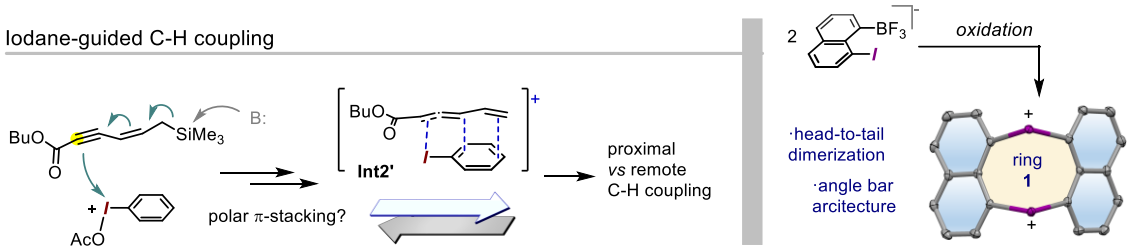
**Reaction and structure development using hypervalent iodine.**

Alexandr Shafir

BISi-Bonds group, Institute for Advanced Chemistry of Catalonia, IQAC-CSIC, Barcelona, Spain.

alexandr.shafir@iqac.csic.es

Hypervalent organoiodine reagents have become ubiquitous in organic synthesis, both as go-to oxidants and as electrophilic group transfer agents. Nevertheless, in recent years several research groups have shown that that the potential of the halogen(III) centers extends way beyond those two applications. This talk will focus our group's recent efforts to discover new reactivity and new molecular architectures based on hypervalent halogen(III) center. With respect to reaction discovery, we have focused on the ability of certain highly reactive λ$^3$-C-I-C intermediates to undergo a sigmatropic rearrangement, such that the $C_{Ar}$-Iodine(III) site acts as a reactivity trampoline for aromatic C–H coupling.[1,2] Our recent mechanistic insights into this process will be illustrated based on a rather versatile iodane-guided *ortho* C–H allylation reaction,[3] and on the newly developed remote C–H functionalization . Additionally, the talk will cover our latest findings on the synthesis and properties of new cyclic scaffolds based on multiple halogen atoms (see the naphthalene-based bis-λ³-iodane dicationic ring **1**). Beyond their sheer synthetic challenge, these molecules are an interesting platform for new "angle bar" molecular geometries (provided a near-90º C-I-C angle), and for exploring new classes of inter-halogen synergistic effects.[4]




**References:**

(1) W. W. Chen, A. B. Cuenca, A. Shafir, The Power of Iodane-Guided C−H Coupling: A Group-Transfer Strategy in Which a Halogen Works for Its Money. *Angew. Chem. Int. Ed*. **2020**, *59*, 16294.

(2) Y. Liang, B. Peng, Revisiting Aromatic Claisen Rearrangement Using Unstable Aryl Sulfonium/Iodonium Species: The Strategy of Breaking Up the Whole into Parts. *Acc. Chem. Res.* **2022**, *55*, 2103.

(3) a) W. W. Chen, A. Cunillera, D. Chen, S. Lethu, A. López de Moragas, J. Zhu, M. Solà, A. B. Cuenca, A. Shafir, *Angew. Chem. Int. Ed*. **2020**, *59*, 20201; b) J. D. Martín-Bernardos, K. Golob, W. W. Chen, O. A. Luongo, I. Sedó, A. B. Cuenca, A. Shafir, *Chem* **2025**, *11*, 102546.

(4) a) W. W. Chen, M. Artigues, M. Font-Bardia, A. B. Cuenca, A. Shafir, Cyclic Homo- and Heterohalogen Di-λ$^3$-diarylhalonium Structures. *J. Am. Chem. Soc.* **2023**, *145*, 13796–13804; b) with Wei Chen, *Maniscript in preparation,* **2026**.