

Supporting Information

Fundamental Functions of Peripheral and Core Pyridine Rings in a Series of Terpyridine Derivatives for High-Performance Organic Light-Emitting Devices

Yuichiro Watanabe,^[a] Ryo Yoshioka,^[a] Hisahiro Sasabe,^{,[a],[b]} Takahiro Kamata,^[a] Hiroshi Katagiri,^{[a],[b]} Daisuke Yokoyama,^{[a],[b]} and Junji Kido^{*,[a],[b],[c]}*

[a] Department of Organic Materials Science, Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata, 992-8510 Japan.

[b] Research Center for Organic Electronics (ROEL), Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata, 992-8510 Japan.

[c] Frontier Center for Organic System Innovations(COI) Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan

E-mail: h-sasabe@yz.yamagata-u.ac.jp; kido@yz.yamagata-u.ac.jp

Table of Contents:

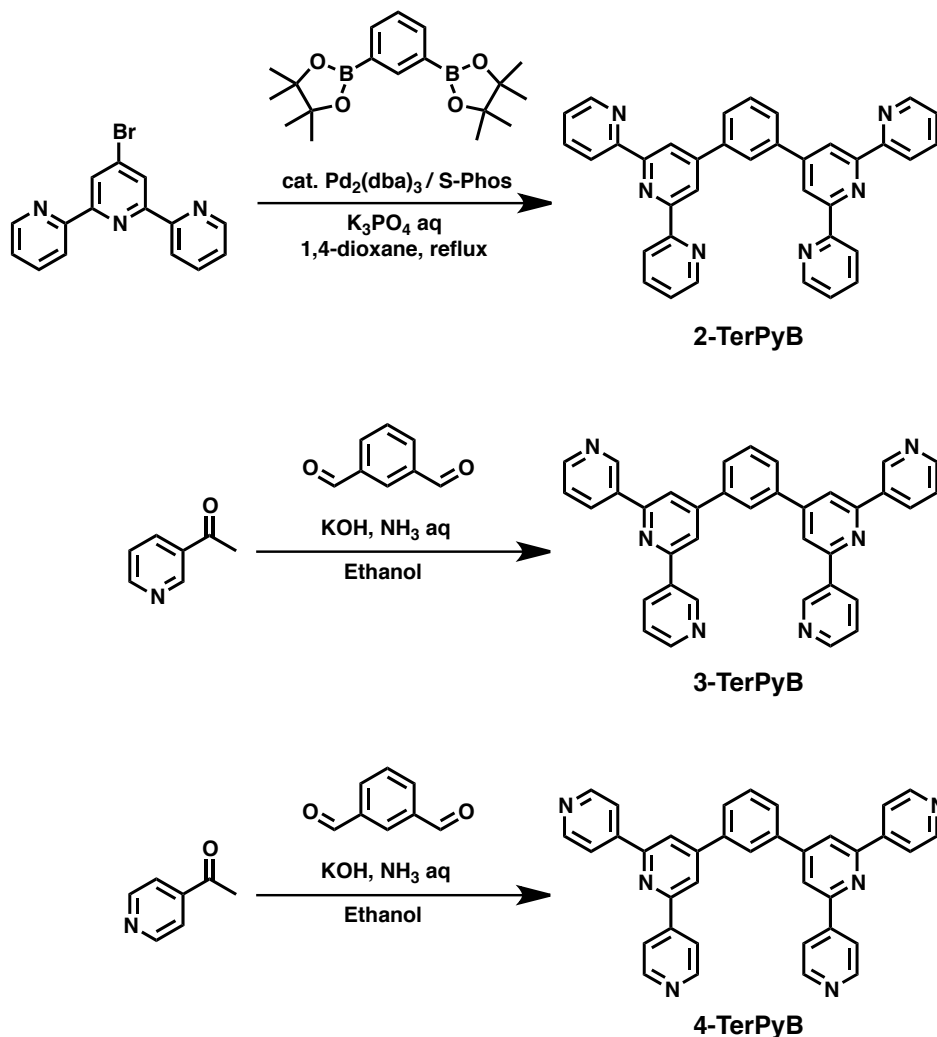
- 1. Synthesis**
- 2. X-Ray Crystal Structure Determination**
- 3. TGA Analysis**
- 4. Optical Properties**
- 5. ¹H NMR analysis of B3PyPB and 3-TerPyB**
- 6. Organic Light-Emitting Devices (OLEDs)**
- 7. References**
- 8. Table of contents**

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. Electrons were described by the Pople's 6-31G(d,p) and 6-311 + G(d,p) basis sets for molecular structure optimization and single-point energy calculations, respectively. ^1H NMR spectrum was recorded on JEOL 400 (400 MHz) spectrometer. Mass spectrum was obtained using a JEOL JMS-K9 mass spectrometer. Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer Diamond DSC Pyris instrument under nitrogen atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$. Thermogravimetric analysis (TGA) was undertaken using a SEIKO EXSTAR 6000 TG/DTA 6200 unit under nitrogen atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$. UV-Vis spectra were measured using a Shimadzu UV-3150 UV-vis-NIR spectrophotometer. Photoluminescence spectra were measured using a FluroMax-2 (Jobin-Yvon-Spex) luminescence spectrometer. The ionization potential (I_p) was determined by a photoelectron yield spectroscopy (PYS) under the vacuum ($\sim 10^{-3}$ Pa). The deposited films for PYS measurement were transported through in nitrogen globe box without atmospherically exposed. AFM images were recorded on a Bruker Dimension Icon.

Device Fabrication and Characterization: CBP and Liq were purchased from eRay. TAPC was purchased from TCI. Ir(ppy)_3 was purchased from Chemipro Kasei. CBP and TAPC were purified by temperature-gradient sublimation in vacuum. Phosphorescent OLEDs were grown on glass substrates precoated with a 130-nm thick material of indium-tin oxide (ITO) having a sheet resistance of $15 \Omega/\text{sq}$. The substrates were cleaned with ultrapurified water and organic solvents, and then dry-cleaned for 30 min by exposure to UV-ozone. The organic materials 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 $2 \text{ mm} \times 2 \text{ mm}$ openings without breaking the vacuum (ca. 10^{-5} Pa). All devices were encapsulated immediately after preparation under a nitrogen atmosphere using epoxy glue and glass lids. 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. Synthesis



Scheme S1. Synthetic route of BPy and BPyPh derivatives.

Synthesis of 2-TerPyB. 4'-chloro-2,2':6',2''-terpyridine (2.40 g, 7.69 mmol) and 1,3-Benzenediboronic acid bis(pinacolate)ester (1.16g, 3.51 mmol) were added to a round bottom flask. 1,4-Dioxane (55 mL) and aqueous K_3PO_4 (1.35 M, 19 mL) were added and nitrogen bubbled through the mixture for 1 hour. Then, $\text{Pd}_2(\text{dba})_3$ (0.067 g, 0.073 mmol) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos) (0.064 g, 0.156 mmol) were added and the resultant mixture was vigorously stirred for 14 hours at reflux temperature under N_2 flow. The precipitate was filtered, and washed with water and methanol. The resulting off-white solid was dissolved in chloroform/Methanol = 20/1 (315 mL), filtered through Celite pad (75 cc). The clear filtrate was further purified by washing with hexane to afford 2-TerPyB as a off white solid (1.86 g, 98%). ^1H NMR (400 MHz, CDCl_3): δ = 8.81 (s, 4H), 8.77–8.68 (m, 8H), 8.34 (s, 1H), 7.98 (d, J = 7.8 Hz, 2H), 7.90 (t, J = 7.8 Hz, 4H), 7.67 (t, J = 7.8 Hz, 1H), 7.42–7.33 (m, 4H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 156.2, 156.0, 150.2, 149.2, 136.9, 128.2, 123.9, 121.4, 119.3 ppm; EI-MS: m/z 541 $[\text{M}+\text{H}]^+$; Anal calcd for $\text{C}_{36}\text{H}_{24}\text{N}_6$: C, 79.98; H, 4.47; N, 15.55%. Found. C, 80.12; H, 4.29; N, 15.63%.

Synthesis of 3-TerPyB. 3-acetyl-pyridine (26.4 mL, 0.242 mol) was added into a solution of isophthalaldehyde (8.05 g, 0.060 mol) in ethanol (966 mL). Then, potassium hydroxide pellets

(18.5 g, 86%, 0.284 mol) and 25% NH_3 *aq* (406 mL, 25%, 5.39 mol) were added to the solution. The resultant mixture was stirred for 6.5 hours at room temperature. The precipitate was filtered, and washed with water and ethanol. The resulting pale-yellow solid was purified by chromatography on silica gel (eluent: $\text{CHCl}_3/\text{CH}_3\text{OH} = 100:2$ to $100:5$ v/v) to afford 3-TerPyB (4.62 g, 14%) as a off white solid. ^1H NMR (400 MHz, CDCl_3): $\delta = 9.41$ (d, $J = 1.8$ Hz, 4H), 8.73 (dd, $J = 1.4, 4.6$ Hz, 4H), 8.54 (dt, $J = 1.8, 7.8$ Hz, 4H), 8.08–8.02 (m, 5H), 7.95–7.84 (m, 2H), 7.78 (t, $J = 7.8$ Hz, 1H), 7.49 (dd, $J = 4.8, 7.8$ Hz, 4H) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 155.7, 150.4, 148.5, 134.6, 134.5, 128.3, 123.7, 117.9$ ppm; EI-MS: m/z 541 $[\text{M}+\text{H}]^+$; Anal calcd for $\text{C}_{36}\text{H}_{24}\text{N}_6$: C, 79.98; H, 4.47; N, 15.55%. Found. C, 80.12; H, 4.37; N, 15.56%.

Synthesis of 4-TerPyB. off white solid (1.46 g, 23% yield). ^1H NMR (400 MHz, CDCl_3): $\delta = 8.84$ – 8.78 (m, 8H), 8.13– 8.08 (m, 12H), 8.02 (s, 1H), 7.91– 7.85 (m, 2H), 7.79 (t, $J = 7.6$ Hz, 1H) ppm; EI-MS: m/z 541 $[\text{M}+\text{H}]^+$. Anal calcd for $\text{C}_{36}\text{H}_{24}\text{N}_6$: C, 79.98; H, 4.47; N, 15.55%. Found. C, 80.26; H, 4.15; N, 15.59%.

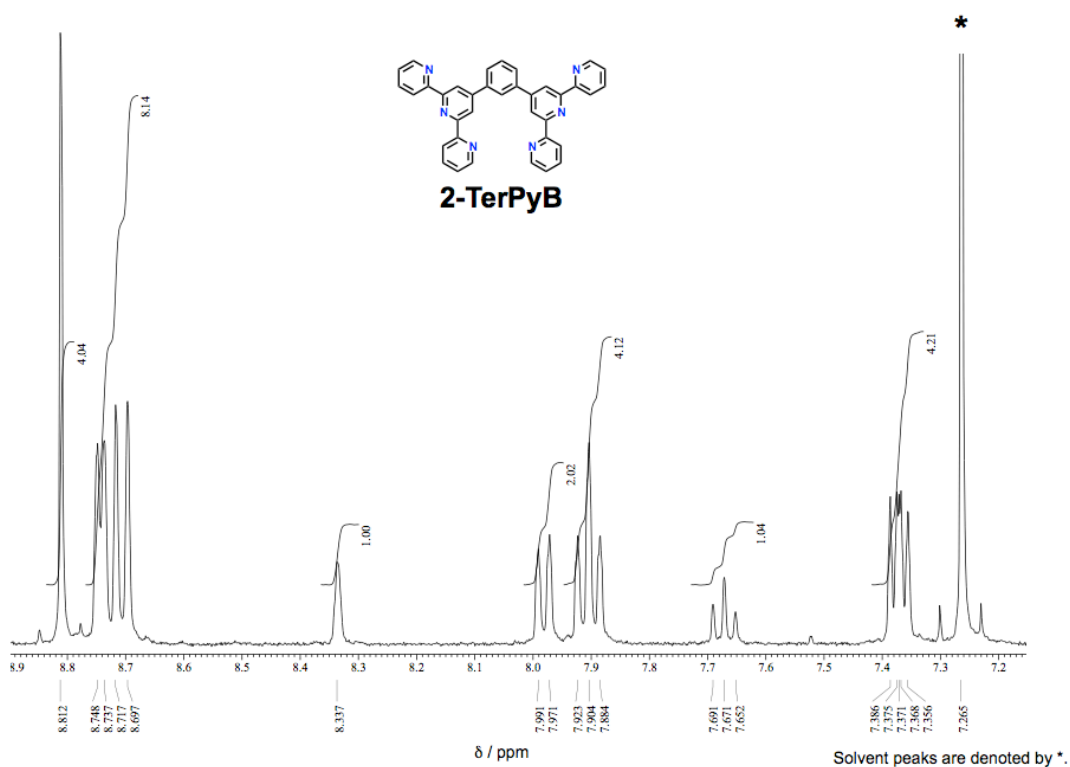
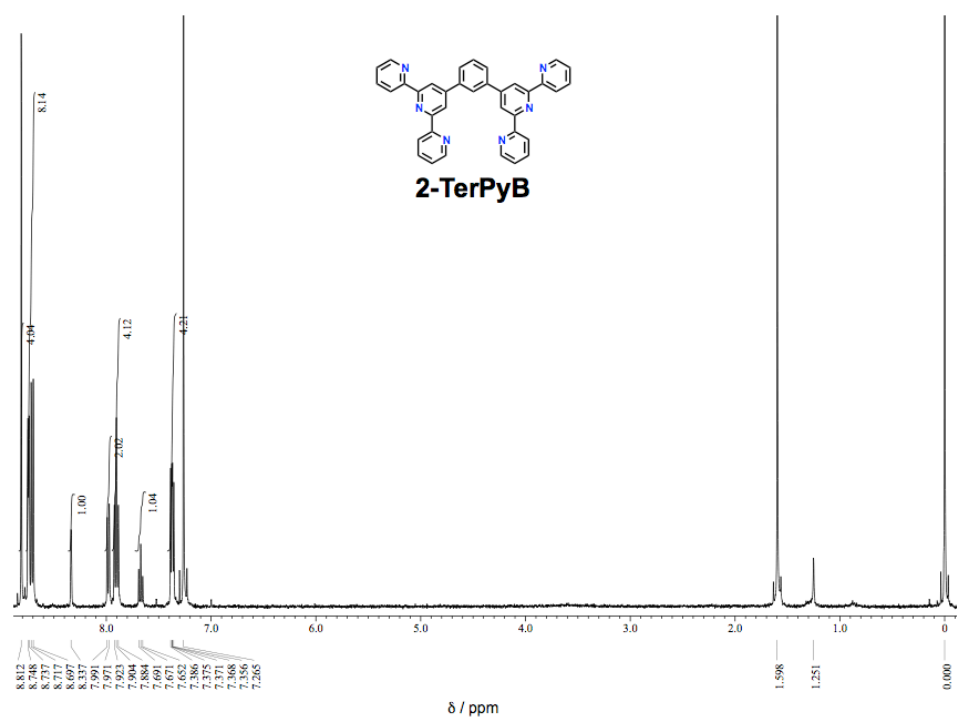


Figure S1. ^1H NMR spectra of 2-TerPyB (400 MHz, CDCl_3).

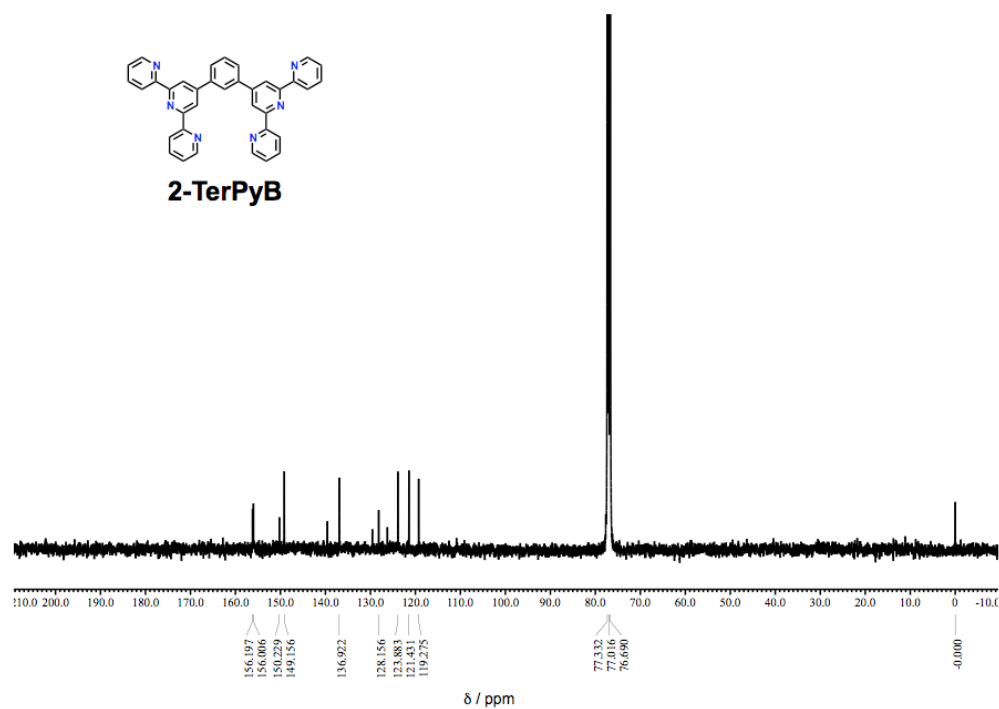


Figure S2. ^{13}C NMR spectra of 2-TerPyB (400 MHz, CDCl_3).

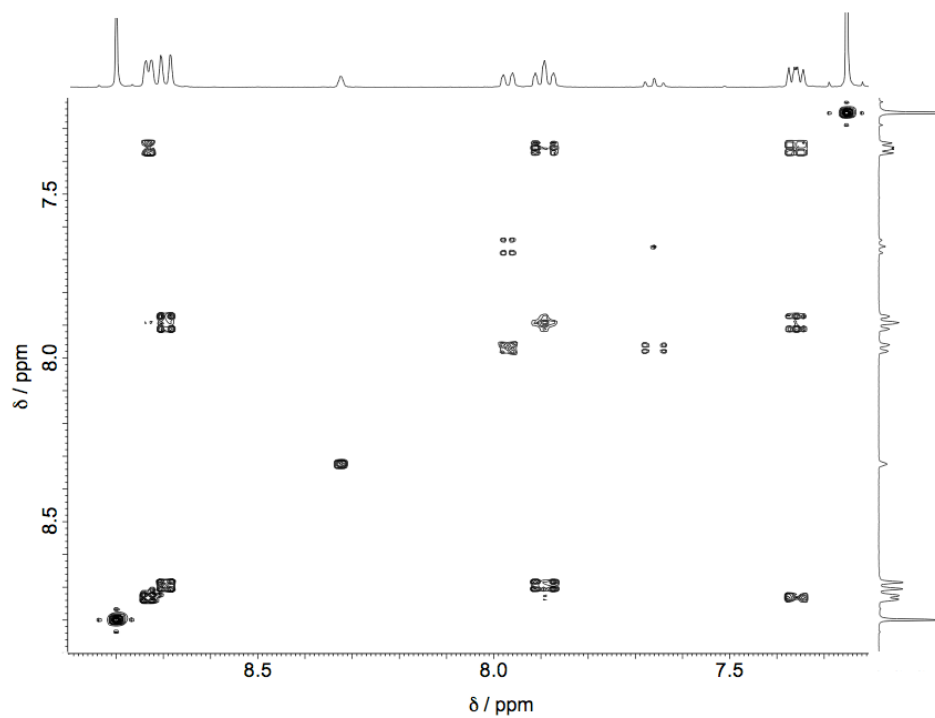


Figure S3. ^1H - ^1H COSY spectrum of 2-TerPyB (400 MHz, CDCl_3).

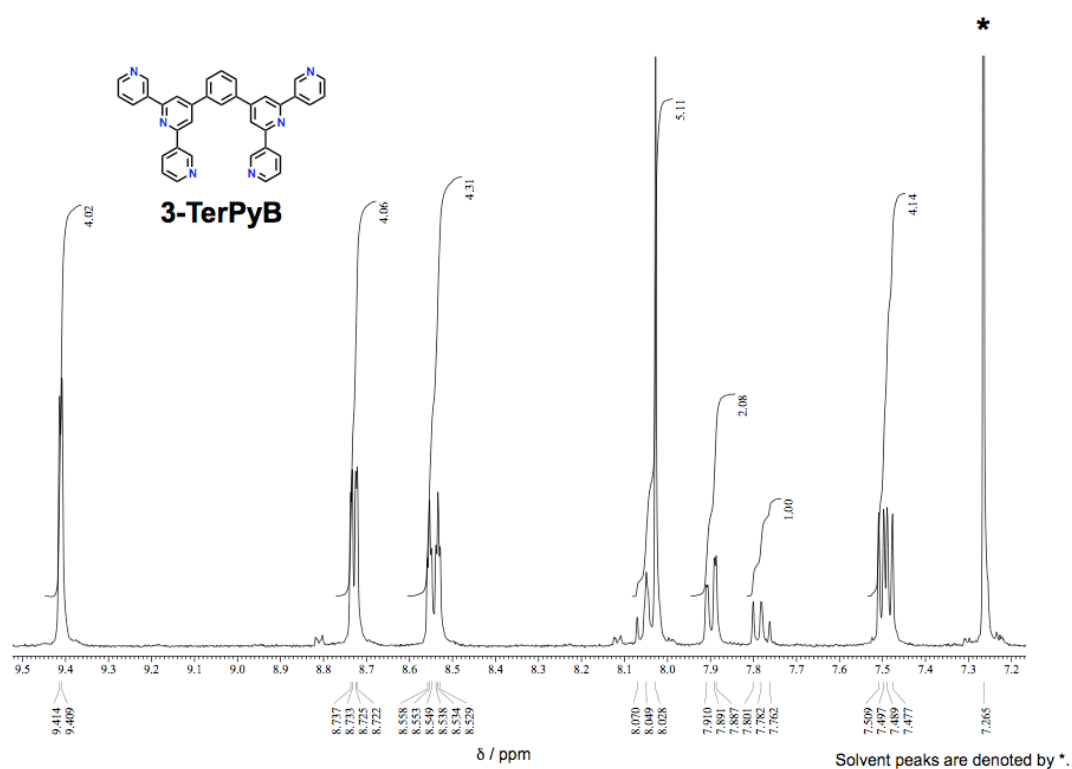
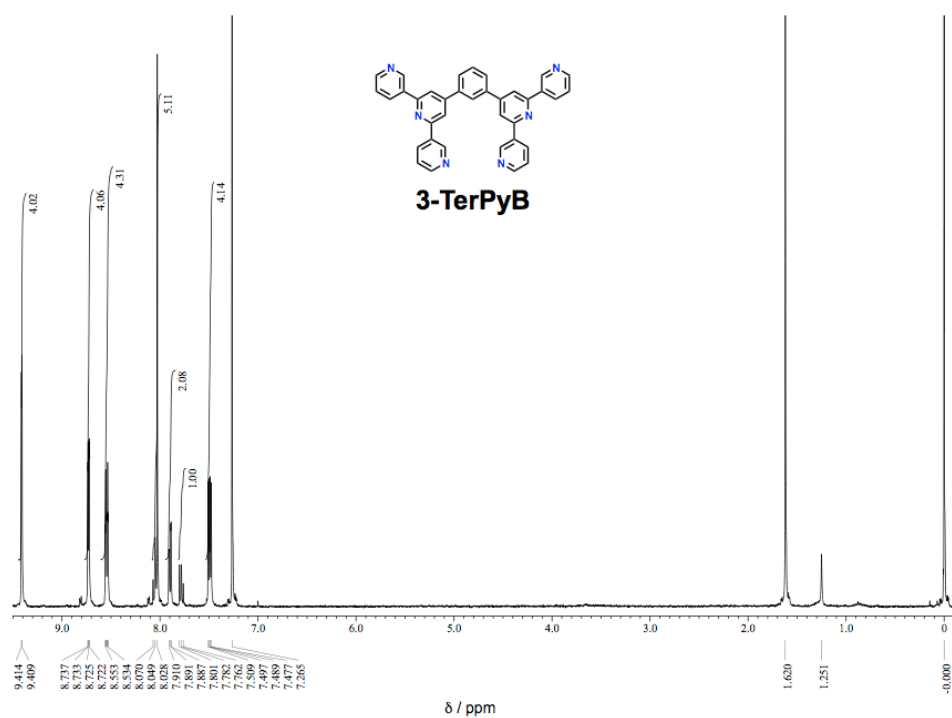


Figure S4. ^1H NMR spectra of 3-TerPyB (400 MHz, CDCl_3).

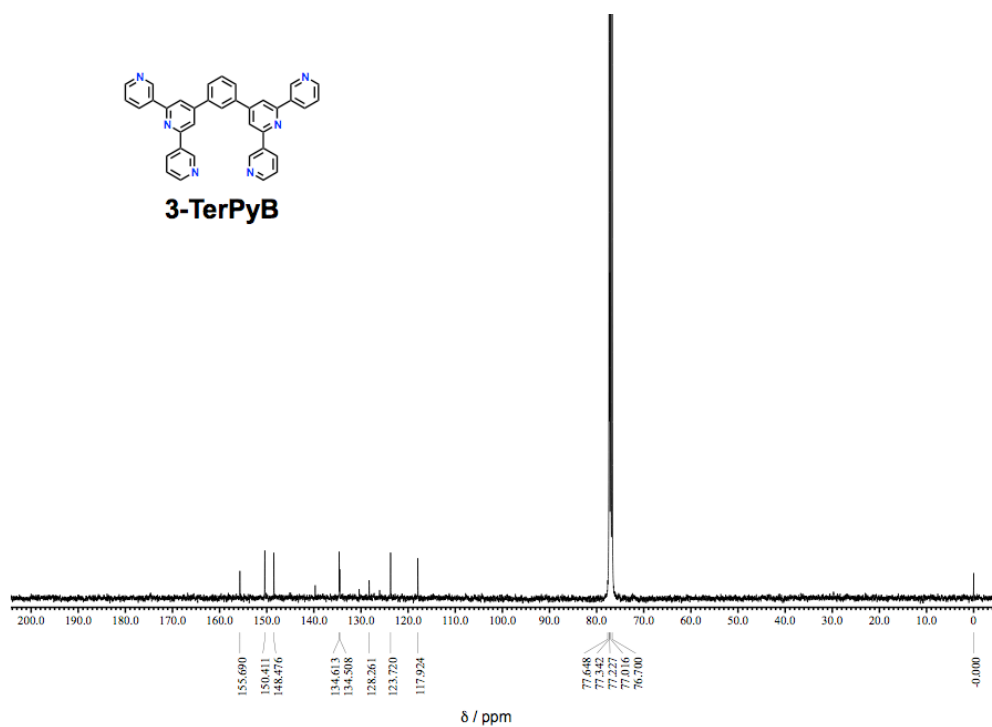


Figure S5. ^{13}C NMR spectra of 3-TerPyB (400 MHz, CDCl_3).

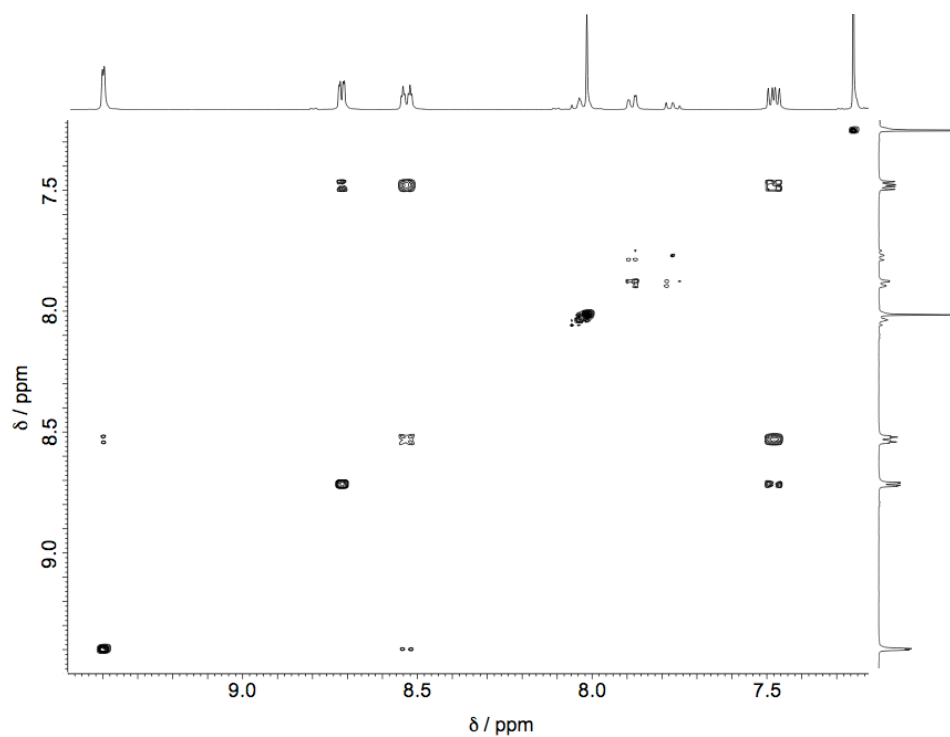


Figure S6. ^1H - ^1H COSY spectrum of 3-TerPyB (400 MHz, CDCl_3).

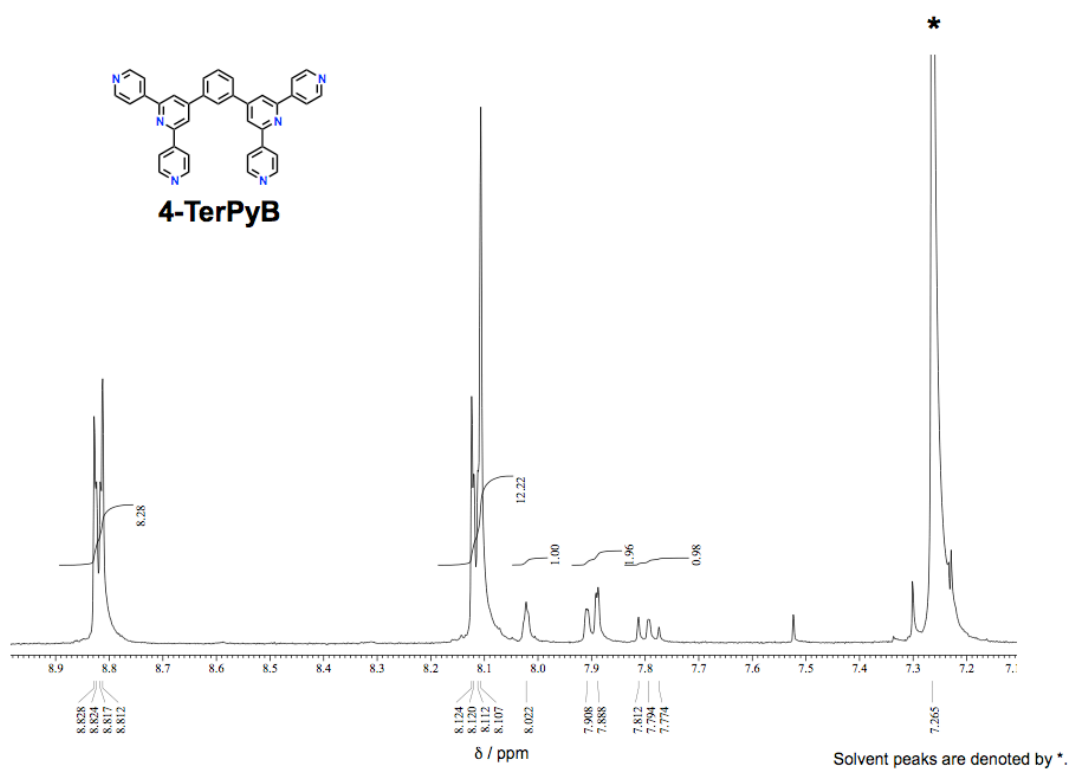
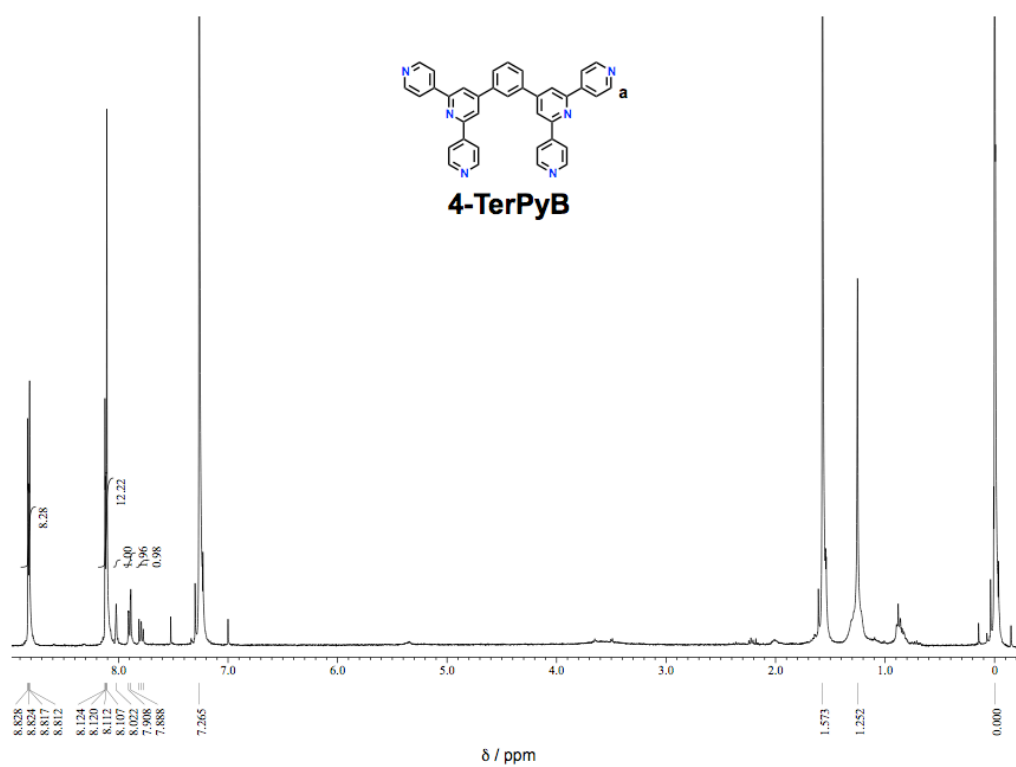


Figure S7. ^1H NMR spectra of 4-TerPyB (400 MHz, CDCl_3).

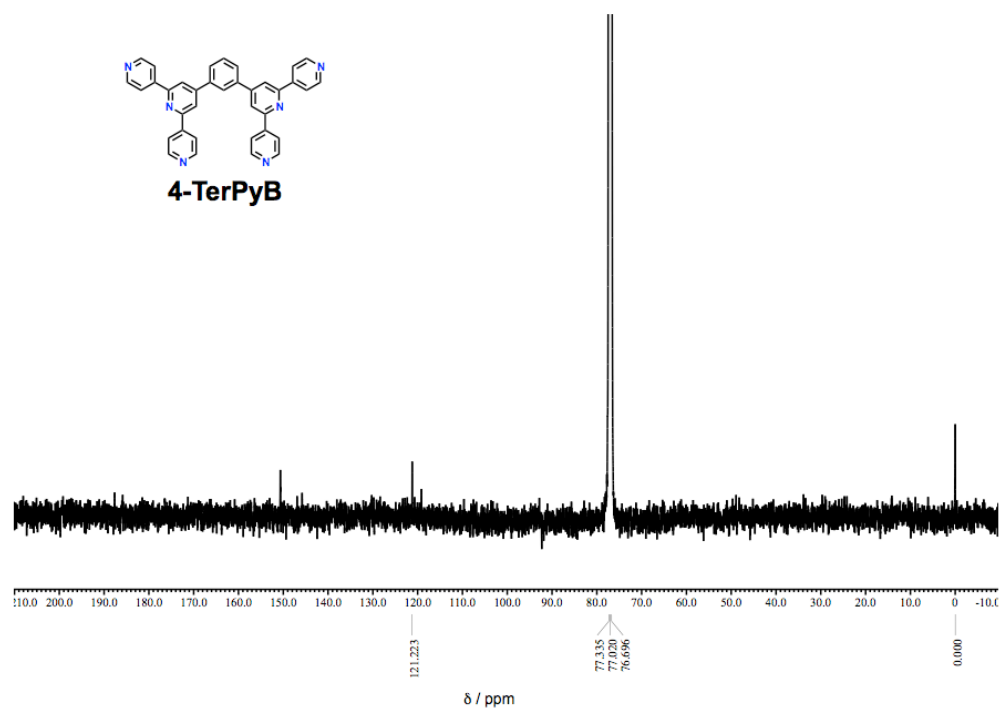


Figure S8. ^{13}C NMR spectra of 4-TerPyB (400 MHz, CDCl_3).

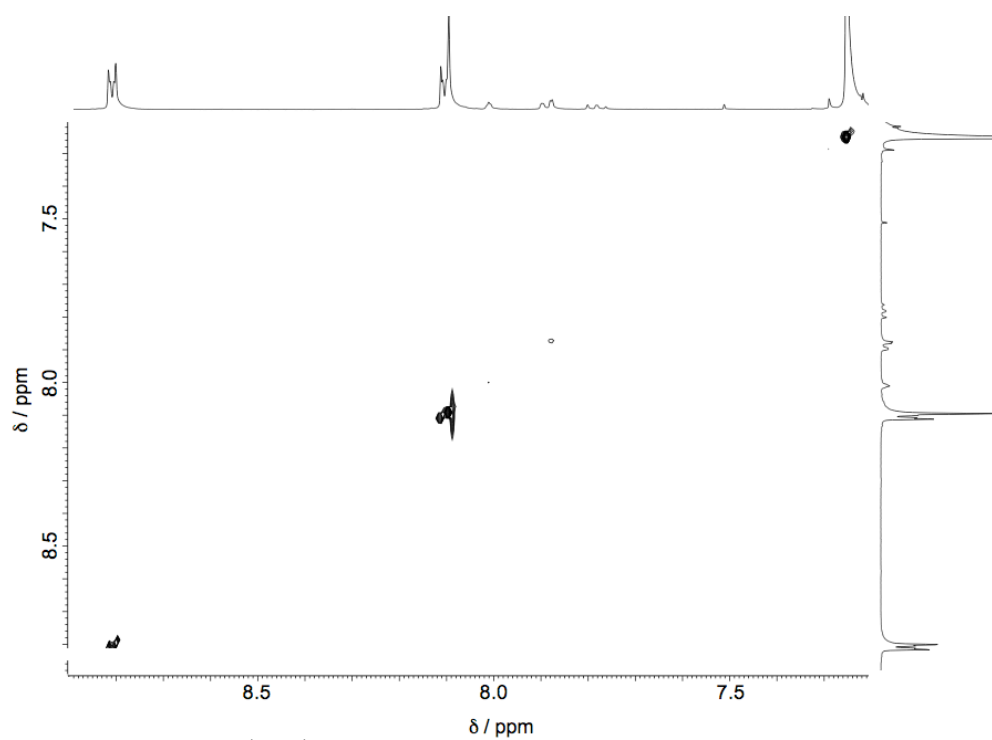


Figure S9. ^1H - ^1H COSY spectrum of 4-TerPyB (400 MHz, CDCl_3).

2. X-ray Crystallographic Structure Determination

4-TerPyB

The X-ray diffraction data for 4-TerPyB was collected on a Rigaku Saturn 724 CCD diffractometer with Mo- $K\alpha$ radiation ($\lambda = 0.71075$ Å) at 93 K. Single crystal of 4-TerPyB [$C_{36}H_{24}N_6$, Mw = 540.61] suitable for X-ray analysis were grown by slow gradient sublimation, and a colourless crystal with dimensions $0.20 \times 0.20 \times 0.20$ mm³ was selected for intensity measurements. The unit cell was monoclinic with the space group $P 2_1/c$. Lattice constants with $Z = 4$, $\rho_{\text{calcd}} = 1.406$ g cm⁻³, $\mu = 0.086$ mm⁻¹, $F(000) = 1128$, and $2\theta_{\text{max}} = 50.48^\circ$ were $a = 7.5568(5)$, $b = 32.8316(17)$ Å, $c = 10.9474(7)$ Å, $\alpha = 90^\circ$, $\beta = 109.928(3)^\circ$, $\gamma = 90^\circ$, and $V = 2553.4(3)$ Å³. A total of 31257 reflections were collected, of which 5821 reflections were independent ($R_{\text{int}} = 0.0293$). Structure was refined to final $R_1 = 0.0449$ for 5821 data [$I > 2\sigma(I)$] with 379 parameters and $wR_2 = 0.1279$ for all data, $GOF = 1.060$, and residual electron density max./min. = 0.400 and -0.229 e.Å⁻³. The ORTEP drawing is shown in **Figure S13**, and the crystal data and structure refinement are listed in **Table S1**. The data collection, cell refinement, and data reduction were conducted using the CrystalClear-SM Expert software^[1]. The structure was solved by direct methods using the program SHELXS-97^[2] and refined by full matrix least squares methods on F^2 using SHELXL-97^[3]. All the materials for publication were prepared using the Yadokari-XG 2009 software^[4]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were calculated geometrically and refined a riding model.

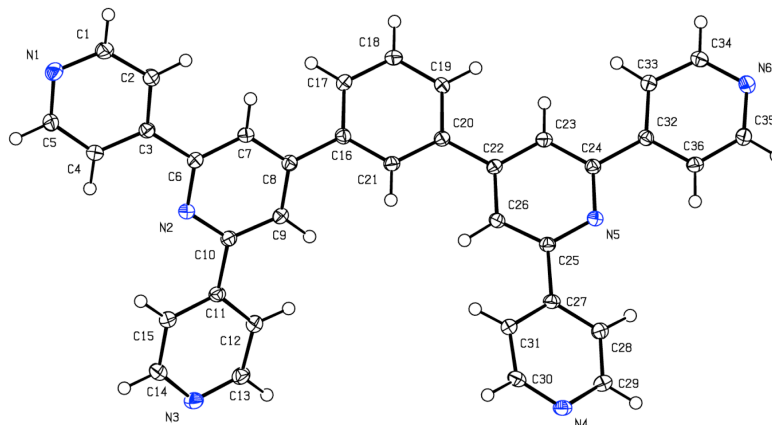


Figure S10. ORTEP diagrams of 4-TerPyB with thermal ellipsoids at 50% probability.

Table S1. Crystal data and structure refinement for 4-TerPyB.

Empirical formula	C ₃₆ H ₂₄ N ₆	
Formula weight	540.61	
Temperature	93 K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ /c	
Unit cell dimensions	<i>a</i> = 7.5568(5) Å	<i>α</i> = 90°
	<i>b</i> = 32.8316(17) Å	<i>β</i> = 109.928(3)°
	<i>c</i> = 10.9474(7) Å	<i>γ</i> = 90°
Volume	2553.4(3) Å ³	
<i>Z</i>	4	
Density (calculated)	1.406 g/cm ³	
Absorption coefficient	0.086 mm ⁻¹	
<i>F</i> (000)	1128	
Crystal size	0.200 × 0.200 × 0.200 mm ³	
Theta range for data collection	3.175 to 27.479°	
Index ranges	−9 ≤ <i>h</i> ≤ 9, −42 ≤ <i>k</i> ≤ 42, −14 ≤ <i>l</i> ≤ 14	
Reflections collected	31257	
Independent reflections	5821 [<i>R</i> (int) = 0.0293]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.925	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	5821 / 0 / 379	
Goodness-of-fit on <i>F</i> ²	1.060	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0449, <i>wR</i> ₂ = 0.1237	
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0488, <i>wR</i> ₂ = 0.1279	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.400 and −0.229 e.Å ⁻³	

3. TGA analysis

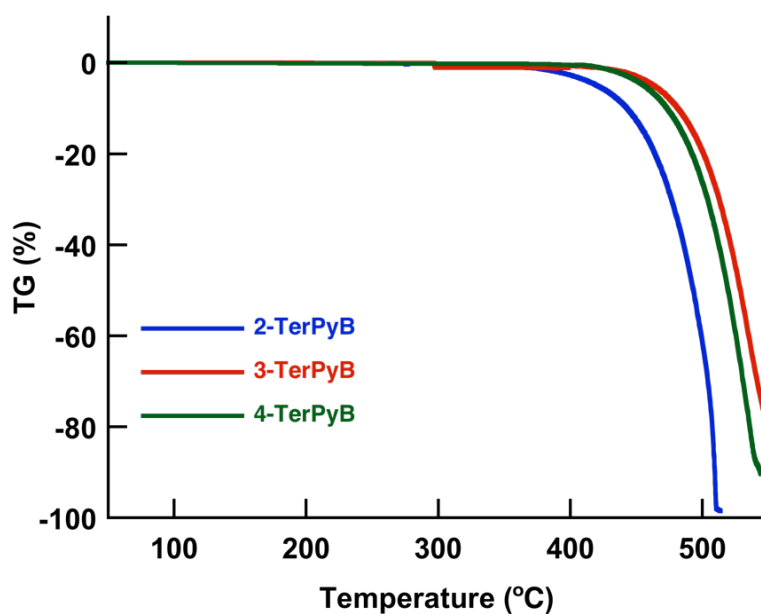


Figure S11. TGA measurement for TerPyBs. The heating rate is 10°C/min under N₂.

4. Optical properties

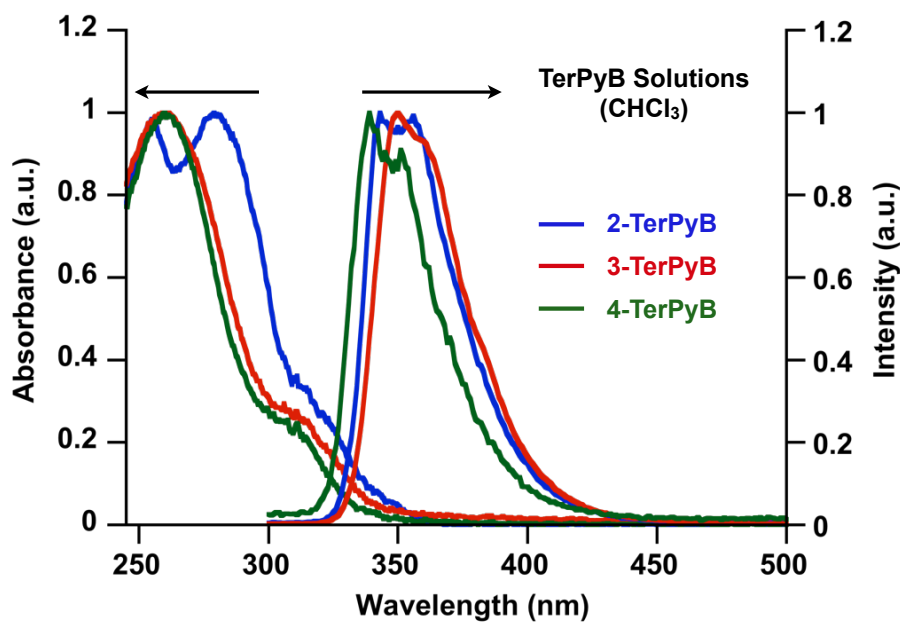


Figure S12. UV-vis, PL spectra of TerPyB in chloroform solution.

5. ^1H NMR analysis of B3PyPB and 3-TerPyB

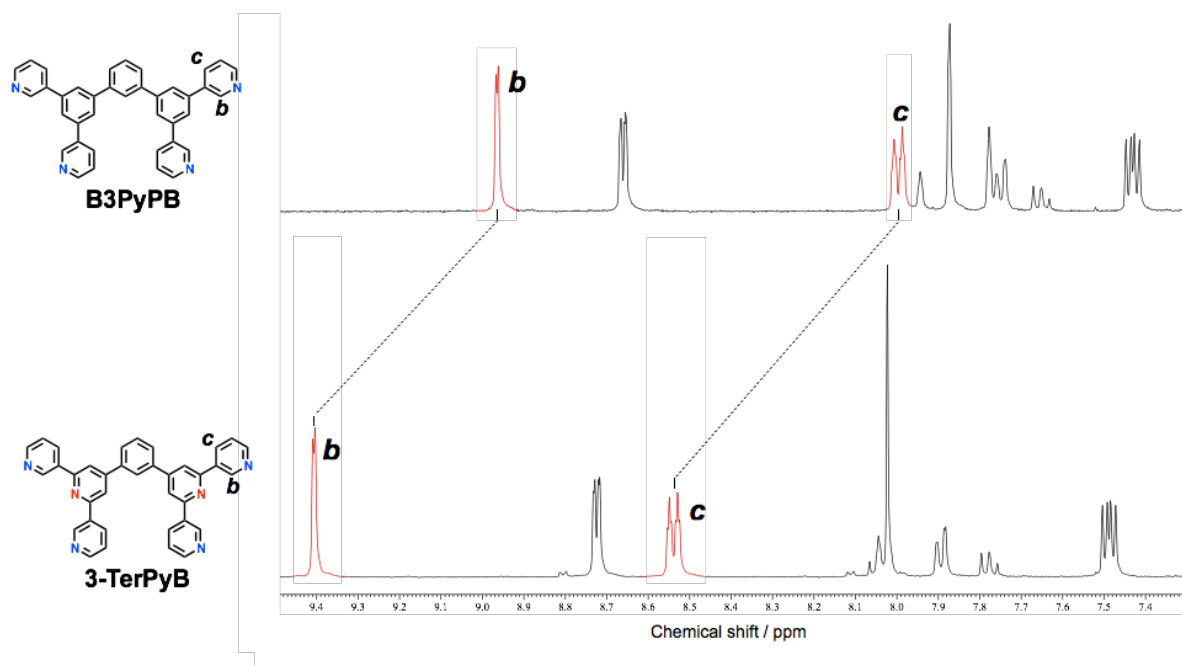


Figure S13. ^1H NMR spectra of B3PyPB and 3-TerPyB in CDCl_3 . The two protons (proton *b* and *c*), which could interact with N atoms of core pyridines were highlighted with red line. The both protons of 3-TerPyB appeared further downfield than those of B3PyPB in CDCl_3 solution. One possible reason is that 3-TerPyB forms intramolecular H-bonds.

6. OLEDs

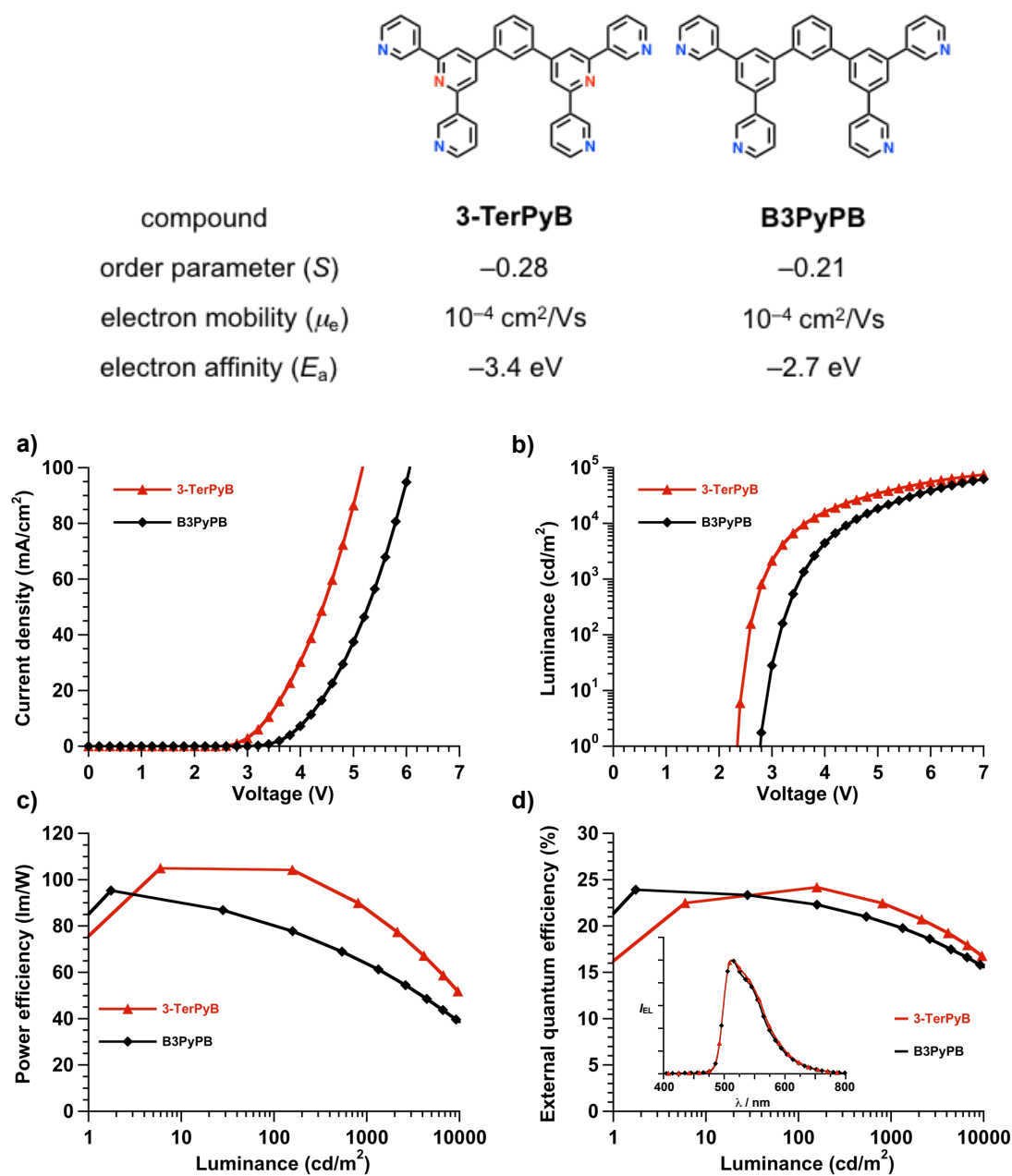


Figure S14. Device performance of the green organic LEDs: a) Current density–voltage characteristics. b) Luminance–voltage characteristics. c) Power efficiency–luminance characteristics. d) External quantum efficiency–luminance characteristics. The inset shows EL spectra at 1 mA.

7. References

- [1] CrystalClear-SM Expart: Rigaku Corporation, Tokyo, Japan, **2011**.
- [2] SHELXS"97: Sheldrick, G. M. Program for the Solution of Crystal Structures; *Acta Crystallogr. A* **2008**, *64*, 112–122.
- [3] SHELXL"97: Sheldrick, G. M. Program for the Refinement of Crystal Structures; *Acta Crystallogr. A* **2008**, *64*, 112–122.
- [4] a) Yadokari"XG: Wakita, K. Software for crystal Structure Analyses, **2001**; b) Yadokari"XG**2009**: C. Kabuto, S. Akine, T. Nemoto, E. Kwon. Release of Software for Crystal Structure Analyses; *J. Cryst. Soc. Jpn.* **2009**, *51*, 218–224.