Electronic Supplementary Information (ESI)

Harnessing Mechanochemical Fluorescence Toward Autonomous Damage-Reporting Coatings

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I. Coating fabrication

A 1-gram scale synthesis of a PU coating on a steel substrate was performed as follows. In a scintillation vial, trimethylolpropane (40.0 mg, 0.298 mmol, 12 equiv OH), **π-AM** (10.0 mg, 0.021 mmol, 0.56 equiv OH), 1,4-butanediol (4.8 mg, 0.054 mmol, 1.44 equiv OH), crushed poly(tetramethylene ether)glycol (746.1 mg, 0.373 mmol, 10 equiv OH), isophorone diisocyanate (199.0 mg, 0.895 mmol, 24 equiv NCO) and anhydrous THF (410 μL) were added. For pigmented coating, 10 mg of the pigment of interest (1 wt.%) was also introduced into the vial, which was sonicated for 5 minutes to ensure proper dispersion of the pigment. The resin mixture was then capped and stirred at 500 rpm for 5 minutes in a 40 °C water bath. After this, a catalyst stock solution of dibutyltin dilaurate (0.05 w/v in THF, 10.8 μL, 0.018 mmol, 0.01 equiv) was added. The final mixture was stirred for 1 minute for mixing and sonicated for 5 minutes for degassing. The mixture was poured onto a steel panel (Q-Lab, QD-36) and applied by a 6-mil bar-shaped film applicator (BYK Instruments). The coated panel was then transferred into a ventilated oven for 30-minute curing at 120 °C. The thickness of the dried and cured coating was measured by an Elcometer digital coating thickness gauge, yielding an approximate thickness of 100 μm.

II. Impact experiments

Impact testing was performed using an SPI Impact Tester (BYK Instruments). A cylindrical weight was dropped down a slotted vertical guide tube from a predetermined height, striking a round-nosed punch (diameter = 12.7 mm), which was positioned on the coated substrate. The impact-induced fluorescence of the coating was analyzed using an Olympus BX63 Microscope equipped with a fluorescence filter cube (U-FUNA) and observed using the DAPI observation method, with a manual exposure time of 25 ms. The average fluorescence intensity in the impacted area was measured from the blue channel using ImageJ.

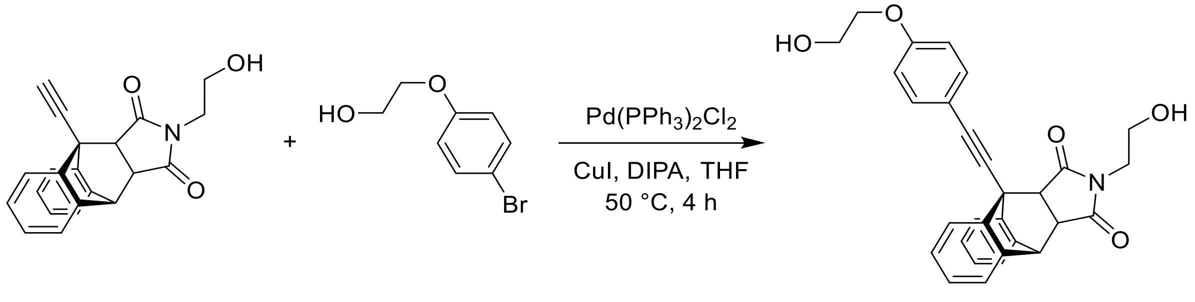
III. Free-standing polyurethane preparation

The formulation of the free-standing polyurethane material was identical to that of the coating, as described in the Experimental Section of the main text. After all the components were mixed in anhydrous THF, the mixture was poured into a Teflon mold with three cutouts according to ASTM D638 Type V (fabricated by the Machine Shop at The University of Akron). The mold containing the resin was then placed in a glass jar and subjected to vacuum. The vacuum was applied until solvent evaporation slowed to one bubble every few seconds. The jar was then backfilled with nitrogen and left to sit overnight. Post-curing was performed at 120 °C for 30 minutes.

IV. Characterization

Nuclear magnetic resonance (NMR) spectroscopy was conducted at the University of Akron Magnetic Resonance Center using a Varian NMR 500MHz spectrometer. The spectra were analyzed by MestReNova. Uniaxial tensile testing was performed on an Instron 5543 universal testing system at a strain rate of 0.5 mm/mm/min using a 100 N load cell. The system was equipped with pneumatic grips, and the gripping pressure was set at 25 psi. Compression was done on an Instron 5969 universal testing system using a 50 kN load cell. For the compression study, a rectangular sample was cut from a dumbbell sample (~13×3 mm^2). The sample was lubricated with soap water and compressed between stainless steel plates at a strain rate of 62.5 mm/mm/min to $H_0/H = 16$ and held for 1 minute. The stretched or compressed samples were analyzed by an Agilent Cary Eclipse fluorescence spectrometer with a solid-state sample mounter, with the excitation wavelength set at 400 nm. Both the excitation and emission slits were set at 2.5 nm. Solution-state fluorescence spectroscopy was performed on an Agilent Cary Eclipse fluorescence spectrometer with the excitation wavelength set at 400 nm. Both the excitation and emission slits were set at 5 nm. The absorbance of the pigmented coatings was measured using an Agilent Cary 60 UV-Vis Spectrophotometer.

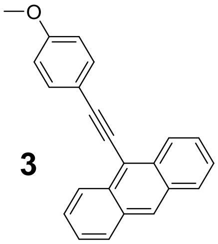
V. Synthesis



1 **2** **π-AM**

1[1] and **2**[2] were synthesized according to literature reports. **1** (649 mg, 1.89 mmol, 1 equiv), **2** (616.6 mg, 2.84 mmol, 1.5 equiv), $Pd(PPh_3)_2Cl_2$ (156 mg, 0.223 mmol, 0.118 equiv), and CuI

(36 mg, 0.189 mmol, 0.1 equiv) were dissolved in a mixture of piperidine (2 mL) and triethylamine (20 mL). The mixture was degassed by purging with nitrogen for 15 minutes. The reaction was stirred and refluxed at 110 °C under nitrogen for 16 hours. Water was added to the mixture. The aqueous phase was extracted with ethyl acetate, and the combined organic phase was dried through sodium sulfate. Subsequent removal of the solvent under vacuum and column chromatography (EtOAc/hexane 50/50) yielded **π-AM** (833.8 mg, 92%) as an off-white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.77 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.73 – 7.66 (m, 2H), 7.58 – 7.50 (m, 2H), 7.30 – 7.17 (m, 5H), 7.11 – 6.99 (m, 2H), 4.92 – 4.86 (m, 1H), 4.83 (d, *J* = 3.1 Hz, 1H), 4.57 (t, *J* = 5.9 Hz, 1H), 4.07 (t, *J* = 5.0 Hz, 2H), 3.75 (q, *J* = 5.0 Hz, 2H), 3.37 – 3.31 (m, 2H), 3.02 (t, *J* = 7.6 Hz, 2H), 2.60 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 176.16, 174.37, 159.62, 141.43, 141.11, 138.82, 138.33, 133.77, 131.97, 131.90, 129.24, 129.15, 127.62, 127.53, 127.21, 127.03, 125.33, 124.75, 123.78, 123.50, 115.39, 114.69, 90.84, 83.73, 70.22, 67.47, 59.99, 56.94, 50.97, 47.53, 47.02, 44.44. HRMS-ESI (m/z): calcd for $C_{30}H_{25}NNaO_5^+$, 502.1625; found, 502.1612.



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The reference compound π-extended anthracene **3** was synthesized according to a literature procedure.[1]

VI. Pigments used in this work

Color	Name
Blue	Pigment Blue 15
Orange	Irgazin Orange EH 1287
White	TiO_2

VII. Supplementary figures

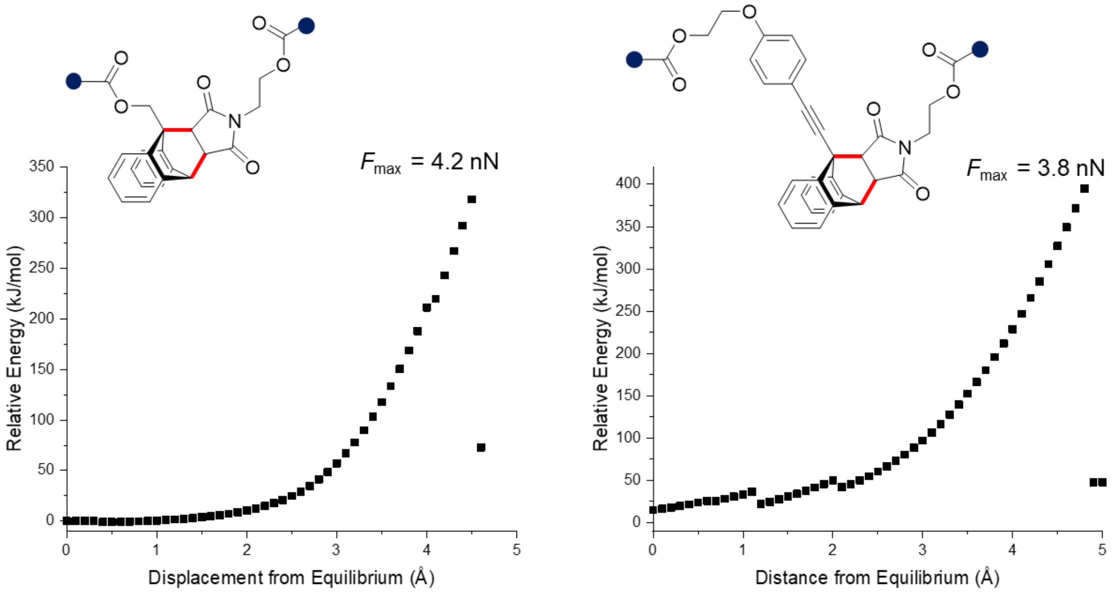

Figure S1. Constrained geometries simulate external force (CoGEF) calculation results for anthracene–maleimide (left) and π-extended anthracene–maleimide (right) cycloadducts.

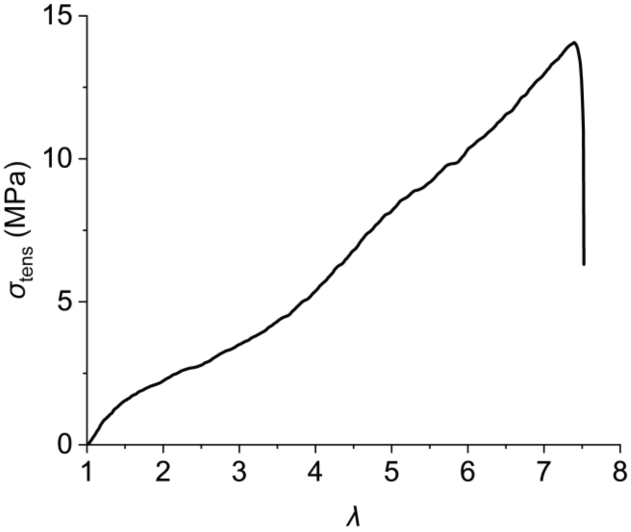

Figure S2. Tensile testing of free-standing polyurethane.

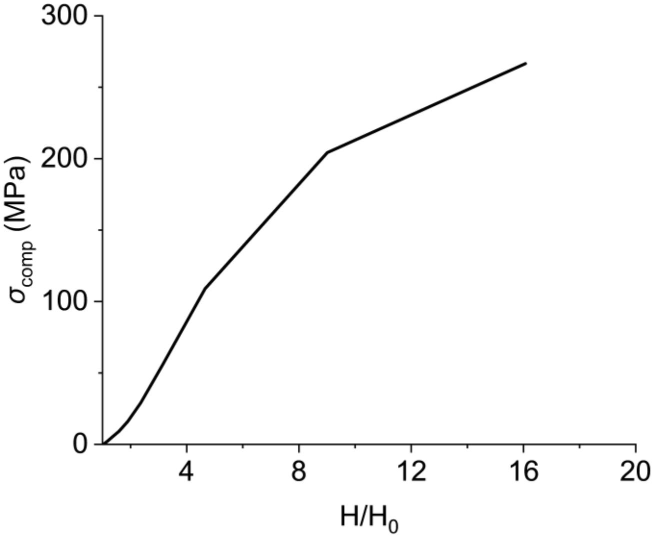

Figure S3. Compressive testing of free-standing polyurethane.

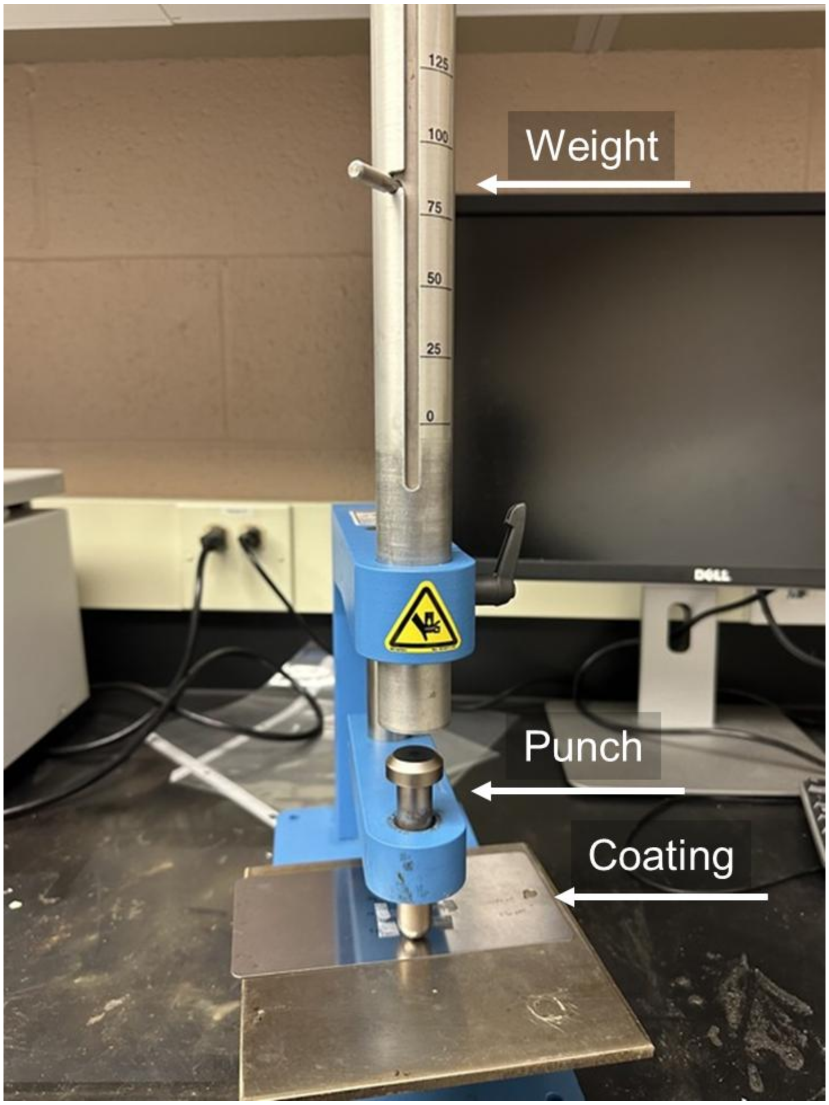

Figure S4. Setup for the impact experiments.

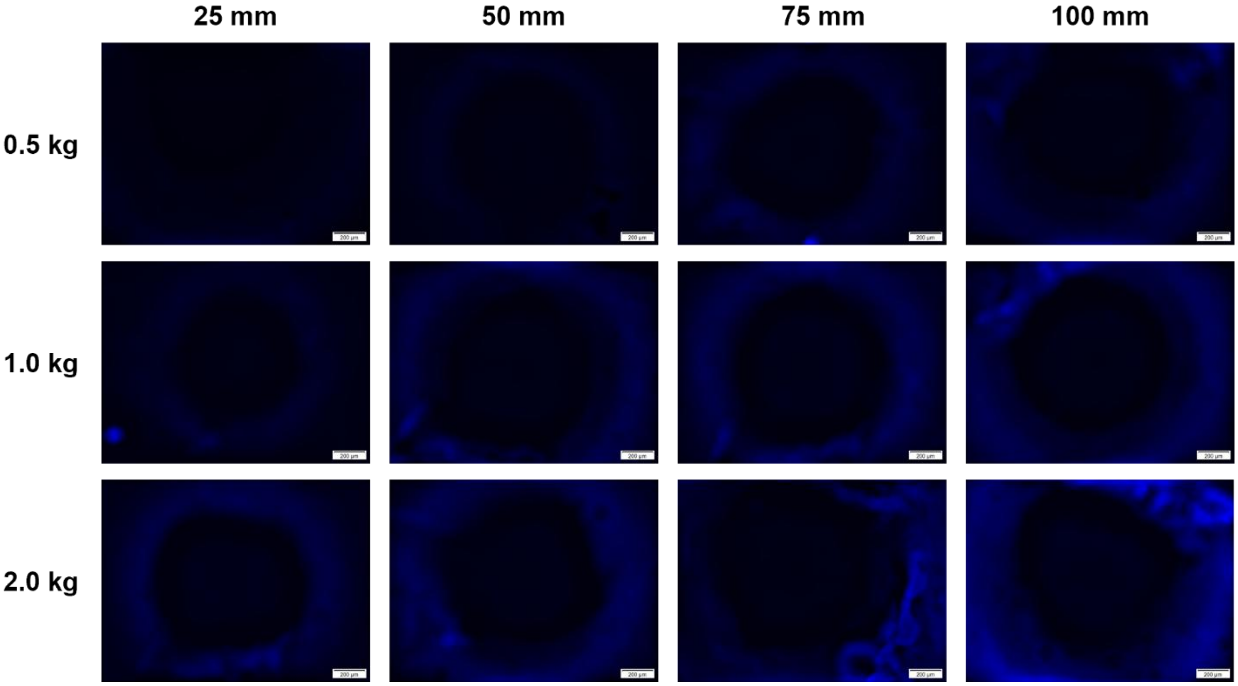

Figure S5. Fluorescence microscopic images of the impact areas of the clear coating that was struck by a falling punch of different weights (left) and from different heights.

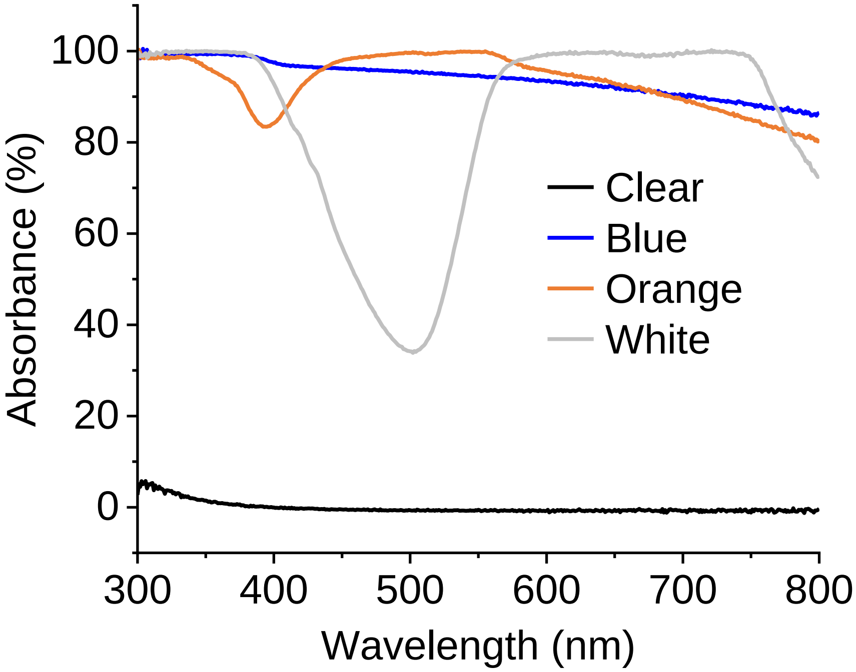

Figure S6. Absorbance profiles of the pigmented coatings.

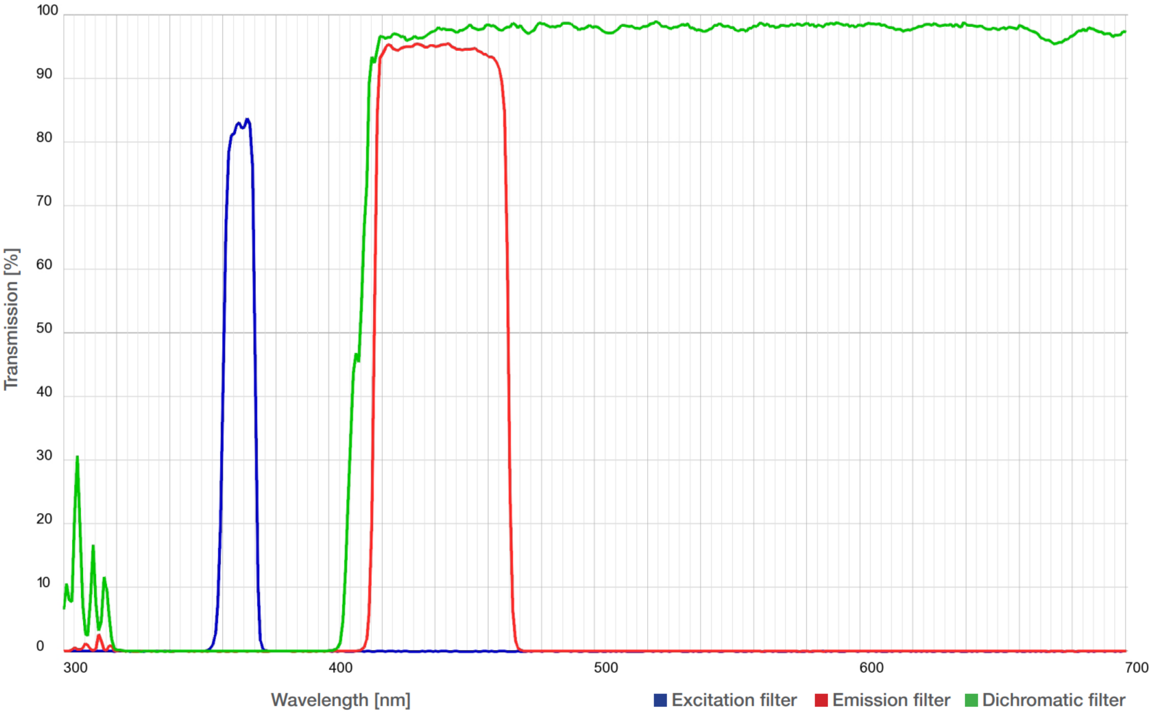

Figure S7. Transmission of the U-FUNA Fluorescence Filter Cube (from manufacturer https://www.olympus-lifescience.com/en/optics/mirror-units/#!cms[focus]=cmsContent6353).

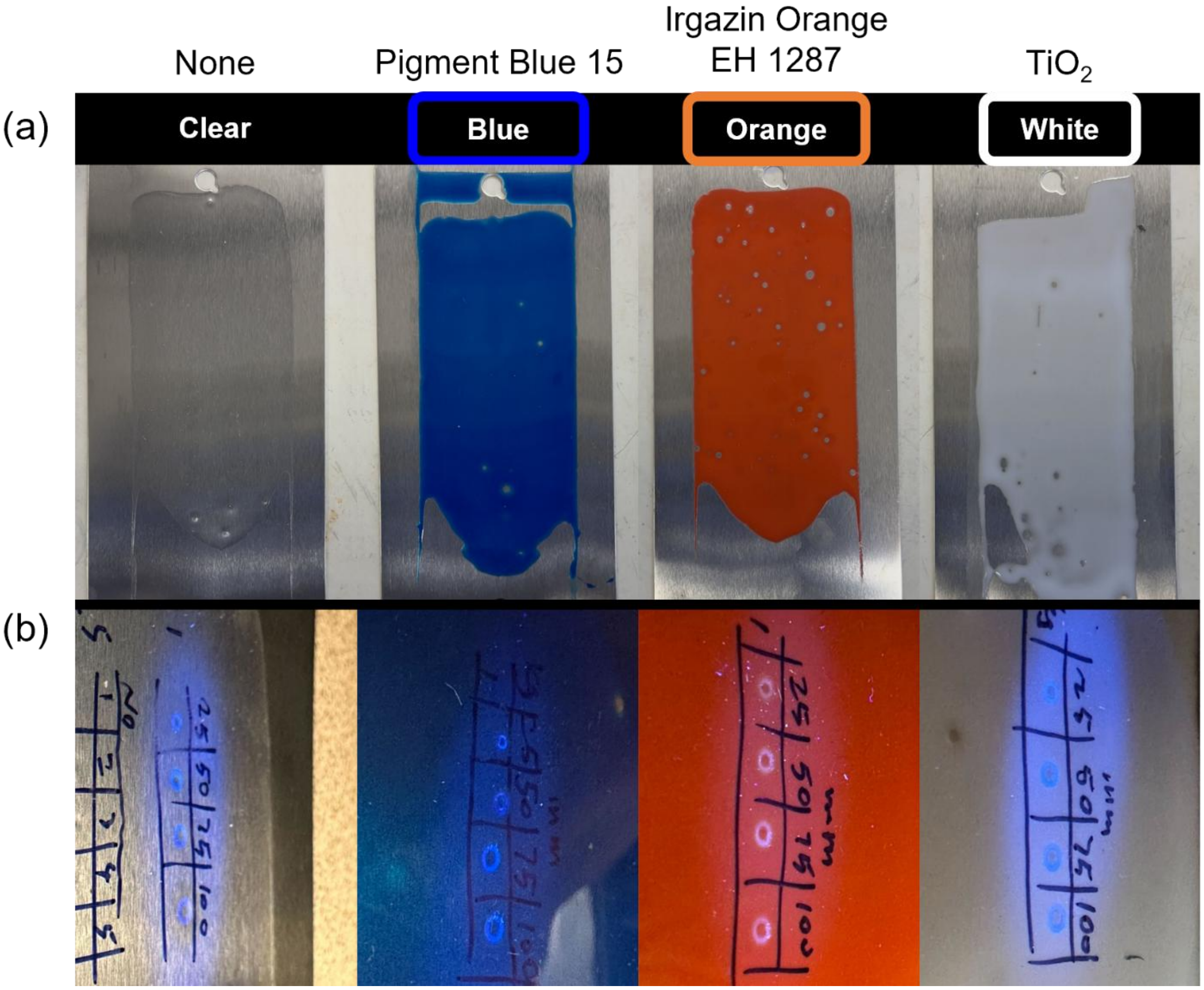

Figure S8. (a) Photos of the clear and pigmented coatings on steel substrate. (b) Photos of the coatings after impact by a punch of 1.0 kg falling from different heights as indicated by the numbers above the spots of impact, on which the mechanically generated fluorescence was visualized under a UV flashlight ($\lambda_{\max}$ = 365 nm).

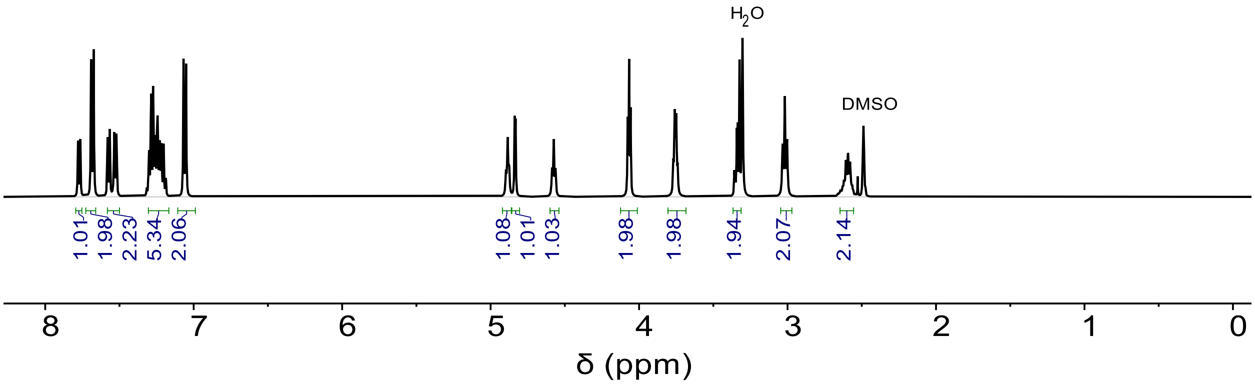

Figure S9. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of π-AM.

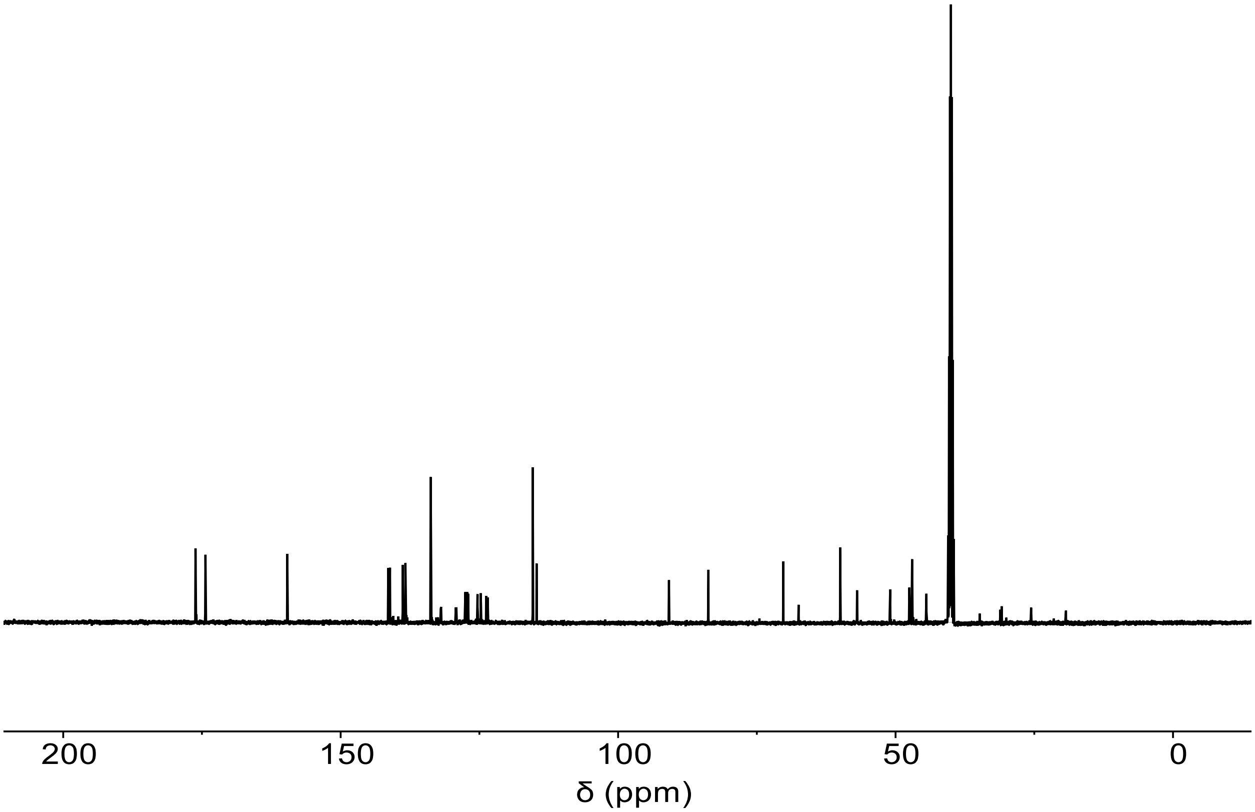

Figure S10. ^{13}C NMR spectrum (125 MHz, DMSO-d_6) of π-AM.

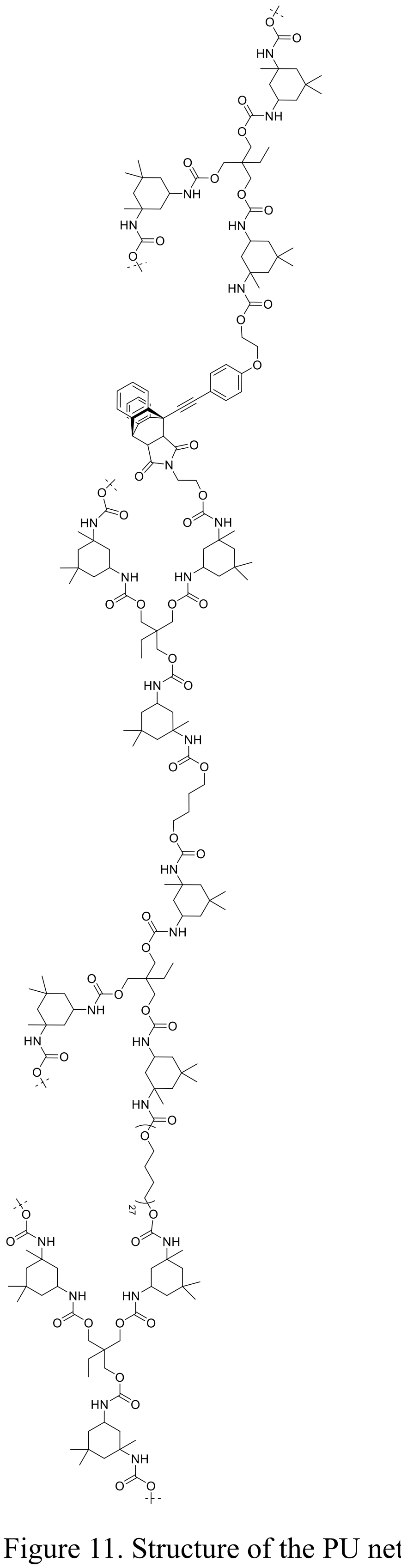

Figure 11. Structure of the PU network.

VIII. References

[1] R. Göstl, R. P. Sijbesma, *Chem. Sci.* **2016**, 7, 370.

[2] O. Bezençon, D. Bur, T. Weller, S. Richard-Bildstein, L. Remeň, T. Sifferlen, O. Corminboeuf, C. Grisostomi, C. Boss, L. Prade, S. Delahaye, A. Treiber, P. Strickner, C. Binkert, P. Hess, B. Steiner, W. Fischli, *J. Med. Chem.* **2009**, 52, 3689.