Electronic supplementary information

A supramolecular hydrogel for generation of a benign DNA-hydrogel

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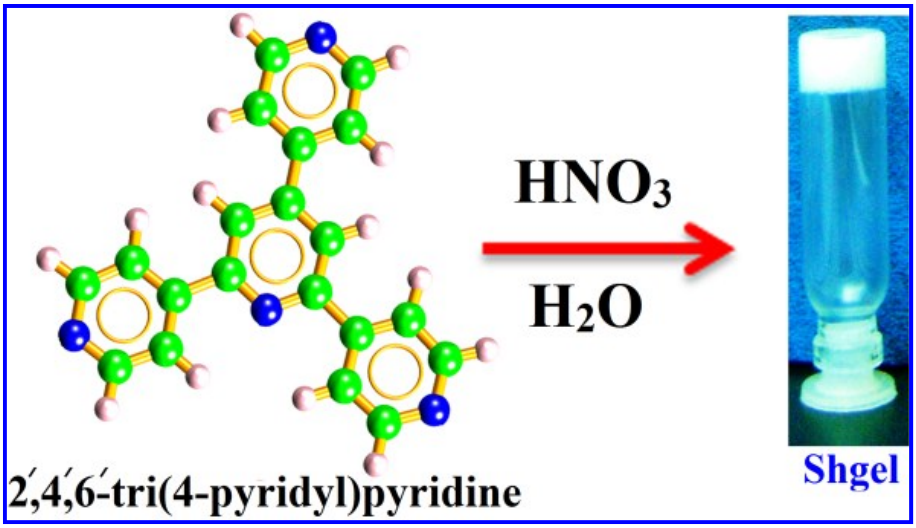
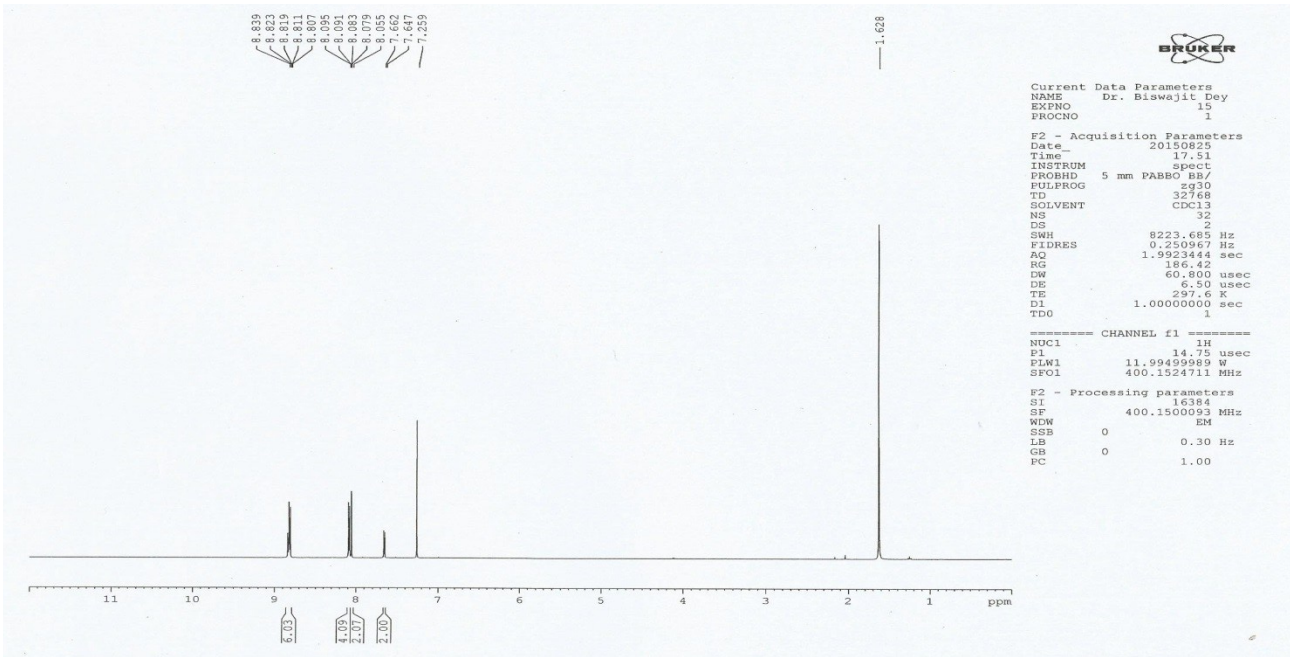
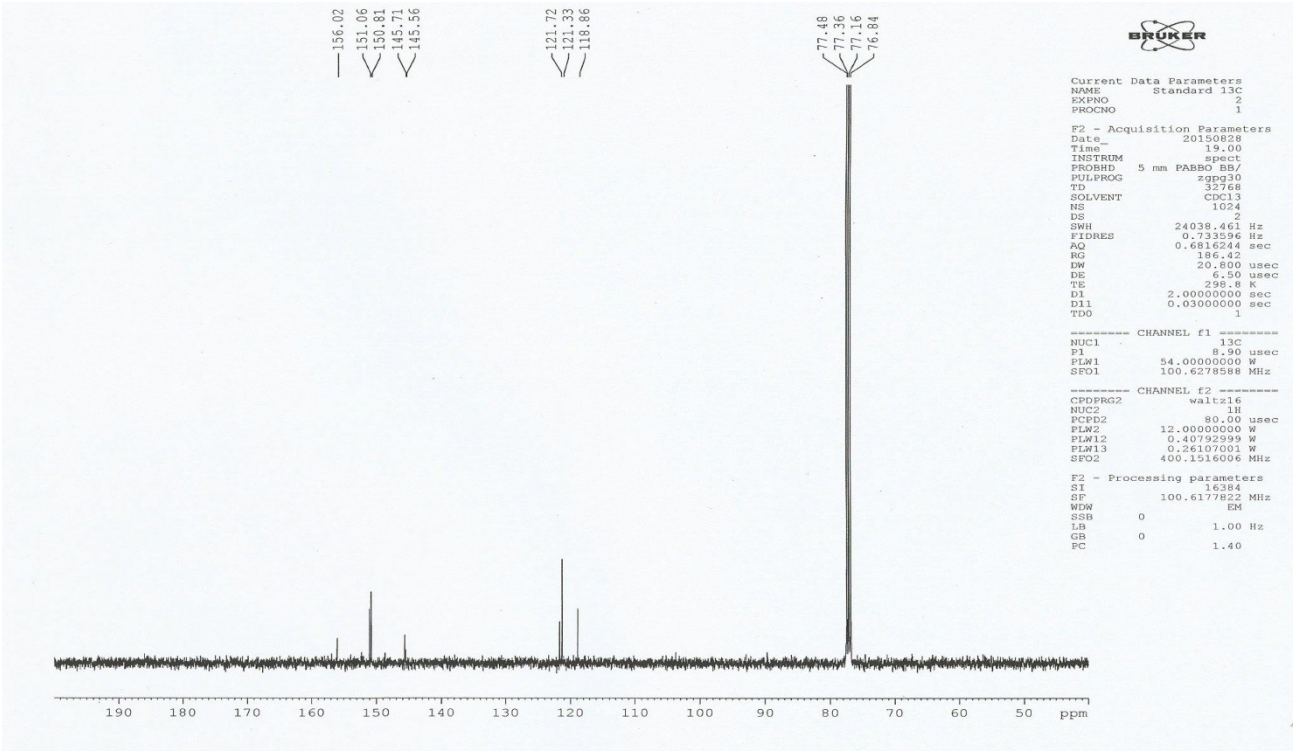


Scheme S1. The synthetic strategy of Shgel synthesis and its photography.

NMR Study:



(a)



(b)

Fig. S1. (a) ^{1}H and (b) ^{13}C NMR spectra of 2′,4′,6′-tri(4-pyridyl)pyridine in $CDCl_3$.

ESI-MS study:

ESI-MS studies (Fig. S2) of pure tetrapyridine ligand (i.e. 2′,4′,6′-tri(4-pyridyl)pyridine) and **Shgel** confirm that protonated tetrapyridinium moieties along with nitrate anions are the basic constructing building block of supramolecular **Shgel** network.

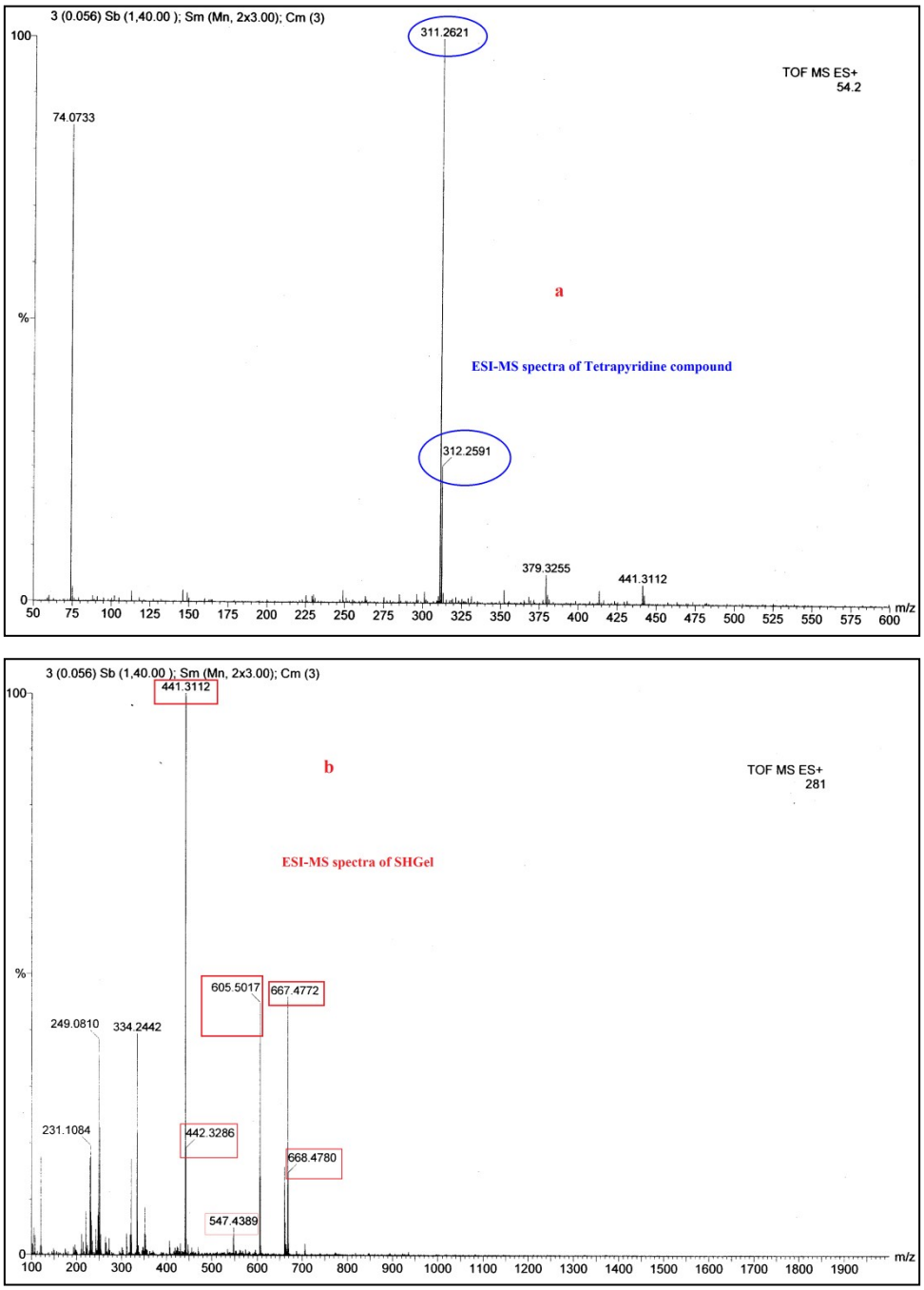


Fig. S2. ESI-MS spectral pattern of tetrapyridine (a) and **Shgel** (b) Here. blue coloured circular marks in (a) shows the presence of 2′,4′,6′-tri(4-pyridyl)pyridine and the red coloured rectangular marks in (b) signify the presence of protonated tetrapyridinium rings along with nitrate anions as the key constituents of **Shgel** network.

Gelation and Thermal study

The critical gelation concentration of the hydrogel was measured to be 2.693 (mg/ml). Gel melting temperature (T_{Gel}) of the hydrogel with the water solution of nitric acid (H_2O:HNO_3 = 1:1 v/v) was obtained from the falling ball method at different concentrations attached by a sophisticated digital water bath.The T_{Gel} vs concentration of hydrogelator plot suggests that the measured T_{Gel} values increase sharply in the low concentration range (Fig S3) and successively attain a near plateau region due to attain the saturation point.Fig S3 clearly shows that T_{Gel} of the **Shgel** is ~ 50˚C. The melting temperature (T_{Gel}) of the **Shgel** also measured by Differential Scanning Calorimetry (DSC) is found to be 45˚C, which is 5 ˚C lower than the gel melting temperature obtained from the falling ball method. The different value of the gel melting points in the two different methods is may be due to adoption of two different measurements. One is heat flow and other is mechanical instability of the ball in the gel matrix with increase of temperature. The measurement by DSC is thermodynamic property and the other method is of kinetic property to break the gel network structure.

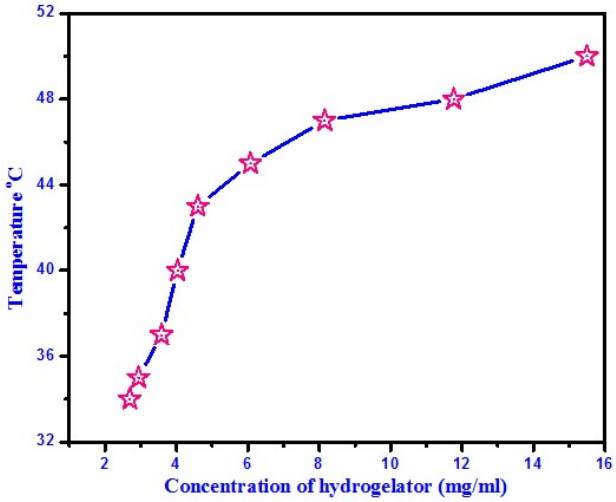


Fig S3. T_{Gel} plot of the **Shgel**.

Dynamic light scattering (DLS) study of Shgel:

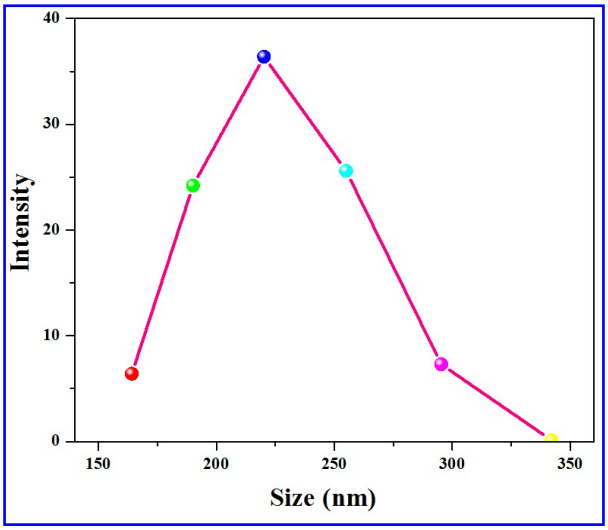
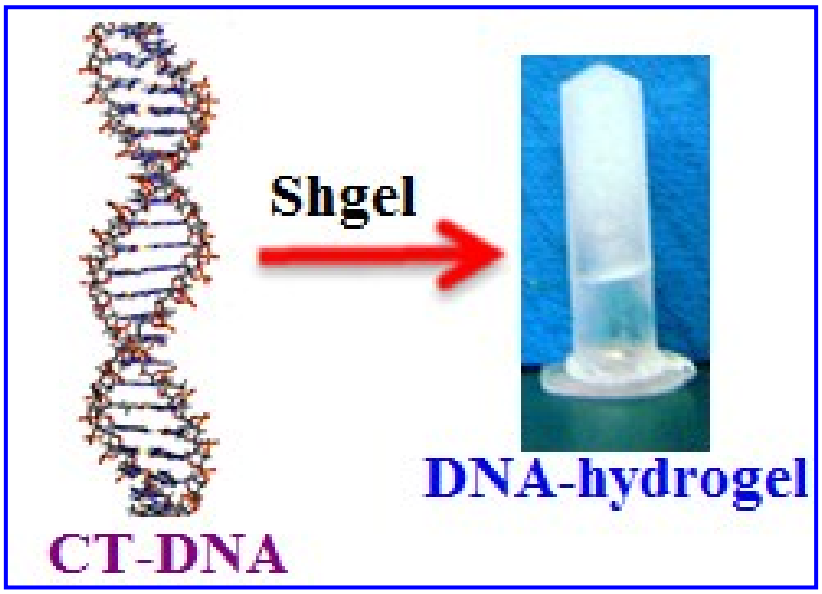
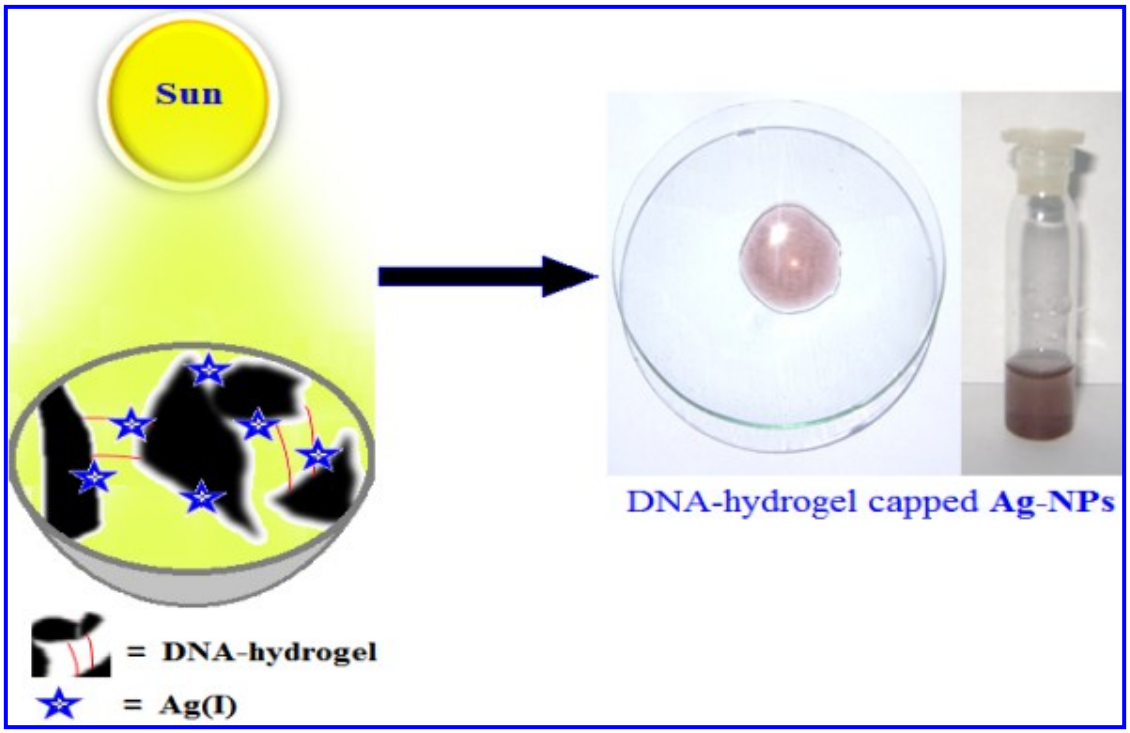


Fig. S4. Size distribution of the aqueous solution of **Shgel** found in DLS study.DLS study shows the average particle size is 220 nm.



Scheme S2. The synthetic strategy of DNA-hydrogel synthesis and its photography.



Scheme S3. Synthesis of DNA-hydrogel capped silver nanoparticles (Ag-NPs) and its photography.

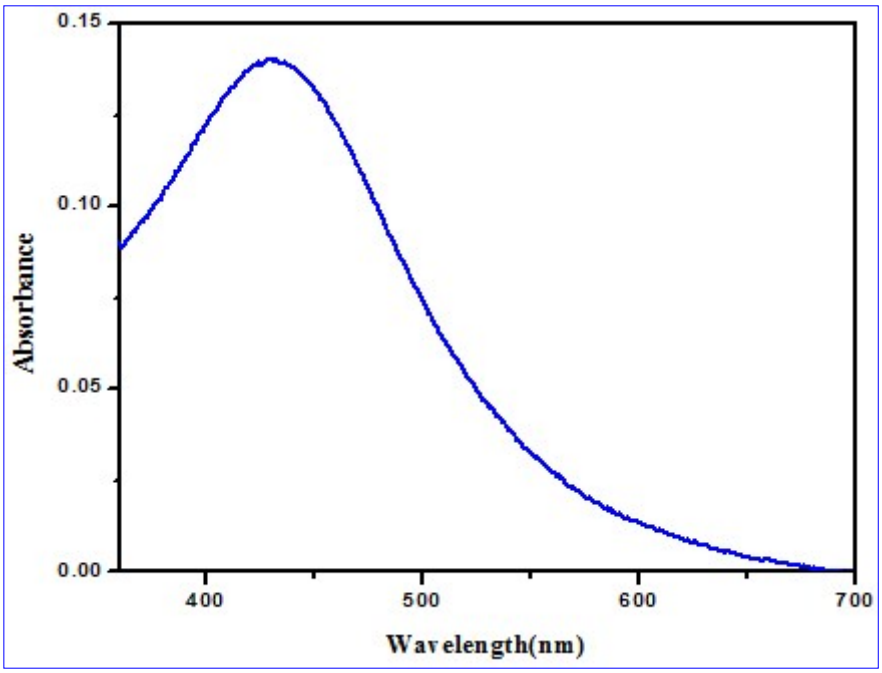


Fig. S5. The control experiment: UV-VIS spectra of the water solution of pure CT-DNA capped photo-chemically synthesized Ag-NPs.

Rheological measurement of Shegl:

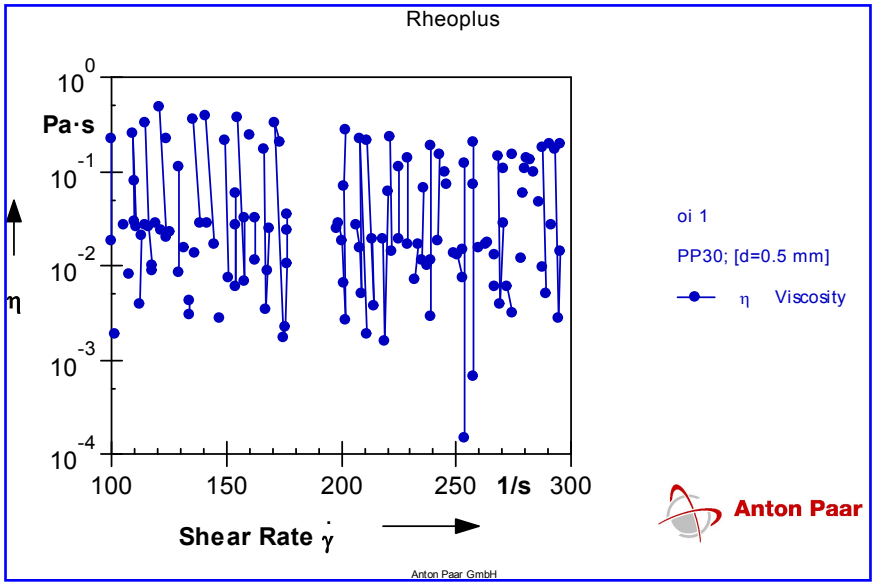


Fig. S6. Viscosity (η) measurement of **Shgel** with a range of shear rate d(gamma)/dt = 100 to 300 1/s at a fixed temperature of 30 °C.

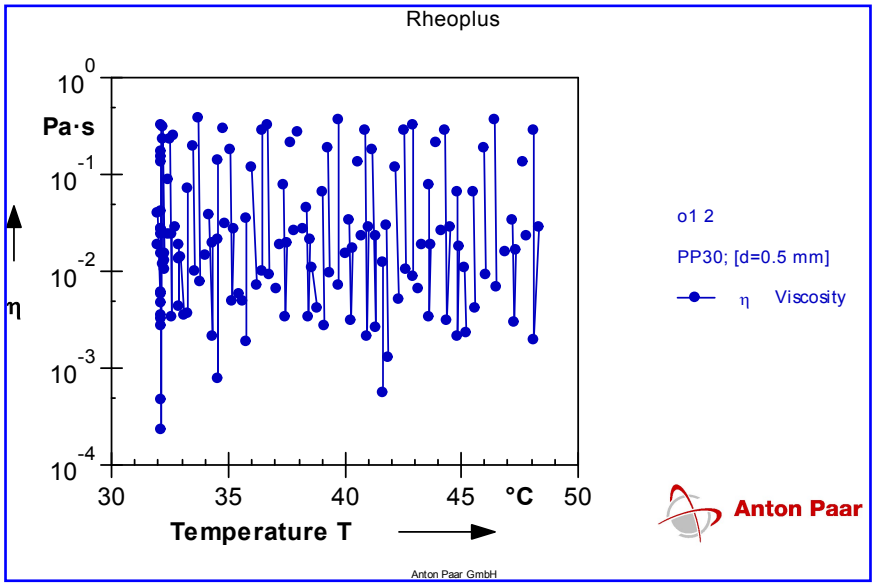


Fig. S7. Viscosity (η) measurement of **Shgel** with a fixed shear rate d(gamma)/dt = 150 1/s in the temperature range of 30 - 50 °C.

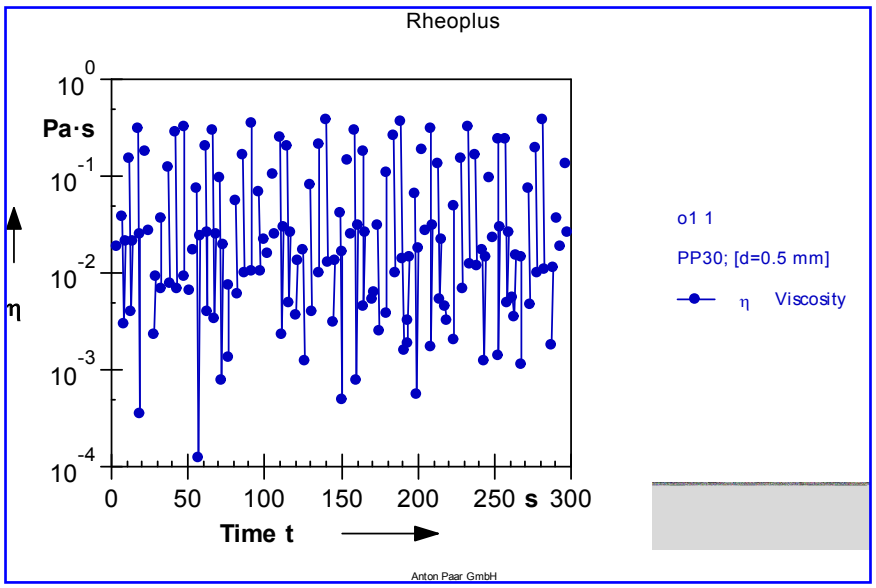


Fig. S8. Viscosity (η) measurement of **Shgel** with a fixed shear rate d(gamma)/dt = 150 1/s at a definite temperature of 30 °C in the duration of 0 - 300 S.

Toxicity studies for Shgel:

Table S1 Hematological and serological parameters in exposed wistar rats for toxicity evaluation.

Parameters	Group I (Cont.)	Group II (Intradermal)	Group III (Intraperitoneal)	Group IV (Gastatory)
W.B.C. (per cmm)	6700 ± 375	6900 ± 286	7100 ± 355	7300 ± 327
Neutrophils (%)	52 ± 13	70 ± 9	67 ± 11	69 ± 8
Lymphocytes (%)	45 ± 11	25 ± 6	30 ± 8	28 ± 9
Basophils (%)	00	00	00	00
Eosinophils (%)	02 ± 1	03 ± 2	02 ± 2	02 ± 1
Monocytes (%)	01 ± 1	02 ± 1	01 ± 1	01 ± 1
Haemoglobin (gm%)	12.0 ± 1.5	10.5 ± 2	11.6 ± 2.4	11.7 ± 1.6
Bilirubin Total (mg%)	0.78 ± 0.11	0.94 ± 0.09	0.85 ± 0.14	1.0 ± 0.09
Bilirubin conjugated (mg%)	0.25 ± 0.06	0.37 ± 0.08	0.26 ± 0.08	0.48 ± 0.04
Bilirubin non-conjugated (mg%)	0.53 ± 0.08	0.57 ± 0.11	0.59 ± 0.06	0.52 ± 0.09
Total Protein (gm%)	7.5 ± 1.1	7.0 ± 0.7	7.8 ± 0.9	7.2 ± 1.2
Albumin (gm%)	4.3 ± 0.6	4.0 ± 0.6	4.5 ± 0.4	4.0 ± 0.7
Globulin (gm%)	3.2 ± 0.7	3.0 ± 0.5	3.3 ± 0.8	3.2 ± 0.3
S.G.P.T. (I.U./L)	37 ± 12	28 ± 7	40 ± 11	39 ± 4
S.G.O.T. (I.U./L)	32 ± 11	20 ± 9	35 ± 11	31 ± 14
Alk. Phosphate (I.U./L)	92 ± 17	105 ± 9	85 ± 12	102 ± 18

Hematological and serological markers in the different rat groups exposed with hydrogel through different routes. (For the corresponding permissible ranges of these parameters please consult literature values.[1]

SEM analysis of DNA-hydrogel:

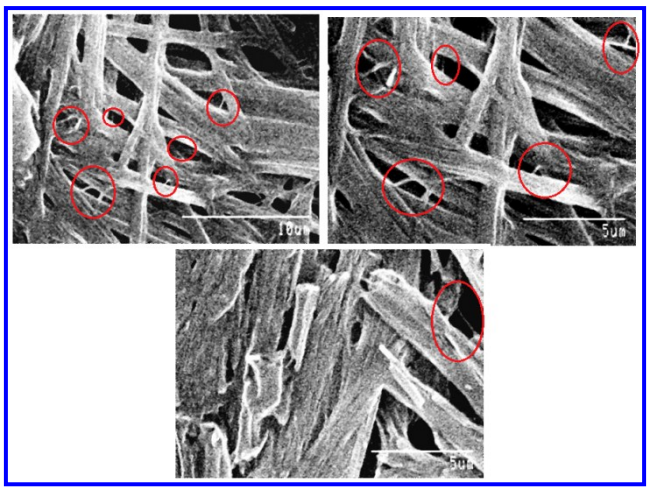


Fig. S9. Microstructure of DNA-hydrogel observed in SEM.

Here, the red coloured circles denote the presence of DNA in DNA-hydrogel network.

Assessment of cytotoxicity

***In vitro* assessment:**

$$\% \text{ Cell viability} = \frac{\text{Absorbance of sample}}{\text{Absorbance of control}} \times 100$$

Table S2 Hematological and serological parameters in exposed wistar rats for toxicity evaluation

Parameters	Group I (Cont.)	Group II (DNA-hydrogel capped Ag-NPs)
W.B.C. (per cmm)	6700 ± 375	5100 ± 265
Neutrophils (%)	52 ± 13	47 ± 6
Lymphocytes (%)	45 ± 11	51 ± 11
Basophils (%)	00	00
Eosinophils (%)	02 ± 1	01 ± 1
Monocytes (%)	01 ± 1	01 ± 1
Haemoglobin (gm%)	12.0 ± 1.5	11.5 ± 2.3
Bilirubin Total (mg%)	0.78 ± 0.11	1.13 ± 0.11
Bilirubin conjugated (mg%)	0.25 ± 0.06	0.83 ± 0.05
Bilirubin non-conjugated (mg%)	0.53 ± 0.08	0.30 ± 0.07
Total Protein (gm%)	7.5 ± 1.1	7.0 ± 0.7
Albumin (gm%)	4.3 ± 0.6	3.9 ± 0.7
Globulin (gm%)	3.2 ± 0.7	3.1 ± 0.6
S.G.P.T. (I.U./L)	37 ± 12	37 ± 13
S.G.O.T. (I.U./L)	32 ± 11	31 ± 8
Alk. Phosphate (I.U./L)	92 ± 17	141 ± 7

Hematological and serological markers in the different rat groups exposed with hydrogel through different routes. (For the corresponding permissible ranges of these parameters please consult literature values.[1]

CD spectral study for the interactions of Ag-NPs with CT-DNA:

CD spectroscopic analysis explores that the non-covalent interactions and minor groove binding dictate the interactional features between Ag-NPs with CT-DNA (Fig. S10). Minor groove binding was revealed by the absence of characteristic changes except the intensity in the CD spectrum showing decoiling of DNA double helix after exposure with Ag-NPs under ambient conditions.

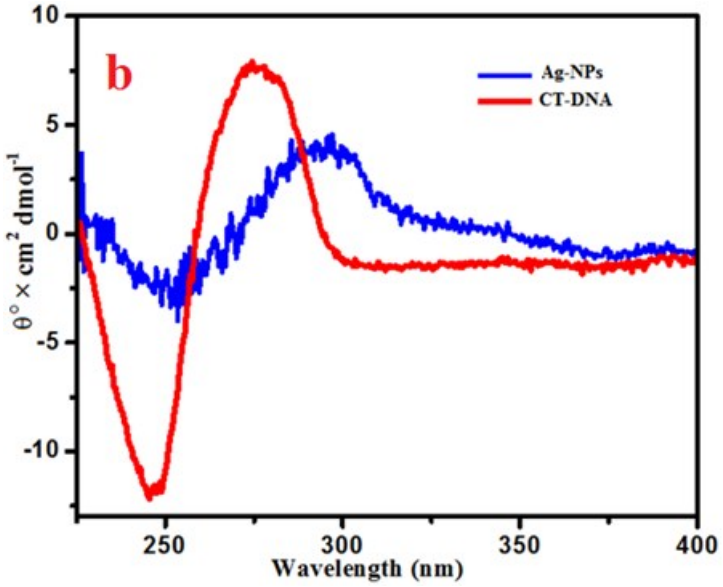


Fig. S10. CD spectra of Ag-NPs with CT-DNA.

Fig. S11(a-c) shows the luminescent property of **Shgel**. This is a thermo-reversible hydrogel with 50 °C as the gel-melting temperature (i.e. the gel-to-sol transition temperature) which is also supported by the temperature dependent solid state UV-absorption study shown as Fig. S11d. The aqueous solution of pure hydrogel (1 μg/ml concentration level) exhibits an intense broad UV-absorption band centred at 350 nm (Fig. S11e) and corresponding fluorescence emission maximum at 562 nm (λ_{ex} = 350nm) at 298K under atmospheric pressure (Fig. S11a).

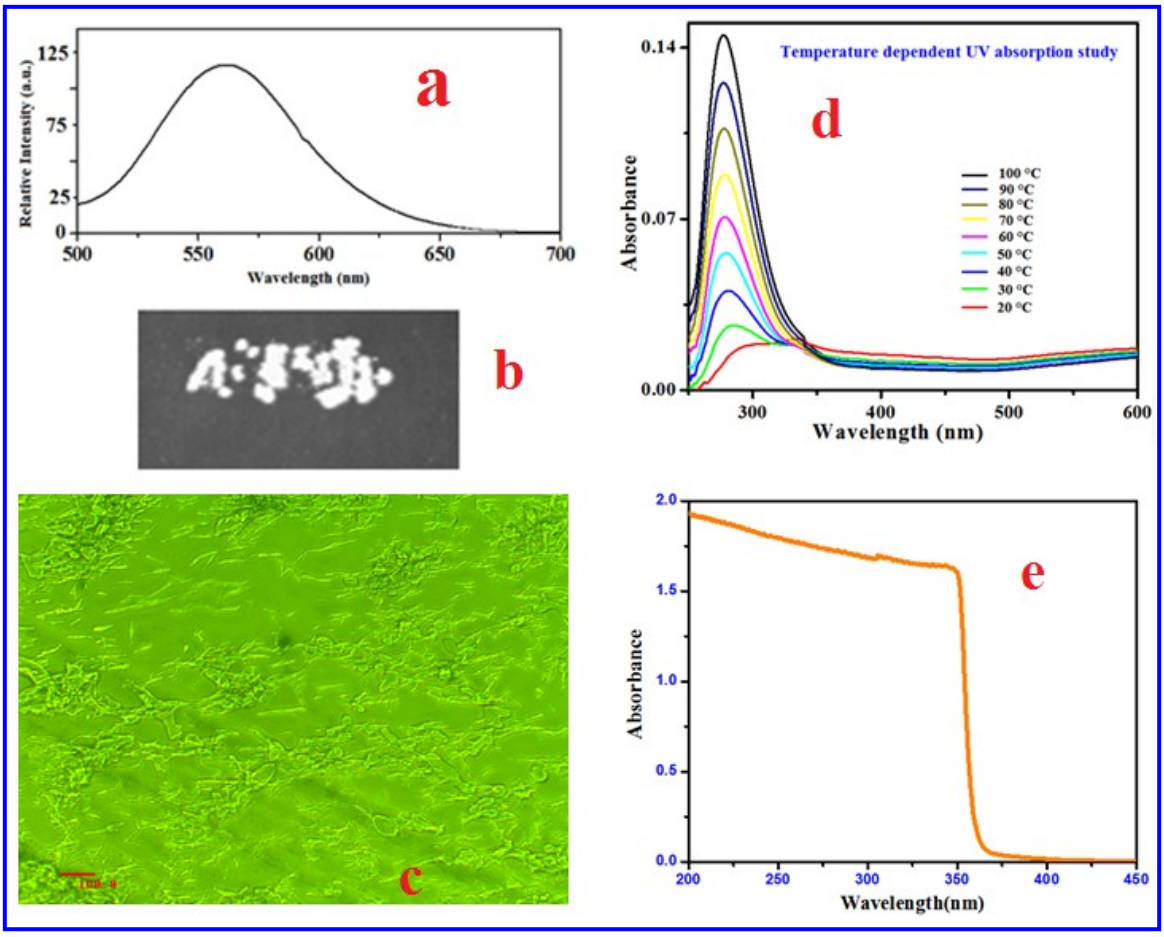


Fig. S11. Spectral characterization of **Shgel**. (a) Fluorescence spectra of water solution of **Shgel**. (b) Luminescence property of pure **Shgel** found in Gel-documentation system with UV-trans illumination. (c) Fluorescent microscopic image of pure **Shgel**. (d) Temperature dependent solid state UV-absorption study of **Shgel**. (e) UV-absorption spectra of the water solution of **Shgel**.

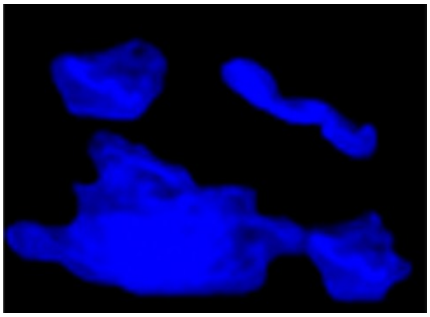


Fig. S12. Fluorescence micrograph of **Shgel**.

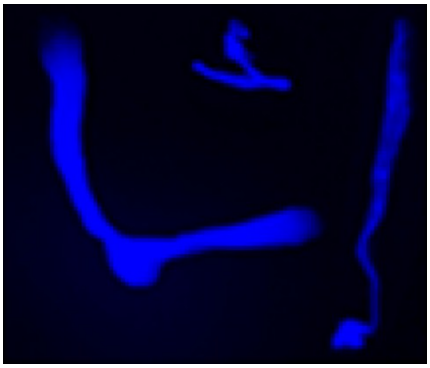


Fig. S13. Fluorescence micrograph of DNA-hydrogel.

Fig. 7a also shows the fluorescence-emission spectral pattern of the dilute aqueous solution of DNA-hydrogel (i.e. fluorescence emission maximum at 562 nm (λ_{ex} = 350 nm) at 298 K and atmospheric pressure) which have been recorded during the fluorimetric measurement of interaction between CT-DNA and **Shgel**.

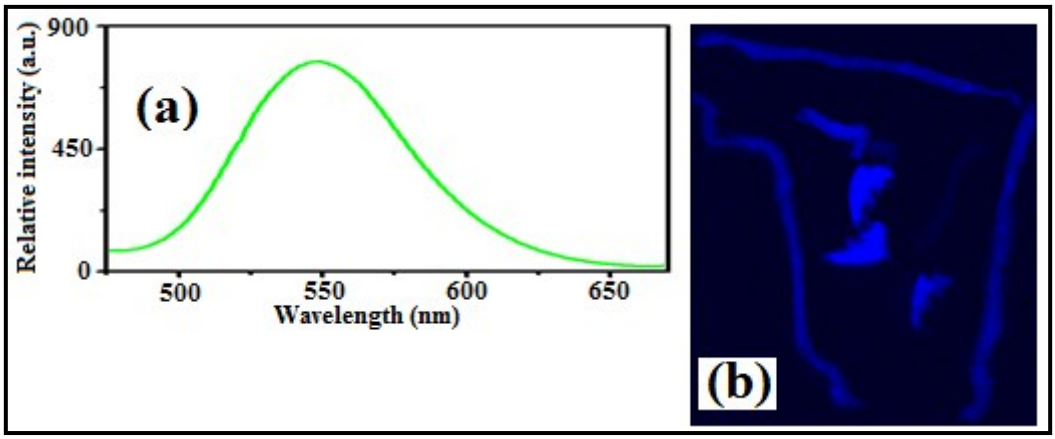


Fig. S14. Fluorescence pattern of DNA-hydrogel capped Ag-NPs: (a) Fluorescence spectra of the water solution of DNA-hydrogel capped Ag-Nps and (b) fluorescence micrograph of DNA-hydrogel capped Ag-NPs.

Circular Dichroism spectroscopic study of Shgel with CT-DNA:

The positive band at 277 nm in CD spectral data signals for base stacking, whereas a negative band at 243 nm designates helicity which is the characteristic marker of right-handed B-DNA.[2-4]These sensitive CD spectral bands are the principal markers for studying interaction of ligands with DNA.[5-6] Intercalation of a ligand with DNA can alter DNA topology but minor groove binders do not perturb the CD spectrum of DNA significantly.[5-6]CD spectral analysis confirms thatduring the sensing process intsead of intercalation there is the groove binding interactions between **Shgel** and DNA strands. Due to this minor groove binding interactions between **Shgel** and DNA strands, there is also a change of intensity of DNA signal in CD spectra. (Fig.8a).

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