A Linear AIE Supramolecular Polymer Based on a Salicylaldehyde Azine-Containing Pillararene and Its Reversible Cross-Linking by Cu(II) and Cyanide

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Supporting Information (17 pages)

1. Materials and Methods S2
2. Syntheses of P5D S3
3. Partial 1H NMR spectra of the host–guest interaction between P5D and G S7
4. Concentration-dependent 1H NMR spectroscopy experiments of the linear supramolecular polymer based on P5D and G S7
5. 2D DOSY NMR spectra of the linear supramolecular polymer based on P5D and G S8
6. Viscosity experiments of the linear supramolecular polymer based on P5D and G S9
7. SEM experiments of the linear supramolecular polymer based on P5D and G S9
8. 1H NMR spectroscopy experiments of the coordination between P5D and Cu(II) S10
9. Fluorescence emission spectroscopy experiments of the coordination between P5D and Cu(II) S10
10. 1H NMR spectroscopy experiments of the reversible cross-linking property of the linear supramolecular polymer based on P5D and G S12
11. 1H NMR spectroscopy experiments of the coordination between P5D and Zn(II) S12
12. Fluorescence emission spectroscopy experiments of the coordination between P5D and Zn(II)/Cu(II) S13
13. 1H NMR spectroscopy experiments of the non-covalent interaction between the linear supramolecular polymer and CN− S14
14. Fluorescence emission spectroscopy experiments of the non-covalent interaction between the linear supramolecular polymer and CN− S15
15. 1H NMR spectroscopy and fluorescence emission spectroscopy experiments of P5D and TBA Cl S15

References S17
1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compounds $1^{S1}$ and $G^{S2}$ were prepared according to published procedures. NMR spectra were recorded with a Bruker Avance DMX 600 spectrophotometer or a Bruker Avance DMX 400 spectrophotometer. High-resolution mass spectrometry experiments were performed with a Waters UPLC H-Class QDA instrument. The melting points were collected on a SGW X-4 automatic melting point apparatus. Scanning electron microscopy investigations were carried out on a TASCAN (LYRA3) instrument. Fluorescent microscopy investigations were carried out on a HORIBA Jobin Yvon FluoroMax-4 fluorescence spectrometer or a JASCO Model FP-8300 fluorescence spectrometer.
2. Syntheses of P5D

Synthesis of 2: A solution of 1 (2.00 g, 2.09 mmol) and 2, 4-dihydroxybenzaldehyde (0.290 g, 2.09 mmol) in acetonitrile (100 mL) was stirred at room temperature. Then potassium carbonate (0.580 g, 4.18 mmol) was added. The reaction mixture was refluxed for 24 h, filtered, and concentrated to give a crude product, which was purified by flash column chromatography (dichloromethane) to afford 2 as a white solid (1.55 g, 73%). The $^1$H NMR spectrum of 2 is shown in Fig. S1. $^1$H NMR (600 MHz, CDCl$_3$, room temperature) $\delta$ 11.51 (s, 1H), 9.72 (s, 1H), 7.42 (d, $J = 6$ Hz, 1H), 6.89–6.78 (m, 10H), 6.49 (m, 1H), 6.42 (d, $J = 6$ Hz, 1H), 3.95 (t, $J = 9$ Hz, 2H), 3.79–3.64 (m, 39H), 3.43 (t, $J = 9$ Hz, 2H), 1.78 (m, 2H), 1.25 (m, 8H), 0.83 (m, 2H), 0.36 (m, 2H), 0.17–0.03 (m, 2H). The $^{13}$C NMR spectrum of 2 is shown in Fig. S2. $^{13}$C NMR (CDCl$_3$, 150 MHz, room temperature,) $\delta$ (ppm): $\delta$ 191.73, 164.15, 162.13, 148.26, 148.20, 148.12, 148.05, 147.87, 147.24, 132.62, 125.94, 125.91, 125.68, 125.65, 125.61, 125.57, 112.35, 111.90, 111.81, 111.64, 111.38, 111.15, 111.06, 106.18, 98.46, 66.38, 65.17, 53.56, 53.26, 53.21, 53.09, 52.93, 29.39, 28.92, 27.67, 27.20, 26.97, 26.86, 26.80, 26.22, 26.04, 25.76, 25.70, 22.62, 22.10, 20.16, 11.61.
**Figure S1.** $^1$H NMR spectrum (600 MHz, CDCl$_3$, room temperature) of 2.

**Figure S2.** $^{13}$C NMR spectrum (150 MHz, CDCl$_3$, room temperature) of 2.
Synthesis of P5D: A solution of 2 (1.50 g, 1.50 mmol) and hydrazine hydrate (0.0375 g, 0.750 mmol) in ethanol (50 mL) was refluxed for 24 h. Then the solution was concentrated to give a crude product, which was purified by flash column chromatography (methanol/dichloromethane, 1:50 v/v) to afford P5D as a light yellow solid (1.15 g, 76%). Mp: 104–106 °C. The \(^1\)H NMR spectrum of P5D is shown in Fig. S3. \(^1\)H NMR (400 MHz, CDCl\(_3\), room temperature) \(\delta\) 11.78 (s, 2H), 8.61 (s, 2H), 7.24 (s, 2H), 6.89–6.78 (m, 20H), 6.57–6.45 (m, 4H), 4.93 (s, 2H), 3.95 (t, \(J = 6\) Hz, 4H), 3.77 (m, 4 Hz, 20H), 3.72–3.65 (m, 54H), 3.53 (t, \(J = 6\) Hz, 4H), 1.85–1.73 (m, 4H), 1.51 (m, 4H), 1.35–1.29 (m, 4H), 1.16 (m, 4H), 1.01–0.89 (m, 4H), 0.87–0.79 (m, 4H), 0.42 (m, 4H), 0.09 (m, 4H). The \(^{13}\)C NMR spectrum of P5D is shown in Fig. S4. \(^{13}\)C NMR (150 MHz, CDCl\(_3\), room temperature) \(\delta\) (ppm): \(\delta\) 158.89, 157.99, 157.06, 146.07, 145.99, 145.95, 145.93, 145.92, 145.89, 145.87, 145.85, 145.69, 145.03, 128.65, 123.67, 123.63, 123.47, 123.42, 123.38, 123.36, 123.34, 123.33, 109.72, 109.55, 109.44, 109.26, 109.23, 109.21, 109.19, 109.01, 108.93, 106.04, 103.11, 96.85, 63.80, 63.04, 51.30, 51.04, 51.01, 50.91, 50.88, 50.76, 50.74, 24.95, 24.80, 24.75, 24.70, 24.64, 24.04, 23.91, 23.81, 23.63, 20.51, 20.07. HRESIMS is shown in Fig. S6: \(m/z\) calcld. for [M + H]\(^+\) \(C_{122}H_{145}N_2O_{24}\), 2023.02153; found 2023.02026; error 0.6 ppm.

*Figure S3.* \(^1\)H NMR spectrum (400 MHz, CDCl\(_3\), room temperature) of P5D.
**Figure S4.** $^{13}$C NMR spectrum (150 MHz, CDCl$_3$, room temperature) of P5D.

**Figure S5.** High-resolution mass electrospray ionization mass spectrum of P5D. Main peak: \textit{m/z} 2023.02026 [M + H]$^+$ (100%).
3. Partial $^1$H NMR spectra of the host–guest interaction between the P5D and G

![Partial $^1$H NMR spectra](image)

**Figure S6** Partial $^1$H NMR spectra (CDCl$_3$, 600 MHz, room temperature): (a) P5D (10.0 mM); (b) P5D (10.0 mM) + G (10.0 mM); (d) G (10 mM).

4. Concentration-dependent $^1$H NMR spectroscopy experiments of the linear supramolecular polymer based on P5D and G

![Concentration-dependent $^1$H NMR](image)

**Figure S7** Partial $^1$H NMR spectra of equimolar mixtures of P5D and G (600 MHz, CDCl$_3$, room temperature) at different concentrations: (a) 100 mM; (b) 80.0 mM; (c) 66.7 mM; (d) 50.0 mM; (e) 40.0 mM; (f) 33.3 mM; (g) 26.7 mM; (h) 20.0 mM; (i) 15.0 mM; (j) 10.0 mM; (k) 5.00 mM; (l) 2.50 mM. Peaks of complexed and uncomplexed P5D and G are designated by c and uc, respectively.
5. 2D DOSY NMR spectroscopy experiments of the linear supramolecular polymer based on P5D and G

Figure S8 2D DOSY NMR spectra of equimolar P5D + G at different concentrations (600 MHz, CDCl₃, room temperature): (a) 2.50 mM; (b) 10.0 mM; (c) 26.7 mM; (d) 50.0 mM; (e) 100 mM.

Figure S9 Schematic illustration of the concentration dependence of diffusion coefficient $D$ (600 MHz, CDCl₃, room temperature) of equimolar P5D and G.
6. Viscosity experiments of the linear supramolecular polymer based on P5D and G

![Graph showing specific viscosity (\(V_S\)) of equimolar P5D and G in chloroform at 298 K versus concentration. The graph displays two slopes: 1.26 and 2.08.](image)

**Figure S10** Specific viscosity \(V_S\) of equimolar P5D and G in chloroform at 298 K versus the concentration.

7. SEM experiment of the linear supramolecular polymer based on P5D and G

![SEM image of a gold-coated fiber drawn from a high concentration solution of equimolar mixtures of P5D and G.](image)

**Figure S11** SEM image of a gold-coated fiber drawn from a high concentration solution of equimolar mixtures of P5D and G.
8. $^1$H NMR spectroscopy experiments of the coordination between P5D and Cu(II)

![Partial $^1$H NMR spectra](image)

**Figure S12** Partial $^1$H NMR spectra (600 MHz, CDCl₃, room temperature): (a) P5D (3.33 mM); (b) after addition of 0.5 molar equiv. Cu(II) to a; (c) after further addition of 0.5 molar equiv. Cu(II) to b; (d) after further addition of 1.0 molar equiv. Cu(II) to c.

9. Fluorescence emission spectroscopy experiments of the coordination between P5D and Cu(II)

In addition, fluorescence titration experiments were carried out to investigate the coordination ratio and binding strength. Fluorescence titration experiments were done with solutions which had a constant concentration of P5D (1.00 × 10⁻⁵ M) and varying concentrations of Cu(II). By a non-linear curve-fitting method, the coordination ratio and binding strength was estimated. By mole ratio plot, 1:2 stoichiometry was obtained for the complexation between P5D and Cu(II). The binding strength was estimated to 9.92 × 10⁴ M⁻¹.

The non-linear curve-fittings were based on the equation:

$$
\Delta F = \frac{\Delta F_c}{[H]_0} \left(0.5[G]_0 + 0.5([H]_0+1/K_a)-(0.5 ([G]_0^2+(2[G]_0(1/K_a-[H]_0)) + (1/K_a+ [H]_0)^2)^{0.5})\right)
$$

Where $\Delta F$ is the fluorescence intensity changes at 510 nm relative to that at $[H]_0$, $\Delta F_c$ is the fluorescence intensity changes at 510 nm when P5D is completely complexed, $[G]_0$ is the initial concentration of Cu(II), and $[H]_0$ is the fixed initial concentration of P5D.³³
Figure S13 Fluorescence spectra of P5D (1.00 × 10⁻⁵ M) in chloroform at room temperature with different concentrations of Cu(II): 0, 0.199, 0.398, 0.791, 0.985, 1.18, 1.94, 2.69, 3.77, 4.65, 7.93, 10.9, 14.4, 18.2 and 23.0 × 10⁻⁵ M⁻¹ chloroform room temperature.

Figure S14 Mole ratio plot for P5D and Cu(II), indicating a 1:2 stoichiometry.
**Figure S15** The fluorescence intensity changes of P5D upon addition of Cu(II). The red solid line was obtained from the non-linear curve-fitting using the above equation.

10. **1H NMR spectroscopy experiments of the reversible cross-linking property of the linear supramolecular polymer based on P5D and G**

![Graph](image)

**Figure S16** Partial 1H NMR spectra (600 MHz, CDCl₃, room temperature): (a) equimolar mixtures of P5D and G (15.0 mM); (b) after addition of 2.0 molar equiv. Cu(II); (c) after further addition of 4.0 molar equiv. of TBACN to part b; (d) after further addition of 6.0 molar equiv. of Cu(II) to part c.

11. **1H NMR spectroscopy experiments of the coordination between P5D and Zn(II)**

To study the quenching phenomenon caused by Cu(II), the addition of Zn(II) to the solution of P5D was studied as a comparison. 1H NMR spectroscopy experiments was carried out to study whether there is complexation between Zn(II) and P5D. As shown in Figure S13, upon gradually addition of Zn(II) to
the solution of **P5D**, no chemical shift changes nor signal changes of the protons on **P5D** was observed, indicating that there is no coordination between **P5D** and Zn(II).

![Figure S17 Partial 1H NMR spectra (600 MH, CDCl3, room temperature): (a) P5D (3.33 mM); (b) after addition of 1.0 molar equiv. Zn(ClO₄)₂•6H₂O (Zn(II)) to a; (c) after further addition of 1.0 molar equiv. Zn(II) to b; (d) after further addition of 2.0 molar equiv. Zn(II) to c.](image)

12. Fluorescence emission spectroscopy experiments of the coordination between **P5D** and Zn(II)/Cu(II)

To study the quenching phenomenon caused by Cu(II), the addition of Cu(II) to the solution of **P5D** was studied. The addition of Zn(II) was investigated as a comparison. As shown in Figure S14, the solution of the **P5D** was gradually added with Zn(II) and Cu(II), respectively. Upon addition of Cu(II), the maximum fluorescence emission at around 510 nm decreased remarkable. While after addition of Zn(II), the maximum fluorescence emission at around 510 nm maintained. These data suggest that Cu(II) could lead to the quenching of the fluorescence of salicylaldehyde azine group and Zn(II) could not.

![Figure S18 Fluorescence emission spectra of **P5D** (1.00 × 10⁻⁵ M) upon gradually addition of Zn(II) (a) and Cu(II) (b).](image)
13. $^1H$ NMR spectroscopy experiments of the non-covalent interaction between the linear supramolecular polymer and CN$^-$

**Figure S19** Partial $^1H$ NMR spectra (600 MHz, CDCl$_3$, room temperature): (a) solution of equimolar P5D and G (15.0 mM); (b) after addition of 2.0 molar equiv. tetrabutylammonium cyanide (30.0 mM) to a.

14. Fluorescence emission spectroscopy experiments of the non-covalent interaction between the linear supramolecular polymer and CN$^-$

**Figure S20** Fluorescence emission spectra of the solution of equimolar P5D and G (40.0 mM) before and after addition of 2.0 molar equiv. tetrabutylammonium cyanide. The excitation wavelength was 350 nm.

15. $^1H$ NMR spectroscopy and fluorescence emission spectroscopy experiments of P5D and tetrabutylammonium chloride

The $^1H$ NMR spectroscopy experiments and fluorescence emission experiments of P5D and tetrabutylammonium chloride (TBACl) were carried out as control experiments to confirm the non-covalent interaction between CN$^-$ and the salicyaldehyde azine group on P5D, not the tetrabutylammonium group. As shown in Figure S17, upon addition of 2.0 molar equiv. TBACl to the
solution of P5D, the $^1$H NMR spectrum didn’t show any changes, especially the peak related to proton H$_{15}$. In addition, as shown in Fig 18, the fluorescence emission spectra also didn’t show any obvious changes after adding TBACl. These results suggested that the tetrabutylammonium group has no interaction with P5D.

Figure S21 Partial $^1$H NMR spectra (600 MHz, CDCl$_3$, room temperature): (a) P5D (3.33 mM); (b) after addition of 4.0 molar equiv. tetrabutylammonium chloride (TBACl) (13.2 mM) to a.

Figure S22 Fluorescence emission spectra of the solution of equimolar P5D (1.00 x 10$^{-5}$ M) before and after addition of 4.0 molar equiv. TBACl (4.00 x 10$^{-5}$ M). The excitation wavelength was 350 nm.
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