Supporting Information

Synthesis of Novel Nonlinear Optical Chromophore to Achieve Ultrahigh Electro-optic Activity

Jieyun Wu[a], Shuhui Bo[b], Jialei Liu[b], Tingting Zhou[a], Hongyan Xiao[b], Ling Qiu[b], Zhen Zhen[b] and Xinhou Liu[b]*

[a] *Graduated University of Chinese Academy of Sciences, Beijing, 100049, China*

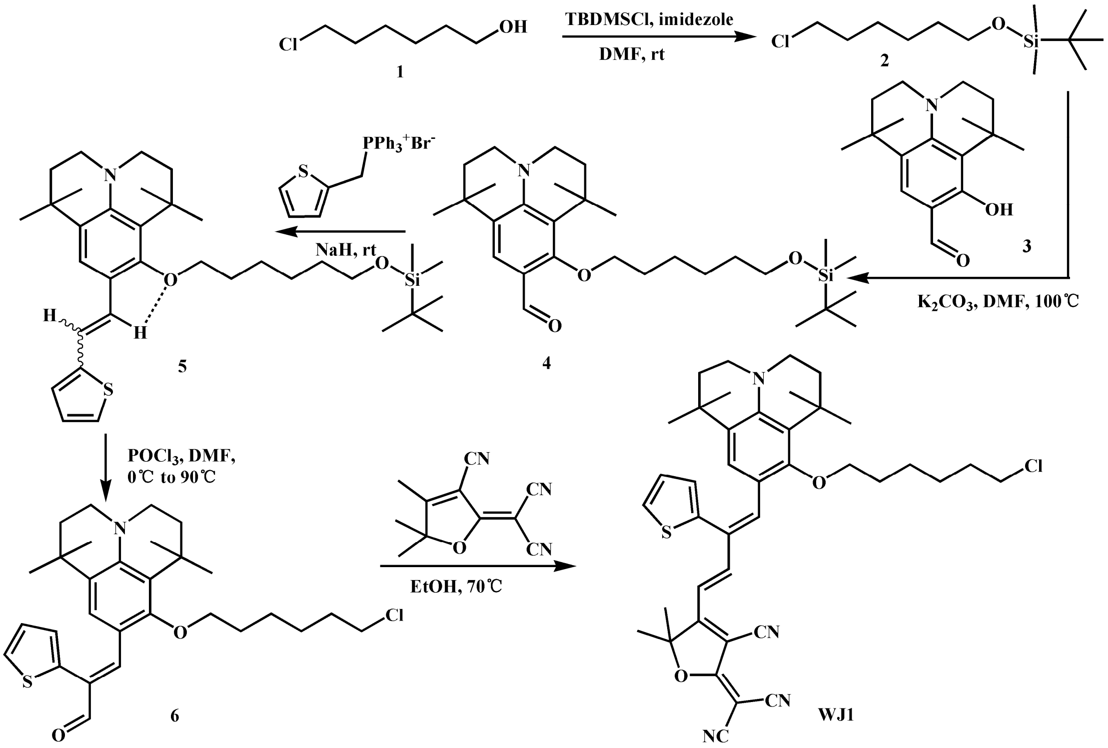
[b] *Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technique Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, 100190, China. E-mail: xinhouliu@yahoo.cn.*

Contents

1. Experimental details

General Procedures

^{1}HNMR spectra were determined by a Varian Gemini 300(300 MHz) NMR spectrometer. The MS spectra were obtained on MALDITOF (Matrix Assisted Laser Desorption/Ionization of Flight) on BIFLEXIII (Broker Inc.) spectrometer. The UV-Vis spectra were performed on Hitachi U2001 photo spectrometer. The fluorescence spectra were performed on Hitachi F-4500 fluorescence spectrometers. The single-crystal X-ray diffraction data were collected with the use of graphite-monochr- -omatized Mo-Ka" radiation (l = 0.71073 A°) at -180 ºC on a Rigaku AFC10 diffractometer equipped with a Saturn CCD detector. Cyclic voltammetry (CV) experiments were performed on a CHI660D electrochemical workstation by a cyclic voltammetry (CV) technique in CH_3CN solution, using two platinum wires as the working and counter electrodes, respectively, and a saturated calomel electrode as the reference electrode in the presence of 1 mM n-tetrabutylammoniumperchlorate as the supporting electrolyte. The DFT calculations using Gaussian 03 were carried out at the hybrid B3LYP level by employing the split valence 6-31 g (d) basis set.[1] All chemicals, commercially available, are used without further purification unless stated. The DMF was freshly distilled prior to its use. 2-dicyanomethylene-3-cyano-4-meth- -yl-2, 5-dihydrofuran (TCF) acceptor was prepared according to the literature.[2]



Scheme 1 Synthetic route of chromophore **WJ1**

Synthesis of compound 2. To a solution of 6-Chlorohexanol (compound **1)** (13.6 g, 100 mmol) and imidazol (10.2 g, 150 mmol) in DMF (40 ml) was added *tert*-butyldimethylsilyl chloride(TBDMSCl) (18 g, 120mmol). The mixture 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 $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was purified by vacuum distillation, to give **2** as a color less oil in 93.2 % yield (23.3 g, 93.2 mmol).

MS (EI), m/z: 250.47.

Synthesis of compound 4. To a solution of compound **3** (5.46 g, 20 mmol) and compound **2** (7.50 g, 30 mmol) in DMF (40 ml) was added anhydrous potassium carbonate (6.4 g, 40 mmol). The mixture was allowed to stir at 100 °C for 12 h and then poured into water. The organic phase was extracted by AcOEt, washed with brine and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography, eluting with (AcOEt:Hexane=1:10) to give **4** as a yellow powder in 78.7 % yield (7.67 g, 15.7 mmol). MS (MALDI-TOF), m/z: 487.481^{1}H NMR (400 MHz, Acetone) δ 9.91 (s, 1H), 7.52 (s, 1H), 3.96 (t, *J* = 6.8 Hz, 2H), 3.66 (t, *J* = 6.2 Hz, 2H), 3.39 – 3.31 (m, 2H), 3.31 – 3.22 (m, 2H), 1.96 – 1.84 (m, 2H), 1.77 – 1.66 (m, 4H), 1.56 (dd, *J* = 14.8, 8.1 Hz, 4H), 1.47 (d, *J* = 6.6 Hz, 2H), 1.42 (s, 6H), 1.24 (s, 6H), 0.89 (s, 9H), 0.04 (s, 6H).

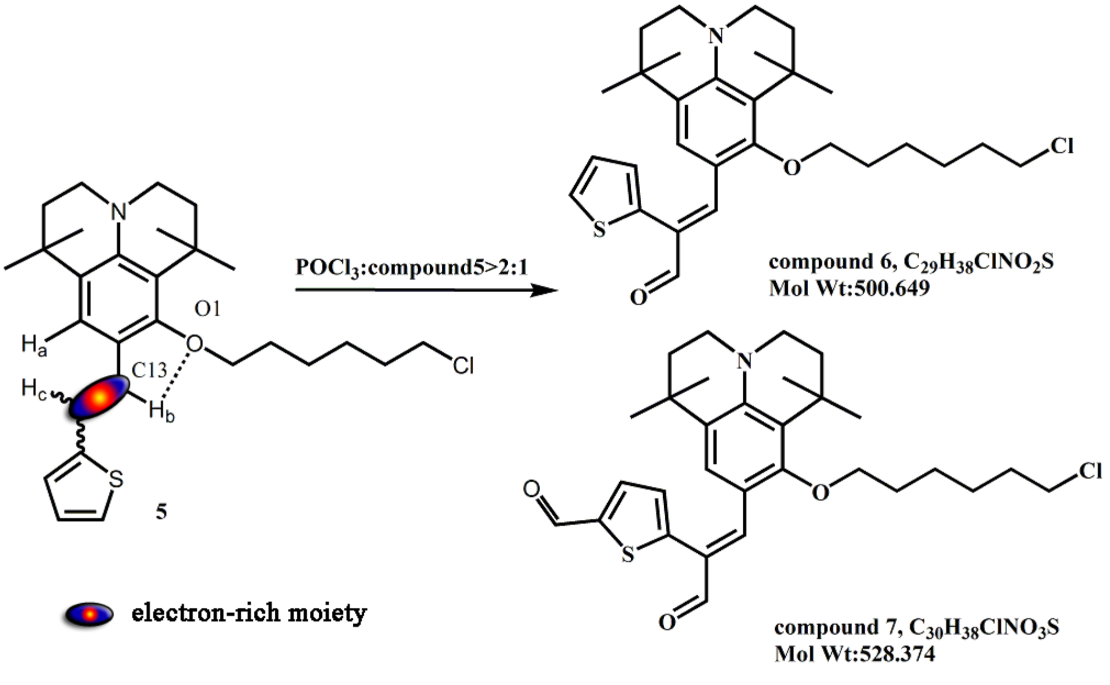
Synthesis of compound 5. To a solution of compound **4** (4.87g, 10 mmol) and 2-thienyl triphenylphosphonate bromide (4.84g, 11 mmol) in ether (25 ml) was added NaH (2.40g, 100 mmol). The solution was allowed to stir for 24h and then poured into water. The organic phase was extracted by AcOEt, washed with brine and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography, eluting with (AcOEt: Hexane = 1:20) to give compound **5** (*E/Z* mixture) as an orange oil in 84.2 % yield (4.76 g, 7.4 mmol). MS (MALDI-TOF), m/z: 567.581. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 0.6H), 7.03 (dd, *J* = 9.5, 5.4 Hz, 1.2H), 7.00 – 6.96 (m, 1H), 6.92 (dd, *J* = 9.6, 6.4 Hz, 1.4H), 6.87 – 6.79 (m, 0.6H), 6.57 (d, *J* = 11.9 Hz, 0.6H), 6.47 (d, *J* = 11.9 Hz, 0.6H), 3.86 – 3.78 (m, 2H), 3.56 (q, *J* = 6.9 Hz, 2H), 3.04 (ddd, *J* = 18.2, 11.6, 5.8 Hz, 4H), 1.75 – 1.61 (m, 6H), 1.50 (ddd, *J* = 21.0, 14.0, 7.1 Hz, 4H), 1.37 (d, *J* = 4.2 Hz, 6H), 1.35 – 1.27 (m, 2H), 1.25 (s, 3H), 1.12 (s, 3H), 0.85 (s, 9H), 0.03 (s, 3H), 0.00 (s, 3H).

Synthesis of compound 6. 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 **5** in 10 ml DMF (1.14 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 $MgSO_4$. 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 **6** as an orange-red solid in 75.9 % yield (0.76 g, 1.52 mmol). MS (MALDI-TOF), m/z: 500.649. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 9.61 (s, 1H), 7.57 (s, 1H), 7.41 – 7.35 (m, 1H), 7.09 (d, *J* = 3.1 Hz, 2H), 7.00 (s, 1H), 3.94 (t, *J* = 6.5 Hz, 2H), 3.57 (t, *J* = 6.6 Hz, 2H), 3.17 (dt, *J* = 11.5, 5.9 Hz, 4H), 1.96 – 1.87 (m, 2H), 1.88 – 1.80 (m, 2H), 1.74 – 1.70 (m, 2H), 1.63 – 1.54 (m, 7H), 1.42 (s, 6H), 0.92 (s, 6H).

Synthesis of chromophore WJ1. To a solution of **6** (1.1 g, 2.2 mmol) and the TCF acceptor (0.48 g, 2.4 mmol) in MeOH (30 ml) was added several drops of triethyl amine. The reaction was allowed to stir at 70 °C for 10 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 = 1:3) to give chromophore **WJ1** as a green solid in 72.0 % yield (1.07 g, 1.29 mmol). MS (MALDI-TOF), m/z: 679.746. Element analysis, found: C69.66, H6.53, N8.21, cal: C70.51, H6.66, N8.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 15.2 Hz, 1H), 7.50 (d, *J* = 5.1 Hz, 1H), 7.44 (s, 1H), 7.20 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.96 (d, *J* = 2.6 Hz, 1H), 6.71 (s, 1H), 5.92 (d, *J* = 15.1 Hz, 1H), 3.91 (t, *J* = 6.5 Hz, 2H), 3.58 (t, *J* = 6.6 Hz, 2H), 3.25 (dd, *J* = 13.4, 8.5 Hz, 4H), 1.98 – 1.89 (m, 2H), 1.89 – 1.80 (m, 2H), 1.76 (d, *J* = 5.6 Hz, 2H), 1.69 – 1.63 (m, 2H), 1.59 (s, 12H), 1.42 (d, *J* = 8.4 Hz, 6H), 1.28 – 1.19 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.79, 173.13, 160.60, 154.71, 147.16, 146.17, 137.22, 128.46, 127.77, 127.56, 127.35, 126.78, 126.33, 122.07, 116.07, 113.14, 112.21, 112.17, 111.01, 96.67, 92.22, 54.01, 47.77, 47.17, 45.22, 39.29, 35.51, 32.59, 32.52, 31.80, 30.06, 29.81, 29.71, 26.88, 26.43, 25.67.

Poling and r_{33} measurements. Guest–host polymers were prepared by formulating chromophore **WJ1** into amorphous polycarbonate (APC) using dibromomethane (CH_2Br_2) 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 40ºC to remove the residual solvent. The poling process was carried out at a temperature of about 10ºC above the T_g of the polymer. The r_{33} values were measured using Teng-Man simple reflection technique at the wavelength of 1310 nm.[3]

2. H-bonding Induced Vilsmeier Reaction of compound 5



Scheme 2 H-bonding Induced Vilsmeier Reaction of compound **5**

Vilsmeier Reaction allows the formylations of electron-rich arenes. Intramolecular H-bonding of C13-Hb…O1 change the electron distribution of compound **5**, resulting in the most electron-rich of double bond. In this reaction (Scheme 2), Formylation reacted primarily at the position of double bond. Two equivalent $POCl_3$ was added into the reaction, only compound **6** was obtained. When excessive (more than two equivalent) $POCl_3$ was added, compound **6** and by-product (compound **7**) was obtained. This result showed that double bond was the primarily position and the thiophene ring was the second position for Vilsmeier Reaction.

3. ^{1}H NMR spectrum of compound 5, 6 and WJ1

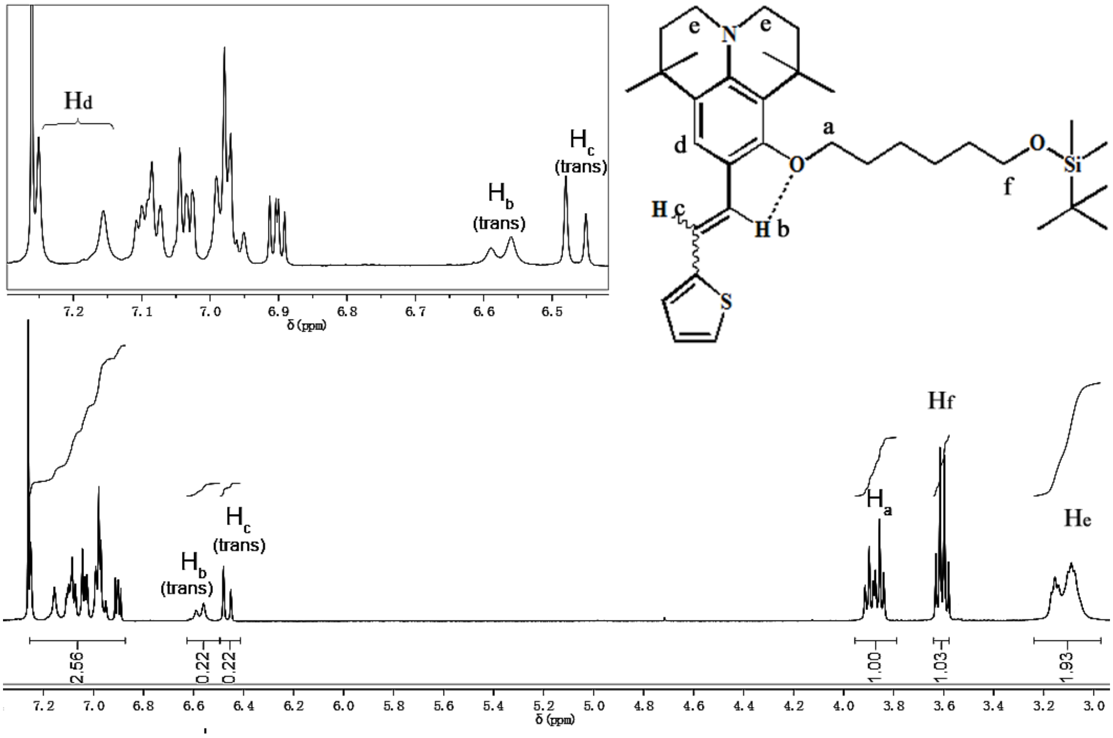


Figure 1 ^{1}H NMR spectra of cis and trans isomer mixtures of compound **5**

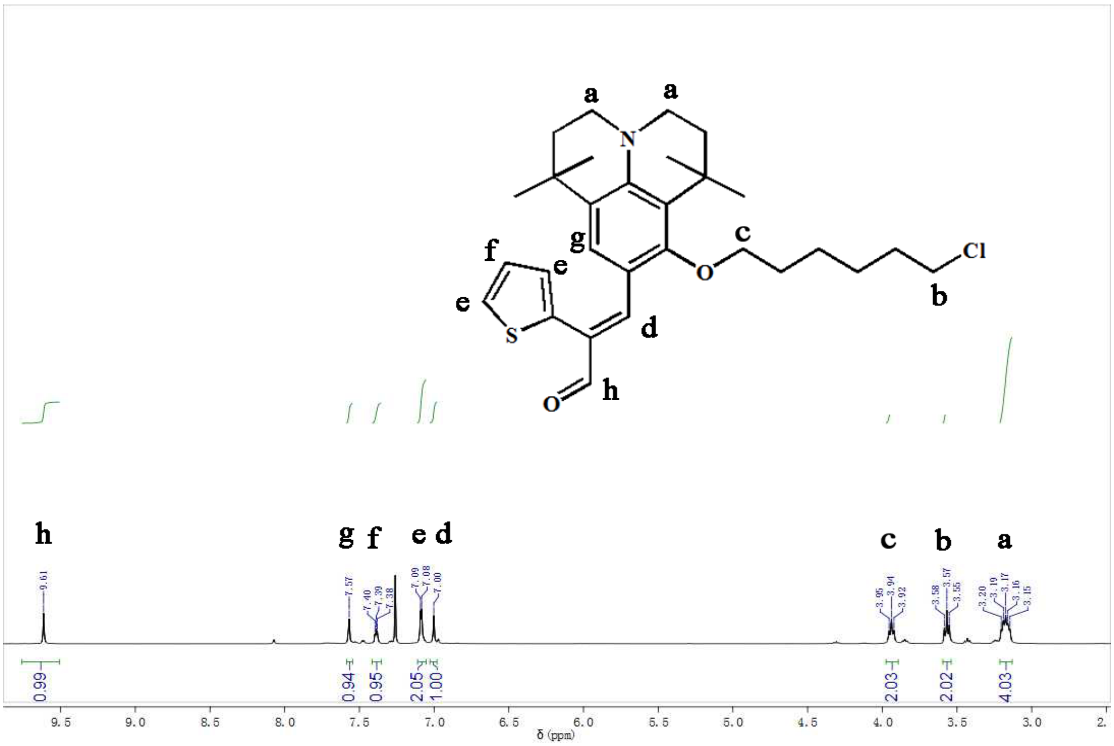


Figure 2 ^{1}H NMR spectra of compound **6**

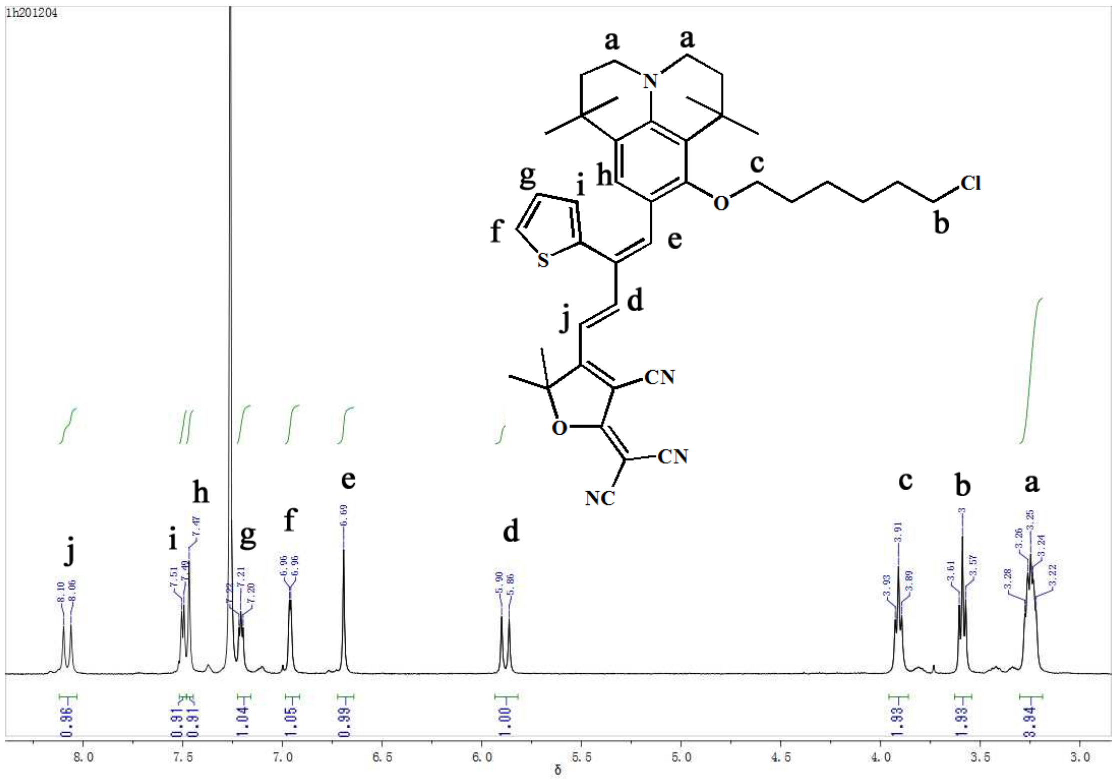


Figure 3 ^{1}H NMR spectra of chromophore **WJ1**

Figure 1 showed the ^{1}H NMR spectra of cis and trans-isomer mixtures of compound **5.** Under the combined action of isomerism and intramolecular H-bonding interaction it was difficult to identify the peak attribution. But the integration of peaks in the low field and H_a in the ratio of 3:1 is in accord with the proton number. Figure 2 and figure 3 showed the ^{1}H NMR spectra of **6** and **WJ1.** Despite of Intramolecular H-bonding of C13-Hb…O1 observed in the crystal analysis, it was difficult to observe the H-bonding effect on proton shift in ^{1}H NMR of **WJ1.** That might be attributed to the trans conformation and the strong electron-withdrawing of TCF acceptor make the charge transfer efficiently.

4. Crystallographic data

The single-crystal X-ray diffraction data of chromophore **WJ1** were collected with the use of graphite-monochromatized Mo-Ka" radiation (l = 0.71073 A°) at -180 ºC on a Rigaku AFC10 diffractometer equipped with a Saturn CCD detector. Figure 4 shows the ORTEP view of the crystal **WJ1**. The crystal data is given as followed: Chemical formula: $C_{40}H_{45}ClN_4O_2S$, M = 681.31, crystal system: triclinic, a = 10.2373(16) Å, b = 12.2791(18) Å, c = 16.455(3) Å, γ = 108.025(9) °, V =1829.0(5) Å3, T = 153(2) K, space group: $P\bar{1}$, NO. of independent reflections: 9607. The final R_1 values were 0.0689 (I > 2σ (I)). The final R_1 values were 0.1024 (all data). The goodness of fit on F^2 was 1.000. The crystallographic data are available as a CIF file from Cambridge Crystallographic Database Centre (CCDC) on quoting the depository number 885141.

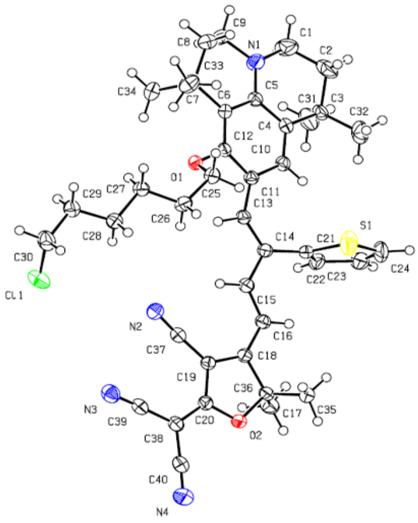


Figure 4 ORTEP view of **WJ1**. Thermal ellipsoids are drawn at 50% probability.

Table 1. Geometric parameters for H-bonding interactions of **WJ1**

Interaction	Symmetry	Distance/Å			D-H….A/°
		D-H	H….A	D….A	
Intra C(13)-H(13)..O(1)	--	0.95	2.31	2.743(3)	107
Intra C(33)-H(33B)..O(1)	--	0.98	2.36	2.883(4)	113
Intra C(34)-H (34B)..O(1)	--	0.98	2.55	3.144(3)	119
Intra C(28)-H(28A)..Cl(1)	--	0.99	2.79	3.200(3)	105
C(25) --H(25A) ..N(3)	2-x,1-y,1-z	0.99	2.56	3.453(4)	151
C(30) --H(30A) ..N(4)	1+x,1+y,z	0.99	2.54	3.482(4)	160

The details of the H-bonding interactions was summaried in Table 1. Intramolecular H-bonding was observed between O1 and C13-H13 with a distance of 2.743 Å. C33-H3B and C34-H34B also formed intramolecular H-bonding with O1. For the high electron density of Cl, non-covalent intramolecular interactions between Cl1 and neighbor CH were found. Besides the intramolecular interactions, there are two type of intermolecular hydrogen bonding of C(25) --H(25A)...N(3) and C(30) --H(30A)...N(4).

The strong nonlinear optical chromophores have large dipole moments which lead to large dipole–dipole interactions. Such strong interactions induce an antiparallel packing of the dipolar molecules. These interactions play significant roles in determining the electro-optic activities. The crystal formed an antiparallel packing as shown in Figure 5. The crystal packing data showed the crystal stacking force of ring-centroid to ring-centroid separations of 4.9 Å to 5.7 Å, which indicates better site isolation than that of below 4.2 Å reported.[4-8]

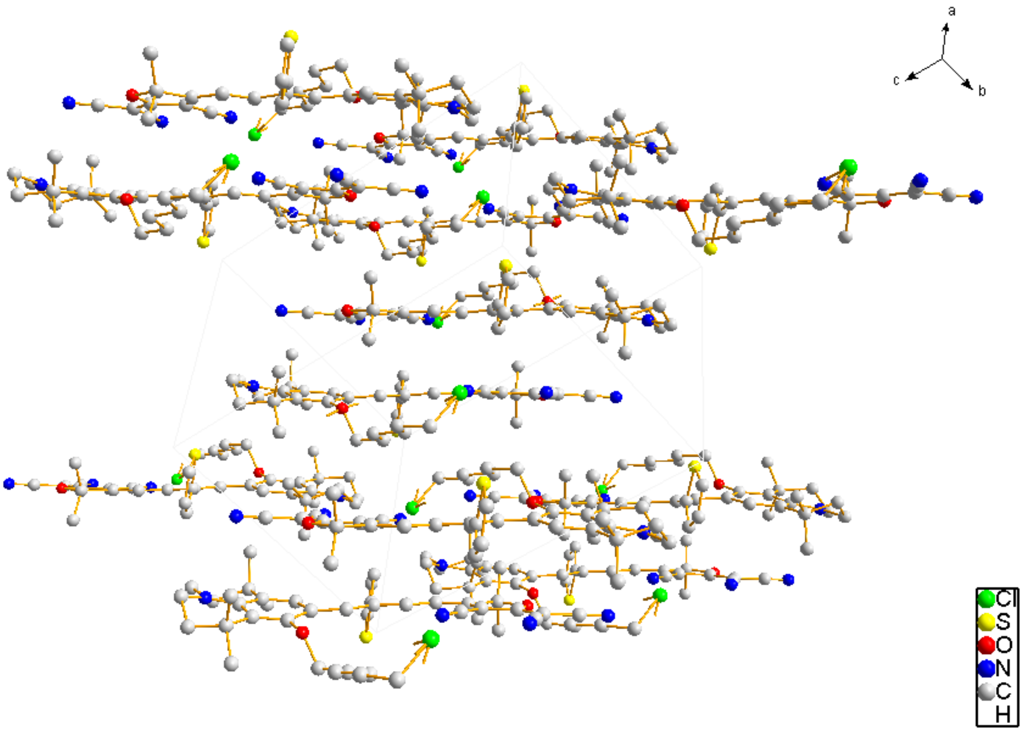


Figure 5 Crystal packing of **WJ1**

5. Photophysical and electrochemical spectrum of WJ1

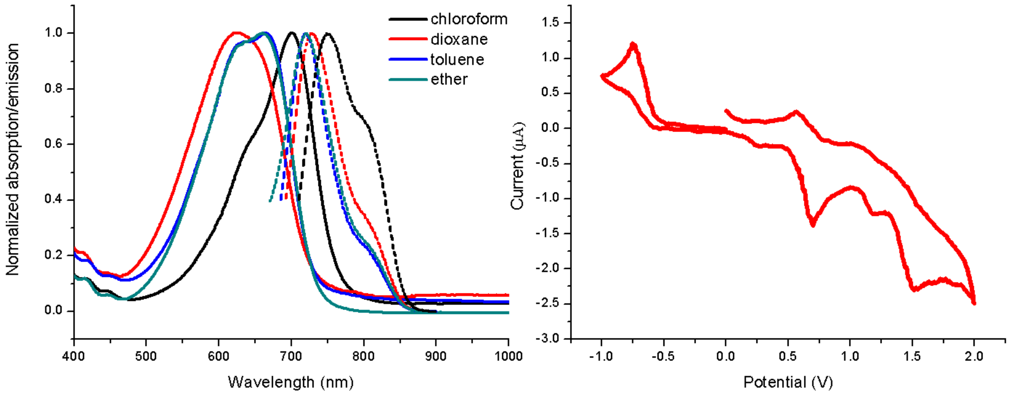


Figure 6 Photophysical (left) and electrochemical (right) spectrum of **WJ1**. The solid line shows the UV-vis absorption spectrum. The dash line shows the fluorescence emission spectrum.

6. Diene reactivity

Diene reactivity was reported as the change of chromophore content after annealing thin films of polymer composites containing the chromophore **WJ1** and excess N-phenylmaleimide moiety.[9] Annealing was accomplished at 150°C for 30 minutes. Comparing the UV-vis spectrum of the films before and after annealing (Figure 7), no additional peak was observed, which indicated that **WJ1** is not reactive to the D-A reaction. The hindrances of chlorohexyloxyl group and thiophene ring rigidify the all-trans π-electron bridge of **WJ1** and elevate the rotational energy barrier of configuration, thereby reducing the diene reactivity of the chromophore.[10, 11] The decrease of the absorption peak after annealing was attributed to the chromophore aggregation.

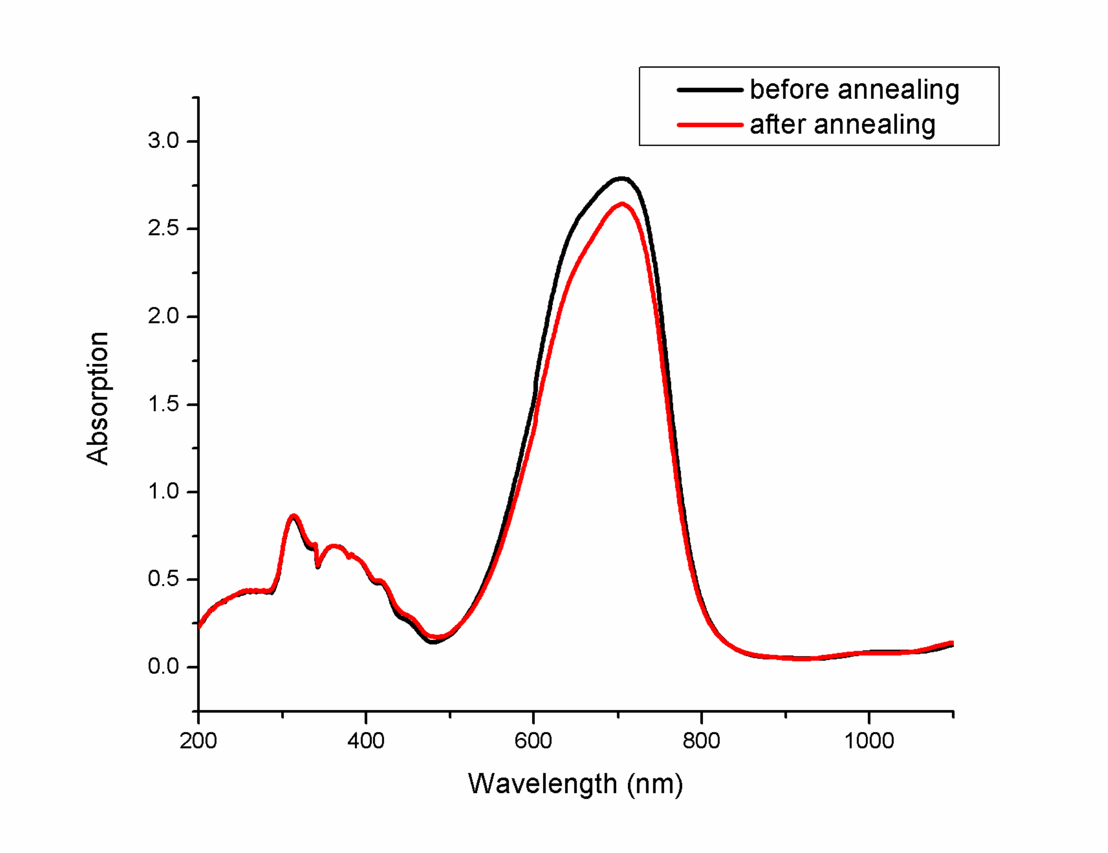


Figure 7 Absorption of EO film containing **WJ1** and N-phenylmaleimide before and after annealing

References:

1. M. J. JR, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain M C, Farkas O, Malick D K, Rabuck A D, Raghavachari K, Foresman J B, Ortiz J V, Cui Q, Baboul A G, Clifford S, Cioslowski J,Stefanov B B, Liu G, Liashenko A, Piskorz P, Ko-maromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA. , *Gaussian 03, Gaussian, Inc., Pittsburgh, PA, 2003.*
2. M. Q. He, T. M. Leslie and J. A. Sinicropi, *Chemistry of Materials*, 2002, **14**, 2393-2400.
3. C. C. M. Teng, H. T., *Appl. Phys. Lett*, 1990, **56**.
4. J. Wu, J. Liu, T. Zhou, S. Bo, L. Qiu, Z. Zhen and X. Liu, *RSC Advances*, 2012, **2**, 1416.
5. O. P. Kwon, S. J. Kwon, M. Jazbinsek, A. Choubey, V. Gramlich and P. Günter, *Advanced Functional Materials*, 2007, **17**, 1750-1756.

---

6. O. P. Kwon, S.-J. Kwon, M. Jazbinsek, J.-Y. Seo, J.-T. Kim, J.-I. Seo, Y. S. Lee, H. Yun and P. Günter, *Chemistry of Materials*, 2011, **23**, 239-246.
7. S. Li, M. Li, J. Qin, M. Tong, X. Chen, T. Liu, Y. Fu, S. Wu and Z. Su, *CrystEngComm*, 2009, **11**, 589.
8. H. Burckstummer, E. V. Tulyakova, M. Deppisch, M. R. Lenze, N. M. Kronenberg, M. Gsanger, M. Stolte, K. Meerholz and F. Wurthner, *Angew Chem Int Ed Engl*, 2011, **50**, 11628-11632.
9. J. Luo, X.-H. Zhou and A. K. Y. Jen, *Journal of Materials Chemistry*, 2009, **19**, 7410.
10. A. Z. Bradley, M. G. Kociolek and R. P. Johnson, *J Org Chem*, 2000, **65**, 7134-7138.
11. J. D. Luo, S. Huang, Y. J. Cheng, T. D. Kim, Z. W. Shi, X. H. Zhou and A. K. Y. Jen, *Org Lett*, 2007, **9**, 4471-4474.