Supporting Information

Kemei Zhu,[a] Yannan Zhou,[a] Chenglin Ma,[a] Yongquan Li,[a] Shenghui Zhou,[a] Li Zhang,[a] Jingru Song,[a] Qikun Sun,[a] Wenjun Yang,[a] and Shanfeng Xue[a]*

[a]State Key Laboratory of Advanced Optical Polymer and Manufacturing Technology, Key Laboratory of Rubber-Plastics of the Ministry of Education, School of Polymer Science and Engineering, Qingdao University of Science and Technology, 53-Zhengzhou Road, Qingdao 266042, PR China.

Corresponding author. E-mail: sfxue@qust.edu.cn

CONTENTS

S1 General Measurements

1. General Measurements

The ^{1}H NMR and ^{13}C NMR spectrum was recorded on a Bruker AC500 spectrometer at 500 and 126 MHz, respectively, using deuterated chloroform ($CDCl_3$) as solvents. The chemical shift for each signal was reported in ppm units with tetramethylsilane (TMS) as a standard internal reference. The MALDI-TOF-MS mass spectra were recorded using an AXIMA-CFRTM instrument. UV-vis absorption and fluorescence spectra of solution and film were recorded by a Hitachi U-4100 spectrophotometer and a Hitachi F-4600 spectrophotometer, respectively. An FLS980 spectrometer measured photoluminescence quantum yield. The lifetime was measured on an Edinburgh FLS-

1000 spectrometer with an EPL-310 optical laser. In the solution-related tests covered in this work, the solution concentration is 10^{-5} M. The single crystals of the molecule is obtained from the sublimation. Single-crystal X-ray diffraction data were collected by Rigaku RAXIS-PRID diffractometer. The PLQY was carried out using a FLS980 spectrometer. The lifetime of the film was measured on an Edinburgh FLS-980 with an EPL-375 optical laser.

2. Electrochemical Measurements

Cyclic voltammetry was performed with a BAS 100 W Bioanalytical system, using a glass carbon disk (Φ = 3 mm) as the working electrode, a platinum wire as the auxiliary electrode with a porous ceramic wick, and Ag/Ag^+ as the reference electrode, standardized for the redox couple ferricinium/ferrocene. All solutions were purged with a nitrogen stream for 10 min before measurement. The procedure was performed at room temperature, and a nitrogen atmosphere was maintained over the solution during the measurements. The energy levels of HOMO and LUMO are calculated according to the Formula below:

$$HOMO = -(E_{ox} \text{ vs. } Ag/Ag^+ - E_{1/2}{}^+ \text{ vs.} Ag/Ag^+ + 4.8)\ eV$$

$$LUMO = -(E_{red} \text{ vs. } Ag/Ag^+ - E_{1/2}{}^- \text{ vs.} Ag/Ag^+ + 4.8)\ eV$$

The E_{ox} vs. Ag/Ag^+ and E_{red} vs. Ag/Ag^+ are oxidation and reduction onset potentials relative to the Ag/Ag^+ electrode. Ferrocene was used as an internal standard. $E_{1/2}{}^+$ vs. Ag/Ag^+ and $E_{1/2}{}^-$ vs. Ag/Ag^+ are half-wave potentials of Fc^+/Fc^- obtained from positive and negative CV scans, respectively.

3. Thermal Stability Measurements

The differential scanning calorimetry (DSC) dates are from the NETZSCH (DSC-204) instrument, which was heated to 20-300 °C at a heating rate of 10 °C /min and a nitrogen flow rate of 80 mL/min. The material was thermal gravimetrically analyzed (TGA) using a Perkin-Elmer thermal analysis system from 40 to 800 ℃ at a heating rate of 10 ℃/min under the nitrogen atmosphere.

4. Device fabrication and characterization

Before the measurement, vacuum sublimation obtained the target molecules as neat products. TPBi, $Ir(ppy)_2acac$, PO-01 and $Ir(MDQ)_2acac$ used in the device were purchased from Jilin OLED Material Tech Co., Ltd., and HATCN, TCTA, TAPC were purchased from Xi'an Polymer Light Technology Corp. ITO-coated glass with a sheet resistance of 10 Ω square^{-1} and was used as the substrate. The pre-treatment of ITO glass included a routine chemical cleaning using detergent and alcohol in sequence, dried in an oven at 120 ℃. After the oxygen plasma was cleaned for 7 min and finally transferred to a vacuum deposition system with a base pressure greater than 1.6×10^{-4} Pa for organic and metal deposition. The current-voltage–luminance characteristics were measured using a Keithley source measurement unit (Keithley 2450 and LS-160). The electroluminescent (EL) spectra and Commission Internationale de l'Eclairage (CIE) coordinates of these devices were measured with a Flame-S (Serial Number: FLMS16791). EQEs were calculated from the luminance, current density, and EL spectrum, all the results were measured in the forward-viewing direction without using any light out-coupling technique.

S2 Supplementary figures and tables

(1) Synthesis of 2-(4-fluoro-3-methylphenyl) benzo[d]oxazole (MePBO-F)

Mix 2-aminophenol (1.0 g, 9.3 mmol), 4-fluoro-3-methylbenzoic acid (1.43 g, 9.3 mmol) and polyphosphoric acid (PPA) (10 g) at 160 ℃ for 5 h under nitrogen. After the mixture was cooled down, 40 mL deionized water was added to the resulting solution and the mixture was extracted with dichloromethane for several times. The organic phase was dried over anhydrous magnesium sulphate. After filtration and solvent evaporation, the given residue was purified through silica gel column chromatography using dichloromethane as eluent to give the product as white solid (1.90 g, 78.0 %).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (ddd, J = 7.3, 2.2, 1.0 Hz, 1H), 8.06 (ddd, J = 8.3, 4.9, 2.3 Hz, 1H), 7.78 – 7.73 (m, 1H), 7.60 – 7.55 (m, 1H), 7.37 – 7.33 (m, 2H), 7.15 (t, J = 8.9 Hz, 1H), 2.38 (d, J = 1.9 Hz, 3H).

(2) Synthesis of 2-(4-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3-methylphenyl) benzo[d]oxazole (MePBODCz)

3,6-Di-*tert*-butyl-9H-carbazole (1.2 g, 7.78 mmol) was added to 50 mL of degassed and dehydrated DMF in a flask. Nitrogen was flushed three times under an ice water bath, and then sodium hydride (2.0 g, 12.97 mmol) was added and stirred for 30 minutes. After the mixture was cooled down, the mixture was extracted with dichloromethane for several times. The organic phase was dried over anhydrous magnesium sulphate. After filtration and solvent evaporation, the given residue was purified through silica gel column chromatography using ethyl petroleum ether/dichloromethane (5/1 ; v/v) as eluent to give the product as white solid (1.67 g, 76.0 %). ^{1}H NMR (500 MHz, Chloroform-d) δ 8.41 – 8.39 (m, 1H), 8.25 (dd, J = 8.2, 2.1 Hz, 1H), 8.18 – 8.15 (m, 2H), 7.85 – 7.81 (m, 1H), 7.66 – 7.61 (m, 1H), 7.51 (d, J = 8.2 Hz, 1H), 7.46 (dd, J = 8.6, 1.9 Hz, 2H), 7.40 (dd, J = 6.0, 3.2 Hz, 2H), 7.01 (dd, J = 8.6, 0.5 Hz, 2H), 2.15 (s, 3H), 1.47 (s, 18H).^{13}C NMR (126 MHz, Chloroform-d) δ 161.55 , 149.88 , 141.78 , 141.14 , 138.69 , 138.31 , 137.01 , 129.72 , 128.74 , 125.94 , 125.41 , 124.31 , 123.73 , 122.70 , 122.24 , 119.13 , 115.35 , 109.66 , 108.19 , 33.73 , 31.02 , 16.96 .MALDI-TOF MS (mass m/z): calcd for $C_{34}H_{34}N_2O$, 486.2671; found, 487.2612 $[M + H]^+$.

S3 Supplementary figures and tables

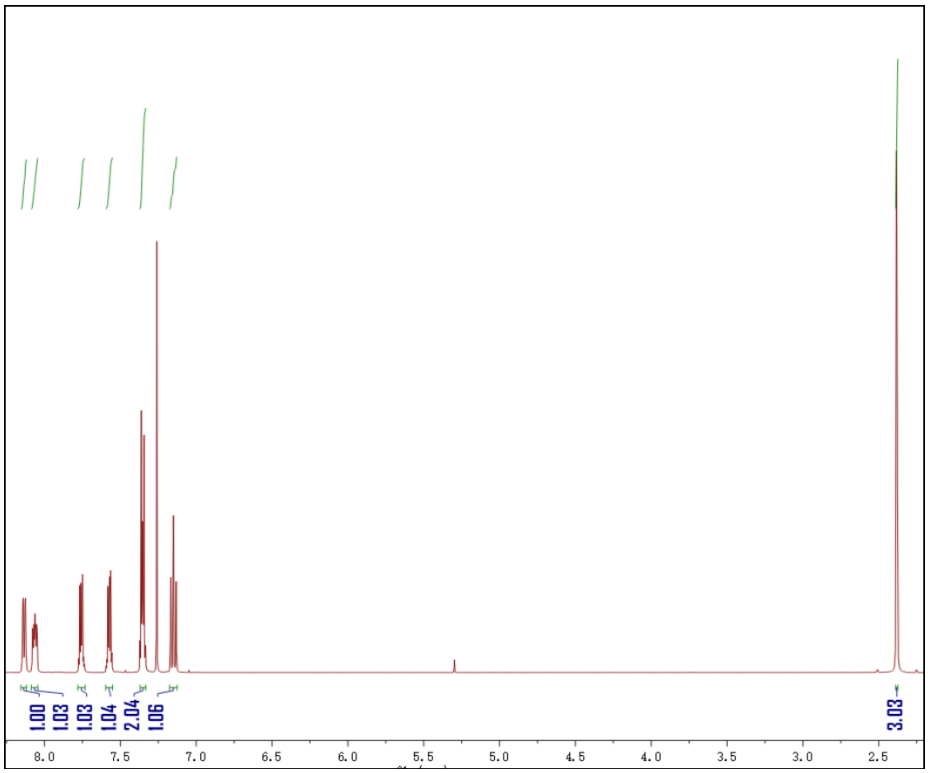

Figure S1. ^{1}H-NMR Spectrum of MePBO-F in $CDCl_3$.

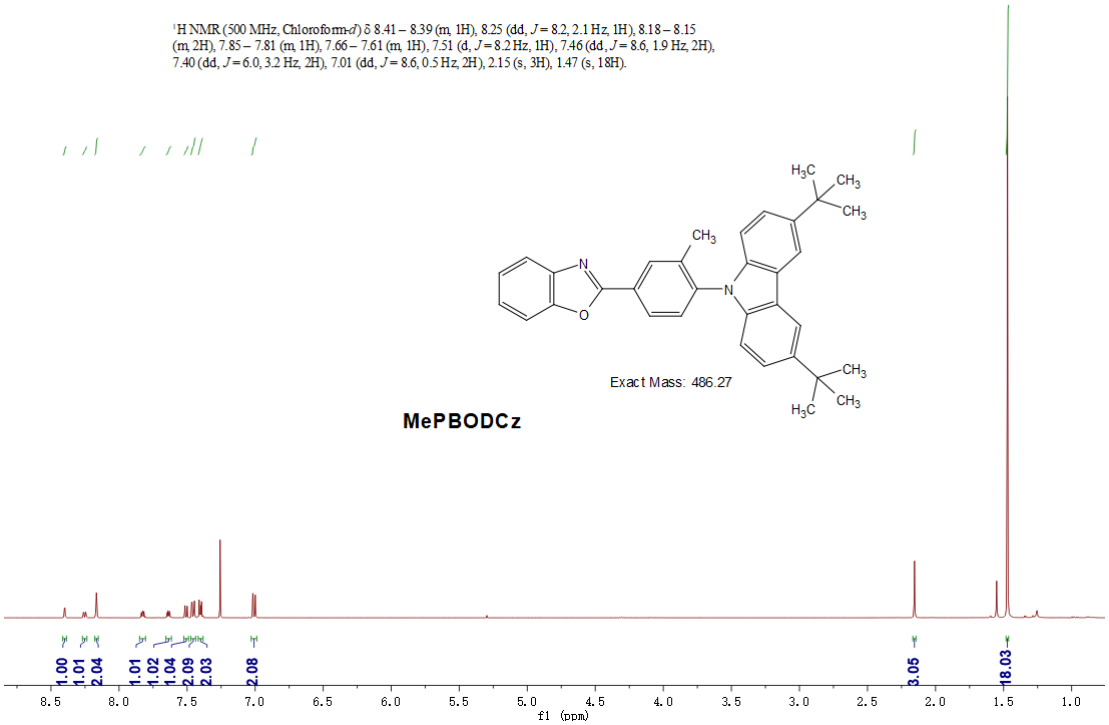

Figure S2. ^{1}H-NMR Spectrum of MePBODCz in $CDCl_3$.

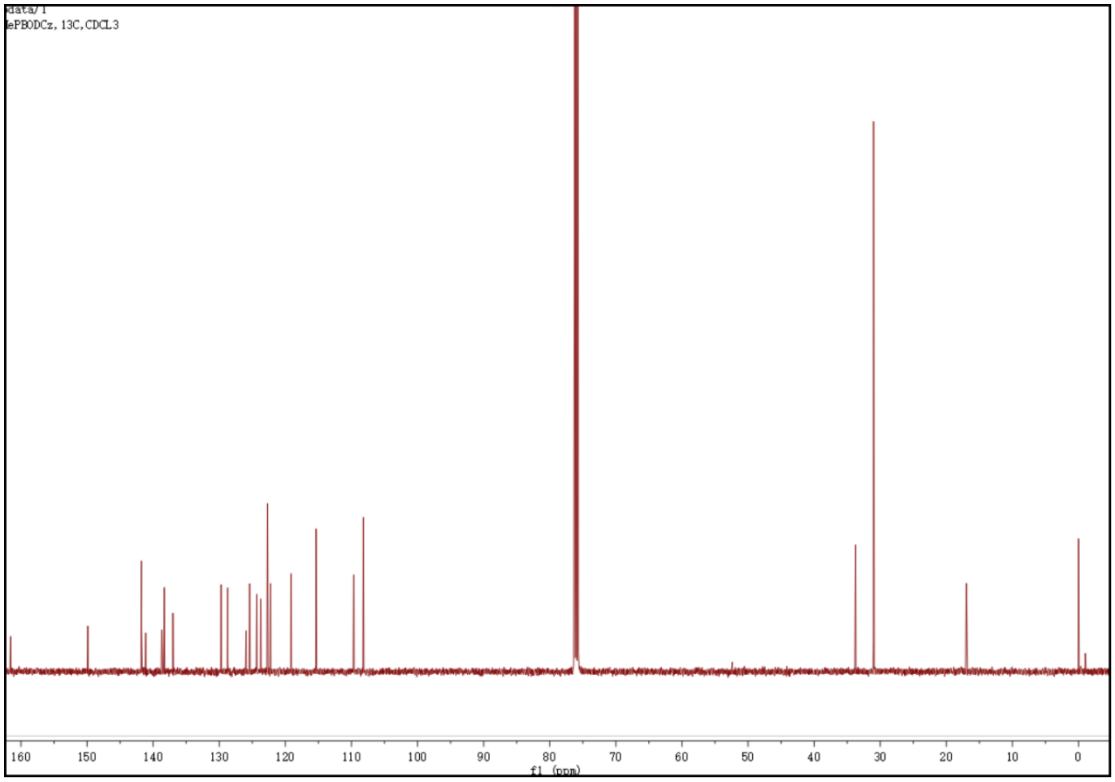

Figure S3. ^{13}C-NMR Spectrum of MePBODCz in $CDCl_3$.

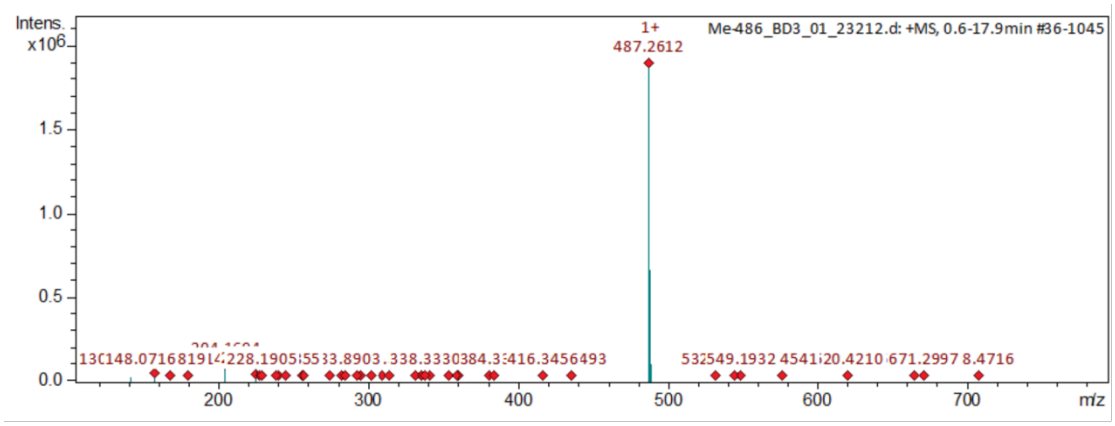

Figure S4. Mass Spectrum $(M+H)^+$ of MePBODCz.

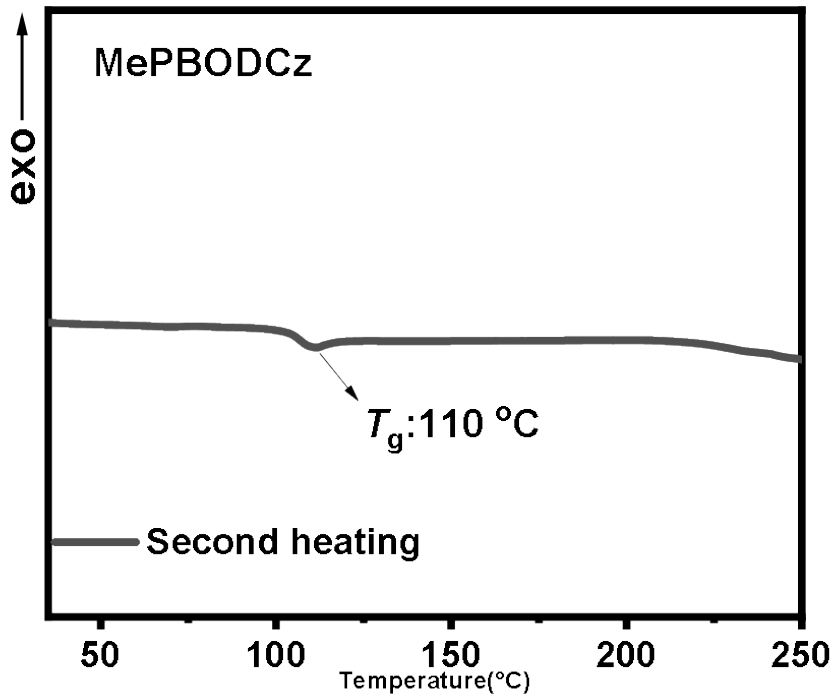

Figure S5. The thermogravimetric analysis (TGA) curves.

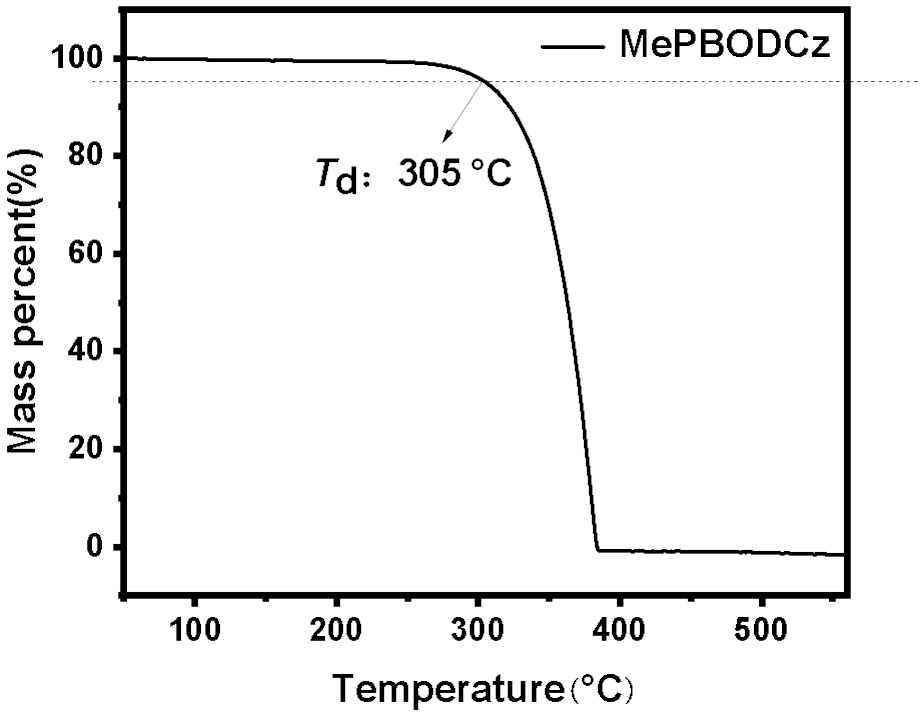

Figure S6. The differential scanning calorimeter (DSC).

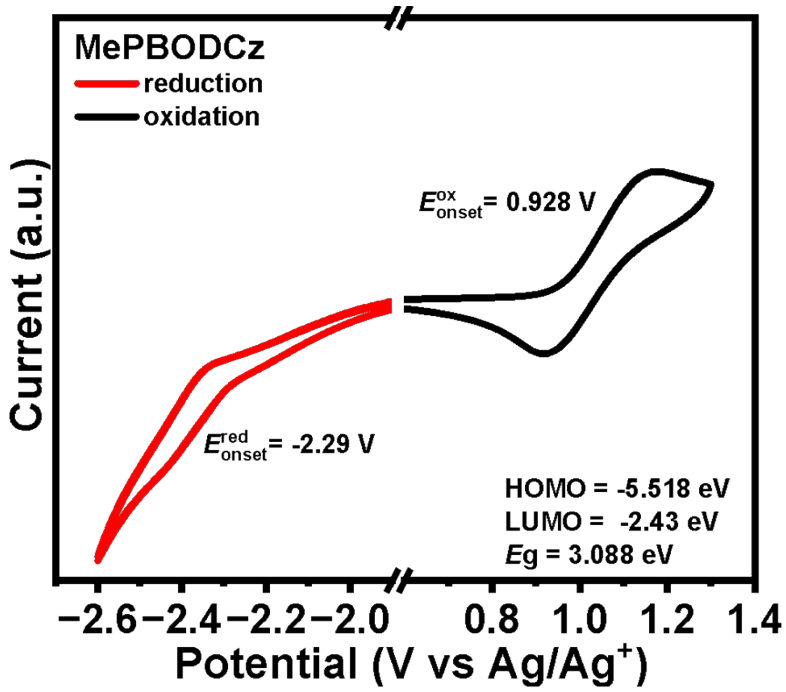

Figure S7. The cyclic voltammetry (CV) curves of MePBODCz.

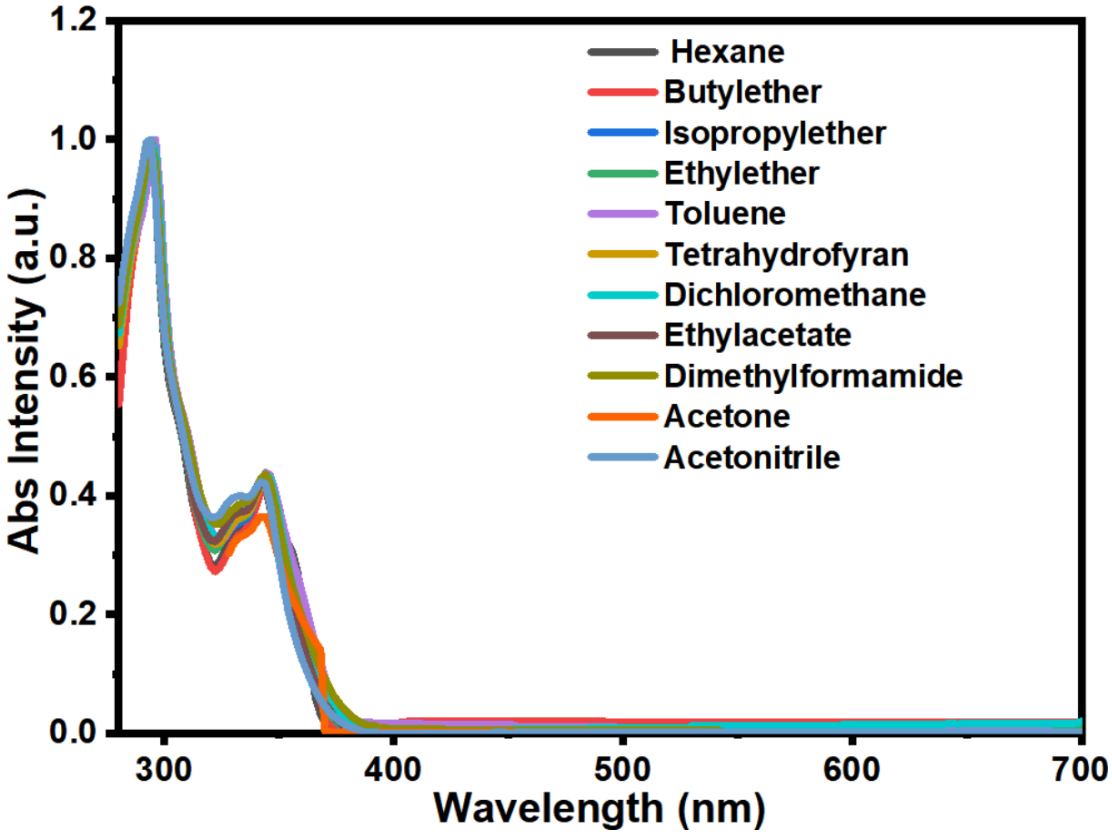

Figure S8. Normalized Abs spectra of MePBODCz in different solvents.

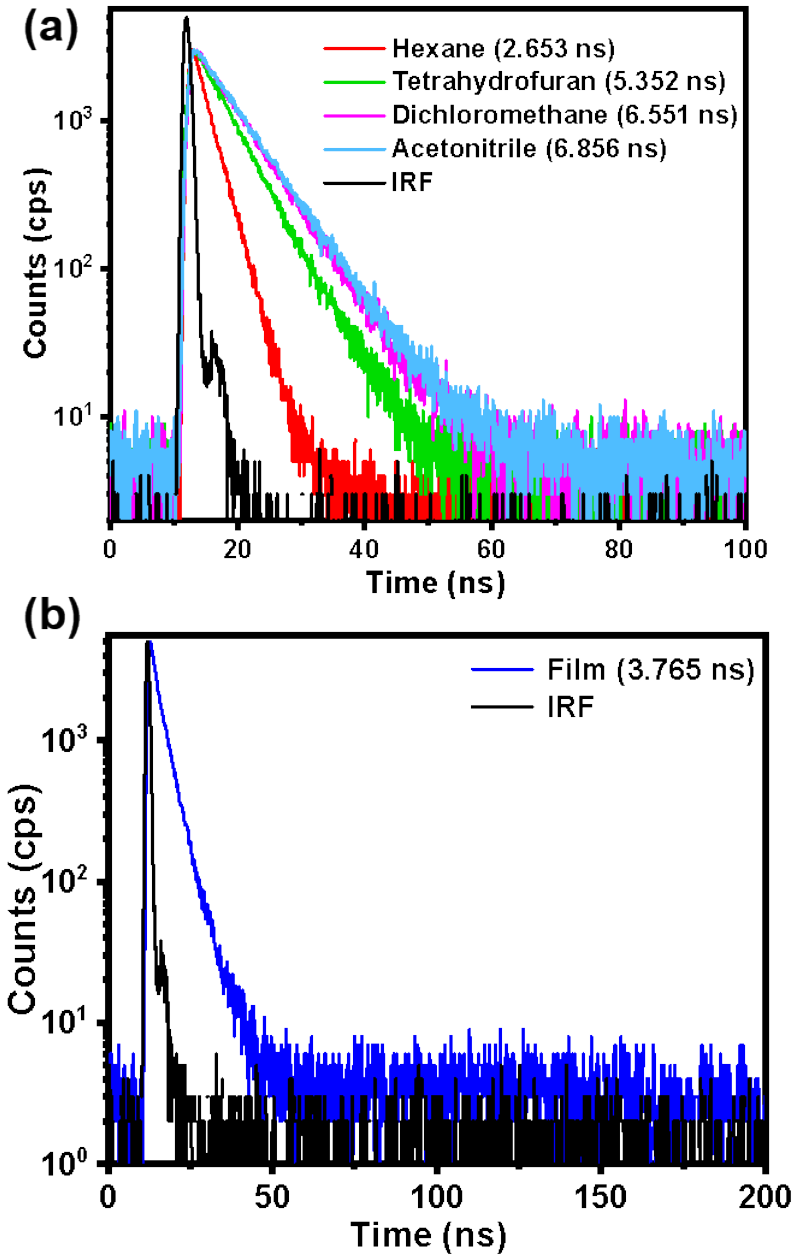

Figure S9. The transient PL decay spectra of MePBODCz in different solvents.

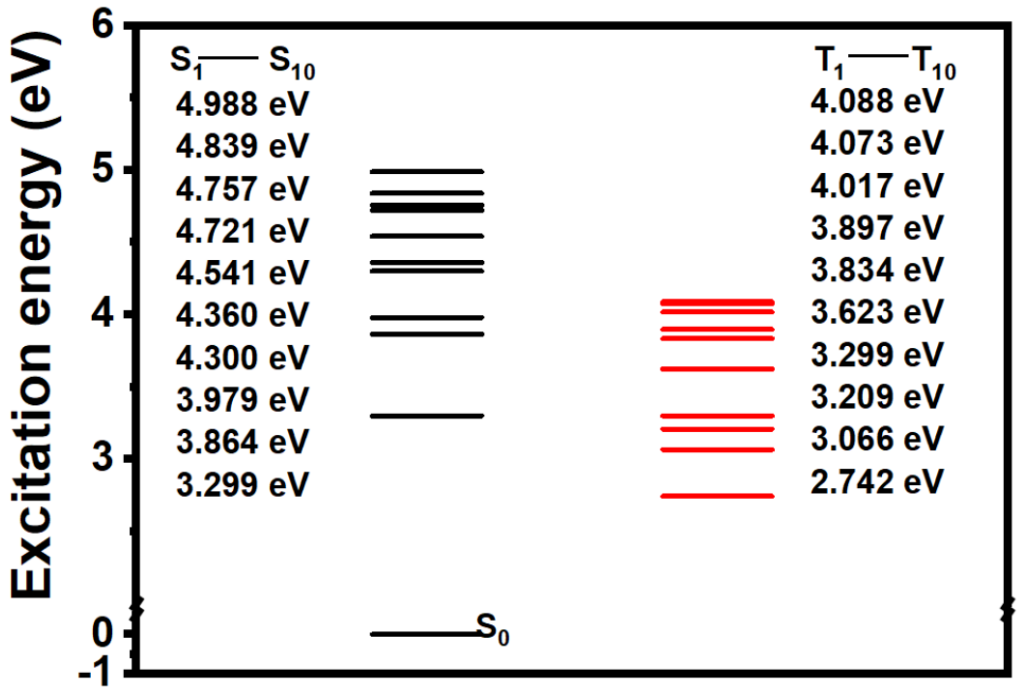

Figure S10. The energy level configuration diagram of excited states of the MePBODCz.

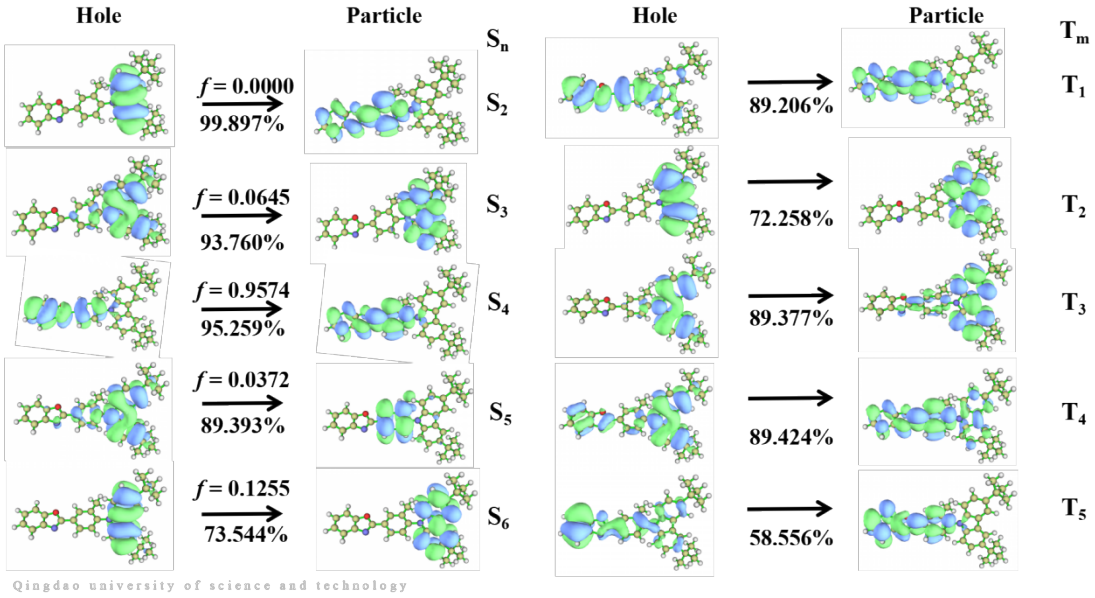

Figure S11. The NTOs of the singlet ($S_{2\text{-}6}$) and triplet ($T_{1\text{-}5}$) excited states for MePBODCz.

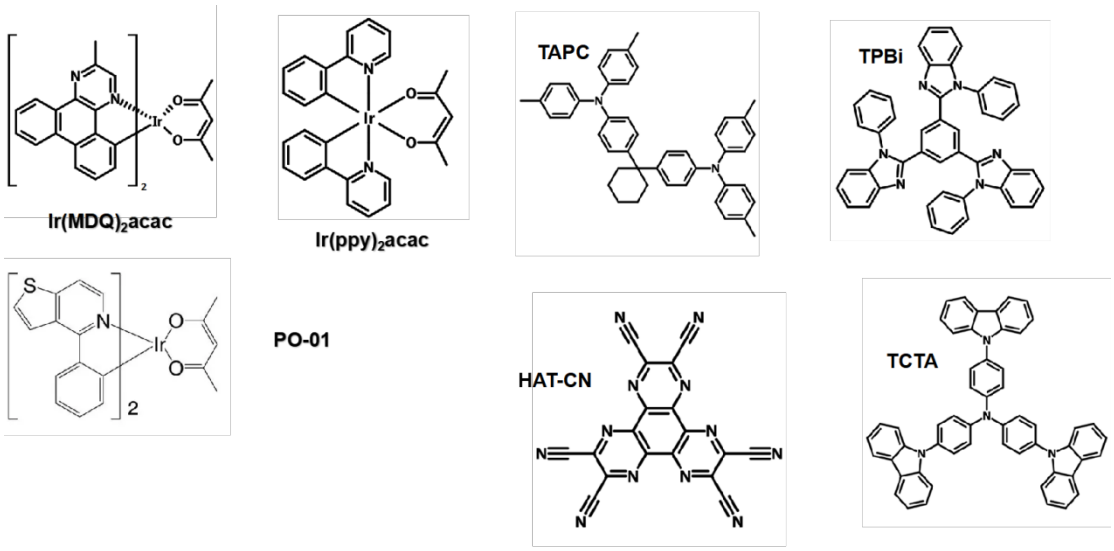

Figure S12. The chemical structure of the relevant materials for OLED devices.

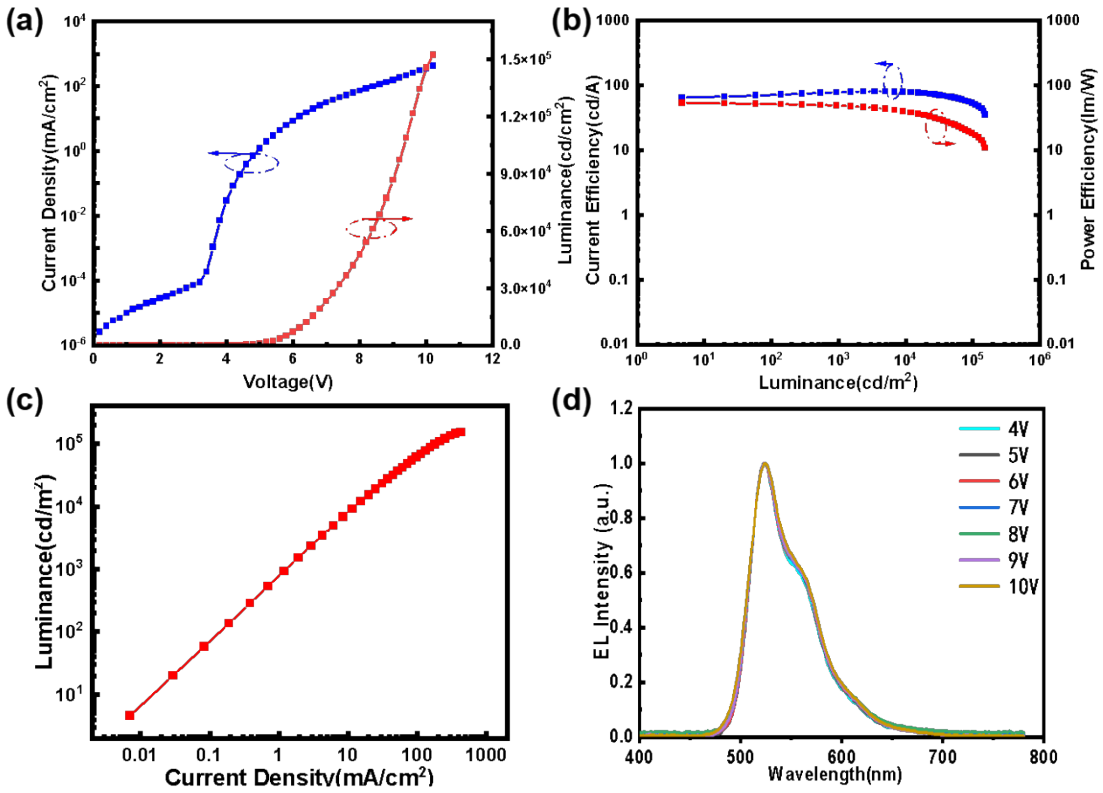

Figure S13. The doped green light PhOLED device using MePBODCz as the host material exhibits the following performance characteristics: a) Current density-voltage-luminance curves; b) Current density-voltage-luminance curves; c) EQE-luminance curves; d) Electroluminescence spectra under

different voltages. The device structure is: ITO / HATCN (20 nm) / TAPC (35 nm) / TCTA (5 nm) / MePBODCz : $Ir(ppy)_2acac$ (8 wt%) (20 nm) / TPBi (35 nm) / LiF (1.5 nm) / Al (100 nm).

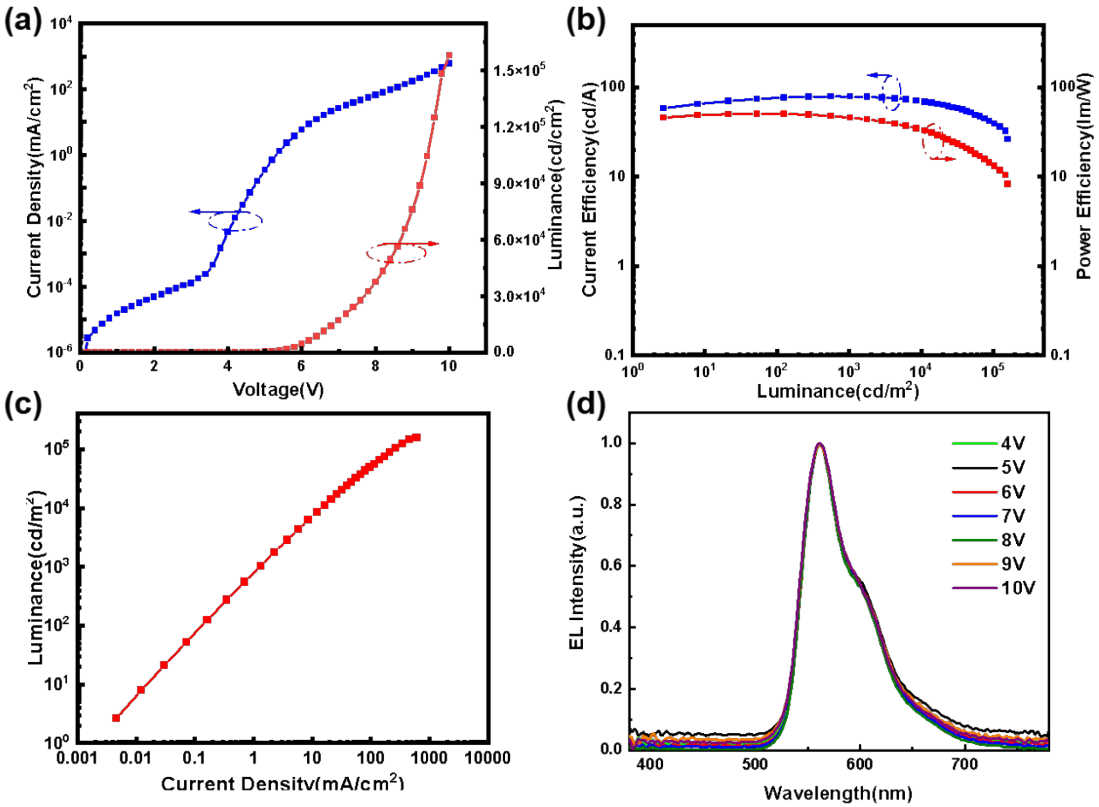

Figure S14. The doped yellow light PhOLED device using MePBODCz as the host material exhibits the following performance characteristics: a) Current density-voltage-luminance curves; b) Current density-voltage-luminance curves; c) EQE-luminance curves; d) Electroluminescence spectra under different voltages. The device structure is: ITO / HATCN (20 nm) / TAPC (35 nm) / TCTA (5 nm) / MePBODCz : PO-01 (5 wt%) (20 nm) / TPBi (35 nm) / LiF (1.5 nm) / Al (100 nm).

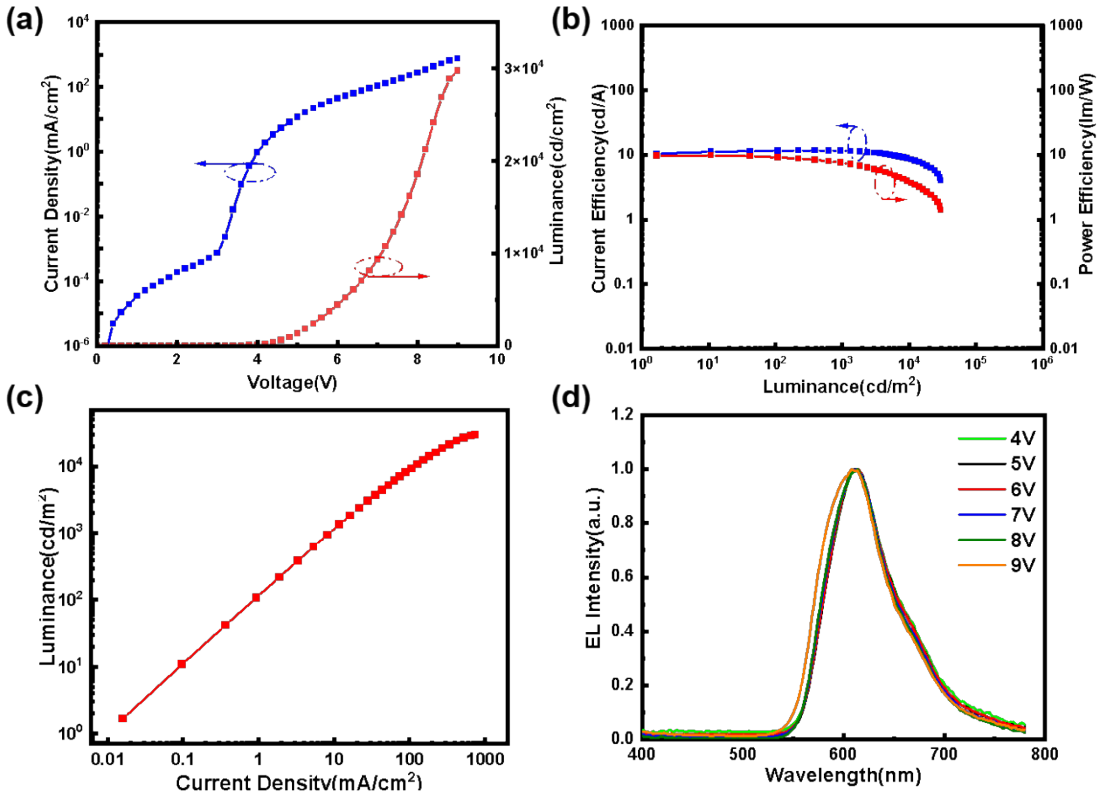

Figure S15. The doped red light PhOLED device using MePBODCz as the host material exhibits the following performance characteristics: a) Current density-voltage-luminance curves; b) Current density-voltage-luminance curves; c) EQE-luminance curves; d) Electroluminescence spectra under different voltages. The device structure is: ITO / HATCN (20 nm) / TAPC (35 nm) / TCTA (5 nm) / MePBODCz : $Ir(MDQ)_2acac$ (5 wt%) (20 nm) / TPBi (35 nm) / LiF (1.5 nm) / Al (100 nm).

Table S1. The maximum peak of photoluminescence under different polar solvents.

Solvent	Butylether	Isopropylether	Diethylether	Toluene	Dichloromethane	Ethyl Acetate	Acetone	N,N-Dimethylformamide	Acetonitrile
MePBODCz	396	402	409	400	448	428	454	461	465

Table S2. PLQY under different polar solvents.

Solvent	Hexane	Isopropylether	Diethylether	THF	Dichloromethane	Acetonitrile
MePBODCz	75%	50%	55%	22%	47%	35%

Table S3 Crystal data for MePBODCz.

Compound	MePBODCz
Chemical formula	$C_{34}H_{34}N_2O$
Formula weight	486.63
Crystal system	Monoclinic
a/Å	23.8493(4)
b/Å	11.7862(2)
c/Å	10.0008(2)
α/°	90
β/°	96.889(1)
γ/°	90
Unit cell volume/ Å3	2790.86(9)
Temperature/K	298 K
Space group	$P2_1/c$
Z	4
Density (calculated) /g cm^{-3}	1.158
F(000)	1040.0
Index ranges	$-28 \le h \le 28$ $14 \le k \le 12$ $-10 \le l \le 12$
Reflections measured	29637
Completeness to theta = 68.37°	98.4%
Min. and max. transmission	0.494 and 0.753
Data / restraints / parameters	5032/1320/372
Goodness-of-fit on F^2	1.128
Final R_1 values ($I > 2\sigma(I)$)	0.0801
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2454
Final R_1 values (all data)	0.0870
Final $wR(F^2)$ values (all data)	0.2530
CCDC number	2526463