*Journal of Materials Chemistry*

## Supporting Information

# A New Class of Non-Conjugated Bipolar Hybrid Hosts for Phosphorescent Organic Light-Emitting Diodes

Lichang Zeng, Thomas Y-H. Lee, Paul B. Merkel and Shaw H. Chen*

### Materials Synthesis

All chemicals, reagents, solvents, and poly(*N*-vinylcarbazole) with a weight-average molecular weight of $1.1 \times 10^6$ g/mole were used as received from commercial sources without further purification except toluene and tetrahydrofuran (THF) that had been distilled over sodium and benzophenone, respectively. Intermediates 9-(2-methylpropyl)carbazole (**1**), [1] 2-chloro-4,6-biphenyl-1,3,5-triazine (**9**), [2] 2,4,6-tris(4-bromophenyl)-1,3,5-triazine (**10**), [3] and 1,3-bis(5-(4-bromophenyl)-1,3,4-oxadiazole-2-yl)benzene (**11**) [4] were synthesized according to the literature procedures. All reactions were carried out under argon and anhydrous conditions unless noted otherwise.

*3,6-Dibromo-9-(2-methylpropyl)carbazole*, **2.** Into a suspension of **1** (10.0 g, 44.8 mmol) and silica gel (230-400 mesh, 100 g) in methylene chloride (400 ml) was added NBS powder (15.9 g, 89.6 mmol) at room temperature. The reaction mixture was stirred in the dark for 3 h before silica gel was removed by filtration. The filtrate was washed with water and dried over $MgSO_4$. Upon evaporating off the solvent, the crude product was purified by column chromatography with hexane as the eluent to yield **2** (16.9 g, 99 %) as white crystals. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.14-8.13 (d, *J*=4.0 Hz 2H), 7.55-7.53 (m, 2H), 7.27-7.25 (m, 2H), 4.04-4.02 (d, *J*=7.6 Hz 2H), 2.32-2.30 (m, 1H), 0.97-0.94 (m, 6H).

*3-Bromo-9-(2-methylpropyl)carbazole*, **3.** The procedure for the synthesis of **2** was followed with 1 eq. NBS to prepare **3** from **1** as white crystals in an 84% yield. $^1$H NMR (400 MHz,

$CDCl_3$): $\delta$ (ppm) 8.20-8.19 (d, *J*=1.6 Hz 1H), 8.05-8.03 (d, *J*=8.0 Hz 1H), 7.53-7.38 (m, 3H), 7.28-7.21 (m, 2H), 4.04-4.02 (m, 2H), 2.32-2.30 (m, 1H), 0.97-0.94 (m, 6H).

*2-(9-(2-Methylpropyl)carbazol-3-yl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane*, **4.** BuLi (2.5 M in hexane, 6.95 ml, 17.4 mmol) was added dropwise into a solution of **3** (4.2 g, 13.9 mmol) in THF (80 ml) at −78 $^oC$, where the mixture was stirred for 3 h before adding 2-*iso*propoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (4.05 g, 21.75 mmol) in one portion. The reaction mixture was allowed to warm up to room temperature over a period of 12 h, quenched with water, and then extracted with ether. The organic extracts were combined, washed with brine and water, and dried over $MgSO_4$. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexane/methylene chloride 3:1 (v/v) as the eluent to yield **4** (3.95 g, 81 %) as a white powder. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.60 (s, 1H), 8.15-8.10 (d, *J*=2.0 Hz 1H), 7.90-7.85 (d, *J*=2.0 Hz 1H), 7.45-7.35 (m, 3H), 7.25-7.15 (m, 1H), 4.10-4.09 (d, *J*=4.0 Hz 2H), 2.42-2.30 (m, 1H), 1.39(s, 12H), 0.97-0.95 (d, *J*=8.0 z 6H).

*3-Bromo-6-(9-(2-methylpropyl)carbazol-3-yl)-9-(2-methylpropyl)carbazole*, **5.** Toluene (30 ml) and $H_2O$ (10 ml) were added into a mixture of **4** (1.2 g, 3.43 mmol), **2** (3.27 g, 8.59 mmol), $Pd(PPh_3)_4$ (0.22 g, 0.17 mmol), and $Na_2CO_3$ (3.43 g, 34 mmol). The reaction mixture was stirred at 90 $^oC$ for 12 h, cooled to room temperature, and extracted with methylene chloride. The organic extracts were combined, washed with water, and dried over $MgSO_4$. Upon evaporating off the solvent, the crude product was purified by gradient column chromatography on silica gel with hexane/methylene chloride 9:1 to 3:1 (v/v) to yield **5** (0.62 g, 34%) as a white powder. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.38-8.34 (m, 2H), 8.29-8.28 (d, *J*=1.6 Hz 1H), 8.19-8.17 (d, *J*=7.6 Hz 1H), 7.85-7.78 (m, 2H), 7.55-7.42 (m, 5H), 7.30-7.23 (m, 2H), 4.15-4.10 (m, 4H), 2.45-2.38 (m, 2H), 1.13-1.10 (m, 12H).

*3-Allyl-6-(9-(2-methylpropyl)carbazol-3-yl)-9-(2-methylpropyl)carbazole*, **6**. THF (20 ml) was added into a mixture of **5** (0.62 g, 1.18 mmol), allyltributyltin (0.78 g, 2.36 mmol), $Pd(PPh_3)_4$ (0.068 g, 0.06 mmol), and LiCl (0.092 g, 3.54 mmol). The reaction mixture was stirred at 90 $^oC$ for 24 h. After evaporating off the solvent, the crude product was purified by gradient column chromatography on silica gel with hexane/methylene chloride 9:1 to 4:1 (v/v) as the eluent to yield **6** (0.35g, 61 %) as a white powder. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.40-8.38 (m, 2H), 8.19-8.17 (d, *J*=7.6 Hz 1H), 8.00 (s, 1H), 7.93-7.79 (m, 2H), 7.50-7.41( m, 4H), 7.34-7.22

(m, 3H), 6.18-6.08 (m, 1H), 5.20-5.10 (m, 2H), 4.15-4.11 (m, 4H), 3.61-3.59 (d, *J*=6.4 Hz 2H), 2.50-2.39 (m, 2H), 1.03-1.01 (m, 12H).

*1-Bromo-4-(3-(6-(9-(2-methylpropyl)carbazol-3-yl)-9-(2-methylpropyl)carbazol-3-yl)propyl)-benzene*, **7.** 9-BBN (0.5 M in THF, 6 ml, 3.0 mmol) was added dropwise into a solution of **6** (0.46 g, 0.95 mmol) in THF (3 ml) at 0 $^{o}$C. The mixture was stirred at room temperature for 15 min and then at 35 $^{o}$C for 18 h before transferring into a mixture of *p*-dibromobenzene (1.12 g, 4.7 mmol), $Pd(PPh_3)_4$ (0.055 g, 0.047 mmol), $K_2CO_3$ (0.98 g, 7.1 mmol), $H_2O$ (3 ml) and THF (5 ml). The reaction mixture was stirred at 85 $^{o}$C for 40 h, cooled to room temperature, and extracted with chloroform. The organic extracts were combined, washed with water, and dried over $MgSO_4$. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexane/chloroform 4:1 (v/v) as the eluent to yield **7** (0.36 g, 59 %) as a white powder. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.40-8.38 (m, 2H), 8.19-8.17 (d, *J*=7.6 Hz, 1H), 7.98-7.97 (d, *J*=0.8 Hz, 1H), 7.81-7.79 (m, 2H), 7.50-7.39 (m, 6), 7.33-7.23 (m, 3H), 7.10-7.08 (d, *J*=8.4 Hz, 2H), 4.15-4.11 (m, 4H), 2.86-2.83 (t, *J*=7.6 Hz, 2H), 2.69-2.65 (t, *J*=7.6 Hz, 2H), 2.44-2.42 (m, 2H), 2.09-2.03 (m, 2H), 1.04-1.01 (m, 12H).

*2-(4-(3-(6-(9-(2-Methylpropyl)carbazol-3-yl)-9-(2-methylpropyl)carbazol-3-yl)propyl)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane*, **8.** The procedure for the synthesis of **4** was followed to prepare **8** from **7** as a white powder in an 88 % yield. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.40-8.38 (m, 2H), 8.19-8.17 (d, *J*=7.6 Hz, 1H), 7.99 (s, 1H), 7.84-7.78 (m, 2H), 7.75-7.74 (d, *J*=8.8 Hz, 2), 7.50-7.43 (m, 4H), 7.32-7.23 (m, 3H), 4.15-4.10 (m, 4H), 2.86-2.83 (t, *J*=7.6 Hz, 2H), 2.69-2.65 (t, *J*=7.6 Hz, 2H), 2.44-2.42 (m, 2H), 2.09-2.03 (m, 2H), 1.34 (s, 12H), 1.04-1.01 (m, 12H).

*3-(9-(2-Methylpropyl)carbazol-3-yl)-9-(2-methylpropyl)carbazole*, **Cz(MP)2**. A solution of **1** (0.3 g, 1.34 mmol) in chloroform (16 ml) was slowly added into a mixture of Iron(III) chloride (0.92 g, 5.37 mmol) and chloroform(30 ml) under argon. The reaction mixture was stirred at room temperature for 4 h, quenched with 10 % sodium hydroxide aqueous solution (100 ml), and extracted with chloroform. The organic extracts were combined, washed with water and dried over $MgSO_4$. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexane/chloroform 1:4 (v/v) as the eluent to yield **Cz(MP)2** (0.23 g, 76 %) as a white powder (Found: C, 86.08; H, 7.22; N, 6.24. Calc. for $C_{32}H_{32}N_2$: C, 86.45; H, 7.25; N, 6.30%.); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.40 (s, 2H), 8.19-8.18 (d,

*J*=3.8Hz, 2H), 7.83-7.81 (m, 2H), 7.50-7.41 (m, 6H), 7.26-7.23 (m, 2H), 4.15 (s, 4H), 2.50-2.39 (m, 2H), 1.03-1.02 (m, 12H).

*2-(4-(3-(6-(9-(2-Methylpropyl)carbazol-3-yl)-9-(2-methylpropyl)carbazol-3-yl)propyl)phenyl)-4,6-diphenyl-1,3,5-triazine*, **TRZ-1Cz(MP)2**. Toluene (10 ml) and $H_2O$ (2 ml) were added into a mixture of **8** (0.34 g, 0.49 mmol), **9** (0.16 g, 0.62 mmol), $Pd(PPh_3)_4$ (0.056 g, 0.049 mmol), and $Na_2CO_3$ (0.39 g, 3.68 mmol). The reaction mixture was stirred at 95 $^oC$ for 40 h, cooled to room temperature, and then extracted with methylene chloride. The organic extracts were combined, washed with water, and dried over $MgSO_4$. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexane/methylene chloride 4:1 (v/v) to yield **TRZ-1Cz(MP)2** (0.28 g, 69 %) as a yellow powder (Found: C, 84.52; H, 6.39; N,8.74. Calc. for $C_{56}H_{51}N_5$: C, 84.71; H, 6.47; N, 8.82%); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.79-8.76 (m, 4H), 8.71-8.69 (d, *J*=8.4 Hz, 2H), 8.41-8.39 (m, 2H), 8.19-8.17 (d, *J*=7.6 Hz, 1H), 8.02 (s, 1H), 7.81-7.79 (m, 2H), 7.60-7.55 (m, 6),7.49-7.42 (m, 6H), 7.35-7.33 (m, 2H), 7.25-7.20 (m, 1H), 4.14-4.11 (m, 4H), 2.93-2.82 (m, 4H), 2.44-2.40 (m, 2H), 2.20-2.10 (m, 2H), 1.03-1.01 (m, 12H). MALD/I TOF MS (DCTB) m/z ($[M]^+$): 793.4.

*2,4,6-Tris(4-(3-(6-(9-(2-methylpropyl)carbazol-3-yl)-9-(2-methylpropyl)carbazol-3-yl)propyl)-phenyl)-1,3,5-triazine*, **TRZ-3Cz(MP)2**. 9-BBN (0.5 M in THF, 3.30 ml, 1.65 mmol) was added dropwise into a solution of **6** (0.21 g, 0.42 mmol) in THF (2 ml) at 0 $^oC$. The mixture was stirred at room temperature for 15 min and then at 35 $^oC$ for 18 h before transferring into a mixture of **10** (0.07 g, 0.13 mmol), $Pd(PPh_3)_4$ (0.030 g, 0.026 mmol), $Na_2CO_3$ (3.82 g, 36.0 mmol), $H_2O$ (18 ml) and toluene (30 ml). The reaction mixture was stirred at 85 $^oC$ for 40 h, cooled to room temperature, and then extracted with chloroform. The organic extracts were combined, washed with water, and dried over $MgSO_4$. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexane/methylene chloride 3:2 (v/v) as the eluent to yield **TRZ-3Cz(MP)2** (0.147 g, 65 %) as a pale yellow powder (Found: C, 85.43; H, 7.01; N, 7.11. Calc. for $C_{126}H_{123}N_9$: C, 85.82; H, 7.03; N, 7.15%). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.69-8.67 (d, 6H), 8.40-8.39 (t, *J*=2.2Hz, 6H), 8.18-8.16 (d, *J*=3.8Hz, 3H), 8.01 (s, 3H), 7.82-7.78 (m, 6H), 7.47-7.30 (m, 27H), 4.12-4.09 (m, 12H), 2.92-2.82 (m, 12H), 2.48-2.35 (m, 6H), 2.19-2.11 (m, 6H), 1.03-0.99 (m, 36H). MALD/I TOF MS (DCTB) m/z ($[M]^+$): 1762.1.

*1,3-Bis(5-(4-(3-(6-(9-(2-methylpropyl)carbazol-3-yl)-9-(2-methylpropyl)carbazol-3-yl)propyl)-phenyl)-1,3,4-oxadiazol-2-yl)benzene*, **OXD-2Cz(MP)2**. 9-BBN (0.5 M in THF, 3.0 ml, 1.50

mmol) was added dropwise into a solution of **6** (0.20 g, 0.41 mmol) in THF (3 ml) at 0 $^{o}$C. The mixture was stirred at room temperature for 15 min and then at 35 $^{o}$C for 18 h before transferring into a mixture of **11** (0.11 g, 0.20 mmol), $Pd(PPh_3)_4$ (0.033 g, 0.029 mmol), $Na_2CO_3$ (0.60 g, 4.35 mmol), $H_2O$ (2 ml) and toluene (5 ml). The reaction mixture was stirred at 85 $^{o}$C for 40 h, cooled to room temperature, and then extracted with chloroform. The organic extracts were combined, washed with water, and dried over $MgSO_4$. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with chloroform/ethyl acetate 50:1 (v/v) as the eluent to yield **OXD-2Cz(MP)2** (0.12 g, 44 %) as a pale yellow powder (Found: C, 82.38; H, 6.42; N, 8.42. Calc. for $C_{92}H_{86}N_8O_2$: C, 82.73; H, 6.49; N, 8.39%) $^1$H NMR (400 MHz, $CDCl_3$): $\delta$(ppm) 8.84 (s, 1H), 8.40-8.39 (m, 4H), 8.32-8.30 (m, 2H), 8.18-8.16 (d, *J*=7.6 Hz, 2H), 8.11-8.08 (d, *J*=8.4 Hz, 4H), 8.00 (s, 2H), 7.82-7.78 (m, 4H), 7.66-7.63 (t, *J*=8.4 Hz, 1H), 7.49-7.32 (m, 16H), 7.25-7.21 (m, 2H), 4.13-4.11 (m, 8H), 2.90-2.88 (t, *J*=7.6 Hz, 4H), 2.82-2.80 (t, *J*=7.6 Hz, 2H), 2.46-2.40 (m, 4H), 2.20-2.10 (m, 4H), 1.03-1.01 (m, 24H). MALD/I TOF MS (DCTB) m/z ($[M]^+$): 1334.8.

**References:**

[1] M. Hammond, R. L. Elliott, M. L. Gillaspy, D. C. Hager, R. F. Hank, J. A. LaFlamme, R. M. Oliver, P. A. Da Silva-Jardine, R. W. Stevenson, C. M. Mack and J. V. Cassella, *Bioorg. Med. Chem. Lett*., 2003, **13**, 1989-1992.

[2] H. Henneberger and M. Wagner, *U.S. Pat.*, *5 438 138*, 1995.

[3] J. R. Norell, *U.S. Pat.*, *3,932,402*, 1976.

[4] R. Cristiano, F. Ely and H. Gallardo, *Liquid Crystals*, 2005, **32**, 15-25.

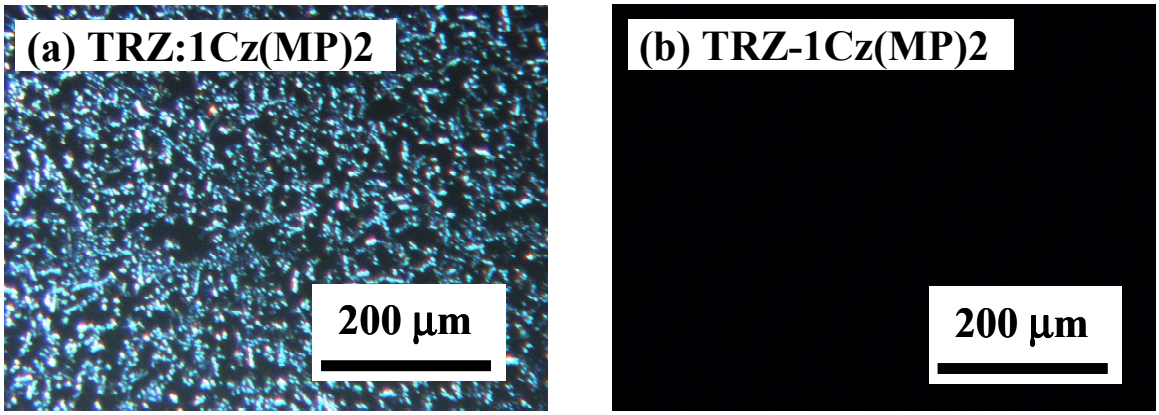


**Figure S1**: Polarizing optical micrographs of spin-cast films of **TRZ:1Cz(MP)2** mixture (a) and **TRZ-1Cz(MP)2** hybrid after thermal annealing at 70 and 120 $^{o}$C, respectively, for ½ h.