

Highly Efficient Blue Thermally Activated Delayed Fluorescence Organic Light Emitting Diodes Based on Tercarbazole Donor and Boron Acceptor Dyads

Durai Karthik, Dae Hyun Ahn, Jae Hong Ryu, Hyuna Lee, Jee Hyun Maeng, Ju Young Lee,
Jang Hyuk Kwon**

Organic Optoelectronic Device Laboratory (OODL), Department of Information Display, Kyung
Hee University, Seoul, Republic of Korea.

*Corresponding author: jhkwon@khu.ac.kr, juyoung105@khu.ac.kr

Supplementary Information

Experimental section

Synthesis

3-bromo-6-methyl-9-phenyl-9H-carbazole (2): Compound **1** (7.90 g, 30.70 mmol) was dissolved in DMF (100 mL) in a round bottom flask (protected from light, covered by aluminium foil). Then, N-bromosuccinimide (5.46 g, 30.70 mmol) was added portion wise over a period of 15 min at room temperature. After, the addition over, it was allowed to stir over night. Then, it was quenched by addition of ice cold water. The formed solids were filtered and washed with water. The collected solids were recrystallized using methanol. White solid, yield 9.06 g (88%); ¹H NMR (CDCl₃, 400 MHz): δ 8.20 (d, *J* = 2.0 Hz, 1H), 7.87 (s, 1H), 7.60-7.57 (m, 2H), 7.51-7.49 (m, 2H), 7.47-7.43 (m, 2H), 7.29-7.22 (m, 3H), 2.53 (s, 3H) ppm.

6,6''-dimethyl-9,9''-diphenyl-9H,9'H,9''H-3,3':6',3''-tercarbazole (M3Cz): A mixture of **2** (5.90 g, 17.54 mmol), 3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (3.50 g, 8.35 mmol), K₂CO₃ (6.92 g, 50.10 mmol) and Pd(PPh₃)₄ (0.58 g, 6 mol%) in THF/water (3:1) (150 mL) was refluxed for 24 hrs under inert atmosphere. Then, it allowed to cool to room temperature and extracted with MC three times and washed thoroughly with water. The combined organic fractions were dried over anhydrous MgSO₄ and adsorbed on silica. Then, it was purified by column chromatography using MC/hexanes (2/3) as eluent. White solid, yield 3.55 g (63%), ¹H NMR (CDCl₃, 400 MHz): δ 8.50 (s, 2H), 8.46 (s, 2H), 8.13 (br, 1H), 8.05 (s, 2H), 7.83-7.77 (m, 4H), 7.65-7.45 (m, 14H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.26-7.24 (m, 2H), 2.58 (s, 6H) ppm.

9'-(5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracen-7-yl)-6,6''-dimethyl-9,9''-diphenyl-9H,9'H,9''H-3,3':6',3''-tercarbazole (M3CzB): A mixture of M3Cz (3.00 g, 4.43 mmol), 7-bromo-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (1.70 g, 4.87 mmol), t-BuONa (0.51 g,

5.32 mmol), t-Bu₃PHBF₄ (19 mg, 1.5 mol%) and Pd(dba)₂ (25 mg, 1 mol%) in toluene was refluxed for 24 hrs. Then, it was allowed to cool to room temperature and the formed solids were filtered through Whatman filter paper. The solids were dissolved in excess MC and filtered through silica-celite pad. The filtrate was concentrated and recrystallized from methanol. Pale green solid, yield 3.23 g (77%). Then, it was purified by sublimation. ¹H NMR (CDCl₃, 400 MHz): δ 8.75 (d, J = 7.6 Hz, 2H), 8.57 (s, 2H), 8.50 (s, 2H), 8.07 (s, 2H), 7.84-7.74 (m, 8H), 7.65-7.58 (m, 12H), 7.52-7.43 (m, 6H), 7.35 (d, J = 8.4 Hz, 2H), 7.25 (s, 2H), 2.58 (s, 6H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ 160.6, 158.4, 140.2, 139.7, 139.6, 138.0, 135.1, 134.6, 133.8, 129.8, 129.4, 127.3, 127.2, 126.9, 126.1, 126.0, 124.8, 123.9, 123.7, 123.1, 120.4, 118.9, 118.8, 118.5, 110.6, 110.0, 109.6, 106.3 21.4 ppm. HRMS ‘Found: [M]⁺ 945.3536; ‘molecular formula C₆₈H₄₄BN₃O₂’ requires [M]⁺ 945.3538.

9'-(2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracen-7-yl)-9,9''-diphenyl-9H,9'H,9''H-3,3':6',3''-tercarbazole (3CzTB): It was synthesized according to the procedure described for M3CzB using M3Cz (1.20 g, 1.85 mmol) and 7-bromo-2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (0.94 g, 2.04 mmol) as starting materials. Pale green solid, yield 1.46 g (77%). ¹H NMR (CDCl₃, 400 MHz): δ 8.82 (s, 2H), 8.59 (s, 2H), 8.52 (s, 2H), 8.27 (d, J = 7.6 Hz, 2H), 7.86-7.83 (m, 8H), 7.65-7.63 (m, 8H), 7.57-7.42 (m, 12H), 7.35-7.32 (m, 2H), 1.53 (s, 18H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ 158.8, 158.6, 145.3, 143.5, 141.3, 140.1, 139.9, 137.8, 135.0, 134.1, 131.6, 130.3, 129.9, 127.4, 127.1, 126.1, 126.0, 125.8, 124.7, 124.0, 123.6, 120.5, 120.0, 119.0, 118.9, 118.0, 110.7, 110.0, 109.9, 106.2, 34.6, 31.6 ppm. HRMS ‘Found: [M]⁺ 1029.4458; ‘molecular formula C₇₄H₅₆BN₃O₂’ requires [M]⁺ 1029.4477.

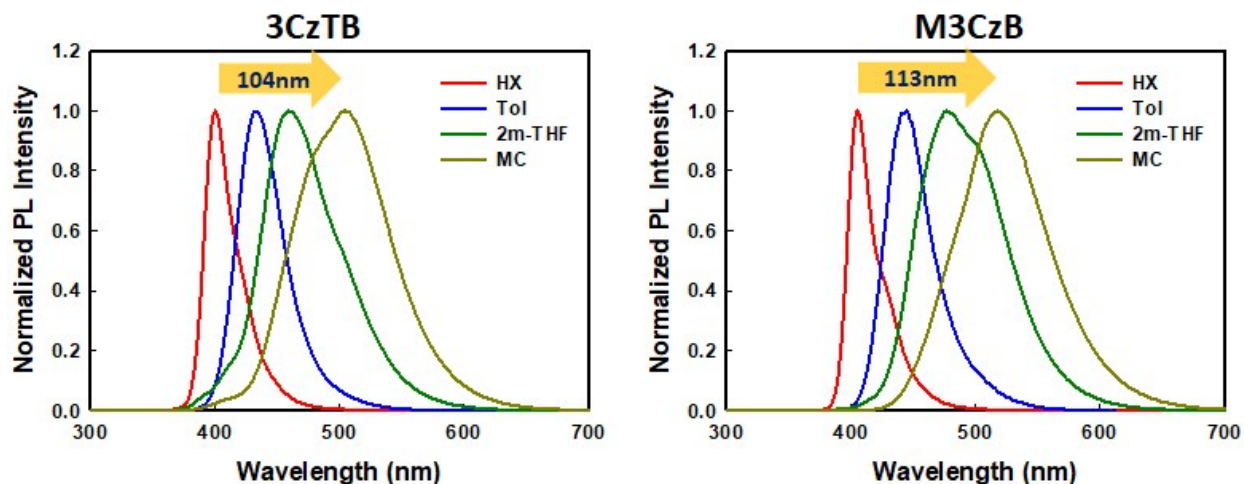


Fig. S1. Photoluminescence solvatochromism of materials in different solvents.

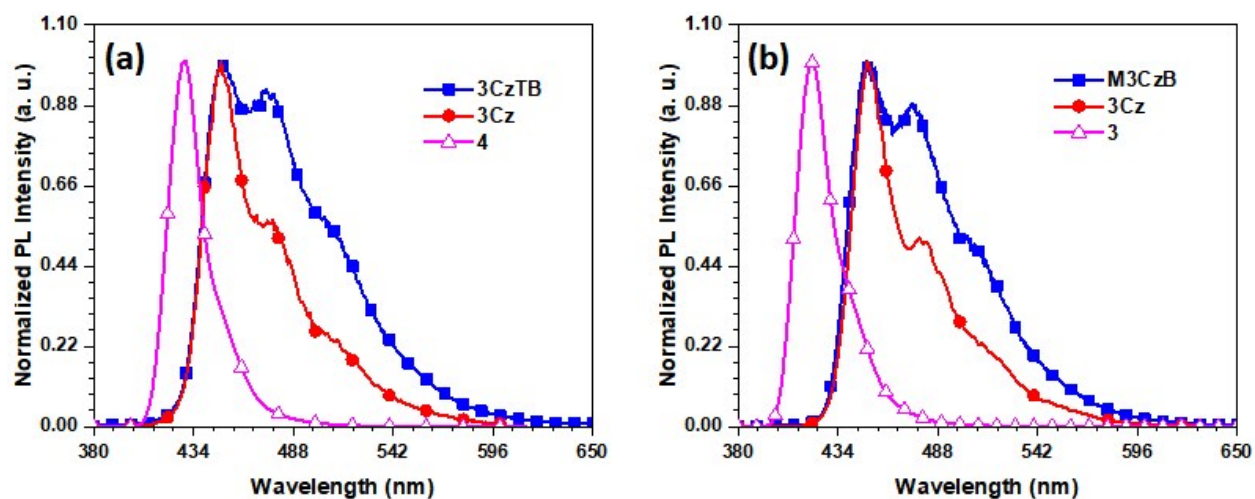


Fig. S2. Photoluminescence spectra of emitters and corresponding donors and acceptors at 77K.

Table S1. Excited state lifetimes and rate constants of materials.

Material	τ_p (ns)	τ_d (μ s)	Φ_{Prompt}	Φ_{Delayed}	k_p^f (10^7) s^{-1}	k_d^f (10^5) s^{-1}	k_{risc} (10^5) s^{-1}	k_{nr}^t (10^4) s^{-1}
3CzTB	23.40	9.32	0.67	0.21	4.27	1.07	1.02	3.90
M3CzB	88.20	7.84	0.69	0.24	1.13	1.28	1.40	2.88

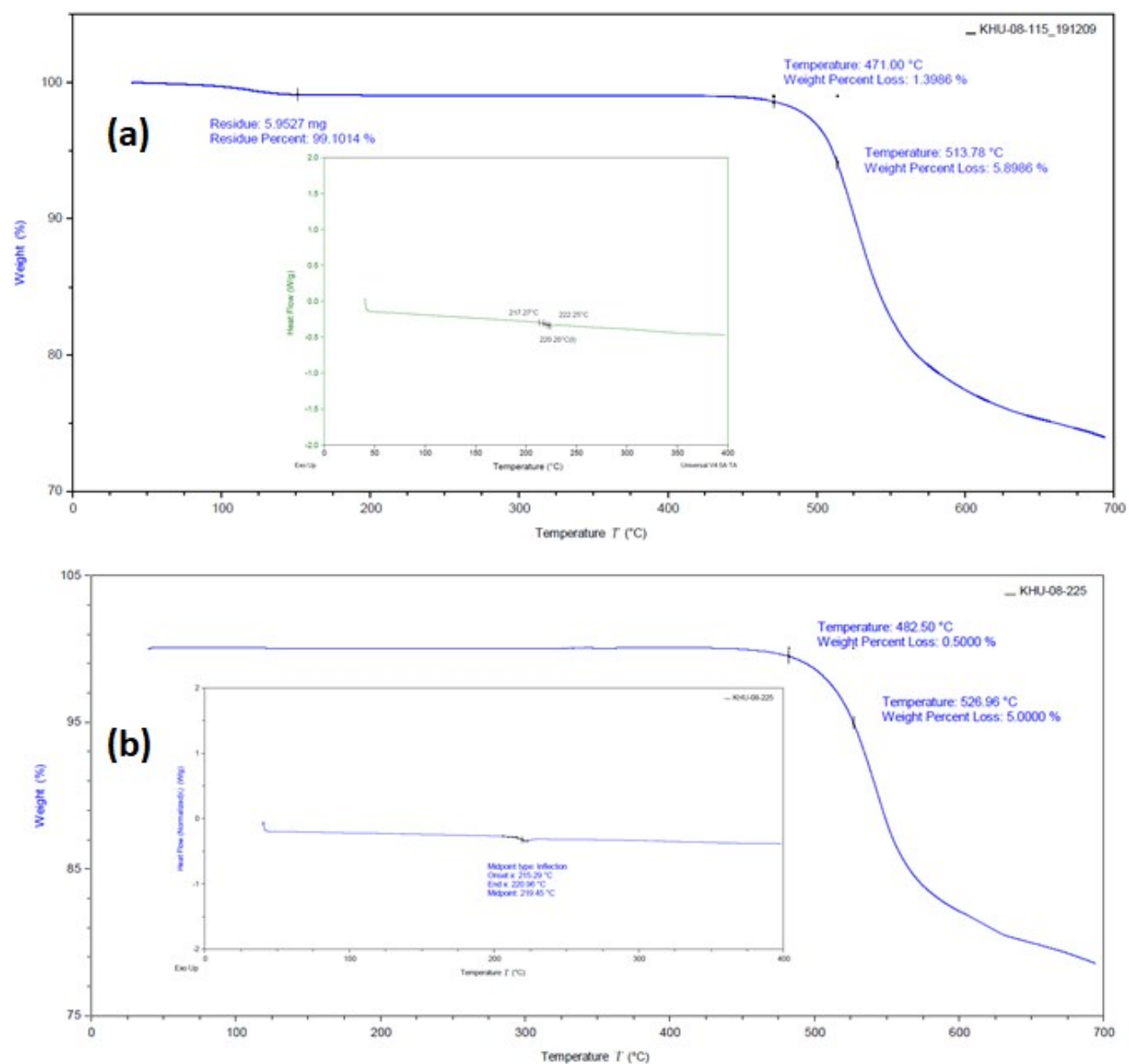


Fig. S3. Thermal properties of materials. TGA graph of **3CzTB** (a) and **M3CzB** (b), inset DSC graph of corresponding materials.

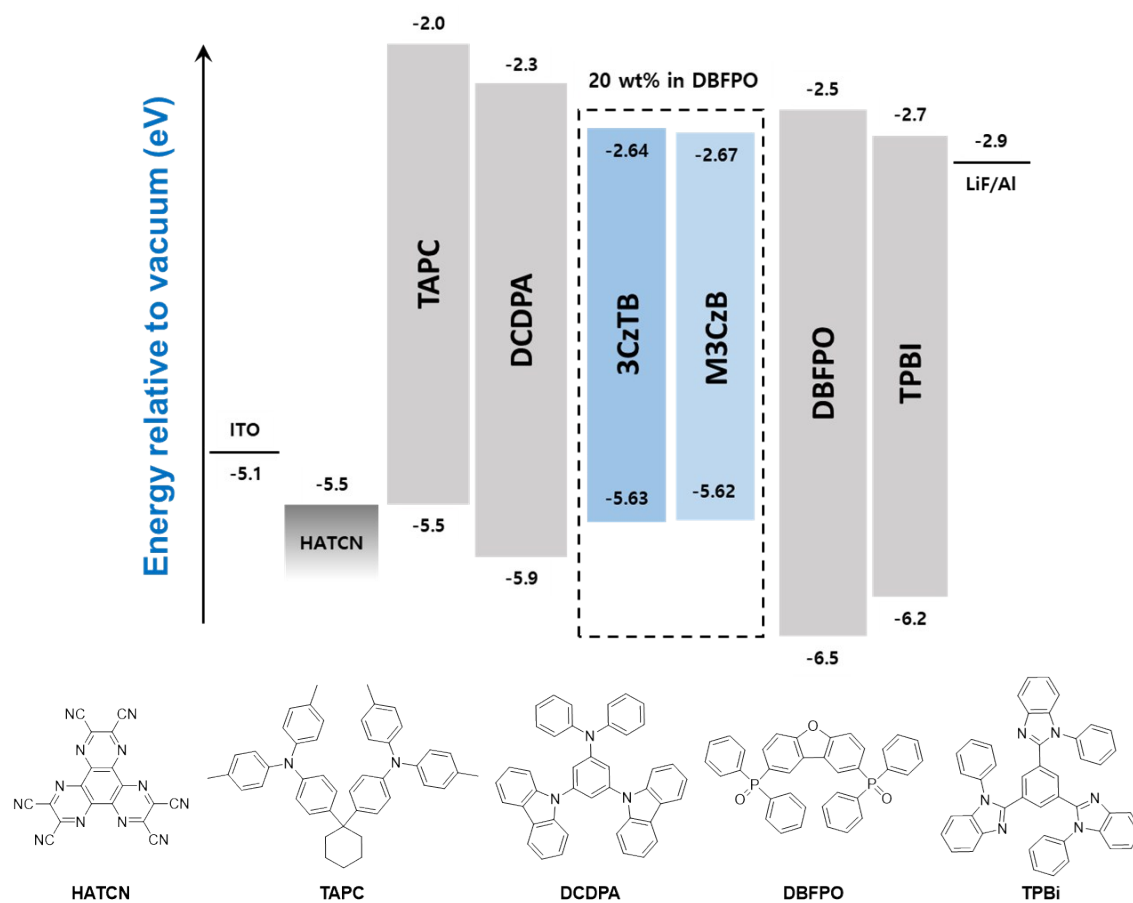


Fig. S4. Energy level diagram and the structure of materials used for the fabrication of blue TADF OLED devices.

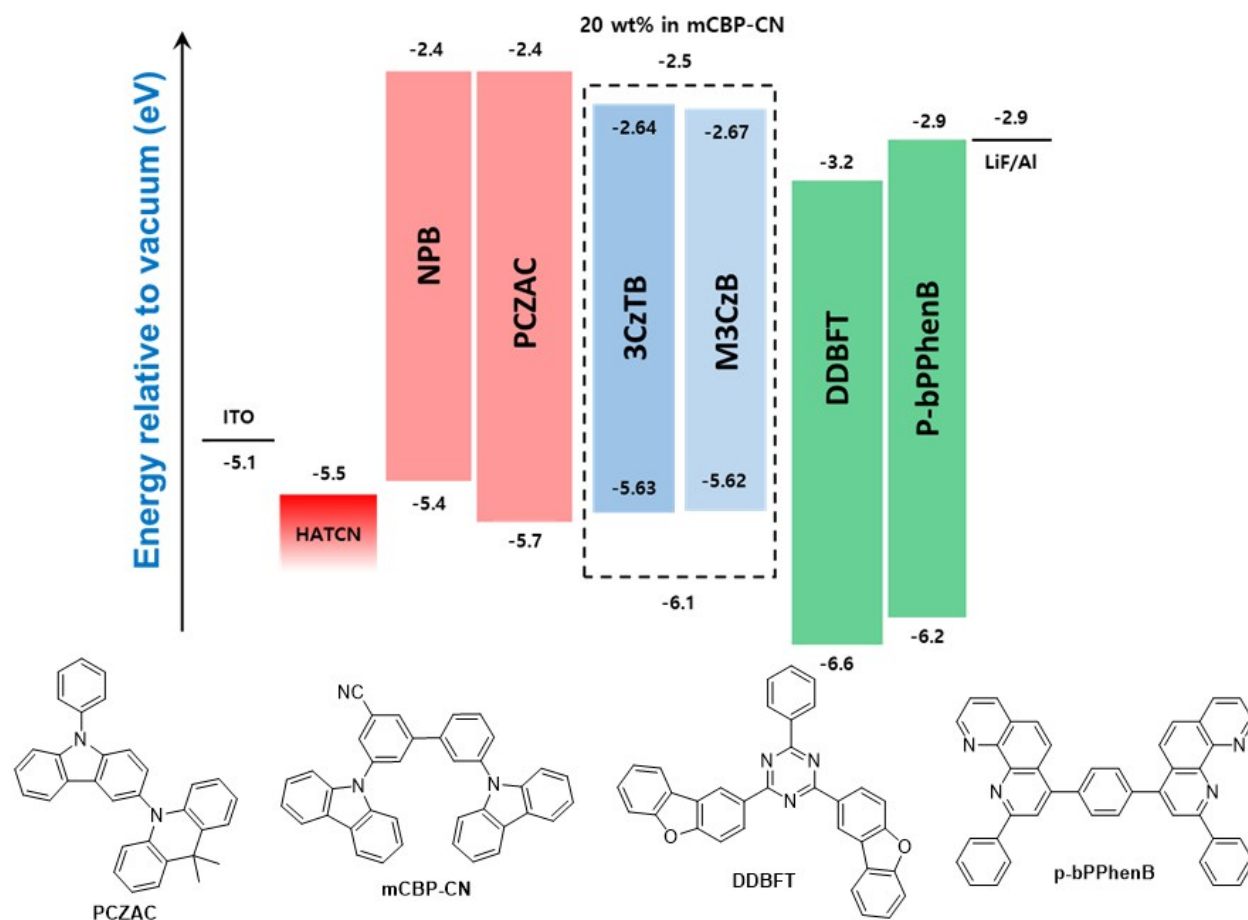


Fig. S5. Energy level diagram and the structure of materials used for the fabrication of lifetime devices. Device configuration: ITO (50 nm)/HATCN (7 nm)/NPB (50 nm)/PCZAC (10 nm)/mCBP-CN:20 wt% dopant (25 nm)/DDBFT (5 nm)/p-bPPhenB (15 nm)/LiF/Al (1.5/100 nm)

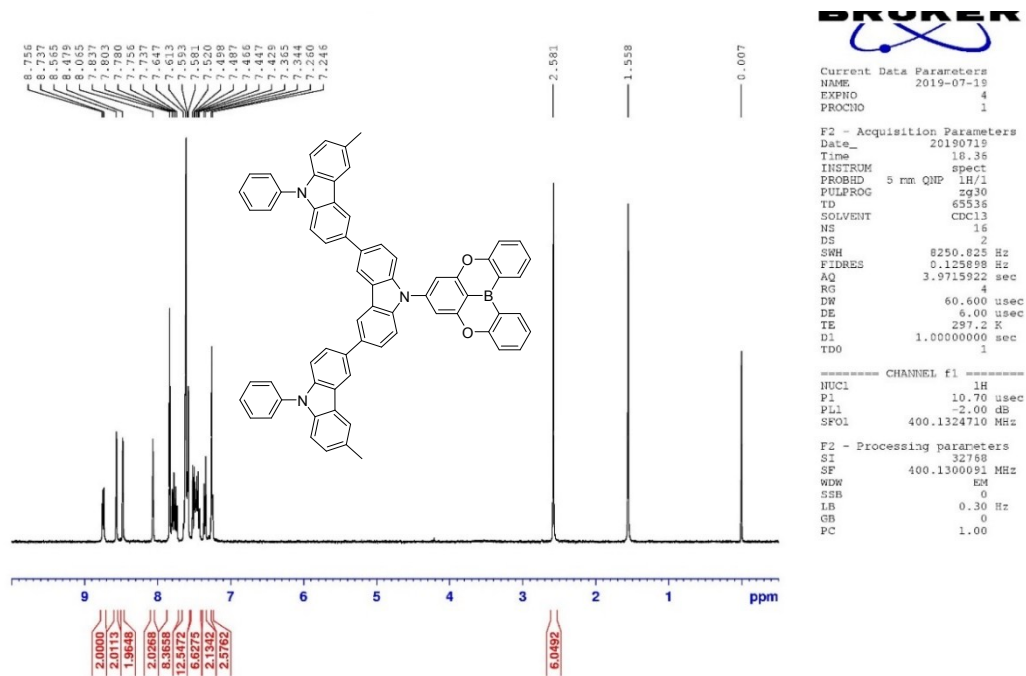


Fig. S10. ^1H NMR spectra of **M3CzB** in CDCl_3 .

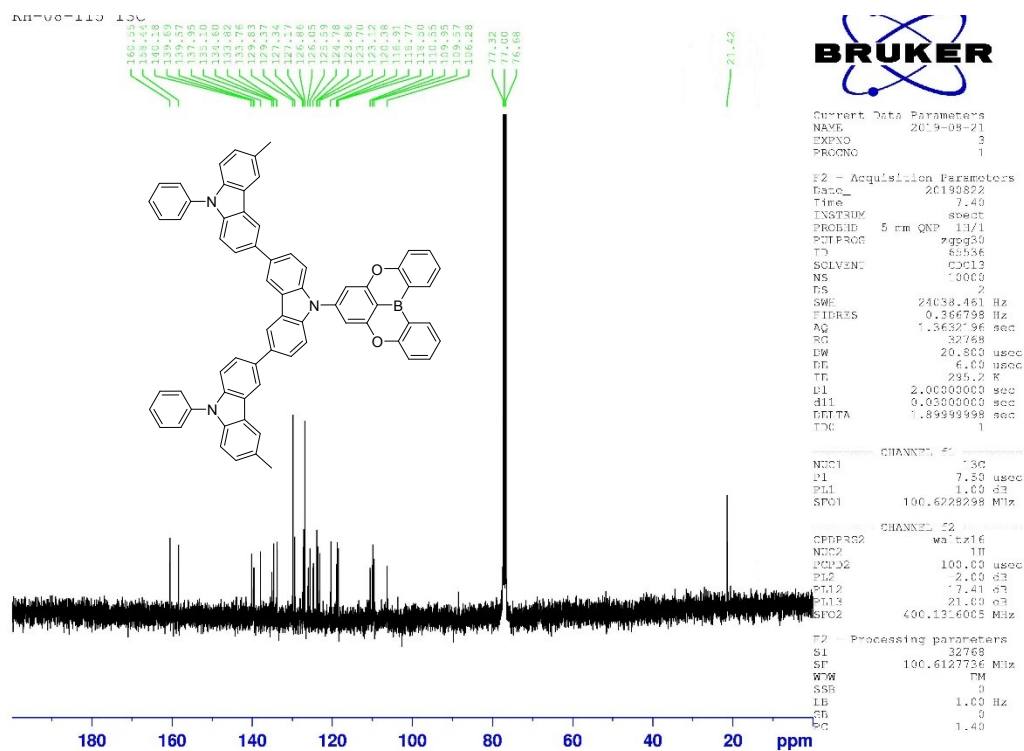


Fig. S11. ^{13}C NMR spectra of **M3CzB** in CDCl_3 .