

Electronic Supporting Information

Imidazolium-type ionic liquid-based carbon quantum dots doped gels for information encryption

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Experimental

Materials

Acetobromoglucose ($C_{14}H_{19}BrO_9$) was purchased from Accela. 1-methylimidazole 1-butylimidazole, Ammonium persulphate (APS) and 1-bromooctane were obtained from Aladdin. Acrylamide (AAM), Hydroxyethyl acrylate (HEA) and N,N-Dimethylacrylamide (DMAA) were obtained from Macklin. N,N,N',N'-Tetramethylethylenediamine (TEMED) and 1-hydroxycyclohexyl phenyl ketone (HCPK) were purchased from TCI. Lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) was purchased from Rhpdia company. Organic solvents, including ethyl alcohol, acetonitrile, ethyl acetate, petroleum ether, ether and Propylene carbonate (PC) were of analytical degree and purchased from Alfa. All chemicals were used as received without any further purification.

Characterizations

1H NMR measurement was performed by a UNITY INOVA 400 MHz nuclear magnetic resonance instrument with DMSO- d_6 as the solvent. ^{13}C NMR spectra were recorded on a Bruker AVANCE 300 at 75 MHz. The morphologies of samples were obtained by transmission electron microscopy (TEM) Tecnai G20 (200 kV acceleration voltage). Tecnai F20 provided high-resolution TEM (HR-TEM) measurements. Energy-dispersive X-ray spectroscopy (EDX) measurements were carried out on a Hitachi Model S-4700 field emission. Fourier transform infrared (FT-IR) spectra were recorded on a Specode 75 model spectrometer. UV-vis absorption spectra were obtained by TU-1800 SPC spectrophotometer, using $BaSO_4$ plates as the reference (100% reflection). The fluorescence emission spectra were obtained on a HITACHI F-4600 fluorescence spectrophotometer at room temperature. Powder X-ray diffraction (PXRD) at ambient pressure was recorded on a Philips X'Pert Pro diffractometer at 35 kV, 25 mA for a Cu-target tube and a graphite monochromator. An XPS-7000 spectrometer offered X-ray photoelectron spectra (XPS). The mechanical tests were conducted by an Instron 5900 system. Field-emission scanning electron microscope (FE-SEM, Hitachi Model S-4700) was used to observe the self-healing process of gel. Thermal behaviors of samples were investigated by a thermogravimetric analyzer (PerkinElmer TGA 4000) under a N_2 flow with a $10\text{ }^\circ\text{C min}^{-1}$ heating rate.

Synthesis of glucose-based IL-Cn

For glucose-based me-IL (IL-C1): The acetobromoglucose and 1-methylimidazole were dissolved in acetonitrile with a molar ratio of 1:1.1 and then degassed with nitrogen gas

and protected from light. The crude product was dispersed in EA and centrifuged to obtain the pure target product.

For glucose-based bu-IL (IL-C4), instead of 1-butylimidazole as added and the crude product was washed with ether.

For glucose-based oc-IL (IL-C8), instead of 1-octyl imidazole as added and the crude product was washed with ether.

Synthesis of IL-based CQD-Cn

For CQD-C1, CQD-C4, CQD-C8: IL-C1 (1.2 g), IL-C4 (1.2 g), IL-C8 (1.2 g) was dissolved in ethanol aqueous solution ($\varphi = 50\%$, 24 mL), respectively. Then the homogeneous solution was transferred to Teflon autoclave, along with heating at 200 °C for 6 h. After the hydrothermal autoclave was cooled to room temperature, the solution was centrifuged at 10,000 rpm, the upper clear liquid was extracted and filtered through a membrane (0.22 μm). The solution was dialyzed for 3 times. To further purify the products, gel filtration chromatography packed with Sephadex LH-20 was applied.

The anion exchange of CQD-Cn

Ethyl acetate was added into 0.1 mg mL⁻¹ CQDs aqueous solution (volume 1:1), followed by gradually adding LiTFSI and constant shaking. Until the bottom water phase was almost clear and transparent, the anion exchange of CQD-Cn ended. The CQD-Cn-TFSI ethyl acetate solution, upper layer, can be obtained through a liquid separator removing water phase.

The preparation of CQD-C1 hydrophilic gel

For the fabrication of hydrophilic gel, 0.9 g AAM, 0.6 g HEA, 1% APS, 0.2% TEMED and 3 mL 8 mg mL⁻¹ CQD-C1 aqueous solution were mixed as pre-polymer solution. Then the solution was cured at 60 °C for several minutes and the CQD-C1 hydrophilic gel has been prepared successfully.

The preparation of CQD-C8 hydrophobic gel

For the fabrication of hydrophobic gel, 0.5 g DMAA, 0.5 g HEA, 1% HCPK and 1 mL 8 mg mL⁻¹, CQD-C8 PC solution were mixed as pre-polymer solution. Then the solution was cured under UV light for several minutes and the CQD-C8 hydrophobic gel has been prepared successfully.

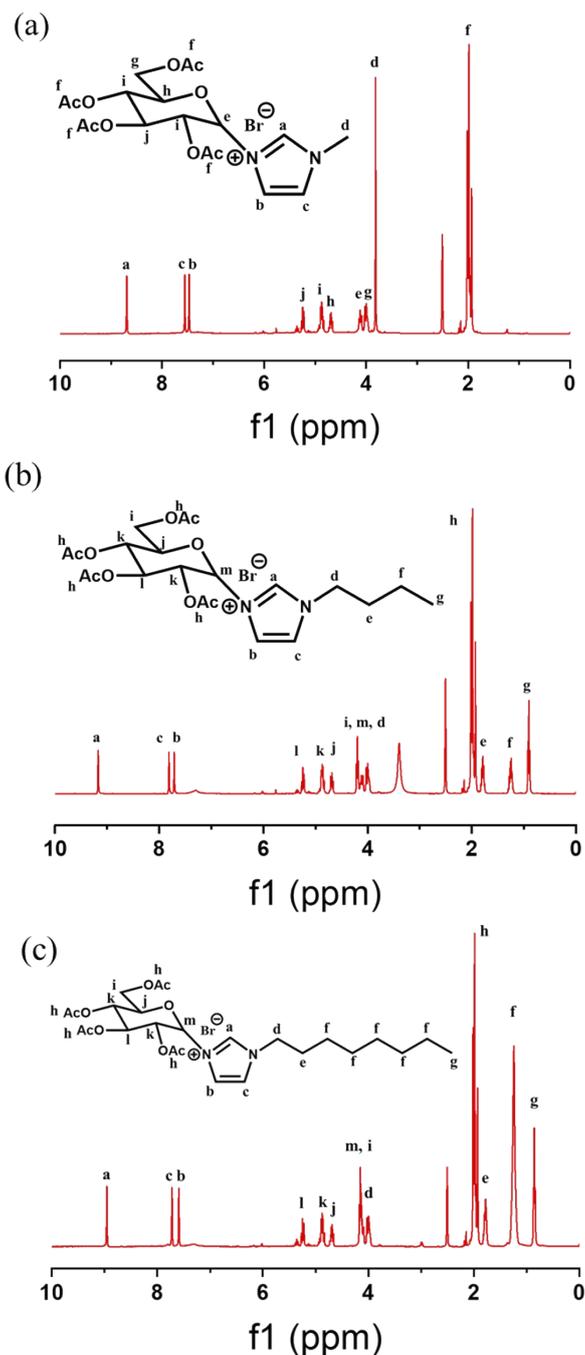


Fig. S1 ^1H NMR spectra of a series of glucose-based IL. a) IL-C1 ^1H NMR (400 MHz, DMSO-d_6) δ 8.69 (s, 1H), 7.55 (s, 1H), 7.47 (s, 1H), 5.24 (t, $J = 9.6$ Hz, 1H), 4.96~4.77 (m, 2H), 4.75~4.62 (m, 1H), 4.17~4.06 (m, 1H), 4.05~3.94 (m, 2H), 3.81 (s, 3H), 2.08~1.88 (m, 12H). b) IL-C4 ^1H NMR (400 MHz, DMSO-d_6) δ 9.17 (s, 1H), 7.81 (s, 1H), 7.71 (s, 1H), 5.24 (t, $J = 9.6$ Hz, 1H), 4.92~4.82 (m, 2H), 4.73~4.64 (m, 1H), 4.24~4.15 (m, 2H), 4.14~4.07 (m, 1H), 4.02 (t, 2H), 2.07~1.89 (m, 12H), 1.79 (m, 2H), 1.26 (m, 2H), 0.92 (t, 3H). c) IL-C8 ^1H NMR (400 MHz, DMSO-d_6) δ 8.96 (s, 1H), 7.72 (s, 1H), 7.59 (s, 1H), 5.30~5.15 (t, 1H), 4.97~4.79 (m, 2H), 4.78~4.64 (m, 1H), 4.13 (m, 3H), 4.02 (t, 2H), 2.09~1.89 (m, 12H), 1.78 (m, 2H), 1.24 (s, 12H), 0.86 (t, 3H).

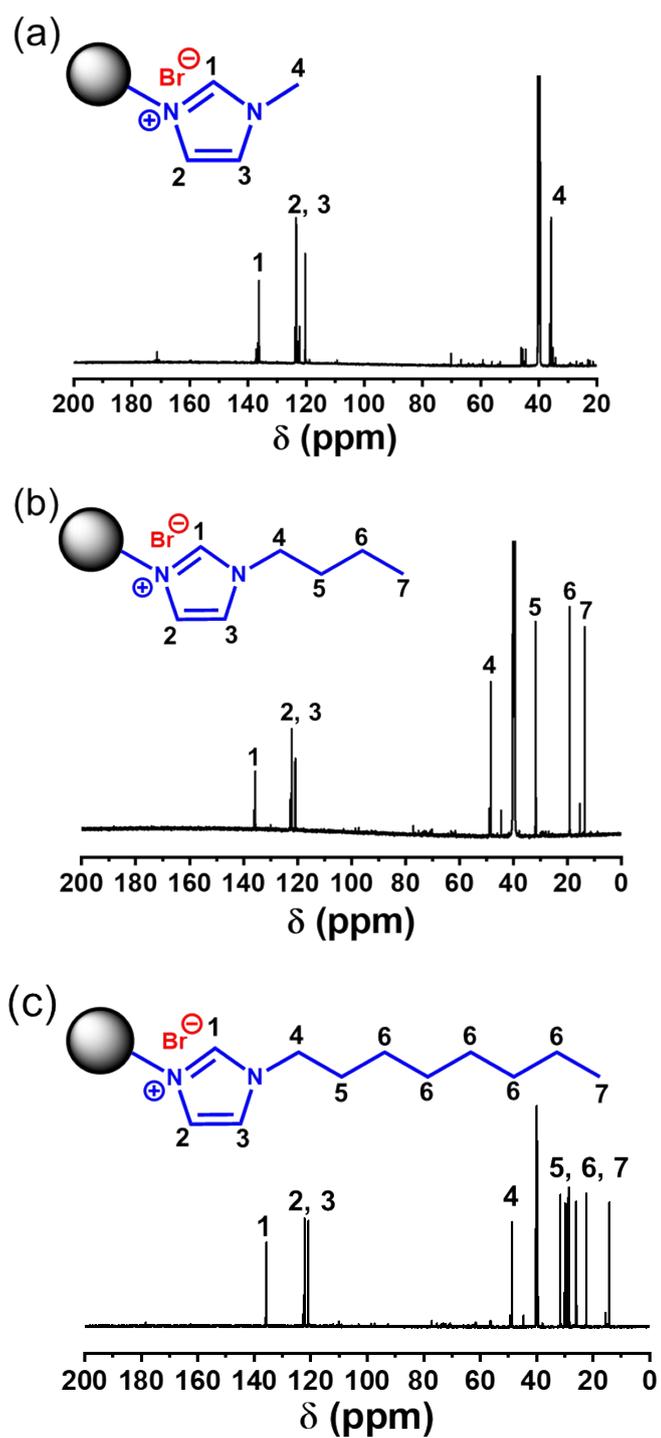


Fig. S2 ^{13}C NMR spectra of a series of IL-modified CQDs a) CQD-C1(DMSO- d_6) b) CQD-C4(DMSO- d_6) and c) CQD-C8(DMSO- d_6).

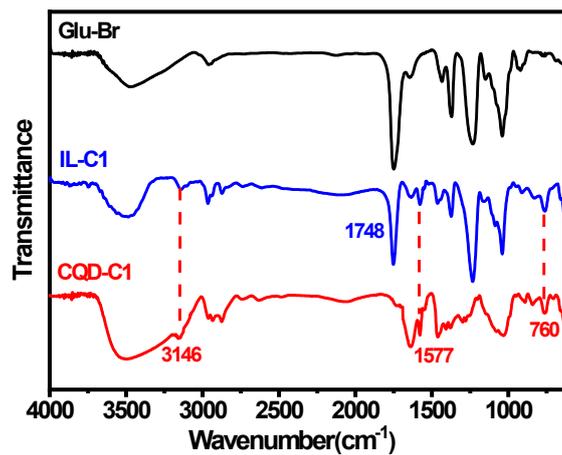


Fig. S3 Comparative FTIR spectra of Glu-Br, IL-C1 and corresponding CQD-C1.

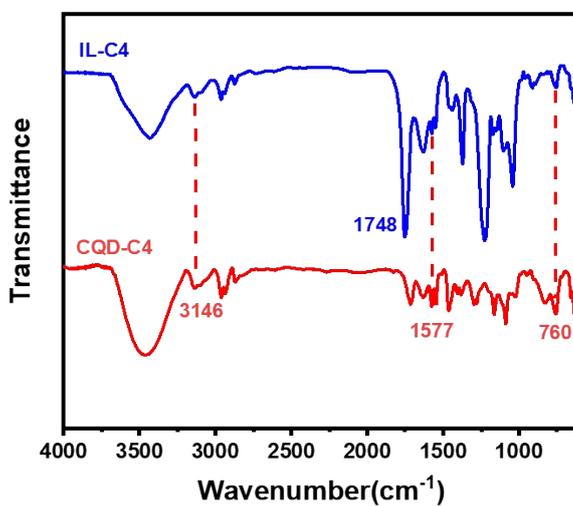


Fig. S4 Comparison of detailed FTIR spectra of IL-C4 and corresponding CQD-C4.

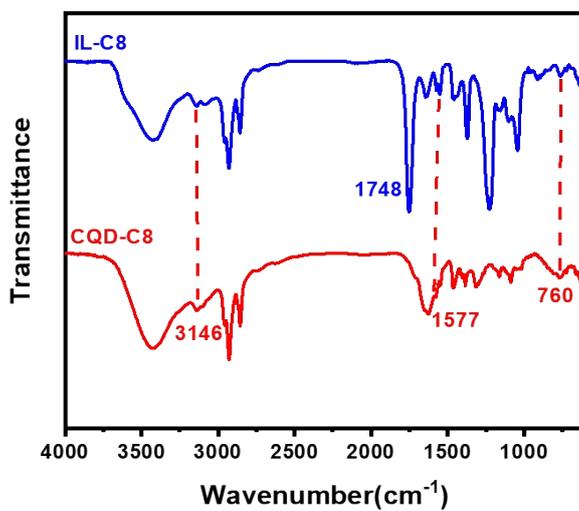


Fig. S5 Comparison of detailed FTIR spectra of IL-C8 and corresponding CQD-C8.

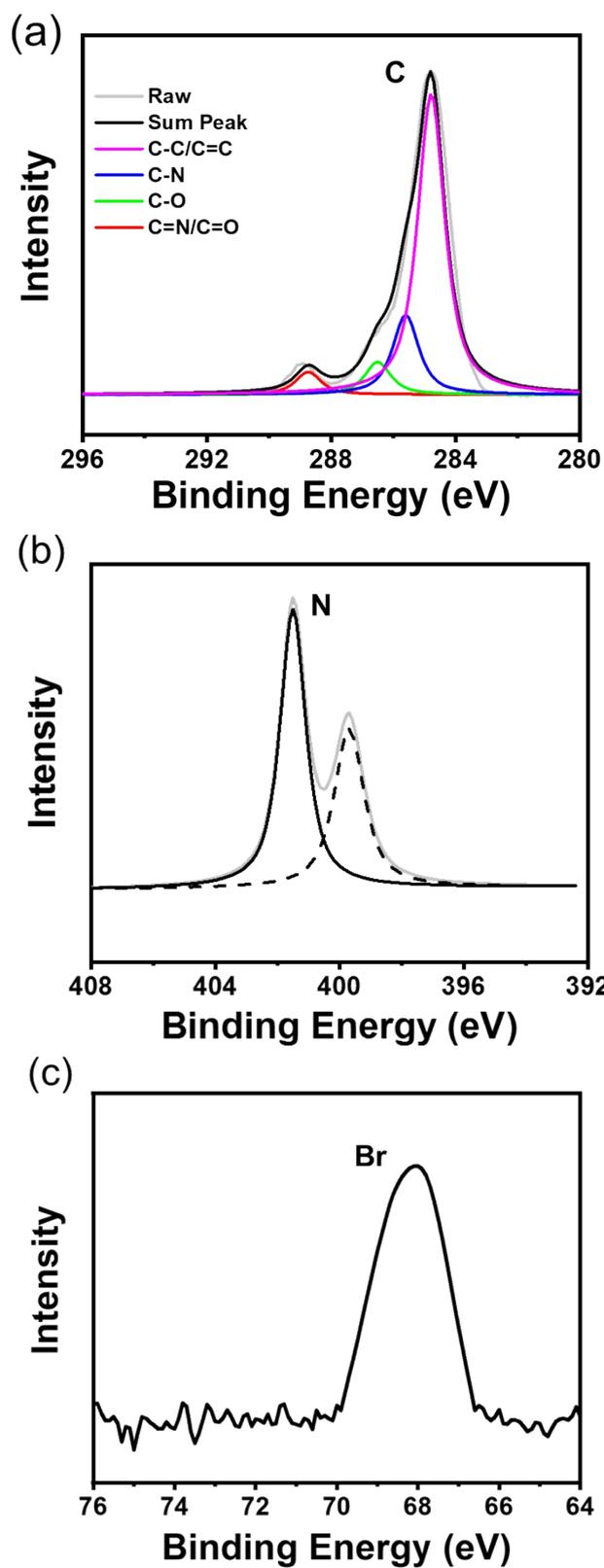


Fig. S6 XPS fine structure spectra of C_{1s}, N_{1s}, and Br_{3d} of CQD-C1.

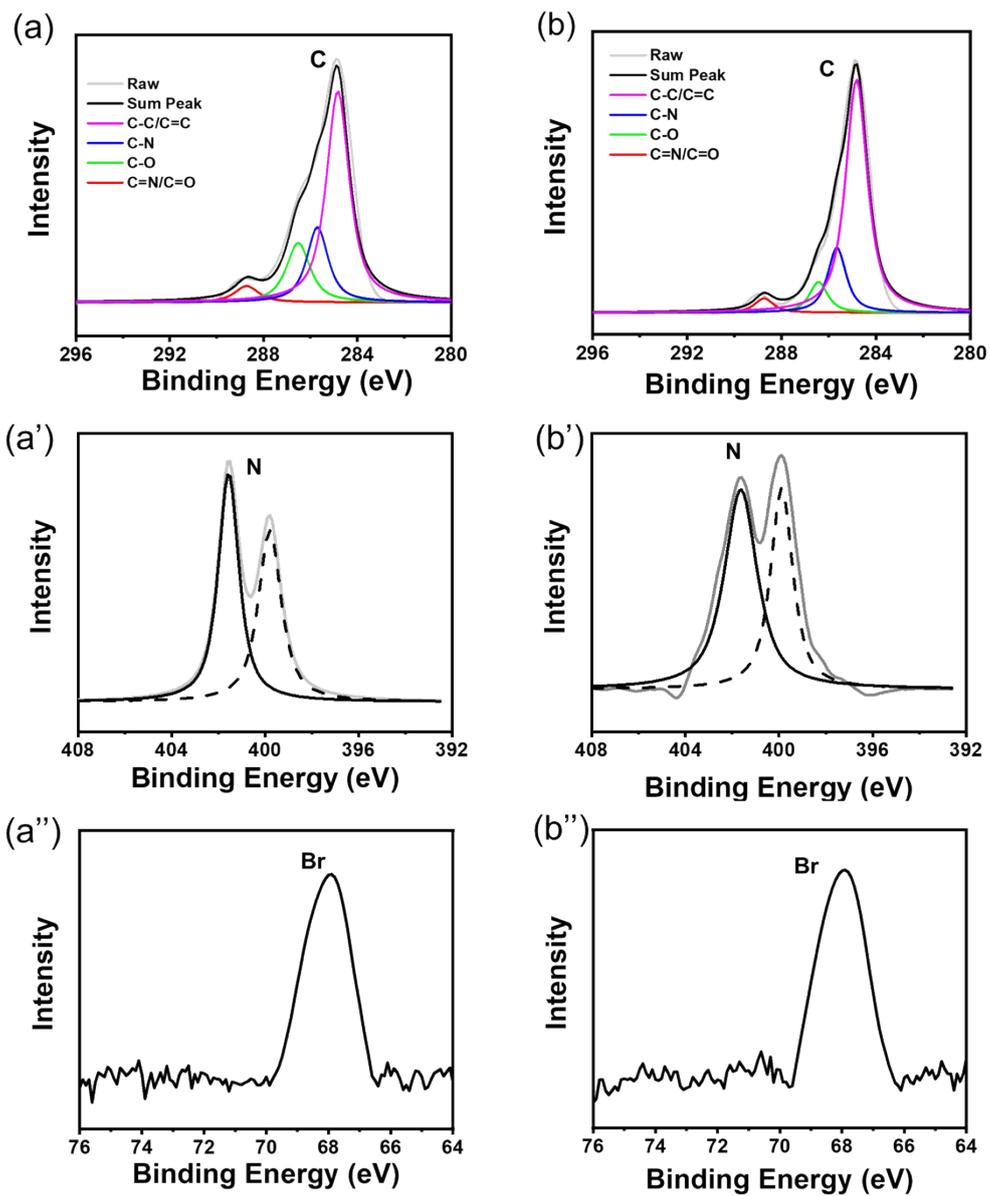


Fig. S7 XPS analysis of a, a', a'') CQD-C4 and b, b', b'') CQD-C8.

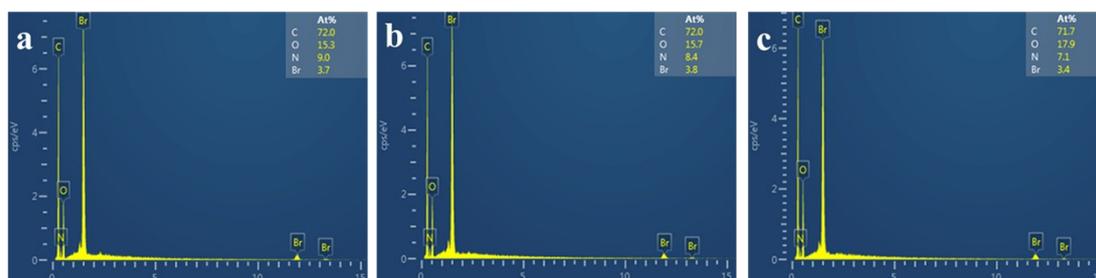


Fig. S8 EDX spectrum of a) CQD-C1 b) CQD-C4 and c) CQD-C8.

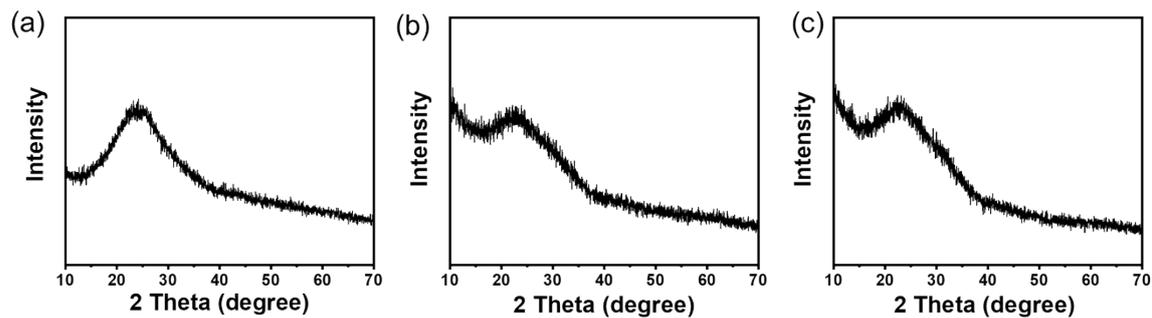


Fig. S9 XRD patterns of a) CQD-C1 b) CQD-C4 and c) CQD-C8.

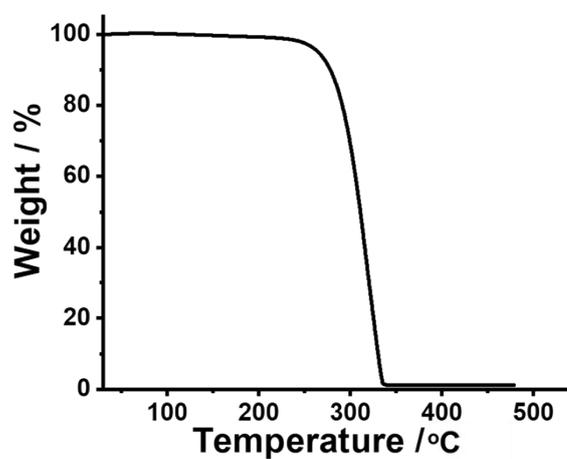


Fig. S10 TGA of imidazolium-type IL under a N₂ flow with a 10 °C min⁻¹ heating rate.

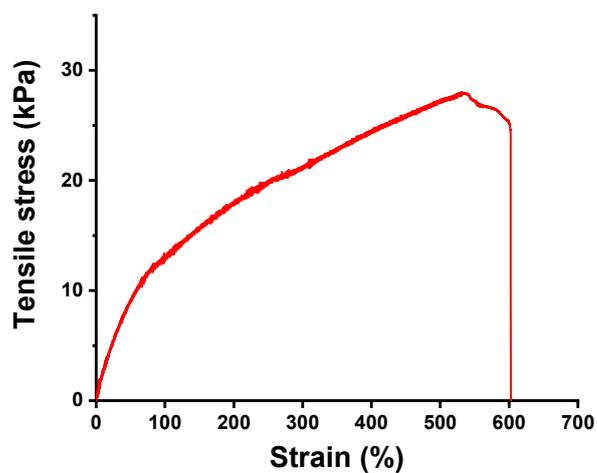


Fig. S11 Tensile stress vs strain curves for healed CQD gel. The sample was tested with a constant strain rate of 10 mm min⁻¹ at room temperature (approximately 25 °C).

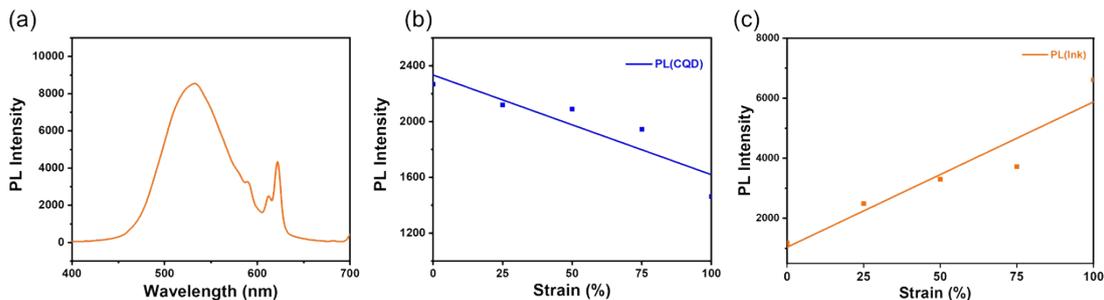


Fig. S12 a) PL emission spectra of yellow ink which was used to print coding information. b) Spectra of luminescence intensity versus strain for the outer hydrophilic CQD gel. c) Spectra of luminescence intensity versus strain for the inner information layer.

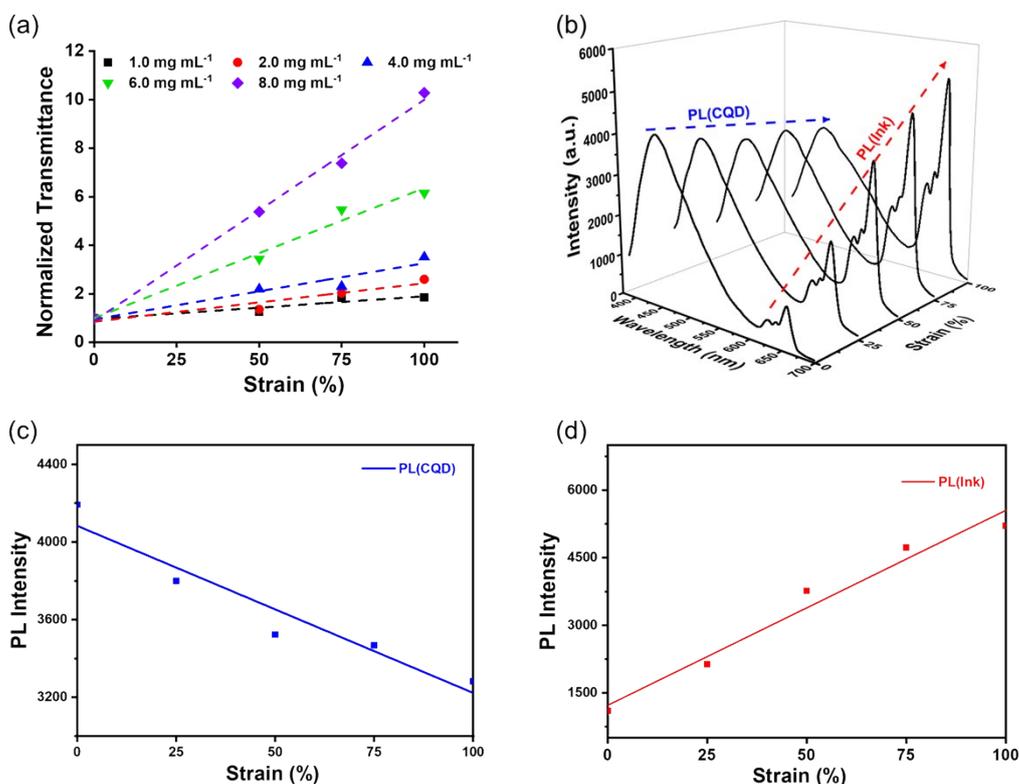


Fig. S13 a) Spectra of normalized transmittance for the CQD hydrophobic gel versus strain at various CQD concentrations. b) The fluorescent spectra of luminescence intensity versus strain for the sandwich-type multilayer gels with 8 mg mL^{-1} CQD-C8 in the outer layer (excitation UV wavelength is 365 nm). The PL spectra of the device displayed two main peaks, corresponding to CQDs at 440 nm and red ink at 655 nm. c) The spectra of luminescence intensity versus strain for the outer hydrophobic CQD gel. d) The spectra of luminescence intensity versus strain for the inner information layer.

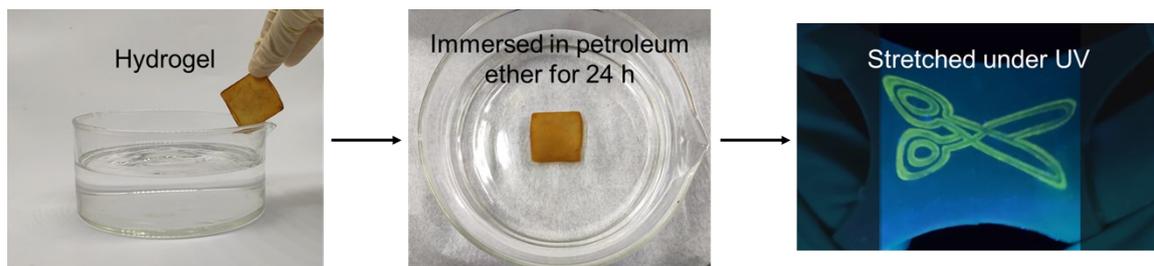


Fig. S14 Sandwich-type multilayer gel with hydrophilic outer layer was immersed in petroleum ether for 24 h.

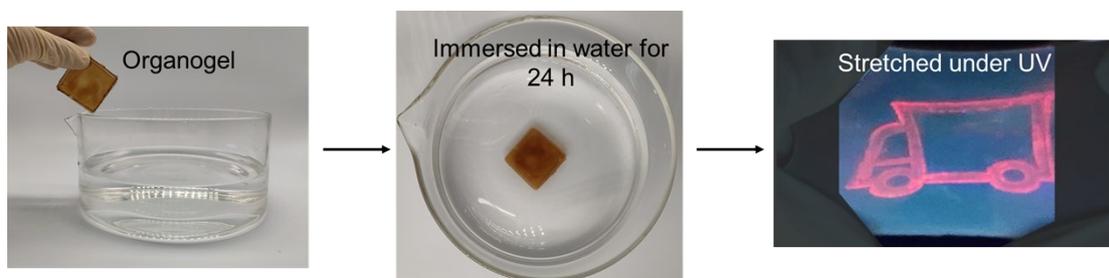


Fig. S15 Sandwich-type multilayer gel with hydrophobic outer layer was immersed in water for 24 h.