Supporting Information for

Synthesis and Properties of NLO Chromophores with Fine-Tuned Electronic Structures

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Section 1. Experimentals.

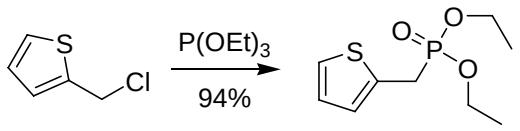
Materials. 1-Methyl-5-(piperidin-1-yl)pyrrole-2-carbaldehyde,[1] 5-(piperidin-1-yl) thiophene-2-carbaldehyde,[1] 2-chloromethyl thiophene,[2] 2-(chloromethyl)thiazole,[3] 2-chloro-5-(chloromethyl)thiazole,[4] thiazole-5-carbaldehyde,[5] 4-methoxy-*N*-(4-methoxyphenyl)-*N*-phenylbenzenamine,[6] 4-(bis(4-methoxyphenyl)amino) benzaldehyde[7] and tetracyanoethene[8] were prepared referring to literature methods. *n*-Butyl lithium (*n*-BuLi) (Acros), 1-iodo-4-methoxybenzene (Zibo Tianyuan Fuli Chemical. Ltd.), potassium *t*-butyloxide (*t*-BuOK) (Alfa Aesar Corp.), tetrabutylammonium perchlorate (Bu_4NClO_4, 99%) (Fluka), 2,2'-bipyridine (Guoyao Corp. of China) and thiazol-2-amine (Beijing Ouhe Ltd.) were purchased and used as received. Phosphorous oxide trichloride ($POCl_3$), trimethylsilane chloride (TMSCl), tetrachloromethane (CCl_4), thionyl chloride, sulfuryl dichloride and aniline were purchased from Beijing Chemical Reagent Ltd. and distilled before use. *N*,*N*-Dimethylformamide (DMF) and tetrahydrofuran were distilled over calcium hydride and metal sodium, respectively, and stored over molecular sieves (3 Å) under nitrogen. All other chemicals were purchased from Beijing Chemical Reagent Ltd. and used as received.

Instruments. ^1H and ^{13}C NMR spectra were recorded on a Varian 300 MHz or a Bruker ARX400 spectrometer using deuterated chloroform ($CDCl_3$) or dimethylsulfoxide (DMSO-d_6) as the solvent. Chemical shifts were reported in ppm scale with tetramethylsilane as the internal standard. Infrared (IR) spectroscopies were measured on a Nicolet Magna 750 Fourier transform infrared spectrometer. UV-Vis absorption spectra were recorded with a DU 640 UV-vis spectrometer. Thermogravimetric analysis (TGA) was performed in nitrigen on a TA TGA-DSC Q600 thermogravimetric analyzer with a heating rate of 20 ^oC / min. Melting points were measured with a SGW-X-4 microscopic melting point instrument. High and low resolution mass spectroscopy was recorded on a ZAB-HS mass spectrometer. Elemental analysis was performed on an Elementar Vario EL instrument (Elementar

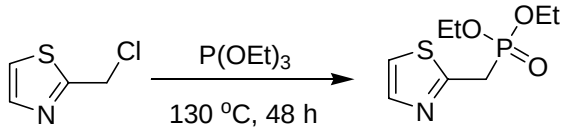
Analysensysteme GmbH). Cyclic voltammetry (CV) was performed on a CHI 600C cyclic voltametric analyzer in a solution of tetrabutylammonium perchlorate (0.1 M) in acetonitrile at a scanning rate of 200 mV/s. Before each measurement, the cell was deoxygenated with argon for 20 min. The working electrode was a glassy carbon disk (diameter 2 mm, freshly polished) for voltammetry. A platinum stick (1 mm thick) was used as the counter-electrode and AgCl/Ag the reference electrode. All potentials are reported versus the AgCl/Ag electrode.

Hyper-Rayleigh scattering (HRS) measurements. HRS measurements of the NLO chromophores were performed at the excitation wavelength of 1000 nm. A third harmonic wave at 355 nm with a pulse duartion of 7 ns (repetition rate, 10 Hz) was supplied by a Q-switched Nd^{3+}:YAG laser, and was used to drive an optical parametric osciallator (MOPO-SL/MOPO-PO, Spectra-Physics) to deliver the light pulses at 1000 nm. The laser beam was passed through a Pelin–Broca prism and other steering optics, and focused into the sample cell with a lens (f = 200 mm). The pulse energy measured in front of the sample cell was 2 mJ/pulse. The HRS signal collected with a camera lens (f/1.4) was further focused *via* a lens (f = 150 mm) onto the entrance slit of a triplet spectrometer (Trivista, SP2500i, Princeton Instruments/Acton), and was detected by an intensified CCD detector (ICCD PI-MAX, Princeton Instruments/Acton) operated with a gate width of 10 ns. For each HRS measurement the sample was exposed to 1000 laser shots, and the accumulated harmonic signal at 500 nm was extracted, *via* spectral deconvolution, from the background fluorescence induced by two-photon absorption. The intensity of HRS signal was calibrated with the Beer-Lambert law for the correction of the chromophore self-absorption. To determine the β value of a chromophore, *p*-nitroaniline (*p*-NA) in dimethylsulfoxide (DMSO) was used as an external standard, whose β value at 1000 nm (34.5×10^{-30} esu) was calculated based on the known β value at 1064 nm (28.8×10^{-30} esu)[9] within the framework of the two-level model. The concentration of *p*-NA in DMSO was in the range of 1×10^{-3} ~ 5×10^{-1} mol/L. All of the sample solutions in chloroform were prepared in the concentration range of 10^{-5} ~ 10^{-4} mol/L.

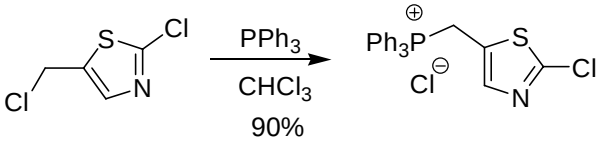
Synthesis of Intermediates.



Diethyl thiophen-2-ylmethyl phosphonate. A solution of 2-chloromethyl thiophene (3.00 g, 22.7 mmol) in triethyl phosphite (7.50 g, 45.2 mmol) was heated to 130 ^{o}C under nitrogen and stirred for 36 h. The excessive amount of triethyl phosphite was removed under vacuum (~0.5 mmHg) to leave a sticky yellow liquid product (5.0 g, 94% yield): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17 -7.20 (1H, m), 6.95 - 7.01 (2H, m), 3.95 -4.10 (4H, m), 3.3 (1H, d, J = 22 Hz), 1.28 (6H, t, J = 7.2 Hz, 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.4, 132.2, 127.3, 127.2, 126.9, 126.8, 124.6, 124.5, 62.3, 62.4, 28.8, 26.9, 16.3, 16.2.

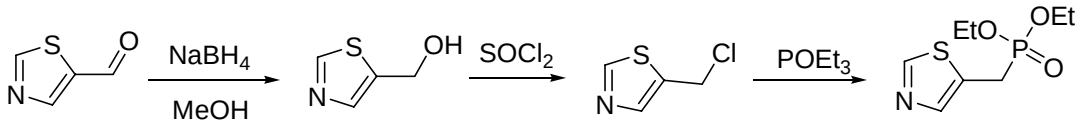


Diethyl thiazol-2-ylmethylphosphonate. A mixture of 2-(chloromethyl) thiazole (4.00 g, 30.0 mmol) and triethyl phosphite (9.96 g, 60.0 mmol) was heated at 130 ^{o}C under nitrogen for 48 h. The excessive amount of triethyl phosphite was removed under vacuum (~ 0.5 mmHg) to give a yellow viscous liquid product (6.80 g, 96% yield): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 (1H, d, J = 3.4 Hz), 7.29 – 7.32 (1H, m), 4.05 – 4.20 (4H, m), 3.70 (2H, d, J = 21.2 Hz), 1.30 (6H, t, J = 7.0 Hz, 7.0Hz).



((2-Chlorothiazol-5-yl)methyl)triphenylphosphonium chloride. A solution of 2-chloro-5-(chloromethyl)thiazole (3.00 g, 17.9 mmol) and triphenylphosphine (11.7 g, 44.6 mmol) in chloroform (30 mL) was stirred at refluxing tempearature for 48 h before filtration to collect the solid product, which was washed with acetone (10 mL)

twice to give a white powdered product (6.20 g, 90% yield): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86 – 7.94 (6H, m), 7.76 – 7.82 (3H, m), 7.63 - 7.68 (6H, m), 7.25 (1H, d, J = 4.2 Hz), 5.70 (2H, d, J = 14.1 Hz).



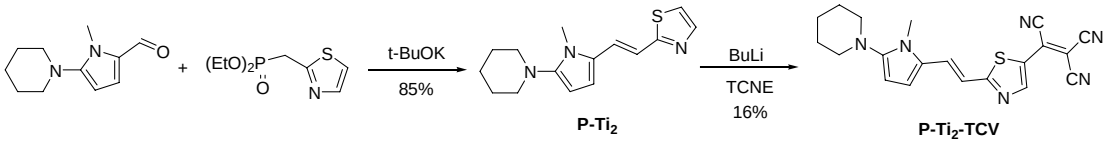
Thiazol-5-ylmethanol. To a solution of thiazole-5-carbaldehyde (0.226 g, 2.00 mmol) in methanol (10 mL), was added powdered sodium borohydride (0.08 g, 1.00 mmol) in portions. The resulting solution was stirred at room temperature for 1 h. After removal of the solvent by rota-evaporation, the liquid residue was purified by a silica-gel column chromatography (eluent: ethanol/ethyl acetate/ligroin = 1/1/4, v/v/v, R_f = 0.31) to give a colorless oily product (0.17 g, 75% yield): ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.75 (1H, s), 7.74 (1H, s), 4.90 (2H, d, J = 4.8Hz), 3.1 (1H, t, J =5.4Hz).

5-(Chloromethyl)thiazole. A mixture solution of thiazol-5-ylmethanol (11.5 g, 100 mmol) and thionyl chloride (2.36 g, 200 mmol) in chloroform was refluxed at 80 ^{o}C for 2 h. It was then poured into water (150 mL) and extracted with ethyl acetate (3×50 mL). The organic extracts were combined, washed with saturated aqueous sodium carbonate solution (30 mL), and dried over anhydrous magnesium sulfate. After removal of the solvent by rota-evaporation, a yellow liquid product was obtained, which was used for the next step of synthesis without further purification (3.5 g, 31% yield): ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.80 (1H, s), 7.80 (1H, s), 4.91 (2H, s).

Diethyl thiazol-5-ylmethylphosphonate. A mixture of 5-(chloromethyl)thiazole (2.00 g, 15.1 mmol) in triethyl phosphite (10.0 mL) was refluxed at 130 ^{o}C for 36 h. The excessive amount of triethyl phosphite was removed under high vacuum (~0.5 mmHg) to give a light-yellow viscous liquid product (2.0 g, 57% yield): ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.75 (1H, d, J = 1.2 Hz), 7.55 (1H, d, J = 1.2 Hz), 3.83 (4H, d, J = 7.2 Hz), 3.36 (2H, d, J = 21 Hz), 1.28 (6H, t, J = 7.2 Hz).

Synthesis of NLO Chromophores.

1. P-Ti$_2$-TCV

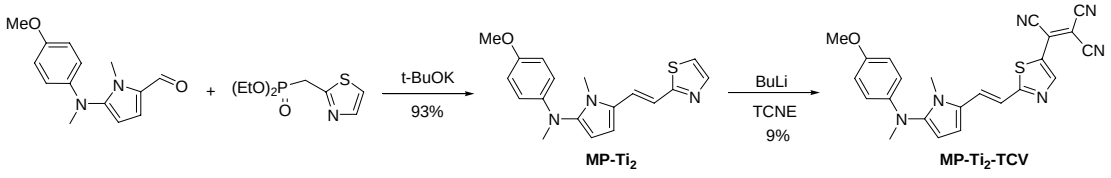


(E)-2-(2-(1-methyl-5-(piperidin-1-yl)-1H-pyrrol-2-yl) vinyl) thiazole (P-Ti$_2$). A solution of 1-methyl-5-(piperidin-1-yl)-1*H*-pyrrole-2-carbaldehyde (1.93 g, 10.0 mmol) and diethyl thiazol-2-ylmethylphosphonate (4.70 g, 20.0 mmol) in anhydrous THF (60.0 mL) was prepared, purged with nitrogen, and cooled with a dry ice/acetone mixture to -78 ^{o}C. To the soludtion was added dropwise a solution of potassium *t*-butyloxide (2.24 g, 20.0 mmol) in anhydrous tetrahydrofuran (60.0 mL). After the addition, the reaction solution was warmed gradually up to room temperature in 3 h and then poured into distilled water (150 mL). The mixture solution was extracted in a separatory funnel with ethyl acetate (3×30 mL). The organic extracts were combined, washed with distilled water (2×30 mL), and dried over anhydrous magnesium sulfate. After removal of the solvent, the solid resdiue was purified with a silica-gel column chromatography (eluent: ethyl acetate/ligroin = 1/4, v/v, R_f = 0.5) and then recrystallized from ligroin to give yellow sheet crystals (2.32 g, 85% yield): mp. 107–108 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (1H, d, J = 3.3 Hz), 7.30 (1H, d, J = 16.2 Hz), 7.13 (1H, d, J = 3.3 Hz), 6.97 (1H, d, J = 15.9 Hz), 6.51 (2H, d, J = 3.9 Hz), 5.71 (2H, d, J = 3.9 Hz), 3.56 (3H, s), 2.83 (4H, t, J = 5.1 Hz, 5.4 Hz), 1.53 - 1.70 (6H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.3, 146.1, 143.0, 126.1, 123.4, 116.3, 114.5, 108.9, 96.3, 53.8, 29.8, 26.0, 24.0; Anal. Calcd. for $C_{15}H_{19}N_3S$: C, 65.90; H, 7.00; N, 15.37; Found: C, 65.90; H, 6.93; N, 15.43.

(E)-2-(2-(2-(1-methyl-5-(piperidin-1-yl)-1H-pyrrol-2-yl)vinyl)thiazol-5-yl) ethene-1,1,2-tricarbonitrile (P-Ti$_2$-TCV). To a solution of **P-Ti$_2$** (0.273 g, 1.00 mmol) in anhydrous tetrahydrofuran (3 mL) at -78 ^{o}C under nitrogen, was added *n*-butyl

lithium (1.6 M in hexane, 0.94 mL, 1.5 mmol). The resulting solution was allowed to warm gradually up to -10 ^{o}C in 2 h and then cooled again to -78 ^{o}C. A solution of tetracyanoethene (0.192 g, 1.50 mmol) in tetrahydrofuran (5 mL) was added dropwise to the solution. After the reaction solution was stirred at -78 ^{o}C for 10 min, hydrochloric acid (1 M, 1 mL) was dropped in. The solution was warmed up to room temperature and poured into distilled water (30 mL). The mixture was extracted in a separatory funnel with dichloromethane (5×30 mL). The organic extracts were combined, washed with distilled water (50 mL) twice, dried over anhydrous magnesium sulfate, and rota-evaporated to give a dark green solid residue, which was purified by silica-gel column chromatography (eluent: ethyl acetate/ligroin, 1/1, v/v, R_f = 0.6) to yield a green solid product (0.060 g, 16% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (1H, s), 7.69 (1H, d, J = 14.8 Hz), 6.96 (1H, d, J = 4.4 Hz), 6.83 (1H, d, J = 14.8 Hz), 5.92 (1H, d, J = 4.4 Hz), 3.60 (3H, s), 3.01 (4H, t, J = 4.8 Hz), 1.71-1.75 (4H, m), 1.63-1.64 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$): 178.2, 157.9, 154.5, 130.1, 128.6, 127.8, 119.7, 113.4, 113.0, 112.6, 110.2, 101.9, 52.8, 31.2, 25.7, 23.9; FT-IR (KBr, cm^{-1}): 2935, 2855, 2192, 1570, 1508, 1439, 1409, 1352, 1226, 1127, 1100, 1026; HRMS for $C_{20}H_{18}N_6S$ (m/z): 374.1314 (Calcd.), 374.1311 (Found).

2. MP-Ti$_2$-TCV



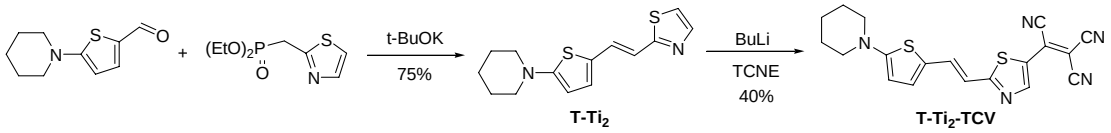
(E)-N-(4-Methoxyphenyl)-N,1-dimethyl-5-(2-(thiazol-2-yl)vinyl)-1H-pyrrol-2-amine (MP-Ti$_2$). To a solution of 5-(*N*-4-Methoxyphenyl *N*-methyl amino)-1-methyl-1*H*-pyrrole-2-carbaldehyde (1.22 g, 5.00 mmol) and diethyl thiazol-2-ylmethylphosphonate (2.56 g, 10.0 mmo) in anhydrous tetrahydrofuran (60.0 mL) at -78 ^{o}C under nitrogen, was added dropwise a solution of potassium

t-butyloxide (1.12 g, 10.0 mmol) in anhydrous tetrahydrofuran (30.0 mL). After the addition, the solution was allowed to warm gradually up to room temperature and then poured into distilled water (100 mL). The mixture was extracted with ethyl acetate (3×30 mL). The organic extracts were combined, washed with distilled water (30 mL) twice, and dried over anhydrous magnesium sulfate. After removal of the solvent, the liquid residue was purified by a silica-gel column chromatography (eluent: ethyl acetate/ligroin = 1/8, v/v, R_f =0.3) to give a sticky liquid product (0.15 g, 93% yield): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (1H, d, J = 3.3 Hz), 7.39 (1H, d, J = 15.9 Hz), 7.18 (1H, d, J = 3.3 Hz), 7.03 (1H, d, J = 15.9 Hz), 6.82 (2H, d, J = 9.0 Hz), 6.58 - 6.63 (3H, m), 5.96 (1H, d, J = 4.2 Hz), 3.76 (3H, s), 3.41(3H, s), 3.23 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.9, 152.9, 143.4, 143.0, 140.9, 126.9, 123.1, 116.8, 115.6, 114.6, 108.6, 103.0, 55.7, 40.8, 29.8.

(E)-2-(2-(2-(5-((4-methoxyphenyl)(methyl)amino)-1-methyl-1H-pyrrol-2-yl)vinyl)thiazol-5-yl)ethene-1,1,2-tricarbonitrile (MP-Ti$_2$-TCV). To a solution of **MP-Ti$_2$** (0. 900 g, 2.77 mmol) in anhydrous tetrahydrofuran (20 mL) at -78 ^{o}C under nitrogen, was added *n*-butyl lithium (1.6 M in hexane, 2.08 mL, 3.33 mmol). The resulting solution was allowed to warm gradually up to 0 ^{o}C in 0.5 h and then cooled again to -78 ^{o}C, to which a solution of tetracyanoethene (0.531 g, 4.15 mmol) in anhydrous tetrahydrofuran (10.0 mL) was added through a syringe in 5 min. After the resulting reaction solution was stirred at -78 ^{o}C for additional 10 min, hydrochloric acid (1 M, 1 mL, 1.00 mmol) was dropped in. The solution was warmed up to room temperature, poured into distilled water (30 mL), and extracted with dichloromethane (3×30 mL). The extracts were combined, washed with distilled water, and dried over anhydrous magnesium sulfate. After rota-evaporation to remove the solvent, the residue was run through a silica-gel column chromatography (eluent: ethyl acetate/ligroin = 1/1, v/v, R_f = 0.55) to give the pure green solid product (0. 10 g, 8.5% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (1H, s), 7.80 (1H, d, J = 15.2 Hz), 7.08 (1H, d, J = 4.4 Hz), 6.81 - 6.89 (5H, m), 6.16 (1H, d, J = 4.4 Hz), 3.80 (3H, s), 3.34 (3H, s), 3.33 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ ; 117.9, 157.7, 155.3, 148.6, 141.5, 129.6, 128.2, 128.1, 127.5, 120.2, 118.3, 114.9, 113.1, 112.8, 112.5, 111.1, 104.9, 55.6, 42.1, 31.1. FT-IR

(KBr, cm^{-1}): 2948, 2208, 1595, 1505, 1462, 1396, 1337, 1233, 1172, 1037; HRMS for $C_{23}H_{18}N_6OS$ (m/z): 426.1263 (Calcd.), 426.1276 (Found).

3. T-Ti$_2$-TCV

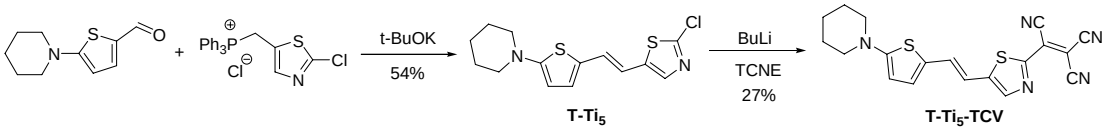


(E)-2-(2-(5-(piperidin-1-yl)thiophen-2-yl)vinyl)thiazole (T-Ti$_2$). To a solution of 5-(piperidin-1-yl)thiophene-2-carbaldehyde (1.95 g, 10.0 mmol) and diethyl thiazol-2-ylmethylphosphonate (4.70 g, 20.0 mmol) in anhydrous tetrahydrofuran (80.0 mL) at -78 ^oC under nitrogen, was added dropwise a solution of potassium *t*-butyloxide (2.24 g, 20.0 mmol) in anhydous tetrahydrofuran (60.0 mL). After the addition, the solution was gradually warmed up to room temperature in 1 h and then poured into distilled water (150 mL). The mixture was extracted with ethyl acetate (3×50 mL). The organic extracts were combined, washed with distilled water (2×30 mL), and dried over magnesium sulfate. After removal of the solvent by rota-evaporation, the solid residue was purified by a silica-gel chromatography (eluent: ethyl acetate/ligroin=1/4, v/v, R_f= 0.7) and recrystallized from ligroin to give yellow needle-like crystals (2.07 g, 75% yield): mp. 111–112 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ 7.70 (1H, d, J = 3.3 Hz), 7.42 (1H, d, J = 15.6 Hz), 7.11 (1H, d, J = 3.3 Hz), 6.86 (2H, d, J = 3.9 Hz), 6.75 (1H, d, J = 15.6 Hz), 5.94 (2H, d, J = 3.9 Hz), 3.19 (4H, m), 1.67 - 1.74 (4H, m), 1.58 – 1.63 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.8, 160.8, 143.0, 130.4, 128.4, 126.0, 116.5, 114.9, 103.7, 51.5, 25.0, 24.0; Anal. Calcd. for $C_{14}H_{16}N_2S_2$: C, 60.83; H, 5.83, N, 10.13; Found: C, 60.73; H, 5.81; N, 10.10.

(E)-2-(2-(2-(5-(piperidin-1-yl)thiophen-2-yl)vinyl)thiazol-5-yl)ethene-1,1,2-tricarbonitrile (T-Ti$_2$-TCV). To a stirring solution of **T-Ti$_2$** (0.273 g, 0.989 mmol) in anhydrous tetrahydrofuran (3.00 mL) at -78 ^oC under nitrogen, *n*-butyl lithium (1.6 M

in hexane, 0.940 mL, 1.50 mmol) was added in drops. After the addition, the solution was allowed to warm up to -10 ^{o}C in 2 h and then cooled again to -78 ^{o}C, to which was added dropwise a solution of tetracyanoethene (0.192 g, 1.50 mmol) in anhydrous tetrahydrofuran (5 mL). After stirring for 5 min, distilled water (3.00 mL) was added and the resulting solution was warmed up to room temperature. After removal of the solvent under vacuum, the residue was washed thoroughly with diethyl ether (2×30 mL) and dichloromethane until the washings were colorless. The dichlormethane washings were combined, dried over anhydrous magnesium sulfate, and rota-evaporated to give a solid residue that was recrystallized from chloroform to yield golden colored crystals (0.150 g, 40% yield): ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (1H, s), 7.89 (1H, d, J = 15.4 Hz), 7.27 (1H, d, J = 4.5 Hz), 6.56 (1H, d, J = 14.4 Hz), 6.14 (1H, d, J = 4.5 Hz), 3.44 (4H, t, J = 4.8 Hz), 1.73-1.70 (6H, m); FT-IR (KBr, cm^{-1}):2942, 2859, 2209, 1581, 1496, 1445, 1411, 1382, 1324, 1234, 1172, 1070, 1011, 943; HRMS for $C_{19}H_{15}N_5S_2$ (m/z): 377.0769 (Calcd.), 377.0769 (Found).

4. T-Ti$_5$-TCV

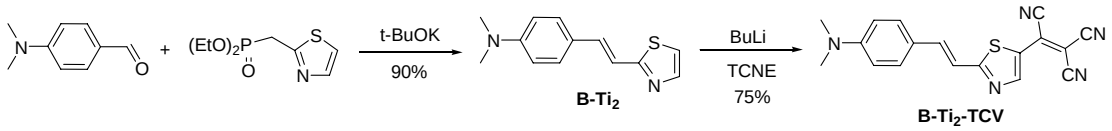


(E)-2-chloro-5-(2-(5-(piperidin-1-yl)thiophen-2-yl)vinyl) thiazole (T-Ti$_5$). To a solution of (2-chlorothiazol-5-yl)methyl triphenyl phosphonium chloride (3.56 g, 8.90 mmol) in toluene (160 mL), was added potassium *t*-butyloxide (1.79 g, 17.8 mmol). The solution was stirred at room temperature for 2.5 h, followed by the addition of 5-(piperidin-1-yl) thiophene-2-carbaldehyde (1.56 g, 8.00 mmol) in toluene (20 mL) in drops. The reaction solution was stirred at room temperature for another 6 h before being poured into distilled water (200 mL). The mixture was extracted in a separatory funnel with ethyl acetate (3×30 mL). The organic extracts were combined, washed with distilled water, dried over anhydrous magnesium sulfate, and rota-evaporated to

give a yellow solid residue that was purified by silica-gel column chromatography (eluent: ethyl acetate/ligroin = 1/10, v/v, R_f= 0.33) and recrystallized from ligroin to yield yellow needle-like crystals (1.30 g, 54% yield): mp: 113-114 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ 7.32 (1H, s), 6.78 (1H, d, J= 15.6 Hz), 6.76 (1H, d, J= 3.9 Hz), 6.50 (1H, d, J=15.6 Hz), 5.91 (1H, d, J=3.9 Hz), 3.18 (3H, t, J=5.4 Hz), 1.56 - 1.74 (6H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.0, 152.7, 147.7, 140.9, 137.6, 128.8, 126.4, 111.4, 103.7, 51.6, 25.1, 23.6. Anal. Calcd. for $C_{14}H_{15}ClN_2S_2$: C, 54.09; H, 4.86; N, 9.01; Found: C, 54.06; H, 4.90; N, 8.96.

(E)-2-(5-(2-(5-(Piperidin-1-yl)thiophen-2-yl)vinyl)thiazol-2-yl)ethene-1,1,2–tricarbonitrile (T-Ti$_5$-TCV). To a solution of **T-Ti$_5$** (0.100 g, 0.323 mmol) in anhydrous tetrahydrofuran (10.0 mL) at -78 ^{o}C under nitrogen, was added dropwise a solution of *t*-butyl lithium (1.5 M in pentane, 0.25 mL, 0.375 mmol). The reaction solution was stirred at -78 ^{o}C for 1 h before tetracyanoethene (0.042 g, 0.328 mmol) in anhydrous tetrahydrofuran (10.0 mL) was added in drops. The color of the solution turned into dark green right away. The solution was stirred at -78 ^{o}C for another 5 min and then poured into distilled water (30.0 mL). Hydrochloric acid (2 M) was added to the mixture solution to adjust the pH value to 5, followed by extraction with dichloromethane (3×20 mL). The organic extracts were combined, washed with distilled water, dried over anhydrous magnesium sulfate, and rota-evaporated to give a dark green solid that was purified by recrystallization from ethyl acetate (0.03 g, 27% yield): ^1H NMR (300 MHz, $CDCl_3$): δ 7.99 (1H, s), 7.32 (1H, d, J = 15 Hz), 7.13 (1H, d, J = 4.5 Hz), 6.54 (1H, d, J = 15 Hz), 6.09 (1H, d, J = 4.5 Hz), 3.38–3.41 (4H, m), 1.54–1.72 (6H, m); FT-IR (KBr, cm^{-1}): 2944, 2856, 2210, 1584, 1499, 1446, 1386, 1347, 1247, 1609, 1012, 919; HRMS for $C_{19}H_{15}N_5S_2$ (m/z): 377.0769 (Calcd), 377.0770 (Found).

5. B-Ti_2-TCV

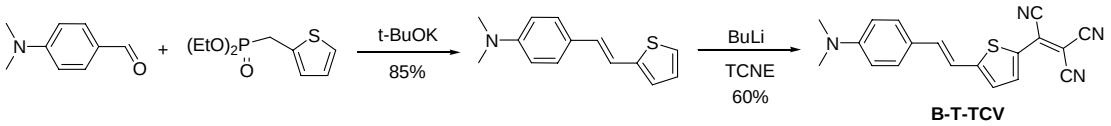


(E)-N,N-Dimethyl-4-(2-(thiazol-2-yl)vinyl)benzenamine (B-Ti_2). To a solution of 4-(dimethylamino)benzaldehyde (1.49 g, 10.0 mmol) and diethyl thiazol-2-ylmethylphosphonate (4.70 g, 20.0 mmol) in anhydrous tetrahydrofuran (100 mL) at -78 ^{o}C under nitrogen, was added dropwise potassium *t*-butyloxide (2.24 g, 20.0 mmol) in anhydrous tetrahydrofuran. The solution was allowed to warm up to room temperature in 0.5 h and then poured into distilled water (100 mL). The resulting mixture was extracted with ethyl acetate (3×30 mL). The organic extracts were combined, washed with distilled water, dried over anhydrous magnesium sulfate, and rota-evaporated to remove most of the solvent. After a flash column chromatography on silica-gel (eluent: ethyl acetate/ligroin = 1/4, v/v, R_f = 0.5), the resulting yellow solid was further purified by recrystallization from ligroin to give yellow sheet-like crystals (2.07 g, 90% yield): mp. 123–124 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (1H, d, J = 3.3 Hz), 7.43 (2H, d, J = 6.9Hz), 7.36 (2H, d, J = 16.2 Hz), 7.10 -7.16 (2H, m), 6.69 (2H, d, J = 6.9Hz), 2.99 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.2, 150.7, 143.0, 134.8, 128.3, 123.6, 116.8, 116.7, 112.0, 40.2.

(E)-2-(2-(4-(Dimethylamino)styryl)thiazol-5-yl)ethene-1,1,2-tricarbonitrile (B-Ti_2-TCV). To a solution of **B-Ti_2** (0.230 g, 1.00 mmol) in anhydrous tetrahydrofuran (3.00 mL) at -78 ^{o}C under nitrogen, was added *n*-buthyl lithium (1.6 M in hexane, 0.94 mL, 1.50 mmol). The resulting solution was stirred at -78 ^{o}C for 1 h before tetracyanoethene (0.192 g, 1.50 mmol) in anhydrous tetrahydrofuran (4 mL) was added. The reaction solution was stirred at -78 ^{o}C for another 10 min and then poured into distilled water (3 mL). The mixture was dried under vacuum with a cold trap and the solid residue was washed with diethyl ether (30 mL) twice and extracted with dichloromethane (30 mL) three times. The dichloromethane extracts were

combined, dried over anhydrous magnesium sulfate, and rota-evaporated to give a dark green residue that was purified by recrystallization from chloroform to yield the dark green solid product (0.371 g, 75% yield): ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.55 (1H, s), 7.80 (1H, d, *J* = 15.6 Hz), 7.54 (2H, d, *J* = 9.0 Hz), 7.13 (1H, d, *J* = 15.6 Hz), 6.73 (2H, d, *J* = 9.0 Hz), 3.11 (6H, s); FT-IR (KBr, cm^{-1}): 2899, 2212 (-CN), 1595, 1510, 1414, 1366, 1232, 1223, 1157, 941, 832; HRMS for $C_{18}H_{13}N_5S$ (m/z): 331.0892 (Calcd.), 331.0896 (Found); Anal. Calcd. for $C_{18}H_{13}N_5$: C, 65.24; H, 3.95; N, 21.13; Found: C, 64.15; H, 4.85; N,22.44.

6. B-T-TCV

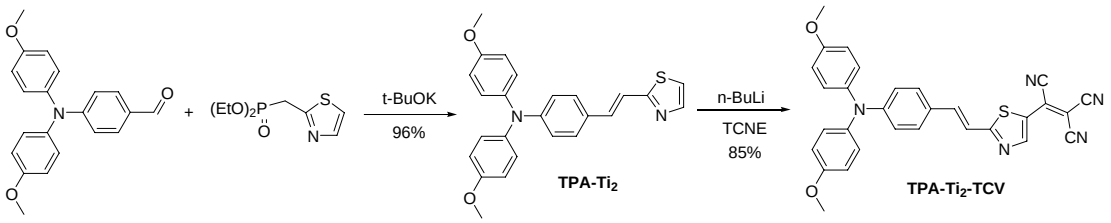


B-T-TCV

(E)-N,N-dimethyl-4-(2-(thiophen-2-yl)vinyl)benzenamine: (B-T). To a soultion of 4-(dimethylamino)benzaldehyde (1.49 g, 10.0 mmol) and diethyl thiophen-2-ylmethylphosphonate (4.68 g, 20.0 mmol) in anhydrous tetrahydrofuran (60 mL) at -78 ^{o}C under nitrogen, was added dropwise potassium t-butyloxide (2.24 g, 20.0 mmol) in anhydrous tetrahydrofuran (60 mL). Afte the addition, the solution was gradually warmed up to room temperature and then poured into distilled water (100 mL). The resulting mixture was extracted with ethyl acetate (3×50 mL). The organic extracts were combined, washed with distilled water (2×30 mL), and dried over magnesium sulfate. After removal of the solvent by rota-evaporation, the solid residue was purified by a silica-gel column chromatography (eluent: ethyl acetate/ligroin = 1/4, v/v, R_f = 0.7) and recrystallized from ligroin to give yellow sheet crystals (1.90 g, 85% yield): mp. 137–139 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 (2H, d, *J* = 8.7Hz), 7.11-12 (1H, m), 7.05 (1H, d, *J* =15.9 Hz), 6.96 – 7.01 (2H, m), 6.87 (1H, d, *J* = 15.9 Hz), 6.71 (2H, d, *J* = 8.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 143.9, 128.6, 127.4, 127.36, 127.32, 124.5, 122.9, 117.6, 112.4, 40.4.

(E)-2-(5-(4-(dimethylamino)styryl)thiophen-2-yl)ethene-1,1,2-tricarbonitrile (B-T-TCV). The synthesis was referred to the literature method [10]: To a solution of **B-T** (0.460 g, 20.0 mmol) in anhydrous DMF (15 mL), tetracyanoethene (0.312 g, 24.0 mmol) in anhydrous DMF (10 mL) was added dropwise. The solution was stirred for 24 h before being poured into distilled water (100 mL). The solid product was collected by filtration and recrystallized from ethyl acetate to give a dark green crystalline product (0.396 g, 60% yield): ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.94 (1H, d, *J* = 4.4 Hz), 7.48 (2H, d, *J* = 9.0 Hz), 7.29 (1H, d, *J* = 15.8 Hz), 7.18 (1H, d, *J* = 4.2Hz), 7.08 (1H, d, *J* = 15.8 Hz), 6.82 (2H, d, *J* = 8.4 Hz), 3.10 (6H, s); FT-IR (KBr, cm^{-1}): 3086, 2804, 2207, 1583, 1513, 1411, 1367, 1292, 1163, 1070, 995, 942, 857, 717; HRMS for $C_{19}H_{14}N_4S$ (m/z): 330.0939 (Calcd), 330.0935 (Found).

7. TPA-Ti$_2$-TCV

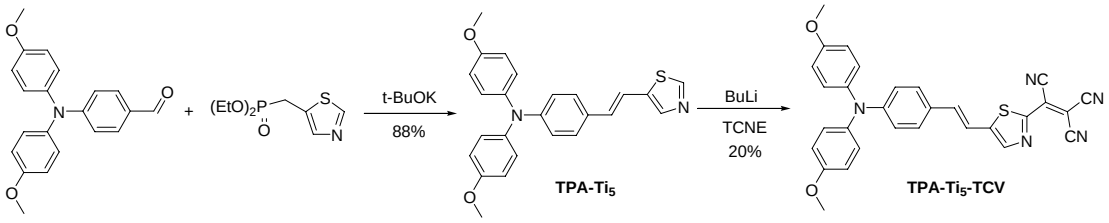


(E)-4-methoxy-N-(4-methoxyphenyl)-N-(4-(2-(thiazol-2-yl)vinyl)phenyl) benzenamine (TPA-Ti$_2$). To a solution of 4-(bis(4-methoxyphenyl)amino)benzaldehyde (1.00 g, 3.00 mmol) and diethyl thiazol-2-ylmethylphosphonate (1.06 g, 4.50 mmol) in anhydrous tetrahydrofuran (30 mL) at -78 ^{o}C under nitrogen, was added dropwise potassium t-butyloxide (0.672 g, 6.00 mmol) in anhydrous tetrahydrofuran. After the addition, the solution was gradually warmed up to room temperature and then poured into distilled water (100 mL). The mixture was extracted with ethyl acetate (3×30 mL). The organic extracts were combined, washed with distilled water (2×30 mL), dried over anhydrous magnesium sulfate, and rota-evaporated to remove the solvent. The solid residue was purified by a silica-gel column chromatography (eluent: ethyl acetate/ligroin = 1/4,

v/v, R_f = 0.5) to give a light yellow solid product (1.19 g, 96% yield): mp. 88–89 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ 7.76 (1H, d, J = 3.3 Hz), 7.32 – 7.37 (3H, m), 7.07 – 7.13 (4H, m), 3.85 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$): 167.8, 156.2, 149.4, 143.2, 140.1, 134.2, 127.9, 127.3, 127.0, 119.4, 118.3, 117.2, 114.72, 55.4; FT-IR (KBr, cm^{-1}): 2954, 1595, 1505, 1327, 1296, 1245, 1178, 1134, 1104, 1031, 968, 832, 719, 573, 533.

(E)-2-(2-(4-(bis(4-methoxyphenyl)amino)styryl)thiazol-5-yl)ethene-1,1,2-tricarbonitrile (TPA-Ti$_2$-TCV). To a stirring solution of **TPA-Ti$_2$** (0.345 g, 0.833 mmol) in anhydrous tetrahydrofuran (10 mL) at -78 ^oC under nitrogen, was added *n*-butyl lithium (1.6 M in hexane, 0.573 ml, 0.917 mmol). The solution was allowed to warmed to room temperature in 3 h and then cooled again down to -78 ^oC. Tetracyanoethane (0.160 g, 1.30 mmol) in anhydrous tetrahydrofuran (5 mL) was added dropwise to the solution. The reaction solution was stirred for another 5 min in cold bath, warmed gradually up to room temperature, and then poured into distilled water (60.0 mL). The mixture was extracted with ethyl acetate (3×30 mL). The organic extracts were combined, washed with distilled water, drived over anhydrous magnesium sulfate, and rota-evaporated to remove the solvent. The solid residue was purified by a silica-gel column chromatography (eluent: ethyl acetate/ligroin = 1/1, v/v, R_f=0.6) to give green crystalline products (0.368 g, 86% yield): mp. 235-237 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 8.56 (1H, s), 7.76 (1H, d, J = 15.6 Hz), 7.41 (2H, d, J = 8.7 Hz), 7.11 – 7.14 (5H, m), 6.86 - 6.92 (6H, m), 3.83 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.3, 157.2, 157.0, 152.0, 143.0, 138.8, 130.3, 128.1, 127.8, 125.8, 118.0, 115.3, 115.0, 112.2, 112.1, 111.8, 55.5; FT-IR (KBr, cm^{-1}): 3038, 2833, 2219, 1581, 15022, 1435, 1391, 1327, 1285, 1240, 1161, 1032, 968, 824; HRMS for $C_{30}H_{21}N_5O_2S$ (m/z): 515.1416 (Calcd.), 515.1416 (Found).

8. TPA-Ti$_5$-TCV



(E)-4-methoxy-N-(4-methoxyphenyl)-N-(4-(2-(thiazol-5-yl)vinyl)phenyl) benzenamine (TPA-Ti$_5$). To a solution of 4-(bis(4-methoxyphenyl) amino) benzaldehyde (0.333 g, 1.00 mmol) and diethyl thiazol-5-ylmethyl phosphonate (0.523 g, 1.20 mmol) in anhydrous tetrahydrofuran (20 mL) at -78 ^{o}C under nitrogen, was added dropwise potassium t-butyloxide (1.34 g, 1.20 mmol) in anhydrous tetrahydrofuran (20 mL). After the addition, the solution was warmed gradually up to room temperature and then poured into distilled water (100 mL). The mixture was extracted with ethyl acetate (3×50 mL). The organic extracts were combined, washed with distilled water (2×30 mL), dried over anhydrous magnesium sulfate, and rota-evaporated to remove the solvent. The solid residue was purified by a silica-gel column chromatography (eluent: ethyl acetate/ligroin = 1/4, v/v, R_f = 0.5) to give a yellow solid product (0.362 g, 88% yield): ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.61 (1H, s), 7.79 (1H, s), 7.26 (2H, d, J= 8.7Hz), 7.07 - 7.10 (5H, m), 6.84 – 6.90 (7H, m), 3.80 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.1, 150.5, 148.8, 140.8, 140.4, 131.9, 128.2, 127.2, 126.8, 119.9, 1115.8, 115.0, 114.7, 55.4.

(E)-2-(5-(4-(bis(4-methoxyphenyl)amino)styryl)thiazol-2-yl)ethene-1,1,2-tricarbonitrile (TPA-Ti$_5$-TCV). To a nitrogen-purged, stirring solution of **TPA-Ti$_5$** (0.200 g, 0.480 mmol) in anhydrous tetrahydrofuran (10.0 mL) at -78 ^{o}C, was added n-butyl lithium (1.6 M in hexane, 0.350 mL, 0.560 mmol) through a syringe. The solution was stirred at -78 ^{o}C for 2 h before tetracyanoethene (0.094 g, 0.730 mmol) in anhydrous tetrahydrofuran (5 mL) was added dropwise. The solution was stirred at -78 ^{o}C for another 5 min and then poured into distilled water (100 mL). The mixture was extracted with ethyl acetate (50 mL) three times. The organic extracts were combined, washed with distilled water (2×20 mL), dried over anhydrous magnesium sulfate, and

rota-evaporated to concentrate the solution to about 20 mL. The resulting golden crystals were collected by filtration and washed with small amount of ethyl acetate (0.05 g, 20% yield): mp. 228–239 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (1H, s), 7.33 (2H, d, J = 8.8 Hz), 7.04 – 7.23 (6H, m), 6.84 – 6.89 (6H, m), 3.82 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): 157.0, 152.1, 151.1, 145.6, 145.4, 139.7, 139.1, 130.8, 129.1, 127.6, 120.1, 118.4, 114.9, 112.4, 112.3, 111.9, 111.7, 55.4; FT-IR (KBr, cm^{-1}): 3069, 2834, 2217, 1583, 1502, 1458, 1384, 1285, 1242, 1152, 1034, 958; HRMS-ESI for $C_{30}H_{21}N_5O_2S$ (m/z): 515.1416 (Calcd.), 515.1420 (Found).

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Section 2. Tables and Figures

Table S-1. Solubility of the NLO chromophores

	Dioxane	Toluene	$CHCl_3$	CH_2Cl_2	THF	DMF
P-Ti_2-TCV	+–	+	+	++	++	++
MP-Ti_2-TCV	+	+	++	++	++	++
T-Ti_2-TCV	+–	+–	+–	+–	+–	+–
T-Ti_5-TCV	+–	+–	+–	+–	+–	+–
B-Ti_2-TCV	+–	+–	+–	+–	+–	+
B-T-TCV	+–	+–	+	+	+	++
TPA-Ti_2-TCV	+	++	++	++	++	++
TPA-Ti_5-TCV	+	++	++	++	++	++

Note: The solubility (η) was tested by dissolving 1.0 mg of chromophore into 1 mL or 0.1 mL of solvent, where "–": insoluble; "+–": $\eta \leq 1$ mg/mL; "+": 1 mg/mL $< \eta \leq 10$ mg/mL; "++": $\eta > 10$ mg/mL.

Table S-2. UV-vis absorption of the NLO chromophores in different solvent.

	λ_{max} (nm)				
	dioxane	$CHCl_3$	THF	acetone	DMF
ε^a	2.21	4.83	7.58	20.7	36.7
P-Ti_2-TCV	660	731	699	715	735
MP-Ti_2-TCV	668	752	715	736	771
T-Ti_2-TCV	680	750	727	745	771
T-Ti_5-TCV	723	840	789	836	854
B-Ti_2-TCV	611	668	630	631	647
B-T-TCV	624	678	645	646	667
TPA-Ti_2-TCV	629	684	631	624	637
TPA-Ti_5-TCV	670	750	684	680	695

[a] Dielectric constant.

(Figure S-1)

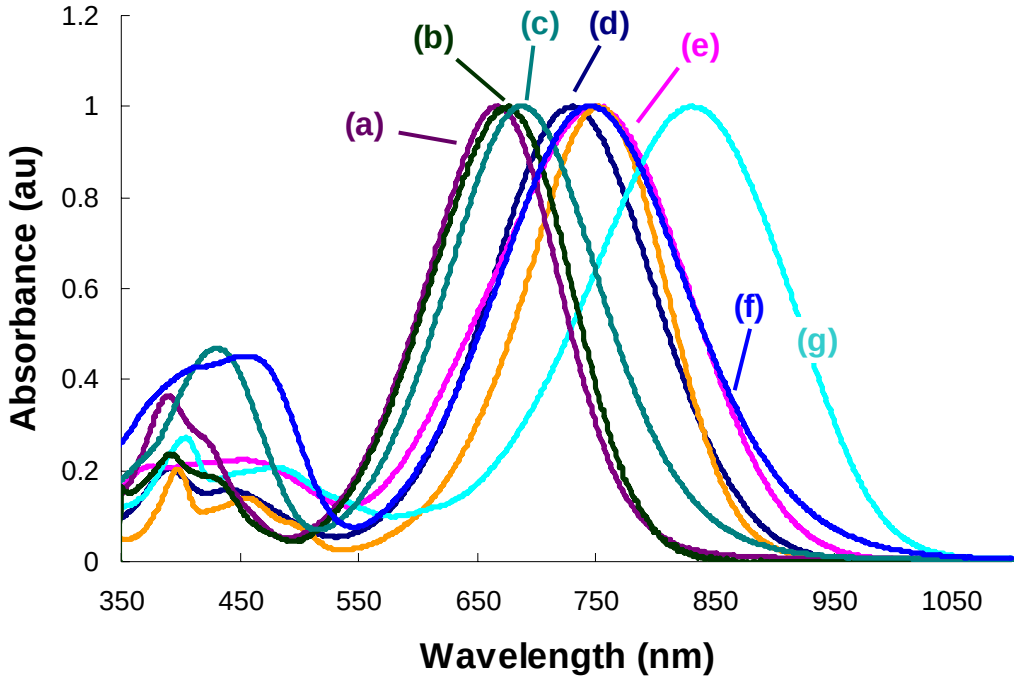

Figure S-1. Normalized UV-vis absorption spectra of the NLO chromophores in chloroform. (a) B-Ti_2-TCV; (b) B-T-TCV; (c) TPA-Ti_2-TCV; (d) P-Ti_2-TCV; (e) MP-Ti_2-TCV; (f) TPA-Ti_5-TCV; (g) T-Ti_5-TCV.

(Figure S-2)

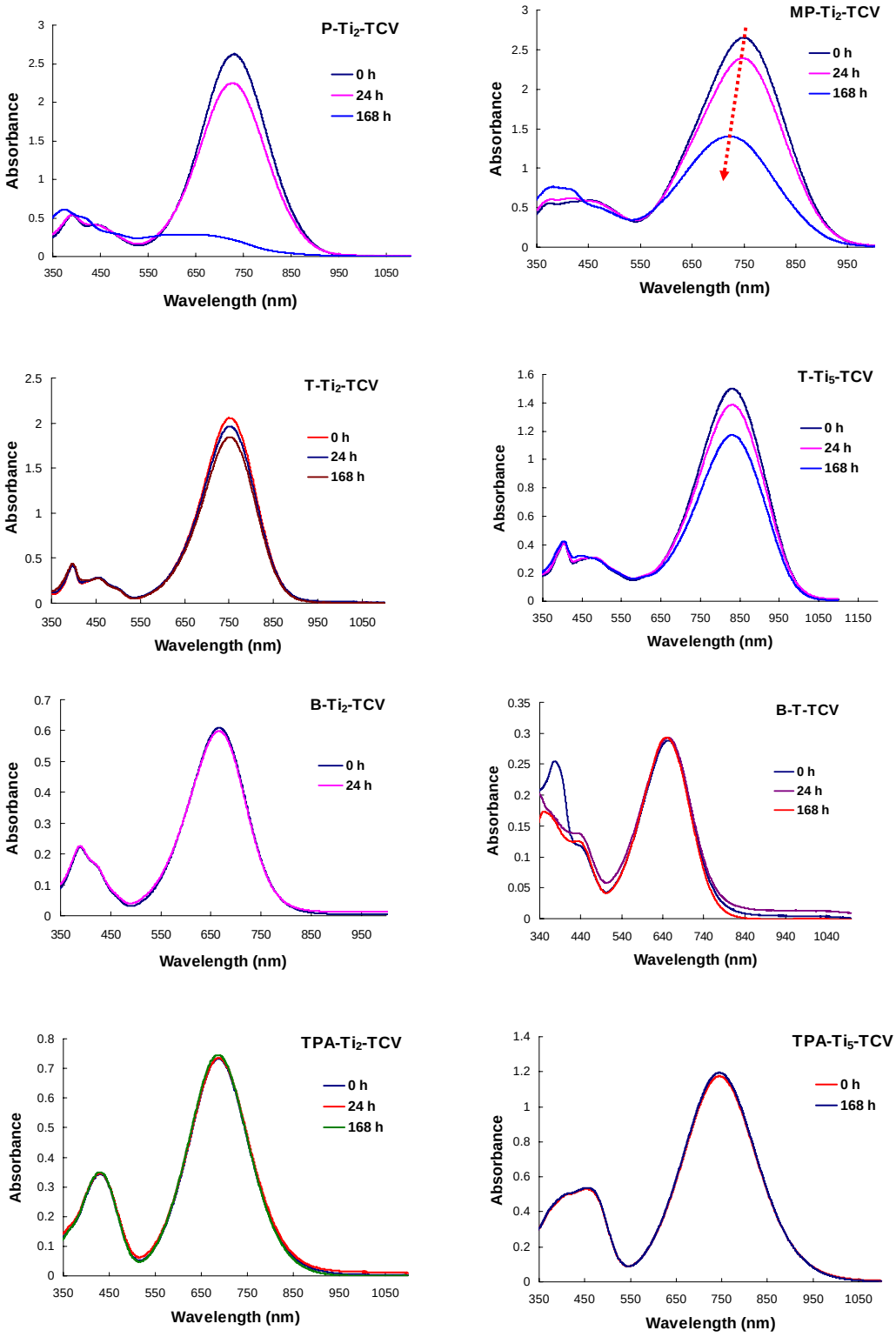

Figure S-2. UV-vis absorption spectra of chromophore solutions in chloroform stored under in-door light for different period of time.