Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic supplementary information

Polyazomethines based on oxadiazolyl or 1,2,4-triazolyl groups: synthesis and hole-buffering application in polymer light-emitting diodes

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Synthesis of 4-bromo-N-(4-bromobenzoyl)benzohydrazide (2). To a two-necked flask were added 4-bromobenzoyl chloride (**1**: 2.19 g, 10 mmol), hydrazine monohydrate (0.25 g, 5 mmol), and N-methyl-2-pyrrolidone (NMP, 20 mL) as solvent. The mixture was stirred for 6 h at room temperature under nitrogen atmosphere. The mixture was poured into a large amount of deionized water. The appearing solid was collected by filtration, dried, and then recrystallized from dimethyl sulfoxide (DMSO) and water to afford compound **2** (yield: 70.2%). ^{1}H NMR (DMSO-d_6, ppm): δ 10.62 (s, 2H, N-H), 7.86-7.84 (d, 4H, Ar-H), 7.75-7.73 (d, 4H, Ar-H).

Synthesis of 2,5-bis(4-bromophenyl)-1,3,4-oxadiazole (3). To a two-necked flask were added **2** (2.02 g, 5.3 mmol) and phosphorus(V) oxychloride ($POCl_3$, excess) as solvent. The mixture was stirred for 7 h at 100°C under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into a large amount of $NaHCO_3$ aqueous solution. The appearing crude product was collected by filtration, dried and then recrystallized from ethyl acetate to afford white crystals of **3** (yield: 77.7%). ^{1}H NMR (DMSO-d_6, ppm): δ 8.08-8.06 (d, 4H, Ar-H), 7.86-7.84 (d, 4H, Ar-H).

Synthesis of 1,2-bis((4-bromophenyl)chloromethylene)hydrazine (4). To a two-necked flask were added **2** (2.39 g, 6.0 mmol), phosphorus pentachloride (PCl_5, 3.12 g, 15.0 mmol), and toluene as solvent. The mixture was stirred at 100°C for 6 h under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into a large amount of $NaHCO_3$ aqueous solution, extracted with dichloromethane. The combined organic layers was dried over $MgSO_4$, concentrated by a rotary evaporator. The residue was further purified by recrystallization from ethanol and chloroform to afford white crystals of **4** (yield: 83.0%). ^1H NMR (DMSO-d_6, ppm): δ 8.00-7.98 (d, 4H, Ar-H), 7.82-7.80 (d, 4H, Ar-H).

Synthesis of 3,5-bis(4-bromophenyl)-4-phenyl-4H-1,2,4-triazole (5). To a two-necked flask were added **4** (2.0 g, 4.6 mmol), aniline (0.86 g, 9.2 mmol), and N,N-dimethylaniline as solvent. The mixture was stirred at 135°C for 12 h under nitrogen atmosphere. After cooling to room temperature, a large amount of 2N $HCl_{(aq)}$ (300 mL) was added and the mixture was stirred for 0.5 h. The appearing solids were collected by filtration, dried, and then purified by recrystallization from ethanol and chloroform to afford solid of **5** (yield: 75.6%). ^1H NMR (Acetone-d_6, ppm): δ 7.59-7.54 (m, 7H, Ar-H), 7.45-7.44 (d, 2H, Ar-H), 7.39-7.37 (d, 4H, Ar-H).

Synthesis of 2,5-bis[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)phenyl]-1,3,4-oxadiazole (6). To a two-necked flask were added **3** (0.76 g, 2.0 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (1.52 g, 6.0 mmol), potassium acetate (1.18 g, 12.0 mmol), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (49 mg, 0.06 mmol), and *p*-dioxane (20 mL) as solvent. The mixture was stirred at 90°C for 24 h under argon atmosphere. After cooling to room temperature, the mixture was poured into a large amount of deionized water. It was extracted with dichloromethane and the combined organic layer was dried over $MgSO_4$ and concentrated by a rotary evaporator. The residue was further purified by silica gel column chromatography using ethyl acetate and *n*-hexane (v/v = 1/6) as eluent to afford white solids of **6** (yield: 75.0%). ^{1}H NMR ($CDCl_3$, ppm): δ 8.15-8.14 (d, 4H, Ar-H), 7.97-7.96 (d, 4H, Ar-H), 1.38 (s, 24H, $-CH_3$).

Synthesis of 3,5-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-4-phenyl-4H-1,2,4-triazole (7). To a two-necked flask were added **5** (0.91 g, 2.0 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'- bi(1,3,2-dioxaborolane) (1.52 g, 6.0 mmol), potassium acetate (1.18 g, 12.0 mmol), $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (49 mg, 0.06 mmol), and *p*-dioxane (20 mL) as solvent. The mixture was stirred at 90°C for 24 h under argon atmosphere. After cooling to room temperature, the mixture was poured into a large amount of deionized water. It was extracted with dichloromethane and the combined organic layer was dried over $MgSO_4$ and concentrated by a rotary evaporator. The residue was further purified by silica gel column chromatography using methanol and dichloromethane (v/v = 1/100) as eluent to afford white solids of **7** (yield: 76.4%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.69-7.68 (d, 4H, Ar-H), 7.54-7.52 (m, 3H, Ar-H), 7.47-7.45 (d, 4H, Ar-H), 7.41-7.39 (d, 2H, Ar-H), 1.33 (s, 24H, $-CH_3$).

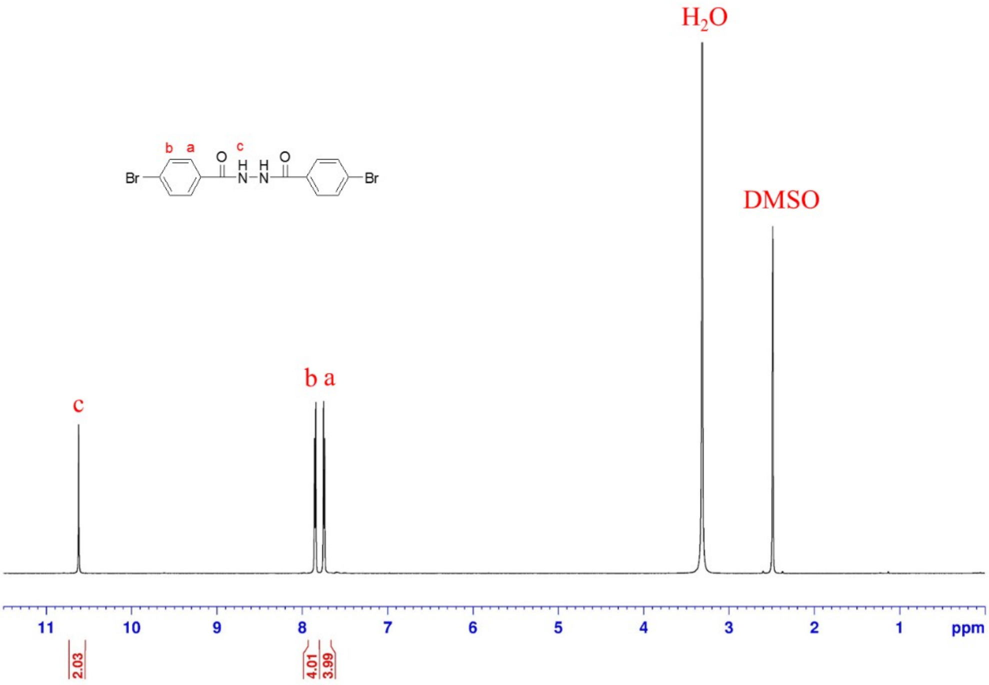

Fig. S1 ^{1}H NMR spectrum of compound **2**.

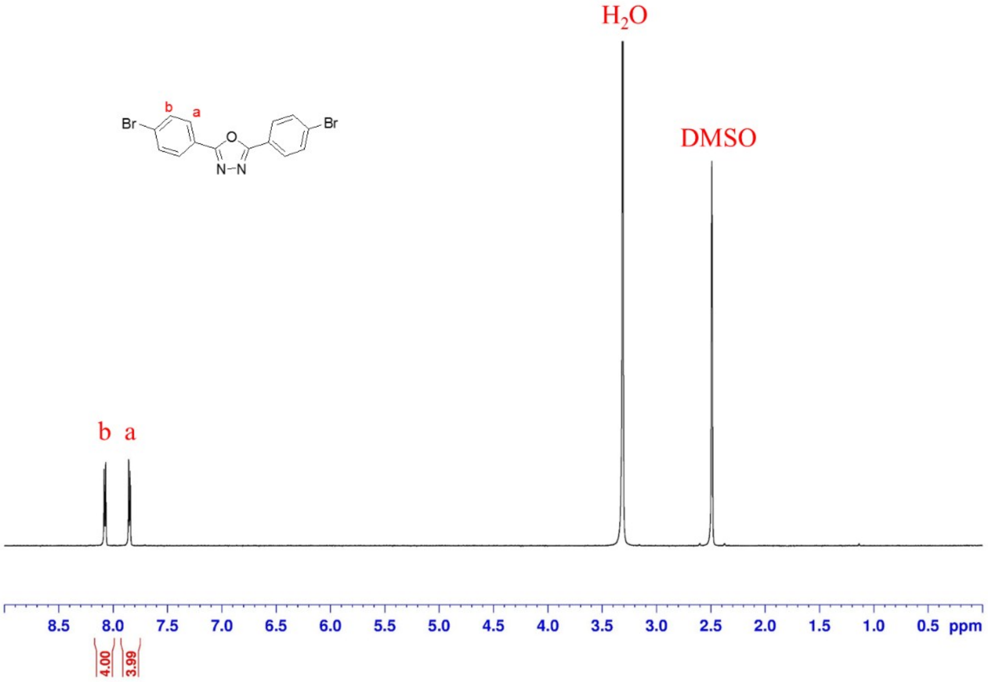

Fig. S2 ^{1}H NMR spectrum of compound **3**.

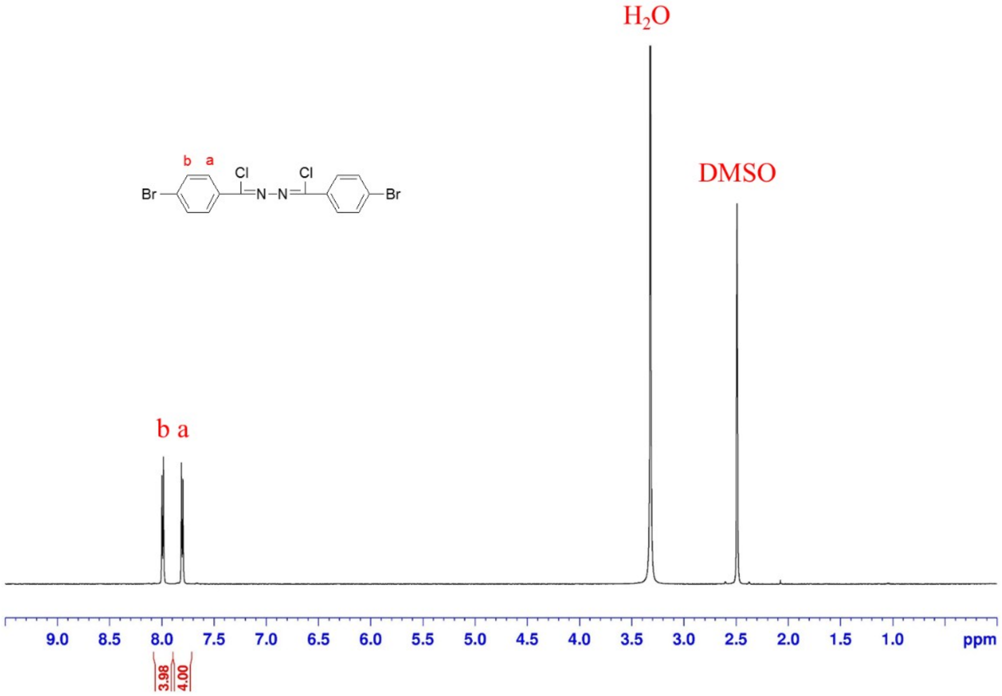

Fig. S3 ^{1}H NMR spectrum of compound **4**.

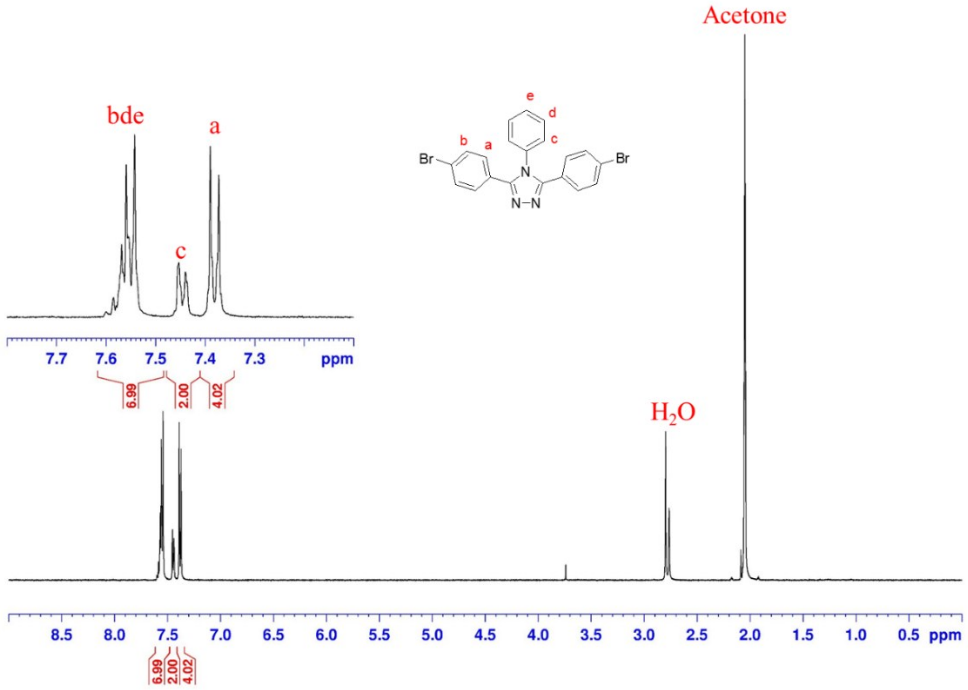

Fig. S4 ^{1}H NMR spectrum of compound **5**.

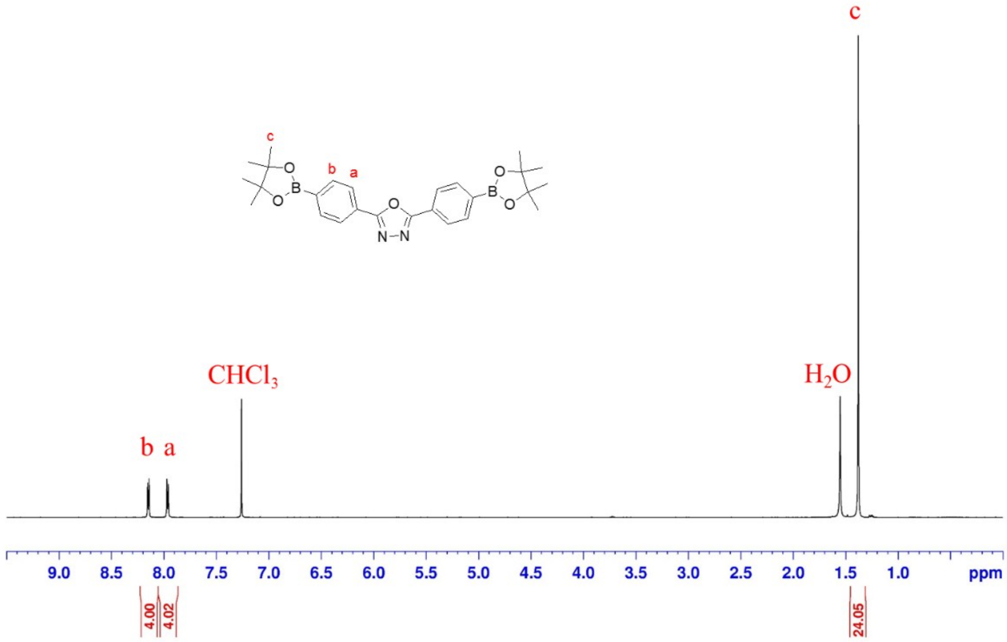

Fig. S5 ^{1}H NMR spectrum of compound **6**.

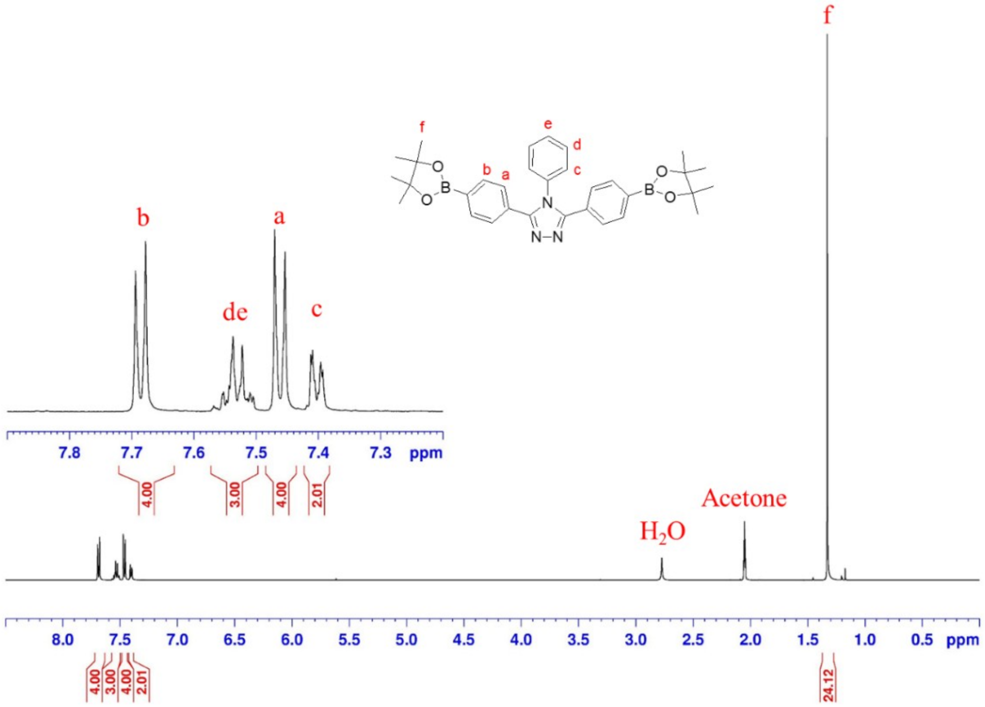

Fig. S6 ^{1}H NMR spectrum of compound **7**.

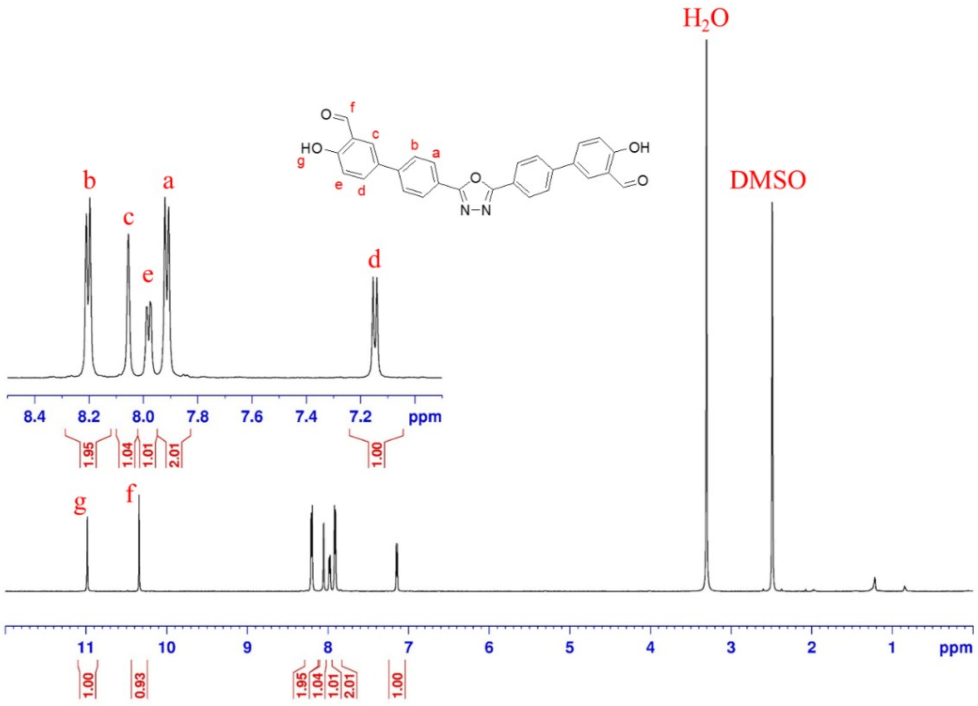

Fig. S7 ^{1}H NMR spectrum of compound **M1**.

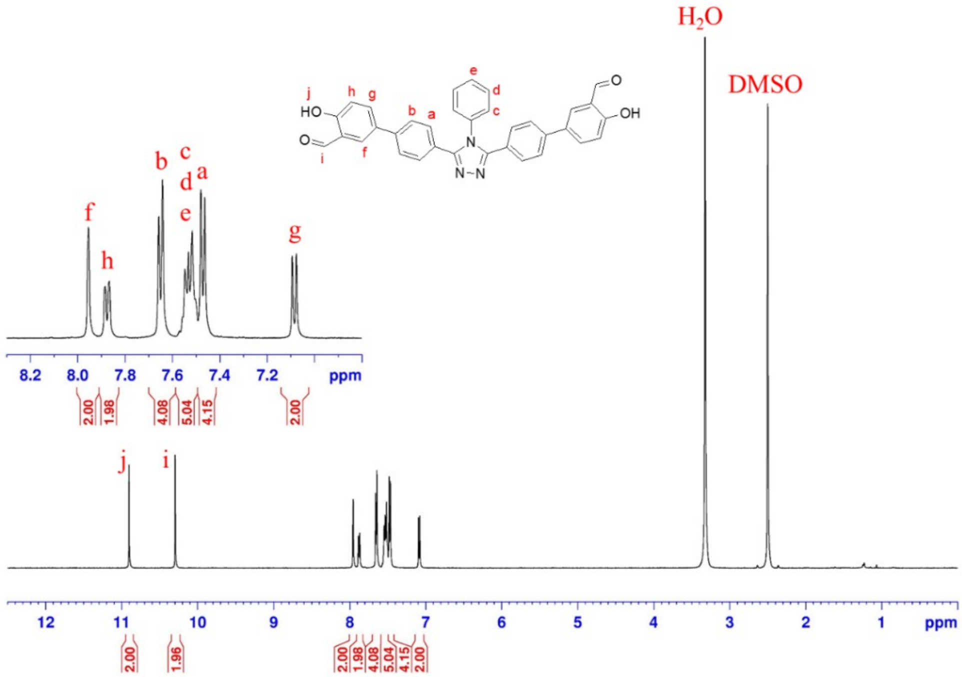

Fig. S8 ^{1}H NMR spectrum of compound **M2**.

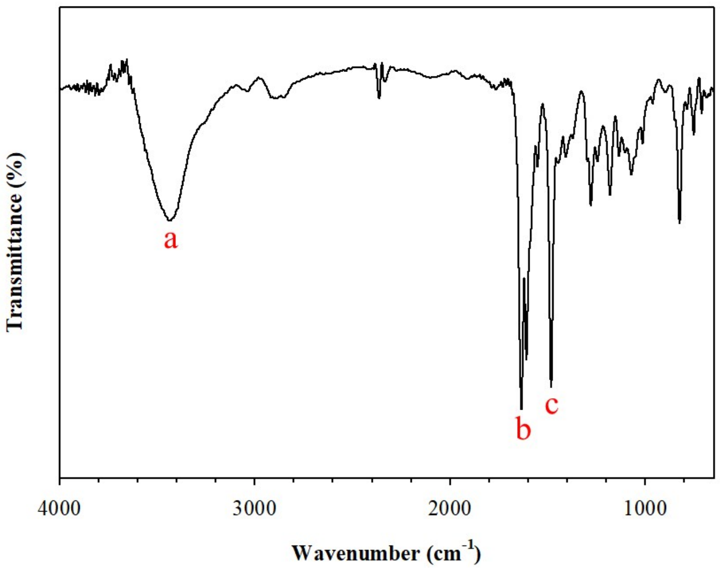

Fig. S9 FT-IR spectrum of **P1**.

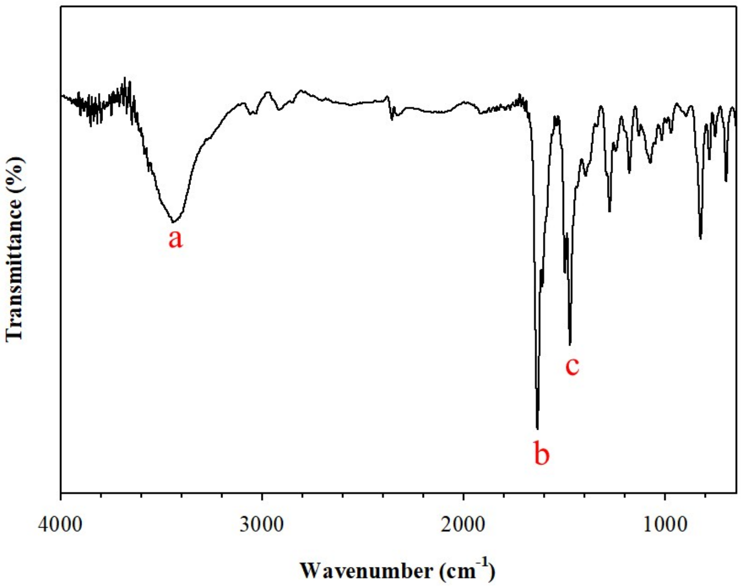

Fig. S10 FT-IR spectrum of **P2**.

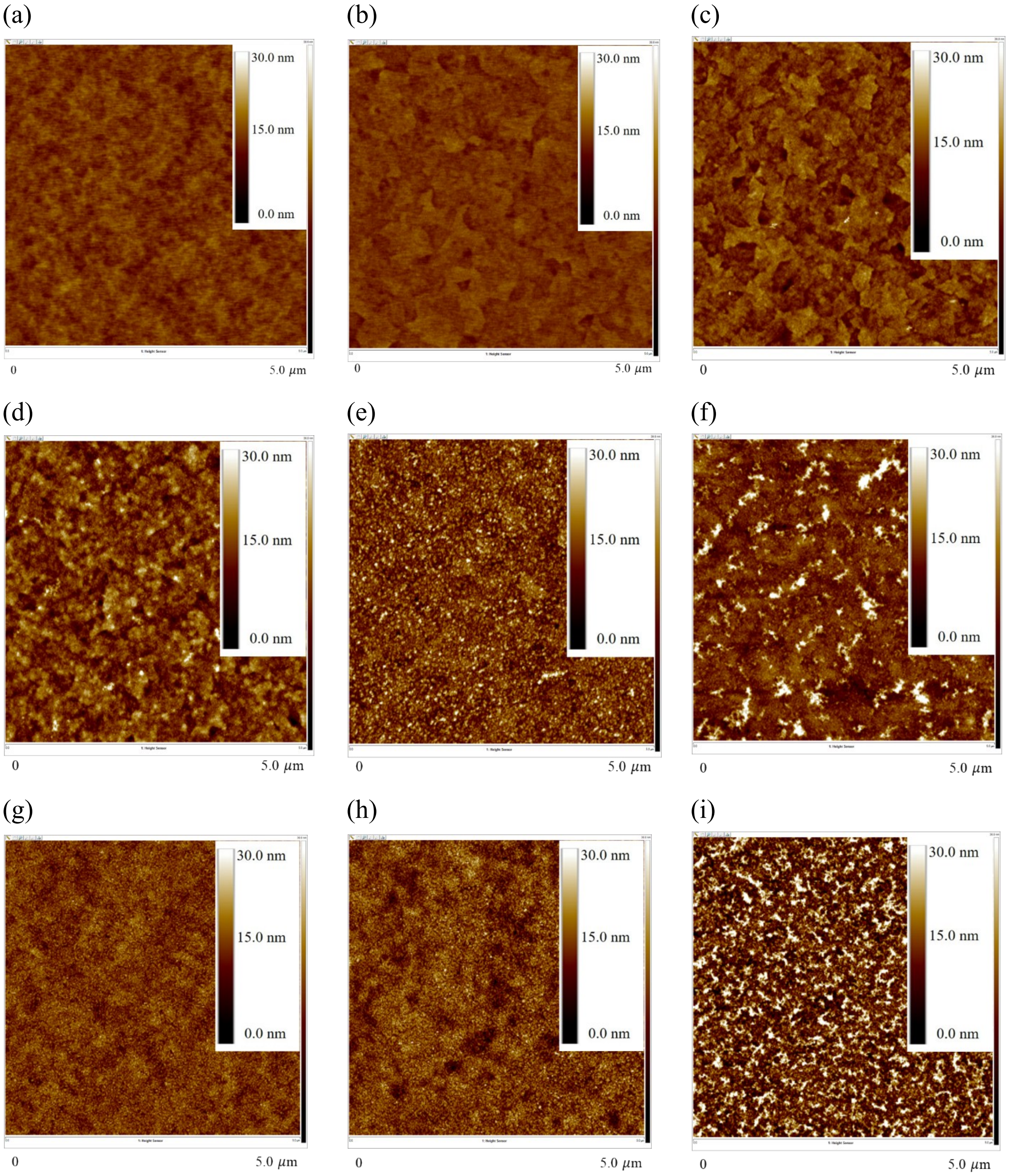

Fig. S11 AFM images of (a) PEDOT:PSS film cast on top of ITO, (b) PEDOT:PSS film after spin-coating with a mixture solvent of formic acid and acetic acid (1/1), (c-f) **P1** films and (g-i) **P2** films spin-coated on top of the PEDOT:PSS layer. The concentrations were (c) 0.5 mg/mL, (d) 1.0 mg/mL, (e) 1.5 mg/mL, (f) 2.0 mg/mL, (g) 1.0 mg/mL, (h) 1.5 mg/mL, and (i) 2.0 mg/mL, respectively, in the mixture solvent.

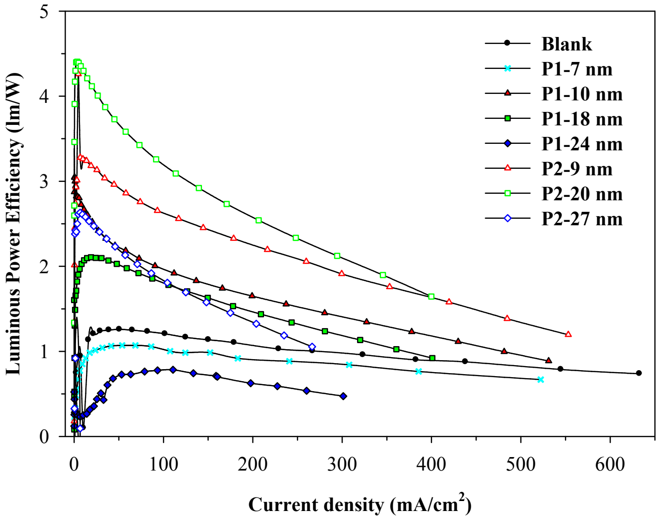

Fig. S12 Power efficiency versus current density characteristics of the PLEDs. Device structure: ITO/PEDOT:PSS/HBL (x nm)/SY-PPV/LiF/Al.

Table S1. Root-mean-square (rms) surface roughness of polymer films.

Polymer films	Concentration (mg/mL)	Surface roughness (nm)
PEDOT:PSS	---	1.32
PEDOT:PSS[a]	---	1.10
P1[b]	0.5	2.22
	1.0	3.19
	1.5	3.38
	2.0	4.13
P2[b]	1.0	2.31
	1.5	3.14
	2.0	6.54

[a] After spin-coating with mixture solvent of formic acid and acetic acid (v/v = 1/1). [b] Films prepared by spin-coating **P1** or **P2** solutions in formic acid and acetic acid (v/v = 1:1) at 3000 rpm on top of the PEDOT:PSS layer.