

***Supporting Information For:***

**Application of hard and soft acid base theory to uncover Lewis bases'  
destructiveness to UiO-66 type metal organic frameworks in aqueous  
solutions**

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## Equations

Vertical ionization potential (VIP): $E(N-1) - E(N)$	Eq.S1
Vertical electron affinity (VEA): $E(N) - E(N+1)$	Eq.S2
Electronegativity ( $\chi$ ): $(VIP+VEA)/2$	Eq.S3
Chemical potential ( $\mu$ ): $-\chi$	Eq.S4
Chemical hardness ( $\eta$ ): $VIP-VEA$	Eq.S5
Softness (S): $1/\eta$	Eq.S6
Fukui functions for electrophilic attack $f^-(\mathbf{r}) = \rho_N(\mathbf{r}) - \rho_{N-1}(\mathbf{r})$	Eq.S7
Local softness for electrophilic attack: $s^-(\mathbf{r}) = Sf^-(\mathbf{r})$	Eq.S8

## Tables

Table.S 1 The solubility of H<sub>2</sub>BDC and NH<sub>2</sub>-H<sub>2</sub>BDC in water at different pH.

	H <sub>2</sub> BDC	NH <sub>2</sub> -H <sub>2</sub> BDC
pH=2	2.1±0.4	90.0±1.4
pH=3	3.1±0.2	88.0±3.3
pH=4	18.4±0.7	360.0±4.7
pH=5	538.3±2.2	>1000mg/L
pH=6	>1000mg/L	>1000mg/L
pH=7	>1000mg/L	>1000mg/L

Table.S 2 The  $\mu$  ( $-\chi$ ) of phosphate species.

	PO <sub>4</sub> <sup>3-</sup>	HPO <sub>4</sub> <sup>2-</sup>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	H <sub>3</sub> PO <sub>4</sub>
$\mu$ ( $-\chi$ )	-2.7	-3.0	-4.1	-5.1

Table.S 3 The  $\mu$  ( $-\chi$ ) and  $\eta$  of ligands of MOFs.

L-bases	I-BDC <sup>2-</sup>	Br-BDC <sup>2-</sup>	F-BDC <sup>2-</sup>	COOH-BDC <sup>2-</sup>	SO <sub>3</sub> H-BDC <sup>2-</sup>	NO <sub>2</sub> -BDC <sup>2-</sup>
$\mu$ ( $-\chi$ )	-3.53	-3.54	-3.76	-3.81	-3.90	-4.34
$\eta$	5.00	5.02	4.86	4.53	4.67	4.08

## Figures

Fig.S 1 The XRD patterns and FT-IR spectra of UiO-66, NH<sub>2</sub>-UiO-66, MIL-101(Fe) and NH<sub>2</sub>-MIL-101(Fe) in pure water at pH 2 and their ligands (H<sub>2</sub>BDC and NH<sub>2</sub>-H<sub>2</sub>BDC).

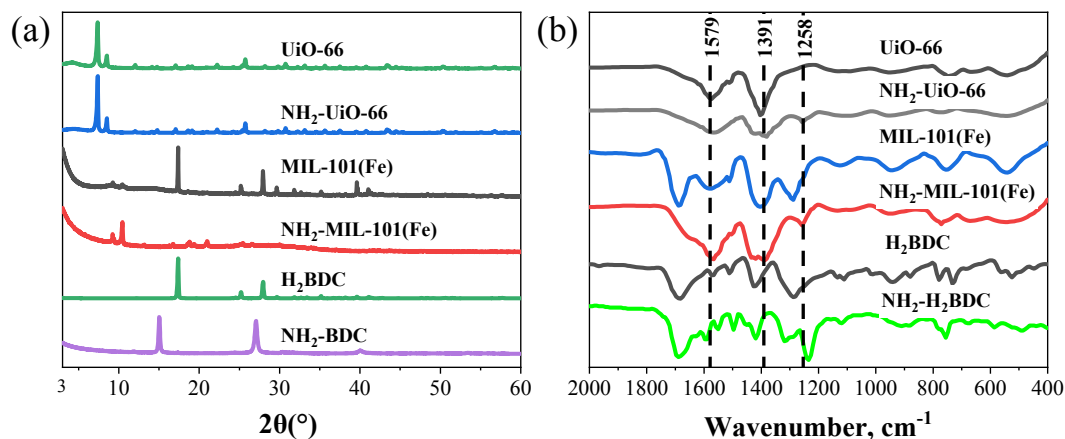


Fig.S 2 XPS analysis of NH<sub>2</sub>-UiO-66 before and after being treated in 3 mM solutions of F<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, AsO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup> at pH 4, respectively: F 1s (b), P 2p (b), As 2p (c) and S 2p (d).

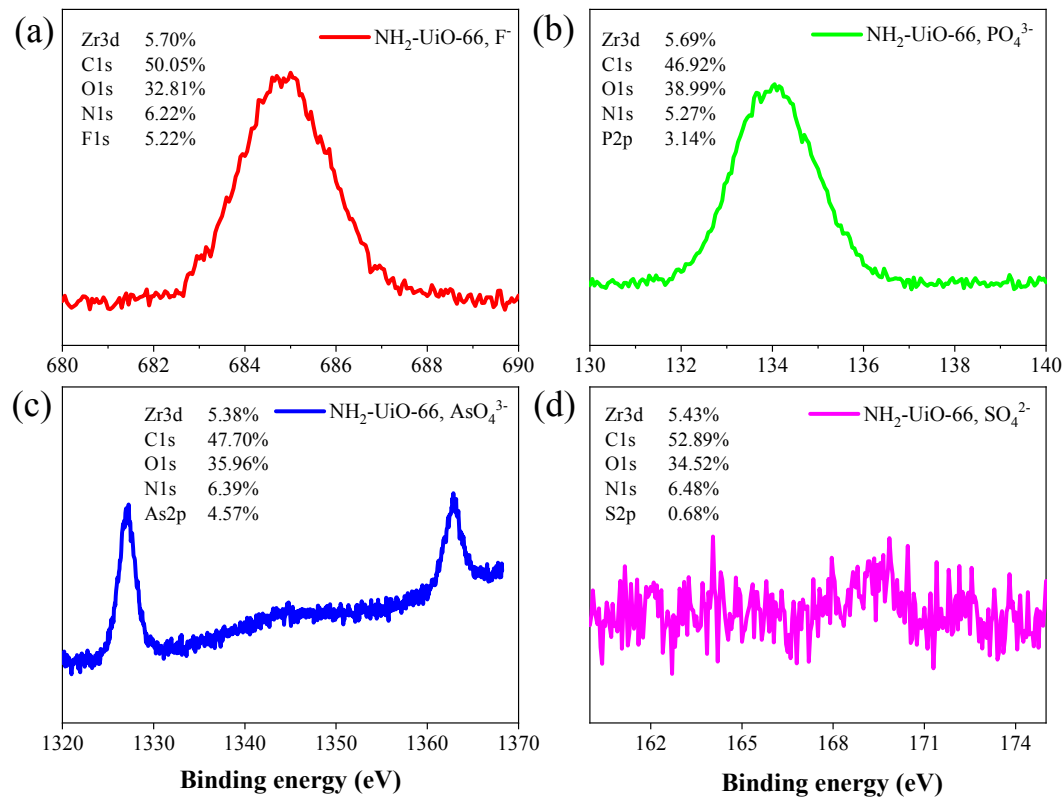


Fig.S 3 FT-IR spectra of UiO-66 and NH<sub>2</sub>-UiO-66 after being treated in 3 mM solution of F<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, AsO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup> at pH 4, respectively.

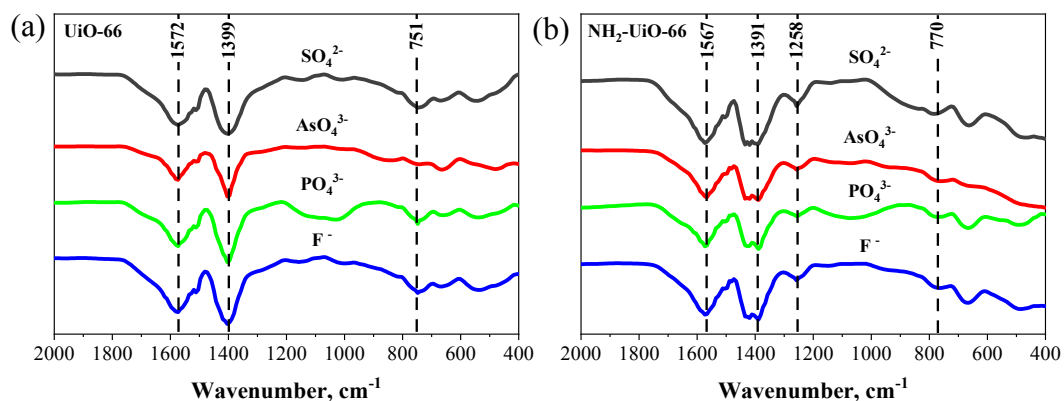


Fig.S 4 Local softness for electrophilic attack (*s*<sup>-</sup>) of L-bases.

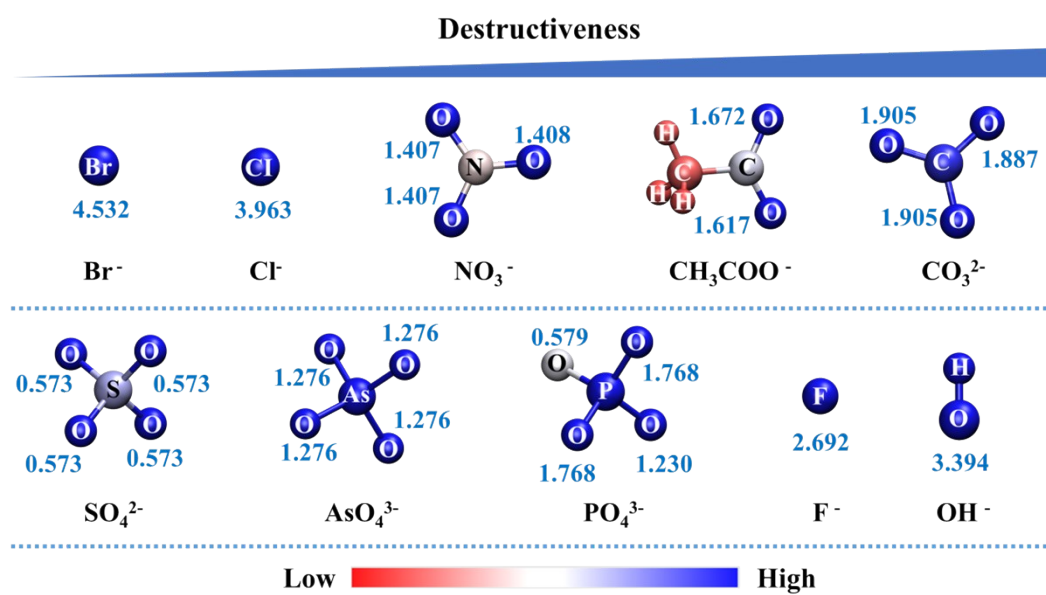


Fig.S 5 Charge of coordinating atoms (CCA) of conjugate acid of different L-bases.

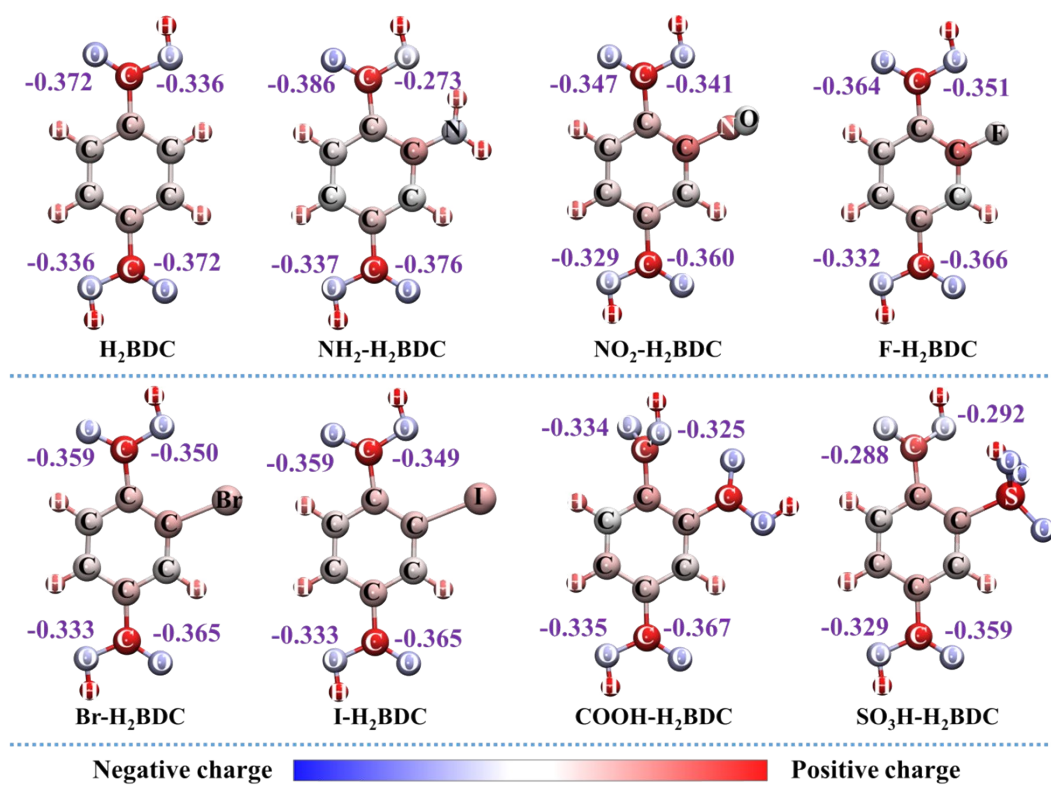


Fig.S 6 Distribution coefficient of phosphate.

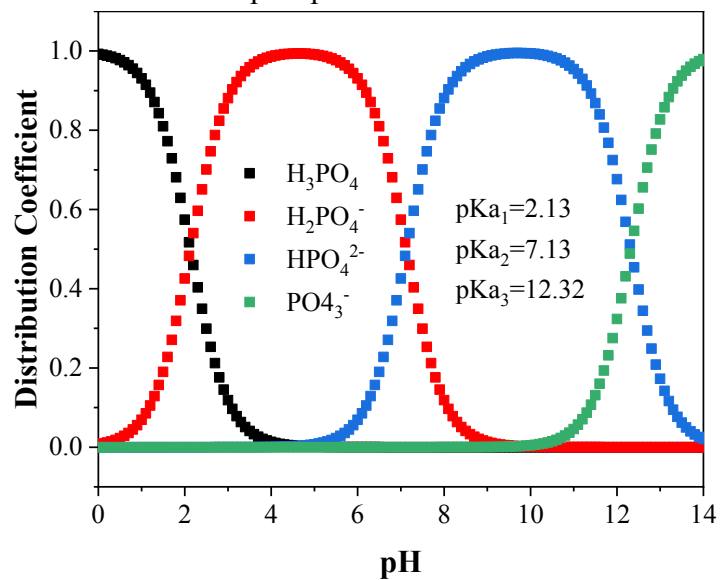


Fig.S 7 The structure and charge distribution of MOFs' ligand.

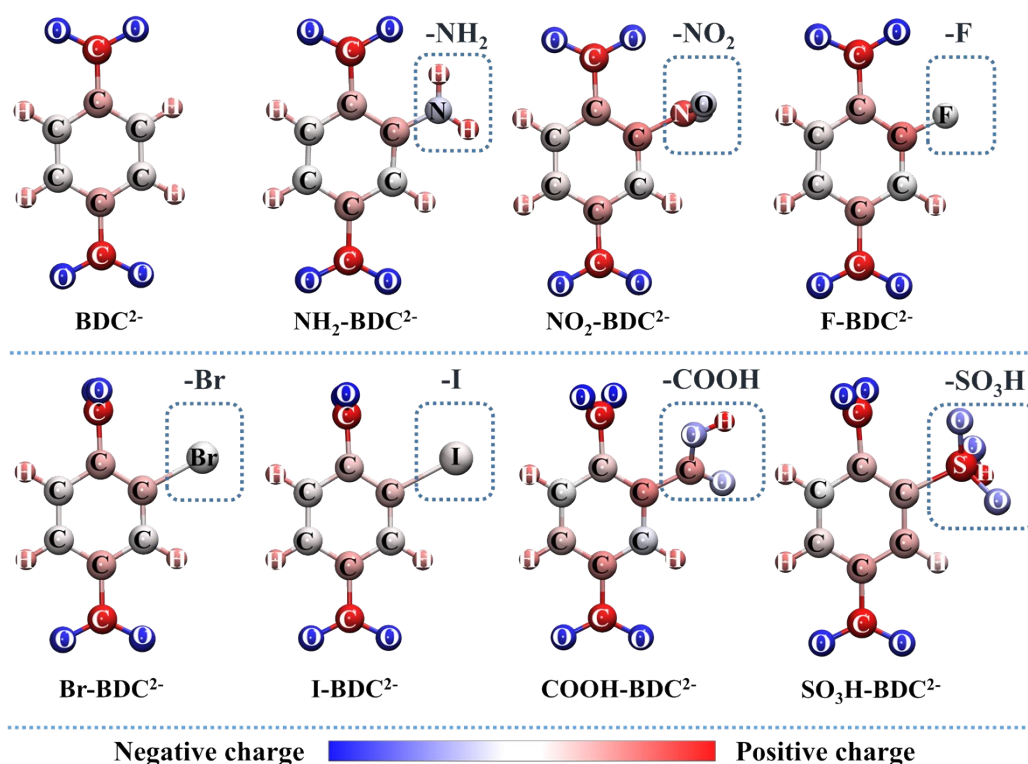
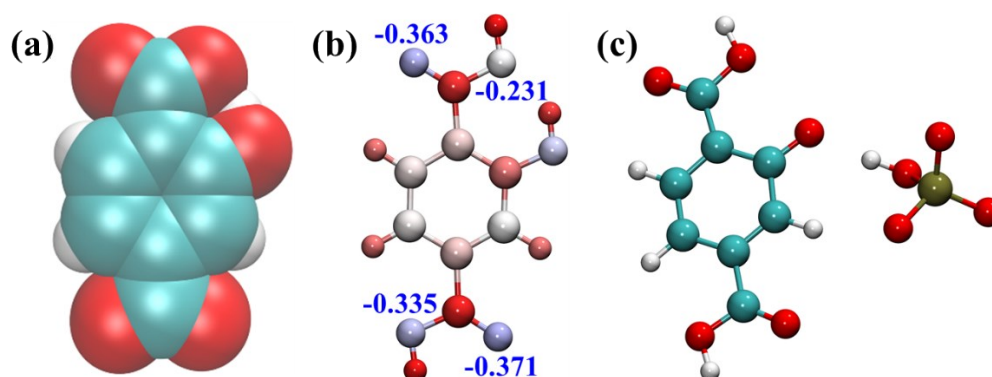


Fig.S 8 The optimized structure of OH-BDC<sup>2-</sup> showed by Van Der Waals radius (a), the CCA of OH-H<sub>2</sub>BDC (b) and the optimized structure of OH-H<sub>2</sub>BDC/PO<sub>4</sub><sup>3-</sup> (c).



As for OH-UiO-66, the symmetry of its carboxy groups was not affected by the -OH (Fig.S 8a) and the  $\mu(-\chi)$  of OH-BDC<sup>2-</sup> was -3.58, which was slightly higher than that of BDC<sup>2-</sup> (-3.68). However, as shown in Fig.S 8b, one of the coordinating atom of OH-H<sub>2</sub>BDC had obvious smaller negative charge (-0.231) than that of H<sub>2</sub>BDC (Fig.S 5). Therefore, it is hard to judge if OH-UiO-66 is more stable than UiO-66, only according to  $\mu(-\chi)$  and CCA. The pKa of -OH on OH-H<sub>2</sub>BDC is not found in the iBond database<sup>[1]</sup>, but the pKa of -OH on different compounds is relatively high, such as salicylic acid (13.2), phenol (9.99) and p-Hydroxybenzoic acid (9.33), implying H-Bond can form between OH-H<sub>2</sub>BDC and PO<sub>4</sub><sup>3-</sup> in a wide range of pH. Beyond expectation, according to the optimized structure of OH-H<sub>2</sub>BDC with PO<sub>4</sub><sup>3-</sup> (Fig.S 8c), the H on -OH on OH-

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H<sub>2</sub>BDC was grabbed by PO<sub>4</sub><sup>3-</sup>, instead of forming stable H-Bond between OH-H<sub>2</sub>BDC and PO<sub>4</sub><sup>3-</sup>. Apparently, -OH can not enhance the stability of MOFs by capturing L-bases.

#### Reference

[1] Internet bond-energy databank (pKa and BDE)--iBonD home page.  
<http://ibond.chem.tsinghua.edu.cn>