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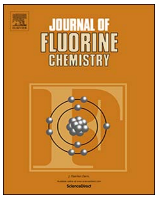

The (2,2′-bipyridine)PtI_2 complex with 5,5′-modification of fluorous side chains: Orthogonal skeleton

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ABSTRACT

Two polyfluorinated PtI_2-containing complexes, [5,5′-bis($R_fCH_2OCH_2$)-2,2′-bpy]PtI_2 [R_f = CF_3- (**5,5′-3F-PtI$_2$**), HCF_2CF_2- (**5,5′-4F-PtI$_2$**)], have been successfully synthesized. Interestingly, these two fluorous Pt-diimine complexes show two different types of structural features. For example, one fluorinated derivative **5,5′-4F-PtI$_2$** along with **5,5′-3F-PtBr$_2$**, which has been reported before, bear similarity to the *C2/c* (bpy)MX_2 platform. This simple (bpy)MX_2 platform with *C2/c* symmetry consists of *orthogonal* synthons in maintaining the synthons as columns and belts to accompany the introduced fluorous interactions. In contrast, the other fluorinated derivative **5,5′-3F-PtI$_2$** has been found to be completely different in the solid state. Its pattern of π···π interactions is a repetition of three molecular planes with the direction of the columns normal to the molecular planes, and its C3,3′—H···I interactions are partially kept though extensively modified. The dimer-monomer units utilize π···π stacking along the *c*-direction and C—H···I hydrogen bonds along approximately the *b*-direction. The less dispersive fluorous components fill in space between the layers of **5,5′-3F-PtI$_2$** molecules parallel to *bc*-planes, where weak C—H···F interactions are then enabled. Additionally, the electrical properties of **5,5′-3F-PtI$_2$** and two polymorphic **5,5′-3F-PtBr$_2$** vs. temperature have been studied. It can be easily seen that the fluorous side chain plays an important role in influencing their molecular packing, which in turn determine their electrical properties.

1. Introduction

The understanding of intermolecular interactions in the context of crystal packing and crystal engineering is important because the packing is based primarily on distance dependent interactions, taking advantages of both strength and directionality [1]. Polymorphism is not yet fully understood in studies of crystalline materials; nonetheless, it is one of the most exciting branches in the study of crystal packing and crystal engineering today [1]. In modern organic electronics, polymorphism serves as an excellent platform for helping the fundamental understanding of charge transport in π···π-stacking systems. The relationship between molecular packing and charge transport can be unequivocally explained since the chemical structures are totally identical among polymorphs, leaving molecular packing as the only variable. In the pharmaceutical industry, just coming up with polymorphic forms of drugs may entitle one to independent patent protection, especially if they show new and improved properties over the previously known crystal forms [2].

The main strategies of crystal engineering in use are deduced from short intermolecular interactions. Herein, the statistically more often occurring ones are known as synthons [3] among which are for instance, coordination complexation [4] and hydrogen bonding [5]. In this paper, the *C2/c*-form, *synthon-orthogonal* (bpy)MX_2 skeleton (bpy = 2,2′-bipyridine, M = Pt, Pd, X = I, Br) was analyzed towards its multiply built-in supramolecular synthons [6]. In rigorous definition, the word ‘synthon' used in this manuscript is the same as supramolecular synthon, which was proposed by Desiraju and nowadays is a well-studied and accepted tool in crystal engineering for designing desired supramolecular structures. A supramolecular synthon may be visualized as a vector denoting its supramolecular interactions such as H-bonding,

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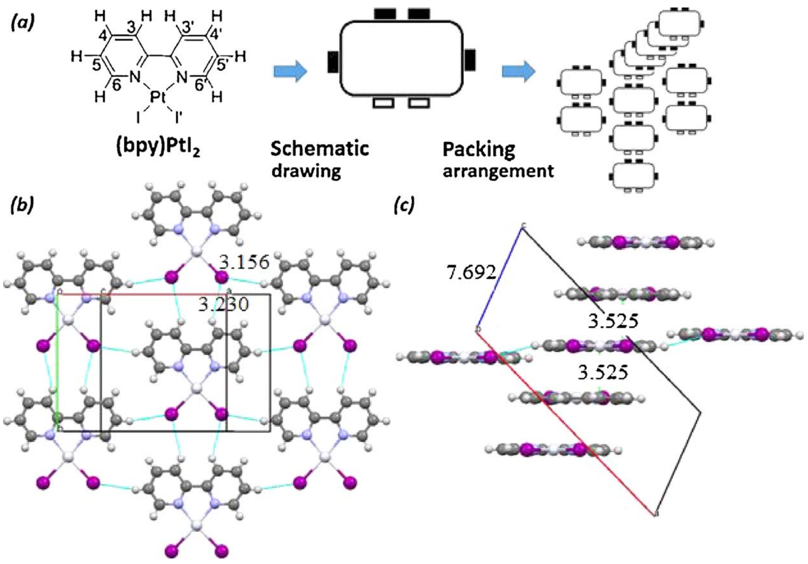


Fig. 1. The *C2/c* form (bpy)PtI_2 synthons. (a) The numbering sequence of (bpy)PtI_2 molecule (Note: Positions 1 and 2 are not noted schematics: central rectangle (bpy)PtI_2 skeleton; small filled rectangle C3,3′—H and C5,5′—H atoms; small empty rectangle I atoms). (b) Projection of (bpy)PtI_2 molecules in one layer. (c) Side view of consecutive (bpy)PtI_2 molecules in a column. (C: gray; N: blue; H: white: H; Pt: silver; I: purple).

π···π interaction, etc. When more than one synthon, relevant to one molecule or a group of molecules, are concurrently present in a crystal structure, and their associated vectors of supramolecular interaction are perpendicular, then the supramolecular synthons are orthogonal. This is how **orthogonality of the synthon** is defined.

A molecule with orthogonal synthons [7] is a great territory in which to work to further advance the understanding of crystal packing, crystal engineering, and polymorphism. For (bpy)MX_2 molecules, the group 10 metal center is square planar in bonding geometry. The bpy ligand is required to be in the *cis* geometry in order to chelate to the metal center, thereby giving opportunities for M···M interaction, π···π stacking, etc. in the crystalline state. Thus, C—H···X hydrogen bonding also plays an important role in packing (Fig. 1). For the fluorous (bpy)MX_2 molecules, they actually have richer structural chemistry than simple (bpy)MX_2 molecules because the fluorous side chains can introduce quite a few weak interactions into the molecules, and so fluorous (bpy)MX_2 complexes are more likely to have polymorphs in solid state packing than their simple (bpy)MX_2 analogues, which usually have one common form of packing.

The compounds (bpy)$PtBr_2$, (bpy)$PdBr_2$, (bpy)PtI_2, and (bpy)PdI_2 are interestingly isomorphous in the space group *C2/c*, and they provide an entry point to study these supramolecular interactions. The crystal packing of parent compound (bpy)PtI_2 can be summarized into C—H···I networks and the π···π stacking:

(a) *CHI networks.* Projected in Fig. 1(b) the (bpy)PtI_2 molecules are seen to self-match on C—H···I interactions along the C3,3′—H direction, forming perfect belts vertically, as evidenced by fully eclipsed (bpy)PtI_2 molecules in Fig. 1(b). The iodides of (bpy)PtI_2 have extra lone pairs of electrons with which to accept C5,5′-H protons horizontally. The two C3,3′—H···I hydrogen bonds are parallel in polarity, whereas the two C5,5′—H···I hydrogen bonds are mostly anti-parallel in polarity. The C5,5′—H···I interaction makes small steps of 0.837 Å between neighboring belts.
(b) *ππ stacking.* Fig. 1(c) is a view from the side of the (bpy)PtI_2 molecular planes with π···π stacked column running parallel to crystallographic *c*-axis. A molecular plane is defined by 15 non-H atoms of the (bpy)PtI_2 molecule, and the π···π distance is 3.525 Å from Pt to the neighboring molecular plane. The stacking (bpy)PtI_2 molecules alternate in polarity, and accordingly the polarity of the C—H···I networks also alternate from layer to layer.

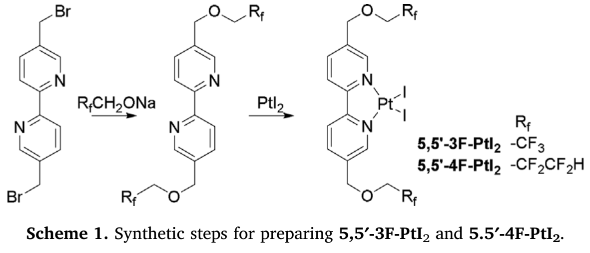
At this point, it was decided to remove the C—H···I hydrogen bonds along the 5,5′-positions by substitution at the 5,5′-positions with fluorous side chains. At about 15% total fluorine content, it should prove interesting to see to what extent the fluorous interactions affect the packing. That is, at least some of the C—H···X hydrogen bonds may be replaced by C—H···F—C hydrogen bonds. The weak C—H···F—C hydrogen bonds are, according to Desiraju et al., on the van der Waals limit (0.25 kcal/mol), much weaker than either those on the electrostatic limit (e.g., $NH_4^+Cl^-$, 15 kcal/mol) or the covalent limit (e.g., HF_2^- anion, 40 kcal/mol) [7].

2. Results and discussion

The fluorinated (bpy)PtI_2 derivatives, abbreviated as 5,5′-3F-PtI_2 and 5,5′-4F-PtI_2 (Scheme 1), were prepared in two steps accommodating an ether linker (—CH_2OCH_2—) prior to connecting the fluorous side chain [8]. Among the strongest bonds in organic chemistry, the C—F bond is not easily polarized [9]. A direct fluorous substitute on the bpy skeleton would more than likely exert unwanted influence on both the physical and chemical properties of the bpy ligand and should preferably be avoided. The ether linker allows additionally non-fluorous methylene H-atoms in the fluorinated region. An extra feature for 5,5′-4F-PtI_2 is the terminal −CF_2H group, in which the sp^3 H-atom has increased acidity due to the electronegative F atoms and behaves as a lipophilic H-donor through hydrogen bonding [10]. The total fluorine content of 5,5′-3F-PtI_2 is 13.7%, while that of 5,5′-4F-PtI_2 17.0%.

2.1. Structure of 5,5′-4F-PtI2

In the solid-state structure of 5,5′-4F-PtI_2, only half of the molecule is required as one asymmetric unit exists in the monoclinic space group *I2/a*. The 5,5′-4F-PtI_2 molecules form columns, attributed to the π···5π interaction, and the neighboring molecular planes within columns are separated by 3.593 Å (Fig. 2). The C6—H6A···F3—C9 contacts, revealed in Fig. 2 as green dotted lines, are believed to reinforce the π···π



Scheme 1. Synthetic steps for preparing **5,5′-3F-PtI_2** and **5.5′-4F-PtI_2**.