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Electronic Supplementary Information

Directly Probing the Effect of the Solvent on a Catalyst Electronic Environment using X-ray Photoelectron Spectroscopy

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Table S1 Structures of the polyatomic ions investigated in this study; note, halide-containing liquids were also studied.

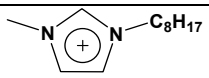
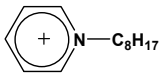
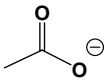
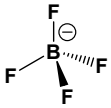
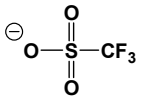
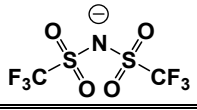
Abbreviation	Structure	Name
$[C_8C_1Im]^+$		1-octyl-3-methylimidazolium
$[C_8Py]^+$		1-octyl-pyridinium
$[OAc]^-$		acetate
$[BF_4]^-$		tetrafluoroborate
$[TfO]^-$		trifluoromethanesulfonate
$[Tf_2N]^-$		bis[(trifluoromethane)sulfonyl]imide

Table S2. Binding Energies of all elements for $[Pd(PPh_3)_4]$ dissolved in $[C_8Py][BF_4]$ and the phosphineimidazolylidene palladium complexes in a range of $[C_8C_1Im]^+$-based ionic liquids. XP spectra for all Pd-containing samples were charge corrected by referencing the C_{alkyl} 1s component to 285.0 eV.. It must be noted that the experimental error associated with measurement of binding energies is ± 0.1 eV.

Ionic Liquid		Binding Energy / eV												
Cation	Anion	Pd $3d_{5/2}$	C_{alkyl}1s	C^2 1s	$C^{4,5}$ 1s (C_{hetero})	$C^{6,7}$ 1s (C_{inter})	N_{cation} 1s	C_{CF3} 1s	N_{anion} 1s	O 1s	F 1s	S $2p_{3/2}$	B 1s	Cl $2p_{3/2}$
$[C_8Py]^+$	$[BF_4]^-$	336.5	285.0		286.9	286.0	402.4				686.0		194.2	
$[C_8C_1Im]^+$	$[Tf_2N]^-$	338.7	285.0	287.7	287.0	286.4	402.1	292.8	399.5	532.6	688.8	168.9		
$[C_8C_1Im]^+$	$[TfO]^-$	338.5	285.0	287.6	286.9	286.4	402.0	292.5		532.0	688.5	168.4		
$[C_8C_1Im]^+$	$[BF_4]^-$	338.4	285.0	287.6	286.9	286.4	402.0				686.0		194.2	
$[C_8C_1Im]^+$	Cl^-	338.2	285.0	287.2	286.6	286.0	401.6							197.0
$[C_8C_1Im]^+$	$[OAc]^-$	337.6	285.0	287.4	286.6	286.0	401.6			530.3				

Table S3. Binding Energies and FWHM of the Pd $3d_{5/2}$ peak for solid $[Pd(PPh_3)_4]$, $[Pd(PPh_3)_4]$ dissolved in $[C_8Py][BF_4]$, and the phosphineimidazolylidene palladium complexes in a range of $[C_8C_1Im]^+$-based ionic liquids. This data is correlated to hydrogen bond acceptor ability (β). The binding energy of Pd $3d_{5/2}$ for solid $[Pd(PPh_3)_4]$ was obtained after charge corrected to $C_{benzene}$ 1s at 284.7 eV. All other peaks were charge corrected by referencing the C_{alkyl} 1s component to 285.0 eV. The error in binding energies is ± 0.1 eV.

Ionic liquid Cation Anion		Binding Energy Pd $3d_{5/2}$ / eV	FWHM / eV	Hydrogen bond Acceptor Ability (β)[a]
Solid Sample		336.4	1.8	
$[C_8Py]^+$	$[BF_4]^-$	336.5	1.1	
$[C_8C_1Im]^+$	$[Tf_2N]^-$	338.7	1.1	0.42
$[C_8C_1Im]^+$	$[TfO]^-$	338.5	0.9	0.57
$[C_8C_1Im]^+$	$[BF_4]^-$	338.4	1.0	0.55
$[C_8C_1Im]^+$	Cl^-	338.2	0.8	0.95
$[C_8C_1Im]^+$	$[OAc]^-$	337.6	1.0	1.09

[a] data available for $[C_4C_1Im]^+$-based $[Tf_2N]^{-1}$, $[TfO]^{-1}$, $[BF_4]^{-1}$, Cl^{-1} and $[OAc]^{-2}$ anions

Reference

1. R. Lungwitz, V. Strehmel and S. Spange, *New J. Chem.*, 2010, **34**, 1135-1140.
2. J. Palgunadi, S. Y. Hong, J. K. Lee, H. Lee, S. D. Lee, M. Cheong and H. S. Kim, *J. Phys. Chem. B*, 2011, **115**, 1067-1074.

Figure S1 XP spectra with component fittings of phoshineimidazolylidene palladium complex in $[C_8C_1Im][BF_4]$ for : (a) survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) B 1s and (f) Pd 3d.

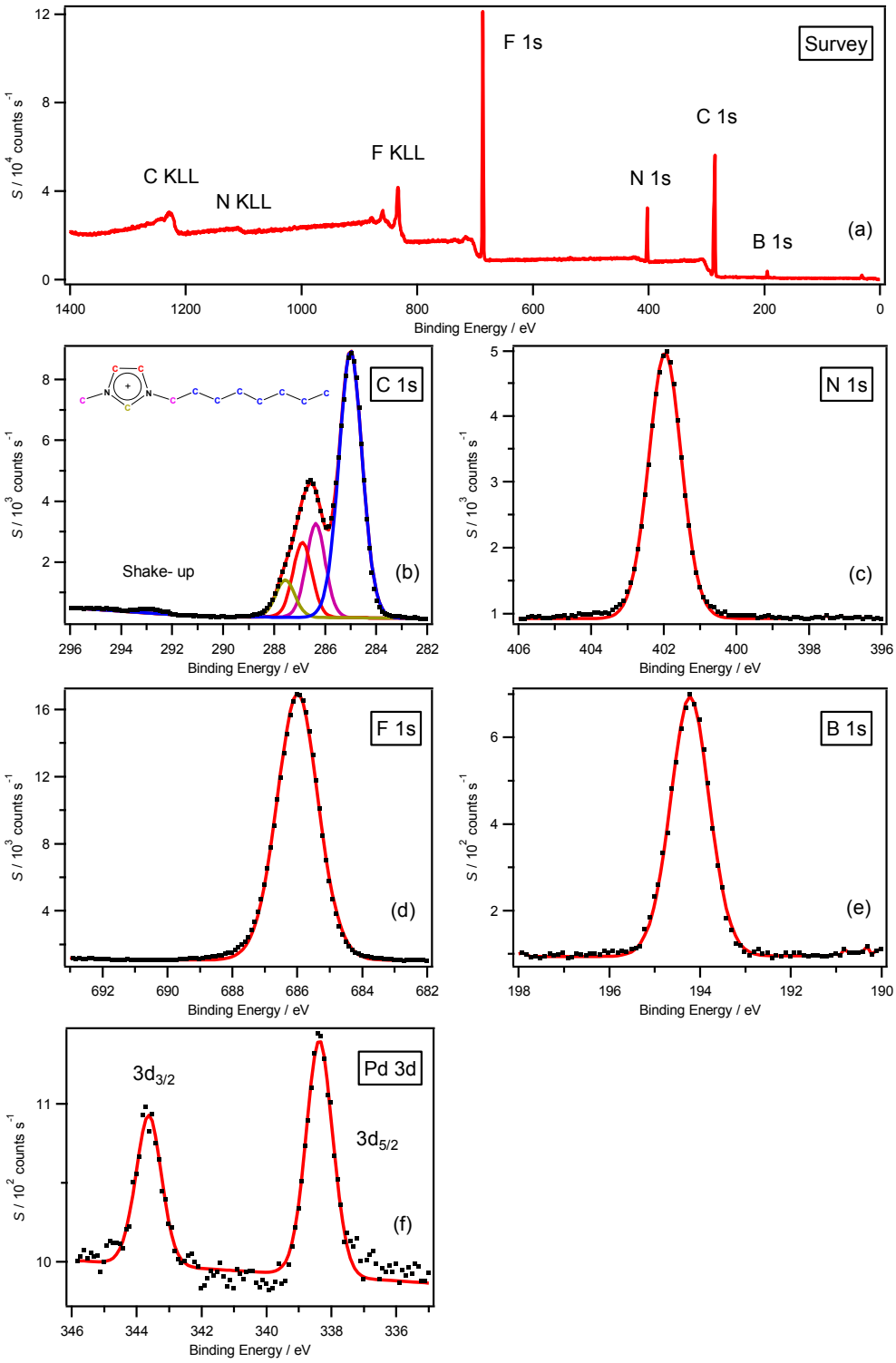


Figure S2 XP spectra with component fittings of phoshineimidazolylidene palladium complex in [C_8C_1Im][OAc] for : (a) survey, (b) C 1s, (c) N 1s, (d) O 1s and (e) Pd 3d.

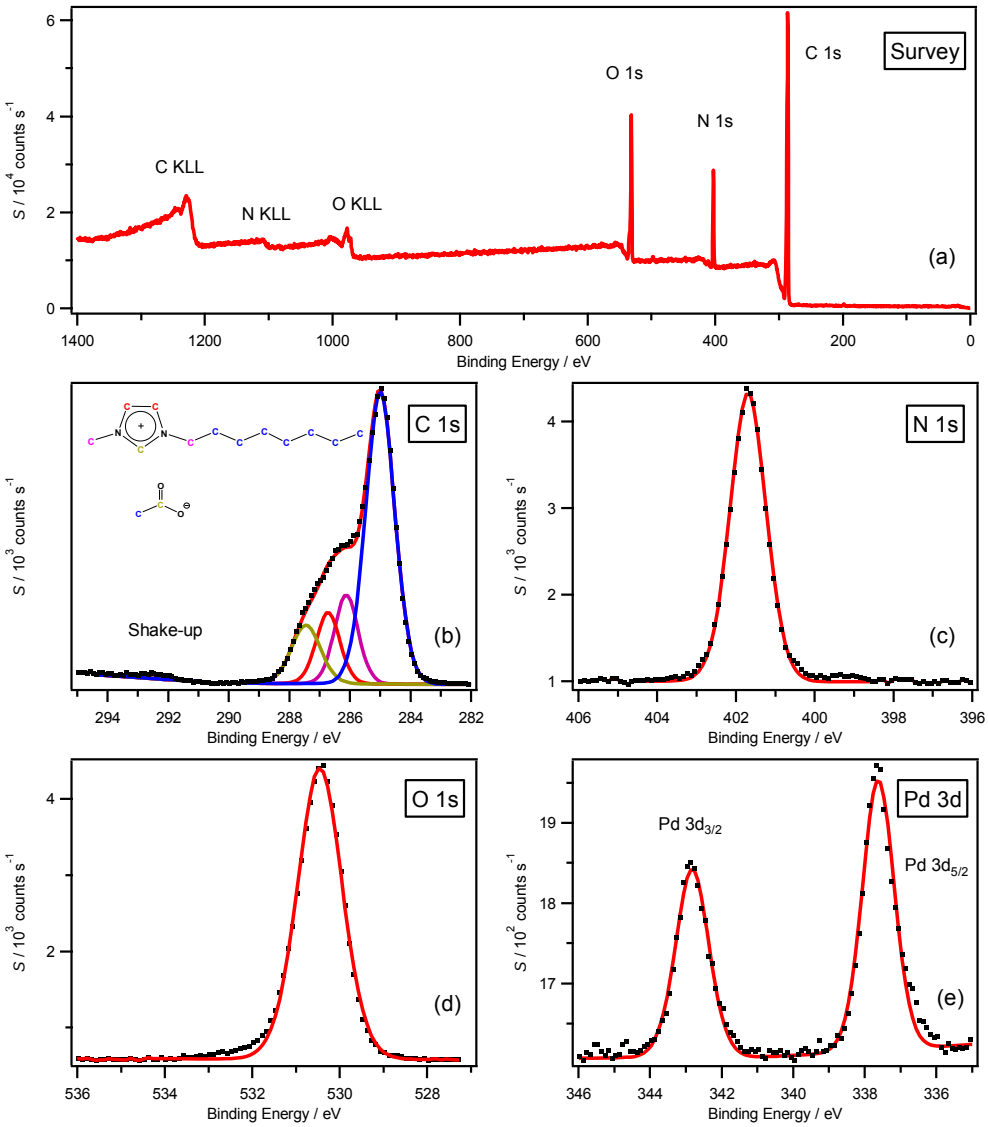


Figure S3 XP spectra with component fittings of phoshineimidazolylidene palladium complex in [C_8C_1Im]Cl for : (a) survey, (b) C 1s, (c) N 1s, (d) Cl 2p and (e) Pd 3d.

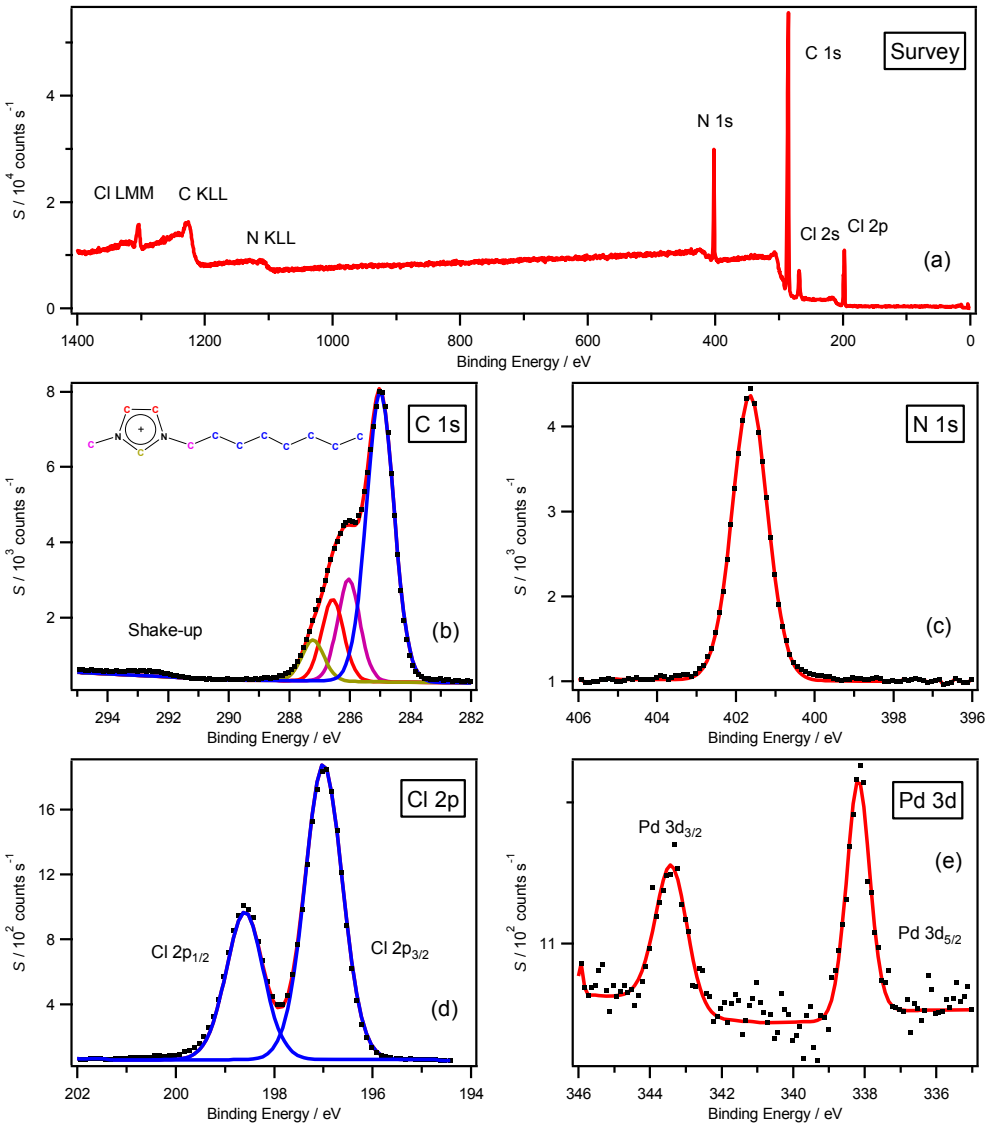


Figure S4 XP spectra with component fittings of phoshineimidazolylidene palladium complex in [C_8C_1Im][TfO] for : (a) survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) O 1s, (f) S 2p and (g) Pd 3d.

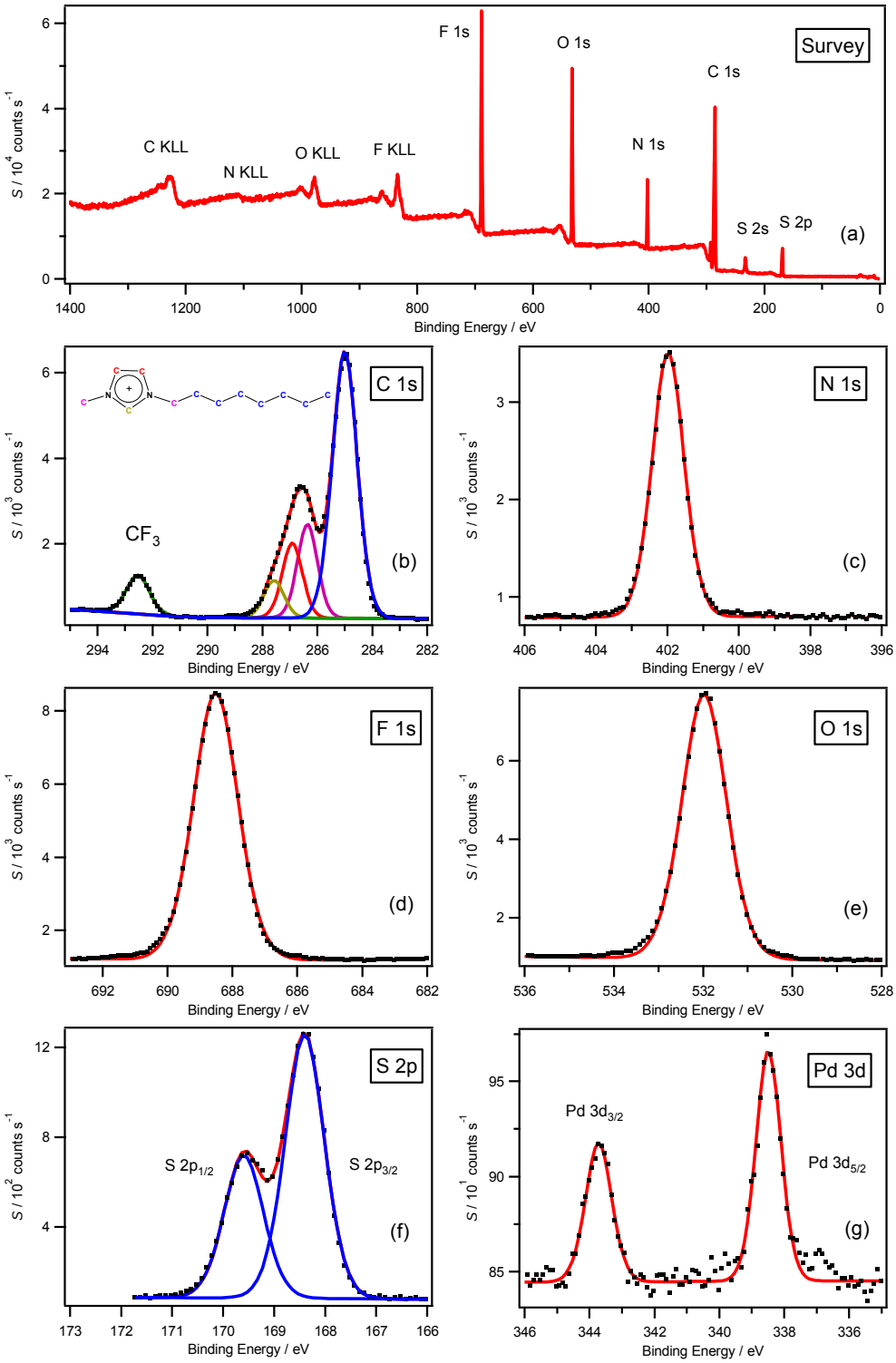


Figure S5 XP spectra with component fittings of phoshineimidazolylidene palladium complex in $[C_8C_1Im][Tf_2N]$ for : (a) survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) O 1s, (f) S 2p and (g) Pd 3d.

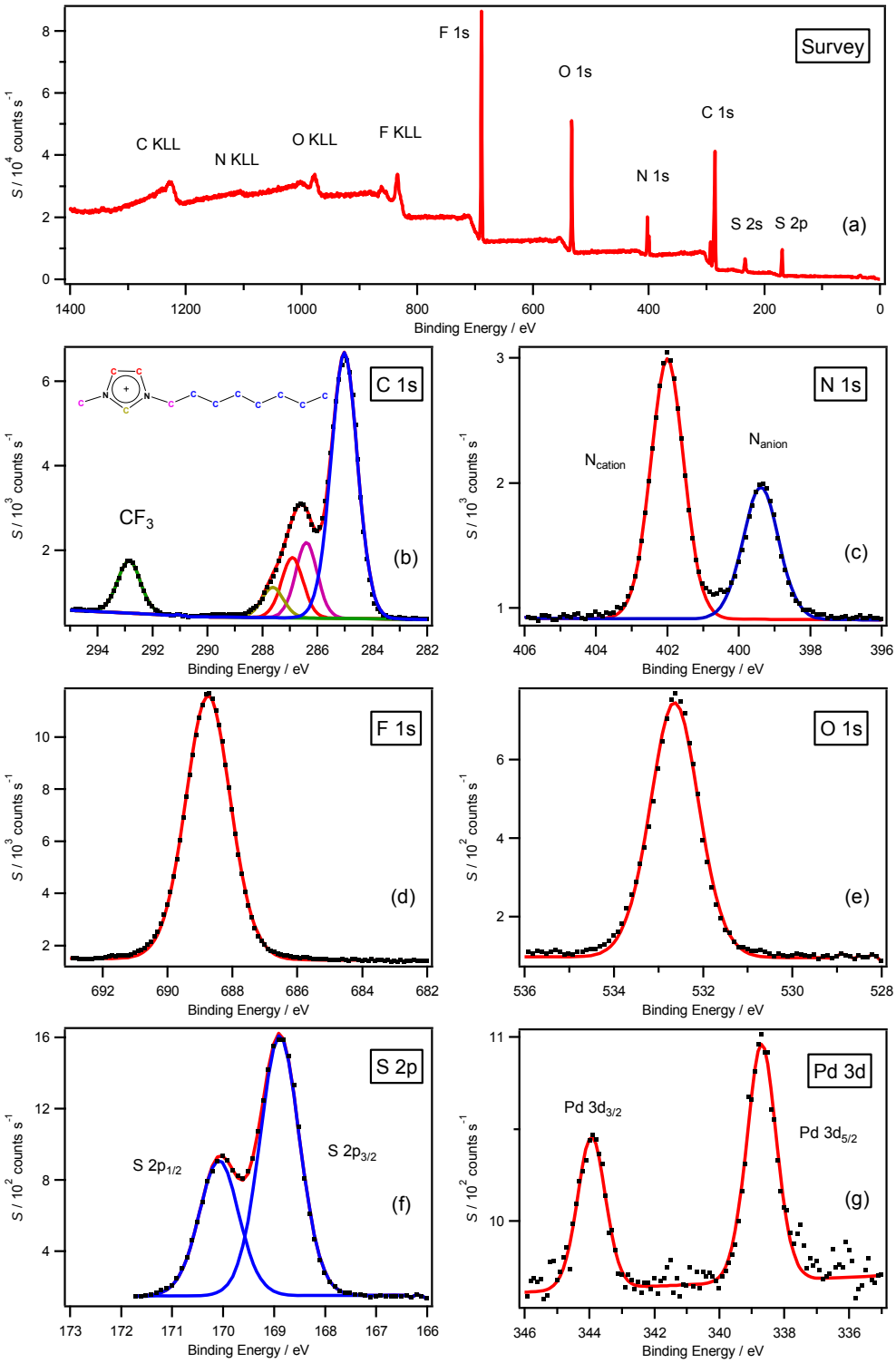


Figure S6 XP spectra with component fittings of $[Pd(PPh_3)_4]$ dissolved in $[C_8Py][BF_4]$ for : (a) survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) B 1s and (f) Pd 3d.

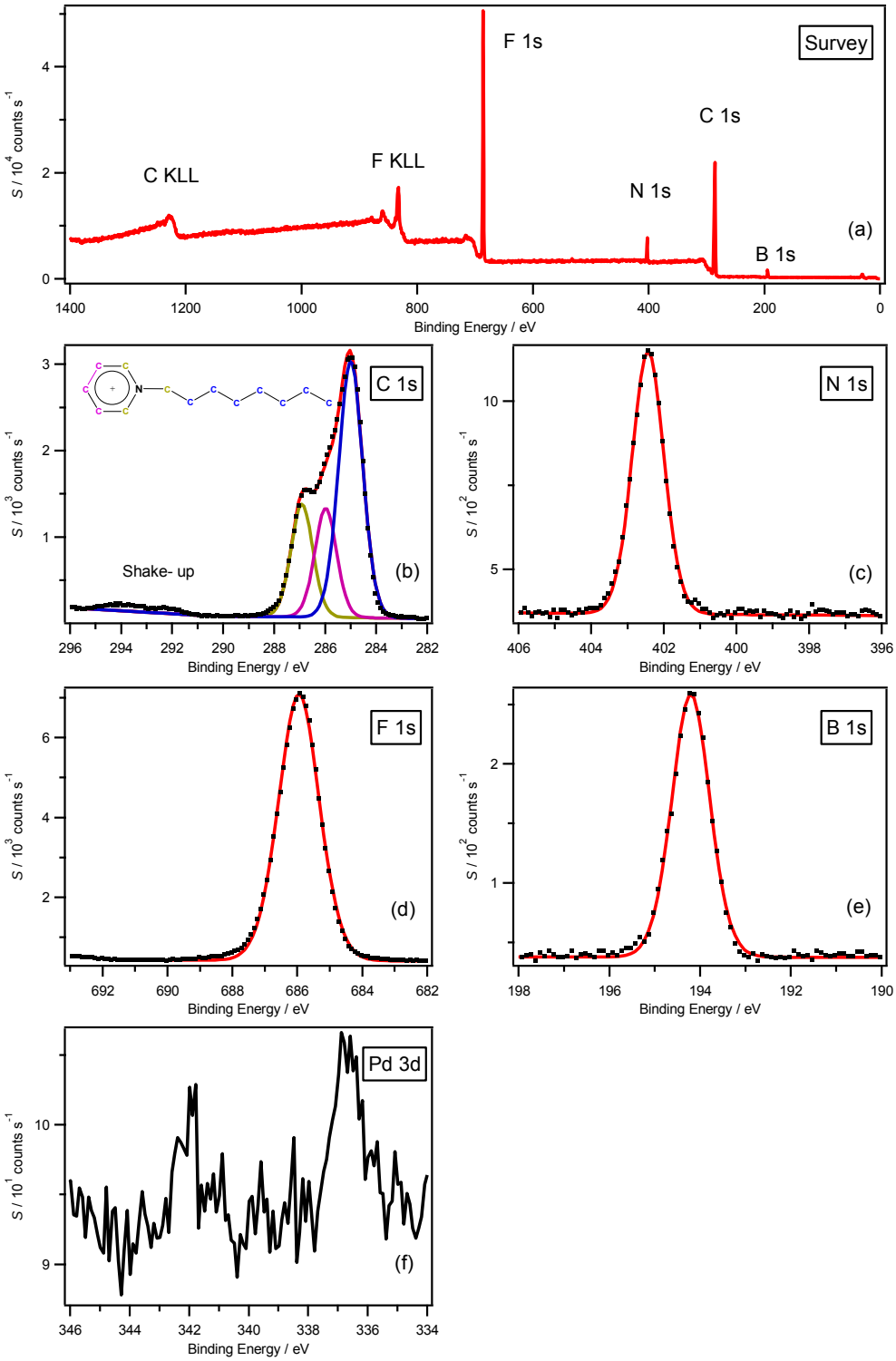


Figure S7 XP spectra with component fittings of Tetrakis(triphenylphosphine) palladium ([$Pd(PPh_3)_4$]) for : (a) survey, (b) C 1s, (c) Pd 3d and (d) P 2p.