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Hole mobility in thieno[3,2-*b*]thiophene oligomers

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1. Experimental Section

Materials**:** All chemicals and reagents for the synthesis were purchased either from local suppliers or from Aldrich or Alfa Aesar. Air- and water-sensitive synthetic steps were performed in argon atmosphere using standard Schlenk techniques. The bisaldehyde **3** was synthesized according to reported procedure.[S1]

Measurements**:** ^{1}H and ^{13}C NMR spectra were recorded on a DPX 500 MHz spectrometer. Melting points were measured using a Mel-Temp-II melting point apparatus and are uncorrected. All the chemical shifts were referenced to $(CH_3)_4Si$ (TMS; δ = 0 ppm) for ^{1}H or $CDCl_3$ (δ = 77 ppm) for ^{13}C. IR spectra were recorded in the solid state (KBr) using Shimadzu IRPrestige-21 Fourier transform infra-red spectrophotometer. MALDI-TOF spectra were recorded on a Ultraflextreme MALDI-TOF/TOF from Bruker Daltonik mass spectrometer.

Electrical measurements**:** Firstly, 2-4 μm thick films of oligomers were deposited by drop casting a chloroform solution of oligomer onto ITO-glass substrates. For MIS-CELIV measurements, devices with the configuration ITO/oligomer/LiF/Al were prepared, where an electron blocking LiF layer (20 nm thick) and a top Al electrode were deposited onto oligomer/ITO-glass specimens by low vacuum (~10^{-6} mbar) thermal evaporation in Edwards Evaporator Auto500. It included a digital USB-oscilloscope (DL-Analog Discovery, Digilent Co.), which plays the roles of master pulse generator and transient current pulse monitor. *RC* constants were at least a factor of 20 smaller than the time scales of interest. The offset voltage prior to the ramp was in the range between 0.6 and 3 V. The bias was swept in the range between 10 and 100 kHz.

J–V characteristics of steady state currents were measured in hole only devices with the configuration ITO/oligomer/Au and recorded by a SMU Keithley 2400. Onto oligomer/ITO-glass specimens, a top Au electrode were thermal evaporated in vacuum as described above. All the electrical measurements were carried out in a MBraun MB200MOD glovebox with argon atmosphere at room temperature.

For MIS-CELIV, according to the consideration of the case of small charge extraction (i.e. at small offset voltage yielding the condition $\Delta j \leq j(0)$), the carriers are extracted as a uniform sheet of charge.[S2] The corresponding small-charge transit time t_{tr} for the sheet of carriers to reach the extracting contact defines the mobility as following

$$\mu = \frac{2d_s^2}{At_{tr}^2}(1+f)$$

where $f \equiv \frac{\varepsilon_s d_i}{\varepsilon_i d_s}$ is the ratio between the geometric capacitance of the semiconductor and the insulator layer. In this study, ε_s is about 3 (for oligomers) and ε_i is 9.17 (for LiF), so the parameter $f \ll 1$ is neglected.

2. Synthetic scheme of the oligomers

Synthesis of 1: Bisaldehyde **3** (215 mg, 0.18 mmol, 1 eq.) and *N*-ethylrhodanine (234 mg, 1.45 mmol, 8 eq.) was dissolved in a solution of dry $CHCl_3$ (15 mL) and then three-four drops of piperidine was added and stirred for 48 hrs under argon at room temperature. The reaction mixture was then diluted with dichloromethane and washed with water and brine. After removal of solvent it was chromatographed on silica gel using $CHCl_3$-Hexane (1:1). Yield: 83%. δ_H (500 MHz, $CDCl_3$, *J*/Hz): 7.78 (s, 2H), 7.29 (s, 2H), 7.23 (d, *J* 3.5, 2H), 7.13 (d, *J* 3.5, 2H), 4.12-4.17 (q, 4H), 2.84-2.77 (m, 8H), 1.73-1.66 (m, 8H), 1.43-1.25 (m, 46 H), 0.89-0.87 (m, 12H). δ_C (125 MHz, $CDCl_3$): 190.97, 166.22, 139.90, 139.86, 138.54, 137.63, 136.54, 136.30, 134.65, 134.05, 133.56, 128.43, 126.12, 125.74, 124.93, 123.80, 119.42, 114.56, 38.87, 30.91, 30.89, 29.40, 29.22, 28.68, 28.62, 28.54, 28.49, 28.45, 28.31, 21.69, 13.13, 11.28. IR (KBr) ν_{max}: 795, 1133, 1253, 1330, 1428, 1503, 1569, 1699, 2330, 3658, 3865 cm-1; MALDI-TOF-MS: m/z = 1422.69 (calcd: 1422.37).

Synthesis of 2: Bisaldehyde **3** (130 mg, 0.12 mmol, 1 eq.) and *N*-octylrhodanine (280 mg, 1.14 mmol, 10 eq.) in the same way as before. The reaction mixture was then diluted with any chlorinated solvent and washed with water and brine. After removal of solvent it was chromatographed on silica gel using chloroform-hexane (1:1). Yield: 85%. δ_H (500 MHz, $CDCl_3$, *J*/Hz): 7.74 (s, 2H), 7.25 (s, 2H), 7.21-7.20 (m, 4H), 7.09 (d, *J* 3.5, 2H), 7.03 (s, 2H), 4.09 (t, *J* 7.5, 4H), 2.82 - 2.75 (m, 8H), 1.69-1.67 (m, 12H), 1.42-1.28 (m, 60H), 0.88 (t, *J* 5, 18H). δ_C (125 MHz, $CDCl_3$): 192.26, 167.52, 141.10, 141.05, 139.39, 138.73, 138.68, 137.55, 137.22, 135.77, 135.28, 134.71, 129.47, 127.26, 126.89, 126.17, 124.80, 120.59, 115.72, 48.86, 39.90, 31.88, 31.77, 30.46, 30.29, 29.69, 29.64, 29.57, 29.48, 29.43, 29.30, 29.28, 29.13, 26.99, 26.80, 22.68, 22.62, 14.10, 14.06. IR (KBr) ν_{max}: 733, 790, 1106, 1169, 1261, 1324, 1423, 1577, 1697, 2851, 2928 cm^{-1}. MALDI-TOF: m/z = 1591.77 for $C_{86}H_{114}N_2O_2S_{12}$ (calcd: 1590.55)

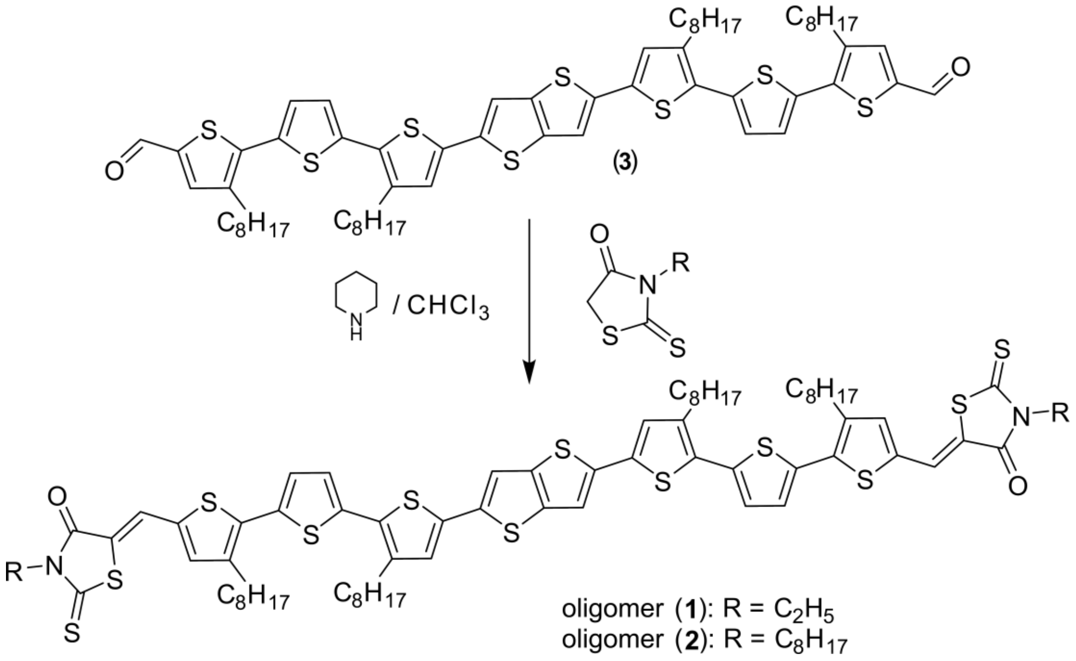
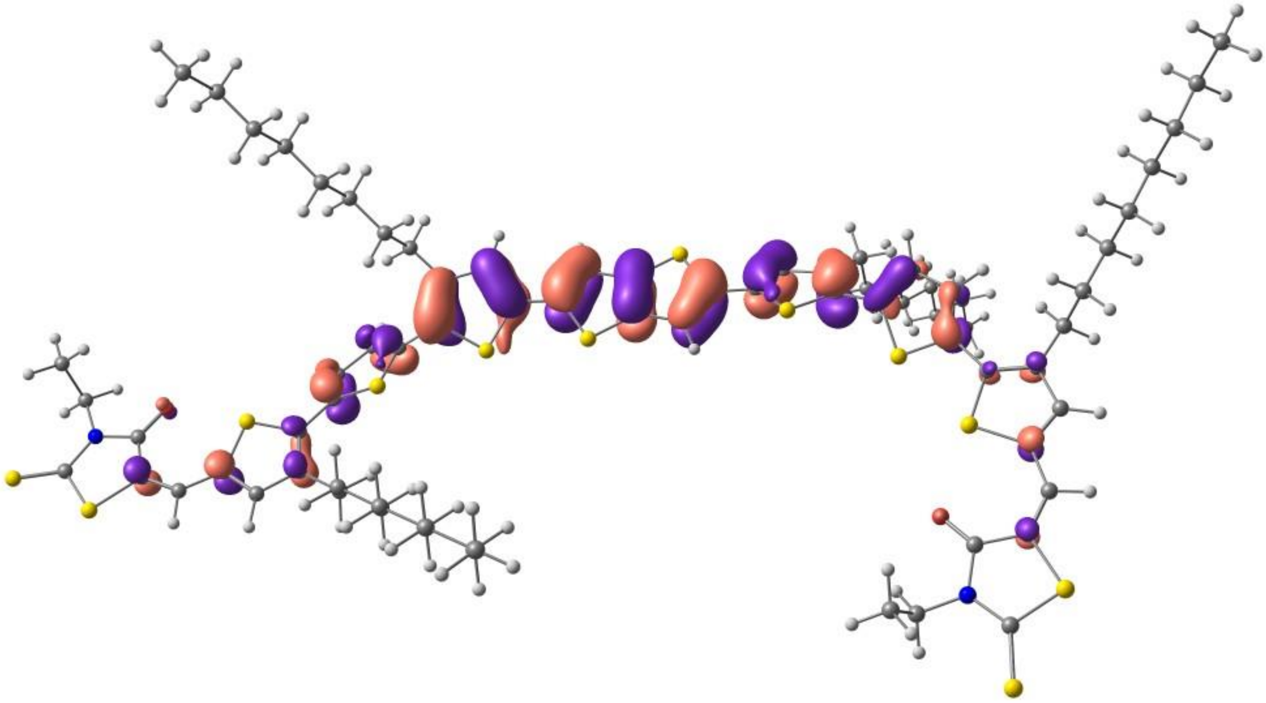


Figure S1. Chemical structures of the oligomers **1**,[S1] **2** under study. Reagents (A) anhydrous chloroform.

3. Theoretical calculations

The theoretical computations of frontier molecular orbitals are based on restricted density functional theory (DFT) and are performed using Becke's three-parameter hybrid method and the Lee-Yang-Parr exchange-correlation energy functional (B3LYP) [S3,S4] with the 6-311G(d,p) basis set for all elements considered.[S5-S8] The geometries of the molecular systems considered are obtained using the GAMESS program package.[S9] All the molecular structures are relaxed until residual forces on atoms are less than 10^{-4} hartree/bohr. The electron density distribution on highest occupied molecular orbital (HOMO) levels are visualized using ChemCraft program package (the value of the contour envelopes is 0.03 a.u.).[S10]

(a)



(b)

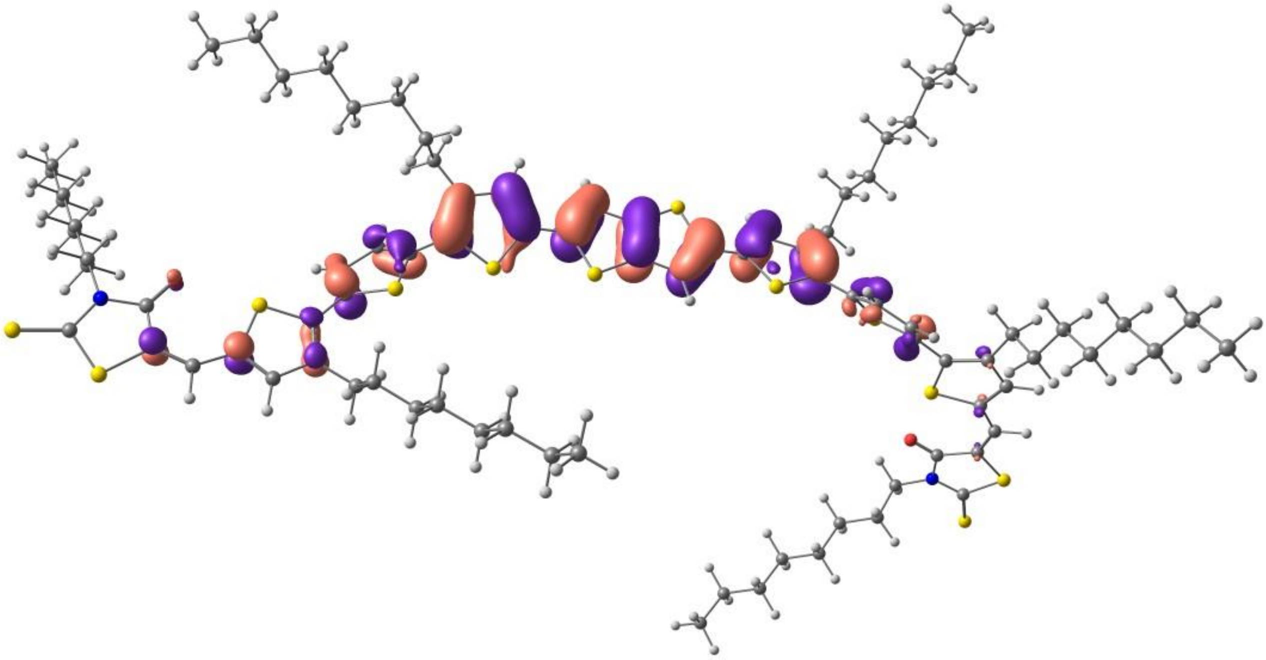


Figure S2. Optimized conformations and calculated spatial electron distributions of HOMO for oligomer **1** (*a*) and **2** (*b*).

4. References

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