Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Synthesis of a Chemically-Reactive and Polymeric Luminescent Gel

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Experimental Section

Materials

Branched poly(ethyleneimine) (BPEI, MW~ 25,000 Da), dipentaerythritol penta-acrylate (5 Acl, MW 524.21 g/mol), and sulphanilamide were procured from Sigma Aldrich, Bangalore, India. Ethyl alcohol was purchased from Tedia Company (United States of America). Glacial acetic acid, sodium nitrite, sodium nitrate, sodium chloride, sodium bromide, sodium sulphate, sodium carbonate, sodium phosphate, sodium hydroxide and hydrochloric acid were procured from Merck Specialities Pvt. Ltd, Mumbai, India. Aniline was purchased from Fisher Scientific.

General Considerations

All glasswares used throughout the experiment were thoroughly cleaned using water and subsequently with acetone prior to use. A Tarsons Spinwin microcentrifuge (Model No. MC03) was used for purification of carbon dots. UV-Visible spectroscopy was carried out in a Perkin Elmer Lambda 25 UV/Vis spectrophotometer and a Thermo Scientific Multiskan GO instrument. Solid state fluorescence spectra were recorded on a Horiba Scientific, Fluoromax-4 Spectrophotometer. Fluorescence intensity analysis was quantified using ImageJ software. Time-resolved fluorescence measurements were carried out in Edinbugrh Instruments Life Spec II instrument. UV lamp images were captured using a Relitech UV lamp (365 nm). Fourier transform infrared (FTIR) spectra of all samples were recorded in a Perkin Elmer instrument in attenuated total reflectance (ATR) mode. Dynamic Light Scattering (DLS) measurements were performed on a

Zetasizer Nano ZS90 (model no ZEN3690) instrument. Transmission Electron Microscopy (TEM) was carried out using a JEOL, JEM 2100 instrument. The surface morphologies of the gel samples were investigated using a Sigma Carl Zeiss Field Emission Scanning Electron Microscope (FESEM). A thin layer of conductive gold coating was deposited on the non-conductive samples prior to perform FESEM imaging. All digital images were captured on a Canon Power Shot SX420 IS digital camera. Mili-Q grade water was used for all experiments. During the demonstration of chemical sensing, the respective error bar was obtained by repeating four sets of the same experiment carried out under exactly identical conditions, where four different sets of samples were used.

Methods

Synthesis of Carbon Dots from branched Poly(ethyleneimine)

Carbon dots were synthesized using hydrothermal method, where branched poly(ethyleneimine) (BPEI) was used as the carbon source. Firstly, an aqueous solution of BPEI was prepared by dissolving 6.75 g of BPEI in 40 mL of Mili-Q water. The aqueous solution of BPEI was then transferred into a Teflon-lined stainless steel autoclave of 50 mL capacity and heated at 160^{o}C for 3 hours. After that, the reaction solution was collected from the autoclave in the form of a sticky yellow product, which was dispersed in ethanol. The ethanolic solution was then centrifuged at 10000 rpm for 10 minutes using a microcentrifuge and the supernatant, that is the carbon dot (BPEI-CDs) solution, was collected and characterized further.

Preparation of Chemically Reactive and Fluorescent Gel (CRFG) and its Post Chemical Functionalization

A chemically reactive fluorescent gel (CRFG) was prepared via a facile 1,4-conjugate addition reaction between the amine functional groups of BPEI-CDs and the acrylate functional groups of 5 Acl. Briefly, the two separate solutions of BPEI-CDs and 5 Acl were prepared in two glass vials by dissolving 0.5 g of BPEI-CDs and 1.325 g of 5 Acl each in 10 mL of ethanol. Next, these solutions of BPEI-CDs and 5 Acl were mixed in 1:1 ratio and allowed to stand undisturbed for 1.5 hours at ambient conditions until all the liquid content in the vial have transformed into CRFG. Subsequently, the CRFG material was rinsed with ethanol for 1 hour to remove traces of all unreacted reagents. After thorough rinsing, the gel material was chemically functionalized with aniline through 1,4-conjugate addition reaction between the amino group of aniline and residual acrylate functional groups of CRFG at ambient conditions. The aniline modified fluorescent gels (AMFG) were further rinsed with ethanol for 1 hour to remove all unreacted aniline. Subsequently, the AMFG were removed from ethanol and transferred to Mili-Q water for about an hour in order to facilitate complete solvent exchange to perform the sensing study at completely aqueous condition. It was observed that upon complete solvent exchange, the gel turned from translucent to milky white. The AMFG materials were further rinsed with water for at least 10 times and finally stored under water, prior to demonstration of parallel 'ON'/ 'OFF' sensing.

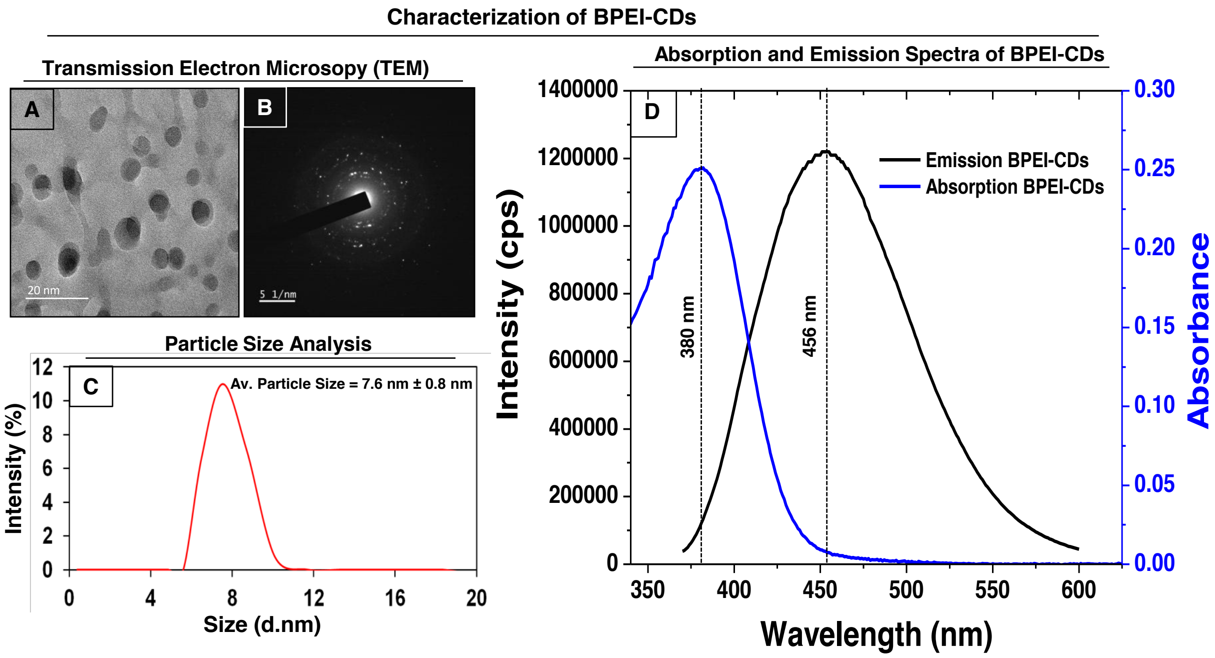

Figure S1. (A) TEM image and (B) the corresponding SAED pattern of BPEI-CDs. (C) DLS analysis of BPEI-CDs. (D) Absorption and emission spectra of BPEI-CDs.

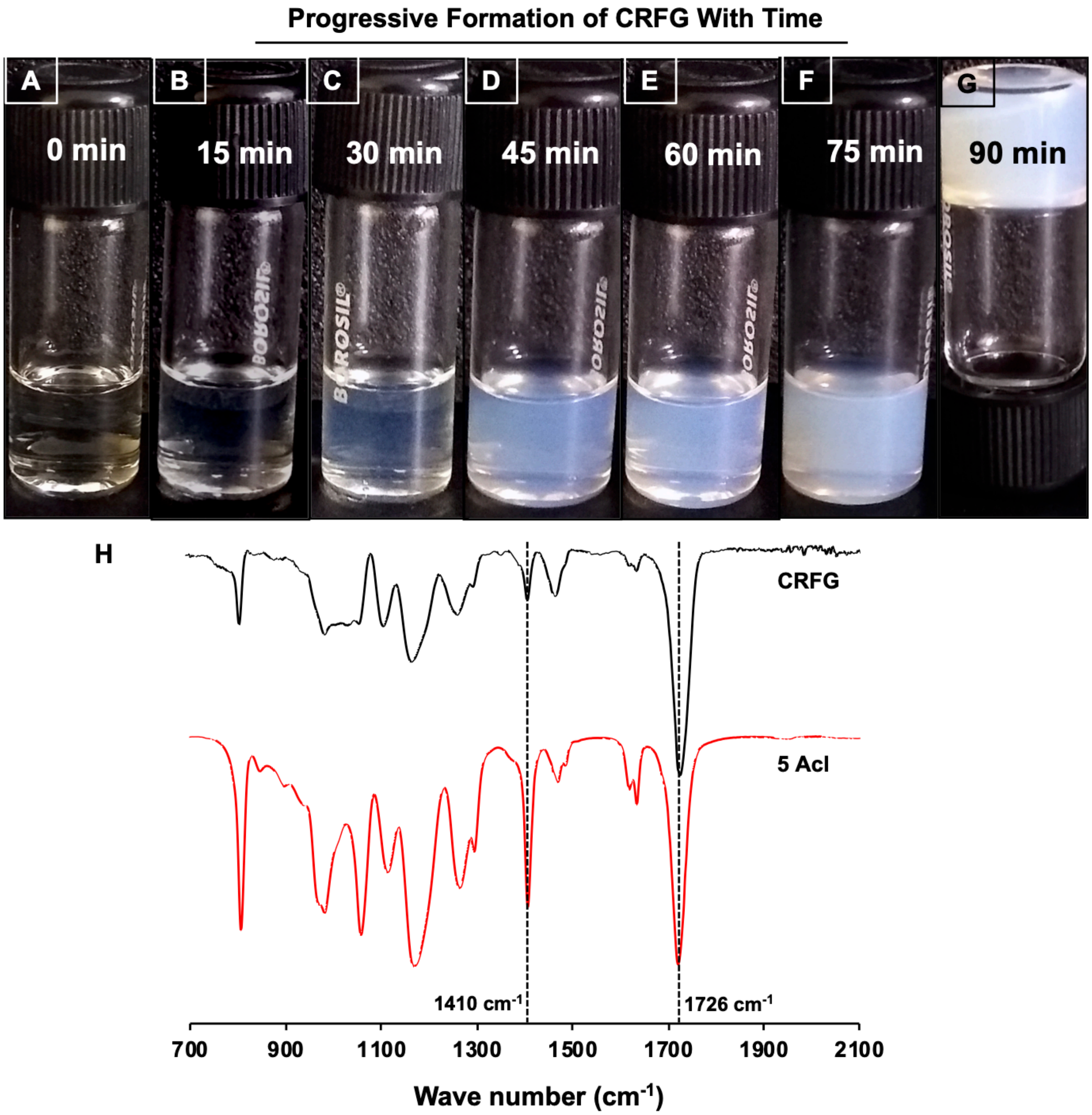

Figure S2. A-G) Digital images illustrating the transformation of a transparent reaction mixture of BPEI-CDs and 5Acl into a chemically reactive fluorescent gel (CRFG) with time. H) ATR-FTIR spectra accounting the crosslinking between BPEI-CDs and 5Acl (red) through 1,4-conjugate addition reaction, which resulted in the formation of covalent crosslinking in CRFG (black). The significant depletion in the IR peak intensity at 1410 cm^{-1} for vinyl group was observed with respect to characteristic carbonyl stretching at 1726 cm^{-1} for acrylate group of 5Acl.

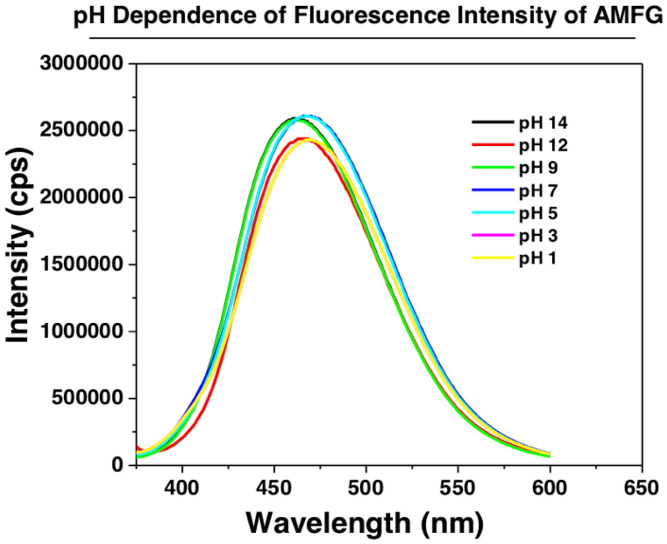

Figure S3. The fluorescence emission spectra accounting the change in fluorescence signal of AMFG at different pH.

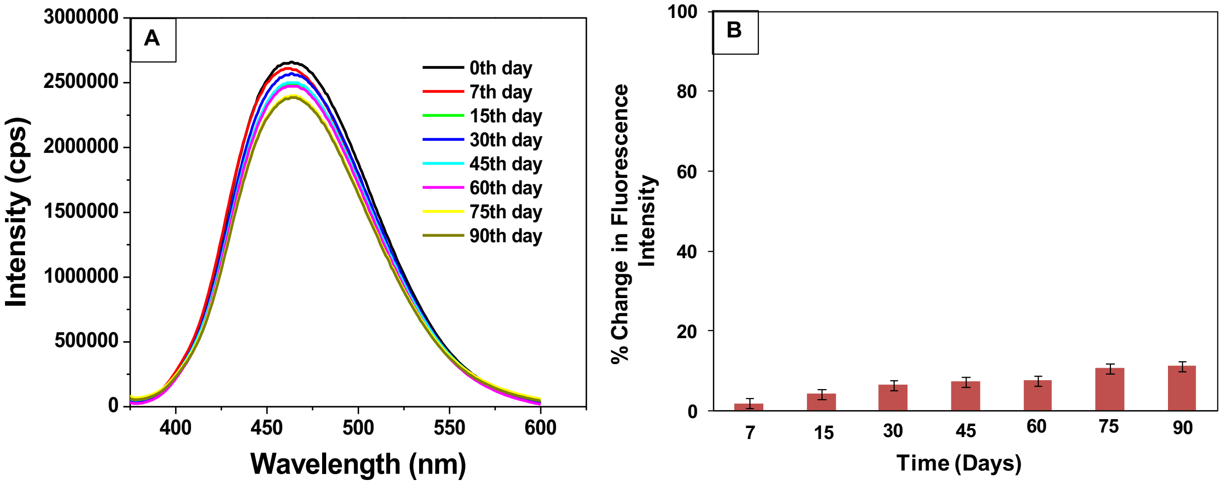

Figure S4: **(**A) Stacked fluorescence emission spectra of synthesized gel over a period of 90 days. (B) Plot of percentage change in fluorescence intensity of polymer gel over a period of 90 days demonstrating the stability of its fluorescence property.

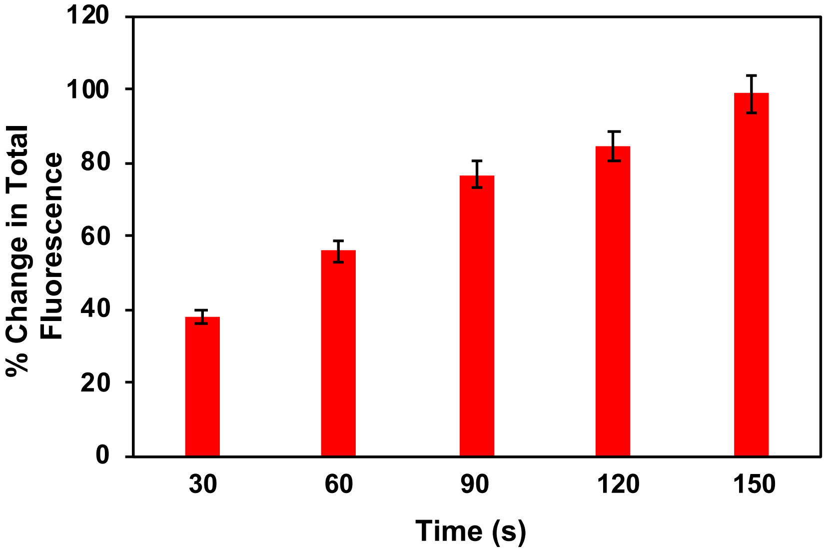

Figure S5: The plot accounting the time-lapse study on the percentage change (due to decrease in fluorescence) in fluorescence during in situ detection of nitrite ions (15 µM) by AMFG.

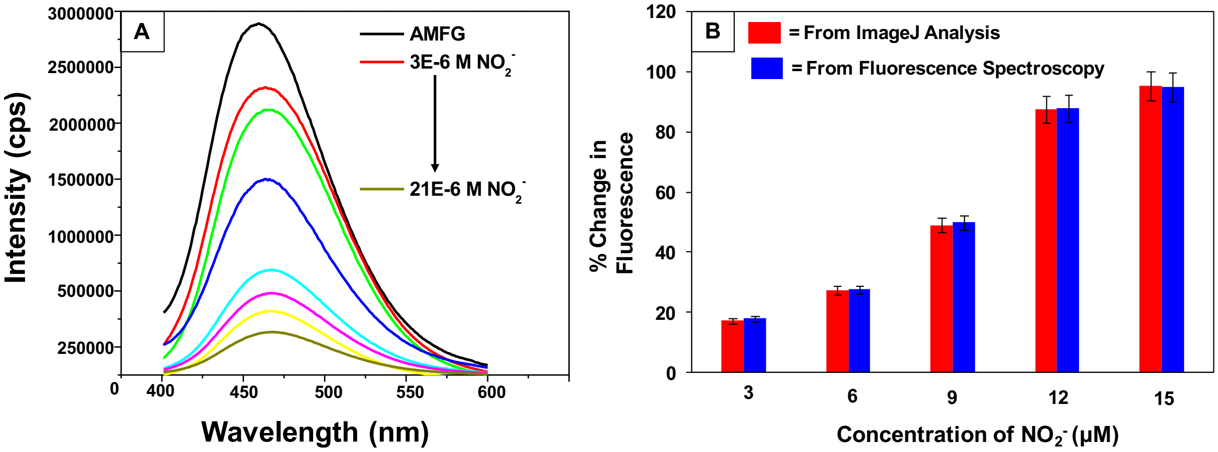

Figure S6. (A) Stacked fluorescence emission spectra of AMFG in presence of different concentrations of NO_2^- ions. (B) The plot accounting the comparative percentage change in fluorescence signals obtained by analyzing both the digital images (using ImageJ software (red bars)) and fluorescence spectra of AMFG after being exposed to different concentrations of NO_2^- ions.

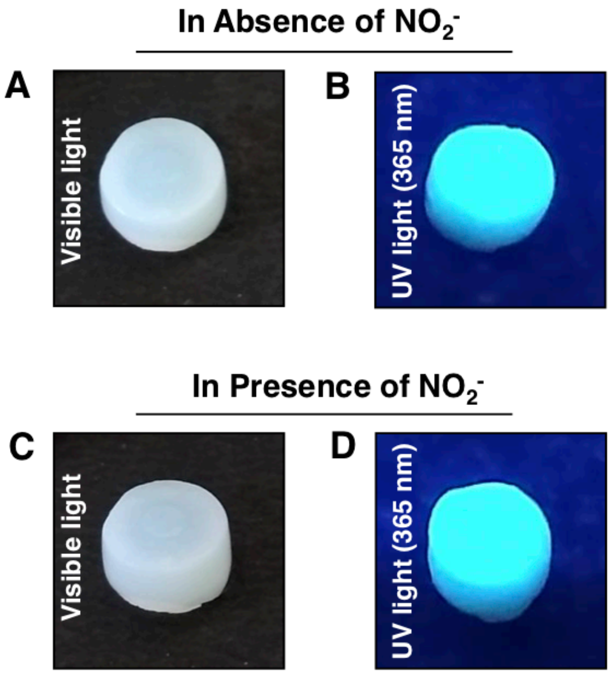

Figure S7. A-D) Digital images of CRFG before (A-B) and after (C-D) exposure to NO_2^- in presence of acidic sulfanilamide, under visible (A,C) and UV (B,D) light.

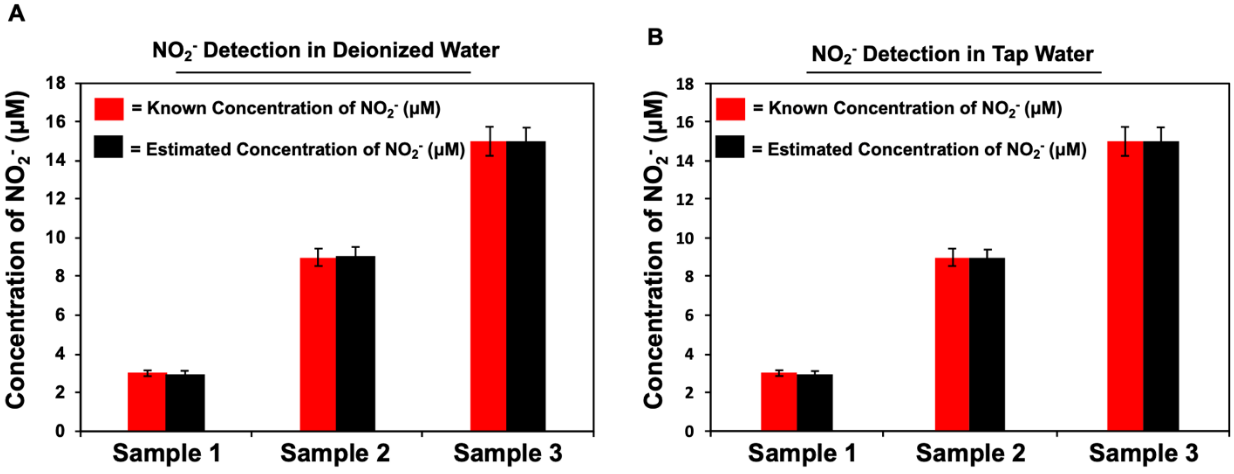

Figure S8. A-B) The graphs accounting the performance of the developed sensor towards estimating the concentration of NO_2^- in both deionized (DI) water (A) and tap water (B) that were contaminated with known amount of NO_2^-. The experimentally determined concentration (black) of NO_2^- matched well with the known concentration (red).

Sample	T_1 (ns)	%	T_2 (ns)	%	T_3 (ns)	%	T_{avg} (ns)
AMFG	1.49202	5.02	3.99325	8	4.79070	86.98	3.4253 ± 0.58
AMFG -NO_2^- (3 μM)	1.45741	5.66	3.95590	8.99	4.777966	85.35	3.3970 ± 0.42
AMFG -NO_2^- (6 μM)	1.43123	5.11	3.93215	8.52	4.75474	86.37	3.37270 ± 0.36
AMFG -NO_2^- (9 μM)	1.42432	5.81	3.92581	8.36	4.75112	85.83	3.36708 ± 0.45

Table S1. Accounting the fluorescence lifetime decay of AMFG before and after exposure to different concentrations of nitrite ions in presence of acidic sulfanilamide.