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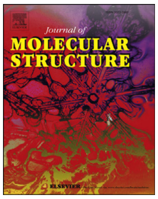

Synthesis, crystal structure and photo physical properties of isomeric fluorinated s-shaped polyaromatic dibenzo[c,l]chrysene derivatives

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ABSTRACT

Two s-shaped fluorinated isomeric polyaromatic dibenzo[c,l]chrysene derivatives have been synthesized by a two step process using the Wittig, Heck and iodine promoted cyclization reactions. These cyclized compounds were characterized by ^{1}H NMR and EI-MS. Further, absolute configurations of isomeric **4a** and **4b** were determined by X-ray diffraction analysis. Compound **4a** crystallized under monoclinic system with space group $P2_1/c$ and compound **4b** crystallized under monoclinic system with space group *Cc*. They have good solubility in common organic solvents such as dichloromethane, chloroform and THF. Photophysical properties of **4a** and **4b** were evaluated by using UV–Visible and Fluorescence spectrophotometer. Compounds **4a** and **4b** showed strong absorption maximum wavelength at 317 nm. The emission spectra of **4a** and **4b** displayed sharp peaks in the visible region from 417 to 441 nm. The shape of the UV–Visible and Fluorescence spectra of **4a** and **4b** looks almost identical. But compound **4a** exhibited better fluorescence intensity than compound **4b.** This difference may be due to the difference in the configuration of compounds **4a** and **4b**.

1. Introduction

Since the discovery of conductivity in organic crystals, the field of organic electronics, which deals predominantly with the π-conjugated materials, has advanced rapidly [1]. Over the past decade significant research has been done and still the search for the new π-conjugated systems has been going on because of the important rapidly growing number of applications in electronic devices such as semiconducting materials [2–5], organic solar cells [6], sensors [7], organic light-emitting diodes (OLEDs, organic field-effect transistors (OFETs), flexible displays. This is due to the π-conjugated materials offers low-cost, large-area, and flexible electronic devices [8–11]. An ideal organic electronic material should have a low HOMO-LUMO energy gap, good solid state packing, stability, solubility and planarity. Despite the large number of molecules explored, only a limited number of families of π-conjugated materials found to satisfy these requirements. One of the fundamental principles in designing an air stable semiconducting material is to incorporating electron withdrawing groups. It was reported that because of the incorporation of electron withdrawing groups, electron affinity of materials increases and LUMO energy gap decreases, consequently band gap also decreases [12–14]. It was also reported that with the introduction of fluorine atoms in the compound increases the thermal stability of the material, which is important for the effective vapor-phase growth of the corresponding thin films [15]. Considering these basic principles, as part of our ongoing research objectives, in this article, we have investigated the synthesis, absolute structure determination and photophysical properties of two fluorinated s-shape π-conjugated organic materials. Earlier we reported the synthesis of various kinds of polyaromatic compounds with extended π-conjugation materials and evaluated their organic photoelectronic properties [16–19]. We believe that understanding of structure-property relationships of these compounds and may be helpful to material chemists in designing new materials with a view to achieve desired performance in electronic devices and circuits.

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2. Results and discussion

Compounds **4a** and **4b** have been synthesized in two steps using different starting materials. Compound **4a** was synthesized by the condensation of 2,6-Bis(triphenylphosphinnomethyl)-naphthalene dichloride **1a** with 2-bromo-5-trifluoromethyl benzaldehyde **2a** via. Wittig reaction generated the intermediate **3a.** In the second step, intermediate **3a** was subjected to palladium acetate assisted Heck reaction yielded corresponding s-shaped polyaromatic compound **4a** in moderate yield (Scheme 1).

Similarly, compound **4b** was synthesized by the condensation of 2,6-naphthalene dialdehyde **1b** with 4-trifluoromethyl triphenylphosphinomethylchloride **2b** via. Wittig reaction generated the intermediates **3b**, followed by iodine assisted photocyclization yielded corresponding s-shaped polyaromatic compound **4b** in moderate yield (Scheme 2).

Compounds **4a** and **4b** were characterized with ^{1}H NMR and EI-MS. ^{1}H NMR spectra for the cyclized products **4a** and **4b** showed downfield shifts of the protons located in the fjord regions which consist of four benzene rings. The NMR shift values are 9.12 ppm and 9.13 ppm for **4a**, 9.07 ppm and 9.31 ppm for **4b**, respectively. The shifts were well explained by the strong ring current effects of the large enhanced π-systems on the compounds.

Compounds **4a** and **4b** displayed good solubility in common organic solvents such as dichloromethane, chloroform and THF. Further to confirm the absolute configuration of these molecules, good crystals suitable for the measurement of X-ray diffraction analysis were prepared in dichloromethane solution using slow diffusion method.

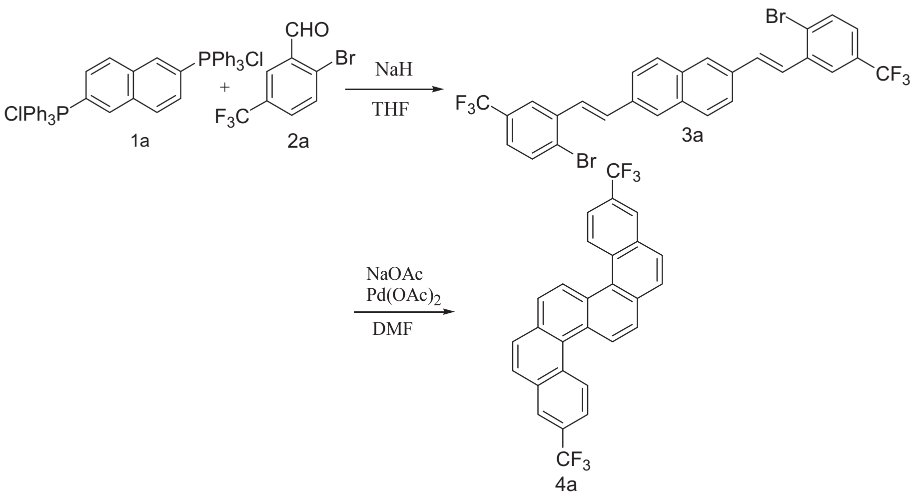
The crystallographic and refinement parameters are summarized in Table 3. Compound **4a** crystallizes with monoclinic crystal system, space group $P2_1/c$ with two non-planar compounds in the unit cell (Fig. 1). The two compounds in the unit cell are arranged side by side with almost planar shape as indicated by the dihedral angel 0.52°. The shape of compound **4a** seems to be the planar, but it is a strained one as indicated by the dihedral angels between the planes of the phenyl rings. The dihedral angle between the planes of the end phenyl rings was quite large (52.57°). Six phenyl ring planes, A (defined by C1,C2,C3,C4,C17,C18), B (defined by C15,C16,C17,C18,C19,C20), C (defined by C13,C14,C19,C20,C21,C22), D (defined by C5,C6,C21,C22,C23,C24), E (defined by C7,C8,C23,C24,C25,C26), F (defined by C9,C10,C11,C12,C25,C26) were slightly leaned (Fig. 1) and the plane angles between six phenyl rings are 11.09° for A–B, 20.08° for A–C, 9.53° for B–C, for C-D, 17.73°, for C-E, 24.84°, C-F, 28.89°, B-E, 41.94° and for A-E, 52.57° respectively.

Compound **4b** also crystallizes with monoclinic crystal system, space group *Cc* with four non-planar compounds in the unit cell (Fig. 2). The four compounds in the unit cell are arranged with a highly strained shape as indicated by the dihedral angels between the planes of the four molecules. In the unit cell two-two sets of compounds are arranged in little strained planar shape indicated by their dihedral angles 4.83°, 3.79°. These two sets of molecules almost aliened perpendicular to each other and the dihedral angles between these planes are 87.35°, 86.35 (Fig. 3). The shape of compound **4b** seems to be planar, but it is not a perfect planar compound because there existed dihedral angels between the planes of the phenyl rings. The dihedral angle between the planes of the end phenyl rings was quite large (43.31°). Six phenyl ring planes, A (defined by C1,C2,C3,C4,C17,C18), B (defined by C5,C6,C17,C18,C19,C20), C (defined by C7,C8,C19,C20,C21,C22), D (defined by C15,C16,C21,C22,C23,C24), E (defined by C13,C14,C23,C24,C25,C26), F (defined by C9,C10,C11,C12,C25,C26) were slightly leaned (Fig. 2) and the plane angles between six phenyl rings are 8.97° for A–B, 13.09° for A–C, 4.52° for B–C, 18.96 for C-D, 23.31° for C-E, 30.53° for C-F, 28.89°, 27.83° for B-E and 43.31° for A-E respectively. The dihedral angle between the planes of the aromatic rings of compound **4b** is relatively more than compound **4a**. This suggests that compound **4b** is more strained than compound **4a**.

Crystal packing of compound **4a** was illustrated in Fig. 4. In the crystal the compounds are assembled like layer shape. Intermolecular short contacts of the molecule **4a** listed in Table 1. The ends of the compounds are linked by C–H···F short contacts. The intermolecular short contacts of compound **4a** showed in Fig. 6. In between the layers the compounds are stacked by C–H···F, C···C and F···F short contacts, forming a flat layer like arrangements. In the packing diagram, dihedral angel between the planes of the molecular layers is ca. 1.0°. This suggests that molecular layers are almost assembled parallel to each other.

Crystal packing of compound **4b** was illustrated in Fig. 5. The molecular packing of the compound is not a planar one. Compound **4b** has herring bone like crystal packing system. The significant intermolecular short contacts of compound **4b** listed in Table 2. The intermolecular short contacts of the molecule **4b** showed in Fig. 7. In the crystal packing diagram, C–H···F, C···C and F···F short contacts together generated three dimensional molecular networks.

Further, we have evaluated the UV–vis absorptions and



Scheme 1. Schematic representation of synthesis of compound **4a.**