Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Modulating Defibrillation by Tryptophan Mediated Photo Cleavage of Disulfide Bonds

Sahabaj Mondal,[a] Surajit Singh,[a] Ananda Shit,[a] Santosh Kumar,[a] and Debasish Haldar*[a]

[a]Department of Chemical Sciences, Indian Institute of science education and Research Kolkata, Mohanpur 741246, Nadia, West Bengal, India.

E-mail: deba_h76@iiserkol.ac.in, deba_h76@yahoo.com.

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Fig. S1: Temperature and pH-responsive nature of the hydrogel.

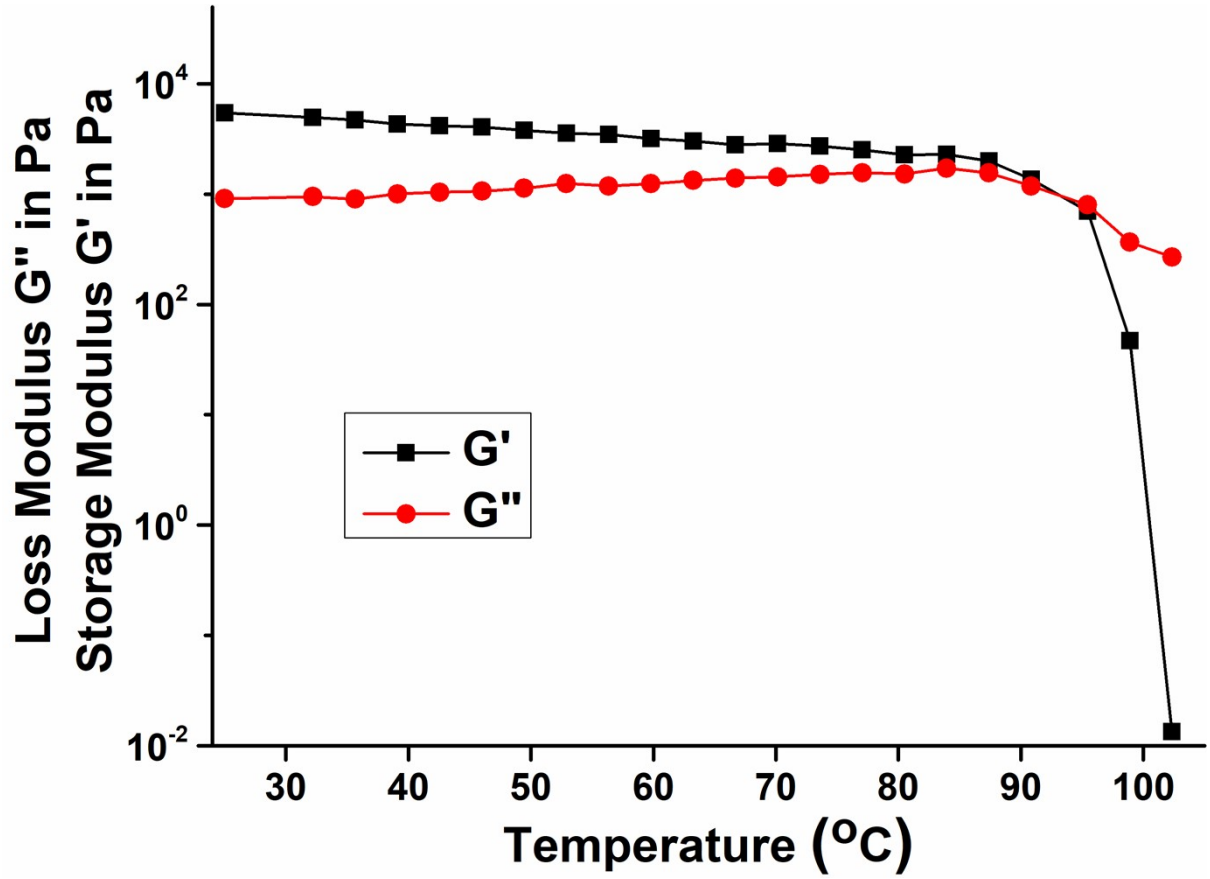


Fig. S2: temperature dependant rheology experiment of ZDC hydrogel.

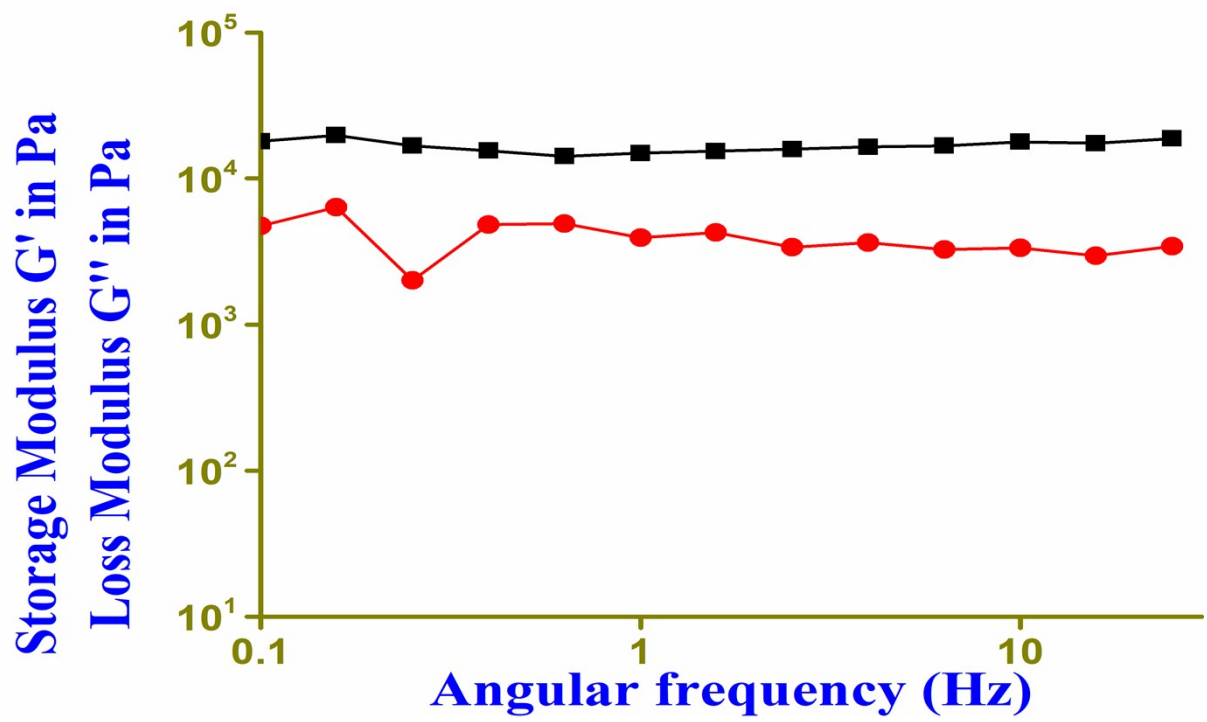


Fig. S3: Frequency-sweep experiment of DZC gel at a constant strain of 0.01%.

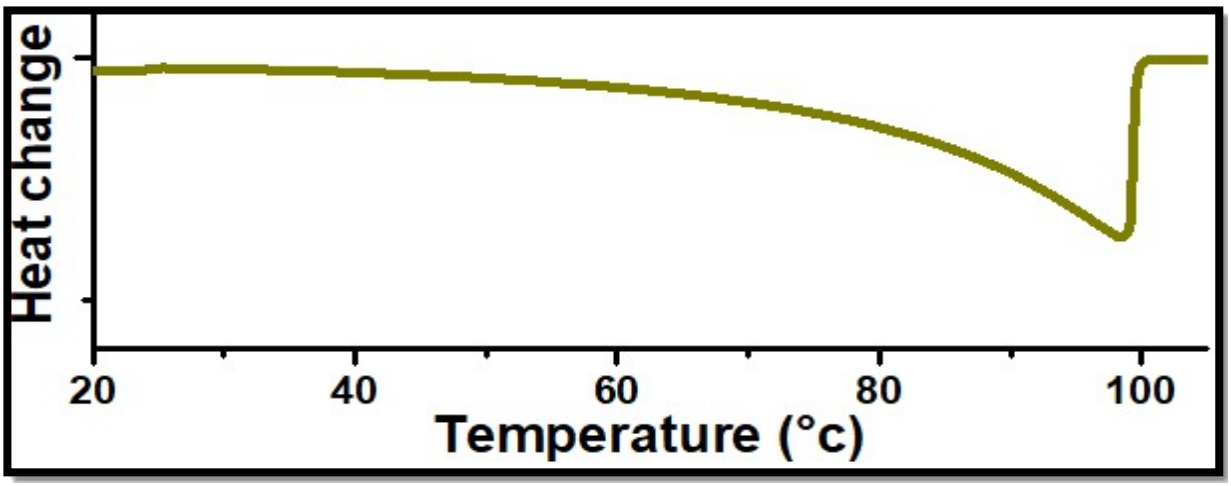


Fig. S4:DSC thermograms of ZDC hydrogels prepared at gelator concentration:6.5 g/L. The T_{DSC} = 98 °C at geletor conc. 6.5 mg/mL.

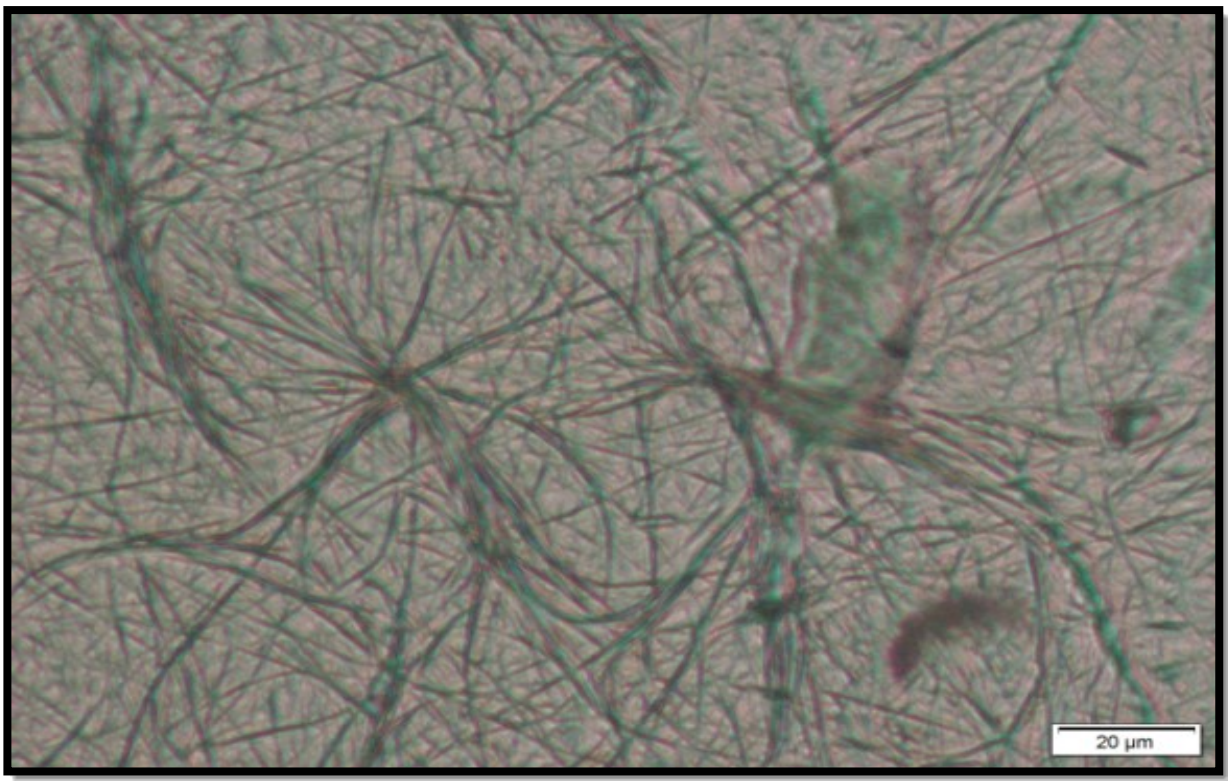


Fig. S5: POM image of DZC xerogel.

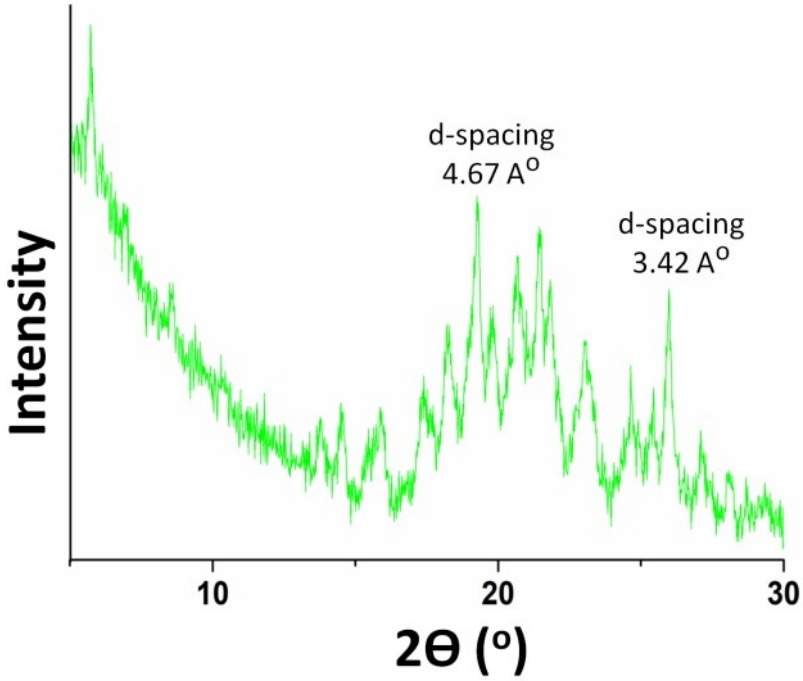


Fig. S6: The wide-angle X-ray scattering (WAXS) patterns of the powder ZDC.

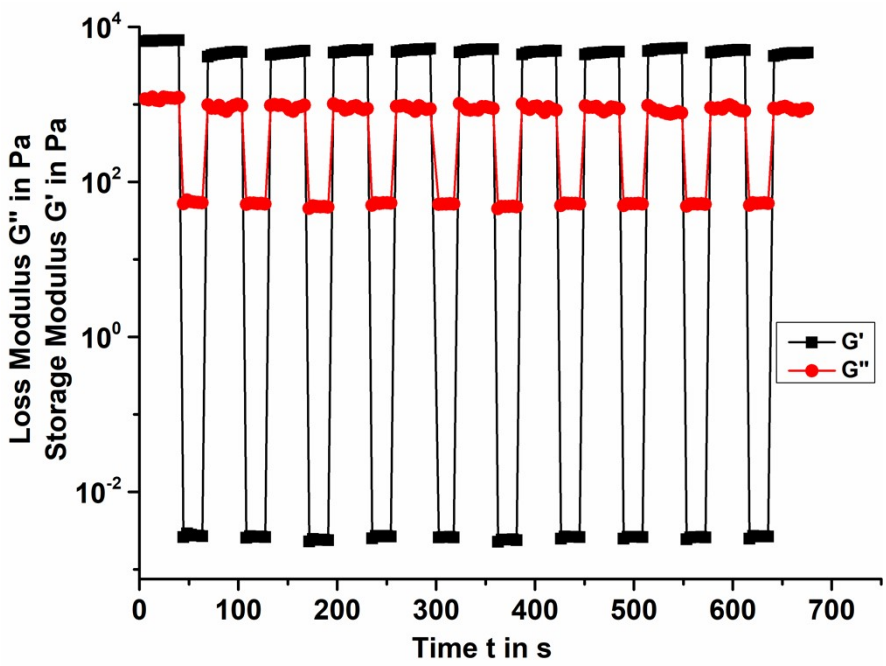


Fig. S7: Rheological recovery behaviors of DZC hydrogel with multiple cycles. (Black and red curves display storage and loss modulus, respectively.)

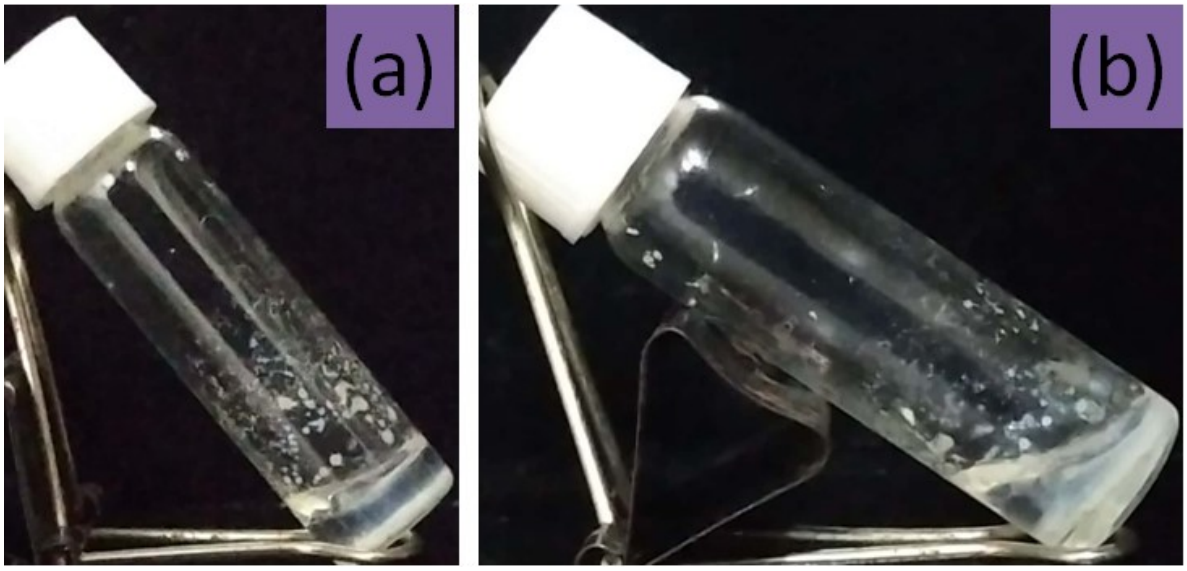


Fig. S8: Vial image of tryptophan-induced hydrogel, (a) without UV-exposure and (b) with UV-exposure.

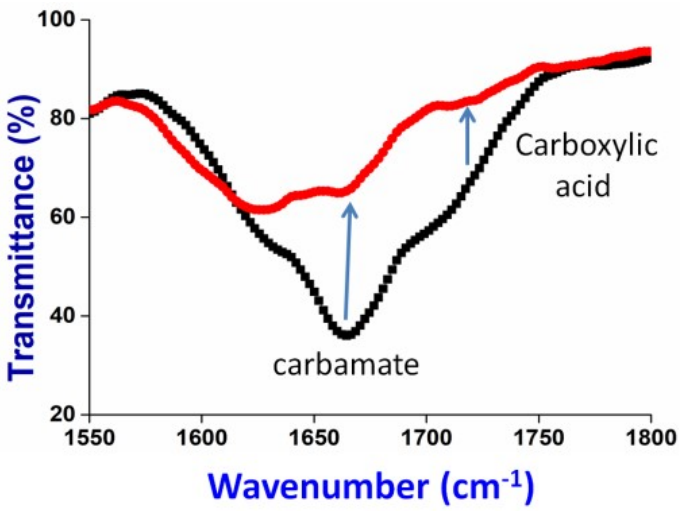


Fig. S9: FTIR spectra of tryptophan-induced hydrogel, without UV-exposure (black) and with UV-exposure (red).

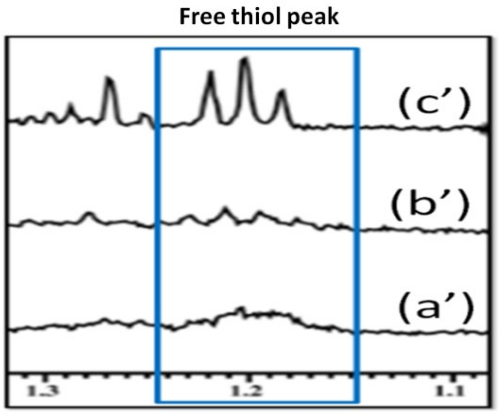


Fig. S10: ^{1}H NMR spectrum of DZC and tryptophan hydrogel, (a' without exposure to sunlight or UV-light, (b') with exposure to sunlight, and (c') with exposure to UV-light for 14h).

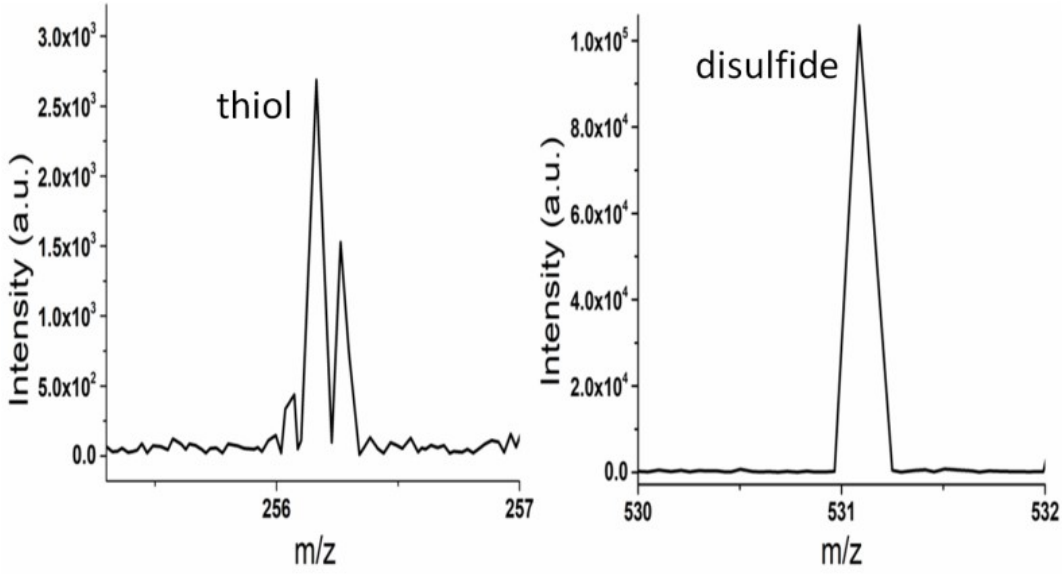


Fig. S11: HR-MS of DZC and tryptophan hydrogel (zoom version).

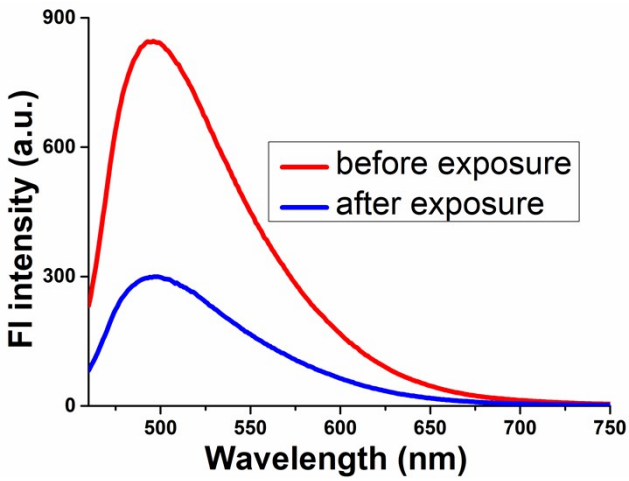


Fig. S12: Th T fluorescence spectra of the DZC and tryptophan-induced hydrogel before (red) and after (blue) exposure to UV light. The excitation wavelength was 450 nm, and the concentration of Th T was 8 μM.

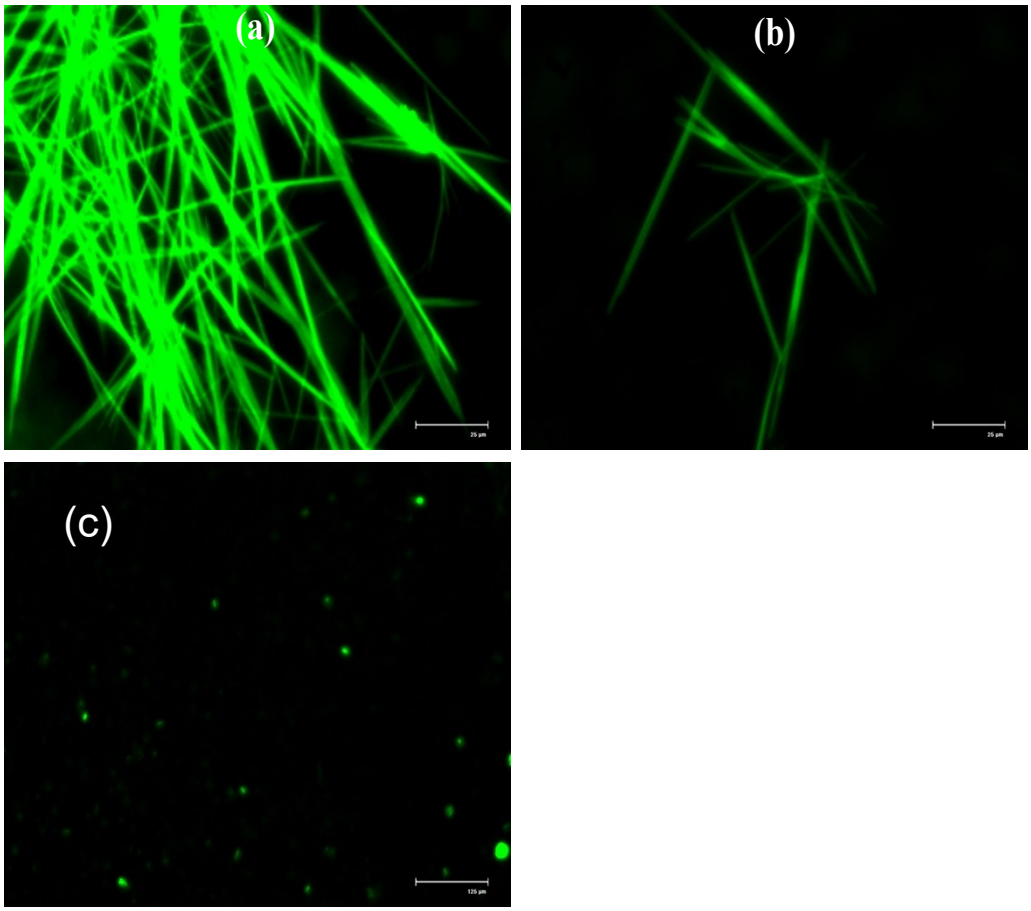


Fig. S13: Fluorescence microscopy images of the DZC and tryptophan-induced hydrogel, (a) before, (b) after exposure to UV light and (c) only with Th T (control).

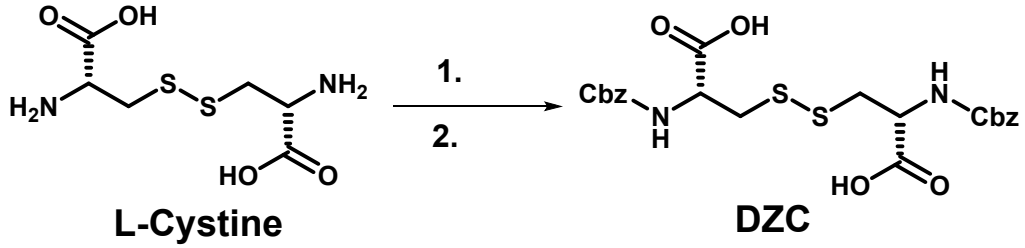
Synthesis

General

L-cystine and Benzyl chloroformate (Cbz-Cl) were purchased from Sigma chemicals.

Synthesis

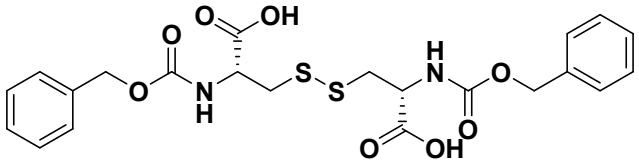
Scheme 1



Steps/Stages:

1. R: NaOH, S: H_2O, S: THF, Cbz-Cl, 10 min, 0°C; overnight, 0°C → rt
2. R: HCl, S: H_2O, rt, pH~1.

Synthesis Procedure:



(N, N'-Di(benzyloxycarbonyl)-*L*-cystine)(DZC): *L*-Cystine (2.4 g, 10 mmol) was stirred with THF (20 mL), and a solution of NaOH (0.85 g, 21.25 mmol) in water (10 mL) was added. The solution mixture was cooled in an ice bath, and then Benzyl chloroformate (CbzCl) (1.8 mL, 12.5 mmol) was added dropwise over 10 min. The reaction was kept to come to room temperature and was stirred overnight. The mixture of the reaction was taken in a separating funnel and washed with hexanes (2 x 20 mL). After that, the aqueous phase was acidified with conc. HCl to pH ~ 1, and the compound was extracted with EtOAc (3 x 30 mL). Combined EtOAc solutions were dried over Na2SO4 and evaporated under a vacuum to obtain the product as a white solid. Yield: 1.88 g (74%).

^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 12.96 (b, 2H, Acid OH), 7.72 (d, J =8.3, 2H, NH),7.39−7.28 (m, 10H, Aromatic H), 5.03 (s, 4H, Benzyl CH2), 4.28 (m, 2H, Cystine-C_αH), 3.15 (dd, 2H, J = 13.65, 4.55 Hz, Cystine-C_βH), 2.92 (dd, 2H, J = 13.45, 10.15 Hz, Cystine-C_βH).

^{13}C NMR (125 MHz, DMSO-d_6, δ ppm): 172.14 (COOH), 156.03 (OCONH), 136.87 (ipso-ArC), 128.34 (ArCH), 127.82 (ArCH), 127.7 (ArCH), 65.55 (Benzyl CH2), 53.03 (Cystine-Cα), 40.02 (Cystine-Cβ).

Mass spectral data: TOF-MS (m/z) calculated of **DZC** $C_{22}H_{24}N_2O_8S_2$ for $[M+Na]^+$:531.56; found : 531.7558 and for $[M+K]^+$: 547.56; found : 547.7732.

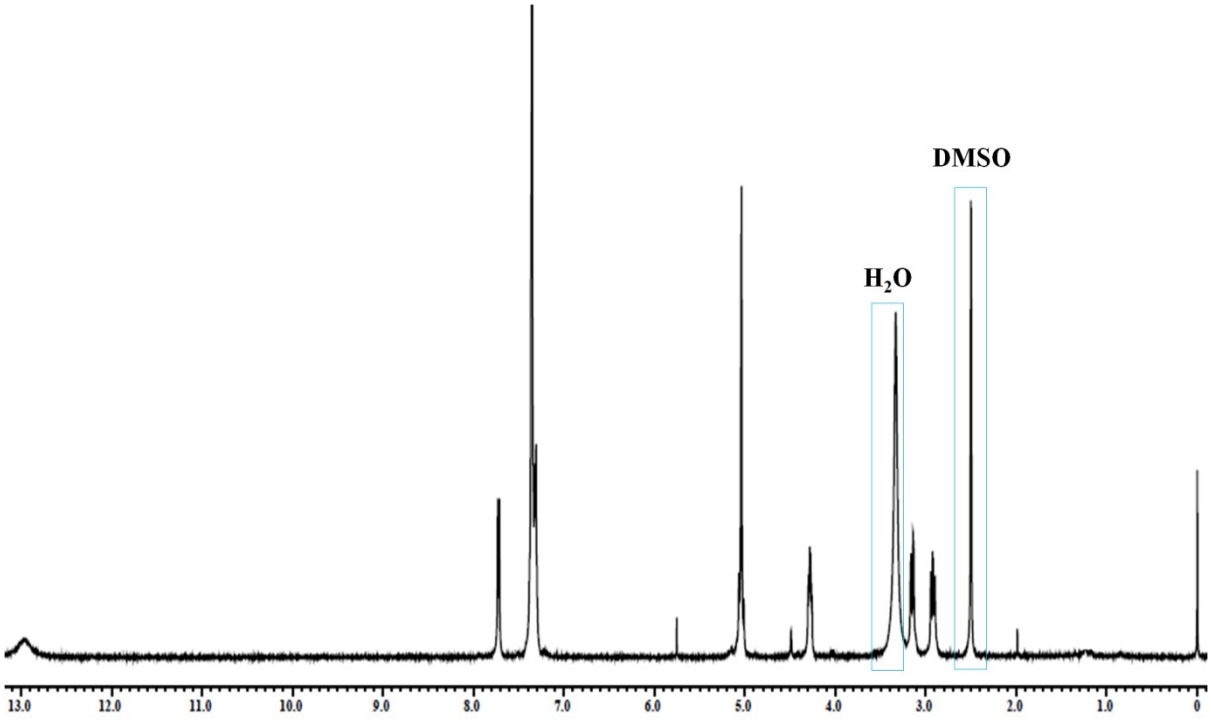


Fig. S14: ^{1}H NMR (500 MHz, DMSO-*d*6) spectrum of DZC.

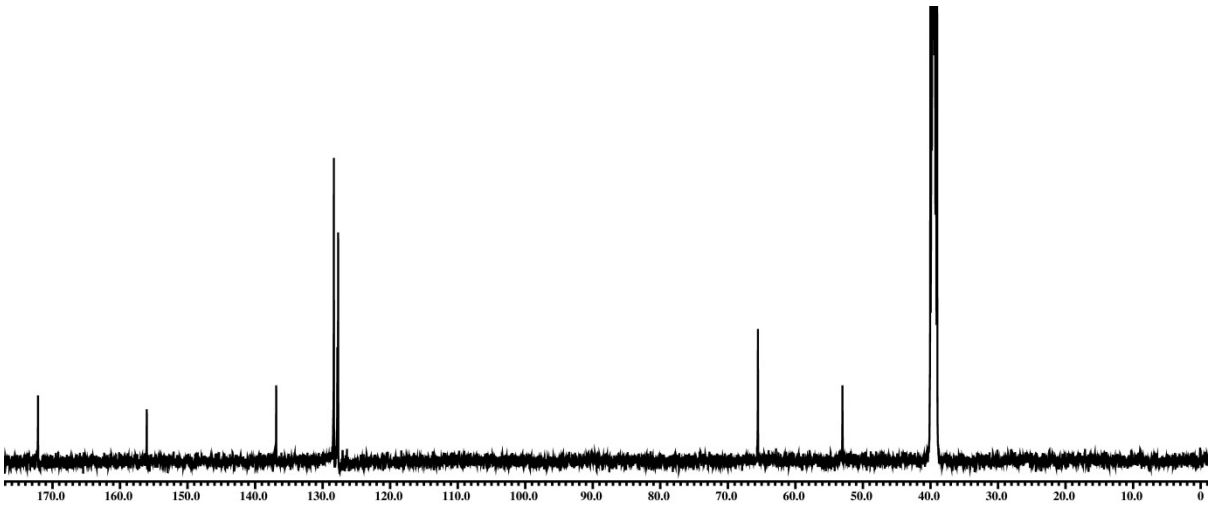


Fig. S15: ^{13}C NMR (125 MHz, DMSO-*d*6) spectrum of DZC.

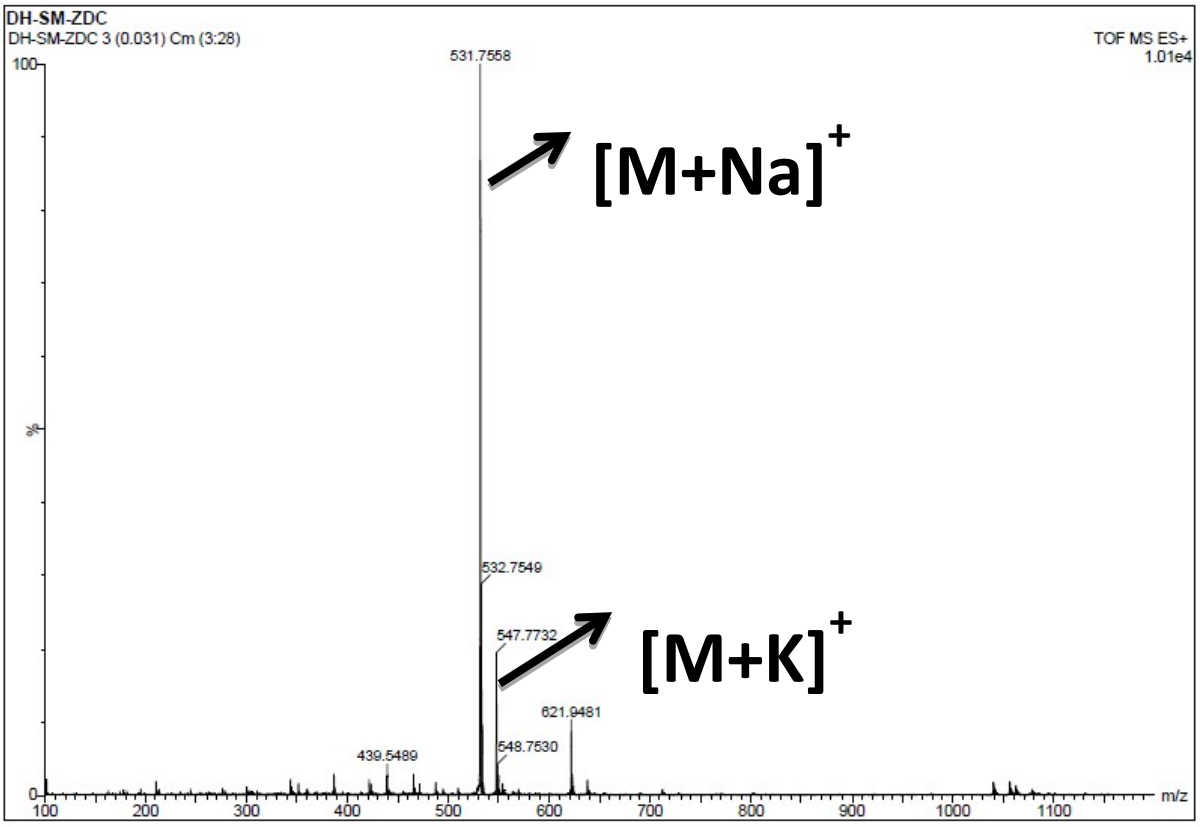


Fig. S16: ESI-MS spectrum of DZC.