Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

High-Efficiency Self-healing Conductive Composite from HPAMAM and CNTs

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Experimental section

Materials: Cystamine dihydrochloride (≥ 98%, Changzhou Furong Chemical Co.), (N-aminoethyl piperazine (AEPZ, 99%, Aladdin Chemicals), Multi-wall carbon nanotubes (CNTs, diameter ≤ 8 nm, length 0.5~2 μm, Beijing Jiaanheng Science & Technology Co. Ltd). Dichloromethane (≥ 99.5%), methanol (≥ 99.5%) and acetone (≥ 99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. N,N'-Cystaminebisacrylamide (CBA) and HPAMAM were synthesized according to the similar method described in our previous publication.[S1]

Preparation of HPAMAM strips: the synthesized HPAMAM was precipitated by acetone twice first, and then dissolved in methanol; the HPAMAM solution was poured into tanks, standing at room temperature for 24 hours; the samples were transferred to a vacuum oven (30 °C, -0.05 MPa) drying for 4 days. The weight of each of the obtained strips was about 0.5 g.

Preparation of Sushi-like self-healing conductive composite: CNTs (0.1 g) were blended with 2 mL HPAMAM/methanol solution first; the mixed solution was then dropped onto the surface of as prepared HPAMAM strip; after drying at 50 °C completely, the CNTs coated strip was rolled up to obtain Sushi-like composite.

Materials characterization: ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a 600MHz NMR spectrometer (Agilent Technologies VNMRS600) with tetramethylsilane as the internal reference. HPAMAM sample was dissolved with deuterated DMSO. The stress-strain behavior of the original HPAMAM sample and the repaired HPAMAM sample was tested on a universal testing machine (Instron 5565A), under a tensile speed of 100 mm/min. The modulus of the HPAMAM samples was determined according to $E = \Delta\sigma/\Delta\varepsilon$, where the E is the modulus, $\Delta\sigma$ is the increment of stress, and $\Delta\varepsilon$ is the corresponding strain in the initial stage of the stress-strain curves. The modulus of HPAMAM was about 6.02±1.03 MPa. Differential scanning calorimetry (DSC) curves were recorded on a DSC-822e (Mettler Toledo, Swiss) in a dry nitrogen atmosphere. The heating rate was 10 °C/min. Fluorescent pictures of the Sushi-like structure was recorded by a digital camera (Olympus SP-620UZ) under UV irradiation with wavelength of 365nm.

Conductivity characterization: An AC power supply of 6 V was used in this work. The resistance of the Sushi-like conductive composites was measured by a digital Ohm meter (Cat-II, Electro-Tek). The surface conductivity of the conductive composites before wrapping was determined by a multifunction digital four-probe tester ST-2258A (Suzhou Jingge Electronic Co., Ltd.).

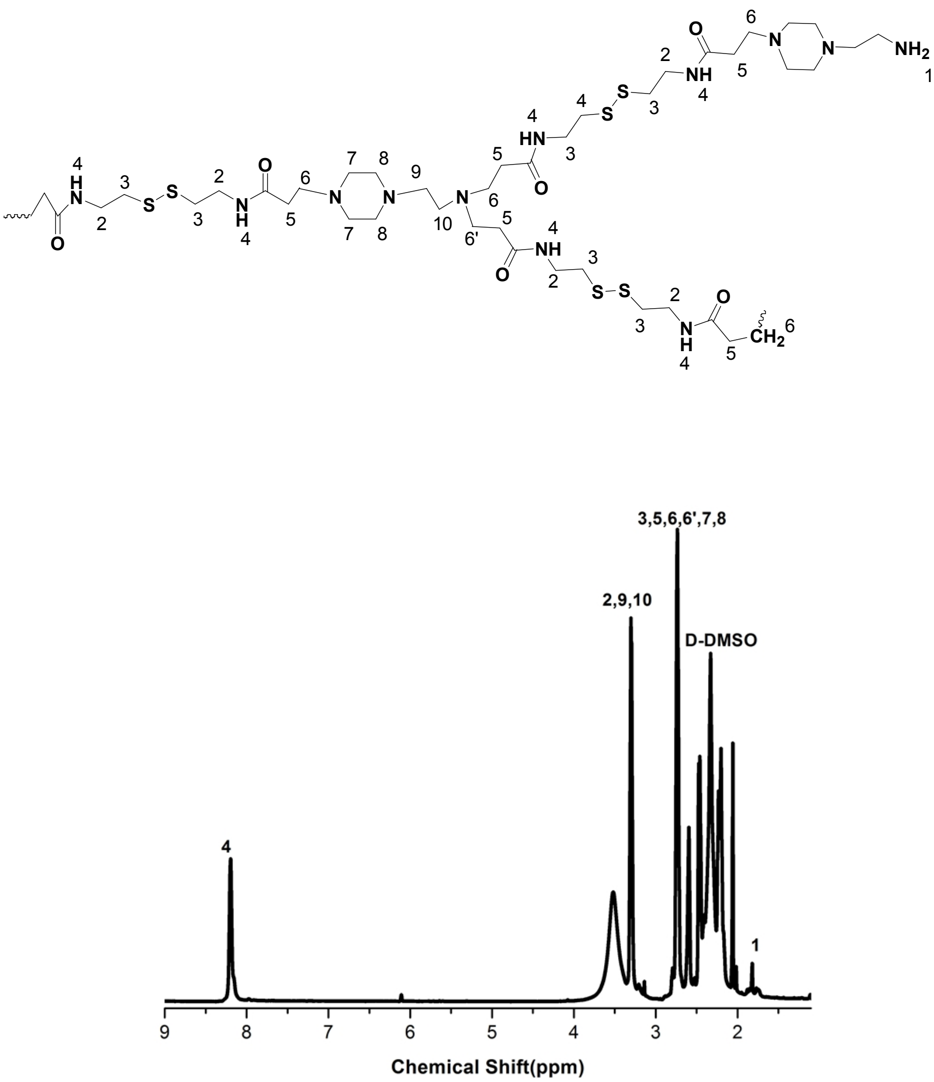

Fig. S1 ^{1}H NMR spectrum of HPAMAM sample

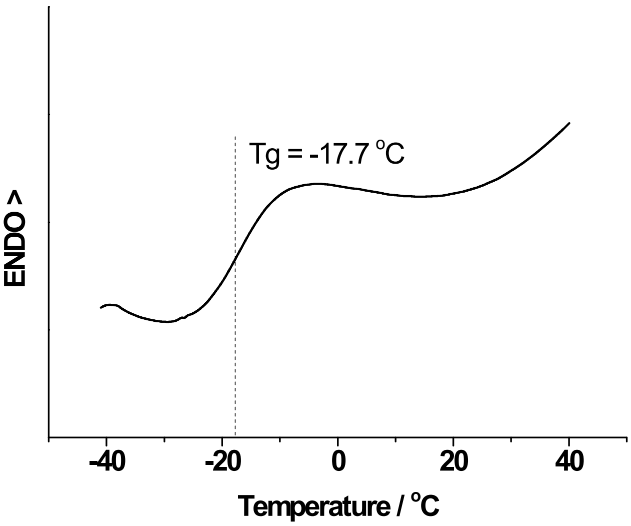

Fig. S2 Glass transition temperature of HPAMAM determined by DSC measurement

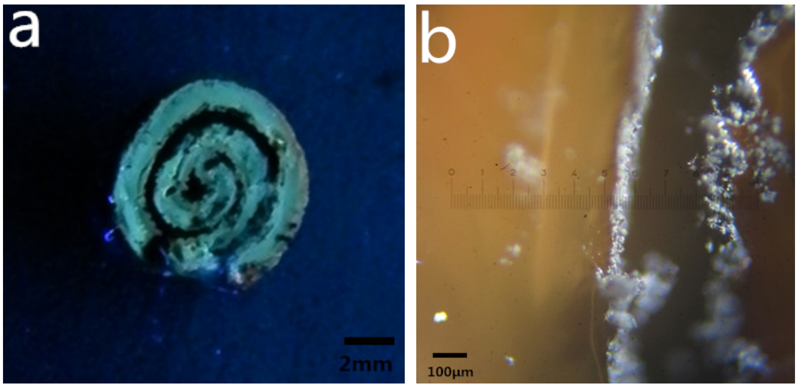

Fig. S3 (a) HPAMAM/CNT self-healing conductive composites under UV irradiation, clear Sushi-like structure could be seen; (b) local parts of the composite, indicating the thickness of the CNT layer to be about 200 μm.

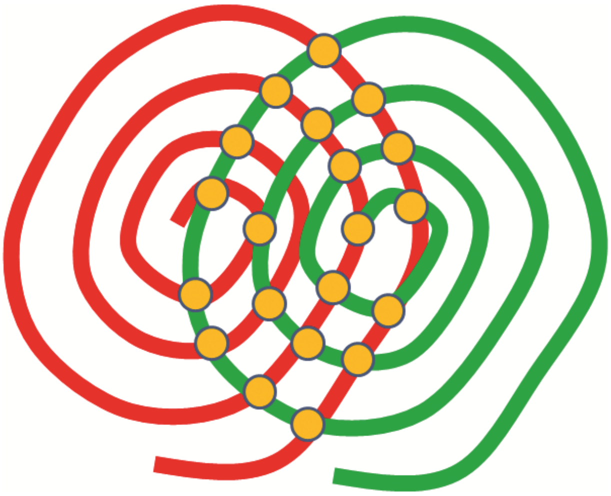

Fig. S4 Overlapping of conductive pathways Conductive Sushi when the fracture surfaces are contact with each other. The yellow points indicate the contact points of conductive pathways.

Fig. S5 (a) HPAMAM sample in original state: the gauge was 10 mm; (b) HPAMAM sample was extended to a length more than 150 mm

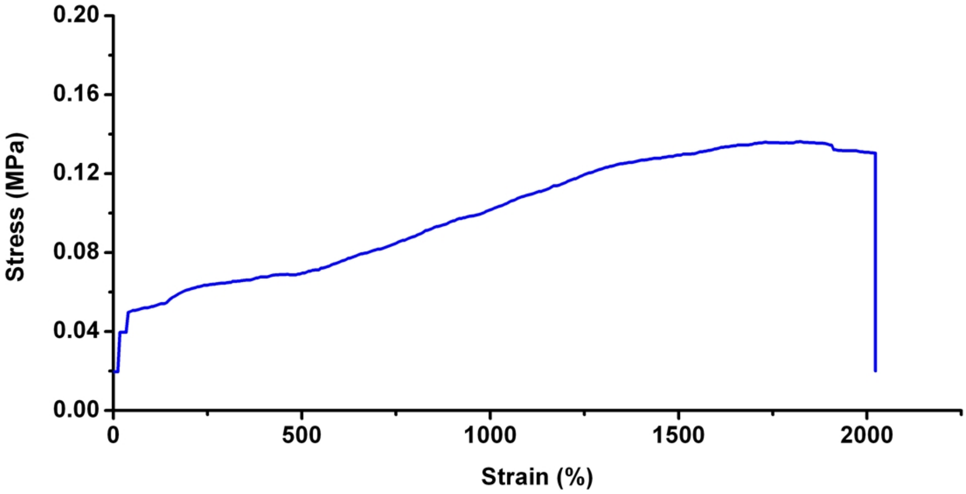

Fig. S6 Stress-strain curve of HPAMAM

At room temperature, the HPAMAM sample showed good flexibility and could be largely extended (Fig. S5†). The stress-strain behavior of the HPAMAM is very special. As shown in Figure S6†, the elongation at break was as large as 2000%. It was only found in a few hydrogels.[S2,S3] For many of the self-healing materials, the strain was less than 1000% (reference to Table S1). On the other hand, the maximum strength of the HPAMAM is about 120 kPa, comparable to that of the supramolecular polymers used in Dickey's report[S4] and in self-healing supercapacitors.[S5] Moreover, the strength of HPAMAM is of great potential to be improved through combining with graphene oxide.[S6] It is highly possible that a lot of functional self-healing materials with better mechanical performance can be obtained with HPAMAM as the substrate polymer.

Table S1 Self-healing ability of polymers materials/hydrogels

No.	Original stress (MPa)	Time for 50% recovery of stress	Time for more than 90% stress recovery	Original strain (%)	Time for 50% recovery of strain	Time for more than 90% strain recovery	Mechanism	References
1	~ 0.5	~ 1 min	~ 1 h	~550	~ 1 min	> 10 min	H-bonds	S6
2	~ 3.1	~ 6 min	~ 60 min	~500	~ 6 min	~ 60 min	ionic interaction	S7
3	~ 0.5	~ 15 min	~ 60 min	~70	~ 15 min	~ 60 min	disulfide bonds	S8
4	~ 3.5	~ 120 min	> 180 min	~650	~ 60 min	~ 180 min	H-bonds	S9
5	~ 0.18	~ 1 h	~ 24 h	~200	> 1 h	~ 24 h	disulfide bonds	S10
6	~ 1.9	> 1 h	~ 24 h	~800	~ 1 h	~ 24 h	H-bonds	S11
7	~ 0.275	> 1 h	> 48 h	~400	~ 1 h	> 48 h	H-bonds	S12
8	~ 0.08	> 1 h	~ 10 h	~1600	> 1 h	~ 10 h	H-bonds	S2
9	~ 0.08	~ 2 h	~ 6 h	~500	> 1 h	~ 6 h	Diaryl-bibenzofuranone bonds	S13
10	~ 0.35	> 2 h	~ 24 h	~5000	~ 1 h	~ 24 h	H-bonds	S3
11	~ 1.35	~ 0.5 h	~ 18 h	~600	> 5 h	> 18 h	H-bonds	S14
12	~ 0.025	> 24 h	> 48 h	~ 100	> 24 h	> 48 h	disulfide bonds/acryl-hydrazone bonds	S15
13	~ 1.5	> 1 day	>10 days	~450	> 1 day	> 10 days	D-A reaction	S16
14	0.13	< 1 min	~ 5 min	~2000	~ 1 min	~ 5 min	H-bonds/disulfide bonds	Present Work*

Note: the dynamic self-healing process of HPAMAM can be found in the online video.

Table S2 Variation of electric resistance of the self-healing conductive composites

Time (min)	Resistance of Sample #1 (kΩ)	Resistance of Sample #2 (kΩ)	Resistance of Sample #3 (kΩ)	Average Resistance (kΩ)	Standard Deviation	
1	1.14	1.20	1.15	1.16	0.03	Before Disconnection
2	1.11	1.21	1.17	1.16	0.05	
3	1.10	1.18	1.20	1.16	0.05	
4	1.08	1.17	1.18	1.14	0.06	
5	1.06	1.15	1.16	1.12	0.06	
6	1.05	1.14	1.16	1.12	0.06	
7	1.04	1.13	1.15	1.11	0.06	
8	1.04	1.13	1.14	1.10	0.06	
9	1.02	1.12	1.13	1.09	0.06	
10	1.02	1.12	1.12	1.09	0.06	
1’	3.74	3.29	3.89	3.64	0.31	After connection
2’	3.51	3.24	3.01	3.25	0.25	
3’	2.96	2.85	2.75	2.85	0.11	
4’	2.68	2.80	2.65	2.71	0.08	
5’	2.56	2.68	2.50	2.58	0.09	
6’	2.40	2.33	2.45	2.39	0.06	
7’	2.29	2.20	2.37	2.29	0.09	
8’	2.23	2.12	2.21	2.19	0.06	
9’	2.14	2.09	2.07	2.10	0.04	
10’	1.98	1.90	1.88	1.92	0.05	
11’	1.79	1.74	1.88	1.80	0.07	
12’	1.67	1.69	1.76	1.71	0.05	
13’	1.58	1.59	1.67	1.61	0.05	
14’	1.43	1.45	1.55	1.48	0.06	
15’	1.31	1.33	1.44	1.36	0.07	
16’	1.27	1.35	1.30	1.31	0.04	
17’	1.16	1.24	1.21	1.20	0.04	
18’	1.15	1.24	1.19	1.19	0.05	

Table S3 Variation of electric resistance of the self-healing conductive composites poorly aligned

Time (min)	Resistance of Sample #1 (kΩ)	Resistance of Sample #2 (kΩ)	Resistance of Sample #3 (kΩ)	Average Resistance (kΩ)	Standard Deviation	
1	1.05	1.10	1.09	1.08	0.03	Before Disconnection
2	1.01	1.08	1.07	1.05	0.04	
3	0.97	1.06	1.07	1.03	0.06	
4	0.96	1.05	1.06	1.02	0.06	
5	0.95	1.06	1.07	1.03	0.07	
6	0.96	1.05	1.03	1.01	0.05	
7	0.95	1.06	1.05	1.02	0.06	
8	0.95	1.05	1.03	1.01	0.05	
9	0.95	1.03	1.01	1.00	0.04	
10	0.94	1.04	1.02	1.00	0.05	
1’	7.50	6.84	7.10	7.15	0.33	After connection
2’	5.31	4.06	5.25	4.87	0.71	
3’	3.01	3.15	3.45	3.20	0.22	
4’	2.51	2.64	2.85	2.67	0.17	
5’	2.42	2.52	2.70	2.55	0.14	
6’	2.21	2.49	2.58	2.43	0.19	
7’	2.18	2.38	2.47	2.34	0.15	
8’	2.14	2.26	2.40	2.27	0.13	
9’	2.10	2.19	2.31	2.20	0.11	
10’	2.01	2.10	2.27	2.13	0.13	
11’	1.98	2.02	2.17	2.06	0.10	
12’	1.94	1.96	2.10	2.00	0.09	
13’	1.92	1.87	1.95	1.91	0.04	
14’	1.90	1.79	1.80	1.83	0.06	
15’	1.87	1.64	1.71	1.74	0.12	
16’	1.80	1.53	1.62	1.65	0.14	
17’	1.71	1.40	1.47	1.53	0.16	
18’	1.64	1.28	1.27	1.40	0.21	

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