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

Dynamic sugar based bio-inspired, self-healing hydrogel exhibiting ESIPT

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Synthesis of 5-(benzo[d]thiazol-2-yl)-4-hydroxyisophthalaldehyde (BTHP)

5-(benzo[d]thiazol-2-yl)-4-hydroxyisophthalaldehyde was synthesized according to the literature procedure.[1] 2-(benzo[d]thiazol-2-yl)phenol (2g, 8.79 mmol) and Hexamine (1.84 g, 13.19 mmol) was dissolved in Trifluoroacetic acid (TFA, 25ml). The solution was refluxed for 12 hrs under Argon atmosphere and the progress of reaction was monitored by TLC. Then the mixture was cooled to room temperature and then 50 ml water was added to the reaction mixture and refluxed for 30 min. Then yellow precipitate formed was filtered and purified by column chromatography using ethyl acetate/petroleum ether (7/3, v/v) as eluent to afford yellow solid (2.07 g, 83 % yield).

^{1}H NMR (DMSO-d$_6$, 400 MHz): δ (ppm): 10.59 (s, 1H), 9.99 (s, 1H), 8.55 (s, 1H), 8.40 (s, 1H), 8.04 (d, 1H, J=8 Hz), 7.98 (d, 1H, J=8 Hz), 7.60-7.49 (m, 2H).

^{13}C NMR (CDCl$_3$, 125 MHz): δ (ppm): 189.53, 151.16, 134.39, 127.49, 126.76, 122.73, 122.00.

MS (ESI MS): (m/z, %): 284.03 (MH^+, 100 %).

Melting Point: > 200°C

^{1}H NMR, ^{13}C NMR and ESI MS spectra of BTHP:

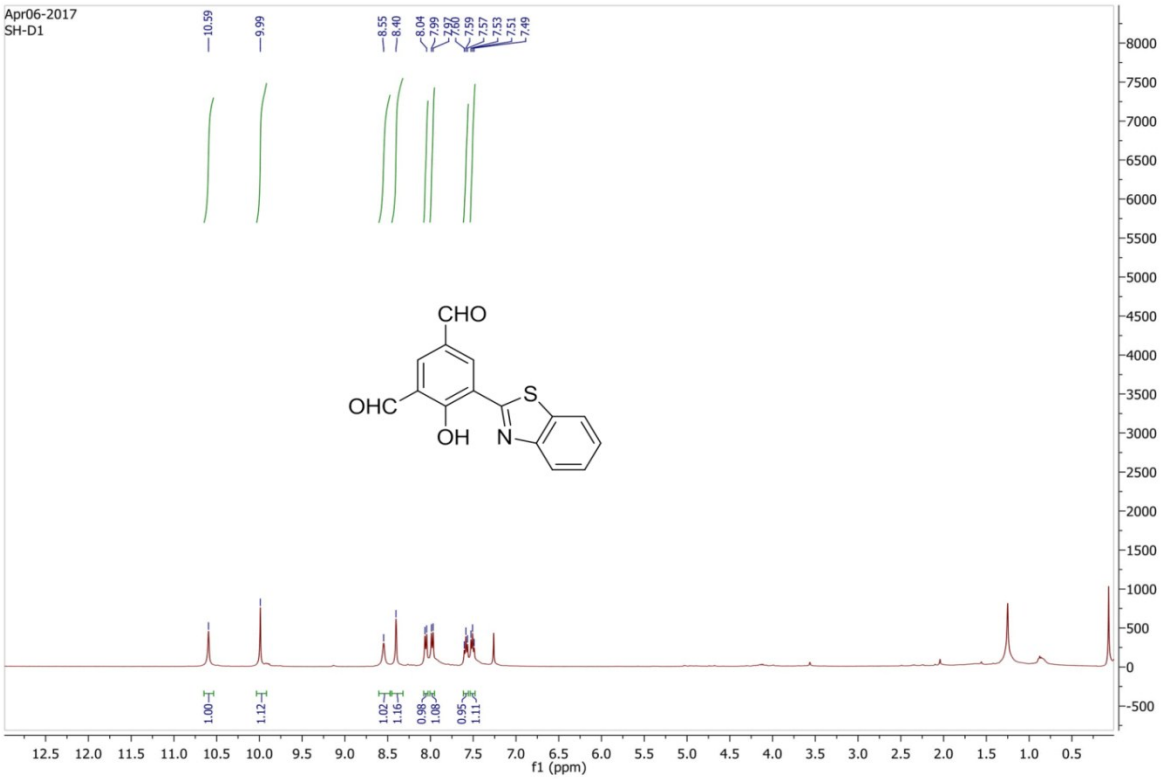

Figure S1: ^{1}H NMR spectrum (400 MHz) of BTHP in DMSO-d$_6$

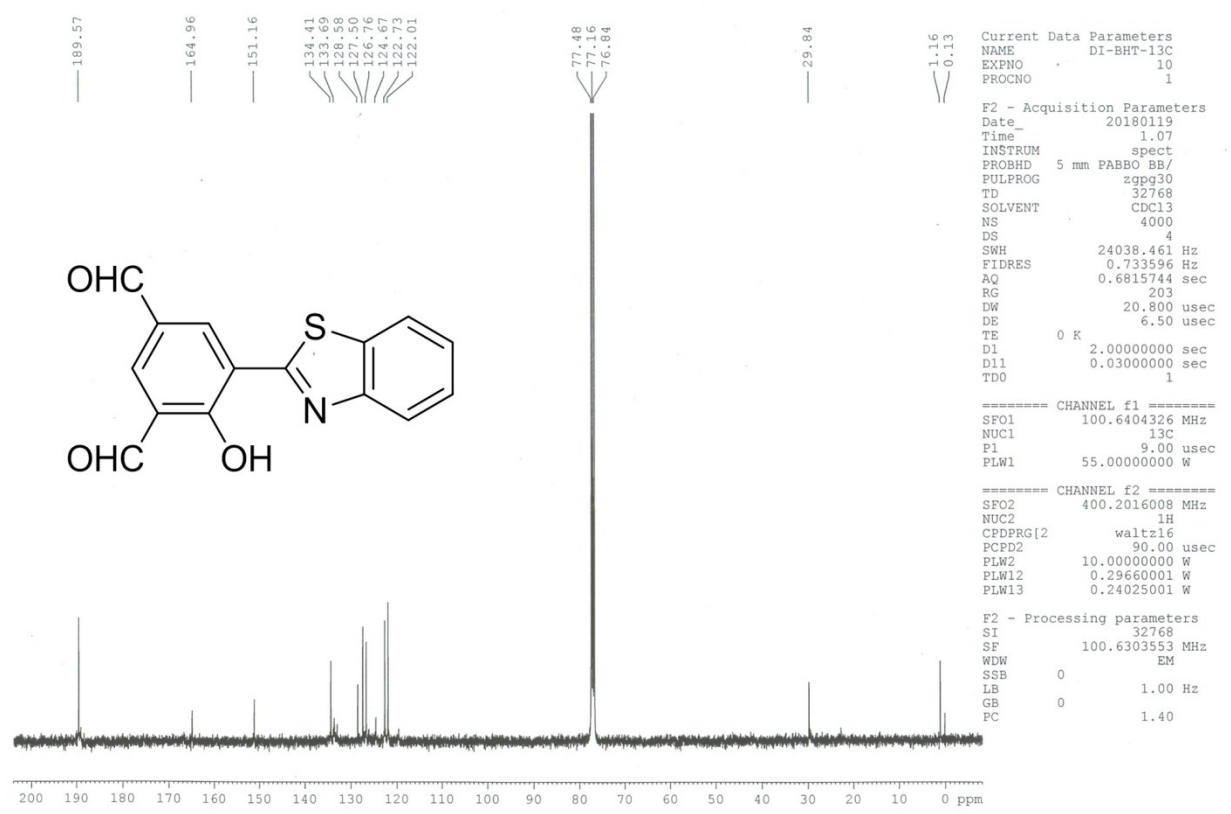

Figure S2: ^{13}C NMR spectrum (100 MHz) of **BTHP** in $CDCl_3$

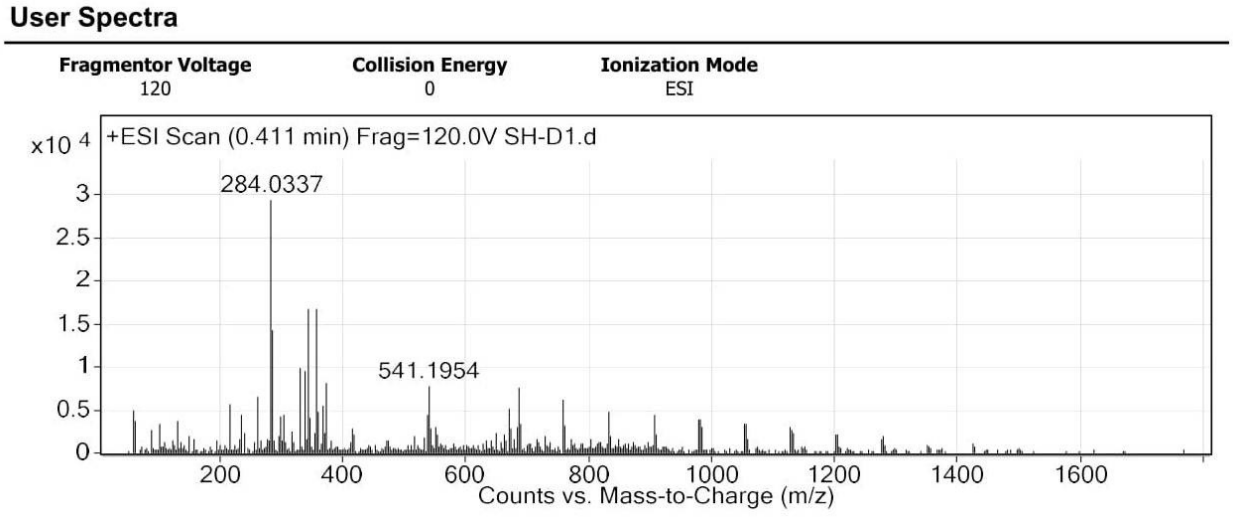

Figure S3: ESI MS of BTHP in MeOH.

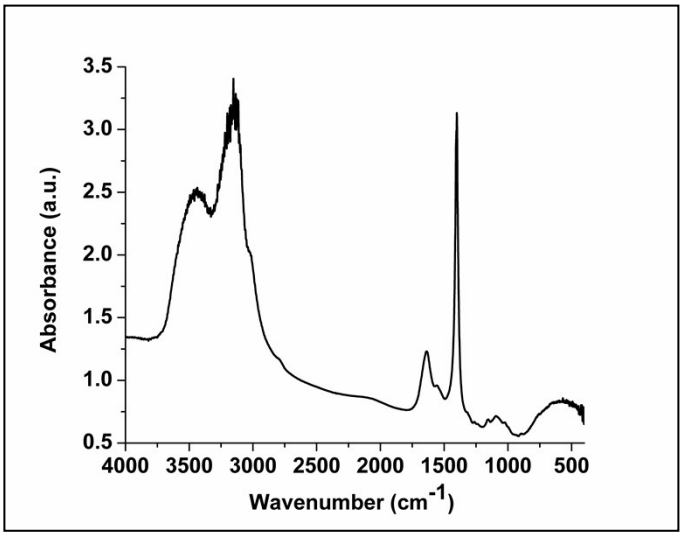

Figure S4: FT-IR spectra of CBTHP.

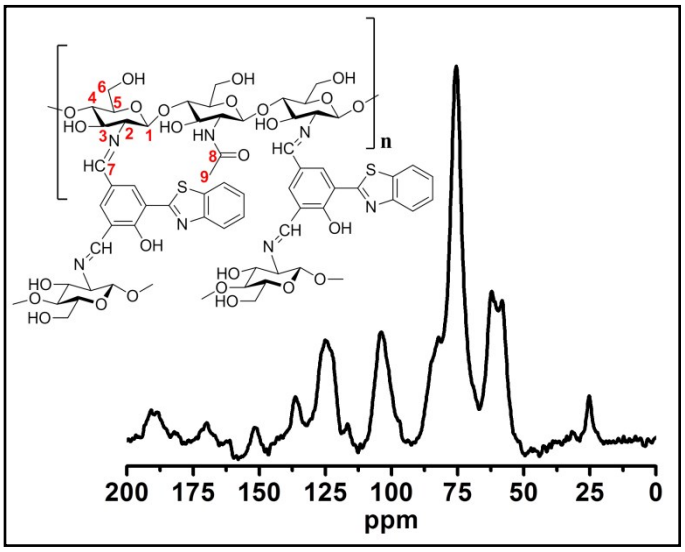

Figure S5: Solid state ^{13}C CP-MAS NMR spectra of CBTHP.

Table S1: Chemical shifts of CBTHP by ^{13}C CP-MAS NMR

C_1	$C_{1'}$	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9
104	97	76	62	82	62	58	161	170	25

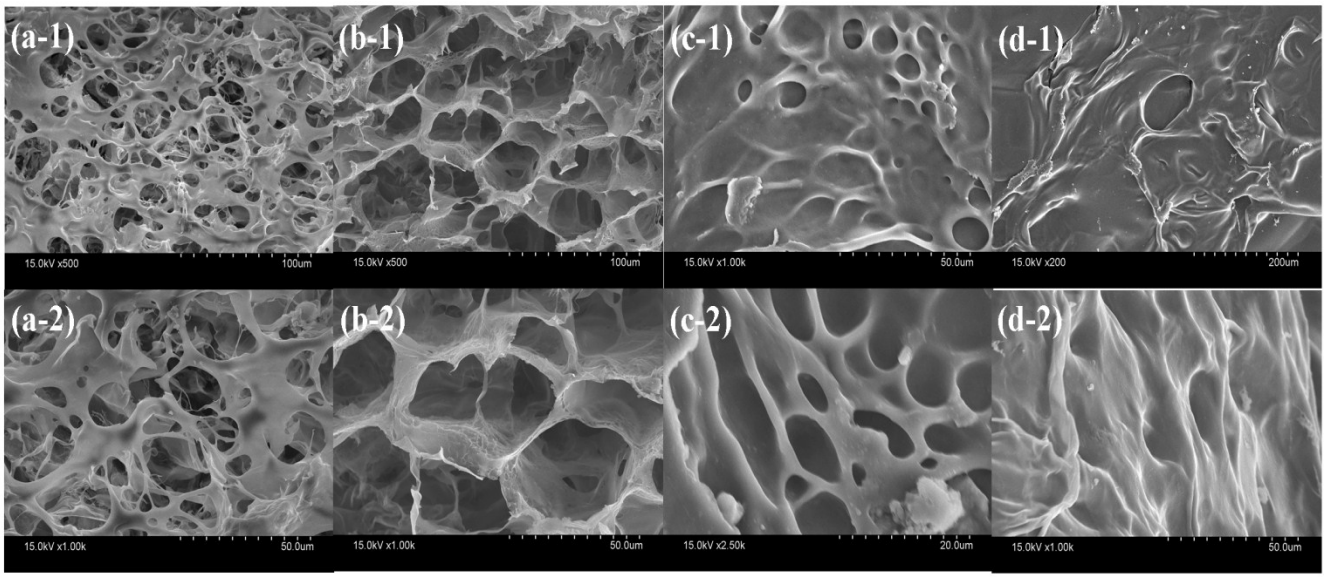

Figure S6: SEM micrographs of freeze-dried CBTHP hydrogels. Surface morphologies of hydrogels with the volume ratio of chitosan and cross-linker (1) are 2:0.5 (a-1 – a-2), 2:1 (b-1 – b-2), 2:1.5 (c-1 – c-2) and 2:2 (d-1 – d-2).

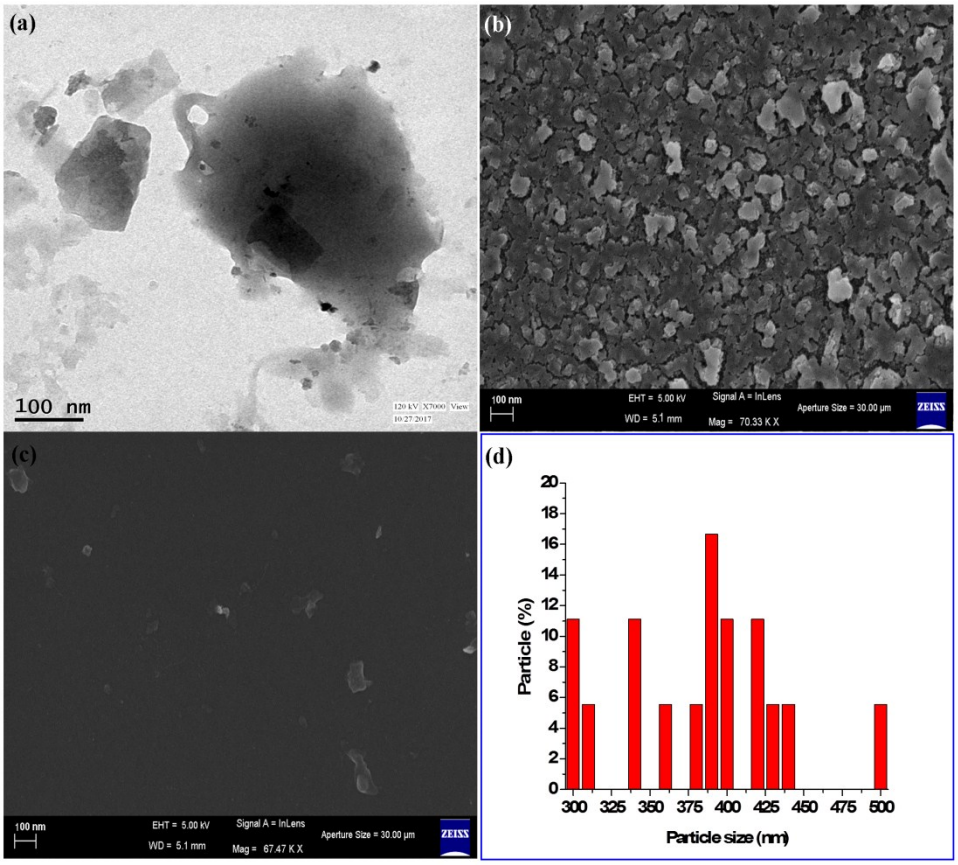

Figure S7: Particle distribution in (a) TEM (b), (c) FE-SEM image; (d) Plot of % of particle vs particle from FE-SEM (fig. (b) and (c)).

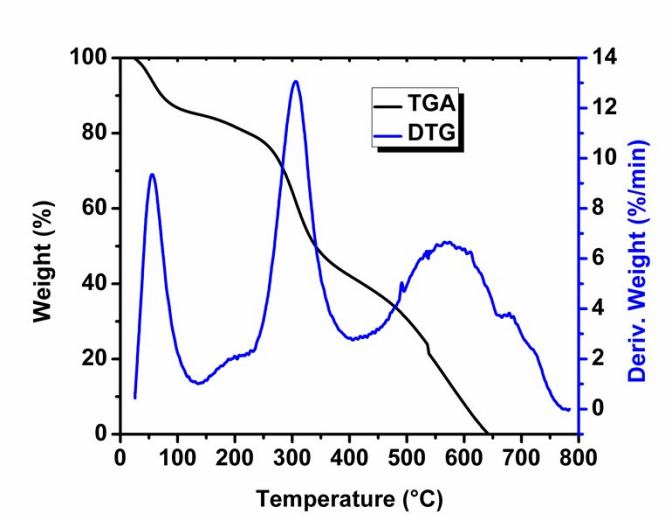

Figure S8: Thermogravimetric analysis of CBTHP.

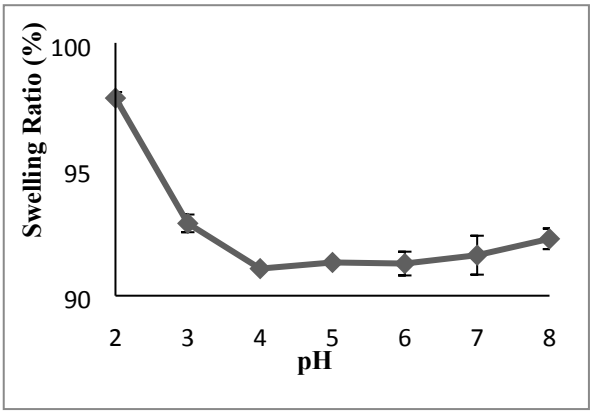

Figure S9: pH dependent swelling study of CBTHP.

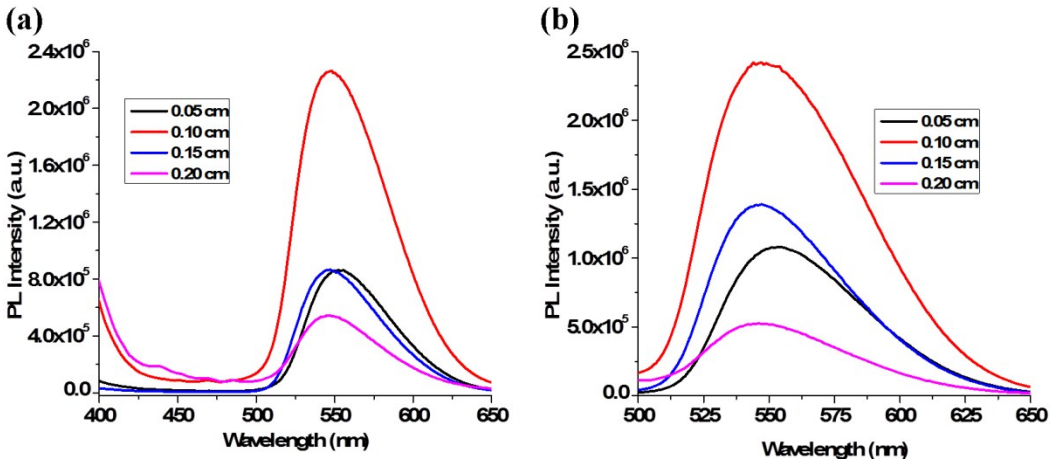

Figure S10: Thickness dependent fluorescence intensity of CBTHP at (a) λ_{ex}=375 nm (b) λ_{ex}=455 nm.

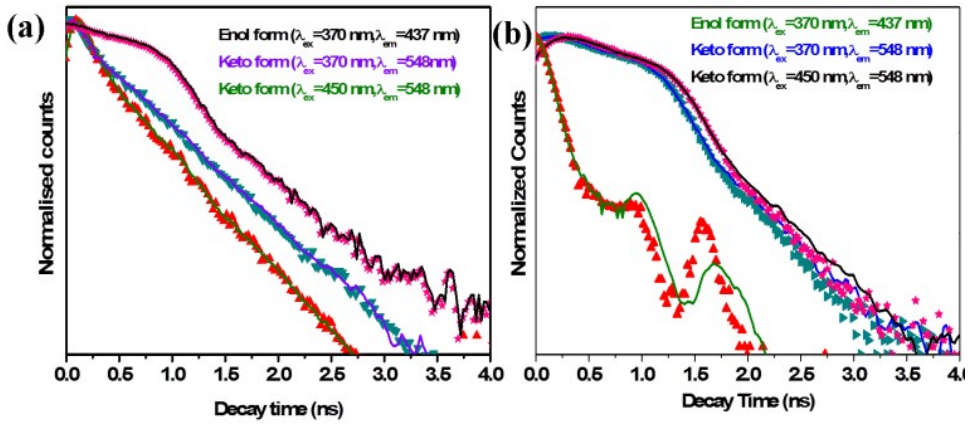

Figure S11: Fluorescence decay profiles in both keto and enol tautomer of CBTHP (a) gel phase (b) solution state.

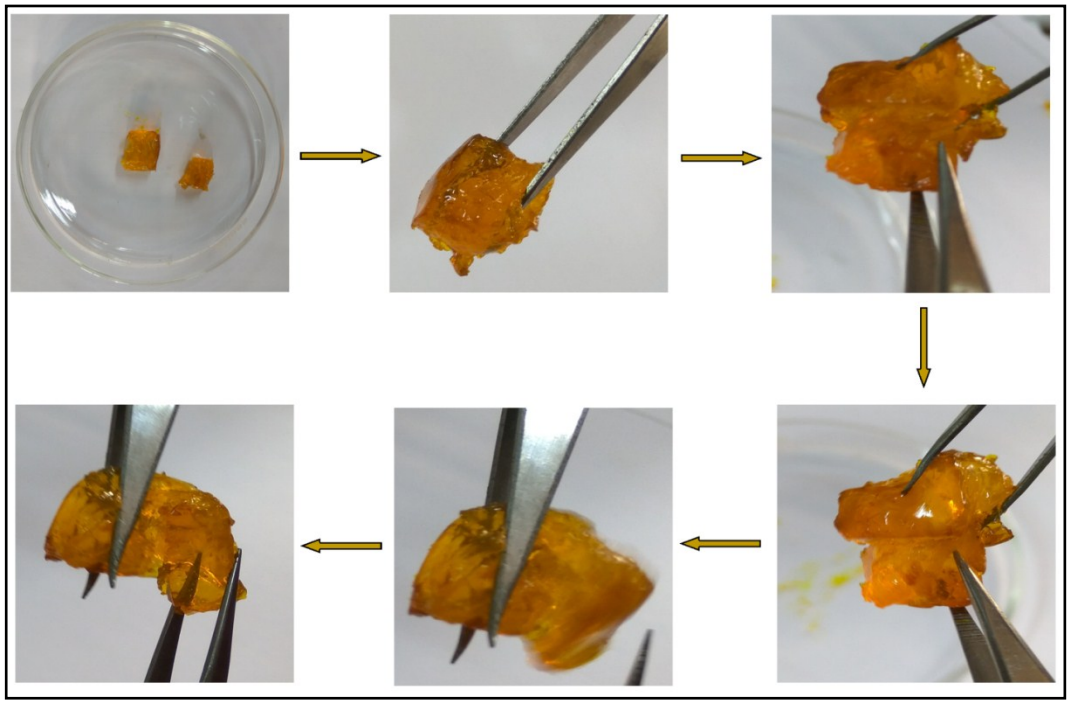

Figure S12: Appearance of spontaneous self-healing of CBTHP hydrogel.

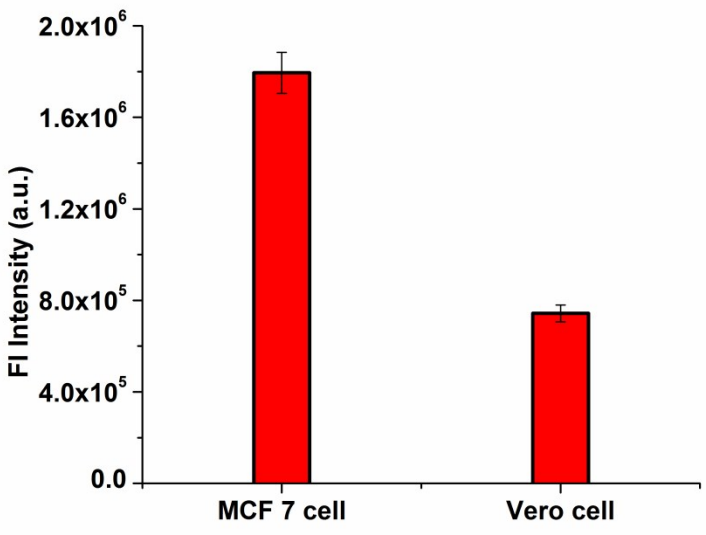

Figure S13: Compression of the fluorescent intensity of MCF 7 cells and Vero cells of the cell images treated with CBTHP (Average intensity of 10 cells has been compared).

Table S2: Comparison of the chitosan-based (imine) fluorescent, self-healing hydrogels

Probe	Type	ESIPT	Self-healing	In-vitro	Reference
Chondroitin sulfate multiple aldehyde (CSMA) and N-succinyl-chitosan based hydrogel	Polymeric hydrogel	No	Yes	Yes	2
Chitosan/polyvinyl alcohol	Polymeric hydrogel	No	Yes	Yes	3
Chitosan–Pluronic	Polymeric hydrogel	No	No	Yes	4
Chitosan-dibenzaldehyde-terminated telechelic poly(ethylene glycol)	Polymeric hydrogel	No	Yes	No	5
Chitosan fibers via cross-linking glutaric dialdehyde (GD)	Polymeric hydrogel (Fluorescent)	No	No	No	6
Pullulan (A-Pul), e-poly-L-lysine (e-PL) and branched polyethyleneimine	Polymeric hydrogel	No	Yes	Yes	7

Chitosan-based hydrogel	Polymeric hydrogel (Fluorescent)	No	No	Yes	8
Chitosan-Graphene oxide	Polymeric hydrogel	No	Yes	No	9
2-(2-Hydroxyphenyl)-benzothiazole-Rhodamine	Small chromophoric system	Yes	No	No	10
2-(2′-Hydroxyphenyl)benzothiazole Derivatives	Small chromophoric system	Yes	No	No	11
BODIPY-chitosan hydrogels	Polymeric hydrogel (Fluorescent)	No	Yes	No	12
chitosan-5-(benzo[d]thiazol-2-yl)-4-hydroxyisophthalaldehyde	Polymeric hydrogel (Fluorescent)	Yes	Yes	Yes	This work

Reference

1. W. E. Smith, *J. Org. Chem.*, 1972, **37**, 3972–3973.

2. S. Lu, C. Gao, X. Xu, X. Bai, H. Duan, N. Gao, C. Feng, Y. Xiong and M. Liu, *ACS Appl. Mater. Interfaces.* 2015, **7**, 13029−13037.

3. G. Chang, Y. Chen, Y. Li, S. Li, F. Huang, Y. Shen and A. Xie, *Carbohydr. Polym.*, 2015, **122**, 336–342.

4. K. M. Park, S. Y. Lee, Y. K. Joung, J. S. Na, M. C. Lee, K. D. Park, Acta Biomater., 2009, **5**, 1956–1965.

5. Y. Zhang, L. Tao, S. Li and Y. Wei, Biomacromolecules, 2011, **12**, 2894–2901.

6. Z. Geng, H. Zhang, Q. Xiong, Y. Zhang, H. Zhao and G. Wang, *J. Mater. Chem. A*, 2015, **3**, 19455–19460.

7. C. Cheng, X. Zhang, Y. Meng, Z. Zhang, J. Chen and Q. Zhang, *Soft Matter,* 2017, **13** , 3003-3012.

8. A. Sachdev, I. Matai, P. Gopinath, Colloids Surf B Biointerfaces, 2016,141, 242–252.

9. D. Han and L. Yan,*ACS Sustainable Chem. Eng.*, 2014, **2**, 296−300.

10. P. Majumdar and J. Zhao, *J. Phys. Chem. B*, 2015, **119**, 2384−2394.

11. J. Cheng, D. Liu, W. Li, L. Bao and K. Han, *J. Phys. Chem. C*, 2015, **119**, 4242−4251.

12. S. Belali, G. Emandi, A. A. Cafolla, B. O'Connell, B. Haffner, M. E. Möbius, A. Karimi and M. O. Senge, *Photochem. Photobiol. Sci.*, 2017, **16**, 1700–1708.