

Supporting Information

Soft Template Induced Phase Selective Synthesis of Fe₂O₃ Nanomagnets: One Step towards Peroxidase-Mimic Activity Rendering Colorimetric Sensing of Thioglycolic Acid

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S1. Materials Used:

All chemicals used, are of analytical grade and no further purification has been done before reaction. Mohr's salt (Merck) [FeSO₄, (NH₄)₂SO₄, 6H₂O] is used as precursor salt for the preparation of Fe₂O₃ NPs. For the synthesis of Schiff bases; aldehydes used are glyoxal (CHO-CHO) (40%, SRL) and glutaraldehyde [CHO-(CH₂)₃-CHO] (25%, Merck), and amines used are ethylenediamine [(CH₂NH₂)₂] and triethylenetetramine [H₂N-C₂H₄-NH-C₂H₄-NH-C₂H₄-NH₂] (SRL). As hydrolysing agent, hydrazine, monohydrate [H₂N-NH₂, H₂O] (80%, Merck) is employed. Distilled water has been used for the entire procedure. Absolute ethanol (99.9%, AR grade) has been used. 3,3',5,5'-tetramethylbenzidine (TMB) (SRL), H₂O₂ (30%), thioglycolic acid (TGA) (Merck) reagents are used of analytical grade.

S2. Instrumentation:

Powder X-Ray diffraction (XRD) was recorded with a SMART APEX II, BRUKER AXS X-ray diffractometer (40kV, 20 mA) using Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$) in the range of 5°-90° at a scanning rate of 0.5° min⁻¹. For analysing the XRD data, JCPDS software guided us. Fourier transform infrared (FTIR) spectral studies were done in KBr pellets in reflectance mode with PERKIN ELMER SPECTRUM RX1 (USA), (LASER HeNe nm < 0.4 mW) FTIR microscope. For the analysis of liquid samples FTIR, NICOLET 6700, THERMOFISHER

SCIENTIFIC INDIA PVT. LMT has been used. Surface morphology was analysed using field emission scanning electron microscopy (FESEM) with a supra, Carl Zeiss Pvt. Ltd. High resolution transmission electron microscopy (HRTEM) analysis was done with the help of JEOL JEM 2100 (JAPAN), Resolution- 1.4 Å, Acceleration VOLT.: 200 kV, Filament: LaB₆. Superconducting quantum interference device (SQUID) magnetometry is carried out in Evercool MPMS SQUID VSM DC magnetometer device. Dried powder samples (TemFe A, TemFe B, TemFe C, TemFe D) were transformed into capsule made by Teflon tape and inserted in a clear brass straw. Zero-field-cooled (ZFC) and field-cooled (FC) were carried out by cooling the sample at 5-300 K by cycling the magnetic field under 100 Oe magnetic field. Isothermal magnetisation as a function of field strength measurements has also been carried out at low (5 K) and high (300 K) temperature within magnetic field sweep of + 2T to -2T. UV-visible spectral analyses were done using SPECTRASCAN UV 2600 digital spectrophotometer (Chemito, INDIA).

Figure S1.

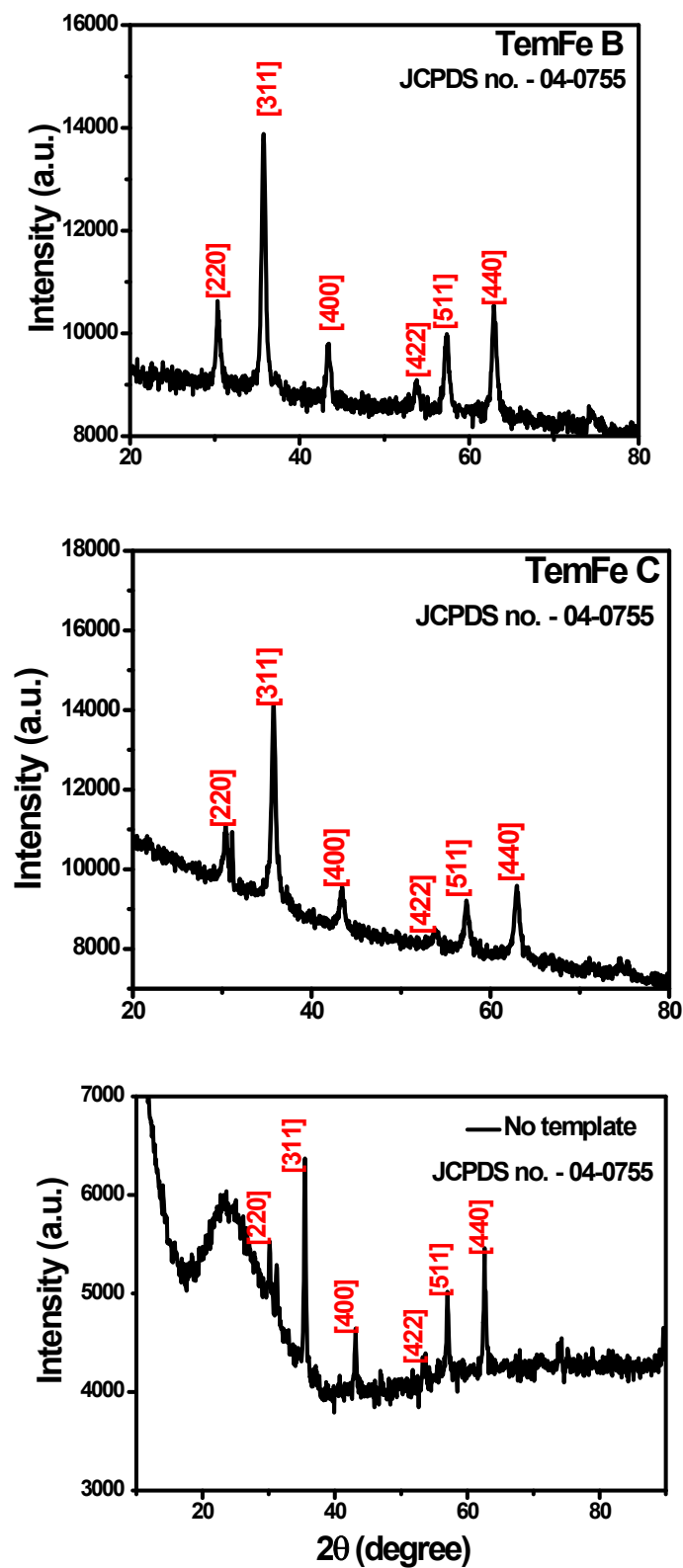


Figure S1. PXRD pattern of TemFe B and TemFe C and product without template corresponds to γ -Fe₂O₃.

Figure S2.

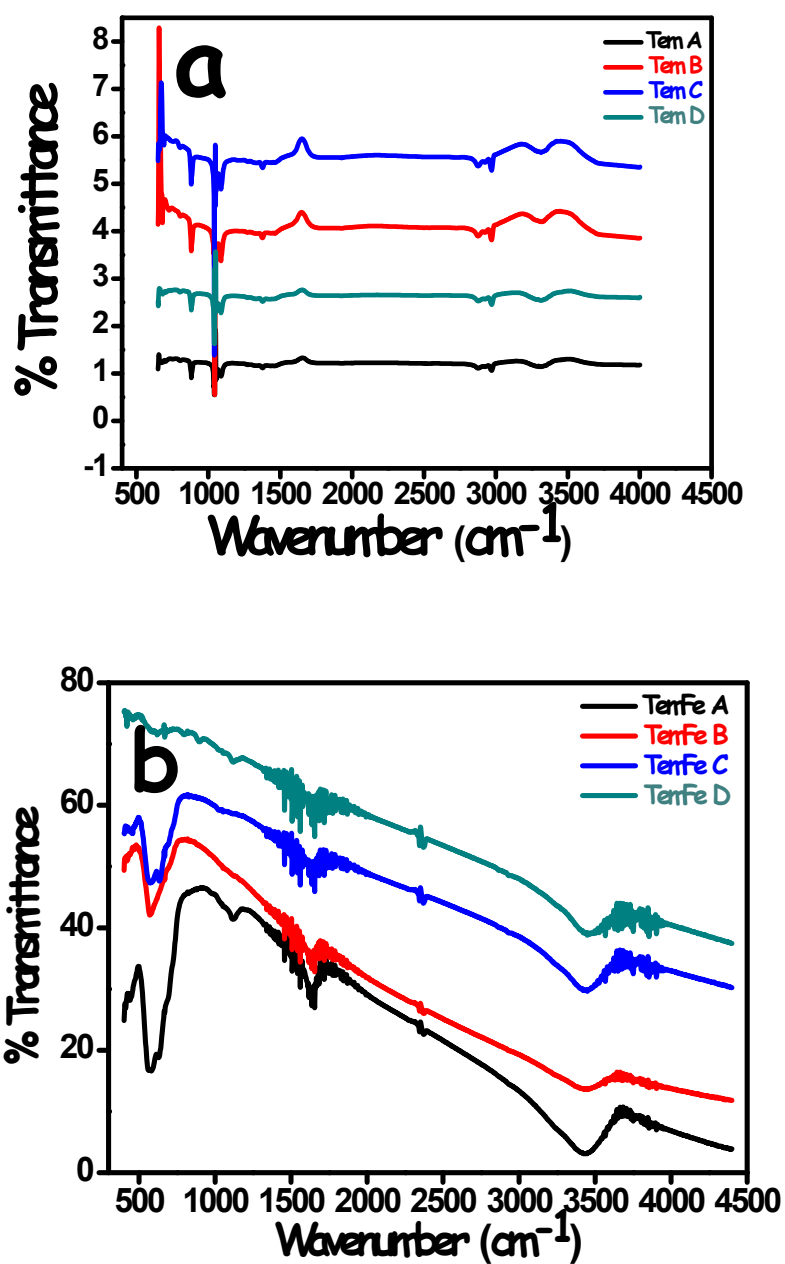


Figure S2. FTIR analysis of (a) four different Schiff bases (Tem A, B, C and D) and (b) α - and γ -Fe₂O₃ nanoparticles (TemFe A, B, C, D) synthesised using those Schiff base templates.

Figure S3.

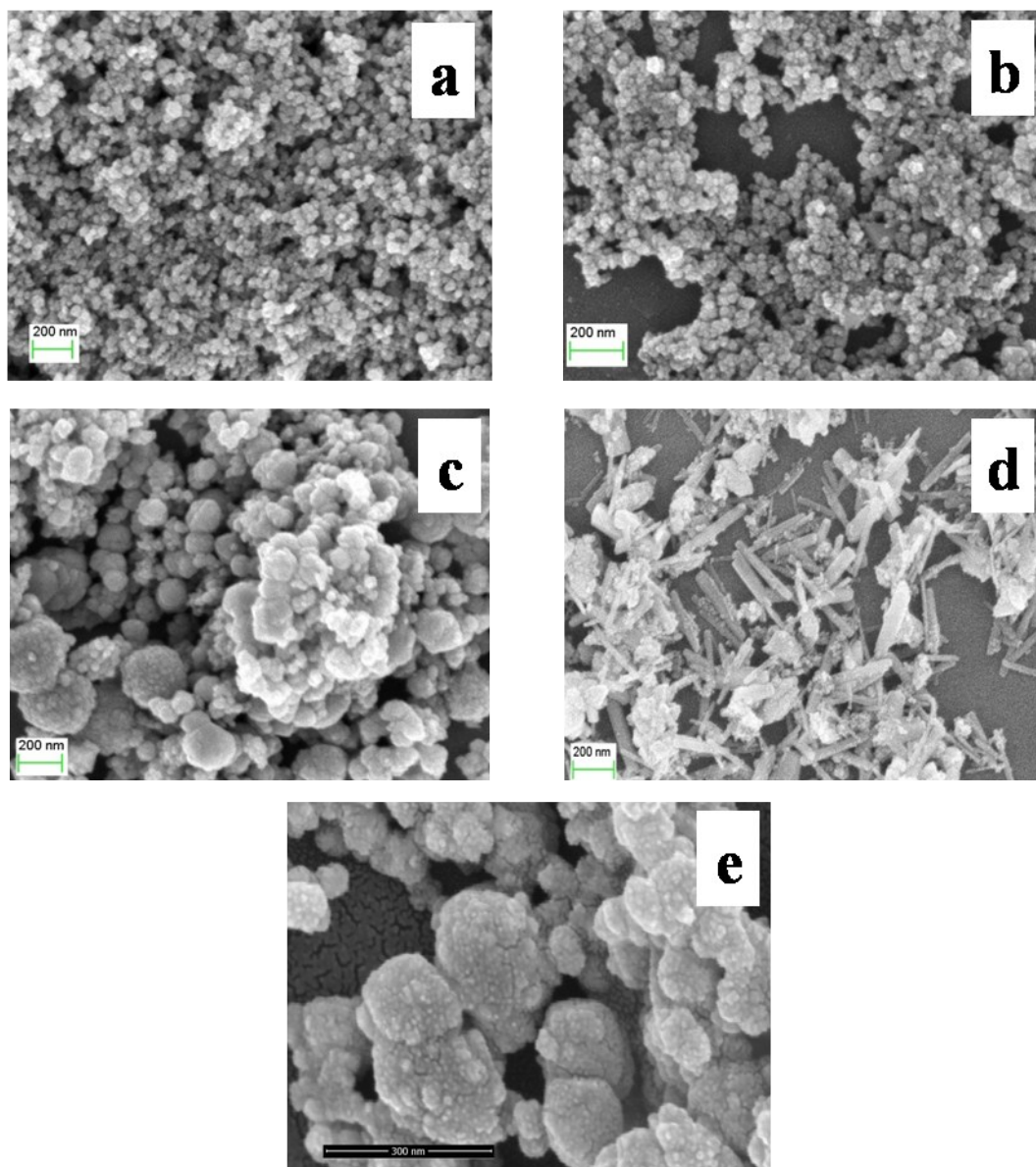


Figure S3. Surface morphology analysis using FESEM (a) TemFe A, (b) TemFe B, (c) TemFe C and (d) TemFe D at magnification of 200 nm and (e) without any template at magnification of 300 nm.

Figure S4.

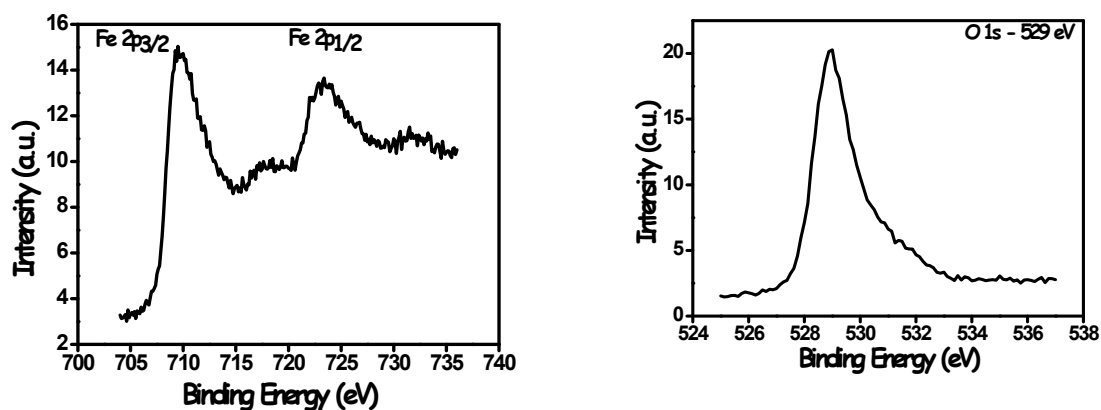


Figure S4: XPS spectra of Fe and O in Fe_2O_3 where reference material is carbon (1s - 284.0 eV).

Table S1: Deconvoluted XPS peak analysis of $\text{Fe}2p_{3/2}$ (Reference C 1s -284.0)									
Catalyst	B.E. (eV)		Height		FWHM		Area		$[\text{Fe}^{+2}] / [\text{Fe}^{+3}]$
	Fe^{+2}	Fe^{+3}	Fe^{+2}	Fe^{+3}	Fe^{+2}	Fe^{+3}	Fe^{+2}	Fe^{+3}	
TemFe A	708.9	710.86	8498	3879	2.25	2.77	21808	12510	1.74
TemFe B	709.39	711.29	7189	3800	2.09	2.77	16842	12257	1.374
TemFe C	709.88	711.39	7101	4471	1.94	2.77	16047	14420	1.112
TemFe D	710.0	711.86	3137	1652	2.21	2.77	7392	5329	1.37

Figure S5.

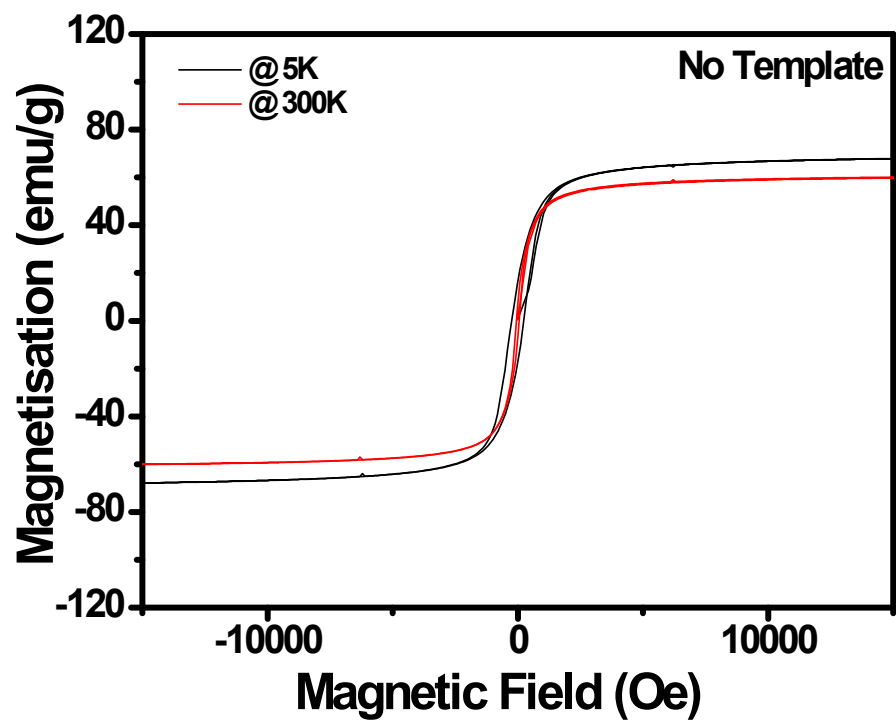


Figure S5: Saturation magnetisation (M-H) data of the sample without template at both 5 and 300 K.

Figure S6(a).

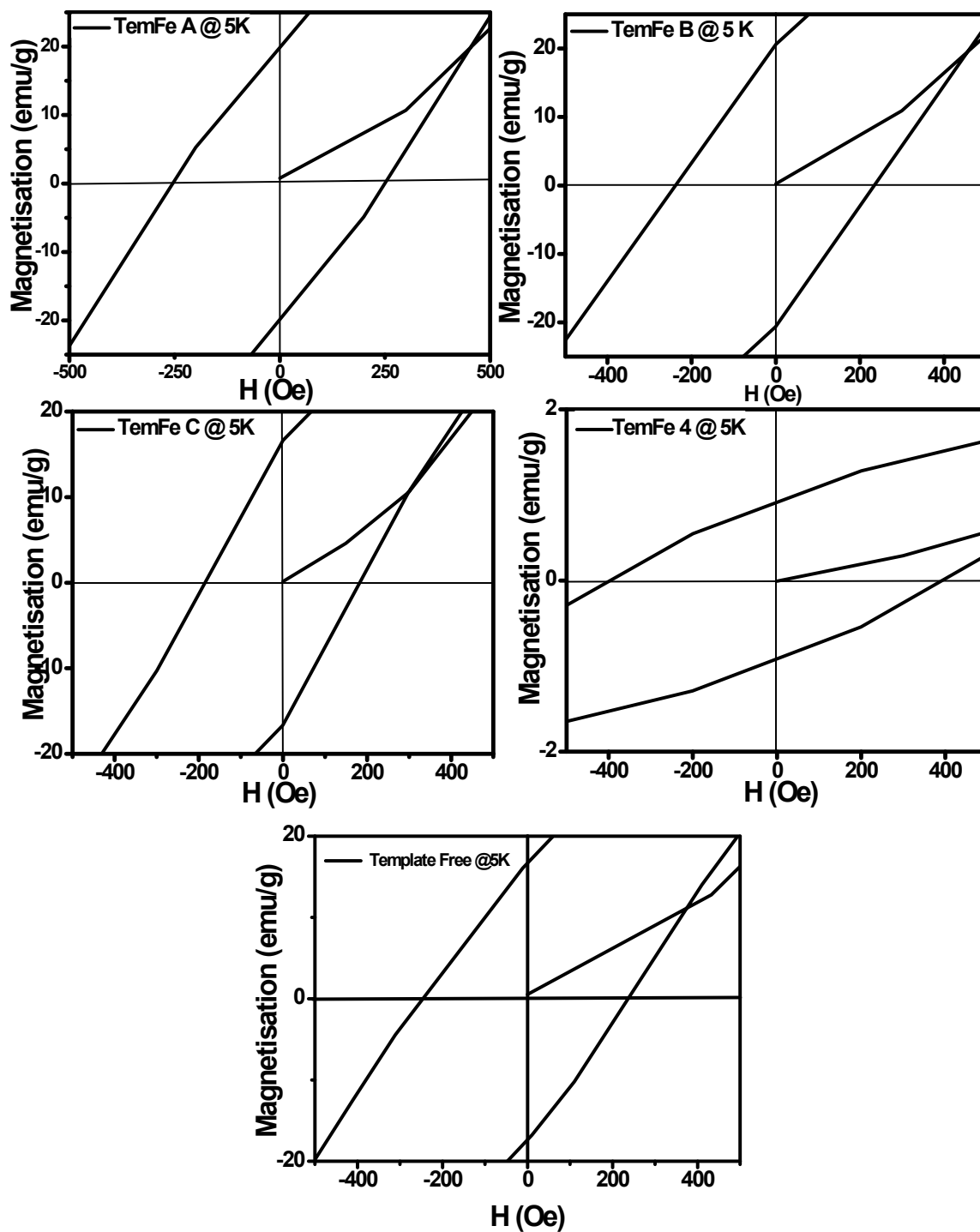


Figure S6(a). Close perception of hysteresis loop of M-H curve for all the TemFes (TemFe A, B, C and D) as well as without template Fe_2O_3 at 5 K.

Figure S6(b).

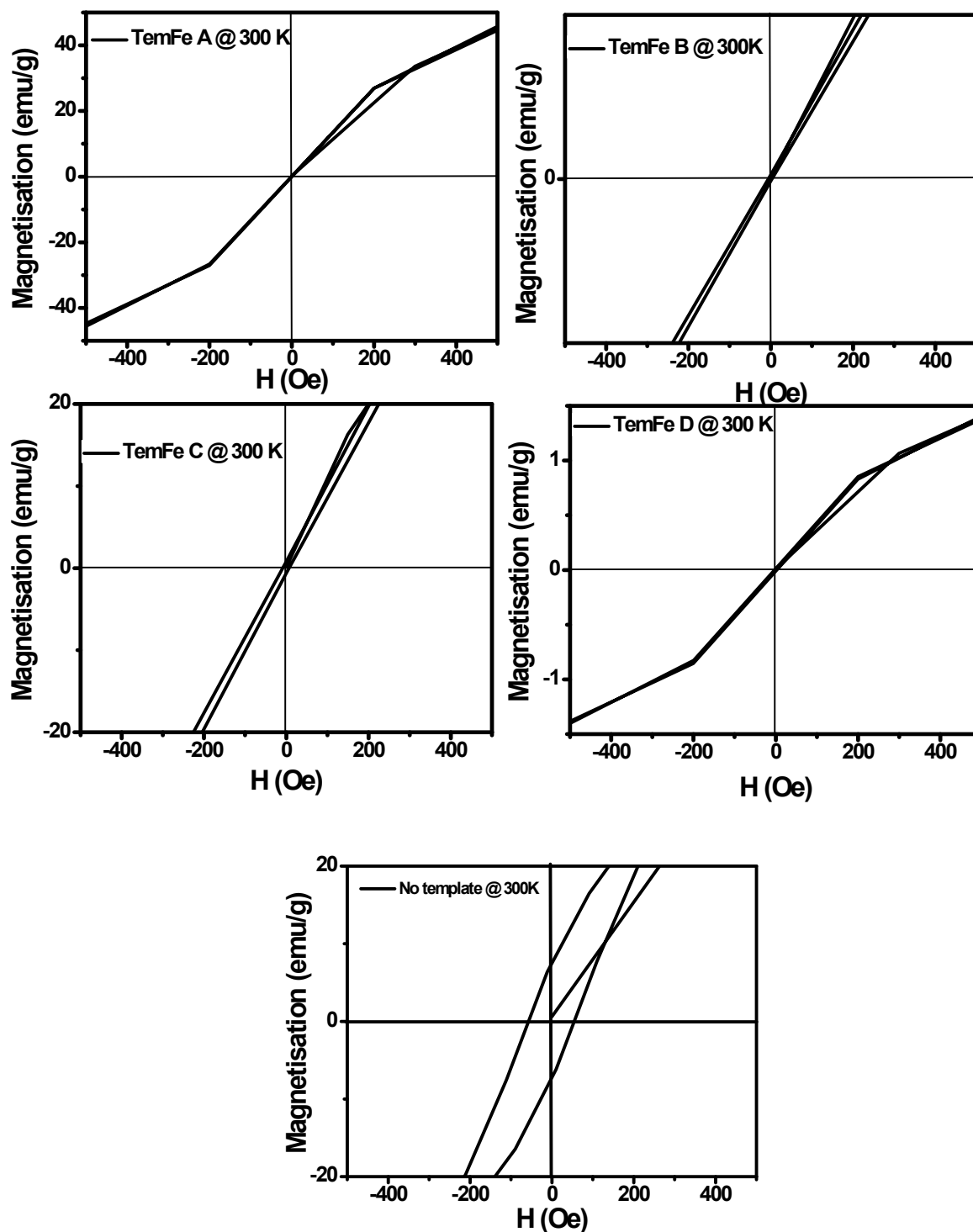


Figure S6(b). Close perception of hysteresis loop of M-H curve for all the TemFes (TemFe A, B, C and D) as well as without template Fe_2O_3 at 300 K.

Figure S7.

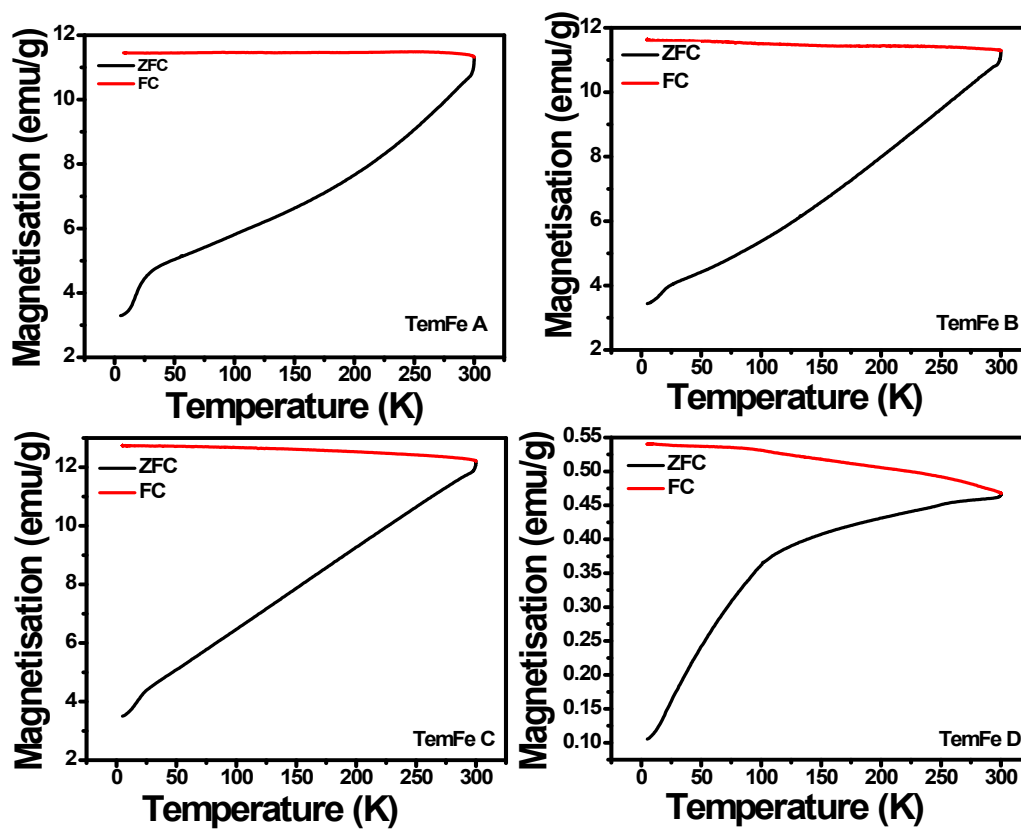


Figure S7. Temperature dependent ZFC-FC curves of TemFe A, B, C and D respectively under the magnetic field of 100 Oe.

Figure S8.

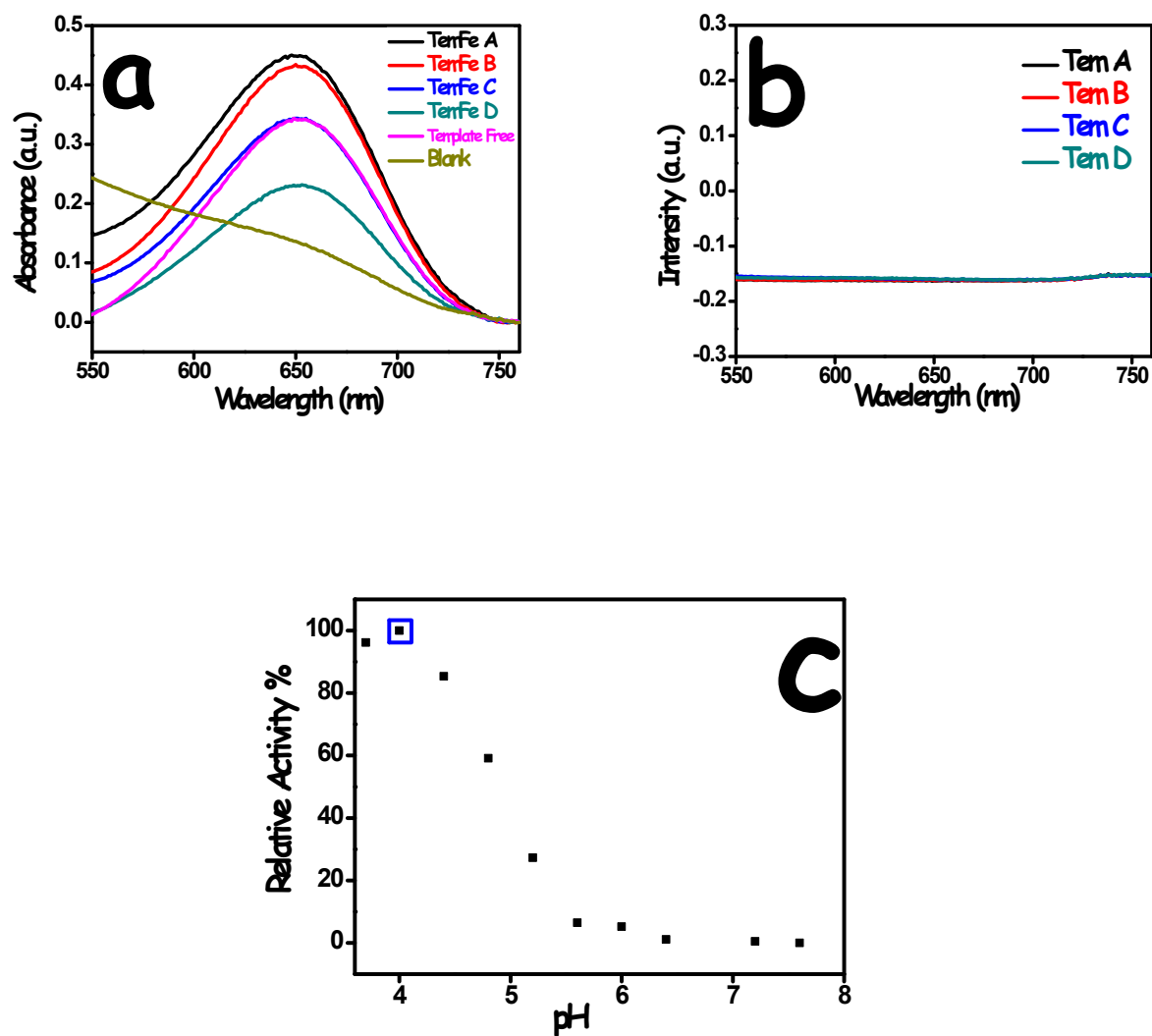


Figure S8: (a) UV-vis spectra of Ox-TMB using H_2O_2 as oxidising agent. Condition: Catalysts are template assisted Fe_2O_3 (TemFe A, B, C, D) and Fe_2O_3 synthesised under template free condition. (b) Control TMB oxidation using only SBs as catalysts. (c) pH-dependent study of peroxidase-like catalytic activity of TemFe A.

Figure S9.

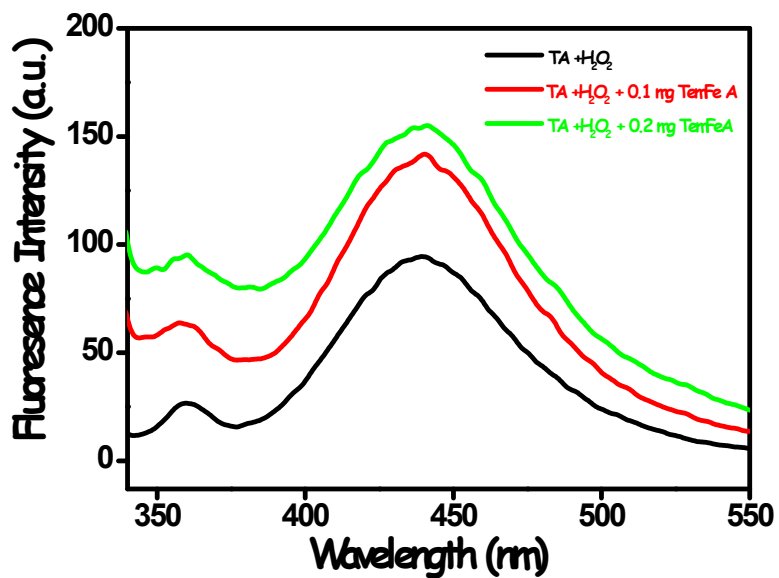


Figure S9: Emission spectra of terephthalic acid (TA) in the presence of H₂O₂ and TemFe A (excitation at 320 nm). Here, 3 mL experimental solution is prepared from 0.1 M acetate buffer solution (pH = 4.0), 0.1 ml (30%) H₂O₂, 2.5×10⁻⁵ M TA.

Figure S10.

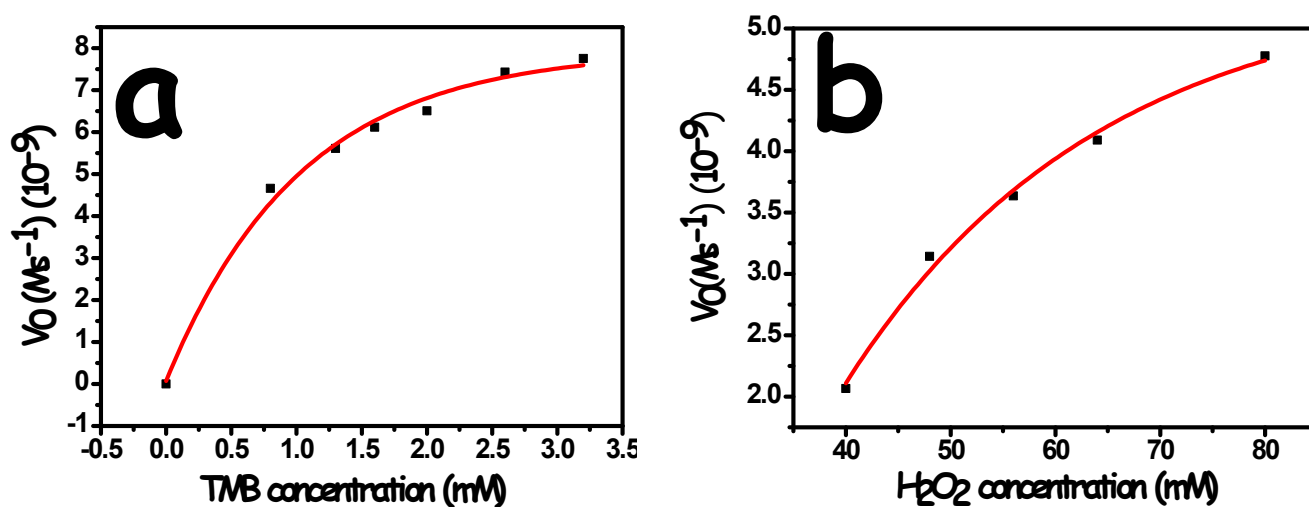


Figure S10. Steady state kinetic analyses using Michaelis-Menten model for TemFe A (a) varying concentration of TMB with fixed amount of H_2O_2 and (b) varying concentration of H_2O_2 with fixed amount of TMB.

Table S2: Comparison of different method of detection of TGA			
Serial No.	Method	TGA detection limit	References
1	Spectroscopy	400 mg	M.K. Tummuru, T.E. Divakar, C.S. Sastry, <i>Analyst</i> 1984, 109 , 1105.
2	High performance Liquid Chromatography	4.2 mg	J.M. Zen, H.H. Yang, M.H. Chiu, Y.J. Chen, and Y. Shih, <i>JAOACInt.</i> 2009, 92 , 574.
3	Ion Chromatography	2.3 mg	Z. Zhong, D. Du, C. Liang, and J. Yao, <i>Wei Sheng Yan Jiu</i> 2004, 33 , 491.
4	Capillary Electrophoresis	0.002 mg	N. Xie, X. Ding, X. Wang, P.Wang, S. Zhao, and Z.Wang <i>Journal of Pharmaceutical and Biomedical Analysis</i> 2014, 88 , 509.
5	Spectroscopy	1.84 mg	This work