Fluorine containing organic substituents are currently used to gain control on the solid state supramolecular organization of both organic and inorganic materials [1]. The introduction of CF$_3$ groups adequately positioned on the rigid core of a molecule, could be sufficient to provide fluorene-fluorine interactions able to modify, in absence of other strong interactions like hydrogen bonding, the packing motifs in the structure of crystalline materials. Moreover, segregation effects of fluorophile-aliphatic groups, in terms of micro-segregation of hydrophilic versus hydrophobic parts of molecules, is a specific tool for the generation of layered and/or columnar structures, which are tailored solid state organizations able to generate specific properties in molecular materials [2]. We have recently used this approach in the generation of new cyclometalated complexes, molecular materials of great interest as a result of their photophysical and mesogenic properties [3]. In particular, fluorine substitution proves to be a useful strategy in the promotion of different and enhanced photophysical properties as well as phase-segregated structures favorable for the appearance of columnar mesomorphism, due to the delicate balance between incompatible parts of the molecules, in acetylacetonate and hexafluoro-acetylacetone cyclopalladated and cycloplatinated complexes [4, 5].

In this communication, the use of fluorophileic groups on both the cyclometalated and the ancillary ligands in novel palladium(II) and platinum(II and IV) complexes, is illustrated with the intention of providing with the term of the ‘organic fluorine’ can be used to drive the solid state supramolecular organization of new crystalline molecular materials and their thermal and photophysical properties. In the case of the Pt(IV) derivatives, - bearing as C=N cyclometallating species the 2-phenylpyridine ligand, - the effects of the variation between aliphatic and fluorophileic ancillary ligands, and the intermolecular interactions eventually introduced by the fluorine atoms, will be discussed in relation with other possible halogen bonding due to the presence of the halides axially coordinated to the metal centre.


**Keywords:** crystal packing, fluorine interactions, organometallic materials

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**MS61.P04**


**Addressing structure solution challenges from light-atom clathrates with very large Z’**

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Inflexible small molecules with strong structure-directing groups, such as carboxylic acids, provide many examples of clathrate assemblies with large unit cells, low space group symmetry and disordered inclusion molecules. Similar to porous coordination frameworks, but lacking metals with higher electron density, these samples provide significant contemporary challenges for chemical crystallography.

We have recently solved the structures of a series of pseudo-polymorphs (differing in degree of solvation) with large Z’ values from an unassuming small molecule comprised of less than 40 carbon and oxygen atoms. These structures presented problems that were at last