ADVANCED MATERIALS

Supporting Information

for

Advanced Materials, adma.200701104

Supporting Information

for

Advanced Materials adma200701104

Three-Color White Electroluminescence from a Single Polymer System with Blue, Green and Red Dopant Units as Individual Emissive Species and Polyfluorene as Individual Polymer Host

Jun Liu, Lei Chen, Shiyang Shao, Zhiyuan Xie, Yanxiang Cheng, Yanhou Geng, Lixiang Wang, Xiabin Jing and Fosong Wang*

Materials All the reagents and solvents used for the syntheses were purchased from Aldrich and Acros companies. 2,7-Dibromo-9,9-dioctylfluorene (**1**), [1] 9,9-dioctyl-2,7-bis(trimethyleneborate)fluorene (**2**), [1] 9-hexyl-9-(6-(4-dimethylamino-1,8-naphthalimide-9-)hexyl)-2,7-dibromofluorene (**Monomer-B1**), [2] 9-hexyl-9-(6-bromohexyl)-2,7-dibromofluorene (**3**), [3] 4,7-dibromo-2,1,3-benzothiadiazole, [4] 4-bromo-7-(4-methoxyphenyl)-2,1,3-benzothiadiazole (**4**) [3], 2-bromo-9,9-dihexylfluorene, [5] 2,7-dibromo-9,9-dihexylfluorene [5] and tributyl(4-(diphenylamino)phenyl)stanne [3] were synthesize according to the procedure from literatures. All reactions were performed under a dry argon atmosphere.

*9,9-dihexylfluorene-2-yl boric acid (**5**)*

To a solution of 9,9-hexyl-2-bromofluorene (21.97 g, 51.5 mmol) in dry tetrahedronfuran (THF) (250 mL) at –78 ^{o}C was added n-butyllithium (38.2 mL 1.6 M solution in hexane, 61.1 mmol). After one hour, $B(OCH_3)_3$ (6.7 mL, 66.5 mmol) was added and the mixture was kept stirred overnight. The reaction mixture was poured into aqueous hydrochloric acid, followed by extraction with ether. The combined extracts was washed with water and then dried with anhydrous Na_2SO_4. Removal of the solvent gave a white solid, which was further purified by silica column chromatography to afford the title compound as a white solid. Yield: 4.20 g (22%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.35 (d, 1H), 8.26 (s, 1H), 7.93 (d, 1H), 7.87-7.84 (m, 1H), 7.45-7.38 (m, 3H), 2.22-2.05 (m, 4H), 1.16 (m, 12H), 0.81-0.72 (m, 10H).

*9,9-dihexyl-2-(9,9-dihexylfluorene-2-yl)-7-bromofluorene (**6**)*

A mixture of **5** (0.89 g, 2.35 mmol), 9,9-dihexyl-2,7-dibromo-fluorene (4.63 g, 9.41 mmol), K_2CO_3 (0.97 g, 7.0 mmol), $Pd(PPh_3)_4$ (0.028 g, 0.024 mmol), toluene (30 mL) and H_2O (3.5 mL) was stirred in dark at 90 ^{o}C for 24 hours. After workup, the mixture was poured into water and extracted with CH_2Cl_2 and then dried with anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue was purified by silica column chromatography to give the title compound as a white solid. Yield: 1.18 g (67%). ^{1}H NMR ($CDCl_3$, 300MHz) δ (ppm): 7.81 (d, 1H), 7.78 (d, 1H), 7.76 (s, 1H), 7.68-7.61 (m, 5H), 7.52 (s, 1H), 7.51 (dd, 1H), 7.41-7.34 (m, 3H), 2.08-2.00 (m, 8H), 1.11 (m, 24H), 0.83-0.73 (m, 20H).

*9,9-dihexyl-2-(9,9-dihexylfluoren-2-yl)-fluoren-7-yl boric acid (**7**)*

The synthesis of **7** is analogous to that of **5** with yield of 59%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.40 (d, 1H), 8.31 (s, 1H), 7.9-7.92 (m, 2H), 7.86-7.67 (m, 7H), 7.43-7.34 (m, 2H), 2.24-2.01 (m, 8H), 1.43-0.97 (m, 24H), 0.79 (m, 20H).

4-(9,9-dihexyl-2-(9,9-dihexylfluorene-2-yl)-fluoren-7-yl)-7-(4-methoxy)-2,1,3-benzothiadiazole (***MC-G2***).

A mixture of **7** (0.60 g, 0.844 mmol), **4** (0.24 g, 0.76 mmol), K_2CO_3 (0.32 g, 2.28 mmol), $Pd(PPh_3)_4$ (0.009 g, 0.0076 mmol), toluene (10 mL), H_2O (1.1 mL) and one drop of Aliquat 336 was stirred in dark at 90 ^{o}C for 24 hours. After workup, the reaction mixture was poured into water and extracted with CH_2Cl_2 and then dried with anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue was purified by silica column chromatography to give the title compound as a green solid. Yield: 0.61 g (89%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.07 (dd, 1H), 8.01-7.99 (m, 3H), 7.93-7.87 (m, 3H), 7.84 -7.77 (m, 3H), 7.73-7.67 (m, 4H), 7.42-7.35 (m, 3H), 7.15 (d, 2H), 3.95 (s, 3H), 2.16-2.07 (m, 8H), 1.16-1.12 (m, 24H), 1.01-0.79 (m, 20H). Anal. calcd.: C, 83.39; H, 8.22; N, 3.09. Found: C, 83.22; H, 8.01; N, 3.15.

*9-hexyl-9-(6-(4-(4-(2-(9,9-dihexylfluorene-2-yl)-9,9-dihexylfluorene-2-yl)-2,1,3-benzothiadiazole-7-yl)-phenyloxy)-hexyl)-2,7-fluorene (**Monomer G2**)*

To a solution of **MC-G2** (0.40 g, 0.44 mmol) in dry CH_2Cl_2 (6 mL) at –78 ^{o}C, BBr_3 (4.0 mL 1 M solution in CH_2Cl_2, 4.0 mmol) was added dropwise and the mixture was stirred at this temperature for 1 hour. Then the mixture was slowly warmed to room temperature and stirred for 24 hours, followed by the addition of several drops of water. After removal of the solvent at room temperature with reduced pressure, the residual was mixed with K_2CO_3 (2.76 g, 20 mmol), **3** (0.55 g, 0.96 mmol) and ethanol (15 mL). The mixture was heated to reflux for 24 hours and then poured into water and extracted with CH_2Cl_2. The organic layer was dried with Na_2SO_4. After filtration and removal of the solvent, the residue was purified by silica column chromatography to give the title compound as a green solid. Yield: 0.16 g (26%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.08-8.05 (m, 2H), 7.98 (d, 2H), 7.94 (s, 1H), 7.92-7.87 (m, 2H), 7.87-7.77 (m, 3H), 7.58-7.52 (m, 6H), 7.50-7.47 (m, 7H), 7.08 (d, 2H), 3.98 (t, 2H), 2.20-1.99 (m, 12H), 1.70-1.60 (m, 2H), 1.29-1.11 (m, 36H), 0.83-0.62 (m, 25H). Anal. calcd.: C, 75.52; H, 7.43; N, 2.02. Found: C, 75.98; H, 7.81; N, 1.76.

*4-(N-phenyl-N-(4-methoxy)phenyl-amino)-1-bromobenzene (**9**)*

A mixture of 4-bromo-diphenylamine (4.50 g, 20.0 mmol), 4-methoxy-1-iodo-benzene (5.76 g, 24.5 mmol), CuCl (0.20 g, 2.0 mmol), 1,10-phenanthroline monohydrate (0.40 g, 2.0 mmol), KOH (11.2 g, 200 mmol) and toluene (45 mL) was heated to reflux and stirred for 36 hours. After workup, the reaction mixture was poured into brine and extracted with CH_2Cl_2. The organic layer was washed with brine and then dried with Na_2SO_4. The solvent was removed and the residue was purified by column chromatography on silica gel to afford the title compound as a white solid. Yield: 4.75 g (67%).

*2-(4-(N-phenyl-N-(4-methoxy)phenyl-amino)phenyl)thiophene (**10**)*

A mixture of **9** (3.59 g, 10.1 mmol), tributyl(thienyl-2-)stanne(4.54 g, 12.2 mmol), $Pd(PPh_3)_4$ (0.11 g, 0.1 mmol) and toluene (60 mL) was stirred in dark at 100 ^oC for 24 hours. After workup, the mixture was poured into aqueous KF and extracted with CH_2Cl_2. The organic layer was washed with water and then dried with Na_2SO_4. The solvent was removed and the residue was purified by column chromatography on silica gel to afford the title compound as a white solid. Yield: 2.00 g (56%). ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.48 (d, 2H), 7.27 (m, 4H), 7.12-7.04 (m, 8H), 6.89 (d, 2H).

*Tributyl(5-(4-(N-phenyl-N-(4-methoxy)phenyl-amino)phenyl)thienyl-2)stannane (**11**)*

To a solution of **10** (1.07 g, 3.0 mmol) in dry THF (30 mL) at –78 ^oC was added n-butyllithium (2.0 mL 1.6 M solution in hexane, 3.2 mmol). After one hour, $(n\text{-}C_4H_9)_3SnCl$ was added to the mixture. The resulting mixture was slowly warmed to room temperature and kept stirred overnight. After workup, the mixture was poured into aqueous $NaHCO_3$ and extracted with hexane. The organic layer was washed with water and then dried with Na_2SO_4. Removal of the solvent afforded the title compound as a light-yellow liquid. Yield: 1.92 g (99%).

*4-(5-(4-(N-phenyl-N-(4-methoxy)phenyl-amino)phenyl)thienyl-2)-7-bromo-2,1,3-benzothiadiazole (**12**)*

A mixture of 4,7-dibromo-2,1,3-benzothiadiazole (2.96 g, 10.1 mmol), **11** (1.92 g, 3.0 mmol), $Pd(PPh_3)_4$ (0.034g, 0.03mmol) and toluene (30 mL) was stirred in dark at 100 ^oC for 24 hours. After workup, the mixture was poured into aqueous KF and extracted with CH_2Cl_2. The organic layer was washed with water and then dried with Na_2SO_4. The solvent was

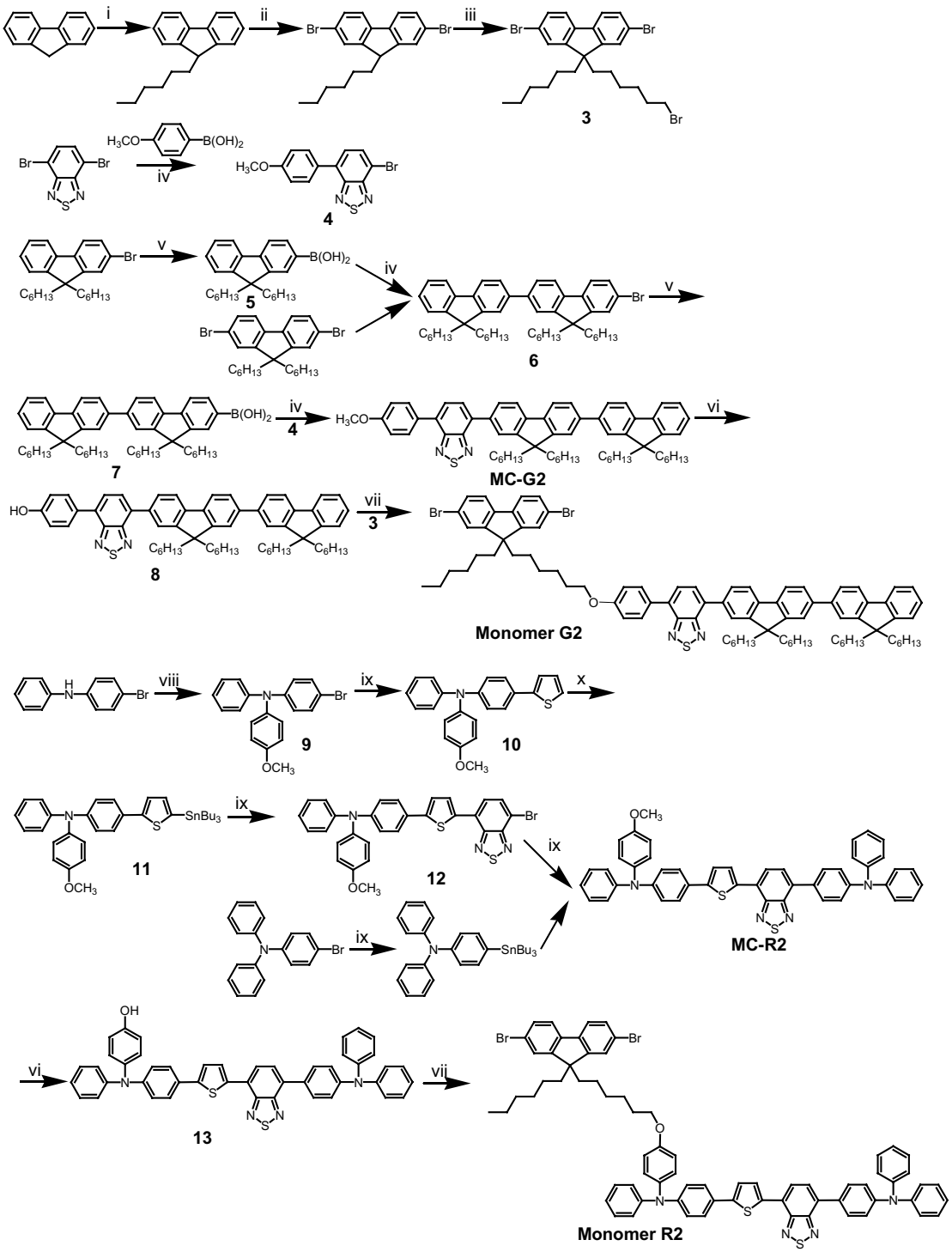
removed and the residue was purified by column chromatography on silica gel to afford the title compound as a deep-red solid. Yield: 0.97 g (57%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.12 (d, 1H), 7.88 (d, 1H), 7.73 (d, 1H), 7.56 (d, 4h), 7.29 (m, 4H), 7.15-7.05 (m, 7H), 6.93 (d, 2H), 3.86 (s, 3H).

*4-(5-(4-(N-phenyl-N-(4-methoxy)phenyl-amino)phenyl)thienyl-2)-7-(4-(diphenylamino)phenyl)-2,1,3-benzothiadiazole (**MC-R2**)*

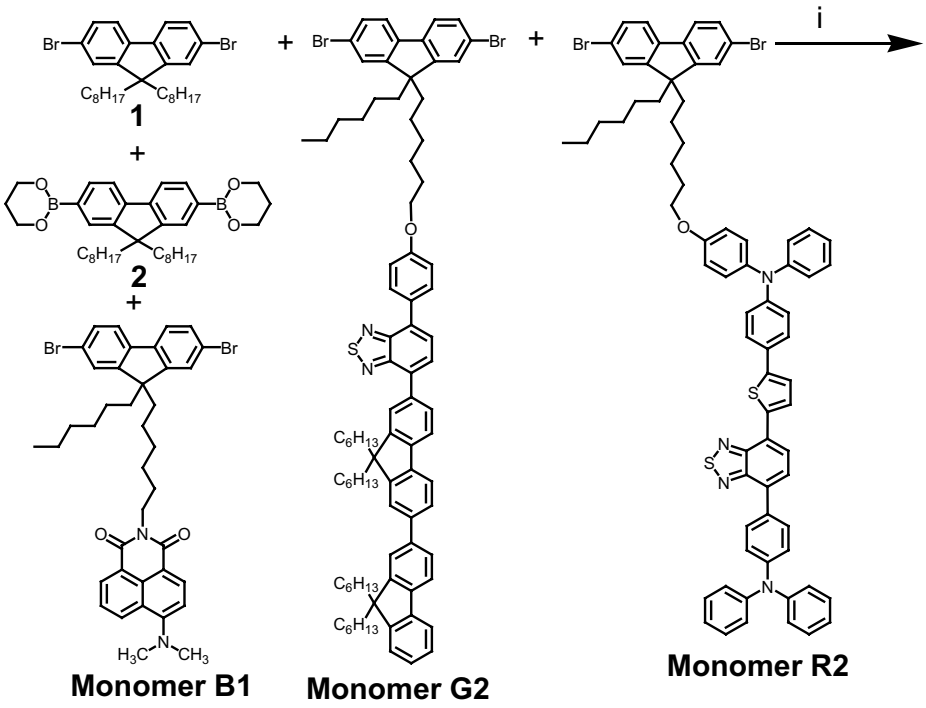
The synthesis of **MC-R2** is analogous to that of **10**. Yield: 78%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.15 (d, 1H), 7.91 (d, 2H), 7.74 (d, 1H), 7.58 (d, 2H), 7.36-7.08 (m, 23H), 6.91 (d, 2H), 3.86 (s, 3H). Anal. calcd.: C, 76.81; H, 4.66; N, 7.62. Found: C, 77.34; H, 4.26; N, 7.09.

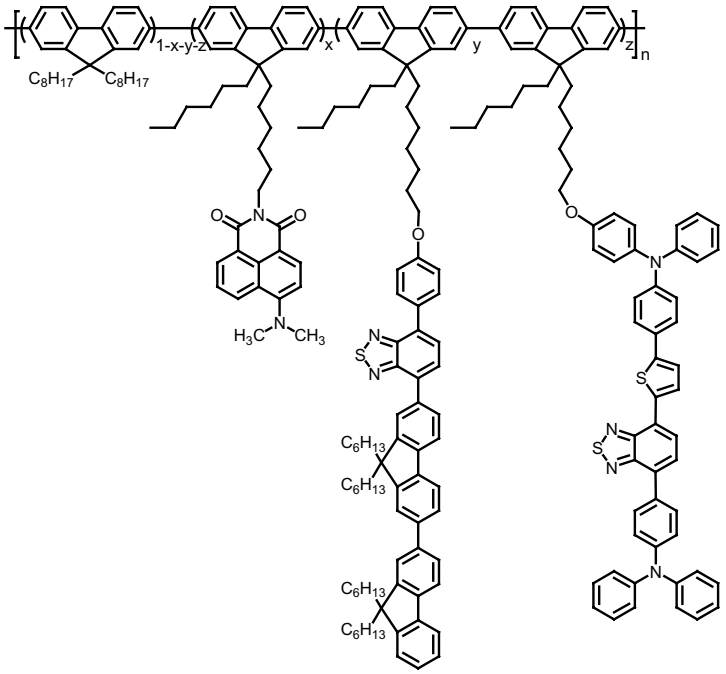
9-hexyl-9-(6-(4-(N-phenyl-N-(4-(5-(4-(4-(diphenylamino)phenyl)-2,1,3-benzothiadiazole-7-)-thienyl-2-)phenyl)amino)phenoxy)hexyl)-2,7-dibromofluorene (**Monomer-R2**)

The synthesis of **Monomer-R2** is analogous to that of **Monomer-G2**. Yield: 17%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.10 (d, 1H), 7.87 (d, 2H), 7.70 (d, 1H), 7.55-7.50 (m, 4H), 7.47-7.44 (m, 4H), 7.36-7.08 (m, 23H), 6.80 (d, 2H), 3.84 (br, 2H), 1.95-1.89 (m, 4H), 1.60 (m, 2H), 1.25-1.05 (m, 10H), 0.78 (t, 3H), 0.61 (br, 4H). Anal. calcd.: C, 70.41; H, 5.16; N, 4.63. Found: C, 71.63; H, 4.98; N, 4.71.



Scheme S1. Synthetic routes of the monomers and model compounds. (Reagents and conditions: (i) a) BuLi, THF, -78 °C, b) n-$C_6H_{13}Br$; (ii) Br_2, $CHCl_3$; (iii) $Br(CH_2)_6Br$, NaOH, Bu_4NBr, toluene, 70 °C; (iv) $Pd(PPh_3)_4$, toluene, K_2CO_3 (aq., 2 M), 90 °C; (v) a) BuLi, THF, -78 °C, b) $B(OCH_3)_3$, c) HCl; (vi) BBr_3, CH_2Cl_2; (vii) K_2CO_3, ethanol, reflux; (viii) CuCl, 1,10-phenanthroline monohydrate, KOH, toluene, reflux; (ix) $Pd(PPh_3)_4$, toluene, 100 °C; (x) a) n-BuLi, THF, -78 °C, b) $(n\text{-}Bu)_3SnCl$).





WP-B2G5R5, x=0.0002,y=0.0005,z=0.0005
WP-B5G5R5, x=0.0005,y=0.0005,z=0.0005
WP-B10G5R5,x=0.0010,y=0.0005,z=0.0005
WP-B5G2R2, x=0.0005,y=0.0002,z=0.0002
WP-B5G5R2, x=0.0005,y=0.0005,z=0.0002
WP-B5G10R2,x=0.0005,y=0.0010,z=0.0002
WP-B5G2R5, x=0.0005,y=0.0002,z=0.0005
WP-B5G10R5,x=0.0005,y=0.0010,z=0.0005

Scheme S2. Synthetic routes of the polymers. (Reagents and conditions: (i) $Pd(PPh_3)_4$, toluene, K_2CO_3 (aq., 2 M), Aliquat 336, 90 ^oC)

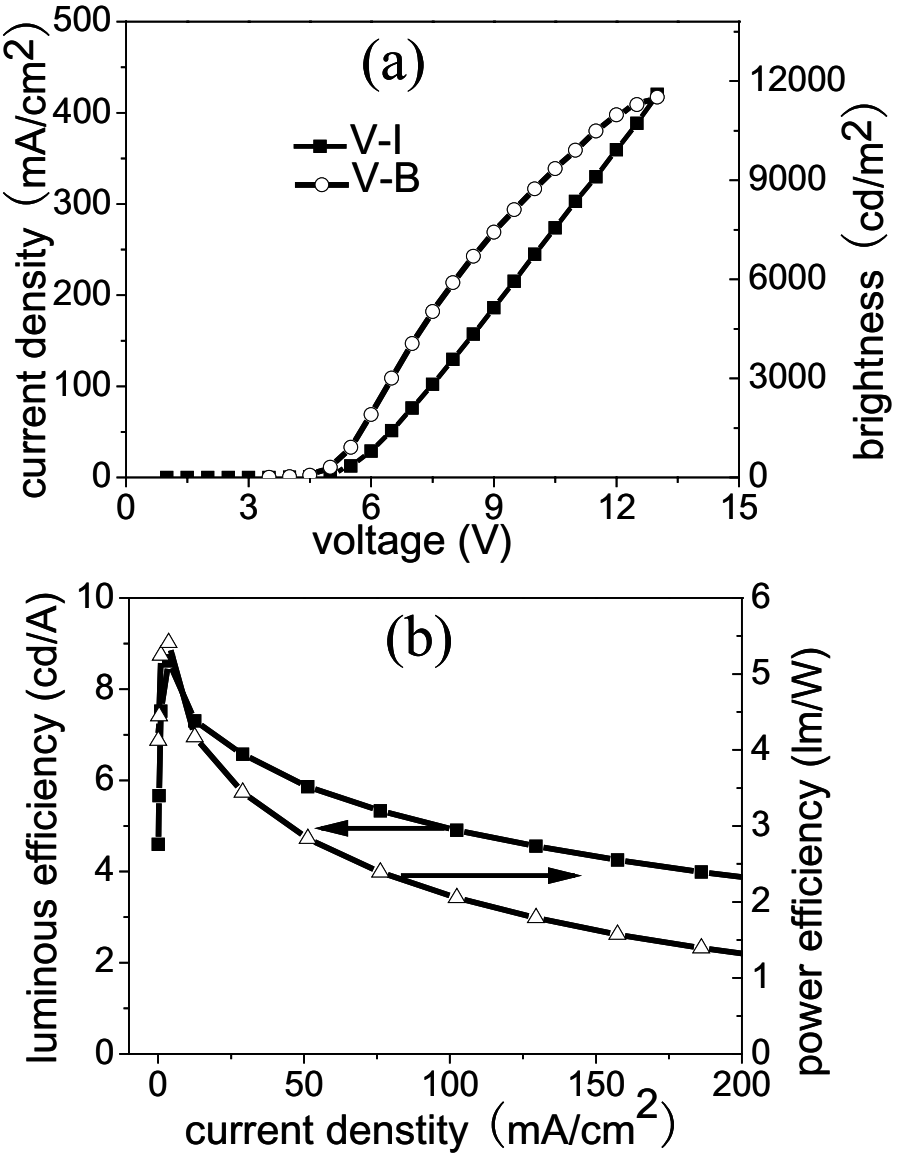


Figure S1. (a) Voltage-current density-brightness characteristic of the device of **WP-B5G5R2**. (b) Dependence of the luminous efficiency and power efficiency on the current density of the device of **WP-B5G5R2**.

Reference

[1] X. W. Chen, J. L. Liao, Y. M. Liang, M. O. Ahmed, H. E. Tseng, S.-A. Chen, *J. Am. Chem. Soc.* **2003**, *125*, 636.

[2] J. Liu, S. Y. Shao, L. Chen, Z. Y. Xie, Y. X. Cheng, Y. H. Geng,L. X. Wang, X. B. Jing, F. S. Wang, *Adv. Mater.* **2007**, adma.200602942, *in press*.

[3] J. Liu, X. Guo, L. J. Bu, Z. Y. Xie, Y. X. Cheng, Y. H. Geng,L. X. Wang, X. B. Jing, F. S. Wang, *Adv. Funct. Mater.* **2007**, adfm.200600988, *in press*.

[4] K. Pilgram, M. Zupan, R. Skiles, *J. Heterocycl. Chem.* **1970**, *7*, 629.

[5] Y. H. Geng, A. Trajkoyska, D. Katsis, J. J. Ou, S. W. Culligan, S. H. Chen, *J. Am. Chem. Soc.* **2002**, *124*, 8337.