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Supporting Information for

Comparison of Nonlinear Optical Chromophores Containing Different Conjugated Electron-bridges: the Relation between Molecular Structure-Properties and the Macroscopic Electro-optic Activities of Materials

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

[a] School of Communication and Information Engineering, University of Electronic Science and Technology of China, Chengdu, 611731, China.

[b] Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technique Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, 100190, China.

1. Experiment

2. photograph of solution and EO film containing chromophores

3. DFT calculations

1. Experiment

1.1 materials and instruction

^{1}HNMR spectra were determined by a Varian Gemini 300(400 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. All chemicals, commercially available, are used without further purification unless stated. The DMF was freshly distilled prior to its use. Compound **1,** chromophore **WJ6** and 2-dicyanomethylene-3-cyano-4-methyl-2, 5-dihydrofuran (TCF) acceptor was prepared according to the literature.[1-3]

1.2 Synthesis

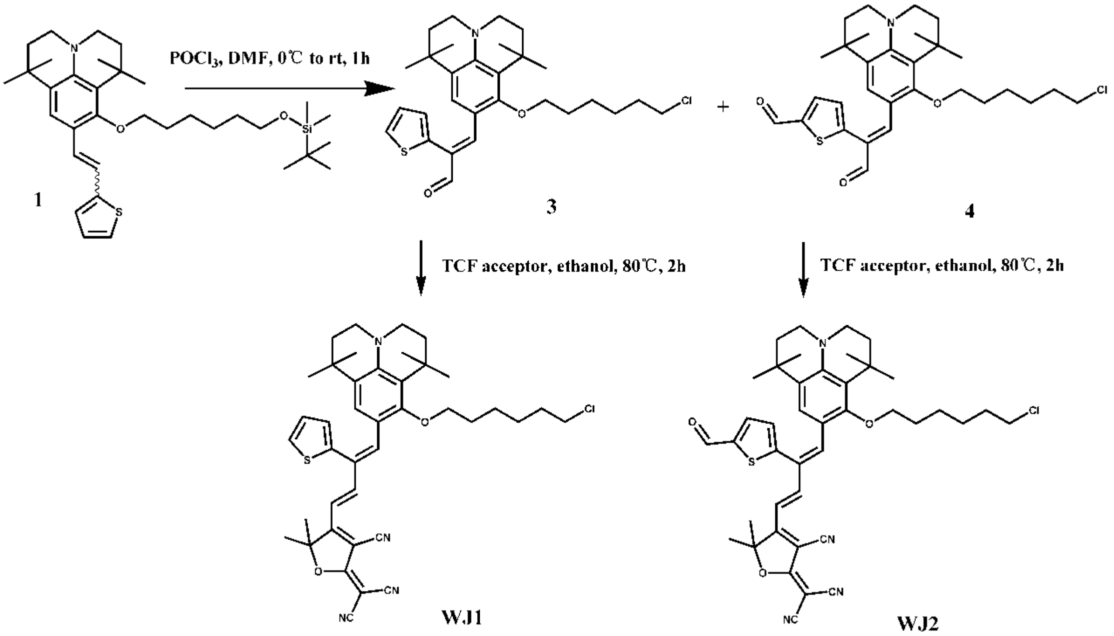

Figure S1. Route 1: acidic formylation to synthesize chromophore WJ1 and WJ2

Synthesis of compound 3

A solution of 20 ml DMF was cooled to 0 °C and was maintained at this temperature during the dropwise addition of phosphorus oxychloride (0.3 g, 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 **1** 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 **3** as an orange-red solid in 89 % yield (0.89 g, 1.78 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). Anal. Calcd (%) for $C_{29}H_{38}ClNO_2S$: C, 69.64; H, 7.66; N, 2.80; found: C, 70.34; H, 7.84; N, 2.83

Synthesis of compound 4

The procedure for compound **3** was followed to prepare compound **4** from compound **1** and $POCl_3$ **(**mole ratio of compound **1** and $POCl_3$**:** 1:3**)** to give an orange-red solid in 44% yield. MS (MALDI-TOF), m/z: 528.467. ^{1}H-NMR (400 MHz, CDCl3) δ 9.82 (s, 1H), 9.51 (s, 1H), 7.68 (d, *J* = 3.7 Hz, 1H), 7.56 (s, 1H), 7.21 (s, 1H), 6.89 (s, 1H), 3.86 (t, *J* = 6.4 Hz, 2H), 3.50 (t, *J* = 6.5 Hz, 2H), 3.17 – 3.10 (m, 4H), 1.88 – 1.80 (m, 2H), 1.80 – 1.73 (m, 2H), 1.71 – 1.58 (m, 4H), 1.57 – 1.44 (m, 4H), 1.35 (s, 6H), 0.85 (s, 6H). Anal. Calcd (%) for $C_{30}H_{38}ClNO_3S$: C, 68.22; H, 7.25; N, 2.65; found: C, 68.84; H, 7.71; N, 2.68.

Synthesis of chromophore WJ1

To a solution of **3** (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 ºC 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. ^{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. Anal. Calcd (%) for $C_{40}H_{45}ClN_4O_2S$: C, 70.51, H, 6.66, N, 8.22; found: C,, 69.66, H, 6.53, N, 8.21.

Synthesis of chromophore WJ2

The procedure of chromophore **WJ1** was followed to prepare chromophore **WJ2** from compound **4** and TCF acceptor to give a dark green solid in 46% yield. MS (MALDI-TOF), m/z: 708.296. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 7.87 (d, J = 15.8 Hz, 1H), 7.52 (s, 1H), 7.36 (d, J = 25.3 Hz, 2H), 7.12 (s, 1H), 6.56 (d, J = 15.7 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 191.12, 175.87, 173.34, 159.82, 150.93, 147.16, 144.98, 140.26, 140.13, 135.26, 130.08, 126.84, 126.16, 126.03, 121.98, 113.65, 112.53, 97.44, 56.79, 47.61, 47.05, 45.09, 39.51, 35.72, 32.68, 32.62, 32.13, 30.45, 30.41, 30.21, 29.92, 29.84, 27.00, 26.56, 26.50, 25.69. Anal.

Calcd (%) for $C_{41}H_{45}ClN_4O_3S$： C69.42, H6.39, N7.90. found: C69.27, H6.34, N7.92.

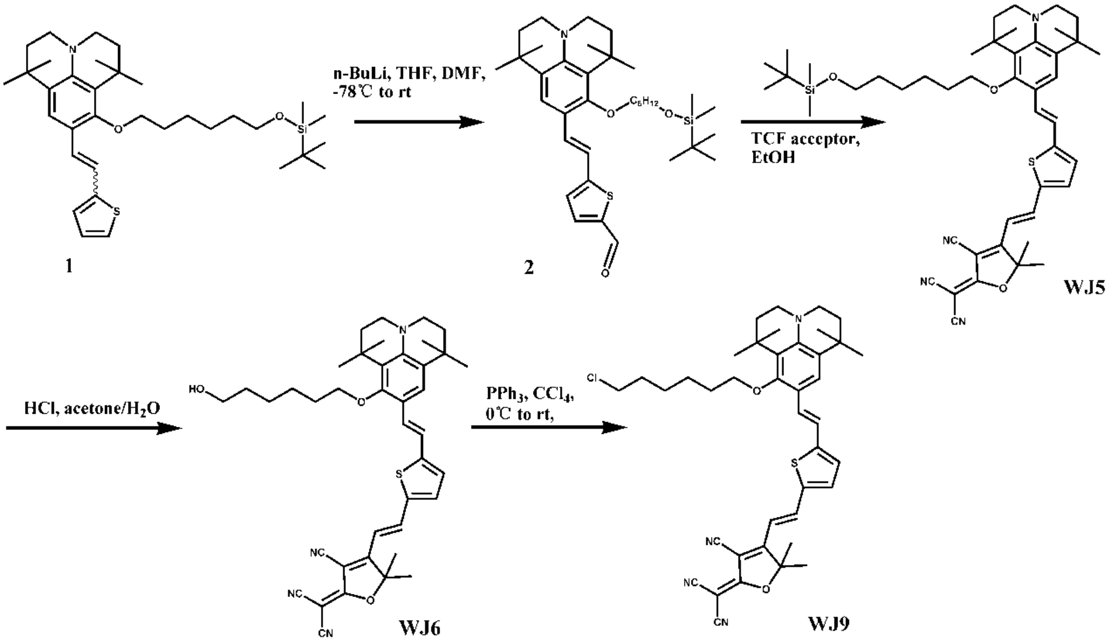

Figure S2. Route 2: alkaline formylation to synthesize chromophore WJ9

Synthesis of Compound 2

To a solution of **1** (*E/Z*, 2.69 g, 4.74 mmol) in THF (30 ml) was cooled to -78 ^{o}C and was maintained at this temperature during the dropwise addition of n-BuLi in hexane (1.6M, 4.5 ml, 7.2 mmol). Following 1 h of stirring at -78 ^{o}C the temperature was kept prior to the dropwise addition of DMF (0.45 g, 6.16 mmol) over 5 minutes. After 1h, solution was gradually warmed to room temperature before being quenched (H_2O, 10 ml). The reaction mixture was poured into water, 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 = 1:5) to give **3a** (*Z*) as orange-red solid (yield: 74.2 %, 2.21 g, 3.51 mmol). MS (MALDI-TOF), m/z: 595.357. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 9.82 (s, 1H), 7.64 (d, *J* = 3.9 Hz, 1H), 7.33 (d, *J* = 16.1 Hz, 1H), 7.29 (s, 1H), 7.06 (d, *J* = 3.9 Hz, 1H), 6.97 (d, *J* = 16.0 Hz, 1H), 3.85 (t, *J* = 8.6 Hz, 2H), 3.63 (t, *J* = 7.8 Hz, 2H), 3.26 – 3.19 (m, 2H), 3.19 – 3.10 (m, 2H), 1.94 – 1.86 (m, 2H), 1.80 – 1.74 (m, 4H), 1.61 – 1.55 (m, 4H), 1.46 (d, *J* = 12.4 Hz, 8H), 1.32 (s, 6H), 0.90 (s, 9H), 0.06 (s, 6H). Anal. Calcd (%) for $C_{35}H_{53}NO_3SSi$: C, 70.54; H, 8.96; N, 2.35; found: C, 70.27; H, 8.75; N, 2.43.

Synthesis of Chromophore WJ5

Chromophore **WJ5** was prepared by condensation of compound **2** with TCF acceptor. A mixture of compound **2** (0.6 g, 1 mmol) and TCF (0.24 g, 1.2 mmol) in methanol (10 ml) was refluxed for 4 h, then cooled to room temperature. The precipitate was collected and washed with methanol. The crude product was purified by column chromatography eluting with (AcOEt: Hexane = 1:3) to give the product as green-black solids (0.42 g, yield: 54.8%). MS (MALDI-TOF), m/z: 777.259.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.83 (d, *J* = 15.6 Hz, 1H), 7.41 (d, *J* = 4.0 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.09 – 7.04 (m, 1H), 7.01 (s, 1H), 6.54 (d, *J* = 15.6 Hz, 1H), 3.85 (t, *J* = 6.7 Hz, 2H), 3.62 (t, *J* = 6.4 Hz, 2H), 3.25 (dt, *J* = 26.4, 5.5 Hz, 4H), 1.90 (m, 2H), 1.76 (s, 6H), 1.58 (dd, *J* = 14.0, 6.7 Hz, 6H), 1.46 (s, 6H), 1.34 (s, 6H), 1.27 (s, 2H), 0.89 (s, 9H), 0.09 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$, ppm): 174.93, 171.76, 171.74, 156.42, 154.99, 143.56, 138.42, 136.98, 135.98, 130.99, 125.82, 125.45, 122.19, 121.38, 115.48, 114.30, 111.45, 110.61, 110.22, 110.03, 95.80, 94.10, 76.23, 74.88, 62.12, 54.47, 46.40, 45.87, 38.87, 35.24, 31.81, 31.66, 31.21, 29.83, 29.18, 29.01, 25.54, 25.18, 24.98, 24.93, 17.36. Anal. Calcd (%) for $C_{46}H_{60}N_4O_3SSi$: C 70.98, H 7.73, N 7.09, Found: C 71.09, H 7.78, N 7.21.

Synthesis of chromophore WJ6

To a solution of chromophore **WJ5** (0.78 g, 1 mmol) in acetone (20 ml) and H_2O (20 ml) was dropwise added 5 ml HCl solution (HCl: H_2O=1:10). The solution was stirred at room temperature for 5 h. After removal of acetone under reduced pressure, the reaction mixture was poured into water, extracted by AcOEt, washed with brine, dried over $MgSO_4$. After removal of solvent, the crude product was purified by silica chromatography, eluting with (AcOEt: Hexane = 1:2) to give the product as green-black solids (0.60 g, yield: 91.2%). MS (MALDI-TOF), m/z: 662.725. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.14 (d, *J* = 15.8 Hz, 1H), 7.67 (d, *J* = 4.0 Hz, 1H), 7.47 (s, 1H), 7.31 (q, *J* = 16.0 Hz, 2H), 7.19 (d, *J* = 4.0 Hz, 1H), 6.79 (d, *J* = 15.8 Hz, 1H), 3.86 (t, *J* = 6.6 Hz, 2H), 3.56 (t, *J* = 6.3 Hz, 2H), 3.30 – 3.13 (m, 4H), 1.98 – 1.88 (m, 2H), 1.87 (s, 6H), 1.76 – 1.68 (m, 5H), 1.67 – 1.56 (m, 4H), 1.55 – 1.48 (m, 2H), 1.42 (s, 6H), 1.28 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): 175.89, 173.00, 157.41, 155.99, 139.33, 137.95, 137.02, 131.89, 130.94, 128.88, 126.78, 122.94, 115.33, 112.43, 111.63, 111.32, 111.20, 96.89, 95.52, 75.93, 65.60, 62.84, 55.61, 47.47, 46.95, 39.90, 36.29, 32.83, 32.73, 32.28, 30.88, 30.62, 30.25, 30.08, 29.73, 26.66, 26.34, 25.94, 19.22, 13.75. Anal. Calcd (%) for $C_{40}H_{46}N_4O_3S$: C 72.48; H 6.99; N 8.45; found: C 73.19, H 7.12, N 8.37.

Synthesis of Chromophore WJ9

To a solution of chromophore **WJ6** (0.66 g, 1 mmol) and excessive triphenylphosphine (PPh_3) in dry THF (20 ml) under N_2 atmosphere was added CCl_4 (0.17 g, 1.1 mmol). The solution was stirred at room temperature for 1 h and then filtered to remove the remove PPh_3. After removal of THF under reduced pressure, the crude product wa purified by silica chromatography, eluting with (AcOEt: Hexane = 1:5) to give the product as green-black solids (0.61 g, yield: 89.3%). MS (MALDI-TOF), m/z: 680.275. 1H NMR (400 MHz, CDCl3) δ 7.70 (d, J = 15.7 Hz, 1H), 7.32 (d, J = 3.6 Hz, 1H), 7.24 (d, J = 18.4 Hz, 2H), 6.93 (d, J = 24.0 Hz, 2H), 6.49 (s, 1H), 3.78 (t, J = 6.5 Hz, 2H), 3.48 (t, J = 6.6 Hz, 2H), 3.28 – 2.92 (m, 4H), 1.84 (dd, J = 13.8, 7.1 Hz, 2H), 1.77 (dd, J = 13.5, 6.7 Hz, 2H), 1.68 (s, 8H), 1.51 (dd, J = 14.8, 11.7 Hz, 6H), 1.36 (s, 6H), 1.24 (s, 6H). 13C NMR (101 MHz, CDCl3) δ 175.98, 172.92, 157.42, 155.79, 144.50, 139.34, 137.87, 137.16, 131.89, 127.17, 126.77, 123.20, 122.66, 115.60, 112.50, 111.70, 111.49, 111.26, 96.95, 95.75, 75.80, 55.82, 47.60, 47.07, 45.20, 39.95, 36.36, 32.82, 32.70, 32.38, 30.99, 30.17, 30.14, 27.03, 26.73, 25.82. Anal. Calcd (%) $C_{40}H_{45}ClN_4O_2S$: C, 70.51; H, 6.66; N, 8.22; found: C, 71.06; H, 6.87; N, 8.75.

Poling and r_{33} measurements.

Guest–host polymers were prepared by formulating chromophore 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 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.[4]

2. photograph of solutions and EO films containing chromophores

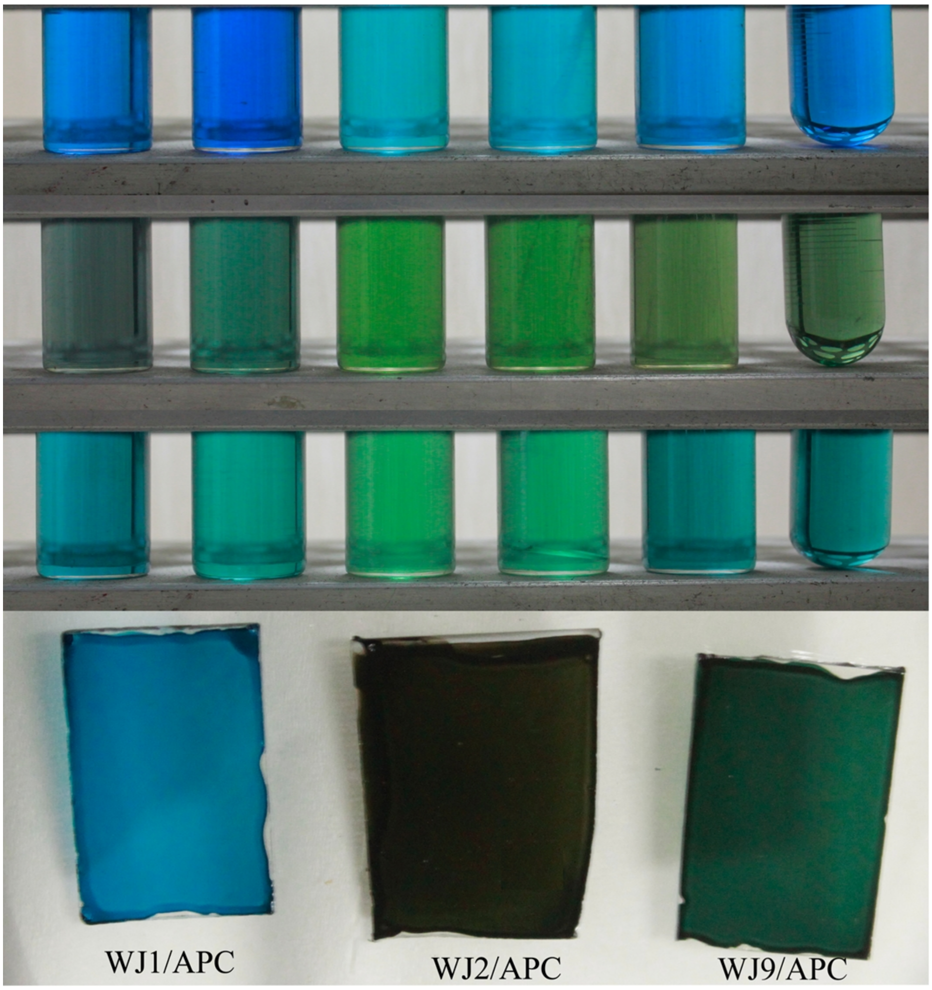

Figure S3. The solutions containing chromophores (2×10^{-5}M) in dioxane, toluene, chloroform, dichlomethane (DCM), acetone and acetonitrile and the guest-host EO polymer films. The first row: WJ1; the second row: WJ2; the third row: WJ9.

3. DFT Calculation

DFT calculations using Gaussian 03 were carried out at the hybrid B3LYP level employing the split valence 6-31G* basis set.[5] Chromophores were rotated into frame such that the x axis was aligned with the dipole axis and $\beta_{xxx} = \beta_{\mu}$. BLA was calculated according to the literature.[6,7]

Table S1. DFT Calculation results[a]

Chromophore	*WJ1*	*WJ2*	*WJ9*
β_{xxx}	-267.01	-253.08	837.05
β_{xxy}	-28.33	-44.86	-91.25
β_{xyy}	12.52	9.66	-9.42
β_{yyy}	0.29	-1.99	-4.30
β_{xxz}	5.30	6.60	2.28
β_{xyz}	0.39	0.38	0.55
β_{yyz}	-0.21	3.02	1.34
β_{xzz}	1.51	1.61	-1.99
β_{yzz}	-0.66	-1.81	-0.31
β_{zzz}	0.044	0.66	1.12
β_{x}	-252.98	-241.81	825.64
β_{y}	-28.70	-48.66	-95.86
β_{z}	5.53	10.28	4.74
β_{total}	254.66	246.87	831.20
α_{x} (esu)	169.96	170.22	231.01
α_{y} (esu)	90.96	98.05	96.38
α_{z} (esu)	-0.78	-2.27	-4.74
α_{total} (esu)	192.77	196.45	250.35
μ_{x} (Debye)	21.10	18.80	18.54
μ_{y} (Debye)	7.71	2.32	11.63
μ_{z} (Debye)	2.74	1.87	2.68
μ_{total} (Debye)	22.63	19.03	22.05
$\mu\beta$(10^{-30}esu*D)	5763	4698	18328
BLA (Å)	0.04812	0.04876	0.03761

a: $\mu_{total} = \sqrt{(\mu_x)^2 + (\mu_y)^2 + (\mu_z)^2}$, $\alpha_{total} = \sqrt{(\alpha_x)^2 + (\alpha_y)^2 + (\alpha_z)^2}$, $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$, $\beta_y = \beta_{yyy} + \beta_{yzz} + \beta_{yxx}$, $\beta_z = \beta_{zzz} + \beta_{zxx} + \beta_{zyy}$, $\beta_{total} = \sqrt{(\beta_x)^2 + (\beta_y)^2 + (\beta_z)^2}$

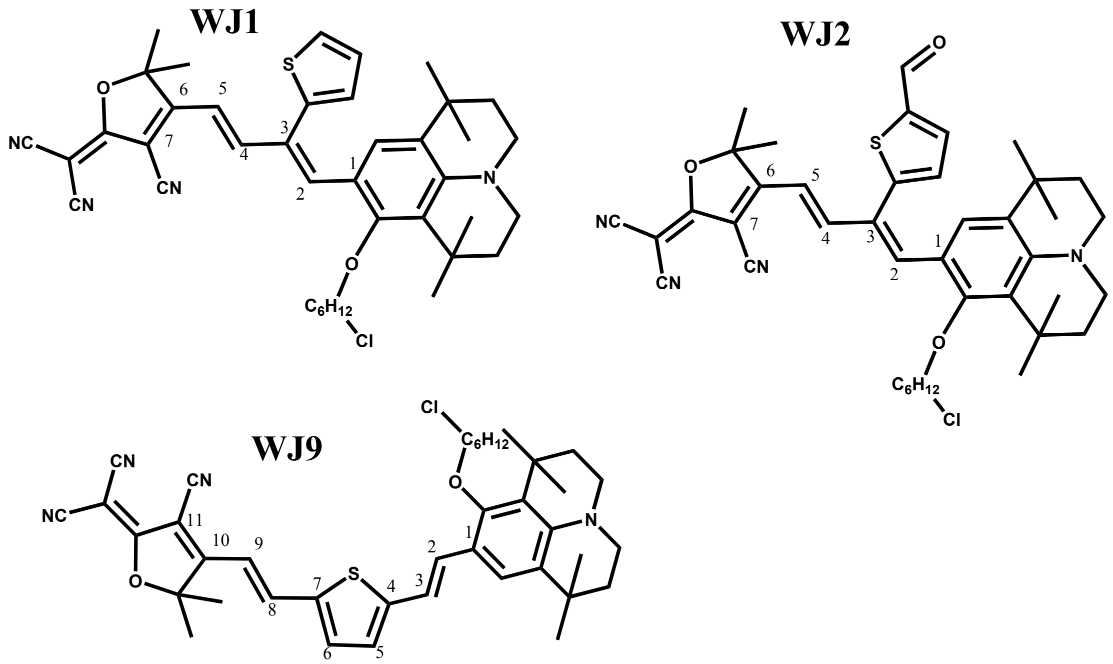

Figure S4. Numbering of the carbon atoms in the conjugated bridge for chromophores

Table S2. Bond Lengths of the conjugated chain of Chromophores **WJ1**, **WJ2** and **WJ9** Obtained by Geometry Optimizations using 6-31G* Basis set (Atom numbering in Figure. S4)

Chromophore	*WJ1*	*WJ2*	*WJ9*
C_1-C_2	1.43703	1.43571	1.44493
C_2-C_3	1.38599	1.38633	1.36591
C_3-C_4	1.43645	1.43664	1.43228
C_4-C_5	1.37652	1.37589	1.39871
C_5-C_6	1.42267	1.42433	1.40088
C_6-C_7	1.38928	1.38818	1.39681
C_7-C_8	-	-	1.41899
C_8-C_9	-	-	1.37632
C_9-C_{10}	-	-	1.41831
C_{10}-C_{11}	-	-	1.38957

Reference:

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