

Carbazole-Substituted Benzobisoxazoles: Near-UV Fluorescent Emitters and Ambipolar Hosts for Organic Light-Emitting Diodes

David L. Wheeler,^a Lloyd Fisher, Jr.,^f Pascal Friederich,^{c,d,e} Christopher Cunningham,^a Angelar K. Muthike,^f Alán Aspuru-Guzik,^{c,d} Theodore Goodson III,^f and Malika Jeffries-EL^{*a,b}

a) Department of Chemistry, Boston University, 590 Commonwealth Ave, Boston, MA 02215, USA.

b) Division of Materials Science and Engineering, Boston University, 15 St Mary's St. #117, Boston, MA. 02215, USA.

c) Department of Chemistry, University of Toronto, 80 St George St, Toronto, ON M5S 3H6, Canada

d) Department of Computer Science, University of Toronto, 214 College St, Toronto, ON M5T 3A1, Canada

e) Institute of Nanotechnology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

f) Department of Chemistry, University of Michigan, Ann-Arbor Michigan 48109-1055, USA.

Supplemental Information

Table of Contents

Materials and Measurements	2
Characterization	3
NMR Spectra.....	3
Experimental Absorbance and Emission Spectra	11
Theoretical Calculations	11
Tables and Figures	11
Cartesian Coordinates	11
References	11

Materials and Measurements

4,8-dibromo-2,6-diethylbenzobisoxazole, bis(hydrochloride) 2,5-diamino-*p*-hydroquinone and 2,4-diaminoresorcinol were synthesized according to literature procedures. THF was dried using an Innovative Technologies solvent purification system. All other chemical reagents were purchased from commercial sources and used without further purification unless otherwise noted. Nuclear magnetic resonance (NMR) experiments were carried out in CDCl₃ at 500 MHz (H¹) and 125 MHz (C¹³). All chemical shifts are given relative to tetramethylsilane and coupling constants are reported in hertz (Hz). High-resolution mass spectra were recorded on a double-focusing magnetic sector mass spectrometer using ESI. Melting points were determined using a MelTemp II apparatus. Ultraviolet photoelectron spectroscopy (UPS) was used to acquire the ionization potentials and approximate the HOMO values for each material. All substrates (positively doped silicon; 10 × 10 mm²) had 40 nm of silver deposited via thermal evaporation. Samples were prepared by dissolution in CHCl₃ at a concentration of 5 mg/mL and stirred for a minimum of 4 h. Each solution was filtered to remove potential aggregates and sequentially spin-coated under a nitrogen atmosphere at 4000 RPM. Spectra were then acquired under ultrahigh vacuum at random positions on the formed film. All UV-Vis and fluorescence spectroscopy were obtained using quartz cuvettes with a 10 mm path length in CHCl₃ for solution-state or as spin-cast thin films on a quartz slide (5 mg/mL solution in CHCl₃ spun at 1500 RPM). UV-vis spectra were collected on a Shimadzu UV-1800 UV spectrophotometer. Photoluminescence spectra were obtained on a Varian Cary Eclipse spectrophotometer.

Characterization

NMR Spectra

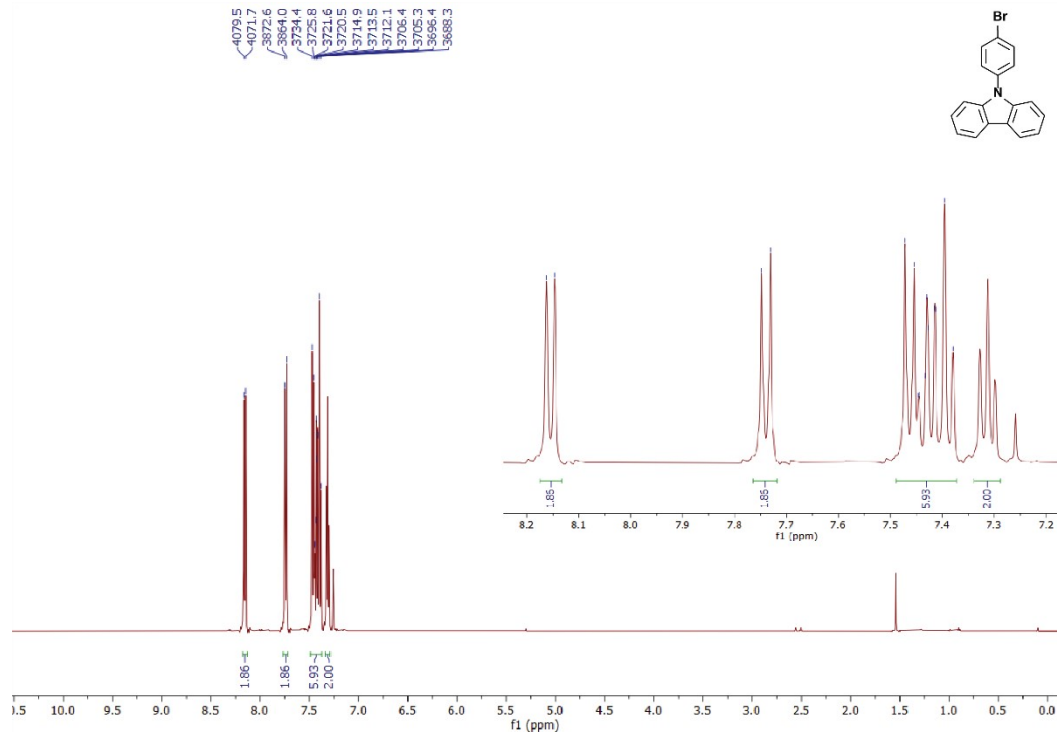


Figure S1. ¹H NMR of 1

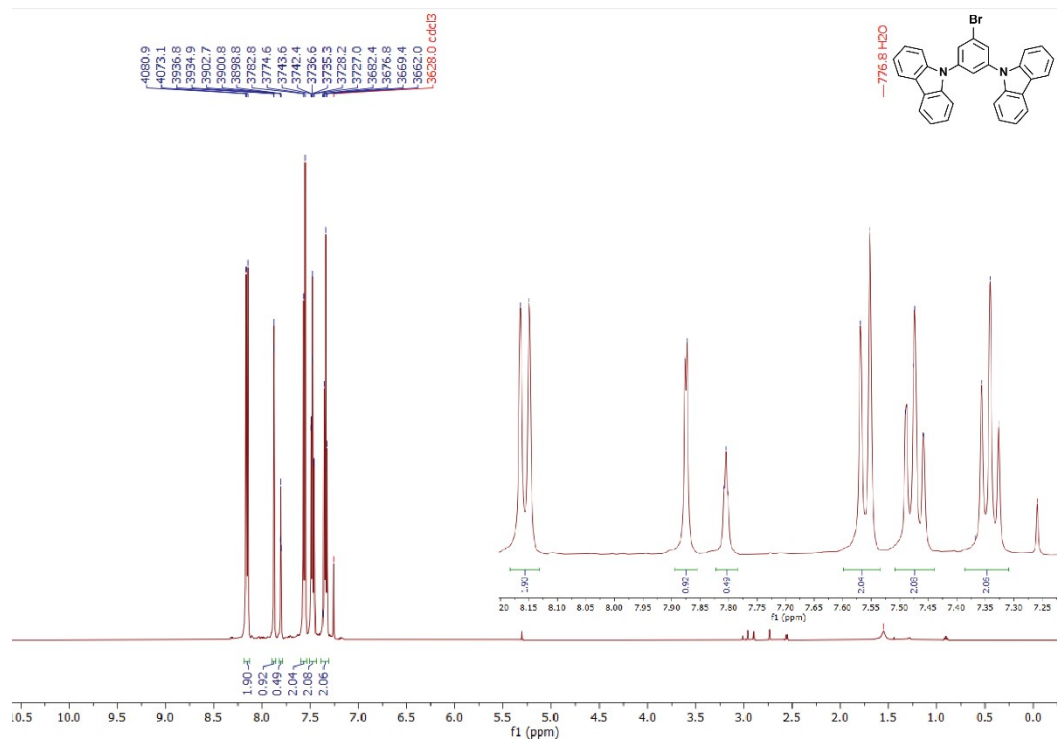


Figure S2. ¹H NMR of 2

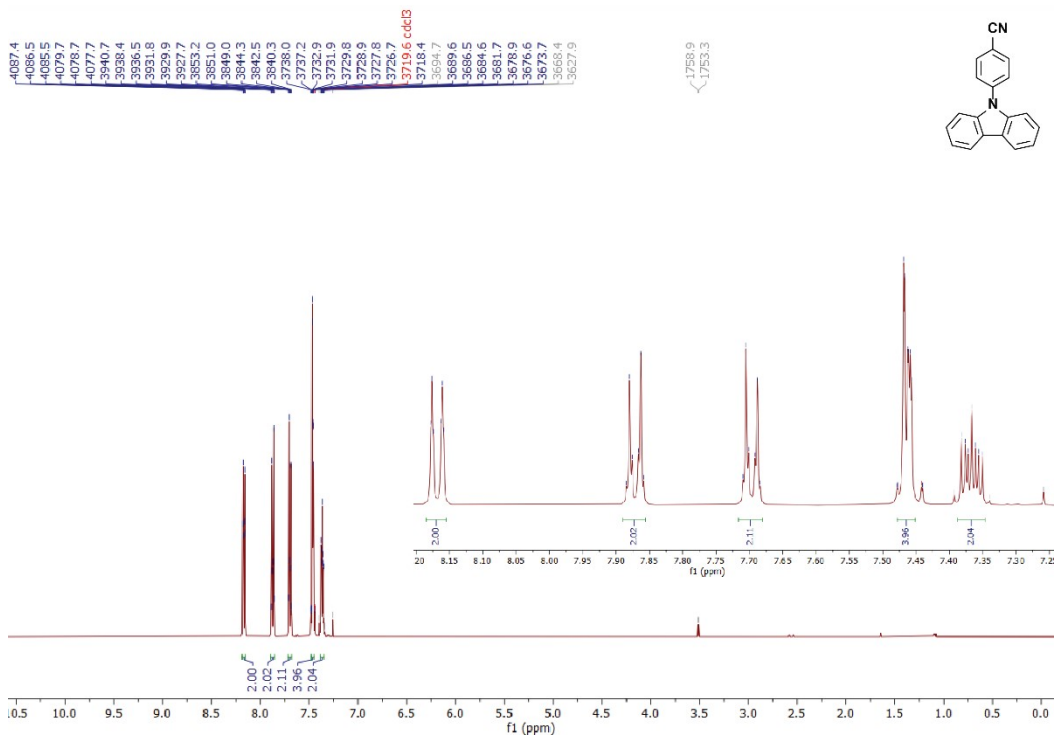


Figure S3. ¹H NMR of 3

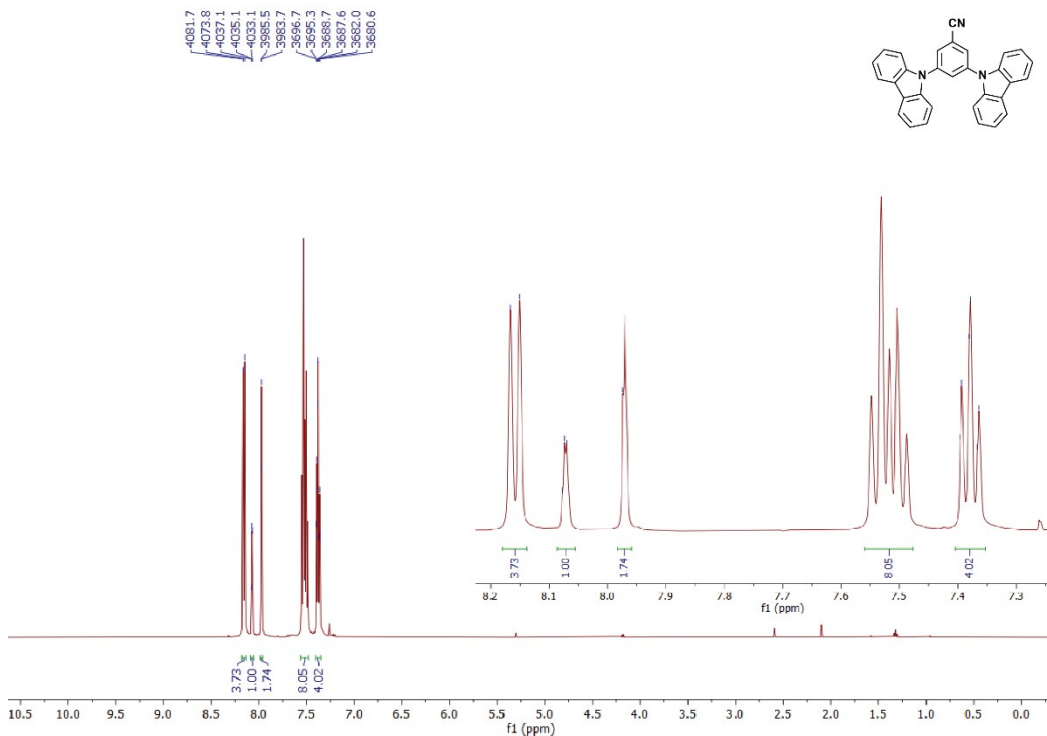


Figure S4. ¹H NMR of 4

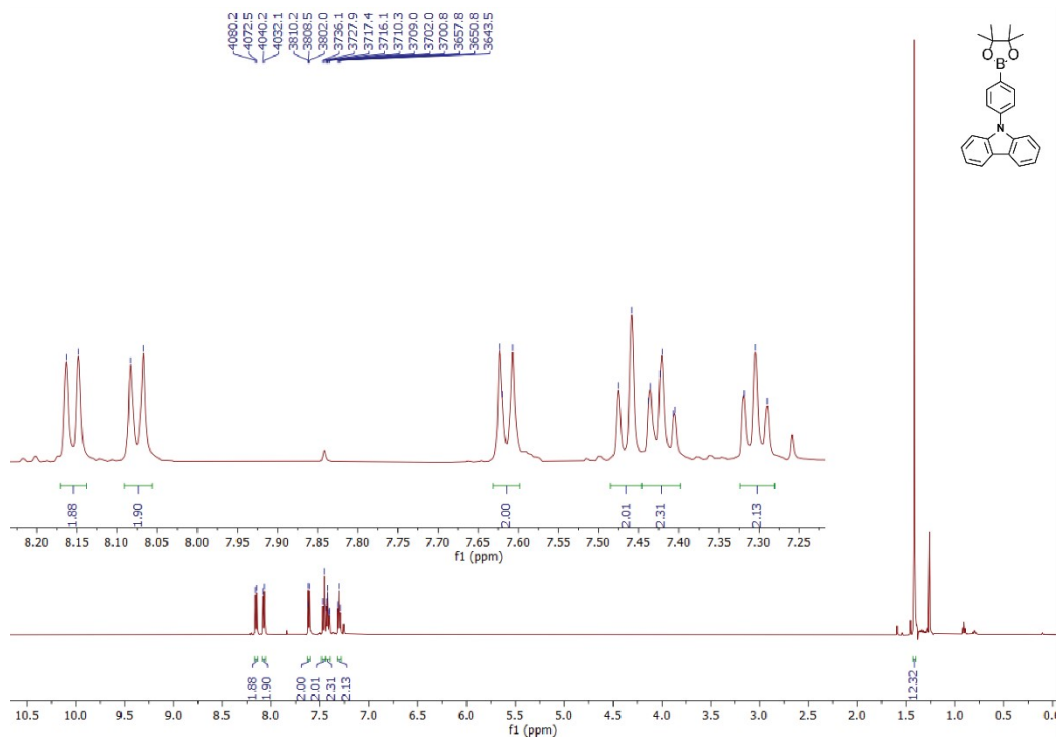


Figure S5. ^1H NMR of 5

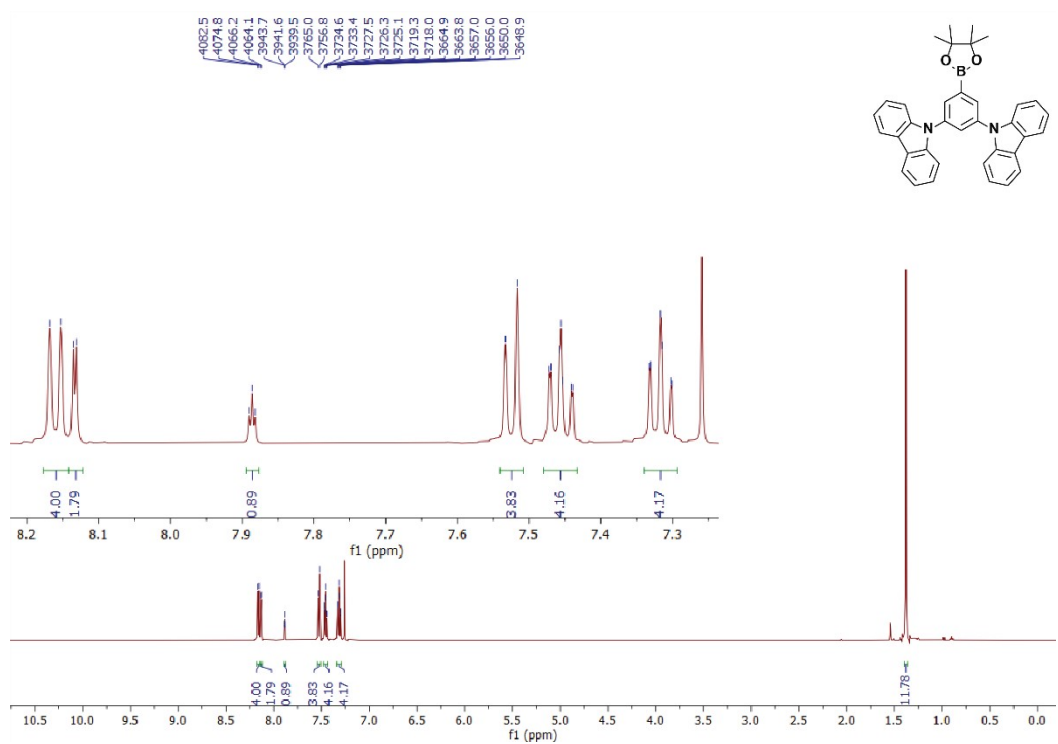


Figure S6. ^1H NMR of 6

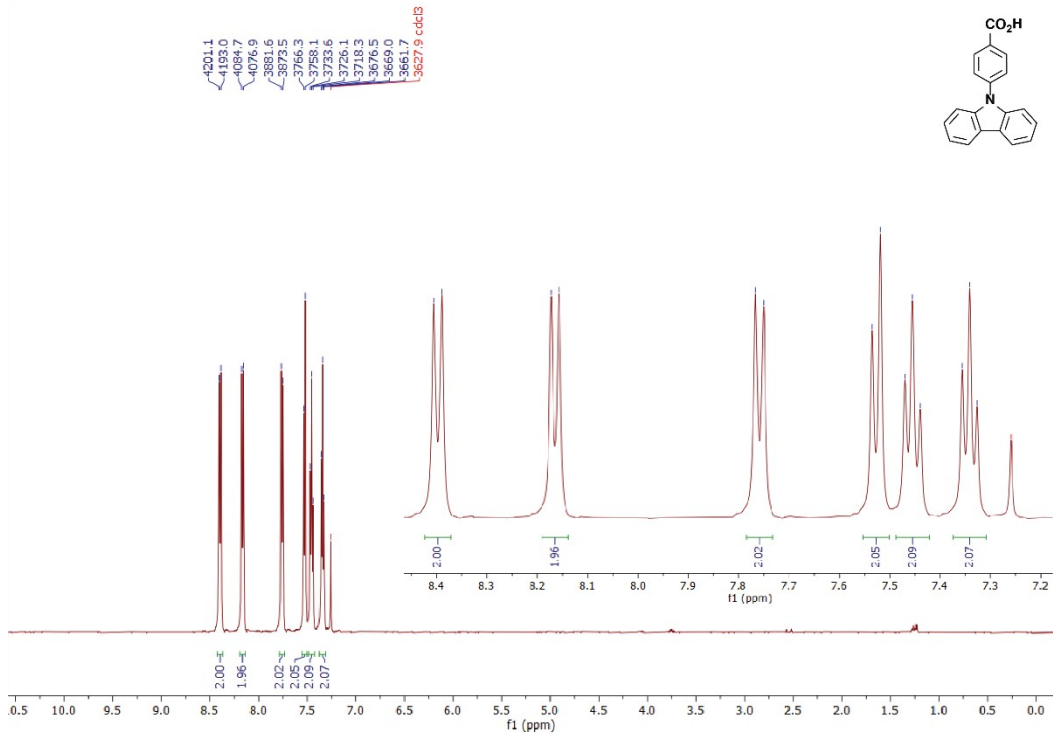


Figure S7. ¹H NMR of 7

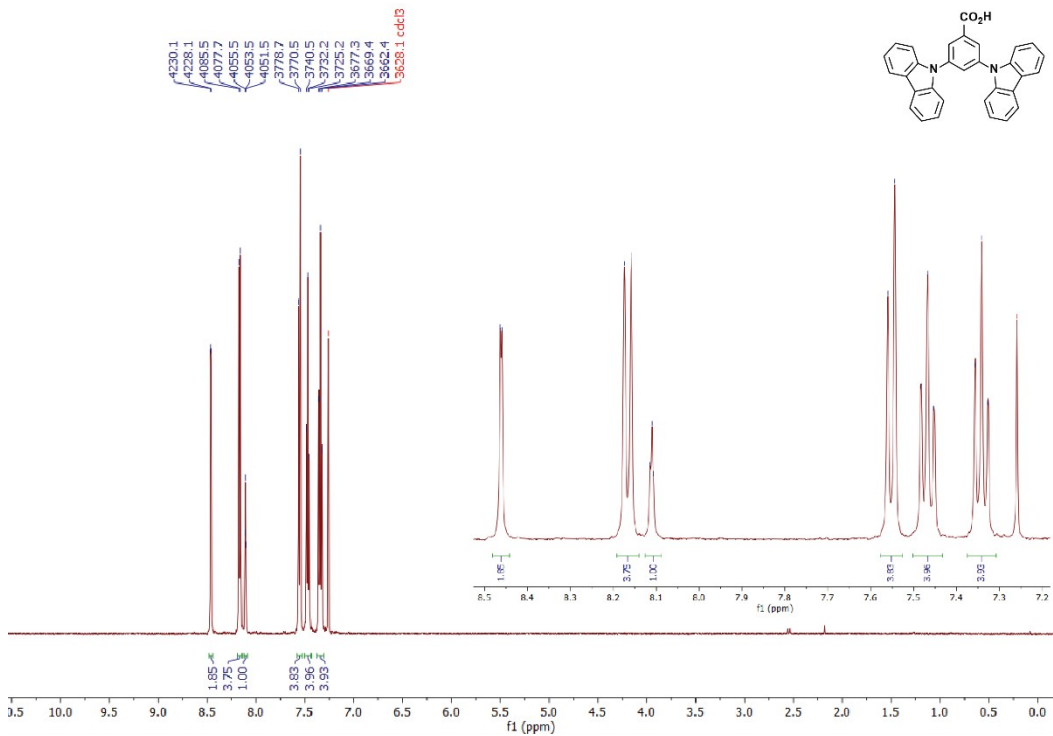


Figure S8. ¹H NMR of 8

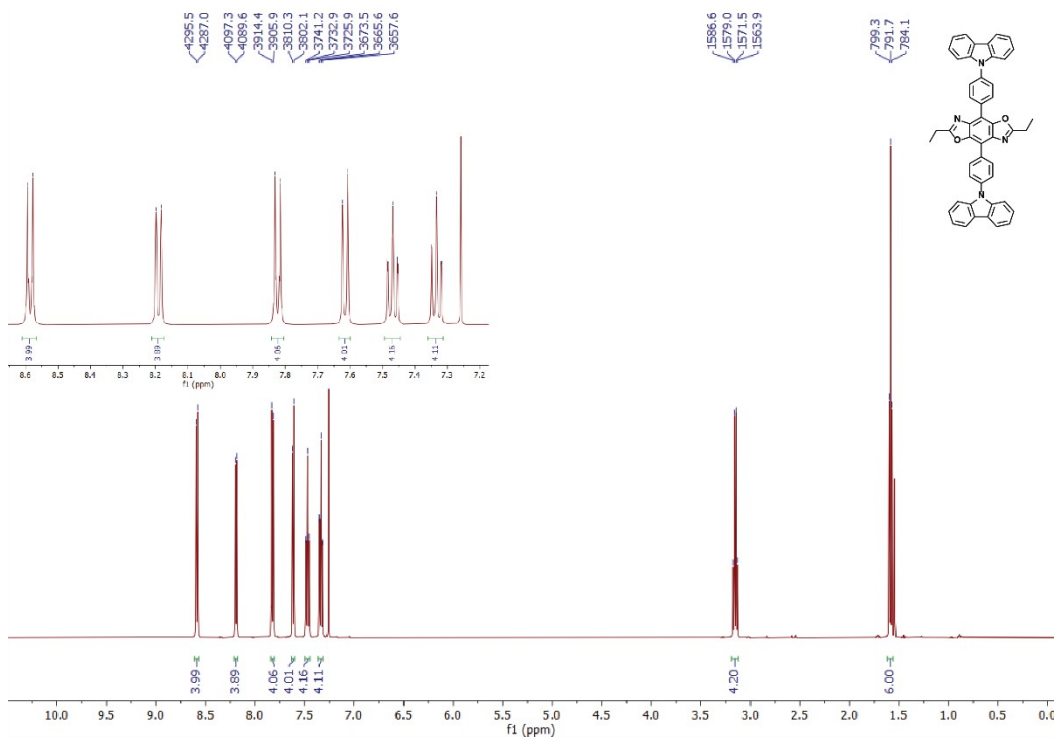


Figure S9. ¹H NMR of C1

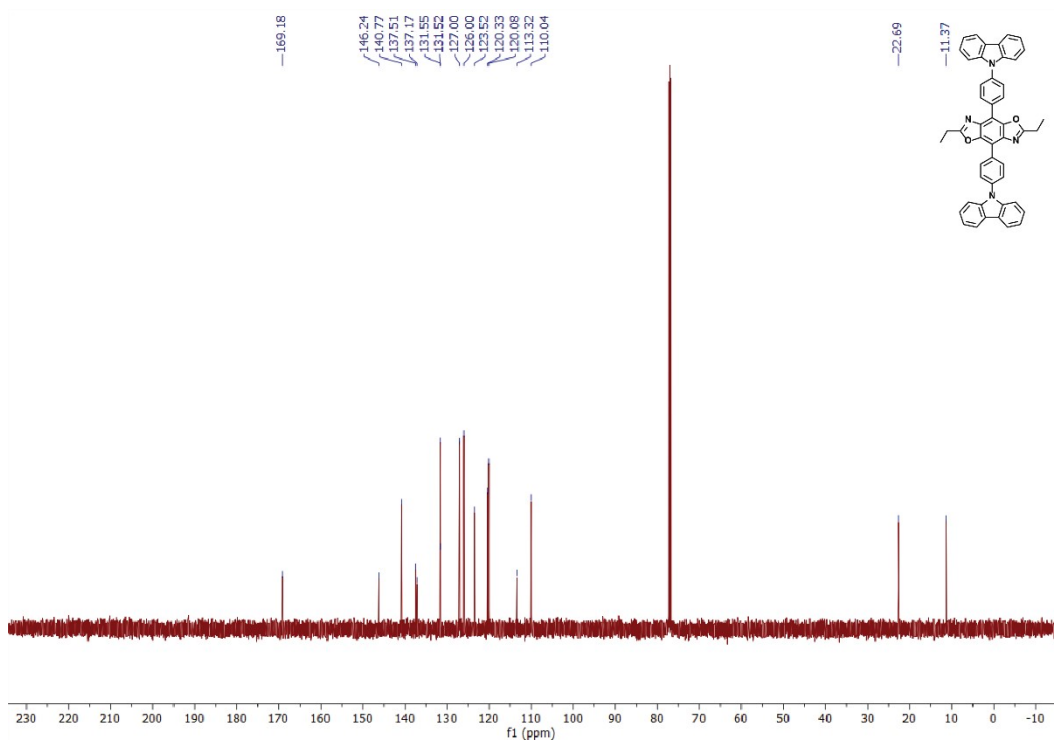


Figure S10. ¹³C NMR of C1

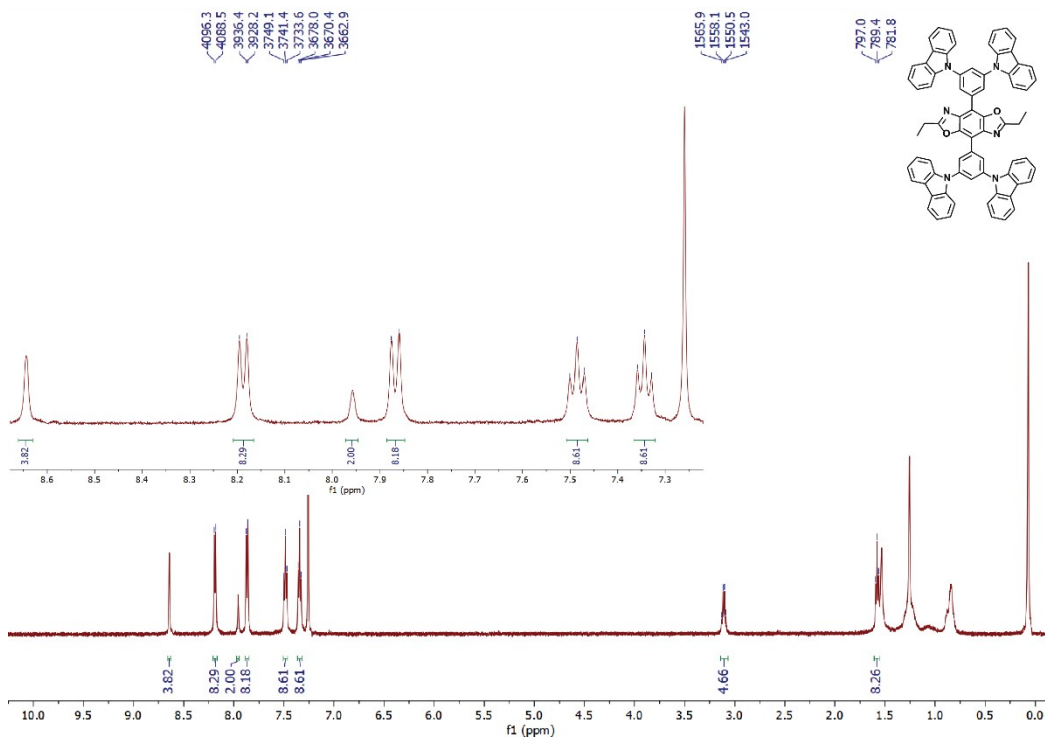


Figure S11. ¹H NMR of C2

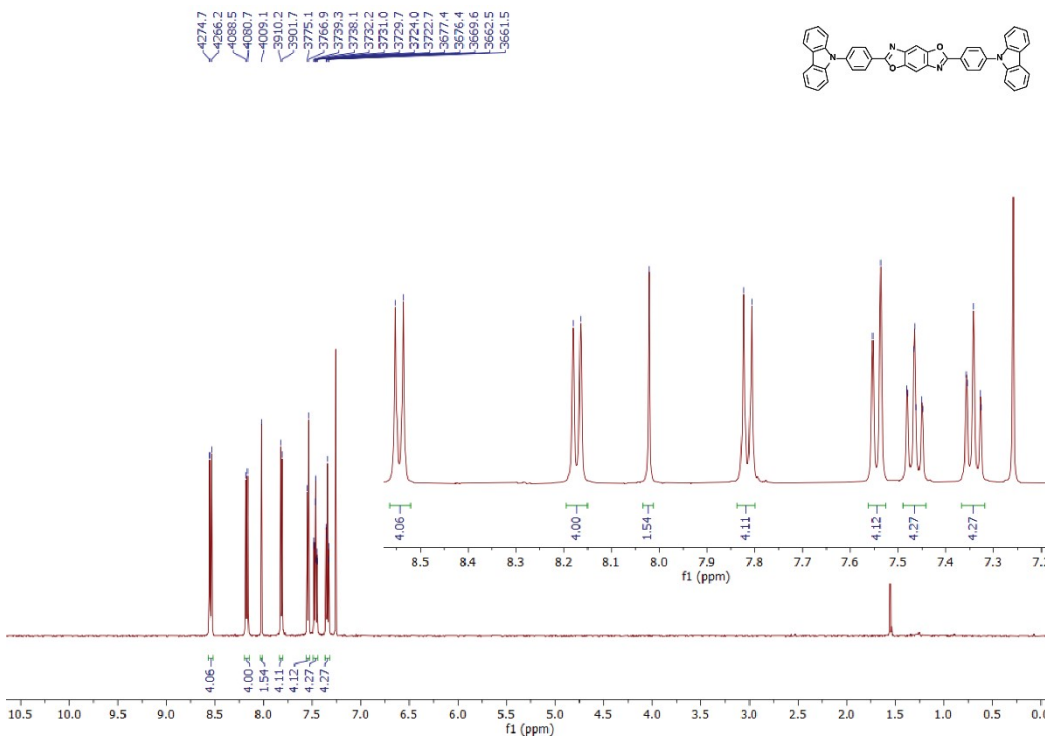


Figure S12. ¹H NMR of C3

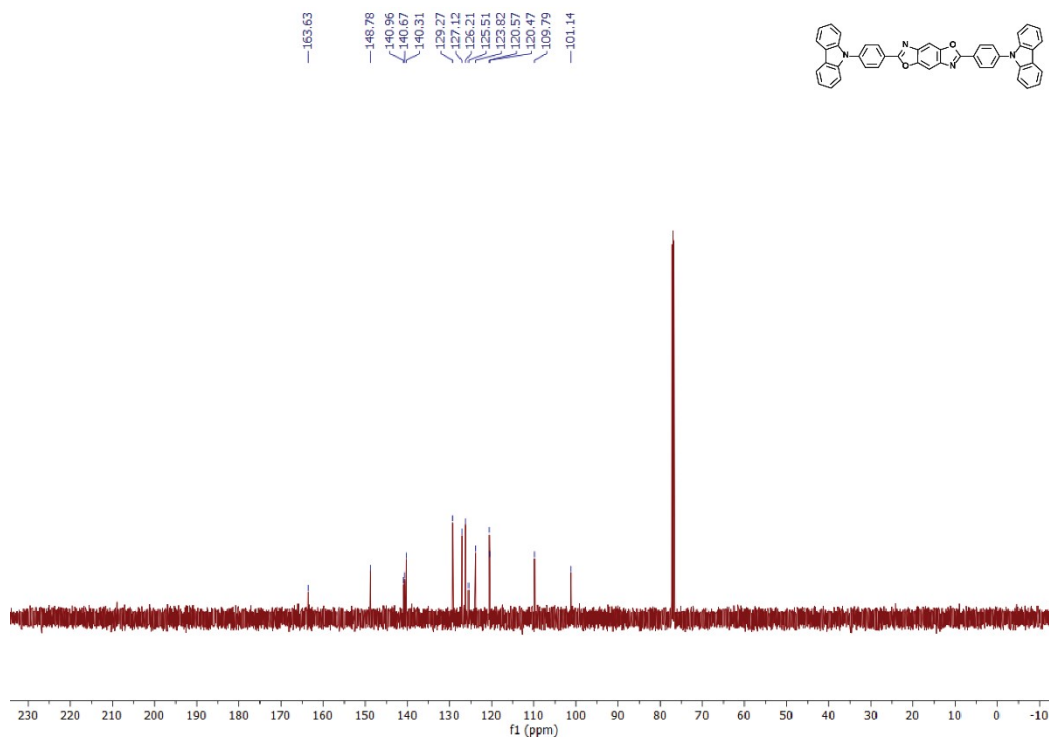


Figure S14. ^{13}C NMR of C3

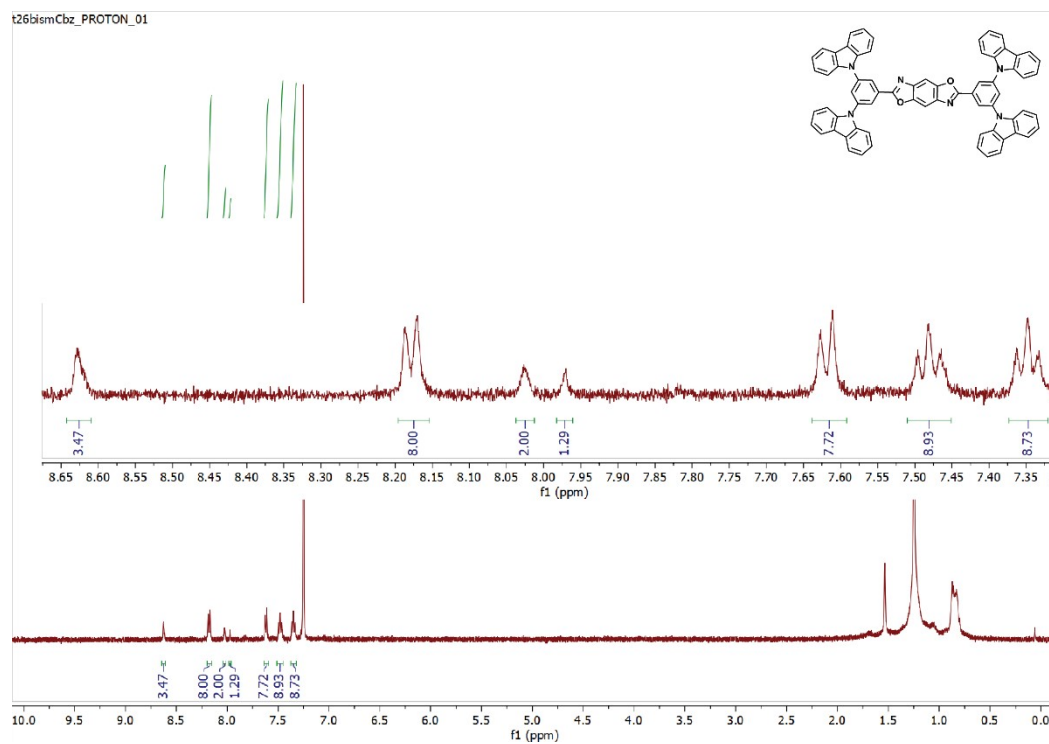


Figure S15. ^1H NMR of C4

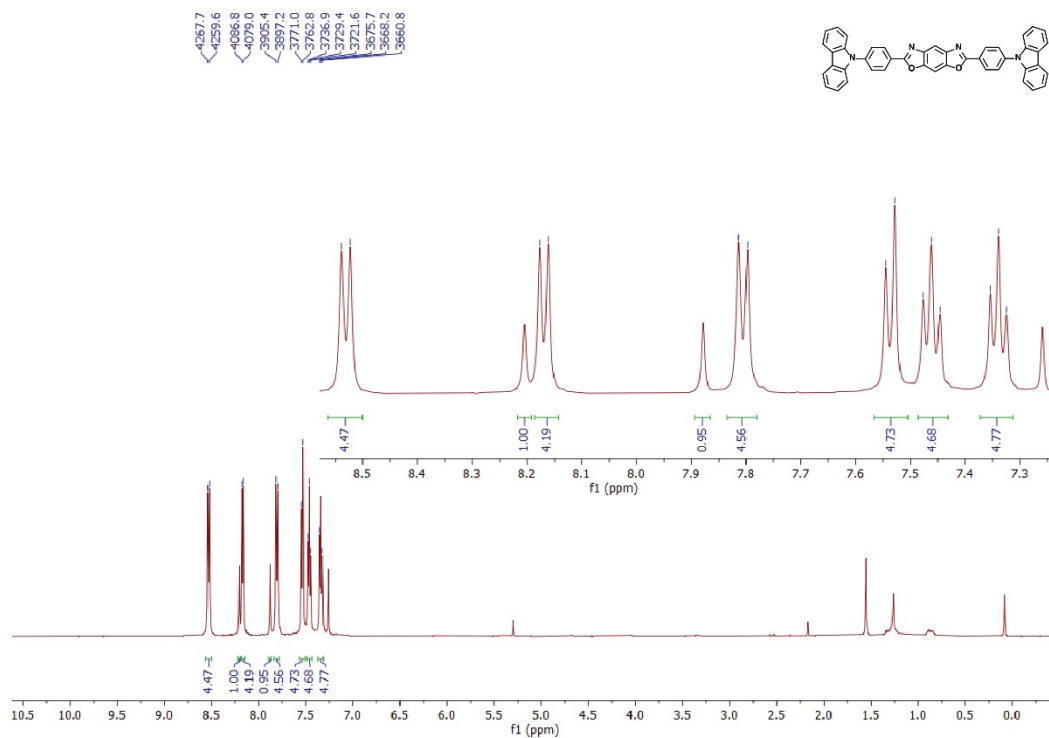


Figure S16. ¹H NMR of C5

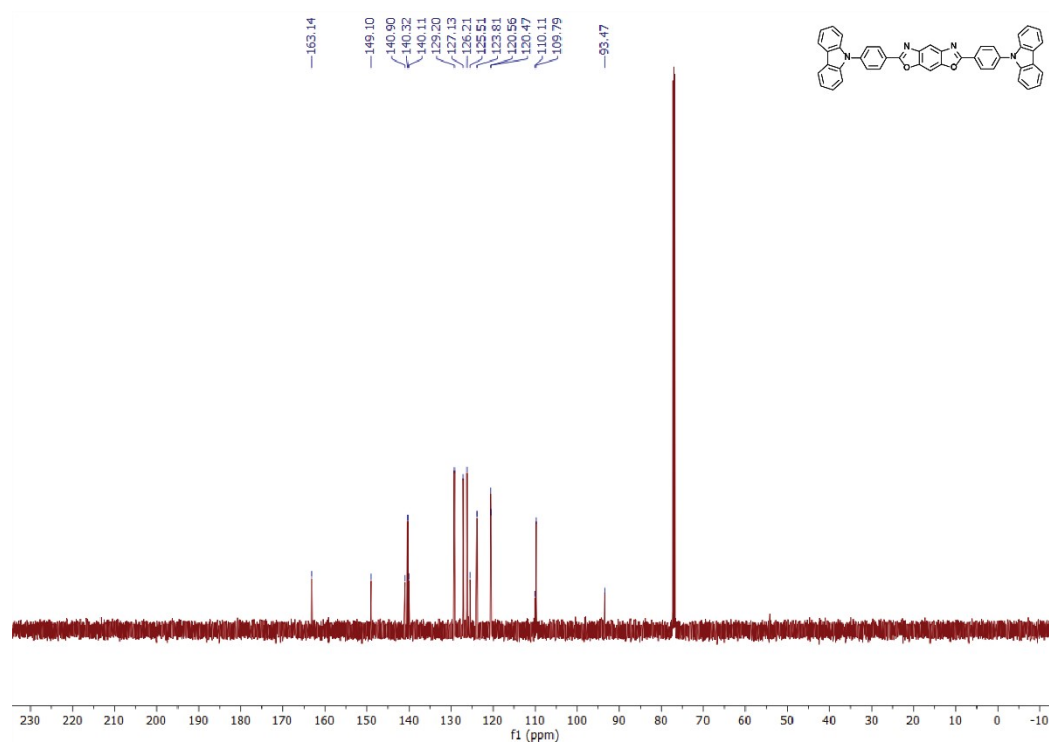
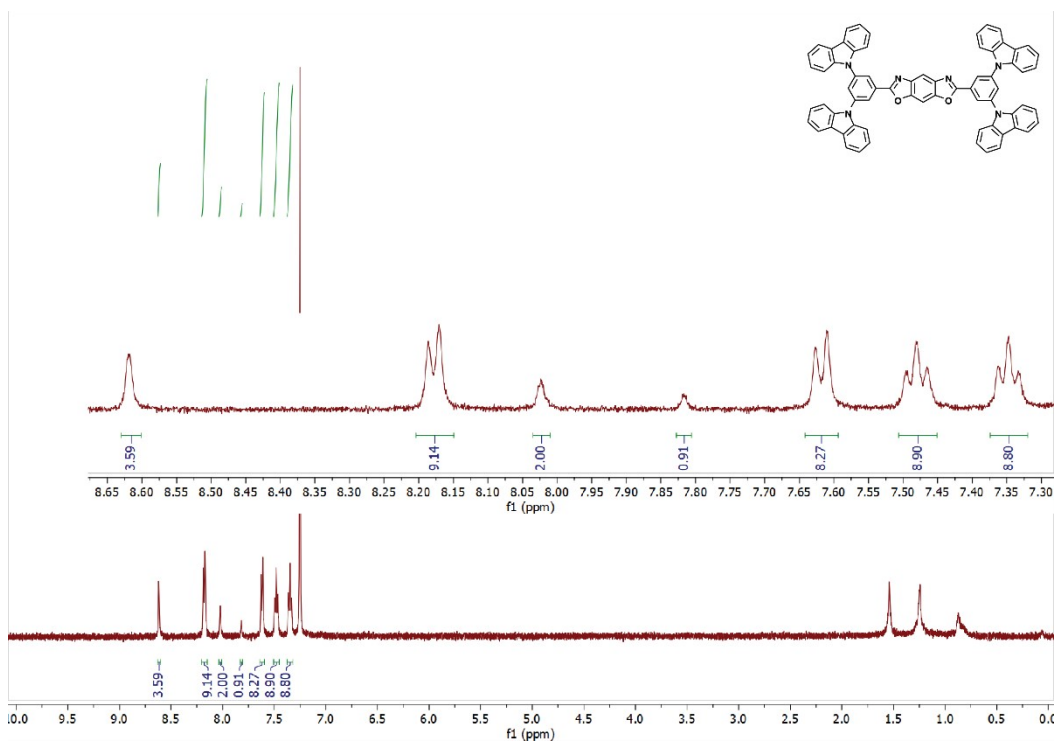


Figure S17. ¹³C NMR of C5



FigureS18 ##. ¹H NMR of C6

Experimental Absorbance and Emission Spectra

Thin film Spectra

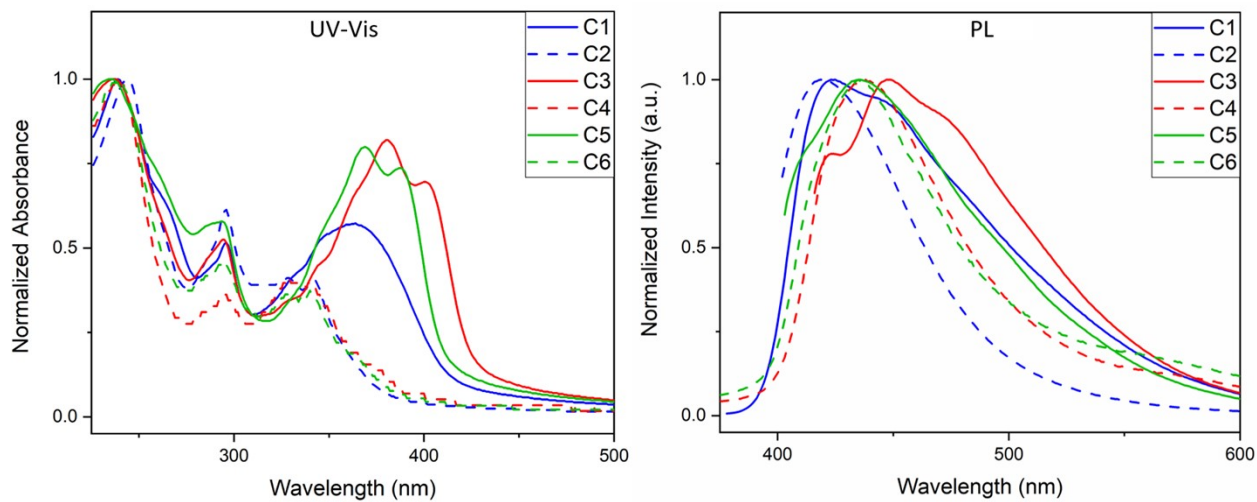


Figure S19. UV-vis (left) and photoluminescence (right) spectra of the six BBOs as thin-films.

BBO	Steady-State			Transient				
	ϕ_{UP} (%)	ϕ_P (%)	ϕ_{TADF}	k_{rISC} (s ⁻¹)	τ_{ESA} (s)	k_{ESA} (s ⁻¹)	τ_{Ph} (s)	k_{Ph} (s ⁻¹)
C1	68	82	0.160	-	-	-	-	-
C2	10	15	0.050	4.30E+04	1.16E-06	8.59E+05	1.92E-06	5.21E+05
C3	42	51	0.110	-	-	-	-	-
C4	3.9	4.7	0.008	5.68E+03	1.41E-06	7.10E+05	1.54E-06	6.51E+05
C5	27	33	0.100	-	-	-	-	-
C6	4.8	6.2	0.014	1.41E+04	9.92E-07	1.01E+06	1.15E+06	8.68E+05

Table S1. Key steady-state and transient data. UP = unpurged. P = purged. rISC = reverse intersystem crossing. ESA = excited state absorption. Ph = phosphorescence.

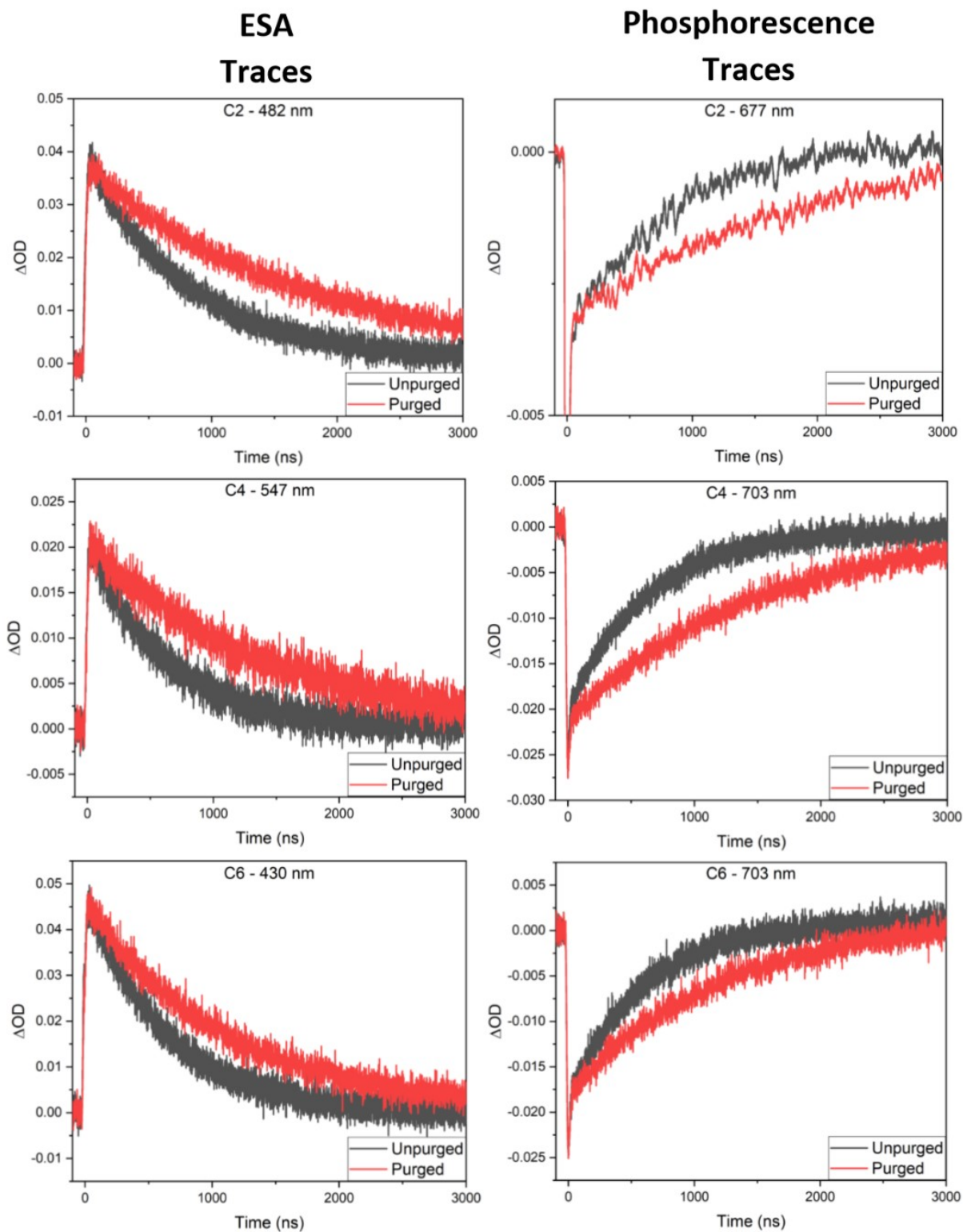


Figure S20. Kinetic traces of the excited state absorbance (right column) and phosphorescent (left column) features. Excitation peak was taken from the maxima of each feature in the transient absorbance curves.

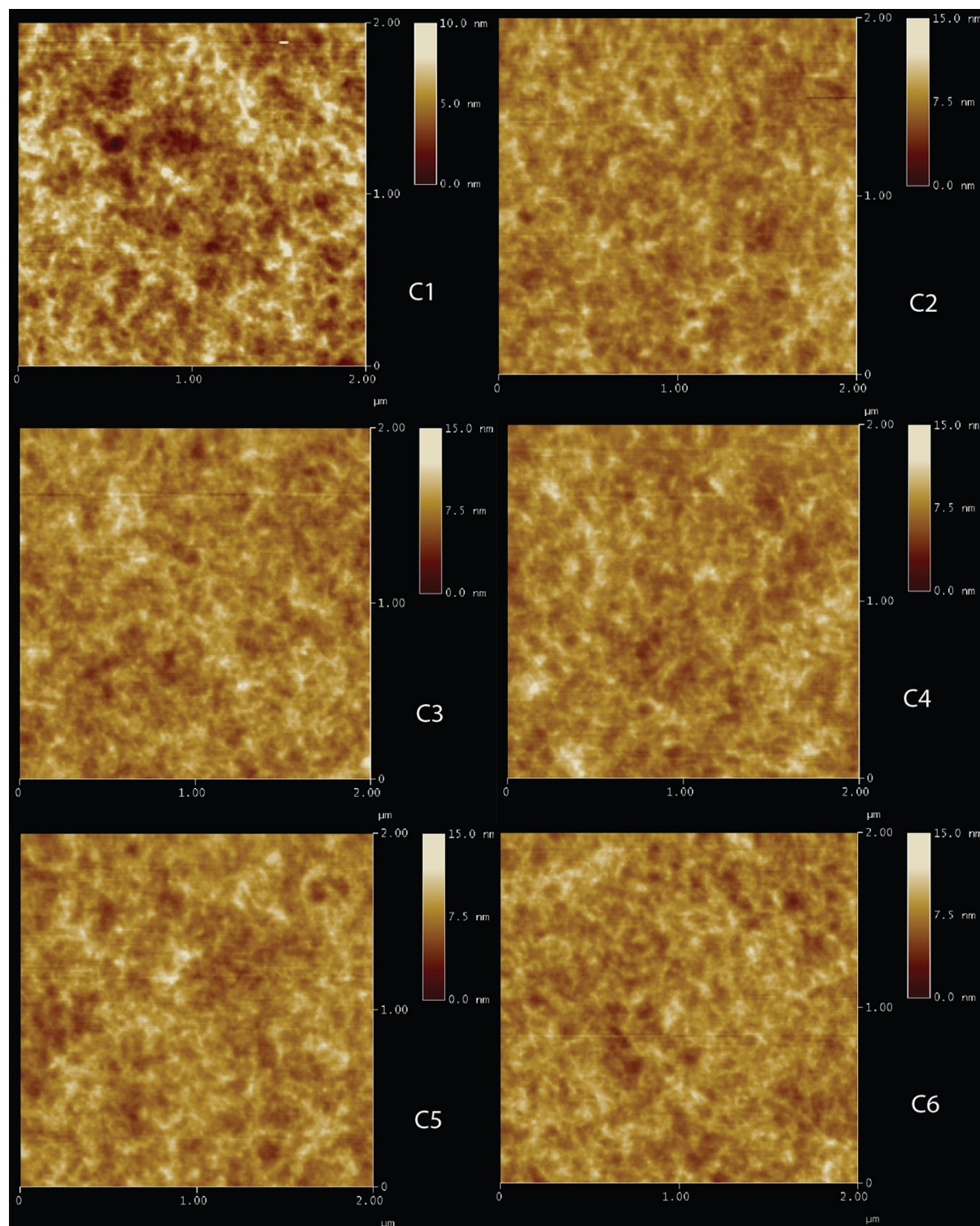


Figure S21. AFM images of the active layer of each OLED device.

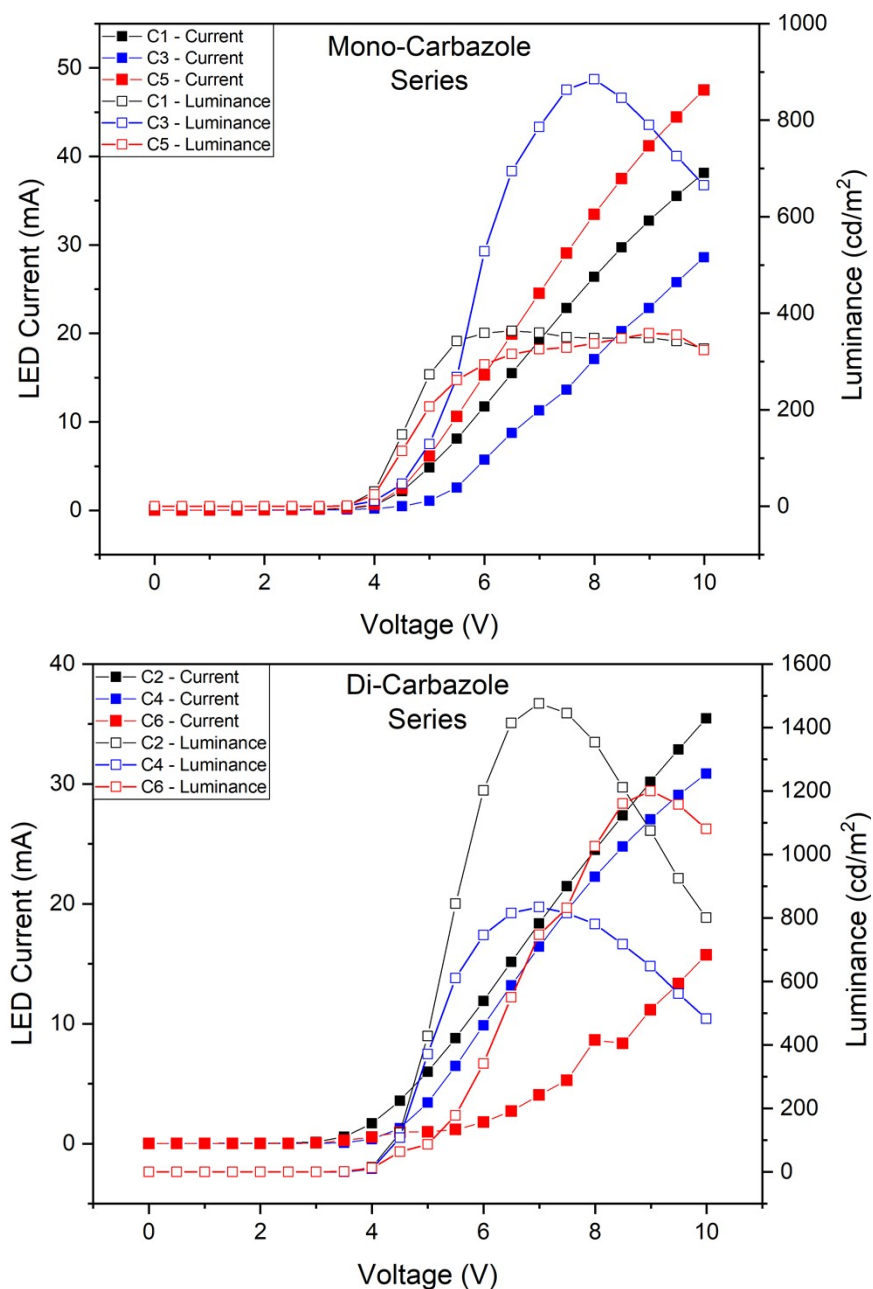


Figure S22. Current-voltage-luminance data of the six BBOs.

References

- (1) Tlach, B. C.; Tomlinson, A. L.; Bhuwarka, A.; Jeffries-EL, M. Tuning the Optical and Electronic Properties of 4,8-Disubstituted Benzobisoxazoles via Alkyne Substitution. *J. Org. Chem.* **2011**, *76* (21), 8670–8681. <https://doi.org/10.1021/jo201078w>
- (2) Tlach, B. C.; Tomlinson, A. L.; Ryno, A. G.; Knoble, D. D.; Drochner, D. L.; Krager, K. J.; Jeffries-El, M. Influence of Conjugation Axis on the Optical and Electronic Properties of Aryl-Substituted Benzobisoxazoles. *J. Org. Chem.* **2013**, *78* (13), 6570–6581. <https://doi.org/10.1021/jo4007927>.

- (3) Mike, J. F.; Makowski, A. J.; Jeffries-EL, M. An Efficient Synthesis of 2,6-Disubstituted Benzobisoxazoles: New Building Blocks for Organic Semiconductors. *Org. Lett.* **2008**, *10* (21), 4915–4918. <https://doi.org/10.1021/ol802011y>.
- (4) Gidron, O.; Dadvand, A.; Sheynin, Y.; Bendikov, M.; Perepichka, D. F. Towards “Green” Electronic Materials. α -Oligofurans as Semiconductors. *Chem. Commun.* **2011**, *47* (7), 1976–1978. <https://doi.org/10.1039/C0CC04699J>.
- (5) Liu, Y.; Wu, P.; Jiang, J.; Wu, J.; Chen, Y.; Tan, Y.; Tan, C.; Jiang, Y. Conjugated Polyelectrolyte Nanoparticles for Apoptotic Cell Imaging. *ACS Appl. Mater. Interfaces* **2016**, *8* (34), 21984–21989. <https://doi.org/10.1021/acsami.6b09347>.
- (6) Shcherbina, M. A.; Borshchev, O. V.; Pleshkova, A. P.; Ponomarenko, S. A.; Chvalun, S. N. When Dendrimers Are Not Better – Rational Design of Nanolayers for High-Performance Organic Electronic Devices. *Nanoscale* **2019**, *11* (10), 4463–4470. <https://doi.org/10.1039/C8NR09241A>.