Supporting Information

Dynamic Encryption Systems Enabled by Novel α-Cyanostilbene-Based AIE-Active Liquid Crystalline Polymers with Self-Assembling Saccharide Units

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1. Experimental section

1.1 Materials

Methyl-α-D-glucopyranoside, terephthalaldehyde, 4-hydroxyphenylacetonitrile, methacrylic acid, 1,6-dibromohexane, azobisisobutyronitrile (AIBN), concentrated sulfuric acid, anhydrous potassium carbonate, sodium bicarbonate, potassium bicarbonate, magnesium sulfate anhydrous, acetone, ethanol, sodium methoxide (CH_3ONa), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), n, n-dimethylmethanamide (DMF), ethyl acetate, hexane and petroleum ether, were purchased from TCI America™, Sigma Aldrich, Anachemia, and Fisher Scientific, and were used directly without further purification.

1.2 Measurements and Characterization

^{1}H NMR spectra of the synthesized chemicals and polymer were recorded on a Bruker Avance-III 300 NMR apparatus at room temperature using DMSO-d_6 as the solvent. X-ray diffraction (XRD) profiles of monomer MM$_6$CN-SachCHO and polymer PMM$_6$CN-SachCHO were recorded on a Bruker AXS Nanostar system equipped with a Microfocus Copper anode at 45 kV/0.65 mA, Montel OPTICS. LC textures of the samples were examined using a POM (Olympus Corporation, BX51-P) equipped with a hot stage (Linkam THMS600). Thermal transition temperatures of all samples were measured using a differential scanning calorimeter (DSC TAQ200) with about 8 mg of the sample under a nitrogen atmosphere (flow rate of 50 mL min^{-1}) at a heating and cooling rate of 10 °C min^{-1}. The UV absorption spectra were measured with a UV–vis spectrometer (Cary 50 Bio, Agilent). Photoluminescence spectra were collected with a fluorescence spectrometer (Cary Eclipse, Varian, Inc) using an excitation wavelength of 365 nm. The solid-state fluorescence quantum yield was measured using a UV-VIS spectrophotometer (Fluorolog FL3-22, Horiba) equipped with a 450 W Xenon lamp, an R928 PMT detector, a double monochromator for both excitation and emission, and a Quanta-phi integrating sphere, enabling precise quantum yield measurements in the solid state. The molecular weight and polydispersity of the polymer were determined by gel chromatography (GPC) using a 1290 Infinity II GPC/SEC System with DMF at 30°C as the mobile phase at a flow rate of 0.4 mL/min. The reversible fluorescence photo-responsiveness was studied by using an OmniCure@Series 1000 UV-vis lamp with a 356 nm filter (20 mW cm^{-2}) and a photochemical reactor with 8 UV lamps (model RPR-100 from Rayonet, 265 nm, 12.6 mW cm^{-2}).

1.3 Synthesis of monomer and polymer

Synthesis of SachCHO

SachCHO was synthesized using a reported method,[1] its ^{1}H NMR spectra was shown in Fig. S1. ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.03 (s, 1H), 7.93 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 5.69 (s, 1H), 5.22 (d, J = 5.0 Hz, 1H), 5.03 (d, J = 6.7 Hz, 1H), 4.64 (d, J = 3.5 Hz, 1H), 4.20 (dd, J = 9.8, 4.6 Hz, 1H), 3.73 (t, J = 10.1 Hz, 1H), 3.59 (td, J = 9.4, 4.9 Hz, 2H), 3.46 – 3.34 (m, 2H), 3.32 (s, 3H).

Synthesis of 2-(4-((6-bromohexyl)oxy)phenyl)acetonitrile

2-(4-((6-bromohexyl)oxy)phenyl)acetonitrile was produced and purified according to an existing procedure with minor modifications as described here.[2] 4-hydroxyphenylacetonitrile (10.0 g, 75.1 mmol), 1,6-dibromohexane (21.8 g, 90.1 mmol), and 120 mL acetone were placed into a 250 mL boiling flask. When 4-hydroxyphenylacetonitrile was dissolved completely, anhydrous potassium carbonate (15.6 g, 112.7 mmol) was added. The mixtures were stirred at 60 °C for 10 h. After that, the mixtures were filtered to remove the inorganic salt. The filtered liquid was collected, and acetone was removed via the rotary evaporation to obtain a crude product. After column chromatographic separation (graded elution: 0 to 30% EtOAc to hexane, increase polarity in increments of 5% per 100 ml of eluent used), the pure product was obtained with a yield of 75%. ^{1}H NMR (δ, ppm, $CDCl_3$): 7.21–7.26 (d, 2H, Ph–H); 6.77–6.93 (d, 2H, Ph–H); 3.94–3.97 (m, 2H, –OCH_2–); 3.64 (s, 2H, –CH_2–CN); 3.41–3.45 (m, 2H, –CH_2–Br); 1.78–1.92 (m, 4H, –CH_2–); 1.50–1.55 (m, 4H, –CH_2–).

Synthesis of BrM$_6$CN-SachCHO

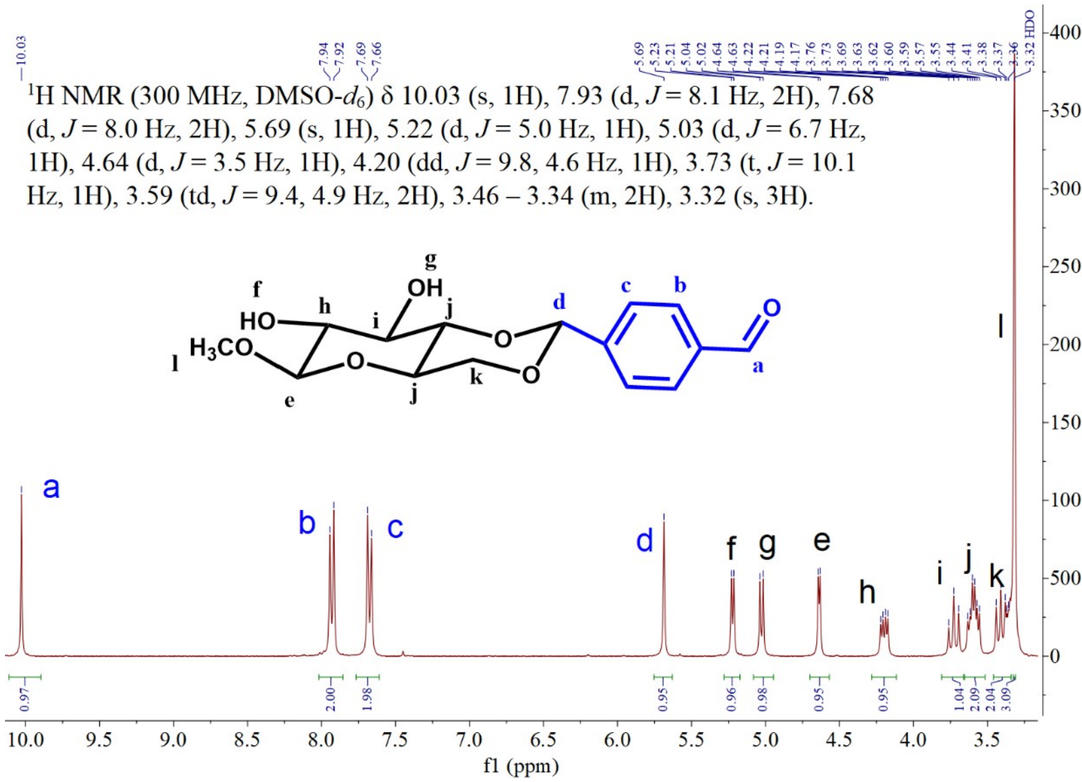
SachCHO (2.126 g, 6.85 mmol) and 120 mL ethanol were placed into a 250 mL boiling flask. When SachCHO was dissolved in ethanol completely, CH_3ONa (0.375 g, 6.85 mmol) was added to the above mixture. Then 2-(4-((6 bromohexyl)oxy)phenyl)acetonitrile (2.0 g, 6.75 mmol) was added. The mixtures were stirred at 25 °C for 6 h. During the reaction, a large number of yellow precipitations were formed gradually. The final reaction mixtures were filtered. The solid products were collected and washed twice with ethanol to obtain the yellow-green solid product. The yield was 50 %. The ^{1}H NMR spectrum was shown in Fig. S2. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.02 – 7.83 (m, 3H), 7.72 (d, J = 8.7 Hz, 2H), 7.60 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 8.8 Hz, 2H), 5.66 (s, 1H), 5.19 (s, 2H), 4.66 (d, J = 3.5 Hz, 1H), 4.22 (dd, J = 9.7, 4.5 Hz, 1H), 4.05 (t, J = 6.4 Hz, 2H), 3.74 (t, J = 10.1 Hz, 1H), 3.67 – 3.52 (m, 4H), 3.34 (s, 4H), 2.02 – 1.62 (m, 4H), 1.47 (s, 4H).

Synthesis of MM$_6$CN-SachCHO

The mixtures of BrM$_6$CN-SachCHO (6.94 g, 11.8 mmol, 1 equiv), potassium bicarbonate (100.115 g/mol, 5.9 g, 59.0 mmol, 5 equiv), methacrylic acid (80.09 g/mol, 3.1 g, 35.4 mmol) and 100 mL DMF were placed into a 250 mL boiling flask. The mixtures were reacted at 100 °C for 24 h. After that, the mixtures were slowly added into cold water. The solid crude products were collected via the filtration method. The yellow green solid product was obtained after purification with silica chromatography. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.94 – 7.85 (m, 3H), 7.75 – 7.63 (m, 2H), 7.58 (d, J = 8.1 Hz, 2H), 7.15 – 6.97 (m, 2H), 6.01 (s, 1H, = CH_2), 5.66 (t, J = 1.7 Hz, 1H, = CH_2), 5.64 (s, 1H), 4.64 (d, J = 3.7 Hz, 1H), 4.19 (dd, J = 9.8, 4.6 Hz, 1H), 4.10 (t, J = 6.5 Hz, 2H, -OCH_2-), 4.03 (t, J = 6.4 Hz, 2H), 3.72 (t, J = 10.1 Hz, 1H), 3.60 (t, J = 9.3 Hz, 2H), 3.32 (s, 5H), 1.87 (t, J = 1.3 Hz, 3H,-CH_3), 1.69 (dt, J = 28.1, 5.6 Hz, 4H), 1.43 (s, 4H) (Fig. S3).

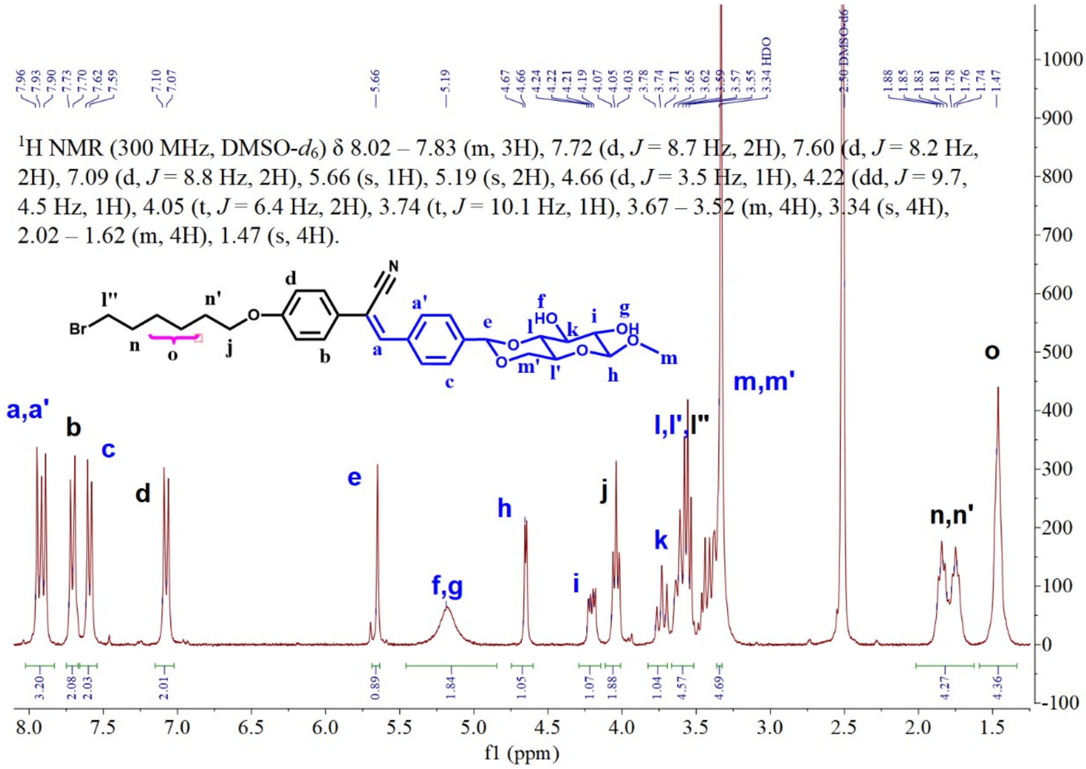
Preparation of SCLLCP containing saccharide units (PMM$_6$CN-SachCHO)

MM$_6$CN-SachCHO (1.0 g, 1.68 mmol), initiator azobisisobutyronitrile (3.96 mg, 0.024 mmol), and solvent-refined DMF (2.33 g) were placed into a glass tube. The glass tube was frozen by liquid nitrogen and was then vacuumed for 3 min to remove O_2. After that, N_2 was injected. After three repetitions, the polymerization glass tube was sealed and the polymerization reaction was conducted at 75 °C. 3 h later, the tube was opened. Then, polymerization mixtures were diluted with refined DMF and were added dropwise into acetone to remove monomers. Polymer PMM$_6$CN-SachCHO was then obtained via the vacuum filtration method. The result of ^{1}H NMR is shown in Fig. S4.



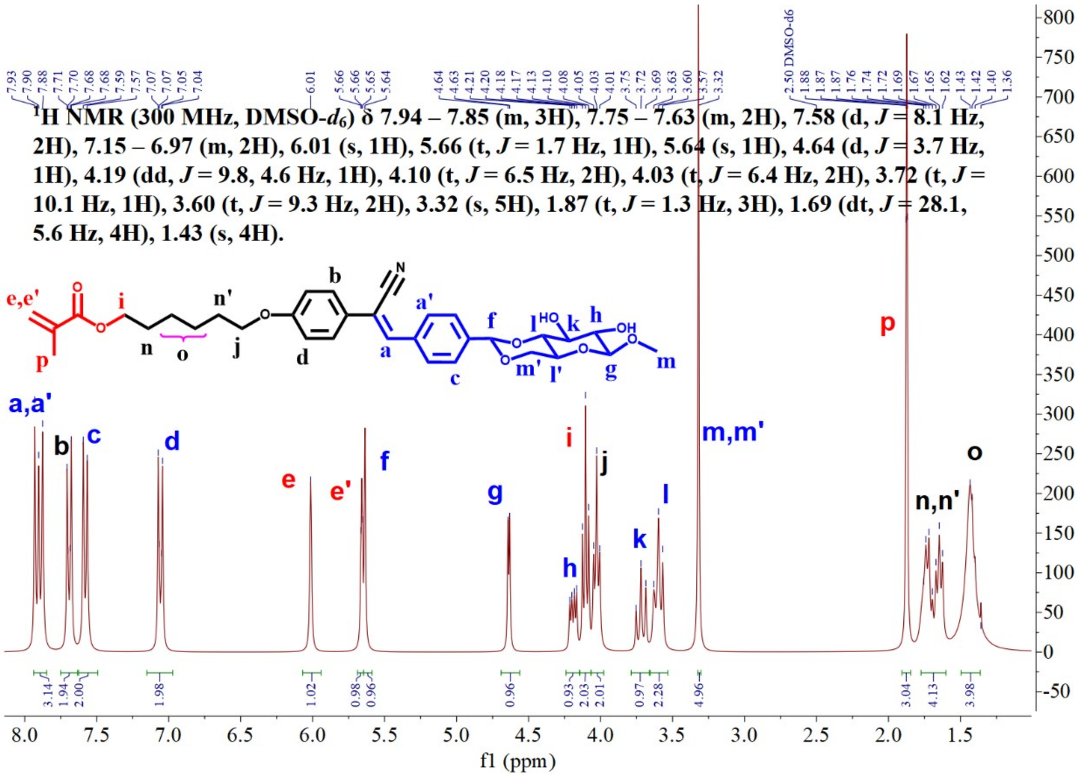
^{1}H NMR (300 MHz, DMSO-d_6) δ 10.03 (s, 1H), 7.93 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 5.69 (s, 1H), 5.22 (d, J = 5.0 Hz, 1H), 5.03 (d, J = 6.7 Hz, 1H), 4.64 (d, J = 3.5 Hz, 1H), 4.20 (dd, J = 9.8, 4.6 Hz, 1H), 3.73 (t, J = 10.1 Hz, 1H), 3.59 (td, J = 9.4, 4.9 Hz, 2H), 3.46 – 3.34 (m, 2H), 3.32 (s, 3H).

Fig. S1. ^{1}H NMR spectrum of SachCHO.



^{1}H NMR (300 MHz, DMSO-d_6) δ 8.02 – 7.83 (m, 3H), 7.72 (d, J = 8.7 Hz, 2H), 7.60 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 8.8 Hz, 2H), 5.66 (s, 1H), 5.19 (s, 2H), 4.66 (d, J = 3.5 Hz, 1H), 4.22 (dd, J = 9.7, 4.5 Hz, 1H), 4.05 (t, J = 6.4 Hz, 2H), 3.74 (t, J = 10.1 Hz, 1H), 3.67 – 3.52 (m, 4H), 3.34 (s, 4H), 2.02 – 1.62 (m, 4H), 1.47 (s, 4H).

Fig. S2. ^{1}H NMR spectrum of BrM$_6$CN-SachCHO.



^{1}H NMR (300 MHz, DMSO-d_6) δ 7.94 – 7.85 (m, 3H), 7.75 – 7.63 (m, 2H), 7.58 (d, J = 8.1 Hz, 2H), 7.15 – 6.97 (m, 2H), 6.01 (s, 1H), 5.66 (t, J = 1.7 Hz, 1H), 5.64 (s, 1H), 4.64 (d, J = 3.7 Hz, 1H), 4.19 (dd, J = 9.8, 4.6 Hz, 1H), 4.10 (t, J = 6.5 Hz, 2H), 4.03 (t, J = 6.4 Hz, 2H), 3.72 (t, J = 10.1 Hz, 1H), 3.60 (t, J = 9.3 Hz, 2H), 3.32 (s, 5H), 1.87 (t, J = 1.3 Hz, 3H), 1.69 (dt, J = 28.1, 5.6 Hz, 4H), 1.43 (s, 4H).

Fig. S3. ^{1}H NMR spectrum of MM$_6$CN-SachCHO.

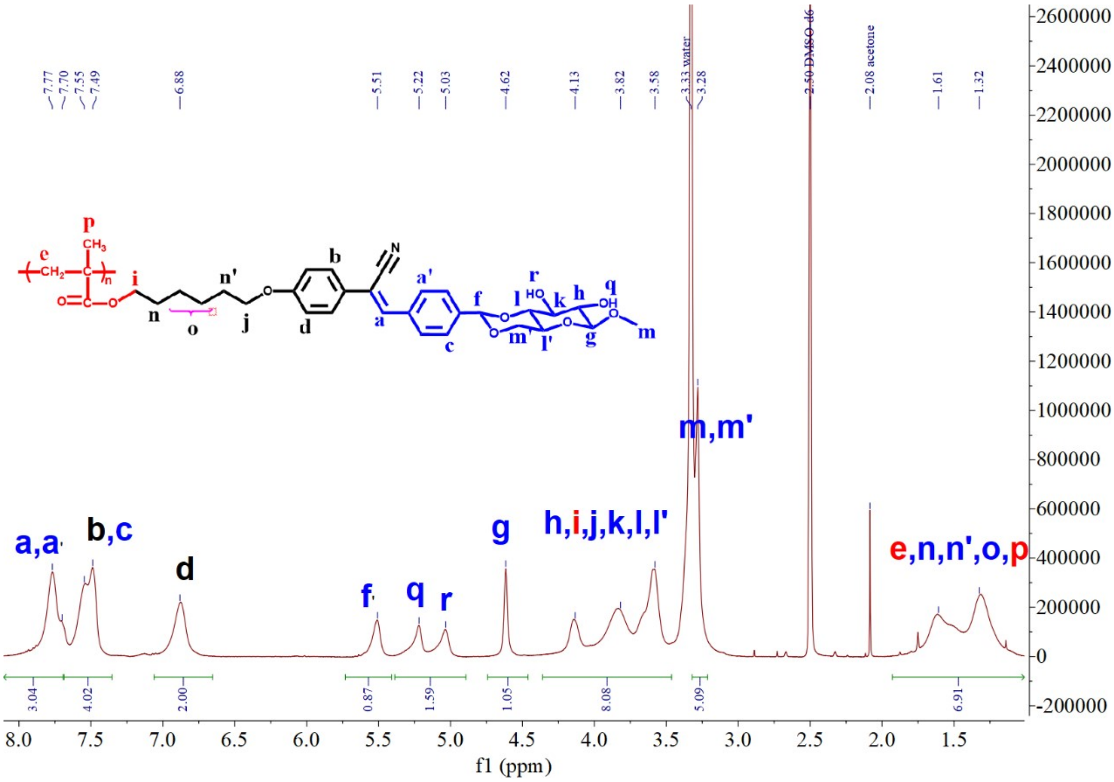


Fig. S4. ^{1}H NMR spectrum of PMM$_6$CN-SachCHO.

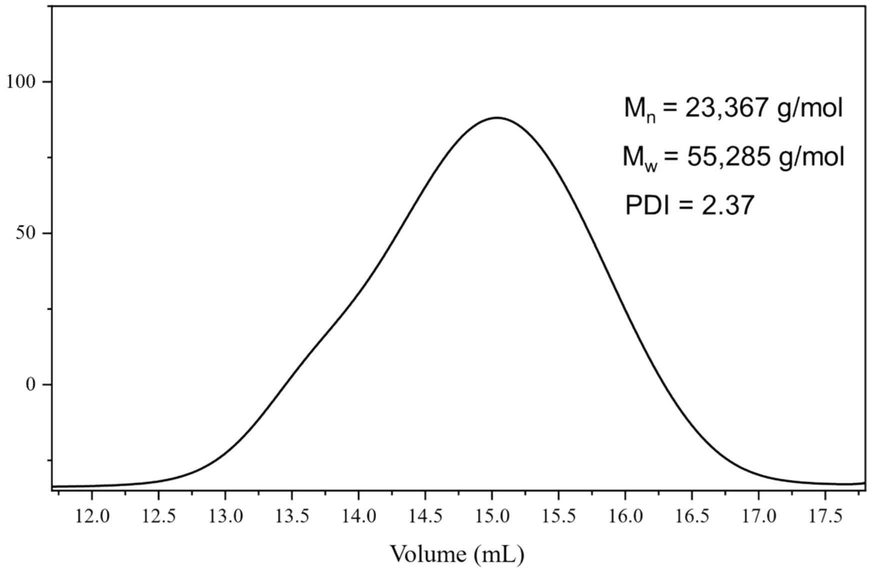


Fig. S5. GPC result of PMM$_6$CN-SachCHO.

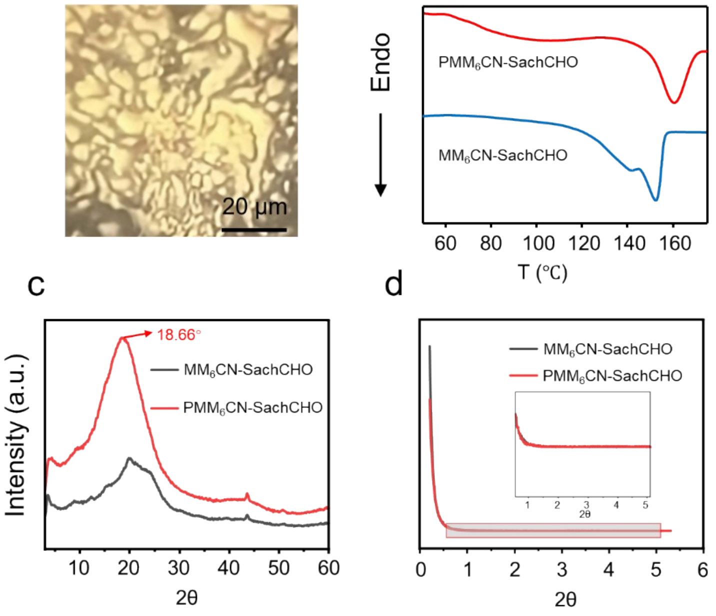


Fig. S6. (a) POM image of PMM$_6$CN-SachCHO captured at 110 °C after cooling from 165 °C. (b) DSC curves of PMM$_6$CN-SachCHO and MM$_6$CN-SachCHO recorded on heating. (c) 1D WAXS patterns of PMM$_6$CN-SachCHO and MM$_6$CN-SachCHO. (d) 1D SAXS diffractograms of PMM$_6$CN-SachCHO and MM$_6$CN-SachCHO, the inset shows an enlarged picture.

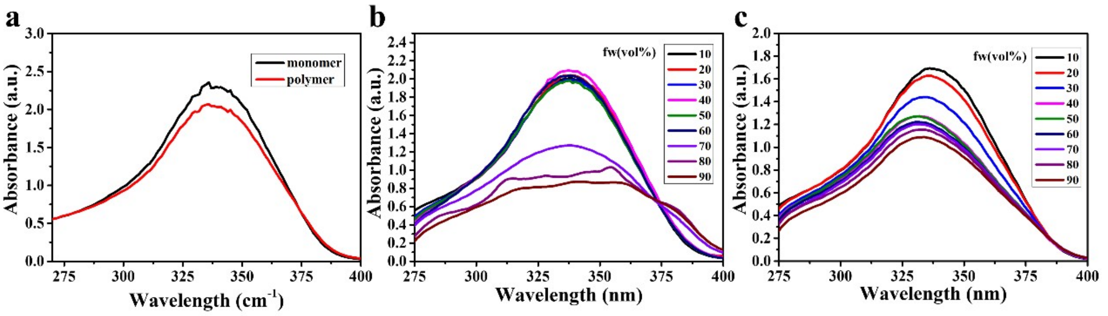


Fig. S7. (a) UV absorption spectra of monomer MM_6CN-SachCHO and polymer PMM_6CN-SachCHO in DMF; (b) and (c) UV absorption spectra of MM_6CN-SachCHO and PMM_6CN-SachCHO in DMF/H_2O mixtures; concentration = 0.05 g/L.

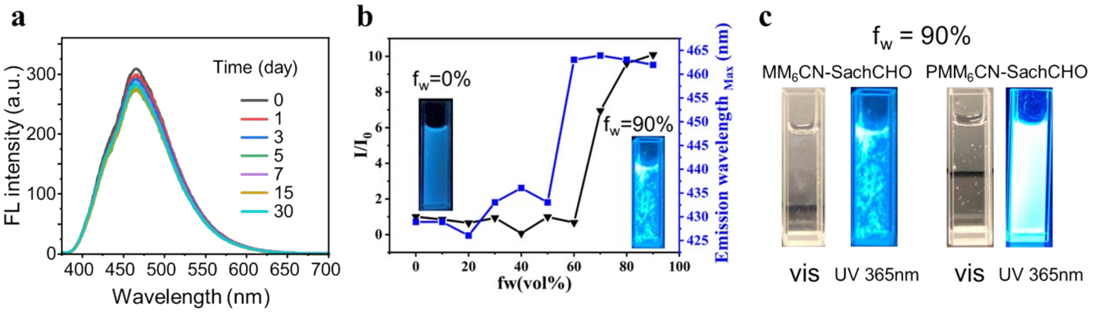


Fig. S8. (a) The fluorescence intensity changes of the PMM_6CN-SachCHO DMF/H_2O mixture with a 90% water fraction over 30 days. (b) Relationship curve of I/I_0 (maximum emission intensity) versus water volume fraction for MM_6CN-SachCHO. (c) Photographs of MM_6CN-SachCHO and PMM_6CN-SachCHO with 90% water volume under visible light and 365 nm UV light. Concentration = 0.05 g/L; excitation wavelength = 365 nm.

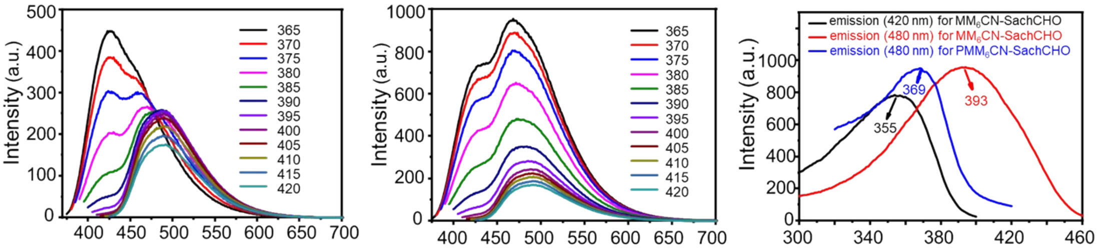


Fig. S9. (a) and (b) Excitation-dependent fluorescence of MM_6CN-SachCHO and PMM_6CN-SachCHO in DMF. (c) Excitation spectra of MM_6CN-SachCHO and PMM_6CN-SachCHO in DMF.

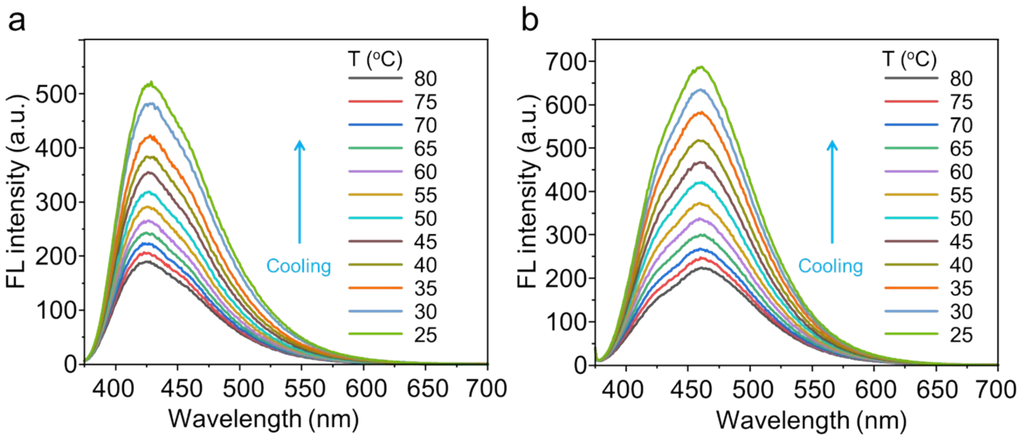


Fig. S10. Thermoresponsive behavior of (a) PMM$_6$CN-SachCHO in DMF and (b) a DMF/H$_2$O mixture (fw=90%) measured during the cooling process.

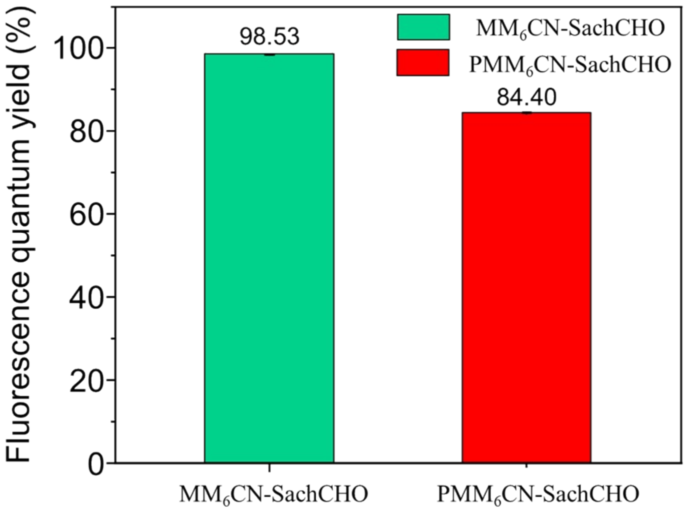


Fig. S11. Solid-state fluorescence quantum yield of MM6CN-SachCHO and PMM6CN-SachCHO. The excitation wavelength was 365 nm.

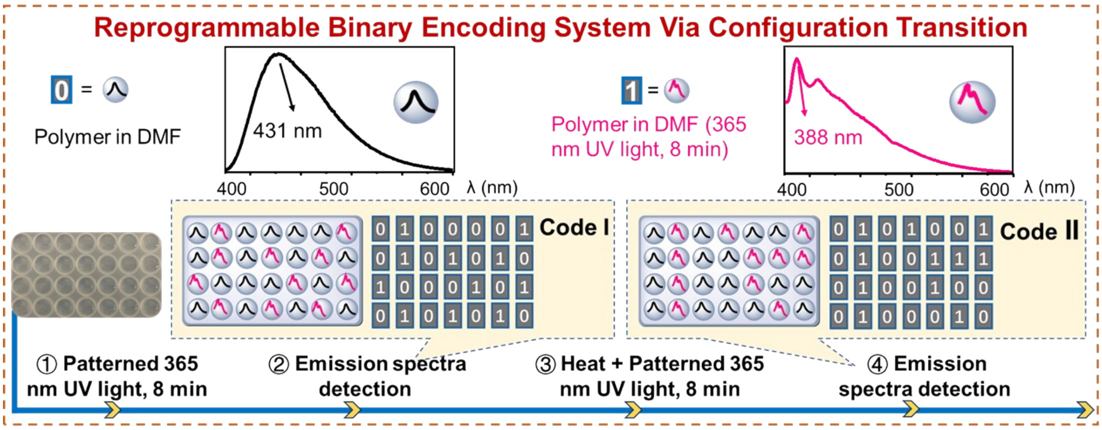


Fig. S12. Reprogramming the binary encoding system using reversible fluorescence photo-responsiveness.

References

1. Q. Chen, Y. Lv, D. Zhang, G. Zhang, C. Liu and D. Zhu, *Langmuir*, 2010, **26**, 3165-3168.
2. Y. Yuan, L. He, J. Li and H. Zhang, *Polymer Chemistry*, 2019, **10**, 2706-2715.