

Electronic Supplementary Information

**Solution-processed High Efficiency OLED Harnessing Thermally Cross-linked
Hole-transporting Layer and Exciplex-forming Emission Layer**

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Experimental Section

Materials

9*H*,9'*H*-3,3'-bicarbazole¹, 1-(4-bromobutyl)-4-vinylbenzene², **BCzC1Sy**³ and PO-T2T⁴ were prepared according to reported literatures. All the chemicals and reagents were used without purification from commercial sources unless otherwise noted. Solvents for analysis and reaction were purified by distillation with drying equipment before use.

Material characterization

Differential scanning calorimetry (DSC) were conducted under a nitrogen atmosphere at a heating rate of 10 °C/min on a platinum pan via Netzsch 204 F1. NMR spectra were measured in CDCl₃ using Varian (Utility 400) spectrometer for ¹H NMR (400 MHz) and ¹³C NMR (100MHz). Steady-state UV-visible absorption spectra in solution were characterized by a UV-vis-NIR spectrophotometer (UV-1650 PC, Shimadzu) and in solid film were recorded by a Thermo spectrophotometer (Evo 201). Photoluminescence (PL) spectra, and phosphorescence spectra were characterized by a spectrofluorimeter (FluoroMax-P, Horiba Jobin Yvon Inc.).

The time-resolved studies were performed using a time-correlated single photon counting (TCSPC) system (TimeHarp 260, PicoQuant) with the pulse LED at 285 nm (PLS280, PicoQuant) as the photoexcitation light source. PLQYs of thin films were determined using quantum yield spectrometer (Hamamatsu C9920-02). All the mass spectra were recorded by the National Taiwan University Mass Spectrometry-based Proteomics Core Facility by Bruker Daltonics Autoflex speed in MALDI-TOF mode.

Cyclic voltammetry

The electrochemical properties were measured by cyclic voltammetry (CHI619B potentiostat). A glassy carbon electrode was used as a working electrode, and a platinum wire was used as a counter electrode. The oxidation potentials were conducted in dried dichloromethane (1.0 mM) with 0.1 M tetrabutylammonium hexafluorophosphate (ⁿBu₄NPF₆) as the supporting electrolyte. All the potentials were recorded versus Ag/AgCl as a reference electrode, further calibrated with the ferrocene/ferrocenium (Fc/Fc⁺) redox couple (0.48 eV in dichloromethane / ⁿBu₄NPF₆).

Device fabrication

OLED devices were constructed with the architecture of indium tin oxide (ITO), PEDOT:PSS (40 nm), **BCzC1Sy** or **BCzC4Sy** (40nm), exciplex blends (BCz3Ph : PO-T2T = 2:1; 40 nm), CNT2T (60 nm), LiF (1 nm),and Al (100 nm). The patterned ITO substrates (18 mm×28 mm) were cleaned by deionized water, acetone, and isopropyl

alcohol for 30 minutes each, and then treated by O₂ plasma cleaning for 10 min to remove the residual organic matter and improve the surface work function. After the O₂ plasma treatment, PEDOT:PSS, used as the hole injection layer (HIL), was spin-coated at 8000 rpm for 40 s on the substrate and annealed at 130 °C for 15 min, resulting in a 40-nm thick layer. The hole-transporting layer (HTLs), prepared using **BCzC1Sy** or **BCzC4Sy**, were dissolved in chlorobenzene at a concentration of 4 mg/mL and then deposited onto the HIL by spin-coating at 6000 rpm for 40 s. The structure of D1 and D2 were using **BCzC1Sy**; D3 and D4 were using **BCzC4Sy**. D1 and D3 were then annealed at 100 °C for 15 min, resulting in a 40-nm thick layer. On the other hand, D2 and D4 were annealed at 170 °C for 30 min, to make cross-linking happened. The emitting layer (EML), prepared using donor–acceptor blends (**BCz3Ph** : PO-T2T = 2:1), were dissolved in chlorobenzene at a concentration of 16 mg/mL and then deposited onto the HTL by spin-coating at 6000 rpm for 40 s. CN-T2T and LiF were used as the electron-transporting and electron-injecting layers, respectively, via vacuum evaporation deposition. After the deposition of organic layers, an Al cathode was deposited using a shadow mask to define the device area of 2 mm×2 mm. Conventional glass encapsulation was performed in an N₂-filled glove box to humidity. A cleaned 0.7-mm thick glass (10 mm×25 mm) was used to cover the active area and UV resin was dispensed on the edges of the glass cover and cured using a UV lamp to seal the OLEDs for protection from oxygen and humidity.

Electroluminescence (EL) spectra, current–voltage–luminance, and external quantum efficiency (EQE) were measured with a LQ-100R spectrometer (Enlitech) with computer control. Photoluminescence (PL) spectra were measured with a FluoroMax-4 fluorescence spectrometer (Horiba Jobin Yvon). All measurements were carried out at room temperature and the devices were encapsulated in a glove box.

Synthesis of 9,9'-di([1,1'-biphenyl]-3-yl)-9*H*,9'*H*-3,3'-bicarbazole (**BCz3Ph**):

9*H*,9'*H*-3,3'-bicarbazole (3.32g, 10 mmol), Cs₂CO₃ (13.00g, 40 mmol) were mixed in a 100 mL two-neck bottle, and then the whole system was evacuated and purged with argon gas. 3-bromo-1,1'-biphenyl (5.00ml, 30mmol) and degassed DMF (20 mL) were then added *via* syringe, and the reaction mixture was heated to 110 °C for 12 hours and then cooled down to room temperature. The reaction mixture was extracted with dichloromethane and brine water, dried over MgSO₄ and concentrated to give a crude product, which was then purified by column chromatography with the eluent of dichloromethane / hexane= 1 / 3 to afford white solid as product of 9,9'-di([1,1'-biphenyl]-3-yl)-9*H*,9'*H*-3,3'-bicarbazole (4.07g, 6.4 mmol, 64%). ¹H NMR (400 MHz, CDCl₃) δ 8.51 (s, 2H), 8.29 (d, *J* = 8 Hz, 2H), 7.88 (s, 2H), 7.83 (d, *J* = 8 Hz, 2H), 7.75–7.70 (m, 8H), 7.63 (t, *J* = 24 Hz, 4H), 7.56–7.52 (m, 8H), 7.50–7.35 (m, 4H). ¹³C

NMR (100 MHz, CDCl₃) δ 143.13, 141.31, 140.10, 139.99, 138.26, 134.40, 130.29, 128.96, 127.85, 127.17, 126.11, 126.09, 125.88, 125.70, 125.61, 124.03, 123.62, 120.46, 120.06, 118.92, 110.08, 109.93. HRMS (m/Z, MALDI) calcd for C₄₈H₃₂N₂ 636.7811 found 636.2585.

Synthesis of 9,9'-bis(4-(4-vinylphenyl)butyl)-9*H*,9'*H*-3,3'-bicarbazole (**BCzC4Sy**):

9*H*,9'*H*-3,3'-bicarbazole (3.32g, 10 mmol), Cs₂CO₃ (13.00g, 40 mmol) were mixed in a 100 mL two-neck bottle, and then the whole system was evacuated and purged with argon gas. 1-(4-bromobutyl)-4-vinylbenzene (5.12ml, 30mmol) and degassed DMF (20 mL) were then added *via* syringe, and the reaction mixture was heated to 110 °C for 12 hours and then cooled down to room temperature. The reaction mixture was extracted with dichloromethane and brine water, dried over MgSO₄ and concentrated to give a crude product, which was then purified by column chromatography with the eluent of dichloromethane / hexane= 1 / 3 to afford white solid as product of 9,9'-bis(4-(4-vinylphenyl)butyl)-9*H*,9'*H*-3,3'-bicarbazole (3.57g, 5.5 mmol, 55%). ¹H NMR (400 MHz, CDCl₃) δ 8.44 (s, 2H), 8.22 (d, *J* = 8 Hz, 2H), 7.84 (d, *J* = 8 Hz, 2H), 7.52–7.25 (m, 12H), 7.11 (t, *J* = 8 Hz, 4H), 6.76–6.68 (m, 2H), 5.74 (dd, *J* = 17.6, 1.2 Hz, 2H), 5.23 (dd, *J* = 10.8, 0.8 Hz, 2H), 4.36 (t, *J* = 13.6 Hz, 4H), 2.65 (t, *J* = 14.8 Hz, 4H), 2.00–1.85 (m, 4H), 1.79–1.74 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 141.56, 140.82, 139.45, 136.59, 135.28, 133.36, 128.53, 126.20, 125.66, 125.53, 123.39, 123.04, 120.44, 118.91, 118.78, 112.99, 108.83, 108.73, 42.96, 35.29, 28.89, 28.56. HRMS (m/Z, MALDI) calcd for C₄₈H₄₄N₂ 648.3505 found 648.3521.

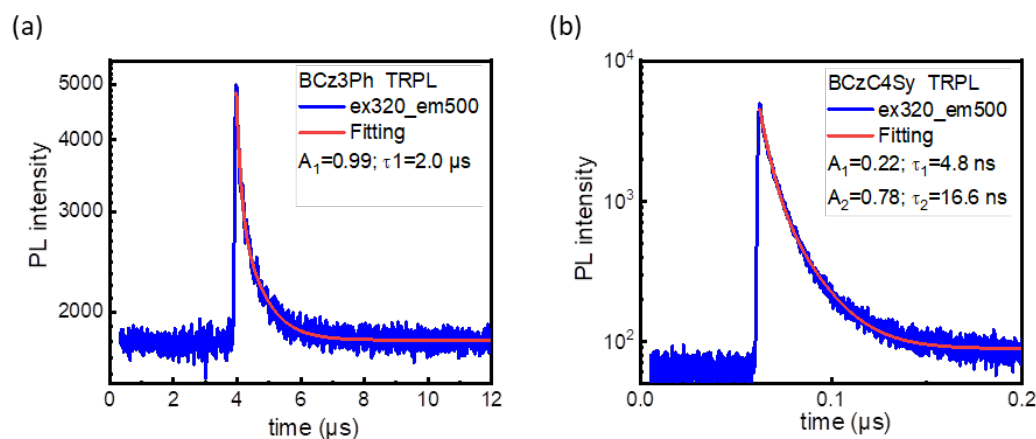


Figure S1. Transient PL decays monitored at 500 nm of (a) **BCz3Ph** (b) **BCzC4Sy** in MeTHF solution at 77 K.

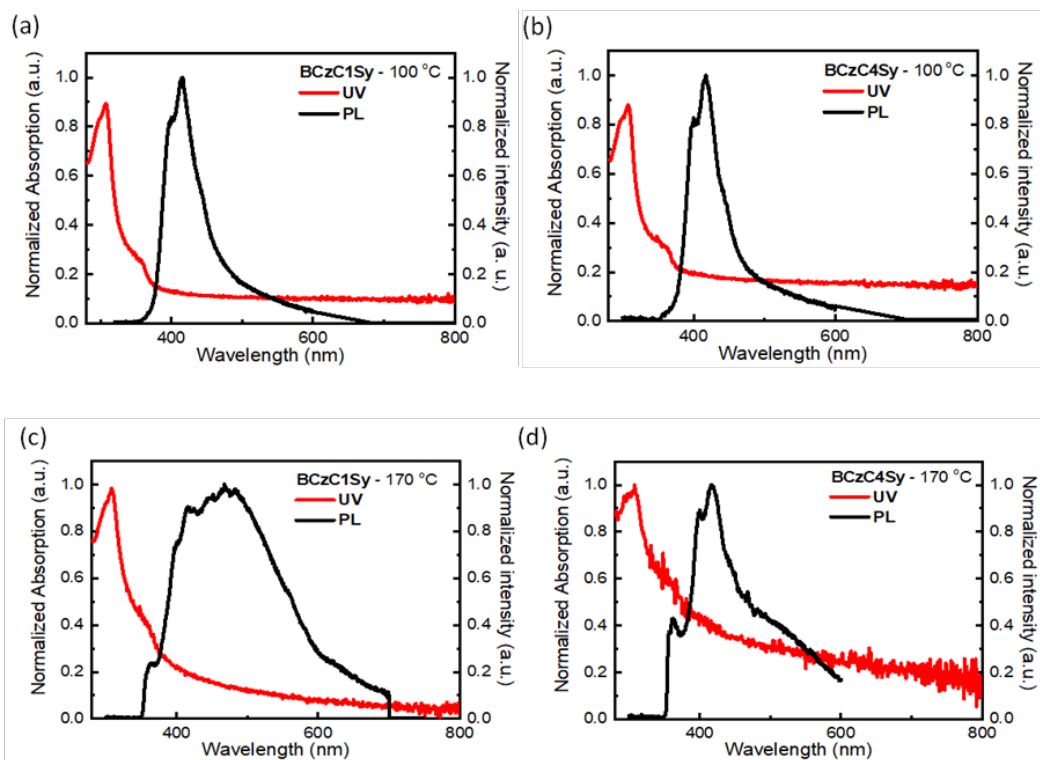


Figure S2. Absorption and emission spectrum of (a) **BCzC1Sy** (b) **BCzC4Sy** films after treating at 100 °C, and (c) **BCzC1Sy** (d) **BCzC4Sy** films after treating at 170 °C.

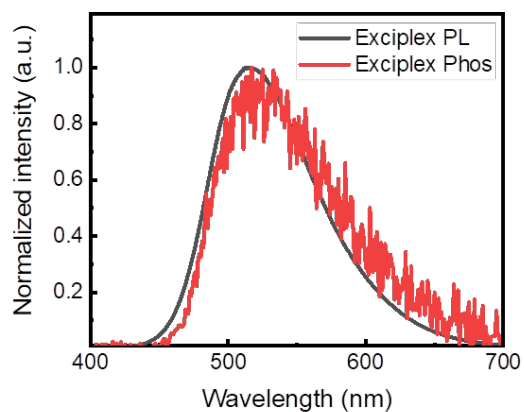


Figure S3. The photoluminescence and phosphorescence of exciplex-forming **BCz3Ph:POT2T (2:1)** blend.

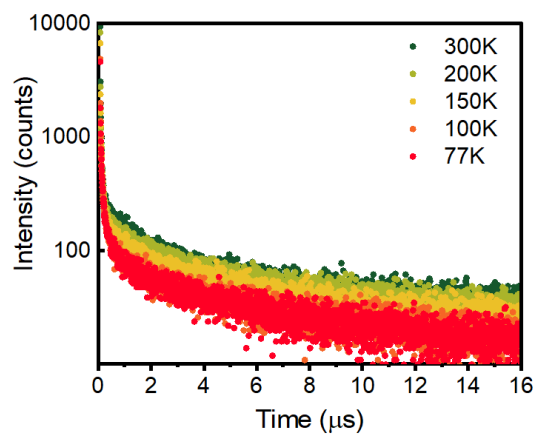


Figure S4. Transient PL decays of the exciplex-forming **BCz3Ph:PO-T2T (2:1)** blend measured from 77 to 300 K under a N₂ atmosphere.

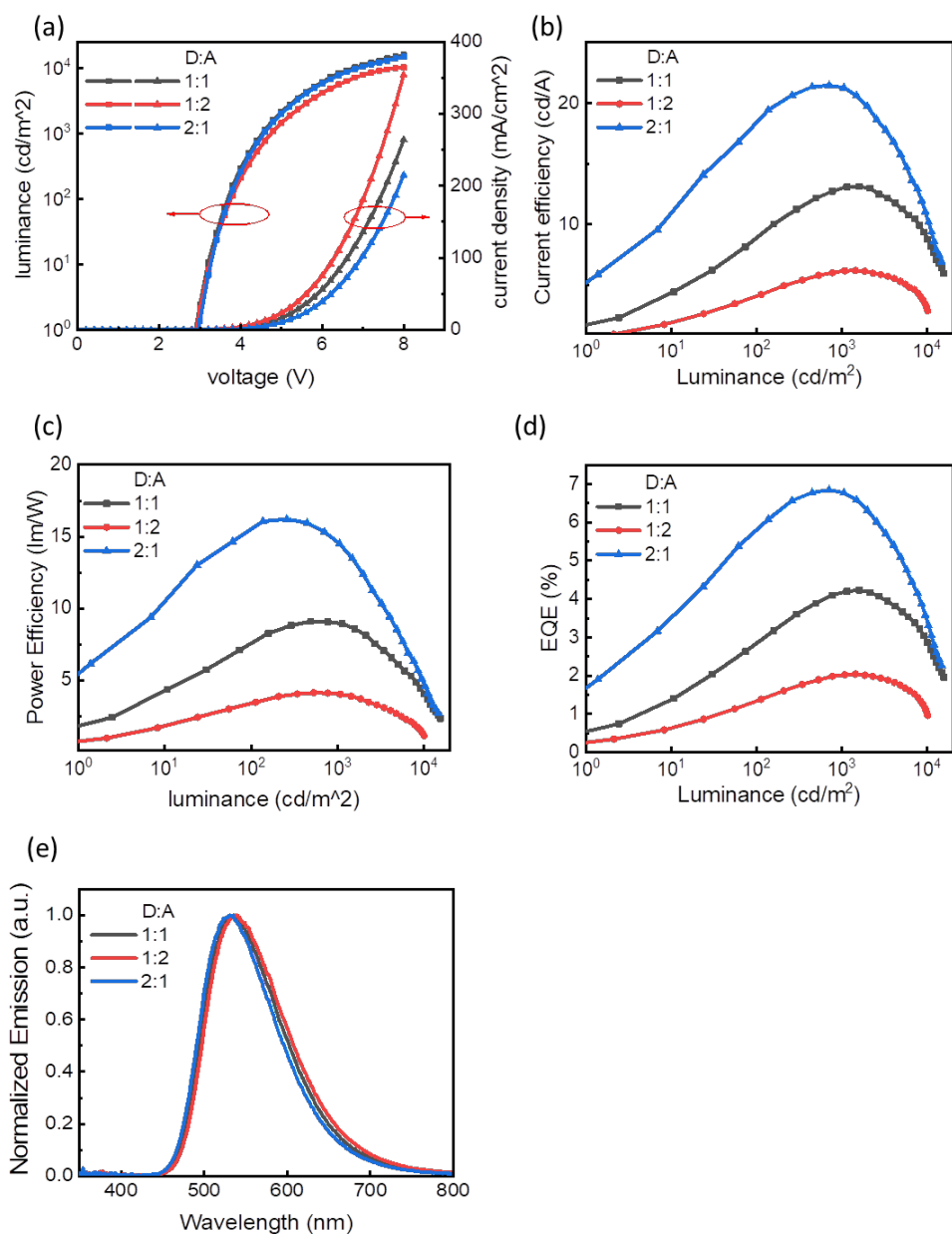


Figure S5. (a) Luminance–voltage–current density characteristics, (b) current efficiency–luminance characteristics, (c) Power efficiency–luminance characteristics, (d) EQE–luminance characteristics and (e) normalized EL spectra for the devices with different ratio of BCz3Ph (D) and PO-T2T (A).

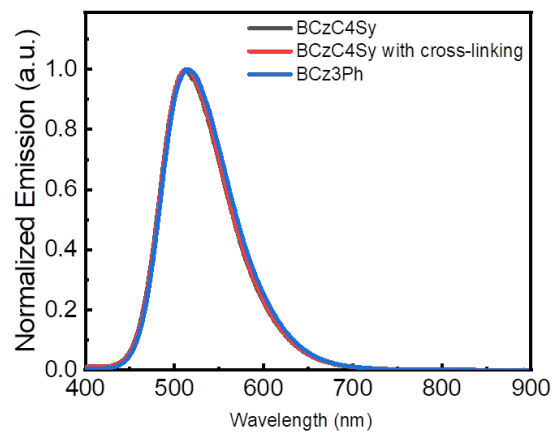


Figure S6. The photoluminescence of two bilayer films and one mixed film: a first layer with either **BCzC4Sy** and **BCzC4Sy** after thermal cross-linking, then spin-coating of PO-T2T as the second layer. The mixed film is the exciplex of **BCz3Ph** with PO-T2T.

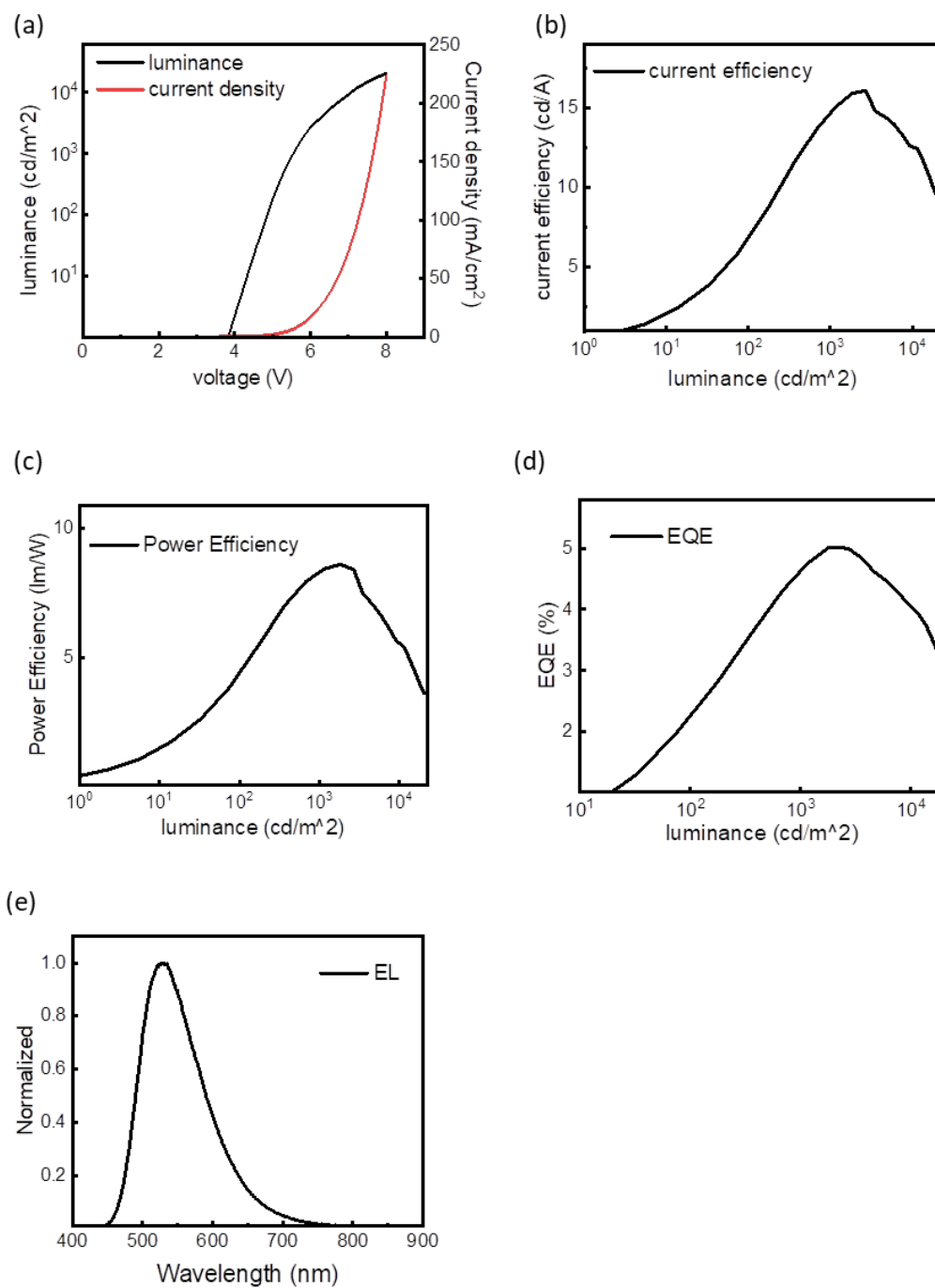


Figure S7. (a) Luminance–voltage–current density characteristics, (b) current efficiency– luminance characteristics, (c) Power efficiency–luminance characteristics, (d) EQE–luminance characteristics and (e) normalized EL spectra for the devices D5 prepared under air condition.

Table S1. The fitting data of the temperature-dependent TRPL spectra of the **BCz3Ph:PO-T2T** (2:1) blend films.

Temperature (K)	TRPL ^a			
	A_1	τ_p (ns)	A_2	τ_d (μ s)
80	0.03	99	0.97	3.50
100	0.03	94	0.97	3.37
150	0.02	70	0.98	3.11
200	0.02	64	0.98	3.01
300	0.02	58	0.98	2.59

^a Measured under an ambient atmosphere, and the decay components were fitted with two exponential decay models as $I(t) = A_1 \exp(-t/\tau_p) + A_2 \exp(-t/\tau_d)$, as shown in Figure S4.

Table S2. The optimization ratio of **BCz3Ph** and PO-T2T.

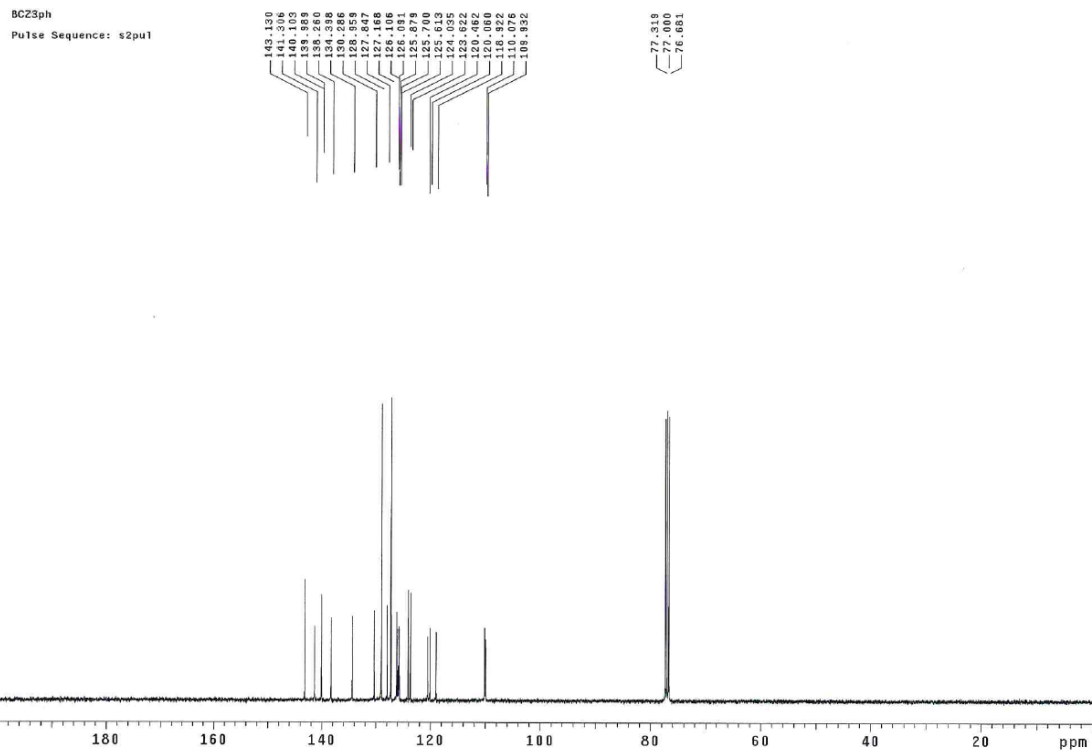
Donor	Donor : PO-T2T	EL λ_{max} (nm)	V_{on} ^a (V)	EQE _{max} /CE _{max} /PE _{max} (%/cd A ⁻¹ /lm W ⁻¹)	At 1000 cd m ⁻² (%/cd A ⁻¹ /lm W ⁻¹) ^b	L_{max} (cd m ⁻²)	CIE (x, y)
BCzC1Sy	1:1	535	2.6	4.23/13.11/9.09	4.01/11.30/8.94	15834	(0.37, 0.56)
BCzC1Sy	1:2	540	2.6	2.04/6.18/4.13	1.96/5.88/4.03	10442	(0.38, 0.55)
BCzC1Sy	2:1	531	2.7	7.15/21.82/18.68	7.07/21.26/15.90	23287	(0.37, 0.55)

^a Turn-on voltage at which emission became detectable.

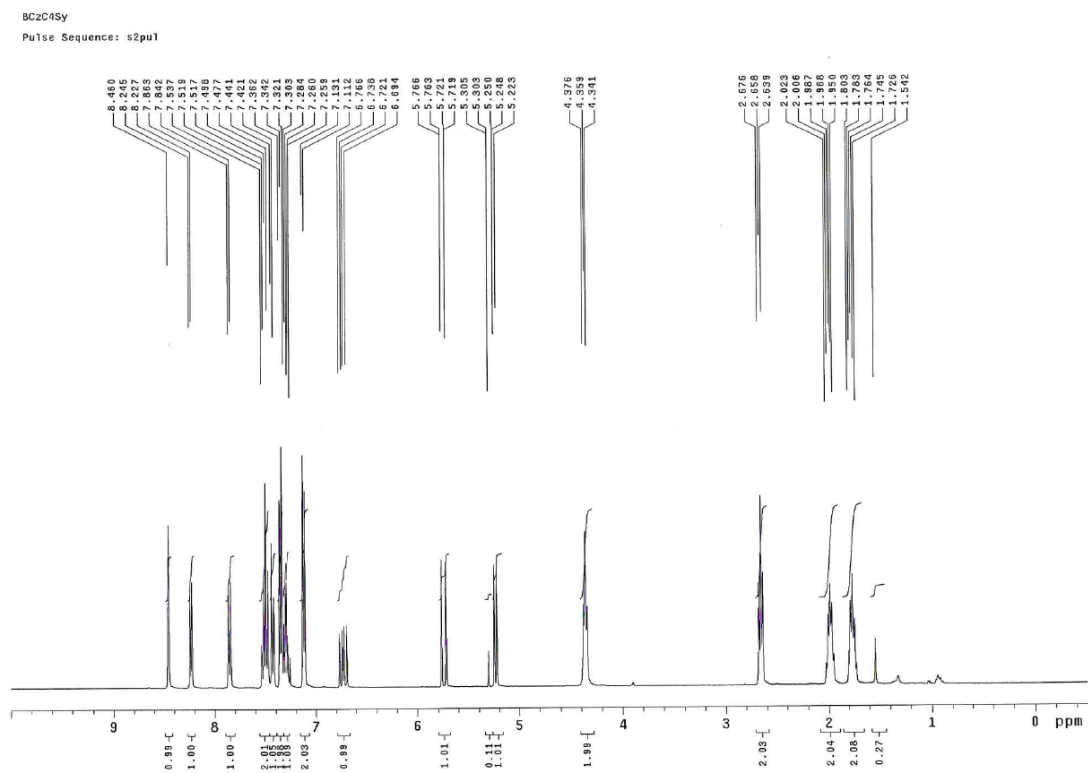
^b The values of EQE ,CE ,PE and driving voltages of device at 1000 cd m⁻²

Table S3. Parameters of slot-die coating

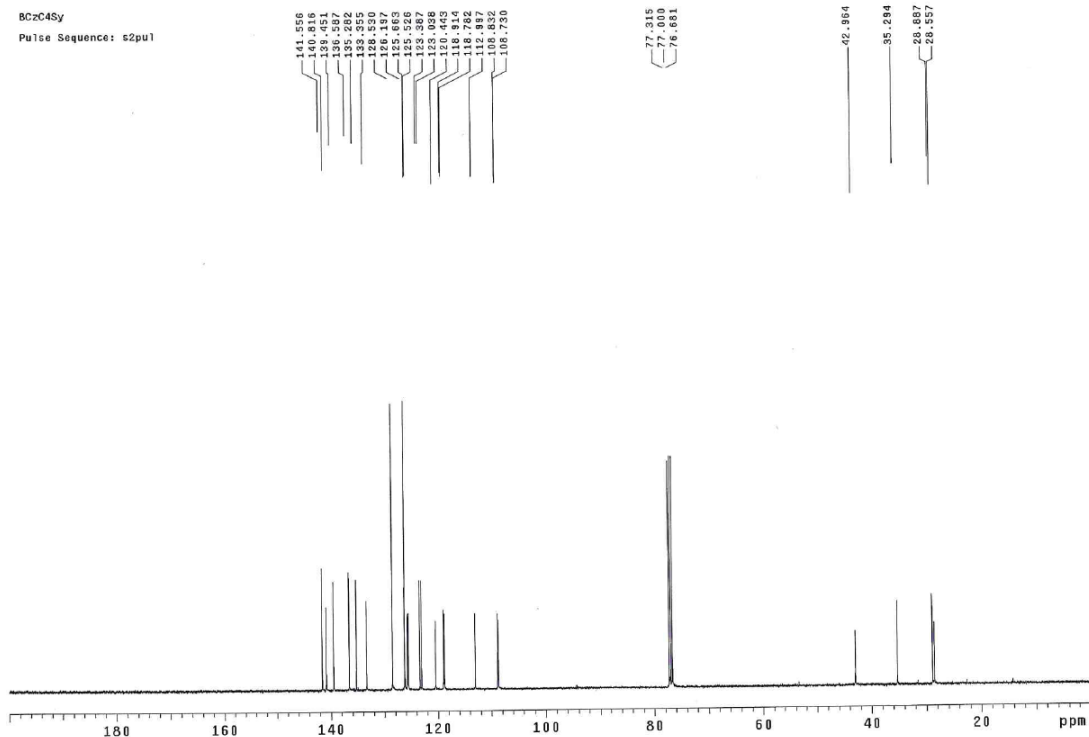
	Concentration (mg/mL)	Flow Rate (mL/hr)	Head Speed (Hz)
PEDOT:PSS	AI 4083:IPA=1:2	90	6000
BCzC4Sy	2	85	13000
BCz3Ph:PO-T2T	8	60	12000



The ^{13}C NMR of BCz3Ph



The ^1H NMR of BCzC4Sy



The ^{13}C NMR of BCzC4Sy

Reference

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4. W.-Y. Hung, G.-C. Fang, S.-W. Lin, S.-H. Cheng, K.-T. Wong, T.-Y. Kuo and P.-T. Chou, The First Tandem, All-exciplex-based WOLED, *Sci. Rep.*, 2014, **4**, 5161.