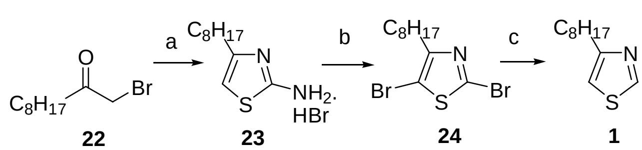
Supplementary Information

The synthetic approach to head-to-tail coupled quaterthiazole **9** commenced with an improved preparation of 4-octylthiazole **1**. The one-step, direct synthesis of **1** from α-bromoketone **22** and thioformamide was hampered by the unavailability of the latter compound. Aminothiazole **23** proved more accessible and was prepared in good yield from addition of thiourea to α-bromoketone **22** (obtained from commercially available 2-decanone by addition of bromine in methanol). After conversion of **23** to the corresponding diazonium salt according to the protocol developed by Doyle (M. P. Doyle, B. Siegfried, J. F. Dellaria, *J. Org. Chem.* **1977**, *42*, 2426), addition of cupric bromide was accompanied by concomitant bromination at the 5-position to provide dibromothiazole **24** as the sole product in an overall yield of 50% from **22**. The structural assignment of this unexpected over-brominated product was fully substantiated by ^{1}H and ^{13}C NMR spectroscopy, mass spectroscopy and elemental analysis. Although neither hydrogenolysis (H_2, Pd/C, EtOH) nor hydride reduction (LAH, THF) proved to be effective in the conversion of **24** to **1**, dibromide **24** can be smoothly debrominated (zinc dust, HOAc, 100 °C) in good yield (90%). It is worth mentioning that this multistep route to **1** is readily amenable to large scale preparations.



Reagents and conditions: a) thiourea, CH_3CN, rt; b) *t*-BuONO, $CuBr_2$, CH_3CN; c) Zn dust, HOAc, 100 °C .

Regioselective lithiation (LDA, THF, -78 °C) of 4-octylthiazole **1** at the 2-position followed by addition of iodine or triisopropylsilyl triflate afforded the

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corresponding iodothiazole **2** or TIPS-protected thiazole **3** in 65% and 60%, respectively. Thiazole **3** was regioselectively lithiated and reacted with tributyltin chloride to give thiazole organostannane **4** in an excellent yield (99%). A subsequent cross-coupling between **2** and **4** was carried out under modified Stille conditions ($Pd_2(dba)_3/PPh_3/Cu_2O$, DMF) to provide head-to-tail coupled TIPS-terminated bithiazole **5** in 55% yield.[28] It is worth mentioning that neither $Pd(PPh_3)_2Cl_2/PPh_3$ nor $Pd(PPh_3)_4$ proved to be effective catalysts for the cross-coupling. The diminished reactivity of thiazole-derived organostannane **4** in comparison to the structurally similar organostannane derived from thiophene under the usual Stille conditions probably reflects electron deficiency of the thiazole moiety. Fluoride-induced (TBAF, THF) desilylation of bithiazole **5** to give **6** was followed by chemoselective iodination (LDA, -78 °C; I_2) to provide iodide **7** in 58% overall yield from **5**. The conversion of **5** to organostannane **8** (excess *n*-BuLi, TMEDA, THF, then Bu_3SnCl) was followed by Stille coupling with **7** to afford completely head-to-tail coupled quaterthiazole **9** in 72%.

The synthesis of the electron-rich hydrophilic oligothiophene (OT) block started from the known bromothiophene **11** bearing a methoxyethoxyethoxymethyl (MEEM) side chain.[29] Lithiation of **11** as previously described,[29] followed by reaction with triisopropylsilyl triflate gave TIPS-substituted thiophene **12**. The added stability provided by the TIPS group over that of a TMS group proved to be crucial as proto-desilylation during silica gel chromatography was not observed. Thiophene **12** was cleanly converted into organostannane **13** in an almost quantitative yield (99%). Cross-coupling **11** and **13** under modified Stille conditions afforded bithiophene **14** in 60%, whereas the usual catalysts $Pd(PPh_3)_2Cl_2/PPh_3$ or $Pd(PPh_3)_4$ proved much less effective when electron-rich **11** was used as the coupling partner. Desilylation of **14** was best effected with TBAF in THF, whereas TFA-mediated desilylation resulted in significant ether cleavage of the MEEM side chain. This was immediately followed by regioselective iodination with *N*-iodosuccinimide (NIS) to afford **15** in excellent yield (99%). Alternatively, TIPS-protected **14** was lithiated with excess *n*-butyllithium and quenched with tributyltin chloride to afford bithiophene tin derivative **16**. Without further purifications, crude mixtures of iodide **15** and tin derivative **16** underwent facile Stille coupling to give quaterthiophene **17** in satisfactory yield.

Physical data. The diblock oligomer **20** and of the reference oligomer **21** were characterized by proton and carbon-13 nuclear magnetic resonance spectroscopy, as well as by mass spectrometry.

The p-n junction diblock oligomer **20** was obtained as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 0.86-0.89 (m, 12 H), 1.28-1.42 (m, 32 H), 1.42-1.48 (m, 8 H), 1.83-1.87 (m, *J* = 7.2 Hz, 8 H), 2.96 (t, *J* = 7.8 Hz, 2 H), 3.07-3.18 (m, *J* = 7.8 Hz, 6 H), 3.37 (s, 6 H), 3.38 (s, 3 H), 3.39 (s, 3 H), 3.55-3.59 (m, 8 H), 3.66-3.69 (m, 8 H), 3.70-3.75 (m, 16 H), 4.57 (s, 2 H), 4.62 (s, 2 H), 4.66 (s, 2 H), 4.67 (s, 2 H), 7.18 (d, *J* = 0.5 Hz, 1 H), 7.21 (s, 1 H), 7.23 (s, 1 H), 7.24 (s, 1 H), 7.26 (d, *J* =0.5 Hz, 1 H), 8.75 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ 14.12, 22.67, 28.74, 28.83, 28.91, 29.23, 29.27, 29.44, 29.52, 29.61, 30.25, 31.14, 31.85, 31.88, 59.04, 66.82, 66.89, 68.52, 69.53, 69.62, 69.70, 70.58, 70.65, 71.92, 123.84, 125.38, 126.81, 126.93, 127.15, 127.21, 129.43, 129.53, 129.98, 131.15, 132.79, 134.09, 134.55, 135.08, 135.13, 135.76, 135.95, 136.00, 140.22, 152.81, 154.08, 154.87, 156.15, 156.85, 156.88, 156.97, 157.62; MS MALDI 1641.2852 ($M + H^+$).

The amphiphilic octithiophene reference oligomer **21** was also obtained as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 0.86-0.89 (m, 12 H), 1.28-1.38 (m, 32 H), 1.39-1.40 (m, 8 H), 1.63-1.69 (m, *J* = 7.1 Hz, 8 H), 2.77-2.80 (m, *J* = 6.9 Hz, 8 H), 3.37 (s, 6 H), 3.38 (s, 3 H), 3.39 (s, 3 H), 3.55-3.59 (m, 8 H), 3.65-3.68 (m, 8 H), 3.70-3.74 (m, 16 H), 4.57 (s, 2 H), 4.61 (s, 2 H), 4.65 (s, 2 H), 4.66 (s, 2 H), 6.93 (s, 1 H), 6.94 (s, 1 H), 6.96 (s, 1 H), 6.97 (s, 1 H), 7.16 (s, 1 H), 7.17 (s, 1 H), 7.18 (s, 1 H), 7.23 (s, 2 H), 7.25 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ 14.06, 22.60, 29.21, 29.34, 29.36, 29.40, 29.45, 29.47, 29.51, 29.62, 30.47, 30.59, 31.82, 58.97, 66.76, 66.83, 66.87, 68.46, 69.46, 69.52, 70.51, 70.54, 70.60, 71.86, 123.51, 123.70, 126.82, 128.38, 128.43, 128.49, 128.67, 129.17, 129.26, 129.90, 130.02, 130.18, 130.21, 130.40, 132.91, 133.04, 133.24, 133.75, 134.00, 134.02, 134.09, 134.42, 134.90, 135.10, 135.66, 135.67, 135.87, 139.52, 139.72, 139.87, 140.11, 140.15; MS MALDI 1637.6295 ($M + H^+$).

Langmuir monolayers of diblock and reference molecules were prepared by spreading 60 μl of dilute chloroform solutions of the respective compounds (~0.5 mg/ml) onto ultra-pure water subphase (Milli-Q; 18 MΩ cm resistivity) in a Langmuir trough (NIMA Technology, type 611, Coventry, England). After injection of sample solutions, the monolayers were equilibrated at room temperature for 30 min. The humidity of the environment was maintained within the range of 25 to 35%. The monolayers were then compressed at 6 cm^2/min (or 0.1 mm/s) to obtain pressure-area isotherms. Au(111) on mica was prepared by evaporation of gold (99.999%) at rate of 0.1 nm/s under vacuum ($<10^{-6}$ Torr) onto freshly cleaved mica (9-11 mil Asheville-Schoonmaker Mica, VA) preheated to 300-350 °C for 12 h as previously described (J. A. Derose, D. B. Lampner, S. M. Lindsay, N. J. Tao, *J. Vac. Sci. Technol. A* **1993**, *11*, 776). A thoroughly cleaned mask made from oxygen-free copper was placed on top of the mica sheet prior to gold evaporation, yielding an effective electrode area of 1.0 cm^2. The gold substrates were thoroughly cleaned and annealed in hydrogen flame immediately prior to use. The gold substrate was rendered hydrophilic by immersion into a 10 mM solution of mercaptoacetic acid (99.9%) in absolute ethanol at room temperature for 12 h, which were then rinsed with copious amount of water and ethanol, and blown dried in a stream of argon (99.95%). The mercaptoacetic acid-modified gold substrate were immediately stored in a desiccator under nitrogen. Langmuir-Blodgett monolayers were deposited onto freshly prepared hydrophilic gold substrates during upstroke lifting with linear speed of 2 mm/min at surface pressure of 35 and 28 mN/m for the diblock and reference molecules, respectively. The decrease in area enclosed by the barriers allows determination of the transfer ratios (1.0 ± 0.05). The LB films were immediately stored in a desiccator under nitrogen and imaged by STM within 12 h of film preparation. Good electrical contact between the gold surface and conducting metal disc necessary for STM experiment was obtained with a thin silver paste (GC Electronics).

Geometry optimizations were performed at the semiempirical AM1 level using Spartan PC *Pro* (Wavefunctions, Irvine, CA), running on an IBM compatible personal computer with a 1 GHz Pentium processor and 512 Mb of RAM.

STM images were recorded with a Nanoscope III (Digital Instruments, Santa Barbara, CA) in the constant-current mode, and scanning tunneling spectroscopy was performed using the routines incorporated in the program. STM imaging was performed under ambient conditions in air. Electrochemically etched Pt/Ir tip (Molecular Imaging, Phoenix, AZ) were used for both STM and STS studies. Ellipsometry thickness measurements were performed with a Gaertner L116C single-wavelength optical ellipsometer equipped with a helium-neon laser operating at the wavelength of 632.8 nm. Measurements were made at an incident angle of 70° to the surface normal, and data were collected from at least 10 different spots on each sample, which were then averaged. An index of refraction of 1.55 was assumed for the LB monolayers of conjugated diblock oligomers.

High impedances (tunneling gap resistance of 60-300 GΩ), which correspond to large separation between STM tip and monolayer surface, are maintained throughout our STM and STS experiments in order to minimize possible mechanical damage or disturbance to the monolayer by the STM tip. The presence of atmospheric oxygen and moisture do not seem to exert a deleterious effect in the *I*-*V* measurement. All of the *I*-*V* curves presented are averaged over 1024 individual curves, of which typically 65-75% of the curves exhibit the observed characteristics and those curves that do not pass through the origin at zero bias were discarded. This measure is necessary to eliminate the possibility of introducing artifacts in the averaging processes.