Supporting Information

Patterning, Morphing, and Coding of Gel Composites by Direct Ink Writing

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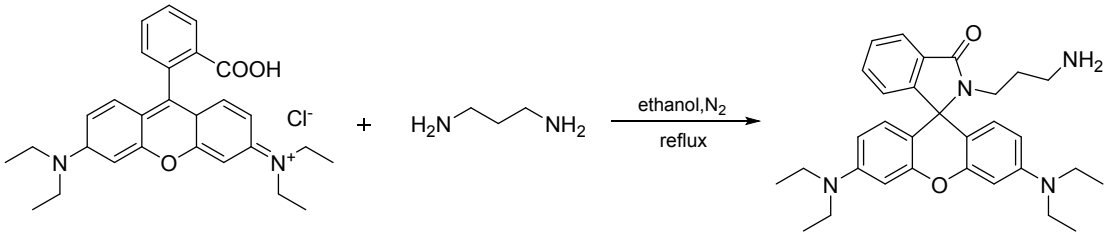
Fabrication of pPFPA gel

Zwitterionic poly(sulfobetaine methacrylate) (10 mg/mL in trifluoroethanol) was spin-coated on a clean Si substrate to form a scarificial layer. Then poly(pentafluorophenyl)acrylate (pPFPA) and 1,3-propyldiamine mixed solution (Table S1) was drop-casted and dried in toluene atomosphere for 2 hours. Subsequent immersing the Si substrate into DI water dissolves the scarificial layer and gives rise to a free-standing flexible and transparent pPFPA gel. The gels are throughly dried for ATR characterization and TGA test.

Synthesis of RA

1,3-Diaminopropane (1.74mL, 10 equiv.) was added to a solution of Rhodamine B (1g, 2.01mmol) in ethanol (50mL). The mixture reaction was refluxed overnight and subsequently

concentrated under a reduced pressure. The crude solid was diluted with DCM, washed with water and brine, dried over $MgSO_4$ and the solvent was removed under vacuum. The residue was purified by silica gel column chromatography to give a pale yellow solid (200mg, 19%). ^{1}H NMR (400 MHz, CDCl3) δ 7.89 (dd, J = 5.9, 2.8 Hz, 1H), 7.43 (dd, J = 5.5, 3.0 Hz, 2H), 7.08 (dd, J = 5.7, 2.8 Hz, 1H), 6.41 (d, J = 8.8 Hz, 2H), 6.37 (d, J = 2.5 Hz, 2H), 6.26 (dd, J = 8.9, 2.5 Hz, 2H), 3.33 (q, J = 7.0 Hz, 8H), 3.20 (t, J = 7.0 Hz, 2H), 2.46 (t, J = 6.5 Hz, 2H), 1.72 (s, 4H), 1.16 (t, J = 7.0 Hz, 12H).



Scheme S1. Synthesis route of RA

Synthesis of CA

Synthesis of tert-Butyl-N-(3-brompropyl)-carbamate (1)

3-Bromopropylamine hydrobromide (3.28 g, 0.02 mol) was added to dichloromethane (100 mL) and triethylamine (4.2 mL) solutions. After stirring for 30 min, the di-tert-butyl dicarbonate (Boc_2O) (0.55g, 2.50 mol) in dichloromethane (10 mL) solutions was added dropwise over 3 h at 0℃. After stirring overnight, the mixture was extracted with water and dichloromethane. The combined organic phases were dried over anhydrous Na_2SO_4, filtered, concentrated, and dried in vacuum. Compound **1** was isolated as clear light-yellow oil in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67 (s, 1H), 3.43 (t, *J* = 6.5 Hz, 2H), 3.27 (d, *J* = 6.4 Hz, 2H), 2.10 – 1.99 (m, 2H), 1.43 (s, 9H).

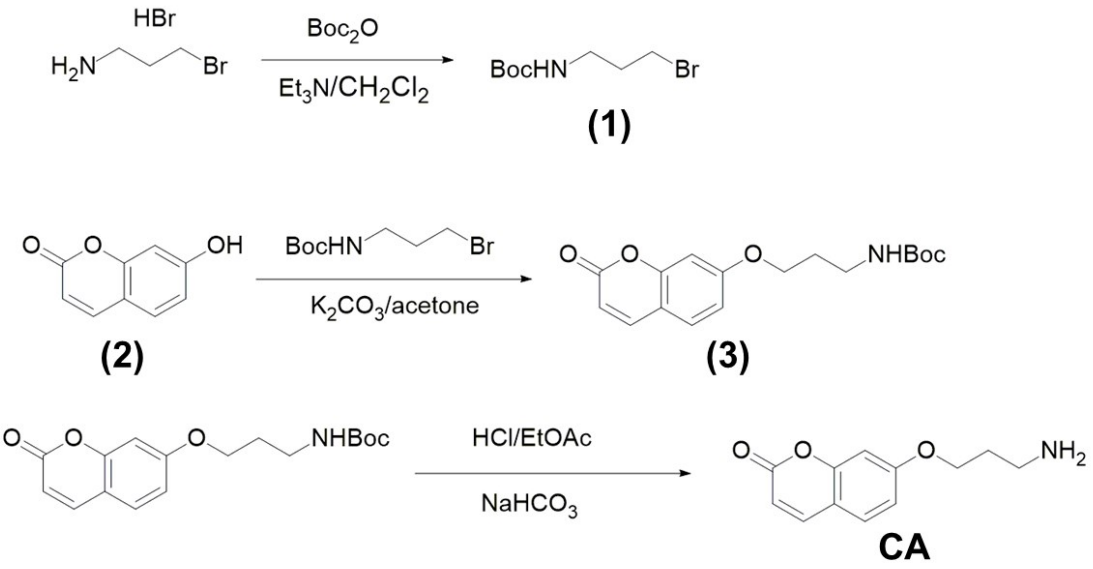
Synthesis Procedure of (3)

Compound **1** (1.33 g, 5.60 mmol), compound **2** (0.75 g, 4.6 mmol), and anhydrous potassium carbonate (1.30 g, 9.4 mmol) were placed into acetone solution (30 mL) and then the mixture was refluxed for 24 h. After the reaction, the precipitate was filtered off and washed three times

with acetone. The filtrate was evaporated and residue dried in vacuum. The obtained powder of **3** was recrystallized from ethanol and dried on air, with the yield 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 9.5 Hz, 1H), 7.36 (d, J = 8.5 Hz, 1H), 6.85 – 6.77 (m, 2H), 6.24 (d, J = 9.5 Hz, 1H), 4.74 (s, 1H), 4.07 (t, J = 6.0 Hz, 2H), 3.33 (d, J = 6.3 Hz, 2H), 2.02 (dd, J = 10.8, 4.5 Hz, 2H), 1.43 (s, 9H).

Synthesis Procedure of CA

Compound **3** (0.99g, 3.10 mmol) was suspended in ethylacetate (2.5 mL), and then 1.25 mL of concentrated hydrochloric acid was added dropwise. The mixture was reacted at ambient atmosphere overnight with intensive stirring. After the reaction, 5% aqueous solution of potassium carbonate was added and the mixture was stirred for 2 h. The resulting mixture was extracted with dichloromethane and the combined organic phases were dried over anhydrous Na_2SO_4, filtered, evaporated, and dried in vacuum at room temperature. As a result, the powder CA was obtained in 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 9.5 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 6.83 (dt, J = 4.3, 2.3 Hz, 2H), 6.25 (d, J = 9.5 Hz, 1H), 4.12 (t, J = 6.1 Hz, 2H), 2.93 (t, J = 6.8 Hz, 2H), 1.99 – 1.93 (m, 2H).



Scheme S2. Synthesis route of CA

Tracking the "in-situ" reaction by NMR

In-situ ^{19}F NMR experiments could well track the reaction progresses. Though pPFPA gels show no signal in ^{19}F NMR spectra due to the solid status in the NMR tube, the side product of the reaction, pentafluorophenol, could readily dissolve in $CDCl_3$ and well-indicate the reaction progress. Therefore, by calculating the peak integral ratio of pentafluorophenol to the hexafluorobenzene (internal standard), the reaction between alkylamine and pPFPA gel could be precisely tracked. Specifically, "In-situ" ^{19}F NMR characterizations of pPFPA gel in different inks with hexafluorobenzene as inner reference are conducted. Here, Chloroform-d and/or water-d/ethanol mixture (volume ratio = 2 : 3) serves as the solvent. To ensure full conversion, large excess alkylmines are applied to the process, with the total amine concentration and the molar ratio of amine to pendant pentafluorophenyl ester group around 1.06 M and 100, respectively. In the experiments, we calibrate the conversion progresses (percentage as the unit) by calculating the peak integral ratio of pentafluorophenol to hexafluorobenzene over time.

Treat pPFPA gel with alkylamines

Prior to treatment, the pPFPA gels are pre-swollen in chloroform for 10 min to expand the gel network and induce a driven force for the diffusion of alkylamines in and out of the gel, and then immersed into desired formulations with gentle agitation at room temperature. Here, the total amine concentration of three formulations are 1.06 M in water/ethanol (volume ratio of 2: 3) or DMSO, depending on the solubility of the alkylamines. Upon completing the treatment, the gels are soaked in water/ethanol to remove the residue amines.

Tensile tests of pPFPA gel: The tensile tests of pPFPA gel (swollen by toluene with a swelling ratio of 1.14) were carried out on an MTS CMT6203 electromechanical universal testing machine at room temperature. The pPFPA gels were cut into rectangular pieces with 24 mm in length (l), 3 mm in width (w) and 0.23 mm in thickness (t). The initial gel length (l_o) between two fixture heads is 14mm, and the crosshead speed was set at 5 mm min^{-1}. The stress is

calculated as $F/(wt)$, and the strain is calculated as (l_t/l_o), where F is the force, l_t is the gel length at a given moment. The moduli of pPFPA gel were obtained by the initial (straight line) linear slope of the stress versus strain curve. At least five samples were used for each test.

Rheological test: The rheological tests were conducted on an DHR-2 rheometer at room temperture using a parallel steel plate with a diameter of 8 mm. A 5% strain and a 200 μm gap is applied during the tests.

Scanning Electron Microscopy characterization: The SEM characterizations were carried out on a SU8010 Scanning Electron Microscopy. The hydrogel samples were freezed-dried prior to the SEM observation.

Calculation of swelling ratio: To determine swelling ratio, we use an optical microscope to measure the dimension change before and after being swollen by the solvent, and the swelling ratio is calculated by following equation with the assumption that the gel is swollen isotropically:

$$SR = \left(\frac{l}{lo}\right)^3$$

Where SR is the swelling ratio, l is the length of the swollen gels, lo is the length of the gel prior to being swollen. At least 12 measurements were taken for each data point.

Bending radius determination: To determine the bending radius, the bent gel is observed under the optical microscope, the software named "TCapture" automatically generates a circle with its arc fits the curve of the bent gel. The radius of the arc is used as the bending radius of the gel. Alternately, we can also manually draw a circle with its arc well-fits the curve of the gel (insert of Fig. 4c), and use the radius of the circle as the bending radius.

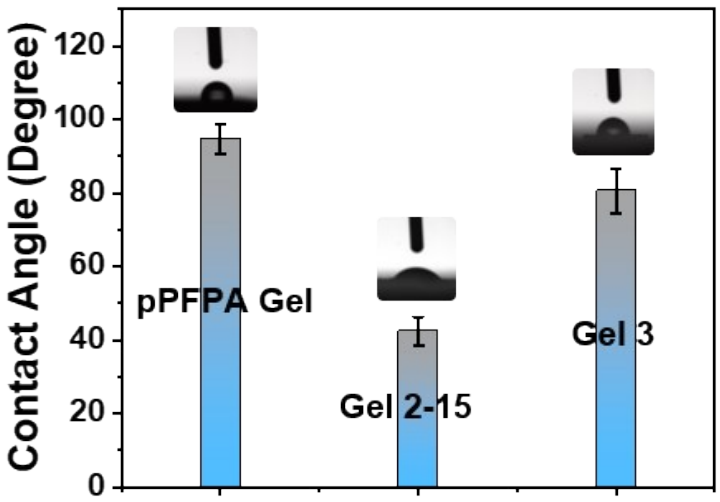


Figure S1. Water contact angle of pPFPA gel, Gel 2-15, and Gel 3. Each data point is the average of 5 repeated tests.

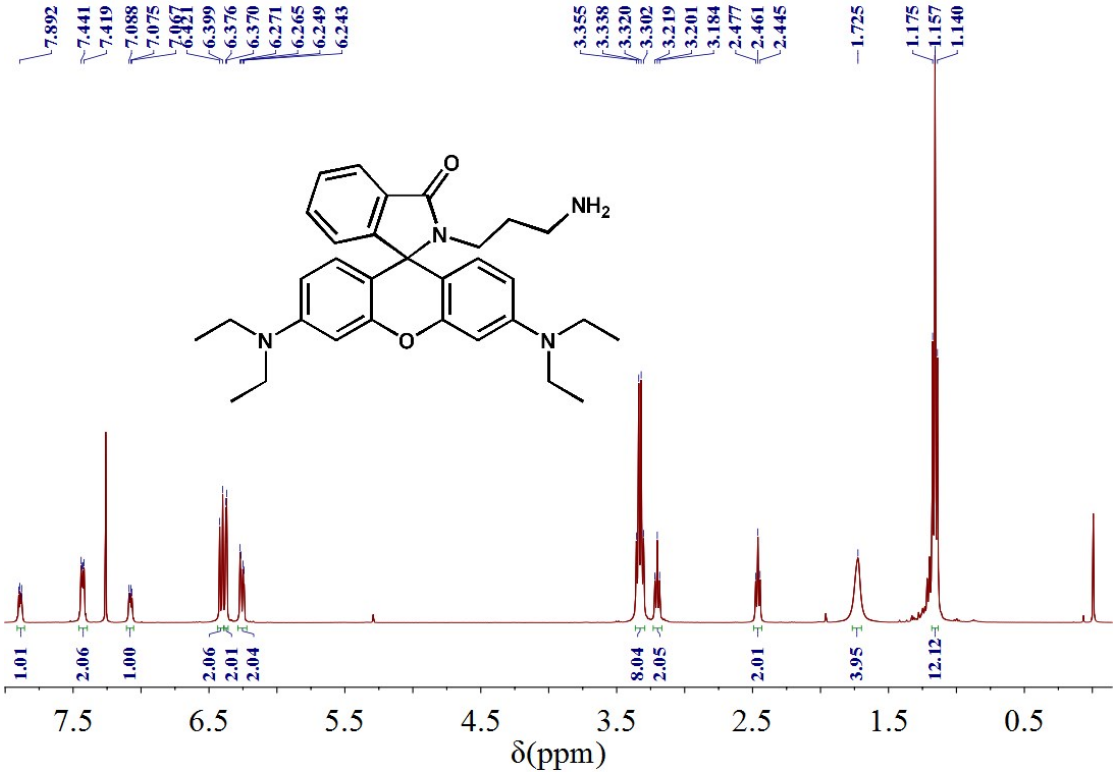


Figure S2. ^{1}H NMR spectrum of RA

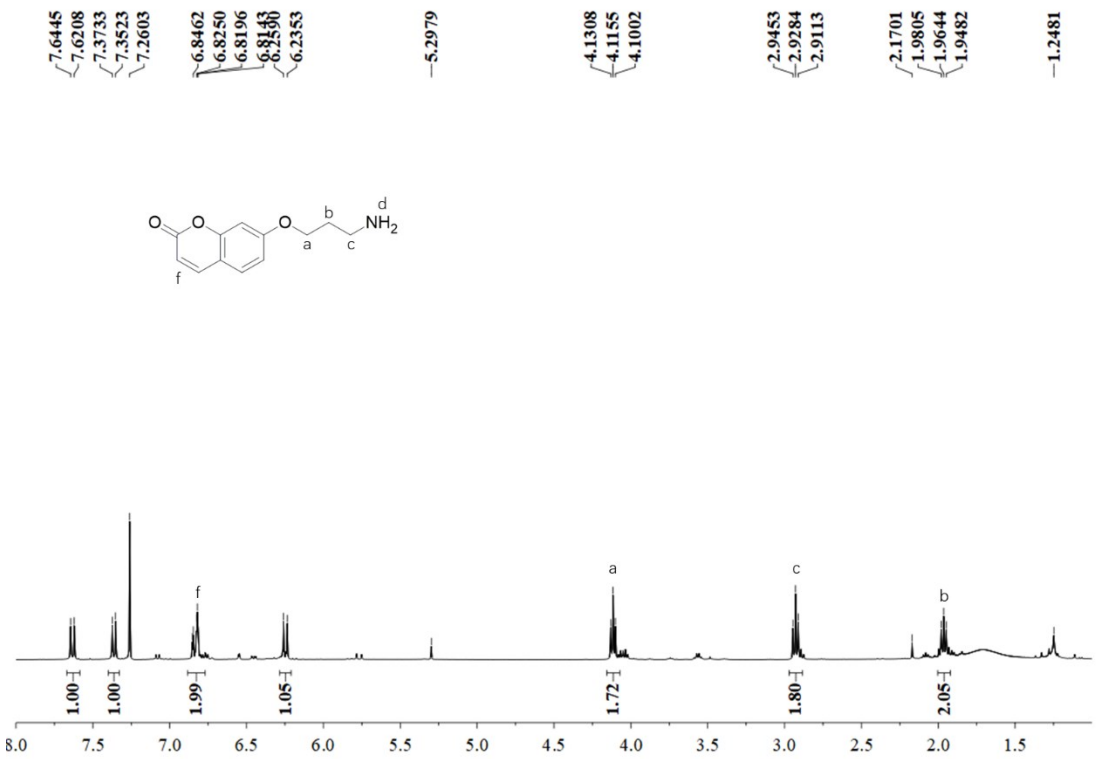


Figure S3. ^{1}H NMR spectrum of CA

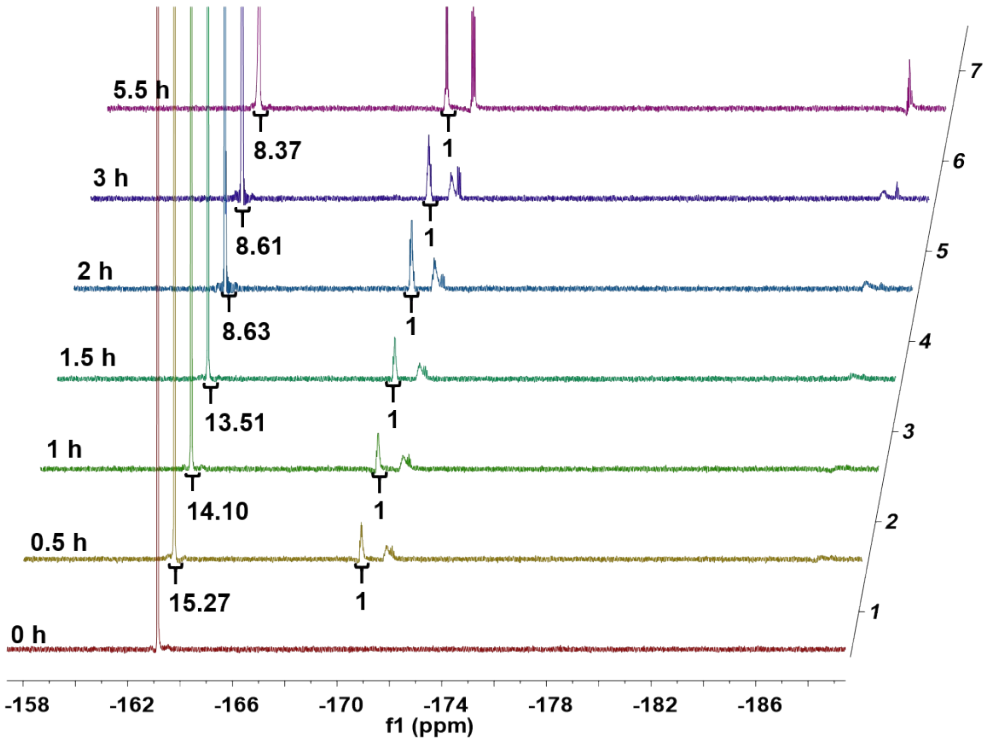


Figure S4. In-situ ^{19}F NMR characterizations of pPFPA gel with hexafluorobenzene as inner reference in IPA Chloroform-*d* solution; The peak at -163.2 ppm is assigned to hexafluorobenzene, and the rest peaks are assigned to pentafluorophenol.

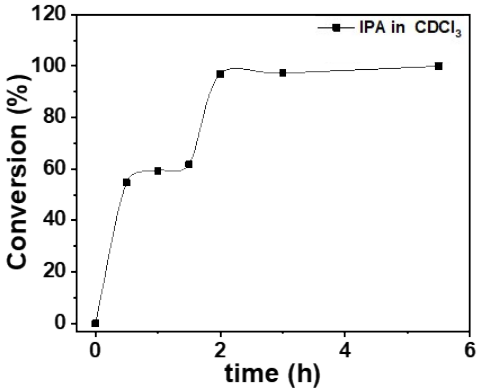


Figure S5. In-situ tracking the reaction between IPA and pPFPA gel by ^{19}F NMR characterizations.

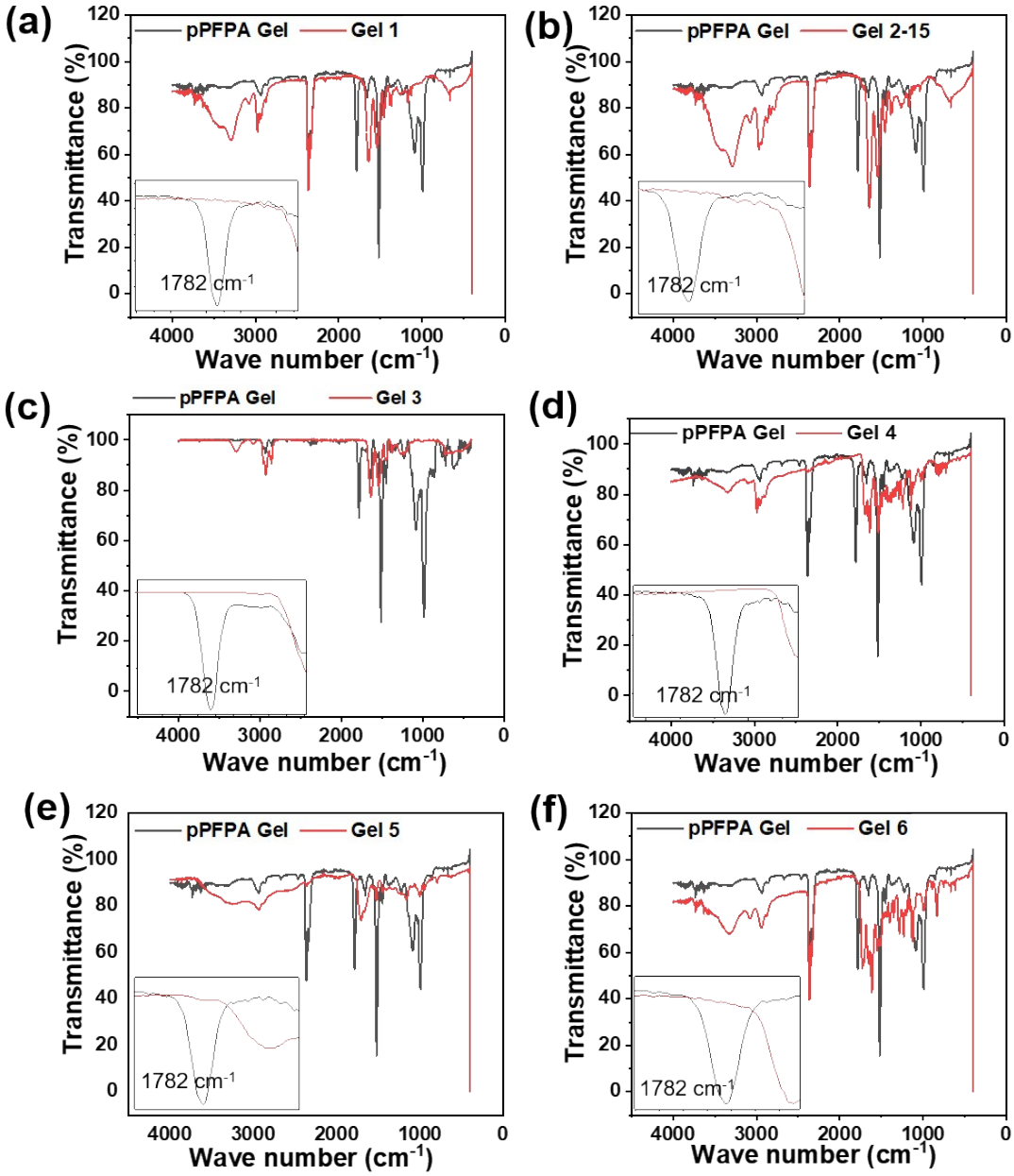


Figure S6. ATR characterizations of the gels after treating by (a) IPA, (b) $IPA_{8.5}/DMPA_{1.5}$, (c) HA, (d) RA, (e) DH and (f) CA. As comparisons, ATR characterizations of pPFPA gel are also presented in all figures. Note that all the samples are thoroughly dried prior to ATR tests.

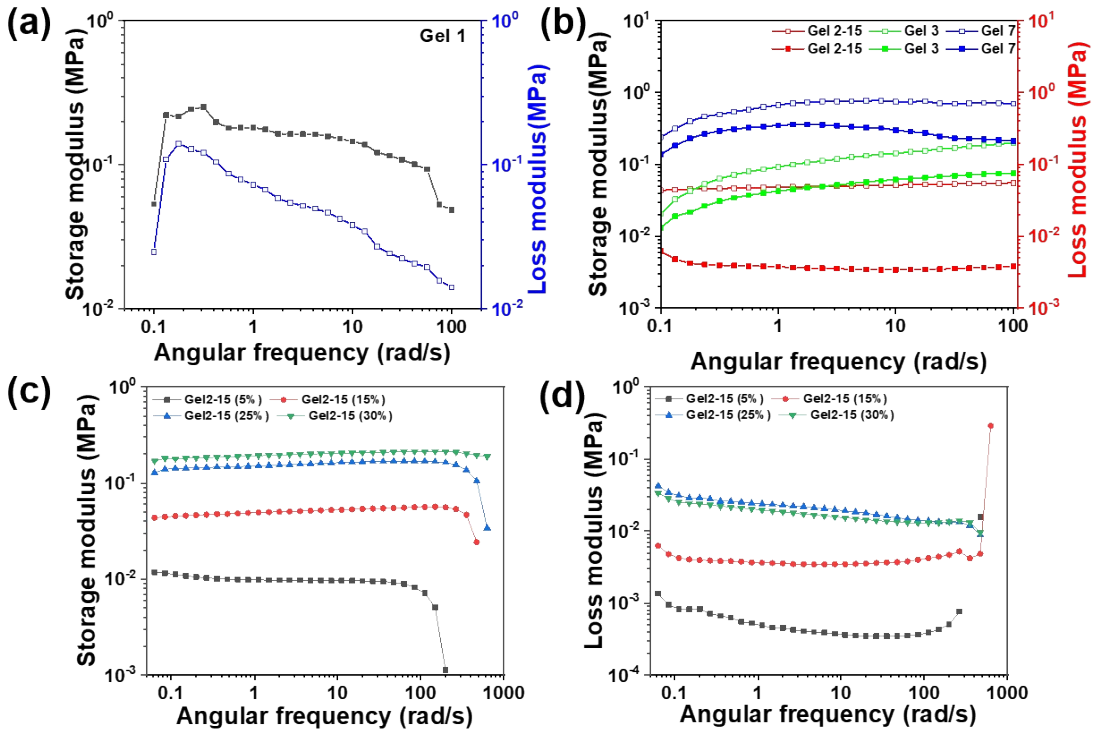


Figure S7. Rheological analysis at 25 ℃ in a of (a) Gel 1, (b) Gel 2-15, Gel 3 and Gel 7 (open square represents storage modulus and solid square indicates loss modulus). (c) storage modulus and (d) loss modulus of Gel 2-15 with different crosslinking density. (The number in the blankets are the crosslinker density of Gel 2-15). All these gels are fully swollen in DI water prior to rheological tests.

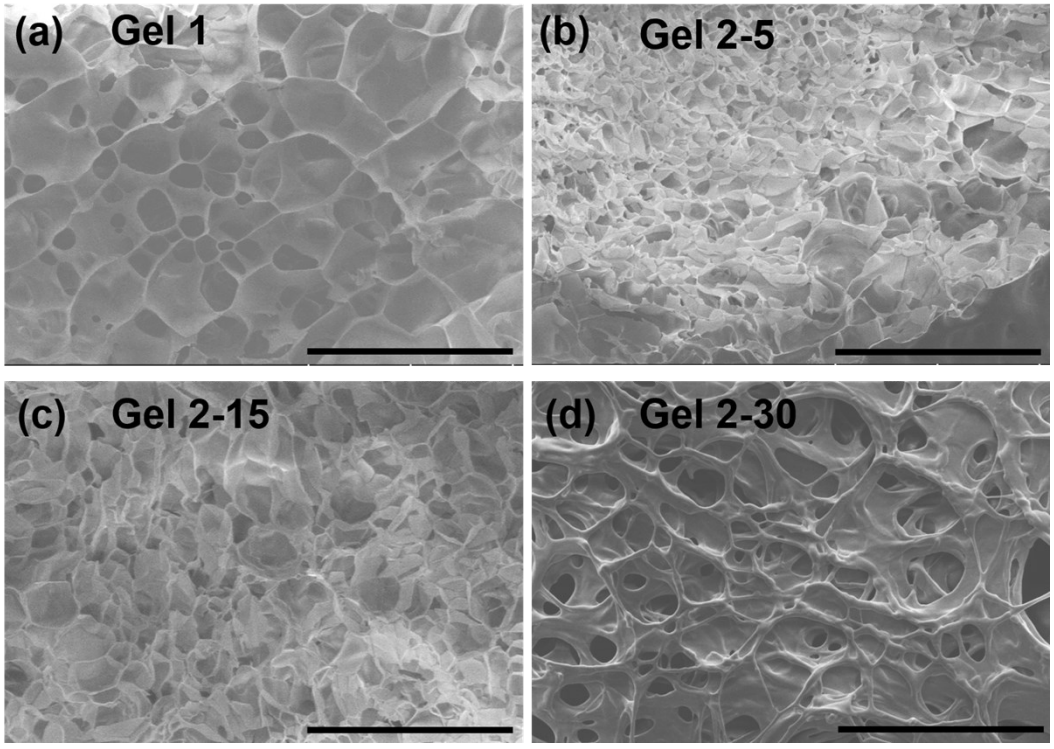


Figure S8. Scanning Electron Microscopy image of (a) Gel 1, (b) Gel 2-5, (c) Gel 2-15 and (d) Gel 2-30. The scale bar in all images is 50 μm.

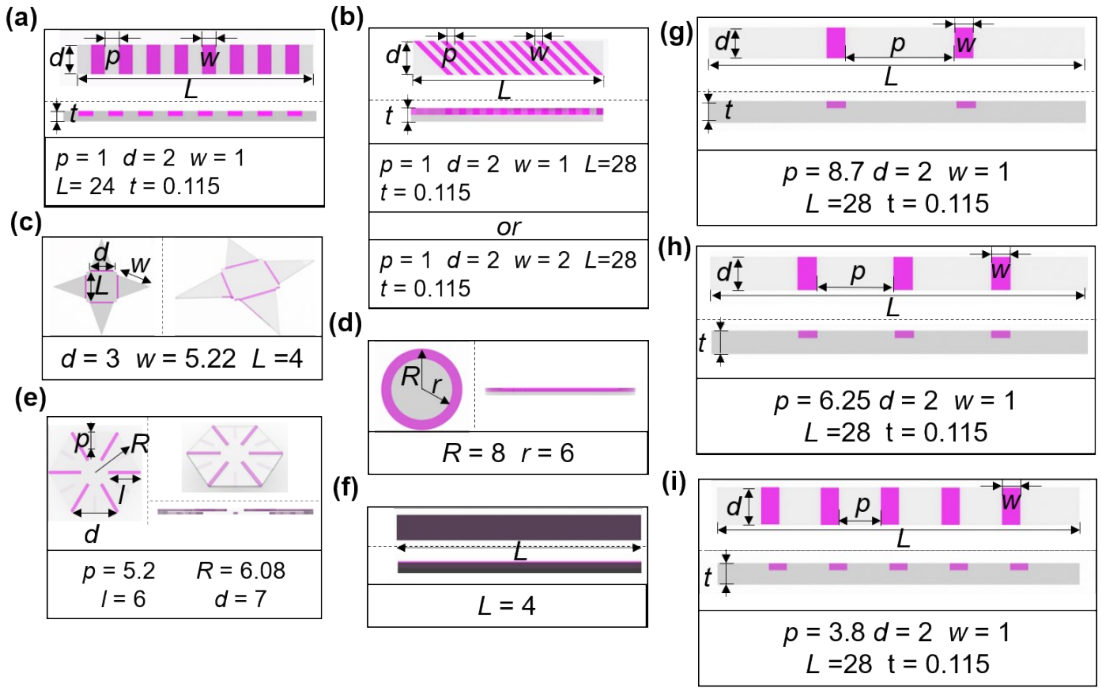


Figure S9. Schematical illustrations of gel pattern dimensions (the unit is "mm" for all patterns). (a) Stripes are parallel to gel short axis. (b) Stripes are 45° with respect to gel short axis. (c) Patterns at the junctions of flower petals and pistil. (d) A ring-shaped pattern on top surface of a cyclic gel. (e) Uniformly distributed patterned lines on both top and bottom surface of a hexagonal gel. (f) Non-transparent bi-layered gel. (g-i) Patterns of trigon, tetragon, and hexagon respectively.

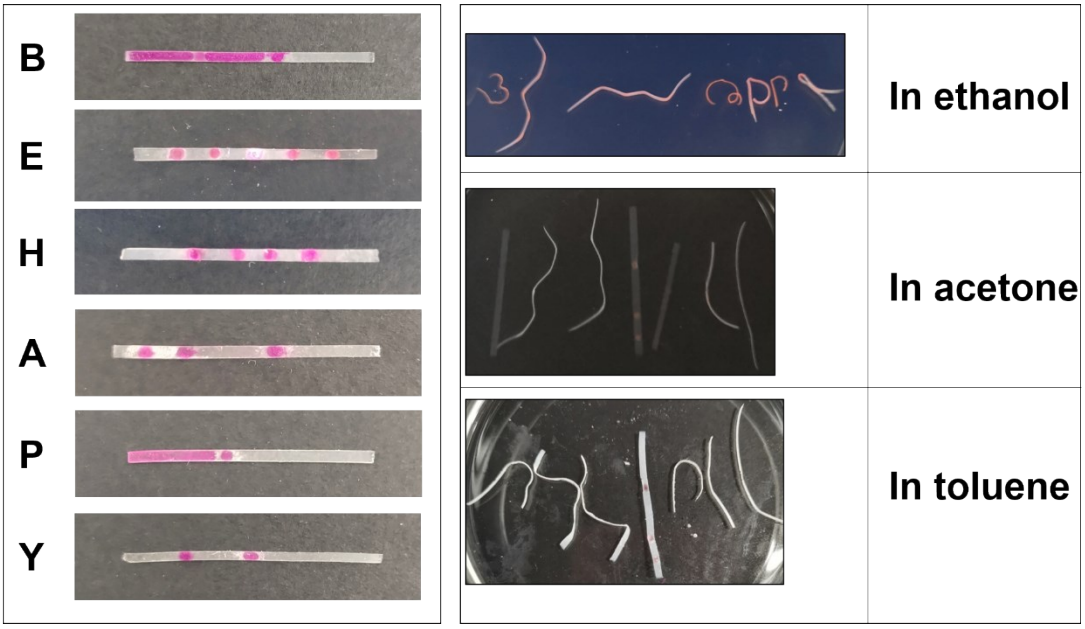


Figure S10. Left: the codes and the corresponding encrypted letters. Right: the decrypted data in improper solvents, such as ethanol, acetone, and toluene. (The dimension of the gel strips is 28 mm in length, 1mm in width, and 0.1 mm in thickness)

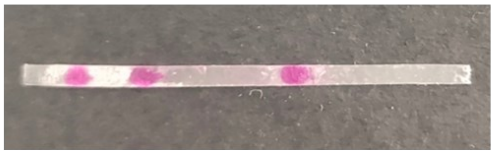
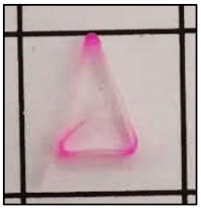
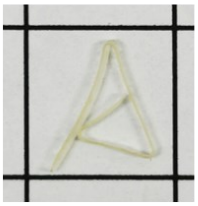
	Codes	Decrypted in H_2O
A dyed		
A undyed		

Figure S11. The code and decryption data with and without dyes on the treated sites. (The dimension of the gel strips is 28 mm in length, 1 mm in width, and 0.1 mm in thickness)

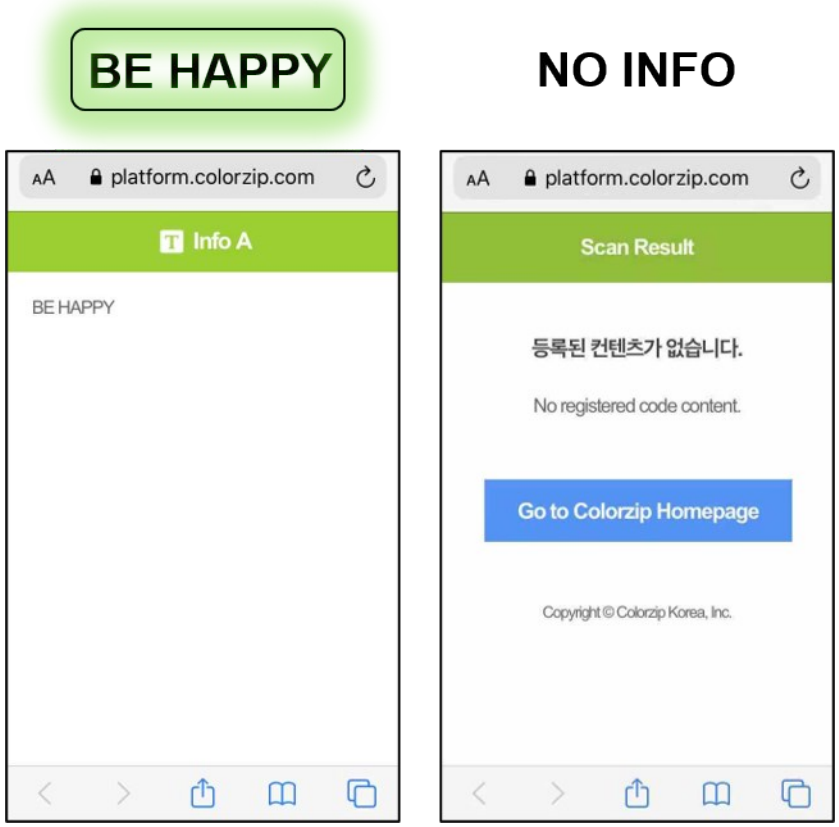


Figure S12. The scanning results of fluorescent gels by smart phone with "COLORCODE" APP.

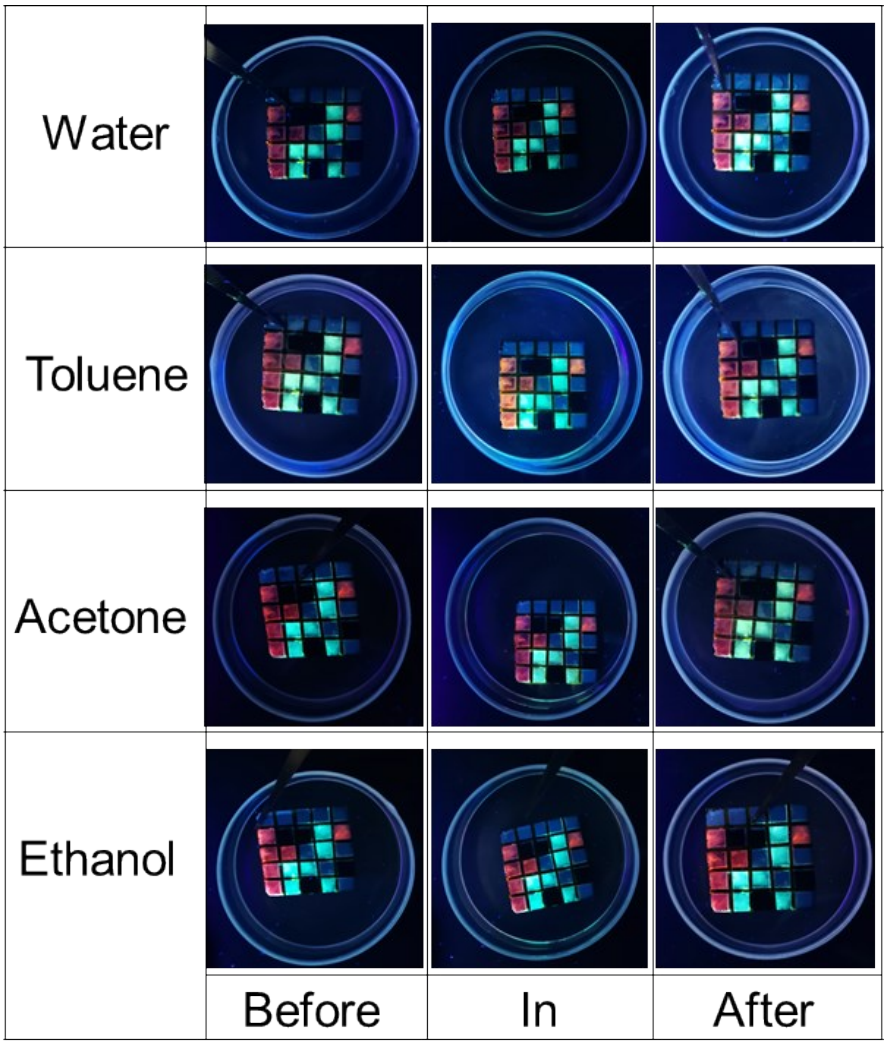


Figure S13. The fluorescent emission change of the gels after being soaked in water, toluene, acetone, and ethanol, respectively.

Table S1: Amount of pPFPA and 1, 3- propyldiamine for fabrication of pPFPA gel with different degree of crosslinking.

Crosslinking degree	0%	5%	10%	15%	25%	30%
pPFPA (600mg/mL in toluene)（μL）	100	100	100	100	100	100
2% 1,3-propyldiamine in toluene（μL）	0	26	52	78	130	156

The solution concentration of pPFPA in the table is 600mg/ mL, and the concentration of 1,3-propyldiamine is 0.02μL/μL.

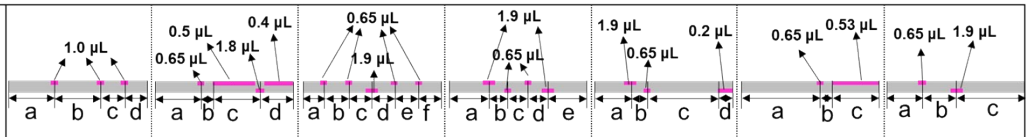
Table S2. Swelling ratio in linear scale of pPFPA gel in different solvents.

Solvent	Acetone	$CHCl_3$	CH_2Cl_2	Toluene	Acetic acetate	Hexane	H_2O
R_{swell}	37%	35.5%	19.5%	24.2%	32%	0.2%	−0.1%

Table S3. Swelling ratio in linear scale of Gel 3 in different solvents.

Solvent	Acetone	Ethanol	Acetic acetate	Hexane	H_2O
R_{swell}	18%	1.8%	28%	2.3%	−0.5%

Table S4. The dimension of treated spots and lines in the codes (side view), and ink volumes applied to each treated site.

Code	
	a = b = 9.3 c = d = 4.6 Unit : mm
	a = 10 b = 2 c = 9 d = 7
	a = b = c = d = e = 5.6
	a = e = 8 b = c = d = 4
	a = 7.4 b = 3.2 c = 14 d = 3.4
	a = 16 b = 2 c = 12
	a = 7 b = 7 c = 14
Data	**A** / **B** / **E** / **H** / **J** / **P** / **Y**

Gel dimensions: L = 28 mm, W = 1 mm, t = 0.1 mm.