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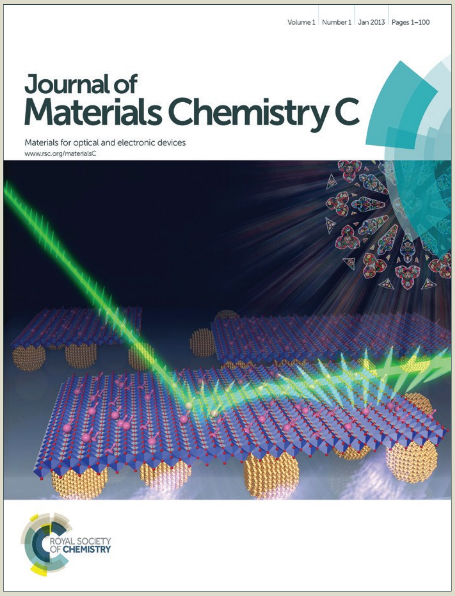

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ARTICLE

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

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Pei-Yang Gu,[a,†] Jing Zhang,[a,†] Guankui Long,[a] Zilong Wang,[a] Qichun Zhang[a,b]*

Although several [1,2,5]thiadiazolo[3,4-*g*]quinoxaline (TQ)-thiophene-based hybrid polymers have been demonstrated for the application in organic field-effect transistors (OFETs), the research on the charge carrier mobility of conjugated donor (D)-acceptor (A) small molecules is rare. To enrich the TQ-containing small molecular family, in this paper, we designed and synthesized three novel TQ derivatives **1**, **2**, and **3** with thiophene units attached onto the TQ cores. The optoelectronic and OFET properties of as-prepared compounds **1**-**3** are investigated. Our results indicate that compounds **1**-**3** show typical p-type characteristic with the mobility as high as 0.012, 0.05 and 0.0055 $cm^2\ V^{-1}\ s^{-1}$ and on/off current ratios of $3×10^5$, $1×10^6$ and $1×10^4$ under the optimized condition, respectively. Due to the steric effect of the substituted bulk group, compound **3** adopts a looser packing mode with larger π-π distance, which subsequently reduces the transport performance. Our results suggest that the D-A π-conjugated small molecules based on TQ could be good candidates for application in organic electronic devices.

Introduction

Soluble low band gap donor (D)-acceptor (A) conjugated molecules and polymers have attracted a lot of interests not only because their optical and electronic properties can be easily tuned through changing the electron donating/accepting ability of substituents, but also because these molecules have a lot of potential applications in organic electronics including organic solar cells (OSCs), organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), organic field-effect transistors (OFETs) and organic memory devices.[1] Due to its high electron affinity nature and good planarity, [1,2,5]thiadiazolo[3,4-*g*]quinoxaline (TQ) as an electron acceptor has been widely incorporated into conjugated D-A molecules[2] to display several interesting properties such as p-type,[3] ambipolar,[4] and n-type characterics.[5] In recent years, thiophene derivatives have been widely introduced into the backbones of conjugated D-A molecules because they can enhance the π-π stacking through intermolecular interactions and result in higher charge-carrier mobility.[6] Although the OFET performance of many TQ-thiophene hybrid polymers have been investigated, the mobility of low band gap D-A small molecules is rarely studied.[7] Compared with TQ-containing polymers, small molecules normally offer several advantages such as reliable synthetic reproducibility, monodispersity, and adjustable structure packing features.

To enrich TQ-containing small molecule family and fully understand their structure-property relationship, we are interested in designing and synthesizing new TQ derivatives **1**, **2**, and **3** (**Scheme 1**) with thiophene units attached onto the TQ cores (fused by phenanthrene, pyrene, and 2,7-*di*-*tert*-butylpyrene groups). We believe that compounds **1-3** could have the following advantages: (1) the introduction of alkyl side-chains could enhance the self-assembling ability with an improvement of structural ordering, leading to a high mobility;[8] (2) the physical properties could be varied through modifying their structures; (3) low band gap might be achieved due to the formation of charge transfer between thiophene segment and TQ unit; (4) pyrene-based semiconductors may exhibit high mobilities because of their highly ordered packing possibility;[9] and (5) compounds **2-3** may display the ability to transport holes and electrons simultaneously based on their electronic structure (the combination of p-type pyrene and n-type TQ).

Experimental

Materials

Thiophene and 4,7-dibromobenzo[*c*][1,2,5]thiadiazole were purchased from Alfa Aesar. Aluminium chloride, *t*-butylchloride, pyrene, 2-ethylhexyl bromide, trimethyltin chloride and *n*-butyllithium were purchased from Sigma-Aldrich Company. Pyrene-4,5-dione and 2,7-*di*-*tert*-

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[a] School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore, E-mail: qczhang@ntu.edu.sg
[b] Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

† Dr P.-Y Gu and J. Zhang contributed equally to this work.

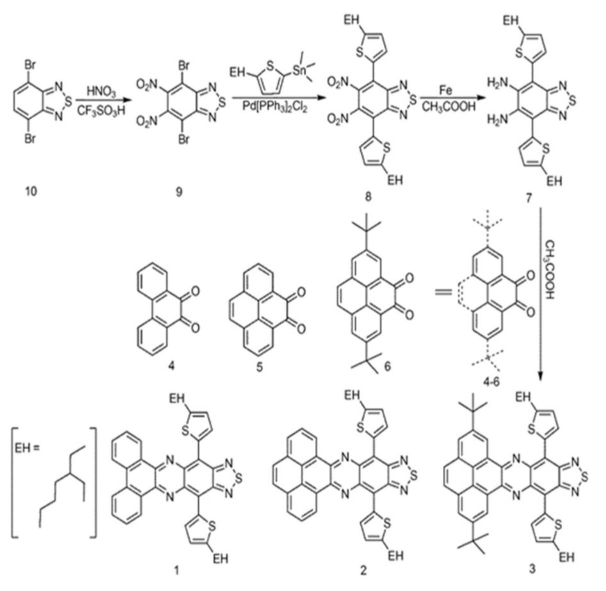
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x butylpyrene-4,5-dione were synthesized according to the reported procedure.[10] Other chemicals and solvents were used directly without further purification.

Characterization

Using $CDCl_3$ or DMSO-d_6 as solvents and tetramethylsilane (TMS) as the internal standard, ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Advance 300 or 400 NMR spectrometer at ambient temperature. UV-Vis absorbance was recorded on a Shimadzu UV-2501 spectrophotometer. High resolution mass spectra (HRMS) were performed on a Waters Q-Tof premier mass spectrometer. Thermogravimetric analysis (TGA) was carried out on a TA Instrument Q500 Thermogravimetric Analyzer at a heating rate of 10 ^{o}C min^{-1}. Cyclic voltammetry measurements were conducted on a CHI 604E electrochemical analyser with glassy carbon (diameter: 1.6 mm; area: 0.02 cm^2) as a working electrode, and platinum wires as a counter electrode and a reference electrode, respectively. Fc^+/Fc was used as an internal standard. Potentials were recorded versus Fc^+/Fc in a solution of anhydrous dichloromethane (DCM) with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as a supporting electrolyte at a scan rate of 100 mV s^{-1}. Employing empirical formulas $E_{LUMO/HOMO}$= -[4.8-E_{Fc} + $E_{re/ox}^{onset}$] eV, where E_{Fc} = 0.14 eV (measured in our setup), the value of HOMO or LUMO can be calculated.

Synthesis

The synthetic procedure for the preparation of compounds **1-3** is depicted in **Scheme 1**. All compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry.



Scheme 1 Synthetic route to compounds **1-3**.

Synthesis of 4,7-dibromo-5,6-dinitrobenzo[*c*][1,2,5]thiadiazole (9)

Compound **9** was synthesized according to the literature-reported procedure.[11] Fuming nitric acid (4.52 mL, 70 mmol) was added dropwise to trifluoromethane sulfonic acid (26.1 mL, 295 mmol) in a two-necked flask at 0 °C and an insoluble complex $2CF_3SO_3H/HNO_3$ was produced immediately. To this mixed acid, 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (**10**, 7.35 g, 25 mmol) was added in portions over 1h. The reaction mixture was stirred at 50 °C overnight. The mixture was poured into ice water slowly, and the excess acid was neutralized by slowly adding sodium hydroxide solution. The resulted precipitate was filtered and washed with water. Purification through recrystallization from 95% ethanol could yield compound **9** as a light yellow powder (7.68 g, 20 mmol, 80%).

Synthesis of 4,7-bis(5-(2-ethylhexyl)thiophen-2-yl)-5,6-dinitrobenzo[*c*][1,2,5]thiadiazole (8)

4,7-Dibromo-5,6-dinitrobenzo[*c*][1,2,5]thiadiazole (**9**, 384 mg, 1.0 mmol) and (5-(2-ethylhexyl)thiophen-2-yl)trimethylstannane (1.08 g, 3.0 mmol) were dissolved in anhydrous tetrahydrofuran (THF, 10 mL). The solution was purged with argon for 30 min and dichlorobis(triphenyl phosphine)palladium(II) ($PdCl_2(PPh_3)_2$ (70.2 mg, 0.10 mmol) was added at room temperature. The mixture was heated at 80 ^{o}C for 24 h under argon atmosphere. After cooling to room temperature, the solvent was evaporated and the target compound **8** was obtained as red crystals (**8**, 300 mg, 0.49 mmol, 49 %) upon standing the saturated hexane solution in refrigerator for 24 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 3.7 Hz, 2H), 6.89 (d, *J* = 3.7 Hz, 2H), 2.86 (d, *J* = 6.8 Hz, 4H), 1.67 (dd, *J* = 12.2, 6.1 Hz, 2H), 1.45 – 1.26 (m, 16H), 0.92 (q, *J* = 7.2 Hz, 12H).

Synthesis of 4,7-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[*c*][1,2,5] thiadiazole-5,6-diamine (7)

A mixture of 4,7-bis(5-(2-ethylhexyl)thiophen-2-yl)-5,6-dinitrobenzo[*c*][1,2,5]thiadiazole (**6**, 1.2 g, 2 mmol) and fine iron powder (1.4 g, 25 mmol) in acetic acid (50 mL) was kept stirring at 80 ^{o}C for 4 h. Then, the reaction mixture was cooled to room temperature, precipitated in 5% aqueous NaOH (150 mL) and extracted three times with DCM (50 mL). The combined organic layers were washed twice with brine, dried with sodium sulfate, and the solvent was removed on a rotary evaporator. The crude product was purified by column chromatography over silica gel, eluting with DCM/hexane to give an orange oil compound **7** (831 mg, 1.5 mmol, 75%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.10 (dt, *J* = 3.2 Hz, 2H), 6.89 (d, *J* = 3.2 Hz, 2H), 5.66 (d, *J* = 29.8 Hz, 4H), 2.78 (d, *J* = 6.6 Hz, 4H), 1.60 – 1.55 (m, 2H), 1.39 – 1.20 (m, 16H), 0.93 – 0.81 (m, 12H).

Synthesis of 2,7-di-tert-butyl-10,14-bis(5-(2-ethylhexyl)thiophen-2-yl)phenanthro[4,5-*abc*][1,2,5]thiadiazolo[3,4-*i*]phenazine (3)

A mixture of 4,7-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole-5,6-diamine (**7**, 554 mg, 1 mmol) and 2,7-*di-tert*-butylpyrene-4,5-dione (**6**, 344 mg, 1 mmol) in acetic acid (50 mL) was stirred at 100 ^{o}C under nitrogen for 24 h. After cooling to room temperature, the mixture was poured into methanol and the crude product was purified by column chromatography over silica gel, eluting with DCM/hexane to give purple compound **3** (690 mg, 0.80 mmol, 80%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.91 (d, *J* = 1.7 Hz, 1H), 8.95 (d, *J* = 3.9 Hz, 1H), 8.27 (d, *J* = 1.8 Hz, 1H), 8.01 (s, 1H), 7.02 (d, *J* = 3.8 Hz, 1H), 2.95 (d, *J* = 6.9 Hz, 2H), 1.88 -1.82 (m, 1H), 1.73 (s, 9H), 1.54 – 1.28 (m, 8H), 0.95 (dt, *J* = 9.7, 7.2 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 151.4, 150.8, 149.9, 144.9, 135.8, 134.0, 133.8, 131.3, 129.2, 127.3, 126.7, 125.4, 125.1, 125.0, 120.7, 41.3, 35.6, 34.6, 32.3, 32.0, 28.8, 25.4, 23.1, 14.2, 10.6. HR-MS, calcd for $C_{54}H_{63}N_4S_3$, 863.4215; found, 863.4219.

Synthesis of 10,14-bis(5-(2-ethylhexyl)thiophen-2-yl)phenanthro[4,5-*abc*][1,2,5]thiadiazolo[3,4-*i*]phenazine (2)

Compound **2** was obtained as purple powder in 78% yield from the reaction between 4,7-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[*c*][1,2,5] thiadiazole-5,6-diamine and pyrene-4,5-dione by following the general procedure described for compound **3**.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.39 (d, *J* = 7.6 Hz, 1H), 8.75 (d, *J* = 3.7 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.89 – 7.73 (m, 2H), 6.88 (d, *J* = 3.5 Hz, 1H), 2.91 (s, 2H), 1.84 - 1.76 (m, 1H), 1.53 -1.27 (m, 8H), 1.06 (t, *J* = 7.4 Hz, 3H), 0.97 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2, 150.3, 143.8, 135.5, 134.2, 133.2, 131.0, 129.7, 129.4, 126.9, 126.8, 126.7, 126.4, 125.3, 120.4, 41.6, 34.0, 32.8, 29.2, 25.7, 23.1, 14.2, 11.1.

HR-MS, calcd for $C_{46}H_{47}N_4S_3$, 751.2963; found, 751.2997.

Synthesis of 10,14-bis(5-(2-ethylhexyl)thiophen-2-yl)dibenzo[*a*,*c*][1,2,5]thiadiazolo[3,4-*i*]phenazine (1)

Compound **1** was obtained as green powder in 70% yield from the reaction between 4,7-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[*c*][1,2,5] thiadiazole-5,6-diamine and phenanthrene-9,10-dione by following the general procedure described for compound **3**.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.31 (d, *J* = 7.9 Hz, 1H), 8.74 (d, *J* = 3.8 Hz, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 3.6 Hz, 1H), 2.98 – 2.80 (m, 2H), 1.88 – 1.75 (m, 1H), 1.54 – 1.26 (m, 8H), 1.04 (t, *J* = 7.4 Hz, 3H), 0.96 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1, 150.2, 143.0, 135.4, 134.1, 133.2, 132.7, 130.6, 130.4, 128.9, 127.8, 125.3, 122.6, 120.4, 41.6, 34.0, 32.7, 29.2, 25.7, 23.1, 14.2, 11.1. HR-MS, calcd for $C_{44}H_{47}N_4S_3$, 727.2963; found, 727.2992.

Results and Discussion

Photophysical, electrochemical, thermal properties, and theoretical calculations

All compounds have good solubility in common organic solvents such as DCM, chloroform and THF. The normalized optical absorption spectra of compounds **1-3** in DCM solution are shown in **Figure 1**. The absorption spectrum of compound **1** shows two absorption bands (250–550 nm and 550–900 nm), which originate from the TQ segments and the D–A interaction between thiophene specie and TQ unit. The absorption spectra of compounds **2-3** are different from that of compound **1** and exhibit three absorption bands (250–450 nm, 450–600 nm and 600–900 nm). There is some small difference in the UV-vis absorption of compounds **2** and **3** due to the structural changes in these two compounds. The absorption edges of compounds **1-3** are similar to each other and extend to ~ 869 nm for all of them, from which the optical band gaps (E_g^{opt}) are estimated to be 1.18 eV. Notably, the similar optical band gap of compounds **1-3** reflects that the extended π–conjugation and intra/intermolecular donor (thiophene)-acceptor (TQ) interactions rather than the extensive delocalization of the π–electrons play a key role to contribute their bandgap.

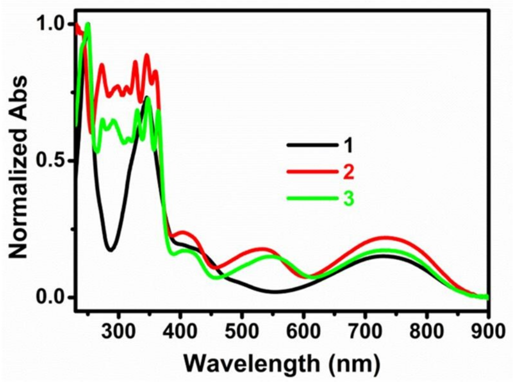


Figure 1 Normalized optical absorption spectra of compounds **1-3** in dilute DCM solution.

Cyclic voltammetry measurements of compounds **1-3** were performed in DCM solution (with 0.1 M $TBAPF_6$ as electrolyte) to investigate the electrochemical properties. As shown in **Figure 2**, all compounds exhibited one reversible reductive and two reversible oxidative waves. The lowest unoccupied molecular orbital (LUMO)/the highest occupied molecular orbital (HOMO) energy levels of compounds **1-3** were calculated from the onset of the first reduction/oxidation peak. The LUMO energy levels of compounds **1-3** were estimated to be -3.89, -3.89 and -3.85 eV from the onset reduction potential with reference to Fc^+/Fc (-4.8 eV) using the equation of $E_{LUMO/HOMO}= -[4.8-E_{Fc} + E_{re/ox}^{onset}]$ eV. Their HOMO energy levels are estimated to be -5.35, -5.37 and -5.37 eV, respectively. The band gaps for compound 1-3 are calculated to be 1.46, 1.48 and 1,52 eV, respectively, which is about 0.3 eV larger than their optical band gaps (1.18, 1.18 and 1.18 eV).

The thermal properties of compounds **1-3** were evaluated by TGA under nitrogen atmosphere. As shown in **Figure S7**, compounds **1-3** exhibit very good thermal stability with onset decomposition temperatures of ~ 341, 341 and 350 °C (considering the 5% weight loss temperature), respectively.

To gain further insight into their electronic structures, the geometry structures of compounds **1-3** were optimized by using DFT calculations (B3LYP/6-31G*),[12] and the frequency analysis was followed to assure that the optimized structures were stable states. All calculations were carried out using Gaussian 09 as shown in Figure **S12**. The electron density distribution of the HOMO for compound **1** mainly locates on thiophene segment while the LUMO is mainly distributed on phenazine ring and TQ unit. Thus, a strong charge-transfer (CT) interaction can occur between the electron donor moieties and the electron acceptor moieties. The calculated results of compounds **2-3** are similar to that of compound **1**.

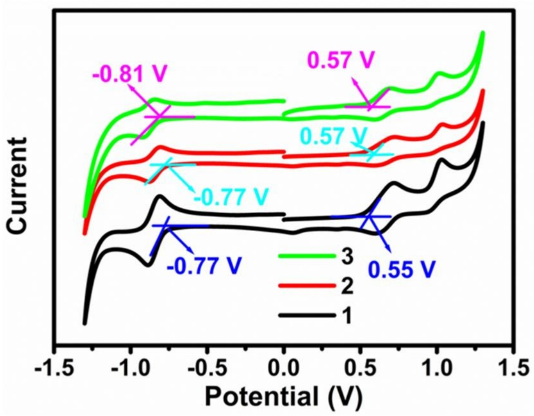


Figure 2 Cyclic voltammogram curves of compounds **1-3** in DCM solution with TBAPF$_6$ (0.1 M) as the supporting electrolyte. Scan rate: 100 mV s^{-1}. Reference to Fc+/Fc (-4.8 eV).

OFET performance:

Thin films (40-60 nm in thickness) were obtained by spin-coating compounds **1-3** onto octadecyltrichlorosilane (OTS)-functionalized SiO$_2$/Si substrates. Then, the as-fabricated thin films were annealed at 100, 150, and 200 °C. Au source/drain electrodes (about 40 nm in thickness) were deposited on the active organic layer through a shadow mask, affording a bottom-gate top-contact device configuration. **Figure 3** shows the device characteristics of compounds **1-3** with the optimized annealing temperature (see **Figure S13**, **S14** and **S15** for the detailed device characteristics of compounds **1-3**). The device performances of compounds **1-3** are summarized in **Table 1**. All devices exhibit typical hole mobility and good current modulation under ambient conditions. The thin-film transistors for compounds **1-3** show typical p-type performance, which are out of our expectation to be ambipolar or n-type. The reason might be that dithienyl groups could affect the molecule packing, which possibly leads to the “pyrene-channel” in the thin film.[9c] For comparison, compound **17** (**Scheme S1**) without pyrene unit like compound **3** with bulky group has been prepared and it didn’t show any FET performance. Although the synthesis and physical properties of a similar compound 4,7-bis(5-octylthiophen-2yl)benzo[c][1,2,5]thiadiazole has been reported, no FET performance was mentioned, which might be due to the shorter conjugated length of this molecule.[13] The poor performance of compound **17** may come from the steric effect of bulky group, which could prevent the dense packing mode. The compound without substituted bulky groups is on the way.

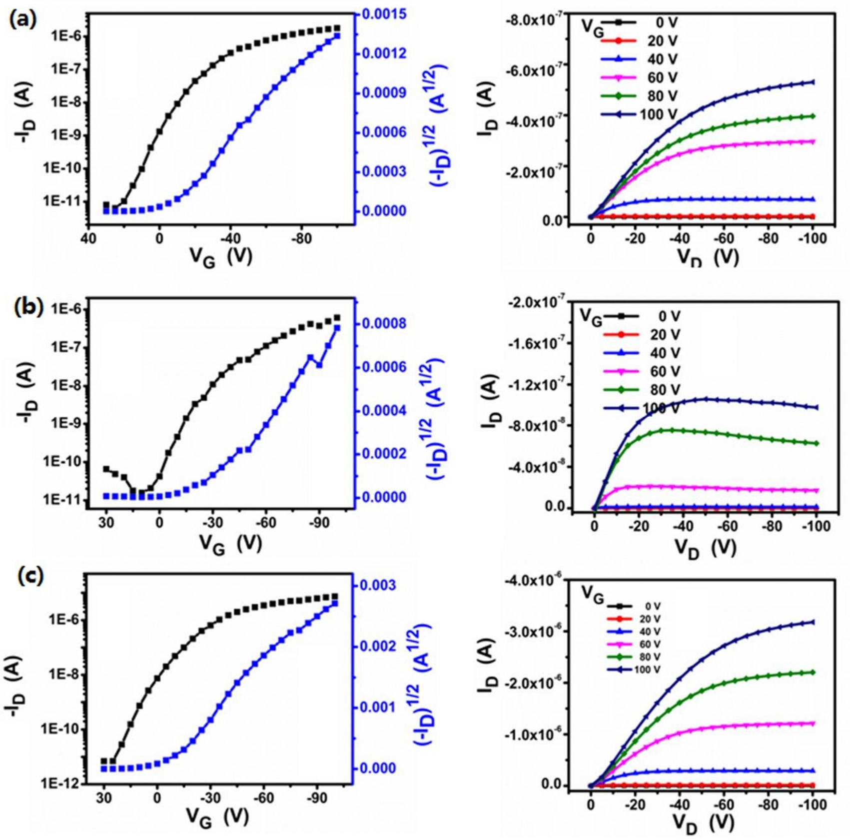


Figure 3 IDS-V plots for OTFT devices fabricated by spin-coating compounds **1-3** onto OTS-treated substrate with optimized annealing temperature, measured under ambient conditions: Output characteristics and transfer characteristics at VDS = -60 V for **1** (a) at 150 °C, **2** (b) at 200 °C and **3** (c) at 150 °C.

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Table 1 The thin-film transistor properties of compounds **1-3** at different annealing temperatures

compound	$T_{annealing}$ (°C)	μ ($cm^2 V^{-1} s^{-1}$)	I_{on}/I_{off}	V_T (V)
1	20	4.4E-04	3×10^4	-17
	100	3.1E-03	1×10^5	0.6
	150	1.2E-02	3×10^5	-5
2	20	2.3E-03	5×10^3	-39
	100	5.0E-03	3×10^2	-27
	150	1.7E-02	4×10^5	-14
	200	5.0E-02	1×10^6	-7
3	100	9.2E-4	8×10^3	-17
	150	5.5E-3(1.2E-2)	1×10^4	-20

Thin films of compounds **1-3,** prepared by different annealing temperatures on OTS-modified SiO_2 substrates, were further characterized by AFM and X-ray diffraction (XRD). Clearly, the higher ordered film morphology could give a positive impact on the improvement of mobility for these three compounds. It should be noted that the threshold voltage of the devices based on compounds **1-2** decreased dramatically after optimization, indicating the less charge traps in optimized films. Further characterizations (using the films of compound **2** as an example) revealed that higher crystallinity as well as bigger grain sizes has been obtained when the annealing temperature increased (**Figure 4**). The device annealed at 200 °C displayed the highest mobility up to 0.05 $cm^2 V^{-1} s^{-1}$ with an on/off current ratio up to 10^6. For compound **1**, AFM images of thin films at individually optimized annealing temperatures are shown in **Figure S16**. Films annealed at 150 °C with clearly larger grain size were much better than those annealed at other temperatures. Further increasing the annealing temperature caused molecules aggregation and form discontinuous clusters, eventually, no charge transport was observed in these devices. Thin films based on compound **3** with extra branching alkyl chains showed totally diverse morphologies, which preferred to self-assemble into ribbon-like architecture as shown in **Figure 5**. The height of the individual ribbon is about 100 nm according to AFM images (**Figure S17**). The device based on one individual microstructure can reach 0.012 $cm^2 V^{-1} s^{-1}$. The microstructure of spin-coated films was investigated by XRD measurement (**Figure S18**). The first intense reflections for compounds **1-3** were observed at $2\theta = 4.41°$, 4.51° and 5.28°, respectively, corresponding to *d*-spacings of 1.99, 1.95 and 1.67 nm. These molecules have almost identical backbones and long alkyl chains, and only one additional isobutyl group were inserted into compound **3**. Thus, we supposed that the diversity in the *d*-spacing resulted from the steric effect of the bulk group. Besides, the π-π distance became larger for its corresponding looser packing mode compared to compounds **1-2**, which caused the relatively low mobility.

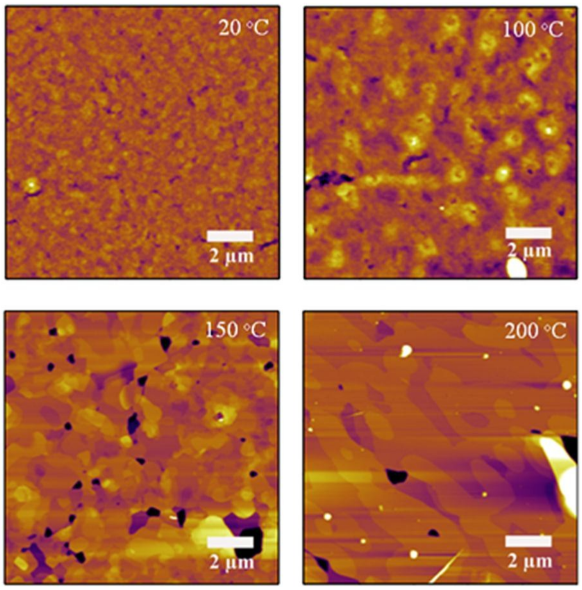

Figure 4 AFM images of thin-films based on compound **2** at different annealing temperatures.

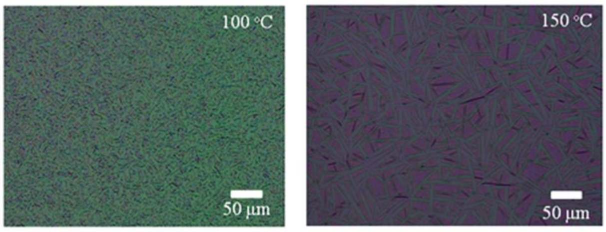

Figure 5 Optical images of thin-films based on compound **3** at different annealing temperatures.

Conclusion

In conclusion, three new [1,2,5]thiadiazolo[3,4-*g*]quinoxaline (TQ)-based derivatives as promising semiconductors for the solution-processed devices have been successfully synthesized and characterized. The optoelectronic and FET properties of compounds **1-3** can be tuned through changing the fused aromatic unit in the TQ core or the side chains. The thin-film transistors for compounds **1-3** show typical *p*-type performance with mobility as high as 0.012, 0.05 and 0.0055 $cm^2 V^{-1} s^{-1}$ and on/off current ratios of 3×10^5, 1×10^6 and 1×10^4 under the optimized condition, respectively. Due to the steric effect of the extra bulk group, compound **3** adopts a looser packing mode with larger π-π distance, which subsequently reduces the transport property. Our results suggest that the D-A π-conjugated small molecules based on TQ could be good candidates for potential application in organic electronics. Future work will focus on the derivatization and the expansion of TQ structures as well as their performance in other organic semiconductor devices.

Acknowledgements

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

Pei-Yang Gu, Jing Zhang, Guankui Long, Zilong Wang, Qichun Zhang

The thin-film transistors for compounds **1**-**3** show typical p-type performance with mobility 0.012, 0.05 and 0.0055 cm^2 V^{-1} s^{-1} and on/off current ratios of 3×10^5, 1×10^6 and 1×10^4, respectively.