Supplementary Information (SI)

New hybrid materials based on the grafting of Pd(II)-amino complexes on the graphitic surface of AC: Preparation, structures and catalytic properties

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1) Complexation of the Ar-S-F molecules with Pd(II).

The complexation capacities of Lys and Tren to Pd(II) are needed because, as it is expected the adsorption of this metal ion by the Merck/Lys and Merck/Tren hybrids is produced by complexation.

In the case of Lys ligand it should be expected the complexing ability to be similar to the reported in the literature[1,2] for the free glycine, which bears the same complexing function than the anchored Lys (Log K_{Gly-Pd} between 11.21-12.25).

In the case of Tren, it has been carried out the study of the reactivity of Pd(II) with a ligand, L, whose complexing function (L = 2,2´-diamino-N-methyldiethylamine), is similar to the F function of Tren. This study was done by using L/Pd(II) mixtures in aqueous solution by using potentiometric methods, following a experimental procedure previously reported.[3] Due to the high stability of the Pd(II)-amino ligands complexes, for the determination of the stability constants by potentiometric techniques, it is required the presence of a competing ligand in the medium. Thus, they were carried out potentiometric titrations of 40 mL of and Pd(II)/L mixtures with 1/1 molar relationship ($[K_2PdCl_4] = 10^{-3}$ M) in aqueous solution, at 298.1 K and [KCl] = 1 M (which provided the competitive ligand Cl^-), using 0.1M KOH as titrating agent. At least three titration experiments were performed in the pH range 2.5-10.5. The measurements (pH= - log $[H^+]$) were done with a 713 Methrom pH-mV meter, equipped with a combined glass electrode and connected to a Methron 765 Dosimat autoburette (1± 0.001 mL). The system was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO_2-free KOH.[4,5] The complex formation equilibria together to the stability constants and the species distribution plot were obtained as described in previous works.[6, 7] The HYPERQUAD software[8] was used to calculate the equilibrium constants from the emf data.

2) Table S1

Table S1. Stability constants of Pd^{2+} with L (L=2,2´-diamino-N-methyldiethylamine), determined by potentiometric measurements (1M KCl, 298.1K)

Equilibrium	log β
$Pd^{2+} + Cl^- + L$ ⇌ $[PdClL]^+$	30.94(4)*
$Pd^{2+} + L + OH^-$ ⇌ $[PdLOH]^+$	21.28(5)

Stability constants of the chloride complexes with Pd(II) are from ref. 9: $Pd^{2+} + Cl^-$ ⇌ $[PdCl]^+$, logβ=4.47; $Pd^{2+} + 2Cl^-$ ⇌ $[PdCl_2]$, logβ = 7.74; $Pd^{2+} + 3Cl^-$ ⇌ $[PdCl_3]^-$, logβ = 10.17; $Pd^{2+} + 4Cl^-$ ⇌ $[PdCl_4]^{2-}$, logβ = 11.54.

Protonation constants of L are: $H^+ + L$ ⇌ HL^+, logβ = 9.76(2); $2H^+ + L$ ⇌ H_2L^{2+}, logβ = 19.34(2); $3H^+ + L$ ⇌ H_3L^{3+}, logβ = 23.11(2).

*From the stability constants of the chloride complex $[PdCl]^+$ (logβ=4.47) it should be estimated the stability constant of PdL complex to be $\log K_{PdL}$=26.47(2).

3) Figure S1.

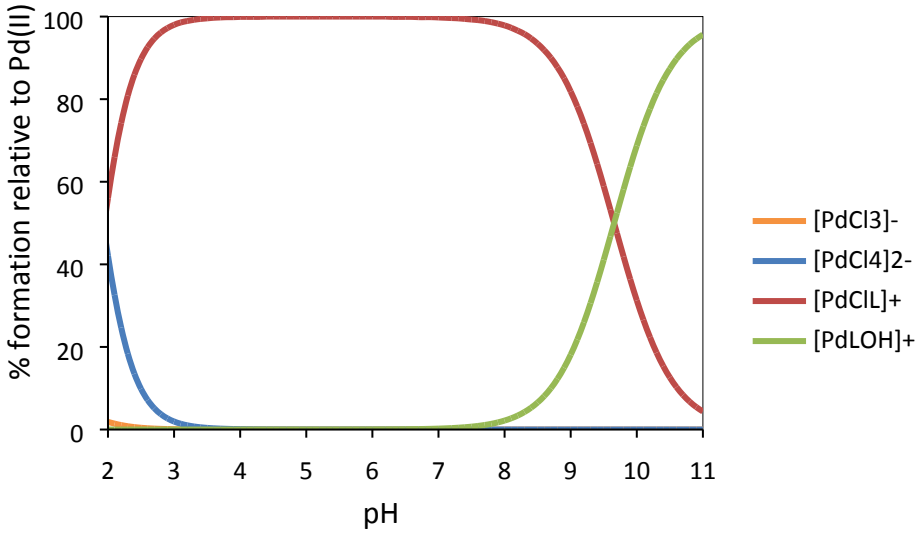

Figure S1. Distribution diagram of the species for the system L/Pd(II) (1 M KCl, 298.1K, [L]=10^{-3}M, [Pd^{2+}]=10^{-3}M)

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