Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary materials to

“Vitruvian” precursor for gas phase deposition: a structural insights into the iridium β-diketonate volatilities

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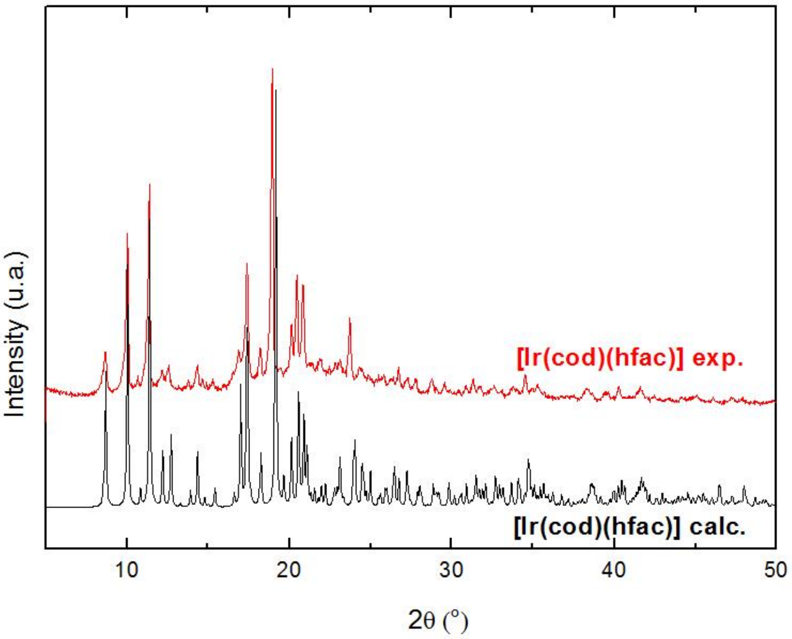
Table S1. The purities and sources of the reagents.

Chemical name	Chemical formula	Source	State	Mass fraction purity *[a]*
Bis(1,5-cyclooctadiene)diiridium(I) dichloride	$Ir_2(C_8H_{12})_2Cl_2$	“Sigma-Aldrich” Ltd. (USA)	Solid	0.97
1,1,1,5,5,5-Hexafluoro-2,4-pentanedione (Hhfac)	$C_5H_2O_2F_6$	“PM-Invest” (Russia)	Liquid	0.99
1,1,1-Trifluoro-2,4-pentanedione (Htfac)	$C_5H_5O_2F_3$	“P&M-Invest” (Russia)	Liquid	0.99
4,4,4-Trifluoro-1-phenyl-1,3-butanedione (Hbtfac)	$C_{10}H_7O_2F_3$	“P&M-Invest” (Russia)	Solid	0.98
Potassium hydroxide	KOH	“Kuzbassorghim” Ltd. (Russia)	Liquid	0.98
Diethyl ether	$(C_2H_5)_2O$	“Reaktiv” JSC (Russia)	Liquid	0.98
Hexane	C_6H_{14}	“Reaktiv” JSC (Russia)	Liquid	0.98

[a] As declared by supplier.

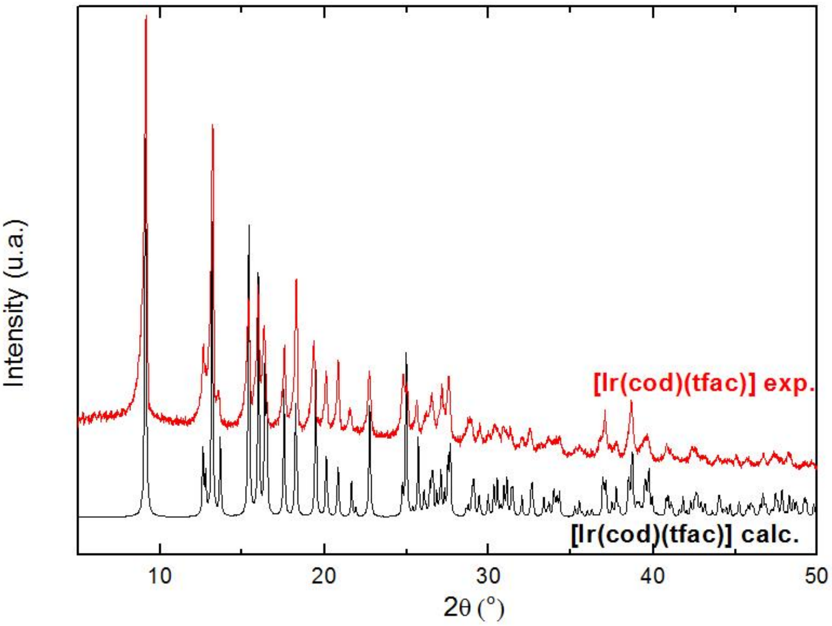
Table S2. Group values for calculation of solid heat capacity of metal β-diketonates at 298.15 K.

Group	Group value / kJ·mol^{-1} [W. Acree and J. S. Chickos, *J. Phys. Chem. Ref. Data*, 2016, **45**, 033101]
$[CH_3]$	36.6
$[CF_3]$	67.1
$[C_6H_5]$	96



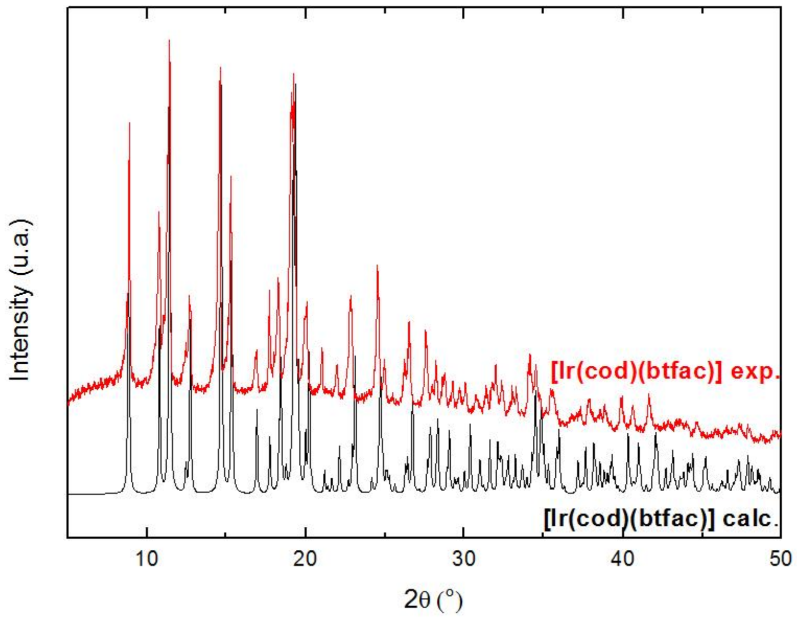
Intensity (u.a.)
[Ir(cod)(hfac)] exp.
[Ir(cod)(hfac)] calc.
10
20
30
40
50
2θ (°)

a



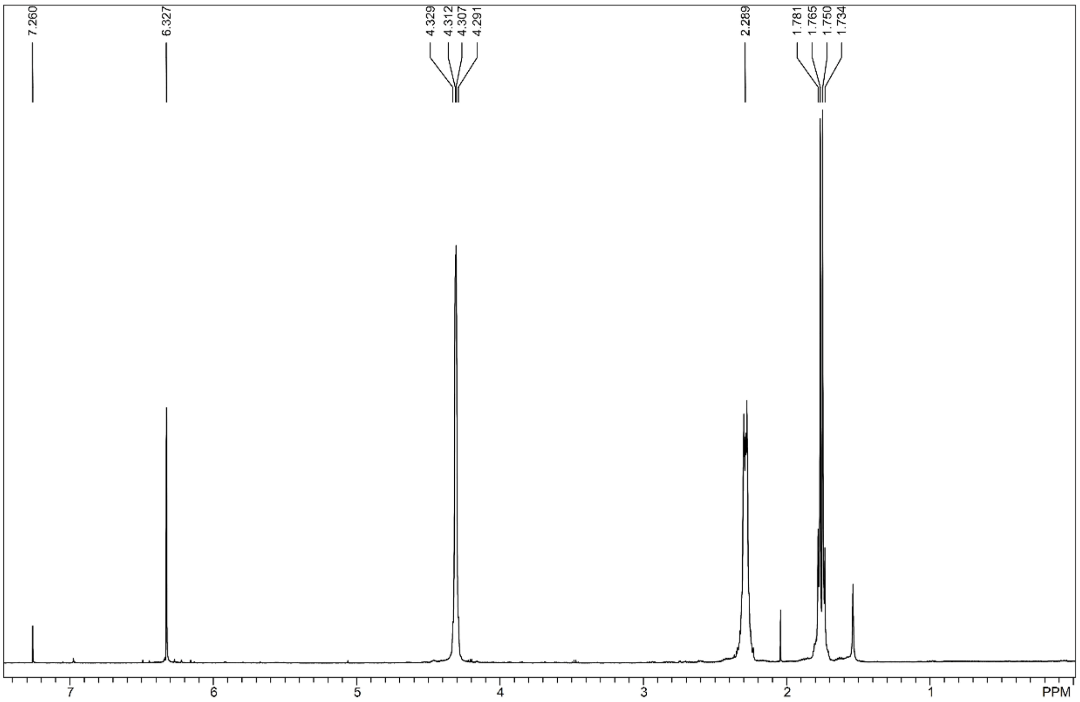
Intensity (u.a.)
[Ir(cod)(tfac)] exp.
[Ir(cod)(tfac)] calc.
10
20
30
40
50
2θ (°)

b



c

Figure S1. P-XRD patterns of the synthesized fluorinated [Ir(cod)(L)] complexes: L = *hfac* (*a*), *tfac* (*b*), *btfac* (*c*).



a

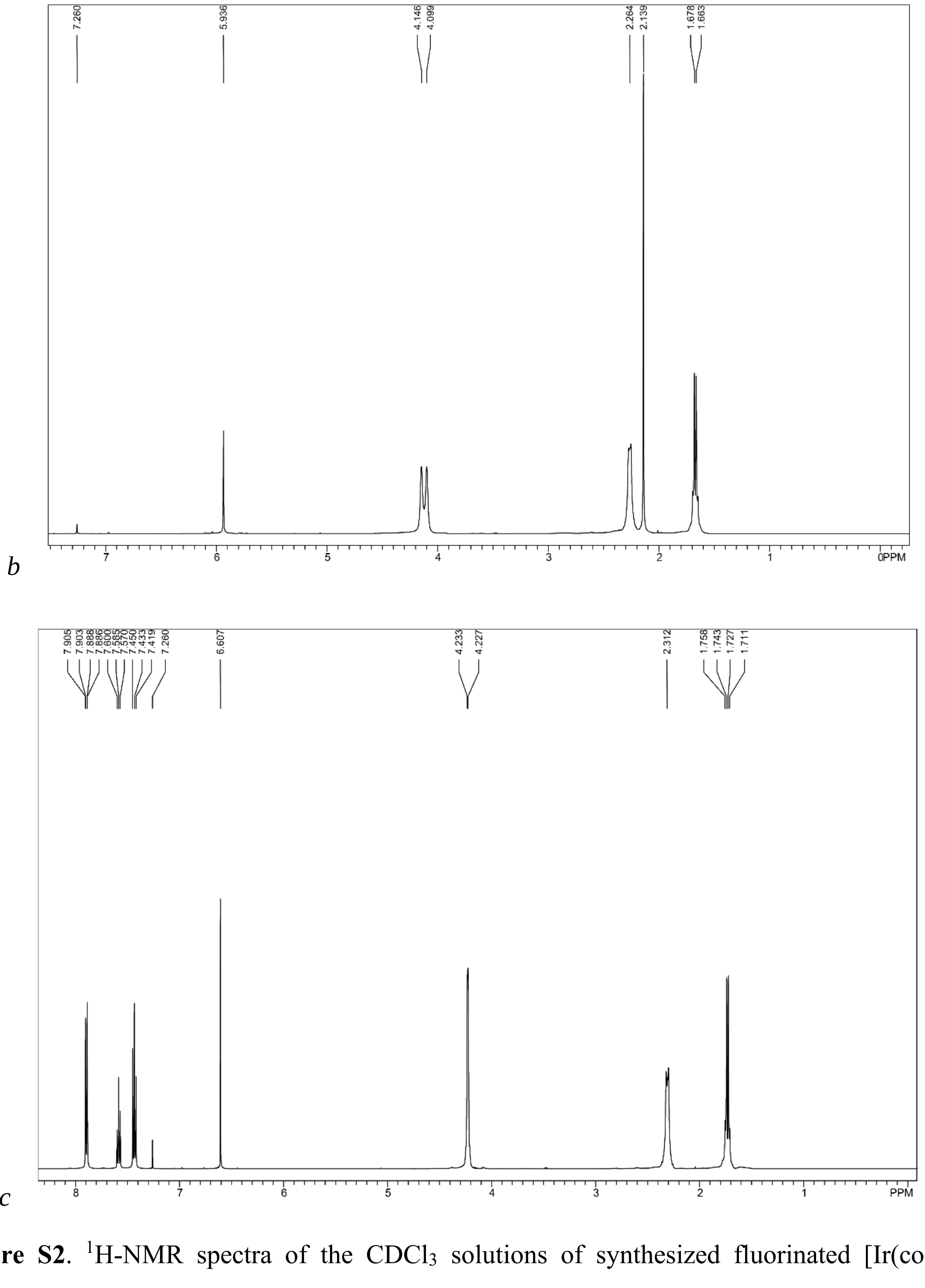


Figure S2. ^{1}H-NMR spectra of the $CDCl_3$ solutions of synthesized fluorinated [Ir(cod)(L)] complexes: L = *hfac* (*a*), *tfac* (*b*), *btfac* (*c*).

Crystal packing description

[Ir(cod)(hfac)]. The structure of the most fluorinated complex is characterized by the largest number of types of interactions are observed in the structure of the most fluorinated complex (Fig. 4*a*). The Ir…H contacts form wave-shaped chains in the direction of the *b* axis. These interactions involve both types of crystallographically independent molecules through the hydrogen atoms of CH-group of the cod-ligand. Each molecule has two such contacts: *d*(Ir…H) = 2.957(2), 3.011(2) Å (Fig. 4*a*). On the other hand, the hydrogen F…H-C contacts form other wave-shaped chains in the new direction: along the *c* axis. The first of these bonds occurs between two adjacent crystallographically equivalent molecules involving the hydrogen atom of the CH_2-group of the *cod*-ligand: *d*(F…C) = 3.393(2) Å (Fig. S5). The second hydrogen bond is realized between crystallographically independent molecules and involves the hydrogen atom of the CH-group of the cod-ligand: *d*(F…C) = 3.525(2) Å (Fig. S5). Thus, each molecule also participates in the formation of two bonds from this hydrogen network. Both of the described networks of the closest interactions form the corrugated layers in which the molecules [Ir(cod)(hfac)] are packed according to a pseudohexagonal motif. It is worth to be emphasized that the network of the shortened F...F contacts is revealed inside these layers: *d*(F…F) = 2.517(2), 2.775(2) Å (Fig. 4*a*, S5). In the rest of the structures of the fluorinated complexes considered here, such interactions are not revealed.

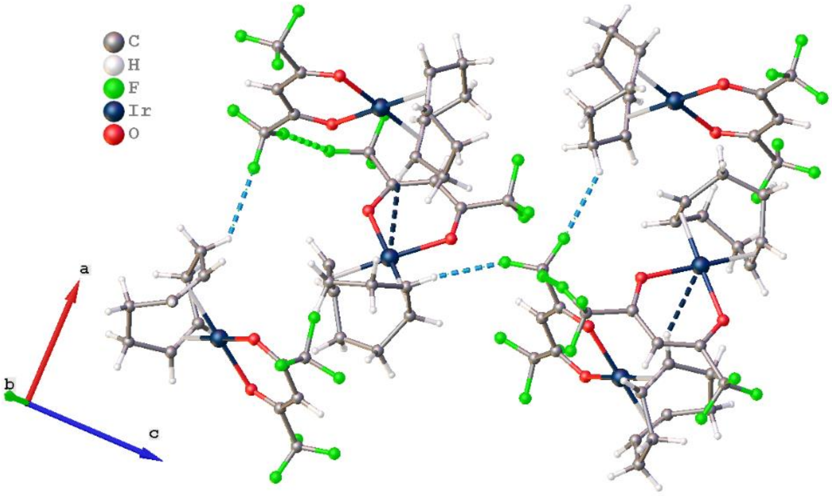
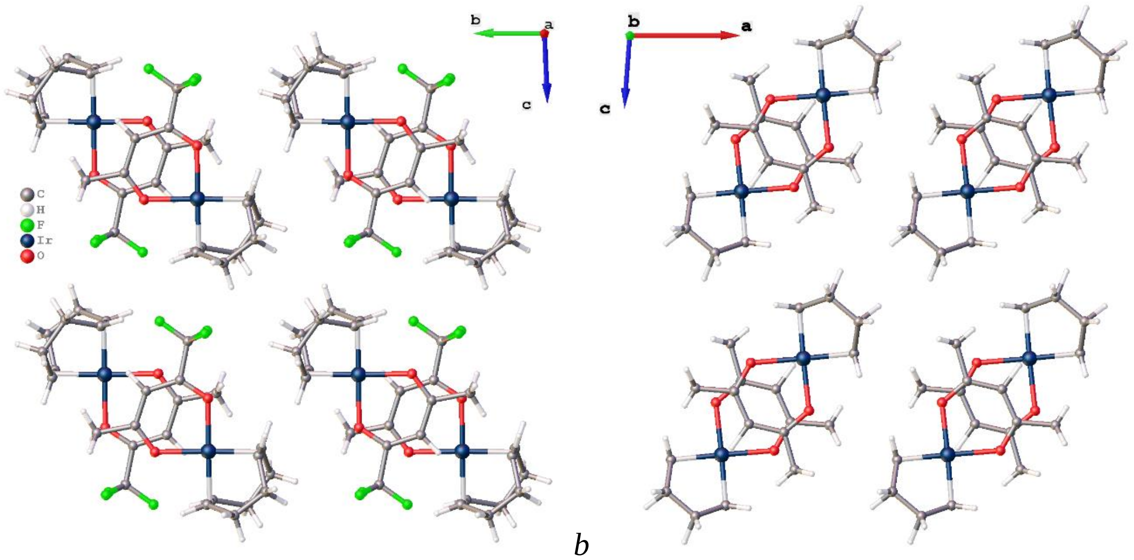


Figure S5. Layered-type crystal packing of [Ir(cod)(hfac)] complex depicted in *bc*-plane. Different types of the intermolecular interactions are shown with dotted lines and highlighted in color: C-H…F in light blue, F…F in green, Ir…H in blue.

[Ir(cod)(tfac)]. In the structure of this complex combined CF_3- and a small CH_3- terminal group, the stacks along *a* axis are formed due to the stacking interactions between the β-diketonate metallocycle rings of adjacent molecules (Fig. 4*b*). The metallocycles in stacks are located in

parallel planes. The distances between the rings centers are 3.653(2) Å and 3.919(2) Å with the shifts of 1.037(2) Å and 1.558(2) Å respectively. Thus, the stacks can be considered irregular. The stacks are supported by the inside paired hydrogen F…H-C interactions involving the hydrogen atoms of CH_3-group of *tfac*-ligand (*d*(F…C) = 3.351(2) Å). These contacts release the nearest pairs of molecules in the stacks, forming pseudo-dimers. It seems to be a reason of the irregularity stack. The stacks are packed in square motive (Fig S6*a*).



a *b*

Figure S6. Stacked-type crystal packing of [Ir(cod)(L)] complexes, L = *tfac* (*a*) and *acac* (*b*).

[Ir(cod)(acac)]. The structure of this complex contained both terminal CH_3-groups is organized in a similar way as for [Ir(cod)(tfac)], except for the absence of hydrogen interactions and regular stack character (Fig. 4*d*, Fig S6*b*). Herein, the stacks are formed along the *b* axis, the distance between the centers of the rings is 3.622(2) Å, and the shift is 1.025(2) Å. As an important difference, it should also be noted that the shortest distance between iridium from neighboring stacks of [Ir(cod)(L)] molecules is 6.638(2) Å and 9.733(2) Å for L = *acac* and L = *tfac*, respectively.

[Ir(cod)(btfac)]. The crystal packing contained aromatic group is the most specific one. It is interesting that no hydrogen F…H-C contacts are observed in this structure unlike other fluorinated complexes. This could be explained *via* the mutual arrangement of the phenyl rings appears to be the important factor determining the packing. Indeed, distinct dimeric units are formed due to the stacking interactions between Ph-group and the chelate metallocycle ring of β-diketonate ligand (Fig. 4*a*). The distance between the centers of such rings is 3.615(2) Å and the shift of the center of the phenyl ring relative to the center of the chelate ring is 1.076(2) Å. This dimer is also supported by the paired Ir…H contacts with the hydrogen atoms of the Ph-groups of the neighboring molecules (*d*(Ir...H) = 3.106(2) Å). In addition, the Ir…H contacts as for

[Ir(cod)(hfac)] structure (involving the hydrogen atoms of the *cod*-ligand) are appears here (*d*(Ir...H) = 3.061(2) Å). Thus, the layers normal to (101) plane are formed where each molecule has four Ir…H contacts with three adjacent ones (see the central molecule in Fig. 4*c*). In this layer, the dimers are arranged not according to the hexagonal but tile motif (Fig. S7).

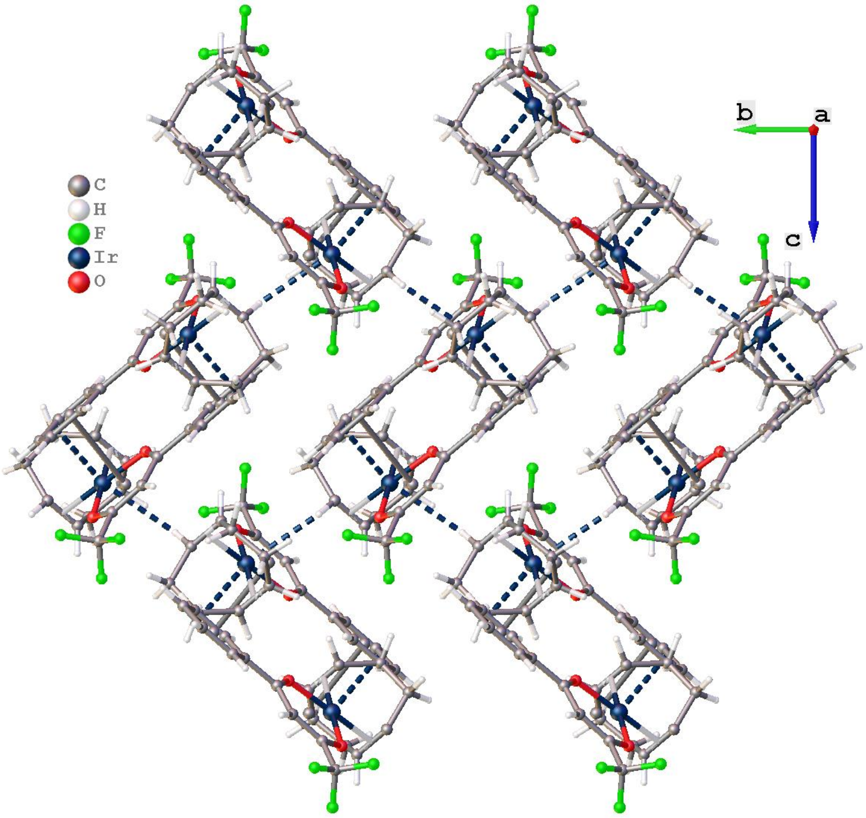


Figure S7. The tile layered packing of the dimeric units in [Ir(cod)(btfac)] structure. The shortened Ir-H contacts are with blue dotted lines. Stacking interactions are not depicted for clarity.