# Supporting Information

# A New Kind of Nonconventional Luminogens Based on Aliphatic Polyhydroxyurethane and its Potential Application in Ink-Free Anticounterfeiting Printing

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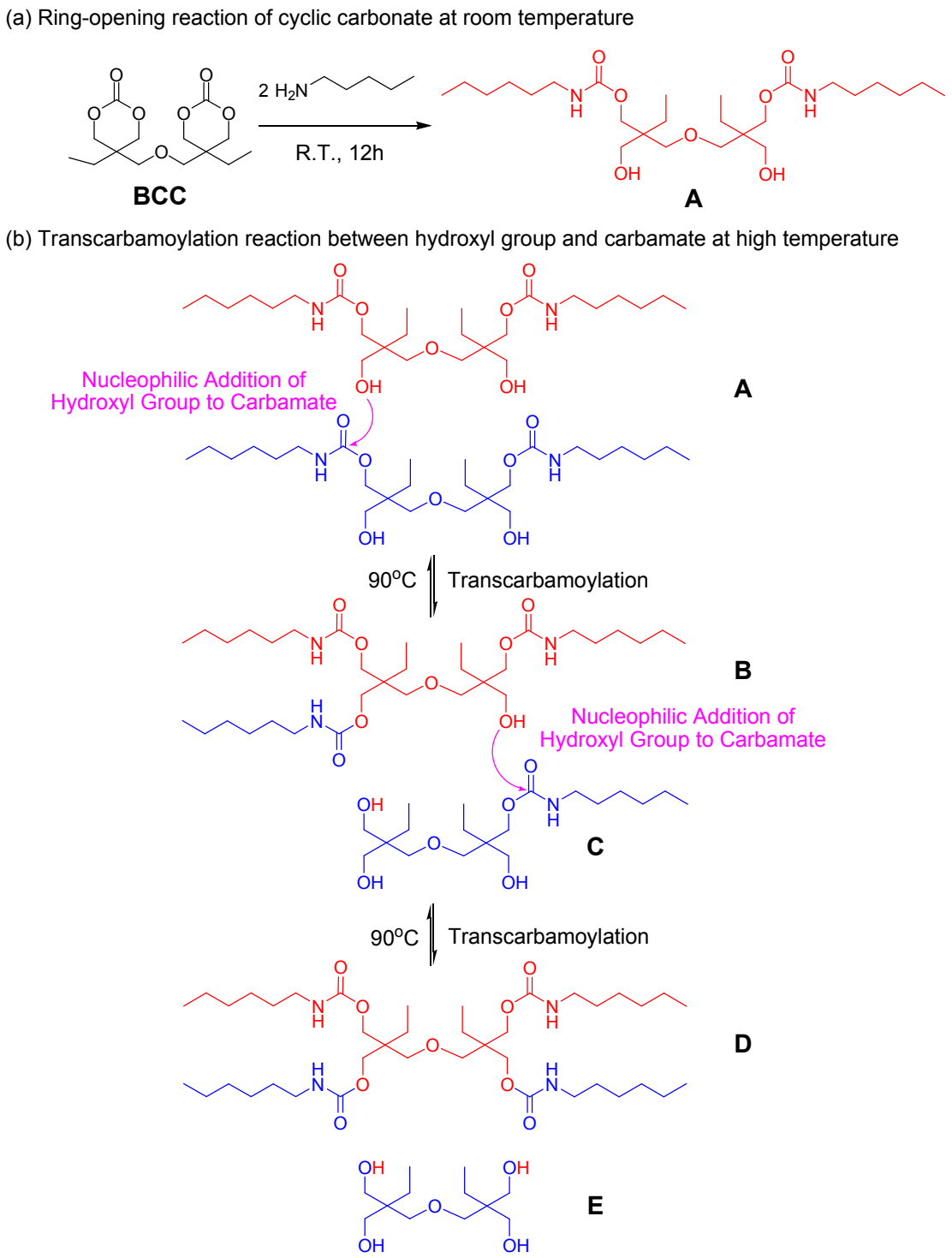


**Scheme S1**. Chemical reactions involved in the synthesis of **PHU1** with fluorescence, (a) ring-opening reaction of cyclic carbonate at room temperature; (b) transcarbamoylation reaction between hydroxyl group and carbamate at high temperature.

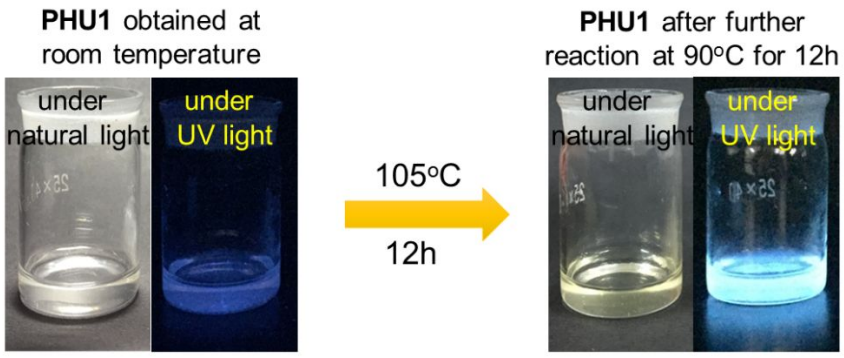


**Figure S1.** Photographic images of **PHU1** upon alternating UV (λ = 365 nm) and natural light irradiation.

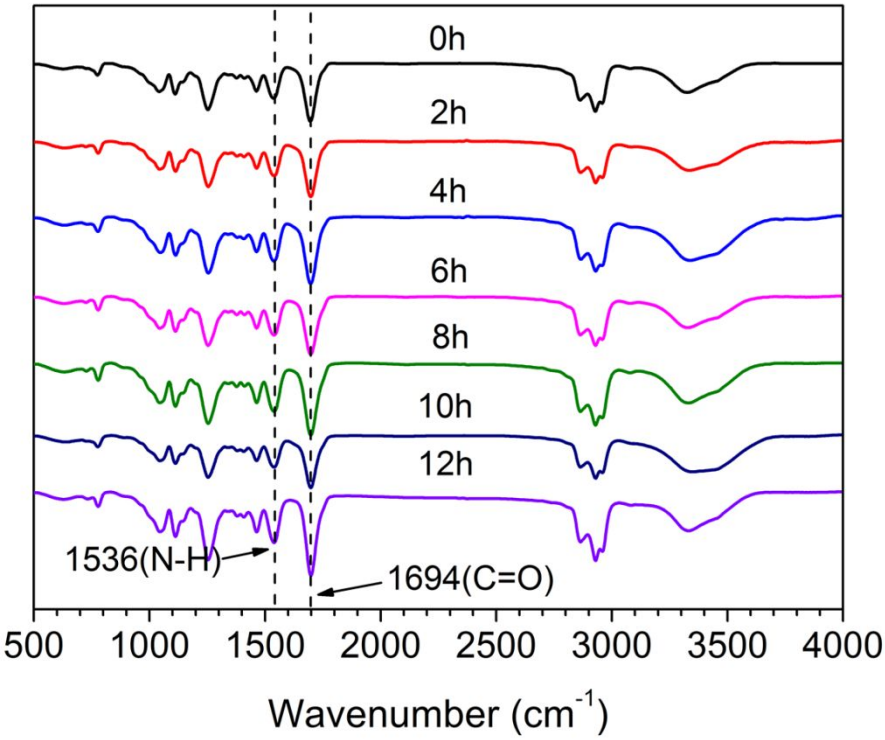


**Figure S2**. FT-IR spectra of **PHU1** taken at different reaction time at 105°C.

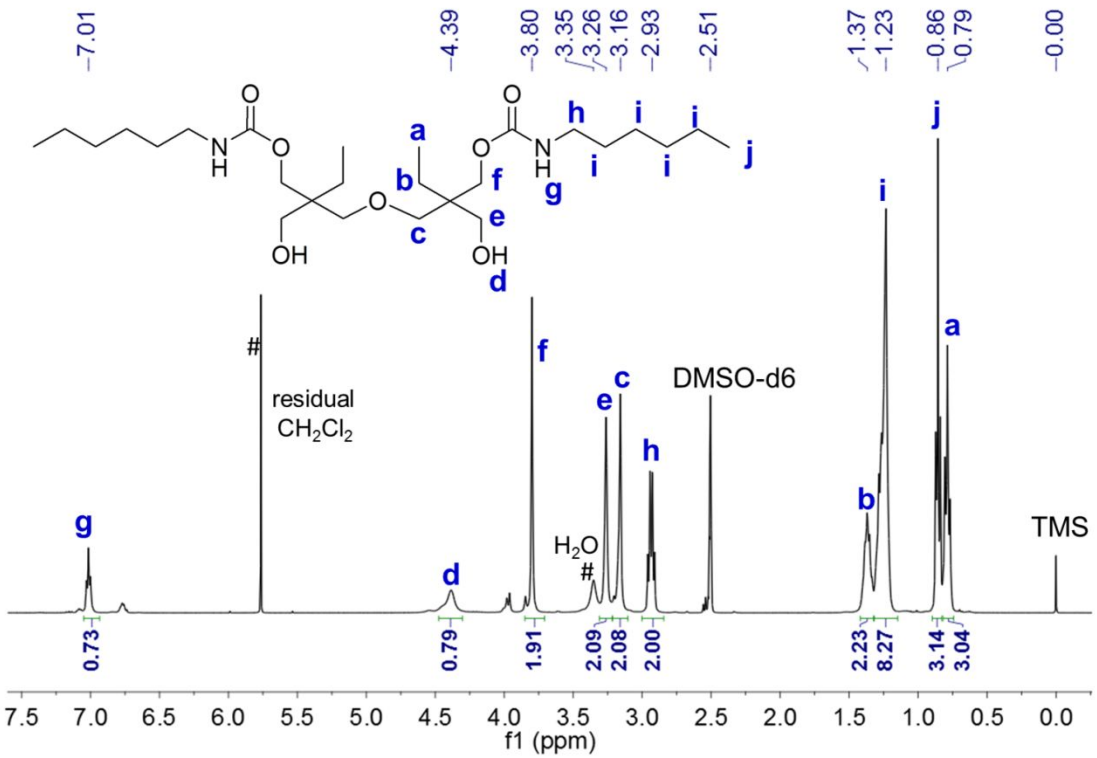


**Figure S3**. $^{1}$H NMR spectrum of **PHU1** obtained at room temperature (DMSO-d6, 500M, 25$^{o}$C).

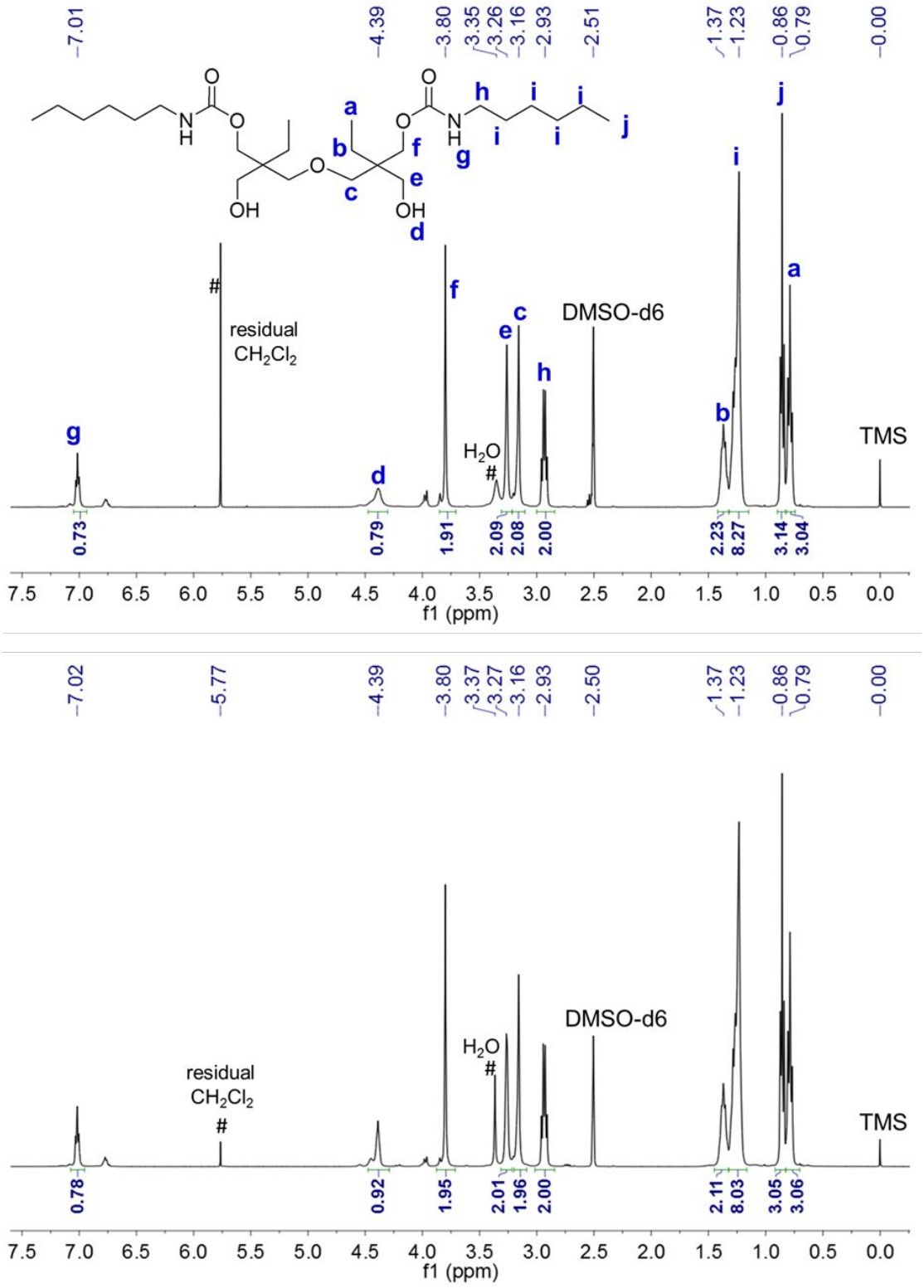


**Figure S4**. $^{1}$H NMR comparative spectra of **PHU1** obtained at room temperature (upper) and after further reaction at 105$^{o}$C for 12h (lower) (DMSO-d6, 500M, 25$^{o}$C).

**Figure S5**. Solid **PHU2** synthesized from tris(2-aminoethyl)amine and bis(cyclic carbonate).

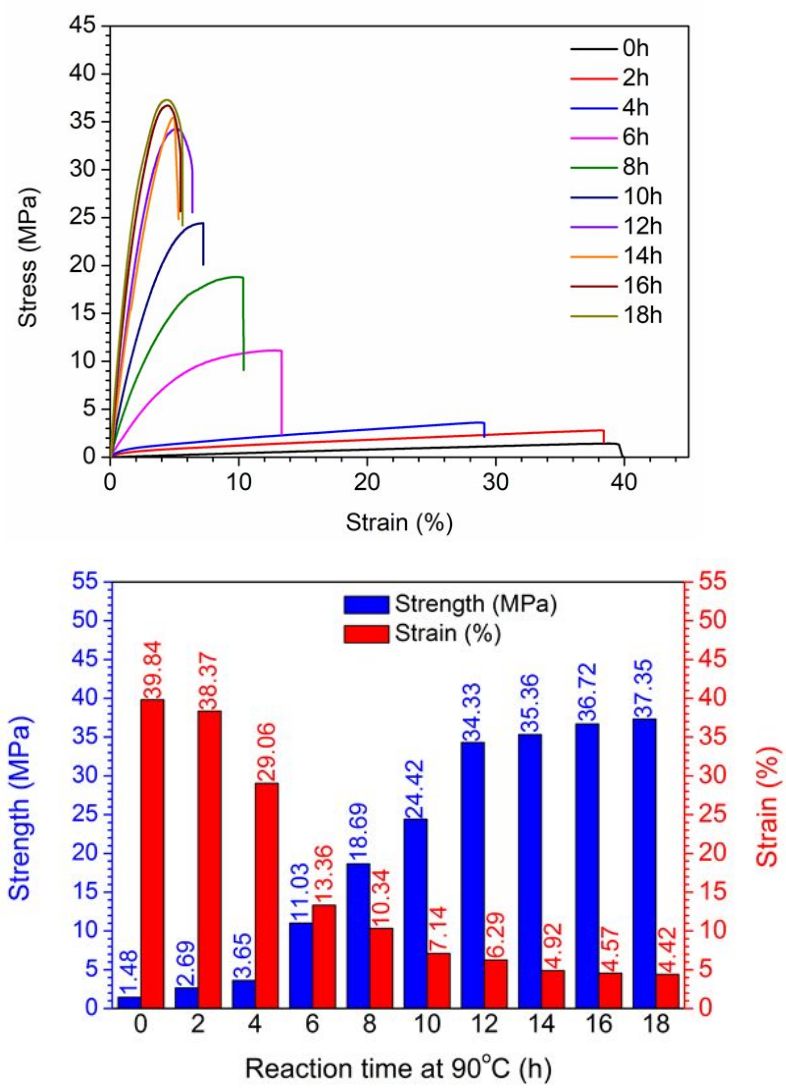


**Figure S6**. Stress-strain curves of **PHU2** taken at different curing time.

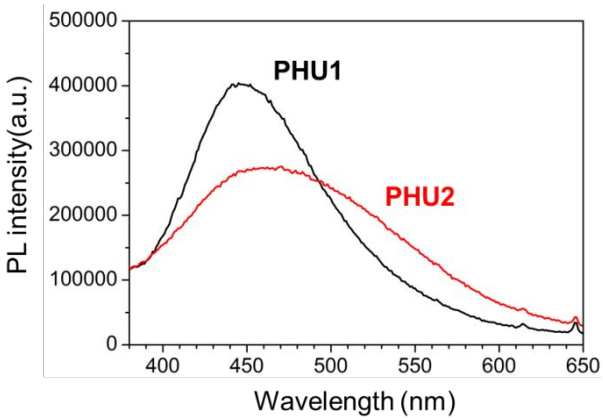


**Figure S7**. Fluorescent spectra of **PHU1** and **PHU2** measured under identical conditions (Both **PHU1** and **PHU2** samples were taken at 12h of reaction at high temperature).

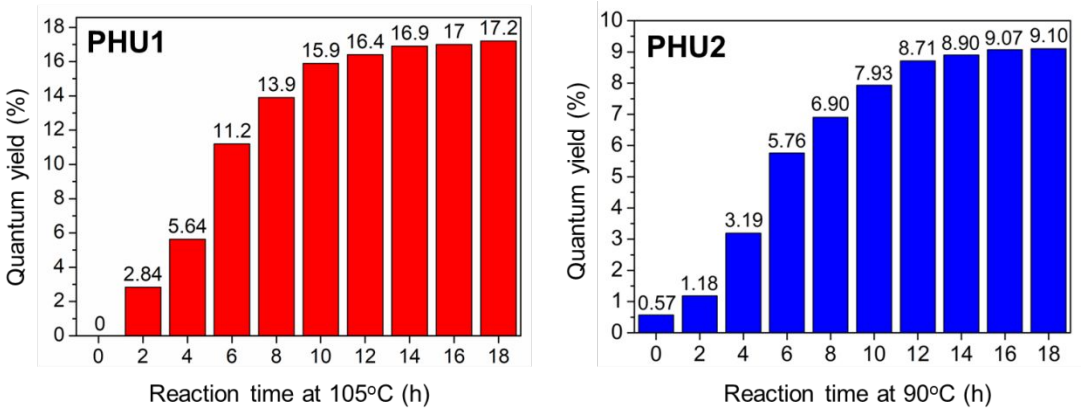


**Figure S8**. Column chart of quantum yields of **PHUs** vs. reaction time.

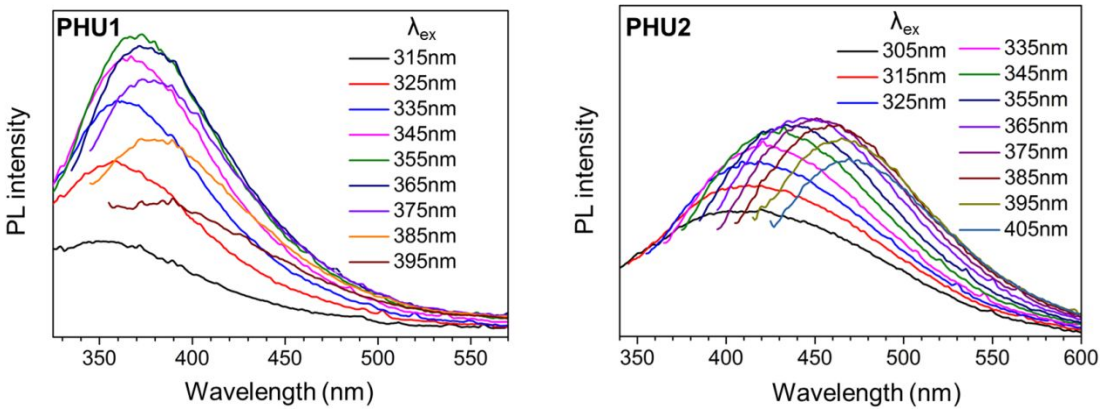


**Figure S9**. Fluorescent spectra of **PHU1** and **PHU2** at different excitation wavelengths. (Excitation at longer wavelength results in a red-shifted emission; the **PHU1** sample was taken at 12h of reaction at 105°C and the **PHU2** sample was taken at 18h of reaction at 90°C.).

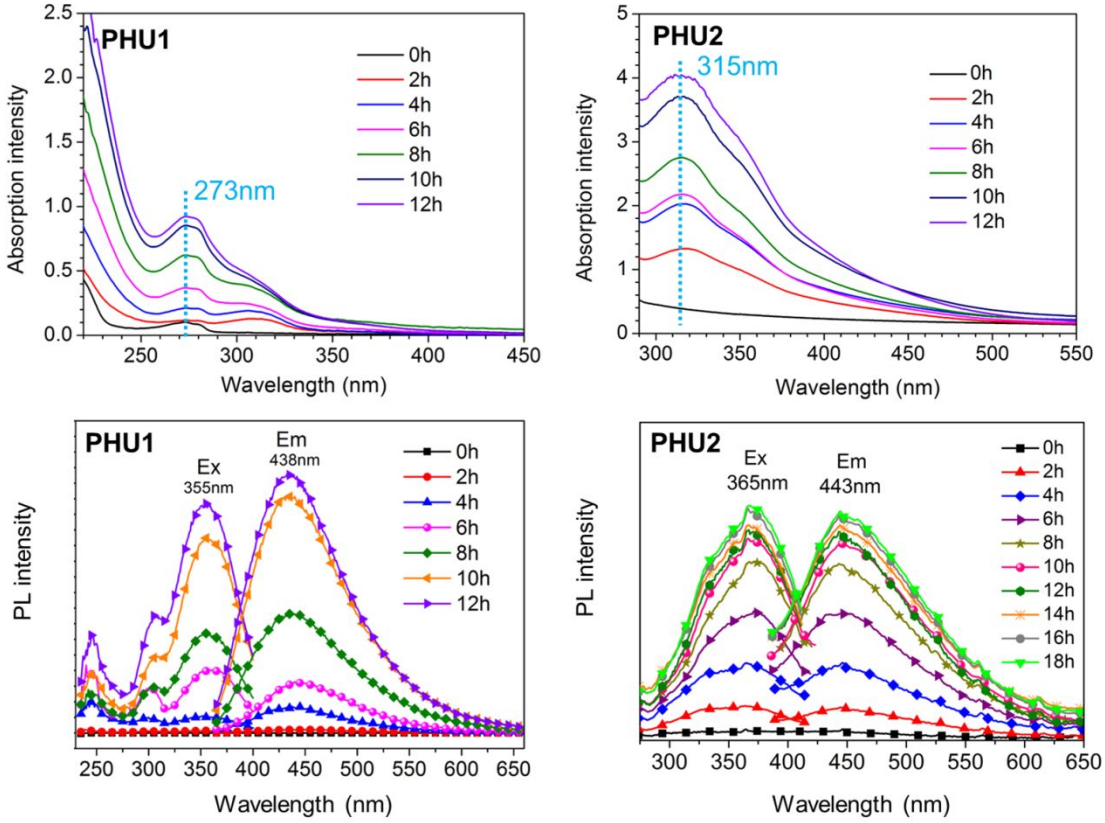


**Figure S10**. UV absorption, excitation and emission spectra of **PHU1** (sampled at different reaction time at 105°C) and **PHU2** (sampled at different reaction time at 90°C).

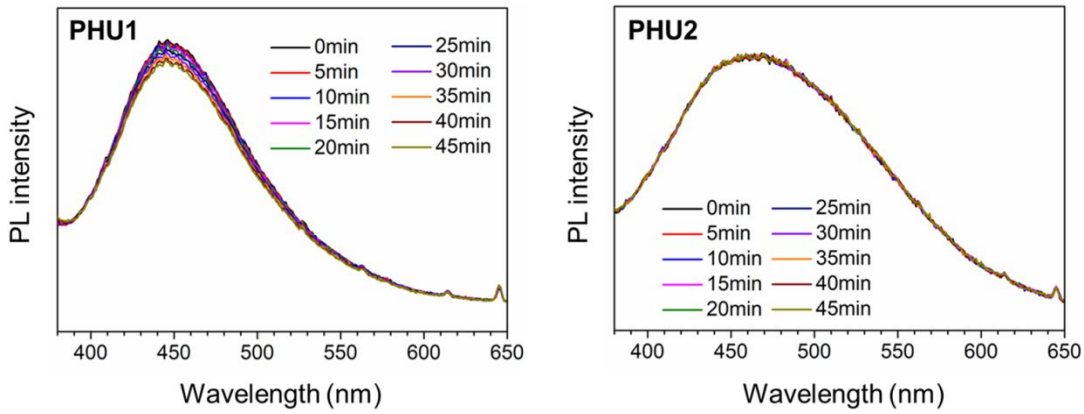


**Figure S11**. Fluorescence spectra of **PHU1** and **PHU2** measured at specific time intervals (the **PHU1** sample was taken at 12h of reaction at 105°C and the **PHU2** sample was taken at 18h of reaction at 90°C.).

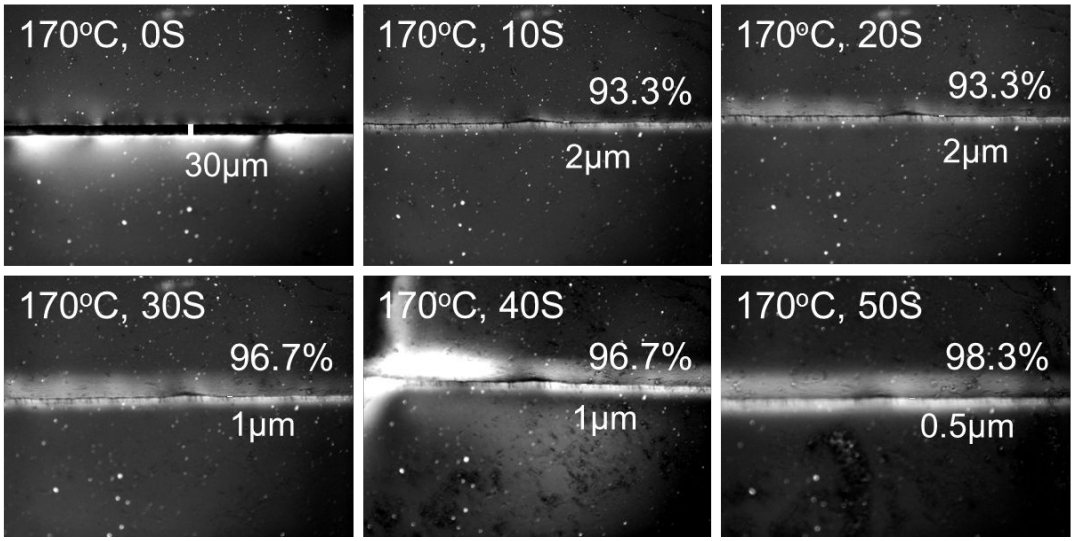


**Figure S12**. Scratch self-healing of PHU2 at 170°C monitored by polarizing microscope (The percentages of self-healing in specific time are labeled in corresponding polarizing microscope photographs.)

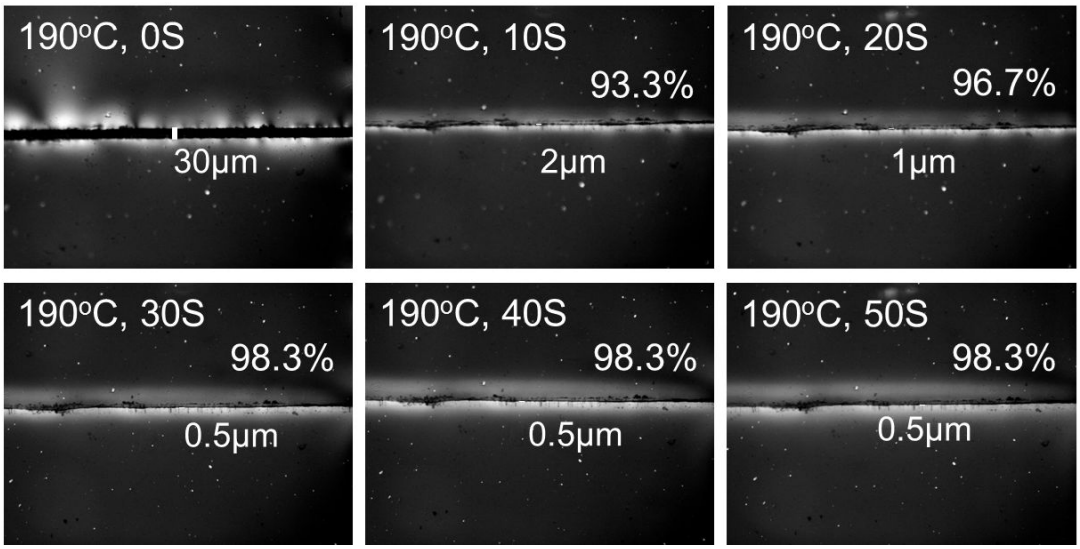


**Figure S13**. Scratch self-healing of PHU2 at 190°C monitored by polarizing microscope (The percentages of self-healing in specific time are labeled in corresponding polarizing microscope photographs.)

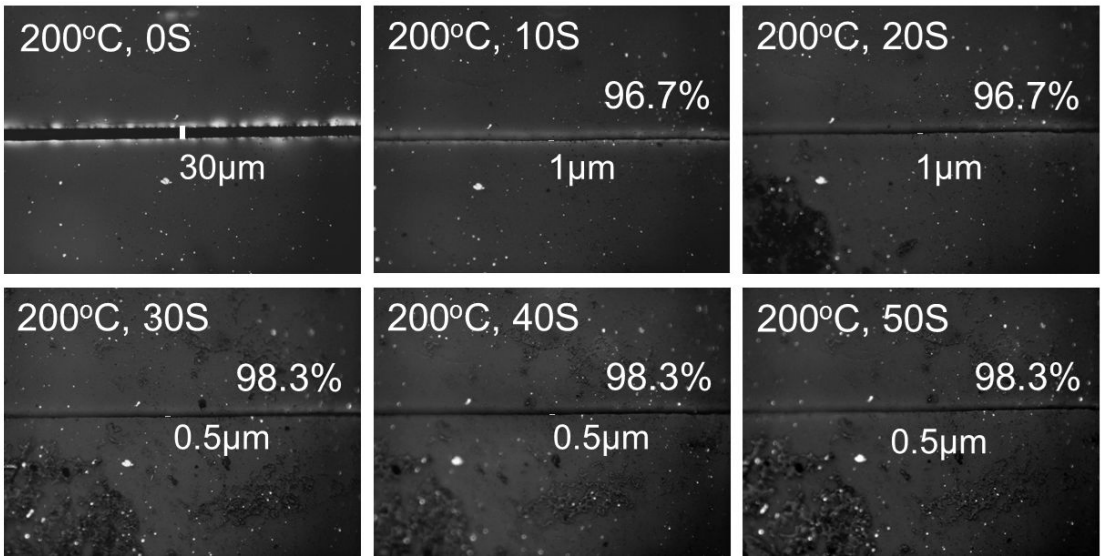


**Figure S14**. Scratch self-healing of PHU2 at 200°C monitored by polarizing microscope (The percentages of self-healing in specific time are labeled in corresponding polarizing microscope photographs.)

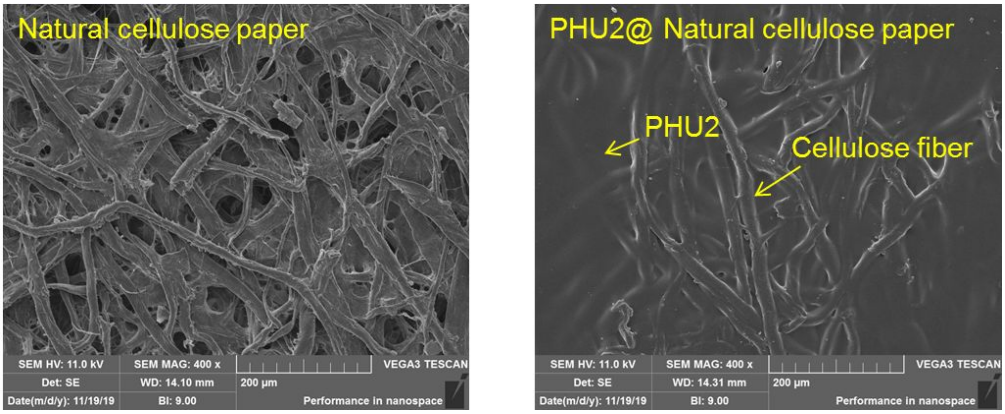


**Figure S15**. SEM images of natural cellulose paper and **PHU2**@paper.

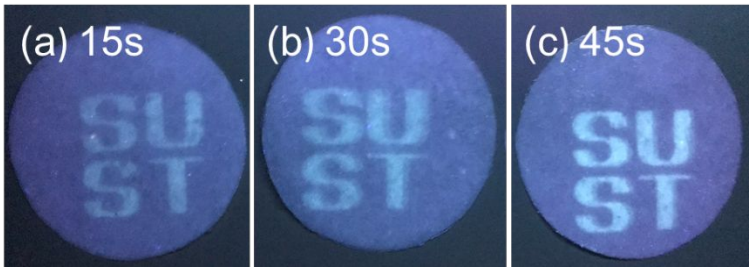


**Figure S16**. Photographic images of paper with "SUST" fluorescence pattern made via hot stamping method (the fluorescence intensity of the pattern can be easily tuned by controlling the stamping time).

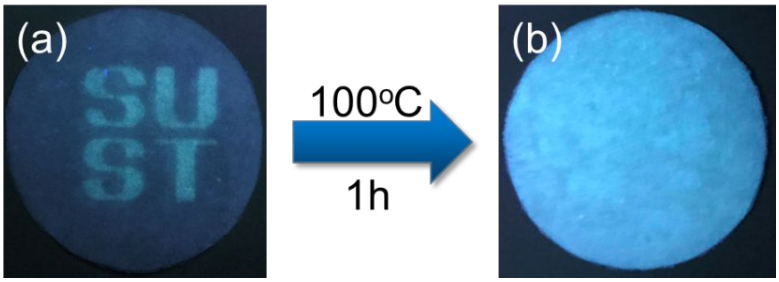


**Figure S17**. Fluorescence pattern erasing by heating (the fluorescence pattern was made by using hot stamping method).

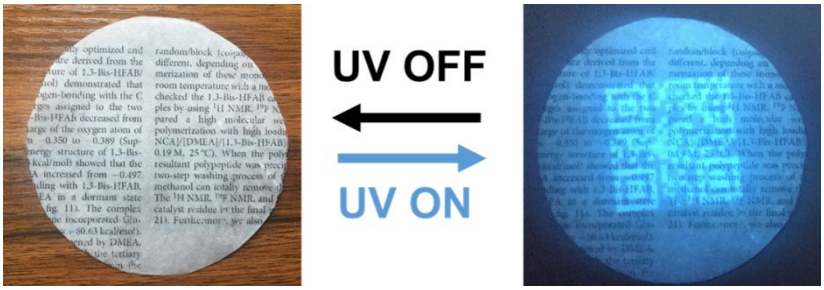


**Figure S18**. Fluorescence pattern-encoded PHU2@paper used for document printing.

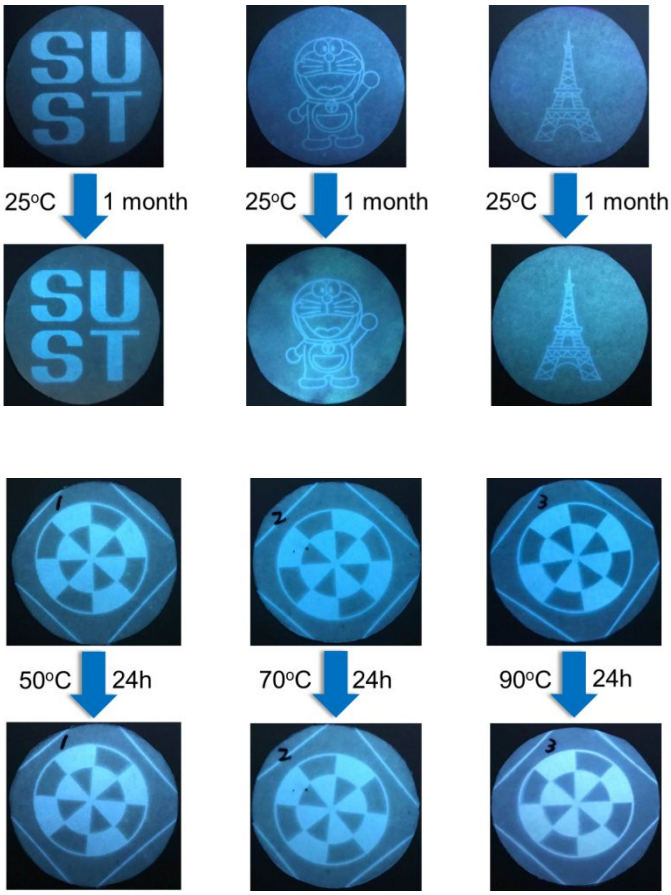


**Figure S19**. Stability investigation of fluorescence patterns at different temperature.

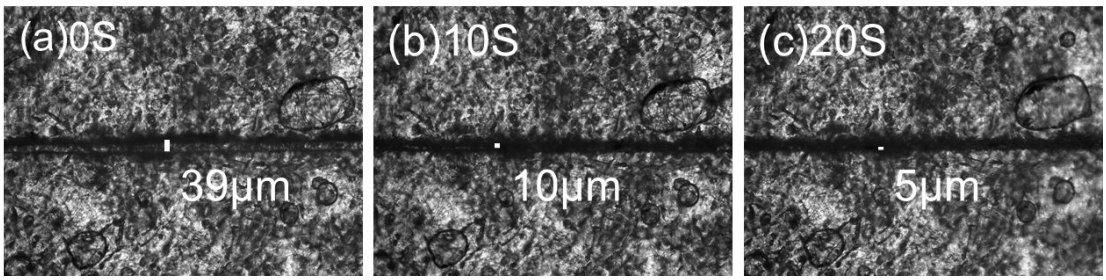


**Figure S20**. Crack Self-healing of **PHU2**@paper after the fluorescence pattern is erased by heating.

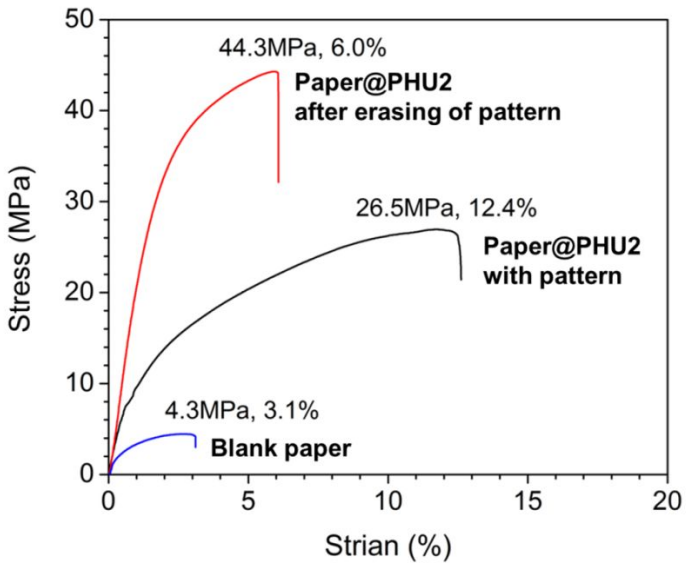


**Figure S21**. Stress-strain curves of blank paper, paper@**PHU2** with pattern and paper@**PHU2** after erasing of pattern by heating (The fluorescence pattern was made via light-mediated screen printing method).

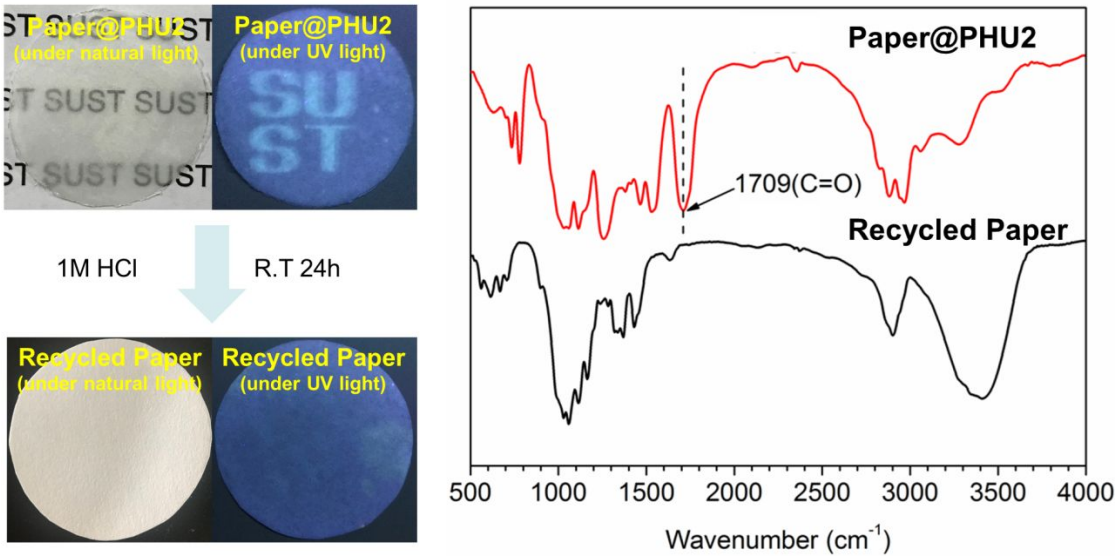


**Figure S22**. Paper recycling from paper@**PHU2** via degradation of **PHU2** in acid solution (the paper@**PHU2** was soaked in 1M HCl solution for 24h).

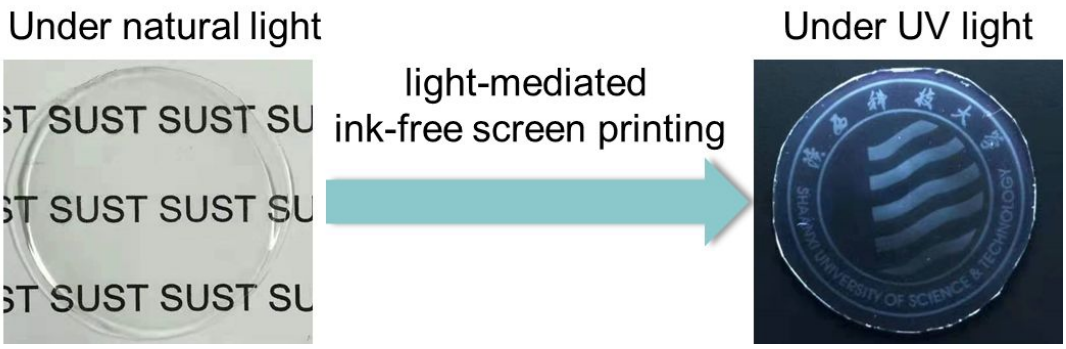


**Figure S23**. Anticounterfeiting patterning on **PHU2** film by light-mediated ink-free screen printing.