

Small Molecular Thienoquinoidal Dyes as Electron Donors for Solution Processable Organic Photovoltaic Cells

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Methods

Device fabrication: OPVs with a typical configuration of ITO/PEDOT:PSS/PC₇₁BM: QT-2 or QT-3/Ca/Al. All devices were fabricated on commercial indium-tin oxide (ITO) coated glass. Before use, the glass was pre-cleaned with deionized water, CMOS grade acetone and isopropanol in turn for 15 min. The organic residues were further removed by treating with UV-ozone for 1 h. Then the ITO glass was modified by spin-coating PEDOT: PSS (poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) layer, 30 nm), dried on a hotplate at 150 °C for 15 min, and then transferred to a N₂ glove box for the remainder of the fabrication and measurement. A mixed chlorobenzene solution (20 mg/ml) of donor (QT-2 or QT-3) and acceptor (PC₇₁BM) with a different weight ratio was spin-coated on the substrate. After the spin coating, the sample was kept at RT for two hours, and then dried at 90 °C for 10 min. Finally, Ca (20 nm) and Al (80 nm) electrode was then subsequently thermally evaporated on the active layer under the vacuum of 1×10^{-6} Torr. The active area of the device was 0.06 cm², and the thickness of the active films was ~60 nm for both the devices.

Photovoltaic characterization: The devices were characterized in nitrogen atmosphere under the illumination of simulated AM 1.5 G, 100 mW cm⁻² using a xenon-lamp-based solar simulator. The current-voltage (*I-V*) measurement of the devices was conducted on a computer-controlled Keithley 2400 Source Measure Unit. The external quantum efficiency (*EQE*) spectra for the devices were performed using a commercial setup (*PV-25 DYE, JASCO*). A 300 W Xenon lamp was employed as light source for generation of a monochromatic beam. Calibrations were performed

with a standard silicon photodiode. EQE is defined by $EQE(\lambda) = hcJ_{sc}/e\phi\lambda$, where h is Planck's constant, c is the speed of light in a vacuum, e is the electronic charge, λ is the wavelength in meters (m), J_{sc} is the short-circuit photocurrent density ($A\ m^{-2}$), and ϕ is the incident radiation flux ($W\ m^{-2}$).

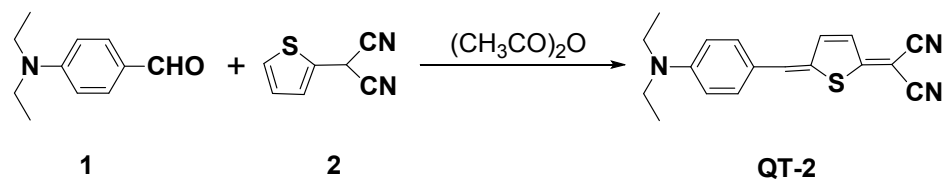
Measurements of the mobility by the space-charge limited current (SCLC)

Sample preparation and measurement were conducted according to the reported methods.¹

Synthesis

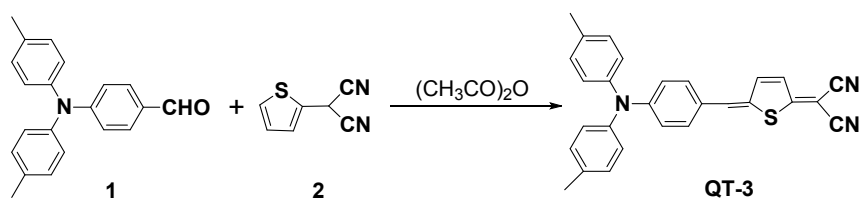
All chemicals and reagents were used as received from commercial sources without purification. Solvents for chemical synthesis were purified by distillation. All chemical reactions were carried out under an argon or nitrogen atmosphere.

1. Synthesis of QT-2:

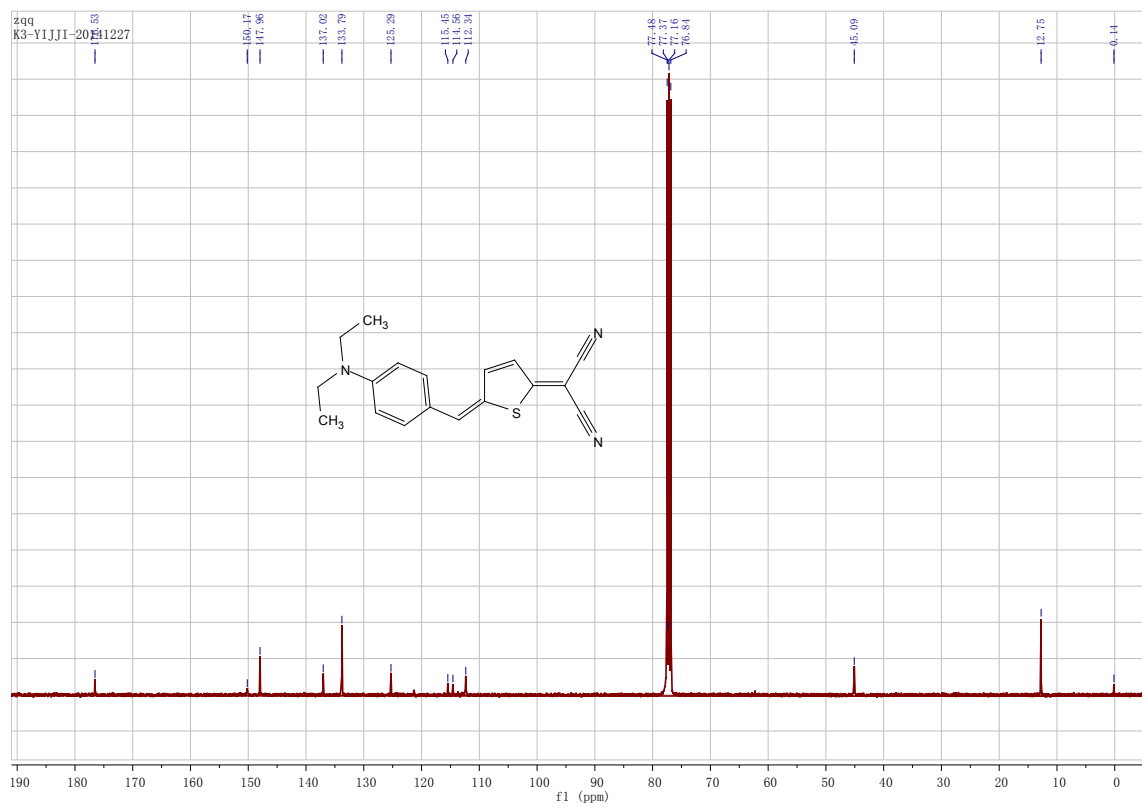
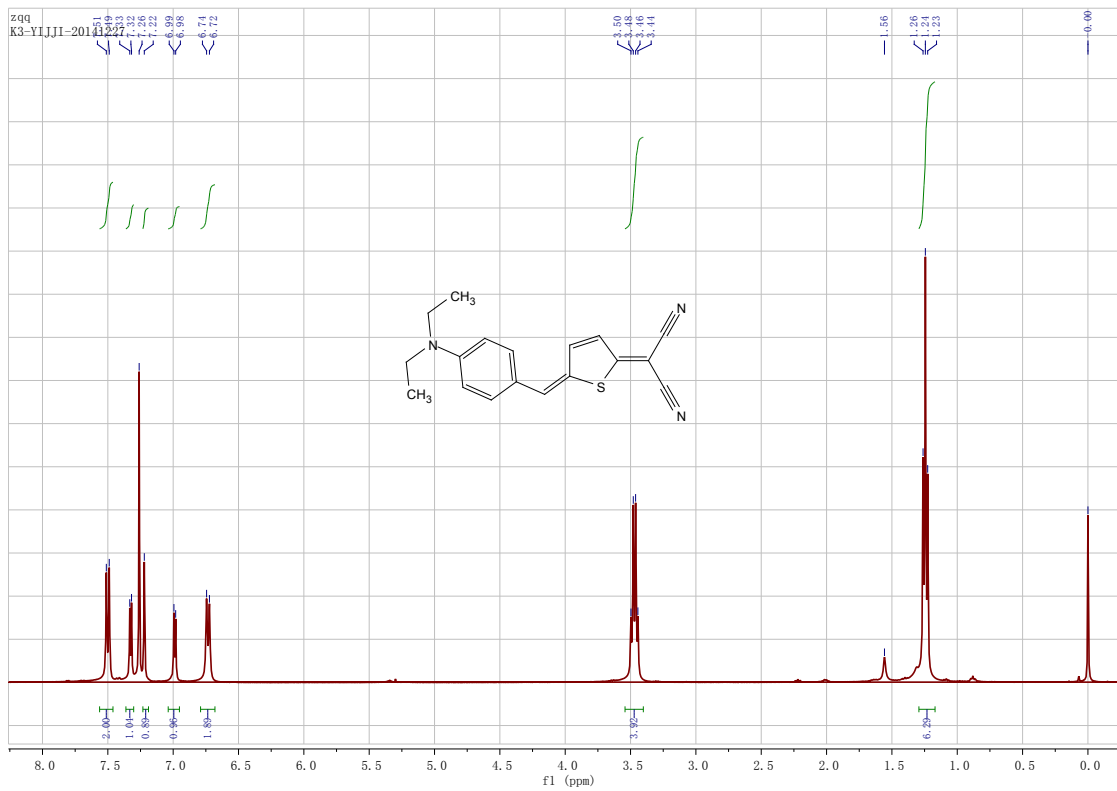


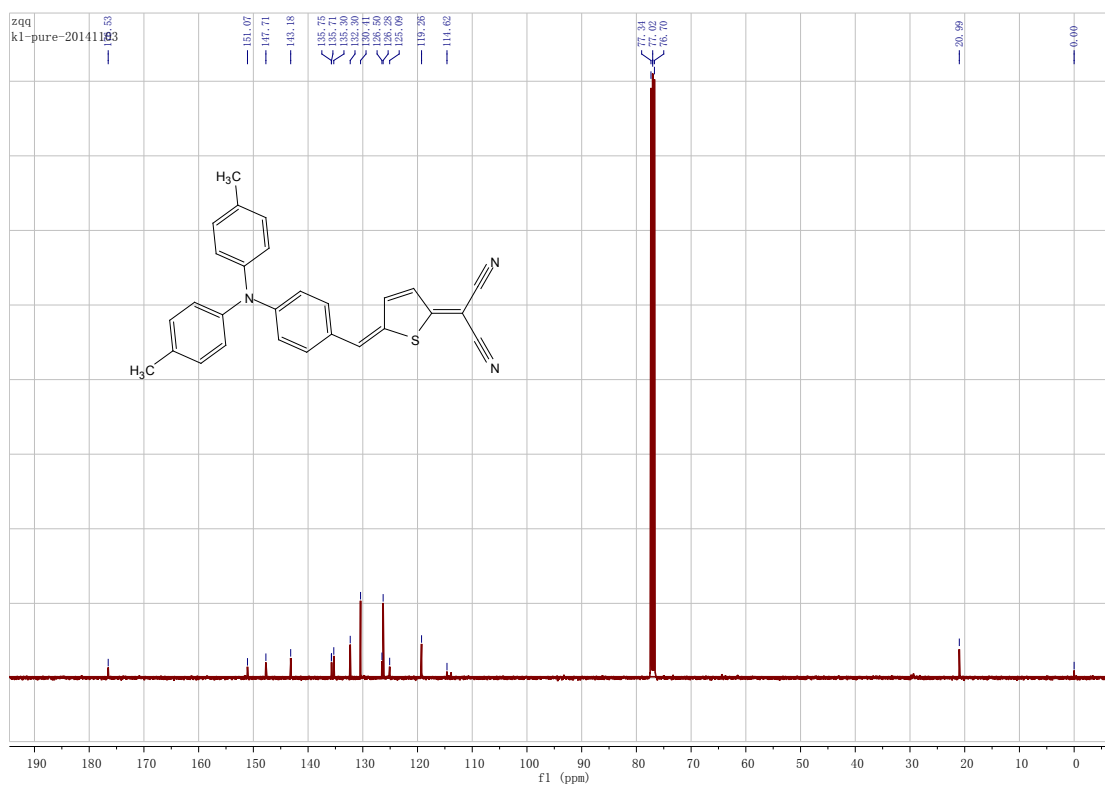
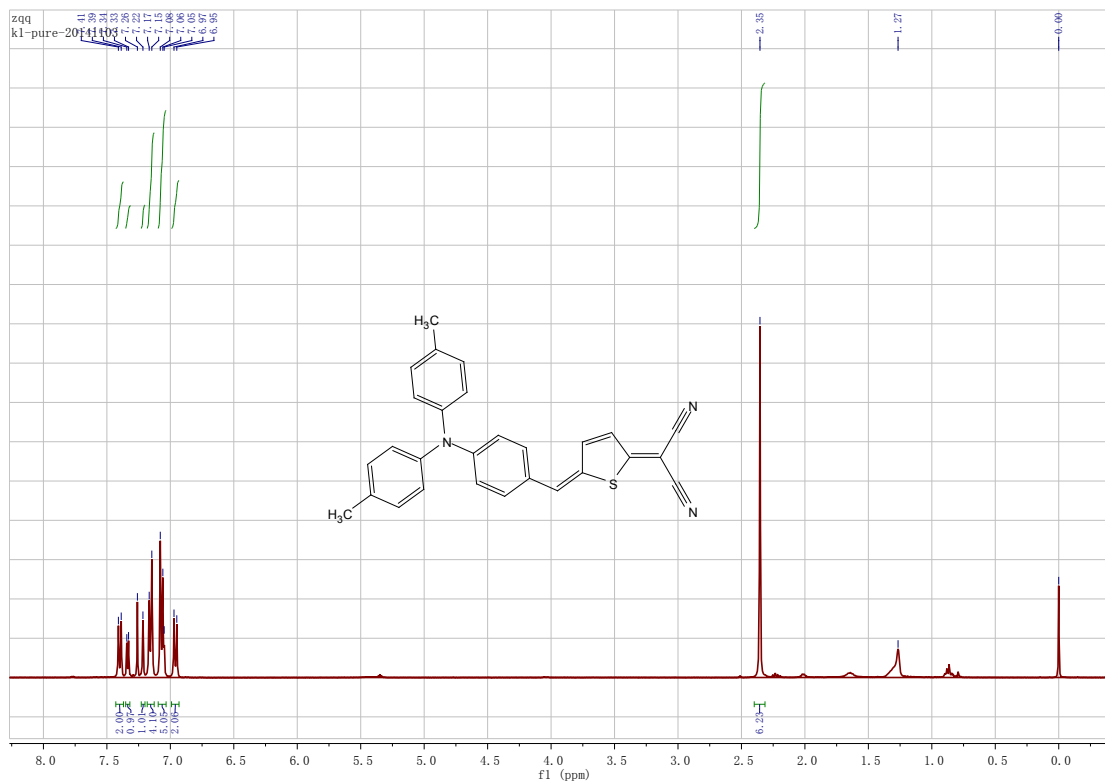
To a 100 ml three-necked round bottom flask were added 4-(diethylamino)benzaldehyde (212 mg, 1.2 mmol) and 2-(thiophen-2-yl)malononitrile² (148 mg, 1.0 mmol) in acetic anhydride (40 mL). The mixture was heated at 100 °C for 6 h under N₂ atmosphere. After cooled to room temperature, the mixture was removed under reduced pressure. The residue was dissolved in DCM (50 mL), washed with 10% NaHCO₃ (50 mL) and brine (50 mL), respectively, and the residue was purified by column chromatography on silica gel with dichloromethane–hexane (2:1) as the eluent yielding a dark blue solid (208 mg, 68%). Melting Point: 182.3 °C. ¹H NMR: (CDCl₃, 400 MHz): δ ppm 7.50 (d, $J=9.2$ Hz, 2H), 7.33 (d, $J=5.2$ Hz, 1H), 7.22 (s, 1H), 6.99 (d, $J=5.2$ Hz, 1H), 6.73 (d, $J=8.8$ Hz, 2H), 3.47 (q, $J=7.2$ Hz, 4H), 1.24 (t, $J=7.2$ Hz, 6H). ¹³C NMR (CDCl₃, 400 MHz): δ ppm 176.5, 150.1, 148.0, 137.0, 133.8, 125.3, 121.3, 115.4, 114.6, 112.3, 45.1, 12.7; HR-MALDI-MS (m/z): [M+Na] calcd for C₂₈H₂₁N₃S: 330.103783 found: 330.103539.

2. Synthesis of QT-3



To a 100 ml three-necked round bottom flask were added 4-(di-p-tolylamino)benzaldehyde (1000 mg, 3.3 mmol) and 2-(thiophen-2-yl)malononitrile (300 mg, 3.1 mmol) in acetic anhydride (20 mL). The mixture was heated at 100 °C for 6 h under N₂ atmosphere. After cooled to room temperature, the mixture was removed under reduced pressure. The residue was dissolved in DCM (50 mL), washed with 10% NaHCO₃ (50 mL) and brine (50 mL), respectively, and the residue was purified by column chromatography on silica gel with dichloromethane–hexane (2:1) as the eluent yielding a light green solid (785 mg, 55%). Melting Point: 171.5 °C. ¹H NMR: (CDCl₃, 400 MHz): δ ppm 7.40 (d, J=8.8 Hz, 2H), 7.34 (d, J=5.6 Hz, 1H), 7.22 (s, 1H), 7.16 (d, J=8.0 Hz, 4H), 7.06 (t, J= 8.0 Hz, 4.4 Hz, 5H), 6.96 (d, J=8.8 Hz, 2H); 2.35 (s, 6H). ¹³C NMR (CDCl₃, 400 MHz): δ ppm 176.5, 151.1, 147.7, 143.2, 135.7, 135.3, 132.3, 130.4, 126.5, 126.3, 125.1, 119.3, 114.6, 113.9, 64.4, 21.0; HR-MALDI-TOF -MS (m/z): [M]⁺calcd for C₂₈H₂₁N₃S: 431.145645 found: 431.145070.





References:

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- 2 S. Inoue, S. Mikami, K. Takimiya, T. Otsubo, Y. Aso, *Heterocycles*, **2007**, 71, 253.