

Supporting Information

Hydrogen Physisorption in Ionic Solid Compounds with Exposed Metal Cations at Room Temperature

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Hydrogen adsorption measurement:

Hydrogen adsorption measurements were performed by following the standard practice guidelines provided by the US Department of Energy to minimize potential errors in the hydrogen uptake measurement. The instrument calibration and the experimental considerations are described as follows. [1-3]

(1) Calibration:

- Calibration of volume, temperature sensors, pressure transducers
- Null calibration (empty sample chamber with zero uptake baseline under isothermal condition) (**Figure S1**)
- Calibration of the instrument with known materials (**Figure S2 and Figure S3**)

(2) Temperature monitoring and control:

- The temperature of the sample chamber was controlled to an acceptable level by applying water bath or liquid N₂ bath.
- The gas reservoir is thermostatted to minimize the room temperature fluctuations.

(3) Sample temperature was monitored continuously throughout the measurement.

(4) Approach to the equilibrium:

- Equilibrium is reached relatively quickly in the physisorption system but the pressure relaxation was measured at each step (data point was taken every minute).

(5) Sample size:

- Sample size was taken carefully to match up with the requirement on the system volume and the pressure measurement.
- Generally, sample size was taken to fill 2/3 volume of the sample chamber (3 cc).

(6) Gas purity: 99.9995 %

(7) Sample degassing was performed under ultra-high vacuum (UHV).

(8) Sample pretreatment: 150 °C under UHV for 12 h.

(9) Leakage was tested using helium and hydrogen at the maximum measurement pressure.

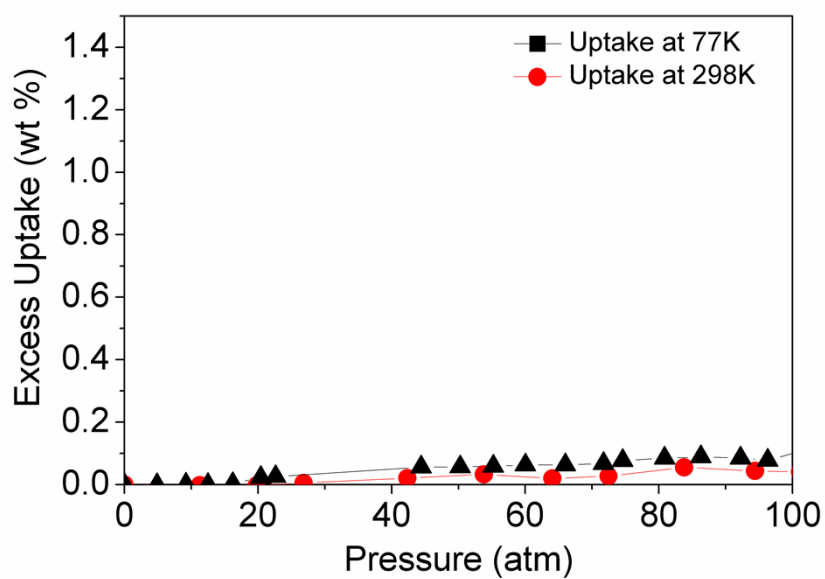


Figure S1: Empty sample holder calibration.

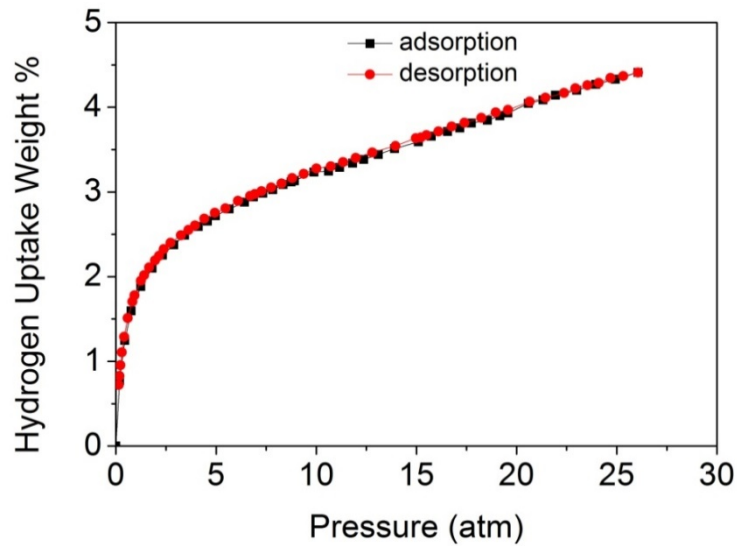


Figure S2: Hydrogen storage capacity of commercially available basolite A100 MOF obtained at 77K in the same instrument under the similar conditions as the MTF-Fe material in this study, in agreement with the reported results in Reference [4].

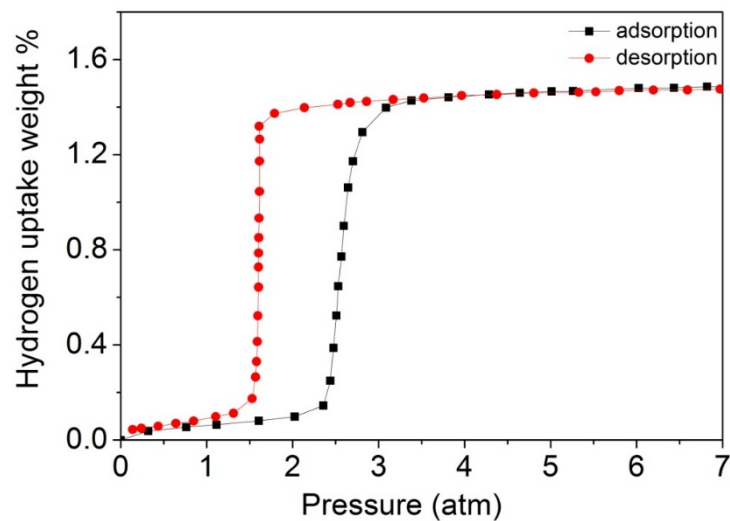


Figure S3: Hydrogen storage capacity of a commercially available LaNi_5 alloy obtained at 298K with the same instrument under the similar condition to the one hydrogen storage in the MTF-Fe material was measured. The results are in excellent agreement with the data shown in Reference [5, 6].

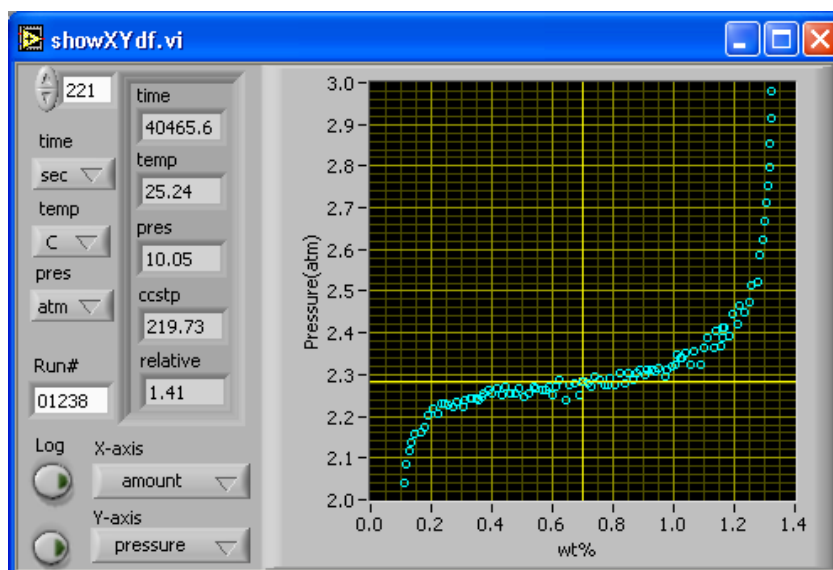


Figure S4: The pressure resolution of the instrument is 0.02 atm (LaNi5 at 298K)

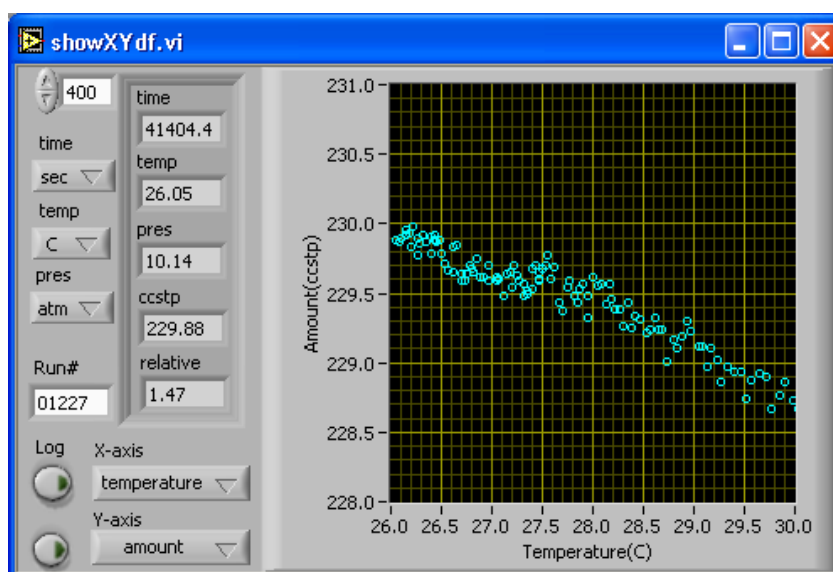


Figure S5: The gas measurement resolution with the GRC instrument is 0.2 ccstp.

Isosteric heat of adsorption:

The enthalpy of the adsorption was calculated using the Clapeyron–Clausius equation by taking the excess hydrogen adsorption data obtained at 323K, 298K and 273K, respectively. The isotherms were fitted using an exponential fit for gas uptake vs. pressure. The exponential equation provides an accurate fit over the pressure up to 100 atm with the goodness of fit (R^2) up to 0.99. The fitted curve was used to obtain the values of P_1 and P_2 at their corresponding amounts of hydrogen adsorbed at T_1 and T_2 , respectively. The heat of adsorption was then calculated using Eq. 2. [7]

$$\Delta H_{iso} = -\frac{RT_1T_2}{T_2 - T_1} \ln \frac{P_2}{P_1} \quad (2)$$

where R is the universal gas constant.

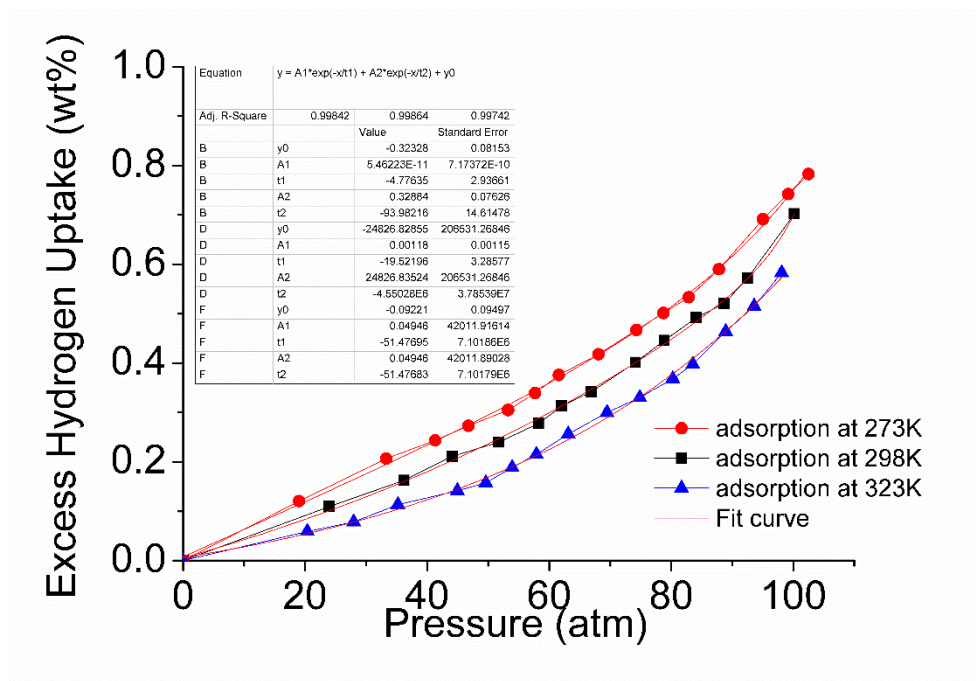


Figure S6: The excess hydrogen uptake of the Ph-INS complex at 323K, 298K and 273K.

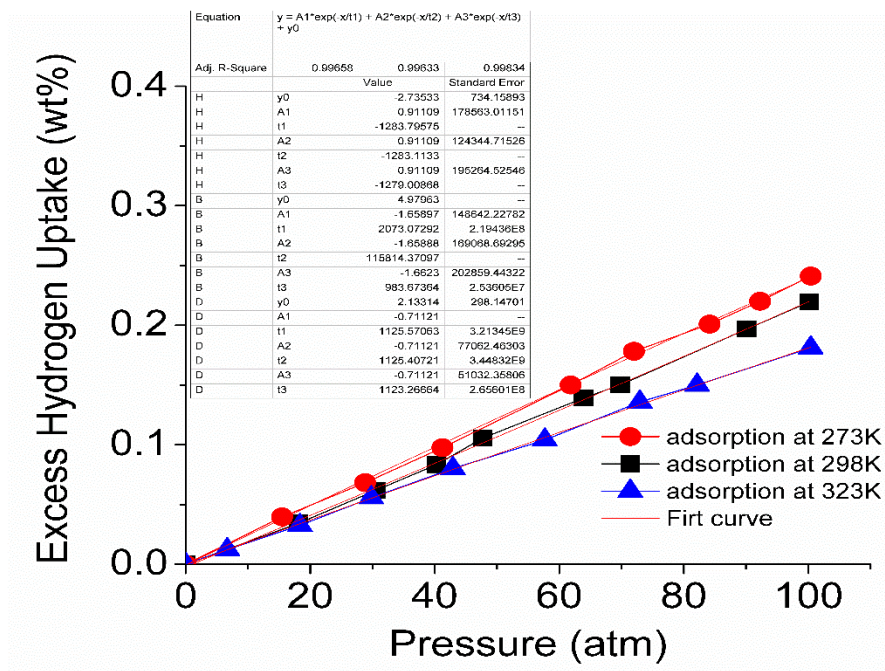


Figure S7: The excess hydrogen uptake of the PhI-INS complex at 323K, 298K and 273K.

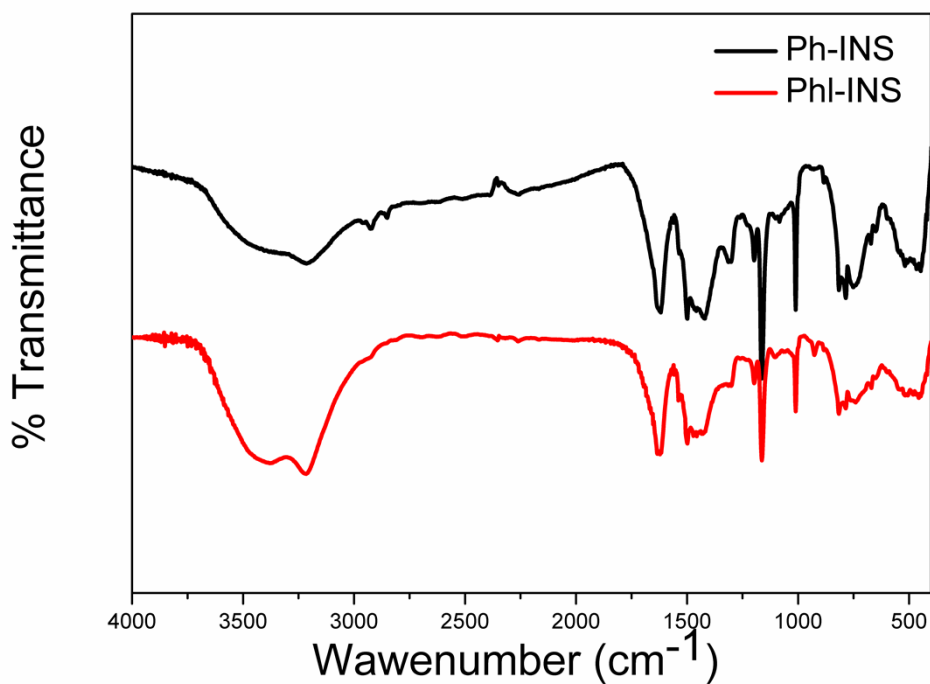


Figure S8: The FTIR spectra of the Ph-INS and PhI-INS materials.

Ph-INS

FTIR (ATR cm^{-1}): 2927 cm^{-1} (C-H str. aromatic), 1616, 1499 and 1414 cm^{-1} (C=C str. aromatic), 1197, 1161 cm^{-1} (B-F str. BF_4), [8] 1066 cm^{-1} (C-O str.) and 3200-3400 cm^{-1} (adsorbed moisture).

Ph-INS

FTIR (ATR cm^{-1}): 2918 cm^{-1} (C-H str. aromatic), 1625, 1509 and 1416 cm^{-1} (C=C str. aromatic), 1190, 1157 cm^{-1} (B-F str. BF_4), [8] 1009 cm^{-1} (C-O str.) and 3200-3400 cm^{-1} (adsorbed moisture).

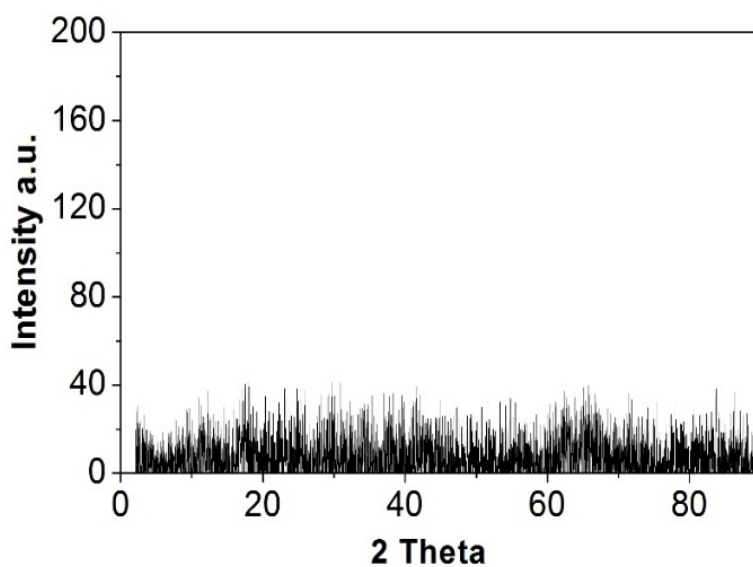


Figure S9: PXRD pattern of the Ph-INS complex.

The powder X-ray diffraction profile of the Ph-INS complex does not contain any sharp signals, which confirms that the material is amorphous with absence of long-range order.

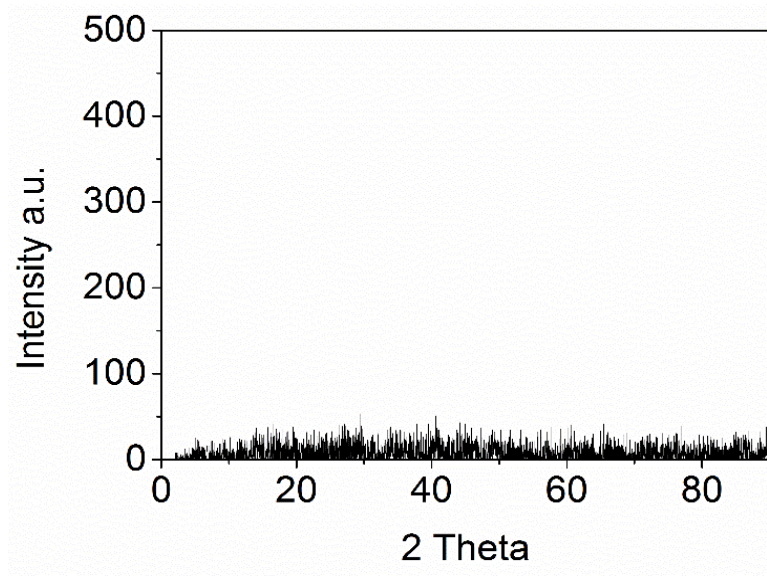


Figure S10: PXRD pattern of the PhI-INS complex.

The powder X-ray diffraction profile of the PhI-INS complex does not contain any sharp signals, which confirms that the material is amorphous with absence of long-range order.

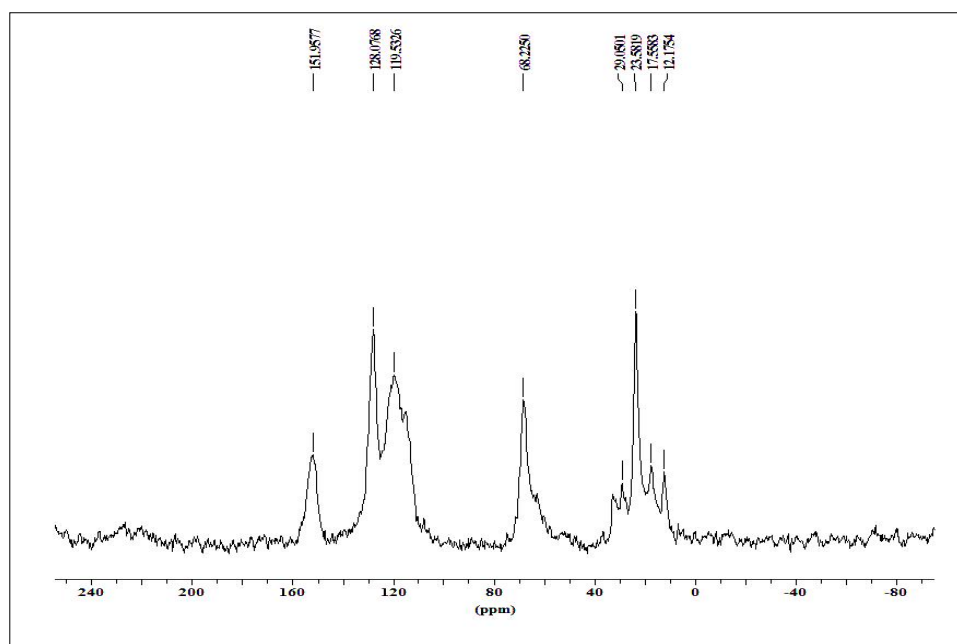


Figure S11: ¹³C CP-MAS NMR of Ph-INS material.

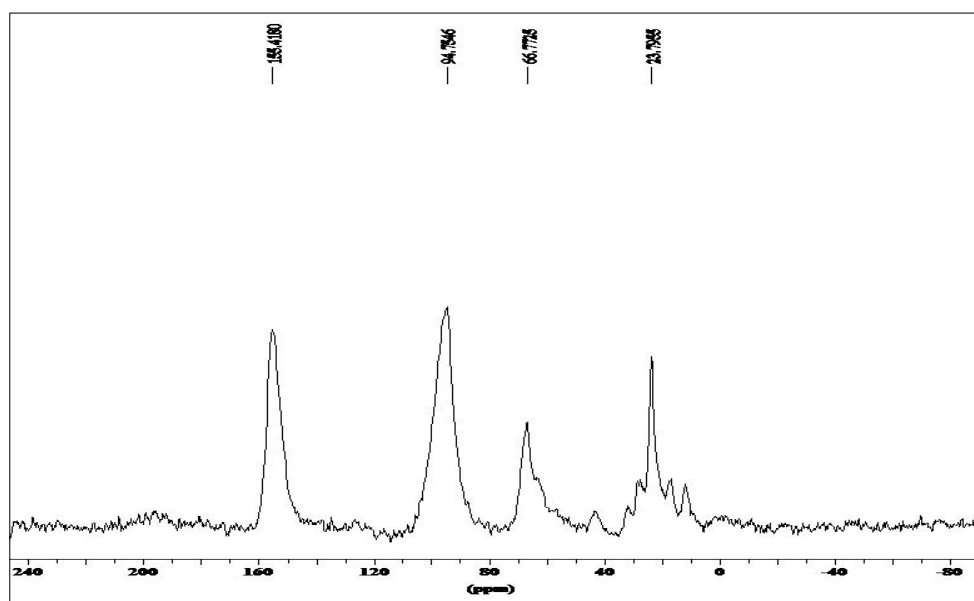


Figure S12: ^{13}C CP-MAS NMR of PhI-INS material.

References:

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