Electronic Supplementary Information

Metal-involving Halogen Bond Ar–I···[d_z^2Pt^{II}] in the Platinum Acetylacetonate Complex

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Variable-temperature XRD studies of the [Pt(acac)$_2$]•2(1,3,5-FIB) complex

Table S1. Main crystallography data and refinement details for [Pt(acac)$_2$]•2(1,3,5-FIB) crystal.

Formula	$C_{22}H_{14}F_6I_6O_4Pt$				
Mass	1412.82				
Crystal system	Monoclinic				
Space group	$P2_1/c$				
Z (Z')	2 (0.5)				
T, K	100	150	200	250	300
a, Å	12.1215(4)	12.1462(4)	12.1714(4)	12.2003(4)	12.2282(5)
b, Å	17.8414(6)	17.8660(6)	17.8866(6)	17.9075(7)	17.9253(7)
c, Å	7.3462(2)	7.3776(2)	7.4115(3)	7.4507(3)	7.4916(3)
α, °	90	90	90	90	90
β, °	99.7390(10)	99.8480(10)	99.9090(10)	99.9350(10)	99.9410(10)
γ, °	90	90	90	90	90
V, Å^3	1565.83(9)	1577.38(9)	1589.45(10)	1603.40(10)	1617.46(11)
d_{calc}, g·cm^{-3}	2.997	2.975	2.952	2.926	2.901
F(000)	1256	1256	1256	1256	1256
$2\theta_{max}$, °	60	60	60	60	60
Reflections measured	20716	20875	21044	21187	21368
Independent reflections	4556	4595	4636	4679	4716
Reflections with I>2σ(I)	4234	4208	4090	4059	3899
Number of parameters	180	180	180	180	180
R_1	0.0219	0.0228	0.0269	0.0286	0.0314
wR_2	0.0470	0.0489	0.0561	0.0596	0.0769
GOF	1.105	1.143	1.211	1.260	1.055
Residual electron density, e·Å^{-3}(d_{min}/d_{max})	0.688/-1.109	0.733/-1.144	0.779/-1.385	0.853/-1.480	0.700/-1.564

According to the VTXRD data the crystal of [Pt(acac)$_2$]•2(1,3,5-FIB) follows smooth anisotropic expansion upon heating (see **Fig. S1** and **Table S2**) and no structural phase transitions were observed within the studied temperature range (100–300 K, 5 XRD experiments with 50 K per step). It is in line with only slight changes of noncovalent interaction angles upon heating (the maximal change is less than 2.1°, see **Table S2**) which could be attributed to variation of bonding pattern peculiarities. **Table S3** summarizes data on thermally induced changes of the shortened intermolecular contacts in [Pt(acac)$_2$]•2(1,3,5-FIB).

Figure S1. Plots of unit cell parameters and volume temperature evolution for [Pt(acac)$_2$]•2(1,3,5-FIB).

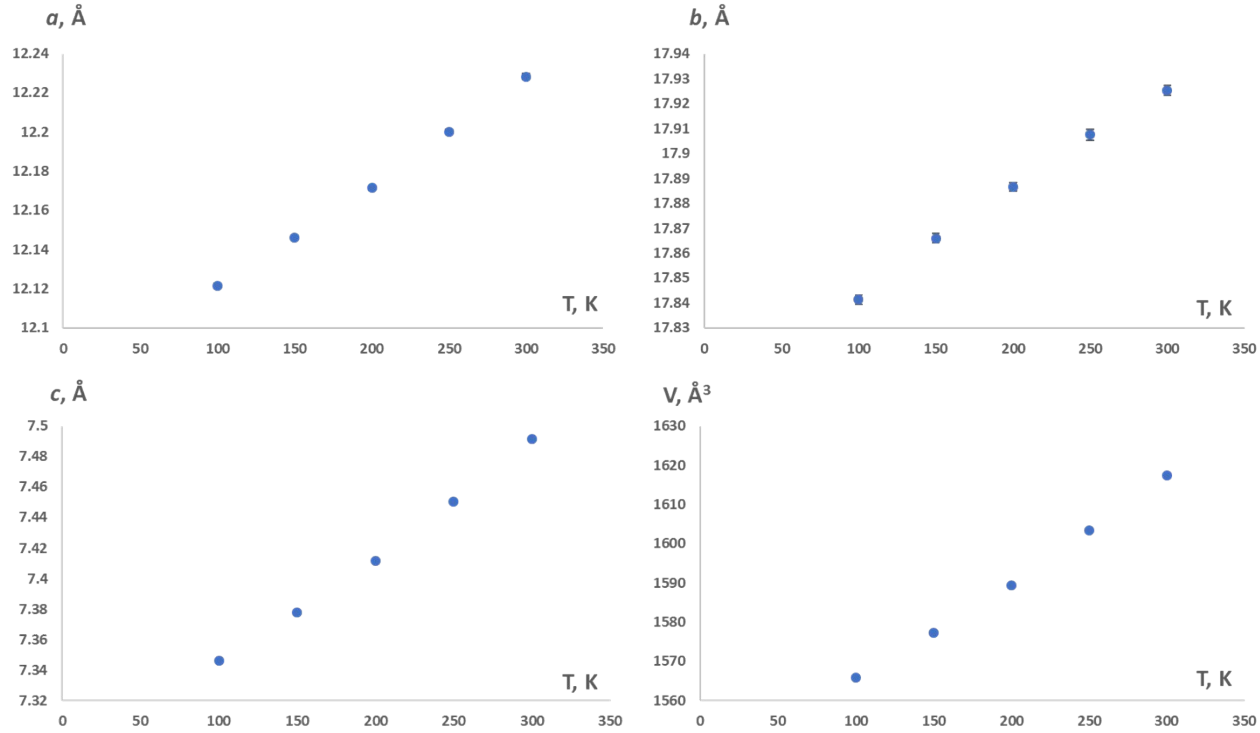

Table S2. The variation of unit cell parameters of [Pt(acac)$_2$]•2(1,3,5-FIB) according to VTXRD.

Temperature	*a*, Å	*b*, Å	*c*, Å	*β*, °	V, Å^3
100	12.1215(4)	17.8414(6)	7.3462(2)	99.739(1)	1565.83(9)
150	12.1462(4)	17.8660(6)	7.3776(2)	99.848(1)	1577.38(9)
200	12.1714(4)	17.8866(6)	7.4115(3)	99.909(1)	1589.45(10)
250	12.2003(4)	17.9075(7)	7.4507(3)	99.935(1)	1603.40(10)
300	12.2282(5)	17.9253(7)	7.4916(3)	99.941(1)	1617.46(11)
Δ[a)]	0.1067	0.0839	0.1454	0.202	51.63

a – difference between data at 300 and 100 K.

Two XBs patterns formed by the I1S and I2S atoms exhibit dramatically different temperature induced changes though both can be attributed to bifurcate XBs, at least geometrically. Surprisingly, the most conservative I1S···O2 geometric contact (lengthening on 0.012 Å upon heating with 3.374 Å at 100 K) is characterized by a rather small interaction angle (the O2···I1S-C2S angle changes from 144.1(3) to 145.8(3)° upon heating), which is nearly inappropriate to classify this contact as directed XB. The more directed (165.9(3)–164.1(4)°) and stronger (3.094–3.175 Å) counterpart of the corresponding bifurcate XB pattern, namely, the I1S···O1 contact lengthens to a significantly larger extent (on 0.081 Å). Thus, the interplay between two interactions is observed: while the weakening of the strong I1S···O1 interaction destabilizes crystal packing, the compensation is achieved by the rigidity of the weak I1S···O2 interaction. This is not the case, however, of the second bifurcate XB involving the metal atom. The I2S···O2 contact, being of the similar geometric characteristics with the I1S···O2 one at 100 K (3.370 Å, the O2···I2S–C4 angle is 153.7(3)°), weakens to a significantly larger extent upon heating (on 0.078 Å). This can be rationalized by a three-center nature of XB formed by the I2S atom and involving the metal center. Assuming the leading role of the I2S···Pt1 contact in the formation of bifurcate XB, one can expect that the weakening of the I2S···Pt1 interaction must be accompanied by the weakening of the I2S···O2 interaction. Indeed, though corresponding to the most directed intermolecular interaction in $[Pt(acac)_2]$•2(1,3,5-FIB) (the Pt1···I2SC4S angle is in the 168.8(3)–168.5(3)° range), the I2S···Pt1 contact still lengthens significantly on 0.058 Å. Finally, a relatively large strength of the XB between the I3S atoms, which can be supposed by the comparison of the I3S···I3S distance with I···I distances in CSD structures stabilized by XBs of Type I,[35] agrees well with a rather insignificant lengthening (on 0.064 Å) upon heating.

The other shortened contact in the crystal packing of $[Pt(acac)_2]$•2(1,3,5-FIB) were found to be more flexible with respect to the temperature change. The H2A···I2S distance corresponding to the H-bond increases on 0.115 Å upon heating (with the C–H bond length being normalized on the ideal value). The largest changes are observed for the stacking interaction between acetylacetonate ligands. The corresponding interplane distance increases on 0.147 Å while the area of overlap of two fragments participating in stacking interaction decreases that follows from even more pronounced lengthening of the shortest intermolecular distance between these fragments (C1···C2 on 0.169 Å).

Table S3. The thermally induced changes of main geometric characteristics of shortened intermolecular contacts in $[Pt(acac)_2]$•2(1,3,5-FIB).

Temperature	100	150	200	250	300	Δ[a)]
Pt1···I2S, Å	3.408	3.421	3.434	3.450	3.466	0.058
Pt1–I2S–C4S, °	168.83	168.70	168.69	168.75	168.46	-0.37
O2···I2S, Å	3.370	3.388	3.403	3.424	3.448	0.078
O2–I2S–C4S, °	153.72	153.45	153.32	153.20	153.17	-0.55
O1···I1S, Å	3.094	3.114	3.135	3.156	3.175	0.081
O1–I1S–C2S, °	165.93	165.38	164.80	164.29	164.08	-1.85
O2···I1S, Å	3.374	3.371	3.375	3.379	3.386	0.012
O2–I1S–C2S, °	144.12	144.65	145.23	145.69	145.88	1.76
H2A···I2S, Å	3.024	3.047	3.072	3.104	3.139	0.115
C2–H2A–I2S, °	162.90	162.34	161.90	161.69	160.84	-2.06
interplane,[b)] Å	3.349	3.386	3.428	3.466	3.496	0.147
C1···C2, Å	3.398	3.440	3.488	3.533	3.567	0.169
I3S···I3S, Å	3.594	3.608	3.624	3.640	3.658	0.064
C6S–I3S–I3S, °	146.76	147.17	147.45	147.70	147.84	1.08

a – difference between data at 300 and 100 K; b – the distance between mean-square planes based on the O1, C1, C2, C3 and O2 atoms of two acetylacetonate ligands participated in a stacking interaction.

Thus, the XBs formed by 1,3,5-FIB were found to be pronouncedly more conservative with respect to changes of external conditions than all other interactions observed in crystal packing of $[Pt(acac)_2]$•2(1,3,5-FIB). This is also supported by the analysis of Hirshfeld surfaces calculated at 100 and 300 K (**Table S4**). In terms of contributions of different intermolecular contacts into the molecular Hirshfeld surface, the least changes are again observed mainly for the contacts formed by the iodine atoms of 1,3,5-FIB. Moreover, the molecular volume of the 1,3,5-FIB, calculated as the volume enclosed by the corresponding molecular Hirshfeld surface, increases to a less extent upon heating than that of the $Pt(acac)_2$ moiety (on 7.44 and 10.79 $Å^3$, respectively, **Table S5**).

The distribution of thermally induced changes of intermolecular interactions agrees well with the anisotropy of crystal thermal expansion (**Table S2**). While the XBs in the crystal of $[Pt(acac)_2]$•2(1,3,5-FIB) are formed in the *ab* plane of unit cell, the stacking interactions and hydrogen bonds stabilize crystal packing in the direction parallel to the *c* vector. In its turn, the *c* parameter increases on 0.1454 Å upon heating while the parameters *a* and *b* change less significantly (on 0.1067 and 0.0839 Å, respectively).

Table S4. The contribution of intermolecular contacts into molecular Hirshfeld surface for the $Pt(acac)_2$ and FIB moieties of $[Pt(acac)_2]$•2(1,3,5-FIB) at 100 and 300 K. The boldface is used to highlight contacts which can in principle be considered as manifestation of intermolecular interactions leading to charge transfer on iodine atoms.

$Pt(acac)_2$				FIB			
Contact	T=100 K	T = 300 K	Δ	Contact	T=100 K	T = 300 K	Δ
Pt···H	0.9	0.7	-0.2	C···C	9.5	9.2	-0.3
Pt···I	2.0	2.1	0.1	C···H	0.1	0.1	0.0
O···I	10.1	10.0	-0.1	**C···I**	1.7	1.7	0.0
O···H	7.6	7.3	-0.3	C···F	4.2	4.1	-0.1
C···C	1.2	0.9	-0.3	**I···Pt**	1.3	1.4	0.1
C···H	3.2	3.4	0.2	**I···O**	8.0	8.0	0.0
C···I	2.0	1.9	-0.1	**I···C**	3.2	3.2	0.0
C···F	1.7	1.5	-0.2	I···H	24.1	24.5	0.4
H···F	19.0	19.4	0.4	**I···I**	6.7	6.6	-0.1
H···I	17.4	18.1	0.7	**I···F**	10.2	10.2	0.0
H···H	26.2	26.2	0.0	F···F	5.6	5.8	0.2
H···C	3.2	3.4	0.2	**F···I**	5.3	5.3	0.0
H···O	5.4	5.1	-0.3	F···H	15.4	15.6	0.2
				F···C	4.6	4.3	-0.3

Table S5. Integral characteristics of the Hirshfeld surface analysis for $Pt(acac)_2$ and FIB moieties of $[Pt(acac)_2]$•2(1,3,5-FIB) at 100 and 300 K.

Moiety	$Pt(acac)_2$			FIB		
Temperature	100	300	Δ	100	300	Δ
Volume	280.91	291.7	10.79	240.36	247.8	7.44
Area	287.05	292.28	5.23	230.66	234.4	3.74
Globularity	0.723	0.728	0.005	0.81	0.814	0.004
Asphericity	0.165	0.161	-0.004	0.105	0.102	-0.003

XRD study of the [Pd(acac)$_2$]•(1,3,5-FIB) complex

Table S6. Main crystallography data and refinement details for [Pd(acac)$_2$]• (1,3,5-FIB) crystal.

Formula	$C_{16}H_{14}F_4I_2O_4Pd$
Mass	814.37
T, K	100
Crystal system	Monoclinic
Space group	$P2_1/n$
Z	4
a, Å	4.34010(10)
b, Å	16.4262(5)
c, Å	30.1450(11)
α, °	90
β, °	93.037(3)
γ, °	90
V, Å^3	2146.06(11)
d_{calc}, g·cm^{-3}	2.521
F(000)	1496
$2\theta_{max}$, °	59
Reflections measured	25130
Number of independent reflections	5407
Reflections with I>2σ(I)	4988
Number of parameters	251
R_1	0.0344
wR_2	0.0633
GOF	1.176
Residual electron density, e·Å^{-3}(d_{min}/d_{max})	1.102/-0.812

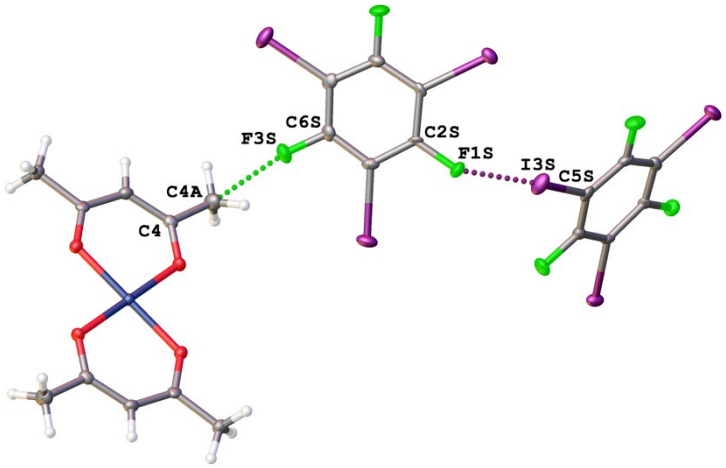

Fig. S2. Short contacts (dotted lines) in the structure of $[Pd(acac)_2]$·1,3,5-FIB; environment of the 1,3,5-FIB molecule.

Table S7. Cartesian atomic coordinates of model supramolecular associates.

Atom	X	Y	Z
I-Pt_100			
Pt	0.000000	8.920700	0.000000
O	0.900487	9.587255	1.642831
O	-0.536680	7.169567	0.761683
C	0.975209	8.883233	2.722364
C	1.720175	9.543365	3.848236
H	1.696794	10.515721	3.730218
H	2.651107	9.236493	3.848236
H	1.299841	9.307858	4.701147
C	0.445357	7.603113	2.899752
H	0.565611	7.216846	3.759904
C	-0.235350	6.826655	1.971542
C	-0.710268	5.450548	2.344419
H	-1.583948	5.284623	1.933168
H	-0.791470	5.386319	3.318968
H	-0.066485	4.785063	2.025845
O	-0.900487	8.254145	-1.642831
O	0.536680	10.671833	-0.761683
C	-0.975209	8.958167	-2.722364
C	-1.720175	8.298035	-3.848236
H	-1.696794	7.325679	-3.730218
H	-2.651107	8.604907	-3.848236
H	-1.299841	8.533542	-4.701147
C	-0.445357	10.238287	-2.899752
H	-0.565611	10.624554	-3.759904
C	0.235350	11.014745	-1.971542
C	0.710268	12.390852	-2.344419
H	1.583948	12.556777	-1.933168
H	0.791470	12.455081	-3.318968
H	0.066485	13.056337	-2.025845
I	-3.484176	6.759928	-0.828583
I	-9.545964	6.736377	-0.455996
I	-6.479079	1.538286	-0.829742
F	-4.157173	3.684606	-0.894905
F	-6.529265	7.731749	-0.742858
F	-8.844599	3.642857	-0.540129
C	-5.316613	4.349376	-0.804401
C	-5.299361	5.734583	-0.784852
C	-6.518935	6.381690	-0.720413
C	-7.724987	5.711746	-0.642941

C	-7.688032	4.328324	-0.639321
C	-6.496807	3.618771	-0.736342
I	3.484176	11.081472	0.828583
I	9.545964	11.105023	0.455996
I	6.479079	16.303114	0.829742
F	4.157173	14.156794	0.894905
F	6.529265	10.109651	0.742858
F	8.844599	14.198543	0.540129
C	5.316613	13.492024	0.804401
C	5.299361	12.106817	0.784852
C	6.518935	11.459710	0.720413
C	7.724987	12.129654	0.642941
C	7.688032	13.513076	0.639321
C	6.496807	14.222629	0.736342
I	8.637324	6.759928	-0.828583
I	2.575536	6.736377	-0.455996
I	5.642421	1.538286	-0.829742
F	7.964327	3.684606	-0.894905
F	5.592235	7.731749	-0.742858
F	3.276901	3.642857	-0.540129
C	6.804887	4.349376	-0.804401
C	6.822139	5.734583	-0.784852
C	5.602565	6.381690	-0.720413
C	4.396513	5.711746	-0.642941
C	4.433468	4.328324	-0.639321
C	5.624693	3.618771	-0.736342
I	-8.637324	11.081472	0.828583
I	-2.575536	11.105023	0.455996
I	-5.642421	16.303114	0.829742
F	-7.964327	14.156794	0.894905
F	-5.592235	10.109651	0.742858
F	-3.276901	14.198543	0.540129
C	-6.804887	13.492024	0.804401
C	-6.822139	12.106817	0.784852
C	-5.602565	11.459710	0.720413
C	-4.396513	12.129654	0.642941
C	-4.433468	13.513076	0.639321
C	-5.624693	14.222629	0.736342
I-Pt_150			
Pt	0.000000	8.933000	0.000000
O	0.904655	9.594935	1.644950
O	-0.541174	7.183740	0.757418
C	0.976408	8.888871	2.715658
C	1.725089	9.535084	3.839428
H	1.776385	10.501635	3.683874
H	2.630534	9.163471	3.885222
H	1.259020	9.365357	4.684073

C	0.444108	7.605556	2.892292
H	0.567666	7.212504	3.747840
C	-0.243855	6.842678	1.957512
C	-0.717788	5.459850	2.329679
H	-1.572177	5.275830	1.884823
H	-0.837783	5.406252	3.300803
H	-0.053853	4.798808	2.045466
O	-0.904655	8.271065	-1.644950
O	0.541174	10.682260	-0.757418
C	-0.976408	8.977129	-2.715658
C	-1.725089	8.330916	-3.839428
H	-1.776385	7.364365	-3.683874
H	-2.630534	8.702529	-3.885222
H	-1.259020	8.500643	-4.684073
C	-0.444108	10.260444	-2.892292
H	-0.567666	10.653496	-3.747840
C	0.243855	11.023322	-1.957512
C	0.717788	12.406150	-2.329679
H	1.572177	12.590170	-1.884823
H	0.837783	12.459748	-3.300803
H	0.053853	13.067192	-2.045466
I	-3.499636	6.768891	-0.804230
I	-9.559068	6.744594	-0.468044
I	-6.491540	1.549340	-0.824220
F	-4.171394	3.692545	-0.875174
F	-6.543632	7.739373	-0.731250
F	-8.853197	3.650560	-0.549528
C	-5.331516	4.361805	-0.794490
C	-5.309716	5.743383	-0.766141
C	-6.528688	6.391919	-0.713078
C	-7.740894	5.722480	-0.636028
C	-7.703698	4.336614	-0.640389
C	-6.509113	3.624118	-0.734885
I	3.499636	11.097109	0.804230
I	9.559068	11.121406	0.468044
I	6.491540	16.316660	0.824220
F	4.171394	14.173455	0.875174
F	6.543632	10.126627	0.731250
F	8.853197	14.215440	0.549528
C	5.331516	13.504195	0.794490
C	5.309716	12.122617	0.766141
C	6.528688	11.474081	0.713078
C	7.740894	12.143520	0.636028
C	7.703698	13.529386	0.640389
C	6.509113	14.241882	0.734885
I	8.646564	6.768891	-0.804230
I	2.587132	6.744594	-0.468044

I	5.654660	1.549340	-0.824220
F	7.974806	3.692545	-0.875174
F	5.602568	7.739373	-0.731250
F	3.293003	3.650560	-0.549528
C	6.814684	4.361805	-0.794490
C	6.836484	5.743383	-0.766141
C	5.617512	6.391919	-0.713078
C	4.405306	5.722480	-0.636028
C	4.442502	4.336614	-0.640389
C	5.637087	3.624118	-0.734885
I	-8.646564	11.097109	0.804230
I	-2.587132	11.121406	0.468044
I	-5.654660	16.316660	0.824220
F	-7.974806	14.173455	0.875174
F	-5.602568	10.126627	0.731250
F	-3.293003	14.215440	0.549528
C	-6.814684	13.504195	0.794490
C	-6.836484	12.122617	0.766141
C	-5.617512	11.474081	0.713078
C	-4.405306	12.143520	0.636028
C	-4.442502	13.529386	0.640389
C	-5.637087	14.241882	0.734885
I-Pt_200			
Pt	0.000000	8.943300	0.000000
O	0.906284	9.599023	1.647092
O	-0.540453	7.192381	0.752727
C	0.980799	8.886063	2.711568
C	1.724785	9.542501	3.831532
H	1.786020	10.506589	3.662150
H	2.627182	9.165094	3.891400
H	1.250066	9.388676	4.674790
C	0.446676	7.603594	2.884600
H	0.572656	7.206511	3.738080
C	-0.245270	6.846990	1.954461
C	-0.728699	5.464356	2.318048
H	-1.607283	5.306954	1.912846
H	-0.801593	5.389233	3.292723
H	-0.092399	4.797186	1.985125
O	-0.906284	8.287577	-1.647092
O	0.540453	10.694219	-0.752727
C	-0.980799	9.000537	-2.711568
C	-1.724785	8.344099	-3.831532
H	-1.786020	7.380011	-3.662150
H	-2.627182	8.721506	-3.891400
H	-1.250066	8.497924	-4.674790
C	-0.446676	10.283006	-2.884600
H	-0.572656	10.680089	-3.738080

C	0.245270	11.039610	-1.954461
C	0.728699	12.422244	-2.318048
H	1.607283	12.579646	-1.912846
H	0.801593	12.497367	-3.292723
H	0.092399	13.089414	-1.985125
I	3.515257	11.109546	0.785727
I	9.571010	11.134587	0.481278
I	6.502826	16.326888	0.822086
F	4.183222	14.183001	0.865161
F	6.559300	10.142418	0.730824
F	8.863121	14.228611	0.560712
C	5.340221	13.516904	0.790692
C	5.321490	12.134269	0.758567
C	6.541217	11.492141	0.708921
C	7.750234	12.157522	0.643943
C	7.714554	13.538368	0.646133
C	6.530216	14.253832	0.730094
I	-3.515257	6.777054	-0.785727
I	-9.571010	6.752013	-0.481278
I	-6.502826	1.559712	-0.822086
F	-4.183222	3.703599	-0.865161
F	-6.559300	7.744182	-0.730824
F	-8.863121	3.657989	-0.560712
C	-5.340221	4.369696	-0.790692
C	-5.321490	5.752331	-0.758567
C	-6.541217	6.394460	-0.708921
C	-7.750234	5.729078	-0.643943
C	-7.714554	4.348232	-0.646133
C	-6.530216	3.632768	-0.730094
I	8.656143	6.777054	-0.785727
I	2.600390	6.752013	-0.481278
I	5.668574	1.559712	-0.822086
F	7.988178	3.703599	-0.865161
F	5.612100	7.744182	-0.730824
F	3.308279	3.657989	-0.560712
C	6.831179	4.369696	-0.790692
C	6.849910	5.752331	-0.758567
C	5.630183	6.394460	-0.708921
C	4.421166	5.729078	-0.643943
C	4.456846	4.348232	-0.646133
C	5.641184	3.632768	-0.730094
I	-8.656143	11.109546	0.785727
I	-2.600390	11.134587	0.481278
I	-5.668574	16.326888	0.822086
F	-7.988178	14.183001	0.865161
F	-5.612100	10.142418	0.730824
F	-3.308279	14.228611	0.560712

C	-6.831179	13.516904	0.790692
C	-6.849910	12.134269	0.758567
C	-5.630183	11.492141	0.708921
C	-4.421166	12.157522	0.643943
C	-4.456846	13.538368	0.646133
C	-5.641184	14.253832	0.730094
I-Pt_250			
Pt	0.000000	8.953750	0.000000
O	0.906140	9.607016	1.652736
O	-0.543617	7.202217	0.749309
C	0.984558	8.887492	2.709548
C	1.727689	9.535744	3.830209
H	1.763545	10.504540	3.681227
H	2.639559	9.177594	3.869105
H	1.268366	9.353087	4.676392
C	0.454074	7.610687	2.875409
H	0.591923	7.207769	3.725261
C	-0.246582	6.860363	1.958037
C	-0.725150	5.468951	2.308106
H	-1.578453	5.293457	1.858227
H	-0.848729	5.400902	3.278318
H	-0.060313	4.811745	2.016015
O	-0.906140	8.300484	-1.652736
O	0.543617	10.705283	-0.749309
C	-0.984558	9.020008	-2.709548
C	-1.727689	8.371756	-3.830209
H	-1.763545	7.402960	-3.681227
H	-2.639559	8.729906	-3.869105
H	-1.268366	8.554413	-4.676392
C	-0.454074	10.296812	-2.875409
H	-0.591923	10.699731	-3.725261
C	0.246582	11.047137	-1.958037
C	0.725150	12.438549	-2.308106
H	1.578453	12.614043	-1.858227
H	0.848729	12.506598	-3.278318
H	0.060313	13.095755	-2.016015
I	3.531626	11.120737	0.772427
I	9.584736	11.148851	0.495601
I	6.514000	16.337908	0.823212
F	4.196632	14.194022	0.851321
F	6.572371	10.158746	0.730961
F	8.876714	14.242551	0.572440
C	5.353746	13.529116	0.778665
C	5.340908	12.146657	0.754446
C	6.554845	11.503420	0.712614
C	7.761721	12.175309	0.655370
C	7.721588	13.550605	0.654636

C	6.541228	14.263324	0.734631
I	-3.531626	6.786763	-0.772427
I	-9.584736	6.758649	-0.495601
I	-6.514000	1.569592	-0.823212
F	-4.196632	3.713478	-0.851321
F	-6.572371	7.748754	-0.730961
F	-8.876714	3.664949	-0.572440
C	-5.353746	4.378384	-0.778665
C	-5.340908	5.760843	-0.754446
C	-6.554845	6.404080	-0.712614
C	-7.761721	5.732191	-0.655370
C	-7.721588	4.356895	-0.654636
C	-6.541228	3.644176	-0.734631
I	8.668674	6.786763	-0.772427
I	2.615564	6.758649	-0.495601
I	5.686300	1.569592	-0.823212
F	8.003668	3.713478	-0.851321
F	5.627929	7.748754	-0.730961
F	3.323586	3.664949	-0.572440
C	6.846554	4.378384	-0.778665
C	6.859392	5.760843	-0.754446
C	5.645455	6.404080	-0.712614
C	4.438579	5.732191	-0.655370
C	4.478712	4.356895	-0.654636
C	5.659072	3.644176	-0.734631
I	-8.668674	11.120737	0.772427
I	-2.615564	11.148851	0.495601
I	-5.686300	16.337908	0.823212
F	-8.003668	14.194022	0.851321
F	-5.627929	10.158746	0.730961
F	-3.323586	14.242551	0.572440
C	-6.846554	13.529116	0.778665
C	-6.859392	12.146657	0.754446
C	-5.645455	11.503420	0.712614
C	-4.438579	12.175309	0.655370
C	-4.478712	13.550605	0.654636
C	-5.659072	14.263324	0.734631
I-Pt_300			
Pt	0.000000	8.962650	0.000000
O	0.905830	9.608678	1.655137
O	-0.546900	7.213320	0.748243
C	0.978067	8.890949	2.708138
C	1.731169	9.543430	3.825337
H	1.759222	10.511396	3.679230
H	2.644593	9.190301	3.853377
H	1.281238	9.353422	4.676149
C	0.452574	7.603912	2.866789

H	0.598096	7.193423	3.710960
C	-0.245347	6.867182	1.951040
C	-0.729287	5.469009	2.291217
H	-1.540879	5.270038	1.779844
H	-0.926635	5.415233	3.249765
H	-0.032799	4.818321	2.063940
O	-0.905830	8.316622	-1.655137
O	0.546900	10.711980	-0.748243
C	-0.978067	9.034351	-2.708138
C	-1.731169	8.381870	-3.825337
H	-1.759222	7.413904	-3.679230
H	-2.644593	8.734999	-3.853377
H	-1.281238	8.571878	-4.676149
C	-0.452574	10.321388	-2.866789
H	-0.598096	10.731877	-3.710960
C	0.245347	11.058118	-1.951040
C	0.729287	12.456291	-2.291217
H	1.540879	12.655262	-1.779844
H	0.926635	12.510067	-3.249765
H	0.032799	13.106979	-2.063940
I	3.547230	11.128743	0.764256
I	9.597335	11.160830	0.511226
I	6.522949	16.346260	0.827126
F	4.207472	14.200423	0.845647
F	6.587949	10.170815	0.729057
F	8.888190	14.254199	0.588854
C	5.374547	13.530016	0.779973
C	5.354041	12.158731	0.750457
C	6.570841	11.518798	0.715037
C	7.768863	12.180241	0.661169
C	7.736235	13.562282	0.658956
C	6.550547	14.279294	0.740126
I	-3.547230	6.796557	-0.764256
I	-9.597335	6.764470	-0.511226
I	-6.522949	1.579040	-0.827126
F	-4.207472	3.724877	-0.845647
F	-6.587949	7.754485	-0.729057
F	-8.888190	3.671101	-0.588854
C	-5.374547	4.395284	-0.779973
C	-5.354041	5.766569	-0.750457
C	-6.570841	6.406502	-0.715037
C	-7.768863	5.745059	-0.661169
C	-7.736235	4.363018	-0.658956
C	-6.550547	3.646006	-0.740126
I	8.680970	6.796557	-0.764256
I	2.630865	6.764470	-0.511226
I	5.705251	1.579040	-0.827126

F	8.020728	3.724877	-0.845647
F	5.640251	7.754485	-0.729057
F	3.340010	3.671101	-0.588854
C	6.853653	4.395284	-0.779973
C	6.874159	5.766569	-0.750457
C	5.657359	6.406502	-0.715037
C	4.459337	5.745059	-0.661169
C	4.491965	4.363018	-0.658956
C	5.677653	3.646006	-0.740126
I	-8.680970	11.128743	0.764256
I	-2.630865	11.160830	0.511226
I	-5.705251	16.346260	0.827126
F	-8.020728	14.200423	0.845647
F	-5.640251	10.170815	0.729057
F	-3.340010	14.254199	0.588854
C	-6.853653	13.530016	0.779973
C	-6.874159	12.158731	0.750457
C	-5.657359	11.518798	0.715037
C	-4.459337	12.180241	0.661169
C	-4.491965	13.562282	0.658956
C	-5.677653	14.279294	0.740126
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I	-0.123092	9.835352	24.986113
I	1.237571	9.916168	19.097129
I	3.070715	14.419083	22.692892
F	-0.012493	9.104714	21.896978
F	1.558902	12.507894	24.722112
F	2.686777	12.545346	20.167881
C	0.780972	10.765731	23.343109
C	2.126253	12.582469	22.437922
C	1.337282	10.798584	20.972525
C	2.044860	11.969772	21.198897
C	0.701930	10.238450	22.067961
C	1.486725	11.946775	23.497536
Pd	1.371496	8.213100	15.051331
O	0.580665	7.817721	16.827689
O	0.582777	6.644398	14.129287
C	-0.210340	6.823443	17.020346
C	-0.205874	5.824731	14.719299
C	-0.605459	5.888793	16.058265
H	-1.202834	5.235030	16.339725
C	-0.737955	4.699536	13.876424
H	-1.697599	4.725818	13.877327
H	-0.440340	3.861800	14.238559
H	-0.415521	4.793165	12.977258
C	-0.706863	6.660824	18.427646
H	0.031474	6.455497	19.006821

H	-1.347112	5.946284	18.461963
H	-1.122850	7.477206	18.717835
O	2.162328	8.608479	13.274973
O	2.160216	9.781802	15.973376
C	2.953333	9.602757	13.082316
C	2.948867	10.601469	15.383363
C	3.348452	10.537407	14.044397
H	3.945826	11.191170	13.762937
C	3.480947	11.726664	16.226238
H	4.440591	11.700382	16.225335
H	3.183333	12.564400	15.864103
H	3.158513	11.633035	17.125405
C	3.449856	9.765376	11.675017
H	2.711518	9.970703	11.095841
H	4.090105	10.479916	11.640699
H	3.865843	8.948994	11.384827
I	2.866085	6.590848	5.116550
I	1.505422	6.510032	11.005533
I	-0.327723	2.007117	7.409770
F	2.755486	7.321486	8.205685
F	1.184091	3.918306	5.380550
F	0.056216	3.880854	9.934782
C	1.962021	5.660469	6.759553
C	0.616740	3.843731	7.664740
C	1.405711	5.627616	9.130137
C	0.698133	4.456428	8.903765
C	2.041063	6.187750	8.034702
C	1.256268	4.479425	6.605126
Pd	-2.968604	8.213100	15.051331
O	-2.177772	8.608479	13.274973
O	-2.179884	9.781802	15.973376
C	-1.386767	9.602757	13.082316
C	-1.391233	10.601469	15.383363
C	-0.991648	10.537407	14.044397
H	-0.394274	11.191170	13.762937
C	-0.859153	11.726664	16.226238
H	0.100491	11.700382	16.225335
H	-1.156767	12.564400	15.864103
H	-1.181587	11.633035	17.125405
C	-0.890244	9.765376	11.675017
H	-1.628582	9.970703	11.095841
H	-0.249995	10.479916	11.640699
H	-0.474257	8.948994	11.384827
O	-3.759435	7.817721	16.827689
O	-3.757323	6.644398	14.129287
C	-4.550440	6.823443	17.020346
C	-4.545974	5.824731	14.719299

C	-4.945559	5.888793	16.058265
H	-5.542934	5.235030	16.339725
C	-5.078055	4.699536	13.876424
H	-6.037699	4.725818	13.877327
H	-4.780440	3.861800	14.238559
H	-4.755621	4.793165	12.977258
C	-5.046963	6.660824	18.427646
H	-4.308626	6.455497	19.006821
H	-5.687212	5.946284	18.461963
H	-5.462950	7.477206	18.717835
Pd	5.711596	8.213100	15.051331
O	4.920765	7.817721	16.827689
O	4.922877	6.644398	14.129287
C	4.129760	6.823443	17.020346
C	4.134226	5.824731	14.719299
C	3.734641	5.888793	16.058265
H	3.137266	5.235030	16.339725
C	3.602145	4.699536	13.876424
H	2.642501	4.725818	13.877327
H	3.899760	3.861800	14.238559
H	3.924579	4.793165	12.977258
C	3.633237	6.660824	18.427646
H	4.371574	6.455497	19.006821
H	2.992988	5.946284	18.461963
H	3.217250	7.477206	18.717835
O	6.502428	8.608479	13.274973
O	6.500316	9.781802	15.973376
C	7.293433	9.602757	13.082316
C	7.288967	10.601469	15.383363
C	7.688552	10.537407	14.044397
H	8.285926	11.191170	13.762937
C	7.821047	11.726664	16.226238
H	8.780691	11.700382	16.225335
H	7.523433	12.564400	15.864103
H	7.498613	11.633035	17.125405
C	7.789956	9.765376	11.675017
H	7.051618	9.970703	11.095841
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H	8.205943	8.948994	11.384827
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I	-0.123092	9.835352	24.986113
I	1.237571	9.916168	19.097129
I	3.070715	14.419083	22.692892
F	-0.012493	9.104714	21.896978
F	1.558902	12.507894	24.722112
F	2.686777	12.545346	20.167881
C	0.780972	10.765731	23.343109

C	2.126253	12.582469	22.437922
C	1.337282	10.798584	20.972525
C	2.044860	11.969772	21.198897
C	0.701930	10.238450	22.067961
C	1.486725	11.946775	23.497536
Pd	-0.798554	16.426200	15.051331
O	0.193872	18.024798	15.675961
O	-0.084676	15.207212	16.443278
C	0.772569	15.580251	17.317159
C	1.295793	16.874635	17.459845
H	1.893713	17.009330	18.157926
C	1.008138	17.980119	16.656405
C	1.225983	14.502692	18.260275
H	0.463585	14.011549	18.576353
H	1.680712	14.901849	19.006821
H	1.823153	13.906421	17.802714
C	1.708142	19.294215	16.919201
H	2.328629	19.473260	16.210284
H	2.181162	19.243293	17.754550
H	1.058283	19.998899	16.962850
O	-1.790979	14.827602	14.426701
O	-1.512432	17.645188	13.659384
C	-2.369676	17.272149	12.785504
C	-2.892900	15.977765	12.642817
H	-3.490820	15.843070	11.944736
C	-2.605245	14.872281	13.446257
C	-2.823091	18.349708	11.842387
H	-2.060692	18.840851	11.526309
H	-3.277820	17.950551	11.095841
H	-3.420260	18.945979	12.299948
C	-3.305249	13.558185	13.183461
H	-3.925736	13.379140	13.892379
H	-3.778269	13.609107	12.348112
H	-2.655390	12.853502	13.139812
Pd	3.541546	16.426200	15.051331
O	4.533972	18.024798	15.675961
O	4.255424	15.207212	16.443278
C	5.112669	15.580251	17.317159
C	5.635893	16.874635	17.459845
H	6.233813	17.009330	18.157926
C	5.348238	17.980119	16.656405
C	5.566083	14.502692	18.260275
H	4.803685	14.011549	18.576353
H	6.020812	14.901849	19.006821
H	6.163253	13.906421	17.802714
C	6.048242	19.294215	16.919201
H	6.668729	19.473260	16.210284

H	6.521262	19.243293	17.754550
H	5.398383	19.998899	16.962850
O	2.549121	14.827602	14.426701
O	2.827668	17.645188	13.659384
C	1.970424	17.272149	12.785504
C	1.447200	15.977765	12.642817
H	0.849280	15.843070	11.944736
C	1.734855	14.872281	13.446257
C	1.517009	18.349708	11.842387
H	2.279408	18.840851	11.526309
H	1.062280	17.950551	11.095841
H	0.919840	18.945979	12.299948
C	1.034851	13.558185	13.183461
H	0.414364	13.379140	13.892379
H	0.561831	13.609107	12.348112
H	1.684710	12.853502	13.139812
I	4.237581	18.048452	20.167881
I	2.876918	18.129268	26.056864
I	1.043774	22.632183	22.461101
F	4.126982	17.317814	23.257016
F	2.555587	20.720994	20.431881
F	1.427713	20.758446	24.986113
C	3.333517	18.978831	21.810884
C	1.988237	20.795569	22.716071
C	2.777207	19.011684	24.181469
C	2.069629	20.182872	23.955097
C	3.412559	18.451550	23.086033
C	2.627764	20.159875	21.656457
I	2.845512	14.803948	9.934782
I	4.206175	14.723132	4.045798
I	6.039319	10.220217	7.641561
F	2.956110	15.534586	6.845646
F	4.527505	12.131406	9.670781
F	5.655380	12.093954	5.116550
C	3.749575	13.873569	8.291778
C	5.094856	12.056831	7.386591
C	4.305885	13.840716	5.921194
C	5.013464	12.669528	6.147566
C	3.670533	14.400850	7.016630
C	4.455329	12.692525	8.446205
I	7.206185	23.017048	5.116550
I	5.845522	22.936232	11.005533
I	4.012377	18.433317	7.409770
F	7.095586	23.747686	8.205685
F	5.524191	20.344506	5.380550
F	4.396316	20.307054	9.934782
C	6.302121	22.086669	6.759553

C	4.956840	20.269931	7.664740
C	5.745811	22.053816	9.130137
C	5.038233	20.882628	8.903765
C	6.381163	22.613950	8.034702
C	5.596368	20.905625	6.605126
Pd	7.881646	16.426200	15.051331
O	8.874072	18.024798	15.675961
O	8.595524	15.207212	16.443278
C	9.452769	15.580251	17.317159
C	9.975993	16.874635	17.459845
H	10.573913	17.009330	18.157926
C	9.688338	17.980119	16.656405
C	9.906183	14.502692	18.260275
H	9.143785	14.011549	18.576353
H	10.360912	14.901849	19.006821
H	10.503353	13.906421	17.802714
C	10.388342	19.294215	16.919201
H	11.008829	19.473260	16.210284
H	10.861362	19.243293	17.754550
H	9.738483	19.998899	16.962850
O	6.889221	14.827602	14.426701
O	7.167768	17.645188	13.659384
C	6.310524	17.272149	12.785504
C	5.787300	15.977765	12.642817
H	5.189380	15.843070	11.944736
C	6.074955	14.872281	13.446257
C	5.857109	18.349708	11.842387
H	6.619508	18.840851	11.526309
H	5.402380	17.950551	11.095841
H	5.259940	18.945979	12.299948
C	5.374951	13.558185	13.183461
H	4.754464	13.379140	13.892379
H	4.901931	13.609107	12.348112
H	6.024810	12.853502	13.139812

We also carried out full geometry optimization procedure in the gas phase (M06/DZP-DKH level of theory) for two model supramolecular associates featuring the I···C XB and I···η^2(O,O) bifurcated XB constructed based on the appropriate experimental X-ray geometry of [Pd(acac)$_2$]·1,3,5-FIB at 100 K as starting point. In both cases, we found corresponding minima on the potential energy surface (see **Table S8** for Cartesian atomic coordinates of their optimized equilibrium structures and **Table S9** for results of QTAIM analysis).

Table S8. Cartesian atomic coordinates for optimized equilibrium structures of two model supramolecular associates constructed based on the appropriate experimental X-ray geometry of $[Pd(acac)_2]$·1,3,5-FIB at 100 K as starting point.

Atom	X	Y	Z
$[Pd(acac)_2]$·1,3,5-FIB featuring I···C XB			
Pd	-3.868445	0.040103	0.255216
O	-3.934209	-0.471660	-1.604814
O	-3.841291	-1.773784	0.914188
C	-3.681061	-2.800703	0.182767
C	-3.614401	-2.800144	-1.223179
H	-3.477160	-3.763137	-1.725424
C	-3.769167	-1.657739	-2.030287
C	-3.499994	-4.085588	0.928229
H	-4.149302	-4.100893	1.818354
H	-2.453254	-4.134142	1.283799
H	-3.694302	-4.967901	0.299057
C	-3.684109	-1.784744	-3.518714
H	-4.432754	-1.131760	-3.995967
H	-3.810047	-2.823026	-3.862159
H	-2.687446	-1.425748	-3.838280
O	-3.757444	0.548600	2.110745
O	-3.839575	1.850409	-0.403734
C	-3.734042	2.888681	0.326359
C	-3.653317	2.897766	1.728666
H	-3.565723	3.867934	2.227646
C	-3.668992	1.747506	2.532765
C	-3.694949	4.177295	-0.435164
H	-4.578178	4.240591	-1.094012
H	-3.663523	5.057535	0.224751
H	-2.807459	4.184255	-1.092624
C	-3.576493	1.872134	4.022294
H	-2.696630	1.310381	4.381947
H	-3.502902	2.918470	4.355497
H	-4.462261	1.402177	4.484520
I	-0.574851	-1.414251	-0.650955
I	5.210283	-2.029088	0.823018
I	3.074838	3.357410	-0.688455
F	2.176891	-2.670074	0.215779
F	0.516262	1.533936	-0.960063
F	5.009855	1.046104	0.210618
C	1.288218	-0.592168	-0.374996
C	2.770718	1.350133	-0.380427
C	3.640425	-0.847653	0.235652
C	3.812682	0.518969	0.024441
C	2.367915	-1.375597	0.026501
C	1.519600	0.767947	-0.572635
$[Pd(acac)_2]$·1,3,5-FIB featuring I···η^2(O,O) bifurcated XB			
I	-4.910589	-2.997305	-0.021877
I	0.286765	0.006784	0.014812
I	-4.926996	2.999967	0.007496
F	-1.832663	-2.324301	-0.008001

F	-5.883713	-0.000770	-0.012601
F	-1.844678	2.344636	0.016456
C	-3.887955	-1.216342	-0.010195
C	-3.894177	1.225248	0.002130
C	-1.772121	0.010237	0.005067
C	-2.501537	1.196497	0.007930
C	-2.495799	-1.179600	-0.004288
C	-4.562765	0.002700	-0.006942
Pd	4.657714	-0.006000	0.002682
O	3.213574	-1.279136	0.032669
O	6.044839	-1.342081	-0.008866
C	3.353006	-2.549643	0.032962
C	5.840139	-2.596538	-0.002763
C	4.579866	-3.223352	0.014759
H	4.563445	-4.318412	0.016915
C	7.069600	-3.454198	-0.015617
H	7.074393	-4.105423	-0.907417
H	7.086172	-4.116142	0.867994
H	7.972830	-2.826181	-0.018442
C	2.069773	-3.318987	0.061050
H	1.521134	-3.085431	0.990982
H	2.231632	-4.405708	-0.002139
H	1.420867	-2.988511	-0.768663
O	6.095987	1.272474	-0.027324
O	3.260807	1.321669	0.012343
C	5.940753	2.537428	-0.035244
C	3.452648	2.581950	-0.002537
C	4.709748	3.209025	-0.025194
H	4.722454	4.304201	-0.035113
C	2.221046	3.436814	0.007400
H	2.216084	4.084672	0.901795
H	2.212806	4.103839	-0.872461
H	1.313728	2.814340	0.004016
C	7.218740	3.317217	-0.056844
H	7.805695	3.034474	-0.948359
H	7.050824	4.404872	-0.060973
H	7.828580	3.044565	0.822330

Table S9. Values of the density of all electrons – $\rho(\mathbf{r})$, Laplacian of electron density – $\nabla^2\rho(\mathbf{r})$, energy density – H_b, potential energy density – $V(\mathbf{r})$, and Lagrangian kinetic energy – $G(\mathbf{r})$ (a.u.) at the bond critical points (3, –1), corresponding to I···C XB and I···η^2(O,O) bifurcated XB in optimized equilibrium structures of two model supramolecular associates constructed based on the appropriate experimental X-ray geometry of [Pd(acac)$_2$]·1,3,5-FIB at 100 K as starting point, bond lengths – l (Å), as well as energies for these contacts E_{int} (kcal/mol), defined by two correlations proposed exclusively for noncovalent interactions involving iodine atoms†.

Contact	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	H_b	$V(\mathbf{r})$	$G(\mathbf{r})$	E_{int}[a]	E_{int}[b]	l
[Pd(acac)$_2$]·1,3,5-FIB featuring I···C XB								
I···C	0.010	0.033	0.001	-0.006	0.007	2.6	2.9	3.389
[Pd(acac)$_2$]·1,3,5-FIB featuring I···η^2(O,O) bifurcated XB								
I···O29	0.010	0.039	0.001	-0.007	0.008	3.0	3.4	3.251
I···O14	0.011	0.043	0.001	-0.008	0.009	3.4	3.8	3.197

† The presence of a linear relationship between the energy of noncovalent interactions and electronic properties at the BCP was verified on the set of complexes featuring typical XBs: NH_3···X–R, H_2S···X–R, H_2O···X–R, HCN···X–R, C_2H_4···X–R, CO···X–R, where X = Cl, Br, I (for details see Ref.[41] in main text).

[a] $E_{int} = 0.68(-V(\mathbf{r}))$

[b] $E_{int} = E_{int} = 0.67G(\mathbf{r})$