Supporting Information For:

Covalent Grafting of Imidiazolium Ionic Liquids to Layered Double Hydroxides: Retardation of Memory Efftect and Exploration of Surface Chemistry

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General

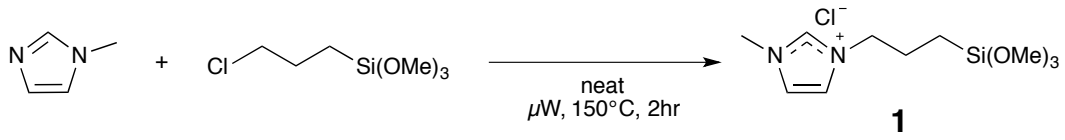
All of the reagents and starting materials were acquired from commercial sources and used as received unless stated otherwise. ^{1}H NMR spectra were obtained using a 400 MHz Agilent spectrometer and the chemical shifts are reported in ppm. CP-MAS spectra were collected on a 500 MHz Bruker Advance III spectrometer. FT-IR spectra were obtained using a Perkin Elmer Frontier FT-IR Spectrometer using KBr pellets. PXRD patterns were obtained using a Rigaku MiniFlex II X-Ray defractometer. Nitrogen isotherms were measured on a Micromertics TriStar surface analyzer at liquid nitrogen temperatures. Samples were degassed under vacuum at 110°C for 3 hours prior to measurement. Surface area was calculated using the BET method. Thermogravometric analysis (TGA) was performed on a Perkin Elmer Pyris 1 TGA. Samples were heated from 30°-650°C at 20°C/min in nitrogen. Elemental composition was determined via EDX using a Shimadzu EDX-700 X-Ray spectrometer.

Synthesis and Characterization

Mg:Al Hydrotalcite

A 300mL solution of $Mg(NO_3)_2 \cdot 6H_2O$ (0.5M) and $Al(NO_3)_3 \cdot 9H_2O$ (0.16M) was added dropwise over 2 hours to 300 ML of 1.66 M Na_2CO_3 solution. The pH was maintained between 9.5 and 10.5 by addition of 0.8 M NaOH. After completing the addition, the solution was heated to 65 °C overnight. The resulting solid was filtered and washed with deionized water until the pH of the filtrate was neutral. The solid was dried at 110°C overnight, then re-suspended in deionized water, filtered and dried overnight at 110°C to give a white solid. If calcined hydrotalcite (mixed metal oxide) was desired, the solid was calcined at 450°C for 24 hours in a furnace. The samples were cooled in a desiccator.

N-3-(3-trimethoxysilyl propyl)-3-methyl imidazolium chloride (1)

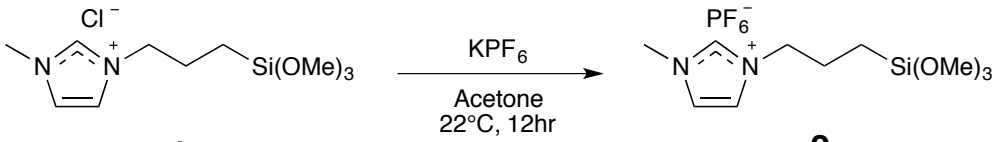


1

An oven-dried 10-mL microwave vial was charged with 1-methylimidazole (1.1316 g, 13.78 mmol) and (3-chloroporpyl)trimethoxy silane (2.7396 g, 13.78 mmol) and heated in a CEM Discover microwave to 150°C for 2 hours. The resulting viscous yellow syrup was found to be analytically pure and used without further purification. The spectral data below agrees with previously reported characterizations.[1]

Yield: <99%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) ∂: 0.57 (t, 2H), 1.97 (m, 2H), 3.52 (s, 9H), 4.08 (s, 3H), 4.28 (t, 2H), 7.31 (m, 1H), 7.47 (m, 1H), 10.67 (s, 1H). ^{13}C NMR (400 MHz, $CDCl_3$, 25°C): ∂5.93, 24.10, 36.56, 50.66, 51.73, 121.65, 123.24, 138.40.

N-3-(3-trimethoxysilyl propyl)-3-methyl imidazolium hexafluorophosphate (2)



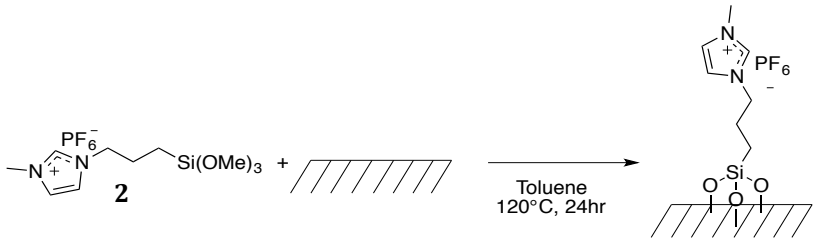
1 **2**

N-3-(3-trimethoxysilyl propyl)-3-methyl imidazolium chloride (***IL-1***, 5 mmol, 1.404g) was added to an oven-dried round bottom flask, placed under a nitrogen atmosphere and diluted with dry acetone (25mL). Another round bottom flask was charged with potassium hexafluorophospahte (5 mmol, 0.920g), placed in a nitrogen atmosphere and diluted with dry acetone (20mL). The solution of KPF_6 was transferred to the flask with ***IL-1*** and stirred at room temperature for 12 hr. The resulting white precipitate was filtered and the filtrate was dried *in vacuo* to yield a

viscous orange liquid which was analytically pure. The spectral data below agrees with previously reported values.[2]

Yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): ∂ 0.57 (t, 2H), 1.95 (m, 2H), 3.51 (s, 9H), 4.07 (s, 3H), 4.27 (t, 2H), 7.34 (m, 1H), 7.56 (m, 1H), 10.53 (s, 1H). ^{13}C NMR (400 MHz, $CDCl_3$, 25°C): ∂ 5.92, 24.12, 36.53, 50.67, 51.69, 121.75, 123.49, 138.05.

Immobilization of 2 to Hydrotalcite



In a dry round bottom flask hydrotalcite (0.400g) was added to a solution of ***IL-2*** (0.300g) in 100 mL dry toluene and refluxed for 24 hours. After cooling to room temperature the solid was filtered and then washed in a Soxholet extractor (refluxing dichloromethane) for 24 hours. The washed solid was then dried in a vacuum oven at 80° C for 12 hr..

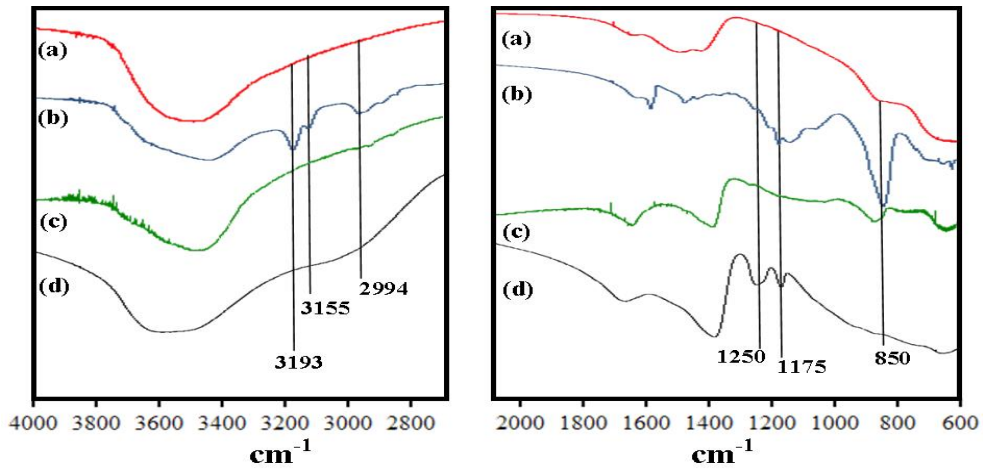


Figure S1. FTIR Spectra of (a) HTc (b) ***HTc-2*** (c) ***HTc-2*** hydrolysis test (d) HTc hydrolysis test.

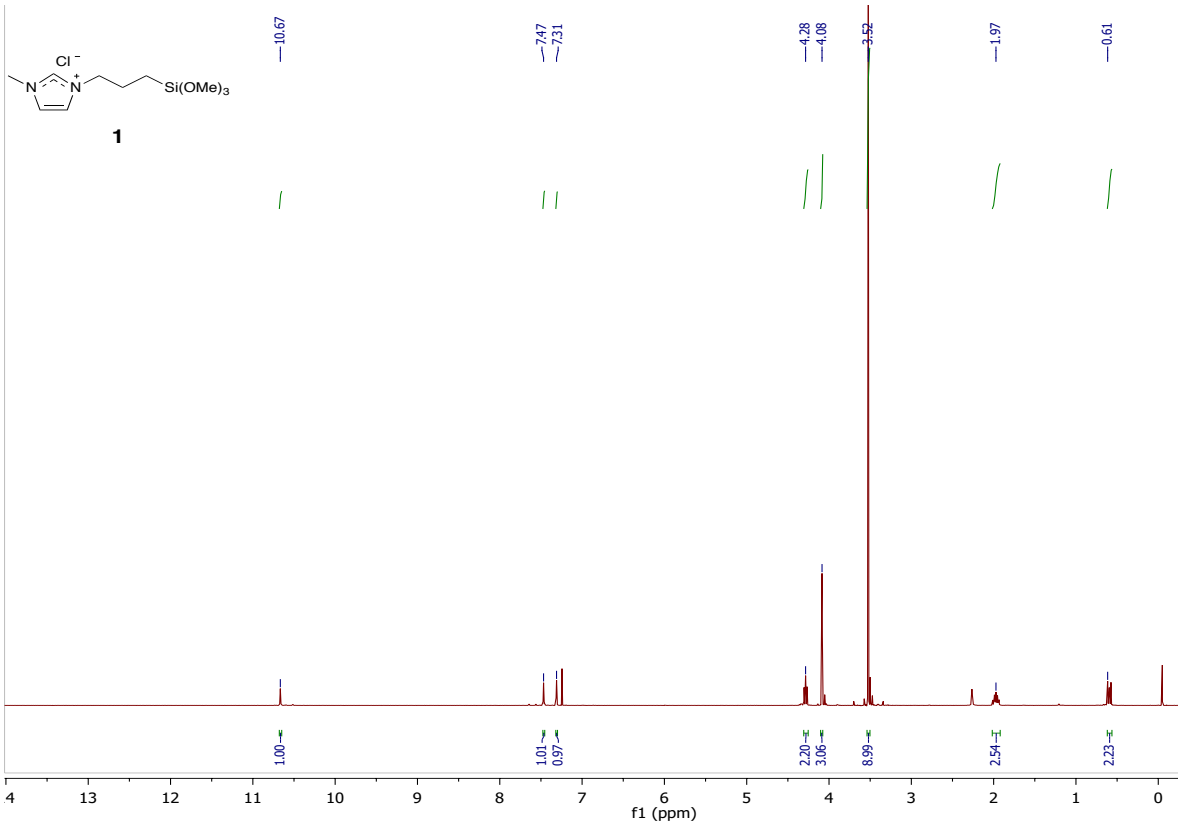


Figure S2. 1H NMR of IL-***1.***

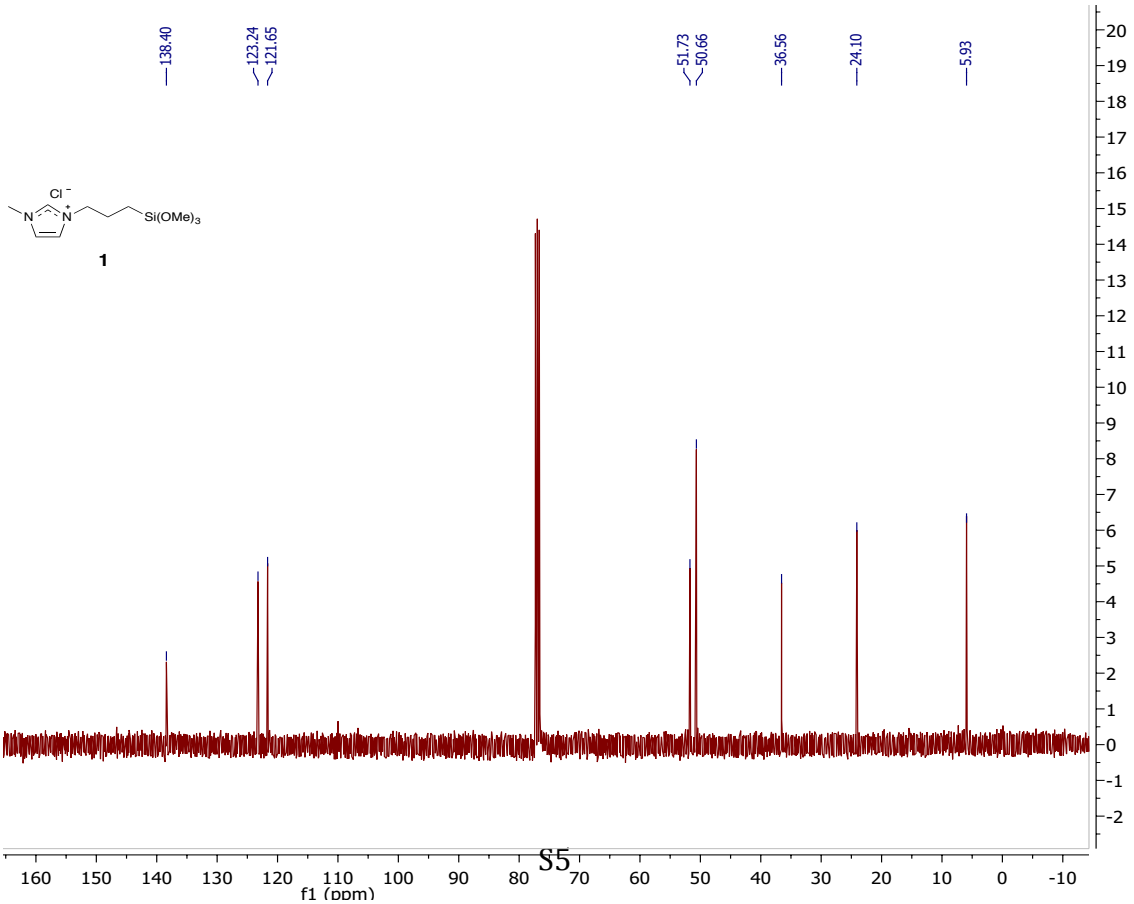


Figure S3. 13C NMR of ***1***

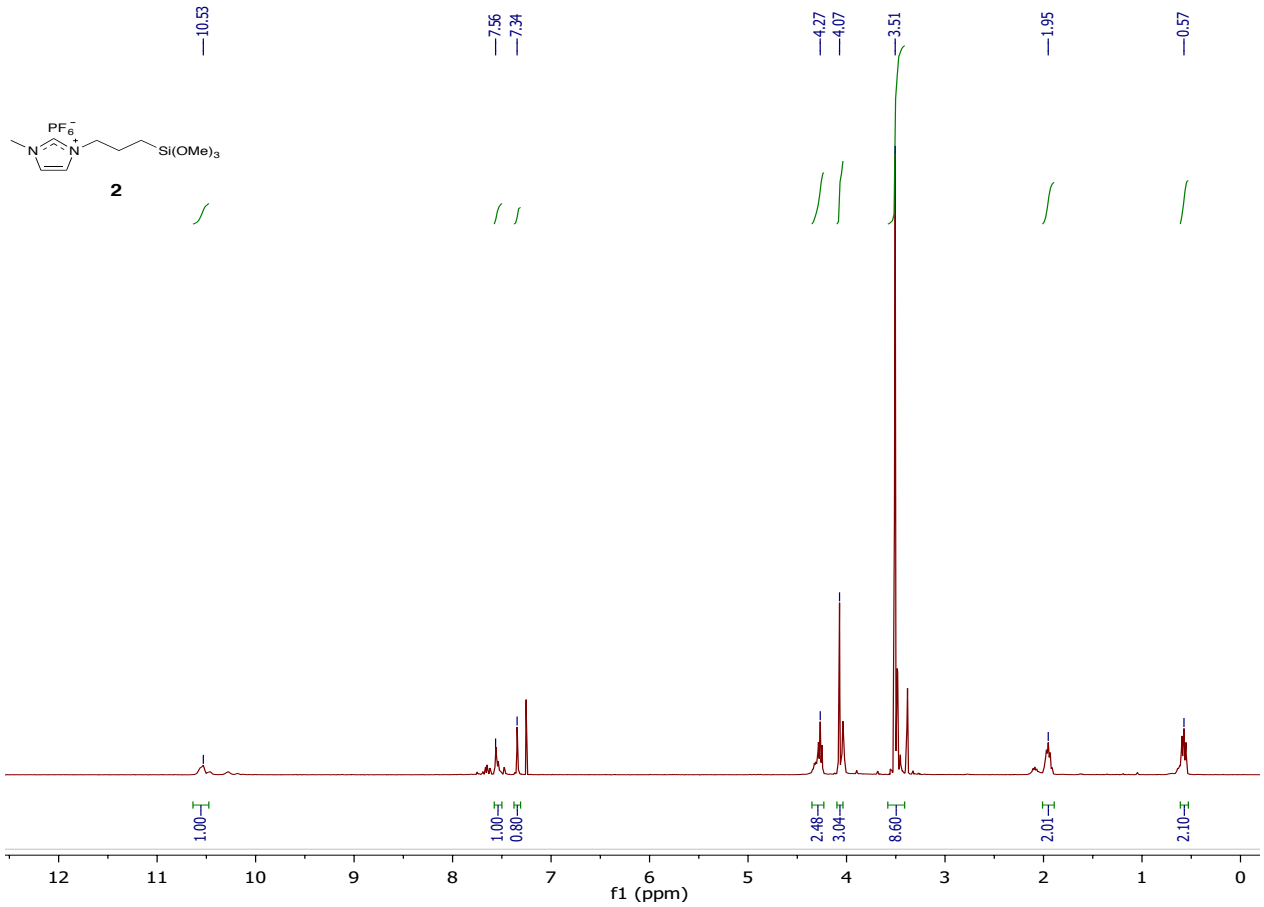


Figure S4. ^{1}H NMR of ***2***

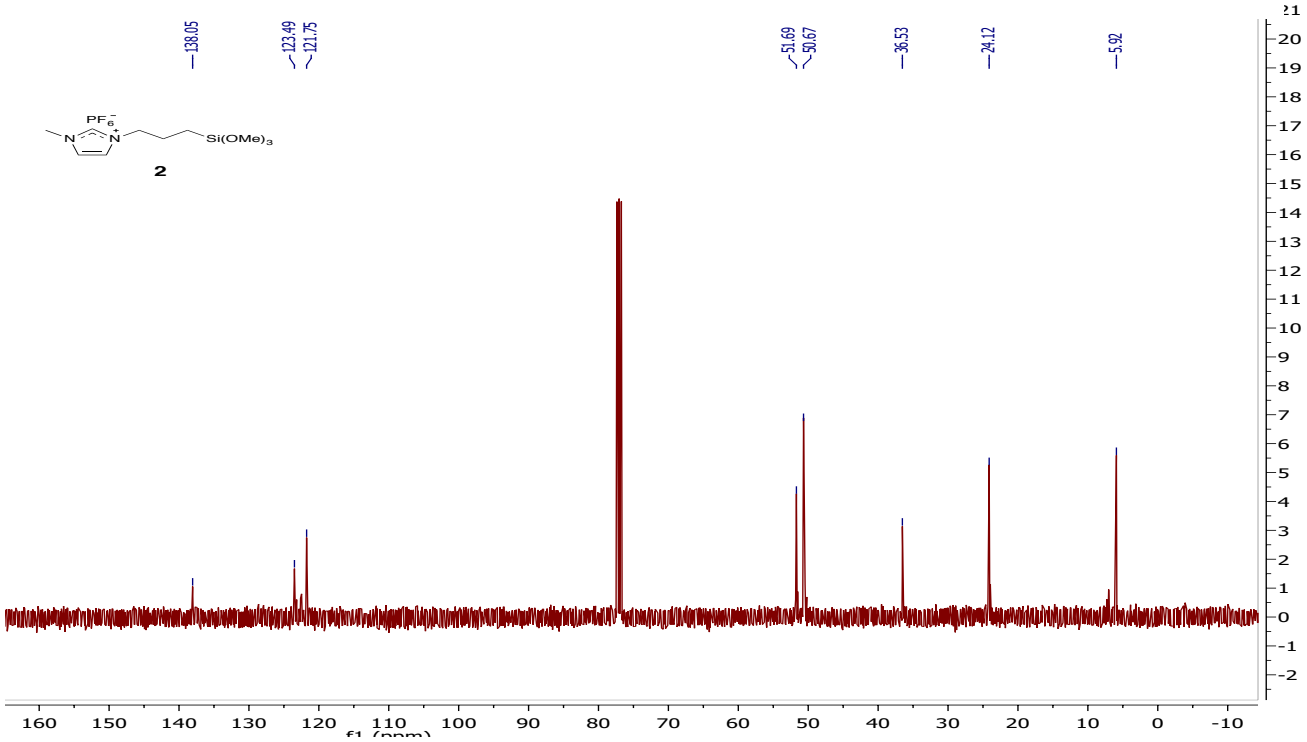


Figure S5. ^{13}C NMR of ***2***

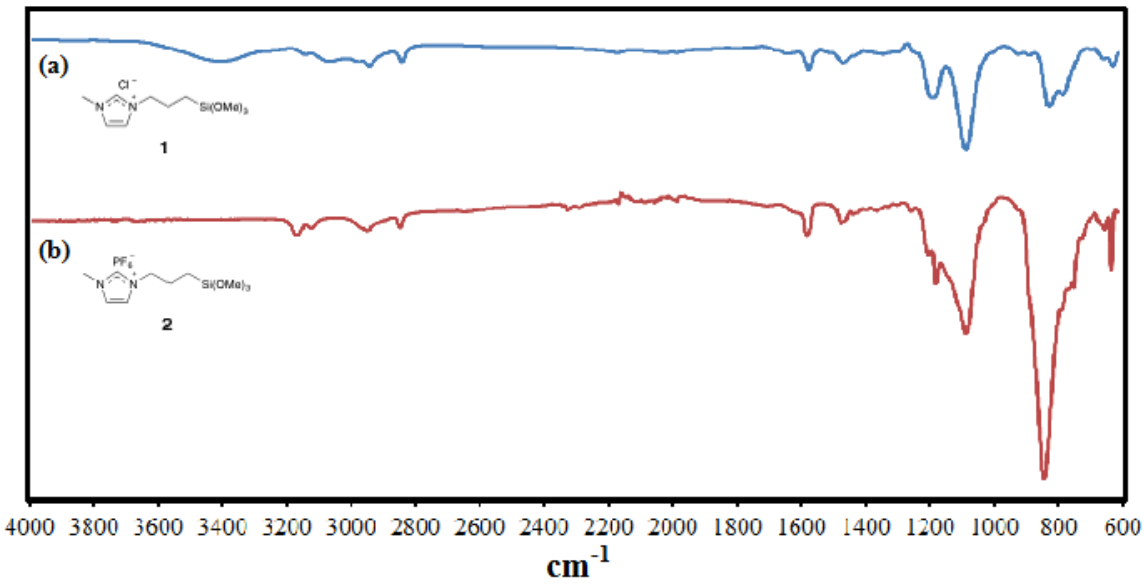


Figure S6. FTIR spectra of unsupported ***1*** (a) and ***2*** (b)

References

1. D. E. Babak Karimi, *Organic Letters*, 2006, 8, 1237-1240.
2. M. Bagherzadeh and S. Ghazali-Esfahani, *Tetrahedron Letters*, 2013, 54, 3765-3768.