

>>> Geometrical structure of 5,10,15,20-tetra(phenyl/perfluorophenyl) platinum(II) porphyrinates

*Ivanovo State University of Chemistry and Technology, Russian Federation

***A. N. Nesmeyanov Institute of Organoelement compounds Russian Academy of Sciences, Russian Federation**

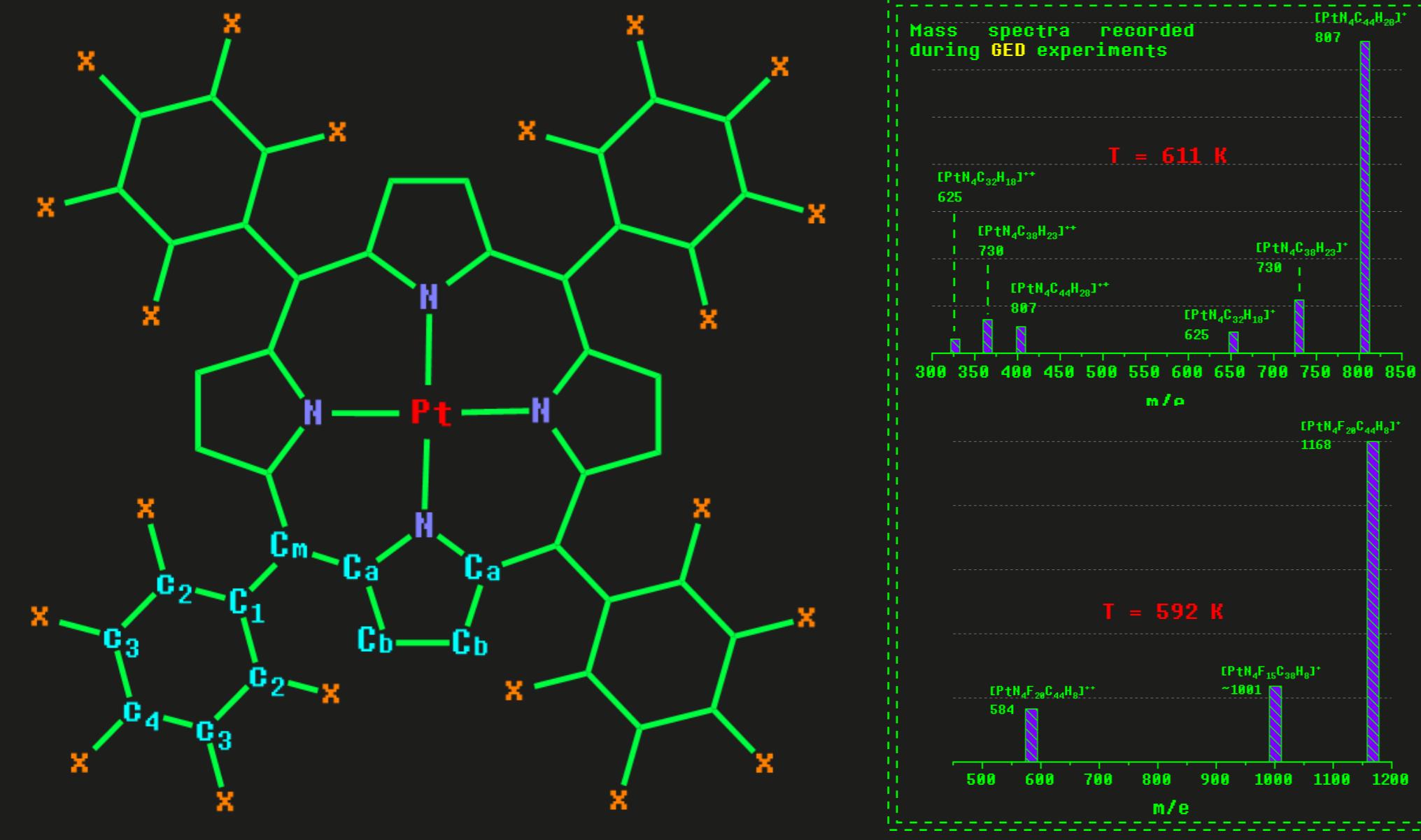
>>> Goal

Determination of experimental geometrical parameters of the investigated molecules and search for structure-property relationships.

>>>Methods

- I. Synchronous gas-phase electron diffraction and mass spectrometry (GED/MS) method
 - II. Quantum chemical methods: DFT (B3LYP, B97D), natural bond orbital analysis (NBO), non-covalent interaction index (NCI), symmetry-adapted perturbation theory analysis (F\I-SAPT0)

>>> Molecular model of PtTPP and PtTF₅PP complexes
(X: H, F) with atom labels



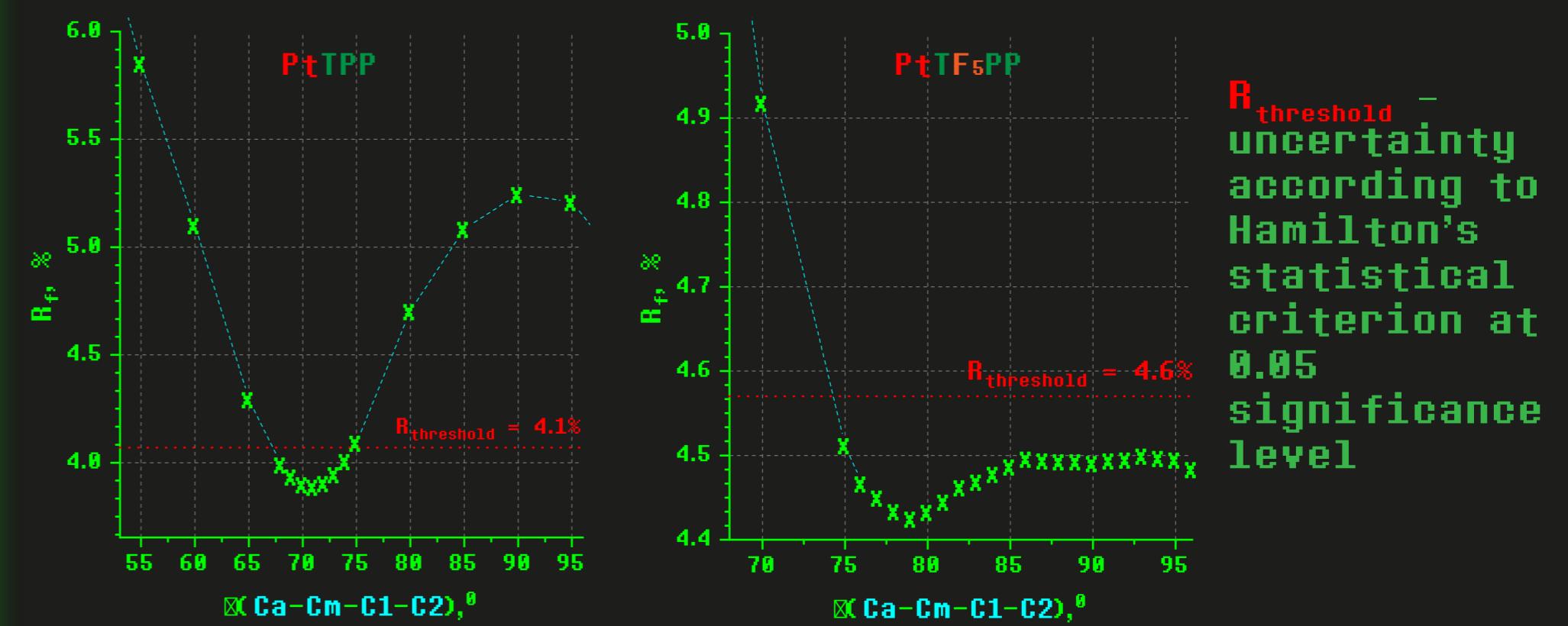
>>> Selected geometrical parameters of PtTPP, and
PtTF5PP by GED and QC calculations (bond length in
Å, angles in °)

Parameter	rh1 (GED)		B3LYP (QC)		B97D (QC)		\AA
	PtTPP	PtTF ₅ PP	PtTPP	PtTF ₅ PP	PtTPP	PtTF ₅ PP	
r(Pt-N)	2.025(4)	2.032(5)	2.027	2.026	2.032	2.030	\AA
r(Ca-N)	1.383(3)	1.378(3)	1.375	1.373	1.383	1.380	\AA
r(Ca-Cb)	1.440(3)	1.437(3)	1.439	1.439	1.440	1.440	\AA
r(Cb-Cb)	1.359(3)	1.354(3)	1.352	1.351	1.360	1.359	\AA
r(Cm-Ca)	1.398(3)	1.378(3)	1.375	1.373	1.383	1.380	\AA
r(Cm-C1)	1.491(3)	1.489(3)	1.497	1.495	1.492	1.492	\AA
r(C-F)	-	1.335(3)	-	1.334	-	1.340	\AA
r(CPh-CPh)ave	1.399(3)	1.396(3)	1.393	1.391	1.399	1.395	\AA
<hr/>							
(Ca-Cm-C1-C2)	71(4)	79(-5 ⁺²⁷)	80.1	90.0	65.3	74.2	\AA
Rf, %	3.9	4.4	-	-	-	-	\AA

QC basis functions: cc-pVTZ (C, N, H, F); aug-cc-pVTZ-PP (Pt)
Refinement of the models of molecules PtTPP and PtTF5PP based
on the force field and the starting geometry from the B97D
calculation gives a better agreement with the experimental

>>> Experimental and theoretical radial distribution functions $F(r)$ for PtTPP and PtTF5PP and residual curves $\Delta F(r)$

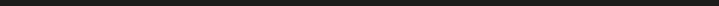
>>>The ratio of disagreement factors Rf as a function of torsion angle (Ca-Cm-C1-C2), responsible for the rotation of C6H5- and C6F5-groups in PtTPP, and PtTF5PP



>>>Preference for the rotated position of meso-substitutes (NCI, F\I-SAPT0, NBO)

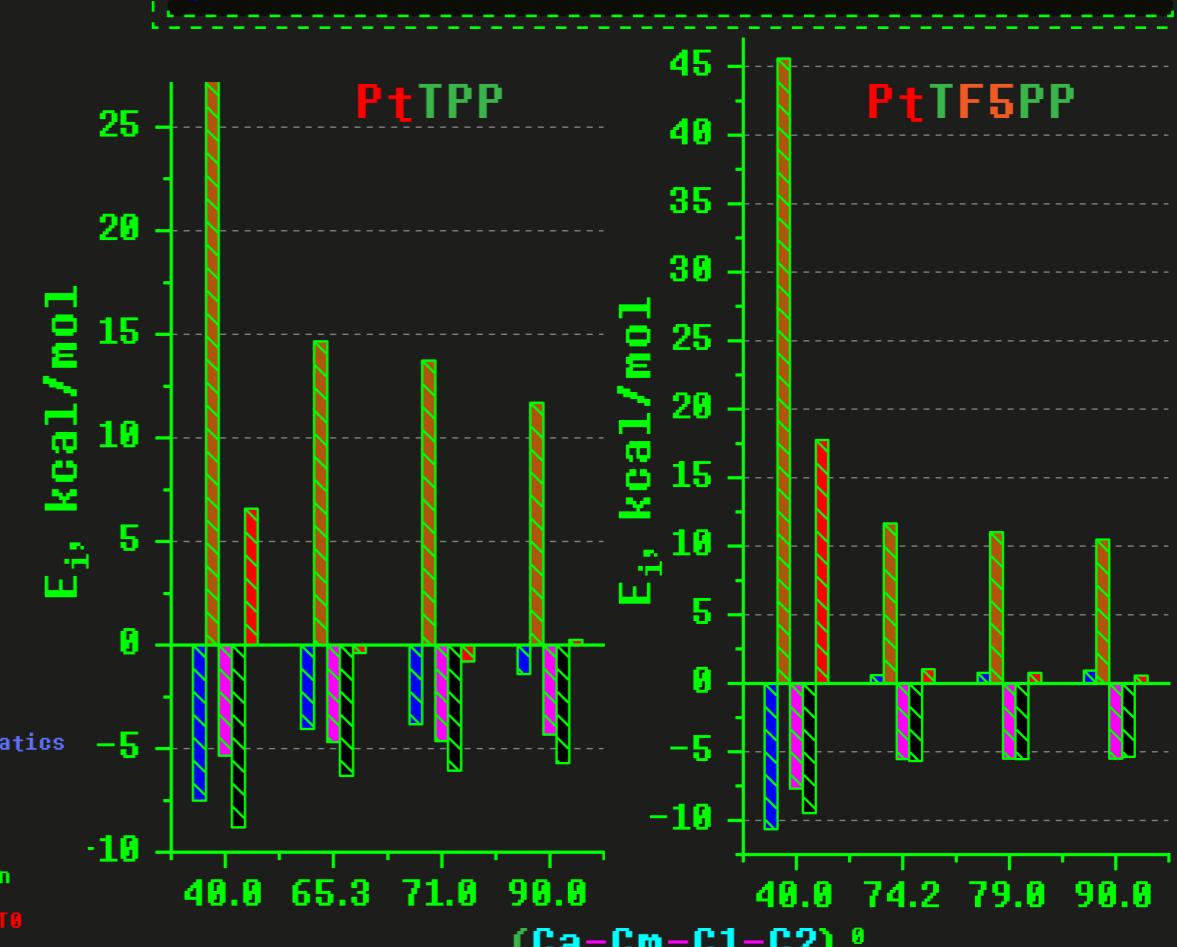
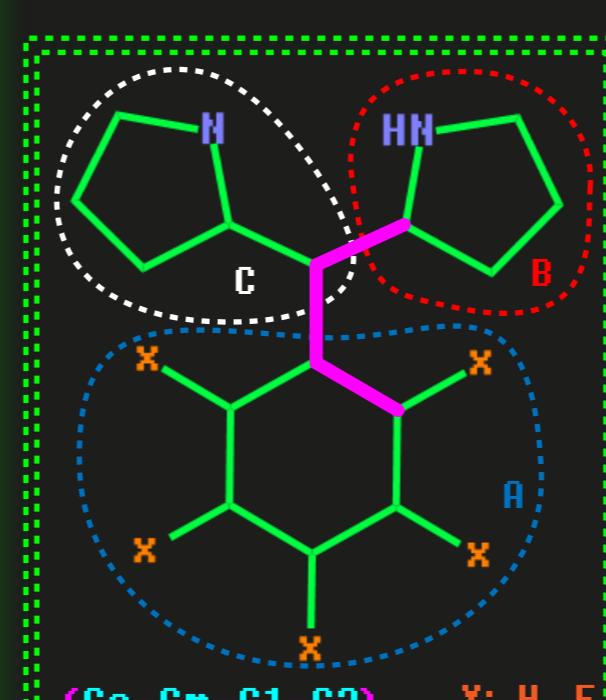
NCI: visual study of weak interactions

color bar for intuitively capture the type
of the weak interaction

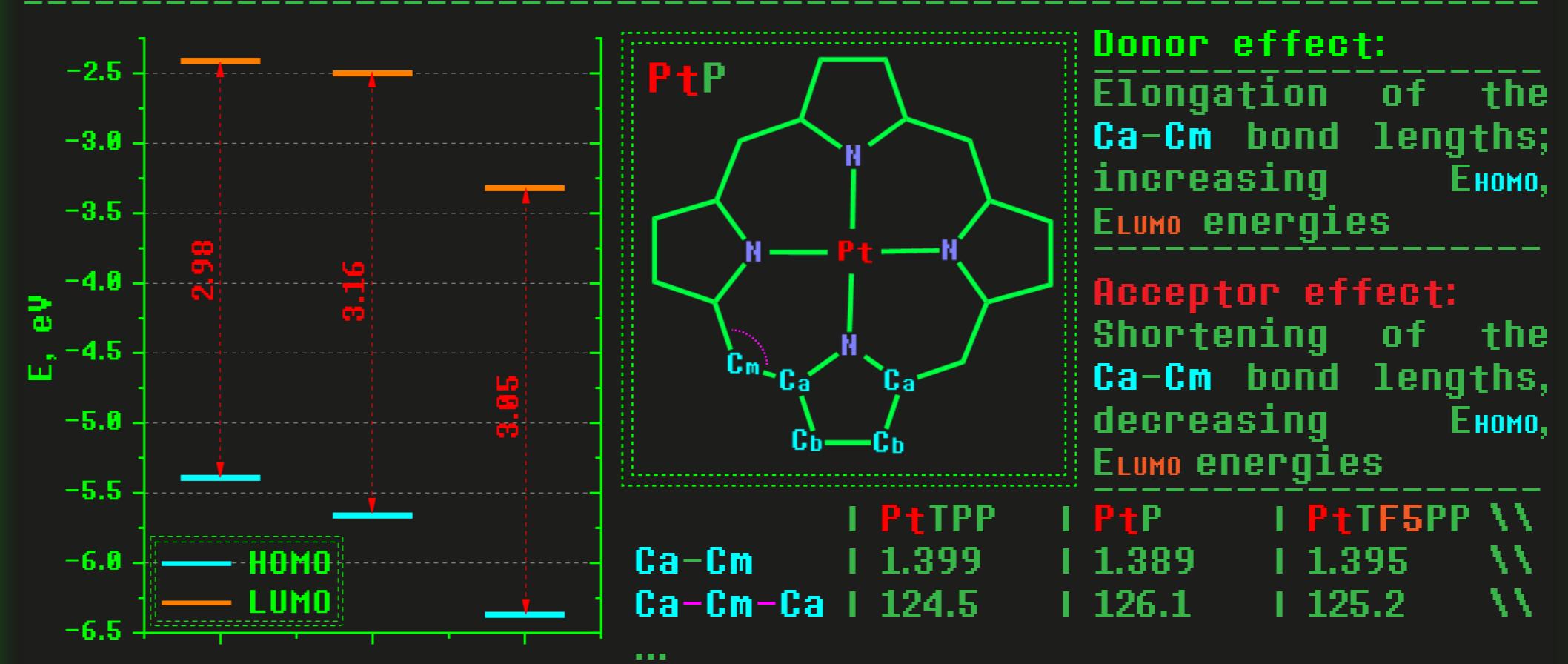


The green isosurface represents the weak interaction region between X-phenol and pyrrol fragments

F/I-SAPT0: C6X5-C5NH3-C4NH4
 fragment being considered by
 F/I-SAPT0 calculations. The
 system is divided into three
 subsystems: A(C6X5-) and B(C4NH4)
 the strength of the interaction
 which we want to assess, as well as
 the link C(-C5NH3-).
 Basis set: jun-cc-pVTZ
 Negative values of E_i energies
 indicate the stabilizing orienta-
 tion of the A, B and C fragments



>>>Effect of the meso-substitution by C₆H₅- and C₆F₅-groups



Conclusions

Experimental structural parameters of PtTPP, and PtTF5PP were determined by synchronous gas electron diffraction for the first time.

time .
Experimental geometrical parameters are close to the calculated
ones in B97D functional.

The strongly skewed position of meso-substituents is confirmed. The factors contributing to such a configuration are considered.