

Supporting Information

Bitrialkylsilylethynyl thienoacenes: Synthesis, molecular conformation and crystal packing, and their Field-Effect Properties

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1. Results of Physical Characterization

Electrochemical Properties

The onset oxidation ($E_{\text{onset}}^{\text{oxd}}$) and onset reduction potential ($E_{\text{onset}}^{\text{red}}$) were estimated in CH_2Cl_2 using platinum disc electrode as a working electrode, platinum wire as a counter electrode, and Ag/AgCl as a reference electrode using 0.1 M of Bu_4NPF_6 as a supporting electrolyte with a scan rate of 100 mV/s and all the potential were calibrated with ferrocene as an external standard. The energy level of the highest occupied molecular orbital (HOMO) for the three fused heteroacenes was calculated from the onset potential according to the following equation (in DCM) :

$$E_{\text{HOMO}} = -(4.40 + E_{\text{onset}}^{\text{oxd}}) \text{ eV};$$

$$E_{\text{LUMO}} = -(4.40 + E_{\text{onset}}^{\text{red}}) \text{ eV}$$

$$E_{\text{energy gap}} = E_{\text{HOMO}} - E_{\text{LUMO}}$$

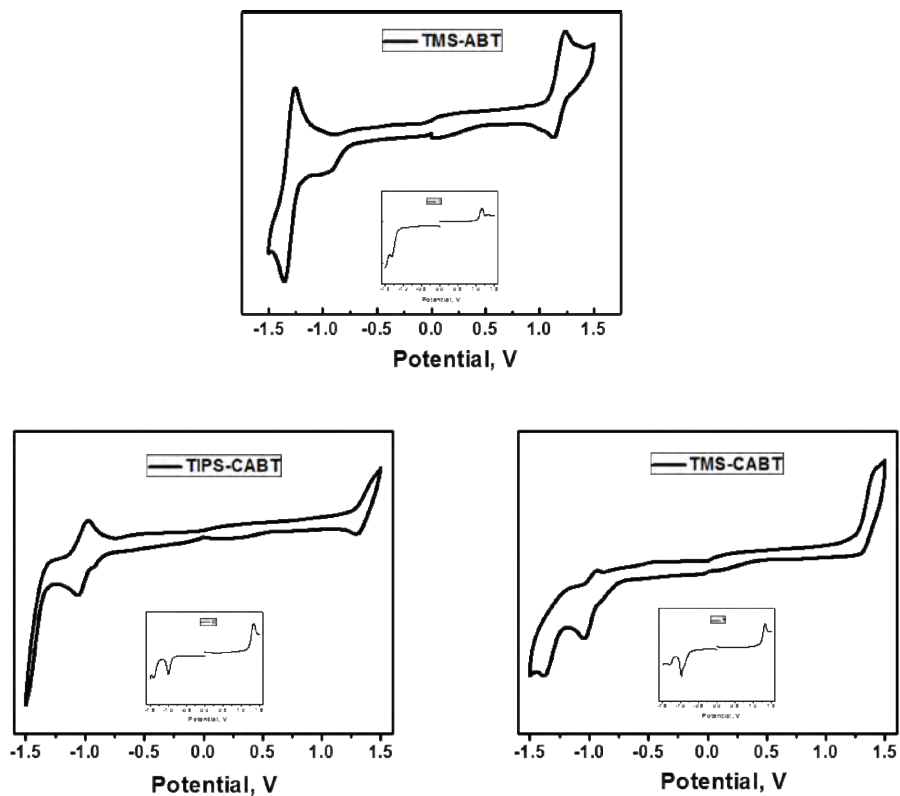


Figure S1 The CV and DPV traces of **TMS-ABT**, **TIPS-CABT**, and **TMS-CABT**

AFM images:

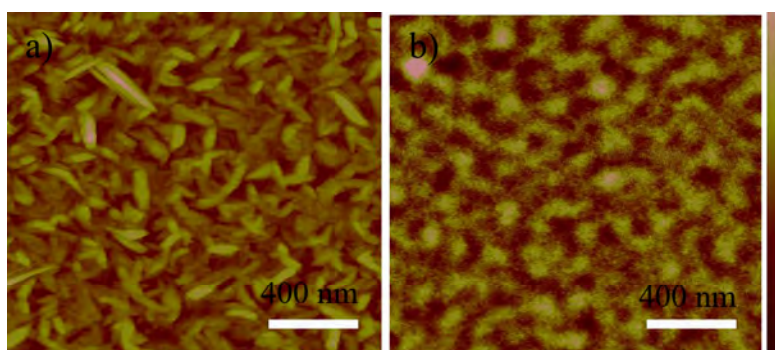


Figure S2 The AFM images ($2\ \mu\text{m} \times 2\ \mu\text{m}$) of pristine thin film of on the OTS-modified **Si/SiO₂** substrates: (a) **TIPS-ABT** (b) **TMS-ABT**

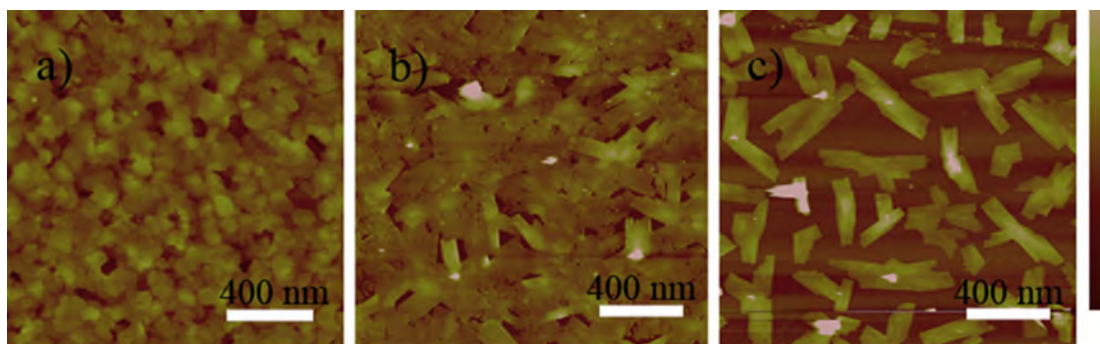


Figure S3 The AFM images ($2\ \mu\text{m} \times 2\ \mu\text{m}$) of the thin films of **TIPS-CABT** on the OTS-modified Si/SiO₂ substrates: (a) pristine thin film and ones after annealing at (b) 100°C and (c) 150 °C

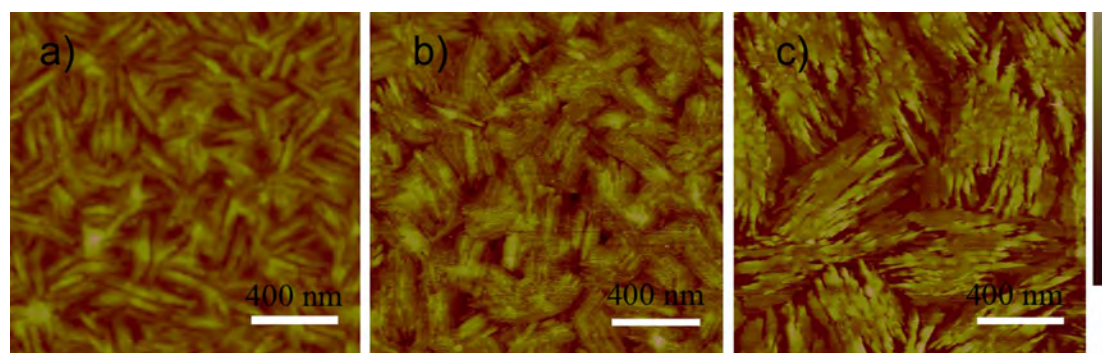


Figure S4 The AFM images ($2\ \mu\text{m} \times 2\ \mu\text{m}$) of the thin films of **TMS-CABT** on the OTS-modified Si/SiO₂ substrates: (a) pristine thin film and ones after annealing at (b) 100°C and (c) 150 °C

2. Calculation Results

Table S1 The adiabatic ionization potentials (AIP) and hole reorganization energies (λ_+) of **TIPS-ABT-1**, **TIPS-ABT-2**, and **TMS-ABT** calculated at the levels of B3LYP/6-31G(d) and B3LYP/6-31+G(d)

| Methods | Molecules | λ_+ (meV) | AIP/eV |
|-----------------|-------------------|-------------------|--------|
| B3LYP/6-31G(d) | TIPS-ABT-1 | 161.6 | 6.062 |
| | TIPS-ABT-2 | 161.7 | 6.063 |
| | TMS-ABT | 172.4 | 6.100 |
| B3LYP/6-31+G(d) | TIPS-ABT-1 | 155.6 | 6.334 |
| | TIPS-ABT-2 | 157.2 | 6.334 |
| | TMS-ABT | 164.0 | 6.387 |

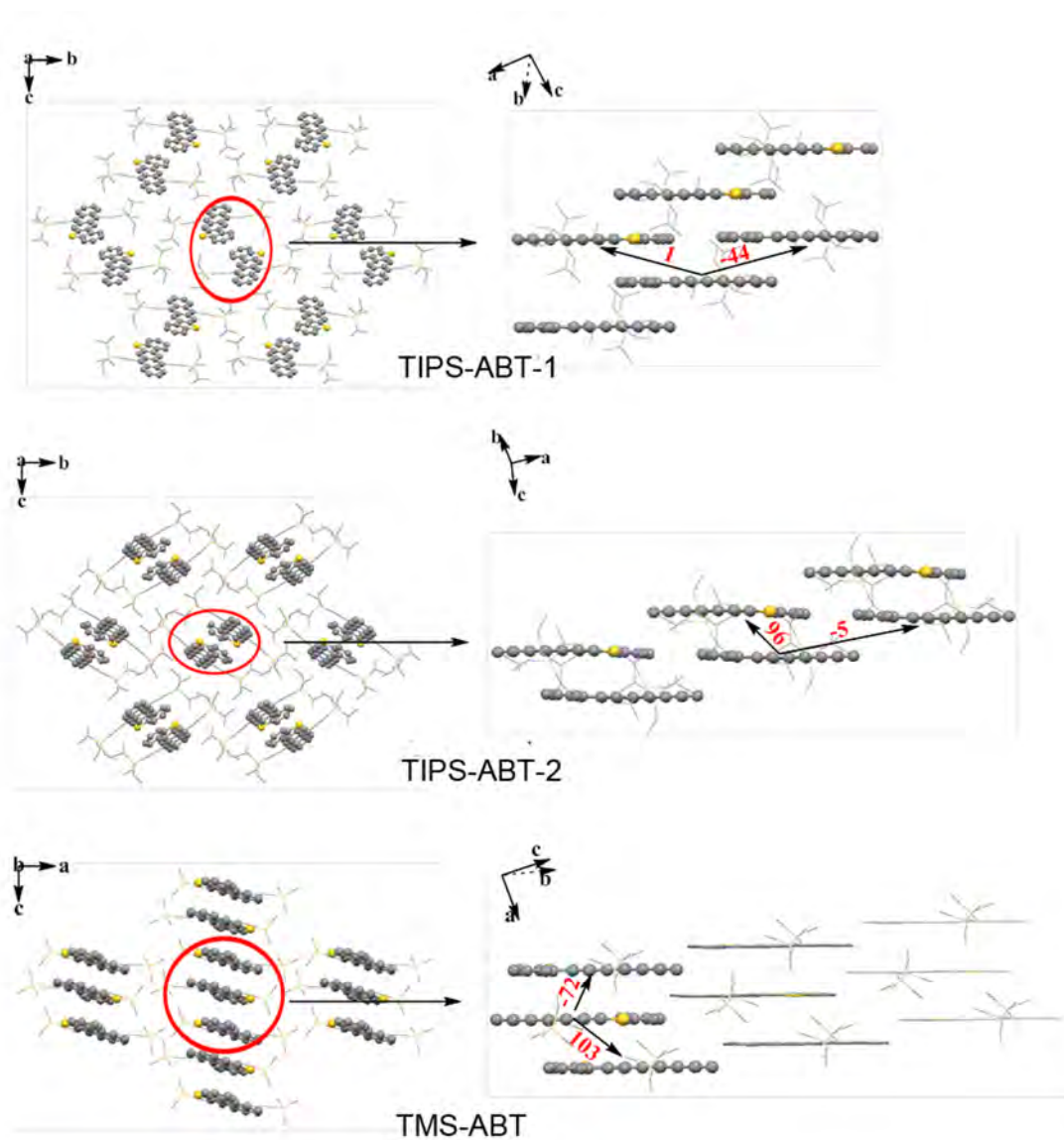


Fig. S5 Crystal packing for TIPS-ABT-1, TIPS-ABT-2, and TMS-ABT with hole transfer integrals (meV) for main carrier hopping pathways.

Theoretical Methodology

To describe the charge-transport properties of systems, the incoherent hopping model was employed in which charge can transfer only between neighboring molecules. Each hopping step has been considered as a nonadiabatic electron-transfer reaction involving a self-exchange charge

from a charged molecule to an adjacent neutral one. The rate of charge transfer between neighboring molecules, k , can be expressed by the standard Marcus equation in terms of the reorganization energy λ , the transfer integral V , and the temperature T as

$$k = \frac{4\pi^2}{h} \frac{1}{\sqrt{4\pi\lambda k_B T}} V^2 \exp\left(-\frac{\lambda}{4k_B T}\right) \quad (1)$$

The reorganization energy λ is evaluated from the adiabatic potential-energy surfaces. The transfer integral V characterizes the strength of electronic coupling between the two adjacent molecules. It could be obtained from the site-energy corrected method:

$$V_{mn} = \frac{V_{mn}^0 - \frac{1}{2}(e_m + e_n)S_{mn}}{1 - S_{mn}^2} \quad (2)$$

Here, $e_{m(n)} = \langle \Phi_{m(n)} | H | \Phi_{m(n)} \rangle$, $V_{mn}^0 = \langle \Phi_m | H | \Phi_n \rangle$, and $S_{mn} = \langle \Phi_m | S | \Phi_n \rangle$, where $\Phi_{m(n)}$ is the frontier molecular orbital of isolated molecule $m(n)$ in the dimer representation. Namely, for hole transport, the highest occupied molecular orbital (HOMO) should be plugged in.

The drift mobility of hopping, μ , can be evaluated from the Einstein relation:

$$\mu = \frac{e}{k_B T} D = \frac{e}{k_B T} \lim_{t \rightarrow \infty} \frac{1}{2n} \frac{\langle l(t)^2 \rangle}{t} \quad (3)$$

where e is the electronic charge, n is the spatial dimensionality, and l is the hopping distance; D is the diffusion coefficient, simulated by the random walk here.