Supporting Information

Stimuli-Responsive Luminescent Supramolecular Polymers Based on Hydrogen Bonding: Molecular Fabrication, Phase Structure, and Controllable-Rewritable Behavior

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1. Materials and Measurements.

4-Bromobenzophenone (98%, Alfa Aesar (China) Chemical Co., Ltd.), 4, 4'dihydroxybenzophenone (98%, TCI (Shanghai) Development Co., Ltd.), 4pyridinylboronic acid (98%, Energy Chemical), titanium tetrachloride (99%, GL45Seal, Energy Chemical), bromobutane (98%, Energy Chemical), zinc (98%, Energy Chemical), tetrakis(triphenylphosphine)palladium(0) (99%, Pd 9% min, Energy Chemical), Poly(vinyl alcohol) 124 (PVA, GR, Sinopharm Chemical Reagent Co., Ltd.) dimethyl sulfoxide (DMSO, AR, Tianjin Kemiou Reagent chemical co), potassium carbonate (K₂CO₃, AR, Tianjin Kemiou Reagent chemical co), Tetrahydrofuran (THF, AR, Tianjin Kemiou Reagent chemical co).

¹H and ¹³C NMR spectra was obtained from a Bruker ARX 400 MHz nuclear magnetic resonance spectrometer. CDCl₃ or DMSO as the solvent and tetramethylsilane (TMS) as the internal standard. Matrix assisted laser desorption ionization tandem time-of-flight mass spectrometry (MALDI-TOF MS) was conducted on a Bruker Daltonics BIFLEX III MALDI-TOF analyzer. Fourier-transform infrared spectroscopy (FT-IR) experiments were performed by a PE Spectrum One FT-IR spectrometer in KBr pellets. UV-vis absorption spectra were recorded on Cary 60, and a flashing xenon lamp as the light source. Photo-luminescence (PL) spectra were performed by using an F-4600 spectrofluorometer. The quantum yields (Φ_F) were determined by a Nanolog FL3-2iHR infrared fluorescence spectrometer by using the integrating sphere, with a R928 photomultiplier as the detector.

Thermogravimetric analysis (TGA) results were recorded on an STD Q600 instrument under a nitrogen atmosphere with a heating rate of 20 °C/min. Polarized optical microscopy (POM, Leica DM-LM-P) was employed to explore the sample textures, with a Mettler FP82HT heating plate. Differential scanning calorimetry (DSC) experiments were performed on a by a TA-Q10 calorimeter in nitrogen atmosphere with a rate of 10 °C/min. One-dimensional wide-angle X-ray diffraction (1D WAXD) powder patterns were recorded on a Bruker D8 Advance diffractometer. The horizontal

placement of samples and reflecting peaks on the stage were calibrated with silver behenate.

2. Synthesis of Supramolecular Polymers PVA(PTPEC₄)_x.



 $PVA(PTPEC_4)_x x = 0.2, 0.4, 0.6, 0.8, 1.0$

Scheme S1. Synthetic route the supramolecular polymers $PVA(PTPEC_4)_x$.

2.1 Synthesis of (4,4'-Dibutanoxy tetraphenylethylene)-1-pyridine (PTPEC₄).

The acceptor PTPEC₄ was synthesized according to our previous work.

¹H NMR (CDCl₃) δ (ppm): 8.61 (d, 2H, pyridine-H), 7.48 (d, 2H, pyridine-H), 7.42 (m, 2H, Ar-H), 7.14 (m, 5H, Ar-H), 7.05 (m, 2H, Ar-H), 6.95 (m, 4H, Ar-H), 6.63 (m, 4H, Ar-H), 3.88 (m, 4H, -OCH₂-), 1.73 (s, 4H, -CH₂-), 1.45 (s, 4H, -CH₂-), 0.96 (s, 6H, -CH₃).

¹³C NMR (CDCl₃) δ (ppm): 157.83 (TPE <u>C</u>-O), 150.11 (pyridine <u>C</u>), 147.92, (pyridine <u>C</u>-TPE), 145.66 (TPE <u>C</u>-pyridine), 144.11 (TPE <u>C</u>-C=C-), 141.20 (TPE-<u>C</u>=C-), 138.07, 135.91, 135.13, 132.61, 127.83, 126.16 (TPE <u>C</u>), 121.27 (pyridine <u>C</u>-C-TPE), 113.68 (TPE <u>C</u>-C-O), 67.54 (TPE-O<u>C</u>H₂-), 31.38 (-O<u>C</u>H₂-), 19.72 (-OCH₂<u>C</u>H₂-), 13.90 (-CH₂<u>C</u>H₃).

MALDI-TOF MS (*m*/*z*): [M + H]⁺ calcd for C₃₉H₃₉NO₂, 553.30; found 554.36. **2.2 Synthesis of PVA(PTPEC₄)**_x. To obtain the resultant polymers $PVA(PTPEC_4)_x$, PVA and $PTPEC_4$ was dissolved in DMSO, and then mixed together with calculated proportion related to x. As x = 0.6 an example, the PVA and $PTPEC_4$ (the molar ratio with PVA was 0.6) was dissolved in DMSO, respectively. Then simply miscible and stirred at room temperature for 24 h. After evaporated the solvent under the vacuum, and then placed at vacuum in 120 °C to remove the residual solution, the $PVA(PTPEC_4)_{0.6}$ was obtained.



3. TGA Data of PVA and PTPEC₄.

Figure S1. TGA curves of PVA (a) and PTPEC₄ (b) in the nitrogen atmosphere with rate at 20 $^{\circ}$ C/min.

4. DSC Date of PVA and PTPEC₄.



Figure S2. DSC traces of PTPEC₄ (a) and PVA (b) at a scanning rate at 10 $^{\circ}$ C/min.

5. POM images of PVA(PTPEC₄)_x.



Figure S3. POM images of PVA(PTPEC₄)_x, (a) x = 1.0, (b) x = 0.8, (c) x = 0.6, (d) x = 0.4, (e) x = 0.2, the scale bar is 50 μ m.



6. 1D WAXD dates of PVA(PTPEC₄)_x.

Figure S4. The variable-temperature 1D WAXD curves of $PVA(PTPEC_4)_x$. x = 1.0 in heating (a), cooling (b) process; x = 0.8 in heating (c), cooling (d) process; x = 0.6 in heating (e), cooling (f) process;

7. UV-vis Results of PVA(PTPEC₄)_x.



Figure S5. Normalized absorption spectrum of $PVA(PTPEC_4)_x$ in film.

8. The pKa Values of the Different Solvent.

Table S1. The pKa values of the solvent in the room temperature.

Solvent	pKa values
aqueous ammonia	15.5
phenol	9.95
acetic acid	4.74
formic acid	3.74
hydrofluoric acid	3.18
trifluoroacetic acid	0.23
hydrochloric	-8.00

9. The Photo-luminescence (PL) Spectra and Repeatability.



Figure S6. Photo-luminescence (PL) spectra of $PVA(PTPEC_4)_{1,0}$ fumed with phenol (a) and trifluoroacetic acid (b) vapors and recovery process.





Figure S7. PL spectra of $PVA(PTPEC_4)_{1,0}$ fumed with acetic acid (a), formic acid (b), hydrofluoric acid (c), and hydrochloric acid (d) vapors and recovery process.