Electronic Supplementary Material (ESI) for New Journal of Chemistry.


# Supporting Information

## Label-free colorimetric detection of deoxyribonuclease I activity based on DNA-enhanced peroxidase-like activity of MIL-53(Fe)

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**Table S1.** The oligonucleotides used in this work.

| Oligonucleotides | Oligonucleotide Sequences |
|---|---|
| **M1** | 5′-A-FAM-3′ |
| **M2** | 5′-CA-FAM-3′ |
| **M3** | 5′-CCA-FAM-3′ |
| **M6** | 5′-TAA CCA-3′ |
| **M12** | 5′-AGG CAG TAA CCA-3′ |
| **M24** | 5′-AGG CAG TAA CCA AGG CAG TAA CCA-3′ |
| **M36** | 5′-AGG CAG TAA CCA AGG CAG TAA CCA AGG CAG TAA CCA-3′ |
| **A20** | 5′-AAA AAA AAA AAA AAA AAA AA-3′ |
| **G20** | 5′-GGG GGG GGG GGG GGG GGG GG-3′ |
| **C20** | 5′-CCC CCC CCC CCC CCC CCC CC-3′ |
| **T20** | 5′-TTT TTT TTT TTT TTT TTT TT-3′ |

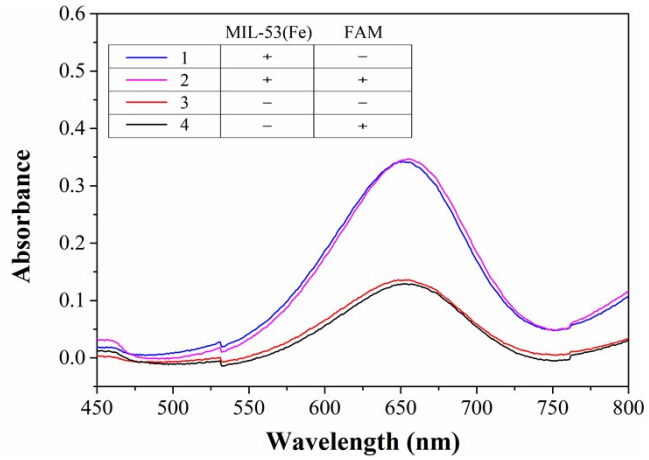


**Figure S1.** UV-vis absorption spectra of TMB and $H_2O_2$ with and without the presence of MIL-53(Fe) or FAM. [TMB] = 0.2 mM, [$H_2O_2$] = 2.5 mM, [MIL-53(Fe)] = 5 μg $mL^{-1}$, [FAM] = 250 nM.

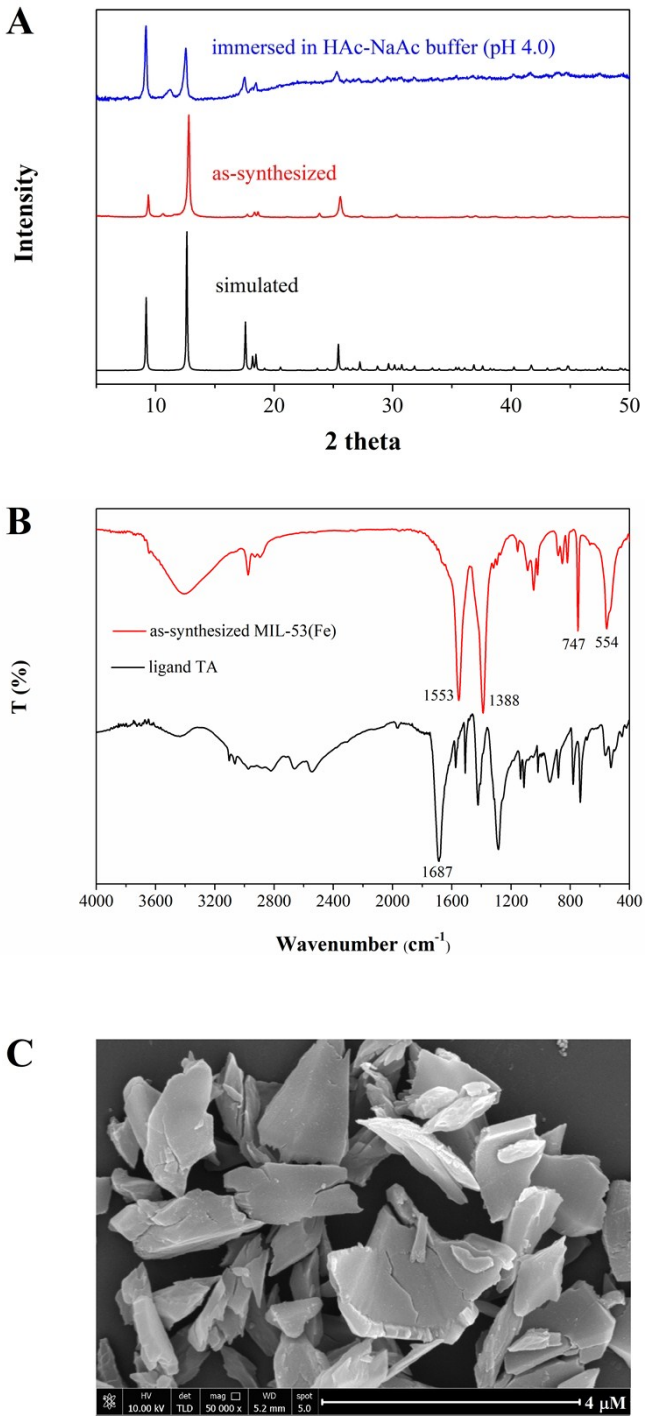


**Figure S2.** (A) PXRD patterns of MIL-53(Fe) under different conditions: simulated, as-synthesized, and immersed in 50 mM HAc-NaAc bu□er (pH 4.0) under 3 h. (B) FTIR spectrum of as-synthesized MIL-53(Fe) and terephthalic acid (TA) ligand. (C) (A) Typical SEM image of MIL-53(Fe).

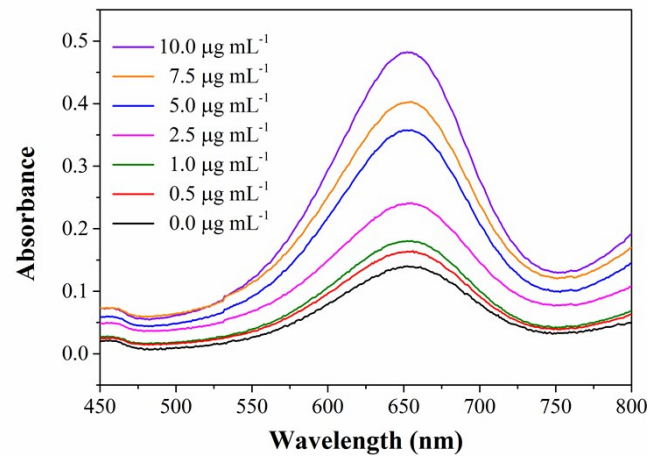


**Figure S3.** UV-vis absorption spectra of TMB and $H_2O_2$ with different concentrations of MIL-53(Fe). [TMB] = 0.2 mM, [$H_2O_2$] = 2.5 mM.

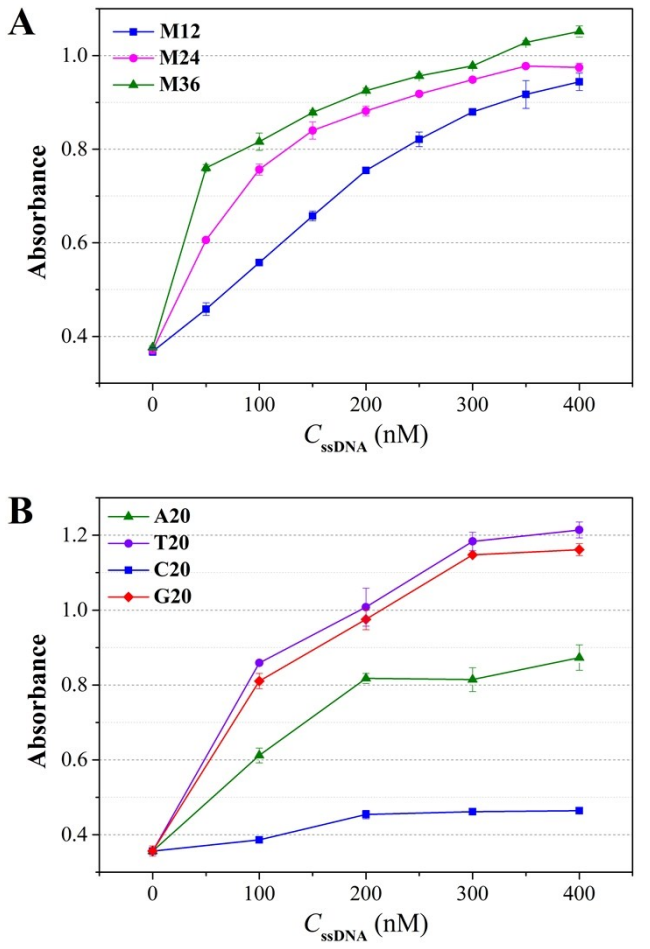


**Figure S4**. (A) Absorbance at 652 nm of reaction systems with different concentrations of **M12**, **M24** and **M36**. (B) Absorbance at 652 nm of reaction systems in the presence of 20-nt homo ssDNAs of **A20**, **G20**, **T20** and **C20**. [ssDNA] = 200 nM.

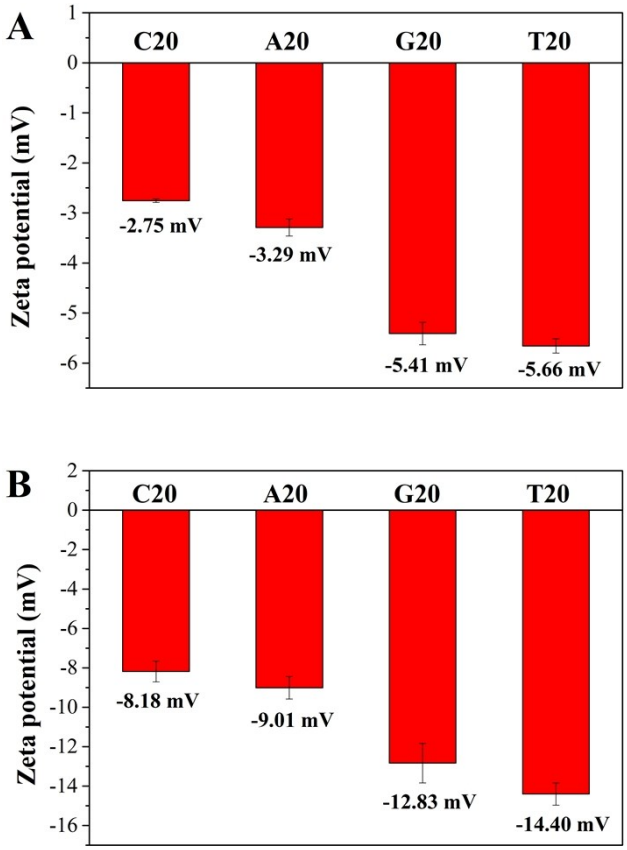


**Figure S5**. Zeta potential of 20-mer DNA homopolymer-modified MIL-53(Fe) (A) and the four types of homopolymers (B) at pH 4.0. [ssDNAs] = 200 nM.

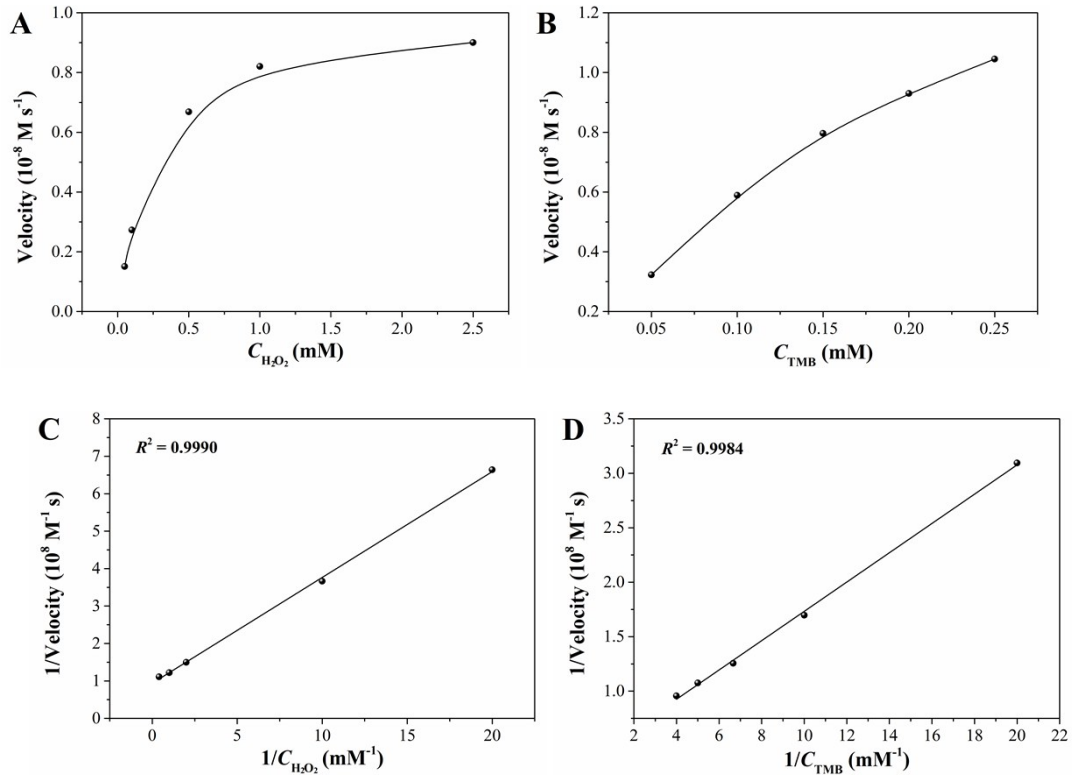


**Figure S6.** Steady-state kinetic assay of **M24**-capped MIL-53(Fe) at pH 4.0. (A) Reaction velocity plots with a fixed TMB concentration (0.2 mM) and various $H_2O_2$ concentration. (B) Reaction velocity plots with a fixed $H_2O_2$ concentration (2.5 mM) and various TMB concentrations. (C and D) Double reciprocal plots of the **M24**-capped MIL-53(Fe) with the concentration of one substrate ($H_2O_2$ or TMB) varied. [**M24**] = 200 nM, [MIL-53(Fe)] = 5 μg $mL^{-1}$.

**Table S2.** The Michaelis−Menten constant ($K_m$) and maximum initial velocity ($V_{max}$) of MIL-53(Fe) and ssDNA-capped MIL-53(Fe) at pH 4.0.

| Catalyst | Substrate | $K_m$ (mM) | $V_{max}$ ($10^{-8}$ M $s^{-1}$) | Reference |
|---|---|---|---|---|
| **MIL-53(Fe)** | $H_2O_2$ | 0.04 | 1.86 | 1 |
| | TMB | 1.08 | 8.78 | |
| **ssDNA-modified MIL-53(Fe)** | $H_2O_2$ | 0.35 | 2.58 | **This work** |
| | TMB | 0.30 | 1.07 | |

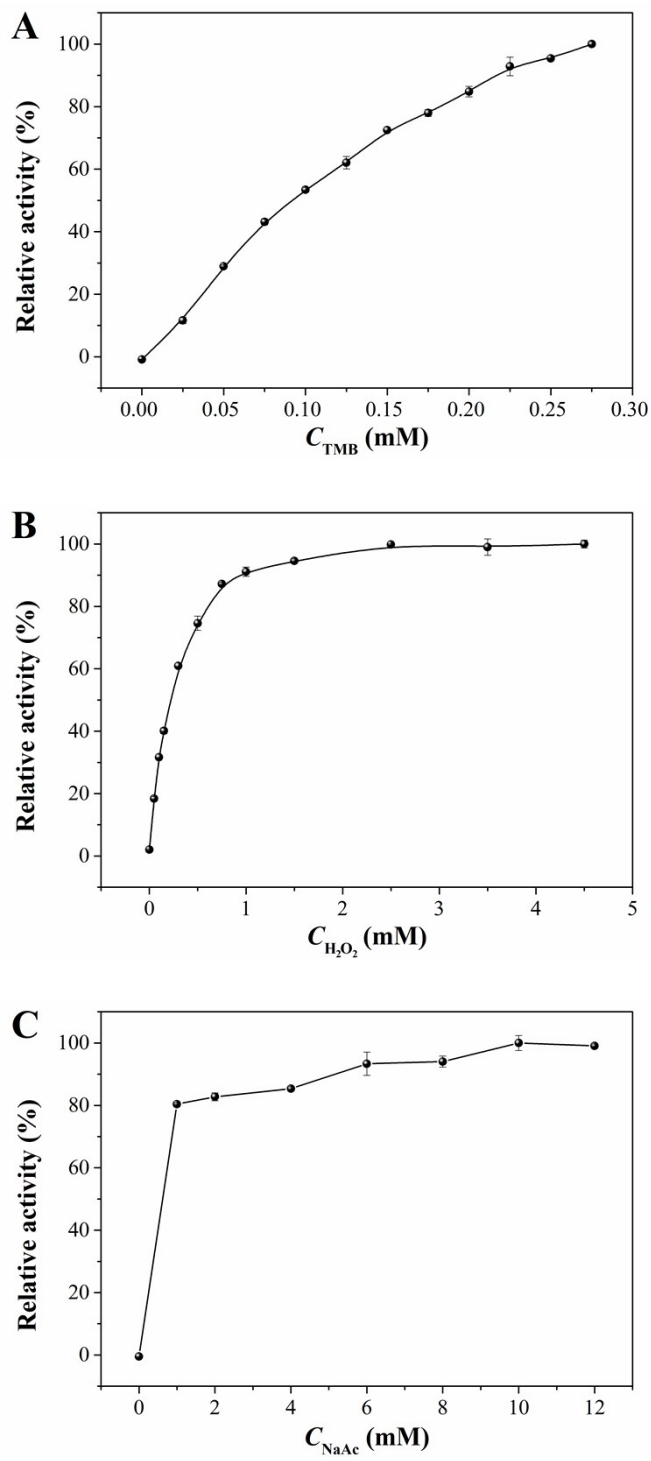


**Figure S7.** Effect of (A) TMB concentration, (B) $H_2O_2$ concentration, (C) NaAc concentration on the peroxidase-like activity of DNA-modified MIL-53(Fe). The absorbance was read at the maximum absorbance of 652 nm and the maximum point in each curve was set as 100 %. [**M24**] = 200 nM, [MIL-53(Fe)] = 5 μg $mL^{-1}$.

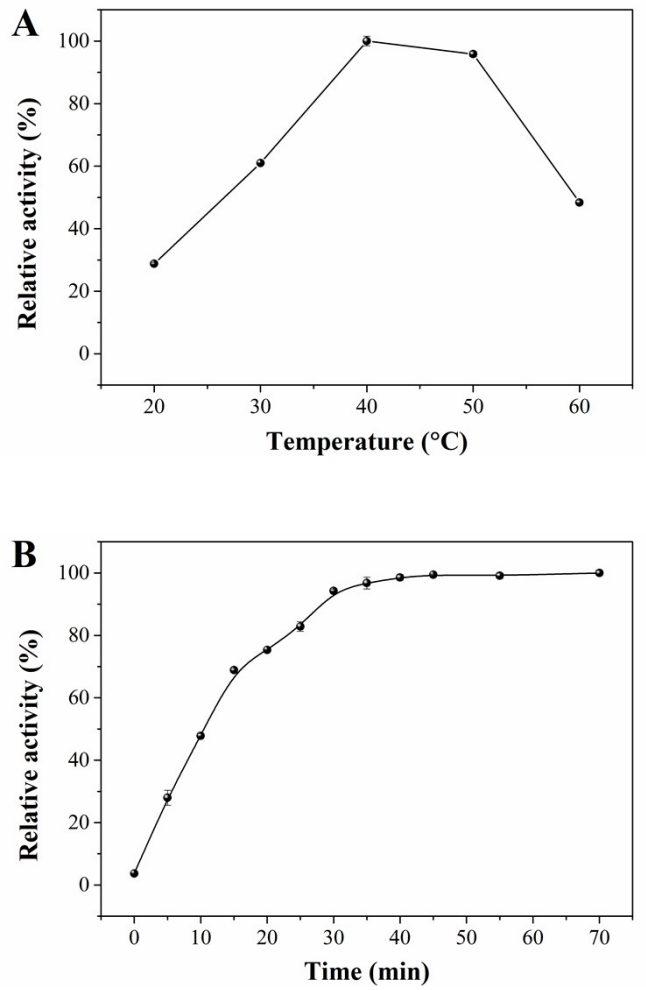


**Figure S8.** Effect of TMB oxidation temperature (A) and time (B) on the peroxidase-like activity of DNA-modified MIL-53(Fe). The absorbance was read at the maximum absorbance of 652 nm and the maximum point in each curve was set as 100 %. [**M24**] = 200 nM, [MIL-53(Fe)] = 5 μg $mL^{-1}$.

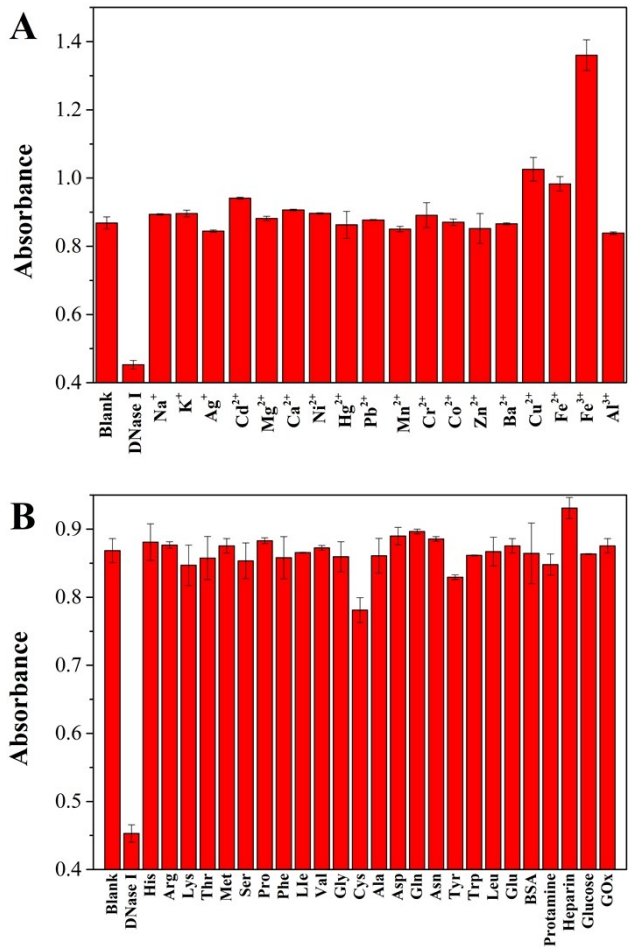


**Figure S9.** The specificity of the DNase I activity assay. Concentrations of BSA, protamine, heparin and GOx are 1 μg $mL^{-1}$. Amounts of metal ions, amino acids and glucose are 1 μM. [DNase I] = 10 U $mL^{-1}$.

**Table S3.** Comparsion of this method with other conventional methods.

| Methods | Linear range ($U\ mL^{-1}$) | Detection limit ($U\ mL^{-1}$) | Reference |
|---|---|---|---|
| **Electrochemical** method based on a gold electrode through the sulfur–gold linkage | 0.10−10 | 0.10 | 2 |
| **Potentiometric** method based on a polycation-sensitive membrane electrode | 1−10 | 0.45 | 3 |
| **Fluorescence** method based on DNA-templated silver nanocluster/graphene oxide nanocomposite | 0−10 | 0.10 | 4 |
| **Fluorescence** method based on a graphene oxide - quenched hairpin probe | 2−70 | 1.0 | 5 |
| **Fluorescence** method based on malachite green/G-quadruplexes | 5−100 | 1.0 | 6 |
| **Fluorescence** method based on graphene oxide as sensing platform | 1.75−70 | 1.75 | 7 |
| **Colorimetric** method based on photoinduced synthesis of AuNPs | 0.5−10 | 1.58 | 8 |
| **Colorimetric** method based on DNA-enhanced peroxidase-like activity of MIL-53(Fe) | 0.2-7 | 0.09 | **This work** |

**Table S4.** Analytical results for DNase I activity in 1% human serum samples.

| Sample | Added ($U\ mL^{-1}$) | Determined ($U\ mL^{-1}$) | Recovery (%) |
|---|---|---|---|
| 1 | 0 | Not detectable | – |
| 2 | 1 | 1.02 ± 0.08 | 102.0 ± 8.0 |
| 3 | 2 | 1.83 ± 0.02 | 91.5 ± 1.0 |

**References**


(1) Ai, L.; Li, L.; Zhang, C.; Fu, J.; Jiang, J. MIL-53(Fe): A Metal-Organic Framework with Intrinsic Peroxidase-Like Catalytic Activity for Colorimetric Biosensing. *Chem. Eur. J.* **2013,** *19*, 15105-15108.

(2) Sato, S.; Fujita, K.; Kanazawa, M.; Mukumoto, K.; Ohtsuka, K.; Waki, M.; Takenaka, S. Electrochemical Assay for Deoxyribonuclease I Activity. *Anal. Biochem.* **2008,** *381*, 233-239.

(3) Ding, J.; Qin, W. Potentiometric Sensing of Nuclease Activities and Oxidative Damage of Single-Stranded DNA Using a Polycation-Sensitive Membrane Electrode. *Biosens. Bioelectron.* **2013,** *47*, 559-565.

(4) Lee, C. Y.; Park, K. S.; Jung, Y. K.; Park, H. G. A Label-Free Fluorescent Assay for Deoxyribonuclease I Activity Based on DNA-Templated Silver Nanocluster/Graphene Oxide Nanocomposite. *Biosens. Bioelectron.* **2017,** *93*, 293-297.

(5) Xu, W.; Xie, Z.; Tong, C.; Peng, L.; Xiao, C.; Liu, X.; Zhu, Y.; Liu, B. A Rapid and Sensitive Method for Kinetic Study and Activity Assay of DNase I in Vitro Based on a GO-Quenched Hairpin Probe. *Anal. Bioanal. Chem.* **2016,** *408*, 3801-3809.

(6) Sun, S. K.; Wang, B. B.; Yan, X. P. A Label-Free Near-Infrared Fluorescent Assay for the Determination of Deoxyribonuclease I Activity Based on Malachite Green/G-Quadruplexes. *Analyst* **2013,** *138*, 2592-2597.

(7) Zhou, Z.; Zhu, C.; Ren, J.; Dong, S. A Graphene-Based Real-Time Fluorescent Assay of Deoxyribonuclease I Activity and Inhibition. *Anal. Chim. Acta* **2012,** *740*, 88-92.

(8) Jung, Y. L.; Lee, C. Y.; Park, J. H.; Park, K. S.; Park, H. G. A Signal-On, Colorimetric Determination of Deoxyribonuclease I Activity Utilizing the Photoinduced Synthesis of Gold Nanoparticles. *Nanoscale* **2018,** *10*, 4339-4343.