Supporting Information

A New Polyboryl-functionalized Triazine as an Electron Transport Material for OLEDs

Christina Sun[1], Zachary M. Hudson[1], Michael G. Helander[2], Zheng Hong Lu[2], Suning Wang[1]*

[1]*Department of Chemistry, Queen's University, 90 Bader Lane, Kingston, Ontario K7L 3N6, Canada*
[2]*Department of Materials Science and Engineering, University of Toronto, 184 College Street, Toronto, Ontario M5S 3E4, Canada*

**suning.wang@chem.queensu.ca*

Content

S1. Materials and Methods

General Procedures. All experiments were performed under a nitrogen atmosphere by standard Schlenk techniques unless otherwise noted. Methylene chloride was dried and distilled over P_2O_5 as solvent for photophysical measurements.

Thin-layer and flash chromatography were performed on silica gel. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz Bruker Avance spectrometer, and deuterated solvents were purchased from Cambridge Isotopes and used without further drying. The high resolution mass spectrum (HRMS) was obtained from an Applied Biosystems QStar XL spectrometer. Elemental analysis was obtained from Laboratoire d'Analyse Élémentaire de l'Université de Montréal, Montréal, Québec, Canada. 2,4,6-tris(*m*-bromophenyl}triazine was synthesized according to a literature procedure.[1]

Electrochemical and Photophysical Measurements. Cyclic voltammetry experiments were performed using a BAS CV-50W analyzer with a scan rate of 0.1-0.2 V/sec using 2 mg sample in 0.5 mL dry THF. The electrochemical cell was a standard three-compartment cell composed of a Pt working electrode, a Pt auxiliary electrode, and an Ag/AgCl reference electrode. CV measurements were carried out at room temperature with 0.1 M tetrabutylammonium hexafluorophosphate (TBAP) as the supporting electrolyte. The LUMO of **B3T** was determined using the reduction potential obtained from square-wave voltammetry relative to $FeCp_2^{0/+}$.[4] Excitation and emission spectra were recorded using a Photon Technologies International QuantaMaster Model 2 spectrometer (CH_2Cl_2 at 1×10^{-5} M). UV/Visible spectra were recorded using a Varian Cary 50Bio UV-vis spectrophotometer. Photoluminescent quantum yields were measured using optically dilute method (1×10^{-5} M, $A \approx 0.1$) at room temperature in CH_2Cl_2 relative to anthracene ($\Phi r = 0.27$ in EtOH). The fluorescence quantum yields were calculated using reported procedures.[2] UPS measurements were performed using a PHI 5500 MultiTechnique system, with attached organic deposition chamber with a base pressure of 10^{-10} Torr.

Density Functional Theory Calculations. Molecular orbital and molecular geometry calculations were performed using the Gaussian 03 program suite using a computational model as the starting point for geometry optimization. Calculations were performed at the B3LYP level of theory using 6-31G* as the basis set.

EL Device Fabrication: Devices were fabricated in a Kurt J. Lesker LUMINOS® cluster tool with a base pressure of ~10^{-8} Torr without breaking vacuum. The ITO anode is commercially patterned and coated on glass substrates 50 x 50 mm^2 with a sheet resistance less than 15 Ω. Substrates were ultrasonically cleaned with a standard regiment of Alconox®, acetone, and methanol followed by UV ozone treatment for 15 min. The active area for all devices was 2 mm^2. The film thicknesses were monitored by a calibrated quartz crystal microbalance and were further verified for single-carrier devices using using capacitance-voltage measurements (Agilent 4294A). I-V characteristics were measured using a HP4140B picoammeter in ambient air. Luminance measurements and EL spectra were taken using a Minolta LS-110 luminance meter and an Ocean Optics USB200 spectrometer with bare fiber, respectively. The external quantum efficiency of EL devices was calculated following the standard procedure.[3]

S2. Synthesis and Characterization

2,4,6-tris(*m*-dimesitylborylphenyl)-1,3,5-triazine (**B3T**)

In a dropwise manner, *n*-butyllithium in hexane (1.6 M, 3.02 mL, 4.83 mmol) was added to a solution of 2,4,6-tris(*m*-bromophenyl}triazine (0.80 g, 1.45 mmol) in 100 mL THF at -78^{o}C. After stirring at -78^{o}C for 1 h, a solution of trimesitylboron fluoride (1.3 g, 4.83 mmol) in 30 mL THF was added dropwise to this mixture. Stirring was continued for 3 h at -78^{o}C and for 2 h at room temperature. THF was evaporated *in vacuo* and the residue was extracted using CH_2Cl_2/sat. NH_4Cl. The organic layer was dried over $MgSO_4$, concentrated, and the residue purified by column chromatography on silica (4:1 hexanes:EtOAc) to afford **1** as a white solid (0.35 g, 23%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.80 (s, 3H, phenyl), 8.52 (d, J = 7.8 Hz, 3H, phenyl), 7.75 (d, J = 7.3 Hz, 3H, phenyl), 7.48 (t, 7.6 Hz, 3H, phenyl), 6.88 (s, 12H, mesityl), 2.36 (s, 18H, mesityl), 2.06 (s, 36H, mesityl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 171.7, 145.6, 141.6, 140.9, 140.4, 138.8, 137.5, 135.8, 132.4, 129.1, 128.2, 23.6, 21.3 ppm. HRMS calc'd for $C_{75}H_{78}B_3N_3$ [M^+] 1053.6493, found 1053.6475. CHN calc'd for $C_{75}H_{78}B_3N_3$: C 84.75, H 7.14, N 3.78 %, found C 85.48, H 7.46, N 3.99 %. The slightly higher observed carbon content is likely caused by the presence of toluene solvent molecules in the crystal lattice that were not fully removed by vacuum. A clean ^{1}H NMR spectrum is provided below.

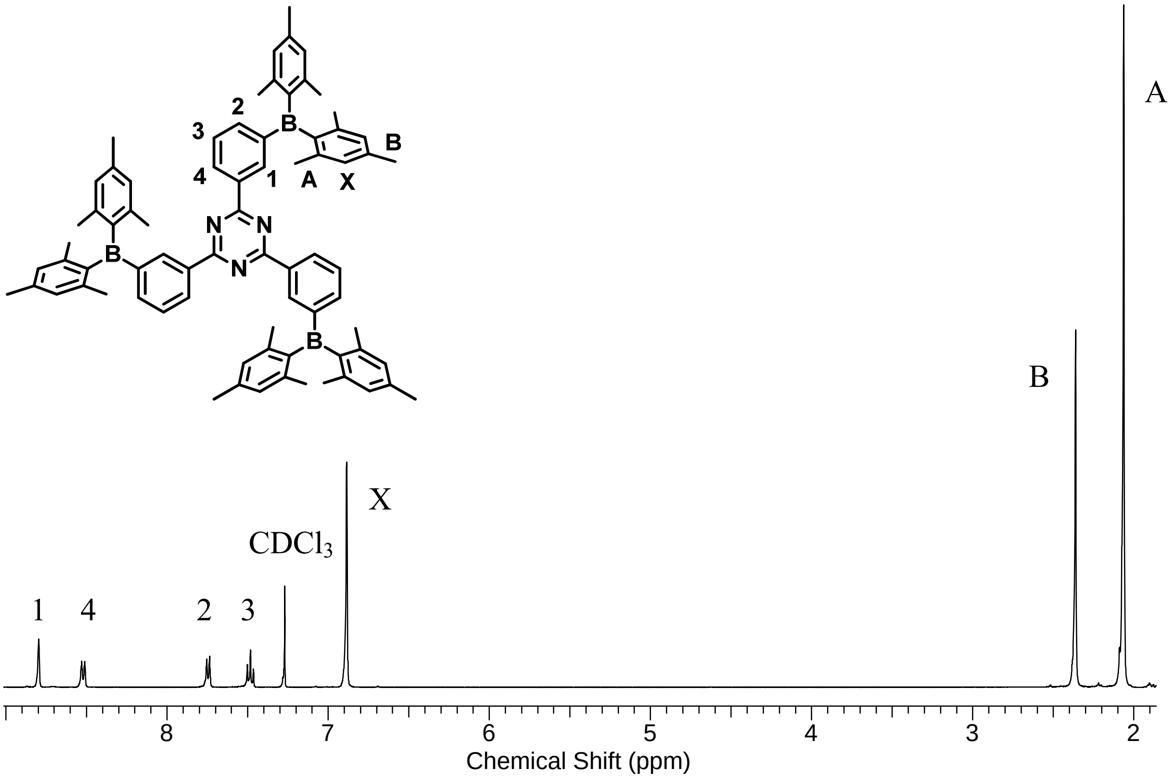

Figure S1. Full ^{1}H NMR spectrum of **B3T** in $CDCl_3$.

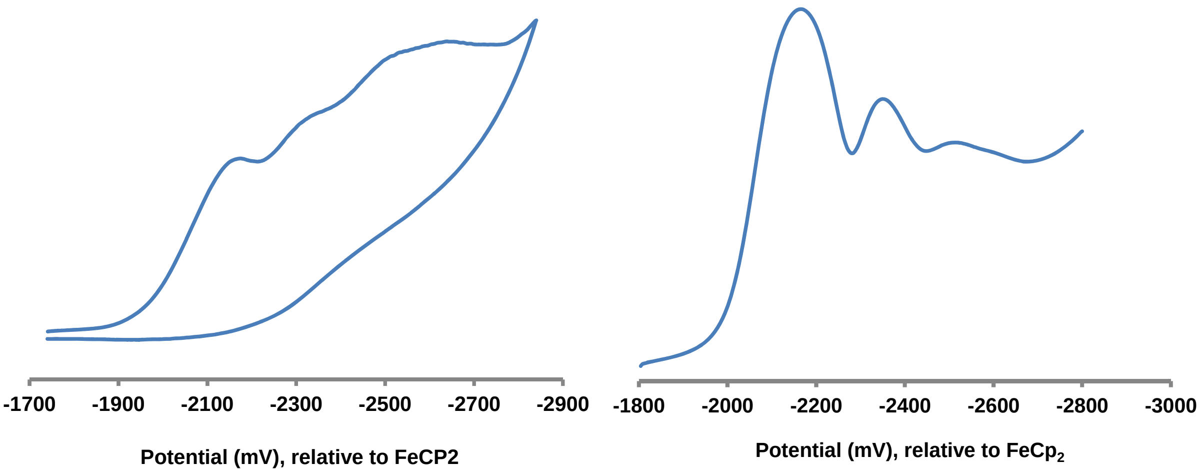

Figure S2. Left: cyclic voltammetry diagrams of **B3T** in THF. Right: square-wave scan diagram of **B3T** in THF. Note: a peak value in a square-wave voltammogram corresponds to the half potential of an ideal CV wave.

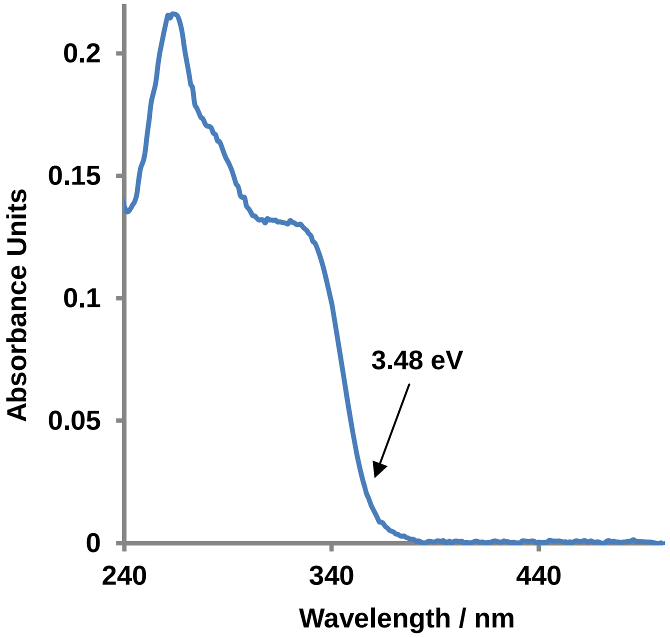

Figure S3. Solid state absorption spectrum of **B3T** film. The arrow indicates the energy gap, E_g.

S3. TD-DFT Results

Excited State	Transition	Energy (eV)	*f*
1	HOMO-1 → LUMO	3.55	0.0431
2	HOMO-2 → LUMO	3.55	0.0828
3	HOMO → LUMO+1 HOMO → LUMO+2	3.55	0.0823

.

S3. Device Characteristics and Performance

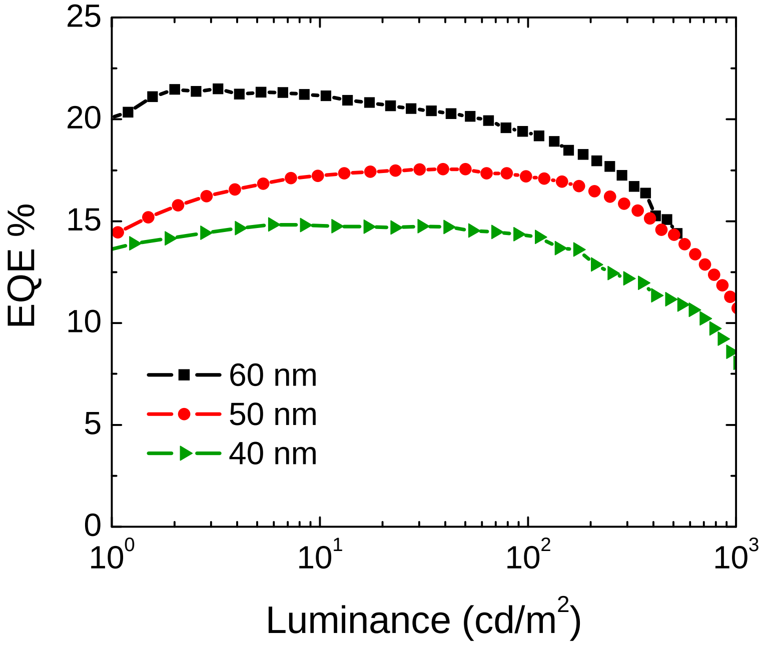

Figure S4. External quantum efficiencies of devices A, B and C.

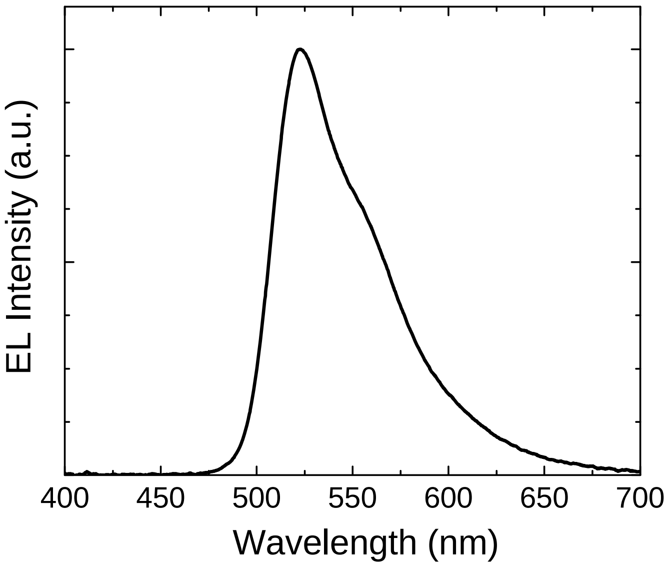

Figure S5. Electroluminescence spectrum of OLED using Ir(ppy)$_2$(acac) as emitter.

S5. References

1. Hsiao-Fan Chen, Shang-Jung Yang, Zhen-Han Tsai, Wen-Yi Hung, Ting-Chih Wang and Ken-Tsung Wong. *J. Mater. Chem.* **2009**, *19*, 8112-8118.
2. Demas, N. J.; Crosby, G. A. *J. Am. Chem. Soc.,* **1970**, *29*, 7262.
3. M. G. Helander, M. T. Greiner, Z. B. Wang, and Z. H. Lu, *Appl. Surf. Sci.* **2010**, *256*, 2602.
4. Pommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bassler, H.; Porsch, M.; Daub, J. *Adv. Mater.* **1995**, *7*, 551.