Supporting information

Ambipolar organic field-effect transistors based on solution-processed single crystal microwires of a quinoidal oligothiophene derivative

Jean-Charles Ribierre,*[abc] Li Zhao,[a] Seiichi Furukawa,[a] Tomoka Kikitsu,[d] Daishi Inoue,[d] Atsuya Muranaka,[b] Kazuto Takaishi,[b] Tsuyoshi Muto,[b] Shinya Matsumoto,[e] Daisuke Hashizume,[d] Masanobu Uchiyama,[b,f] Pascal André,[b,c] Chihaya Adachi,*[a] and Tetsuya Aoyama*[b]

Experimental Procedure

Preparation of the single crystal microwires:
The QQT(CN)4 molecules, synthesized following an improved method previously described in the literature,[1] were dissolved in chloroform at 10 mg/mL. The solution was then drop-casted on top a substrate and left for about 2-3 hours in chloroform saturated atmosphere to ensure a slow evaporation of the solvent. Using this method, a network of single crystal microwires of QQT(CN)4 is formed on the substrates via self-assembly occurring through π−π stacking, as displayed in Figure S1. The samples were then sonicated for 2 seconds in hexane, which is a very poor solvent for QQT(CN)4. The obtained suspension of microwires could then be drop-casted with the desired density of microwires on the surface of interest being controlled by the concentration of the microwires in the hexane suspension and the amount of suspension deposited onto the substrate.

Characterization of the microwires:
The morphological and structural properties of the single crystal microwires were examined using a polarized optical microscope (Nikon, ECLIPSE E600 POL), an optical microscope (Olympus, model OLS4000), a scanning electron microscope (SEM; JEOL, JSM-6330F) with an accelerating voltage of 3 kV, and a transmission electron microscope (TEM; JEOL, JEM-2100F) with an accelerating voltage of 200 kV. For the TEM measurements, the microwires in hexane suspension were deposited onto a micro-grid and air dried. For the SEM measurements, the microwires in hexane suspension were deposited onto a silicon substrate. The microwires were dried in the air, and then coated with osmium (Filgen, OPC80N). XRD measurements were carried out with an X-ray diffractometer (Rigaku, SmartLab) using Cu *K*α radiation. For the in-plane XRD measurements, the incident beam was fixed at 0.2 degrees. The microwire sample was prepared by drop-casting the QQT(CN)4 chloroform solution onto a fused silica plate in chloroform saturated atmosphere.

Fabrication and characterization of OFETs based on individual QQT(CN)4 single crystal microwires:
The bottom-gate top-contact OFETs were fabricated onto silicon wafer substrates with a thermally grown 300 nm thick SiO_2 layer. The QQT(CN)4 single crystal microwires were drop-casted on the substrates from an hexane suspension. Gold s/d electrodes with a thickness of 250 nm were then deposited on top of the microwires by thermal evaporation through shadow mask. A semiconductor device analyzer (Agilent Technologies, B1500A) and a probe station were used to measure the electrical characteristics of the devices. The dimensions of the individual QQT(CN)4 microwires were determined before the electrical measurements, using the optical microscope mentioned above. This approach certainly leaves room for improvement in terms, for instance, of controlling accurately the micro-positioning of each microwire. It is noticeable that the random distribution and orientation of the microwires herein reported on is a fair limitation to future applications relying on the proposed organic ambipolar microwire based technology.

However, addressing these issues go beyond the scope of the present work, which instead focus on the preparation method and the investigation the microwires intrinsic electronic properties. Further efforts are nonetheless on-going to reduce the size distribution of the microwires through temperature control and addition of co-vapor solvents during the molecular assembly process. Similarly, to better control the device performances, it might be possible to orient the microwires by drop-casting them on top of biased electrodes and to use self-assembled monolayer to locally treat the gate dielectric of the OFETs and to preferentially position the microwires.

Quantum chemical calculations:
The semi-empirical Hartree-Fock-based ZINDO/s method was used to determine the electronic structure of QQT(CN)4 in 3-dimensional molecular clusters in configurations found in the crystalline structure of QQT(CN)4 at room temperature. These calculations were carried out using the Gaussian 09 suites of programs,[2] following the method already detailed in previous studies.[3,4]

1 H. Higuchi, T. Nakayama, H. Koyama, J. Ojima, T. Wada and H. Sasabe, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 2363.

2 M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E.Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski and D.J. Fox, *Gaussian 09*, revision C.01; Gaussian, Inc.: Wallingford, CT, 2010.

3 J. Cornil, J.P. Calbert, D. Beljonne, R. Silbey and J.L. Bredas, *Adv. Mater.,* 2000, **12**, 978.

4 J.C. Ribierre, Y. Yokota, M. Sato, A. Ishizuka, T. Tanaka, S. Watanabe, M. Matsumoto, A. Muranaka, S. Matsumoto, M. Uchiyama, T. Aoyama, *RSC Adv*. 2014, **4**, 36729.

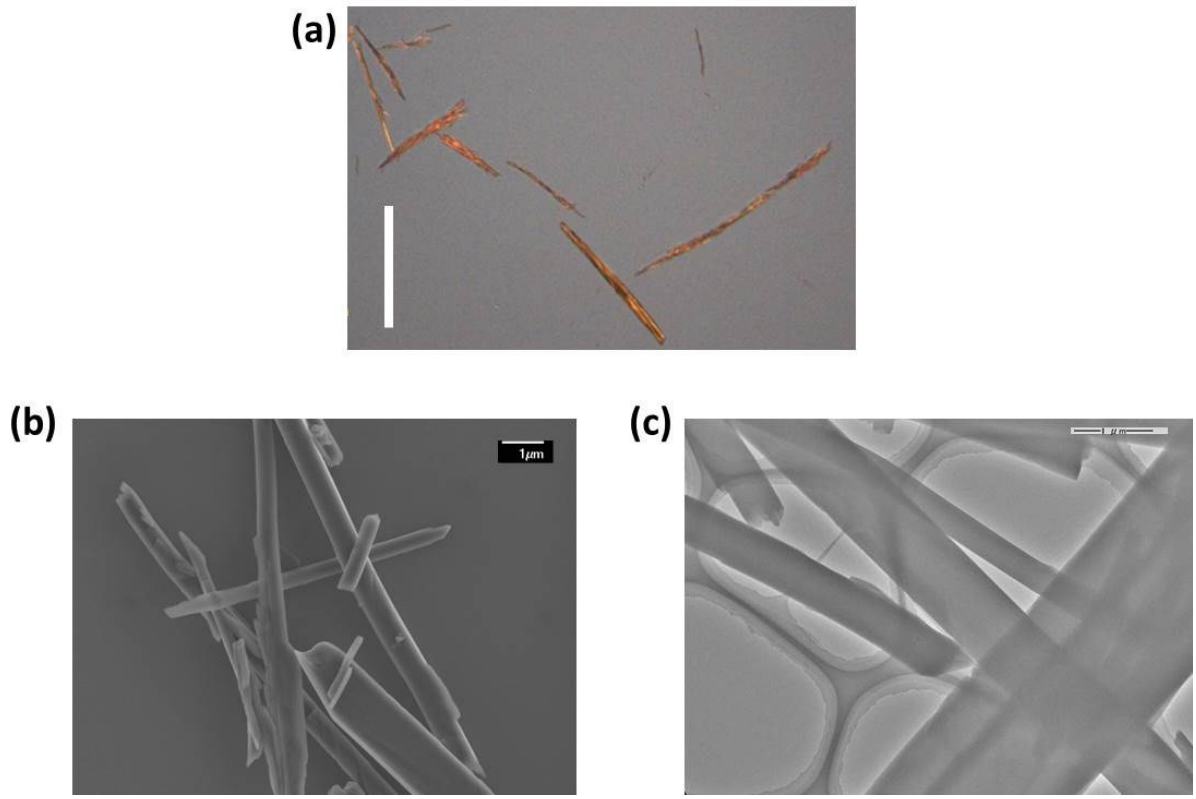


Figure S1. (a) Optical microscope image of QQT(CN)4 single crystal microwires. The scale bar is 100 μm. (b) SEM image of solution-processed QQT(CN)4 single crystalline microwires. The scale bar is 1 μm. (c) TEM image of solution-processed QQT(CN)4 single crystal microwires. The scale bar is 1 μm. These SEM and TEM images show that the width of the QQT(CN)4 single crystal structures can, in some cases, be shorter than 1 μm.

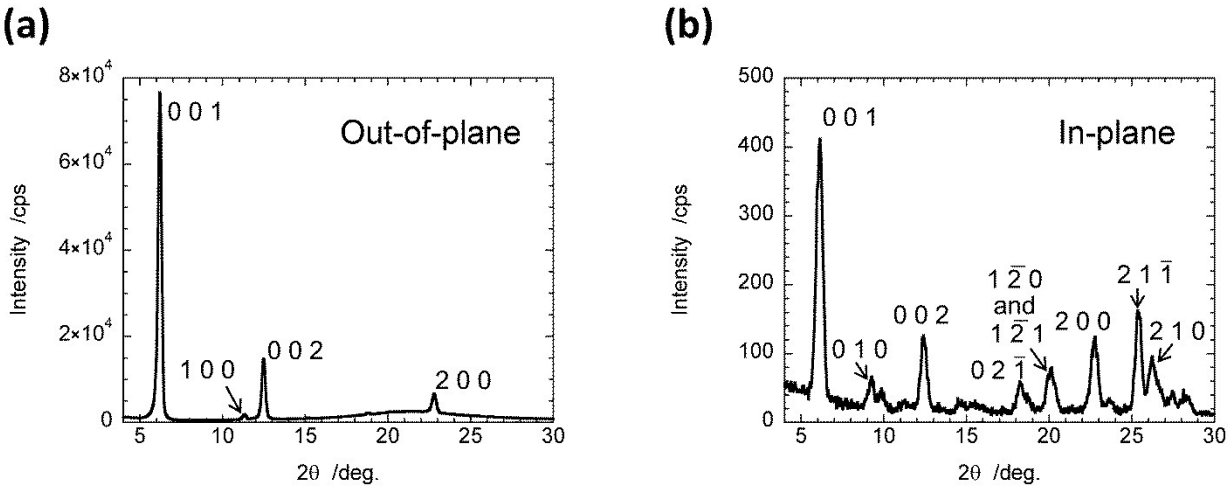
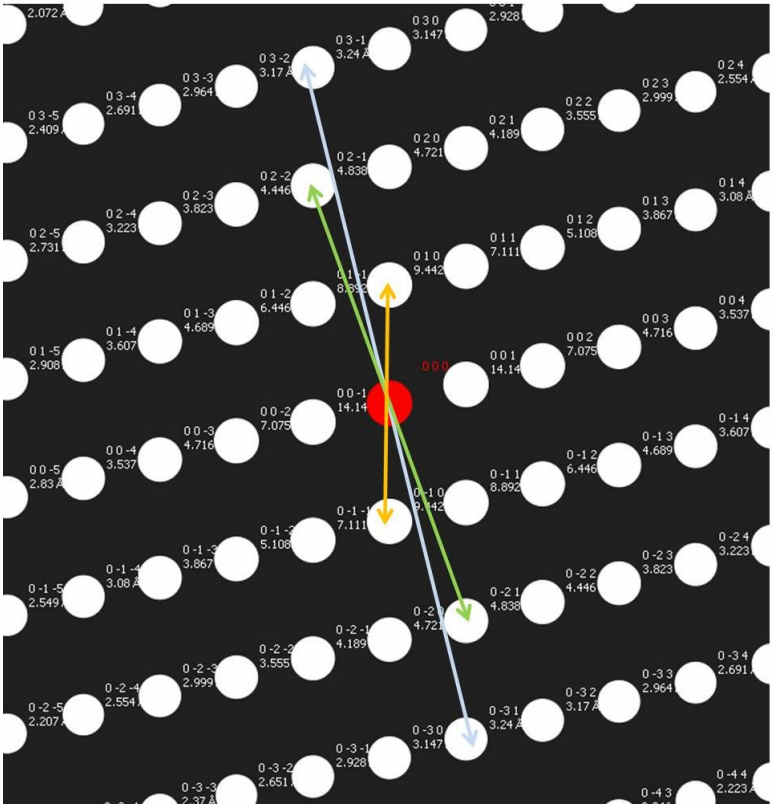


Figure S2. (a) Out-of-plane and (b) in-plane X-ray diffraction patterns of the QQT(CN)4 microwires prepared on fused silica.



Crystalline structure

triclinic

a = 8.04361

b = 9.83650

c = 14.74575

α = 102.0657

β = 98.8948

γ = 98.7524

Calculated d-spacing

0 1 0 : 9.442 Å

0 2 −1: 4.838 Å

0 3 −1: 3.240 Å

d-values measured from TEM diffraction

d = 9.4 Å

d = 4.9 Å

d = 3.2 Å

Figure S3. Crystal data and determination of the d-spacing values in the QQT(CN)4 microwire using the software Recipro ver4.24 (http://pmsl.planet.sci.kobe-u.ac.jp/~seto/?page_id=19&lang=en). By comparing the d values calculated from the powder X-ray diffraction data with those obtained from TEM diffraction experiments, the orange arrow shown in Figure 2a can be assigned to the d-spacing for the (0 1 0) face. Accordingly, because the green arrow in Figure 2a is parallel to the long axis direction of the single crystal microwire, the (0 2 -1) face is found to be perpendicular to the long axis. In addition, the blue arrow in Figure 2a could be assigned to the d-spacing for the (0 3 -1) face.

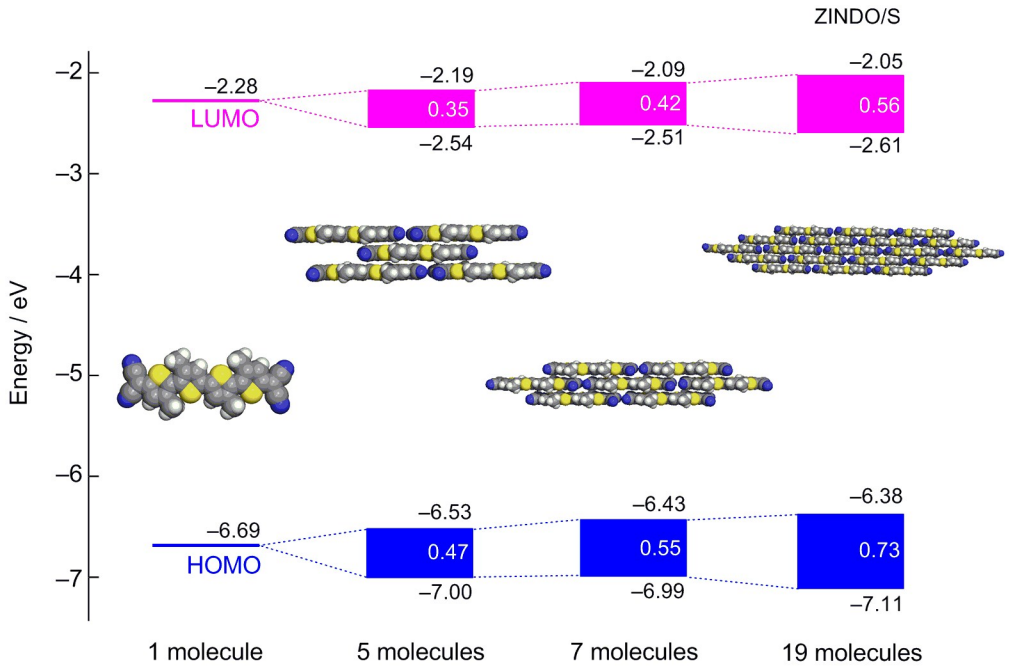


Figure S4. HOMO and LUMO energies and splittings calculated in crystalline QQT(CN)4 molecular clusters of different sizes. Note that the alkyl side-chains were replaced by methyl groups to reduce the computational cost.

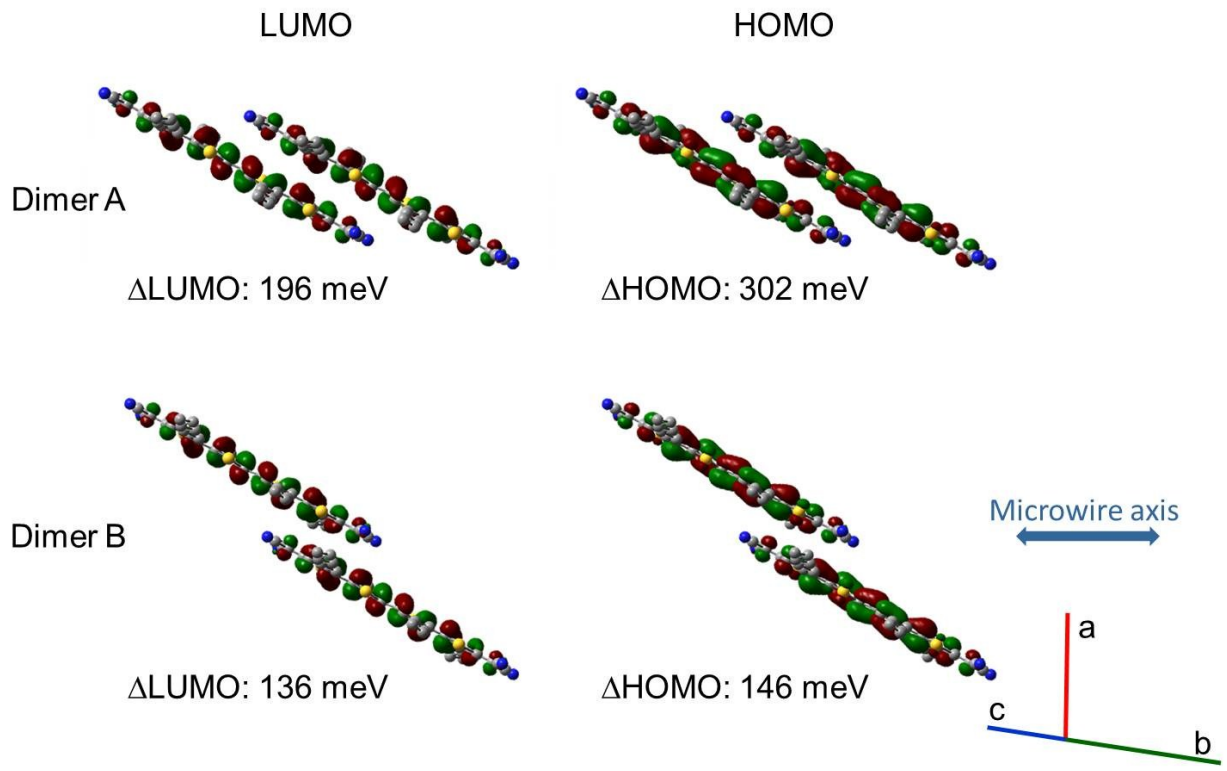


Figure S5. LUMO and HOMO splittings calculated in the two types of dimers, noted A and B, present in the crystalline structure of the QQT(CN)4 microwires.

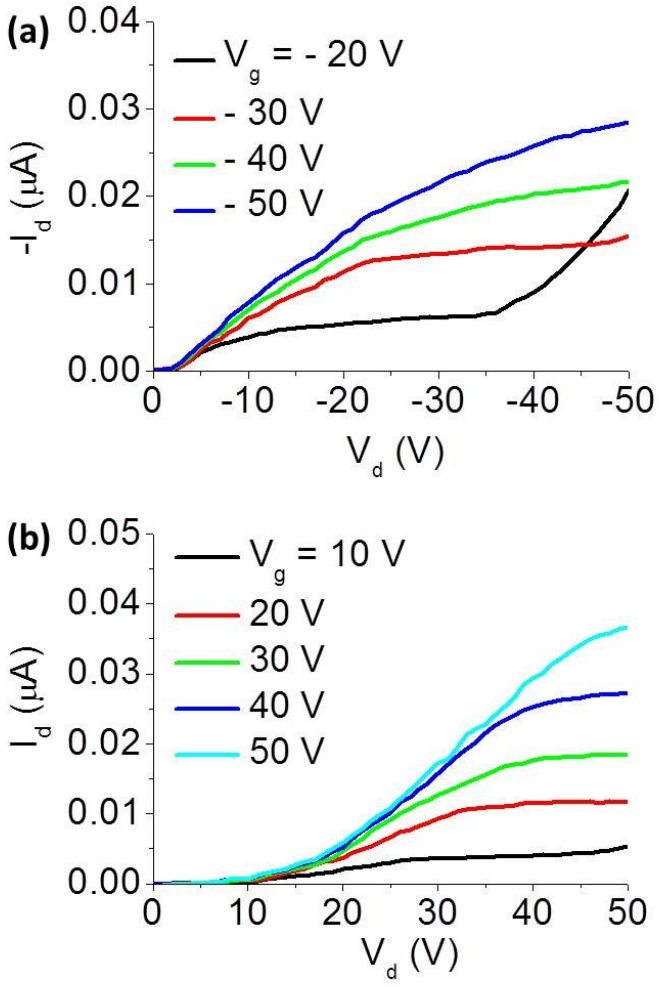


Figure S6. Output characteristics of a representative QQT(CN)4 single crystal microwire OFET measured at (a) negative and (b) positive applied voltages.

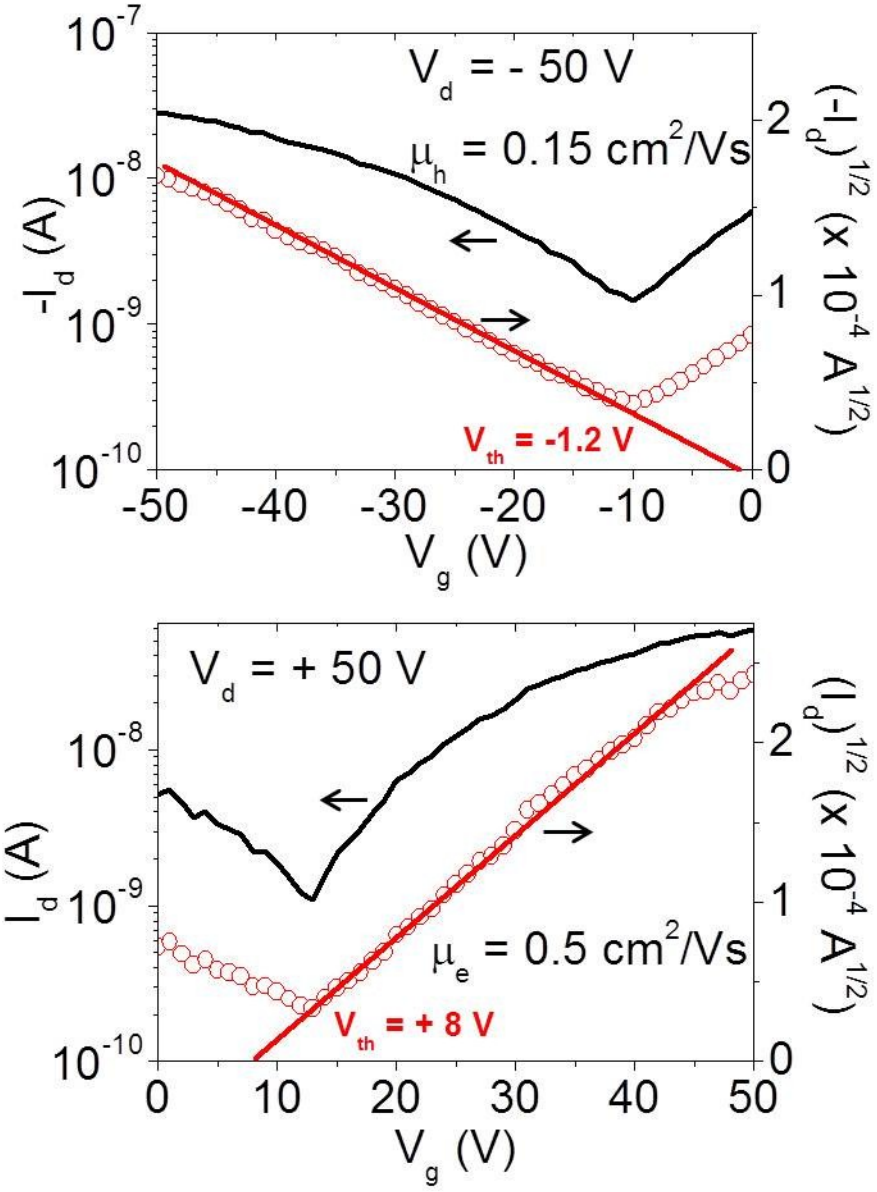


Figure S7. Transfer characteristics of the ambipolar QQT(CN)4 single crystal microwire OFET with the highest electron mobility. The device was based on a bottom-gate, top-contact architecture with a 300 nm SiO_2 dielectric layer and Au s/d electrodes. The channel width and length of the device were 1 and 67 μm, respectively.

Table 1
Electron mobility (μ_e), hole mobility (μ_h), ratio between the electron and hole mobilities (μ_e /μ_h) as well as the microwire width (w_m) and the channel length (l_m) in the OFETs fabricated in this work.

Device #	μ_h (cm^2/Vs)	$V_{th,h}$ (V)	μ_e (cm^2/Vs)	$V_{th,e}$ (V)	μ_e /μ_h	w_m (μm)	l_m (μm)
1	0.15	-1.2	0.5	+ 8	3.3	1.5	67
2	0.4	-18.8	0.15	-2.2	0.37	2	28
3	0.35	-8.1	0.3	+3.6	0.86	1.5	41
4	0.08	-22.1	0.35	-6.9	4.38	3	59
5	0.1	-3.8	0.4	+6.4	4	1	33
6	0.35	-11.1	0.25	+4.3	0.71	1.5	48
7	0.2	-5.8	0.35	+15.2	1.75	1	63
8	0.3	-14.3	0.35	-4.8	1.17	2	50
9	0.35	-24.2	0.4	-5.5	1.14	2.5	53
10	0.35	-16.4	0.3	-3.4	0.86	3	38
11	0.25	-31.8	0.4	-8.4	1.6	2.5	46
12	0.15	-7.6	0.45	+19.6	3	1.5	39