient of a poled film containing 25 wt% of C2 doped in APC afforded a value of 40 pm/V at 1310 nm, while the film of C1 of the same concentration only gave a value of 22 pm/V. In addition, the excellent thermostability (the decomposition temperature is 294

 $^{\circ}$ C) of C2 made itself a favourable candidate for practical application.

Experimental section

Materials and instrument

All chemicals are commercially available and are used without further purification unless otherwise stated. The DMF, toluene and THF were freshly distilled prior to their use. TCF acceptor was prepared according to the literature.³⁹ ¹H NMR spectra were determined by an Advance Bruker 400M (400 MHz) NMR spectrometer (tetramethylsilane as internal-reference). The MS spectra were obtained on MALDI-TOF (Matrix Assisted Laser Desorption/Ionization of Flight) on BIFLEXIII (Broker Inc.) spectrometer. The UV-Vis experiments were performed on Cary 5000 photo spectrometer. The TGA was determined by TA5000-2950TGA (TA co) with a heating rate of 10 °C /min under the protection of nitrogen. The glass transition temperatures and melting points were obtained by TA DSC Q10 under N₂ at a heating rate of 10 °C/min. 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 counterelectrode, and Ag/AgCl as the reference electrode at a scan rate of 100 mV/s. The 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF) in acetonitrile is the electrolyte.

Poling process and r₃₃ measurements

To study the EO property derived from the chromophores, polymers were prepared guest-host by formulating chromophores C1 and C2 into amorphous polycarbonate (APC) using dibromomethane as the solvent. The resulting solutions were filtered through a 0.22 µm Teflon membrane filter and spin-coated onto indium tin oxide (ITO) glass substrates. Films of doped polymers were baked in a vacuum oven at 40 °C overnight to remove the residual solvent. We used the corona poling method. The r₃₃ values of poled films were measured by the Teng-Man simple reflection method at a wavelength of 1310 nm using a carefully selected thin ITO electrode with low reflectivity and good transparency in order to minimize the contribution from multiple reflections.^{40,41}

Synthesis

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Compound z. Yellow mercury oxide (1.3 g, 6 mmol) was added to the mixture of concentrated sulfuric acid (1.9 mL) and deionized water (10 mL). Below 70 °C, 2-methyl-3-butyn-2-ol (8.4 g, 0.1 mol) was added dropwise and stirred at 70 °C for 30 minutes. When it was cooled to room temperature, the mixture was poured into aqueous sodium bicarbonate, extracted with dichloroethane (CH₂Cl₂), and dried by anhydrous magnesium sulfate (MgSO₄). After the removal of the solvent, the pale yellow liquid was obtained by collecting the 140 °C fraction (4.56 g, yield: 32.2%).

TCF. A solution of metal lithium (0.05 g, 7 mmol) in absolute anhydrous ethanol (1 mL) was slowly added to a solution of compound z (1.7 g, 0.017 mol) and malononitrile (2.2 g, 0.033 mol) in THF (20 mL). The mixture was refluxed overnight. After removing the THF, the crude product was recrystallized from ethanol, washed with cold ethanol and dried to afford a pale yellow solid (2.33 g, yield: 35%).

Compound 2. To a solution of compound **1** (15 g, 90.3 mmol) and 1-Bromobutane (25 mL) in DMF (50 mL), potassium tert-butoxide (25 g, 223 mmol) was added. The mixture was allowed to stir at room temperature for 1 h and then poured into water. The organic phase was extracted by AcOEt, washed with brine and dried over MgSO₄. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography to give **2** as a white powder in 60 % yield (15 g, 54 mmol). MS, m/z: 278.311 (M⁺), ¹H NMR (400 MHz, Acetone) δ 7.80 – 7.77 (m, 2H), 7.43 (ddd, *J* = 6.8, 4.1, 2.8 Hz, 2H), 7.35 – 7.29 (m, 4H), 2.04 (dd, *J* = 7.8, 3.4 Hz, 4H), 1.10 – 1.02 (m, 4H), 0.64 (t, *J* = 7.4 Hz, 6H), 0.59 – 0.49 (m, 4H).

Compound 3. To a solution of compound **2** (7 g, 25.2 mmol) in propylene carbonate (40 mL), was added Nbromosuccinimide (4.48 g, 25.2 mmol) at 57 °C in one portion, and the mixture was stirred for 30 min at 60 °C and then poured into water. The organic phase was extracted by AcOEt, washed with brine and dried over MgSO₄. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography to give **3** as a white powder in 83.7 % yield (7.5 g, 21.1 mmol). MS, m/z: 356.109, ¹H NMR (400 MHz, CDCl₃) δ 7.64 (dt, *J* = 10.3, 3.5 Hz, 1H), 7.57 – 7.41 (m, 4H), 7.32 (dd, *J* = 7.9, 4.9 Hz, 2H), 2.02 – 1.86 (m, 4H), 1.15 – 1.00 (m, 4H), 0.70 – 0.64 (m, 6H), 0.62 – 0.52 (m, 4H).

Compound 4. A solution of compound **3** (4 g, 11.2 mmol) in anhydrous THF (10 mL) was prepared in a three neck flask which was purged with nitrogen, then the solution was cooled to -78 $\$ and dropwise added n-BuLi (5.6 mL, 2.5 M in hexane), after this, the resulting mixture was stirred for 1 h. Anhydrous N,N-dimethylformamide (DMF) (2 mL) was added, and the mixture was stirred for one more hour, then the temperature rose to 0 $\$ and treated with aqueous HCl (2 mL of concentrated HCl diluted and 16 mL of water). The mixture was then warmed to room temperature and poured into water, the organic layer was extracted with dichloromethane (3 \times 50 mL) and washed with dilute NaHCO₃ solution, dried over anhydrous MgSO₄. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography to give **4** as a yellow powder in 81.6 % yield (2.8 g, 9.2 mmol). MS, m/z: 306.437 (M⁺), ¹H NMR (400 MHz, CDCl₃) δ 9.99 (s, 1H), 7.82 – 7.79 (m, 1H), 7.79 – 7.74 (m, 2H), 7.73 – 7.69 (m, 1H), 7.34 – 7.27 (m, 3H), 1.94 (m, *J* = 13.5, 6.8 Hz, 4H), 1.07 – 0.92 (m, 4H), 0.58 (t, *J* = 7.4 Hz, 6H), 0.53 – 0.42 (m, 4H).

Compound 5a. To a solution of compound **4** (1.5 g, 4.9 mmol) and 2-thienyl triphenylphosphonate bromide (2.58 g, 5.9 mmol) in absolute ether (30 mL) was added NaH (1.17 g, 48.7 mmol). The solution was allowed to stir at room temperature for 24 h and then poured into water. The organic phase was extracted by AcOEt, washed with brine and dried over MgSO₄. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography to give **5a** as a yellow oil in 88.9 % yield (1.68 g, 4.4 mmol). MS, m/z: 386.198 (M⁺), ¹H NMR (400 MHz, Acetone) δ 7.80 – 7.75 (m, 2H), 7.70 (s, 1H), 7.56 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.51 (d, *J* = 16.2 Hz, 1H), 7.44 (dt, *J* = 6.9, 2.9 Hz, 1H), 7.36 (d, *J* = 5.4 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.19 (d, *J* = 3.5 Hz, 1H), 7.13 – 7.03 (m, 2H), 2.15 – 2.06 (m, 4H), 1.08 (dd, *J* = 14.9, 7.4 Hz, 4H), 0.67 – 0.62 (m, 6H), 0.63 – 0.53 (m, 4H).

Compound 5b. To a solution of compound 4 (1 g, 3.3 mmol) and 5,5-dimethyl-2-cyclohexenone (0.53 mL) in absolute ethanol (5 mL) was added NaOEt (0.68 g, 3.96 mmol). The solution was allowed to stir at 85 °C for 2 h, then drops of water was added to quench the reaction. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography to give **5b** as a yellow oil in 79.1 % yield (1.1 g, 2.6 mmol). MS, m/z: 426.153 (M⁺), ¹H NMR (400 MHz, Acetone) δ 7.84 (dd, J = 7.6, 3.5 Hz, 2H), 7.79 (s, 1H), 7.66 (dd, J = 7.9, 1.3 Hz, 1H), 7.48 (dd, J = 5.9, 2.7 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.30 (s, 1H), 7.27 (s, 1H), 6.07 (s, 1H), 2.63 (s, 2H), 2.29 (s, 2H), 2.15 – 2.09 (m, 4H), 1.16 – 1.07 (m, 10H), 0.70 – 0.57 (m, 10H).

Compound 6a. A solution of compound 5a (1.35 g, 3.5 mmol) in anhydrous THF (10 mL) was prepared in a three neck flask which was purged with nitrogen, then the solution was cooled to -78 °C and dropwise added n-BuLi (1.8 mL, 2.5 M in hexane), after this, the resulting mixture was stirred for 1 h. Anhydrous N,N-dimethylformamide (DMF) (0.6 mL) was added, and the mixture was stirred for one more hour, then the temperature rose to 0 °C and reacted for 30 min. 10 mL water was added to the solution to quench the reaction, the mixture was then warmed to room temperature and poured into water, the organic layer was extracted with dichloromethane (3×50) mL) and dried over anhydrous MgSO₄. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography to give **6a** as an orange oil in 83.4 % yield (1.21 g, 2.9 mmol). MS, m/z: 414.419 (M⁺), ¹H NMR (400 MHz, Acetone) δ 9.79 (s, 1H), 7.77 (d, J = 3.9 Hz, 1H), 7.69 (dd, J = 9.6, 5.2 Hz, 3H), 7.51 (d, J = 7.9 Hz, 1H), 7.49 -7.42 (m, 1H), 7.36 - 7.31 (m, 1H), 7.29 (s, 1H), 7.27 - 7.20 (m, 3H), 1.96 (ddd, J = 10.2, 6.3, 3.3 Hz, 4H), 1.01 - 0.89 (m, 4H), 0.55 - 0.41 (m, 10H).

Compound 6b. To a solution of diethyl cyanomethylphosphonate (0.5 mL) and NaH (0.07 g, 2.9 mmol)

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in anhydrous THF (10 mL) was dropwise added solution of compound **5b** (0.6 g, 1.4 mmol) in anhydrous THF at 0 °C under N₂ circumstance, then the solution heated up to 70 °C for 3 h. After the reaction completed, poured the solution into saturated ammonium chloride solution. The organic phase was extracted by AcOEt, washed with brine and dried over MgSO₄. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography to give **6b** as a yellow oil in 87.3 % yield (0.55 g, 1.2 mmol). MS, m/z: 449.587 (M⁺), ¹H NMR (400 MHz, Acetone) δ 7.64 (ddd, *J* = 30.4, 17.1, 10.7 Hz, 3H), 7.45 (ddd, *J* = 14.7, 7.9, 1.2 Hz, 1H), 7.31 (dd, *J* = 8.0, 4.6 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.17 – 6.90 (m, 2H), 6.55 (dd, *J* = 71.5, 42.1 Hz, 1H), 5.33 – 5.03 (m, 1H), 2.38 – 2.17 (m, 4H), 2.05 – 1.93 (m, 4H), 1.09 – 0.77 (m, 10H), 0.77 – 0.37 (m, 10H).

Compound 7b. A solution of compound 6b (0.55 g, 1.2 mmol) in anhydrous toluene (10 mL) was prepared in a three neck flask which was purged with nitrogen, then the solution was cooled to -78 °C and dropwise added DIBAH (2.5 mL), after this, the resulting mixture was stirred for 2 h. Wet silicagel powder was added to the solution to quench the reaction, then the temperature rose to 0 °C and reacted for 1 h. The organic phase was extracted by AcOEt, washed with brine and dried over MgSO₄. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography to give 7b as an orange oil in 72.2 % yield (0.4 g, 0.9 mmol, Z/E=1/0.59). MS, m/z: 452.322 (M⁺), ¹H NMR (400 MHz, Acetone) δ 10.15 (d, J = 7.9 Hz, 1H), 9.99 (d, J = 8.1 Hz, 0.59H), 7.70 – 7.63 (m, 3H), 7.59 (d, J = 2.0 Hz, 1.5H), 7.45 (dd, J = 7.9, 1.4 Hz, 1.5H), 7.36 (d, J = 11.5 Hz, 1H), 7.35 -7.28 (m, 1.6H), 7.25 - 7.17 (m, 3H), 7.09 (t, J = 17.5 Hz, 1.7H), 6.94 (dd, J = 16.2, 9.6 Hz, 1.6H), 6.36 (s, 0.6H), 5.76 (d, J = 8.1 Hz, 0.67H), 5.58 (d, J = 7.8 Hz, 1H), 2.34 (d, J = 2.8 Hz, 3H), 2.20 (t, J = 17.4 Hz, 2.5H), 2.09 - 1.94 (m, 6.4H), 1.02 -0.72 (m, 16H), 0.58 – 0.32 (m, 16H).

Chromophore C1. A solution of compound 6a (0.5 g, 1.2 mmol) and TCF acceptor (0.28 g, 1.4 mmol) in ethanol (20 mL) was allowed to stir at 80 °C for 12 h, then after removal of the solvent under reduced pressure, the crude product was purified by silica chromatography to give C1 as a purple solid in 41.2 % yield (0.3 g, 0.5 mmol). m.p. : 169.22 °C. MS, m/z: 595.733 (M^+) , ¹H NMR (400 MHz, Acetone) δ 8.04 (d, J = 16.0 Hz, 1H), 7.70 (dd, J = 7.3, 4.4 Hz, 3H), 7.59 (d, J = 4.0 Hz, 1H), 7.51 (dd, J = 18.1, 12.0 Hz, 2H), 7.37 - 7.28 (m, 2H), 7.27 - 7.18 (m, 2H)3H), 6.78 (d, J = 16.0 Hz, 1H), 2.02 – 1.94 (m, 4H), 1.86 – 1.70 (m, 6H), 1.03 - 0.88 (m, 4H), 0.58 - 0.34 (m, 10H). ¹³C NMR (100 MHz, Acetone) & 175.68, 173.58, 150.75, 150.69, 150.44, 141.63, 140.07, 138.94, 138.51, 136.35, 134.88, 132.89, 127.83, 126.89, 126.37, 125.90, 122.35, 120.80, 119.86, 119.41, 119.29, 112.73, 111.52, 110.86, 109.98, 97.85, 97.63, 54.32, 39.21, 25.36, 24.70, 22.09, 12.49. Anal. Calcd. for C₃₉H₃₇N₃OS (%): C, 78.62; H, 6.26; N, 7.05. Found: C, 78.59; H, 6.25; N, 7.08.

Chromophore C2. A solution of compound **7b** (0.2 g, 0.44 mmol) and **TCF** acceptor (0.11 g, 0.55 mmol) in ethanol (20 mL) was allowed to stir at 75 $^{\circ}$ C for 12 h, then after removal of the solvent under reduced pressure, the crude product was

purified by silica chromatography to give C2 as a blue solid in 67.9 % yield (0.19 g, 0.3 mmol). m.p. : 143.87 °C. MS, m/z: 633.109 (M⁺), ¹H NMR (400 MHz, Acetone) δ 8.14 (dd, J = 15.1, 12.0 Hz, 1H), 7.84 - 7.71 (m, 3H), 7.69 - 7.63 (m, 1H), 7.62 - 7.56 (m, 1H), 7.48 - 7.44 (m, 1H), 7.38 - 7.31 (m, 2H), 7.28 - 7.17 (m, 1H), 7.11 (d, J = 16.1 Hz, 1H), 6.65 (dd, J =23.0, 9.1 Hz, 2H), 2.51 (dd, J = 36.2, 29.0 Hz, 4H), 2.08 (ddd, J = 6.3, 5.7, 2.2 Hz, 4H), 1.82 (d, J = 15.3 Hz, 6H), 1.11 - 0.92 (m, 10H), 0.70 - 0.45 (m, 10H). ¹³C NMR (100 MHz, CDCl₃) δ 175.89, 173.29, 154.05, 151.57, 151.23, 146.97, 143.67, 142.39, 140.57, 135.59, 134.06, 133.69, 131.15, 129.82, 128.39, 127.58, 127.00, 126.38, 123.01, 121.40, 120.12, 119.97, 116.36, 112.24, 111.58, 111.39, 96.89, 95.52, 55.03, 40.27, 39.97, 39.61, 31.43, 28.49, 28.29, 26.45, 26.04, 23.08, 13.77. Anal. Calcd. for C₄₄H₄₇N₃O (%): C, 83.37; H, 7.47; N, 6.63. Found: C, 83.39; H, 7.41; N, 6.70.

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Notes and references

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Graphical abstract

Chromophore C2 (below) has better electro-optic performance than chromophore C1 (above).

