

Chemically Robust Amine-grafted Zn(II)-based Smart Supramolecular gel as a Regenerative Platform for Trace Discrimination of Nitro-antibiotics and Assorted Environmental Toxins

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Experimental Details

All reagents and solvents for synthesis and analyses were commercially available and used as received without further purification. N, N-Dimethylformamide (DMF) purchased from Finar. Zinc(II) acetate tetrahydrate $[\text{Zn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}]$, Hydrochloric acid (HCl), Sodium Hydroxide pellets, Ammonia solution, Ammonium thiocyanate, Glacial Acetic acid, Ethylenediaminetetraacetic acid (EDTA) were procured from Fisher Scientific (SQ grade, Qualigens), Rankem (LR grade), Merck, Qualigens (SQ grade), Fisher Scientific (Certified ACS grade), Fisher scientific (SQ grade, Qualigens) and SD Fine Chemicals (AR grade) respectively. Triphenylphosphine, Tetra-butyl Ammonium bromide, Silver nitrate, Lithium fluoride, Sodium chloride, Potassium bromide, Potassium iodide and picric acid were purchased from Loba Chemie, Spectrochem, Qualigens, SD Fine Chemicals, Fisher scientific, SD Fine Chemicals, Qualikems and Loba Chemie respectively. 2,4-dinitrotoluene, 4-nitrotoluene, 3-nitrotoluene, 2-nitrotoluene, 2,4-dinitrophenol, 3-nitrophenol, 2-nitrophenol and 4-nitrophenol were procured from TCI Chemicals. 3,5-diammino-1,2,4-traizole, 3-nitrobenzoic acid and *p*-nitrobenzoic acid were obtained from Sigma Aldrich and used as received. Furazolidone, nitrofurantoin, ornidazole, secnidazole and tinidazole were obtained from reliable commercial sources and were used without further purifications.

Instrument Details

The synthesized metallogel and corresponding xerogel were characterized using several techniques such as PXRD, FT-IR, UV-vis, Emission analysis, TEM, SEM and dynamic rheological studies. The powder X-ray diffraction (PXRD) analysis was done using Philips X'pert MPD system (PANalytical diffractometer) with Cu $K\alpha_1$ radiation ($\lambda = 0.15406 \text{ nm}$). The diffraction pattern was measured from $5\text{-}90^\circ$ 2θ range at operating voltage of 40 kV and 30 mA current, with a scan speed of 3° min^{-1} and a step size of 0.013° in 2θ at RT with a scan step time 58.395 sec. Anode Material was Cu and the value of $K_{\alpha 1}$, $K_{\alpha 2}$ and K_{β} were 1.54060

[Å], 1.54443 [Å] and 1.39225 [Å] respectively. $K_{\alpha 2}/K_{\alpha 1}$ Ratio was 0.50000. Fourier transform Infrared Spectra analysis (FT-IR) was recorded on Perkin Elmer-Spectrum G-FTIR spectrometer (Germany) from 400-4000 cm^{-1} with a resolution of 4 cm^{-1} using KBr pellets. The UV-visible (UV-vis) spectra and emission spectra of samples were recorded using UV 3600, Shimadzu (Japan) and Fluorolog Horiba Jobin fluorometer respectively. The slit-width for the fluorescence experiment was kept at 5 nm (excitation) and 5 nm (emission) and the excitation wavelength was set at 275 nm. The surface morphology of prepared gel material was analyzed by Field Emission-Scanning Electron Microscope JEOL JSM 7100F (using accelerating voltage of 5–15 kV with 10 μA of emission current) and by transition electron microscope (TEM) JEOL, JEM 2100. LEICA EM ACE200 sputter coater was used for gold coating of the samples before analyzed under the Field Emission-Scanning Electron Microscope. The exact mass analyses of samples were analyzed by LC-MS analysis (LC Waters, MS Micromass). The rheological properties of samples were measured by the Anton Paar Rheometer with a plate probe of 40 nm diameter. For the amplitude sweep experiment (Dynamic strain sweep, DSS) and thixotropic loop test, the operating frequency was kept constant at 1 rad s^{-1} . For the dynamic frequency sweep measurements, the operating strain was kept constant at 0.1% over the entire frequency range.

Details of the Density functional theory calculations

The 3D structures for nitroaromatics and nitro-antibiotics were generated using the builder panel in Maestro GUI. The geometry of NACs and NDs are then optimized by semi-empirical PM3¹ using Gaussian09 package². The optimized interaction of Nit/4-NP@ZnGel is proposed using B3LYP functional^{3,4} and 6-311++G(d,p) basis set⁵. The energy values corresponding to highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were obtained from this quantum chemical calculations. The HOMO-LUMO energy gap value predicts the chemical reactivity of the molecules. The

distribution of HOMO-LUMO orbitals were generated using Cubegen utility in Gaussian09 software.

Analytical data

ZnGel: FT-IR (KBr) $\nu_{\text{max}}(\text{cm}^{-1})$: 3471 (m, br), 3072 (w), 2932 (m), 2872 (w), 2593 (w), 2515 (w), 2337 (w), 2274 (w), 2181 (w), 2119 (w), 2051 (w), 1965 (w), 1671 (s), 1498 (m), 1438 (w), 1390 (s), 1252 (s), 1097 (s), 868 (m), 762 (w), 666 (s), 616 (w), 408 (m).

ZnXero: FT-IR (KBr) $\nu(\text{cm}^{-1})$: 3376 (m,br), 2936 (w), 1671 (m), 1589 (s), 1539 (w), 1519 (w), 1408 (m), 1389 (w), 1338 (m), 1103 (w), 1069 (w), 1022 (w), 936 (w), 850 (w), 764 (m), 681 (m), 623 (w), 562 (w), 505 (w), 412 (m).

Absorbance spectrum of ZnGel

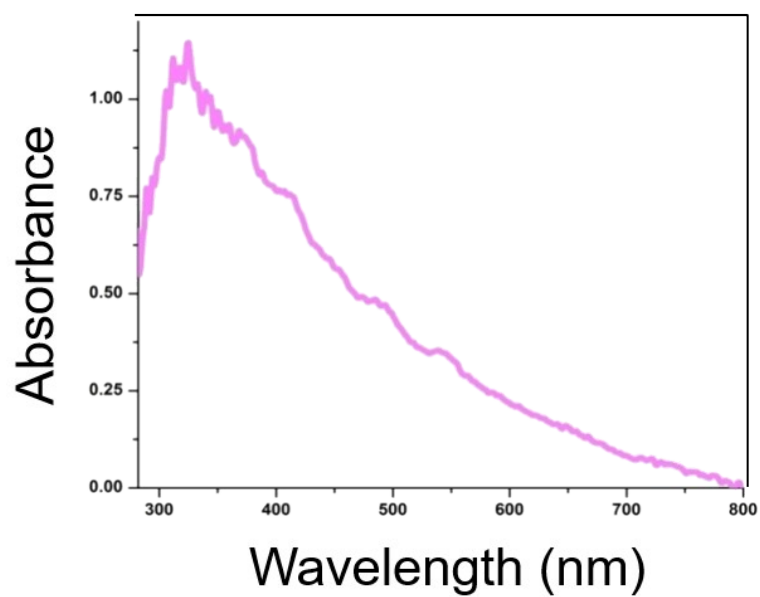


Figure S1. Absorbance spectrum of **ZnGel**.

FT-IR spectrum of ZnGel and ZnXero

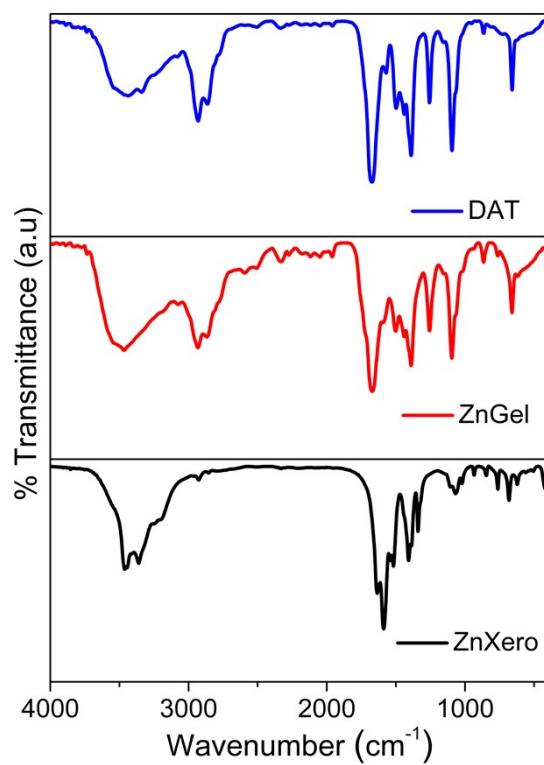


Figure S2. FT-IR spectrum of **DAT**, **ZnGel** and **ZnXero**.

PXRD pattern of the ZnGel and ZnXero

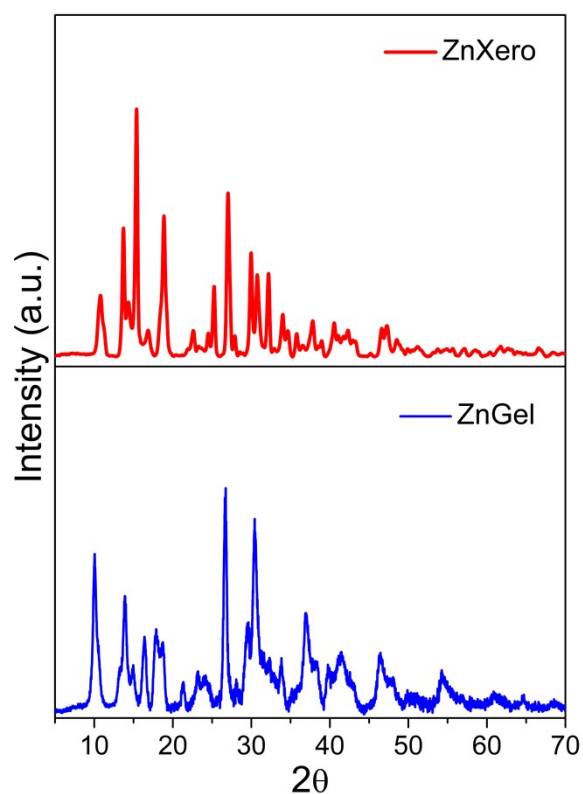


Figure S3. PXRD pattern of the **ZnGel** and **ZnXero**.

Mass spectrum of ZnGel

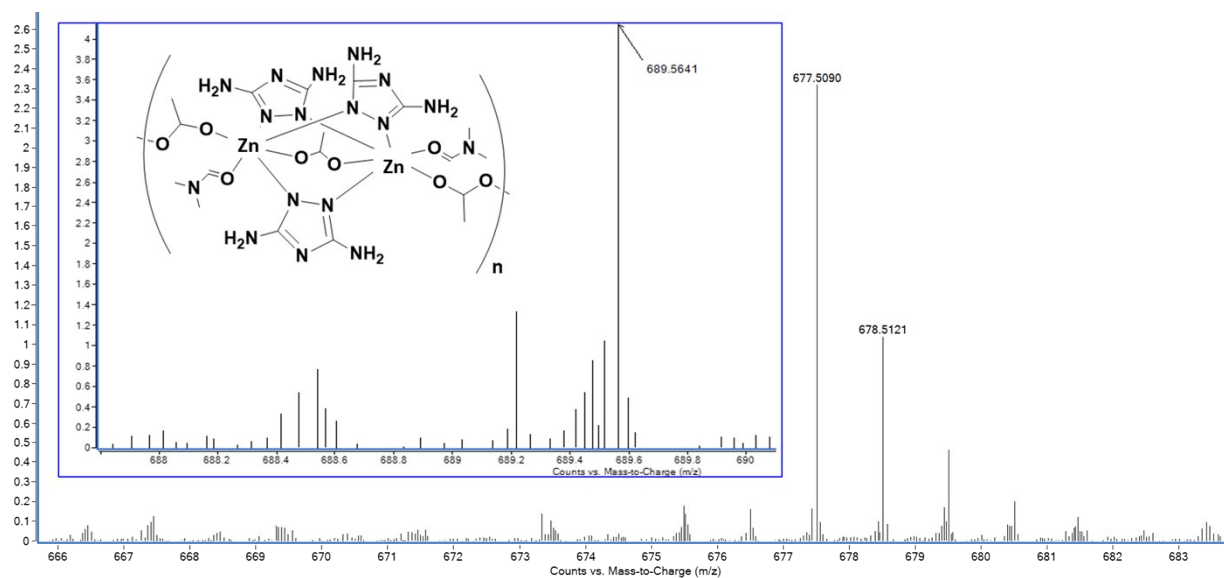


Figure S4. Mass spectrum of **ZnGel** (inset: the local structure of **ZnGel** and the corresponding molecular ion peak at $m/z = 689.56$).

SEM images (including EDX analysis) of ZnGel and analyte incorporated ZnGel

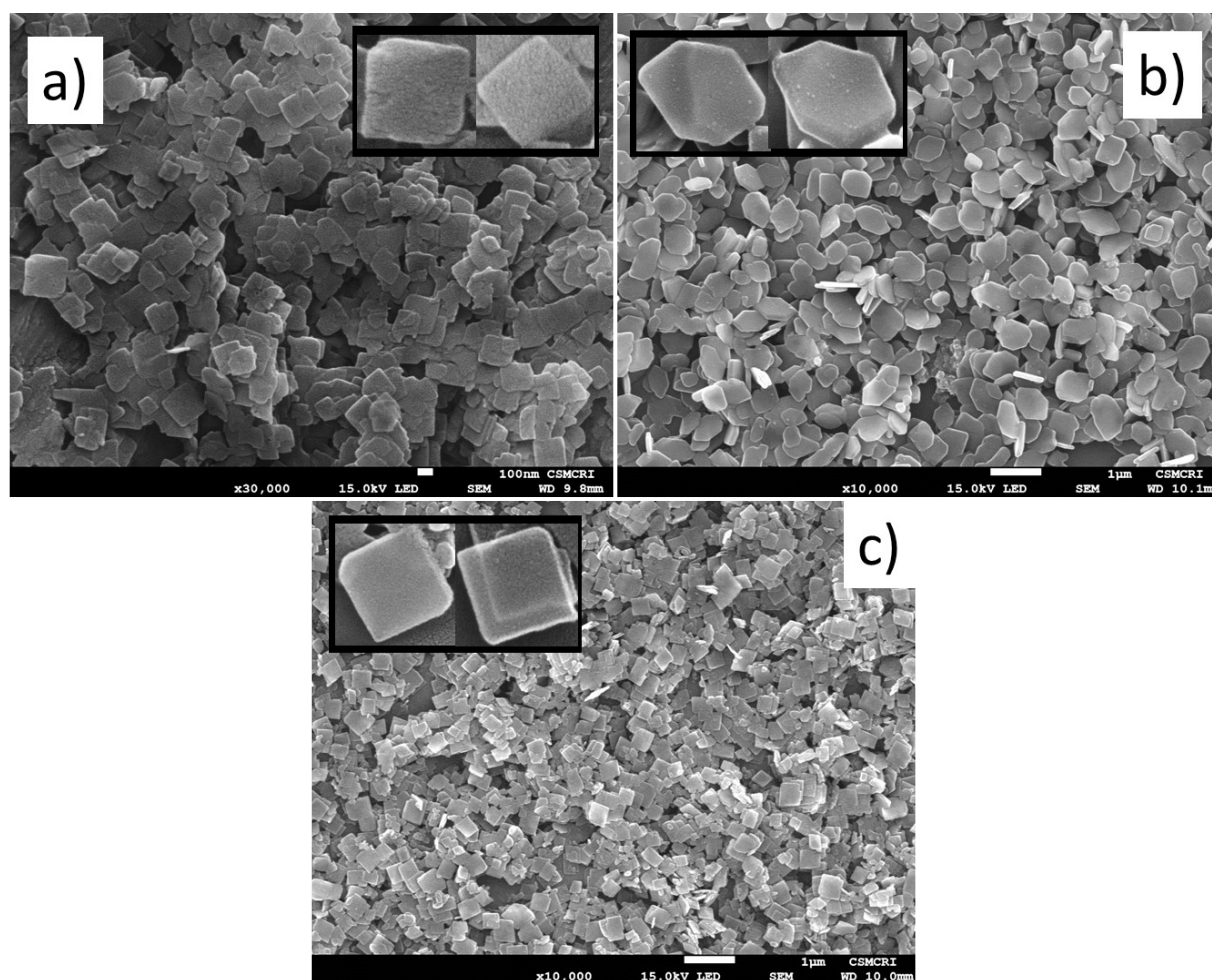


Figure S5. FE-SEM images of a) ZnGel, b) PA@ZnGel, and c) Nit@ZnGel respectively.

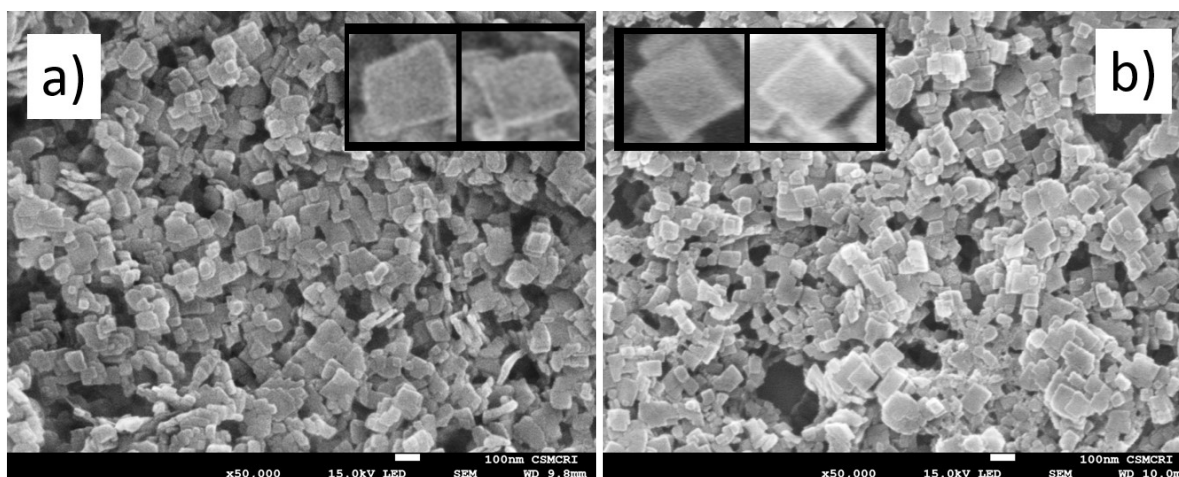


Figure S6. FE-SEM images of a) Fe(III)@ZnGel and b) Pd(II)@ZnGel respectively.

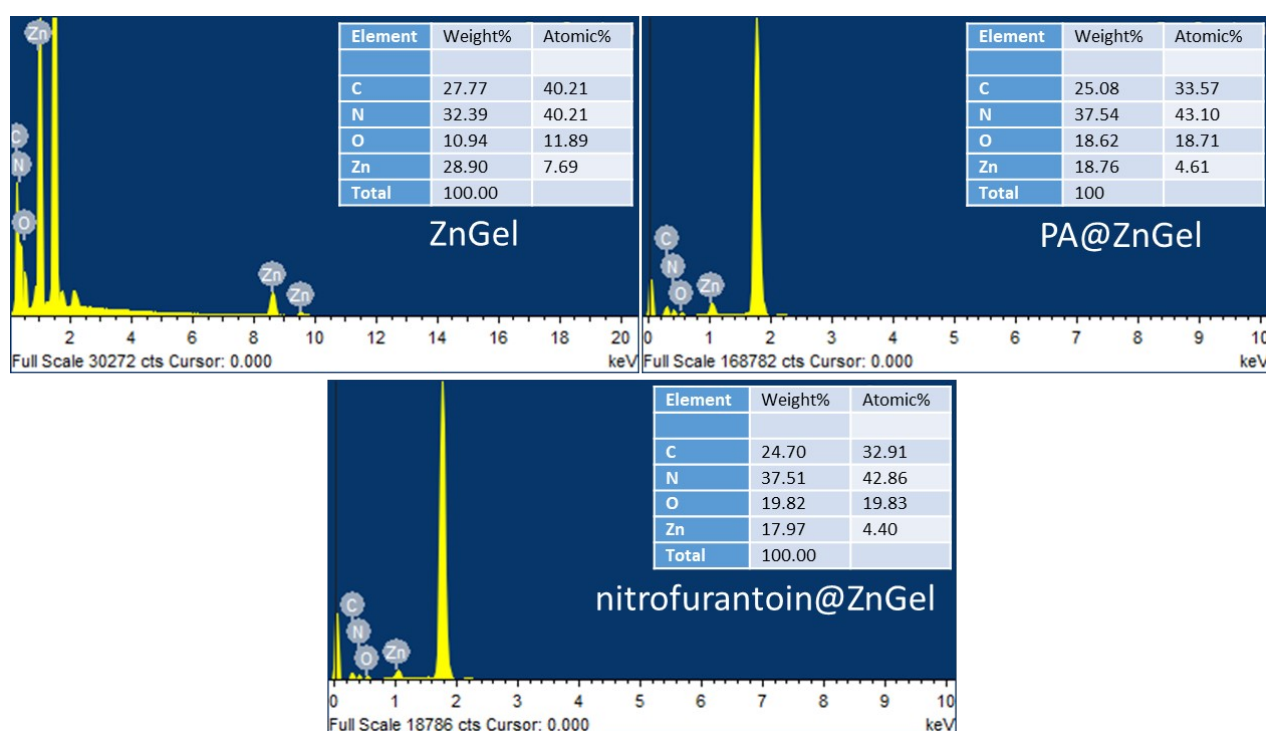


Figure S7. FE-SEM EDX analysis of a) ZnGel, b) PA@ZnGel, and c) Nit@ZnGel respectively.

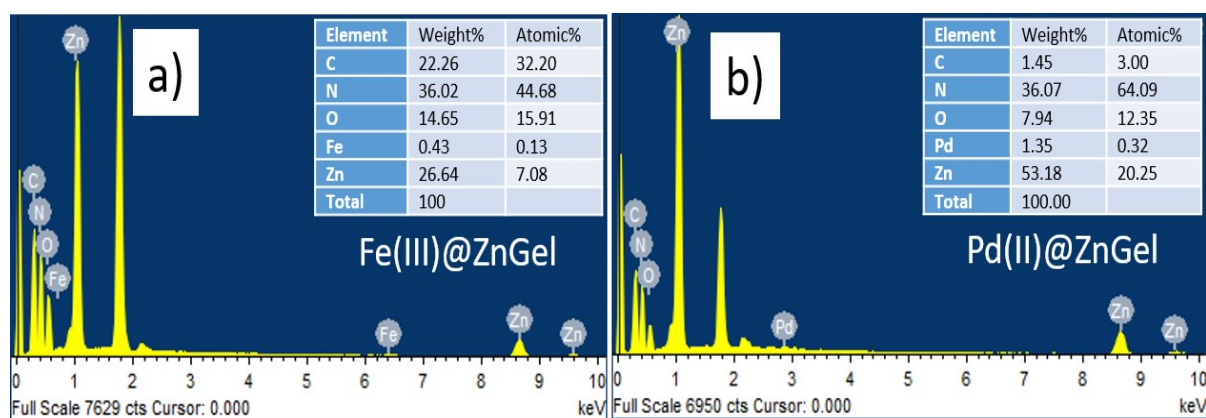


Figure S8. FE-SEM EDX analysis of a) Fe(III)@ZnGel and b) Pd(II)@ZnGel respectively.

TEM images (including EDX analysis) of ZnGel and analyte incorporated ZnGel

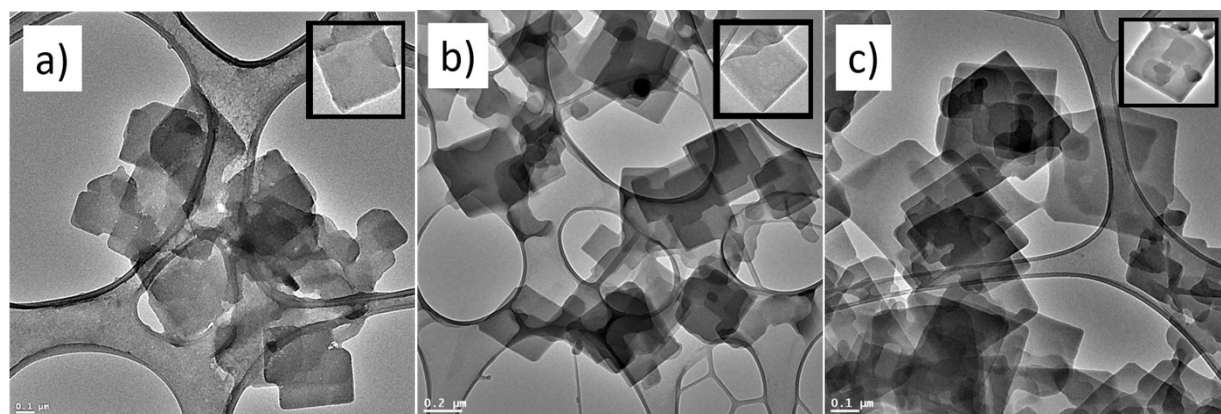


Figure S9. TEM images of a) ZnGel, b) Nit@ZnGel and c) Furz@ZnGel respectively.

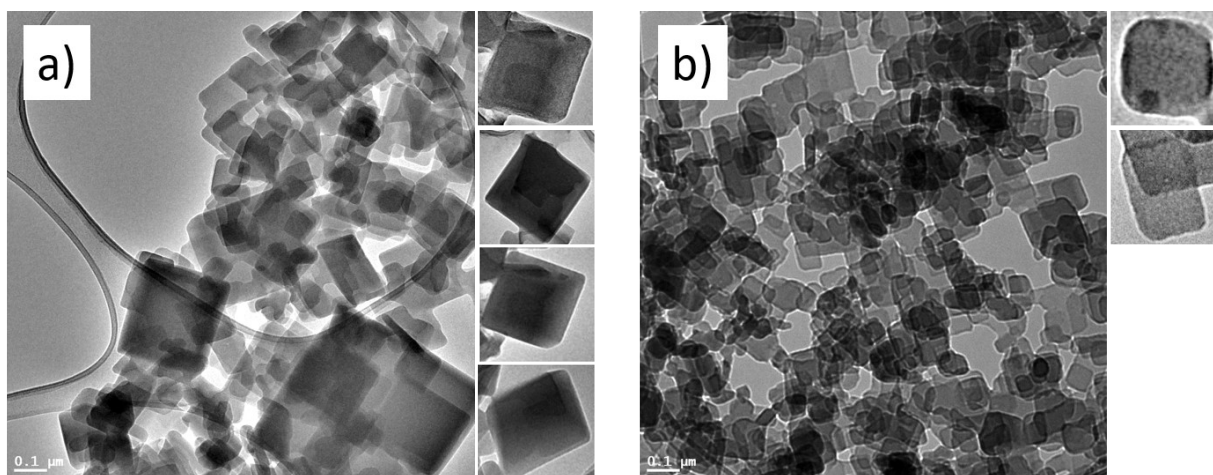


Figure S10. TEM images of a) PA@ZnGel and b) Fe(III)@ZnGel respectively.

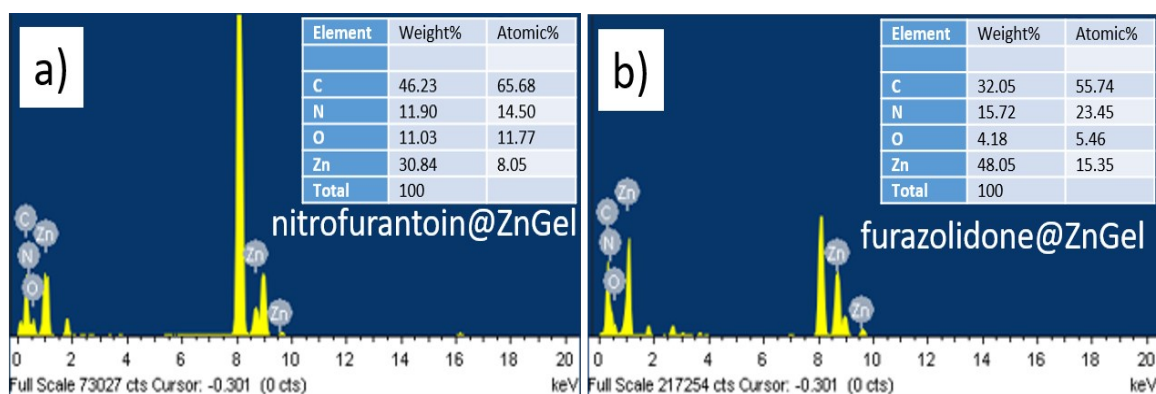


Figure S11. TEM EDX analysis of a) Nit@ZnGel and b) Furz@ZnGel respectively.

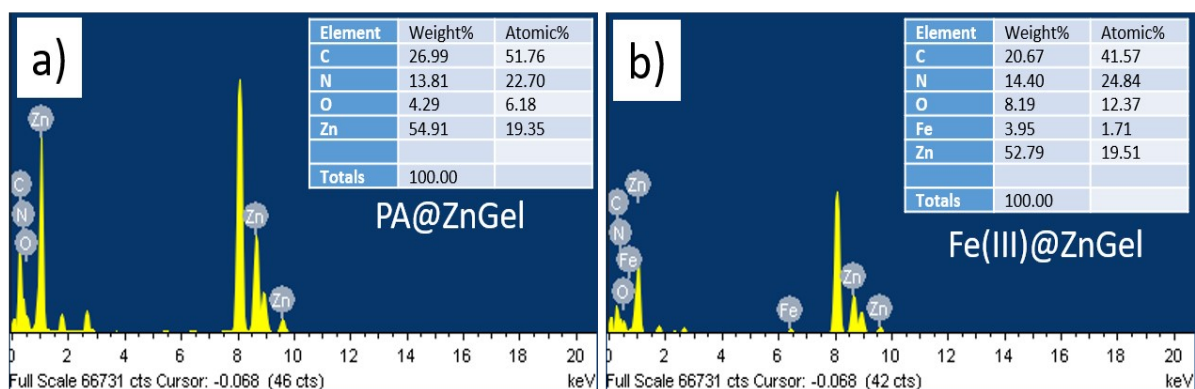


Figure S12. TEM EDX analysis of a) PA@ZnGel and b) Fe(III)@ZnGel respectively.

Injectable nature of ZnGel



Figure S13. Injectable nature of **ZnGel**.

Response of ZnGel towards treatment with PPh_3 and with external halide stimuli

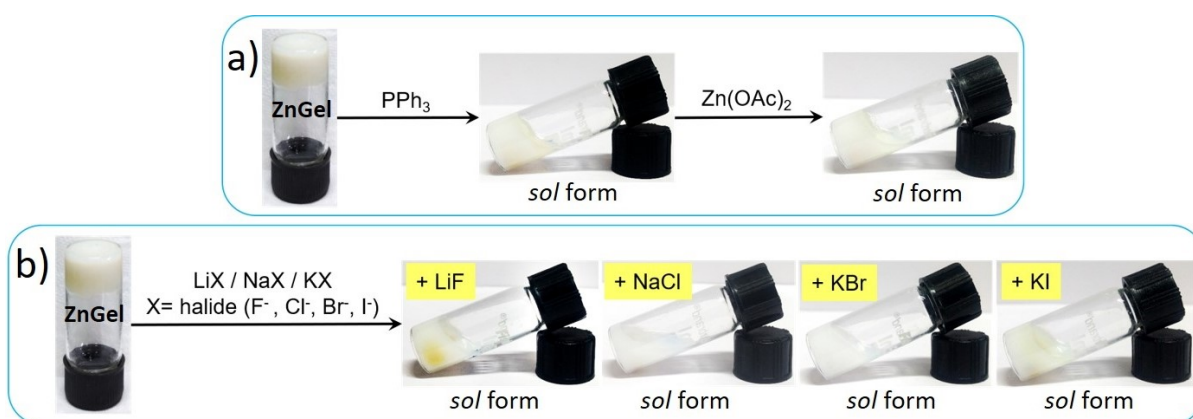


Figure S14. Response (i.e. irreversible *gel-to-sol* transformation of **ZnGel** a) towards treatment with PPh_3 followed by Zn^{II} -precursor; b) upon addition of external halide stimuli.

Fluorescence titration of ZnGel in DMF in presence of different NDs

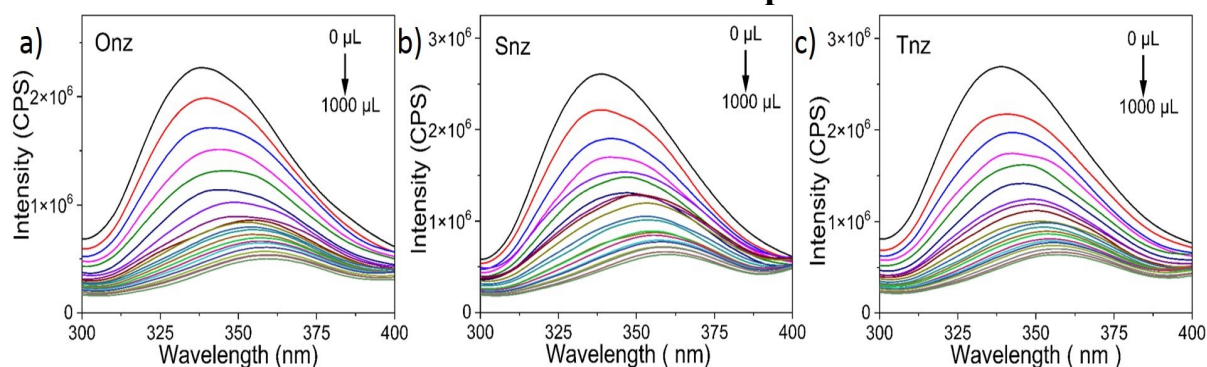


Figure S15. Fluorescence titrations of **ZnGel** in DMF ($\lambda_{\text{ex}} = 275$ nm) with a) Onz, b) Snz and c) Tnz respectively.

Stern-Volmer plots of ZnGel in DMF in presence of different NDs

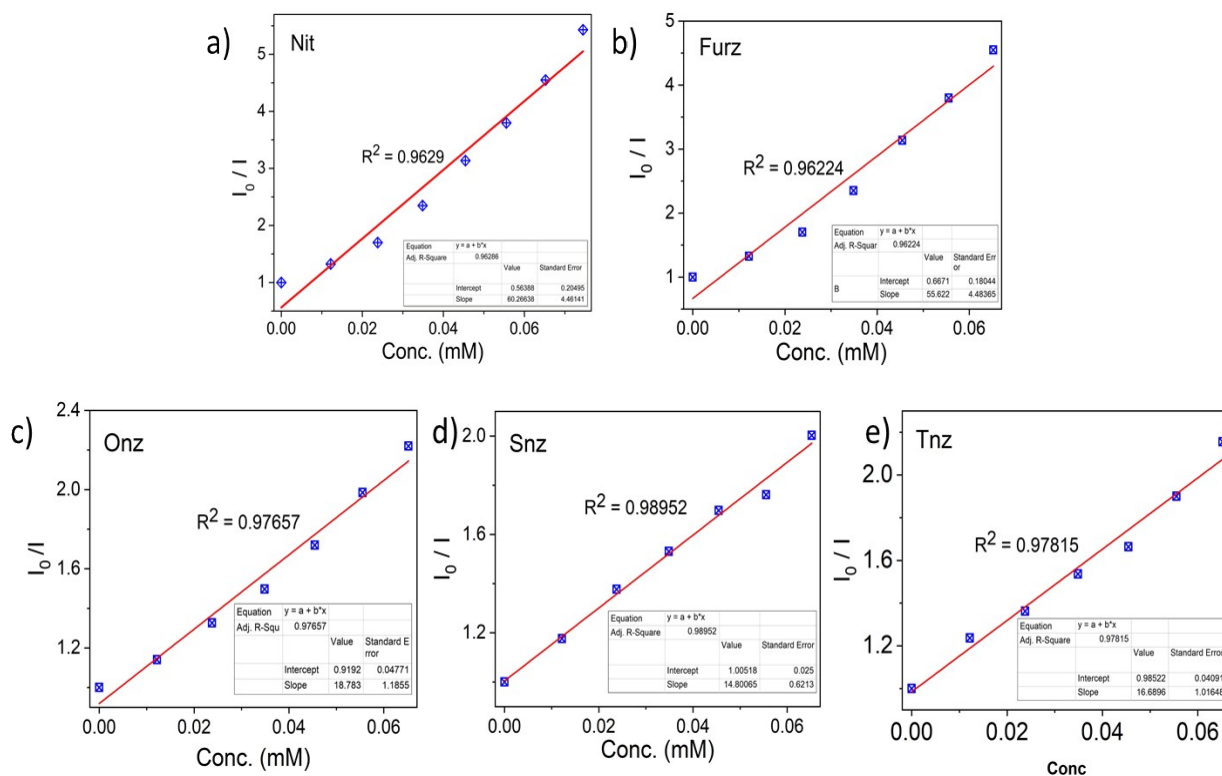


Figure S16. Stern-Volmer plots of **ZnGel** in DMF ($\lambda_{\text{ex}} = 275$ nm) with a) Nit, b) Furz, c) Onz, d) Snz and e) Tnz respectively.

Intensity of ZnGel vs concentration of the NDs plot

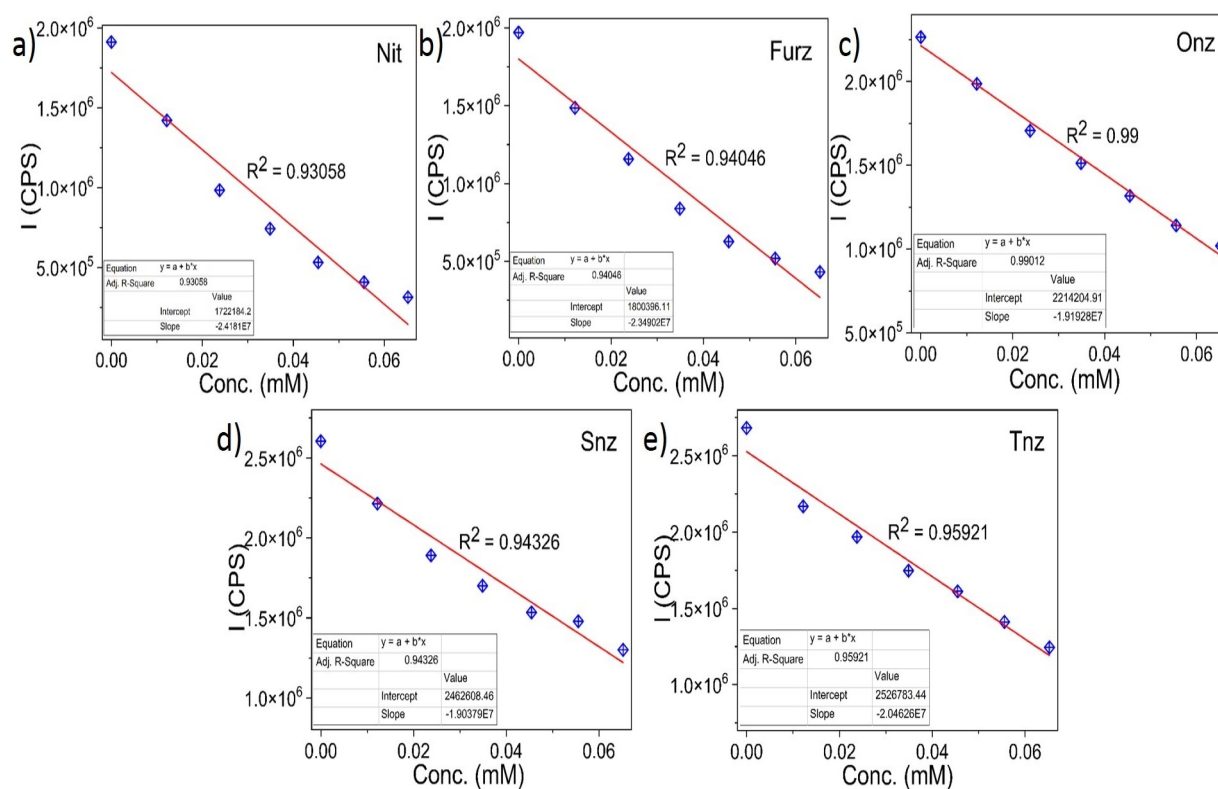


Figure S17. C vs I plots of ZnGel in DMF ($\lambda_{ex} = 275$ nm) with a) Nit, b) Furz, c) Onz, d) Snz and e) Tnz respectively.

Fluorescence titrations of ZnGel in DMF in presence of different NACs

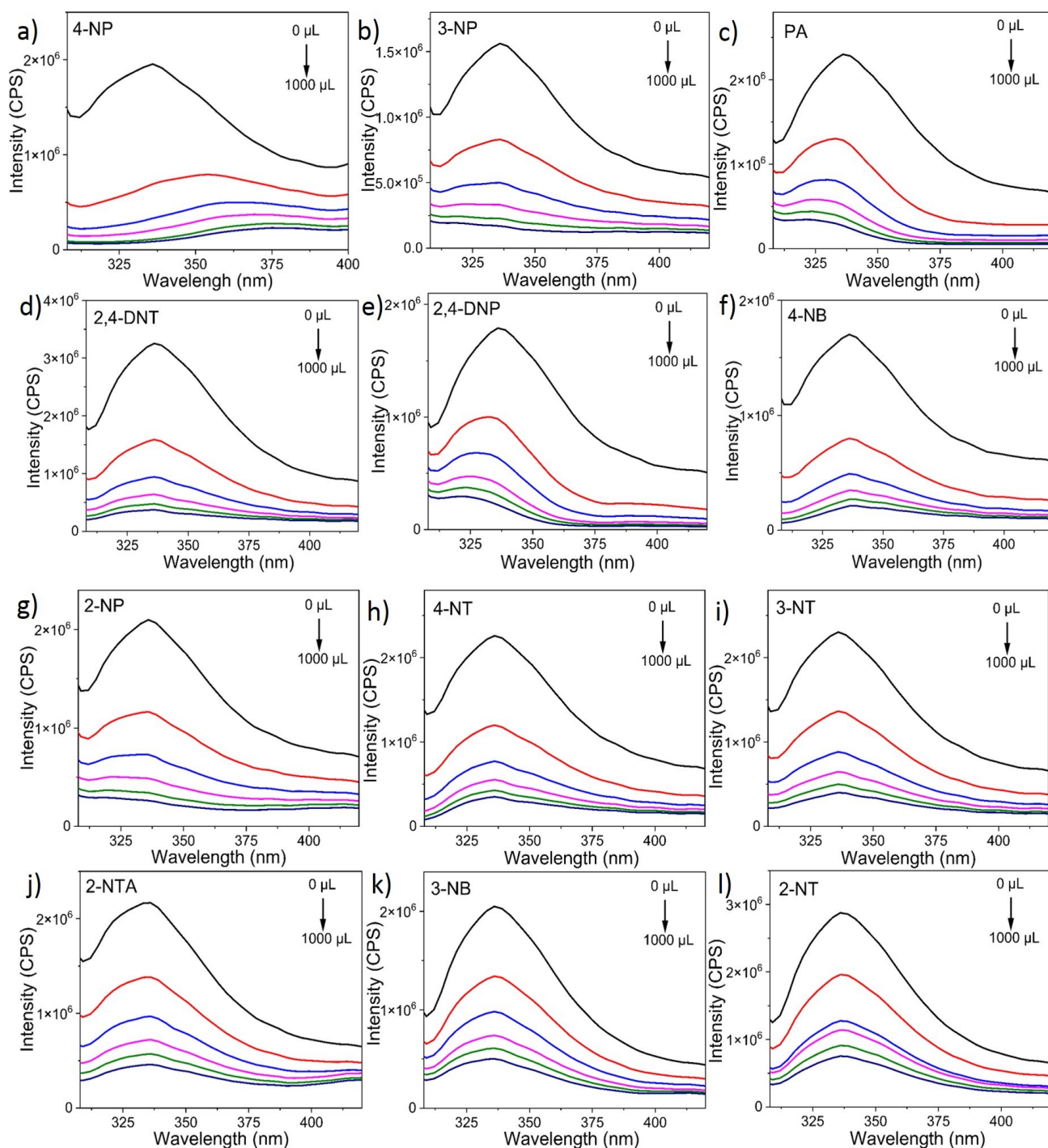


Figure S18. Fluorescence titrations of **ZnGel** in DMF ($\lambda_{\text{ex}} = 275 \text{ nm}$) with a) 4-NP; b) 3-NP; c) PA; d) 2,4-DNT; e) 2,4-DNP; f) 4-NB; g) 2-NP; h) 4-NT; i) 3-NT; j) 2-NTA; k) 3-NB; and l) 2-NT respectively.

Stern-Volmer plots of ZnGel in DMF in presence of different NACs

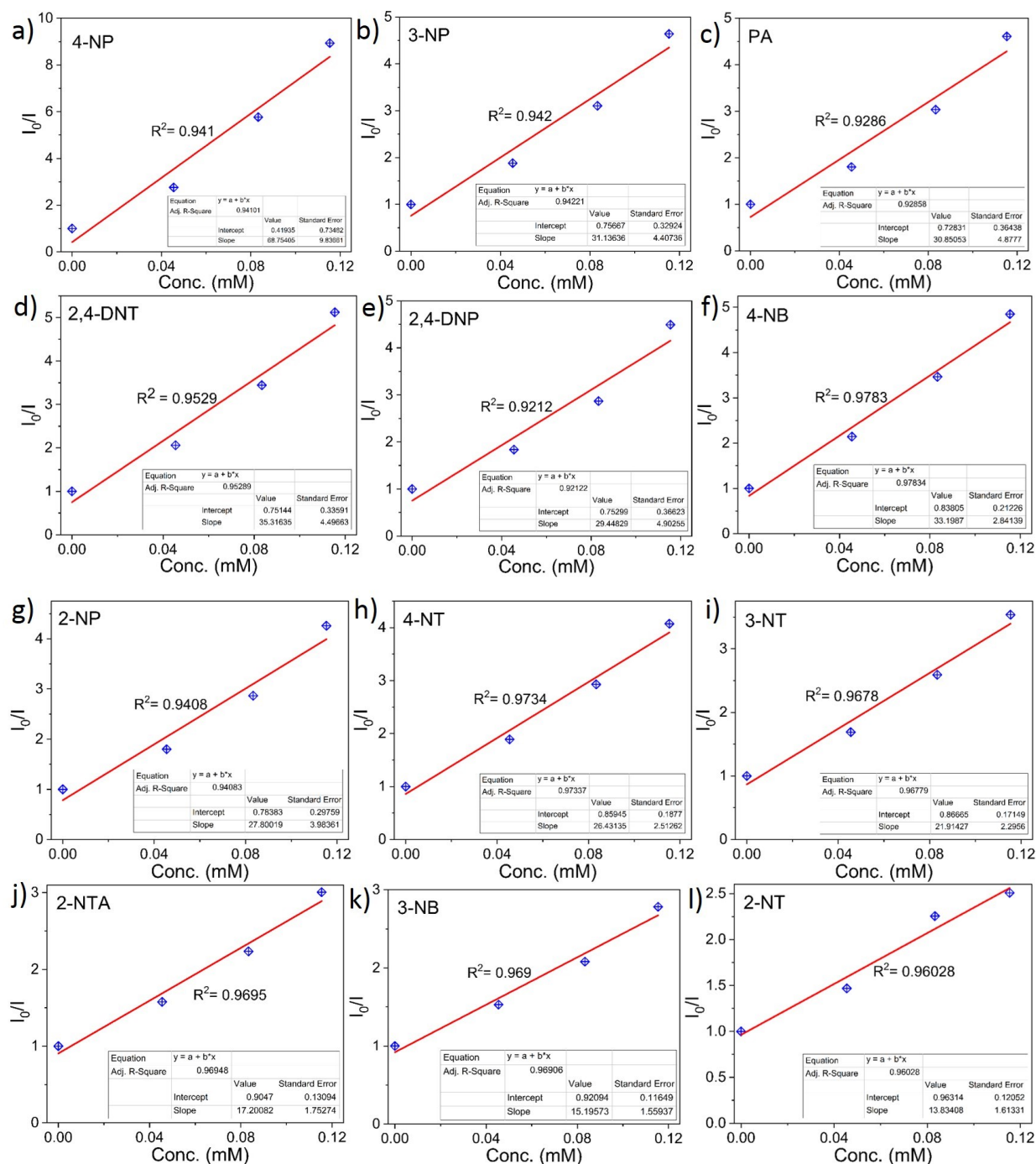


Figure S19. Stern-Volmer plots of **ZnGel** in DMF ($\lambda_{ex} = 275$ nm) with a) 4-NP; b) 3-NP; c) PA; d) 2,4-DNT; e) 2,4-DNP; f) 4-NB; g) 2-NP; h) 4-NT; i) 3-NT; j) 2-NTA; k) 3-NB; and l) 2-NT respectively.

Intensity of ZnGel vs concentration of the NACs plot

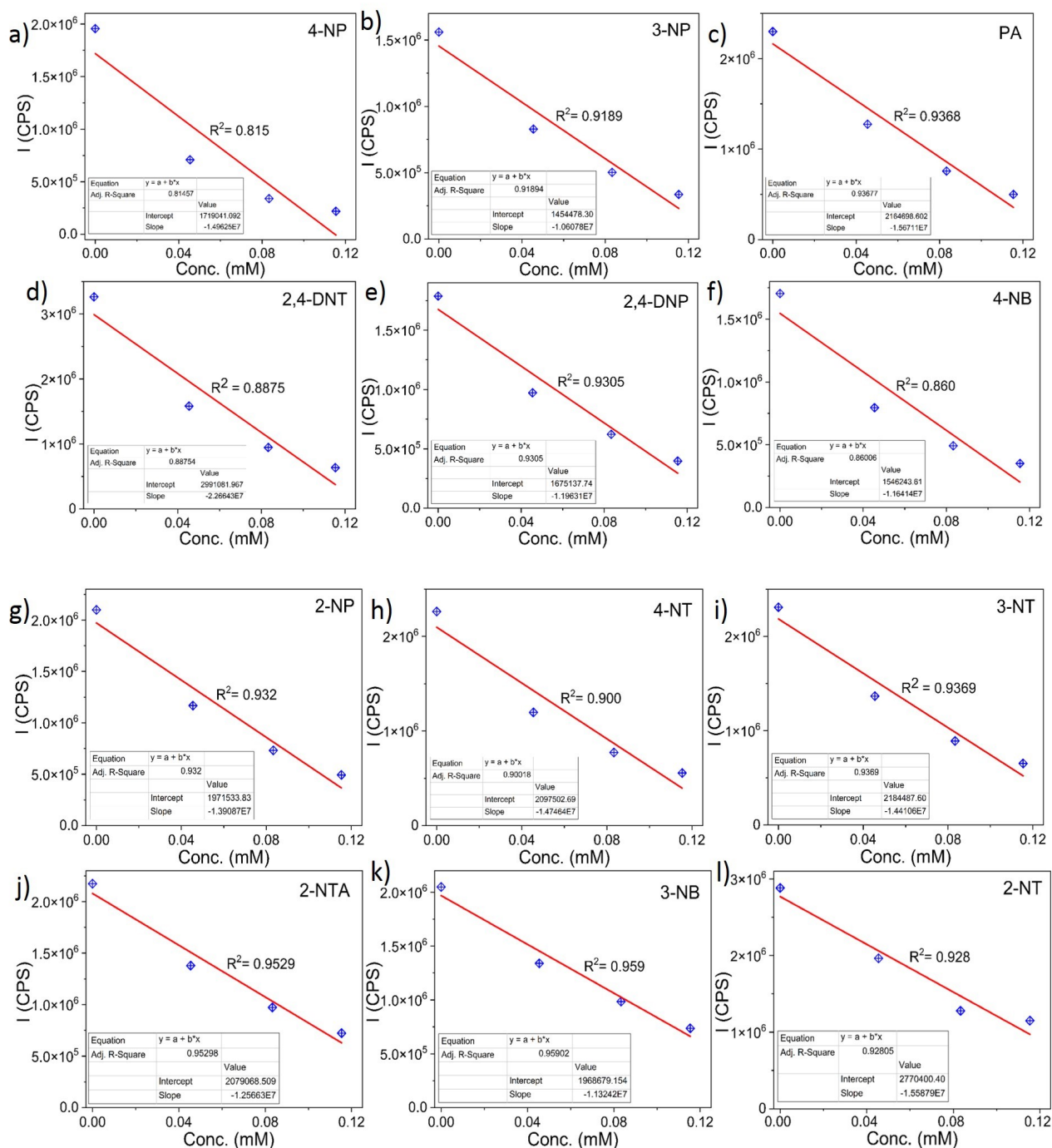


Figure S20. C vs I plots of **ZnGel** in DMF ($\lambda_{\text{ex}} = 275 \text{ nm}$) with a) 4-NP; b) 3-NP; c) PA; d) 2,4-DNT; e) 2,4-DNP; f) 4-NB; g) 2-NP; h) 4-NT; i) 3-NT; j) 2-NTA; k) 3-NB; and l) 2-NT respectively.

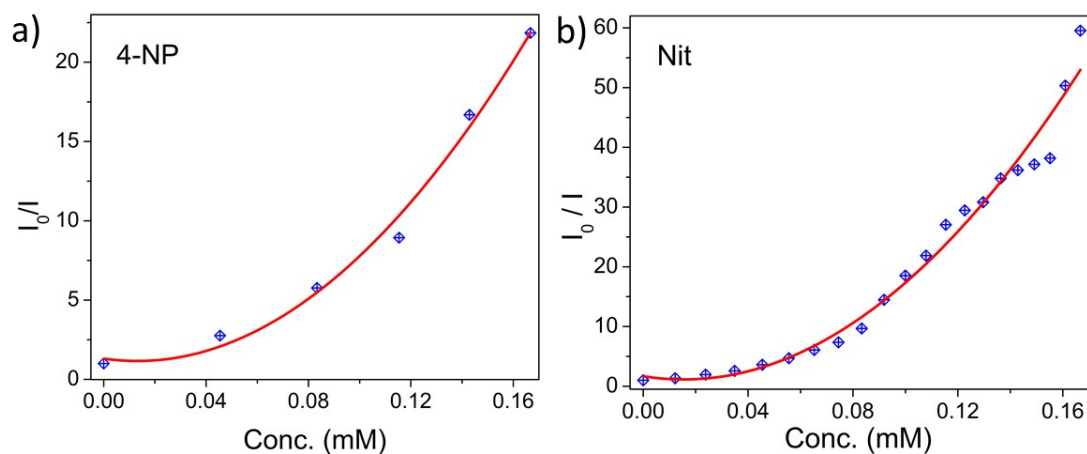


Figure S21. The non-linear Stern-Volmer plot of **ZnGel** in DMF ($\lambda_{\text{ex}} = 275$ nm) with a) 4-NP and b) Nit at concentration range 0-0.17 mM.

Fluorescence titrations of ZnGel in DMF in presence of different metal ions

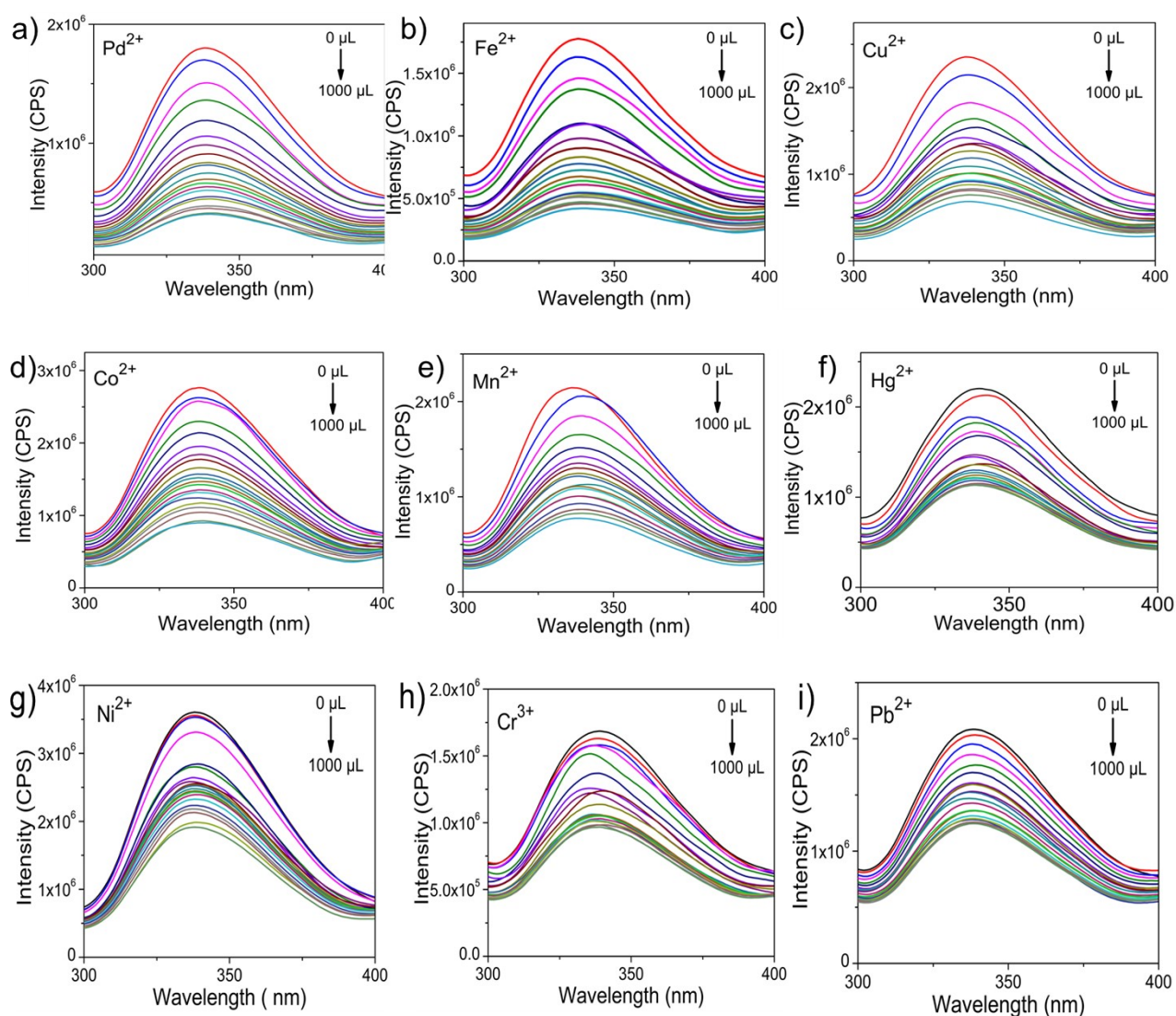


Figure S22. Fluorescence titrations of **ZnGel** in DMF ($\lambda_{\text{ex}} = 275 \text{ nm}$) with a) Pd^{2+} , b) Fe^{2+} , c) Cu^{2+} , d) Co^{2+} , e) Mn^{2+} , f) Hg^{2+} , g) Ni^{2+} , h) Cr^{3+} and i) Pb^{2+} respectively.

Stern-Volmer plots of ZnGel in DMF in presence of different metal ions

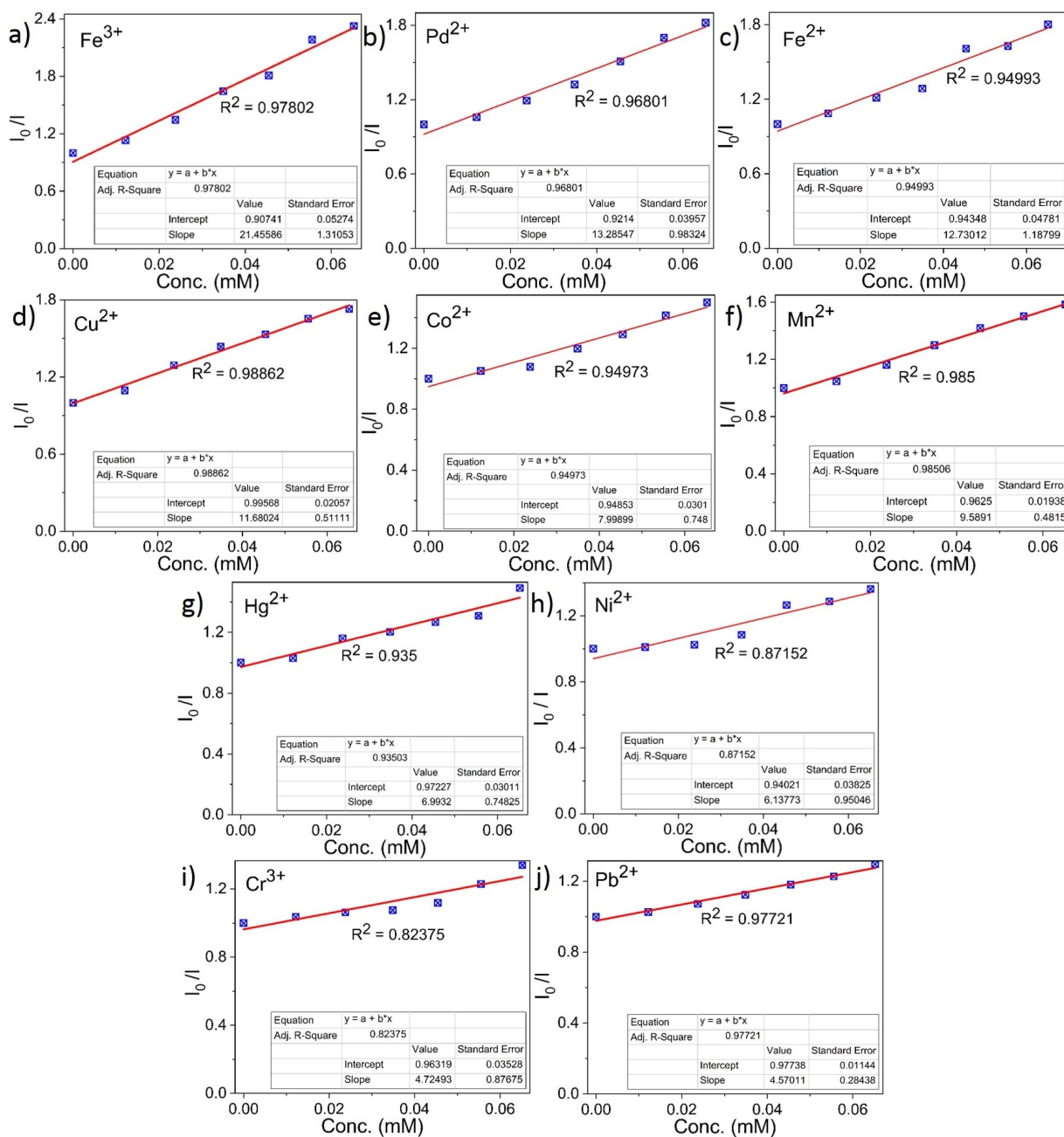


Figure S23. Stern-Volmer plots of ZnGel in DMF ($\lambda_{ex} = 275$ nm) with a) Fe^{3+} , b) Pd^{2+} , c) Fe^{2+} , d) Cu^{2+} , e) Co^{2+} , f) Mn^{2+} , g) Hg^{2+} , h) Ni^{2+} , i) Cr^{3+} and j) Pb^{2+} respectively.

Intensity of ZnGel vs concentration of the metal ions plot

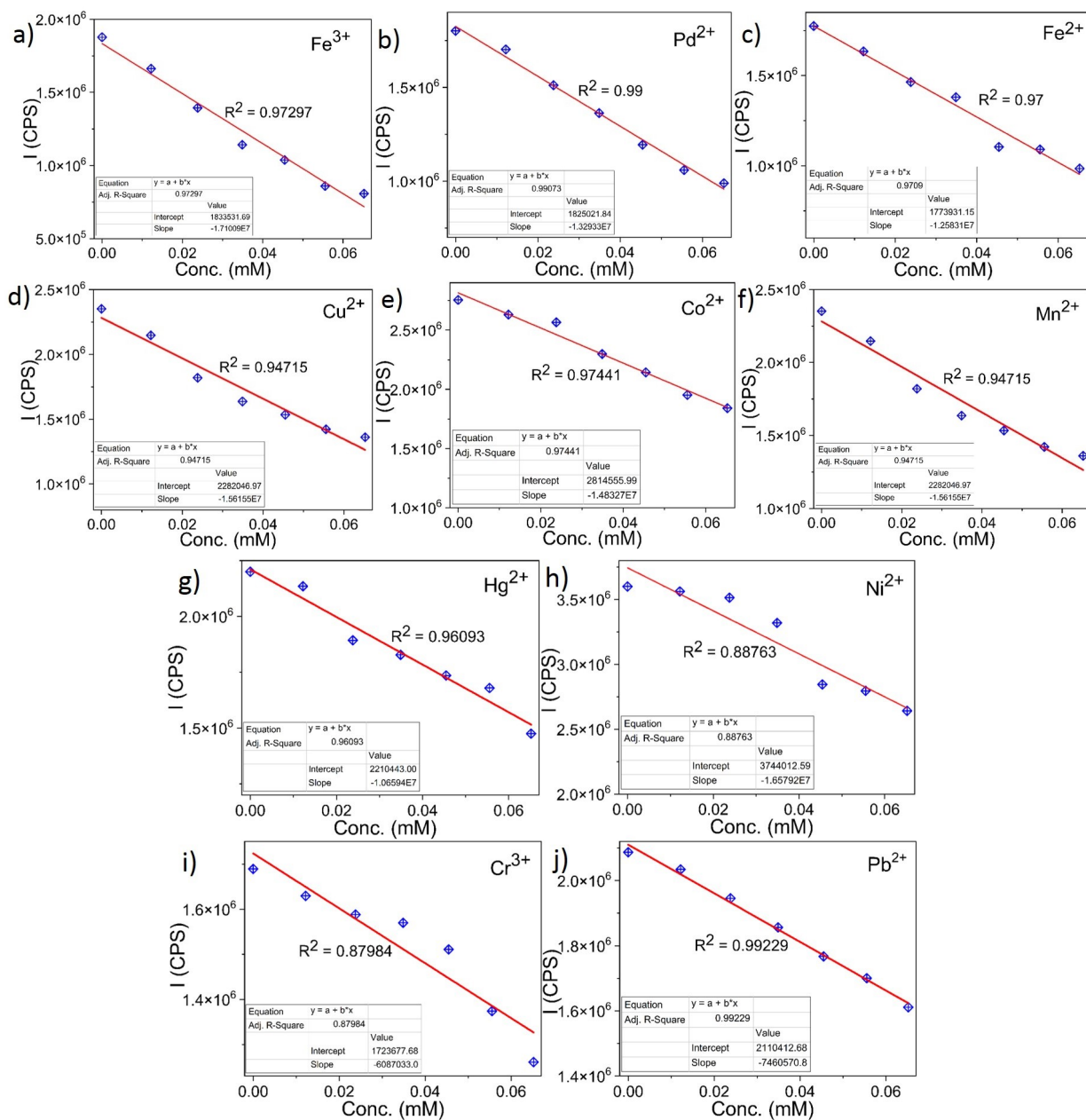


Figure S24. C vs I plots of **ZnGel** in DMF ($\lambda_{\text{ex}} = 275 \text{ nm}$) with a) Fe^{3+} , b) Pd^{2+} , c) Fe^{2+} , d) Cu^{2+} , e) Co^{2+} , f) Mn^{2+} , g) Hg^{2+} , h) Ni^{2+} , i) Cr^{3+} and j) Pb^{2+} respectively.

Doping/ Uptake-study of NDs, NACs and metal ions into the gel: Naked-eye sensing in gel-to-gel states

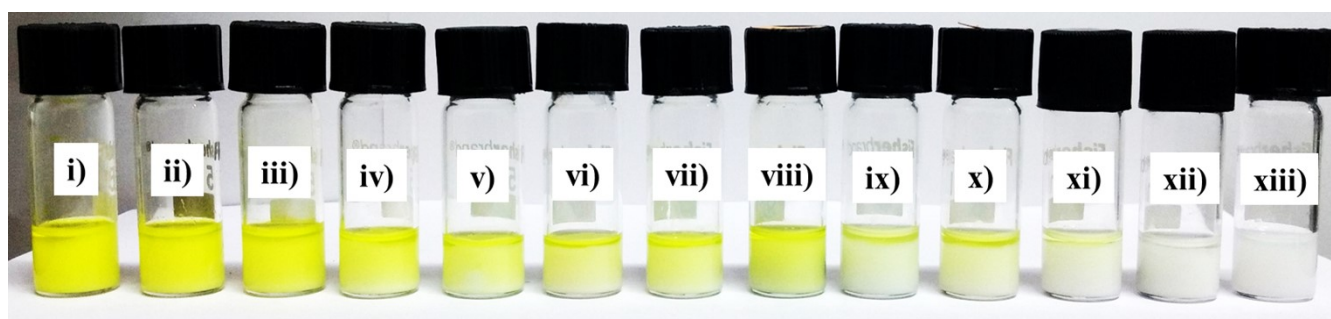
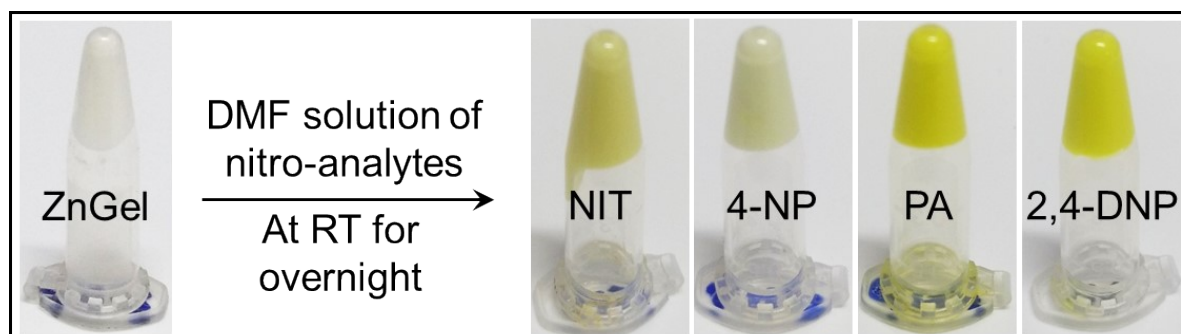


Figure S25. **Top Panel** shows the visual changes in **ZnGel** respectively upon nitro-analyte uptake. **Bottom Panel:** Naked-eye response of the metallogel when incubated with ethanolic solution of picric acid having varying concentrations [i) 5×10^{-2} M, ii) 2.5×10^{-2} M, iii) 1.0×10^{-2} M, iv) 5×10^{-3} M, v) 2.5×10^{-3} M, vi) 1.0×10^{-3} M, vii) 5×10^{-4} M, viii) 2.5×10^{-4} M, ix) 1.0×10^{-4} M, x) 5×10^{-5} M, xi) 1.0×10^{-5} M, xii) 1.0×10^{-6} M and xiii) 1.0×10^{-7} M respectively]. Naked-eye detection is possible only up to 10 μ M solution.

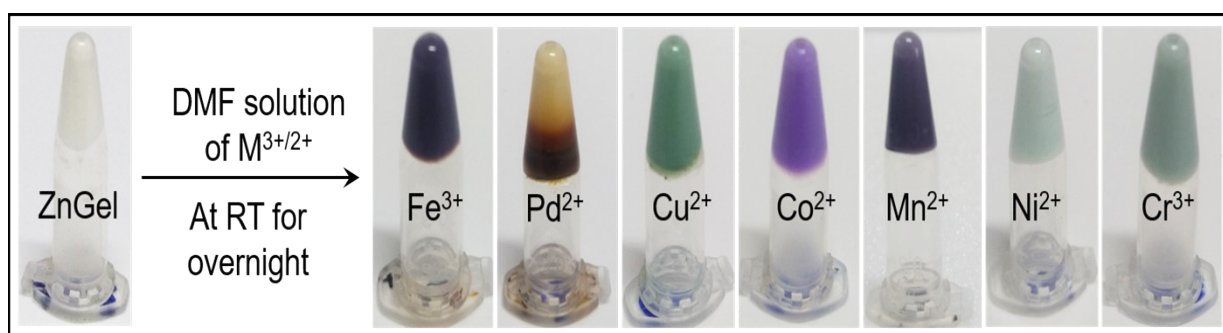


Figure S26. Shows the visual changes in **ZnGel** respectively upon metal uptake.

Spectral overlap between the emission spectrum of ZnGel with the absorption spectra of different NACs

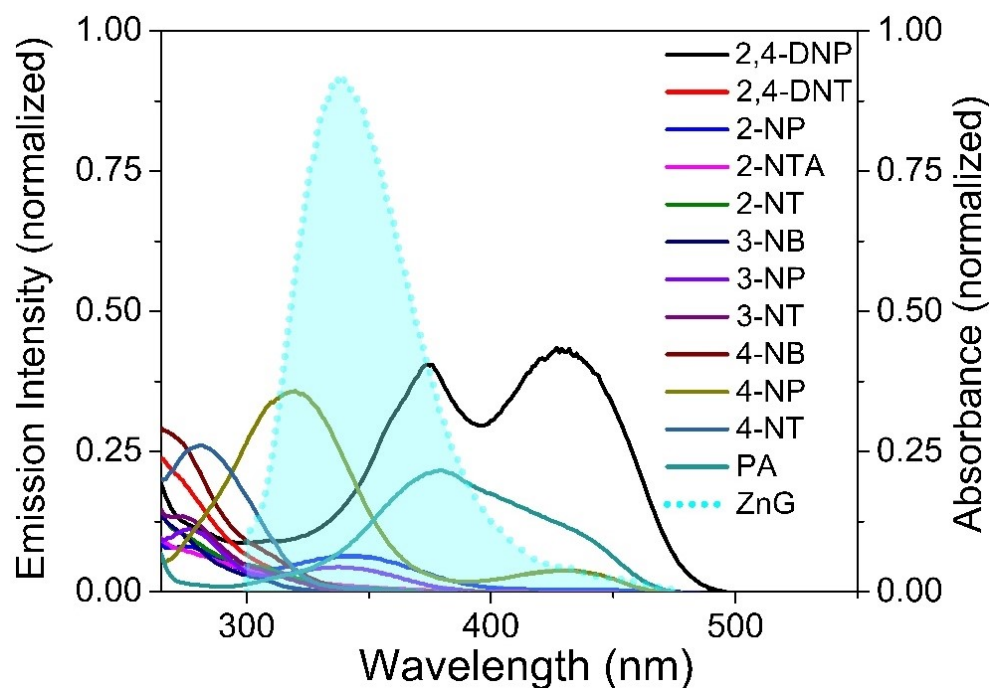
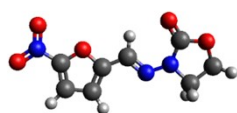
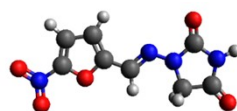


Figure S27. Spectral overlap between the emission spectrum of **ZnGel** (here ZnG) with the absorption spectra of respective NACs.

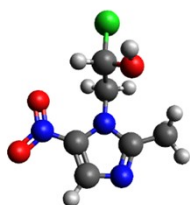
DFT optimized structures of the nitro analytes



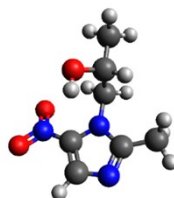
Furazolidone



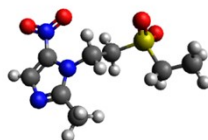
Nitrofurantoin



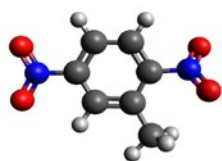
Ornidazole



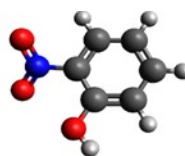
Secnidazole



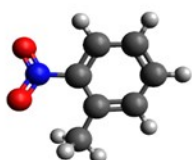
Tinidazole



2,4-dinitrotoluene



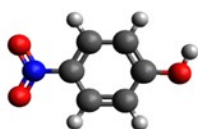
2-nitrophenol



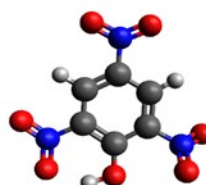
2-nitrotoluene



3-nitrotoluene



4-nitrophenol



picric acid

Figure S28. DFT-optimized structures of the antibiotics and nitro aromatics.

Frontier orbital energy levels from DFT

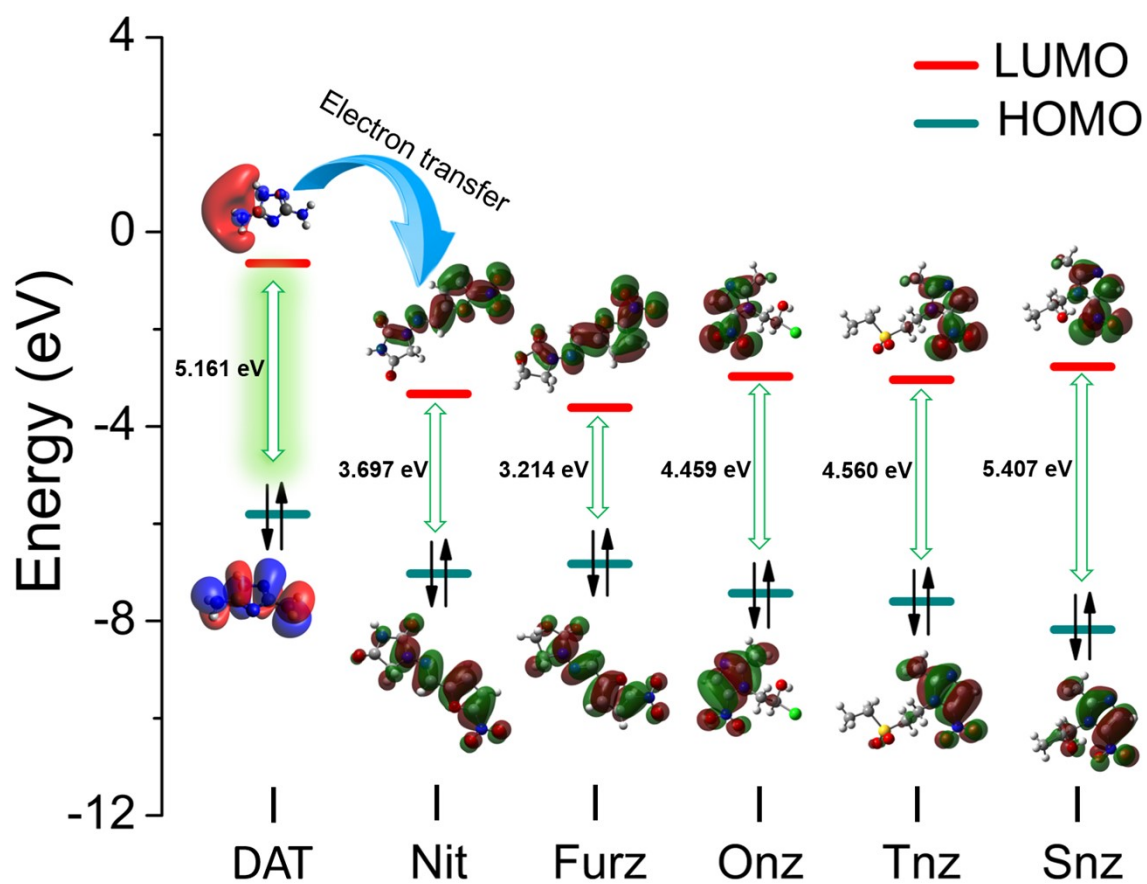


Figure S29. HOMO-LUMO energy (eV) plot for the antibiotics.

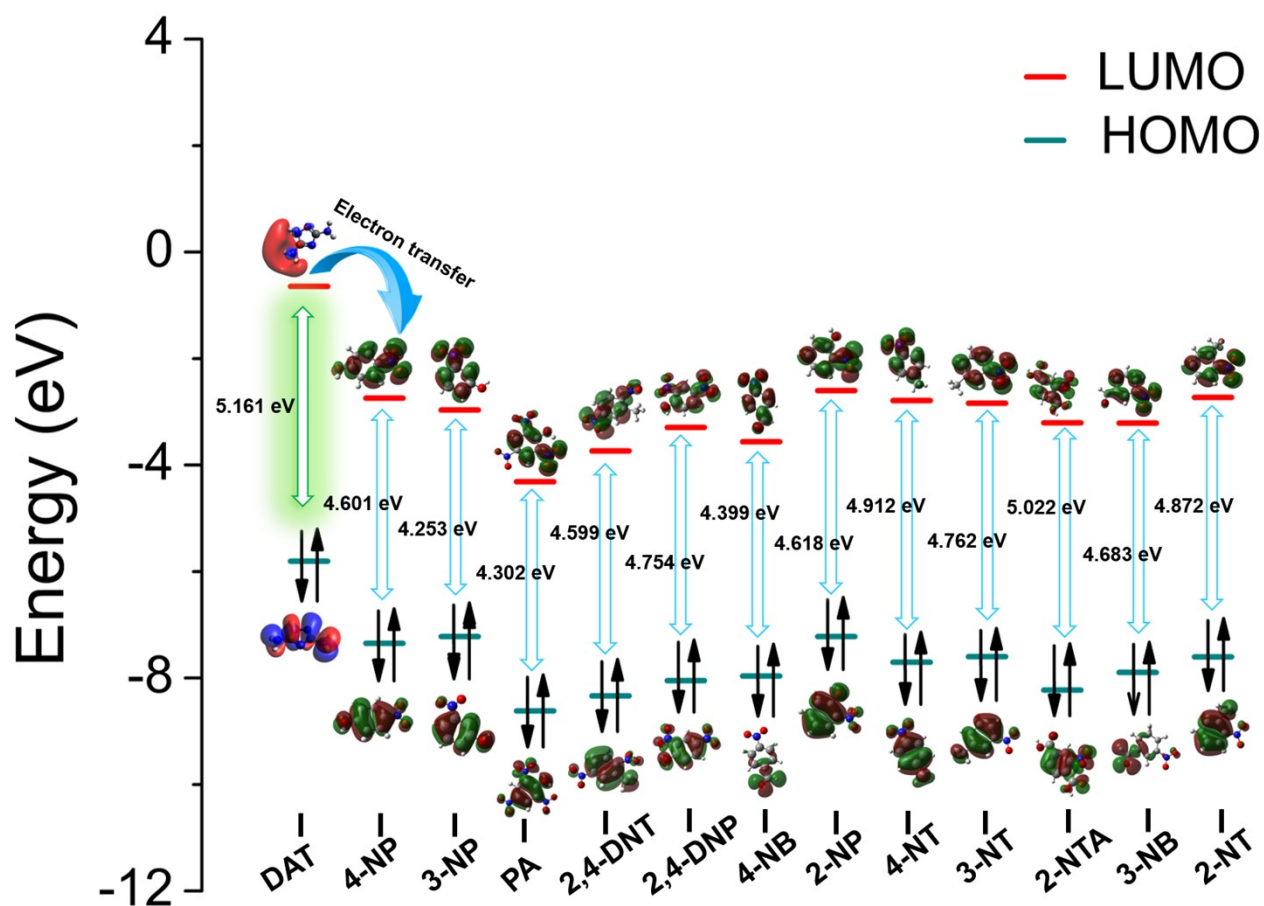


Figure S30. HOMO-LUMO energy (eV) plot for the nitroaromatics.

Anti-interference experiments

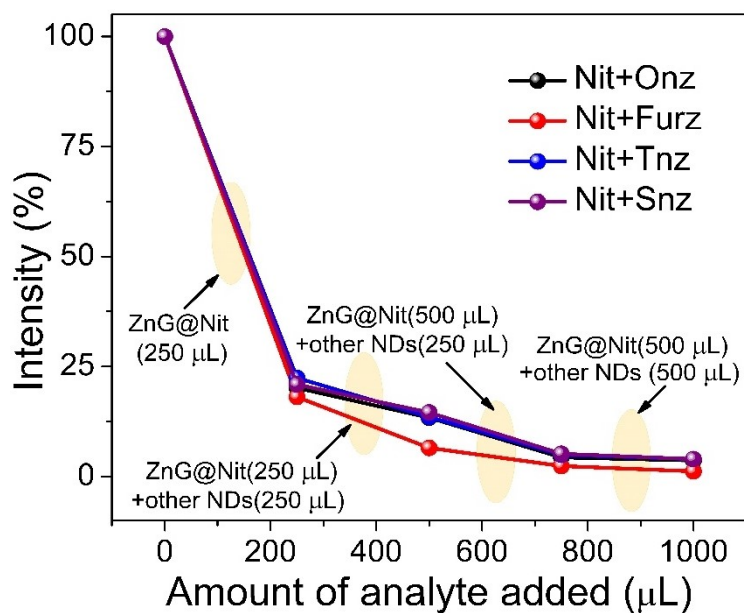


Figure S31. Quenching of the PL efficiency of **ZnGel** (here ZnG) by Nit, in presence of other competing nitro antibiotics.

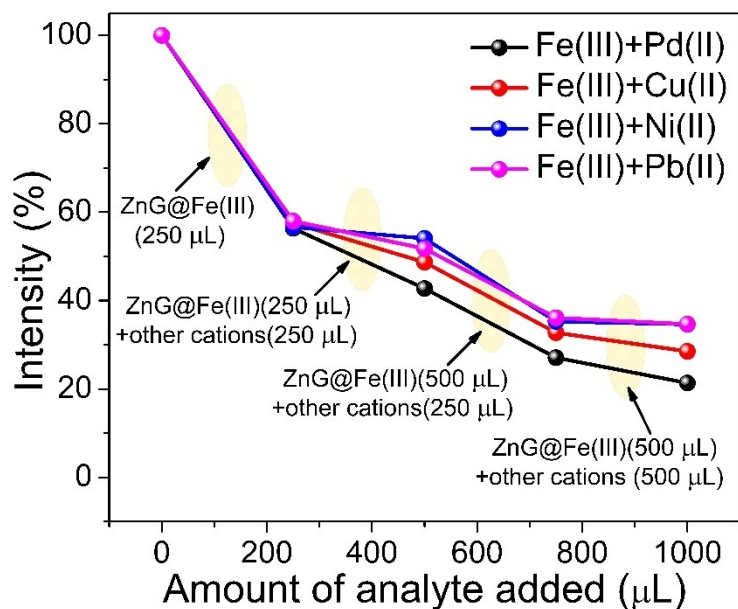


Figure S32. Quenching of the PL efficiency of **ZnGel** (here ZnG) by Fe(III), in presence of other competing metal ions.

Rapid detection of analytes

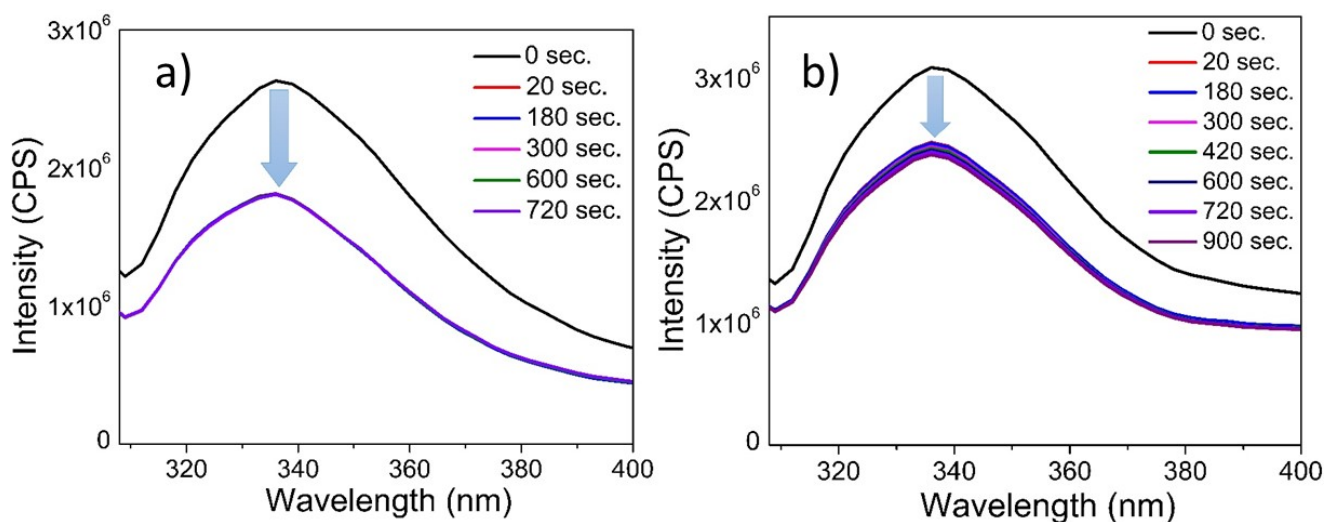


Figure S33. Rapid response of **ZnGel** within the first 20 seconds, in the detection of a) nitrofurantoin and b) furazolidone.

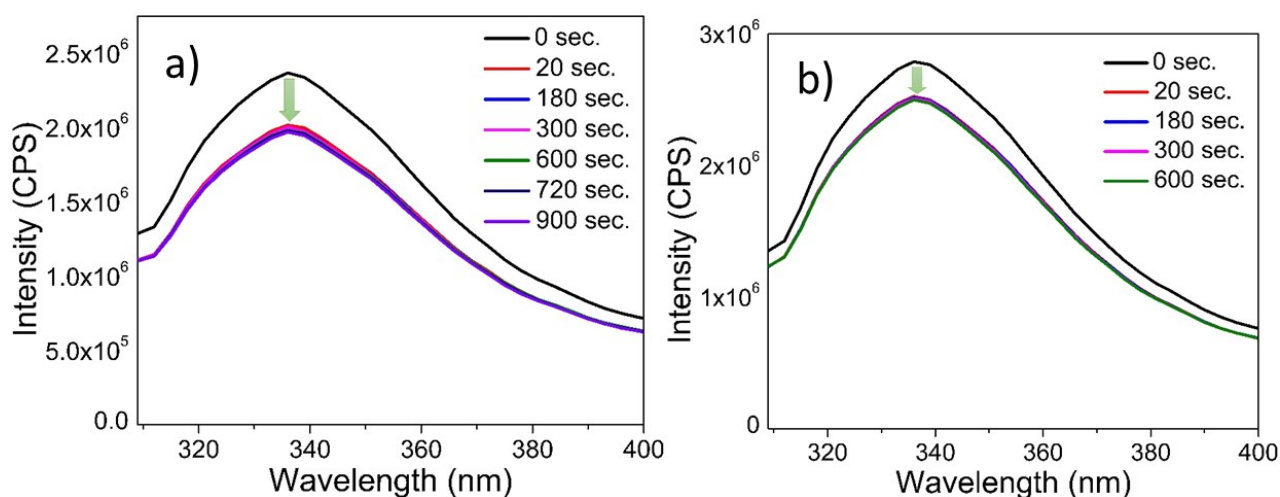


Figure S34. Rapid response of **ZnGel** within the first 20 seconds, in the detection of metal salts a) Fe³⁺ and b) Pd²⁺.

Calculation for the Limit of Detection for respective analytes using ZnGel as the probe

Table S1. Calculation of standard deviation of fluorescence intensity and limit of detection for **ZnGel** towards nitrofurantoin.

Blank Readings (ZnGel)	Fluorescence Intensity (CPS)
Reading 1	1870240.76
Reading 2	1965361.88
Reading 3	1912174.20
Reading 4	2269097.03
Reading 5	2018221.20
Standard Deviation (σ)	156723.899
Slope from Curve (K)	$2.4181 \times 10^7 \text{ mM}^{-1}$
Detection Limit ($3\sigma/K$)	0.0194 mM
Limit of Detection (LOD)	4.62 ppm

Table S2. Calculation of standard deviation of fluorescence intensity and limit of detection for **ZnGel** towards furazolidone.

Blank Readings (ZnGel)	Fluorescence Intensity (CPS)
Reading 1	1870240.76
Reading 2	1965361.88
Reading 3	1912174.20
Reading 4	2269097.03
Reading 5	2018221.20
Standard Deviation (σ)	156723.899
Slope from Curve (K)	$2.34902 \times 10^7 \text{ mM}^{-1}$
Detection Limit ($3\sigma/K$)	0.02 mM
Limit of Detection (LOD)	4.50 ppm

Table S3. Calculation of standard deviation of fluorescence intensity and limit of detection for **ZnGel** towards Fe^{3+} .

Blank Readings (ZnGel)	Fluorescence Intensity (CPS)
Reading 1	1686257.90
Reading 2	1776526.68
Reading 3	1879131.23
Reading 4	2084091.26
Reading 5	1801332.14
Standard Deviation (σ)	150102.47
Slope from Curve (K)	$1.71009 \times 10^7 \text{ mM}^{-1}$
Detection Limit ($3\sigma/K$)	0.0263 mM
Limit of Detection (LOD)	6.13 ppm

Table S4. Calculation of standard deviation of fluorescence intensity and limit of detection for **ZnGel** towards 4-NP.

Blank Readings (ZnGel)	Fluorescence Intensity (CPS)
Reading 1	1686257.90
Reading 2	1776526.68
Reading 3	1879131.23
Reading 4	2084091.26
Reading 5	1801332.14
Standard Deviation (σ)	150102.47
Slope from Curve (K)	$1.49625 \times 10^7 \text{ mM}^{-1}$
Detection Limit ($3\sigma/K$)	0.0301 mM
Limit of Detection (LOD)	4.18 ppm

Table S5. Comparative Study with reported sensor materials for Nitrofurantoin

Sl. No.	Name of the analytes	Sensor (probe) material used	Limit of Detection (LOD)	References
1.	Nitrofurantoin	Zn(II)-based metallogel	4.62 ppm (0.0194 mM)	<i>This work</i>
2.	Nitrofurantoin	Copper nanoclusters	0.73 μM	6
3.	Nitrofurantoin	Luminescent drug-based carbon nanodots	1.4 μM	7
4.	Nitrofurantoin	Zn(II)-Coordination Polymer	-	8
5.	Nitrofurantoin	bismuth titanate enclosed carbon nanofiber	0.005 μM	9
6.	Nitrofurantoin	Amide based low-molecular weight gelator (LMWG)	150 nM	10

Table S6. Comparative Study with reported sensor materials for Furazolidone

Sl. No.	Name of the analytes	Sensor (probe) material used	Limit of Detection (LOD)	References
1.	Furazolidone	Zn(II)-based metallogel	4.50 ppm (0.02 mM)	<i>This work</i>
2.	Furazolidone	<i>Pyoverdine</i>	0.5 mM	11
3.	Furazolidone	Carbon dots	0.096 μM	12
4.	Furazolidone	silica nanoparticles (type 1, FMSN-1)	$4.46 \times 10^{-6} \text{ M}$	13
5.	Furazolidone	glutathione-templated copper nanoclusters	0.012 μM	14
6.	Furazolidone	Pyoverdine	0.5 μM	15

Table S7. Comparative Study with reported sensor materials for Fe³⁺ ion

Sl. No.	Name of the analytes	Sensor (probe) material used	Limit of Detection (LOD)	References
1.	Fe ³⁺	Zn(II)-based metallogel	6.13 ppm (0.0263 mM)	<i>This work</i>
2.	Fe ³⁺	[Zn ₃ (bpg) _{1.5} (azdc) ₃]·(DMF) _{5.9} ·(H ₂ O) _{1.05}	1.71 ppm (1.29 μM)	16
3.	Fe ³⁺	[Cd(L1)(oba)]·DMF	103 ppb	17
4.	Fe ³⁺	[Zn ₂ (L1) ₂ (HBPT) ₂]·H ₂ O	72 ppb	17
5.	Fe ³⁺	[Zr ₆ O ₄ (OH) ₄ (C ₈ H ₂ O ₄ S ₂) ₆]·DMF·18H ₂ O	1.26 × 10 ⁻⁶ M	18
6.	Fe ³⁺	Cd(PAM)(4-bpdb)1.5]·DMF	0.3 μM	19
7.	Fe ³⁺	Zn ₂ (TPOM)(NDC) ₂]·3.5H ₂ O	2 μM	20
8.	Fe ³⁺	[Zn ₅ (hfipbb) ₄ (trz) ₂ (H ₂ O) ₂]	~0.20 mmol·L ⁻¹	21
9.	Fe ³⁺	Zn-based coordination compound [Zn(OOCC ₆ F ₅)(H ₂ O)(C ₁₂ H ₈ N ₂) ₂] (OOCC ₆ F ₅)	0.240 μM	22
10.	Fe ³⁺	Carbon dots and quantum dots-based nanohybrid	0.26 μM	23
10.	Fe ³⁺	imidazole-based chemosensor	0.27 μM	24
12.	Fe ³⁺	Rhodamine based chemosensor	9.2 × 10 ⁻⁸ M (5.5 μg/L)	25
13.	Fe ³⁺	4-(diethylamino)-2-(hydroxy)-phenyl imine functionalized naphthalimide	3.95 × 10 ⁻⁸ M	26
14.	Fe ³⁺	Fe ₃ O ₄ @ZnO	3 nmol L ⁻¹	27
15.	Fe ³⁺	Au nanoclusters functionalized with 3,4-Dihydroxyphenylalanine	3.5 μM	28
16.	Fe ³⁺	Au nanorods	1.79 μM	29
17.	Fe ³⁺	Anionic Zn-MOF based on H ₆ TDPAT (2,4,6-tris(3,5-dicarboxylphenylamino)-1,3,5-triazine)	0.0233 mM	30
18.	Fe ³⁺	bi-component supramolecular polymer hydrogel based on tripodal gelators	5.33 × 10 ⁻⁹ M and 1.61 × 10 ⁻⁸ M	31
19.	Fe ³⁺	pillar[5]arene-based supramolecular organic framework gel	0.102 nM	32

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