

Supporting Information

Synthesis and photo- and electroluminescence properties of 3,6-disubstituted phenanthrenes: alternative host material for blue fluorophores

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Experimental Section

General Information.

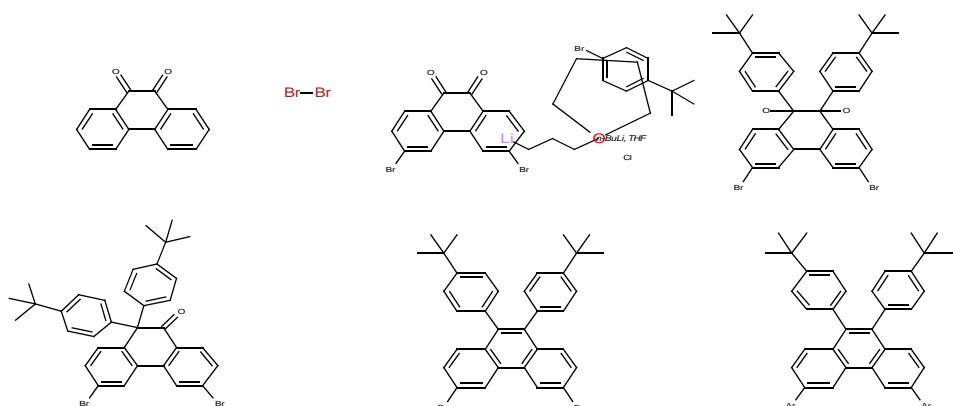
^1H and ^{13}C NMR spectra were carried out on a Bruker AV-400 MHz NMR spectrometer. Mass spectra were determined using a JMS-700 HRMS instrument. UV-Vis spectra were recorded on a Hitachi U-3300 model, while PL spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer. The TGA and DSC measurements were carried out using TA Instruments Q50 and Q20 at a speed of 20 and 10 °C/min under a nitrogen gas atmosphere, respectively. The PL quantum yields of the vacuum deposited films (30 nm) were determined by the integrating sphere method using a Labsphere SP-150M equipment.

The HOMO and LUMO levels were estimated from the oxidation potential ($E_{1/2}$) in CH_2Cl_2 and the reduction potential ($E_{1/2}$) in THF solution at 10^{-3} M obtained from the cyclic voltammetry (CV) measurement with Pt wire as the counter electrode, Pt/(Au/Hg) electrodes as working electrode. The potentials were measured against an Ag/Ag^+ ($\text{Ag}/0.01$ M AgNO_3) reference electrode. The final results were calibrated with the ferrocene/ferrocenium (Fc/Fc^+) couple. Under the assumption that the energy level of ferrocene/ferrocenium is 4.8 eV below vacuum, the HOMO and LUMO levels of phenanthrene derivatives were determined from the equation: $-(4.8 \text{ eV} + E_{1/2}$ (versus Fc/Fc^+)). The energy gap (E_g) was estimated by subtracting the LUMO energy level from the HOMO energy level.

The molecular geometry optimizations and electronic properties were computed by carrying out the Gaussian 03 program with density functional theory (DFT) and time-dependent DFT (TDDFT) calculations, in which the Becke's three-parameter functional combined with Lee, Yang, and Parr's correlation functional (B3LYP) hybrid exchange-correlation functional with the 6-31G* basic set were used. The molecular orbitals were visualized on the Gaussview 4.1 software.

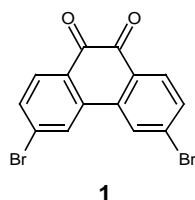
The current density-voltage-luminance measurements were recorded on a Keithley model 2400 source meter and a Newport 1835-C optical meter equipped with a Newport 818-ST silicon photodiode. The EL spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer.

Synthesis of phenanthrene derivatives:

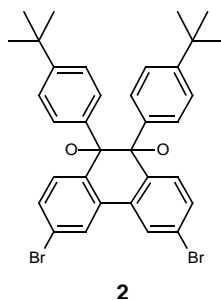


Procedures for the synthesis of phenanthrene derivatives¹:

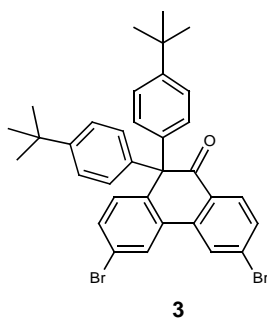
The reaction involves the addition of two 4-*tert*-butylphenyl lithium to dibromodione **1** to give diol **2** followed by a skeleton rearrangement to provide ketone **3**. Reduction with LiAlH₄ and the subsequent dehydration led to product **4**. Further treatment of phenanthrene derivatives with phenyl-, 2-naphthyl- and 1-pyrenylboronic acid under Suzuki coupling conditions afforded TPhP, TNaP and TPyP, respectively.



3,6-Dibromophenanthrene-9,10-dione (**1**): Phenanthrenequinone (1.0 g, 4.80 mmol), Br₂ (1.0 mL, 19.7 mmol), and benzoyl peroxide (100 mg) were added to nitrobenzene (15.0 mL). The mixture was exposed to a 300 W tungsten lamp for 1 h. After 30 min, the mixture was cooled to room temperature and filtered. The crude product was washed with MeOH and Et₂O, and dried under vacuum to give **1** (1.47 g, 84%). ¹H NMR (400 MHz, CDCl₃): δ 8.10 (d, *J* = 1.6 Hz, 2H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.65 (dd, *J* = 7.2 Hz, *J* = 1.6, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 178.2, 153.9, 133.4, 132.1, 129.9, 127.4. HRMS (*m/z*): [*M*⁺] calcd. for C₁₄H₆Br₂O₂, 363.8735; found 363.87130.

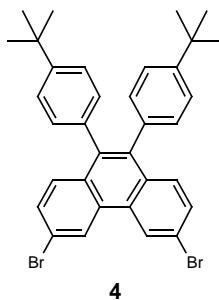


3,6-Dibromo-9,10-bis(4-tert-butylphenyl)-9,10-dihydrophenanthrene-9,10-diol (2): *n*-Butyllithium in hexane (2.5 M, 16.8 mL) was added slowly under nitrogen to a solution of 1-bromo-4-*tert*-butylbenzene (8.52 g, 40.0 mmole) in anhydrous THF (60 mL) at -78 °C. The mixture was stirred for 30 min at -78 °C and then a solution of 3,6-dibromophenanthrene-9,10-dione (3.66 g, 10.0 mmole) in anhydrous THF (100 mL) was added dropwise. This mixture was cooled to room temperature and stirred overnight. Thereafter, the reaction mixture was quenched with aqueous HCl (2.0 M, 10 mL) and extracted with CH₂Cl₂ (2 × 50 mL). The collected organic phase was dried over MgSO₄ and concentrated under reduced pressure. The residue was purified through a silica gel column (CH₂Cl₂/*n*-Hexane = 1:4) to give **1** (2.85 g, 45%). ¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, *J* = 1.6 Hz, 2H), 7.39-7.34 (m, 4H), 7.29-7.26 (m, 4H), 7.21-7.19 (m, 4H), 2.26 (s, 2H), 1.21 (s, 18H). ¹³C NMR (100 MHz, CDCl₃): δ 150.8, 141.0, 136.2, 134.3, 132.4, 129.0, 127.3, 126.0, 125.4, 122.8, 80.4, 34.4, 31.1. HRMS (*m/z*): [*M*⁺] calcd. for C₃₄H₃₄Br₂O₂ 632.0926; found 632.0923.

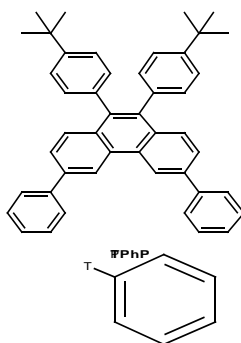


3,6-Dibromo-10,10-bis(4-tert-butylphenyl)phenanthren-9(10H)-one (3): A solution of HCl (12 M, 11.0 mL) in AcOH (25 mL) was added dropwise to a solution of **1** (16.0 g, 25.2 mmol) in AcOH (75 mL). The mixture was heated under reflux for 30 min and was then poured into cold water. The mixture was extracted with CH₂Cl₂ (100 mL). The combined organic layer was washed with H₂O (100 mL × 2), saturated NaHCO₃ (100 mL × 2) aqueous solution and dried with anhydrous MgSO₄. The crude product was purified through a silica gel column (CH₂Cl₂/*n*-hexane = 1:6) to give **2** (13.6 g, 87%). ¹H NMR (400 MHz, CD₂Cl₂): δ 8.11 (s, 1H), 8.06 (s, 1H), 7.81 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.6 Hz,

4H), 6.81 (d, $J = 7.6$ Hz, 4H), 6.67 (d, $J = 8.8$ Hz, 1H), 1.28 (s, 18H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 198.7, 150.4, 141.0, 137.9, 136.9, 134.0, 132.1, 132.0, 131.8, 130.0, 129.6, 129.4, 128.9, 127.1, 126.1, 125.2, 122.1, 67.1, 34.4, 31.3. HRMS (m/z): [M^+] calcd. for $\text{C}_{34}\text{H}_{32}\text{Br}_2\text{O}$, 614.0820; found 614.0812.

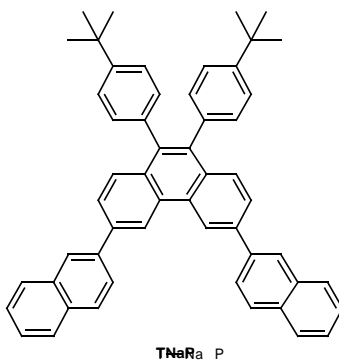


3,6-Dibromo-9,10-bis(4-tert-butylphenyl)phenanthrene (4): Compound **2** (13.6 g, 22.06 mmol) was dissolved in anhydrous THF (100 mL) and degassed with nitrogen. To the mixture was added LiAlH_4 (1.47 g, 38.8 mmol) and the mixture was refluxed under nitrogen for 2 h, cooled to room temperature, quenched with dilute HCl (2.0M, 10 mL) in an ice bath and extracted with CH_2Cl_2 (100 mL \times 2). The collected organic layer was dried over MgSO_4 and concentrated under reduced pressure. Then the residue was dissolved in an acetic acid solution (200 mL) and refluxed for 2 h. The reaction mixture was cooled and then extracted with CH_2Cl_2 (100 mL). The organic layer was washed with H_2O (100 mL \times 2), saturated NaHCO_3 (100 mL \times 2) aqueous solution and dried with anhydrous MgSO_4 . The crude product was purified by using column chromatography with *n*-hexane as the eluent to afford **3** (12.5 g, 94%). ^1H NMR (400 MHz, CDCl_3): δ 8.80 (s, 2H), 7.56 (s, 4H), 7.18 (d, $J = 8.0$ Hz, 4H), 6.95 (d, $J = 8.0$ Hz, 4H), 1.24 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3): δ 149.5, 137.7, 135.6, 130.9, 130.5, 130.4, 130.2, 129.8, 125.3, 124.3, 121.1, 34.4, 31.3. HRMS (m/z): [M^+] calcd. for $\text{C}_{34}\text{H}_{32}\text{Br}_2$, 598.0871; found 598.0863.

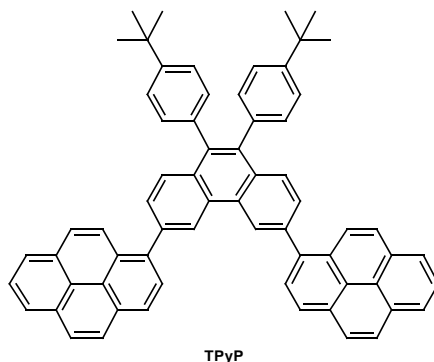


3,6-Diphenyl-9,10-bis(4-tert-butylphenyl)phenanthrene (TPhP): Phenylboronic acid (1.35 g, 4.50 mmol), 3,6-dibromo-9,10-bis(4-tert-butylphenyl)phenanthrene (**3**) (1.00

g, 1.84 mmol), aqueous K_2CO_3 (2.0 M, 10 mL), tetrakis (triphenylphosphine)palladium (*ca.* 213 mg), and toluene (30 mL) was mixed in a flask and refluxed under nitrogen for 24 h. The reaction mixture was cooled to room temperature and then extracted with CH_2Cl_2 (100 mL \times 2). The combined organic layers were washed with H_2O (100 mL \times 2) and dried with anhydrous $MgSO_4$. The crude product was purified through a silica gel column (CH_2Cl_2/n -hexane, 1:20) to afford TPhP as a white powder (0.862 g, 78%). 1H NMR (400 MHz, $CDCl_3$): δ 9.05 (d, $J = 1.2$ Hz, 2H), 7.81-7.79 (m, 6H), 7.74 (dd, $J = 8.4$, $J = 1.6$ Hz, 2H), 7.53 (t, $J = 7.6$ Hz, 4H), 7.41 (t, $J = 7.2$ Hz, 2H), 7.22 (d, $J = 8.0$ Hz, 4H), 7.06 (d, $J = 8.4$ Hz, 4H), 1.28 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 141.5, 139.1, 137.5, 136.4, 131.4, 130.7, 130.3, 128.9, 128.6, 127.7, 127.4, 126.0, 124.2, 121.0, 34.4, 31.3. HRMS (m/z): $[M^+]$ calcd. for $C_{46}H_{42}$, 594.3287; found, 594.3276. Anal. calcd for $C_{46}H_{42}$: C, 92.88; H, 7.12; found: C, 92.82; H, 7.18.



3,6-Di(naphthalen-2-yl)-9,10-bis(4-tert-butylphenyl)phenanthrene (TNaP): Prepared as a white solid (0.463 g, 80%) according to a procedure similar to the above one by using 2-naphthylboronic acid as one of the reagents. 1H NMR (400 MHz, $CDCl_3$): δ 9.21 (d, $J = 0.8$ Hz, 2H), 8.25 (s, 2H), 8.01-7.95 (m, 6H), 7.92-7.84 (m, 6H), 7.55- 7.48 (m, 4H), 7.24 (d, $J = 8.4$ Hz, 4H), 7.09 (d, $J = 8.4$ Hz, 4H), 1.29 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 139.0, 138.9, 137.6, 136.5, 133.8, 132.7, 131.5, 130.8, 130.4, 128.7, 128.6, 128.3, 127.7, 126.4, 126.3, 126.3, 126.1, 126.0, 124.2, 121.3, 34.4, 31.3. HRMS (m/z): $[M^+]$ calcd. for $C_{54}H_{46}$, 694.3600; found, 694.3604. Anal. calcd for $C_{54}H_{46}$: C, 93.33; H, 6.67; found: C, 93.16; H, 6.77.



3,6-Di(pyrene-1-yl)-9,10-bis(4-tert-butylphenyl)phenanthrene (TPyP): Prepared as a white solid (0.518 g, 74%) according to procedure similar to the above one by using 1-pyreneboronic acid as one of the reagents. ^1H NMR (400 MHz, CDCl_3): δ 9.08 (d, $J = 1.6$ Hz, 2H), 8.26 (d, $J = 9.2$ Hz, 2H), 8.21 (d, $J = 8.0$ Hz, 2H), 8.15 (d, $J = 8.0$ Hz, 2H), 8.10 (d, $J = 8.0$ Hz, 4H), 8.06 (s, 4H), 7.99-7.95 (m, 6H), 7.82 (dd, $J = 8.2$, $J = 1.4$ Hz, 2H), 7.29 (d, $J = 8.4$ Hz, 4H), 7.20 (d, $J = 8.4$ Hz, 4H), 1.30 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3): δ 149.2, 139.2, 137.8, 136.5, 131.5, 131.4, 130.9, 130.8, 130.7, 130.0, 129.4, 128.7, 128.0, 127.9, 127.7, 127.5, 127.4, 126.0, 125.3, 125.1, 125.0, 124.8, 124.8, 124.7, 124.5, 124.3, 34.5, 31.3. HRMS (m/z): $[\text{M}^+]$ calcd. for $\text{C}_{66}\text{H}_{50}$, 842.3913; found, 842.3926. Anal. calcd for $\text{C}_{66}\text{H}_{50}$: C, 94.02; H, 5.98; found: C, 94.01; H, 5.96.

References:

- (a) H. J. Kim, E. Lee, H. S. Park and M. Lee, *J. Am. Chem. Soc.*, 2007, **129**, 10994; (b) Y. Shirai, A. J. Osgood, Y. Zhao, Y. Yao, L. Saudan, H. Yang, Y. H. Chiu, L. B. Alemany, T. Sasaki, J. F. Morin, J. M. Guerrero, K. F. Kelly and J. M. Tour. *J. Am. Chem. Soc.*, 2006, **128**, 4854; (c) B. He, H. Tian, Y. Geng, F. Wang and K. Müllen, *Org. Lett.*, 2008, **10**, 773; (d) H. Kurata, Y. Takehara, T. Kawase, and M. Oda, *Chemistry Letters*, 2003, **32**, 538; (e) Y. H. Lai, *J. Chem. Soc. Perkin Trans. II*, 1986, 1667.

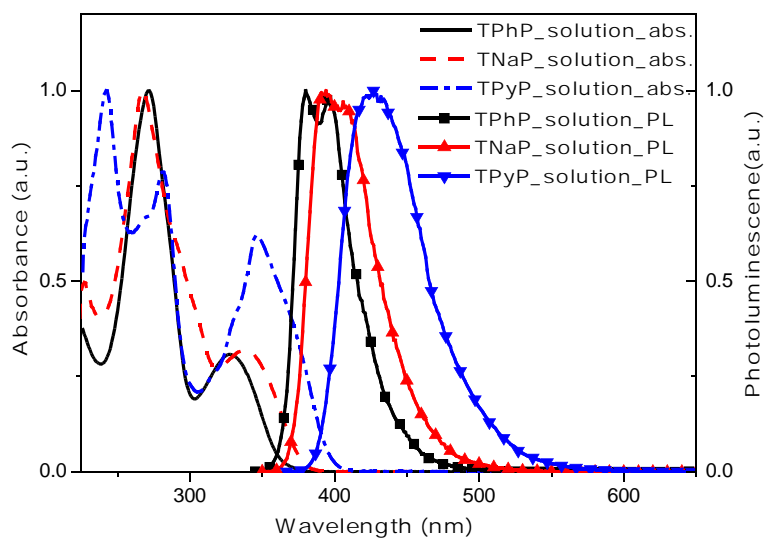


Fig S1. Absorption and emission spectra of TPhP, TNaP and TPyP in dichloromethane at concentration = 1.0×10^{-5} M.

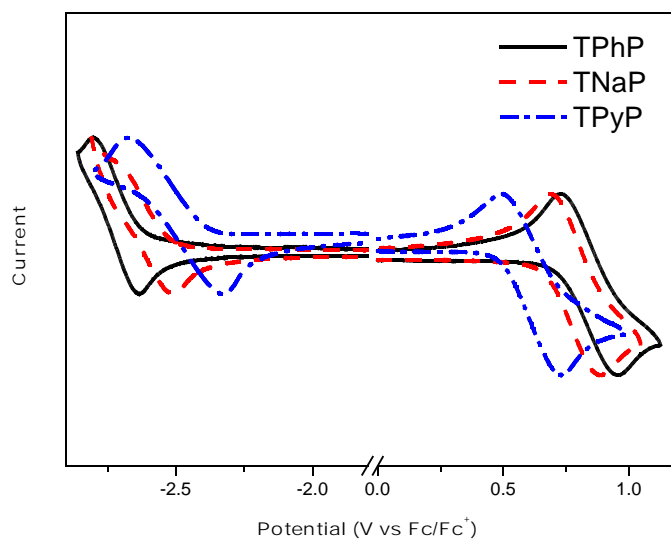


Fig S2. Cyclic voltammograms of TPhP, TNaP and TPyP.

Table S1. The $E_{1/2}^{ox}$ and $E_{1/2}^{re}$ (versus Fc/Fc⁺) of phenanthrene derivatives.

Compound	$E_{1/2}^{ox}$ (eV)	$E_{1/2}^{re}$ (eV)
TPhP	1.0	-2.7
TNaP	0.9	-2.6
TPyP	0.8	-2.5

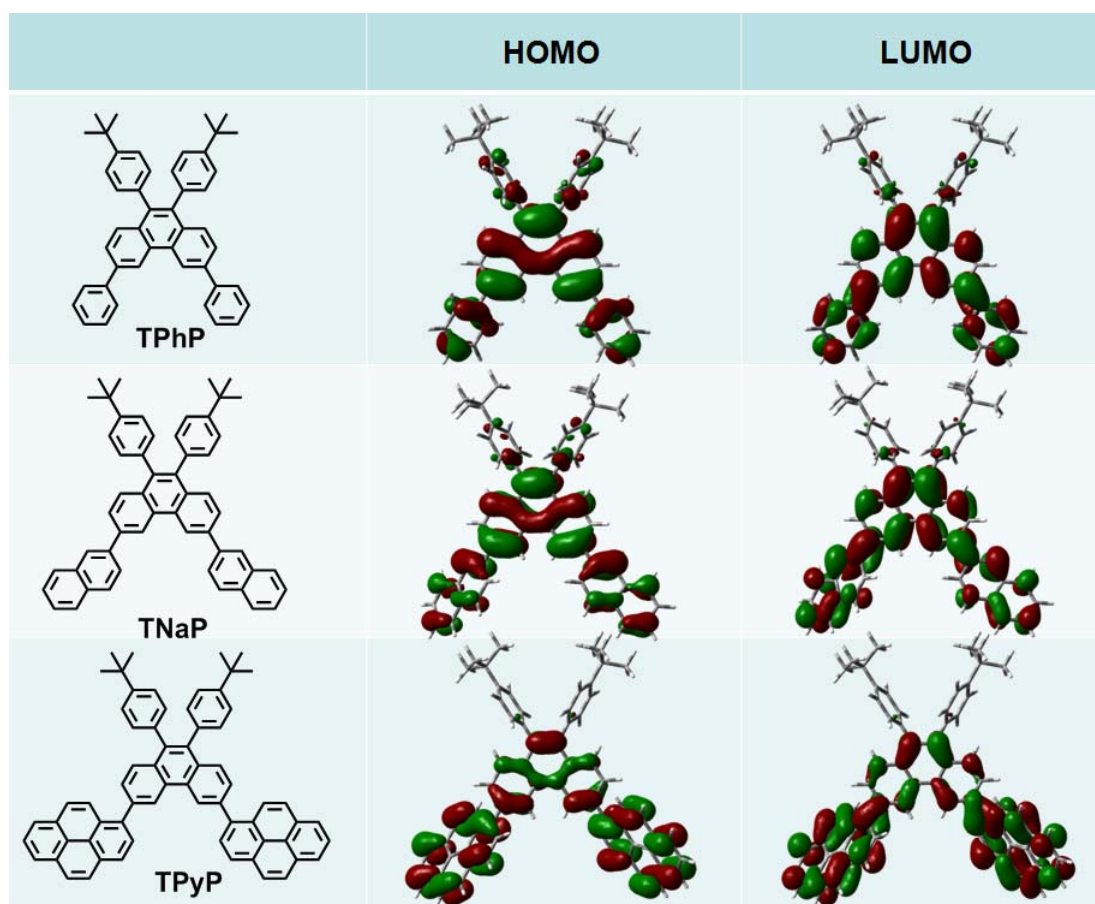


Fig S3. Calculated HOMO and LUMO density maps of TPhP, TNaP and TPyP.

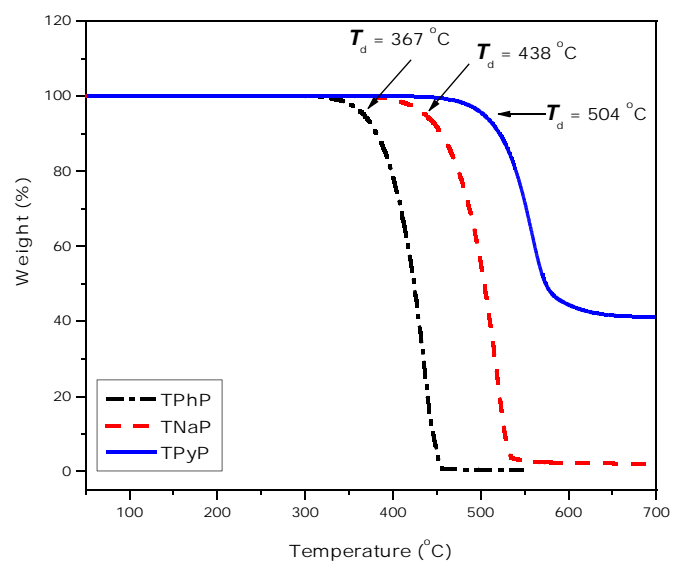


Fig S4. TGA thermograms of TPhP, TNaP and TPyP.

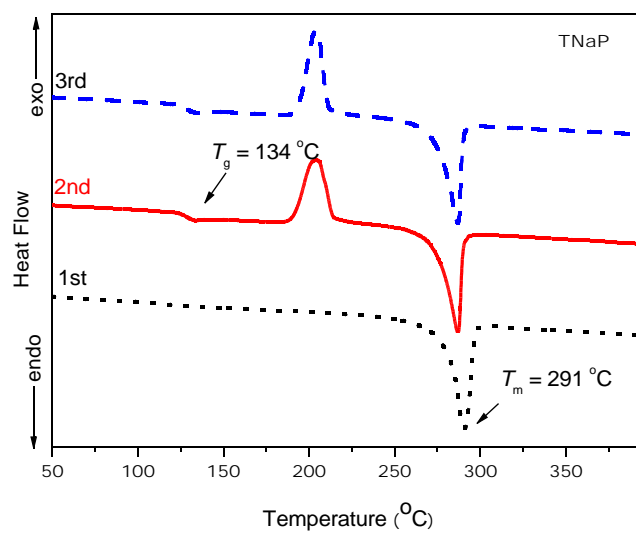


Fig S5. DSC thermograms of TNaP.

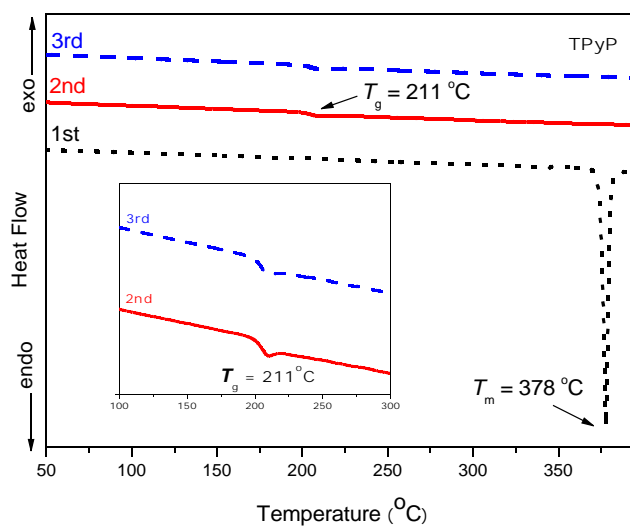


Fig S6. DSC thermograms of TPyP.

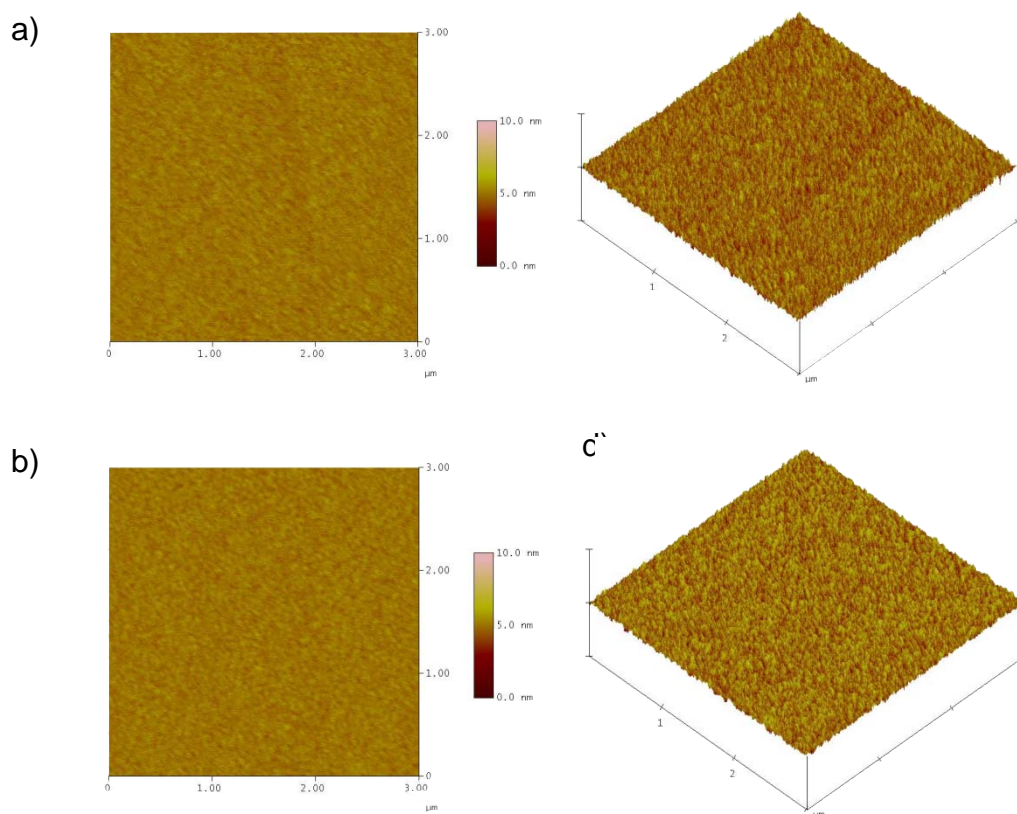


Fig S7. AFM topographic images (top and angled views) of TPyP doped with 5% BCzVBi. (a) TPyP without annealing; (b) after annealing at 110 °C for 18 h under one nitrogen atmosphere. (the root-mean-square roughness values of (a) and (b) are 0.237 and 0.220, respectively).

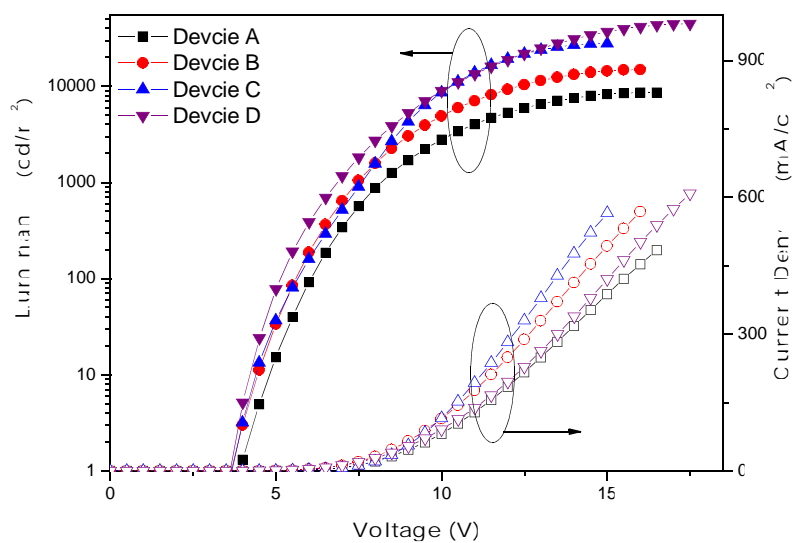


Fig S8. The voltage versus luminance and current density curves of devices A-D.

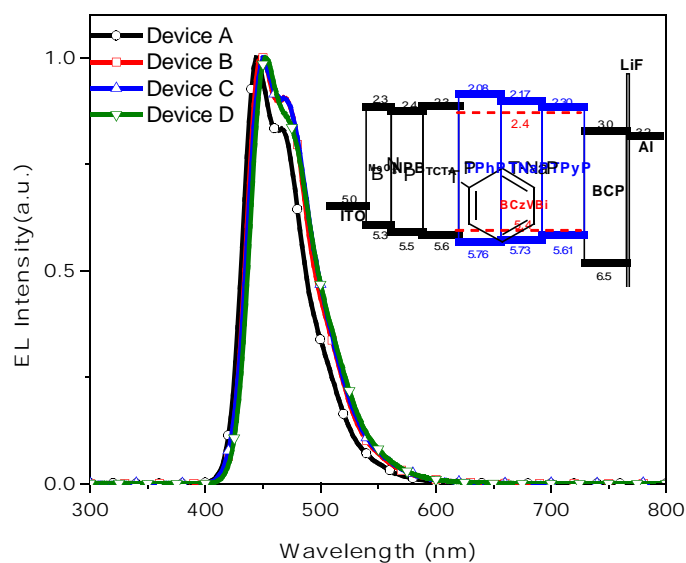


Fig S9. The EL spectra of devices A-D. Inset: Schematic energy diagram of the materials in the devices.

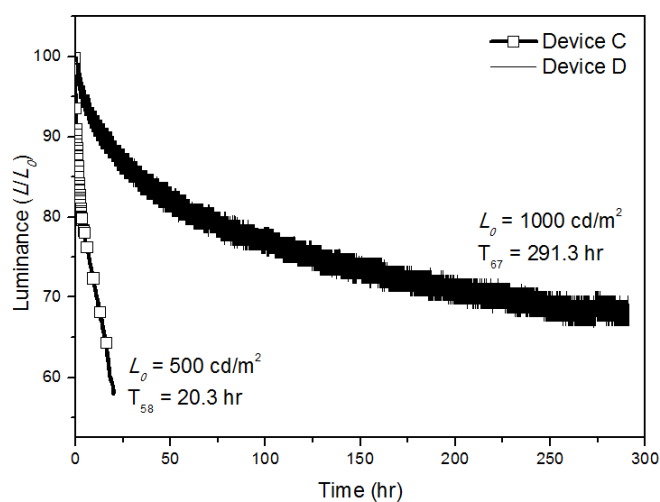


Fig S10. The L/L_0 versus operation time of devices C and D, where L is luminance and L_0 is the luminance at time = 0.

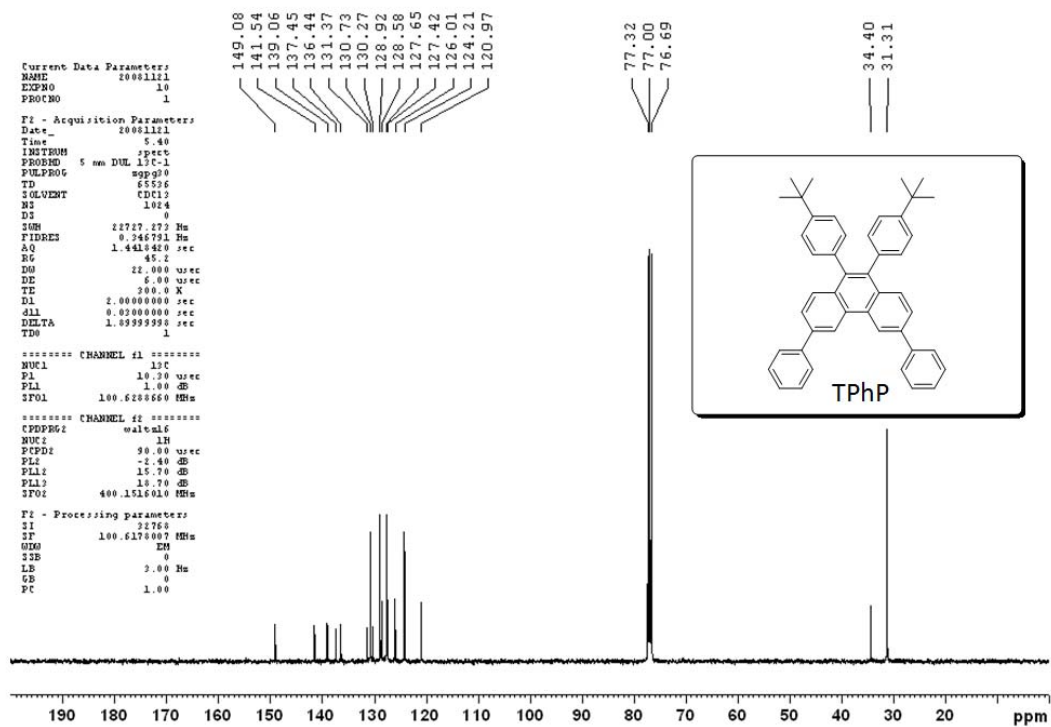
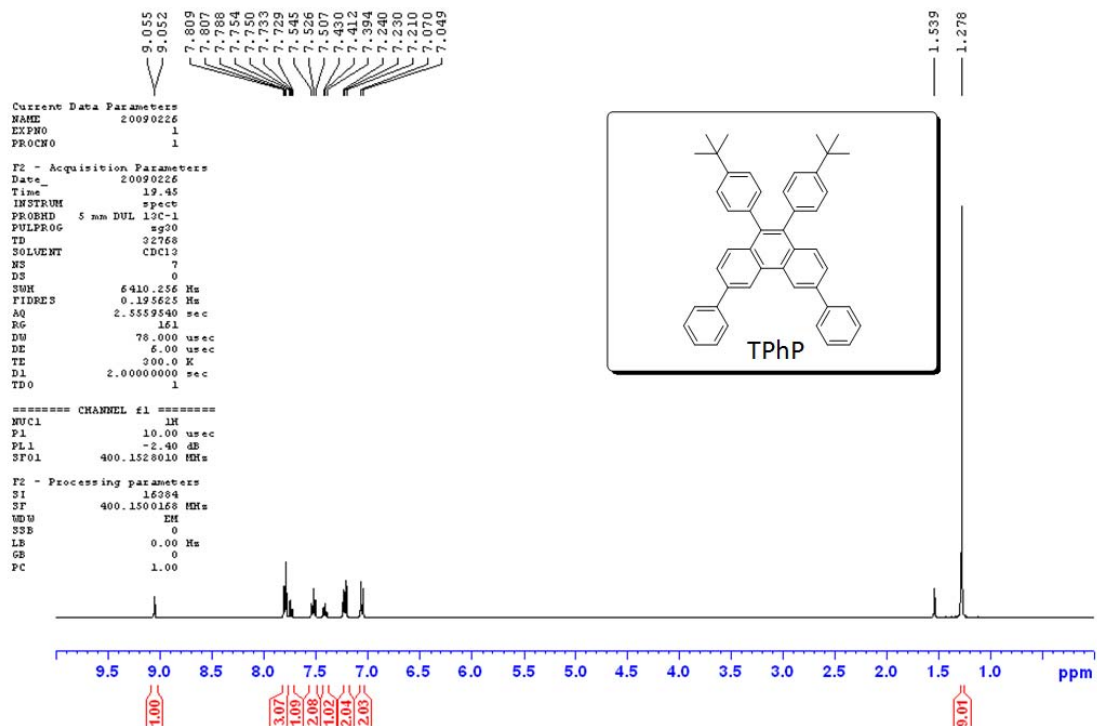


Fig S11. ¹H and ¹³C NMR spectra of TPhP.

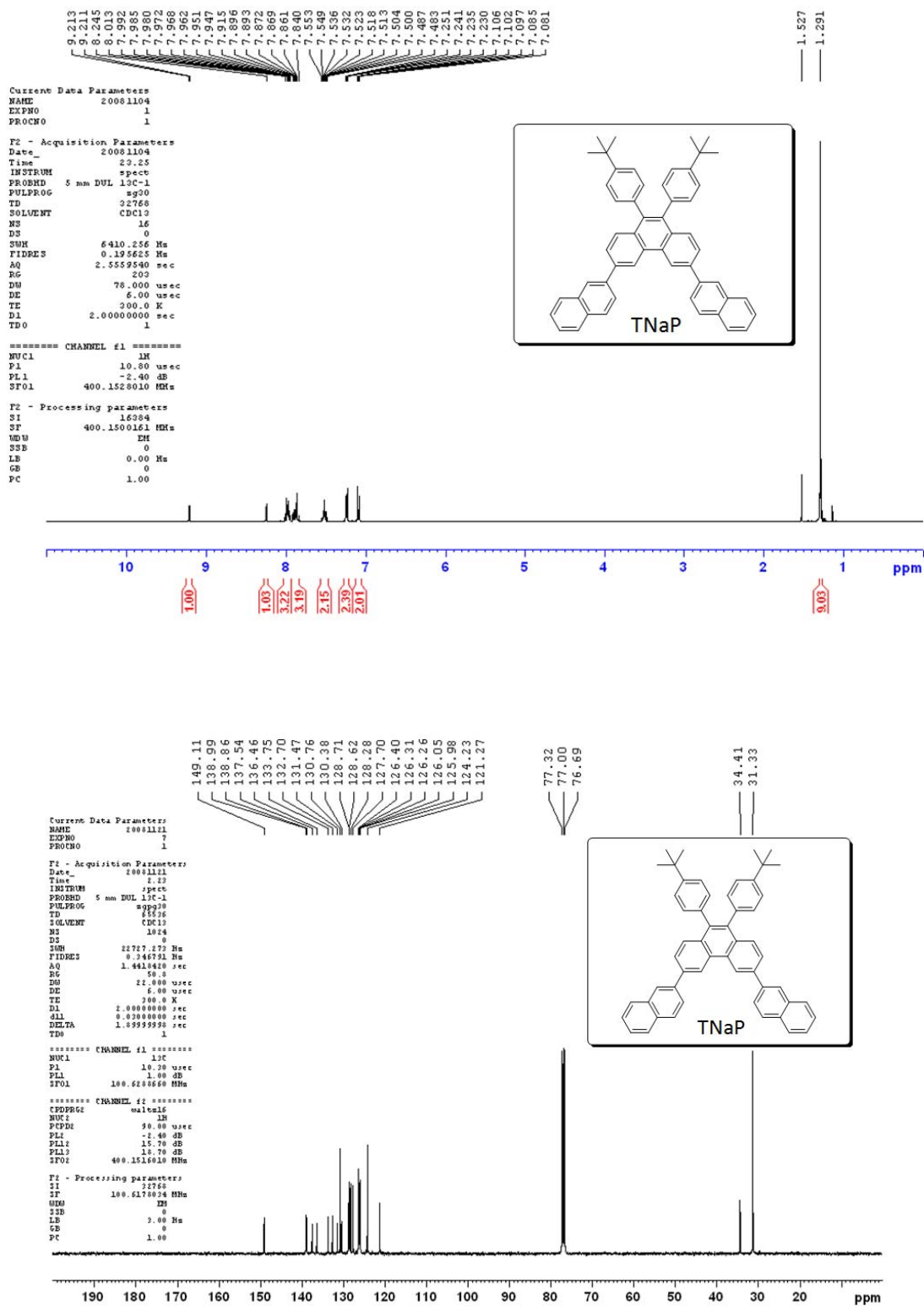


Fig S12. ¹H and ¹³C NMR spectra of TNaP.

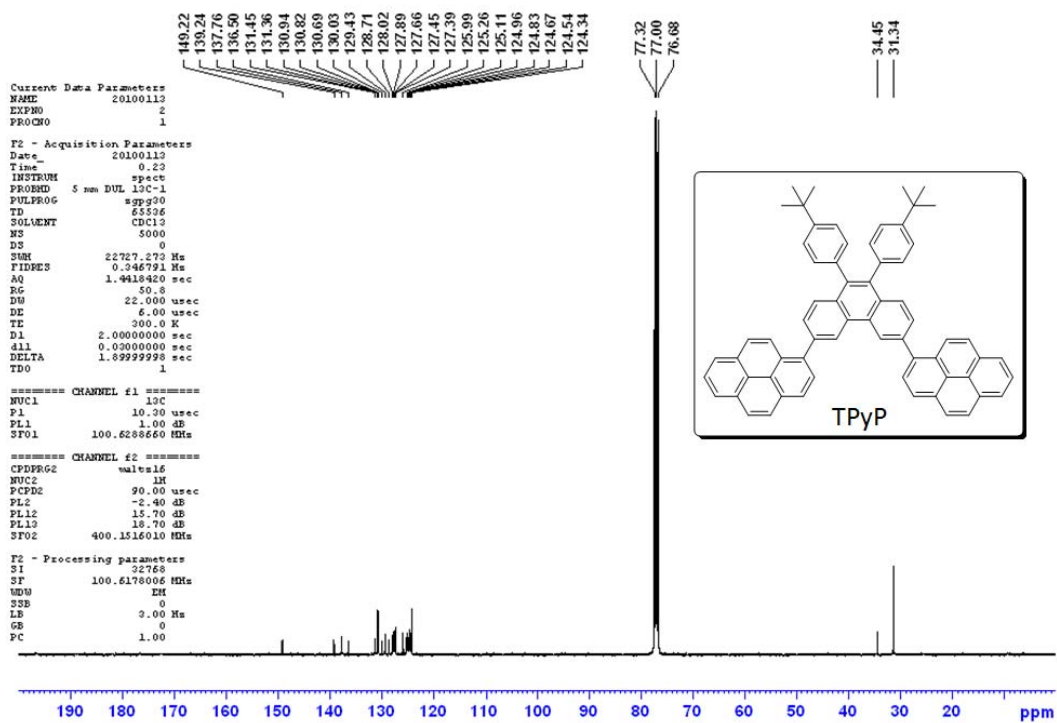
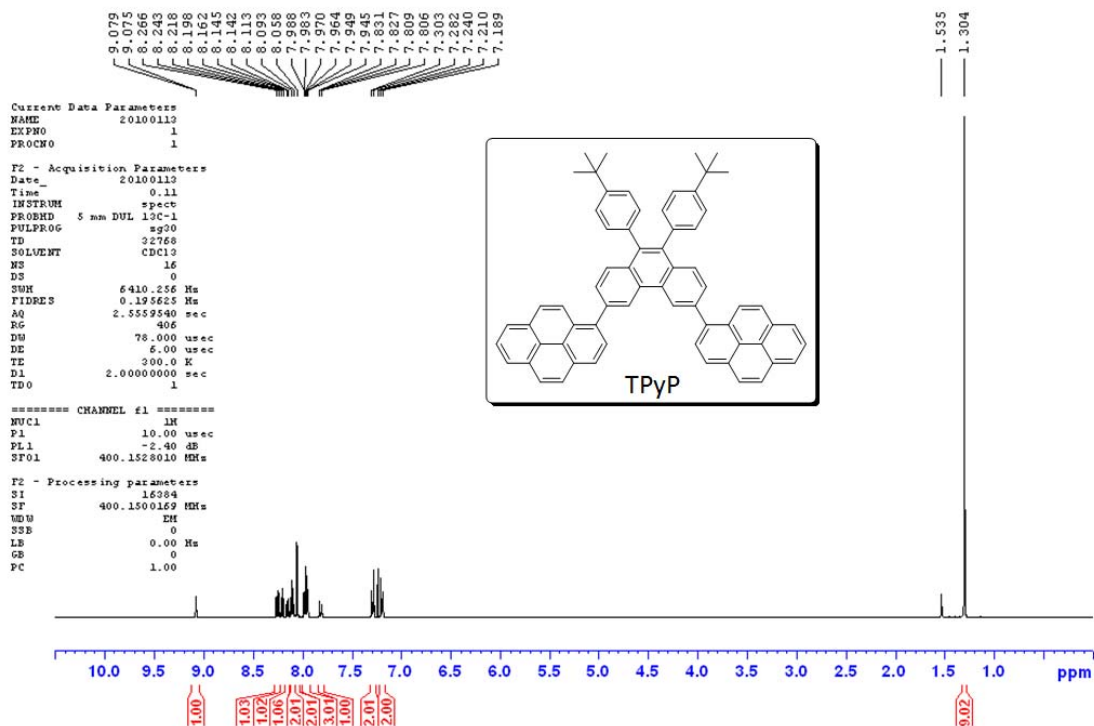


Fig S13. ¹H and ¹³C NMR spectra of TPyP.