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Supporting Information

Rational design and microwave-assisted synthesis of a novel terthiophene derivative for facile preparation of binder-free polymer/metal oxide-based binary composite electrodes with high electrochemical performance

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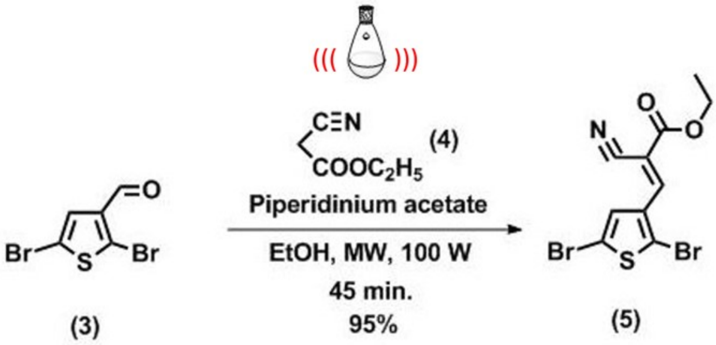
Contents

- **Synthesis of ethyl 2-cyano-3-(2,5-dibromothiophene-3-yl)acrylate (5)**



General procedure: Piperidine (0.07 g, 0.85 mmol) was dissolved in 10 mL ethanol and placed in a microwave reaction vessel (30 mL). Piperidinium acetate was prepared by adding acetic acid (0.035 g, 0.55 mmol) dropwise to the piperazine solution. Then, 2,5-dibromo-3-thiophenecarboxaldehyde (3 g, 11.1 mmol) (3) and ethyl cyanoacetate (1.25 g, 11.1 mmol) (4) were added to the piperidinium acetate solution. The reaction mixture was irradiated at 80°C under 100 W single-mode microwave power for 45 min. After the completion reaction, precipitated light yellow solid product was filtered and washed with cold ethanol (20 mL). The crude product was crystallized from hexane. Ethyl 2-cyano-3-(2,5-dibromothiophene-3-yl)acrylate (5) was obtained as a light yellow solid (3.85 g, 10.5 mmol, 95%, mp 126-128°C). ^{1}H NMR (400 MHz, $CDCl_3$) δH/ppm: 1.39 (t, J=7.2 Hz, 3H, ester –CH_3), 4.38 (q, J=6.8 Hz, 2H, ester –CH_2-), 8 ppm (s, 1H, Th-H), 8.15 (t, 1H, -CH=C-). ^{13}C NMR (400 MHz, $CDCl_3$) δC/ppm: 14 (ester –CH_3), 62.9 (ester –CH_2-), 103.4 (-CH=C-), 113.9 (Th-2C), 114.9 (Th-5C), 124.9 (-CN), 128.1 (Th-4C), 134 (Th-3C), 143.8 (-CH=C-), 162.1 (ester –C=O). (EI) m/z (%) calcd for $C_{10}H_7Br_2NO_2S$: 365; found: 364.9 (M^+, 20), 319.8 (10), 286 (5), 257.9 (100), 229.9 (30), 212.9 (15), 172.9 (3), 160 (10), 132 (15), 106.1 (5), 88.1 (10), 69.1 (5). FTIR (ATR) ν_{max}/cm^{-1} 3104 (w, aromatic C-H strecthing), 2984, 2906 (w, aliphatic C–H stretching), 2226 (m, -CN strecthing), 1724 (s, ester –C=O strecthing), 1642, 1604, 1506 (m, aromatic –C=C- strecthing), 1402, 1376 (m, aliphatic C-H bending), 1252 (s, -C-O- strecthing), 758 (s, thiophene-Br strecthing).

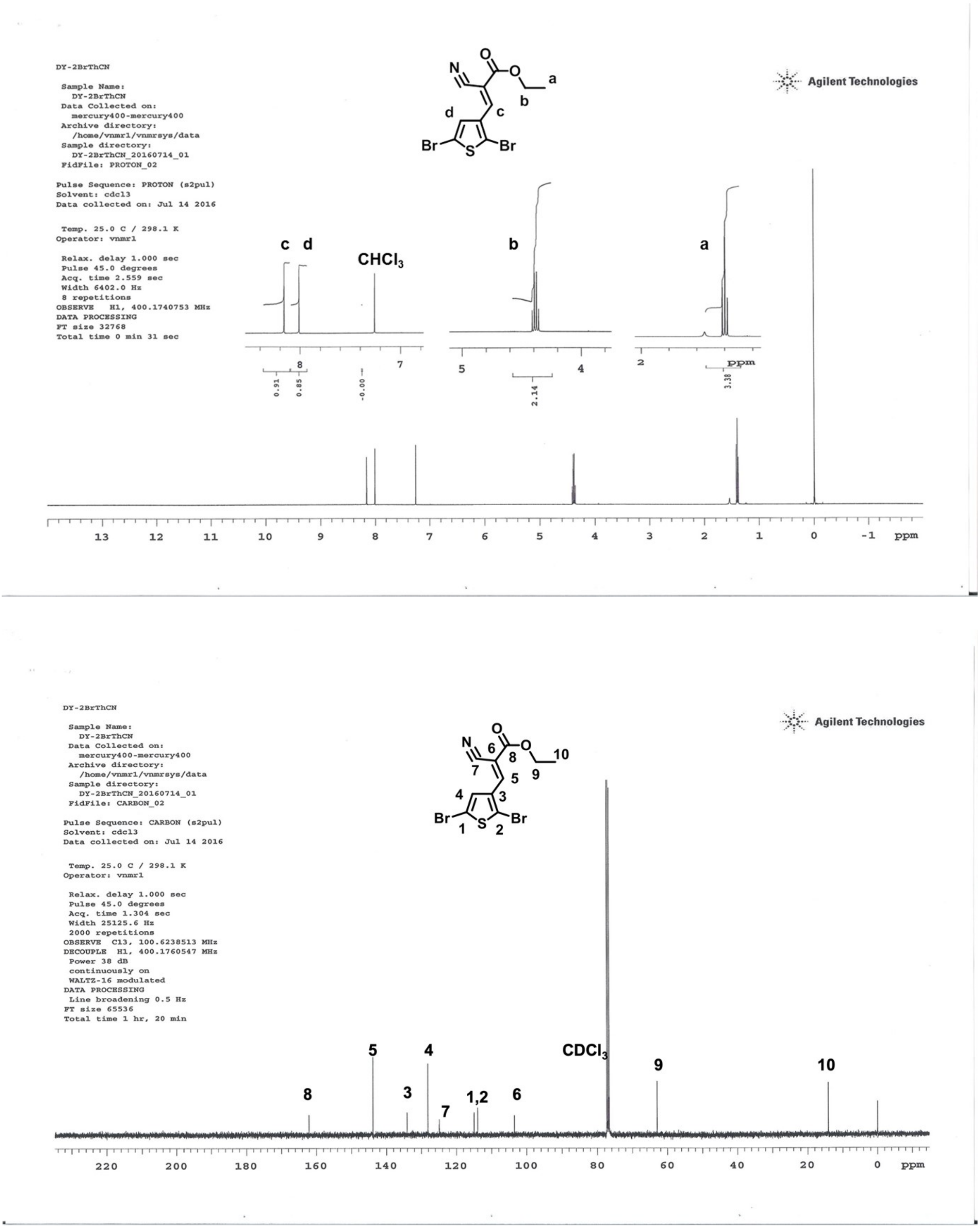


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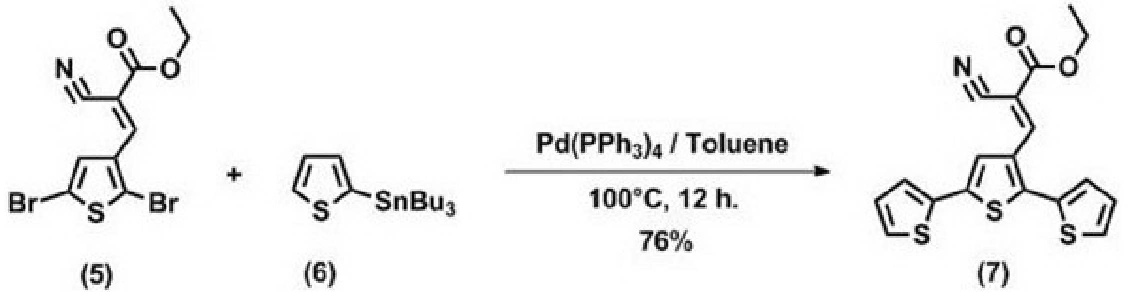
Fig. S1. ^1H NMR and ^{13}C NMR spectra of ethyl 2-cyano-3-(2,5-dibromothiophene-3-yl)acrylate (5)

❖ Synthesis of ethyl 3-[(2,2′:5′,2″-terthiophene-3′-yl)]-2-cyanoacrylate (7)



General procedure: In a 50 mL two-necked round-bottom flask fitted with a condenser and nitrogen inlet, ethyl 2-cyano-3-(2,5-dibromothiophene-3-yl)acrylate (0.5 g, 1.345 mmol) (5) and $Pd(PPh_3)_4$ (0.04 g, 0.035 mmol, 0.025 eqv.) were dissolved in dry toluene (20 mL). The toluene solution was intensely stirred for 25 min and then, 2-(tributylstannyl)thiophene (1.25 g, 3.375 mmol, 2.5 eqv) (6) was added. The resulting reaction mixture was refluxed under a nitrogen atmosphere for 12 h. Following the completion of the reaction, toluene was removed under reduced pressure and the oily crude product was extracted with chloroform (3 x 25 mL), washed brine solution and dried over Na_2SO_4. After removal of chloroform by evaporation, the crude product was purified by column chromatography using hexane–ethyl acetate (4:1 v/v) as eluent. Ethyl 3-[(2,2′:5′,2″-terthiophene-3′-yl)]-2-cyanoacrylate (7) was obtained as a orange solid (0.38 g, 1.02 mmol, 76%, mp: 141-143°C). ^{1}H NMR (400 MHz, $CDCl_3$) δH/ppm: 1.38 (t, J=7.6 Hz, 3H, ester $–CH_3$), 4.37 (q, J=7.6 Hz, 2H, ester $–CH_2$-), 7.06 (dd, J=8 Hz and J=3.6 Hz, 1H, Th-H), 7.19 (m, 2H, Th-H), 7.28 (d, J=4 Hz, 1H, Th-H), 7.31 (d, J=4 Hz, 1H, Th-H), 7.52 (dd, J=6 Hz and J=1.6 Hz, 1H, Th-H), 8.13 ppm (s, 1H, Th-H), 8.41 (t, 1H, -CH=C-). ^{13}C NMR (400 MHz, $CDCl_3$) δC/ppm: 14.2 (ester $–CH_3$), 62.6 (ester $–CH_2$-), 101.8 (-CH=C-), 115.7 (-CN), 122.2 (Th-C), 125.2 (Th-C), 126 (Th-C), 128 (Th-C), 128.6 (Th-C), 129.1 (Th-C), 130.7 (Th-C), 132. 8 (Th-C), 135.3 (Th-C), 137.6 (Th-C), 145.2 (Th-C), 146.3 (-CH=C-), 162.9 (ester –C=O). (EI) m/z (%) calcd for $C_{18}H_{13}NO_2S_3$: 371.4; found: 371 (M^+, 100), 343 (5), 298 (98), 265 (20), 252 (5), 210 (3), 170 (2), 127 (5), 114 (2), 69 (3). FTIR (ATR) ν_{max}/cm^{-1} 3066 (w, aromatic C-H strecthing), 2980 (w, aliphatic C–H stretching), 2218 (m, -CN strecthing), 1716 (s, ester –C=O strecthing), 1581, 1556 (m, aromatic –C=C- strecthing), 1444, 1365 (m, aliphatic C-H bending), 1238, 1200 (m, -C-O- strecthing).

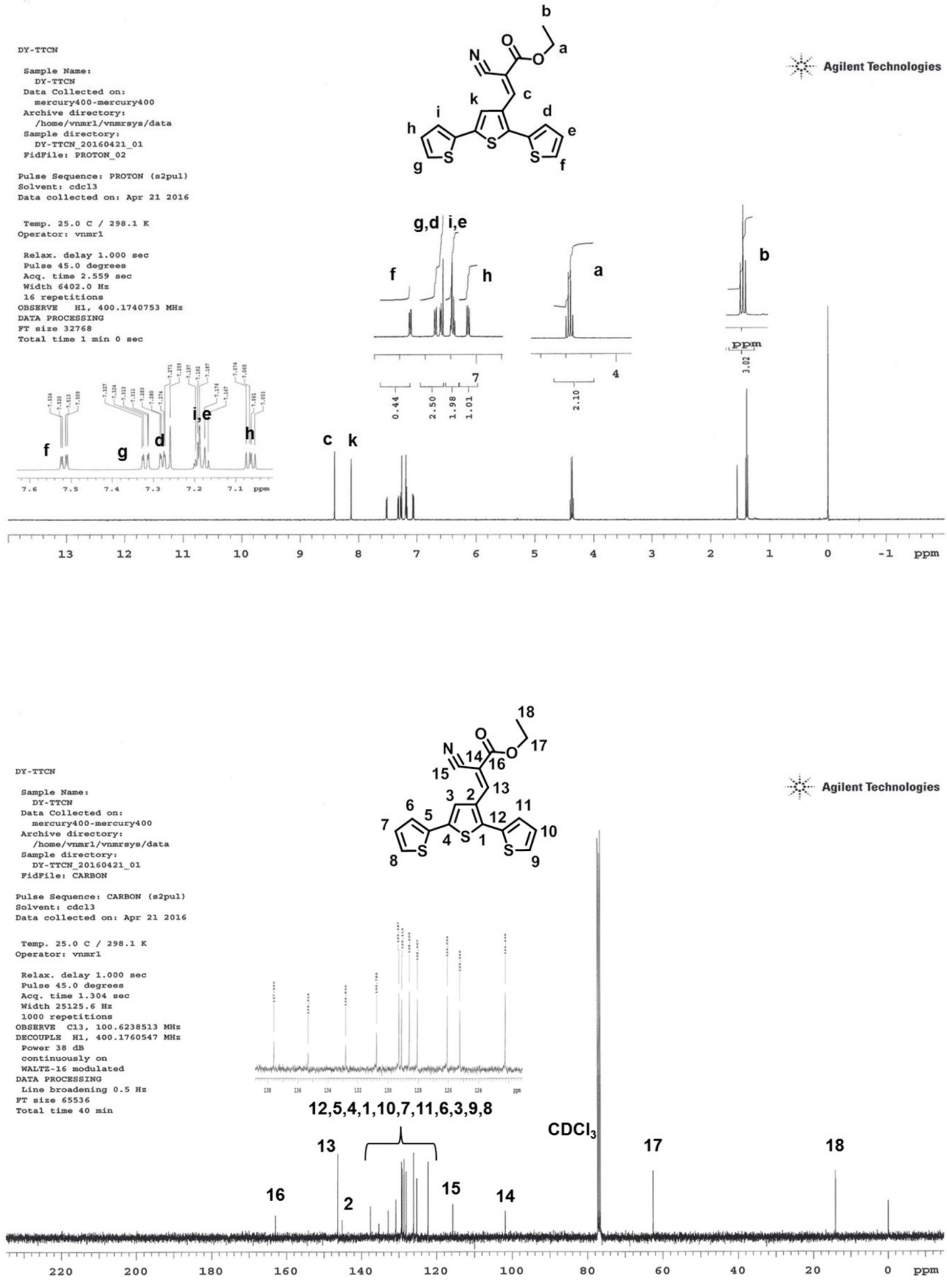


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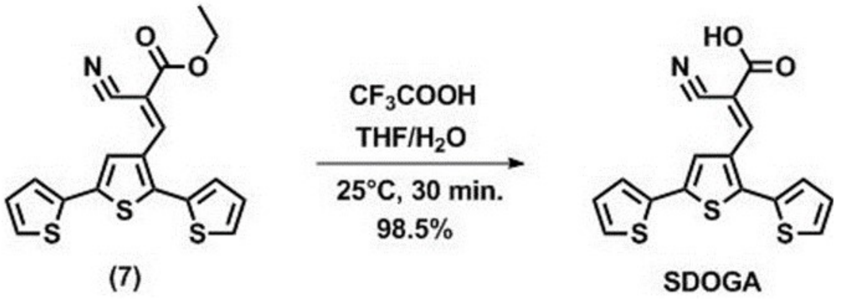
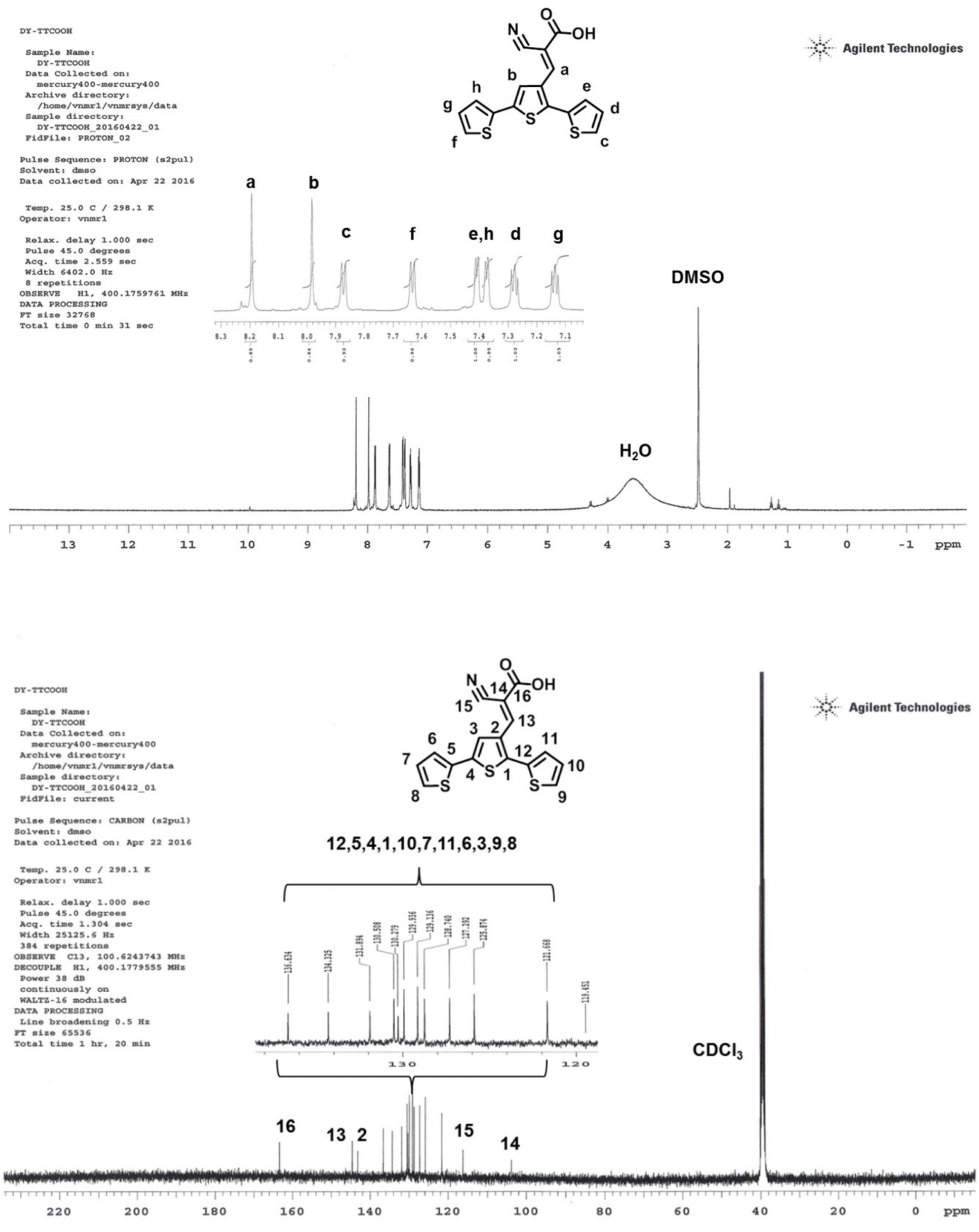
Fig. S2. ^{1}H NMR and ^{13}C NMR spectra ethyl 3-[(2,2′:5′,2″-terthiophene-3′-yl)]-2-cyanoacrylate (7)

❖ Synthesis of 3-[(2,2′:5′,2″-terthiophen-3′-yl)]-2-cyanoacrylic acid (SDOGA)



General procedure: In a 50 mL one-necked round-bottom flask, trifluoroacetic acid (4 mL) was added to the suspension of ethyl 3-[(2,2′:5′,2″-terthiophene-3′-yl)]-2-cyanoacrylate (1.25 g, 3.36 mmol) (7) in tetrahydrofuran/water (20 mL, 1:1, v/v). The orange suspension was stirred at room temperature for 30 min. The precipitated solid was filtered and washed with cool HCl solution several times. The crude product was recrystallized from ethanol to afford target monomer. 3-[(2,2′:5′,2″-terthiophen-3′-yl)]-2-cyanoacrylic acid (SDOGA) was obtained as a burgundy solid (1.13 g, 3.30 mmol, 98.5%, mp > 195°C). ^{1}H NMR (400 MHz, CDCl$_3$) δ_H/ppm: 7.13 (dd, *J*=8.4 Hz and *J*=3.6 Hz, 1H, Th-H), 7.28 (dd, , *J*=8.2 Hz and *J*=3.6 Hz, 1H, Th-H), 7.37 (d, *J*= 3.6 Hz, 1H, Th-H), 7.63 (d, *J*= 4.4 Hz, 1H, Th-H), 7.87 (d, *J*= 4.4 Hz, 1H, Th-H), 7.98 ppm (s, 1H, Th-H), 8.2 (t, 1H, -CH=C-). ^{13}C NMR (400 MHz, CDCl$_3$) δ_C/ppm: 103.9 (-CH=C-), 116.2 (-CN), 121.7 (Th-C), 125.9 (Th-C), 127.3 (Th-C), 128.7 (Th-C), 129.1 (Th-C), 129.9 (Th-C), 130.3 (Th-C), 130.5 (Th-C), 131.9 (Th-C), 134.3 (Th-C), 136.6 (Th-C), 143.3 (Th-C), 144.6 (-CH=C-), 163.4 (carboxylic acid –C=O). (EI) m/z (%) calcd for $C_{16}H_9NO_2S_3$: 343.4; found: 343 (M+, 95), 297 (90), 264.4 (35), 251.6 (7), 209.7 (5), 170.1 (4), 126.9 (8), 113.2 (2), 68.6 (5). FTIR (ATR) v_{max}/cm^{-1} 3100-2472 (w, b, carboxylic acid –OH strecthing), 3101, 3070 (w, aromatic C-H strecthing), 2218 (m, -CN strecthing), 1672 (s, carboxylic acid –C=O strecthing), 1554, 1502 (m, aromatic –C=C- strecthing), 1273, 1242, 1224 (m, -C-O- strecthing). Elemental analysis: anal. cald for $C_{16}H_9NO_2S_3$ (343.4): C 55.95 H 2.64 N 4.08; found: C 55.64 H 2.53 N 3.96**.**



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DY-TTCOOH

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DATA PROCESSING
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FT size 65536
Total time 1 hr, 20 min
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Fig. S3. ^{1}H NMR and ^{13}C NMR spectra of 3-[(2,2′:5′,2″-terthiophen-3′-yl)]-2-cyanoacrylic acid (SDOGA)

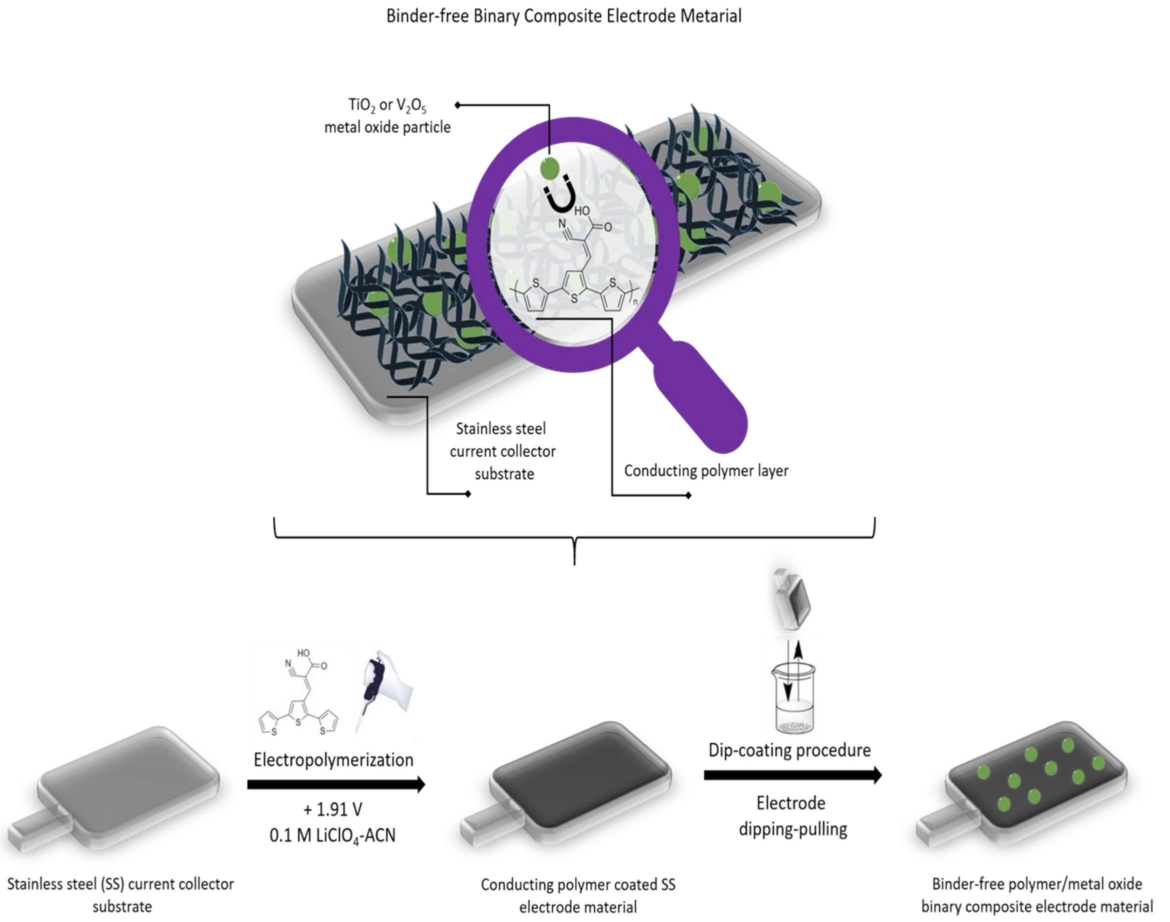

Fig. S4. Schematic fabrication procedure of the binder-free binary composite electrode material

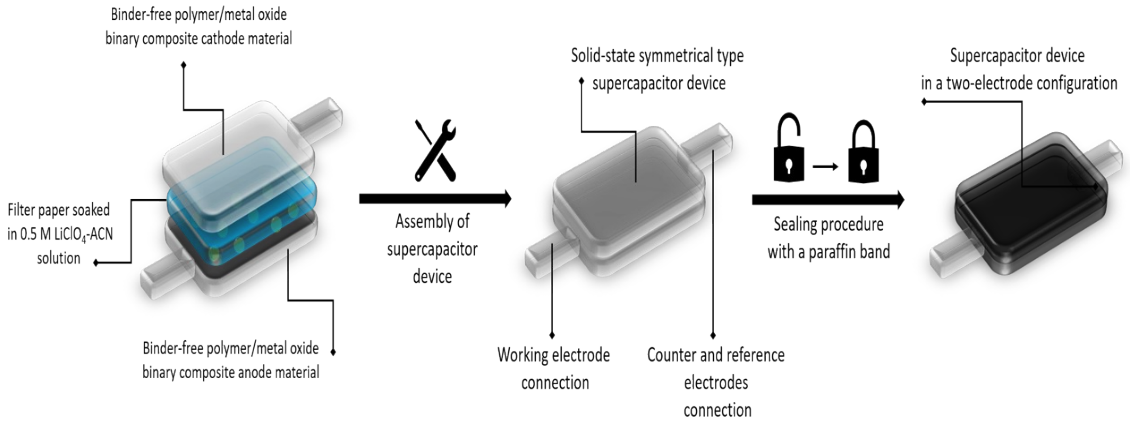

Fig. S5. Schematic representation for the assembly procedure of solid-state symmetrical type supercapacitor device

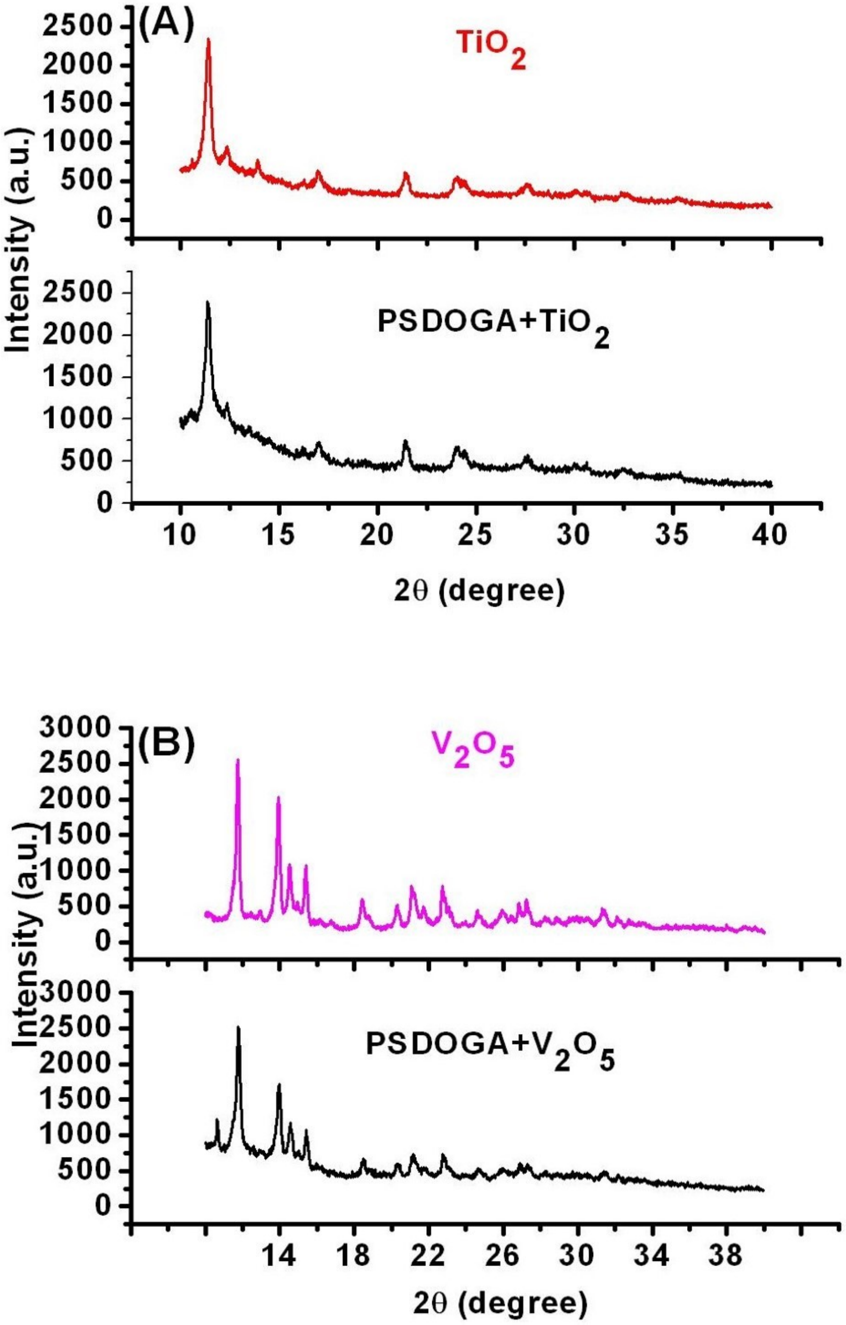

Fig. S6. XRD patterns of (a) PSDOGA/TiO_2 and (b) PSDOGA/V_2O_5 binder-free binary composite materials

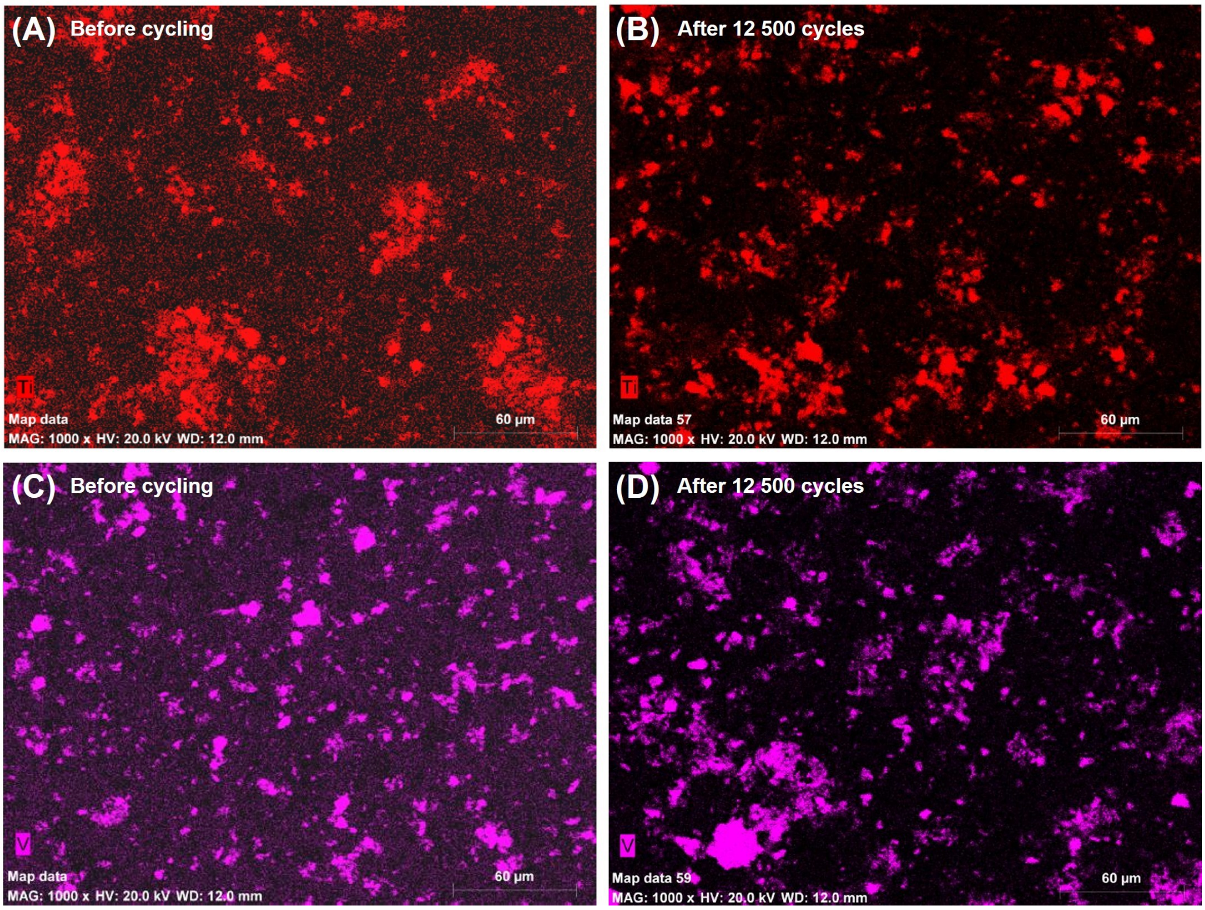

Fig. S7. SEM-EDX elemental mapping images of (a) PSDOGA/TiO_2 composite electrode before cycling, (b) PSDOGA/TiO_2 composite electrode after 12 500 charge/discharge cycles, (c) PSDOGA/V_2O_5 composite electrode before cycling and (d) PSDOGA/V_2O_5 composite electrode after 12 500 charge/discharge cycles