Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Dynamically Crosslinked Carbon Dots/Biopolymer Hydrogels Exhibiting Fluorescence and Multi-stimuli Logic-gate Response

Chun Shen, [a,] * Yue Zhao, [b] Hou Liu, [b] Yingnan Jiang, [c] Na Li, [d] Shaowei Lan, [d] Huizheng Bao, [d] Bai Yang, [b] Quan Lin [b,] *

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Experimental section

Material: Ethylene glycol, hydrogen peroxide (H_2O_2, ~30 wt.%), acetic acid (HAc, ~99.5%), sodium acetate trihydrate ($NaAc•3H_2O$, ~99.0%), copper sulfate ($CuSO_4$, ~99.0%) hydrochloric acid were obtained from Beijing chemical works (Beijing, China). Polyethylenimine (PEI-1800, branched form), phytic acid, vitamin B6, lysine, hyaluronidase, and sodium (meta) periodate were purchased from Aladdin. Sodium hyaluronate was obtained from Yuanye Biological Technology Co., Ltd (Shanghai, China). All other chemicals were analytical grade and used without further purification. The ultra-pure water used throughout the experiments was purified with a Milli-Q A10 filtration system (Millipore, Billerica, MA, USA).

Synthesis of HA-ALD: Sodium hyaluronate (1g) and sodium periodate (1g) were dissolved in 100 mL deionized water. The mixture was stirred in dark for 3-5 h at room temperature. After that, the reaction was stopped by adding 3 mL ethylene glycol, dialysing against deionized water for 3 days, freezing and lyophilizing for further use.

Synthesis of carbon dots: PEI (3mL, Mw=1800) and citric acid (20 mg) were dissolved in 7 mL of water. The mixture was stirred for 10 minutes and then transferred to a poly (tetrafluoroethylene) (Teflon)-lined autoclave chamber (30 mL). After that, the chamber was heated at 200 °C for 10 h in an oven. The reactor was automatically cooled to room temperature by naturally. The product, which was faint yellow, and transparent, was subjected to dialysis in order to remove the impurities, dialyzing against deionized water to remove traces of low-molecular-weight impurities

Synthesis of hydrogels: HA-ALD and CDs were dissolved in HAc-NaAc (pH=6.0, 7.0) buffer solutions, respectively. Then the aqueous solution of HA-ALD was added to the solution of CDs with stirring. The pH value of the final solution was kept at 6.0 or 7.0. The mixed solution immediately changed from sol to gel, and a transparent crosslinked hydrogels were homogeneously formed. The in situ formation of fluorescent hydrogel was facile, requiring simply that the CDs solutions be homogeneously mixed with the HA-ALD solution at room temperature (25 ℃). The interwoven networks are attributed to imine bonds, which are obtained via the reaction of aldehyde groups in HA-ALD with the amino groups from CDs. Because the dynamic imine bonds can undergo the reversible reaction under neutral conditions, preparation of all precursor solutions was at the appropriate pH values by using HAc-NaAc (pH=6.0, 7.0) buffer solutions.

Characterization: Fluorescence data were collected on a Shimadzu RF–5301 PC spectrofluorimeter using a quartz cell of 1 cm path length at room temperature. UV-vis absorption experiments were performed with a Lambad 800 spectrophotometer using the same quartz cell at room temperature. Fluorescence life data were obtained on a FLS980 steady/transient fluorescence spectrometer. Fourier transform infrared (FTIR) spectroscopy of HA-ALD, CDs, and HA-ALD/CDs hydrogels was performed

on a BLUCK spectrophotometer using the KBr pellet method. The morphology of the CDs was determined using a TECNA F20 transmission electron microscope with an accelerating voltage of 200 kV using copper grids with ultrathin carbon film and a drop of solution dried at room temperature. The morphology of freeze-dried hydrogels was analyzed using JEOL JSM-6700F scanning electron microscope operated at an acceleration voltage of 3 kV. The zeta potential was obtained on a Zetasizer-nanozs. All photographs were taken by a digital camera (Canon camera).

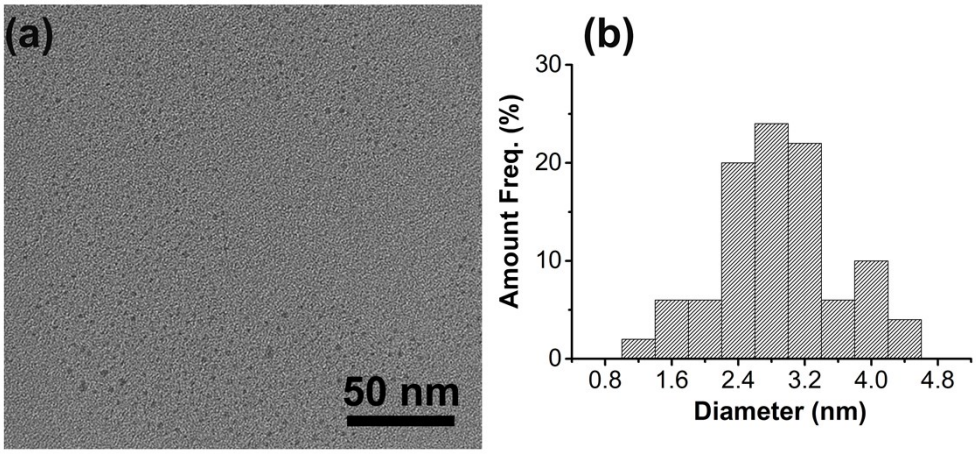

Figure S1. (a) The typical TEM image for the CDs. (b) The corresponding size of the CDs.

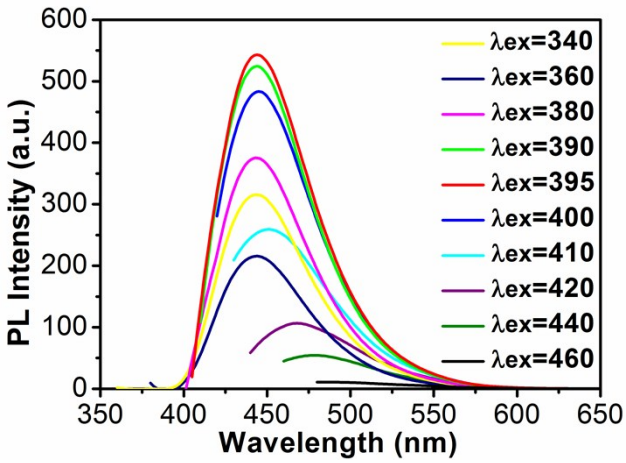

Figure S2. The excitation-dependent PL behavior of CDs.

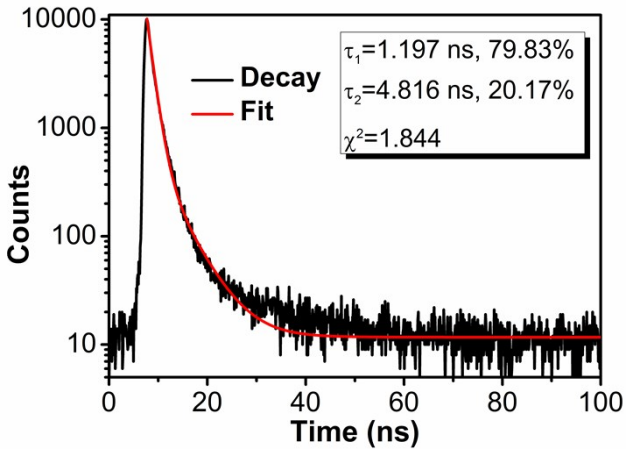

Figure S3. The lifetime of CDs at 375 nm excitation.

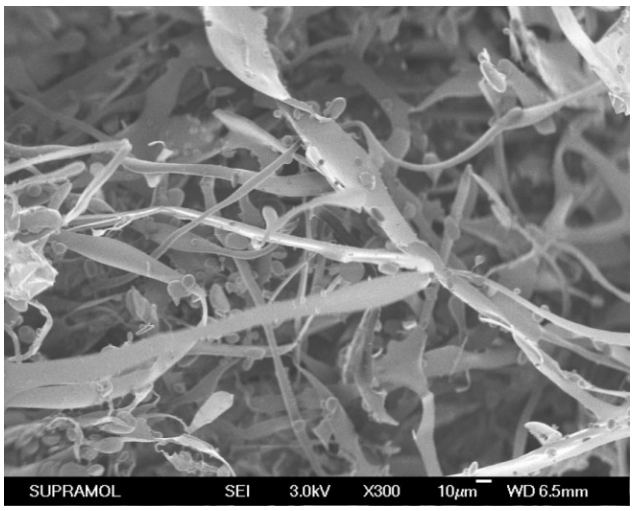

Figure S4. The typical SEM image of HA-ALD biopolymers.

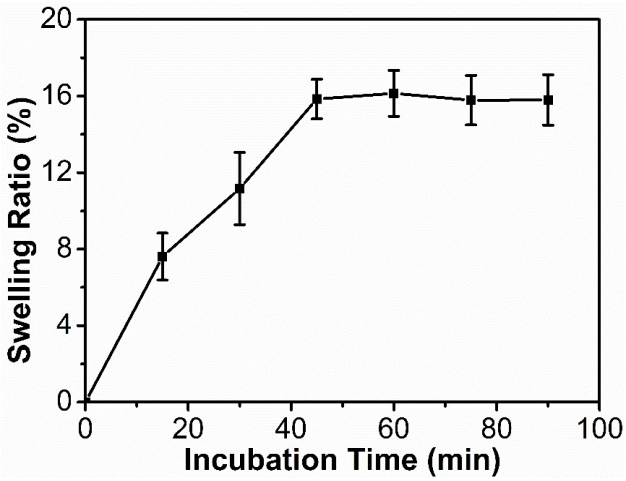

Figure S5. The swelling property of fluorescent hydrogels.

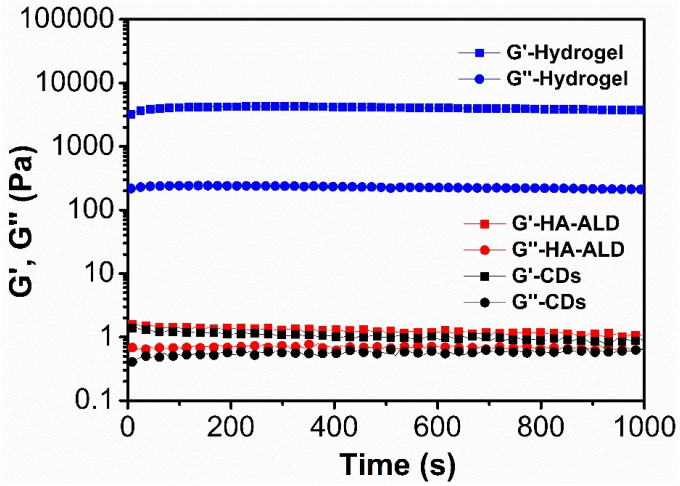

Figure S6. The rheological experiment results of the HA-ALD solution, the CDs solution, and fluorescent hydrogels. As displayed in Figure S6, when the shear strain was about 10 %, both the storage modulus (G') and the loss modulus (G'') of the resultant solutions gradually increased with time after the HA-ALD biopolymers solution reacting with the CDs solution, and the G' values dominate over the G'' values all the time indicating the formation of hydrogels. In contrast, the HA-ALD biopolymers and the CDs solution were liquefied all the time because the G'' values were larger than G' value. This change in the rheological data could be readily indicate that the gelation networks were synthesized through $-NH_2$ and -CHO binding sites between the CDs and the HA-ALD biopolymer chains.

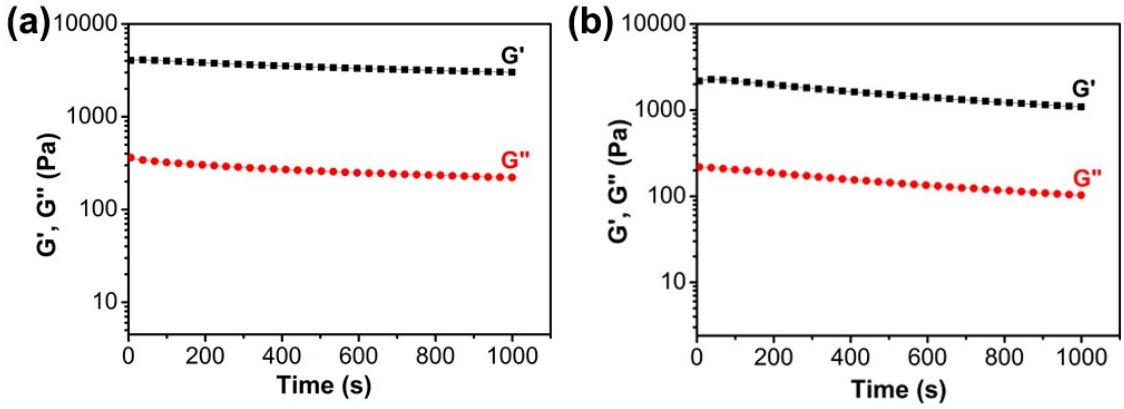

Figure S7. The rheological measurement of fluorescent hydrogels obtained from HA-ALD biopolymers, prepared from 4 hours reaction time (a) and 5 hours reaction time (b).

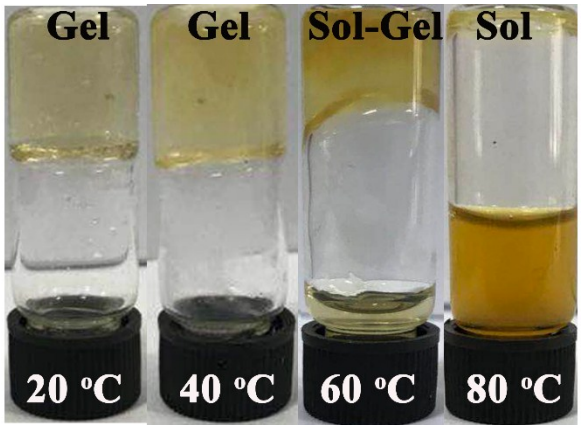

Figure S8. The thermal stability of hydrogels. Figure S8 shows the phase state of the CDs hydrogel in aqueous solution upon increasing the temperature. When the CDs hydrogel was incubated in water bath at 20 ℃ or 40 ℃, the hydrogel was stable without obvious phase change. After further increased the incubation temperature to 60 ℃, the state of hydrogel was between solid and fluid. However, the networks were destroyed seriously and transited to the solution state above 60 ℃ in few minutes. This is because the gelation networks are synthesized through the Schiff' base bonds capable of the reversibility of noncovalent bond. And temperature can influence the chemical equilibrium in dynamic reaction.