Supplementary Information

Cleaving DNA-model Phosphodiester with Lewis Acid-Base Catalytic Sites in Bifunctional Zr-MOFs

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Experimental Section

Materials. $ZrCl_4$ (Sinopharm Chemical Reagent), 2,2'-bipyridine-5,5'-dicarboxylic acid (H_2bpydc, Energy Chemical Reagent), benzoic acid (Adamas Chemical Reagent), bis(p-nitrophenyl) phosphate (BNPP, Sinopharm Chemical Reagent), zinc perchlorate hexahydrate ($Zn(ClO_4)_2 \cdot 6H_2O$, Energy Chemical Reagent), tris (Energy Chemical Reagent), sodium perchlorate ($NaClO_4$, Aladdin), hydrochloric acid (Energy Chemical Reagent), sodium hydroxide (NaOH, Sinopharm Chemical Reagent), *N*,*N'*-dimethylformamide (DMF, Energy Chemical Reagent) and methanol (CH_3OH, Sinopharm Chemical Reagent) were used as obtained. Deionized water was utilized in all experiments. The zinc complex with 2,2'-bipyrdine ligand was synthesized according to a previously reported method,[S1] and confirmed by XRD (Figure S5). The contents of zinc and zirconium in UiO-67-bpydc-Zn were quantified by an Optima 7300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES). X-ray photoelectron spectroscopy (XPS) was surveyed by a Thermo Fisher Scientific ESCALAB 250X imaging electron spectrometer. Thermogravimetric analyses were carried out at a ramp rate of 5 °C/min under a nitrogen flow with a model SDT Q60 thermogravimetric analyzer (ThermoElectron, Inc.).

Synthesis of UiO-67-bpydc: UiO-67-bpydc was prepared according to the literature with minor modification.[S2] Briefly, 26 mg of $ZrCl_4$, 26 mg of H_2bpydc, and 363 mg of benzoic acid were dissolved in 5 mL of DMF by sonication. The mixture was heated at 393 K for 24 h. After cooling to room temperature, the white product was isolated by centrifugation, and subsequently washed with DMF then methanol three times. Finally, the product was dried at 353 K under vacuum overnight.

Synthesis of UiO-67-bpydc-Zn: 30 mg of UiO-67-bpydc was loaded in a round-bottom flask containing 10 mL methanol, then ultrasonicated for 20 min. Subsequently, $Zn(ClO_4)_2 \cdot 6H_2O$ (74 mg) was added to the solution under magnetic stirring. Next, the mixture was heated at 333 K for 24 h under stirring. Finally, the product was washed three times with methanol and dried at 353 K under vacuum overnight. The content of Zn and Zr was determined as 1.42 wt% and 20.50 wt%, by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Hydrolysis of BNPP: The cleavage of BNPP was monitored by enhancement of the absorbance at 400 nm, due to the formation of the *p*- nitrophenolate anion.[S3,S4] The pH of the aqueous solution (7.0, 7.3, 7.5, 7.8 and 8.2) was controlled using tris buffer, and the ionic strength (0.1 M) was adjusted by $NaClO_4$. The catalytic hydrolysis of BNPP was performed heterogeneously in 20 mL buffer solution containing 5 mg of the catalyst, BNPP (0.75 mM), under stirring at 308 K. UV-Vis spectroscopy was periodically monitored at 400 nm by extracting a 10 μL aliquot from the reaction mixture and diluting with buffer (3 mL), followed by centrifugation. The A_∞ values for each set were determined after a week (308 K). The observed first-order rate constant k_{obs} was determined by the initial rate method.

Potentiometric Titration: The entire process of potentiometric titration was completed at 308 K with a ZDJ-4A automatic potentiometric titrator.[S4,S5] The catalyst (25 mg) was added to 30 mL of 0.1 M $NaClO_4$ solution, resulting in a uniform ultrasonic dispersion. The pH was adjusted to 3 with 0.1 M HCl solution, then titrated with fresh 0.1 M NaOH solution under stirring.

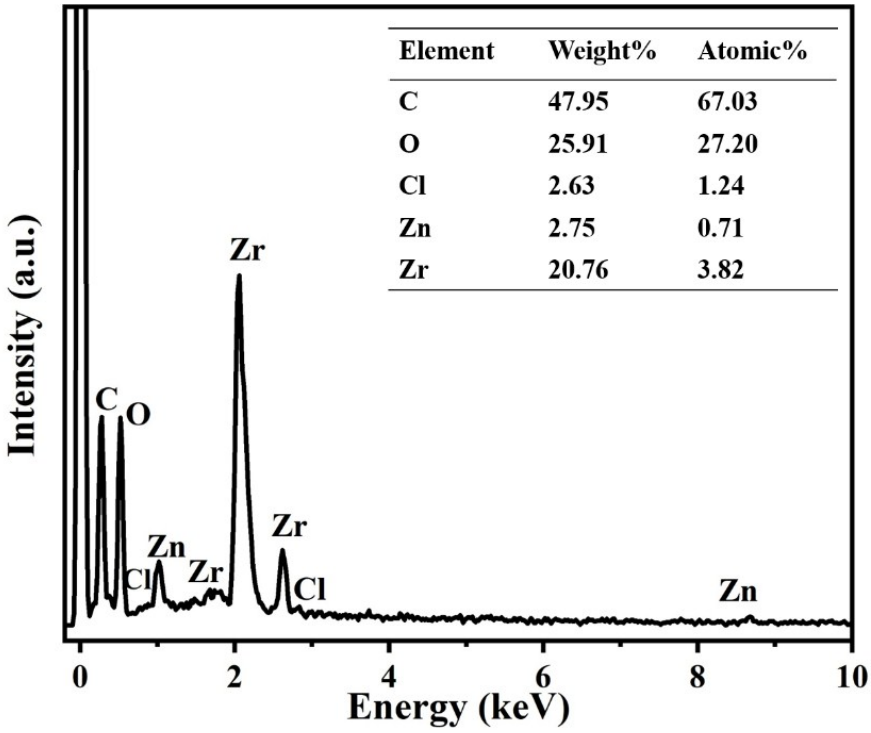

Fig. S1. EDX patterns of UiO-67-bpydc-Zn.

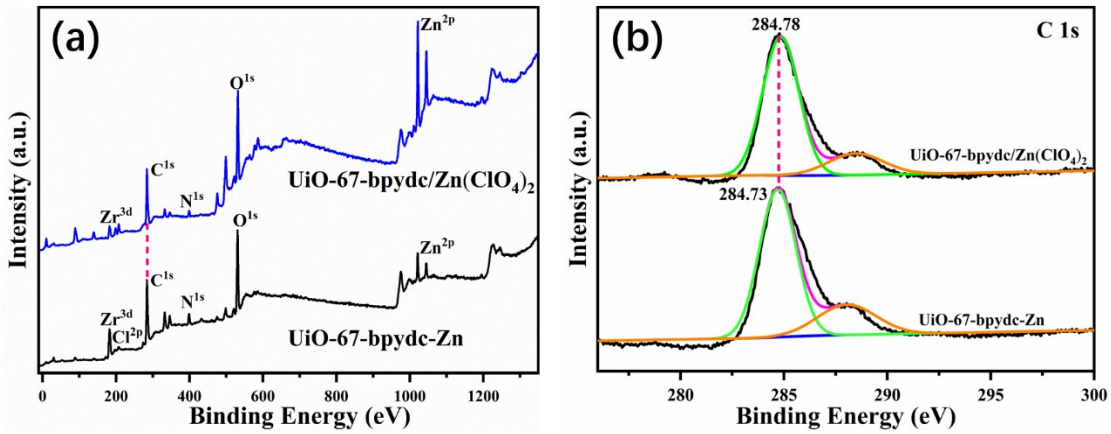

Fig. S2. (a) XPS spectra and (b) C 1s of UiO-67-bpydc-Zn compared to the mixture of UiO-67-bpydc and $Zn(ClO_4)_2 \cdot 6H_2O$.

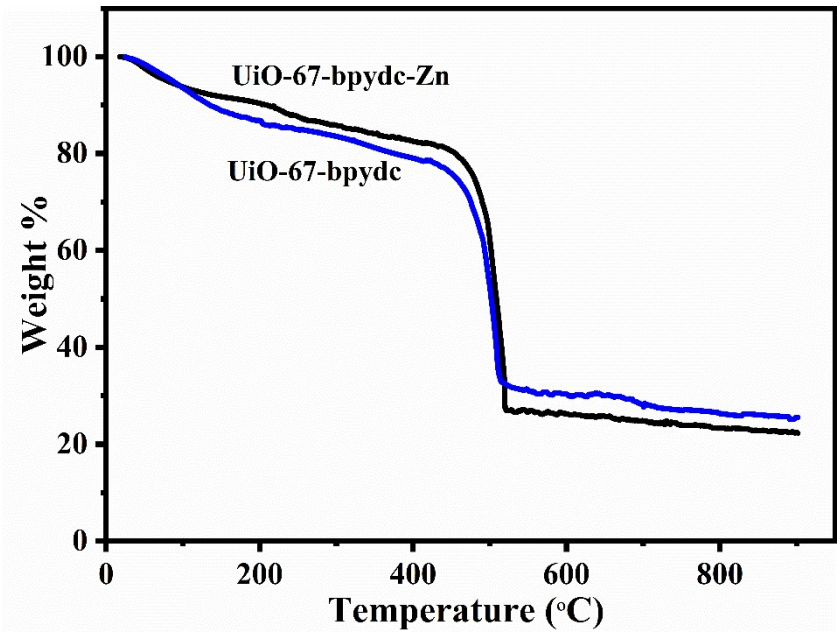

Fig. S3. TGA profiles of UiO-67-bpydc-Zn and UiO-67-bpydc under nitrogen atmosphere at a heating rate of 5 °C/min.

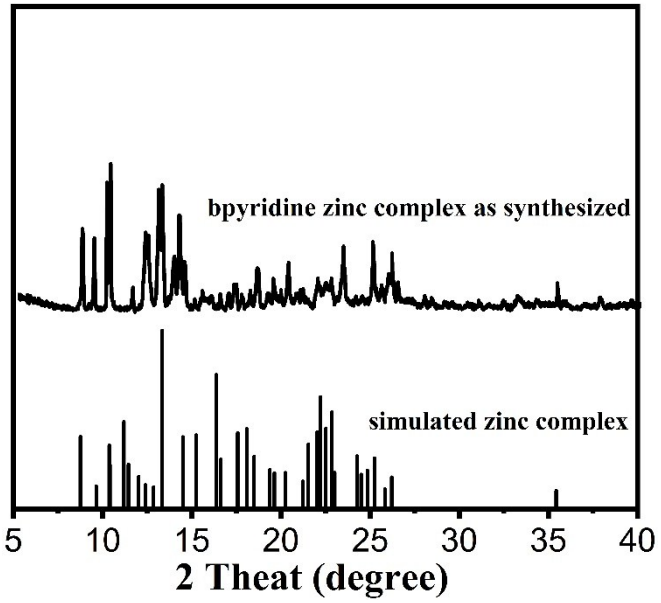

Fig. S4. XRD pattern of 2,2'-bpyridine zinc complex.

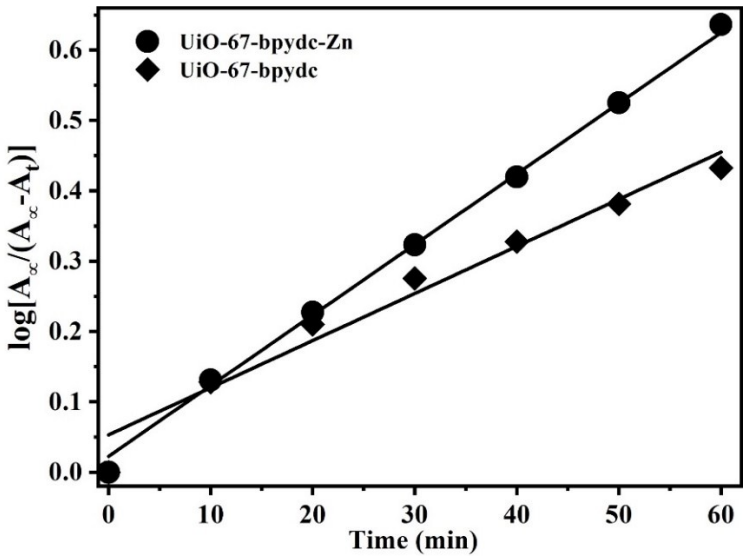

Fig. S5. Plots of log [A∞/(A∞ − At)] *versus* time for 60 min during BNPP hydrolysis catalyzed by UiO-67-bpydc or UiO-67-bpydc-Zn, respectively.

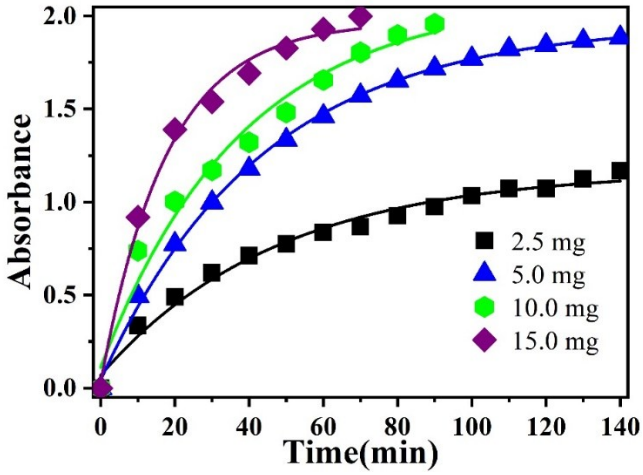

Fig.S6. 0.75 mM BNPP hydrolysis with various amounts of catalyst at varying pH in 20 mL buffer solution (308 K). Absorption was measured at 400 nm.

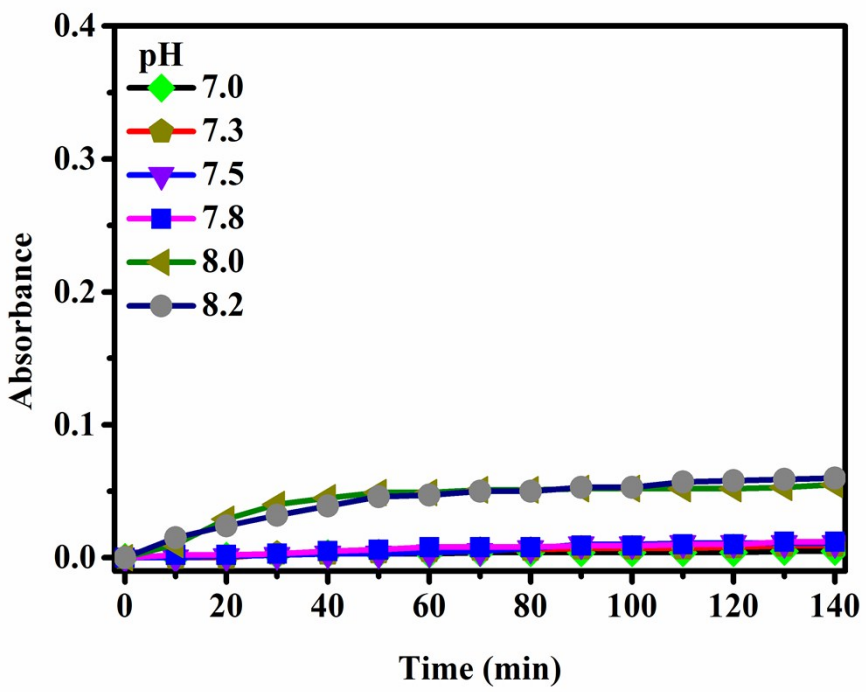

Fig.S7. 0.75 mM BNPP hydrolysis without catalyst at varying pH in 20 mL buffer solution at 308 K. Absorptions was measured at 400 nm.

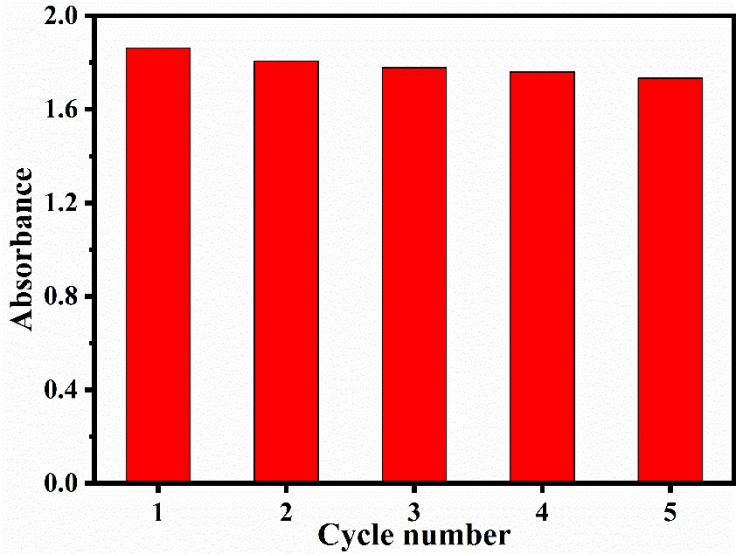

Fig. S8. Recyclability test for BNPP hydrolysis catalyzed by UiO-67-bpydc-Zn at 308 K and pH 7.8.

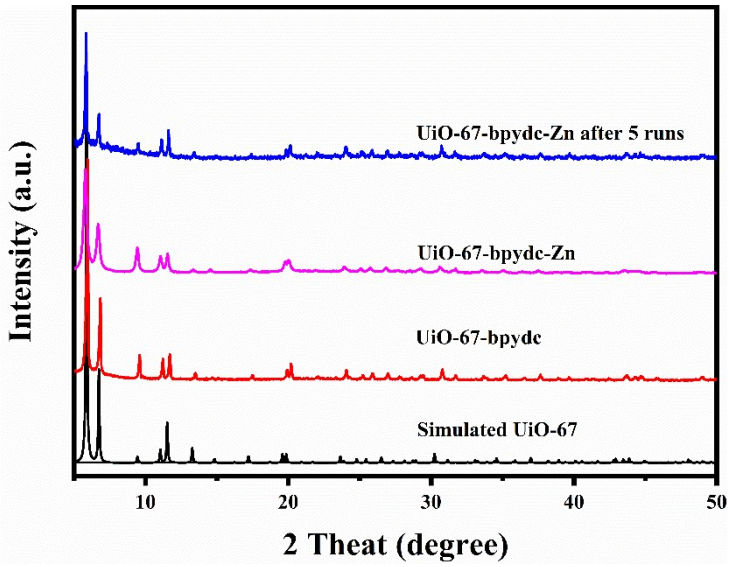

Fig. S9. PXRD patterns of UiO-67-bpydc-Zn after five runs.

References

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