Electronic Supporting Information

Tetrachloroplatinate(II) Anion as a Square-planar Tecton for XB-Involving Crystal Engineering

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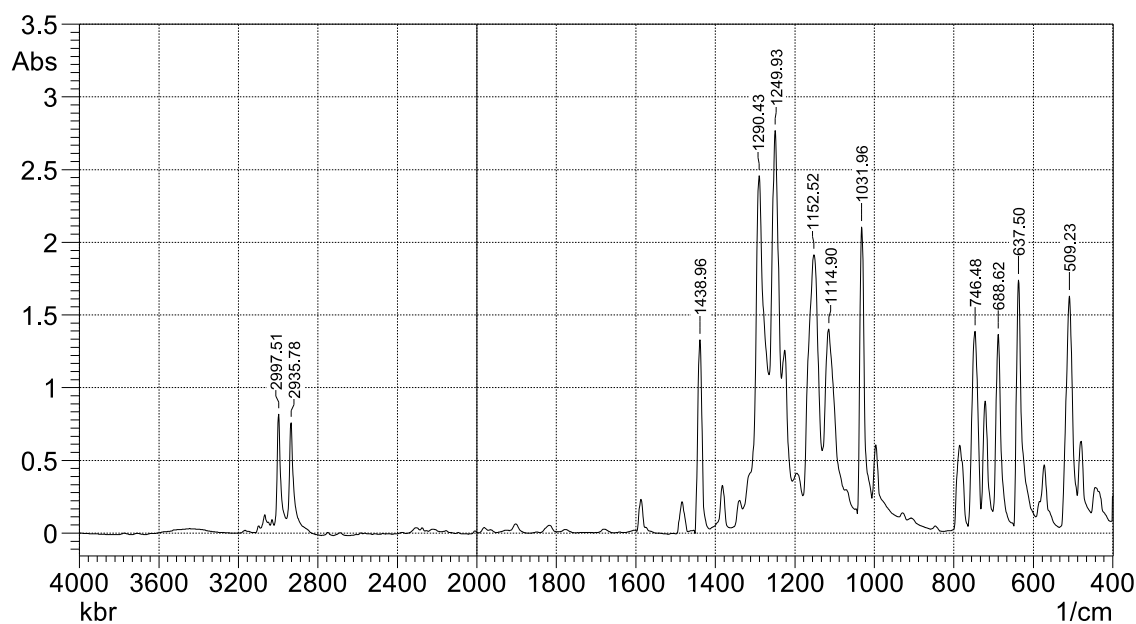
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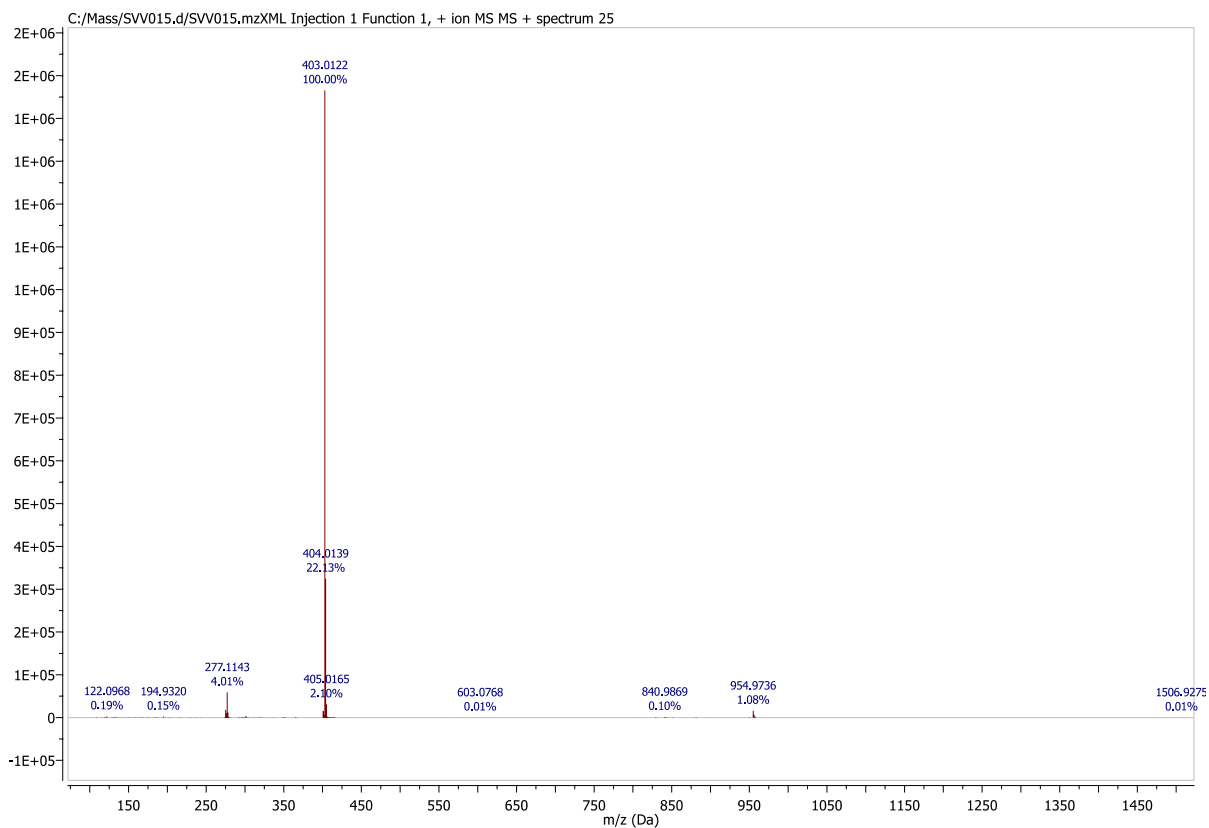
Figure S1. HRESI-MS$^+$ spectrum of [Ph$_3$PCH$_2$I](CF$_3$SO$_3$).
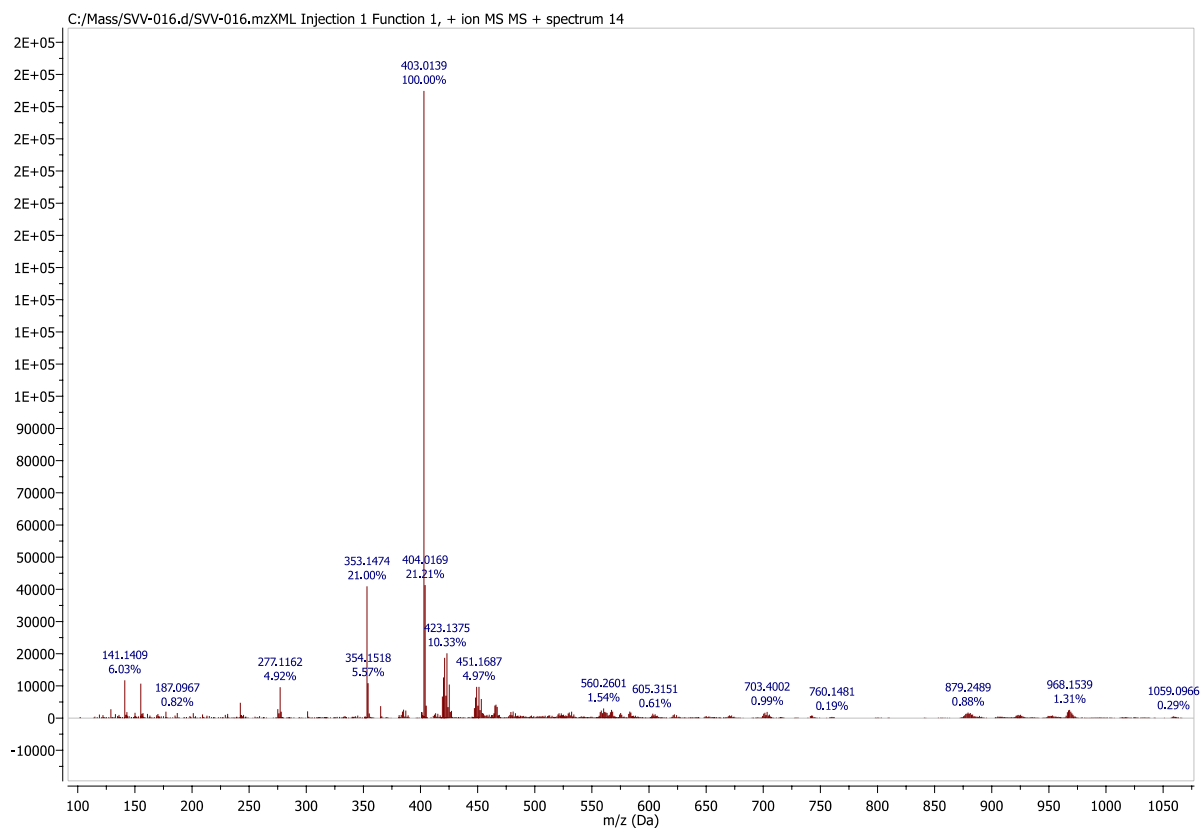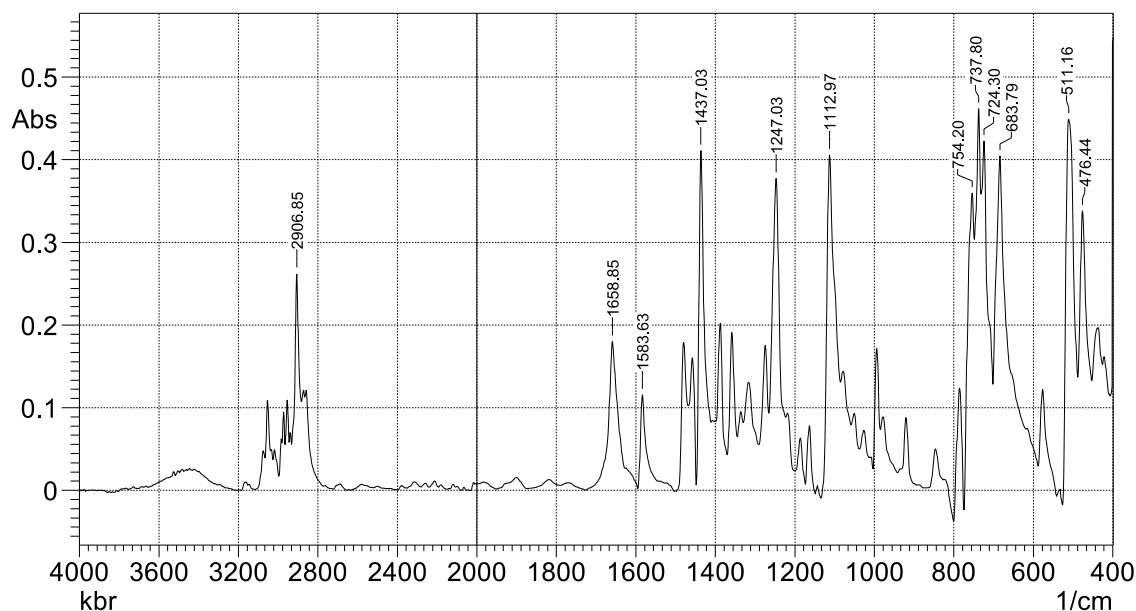

Figure S2. HRESI-MS$^+$ spectrum of **2**.

Figure S3. IR spectrum of [Ph$_3$PCH$_2$I](CF$_3$SO$_3$).

Figure S4. IR spectrum of [Ph$_3$PCH$_2$I](CF$_3$SO$_3$).

Table S1. Crystal data and structure refinement for [Ph$_3$PCH$_2$I](CF$_3$SO$_3$), **2**, and **1**·FIB.

Sample	[Ph$_3$PCH$_2$I](CF$_3$SO$_3$)	**2**	**1**·FIB
Identification code	10622-13266_SVV015	10622-13309_SVV016_MeNO2	EAA028
Empirical formula	C$_{20}$H$_{17}$F$_3$IO$_3$PS	C$_{38}$H$_{34}$Cl$_4$I$_2$P$_2$Pt	C$_{78}$H$_{60}$Cl$_4$F$_4$I$_2$N$_2$P$_4$Pt
Formula weight	552.26	1143.28	1815.85
Temperature/K	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1$/n	$P2_1$/c	P-1
a/Å	10.4024(3)	18.3265(6)	10.8208(5)
b/Å	15.8557(5)	13.0690(3)	12.0593(6)
c/Å	12.7928(4)	18.5735(6)	14.2648(7)
α/°	90	90	109.418(4)
β/°	97.894(2)	119.538(4)	92.227(4)
γ/°	90	90	97.782(4)
Volume/Å^3	2090.02(10)	3870.3(2)	1732.36(15)
Z	4	4	1
ρ_{calc}g/cm^3	1.755	1.962	1.741
μ/mm^{-1}	1.754	5.607	3.221
F(000)	1088.0	2176.0	890.0
Crystal size/mm^3	0.2 × 0.2 × 0.15	0.2 × 0.2 × 0.2	0.2 × 0.15 × 0.15
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.006 to 54.996	5.43 to 55	5.212 to 62.824
Index ranges	-12 ≤ h ≤ 13, -18 ≤ k ≤ 20, -16 ≤ l ≤ 9	-21 ≤ h ≤ 23, -16 ≤ k ≤ 15, -24 ≤ l ≤ 22	-14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -20 ≤ l ≤ 20
Reflections collected	10364	16758	18135
Independent reflections	4806 [R$_{int}$ = 0.0244, R$_{sigma}$ = 0.0351]	8873 [R$_{int}$ = 0.0304, R$_{sigma}$ = 0.0504]	10013 [R$_{int}$ = 0.0297, R$_{sigma}$ = 0.0518]
Data/restraints/parameters	4806/0/262	8873/0/424	10013/0/430
Goodness-of-fit on F^2	1.069	1.182	1.045
Final R indexes [I>=2σ (I)]	R$_1$ = 0.0258, wR$_2$ = 0.0562	R$_1$ = 0.0456, wR$_2$ = 0.0944	R$_1$ = 0.0308, wR$_2$ = 0.0663
Final R indexes [all data]	R$_1$ = 0.0320, wR$_2$ = 0.0591	R$_1$ = 0.0534, wR$_2$ = 0.0976	R$_1$ = 0.0378, wR$_2$ = 0.0708
Largest diff. peak/hole / e Å^{-3}	0.44/-0.55	2.87/-1.64	1.60/-1.74
CCDC number	1989400	1989401	1989402
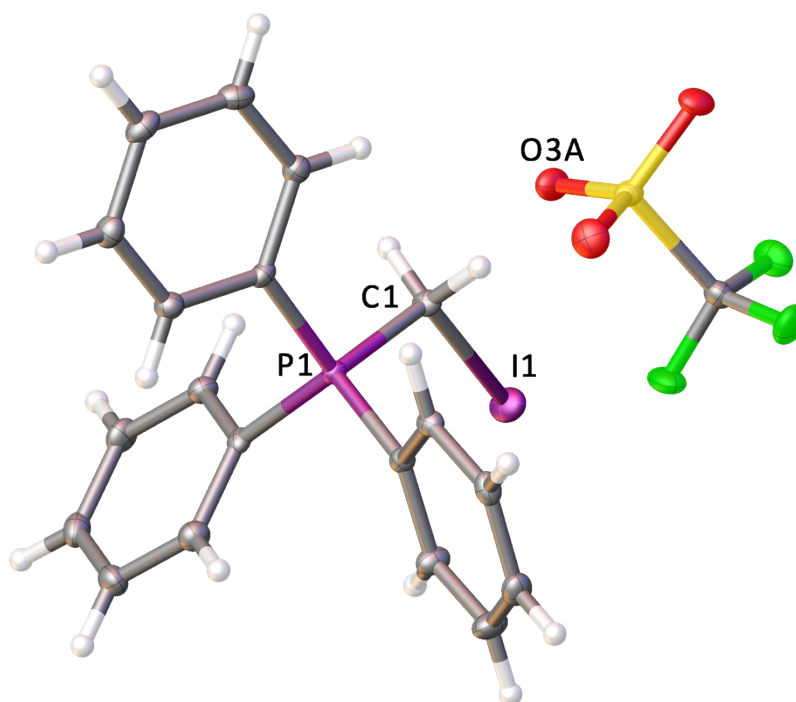
Figure S5. View of the molecular structure of [Ph$_3$PCH$_2$I](CF$_3$SO$_3$).
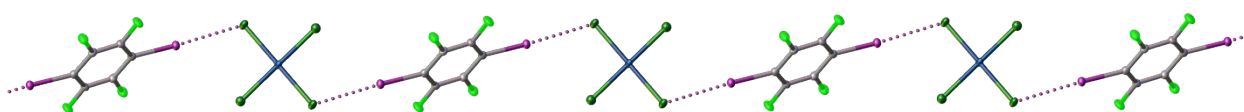
Fig. S6. The 1D chain formed by [PtCl$_4$]$^{2-}$ and FIB; the contacts shorter than ΣR_{vdW} are represented by dotted lines. Thermal ellipsoids are shown with the 50% probability.

Table S2. Distribution of electron density ρ(**r**) and electrostatic potential ESP along the bond path for contacts I···Cl in **1**·FIB and **2**.

System	**1**·FIB		**2**
Contact I···Cl	Type I, 3.743 Å	Type II, 3.091 Å	Type I or II, 3.489 Å
Position of $\rho(\mathbf{r})_{max}$(I), Å	0.796	0.795	0.795
Position of $\rho(\mathbf{r})_{min}$, Å	2.747	2.354	2.603
Position of $\rho(\mathbf{r})_{max}$(Cl), Å	4.538	3.887	4.285
Distance between $\rho(\mathbf{r})_{max}$(I) and $\rho(\mathbf{r})_{min}$, Å	1.951	1.559	1.808
Distance between $\rho(\mathbf{r})_{max}$(Cl) and $\rho(\mathbf{r})_{min}$, Å	1.791	1.533	1.682
Value of $\rho(\mathbf{r})_{max}$(I), a.u.	245620.090	439813.690	461651.540
Value of $\rho(\mathbf{r})_{min}$, a.u.	0.008	0.023	0.010
Value of $\rho(\mathbf{r})_{max}$(Cl), a.u.	3897.851	3982.246	3984.531
Position of ESP_{max}(I), Å	0.800	0.805	0.802
Position of ESP_{min}, Å	3.007	2.573	2.823
Position of ESP_{max}(Cl), Å	4.552	3.893	4.295
Distance between ESP_{max}(I) and ESP_{min}, Å	2.207	1.768	2.021
Distance between ESP_{max}(Cl) and ESP_{min}, Å	1.545	1.320	1.472
Value of ESP_{max}(I), a.u.	5503.339	16578.570	15687.031
Value of ESP_{min}, a.u.	-0.296	-0.171	-0.118
Value of ESP_{max}(Cl), a.u.	1800.527	5357.494	5071.459

Table S3. Cartesian atomic coordinates for model supramolecular associates.

Atom	X	Y	Z
1·FIB			
Pt	8.633607	7.085965	13.399087
Cl	7.839677	7.749003	11.349027
Cl	10.565030	6.225891	12.467717
Cl	9.427537	6.422926	15.449148
Cl	6.702184	7.946038	14.330458
I	8.978019	5.975938	9.086859
F	7.160946	3.865320	7.517826
F	7.739285	1.961270	5.754908
C	9.419114	4.565291	7.622741
C	8.445279	3.717911	7.122955
C	8.742817	2.725084	6.223876
I	10.476388	1.110026	4.312228
F	12.293461	3.220644	5.881261
F	11.715122	5.124695	7.644179
C	10.035293	2.520673	5.776347
C	11.009128	3.368054	6.276133
C	10.711590	4.360881	7.175211
2			
Pt	4.474065	5.483752	0.041691
Cl	3.708586	7.171483	1.454677
Cl	5.592840	7.068238	-1.241533
Cl	3.419450	3.906324	1.365638

Cl	5.167245	3.777072	-1.374041
I	1.091715	1.704328	2.747435
P	-1.637891	-0.041167	3.288939
C	-4.243706	-0.650836	4.044718
H	-4.477738	-0.551512	3.128476
C	-5.193563	-1.032451	4.970657
H	-6.087094	-1.197120	4.687866
C	-1.080595	-3.707675	1.661195
H	-1.558233	-4.293167	1.084301
C	-4.868648	-1.177517	6.302198
H	-5.531816	-1.446738	6.925954
C	-3.565460	-0.931820	6.735272
H	-3.342423	-1.021996	7.654747
C	-2.312958	0.857326	1.895507
C	-0.443689	1.021996	4.088349
H	-0.022795	0.527988	4.836533
H	-0.911778	1.806136	4.468097
C	-1.589030	-2.462200	1.973073
H	-2.427611	-2.191671	1.615948
C	-2.329475	1.421907	-0.439538
H	-2.102588	1.216724	-1.338005
C	-2.937771	-0.414287	4.472945
C	-2.594526	-0.554126	5.814182
H	-1.701911	-0.392070	6.098589
C	-1.926795	0.565888	0.586589

H	-1.399985	-0.199956	0.397523
C	-3.056906	2.007398	2.163755
H	-3.306703	2.208661	3.057374
C	0.322988	-2.013933	3.375716
H	0.791470	-1.441511	3.972001
C	-0.885875	-1.600952	2.802054
C	0.151165	-4.097132	2.207385
H	0.517606	-4.945310	1.984384
C	-3.426594	2.849042	1.147323
H	-3.935079	3.629261	1.333157
C	-3.048679	2.551069	-0.163211
H	-3.293622	3.137867	-0.869380
C	0.827757	-3.265943	3.060606
H	1.651686	-3.550847	3.440354