



Cite this: *J. Mater. Chem. C*, 2016,
4, 3765

Benzobisoxazole cruciforms: a tunable, cross-conjugated platform for the generation of deep blue OLED materials†

Ramiro Chavez III,^a Min Cai,^b Brian Tlach,^a David L. Wheeler,^c Rajiv Kaudal,^b Ayuna Tsyrenova,^{bd} Aimée L. Tomlinson,^c Ruth Shinar,^e Joseph Shinar^b and Malika Jeffries-EL^{*a}

Four new cross-conjugated small molecules based on a central benzo[1,2-*d*:4,5-*d'*]bisoxazole moiety possessing semi-independently tunable HOMO and LUMO levels were synthesized and the properties of these materials were evaluated experimentally and theoretically. The molecules were thermally stable with 5% weight loss occurring well above 350 °C. The cruciforms all exhibited blue emission in solution ranging from 433–450 nm. Host–guest OLEDs fabricated from various concentrations of these materials using the small molecule host 4,4'-bis(9-carbazolyl)-biphenyl (CBP) exhibited deep blue-emission with Commission Internationale de L'Eclairage (CIE) coordinates of ($0.15 \leq x \leq 0.17$, $0.05 \leq y \leq 0.11$), and maximum luminance efficiencies as high as $\sim 2 \text{ cd A}^{-1}$. These results demonstrate the potential of benzobisoxazole cruciforms as emitters for developing high-performance deep blue OLEDs.

Received 3rd November 2015,
Accepted 19th January 2016

DOI: 10.1039/c5tc03622d

www.rsc.org/MaterialsC

Introduction

Due to the multitude of everyday applications conceivable for organic semiconductors, the field of organic electronics is rapidly developing.¹ Research in this area is motivated by the many benefits of these materials, which include the relative abundance of carbon, the reduced fabrication cost attained *via* solution processing, and the opportunity to optimize the material properties for specific applications through organic synthesis. Initially, conjugated polymers were investigated for organic electronic applications.² However, since the properties of conjugated polymers are a function of the materials structure and morphology, variations in the molecular weight, dispersity, defects and purity can dramatically impact their performance.³ Furthermore, current methods for the synthesis of conjugated polymers make consistency between batches difficult. As a result the reported performance

of conjugated polymers in organic solar cells (OSC)s, organic light emitting diodes (OLED)s, and organic field effect transistors can vary widely. In contrast, mono-disperse conjugated molecules possess well-defined molecular structures, and can be consistently synthesized with high purity.⁴ Initially, studies on these molecules focused on simple systems comprising one building block.⁵ In recent years, combining alternating electron donating (D) and electron accepting (A) moieties within the same (macro)molecule has emerged as an effective way to manipulate the position of its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). To date, a number of different donor–acceptor molecules have been synthesized and OSCs using small molecules as the active layer have recently reached record-breaking efficiencies above 9.0%.⁶ Small molecules are the materials of choice in commercial OLEDs due to their superior efficiency and color purity in comparison to polymers.⁷ However, until recently, small molecule OLEDs (SMOLEDs), have suffered from limited solubility.⁸ Therefore there is a need for the development of new materials that can be solution-processed.

While the donor–acceptor approach enables the tuning of the materials' frontier molecular orbitals (FMO)s, due to the extensive delocalization of electrons within conjugated systems most chemical modifications impact the position of both the HOMO and LUMO levels. One tactic to circumvent this phenomenon is through the synthesis of two-dimensional cross-conjugated molecules comprising two perpendicular π -conjugated linear units that intersect *via* a central aromatic core. As a result

^a Department of Chemistry, Iowa State University, 1605 Gilman Hall, Ames IA, 50011, USA. E-mail: malikaj@iastate.edu

^b Ames Laboratory-USDOE and Department of Physics and Astronomy, Iowa State University, Ames IA, 50011, USA

^c Department of Chemistry and Biochemistry, University of North Georgia, 82 College Circle, Dahlonega GA, 30041, USA

^d National University of Science & Technology (NUST MISIS), Moscow, Russia

^e Microelectronics Research Center and Department of Electrical and Computer Engineering, Iowa State University, Ames, IA 50011, USA

† Electronic supplementary information (ESI) available: ¹H and ¹³C NMR spectra, cyclic voltammograms and details for the synthesis of intermediates. See DOI: 10.1039/c5tc03622d





Scheme 1 Synthesis of BBO cruciform.

Fig. 1 Photoluminescence spectra of **SM 1–SM 4**.

strong blue-emission in solution (433–450 nm). **SM 1**, **SM 2** and **SM 4** all had broad, featureless peaks, whereas **SM 3** had a fairly shifted shoulder. The fluorescence quantum yields in solution as **SM 1** was the lowest, **SM 4** the highest and the constitutional isomers, **SM 2** and **SM 3** were identical. The electrochemical properties of the BBOs were investigated by cyclic voltammetry (CV) using a platinum working electrode in acetonitrile, with 0.1 M Bu_4NPF_6 as the electrolyte and an Ag/Ag^+ reference electrode. The onsets were referenced to Fc/Fc^+ and the results are summarized in Table 1. All of the materials exhibited measurable and reproducible oxidation and reduction processes. The HOMO values of the BBOs were similar,¹⁵ ranging from -6.0 to -6.2 eV, whereas the LUMO levels ranged from -2.7 to -3.7 eV. **SM 1**, with phenyl substituents in all four positions, had the deepest HOMO level (-6.2 eV), and the highest-lying LUMO level (-2.7 eV), resulting in the widest band gap. For the mixed systems possessing both fluorenyl and phenyl groups

Table 1 Optical and electronic properties for **SM 1–SM 4**

BBO	Abs $\lambda_{\text{max}}^{\text{film}}$ (nm)	PL $\lambda_{\text{max}}^{\text{film}}$ (nm)	Φ_{PL}	$E_{\text{g}}^{\text{opt}a}$ (eV)	HOMO ^b (eV)	LUMO ^c (eV)	$E_{\text{g}}^{\text{EC}d}$ (eV)
SM 1	355	433	0.34	3.1	-6.2	-2.7	3.5
SM 2	364	441	0.51	2.9	-5.7	-3.5	2.2
SM 3	386	444	0.51	2.9	-6.0	-3.7	2.3
SM 4	395	450	0.71	2.8	-6.0	-3.5	2.5

^a Estimated from the absorption onset of the film. ^b HOMO = $-(E_{\text{onset}}^{\text{ox}} + 4.8)$ eV. ^c LUMO = $-(E_{\text{onset}}^{\text{red}} + 4.8)$ eV. ^d $E_{\text{g}}^{\text{EC}} = \text{LUMO} - \text{HOMO}$.



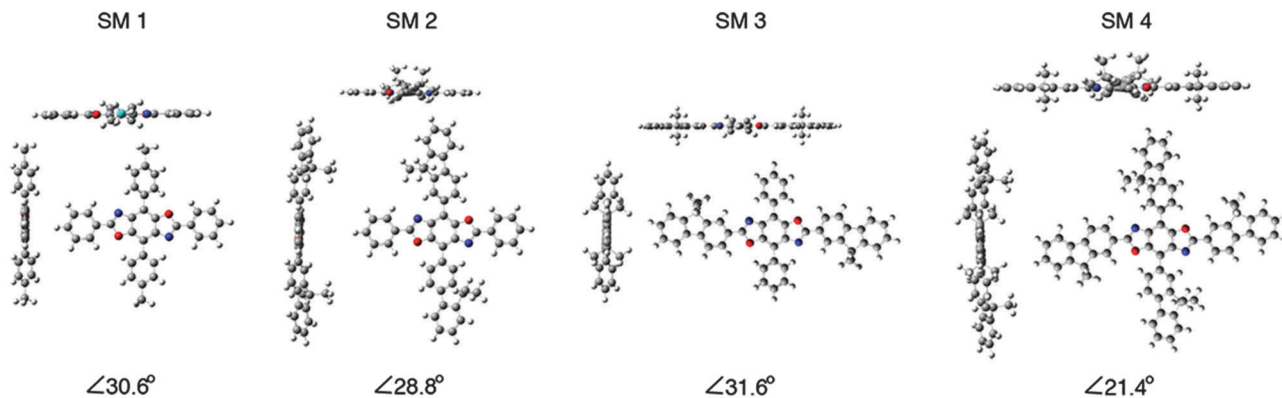


Fig. 3 Optimized geometries for **SM 1–SM 4**.

diagrams and the EL spectra of devices comprising the CBP host and 10% of the guest (**SM 1**, **SM 2** or **SM 3**) are shown in Fig. 4 and 5a, respectively. Due to the poor performance of the device from **SM 1**, the EL spectra could not be obtained. This result is not surprising as both the HOMO and LUMO levels for **SM 1** are outside those for the CBP host. The emission maximum of **SM 2** is red-shifted 11 nm from **SM 3**, demonstrating the influence of the direction of the extended conjugation axis. Similarly, the emission maximum of **SM 4** was red-shifted 22 nm relative to **SM 3** as a result of extended conjugation. The EL spectrum for **SM 3** is similar in width and shape to its emission spectrum, but the peak widths at half-maximum for the EL spectra of **SM 2** and **SM 4** are considerably narrower than their emission spectra. The normalized electroluminescent spectra of devices with different weight% concentrations of the BBO's in the CBP host are shown below in Fig. 5. The key performance parameters of these OLEDs are summarized in Table 3. It can be seen from these plots that the host is quenched upon the addition of ~5% of the guest molecule, indicating that there is efficient energy transfer from the host to the emitters. Interestingly, the best devices were obtained when 10 wt% of the guest was used. These results are also an

improvement from our previous work where BBO polymer: CBP host systems were studied, as emission was not observed with 10% doping levels.¹⁹ This relatively high concentration of the guest suggests that excellent guest–host mixing is occurring in this system, as OLEDs based on neat films of the cruciforms exhibited strong concentration quenching. Such quenching is often a result of strong π -stacking within conjugated systems. Based on the optimized geometries in Fig. 3, we could surmise that **SM 2**, was the least planar and thus least susceptible to intermolecular aggregation. Indeed, **SM 2**, gave the best performance of all the molecules with an efficiency of $\sim 2 \text{ cd A}^{-1}$ and a peak emission at 443 nm, when doped into the host at 10 wt%. The CIE 1931 coordinates for **SM 2** of $x = 0.16$, $y = 0.05$, were well into the deep blue region. Interestingly, switching the conjugation axis had a detrimental impact on the OLED performance as **SM 3** had the lowest efficiency, luminescence and EQE regardless of the doping level. This may be a result of the difference in the distribution of the electron density within the system as seen in the frontier orbitals, Fig. 3. Another contributing factor is that the deep HOMO level of **SM 3** is close to that of the CBP guest. However, since **SM 4** has the same HOMO level as **SM 3** and performed significantly better, energy level misalignment is not likely the cause of the poor performance. In the future we will utilize a wider band gap host to further evaluate this phenomena. The device made using 2% of **SM 4** gave the second best performance an efficiency of $\sim 1.9 \text{ cd A}^{-1}$, with peak emission at 443 nm, and CIE 1931 coordinates $x = 0.15$, $y = 0.09$, which are close to the National Television System Committee (NTSC) blue color standard (0.14, 0.08).^{18,20} These are very promising materials considering that the photopic factor is only 0.023 at $\sim 445 \text{ nm}$. Furthermore, considering that the PL quantum yield is only 0.5, the maximum internal quantum efficiency is only $\sim 0.25 \times 0.5 = 0.125$ (yield of singlets times PL quantum yield), and the EQE is about $\sim 0.2 \times 0.125 = 0.025 = 2.5\%$, since the outcoupling factor in these conventional bottom-emitting-through-the-glass OLEDs with ITO is $< 20\%$. Hence, based on the Φ_{PL} of the emitting materials, the EQE of the deep blue fluorescent OLEDs based on **SM 2** and **SM 4** are close to the maximal possible values.



Fig. 4 Energy level diagram of **SM 1–SM 4** and CBP host.





Fig. 5 Electroluminescence spectra of SM 2–SM 4 (top left), and EL emission at various concentrations as noted.

Table 3 Device characteristics of SMOLEDs based on BBO cruciforms

Dopant	Device wt%	V_{on} [V]	Drive voltage [V]	Current density J , [mA cm ⁻²]	Brightness [cd m ⁻²]	Efficiency [cd A ⁻¹ , lm W ⁻¹ (% EQE)]	λ_{max}^{EL} [nm]	CIE 1931 [x, y, y']
SM 2	1.0	4.2	6.2	392	1155	0.93, 0.61, 1.82	433, 400	0.16, 0.05, 0.79
	2.0	4.0	6.0	439	2152	1.30, 0.85, 2.33	436, 400	0.16, 0.05, 0.79
	5.0	4.4	6.6	489	1141	0.71, 0.45, 1.08	439, 400	0.16, 0.06, 0.78
	10.0	4.0	7.0	336	1051	2.05, 1.40, 2.95	443, 400	0.16, 0.05, 0.79
SM 3	1.0	5.0	8.0	365	275	0.33, 0.20, 0.60	425, 400	0.17, 0.06, 0.78
	2.0	5.2	6.4	74	148	0.25, 0.13, 0.37	428, 400	0.16, 0.07, 0.77
	5.0	4.8	8.4	497	801	0.45, 0.25, 0.58	430, 400	0.17, 0.08, 0.76
	10.0	4.2	8.2	583	779	0.50, 0.33, 0.76	430, 400	0.16, 0.06, 0.78
SM 4	1.0	4.0	6.3	360	1649	1.23, 0.77, 1.55	450, 400	0.15, 0.09, 0.76
	2.0	4.0	6.4	350	1568	1.93, 1.24, 2.22	450, 400	0.15, 0.09, 0.76
	5.0	3.9	6.4	404	1412	1.09, 0.67, 1.01	450, 400	0.16, 0.11, 0.73
	10.0	3.6	6.9	606	1159	1.29, 0.97, 1.20	450, 400	0.15, 0.11, 0.74

Conclusions

In summary, we have synthesized four cross-conjugated, blue light emitting materials based on benzo[1,2-*d*:4,5-*d'*]bisoxazole. The HOMO and LUMO levels of these materials were readily tuned *via* substitution pattern to afford materials with wide-band gaps. Structure–property studies reveal that such modifications not

only impact the energy levels and band gaps, but they also affect the electron density and planarity within the systems. As a result, the performance of the OLEDs varied depending upon structure. Non-optimized OLEDs achieved EQE approaching 3% and efficiency of ~ 2 cd A⁻¹ with a relatively narrow EL band peaking at 443 nm and a CIE_y ≤ 0.05 . Collectively these results indicate that the synthesis of BBO cruciforms is a



promising strategy for the design of efficient deep-blue OLEDs. Future work is ongoing in our labs on OLED optimization and synthesis of new materials. These will be reported in due course.

Experimental

Materials and measurements

Br-DAHQ (**1**),²¹ polyphosphoric acid, silyl ester (PPSE),²² were synthesized according to literature procedures. THF and toluene were 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 600 MHz (¹H) AND 800 MHz (¹³C). In all spectra, chemical shifts are given in δ relative to tetramethylsilane. Coupling constants are reported in hertz (Hz). High-resolution mass spectra were recorded on a double-focusing magnetic sector mass spectrometer using ESI or APCI. Melting points were obtained on a melting point apparatus with 260 °C upper limit and are uncorrected. All UV-Vis and fluorescence spectroscopy were obtained using CHCl₃ solutions unless otherwise noted. Relative solution fluorescence quantum yields were obtained using 9,10-diphenylanthracene (Φ_{PL} = 0.885 in ethanol)²³ as a standard with excitation at 372 nm.

4,8-Dibromo-2,6-diphenylbenzo[1,2-*d*:4,5-*d'*]bis(oxazole) (**2**).

In a dried round-bottomed flask (RBF), a fresh prepared solution of poly-phosphosilylether (PPSE) (5 g in 20 mL of *o*-DCB) and **1** was degassed for 20 minutes. Benzoyl chloride was added and the solution was refluxed for 2 days under argon. The solution was allowed to cool to room temperature and crashed into cold methanol (−78 °C). The precipitate was filtered and refluxed in EtOH to remove the red color, resulting in a tan powder. The resulting product was used without further purification. M.P. > 260 °C Due to the poor solubility of the product, NMR spectra were not obtained.

4,8-Dibromo-2,6-bis(9,9-dihexyl-9H-fluoren-2-yl)benzo[1,2-*d*:4,5-*d'*]bis(oxazole) (**6**).

In a dried RBF, compound **1** (1.49 g, 5 mmol) and a fresh prepared solution of poly-phosphosilylether (PPSE) (2 g in 20 mL of DCE) were degassed for 20 minutes and then heated at reflux for 3 days under argon. The solution was allowed to cool to room temperature and quenched with 2 M sodium hydroxide and extracted with methylene chloride. The combined organic layers were washed with 2 M hydrochloric acid, water, brine and dried over sodium sulphate then concentrated. The resulting residue was filtered a small silica gel column with CH₂Cl₂ and concentrated *in vacuo*. The residue was put through a second column with 80/20 v/v hexanes/CH₂Cl₂. The solution was concentrated and recrystallized from ethyl acetate.

M.P. > 260 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.36 (2H, d, *J* = 4), 8.30 (2H, s), 7.86 (2H, d, *J* = 8), 7.79 (2H, dd, *J* = 4,4), 7.39 (6H, d, *J* = 4), 2.10 (9H, m), 1.06 (24H, m), 0.75 (12H, t), 0.60 (9H, m); HRMS (ESI) calcd for C₅₈H₆₆N₂O₂Br₂ 981.3564 [M + H]⁺, found 981.3559.

4,8-Bis(4-octylphenyl)-2,6-diphenylbenzo[1,2-*d*:4,5-*d'*]bis(oxazole) (**SM 1**).

In a dried, 3-necked RBF purged with argon, fitted with

an condenser, monomers **2** (117.5 mg, 0.25 mmol) and **3** (174 mg, 0.55 mmol) and were dissolved in degassed toluene. One drop of Aliquot 336 (surfactant) was added to the reaction flask, followed by sodium carbonate (6 mL, 10 mmol). The reaction solution was then deoxygenated for 30 min by pumping argon through the solution. PEPPSI-*i*Pr catalyst (0.0125 mmol) was added and the reaction refluxed for 3 days under argon. The solution was then diluted with toluene and layers separated. Aqueous layer was extracted twice with toluene (2 × 20 mL portions). The combined organic layers were washed with 1 M hydrochloric acid, water, brine and dried with sodium sulfate. After concentration, the residue was purified by column chromatography (gradient hexanes to 50/50 v/v hexanes/dichloromethane). The eluents were concentrated and dissolved in 1.5 mL of chloroform and crashed out into methanol (−78 °C). The resulting powder was taken through a second column by dry packing to silica, following the same gradient then precipitated into MeOH to give the product as a white powder (87 mg, 50%).

M.P. 242 °C, ¹H NMR (600 MHz, CDCl₃) δ 8.34–8.37 (8H, m, *J* = 6, 6 Hz), 7.54 (6H, d, *J* = 6 Hz), 7.47 (4H, d, *J* = 6 Hz), 2.75 (4H, m), 1.75 (4H, m) 1.55 (13H, s) 1.45 (5H, m), 1.38 (4H, m) 1.32 (10H, m) 0.90 (6H, t); ¹³C (400 MHz, CDCl₃) δ 165.68, 152.10, 152.00, 147.37, 146.04, 140.35, 140.21, 128.91, 127.95, 127.53, 124.95, 123.50, 122.84, 121.61, 120.61, 91.86, 56.03, 40.83, 32.01, 30.12, 24.22, 23.03, 14.46; HRMS (ESI) calcd for C₄₈H₅₂N₂O₂ 689.4102 [M + H]⁺, found 689.4087.

4,8-Bis(9,9-dioctyl-9H-fluoren-2-yl)-2,6-diphenylbenzo[1,2-*d*:4,5-*d'*]bis(oxazole) (**SM 2**).

SM 2 was synthesized similarly to **SM 1** from **2** and **4**. The product was obtained as a bright yellow powder (90 mg, 76%).

M.P. 149–152 °C, ¹H NMR (800 MHz, CDCl₃) δ 8.50 (2H, m, *J* = 8,8 Hz), 8.45 (2H, s), 8.37 (4H, dd, *J* = 8,8 Hz), 7.99 (2H, d, *J* = 8 Hz), 7.84 (4H, d, *J* = 8 Hz), 7.75 (2H, d, *J* = 8 Hz), 7.45 (2H, d, *J* = 8 Hz) 7.42 (2H, td, *J* = 8 Hz); 7.38 (2H, td, *J* = 8 Hz), 2.15 (10H, m), 1.17 (18H, m), 0.95 (4H, m), 0.82 (4H, m), 0.78 (14H, t, *J* = 8 Hz); ¹³C (800 MHz, CDCl₃) δ 163.66, 151.51, 150.88, 146.62, 141.28, 141.05, 138.60, 131.61, 131.33, 129.29, 129.27, 129.01, 127.80, 127.50, 127.39, 127.00, 125.07, 125.05, 123.15, 120.16, 119.97, 114.99, 55.37, 40.82, 31.92, 31.90, 30.53, 29.54, 29.53, 29.46, 24.20, 22.73, 22.72, 14.19, 14.18 HRMS (ESI) calcd for C₇₈H₉₂N₂O₂ 1089.7232 [M + H]⁺, found 1089.7228.

2,6-Bis(9,9-dihexyl-9H-fluoren-2-yl)-4,8-diphenylbenzo[1,2-*d*:4,5-*d'*]bis(oxazole) (**SM 3**).

SM 3 was synthesized similarly to **SM 1** from **6** and phenyl boronic ester. The resulting residue was purified by column chromatography (gradient hexanes to 50/50 v/v hexanes/dichloromethane). The product was obtained as light-yellow flakes (97 mg, 40%).

M.P. 214 °C, ¹H NMR (600 MHz, CDCl₃) δ 8.49 (2H, dd, *J* = 6 Hz), 8.44 (2H, s), 8.37 (4H, m), 7.98 (2H, d, *J* = 6 Hz), 7.82 (2H, d), 7.56 (6H, m), 6.14 (6H, m), 2.14 (9H, ddq), 1.13 (45H, dd), 0.76 (14H, t); ¹³C (800 MHz, CDCl₃) δ 164.81, 151.88, 151.68, 146.74, 144.99, 140.37, 138.84, 133.03, 130.69, 130.67, 130.66, 129.01, 128.61, 128.44, 127.34, 127.29, 125.89, 123.30, 122.38, 120.31, 114.45, 55.72, 40.60, 31.85, 29.95, 24.07, 14.31; HRMS (ESI) calcd for C₇₀H₇₆N₂O₂ 977.598 [M + H]⁺, found 977.5982.



2,6-Bis(9,9-dihexyl-9H-fluoren-2-yl)-4,8-bis(9,9-dioctyl-9H-fluoren-2-yl)benzo[1,2-d:4,5-d']bis(oxazole) (SM 4). SM 4 was synthesized similarly to SM 1 from 4 and 6. The product was obtained as yellow crystals (208 mg, 52%).

M.P. 144–146 °C, ¹H NMR (600 MHz, CDCl₃) ¹H NMR (600 MHz, CDCl₃) 8.62 (2H, d, *J* = 6 Hz), 8.55 (2H, s), 8.32 (4H, m, *J* = 12 Hz), 7.99 (2H, d, *J* = 6 Hz), 7.81 (4H, t, *J* = 6 Hz), 7.73 (2H, dd), 7.40 (2H, d, *J* = 6 Hz) 7.33 (10H, m, *J* = 6,6 Hz); ¹³C (800 MHz, CDCl₃) δ 164.44, 151.76, 151.53, 151.11, 146.87, 144.99, 141.48, 141.35, 140.45, 138.90, 131.83, 129.53, 129.50, 128.47, 127.56, 127.32, 127.15, 126.16, 125.05, 125.02, 123.37, 123.32, 122.22, 120.69, 120.34, 120.31, 120.18, 114.70, 55.81, 55.66, 41.13, 40.83, 32.11, 31.89, 30.76, 30.04, 29.70, 29.68, 24.39, 24.10, 22.90, 14.33, 14.31; HRMS (ESI) calcd for C₁₁₆H₁₄₈N₂O₂ 1602.1614 [M + H]⁺, found 1602.1583.

OLED fabrication and characterization

OLEDs were fabricated on nominally 10–20 ohms sq⁻¹, 120–160 nm thick ITO-coated glass substrates (Colorado Concept Coatings). The substrates were first cleaned with a detergent and organic solvents and then treated in a UV/ozone oven to increase the work function of the ITO and hence facilitate hole injection, as described elsewhere. A 60 nm poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) layer was spin-coated onto the ITO and then baked in air at 120 °C for 1 h and next in an argon-filled glove box at 120 °C for another 30 min. Blends of 4,4'-bis(9-carbazolyl)-biphenyl (CBP) and 1, 2, 5 and 10 wt% of SM 1–SM 4 in chlorobenzene solutions were spin-coated on top of the PEDOT:PSS layer in the argon-filled glovebox. The combined concentration of the CBP and guest material was kept constant at 9 mg mL⁻¹. The solution was spin-coated at 4000 rpm for 60 s. The fabricated structure was then annealed at 60 °C for 30 min. Following this annealing step, the samples were transferred to a thermal evaporator within the glovebox, and the 4,7-diphenyl-1,10-phenanthroline (BPhen), LiF, and Al layers were deposited sequentially by thermal evaporation at a base pressure of ~1 × 10⁻⁶ Torr. The OLEDs were characterized by monitoring their electroluminescence (EL) spectra and brightness as a function of the applied voltage, and the luminous and power efficiencies were determined.

Computational details

All of the calculations on these oligomers studied in this work were studied using the Gaussian 03W with the GaussView 4 GUI interface program package. All electronic ground states geometries were optimized using density functional theory (DFT) employing an SVP functional and a 6-31G* basis set. Excited states were generated through time dependent density functional theory (TD-DFT) applied to the optimized ground state for each oligomer. The HOMO, LUMO, band gap, first ten excited states, and UV-Vis simulations were generated from these excited computations. All computations were performed using Gaussian 09 using the Marcy cluster provided by the MERCURY consortium.

Acknowledgements

We would like to thank Dr Sarah Cady, Dr Kamel Harrata and Mr Steven Veysey of Iowa State University (ISU) Chemical Instrumentation Facility for compound analysis. We thank Eeshita Manna for technical assistance. We also thank the National Science Foundation (CHE-1413173) for financial support of this work. RK and JS were partially supported by Basic Energy Sciences, Division of Materials Science and Engineering, USDOE. Ames Laboratory is operated by Iowa State University for the US Department of Energy (USDOE) under Contract No. DE-AC 02-07CH11358. Computational resources were provided in part by the MERCURY consortium (<http://mercuryconsortium.org/>) under NSF grants CHE-0116435, CHE-0521063, CHE-0849677, and CHE-1229354.

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