

A Field-Depending Organic LED Consisting of Two New High T_g Blue Light Emitting Organic Layers – A Possibility of Attainment of A White Light Source

Soon Wook Cha and Jung-Il Jin *

Department of Chemistry and the Center for Electro- and Photo-Responsive Molecules,

Korea University, Seoul 136-701, Korea

Experimental

Synthesis of Cz3d and Oxa3d

The synthesis of Cz3d and Oxa3d was performed via the routes showing in scheme 1 and 2, respectively. The numbers given in this part are the same as those given in the schemes.

9-p-Tolyl-9H-carbazole (1) :

Carbazole (20 g: 0.12 mol), 4-bromotoluene (30 g: 0.18 mol), Cu powder (15 g), potassium carbonate (65g: 0.47 mol) and dibenzo-18-crown-6 (4.4 g: 1.2×10^{-2} mol) were placed in a three-necked round-bottomed flask containing 300 mL of 1,2-dichlorobenzene. The mixture was refluxed under a nitrogen atmosphere for 24 h. Insoluble precipitates were removed by filtration. Crude product was obtained by distilling out the dichlorobenzene solvent from the filtrate. Purification was conducted by column chromatography on a silica gel column using a mixture of methylene chloride and n-hexane (1: 6 by volume) as an eluent, and then dried in a vacuum oven

for 1 day. The yield was 67 % (30.9 g). m.p.: 107 °C.

¹H NMR spectrum (CDCl₃, δ ppm): 2.49 (s, 3H), 7.20-7.44 (m, 10H), 8.14 (d, 2H).

FTIR (KBr, cm⁻¹): 3064 (Ar C-H stretching), 2964 (aliphatic C-H stretching), 1597,

1510 (Ar C=H stretching), 1278, 1224 (C-N stretching). Elemental analysis: Calcd. [%]

for C₁₉H₁₅N: C 88.68 H 5.88 N 5.44 %. Found: C 88.60 H 5.93 N 5.40 %.

3,6-Dibromo-9-p-tolyl-9H-cabazole (2) :

Compound 1 (10 g: 39 mmol) was dissolved in 200 mL of CCl₄. Bromine (2 mL, 39 mmol) dissolved in 50 mL of CCl₄ were added to the reaction flask through a dropping funnel over a period of 20 min. White precipitates were generated. After being stirred for 2 h, the precipitate was collected on a filter and washed with water and then dried in a vacuum oven. The yield was 70 % (11.3 g). m.p.: 208 °C.

¹H NMR spectrum (CDCl₃, δ ppm): 2.46 (s, 3H, -CH₃), 7.23 (d, 2H, Ar-H), 7.34-7.42

(m, 4H, Ar-H), 7.48 (d, 2H, Ar-H), 8.19 (s, 2H, Ar-H). FTIR (KBr, cm⁻¹): 3064 (Ar C-H

stretching), 2964 (aliphatic C-H stretching), 1598, 1513 (Ar C=H stretching), 1276,

1220 (C-N stretching). Elemental analysis: Calcd. [%] for C₁₉H₁₃Br₂N: C 54.97 H 3.16

N 3.37 %. Found: C 54.89 H 3.25 N 3.39 %.

3,6-Dibromo-9-(vinylphenyl)-9H-cabazole (3) :

Compound 3 was synthesized in the same manner as described below in the

preparation of compound 8. m.p.: 160 °C.

¹H NMR spectrum (CDCl₃, δ ppm): 5.40, 5.89 (d, d, 1H, 1H, -CH=CH₂), 6.87 (m, 1H, -CH=CH₂), 7.28 (d, 2H, Ar-H), 7.44-7.52 (m, 4H, Ar-H), 7.65 (d, 2H, Ar-H), 8.20 (s, 2H, Ar-H). FTIR (KBr, cm⁻¹): 3063 (Ar C-H stretching), 2965 (aliphatic C-H stretching), 1597, 1512 (Ar C=C stretching), 1279, 1226 (C-N stretching). Elemental analysis: Calcd. [%] for C₂₀H₁₃Br₂N: C 56.24 H 3.07 N 3.28 %. Found: C 56.29 H 3.05 N 3.32 %.

3,6-Bis(4-t-butylphenyl) -9-(vinylphenyl)-9H-cabazole (4) :

Compound 3 (5 g, 12 mmol) dissolved in 150 mL of toluene was mixed with (PPh₃)₄Pd (0.7 g, 0.6 mmol) and 40 mL of 2M Na₂CO₃ under nitrogen atmosphere. 4-t-Butylphenylboronic acid (5.3 g, 30.0 mmol) dissolved in 20 mL of ethanol was charged into the reaction flask. The reaction mixture was refluxed for 24 h. Dark impurities formed were removed by filtration using celite and charcoal as a filter aids. Then, solvent in the filtrate were evaporated out under a reduced pressure and the crude product was purified by column chromatography on a silica gel column using n-hexane/methylene chloride = 9/1 (v/v) as an eluent. The yield was 64 % (4.1 g). m.p.: 218 °C.

¹H NMR spectrum (CDCl₃, δ ppm): 1.40 (s, 18H, -C(CH₃)₃), 5.40, 5.90 (d, d, 1H, 1H, -CH=CH₂), 6.89 (m, 1H, -CH=CH₂), 7.43-7.70 (m, 16H, Ar-H), 8.38 (s, 2H, Ar-H).

FTIR (KBr, cm^{-1}): 3062 (Ar C-H stretching), 2964 (aliphatic C-H stretching), 1599, 1511 (Ar C=H stretching), 1280, 1228 (C-N stretching). Elemental analysis: Calcd. [%] for $\text{C}_{40}\text{H}_{39}\text{N}$: C 90.01 H 7.36 N 2.62 %. Found: C 90.10 H 7.28 N 2.68 %. MALDI-TOF MS: Calcd. for $\text{C}_{40}\text{H}_{40}\text{N}$ (MH^+) 534.3, Found: 534.7.

3,6-Bis(2-{4-[3,6-Bis(4-*t*-butylphenyl)cabazole-9-yl]phenyl}vinyl)-9-*p*-tolyl-9H-cabazole (Cz3d) :

Cz3d was synthesized using compound 2 and compound 4 in the same manner as described below in the preparation of OXA3d.

^1H NMR spectrum (CDCl_3 , δ ppm): 1.40 (s, 36H, $-\text{C}(\text{CH}_3)_3$), 2.53 (s, 3H, $-\text{CH}_3$), 7.34-7.80 (m, 54H, Ar-H), 8.40 (s, 6H, Ar-H). FTIR (KBr, cm^{-1}): 3064 (Ar C-H stretching), 2965 (aliphatic C-H stretching), 1596, 1508 (Ar C=H stretching), 1276, 1220 (C-N stretching). Elemental analysis: Calcd. [%] for $\text{C}_{99}\text{H}_{89}\text{N}_3$: C 90.03 H 6.79 N 3.18 %. Found: C 90.12 H 6.88 N 3.20 %. MALDI-TOF MS: Calcd. for $\text{C}_{99}\text{H}_{90}\text{N}_3$ (MH^+) 1320.7, Found: 1322.0.

2-(4-*t*-Butylphenyl)-5-(4-methylphenyl)-1,3,4-oxadiazole (6) :

A mixture of methyl 4-methylbenzoate (30.0 g, 0.20 mol) and hydrazine

monohydrate (31.2 g, 0.62 mol) was refluxed for 24 h in 600 mL of ethanol. After the reaction was completed, the mixture were cooled to room temperature, and then poured into cold water to precipitate the white solid, which was collected on a filter and washed with hexane and small amount (ca. 100 mL) of cold water to remove the unreacted starting materials. The product, 4-methylbenzhydrazide (5), was dried for 1 h by vacuum filtration followed by drying in a vacuum oven for 1 day. The product yield was 83 % (24.9 g).

17.8 g (0.10 mol) of 4-*t*-butylbenzoic acid was added to 50 mL of SOCl₂ and refluxed for 6 h to give 4-*t*-butylbenzoyl chloride. The excess SOCl₂ was removed by vacuum distillation and the reaction mixture was cooled to room temperature. After 30 min, 20.0 g (0.13 mol) of 4-methylbenzylhydrazide dissolved in 200 mL of pyridine were added to the reaction flask containing 4-*t*-butylbenzoyl chloride through a dropping funnel over a period of 20 min. After being stirred for 2 h, the reaction mixture was poured into distilled water. The product was collected on a filter and washed with water and then dried in a vacuum oven. The yield was 79 % (24.5 g).

The product (24 g, 77.4 mmol) was placed in a 500 mL 2-necked round bottomed flask. POCl₃ (250 mL) was added to the flask. The mixture was refluxed for 6 h under nitrogen atmosphere. After the completion of the reaction, the reaction mixture was

slowly poured into cold water in a ice bath and 0.5 M NaOH solution was added to neutralize the reaction mixture. Then the precipitate was collected on a filter, washed with distilled water, and finally recrystallized from ethanol/water = 3:1 (v/v). The yield was 84 % (19.0 g). m.p.: 110 °C. ¹H NMR (300 MHz, CDCl₃, ppm): 1.37 (s, 9H, -C(CH₃)₃), 2.44 (s, 3H, -CH₃), 7.32 (d, 2H, Ar-H), 7.56 (d, 2H, Ar-H), 8.01-8.07 (d, 2H, 2H, Ar-H). FTIR (KBr, cm⁻¹): 3064 (Ar C-H stretching), 2964 (aliphatic C-H stretching), 1613, 1494 (Ar C=H stretching), 1575 (C=N stretching), 1012 (C-O-C stretching). Elemental analysis: Calcd. [%] for C₁₉H₂₀N₂O: C 78.05, H 6.89, N 9.58; found: C 78.10, H 6.85, N 9.51.

2-(4-Bromomethylphenyl)-5-(4-*t*-butylphenyl)-1,3,4-oxadiazole (7) :

A mixture of compound 6 (2.92 g, 10.0 mmol), N-bromosuccinimide (3.92 g, 22.0 mmol), and benzoyl peroxide (0.48 g, 2.0 mmol) was dissolved in 200 mL of CCl₄ and the mixture was heated slowly to and kept 76 °C under nitrogen atmosphere for 4 h. After the completion of the reaction, the mixture was cooled down to room temperature. And the insolubles were removed by filtration. The CCl₄ solvent was removed by evaporation under a reduced pressure to obtain a crude product. The product was purified by column chromatography on a silica gel column using n-hexane/ethyl acetate = 5/1 (v/v) as an eluent. The yield was 67 % (2.48 g). m.p.: 160 °C. ¹H NMR (300

MHz, CDCl₃, ppm): 1.37 (s, 9H, -C(CH₃)₃), 4.54 (s, 2H, -CH₂Br), 7.57 (d, 4H, Ar-H), 8.08 (d, 2H, Ar-H), 8.13 (d, 2H, Ar-H). FTIR (KBr, cm⁻¹): 3064 (Ar C-H stretching), 2962 (aliphatic C-H stretching), 1615, 1493 (Ar C=C stretching), 1576 (C=N stretching), 1015 (C-O-C stretching). Elemental analysis: Calcd. [%] for C₁₉H₁₉BrN₂O: C 61.47, H 5.16, N 7.55; found: C 61.54, H 5.20, N 7.60.

2-(4-*t*-Butylphenyl)-5-(4-vinylphenyl)-1,3,4-oxadiazole (8) :

A mixture of compound 7 (2.48 g, 6.7 mmol) and triphenylphosphine (2.62 g, 10.0 mmol) was refluxed for 4 h in 50 mL of benzene. White precipitate was generated. It was cooled down to room temperature and then collected by filtration. The product, phosphonium salt, was dried in a vacuum oven for 1 day. The yield was 92 % (3.90 g). The phosphonium salt (3.9 g, 6.2 mmol) was dissolved in 100 mL of 1N NaOH solution. 50 mL of formaldehyde (37 % solution in water) was added in the mixture. After being stirred for 2 h, white precipitate was collected on a filter. The product was purified by column chromatography on a silica gel column using n-hexane/ethyl acetate = 5/1 (v/v) as an eluent, and then dried in a vacuum oven for 1 day. The yield was 90 % (1.70 g). m.p.: 115 °C.

¹H NMR (300 MHz, CDCl₃, ppm): 1.38 (s, 9H, -C(CH₃)₃), 5.42, 5.92 (d, d, 1H, 1H, -CH=CH₂), 6.83 (q, 1H, -CH=CH₂), 7.54, 7.58 (d, d, 2H, 2H, Ar-H), 8.05, 8.11 (d, d, 2H,

2H, Ar-H). FTIR (KBr, cm^{-1}): 3064 (Ar C-H stretching), 2969 (aliphatic C-H stretching), 1612, 1496 (Ar C=H stretching), 1584 (C=N stretching), 1010 (C-O-C stretching). Elemental analysis: Calcd. [%] for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}$: C 78.92, H 6.62, N 9.20; found: C 78.85, H 6.66, N 9.05. MALDI-TOF MS: Calcd. for $\text{C}_{15}\text{H}_{11}\text{Br}_2\text{N}_2\text{O}$ (MH^+) 305.2, Found: 305.4.

2-(3,5-Dibromophenyl)-5-(4-methylphenyl)-1,3,4-oxadiazole (9) :

Compound 9 was synthesized in the same manner as described above in the preparation of compound 6. 3,5-Dibromobenzoic acid was used instead of 4-*t*-butylbenzoic acid. m.p.: 180 °C.

^1H NMR (300 MHz, CDCl_3 , ppm): 2.45 (s, 3H, $-\text{CH}_3$), 7.46 (d, 2H, Ar-H), 8.03 (s, H, Ar-H), 8.11 (d, 2H, Ar-H), 8.33 (d, 2H, Ar-H).

FTIR (KBr, cm^{-1}): 3064 (Ar C-H stretching), 2964 (aliphatic C-H stretching), 1613, 1494 (Ar C=H stretching), 1575 (C=N stretching), 1012 (C-O-C stretching). Elemental analysis: Calcd. [%] for $\text{C}_{15}\text{H}_{10}\text{Br}_2\text{N}_2\text{O}$: C 45.72, H 2.56, N 7.11; found: C 45.78, H 2.62, N 7.06.

2-[3,5-Bis(2-{4-[5-(4-*t*-Butylphenyl)-1,3,4-oxadiazole-2-yl]phenyl}vinyl)phenyl]-5-(4-methylphenyl)-1,3,4-oxadiazole (Oxa3d) :

Compound 8 (1.7 g, 5.6 mmol) and compound 9 (0.9 g, 2.3 mmol) were dissolved in

20 mL of dimethyl formamide (DMF) and 10 mL of triethylamine. The mixture was heated slowly to and kept 90 °C under nitrogen atmosphere for 30 min. and then added palladium(II) acetate (67 mg, 0.3 mmol) and tri-*o*-tolylphosphine (180 mg, 0.6 mmol) in the reaction mixture. It was stirred for 12 h. After the completion of the reaction, the mixture was cooled down to room temperature. And then the mixture was poured into methanol to precipitate the solid, which was collected on a filter. The product was purified by column chromatography on a silica gel column using chloroform/diethyl ether = 10/1 (v/v) as an eluent, and then dried in a vacuum oven for 1 day. The yield was 62 % (1.20 g). m.p.: 218 °C.

¹H NMR (300 MHz, CDCl₃, ppm): 1.39 (s, 18H, -C(CH₃)₃), 2.44 (s, 3H, -CH₃), 7.30 (s, 4H, -CH=CH-), 7.36 (d, 2H, Ar-H), 7.57 (d, 4H, Ar-H), 7.72 (d, 4H, Ar-H), 7.81 (s, 1H, Ar-H), 8.05-8.19 (m, 12H, Ar-H). FTIR (KBr, cm⁻¹): 3064 (Ar C-H stretching), 2964 (aliphatic C-H stretching), 1613, 1494 (Ar C=H stretching), 1575 (C=N stretching), 1012 (C-O-C stretching). Elemental analysis: Calcd. [%] for C₅₅H₄₈N₆O₃: C 78.55, H 5.75, N 9.99; found: C 78.45, H 5.80, N 9.89. MALDI-TOF MS: Calcd. for C₅₅H₄₉N₆O₃ (MH⁺) 841.4, Found: 842.6.