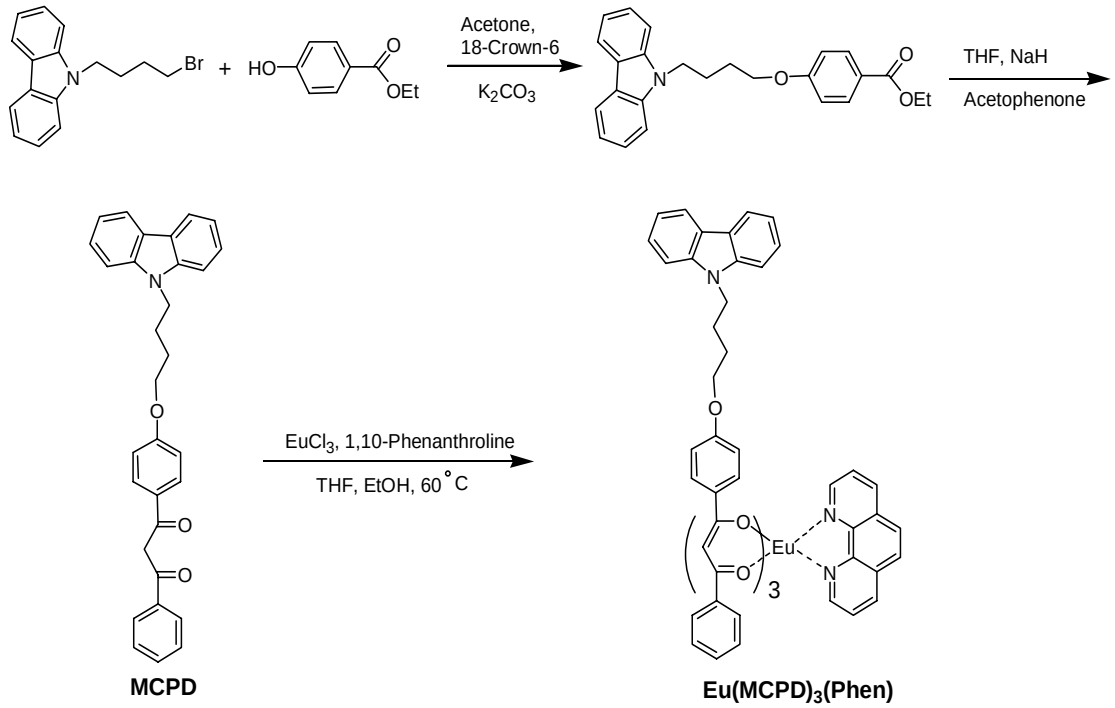
Electronic Supplementary Information (ESI)

Dendritic europium complex as single dopant for white-light electroluminescent device

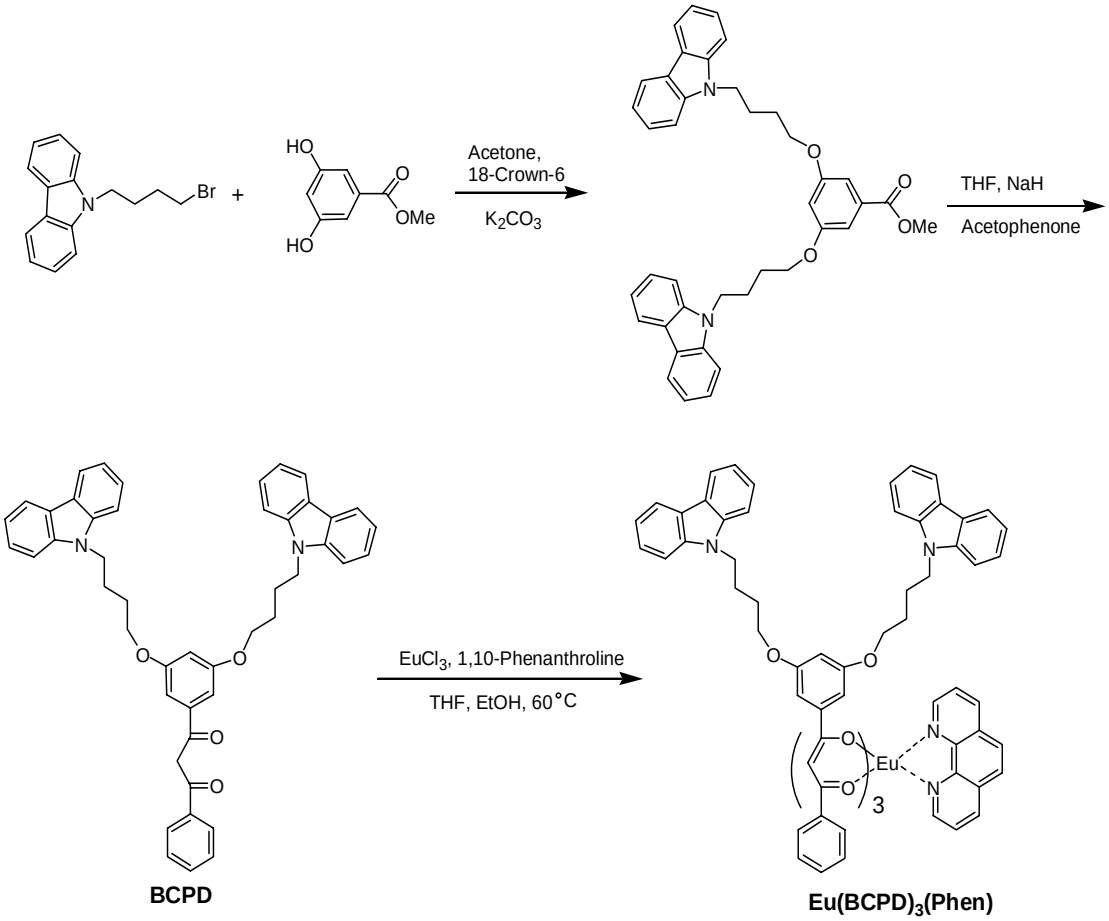
Shangfeng Li,[#] Gaoyu Zhong,[‡] Weihong Zhu,[#] Fuyou Li,[‡] Jianfeng Pan,[#] Wei Huang[‡] and He Tian[*#]

[#] *Lab for Advanced Materials and Institute of Fine Chemicals, East China University of Science & Technology, Shanghai 200237, P. R. China*

[‡] *Institute of Advanced Materials, Fudan University, Shanghai 200433, P. R. China*



Scheme S1. Synthetic route of $Eu(MCPD)_3(Phen)$.



Scheme S2. Synthetic route of $Eu(BCPD)_3(Phen)$.

Synthesis of ethyl 4-[4-(9*H*-carbazol-9-yl)butoxy]benzoate

A mixture of 9-(4-bromobutyl)-9*H*-carbazole (2.00 g, 6.62 mmol), ethyl 4-hydroxybenzoate (1.43 g, 8.61 mmol), potassium carbonate (1.30 g, 9.42 mmol) and 18-crown-6 (0.13 g, 4.72 mmol) in anhydrous acetone (60 mL) was heated at reflux and stirred vigorously under nitrogen for 56 h. The mixture was allowed to cool and evaporate to dryness under reduced pressure. The residue was washed with water and a large amount of precipitate appeared followed by filtration. After recrystallization, a white needle-like crystal was obtained. (1.71 g), yield 66%. mp: 80 - 82 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 1.37 (t, 3H, CH_3), 1.87 (m, 2H, CH_2), 2.10 (m, 2H, CH_2), 3.98 (t, 2H, -OCH_2), 4.32 (dd, 2H, -NCH_2), 4.40 (t, 2H, -OCH_2), 6.84 (d, 2H, J = 8.8 Hz, Ph-H), 7.23 (t, 2H, J_1 = 7.0 Hz, J_2 = 8.2 Hz, Ph-H), 7.43 (d, 2H, J = 8.1 Hz, Ph-H), 7.47 (t, 2H, J_1 = 7.2 Hz, J_2 = 8.3 Hz, Ph-H), 7.96 (d, 2H, J = 8.7 Hz, Ph-H), 8.10 (d, 2H, J = 7.6 Hz, Ph-H).

Synthesis of methyl 3,5-bis[4-(9*H*-carbazol-9-yl)butoxy]benzoate

A mixture of 9-(4-bromobutyl)-9*H*- carbazole (3.00 g, 9.93 mmol), methyl 3,5-dihydroxybenzoate (0.78 g, 4.64 mmol), potassium carbonate (1.82 g, 13.1 mmol) and 18-crown-6 (0.13 g, 4.7 mmol) in anhydrous acetone (100 mL) was heated at reflux and stirred vigorously under nitrogen for 56 h. The mixture was allowed to cool and evaporate to dryness under reduced pressure. The residue was washed with water and a large amount of precipitate appeared followed by filtration. After recrystallization with ethanol, a white powder was obtained (2.5 g), yield 88%. mp: 124 - 127 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 1.89 (m, 4H, CH_2), 2.11 (m, 4 H, CH_2), 3.88 (s, 3H, -OCH_3), 3.99 (t, 4H, -OCH_2), 4.41 (t, 4H, -NCH_2), 6.54 (s, 1H, Ph-H), 7.14 (s, 2H, Ph-H), 7.23 (t, 4H, J_1 = 7.2 Hz, J_2 = 7.4 Hz, Ph-H), 7.42 (d, 4H, J = 8.1 Hz, Ph-H), 7.46 (t, 4H, J_1 = 7.4 Hz, J_2 = 7.8 Hz, Ph-H), 8.10 (d, 4H, J = 7.8 Hz, Ph-H). Anal. Calcd for $C_{40}H_{38}N_2O_4$: C, 78.66; H, 6.27. Found: C, 78.40; H, 6.00.

Synthesis of methyl 3,4,5-tris[4-(9*H*-carbazol-9-yl)butoxy]benzoate

A mixture of 9-(4-bromobutyl)-9*H*-carbazole (3.00 g, 9.93 mmol), methyl 3,4,5-trihydroxy benzoate (0.60 g, 3.31 mmol), potassium carbonate (1.51 g, 10.9 mmol) and 18-crown-6 (0.13 g, 4.7 mmol) in anhydrous acetone (60 mL) was stirred vigorously, and refluxed for 56 h under the protection of nitrogen. After cooled, removed solvents under reduced pressure, the resulting solid was filtrated, and recrystallized from ethanol to give a white needle-like crystal (2.13 g), yield 75%. mp 86 - 88 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 1.55 (m, 2H, CH_2), 1.69 (m, 4H, CH_2), 1.89 - 1.98 (m, 6H, CH_2), 3.84 (m, 5H, -OCH_3, -OCH_2), 3.91 (t, 4H, -OCH_2), 4.10 (t, 2H, -NCH_2), 4.21 (t, 4H, -NCH_2), 7.17 (s, 2H, Ph-H), 7.19 (m, 6H, Ph-H), 7.24 (t, H, J_1 = 1.3 Hz, J_2 = 7.2 Hz, Ph-H), 7.29 (d, 4H, J = 8.2 Hz, Ph-H), 7.36 - 7.42 (m, 6H, Ph-H), 8.05 (d, 2H, J = 7.7 Hz, Ph-H), 8.06 (d, 4H, J = 5.0 Hz, Ph-H). MALDI-TOF MS (FAB): *m/z* 847.9 [M^+ + 1], 846.9 [M^+]. Anal. Calcd for $C_{56}H_{53}N_3O_5$: C, 79.31; H, 6.30. Found: C, 79.08; H, 6.11.

Synthesis of 1-[4-[4-(9*H*-carbazol-9-yl)butoxy]phenyl]-3-phenylpropane-1,3-dione

(MCPD)

To a dry flask containing a solution of acetophenone (0.37 g, 3.08 mmol) and ethyl 4-(4-(9*H*-carbazol-9-yl)butoxy)benzoate (1.20 g, 3.09 mmol) in THF (60 mL) was added quickly 60% sodium hydride (0.30 g, 7.5 mmol). The reaction mixture was heated under argon at 60 °C for 90 h. The solution was then acidified with dilute HCl and extracted with CH_2Cl_2. After solvent removal, the solid residue was separated over a silica gel column CH_2Cl_2/CCl_4 (1:2/v:v) as eluent and get a light yellow solid (0.23 g), yield 16%. mp: 159 - 162 ºC. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 1.89 (m, 2H, CH_2), 2.11 (m, 2H, CH_2), 4.01 (t, 2H, -OCH_2), 4.43 (t, 2H, -NCH_2), 6.79 (s, 1H, =CH), 6.91 (d, 2H, J = 5.23 Hz, Ph-H), 7.25 (t, 2H, J_1 = 4.88 Hz, J_2 = 4.90 Hz, Ph-H), 7.42 (d, 2H, J_2 = 8.06 Hz, Ph-H), 7.44-7.50 (m, 4H, Ph-H), 7.53 (t, 1H, J_1 = 1.42 Hz, J_2 = 1.17 Hz, Ph-H), 7.93-7.97 (m, 4H, Ph-H), 8.11 (d, 2H, J = 7.63 Hz, Ph-H). MS (FAB): *m/z* 463 [M^+ + 2], 462 [M^+ + 1], 461 [M^+], 222 (26.13%), 180 (100%). Anal. Calcd for $C_{31}H_{27}NO_3$: C, 80.67; H, 5.90. Found: C, 80.38; H, 5.69.

Synthesis of 1-[3,5-bis[4-(9*H*-carbazol-9-yl)butoxy]phenyl]-3-phenylpropane-1,3-dione (BCPD)

To a dry flask containing a solution of acetophenone (0.39 g, 3.3 mmol) and Methyl 3,5-bis(4-(9*H*-carbazol-9-yl)butoxy)benzoate (2.00 g, 3.28 mmol) in THF (80 mL) was added quickly 60% sodium hydride (0.20 g, 5.0 mmol). The reaction mixture was heated under argon at 60 ºC for 90 h. The solution was then acidified with dilute HCl and extracted with CH_2Cl_2. After solvent removal, the solid residue was separated over a silica gel column CH_2Cl_2/CCl_4 (1:5 / v:v) as eluent and get a light yellow solid (0.43 g), yield 19%. mp: 57 - 59 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 1.88 (m, 4H, CH_2), 2.11 (m, 4H, CH_2), 3.98 (t, 4H, -OCH_2), 4.41 (t, 4H, -NCH_2), 6.53 (s, 1H, Ph-H), 6.75 (s, 1H, =CH), 7.04(s, 2H, Ph-H), 7.25 (t, 4H, J_1 = 7.2 Hz, J_2 = 7.3 Hz, Ph-H), 7.42 - 7.51 (m, 10H, Ph-H), 7.55 (t, 1H, J_1 = 7.2 Hz, J_2 = 7.0 Hz, Ph-H), 7.97 (d, 2H, J = 7.6 Hz, Ph-H), 8.11 (d, 4H, J = 7.7 Hz, Ph-H). MS (FAB): *m/z* 700 [M^+ + 2] (7.6%), 699 [M^+ + 1] (59%), 698 [M^+] (95%), 218 (38.7%), 222 (54.3%), 180 (100%). Anal. Calcd for $C_{47}H_{42}N_2O_4$: C, 80.78; H, 6.06. Found: C, 80.50; H, 5.85.

Synthesis of 1-[3,4,5-tris[4-(9*H*-carbazol-9-yl)butoxy]phenyl]-3- phenylpropane-1,3-dione (TCPD)

To a dry flask containing a solution of acetophenone (0.21 g, 1.76 mmol) and methyl 3,4,5-tris(4-(9*H*-carbazol-9-yl)butoxy)benzoate (1.50 g, 1.76 mmol) in THF (60 mL) was added quickly 60% sodium hydride (0.10 g, 2.5 mmol). The reaction mixture was heated at 60 ºC for 90 h under argon. The solution was then acidified with dilute HCl, and extracted with CH_2Cl_2. After solvent removal, the solid residue was purified via a silica gel column CH_2Cl_2/CCl_4 (1:2 / v:v) as eluent to get a light yellow oil (0.49 g), yield 30%. mp 71 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 1.60 (m, 2H, CH_2), 1.74 (m, 4H, CH_2), 1.94 (m, 6H, CH_2), 3.88 (t, 2H, -OCH_2), 3.94 (t, 4H, -OCH_2), 4.12 (t, 2H, -NCH_2), 4.22 (t, 4H, -NCH_2), 6.65 (s, 1H, =CH), 7.08 (s, 2H, Ph-H), 7.17 - 7.21 (m, 6H, Ph-H), 7.25 - 7.28 (m, 2H, Ph-H), 7.30 - 7.32 (d, 4H, J = 8.2 Hz, Ph-H), 7.37 - 7.41 (m, 6H, Ph-H), 7.47 (t, 2H, J_1 = 7.8 Hz, J_2 = 7.5 Hz, Ph-H), 7.54 (t, 1H, J_1 = 7.9 Hz, J_2 = 7.8 Hz), 7.92 (d, 2H, J = 7.2 Hz), 8.07 (t, 6H, J_1 = 7.6 Hz, J_2 = 6.8 Hz, Ph-H). MS (FAB): *m/z* 974.4 [M^+ + K], 958.4 [M^+ + Na]. Anal. Calcd for $C_{63}H_{57}N_3O_5$: C, 80.83; H, 6.14. Found: C, 80.58; H, 5.87.

Synthesis of Tris[1-[4-[4-(9*H*-carbazol-9-yl)butoxy]phenyl]-3-phenylpropane-1,3-dione] (1,10-phenanthroline) Europium (III) (Eu(MCPD)$_3$(Phen))

To a solution of MCPD (120 mg, 0.26 mmol) and 1,10-phenanthroline monohydrate (18 mg, 90.9 μmol) in THF (10 mL), 1 M aqueous NaOH (0.2 mL) was syringed dropwise followed by aqueous $EuCl_3$ hexahydrate (31.7 mg, 87.4 μmol). After injection of argon repeatedly, the mixture was stirred at 60 °C for 4 h and then cooled. The product was collected by filtration and washed with deionized water twice before crystallization with acetone and vacuum drying. (112 mg), yield 76%. mp: 110 - 113 ºC. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 1.72 (s, 6H, CH_2), 2.17 (s, 6H, CH_2), 3.77 (s, 6H, CH_2), 4.35 (s, 6H, CH_2), 5.59 (s, 6H, =CH, Ph-H), 5.95 (s, 6H, Ph-H), 6.20 (s, 6H, Ph-H), 6.61 (m, 12H, Ph-H), 7.26 - 7.46 (m, 15H, Ph-H), 8.11 (d, 9H, Ph-H), 8.97 (s, 2H, Ph-H), 9.90 (s, 2H,

Ph-H), 10.64 (s, 2H, Ph-H), 11.01 (s, 2H, Ph-H); MS (FAB): *m/z* 1752.6 [M^+ + K], 1736.7 [M^+ + Na], 1714 [M^+]. Anal. Calcd for $C_{105}H_{86}EuN_5O_9$: C, 73.59; H, 5.06. Found: C, 73.21; H, 4.69.

Synthesis of Tris[1-[3,5-bis[4-(9*H*-carbazol-9-yl)butyloxy]phenyl]-3-phenylpropane-1,3-dione] (1,10-phenanthroline) Europium (III) (Eu(BCPD)$_3$(Phen))

To a solution of BCPD (0.10 g, 0.14 mmol) and 1,10-phenanthroline monohydrate (11.3 mg, 57.2 μmol) in THF (10 mL), 1 M aqueous NaOH (0.20 mL) was syringed dropwise followed by aqueous $EuCl_3$ hexahydrate (17.5 mg, 48.2 μmol). After injection of argon repeatedly, the mixture was stirred at 60 °C for 4 h and then cooled. The product was collected by filtration and washed with deionized water twice before crystallization with acetone and vacuum drying (57 mg), yield 49%. mp: 89 - 92 ºC. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 1.56 (s, 12H, CH_2), 1.86 (s, 12H, CH_2), 3.51 (s, 12H, CH_2), 4.24 (s, 12H, CH_2), 5.67 (s, 3H, =CH), 6.00 (s, 6H, Ph-H), 6.61 (m, 9H, Ph-H), 7.26 (m, 12H, Ph-H), 7.40 (m, 30H, Ph-H), 8.10 (s, *J* = 5.5 Hz, 15H, Ph-H), 7.97 (d, *J* = 7.4 Hz, 2H, Ph-H), 8.52 (s, 2H, Ph-H), 10.42 (s, 2H, Ph-H), 10.73 (s, 2H, Ph-H); MALDI-TOF MS: *m/z* [M^+] 2425. Anal. Calcd for $C_{153}H_{131}EuN_8O_{12}$: C, 75.76; H, 5.44. Found: C, 75.28; H, 5.07.

Synthesis of Tris[1-[3,4,5-tris[4-(9*H*-carbazol-9-yl)butoxy]phenyl]-3-phenyl-propane- 1,3- dione] (1,10- phenanthroline) Europium (III) (Eu(TCPD)$_3$(Phen))

To a solution of TCPD (226 mg, 240 μmol) and 1,10-phenanthroline monohydrate (16 mg, 81 μmol) in THF (10 mL), 1 M aqueous NaOH (0.38 mL) was syringed dropwise, followed by aqueous $EuCl_3 \cdot 6H_2O$ (29.4 mg, 80 mmol). The mixture was stirred at 60 °C for 4 h under the protection of nitrogen. After cooled, the product was filtrated, washed with deionized water, and recrystallized from acetone to give Eu(TCPD)$_3$(Phen) (180 mg), yield 72%. mp 84 – 87 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 1.22 - 2.03 (m, 36H, CH_2), 3.28 - 4.40 (s, 36H, CH_2), 6.19 (s, 3H, =CH), 6.44 (s, 6H, Ph-H), 7.08 - 7.47 (m, 66H, Ph-H), 7.93 - 8.06 (m, 21H, Ph-H), 8.52 (s, 2H, Ph-H), 9.21 (s, 2H, Ph-H), 10.36 (s, 2H, Ph-H), 10.64 (s, 2H, Ph-H). MALDI-TOF MS: *m/z* [M^+] 3143.6. Anal. Calcd for $C_{201}H_{176}EuN_{11}O_{15}$: C, 76.94; H, 5.65 Found: C, 76.58; H, 5.28.

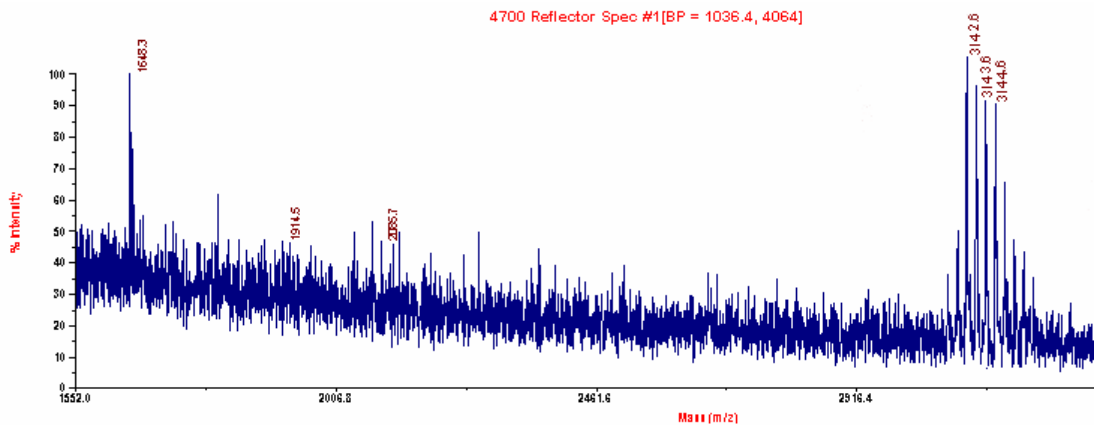


Fig. S1 MALDI-TOF mass spectrum of dendritic Europium complex Eu(TCPD)$_3$(Phen).

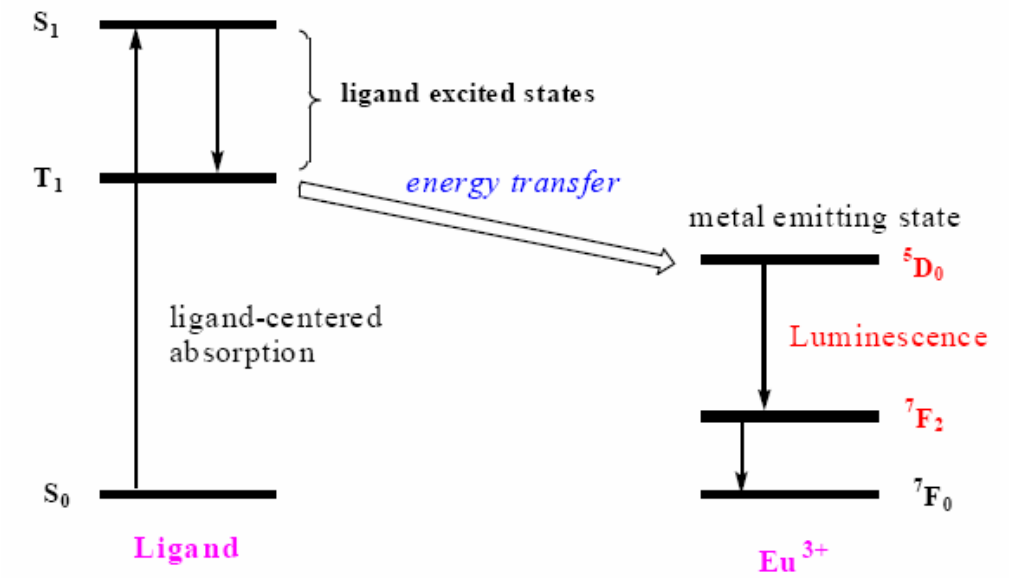


Fig. S2 Schematic diagram of energy transfer in Eu (III) complexes. D and F are corresponding to Eu (III) ion energy levels.

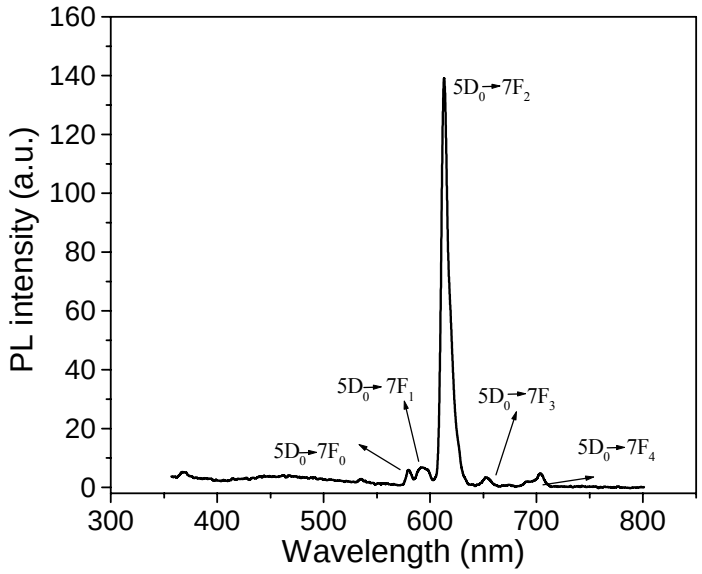


Fig. S3 Five peaks at 586, 591, 615, 651 and 702 nm are corresponding to $^5D_0 \rightarrow {}^7F_j$ (j = 0 - 4) transitions, respectively.

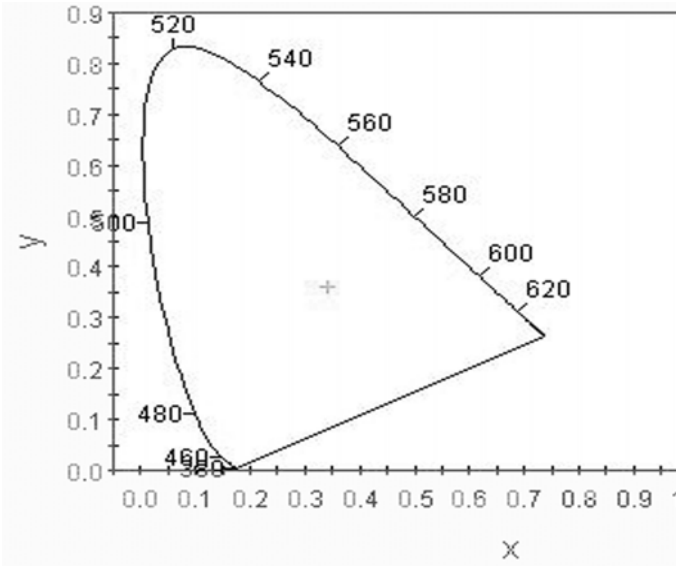


Fig. S4 CIE chromaticity coordinate (0.333, 0.348) of EL device with the configuration of ITO/NPB/CBP:Eu(TCPD)$_3$(Phen)/BCP/Mg:Ag at the applied voltage of 16.2 V.