

# Stable 7,14-Disubstituted-5,12-Dithiapentacenes with Quinoidal Conjugation

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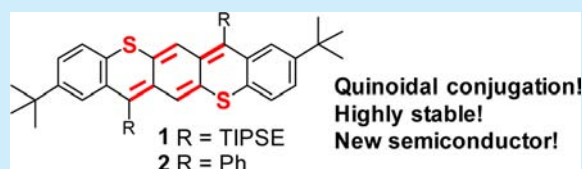
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## S Supporting Information

**ABSTRACT:** Two 7,14-disubstituted-5,12-dithiapentacenes (**1** and **2**) with quinoidal conjugation were synthesized. Their ground-state quinoidal structures were proven by X-ray crystallographic analysis. They showed very different electronic and optical properties from those of the corresponding pentacene derivatives with diene conjugation, and their stability was significantly improved. Organic field effect transistors based on solution processed thin films of **1** and **2** exhibited a hole mobility of up to  $0.032 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .



Acene-based molecular materials have been demonstrated to be useful semiconductors and chromophores.<sup>1</sup> However, one drawback which hampers their general applications is their intrinsic instability.<sup>2</sup> For all acene molecules, only one aromatic sextet ring (highlighted in green color in Scheme 1) can be drawn, and thus the diene character increases with the extension of molecular length, which results in high reactivity for acenes longer than anthracene. Typical reactions of acenes related to the diene conjugation include addition with singlet oxygen to form endoperoxide and dimerization under light irradiation. Several strategies have been employed to increase the robustness of acenes, such as substitution by trialkylsilyl ethynyl groups,<sup>3</sup> electron-withdrawing fluorine atoms,<sup>4</sup> cyano groups<sup>5</sup> and carboximide groups.<sup>6</sup> Another strategy is to disturb the diene-type conjugation by fusion of five-membered rings onto the zigzag edges of acenes.<sup>7</sup>

Herein, we propose to develop stable heteroacenes by incorporation of a quinoidal moiety into the acene framework. Taking pentacene as an example, a *p*-quinodimethane (*p*-QDM) bridged heteropentacenes containing two sulfur, nitrogen, or oxygen atoms can be drawn with two aromatic sextet rings (Scheme 1), and thus they could show improved stability. In addition, the pro-aromatic *p*-QDM unit can dramatically change their electronic and optical properties. In fact, quinoidal  $\pi$ -conjugated systems have drawn increasing attention recently due to their small energy gap and intrinsic biradical character,<sup>1e,8</sup> which lead to promising applications as nonlinear optical chromophores<sup>9</sup> and ambipolar/*n*-type semiconductors.<sup>10</sup> To date, the heteroacenes and their isoelectronic structures with quinoidal conjugation have been rarely investigated.<sup>11</sup> In this work, we focused on the 5,12-dithiapentacene framework and two stable derivatives **1** and **2**

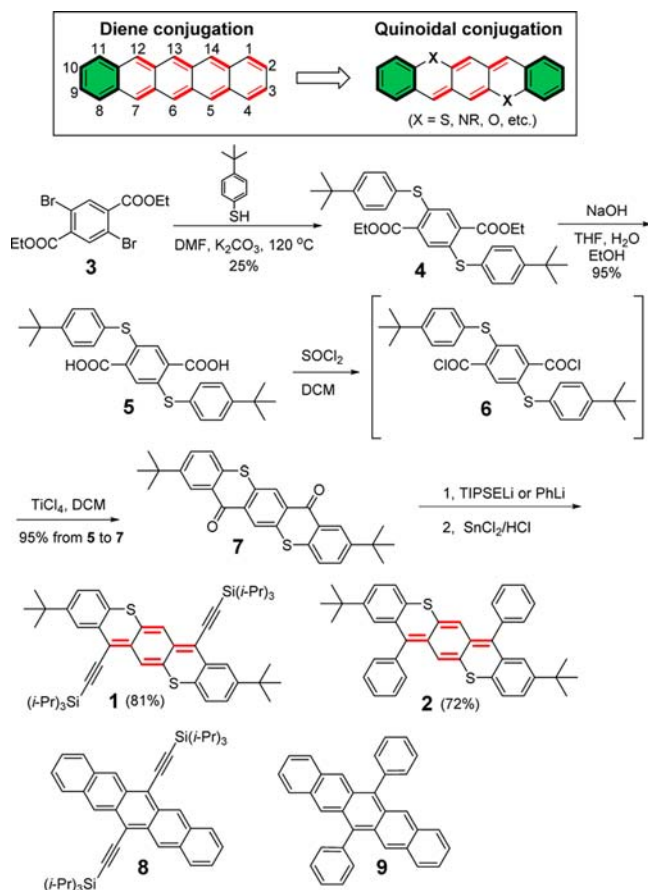
were successfully synthesized (Scheme 1). Their ground-state geometric structures, optical properties, and electronic properties were investigated in detail and compared with their pentacene counterparts, the bis(triisopropylsilyl ethynyl)pentacene (TIPS-pentacene) **8** and the 6,13-diphenylpentacene (DPP) **9** (Scheme 1). Their potential as charge transporting materials was also evaluated in organic field effect transistors (OFETs).

Synthesis of the 5,12-dithiapentacenes **1** and **2** was outlined in Scheme 1. Diethyl 2,5-dibromoterephthalate<sup>12</sup> underwent a nucleophilic attack reaction by *tert*-butylthiophenol to give compound **4** in 25% yield. The diester **4** was then hydrolyzed by sodium hydroxide to quantitatively afford the diacid intermediate **5**, which was then converted to the diacyl chloride **6** in the presence of thionyl chloride. The intramolecular Friedel–Crafts acylation reaction of **6** was carried out with  $\text{TiCl}_4$  to generate the key intermediate dithioquinacridone **7**. The overall yield from **4** to **7** was 90%. The attachment of two *tert*-butyl groups was necessary to afford sufficient solubility for **7** and also for the subsequent synthesis. The triisopropylsilyl ethynyl (TIPSE) and the phenyl substitution groups were introduced to the 7,14-positions by nucleophilic addition of **7** with the corresponding lithium reagents. Subsequent reduction of the generated diols with tin(II) chloride afforded the target compounds **1** and **2** in good yields. Compounds **1** and **2** showed good stability and solubility in normal organic solvents (e.g., hexane, chloroform), and their structures were confirmed by NMR, mass spectrometry, elemental analysis (EA), and X-ray crystallographic analysis (*vide infra*).

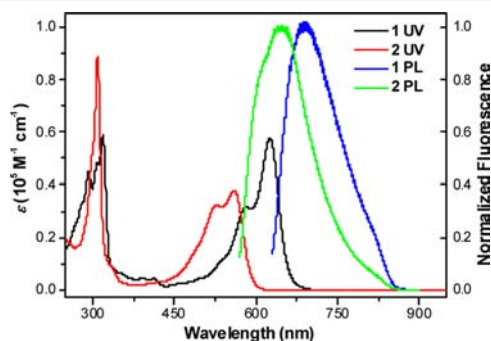
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**Scheme 1. Schematic Representation of Diene Conjugation in Pentacene and Quinoidal Conjugation in Heteropentacenes, and Synthetic Route of Compounds 1 and 2**



The UV–vis absorption and photoluminescence (PL) spectra of compounds 1 and 2 were recorded in diluted chloroform solutions (Figure 1 and Table S1 in the Supporting

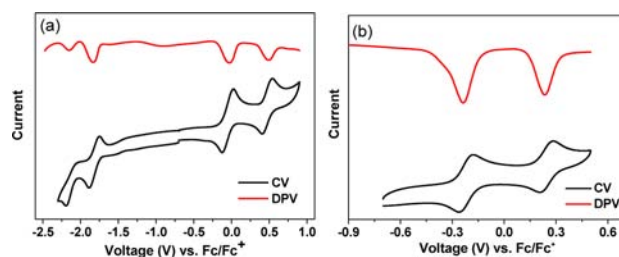


**Figure 1.** UV–vis and PL spectra of compounds 1 and 2 in chloroform solution ( $10^{-5}$  M for UV–vis absorption measurements and  $10^{-6}$  M for PL measurements).

Information (SI)). The 7,14-bisTIPSE substituted compound 1 mainly absorbed in the region 500–650 nm with the maximum at 625 nm. For the 7,14-diphenyl-substituted compound 2, the absorption maximum was hypsochromically shifted to 558 nm. This could be rationally explained by more extended conjugation along the TIPSE substitution for compound 1. For compound 2, the phenyl groups were found to be almost

perpendicular to the central dithiapentacene plane, which limited the effective  $\pi$ -extension along the phenyl groups (*vide infra*). For comparison, the absorption maxima of the TIPS-pentacene (8) and DPP (9) are located at 644 and 603 nm, respectively.<sup>3b,13</sup> It is worthy to note that, for both compounds 1 and 2, they have superior stability in solution compared with the pentacene derivatives 8 and 9. The chloroform solution of 1 was stored at ambient conditions for over 2 months, and no obvious decomposition was observed. Under the same conditions, the TIPS-pentacene 8 gradually decomposed within 1 day. The substantially increased stability of these quinoidal heteropentacenes would most likely originate from the disruption of the normal diene conjugation of acenes and hence interrupting the decomposition pathways although they have two more electrons than that of 8 and 9. Compounds 1 and 2 showed weak emission with the maximum at 692 and 648 nm, respectively. For comparison, compounds 8 and 9 showed modest fluorescence in chloroform with the maximum at 648 and 611 nm, respectively. Thus, the quinoidal heteropentacenes 1 and 2 showed much larger Stokes shifts compared to 8 and 9. The optical energy gaps were determined as 1.88 and 2.09 eV for 1 and 2, respectively, from the longest absorption wavelength onset.

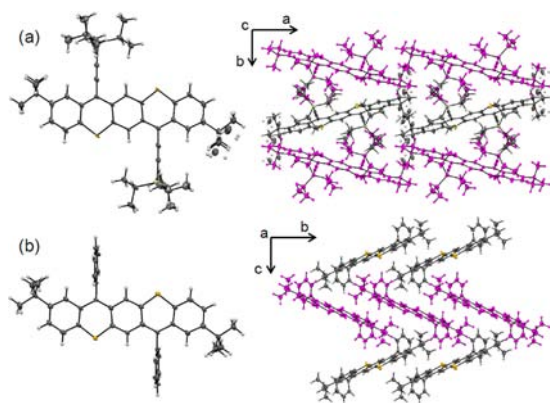
The electrochemical properties of compounds 1 and 2 were measured by cyclic voltammetry and differential pulse voltammetry in dry  $\text{CH}_2\text{Cl}_2$  (Figure 2 and Table S1 in the



**Figure 2.** Cyclic voltammograms and differential pulse voltammograms of 1 (a) and 2 (b) measured in dry  $\text{CH}_2\text{Cl}_2$ .

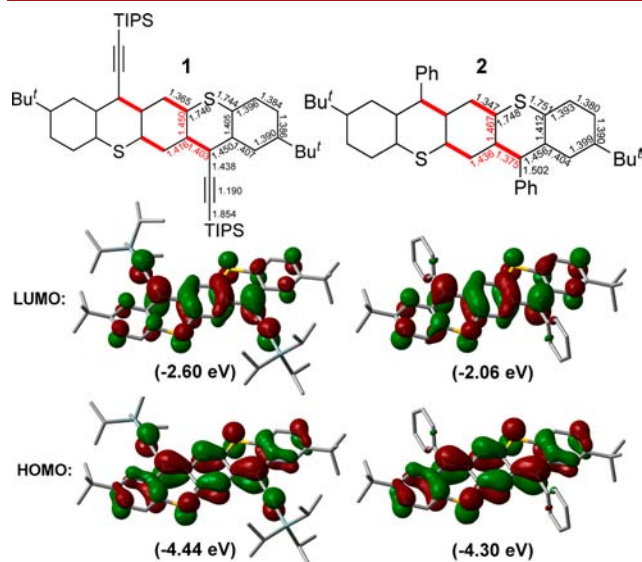
SI). Compound 1 showed two reversible oxidation waves and one reversible reduction wave, with the half-wave potential ( $E_{1/2}$ ) at  $-0.02$ ,  $0.49$ , and  $-1.83$  V (vs  $\text{Fc}/\text{Fc}^+$ ,  $\text{Fc}$ : ferrocene), respectively. Compound 2 showed two reversible oxidation waves with  $E_{1/2}$  at  $-0.24$  and  $0.23$  V, and one irreversible reduction wave. The HOMO energy levels were determined to be  $-4.67$  and  $-4.52$  eV for 1 and 2 according to the following equation:  $\text{HOMO} = -(4.8 + E_{\text{ox onset}})$ ,<sup>14</sup> respectively, where  $E_{\text{ox onset}}$  is the onset potential of the first oxidation wave. For comparison, the HOMO energy levels of 8 and 9 are  $-5.16$  and  $-5.04$  eV respectively,<sup>13,15</sup> which are 0.5 eV lower than that of the corresponding quinoidal heteropentacene analogues 1 and 2. The electron-donating nature of the thioether linkage in the backbone would account for the increased HOMO energy levels for the 5,12-dithiapentacenes 1 and 2 which have two more electrons than their counterparts 8 and 9.

Single crystals suitable for X-ray crystallographic analysis were obtained for both 1 and 2 by slow diffusion of methanol to the chloroform solutions (Figure 3). For both compounds, the 5,12-dithiapentacene backbone is essentially planar. For 2, the substituted phenyl rings are tilted to the central plane by about  $80^\circ$  and this explains the observed shorter wavelength of absorption maximum compared with 1. Similar to pentacene and heavily substituted heptacene,<sup>16</sup> both 1 and 2 pack in a



**Figure 3.** X-ray crystallographic structures and molecular packing of **1** (a) and **2** (b).

herringbone motif. There is no  $\pi$ - $\pi$  stacking between the 5,12-dithiapentacene backbone in both cases, but close contact between the outmost benzene rings (in **1**) or the diphenyl rings (in **2**) and the *tert*-butyl group were observed (Figure S1 in the SI). For comparison, TIPS-pentacene **8** packs in a two-dimensional slipped face-to-face packing motif<sup>3a</sup> and the DPP **9** packs in columns of cage-like dimers.<sup>17</sup> By analyzing the bond lengths of **1** and **2**, both compounds had typical quinoidal type conjugation (Figure 4). For compound **1**, the bond length alternation is smaller than that of **2**, which would be due to the more extended  $\pi$ -conjugation to the attached ethynyl moieties.



**Figure 4.** Selected bond lengths, and calculated HOMO/LUMO profiles and energy levels of **1** and **2**.

Density functional theory (DFT, B3LYP/6-31G\*\*) calculations were conducted to better understand the electronic and optical properties of the quinoidal 5,12-dithiapentacenes **1** and **2**. For compound **1**, the HOMO/LUMO coefficients are distributed along the whole conjugated framework including the ethynyl units, while the phenyl rings in **2** are nearly nonconjugated to the dithiapentacene backbone (Figure 4). The largest molecular orbital coefficient is located at the *p*-QDM unit. The HOMO/LUMO energy levels were calculated to be  $-4.44/-2.60$  eV for **1** and  $-4.30/-2.06$  eV for **2**. Time-dependent DFT calculations predicted the longest wavelength

HOMO  $\rightarrow$  LUMO transition at 638.5 nm (oscillator strength  $f = 0.8551$ ) for **1** and 546.7 nm ( $f = 0.8915$ ) for **2** (Figures S2–S3 in the SI), which is consistent with the experimental data.

To probe the charge transport properties of compounds **1** and **2**, thin-film field effect transistors were fabricated by a solution processing method. Both compounds showed *p*-type behavior under negative gate voltage bias in the device, and the typical transfer and output curves are shown in Figure S4 in the SI. The devices revealed an average hole mobility of  $0.032 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $0.013 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in the saturation region for compounds **1** and **2**, respectively, in nitrogen. The current on/off ratio of **1** and **2** is about  $10^5$ – $10^6$ , and the threshold voltage is around  $-7$  and  $0$  V, respectively. When operated in air, the hole mobility declined to  $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for **1** and  $0.002 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for **2** with a large negative threshold voltage shift and decreased on/off ratio of  $10^3$ – $10^4$ . This is due to the low ionization energy for these two compounds, and the semiconductor layer might be easily doped by molecular oxygen from an ambient environment.<sup>18</sup>

Atomic force microscope (AFM) and X-ray diffraction (XRD) techniques were employed to investigate the thin film morphology, and the results are shown in Figures S5–S6 in the SI. Compound **1** exhibited well-resolved terrace-like layer-by-layer morphology in the thin film. The thickness of one layer was estimated to be 1.8 nm based on the AFM measurement, which is correlated to the length of **1** along the dithiapentacene backbone. Compound **2** exhibited similar terrace-like morphology with a smaller crystal size. Homogeneity and continuity of the layers are also envisaged, which are beneficial for charge transport in the thin film. The XRD diffraction peaks correspond well to a layer-like lamellar packing motif with a  $d$  spacing value of 1.67 and 1.36 nm for thin films of **1** and **2**, respectively, which was approximately the thickness of one layer of the terrace. The strong crystallinity of the thin film was also reflected by the observation of the long-range order of Bragg diffraction peaks. All these factors made compound **1** and **2** favorable as hole charge transporting materials in the transistor device.

In summary, two 7,14-disubstituted-5,12-dithiapentacenes **1** and **2** were successfully prepared and their ground-state geometry and physical properties were investigated in detail. Both compounds have a typical quinoidal structure and packed in a herringbone motif in the crystal. They showed much improved stability compared with the corresponding diene-type conjugated pentacenes although they have much higher lying HOMO energy levels. They can be reversibly oxidized into the radical cation and dication forms. Although there is no typical  $\pi$ - $\pi$  stacking in the crystalline form, the thin films of **1** and **2** showed moderate field effect hole mobilities due to their ordered packing and the existence of intermolecular close contacts. Synthesis of quinoidal heteroacenes with more extended conjugation is underway in our laboratory.

## ■ ASSOCIATED CONTENT

### § Supporting Information

Synthetic procedures and characterization data for all new compounds, DFT calculation details, X-ray crystallographic data, AFM and XRD data, and more data on device fabrication and characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.



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## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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