Supplementary Information

Metal Ion Binding by Pyridylethyl-Containing Polymers: Experimental and Theoretical Study

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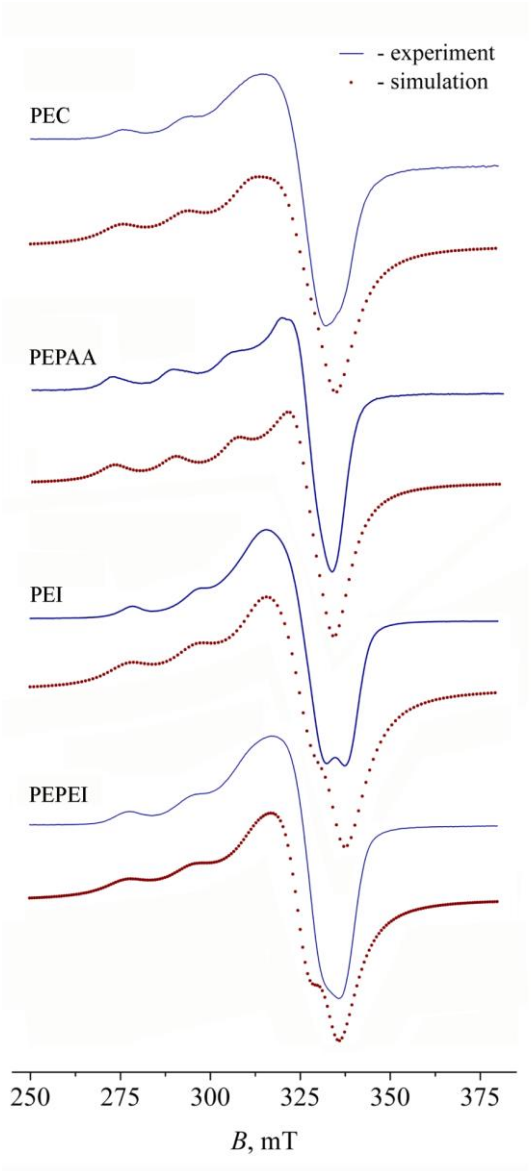

Fig.1S. Experimental (solid lines) and simulated (dotted lines) ESR spectra of the investigated complexes at 77 K. The parameters of ESR spectra used in simulations are presented in Table 4.

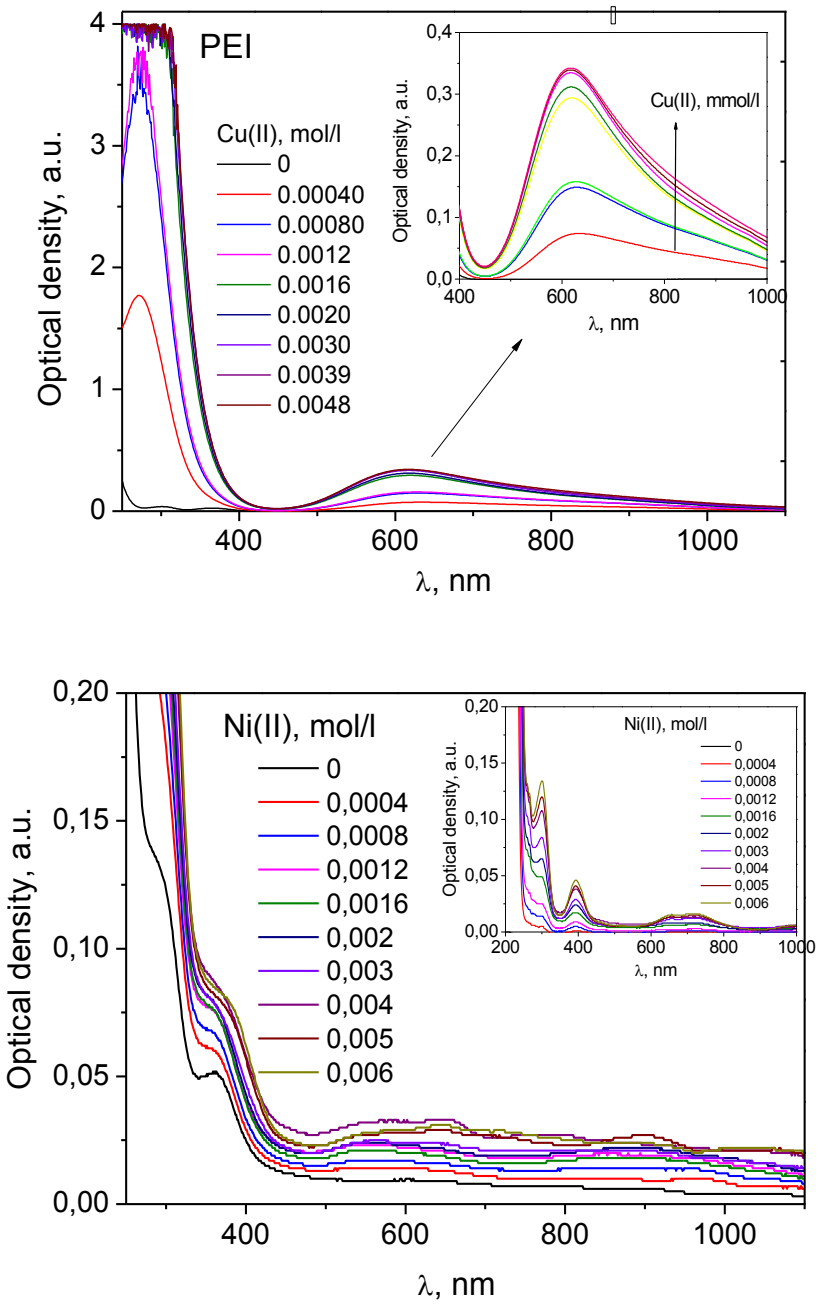

Figure 2S. UV-Vis spectra for titration of PEI with $Cu(NO_3)_2$ and $Ni(NO_3)_2$. Insert in the Figure for titration of PEI with $Ni(NO_3)_2$ shows UV-vis spectra of $Ni(NO_3)_2$ solution without polymers. PEI concentration – 5 mmol (monomer)/l.

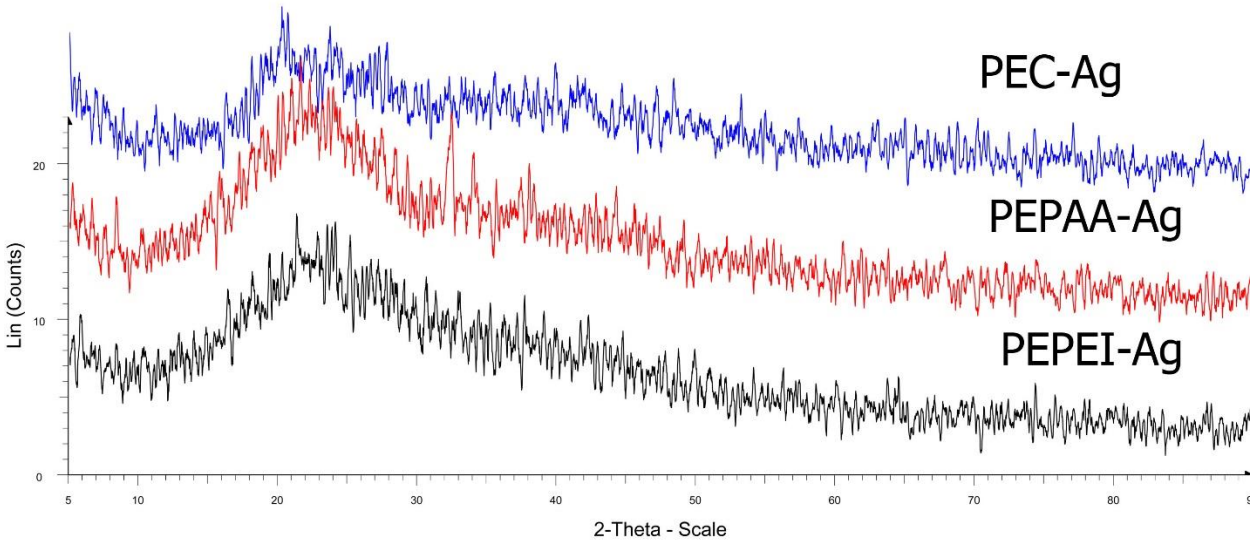

Figure 3S. XRD pattern of PEC, PEPAA, and PEPEI after Ag(I) sorption.

X-ray diffraction analysis of the materials after Ag(I) sorption has been performed using DRON-3 multipurpose diffractometer (Russia) equipped with CuKα- irradiation source, Ni-filter, medium wavelength (λ) 1.5418 Å.

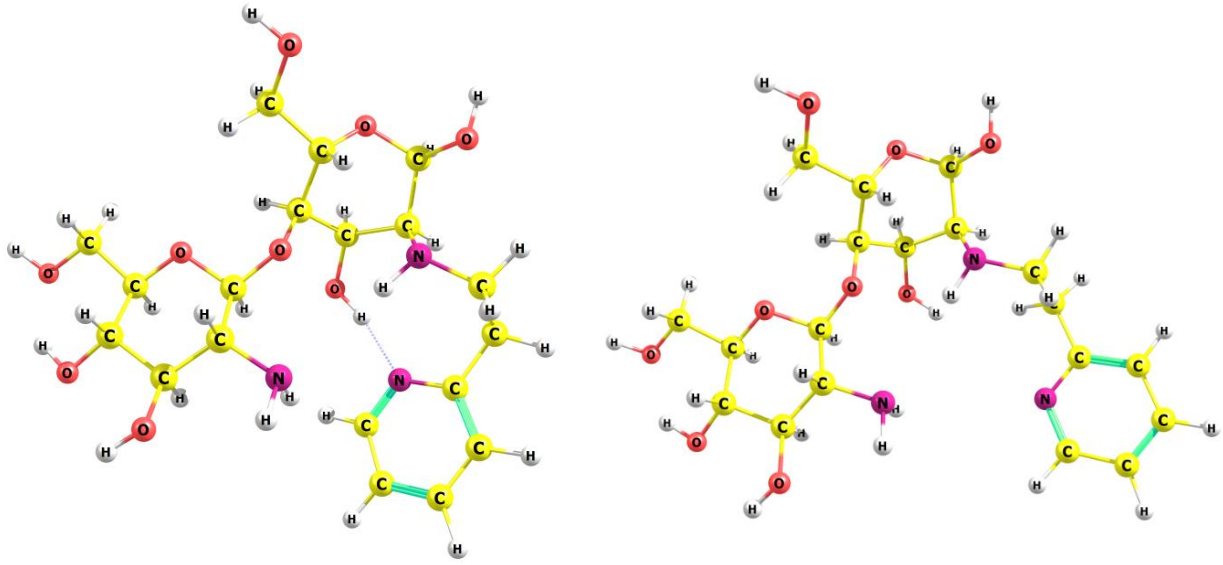

Figure 4S. Structures of investigated model PEC clusters with (left structure, E_{tot} = -784435 kJ/mol) and without (right structure, E_{tot} = -784386 kJ/mol) N - HO hydrogen bonding.

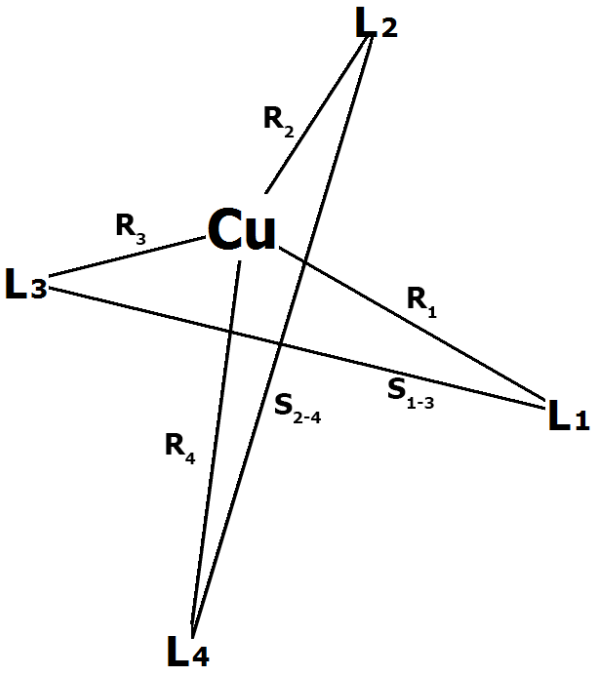

Figure 5S. Illustration for calculation of deviation (D) from the square planar geometry for Cu(II) complexes.

$D = \sum R / \sum S$, where

$\sum R = R_1 + R_2 + R_3 + R_4$ is the sum of distances from central metal ion (Cu^{2+}) to four closest atoms (N or O) of the ligand

$\sum S = S_{1-3} + S_{2-4}$ is the sum of diagonals of the tetragon formed by four closest to central metal ion (Cu2+) atoms (N or O) of the ligand.

In the square complex $\sum R = \sum S$, and D = 1.

Table 1S. Parameters of Langmuir equation for sorption isotherms. K_L-Langmuir constant, Q_{max} – maximum sorption capacity, mmol/g

	Cu(II)			**Ag(I)**			**Ni(II)**		
	K_L	Q_{max}	R	K_L	Q_{max}	R	K_L	Q_{max}	R
PEC	1.25	1.55	0.92	2.59	1.34	0.99	3.18	0.48	0.97
PEPAA	0.783	0.4	0.92	3.96	0.902	0.92	2.35	0.256	1
PEPEI	1.17	2.098	0.89	4.39	1.00	0.92	1.03	0.84	0.98

Table 2S. Binding energies (eV) for pyridylethyl derivatives and their complexes with Cu(II) and Ag(I)

Sample	**N 1s**		**Ag 3d/Cu 2p**	
PEPEI-Ag(I)	399.2	401.9	368.4	374.4
PEPEI-Cu(II)	399.0	401.5	933.3	942.1
PEPEI	398.9	401.5		
PEC-Ag(I)	398.9	401.4	368.5	374.5
PEC-Cu(II)	399.3	401.6	933.1	942.6
PEC	399.3	401.5		
PEI-Cu(II)	399.3	401.6	933.8	943.7
PEI	399.0	401.5		
PEPAA-Ag(I)	399.15	400.8	368.4	374.5

Table 3S. Distances from central metal ion (Cu^{2+}) to four closest atoms (N or O) of the ligand (R_1, R_2, R_3, R_4), sum of the distances ∑R, sum of the diagonals of the tetragon formed by four closest to central metal ion (Cu2+) atoms (N or O) of the ligand, D - deviation from the square planar geometry for Cu(II) complexes (see Figure 5S for details)

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Complex	**R_1**	**R_2**	**R_3**	**R_4**	**∑R**	**∑S**	**D**
PEPAA(0.5)-Cu^{2+}	1.99	1.97	2.02	2.14	2.03	1.87	1.09
PEI-Cu^{2+}	2.02	2.04	2.04	2.06	2.01	1.99	1.01
PEPEI(0.5)-Cu^{2+}	2.08	2.09	2.16	2.20	2.00	1.87	1.07
PEC(0.5)-Cu^{2+}	2.01	2.03	2.04	2.23	2.06	2.04	1.01