Supporting Information

Size-dependent fluorescence of conjugated polymer dots and correlation with the fluorescence in solution and in the solid phase of the polymer

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Experimental Section

1. Materials and instrumentation

1,4-Dibromo-2,5-bis(octyloxy)benzene (M1), 2,5-bis(octyloxy)phenyldiboronic acid (M2), and 4,7-dibromo-2,1,3-benzothiadiazole (M3) were synthesized using previously published methods.[X1,X2] Tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) was purchased from Sigma Aldrich (U.S.A.). Acetonitrile and chloroform were obtained from Samchun Chemicals (Korea). ^{1}H and ^{13}C NMR spectra were obtained with a Bruker DRX-300 spectrometer with tetramethylsilane as the internal standard (Korea Basic Science Institute). Elemental analysis was performed with an Elemental Analyzer EA 1108 (Fisons Instruments). Fourier transform infrared (FT-IR) spectra were recorded on a Bruker FT-IR spectrometer. Ultraviolet-visible (UV-vis) absorption spectra were recorded on a PerkinElmer Lambda 35 spectrometer. Photoluminescence spectra were taken using a Varian Cary Eclipse spectrophotometer equipped with a Xe lamp excitation source. A gel permeation chromatograph (GPC) equipped with GMHHRM columns and a Bischoff LAMBDA 1000 detector was used for determination of molecular weights against polystyrene standards (at 1.32K, 2.78K, 6.77K, 19.5K, 51.2K, 126K, 282K, and 791K g/mol) using tetrahydrofuran (THF) as the eluent. The amount of Se in the polymers was determined using an inductively coupled plasma-mass spectrometer (ICP-MS, ELAN 6000, ELAN DRC II, PerkinElmer). The Pdot sizes were measured using dynamic light

scattering (DLS, Zetasizer Nano ZS, Malvern).

2. Synthesis of CPs

2.1. CP-W1

M1 (492.3 mg, 1.0 mmol), M2 (591.0 mg, 1.4 mmol), and M3 (13.6 mg, 0.04 mmol) were placed in a three-necked round-bottom flask containing a mixture of dry toluene and THF and 2 M aqueous potassium carbonate solution (8 mL) under N_2 atmosphere. After addition of $(PPh_3)_4Pd(0)$ (81 mg, 0.07 mmol) and a few drops of a phase transfer catalyst (Aliquat 336), the reaction mixture was stirred at 90 °C for 36 h. After polymerization, the mixture was cooled to room temperature and added slowly to a large volume of methanol (120 mL). The resulting precipitate was isolated by filtration and washed repeatedly with water, methanol, and acetone. The polymer was dissolved in chloroform and precipitated consecutively from methanol and acetone. Finally, a yellow powder was obtained after drying under vacuum (yield 0.45 g, 66%).

^1H NMR (300 MHz, $CDCl_3$): δ 7.66–7.52 (br), 7.2–7.0 (br), 4.2–4.0 (br), 3.8–3.7 (br), 3.1–2.9 (br), 2.3–1.7 (br), 1.6–1.3 (br) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 150.45, 129.09, 116.30, 77.22, 69.63, 31.84, 29.72, 29.40, 29.29, 26.13, 22.68, 14.11 ppm. FT-IR (KBr pellet): 2925–2852 (sp^2 C–H), 1638 (C=N), 1490 (C=C), 1381 (aryl C–N), 1328 (–CH_2–) 826 cm^{-1} (C–O). Elemental analysis found (%): C 76.32, H 10.45, N 0.47, S 0.05.

2.2. CP-W2

M1 (492.3 mg, 1.0 mmol), M2 (591.0 mg, 1.4 mmol), and M3 (34.1 mg, 0.1 mmol) were placed in a three-necked round-bottom flask containing a mixture of dry toluene and THF and 2 M aqueous potassium carbonate solution (8 mL) under N_2 atmosphere. Subsequent procedures were the same that used for CP-W1. Finally, a orange powder was obtained after drying under vacuum with a yield of 0.38 g (53.3%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.68–7.60 (br), 7.48–7.32 (br), 7.20–6.81 (br), 6.66 (s), 5.78 (s), 5.67 (s), 4.03–3.90 (br), 1.90–1.52 (br), 1.46–1.07 (br), 0.87 (s) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 150.06, 117.33, 77.26, 69.56, 31.92, 29.61, 29.49, 29.36, 26.15, 22.69, 14.09 ppm. FT-IR (KBr pellet): 2924–2852 (sp^2 C–H), 1637 (C=N), 1489 (C=C), 1379 (aryl C–N), 1323 (–CH_2–) 827 cm^{-1} (C–O). Elemental analysis found (%): C 77.85, H 10.59, N 0.90, S 0.11

2.3. CP-W3

M1 (492.3 mg, 1.0 mmol), M2 (591.0 mg, 1.4 mmol), and M3 (68.2 mg, 0.2 mmol) were placed in a three-necked round-bottom flask containing a mixture of dry toluene and THF and 2 M aqueous potassium carbonate solution (8 mL) under N_2 atmosphere. Subsequent procedures were the same that used for CP-W1. Finally, a gray powder was obtained after drying under vacuum with a yield of 0.43 g (55.4%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.76–7.59 (br), 7.38–7.31 (br), 7.22–6.76 (br), 6.66 (s), 5.67 (s), 4.03–3.73

(br), 1.86–1.78 (br), 1.75–1.46 (br), 1.42–1.07 (br), 1.42–1.07 (br), 0.87 (s) ppm. ^{13}C NMR

(75.5 MHz, CDCl$_3$): δ 77.21, 69.53, 31.91, 29.61, 29.49, 29.36, 26.15, 22.68, 14.10 ppm. FT-

IR (KBr pellet): 2925–2851 (sp^2 C–H), 1638 (C=N), 1487 (C=C), 1380 (aryl C–N), 1323 (–

CH$_2$–) 825 cm^{-1} (C–O). Elemental analysis found (%): C 74.95, H 9.08, N 0.95, S 1.63.

3. Preparation of Pdots

Pdots from CP-W1, CP-W2 and CP-W3 with various sizes were prepared by the

conventional reprecipitation method. The fabrication was carried out in an aqueous

medium at room temperature. The polymer was dissolved in THF with concentrations

of 0.001 to 0.5 mg/mL. The polymer solution (1 mL) was quickly added into Milli-Q

water (12 mL) under vigorous sonication, allowing the formation of nanoparticles, and

then the THF was removed by nitrogen stripping. The solution was filtered with a 0.45

µm syringe filter. The aqueous medium containing finely dispersed Pdots was

transparent and stable for more than 2 weeks without any aggregation. Pdots with

sizes ranging from 30 to 113 nm (as determined by DLS) were obtained. The Pdots

were denoted by their average diameter as determined with DLS. For example, CP-

W1dot92 and CP-W1dot31 were fabricated using CP-W1 and their hydrodynamic

diameters were 91.8 and 31.28 nm, respectively.

4. Cyclic voltammetry (CV)

CV was performed with a BAS 100B electrochemical analyzer in a three-electrode cell with a Pt wire counter electrode, a Ag/AgCl reference electrode, and a glassy carbon working electrode at a scan rate of 10 mV s^{-1} with 0.1 M Bu$_4$NPF$_6$ as the supporting electrolyte in anhydrous acetonitrile solution purged with N$_2$ at room temperature. CP films were fabricated by drop-casting of their chloroform solutions on a glassy C working electrode to perform electrochemical analysis.

5. Calculation of the number of CP chains in a single Pdot

The number of CP chains in a single Pdot (n) was calculated from the hydrodynamic size of Pdots, determined by DLS.[X3] For the calculation of n, Pdot shape was assumed to be spherical and following equation (1) was used.

$$n = \rho V \frac{N}{M_w} = \rho \frac{\pi D^3 N}{6 M_w}, \quad (1)$$

where M$_n$, N, V, D, and ρ are number-average molecular weight of CP (g/mol), Avogadro constant, volume of a Pdot (cm^3), hydrodynamic size of Pdot (cm), and density of Pdot, respectively. The density of Pdot was assumed to be 1.1 g/cm^3, because CP is compactly packed within Pdot dispersed in water. For example, the number of CP-W2 chains in a CP-W2dot38 was calculated as follow:

$$n = 1.1 \times \frac{1g}{cm^3} \times \frac{3.14 \times (37.81 \times 10^{-7} cm)^3 \times (6.02 \times 10^{23} mol^{-1})}{6 \times 31000 mol^{-1} g} = 6.04 \times 10^2.$$

The number of CP chains in a Pdot with various sizes are tabulated in Table 3.
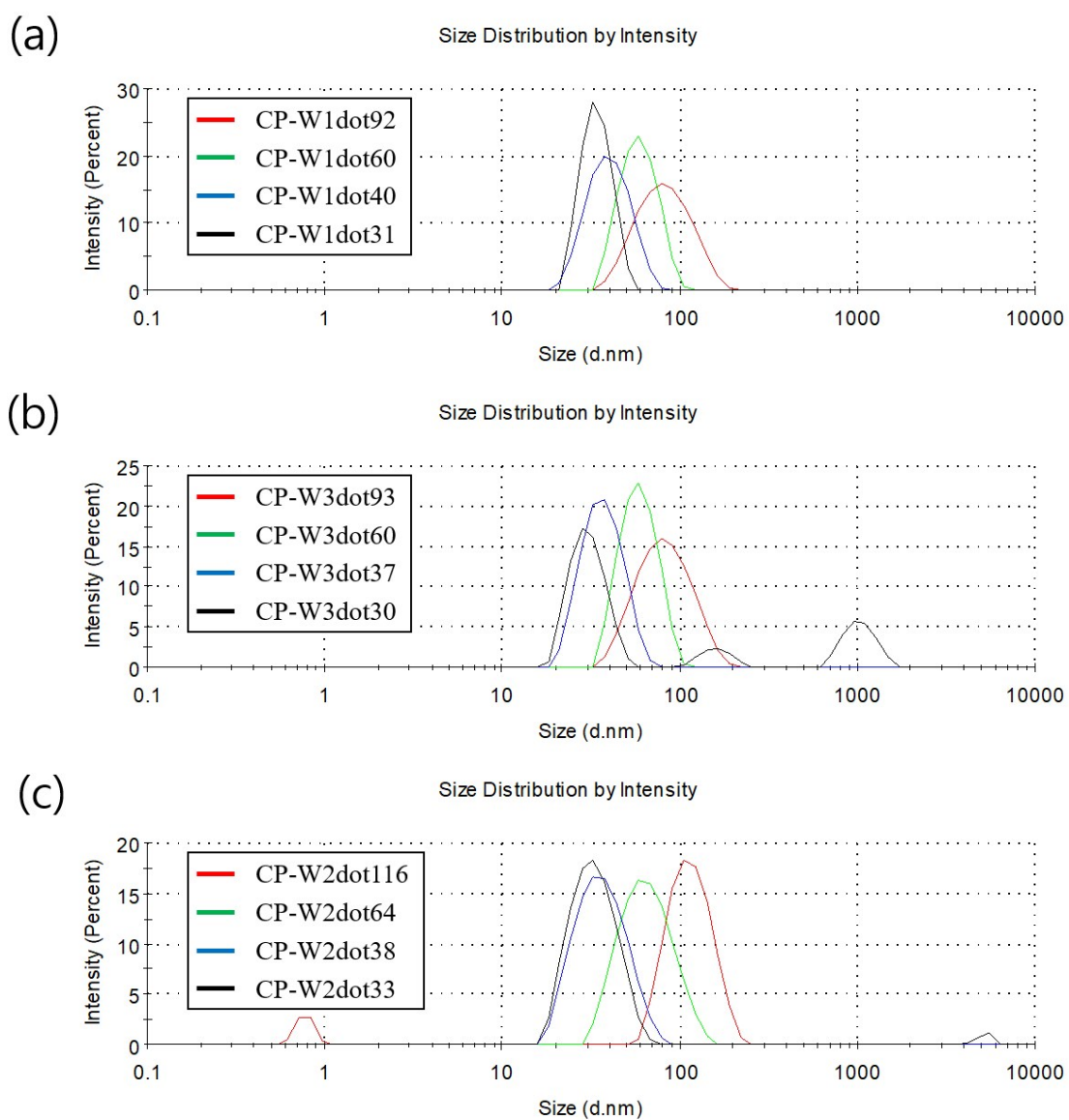
(a)

Size Distribution by Intensity

Legend:
- CP-W1dot92 (red)
- CP-W1dot60 (green)
- CP-W1dot40 (blue)
- CP-W1dot31 (black)

x-axis: Size (d.nm); y-axis: Intensity (Percent)

(b)

Size Distribution by Intensity

Legend:
- CP-W3dot93 (red)
- CP-W3dot60 (green)
- CP-W3dot37 (blue)
- CP-W3dot30 (black)

x-axis: Size (d.nm); y-axis: Intensity (Percent)

(c)

Size Distribution by Intensity

Legend:
- CP-W2dot116 (red)
- CP-W2dot64 (green)
- CP-W2dot38 (blue)
- CP-W2dot33 (black)

x-axis: Size (d.nm); y-axis: Intensity (Percent)

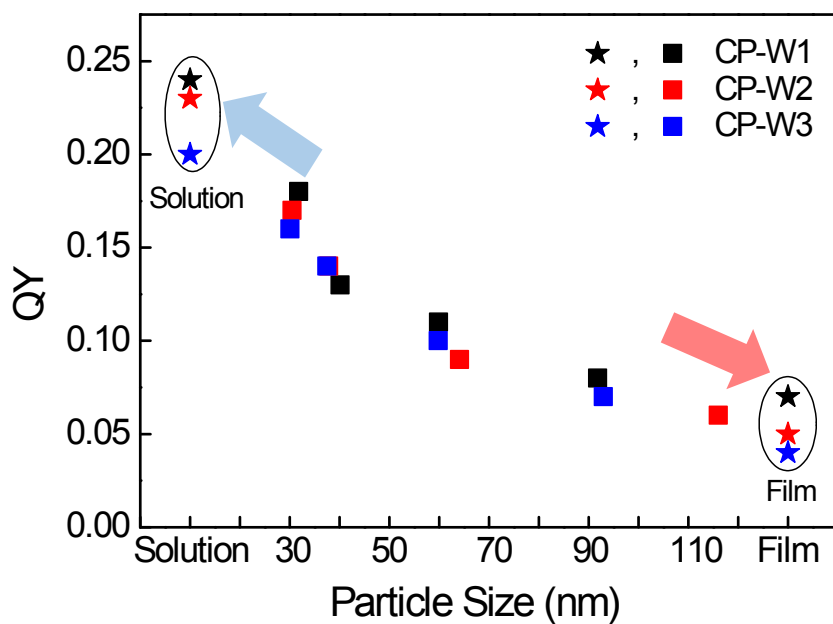**Fig. S1**. DLS data of (a) CP-W1dots, (b) CP-W2dots, and (c) CP-W3dots.

Fig. S2. Changes in the QYs of CP-W1, CP-W2, and CP-W3 in their THF solutions and in the solid films, and in the forms of Pdots with different sizes. Excitation wavelength: 357 nm (CP-W1); 336 nm (CP-W2); 333 nm (CP-W3). QYs were determined relative to rhodamine B.
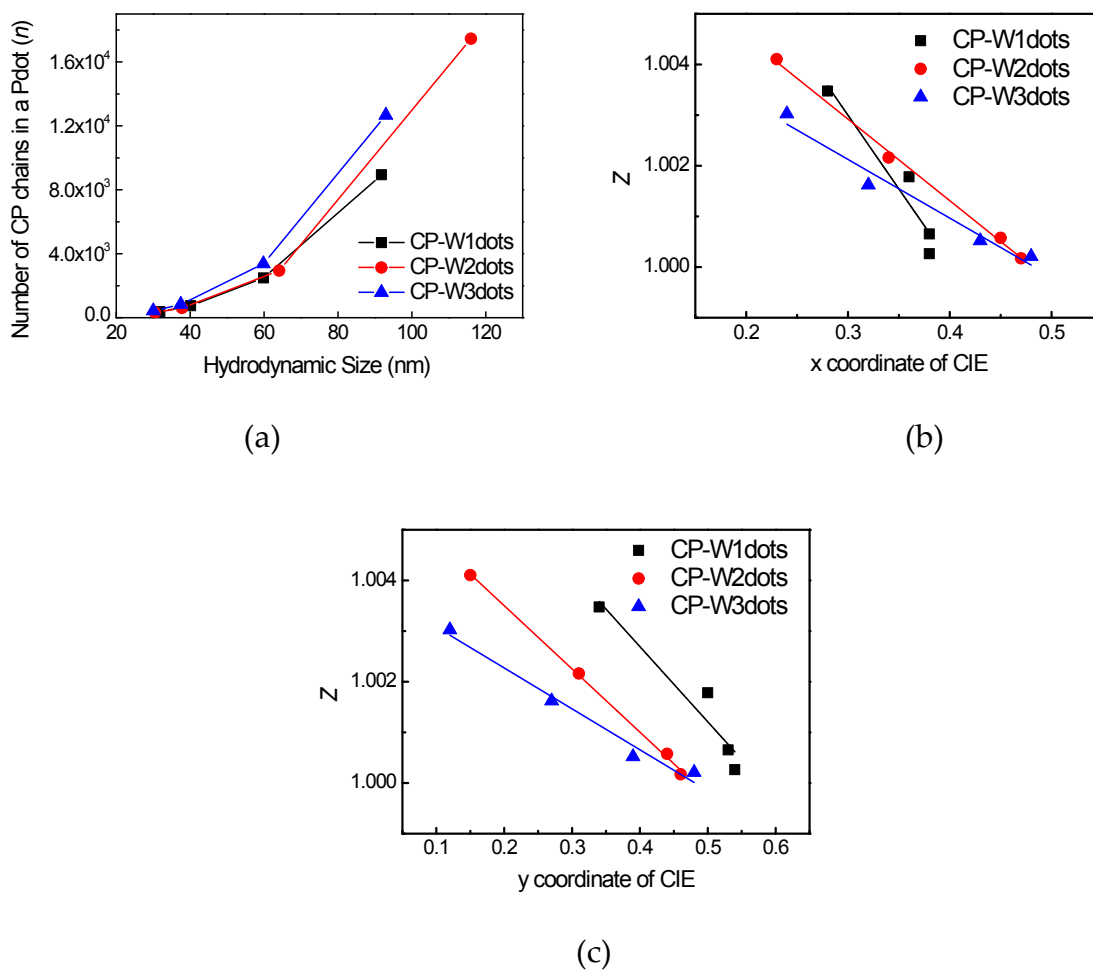
(a)

(b)

(c)

Fig. S3. (a) Change in the number of CP chains in a Pdot with various sizes. Relationship between the number of CP chains in a Pdot and CIE coordinates (b) x and (c) y. $Z = exp^{1/(\log(n))^6}$

Table S1. Monomer Feed Ratios and Molecular Weights of the CPs

	M1	M2	M3	$M_n{}^a$	$M_w{}^a$	PDI	Se content (wt%)[b]	m : n[c]
CP-W1	1	1.4	0.04	1.8×10^4	3.0×10^4	1.69	0.44	0.963 : 0.037
CP-W2	1	1.4	0.1	1.9×10^4	3.1×10^4	1.58	0.77	0.936 : 0.064
CP-W3	1	1.4	0.2	1.5×10^4	2.2×10^4	1.50	1.84	0.850 : 0.150

[a] determined by GPC

[b] determined by ICP

[c] calculated based on the Se content

Table S2. Optical Properties of CPs

polymers	$\lambda_{Abs.max}$ (nm)		$\lambda_{Em.max}$ (nm)		$E_{g.opt}^{c}$ (eV)	E_{HOMO}^{d} (eV)	E_{LUMO}^{e} (eV)	$E_{ox.onset}$ (V)
	solution[a]	film[b]	solution[a]	film[b]				
CP-W1	348	357	411	550	2.51	-5.79	-3.28	0.99
CP-W2	335	336	401	583	2.47	-5.54	-3.07	0.74
CP-W3	333	333	404	583	2.41	-5.43	-3.02	0.63

[a] in THF.

[b] Thin film of CPs on slide glass, formed by spin-coating 1wt% CP solution in $CHCl_3$.

[c] Optical bandgap calculated from the film-state absorption onset wavelength.

[d] HOMO levels were determined from onset potential of the first oxidation cyclic voltammogram with reference to ferrocene at -4.8 eV.

[e] LUMO levels were calculated from the HOMO and $E_{g.opt}$

Table S3. Sizes of Pdots and Caculated Number of CP chains (*n*) in a Single Pdot

CPs	Concentrations[a] (mg/mL)	Pdots	Hydrodynamic sizes (nm)[b]	n^c	Z^d
CP-W1	0.5	CP-W1dot92	91.80	8.94×10^3	1.000263
	0.05	CP-W1dot60	59.89	2.48×10^3	1.000654
	0.01	CP-W1dot40	40.13	7.47×10^2	1.00178
	0.001	CP-W1dot31	31.81	3.72×10^2	1.003474
CP-W2	0.5	CP-W2dot116	116.02	1.75×10^4	1.000172
	0.05	CP-W2dot64	64.08	2.94×10^3	1.000574
	0.01	CP-W2dot38	37.81	6.04×10^2	1.002163
	0.001	CP-W2dot33	30.47	3.16×10^2	1.004104
CP-W3	0.5	CP-W3dot93	92.97	1.27×10^4	1.0002098
	0.05	CP-W3dot60	59.84	3.38×10^3	1.0005184
	0.01	CP-W3dot37	37.47	8.29×10^2	1.0016198
	0.001	CP-W3dot30	30.04	4.27×10^2	1.0030232

[a] Concentrations (mg/mL of THF) used for fabrication of Pdots

[b] Determined by DLS

[c] Calculated from equation 1

[d] $Z = exp^{1/(\log(n))^6}$

Table S4. CIE Coordinates of CPs in THF solutions and in the Films, and Pdots

	CIE coordinates (x, y)					
CP-W1	Film	CP-W1dot92	CP-W1dot60	CP-W1dot40	CP-W1dot31	Solution
	(0.38, 0.55)	(0.38,0.54)	(0.38,0.53)	(0.36,0.50)	(0.28,0.34)	(0.20, 0.11)
CP-W2	Film	CP-W2dot116	CP-W2dot64	CP-W2dot38	CP-W2dot33	Solution
	(0.47, 0.47)	(0.47,0.46)	(0.45,0.44)	(0.34,0.31)	(0.23,0.15)	(0.20, 0.08)
CP-W3	Film	CP-W3dot93	CP-W3dot60	CP-W3dot37	CP-W3dot30	Solution
	(0.49,0.47)	(0.48, 0.48)	(0.43,0.39)	(0.32,0.27)	(0.24, 0.12)	(0.20,0.12)

Table S5. Quantum yields of CPs in THF solutions and in the Films, and Pdots

	QY[a]					
CP-W1	Film	CP-W1dot92	CP-W1dot60	CP-W1dot40	CP-W1dot31	Solution
	0.07	0.08	0.11	0.13	0.18	0.24
CP-W2	Film	CP-W2dot116	CP-W2dot64	CP-W2dot38	CP-W2dot33	Solution
	0.05	0.06	0.09	0.14	0.17	0.23
CP-W3	Film	CP-W3dot93	CP-W3dot60	CP-W3dot37	CP-W3dot30	Solution
	0.04	0.07	0.10	0.14	0.16	0.20

[a] relative to rhodamine B

Reference

X1. C. Kim, S. -Y. Kim, Y. T. Lim and T. S. Lee, *Macromol. Res.*, 2017, **25**, 572-577.

X2. R. Yang, R. Tian, J. Yan, Y. Zhang, J. Yang, Q. Hou, W. Yang, C. Zhang and Y. Cao, *Macromolecules*, 2005, **38**, 244–253.

X3. G. Feng, K. Li, J. Liu, D. Ding and B. Liu, *Small*, 2014, **10**, 1212–1219.