Electronic Supplementary Information

Extremely Tough and Healable Elastomer Realized via Reducing the Crystallinity of Rigid Domain

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Materials

Hexamethylene diisocyanate (HDI), poly (tetrahydrofuran) (PTMG, M_n = 1000 g/mol) and dibutyltin dilaurate (DBTDL) were purchased from Sigma-Aldrich. 2,2-Bis (hydroxymethyl) propionic acid (DMPA) was purchased form J&K. **Anhydrous** $FeCl_3$, $ZnCl_2$ and $CuCl_2$ were purchased from Alfa Aesar. *N,N*-dimethyl Formamide (DMF) was purchased from Shanghai Titan Chemistry Co., Ltd.. HDI, PTMG and DMPA should be dried at 85 °C in vacuum oven for 12h before used, DMF was distilled and preserved with 4A molecular sieve.

Synthesis of metal ion-carboxyls coordinated PU

DBTDL catalyst (5 μL) was dropped into a mixture of dried HDI (12 mmol, 2.016 g) and dried PTMG (M_n = 1000, 6 mmol, 6.0 g) at 55 °C with argon protection to synthesize the prepolymer. After reaction for 1.5h, the temperature rose to 70 °C and a mixture of DMPA (0.804 g, 6 mmol) and **anhydrous** $FeCl_3$, $ZnCl_2$ or $CuCl_2$ (0-1.5mmol, the detail amount could be found in **Table S1**.) was dissolved in distilled DMF and added to the prepolymer. After a 15-60min stirring (**FePU**/**CuPU** 15-30min, **ZnPU** ~60min), the viscous mixture was degassed and then transferred into a polytetrafluoroethylene plate and cured for 12h at 70 °C.

Characterizations

The tensile tests were performed by stretching dumbbell samples with a rate of 50 mm/min under ambient atmosphere (23±2 °C) on an INSTRON 5944 machine. For self-healing test, the sample was cut into two pieces and then contacted with each other in 30 s, and then cured at 60±5 °C (40±10% RH). The fracture tests were carried out by using classical single-edge test and the calculation of fracture toughness (G_c) was expressed by following equation:

$$G_c = \frac{2\pi\alpha W_c}{\sqrt{\lambda_c}}$$

where α is the notch length, λ_c is the stretch ratio of notched samples, W_c is the strain energy calculated by integration of stress-strain curve of origin samples until λ_c. The detail data could be seen in **Table S2**, the W_0 in **Table S2** is the toughness which calculated by integration of stress-strain curve of origin samples.

The ITC titration was carried out using a GE ITC200 instrument, samples were

prepared in a solution of anhydrous methanol at 25 °C.

DMA tests were performed on a DMA Q800, samples were performed from -80 to 150 °C with a 0.2% strain, 10Hz. The fourier transform infrared spectra (FTIR) were recorded on a TENSOR27 spectrophotometer (ATR mode, scanned from 4000 to 400 cm^{-1}).

The SAXS measurement was carried out using Beamine 4-2 at Stanford Synchrotron Radiation Lightsource (SSRL) of SLAC National Accelerator Laboratory (SLAC). The incident x-ray beam with an energy of 15 keV was used.

The XRD measurement was performed from a BRUKER D8 ADVANCE diffractometer with a Cu Kα X-ray source (λ = 1.540598 Å). The morphologies of polyurethane samples were observed by transmission electron microscopy (TEM) (JEM-2100), the sample was prepared by dropping diluted mixture of prepolymer and chain extender on bronze net and then cured at 70 °C for 12h.

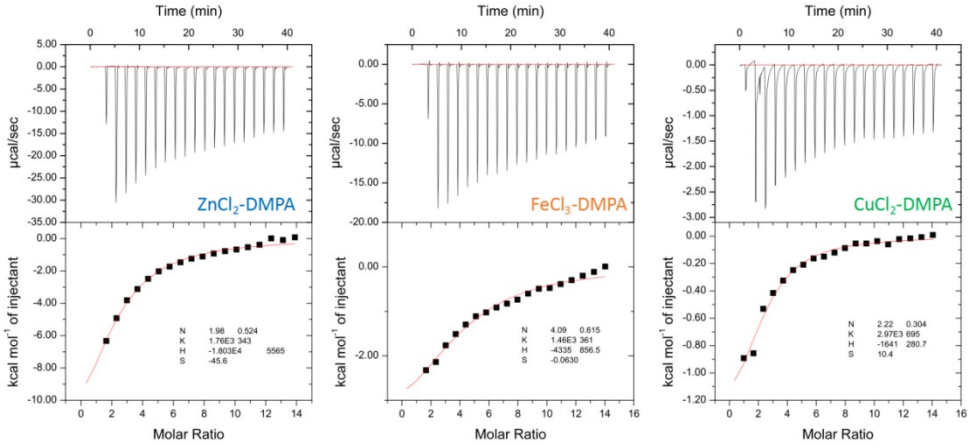

Figure S1. The ITC titration curve of the DMPA mixed with $ZnCl_2$, $FeCl_3$ and $CuCl_2$ in anhydrous methanol at 25 °C.

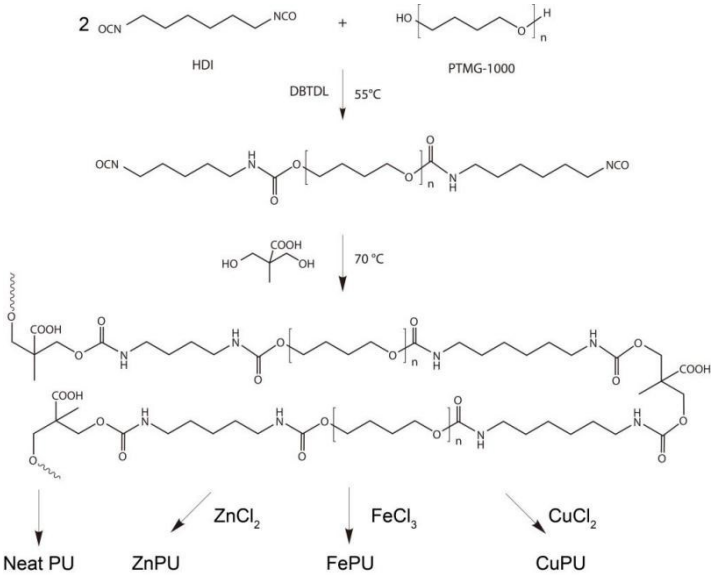

Figure S2. The detail synthetic route of **Neat PU**, **FePU**, **ZnPU** and **CuPU**.

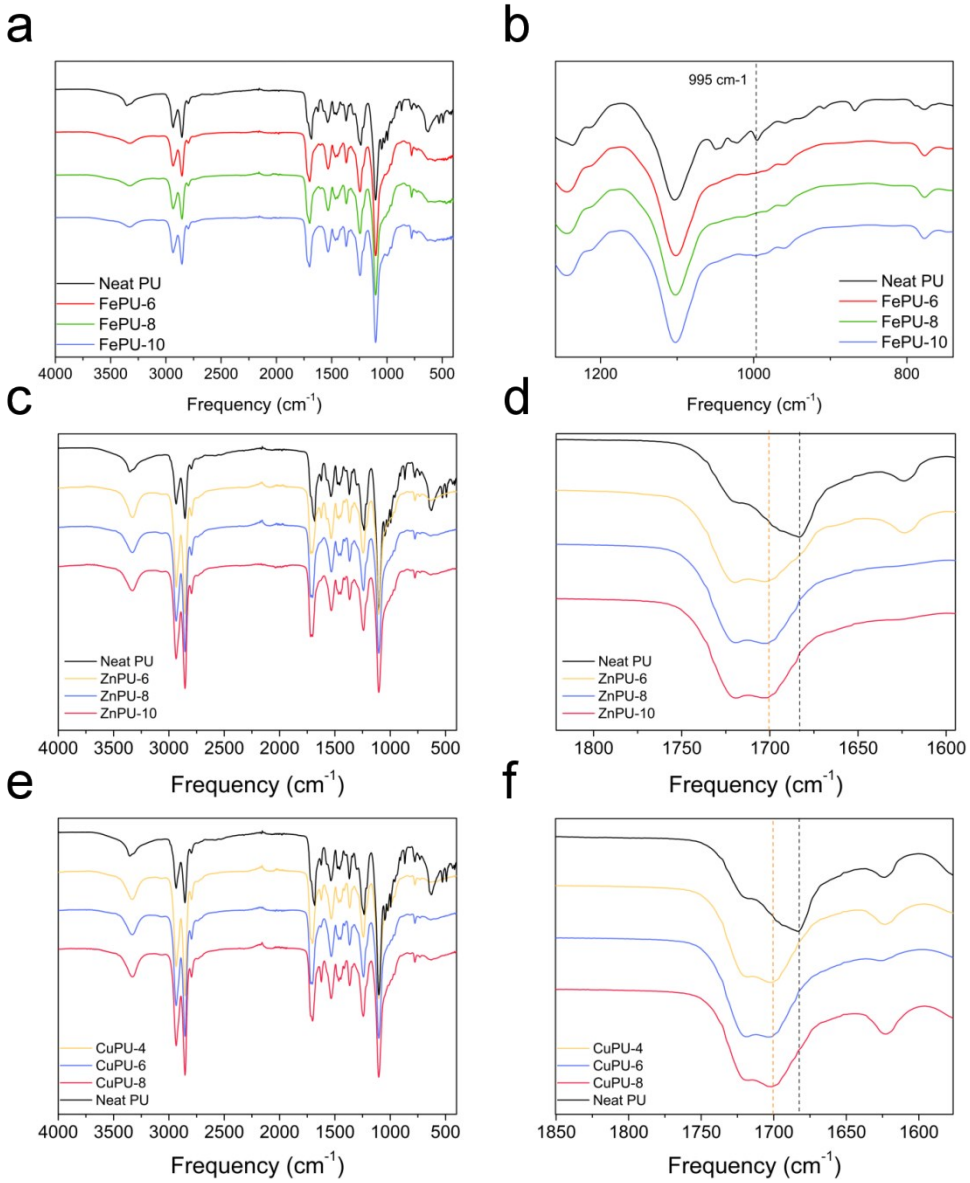

Figure S3. (a) FT-IR spectrum of **Neat PU**, **FePU-6**, **FePU-8** and **FePU-10** (b) Detail FT-IR spectrum of crystalline peak related to hard segment in **Neat PU, FePU-6, FePU-8 and FePU-10.** (c) FT-IR spectrum of **Neat PU**, **ZnPU-6**, **ZnPU-8** and **ZnPU-10**. (d) Detail FT-IR spectrum of amide I region of **Neat PU**, **ZnPU-6**, **ZnPU-8** and **ZnPU-10**. (e) FT-IR spectrum of **Neat PU**, **CuPU-4**, **CuPU-6** and **CuPU-8**. (f) Detail FT-IR spectrum of amide I region of **Neat PU**, **CuPU-4**, **CuPU-6** and **CuPU-8**.

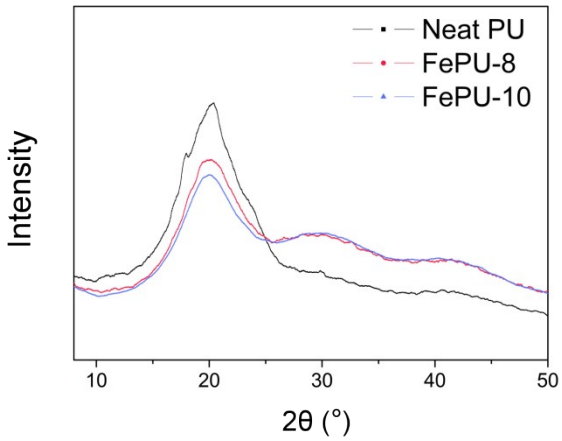

Figure S4. XRD of **Neat PU**, **FePU-6** and **FePU-8**.

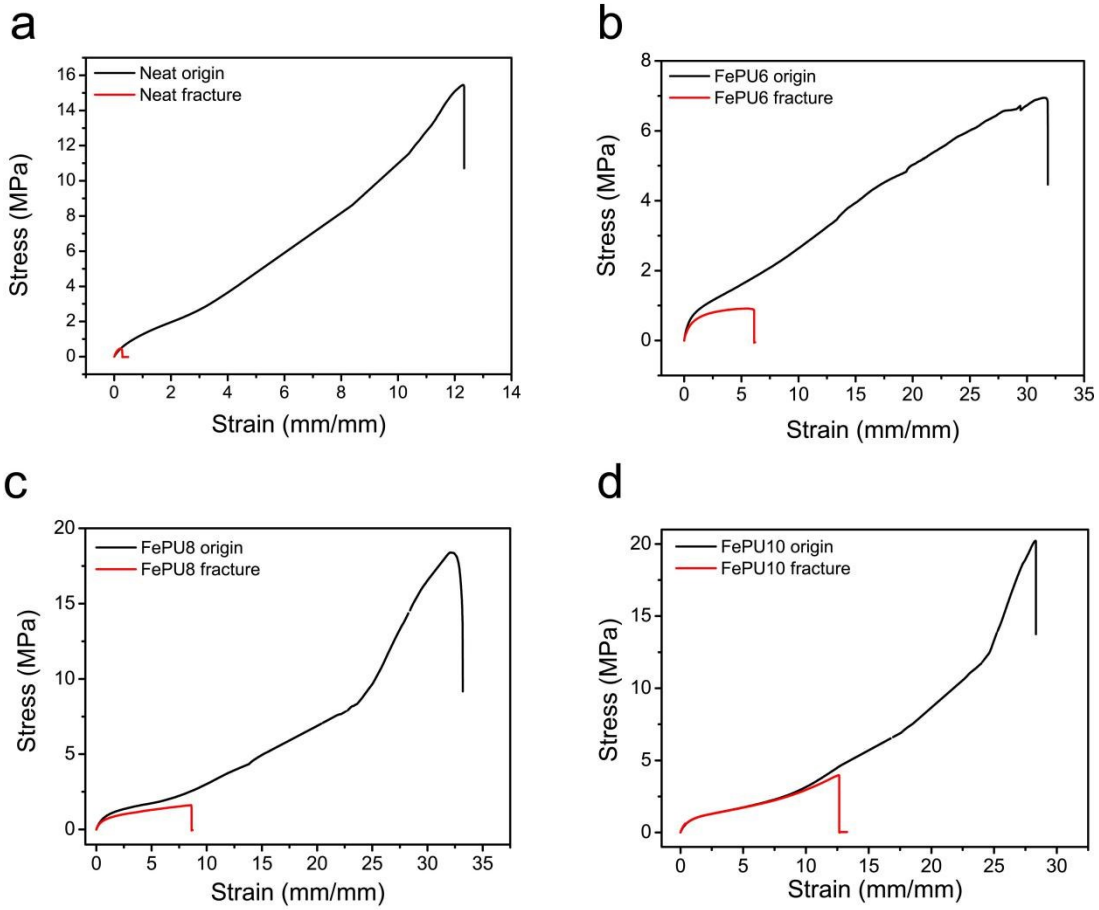

Figure S5. Stress−strain curves for a) **Neat PU** b) **FePU-6** c) **FePU-8** d) **FePU-10** in single-edge test.

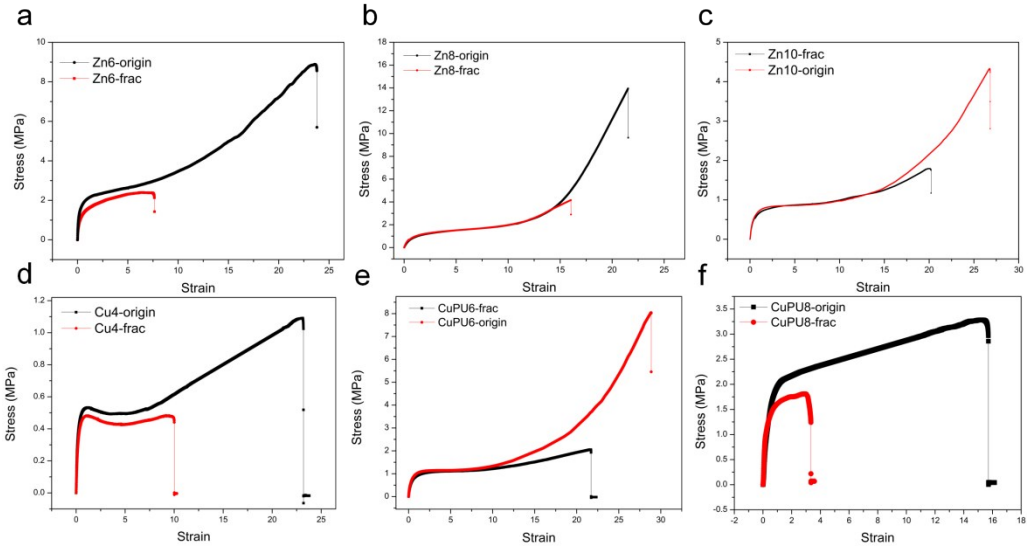

Figure S6. Stress−strain curves for a) **ZnPU-6** b) **ZnPU-8** c) **ZnPU-10** d) **CuPU-4**. e) **CuPU-6** and f) **CuPU-8** in single-edge test.

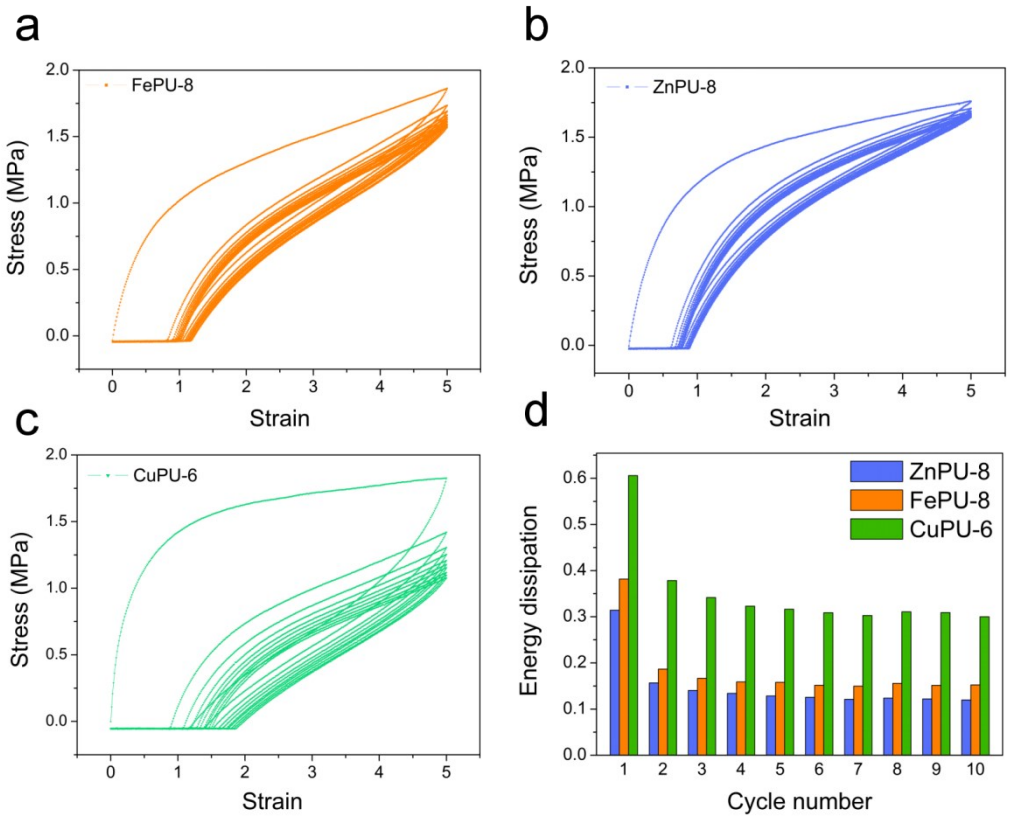

Figure S7. (a) The stress-strain curve in cycle tensile test of **FePU-8**. (b) The stress-strain curve in cycle tensile test of **ZnPU-8**. (c) The stress-strain curve in cycle tensile test of **CuPU-6**. (d) Energy dissipation in 1-10 cycles of **ZnPU-8** (blue), **FePU-8** (orange) and **CuPU-6** (green).

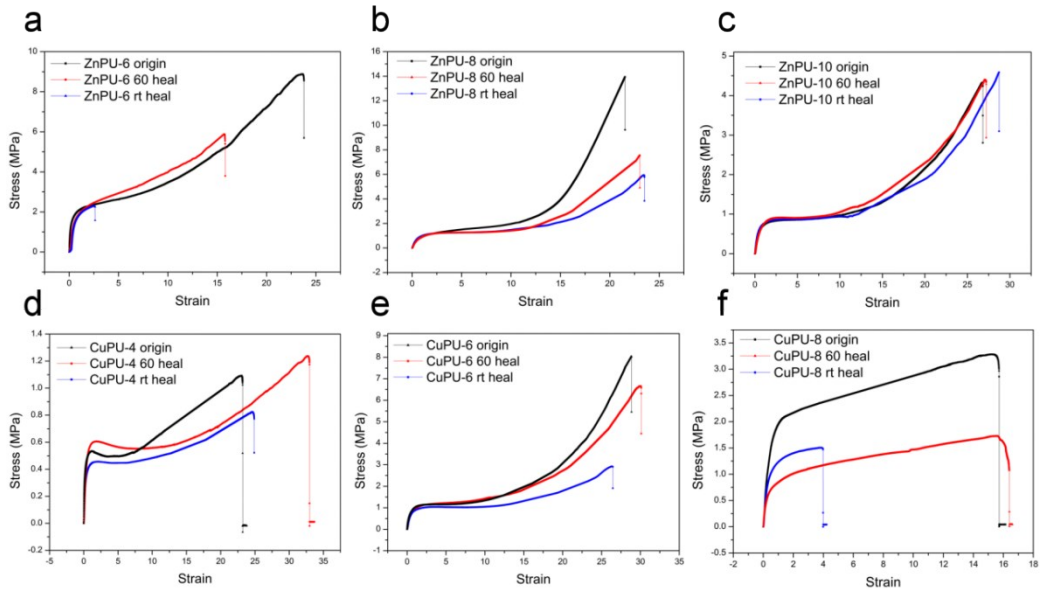

Figure S8. The stress-strain curve of hurt (a) **ZnPU-6** (b) **ZnPU-8** (c) **ZnPU-10** (d) **CuPU-4** (e) **CuPU-6** (f) **CuPU-8** after 24h self-healing at room temperature (blue) and 60 °C (red), the black line was their origin stress-strain curve.

Table S1. The dosage of each raw material applied in **Neat PU** and various metal ion-carboxyls coordinated PU.

Sample ID	n(HDI) / mmol	n(PTMG-1000) / mmol	n(DMPA) / mmol	n(metal salt) / mmol
Neat PU	12	6	6	0
FePU-3	12	6	6	2
FePU-4	12	6	6	1.5
FePU-6	12	6	6	1
FePU-8	12	6	6	0.75
FePU-10	12	6	6	0.6
ZnPU-6	12	6	6	1
ZnPU-8	12	6	6	0.75
ZnPU-10	12	6	6	0.6
CuPU-4	12	6	6	1.5
CuPU-6	12	6	6	1
CuPU-8	12	6	6	0.75

Table S2. The toughness (W_0) and fracture toughness (G_c) of **Neat PU**, **FePU**s, **ZnPU**s and **CuPU**s.

Sample ID	W_0 / MJ·m^{-3}	α / mm	W_c / MJ·m^{-3}	λ_c	G_c / kJ·m^{-2}
Neat PU	81.38	2.00	0.085	1.28	0.948
FePU-6	127.02	2.00	7.36	7.12	34.7
FePU-10	185.15	1.00	27.96	13.65	47.5
ZnPU-6	108.31	2.00	18.692	8.65	79.8
ZnPU-8	83.04	2.00	32.14	16.04	97.8
ZnPU-10	43.65	2.00	22.79	21.21	62.2
CuPU-4	16.49	1.00	5.3176	11.27	9.95
CuPU-6	77.82	2.00	41.21	22.70	106.3
CuPU-8	41.26	2.00	11.87	5.60	38.73

Table S3. Comparison of toughness with other self-healing material in previous literatures [1-14].

Sample Name	**Stress / MPa**	**Toughness / MJ·m^{-3}**	**Reference**
FePU-8	18.36	228.86	This work
PDM-2.5	29	121.8	1
Cu-DOU-CPU	14.8	87	2
PI-xNa	7	70	3
PPGTD-IDA	4.83	65.49	4
IP-SS	6.76	26.9	5
PEG-DE-CAT-DAB	21.9	22	6
PEIs	4.4	12	7
CB[8] based networks	0.5	11	8
HBPs	1.9	10	9
U-PDMS	1.11	7.14	10
P(DA-*co*-BA)	3.5	6.8	11
PSeD-U20-12h	2.42	4.59	12
Fe-Hpdca-PDMS	0.23	3.8	13
PDMS-PtL	0.3	3.4	14

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