# **Supporting Information**

# Design of Lewis Pair-Functionalized Metal Organic Frameworks for CO<sub>2</sub> Hydrogenation

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#### 1. Optimized structures of the unit cell and primitive cell of UiO-66



Figure S1. Optimized structure of (a) UiO-66 unit cell and (b) UiO-66 primitive cell

#### 2. Optimization the CUTOFF and REL\_CUTOFF values

We tested the CUTOFF and REL\_CUTOFF values for the primitive cell of UiO-66. CUTOFF ranged from 300 Ry to 400 Ry in 10 Ry increments and REL\_CUTOFF was set to either 60 Ry or 80 Ry. Both REL\_CUTOFF values give essentially identical results, as seen in Figure S2. Also seen in this figure, a CUTOFF value of 330 Ry is converged.



Figure S2. Convergence of CUTOFF and REL\_CUTOFF for the total energy of a primitive cell of UiO-66. The lines are drawn as a guide to the eye.

#### 3. Basis set size tests

Finite basis sets have the potential to generate basis set superposition errors (BSSE) when computing adsorption or interaction energies. We have tested the size of basis sets to make sure the BSSE error is sufficiently small so that the adsorption energies are not significantly affected. The results are summarized in Table S1. The TZV2PX-MOLOPT basis set is the largest available in CP2K for the Quickstep method. The adsorption energy of CO<sub>2</sub> and H<sub>2</sub> calculated using the TZV2PX-MOLOPT basis set is very close to that calculated with the DZVP-MOLOPT basis set. As a result, we use DZVP-MOLOPT for all the calculations in this work.

	CP2K	CP2K	VASP
Eads (eV)	DZVP-MOLOPT	TZV2PX-MOLOPT	PAW
H <sub>2</sub> *	-0.59	-0.53	-0.44
$CO_2^*$	-0.93	-0.91	-0.95

Table S1. Adsorption energies of  $H_2$  and  $CO_2$  in UiO-66-P-BF<sub>2</sub> computed using different basis sets within CP2K. Adsorption energies computed from VASP are also reported.

Note: Energy data in this table are without ZPE correction.

#### 4. Accuracy of CP2K

#### 4.1 CP2K vs VASP for periodic systems

We compared the adsorption energy of CO<sub>2</sub> and H<sub>2</sub> calculated from CP2K<sup>1</sup> with VASP.<sup>2,3</sup> The parameters for VASP calculations are same as used previously.<sup>4-6</sup> The Perdew-Burke-Ernzerhof functional<sup>7</sup> was used to describe electron exchange-correlation with an energy cutoff of 400 eV and a  $2\times2\times2$  k-point grid generated from the Monkhorst-Pack scheme. Geometry optimizations were performed until the maximum force on each atom was less than 0.03 eV/Å. The results of these calculations are included in Table S1. We can see that the adsorption energy for CO<sub>2</sub> computed from VASP is very close to the CP2K result, whereas the adsorption energy of H<sub>2</sub> computed from VASP is 0.09 eV smaller (less favorable) than from CP2K.

#### 4.2 CP2K vs Gaussian for molecules

As a test of the accuracy of using DFT for the systems studied in this work, we compared the adsorption energy of H<sub>2</sub> on gas phase P-BF<sub>2</sub> (not bound to UiO-66) calculated from CP2K with post-Hartree-Fock wavefunction calculations computed from Gaussian09.<sup>8</sup> We see from Table S2 that the CP2K DFT adsorption energy is in reasonably good agreement with our MP2, MP4SDTQ, and CCSD(T) results. The error in the DFT energy is about 0.08 eV. We also compare our CP2K calculations for CO<sub>2</sub> and H<sub>2</sub> on **FLP1**, with and without ZPE corrections, to Gaussian calculations with the M06-2X functional. Table S3 reports energy differences for five processes from our CP2K calculations and M06-2X functional calculations reported by Theuergarten et al.<sup>9,10</sup> H<sub>2(cis)</sub>\* is the adsorption energy of H<sub>2</sub> resulting in dissociated H atoms facing each other in the cis configuration (see 2H\* in Figure S7b). H<sub>2(trans)</sub>\* is the adsorption energy of H<sub>2</sub> where the H atoms are facing away from each other in a trans configuration.  $\Delta E$ H<sub>2(cis→trans)</sub> denotes the energy difference between H<sub>2(cis)</sub>\* and H<sub>2(trans)</sub>\* adsorption energy for CO<sub>2</sub>. We see that the CP2K calculations are in good agreement with the results calculated from the more accurate M06-2X functional.<sup>9,10</sup>

	CP2K	Gaussian	Gaussian	Gaussian
	DFT	MP2	MP4SDTQ	CCSD(T)
E <sub>ads</sub> (eV)	DZVP-MOLOPT	6-311++g(d,p)	6-311++g(d,p)	6-311++g(d,p)
H <sub>2</sub> adsorption in P-BF <sub>2</sub>	-0.34	-0.27	-0.26	-0.26

Table S2. The adsorption energy of H<sub>2</sub> in P-BF<sub>2</sub> using different methods.

Note: Energy data in this table are without ZPE correction.

	$E_{ m ads}$ (H <sub>2(cis)</sub> *)	$E_{ m ads}$ (H <sub>2(trans)</sub> *)	$\frac{\Delta E}{(\mathrm{H}_{2(\mathrm{cis} \rightarrow \mathrm{trans})})}$	$\Delta E_{\rm a}$ (H <sub>2</sub> dissociation)	Eads (CO <sub>2</sub> *)
CP2K(with ZPE)	-0.92	-1.07	-0.15	0.43	-0.91
CP2K(without ZPE)	-1.25	-1.44	-0.19	0.37	-1.22
Gaussian(without ZPE)	$-1.10^{8}$	-1.249	$-0.14^{8}$	0.438	$-1.29^{10}$

Table S3. Comparison of the energy differences for five different processes in **FLP1** computed from two different methods. Gaussian calculations employed the M06-2X functional and 6- $311++G^{**}$  basis set were used for all elements.

## 5. Lattice constants of UiO-66, UiO-66-P-BF2 and UiO-66-P-BF2 with adsorbed H2 or CO2

Table S4. The optimized lattice constants of UiO-66, UiO-66-P-BF<sub>2</sub>, and UiO-66-P-BF<sub>2</sub> with adsorbed  $H_2$  or CO<sub>2</sub> (lattice parameter: Å, angle: degrees)

		UiO-66	UiO-66-P- BF <sub>2</sub>	$H_2*$	CO <sub>2</sub> *
Lattice	а	14.788	14.784	14.776	14.762
constants	b	14.788	14.777	14.770	14.776
	с	14.788	14.777	14.791	14.800
	α	60	60	60	60
Angle	β	60	60	60	60
	γ	60	60	60	60
Energy (hartree)	Optimized cell	-1087.15593	-1183.024518	-1220.820035	-1184.208074
	Fixed cell		-1183.024482	-1220.819943	-1184.208022
Energy difference (eV) <sup>a</sup>			0.000978	0.002488	0.001419

Note: <sup>a</sup> Energy difference calculated by the equation  $\Delta E = E(\text{Fixed cell}) - E(\text{Optimized cell})$ 

#### 6. Physorption energies of H<sub>2</sub> and CO<sub>2</sub> in UiO-66

MD calculation runs at 1000 K with 0.5 fs time step for 3000 steps, for a total simulation time of 1.5 ps. We selected different low-energy configurations from the MD run and optimized these configurations to find local minima.

Table S5. The physorption energies for ten different configurations of  $H_2$  and  $CO_2$  in UiO-66 with (without) ZPE corrections.

Eads (eV)	1	2	3	4	5	6	7	8	9	10
H <sub>2</sub>	-0.19	-0.18	-0.16	-0.18	-0.18	-0.12	-0.10	-0.19	-0.18	-0.11
	(-0.17)	(-0.16)	(-0.14)	(-0.16)	(-0.16)	(-0.10)	(-0.08)	(-0.17)	(-0.16)	(-0.09)
$CO_2$	-0.22	-0.18	-0.26	-0.16	-0.14	-0.17	-0.19	-0.22	-0.16	-0.26
	(-0.19)	(-0.15)	(-0.23)	(-0.13)	(-0.11)	(-0.14)	(-0.16)	(-0.19)	(-0.13)	(-0.23)

# 7. Structural details of configurations in Figures 3 and 4 $H_{2(vdW)}: d_{H_a-H_b} = 0.732 \text{ Å}, d_{H_a-B} = 3.057 \text{ Å}, d_{H_b-N_b} = 2.800 \text{ Å};$ TS1: $d_{H_a-H_b} = 0.904 \text{ Å}, d_{H_a-B} = 1.492 \text{ Å}, d_{H_b-N_b} = 1.479 \text{ Å}$ $CO_{2(vdW)}: d_{C-O_a} = 1.176 \text{ Å}, d_{C-O_b} = 1.175 \text{ Å}, \angle_{O_a-C-O_b} = 177.86^\circ, d_{O_a-B} = 3.323 \text{ Å}, d_{C-N_b} = 3.129$ Å; TS2: $d_{C-O_a} = 1.205 \text{ Å}, d_{C-O_b} = 1.182 \text{ Å}, \angle_{O_a-C-O_b} = 158.05^\circ, d_{O_a-B} = 2.194 \text{ Å}, d_{C-N_b} = 2.130 \text{ Å}$

#### 8. Reaction energy profiles for reactions of Figure 5



Figure S3. Reaction energy profile for  $H_2$  dissociative adsorption in UiO-66-P-BF<sub>2</sub>. The curve is drawn as a guide to the eye.



Figure S4. Reaction energy profile for CO<sub>2</sub> adsorption in UiO-66-P-BF<sub>2</sub>. The curve is drawn as a guide to the eye.



Figure S5. Reaction energy profile of physisorbed  $CO_2$  reacting with dissociatively adsorbed H atoms in UiO-66-P-BF<sub>2</sub>. The curve is drawn as a guide to the eye.



Figure S6. Reaction energy profile of physisorbed  $H_2$  reacting with chemisorbed  $CO_2$  in UiO-66-P-BF<sub>2</sub>. The curve is drawn as a guide to the eye.

# **9.** Structural details of configurations involving the reaction pathways of Figure 5 CO<sub>2</sub>+2H\*:

 $\begin{aligned} &d_{c-o_a} = 1.183 \text{ Å, } d_{c-o_b} = 1.169 \text{ Å, } \angle_{o_a - c - o_b} = 178.15^\circ, \ d_{o_b - H_b} = 1.999 \text{ Å, } d_{c-H_a} = 2.554 \text{ Å, } d_{H_b - N_b} \\ &= 1.021 \text{ Å, } d_{H_a - B} = 1.214 \text{ Å.} \end{aligned}$  **TS3:**  $&d_{c-o_a} = 1.280 \text{ Å, } d_{c-o_b} = 1.214 \text{ Å, } \angle_{o_a - C - o_b} = 133.83^\circ, \ d_{o_b - H_b} = 1.296 \text{ Å, } d_{c-H_a} = 1.217 \text{ Å, } d_{H_b - N_b} \\ &= 1.210 \text{ Å, } d_{H_a - B} = 1.632 \text{ Å.} \end{aligned}$  **HCOOH:**  $&d_{c-o_a} = 1.355 \text{ Å, } d_{c-o_b} = 1.216 \text{ Å, } \angle_{o_a - C - o_b} = 123.14^\circ, \ d_{o_b - H_b} = 1.001 \text{ Å, } d_{c-H_a} = 1.106 \text{ Å, } d_{H_b - N_b} \\ &= 1.860 \text{ Å, } d_{H_a - B} = 2.911 \text{ Å.} \end{aligned}$  **H2+CO2\*:**  $&d_{H_a - H_b} = 0.727 \text{ Å, } d_{H_b - C} = 3.165 \text{ Å, } d_{H_a - O_a} = 3.810 \text{ Å, } d_{c-o_a} = 1.312 \text{ Å, } d_{c-o_b} = 1.209 \text{ Å, } \\ &\angle_{o_a - C - o_b} = 130.69^\circ, \ d_{c-N_2} = 1.457 \text{ Å, } d_{o_a - B} = 1.523 \text{ Å.} \end{aligned}$  **TS4:**  $&d_{H_a - H_b} = 1.003 \text{ Å, } d_{H_b - C} = 1.455 \text{ Å, } d_{H_a - O_a} = 1.324 \text{ Å, } d_{c-o_a} = 1.548 \text{ Å, } d_{c-o_b} = 1.212 \text{ Å, } \\ &\angle_{o_a - C - o_b} = 123.41^\circ, \ d_{c-N_b} = 1.477 \text{ Å, } d_{o_a - B} = 1.514 \text{ Å.} \end{aligned}$ 

## [HCO+OH]\*:

 $d_{H_a-H_b} = 2.520$  Å,  $d_{H_b-C} = 1.096$  Å,  $d_{H_a-O_a} = 0.970$  Å,  $d_{C-O_a} = 2.392$  Å,  $d_{C-O_b} = 1.208$  Å,  $d_{C-N_b} = 1.463$  Å,  $d_{O_a-B} = 1.448$  Å.

10. Structural details of configurations involving the reaction pathways of Figure 6.

**(a)** 









Figure S7. Structural details of  $CO_2$  hydrogenation (a) in the gas phase, (b) catalyzed by **FLP1**, (c) catalyzed by P-BF<sub>2</sub>.



Figure S8. Reaction energy profile for  $CO_2$  hydrogenation occurring in the gas phase. The curve is drawn as a guide to the eye.



Figure S9. Reaction energy profile for  $H_2$  dissociation on **FLP1.** The curve is drawn as a guide to the eye.



Figure S10. Reaction energy profile for physisorbed  $CO_2$  reacting with dissociatively adsorbed  $H_2$  on **FLP1**. The curve is drawn as a guide to the eye.



Figure S11. Reaction energy profile for  $H_2$  dissociation on P-BF<sub>2</sub>. The curve is drawn as a guide to the eye.



Figure S12. Reaction energy profile for physisorbed  $CO_2$  reacting with dissociatively adsorbed  $H_2$  on P-BF<sub>2</sub>. The curve is drawn as a guide to the eye.

## 11. Effect of zero point energy (ZPE) correction



Figure S13. Potential energy surface for  $CO_2$  hydrogenation in UiO-66-P-BF<sub>2</sub> through physisorbed  $CO_2$  reacting with 2H\*.



Figure S14. Potential energy surface for  $CO_2$  hydrogenation in UiO-66-P-BF<sub>2</sub> though physisorbed H<sub>2</sub> reacting with  $CO_2^*$ .



Figure S15. Relative energy profiles for  $CO_2$  hydrogenation without ZPE corrections in the gas phase (black line), catalyzed by FLP1 (yellow line), catalyzed by P-BF<sub>2</sub> (blue line) and catalyzed by UiO-66-P-BF<sub>2</sub> (green line).

# 12. Structural details of Lewis pair sites

Table S6. Structur	ral details	of three	different I	Lewis pair sit	es, with and	d without cher	nisorbed H	<b>H</b> <sub>2</sub> .
Bond lengths, bond angles, torsion angles and the base-acid site distances, $N_b$ B are reported								
(lengths: Å, angles: degrees). Atom labels are identified in Figure S16.								
Lewis Pair	Bond	Bond	Bond	Angle	Angle	Torsion	Dist	

Lewis Pair	Bond	Bond	Bond	Angle	Angle	Torsion	Dist
	N <sub>a</sub> -B	$N_a$ - $N_b$	B-F <sub>a</sub>	N <sub>b</sub> -N <sub>a</sub> -B	N <sub>a</sub> -B-F <sub>a</sub>	$N_b-N_a-B-F_a$	$N_b {\cdots} B$
			(Ca)		(Ca)	(Ca)	
FLP1	1.46	1.39	1.57	110.90	117.60	48.91	2.35
FLP1/2H*	1.61	1.36	1.62	112.55	110.86	131.03	2.48
P-BF <sub>2</sub>	1.43	1.36	1.31	121.66	122.01	0.08	2.46
P-BF <sub>2</sub> /2H*	1.67	1.35	1.40	119.25	105.46	120.78	2.61
UiO-66-P-BF <sub>2</sub>	1.44	1.39	1.34	122.22	122.34	22.84	2.48
UiO-66-P-	1.66	1.35	1.40	118.96	106.44	136.62	2.60
$BF_2/2H^*$							



Figure S16. Torsion angles in (a) **FLP1**, (b)  $P-BF_2$  and (c) UiO-66-P-BF<sub>2</sub>.

## **13.** Lewis acidity and basicity

Table S7. Hydride and proton attachment energies computed from Gaussian 09.8

	$\Delta G_{pa}(eV)$	$\Delta G_{ha}(eV)$	$\Delta G_{ha} + \Delta G_{pa} (eV)$
FLP1	-9.55	-4.25	-13.80
P-BF <sub>2</sub>	-9.07	-3.21	-12.28
Note:	$\Delta G_{\rm pa} = G([\rm XH]^+) - G$	$G(\mathbf{X}) - G([\mathbf{H}]^+)$	(1)
	$\Delta G_{\rm ha} = G([\rm XH]^{-}) - G$	$G(\mathbf{X}) - G([\mathbf{H}]^{-})$	(2)

where G(X),  $G([H]^-)$ ,  $G([H]^+)$ ,  $G([XH]^-)$  and  $G([XH]^+)$  represent Gibbs free energies of X (X= **FLP1** or P-BF<sub>2</sub>), hydride, proton,  $[XH]^-$  and  $[XH]^+$ , respectively.  $\Delta G_{ha}$  and  $\Delta G_{pa}$  represent the Gibbs free energies for proton attachment and hydride attachment, respectively. A more negative  $\Delta G_{pa}$  value corresponds to a stronger basicity, and a more negative  $\Delta G_{ha}$  value corresponds to a stronger acidity.<sup>11</sup>

# 14. Charge distributions

The density derived electrostatic and chemical (DDEC) method<sup>12,13</sup> was used to analyze the atomic charge distribution for **FLP1**, P-BF<sub>2</sub>, and UiO-66-P-BF<sub>2</sub>, with and without chemisorbed H<sub>2</sub>. The purpose of these calculations is to identify differences in electronic effects due to the substituent groups or presence of the framework. The results of the calculations are shown in Table S8.

Table S8. The DDEC charges of Lewis acid (B) and base ( $N_b$ ) sites of **FLP1**, P-BF<sub>2</sub> and UiO-66-P-BF<sub>2</sub> without and with chemisorbed H<sub>2</sub>.

Charge(e)	Lewis acid	Lewis base	ŀ	$\mathbf{I}_2$
	В	$N_b$	Ha	$H_{b}$
FLP1	+0.59	-0.36		
<b>FLP1</b> /2H*	+0.19	-0.20	-0.13	+0.31
P-BF <sub>2</sub>	+0.88	-0.29		
$P-BF_2/2H^*$	+0.58	-0.12	-0.24	+0.32
UiO-66-P-BF <sub>2</sub>	+0.90	-0.29		
UiO-66-P-BF <sub>2</sub> /2H*	+0.58	-0.13	-0.23	+0.32

## 15. The effect of van der Waals interaction

Table S9. The adsorption energies of H<sub>2</sub> and CO<sub>2</sub>+2H\* in P-BF<sub>2</sub> and UiO-66-P-BF<sub>2</sub> with/without D3 dispersion corrections.<sup>14</sup> Zero point energy corrections have not been applied (see Figure S15).

E <sub>ads</sub> (eV)	P-BF <sub>2</sub> /	UiO-66-P-BF <sub>2</sub> /	P-BF <sub>2</sub> /	UiO-66-P-BF <sub>2</sub> /
	2H*	2H*	$CO_2+2H^*$	CO <sub>2</sub> +2H*
Without vdW functional	-0.30	-0.53	-0.43	-0.66
With vdW functional	-0.34	-0.59	-0.52	-0.99

#### 16. Proposed synthetic pathway for UiO-66-P-BF2

We here sketch out a potential pathway for synthesis of UiO-66-PBF<sub>2</sub> based on combining the ideas for the synthesis of **FLP1**<sup>10</sup> with those for synthesis of UiO-66.<sup>15</sup> Synthesis of UiO-66-PBF<sub>2</sub> could potentially be carried out by attaching a pyrazole group to the BDC linker, followed by synthesis of UiO-66 using a mixture of the functionalized and non-functionalized BDC linkers and then attaching a  $-BF_2$  group to the functional groups embedded into UiO-66 using post-synthetic modification. Attaching the  $-BF_2$  group after the pyrazole functionalized linker is incorporated into the MOF means that quenching of the Lewis pair cannot occur, since the Lewis pair is formed in situ. The steps for the proposed synthesis of are UiO-66-PBF<sub>2</sub> shown schematically in Scheme S1.



Scheme S1. Potential synthesis pathway for UiO-66-P-BF<sub>2</sub>.

The first step in Scheme S1 involves synthesis of a *H*-prazole functionalized H<sub>2</sub>BDC precursor via Negishi coupling that has been used for similar systems.<sup>16</sup> In step 2 the methyl groups on the functionalized dimethylbenzyl species can then be converted to carboxylic acid groups via the Amoco process.<sup>17</sup> We note that an alternate procedure using milder conditions, such as oxidation by H<sub>2</sub>O<sub>2</sub>, might offer higher selectivity. The resulting *H*-pyrazole functionalized H<sub>2</sub>DBC linker can be incorporated into UiO-66 in small quantities by mixing with unfunctionalized H<sub>2</sub>DBC, as shown in Step 3, where 10% functionalized linkers are used, for example, so that on average slightly less than one functionalized BDC will be found in each primitive cell. The resulting functionalized UiO-66 is denoted UiO-66-P. This material can then be exposed to HBF<sub>2</sub>, which will react with the pyrazole ring on the functionalized BDC linkers to produce a hydrogenated UiO-66-PBF<sub>2</sub> with chemisorbed 2H\*, as occurs in the synthesis of **FLP1**.<sup>10</sup> This material can be heated to release H<sub>2</sub> if the pure UiO-66-PBF<sub>2</sub> is desired.

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