Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

ESI

Solution-processable thiadiazoloquinoxaline-based donor–acceptor small molecules for Thin-Film Transistors

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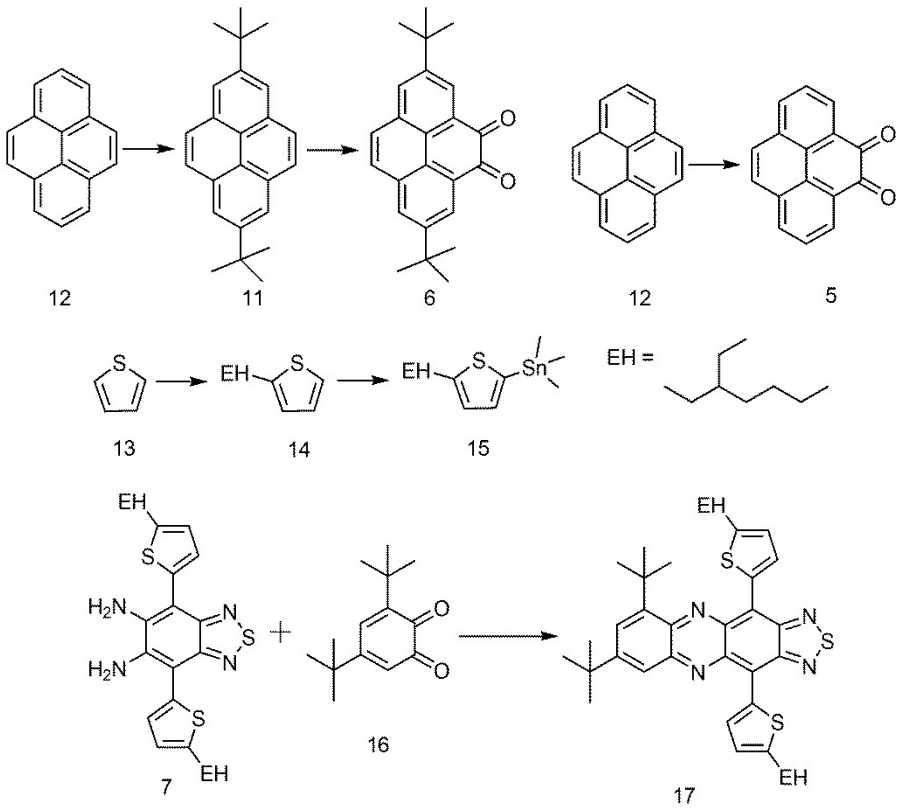
Experimental Section



Scheme S1 Synthetic route of compounds **5**, **6** and **15**.

Synthesis of 2,7-di-t-butyl-pyrene (**11**)

Compound **11** was synthesized according to the literature procedure [reference].[1] Pyrene (10.1 g, 50 mmol) was dissolved in anhydrous dichloromethane (100 mL) and aluminum chloride (1.33 g, 10 mmol) was added in portions and then a solution of *t*-butylchloride (10 g, 109 mmol) in anhydrous dichloromethane (15 mL) was added dropwise under argon below 5 ^{o}C. Then the mixture was stirred overnight at room temperature. Solvent was evaporated under vacuum and the crude product was purified by column chromatography over silica gel, eluting with hexane to give white crystals compound **11** (14.1, 45 mmol, 90%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (s, 4H), 8.05 (s, 4H), 1.61 (s, 18H).

Synthesis of 2,7-di-tert-butylpyrene-4,5-dione (**6**)

Compound **6** was synthesized according to the literature procedure.[1] To a solution of 2,7-di-t-butyl-pyrene (3.14 g, 10 mmol) in dichloromethane (40.0 mL) and acetonitrile (40.0 mL), were added $NaIO_4$ (10.0 g, 46.8 mmol), water (50.0 mL), and $RuCl_3$*H_2O (0.20 g, 0.96 mmol). The dark brown suspension was stirred at room temperature overnight. The reaction mixture was poured into 500 mL water and the organic phase was separated. The aqueous phase was extracted

three times with dichloromethane (50 mL). The dichloromethane extracts were combined with the organic phase and washed with water to give a dark orange solution. Solvent was evaporated under vacuum and the crude product was purified by column chromatography over silica gel, eluting with dichloromethane/hexane to give orange compound **6** (1.23 g, 3.6 mmol, 36%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (d, *J* = 2.0 Hz, 2H), 8.14 (d, *J* = 2.0 Hz, 2H), 7.82 (s, 2H), 1.51 (s, 18H).

Synthesis of pyrene-4,5-dione (**5**)

Compound **5** was synthesized as an orange powder in 38% yield by following the general procedure described for compound **6**.^{1}H NMR (300 MHz, $CDCl_3$) δ 8.46 (dd, *J* = 7.4, 1.2 Hz, 2H), 8.15 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.82 (s, 21H), 7.74 (t, *J* = 7.7 Hz, 2H).

Synthesis of 2-(2-ethylhexyl)thiophene (**14**)

n-Butyllithium (*n*-BuLi, 110 mmol, 2.0 M in *n*-hexane, 55 mL) was added dropwise to an anhydrous THF (50 mL) solution of thiophene (8.40 g, 100 mmol), and cooled to -40 °C. The mixture was allowed to stay at this temperature for 1 h and then stirred for another 1 h at room temperature, then, the mixture cooled to -40 °C, followed by the addition of 2-ethylhexyl bromide (20.2 g, 105 mmol). The reaction was allowed to stay at this temperature for 1 h and then stirred at room temperature overnight. The mixture was poured into cold water and extracted with hexanes. The organic extracts were dried over $MgSO_4$, filtered and concentrated by evaporation *in vacuo*. The residue was not further purified and used directly in the next step.

Synthesis of (5-(2-ethylhexyl)thiophen-2-yl)trimethylstannane (**15**)

n-Butyllithium (*n*-BuLi, 22 mmol, 2.0 M in n-hexane, 11 mL) was added dropwise to an anhydrous THF (100 mL) solution of 2-(2-ethylhexyl)thiophene (3.92 g, 20 mmol) at -78 °C. Then the mixture was allowed to stay at this temperature for 1 h and then stirred for 1 h at 0 ^{o}C and again cooled to -78 °C, followed by addition of a solution of Me_3SnCl (20 mmol, 1.0 M in THF, 20 mL). The reaction was allowed to react at this temperature for 1 h and then stirred at room temperature overnight. The mixture was poured in cold water and extracted with hexanes. The organic extracts were dried over MgSO4, filtered and concentrated by evaporation in vacuo. The residue was not further purified and used directly in the next step.

Synthesis of 6,8-di-tert-butyl-4,11-bis(5-(2-ethylhexyl)thiophen-2-yl)[1,2,5]thiadiazolo [3,4-*b*]phenazine (**17**)

Compound **17** was obtained as red powder in 75% yield from the reaction between 4,7-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[*c*][*1*,*2*,*5*] thiadiazole-5,6-diamine and 3,5-di-tert-butylcyclohexa-3,5-diene-1,2-dione by following the general procedure described for compound **3**.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.76 (d, *J* = 3.8 Hz, 1H), 7.31 (d, *J* = 1.5 Hz, 1H), 7.13 (d, *J* = 1.5 Hz, 1H), 6.99 (d, *J* = 3.4 Hz, 2H), 6.79 (d, *J* = 3.5 Hz, 1H), 2.92 (d, *J* = 7.0 Hz, 2H), 2.84 (d, *J* = 6.8 Hz, 2H), 1.77 (m, 1H), 1.69 (m, 1H), 1.48 – 1.27 (m, 25H), 1.22 (s, 9H), 0.95 (dd, *J* = 9.6, 4.7 Hz, 12H).

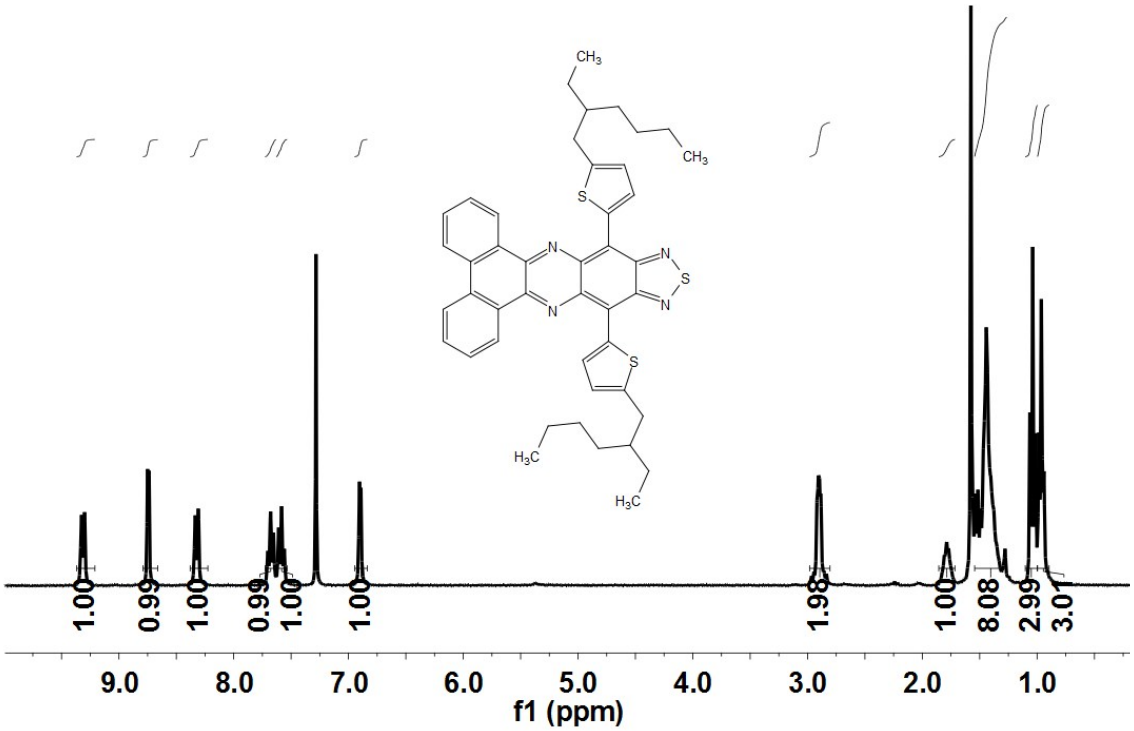


Figure S1 ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

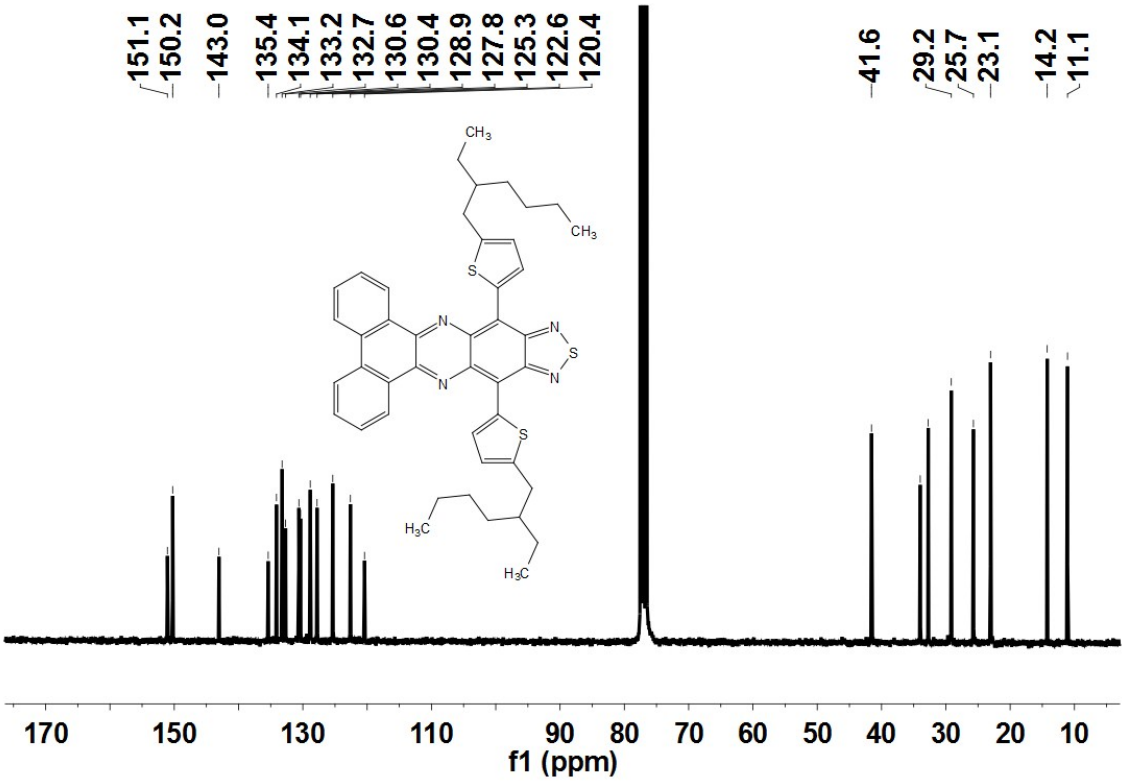


Figure S2 ^{13}C NMR spectrum of compound **1** in $CDCl_3$.

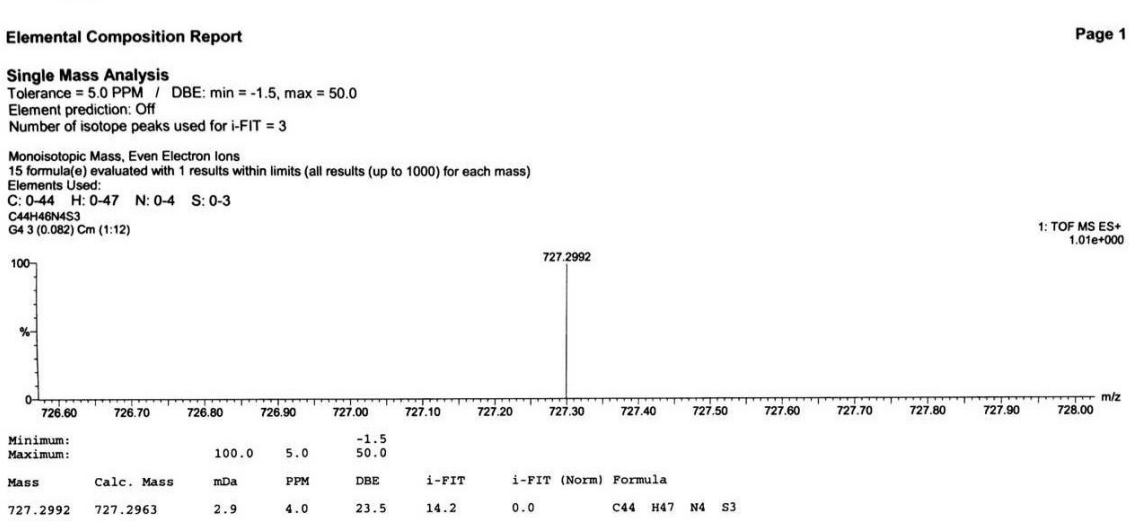


Figure S3 HRMS spectrum of compound **1**.

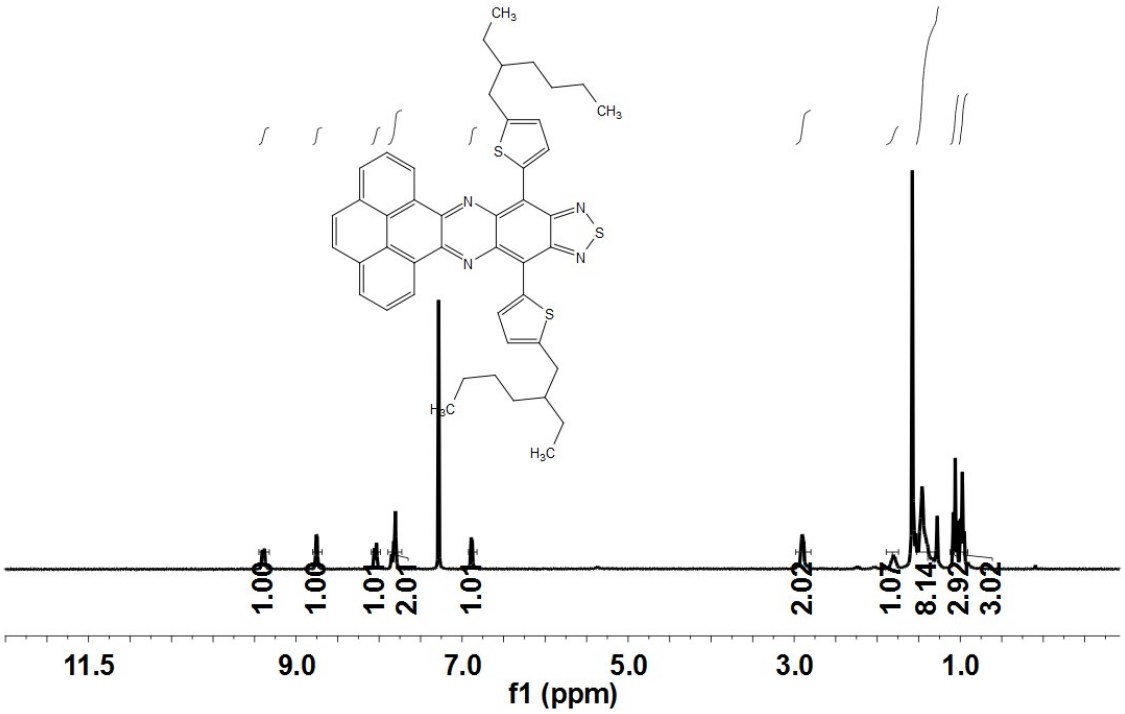


Figure S4 ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

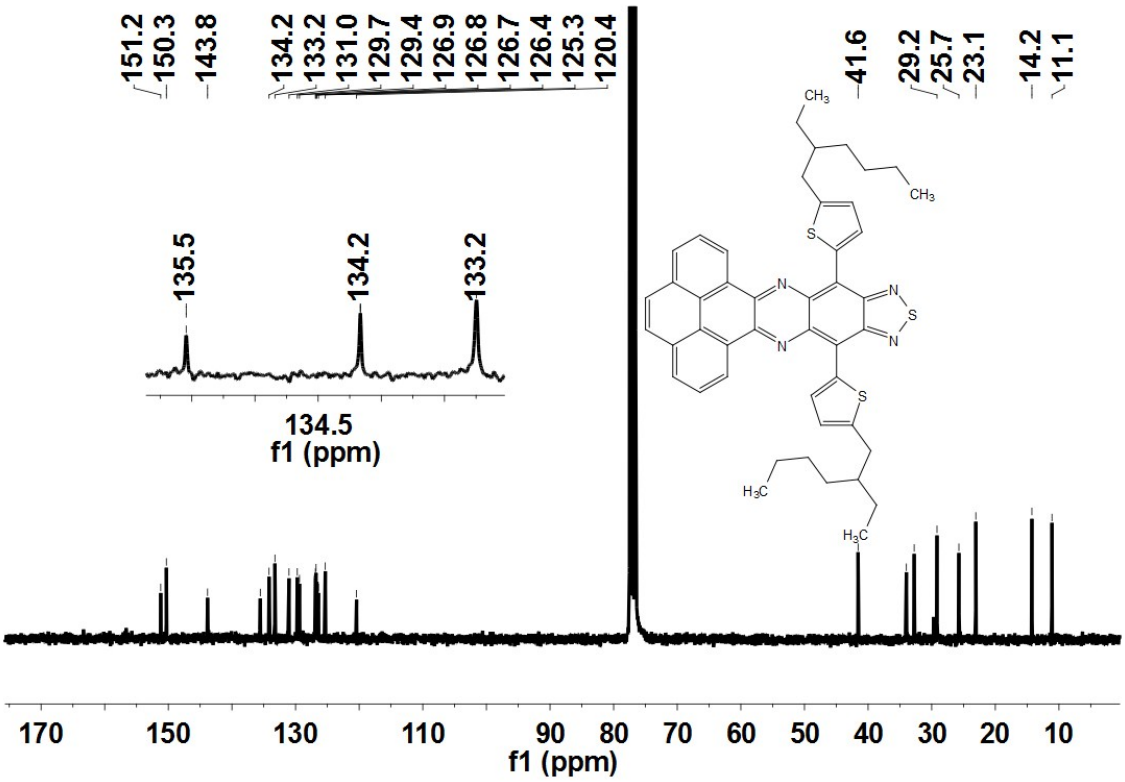


Figure S5 ^{13}C NMR spectrum of compound **2** in $CDCl_3$.

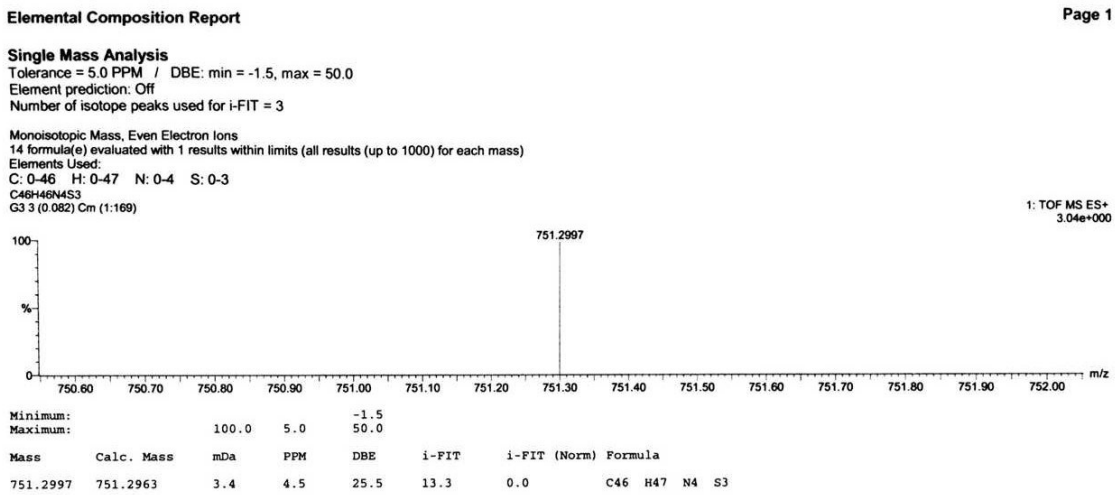


Figure S6 HRMS spectrum of compound **2**.

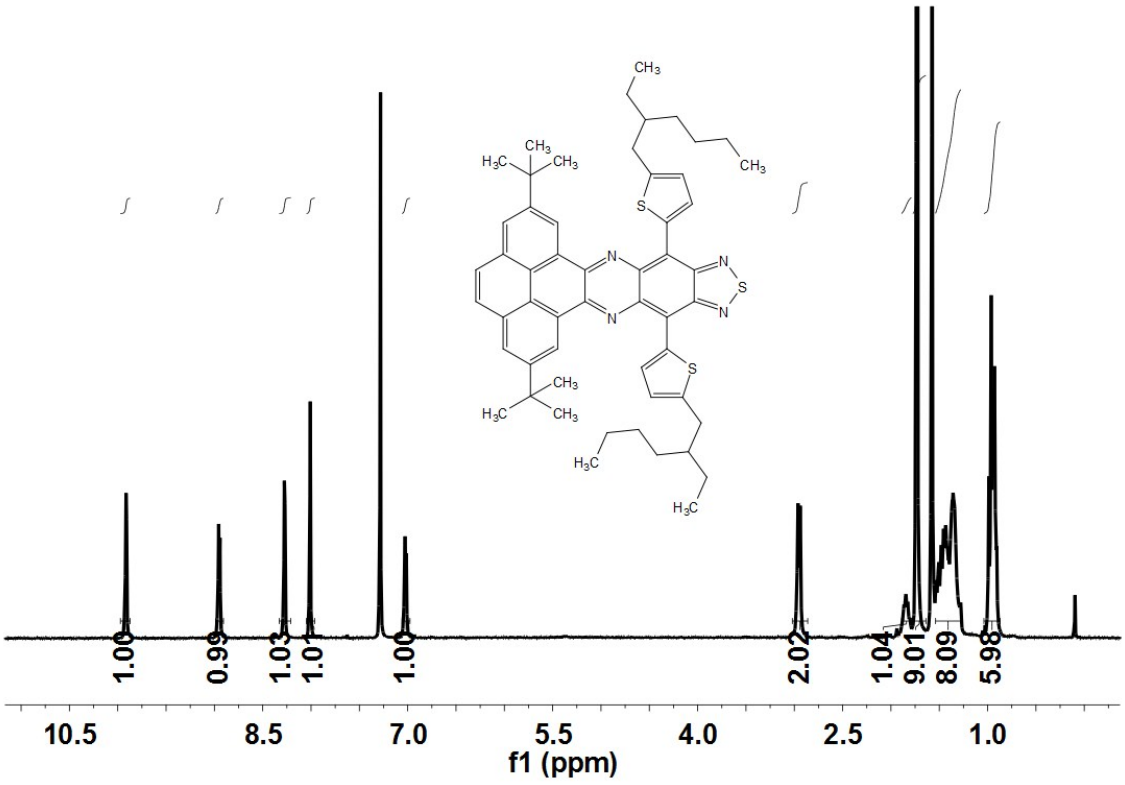


Figure S7 ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

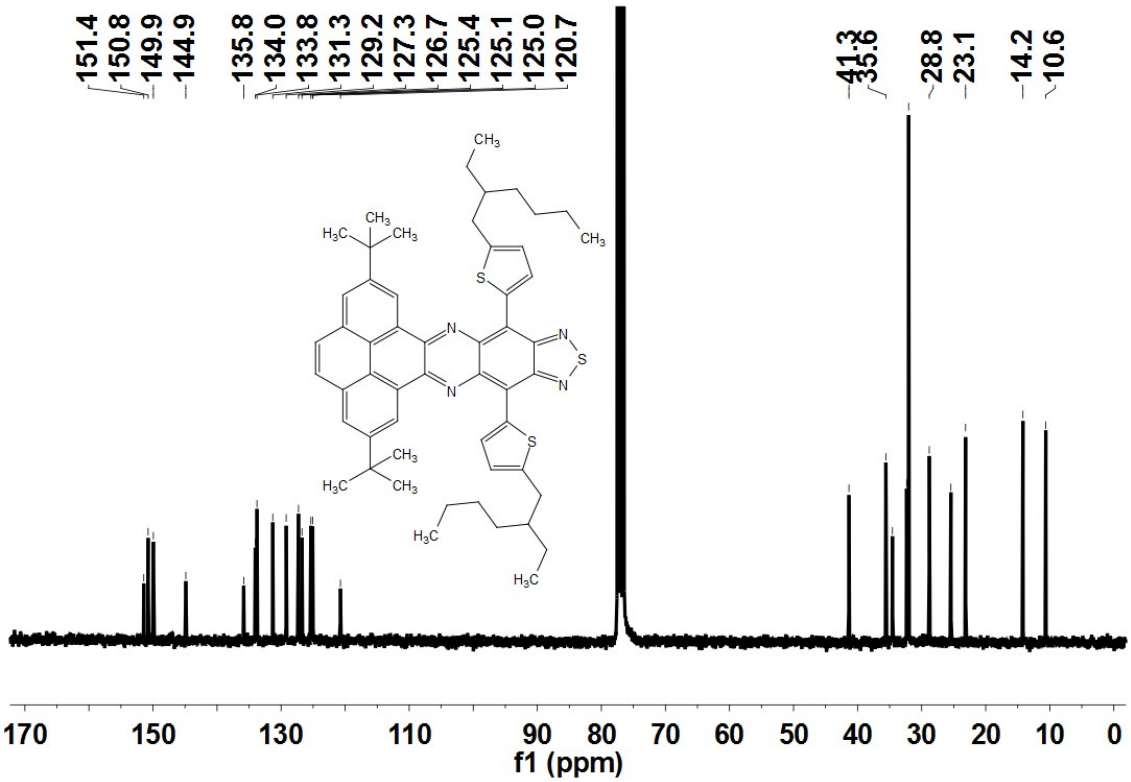


Figure S8 ^{13}C NMR spectrum of compound **3** in $CDCl_3$.

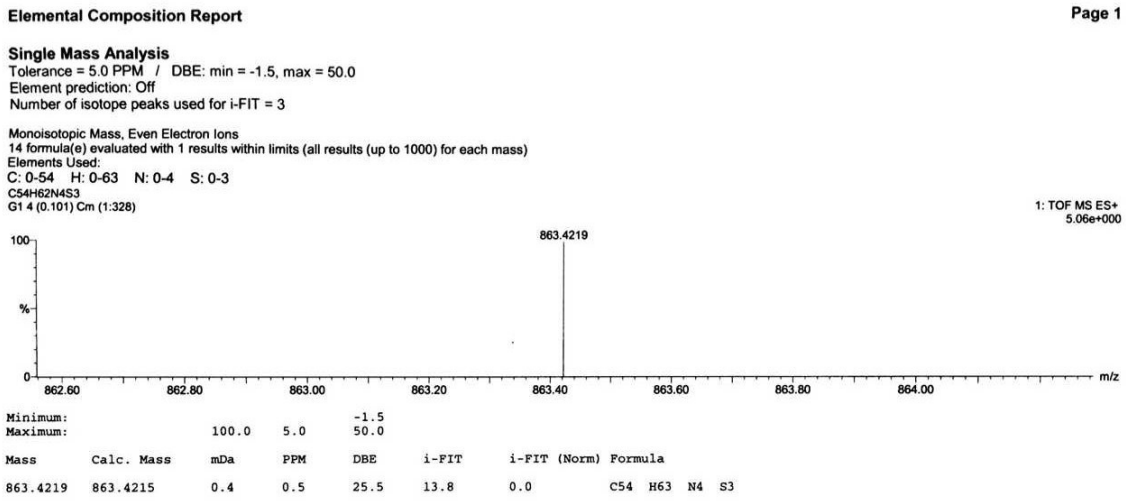


Figure S9 HRMS spectrum of compound **3**.

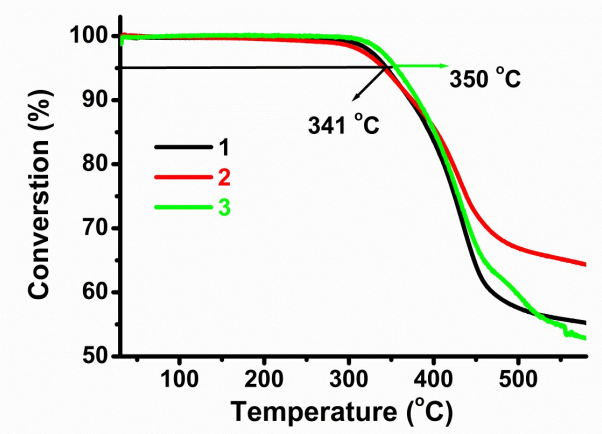


Figure S10 TGA curves of compounds **1-3** with a heating rate of 10 ^{o}C min^{-1} under N_2.

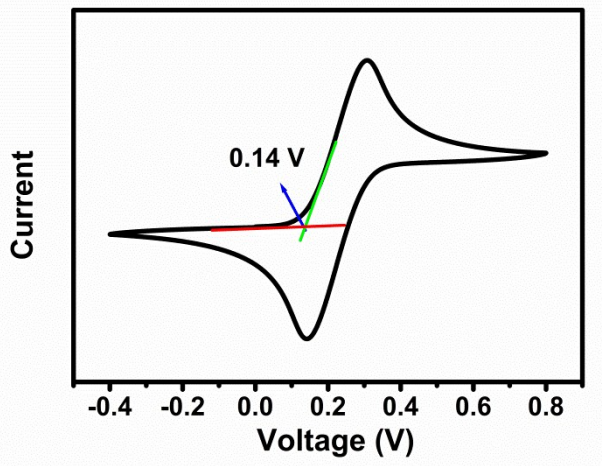


Figure S11 Cyclic voltammogram of the ferrocene standard in DCM solution at the scan rate of 100 mV S^{-1}.

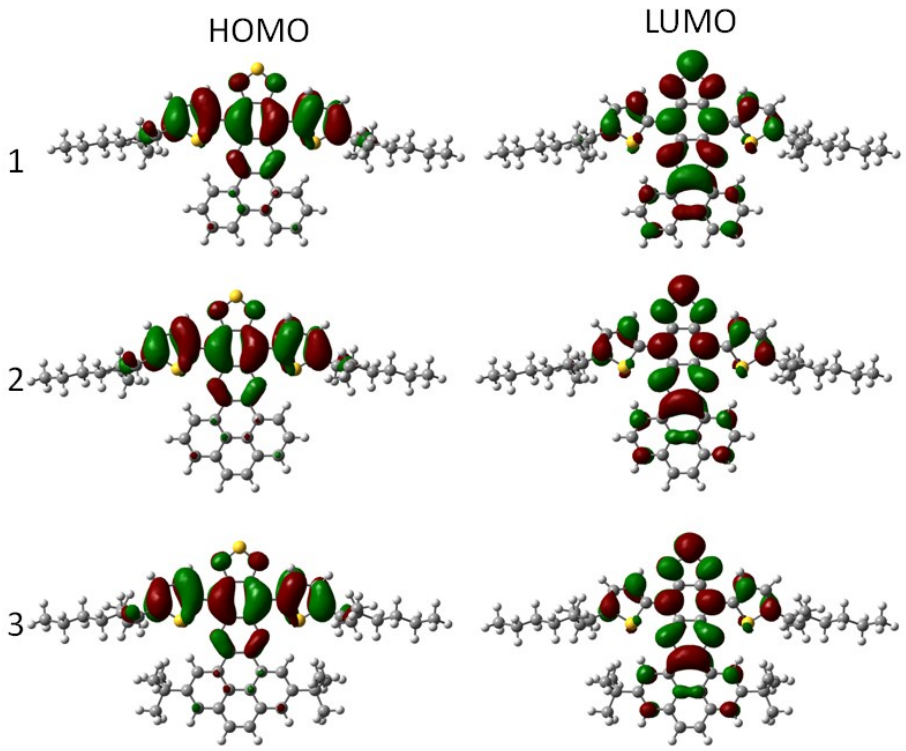


Figure S12 HOMO and LUMO levels of compounds **1-3**.

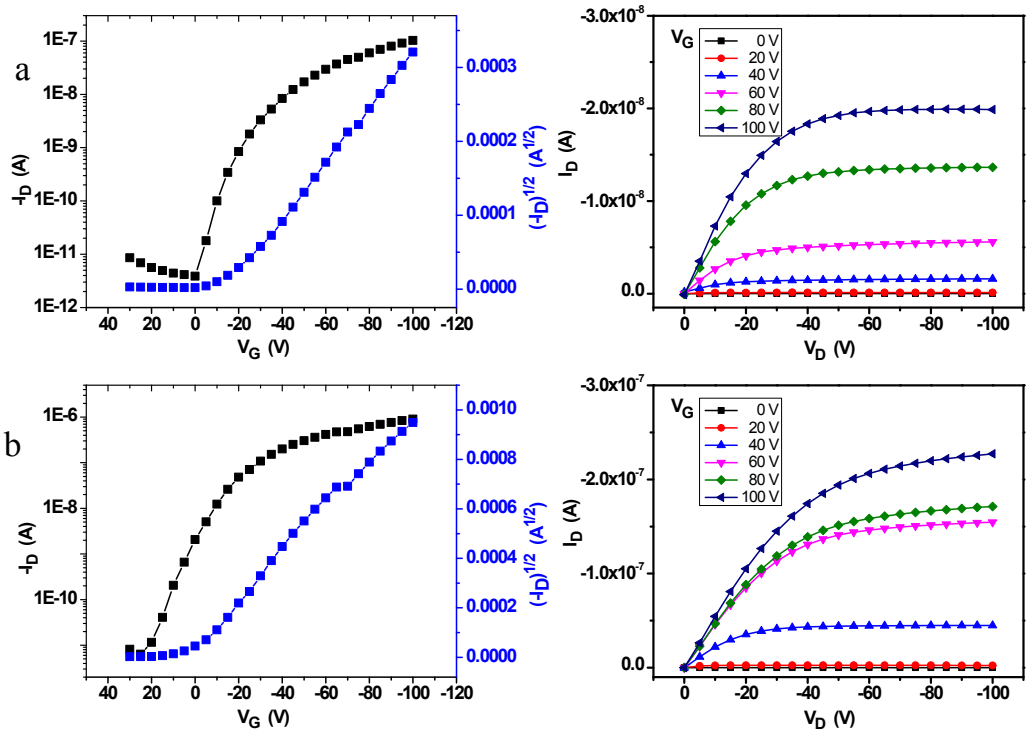


Figure S13 Transfer and output characteristics of OTFT devices based on compound **1** annealed at 20 °C (a) and 100 °C (b).

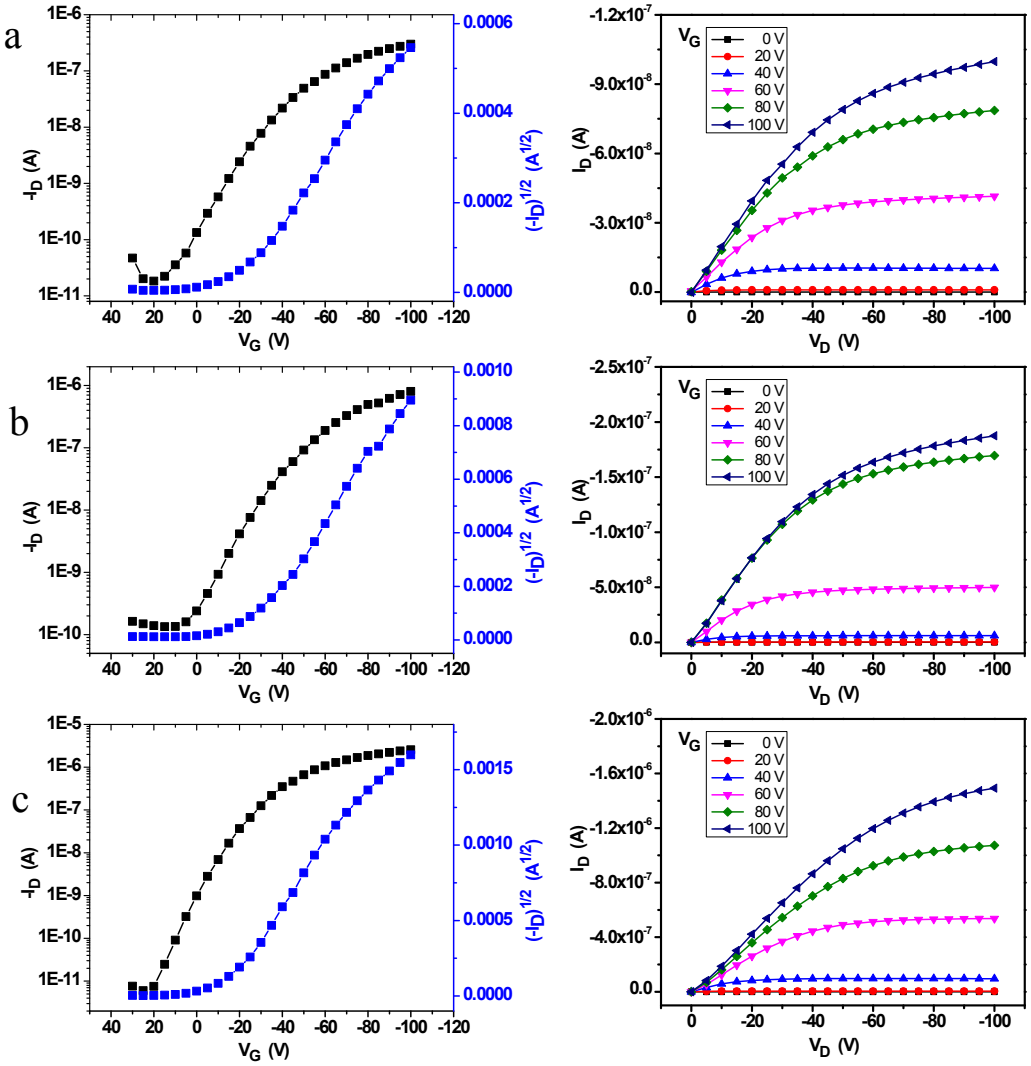


Figure S14 Transfer and output characteristics of OTFT devices based on compound **2** annealed at 20 °C (a), 100 °C (b) and 150 °C (c).

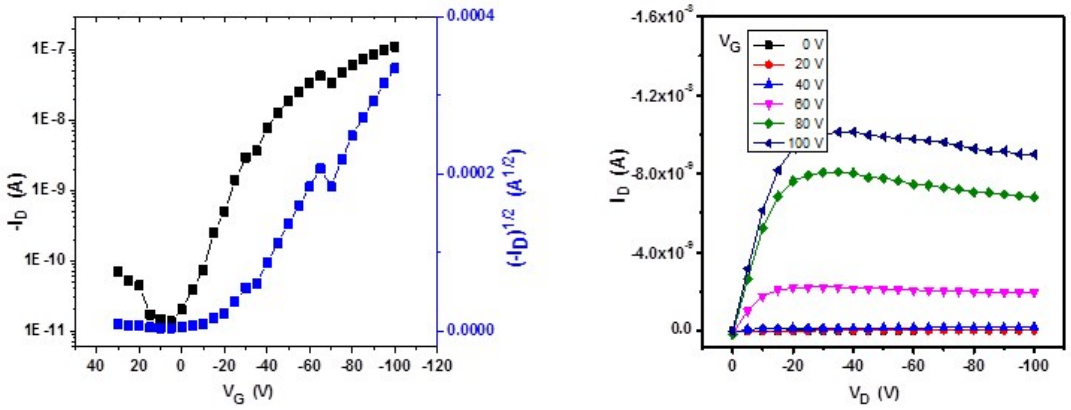


Figure S15 Transfer and output characteristics of OTFT devices based on compound **3** annealed at 100 °C.

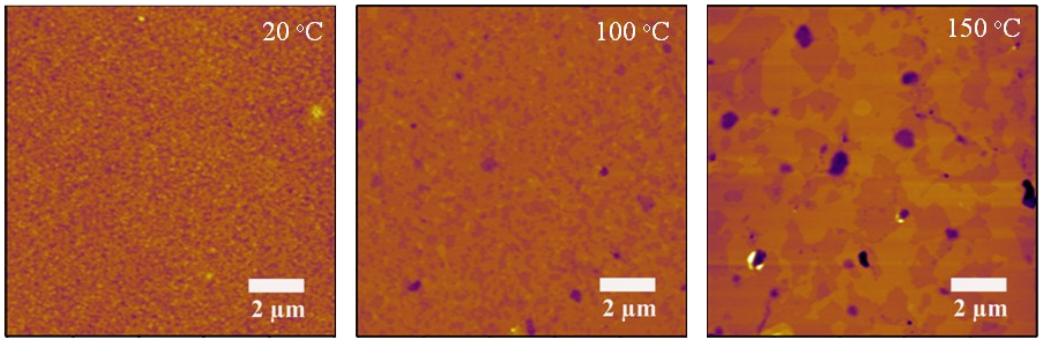


Figure S16 AFM images of thin-films based on compound **1** at different annealing temperatures.

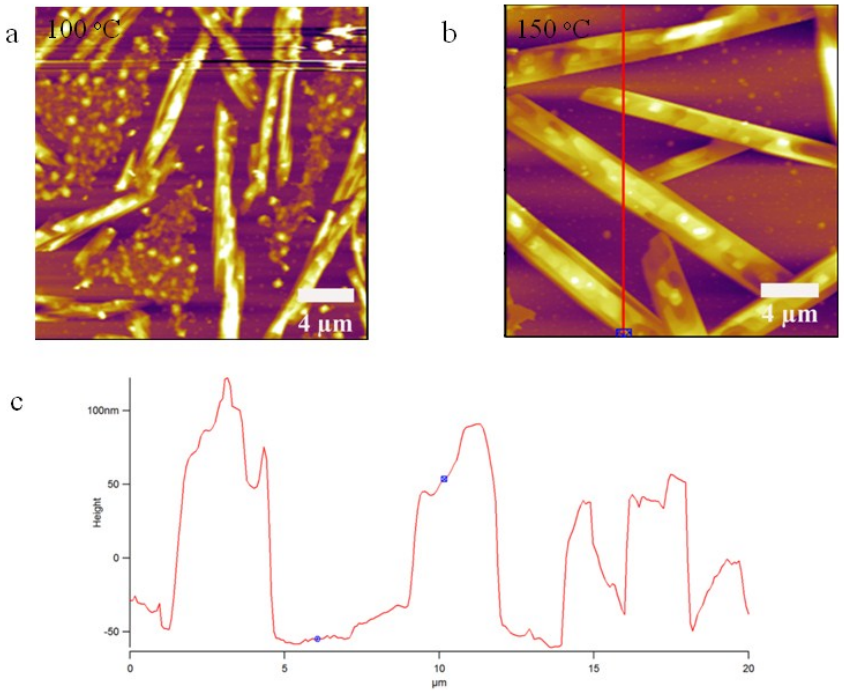


Figure S17 (a) and (b) AFM images of annealed thin-films based on compound **3**, (c) height image of the reassembled ribbon.

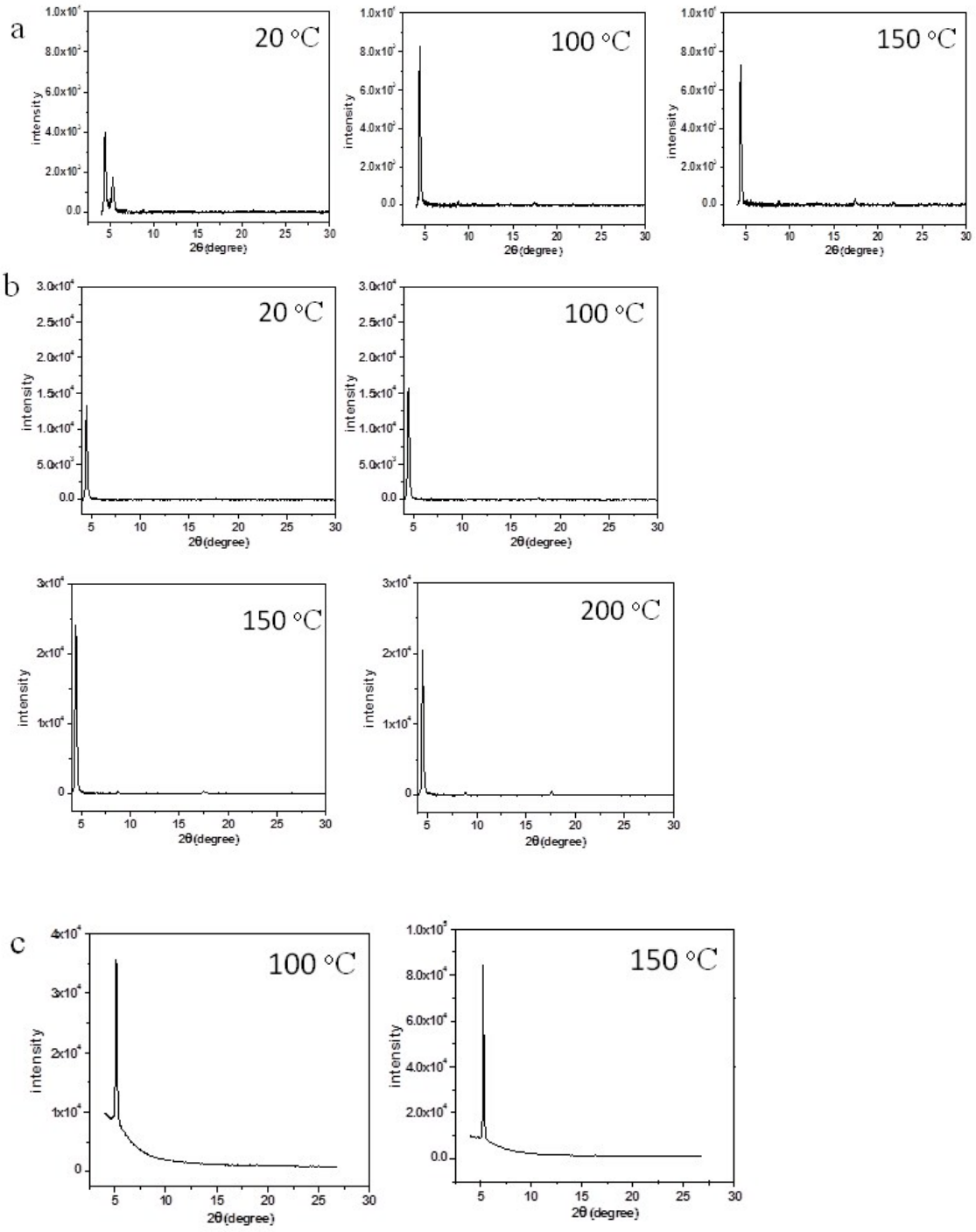


Figure S18 XRD of thin-films based on compounds **1** (a), **2** (b) and **3** (c) at different annealing temperatures.

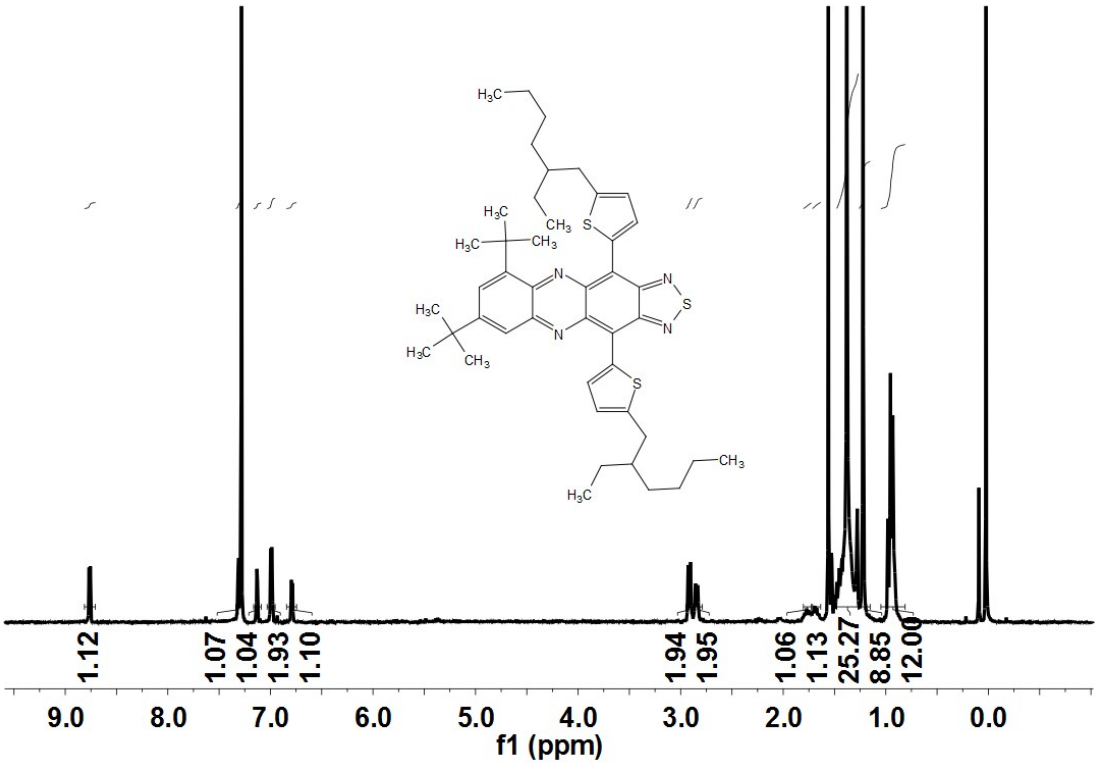


Figure S19 ^{1}H NMR spectrum of compound **17**.

Reference

1 J. Hu, D. Zhang and F. W. Harris, *J. Org. Chem.*, 2005, **70**, 707-708.