

Supporting Information

Microwave-Assisted Solvothermal Synthesis of UiO-66-NH₂ and Its Catalytic Performance towards the Hydrolysis of a Nerve Agent Simulant

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1. Size distribution of obtained MOFs

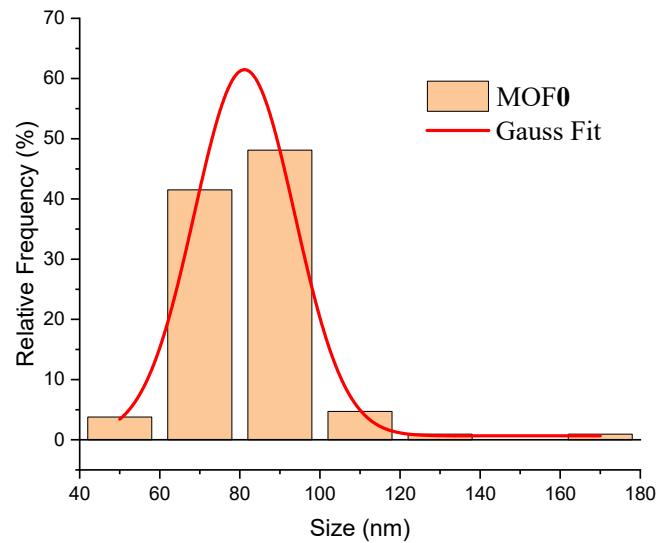


Figure S1. Size distribution of obtained MOF0 nanocrystals

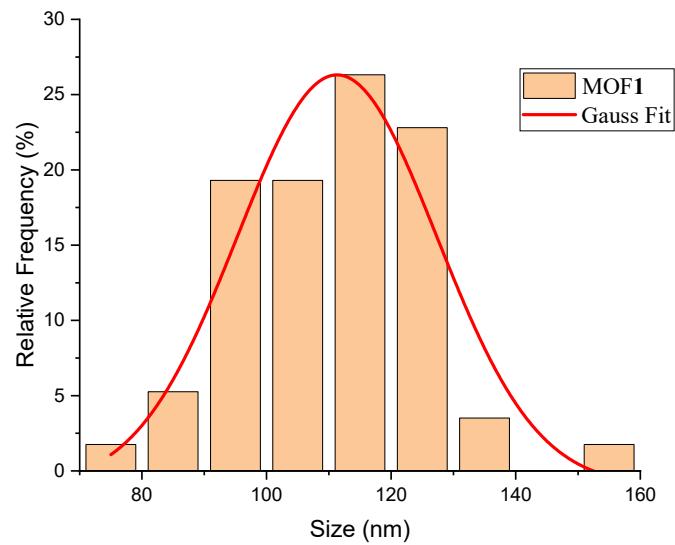


Figure S2. Size distribution of obtained MOF1 nanocrystals

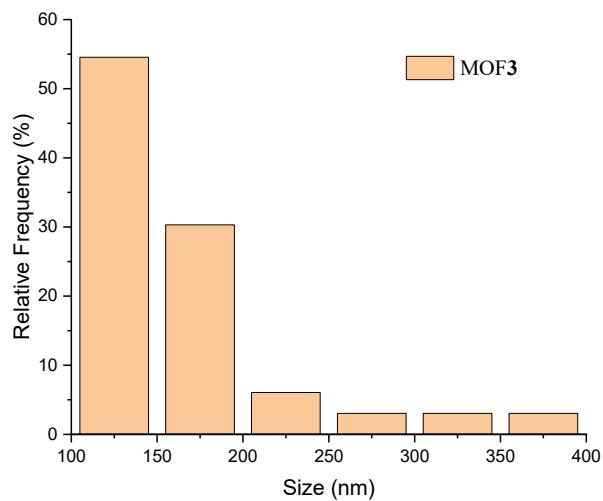


Figure S3. Size distribution of obtained MOF3 nanocrystals

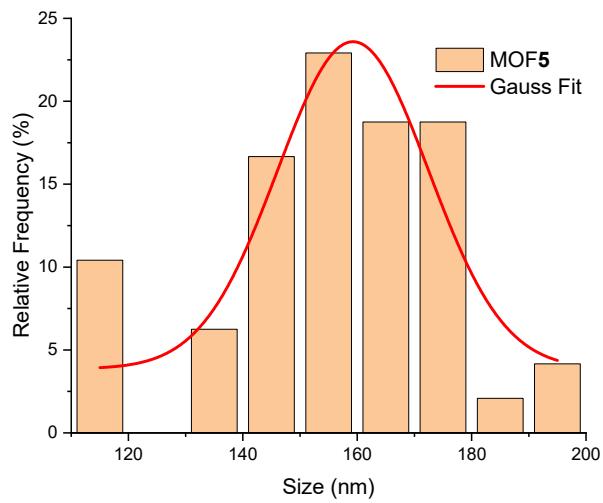


Figure S4. Size distribution of obtained MOF5 nanocrystals

2. The pore size distribution of obtained MOFs

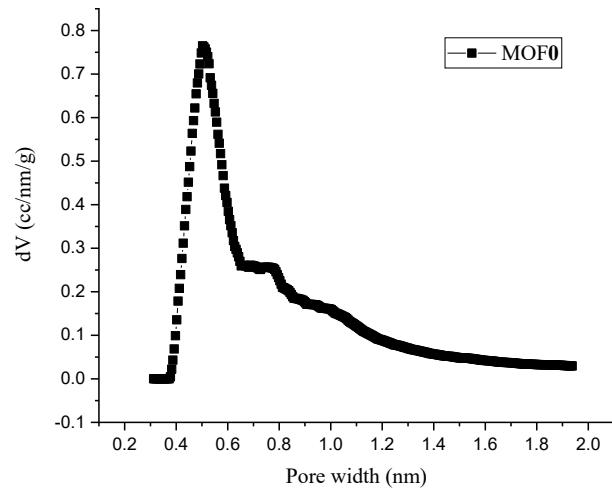


Figure S5. The micropore size of obtained MOF0 analyzed by the Horvath–Kawazoe (HK) method

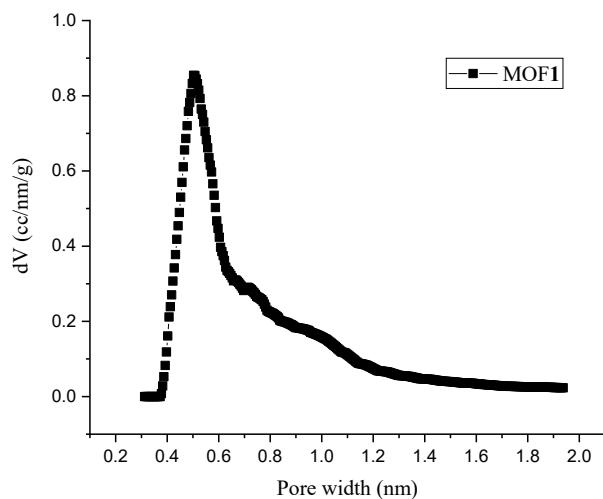


Figure S6. The micropore size of obtained MOF1 analyzed by the HK method

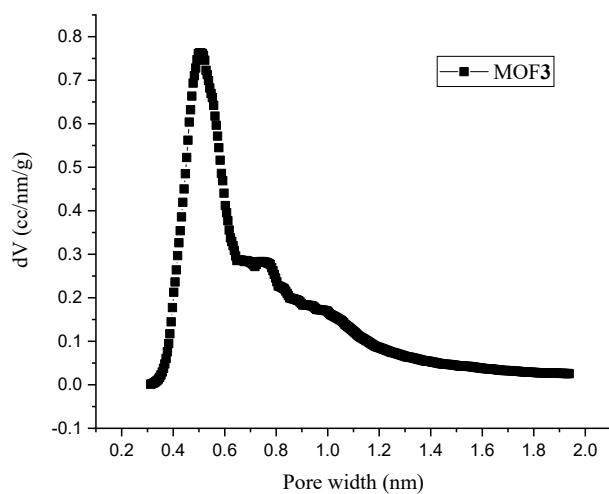


Figure S7. The micropore size of obtained MOF3 analyzed by the HK method

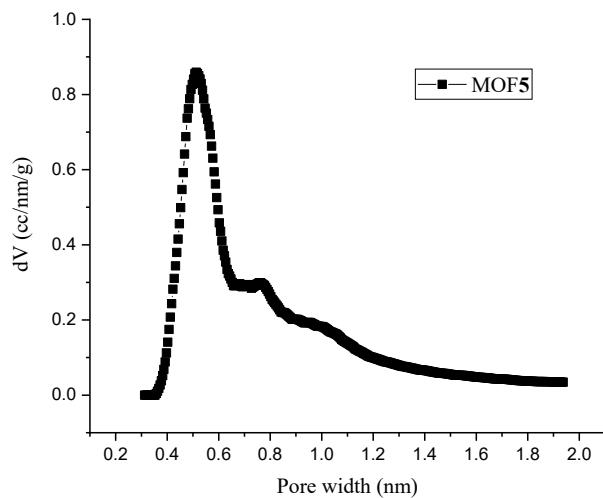


Figure S8. The micropore size of obtained MOF5 analyzed by the HK method

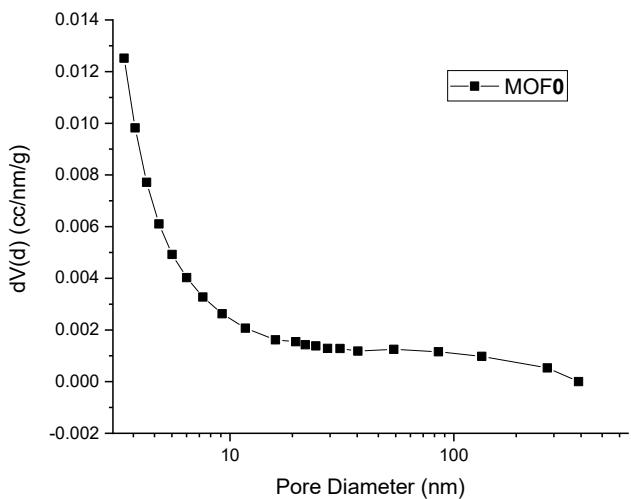


Figure S9. The Barrett-Joyner-Halenda (BJH) pore size of obtained MOF0

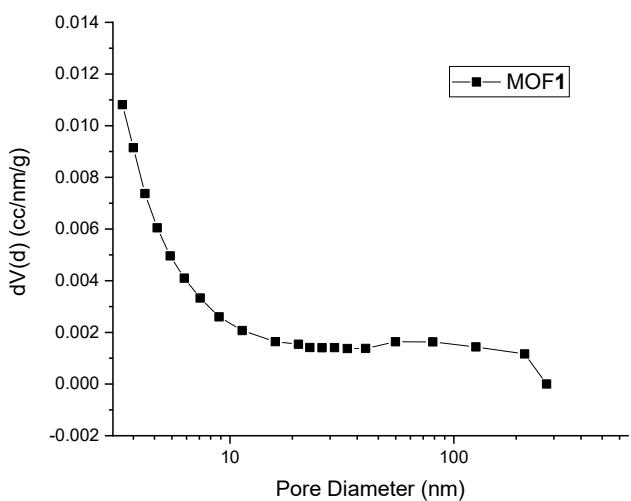


Figure S10. The BJH pore size of obtained MOF1

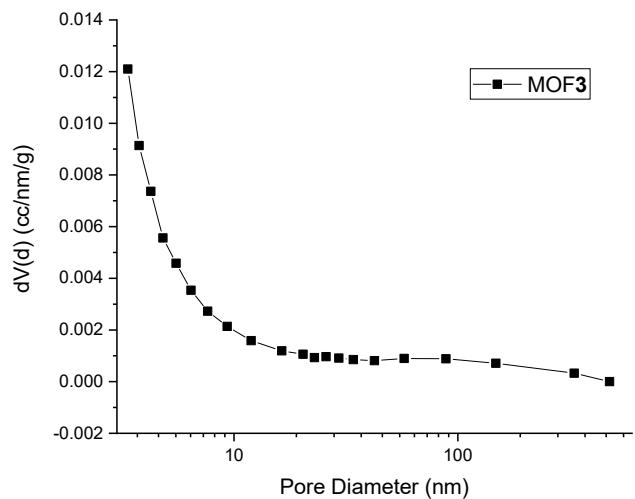


Figure S11. The BJH pore size of obtained MOF3

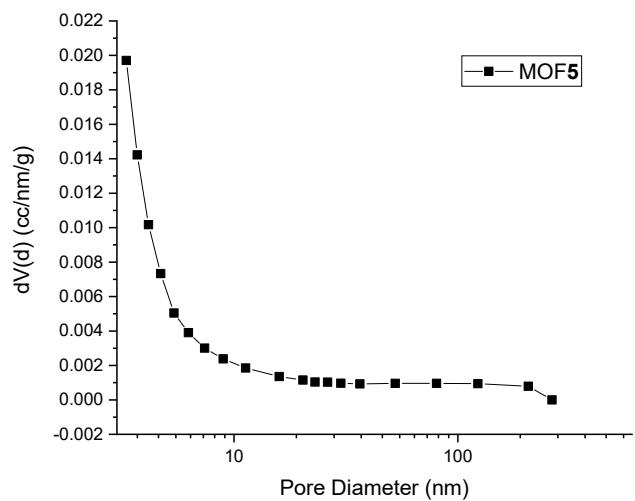


Figure S12. The BJH pore size of obtained MOF5

3. The NMR spectra of obtained MOFs

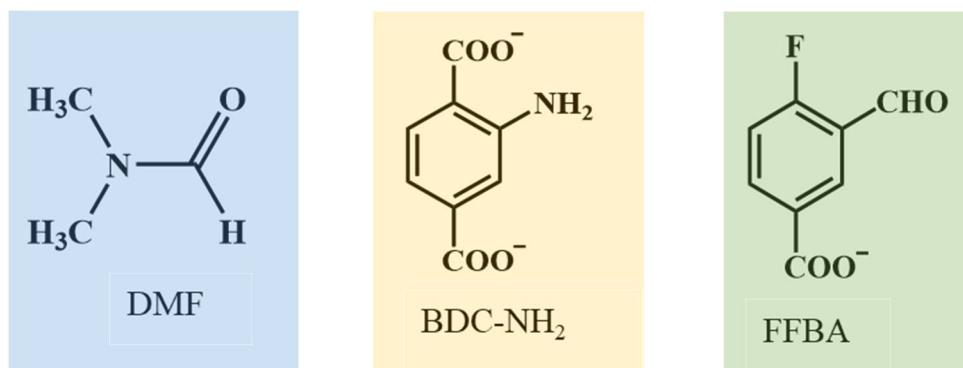


Figure S13. The chemical structures of DMF, BDC-NH₂ and FFBA in NMR test

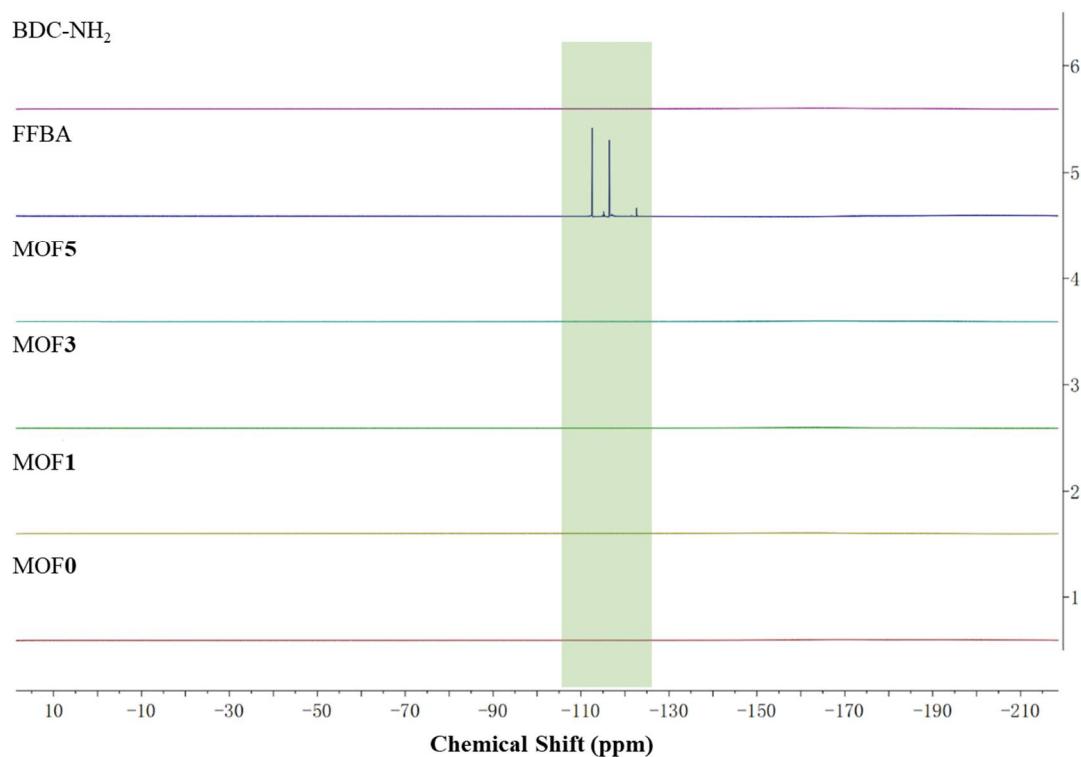


Figure S14. The ¹⁹F NMR spectra of BDC-NH₂, FFBA and four obtained MOF products digested in 10wt% NaOD/D₂O

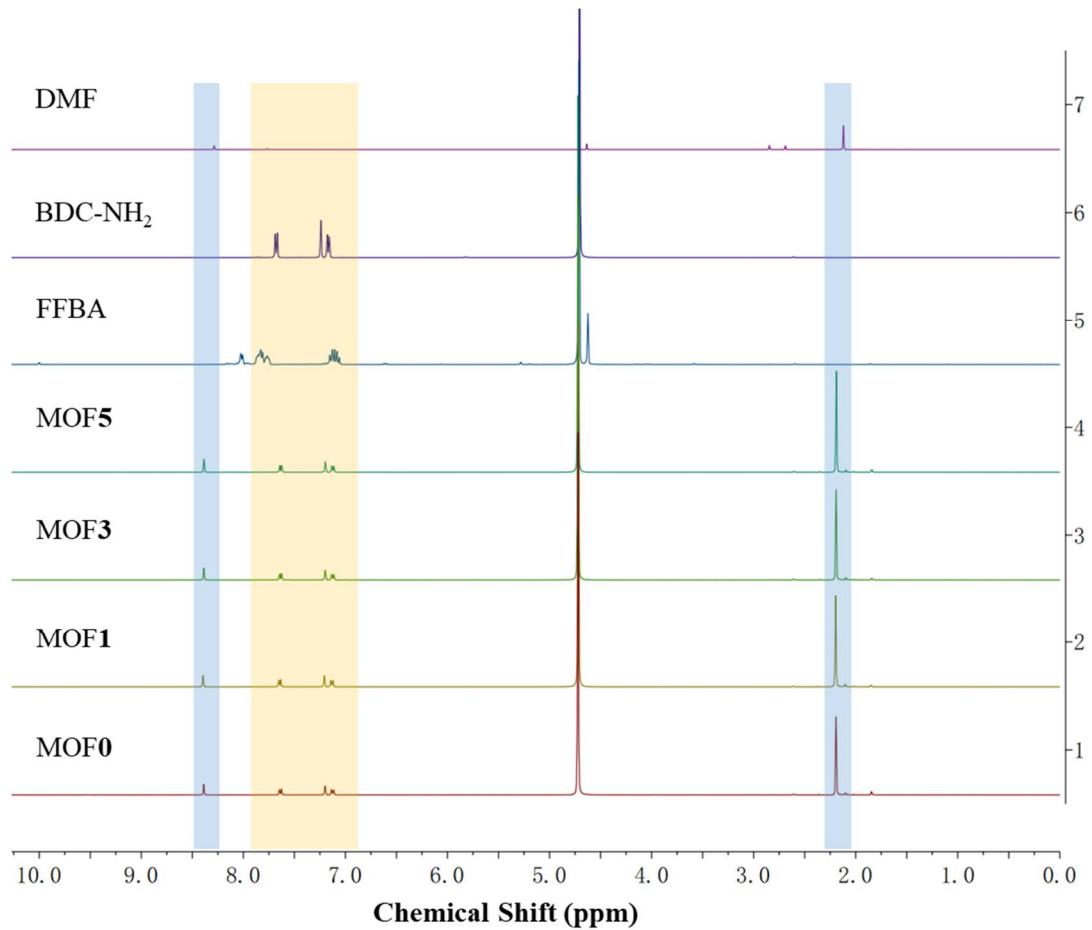


Figure S15. The ¹H NMR spectra of DMF, BDC-NH₂, FFBA and four obtained MOF products digested in 10wt% NaOD/D₂O

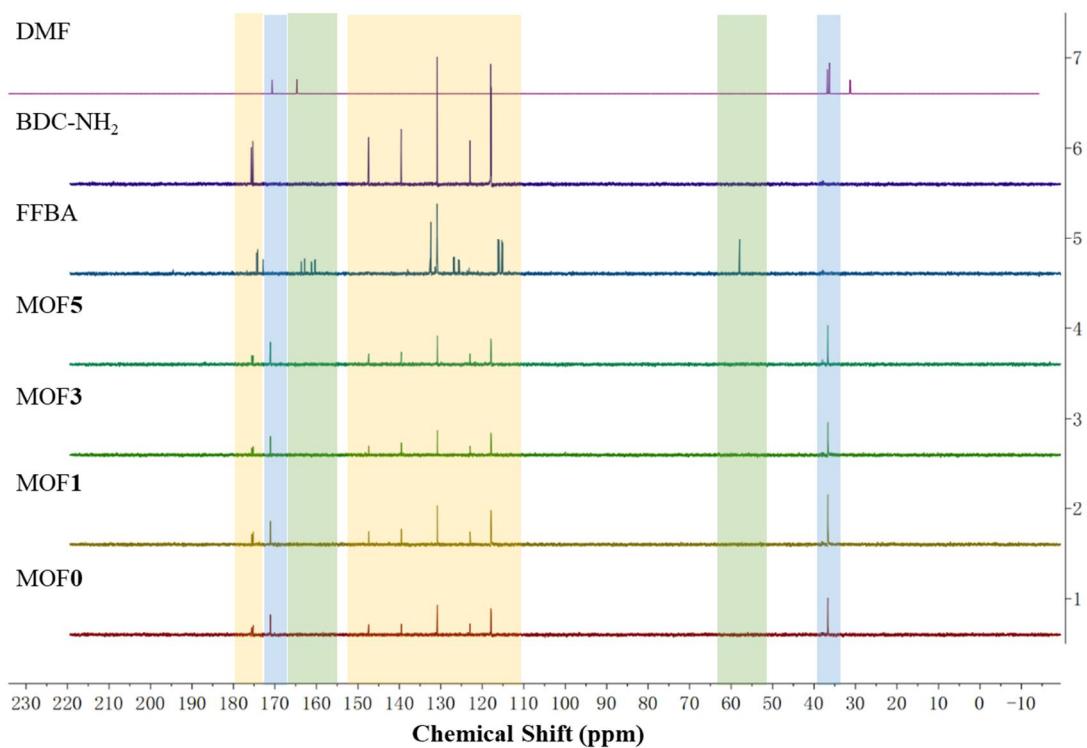


Figure S16. The ^{13}C NMR spectra of DMF, BDC-NH₂, FFBA and four obtained MOF products digested in 10wt% NaOD/D₂O

4. Observed UV-vis spectra

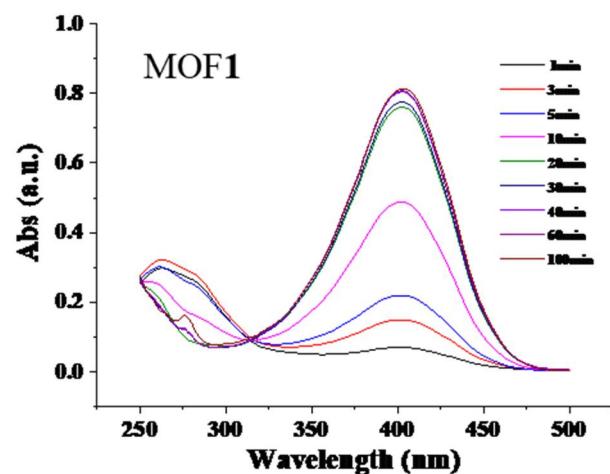


Figure S17. Hydrolysis reaction for DMNP using MOF1 as a catalyst

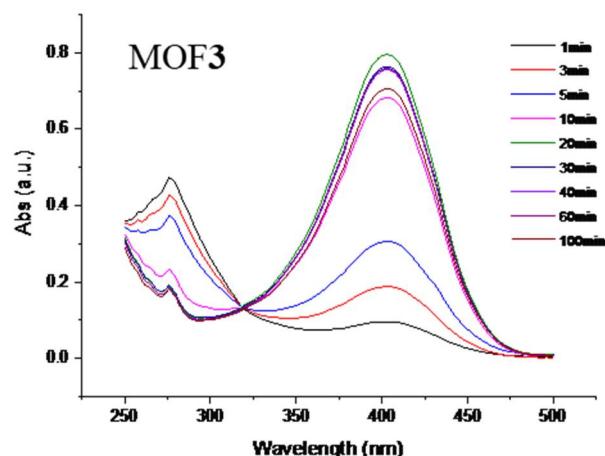


Figure S18. Hydrolysis reaction for DMNP using MOF3 as a catalyst

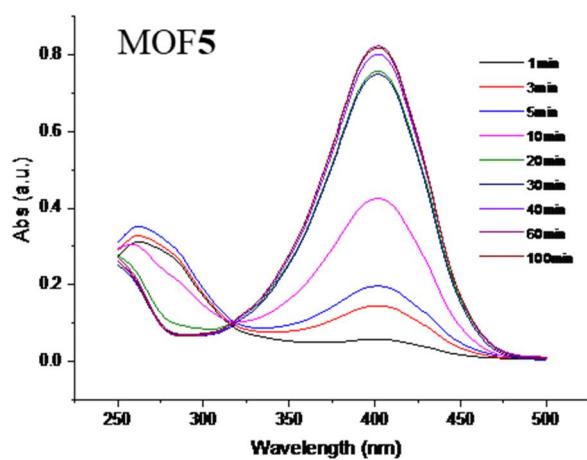


Figure S19. Hydrolysis reaction for DMNP using MOF5 as a catalyst

5. Kinetic analysis

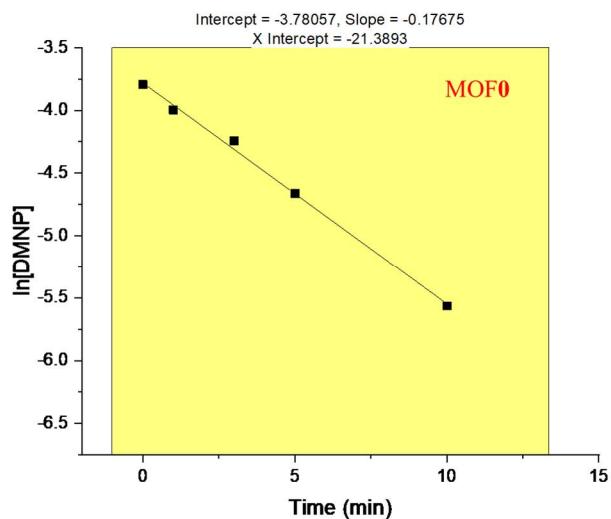


Figure S20. Kinetic analysis using MOF0 as a catalyst.

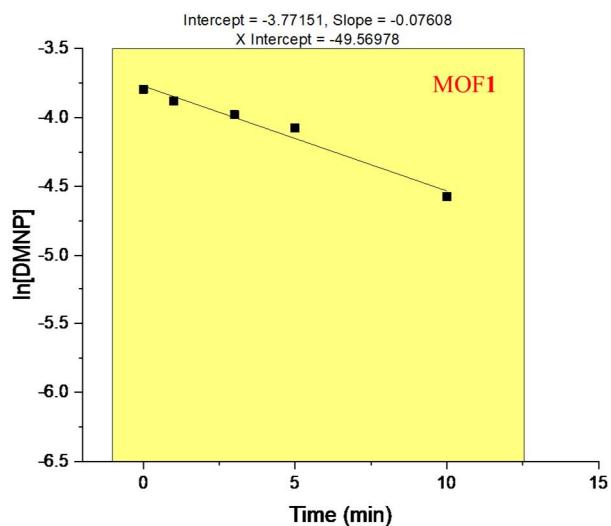


Figure S21. Kinetic analysis using MOF1 as a catalyst.

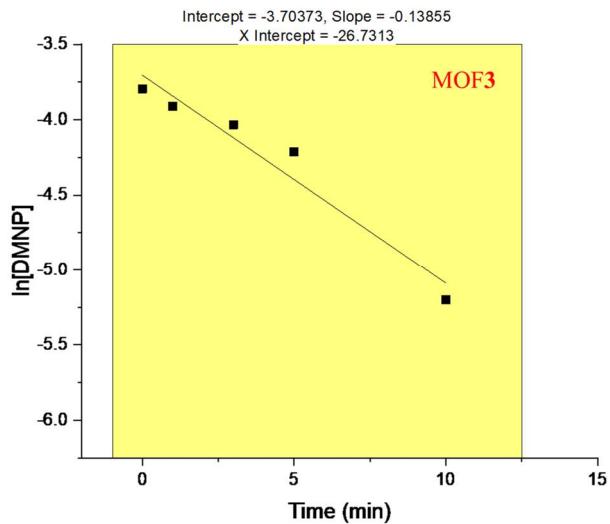


Figure S22. Kinetic analysis using MOF3 as a catalyst.

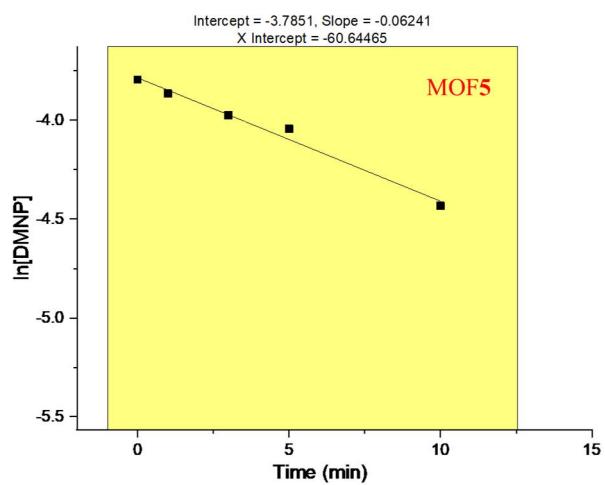


Figure S23. Kinetic analysis using MOF5 as a catalyst.

6. The comparison of catalytic activity of Zr-MOFs reported in the literatures

Table S1. The kinetic parameters of DMNP hydrolysis catalyzed different Zr-MOFs reported in the literatures

Samples	k_1 (min ⁻¹)	$t_{1/2}$ (min)	Refs.
MOF0	0.18	3.9	This work
MOF1	0.08	9.1	This work
MOF3	0.14	5.0	This work
MOF5	0.06	11.1	This work
UiO-66-NH ₂	0.14	4.8	[1]
UiO-66-NH ₂		< 1	[2]
UiO-66-NH ₂	0.3~1.4×10 ⁻³	24~495	[3]
UiO-66-NH ₂	0.16	4.4	[4]
UiO-66	0.02	35	[5]
UiO-67	0.2	3.5	[6]
NU-1000	0.05	15	[7]
NU-1000(dehydrated)	0.46	1.5	[7]
MOF-808	1.40	0.5	[8]

7. References

1. Chen, R.; Tao, C.-a.; Zhang, Z.; Chen, X.; Liu, Z.; Wang, J. Layer-by-layer Fabrication of Core-Shell Fe₃O₄@UiO-66-NH₂ with High Catalytic Reactivity toward the Hydrolysis of Chemical Warfare Agent Simulants. *ACS Applied Materials & Interfaces* **2019**, *11*, 43156–43165, doi:10.1021/acsami.9b14099.
2. Peterson, G.W.; Moon, S.; Wagner, G.W.; Hall, M.G.; Decoste, J.B.; Hupp, J.T.; Farha, O.K. Tailoring the Pore Size and Functionality of UiO-Type Metal–Organic Frameworks for Optimal Nerve Agent Destruction. *Inorganic Chemistry* **2015**, *54*, 9684–9686, doi:10.1021/acs.inorgchem.5b01867.
3. Peterson, G.W.; Destefano, M.R.; Garibay, S.J.; Ploskonka, A.M.; McEntee, M.; Hall, M.G.; Karwacki, C.J.; Hupp, J.T.; Farha, O.K. Optimizing Toxic Chemical Removal through Defect-Induced UiO-66-NH₂ Metal–Organic Framework. *Chemistry - A European Journal* **2017**, *23*, 15913–15916, doi:10.1002/chem.201704525.
4. Lu, A.X.; McEntee, M.; Browne, M.A.; Hall, M.G.; DeCoste, J.B.; Peterson, G.W. MOFabric: Electrospun Nanofiber Mats from PVDF/UiO-66-NH₂ for Chemical Protection and Decontamination. *Acs Applied Materials & Interfaces* **2017**, *9*, 13632–13636, doi:10.1021/acsami.7b01621.
5. Katz, M.J.; Mondloch, J.E.; Totten, R.K.; Park, J.K.; Nguyen, S.T.; Farha, O.K.; Hupp, J.T. Simple and compelling biomimetic metal-organic framework catalyst for the degradation of nerve agent simulants. *Angewandte Chemie International Edition* **2014**, *53*, 497–501, doi:10.1002/anie.201307520.
6. Katz, M.J.; Moon, S.; Mondloch, J.E.; Beyzavi, M.H.; Stephenson, C.J.; Hupp, J.T.; Farha, O.K. Exploiting parameter space in MOFs: a 20-fold enhancement of phosphate-ester hydrolysis with UiO-66-NH₂. *Chemical Science* **2015**, *6*, 2286–2291, doi:10.1039/C4SC03613A.
7. Mondloch, J.E.; Katz, M.J.; Isley, W.C.; Ghosh, P.; Liao, P.; Bury, W.; Wagner, G.W.; Hall, M.G.; Decoste, J.B.; Peterson, G.W. Destruction of chemical warfare agents using metal–organic frameworks. *Nature Materials* **2015**, *14*, 512–516, doi:10.1038/nmat4238.
8. Moon, S.-Y.; Liu, Y.; Hupp, J.T.; Farha, O.K. Instantaneous Hydrolysis of Nerve-Agent Simulants with a Six-Connected Zirconium-Based Metal–Organic Framework. *Angewandte Chemie International Edition* **2015**, *54*, 6795–6799, doi:10.1002/anie.201502155.