Supporting Information

Dual-dynamic Crosslinked Polyurethanes with Synergistic Mechanical Reinforcement, Self-Healing, Recycling and Photoluminescence

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Table S1 Double dynamic crosslinked polyurethane synthesis formula

Sample	IPDI	PTMG	MDEA	DU	CA
HPU	2.25	1	0	0.5	0
HIPU-1	2.25	1	0.25	0.375	0.25
HIPU-2	2.25	1	0.5	0.25	0.5
HIPU-3	2.25	1	0.75	0.125	0.5
IPU	2.25	1	1	0	1

Crosslinking density and gel content

The crosslinking density and gel content were examined by swelling method based on the Flory–Rehner theory. All dried samples (m_d) were immersed in ethyl acetate (EA) at room temperature to reach equilibrium. Then, the swollen sample were taken out, gently blot off surface solvent with filter paper and weight (m_s). In addition, the swollen sample were dried to constant weight (m_{d2}). The crosslink density ν (mol/cm³), molecular weight between crosslinks M_c (g/mol) and gel content (%) are calculated from:

$$\nu = \frac{-In\left(1-V_r\right)-V_r-\chi V_r^2}{V_e\left(V_r^{1/3}-V_r/2\right)}$$

$$M_c = \frac{\rho_p}{\nu}$$

$$gel\ content\ = \frac{m_{d2}}{m_d} \times 100\%$$

where, ν is crosslinking density (mol/cm³), V_r is polyurethane volume fraction in swollen gel (V_r=m_d/m_s), V_e is molar volume of the EA solvent (cm³/mol), χ is the polyurethane–EA solvent interaction parameter (0.43). M_c is molecular weight between crosslinks (g/mol), ρ_p is the density of HIPUs (1.15 g/cm³).

Table S2 Crosslink density, molecular weight between crosslinks and gel content of HIPUs

Samples	HPU	HIPU-1	HIPU-2	HIPU-3	IPU
m_d (g)	0.2730	0.1525	0.3450	0.2438	0.0811
m_s (g)	0.5053	0.3140	0.9891	0.8692	0.3200
m_{d2} (g)	0.2639	0.1312	0.2394	0.1259	0.0302
ν（mol/cm³）	1.41×10^{-3}	9.68×10^{-4}	3.42×10^{-4}	1.85×10^{-4}	1.44×10^{-4}
Mc（g/mol）	817	1188	3366	6231	7969
Gel content（%）	96.67	86.03	69.39	51.66	37.24

Table S3 Mechanical properties of HIPU-2 after varied hot-pressing cycles

Cycles	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Toughness (MJ/m^3)
0	25.68	802	5.01	68.02
1	24.80	782	7.92	62.49
3	22.84	758	8.21	59.52
5	20.00	750	3.65	54.39

Table S4 Comparison of self-healing, recycling efficiencies and photoluminescence of self-healing polyurethanes in previous literatures

Ref.	Self-healing motif	Healing conditions	Healing efficiency (%)	Recycling conditions	Recycling cycle and ratio (%)	Photoluminescence
This work	Ionic interactions and H-bonds	80 ℃, 12 h	88.94	100 °C under 5 MPa for 5 min	92	Yes (without quantum yield)
4	H-bonds [Multiple H-bonding chain extender-based]	25 ℃, 6 h	87.6	/	/	Yes (without quantum yield)
13	H-bonds and disulfide bonds	25 ℃, 48 h 60 ℃, 3 h	81 99	DMF solvent	3, without ratio	No
15	Ionic interactions and H-bonds	25 ℃, 168 h	92.8	Ethanol solvent	5, without ratio	No
26	H-bonds and coordinate interactions	80 ℃, 10 h	91.7	/	/	Yes (without quantum yield)
27	H-bonds and disulfide bonds	80 ℃, 12 h	86.1	DMF solvent	3, without ratio	No
28	Disulfide bonds and H-bonds	50 ℃, 12 h	81.47	DMF solvent	5, 91.26	No

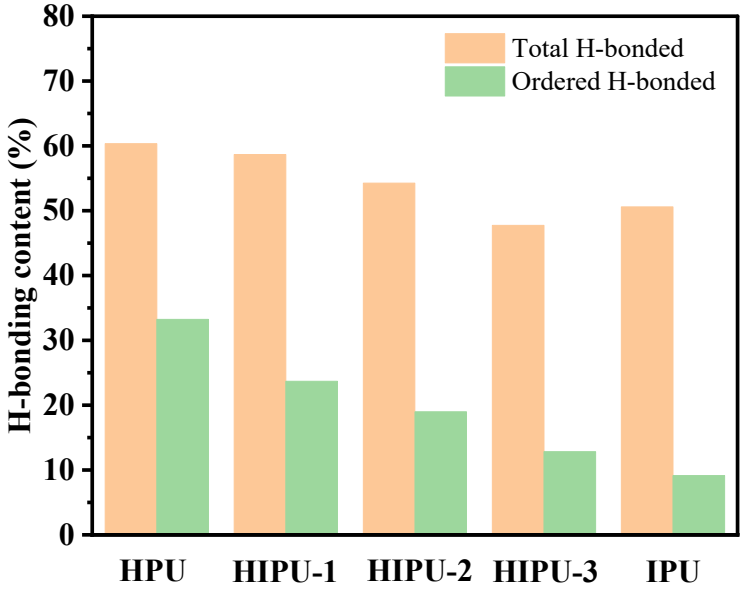

Fig.S1 H-bonding content of HIPUs

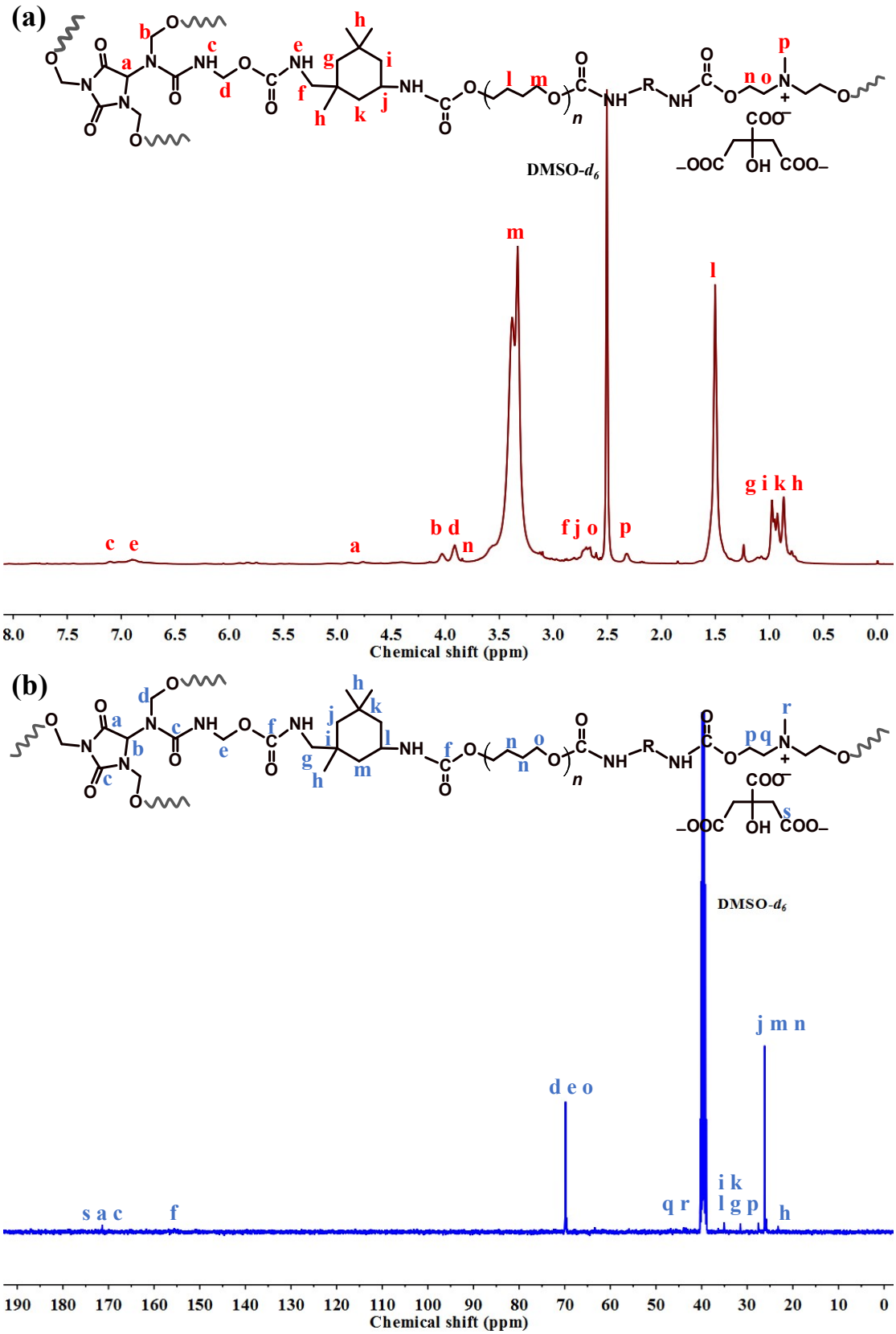

Fig.S2 (a) ^{1}H NMR and ^{13}C NMR spectra of HIPU-2

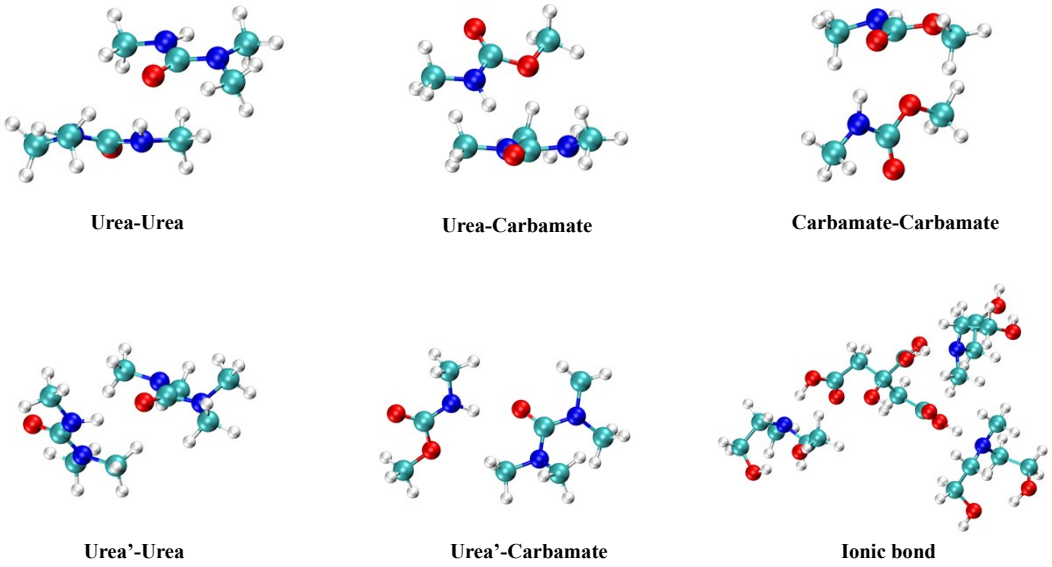

Fig. S3 Optimized structures of hydrogen bonds and ionic bonds

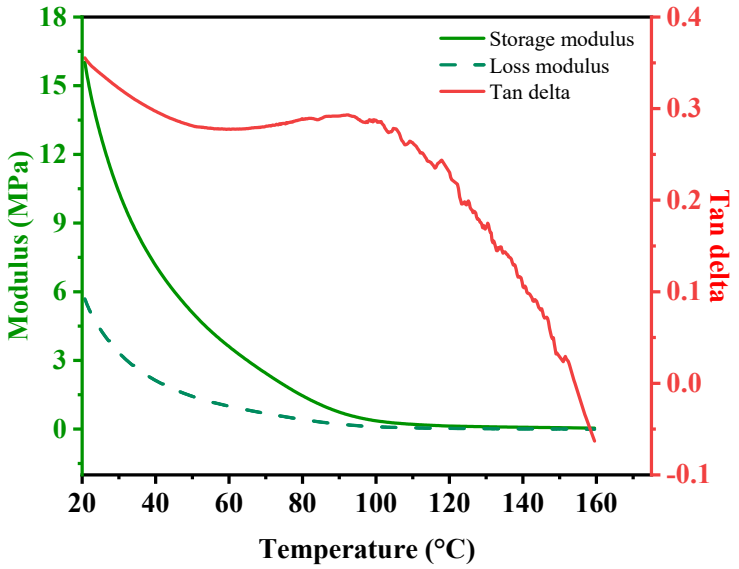

Fig. S4 The storage modulus, loss modulus and tan delta of HIPU-2

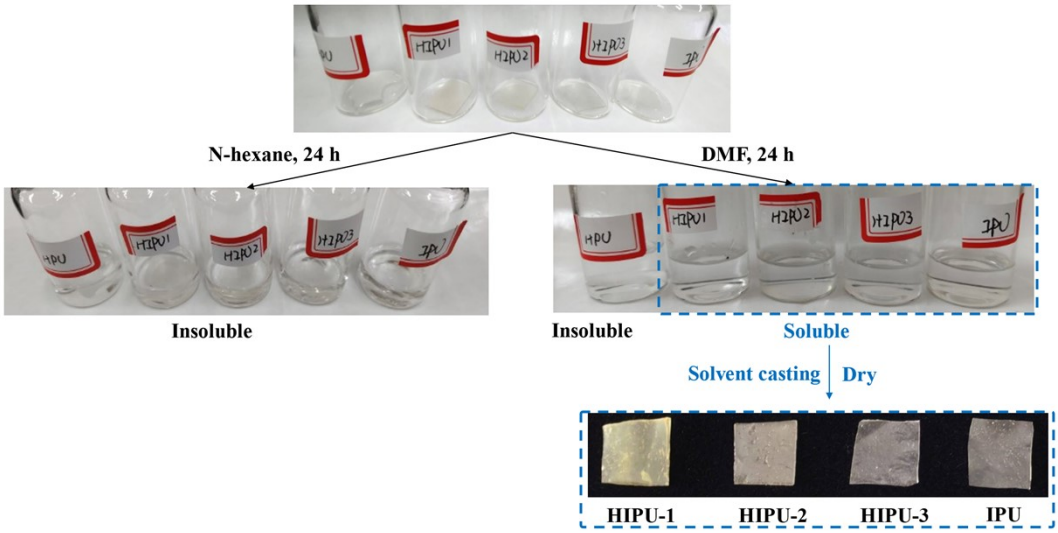

Fig. S5 Solubility and processability of HIPUs in n-hexane and DMF

As shown in Fig.S5, the HIPUs (except HPU) are soluble in polar solvents (e.g., DMF) at room temperature after 24 h, forming a clear homogeneous solution. This is because these strong polar solvents effectively disrupt the intermolecular hydrogen bonds and ionic interactions, confirming the dynamic and reversible nature of the supramolecular network. Moreover, a new film can be re-formed after solvent evaporation, demonstrating solution processability. HIPUs are insoluble in non-polar solvents (e.g., n-hexane), further supporting that the network is non-covalent.

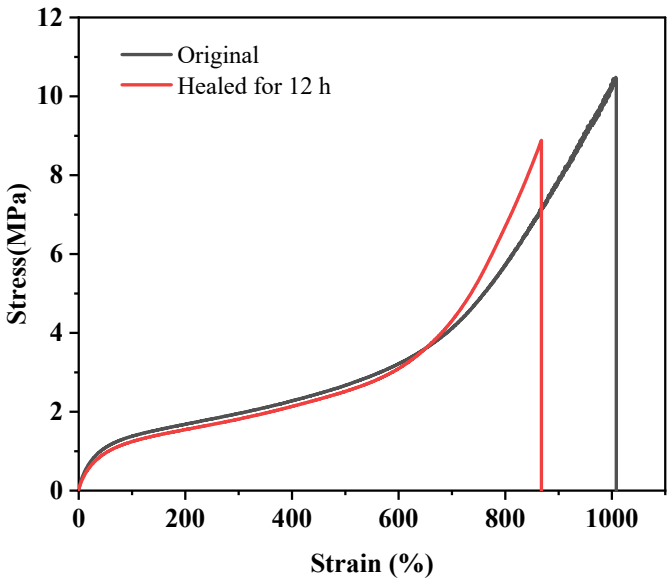

Fig. S6 Stress-strain curves of IPU healed at 80 °C for 12 h

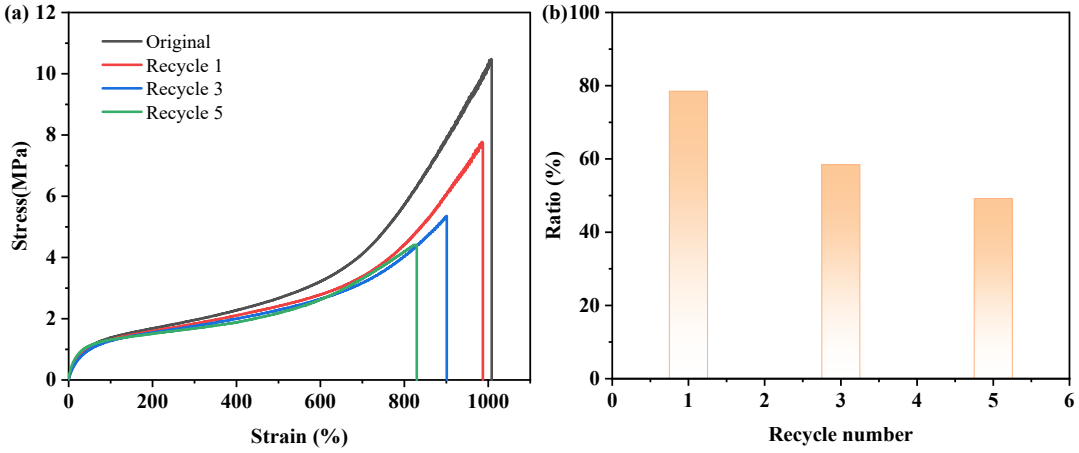

Fig. S7 Recycling properties of IPU: (a) Recyclability of IPU film through hot-pressing; (b) Recycling ratio of IPU

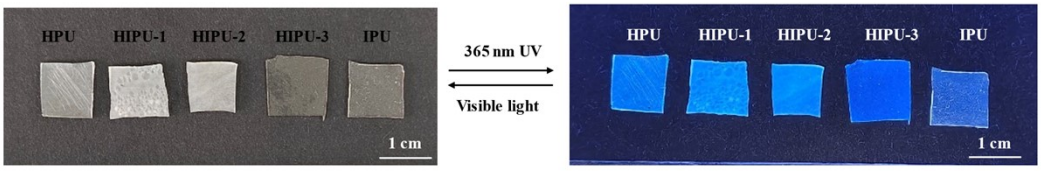

Fig. S8 Photographs of HIPUs under UV irradiation at 365 nm

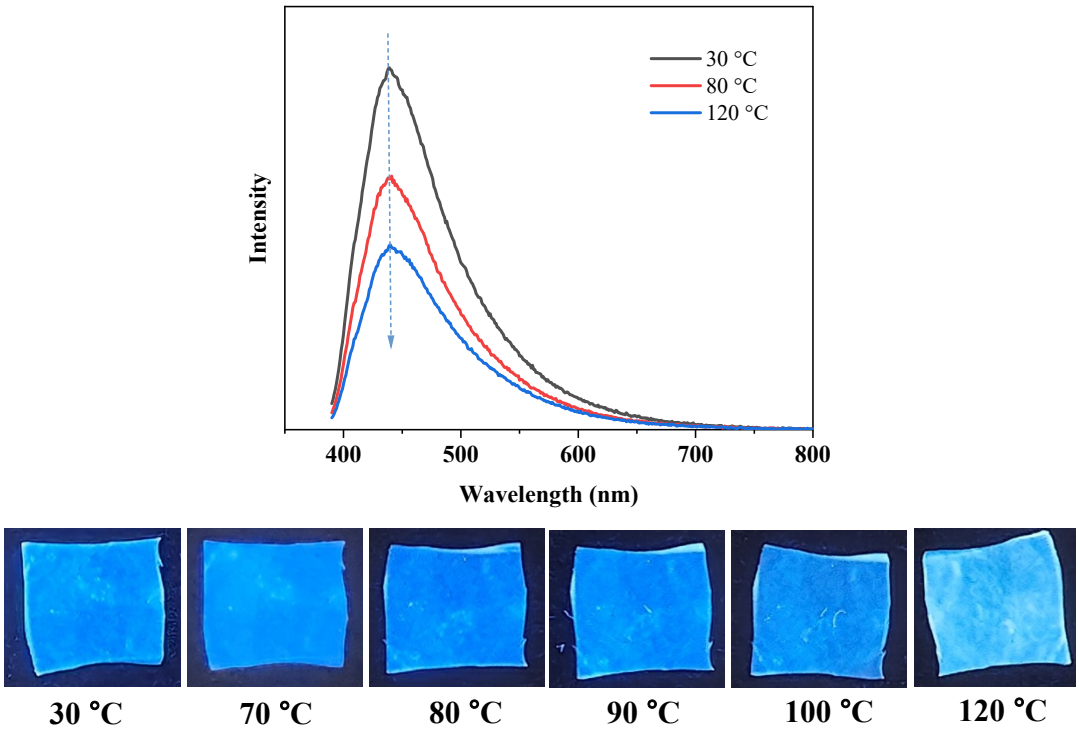

Fig. S9 Photoluminescence spectra of HIPU-2 at different temperatures

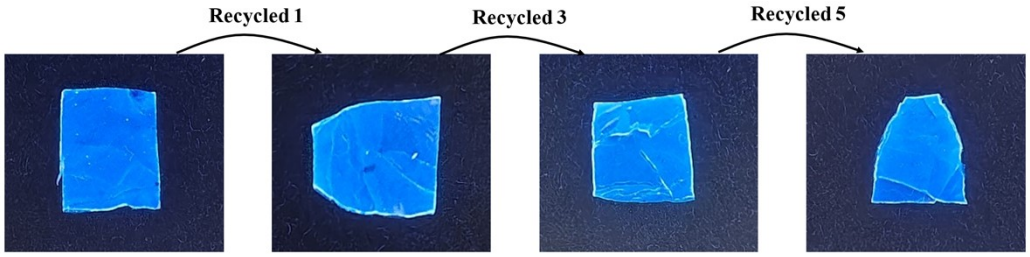

Fig. S10 Photographs of HIPU-2 luminescence after five recycling cycles

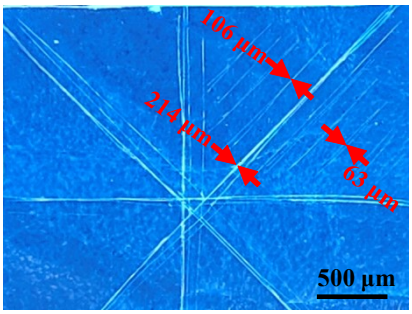

Fig. S11 Luminescent crack detection in HIPU-2