Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Hydrogel based on Fe(II)-GMP demonstrates Tunable Emission, Self-healing Mechanical Strength and Fenton Chemistry mediated Notable Antibacterial Properties

Umesh,[a]† *Vysakh C. Chandran,*[a]† *Pranoy Saha,*[b] *Debasish Nath ,*[a] *Sayan Bera,*[b] *Santanu Bhattacharya**[, b,c] *and Asish Pal**[,a]

[a] *Chemical Biology Unit, Institute of Nano Science and Technology, Knowledge City, Sector 81, Mohali, Punjab 140306 (India) E-mail: apal@inst.ac.in*

[b] *School of Applied &Interdisciplinary Sciences, Indian Association for the Cultivation of Science, Kolkata, 700032 (India) E-mail: sb23in@yahoo.com*

[c] *Department of Chemistry, Indian Institute of Science Education and Research Tirupati, Yerpedu Mandal, Tirupati District, Andhra Pradesh, 517619 (India)*

†Umesh and Vysakh contributed equally.

TABLE OF CONTENTS

Materials and Methods **S2**

Synthesis of Tetra(4-carboxylphenyl) ethylene (1) **S2**

NMR characterization of 1_{GMP} & Angular sweep oscillatory rheology of 1_{GMP} **S3**

Characterization and properties of metallogels **S4**

Control gelation experiments **S5**

Fenton reaction and mechanical properties **S5**

Rheological studies of Fe-1_{GMP} V/S Fe-1_{GMP}+AA **S6**

Antimicrobial and Biocompatibility studies **S7**

Reference **S7**

Materials and methods

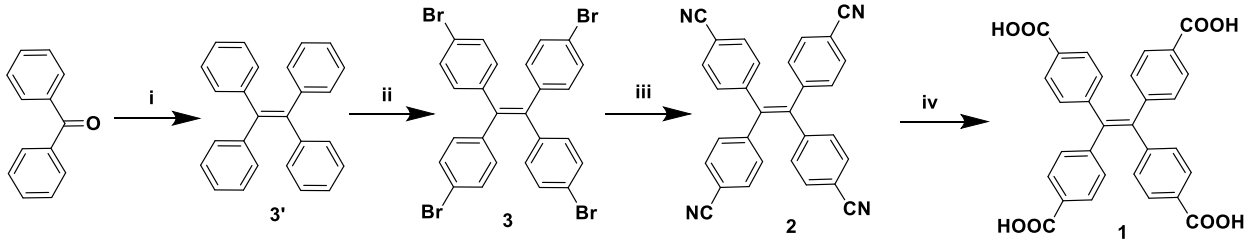
Materials

All reagents, both chemical and biological, employed in this study were sourced from reputable manufacturers and maintained the highest quality standards. Sigma supplied 5'-GMP and $FeCl_2.4H_20$, while spectrochem chemicals provided $MgCl_2$ and $CaCl_2$. Biological materials, including bacterial growth media such as Luria Bertani broth and Nutrient agar, were obtained from HIMEDIA. Nuclear Magnetic Resonance spectra (^{1}H-NMR) were recorded using a FT-NMR Bruker 400 MHz NMR spectrometer. UV–visible spectra were recorded using an Agilent Cary 60 spectrophotometer. Circular Dichroism (CD) spectra were obtained using a JASCO J-1500 Circular Dichroism Spectrometer in Easton, MD, USA. Fluorescence spectra were recorded with an Edinburgh Instruments Spectrofluorometer FS5. X-ray diffraction (XRD) studies were conducted using a Bruker D8 Advance Powder X-ray Diffractometer. Scanning Electron Microscopy (FESEM) images were acquired using a JEOL JEM 2100 scanning electron microscope from Tokyo, Japan.

Synthesis of Tetra(4-carboxylphenyl) ethylene (1)

The molecule TPE, **1** was synthesized by following the previously reported procedure[S1] and characterized by ^{1}H-NMR spectroscopy.

Scheme 1



Reagents & Conditions: (i) $TiCl_4$, Zn Powder, Dry THF, 0 -70°C, overnight; (ii) Br_2, Glacial Acetic acid, DCM, 0 °C, 3h; (iii) CuCN, DMF, reflux, 2 days; (iv) KOH, ethylene glycol, 200 °C, 3 days.

^{1}H-NMR (DMSO-*d*6) of **3**, δ (ppm): 12.93 (br *s*, 4H), 7.73 (*d*, 2H), 7.13 (*d*, 2H).

NMR characterization of 1_{GMP} hydrogel

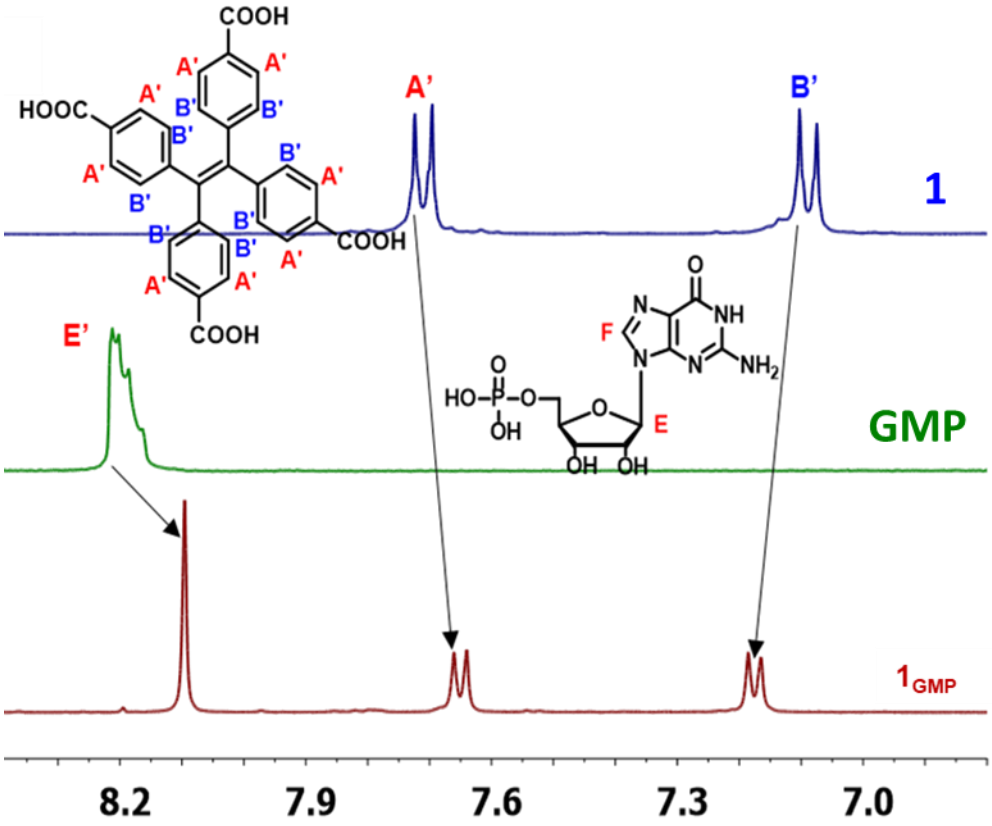


Fig. S1 ^{1}H-NMR spectra for the **1** in DMSO-d_6, 5'-GMP in D_2O and $\mathbf{1_{GMP}}$ in D_2O, showing the shifts in peak position of the aromatic protons.

Characterization and properties of metallogels, M-1$_{GMP}$

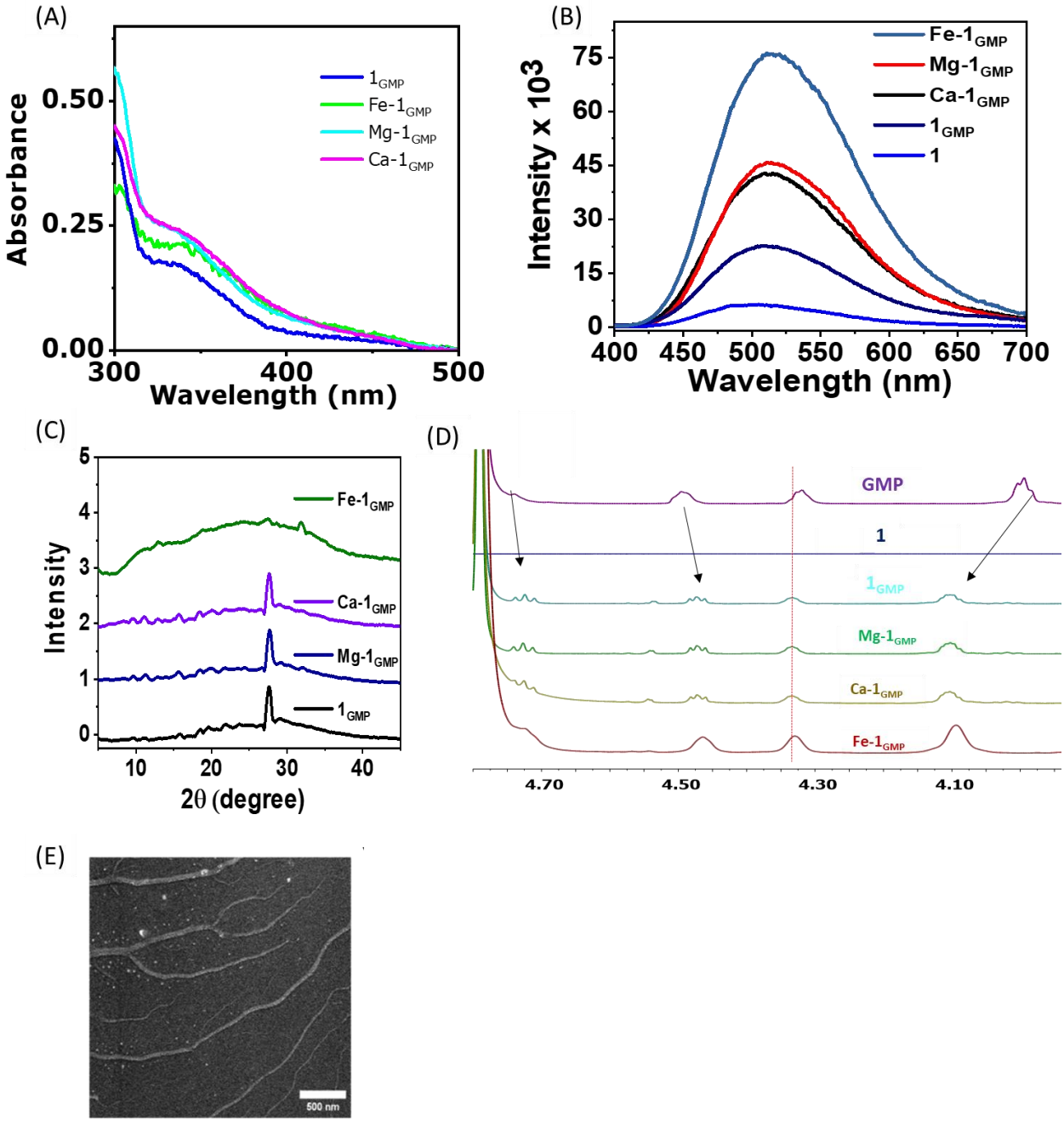


Fig. S2 (A) Comparative UV-vis spectra of the metallogels, **M-1$_{GMP}$** with **1$_{GMP}$**. (B) Fluorescence spectra showing enhanced emission of metallogels, M-**1$_{GMP}$**. (C) PXRD data showing absence of peak at 2θ = 27.5° corresponding to G4-quadruplex. (D) ^{1}H NMR spectra of the metallogels, **M-1$_{GMP}$** showing shift of the pentose sugar protons. (E) FE-SEM image of **Fe-1$_{GMP}$** showing fibrous morphology.

Gelation studies

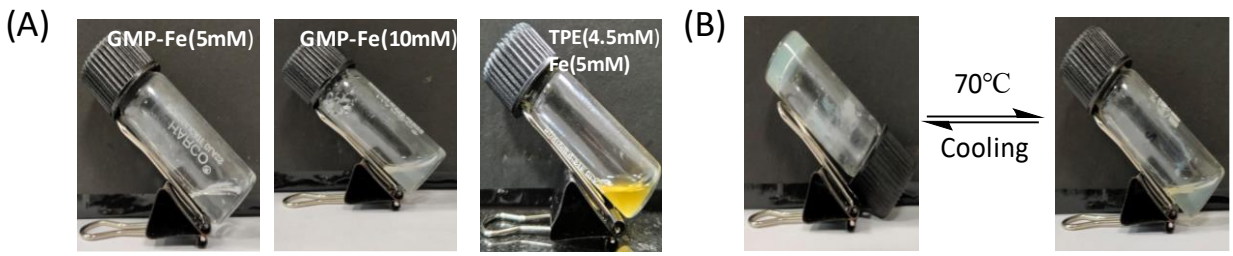


Fig. S3 (A) Control gelation experiment of G-quartet of GMP with TPE (**1**) and Fe. (B) Reversible hydrogel formation of **Fe-1$_{GMP}$** by subsequent heat-cool cycles.

Fenton reaction in metallogels, M-1$_{GMP}$

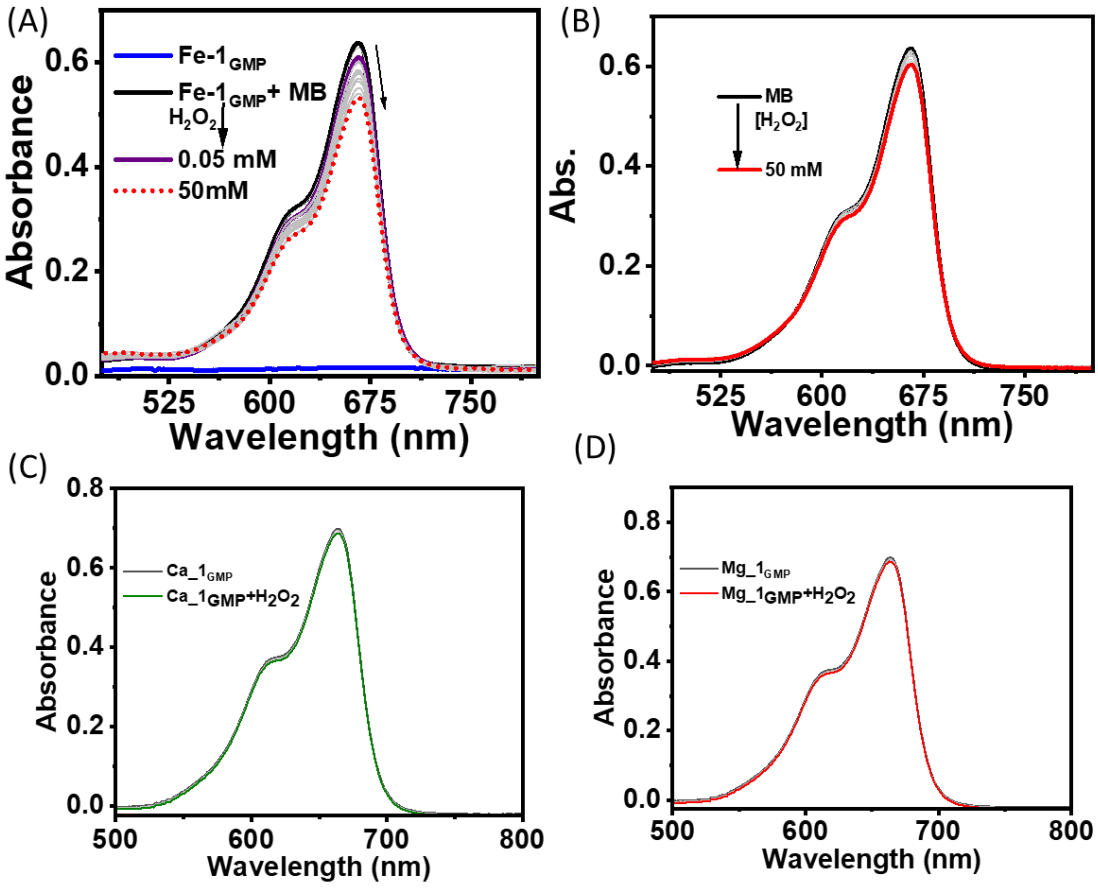


Fig. S4 (A) Concentration dependent degradation of MB dye with addition of H_2O_2 in presence of **Fe-1$_{GMP}$**. (B) Degradation MB in presence of H_2O_2 only. (C-D) Control experiments showing no ROS formation in the hydrogels of **Ca-1$_{GMP}$** & **Mg-1$_{GMP}$**.

Rheological studies of Fe-1_{GMP} V/S Fe-1_{GMP}+AA

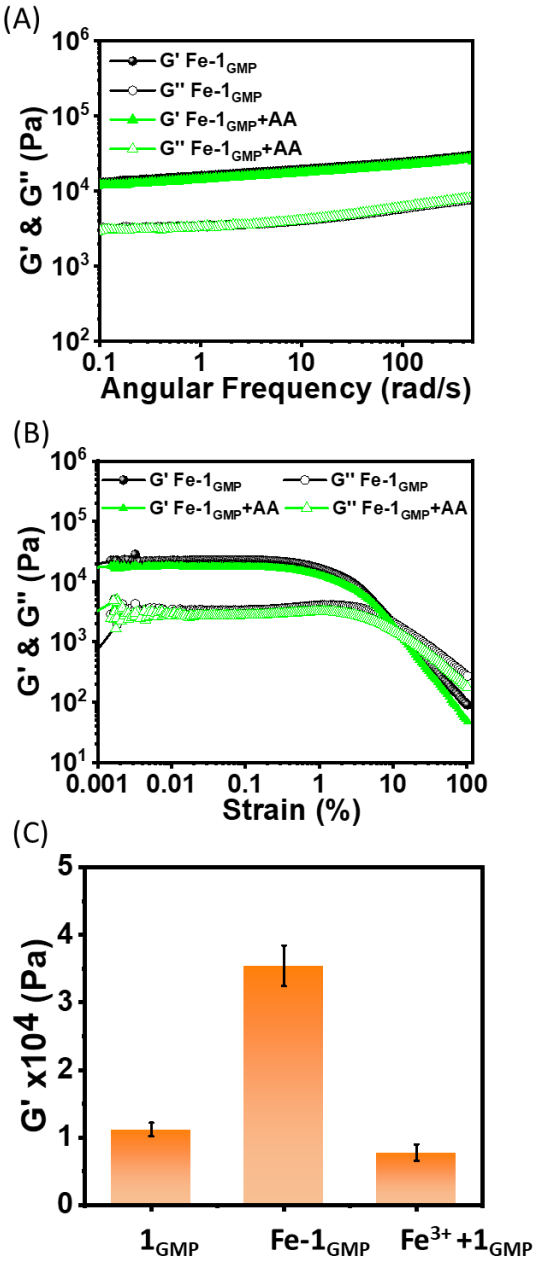


Fig. S5 (A-B) Frequency sweep and amplitude sweep rheological study of **Fe-1_{GMP}** after loading AA. (C) Comparison of the storage moduli of **1_{GMP}**, **Fe-1_{GMP}+AA** and **Fe^{3+}** loaded **1_{GMP}**.

Antimicrobial and Biocompatibility studies

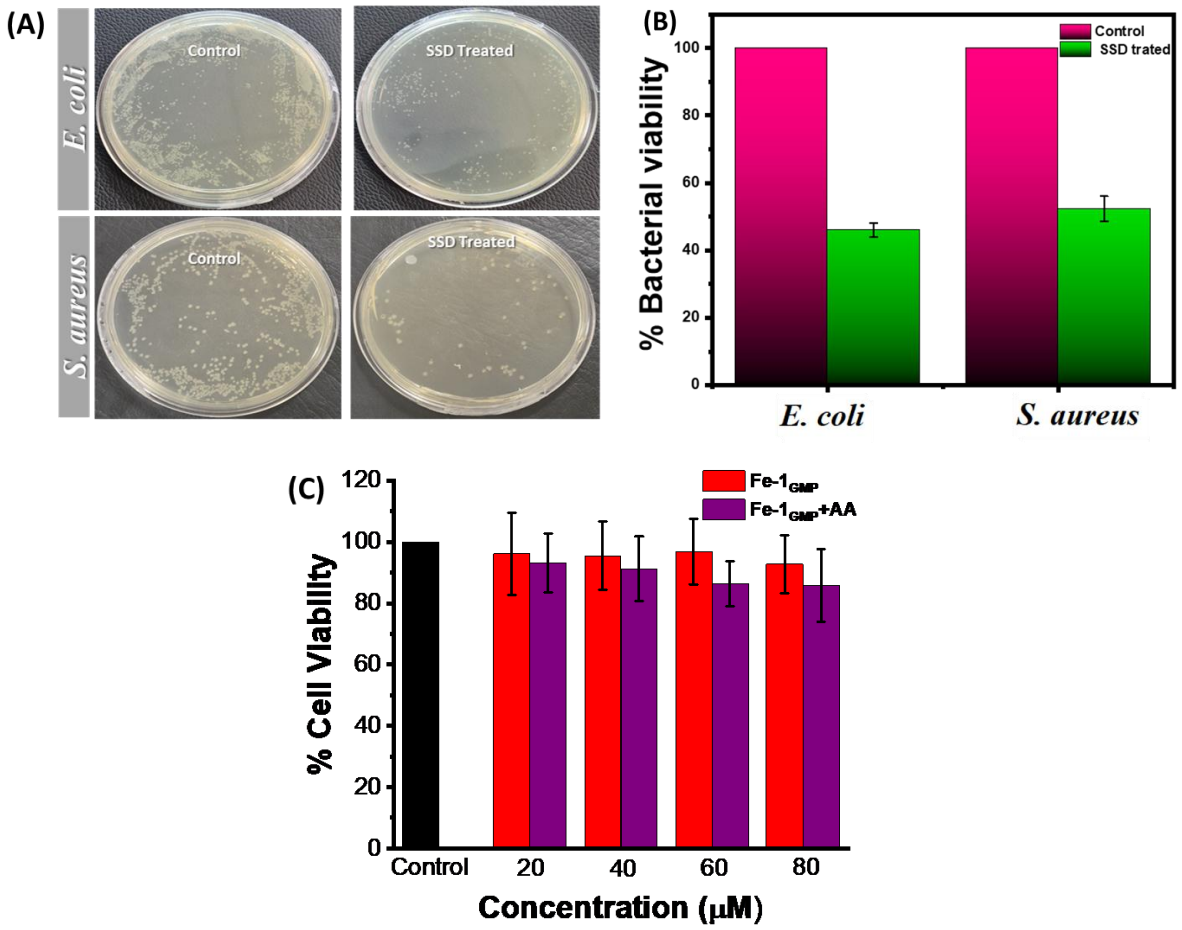


Fig. S6 (A) Images of bacterial colonies formed treating silver sulfadiazine (SSD) at its MIC, *E. coli* 23.7 µg/mL (upper panel) *S. aureus* 47.5 µg/mL (lower panel) and (B) corresponding histogram of comparison of survival percentage of bacterial cells. Control is without SSD administration. (C) MTT assay for **Fe-1$_{GMP}$** and **Fe-1$_{GMP}$ + AA** loaded hydrogels in L929 cell line.

Reference:

S1. A. Bhunia, V. Vasylyevaa, C. Janiak, *Chem. Commun.*, 2013, **49**, 3961-3963.