Syntheses and Structures of Pyrene Derivatives Functionalized with Thienyl Groups

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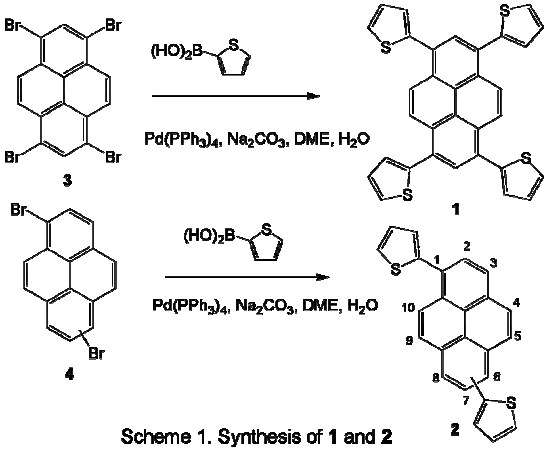
We focus on pyrene backbone as a substrate for systematical study of molecular design and packing associated with field effect properties. We report synthesis and crystal structures of functionalized pyrene derivatives with thienyl groups (Scheme 1), and 1,3,6,8-tetraphenylpyrene which is tetraphenyl analogue of the compound **1**. The synthesis of the present compounds **1** and **2** is shown in scheme 1, where tetrathienylpyrene **1** was recently synthesized by the similar manner.[1] The starting tetrabromopyrene **3** and dibromopyrene **4** were synthesized according to the previous reports.[2,3] **4** was obtained as a mixture of three possible isomers with respect to the position of the bromines, but main products were 1,6- and 1,8-dibromo isomers.[3] **1** and **2** were synthesized via conventional Suzuki coupling reactions of **3** and **4** with 2-thiopheneboronic acid, respectively. Owing to the existence of the starting three positional isomers, **2** was obtained as a mixture of the three isomers. To our best knowledge, the compound **2** is first reported. In the crystal of 1,3,6,8-tetraphenylpyrene, the pyrene core is almost planar and the peripheral phenyl groups are twisted out of the pyrene plane. The tetraphenylpyrene molecules do not stack in the crystal. We have obtained the crystal of **1** (monoclinic, space group $P2_1/n$) different from the reported one with the herringbone motif (monoclinic, space group $P2_1/c$).[1] Although the molecular geometry of **1** is similar to that of tetraphenylpyrene, the molecules in the crystal of **1** form uniform stacks along the *a* axis (Fig. 1). Among the isomers of **2**, the single crystal of 1,8-dithienyl isomer was obtained. Similar to the structure of **1**, the crystal of **2** exhibits uniform stacks. The OFET characteristics using the single crystal of the present compounds are investigated.



Scheme 1. Synthesis of **1** and **2**

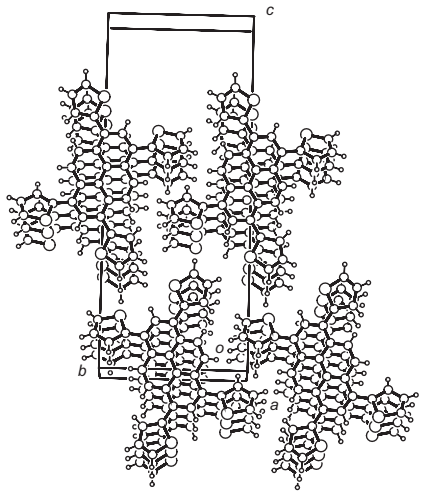


Fig. 1 Crystal structure of **1**.

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