



## An electron-deficient tetrathiafulvalene-conjugated bistetracene



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### ABSTRACT

An electron-deficient tetrathiafulvalene (TTF)-conjugated bistetracene **2** was synthesized as the counterpart of phenyl-substituted TTF-conjugated bistetracene **1**, and was characterized in the molecular electronic structures based on the spectroscopic measurements. UV–vis absorption spectrum of **2** is slightly broader than that of **1** and fluorescence spectrum of **2** is red-shifted, reflecting the red-shifted absorption spectrum. The energy level of the highest occupied molecular orbital (HOMO) of **2** was directly determined by the atmospheric-photoelectron yield spectroscopy in powder to be  $-5.8$  eV, which is remarkably lower than that of **1** ( $-5.2$  eV).

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### Introduction

Compared to the p-type semiconductors, the line-up of n-type semiconductors is not fully developed, and higher performances are demanded. The creation of excellent n-type materials is crucial for the fabrication of p–n junctions, bipolar transistors, and organic photovoltaic devices.<sup>1</sup> To obtain the high electron mobility, the organic semiconductor layer should be highly ordered with strong intermolecular interactions and also have a lower LUMO energy level.

Tetrathiafulvalene (TTF) derivatives are promising candidates for semiconductors, giving high performance FETs because of their self-assembling properties leading to strong intermolecular interactions.<sup>2</sup> However, because of the electron-rich properties, the compounds are generally weak to oxygen.<sup>3</sup> In our previous work, we introduced fused aromatic rings to the TTF skeleton to enhance the intermolecular interaction, which consequently lead to the large charge transfer integral in the calculations based on the crystal structure (Chart 1, compound **1**).<sup>4</sup> High performance n-type organic semiconductors have recently been obtained by introducing electron-withdrawing substituents into electron-donating  $\pi$ -conjugated systems.<sup>1,5</sup> Therefore, we have now introduced p-trifluoromethyl-substituent as an electron-accepting group to the peripheral aryl groups on TTF derivative **1**. We report here the synthesis and physical properties of electron deficient TTF

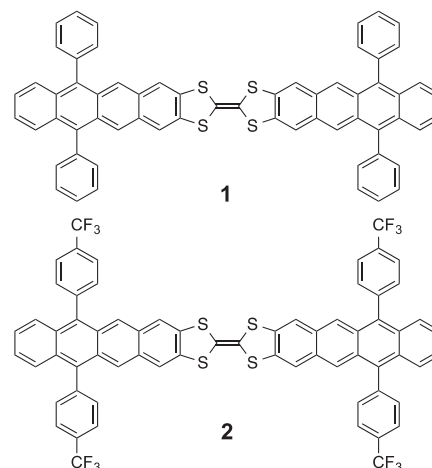


Chart 1.

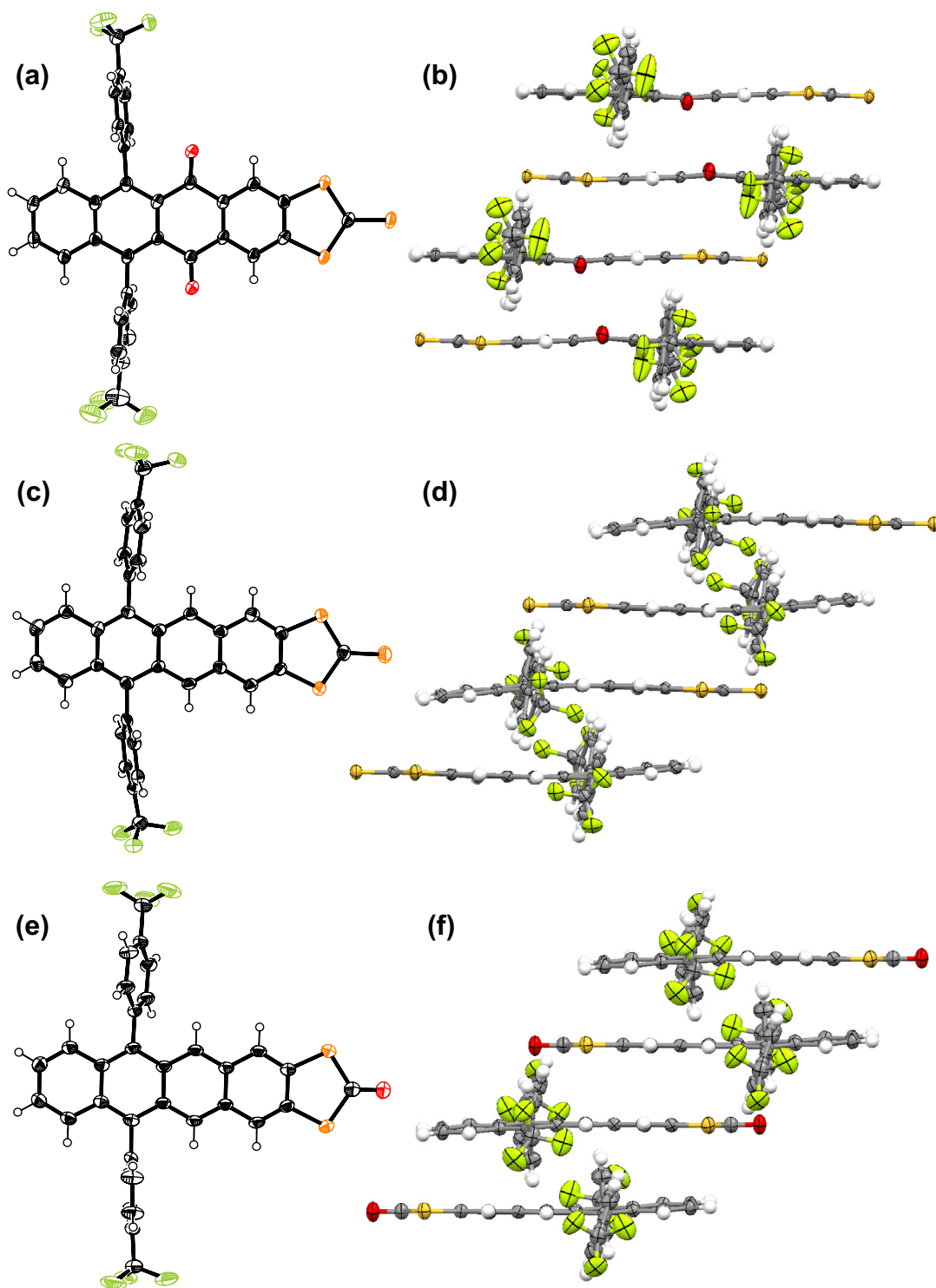
derivative **2**. New TTF derivative **2** was synthesized by a phosphite coupling reaction and characterized by conventional chemical and physical methods.

### Synthesis and characterization

The route for the synthesis of the p-CF<sub>3</sub>-tetraphenyl TTF-conjugated bistetracene **2** starts from a Diels–Alder reaction of the quinone **4**<sup>6</sup> with 1,3-bis(p-trifluoromethylphenyl)-isobenzofurane **3**<sup>7</sup>

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**Figure 1.** Crystal structures of (a) top view and (b) packing diagram of **5**, (c) top view and (d) packing diagram of **6**, and (e) top view and (f) packing diagram of **7**. Solvent molecules are omitted for clarity. Thermal ellipsoids represent 50% probability.

to form an adduct, then subsequent dehydration provided the tetracenequinone **5** (Scheme 1). The quinone **5** was reduced with  $\text{NaBH}_4$  and  $\text{SnCl}_2$  to afford tetracene thione **6** in high yield, which was interconverted to dioxol-2-one **7** with  $\text{Hg}(\text{OAc})_2$  in 87% yield.

The structures of **5**, **6**, and **7** were confirmed by their  $^1\text{H}$  NMR and high-resolution mass spectroscopies. All those were also revealed by single crystal X-ray diffraction analysis (Fig. 1).<sup>8</sup> The structures exhibit perfectly planar skeletons unambiguously, in

which the phenyl groups take perpendicular orientation. In the solid state, all **5**, **6**, and **7** form a face-to-face anti-parallel dimeric structure with a stacking distance of  $\sim 3.4$  Å.

Then, we tried to prepare the target compound **2** from **6** and **7** based on the phosphonate-induced coupling reaction. After several experiments, we obtained **2** in 56% yield as a purple solid. The solubility of **2** in common organic solvents is quite low, rather than that of **1**. High resolution spiral MALDI-TOF-mass spectroscopy

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