Supplementary Information

Hole-transporting materials based on thiophene-fused arenes from sulfurmediated thienannulations

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1. Optical microscope and AFM measurement

Optical microscope (Keyence, VHX-2000) images of the drop-cast films of **1** and **2** are shown in Figs. S1(a) and S1(b), respectively. Tapping mode AFM (Bruker, Dimension FastScan) was carried out using cantilevers (Bruker, Fastscan-C) with a spring constant of ~0.8 N/m. The measurements were carried out in the air at room temperature with scan rates of ~1.0 Hz line. Scan areas of $10 \times 10 \ \mu\text{m}^2$ were explored with resolution of 512×512 pixels. AFM height images of drop-cast film of **1** and **2** are shown in Figs. S1(c) and S1(d), respectively. The optical microscope and AFM images revealed no crystalline structures^{S1,2} of drop-cast film of **1** and **2**.



Figure S1. Optical microscope (a,b) and AFM (c,d) images of the drop-cast films of 1 (a,c) and 2 (b,d).

- S1. R. Dabirian, X. Feng, L. Ortolani, A. Liscio, V. Morandi, K. Müllen, P. Samorí, and V. Palermo, *Phys. Chem. Chem. Phys.*, 2010, 12, 4473-4480.
- S2. E. H. H. Chow, D.-K. Bučar, and W. Jones, Chem. Commun., 2012, 48, 9210-9226.

2. Theoretical study

compound	Ē	E + ZPE	Н	G
1	-3289.80888562	-3288.985640	-3288.931352	-3289.083019
2	-3597.08405661	-3596.166989	-3596.107301	-3596.269856
8	-1875.45933261	-1875.067640	-1875.041576	-1875.125344
9	-2182.73498724	-2182.249445	-2182.217994	-2182.312794

Table S1. Uncorrected and thermal-corrected (298 K) energies of stationary points (Hartree).^a

a) *E*: electronic energy; *ZPE*: zero-point energy; $H (= E + ZPE + E_{vib} + E_{rot} + E_{trans} + RT)$: sum of electronic and thermal enthalpies; G (= H - TS): sum of electronic and thermal free energies.

8.50





S4



Compound 1



Compound 2

