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ZWITTERIONIC IODONIUM SALTS AS TECTONS FOR DESIGN OF HALOGEN BONDED ORGANIC FRAMEWORKS (XOFs)

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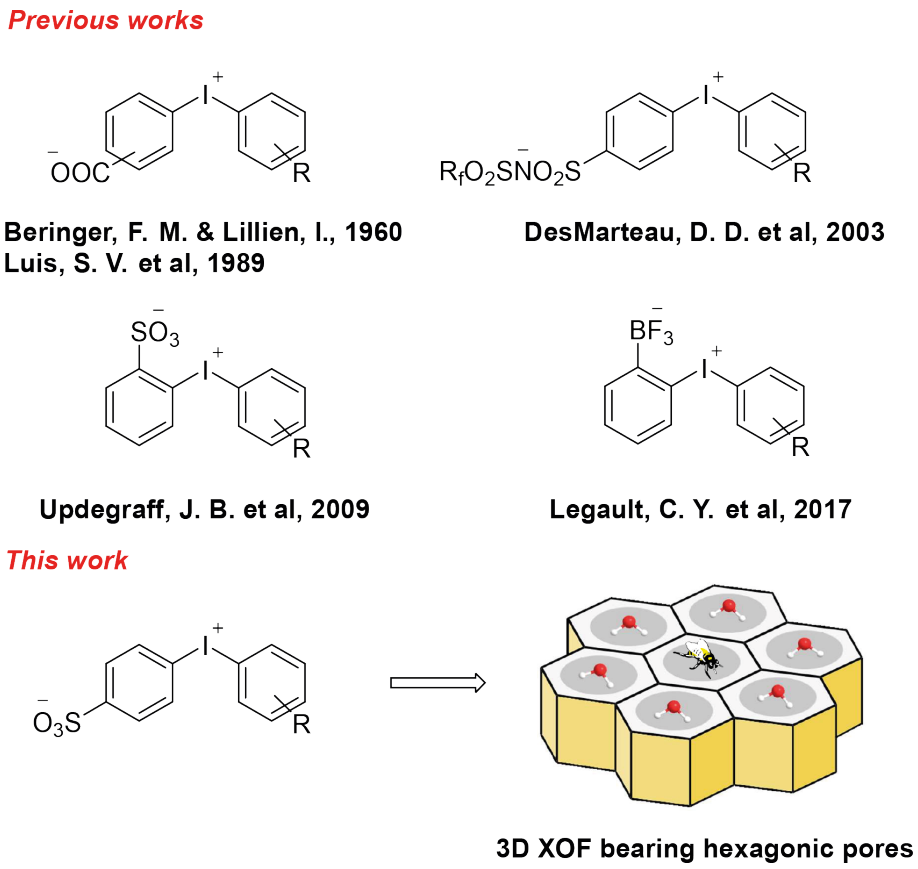
Noncovalent organic frameworks (nCOFs) are porous compound formed by various noncovalent interactions as hydrogen bonding, halogen bonding, π-π stacking and etc. [1, 2]. Halogen bonded organic framework (XOFs) is relatively new type of noncovalent organic frameworks formed by halogen bonding (XB). Currently only several examples of XOFs were reported [3–6]. All reported XOFs were formed with monovalent organic halides as 1,4-diiodotetrafluorobenzene or tetrabromobenzene-1,4-dicarboxylic acid.

Hypervalent iodine compounds, particularly iodonium salts are a relatively new object of research for the chemistry of halogen bonding [7–9].



Scheme 1. *Zwitterionic iodonium salts as tectons for synthesis of XOFs*

Halogen bonding in iodonium salts is more strength due to charge assistance that can be useful for mechanical properties of XOFs formed by iodonium salts. In particular zwitterionic iodonium salts often exhibit 1D and 2D supramolecular structures that can be useful for the design of various XOFs.

In this work we prepared a range of 4-(aryliodonio)-benzenesulfonates from the 4-iodobenzoic acid and arene with Oxone as oxidant. Importantly, that new zwitterionic iodonium salts 4-(aryliodonio)-benzenesulfonate can be utilized for synthesis of first 3D XOFs bearing hexagonal pores filled with disordered water (Scheme 1).

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INTERIONIC HALOGEN BONDING IN HEXAIODODIPLATINATES(II)

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Noncovalent interactions play an important role in many advanced areas of modern science spanning from supramolecular chemistry to molecular biology. While amount of studies on hydrogen bonding, metallophilic interactions and π-stacking is gradually stabilized, many novel types of noncovalent forces including halogen bonding (XB) were recognized only recently thus providing a new tool for crystal engineering.

It was previously shown that hexaiododiplatinates(II) can be co-crystallized with iodine-based organic compounds, forming C–I···I–Pt interactions through iodide ligands. X-ray diffraction (XRD) studies revealed that $[Pt_2I_6]^{2-}$ anions behave as rectangular nucleophiles, forming XBs via two, three, and even four terminal ligands [1]. In the present work, two new compounds are discussed, viz. $[Ar^1IAr^2]_2[Pt_2I_6]$ and $[Ar^2IAr^3]_2[Pt_2I_6]$ (Ar^1 – Ph, Ar^2 – $Ph(OMe)_3$, Ar^3 – PhCl). The complexes were obtained by the treatment of tetraethylammonium hexaiododiplatinate(II) with diaryliodonium salts. In the obtained co-crystals, we identified interionic C–I···I–Pt XBs formed between the iodide ligands of the anions and I centers of the cations (Fig. 1).

The $[Pt_2I_6]^{2-}$ anions are linked to the diaryliodonium cations by the C–I···I–Pt XBs thus forming extended 1D-chains consisting of heterotetrameric clusters (Fig. 2). To the best of our knowledge, this is the first example of interionic XB involving hexaiododiplatinates(II). The distances I···I are less than the sum of van der Waals radii (3.8044(7) and 3.6328(6) Å for $[Ar^1IAr^2]_2[Pt_2I_6]$; 3.6954(6), 3.5888(5) and 3.9183(5) Å for $[Ar^2IAr^3]_2[Pt_2I_6]$),