Supporting Information

Enhanced Mechano-responsive Luminescence in Polyurethanes by Supramolecular Mechanophores based on Synergy between Quadruple H-Bonding and π-π Stacking

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I. Experimental

General Methods

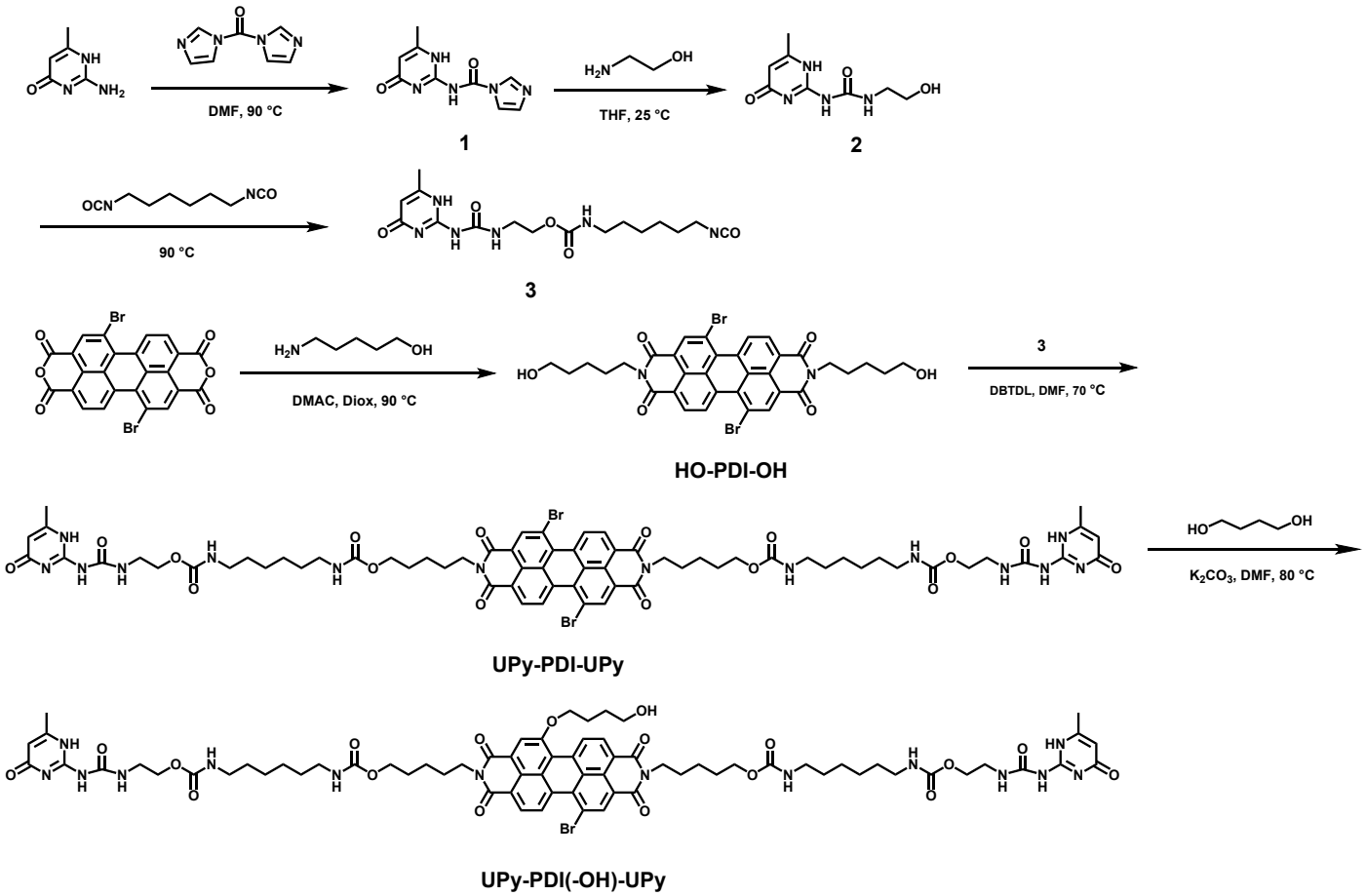
Unless otherwise stated, all oxygen or moisture-sensitive reactions were performed under a nitrogen atmosphere. All chemicals and solvents were used as received from Alfa Chemical Co. Chloroform and N,N-methylene formamide (DMF) were distilled with calcium hydride before use. Compounds **1** and **2** were prepared according to the literatures[S1,S2].

The ^{1}H (400 MHz) NMR spectra were recorded on a Bruker NMR 400 spectrometer with tetramethylsilane (TMS) as the internal reference and DMSO-d_6 or $CDCl_3$ as the solvent. Chemical shifts are reported in parts per million (ppm) relative to the residual peak of the solvent (2.50 ppm for DMSO-d_6 or 7.26 ppm for $CDCl_3$). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), and m (multiplet), and the coupling constants J are given in Hz. Mass spectrometric measurements were performed on a Ultraflex MALDI-TOF/TOF mass spectrometer, with α-cynao-4-hydroxycinnamic acid (CHCA) as the matrix. Elemental analyses were performed on a Vario EL III elemental analyzer. Gel permeation chromatography (GPC) was recorded by Aglient 1260 Infinity II GPC/SEC system with $CHCl_3$ as the mobile phase and narrow linear PS as the standards (1132 – 3051140 g/mol).

The UV-vis absorption spectra were recorded on a HITACHI U-3900 spectrometer. The fluorescence spectra were recorded on a HITACHI F-4700 FL spectrometer excited at 380 nm.

At room temperature, the tensile properties of polymer films were characterized by universal material testing machine. The tensile rate was maintained at 10 mm/min. The Young's modulus is determined by the initial slope of the stress-strain curve.

Synthesis of the compounds



Scheme S1. Synthetic routes to **HO-PDI-OH**、**UPy-PDI-UPy** and **UPy-PDI(-OH)-UPy**.

Synthesis of 2-(1-imidazolylcarbonylamino)-6-methyl-4[1*H*]-pyrimidinone[S1] (1)

To DMF (110 mL) was added 2-amino-6-methylpyrimidin-4(1*H*)-ketone (6.00 g, 0.048 mol) and N,N'-carbonyldiimidazole (CDI) (9.40 g, 0.058 mol). The mixture was stirred at 90 °C for 5 h and then cooled to room temperature. After acetone (150 mL) was added as the precipitant, the precipitates were filtered, washed with acetone and dried in vacuo at 50 °C to obtain **1** as a white solid (7.80 g, 0.036 mol, 74%).

Synthesis of 1-(2-hydroxyethyl)-3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)urea[S2] (2)

To THF (120 mL) was added **1** (6.00 g, 0.027 mol) and ethanolamine (2.50 g, 0.041 mol), and the mixture was stirred at 25 °C for 3 hours. The solvent was concentrated, and distilled water (400 mL) was added as the precipitant. The precipitates were filtered, washed with deionized water and acetone successively, and dried in vacuo at 50 °C to yield **2** as a white solid (4.50 g, 0.021 mol, 79%).^{1}H NMR (400 MHz, DMSO-d_6) δ 11.55

(s, 1H), 9.76 (s, 1H), 7.46 (s, 1H), 5.78 (s, 1H), 4.83 (t, J = 5.1 Hz, 1H), 3.46 (q, J = 5.5 Hz, 2H), 3.20 (q, J = 5.6 Hz, 2H), 2.10 (s, 3H).

Synthesis of 2-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)ethyl (6-isocyanatohexyl) carbamate (3)

Compound **2** (1.50 g, 7 mmol) was dissolved in 1,6-diisocyanate (HDI) (15 mL), and the mixture was stirred at 90 °C for 24 hours. The reaction mixture was cooled to room temperature, and ethyl acetate (100 mL) was added as the precipitant. The precipitates were filtered, washed with toluene and acetone successively, and dried in vacuo at 50 °C to obtain **3** as a white solid (1.76 g, 4.6 mmol, 66%). ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 13.10 (s, 1H), 11.85 (s, 1H), 10.17 (s, 1H), 5.83 (s, 1H), 4.47 (t, J = 7.9 Hz, 1H), 3.66 (s, 2H), 3.52 – 2.90 (m, 6H), 2.23 (s, 3H), 1.62 (t, J = 7.1 Hz, 4H), 1.43 – 1.34 (m, 4H). MS (MALDI-TOF, *m/z*): $[M-H]^-$ calcd for $C_{16}H_{23}N_6O_5$, 379.18, found 379.09.

Synthesis of N,N′-bis(5-hydroxypentyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxylic diimide (HO-PDI-OH)

To anhydrous N,N-dimethylacetamide (DMAC, 10 mL) and 1,4-dioxane (10 mL) solution was added 1,7-dibromo-3,4,9,10-perylenetetracarboxylic dianhydride (400 mg, 0.85 mmol) and 5-amino-1-pentanol (200 mg, 2 mmol). The reaction was carried out at 95 °C for 50 minutes. After the reaction was completed, the mixture was cooled to room temperature, and deionized water (400 mL) was added as the precipitant. The precipitates were filtered, washed with deionized water, and dried at 65 °C in vacuo. The crude product was purified by column chromatography (MeOH / DCM = 1/25, v/v) to yield **4** as a red solid (290 mg, 0.403 mmol, 47%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.15 (s, 2H), 8.41 (s, 4H), 4.39 (d, J = 5.3 Hz, 2H), 4.00 (s, 4H), 3.44 – 3.37 (m, 4H), 1.52 – 1.37 (m, 12H). MS (MALDI-TOF, *m/z*): $[M+H]^+$ calcd for $C_{34}H_{29}Br_2N_2O_6$, 720.03, found 721.01.

Synthesis of 5-(5,12-dibromo-9-(1-((6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)amino)-1,6,15-trioxo -

5,16-dioxa-2,7,14-triazahenicosan-21-yl)-1,3,8,10-tetraoxo-3,8,9,10-tetrahydroanthra[2,1,9-def:6,5,10-d'e'f']diisoquinolin-2(1H)-yl)pentyl (2-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)ethyl) hexane-1,6-diyldicarbamate (UPy-PDI-UPy)

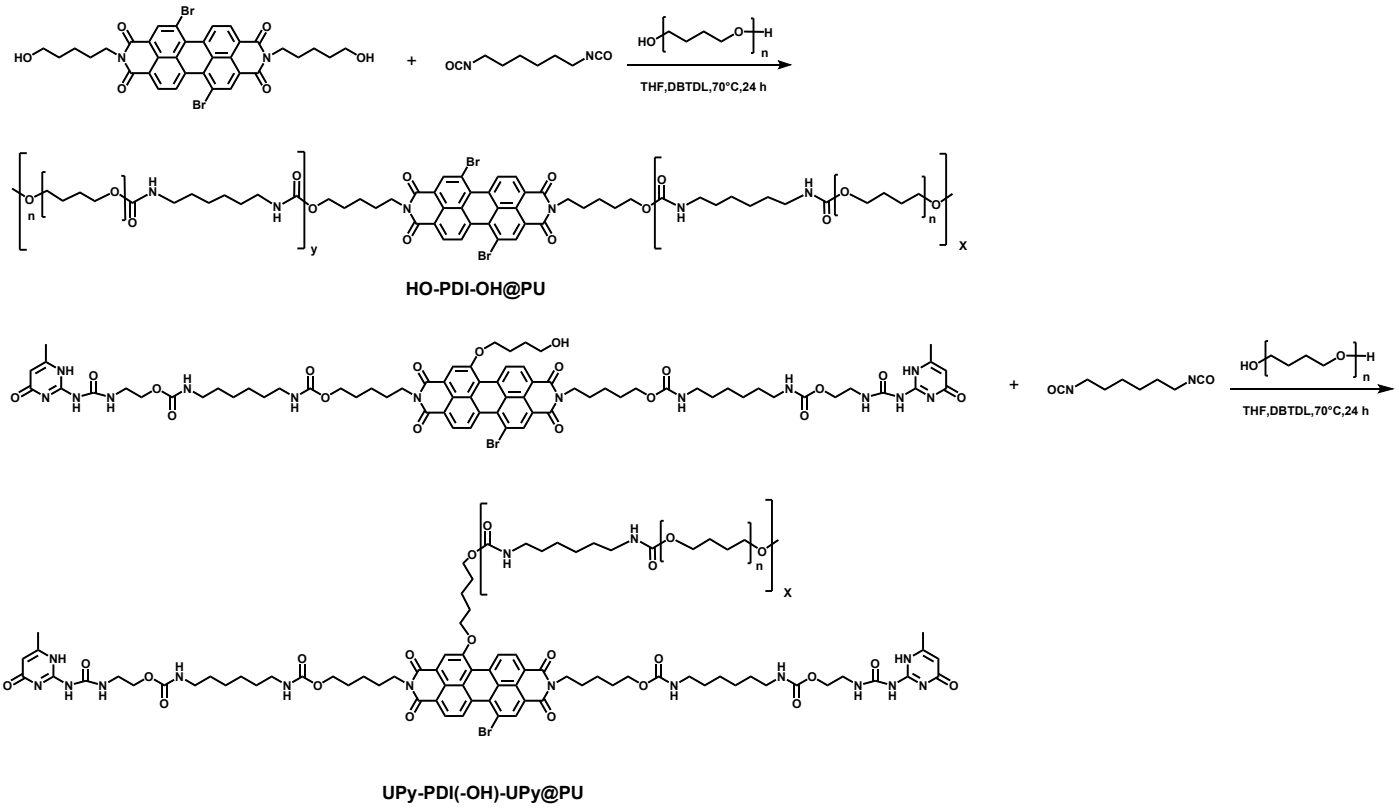
To dry DMF (110 mL) was added compounds **3** (467 mg, 1.23 mmol), **4** (300 mg, 0.41 mmol), and catalyst dibutyltin dilaurate (DBTDL) (30 μL). The reaction was carried out at 70 °C for 24 hours. After the reaction was completed, the mixture was cooled to room temperature, and hexane (300 mL) was added as the precipitant. The precipitates were filtered, washed with EtOH, and dried in vacuo. The crude product was purified by column chromatography (MeOH/DCM = 1/20, v/v) to yield **UPy-PDI-UPy** as a red solid (326 mg, 0.22 mmol, 53.7%).^{1}H NMR (400 MHz, DMSO-d_6) δ 11.52 (s, 2H), 9.68 (s, 1H), 9.63 (s, 1H), 9.24 (d, J = 8.6 Hz, 2H), 8.78 – 8.22 (m, 4H), 7.46 – 7.31 (m, 2H), 7.03 (s, 2H), 5.86 – 5.64 (m, 4H), 4.23 – 3.69 (m, 6H), 3.34 (d, J = 6.2 Hz, 8H), 3.16 – 2.87 (m, 10H), 2.05 (s, 6H), 1.58 – 1.20 (m, 28H). MS (MALDI-TOF, *m/z*): $[M\text{-}C_{16}H_{25}N_6O_5]^+$ calcd for $C_{50}H_{51}Br_2N_8O_{11}$,1097.20, found 1097.36.

Synthesis of 5-(5-bromo-12-(4-hydroxybutoxy)-9-(1-((6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)amino)-1,6,15-trioxo-5,16-dioxa-2,7,14-triazahenicosan-21-yl)-1,3,8,10-tetraoxo-3,8,9,10-tetrahydroanthra[2,1,9-def:6,5,10-d'e'f']diisoquinolin-2(1H)-yl)pentyl (2-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)ethyl) hexane-1,6-diyldicarbamate (UPy-PDI(-OH)-UPy)

To dry DMF (30 mL) was added **UPy-PDI-UPy** (200 mg, 0.13 mmol), butanediol (13.78 mg, 0.13 mmol), and K_2CO_3 (64 mg, 0.46 mmol). The reaction was carried out at 80 °C for 50 minutes. After the reaction was completed, the mixture was cooled to room temperature, and deionized water (400 mL) with dilute hydrochloric acid (1 M, 2 mL) was added as the precipitant. The precipitates were filtered, washed with deionized water, and dried in vacuo at 65 °C. The crude product was purified by column chromatography (MeOH/DCM = 1/20,v/v) to yield **UPy-PDI(-OH)-UPy** as a red solid (121 mg, 0.081 mmol, 63%).^{1}H NMR (400 MHz, DMSO-d_6) δ 11.51 (s, 2H), 9.64 (s, 2H), 9.04 (d, J = 6.9 Hz, 2H), 8.54 (s, 1H), 8.41 – 8.26 (m,

4H), 8.21 (s, 1H), 7.33 (s, 2H), 7.04 (d, *J* = 5.3 Hz, 2H), 5.74 (m, 2H), 4.45 – 4.32 (m, 4H), 4.07 – 3.85 (m, 8H), 3.60 (t, *J* = 6.5 Hz, 1H), 3.43 (m, 8H), 3.11 (q, *J* = 6.5 Hz, 4H), 2.99 – 2.88 (m, 4H), 2.10 (s, 6H), 1.64 (s, 6H), 1.53 – 1.47 (m, 4H), 1.47 – 1.32 (m, 14H), 1.30 – 1.18 (m, 8H), 1.06 (t, J = 7.0 Hz, 3H). MS (MALDI-TOF, *m/z*): $[M\text{-}C_{21}H_{30}N_{10}O_8+H]^+$ calcd for $C_{49}H_{56}BrN_4O_{10}$, 939.31, found 939.44.

3. Preparation of the Polymers



Scheme S2. Synthetic routes to **HO-PDI-OH@PU** and **UPy-PDI(-OH)-UPy@PU**.

Synthesis of 0.1 mol% HO-PDI-OH@PU

Polytetrahydrofuran (PTMG) (1.95 g, 3 mmol, M_n = 650 g/mol), DBTDL (30 μL) and HDI (0.525 g 3.02 mmol) were dissolved in dry THF (30 mL) and pre-polymerized at 70 °C for 1 h. **HO-PDI-OH** (2.2 mg, 0.003 mmol) dissolved in dry THF (10 mL) was then added and the reaction mixture was stirred for 23 hours. The mixture was cooled to room temperature and poured into n-hexane (200 mL). The orange precipitate was filtered and dried in vacuo at 50 °C (2.20 g, 89%, M_n = 151.8 kDa).

0.3 mol% **HO-PDI-OH@PU** and 0.5 mol% **HO-PDI-OH@PU** were prepared according to the above

procedure with the amount of **HO-PDI-OH** of 6.6 and 11 mg, respectively.

Synthesis of 0.1 mol% UPy-PDI-UPy in PU

Polytetrahydrofuran (PTMG) (1.95 g, 3 mmol, M_n = 650 g/mol), DBTDL (30 μL) and HDI (0.525 g 3.02 mmol) were dissolved in dry THF (30 mL) and pre-polymerized at 70 °C for 1 h. **UPy-PDI-UPy** (4.4 mg, 0.003 mmol) dissolved in dry THF (10 mL) was then added and the reaction mixture was stirred for 23 hours. The mixture was cooled to room temperature and poured into n-hexane (200 mL). The red precipitate was filtered and dried in vacuo at 50 °C (2.20 g, 89%, M_n = 139.6 kDa).

0.3 mol% **UPy-PDI-UPy in PU** and 0.5 mol% **UPy-PDI-UPy in PU** were prepared according to the above procedure with the amount of **UPy-PDI-UPy in PU** of 13.2 and 22 mg, respectively.

Synthesis of 0.1 mol% UPy-PDI(-OH)-UPy@PU

Polytetrahydrofuran (PTMG) (1.95 g, 3 mmol, M_n = 650 g/mol), DBTDL (30 μL) and HDI (0.525 g 3.02 mmol) were dissolved in dry THF (30 mL) and pre-polymerized at 70 °C for 1 h. **UPy-PDI(-OH)-UPy** (4.5 mg, 0.003 mmol) dissolved in dry THF (10 mL) was then added and the reaction mixture was stirred for 23 hours. The mixture was cooled to room temperature and poured into n-hexane (200 mL). The orange precipitate was filtered and dried in vacuo at 50 °C (2.23 g, 90%, M_n = 165.8 kDa).

0.3 mol% **UPy-PDI(-OH)-UPy@PU** and 0.5 mol% **UPy-PDI(-OH)-UPy@PU** were prepared according to the above procedure with the amount of **UPy-PDI(-OH)-UPy@PU** of 13.5 and 22.5 mg, respectively.

Preparation of the PU films

The polyurethane (3 g) was dissolved in chloroform (30 mL) to form a uniform mixture, and the solution was then poured into a poly(tetrafluoroethylene) mold of 12 cm×12 cm. The polyurethane films were prepared into a dumbbell shaped poly(tetrafluoroethylene) of 5 mm×15 mm. The film with a thickness of about 0.06 mm was prepared after 12 hours of volatilization of the solvent at room temperature.

II. Photophysical properties of fluorescent mechanophores

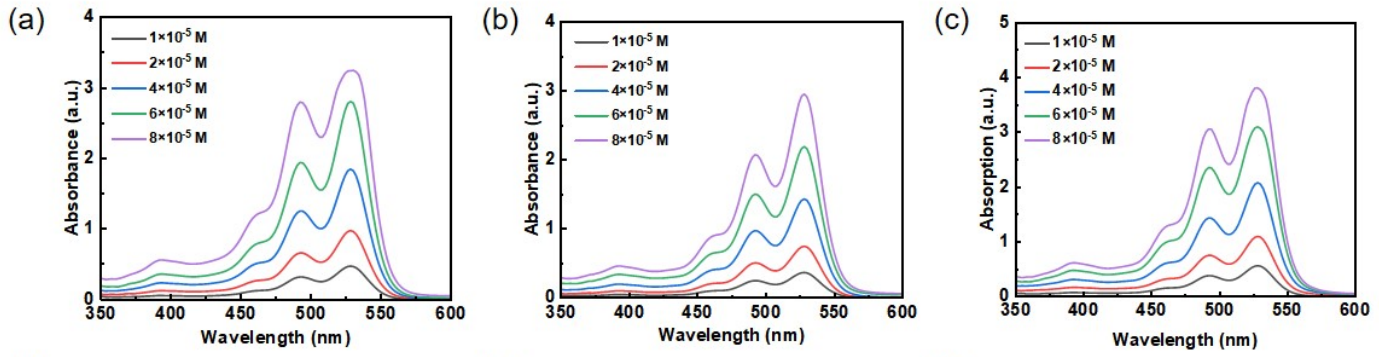


Figure S1. UV-Vis absorption spectra of (a) **HO-PDI-OH**, (b) **UPy-PDI-UPy** and (c) **UPy-PDI(-OH)-UPy** in chloroform with different concentrations.

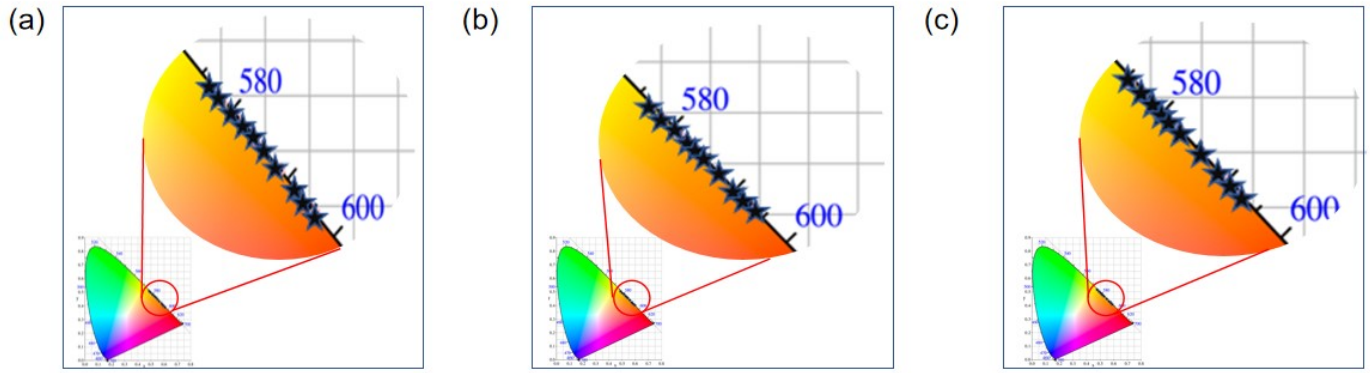


Figure S2. CIE coordinates of (a) **HO-PDI-OH**、(b) **UPy-PDI-UPy** and (c) **UPy-PDI(-OH)-UPy** with different concentrations.

III. Mechanical properties of mechanoresponsive luminescent polymers

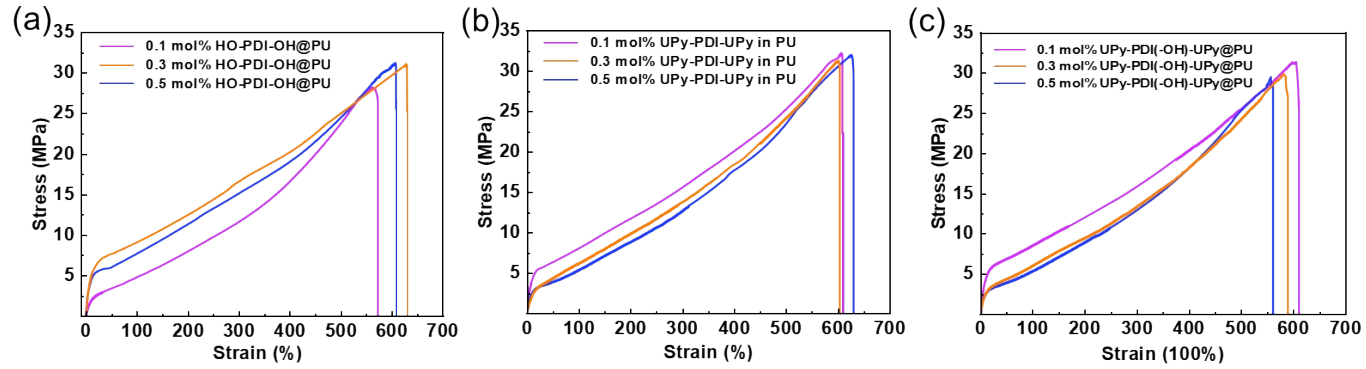


Figure S3. Stress-strain curves of different contents (a) **HO-PDI-OH@PU**, (b) **UPy-PDI-UPy in PU** and (c) **UPy-PDI(-OH)-UPy@PU**.

Table S1. Summary of the mechanical properties of different types of PU elastomers

Sample	Fracture Stress (Mpa)	Fracture Strain (100%)	Young's Modulus (Mpa)	Toughness (kJ/m^3)
blank PU	26.12	5.25	4.98	67.12
0.1 mol% **HO-PDI-OH@PU**	28.12	5.72	4.92	72.56
0.3 mol% **HO-PDI-OH@PU**	30.93	6.29	4.93	101.88
0.5 mol% **HO-PDI-OH@PU**	31.27	6.08	5.13	97.67
0.1 mol% **UPy-PDI-UPy in PU**	32.31	6.15	5.24	101.83
0.3 mol% **UPy-PDI-UPy in PU**	31.22	6.04	5.30	90.34
0.5 mol% **UPy-PDI-UPy in PU**	31.96	6.24	4.61	94.15
0.1 mol% **UPy-PDI(-OH)-UPy@PU**	31.48	6.02	5.23	109.36
0.3 mol% **UPy-PDI(-OH)-UPy@PU**	29.80	5.89	5.06	84.63
0.5 mol% **UPy-PDI(-OH)-UPy@PU**	29.49	5.60	5.26	75.38

IV. Mechanoresponsive luminescent properties of polymers

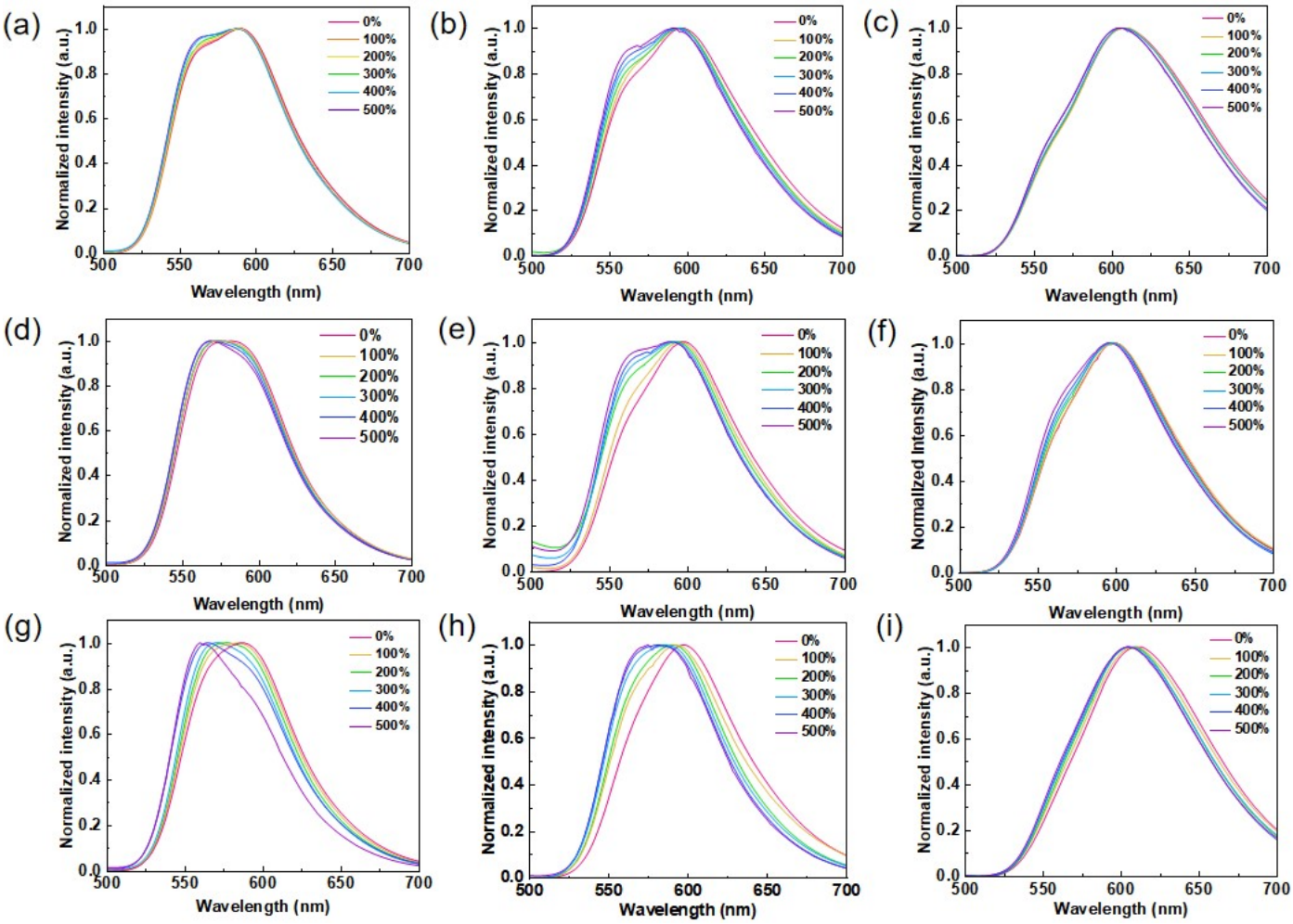


Figure S4. Normalized PL spectra under different strains of (a-c) 0.1, 0.3, 0.5 mol% **HO-PDI-OH@PU**; (d-f) 0.1, 0.3, 0.5 mol% **UPy-PDI-UPy in PU**; (g-i) 0.1, 0.3, 0.5 mol% **UPy-PDI(-OH)-UPy@PU**

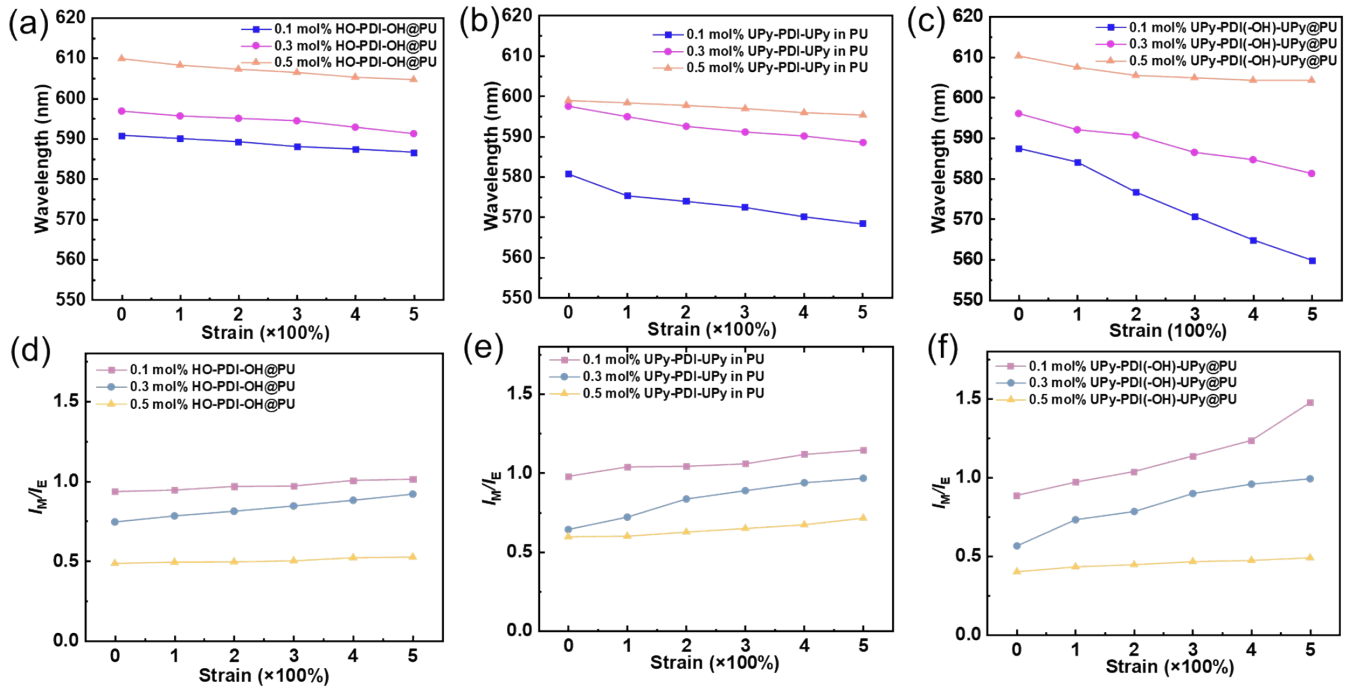


Figure S5. The wavelength changes under different strains of 0.1, 0.3 and 0.5 mol% (a) **HO-PDI-OH@PU**, (b) **UPy-PDI-UPy in PU**, (c) **UPy-PDI(-OH)-UPy@PU**. The I_M/I_E values under different strains of 0.1, 0.3 and 0.5 mol% of (d) **HO-PDI-OH@PU**, (e) **UPy-PDI-UPy in PU** and (f) **UPy-PDI(-OH)-UPy@PU**

Table S2. The mechanoresponse performance of the PU elastomers under 0-500% strain

Sample	$\Delta I_M/I_E$	$\Delta\lambda_{max}$ (nm)
0.1 mol% **HO-PDI-OH@PU**	0.08	4.4
0.3 mol% **HO-PDI-OH@PU**	0.17	6.3
0.5 mol% **HO-PDI-OH@PU**	0.04	5.4
0.1 mol% **UPy-PDI-UPy in PU**	0.32	12.4
0.3 mol% **UPy-PDI-UPy in PU**	0.11	9.2
0.5 mol% **UPy-PDI-UPy in PU**	0.07	4.6
0.1 mol% **UPy-PDI(-OH)-UPy@PU**	0.59	27.6
0.3 mol% **UPy-PDI(-OH)-UPy@PU**	0.43	15.5
0.5 mol% **UPy-PDI(-OH)-UPy@PU**	0.09	6.7

V. ^{1}H NMR spectra

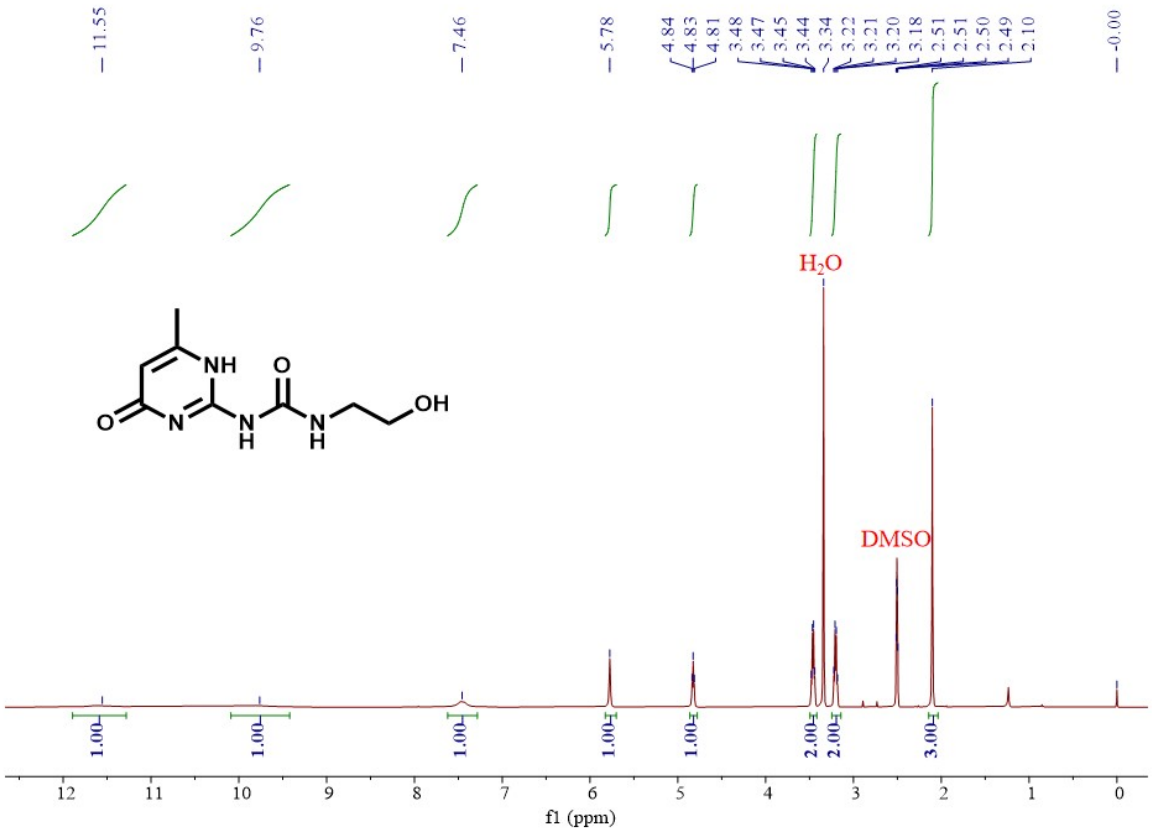


Figure S6 ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **2**.

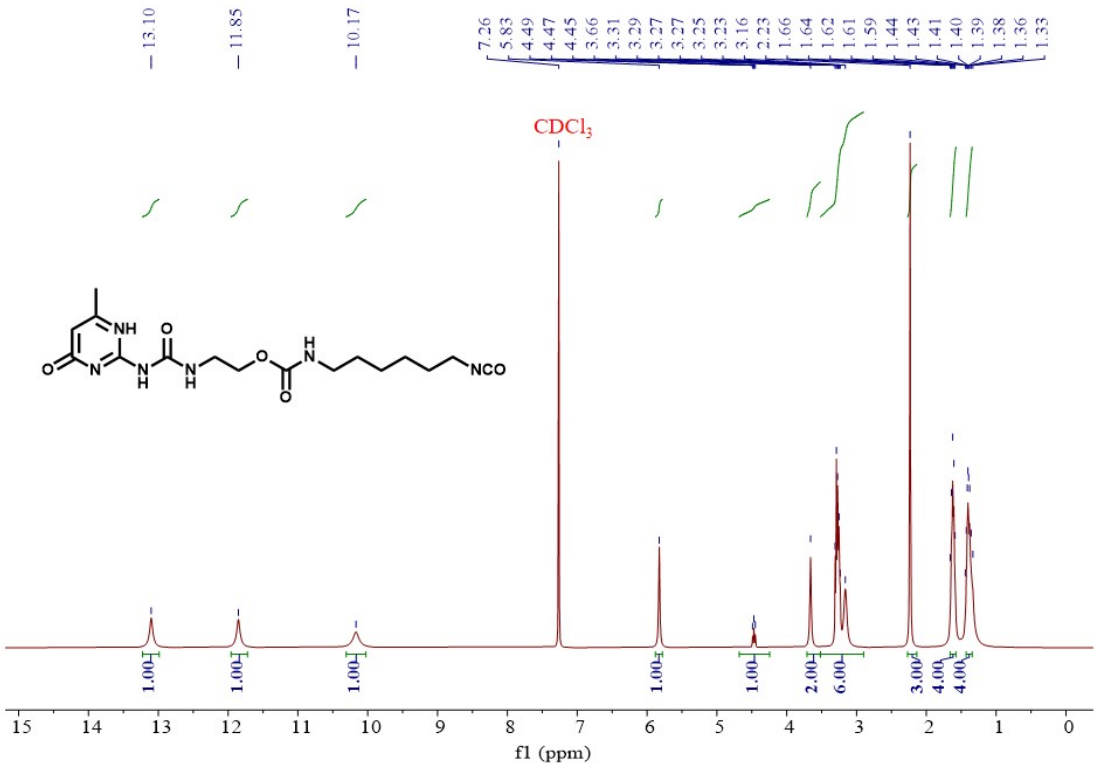


Figure S7 ^{1}H NMR spectrum (400 MHz, $CDCl_3$-d) of **3**.

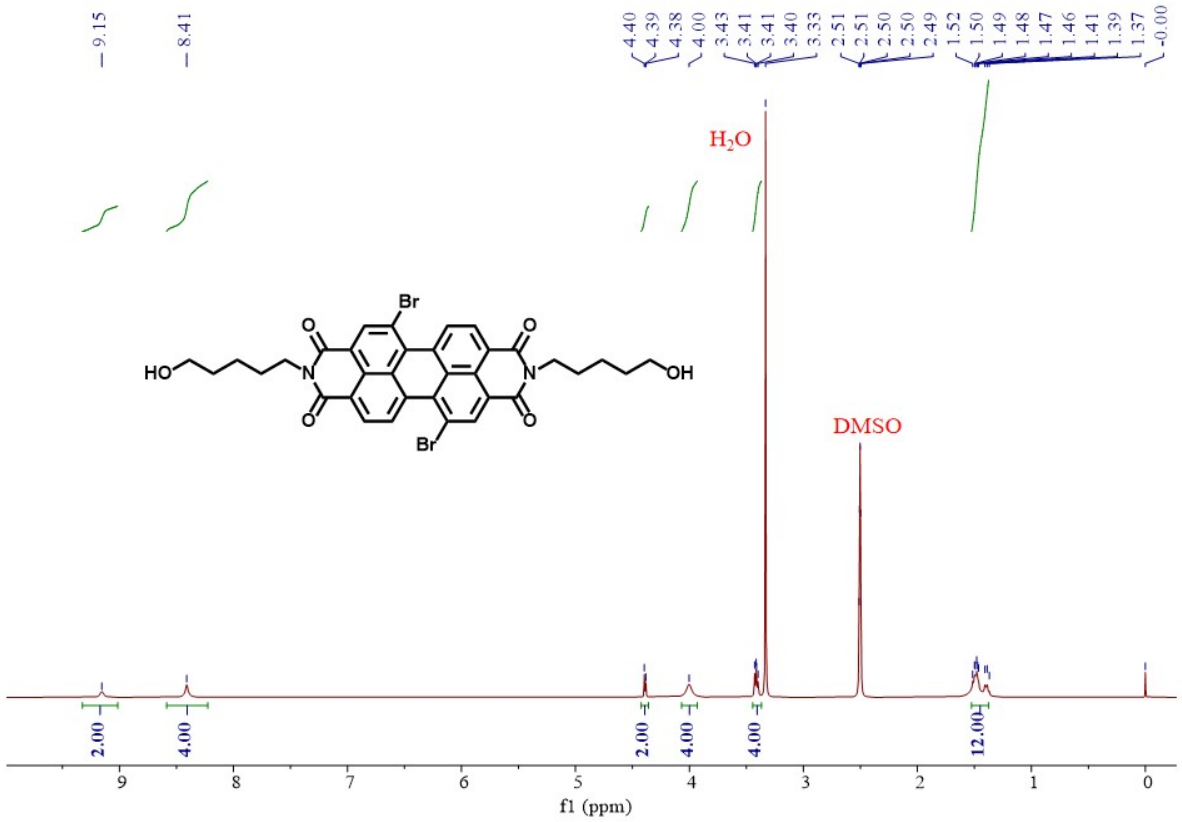


Figure S8 ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **HO-NDI-OH**.

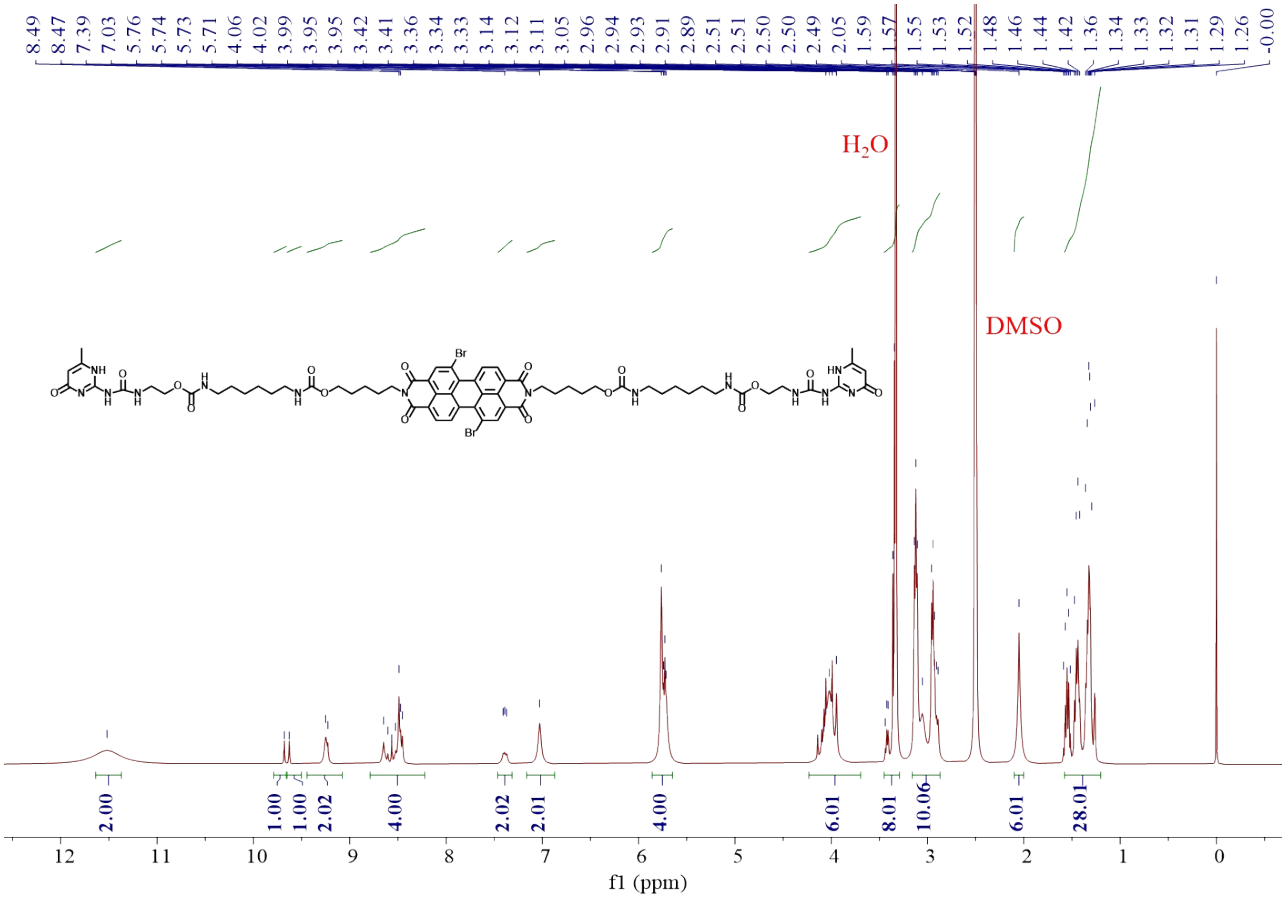


Figure S9 ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **UPy-PDI-UPy**.

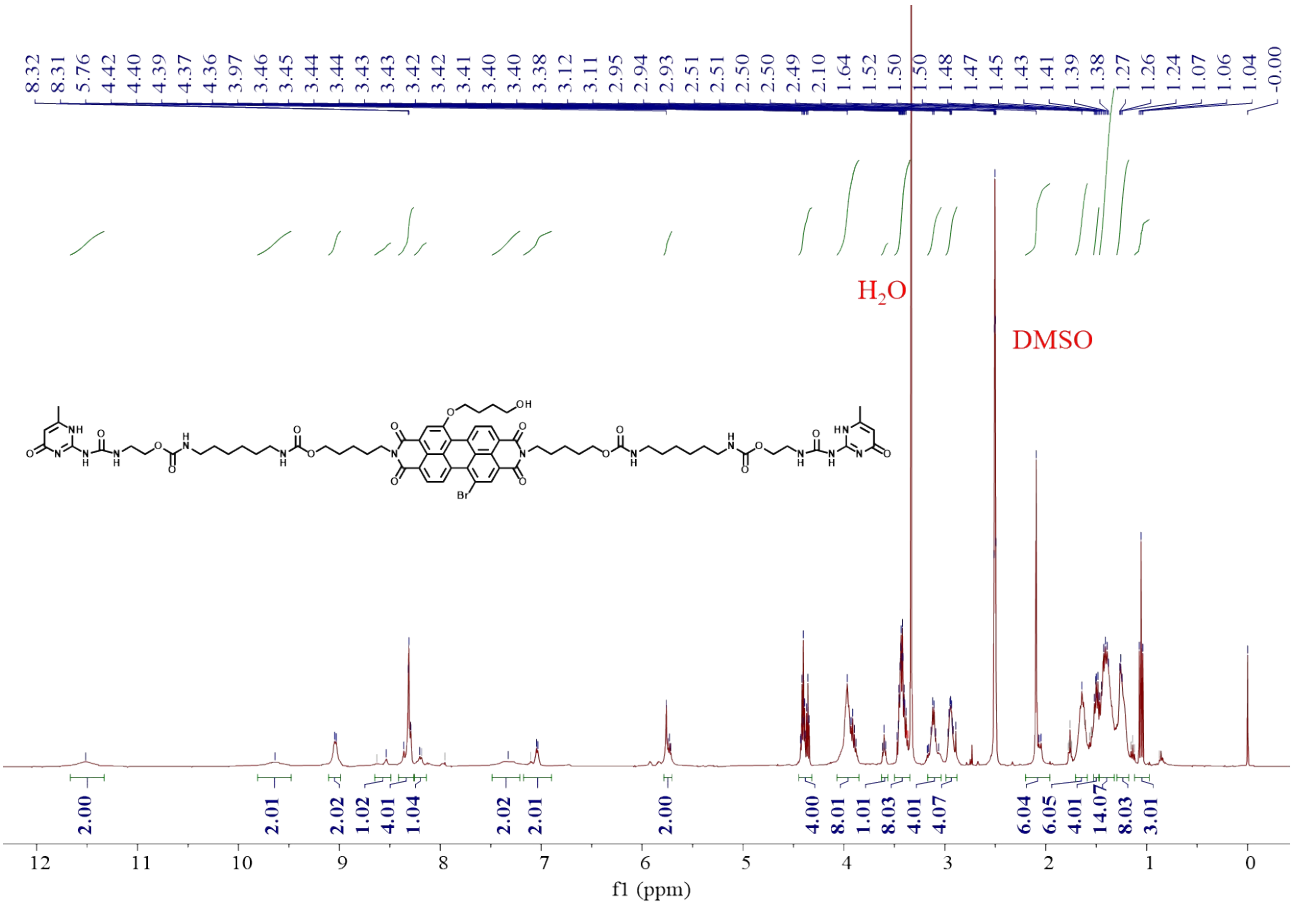


Figure S10 ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **UPy-PDI(-OH)-UPy**.

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