Supporting Information

Non-covalent Assembly Super-tough, Highly Stretchable and Environmentally Adaptable Self-healing Material Inspired by Nacre

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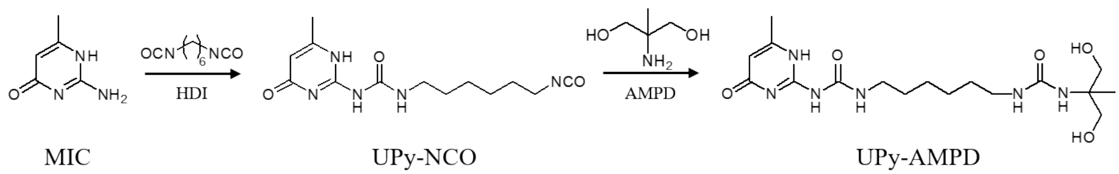

Fig. S1 Synthetic route of UPy-AMPD.

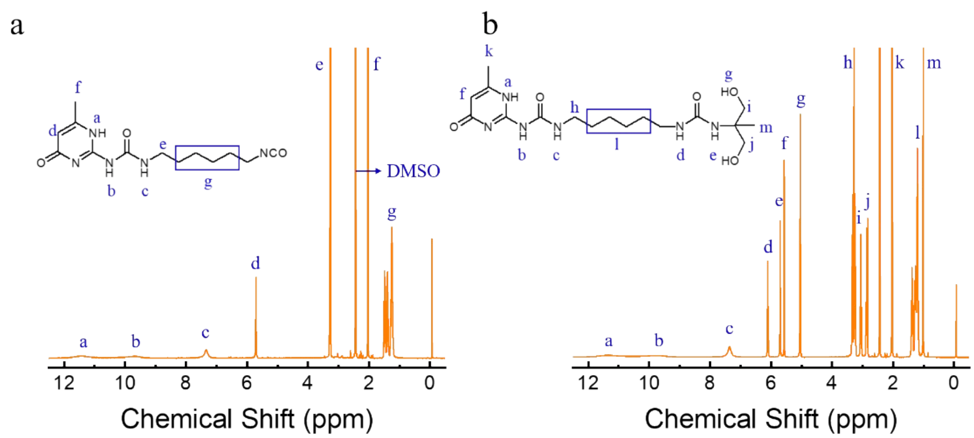

Fig. S2 ^{1}H NMR spectra (DMSO-d6) of (a) UPy-NCO and (b) UPy-AMPD.

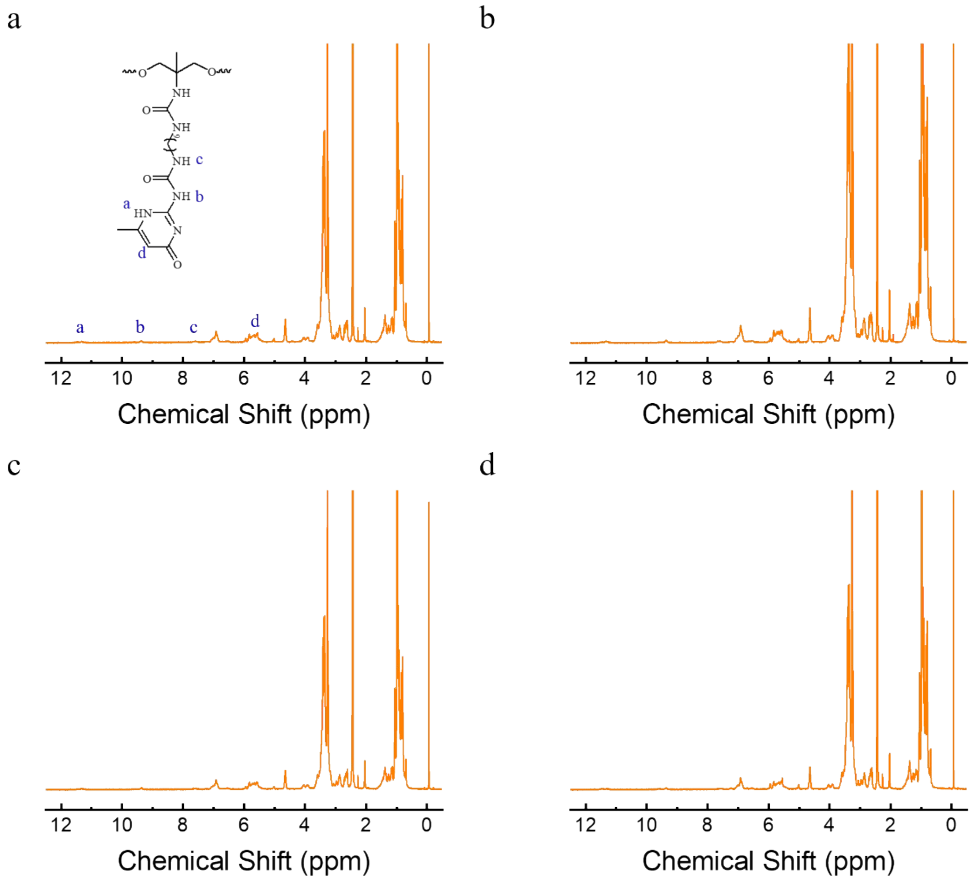

Fig. S3 ^{1}H NMR spectra (DMSO-d6) of (a) PU-UPy-AMPD, (b) PU-PDG-0.2%, (c) PU-PDG-0.5%, and (d) PU-PDG-1.0%.

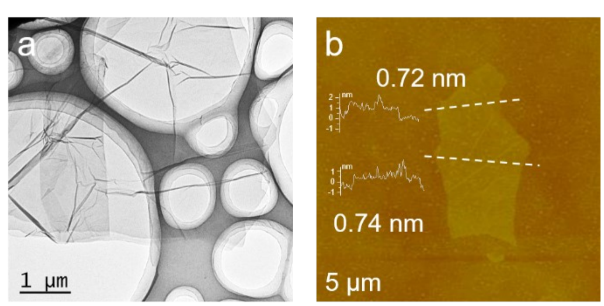

Fig. S4 (a) TEM and (b) SPM images of GO nanosheets.

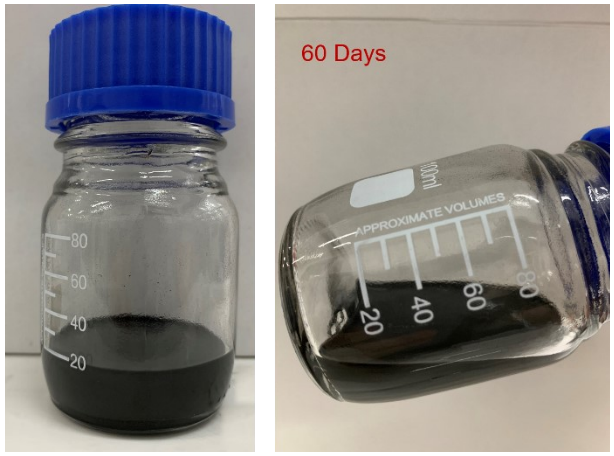

Fig. S5 Optical picture of the dispersibility of PDG nanosheets in water.

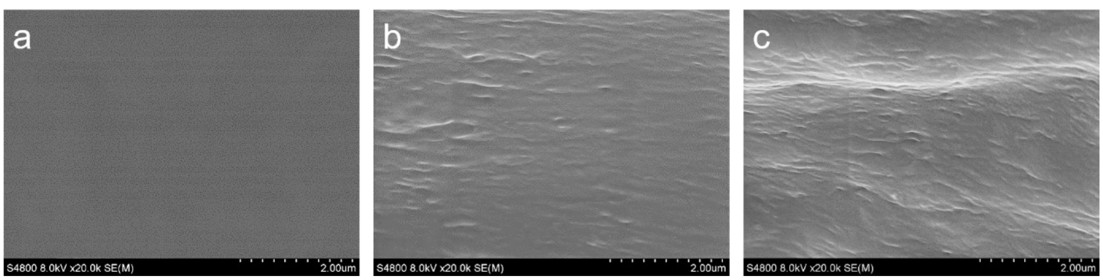

Fig. S6 Cross-sectional SEM images of (a) PU-UPy-AMPD, (b) PU-PDG-0.2%, and (c) PU-PDG-1.0%.

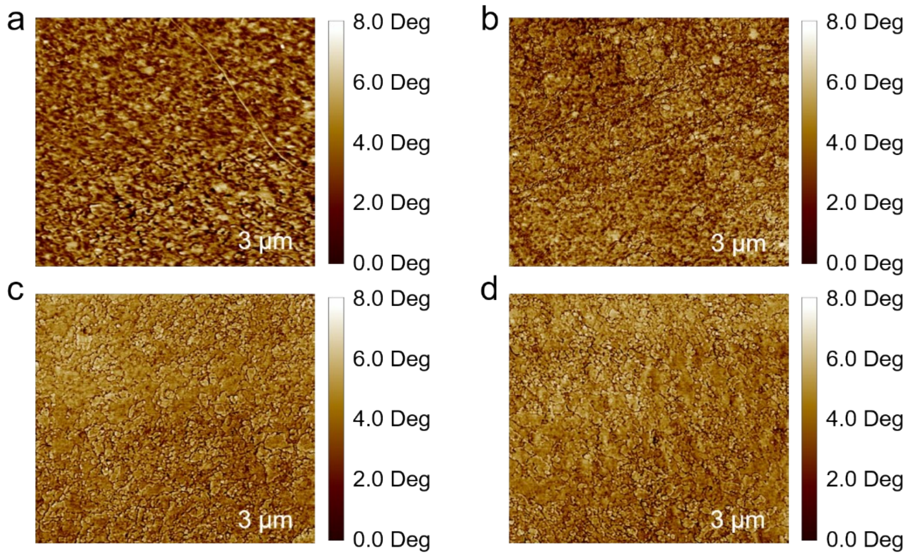

Fig. S7 SPM images of (a) PU-UPy-AMPD, (b) PU-PDG-0.2%, (c) PU-PDG-0.5%, and (d) PU-PDG-1.0%.

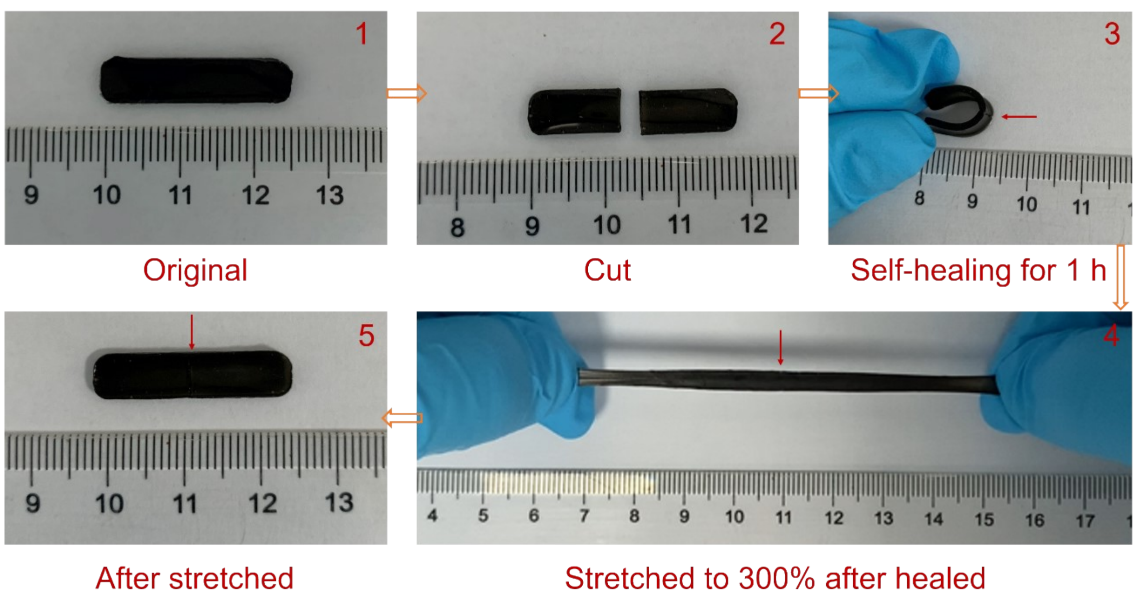

Fig. S8 Optical photo of PU-PDG-0.5% stretching process after healed at room temperature for 1 hour.

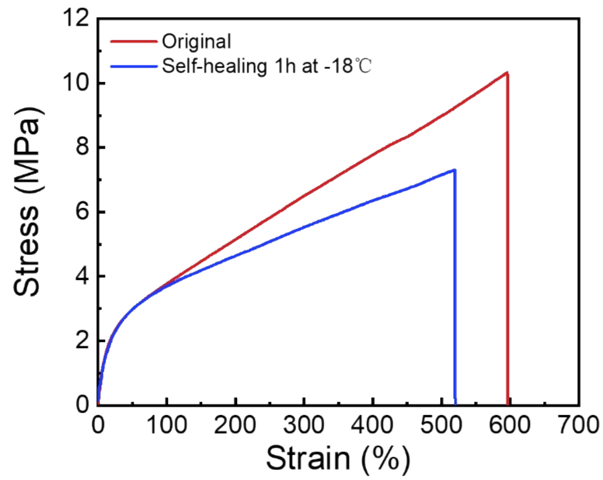

Fig. S9 Stress-strain curve of PU-PDG-0.5% after self-healing at -18 °C for 1 h.

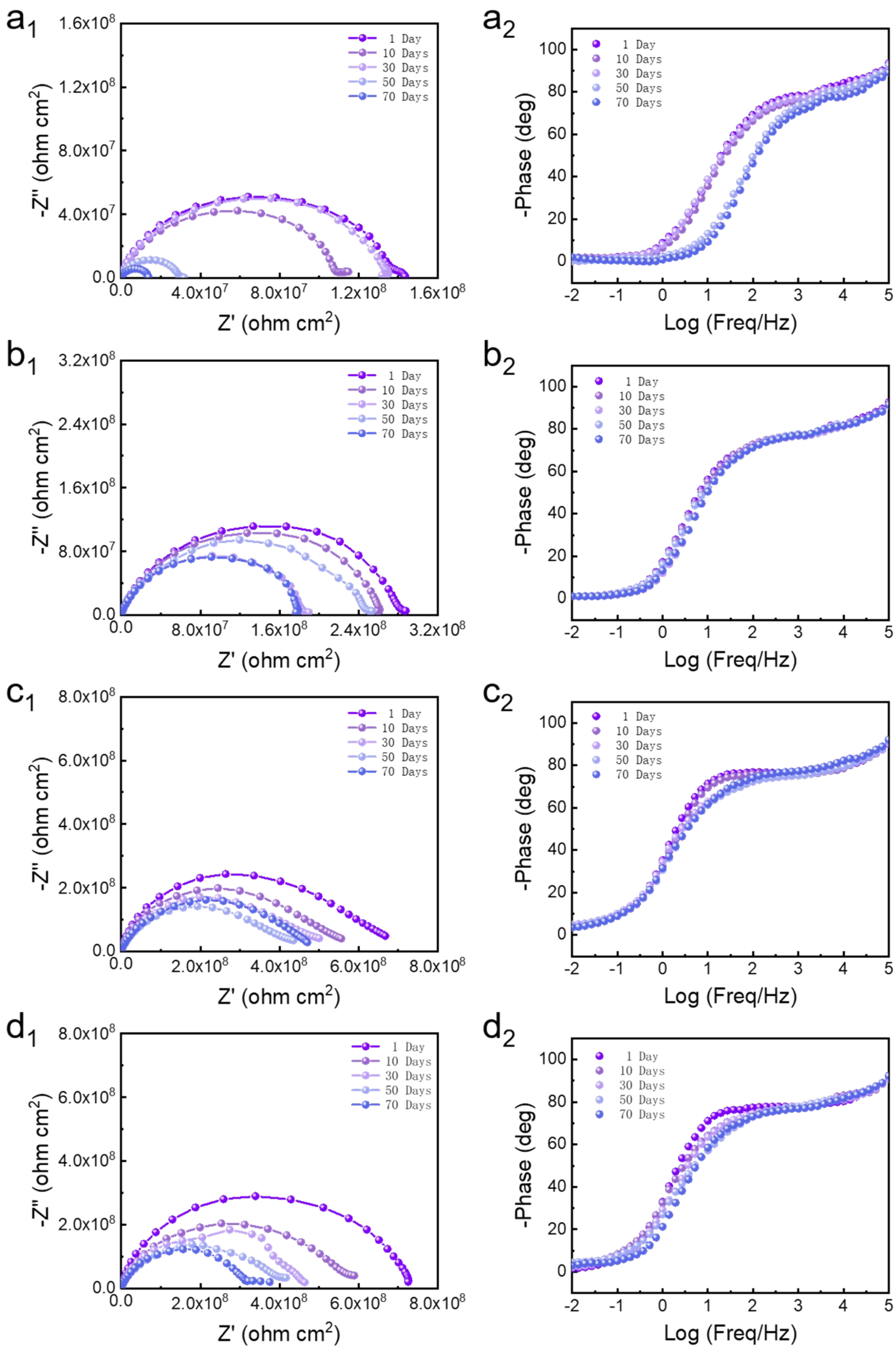

Fig. S10 Nyquist and Bode-Phase plots of (a) PU-UPy-AMPD, (b) PU-PDG-0.2%, (c) PU-PDG-0.5%, and (d) PU-PDG-1.0%.

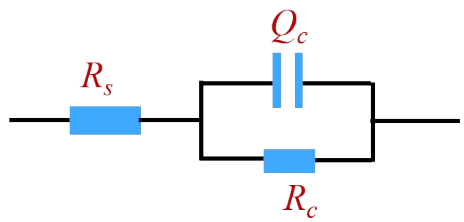

Fig. S11 Electrochemical simulation circuit diagram of the PU composite materials.

In the equivalent circuit model diagram, R_s represents solution resistance, R_c represent the resistance of coating, and *Qc* is the capacitance of the coating.

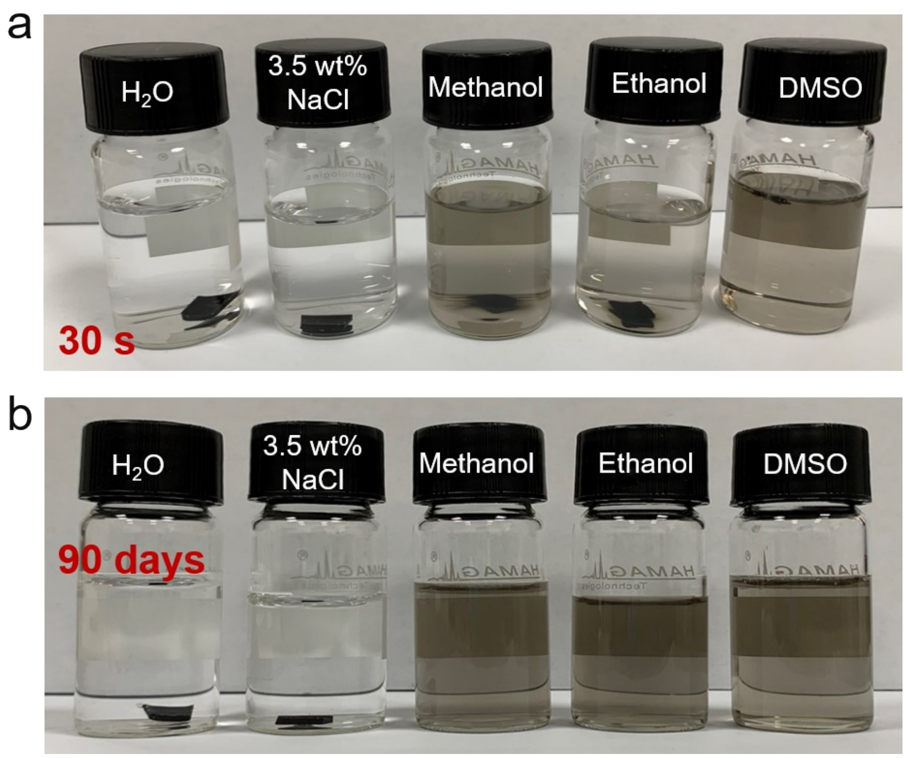

Fig. S12 Optical photos of PU-PDG-0.5% immersed in different solvents for different time.

Table S1 Comparison of elongation at break, ultimate tensile strength, Young's modulus, toughness, and self-healing efficiency of samples.

Samples	Elongation at break (%)	Ultimate tensile strength (MPa)	Young's modulus (MPa)	Toughness (MJ m^{-3})	Self-healing efficiency (%)
PU-UPy-AMPD	612.3±11.4	6.6±0.1	22.7±0.3	25.3±0.4	90.7±2.4
PU-PDG-0.2%	600.7±14.8	8.0±0.2	20.24±0.5	29.5±0.6	90.3±2.2
PU-PDG-0.5%	596.2±8.2	10.3±0.5	31.5±0.6	37.8±0.8	89.3±1.8
PU-PDG-1.0%	574.0±8.4	8.8±0.2	46.5±0.8	31.1±0.7	80.1±1.6

Table S2 Comparison of elongation at break, ultimate tensile strength, toughness, and self-healing efficiency of various self-healing polymers.

Ref.	Elongation at break (%)	Ultimate tensile strength (MPa)	Toughness (MJ m^{-3})	Self-healing efficiency (%)	Self-healing conditions
This work	596	10.4	37.8	89.1	RT. 1 h
1	923	6.8	26.9	76.6	RT. 2 h
2	1700	1.7	15.3	78.0	RT. 48 h
3	310	1.1	1.4	76.0	RT. 48 h
4	1200	0.6	3.6	93.0	NIR 1 min
5	560	4.4	12.0	91.6	RT. 120 h
6	780	1.9	10.0	80.0	RT. 24 h
7	600	3.4	8.0	75.0	RT. 3 h
8	310	3.5	6.8	77.9	RT. 24 h
9	700	2.1	6.6	76.2	RT. 24 h
10	58	4.4	1.4	85.7	RT. 72 h
11	780	1.9	11.4	87.6	RT. 6 h

RT. stands for room temperature, NIR stands for near-infrared, self-healing efficiency = $\sigma_{healing}/\sigma_{original}$.

Table S3 Comparison of elongation at break, ultimate tensile strength, Young's modulus, toughness, and self-healing efficiency of PU-PDG-0.5% under different healing time.

Healing times (min)	Elongation at break (%)	Ultimate tensile strength (MPa)	Young's modulus (MPa)	Toughness (MJ m^{-3})	Self-healing efficiency (%)
5	429.8±8.1	3.3±0.6	17.5±0.7	8.5±0.7	32.0±1.7
15	492.0±6.2	6.0±0.4	24.0±0.2	18.3±0.4	58.3±2.1
30	513.7±6.8	6.7±0.5	24.2±0.5	22.8±0.6	65.0±1.6
45	531.0±5.6	8.1±0.3	26.8±0.4	28.1±0.9	78.6±1.9
60	564.7±7.4	9.2±0.5	28.8±0.6	33.5±0.8	89.3±1.8

Table S4 Comparison of Log ($Z_{f=0.01\mathrm{Hz}}$) of different samples under different immersion time.

Log ($Z_{f=0.01\mathrm{Hz}}$/ohm)	Immersion times (day)				
	1	10	30	50	70
PU-UPy-AMPD	8.16±0.24	8.06±0.19	8.12±0.23	7.50±0.16	7.14±0.11
PU-PDG-0.2%	8.46±0.22	8.42±0.24	8.28±0.22	8.40±0.28	8.25±0.25
PU-PDG-0.5%	8.83±0.52	8.75±0.45	8.70±0.49	8.64±0.29	8.67±0.23
PU-PDG-1.0%	8.86±0.78	8.77±0.46	8.67±0.61	8.62±0.44	8.57±0.28

Table S5 Comparison of Log R_s of different samples under different immersion time.

R_s (ohm)	Immersion times (day)				
	1	10	30	50	70
PU-UPy-AMPD	$1.37\pm0.58\times10^8$	$1.09\pm0.46\times10^8$	$1.31\pm0.53\times10^8$	$3.00\pm1.64\times10^7$	$1.38\pm0.83\times10^7$
PU-PDG-0.2%	$2.82\pm0.49\times10^8$	$2.63\pm0.54\times10^8$	$1.86\pm0.48\times10^8$	$2.48\pm0.62\times10^8$	$1.77\pm0.59\times10^8$
PU-PDG-0.5%	$6.76\pm1.12\times10^8$	$5.62\pm0.86\times10^8$	$5.01\pm1.02\times10^8$	$4.36\pm0.66\times10^8$	$4.67\pm0.54\times10^8$
PU-PDG-1.0%	$7.24\pm1.54\times10^8$	$5.88\pm0.99\times10^8$	$4.67\pm1.25\times10^8$	$4.16\pm0.91\times10^8$	$3.27\pm0.68\times10^8$

Supporting References

[1] S. M. Kim, H. Jeon, S. H. Shin, S. A. Park, J. Jegal, S. Y. Hwang, D. X. Oh, J. Park, *Adv. Mater.* **2017**, *30*, 1705145.

[2] J. Kang, D. Son, G. Wang, Y. Liu, J. Lopez, Y. Kim, J. Y. Oh, T. Katsumata, J. Mun, Y. Lee, *Adv. Mater.* **2018**, *30*, 1706846.

[3] Y. L. Rao, A. Chortos, R. Pfattner, F. Lissel, Y. C. Chiu, V. Feig, J. Xu, T. Kurosawa, X. Gu, W. Chao, *J. Am. Chem. Soc.* **2016**, *138*, 6020.

[4] P. Song, H. Qin, H. L. Gao, H. P. Cong, S. H. Yu, *Nat. Commun.* **2018**, *9*, 2786.

[5] A. Susa, R. K. Bose, A. M. Grande, V. Sybrand, S. J. Garcia, *ACS Appl. Mater. Inter.* **2016**, *8*, 34068.

[6] Y. Chen, A. M. Kushner, G. A. Williams, Z. Guan, *Nat. Chem.* **2012**, *4*, 467.

[7] C. Philippe, T. Franois, S.-Z. Corinne, L. Ludwik, *Nature* **2008**, *451*, 977.

[8] J. Li, H. Ejima, N. Yoshie, *ACS Appl. Mater. Inter.* **2016**, *8*, 19047.

[9] H. Sardon, J. Zhu, L. Irusta, D. Mecerreyes, X. An, R. Hernandez, N. Aramburu, F. Ruipérez, J. M. Matxain, X. Pan, *Polym. Chem.* **2017**, 10.1039.C7PY00448F.

[10] J. J. Cash, T. Kubo, A. P. Bapat, B. S. Sumerlin, *Macromolecules* **2015**, *48*, 2098.

[11] Y. Yao, Z. Xu, B. Liu, M. Xiao, J. Yang, W. Liu, *Adv. Funct. Mater.* **2020**, 2006944.