Supporting Information

Mechanical Bond Approach to Introducing Self-Adaptive Active Sites in Covalent Organic Frameworks for Zinc-Catalyzed Organophosphorus Degradation

Xianghui Ruan, Yajie Yang, Weixu Liu, Xujiao Ma, Cheng Zhang, Qinghao Meng, Zeyu Wang, Fengchao Cui, Jiahui Feng, Fuli Cai, Ye Yuan,* and Guangshan Zhu*

Key Laboratory of Polyoxometalate and Reticular Material Chemistry of Ministry of Education, Northeast Normal University, Renmin Avenue, Changchun, 130024, China
E-mail: Yuany101@nenu.edu.cn and Zhugs100@nenu.edu.cn

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1 Materials and methods

Materials

No unexpected or unusually high safety hazards were encountered. Paraoxon-ethyl, paraoxon-methyl, and parathion-methyl were purchased from Sigma-Aldrich. All other starting materials and organic solvents were purchased from commercial suppliers and used without further purification unless otherwise noted.

General instrumentation and methods

$^1$H, $^{13}$C NMR spectra were recorded on Varian Inova 500 MHz NMR spectrometer. FT-IR measurements were performed on the Nicolet IS50 Fourier transforms infrared spectrometer. TGA was measured on the METTLER-TOLEDO TGA/DSC 3 analyzer at the 10 °C·min$^{-1}$ heating rate in air atmosphere. N$_2$-adsorption isotherms and pore size distribution were obtained at 77 K using an Autosorb iQ2 adsorptometer, Quantachrome Instrument. SEM and EDS elemental mapping were implemented on the field emission scanning electron microscopy (FE-SEM, SU-8010, Hitachi). Transmission electron microscopic (TEM) images were generated with JEOL 2100PLUS instrument at an accelerating voltage of 200 kV. PXRD measurements were carried out on the Rigaku SmartLab X-ray diffractometer with Cu-Kα radiation (40 kV, 30 mA, λ = 1.5418 Å). XPS were recorded on an Escalab-MK II photoelectronic Spectrometer with Al Kα (1200 eV). $^{13}$C CP/MAS solid-state NMR spectra were obtained using a Bruker Avance III model 400 MHz NMR spectrometer at a MAS rate of 5 kHz. UV-Vis spectra were recorded on a Cary 500 UV-Vis-NIR spectrophotometer. The elemental analyses were measured by Inductively Coupled Plasma - Atomic Emission Spectrometer (ICP-AES) on a LEEMAN Prodigy. In-situ-IR date was measured by METTLER-TOLEDO ResctIR-15.

2 Synthetic procedure

2.1 Synthesis of $2H^+$-BPDA.

$\begin{array}{c}
\text{BPDA} \\
\text{CH}_2\text{Cl}_2, \text{TOH}
\end{array}$

$\text{0°C, 4 h}$

$\begin{array}{c}
\text{H}
\end{array}$

$\text{2H}^+$-BPDA

$2H^+$-BPDA was synthesized following the previous literature. A solution of 2,2’-bipyridyl-5,5’-dialdehyde (BPDA: 100 mg, 0.47 mmol) in dichloromethane (20 mL) was stirred at ice-water bath for 10 min. Trifluoromethanesulfonic acid (TfOH: 177 mg, 1.2 mmol) in 6 mL dichloromethane was slowly added to the above reaction system by dropping funnel and stirring for 4 h; the buff solid was precipitated from clear solution. The solid was filtered and re-crystallized in a mixture of acetonitrile and diethyl ether to get 154 mg white solid. 2, 2’-Bipyridyl-5, 5’-dialdehyde-salt ($2H^+$-BPDA) was obtained with a yield of 64%. m.p. 160-162 °C. $^1$H NMR (500 MHz, CD$_3$CN) δ: 10.24 (s, 2H), 9.31 (s, 2H), 8.85 (dd, J = 8.2, 1.3 Hz, 2H), 8.73 (d, J = 8.3 Hz, 2H). $^{13}$C NMR (151 MHz, CD$_3$CN) δ: 189.79, 149.80, 148.26, 143.65, 134.66, 125.56, 121.32 (q, $^1J_{CF} = 749.0$ Hz, C: TfO$^-$). $^{19}$F NMR (470 MHz, CD$_3$CN) δ: -74.01 (s). HRMS (m/z), calcd for $C_{12}H_{10}N_3O_2$ [M]$^{2+}$ 107.0367, found 107.0397.
Figure S1. $^1$H NMR spectra of $2H^+$-BPDA and BPDA in CDCl$_3$ at 500 MHz.

Figure S2. $^{13}$C NMR spectrum of $2H^+$-BPDA in CDCl$_3$ at 151 MHz.
Figure S3. $^{19}$F NMR spectrum of 2H$^+$-BPDA in CDCl$_3$ at 470 MHz.

Figure S4. HRMS (m/z) spectrum of 2H$^+$-BPDA, calcd for C$_{12}$H$_{10}$N$_3$O$_2$ [M]$^{2+}$ 107.0367, found 107.0306.
Figure S5. FTIR spectra of 2H⁺-BPDA and BPDA.
2.2 Synthesis of pseudorotaxane.

The binding patterns for the mixture of dibenzo-24-crown-8 (DB-24-C-8) and BPDA-salt with stoichiometric of 1:1 was explored by FTIR and $^1$H NMR analysis (Figure S6). Weighting 2H$^+$-BPDA (20 mg, 39 μmol) and DB-24-C-8 (17.5 mg, 39 μmol), the mixture was dissolved in acetonitrile (CH$_3$CN, 10 mL), and stirred at room temperature for 24 h. The yellow solid (pseudorotaxane) was collected by removing solvent molecules under vacuum. $^1$H NMR (500 MHz, CD$_3$CN) δ: 10.24 (s, 2H), 9.31 (d, $J$ = 1.3 Hz, 2H), 8.77 (dd, $J$ = 8.3, 1.7 Hz, 2H), 8.65 (d, $J$ = 8.3 Hz, 2H), 6.88 – 6.78 (m, 8H), 4.03 (dd, $J$ = 5.2, 3.3 Hz, 8H), 3.83 – 3.77 (m, 8H), 3.72 (s, 8H).

We compared the binding patterns for DB-18-C-6/bipyridine and DB-24-C-8/bipyridine (Figures S6 and S7). The results showed slight changes in chemical shifts in complex of DB-18-C-6 and 2H$^+$-BPDA, indicating that the crown ether rings with different sizes affected the extent of complexation between the host and guest. Obviously, DB-24-C-8 was more suitable for building pseudorotaxane structure.

As illustrated in $^1$H NMR spectra, the chemical shifts of the protons a, b, c, and d on the crown ether were shifted by -0.07, -0.07, -0.6, and -0.01 ppm, respectively, which indicated that the hydrogen bonding between –O– groups and the quaternary-nitrogen proton (Figure S6).

The weakened strength of the pyridine stretching vibration coupled with the decrease wavenumber from 1635.4 to 1628.1 cm$^{-1}$ were observed after the impregnation of DB-24-C-8 and 2H$^+$-BPDA. These phenomena were attributed to that crown ether rings with a large number of electronegative oxygen atoms possessed a strong induction action for the protonated bipyridine groups, demonstrating the hydrogen bonding between –O– groups and the quaternary-nitrogen proton (Figure S7).
Figure S6. $^1$H NMR spectra of pseudorotaxane (DB-24-C-8:2H$^+$-BPDA = 1:1) and mixture (DB-18-C-6:2H$^+$-BPDA = 1:1) in CD$_3$CN at 500 MHz.

Figure S7. FTIR spectra of pseudorotaxane (DB-24-C-8:2H$^+$-BPDA = 1:1) and raw materials.
2.3 Synthesis of dumbbell molecule.

BPDA (30 mg, 141.4 μmol) and 4-tritylaniline (95 mg, 283 μmol) were added into 20 mL of N, N-dimethylformamide (DMF). The mixture was stirred at 60 °C for 10 min. Then, anhydrous acetic acid (500 μL) was added to the reaction system and the mixture was stirred at 60 °C for one day. After the reaction was completed (as indicated by TLC; petroleum ether/ethyl acetate=1:1, v/v), the mixture was diluted with water (200 mL) and extracted with dichloromethane (30 mL×3). The combined dichloromethane extracts were dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo; and the crude product was purified by column chromatography (silica gel) using ethyl acetate/dichloromethane (10:1, v/v) as the eluent to afford a dumbbell molecule. The dumbbell molecule was obtained with a yield of 70.2%. m.p. >320 °C. ¹H NMR (500 MHz, CDCl₃) δ: 8.67 (d, J = 11.5 Hz, 2H), 8.36 (d, J = 1.5 Hz, 2H), 7.51 (d, J = 11.2 Hz, 2H), 7.41 (d, J = 8.7 Hz, 4H), 7.12 (s, 2H), 6.95 (d, J = 8.7 Hz, 4H).

Figure S8. ¹H NMR spectrum of dumbbell molecule in CDCl₃.
Figure S9. $^{13}$C NMR spectrum of dumbbell molecule in CDCl$_3$.

Figure S10. HRMS (m/z) spectrum of dumbbell molecule, calcd for C$_{62}$H$_{48}$N$_4$Na [M+Na]$^+$ 871.3771, found 871.3730.
2.4 Synthesis of [2]rotaxane molecule.

A glass ampule (20 mL) was charged with 4-tritylaniline (70 mg, 208 μmol) and 4 mL mesitylene. Dissolving the prepared pseudorotaxane (2H⁺-BPDA: 52.2 mg, 102 μmol and DB-24-C-8: 50.2 mg, 111.9 μmol) in 4 mL of acetonitrile, the system was added by 100 μL of acetic acid, sealed, and reacted at 60 ºC for 72 h. The reaction solution was added to 200 mL water to dilute and extracted with dichloromethane (30 mL×3). The collect dichloromethane extracts were dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo, and the crude product was purified by column chromatography (silica gel) using ethyl acetate/dichloromethane/triethylamine (10:1:0.01, v/v/v) as the eluent to afford the [2]rotaxane molecule with a 10.7% yield. m.p. 263 ºC. ¹H NMR (500 MHz, CDCl₃) δ 8.32 (d, J = 17.9 Hz, 2H), 8.13 (s, 2H), 7.36 (d, J = 25.9 Hz, 2H), 7.29-7.18 (m), 6.97 (d, J = 6.7 Hz, 2H), 6.81 (s, 6H), 6.61 (d, J = 20.6 Hz), 4.17 (s), 3.78 (s, 6H), 3.59 (s).

Figure S11. ¹H NMR spectrum of [2]rotaxane in CDCl₃.
Figure S12. $^{13}$C NMR spectrum of [2]rotaxane in CDCl$_3$.

Figure S13. HRMS (m/z) spectrum of [2]rotaxane, calcd for C$_{86}$H$_{80}$N$_4$O$_8$Na [M+2H+Na]$^{3+}$ 439.8619, found 439.8633.

2.5 Preparation of [Zn(2,2’-bpy)Cl$_2$], [(bpy-OH)Zn(Trop)Cl], [(bpy-OH)Zn(Trop)$_2$], dumbbell-Zn, [2]rotaxane-Zn.

[Zn(2,2’-bpy)Cl$_2$],$^{2a}$ [(bpy-OH)Zn(Trop)Cl],$^{2b}$ and [(bpy-OH)Zn(Trop)$_2$]$^{2b}$ were synthesized according to the reference literatures. Weighting respective dumbbell compound (11.6 mg, 12.5 μmol)
and [2]rotaxane compound (10.2 mg, 7.9 μmol) dissolved in 10 mL, the corresponding 4 mL and 6.3 mL of 2 mM ZnCl$_2$ ethanol solutions were poured into the system. After standing at room temperature for 1 week, the resulting dumbbell-Zn, [2]rotaxane-Zn were obtained with masses of 5.4 mg (43.9%) and 3.1 mg (28.1%), respectively.

2.6 Preparation of BP-COF.

1,3,5-Tris(4-aminophenyl)benzene (TAPB, 23 mg, 66 μmol) and 2,2'-bipyridine-5,5'-dicarboxaldehyde (BPDA, 21 mg, 99 μmol) were weighed into a glass ampule (volume 10 mL with a body length of 16 cm and a neck length of 5 cm), and added by 2.0 mL of mesitylene and 2 mL acetonitrile. The mixture was added 50 μL of acetic acid. The glass ampule was flash frozen in a 77 K (liquid N\textsubscript{2} bath), evacuated to an internal pressure of 19 mbar and flame sealed, reducing the total length by 4-5 cm. Thaw at room temperature, the glass ampule was placed in an oven at 60 °C and left undisturbed for 72 h, yielding a yellow solid at the bottom of the ampule which was isolated by filtration and embathed with anhydrous THF and anhydrous methyl alcohol for 12 h, respectively. The obtained solid by filtration after embathed and dried at 80 °C under vacuum for 12 h to yield BP-COF as a yellow powder (32.8 mg, 73% yield).

2.7 Preparation of Crown-COF.

A glass ampule (10 mL) was charged with 1,3,5-tris(4-amino-phenyl) benzene (10 mg, 28.5 μmol) and 2 mL mesitylene. The prepared pseudorotaxane was dissolved in 2 mL of acetonitrile and added by 40 μL of acetic acid. The solution of pseudorotaxane was poured into the glass ampule and flash frozen at liquid nitrogen bath, evacuated to an internal pressure and flame sealed. Upon sealing, the length of the glass ampule was reduced by 4-5 cm. Thaw at room temperature, the reaction was heated at 60 °C for 72 h yielding a red solid at the bottom of the ampule, which was isolated by filtration and washed with anhydrous THF and anhydrous methyl alcohol for 12 h respectively. Collect the powder by filtration and continue washed with mixture (Et\textsubscript{3}N/CH\textsubscript{3}CN/H\textsubscript{2}O= 0.1:1:1, v/v/v; 10 mL×2), then decanted the solvent and dried at 80 °C under vacuum for 12 h to afford the tan powder of Crown-COF (Yield: 17.3 mg, 51.6%).
2.8 Preparation of BP-COF-Zn and Crown-COF-Zn.

BP-COF was weighed 20 mg into 20 mL in a vial, and added the 15 mL methyl alcohol, ultrasonic dispersion for 10 minutes at 45 Hz, then added 5.0 mg ZnCl₂. The mixture was stirred at room temperature for 4 h, which was isolated by filtration and the obtained solid dried BP-COF-Zn at 90 °C under vacuum for 12 h.

20 mg Crown-COF was weighed and poured into 20 mL in a vial, and added the 15 mL methyl alcohol, ultrasonic dispersion for 10 minutes at 45 Hz. The dispersion was transferred into a centrifuge tube and washed with centrifuge the tube to remove supernatant, then transferred to vial again and added 4.5 mg ZnCl₂. It was stirred at room temperature for 4 h, which was isolated by filtration and the obtained solid dried Crown-COF-Zn at 90 °C under vacuum for 12 h.

2.9 Preparation of small molecules in a discrete mode.

Based on the amount of 2 mg of Crown-COF-Zn, it is calculated to contain 2,2-bipyridyl (0.692 mg, 4.44×10⁻³ mmol), DB-24-C-8 (0.597 mg, 2.49×10⁻³ mmol), and ZnCl₂ (0.945 mg, 6.93×10⁻³ mmol). 3 mL of the above mixture of acetonitrile and water (1/1, v/v) solution was stirred at room temperature for 1 h, subsequently dried under vacuum for further investigation.
3 Characterizations

Figure S14. XPS Zn 2p spectrum of Crown-COF-Zn, the curve-fitting was conducted based on the characteristic signals of Zn-O, Zn-N, and Zn-Cl.

Figure S15. XPS Zn 2p spectra of [Zn(2,2'-bpy)Cl2] and [Zn-dumbbell]. The binding energy of Zn-Cl centered at 1023.6 eV according to the previous report for ZnCl2 binding energy.
Figure S16. High-resolution XPS spectra of c N 1s region of Crown-COF, d N 1s region of Crown-COF-Zn, e O 1s region of Crown-COF, and f O 1s region of Crown-COF-Zn.
Figure 17. TGA and DSC curves of a BP-COF, b Crown-COF, c DB-24-C-8, d DB-24-C-8 + BP-COF (Physical adsorption), e Crown-COF-1/6Zn, and f Crown-COF-Zn.
Figure S18. PXRD spectra of BP-COF and Crown-COF.

Figure S19. N\textsubscript{2} adsorption-desorption isotherms at 77 K of BP-COF and Crown-COF (solid symbols, adsorption; open symbols, desorption).
Figure S20. Simulated $^{13}$C NMR chemical shifts for Crown-COF and DB-24-C-8, obtained from MestReNova.

Figure S21. FTIR spectra of Dumbbell, [2]Rotaxane, and [2]Rotaxane-Zn.
Figure S22. a SEM image of BP-COF, b SEM image of Crown-COF, c TEM image of BP-COF, and d TEM image of Crown-COF.
Figure S23. EDS element mappings of Crown-COF-Zn for carbon, oxygen, nitrogen, and zinc. Scale bar: 500 nm.
4 Catalytic tests

Scheme S1. Degradation of organophosphorus agents.

Hydrolysis assay.

Based on previously described hydrolysis assay, the hydrolysis activity was tested under 5 mM of paraoxon-ethyl. The result was measured using ultraviolet and visible spectrophotometry (UV) by monitoring the characteristic peak of product (p-nitrophenol, p-NP). BP-COF, BP-COF-Zn, and Crown-COF-Zn (2 mg) was dispersed in 1 mL solution of acetonitrile and water (CH$_3$CN/H$_2$O=1:1, v/v), respectively. After immersion for 10 min, we extracted 900 μL of supernatant, then added 800 μL (20 mM) Tris-HCl buffer (pH = 9.0), then 100 μL paraoxon-ethyl in acetonitrile was poured into the solution. Subsequently, the mixture was shaken at 2000 rpm in a shaker. After respective 10, 20, 30, 40, 50, 60, 90, 120, 180, 240, 300, 360, 420 and 480 minutes, 40 μL of the solution was sampled and diluted with Tris-HCl buffer (pH = 9.0) to make 4 mL. The absorbance at 275 nm and 400 nm were measured by UV spectrophotometry, then Beer-Lambert law was applied to determine the amount of product. All results were averaged from more than three measurements.

Some other test conditions should be noted that the 0 °C and 60 °C reaction environments should be tested in a sample bottle with good airtightness.

Beer–Lambert’s Law: When the concentration is controlled within certain bounds, it presents a linear relationship with optical intensity, which is calculated by Equation (1) as follow:

$$ A = \log \frac{1}{T} = Kbc \quad (1) $$

where $A$ is the absorbance, $T$ represents the transmittance, $K$ is the molar absorption coefficient, $b$ is the thickness of absorbing layer, and $c$ is the concentration of substrate. The initial intensity of p-nitrophenol ($0.11 \times 10^{-3} \text{ M}$) is 1.72 in UV spectrophotometry-set as the standard.
Figure S24. UV spectra of p-NP 0.1 mM in water. Inset showing two forms of p-NP in acidic and basic media. Therefore, the pH=9 tris-HCl was used to dilute the sampling solution during the OP degradation rate.

Figure S25. Calibration plot of p-NP in buffer tris-HCl pH = 9.
Figure S26. UV spectra during the hydrolysis process for 5 mM POM by different materials at 30 °C in tris-HCl buffer pH = 9. a Crown-COF, b PB-COF-Zn, c Crown-COF-Znrotaxane (with an amount of 16.7% pseudorotaxane), and d Crown-COF-Zn.

In order to prove the synergistic effect originated from the crown-ether coordinated Zn(II) and bipyridine coordinated Zn(II), BP-COF-Zn with bipyridine coordinated Zn(II) and Crown-COF-Znrotaxane with crown-ether coordinated Zn(II) were used for the hydrolysis of paraoxon-methyl. It was found that the initial hydrolysis rates of BP-COF-Zn and Crown-COF-Znrotaxane were 7.4 and 6.5 μM/min, respectively, which were far lower than Crown-COF-Zn (94.4 μM/min). This result proves the synergistic effect originated from the crown-ether coordinated Zn(II) and bipyridine coordinated Zn(II).
Figure S27. UV spectra recording the hydrolysis of paraoxon-methyl in different models. a 2 mg [2]rotaxane-Zn model (insert: the model in the schematic diagram is a stacked graph because it does not dissolve in the solution). b 2 mg discrete small molecules.
Michaelis-Menten Model: It describes the rate of enzymatic reaction by relating the rate \( v \) to \([S]\), which is calculated with Equation (2):

\[
v = \frac{V_{\text{max}} [S]}{K_m + [S]}
\]  

(2)

where \( v \) represents the reaction rate, \( V_{\text{max}} \) is the maximum rate, \( K_m \) represents the substrate concentration when the rate value is half of the \( V_{\text{max}} \), and \([S]\) represents the initial concentration of the substrate. Taking the reciprocal of Equation (3) gives:

\[
\frac{1}{v} = \frac{K_m}{V_{\text{max}}} \times \frac{1}{[S]} + \frac{1}{V_{\text{max}}}
\]

(3)

Figure S28. a, the initial paraoxon-methyl hydrolysis profile catalyzed by Crown-COF-Zn. b, Lineweaver-Burk plot of the paraoxon-methyl catalyzed by Crown-COF-Zn. The catalytic performances of Crown-COF-Zn were tested using the hydrolysis of paraoxon-methyl in a Tris-HCl buffer (pH = 9.0) at 30 °C.
Figure S29. Possible hydrolysis mechanism of Crown-COF-Zn.
Figure S30. a-c XPS spectra of Zn, N, and O elements for paraoxon-methyl adsorbed [2]rotaxane-Zn. d FTIR spectra of paraoxon-methyl adsorbed Crown-COF-Zn. e In-situ infrared spectra of Crown-COF-Zn after deducting organic solvents and substrates at 31 °C, C=N and C–O–C interaction with Zn infrared absorbance curve with time.
Figure S31. Five states during the reaction process based on possible mechanisms. The structure is characterized by a double layer and the initial unit cell thickness is 5 Å. The modeled small base block is first optimized by Gaussian 0.9 for DFT structure, and then the organic structure is constructed. After optimized by all-atom simulations using the Forcite module in Materials Studio 7.0, the ZnCE-ZnDipy distance of the established reaction site is averaged to obtain the result in Figure 4a.
Figure S32. a UV spectra of hydrolyzed process POM by Crown-COF-Zn at 60 °C in methyl alcohol. b Concentration curve of POM and NP in the hydrolysis reaction of methanol environment. Acute toxicity data: 4-Nitrophenol’s LD<sub>50</sub> (lethal dose 50 percent kill) = 202 mg/kg, 4-Nitroanisole’s LD<sub>50</sub>=2300 mg/kg (PubChem database).
Figure S33. $^1$H NMR spectrum of 4-nitroanisole in CDCl$_3$ at 500 MHz.

Figure S34. $^{13}$C NMR spectrum of 4-nitroanisole in CDCl$_3$ at 500 MHz.
Figure S35. UV spectra recording the hydrolysis of paraoxon-methyl in presence of Crown-COF-Zn. The corresponding reaction temperatures for a, b, c, and d were 0, 20, 30, and 60 °C, respectively. e Stability of Crown-COF-Zn against pH and f stability of Crown-COF-Zn against cycle-used.
Figure S36. UV spectrum of 1/6Crown-COF-Zn during the hydrolysis process for 5 mM POM by different materials at 30 °C in tris-HCl buffer pH = 9.

In this work, we adjusted the proportion of pseudo-rotaxane building monomer to 1/6 of the original one, denoted 1/6Crown-COF-Zn. The catalytic rate of the 1/6Crown-COF-Zn sample was 13% of the original catalytic rate of Crown-COF-Zn (Figure 5). This apparent reduction proves that the doping amount of the crown-ether coordinated Zn(II) directly affects the catalytic performance.
Figure S37. FT-IR spectra of Crown-COF-Zn after soaked in different solvents for 12 hours.

We measured the water/chemical stability of Crown-COF-Zn in different solvents, and characterized the structural integrity by FT-IR spectroscopy. As shown in Figure 6, the characteristic peak of C=N stretching band (1620 cm$^{-1}$) has not significant change, which shows the high water/chemical stability of Crown-COF-Zn.
Table S1. Comparison of catalyst characteristics with other catalysts: Hydrolysis temperature, pH, catalyst dosage, substrate condition and hydrolysis rates.

| Sample                  | Temperature (°C) | pH   | Catalyst dosage (mg) | Substrate (mM) | Rate (μM min⁻¹) | Rate per unit mass (μM mg⁻¹ min⁻¹) |
|-------------------------|------------------|------|----------------------|----------------|-----------------|-----------------------------------|
| OPH[4]a                 | RT               | 8.5  | 10                   | 30             | 9.7             | 0.97                              |
| LT-nCeO₃[5]b            | RT               | 9    | 17.2                 | 2              | 16.7            | 0.97                              |
| Free His6-EcPepQ[6]b    | 70               | 8    | 7.8                  | 20             | 17.5            | 2.24                              |
| OPH-PCD[4]c             | RT               | 8.5  | 10                   | —              | 7.4             | 0.74                              |
| LaA₂B₁[7]e              | 60               | MeOH | 4                    | 25             | 42              | 10.50                             |
| LaA₂C₁[7]e              | 60               | MeOH | 4                    | 25             | 102             | 25.50                             |
| LaA₂C₁[7]e              | 60               | 10   | 4                    | 25             | 66              | 16.50                             |
| UiO-66[8]d              | 30               | MeOH | 2.5                  | 10             | 5               | 2.00                              |
| MTV-Uio-66-BE[9]d       | RT               | MeOH | 6                    | 1.25           | 26.4            | 4.40                              |
| MIPAF-9[3]d             | 30               | 9    | 2                    | 40             | 27.5            | 13.75                             |
| OpdA@MIL-88A[10]d      | 37               | 8    | —                    | 0.2            | 37.2            |                                   |
| Crown-COF-Zn e          | 30               | 9    | 2                    | 5              | 62.8            | 31.40                             |
| Crown-COF-Zn f          | 60               | 9    | 2                    | 5              | 94.4            | 47.20                             |
| Crown-COF-Zn g          | 60               | MeOH | 1.3                  | 25             | 215.8           | 166.00                            |

a, Organophosphorus hydrolase. b, Nanoparticles. c, Functionalized polymers. d, the framework materials. e, Hydrolysis rates of Crown-COF-Zn were tested in Tris-HCl buffer (pH = 9.0) at 30 °C by paraoxon 9.7 n-methyl in first 10 min. f and g, The temperature was set at 60 °C and the other conditions are as the same as e.
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