Supporting information

Light Metals Decorated Covalent Triazine-Based Frameworks as High Capacity Hydrogen Storage Medium

Xiaowei Chen,[a] Feng Yuan, [a] Qinfen Gu, [b] Xuebin Yu [a]*

[a] *Department of Materials Science, Fudan University, Shanghai 200433, China*

[b] *Australian Synchrotron, Clayton, Victoria 3168, Australia*

* To whom correspondence should be addressed. Phone and Fax: +86-21-5566 4581.

E-mail: yuxuebin@fudan.edu.cn

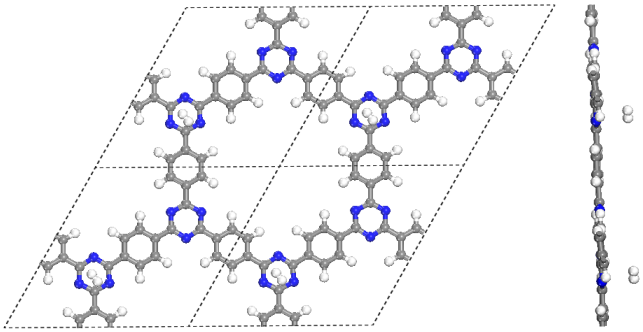

Figure S1. The most stable geometry of H_2 adsorbed on CTF shown in (a) top and (b) side views. The molecule is positioned over the center of an empty carbon hexagon with its axis parallel to the CTF plane. The dark gray, blue and white spheres represent carbon, nitrogen and hydrogen atoms, respectively.

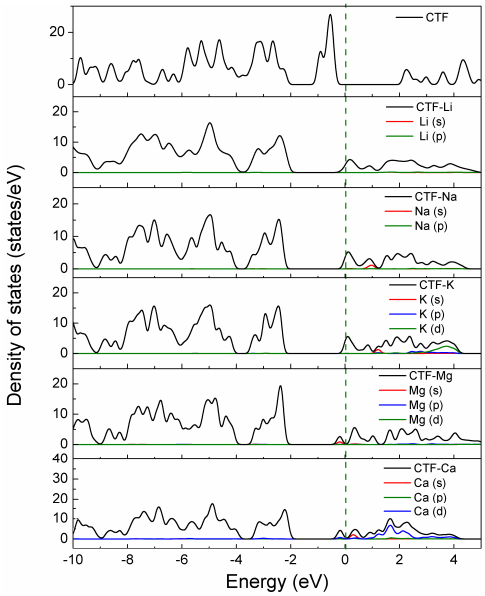

Figure S2. The density of states (DOS) of CTF and CTF–M (M= Li, Na, Mg, K, Ca) complexes. The Fermi level is set to zero and indicated by the dotted line.

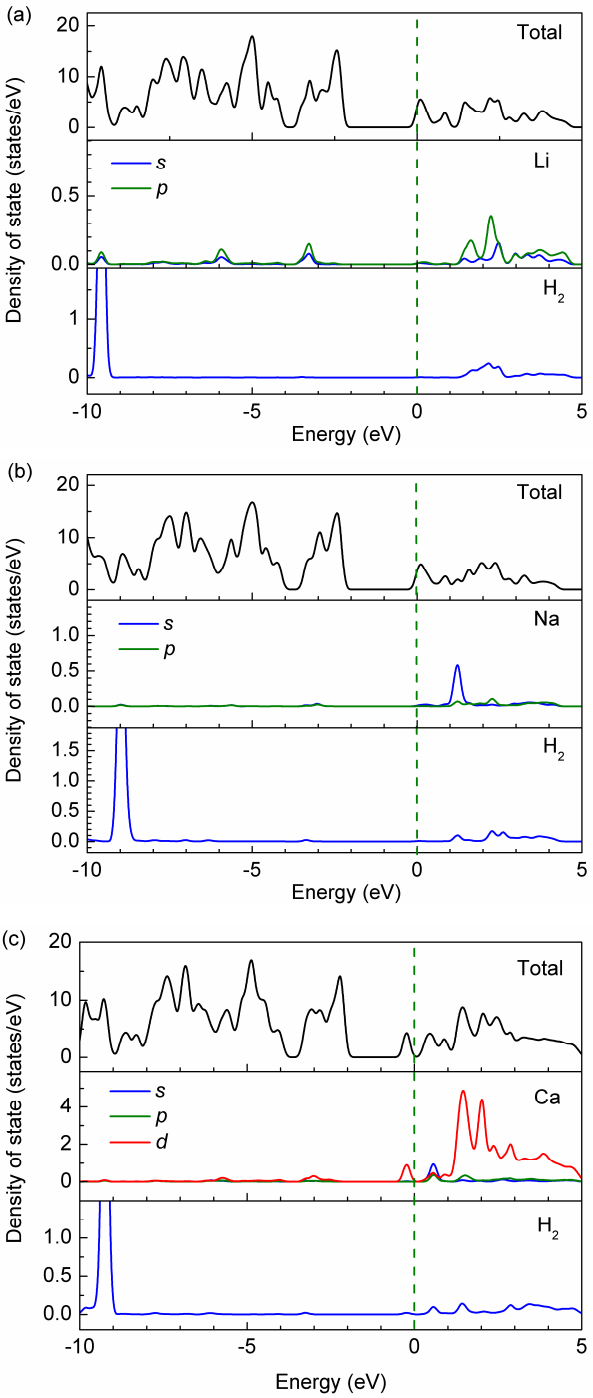

Figure S3 The density of states (DOS) of (a) CTF–Li, (b) CTF–Na and (c) CTF–Ca, where the metal atoms are located on top site of a hexagonal carbon ring. The Fermi level is set to zero and indicated by the dotted line.

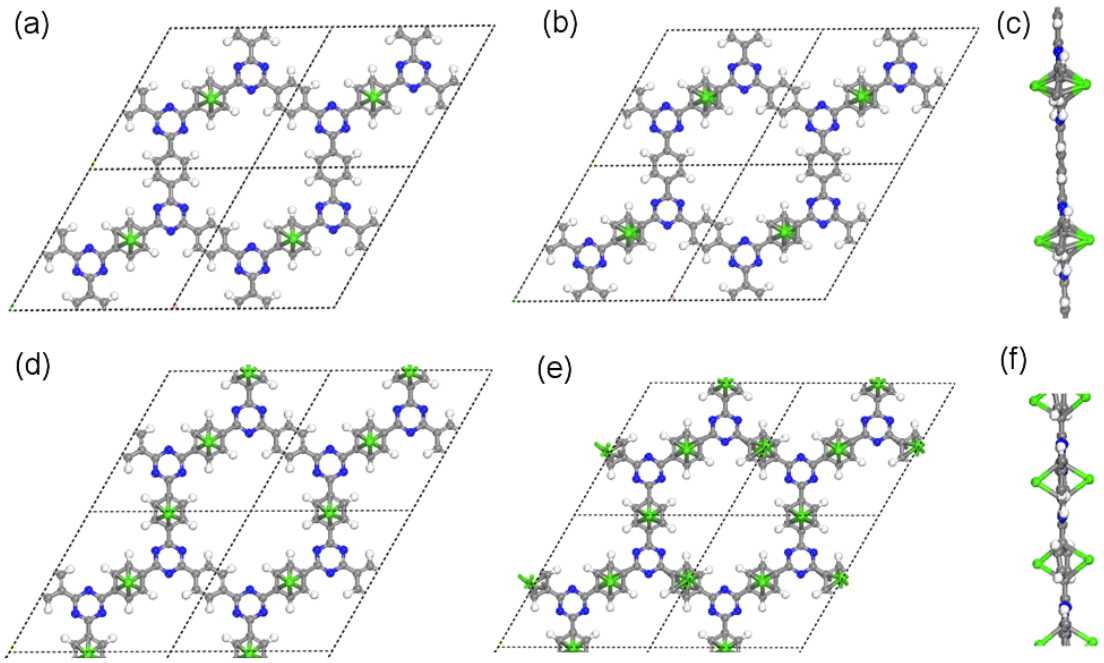

Figure S4. Optimized structure of various coverages of metal atoms decorated CTF-1. (a) top view of a Ca atom on signal side, (b) top view and (c) side view of two Ca atoms on both sides, (d) top view of two Ca atoms on signal side, (e) top view and (f) side view of six Ca atoms on both sides. The green, dark gray, blue and white spheres represent calcium, carbon, nitrogen and hydrogen atoms, respectively. Li and Na decorated CTF-1 have a similar geometry.

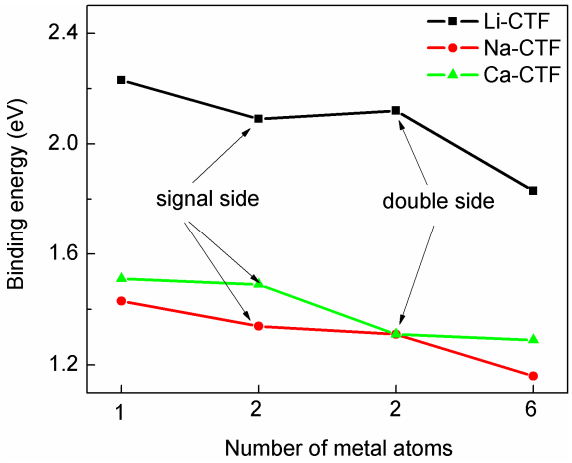

Figure S5. The calculated average binding energies of Li, Na and Ca decorated CTF with various coverages.

Table S1. The bond lengths, binding energies and bader charges of CTF–M complexes.

	bond length (Å)		M–CTF binding	Charge on the metal
system	Metal–Nitrogen	Metal–Carbon	energy (eV)	atoms (e)
CTF–Li–B_{CN}	1.87	2.49	2.09	+0.91
CTF–Li–T_C	——	2.27	2.23	+0.90
CTF–Na–B_{CN}	2.28	2.83	1.53	+0.88
CTF–Na–T_C	——	2.65	1.43	+0.91
CTF–Mg–B_{CN}	2.16	3.02	0.45	+0.63
CTF–Mg–T_C	——	3.61	0.09	+0.32
CTF–K–B_{CN}	2.65	3.15	1.71	+0.89
CTF–K–T_C	——	2.98	1.72	+0.89
CTF–Ca–B_{CN}	2.21	2.54	1.52	+1.36
CTF–Ca–T_C	——	2.41	1.51	+1.38

Table S2. The bond lengths, binding energies and bader charges of CTF–M complexes after the adsorption of H_2 molecules.

atoms	M–H bond length (Å)	H–H bond length (Å)	Charge on metal (e)	E_b (eV)
Li	1.98	0.76	+0.98	0.26
Na	2.32	0.76	+0.90	0.16
K	2.85	0.76	+0.90	0.13
Ca	2.44	0.77	+1.45	0.26

Table S3. The H_2 binding energies on the Na atom decorated B_{CN} sites of CTF.

No. of H_2 molecules	1	2	3	4	5
E_b	0.16	0.17	0.19	0.18	0.17