Electronic Supplementary Information

Self-healing Responsive Chiral Photonic Film for Sensing and Encoding

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Fig. S1 a) Dynamic equilibrium of the formation of boronic ester. b) ¹H NMR (500 MHz, D₂O, δ) spectra of PVA, 3-Acrylamidophenylboronic acid (3-ABA) with ammonium hydroxide (NH₃•H₂O), and PVA/3-ABA/ NH₃•H₂O, respectively. c) Partial ¹H NMR showing

that the Ha signal (the H atom connected to the C atom next to the hydroxyl of the PVA) of the PVA solution in D_2O exhibited partly down field shifts when mixed with 3-ABA and ammonium hydroxide.

According to the partial ¹H NMR of Fig. S1c, an additional signal of Ha' appeared after the adding of 3-ABA and ammonium hydroxide, with the integral area of Ha' : (Ha+ Ha') =1 : 5.51=18.15% which was close to the molar ratio of boronic acid to the diol groups (2*mol_{3-ABA}: mol_{repeating units of PVA}=15.37%), supporting that most of the 3-ABA could react with PVA to form the boronic ester.

¹H NMR of PVA: ¹H NMR (500 MHz, D₂O, δ) 4.18-3.33 (m, 41H, CH), 3.25 (s, 4H, COCH₃), 1.81-1.17 (m, 81H, CH₂).

¹H NMR of 3-ABA with NH₃•H₂O: ¹H NMR (500 MHz, D₂O, δ) 7.36 (s, 1H, 5-Ar H), 7.34 (d, *J* = 2.2 Hz, 1H, 4-Ar H), 7.32 (d, *J* = 2.1 Hz, 1H, 2-Ar H), 7.23 (t, *J* = 7.6 Hz, 1H, 3-Ar H), 6.35 (dd, *J* = 17.1, 10.3 Hz, 1H, 7-=CH), 6.23 (dd, *J* = 17.0, 0.8 Hz, 1H, 8-=CH₂), 5.77 (d, *J* = 10.8 Hz, 1H, 9-=CH₂).



Fig. S2 a) Dynamic equilibrium of the ionization of the boronic acid (3-ABA). b) ¹H NMR (500 MHz, DMSO-*d*6, δ) spectra of 3-ABA, 3-ABA/NH₃•H₂O=1 : 1, 3-ABA/NH₃•H₂O=1 : 10, and 3-ABA/NH₃•H₂O=1 : 1 with PVA, respectively.

To follow the H₁ signal of 3-ABA, ¹H NMR in DMSO-*d*6 was collected because H₁ signals would disappeared in D₂O due to the ion exchange with D₂O during ionization. In addition, the H₁ signal of 3-ABA also disappeared in DMSO-*d*6 after the ionization. When a proper amount of ammonium hydroxide was added to 3-ABA (mole ratio 1 : 1), partial ionization led to reduced H₁ signal, while excess amount of ammonium hydroxide (3-ABA/NH₃•H₂O=1 : 10) could lead to disappearance of H₁ signal. After the introduction of

PVA to the system of 3-ABA/NH₃•H₂O=1 : 1, the disappearance of H₁ signal indicated that the PVA promote ionization of 3-ABA via equilibrium shifting, supporting the formation of boronic ester of 3-ABA with PVA.



Fig. S3 a) Stress-strain curve of PVA-PAM hydrogel with water content of 50%. b) Stress-strain curve of a SCPF (m_{PVA-PAM}/m_{CNC}=14%) in dry state.



Fig. S4 Digital photos of self-healing process of the PVA-PAM hydrogel segments. The successful self-healing was confirmed by the external tensile force.



Fig. S5 (a) Frequency sweep of the PVA-PAM hydrogel at pH 8.5. Strain was constant at 4%. b) The change in modulus during the strain ramp described in c), demonstrating the self-healing of PVA-PAM hydrogel at pH 8.5 after the fracture. The hydrogels fractured during the strain ramp up to 300% and rapidly healed after the strain was reduced. The angular frequency for b) and c) was constant at 10 rad/s.



Fig. S6 Self-healing process of cut sections with age time for 2 days. a) Cut sections of PVA-PAM hydrogel aged for 2 days. b) The healed sections of the PVA-PAM hydrogel. c) The successful self-healing confirmed by the external tensile force. d) The broken PVA-PAM hydrogel under the external tensile force, indicating the breaking position located out of the healing interface. e) Cut sections of SCPFs ($m_{PVA-PAM}/m_{CNC}=14\%$) aged for 2 days. f) The healed sections of the aged SCPFs.



Fig. S7 Self-healing process of a completely dried PVA-PAM film, indicating that the water containment did not significantly affect the self-healing property.



Fig. S8 The FT-IR spectra of CNC, self-healing chiral photonic hydrogel (SCPF, $m_{PVA-PAM}/m_{CNC}=14\%$) and pure hydrogel of PVA-PAM.

Table S1. Former reported time scales for self-healing by boronic ester at room temperatu
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Materials	Time scales for self-healing at room temperature	Reference	
Poly (2-acrylamidophenylboronic acid – co – DMA) crosslinked with PVA or a catechol-functionalized copolymer	1 hour	ACS Macro Lett., 2015, 4, 220.	
Catechol functionalized hyperbranched polyurethane crosslinked with H ₃ BO ₃	24 hours	J. Mater. Chem. A, 2016, 4, 14122.	
Boronic acid-modified alginate	0.5 hour	Chem. Commun., 2017, 53 , 3350.	
Telechelic diboronic ester with 1,2- diol-containing polymer backbones	16 hours	J. Am. Chem. Soc., 2015, 137 , 6492.	
Boronic acids and 1,2-diols crosslinked PDMS	10 minutes	Macromol. Rapid Commun., 2016, 37, 1052.	



Fig. S9 a) The SCPFs incorporated onto the porous substrates of (from left to right) carbon cloth, stainless steel mesh, nickel foam, nylon mesh, and filter paper through self-healing process, respectively. b) The wetted SCPFs bent with the porous substrates that attached on a glove to form wearable materials.



Fig. S10 SEM images of the porous substrates with and without the self-healing hydrogel coatings: Carbon cloth a) with and b) without the coating, scale bar: 500 μ m. Stainless steel mesh c) with and d) without the coating, scale bar: 200 μ m. Nickel foam e) with and f) without the coating, scale bar: 200 μ m. Nylon mesh g) with and h) without the coating, scale bar: 200 μ m. Filter paper i) with and j) without the coating, scale bar: 50 μ m.



Fig. S11 DRS patterns of a single layer SCPF ($m_{PVA-PAM}/m_{CNC}=14\%$) sample responding to different solvents: a) water, b) DMSO, c) DMF, d) DMA, e) acetic acid, f) MeOH, g) EtOH, h) isopropanol, and i) acetone. The insets in a) and b) showed the enlarged views for the initial DRS patterns.

Solvent	Polarity	Refractive index (25°C)	Viscosity (cp, 20°C)
water	10.2	1.33	1.0
dimethyl sulfoxide	7.2	1.48	2.24
N,N-dimethylformamide	6.4	1.43	0.92
N,N-dimethylacetamide	6.5	1.44	0.80
acetic acid	6.2	1.37	1.28
methanol	5.1	1.33	0.6
ethanol	4.3	1.36	1.2
isopropanol	3.9	1.38	2.37
acetone	5.1	1.36	0.32

Table S2. Polarity indexes, refractive indexes and viscosity of several solvents.

For the SCPF ($m_{PVA-PAM}/m_{CNC}=14\%$), solvents with polarity over 6 could lead to significant

red-shift and split of the reflectance band during the response.



Fig. S12 DRS patterns of a single layer SCPF ($m_{PVA-PAM}/m_{CNC}=7\%$) sample responding to different solvents: a) water, b) DMSO, c) DMF, d) DMA, e) acetic acid, f) MeOH, g) EtOH, h) isopropanol, and i) acetone.



Fig. S13 DRS patterns of the SCPF (m_{PVA-PAM}/m_{CNC}=7%) immersed in solvents of a) water, b) DMSO, c) DMF, d) DMA, e) acetic acid and f) MeOH. (a', b', c', d', e' and f') Time evolution of the spectrum denoted as horizontal white dashed lines in the DRS patterns except the starting time and ending time. The arrows indicated the shift of the reflectance peaks.



Fig. S14 a) Schematics of the dynamic reflection spectra (DRS) measurement with a single layer SCPF ($m_{PVA-PAM}/m_{CNC}=14\%$) sample. The reflection spectra were continuously recorded in steps of 1 second for 2 minutes under a normal incident light. The tested solvent (15 µl) was injected onto the surface of the SCPFs and the system was covered to prevent evaporation of the solvent. b) to l) The 2D contour map of the single layer SCPF responding to water/acetone in different volume ratios from (b) 100: 0 to (l) 0: 100.

As shown in Figure S14, with increasing contents of water from 0 to 100% in the mixtures, the reflectance maxima at 120 seconds red shifted from 419 nm in pure acetone and 750 nm in pure water, along with the continually increasing speed of the redshift. The

corresponding structural color shifted throughout the entire visible spectrum, indicating the swelling of SCPF was very sensitive to the water contents in the solvent mixtures within the observing time.



Fig. S15 a) Schematic illustration of the experiment method for Figure 7. b) The measured tansmittance spectra of the used circularly polarized filter.



Fig. S16 Schematic illustrations showing the encryption and recognition of the paper printed QR codes encoded by SCPFs with a multiple layer structure ($m_{PVA-PAM}/m_{CNC}=40\%$ for the bottom layer and $m_{PVA-PAM}/m_{CNC}=30\%$ for the triangle layer on top). The optical images of SCPF-encoded QR codes were taken under normal incident light.



Fig. S17 Reflatance spectra and optical images of the SCPF ($m_{PVA-PAM}/m_{CNC}=14\%$) encoded QR codes under normal incident L-CPL and R-CPL.

The dissymmetry factor, **g**, can be calculated in the equation as follows:

$$g = \frac{I_{\rm L} - I_{\rm R}}{\frac{1}{2}(I_{\rm L} + I_{\rm R})}$$

Where I_L and I_R are the intensities of L-CPL and R-CPL respectively. (Adv. Mater., 2018,

1705948; Chem. Rev., 1986, 86, 1; Chem. Rev., 1977, 77, 6.)