

Supporting Information

A terpyridine-modified chrysene derivative as an electron transporter to improve lifetime in phosphorescent OLEDs

Tsukasa Owada¹, Hisahiro Sasabe*^{1,2,3}, Yoshihito Sukegawa¹, Taiki Watanabe¹, Tomohiro Maruyama¹, Yuichiro Watanabe^{1,2,3}, Daisuke Yokoyama^{1,2}, Junji Kido*^{1,2,3}

¹Department of Organic Materials Science, Graduate School of Organic Materials Science, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan, ²Research Center for Organic Electronics (ROEL), Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan, ³Frontier Center for Organic Materials (FROM), Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan

E-mail: h-sasabe@yz.yamagata-u.ac.jp, kid@yz.yamagata-u.ac.jp

Table of Contents

- 1. Experimental Section**
- 2. Syntheses of B3TPyC**
- 3. ¹H NMR, Mass analyses of B3TPyC**
- 4. OLED performances**
- 5. References**

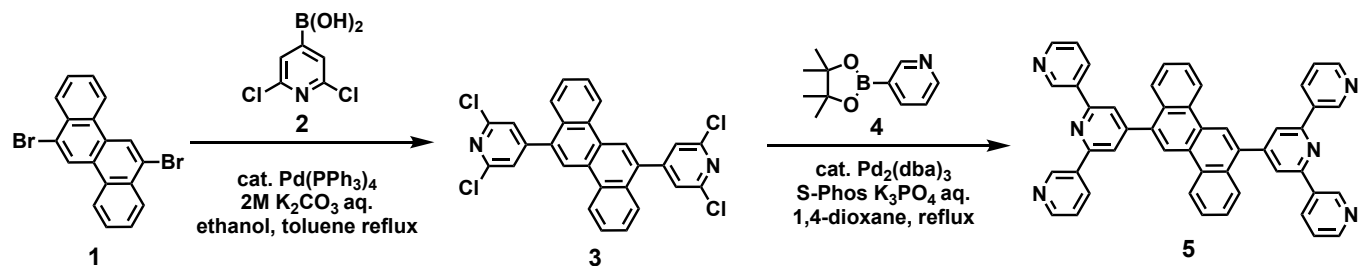
1. Experimental Section

General Considerations: Quantum chemical calculations were performed using the hybrid density functional theory (DFT) functional Becke and Hartree-Fock exchange and Lee Yang and Parr correlation (B3LYP) as implemented by the Gaussian 09 program packages.¹ Electrons were described by the Pople's 6-31G(d) and 6-311+G(d,p) basis sets for molecular structure optimization and single-point energy calculations, respectively. ¹H NMR spectra were recorded on JEOL 400 (400 MHz) spectrometer. Mass spectrum were obtained using a Waters SQD2 mass spectrometer with atmospheric pressure solid analysis probe (ASAP). Different scanning calorimetry (DSC) was performed using a Perkin-Elmer Diamond DSC Pyris instrument under nitrogen atmosphere at a heating rate of 10 °C min⁻¹. Thermogravimetric analysis (TGA) was undertaken using a SEIKO EXSTAR 6000 TG/DTA 6200 unit under nitrogen atmosphere at a heating rate of 10 °C min⁻¹. UV-vis spectra was measured using a Shimadzu UV-3150 UV-vis-NIR spectrophotometer. Photoluminescence spectra were measured using a FluoroMax-2 (Jobin-Yvon-Spex) luminescence spectrometer. The ionization potential (Ip) was determined by a photoelectron yield spectroscopy (PYS)² under the vacuum (~10⁻³ Pa). The deposited films for PYS measurement were transported through in nitrogen glove box without atmospherically exposed.

Device fabrication and characterization : All organic materials were purified by temperature gradient sublimation in vacuum. The substrates were cleaned with organic solvents (chloroform and acetone) and ultrapurified water and then dry-cleaned for 10 min by exposure to UV-ozone. The organic layers were deposited onto the ITO substrate under the vacuum (ca. 10⁻⁵ Pa), successively. Al was patterned using a shadow mask with an array of 2 mm × 2 mm openings without breaking the vacuum (ca. 10⁻⁵ Pa). The EL spectra were taken using an optical multichannel analyzer Hamamatsu Photonics PMA-11. The current density-voltage and luminance-voltage characteristics were measured using a Keithley source measure unit 2400 and a Minolta CS200 luminance meter, respectively.

2. Syntheses of B3TPyC

Synthesis of B3TPyC



6,12-Dibromochrysene **1** (2.00 g, 5.18 mmol) and 2,6-dichloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine **2** (3.12 g, 11.4 mmol) were added to a round bottom flask. Toluene (35 mL) and ethanol (18 mL) and aqueous K_2CO_3 (2.0 M, 20.7 mL) were added and nitrogen bubbled through the mixture for 1 hour. Then, tetrakis(triphenylphosphine)palladium(0) ($\text{Pd}(\text{PPh}_3)_4$) (359 mg, 0.31 mmol) was added and the resultant mixture, and was vigorously stirred for 20 hours at reflux temperature under N_2 flow. Upon cooling to room temperature, water (100 mL), toluene (200 mL) were added and stirred. The resulting white solid was dissolved in chloroform, and was purified by column chromatography on silica gel to obtain the crude product of tetrachloride **3**. Then, the crude product of **3** (3.00 g, 5.8 mmol) and 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (3.57 g, 17.4 mmol) were added to a round bottom flask. 1,4-Dioxane (105 mL) and aqueous K_3PO_4 (1.35 M, 78 mL) were added and nitrogen bubbled through the mixture for 1 hour. Then, $\text{Pd}_2(\text{dba})_3$ (359 mg, 0.31 mmol) and S-Phos (131 mg, 0.324 mmol) were added and the resultant mixture was vigorously stirred for 73 hours at reflux temperature under N_2 flow. Upon cooling to room temperature, water (100 mL), and toluene (200 mL) were added, and were vigorously stirred. After filtration of the mixture, the organic layer was extracted, and was evaporated under reduced pressure. The resulting white solid was dissolved in chloroform, and was purified by column chromatography on silica gel to obtain white solid of B3TPyC **5** (1.39 g, 35%); $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 9.46 (d, $J = 1.4$ Hz, 4H), 8.95 (d, $J = 8.7$ Hz, 2H), 8.83 (s, 2H), 8.74 (dd, $J = 5.0, 1.4$ Hz, 4H), 8.59 (dt, $J = 7.9, 1.8$ Hz, 4H), 8.09 (d, $J = 9.6$ Hz, 6H), 7.81 (dd, $J = 8.2, 6.9$ Hz, 2H), 7.69 (dd, $J = 8.2, 6.9$ Hz, 2H), 7.51 (dd, $J = 8.0, 4.8$ Hz, 4H); MS: m/z 691 $[\text{M}+\text{H}]^+$ (ASAP); Anal calcd for $\text{C}_{48}\text{H}_{30}\text{N}_6$: C, 83.46; H, 4.38; N, 12.17%. Found. C, 83.64; H, 4.25; N, 12.25%.

3. $^1\text{H-NMR}$, Mass analyses of B3TPyC

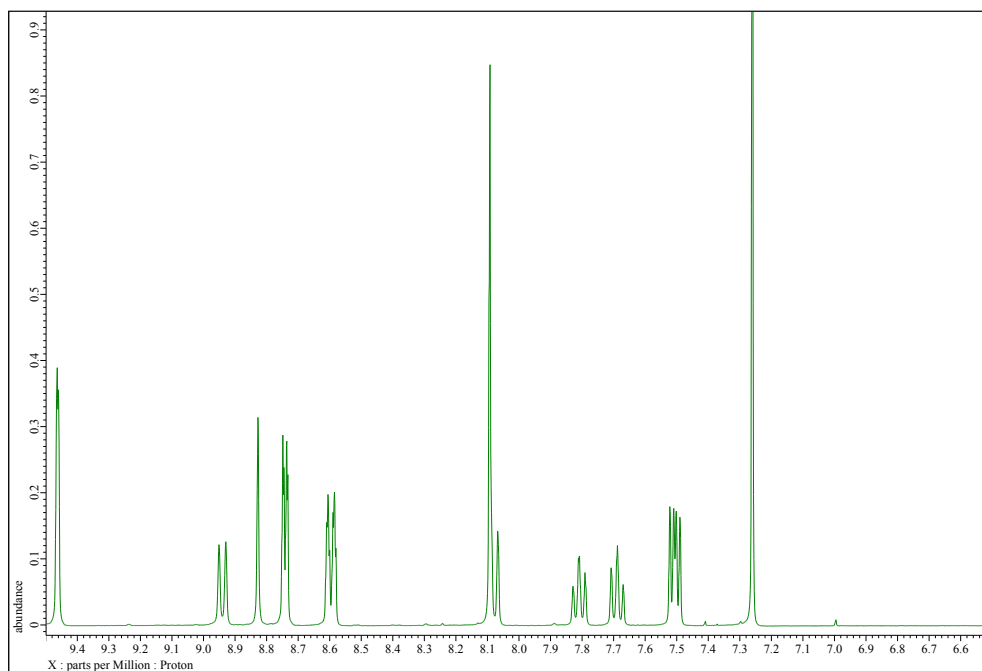


Figure S1. $^1\text{H-NMR}$ spectrum of B3TPyC (400 MHz, CDCl_3).

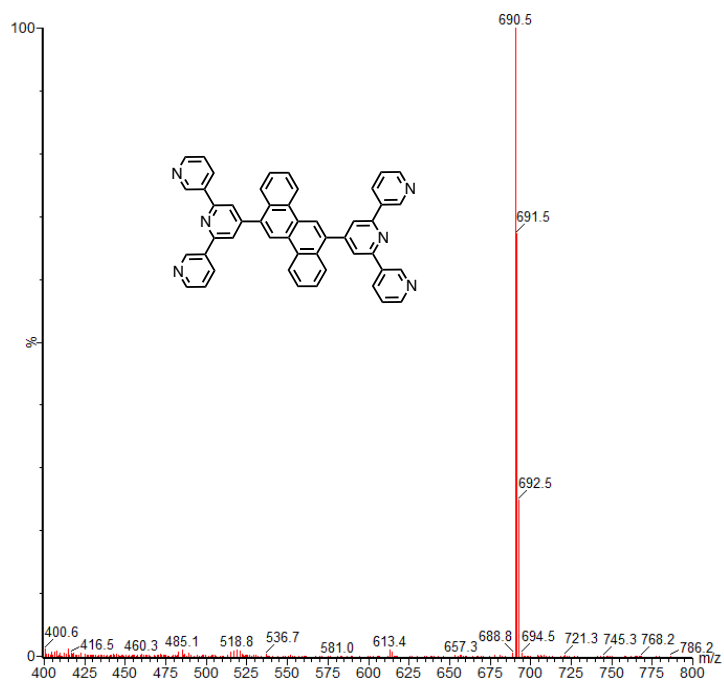


Figure S2. MS spectrum of B3TPyC (ASAP).

4. OLED performances

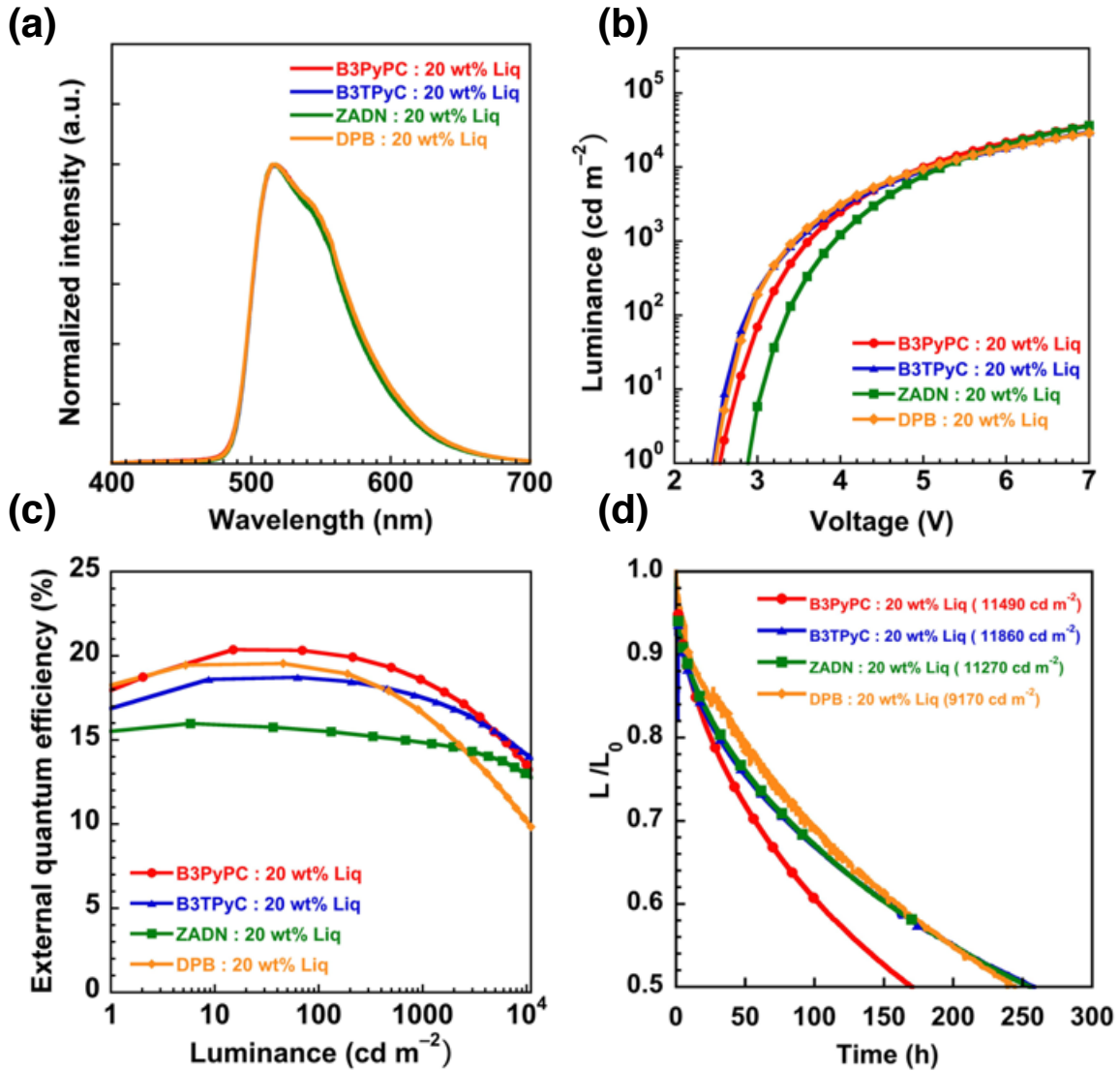


Figure S3. Device performances of OLED: a) EL spectra, b) L - V characteristics, c) η_{ext} - L characteristics and d) normalized luminance of devices as a function of operation time at the initial luminance of 25 mA cm^{-2} .

Table S1. Summary of OLED performances.

ETL	V_{on}^a (V)	$V_{100}/\eta_c,100/\eta_p,100/\eta_{ext,100}^b$ (V/cd A ⁻¹ /lm W ⁻¹ %)	$V_{1000}/\eta_c,1000/\eta_p,1000/\eta_{ext,1000}^c$ (V/cd A ⁻¹ /lm W ⁻¹ %)	LT ₅₀ ^d (h) @ 25 mA cm^{-2}	LT ₅₀ ^e (h) @ 1000 cd m^{-2}
B3TPyC	2.42	2.85/74.2/67.3/18.7	3.46/57.4/63.3/17.5	258	≈ 19000
B3PyPC	2.51	3.04/75.3/72.9/20.2	3.61/58.1/66.8/18.6	170	≈ 12000
ZADN	2.83	3.33/53.1/56.2/15.6	3.92/43.1/53.7/14.9	256	≈ 17000
DPB	2.43	2.88/76.1/69.5/19.3	3.43/54.9/59.9/16.6	243	≈ 11000

^a Turn-on voltage at 1 cd m^{-2} . ^b Voltage, current efficiency (η_c), power efficiency (η_p), and external quantum efficiency (η_{ext}) at 100 cd m^{-2} . ^c Voltage, η_c , η_p , and η_{ext} at $1,000 \text{ cd m}^{-2}$. ^d Operation lifetime at 50% of the initial luminance of approximately 11000 cd m^{-2} (current density : 25 mA cm^{-2}) ^e Operation lifetime at 50% of the initial luminance of approximately 1000 cd m^{-2} estimated using the well known stretched exponential decay function^[3].

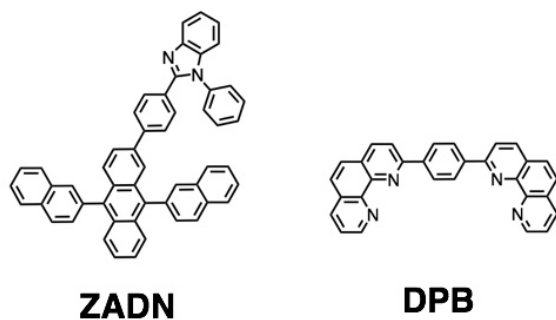


Figure S4. Chemical structures of ZADN and DPB used as ETLs.

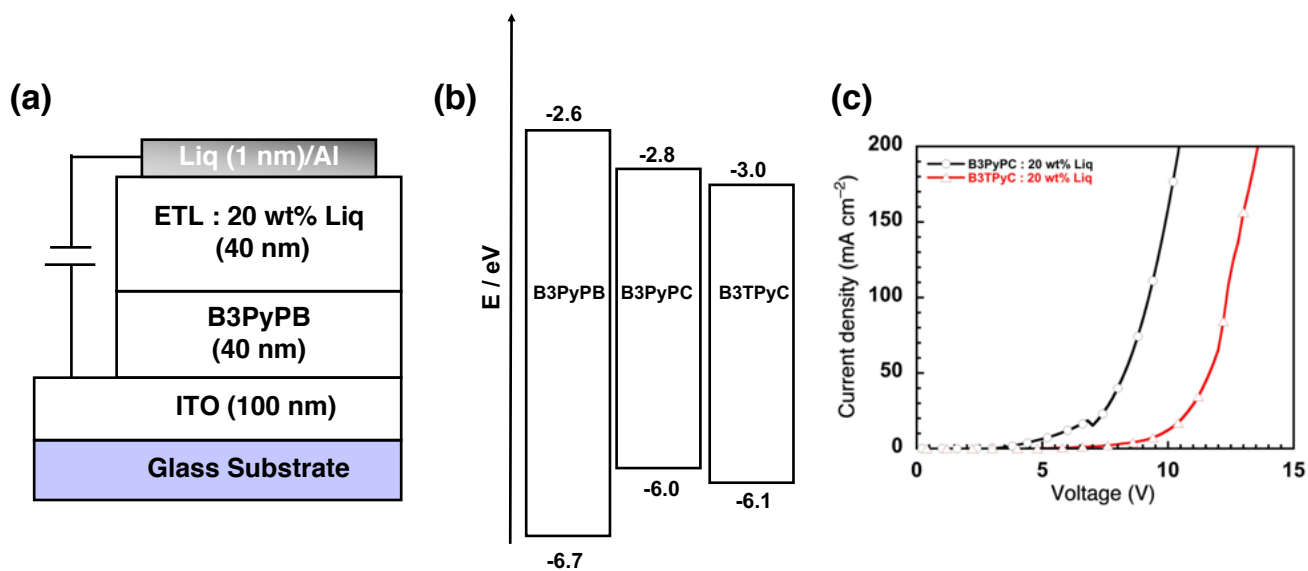


Figure S5. a) Device structure, b) energy diagram, and c) J–V characteristics of the electron only devices using B3PyPC and B3TPyC.

References

- (1) M. J. Frisch et al. Gaussian 09; Gaussian Inc.: Pittsburgh, PA 2009.
- (2) H. Ishii, D. Tsunami, T. Suenaga, N. Sato, Y. Kumura, M. Niwano, *J. Surf. Sci. Jpn.* **2007**, *28*, 26
- (3) D. Zhang, M. Cai, Y. Zhang, D. Zhang, L. Duan, *Mater Horiz.* **2016**, *3*, 145.

