Supporting Information

Materials

Fe-MSN was synthesized by a procedure as reported earlier. [1] Catalase, Horseradish peroxidase (HRP), 3, 3′, 5, 5′-Tetramethylbenzidine (TMB) were obtained from sigma Aldrich and used without further purification. Potassium dihydrogen phosphate, hydrogen peroxide used is from Merck India and sodium cyanide from S. D Fine chemicals. De-ionized water was used for all the experiments.

Physical measurements

All the UV-VIS measurements were carried in Cary300 spectrophotometer. For the calibration curve optcal density(OD) was measured at 650 nm, green colored oxidized TMB. pH meter used was from Lab India and ICP-OES (Inductively coupled plasma – optical emission spectroscopy) from Spectro arcos.

Detection of cyanide in the linear range of 0 to 156 ppb

Preparation of phosphate buffers: Stocks of 1.0 M phosphate buffer of pH 7 was prepared using potassium dihydrogen phosphate. pH was adjusted by adding aqueous potassium hydroxide solution and persevered at 4 ˚C for further use.

Stock solutions:
1) 50 mM sodium cyanide: 24.50 mg was dissolved in DI water (10 mL). This was further diluted to have the desired strength.
2) 0.1 mg/mL Catalase: 10 mg of solid was dissolved in 100 mL of 10 mM PB of pH 7 (~0.4 μM considering tetramer molecular weight ~250 KDa)
3) 0.8 M hydrogen peroxide: Desired volume of commercial hydrogen peroxide in DI water. Molar extinction coefficient of 72.8 $M^{-1}cm^{-1}$ at 230 nm was used to find the concentration of commercial stock.
4) 50 mM solution of TMB: 12 mg of solid was dissolved in 1 mL of 0.1N aqueous hydrochloric acid. Gently heated to warm, if necessary.
5) 1 mg/mL of Fe-MSN: 2 mg of solid Fe-MSN was dispersed well in DI water (2 mL) by sonication.
6) 50 mM solution of different anions: Following amounts (Table S1) of salts were dissolved in 1 mL of DI water

Table S1: Amounts of metal salts to make stock of 50 mM strength

Salt	Mol.wt	Weight/ mg
KF	58.1	2.905
NaCl	58.4	2.92
KBr	119.0	5.95

NaI	149.89	7.49
$NaHCO_3$	84.01	4.2
$MgSO_4$	120.37	6.02
CH_3COONa	82.0	4.1
$NaNO_3$	85.0	4.25
$HCOONH_4$	63.06	3.15
KSCN	97.18	4.86
NaCN	49	2.45

Procedure: In a 2.0 mL eppendorf tube, 410 µL of de-ionized water, 5 µL of phosphate buffer (1 M, pH 7), desired volume of 0.5 mM NaCN and 35 µL of 0.1 mg/mL catalase stock solutions were mixed and allowed to stand at room temperature with occasional shaking for 5 min. 5 µL of 0.8 M hydrogen peroxide solution was added to the mixture and allowed to stand for another 5 min with gentle shaking. Evolution of bubbles confirmed the disproportionation of hydrogen peroxide to water and oxygen. Then 5 µL of 50 mM TMB solution and 35 µL of 1 mg/mL Fe-MSN stock were added to it (Fe-MSN particles were dispersed by sonication each time before addition to the reaction mixture). DI water was used to adjust final volume of 500 µL in each case. The reaction mixture was mixed well by shaking for seven to eight minutes and then 400 µL of reaction mixture was diluted to 800 µL (hence OD was multiplied by 2 for the calculation of $[TMB]_{oxidized}$, Table S2) by adding DI water and absorbance at 650 nm was taken at the 10th minute of catalyst addition.

Final concentrations:
1) Cyanide: (0 to 12 µM or 0 to 312 ppb)
2) Catalase: ~0.028 µM
3) Hydrogen peroxide: 8 mM
4) TMB: 0.5 mM
5) Fe-MSN: 70 µg/mL($[Fe^{III}(biuret-amide)]$ = 3.5 µM, by ICP 0.05 mmoles of catalysts are present per gram of Fe-MSN).

Table S2: Cyanide detection in the linear range of 0 to 156 ppb

Sl. No.	Vol. of 0.5 mM CN^-/ µL	$[CN^-]$/ µM	$[CN^-]$/ ppb	Abs at 650 nm	*$[TMB]_{oxidized}$/ µM	$[CN^-] : [TMB]_{oxidized}$
1	0	0	0	0.077	3.95	-
2	0.75	0.9	23.4	0.253	12.97	1 : 14.41
3	1.50	1.8	46.8	0.357	18.31	1 : 10.17
4	2.50	3.0	78.0	0.547	28.05	1 : 9.35
5	3.50	4.2	109.2	0.696	35.70	1 : 8.50
6	5.0	6.0	156.0	1.040	53.33	1 : 8.88

| 7 | 7.50 | 9.0 | 234.0 | 1.263 | 64.77 | 1 : 7.19 |
| 8 | 10.0 | 12.0 | 312.0 | 1.310 | 67.18 | 1 : 5.59 |

*$[TMB]_{oxidized} = (2 \times OD$ at 650 nm$)/ 39000$, $\varepsilon_{650\,nm} = 39000$ M^{-1}cm^{-1}
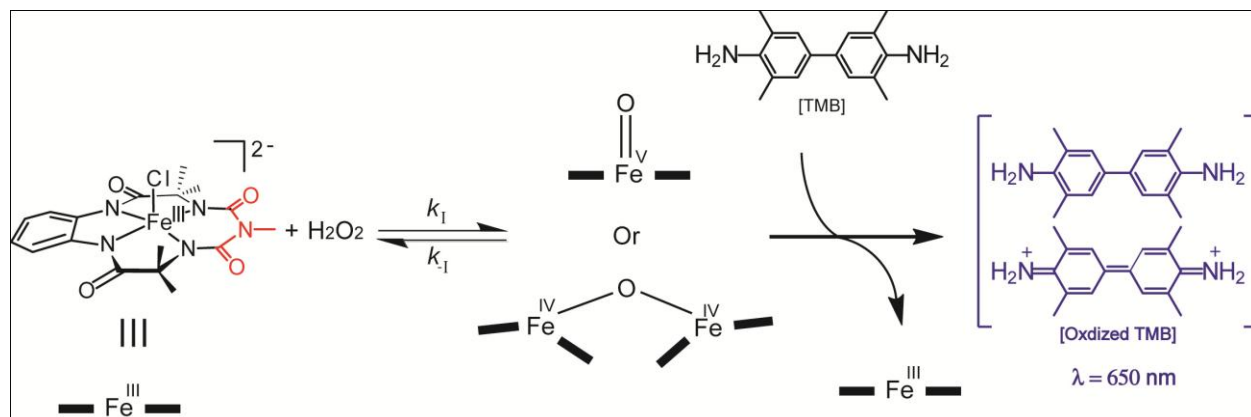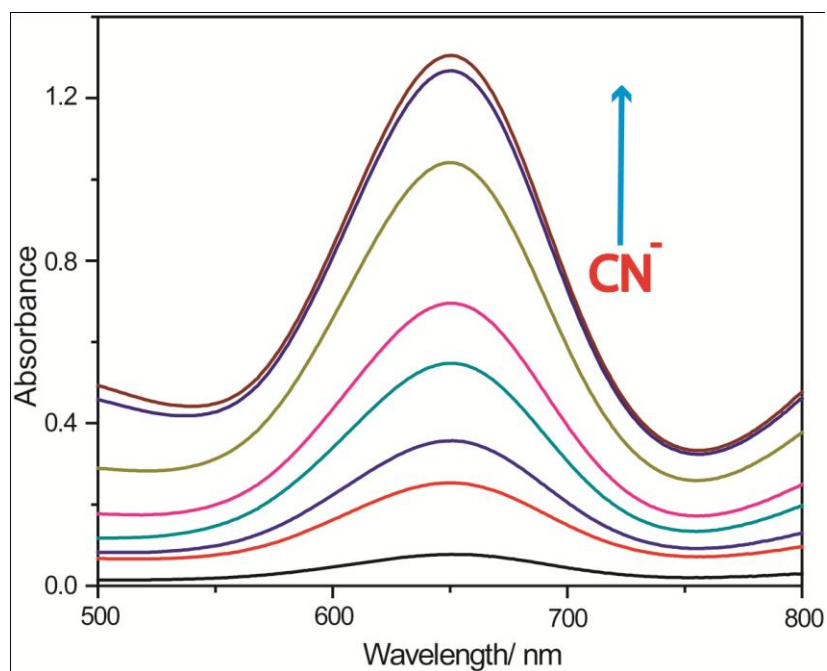

Scheme S1: Proposed mechanism of TMB oxidation

Figure S1: Plot of absorbance of $[TMB]_{oxidized}$ *vs.* wavelength with cyanide increase

Detection of cyanide in the linear range of 0 to 5.2 ppm

The same above procedure was followed only difference being addition of 10 µL of 1mg/mL catalase in place of 35 µL of 0.1 mg/mL catalase and desired volume of 5 mM cyanide in place of 0.5 mM cyanide. DI water was used to compensate the volume difference.

Table S3: Cyanide detection in the linear range of 0 to 5.2 ppm

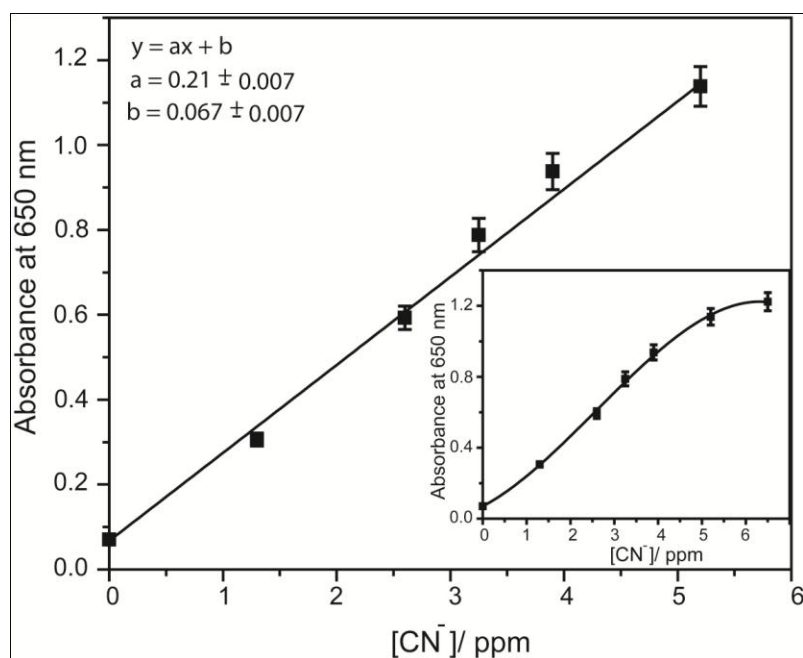| Sl. No.	Vol. of 5 mM CN^-/ µL	$[CN^-]$/ µM	$[CN^-]$/ ppm	Abs at 650 nm	*$[TMB]_{oxidized}$/ µM	$[CN^-] : [TMB]_{oxidized}$
1	0	0	0	0.070	3.60	-
2	5.0	50	1.3	0.310	15.70	1 : 0.31
3	10.0	100	2.6	0.593	30.05	1 : 0.30
4	12.5	125	3.25	0.789	40.41	1 : 0.32
5	15.0	150	3.9	0.938	48.10	1 : 0.32
6	20.0	200	5.2	1.140	58.37	1 : 0.29
7	25.0	250	6.5	1.220	62.74	1 : 0.25

Figure S2: Detection of cyanide in the linear range 0 to 5.2 ppm

Selectivity towards CN⁻ over other common anions

The same above procedure was followed with addition 10 µL of 0.5 mM CN⁻ or 50 mM other anions.

Figure S4:

Sl. No.	Anion	[Anion]/ µM	Abs at 650 nm
1	No anion	-	0.069 ± 0.003
2	Cyanide	5	1.200 ± 0.060
3	Bromide		0.072 ± 0.004
4	Chloride		0.082 ± 0.004
5	Acetate		0.065 ± 0.003
6	Fluoride		0.075 ± 0.004
7	Bicarbonate	500	0.069 ± 0.003
8	Formate		0.071 ± 0.003
9	Iodide		0.070 ± 0.003
10	Nitrate		0.068 ± 0.003
11	Thiocyanate		0.065 ± 0.003
12	Sulphate		0.071 ± 0.003

HRP inhibition by Cyanide

To 900 µL of 2 mg/mL HRP (~45 µM) stock in 10 mM PB of pH 7 was added 100 µL of desired concentrations of cyanide stock. The mixture was allowed to stand for 2 min and UV-VIS absorbance spectra were taken (Figure S3). The typical soret band was shifted from 403 nm to 420 nm with the increase of cyanide concentration. The OD change at 403 nm for each cyanide addition was measured. (Table S5, Figure S3)

Final concentrations:

1) HRP: ~40.5 µM

2) Sodium cyanide: Table S5

Table S5: Spectral data of HRP soret band with cyanide increase.

Sl. No.	[CN⁻]$_{final}$/ µM	OD at 403 nm	ΔAbs at 403 nm
1	0	0.814	0
2	0.5	0.811	0.003
3	2.5	0.761	0.053

4	5	0.705	0.109
5	9	0.649	0.164
6	12.5	0.632	0.182
7	25	0.617	0.197
8	50	0.579	0.234
9	200	0.559	0.255
10	500	0.549	0.265

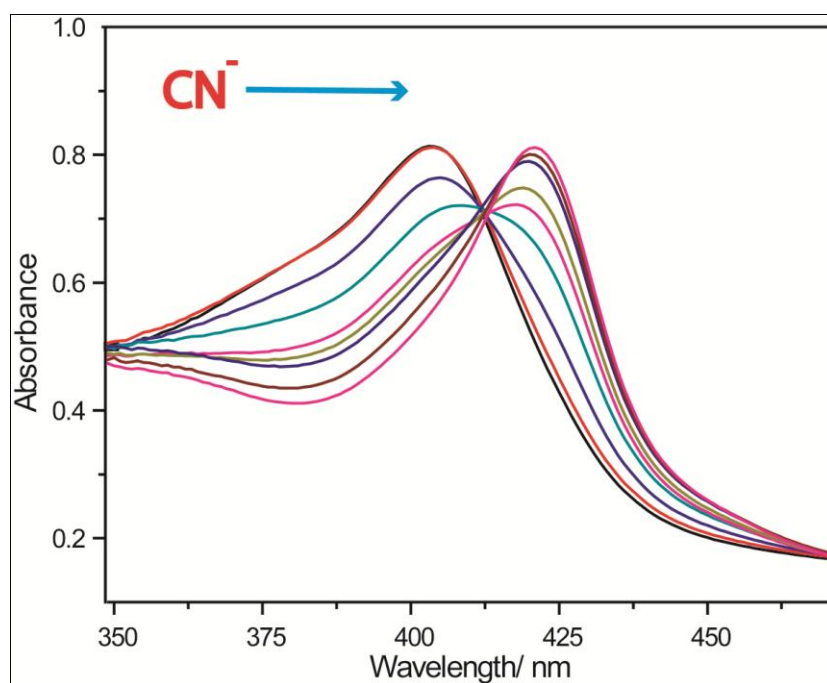**Figure S3:** Shift of HRP soret band with cyanide addition

Catalase inhibition by cyanide

To 900 µL of 5 mg/mL catalase (~20 µM) stock in 10 mM PB, pH 7 was added 100 µL of desired concentrations of cyanide stock. The mixture was allowed to stand for 2 min and UV-Vis absorbance spectra were taken. The typical soret band was shifted from 405 nm to 425 nm with the increase of cyanide concentration. The OD change at 405 nm for each cyanide addition was measured. (Table S6, Figure S4)

Final concentrations:

1) Catalase: ~18 µM

2) Sodium cyanide: Table S6

Table S6:

Sl. No.	$[CN^-]_{final}/$ μM	OD at 405 nm	ΔAbs at 405 nm
1	0	0.969	0
2	5	0.951	0.017
3	25	0.893	0.075
4	50	0.860	0.109
5	150	0.822	0.147
6	250	0.815	0.154
7	500	0.807	0.162
8	2500	0.767	0.202

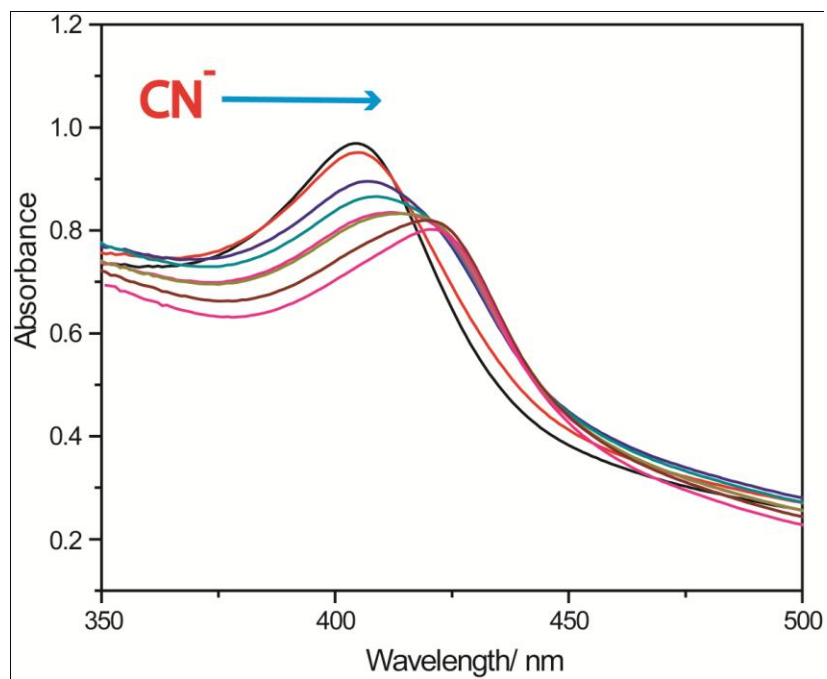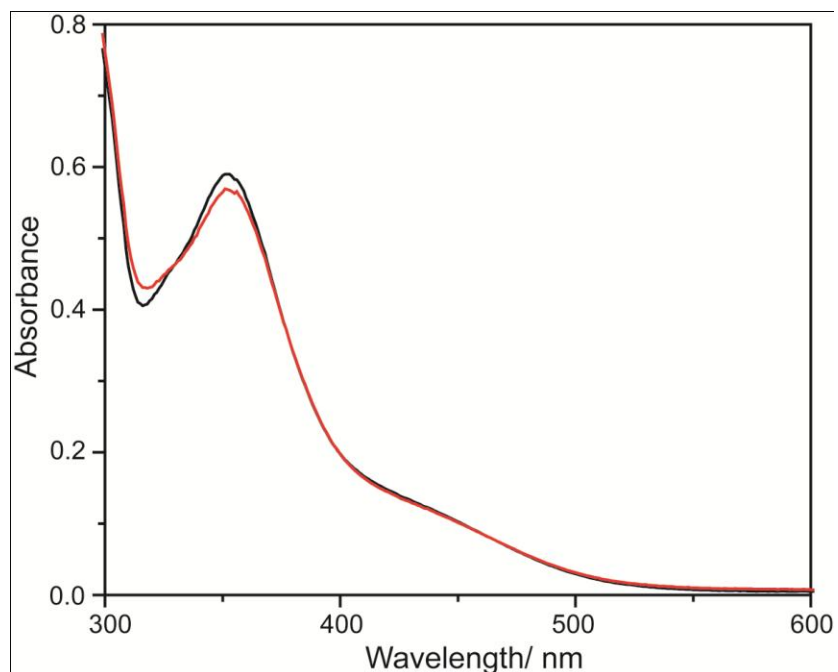**Figure S4:** Shift of catalase soret band with cyanide addition

Figure S5: UV-VIS spectrum of 1.5×10^{-3} M [Fe^{III}(biuret-amide)] in presence (red) and absence (black) of cyanide in water.

Reactivity comparison of HRP and Fe-MSN in presence of cyanide

To 960 µL of DI water, 10 µL of 1 M PB of pH 7 and 10 µL HRP (0.1 mg/ mL) or Fe-MSN (1 mg/ mL), desired volume of 50 mM cyanide solution was added and allowed to stand for 5 minutes. Then 10 µL each of TMB (50 mM) and H_2O_2 (0.8 M) were added, waited for one minute and then UV-VIS spectra were taken. The total volume of reaction mixture was adjusted to 1000 µL varying DI water.

Table S7:

Sl. No.	Vol of 50 mM CN⁻/ µL	[CN⁻]$_{final}$/ mM	HRP		Fe-MSN	
			OD$_{650 nm}$	% Reactivity	OD$_{650 nm}$	% Reactivity
1	0	0	2.670	100	1.430	100
2	10	0.5	1.825	68	1.358	95
3	20	1.0	1.456	54	1.429	100
4	40	2.0	1.310	49	1.432	100
5	50	2.5	1.010	38	1.415	99
6	70	3.5	0.904	34	1.287	90
7	100	5.0	0.707	26	1.359	95

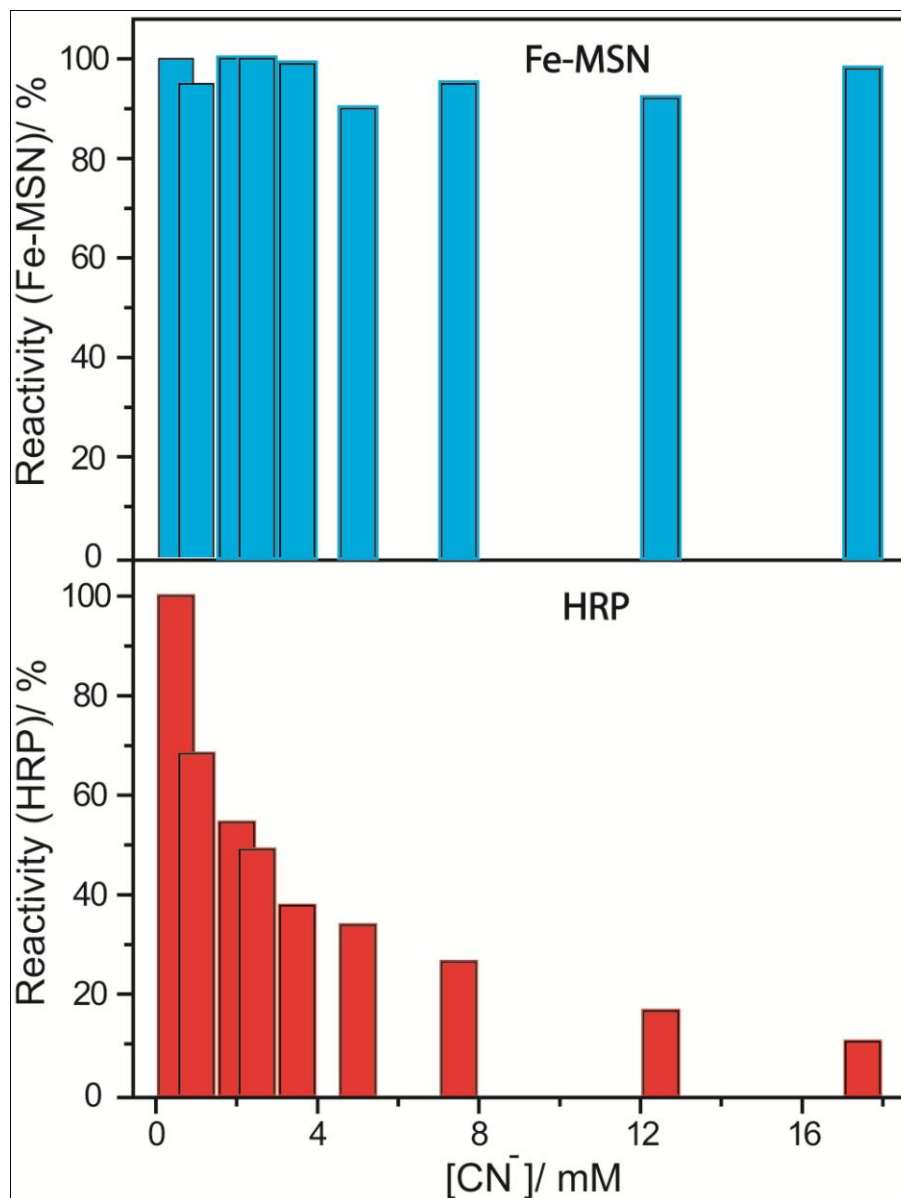| 8 | 150 | 7.5 | 0.444 | 17 | 1.320 | 92 |
| 9 | 250 | 12.5 | 0.279 | 10 | 1.400 | 98 |

Figure S6: Comparison of HRP (red bars) and Fe-MSN (blue bars) reactivity in presence of cyanide.

Oxidation of TMB by Fe-MSN in presence of cyanide and other anions

To 960 µL of DI water 10 µL of 1 M PB of pH 7 and 10 µL of Fe-MSN (1 mg/ mL), 10 µL of 50 mM cyanide or other anions were added and allowed to stand for 5 minutes. Then 10 µL each

of TMB (50 mM) and H_2O_2 (0.8 M) were added, mixed for one minute and UV-VIS spectra were taken. The total volume of reaction mixture was adjusted to 1000 µL varying DI water.

Table S8:

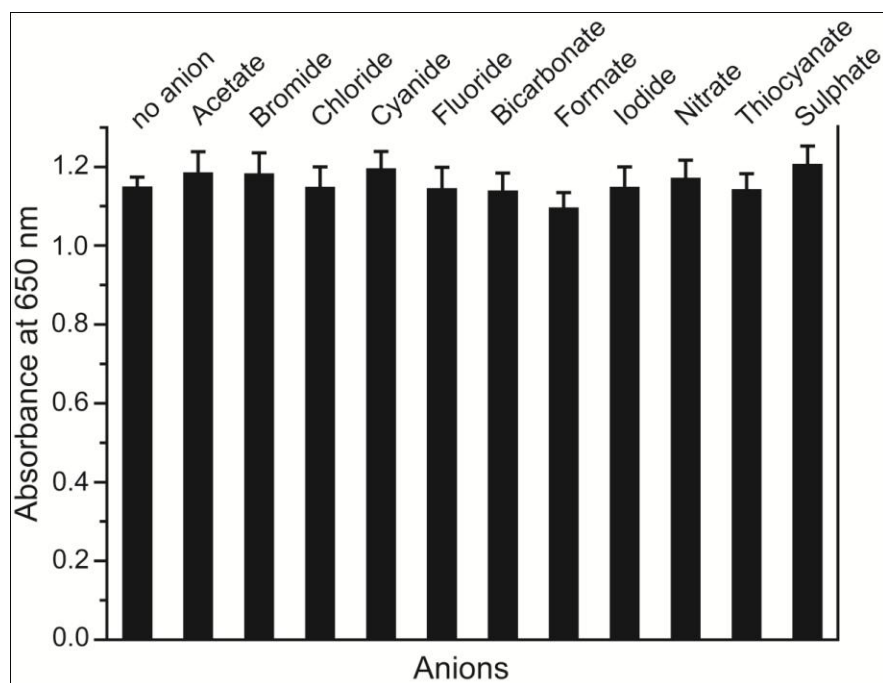| Sl. No.	Anion	$OD_{650 \, nm}$	% Reactivity
1	No anion	1.143 ± 0.031	100
2	Acetate	1.180 ± 0.050	~ 100
3	Bromide	1.177 ± 0.052	
4	Chloride	1.142 ± 0.063	
5	Cyanide	1.189 ± 0.045	
6	Fluoride	1.139 ± 0.061	
7	Bicarbonate	1.133 ± 0.050	
8	Formate	1.090 ± 0.040	
9	Iodide	1.143 ± 0.057	
10	Nitrate	1.165 ± 0.051	
11	Thiocyanate	1.143 ± 0.052	
12	Sulphate	1.200 ± 0.052	

Figure S7: Bar plot for TMB oxidation in presence of different anions.

Spectrophotometric determination of half lives of H_2O_2 in presence of cyanide[2]

In a 2.0 mL eppendorf tube, 900 - 910 µL of de-ionized water, 10 µL of phosphate buffer (1 M, pH 7), desired volume of 0.5 mM NaCN and 70 µL of 0.1 mg/mL catalase stock solutions were mixed and allowed to stand at room temperature with occasional shaking for 5 min. 10 µL of 0.8 M hydrogen peroxide solution was added to the mixture. Immediately mixing within 10 seconds the disproportionation is followed spectrophotometrically by tracking the rate of decrease of absorbance at 230 nm typical for hydrogen peroxide ($\varepsilon = 72.8$ $M^{-1}cm^{-1}$). The duration of each kinetic run was chosen such that there was no effect from bubble formation. The decay curve was very smooth and fitted very nicely according to first order rate law. The $t_{1/2}$ of each set containing various amount of cyanide was calculated and the number of half lives in 5 minutes was calculated from these values (H_2O_2 decomposition duration for the cyanide detection experiment). The UV-VIS spectral kinetics data indicated number of half lives decrease with increasing cyanide concentration.

Table S9: Half life calculations for H_2O_2 in presence of cyanide

Sl. No.	Vol. of 0.5 mM CN⁻/ µL	$[CN^-]_{final}$/ µM	k_{obs}/ s^{-1}	$t_{1/2}$/ s^{-1}	No. of half lives in 5 min
1	0.0	0.00	0.023	30	10.0
2	0.5	0.25	0.019	36	8.33
3	1.0	0.50	0.016	43	7.00
4	2.5	1.25	0.015	47	6.40
5	5.0	2.50	0.013	52	5.77
6	10.0	5.00	0.011	62	4.84

References:

[1]   B. Malvi, C. Panda, B. B. Dhar, S. S. Gupta, *Chemical Communications* **2012**, *48*, 5289-5291.

[2]   R. F. Beers, I. W. Sizer, *J. Biol. Chem.* **1951**, 133-140.