



## TTF and TCNQ analogues derived from a new benzo-fused thiopyranyl building block

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### ABSTRACT

TTF-type and TCNQ-type analogues (**9–12**) have been prepared from a new benzo-fused thiopyranyl precursor **8**. The synthetic conditions of **8** were optimized. An anomaly was observed in the <sup>1</sup>H NMR spectrum of **9**. The crystal structures of **9** and **10** show distorted conformations and ordered packing geometries connected by short contacts. Electronic and redox properties of **9–12** were investigated by UV–vis spectroscopy and cyclic voltammetry. Both **9** and **10** exhibited *p*-type OFET performances.

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Over the past decades, there has been increasing interest in the synthesis of  $\pi$ -extended tetrathiafulvalene and tetracyano-*p*-quinodimethane analogues (exTTFs and exTCNQs) due to their versatile applications in many areas such as supramolecular and organic electronic materials chemistry.<sup>1</sup> Different  $\pi$ -spacers spanning from planar<sup>2</sup> to nonplanar<sup>3</sup> conjugated units, have been employed to construct new exTTFs and exTCNQs. Among numerous examples, anthraquinone-derived exTTFs (such as TTFAQ) and exTCNQs (such as TCAQ)<sup>4</sup> are mostly studied, and exhibit attractive redox and structural properties. In these systems, the electroactive units, that is, the 1,3-dithiole rings or dicyanomethylene fragments are in a relative *para*-position, and the molecules adopt twisted butterfly shaped geometries in neutral state due to the steric interaction of the aromatic *peri*-hydrogens with the electroactive units. Another interesting system, in which the electroactive units are in a relative *meta*-position, is less studied, and only a few examples, such as azulene<sup>5</sup> or pyridine-bridged<sup>6</sup> exTTFs have been reported. The *meta*-linkage would lead to electronic decoupling of the electroactive units in the ground states, and to electronic coupling in the excited states.

To shed more light on the relationship between the electronic states and the different linking mode of the electroactive units relative to the  $\pi$ -spacer, we report herein on the synthesis and properties of a class of TTF and TCNQ analogues (**9–12**) derived from a new benzo-fused thiopyranyl building block. As we know, 2-(thiopyran-4'-ylidene)-1,3-dithiole (TPDT) was synthesized about twenty years ago,<sup>7</sup> and the  $\pi$ -extension of TPDT was achieved by the benzo-fusing on the dithiole ring.<sup>8</sup> However, the benzo-fusing on the thiopyran ring was rarely reported, and novel structural benzo-fused thiopyranyl systems are not at hand. Therefore, rea-

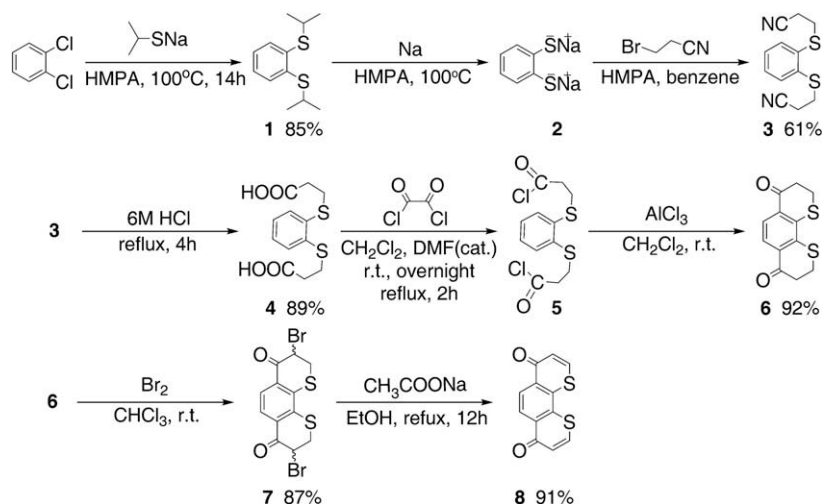
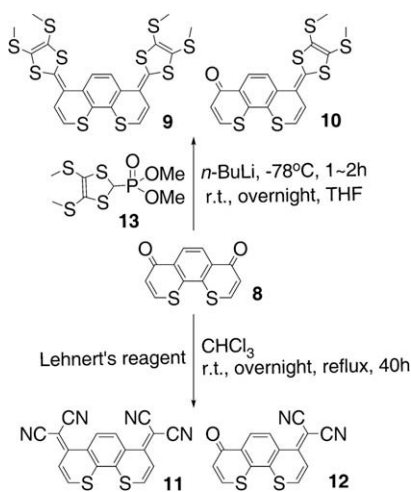
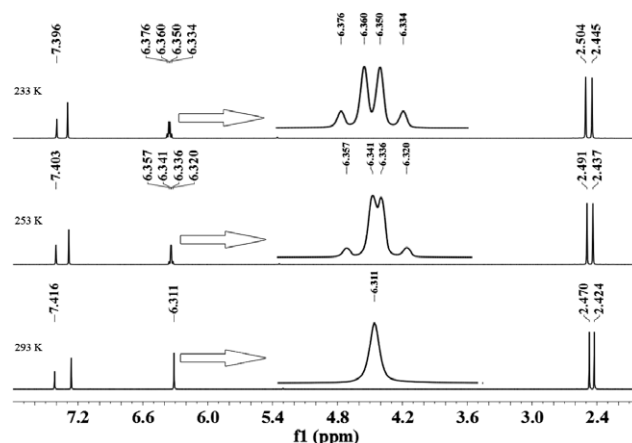
sonable design and synthesis of new  $\pi$ -spacers based on thiopyranyl systems are necessary for the development of new exTTFs and exTCNQs.

The main structural feature of our compounds includes a thiopyrano[3,2-*h*]thiochromene moiety, which was introduced by the Wittig–Horner or Knoevenagel reaction of the precursor **8** with phosphonate ester **13** or malononitrile, respectively. As shown in Scheme 1, **8** was obtained through eight steps. The synthesis began with a nucleophilic aromatic substitution of *o*-dichlorobenzene with thiolate ions in hexamethylphosphoramide (HMPA) at 100 °C. We had improved the yield of **1** to ca. 85% and shortened the reaction time to ca. 14 h by using high concentration of the freshly prepared sodium 2-propanethiolate (2 mol/L in HMPA). The following dealkylation of **1** was conducted smoothly according to the well-established methods reported by M. Tiecco's group,<sup>9</sup> then the intermediate **2** was added reversely into the benzene solution of 3-bromopropionitrile to give **3** with a yield of ca. 60%. **3** was converted to the corresponding diacid (**4**) in a satisfactory yield of 89% by boiling it in concentrated HCl (6 M) for 4–5 h. Due to the failure of the direct phosphoric acid (PPA) ring-closure of **4**, it was firstly transformed into the diacyl chloride **5** by oxalyl chloride, then **5** was cyclized to **6** quantitatively and neatly under Friedel–Crafts condition (AlCl<sub>3</sub> as a catalyst) at room temperature.<sup>10</sup> The conventional dehydrogenation methods<sup>11</sup> could not succeed in the conversion of **6** into **8**, and the halogenation-dehydrohalogenation sequence turned out to be the method of choice.<sup>12</sup> The  $\alpha$ -dibromination of diketone **6** yielded a mixture of diastereomers (**7**),<sup>13</sup> which gave rise to **8** by treatment with sodium acetate in refluxing ethanol. The overall yield was 34% for the whole synthetic route.

The synthesis of TTF and TCNQ analogues (**9–12**) is shown in Scheme 2. The TCNQ analogues (**11** and **12**) were prepared from **8** by Knoevenagel condensation using Lehnert's reagent (malononitrile, TiCl<sub>4</sub>, and pyridine).<sup>14</sup> The conjugated olefinic structure

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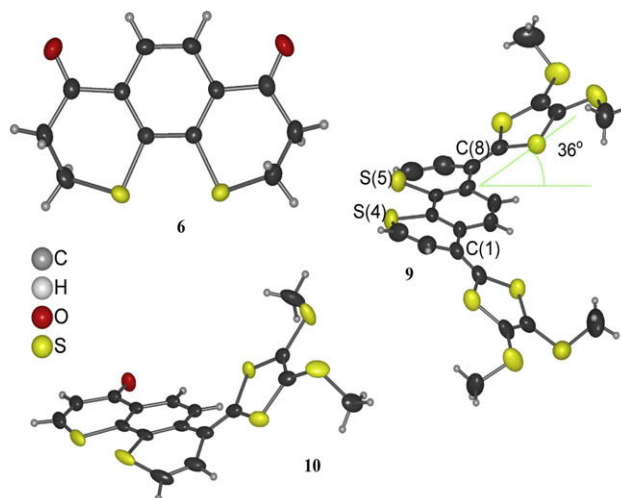
Scheme 1. Synthetic route of the precursor **8**.Scheme 2. Synthesis of **9–12**.Figure 1. Variable-temperature  $^1\text{H}$  NMR of **9** in  $\text{CDCl}_3$ .

and the poor solubility of **8** may account for the low yield of **11** and **12**.<sup>15</sup>

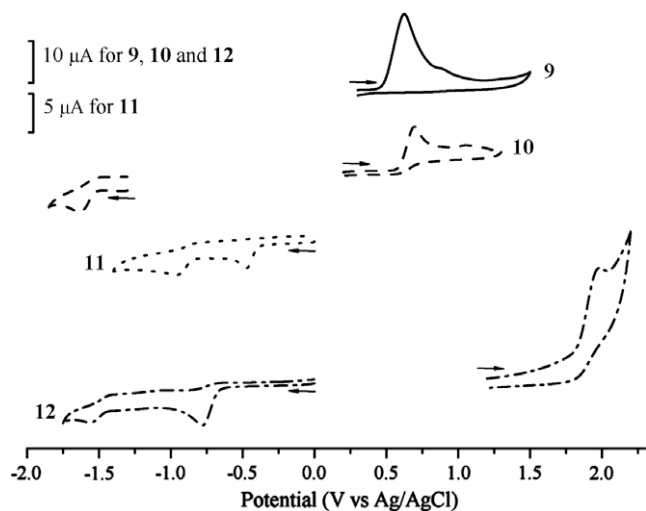
The TTF analogues (**9** and **10**) were synthesized by Wittig-Horner reaction using in situ-generated carbanion of **13** in the presence of *n*-BuLi at  $-78^\circ\text{C}$ . The precise addition of *n*-BuLi and the fine grinding of **8** are necessary for the success of the procedure.<sup>16</sup>

Two vicinal olefinic hydrogens on one of the thiopyran rings of **9** are in an AB spin system, and should display a set of two skewed doublets in the  $^1\text{H}$  NMR spectrum. However, the  $^1\text{H}$  NMR spectrum of **9** in  $\text{CDCl}_3$  at room temperature showed a singlet peak at ca. 6.31 ppm corresponding to the hydrogen signal on thiopyran ring. By performing the variable-temperature (VT)  $^1\text{H}$  NMR experiment, the singlet peak gradually restored into two doublet peaks with the decrease of the temperature (from 293 K to 233 K) as shown in Figure 1. This phenomenon may be explained by the random conformation promoted by halogenated solvents in which the interactions between solute (donor molecules) and solvent may be involved.<sup>17</sup>

Single crystals of **6**, **9**, and **10** were obtained by slow evaporation or diffusion method, and their crystal structures (as shown in Fig. 2) were investigated by X-ray crystallographic analysis. **6** adopts almost planar conformation, and in the packing mode of **6**, the molecules form two kinds of opposite-oriented chains

Figure 2. The crystal structures of **6**, **9**, and **10**.

through the short contacts (see Figure S3 in SI-1). **9** displays a distorted structure, in which two TPDT parts take boat conformations with opposite orientations, and the dithiole ring is tilted to  $36^\circ$  with respect to the  $\text{C}(1)\text{S}(4)\text{C}(8)\text{S}(5)$  plane. Compound **9** stacks in



**Figure 3.** Cyclic voltammograms of **9–12** measured in  $\text{CH}_2\text{Cl}_2$  (**9** and anodic part of **10**), DMSO (**11**) and benzonitrile (**12** and cathodic part of **10**) at room temperature (V vs Ag/AgCl, 100 mV/s, 0.1 M  $(n\text{-Bu})_4\text{N}^+\text{ClO}_4^-$ ).

a row along *a* direction, and the face to face contacts only occur between two neighboring dithiole rings within the row (the average distance between the mean planes of two neighboring dithiole rings falls in the range of 3.55–3.65 Å, while the average distance between the mean planes of two neighboring thiopyrano[3,2-*h*]thiochromene moieties falls in the range of 4.06–4.08 Å) (see Figure S5 in SI-1). There exist interactions through S...S short contacts (ca. 3.63 Å) between the methylthio groups (see Figure S4 in SI-1). The boat conformation of the TPDT part of **10** is similar to that of **9**, and the existence of O...S short contacts (ca. 3.15 Å) may account for the complicated packing mode (see Figure S6 in SI-1).

The solution UV–vis spectra of **9–12** were shown in Figure S7 and the absorption maxima were collated in Table S3. All compounds feature strong absorptions in the range between 350 nm and 500 nm, which could be assigned to the transitions involving the thiopyrano[3,2-*h*]thiochromene moiety.<sup>7</sup> For **10**, the tail of absorption band above 500 nm indicated the existence of possible weak intramolecular charge transfer (ICT) interactions between the 1,3-dithiole ring and the thiopyrano[3,2-*h*]thio-chromene fragment.

Electrochemical redox properties of **9–12** were investigated by cyclic voltammetry (CV) as shown in Figure 3, and the redox potentials were listed in Table S3. **9** and **10** show irreversible oxidation waves on anodic scanning, and the oxidation potentials are higher than those of TTF ( $E_{1/2}$ , +0.34 and +0.71 V)<sup>18</sup> or TPDT ( $E_{1/2}$ , +0.23 and +0.61 V).<sup>7</sup> These waves could be attributed to the formation of radical cations. Compound **10** also gives an irreversible reduction wave at -1.64 V corresponding to one-electron reduction of carbonyl group. The coalescence of the oxidation waves of **9** and **10** could be resolved in THF as shown in Figure S8. Compound **9** gives two slightly resolved irreversible electron transfers corresponding to a two-electron oxidation step on two 1,3-dithiole rings and a one-electron oxidation step on the thiopyrano[3,2-*h*]thiochromene moiety. Compound **10** shows two well-resolved irreversible electron transfers corresponding to a one-electron oxidation step on the 1,3-dithiole ring and a one-electron oxidation step on the thiopyrano[3,2-*h*]thiochromene moiety. The coalescence of the oxidation waves of **9** and **10** may be resulted from the distorted geometry of the two donors which had been suggested by other researchers.<sup>19</sup> The acceptor molecule **11** show irreversible reduction waves at -0.47 V and -0.95 V on cathodic scanning, and the reduction potentials are more negative than those of TCNQ ( $E_{pc}$ , -0.09 and -0.75 V)<sup>1b</sup> or TCAQ ( $E_{1/2}$ , -0.285,

-2.06 and -2.58 V).<sup>1b</sup> These waves could be attributed to the formation of radical anions. **12** gives two irreversible reduction waves at -0.78 and -1.56 V corresponding to two one-electron reduction steps located on the dicyanomethylidene and carbonyl groups separately, and one irreversible oxidation wave at 1.98 V corresponding to the one-electron oxidation of thiopyrano[3,2-*h*]thiochromene unit. The difference in the first reduction potentials of **11** and **12** may be ascribed to the worse accepting ability of carbonyl group compared to dicyanomethylidene group.

Preliminary results of spin coating and OFET device performance of **9** and **10** (see page S13 and S14 in SI-1) indicated that these  $\pi$ -extended TTFs with thiopyrano[3,2-*h*]thiochromene moiety can form homogeneous thin-films. Both **9** and **10** exhibited *p*-type transistor performances, although the field-effect mobilities and the current ratios are not high compared to those of other attractive  $\pi$ -extended TTFs.<sup>20</sup>

In summary, a new class of TTF and TCNQ analogues (**9–12**) have been synthesized from the precursor **8**. Compound **8** may be a promising candidate for versatile synthesis of electron donors and acceptors in the near future. The electrochemical study reveals moderate donating ability of **9** and **10**, and poor accepting ability of **11** and **12**. The distorted geometries of **9** and **10** established by X-ray single crystal analysis may account for the coalescence of their oxidation process and *p*-type performances of their OFET devices. Further experiments to optimize the device fabrication and to modify the  $\pi$ -extended structure are currently underway.

## Acknowledgments

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## Supplementary data

Experimental procedures (SI-2); copies of <sup>1</sup>H and <sup>13</sup>C NMR spectra for new compounds (SI-2); a scheme for donors and acceptors involved in this Letter; crystal data (Table S2 in SI-1) for **6** (CCDC 702881), **9** (CCDC 702882) and **10** (CCDC 702883); details for the OFET devices fabrication/characterization of **9** and **10**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.03.101.

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