SUPPORTING INFORMATION

Benzophenones as Generic Host Materials for Phosphorescent Organic Light-Emitting Diodes (PhOLEDs)

Samik Jhulki,[a] Saona Seth,[a] Avijit Ghosh,[b] Tahsin J. Chow,[b],* and Jarugu Narasimha Moorthy[a],*

[a]*Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India*
[b]*Institute of Chemistry, Academia Sinica, Taipei, Taiwan 115, Republic of China*

Email: chowtj@gate.sinica.edu.tw; moorthy@iitk.ac.in

Table of Contents

EXPERIMENTAL SECTION

General Aspects. ^{1}H NMR spectra were recorded on JEOL (400/500 MHz) spectrometers in $CDCl_3$ as a solvent. ^{13}C NMR spectra were recorded on JEOL-Lambda (100/125 MHz) spectrometers with complete proton decoupling. ESI and EI mass spectra analyses were carried out on Waters ^{Q}TOF and GCT premier mass spectrometers, respectively. IR spectra were recorded on an Agilent FT-IR spectrophotometer. X-ray powder patterns were recorded on a Rigaku X-ray diffractometer. The TGA and DSC measurements were carried out using SDT Q600 instruments at a scan rate of 10 ºC/min under a nitrogen gas atmosphere. UV-Vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Fluorescence and phosphorescence measurements were carried out using FluoroMax-4, FM4-3000 spectrofluorometer, Horiba Scientific. UPS spectra were recorded in photoelectron spectrometer (AC2 instrument, Riken Keiki). Solvents were distilled prior to use and HPLC grade solvents used for UV-vis and PL measurements were procured from commercial sources (Merck). Column chromatography was conducted with silica-gel of 100-200µ mesh. All the reactions were monitored by analytical thin layer chromatography (TLC) using commercial aluminum sheets pre-coated with silica gel (Merck).

Materials. The starting materials, namely, 1,3,5-triphenylmesitylene[1] and 3,3',5,5'-tetraphenylbimesitylene[2] were synthesized following literature-reported procedures. **BP2-4** were synthesized by benzoylation reaction, vide infra. ITO-coated glass slides of thickness 0.7 mm and resistance 11 Ω, and materials such as NPB, *m*CP, CBP, FIrpic, $Ir(ppy)_3$, PO-01, $Ir(btp)_2acac$, TmPyPB, BCP, Alq_3, LiF and Al, which were employed for device fabrications, were procured from commercial sources.

Device Fabrication. Fabrication of the devices was carried out following previously-reported procedure.[3-4]

Synthesis and Characterization Data.

Synthesis of 1,4-diphenyldurene. A mixture of toluene (15 mL), EtOH (10 mL) and water (5 mL) contained in a two-necked round bottom flask was degassed by bubbling N_2 for 10 min. Subsequently, 1,4-dibromodurene (1.0 g, 3.42 mmol), phenylboronic acid (1.25 g, 10.27 mmol), NaOH (0.54 g, 1.37 mmol) and $Pd(PPh_3)_4$, (0.59 g, 0.51 mmol) were added to the flask. The resulting suspension was heated at 110 °C under N_2 atmosphere during which the reaction mixture becomes clear pale yellow solution. The progress of the reaction was monitored by TLC analysis. At the end of for 24 h, the reaction was judged to be complete. Subsequently, toluene and EtOH were removed in vacuo and the residue was extracted with chloroform three times. The combined organic extract was dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo to obtain the crude product, which was purified by silica-gel column chromatography to afford the 1,4-diphenyldurene as a colorless solid, yield 0.65 g (64 %); IR (KBr) cm^{-1} 3056, 3019, 2921, 1598, 1415, 1378; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.97 (s, 12H), 7.20-7.22 (m, 4H), 7.34-7.37 (m, 2H), 7.43-7.46 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.1, 126.3, 128.3, 129.5, 131.8, 141.2, 142.8; EI-MS$^+$ m/z $[M]^+$ Calcd for $C_{22}H_{22}$ 286.1721, found 286.1719.

Synthesis of BP2. Anhydrous $AlCl_3$ (4.66 g, 34.9 mmol) and 1,4-diphenyldurene (1.0 g, 3.49 mmol) were added to 40 mL of CS_2 taken in a 2-necked round bottom flask. The resulting mixture was cooled to 0 °C and benzoyl chloride (3.65 mL, 31.4 mmol) was introduced slowly into the flask. The resulting dark-brown mixture was warmed to room temperature over a period of 30 minutes. Subsequently, it was heated at reflux for 10 h. At the end of this period, the reaction mixture was poured into crushed ice and extracted three times with chloroform. The combined organic mixture was dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo to obtain the crude product, which was purified by column chromatography to obtain **BP2** as a colorless solid, yield 1.50 g (87%). IR (KBr) cm^{-1} 2994, 2919, 1648, 1600, 1445, 1401, 1311; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.99 (s, 12H), 7.32 (d, J = 8.55 Hz, 4H), 7.51-7.55 (m, 4H), 7.61-7.64 (m, 2H), 7.89 (d, J = 7.30 Hz, 4H), 7.93 (d, J = 7.95 Hz, 4H); ^{13}C NMR ($CDCl_3$, 125

MHz) δ 18.1, 128.3, 129.5, 130.0, 130.4, 131.7, 132.3, 135.8, 137.7, 140.6, 147.4, 196.5; ESI-MS$^+$ m/z [M+H]$^+$ Calcd for $C_{36}H_{30}O_2$ 494.2245, found 494.2244.

Synthesis of BP3. A similar procedure described for the synthesis of **BP2** was followed to synthesize **BP3**. Reaction between anhydrous $AlCl_3$ (1.91 g, 14.35 mmol) and 1,3,5-triphenylmesitylene (0.50 g, 1.43 mmol) and benzoyl chloride (1.5 mL) in 20 mL of CS_2 for 7 h afforded, subsequent to purification by column chromatography, **BP3** as a colorless solid, yield 0.86 g (93 %). IR (KBr) cm^{-1} 3030, 2919, 1664, 1602, 1446, 1398, 1312; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.77 (s, 9H), 7.37 (d, J = 8.00 Hz, 6H), 7.50-7.53 (m, 6H), 7.60-7.62 (m, 3H), 7.86 (d, J = 6.90 Hz, 6H), 7.92 (d, J = 8.60 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.5, 128.3, 129.4, 130.0, 130.6, 132.4, 133.0, 136.0, 137.6, 139.2, 146.3, 196.5; ESI-MS$^+$ m/z [M+H]$^+$ Calcd for $C_{48}H_{37}O_3$ 661.2742, found 661.2744.

Synthesis of BP4. Synthesis of **BP4** was carried out following reported procedure from our group.[2] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.75 (s, 12H), 1.77 (s, 6H), 7.36 (d, J = 8.05 Hz, 8H), 7.50-7.53 (m, 8H), 7.59-7.62 (m, 4H), 7.87 (d, J = 6.85 Hz, 8H), 7.91 (d, J = 8.05 Hz, 8H).

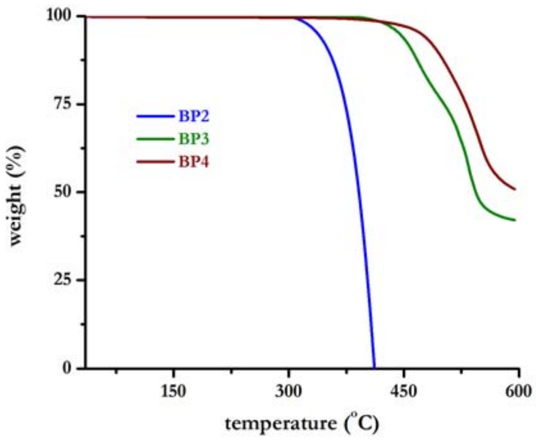


Figure S1. TGA profiles of the benzophenones.

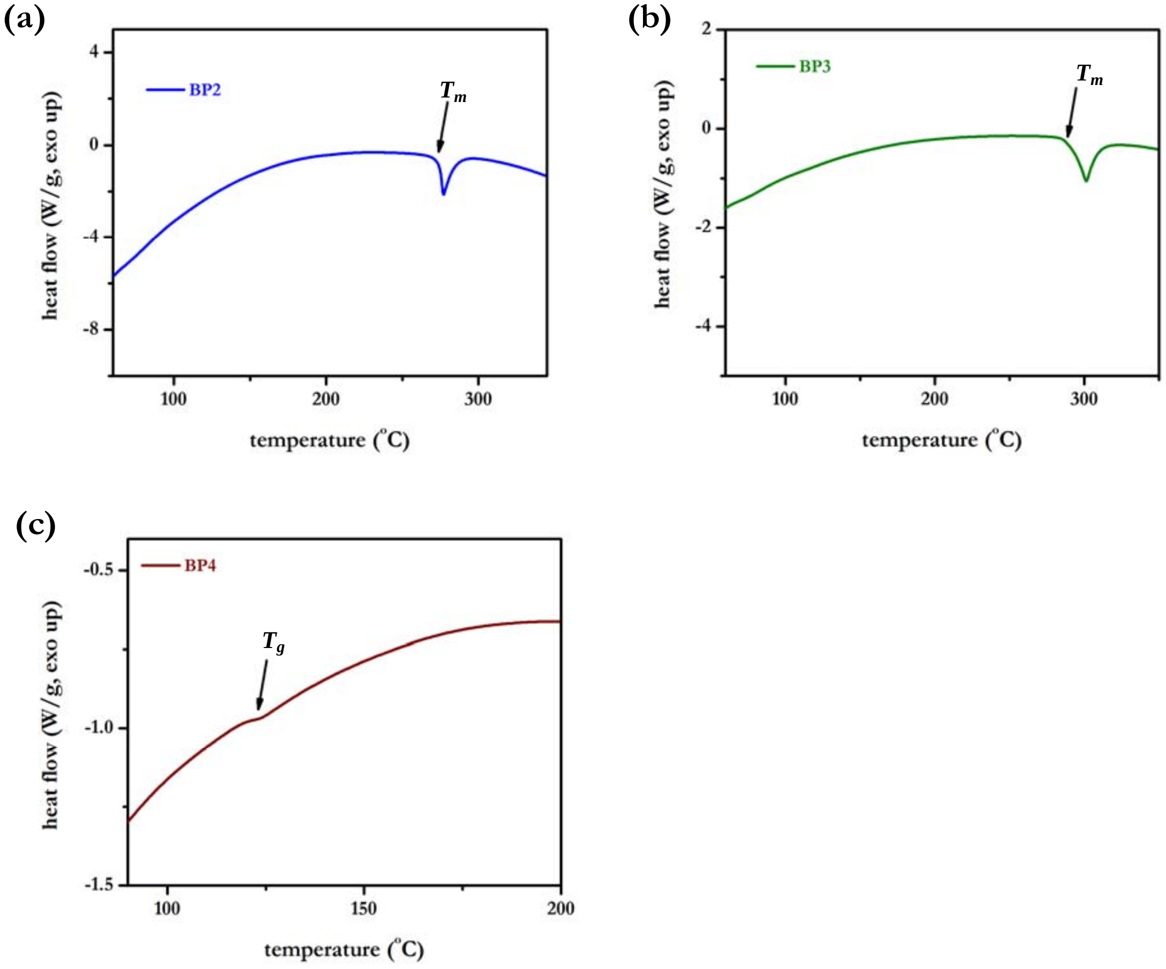


Figure S2. DSC profiles of the **BP2** (a), **BP3** (b) and **BP4** (c).

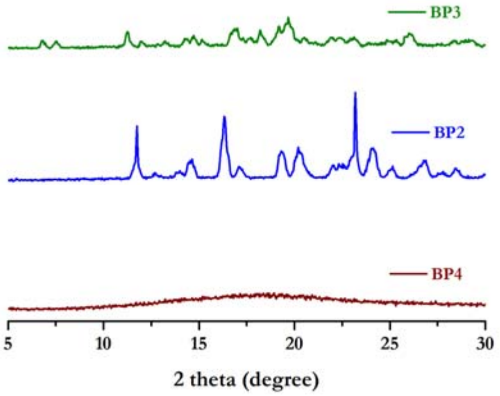


Figure S3. Powder X-ray diffraction profiles of the benzophenones.

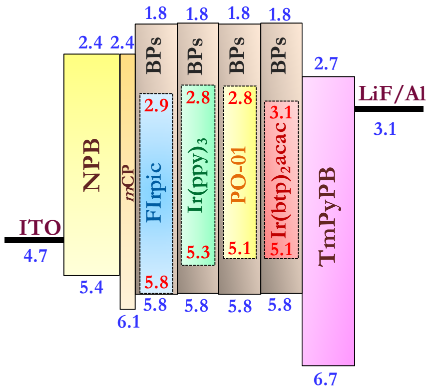


Figure S4. Energy level diagrams for the devices of configurations B–R.

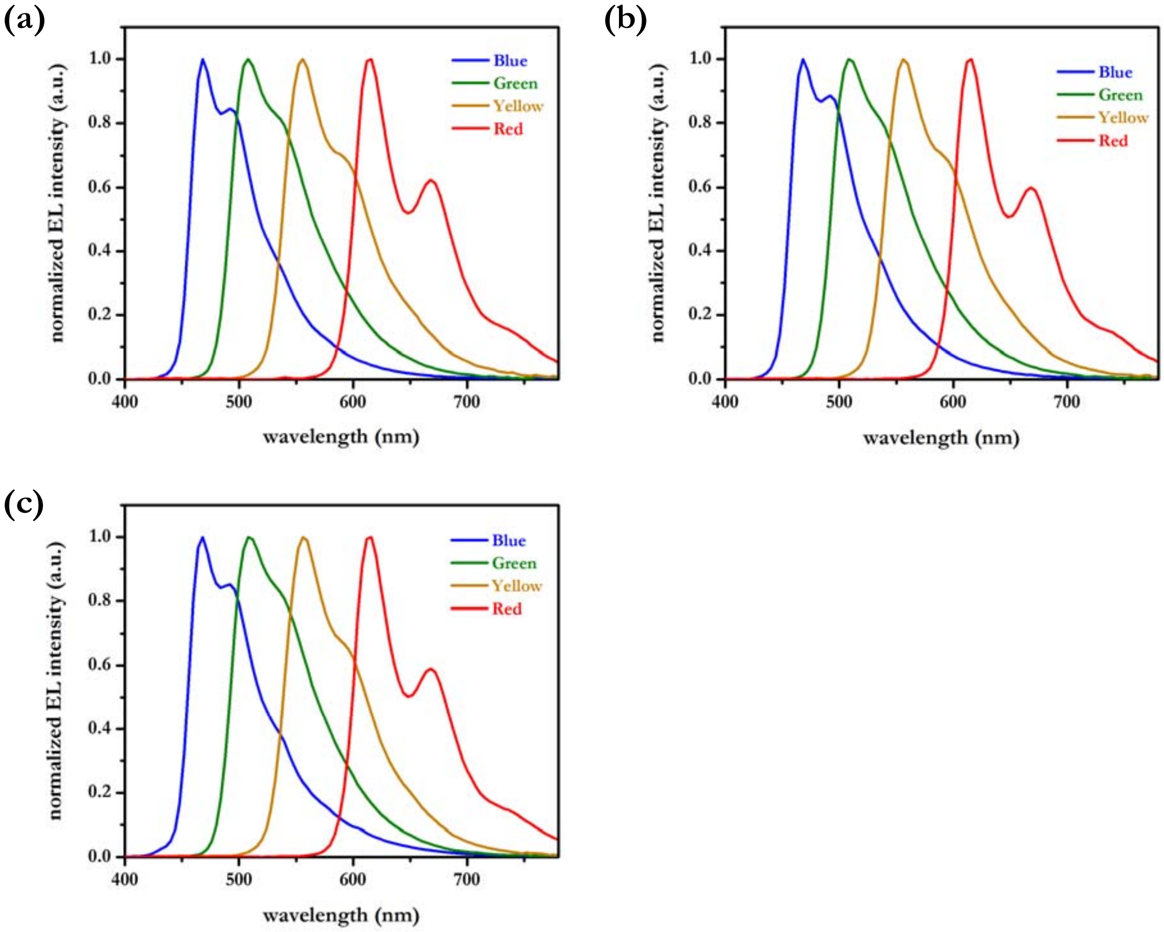


Figure S5. EL spectra recorded at 10 V of the doped devices fabricated with **BP2** (a), **BP3** (b) and **BP4** (c). The colors in each curve represent the colors of the emitted lights, which are blue to green to yellow to red from left to right.

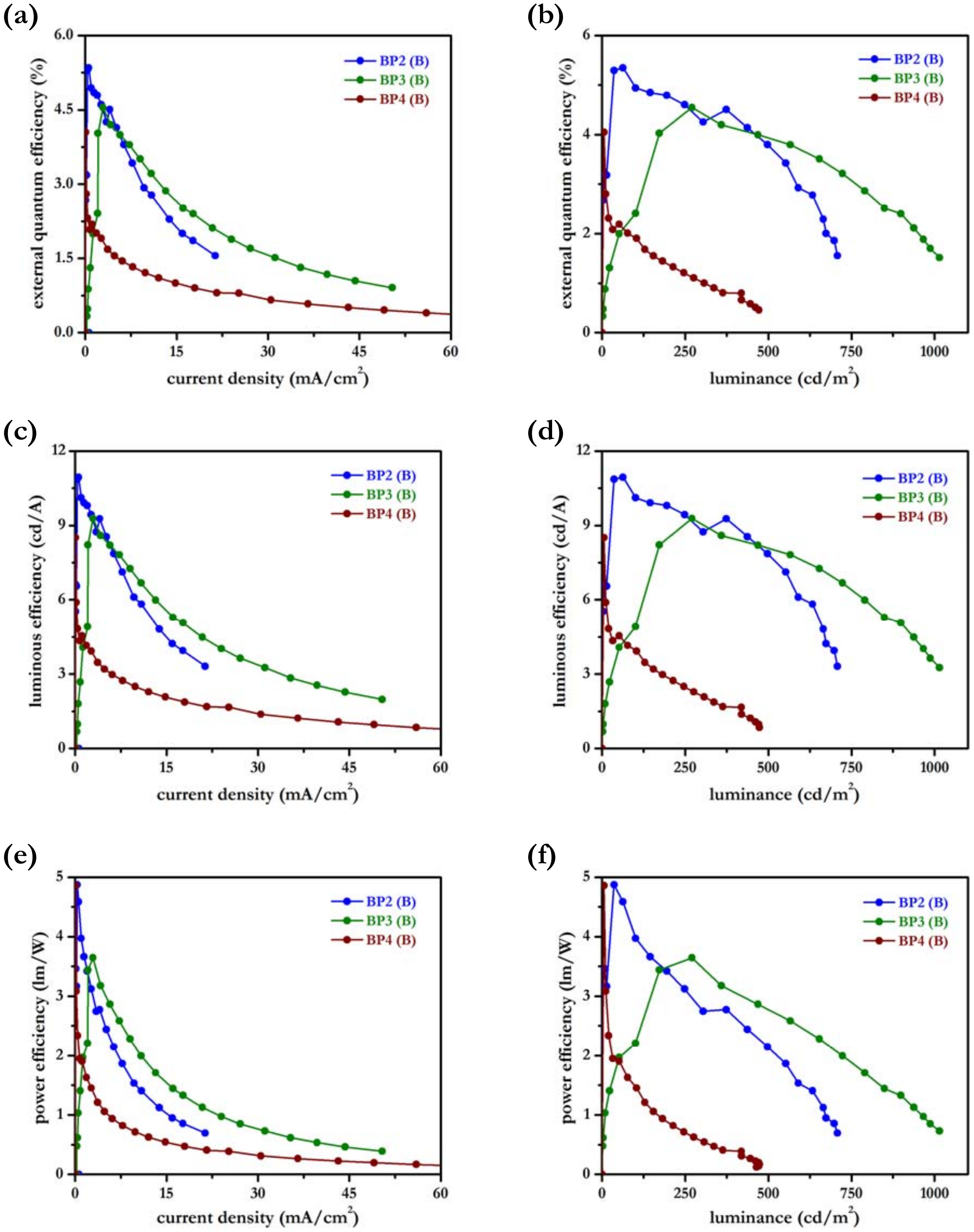


Figure S6. Plots of external quantum efficiency vs. current density (a), external quantum efficiency vs. luminance (b), luminous efficiency vs. current density (c), luminous efficiency vs. luminance (d), power efficiency vs. current density (e) and power efficiency vs. luminance (f) for the devices of configuration B, refer to text.

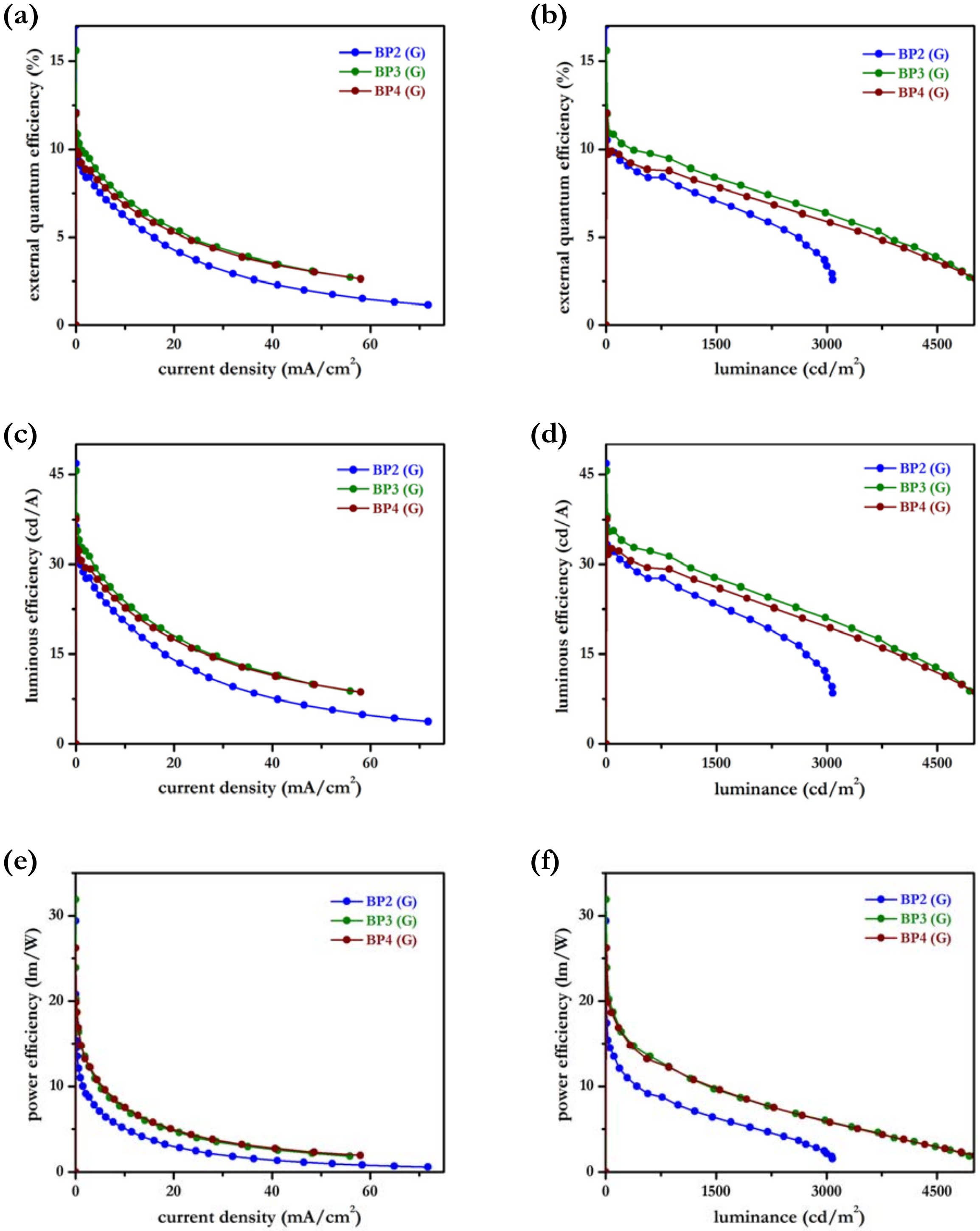


Figure S7. Plots of external quantum efficiency vs. current density (a), external quantum efficiency vs. luminance (b), luminous efficiency vs. current density (c), luminous efficiency vs. luminance (d), power efficiency vs. current density (e) and power efficiency vs. luminance (f) for the devices of configuration G, refer to text.

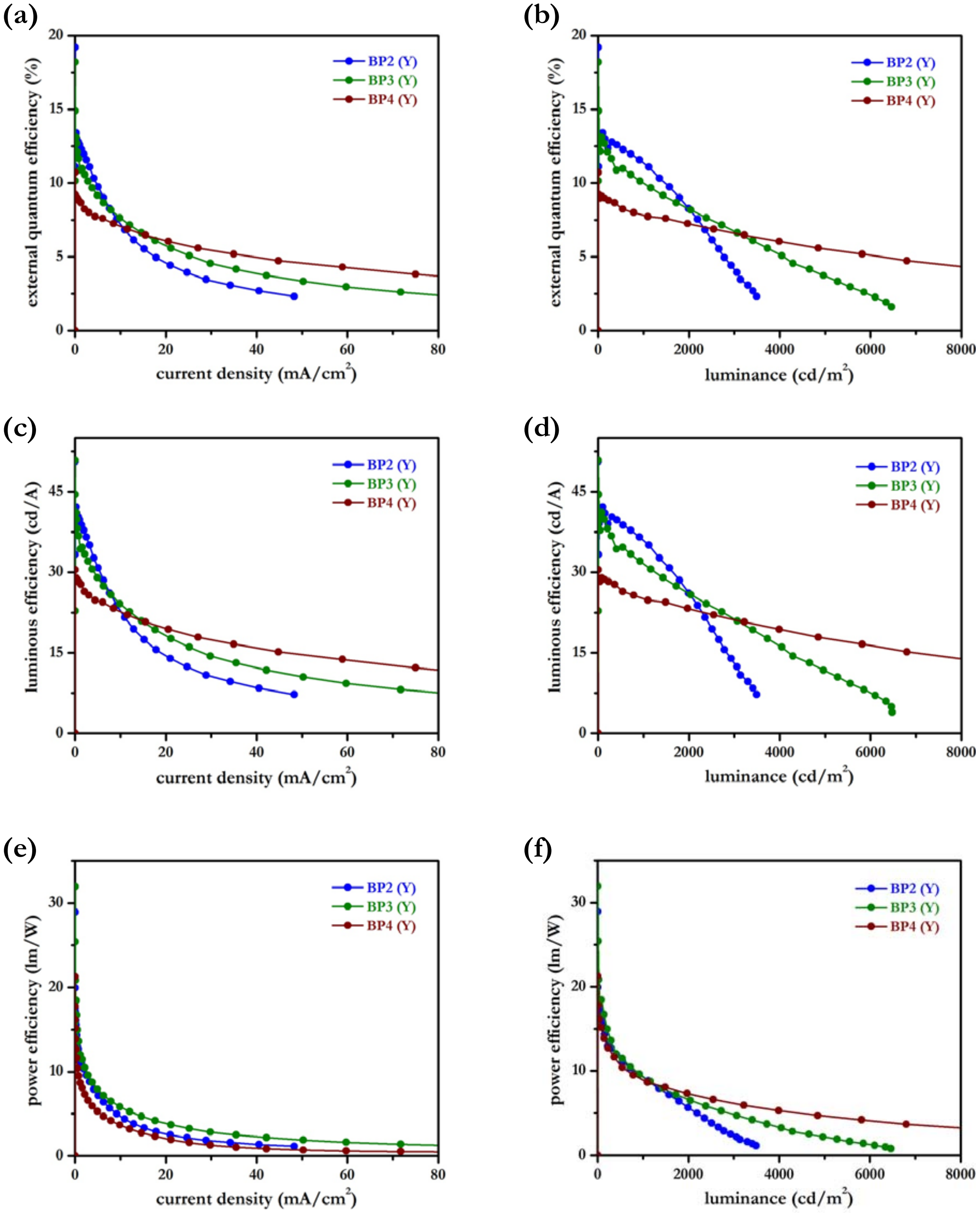


Figure S8. Plots of external quantum efficiency vs. current density (a), external quantum efficiency vs. luminance (b), luminous efficiency vs. current density (c), luminous efficiency vs. luminance (d), power efficiency vs. current density (e) and power efficiency vs. luminance (f) for the devices of configuration Y, refer to text.

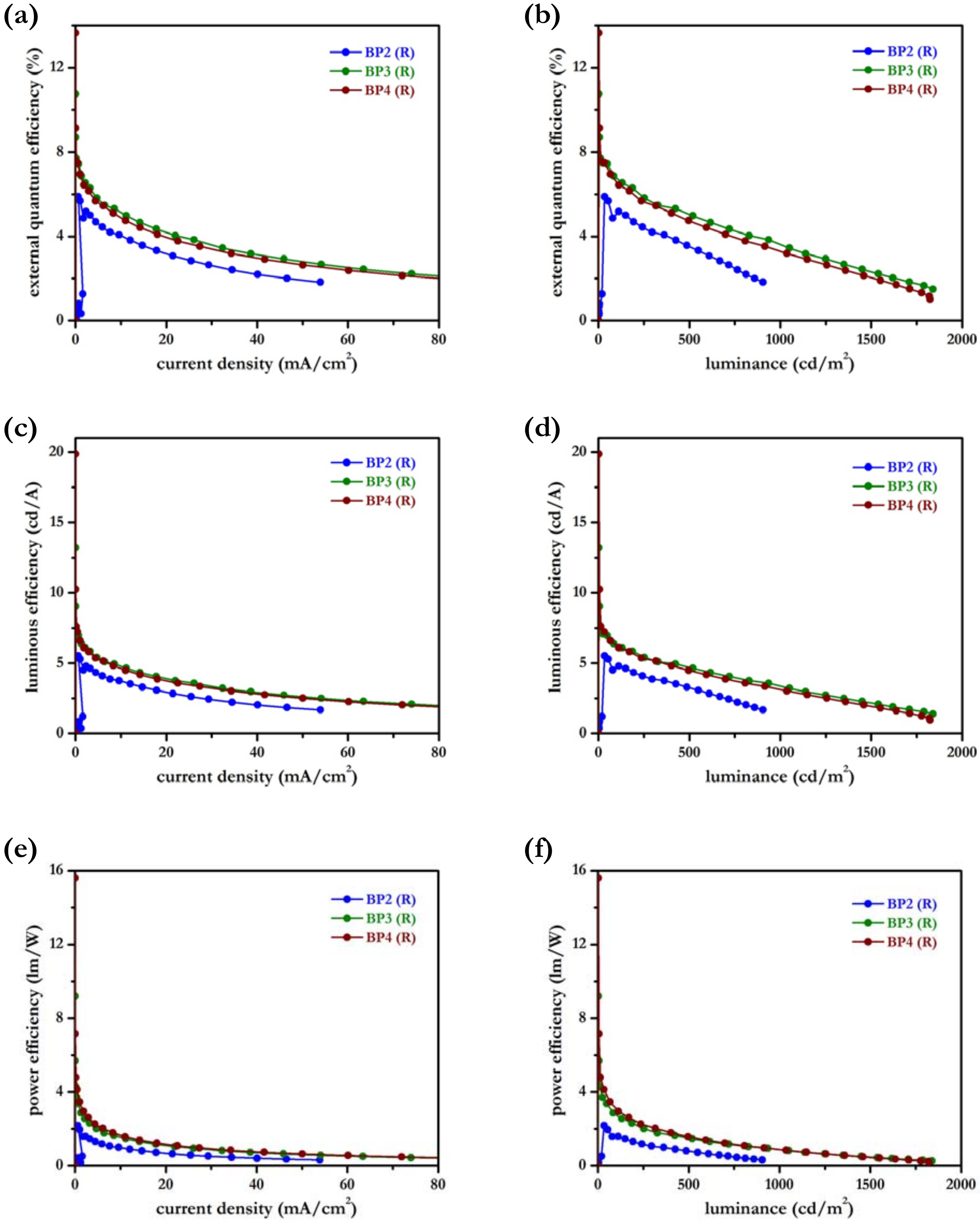


Figure S9. Plots of external quantum efficiency vs. current density (a), external quantum efficiency vs. luminance (b), luminous efficiency vs. current density (c), luminous efficiency vs. luminance (d), power efficiency vs. current density (e) and power efficiency vs. luminance (f) for the devices of configuration R, refer to text.

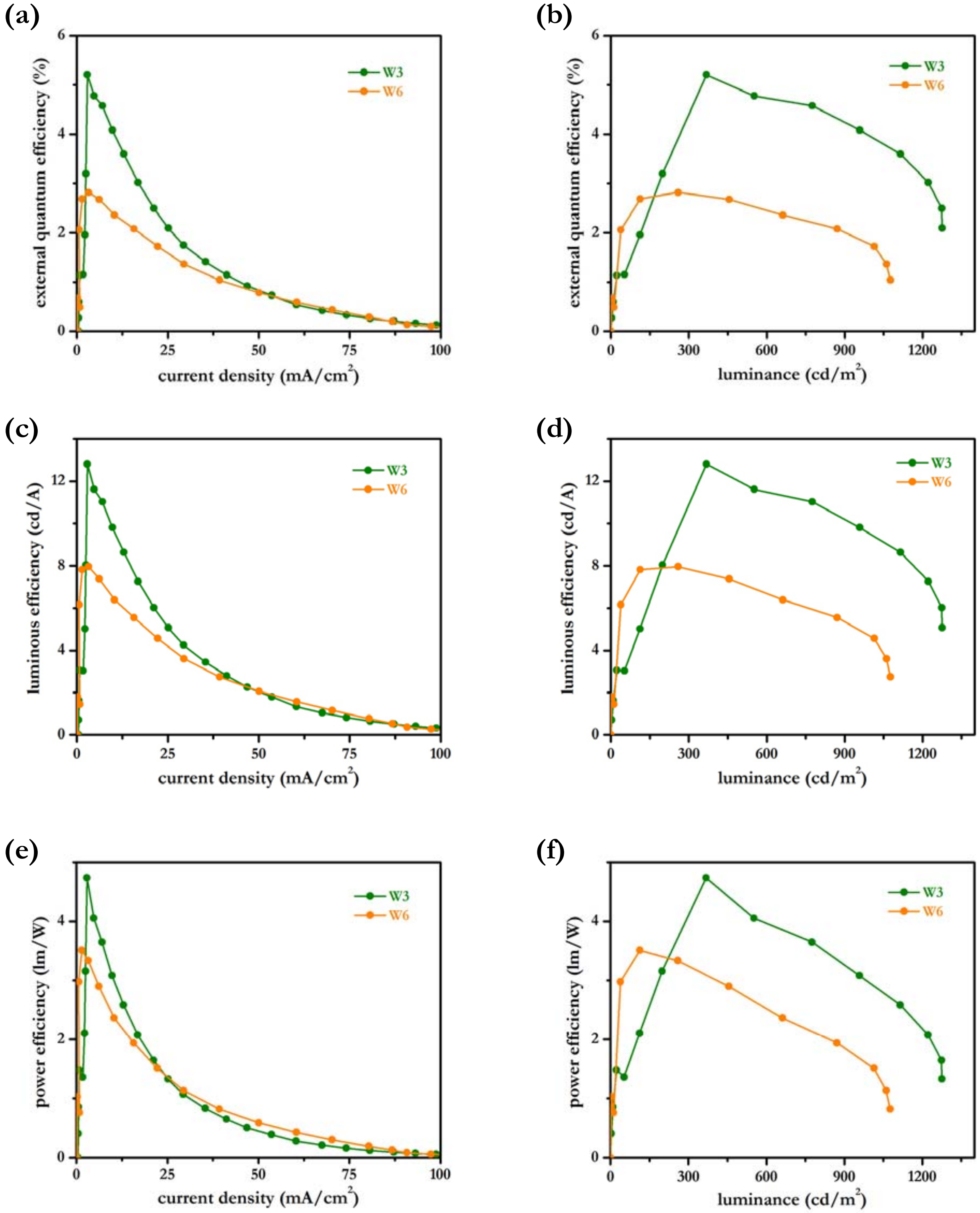


Figure S10. Plots of external quantum efficiency vs. current density (a), external quantum efficiency vs. luminance (b), luminous efficiency vs. current density (c), luminous efficiency vs. luminance (d), power efficiency vs. current density (e) and power efficiency vs. luminance (f) for the devices of configurations W3 and W6, refer to text.

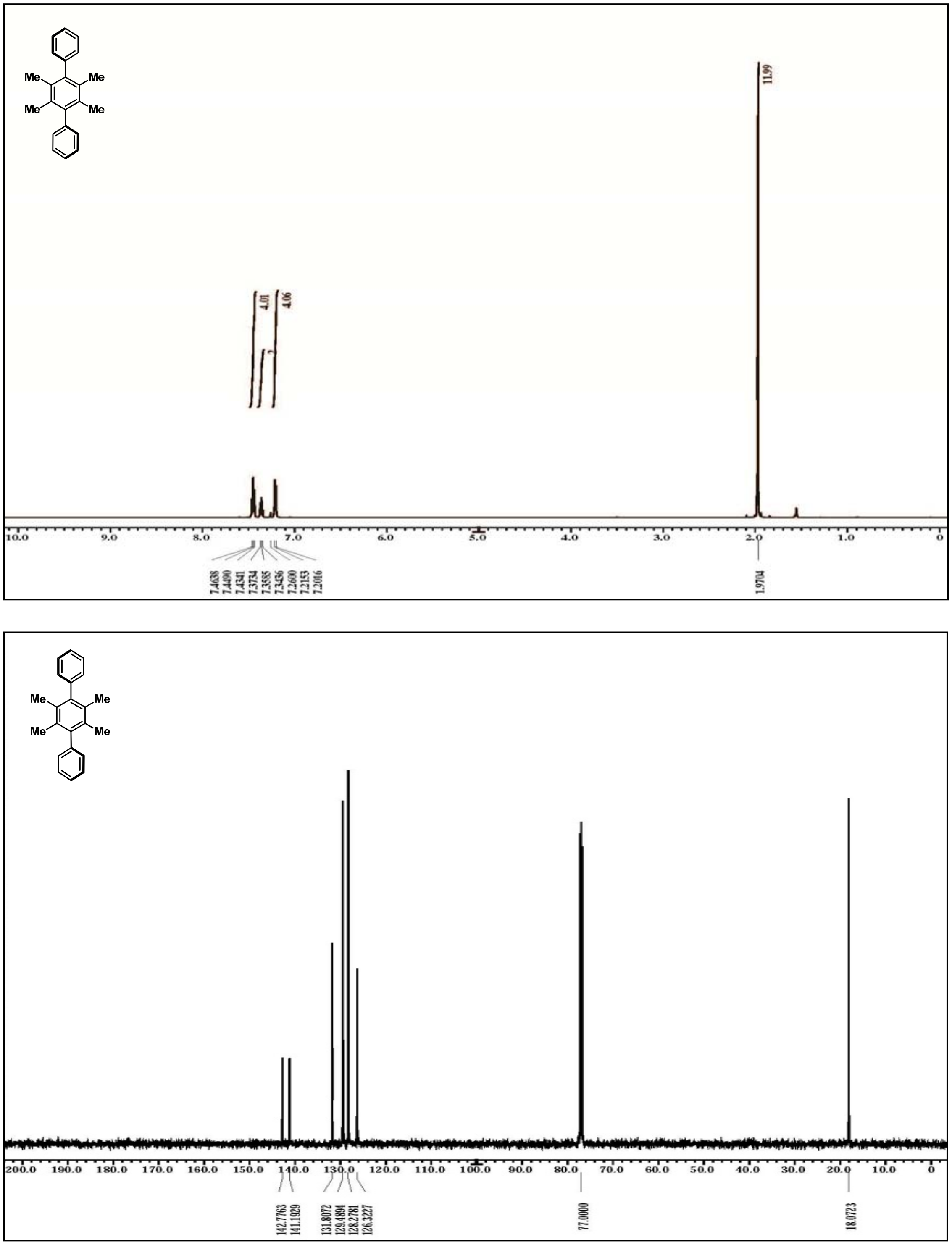


Figure S11. ^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of 1,4-diphenyldurene in CDCl$_3$.

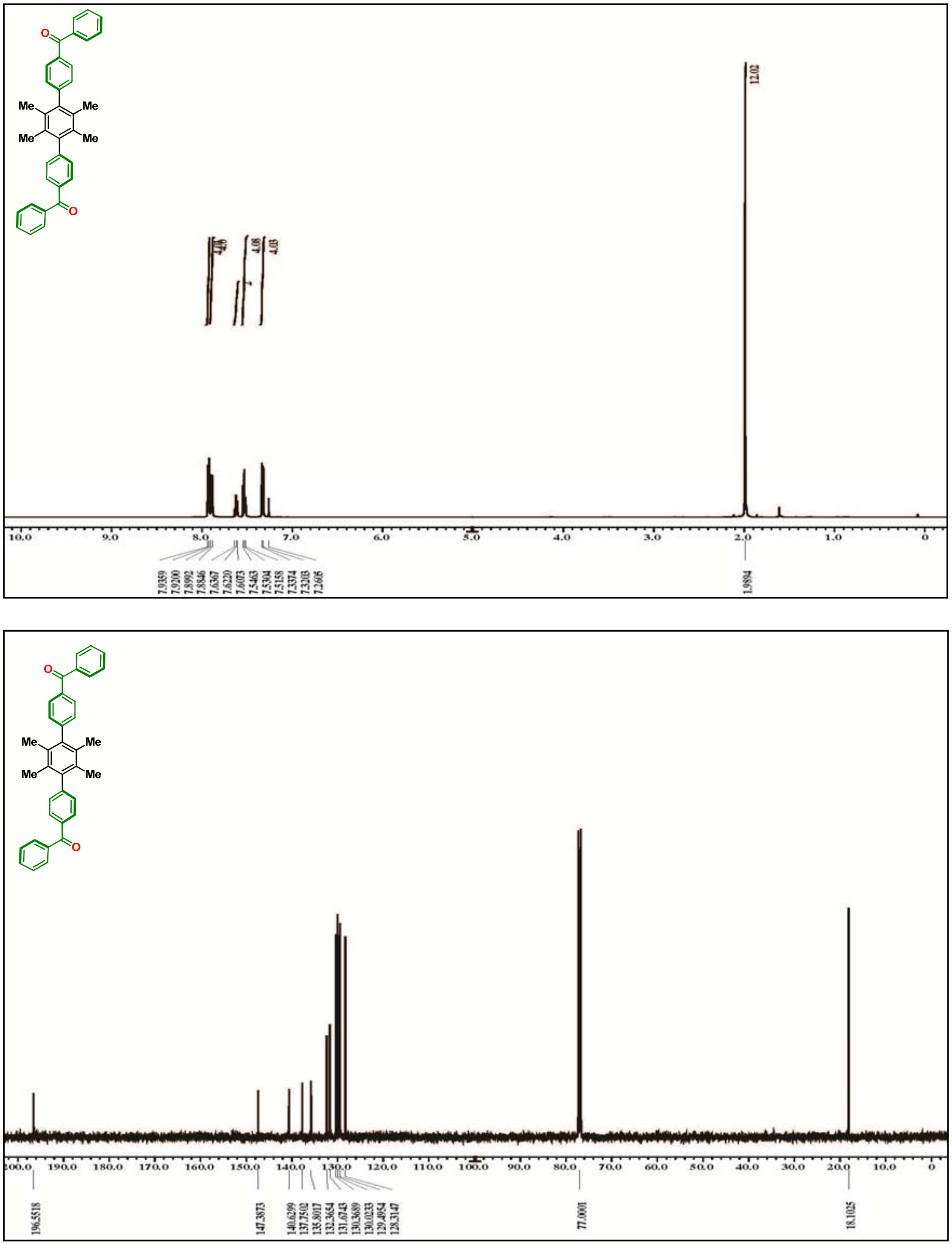
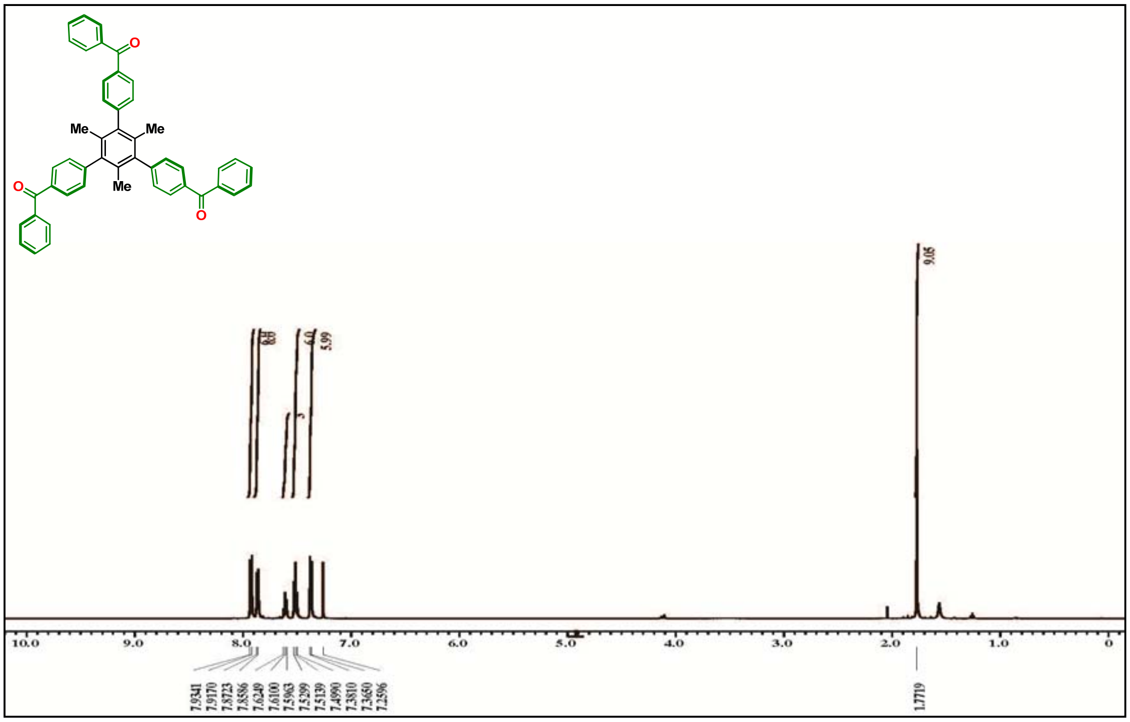


Figure S12. ^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of **BP2** in $CDCl_3$.



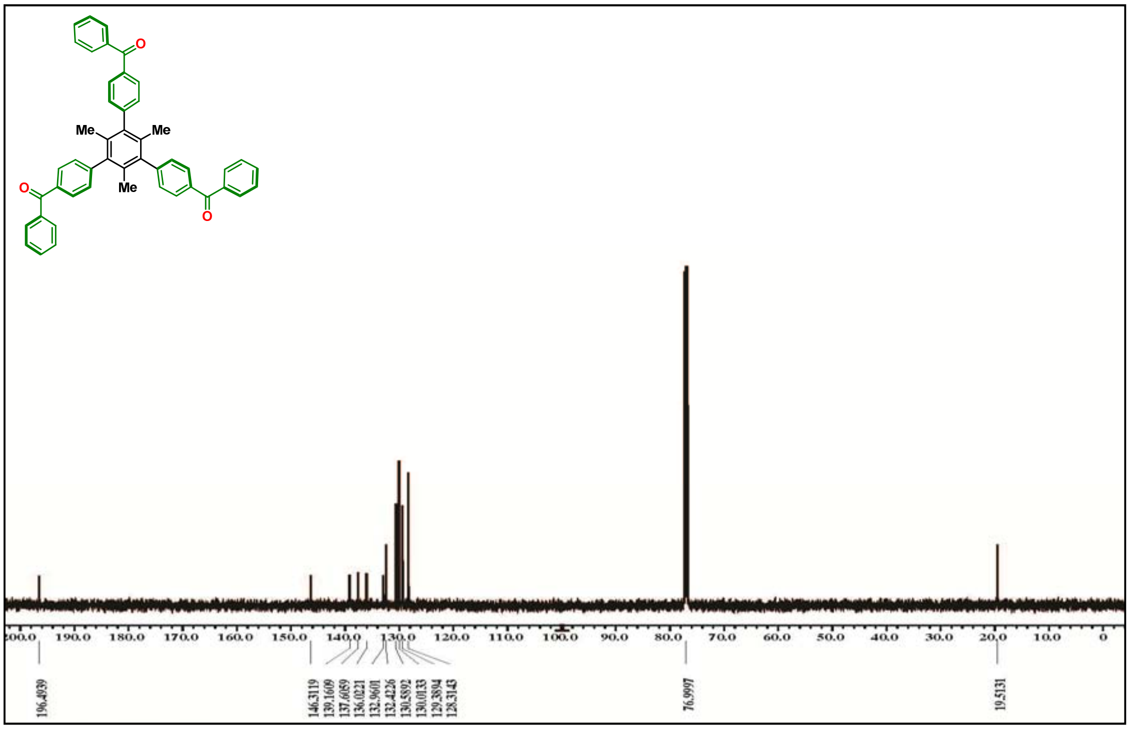


Figure S13. ^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of **BP3** in $CDCl_3$.

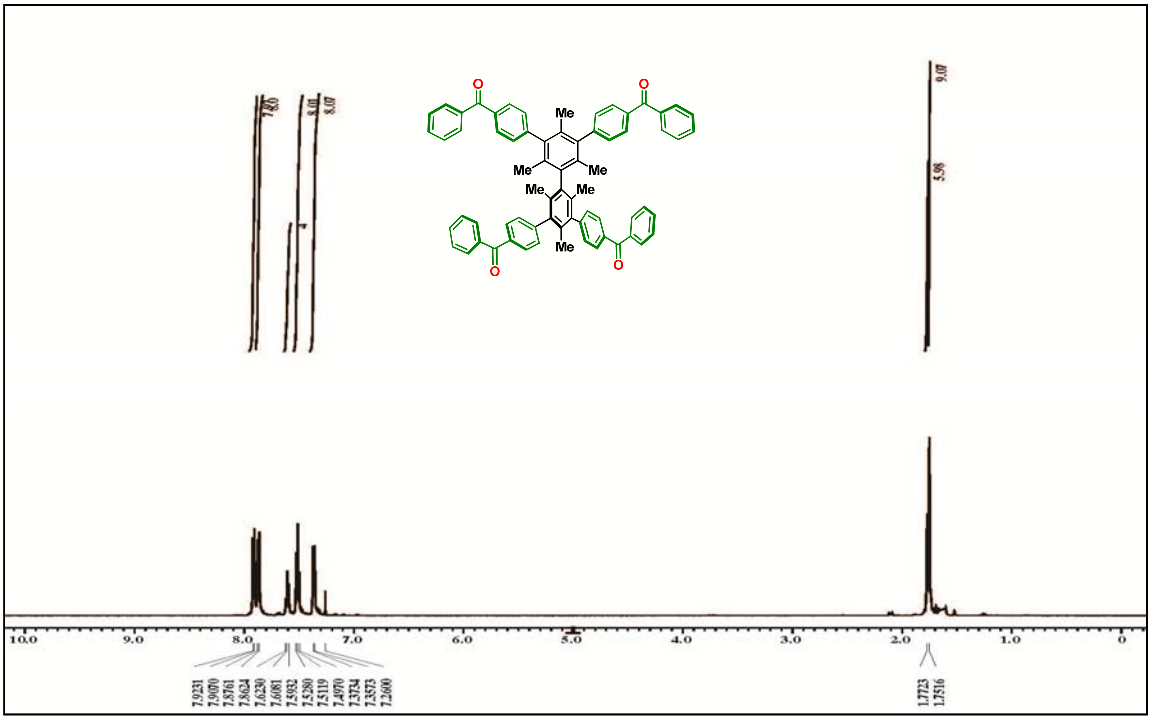


Figure S14. ^{1}H (500 MHz) spectrum of **BP4** in $CDCl_3$.[2]

References

(1) Lehmann, M.; Maier, P. Shape-Persistent, Sterically Crowded Star Mesogens: From Exceptional Columnar Dimer Stacks to Supermesogens. *Angew. Chem., Int. Ed.* **2015**, *54*, 9710 –9714.

(2) Moorthy, J. N.; Venkatakrishnan, P.; Natarajan, P.; Lin, Z.; Chow, T. J. Nondoped Pure-Blue OLEDs Based on Amorphous Phenylenevinylene-Functionalized Twisted Bimesitylenes. *J. Org. Chem*. **2010**, *75*, 2599–2609.

(3) Neogi, I.; Jhulki, S.; Ghosh, A.; Chow, T. J.; Moorthy, J. N. Bifunctional Organic Materials for OLEDs Based on Tröger's Base: Subtle Structural Changes and Significant Differences in Electroluminescence. *Org. Electron.* **2014**, *15*, 3766–3772.

(4) Neogi, I.; Jhulki, S.; Ghosh, A.; Chow, T. J.; Moorthy, J. N. Amorphous Host Materials Based on Tröger's Base Scaffold for Application in Phosphorescent Organic Light-Emitting Diodes. *ACS Appl. Mater. Interfaces* **2015**, *7*, 3298–3305.