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Supporting Information

Investigating the Effect of Ligand and Cation on the Properties of Metal Fluorinated Acetylacetone Based Magnetic Ionic Liquids

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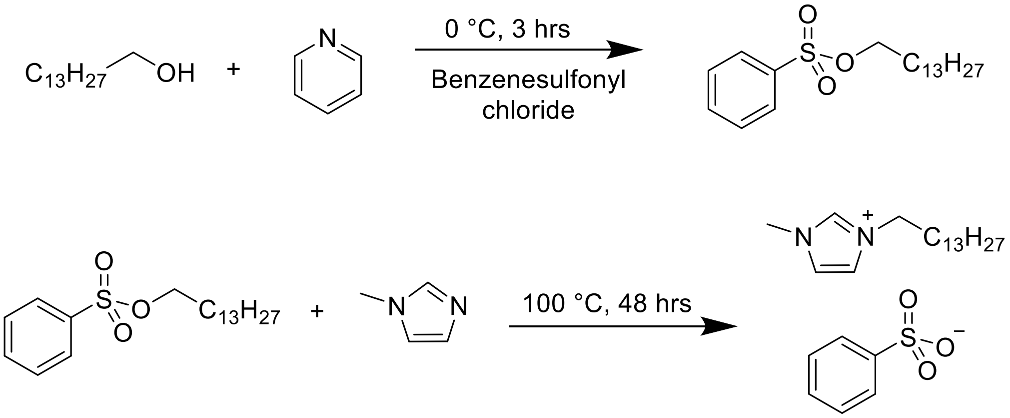
1: Synthesis of [$C_{14}MIM^{+}$][BS^{-}]

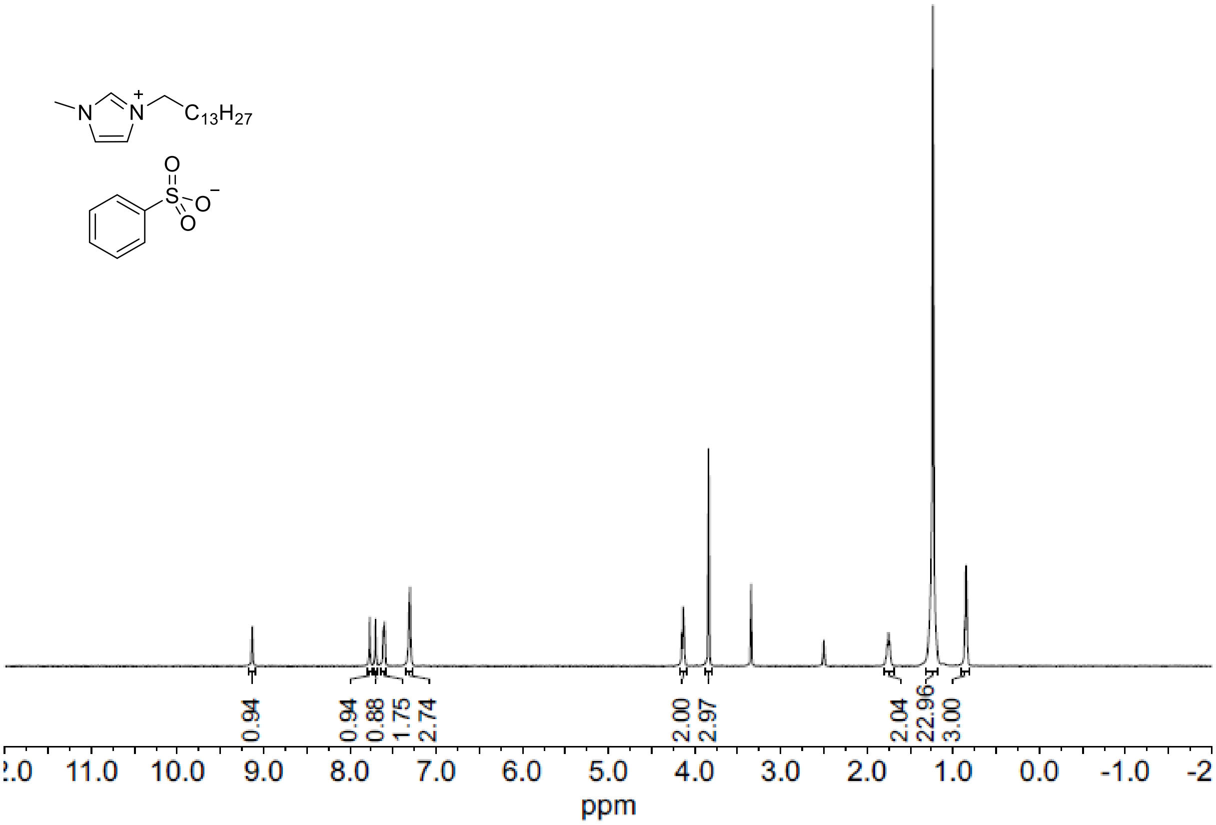
Firstly, tetradecyl benzene sulfonate was synthesized following the method reported by Sekera et al.,[1] where one equivalent of tetradecanol was mixed with four equivalents of pyridine. The temperature was decreased to 0 °C and after a few minutes, 1.1 equivalents of benzenesulfonyl chloride were added. The reaction mixture was allowed to stir for 3 hours and then an excess of ice cold dilute hydrochloric acid was added to quench the reaction. The product was then collected by filtration and recrystallized by methanol.

In the second step of reaction, tetradecyl benzene sulfonate ester and 1-methylimidazole were added to a round bottom flask in 1:1 molar ratio. The reaction mixture was heated up to 100 °C for 48 hours. The crude product was again recrystallized from methanol to obtain a pure white solid [$C_{14}MIM^{+}$][BS^{-}].

Scheme 1: Synthesis of [$C_{14}MIM^{+}$][BS^{-}]

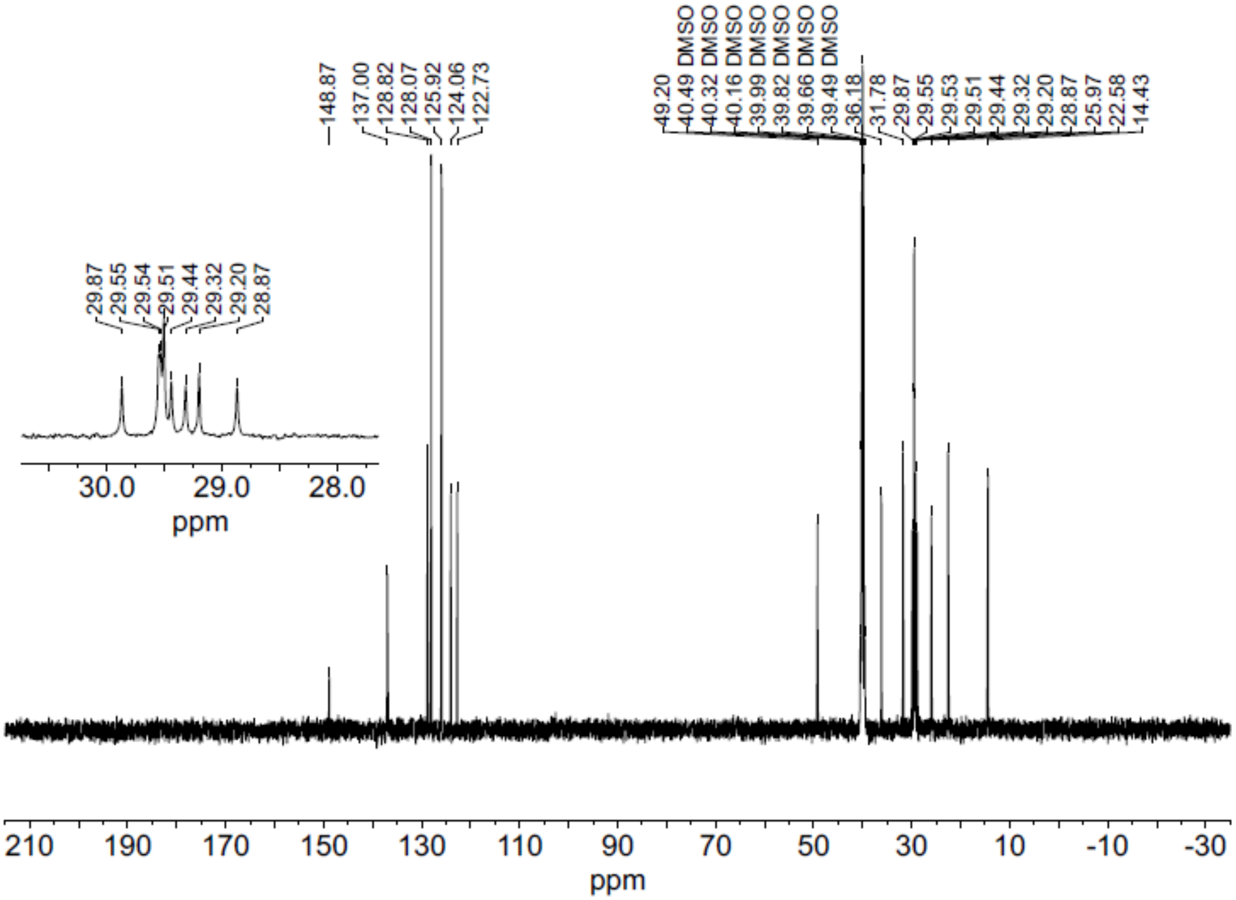


2: ^{1}H NMR of [$C_{14}MIM^+$][BS^-]



^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 9.13 (s, 1H), 7.77 (t, J = 1.9 Hz, 1H), 7.70 (t, J = 1.8 Hz, 1H), 7.61 (dd, J = 7.2, 2.2 Hz, 2H), 7.35 – 7.27 (m, 3H), 4.13 (t, J = 7.2 Hz, 2H), 3.84 (s, 3H), 1.75 (p, J = 7.2 Hz, 2H), 1.23 (s, 22H), 0.85 (t, J = 6.7 Hz, 3H).

2: ^{13}C NMR of [C_{14}MIM$^+$][BS$^-$]



^{13}C NMR (126 MHz, DMSO-d_6, ppm) δ 148.87, 137.00, 128.82, 128.07, 125.92, 124.06, 122.73, 49.20, 40.49, 40.32, 40.16, 39.99, 39.82, 39.66, 39.49, 36.18, 31.78, 29.87, 29.55, 29.54, 29.51, 29.44, 29.32, 29.20, 28.87, 25.97, 22.58, 14.43.

3: TGA of MIL 7 and MIL 10

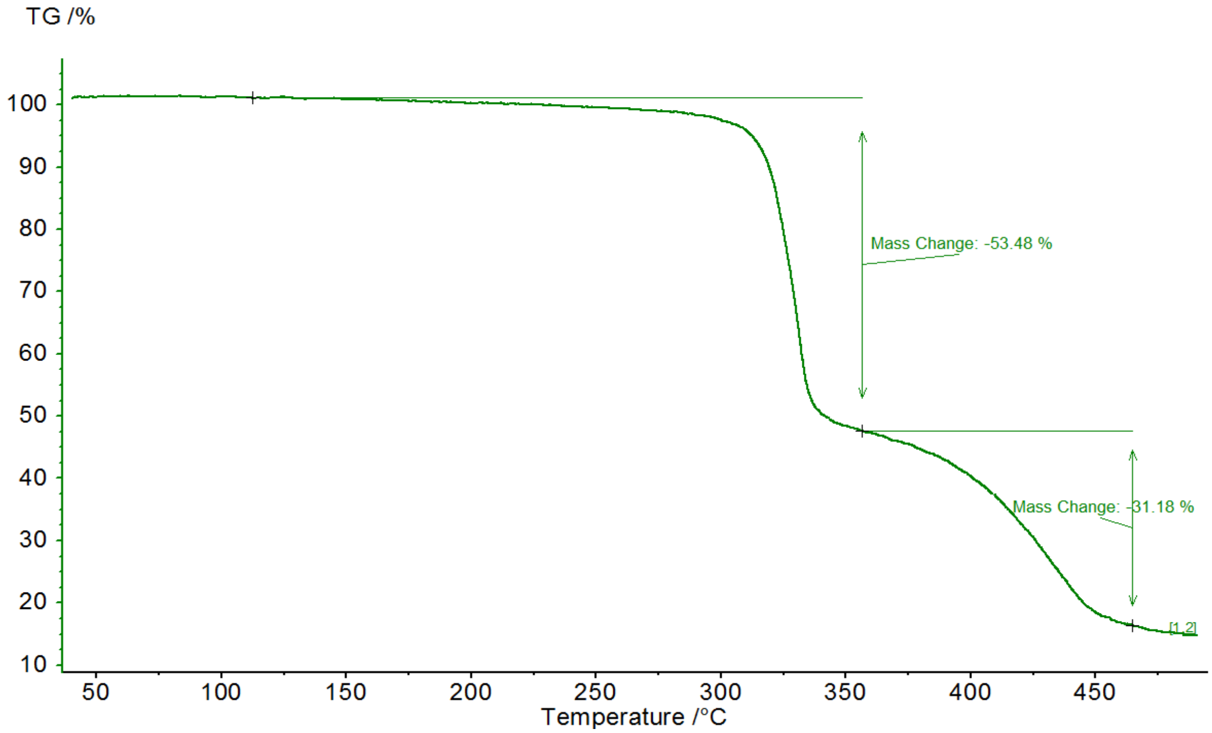


Figure S1 Thermogram of MIL **7** ([P_{66614}^{+}][Ni(P_{h}tfacac)$_3^{-}$]) at a rate of 5 °C/min.

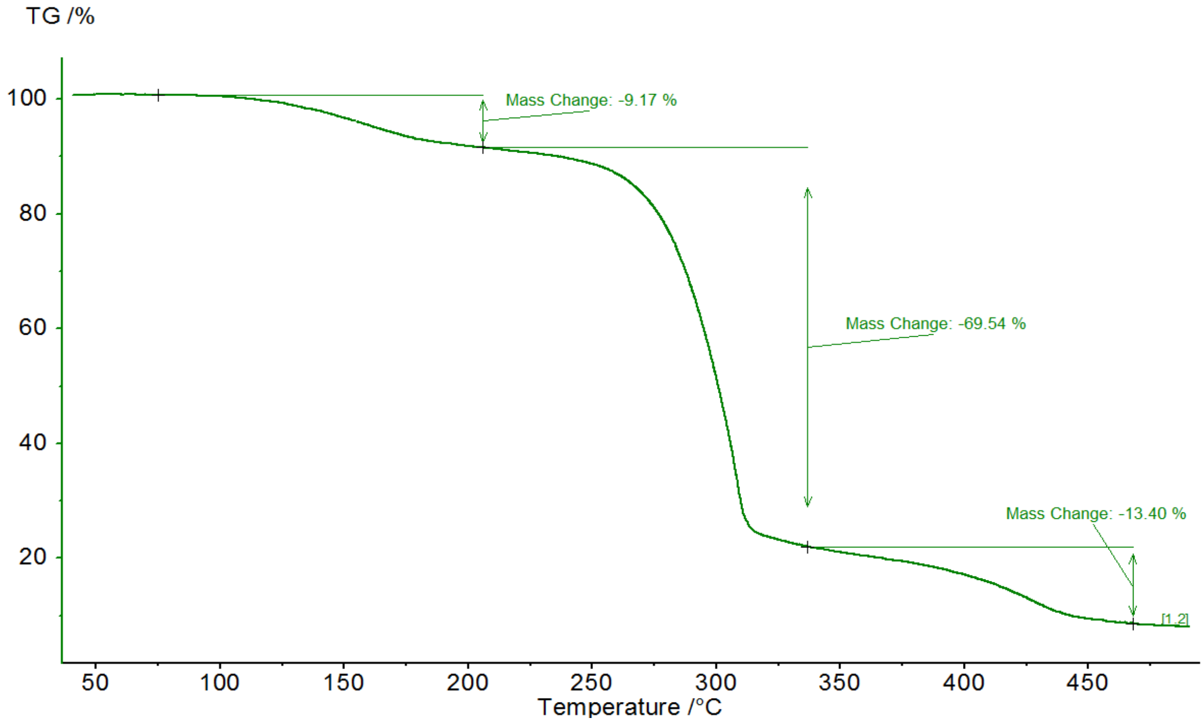


Figure S2 Thermogram of MIL **10** ([P_{66614}^{+}][Ni(tfacac)$_3^{-}$]) at a rate of 5 °C/min.

4: SQUID plots of transition metal-based MILs

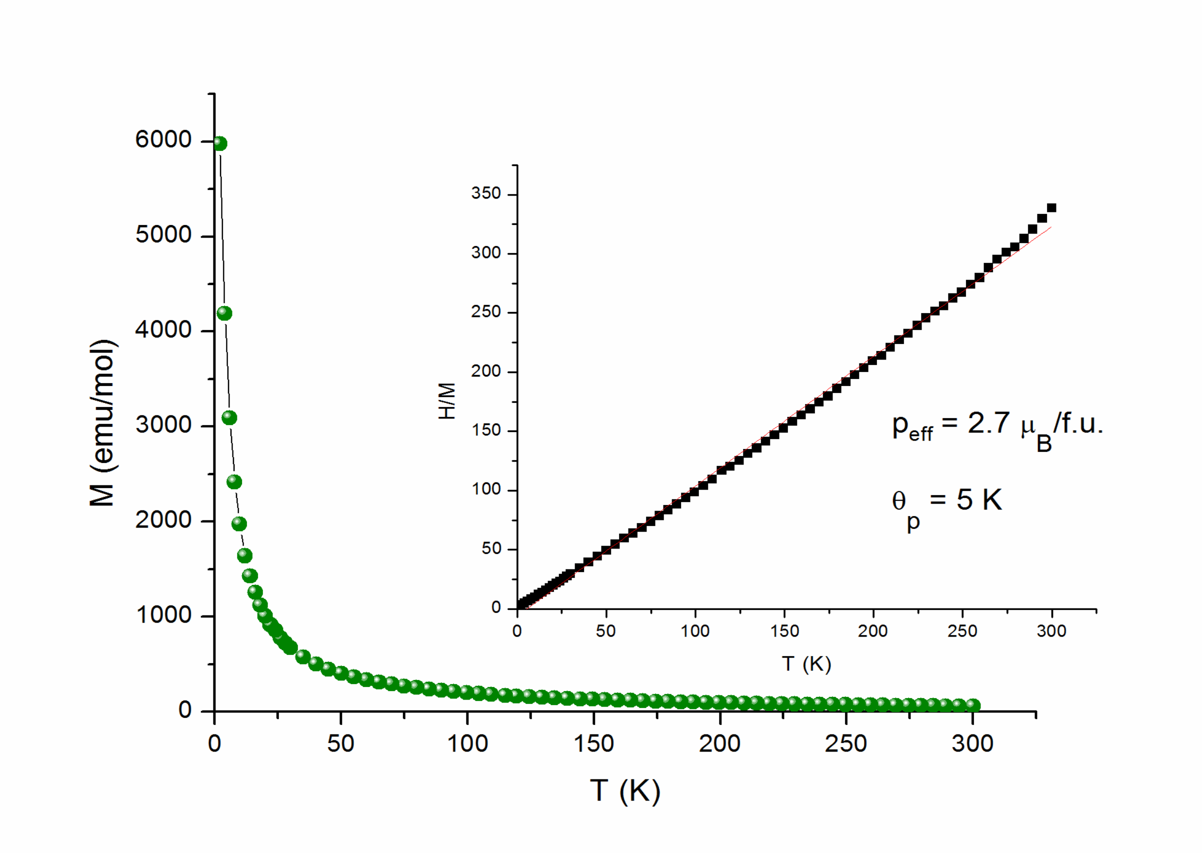


Figure S3 Magnetization of the $[P_{66614}^{+}][Ni(P_{h}tfacac)_{3}^{-}]$ MIL as a function of temperature in applied magnetic field of H = 20 kOe between 2 and 300 K. The inset shows the Curie-Weiss fit of reciprocal magnetic susceptibility vs temperature.

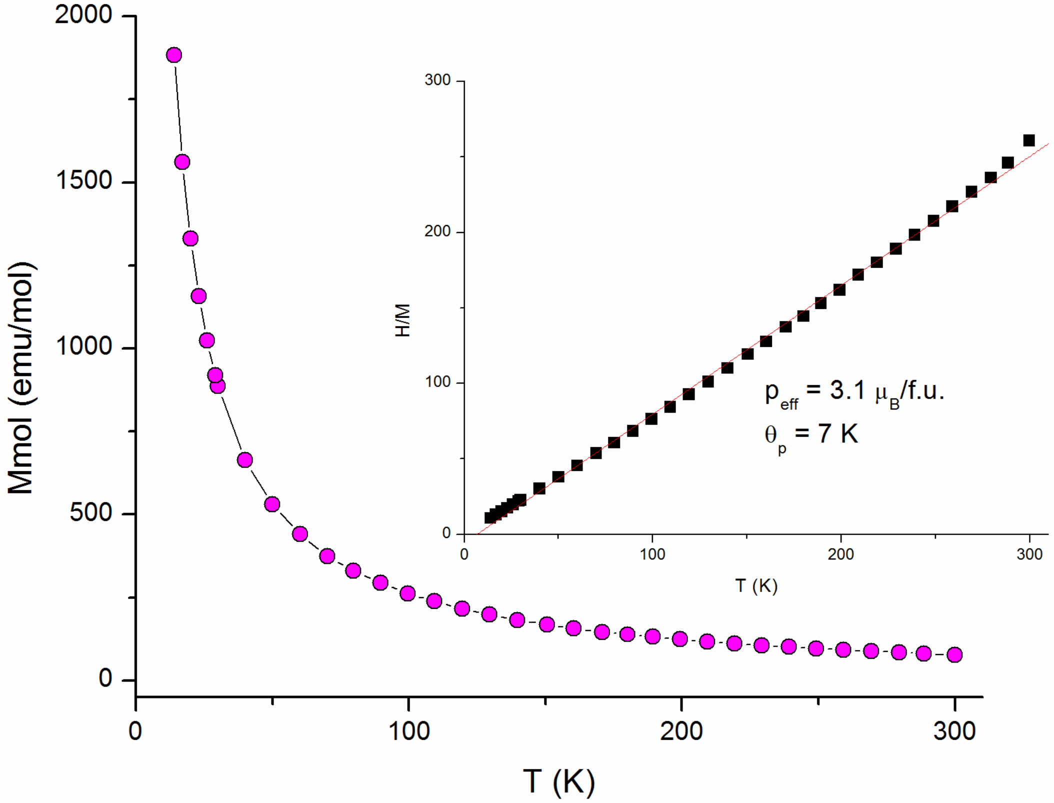


Figure S4 Magnetization of the $[P_{66614}^{+}][Ni(T_htfacac)_3^{-}]$ MIL as a function of temperature in applied magnetic field of H = 20 kOe between 2 and 300 K. The inset shows the Curie-Weiss fit of reciprocal magnetic susceptibility vs temperature.

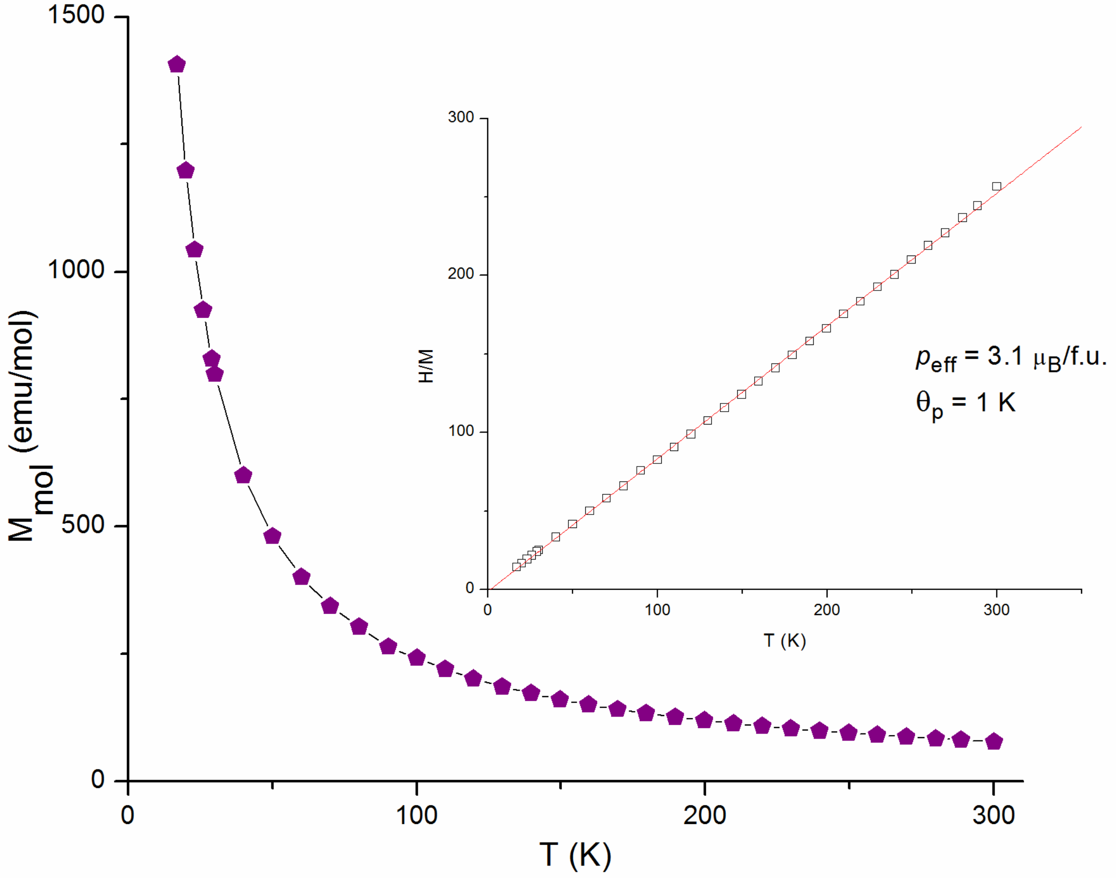


Figure S5 Magnetization of the [$C_{14}MIM^+$][$Ni(T_htfacac)_3^-$] MIL as a function of temperature in applied magnetic field of H = 20 kOe between 2 and 300 K. The inset shows the Curie-Weiss fit of reciprocal magnetic susceptibility vs temperature.

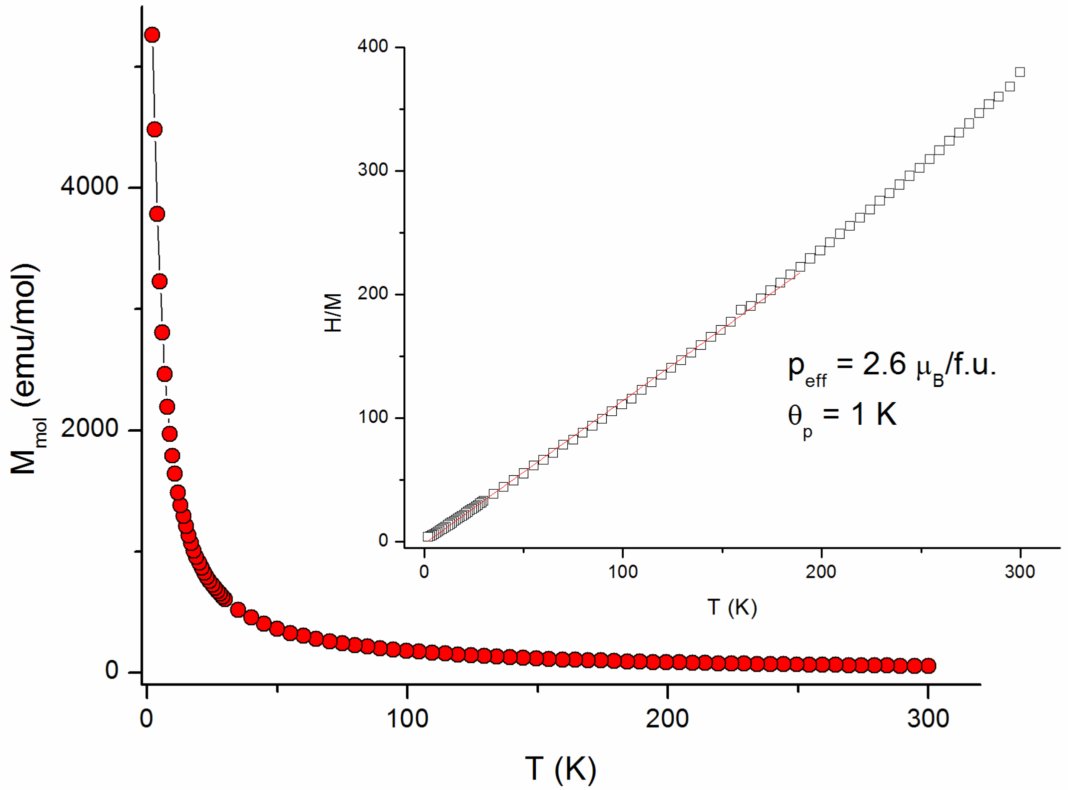


Figure S6 Magnetization of the [P_{66614}^{+}][$Ni(N_ptfacac)_3^{-}$] MIL as a function of temperature in applied magnetic field of H = 20 kOe between 2 and 300 K. The inset shows the Curie-Weiss fit of reciprocal magnetic susceptibility vs temperature.

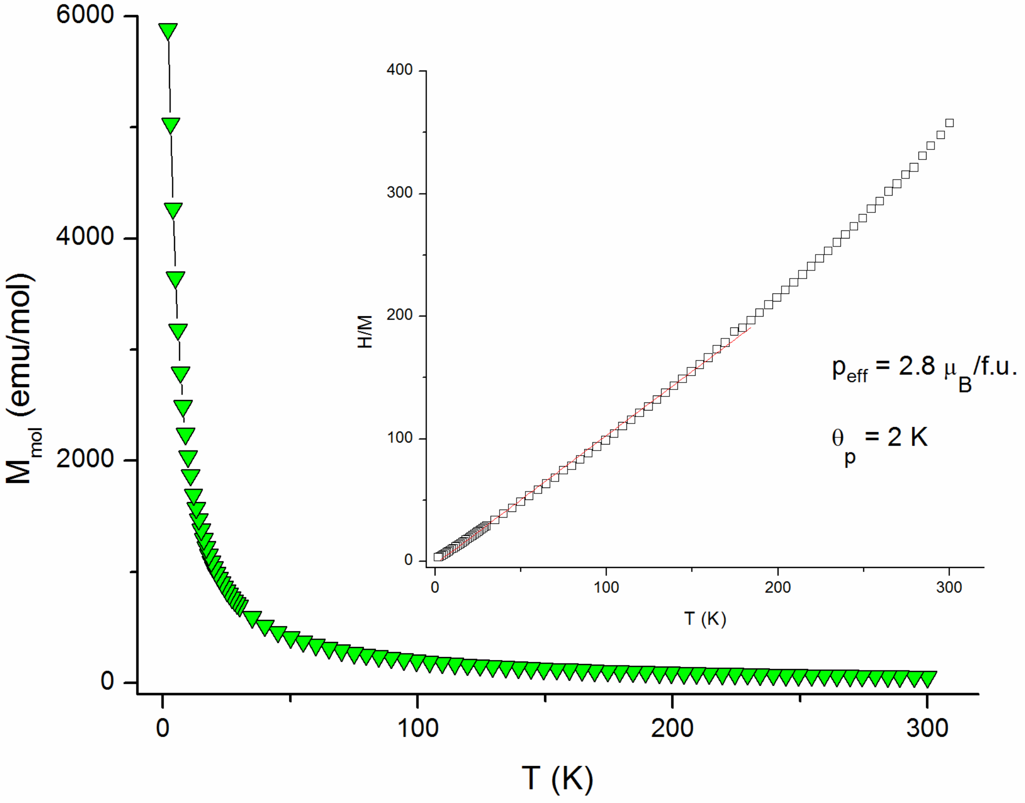


Figure S7 Magnetization of the $[C_{14}MIM^{+}][Ni(N_{p}tfacac)_{3}^{-}]$ MIL as a function of temperature in applied magnetic field of H = 20 kOe between 2 and 300 K. The inset shows the Curie-Weiss fit of reciprocal magnetic susceptibility vs temperature.

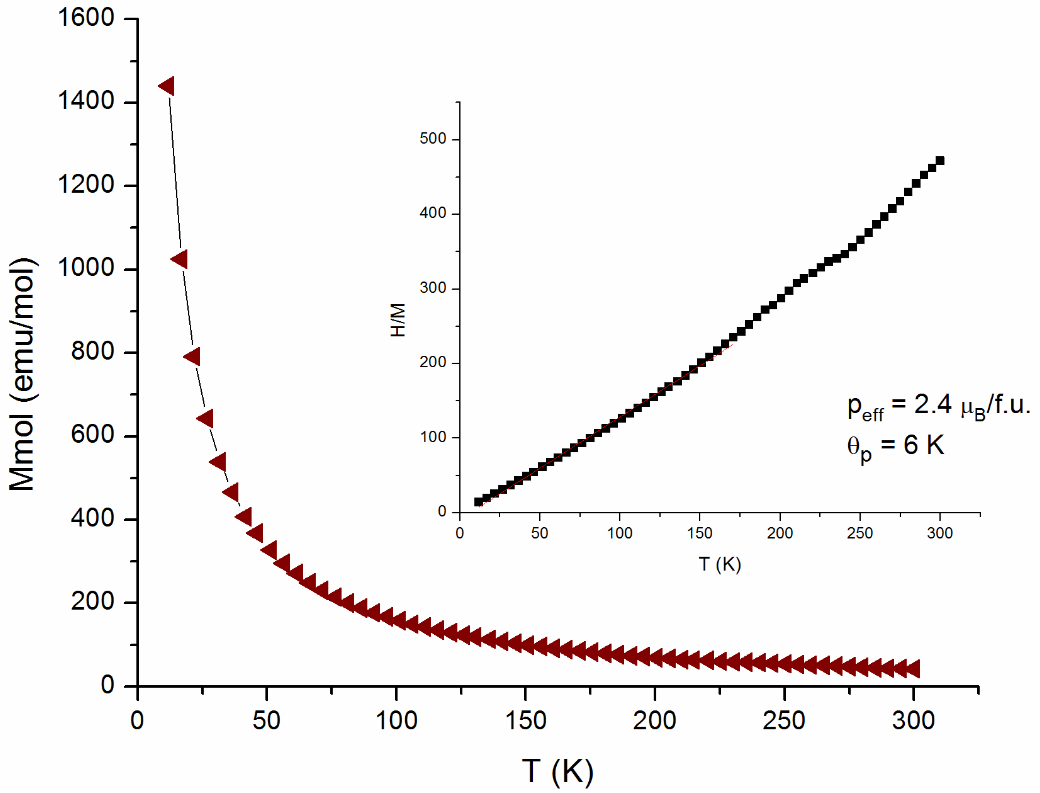


Figure S8 Magnetization of the [P_{66614}^+][$Ni(tfacac)_3^-$] MIL as a function of temperature in applied magnetic field of H = 20 kOe between 2 and 300 K. The inset shows the Curie-Weiss fit of reciprocal magnetic susceptibility vs temperature.

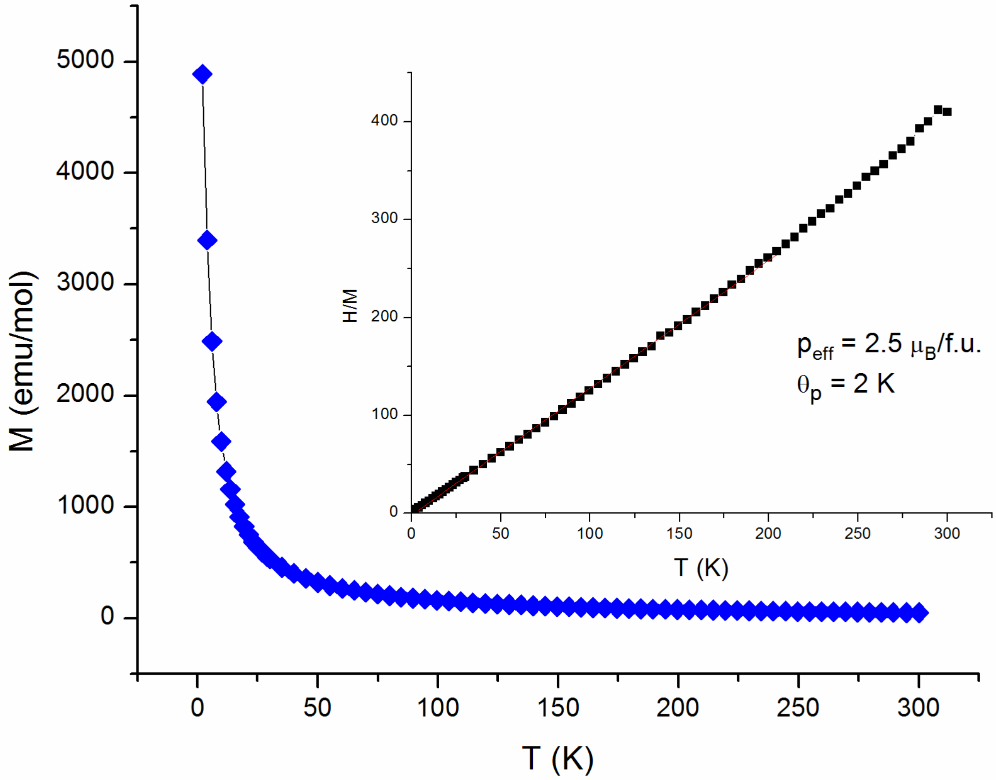


Figure S9 Magnetization of the [$C_{14}MIM^+$][$Ni(tfacac)_3^-$] MIL as a function of temperature in applied magnetic field of H = 20 kOe between 2 and 300 K. The inset shows the Curie-Weiss fit of reciprocal magnetic susceptibility vs temperature.

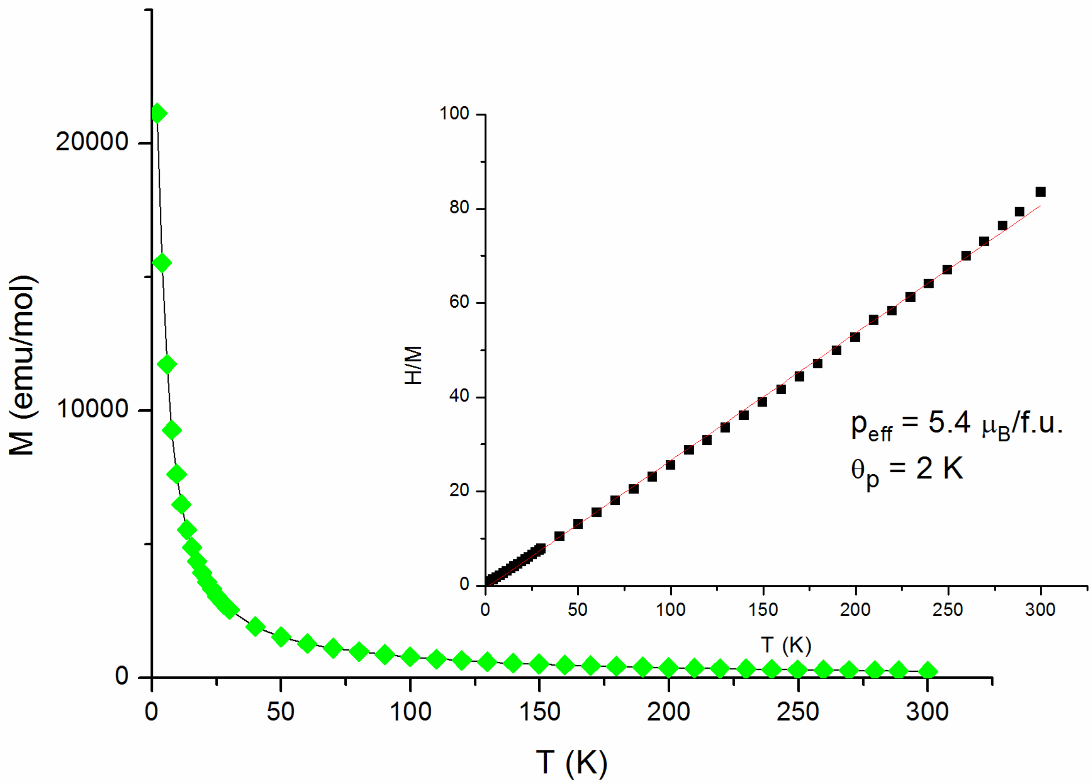


Figure S10 Magnetization of the $[P_{66614}^{+}][Mn(P_htfacac)_3^{-}]$ MIL as a function of temperature in applied magnetic field of H = 20 kOe between 2 and 300 K. The inset shows the Curie-Weiss fit of reciprocal magnetic susceptibility vs temperature.

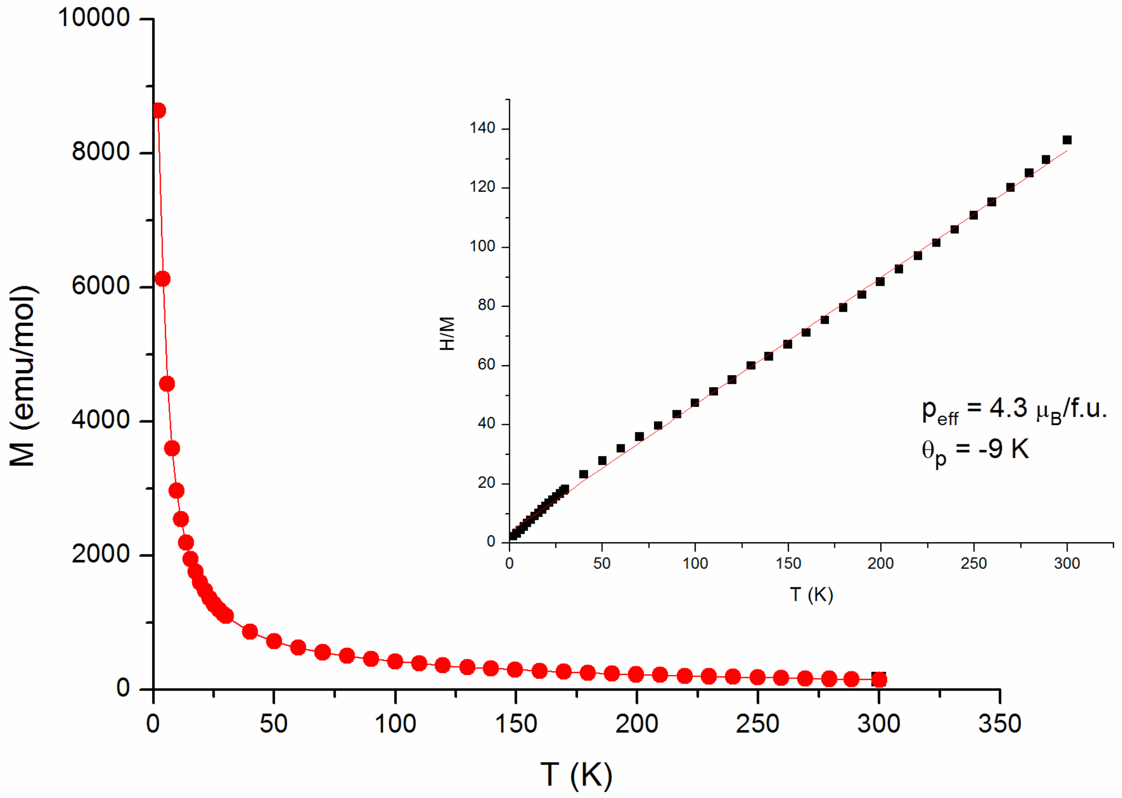


Figure S11 Magnetization of the $[P_{66614}^{+}][Co(P_{h}tfacac)_{3}^{-}]$ MIL as a function of temperature in applied magnetic field of H = 20 kOe between 2 and 300 K. The inset shows the Curie-Weiss fit of reciprocal magnetic susceptibility vs temperature.

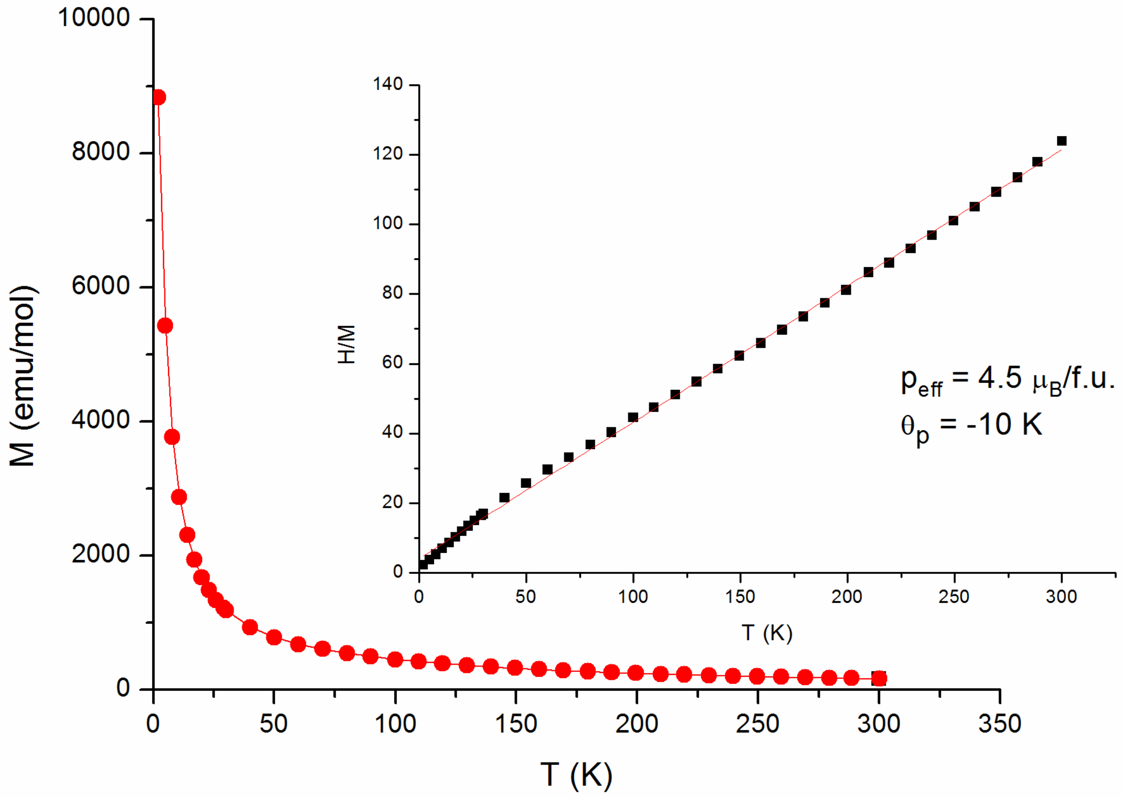


Figure S12 Magnetization of the [$C_{14}MIM^+$][$Co(P_htfacac)_3^-$] MIL as a function of temperature in applied magnetic field of H = 20 kOe between 2 and 300 K. The inset shows the Curie-Weiss fit of reciprocal magnetic susceptibility vs temperature.

Reference

(1) Sekera, V. C.; Marvel, C. S. Higher Alkyl Sulfonates. *J. Am. Chem. Soc.* **1933**, *55*, 345–349.