Supporting Information

for

Synthesis of Fluorescent Conjugated Polymer Nanoparticles and Their Immobilization on a Substrate for White Light Emission

Choongho Kim,* Young Jin Gwon,* Jongho Kim, Taek Seung Lee**

Organic and Optoelectronic Materials Laboratory, Department of Advanced Organic Materials and Textile System Engineering, Chungnam National University, Daejeon 34134, Korea

*These authors contributed equally.

**Corresponding author: TSL (tslee@cnu.ac.kr)

Synthesis of monomers

1,4-Bis(octyloxy)benzene (1)

Hydroquinone (7 g, 63.5 mmol) and potassium hydroxide (7.06 g, 126 mmol) were dissolved in DMSO (100 mL) in a three-neck flask equipped with a reflux condenser. Then 1-bromooctane (23.94 mL, 138.6 mmol) was added dropwise to the mixture. The reaction was carried out at 85 °C for 4 h. After the reaction, the mixture was precipitated in distilled water. The product was washed with ethanol and recrystallized from ethanol to yield 14 g (64 %) of 1. ¹H NMR (300 MHz, CDCl₃) δ_{ppm} = 6.82 (s, 4H), 3.82–3.87 (t, 4H), 1.80–1.70 (m, 4H), 1.46–1.41 (m, 4H), 1.38–1.28 (m, 16H), 0.91–0.86 (t, 6H).

1,4-Dibromo-2,5-bis(octyloxy)benzene (2)

1 (2.0 g, 6.0 mmol) was dissolved in chloroform (20 mL) in a three-neck flask. A mixture of chloroform (5 mL) and bromine (1.23 mL, 24 mmol) was added dropwise to the flask at 0 °C for 1 h. After 1 h, the temperature was increased to room temperature and the mixture was stirred for an additional 6 h and then quenched with NaHSO₃ solution (40 mL). The organic mixture was extracted with brine. The organic phase was dried over anhydrous MgSO₄, isolated by filtration, and concentrated with a rotary evaporator. The crude product was recrystallized from n-hexane to yield 1.9 g (65 %) of **2**. ¹H NMR (300 MHz, CDCl₃) $\delta_{ppm} = 7.09$ (s, 2H), 3.97–3.92 (t, 4H), 1.83–1.78 (m, 4H), 1.56–1.45 (m, 4H), 1.32–1.29 (m, 16H), 0.91–0.87 (t, 6H)

2,5-Dioctyloxyphenyldiboronic acid (3)

n-BuLi (8.9 mL, 2.0 M in cyclohexane) was added to a solution of **2** (3.8 g, 7.7 mmol) in a dry ether (30 mL) at -20 °C under argon atmosphere and then trimethylborate (19.3 mmol, 2.2 mL) was added. The temperature was raised to room temperature and stirred for 12 h. 2 M HCl solution (20mL) was added to the reaction mixture and the precipitate was collected by filtration and washed with ether (20 mL) and water (10 mL), affording colorless solid (yield 2.5 g, 74 %). ¹H NMR (300 MHz, DMSO-*d*₆) $\delta_{ppm} = 7.80$ (s, 4H), 7.19 (s, 2H), 4.00 (t, 4H), 1.73 (t, 4H), 1.27 (m, 16H), 0.73 (t, 6H). B NMR (400 MHz, DMSO-*d*₆) 3.47 (s).

4,7-Dibromo-2,1,3-benzothiadiazole (4)

A mixture of 2,1,3-benzothiadiazole (10.0 g, 73.4 mmol) in 48% hydrobromic acid (100 mL) was refluxed with stirring while bromine (35.6 g, 11.3 mL, 220.3 mmol) was added slowly. After completion of the bromine addition, the reaction mixture became a suspension of solid in hydrobromic acid. More hydrobromic acid (10 mL) was added and the mixture was heated under reflux for another 2.5 h. The mixture was isolated by filtration, washed thoroughly with water, recrystallized from chloroform, and dried in a vacuum oven to give white needle crystals (yield 12 g, 70%). ¹H NMR (300 MHz, CDCl₃) $\delta_{ppm} = 7.74$ (s, 2H).

4,7-Di-2-thienyl-2,1,3-benzothiadiazole (5)

To a solution of **4** (1 g, 3.4 mmol) and tributyl(2-thienyl)stannane (3.17 g, 8.5 mmol) in THF (50 mL), Pd(PPh₃)₄ (0.078 g, 0.068 mmol) was added. The mixture was refluxed under a nitrogen atmosphere for 3 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (eluent: CH₂Cl₂–hexane; 1:1). Recrystallization from ethanol gave **5** as red needles (yield 0.9 g, 88 %). ¹H NMR (300 MHz, CDCl₃) $\delta_{ppm} = 8.13$ (m, 2H), 7.87 (s, 2H), 7.47 (d, 2H), 7.22 (m, 2H).

4,7-Bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (6)

To a mixture of chloroform (100 mL) and acetic acid (100 mL), **5** (5.0 g, 16.7 mmol) was added under a nitrogen flow. After the solid was dissolved completely, N-bromosuccinimide (NBS, 7.404 g, 41.6 mmol) was added in one portion. The reaction mixture was stirred at room temperature overnight, and the dark red precipitate formed was filtered off and recrystallized from DMF to give **6** (yield 2.0 g, 26 %) as shiny red crystals. ¹H NMR (300 MHz, CDCl₃) δ_{ppm} = 7.81 (m, 4H), 7.17 (d, 2H).



Scheme S1. Preparation of CPdots from CPs.





Figure S1. Changes in fluorescence spectra of (a) GP and (b) RP in the solid and solutions with various concentrations in chloroform.





Figure S2. (a) Cyclic voltammetry of RP, GP and BP (vs. Ag/Ag^+ in acetonitrile solution with 0.1 M *n*-Bu₄NPF₆ as supporting electrolyte). (b) Energy level diagrams of RP, GP, and BP and interparticle energy transfer between them..



(b)

(c)



(d)

Figure S3. SEM images and DLS of (a) BCPdots; (b) GCPdots; (c) RCPdots. (d) TEM images of RCPdots.



Figure S4. Calibration curves of (a) BP, (b) GP, and (c) RP in chloroform solutions, derived from UV absorbance.





Figure S5. Fluorescence spectra of mixed solutions containing (a) BCPdots and GCPdots; (b) BCPdots and RCPdots; (c) GCPdots and RCPdots (The sample numbers are illustrated in Table S2).





Figure S6. SEM image of TPEON (a) before and (b) after immersion in water for 4 h.



Figure S7. (a) FT-IR spectra of PEO nanofibers and TPEON. (b) XPS spectra of TPEON and (c) amine-modified TPEON.





Figure S8. Contact angle images of (a) TPEON and (b) amine-modified TPEON. Contact angles: (a) 111.68° and (b) 81.48°.





(b)



(c)

Figure S9. SEM images of (a) TPEON, (b) amine-modified TPEON, and (c) CPdotsimmobilized WLE TPEON.



Figure S10. Photographs of WLE nanofibers (a) and WLE glass (b) on LED lamp (emission wavelength: 365 nm).

	$\lambda_{ ext{PL}}$ [nm]	E _{g,opt} [eV] ^{a)}	E _{red,onset} [V] ^{b)}	LUMO [eV] ^{c)}	HOMO [eV] ^{d)}
RP	625	1.98	-1.09	-3.35	-5.33
GP	534	2.58	-1.43	-3.01	-5.59
BP	425	3.59	-1.34	-3.10	-5.69

Table S1. Optical and Electrochemical Properties of Polymers

a) Estimated from the absorption onset (E_g = $1240/\lambda_{onset}$).

- b) Versus Ag/Ag⁺ in acetonitrile solution with 0.1 M *n*-Bu₄NPF₆ as supporting electrolyte, at a scan speed of 50 mV s⁻¹, $E_{1/2,F_c,F_c+} = 0.36$ V.
- c) The LUMO levels of polymers were calculated according to the formula: LUMO = $-(E_{red,onset} E_{1/2,Fc,Fc+} + 4.8) = -(E_{red,onset} + 4.44)$ eV, where $E_{red,onset}$ was determined from the onset potentials of the reduction waves.
- d) Estimated from $E_{HOMO} = E_{LUMO} E_{g,opt}$.

	BCPdots (µg/mL)	GCPdots (µg/mL)	RCPdots (µg/mL)
1	3.35		
2	6.76	1 21	
3	13.18	1.51	
4	26.75		
5	3.98		
6	6.82		4.43
7	12.69		4.43
8	23.32		
9		1.30	
10		1.46	4 43
11		1.54	4.40
12		1.83	

Table S2. Manipulation of the Concentration of CPdots to Obtain Non-energyTransfer between CPdots Based on Fluorescence Intensity (Related to Figure S5)

	Green arrow				Red arrow			
CPdots (µg/mL)	1	2	3	4	5	6	7	8
BCPdots	30.68	30.68	30.68	30.68	30.68	30.68	30.68	30.68
GCPdots	1.28	1.96	2.91	4.43	5.16	2.91	2.91	2.91
RCPdots	0	0	0	0	0	3.00	4.67	5.49

Table S3. Manipulation of CPdot Concentrations for Construction of WLENanofibers (Related to Figure 3a)

Table S4. Quantum Yields of WLEMs

	Sample name	Quantum yields (%)ª
	WLE CPdots solution	20
	WLE glass coated with CPdots	24
、减	WLE nanofibers coated with CPdots	38

^aQYs were determined using calibrated integrating sphere. Excitation source: 365 nm

laser.