

Silica supported ionic liquids for the efficient
and selective recovery of platinum and
palladium from aqueous media

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Supporting equations

Kinetic and isotherm models

The sorption kinetics indicates the speed that the sorbate is removed by the sorbent, from the moment they come into contact (t_0) until the moment at which the sorbent cannot retain more sorbate, i.e., the equilibration time (t_e). Within this period, the concentration of sorbate on the sorbent material (q_t) progressively increases as the concentration in the liquid fraction (C_t) decreases relative to the initial value (C_0). When equilibrium is attained, the sorbate concentration on the sorbent achieves its maximum (q_e), while the concentration of free sorbate is in its minimum (C_e). The total amount of sorbate retained by the sorbent material in a certain time t (q_t) and when equilibrium is attained (q_e) can be determined from the following mass balance equations:

$$q_t = \frac{(C_0 - C_t)}{m} * V \quad (\text{S1})$$

$$q_e = \frac{(C_0 - C_e)}{m} * V \quad (\text{S2})$$

where m is the mass of sorbent in a given volume V of solution.

Among the various kinetic models available in the literature, the kinetic models of pseudo 1st order (or model of Lagergren) and pseudo 2nd order are mathematical models widely used. The pseudo 1st order model is expressed by the following equation ¹:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \xrightarrow[t=0(q_t=0) \text{ to } t=t(q_t=q_t)]{\text{integration}} q_t = q_e(1 - e^{-k_1 t}) \quad (\text{S3})$$

where k_1 (1/h) is the rate constant of the model. This model has the disadvantage of not adjusting well to the experimental data near the equilibrium.

The pseudo 2nd order model generally adjusts better to the experimental data throughout the entire period of the sorption process ²:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \xrightarrow[t=0(q_t=0) \text{ to } t=t(q_t=q_t)]{\text{integration}} q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (\text{S4})$$

where k_2 (1/h) is the kinetic constant of the model.

Another common kinetic model is the Elovich's model, firstly used to describe the sorption of gas onto solid systems ³. However, in the last years this model began to be applied to the sorption of chemical species in aqueous solutions ⁴. This model is based on the following equation:

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \xrightarrow[t=0(q_t=0) \text{ to } t=t(q_t=q_t)]{\text{integration}} q_t = \left(\frac{1}{\beta}\right) \ln(1 + \alpha\beta t) \quad (\text{S5})$$

where α and β are, respectively, the initial sorption rate, and the desorption constant.

In order to evaluate the effectiveness of the process, the removal percentages are calculated using equation 1.6. The variation of ion concentration along the contact time with the sorbent material is expressed in terms of normalized concentrations (equation 1.7). This allows the comparison of the removal process of various sorbates for a given sorbent, or using the same sorbate but different sorbents, regardless of the initial sorbate concentration.

$$\text{Removal (\%)} = \frac{(C_0 - C_t)}{C_0} * 100 \quad (\text{S6})$$

$$C'_t = \frac{C_t}{C_0} \quad (\text{S7})$$

In addition to the kinetic study, a sorption process may be characterized by equilibrium studies. These studies are carried out at controlled and constant temperatures (hence, the respective associated mathematical models are often referred to as isothermal) and involve studying q_e vs C_e , being useful to determine the maximum sorption capacity,

affinity and surface properties of a particular sorbent for a given sorbate, as well as to understand the sorption mechanism ^{5,6}. The Langmuir and Freundlich models are the most common to predict these properties, since they can generally better fit the experimental results.

The Langmuir model assumes that the maximum sorption of a given sorbent corresponds to the formation of a monolayer of sorbate molecules on the surface of the sorbent. As this surface is uniform, the active sites have the same affinity for the sorbate, so there are no interactions between sorbed molecules ⁷. The equation on which this model is based is the following:

$$q_e = \frac{q_{max}K_L C_e}{1 + K_L C_e} \quad (S8)$$

where K_L (L/mg) is the sorption equilibrium constant of the model and q_{max} (mg/g) is the maximum capacity of the sorbent.

The Freundlich model, unlike the Langmuir model, assumes the existence of a multi-layer of sorbate molecules on the surface of the sorbent, which is heterogeneous, and is expressed by the following equation ⁸:

$$q_e = K_F C_e^{1/n} \quad (\text{S9})$$

where K_F ($\text{mg}^{1-1/n} \text{L}^{1/n}/\text{g}$) and n are empirical constants of the model. Note that n (sorption intensity) varies between 1 and 10 and is related to non-linearity of the Freundlich model.

Another common isotherm model is the Dubinin-Radushkevich's model, which assumes that sorption occurs by micropore volume filling instead of the formation of one or more layers on the surface of the sorbent. This model is based on the following equations ⁹:

$$q_e = q_{max} e^{-B_{DR}\varepsilon} \quad (\text{S10})$$

$$\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \quad (\text{S11})$$

where q_{max} (mg/g) is the maximum capacity of the sorbent, B_{DR} (mol^2/J^2) is the Dubinin-Radushkevich constant, ε (J/mol) is the Polanyi potential, R ($8.314 \text{ J}/\text{mol}/\text{K}$) is the universal gas constant and T (K) is the absolute temperature.

Supporting tables

Table S1. Equilibrium concentration of Pt and Pd after sorption (C_e), sorption efficiency (%R), and concentration of sorbate in the solid phase (q_e) of $[\text{Si}][\text{N}_{3222}]\text{Cl}$ with PGEs solution.

$[\text{Si}][\text{N}_{3222}]\text{Cl}$						
	Pt			Pd		
Time / min	C_e ($\mu\text{g/L}$)	%R	q_e (mg/g)	C_e ($\mu\text{g/L}$)	%R	q_e (mg/g)
0	936	0	0.00	966	0	0.00
5	304	68	2.53	841	13	0.50
15	152	84	3.13	810	16	0.62
30	109	88	3.31	805	17	0.64
45	94	90	3.37	815	16	0.60
60	82	91	3.41	802	17	0.66

90	83	91	3.41	794	18	0.69
120	78	92	3.43	805	17	0.64
240	69	93	3.47	806	17	0.64
480	84	91	3.41	810	16	0.62

Table S2. Equilibrium concentration of Pt and Pd after sorption (C_e), sorption efficiency ($\%R$), and concentration of sorbate in the solid phase (q_e) of $[\text{Si}][\text{N}_{3444}]\text{Cl}$ with PGEs solution.

$[\text{Si}][\text{N}_{3444}]\text{Cl}$						
	Pt			Pd		
Time / min	C_e ($\mu\text{g/L}$)	$\%R$	q_e (mg/g)	C_e ($\mu\text{g/L}$)	$\%R$	q_e (mg/g)
0	961	0	0.00	967	0	0.00
5	821	15	0.56	947	2	0.08

15	805	16	0.62	956	1	0.04
30	795	17	0.66	950	2	0.07
45	786	18	0.70	954	1	0.05
60	774	19	0.74	932	4	0.14
90	778	19	0.73	925	4	0.17
120	779	19	0.72	936	3	0.12
240	768	20	0.77	932	4	0.14
480	761	21	0.80	921	5	0.18

Table S3. Equilibrium concentration of Pt and Pd after sorption (C_e), sorption efficiency (%R), and concentration of sorbate in the solid phase (q_e) of $[\text{Si}][\text{N}_{366}]\text{Cl}$ with PGEs solution.

$[\text{Si}][\text{N}_{366}]\text{Cl}$

	Pt			Pd		
Time / min	C_e ($\mu\text{g/L}$)	%R	q_e (mg/g)	C_e ($\mu\text{g/L}$)	%R	q_e (mg/g)
0	974	0	0.00	944	0	0.00
5	901	7	0.29	946	0	---
15	893	8	0.32	944	0	0.00
30	895	8	0.32	946	0	---
45	878	10	0.38	949	---	---
60	890	9	0.34	940	0	0.02
90	878	10	0.38	927	2	0.07
120	866	11	0.43	927	2	0.07
240	856	12	0.47	921	2	0.09
480	851	13	0.49	917	3	0.11

Table S4. Equilibrium concentration of Pt and Pd after sorption (C_e), sorption efficiency (%R), and concentration of sorbate in the solid phase (q_e) of [Si][N₃₈₈₈]Cl with PGEs solution.

[Si][N ₃₈₈₈]Cl						
	Pt			Pd		
Time / min	C_e ($\mu\text{g/L}$)	%R	q_e (mg/g)	C_e ($\mu\text{g/L}$)	%R	q_e (mg/g)
0	998	0	0.00	962	0	0.00
5	979	2	0.08	962	0	0.00
15	962	4	0.14	962	0	0.00
30	953	5	0.18	962	0	0.00
45	950	5	0.19	956	1	0.02
60	959	4	0.16	943	2	0.08
90	955	4	0.17	948	1	0.06

120	1005	---	---	972	---	---
240	1041	---	---	995	---	---
480	997	0	0.00	951	1	0.04

Table S5. Equilibrium concentration of Pt and Pd after sorption (C_e), sorption efficiency (%R), and concentration of sorbate in the solid phase (q_e) of $[\text{Si}][\text{N}_{3114}]\text{Cl}$ with PGEs solution.

$[\text{Si}][\text{N}_{3114}]\text{Cl}$						
	Pt			Pd		
Time / min	C_e ($\mu\text{g/L}$)	%R	q_e (mg/g)	C_e ($\mu\text{g/L}$)	%R	q_e (mg/g)
0	988	0	0.00	1022	0	0.00
5	102	90	3.54	351	66	2.68
15	73	93	3.66	239	77	3.13

30	49	95	3.76	199	81	3.29
45	49	95	3.76	196	81	3.30
60	42	96	3.78	194	81	3.31
90	39	96	3.80	186	82	3.34
120	38	96	3.80	197	81	3.30
240	40	96	3.79	197	81	3.30
480	37	96	3.80	206	80	3.26

Table S6. Equilibrium concentration of Pt and Pd after sorption (C_e), sorption efficiency (%R), and concentration of sorbate in the solid phase (q_e) of $[\text{Si}][\text{N}_{3118}]\text{Cl}$ with PGEs solution.

$[\text{Si}][\text{N}_{3118}]\text{Cl}$	
Pt	Pd

Time / min	C_e ($\mu\text{g/L}$)	%R	q_e (mg/g)	C_e ($\mu\text{g/L}$)	%R	q_e (mg/g)
0	961	0	0.00	979	0	0.00
5	120	88	3.36	525	46	1.81
15	59	94	3.60	316	68	2.65
30	34	96	3.70	218	78	3.04
45	39	96	3.68	193	80	3.14
60	35	96	3.70	178	82	3.20
90	27	97	3.73	163	83	3.26
120	28	97	3.73	154	84	3.29
240	24	98	3.74	164	83	3.25
480	29	97	3.72	175	82	3.21

Table S7. Equilibrium concentration of Pt and Pd after sorption (C_e), sorption efficiency (%R), and concentration of sorbate in the solid phase (q_e) of $[\text{Si}][\text{C}_3\text{C}_1\text{Im}]\text{Cl}$ with PGEs solution.

$[\text{Si}][\text{C}_3\text{C}_1\text{Im}]\text{Cl}$						
	Pt			Pd		
Time / min	C_e ($\mu\text{g/L}$)	%R	q_e (mg/g)	C_e ($\mu\text{g/L}$)	%R	q_e (mg/g)
0	958	0	0.00	965	0	0.00
5	327	66	2.52	446	54	2.07
15	206	78	3.00	236	76	2.91
30	126	87	3.32	158	84	3.22
45	85	91	3.49	138	86	3.30
60	69	93	3.55	132	86	3.33
90	52	95	3.62	111	88	3.41

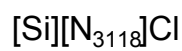
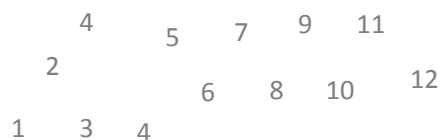
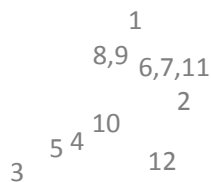
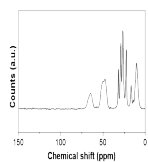
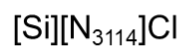
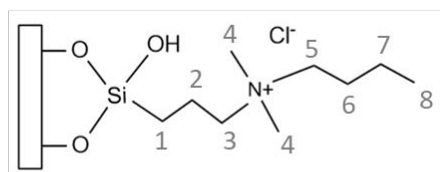
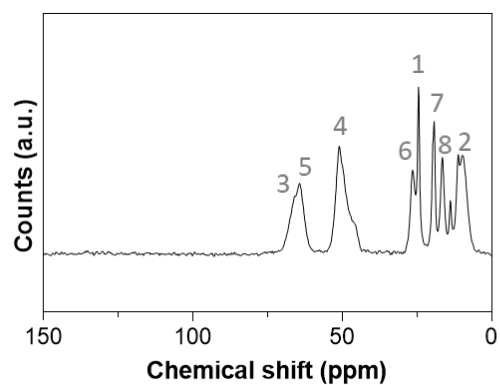
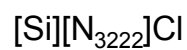
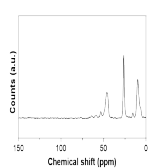
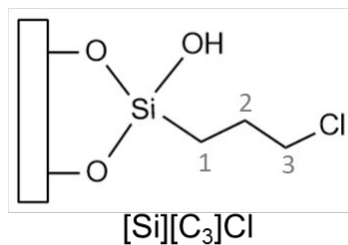
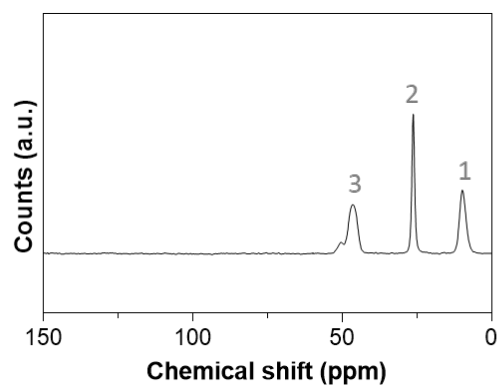
120	43	96	3.65	107	89	3.43
240	29	97	3.71	109	89	3.42
480	21	98	3.74	111	88	3.41

Table S8. Equilibrium concentration of Pt and Pd after sorption (C_e), and concentration of sorbate in the solid phase (q_e) of $[\text{Si}][\text{C}_3\text{C}_1\text{Im}]\text{Cl}$ with PGEs solution, at 25 °C.

Pt		Pd	
C_e (mg/L)	q_e (mg/g)	C_e (mg/L)	q_e (mg/g)
9.7	48.0	8.8	22.0
9.2	51.0	8.6	22.3
8.8	45.9	7.8	18.6
6.5	37.5	7.3	19.0

3.3	47.4	6.7	21.4
2.7	37.5	6.0	19.1
1.3	35.4	5.4	17.5
1.1	30.5	4.1	18.9
0.70	23.8	2.3	18.7
0.67	19.3	1.6	16.5
0.51	13.0	1.2	11.6
0.36	9.8	0.88	8.9
0	0	0	0

Supporting figures



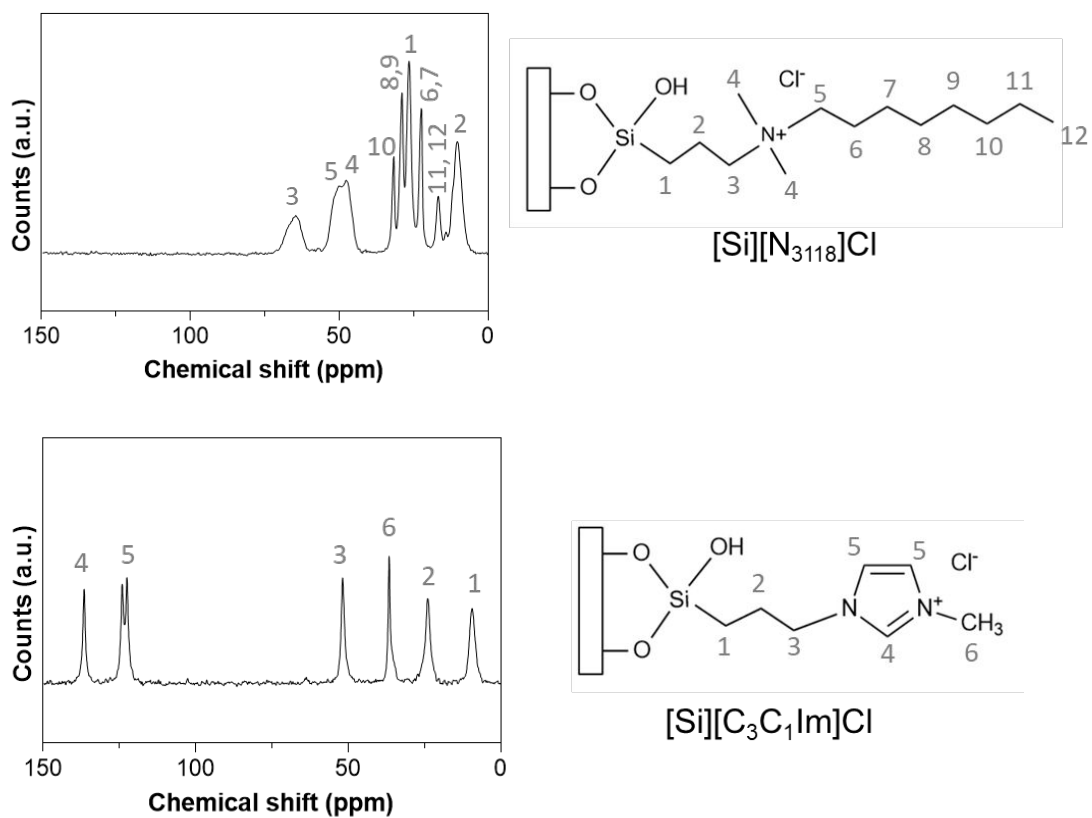


Figure S1. Solid-state ^{13}C NMR spectra of chloropropyl silica, $[\text{Si}][\text{N}_{3222}]\text{Cl}$, $[\text{Si}][\text{N}_{3114}]\text{Cl}$, $[\text{Si}][\text{N}_{3118}]\text{Cl}$ and $[\text{Si}][\text{C}_3\text{C}_1\text{Im}]\text{Cl}$.

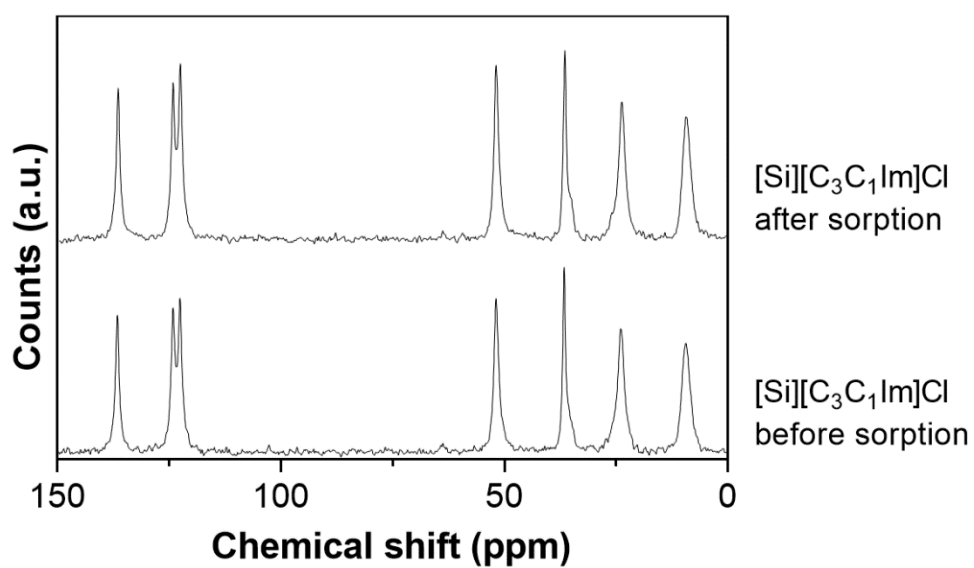
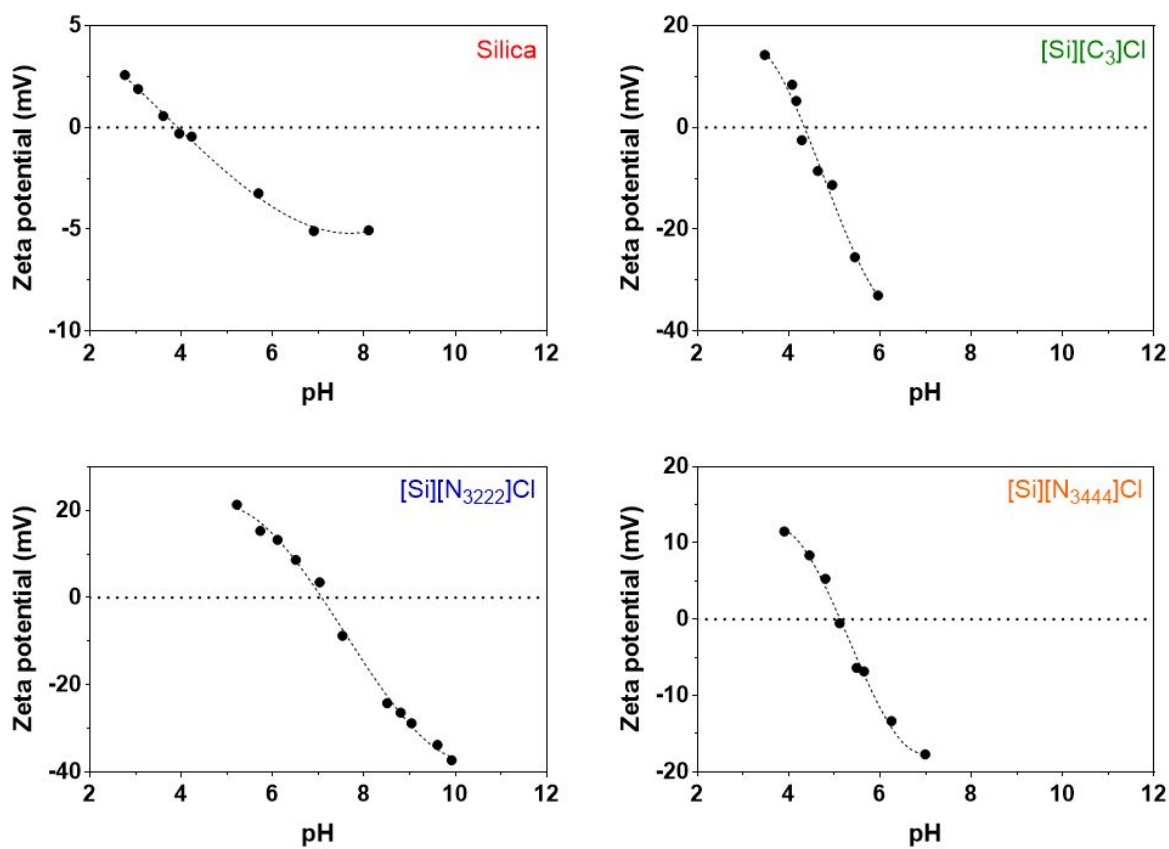


Figure S2. Solid-state ^{13}C NMR spectra of the $[\text{Si}][\text{C}_3\text{C}_1\text{Im}]\text{Cl}$ sample, after and before sorption experiments at pH 4.



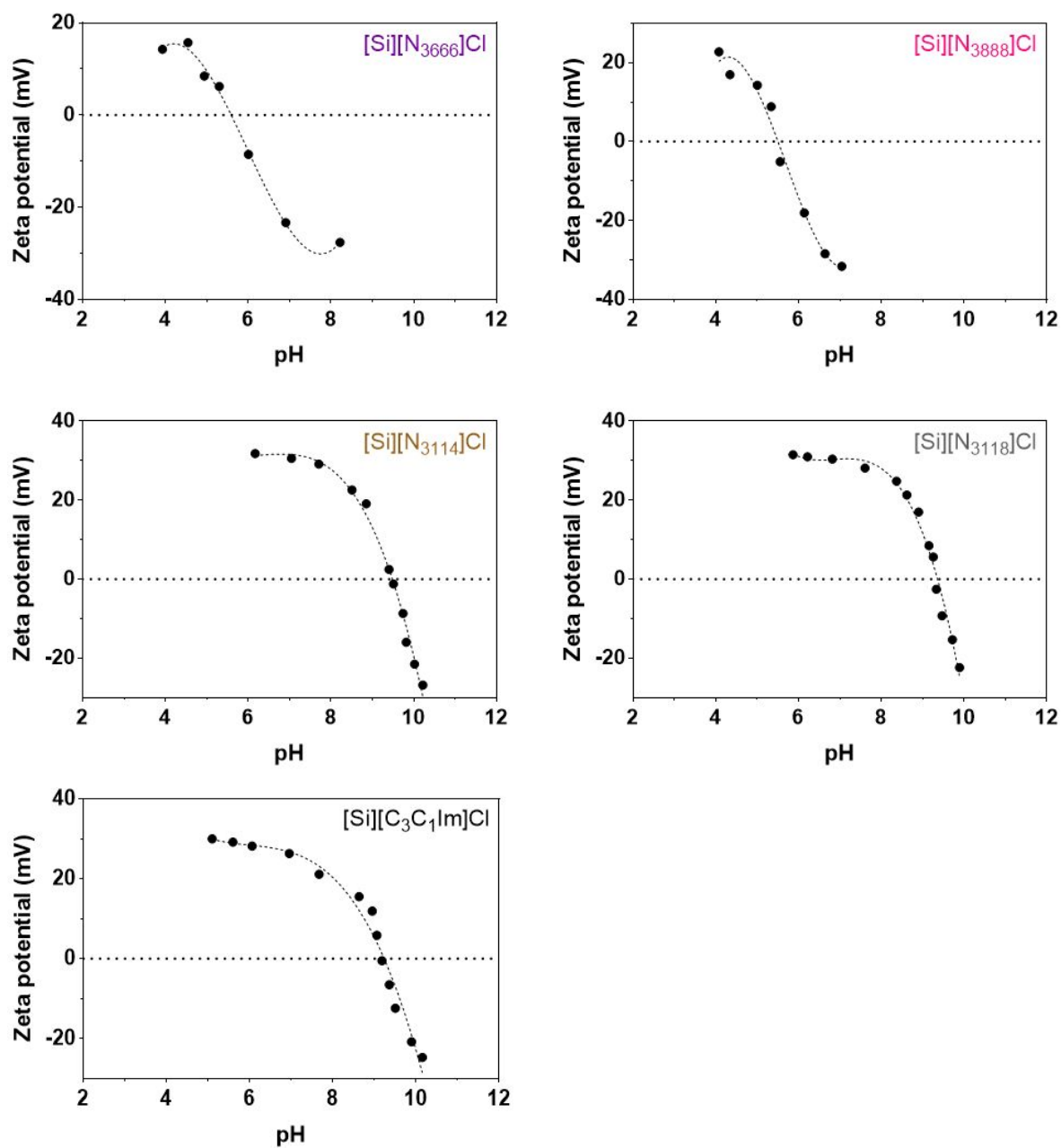


Figure S3. Zeta potential as a function of pH for the activated silica, chloropropyl silica and synthesized SILs.

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