

Supporting Information

Colorful Luminescence of Conjugated Polyelectrolytes Induced by Molecular Weight

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Synthesis of 2-(C₄H₈SO₃Na)-2H-benzo[1,2,3]triazole

Benzotriazole (28.6 mmol, 3.4 g) and tetrabutylammonium bromide (460 mg, 1.43 mmol) were dissolved in 140 mL anhydrous DMSO, which was degassed by N₂ for about 5 min. A 16 mL NaOH (14 g) aqueous solution was added using a syringe, which was followed by the addition of 1,4-butanediol (3500 µL, 66.8 mmol). After stirring for 3 hours at room temperature, the reaction mixture was poured into acetone. After filtration and washing it with acetone, the white precipitate was obtained. The purification by chromatography (reversed phase silica gel C-18, 10:1 H₂O:MeOH) provided the title product as a white solid (41% yield). ¹H NMR (500 MHz, D₂O) δ 7.53 (d, 2H), 7.86 (d, 2H), 4.79 (t, 2H), 2.89 (t, 2H), 2.24 (m, 2H), 1.74 (m, 2H). MS m/z calcd for C₁₀H₁₂N₃SO₃Na: 277 g/mol found: 254.29 (C₁₀H₁₂N₃SO₃⁻). See below spectra in Figures S1 and S2, which were cited from [1].

Synthesis of 4,7-dibromo-2-(C₄H₈SO₃Na)-2H-benzo[1,2,3]triazole (BTzBr₂-SO₃Na)

BTz-C₄H₈SO₃Na (0.73 mmol, 0.201 g) and an aqueous HBr solution (33 wt%, 1.3 mL) were added to a round bottom flask, and the mixture was stirred for one hour at 100 °C. After cooling it down to room temperature, bromine (0.33 g, 0.106 mL) was added. The solution was stirred for 12 h at 80 °C. After cooling it down to room temperature again, an aqueous solution of NaHCO₃ was added, and the reaction was stirred in another 2 hours. The purification by chromatography (reversed phase silica gel C-18, 10:1 H₂O:MeOH) provided the title product as a white solid (83% yield). ¹H NMR (400 MHz, D₂O) δ 7.59 (s, 2H), 4.88 (t, 2H), 2.90 (t, 2H), 2.25 (m, 2H), 1.74 (m, 2H). MS m/z calcd for C₁₀H₁₀Br₂N₃SO₃Na: 435 g/mol found: 411.71 (C₁₀H₁₀Br₂N₃SO₃⁻). See below spectra in Figures S3 and S4, which were cited from [1].

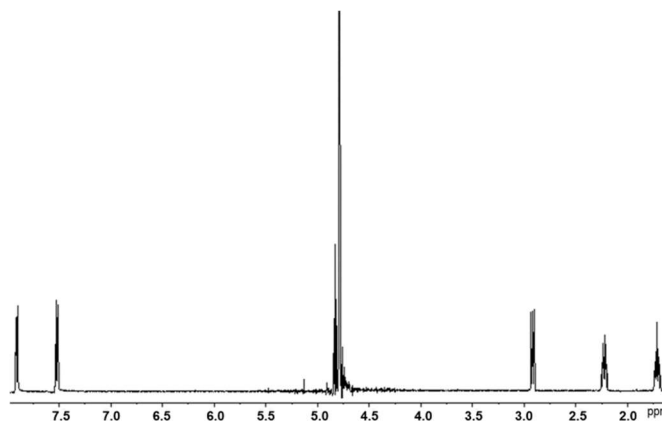


Figure S1. The ¹H NMR spectrum of 2-(C₄H₈SO₃Na)-2H-benzo[1,2,3]triazole in D₂O.

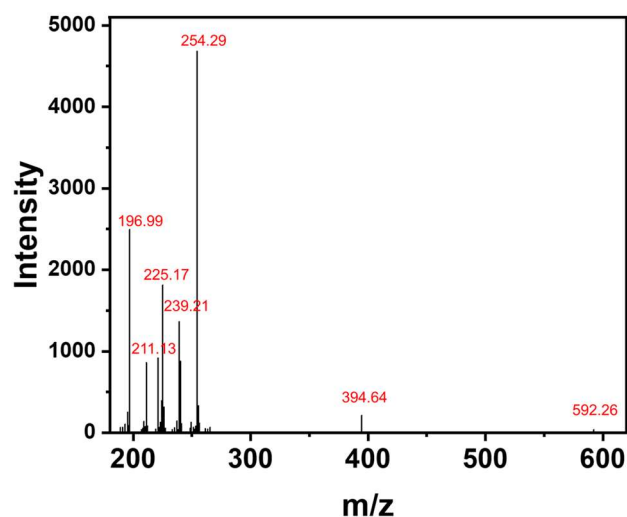


Figure S2. The mass spectrum of 2-(C₄H₈SO₃Na)-2H-benzo[1,2,3]triazole in D₂O.

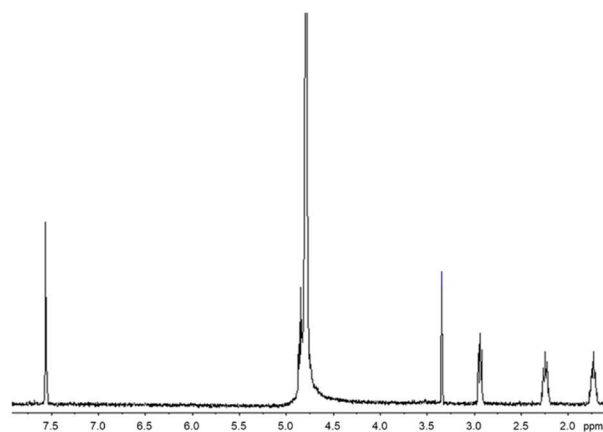


Figure S3. The ¹H NMR spectrum of BTzBr₂-SO₃Na in D₂O.

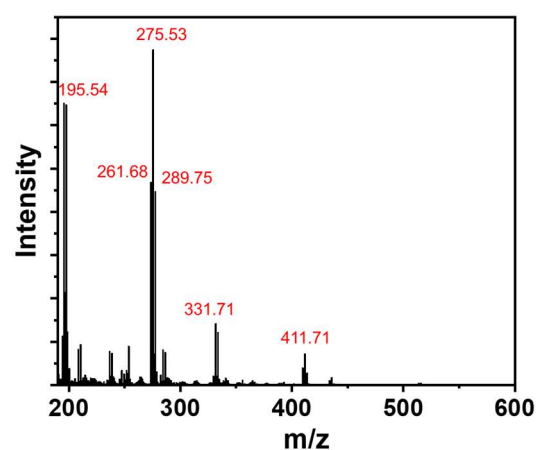


Figure S4. The mass spectrum of BTzBr₂-SO₃Na in D₂O.

Suzuki coupling polymerization of PBTBTz-SO₃Na with different molecular weights

Dibromide (1.0 equiv), diboronic ester (1.0 equiv), Na₂CO₃ (5 equiv), and Pd(PPh₃)₄ (2 mol%) were combined in the microwave tube using a stir bar in a glove box. The tube was sealed and taken out of the glove box. A mixture of DMF and H₂O (4/1 vol/vol) was degassed with argon for 5 min, then, it was transferred into the above tube under an argon atmosphere. The solution was placed into an oil bath, and heated to 80 °C, at which temperature the mixture turned dark red in ~20 min. The reaction was conducted at about 80

°C for 24 h, and it was poured into acetone. The red precipitate was collected by filtration and washed with acetone and MeOH. The red products were dissolved in millipore H₂O, and then, they were transferred into a dialysis tube (MWCO: 3500-5000). The tube was placed into the millipore H₂O for dialysis which took place after a week, and the millipore H₂O was changed every 12 h. After freeze-drying, the P1 was obtained as a dark red solid.

Dibromide (1.0 equiv), diboronic ester (1.0 equiv), Na₂CO₃ (5 equiv), and Pd(PPh₃)₄ (1.8 mol%) were combined in the microwave tube using a stir bar in a glove box. The tube was sealed and taken out of the glove box. A mixture of DMF and H₂O (3/1 vol/vol) was degassed with argon for 5 min, and then, it was transferred into the above tube under an argon atmosphere. The solution was placed into an oil bath and heated to 80 °C, at which temperature the mixture turned dark red in ~20 min. The reaction was conducted at about 80 °C for 24 h, and it was poured into acetone. The red precipitate was collected by filtration and washed with acetone and MeOH. The red products were dissolved in millipore H₂O, and then, they were transferred into a dialysis tube (MWCO: 3500-5000). The tube was placed into the millipore H₂O for dialysis which took place after a week, and the millipore H₂O was changed every 12 h. After freeze-drying, the P2 was obtained as a dark red solid.

Dibromide (1.0 equiv), diboronic ester (1.0 equiv), Na₂CO₃ (5 equiv), and Pd(PPh₃)₄ (1.5 mol%) were combined in the microwave tube using a stir bar in a glove box. The tube was sealed and taken out of the glove box. A mixture of DMF and H₂O (3/1 vol/vol) was degassed with argon for 5 min, and then, it was transferred into the above tube under an argon atmosphere. The solution was placed into an oil bath and heated to 80 °C, at which temperature the mixture turned dark red in ~20 min. The reaction was conducted at about 80 °C for 24 h, and it was poured into acetone. The red precipitate was collected by filtration and washed with acetone and MeOH. The red products were dissolved in millipore H₂O, and then, they were transferred into a dialysis tube (MWCO: 3500-5000). The tube was placed into the millipore H₂O for dialysis which took place after a week, and the millipore H₂O was changed every 12 h. After freeze-drying, the P3 was obtained as a dark red solid.

Characterizations

General Information for Synthesis

All of the glasses were oven dried. The chemicals were commercially available, and they were used as received. Thin layer chromatography (TLC) was performed using EM Science Silica Gel 60 F254 glass plates. Flash chromatography was performed using 60 Å silica gel (37-75 µm). The dialysis membrane (MWCO: 3500-5000 Da) was purchased from Spectrum® Laboratories Inc. The ¹H NMR spectra were recorded at either 400 MHz or 500 MHz in D₂O. The GPC of PBTBTz-SO₃TBA was measured using DMF as the solvent.

Cyclic voltammetry (CV) measurements

The cyclic voltammetry (CV) was performed using a CHI instrument model 730B in a standard three-electrode, with one compartment configuration being equipped with a Ag wire quasi reference electrode, a Pt wire counter electrode, and a glassy carbon working electrode. Additionally, the glass carbon electrodes were polished with alumina. The polyelectrolytes formed the films by dripping 5 µL of 5 mg/mL solution on the carbon working electrode, then, they were dried under a vacuum overnight before we took the measurements. The CV experiments were processed in anhydrous acetonitrile solution (PBTBTz-SO₃Na was performed in DMF) with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte at a scan rate of 100 mV/s. The electrochemical solutions were purged with argon for 15 minutes to deoxygenate the solutions. Ferrocene was used as the internal standard.

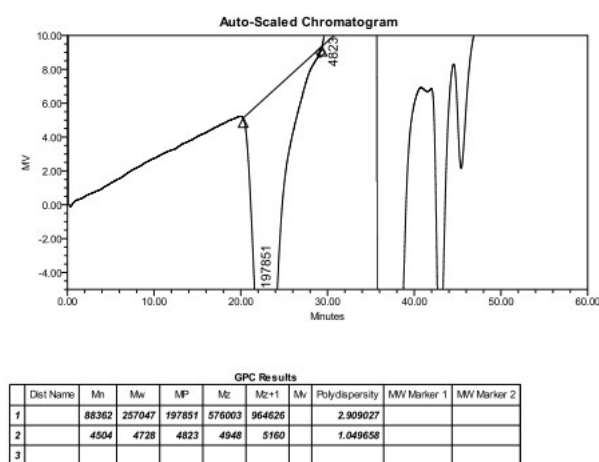


Figure S5. The original test picture of P1.

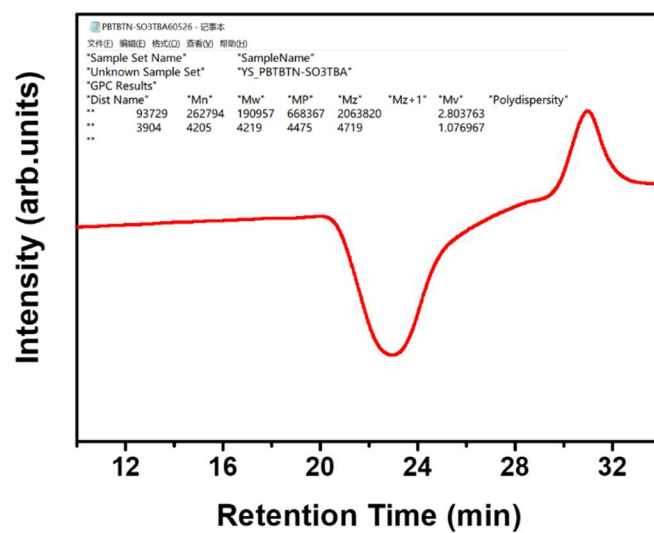
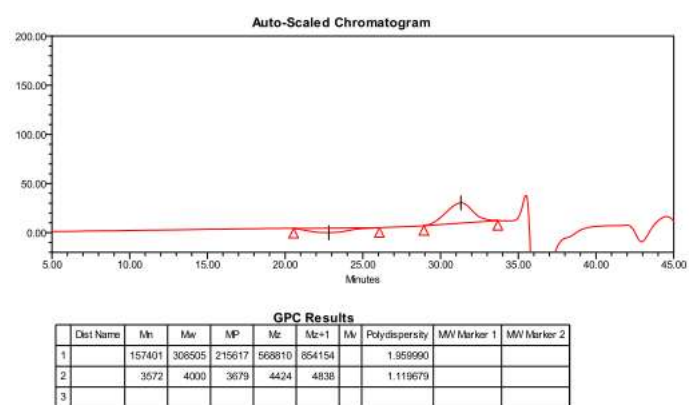


Figure S6. The original test picture of P2.



Processed Channel:

| Peak Name | Retention Time (min) | Area | % Area | Height |
|-----------|----------------------|---------|--------|--------|
| 1 Peak3 | 22.814 | 787272 | 24.03 | -4595 |
| 2 Peak4 | 31.315 | 2488513 | 75.97 | 20953 |
| 3 Peak2 | 36.476 | | | |

Figure S7. The original test picture of P3.

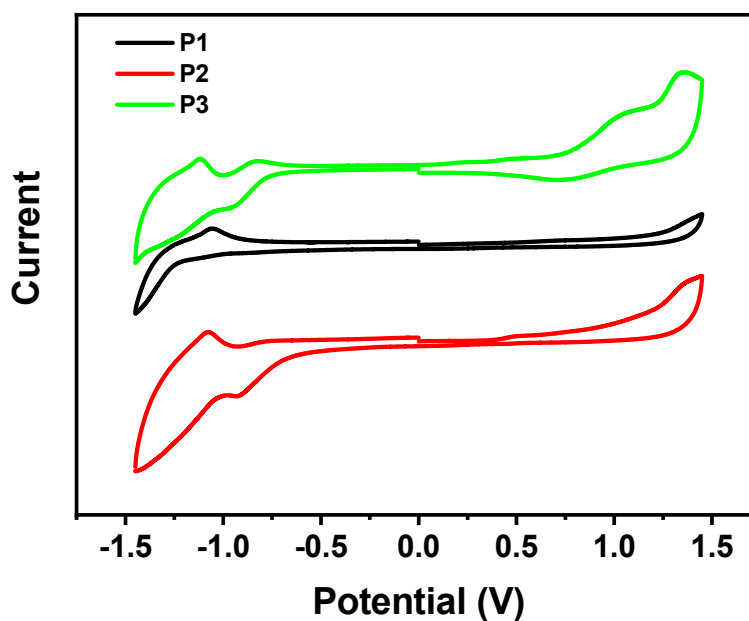


Figure S8. The CV curves of P1, P2 and P3.

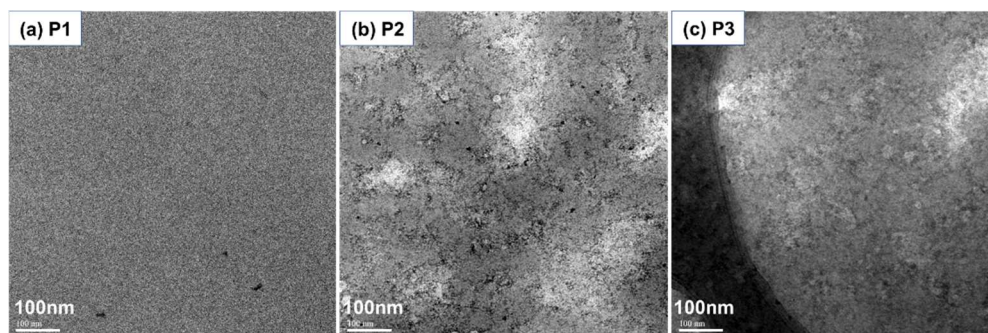


Figure S9. The larger TEM images of P1, P2 and P3.

UV-vis absorptions

The UV-vis absorption measurements were performed using a Perkin Elmer Lambda 750 spectrophotometer. The films were prepared by spin coating from the corresponding solutions (5 mg/mL) onto the glass substrates. The concentration of the solution was 0.016 mg/mL.

Fluorescence Quantum Yield (Φ)

The concentration of each sample was 0.016 mg mL⁻¹. The fluorescence quantum yields of P1, P2 and P3 in H₂O were determined relative to a reference sample of a known quantum yield Φ (rhodamine 101 inner salt in H₂O) with the possibility of correcting for the differences between the refractive index of the reference n_r and the sample solutions n_s using the following equation [2].

$$\Phi_s = \frac{S_s}{S_r} \frac{n_s^2}{n_r^2} \Phi_r$$

The subscripts s and r denote the samples and reference, respectively. The S represents the integral of the corrected emission spectra at the wavelength of excitation. The

n stands for the refractive index of the solution. The Φ is the fluorescence quantum yields. The Φ_r value of rhodamine 101 inner salt is 100%.

The integrated emission S was obtained in three steps. The first step was the UV-vis absorption of the sample and reference to obtain the excitation wavelength. Here, the excitation wavelengths were 440 nm, 461 nm and 443 nm for P1, P2 and P3, respectively. The second step was the fluorescence emission spectra of the sample, reference and blank. The third step was subtracting the blank from the sample and the reference, respectively, to obtain the fluorescence integrals of the sample and the reference shown in the Figure 4d.

References

1. Shi, Y.; Mai, C.-K.; Fronk, S.L.; Chen, Y.; Bazan, G.C. Optical properties of Benzotriazole-based Conjugated Polyelectrolytes. *Macromolecules* **2016**, *49*, 6343–6349.
2. Morrls, J.V.; Mahaney, M.A.; Huber, J.R. Fluorescence Quantum Yield Determinations. 9,10-Diphenylanthracene as A Reference Standard in Different Solvents. *J. Phys. Chem.* **1976**, *80*, 969–974.