Supporting Information

Tunable Gravimetric and Volumetric Hydrogen Storage Capacities in Polyhedral Oligomeric Silsesquioxane Frameworks

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S1. The Lennard-Jones parameters for the calculation of V_p

Equation 3 of the main text, which is used to determine the specific pore volume V_p, contains an $E(r)$ term that is calculated as:

$$E(r) = \sum_{j}^{\substack{Atoms\ in \\ Framework}} -4\varepsilon_{He,j} \left[\left(\frac{\sigma_{He,j}}{r_{He,j}} \right)^6 - \left(\frac{\sigma_{He,j}}{r_{He,j}} \right)^{12} \right] \tag{S1}$$

with

$$\sigma_{He,j} = (\sigma_{He} + \sigma_j)/2 \tag{S2}$$

and

$$\varepsilon_{He,j} = \sqrt{\varepsilon_{He}\varepsilon_j}. \tag{S3}$$

The values of ε_j and σ_j used for different elements j are shown Table S1.

Table S1. The Lennard-Jones parameters[a] used for calculating specific pore volumes (V_p).

	σ (Å)	ε/k_B (K)
He	2.64	10.9
C	3.473	47.856
B	3.581	47.806
H	2.846	7.649
Si	3.804	155.997
O	3.033	48.156

[a] Parameters from Refs S1, S2

S2. Geometrical parameters and H_2 capacities for the T_8 based and $T_{12}+T_6$ based frameworks

Table S2. Chemical formulas, lattice constants (a), specific volumes (V_{total}), specific pore volumes (V_p), theoretical maximum gravimetric (D_g) and volumetric capacities (D_v) of adsorbed H_2 for frameworks built with $\underline{T_8}$ cages. D_g and D_v are estimated based on the assumption that each Sc and Ti center can bind 5 and 4 H_2 molecules, respectively.

Linker	Chemical formula[a]	a (Å)[a]	V_{total} (cm³/g)	V_p (cm³/g)	D_g (wt%)		D_v (g/L)	
					Sc	Ti	Sc	Ti
B-benzene	$C_{16}B_8H_{16}Si_8O_{12}$	14.12	1.19	0.57	7.0[b]	5.6	95.1[b]	76.1
(B-biphenyl)[cd]	$C_{32}B_{16}H_{32}Si_8O_{12}$	19.26	2.14	1.54	8.5	6.8	75.0	60.0
(B-phenanthrene)[cd]	$C_{40}B_{16}H_{32}Si_8O_{12}$	19.37	1.99	1.44	8.1	6.5	73.7	58.9
(B-E-1,2-diphenylethylene)[c]	$C_{40}B_{16}H_{40}Si_8O_{12}$	21.89	2.84	2.26	8.1	6.4	51.1	40.8
(B-diphenylacetylene)[c]	$C_{40}B_{16}H_{32}Si_8O_{12}$	22.16	2.97	2.39	8.1	6.5	49.2	39.4

[a] The chemical formula is given in terms of the primitive bcc unit cell, which was used for the actual simulation. For the sake of an easier comparison, the lattice constant a is given in terms of the conventional cubic cell of bcc. [b] The systems encounter the problem of steric effects among absorbed H_2. [c] The D_g and D_v are only estimated with the assumption of 5(4) H_2 molecules adsorbed on each Sc(Ti) site without real modeling. [d] The metal decorated frameworks are most likely not stable.

Table S3. Chemical formulas, lattice constants (a/c), specific volumes (V_{total}), specific pore volumes (V_p), theoretical maximum gravimetric (D_g) and volumetric capacities (D_v) of adsorbed H_2 for frameworks built with $\underline{T_{12}}$ and $\underline{T_6}$ cages. D_g and D_v are estimated based on the assumption that each Sc and Ti center can bind 5 and 4 H_2 molecules, respectively.

Linker	Chemical formula	a (Å)	c (Å)	V_{total} (cm³/g)	V_p (cm³/g)	D_g (wt%)		D_v (g/L)	
						Sc	Ti	Sc	Ti
B-benzene	$C_{48}B_{24}H_{48}Si_{24}O_{36}$	17.92	13.84	1.09	0.63	7.0[b]	5.6[a]	104[b]	83.5[a]
(B-biphenyl)[bc]	$C_{96}B_{48}H_{96}Si_{24}O_{36}$	24.90	18.49	1.98	1.47	8.5	6.8	80.9	64.7
(B-phenanthrene)[bc]	$C_{120}B_{48}H_{96}Si_{24}O_{36}$	24.87	18.15	1.77	1.31	8.1	6.5	82.6	66.1
(B-E-1,2-diphenylethylene)[b]	$C_{120}B_{48}H_{120}Si_{24}O_{36}$	27.72	21.48	2.58	2.06	8.1	6.4	56.2	45.0
(B-diphenylacetylene)[b]	$C_{120}B_{48}H_{96}Si_{24}O_{36}$	28.14	21.84	2.72	2.21	8.1	6.5	53.6	42.9

[a] The systems encounter the problem of steric effects among absorbed H_2. [b] The D_g and D_v are only estimated with the assumption of 5(4) H_2 molecules adsorbed on each Sc(Ti) site without real modeling. [c] The metal decorated frameworks are most likely not stable.

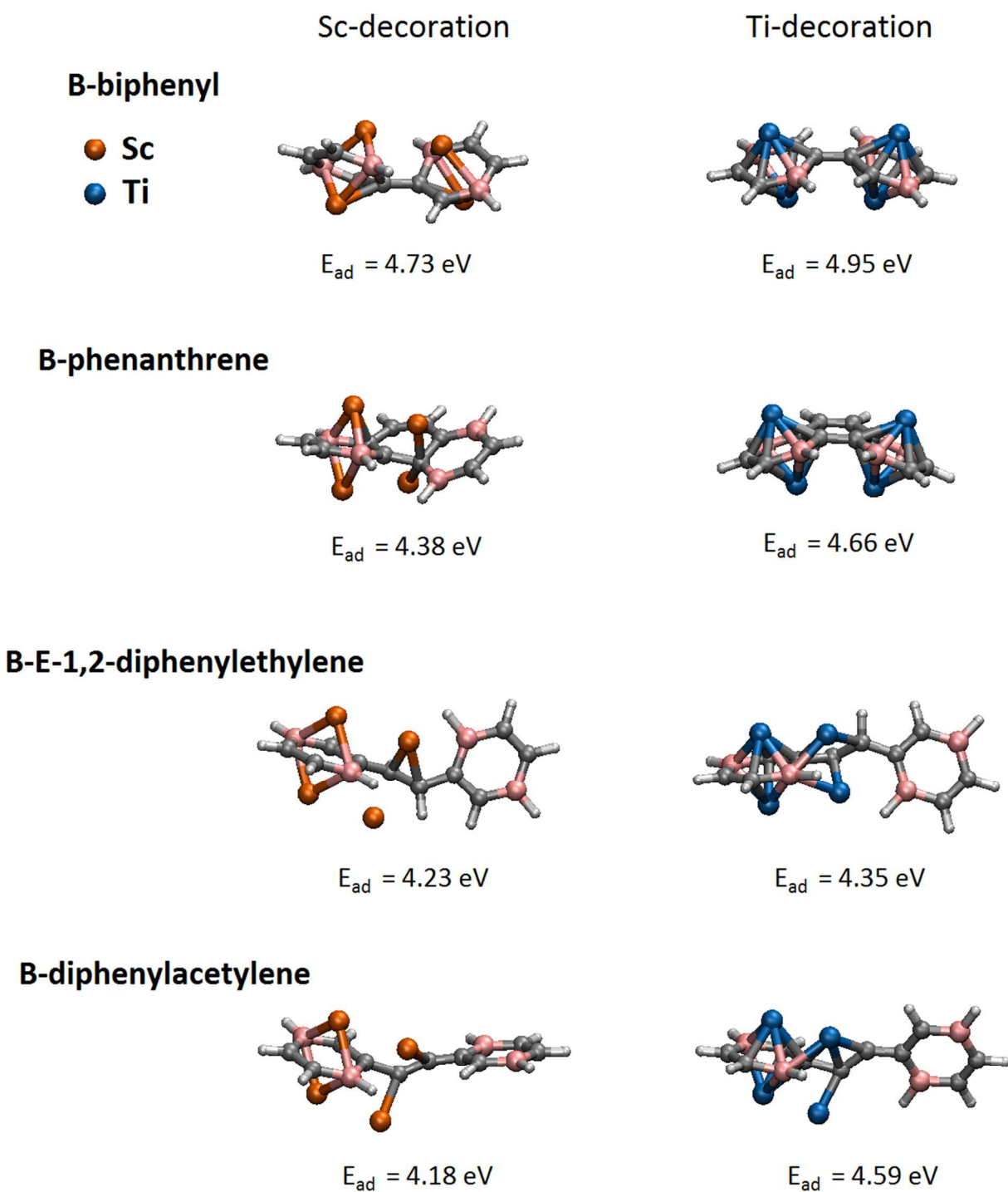## S3. Optimized molecular structures

Figure S1. The structures of distorted linker molecules with metal adsorption (labeled with the average metal adsorption energy). Orange: Sc, blue: Ti, grey: C, pink: B, white: H.
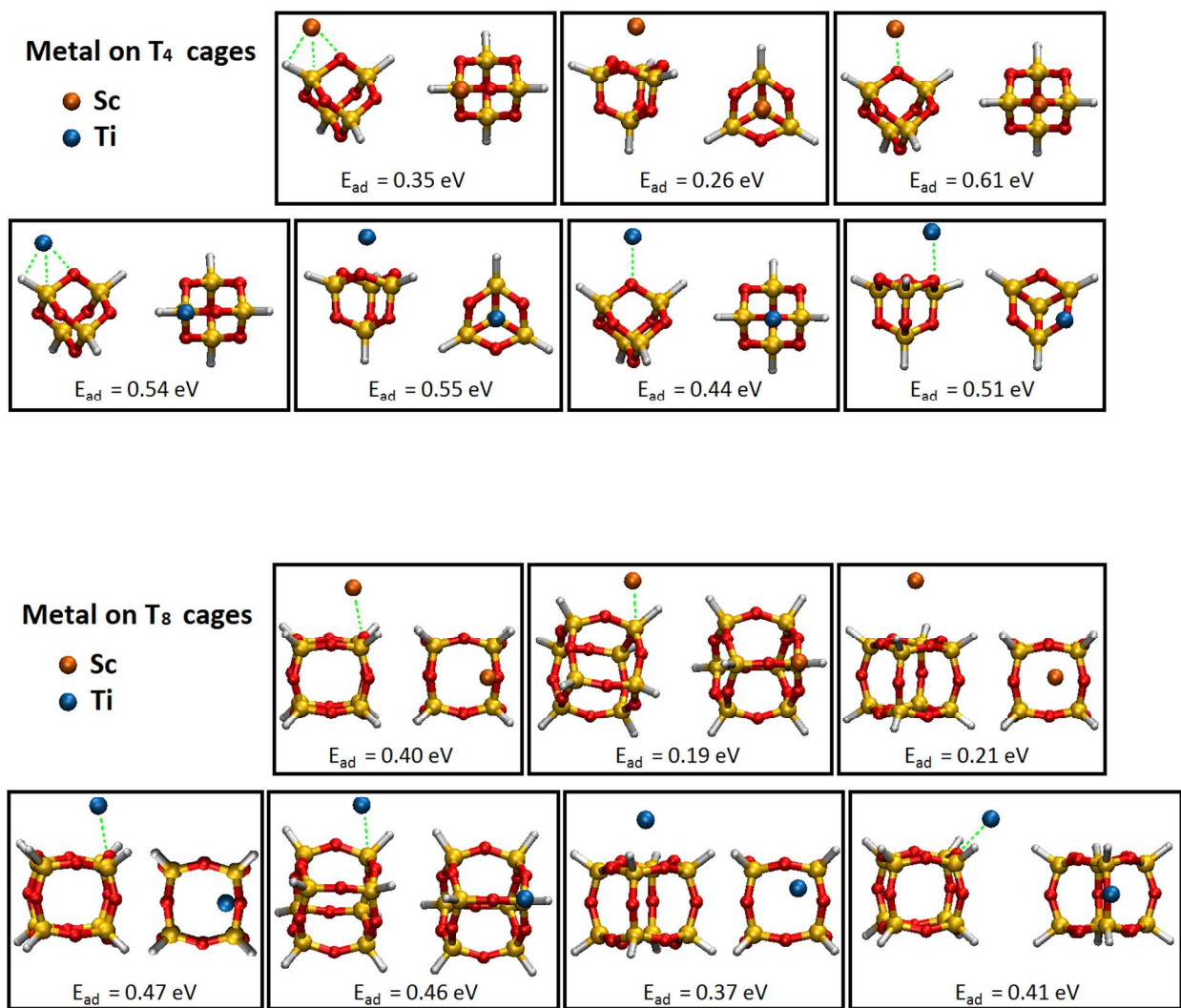
Metal on T₄ cages
- Sc
- Ti

$E_{ad} = 0.35$ eV $E_{ad} = 0.26$ eV $E_{ad} = 0.61$ eV

$E_{ad} = 0.54$ eV $E_{ad} = 0.55$ eV $E_{ad} = 0.44$ eV $E_{ad} = 0.51$ eV

Metal on T₈ cages
- Sc
- Ti

$E_{ad} = 0.40$ eV $E_{ad} = 0.19$ eV $E_{ad} = 0.21$ eV

$E_{ad} = 0.47$ eV $E_{ad} = 0.46$ eV $E_{ad} = 0.37$ eV $E_{ad} = 0.41$ eV

Figure S2. Optimized structures of Sc and Ti adsorbed on T_4 and T_8 cages viewed from different perspectives. The corresponding metal adsorption energies are indicated. Orange: Sc, blue: Ti, yellow: Si, red: O, white: H.
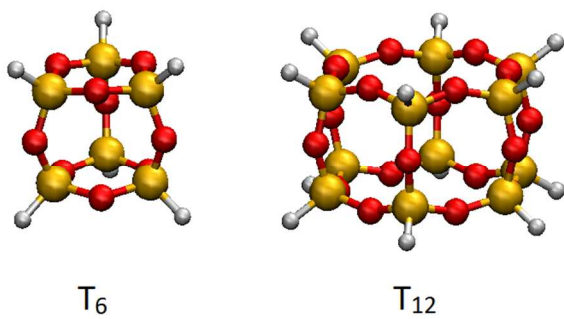
Figure S3. Optimized structures of T_6 and T_{12} cages. Yellow: Si, red: O, white: H

S4. Comment on the H$_2$ expulsion from the Sc coordination sphere

As mentioned in Section 3.2 of the main text, Sc decorated, isolated B-biphenyl and B-phenanthrene can only bind 19 H$_2$ molecules instead of 20 H$_2$. This can be related to the fact that on these linker molecules, neighboring Sc centers start to interact, which renders the space around the Sc atoms too crowded to fit 5 H$_2$ molecules per metal atom. This in return results in the expulsion of one H$_2$ molecule from the Sc coordination sphere, as shown by the long Sc-H distances of over 4 Å (**Figure 4a** of main text). However, the expelled H$_2$ molecule is not completely separated from the Sc-(H$_2$)$_x$ moiety. That H$_2$ still interacts via dispersive forces with the other H$_2$ molecules that are still coordinated to the Sc. This can be shown by the center to center distance between the expelled H$_2$ and the closest H$_2$ of 3.02 Å, which is close to the optimized distance between two free H$_2$ molecules (3.18 Å) in PBE-D3.

To cross check our observation of H$_2$ expulsion, we have also optimized the geometries of the concerned structures using the optB88-vdW functional[S3] and the PBE-TS functional.[S4] Both approaches attempt to account for dispersive interactions, similar to the PBE-D3 functional used in this study. The calculations at both optB88-vdW and PBE-TS levels predict that H$_2$ expulsion does occur on Sc decorated B-biphenyl and B-phenanthrene, but not to the counterparts with Ti decoration. In other words, the optB88-vdW level and PBE-TS results are consistent with the PBE-D3 results.

References :

(S1) Li, X.-D.; Zhang, H.; Miyamoto, Y.; Tang, Y.-J.; Wang, G.-Y. Computational Design of Tetrahedral Silsesquioxane-Based Porous Frameworks with Diamond-Like Structure as Hydrogen Storage Materials. *Struct. Chem.* **2014**, *25*, 177–185.

(S2) Li, X.-D.; Zang, H.-P.; Wang, J.-T.; Wang, J.-F.; Zhang, H. Design of Tetraphenyl Silsesquioxane Based Covalent-Organic Frameworks as Hydrogen Storage Materials. *J. Mater. Chem. A* **2014**, *2*, 18554-18561.

(S3) Klimeš, J.; Bowler, D. R.; Michaelides, A. Chemical Accuracy for the Van Der Waals Density Functional. *J. Phys.: Condens. Matter* **2010**, *22*, 022201.

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