

Supporting Information for

A Push-Pull Thienoquinoidal Chromophore for Highly Efficient P-Type Dye-Sensitized Solar Cells

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Experimental

General methodology All the chemicals were purchased from commercial sources and used without further purification, and all solvents were dried according to standard procedures. NMR spectra were recorded on a BRUKER AVANCE 400 MHz instruments. The residual solvent protons (^1H) or the solvent carbons (^{13}C) were used as internal standards. ^1H NMR data are presented as follows: chemical shift in ppm (δ) downfield from tetramethylsilane (multiplicity, coupling constant (Hz), integration). Mass spectra were measured on a Bruker Daltonics BIFLEX III MALDI-TOF or ESI-MS. The electrochemical cyclic voltammetry (CV) was performed using a CH Instruments electrochemical workstation (model 660A) in a $0.1 \text{ mol}\cdot\text{l}^{-1}$ tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) dichloromethane (DCM) solution with a scan speed at 0.1 V s^{-1} . A Pt wire and Ag/AgCl were used as the counter and reference electrodes, respectively. The potentials are quoted against the ferrocene internal standard. The absorption and emission spectrum were measured on Hitachi U-3010 UV-vis spectrophotometer and Horiba FluoroMax-4-NIR spectrophotometers, respectively.

Synthesis of dimethyl 4,4'-((4-((5-(dicyanomethylene)thiophen-2(5H)-ylidene)methyl)phenyl)azanediy)dibenzoate) (3): To a 100 ml three-necked round bottom flask were

added dimethyl 4,4'-((4-formylphenyl)azanediyl)dibenzoate¹ (492 mg, 1.2 mmol) and 2-(thiophen-2-yl)malononitrile² (298 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, and the residue was purified by column chromatography on silica gel with dichloromethane–hexane (2 : 1) as the eluent yielding a deep blue solid (407 mg, 62%). ¹H NMR: (CDCl₃, 400 MHz, ppm): δ 3.91 (s, 6H), 7.15 (m, 7H), 7.26 (s, 1H), 7.37 (d, J=5.6 Hz, 1H), 7.51 (d, J=8.8 Hz, 2H), 7.98 (d, J=8.8 Hz, 4H). ¹³C NMR (CDCl₃, 400 MHz, ppm): δ 52.1, 53.4, 67.0, 113.1, 113.9, 124.1, 124.3, 126.1, 128.1, 129.1, 131.3, 132.0, 134.2, 138.1, 147.5, 149.9, 166.3, 176.4. MS (MALDI-TOF) m/z ([M+H]⁺): calcd for C₃₀H₂₁N₃O₄S:520.1, found 520.2.

Synthesis of 4,4'-((4-((5-(dicyanomethylene)thiophen-2(5H)-ylidene)methyl)phenyl)azanediyl)dibenzoic acid (4): **3** (198 mg, 0.4 mmol) was dissolved in a tetrahydrofuran (40 ml)/methanol (2 ml) mixture in a 100 ml round bottom flask. To the solution was slowly added sodium hydroxide aqueous solution (1.5 N, 5ml) with stirring. After the addition, the mixture was heated at 40 °C for 2 h. After cooled to room temperature, the mixture was adjusted to the pH=2 with 1N hydrochloride acid. The crude product was filtered, and further purified by silica gel column chromatography using dichloromethane and methanol (1:1), yielding the purplish blue product (150 mg, 67%). ¹H NMR (400 MHz, MeOD-d₄, ppm): δ 7.18 (m, 7H), 7.60 (d, J=3.2 Hz, 1H), 7.63 (s, 1H), 7.69 (d, J=5.2 Hz, 1H), 7.98 (d, J=8.4 Hz, 4H). ¹³C NMR (CDCl₃, 400 MHz, ppm): δ 114.4, 115.3, 123.9, 125.6, 128.3, 129.5, 129.9, 130.9, 132.2, 133.4, 137.2, 138.5, 149.9, 150.5, 151.1, 178.3. HRMS-ESI (negative mode) m/z ([M-H]⁻): calcd for C₂₈H₁₇N₃O₄S 490.086373, found 490.086701.

Solar Cell Fabrication A precursor solutions of NiO were prepared by dissolving anhydrous NiCl₂ (1 g) and the triblock co-polymer F88 (1 g) into a mixture of deionized water (3 g) and ethanol (6 g). The solution was left for 3 days at room temperature, and then filtered. The filtrate was deposited on an FTO glass substrate by

doctor blade method using Scotch tape) as a spacer to adjust the film thickness. The film was dried for 20 min at room temperature, and then calcined in air at 450 °C for 30 min. After cooling to room temperature, the substrate was immersed in a dye bath containing 0.3 mM **QT-1** in acetonitrile, and kept for 24 h at room temperature. The dyed electrodes were then rinsed with the mixed solvent to remove excess dye. A platinum-coated FTO-glass as a counter electrode was used with two holes drilled on its opposite sides. The two electrodes were sealed together with a 25 μm thick thermoplastic Surlyn frame. An electrolyte solution was then introduced through one of the two holes in the counter electrode, and the holes were sealed with the thermoplastic Surlyn. Two different electrolytes were employed. The I⁻/I₃⁻ based electrolyte (**EL1**) is composed of 0.68 M dimethyl imidazolium iodide, 0.03 M iodine, 0.10 M LiI, 0.05 M guanidinium thiocyanate, and 0.40 M *tert*-butylpyridine in the mixture of acetonitrile and valeronitrile (85:15, *v/v*), and the Co²⁺/Co³⁺ based liquid electrolyte (**EL2**) contains 0.1 M [Co(L)₃](PF₆)₃ and 0.1 M [Co(L)₂](PF₆)₂ in acetonitrile, where L represents 2-(1H-pyrazol-1-yl)pyridine). All the devices were prepared with a photoactive area of about 0.3 cm², and a metal mask of 0.165 cm² was covered on the device for photovoltaic property measurements.

Photovoltaic Characterization The photocurrent-voltage (*J-V*) characteristics were recorded at room temperature using a computer-controlled Keithley 2400 source meter under air mass (*AM*) 1.5 simulated illumination (100 mW cm⁻², Oriel, 67005), and each data was averaged by three parallel samples. The external quantum efficiency (*EQE*) spectra for solar cells 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).

1. Liu, B.; Zhang, Q.; Ding, H.; Hu, G.; Du, Y.; Wang, C.; Wu, J.; Li, S.; Zhou, H.; Yang, J.; Tian, Y. *Dyes Pigments* **2012**, 95 149-160.
2. Inoue, S.; Mikami, S.; Takimiya, K.; Otsubo, T.; Aso, Y. *Heterocycles*, **2007**, 71, 253-268.

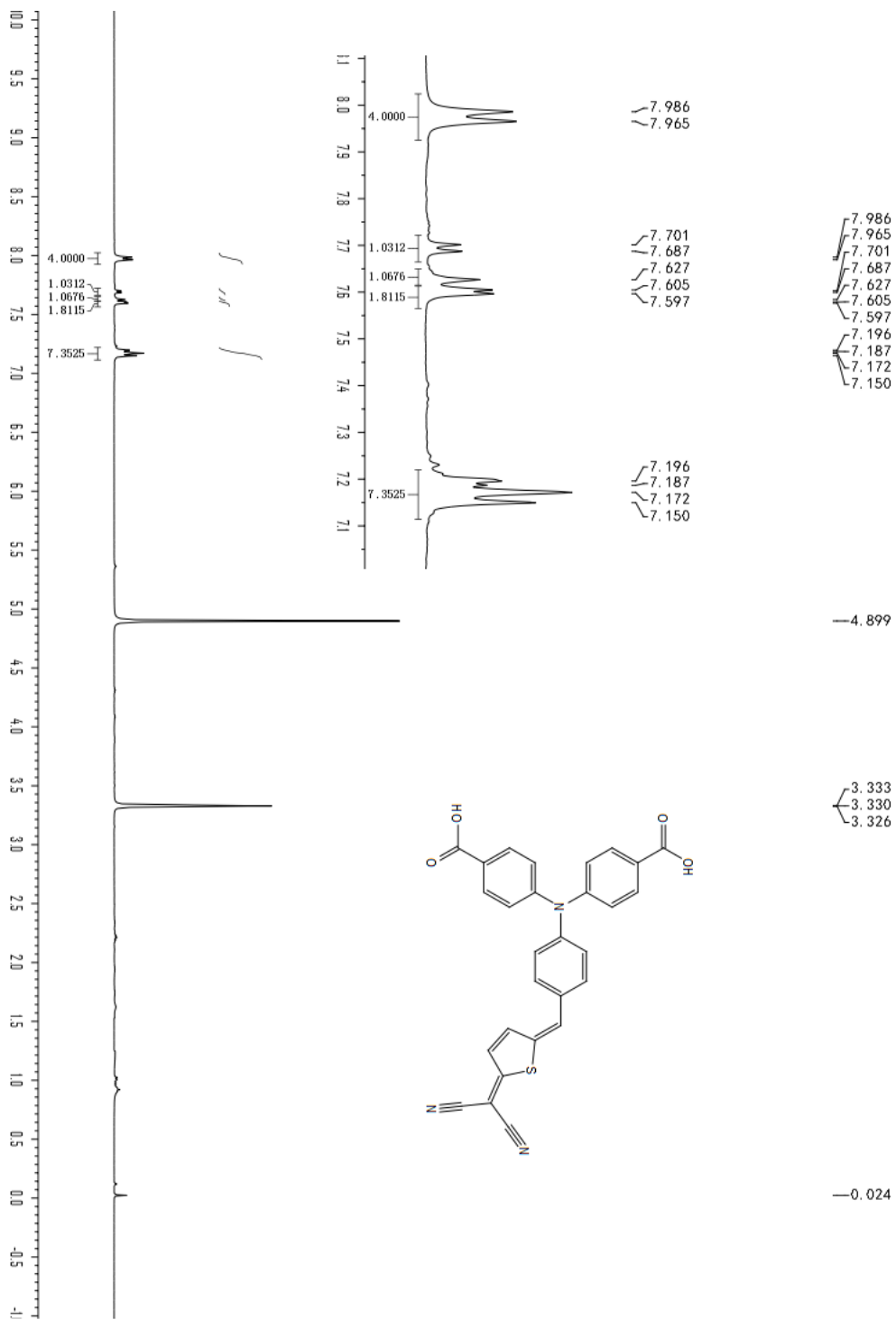


Fig. S1 ^1H NMR spectrum of QT-1.

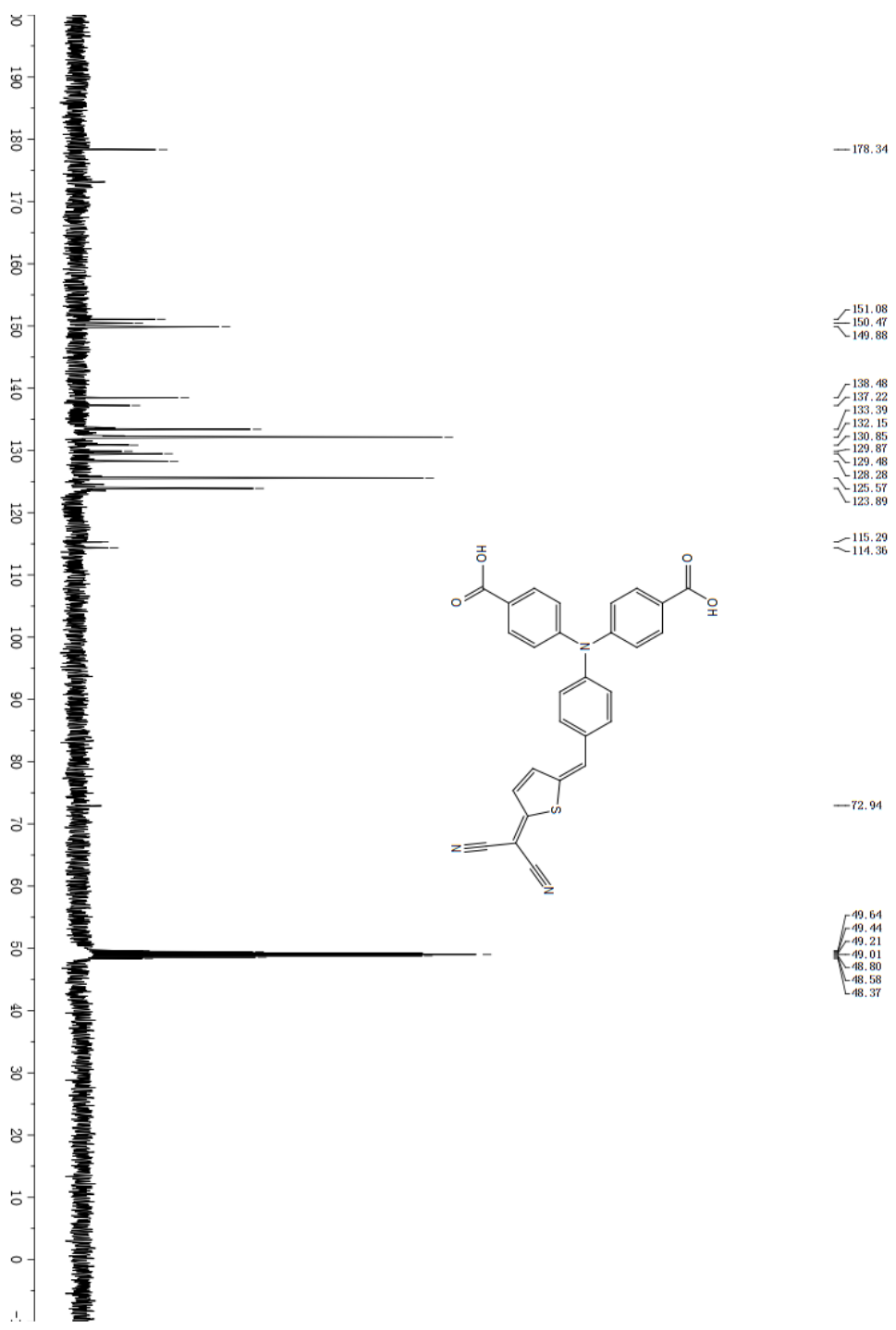


Fig. S2 ¹³C NMR spectrum of QT-1.

