



## The synthesis and ambipolar charge transport properties of 1,2,3,4-tetrafluoropentacene

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### ABSTRACT

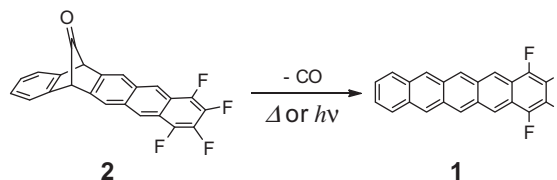
1,2,3,4-Tetrafluoropentacene is prepared from a soluble precursor containing a carbonyl bridge across the central benzene ring. It underwent dimerization readily in solution, yet displayed a high stability in the solid state. While fabricated into OFET devices, it exhibited an ambipolar charge transport characteristic. Its spectral and electronic properties are described.

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Pentacene and its derivatives have attracted a great deal of interest recently in the field of organic materials chemistry.<sup>1</sup> For example, it displayed a high hole mobility in organic field effect transistors (OFET).<sup>2</sup> However, due to its low solubility in solution and the low stability in the air, the preparation of pentacene derivatives remains to be a challenge to chemists. Recently, we have developed a new method to synthesize acenes, including pentacene, of high quality by way of their carbonyl adducts.<sup>3</sup> These adducts can act as efficient acene precursors for the production of acenes through cheletropic cyclo-reversion reactions, which can be done either by heating or by the irradiation of light.<sup>4</sup> The carbon monoxide (CO) expulsion reactions can proceed without solvent, therefore avoiding the exposure of sensitive compounds in solutions. For example, the preparation of pure hexacene has been achieved through the corresponding precursor in the solid state.<sup>5</sup> In this Letter, we reported the synthesis of the precursor compound **2**, and its transformation to 1,2,3,4-tetrafluoropentacene (**1**) (Fig. 1). Compound **1** has been regarded as a typical example of an ambipolar derivative of pentacene, which may act both as a p-type as well as an n-type semiconductor. Although compound **1** was found to be unstable in solution, it was quite stable in the solid state and can be processed into workable devices.

The synthesis of compound **2** started from 9-(propanylidene)-1,4-dihydro-1,4-methanonaphthalene (**3**) as depicted in Scheme 1. Cycloaddition of 1,1-dimethylbenzofulvene, which was generated from **3**, with 5,6,7,8-tetrafluoroanthracene-1,4-dione yielded **4** as a pair of stereoisomers (*exo/endo* = 4:1) in a total yield of 91%.

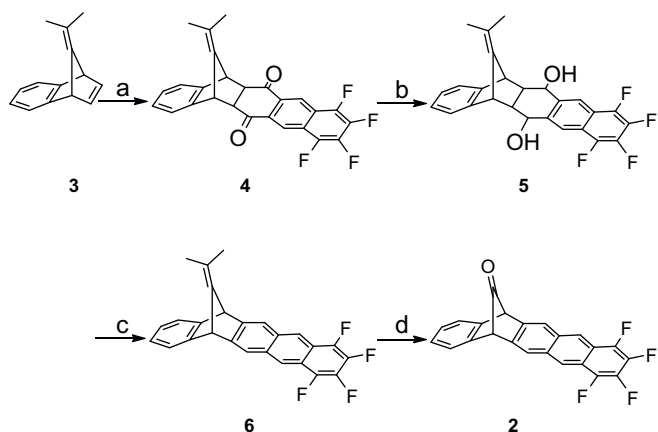
The structure of *exo/endo* isomers can be distinguished by the chemical shifts in <sup>1</sup>H NMR spectra (Figs. S1–S4). The singlet bridgehead protons of *exo-4* ( $\delta = 1.19$  ppm) appeared at a higher field than those of *endo-4* ( $\delta = 1.71$  ppm), due to the ring-current effect from understated of 1,2,3,4-tetrafluoro naphthalene moiety. In the aromatic region of *endo-4*, three sets of signals appear at  $\delta = 8.48$ , 6.96, and 6.63 ppm, while those of *exo-4* at 8.84, 7.39, and 7.20 ppm. The molecular structures of *exo/endo-4* were unambiguously identified by X-ray crystallographic analysis (Fig. S15). In the next step, the carbonyl groups of *exo/endo-4* was reduced by



**Figure 1.** Thermal or photo conversion of 1,2,3,4-tetrafluoro pentacene **1** from mono ketone precursor **2**.

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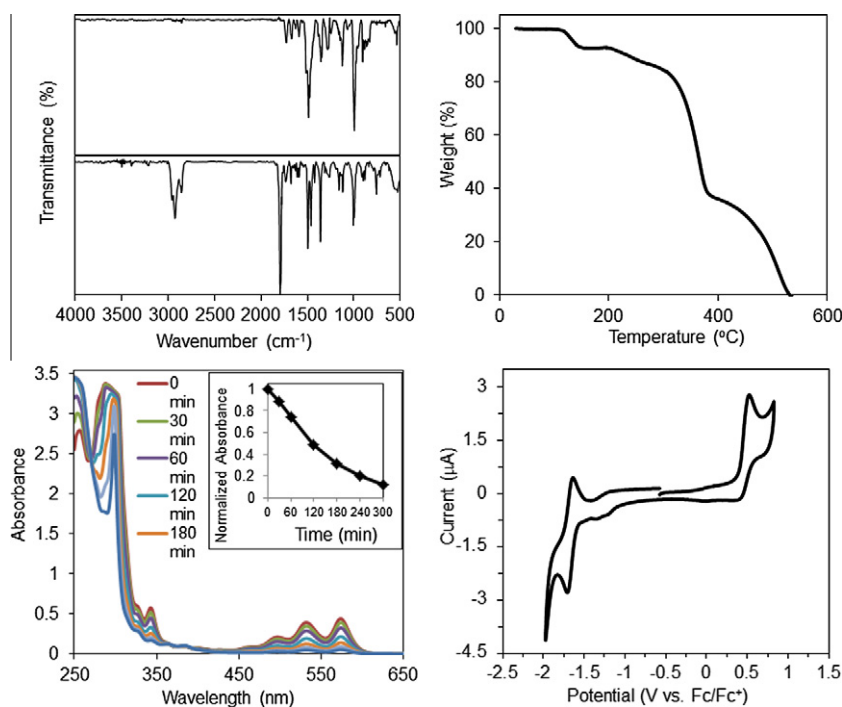
**Scheme 1.** Synthetic route of 1,2,3,4-tetrafluoropentacene precursor **2**. (a) 5,6,7,8-Tetrafluoroanthracene-1,4-dione, 3,6-di(pyridin-2-yl)-1,2,4,5-tetrazine,  $\text{CHCl}_3$ , 91%, (b)  $\text{NaBH}_4$ , MeOH–THF, 90%, (c)  $\text{POCl}_3$ , pyridine, 40%, (d)  $\text{O}_3$ ,  $\text{CH}_2\text{Cl}_2$ , then dimethyl sulfide, 61%.

$\text{NaBH}_4$  in methanol/tetrahydrofuran (MeOH/THF) to give the *exo/endo*-diol **5** (90%), which was aromatized by reacting with  $\text{POCl}_3$  to yield compound **6** in 40%. The double bond of **6** was cleaved by ozonolysis to yield the ketone **2** in 61%. The total yield of **2** starting from **3** was 20%. The carbonyl group of **2** was confirmed by the absorption at  $1794\text{ cm}^{-1}$  in infrared region, and the peak at 191.5 ppm in  $^{13}\text{C}$  NMR spectrum. It is soluble in most organic solvents, for example, dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), chloroform ( $\text{CHCl}_3$ ), and THF (all  $>1.0\text{ g L}^{-1}$ ).

The CO extrusion reaction of compound **2** can be monitored by a thermal gravitational analysis (TGA). In the TGA plot, it showed a weight loss of 7.6%, that occurred at ca.  $120\text{ }^\circ\text{C}$ , corresponding to the expulsion of a carbonyl group (calcd 7.5%) to form tetrafluoropentacene **1** (Fig. 2b). After CO expulsion compound **1** stayed stable

until ca.  $200\text{ }^\circ\text{C}$ , when another weight loss began due to vaporization. This thermal fragmentation pattern was quite similar to that of the pentacene monoketone precursor, which happened at  $128\text{ }^\circ\text{C}$  as described in a previous report.<sup>3b</sup> In the infrared spectrum (1 wt % in KBr), the carbonyl peak at  $1794\text{ cm}^{-1}$  diminished within 150 s (Figs. 2a and S14). The thermal generation of tetrafluoropentacene **1** was again confirmed by the molecular ion signal at  $m/z$  351.0803 ( $\text{MH}^+$ , calcd 351.0797, error = 1.7 ppm) in matrix assisted laser desorption/ionization mass spectrum (MALDI/MS) (Fig. S16). The  $^1\text{H}$  NMR spectrum of **1** after thermal generation in dilute condition (ca.  $1 \times 10^{-4}\text{ M}$  in THF- $d_8$ ) indicated that **1** was produced in a very high purity. The aromatic protons of **1** showed five absorption peaks at  $\delta$  9.17, 9.00, 8.81, 8.00, and 7.38 ppm, distinctively (Fig. S13), at low field without other observable contaminants. However, when a solution of **1** was kept for a longer period of time, other species appeared as described in the following paragraph.

The color of the solids transformed from white to purple upon losing CO. In absorption spectrum, compound **2** ( $1.0 \times 10^{-4}\text{ M}$  in THF) displayed a characteristic  $^1A \rightarrow ^1L_a$  transition of anthracene with vibronic progressions at 383 ( $\log \epsilon = 3.70$ ), 363 (3.79), 345 (3.66), and 330 nm (3.41) (Fig. S17). After thermal conversion, compound **1** ( $1.0 \times 10^{-4}\text{ M}$  in THF) displayed a series of new peaks at 574 ( $\log \epsilon = 3.64$ ), 532 (3.59), 497 (3.32), and 465 nm (2.95), corresponding to the  $\pi-\pi^*$  transition of tetrafluoropentacene (Figs. 2c and S17). These  $\pi-\pi^*$  transition bands matched well with those of pentacene at ca. 582 nm (Fig. S18). In the short wavelength region, that is, 250–350 nm, some absorptions deriving from the dimer of **1** were also detected (Fig. 2c). The redox behavior of **1** was estimated by cyclic voltammetry. The measurements were performed in  $\text{CH}_2\text{Cl}_2$  in the presence of tetra(*n*-butyl)ammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) (0.1 M) using ferrocene/ferrocenium couple ( $\text{Fc}/\text{Fc}^+$ ) as an internal standard (Fig. 2d). A quasi-reversible one-electron oxidative wave was found at  $^{\text{ox}}E_{1/2}(I) = +0.46\text{ V}$ , while a reversible one electron reductive wave was found at  $^{\text{red}}E_{1/2}(I) = -1.67\text{ V}$ . From these data, the highest occupied molecular orbital



**Figure 2.** Physical and electronic properties. (a) Infrared spectra of **2**: before heat (bottom) and after heating at  $120\text{ }^\circ\text{C}$  for 150 s (top). (b) TGA profile of **2** from  $30\text{ }^\circ\text{C}$  to  $600\text{ }^\circ\text{C}$ . (c) Time-dependent absorption spectra of tetrafluoropentacene (**1**) in THF solution ( $1.0 \times 10^{-4}\text{ M}$  in an  $\text{O}_2$  free environment). Inset: relative intensity of 574 nm peak at different measurement times. (d) Cyclic voltammogram of **1** in  $\text{CH}_2\text{Cl}_2$  in the presence of  $\text{Bu}_4\text{NPF}_6$  (0.1 M) at a scan rate of  $20\text{ mV s}^{-1}$ .

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