Electronic Supplementary Material (ESI) for Analytical Methods.

SUPPORTING INFORMATION

Micellar catalysis of an Iron (III)-MOF: Enhanced Biosensing Characteristics

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Peroxidase and catalase mimicking mechanism of PCN-222(Fe) as catalyst

One of the applications that emerge from previous studies on MOFs is their ability to catalyze oxidation reactions, which so far has only been imputed to the peroxidase enzymes mimics. PCN-222(Fe) with porphyrin rings that functions similar to the active site of peroxidase (horseradish peroxidase) is one of the best candidates as enzyme mimetics.
Our findings in this report, suggest a possible catalytic mechanism mediated by the PCN-222(Fe) in two simultaneous stages based on porphyrin rings. The active sites of PCN-222(Fe) react in an initial step with H_2O_2 to generate free radicals to react with a hydrogen donor (ABTS) to form the $ABTS^+$ species.

$$\mathbf{H_2O_2 + ABTS \xrightarrow{PCN\text{-}222(Fe)} 2H_2O + oxidized\ ABTS}$$

Also, kinetic rate constant (k_1,k_3) calculations were performed to show the peroxidase-like activity of PCN-222(Fe) according to following equations(similar to HRP):

$$\mathbf{HRP + H_2O_2 \xrightarrow{K_1} Compound\text{-}I\ (HRP\text{-}Fe{=}O) + H_2O}$$

$$\mathbf{Compound\text{-}I\ (HRP\text{-}Fe{=}O) + AH \xrightarrow{K_2} Compound\text{-}II\ (HRP\text{-}Fe\text{-}OH) + A^{\bullet}}$$

$$\mathbf{Compound\text{-}II\ (HRP\text{-}Fe\text{-}OH) + AH \xrightarrow{K_3} HRP + H_2O + A^{\bullet}}$$

Using the peroxidase enzyme pattern, Initial reaction rate variation against catalyst concentration can be calculated as:

$$Rate = \frac{dx}{dt} = \frac{[catalyst]}{(1/k_1\,[H_2O_2] + (1/k_3[S]_0)}$$

These findings (k values) are in agreement with those of HRP, that prove the sensible catalytic activity of PCN-222(Fe)(Table. S1).

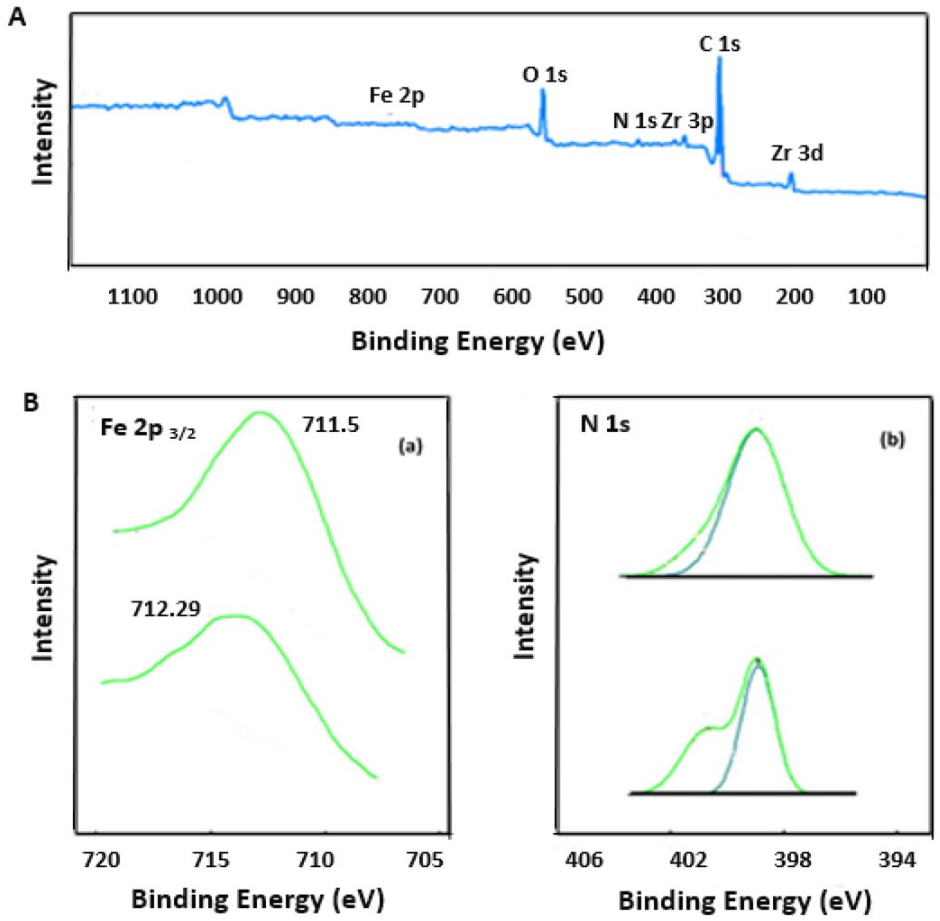

Figure S1. (A) XPS spectra of PCN-222 and (B) a) Fe 2p3/2 core-level XPS spectra of PCN-222 (B) N1s core-level XPS spectra of PCN-222(Fe).

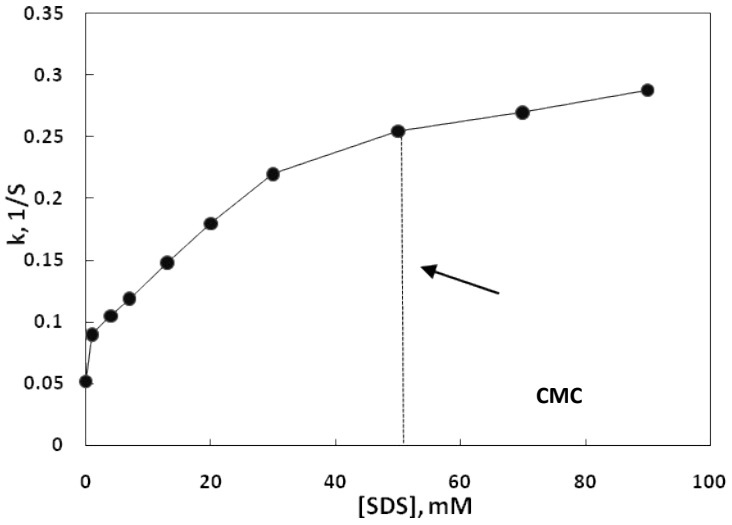

Figure S2. Micellization profile of PCN-222(Fe) in presence of various concentration of SDS

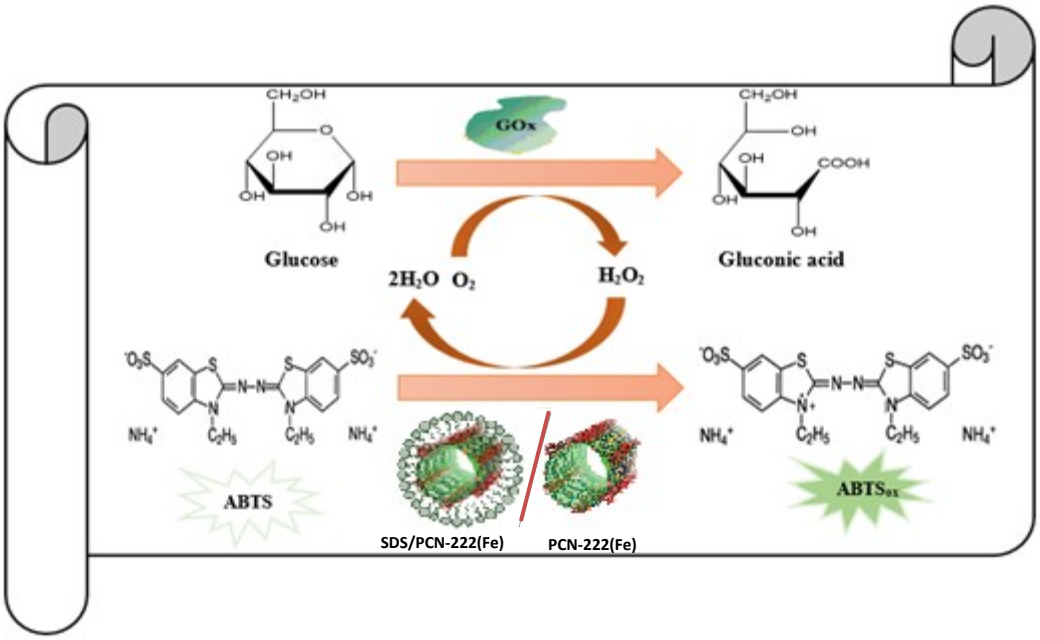

Figure S3. Schematic illustration of detection mechanism for glucose sensing using glucose oxidase (GOx). and PCN-222(Fe) and SDS/PCN-222(Fe) as artificial enzymes.

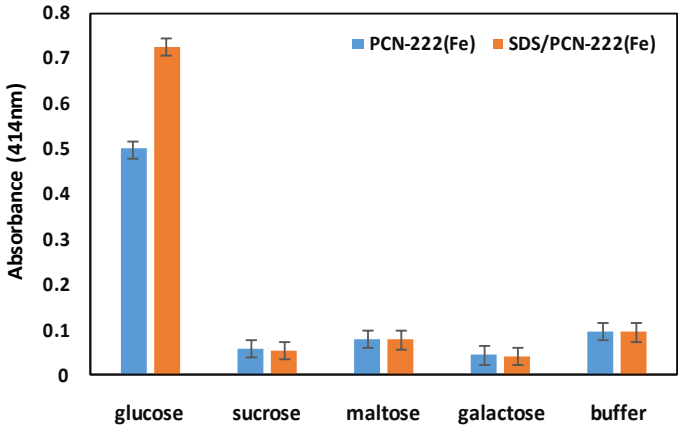

Fig. S4. Evaluation of Selective analysis of the glucose assay with SDS/PCN-222(Fe), PCN-222(Fe) and other control compounds.

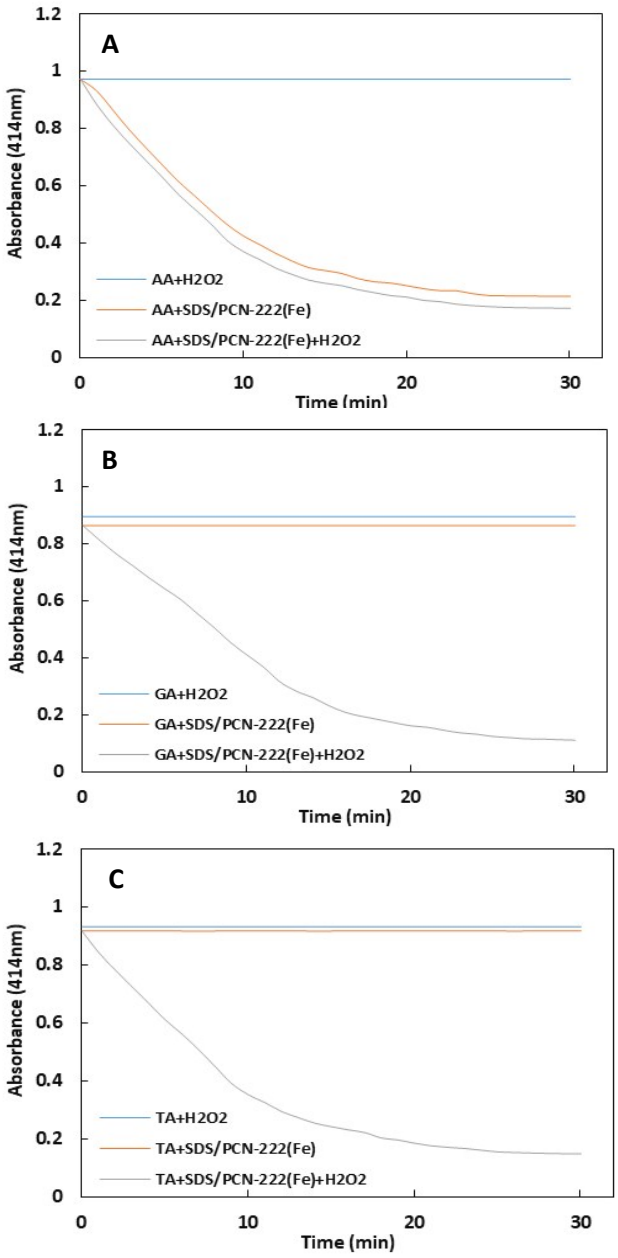

Fig. S5. The absorbance evolutions of AA (A) , GA (B) and TA (C) over time in the absence and presence of H_2O_2 or SDS/PCN-222(Fe) without ABTS.

Table. S1 Comparative rate constants value for HRP and PCN-222(Fe) catalysts

Catalyst	**k_1($M^{-1}s^{-1}$)**	**K_3($M^{-1}s^{-1}$)**
PCN-222(Fe)	6.89×10^{-5}	6.03×10^{-4}
HRP	5.37×10^{-7}	3.03×10^{-5}

Table. S2DLS and Zeta-potential Parameters for the various catalysts

Compounds	diameter (nm)	zeta-potential (mV)
PCN-222(Fe)	73.2	- 0.529
SDS/PCN-222(Fe)	306.9	- 24.7

Table. S3 Determination of AA in real samples

Samples	Detected(μM)	Added(μM)	Found(μM)	Recovery(%)	RSD(%)
1	15.75	3	18.68	99.63	0.6
		15	30.42	98.93	0.8
		20	35.47	99.22	0.7
2	16.19	3	18.91	98.54	2.2
		15	30.73	98.53	1.3
		20	35.78	98.87	1.16
3	17.32	3	20.27	99.75	0.2
		15	31.93	98.79	1.5
		20	37.17	99.60	0.3