



### Abstract:

Eight platinum(II) biphenyl complexes containing 1,10-phenanthroline derivatives were synthesized and their physical and photophysical properties were examined. X-ray crystal structures were obtained for five of the complexes with two different motifs giving rise to two different circular dichroism spectra. Structures obtained by density functional theory were in agreement with the parameters obtained by x-ray diffraction. Electron density of the HOMO is located on the metal center and the biphenyl ligand; for the LUMO it is located primarily on the phenanthroline ligand. The results for time dependent density functional theory calculations are in agreement with a MLCT (metal-to-ligand charge transfer) low energy electronic transition assignment. The optical, emission and reduction potentials correlated with Hammett Sigma functions giving rise to excellent free-energy correlations for the series of complexes.

### Introduction:

Square planar platinum(II) complexes containing bidentate biphenyl chelating ligands are attractive emitters with promising applications in optoelectronic devices, chemosensory materials and catalysis. The complexes display rich emission properties both in solution and in the solid state. In dilute solution, emission was assigned either to a <sup>3</sup>LC (triple ligand-centered) or a <sup>3</sup>MLCT (triplet metal-to-ligand charge transfer) state. But in concentrated solution, molecular aggregation gave rise to different emission maxima due to  $\pi$ - $\pi$  stacking which results from Pt...Pt orbital overlap. Both electronic absorption & emission properties vary with substituents on the phenanthroline (phen) ligand.

### Methodology:

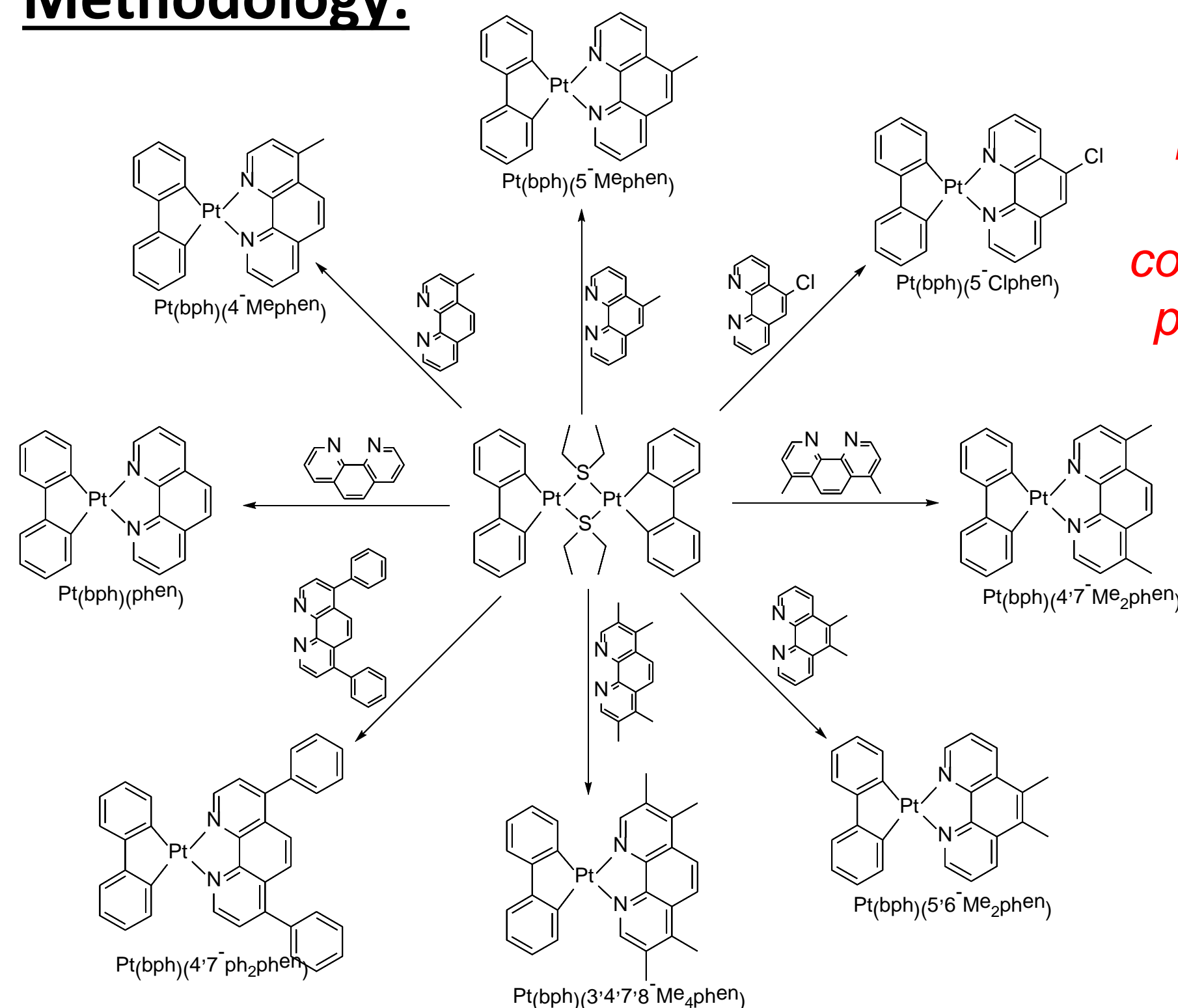


Figure 1. Synthesis of Pt(II)-biphenyl complexes containing 1,10-phenanthroline derivatives

Figure 1 shows the synthesis of all the Pt(II)-biphenyl complexes containing 1,10-phenanthroline ligands. One can see that the substituents were varied based on their electron-withdrawing and electron-releasing nature. All syntheses were carried out under Ar conditions; and all structures were confirmed using X-ray crystallography.

### Results and Discussion:

Figure 1 shows the synthesis of all the Pt(II)-biphenyl complexes containing 1,10-phenanthroline ligands. One can see that the substituents were varied based on their electron-withdrawing and electron-releasing nature. All syntheses were carried out under Ar conditions; and all structures were confirmed using X-ray crystallography. Figure 2 contains the Pt-Pt stacking from X-ray data. Figure 3 shows frontier orbitals of the Pt(II)-biphenyl-1,10-phenanthroline (Pt(II)bphphen) complex that are involved during absorption/emission. These orbital surfaces were calculated using density-functional theory (DFT). Figure 4 shows correlation among electrochemical, electronic absorption & emission, and LUMO energies with Hammett-sigma constant ( $\sigma_p$ ).

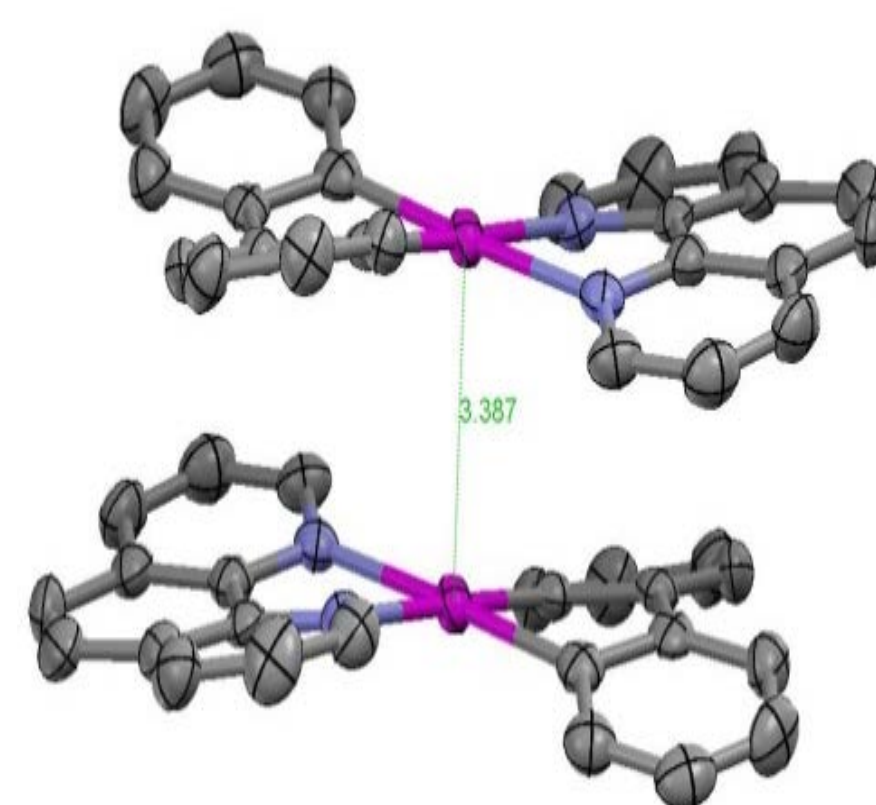


Figure 2. Pt...Pt stacking in Pt(II)bphphen from X-ray data

### Conclusions:

Square planar platinum(II) containing biphenyl and 1,10-phenanthroline ligand derivatives were synthesized. Linear correlation among electrochemical, spectroscopic and LUMO energies vs  $\sigma_p$  were observed. These correlations were attributed to the inductive effect caused by the substituents on the <sup>3</sup>MLCT excited state. The NH<sub>2</sub> group increased the HOMO-LUMO band gap the most while the COOC<sub>2</sub>H<sub>5</sub> has the least. This shows that COOC<sub>2</sub>H<sub>5</sub> has a stabilizing effect on the phen ring electron density.

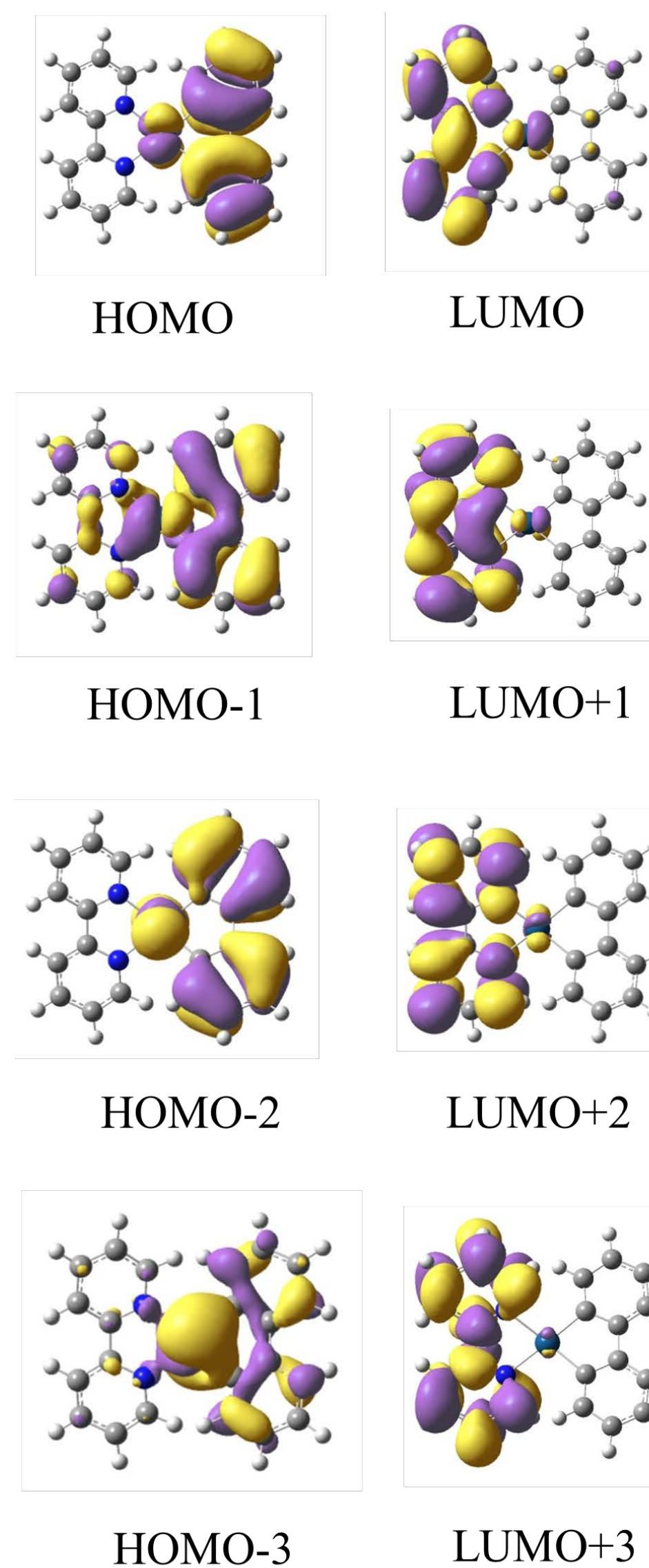


Figure 3. Frontier Orbitals of Pt(II)(bph)(phen)

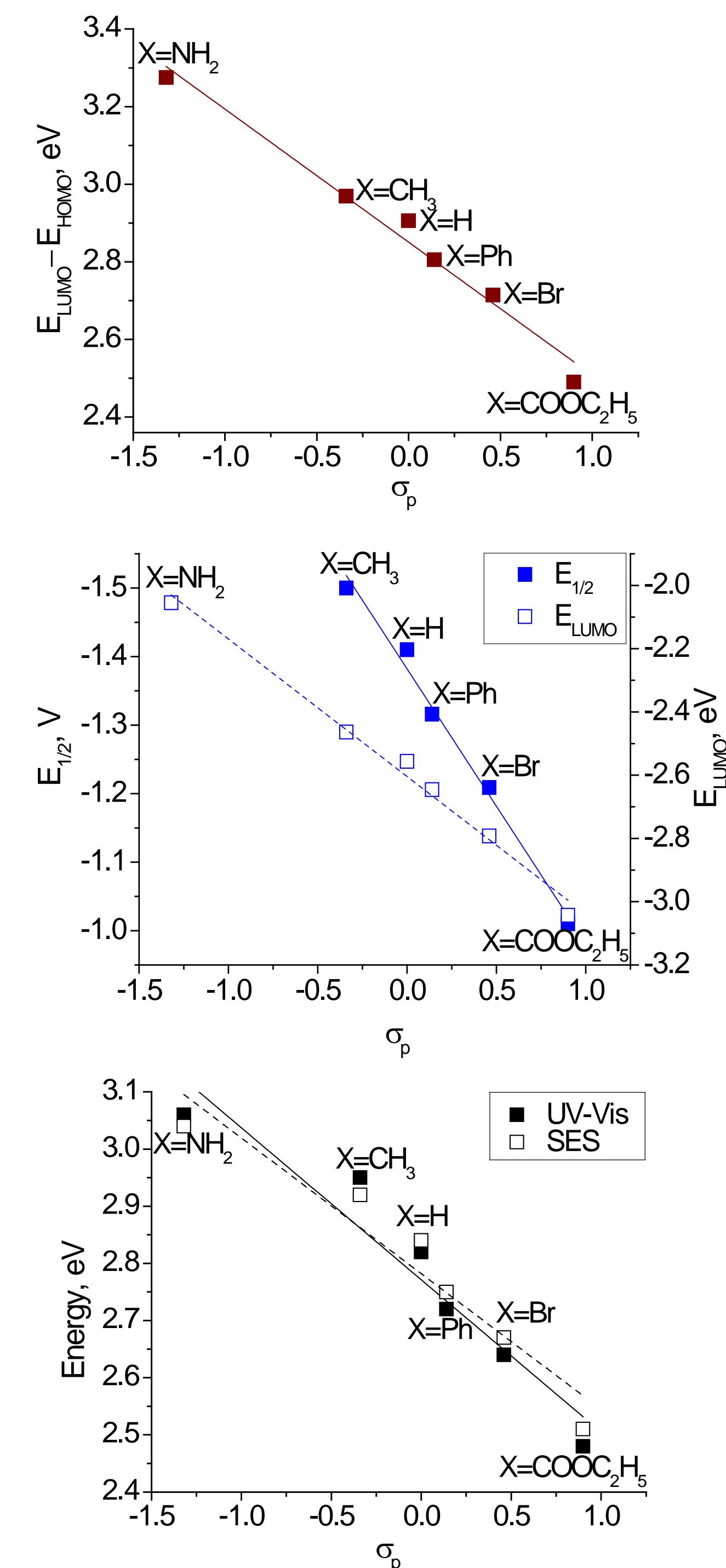


Figure 4. Electrochemical, Spectroscopic and  $E_{LUMO}$  correlations with  $\sigma_p$ .

### References:

- Hansch et al. Chem. Rev. **1991**, 165-195.
- Cruz et al. Dalton Trans **2015**, 44, 17075-17090.
- Cruz et al. J. Mol. Struct. **2013** 1041, 82-91.