Supporting Information

3D Printable and Stimuli-Responsive Colorimetric Silicone Composites

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Materials and Characterizations

All reagents and solvents were purchased from Sigma-Aldrich, Macklin, and Energy Chemicals (China) and used without further purification unless otherwise stated. Fluorescein-free acid, bromocresol green and cresol red were purchased from Sigma-Aldrich. The derivatives of rhodamine (denoted as Rho-1) and zinc phthalocyanine (denoted as ZnPC) were synthesized according to the procedures from literature.^{1,2} Histamine, triethylamine, 1,4-diaminobutane, and 1,5-diaminopentane were purchased from Macklin. Silicone gel DOWSIL SE 1700 Clear Base and corresponding curing agent for 3D printing were purchased from DOW. Electrospray ionization-mass spectrometry (ESI-MS) spectrum was obtained on a Waters Xevo G2-XS Tof using acetonitrile as solvent. UV-vis spectra were recorded using a UV-vis spectrophotometer (UV 1900, Shimadzu). Steady-state photoluminescence (PL) spectra were recorded on a SPEX Fluorolog spectrofluorometer (Jobin Yvon/SPEX, Edison, New Jersey).



Scheme S1. Chemical structure of zinc phthalocyanine (ZnPC).

Preparation of DUCS-1 sensor by 3D-Printing.

Rho-1 ethanol solution (0.01 M, 300 μ L) and fluorescein ethanol solution (0.01 M, 300 μ L) were mixed with hydrochloric acid (1 M, 300 μ L) by continuous stirring. The mixed solution was added to silicone gel (DOWSIL SE 1700 Clear Base, 7.8 g) and the matched curing agent (0.9 g), and homogenized with a vacuum spinner for 10 min. Then the mixture was added to the customized Independent Dual Extrusion 3D printer based on a Cartesian gantry system and printed through DIW. The printed samples stood at room temperature for 24 h to volatilize the liquid solvent, and then heated at 120 °C for 30 min in the oven to solidify the silicone composites.



Figure S1. Rheological properties of printable inks. (a) Storage (G') and loss (G'') moduli versus shear stress for the printable inks. (b) Apparent viscosity of the printable inks as a function of shear rate.



Figure S2. ¹H NMR (CDCl₃, 500 MHz) spectrum of Rho-1.



Figure S3. UV-vis absorption spectra of (a) **Rho-1** ethanol solution $(1 \times 10^{-3} \text{ M})$, (b) fluorescein ethanol solution $(1 \times 10^{-4} \text{ M})$, with and without HCl (0.1 M in water); (c-d) Digital photographs of (a) and (b) under visible light and 365-nm UV light.



Figure S4. UV-vis absorption (a) and steady-state PL emission spectra (excited at 470 nm) (b) and digital photographs (c) of **DUCS-1** samples before and after being heated at 120 °C for 8 h.



Figure S5. UV-vis absorption spectra of **DUCS-1** films before and after being soaked in aqueous media at different pH values: (a) pH 6, (b) pH 7 and (c) pH 8 for 48 h.



Figure S6. UV-vis absorption spectra of **DUCS-1** (a) with original concentration (Rho-1: 0.01 M, 300 μ L, and fluorescein (0.01 M, 300 μ L) in silicone gel (7.8 g) with the curing agent (0.9 g)), and concentrations of Rho-1 and fluorescein doubled (b) based on those in (a). All the samples were treated with ammonia at 10⁴ ppm for 15 min before the measurement.



Figure S7. UV-vis absorption spectra (a, b) and digital photographs (c, d) of (a, c) bromocresol green (BG) (2×10^{-4} mmol/mL in ethanol), and (b, d) cresol red (CR) (2×10^{-4} mmol/mL in ethanol), with and without 0.1 mmol/mL HCl.



Figure S8. Monitoring of shrimp freshness by the **DUCS-1** sensor. Digital photographs of the sensor strips to monitor the freshness of 2 shrimps stored at (a) 4 °C and (b) -18 °C, respectively, under room light and UV (365 nm) light.

References:

- 1. H. Zhang, X. Wei, M. B. Chan-Park and M. Wang, ACS Food Sci. Technol., 2022, 2, 703–711.
- Z. Xu, L. Mei, Y. Shi, M. Yun, Y. Luan, Z. Miao, Z. Liu, X.-M. Li, M. Jiao, *Biomacromol.* 2022, 23, 2778-2784.