Supplementary Information

Exploring the Interfacial Behavior of Ruthenium Complexes in Ionic Liquids: Implications for Supported Ionic Liquid Phase Catalysts

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The supporting information (SI) presents fitting procedures and full sets of all relevant core levels recorded from neat $[C_4C_1Im][PF_6]$ (*Figure S1*) and $[C_2C_1Im][OAc]$ (*Figure S2*) and the solutions of $[Ru(tpy)(bpy)Cl][PF_6]$ in $[C_4C_1Im][PF_6]$ (*Figure S4*) and $[C_2C_1Im][OAc]$ (*figure S5*), as well as $[Ru(tpy)(dcb)Cl][PF_6]$ in $[C_2C_1Im][OAc]$ (*Figure S8*) with $2.5\%_{mol}$ nominal concentration. Since a surface-active contamination was found for one of the latter solutions, C 1s and O 1s ARXP spectra are shown on top of each other before and after surface cleaning using Ar^+-sputtering (*Figure S7*). In addition, Si 2p spectra are depicted for all samples to confirm absence of other common surface-active contaminations observed in previous studies[1]. For neat $[C_2C_1Im][OAc]$ and the solution of $[Ru(tpy)(bpy)Cl][PF_6]$ in $[C_2C_1Im][OAc]$, mass spectra are shown at room temperature and 50 °C (*Figure S3*). In order to rule out X-ray induced alterations of the samples, all region spectra acquired initially are contrasted with spectra taken after more than 90 min of X-ray exposure for the solution of $[Ru(tpy)(bpy)Cl][PF_6]$ in $[C_2C_1Im][OAc]$ (*Figure S6*). Finally, the weighed proportions for preparation of the solutions are given (*Table S2*).
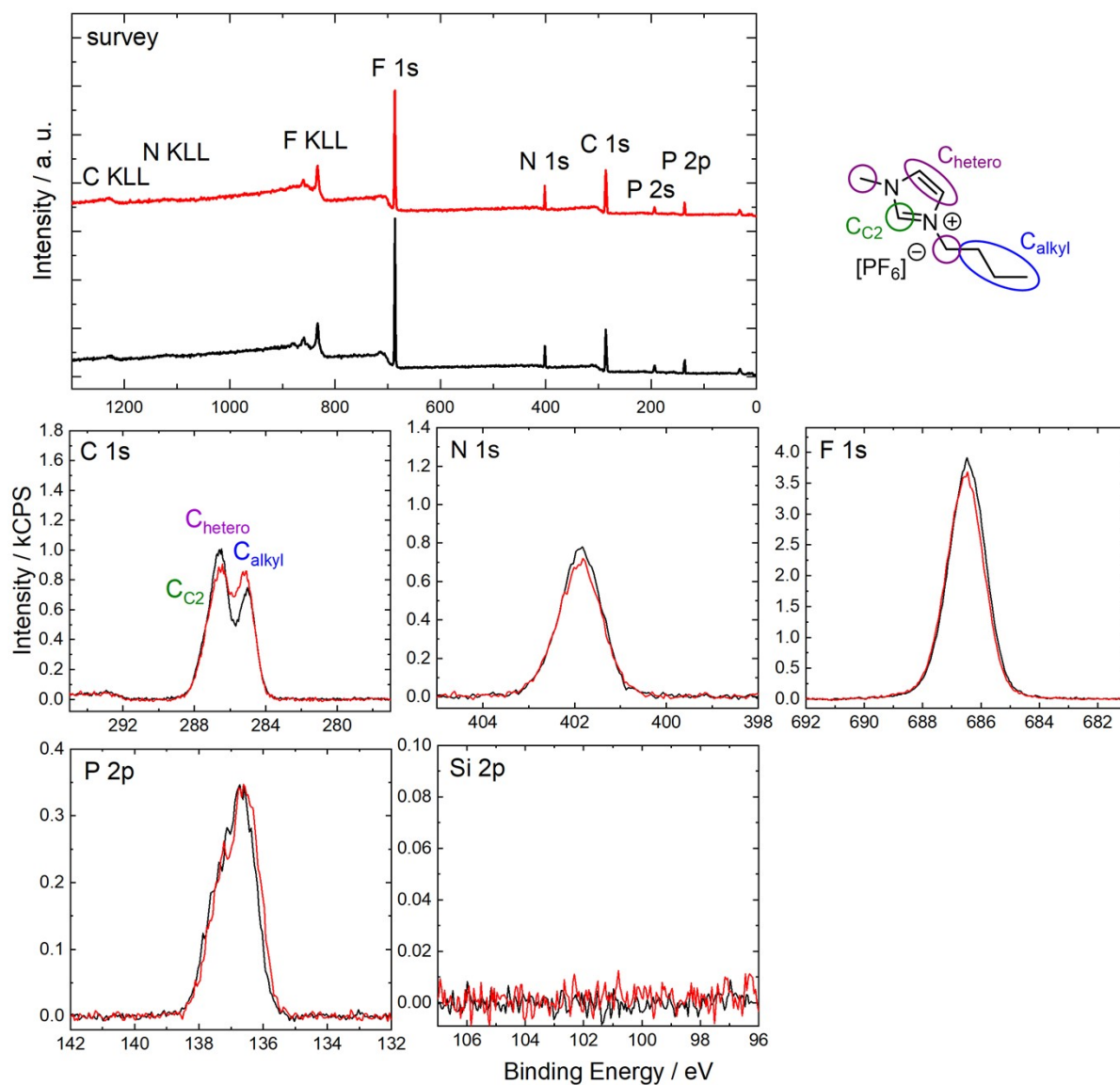
Figure S1*: Survey, C 1s, N 1s, F 1s, P 2p and Si 2p XP spectra of neat [C_4C_1Im][PF_6] in 0° (black) and 80° (red) emission recorded at room temperature with assignment of peaks to the molecular structure.*

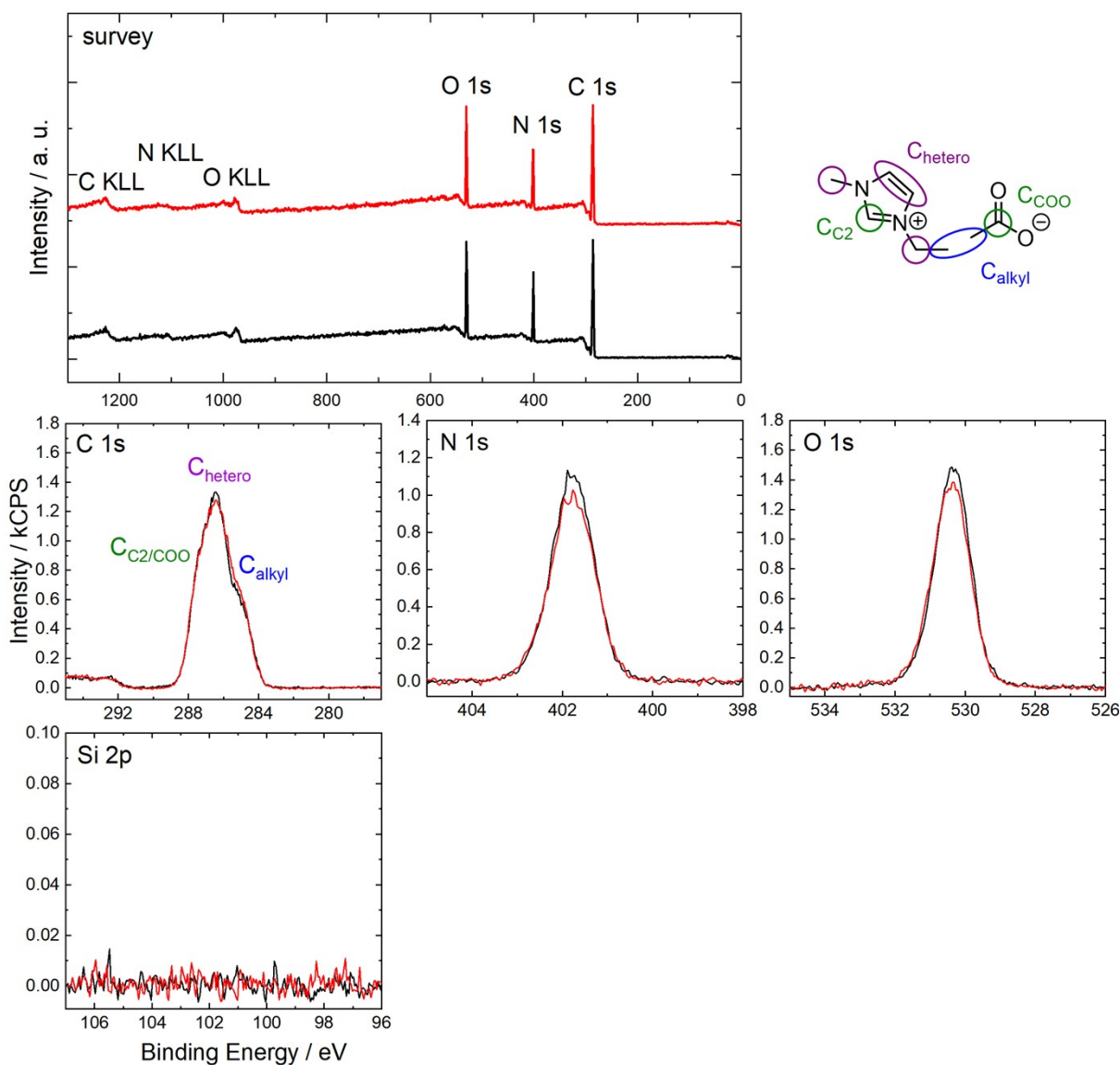The fitting procedure of the C 1s region is presented in Ref. 2.

Figure S2: *Survey, C 1s, N 1s, O 1s and Si 2p XP spectra of neat [C₂C₁Im][OAc] in 0° (black) and 80° (red) emission recorded at room temperature with assignment of peaks to the molecular structure.*

Fitting of the C 1s region was achieved by slightly adapting the established procedure used for 1,3-dialkylimidazolium ionic liquids (ILs)[3]: Area of C_{hetero} was set equal to twice the intensity of $C_{C2/COO}$. The full width a half maximum (FWHM) of C_{hetero} and C_{alkyl} was constraint using a factor of 1.1 to the FWHM of the $C_{C2/COO}$ peak.
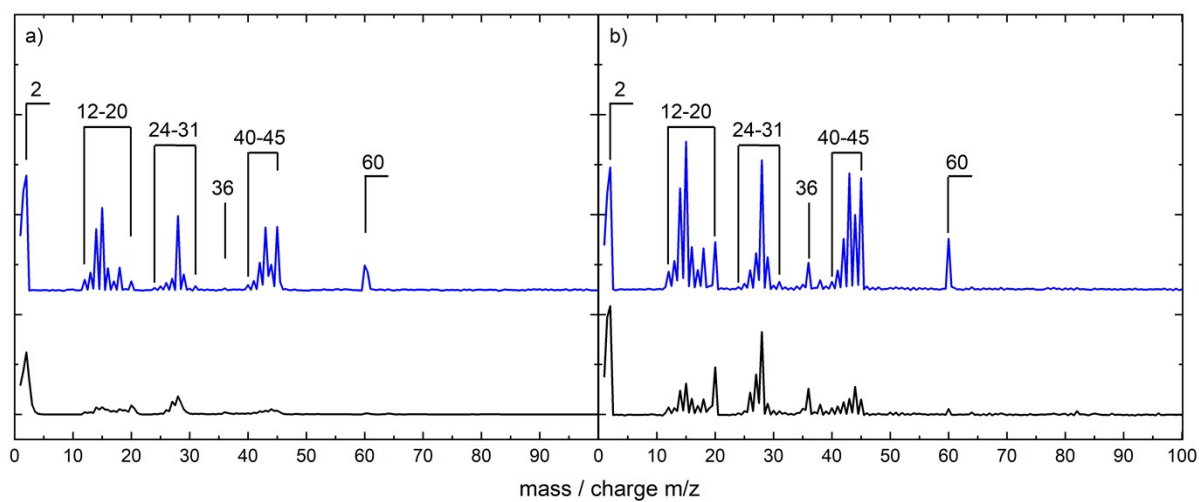
Figure S3: Mass spectra of a) neat [C_2C_1Im][OAc] and a 2.5%$_{mol}$ solution of [Ru(tpy)(bpy)Cl][PF_6] in [C_2C_1Im][OAc] at room temperature (black) and 50 °C (blue). Note that signals at 19 and 20 amu correspond to HF, which is a typical residual gas when working with ILs, including PF6--based ILs. Note further that also signal at 36 amu corresponds to residual HCl gas from previous experiments.
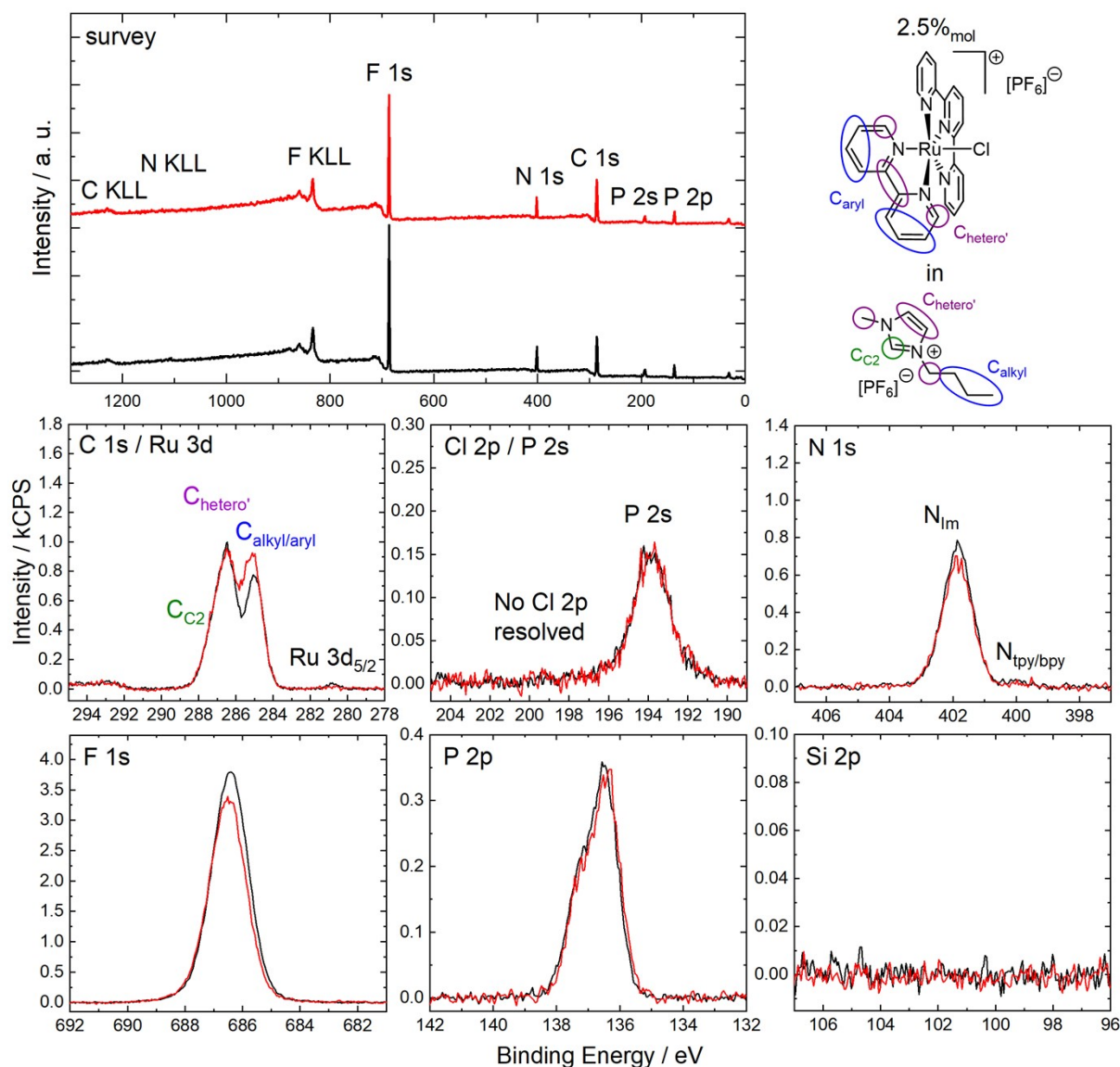
Figure S4: *Survey, C 1s/Ru 3d, Cl 2p/P 2s, N 1s, F 1s, P 2p and Si 2p XP spectra of a 2.5%$_{mol}$ solution of [Ru(tpy)(bpy)Cl][PF$_6$] in [C$_4$C$_1$Im][PF$_6$] in 0° (black) and 80° (red) emission recorded at room temperature with assignment of peaks to the molecular structure. Note that for sake of clarity the assignment of carbon species from the ligands is only shown for bpy. XPS signals from the tpy ligand are assigned accordingly.*

By analogy to the established fitting procedure of the C 1s region applied for neat [C$_4$C$_1$Im][PF$_6$] (see above), the area of C$_{hetero'}$ was constraint according to the nominal composition of the mixture, which is a 1:4.3 ratio between C$_{C2}$ and C$_{hetero'}$ (note that the C$_{hetero'}$ peak includes carbon atoms bound to heteroatoms from both ligand system and solvent IL). The FWHM of C$_{hetero'}$ and C$_{alkyl/aryl}$ was constraint using a factor of 1.1 and 1.0 to the FWHM of the C$_{C2}$ peak, respectively. The position of C$_{hetero'}$ was set to 0.9 eV to lower binding energy with respect to the C$_{C2}$ peak. The FWHM of N$_{Im}$ and N$_{tpy/bpy}$ was set to equal values.
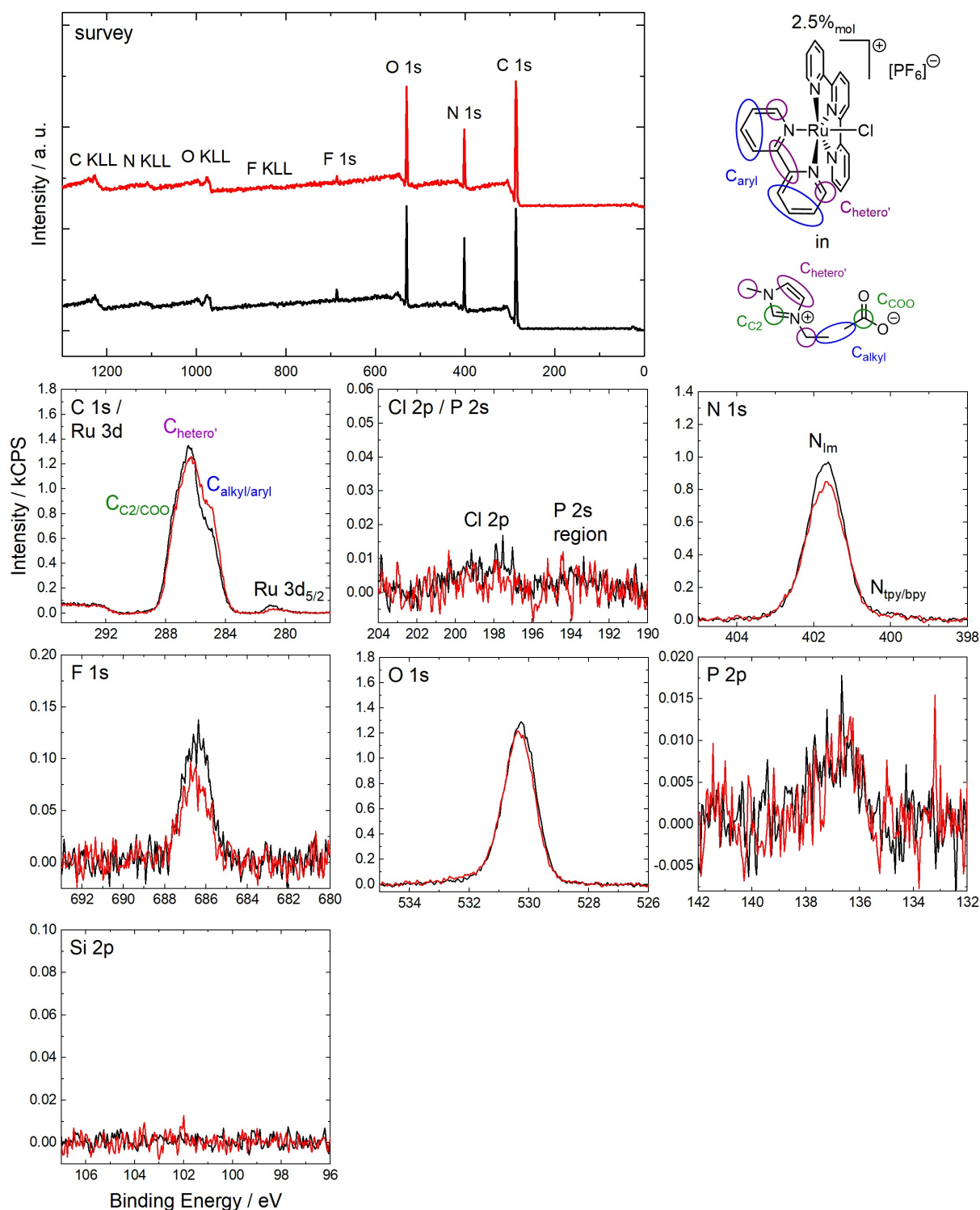
Figure S5: *Survey, C 1s/Ru 3d, Cl 2p/P 2s, N 1s, F 1s, O 1s, P 2p and Si 2p XP spectra of a 2.5%$_{mol}$ solution of [Ru(tpy)(bpy)Cl][PF$_6$] in [C$_2$C$_1$Im][OAc] in 0° (black) and 80° (red) emission recorded at room temperature with assignment of peaks to the molecular structure. Note that for sake of clarity the assignment of carbon species from the ligands is only shown for bpy. XPS signals from the tpy ligand are assigned accordingly.*

Fitting was achieved by analogy to fitting procedures applied for neat [C$_2$C$_1$Im][OAc] (see above): Area of C$_{hetero'}$ was constraint according to the nominal composition of the mixture, which is a 1:2.1 ratio between C$_{C2/COO}$ and C$_{hetero'}$. The FWHM of C$_{hetero'}$ and C$_{alkyl/aryl}$ was constraint using a factor of 1.1 to the FWHM of the C$_{C2}$ peak. The FWHM of N$_{Im}$ and N$_{tpy/bpy}$ was set to equal values.
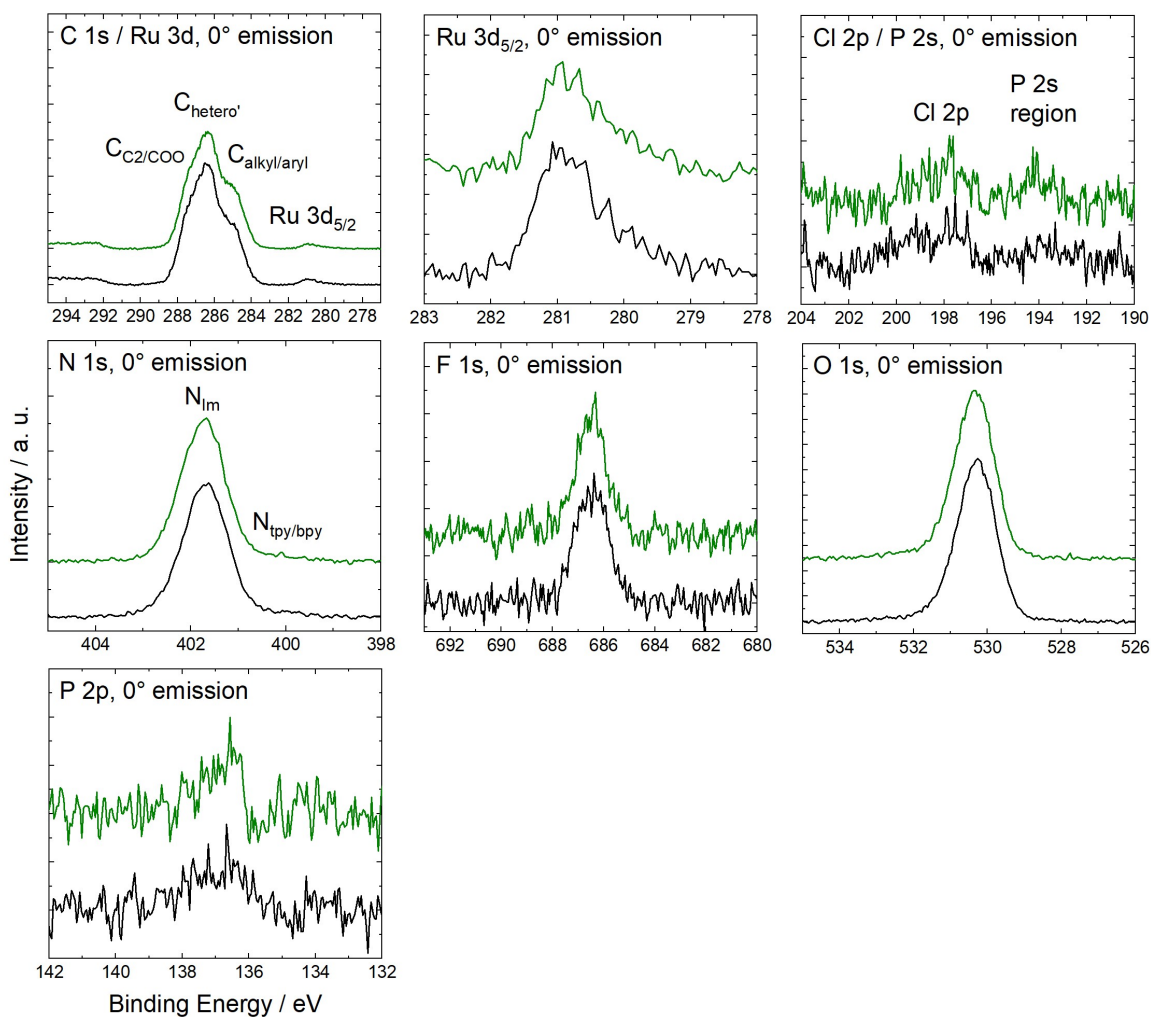
Figure S6: *C 1s/Ru 3d, Ru 3d, Cl 2p/P 2s, N 1s, F 1s, O 1s and P 2p XP spectra of a 2.5%$_{mol}$ solution of [Ru(tpy)(bpy)Cl][PF$_6$] in [C$_2$C$_1$Im][OAc] in 0° emission recorded at room temperature. The black spectra were recorded after initially introducing the sample in the X-ray beam, the C 1s/Ru 3d spectrum was recorded first, all other regions were recorded subsequently. The green set of spectra was recorded after 90 min of X-ray exposure, again the C1s/ Ru 3d spectrum was recorded first. No changes could be identified.*
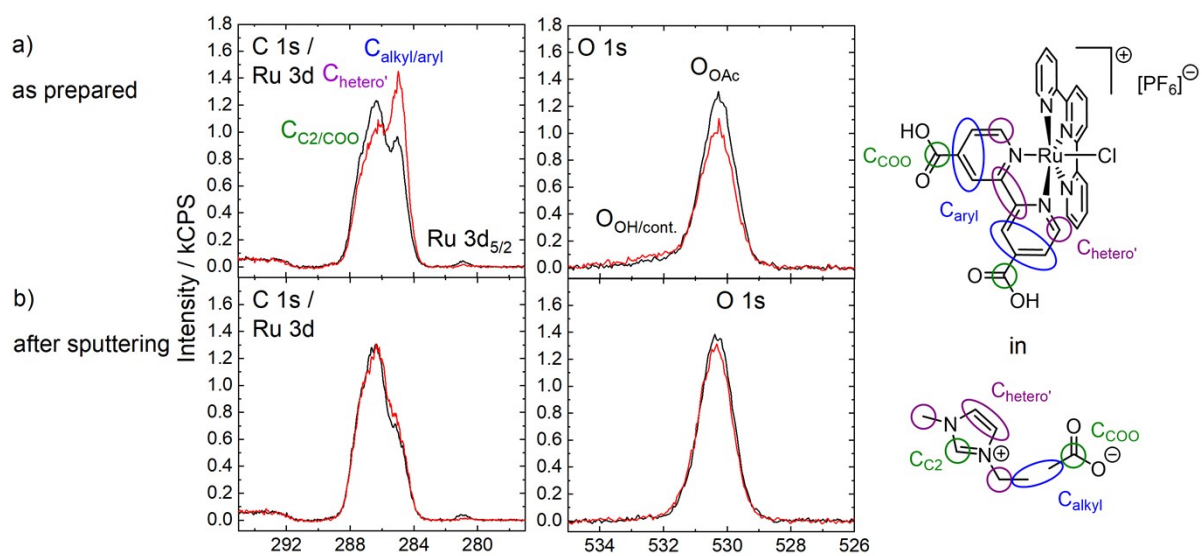
Figure S7: *C 1s/Ru 3d and O 1s XP spectra of a 2.5%$_{mol}$ solution of [Ru(tpy)(dcb)Cl][PF$_6$] in [C$_2$C$_1$Im][OAc] in 0° (black) and 80° (red) emission recorded at room temperature a) as prepared and b) after mild Ar$^+$-sputtering. Color-code identifies assignment of C 1s peaks to the molecular structure. Note that for sake of clarity the assignment of carbon species from the ligands is only shown for dcb. XPS signals from the tpy ligand are assigned accordingly.*

Figure S8: Survey, C 1s/Ru 3d, Cl 2p/P 2s, N 1s, F 1s, O 1s, P 2p and Si 2p XP spectra of a 2.5%$_{mol}$ solution of [Ru(tpy)(dcb)Cl][PF$_6$] in [C$_2$C$_1$Im][OAc] in 0° (black) and 80° (red) emission recorded at room temperature with assignment of peaks to the molecular structure. Note that for sake of clarity the assignment of carbon species from the ligands is only shown for dcb. XPS signals from th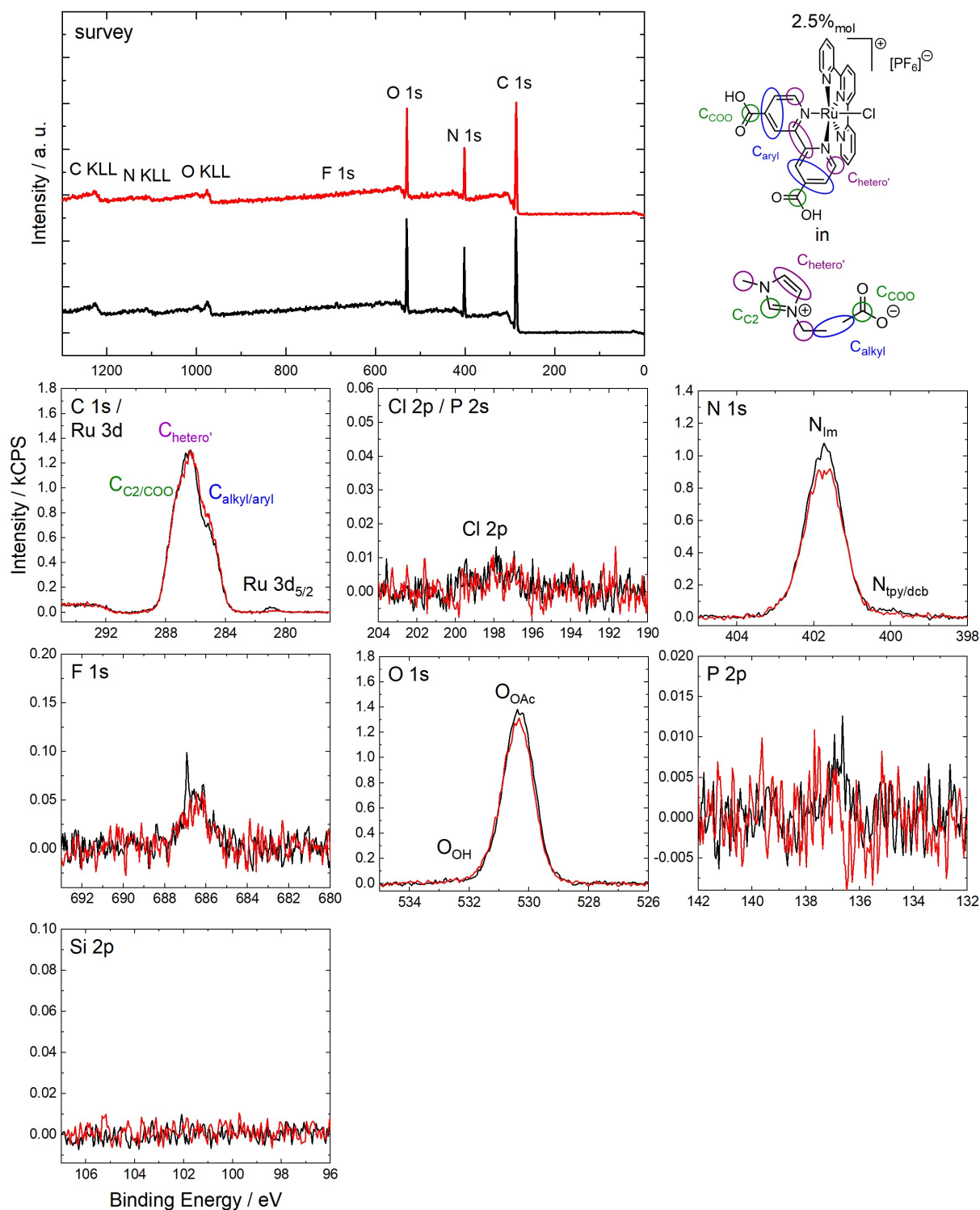e tpy ligand are assigned accordingly. Since an unwanted surface-active contamination was found, the surface was cleaned by mild Ar$^+$-sputtering.

Fitting was achieved in analogy to fitting procedures applied above: Area of C$_{hetero'}$ was constraint according to the nominal composition of the mixture, which is a 1:2.1 ratio between C$_{C2/COO}$ and C$_{hetero'}$. The FWHM of C$_{hetero'}$ and C$_{alkyl/aryl}$ was constraint using a factor of 1.1 to

the FWHM of the C_{C2} peak. The FWHM of N_{Im} and $N_{tpy/bpy}$ was set to equal values. The FWHM of O_{OH} was constraint to the FWHM of the O_{OAc} signal.

Table S1: Weighed proportions for preparation of solutions investigated.

	2.5%$_{mol}$ [Ru(tpy)(bpy)Cl][PF$_6$] in [C$_4$C$_1$Im][PF$_6$]	2.5%$_{mol}$ [Ru(tpy)(bpy)Cl][PF$_6$] in [C$_2$C$_1$Im][OAc]	2.5%$_{mol}$ [RuCl(tpy)(dcb)][PF$_6$] in [C$_2$C$_1$Im][OAc]
Mass [Ru(bpy)(tpy)Cl][PF$_6$] / mg	21.8	20.4	30.0
Amount of substance [Ru(bpy)(tpy)Cl][PF$_6$] / mmol	0.032	0.030	0.040
Mass [C$_4$C$_1$Im][PF$_6$] / mg	370		
Amount of substance [C$_4$C$_1$Im][PF$_6$] / mmol	1.29		
Mass [C$_2$C$_1$Im][OAc] / mg		208	268
Amount of substance [C$_2$C$_1$Im][OAc] / mmol		1.20	1.54
Exact molar concentration of complex in IL / %$_{mol}$	2.46	2.48	2.50
Exact ratio IL:complex$_l$	39.7:1	39.4:1	39.0:1

$M_{[Ru(tpy)(bpy)Cl][PF_6]} = 670.94$ g/mol, $M_{[Ru(tpy)(dcb)Cl][PF_6]} = 758.96$ g/mol,

$M_{[C_4C_1Im][PF_6]} = 284.18$ g/mol, $M_{[C_2C_1Im][OAc]} = 170.21$ g/mol

Purity [C$_4$C$_1$Im][PF$_6$]: 99%, purity [C$_2$C$_1$Im][OAc]: 98%

References

1.   J. M. Gottfried, F. Maier, J. Rossa, D. Gerhard, P. S. Schulz, P. Wasserscheid and H. P. Steinrück, *Zeitschrift für Physikalische Chemie*, 2006, **220**, 1439 - 1453.
2.   B. S. J. Heller, M. Lexow, F. Greco, S. Shin, G. Partl, F. Maier and H.-P. Steinrück, *Chemistry – A European Journal*, 2020, **26**, 1117-1126.
3.   I. Niedermaier, C. Kolbeck, H.-P. Steinrück and F. Maier, *Rev. Sci. Instrum.*, 2016, **87**, 045105.