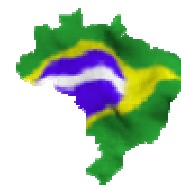


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## Quantitative Structure-Property Relationship (QSPR) study of phenolic passivation at the platinum electrode

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# OUTLINE



**INTRODUCTION**

**EXPERIMENTAL AND THEORETICAL METHODS**

**RESULTS AND DISCUSSION**

**CONCLUSIONS**

# INTRODUCTION

Phenols are of interest as

natural and bioactive compounds  
chemicals  
industrial products  
pollutants and drugs

OUR MAIN INTEREST:

To use electroanalytical methods to degradate phenols in waste water treatments.

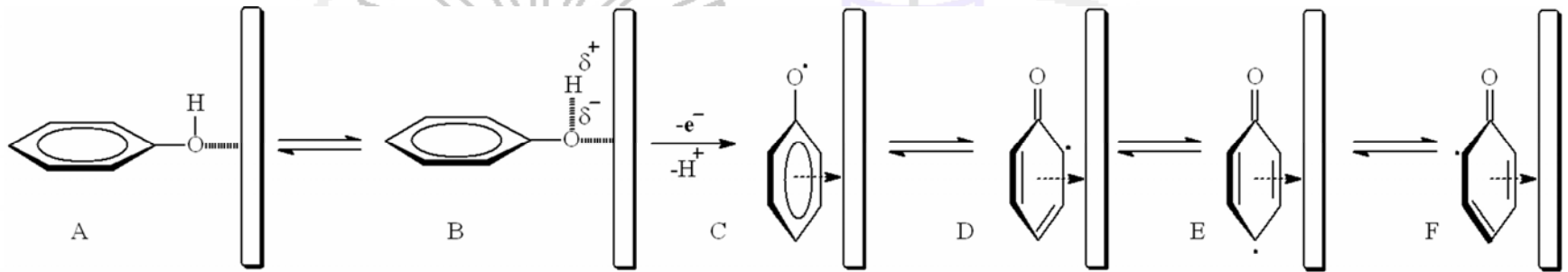
Instead of total decomposition, many phenols partially oxidize and then polymerize at the electrode surface.

The electrode becomes inactive and in some cases hard to be recuperated.

PASSIVATION

Passivation is affected by experimental conditions:

Solvent                      pH                      electrode material  
current oxidation                      potential  
phenol concentration and structure



Mechanism of the first phenolic electrooxidation:

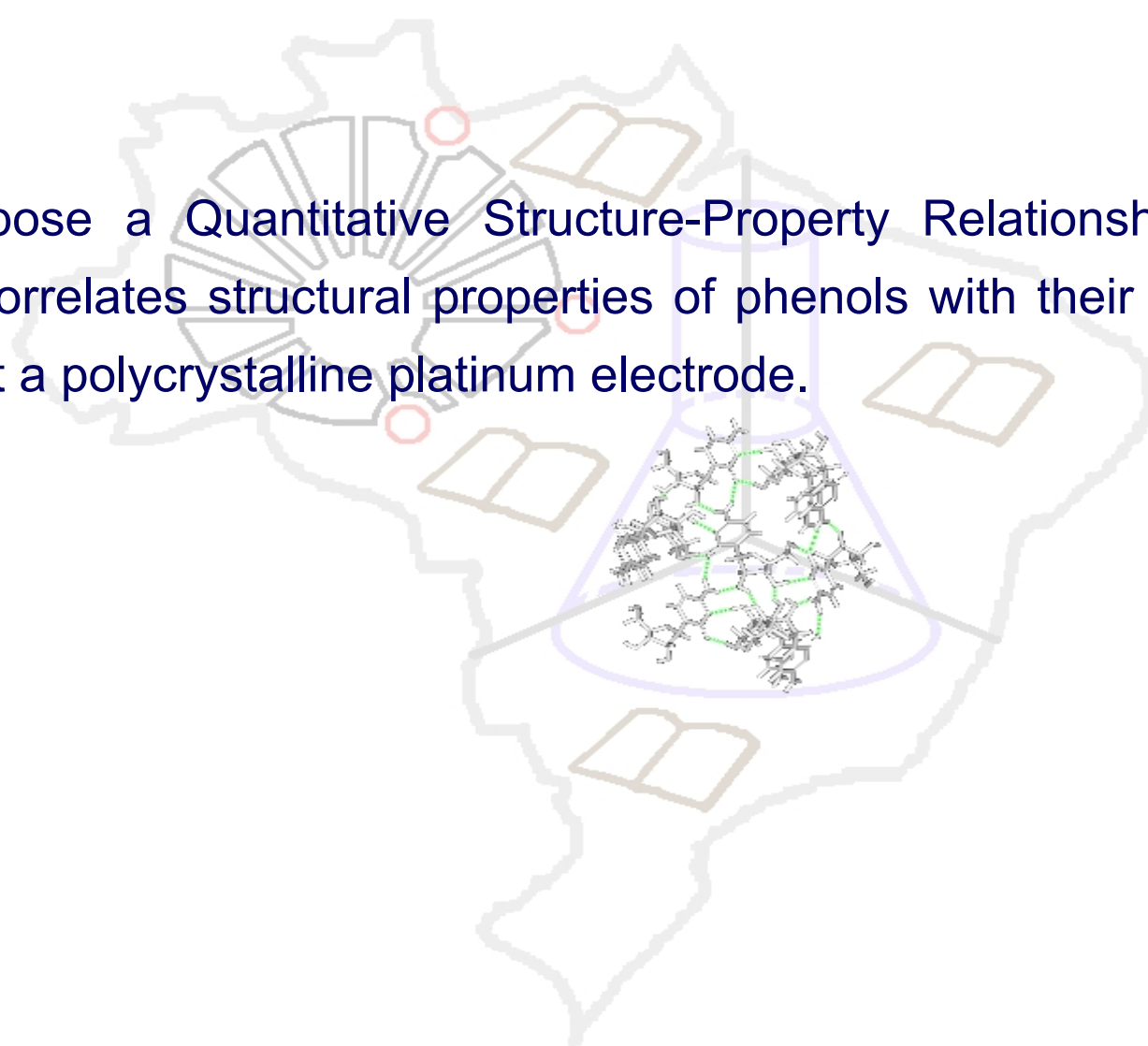
- A) adsorption at the electrode surface
- B) O-H bond polarization and oxidation with O-H dissociation
- C-F) stabilization of the phenoxyl radical by resonance

Mechanism is based in the analysis of the polymeric film

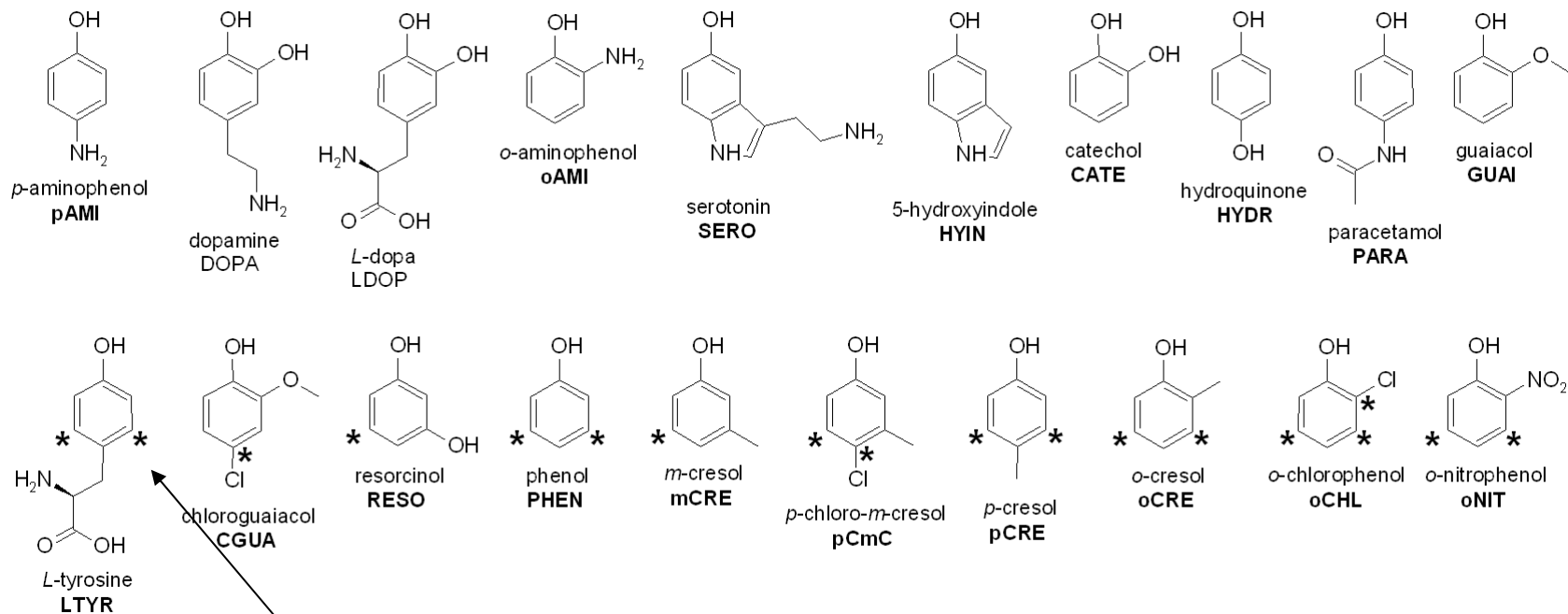
**NO ATTENTION HAS BEEN PAID TO THE MONOMER!**

# GOAL

To propose a Quantitative Structure-Property Relationship (QSPR) which correlates structural properties of phenols with their passivation ability at a polycrystalline platinum electrode.



# STUDIED PHENOLIC COMPOUNDS



sites for nucleophilic aromatic substitution

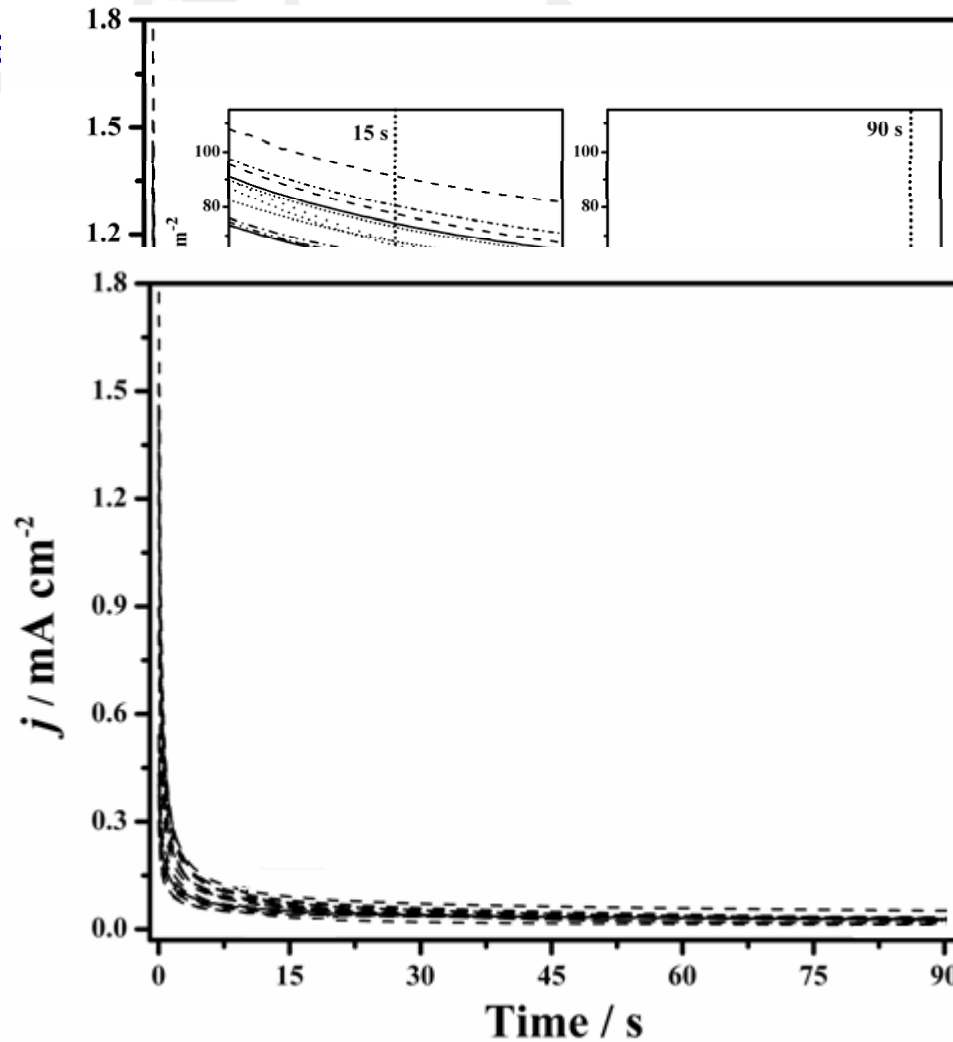
Chemical reactivity is proportional to the number of these sites (NU).

# EXPERIMENTAL PART

## Chronoamperometry:

The current de  
recorded each  
oxidation peak

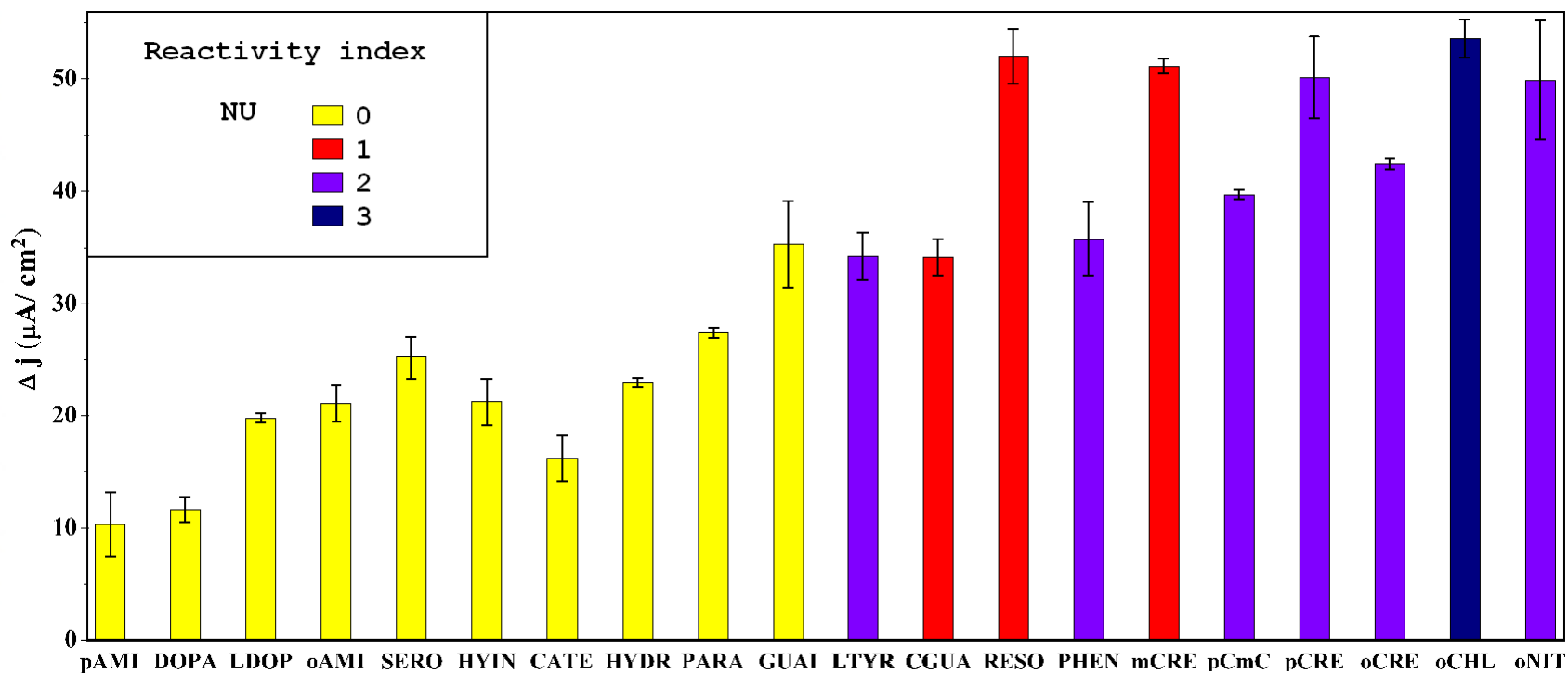
for 90 s and  
nV above the



for 15 s and

PASSIVATIO  
90 s in its log

# EXPERIMENTAL RESULTS



The current density difference  $\Delta j$  is related to the chemical reactivity of the phenolic rings (the NU number).



# THEORETICAL METHODS

## Molecular modeling:

Experimental crystallographic geometries were extracted from the Cambridge Structural Database (CSD) and optimized at the DFT level, using the B3LYP method and 6-31G\*\* basis set.

## Molecular descriptors:

Optimized geometries were used to generate various **quantum chemical** descriptors of steric and electronic nature. Other descriptors (compositional, topological and mixed) were obtained **manually** and by using the **Dragon software**.

Total descriptors: 700

# CHEMOMETRICS

## *Variable selection*

$y$ - $X$  correlation ~~coefficient~~  $< 0.5$

30 descriptors selected

Manual selection in order to achieve descriptors

- ☺ with the best predictive ability
- ☺ differently obtained/defined
- ☺ computationally simple
- ☺ chemically interpretable

5 descriptors selected

## *Regression analysis*

PLS model on autoscaled descriptors

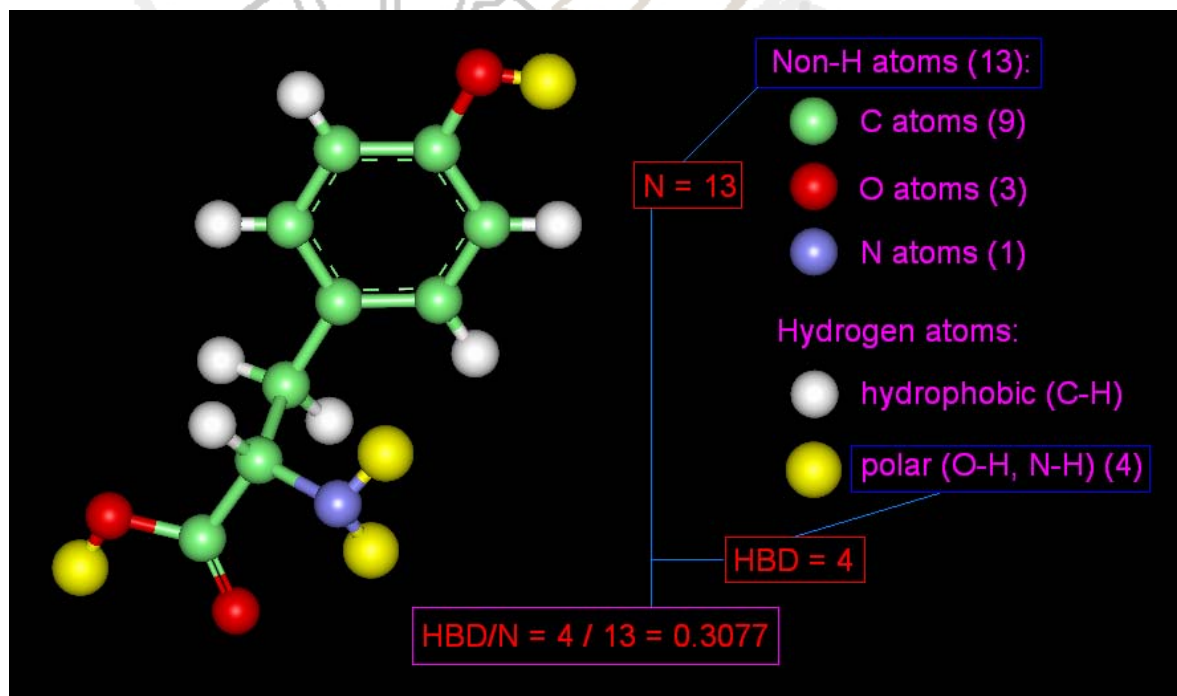
Validation: external validation

Y-randomization

Prediction (4 samples in the prediction set).

# FIVE SELECTED MOLECULAR DESCRIPTORS

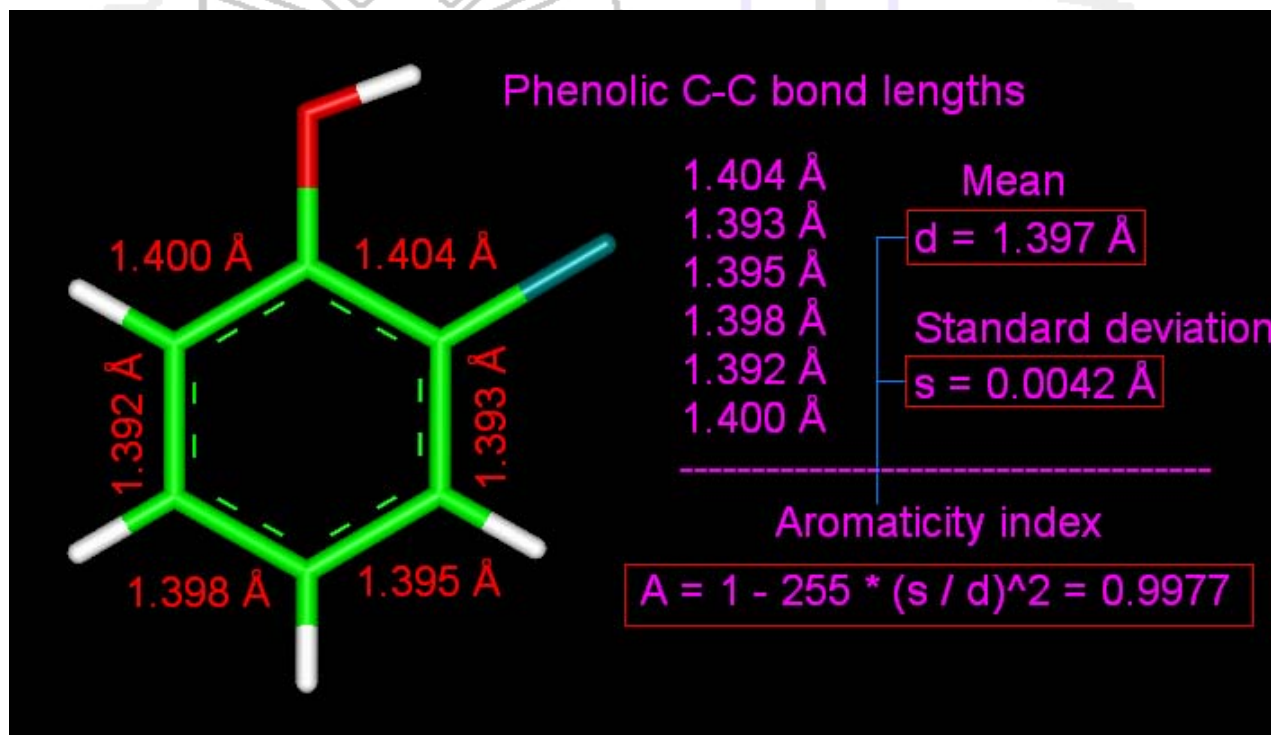
**HBD/N** → a **hydrogen bonding descriptor**: the number of polar hydrogen atoms divided by the number of non-hydrogen atoms.



Higher values result in weaker passivation  
Presence of polar groups can partially inhibit phenolic polymerization

**Mor06u** ⇒ a steric descriptor (size of the group) for chemical reactions by and on the phenolic skeleton to become parallel to the electrode surface and interact with Pt atoms.

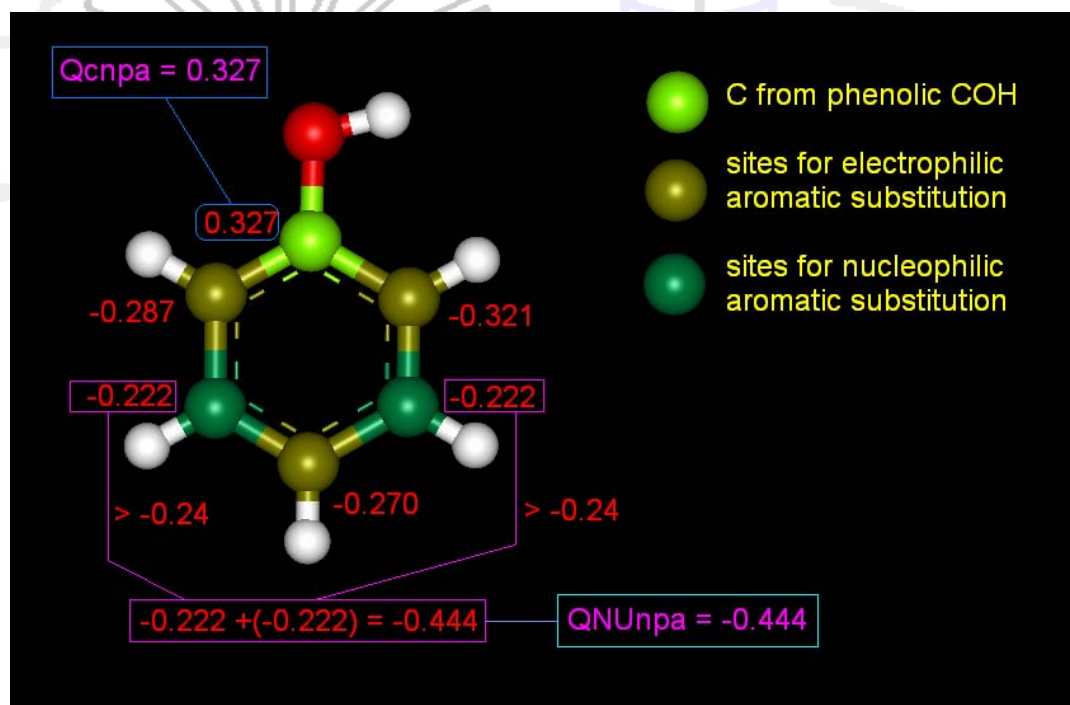
**Ar** → a modified Julg's **aromaticity index**: calculated from the phenolic C-C bond lengths.



Higher ring's aromaticity is related to higher passivation which means weaker electron delocalization between the ring and phenolic oxygen

**Qcnpa** → the NPA **atomic charge** of the phenolic carbon atom.  
It directly reflects the electronic properties of the OH group.

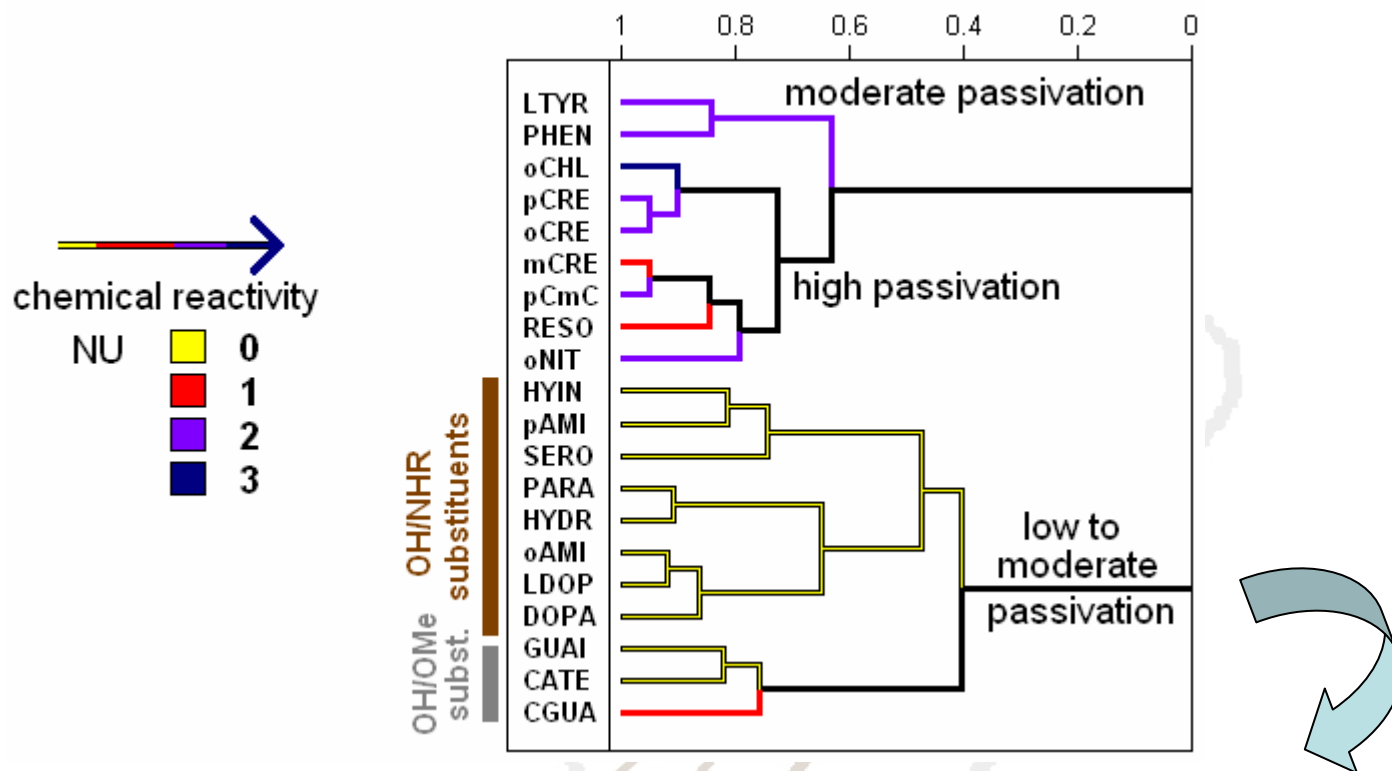
**QNUnpa** → the sum of NPA **atomic charges** at the sites for nucleophilic aromatic substitution (including halogen-occupied sites).



More negative the sum → higher passivation. This descriptor is directly related to the number of sites for nucleophilic substitution.

# EXPLORATORY ANALYSIS

## Hierarchical Cluster Analysis



They have bulky or electronegative substituents and no sites for nucleophilic substitution

# THE PLS MODEL (20 samples)

The  $y$  variable:

$$y = \log(\Delta j / \text{mA cm}^{-2})$$

The model's basic statistics:

1 LV

Leave-one-out crossvalidation:

$$\text{SEV} = 0.097$$

$$Q^2 = 0.786$$

Prediction:

$$\text{SEP} = 0.086$$

$$R^2 = 0.851$$

Relative errors:

-mean: 5.1%

-max.: 13.9%

-samples with >10%: 3

Regression vector:

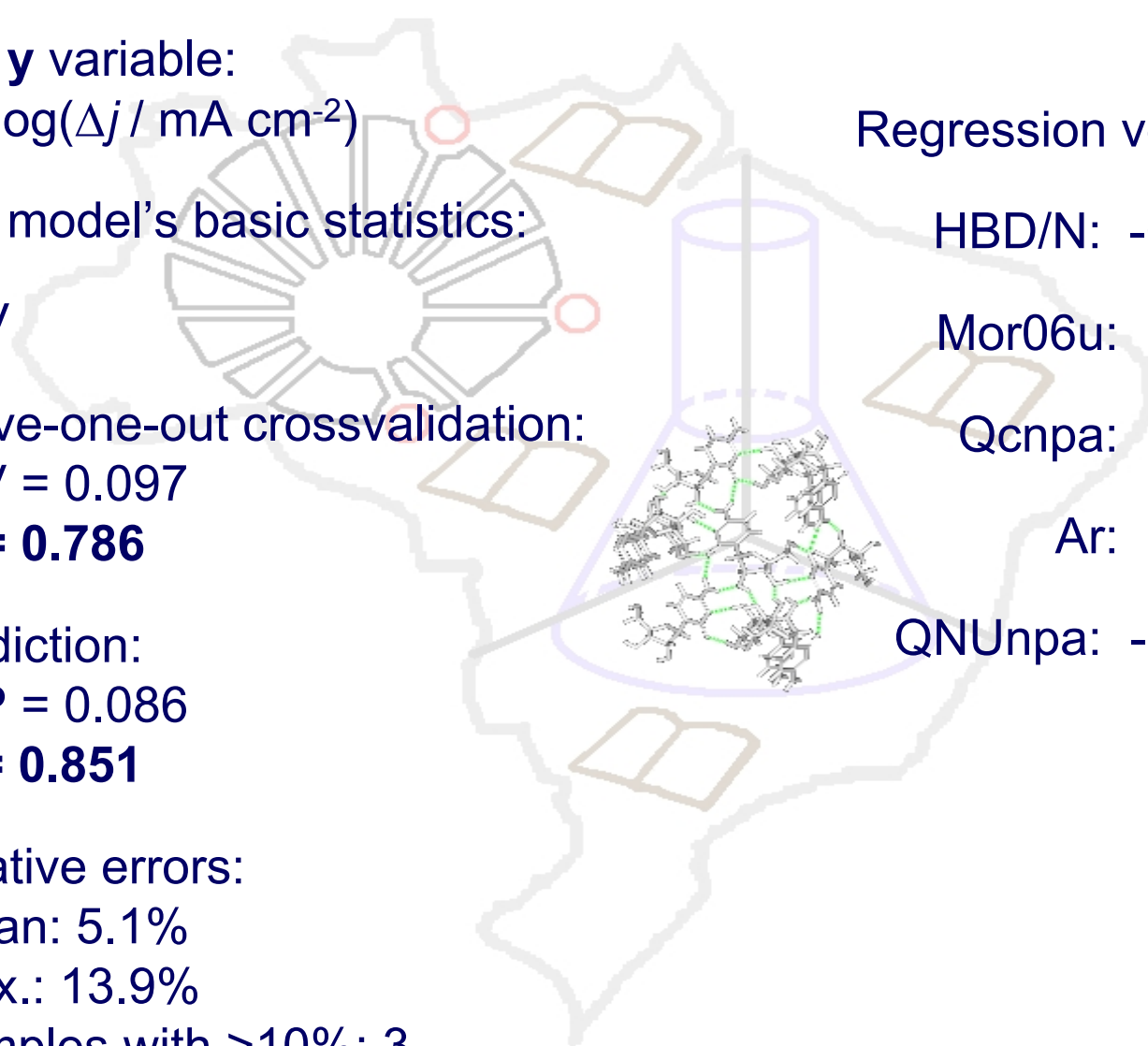
$$\text{HBD/N: } -0.276$$

$$\text{Mor06u: } 0.201$$

$$\text{Qcnpa: } 0.279$$

$$\text{Ar: } 0.208$$

$$\text{QNUnpa: } -0.261$$



## External validation

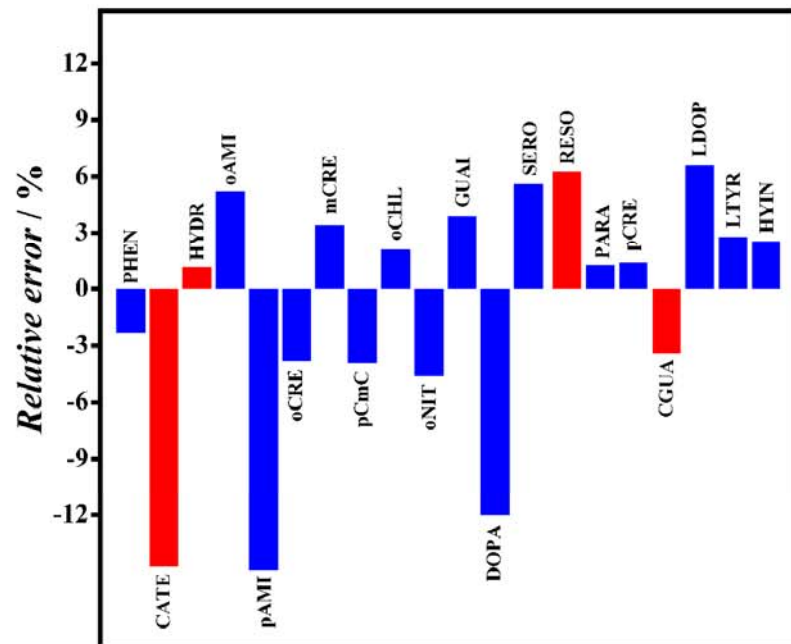
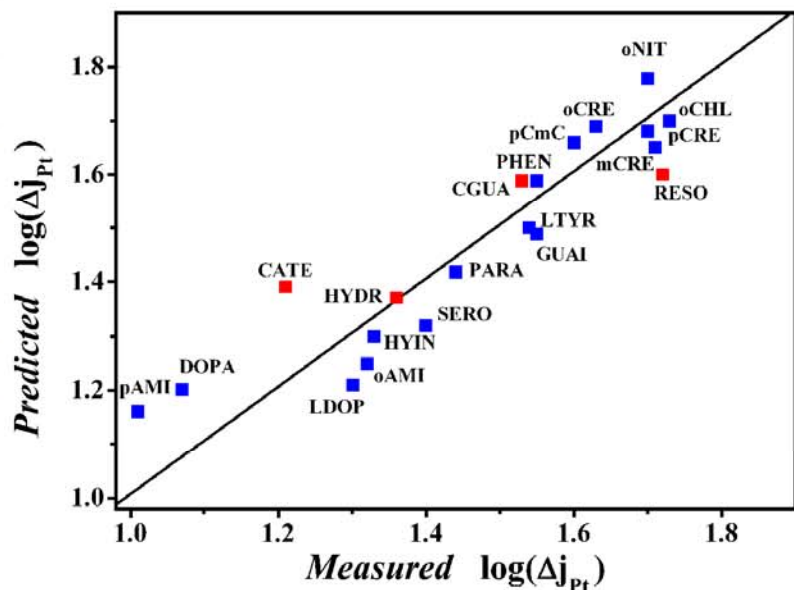
Training set: 16 samples

External validation set: 4 samples

1 LV (63.5%)

SEV = 0.092,  $Q^2 = 0.817$

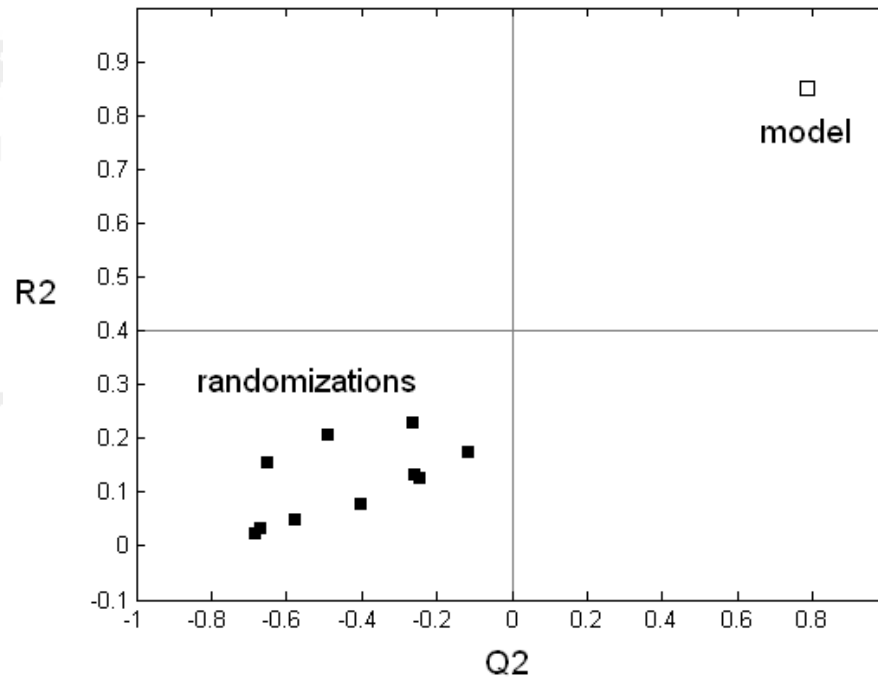
SEP = 0.078,  $R^2 = 0.884$



■ training set  
■ external validation set

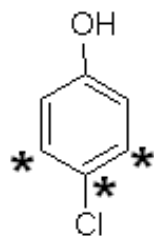


## Y-randomization test



No chance correlation has been found. The randomized models are far away from the real model.

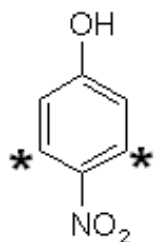
## Prediction



*p*-chlorophenol

Prediction: **1.71**

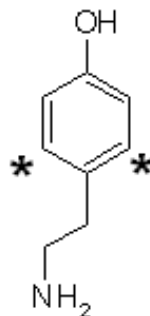
Comparison:  
*o*-chlorophenol  
**1.73** (exp)  
**1.69** (pred.)



*p*-nitrophenol

Prediction: **1.73**

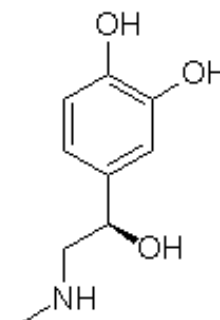
Comparison:  
*o*-nitrophenol  
**1.70** (exp)  
**1.79** (pred.)



tyramine

Prediction: **1.51**

Comparison:  
*L*-tyrosine  
**1.54** (exp)  
**1.52** (pred.)



adrenaline

Prediction: **1.27**

Comparison:  
*L*-dopa  
**1.30** (exp)  
**1.20** (pred.)

Predicted values are close to the experimental and predicted values for similar samples from the training set.

# CONCLUSIONS

To our knowledge, this is the first time that phenolic passivation is studied at a quantitative level (QSPR).

The presented QSPR approach is interpretable in terms of chemical concepts.

The PLS model can be used for prediction of phenolic passivation in practice, using relatively fast and simple calculations.

