

## Supporting information

### Unprecedented toughness in transparent, luminescent, self-healing polymers achieved via hierarchical rigid domain design

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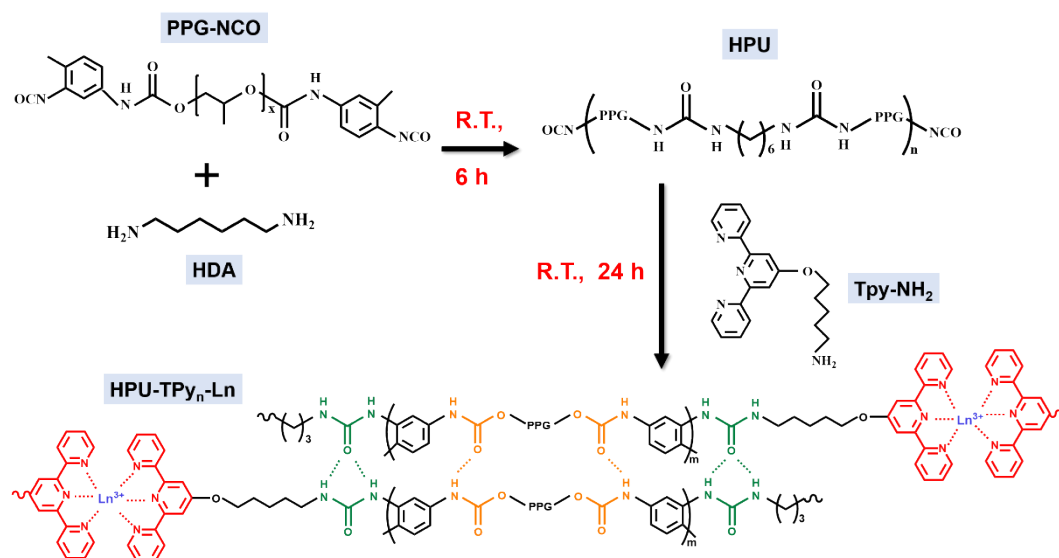
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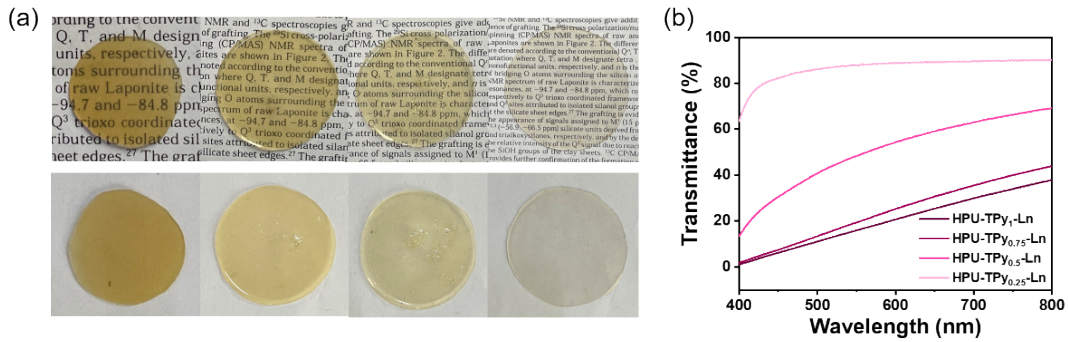
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Sample	PPG-NCO (mg/mmol)	HDA (mg/mmol)	TPy-NH <sub>2</sub> (mg/mmol)	Ln <sup>3+</sup> (mL/mmol)
HPU-TPy <sub>1</sub> -Ln	2300/1	58/0.5	334/1	5/0.5
HPU-TPy <sub>0.75</sub> -Ln	2300/1	72.5/0.625	250.5/0.75	3.75/0.375
HPU-TPy <sub>0.5</sub> -Ln	2300/1	87/0.75	167/0.5	2.5/0.25
HPU-TPy <sub>0.25</sub> -Ln	2300/1	101.5/0.875	83.5/0.25	1.25/0.125
HPU-TPy <sub>0</sub>	2300/1	116/1	0/0	0/0

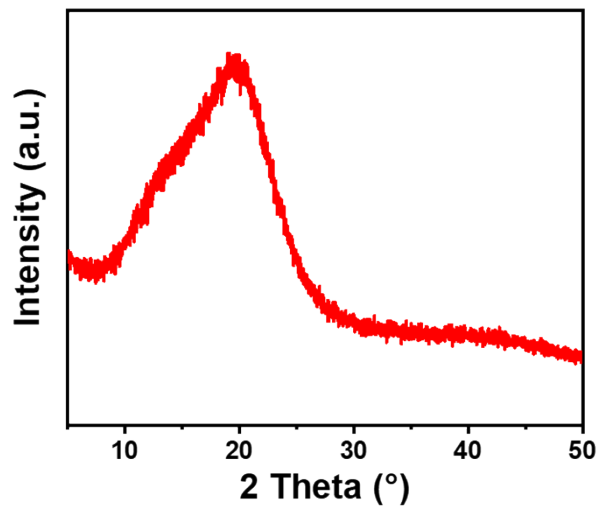
**Table S1.** The feed ratios of various HPU-TPy<sub>n</sub>-Ln



**Figure S1.** Synthetic route of HPU-TPy<sub>n</sub>-Ln.



**Figure S2.** (a) Photographs of a range of materials HPU-TPy<sub>n</sub>-Ln under two different backgrounds, from left to right: n=1, 0.75, 0.5 and 0.25, respectively. (b) Transmittance spectra of HPU-TPy<sub>n</sub>-Ln films with a thickness of 0.2 mm.



**Figure S3.** WAXD spectrum of the HPU-TPy<sub>0.25</sub>-Ln elastomers.

The wide-angle X-ray diffraction (WAXD) spectrum of the HPU-TPy<sub>0.25</sub>-Ln elastomers only show broadband absorption without sharp XRD peaks, which are the representative WAXD patterns of amorphous polymers.

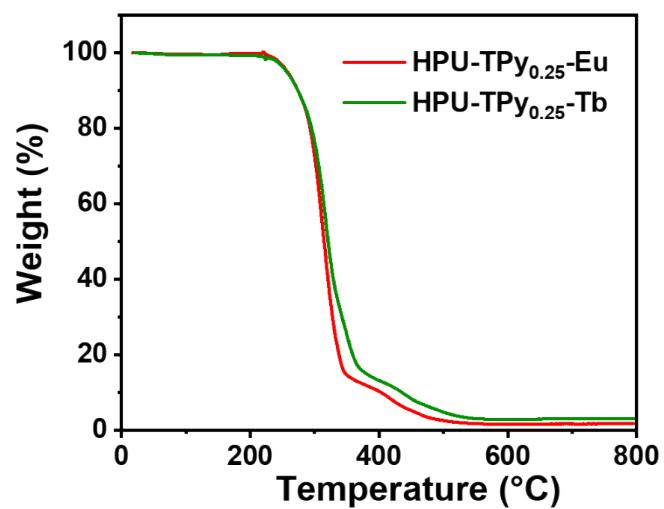


Figure S4. TG curves of HPU-TPy<sub>0.25</sub>-Ln.

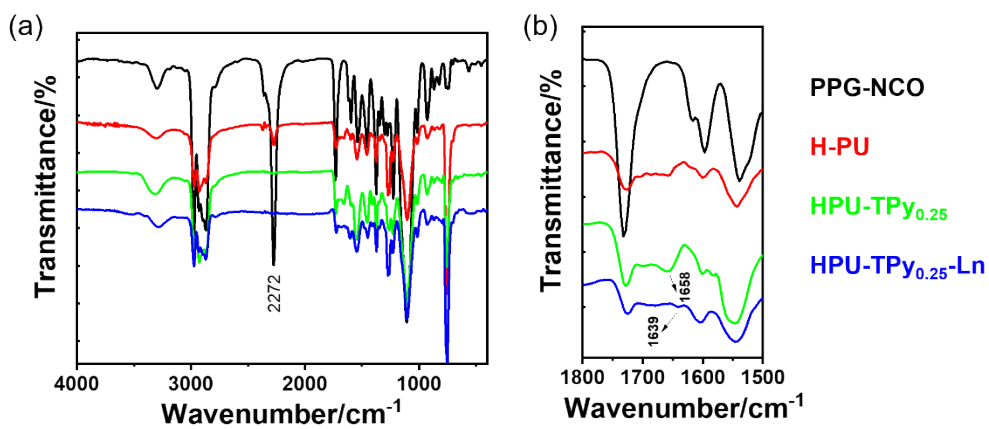


Figure S5. Infrared spectra of a series of products.

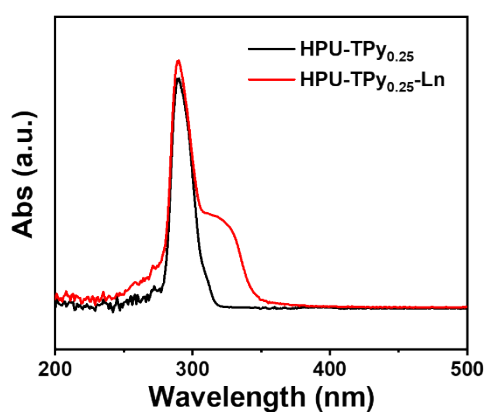
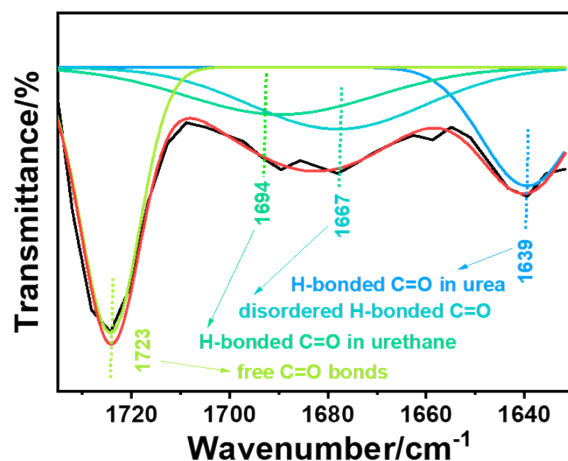
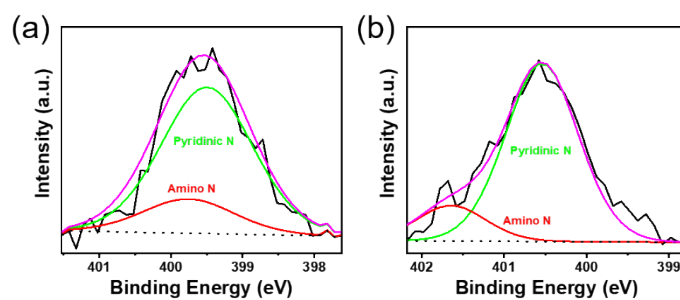


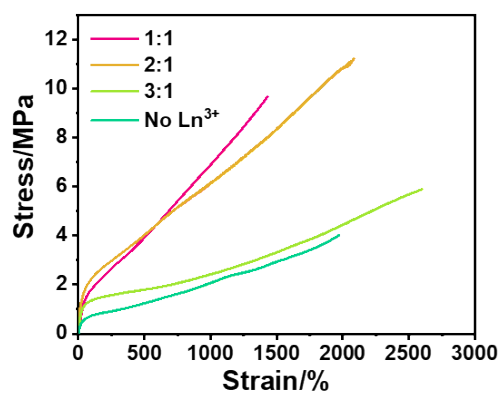
Figure S6. UV-vis spectra of HPU-TPy<sub>0.25</sub> and HPU-TPy<sub>0.25</sub>-Ln in the solution phase (CH<sub>2</sub>Cl<sub>2</sub>).



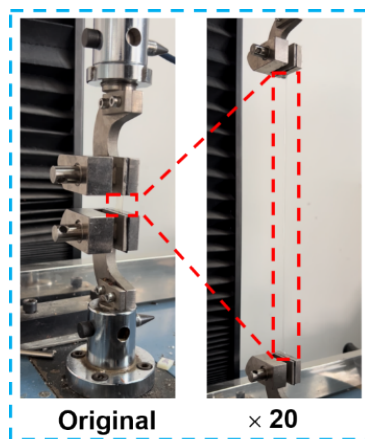
**Figure S7.** Transmittance spectra in the C=O stretching region (1631~1735  $\text{cm}^{-1}$ ) of the obtained HPU-TPy<sub>0.25</sub>-Ln material. The dashed lines are the fitted bands at 1723, 1694, 1667 and 1639  $\text{cm}^{-1}$ .



**Figure S8.** XPS spectra of (a) HPU-TPy<sub>0.25</sub> and (b) HPU-TPy<sub>0.25</sub>-Ln.



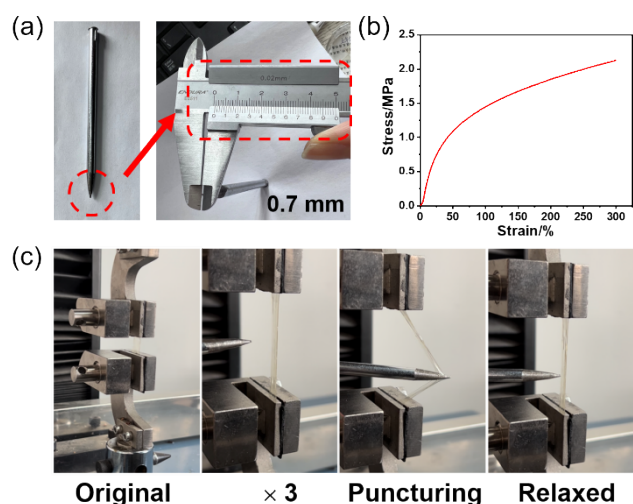
**Figure S9.** Stress-strain curves of HPU-TPy<sub>0.25</sub>-Ln with different feed molar ratios of the TPy-NH<sub>2</sub> to Ln<sup>3+</sup>.



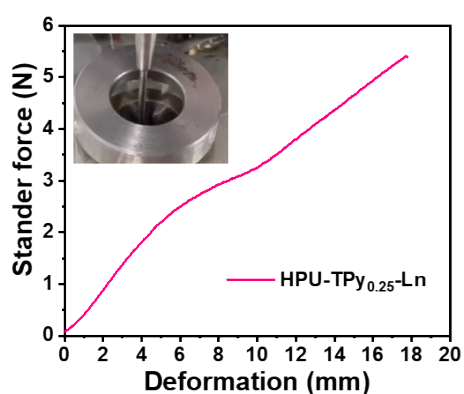
**Figure S10.** Photos of HPU-TPy<sub>0.25</sub>-Ln before and after stretching.

Sample name	Strength (MPa)	Toughness (MJ m <sup>-3</sup> )	Ref.
HPU-TPy <sub>0.25</sub> -Ln	11.21	133.35	This work
Polymer-Phen-Ln <sup>3+</sup>	2.27	8.4	21
Polymer-Phen-Eu(tta) <sub>3</sub>	1.59	9.28	21
Eu-Ppdc	0.4	1.8	13
Ln <sup>3+</sup> -Tpy-PPG	0.48	~10	22
PIB-Eu-TTA	0.58	6.27	11
H-PU-Ln	0.58	1.68	12
P1-3	0.21	~0.3	23
Eu-to-IDA	6.1	6.4	24
Eu-DPA	2	4.4	25
p(HFBM-co-SBMA)	1.87	7.26	26
Ln-Bipy-PDMS	1.55	~3	27

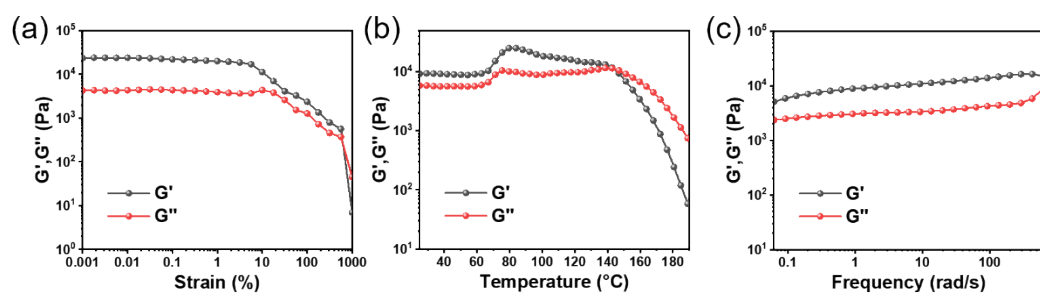
**Table S2.** Comparison of mechanical properties of HPU-TPy<sub>0.25</sub>-Ln elastomer with synthetic room-temperature self-healing luminescent materials in the previous literatures.<sup>1-5</sup>



**Figure S11.** (a) A needle with a tip of 0.7mm. (b) Stress-strain curve of 300% stretching. (c) Images of puncture resistance ability of HPU-TPy<sub>0.25</sub>-Ln elastomer.

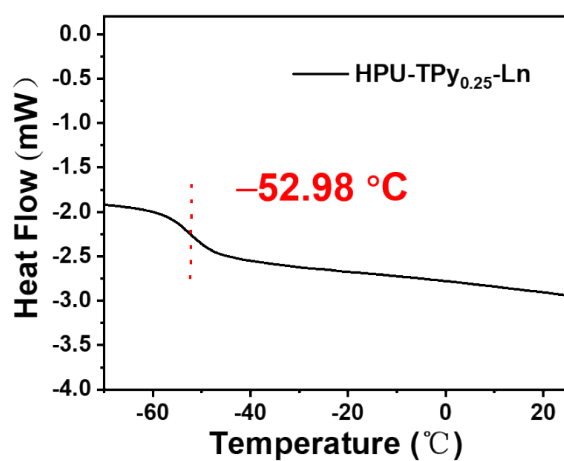


**Figure S12.** Force-displacement curves of HPU-TPy<sub>0.25</sub>-Ln, measured by the puncture resistance tests.



**Figure S13.** Rheological measurements of (a) strain sweep tests (b) temperature dependence and (c) frequency sweep curves of storage modulus ( $G'$ ) and loss modulus ( $G''$ ) of HPU-TPy<sub>0.25</sub>-Ln.

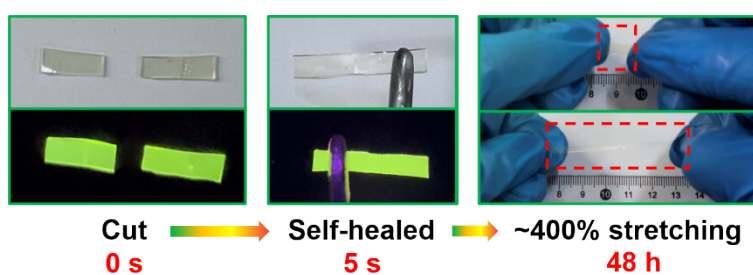




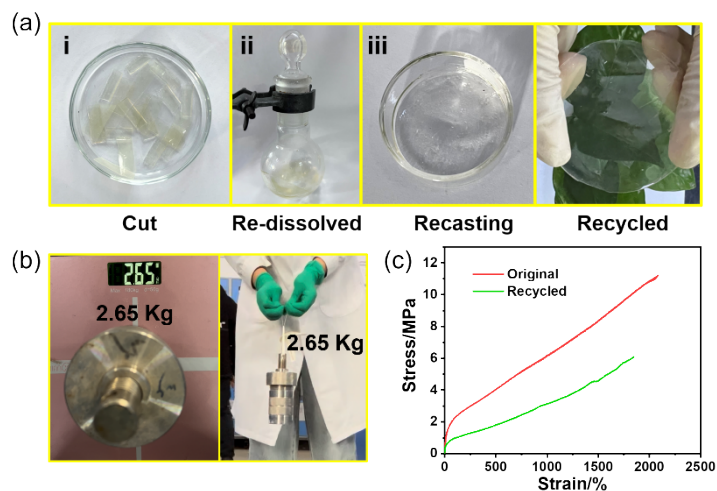
**Figure S14.** DSC curves of HPU-TPy<sub>0.25</sub>-Ln.

Sample	First	Second	Third	Fourth
HPU-TPy <sub>0.25</sub> -Ln	296.38	154.8	129.6	121.6

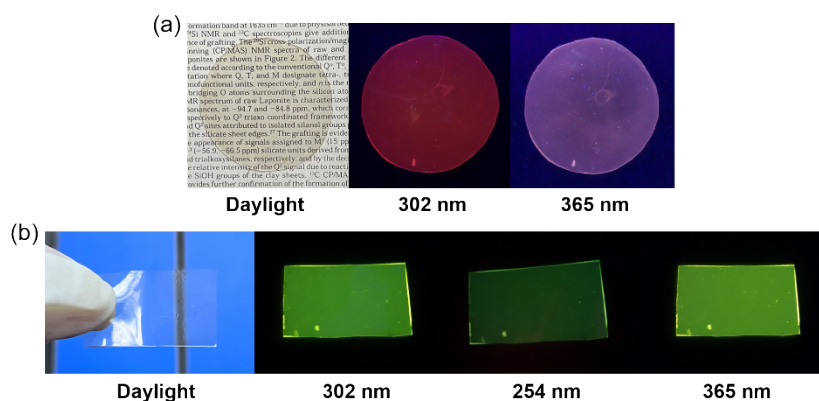
**Table S3.** Energy dissipation in continuous cyclic loading and unloading of HPU-TPy<sub>0.25</sub>-Ln (KJ m<sup>-3</sup>).



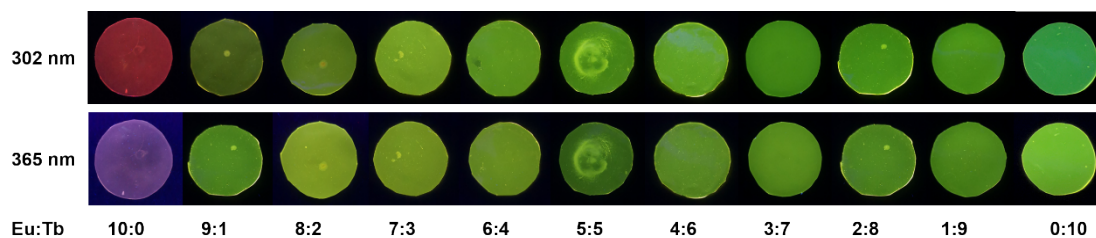
**Figure S15.** Self-healing behavior of HPU-TPy<sub>0.25</sub>-Ln.



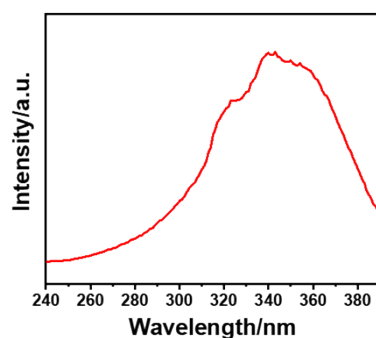
**Figure S16.** The recycling process of HPU-TPy<sub>0.25</sub>-Ln films. (b) 2.65 kg weight lifted by a recycled HPU-TPy<sub>0.25</sub>-Ln elastomer strip (weight: 38.1 mg, 40 mm (L) × 7 mm (W) × 0.15 mm (T)). (c) Stress-strain curves of original and recycled HPU-TPy<sub>0.25</sub>-Ln.



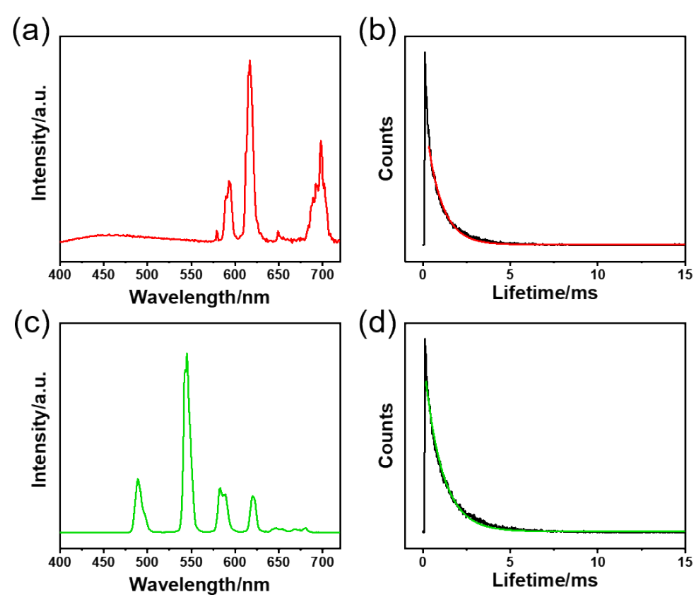
**Figure S17.** Photographs of (a) HPU-TPy<sub>0.25</sub>-Eu and (b) HPU-TPy<sub>0.25</sub>-Tb under daylight and UV light.



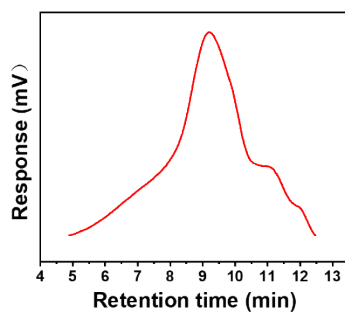
**Figure S18.** Photographs of HPU-TPy<sub>0.25</sub>-Eu<sub>x</sub>Tb<sub>y</sub> under UV light.



**Figure S19.** (a) The excitation curves of HPU-TPy<sub>0.25</sub> monitored at 544 nm.



**Figure S20.** The emission spectra of (a) HPU-TPy<sub>0.25</sub>-Eu and (c) HPU-TPy<sub>0.25</sub>-Tb excited at 340 nm. The luminescence decay curves of (b) HPU-TPy<sub>0.25</sub>-Eu and (d) HPU-TPy<sub>0.25</sub>-Tb.



**Figure S21.** GPC curve of HPU-TPy<sub>0.25</sub>.