

Synthesis and crystal structure of 5,12-diphenyl-6,11-bis(thien-2-yl)tetracene

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Abstract

5,12-Diphenyl-6,11-bis(thien-2-yl)tetracene (**1**) was prepared by reduction of 5,12-diphenyl-6,11-bis(thien-2-yl)-6,11-tetracenediol (**3**) with NaBH₃CN in the presence of weak Lewis acid ZnI₂. A rearranged byproduct, 6,11-dihydro-5,12-diphenyl-6,6'-bis(thien-2-yl)-11,11'-dihydrotetracene (**5**), was also obtained under this condition. Treatment of compound **3** with HI or other strong Lewis acid led to rearrangement and afforded 5,12-diphenyl-6,6'-bis(thien-2-yl)tetracene-11-one (**4**). The structures of compounds **1**, **4** and **5** were confirmed by single crystal X-ray diffraction. The central tetracene rings of molecules **1** are twisted and assemble into arrays with slip parallel molecules in the crystal structure. There is no π - π overlap among the tetracene rings or among the pendant phenyl rings and thienyl rings. © 2008 Elsevier B.V. All rights reserved.

Keywords: Tetracene; Crystal structure; Synthesis; Rearrangement; Reduction

1. Introduction

The polycyclic aromatic hydrocarbon (PAH), rubrene (5,6,11,12-tetraphenyltetracene) has been widely investigated for more than three decades [1,2]. Over past few years, rubrene has offered one of the best materials for organic electronic and optoelectronic devices due to its high mobility. And it has been successfully used in organic light-emitting diodes (OLED) [3–5] and organic field-effect transistors (OFETs) [6–9]. For its wide variety of interesting properties, there has been an increasing interest in the synthesis of new specifically substituted rubrene derivatives in the last years. However, these rubrene derivatives were mostly prepared by introduction of substituent on the pendant phenyl rings, rather than directly on the tetracene backbone ring [10–12]. As an electron-rich substituent, thienyl has been used as a popular building block for many

peculiar electronic and optoelectronic materials, which has been successfully used in many organic semi-conductor devices [13–15]. Herein we wish to report the synthesis of a new thienyl substituted rubrene derivative, 5,12-diphenyl-6,11-bis(dithien-2-yl)tetracene (**1**) (Chart 1). Although chemical structure of compound **1** is very similar to that of rubrene, the synthesis procedure and the crystal structure of **1** are obviously different from those of rubrene. And two rearranged compounds were also obtained, unexpectedly. Their structures were all confirmed by the single crystal X-ray diffractions.

2. Experimental

2.1. General

NMR spectra were obtained on a Bruker AC-300 Spectrometer (300-MHz) as CDCl₃ solution using TMS as the internal standard. Elemental analyses were performed using a Thermo Electron FLASH/EA 1112 instrument. Mass spectra were carried out on a Thermofinnigan LCQ

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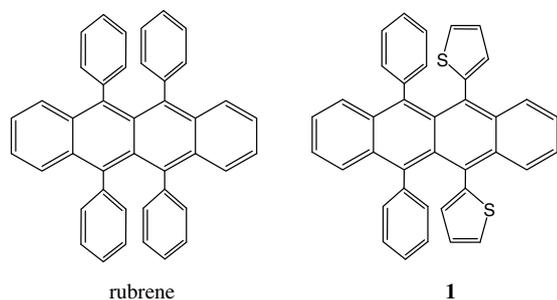


Chart 1. Chemical structures of rubrene and compound 1.

Advantage mass spectrometer. All reagents are commercially available and purified by standard methods prior to use. 6,11-Diphenyl-5,12-tetracenequinone (**2**) was synthesized as described in the literature [16].

2.2. Synthesis

2.2.1. 5,12-Diphenyl-6,11-bis(thien-2-yl)-6,11-tetracenediol (**3**)

To 6,11-diphenyl-5,12-tetracenequinone (5.1 g, 12.5 mmol) in 150 ml dry THF at $-78\text{ }^{\circ}\text{C}$ under argon atmosphere, 1 M 2-thienyllithium THF solution (30 mL) was added slowly. The mixture was allowed to slowly warm up to room temperature and stirred overnight. The reaction was worked up with aqueous solution of saturated NH_4Cl , and extracted with Et_2O . The combined organic extracts were dried (MgSO_4) and then concentrated in vacuum. The resulting solid was washed thoroughly with 4:1 hexanes– Et_2O to give an off-white solid (yield 87%). M_p 172–174 $^{\circ}\text{C}$. ^1H NMR (400 MHz, *d*-acetone): δ 7.62 (d, $J = 7.4$ Hz, 2H), 7.48–7.45 (m, 4H), 7.31 (t, $J = 7.4$ Hz, 2H), 7.20–7.19 (m, 2H), 7.09–6.98 (m, 8H), 6.65 (t, $J = 4.3$ Hz, 2H), 6.44 (d, $J = 5.4$ Hz, 2H), 6.22 (d, $J = 7.5$ Hz, 2H), 5.62 (s, 2H). MS (EI) m/z 578 (M^+). Elemental analysis calcd for $\text{C}_{38}\text{H}_{26}\text{O}_2\text{S}_2$: C, 78.86; H, 4.53; O, 5.53; S, 11.08%. Found: C, 78.79; H, 4.51; O, 5.58; S, 11.12%.

2.2.2. 5,12-Diphenyl-6,6'-bis(thien-2-yl)tetracene-11-one (**4**)

To a 50 mL Et_2O solution of diol **3** (1.15 g, 2 mmol), 57% HI water solution (50 mL) was added at room temperature. The mixture was stirred for 0.5 h before addition of a saturated aqueous solution of sodium metabisulfite. The aqueous portion was extracted with Et_2O , and the combined organic extracts immediately dried (MgSO_4) and concentrated in vacuo to give a red solid, which was recrystallized from CHCl_3 –acetone to give **4** as a bright red crystalline solid (yield 82%). M_p 262–264 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 7.82 (d, $J = 7.6$ Hz, 1H), 7.64–7.51 (m, 4H), 7.45–7.43 (m, 2H), 7.39–7.29 (m, 2H), 7.21–7.18 (m, 3H), 7.08–7.06 (m, 4H), 7.02–6.97 (m, 2H), 6.71 (d, $J = 3.7$ Hz, 2H), 6.64 (t, $J = 5.1$ Hz, 2H), 6.57 (d, $J = 8.1$ Hz, 2H). MS (ESI) m/z 561 (MH^+). Elemental analysis calcd

for $\text{C}_{38}\text{H}_{24}\text{OS}_2$: C, 81.40; H, 4.31; O, 2.85; S, 11.44%. Found: C, 81.44; H, 4.26; O, 2.81; S, 11.49%.

2.2.3. 5,12-Diphenyl-6,11-bis(thien-2-yl)tetracene (**1**) and 6,11-dihydro-5,12-diphenyl-6,6'-bis(thien-2-yl)-11,11'-dihydrotetracene (**5**)

A suspension of diol **3** (0.64 g, 1.1 mmol), ZnI_2 (1.01 g, 3.4 mmol) and NaBH_3CN (0.69 g, 11 mmol) in 1,2-dichloroethane (10 mL) was refluxed (under argon and protected from light) for 20 h. After cooling to room temperature, dichloromethane (30 mL) was added and the solids were filtered off. The clear filtrate was washed with diluted HCl (3 M, 3×30 mL) and dried (MgSO_4), then concentrated in vacuum. The residue was purified by column chromatography (SiO_2 , eluent–hexanes) to give compound **1** (yield 57%) as red crystals and the byproduct **5** as white crystals (yield 30%).

Compound **1** was a red solid: M_p 248–250 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 7.57–7.54 (m, 2H), 7.42 (broad, 2H), 7.23–7.13 (m, 14H), 6.93 (broad, 2H), 6.73 (broad, 2H), 6.44 (broad, 2H). MS (EI) m/z 544 (M^+). Elemental analysis calcd for $\text{C}_{38}\text{H}_{24}\text{S}_2$: C, 83.79; H, 4.44; S, 11.77%. Found: C, 83.85; H, 4.47; S, 11.68%.

Compound **5** was a white solid: M_p 286–288 $^{\circ}\text{C}$. ^1H NMR (400 MHz, *d*-acetone): δ 7.62–7.53 (m, 3H), 7.44–7.39 (m, 3H), 7.28 (t, $J = 6.6$ Hz, 1H), 7.17 (t, $J = 7.4$ Hz, 1H), 7.07–6.90 (m, 10H), 6.83 (d, $J = 6.8$ Hz, 2H), 6.65–6.60 (m, 4H), 3.86 (s, 2H). MS (EI) m/z 546 (M^+). Elemental analysis calcd for $\text{C}_{38}\text{H}_{26}\text{S}_2$: C, 83.48; H, 4.79; S, 11.73%. Found: C, 83.54; H, 4.75; S, 11.71%.

2.3. X-ray crystallography

The diffraction-quality single crystals of **1**, **4**, **5** were mounted on glass fibers in random orientation using epoxy-glue. Bruker SMART 1000 CCD automatic diffractometer was used for data collection at $T = 294(2)$ K using graphite monochromated $\text{MoK}\alpha$ -radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods, and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the SHELXTL package. More details on data collection and structure calculation are summarized in Table 1. Crystallographic data for all structures reported here have been deposited with the Cambridge Crystallographic Data Centre; CCDC numbers are given in Table 1.

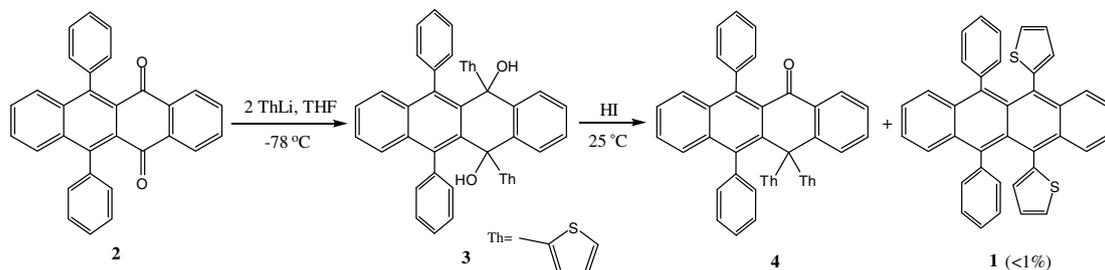
3. Results and discussion

3.1. Synthesis

The key intermediate, 5,12-diphenyl-6,11-bis(thien-2-yl)-6,11-tetracenediol (**3**), was synthesized, by the addition of 5,12-diphenyl-6,11-tetracenequinone (**2**) with thienyllithium (Scheme 1), and fully characterized. HI has been used widely to reduce tetracenediols for rubrene derivatives

Table 1
Experimental data for the X-ray diffraction studies of prepared compounds at 294(2) K

	1	4	5
No. in CCDC	659,313	659,311	659,312
Empirical formula	C ₃₈ H ₂₄ S ₂	C ₃₈ H ₂₄ OS ₂ ·1.5C ₄ H ₈ O	C ₃₈ H ₂₆ S ₂
Formula weight	544.69	668.85	546.71
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2 ₁ /c	C2/c	P2 ₁ /n
a (Å)	22.036(4)	35.265(5)	18.463(6)
b (Å)	8.8034(17)	9.4510(14)	8.190(3)
c (Å)	30.252(6)	23.373(4)	18.624(7)
α (°)	90	90	90
β (°)	104.921(4)	115.779(3)	98.288(6)
γ (°)	90	90	90
V (Å ³)	5671(2)	7014.7(18)	2786.7(16)
Z	8	8	4
D _{calcd} (mg/m ³)	1.276	1.267	1.303
Crystal size (mm)	0.22 × 0.20 × 0.18	0.20 × 0.18 × 0.14	0.20 × 0.16 × 0.10
μ (mm ⁻¹)	0.214	0.191	0.218
F (000)	2272	2816	1144
θ Range for data col. (°)	1.39–25.02	1.80–25.01	1.45–25.02
Index ranges	–16 ≤ h ≤ 26, –10 ≤ k ≤ 10, –36 ≤ l ≤ 33	–39 ≤ h ≤ 41, –11 ≤ k ≤ 10, –27 ≤ l ≤ 19	–21 ≤ h ≤ 21, –9 ≤ k ≤ 5, –22 ≤ l ≤ 21
Completeness (%)	100	98.4	98.1
Reflections collected/unique	28,527/10,019	17,383/6084	13,229/4832
R _{int}	0.1077	0.0618	0.1674
Data/restraints/parameters	10,019/0/721	6084/269/501	4832/167/399
Goodness-of-fit on F ²	1.008	1.064	1.030
Final R indices [I > 2σ(I)]	R ₁ = 0.0691, wR ₂ = 0.1491	R ₁ = 0.0760, wR ₂ = 0.1920	R ₁ = 0.0783, wR ₂ = 0.1488
R indices (all data)	R ₁ = 0.1981, wR ₂ = 0.1984	R ₁ = 0.1561, wR ₂ = 0.2468	R ₁ = 0.2369, wR ₂ = 0.2049
Largest diff. peak and hole (e Å ⁻³)	0.313 and –0.422	0.509 and –0.384	0.330 and –0.369



Scheme 1. Synthesis of compound 3. Reaction of 3 with HI mainly to give rearranged compound 4.

[16]. However, when 5,12-diphenyl-6,11-bis(thien-2-yl)-6,11-tetracenediol (**3**) was reacted with HI acid under the literature condition, the expected 5,12-diphenyl-6,11-bis(thien-2-yl)tetracene (**1**) was produced in rather small yield (<1%) and the main product was a rearranged compound, 5,12-diphenyl-6,6'-bis(thien-2-yl)tetracene-11-one (**4**, Scheme 1). The structure of compound **4** was confirmed by single crystal X-ray diffraction study (Fig. 1). Apparently, the unexpected product **4** is formed by migration of the thienyl ring.

Indeed, some electron-rich substituents favor rearrangement in the preparation of substituted anthracene and pentacene derivatives [17–19]. We also used KI/NaH₂PO₂ to try the reduction reaction in refluxing ace-

tic acid. Similarly, this method also converted the diol **3** mainly to the rearranged product **4**. It is obvious that the thienyl ring on the tetracene migrates quite easily under strong Lewis acid condition such as in HI or acetic acid. We noticed that the reduction of analogous anthracenediol derivatives was successfully achieved by treating them with ZnI₂ (as weak Lewis acid) and NaBH₃CN (as reductant) in 1,2-dichloroethane [20]. So we used the same method to reduce the diol **3**. Indeed, this condition gave the desired compound **1** with 57% yield (Scheme 2). Interestingly, another byproduct was isolated under this condition. By X-ray crystallographic analysis, we found that it was another rearranged compound, 6,11-dihydro-5,12-diphenyl-6,6'-bis(thien-2-yl)-

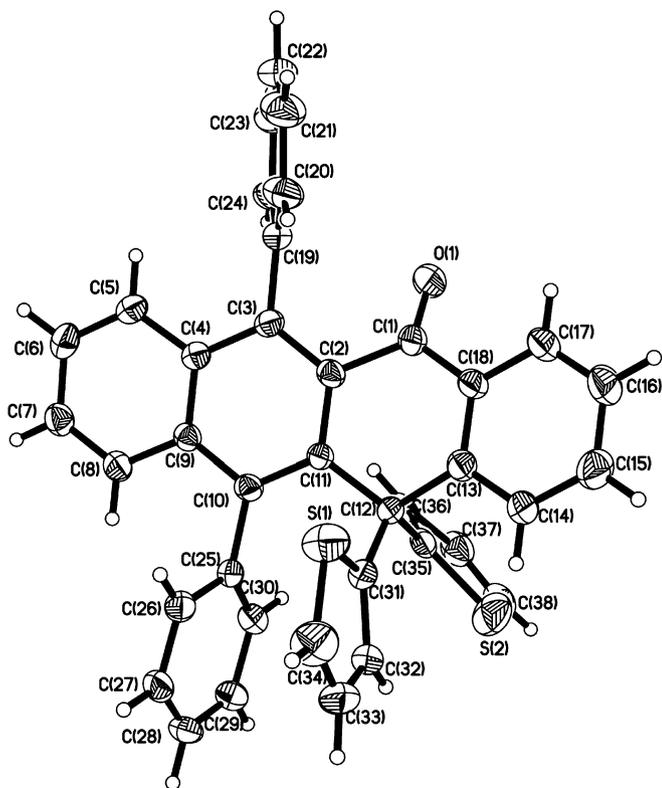


Fig. 1. Molecular structure of compound 4. Thermal ellipsoids have been drawn at the 30% probability level.

11,11'-dihydrotetracene **5** (Fig. 2). Because NaBH_3CN can reduce ketones and alcohols to the corresponding alkanes in the presence of ZnI_2 [18,21], we suspect that this byproduct was formed by the reduction of the rearranged product **4**. Although the side-reactions seemed inevitable, this reduction condition provided acceptable yield of compound **1**. The absorption and photoluminescent (PL) spectra of compound **1** in CH_2Cl_2 solution are presented in Fig. 3. The maximum absorption of compound **1** is at 300 nm. And there also have broad weak absorptions about at 450–550 nm. Compound **1** shows strong orange fluorescence in CH_2Cl_2 solution [$\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2) = 589 \text{ nm}$, quantum yield = 45%].

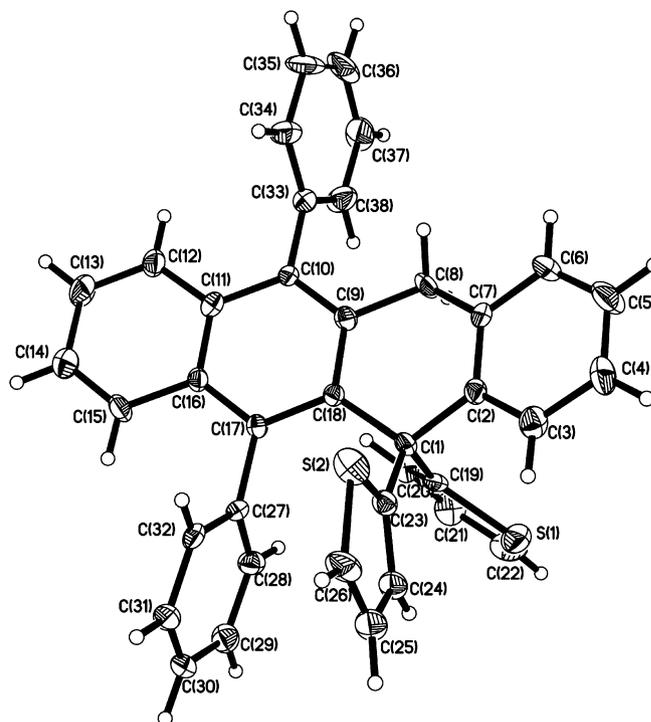
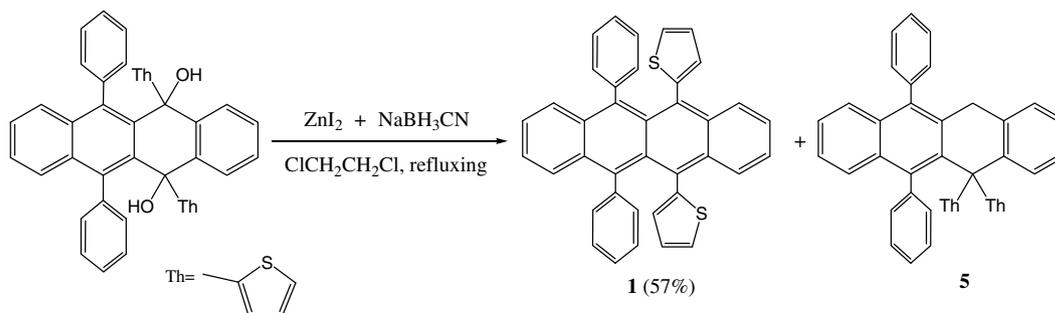


Fig. 2. Molecular structure of compound 5. Thermal ellipsoids have been drawn at the 30% probability level.

3.2. Crystal structures

Compound **4** easily crystallized as bright red prisms from tetrahydrofuran (THF) in monoclinic space group $C2/c$ ($Z = 8$). The crystal structure of **4** consists of one molecule of **4** and two THF solvate molecules, one with partial occupancy (50%). Compound **5** crystallized as white prisms from CHCl_3 -acetone in monoclinic space group $P2_1/n$ ($Z = 4$). Lattice parameters and other crystallographical data of **4** and **5** are given in Table 1.

The single crystal suitable for the X-ray diffraction study of compound **1** was grown from CH_2Cl_2 -MeOH solution. Compound **1** crystallizes in the common monoclinic space group $P2_1/c$ ($Z = 8$). The crystal structure of compound **1** is depicted in Fig. 4. Two molecules of **1** were present in the crystal as crystallographically independent molecules. Clearly, the tetracene ring of **1** is twisted,



Scheme 2. Reaction of **3** with ZnI_2 and NaBH_3CN to give compound **1** and rearranged compound **5**.

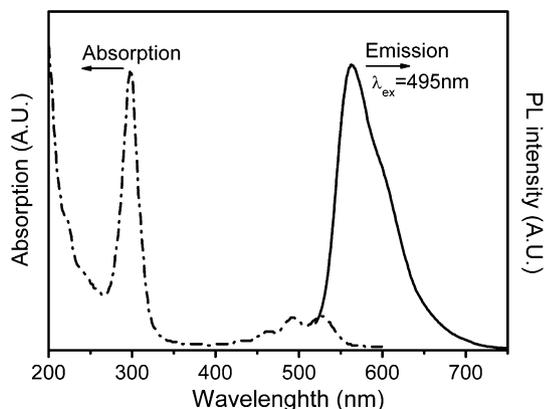


Fig. 3. UV-vis absorption and photoluminescence (PL) spectra of compound **1** measured in dilute CH_2Cl_2 solution. Compound **1** shows strong orange fluorescence [$\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2) = 589 \text{ nm}$].

not as expected as planar. To the two independent molecules, the twist directions of the tetracene rings are reversed and the two twist angles are different. The end to end twist of molecule **I** is 27.9° ; that of molecule **II**

is 36° . The stacking of molecules **1** is illustrated in Fig. 5. The tetracene rings of molecules **1** assemble into an array with slip parallel molecules and the adjacent two molecules are not face to face directly in the array. The separation between two adjacent parallel molecules is 6.8 Å. This length is larger than the typical van der Waals interaction distance in a C–C π -stack [22,23]. So there is no π – π stacking interaction among the tetracene rings in the arrays. Also because of the twist of the tetracene ring, the pendant phenyl rings and thienyl rings have no overlap in the individual molecule. These structure characteristics are quite different from that of rubrene [9,22], where the tetracene ring is nearly planar and the tetracene rings form π – π overlap in the crystal. The replacement of the two pendant phenyl rings with two thienyl rings results in significant change of the molecular structures.

We had expected that compound **1** might show high mobility. Thus high pure single crystal of compound **1** was grown by horizontal physical vapor transport in a stream of ultra high purity argon. We have fabricated

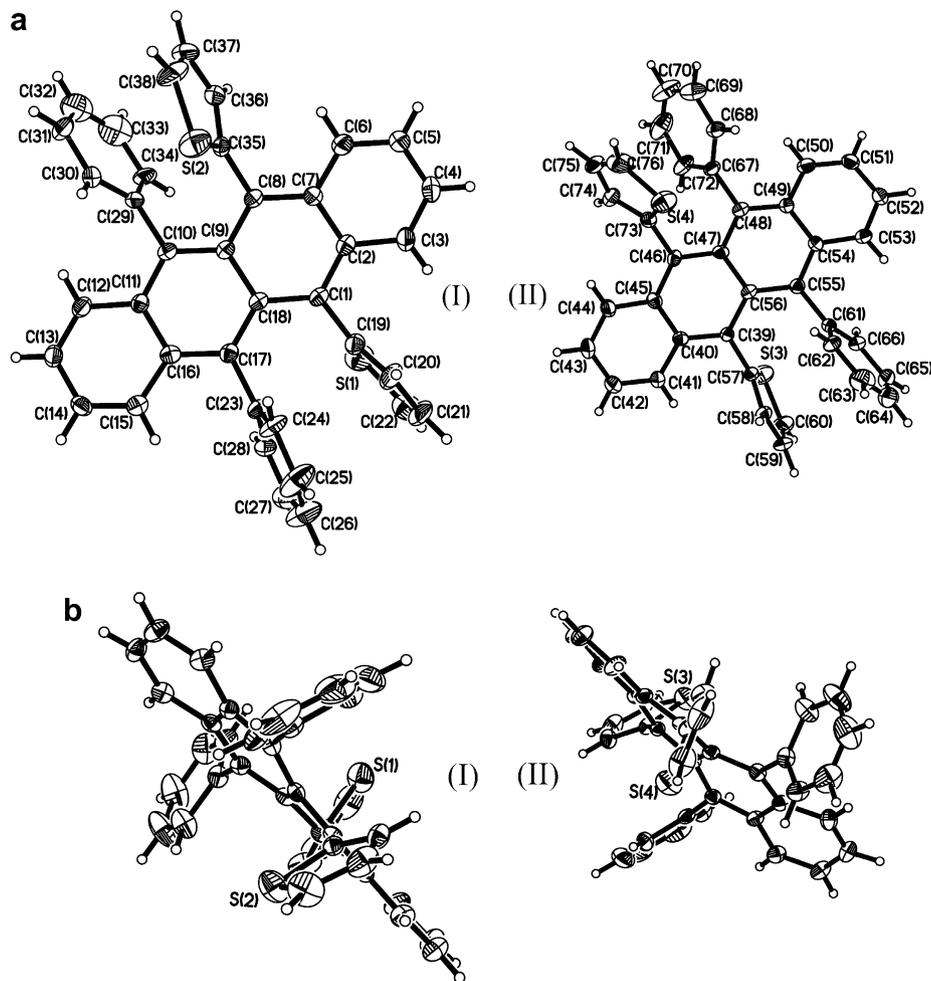


Fig. 4. (a) Molecular structure of compound **1**; both of the crystallographically independent molecules are shown. (b) Stereoview of the crystallographically independent molecules. Thermal ellipsoids have been drawn at the 30% probability. To the two independent molecules, the twist directions of the tetracene rings are reversed.

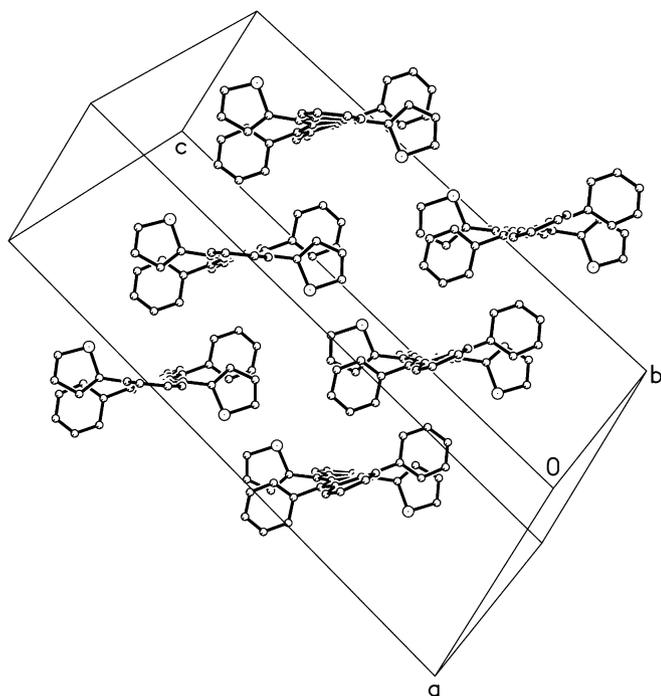


Fig. 5. Packing structure of molecule **1** in single crystal. Hydrogen atoms have been omitted for clarity and thermal ellipsoids have been drawn at the 30% probability level. The tetracene rings of molecules **1** assemble into an array with slip parallel molecules.

FET devices using its single crystals, but disappointingly no FET property was observed. This is probably due to the twist of the tetracene ring of **1** as discussed above, which makes it difficult to form the enhanced intermolecular π – π overlap as rubrene, and no FET property could be observed.

4. Conclusions

In summary, 5,12-diphenyl-6,11-bis(thien-2-yl)tetracene (**1**) was successfully synthesized by the reduction of 5,12-diphenyl-6,11-bis(thien-2-yl)-6,11-tetracenediol (**3**) with NaBH_3CN in the presence of ZnI_2 . Because of the thienyl migration, two rearranged products, **4** and **5**, were also obtained. The structure of **1** is quite different from that of rubrene and the significant twist of the tetracene ring of **1** destroys the π – π overlap existed in rubrene.

Acknowledgements

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Appendix A. Supplementary data

Crystallographic data for all structures reported here have been deposited with the Cambridge Crystallographic Data Centre; CCDC numbers are given in Table 1. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

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