Supplementary Materials

Mechanistic aspects of functional layer formation in hybrid one-step designed GOx/Nafion/Pd-NPs nanobiosensors

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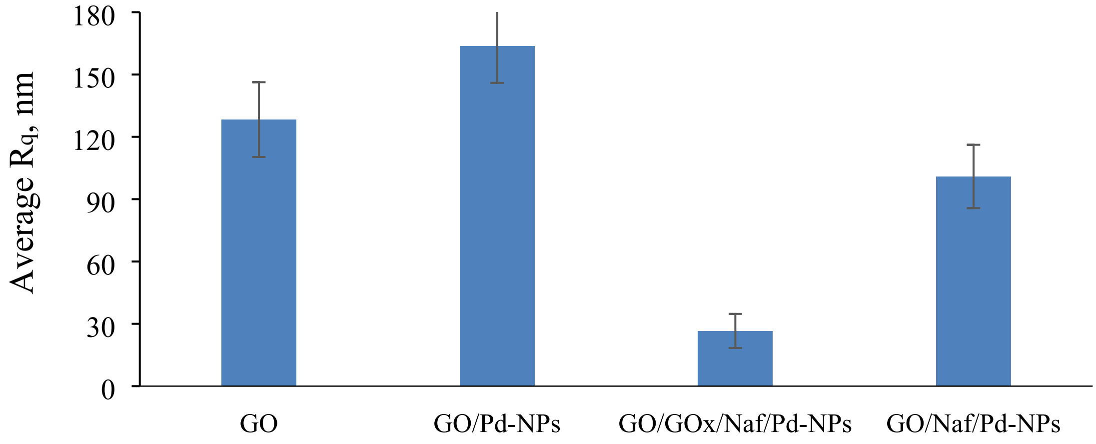

Figure S1 The estimation of roughness (R_q) for pristine GO and GO modified by Pd-NPs (GO/Pd-NPs), by mixture of Nafion and Pd-NPs (GO/Naf/Pd-NPs), and hybrid GO/GOx/Nafion/Pd-NPs. *Note*: all the deposition parameters were as follows: I_k = -2.5 mA; t_{el} = 30 s.

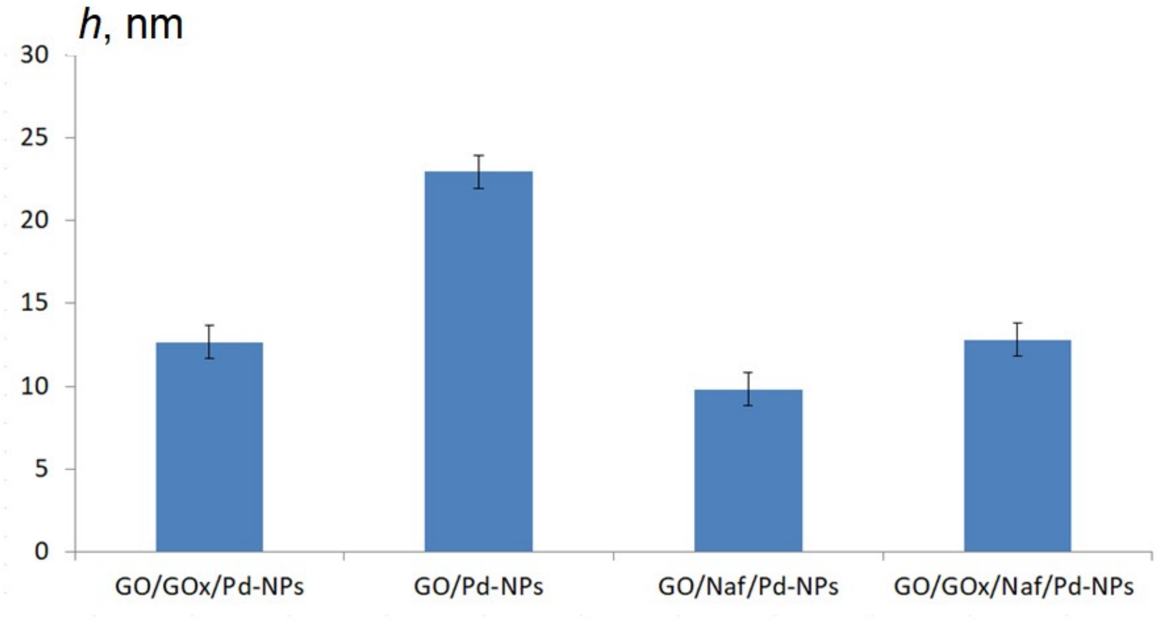

Figure S2. The summary of the thickness (*h,* nm) of the hybrid layer in various systems. *Note:* the thickness (*h*, nm) was calculated according to *Faraday's* law. The masses of the hybrid co-deposits were evaluated by QCM (the given mass was calculated in *ng*).

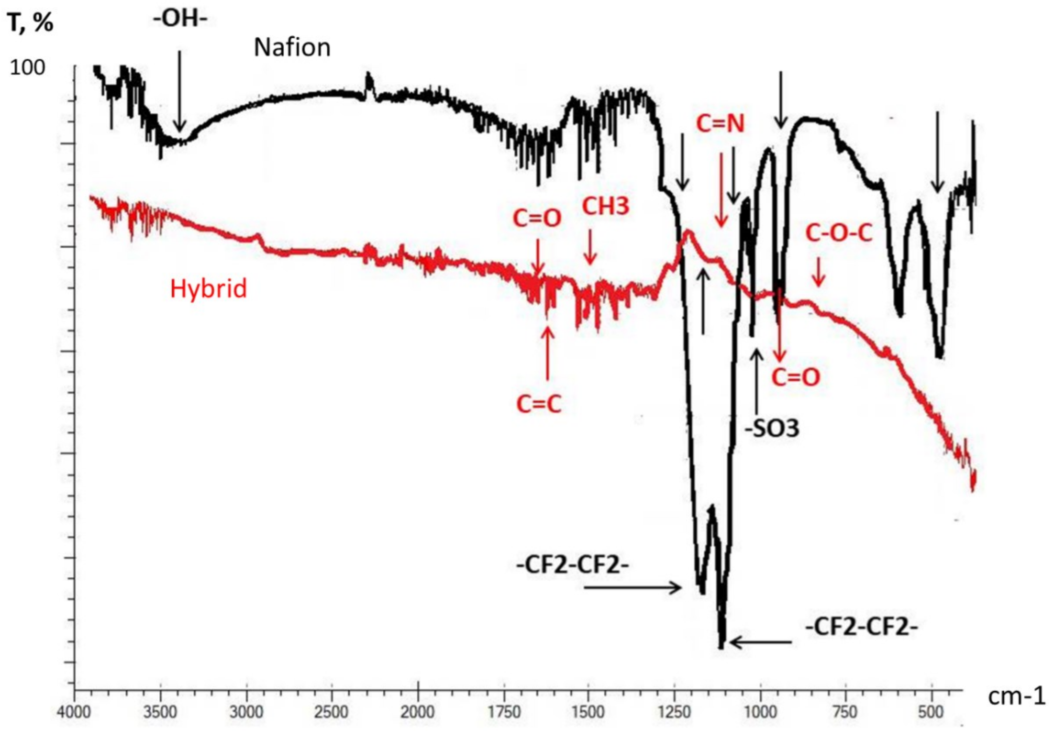

Figure S3. FT-IR spectra recorded in a transmission mode from Nafion film dried at the ambient conditions and scratched dried film from the hybrid one-step designed nanobiosensor. *Note:* all experiments were performed at least in a triplicate with the same results.

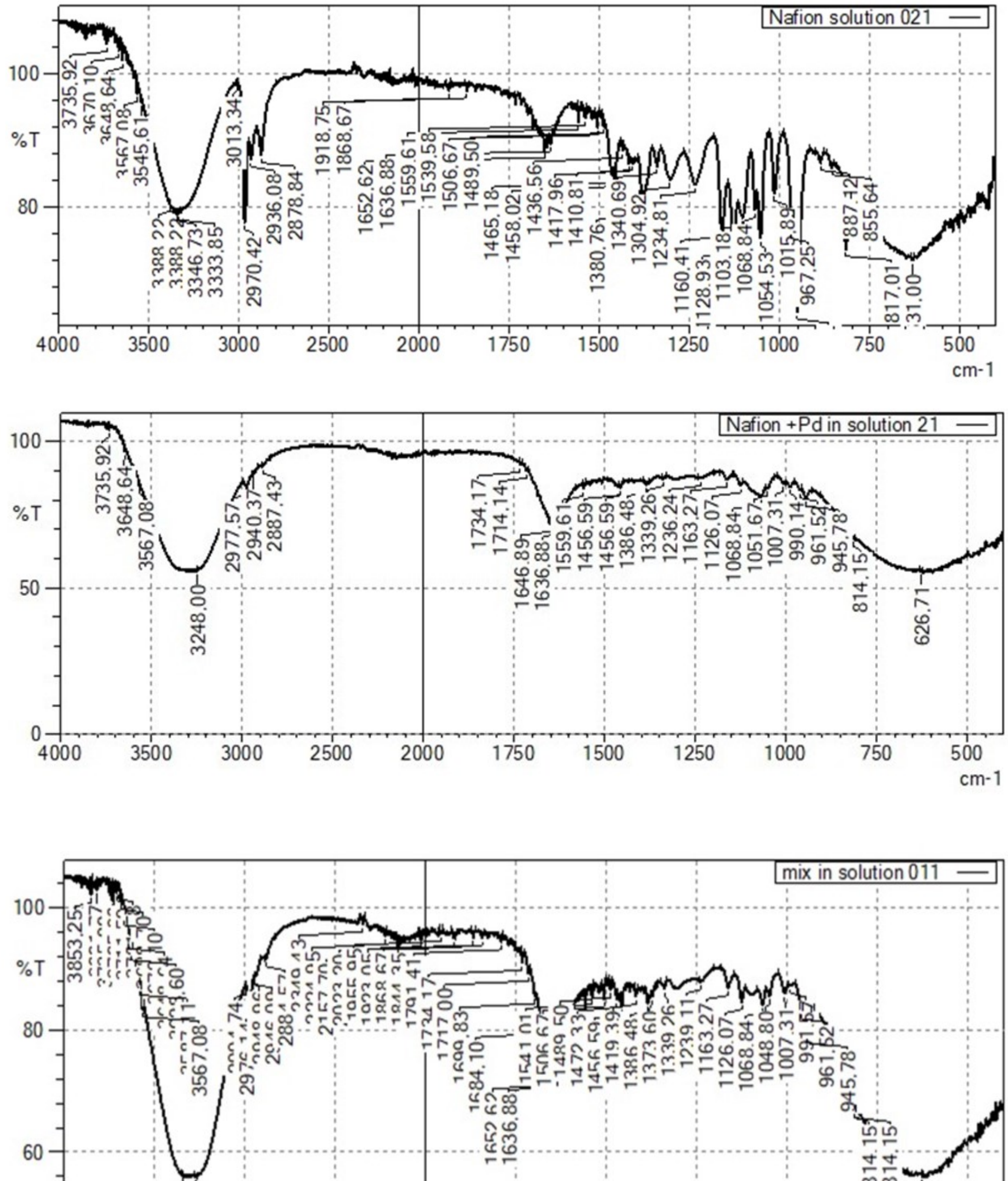

Figure S4. FT-IR spectra of the water-alcohol solutions of Nafion (*top*); Nafion+Pd-electrolyte (*middle*); Nafion + Pd-electrolyte + GOx (*bottom*).

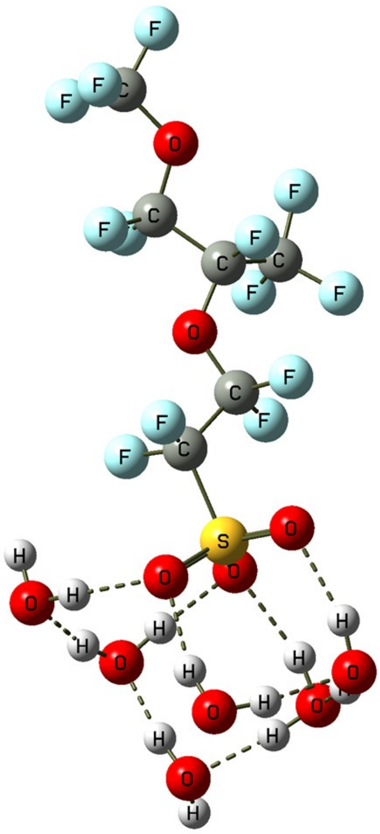

Figure S5. The optimized structure of a representative Nafion fragment with six water molecules in the water environment (PCM model).

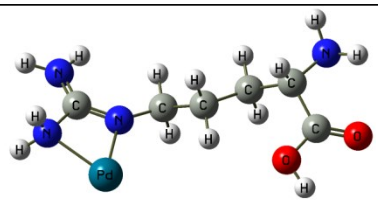	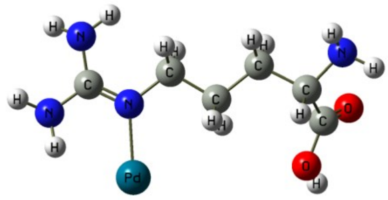	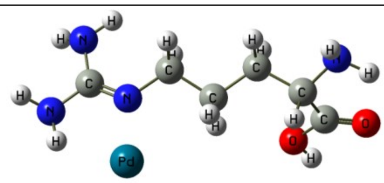
Pd^{2+} - Arg in Water, R_{PdN1} =1.96 Å R_{PdN2} = 2.09 Å	Pd^{0} – Arg in Water, R_{PdN} = 2.08 Å	Pd^{0} – Arg in Air, R_{PdN} = 2.12 Å

Figure S6. The optimized structures of Pd^{2+} and Pd^{0} complexes with Arg in water and air.

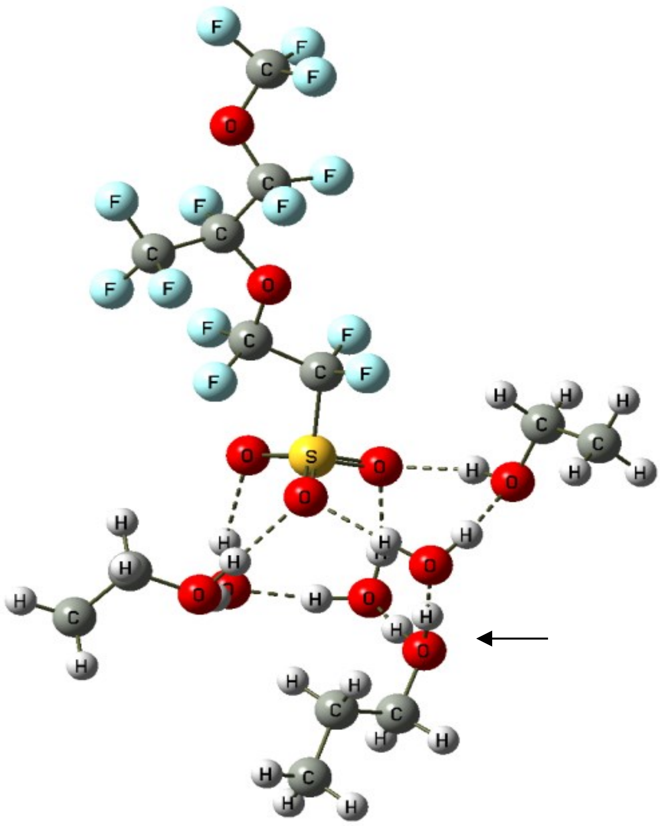

Figure S7. The optimized structure of the Nafion fragment in an aqueous-alcoholic solution. Note: the sulfonate group is surrounded with six molecules of solvent (three H_2O, two EtOH (ethanol), and PrH^+ (protonated propanol-1) as shown by the arrow). Two EtOH molecules are located in the first hydrate shell of the sulfo group and PrH^+ – are in the second. The hydrogen bonds are shown by the dash lines. During optimization, the structure was placed in a medium with Ɛ = 30.

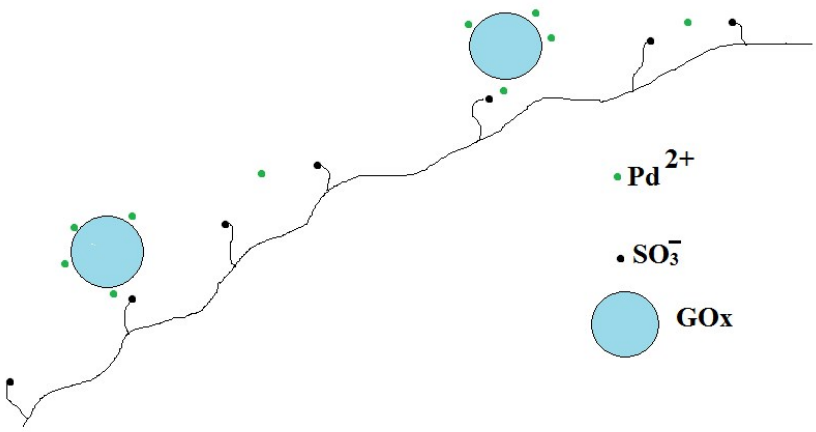

Figure S8. The fragment of the assumed structure of Nafion with Pd^{2+} cations and $GOx \cdot nPd^{2+}$ in the GOx/Naf/Pd solution.

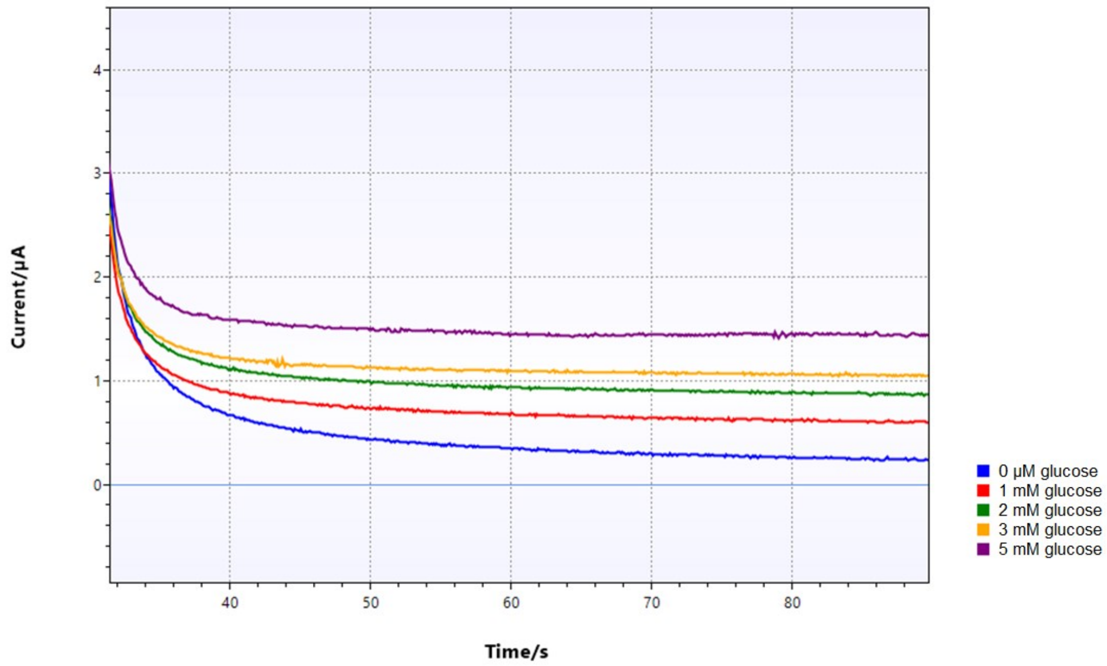

Figure S9. The responses obtained from the hybrid one-step designed nanobiosensor with encapsulated GOx in the presence of glucose at the applied potential of 0.2 V in multistep amperometric mode (MAM).

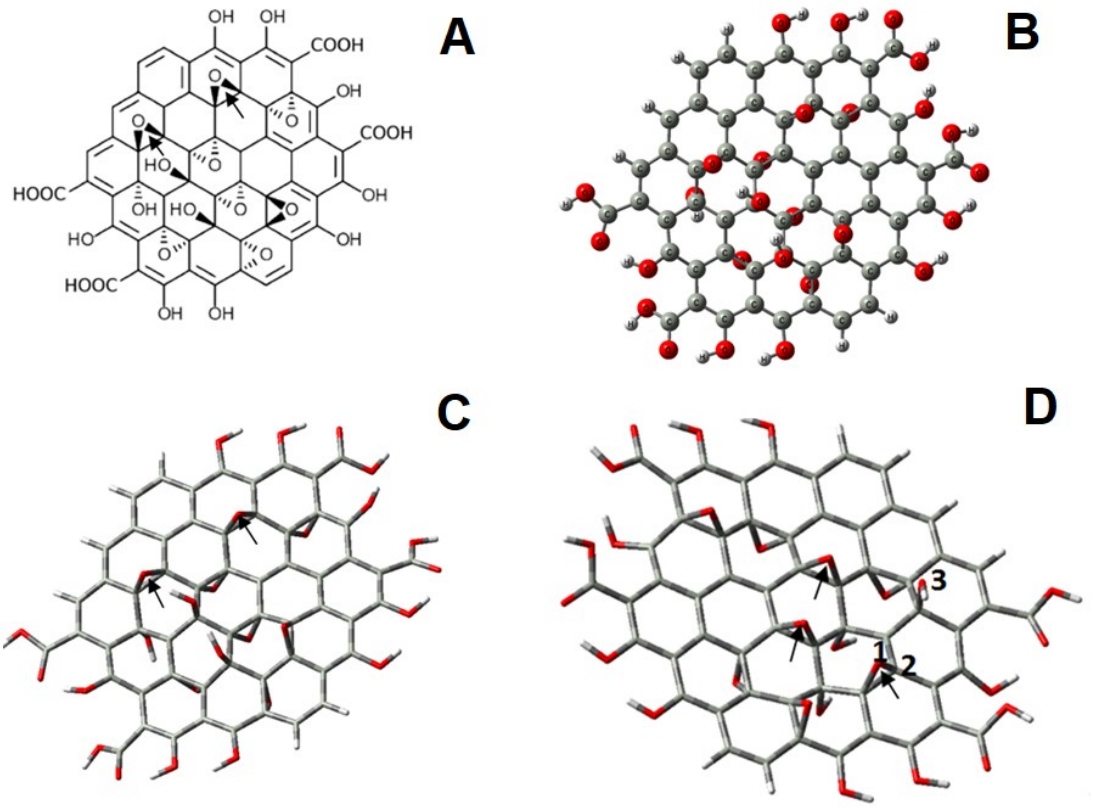

Figure S10. The models of GO (an oxidized circumcoronene molecule, OCM): **A** – the structure of OCM in according to an algorithm of successive addition of new oxygen-containing groups to the surface of graphene depending on the relative reactivity of non-oxidized sites.[50] **B,C,D** – various representations of the optimized OCM structure (**B** – “ball and stick”; **C** – a “tube” form; **D** – the reverse side of models **A, B** and **C** in the “tube” form). *Note:* 1 – the number of the oxygen atom of the epoxy group on the surface of GO; 2 – the number of the carbon atom of the same epoxy group; 3 – the number of the oxygen atom of the hydroxyl group. Colors of atoms: O (oxygen) - red, C (carbon) - grey, H (hydrogen) - white.

Table S1. The symmetric stretching vibration of SO_3^- anion, cm^{-1}, in the Nafion (Naf) solution; Nafion/Pd-electrolyte (Naf/Pd); glucose oxidase/Naf/Pd-electrolyte (GOx/Naf/Pd) selected from experimental FT-IR spectra, Figure S4

Number of characteristic peak	Naf	Naf/Pd	GOx/Naf/Pd
1	1069	1069	1069
2	1055	1052	1049

Table S2. The interaction energy between Pd^{2+}, Na^+, Pd^0 and sides radicals of the selected aminoacids acids and NMA (kcal/mol) in different mediums

Medium	Water	Water	Air	Water
Ion / Ligand	$E_{Pd}{}^{2+}$,	$E_{Pd}{}^{0}$,	$E_{Pd}{}^{0}$,	$E_{Na}{}^{+}$
Arg	96.8	22.0	18.1	9.2
Lys	83.9	20.4	17.8	9.6
His	79.7	19.9	17.1	11.7
Met	71.6	21.0	17.9	2.8
Gln	63.3	11.6	10.4	9.4
Cys	62.8	19.8	16.7	2.0
Ser	53.9	14.9	6.4	7.9
Asn	53.4	6.9	9.7	9.3
Glu	51.8	13.2	11.2	6.7
Asp	50.0	6.9	12.5	6.9
NMA	64.9	11.7	10.1	10.1