Supporting Information

Effects of Metal Ions and Ligand Functionalization on Hydrogen Storage in Metal-Organic Frameworks by Spillover

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Table S1. H_2 Uptakes at 298 K and 7.3 MPa for the MIL-53 (Al, Cr, or Fe) and MIL-68 (V) materials.

MOF	Formula unit	Formula weight (g/mol)	Expected H_2 capacity, q_e (wt%)[a]	Net H_2 uptake by spillover, q_n (wt%)[b]	Enhancement factor
MIL-53 (Al)	Al(OH)(BDC)	208	0.18	0.23	2.25
MIL-53 (Cr)	Cr(OH)(BDC)	233	0.18	0.20	2.09
MIL-53 (Fe)	Fe(OH)(BDC)	237	0.16	0.20	2.26
MIL-68 (V)	V(OH)(BDC)	232	0.20	0.20	2.00

[a] Based on the weighted average of the Pt/C-MOF mixture assuming no spillover. $q_e = 0.9 \times q_{mof} + 0.1 \times q_{catalyst}$, q_{mof}, and $q_{catalyst}$ are the H_2 uptakes of pristine MOF, and catalyst, respectively. [b] The net spillover enhancement for the Pt/C-MOF mixture over the expected H_2 uptake ($q_n = q - q_e$, here q is the total H_2 uptake measured on the Pt/C-MOF mixture).

Table S2. H_2 Uptakes at 298 K and 7.3 MPa for the IRMOF type materials.

MOF	Formula unit	Formula weight (g/mol)	Expected H_2 capacity, q_e (wt%)[a]	Net H_2 uptake by spillover, q_n (wt%)[b]	Enhancement factor	H_s/(x-BDC)[c]
IRMOF-1	$Zn_4O(BDC)_3$	770	0.28	0.27	1.96	0.69
IRMOF-2	$Zn_4O(Br\text{-}BDC)_3$	1006	0.25	0.51	3.00	1.89
MTV-MOF-5-AE	$Zn_4O(BDC)_{2.1}$ $(NO_2\text{-}BDC)_{0.9}$	810	0.25	0.34	2.37	1.43[d]
IRMOF-3	$Zn_4O(NH_2\text{-}BDC)_3$	815	0.29	0.17	1.60	0.51
MTV-MOF-5-AF	$Zn_4O(BDC)_{1.3}$ $((CH_3)_2\text{-}BDC)_{1.7}$	817	0.23	0.15	1.67	0.29[e]

[a] Based on the weighted average of the Pt/C-MOF mixture assuming no spillover. $q_e = 0.9 \times q_{mof} + 0.1 \times q_{catalyst}$, q_{mof}, and $q_{catalyst}$ are the H_2 uptakes of pristine MOF, and catalyst, respectively. [b] The net spillover enhancement for the Pt/C-MOF mixture over the expected H_2 uptake ($q_n = q - q_e$, here q is the total H_2 uptake measured on the Pt/C-MOF mixture). [c] Average amount of H_s per BDC linker. [d] $H_s/(NO_2\text{-}BDC)$. [e] $H_s/((CH_3)_2\text{-}BDC)$.

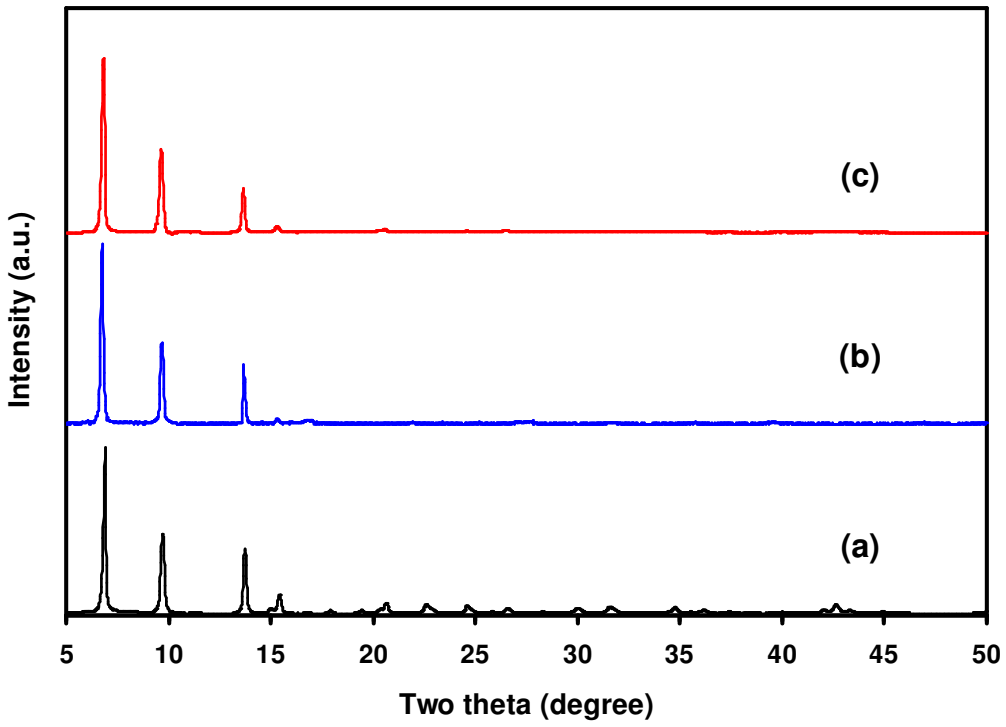

Figure S1. Powder XRD patterns of IRMOF-3 samples: (a) pristine IRMOF-3; (b) Pt/C-IRMOF-3 physical mixture; (c) Pt/C-IRMOF-3 after H_2 exposure.

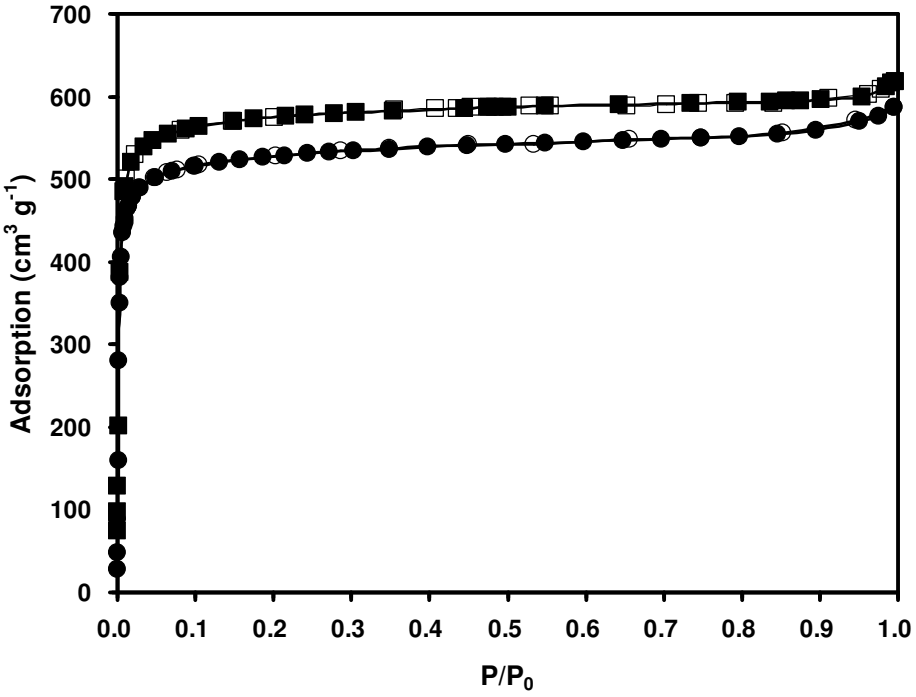

Figure S2. Nitrogen adsorption isotherms for IRMOF-3 at 77 K. Symbols: ■ pristine IRMOF-3; ● Pt/C-IRMOF-3 physical mixture. Open symbols indicate desorption branches. The BET surface area of the Pt/C-IRMOF-3 mixture is ca. 2015 m^2/g.

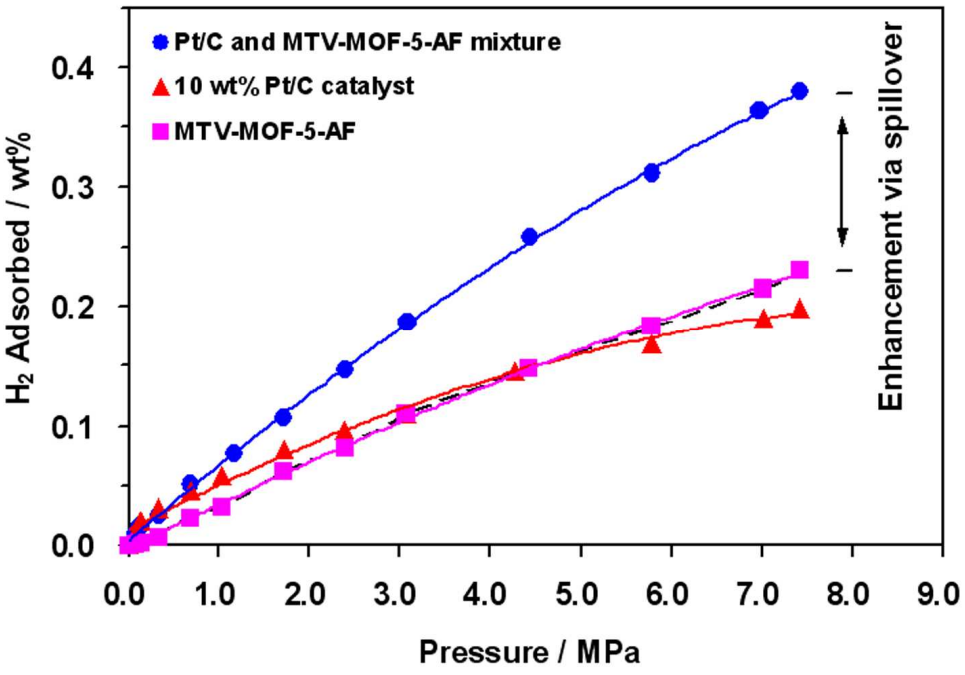

Figure S3. High-pressure hydrogen adsorption at 298 K for the MTV-MOF-5-AF. Dotted line is prediction based on the weighted average of the mixture.

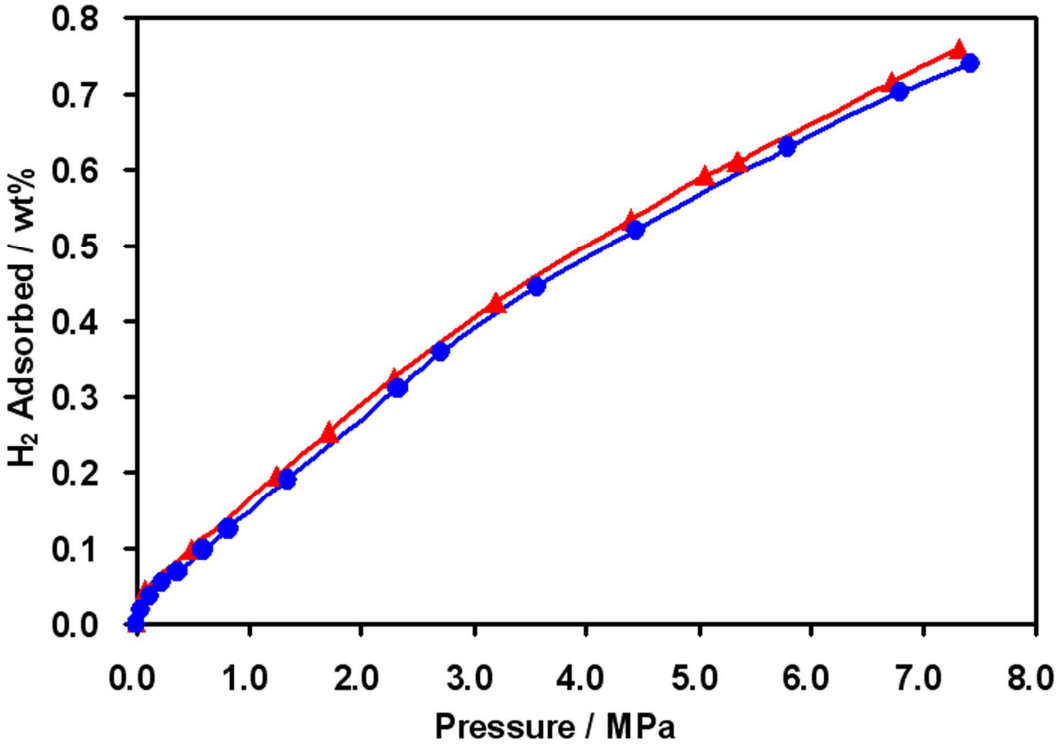

Figure S4. High-pressure hydrogen isotherms at 298 K for two Pt/C–IRMOF-2 physical mixtures prepared independently.

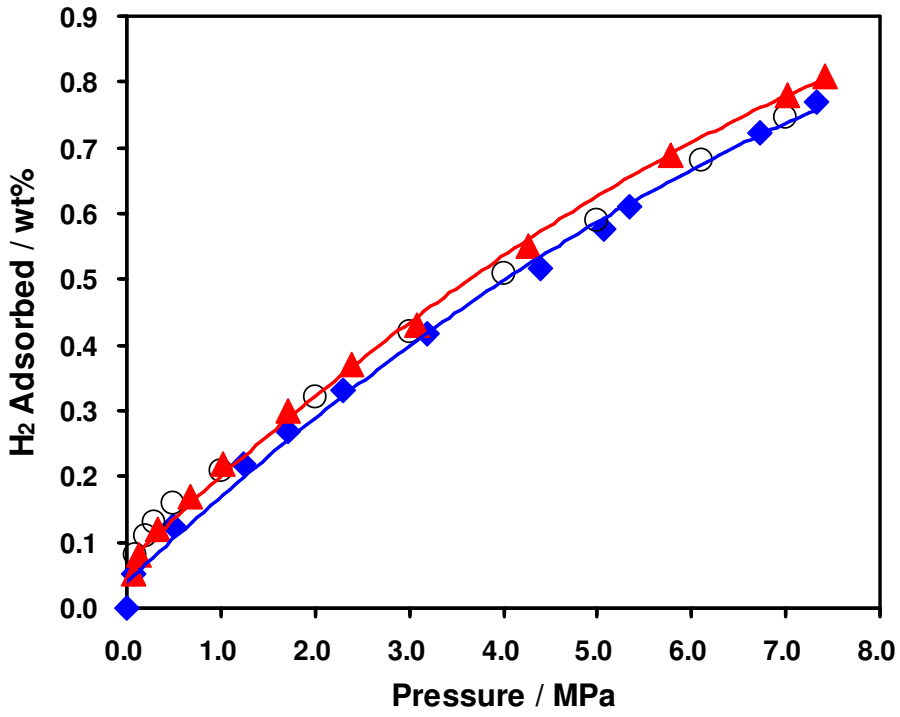

Figure S5. High-pressure hydrogen adsorption at 298 K for the Pt/C–IRMOF-2 physical mixture: first adsorption (◆), desorption (○), and second adsorption (▲).