Supporting Information for

Mechanically Robust 3D Nanostructure Chitosan-Based Hydrogels with Autonomic Self-Healing Properties

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1. The synthesis procedure for zinc phthalocyanine tetra-aldehyde (ZnPcTa)

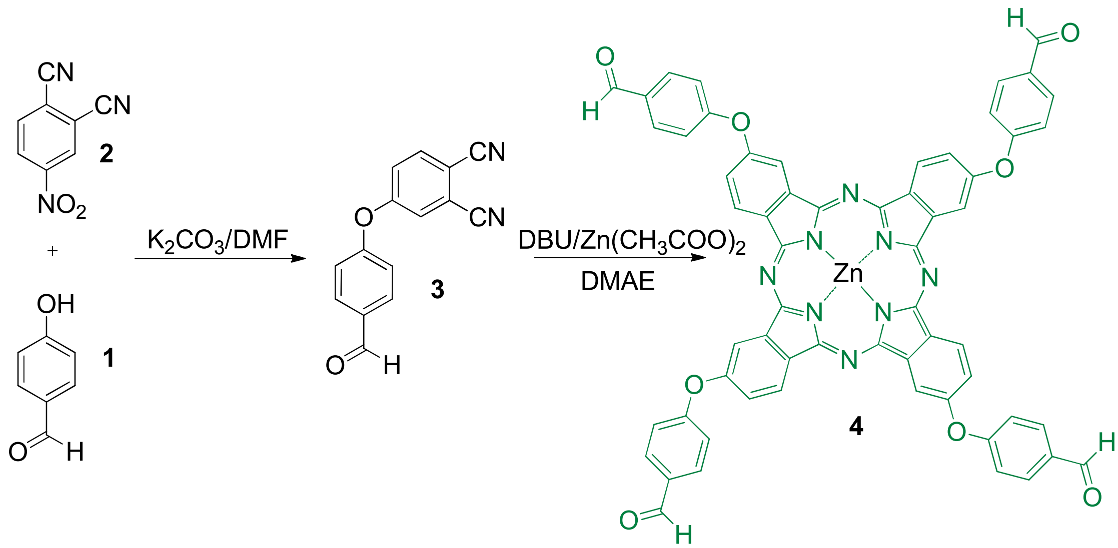

Figure S1. Synthesis of zinc phthalocyanine tetra-aldehyde (ZnPcTa)

2. Additional analyses of cross-linker

The IR spectrum of FPPht clearly indicate the presence of CN band. **Figure S2** shows after cyclotetramerization of FPPht, the IR spectrum of phthalocyanine lacked the CN band, completely.

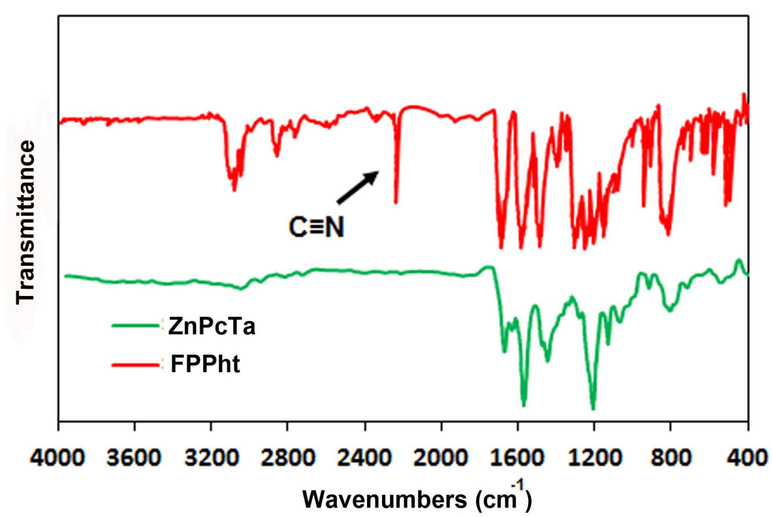

Figure S2. FT-IR spectra of FPPht and ZnPcTa

3. Pore-size of hydrogels with different wt% ZnPcTa.

As shown in **Figure S3,** the ZnPcTa concentrations show very strong regulation on the pore size distribution of the hydrogels.

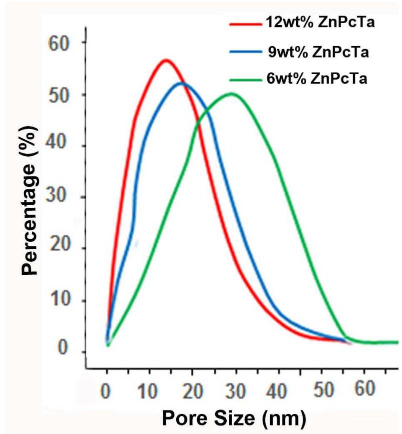

Figure S3. Pore-size distributions of the hydrogels with different wt% ZnPcTa

4. Morphology of the non-functional MWCNT hydrogel nanocomposite.

Scanning electron microscopy (SEM) analysis of the non-functional MWCNT exhibited aggregates of carbon nanotubes associated with hydrogel network.

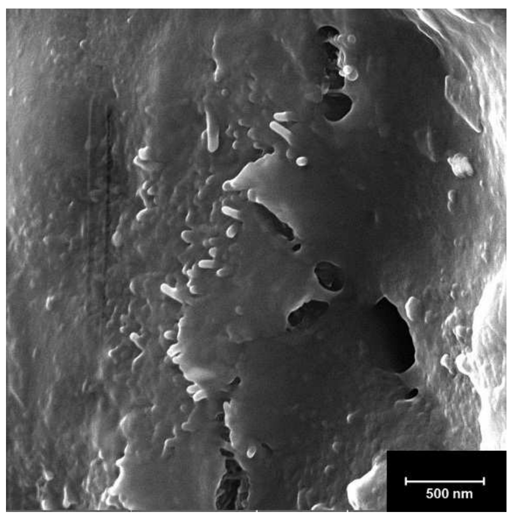

Figure S4. SEM image of hydrogel nanocomposite with 2 wt% non-functionalized MWCNTs

5. Rheological analyses of hydrogels and hydrogel nanocomposites.

The data of loss modulus (G″) versus frequency (ω) of hydrogels with different concetrain of ZnPcTa and hydrogel nanocomposites with the same concetrain of ZnPcTa and different MWCNT contents are shown in **Figure S5- S6.**

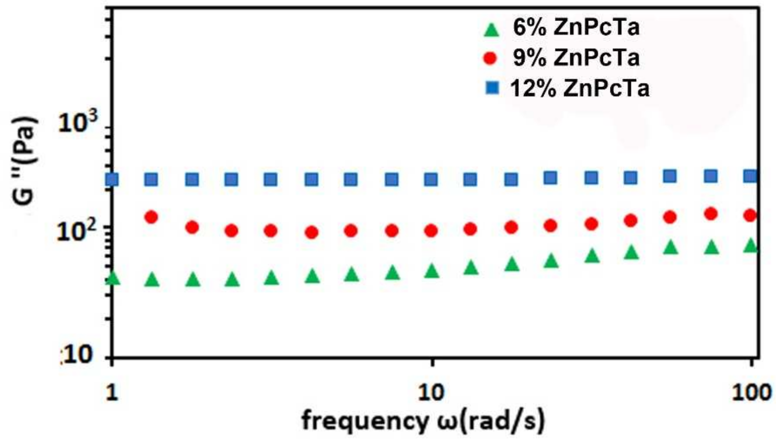

Figure S5. The loss modulus G″ of the hydrogels with different wt% ZnPcTa at a fixed strain, γ = 5.0%.

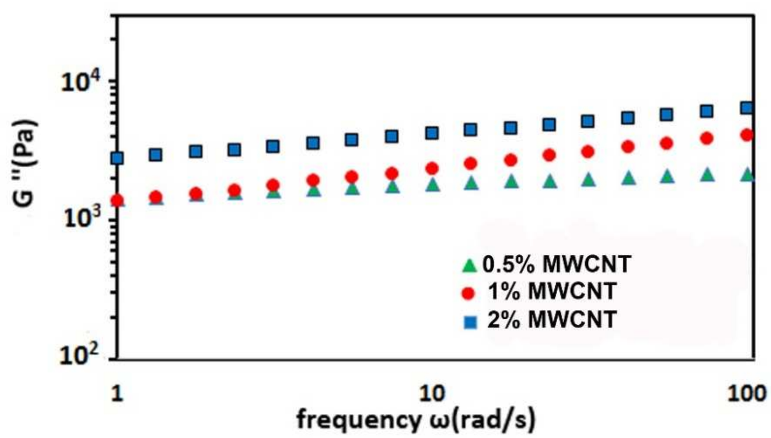

Figure S6. The loss modulus G″ of the hydrogel nanocomposites with 12 wt% ZnPcTa and different wt% MWCNTs at a fixed strain, γ = 5.0%.

5. The effect of various wt% MWCNTs on the healing rate of self-healing hydrogel nanocomposites.

As shown in **Figure S7,** the hydrogel nanocomposites prepared with 12 wt% ZnPcTa and 0, 0.5, 1, and 2 wt% MWCNT, respectively, show healing time of 15 min (m), 18 m, 20 m and 30 m, respectively. These observations are consistent with the previous report that the hydrogel nanocomposites with high wt% MWCNT resulted in a slight decrease in recovery time.

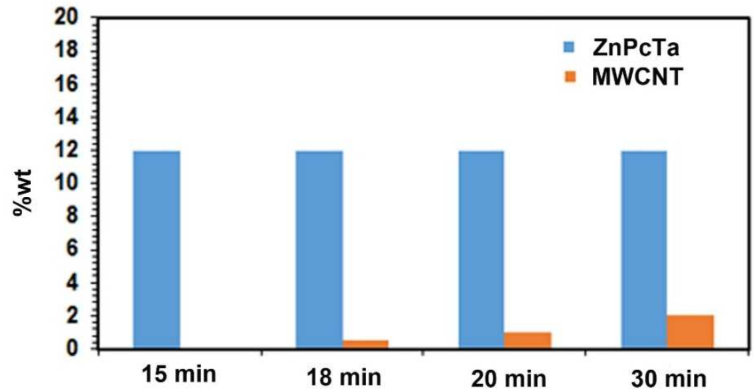

Figure S7. The effect of MWCNTs content on the healing rate of the hydrogel nanocomposites.

6. Self-healing recovery and mechanical properties of some self-healing hydrogels based on dynamic covalent Schiff-base linkage.

We investigate self-healing hydrogels with a focus on methods to test for the efficiencies of self-healing and recovery. This is followed by an explanation of the development of hydrogels that possess both self-healing and robust mechanical properties**.**

Table S1. Self-healing recovery and mechanical properties of some self-healing chemical hydrogels.

Polymer/materials	**Self-healing mechanisms**	**Healing test**	**Self-recovery[%]**	**Mechanical properties**	**Ref**
Telechelic difunctional poly(ethylene glycol) (PEG), and chitosan	Schiff base (imine linkage)	2 h, RT [a)]	100%, <100 s, (2 cycles of γ =20% and 200%, f =1 Hz) [b)]	≈1150 Pa [c)]	**1**
Telechelic difunctional poly(ethylene glycol) (PEG), and glycol chitosan	Schiff base (imine linkage)	12 h, RT [a)]	100%, < 10 s, (3 cycles of γ =1% and 300%, f =1 Hz) [b)]	~0.8 kPa at 25 °C and ~1.5 kPa at 37 °C [c)]	**2**
Chondroitin sulfate multiple aldehyde and N-succinyl-chitosan	Schiff base (imine linkage)	2 h, RT [a)]	-	≈103 Pa [c)]	**3**
zinc phthalocyanine tetra-aldehyde (ZnPcTa)[d)], and chitosan	Schiff base (imine linkage)	15 min, RT [a)]	100%, <100 s, (3 cycles of γ =1% , 80%, 300%,800% f =1 Hz) [b)]	≈2500 Pa at 25 °C [c)]	**-**

[a)] Pieces of cut hydrogel rejoined, [b)] alternative step strain deformation, [c)] storage modulus G′[Pa], [d)] hydrogel with 12 wt% ZnPcTa.

7. The electrical conductance of self-repaired nanocomposites with 12 wt% ZnPcTa and different MWCNT-COOH contents.

Table S2. Electrical healing for 3 cuts at the same severed location of nanocomposites with different MWCNT-COOH contents.

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No.	MWCNT-COOH (wt%)	Conductivity (S/cm)[b]	Conductivity (S/cm)[c]	Conductivity (S/cm)[d]
1[a]	-	4.10×10^{-6}	4.06×10^{-6}	3.96×10^{-6}
2[a]	0.5	2.95×10^{-5}	2.90×10^{-5}	2.87×10^{-5}
3[a]	1	3.19×10^{-4}	3.16×10^{-4}	3.10×10^{-4}
4[a]	2	2.92×10^{-3}	2.87×10^{-3}	2.85×10^{-3}

[a] 12 wt% ZnPcTa; [b] 1st cutting–healing process; [c]2st cutting–healing process; [d] 3st cutting–healing process.

REFERENCES

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