Supporting Information for：

Solution-Processible Hyperbranched Conjugated Polymer Nanoparticles with Tunable Particle Sizes by Suzuki Polymerization in Miniemulsion

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Experimental Section:

Measurement and Characterization. ^{1}H NMR and ^{13}C NMR spectra were obtained with a Bruker Avance 300 or 400 NMR spectrometer. The chemical shifts with respect to tetramethylsilane as an internal reference are reported in parts per million. ^{13}C CP/MAS NMR spectra were recorded on a Bruker AVANCE III 400 WB spectrometer at a MAS rate of 12 KHz. The elemental analysis was performed on a Bio-Rad elemental analysis system. IR spectra were obtained on FT-IR Bruker Vertex 70 spectrometer at a norminal resolution of 2 cm^{-1}. The samples were prepared by adding model compound and polymer into KBr and the mixture was ground to a fine power and pressed to form disk. Number average molecular weights and the polydispersity of the polymers were determined by gel permeation chromatography (GPC) on a Waters 410 instrument with polystyrene as a standard and THF as the eluent. Electron microscopy was performed on a Zeiss XL30 Field Emission Scanning electron microscopy operating at 25 keV. A commercial LLS spectrometer (ALV CGS-3), equipped with a multi-τ digital time correlation (ALV7000) and a cylindrical 22 mW He_Ne laser (λ = 632.8 nm, Uniphase) as light source, was used for dynamic light scattering. The samples were measured at 25 °C with a scattering angle of 90 degrees. Thermal properties of the polymers were analyzed with a Perkin-Elmer-TGA 7 instrument under nitrogen at a heating rate of 10 °C/min. UV–Vis absorption spectra were recorded by a Perkin-Elmer Lambda 35 UV–Vis spectrometer. PL spectra were recorded using a Perkin-Elmer LS50B spectrofluorometer.

Materials

1,3,5-tribromobenzene was purchased from Acros Asear. 1,3-dibromobenzene, 1,4-dibromobenzene, 4-bromoanisole, hexadecyltrimethylammonium bromide(CTAB) and picric acid were purchased from Aladdin Reagent Inc. 9,9-Dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester and 4-methoxybenzeneboronic acid (1,3-propanediol) ester was synthesized according to literatures.[1]

Typical procedure for a miniemulsion Suzuki polymerization (P1): Under an inert atmosphere, the solution of 1,3,5-tribromobenzene (0.0628 g, 0.2 mmol), 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (0.1675 g, 0.3 mmol) and $Pd(PPh_3)_4$ (1.4 mg, 0.0012 mmol) in 1.5 mL toluene was added to the aqueous solution of CTAB (2.184 g, 6 mmol). The emulsion was stirred vigorously for one hour and ultrasonicated for half an hour to make itself a transparent light-yellow emulsion. 1.2 mL of 2 M K_2CO_3 aqueous (4 equivalent (4 eq.)) was added to the emulsion. Then, the emulsion was placed in an oil bath at 80 ^{o}C and stirred for 24 hours. After cooling, the latex was extracted with CH_2Cl_2 for three times. The organic phase was washed with saturated NaCl aqueous for five times and dried with anhydrous Na_2SO_4. The organic phase was concentrated and subsided in methyl alcohol. The light yellow powder was collected and dried under vacuum, with a yield of 50 ~ 70%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.2~7.4 (br, 8H), 2.4–1.8 (br, 4H), 1.2–0.95 (br, 20H), 0.95–0.6 (br, 10H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 152.3, 144.6, 143.3, 140.9, 129.4, 126.7, 125.5, 123.7, 122.0, 120.7, 55.9, 40.8, 32.1, 30.4, 29.6, 24.2, 23.0, 14.4. IR (KBr pellet): 3030, 2924, 2852, 1592, 1467, 1261, 1003, 876, 819, 741. Elemental Analysis Calculated (Anal. Calcd.): C, 90.07%; H, 9.93%; Found: C, 84.34%; H, 8.92%. Decomposition Temperature (T_d), 5% weight loss): 375 °C.

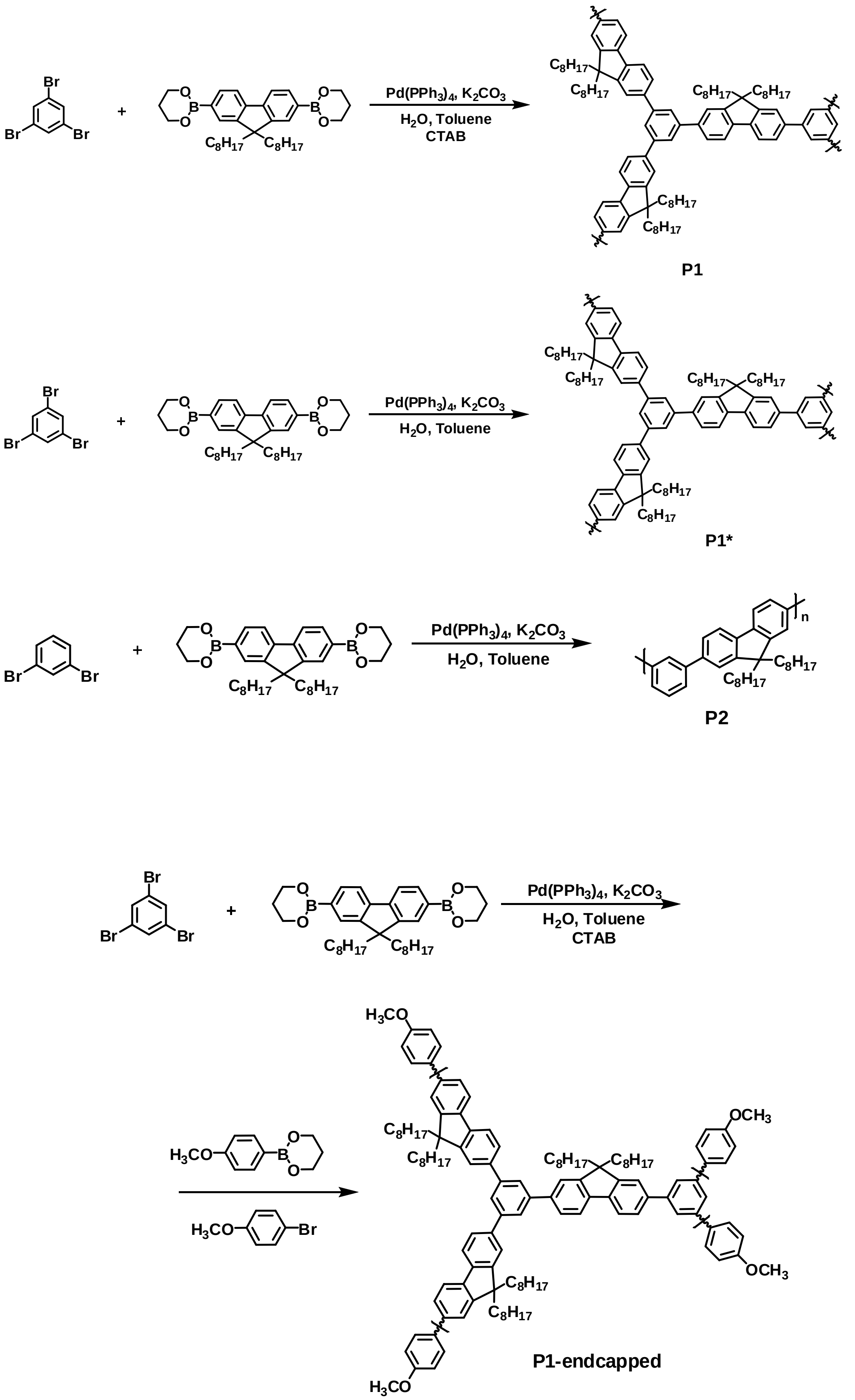
Typical procedure for a endcapped nanoparticles prepared by miniemulsion Suzuki polymerization (P1-endcapped): Under an inert atmosphere, the solution of 1,3,5-tribromobenzene (0.0628 g, 0.2 mmol), 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (0.1675 g, 0.3 mmol) and $Pd(PPh_3)_4$ (1.4 mg, 0.0012 mmol) in 1.5 mL toluene was added to the aqueous solution of CTAB (2.184 g, 6 mmol). The emulsion was stirred vigorously for one hour and ultrasonicated for half an hour to make itself a transparent light-yellow emulsion. 1.2 mL of 2 M K_2CO_3 aqueous (4 eq.) was added to the emulsion. Then, the emulsion was placed in an oil bath at 80 °C and stirred for 24 hours. 4-methoxybenzeneboronic acid (1,3-propanediol) ester (0.025 g, 0.12 mmol) in 0.5 mL toluene was added to the emulsion, which was kept at the reaction condition for 6 hours. Another endcapping reagent, 4-bromoanisole (25 μL, 1 mmol), was added to the emulsion, which was also kept at the reaction condition for 6 hours. After cooling, the latex was extracted with CH_2Cl_2 for three times. The organic phase was washed with saturated NaCl aqueous for five times and dried with anhydrous Na_2SO_4. The organic phase was concentrated and subsided in methyl alcohol. The light yellow powder was collected and dried under vacuum, with a yield of 70%. ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.2~7.4 (br, 8H), 4.0~3.8 (br, 0.1H), 2.4–1.8 (br, 4H), 1.2–0.95 (br, 20H), 0.95–0.6 (br, 10H). IR (KBr pellet): 3030, 2925, 2852, 1593, 1467, 1266, 1005, 874, 818, 740. Anal. Calcd.: C, 90.07%; H, 9.93%; Found: C, 86.03%; H, 9.30%. T_d (5% weight loss): 408 °C.

Typical procedure for a conventional Suzuki polymerization (P1*): Under an inert atmosphere, 1,3,5-tribromobenzene (0.0628 g, 0.2 mmol), 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (0.1675 g, 0.3 mmol), $Pd(PPh_3)_4$ (1.4 mg, 0.0012 mmol) and two drops of Trioctylmethylammonium chloride (aliquot 336) was solved by 5 mL of toluene. After adding 1.2 mL of 2 M K_2CO_3 to the solution, the mixture was placed in 80 °C oil bath and stirred for 24 hours. After cooling, the mixture was poured into methyl alcohol. The solid powder was filtered and washed with methyl alcohol and dichloromehtane for three times. Then, the solid powders was collected and dried under vacuum, with a yield about 50%. ^{13}C CP/MAS NMR(100 MHz) δ (ppm): 151.9, 141.0, 126.7, 120.6, 55.6, 40.9, 30.3, 23.2, 14.3. IR (KBr pellet): 3030, 2924, 2852, 1591, 1466, 1003, 876, 818, 739. Anal. Calcd.: C, 90.07%; H, 9.93%; Found: C, 84.93%; H, 9.11%. T_d (5% weight loss): 336 °C.

P2: Under an inert atmosphere, 1,3-dibromobenzene (0.071 g, 0.3 mmol), 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (0.168 g, 0.3 mmol), $Pd(PPh_3)_4$ (2 mg, 0.0012 mmol) and two drops of aliquot 336 was solved by 5 mL of toluene. After adding 1.2 mL of 2 M K_2CO_3 (4 eq.) to the solution, the mixture was placed in 80 °C oil bath and stirred for 24 hours. After cooling, the mixture was diluted with CH_2Cl_2, washed with water for three times and dried with anhydrous Na_2SO_4. The organic phase was concentrated and subsided in methyl alcohol. The solid powders was collected and dried under vacuum, with a yield about 90%. ^1H NMR ($CDCl_3$, 300 MHz) δ(ppm): 8.0–7.9 (br, 1H), 7.9–7.78 (br, 2H), 7.72–7.62 (br, 6H), 7.62–7.52 (br, 1H), 2.2–1.95 (br, 4H), 1.22–0.95 (br, 20H), 0.9–0.6 (br, 10H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 152.2, 142.8, 140.6, 129.6, 126.6, 122.1, 120.5, 55.8, 40.9, 32.2, 30.5, 29.6, 24.3, 23.0, 14.5. IR (KBr pellet): 3059, 3030, 2926, 2853, 1599, 1462, 1005, 884, 822, 790, 700. Anal. Calcd.: C, 90.46%; H, 9.54%; Found: C, 89.34%; H, 9.37%. GPC results: *M*n=10.4 kDa, PDI=1.9.

Procedure for the dispersing polymers in miniemulsion: 1.5 mL dichloromethane solution of 13 mg Polymer **P2** was quickly injected to 45 mL aqueous solution of 0.291 g CTAB. After vigorous stirring for half an hour and ultrasonicating for half an hour, the polymer emulsion was obtained. Then, the emulsion was kept stirring uncovered for 3 days at room temperature to evaporate the remaining dichloromethane.

Fluorescence Titration Procedure: A 10×10 mm quartz cuvette was used for solution spectra, and emission was collected at 90° relative to the excitation beam. The emulsions of **P1**, **P2** were diluted to about 2 mg/L in distilled de-ionized water (based on the absorption intensity around 335 nm). Solution of picric acid (PA) with the concentration of typically 1×10^{-3} M was prepared in water, and the solution was diluted to 1.0×10^{-4}, 1.0×10^{-5}, and 1.0×10^{-6} M with water. Fluorescent responses of the emulsions to the varied concentrations of PA were studied by adding small aliquots of PA solutions to 3.00 mL of the diluted emulsions.



Scheme S1 The synthesis of **P1, P1*, P2** and **P1-endcapped.**

Table S1. Polymerization of 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester and 1,3,5-tribromobenzene.

Entry	CTAB / mmol	Yield / %	diameter/nm[c]
1[a](P1)	4	50	460
2[a](P1)	5	62	200
3[a](P1)	6	56	146
4[a](P1)	8	61	110
5[a](P1)	10	55	75
6[a](P1)	12	60	60
7[b](P1*)	0	80	-

[a] Polymerization condition: 1.5 mL of toluene; 45 mL water; 1.4 mg $Pd(PPh_3)_4$; 1.2 mL 2 M K_2CO_3; 80 °C; 24 hours. [b] Conventional Suzuki polymerization condition. [b] DLS results of the emulsion dispersions.

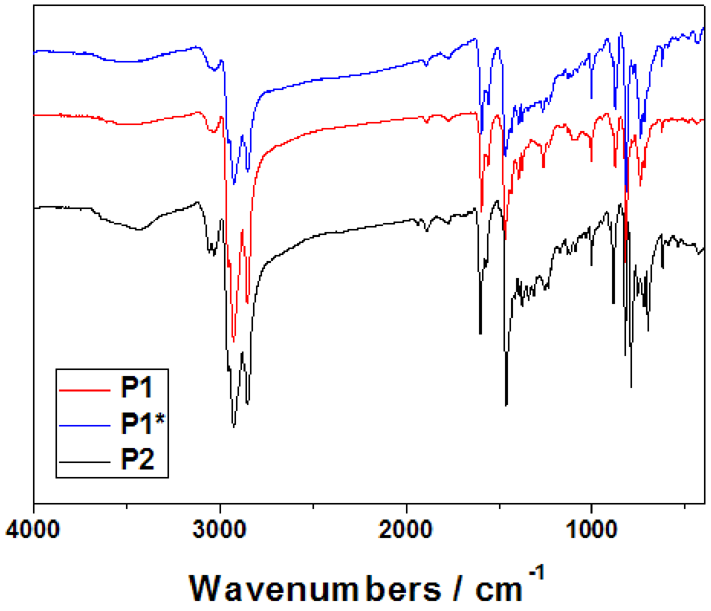


Figure S1: FT-IR spectra of **P1**, **P1*** and **P2**.

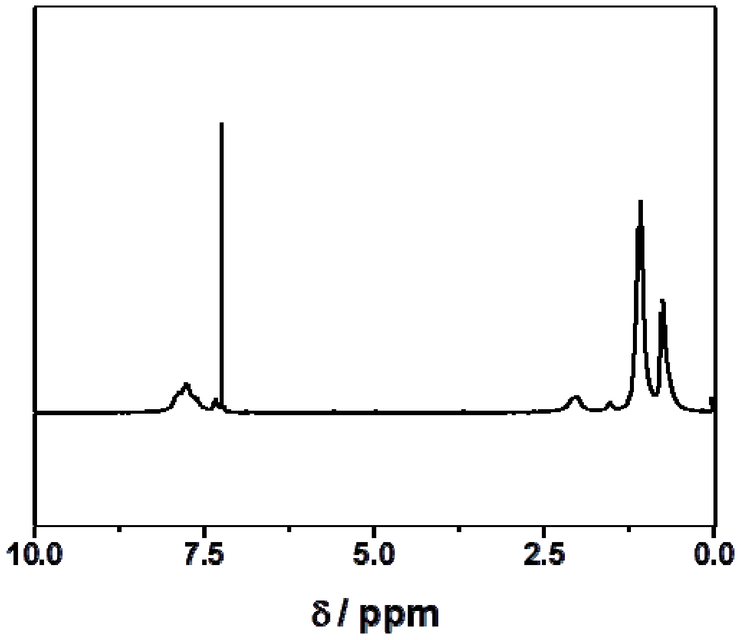


Figure S2 ^{1}H NMR spectrum of **P1**

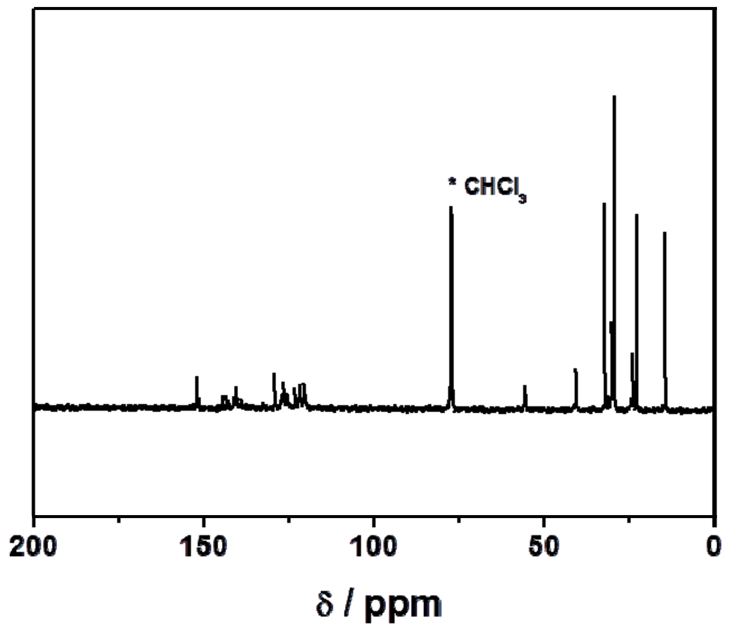


Figure S3 ^{13}C NMR spectrum of **P1**

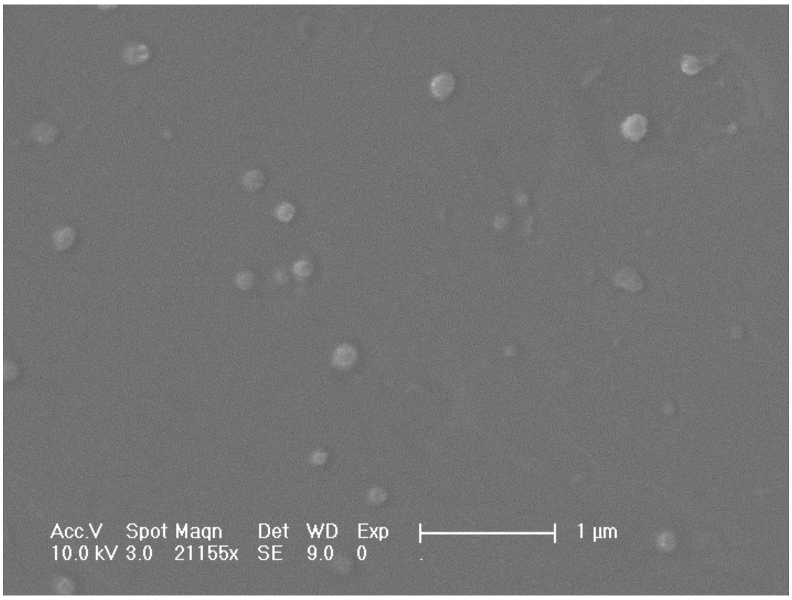
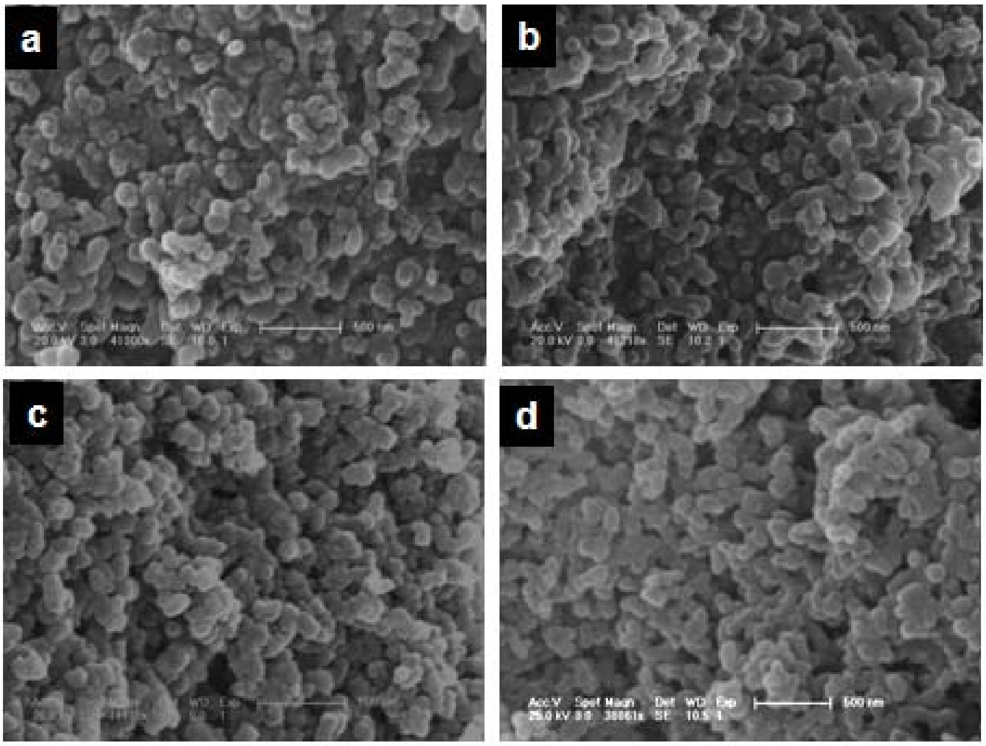
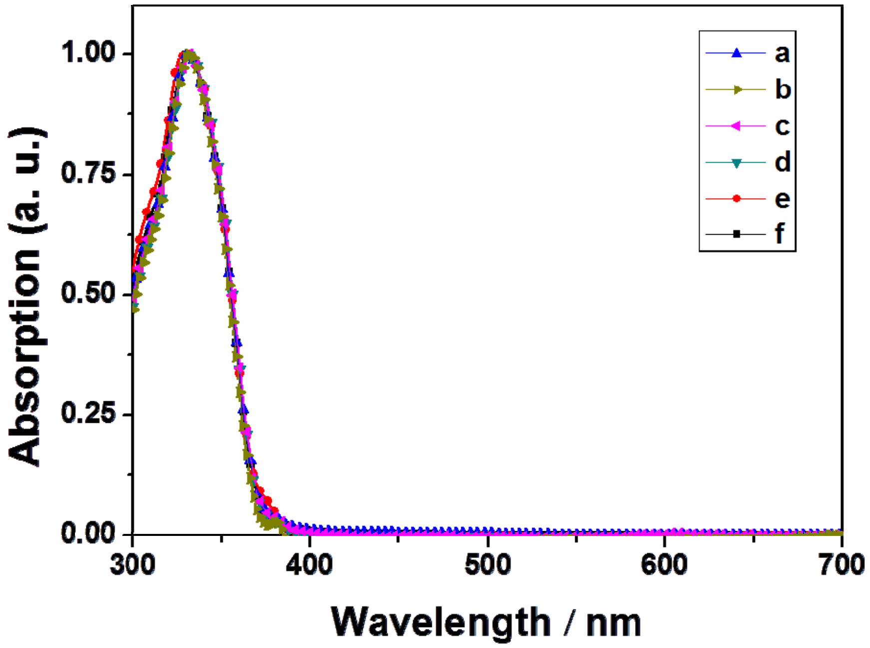


Figure S4: SEM image of **P1** emulsion (scale bar: 1 μm)



Fiure S5: SEM image of **P1** solid powders prepared for different reaction time: 6 h (**a**), 12 h (**b**), 24 h (**c**), 48 h (**d**). (scale bar: 500 nm)

a


Absorption (a. u.)
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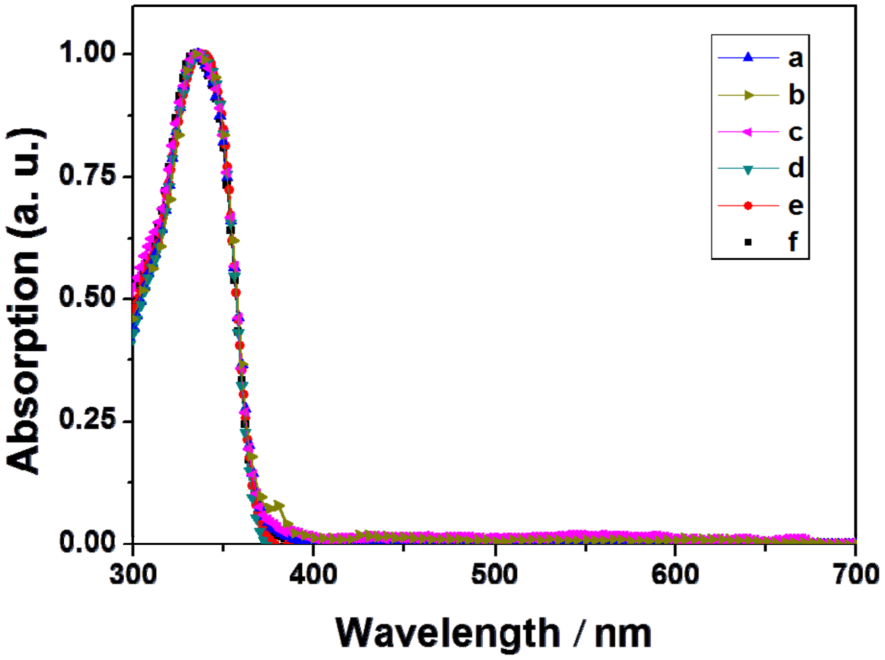
0.25
0.00
300
400
500
600
700
Wavelength / nm
a
b
c
d
e
f

b


Absorption (a. u.)
1.00
0.75
0.50
0.25
0.00
300
400
500
600
700
Wavelength / nm
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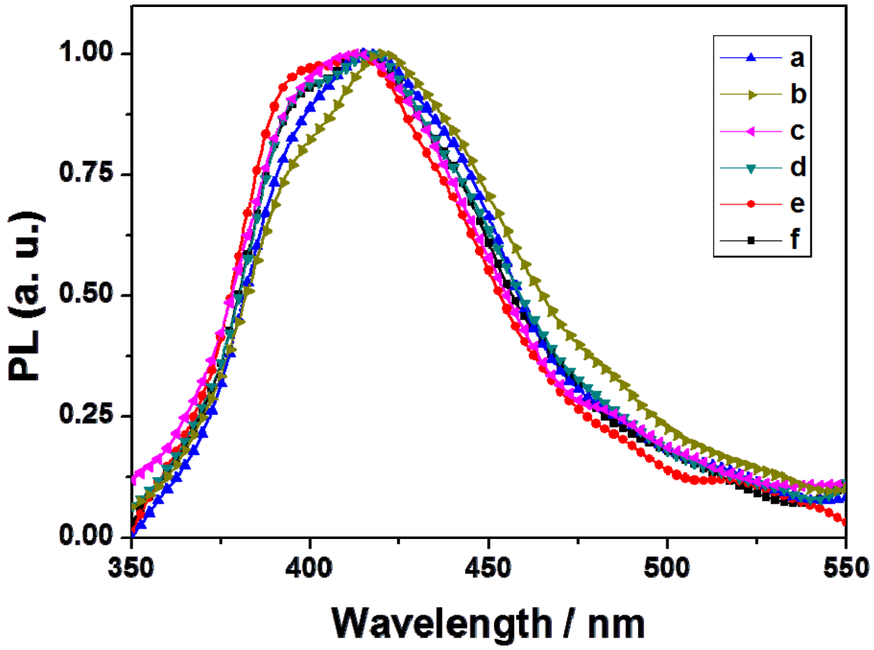
c
d
e
f

c



d

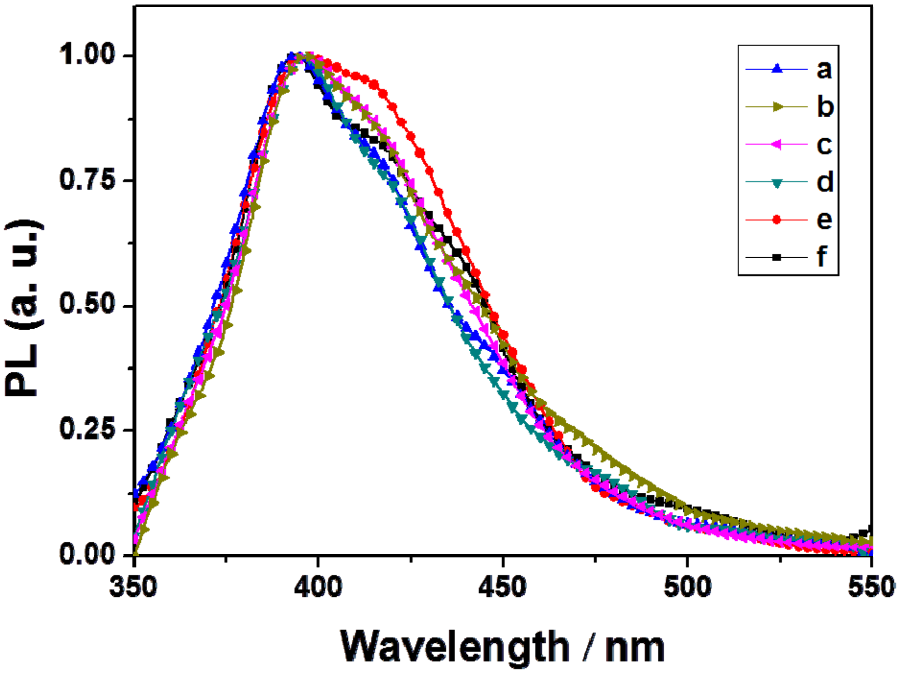


Figure S6: Absorption for **P1** (Entry 1~6) emulsion (**a**) and THF (**b**) solution; and emission for **P1** (Entry 1~6) emulsion (**c**) and THF (**d**) solution.

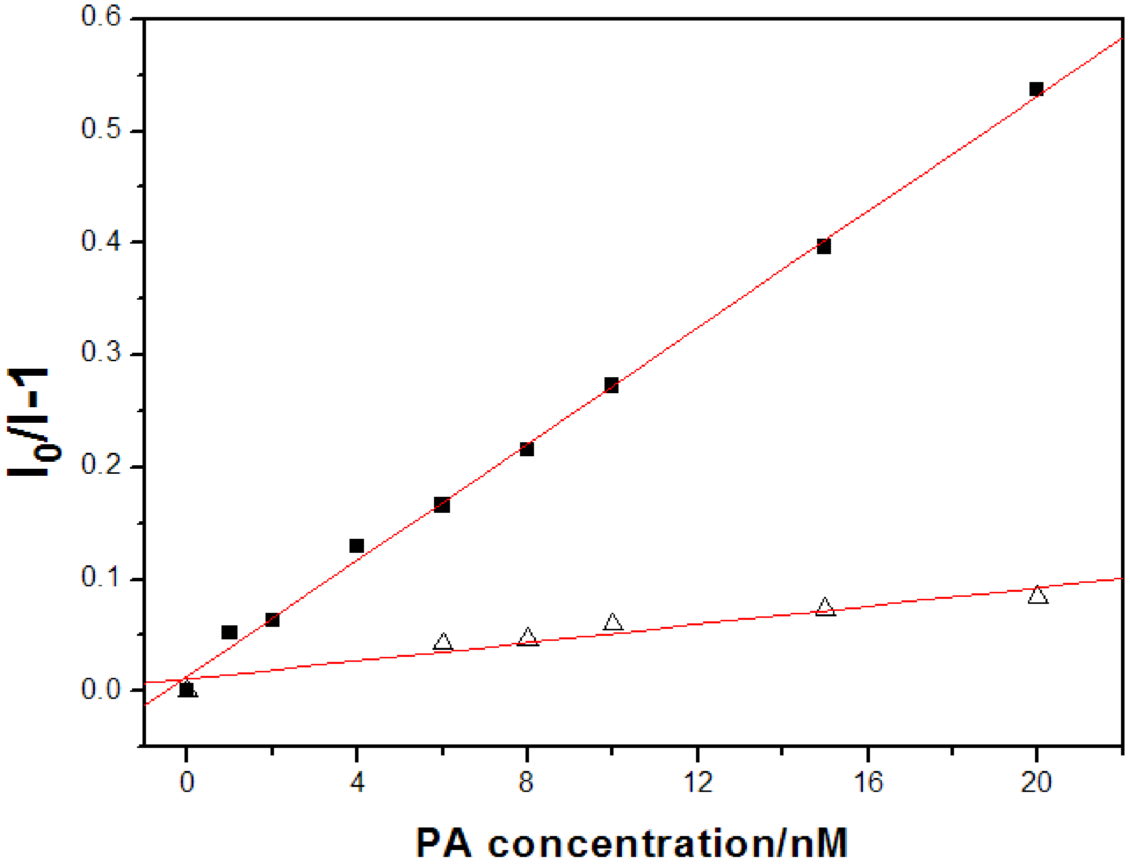


Figure S7: Stern-Volmer plot of the emission quenching of **P1 (■)** and **P2 (Δ)** emulsion by PA (at the low PA concentration region).

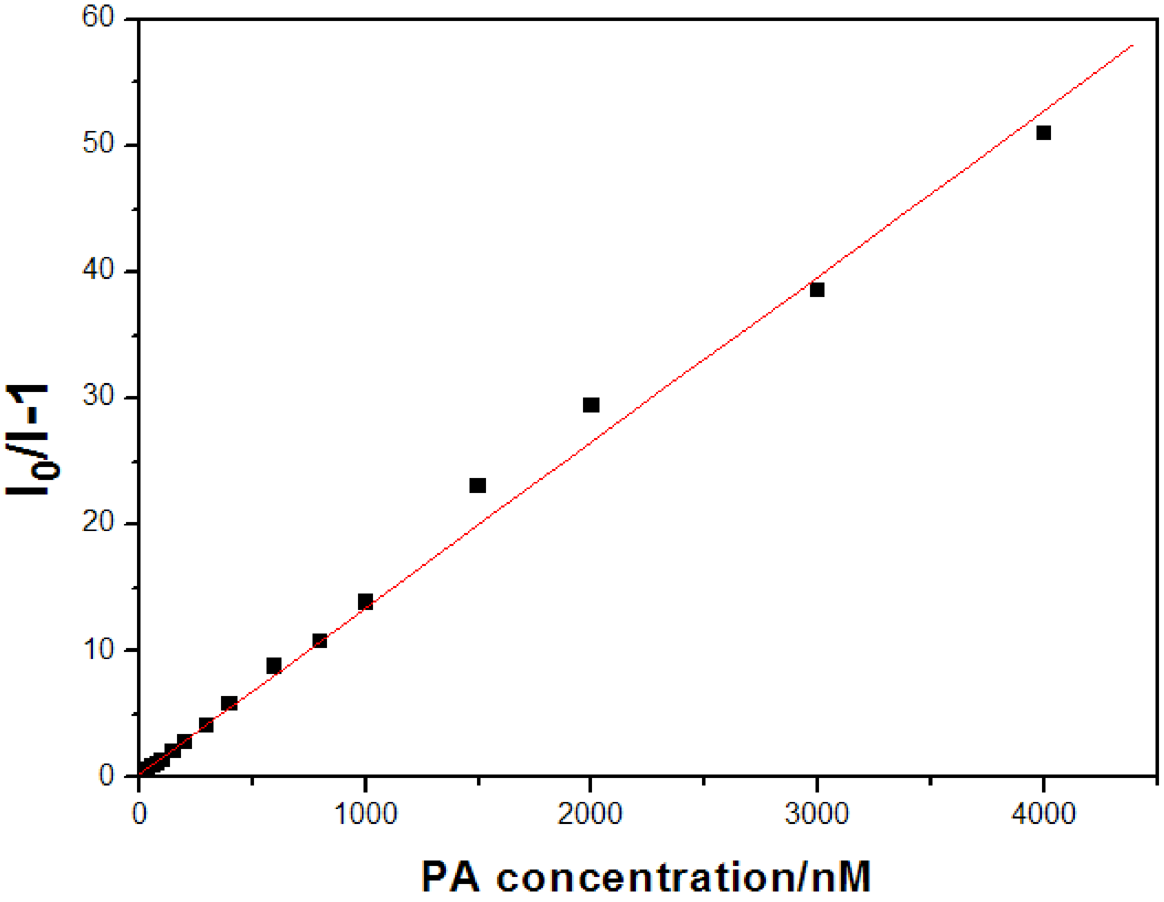


Figure S8: Stern-Volmer plot of the emission quenching of **P1 (■)** emulsion by PA.

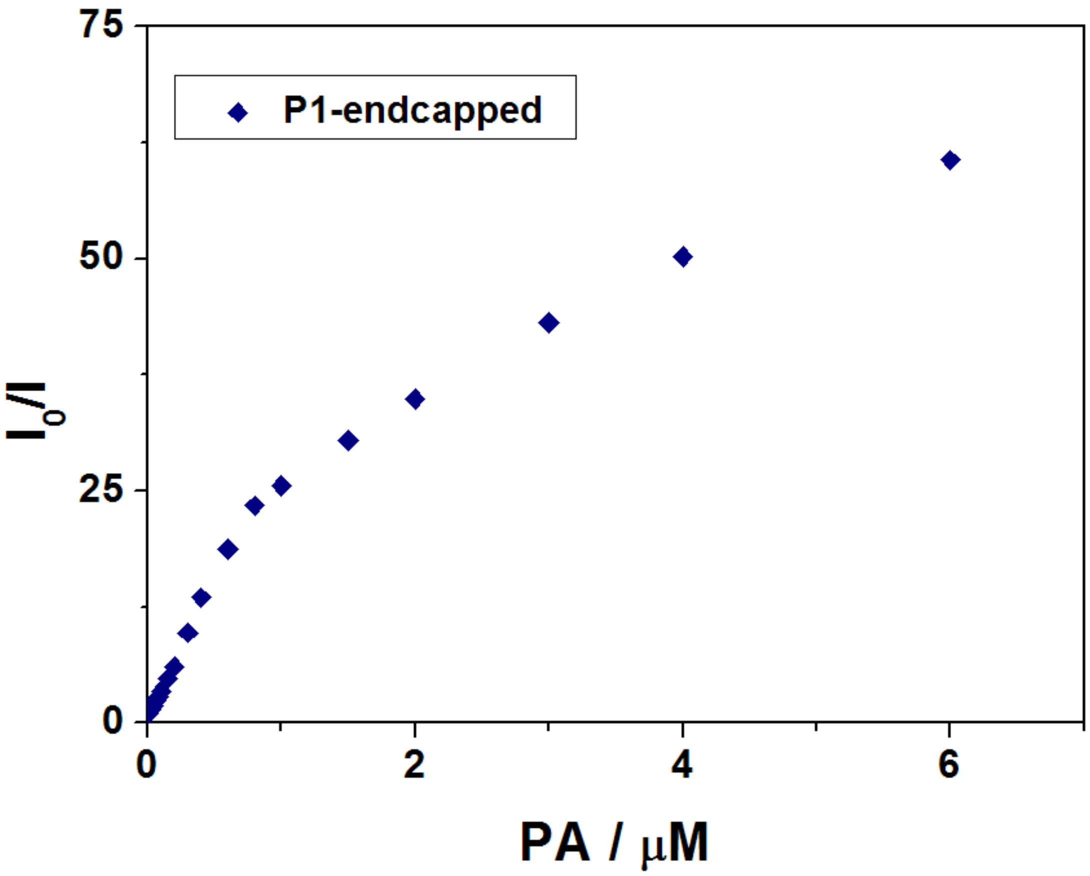


Figure S9: Stern-Volmer plot of **P1-endcapped** emulsion in the presence of different concentrations of picric acid in aqueous solution.

Hyperbranched polymers will have numerous end groups, which might have influence on their sensing properties. Thus, we prepared **P1** endcapped with 4-methoxybenzeneboronic acid (1,3-propanediol) ester and 4-bromoanisole. Anyway, **P1-endcapped** exhibits similar absorption and emission spectra and particle size as **P1**. The quenching behavior of **P1-endcapped** (**Figure S7**) is also close to **P1**, both of which are much better than that of **P2** **(Figure 4)**.

Reference:

1. Y. Xin, G. A.Wen, W. J. Zeng, L. Zhao, X. R. Zhu, Q. L. Fan, J. C. Feng, L. H. Wang, W. Wei, B. Peng, Y. Cao, W. Huang, *Macromolecules* 2005**, 38**, 6755.