[Supporting Information (SI) to accompany:]

# Synthesis of Nanocrystals of Zr-based Metal-Organic Frameworks with csq-Net: Significant Enhancement in the Degradation of a Nerve Agent Simulant

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**Section S1. General procedures, materials, and instrumentations.**

**Materials.** Zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) and benzoic acid ($C_6H_5COOH$) were purchased from Sigma-Aldrich and used as received, Fe(III) meso-Tetra(4-carboxyphenyl)porphine chloride (FeTCPP) was purchased from Frontier Scientific and used without further purification. The ligand 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene ($H_4$TBAPy) was synthesized following the published procedure.[1]

**Methods of Characterization and Instrumentations.**

Powder X-ray diffraction data were collected on a Rigaku model ATX-G diffractometer equipped with a Cu rotating anode X-ray source. This work made use of the J.B. Cohen X-ray Diffraction Facility supported by the MRSEC program of the National Science Foundation (DMR-1121262) at the Materials Research Center of Northwestern University.

Thermogravimetric analyses (TGA) were performed on a TGA/DCS 1 system (Mettler-Toledo AG, Schwerzenbach, Switzerland), which runs on a PC with STAR$^e$ software. Samples were heated from 25 to 600 ℃ at a rate of 10 ℃/min under flowing $N_2$.

$N_2$ sorption isotherm measurements were performed on a Micromeritics Tristar II 3020 (Micromeritics, Norcross, GA) at 77K. Between 30 and 100 mg of material was used for each measurement. Surface areas were estimated by applying the Brunauer–Emmett–Teller (BET) equation. T-plot internal and external surface area were determined by Harkins and Jura equation in the second linear regions of $N_2$ isotherms (0.26 $P/P_0$ to 1.0 $P/P_0$).[2]

Scanning electron micrographs (SEM) images were taken using a Hitachi SU8030 or a Hitachi S4800-II at the EPIC facility (NU*ANCE* Center-Northwestern University), which has received support from the MRSEC program (NSF DMR-1121262) at the Materials Research Center; the Nanoscale Science and Engineering Center (NSF EEC–0647560) at the International Institute for Nanotechnology; and the State of Illinois, through the International Institute for Nanotechnology.

Dynamic light scattering measurements of hydrodynamic radii were made on a

Malvern Zetasizer Nano-ZS (Malvern Instruments). Results were averaged over five measurements.

Hydrolysis profiles of methyl paraoxon were recorded by in-situ $^{31}P$ NMR measurement (400 MHz Agilent DD MR-400 at IMSERC (Integrated Molecular Structure Education and Research Center) of Northwestern University) at room temperature (National Science Foundation (CHE-9871268) and International Institute of Nanotechnology).

**Hydrolysis of Methyl Paraoxon with Different Sized NU-1000**

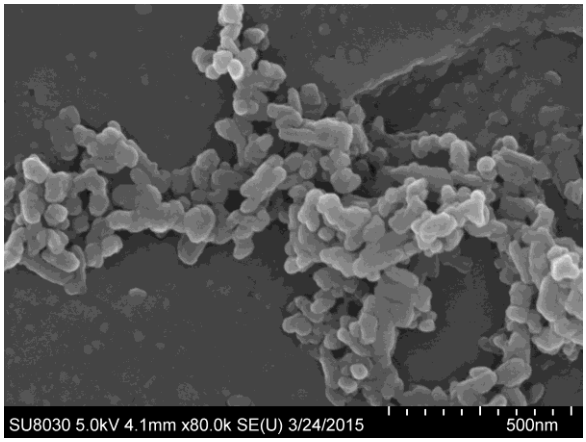
NU-1000 (F.W: 2160.55, 0.8 mg, 0.37 μmol) was loaded into a 1.5 dram vial and 1 mL of 0.4 M *N*-ethylmorpholine solution (0.05 mL *N*-ethylmorpholine, 0.9 mL DI water/0.1 mL $D_2O$) was added. The reaction mixture was stirred for 15 min to disperse the MOF particles homogeneously, and then 4 μL (25 μmol) of methyl paraoxon were added and the reaction was swirled for 10 s. The reaction mixture was then transferred to a NMR tube and the spectrum was immediately measured; the first data point was collected 150 s after the start of the reaction. The progress of the reaction was monitored with 1 min increments for 1 h (number of scans = 16, delay time = 28 s). The solvent was 10 % $D_2O/H_2O$. To measure reaction conversions at 30 s, the reaction mixture was prepared under identical conditions and filtered using a commercial 200 nm syringe filter or 20 nm AAO (anodic aluminium oxide) membrane at 30 s, thereby stopping the reaction and permitting the degree of completion to be assessed by $^{31}P$ NMR.

**Section S2. Synthesis of NU-1000 and PCN-222/MOF-545particles with different sizes**

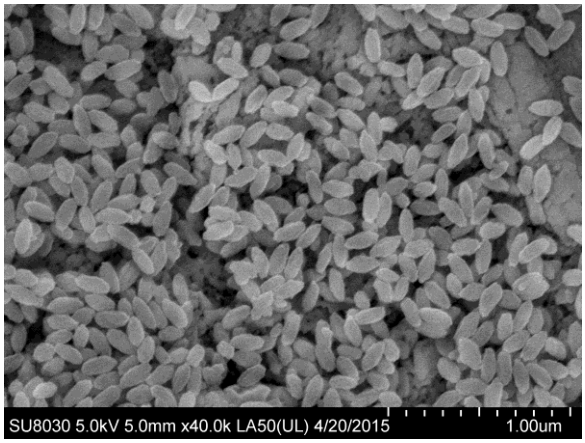
Solution **A:** 970 mg (3.00 mmol) of $ZrOCl_2 \cdot 8H_2O$ and 16.0 g (131 mmol) of benzoic acid were dissolved in 80 mL of DMF in a 100 ℃ oven.

Solution **B:** 200 mg (0.300 mmol) of the 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene ($H_4$TBAPy) ligand was dissolved in 80 mL of DMF in a 100 ℃ oven.

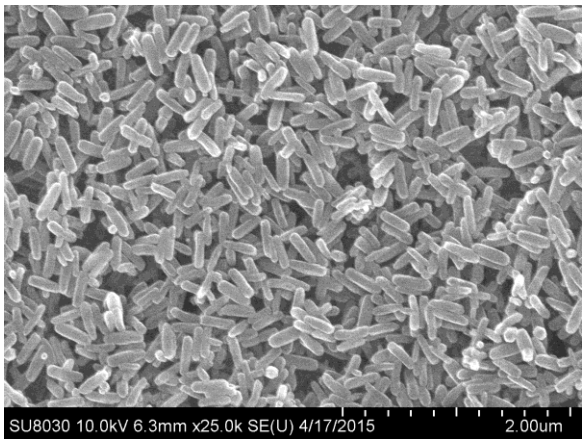
**Synthesis of NU-1000-75nm**. 1 mL of solution **A** and 1 mL of solution **B** were added to a 1.5-dram vial containing 20 μL trifluoroacetic acid (0.26 mmol), resulting in a translucent yellow solution. 10 sample vials were prepared under the same conditions at once and were placed into an oven at 100 ℃ for 30 min, during which time a yellow suspension formed. After cooling down to room temperature, the 10 vials were combined and the suspension was isolated by centrifugation at 7800 rpm for 10 min. The sample was further washed with DMF and acetone twice, then subsequently activated with HCl (see below).




**Synthesis of NU-1000-150nm**. 1 mL of solution **A** and 1 mL of solution **B** were added to a 1.5-dram vial containing 20 μL trifluoroacetic acid (0.26 mmol), resulting in a translucent yellow solution. 10 sample vials were prepared under the same conditions at once and placed into an oven at 100 ℃ for 1 h, during which time a yellow suspension formed. After cooling down to room temperature, the 10 vials were combined and the suspension was isolated by centrifugation at 7800 rpm for 10 min. The sample was further washed with DMF and acetone twice, then subsequently activated with HCl.

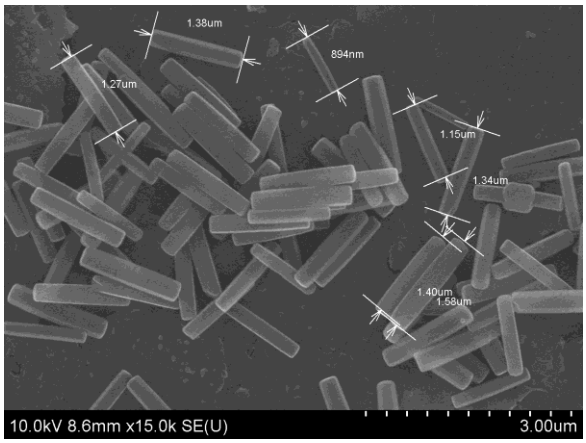



**Synthesis of NU-1000-500nm**. 1 mL of solution **A** and 1 mL of solution **B** were added to a 1.5-dram vial containing 20 μL trifluoroacetic acid (0.26 mmol), resulting in a translucent yellow solution. 10 sample vials were prepared under the same conditions at once and placed into an oven at 120 ℃ for 30 min, during which time a yellow suspension formed. After cooling down to room temperature, the 10 vials were combined and the suspension was isolated by centrifugation at 7800 rpm for 10 min. The sample was further washed with DMF and acetone twice, then subsequently activated with HCl.




**Synthesis of NU-1000-1200nm**. 1 mL of solution **A** and 1 mL of solution **B** were added to a 1.5-dram vial, resulting in a translucent yellow solution. 10 sample vials were prepared under the same conditions at once and placed into an oven at 120 ℃ for 1 h, during which time a yellow suspension formed. After cooling down to room temperature, the 10 vials were combined and the suspension was isolated by centrifugation at 7800 rpm

for 10 min. The samples was further washed with DMF and acetone twice, then subsequently activated with HCl.



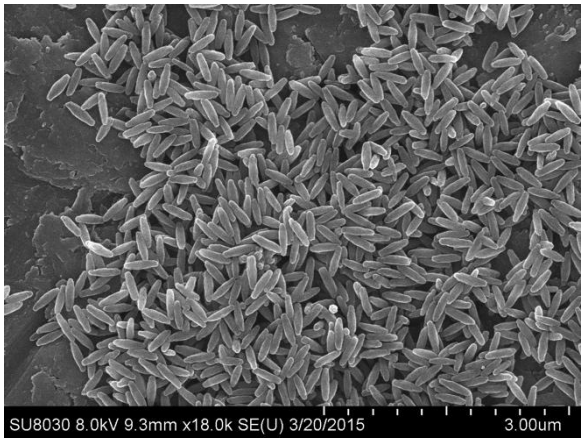

**Synthesis of NU-1000-15000nm**. 70 mg of $ZrCl_4$ (0.30 mmol) and 2700 mg (22 mmol) of benzoic acid were mixed in 8 mL of DEF (in a 6-dram vial) and ultrasonically dissolved. The clear solution was incubated in an oven at 80 °C for 1h. After cooling down to room temperature, 40 mg (0.06 mmol) of $H_4$TBAPy was added to this solution and the mixture was sonicated for 20 min. The yellow suspension was heated in an oven at 120 °C for 48 h. After cooling down to room temperature, yellow single crystals were present on the vial walls. The sample was washed with DMF and acetone and subsequently activated with HCl.

**Activation procedure for nano-NU-1000.** Approximately 50 mg of sample was soaked in 20 mL of DMF and 4 mL of 8 M aqueous HCl was added. This mixture was heated in an oven at 100 °C for 24 h. After cooling to room temperature, the filtrate was decanted and the material was washed twice with DMF to remove HCl impurities. Subsequently, the solid residue was washed with acetone (2×) and soaked in acetone for an additional 12 h. The solid was filtered, briefly dried on a filter paper and activated at 120 °C under vacuum for 12 h before adsorption measurements.

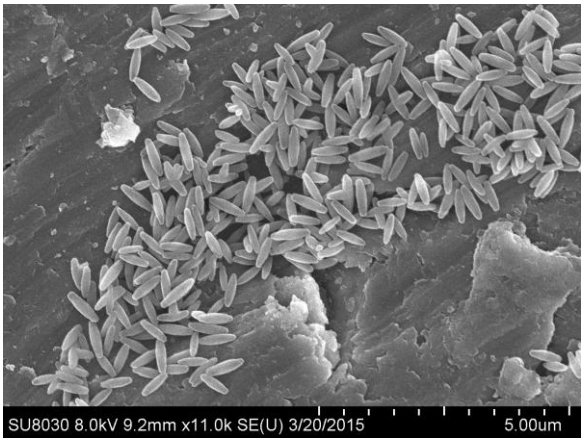
**Synthesis of PCN-222/MOF-545 (nanoscale)**. 50 mg of $ZrOCl_2 \cdot 8H_2O$ (0.155 mmol) and 0.750 g (6.14 mmol) of benzoic acid were mixed in 8 or 10 mL of DMF (in a 6-dram vial) and ultrasonically dissolved. The colorless solution was incubated in an oven at 80 ℃ for 1 h. After cooling down to room temperature, 25 mg (0.0284 mmol) of FeTCPP(FeTCPP) was added to this solution and the mixture was sonicated for 5 min. The dark brown suspension was placed in an oil bath at 120 ℃ for 1 h. After cooling down to room temperature, dark brown microcrystalline powder was isolated by centrifugation and washed with DMF and acetone.

In our hands, between multiple vials set up on the same day, we observed a very narrow particle size range typically +/− 25–75 nm (SEM images represent 2–3 vials combined into one batch); however, between batches on different days, we observe the center of the distribution varies with the 8 mL scale giving particles with a size range of 600–1000 nm and the 10 mL scale giving a size range between 300–750 nm.

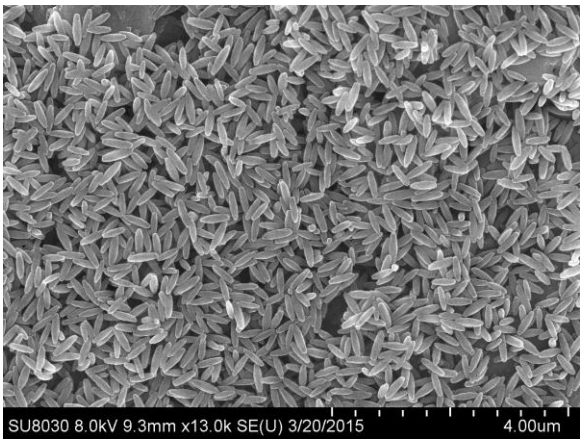
10-mL synthesis (SEM images show 2–4 vials prepared simultaneously combined into one batch).




300–400 nm

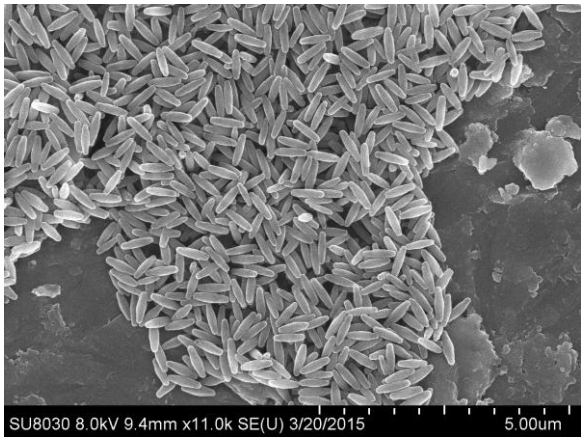



450–500 nm

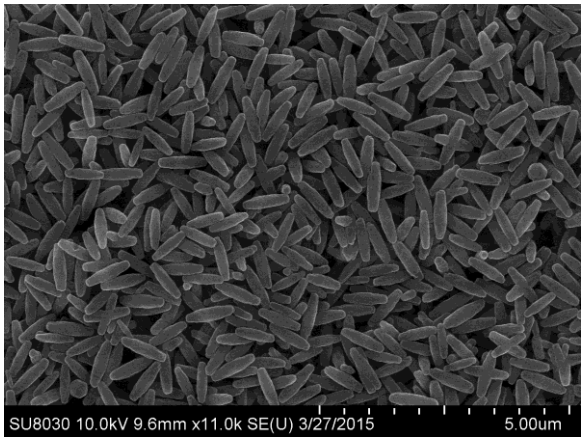



500–750 nm

8-mL synthesis (SEM images show 2–4 vials prepared simultaneously combined into one batch)



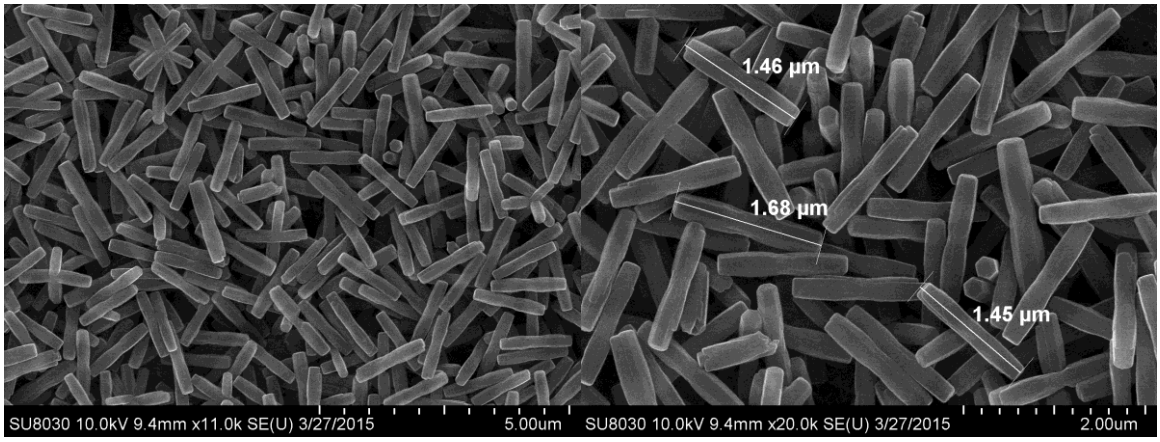

600–700 nm



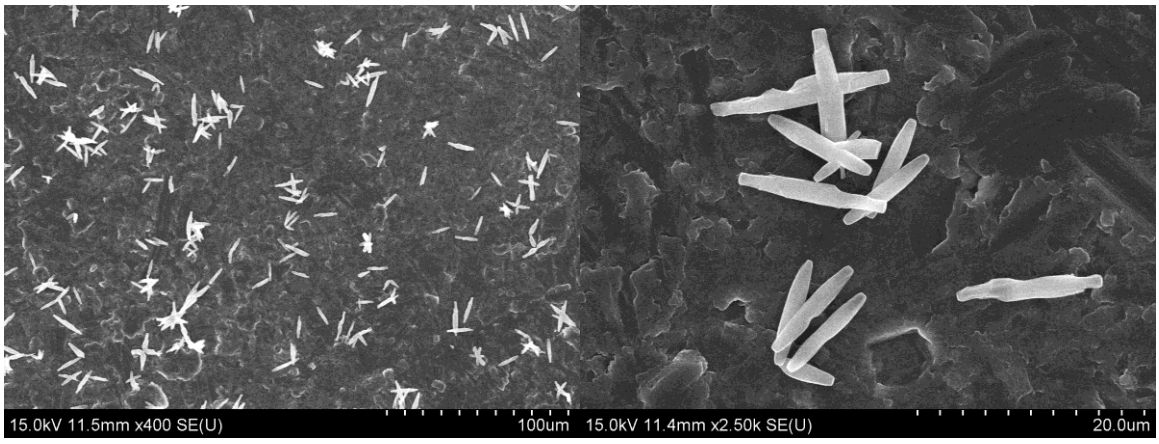

850–1000 nm

**Synthesis of PCN-222/MOF-545(1.45–1.7 μm)**. 0.240 g of $ZrOCl_2 \cdot 8H_2O$ (0.745 mmol) and 6.694 g (0.0548 mol) of benzoic acid were mixed in 15 mL of DMF (in a 100 mL jar) and ultrasonically dissolved. 0.124 g (0.141 mmol) of FeTCPP were mixed in 15 mL of DMF (in a 100 mL jar) and ultrasonically dissolved. Both the Zr/benzoic acid and the FeTCPP solutions were incubated in an oven at 100 ℃ for 1h. After cooling down to room temperature, 1 mL of the Zr/benzoic acid solution was added to a 1.5-dram vial, followed by 1 mL of the FeTCPP solution and the dark brown reaction mixture was ultrasonically dissolved, then incubated in a 120 ℃ oven for 1 h 40 min. After cooling down to room temperature, dark brown microcrystalline material was isolated by centrifugation and washed with DMF and acetone.

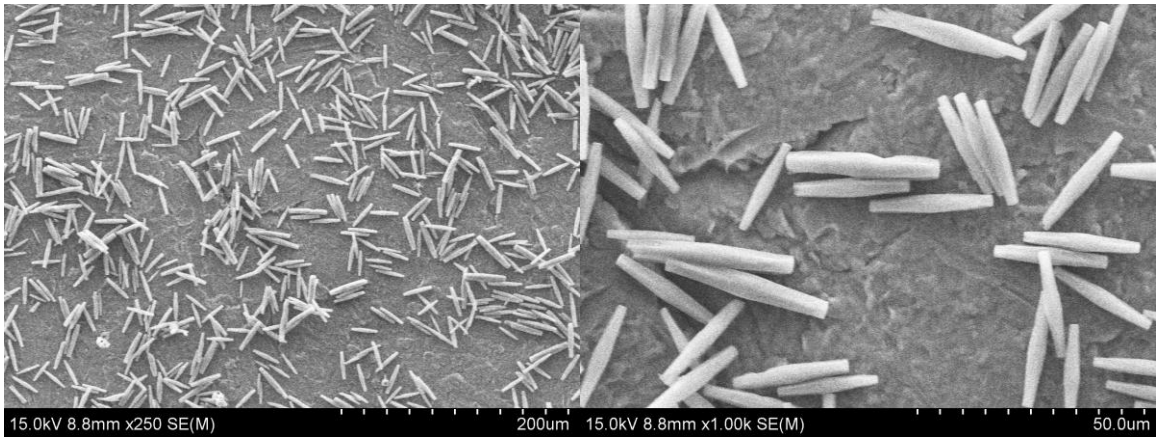
1.45–1.7 μm (SEM images show 13 vials prepared simultaneously and combined into one batch):



**Synthesis of PCN-222/MOF-545 (10–12 μm)**. 32 mg of $ZrOCl_2 \cdot 8H_2O$ (0.0993 mmol) and 0.893 g (2.77 mmol) of benzoic acid, and 16.5 mg (0.0187 mmol) of FeTCPP were mixed in 16 mL of DMF (in an 8-dram vial), then 120 μL of trifluoroacetic acid was added. The dark brown solution was ultrasonically dissolved, then incubated in an oven at 120 ℃ for 20 h. After cooling down to room temperature, dark purple microcrystalline material was isolated by centrifugation and washed with DMF and acetone.



**Synthesis of PCN-222/MOF-545 (25–35 μm)**. 64 mg of $ZrOCl_2 \cdot 8H_2O$ (0.199 mmol) and 1.785 g (14.6 mmol) of benzoic acid were mixed in 8 mL of DMF (in a 6-dram vial) and ultrasonically dissolved. The colorless solution was incubated in an oven at 80 ℃ for 1 h. After cooling down to room temperature, 33 mg (0.0375 mmol) of FeTCPP was added to this solution and the mixture was sonicated for 5 min. The dark brown suspension was placed in an oven at 120 ℃ for the indicated amount of time. After cooling down to room temperature, dark purple microcrystalline material was isolated by centrifugation and washed with DMF and acetone.



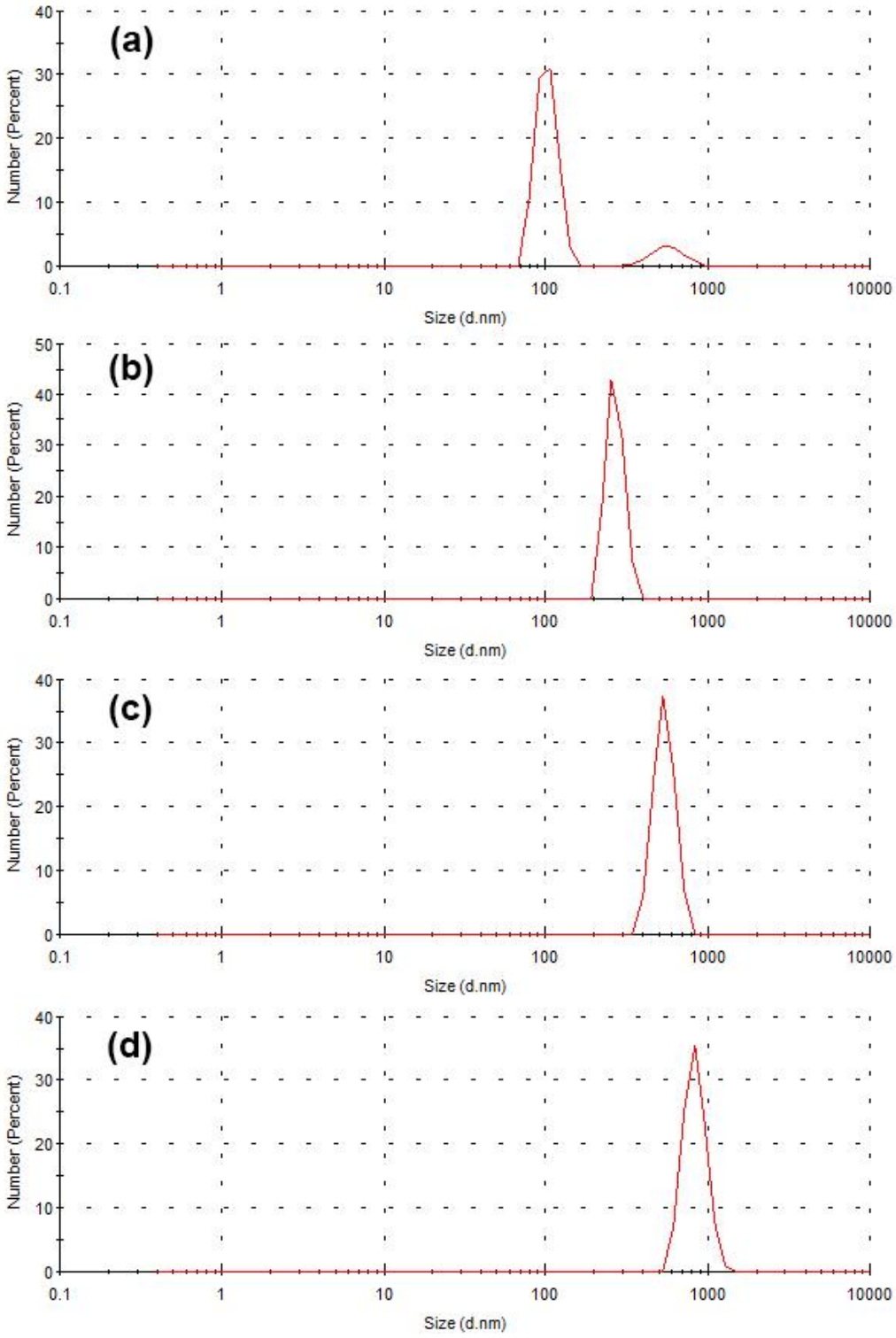



Figure S1. Particle size distributions of NU-1000 nanocrystals from DLS measurements. (a) 50–100 nm (b) 100–200 nm (c) 300–700 nm, and (d) 800–1600 nm.

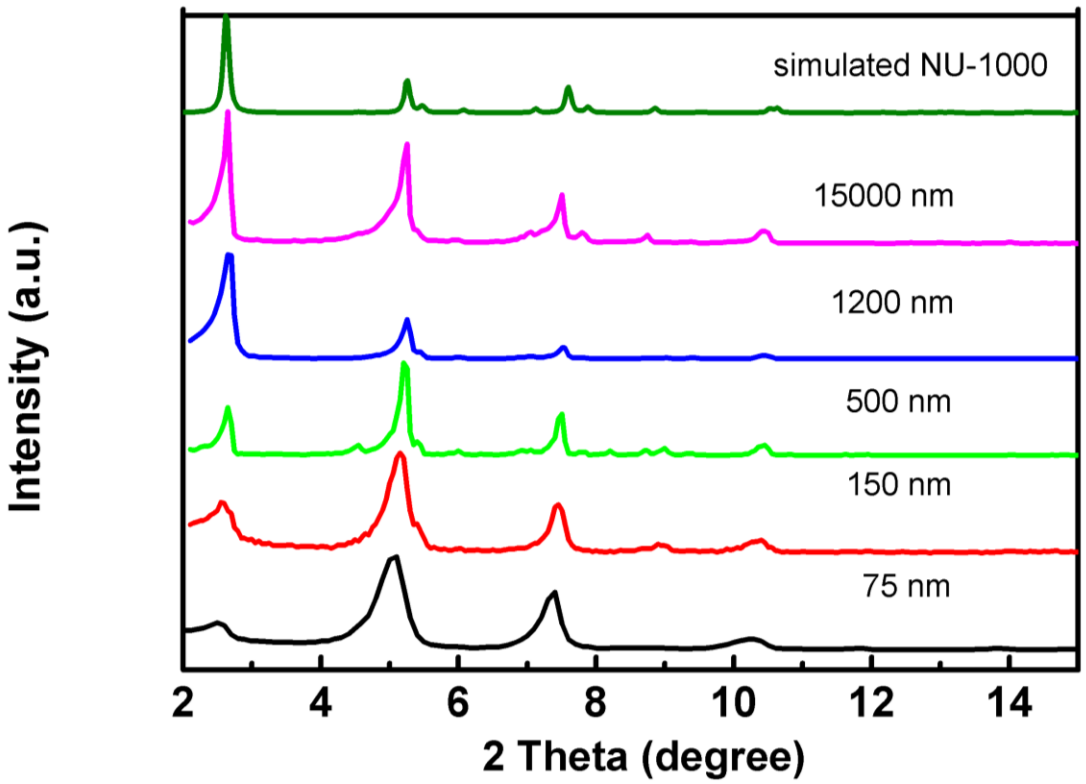



Figure S2. Powder X-ray diffraction patterns of NU-1000 samples with different particle sizes.

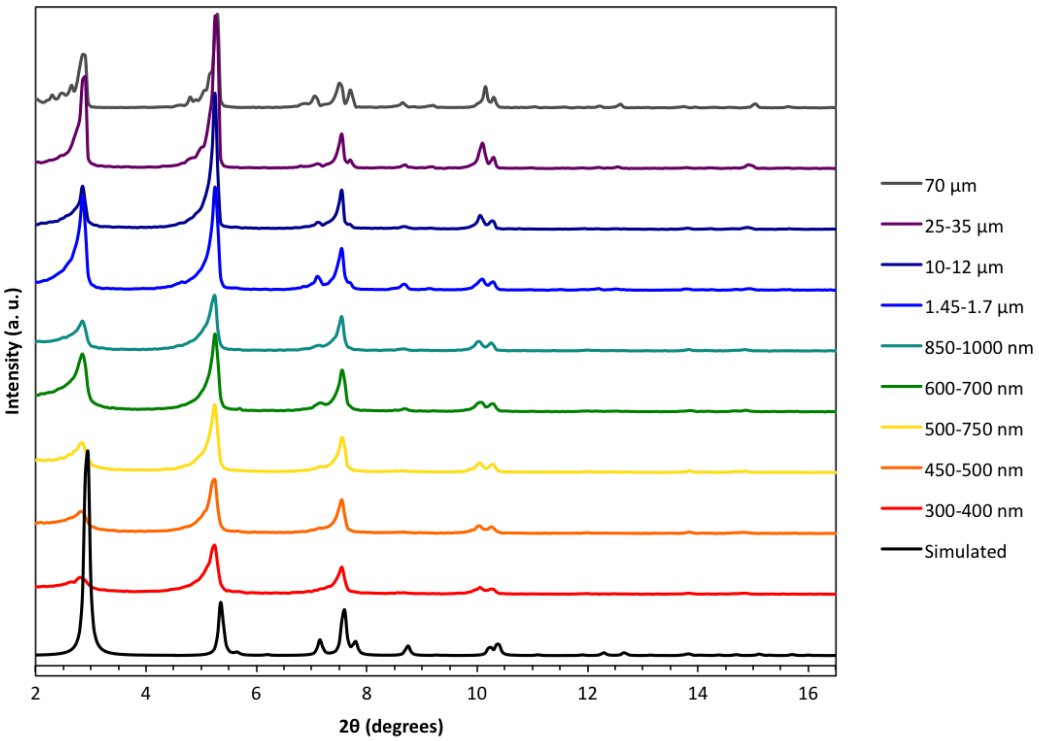



Figure S3. Powder X-ray diffraction patterns of PCN-222/MOF-545 samples with different particle sizes.

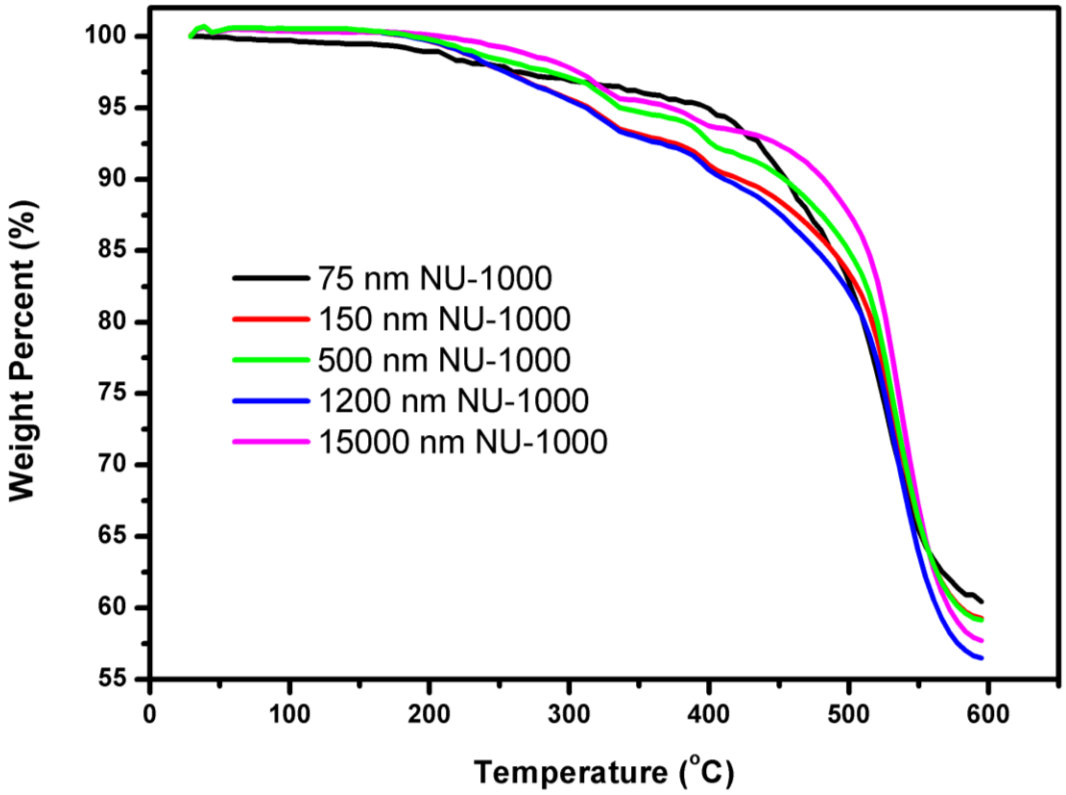



Figure S4. Thermogravimetric analysis curves of NU-1000 samples with different particle sizes.

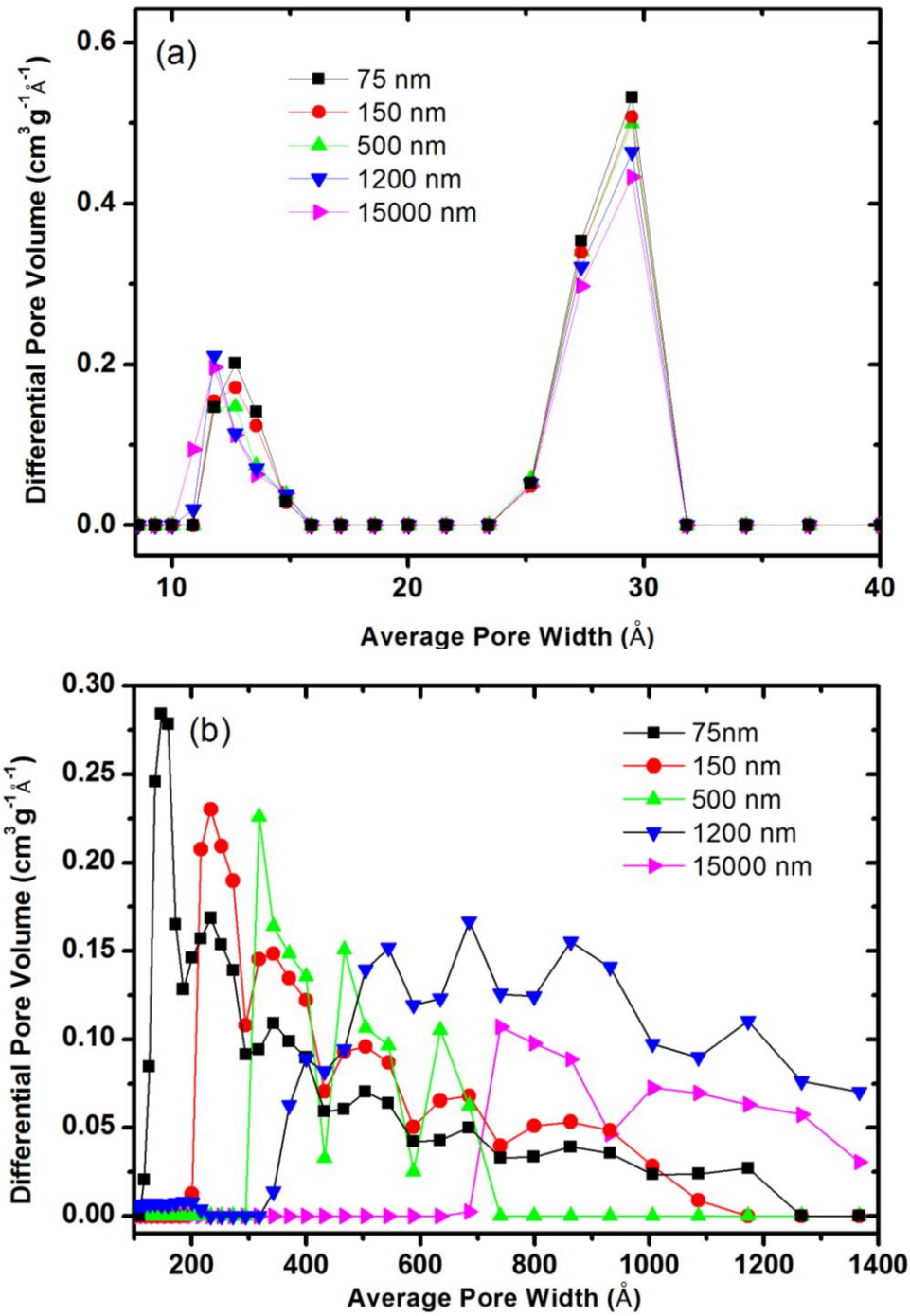
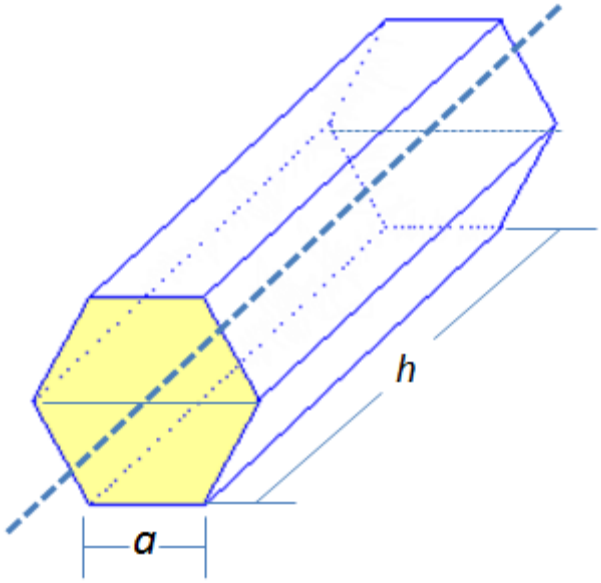



Figure S5. Pore size distribution of NU-1000 samples with different particle sizes in the region from (a) 0.8 nm to 4 nm and region from (b) 10 nm to 150 nm.

Table S1. Half-life for the hydrolysis of methyl paraoxon for NU-1000 particles with different sizes.

| Particles size (nm) | Half-life ($t_{1/2}$) (min) |
|---|---|
| 75 | 2 |
| 150 | 5 |
| 500 | 12 |
| 1200 | 38 |
| 15000 | 80 |

**Calculation of the Ratio of Surface Area over Volume in an Ideal Hexagonal Rod NU-1000 Particle**




Assuming NU-1000 particles are hexagonal cylinders with width *a* and length *h*, the volume of an NU-1000 particle is:

$$V_{NU-1000} = h \times a^2 \times \frac{3\sqrt{3}}{2} = \frac{3\sqrt{3}}{2} ha^2$$

the surface area of an NU-1000 particle is

$$S_{NU-1000} = 3\sqrt{3}a^2 + 6ah$$

$$\frac{S_{NU-1000}}{V_{NU-1000}} = \frac{3\sqrt{3}a^2 + 6ah}{\frac{3\sqrt{3}}{2} ha^2} = \frac{2}{h} + \frac{4\sqrt{3}}{3a} \approx \frac{2}{h} + \frac{2.3}{a}$$

Table S2. Particle size and approximate relative surface area over total volume (S/V) ratio for the five different sizes of NU-1000 particles.

| Particles size (nm) | S/V ($nm^{-1}$) |
|---|---|
| 75 | 0.18 |
| 150 | 0.09 |
| 500 | 0.027 |
| 1200 | 0.01125 |
| 15000 | 0.0009 |

**Calculation of t-plot Internal and External Surface in NU-1000**

t-plot analysis performed using Harkins and Jura equation:

$$t = [\ 13.99 / (\ 0.034 - \log(P/Po)\ )\ ]^{0.5}$$

Table S3. Calculation of t-plot internal and external surface area for the five different sizes of NU-1000 particles.

| Particles size (nm) | t-plot internal surface area ($m^2/g$) | t-plot external surface area ($m^2/g$) | % of external surface area |
|---|---|---|---|
| 75 | 2100 | 200 | 9.5 |
| 150 | 2100 | 150 | 7.1 |
| 500 | 2200 | 71 | 3.2 |
| 1200 | 2200 | 33 | 1.5 |
| 15000 | 2000 | 13 | 0.65 |

## References

1. J. E. Mondloch, W. Bury, D. Fairen-Jimenez, S. Kwon, E. J. DeMarco, M. H. Weston, A. A. Sarjeant, S. T. Nguyen, P. C. Stair and R. Q. Snurr, *J. Am. Chem. Soc.*, 2013, 135, 10294-10297.

2. F. Villemot, A. Galarneau and B. Coasne, *Adsorption*, 2014, 20, 349-357.