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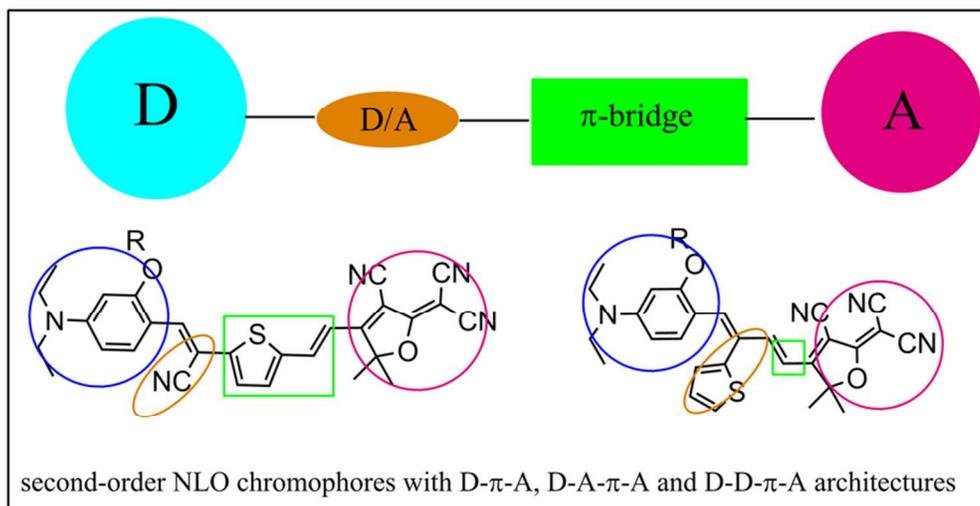


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## Comparison of second-order nonlinear optical chromophores with D- $\pi$ -A, D-A- $\pi$ -A and D-D- $\pi$ -A architectures: diverse NLO effects and interesting optical behavior

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Four second-order nonlinear optical chromophores with D- $\pi$ -A, D-A- $\pi$ -A and D-D- $\pi$ -A architectures had been synthesized and systematically characterized. Chromophores A and C had been synthesized with additional acceptor (-CN) or donor group (thiophene) on the  $\pi$  bridge, termed the D-A- $\pi$ -A and D-D- $\pi$ -A configurations. D- $\pi$ -A structural chromophores B and D were chosen as reference compounds for comparison. The results show that incorporation of the -CN group could increase poling efficiency possibly due to reduced intermolecular dipole-dipole interactions which results in comparable  $r_{33}$  values (48 pm/V).  $R_{33}$  value of 45 pm/V was obtained for film C/APC suggesting significant site isolation. Compare with the D- $\pi$ -A structural chromophores B and D, Chromophores A and C demonstrated similar or enhanced NLO effects and better optical transparency.

### 1. Introduction

In recent years, organic electro-optic (OEO) materials have attracted much attention and been extensively studied owing to their potential applications in optical switches, optical sensors, information processors, and telecommunications etc.<sup>1-4</sup> The second-order nonlinear optical (NLO) chromophores are the key constructing blocks for OEO materials.<sup>5</sup> To meet the stringent requirements for the using of devices, NLO chromophores should exhibit good properties such as high thermal and chemical stabilities, large nonlinearity, and good transparency, as well as easy syntheses. However, experimentally observed trade-offs, such as nonlinearity-transparency trade-off make it hard to achieve all of these requirements simultaneously.<sup>6, 7</sup> In addition, organic NLO chromophores, especially those demonstrating high  $\beta$  values, typically have large dipole moments. The strong inter chromophore dipole-dipole interactions may lead to unfavorable antiparallel packing of the chromophores, thus

reducing the optical nonlinearities.<sup>8</sup> Several approaches have been found to solve these problems in some degree.<sup>6, 7, 9, 10</sup>

The second-order NLO chromophores are based on a push-pull system, which consists of an electron-donating group (Donor) and an electron-withdrawing group (Acceptor) coupled through a  $\pi$ -conjugated bridge.<sup>11, 12</sup> To date, most of these chromophores have been constructed with a typical electron donor- $\pi$  bridge-electron acceptor (D- $\pi$ -A) configuration. Previous studies have shown that, we could construct different types of structural motifs by inserting electron-rich ring or an electron-poor ring into the  $\pi$  bridge of chromophore, which may lead to enhanced strength of the donor and acceptor.<sup>13-15</sup>

Recently, it has been found that incorporation of additional electron-withdrawing units (such as cyanovinyl, thiazole) into the  $\pi$  bridge as internal acceptors, termed the "D-A- $\pi$ -A" configuration, displays several advantages such as tuning of the molecular energy levels, red-shift of the charge-transfer absorption band. They had been widely studied in the dye-sensitized solar cells (DSCs) area.<sup>16-18</sup> There were articles

about tricyanopyrrolidene-based chromophores containing thiophene as a lateral moiety to the  $\pi$  bridge which form the “D–D– $\pi$ –A” configuration.<sup>19, 20</sup> Based on the excellent work on the different structures of dyes, we were wondering if it is possible to introduce additional acceptor or donor group on the  $\pi$  bridge but without changing the conjugated length of the chromophores. Perhaps, the introduced acceptor or donor group could isolate the chromophores from each other more effectively, thus improving the NLO effect. And they may have different influences on electron transfer and optical properties.

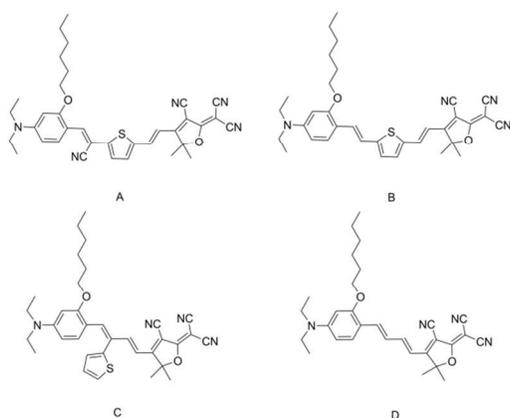


Chart 1 Chemical structure for chromophores A-D.

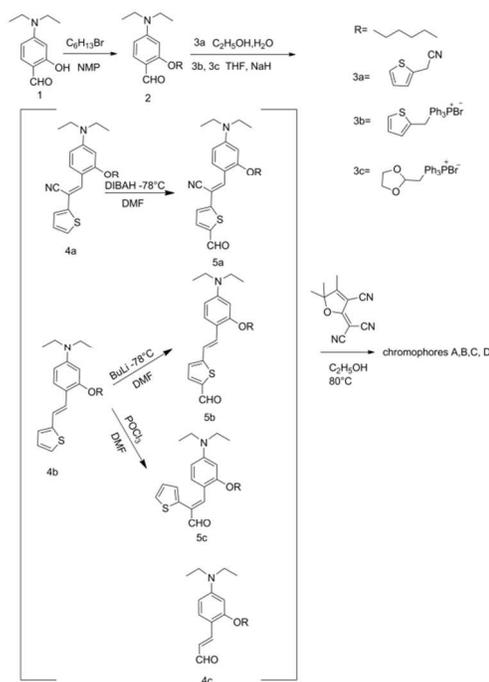
So, in our paper, we would like to compare the structure–property relationship between the three architectures of the second-order chromophores: D– $\pi$ –A, D–A– $\pi$ –A and D–D– $\pi$ –A configurations. We had designed and synthesized chromophores A-D based on the 4-(diethylamino) aryl group donor and strong tricyanovinylidene (TCF) acceptor in simple three or four step reactions. Chromophores A and C had been synthesized with additional acceptor (–CN) or donor group (thiophene) on the  $\pi$  bridge to form the D–A– $\pi$ –A and D–D– $\pi$ –A configurations. D– $\pi$ –A structural chromophores B and D were chosen as reference compounds for comparison. The synthesis, UV-Vis, solvatochromic, DFT calculations, thermal stabilizes and EO activities of these chromophores were systematically studied and compared to illustrate the architectural influence on rational NLO chromophore designs.

## 2. Results and discussion

### 2.1 Synthesis and characterization of chromophores

Scheme 1 shows the synthetic approach for the new chromophores A-D. Starting from the amine donor aldehyde intermediate compound 3, chromophores A-D were synthesized in good overall yields through simple three or four step reactions: the free hydroxyl group on the donor was protected by the alkyl group to improve the solubility through Williamson ether synthesis, after introduction of the bridge by Wittig condensation, compounds 4a-c were prepared with a

high yield. Treatment of compound 4b with  $\text{POCl}_3$  and DMF gave an aldehyde 5c. Treatment of compound 4a-b with *n*-BuLi and DMF gave an aldehyde 5a-b. And the final condensations with the TCF acceptor give chromophores A-B as green solids and chromophores C-D as blue solids. All of the chromophores were fully characterized by  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , elemental analysis and mass spectroscopy. These chromophores possess good solubility in common organic solvents, such as dichloromethane, chloromethane and acetone.



Scheme 1 Chemical structures and synthetic routes for chromophores A-D.

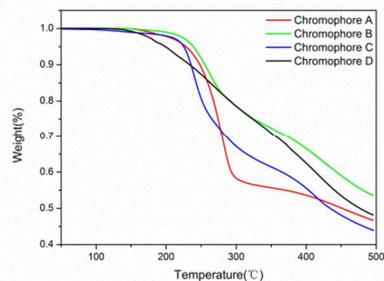
### 2.2 Thermal stability

The NLO chromophores must be thermally stable in order to withstand the poling process and subsequent processing for use. The thermal stability of the chromophores was investigated using thermo gravimetric analysis (TGA) as shown in Figure 1. All the chromophores exhibited good thermal stabilities with the decomposition temperatures ( $T_d$ ) higher than 200 °C as showed in Table 1. The chromophore D had the minimum decomposition temperature ( $T_d=200$  °C). It may be attributed to the reason that the extended polyenes are typically not sufficiently stable.<sup>21</sup> The chromophore A-C showed different decomposition temperatures from 225 °C to 236 °C, which was high enough for the application in EO device preparation.<sup>22</sup>

### 2.3 Optical properties

In order to reveal the effect of different structures on the intramolecular charge transfer (ICT) of dipolar chromophores,

UV-Vis absorption spectra of the four chromophores were measured in series solvents with different dielectric constants, as shown in Figure 2.

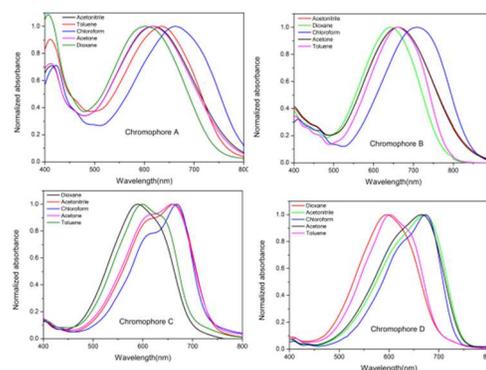


**Fig. 1** TGA curves of chromophores A-D with a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  in nitrogen atmosphere.

The spectrum data are summarized in Table 1. Depending on different structures, the resulting NLO chromophores exhibited diverse intramolecular charge-transfer (ICT) absorption properties. It may see from the Figure 2 that chromophore A, B, C and D showed the maximum absorption ( $\lambda_{\text{max}}$ ) from 663 nm to 709 nm in chloroform. Incorporation of additional electron-withdrawing -CN unit into the  $\pi$  bridge did not red-shift the maximum absorption band as reported in the dye-sensitized solar cells (DSCs) molecules containing cyanoacrylic acid acceptor.<sup>16-18</sup> Compared to chromophore B, chromophore A showed large blue-shift ( $\Delta\lambda=46\text{nm}$ ), it attribute to the different acceptors: the -CN group would enhance the electron-withdrawing ability of cyanoacrylic acid, but such an enhancement may weaken if the acceptor become much stronger acceptor TCF. And, it may somehow weak the strength of the donor. Chromophores C and D exhibit the absorption maximum ( $\lambda_{\text{max}}$ ) at 668 and 673 nm in chloroform, respectively. This may be explained by that chromophore C possessed a less coplanar geometry due to the steric hindrance of the lateral group thiophene.

Besides, the solvatochromic behavior was also an important aspect to investigate the polarity of chromophores. It was found that both chromophores C and D showed very large bathochromic shifts of 79 and 78nm, from dioxane to chloroform, displaying larger solvatochromism than CLD (60 nm) and the similar single donor FTC (61 nm).<sup>23, 24</sup> Chromophore A and B showed moderate bathochromic shifts of 61 and 66 nm from dioxane to chloroform. This confirms that chromophores C and D are more easily polarizable than Chromophore A and B.<sup>9, 25</sup> With a further increase of solvent polarity, a saturation behavior was found for four chromophores in more polar solvents, such as acetone, and acetonitrile. For example, compounds A and B showed hypsochromic shifts of -45nm and -47nm, respectively, from chloroform to acetone. Chromophores C and D also exhibited similar solvatochromic behavior. Such a phenomenon was reported by Davies<sup>9</sup> and was ascribed to the back electron

transfer from the acceptor side to the donor side in polar solvents which causing blue-shift from the absorption.<sup>14</sup>



**Fig. 2** UV-Vis absorption spectra of chromophore A-D in six kinds of aprotic solvents with varying dielectric constants ( $\epsilon$ )

## 2.4 Theoretical calculations

The DFT calculations were carried out at the hybrid B3LYP level by employing the split valence 6-311g (d, p) basis set<sup>26, 27</sup> to understand the ground-state polarization of the chromophores with different configurations. All molecules were assumed to be in trans-configurations. The HOMO-LUMO energy gap, dipole moment ( $\mu$ ), and first hyperpolarizability ( $\beta$ ) 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.<sup>22, 28</sup> Fig.3 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 and LUMO energies were calculated by DFT method and summarized in Table 2. As showed in Table, the HOMO energy of chromophore A is 0.29 eV lower than that of chromophore B (-5.580 eV vs. -5.290 eV), while the LUMO energy of chromophore A is 0.2 eV lower than that of chromophore B (-3.459 eV vs. -3.259 eV). The cyanovinyl unit has the potential of lowering the LUMO energy and hence a lower excitation energy.<sup>29</sup> However, in chromophore A, the -CN unit also had potential of lowering the HOMO energy to a greater extent than the LUMO energy. These two factors increase the gap between the HOMO and LUMO by 0.09eV. The HOMO-LUMO gap of chromophore C was little larger than chromophore D, this may be explained by that conjugate structure was somehow wrecked by the lateral group thiophene. As  $\Delta E$  is reduced, resulting in a bathochromic shift of  $\lambda_{\text{max}}$  within the series of compounds. These results correspond with the conclusion of UV-Vis spectra analysis.

To get more information from the frontier orbitals, the composition of the HOMOs and LUMOs has been calculated

using the Multiwfn program.<sup>30</sup> As shown in Table 3, the whole chromophore molecule was segmented as donor,  $\pi$ -bridge, and acceptor. At the same time, the attributions of the substituent groups (-CN, thiophene) located in bridge moiety were listed separately. For the chromophores A and B, the LUMO was largely stabilized by the contributions from acceptors (43.76%-44.27%) and the  $\pi$ -bridges (38.99%-39.77%), while the HOMO was largely stabilized by the contributions from donors (46.57%-52.21%) and  $\pi$ -bridges (28.95%-30.93%). For the chromophores C and D, the LUMO and HOMO were largely stabilized by the contributions from acceptors and donors. The difference attribute to the different properties of thiophene and polyenes. For chromophore C, when compare LUMO to HOMO level, the contribution of thiophene ring decreased to 0.26% from 2.52%. The comparison of HOMO and LUMO electron distribution in the thiophene ring indicated the easy delocalization of electrons in the thiophene ring. Consequently, the thiophene ring can be treated as another donor, which efficiently enhances the electron density of the conjugated

system and increases the polarizability of chromophore C.<sup>31</sup> This corresponded well with the results of solvatochromism study. Similarly, the comparison of HOMO and LUMO electron distribution in the -CN group indicated that the -CN can be treated as another acceptor.

**Table 1** Thermal and Optical Properties data of the Chromophores.

Chromophores	T <sub>d</sub> (°C)	$\lambda_{\max}^a$ (nm)	$\lambda_{\max}^b$ (nm)	$\Delta\lambda^c$ (nm)
A	228	602	663	61
B	238	643	709	66
C	225	589	668	79
D	200	595	673	78

<sup>a</sup>  $\lambda_{\max}$  was measured in dioxane. <sup>b</sup>  $\lambda_{\max}$  was measured in chloroform. <sup>c</sup>  $\Delta\lambda$  was the difference between <sup>a</sup>  $\lambda_{\max}$  and <sup>b</sup>  $\lambda_{\max}$ .

**Table 2** Summary of DFT Data

Chromophore	$\Delta E(\text{DFT})^a(\text{V})$	HOMO <sup>b</sup> (eV)	LUMO <sup>c</sup> (eV)	$\beta_{\text{tot}}^d(10^{-30}\text{esu})$	$\mu^e$ (D)
A	2.12	-5.580	-3.459	518.57	15.05
B	2.03	-5.290	-3.259	678.72	20.53
C	2.49	-5.514	-3.018	208.61	20.67
D	2.44	-5.507	-3.065	226.73	21.49

<sup>a</sup>  $\Delta E(\text{DFT})$  was calculated from DFT calculations. <sup>b</sup> calculated from DFT calculations. <sup>c</sup> calculated from DFT calculations. <sup>d</sup>  $\beta_{\text{tot}}$  is the first-order hyperpolarizability, and where  $\beta_{\text{tot}} = \sqrt{(\beta_x)^2 + (\beta_y)^2 + (\beta_z)^2}$ , calculated from DFT quantum mechanical methods. <sup>e</sup>  $\mu$  is the total dipole moment.

**Table 3** The Molecular Orbital Composition (%) in the Ground State for Chromophores A-D.

Chromophore	A		B		C		D	
	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
donor	46.57%	17.13%	52.21%	15.96%	47.57%	36.10%	49.47%	36.28%
$\pi$ bridge	30.93%	38.99%	28.95%	39.77%	11.45%	16.26%	10.42%	16.36%
acceptor	19.55%	43.76%	18.84%	44.27%	38.47%	47.38%	40.11%	47.36%
thiophene					2.52%	0.26%		
CN	2.96%	0.13%						

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

First hyperpolarizability is a third rank tensor that can be described by a  $3 \times 3 \times 3$  matrix. The components of  $\beta$  can be calculated using the following equation<sup>32</sup>:

$$\beta_{\text{tot}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

Where

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

When used carefully and consistently, this method of DFT has been shown to give relatively consistent descriptions of

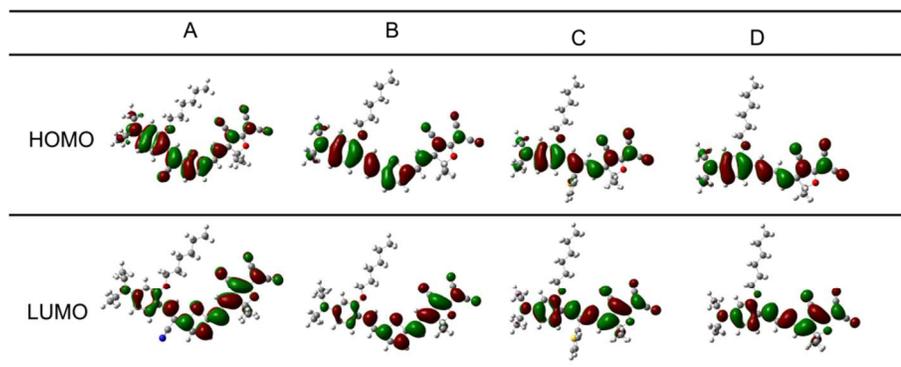
first-order hyperpolarizability for a number of similar chromophores.<sup>27,33</sup>

As reported earlier, the  $\beta$  value has a close relationship with the substituents, steric hindrance, and intramolecular charge-transfer,  $\pi$ -conjugation length and so on.<sup>34,35</sup> The  $\beta$  value of chromophore B was larger than that of chromophore A due to narrower energy gap between HOMO and LUMO as shown in Table 2. It attribute to the introduction of electron-withdrawing units -CN. It may weak the strength of the donor probable due to its nearby to the donor. The  $\beta$  value of chromophore C was little smaller than that of chromophore D. This may be explained by that chromophore C possessed a less coplanar

geometry due to the steric hindrance of the lateral group thiophene.

The calculated results indicated that the total dipole moment ( $\mu$ ) of chromophore A is smaller than that of chromophores B-D. The -CN substitution would create another local dipole

moment in other direction which may reduce the total dipole moment. The smaller  $\mu$  can reduce the aggregation of chromophore A in organic materials which was in accordance with the Electro-Optic performance study.<sup>36</sup>



**Fig. 3** The frontier molecular orbitals of chromophores A-D.

## 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- $\mu\text{m}$  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.<sup>37-39</sup>

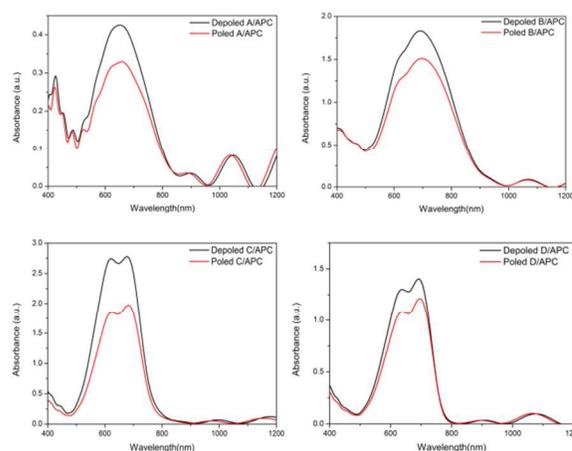
The measured  $r_{33}$  values depend on the chromophore number density ( $N$ ),  $\beta$  value, and poling efficiency, described by the  $\cos^3(\theta)$  order parameter, as indicated by<sup>40</sup>

$$r_{33} \approx \left[ 2N\beta f \langle \cos^3 \theta \rangle / n^4 \right]$$

Where the  $f$  term describes electric-field factors and  $n$  is the refractive index of the film, both of which remain relatively constant for related chromophores at similar loading densities.  $\cos^3(\theta)$  is the acentric order parameter.  $\theta$  is the angle between the permanent dipole moment of chromophores and the applied electric field. At low concentration, the electro-optic activity increased with chromophore density, dipole moment and the strength of electric poling field. However, when the concentrations of chromophores increased to a certain extent, the  $N$  and  $\cos^3(\theta)$  are no longer independent factor. Then,

$$\langle \cos^3(\theta) \rangle = (\mu F / 5kT) \left[ 1 - L^2(W / kT) \right]$$

Where  $k$  is the Boltzmann constant and  $T$  is the Kelvin (poling) temperature.  $F = [f(0) E_p]$  where  $E_p$  is the electric poling field.  $L$  is the Langevin function, which is a function of  $W/kT$ , the ratio of intermolecular electrostatic energy ( $W$ ) to the thermal energy ( $kT$ ).  $L$  is related to electrostatic interactions between molecules.



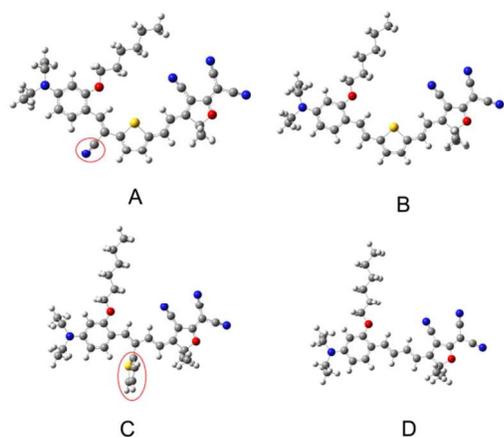
**Fig. 4** UV-Vis absorption spectra of E-O polymers before and after poling (25%wt).

When the intermolecular electrostatic interactions are neglected, the electro-optic coefficient ( $r_{33}$ ) should increase linearly with chromophore density, 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 (N) 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.<sup>41</sup>

To evaluate their EO activity, 25 wt% of the chromophores A-D were doped into APC and formulated as the typical guest–host polymer. For this series of chromophores, the poled films of A/APC, B/APC, C/APC and D/APC afforded  $r_{33}$  values of 48, 52, 45 and 21 pmV<sup>-1</sup>, respectively. In order to conclusively determine the relative contributions of  $\beta$  values to the  $r_{33}$  values obtained for the four chromophore with quite different  $\beta$  value, further investigation is necessary.

To identify the underlying mechanism for the difference in achievable EO performance, the order parameter ( $\Phi$ ) was calculated by measuring UV-Vis absorption spectra. After the corona poling, the dipole moments of the chromophore moieties in the polymer were aligned, and the absorption curve decreased due to birefringence<sup>25</sup>. The order parameter ( $\Phi$ ) for films can be calculated from the absorption changes according to the following equation:  $\Phi = 1 - A/A_0$ <sup>42</sup>, in which A and A<sub>0</sub> are the respective absorptions of the polymer films after and before corona poling. The order parameter ( $\Phi$ ) of poled films was calculated. The  $\Phi$  values of film-A/APC, B/APC, C/APC and D/APC are 22.48 %, 16.05 %, 28.95%, 13.52% respectively as shown in Figure 4. This suggests the poling efficiencies of the four chromophores may indeed be quite different.<sup>43</sup>



**Fig. 5** The optimized structure of chromophore A-D.

For chromophores A and B, DFT calculations suggest that the  $\beta$  value of chromophore B is 30% larger than that of chromophores A, while their  $r_{33}$  values were nearly. The larger order parameter (22.48 % and 16.05 %) indicates that film-A/APC has weaker inter chromophore electrostatic interactions than film-B/APC in this density. While the small structural differences between chromophores A and chromophores B likely have little effect on the steric of poling, it may have a larger influence on the electrostatics of it. For chromophore A, the introduction of the -CN group on the  $\pi$  bridge produces a

decrease of the dipole moment of the push-pull molecule from about 20 to 15 D, the decrease of dipole moment can efficiently reduce the intermolecular electrostatic interactions. Moreover, the side -CN group may somehow act as the isolation group to suppress the possible charge transport between chromophores. So, the film A/APC achieves similar  $r_{33}$  values with that of film B/APC (48 and 52 pmV<sup>-1</sup>), even though it has relatively lower  $\beta$ . Meanwhile, it offers a pleasant surprise to the nonlinearity–transparency trade off that almost inevitably occurs in the dipolar donor– $\pi$ –acceptor systems with a 41 nm hypsochromic shift of absorption maximum.

The poled films of C/APC and D/APC afforded  $r_{33}$  values of 45 and 21 pmV<sup>-1</sup>, respectively, although chromophores C and chromophores D have similar  $\beta$  value. The EO coefficient measurements clearly indicate that the chromophores C show significant improvements in  $r_{33}$  value as compared to the chromophores D. The largest order parameter (28.95%) indicates that film-C/APC has weaker inter chromophore electrostatic interactions than other films in this density and chromophores C is more polarizable.<sup>43</sup> This corresponded well with the results of solvatochromism study. When at a low-density range, the intermolecular dipolar interactions are relatively weak. The intermolecular dipole-dipole interactions would become stronger and stronger, accompanying with the increased concentration of NLO chromophore moieties in the polymer which would finally lead to a decreased NLO coefficient. As for chromophore C, it may be revealed by the optimized configurations (Fig.5) that the side thiophene ring group was perpendicular to the direction of the dipole moment of the chromophore which could act as the isolation group to suppress the possible aggregation. The larger  $r_{33}$  values indicates that film-C/APC has weaker inter chromophore electrostatic interactions than film-D/APC in this density. Larger  $r_{33}$  values are obtained for the chromophore C than that of chromophore D (45 and 21 pmV<sup>-1</sup>), suggesting the side thiophene ring group can reduce the inter chromophore dipole–dipole interactions more effectively, thereby enhancing the NLO effects of the chromophores.

### 3. Conclusion

Four organic NLO chromophores based on the 4-(diethylamino) aryl group donor and strong tricyanovinylidihydrofuran (TCF) acceptor with D– $\pi$ –A, D–A– $\pi$ –A and D–D– $\pi$ –A architectures had been synthesized and systematically characterized. The chromophores obtained high thermal and chemical stabilities, large nonlinear optical coefficients, and good solubility in all common solvents. Chromophores A and C had been synthesized with additional acceptor (-CN) or donor group (thiophene) on the  $\pi$  bridge. D– $\pi$ –A structural chromophores B and D were chosen as reference compounds for comparison.

The results show that incorporation of the -CN group could reduce intermolecular dipole–dipole interactions due to reduced  $\mu$  which results in comparable  $r_{33}$  values (48 pm/V).  $r_{33}$  values of 45 pm/V are obtained for the film C/APC suggesting

significant site isolation. Compare with the D- $\pi$ -A structural chromophores B and D, Chromophores A and C demonstrated similar or enhanced NLO effects and better optical transparency. These investigations suggest that substituent groups play a critical role in affecting the nonlinearity of D- $\pi$ -A chromophores, which could provide a general tool to guide the future molecular design of highly efficient nonlinear optical chromophores.

#### 4. Experimental section

##### 4.1 Materials and instrument

All chemicals are commercially available and were used without further purification unless otherwise stated. N, N-dimethyl formamide (DMF), Phosphorus oxychloride (POCl<sub>3</sub>), tetrahydrofuran (THF) and ether was distilled over calcium hydride and stored over molecular sieves (pore size 3Å). The 2-dicyanomethylene-3-cyano-4-methyl-2, 5-dihydrofuran (TCF) acceptor was prepared according to the literature.<sup>44</sup> 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).

##### 4.2 Measurements and instrumentation

<sup>1</sup>H-NMR and <sup>13</sup>C-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 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<sup>-1</sup> under the protection of nitrogen. The elemental analysis was measured on Flash EA 1112 Elemental Analyzer.

##### 4.3 Synthesis and characterization

###### Compound 2

To a solution of 4-(diethylamino)-2-hydroxybenzaldehyde 1a (11.59 g, 60.00 mmol) and 1-bromohexane (14.99 g, 90.80 mmol) in NMP (100 ml) was added anhydrous potassium carbonate (19.03 g, 137.70 mmol). The mixture was allowed to stir at 120 °C for 24 h and then poured into water. The organic phase was extracted by AcOEt, washed with brine and dried over MgSO<sub>4</sub>. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography, eluting with (Acetone: Hexane=1:10) to give 4 as an orange oil in 91.3% yield (15.19 g, 54.78 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.18 (s, 1H, CHO), 7.70 (d, J = 9.0 Hz, 1H, ArH), 6.25 (d, J = 9.0 Hz, 1H, ArH), 6.01 (s, 1H, ArH), 4.02 (t, J = 6.3 Hz, 2H, CH), 3.41 (q, J = 7.1 Hz, 4H, CH<sub>2</sub>), 1.87 – 1.75 (m, 2H, CH<sub>2</sub>), 1.55 – 1.43 (m, 2H, CH<sub>2</sub>),

1.35 (dt, J = 7.3, 4.8 Hz, 4H, CH<sub>2</sub>), 1.21 (t, J = 7.1 Hz, 6H, CH<sub>3</sub>), 0.90 (t, J = 7.0 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  186.61, 163.65, 153.65, 129.72, 114.20, 104.12, 92.73, 67.91, 44.68, 31.49, 29.06, 25.75, 22.45, 13.80, 12.13. MS (EI) (M<sup>+</sup>, C<sub>17</sub>H<sub>27</sub>NO<sub>2</sub>): calcd: 277.40; found: 277.20.

###### Compound 4a

2-Thiopheneacetonitrile (1.35g, 11.00 mmol) and an aqueous solution of NaOH (0.02 g, 10 mol %) was added to a flask containing 2 (2.77 g, 10.00 mmol) in EtOH (120 mL). The solution was stirred for 5 h, and EtOH was removed by rotatory evaporator. The organic product was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The collected organic extracts were dried with MgSO<sub>4</sub> and filtered. The filtrate was dried under a vacuum and the residue was further purified by silica chromatography, eluting with (Acetone: Hexane=1:20) to give 4a as an orange powder in 76.5% yield (2.92 g, 7.65mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.15 (d, J = 9.0 Hz, 1H, ArH), 7.76 (s, 1H, CH), 7.15 (m, 1H, CH), 7.10 (d, J = 5.1 Hz, 1H, CH), 6.97 – 6.92 (m, 1H, CH), 6.28 (m, 1H, ArH), 6.01 (d, J = 17.5 Hz, 1H, ArH), 3.93 (t, J = 6.4 Hz, 2H, CH<sub>2</sub>), 3.34 (q, J = 7.1 Hz, 4H, CH<sub>2</sub>), 1.82 – 1.69 (m, 2H, CH<sub>2</sub>), 1.50 – 1.41 (m, 2H, CH<sub>2</sub>), 1.32 – 1.27 (m, 4H, CH<sub>2</sub>), 1.15 (t, J = 7.1 Hz, 6H, CH<sub>3</sub>), 0.85 (q, J = 8.8 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  158.91, 140.62, 133.85, 128.00, 126.76, 123.36, 122.92, 117.93, 103.51, 93.42, 69.54, 67.25, 43.66, 30.57, 24.73, 21.68, 13.02, 11.67. MS (MALDI) (M<sup>+</sup>, C<sub>23</sub>H<sub>30</sub>N<sub>2</sub>OS): calcd: 382.56; found: 382.21

###### Compound 4b

Under a N<sub>2</sub> atmosphere, to a solution of compound 2 (1.39g, 5.00 mmol) and 3b (3.47g, 6.00 mmol) in ether (100 ml) was added NaH (0.71g, 30.00 mmol). The solution was allowed to stir for 48h and then poured into water. The organic phase was extracted by AcOEt, washed with brine and dried over MgSO<sub>4</sub>. 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 4b as orange oil in 83.7% yield (1.50 g, 4.18 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.26 (d, J = 8.7 Hz, 1H, CH), 7.15 (d, J = 11.7 Hz, 1H, CH), 7.07 (d, J = 11.7 Hz, 1H, CH), 7.00 (d, J = 4.6 Hz, 1H, CH), 6.87 (m, 2H, CH, PhH), 6.20 (d, J = 10.3 Hz, 1H, CH), 6.09 (s, 1H, PhH), 3.92 (t, J = 6.4 Hz, 2H, CH<sub>2</sub>), 3.28 (q, J = 7.0 Hz, 4H, CH<sub>2</sub>), 1.83 – 1.72 (m, 2H, CH<sub>2</sub>), 1.46 (m, 2H, CH<sub>2</sub>), 1.30 (m, 4H, CH<sub>2</sub>), 1.10 (t, J = 7.0 Hz, 6H, CH<sub>3</sub>), 0.85 (t, J = 6.7 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  157.00, 147.66, 144.05, 126.80, 126.24, 123.34, 122.66, 121.42, 116.25, 112.77, 103.20, 94.93, 67.17, 43.49, 30.60, 28.37, 24.9, 21.58, 13.01, 11.72. (MALDI) (M<sup>+</sup>, C<sub>22</sub>H<sub>31</sub>NOS): calcd: 357.55; found: 357.86

###### Compound 5a

Under a N<sub>2</sub> atmosphere, LDA (3.50 ml, 7.00mmol), was added dropwise into the solution of 4a (2.00 g, 5.23mmol) in 30 mL of THF prechilled to -78 °C. After the completion of the addition, the solution was warmed to room temperature and stirred for 1 h. The solution was then cooled to -78 °C and

stirred for 3 h after the addition of N-formylpiperidine (0.62g, 5.54 mmol). The reaction was quenched by 1 N HCl and extracted with diethyl ether. The combined organic extracts were dried over MgSO<sub>4</sub> and the residue was further purified by silica chromatography, eluting with (Acetone: Hexane = 1:10) to give compound 5a as a red solid in 74.3% yield (1.59g, 3.89mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.73 (s, 1H,CHO), 8.21 (d, *J* = 9.2 Hz, 1H, ArH), 7.95 (s, 1H,CH), 7.57 (d, *J* = 4.0 Hz, 1H,CH), 7.18 (d, *J* = 4.0 Hz, 1H,CH), 6.26 (dd, *J* = 9.2, 2.4 Hz, 1H,ArH), 5.97 (d, *J* = 2.4 Hz, 1H,ArH), 3.92 (t, *J* = 6.5 Hz, 2H,CH<sub>2</sub>), 3.34 (q, *J* = 7.1 Hz, 4H,CH<sub>2</sub>), 1.83 – 1.72 (m, 2H,CH<sub>2</sub>), 1.50 – 1.39 (m, 2H,CH<sub>2</sub>), 1.35 – 1.26 (m, 4H,CH<sub>2</sub>), 1.14 (t, *J* = 7.1 Hz, 6H,CH<sub>3</sub>), 0.84 (t, *J* = 7.0 Hz, 3H,CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 182.23, 160.62, 152.18, 140.74, 137.67, 137.52, 129.65, 124.36, 118.28, 110.05, 104.90, 95.38, 93.87, 68.46, 44.82, 31.56, 29.14, 25.88, 22.66, 14.05, 12.67. (MALDI) (M<sup>+</sup>, C<sub>24</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub>S): calcd: 410.57; found: 410.20

#### Compound 5b

Under a N<sub>2</sub> atmosphere, 4b (0.36g, 1mmol) was dissolved in 150 mL of freshly distilled THF and cooled to -78 °C. Approximately 2 equivalents of 2.5 Mn BuLi in hexanes (20mL,5mmol) was added drop wise over 20 min. Reaction continued at -78 °C for 1 h at which time DMF (0.37g, 5mol) 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<sub>4</sub>. 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 5b as an orange oil in 77.1% yield (0.30 g, 0.77 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.69 (s, 1H,CHO), 7.46 (d, *J* = 4.0 Hz, 1H,CH), 7.23 – 7.12 (m, 1H, ArH), 7.00 (d, *J* = 4.0 Hz, 1H,CH), 6.70 (d, *J* = 11.9 Hz, 1H,CH), 6.42 (d, *J* = 11.9 Hz, 1H,CH), 6.13 (dd, *J* = 8.6, 2.3 Hz, 1H,ArH), 6.08 (d, *J* = 2.3 Hz, 1H,ArH), 3.87 (t, *J* = 6.5 Hz, 2H,CH<sub>2</sub>), 3.30 (q, *J* = 7.1 Hz, 4H,CH<sub>2</sub>), 1.72 – 1.54 (m, 2H,CH<sub>2</sub>), 1.37 – 1.29 (m, 2H,CH<sub>2</sub>), 1.26 – 1.20 (m, 4H,CH<sub>2</sub>), 1.12 (t, *J* = 7.1 Hz, 6H,CH<sub>3</sub>), 0.80 (t, *J* = 6.8 Hz, 3H,CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 181.71, 157.27, 150.76, 148.69, 139.96, 135.30, 129.61, 126.94, 118.03, 111.11, 102.65, 94.32, 67.16, 43.45, 30.44, 28.27, 24.72, 21.62, 13.03, 11.70. (MALDI) (M<sup>+</sup>, C<sub>23</sub>H<sub>31</sub>NO<sub>2</sub>S): calcd: 385.56; found: 385.74

#### Compound 5c

A solution of 20 ml DMF was cooled to 0 °C and was maintained at this temperature during the dropwise addition of phosphorus oxychloride (0.64 g, 4.2 mmol). The solution was kept for 2 h of stirring at 0 °C and the temperature was kept during the dropwise addition of compound 4b in 10 ml DMF (0.72 g, 2 mmol). The solution was gradually warmed to room temperature and stirred for 3 h of stirring at 90 °C before being poured into 150 ml solution of sodium carbonate (10 %) for quench. The reaction mixture was extracted by AcOEt, washed with brine, dried over MgSO<sub>4</sub>. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography, eluting with (AcOEt: Hexane = 1:10) to give

compound 5c as an orange-red solid in 73.3% yield (0.56 g, 1.47 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.87 (s, 0.11H, CHO), 9.52 (s, 0.89H, CHO), 8.17 (s, 0.11H, CH), 7.79 (s, 0.89H, CH), 7.31 (d, *J* = 6.2 Hz, 1H, CH), 7.00 (dd, *J* = 5.1, 3.5 Hz, 1H, CH), 6.98 (m, 1H,CH) 6.95 (dd, *J* = 8.6, 5.1 Hz, 1H, PrH), 5.98 (d, *J* = 2.0 Hz, 1H, PrH), 5.95 (m, 1H,PrH), 3.95 (t, *J* = 6.4 Hz, 2H,CH<sub>2</sub>), 3.27 (q, *J* = 7.1 Hz, 4H,CH<sub>2</sub>), 1.83 – 1.73 (m, 2H,CH<sub>2</sub>), 1.50 – 1.40 (m, 4H,CH<sub>2</sub>), 1.35 – 1.25 (m, 2H,CH<sub>2</sub>), 1.14 (t, *J* = 7.1 Hz, 0.66H,CH<sub>3</sub>), 1.09 (t, *J* = 7.1 Hz, 5.34H,CH<sub>3</sub>), 0.84 (t, *J* = 7.4 Hz, 3H,CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 191.95, 159.53, 150.49, 146.18, 134.43, 130.66, 126.45, 126.20, 125.36, 109.68, 103.06, 93.01, 67.40, 43.38, 30.47, 28.16, 24.73, 21.46, 13.00, 11.66. (MALDI) (M<sup>+</sup>, C<sub>23</sub>H<sub>31</sub>NO<sub>2</sub>S): calcd: 385.56; found: 385.80

#### Compound 4c

Under a N<sub>2</sub> atmosphere, to a solution of compound 2 (0.50g, 1.80 mmol) and 3c (0.99g, 2.70 mmol) in ether (100 ml) was added NaH (0.33g, 13.50mmol). The solution was allowed to stir for 48h and then poured into water. The organic phase was extracted by AcOEt, washed with brine and dried over MgSO<sub>4</sub>. After removal of the solvent under reduced pressure, the crude product was added 10ml HCL (10%) dropwise into the 30 mL of THF and stirred for 1 h. The organic phase was extracted by dichloromethane and then purified by silica chromatography, eluting with (Acetone: Hexane = 1:10) to give compound 4c as orange oil in 86.7% yield (0.47 g, 1.56 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.55 (d, *J* = 8.1 Hz, 1H,CHO), 7.70 (d, *J* = 15.4 Hz, 1H,CH), 7.39 (d, *J* = 8.4 Hz, 1H,PhH), 6.60 (dd, *J* = 15.4, 8.1 Hz, 1H,CH), 6.28 (d, *J* = 8.4 Hz, 1H,PhH), 6.09 (s, 1H, PhH), 4.01 (t, *J* = 5.2 Hz, 2H,CH<sub>2</sub>), 3.43 (q, *J* = 7.1Hz,4H,CH<sub>2</sub>), 1.92 – 1.77 (m, 2H,CH<sub>2</sub>), 1.49 (m, 4H,CH<sub>2</sub>), 1.40 – 1.32 (m, 2H,CH<sub>2</sub>), 1.21 (t, *J* = 7.1 Hz,6H,CH<sub>3</sub>), 0.93 – 0.89 (t, *J* = 7.1Hz,3H,CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 193.31, 159.18, 150.81, 148.30, 129.80, 122.68, 103.68, 93.72, 67.39, 43.71, 30.56, 28.19, 24.84, 21.55, 12.94, 11.69. MS (EI) (M<sup>+</sup>, C<sub>19</sub>H<sub>29</sub>NO<sub>2</sub>): calcd: 303.44; found: 303.23

#### Chromophore A

To a solution of 5a (0.21 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 °C 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 46.7% yield (0.14 g, 0.23 mmol). <sup>1</sup>H NMR (400 MHz, Acetone) δ 8.26 (d, *J* = 9.2 Hz, 1H, PrH), 8.15 (d, *J* = 16.0 Hz, 1H,CH), 8.06 (s, 1H,CH), 7.74 (d, *J* = 4.1 Hz, 1H,CH), 7.30 (d, *J* = 4.1 Hz, 1H,CH), 6.88 (d, *J* = 16.0 Hz, 1H,CH), 6.53 (dd, *J* = 9.2, 2.3 Hz, 1H,PrH), 6.33 (d, *J* = 2.3 Hz, 1H,PrH), 4.17 (t, *J* = 6.2 Hz, 2H,CH<sub>2</sub>), 3.57 (q, *J* = 7.1 Hz, 4H,CH<sub>2</sub>), 1.90 (s, 6H,CH<sub>3</sub>), 1.64 – 1.52 (m, 2H,CH<sub>2</sub>), 1.47 – 1.36 (m, 4H,CH<sub>2</sub>), 1.34 – 1.27 (m, 2H,CH<sub>3</sub>), 0.92 (t, *J* = 7.1 Hz, 3H,CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, Acetone) δ 178.18, 175.67, 161.74, 153.72, 151.07, 140.05, 139.19, 138.16, 137.63,

130.15, 126.30, 118.91, 114.04, 112.67, 111.68, 110.89, 106.30, 98.75, 95.21, 69.26, 45.28, 32.25, 26.94, 26.21, 24.10, 23.34, 14.37, 13.01. (MALDI) (M<sup>+</sup>, C<sub>35</sub>H<sub>37</sub>N<sub>5</sub>O<sub>2</sub>S): calcd: 591.77; found: 591.23. Anal. Calcd (%) for C<sub>35</sub>H<sub>37</sub>N<sub>5</sub>O<sub>2</sub>S: C, 71.04; H, 6.30; N, 11.83; found: C, 71.09; H, 6.37; N, 11.79;

### Chromophore B

The procedure for chromophore A was followed to prepare chromophore B from 5b as a green solid in 48.9% yield (0.14 g, 0.25 mmol). <sup>1</sup>H NMR (400 MHz, Acetone) δ 8.13 (d, *J* = 15.7 Hz, 1H, CH), 7.66 (d, *J* = 4.1 Hz, 1H, CH), 7.47 (d, *J* = 9.2 Hz, 1H, CH), 7.37 (d, *J* = 3.2 Hz, 1H, PrH), 7.31 (d, *J* = 9.2 Hz, 1H, CH), 7.14 (d, *J* = 4.1 Hz, 1H, CH), 6.77 (d, *J* = 15.7 Hz, 1H, CH), 6.37 (dd, *J* = 8.8, 2.3 Hz, 1H, PrH), 6.30 (d, *J* = 2.3 Hz, 1H, PrH), 4.13 (t, *J* = 6.4 Hz, 2H, CH<sub>2</sub>), 3.47 (q, *J* = 7.0 Hz, 4H, CH<sub>2</sub>), 1.88 (s, 6H, CH<sub>3</sub>), 1.63 – 1.52 (m, 2H, CH<sub>2</sub>), 1.47 – 1.38 (m, 4H, CH<sub>2</sub>), 1.31 (dd, *J* = 13.6, 6.6 Hz, 2H, CH<sub>2</sub>), 1.19 (t, *J* = 7.0 Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, Acetone) δ 177.16, 174.06, 158.70, 154.75, 149.75, 139.50, 137.61, 136.60, 129.67, 128.88, 126.05, 115.40, 112.20, 111.15, 110.46, 104.28, 97.46, 94.77, 77.55, 67.52, 43.87, 31.68, 25.38, 24.9, 21.95, 12.96, 11.45. (MALDI) (M<sup>+</sup>, C<sub>34</sub>H<sub>38</sub>N<sub>4</sub>O<sub>2</sub>S): calcd: 566.76; found: 566.29. Anal. Calcd (%) for C<sub>34</sub>H<sub>38</sub>N<sub>4</sub>O<sub>2</sub>S: C, 72.05; H, 6.76; N, 9.89; found: C, 72.08; H, 6.83; N, 9.91;

### Chromophore C

The procedure for chromophore A was followed to prepare chromophore B from 5c as a green solid in 43.9% yield (0.12 g, 0.22 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94 (d, *J* = 15.1 Hz, 1H, CH), 7.76 (s, 1H, CH), 7.49 (d, *J* = 5.0 Hz, 1H, CH), 7.18 (dd, *J* = 5.0, 3.5 Hz, 1H, CH), 6.92 (d, *J* = 3.0 Hz, 1H, CH), 6.58 (d, *J* = 9.8 Hz, 1H, PrH), 6.00 (d, *J* = 7.2 Hz, 2H, PrH), 5.89 (d, *J* = 15.1 Hz, 1H, CH), 4.03 (t, *J* = 6.6 Hz, 2H, CH<sub>2</sub>), 3.38 (q, *J* = 7.0 Hz, 4H, CH<sub>2</sub>), 1.62 (s, 6H, CH<sub>3</sub>), 1.54 – 1.49 (m, 2H, CH<sub>2</sub>), 1.44 – 1.36 (m, 4H, CH<sub>2</sub>), 1.30 (m, 2H, CH<sub>2</sub>), 1.18 (t, *J* = 7.0 Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, Acetone) δ 176.98, 173.90, 161.14, 154.01, 152.14, 143.53, 131.61, 127.66, 127.17, 126.84, 125.59, 123.75, 112.31, 111.57, 110.72, 104.69, 96.82, 93.70, 67.83, 43.94, 32.78, 30.89, 25.16, 25.03, 21.89, 12.92, 11.60. (MALDI) (M<sup>+</sup>, C<sub>34</sub>H<sub>38</sub>N<sub>4</sub>O<sub>2</sub>S): calcd: 566.76; found: 566.21. Anal. Calcd (%) for C<sub>34</sub>H<sub>38</sub>N<sub>4</sub>O<sub>2</sub>S: C, 72.05; H, 6.76; N, 9.89; found: C, 72.01; H, 6.82; N, 9.83;

### Chromophore D

The procedure for chromophore A was followed to prepare chromophore B from 4c as a green solid in 56.8% yield (0.14 g, 0.28 mmol). <sup>1</sup>H NMR (400 MHz, Acetone) δ 7.88 (dd, *J* = 14.9, 11.4 Hz, 1H, CH), 7.66 (d, *J* = 14.8 Hz, 1H, CH), 7.57 (d, *J* = 9.0 Hz, 1H, PrH), 7.24 (dd, *J* = 14.8, 11.4 Hz, 1H, CH), 6.48 (d, *J* = 15.0 Hz, 1H, CH), 6.44 (d, *J* = 2.3 Hz, 1H, PrH), 6.29 (d, *J* = 2.3 Hz, 1H, PrH), 4.15 (t, *J* = 6.5 Hz, 2H, CH<sub>2</sub>), 3.54 (q, *J* = 7.1 Hz, 4H, CH<sub>2</sub>), 1.87 (t, *J* = 14.0 Hz, 2H, CH<sub>2</sub>), 1.79 (s, 6H, CH<sub>3</sub>), 1.60 – 1.49 (m, 2H, CH<sub>2</sub>), 1.38 (dd, *J* = 7.1, 3.6 Hz, 4H, CH<sub>2</sub>), 1.22 (t, *J* = 7.1 Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, Acetone) δ 176.47, 173.15, 160.63, 152.14, 151.70, 144.85, 131.13, 122.86, 112.82, 111.81, 111.10, 105.16, 96.91, 94.00, 92.22, 77.53, 67.55,

44.04, 30.85, 25.22, 25.15, 21.86, 12.98, 11.63. (MALDI) (M<sup>+</sup>, C<sub>30</sub>H<sub>36</sub>N<sub>4</sub>O<sub>2</sub>): calcd: 484.63; found: 484.28. Anal. Calcd (%) for C<sub>30</sub>H<sub>36</sub>N<sub>4</sub>O<sub>2</sub>: C, 74.35; H, 7.49; N, 11.56; found: C, 74.41; H, 7.52; N, 11.51;

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### Notes and references

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