

Supporting Information

Photo-gated polymer mechanochromism from excited-state intramolecular proton transfer

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1. Materials and General Methods

All the solvents and reactants were purchased from commercialized companies and used as received without further purification except for specifying otherwise.

In-situ fluorescence spectra under 365 nm irradiation light were recorded using Seeman S5000UV miniature spectrometer equipped with Seeman FS120 quartz optical fiber as detector and SHENYAN 365 nm UV lamp as the light source. The size of the rectangularshaped sample for the test was 30 mm × 5 mm × 1 mm. The sample was fixed on the stretching device (Beijing PDV Instrument Co., Ltd) and then was stretched from 0 (10 mm) to 500% (60 mm) at 100% intervals to record the fluorescence spectra at different elongations. Stress–strain measurements were carried out under ambient conditions on ZGDR tensile testing machine at a strain rate of 50 mm/min. ¹H NMR and ¹³C NMR spectra were recorded on the 400 MHz (Bruker ARX400) were recorded on the Bruker 101 MHz spectrometer at room temperature with CDCl₃ or DMSO-*d*₆ as the solvent and tetramethylsilane (TMS) as the internal standard. High resolution mass spectra (HRMS) were obtained from a Bruker Solarix XR time-of-flight mass spectrometer (ESI+). UV-Vis spectra were acquired on the Hitachi U-3900H UV-vis spectrophotometer. Photoluminescence spectra were performed on the Hitachi F-4600 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) measurement was carried out by using TA instruments Q100 DSC.

2. Synthesis of HBIA-COOH, HBIA-COOH-M and HBIA-2OH.

Compound HBIA-COOH: 2-(1H-Benzo[d]imidazol-2-yl)aniline (2.09 g, 10 mmol) and succinic anhydride (1.50 g, 15 mmol) were placed in a 150 ml round-bottomed flask. Trichloromethane (50 ml) was then added and the solution was refluxed at 60 °C for 1 h. The mixture was cooled down to room temperature. And the precipitation was filtered and then dried to give 3.03 g HBIA-COOH as a white solid. Yield: 98%.

¹H NMR (400 MHz, DMSO-*d*₆) δ: 13.16 (s, 1H), 13.08 (s, 1H), 12.20 (s, 1H), 8.69 (d, J = 7.9 Hz, 1H), 8.16 – 8.09 (m, 1H), 7.76 (d, J = 7.7 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 16.8 Hz, 1H), 7.37 – 7.21 (m, 3H), 2.78 (t, J = 6.3 Hz, 2H), 2.66 (s, 2H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ: 131.13, 127.77, 123.15, 120.28, 40.40, 40.19, 39.98, 39.77, 39.57, 39.36, 32.87, 29.28.

Compound HBIA-COOH-M: HBIA-COOH (1.54g, 5 mmol), CsCO₃ (2.44g, 7.5 mmol) and methyl bromoacetate (1.15g, 7.5 mmol) were placed in a 150 ml round-bottomed flask. Acetonitrile (50 ml) was then added and the solution was kept stirring at room temperature for 24 h. And the precipitation was filtered and then dried to give 1.33 g HBIA-COOH-M as a yellow solid. Yield: 70%.

¹H NMR (400 MHz, Chloroform-*d*) δ: 7.74 (d, J = 8.2 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.58 – 7.51 (m, 1H), 7.42 (d, J = 8.1 Hz, 1H), 7.33 – 7.25 (m, 3H), 4.80 (s, 2H), 3.84 (s, 3H), 2.70 – 2.55 (m, 4H).

¹³C NMR (101 MHz, Chloroform-*d*) δ: 176.29, 131.09, 130.71, 129.33, 129.11, 123.52, 122.85, 120.07, 109.82, 77.39, 77.07, 76.75, 52.87, 46.23, 28.41.

Compound HBIA-COOH-M: HBIA-COOH-M (0.76 g, 2 mmol), NaBH₄ (0.38 g, 10 mmol) and ZnCl₂ (0.27g, 2 mmol) were placed in a 100 ml round-bottomed flask. Tetrahydrofuran (30 ml) was then added and the solution was refluxed at 70 °C for 48 h. And then the mixture was cooled down to room temperature and some water was added to quench the excess NaBH₄. The reaction mixture was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (5~10% ethanol/dichloromethane) to give 0.20 g HBIA-2OH as a white powder. Yield: 30%.

¹H NMR (400 MHz, DMSO-*d*₆) δ: 9.99 (s, 1H), 8.13 (d, J = 8.2 Hz, 1H), 7.76 – 7.66 (m, 3H), 7.51 (t, J = 8.4 Hz, 1H), 7.29 (q, J = 8.2, 7.2 Hz, 3H), 5.00 (d, J = 11.0 Hz, 1H), 4.48 (s, 1H), 4.24 (t, J = 5.5 Hz, 2H), 3.71 (q, J = 5.5 Hz, 2H), 3.44 – 3.35 (m, 2H), 2.25 (t, J = 7.6 Hz, 2H), 1.70 – 1.61 (m, 2H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ: 131.24, 130.52, 124.02, 123.32, 122.90, 122.46, 119.44, 111.86, 60.50, 47.44, 40.41, 40.20, 40.00, 39.79, 39.58, 39.37, 33.77, 28.72.

HRMS (ESI, m/z): Calcd for C₁₉H₂₁N₃O₃ (M+H)⁺: 340.1661. Found: 340.1696.

3. Characterization of target molecules

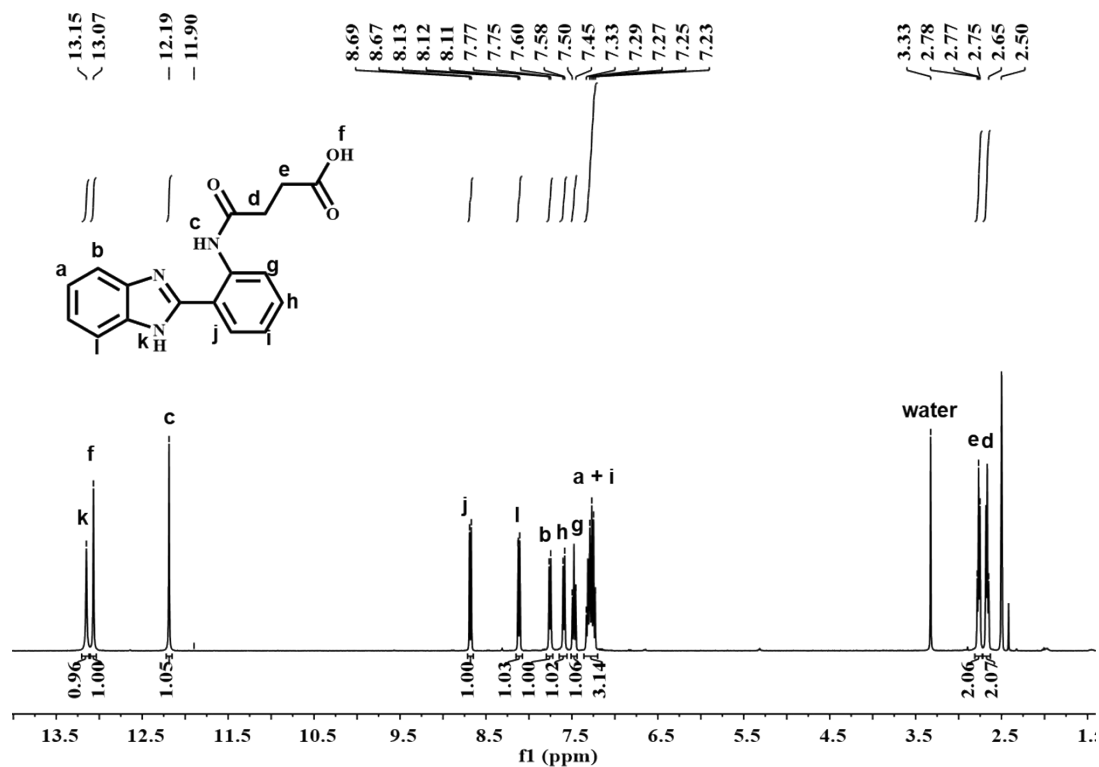


Fig. S1 ^1H NMR spectrum of **HBIA-COOH** in $\text{DMSO-}d_6$.

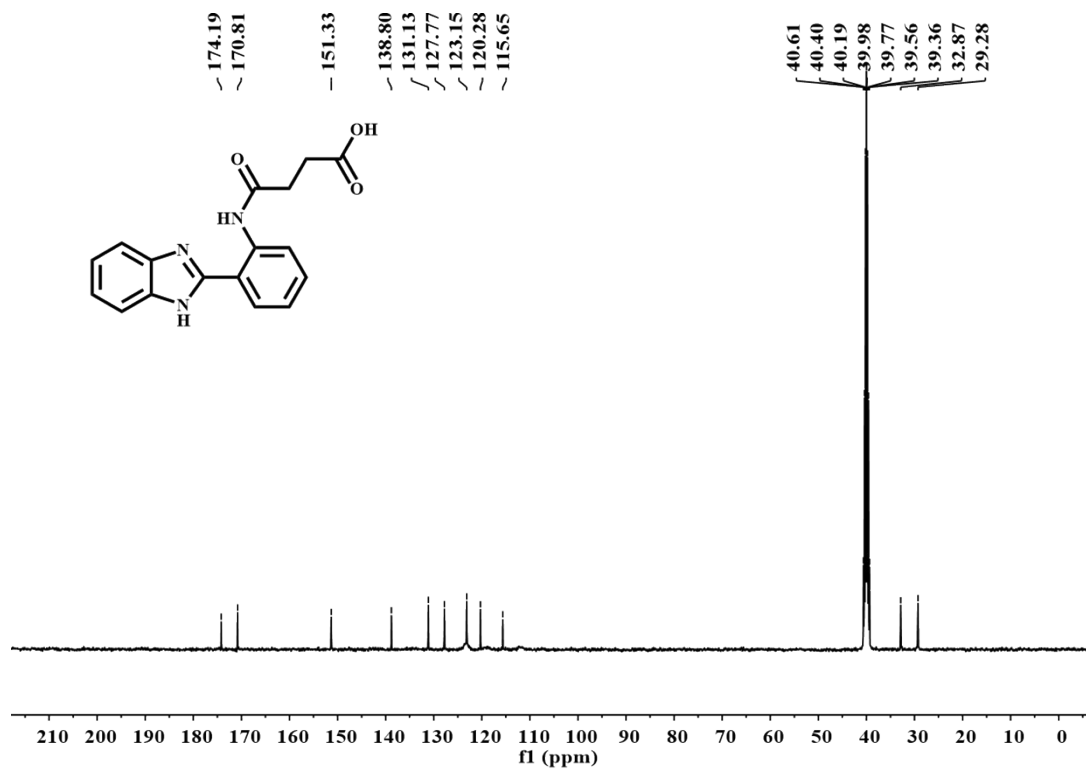


Fig. S2 ^{13}C NMR spectrum of **HBIA-COOH** in $\text{DMSO-}d_6$.

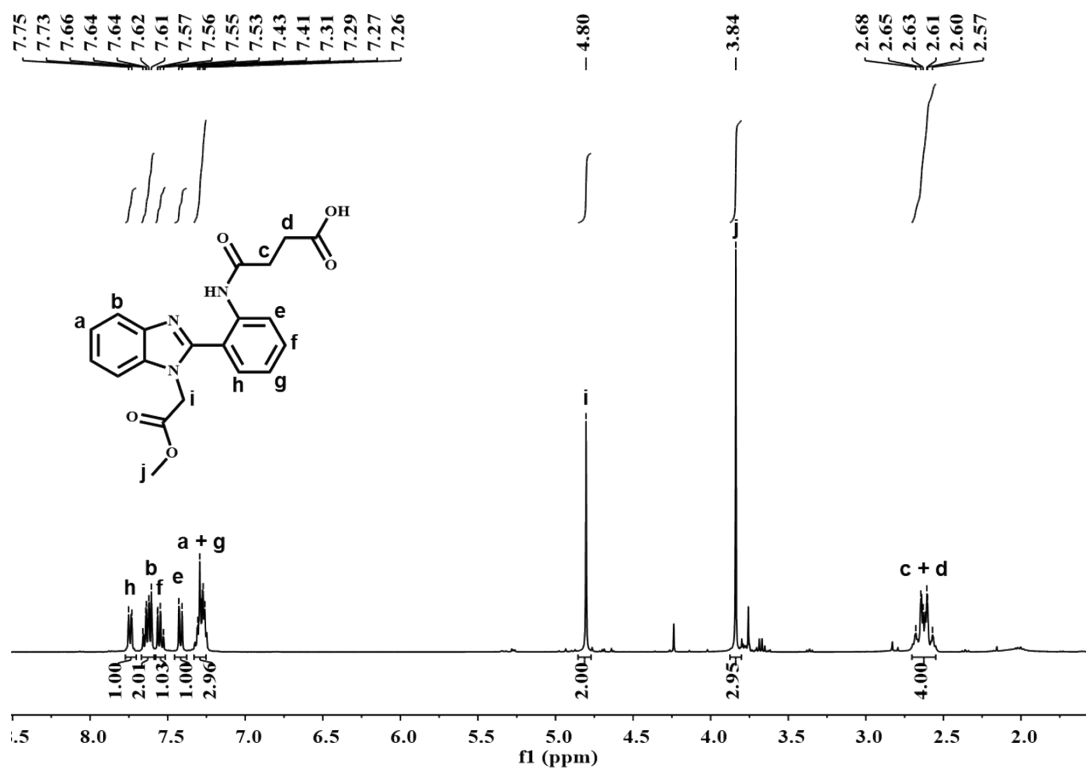


Fig. S3 ^1H NMR spectrum of **HBIA-COOH-M** in CDCl_3 .

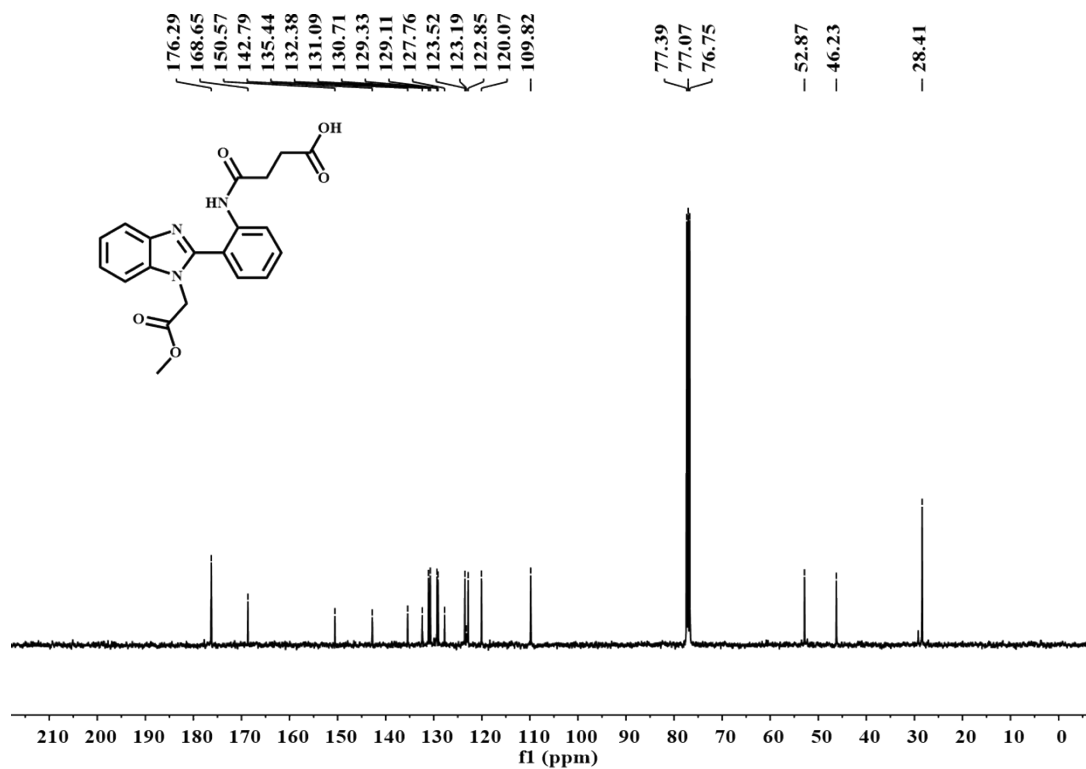


Fig. S4 ^{13}C NMR spectrum of **HBIA-COOH-M** in CDCl_3 .

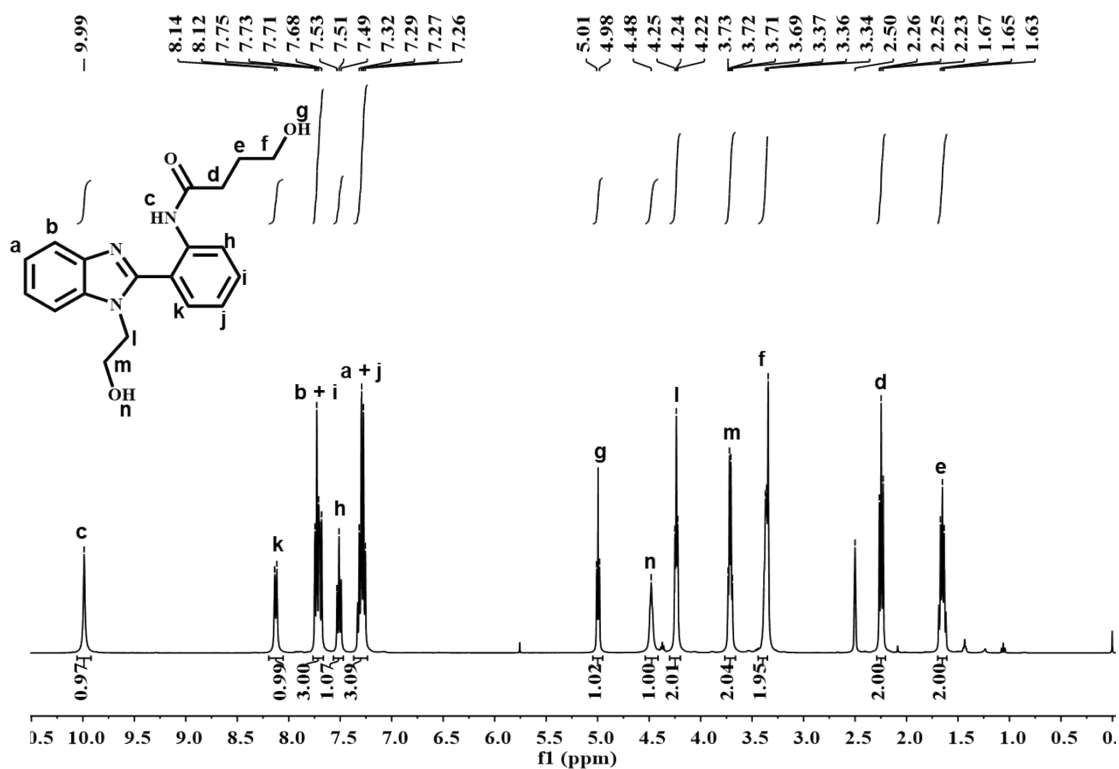


Fig. S5 ^1H NMR spectrum of HBIA-2OH in $\text{DMSO-}d_6$.

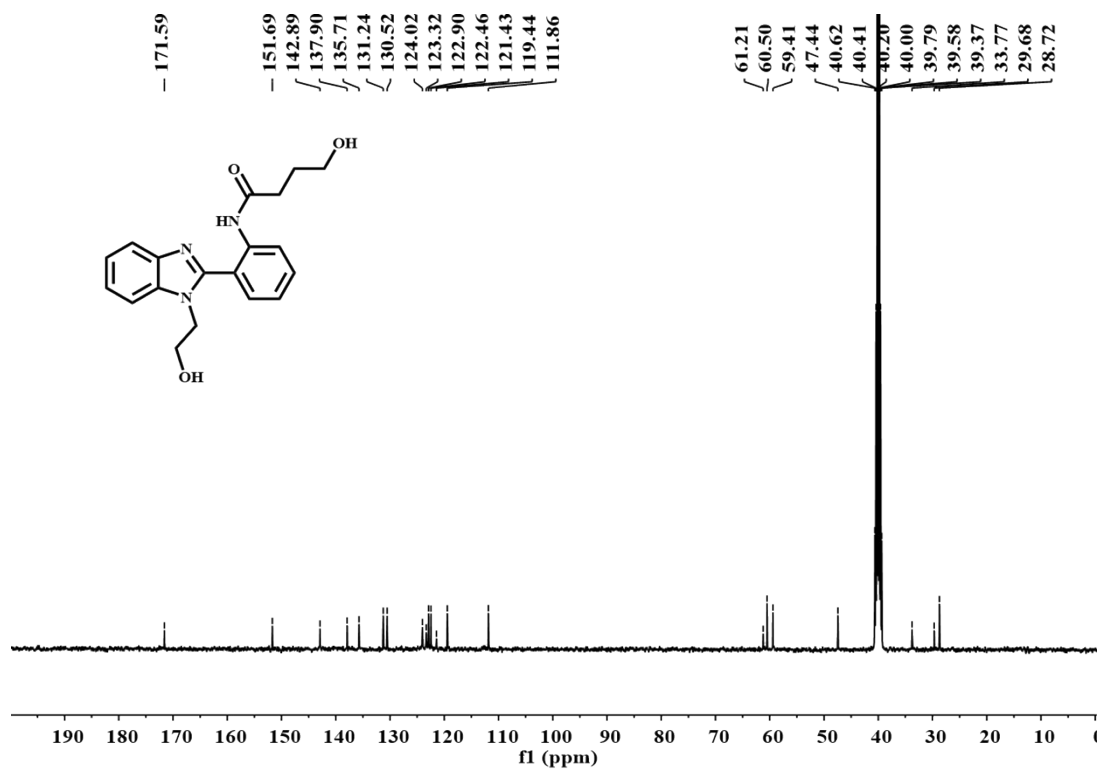


Fig. S6 ^{13}C NMR spectrum of HBIA-2OH in $\text{DMSO-}d_6$.

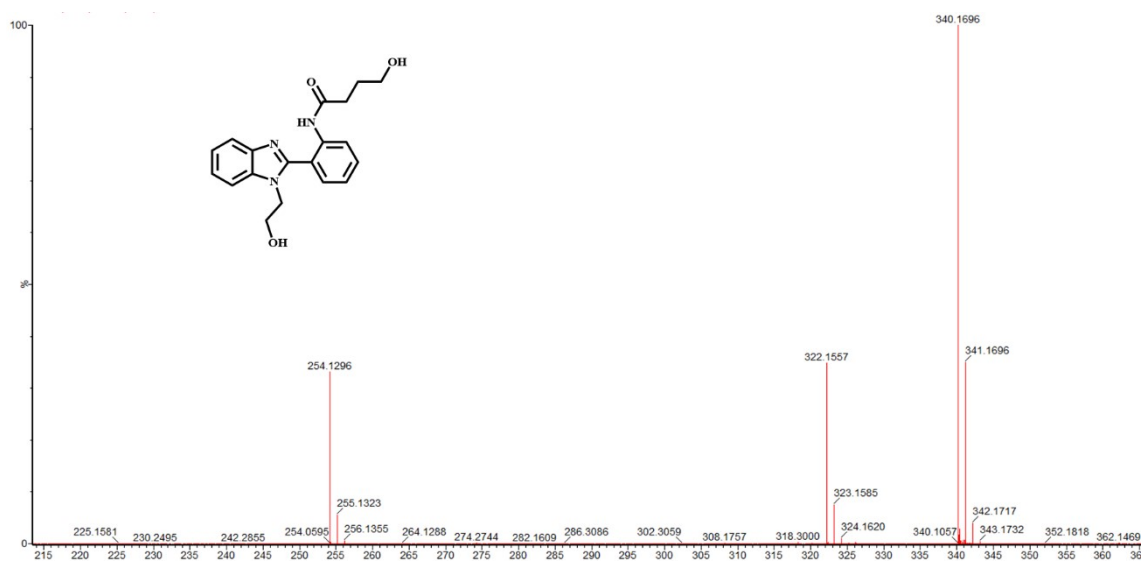


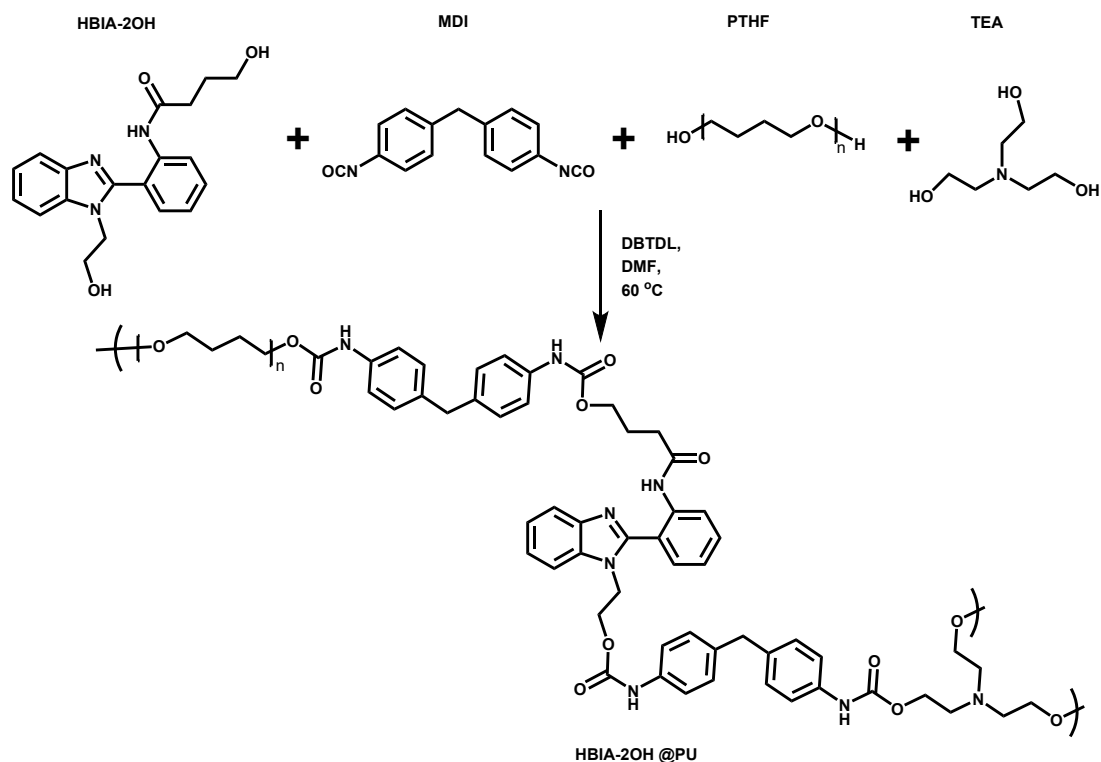
Fig. S7 HR-MS spectrum of compound HBIA-2OH.

4. Preparation and characterization of polyurethane films

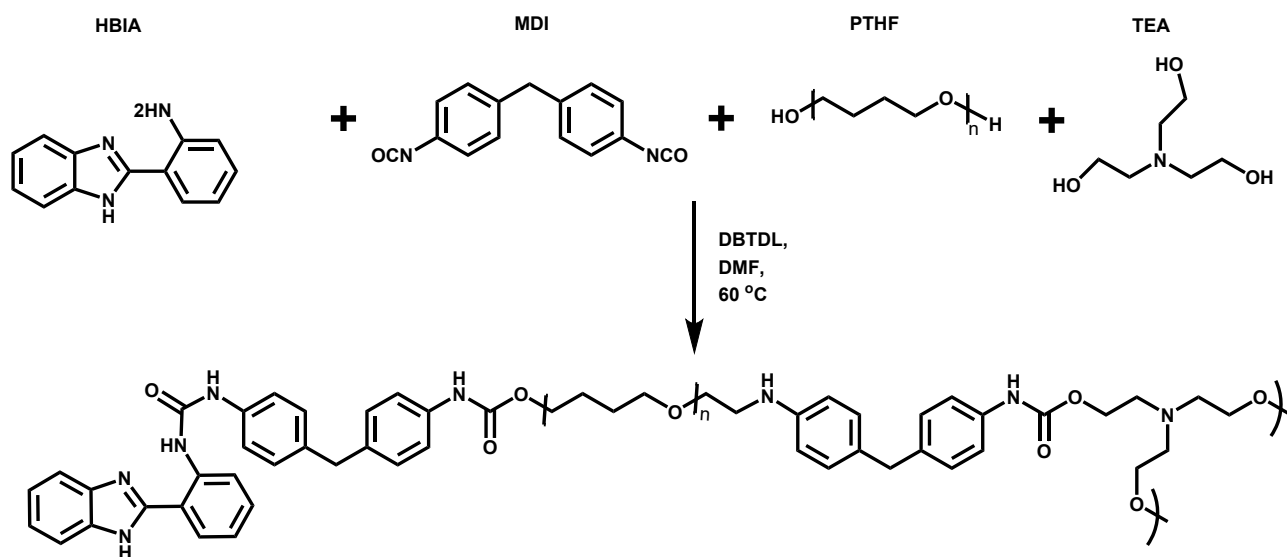
General procedure for the synthesis of polyurethanes containing HBIA-2OH Mechanophore (HBIA-2OH@PU) and HBIA Mechanophore (HBIA@PU): The preparation process was referenced to our previous work¹ and the moles of each monomer were in Table S1.

Table S1. Each monomer amount in the polymerization of polyurethane.

	PTHF/mmol	MDI/mmol	TEA/mmol	mechanophore/mmol
0.56 % HBIA-2OH@PU	1.10	2.12	0.33	0.02
1.38 % HBIA-2OH@PU	1.10	2.15	0.33	0.05
2.68 % HBIA-2OH@PU	1.10	2.20	0.33	0.10
1.38 % HBIA@PU	1.10	2.15	0.33	0.05



Scheme S1 The synthetic route for the HBIA-2OH @PU films.



Scheme S2 The synthetic route for the HBIA @PU film.

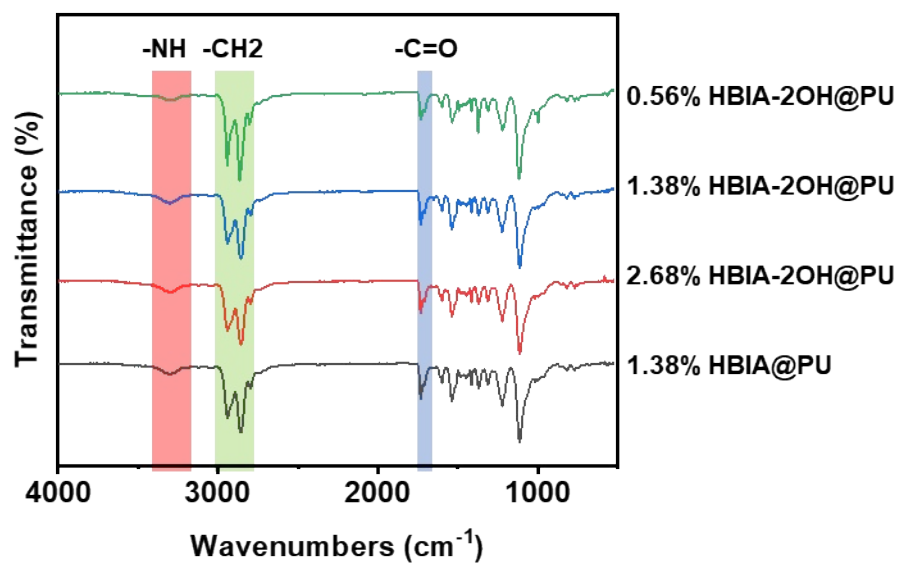


Fig. S8 FT-IR spectra of polyurethane films.

5. The mechanical properties of polyurethane films

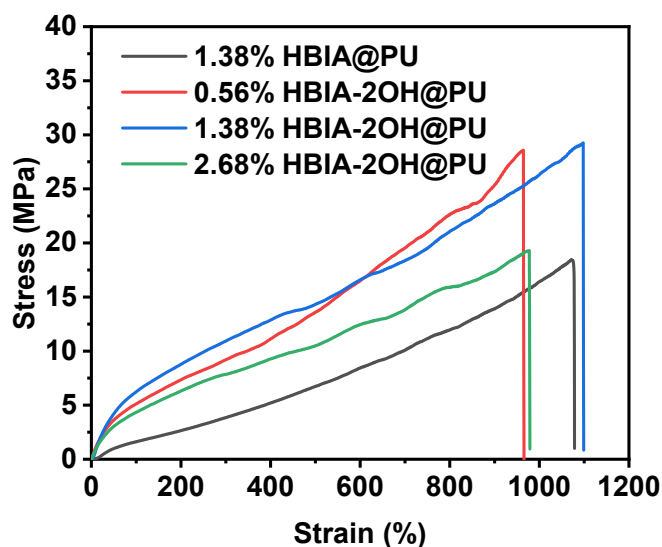


Fig. S9 Stress-strain curves of polyurethane films. The experiments were conducted with a strain rate of 50 mm/min.

Table S2. Mechanical data of the polyurethane films extracted from tensile tests. ^(a)

sample	Young's modulus (MPa)	Stress at break (MPa)	Strain at break (%)
0.56 % HBIA-2OH@PU	13.02	28.58	964
1.38 % HBIA-2OH@PU	9.05	29.25	1098
2.68 % HBIA-2OH@PU	10.54	19.30	978
1.38 % HBIA@PU	0.50	18.40	1074

^(a) All data were extracted from the stress-strain curves shown in Fig. S8 according to test standard ASTM D 882.

6. Photophysical properties of HBIA, HBIA-2OH and HBIA-2OH@PUs.

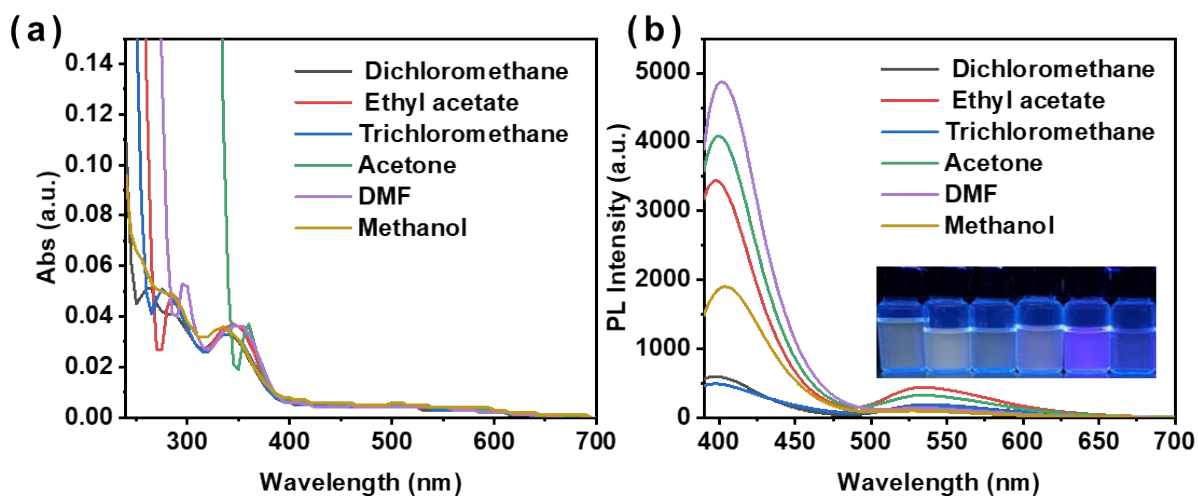


Fig. S10 (a) Absorption spectra of HBIA in different organic solvents (10 μM) and (b) PL spectra of HBIA in different organic solvents (20 μM , $\lambda_{\text{ex}} = 365 \text{ nm}$). The inserts in (b) were photographs of HBIA in different organic solvents under 365 nm UV light, respectively. (From left to right: dichloromethane, ethyl acetate, trichloromethane, acetone, DMF, methanol).

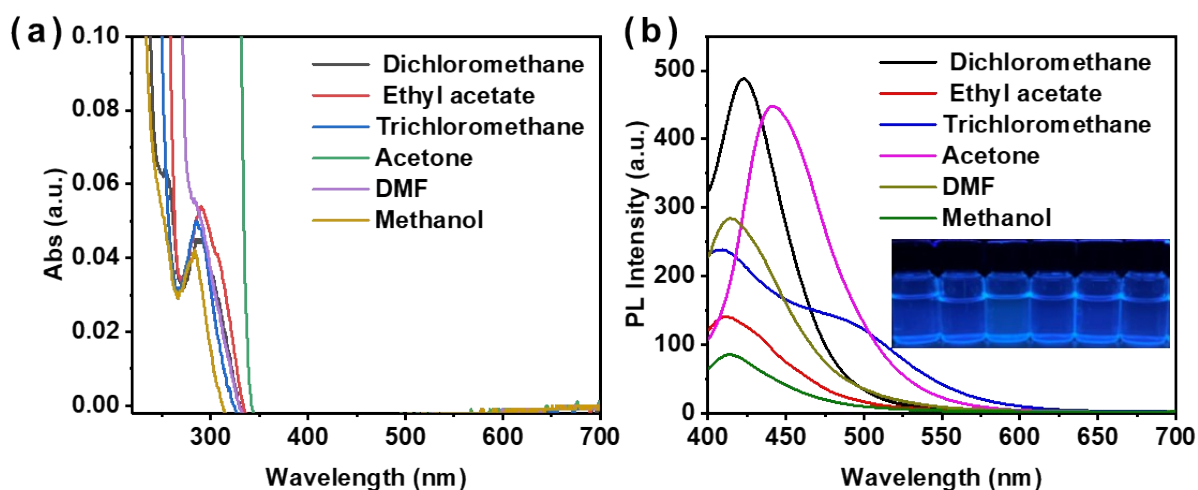


Fig. S11 (a) Absorption spectra of HBIA-2OH in different organic solvents (10 μM) and (b) PL spectra of HBIA-2OH in different organic solvents (20 μM , $\lambda_{\text{ex}} = 365 \text{ nm}$). The inserts in (b) were photographs of HBIA-2OH in different organic solvents under 365 nm UV light, respectively. (From left to right: dichloromethane, ethyl acetate, trichloromethane, acetone, DMF, methanol).

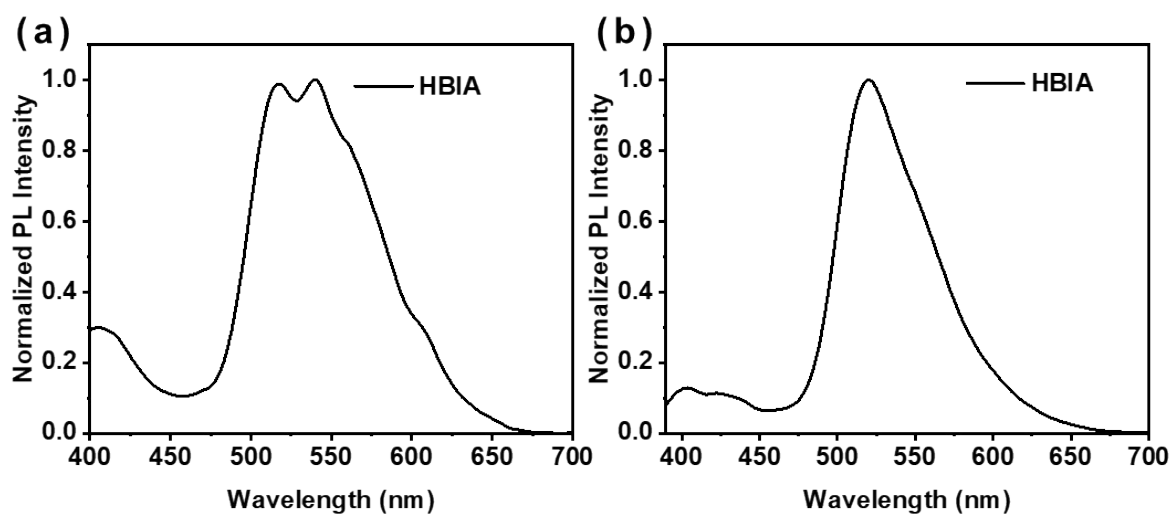


Fig. S12 Normalized PL spectra of HBIA solid power measured by (a) Seeman S5000UV miniature spectrometer (b) FL4600. (Note: the peak at 540 nm is the noise of the device)

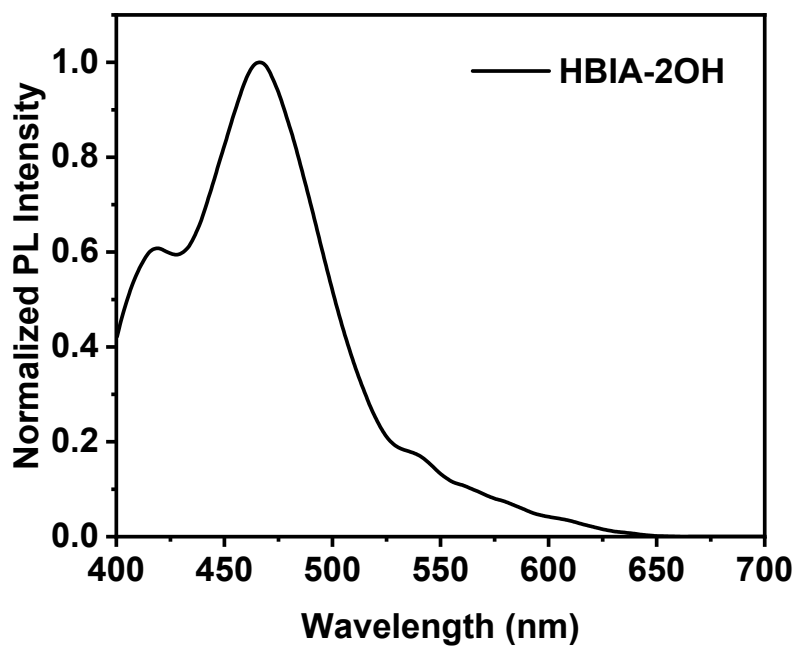


Fig. S13 Normalized PL spectrum of HBIA-2OH solid power.

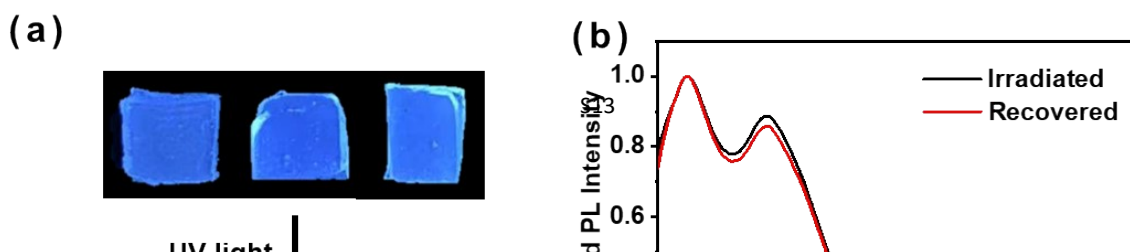


Fig. S14 (a) Photographs of 0.56 %, 1.38% and 2.68% HBIA-2OH@PU before and after irradiated from left to right. (b-d) Normalized PL spectra of (b) 0.56 %, (c) 1.38% and (d) 2.68% HBIA-2OH@PU irradiated for 5 min and recovered for 5 min at room temperature.

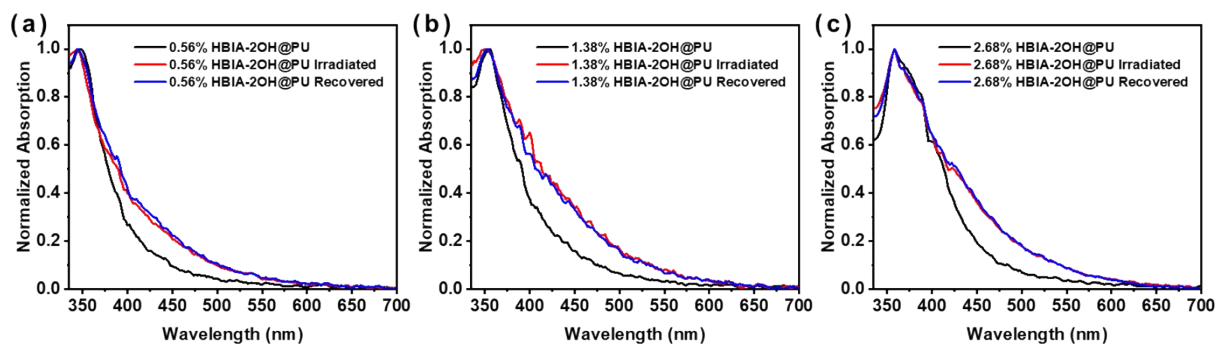


Fig. S15 Normalized absorption spectra of 0.56 %, 1.38% and 2.68% HBIA-2OH@PU before and after irradiated and recovered for 5 min at room temperature.

7. Differential scanning calorimetry (DSC)

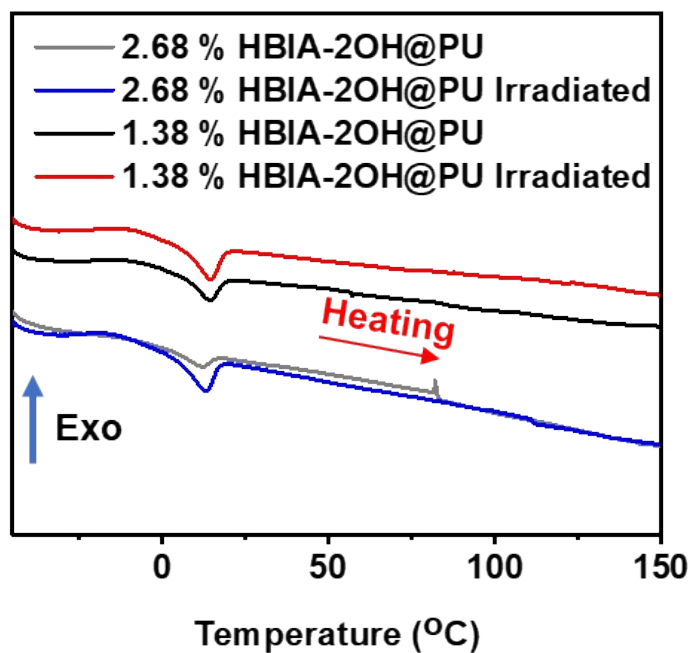


Fig. S16 DSC curves of 1.38 % HBIA-2OH@PU and 2.68 % HBIA-2OH@PU before and after 365 nm light irradiation under nitrogen atmosphere (heating rate: 10 K min⁻¹).

8. Fluorescence spectra of HBIA-2OH@PU

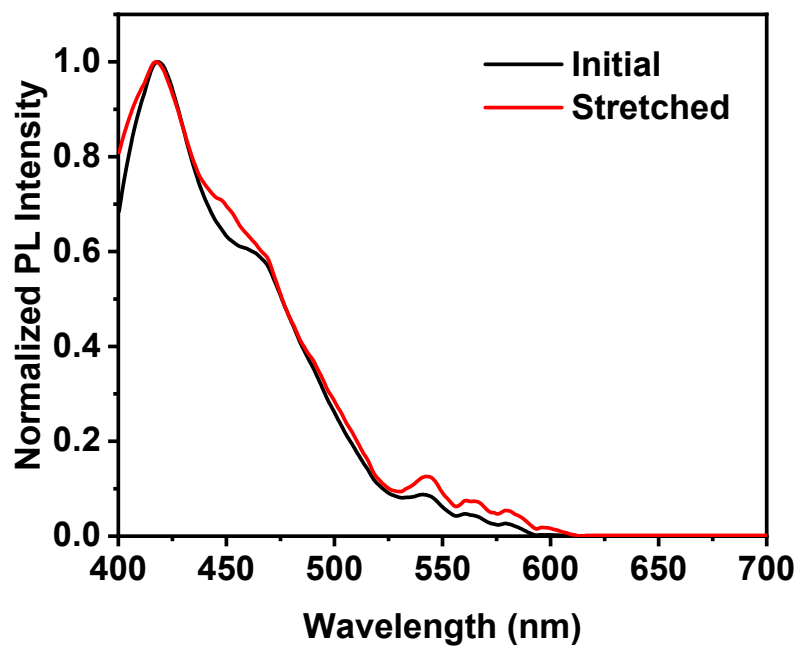


Fig. S17 Normalized fluorescence spectra of HBIA-2OH@PU before and after stretching.

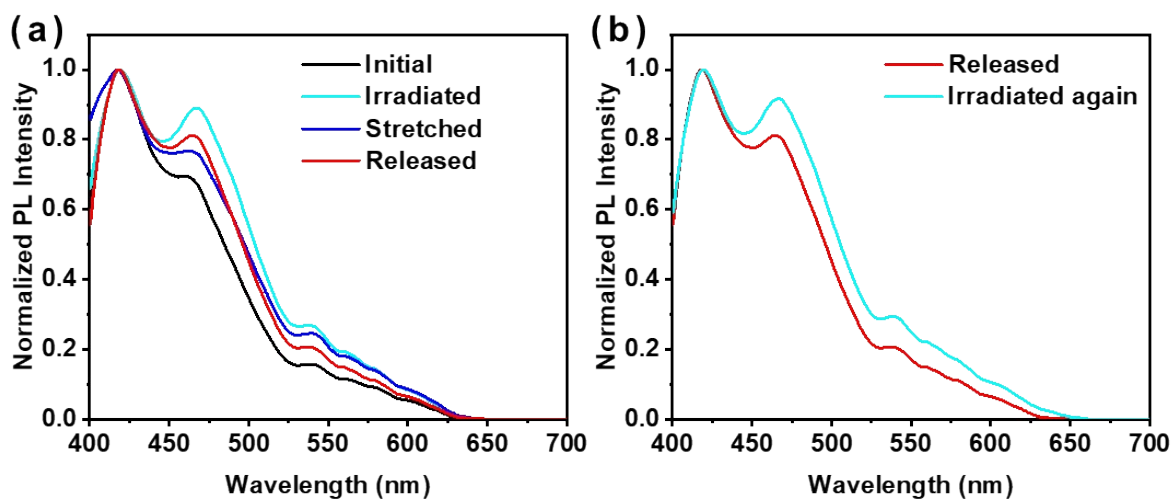


Fig. S18 Normalized PL spectra of HBIA-2OH@PU (a) before and after irradiation, and irradiated HBIA-2OH@PU after being stretched to 500% elongation and released, (b) the HBIA-2OH@PU after being released and irradiated again.

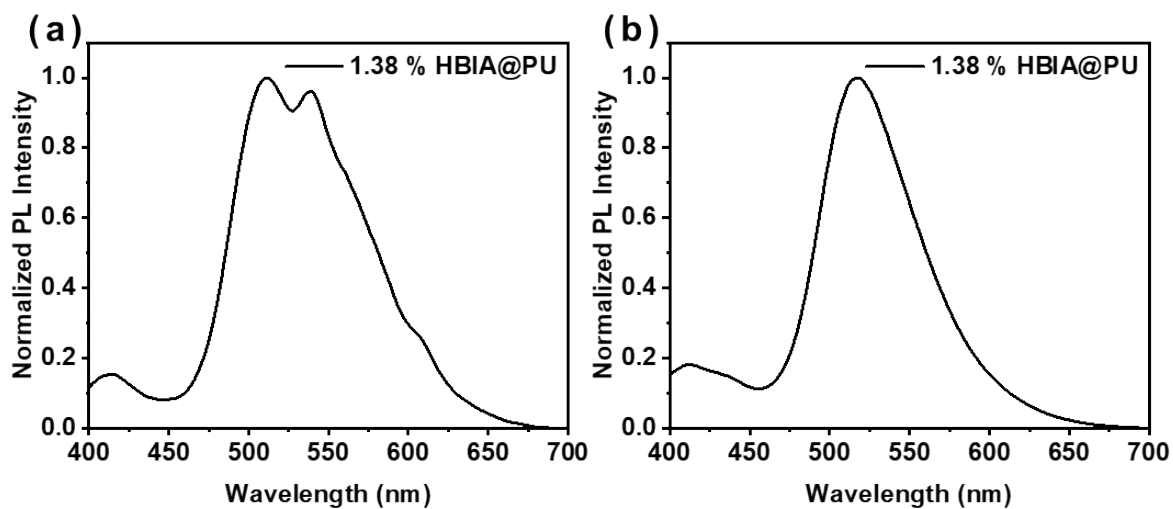


Fig. S19 Normalized PL spectra of 1.38 % HBIA@PU measured by (a) Seeman S5000UV miniature spectrometer (b) FL4600. (Note: the peak at 540 nm is the noise of the instrument)

9. DFT calculations

All DFT calculations were performed with Gaussian 16 package. Geometry optimizations were calculated in vacuum by using B3LYP functional with the 6-31G(d, p) basis set.

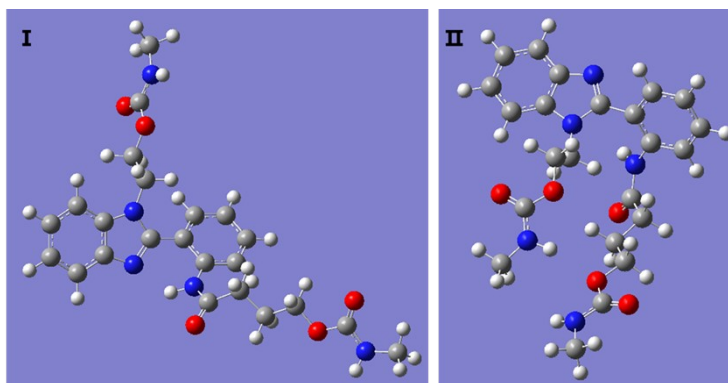


Fig. S20 Optimized structure of HBIA-2OH@PU.

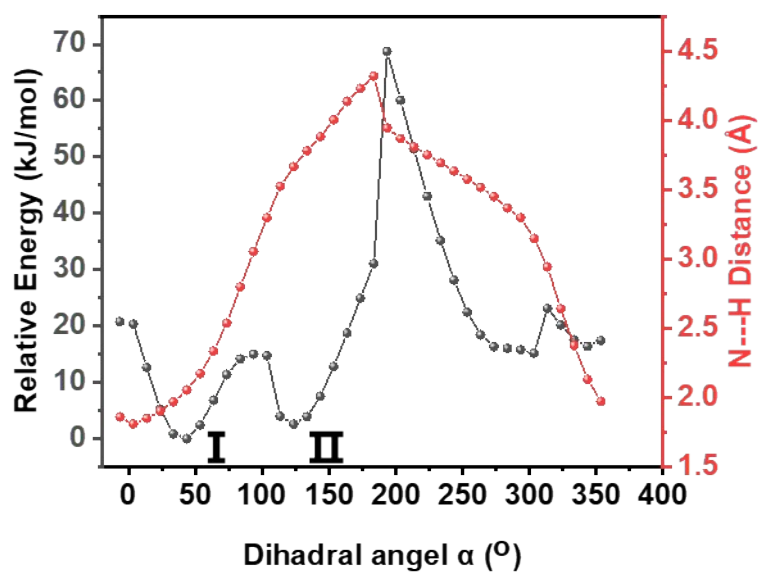


Fig. S21 The relative energy of S_0 and the N...H distance (=N- as the hydrogen bond acceptor and -NH as the hydrogen bond donor) were plotted with the increasing dihedral angle for the model molecule of HBIA-2OH@PU.

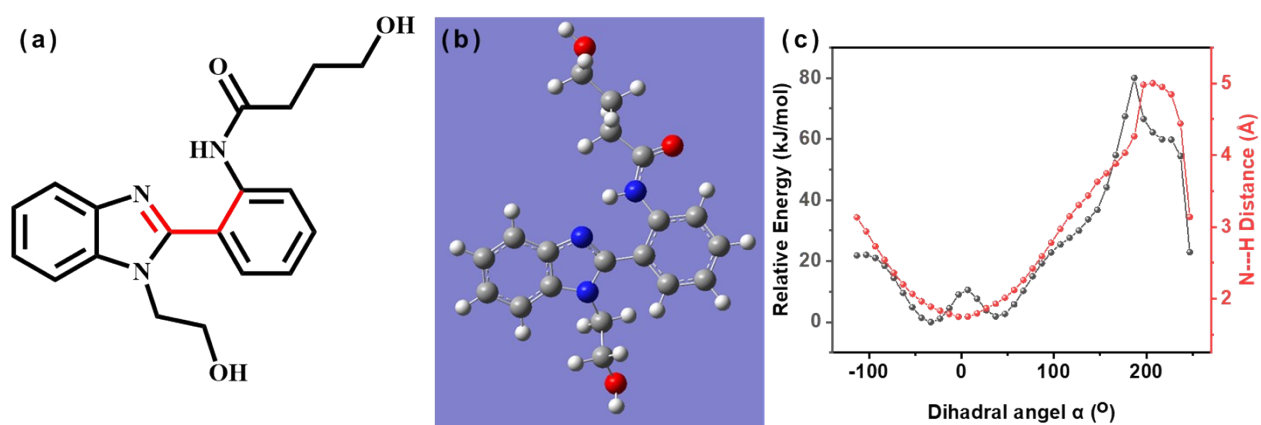


Fig. S22 (a) Chemical structure and (b) optimized structure of HBIA-2OH. (c) The relative energy of S_0 and the N...H distance (=N- as the hydrogen bond acceptor and -NH as the hydrogen bond donor) were plotted with the increasing dihedral angle for the model molecule of HBIA-2OH.

REFERENCES

- (1) Hu, H.; Cheng, X.; Ma, Z.; Sijbesma, R. P.; Ma, Z. Polymer Mechanochromism from Force-Tuned Excited-State Intramolecular Proton Transfer. *J. Am. Chem. Soc.* **2022**, *144* (22), 9971-9979.