Preparation of a white-light-emitting fluorescent supramolecular polymer gel with a single chromophore and use of the gel to fabricate a protected quick response code

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Electronic Supplementary Information

1. Materials and methods

Compounds **3**[S1] and **4**[S2] were prepared according to literature procedures. Solvents were either employed as purchased or dried according to procedures described in the literature. ^{1}H NMR spectra were collected on a Bruker Avance DMX-400 spectrometer with internal standard TMS. Molecular weight distributions were measured on a conventional gel permeation chromatography (GPC) system equipped with a Waters 1525 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (HR1, HR2 and HR4, 7.8 mm × 300 mm). GPC measurements were carried out at 35 °C using DMF as the solvent with a flow rate of 1.0 mL/min. The system was calibrated with linear polystyrene standards. SEM investigations were carried out on a JEOL 6390LV instrument. The fluorescence spectra were recorded on a Perkin Elmer LS55 fluorescence spectrophotometer.

*2. Synthesis of polymer **1***

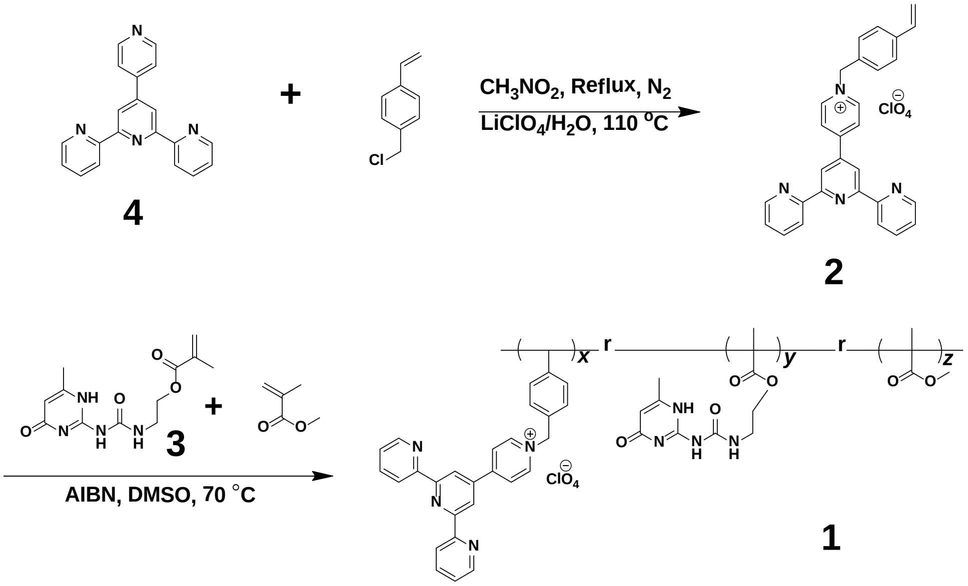

Fig. S1. Synthetic route to polymer **1**.

Compound **2**:

A mixture of **4**^{S2} (350 mg, 1.13 mmol) and 1-(chloromethyl)-4-ethenylbenzene (258 mg, 1.69 mmol) were added to CH_3NO_2 (50.0 mL) under the protection of N_2 and the solution was stirred at 103 °C for 24 hours. After addition of excess diethyl ether to the reaction system, the yellow gray solid powder was filtered and well washed with diethyl ether. Then, the yellow gray solid was dissolved in water and $LiClO_4$ was added into this solution to form a white solid powder (320 mg, 53%). Mp: 179.1–181.2 °C. The ^{1}H NMR spectrum of compound **2** is shown in Fig. S2. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm): 9.36 (d, J = 6.8 Hz, 2H), 8.91 (s, 2H), 8.86–8.77 (m, 4H), 8.72 (d, J = 7.9 Hz, 2H), 8.09 (m, 3H), 7.59 (s, 6H), 6.77 (m, 2H), 5.93 (s, 3H), 5.34 (d, J = 11.1 Hz, 1H). The ^{13}C NMR spectrum of **3** is shown in Fig. S3. ^{13}C NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm): 156.36, 154.22, 153.23, 149.44, 145.31, 143.93, 138.14, 137.73, 135.80, 133.73, 129.16, 126.86, 126.46, 125.04, 122.04–120.08, 118.88, 115.73, 62.67. LRESIMS of **2** is shown in Fig. S4: m/z 427.3 $[M - ClO_4]^+$ (100%). HRESIMS: m/z calcd for $[M - ClO_4]^+$ $C_{29}H_{23}N_4^+$, 427.1917; found 427.1919; error 0.5 ppm.

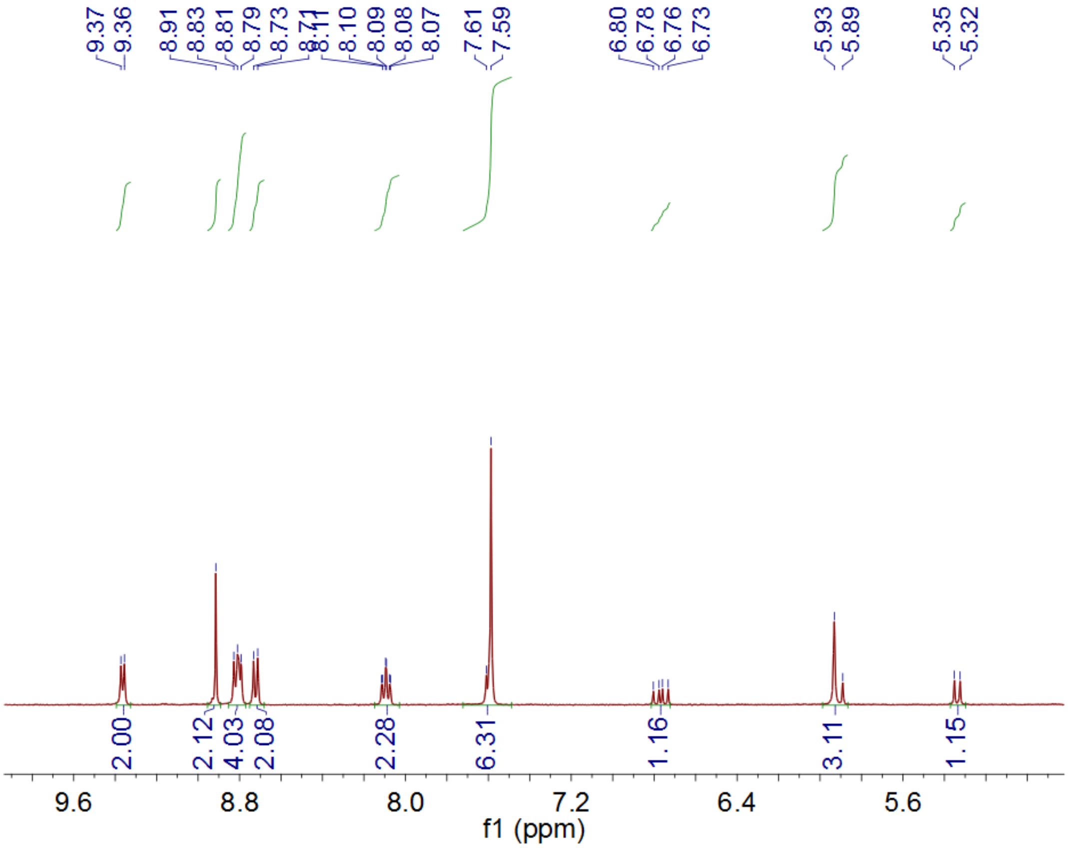

Fig. S2. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of compound **2**.

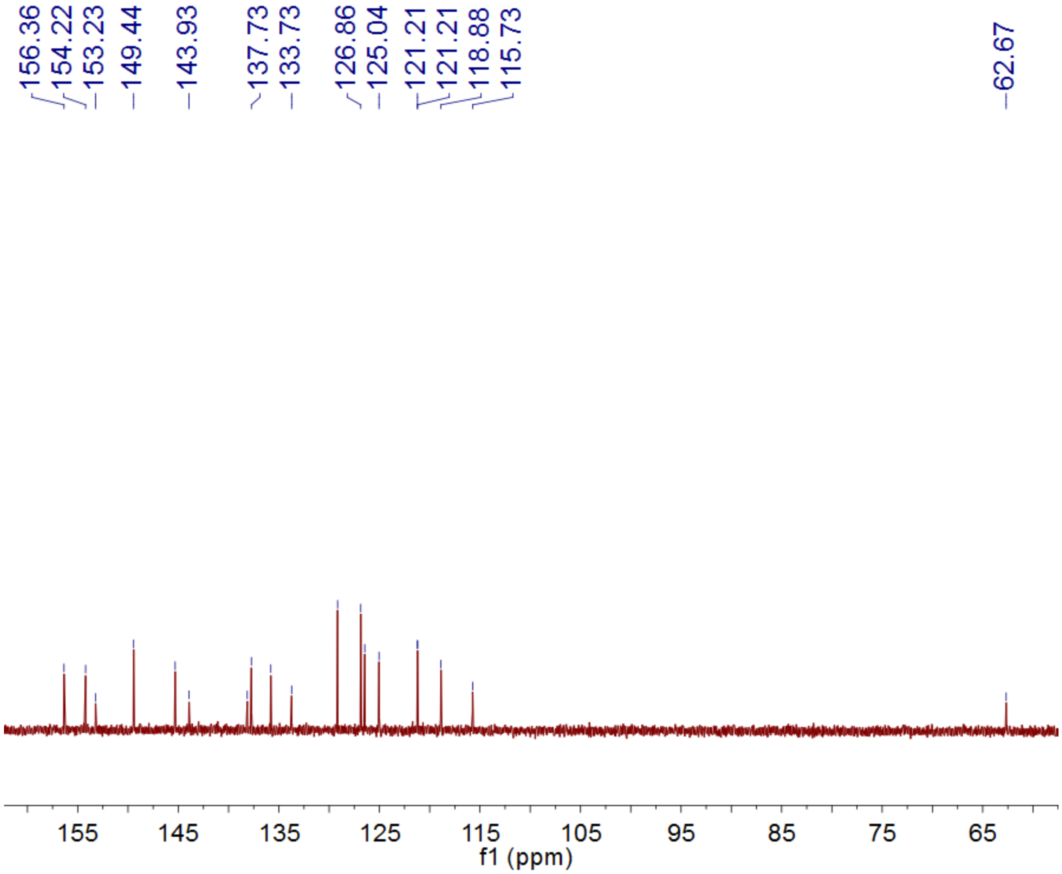

Fig. S3. ^{13}C NMR spectrum (400 MHz, DMSO-d_6, 298 K) of compound **2**.

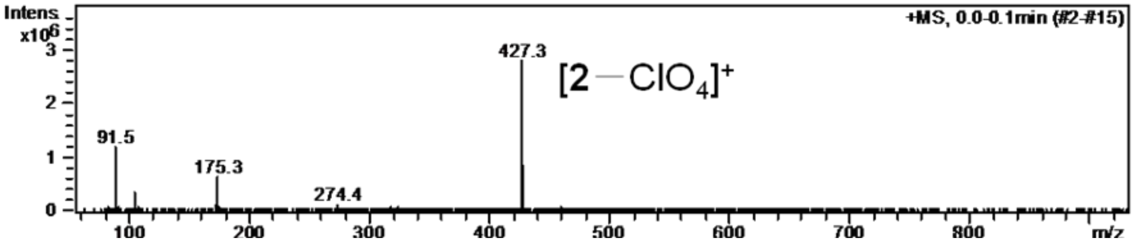

Fig. S4. LRESI mass spectrum of compound **2**.

Polymer **1**:

Polymer **1** was prepared from monomers **2**, **3**,[S1] and methyl methacrylate by free radical copolymerization. A mixture of compound **2** (200 mg, 0.380 mmol), compound **3** (180 mg, 0.500 mmol), and methyl methacrylate (1.72 mL, 16.0 mmol) in 50 mL of DMSO was stirred at room temperature. A stream of argon (Ar) was bubbled through for 30 min. In one portion was added 5.00 mg (0.0300 mmol) of azobisisobutyronitrile (AIBN) and the mixture was stirred for 10 min, sealed with a rubber septum, and heated at 70 °C for 24 h. The polymerization was quenched by rapid freezing in liquid nitrogen. The solution was dropped into 500 mL of diethyl ether, and the precipitated solid was collected by vacuum filtration. This process was repeated three times and the collected polymer was dried in vacuo (1.28 g, 65%). ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ (ppm): 12.93 (s, N*H*), 11.93 (s, N*H*), 10.45 (s, N*H*), 9.03 (s, C*H*), 8.76 (s, C*H*), 8.63 (s, C*H*), 8.42 (s, C*H*), 8.38 (s, C*H*), 7.83 (s, C*H*), 7.43 (s, C*H*), 7.41 (s, C*H*), 7.13 (s, C*H*), 5.91–5.80 (m, CH_2), 5.32 (s, C*H*), 4.04–3.75 (m, CH_2), 3.57–3.37 (m, OCH_3), 2.42–0.80 (m, CH_3).

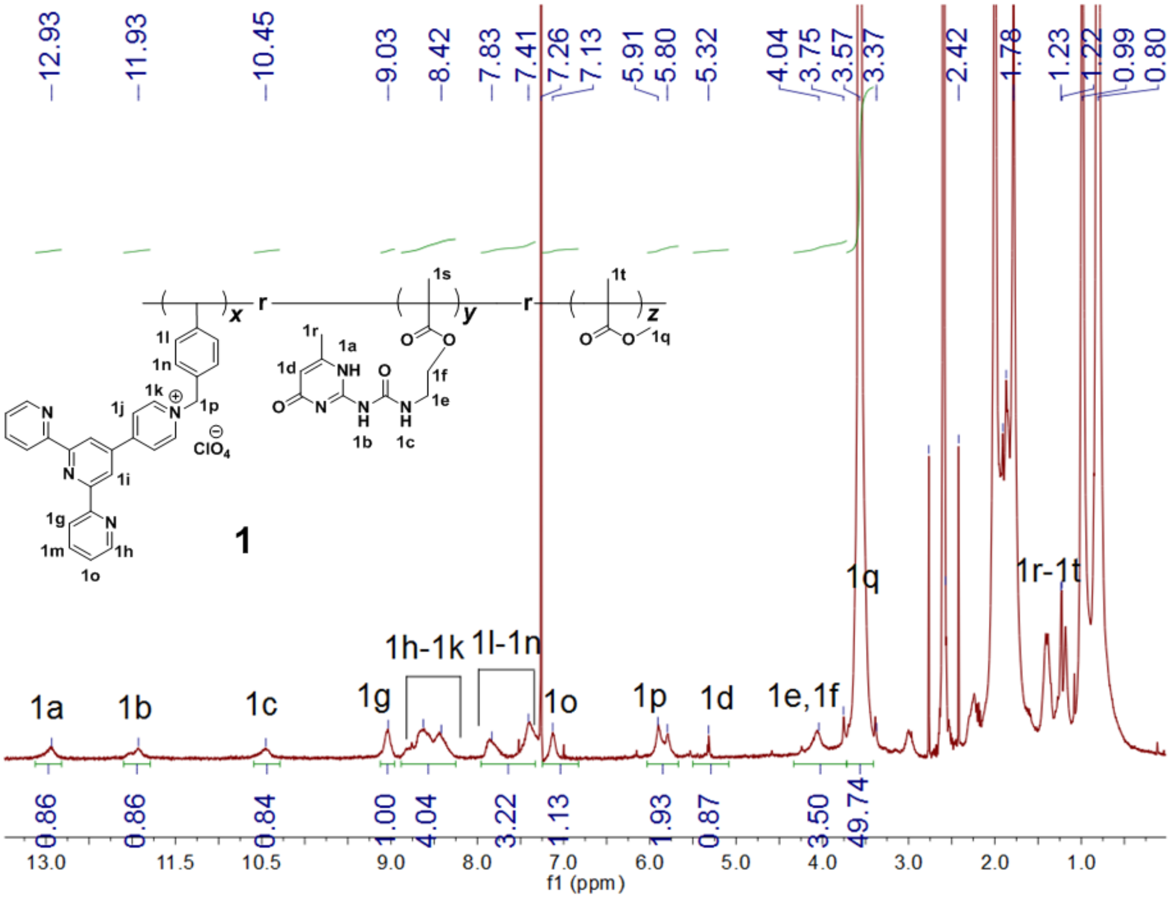

Fig. S5. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of polymer **1**.

The ratio of *x*/*y*/*z* was (1.34)/(1)/(59.34/3), namely 1.34/1/19.78, for polymer **1**, as calculated based on the integrations of the peaks of H_{1g}, H_{1d}, and H_{1q}. Because of the intramolecular and intermolecular hydrogen bonding, the integration of the peak of H_{1a}, H_{1b}, or H_{1c} is not equal to that of H_{1d}.

Table S1. GPC analysis of polymer **1** using conventional calculations with polystyrene as the standard and DMF as the solvent.

M_n	M_w	M_p	M_z	PDI
3.6×10^4	6.3×10^4	6.5×10^4	9.5×10^4	1.78

According to M_n and the ratio of $x/y/z$, the values of x, y, and z were calculated to be 16.1, 12.0 and 237.4, respectively.

*3. Emission spectra of monomer **2** dissolved in chloroform under various excitation wavelengths*

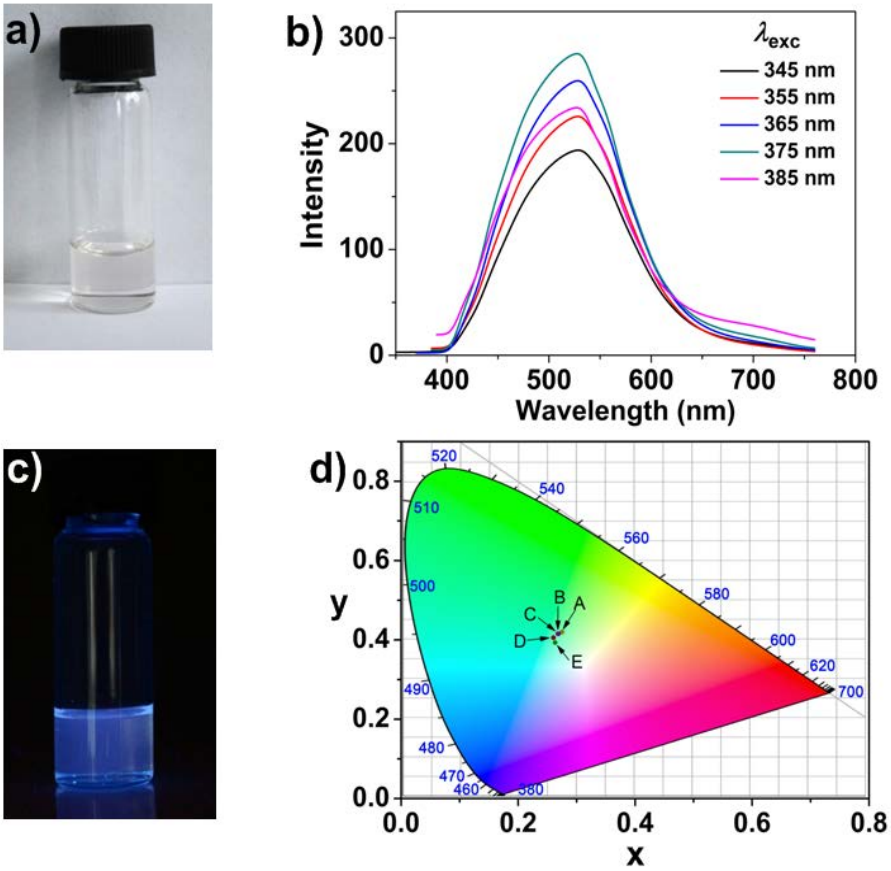

Fig. S6. (a) Photo of 1.0 mM monomer **2** dissolved in chloroform under natural light. (b) Fluorescence emission spectra of 1.0 mM monomer **2** under different excitation wavelengths. (c) Photo of monomer **2** dissolved in chloroform under 365 nm UV light. (d) CIE chromaticity coordinates of monomer **2** under different excitation wavelengths: A, (0.2753, 0.4198) at 345 nm; B, (0.2690, 0.2155) at 355 nm; C, (0.2680, 0.4156) at 365 nm; D, (0.2604, 0.4057) at 375 nm; E, (0.2633, 0.3933) at 385 nm.

4. Spectra with normalized intensity of gel ***G***

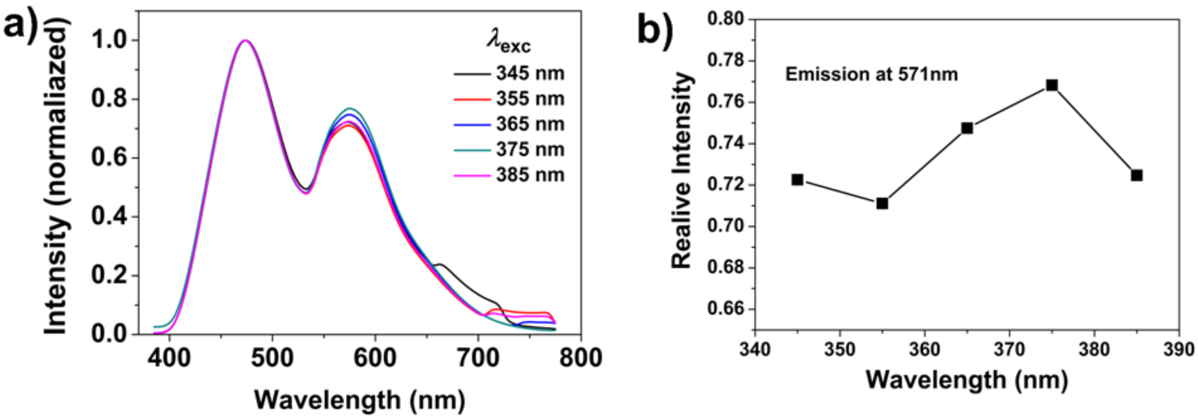

Fig. S7. (a) Spectra with normalized intensity of the high-energy emission at λ_{max} = 474 nm of gel. (b) The trend in the relative intensity of the low-energy emission at λ_{max} = 571 nm versus excitation wavelength of gel **G**.

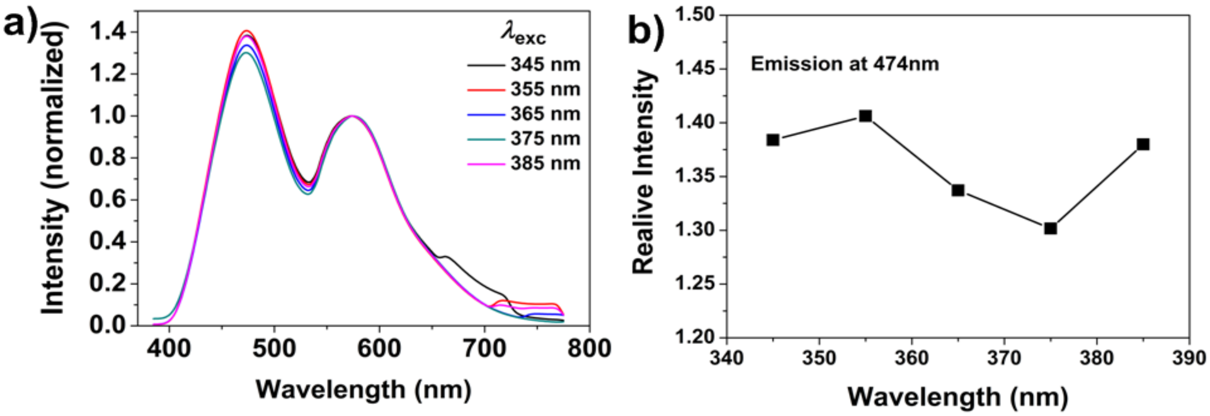

Fig. S8. (a) Spectra with normalized intensity of the low-energy emission at λ_{max} = 571 nm of gel **G**. (b) The trend in the relative intensity of the high-energy emission with λ_{max} = 474 nm versus excitation wavelength of gel **G**.

References:

S1. K. Yamauchi, J. R. Lizotte and T. E. Long, *Macromolecules*, 2003, **36**, 1083–1088.

S2. J. Wang and G. S. Hanan, *Synlett*, 2005, **8**, 1251–1254.