Electronic Supplementary Information for

D-D-π-A Organic Dyes Containing 4,4'-Di(2-thienyl)triphenylamine Moiety for Efficient Dye-Sensitized Solar Cells

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Synthesis and characterization of the dyes:

Materials: All reagents and chemicals were purchased from commercial suppliers. *N*, *N*-Dimethylformamide (DMF), 1,2-dichroloethane and Tetrahydrofuran (THF) were distilled with CaH_2, while acetonitrile was distilled with P_2O_5. Other chemicals and reagents were used as received without further purifications.

Characterizations: The molecular structures of TTC104, TTC105 and intermediates were confirmed by ^{1}H NMR, ^{13}C NMR, and mass spectra, as summarized in the supporting materials. . The attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were measured with a Thermo Scientific Nicolet iS10 FT-IR Spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were recorded in solution of $CDCl_3$ or DMSO-d_6 on a Bruker DRX (500 MHz) NMR spectrometer with tetramethylsilane (TMS) as the internal standard. MALDI-TOF (matrix-assisted laser desorption ionization time-of-flight) analysis was performed on Bruker Daltonics Ultraflex MALDI TOF/TOF Mass Spectrometer, using α-Cyano-4-hydroxycinnamic acid as matrix. Electron spray mass spectrometry was measured in Thermo LCQ Fleet Electro-Spray Mass Spectrometer.

Synthesis of 9-ethyl-3,6-di(thiophen-2-yl)-9H-carbazole (1). A mixture of 3,6-dibromo-9-ethylcarbazole (3.530 g, 10.0 mmol), $Pd(PPh_3)_4$ (0.580 g, 0.5 mmol), 2-thienyl acid (2.952 g, 24.0 mmol), 0.5 mM K_2CO_3 (50.0 mL, 25.0 mmol) and 1,4-dioxane (100 mL) were degassed with a steady stream of N_2 for 15 min at room temperature. The reaction mixture was then heated to reflux for 18 h under N_2. After cooling to room temperature, the reaction mixture was extracted by $CHCl_3$ (3×150 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography with CH_2Cl_2 : hexane (v : v, 1 : 100) as eluent to give the target compound **1** as pale yellow solid (3.100 g, 86%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ, [ppm]: 8.60 (s, 2H), 7.75 (d, J = 8.5, 2H), 7.61 (d, J = 8.5, 2H), 7.54 (d, J = 3.5, 2H), 7.48 (d, J = 5.0, 2H), 7.15 (t, J = 5.0, 2H), 4.43 (q, J = 7.5, 2H), 1.32 (t, J = 7.5, 3H); MS (MALDI-Tof): Calcd for $C_{22}H_{17}NS_2$, 359.08; found, 359.407.

Synthesis of 5-(9-ethyl-6-(thiophen-2-yl)-9H-carbazol-3-yl)thiophene-2-carbaldehyde (2). To an ice-cooled solution of distilled dimethylformamide (0.402 g, 5.5 mmol) and compound **1** (1.798 g, 5.0 mmol) in dry 1,2-dichloroethane (20.0 mL) under N_2, phosphorus oxychloride (0.767 g, 5.0 mmol) was added drop wise. The resulting mixture was slowly brought to room temperature and then stirred at 85 °C for 18 h. After refluxing, the solution was cooled to room temperature. Then the solution was poured into a saturated sodium acetate aqueous solution (50.0 mL), and stirred for 6 h to complete the hydrolysis. The hydrolyzed solution was extracted with dichloromethane (3×50 mL). The combined dichloromethane solutions were dried over anhydrous $MgSO_4$, and then concentrated by distillation under reduced pressure. After purification by silicagel column chromatography using CH_2Cl_2 : hexane (v : v, 1 : 10) as eluent, title compound **2** was obtained as yellow liquid. Yield: 1.300 g (67%) .^{1}H NMR (DMSO-d_6, 500 MHz): δ, [ppm]: 9.91 (s, 1H), 8.82 (s, 1H), 8.64 (s, 1H), 8.07 (d, J = 4.0, 1H), 7.93 (d, J = 8.5, 1H), 7.80-7.83 (m, 2H), 7.72 (d, J = 8.5, 1H), 7.69 (d, J = 8.5, 1H), 7.55 (d, J = 3.0, 1H), 7.52 (d, J = 5.5, 1H), 7.18 (t, J = 5.0, 1H), 4.50 (q, J = 7.0, 2H), 1.36 (t, J = 7.0, 3H); MS (MALDI-Tof): Calcd for $C_{23}H_{17}NOS_2$,

387.08; found, 387.178.

Synthesis of 5-(6-(5-bromothiophen-2-yl)-9-ethyl-9H-carbazol-3-yl)thiophene-2-carbaldehyde (3). N-bromosuccinamide (NBS) (0.534 g, 3 mmol) was added over a period of 20 min into an ice-cooled solution of compound **2** (1.163 g, 3 mmol) in THF (30 mL) under N_2. The mixture was stirred at room temperature for 3 h. Then 5.0 mL water was added and stirred for additional 0.5 h. 50 mLCH_2Cl_2 was added and the solution was washed with water (3×50 mL). The combined organic layer was dried over anhydrous $MgSO_4$, and then concentrated by distillation under reduced pressure. After purification by silicagel column chromatography using CH_2Cl_2 : hexane (v : v, 1 : 10) as eluent, title compound **3** was obtained as yellow liquid. Yield: 1.150 g (82%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ, [ppm]: 9.91 (s, 1H), 8.80 (s, 1H), 8.61 (s, 1H), 8.07 (d, J = 4.0, 1H), 7.94 (d, J = 8.0, 1H), 7.79 (d, J = 4.0, 1H), 7.76 (d, J = 8.5, 1H), 7.73 (d, J = 9.0, 1H), 7.69 (d, J = 8.5, 1H), 7.39 (d, J = 4.0, 1H), 7.28 (d, J = 4.0, 1H), 4.49 (q, J = 7.0, 2H), 1.35 (t, J = 7.0, 3H); MS (MALDI-Tof): Calcd for $C_{23}H_{16}BrNOS_2$, 464.99; found, 465.012.

Synthesis of 3,6-bis(5-bromothiophen-2-yl)-9-ethyl-9H-carbazole (4). N-bromosuccinamide (NBS) (1.068 g, 6 mmol) was added over a period of 20 min into an ice-cooled solution of compound **1** (1.163 g, 3 mmol) in THF (40 mL) under N_2. The mixture was stirred at room temperature for 3 h. Then 5.0 mL water was added and stirred for additional 0.5 h. 80 mLCH_2Cl_2 was added and the solution was washed with water (3×50 mL). The combined organic layer was dried over anhydrous $MgSO_4$, and then concentrated by distillation under reduced pressure. After purification by silicagel column chromatography using CH_2Cl_2 : hexane (v : v, 1 : 100) as eluent, title compound **3** was obtained as yellow liquid. Yield: 1.440 g (93%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ, [ppm]: 8.57 (s, 2H), 7.75 (d, J = 8.5, 2H), 7.68 (d, J = 8.5, 2H), 7.39 (d, J = 3.5, 2H), 7.28 (d, J = 3.5, 2H), 4.48 (q, J = 7.0, 2H), 1.34 (t, J = 7.0, 3H); MS (MALDI-Tof): Calcd for $C_{22}H_{15}Br_2NS_2$, 514.90; found, 514.849.

Synthesis of 4-bromo-N,N-bis(4-(thiophen-2-yl)phenyl)aniline (5). A mixture of tris(4-bromophenyl)amine (4.82 g, 10 mmol), $Pd(PPh_3)_4$ (0.580 g, 0.5 mmol), 2-thiopheneboronic acid (2.56 g, 20 mmol), 0.5 mM K_2CO_3 (50.0 mL, 25 mmol) and 1,4-dioxane (100 mL) were degassed with a steady stream of N_2 for 15 min at room temperature. The reaction mixture was then heated to reflux for 18 h under N_2. After cooling to room temperature, the reaction mixture was extracted by $CHCl_3$ (3×150 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography with CH_2Cl_2 : hexane (v : v, 1 : 100) as eluent to give the target compound **5** as yellow solid (2.05 g, 42%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ, [ppm]: 7.01 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.5 Hz, 4H), 7.12 (dd, J = 3.5, 5.0 Hz, 2H), 7.43 (d, J = 2.5 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 5.0 Hz, 2H), 7.61 (d, J = 8.5 Hz, 4H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ, [ppm]: 115.30, 123.58, 124.79, 125.60, 126.00, 127.22, 128.93, 129.47, 132.86, 143.45, 146.27, 146.52. MS (MALDI-Tof): Calcd for $C_{26}H_{18}BrNS_2$, 487.01; found, 487.221.

Synthesis of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N,N-bis(4-(thiophen-2-yl) phenyl)aniline (6). A mixture of compound **5** (1.952 g, 4 mmol), Bis(pinacolato)diboron (1.524 g, 6.0 mmol), 2-thiopheneboronic acid (2.56 g, 20.0 mmol), AcOK (1.178 g, 12.0 mmol) and DMF

(15 mL) were degassed with a steady stream of N_2 for 15 min at room temperature. Then, $Pd(dppf)_2Cl_2$•CH_2Cl_2 (0.1630 g, 0.2 mmol) was added and stirred at 100 ^oC for 2 h. After cooling to room temperature, the reaction mixture was poured into 100 mL water and extracted by $CHCl_3$ (3×50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography with CH_2Cl_2 : hexane (v : v, 1 : 50) as eluent to give the target compound **6** as yellow solid (1.540 g, 72%). ^1H NMR (DMSO-d_6, 500 MHz): δ, [ppm]: 7.61 (d, J = 8.5, 4H), 7.59 (d, J = 8.5, 2H), 7.50 (d, J = 5.0, 2H), 7.44 (d, J = 3.5, 2H), 7.12 (d, J = 5.0, 2H), 7.08 (d, J = 9.0, 4H), 7.01 (d, J = 8.5, 2H), 1.28 (s, 12H); MS (MALDI-Tof): Calcd for $C_{32}H_{30}BNO_2S_2$, 535.18; found, 535.359.

Synthesis of 5-(6-(5-(4-(bis(4-(thiophen-2-yl)phenyl)amino)phenyl)thiophen-2-yl)-9-ethyl-9H-carbazol-3-yl)thiophene-2-carbaldehyde (7). A mixture of compound **3** (0.466 g, 1.0 mmol), $Pd(PPh_3)_4$ (0.058 g, 0.05 mmol), compound **6** (0.536 g, 1.0 mmol), 0.5 mM K_2CO_3 (3.0 mL, 1.5 mmol) and 1,4-dioxane (10 mL) were degassed with a steady stream of N_2 for 15 min at room temperature. The reaction mixture was then heated to reflux for 18 h under N_2. After cooling to room temperature, the reaction mixture was extracted by $CHCl_3$ (3×15 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography with CH_2Cl_2 : hexane (v : v, 1 : 10) as eluent to give the target compound **7** as yellow solid (0.453 g, 57%). ^1H NMR (DMSO-d_6, 500 MHz): δ, [ppm]: 9.91 (s, 1H), 8.85 (s, 1H), 8.69 (s, 1H), 8.08 (d, J = 3.5, 1H), 7.95 (d, J = 8.5, 1H), 7.87 (d, J = 8.5, 1H), 7.82 (d, J = 3.5, 1H), 7.75 (d, J = 8.5, 2H), 7.72 (d, J = 8.5, 1H), 7.69 (d, J = 8.5, 2H), 7.65 (d, J = 8.5, 4H), 7.58 (d, J = 3.5, 1H), 7.52 (d, J = 5.0, 2H), 7.46 (d, J = 3.0, 2H), 7.10-7.16 (m, 8H), 4.52 (q, J = 6.5, 2H), 1.35 (t, J = 6.5, 3H); MS (MALDI-Tof): Calcd for $C_{49}H_{34}N_2OS_4$, 794.16; found, 793.905.

Synthesis of 4-(5-(6-(5-bromothiophen-2-yl)-9-ethyl-9H-carbazol-3-yl)thiophen-2-yl)-N,N-bis(4-(thiophen-2-yl)phenyl)aniline (8). A mixture of compound **4** (0.517 g, 1.0 mmol), $Pd(PPh_3)_4$ (0.058 g, 0.05 mmol), compound **6** (0.536 g, 1.0 mmol), 0.5 mM K_2CO_3 (3.0 mL, 1.5 mmol) and 1,4-dioxane (10 mL) were degassed with a steady stream of N_2 for 15 min at room temperature. The reaction mixture was then heated to reflux for 18 h under N_2. After cooling to room temperature, the reaction mixture was extracted by $CHCl_3$ (3×15 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography with CH_2Cl_2 : hexane (v : v, 1 : 50) as eluent to give the target compound **8** as yellow solid (0.347 g, 41%). ^1H NMR (DMSO-d_6, 500 MHz): δ, [ppm]: 8.64 (s, 1H), 8.60 (s, 1H), 7.84 (d, J = 8.5, 1H), 7.74 (d, J = 8.5, 1H), 7.68 (d, J = 8.0, 4H), 7.64 (d, J = 8.0, 4H), 7.57 (d, J = 3.5, 1H), 7.48-7.54 (m, 3H), 7.46 (d, J = 3.5, 2H), 7.41 (d, J = 4.0, 1H), 7.28 (d, J = 3.5, 1H), 7.10-7.17 (m, 8H), 4.49 (q, J = 7.0, 2H), 1.35 (t, J = 7.0, 3H); MS (MALDI-Tof): Calcd for $C_{48}H_{33}BrN_2S_4$, 844.07; found, 843.684.

Synthesis of (E)-3-(5-(6-(5-(4-(bis(4-(thiophen-2-yl)phenyl)amino)phenyl)thiophen-2-yl)-9-ethyl-9H-carbazol-3-yl)thiophen-2-yl)-2-cyanoacrylic acid (TTC104). To a solution of compound **7** (0.318 g, 0.4 mmol), cyanoacetic acid (68.0 mg, 0.8 mmol) in dry CH_3CN (5 mL) and THF (5 mL), and a few drops of piperidine was added and heated to reflux for 2 h. After cooling to room temperature, solvents were removed by rotary evaporation. The residue was

purified by silica gel column chromatography with CH_2Cl_2 : MeOH (v : v, 10 : 1) as eluent to afford the dye TTC104 as a red solid (0.203 g, 59%). M.P. 163-167 °C; ^{1}H NMR (DMSO-d_6, 500 MHz): δ, [ppm]: 8.70 (s, 1H), 8.65 (s, 1H), 8.12 (s, 1H), 7.84 (t, J = 9.0, 2H), 7.75 (d, J = 4.0, 1H), 7.66-7.74 (m, 5H), 7.62 (d, J = 8.5, 4H), 7.58 (d, J = 4.0, 1H), 7.36-7.54 (m, 3H), 7.44 (d, J = 2.5, 2H), 7.08-7.16 (m, 8H), 4.49 (q, J = 7.0, 2H), 1.35 (t, J = 7.0, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ, [ppm] 168.35, 154.03, 146.48, 146.21, 144.06, 144.01, 142.03, 140.56, 139.69, 139.63, 138.25, 138.16, 134.59, 129.42, 129.24, 128.04, 126.85, 126.38, 126.16, 124.36, 124.21, 123.43, 123.26, 123.23, 123.13, 123.04, 122.70, 122.45, 118.96, 118.93, 118.89, 118.39, 117.53, 117.48, 117.17, 108.92, 37.63, 13.82; MS (MALDI-Tof): Calcd for $C_{52}H_{35}N_3O_2S_4$, 861.16; found, 860.780. The attenuated total reflection Fourier transform infrared (ATR-FTIR) spectrum of TTC104 is shown in Fig. S4.

Synthesis of 4-(5-(9-ethyl-6-(5-(pyridin-4-yl)thiophen-2-yl)-9H-carbazol-3-yl)thiophen-2-yl)-N,N-bis(4-(thiophen-2-yl)phenyl)aniline (TTC105). A mixture of compound **8** (0.296 g, 0.35 mmol), $Pd(PPh_3)_4$ (29.0 mg, 0.025 mmol), Pyridine-4-boronic acid (21.5 mg, 0.5 mmol), 0.5 mM K_2CO_3 (2 mL, 1 mmol) and 1,4-dioxane (10 mL) were degassed with a steady stream of N_2 for 15 min at room temperature. The reaction mixture was then heated to reflux for 18 h under N_2. After cooling to room temperature, the reaction mixture was extracted by $CHCl_3$ (3×15 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography with EtOAc as eluent to give the target dye TTC105 as a yellow solid (0.204 g, 69%). M.P. 152-155 °C; ^{1}H NMR (DMSO-d_6, 500 MHz): δ, [ppm]: 8.74 (s, 1H), 8.67 (s, 1H), 8.60 (d, J = 6.0, 2H), 7.90 (d, J = 4.0, 1H), 7.87 (t, J = 9.0, 2H), 7.73 (d, J = 8.5, 2H), 7.68-7.71 (m, 5H), 7.62 (d, J = 8.5, 4H), 7.54-7.59 (m, 3H), 7.53 (d, J = 6.0, 2H), 7.47 (d, J = 3.0, 2H), 7.14 (m, 7H), 4.51 (q, J = 7.5, 2H), 1.37 (t, J = 7.5, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ, [ppm] ;149.74, 148.15, 146.53, 146.38, 144.18, 144.10, 142.25, 140.38, 140.17, 140.00, 133.02, 132.15, 132.07, 131.93, 131.69, 129.40, 129.33, 128.54, 128.45, 128.04, 126.91, 126.43, 126.23, 125.18, 124.51, 124.43, 124.25, 123.44, 123.37, 123.11, 122.48, 119.43, 118.14, 117.71, 109.17, 37.92, 13.91; MS (MALDI-Tof): Calcd for $C_{53}H_{37}N_3S_4$, 843.19; found, 842.892. The attenuated total reflection Fourier transform infrared (ATR-FTIR) spectrum of TTC105 is shown in Fig. S5.

Bode phase plots of electrochemical impedance spectroscopy,

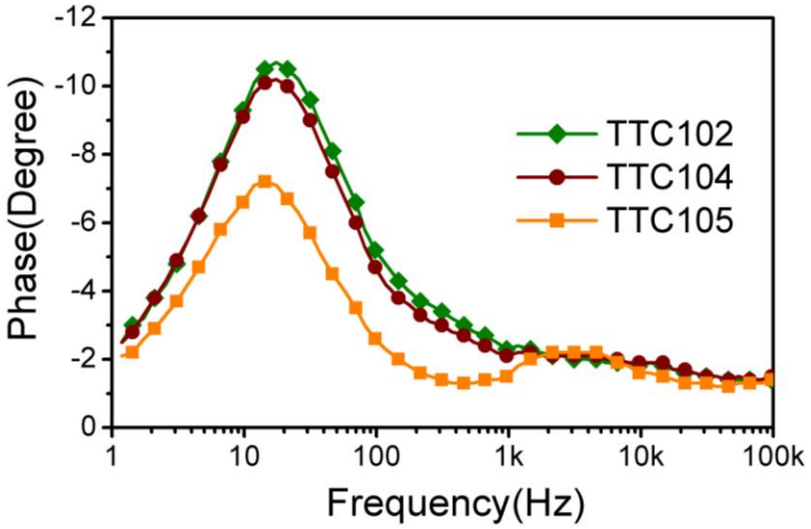

Fig. S1 Bode phase plots of electrochemical impedance Spectroscopy, scanned from 10^5 to 1

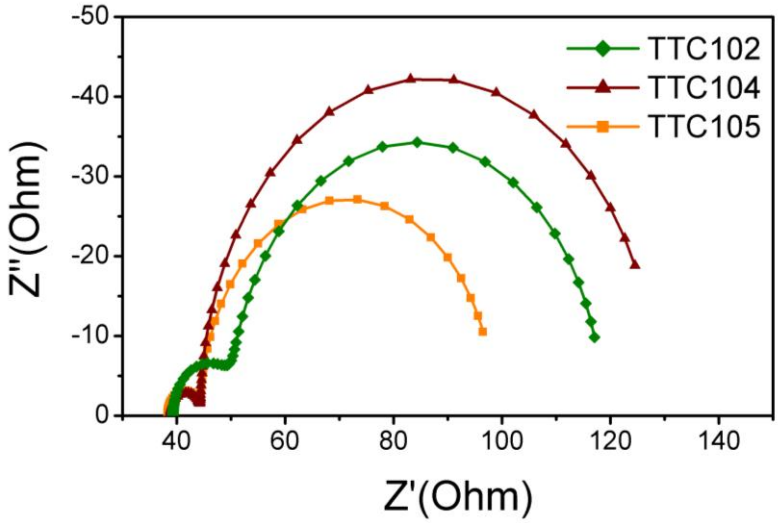

Fig. S2 Nyquist plots of Electrochemical impedance Spectroscopy (under dark) of DSSCs based on TTC102, TTC104, and TTC105, scanned from 10^5 to 1 Hz. The applied potential and ac amplitude were set as -0.4 V and 10 mV, respectively.

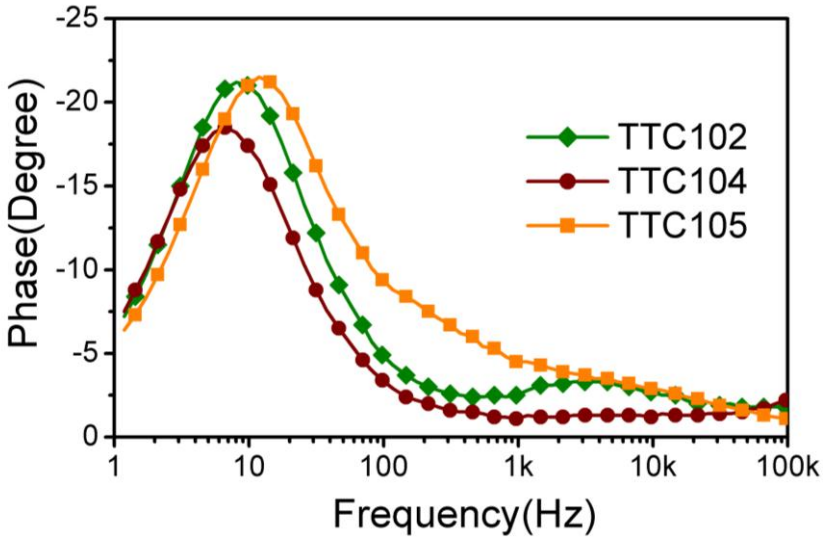

Fig. S3 Bode phase plots of Electrochemical impedance Spectroscopy (under dark) of DSSCs based on TTC102, TTC104, and TTC105, scanned from 10^5 to 1 Hz. The applied potential and ac amplitude were set as -0.4 V and 10 mV, respectively.

The attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of TTC104 and TTC105.

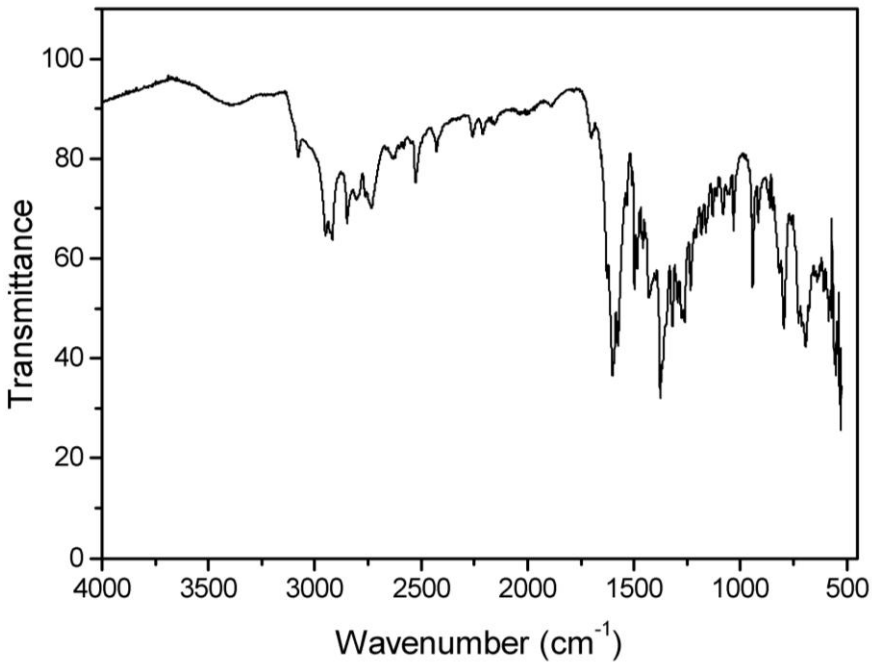

Fig. S4 The attenuated total reflection Fourier transform infrared (ATR-FTIR) spectrum of TTC104.

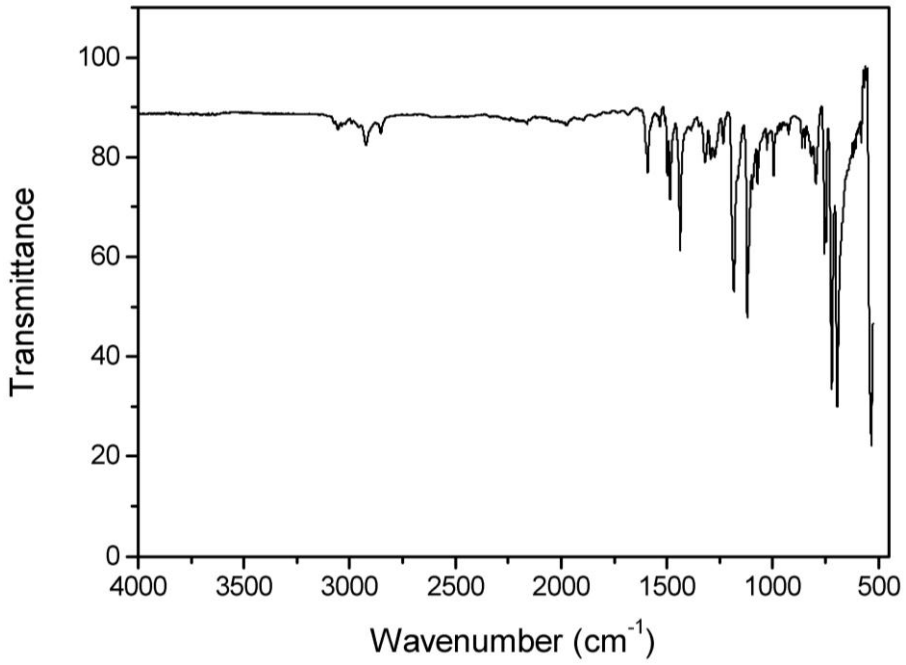

Fig. S5 The attenuated total reflection Fourier transform infrared (ATR-FTIR) spectrum of TTC105.