Supplementary Information

Structure Engineering through Modulator Incorporation in UiO-66-NH_2 Metal-Organic Frameworks for Piezoresponse Regulation

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1. Supplementary Text

Experimental Chemical Formula Calculation through TGA and NMR

To quantitively acquire the experimental dehydrated chemical formula of UiO-66-NH_2 (Zr, Hf) with different modulators, the details are discussed below, followed by a reported work[1].

First, the theoretical dehydrated chemical formula of UiO-66-NH_2 (Hf) is $Hf_6O_6(BDC\text{-}NH_2)_6$. Then, it undergoes the reaction through a heating process as follows: $Hf_6O_6(BDC\text{-}NH_2)_6$ (s) + O_2 (g) → HfO_2 (s) + CO_2 (g) + NO_2 (g) + H_2O (g), where the only remaining solid is HfO_2. As 1 mol $Hf_6O_6(BDC\text{-}NH_2)_6$ produces 6 mol HfO_2 and the molar weight of $Hf_6O_6(BDC\text{-}NH_2)_6$ and HfO_2 are 2241.84 g/mol and 210.49 g/mol, the normalized weight of $Hf_6O_6(BDC\text{-}NH_2)_6$ can be calculated as 2241.84/ (6×210.49) ≈177.5% if the final weight of HfO_2 is set as 100%. The contribution of one ligand molecule to the weight is calculated as (177.5%-100%)/6≈12.92%.

Meanwhile, the experimental dehydrated chemical formal with modulators can be noted as $Hf_6O_{6+x-y-z}(BDC\text{-}NH_2)_{6-x}(CH_3COO)_{2y}(HCOO)_{2z}$, where x, 2y, and 2z is the deficiency of $BDC\text{-}NH_2^{2-}$, the incorporated AA^-, and the incorporated FA^-, respectively.

Take Hf/70 AA for example, its normalized weight at 300 ˚C is 161.80% from the TGA result, so we can obtain this equation: 6-x= (161.80%-100%)/12.92% ≈4.78 and x is 1.22. It is also acquired that the $AA^-/BDC\text{-}NH_2^{2-}$ and $FA^-/BDC\text{-}NH_2^{2-}$ ratio from NMR peak area is 0.11 and 0.06, then 2y=4.78×0.11≈0.53 and 2z=4.78×0.06≈0.29. Finally, the dehydrated chemical formal of Hf/70 AA is $Hf_6O_{6.81}(BDC\text{-}NH_2)_{4.78}(CH_3COO)_{0.53}(HCOO)_{0.29}$.

Similarly, the normalized weight of $Zr_6O_6(BDC\text{-}NH_2)_6$ can be calculated as 232.4% and one ligand contribution is 22.07%, consistent with the reported work[2]. And its experimental dehydrated chemical formal with modulators can be noted as $Zr_6O_{6+x-y-z}(BDC\text{-}NH_2)_{6-x}(CH_3COO)_{2y}(HCOO)_{2z}$.

The calculated dehydrated chemical formulas of all samples are listed in **Table 1**.

2. Supplementary Figures

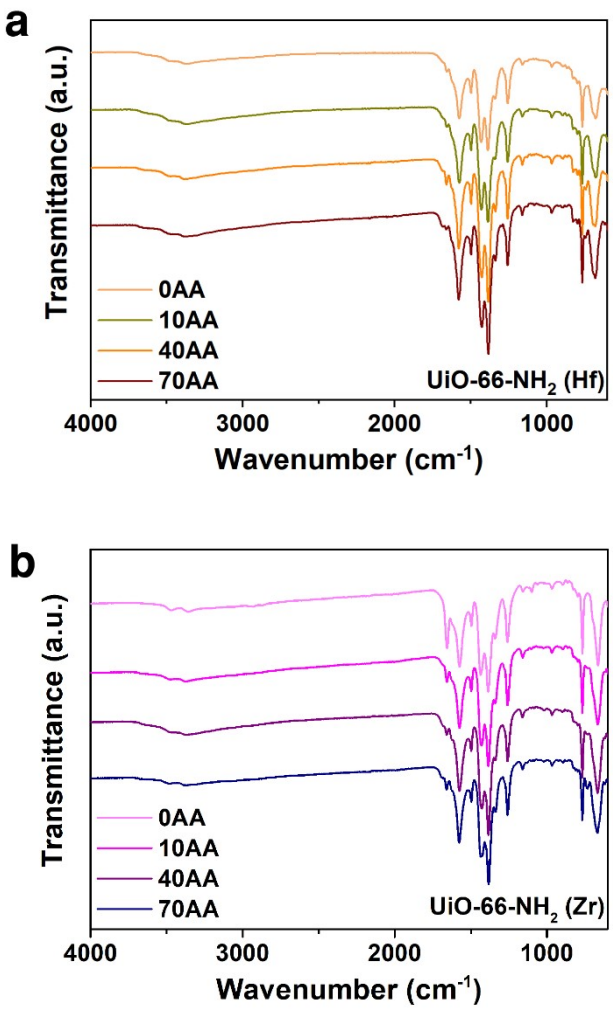

Figure S1. FTIR spectra of (a) UiO-66-NH_2 (Hf) and (b) UiO-66-NH_2 (Zr) with different amount of added AA.

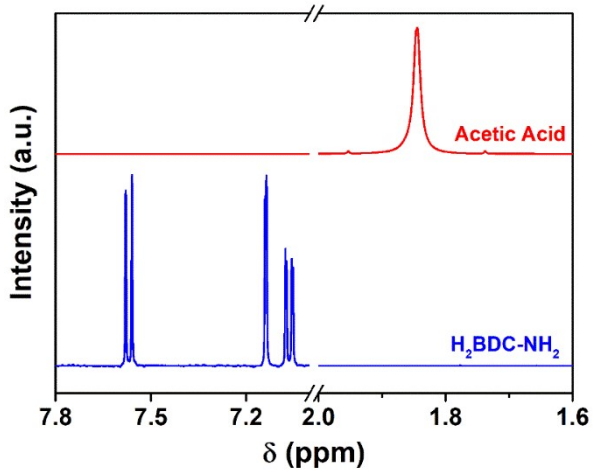

Figure S2. NMR of pure AA and $H_2BDC\text{-}NH_2$ in 1M NaOH D_2O.

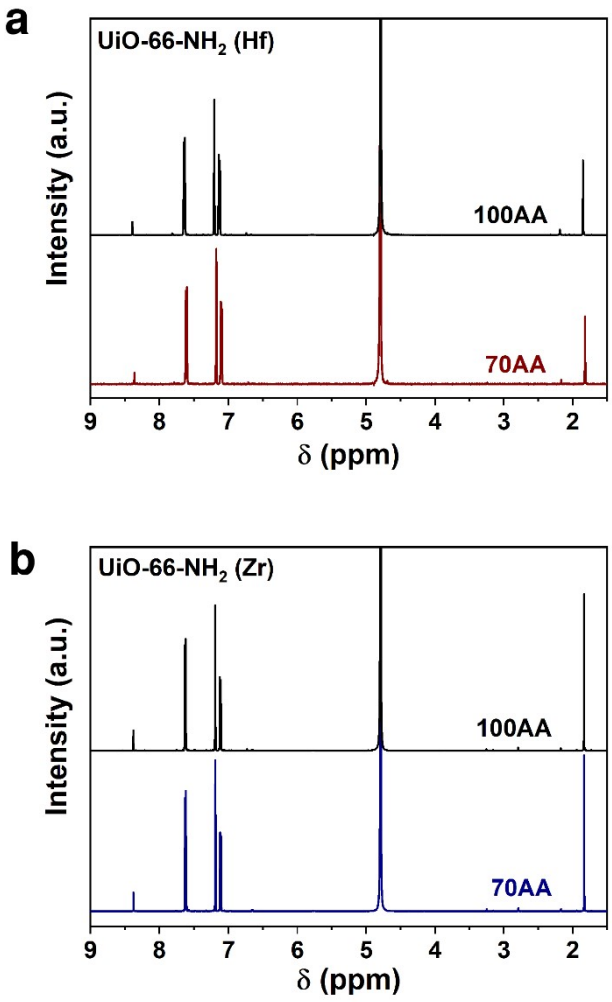

Figure S3. NMR spectra of (a) UiO-66-NH_2 (Hf) and (b) UiO-66-NH_2 (Zr) with 70 AA and 100 AA.

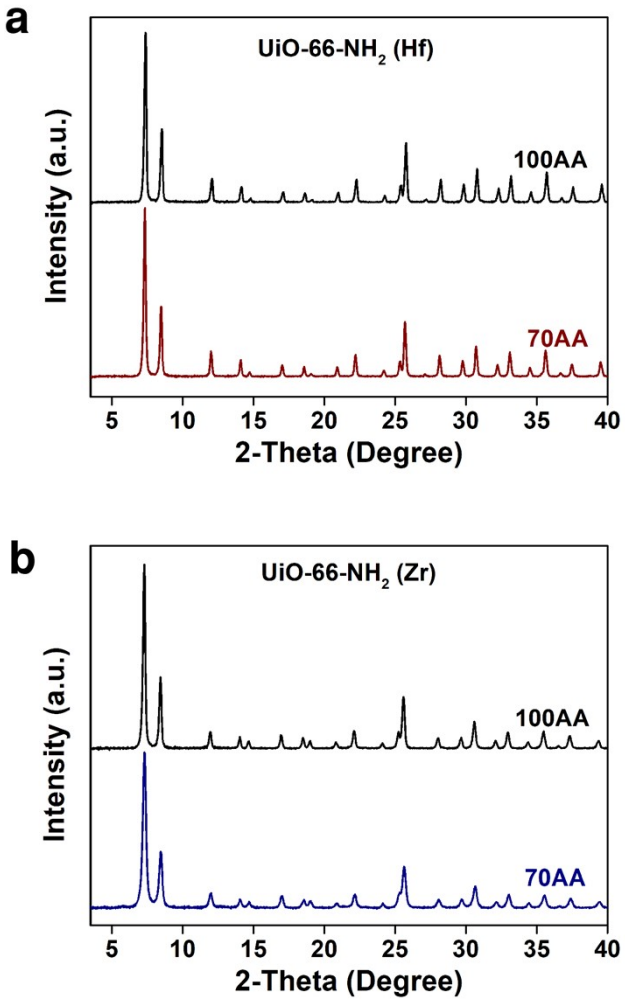

Figure S4. XRD patterns of (a) UiO-66-NH_2 (Hf) and (b) UiO-66-NH_2 (Zr) with 70 AA and 100 AA.

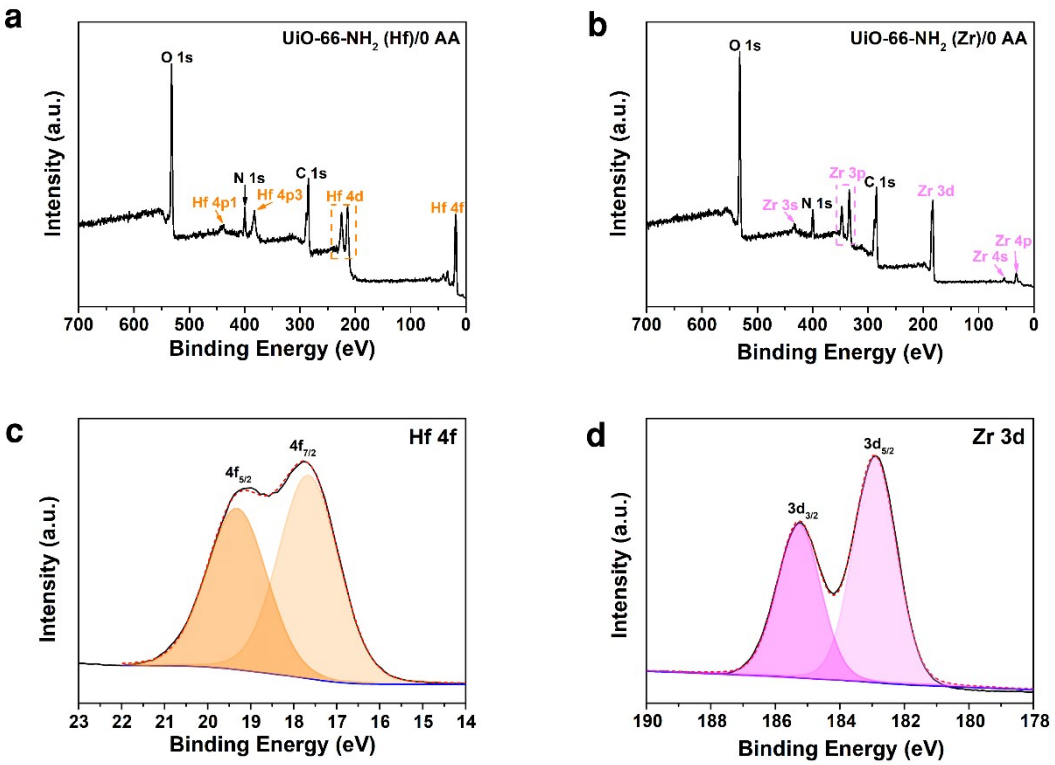

Figure S5. XPS survey spectra of (a) Hf/0 AA and (b) Zr/0 AA. (c) Hf 4f XPS peak of Hf/0 AA. (d) Zr 3d XPS peak of Zr/0 AA.

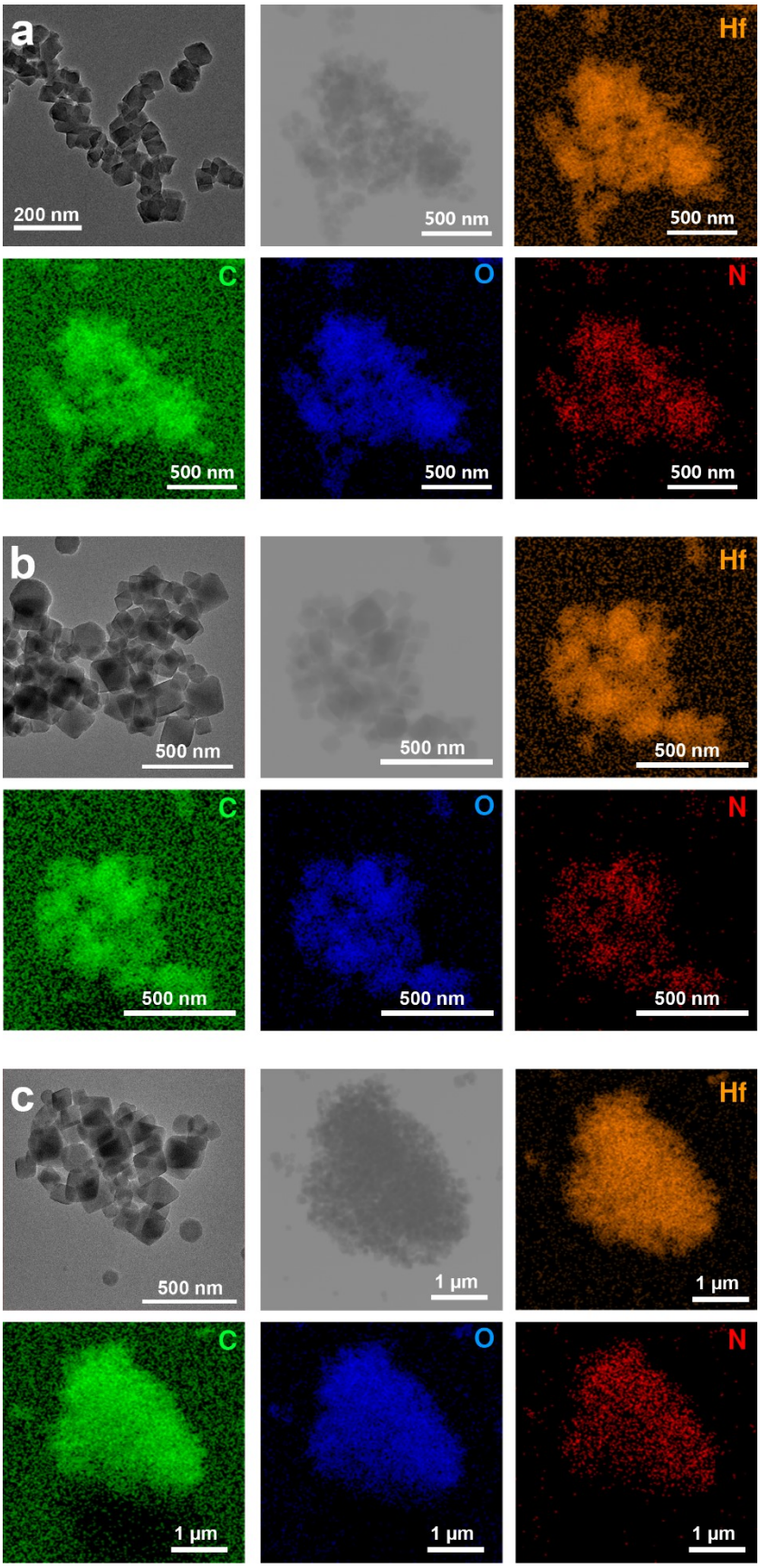

Figure S6. TEM and dark field images as well as the corresponding EDS elements mapping of (a) Hf/0 AA, (b) Hf/10 AA, and (c) Hf/40 AA.

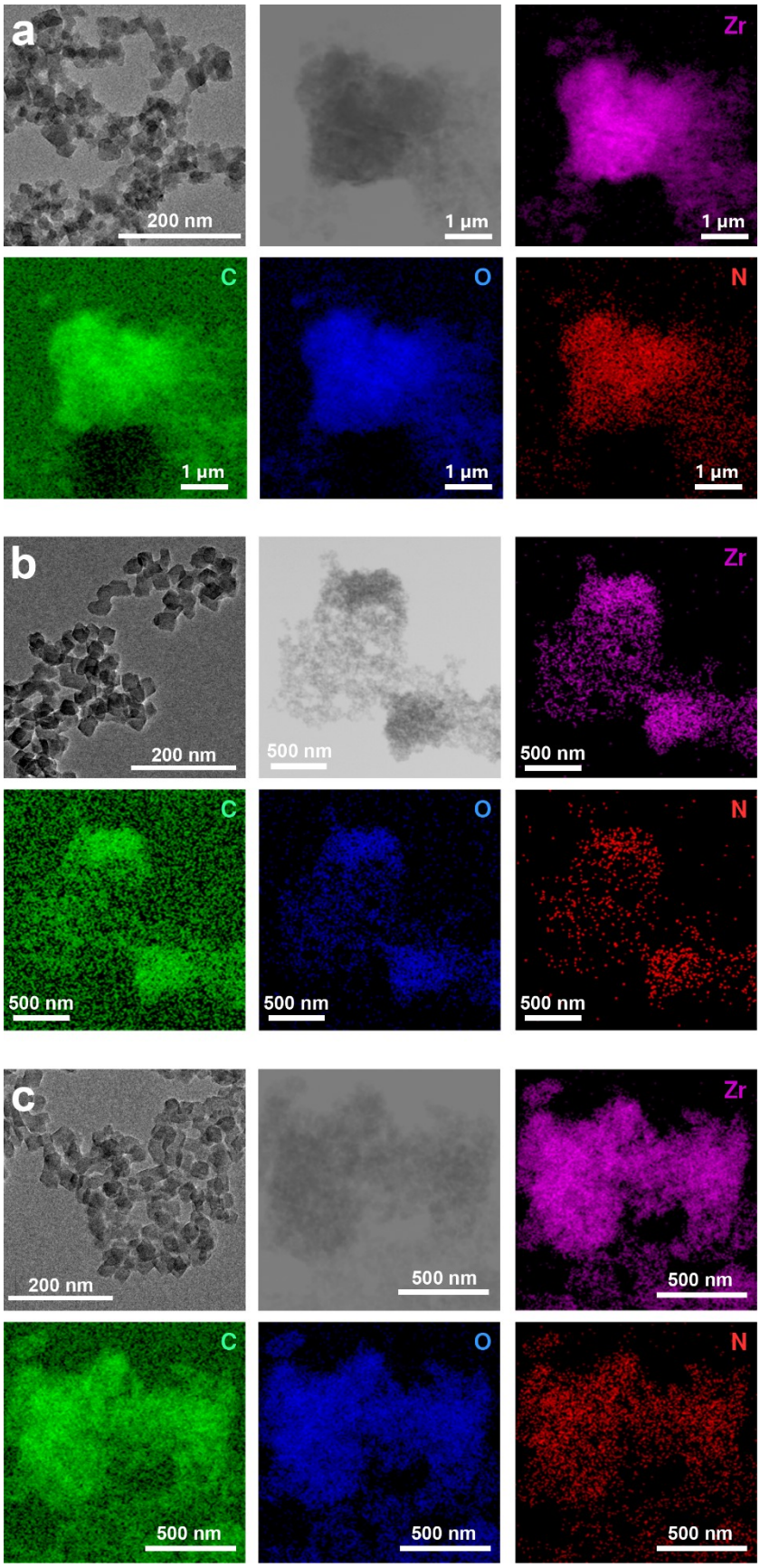

Figure S7. TEM and dark field images as well as the corresponding EDS elements mapping of (a) Zr/0 AA, (b) Zr/10 AA, and (c) Zr/40 AA.

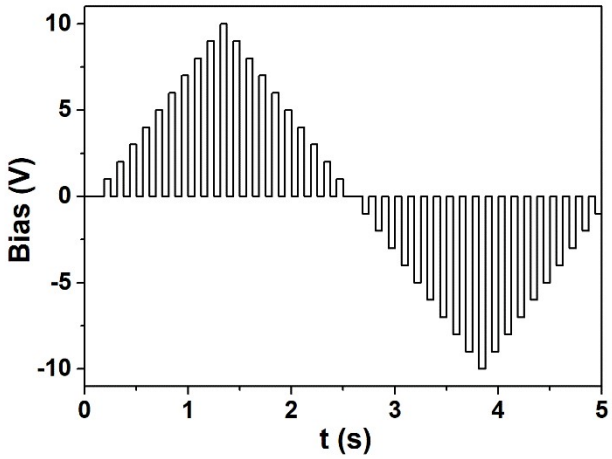

Figure S8. PFM bias waveform.

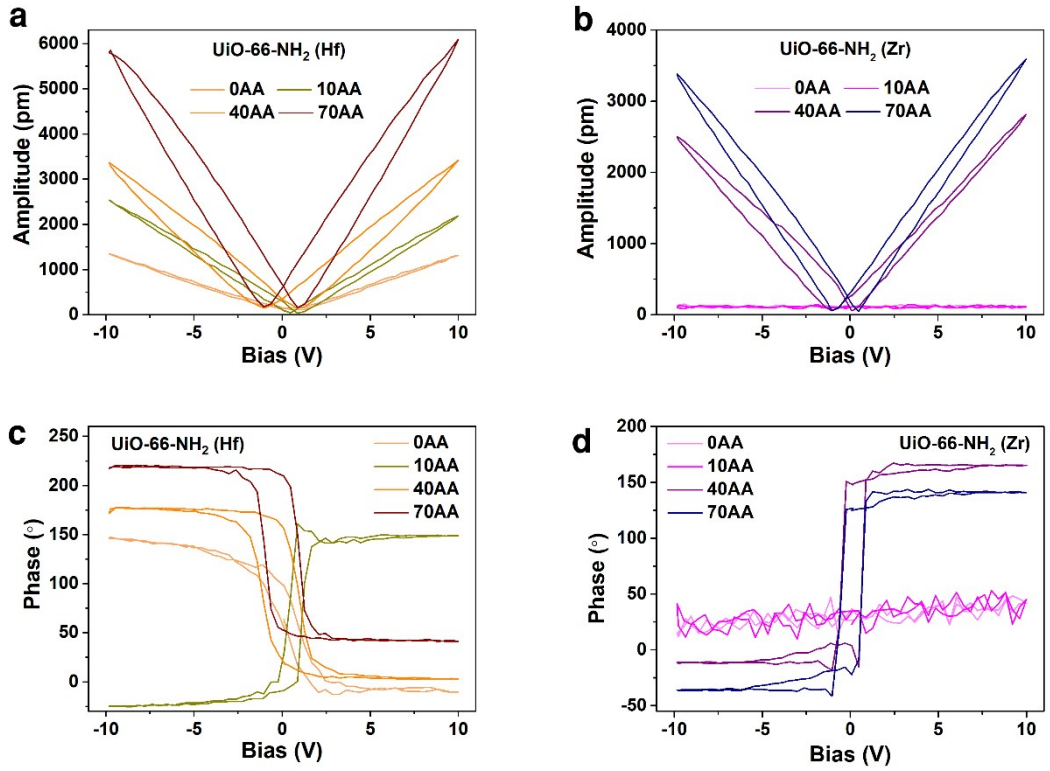

Figure S9. PFM bias-on state amplitude curves of (a) UiO-66-NH_2 (Hf) and (b) UiO-66-NH_2 (Zr) with different amount of added AA and (c-d) their corresponding PFM phase curves.

3. Supplementary Tables

Table S1. Crystallinity of UiO-66-NH_2 (Hf, Zr) with Different Amount of Added AA.

	UiO-66-NH_2 (Hf)				UiO-66-NH_2 (Zr)			
	0 AA	10 AA	40 AA	70AA	0 AA	10 AA	40 AA	70AA
Crystallinity (%)	72.5	78.4	80.3	79.1	73.9	80.1	79.9	81.6

Table S2. Relative AA^-/BDC-NH_2^{2-} and FA^-/BDC-NH_2^{2-} Ratio of UiO-66-NH_2 (Hf, Zr) with Different Amount of Added AA from NMR Peak Area.

	UiO-66-NH_2 (Hf)				UiO-66-NH_2 (Zr)			
Amount Ratio	0 AA	10 AA	40 AA	70AA	0 AA	10 AA	40 AA	70AA
AA^-/BDC-NH_2^{2-}	0	0.05	0.09	0.11	0	0.08	0.14	0.18
FA^-/BDC-NH_2^{2-}	0.04	0.04	0.05	0.06	0.04	0.05	0.05	0.07

Table S3. Atomic Percentage of (Hf, Zr)/70 AA.

Atomic Percentage (%)	Hf	Zr	C	N	O
UiO-66-NH_2 (Hf)	5.41	/	51.88	8.22	34.49
UiO-66-NH_2 (Zr)	/	7.5	52.15	6.38	33.96

Table S4. BET Surface Area, Micropore Volume, and Median Pore Width of UiO-66-NH_2 (Hf, Zr) with Different Amount of Added AA.

	UiO-66-NH_2 (Hf)				UiO-66-NH_2 (Zr)			
	0 AA	10 AA	40 AA	70AA	0 AA	10 AA	40 AA	70AA
S_{BET} (m^2/g)	437.68	564.03	739.25	830.72	667.98	859.32	932.26	1,042.52
V_p (cm^3/g)	0.1674	0.2244	0.3036	0.336	0.2668	0.3401	0.3645	0.4188
W_p (Å)	7.23	7.03	7.07	7.53	7.08	7.26	7.30	7.40

References

1. G. C. Shearer, S. Chavan, S. Bordiga, S. Svelle, U. Olsbye and K. P. Lillerud, *Chem. Mat.*, 2016, **28**, 3749-3761.
2. G. Fang, J. N. Hu, L. C. Tian, J. X. Liang, J. Lin, L. Li, C. Zhu and X. Wang, *Angew. Chem. Int. Ed.*, 2022, **61**, e202205077.