

Syntheses of Soluble,  $\pi$ -Stacking  
Tetracene Derivatives

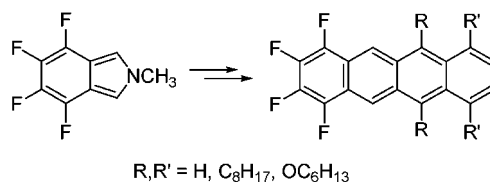
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## ABSTRACT



The syntheses of a series of fluorine- and alkyl/alkoxy-functionalized tetracenes are reported. These functional groups are found to improve the solubility in common organic solvents and tune molecular arrangement in solids. The crystal packing, electrochemical behavior, and UV–vis absorbance spectroscopy of these materials are discussed.

Oligoacenes, typically pentacene and tetracene, have been widely studied as the channel materials for organic field effect transistors (OFETs).<sup>1</sup> Pentacene-based devices were reported to show field effect mobilities of greater than  $2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , which are comparable to the performance of amorphous silicon thin film devices.<sup>2</sup> It is generally believed that the charge-carrier mobility in organic materials at room temperature is dominated by  $\pi$ – $\pi$  interactions between molecules via a charge-hopping transport mechanism.<sup>3</sup> Therefore, the molecular stacking in the solid state has a strong influence on the field effect mobility. It is well recognized that the intermolecular distance and the extent of  $\pi$ -orbital overlap between neighboring molecules are two important parameters for investigating the electrical properties of organic semiconductors.<sup>4</sup> However, the herringbone-like stacking superstructure of oligoacenes is not the optimum packing for high-mobility devices because the edge–face

packing reduces the  $\pi$ -overlap between adjacent molecules.<sup>5</sup> Recently, several novel organic semiconducting compounds with cofacial  $\pi$ -stacking arrangements have been synthesized and their devices showed promising charge-carrier mobilities.<sup>6</sup> The excellent intrinsic electrical properties of oligoacenes have also inspired chemists to design and synthesize oligoacene derivatives with improved  $\pi$ -stacking in the solid state.<sup>7–10</sup> Additionally, the often poor solubility of

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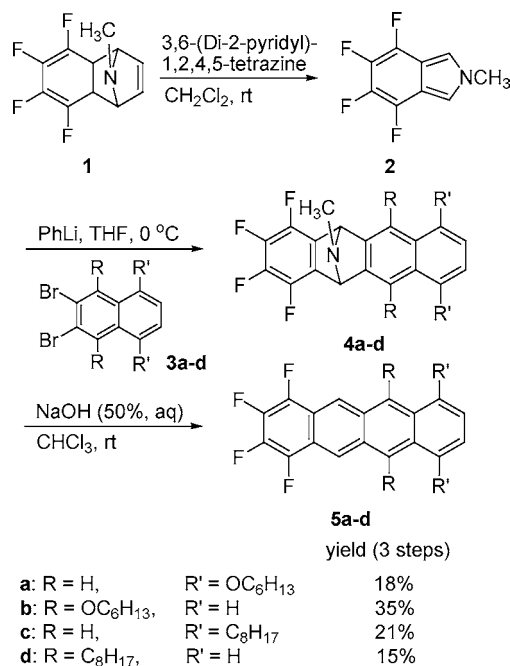
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oligoacenes in organic solvents at room temperature has been a hurdle in fully realizing the advantages of organic electronics, such as low-cost patterning and low-temperature processing. Therefore, it is necessary to develop new, soluble,  $\pi$ -stacking organic semiconductors for OFETs.<sup>11</sup>

In this work, we report a family of partially fluorinated and alkyl/alkoxy-substituted tetracene molecules that are soluble in common organic solvents and have significant  $\pi$ -stacking motifs in crystal lattices. Fluorine has been applied extensively to tune the electronic and structural properties of organic semiconducting materials because of its strong electronegativity and significantly small size.<sup>7a,12</sup> Recently, Watson and co-workers have reported that partial fluorination overcame the herringbone crystal packing of tetracyclic aromatic compounds, leading to a cofacial packing with a  $\pi$ -distance of 3.37 Å.<sup>12a</sup> Partially fluorinated silylethynyl pentacenes were also found to reduce the intermolecular distances.<sup>7a</sup> Incorporation of long alkyl or alkoxy chains is widely used to improve the solubility of small molecules and polymers and to facilitate formation of semiconductor thin films by cost-effective solution deposition techniques.<sup>13</sup> In our studies, we found that the regiochemistry of the side-chain attachment on the tetracene backbone not only improved the solubilities but also tuned the electrochemical properties and packing motifs. Furthermore, the incorporation of both donor and acceptor substituents to the main chain was added to induce a strong dipole moment. Strong dipole-dipole interactions between neighboring molecules were previously demonstrated to afford  $\pi$ -stacking with short intermolecular distances and self-assembly properties.<sup>9</sup>

The key steps of our synthetic strategy to the tetracene derivatives, as outlined in Scheme 1, were adapted from a methodology previously reported by Gribble.<sup>14</sup> *N*-Methyl-4,5,6,7-tetrafluoroisindole (**2**), which is a moderately stable compound and should be prepared freshly, could be easily prepared from a reaction between **1** and 3,6-di(2-pyridyl)-1,2,4,5-tetrazine, via a Diels–Alder (D–A) reaction and subsequent thermally allowed electrocyclic fragmentation.<sup>15</sup> In the presence of **2**, dibromonaphthalenes **3a–d** were treated with phenyllithium (PhLi) at 0 °C, leading to the formation of corresponding naphthalene, which readily reacted with **2** via the D–A reaction. Imines (**4a–d**) were obtained as colorless or slightly yellow solids in 40–65% yields. The deamination was carried out by the treatment of an aqueous solution of NaOH (50%, w/w) to the stirred chloroform

Scheme 1. Syntheses of **5a–d**



solution of **4a–d** and phase-transfer catalyst benzyltriethylammonium chloride at room temperature. This reaction was proposed to proceed by way of the in-situ-formed dichlorocarbene, which combined with **4a–d** to form ammonium ylide intermediates.<sup>16</sup> The aromatic acenes were then generated from the rapid cheletropic loss of methyl isocyanide dichloride. Tetracene derivatives **5a–d** were obtained as red or orange crystals from recrystallization in hexane, with yields of 15–35% over three steps. The solubility of **5a–d** in organic solvents, such as methylene chloride, chloroform, and toluene, was found to be much better than that of their parent tetracene, owing to the long linear side chains.

Scheme 2 shows the synthetic routes to dibromonaphthalenes (**3a–d**), which are used in Scheme 1. Hexyloxy-substituted naphthalenes were prepared from corresponding naphthoquinone (**6** and **7**) via a reduction to naphthalenehydroquinone and then alkylation under basic conditions.<sup>17</sup> The bromination of 1,4-bis(hexyloxy)naphthalene (**8**) was carried out by a treatment of *N*-bromosuccinimide (NBS) in methylene chloride.<sup>18</sup> Both **3a** and **3b** were obtained as colorless crystals. Dioctyl-substituted dibromonaphthalenes (**3c–d**) were prepared in two steps with good yields. In the presence of an excess of furans, tetrabromobenzenes (**9a–b**) were treated with *n*-butyllithium (*n*-BuLi) at low temperature, leading to the epoxides (**10a–b**) via a D–A reaction between corresponding benzynes and furans.<sup>19</sup> Low-valent Ti, prepared in situ from a reaction between zinc and

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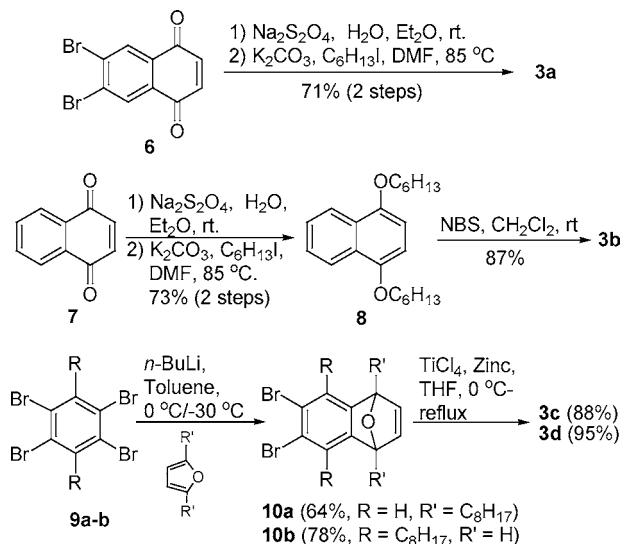
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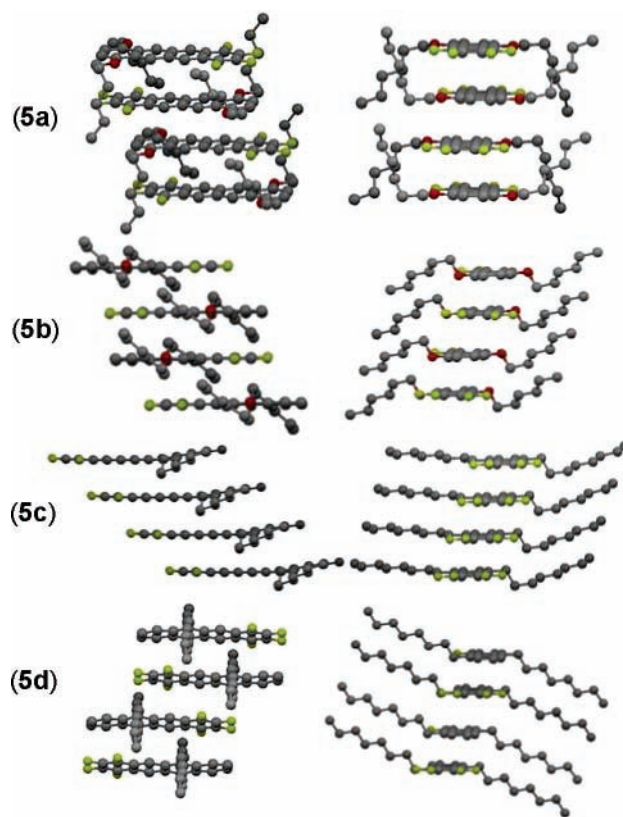
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**Scheme 2.** Syntheses of **3a–d**



$\text{TiCl}_4$ , was applied for the deoxygenation of **10a–b**,<sup>19,20</sup> to give **3c–d** as white solids.

The molecular and crystal structures of **5a–d** were determined by X-ray structure analysis on single crystals, which were obtained by solvent diffusion at low temperature. The packing diagrams of **5a–d** are displayed in Figure 1. All four compounds show primarily face–face slipped  $\pi$ -stacking in the crystals, and the selected structural data are summarized in Table 1. The hexyloxy-substituted molecules, **5a** and **5b**, adopt antiparallel cofacial arrangements. The  $\pi$ -stacked column has regular alternating intermolecular distances (Table 1), forming face–face  $\pi$ -stacks of  $\pi$ -dimers.<sup>4</sup> In the crystal structure of **5a**, we found that the two hexyloxy chains are in a conformation which extends them out of the aromatic plane, holding the  $\pi$ -dimer like a shield. The remarkably short intermolecular distances (3.22 and 3.24 Å) indicate the existence of strong intermolecular interactions, which are expected to enhance the charge-carrier mobility. The relatively large intermolecular distances in **5b** may be attributed to the repulsion from the side chains, which have a kink in their otherwise extended conformation. However, the relatively small roll displacement<sup>4</sup> (0.99 and 0.89 Å) is suggestive of a large  $\pi$ -orbital overlap.<sup>5</sup> In contrast to the crystal structures of **5a** and **5b**, octyl-substituted **5c** crystallizes in a parallel cofacial molecular arrangement, with the intermolecular distance of 3.35 Å and roll displacements of 1.15 Å. The molecules in each column are slipped lengthwise by about one benzene ring. **5d** has a face–face antiparallel  $\pi$ -stacking motif, similar to that of **5a** and **5b**. However, the stacks of **5d** are packed with alternating columns that are at an angle of 141° between the short axes of the molecules in neighboring columns (Supporting Information Figure S6). Interestingly, **5d** exhibits the shortest interplanar distance (3.18 and 3.20 Å) among these four compounds, but it has the biggest pitch and roll displacements, which are expected



**Figure 1.** Packing diagrams of **5a–d** showing that the molecules stack in a slipped cofacial motif. (Left: view along the short molecular axis. Right: view along the long molecular axis.)

**Table 1.** Comparison between the Intermolecular Distances and Pitch/Roll Displacements of **5a–d**

compd	$d$ (Å) <sup>a</sup>	$d_p$ (Å) <sup>b</sup>	$d_r$ (Å) <sup>c</sup>
<b>5a</b>	3.22	1.37	1.16
	3.24	1.68	1.36
<b>5b</b>	3.44	3.41	0.99
	3.53	1.21	0.89
<b>5c</b>	3.35	3.46	1.15
<b>5d</b>	3.18	1.22	1.45
	3.20	4.68	1.75

<sup>a</sup> Intermolecular distance. <sup>b</sup> Pitch displacement. <sup>c</sup> Roll displacement (see ref 4).

to reduce the extent of  $\pi$ -orbital overlap.<sup>4,5</sup> These displacements are probably due to the out of plane conformation of the octyl chains. The crystal features of **5a–d** clearly demonstrate the effect of substitution regiochemistry on molecular packings.<sup>21</sup> A close inspection of the  $\pi$ -dimers in **5a**, **5b**, and **5d** reveals that the electron-poor ring (fluorinated ring) faces the electron-rich ring (hexyloxy- or octyl-substituted ring), indicating the effect of the arene–perfluoroarene interaction on the molecular stacking.<sup>22</sup> A similar packing motif was previously observed in the crystal structure

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of 2,3,4,5,6-pentafluorodiphenyl diacetylene by Grubbs.<sup>23</sup> Extensive studies on the interactions of phenyl and perfluorophenyl groups, especially the 1:1 mixture of benzene and hexafluorobenzene, have supported that this cofacial stacking arrangement results from the electrostatic attractions between adjacent molecules.<sup>22–24</sup> Our results suggest that the noncovalent electrostatic interactions between donor- and acceptor-substituted arenes can be employed to design novel  $\pi$ -stacking organic semiconductors.<sup>9,25</sup>

The electrochemical behaviors of tetracene and compounds **5a–d** together with the spectroscopic data are summarized in Table 2. All five compounds show one quasireversible

**Table 2.** Optical Band Gap and Cyclic Voltammogram Data of Tetracene and **5a–d**

compd	$E_g^{\text{Op}}$ (eV) <sup>a</sup>	$E_{\text{ox}}^{\text{onset}}$ (V) <sup>b</sup>	$E_{\text{red}}^{\text{onset}}$ (V) <sup>b</sup>	$E_g^{\text{EChem}}$ (eV) <sup>c</sup>
tetracene	2.57	0.41	−2.05	2.46
<b>5a</b>	2.25	0.31	−1.92	2.23
<b>5b</b>	2.34	0.44	−1.84	2.28
<b>5c</b>	2.47	0.56	−1.89	2.45
<b>5d</b>	2.40	0.48	−1.91	2.39

<sup>a</sup> Calculated from the onset of UV absorbance spectra measured in  $\text{CH}_2\text{Cl}_2$  solution. <sup>b</sup> Performed in 0.1 M solution of TBAPF<sub>6</sub> in  $\text{CH}_2\text{Cl}_2$ , with a Pt electrode, a scan rate of 100 mV/s, and ferrocene as the internal standard. <sup>c</sup> Calculated from the onset of CVs.

reduction wave with onset reduction potentials between −2.05 and −1.84 eV (vs the Fc/Fc<sup>+</sup> couple). The cyclic voltammogram (CV) of **5a** exhibits two separate one-electron reversible oxidation waves at  $E_{1/2} = 0.39$  and 0.97 V. Similarly, **5b** has two sequential oxidation waves over the range of scan rates investigated (10–100 mV/s). However,

the return reduction processes were scan-rate dependent, displaying the expected two waves (0.47 and 0.66 V) at slow scan rates (10 mV/s) and an unexpected third wave with large potential shifts (0.19, 0.45, and 0.65 V) at 100 mV/s. The electrochemical irreversibility of **5b** probably indicates slow electron-transfer kinetics and/or strong intermolecular interactions. Both the CVs of **5c** and **5d** show one reversible oxidation wave and a second quasireversible oxidation wave, with the first waves at  $E_{1/2} = 0.65$  and 0.58 V for **5c** and **5d**, respectively. We found that the introduction of both fluorine and a hexyloxy group offered a slight change on oxidation potentials, as compared to the  $E_{1/2}$  potential of tetracene. However, **5c** and **5d** exhibited relatively higher oxidation potentials due to the modest electron-donating ability of the alkyl group. Our CV studies reveal that the position of alkoxy/alkyl substituents could significantly tune the electrochemical properties of these molecules. The band gaps, determined from the onset of oxidation and reduction (scan rate = 100 mV/s), correspond with the values calculated from the onset of UV–vis absorption spectra measured in methylene chloride solution (Table 2). The small band gaps of these compounds are expected to make them promising candidates for use in organic electronics.

In summary, we have shown the syntheses of a series of partially fluorinated tetracene derivatives with *N*-methyl-1,2,4,5-tetrafluoroisindole as a synthetic building block. **5a**, **5b**, and **5d** were found to crystallize with antiparallel, cofacial, stacked column superstructures, and **5c** exhibited a slipped parallel  $\pi$ -stacking arrangement in crystals. We found that the substitution of alkyl/alkoxy groups on the main chain not only provided better solubility in common organic solvents but also subtly tuned the crystal structures and electrochemical behaviors. Studies of charge-carrier mobilities of these novel tetracene derivatives in OFETs will be forthcoming.

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**Supporting Information Available:** Experimental details, spectroscopic data, and crystallographic CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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