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Synthesis of benzobisoxazole-based D-π-A-π-D organic chromophores with variable optical and electronic properties*

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Abstract: A series of symmetrical D-π-A-π-D molecules comprised of benzo[1,2-*d*;4,5-*d'*]bisoxazole (BBO) and various arylenevinylenes was synthesized via a Knoevenagel condensation of 2,6-dimethyl BBO and the corresponding aryl aldehydes. The resulting compounds had energy levels that were easily modulated and broad absorptions in the visible spectrum. They also demonstrated high fluorescence quantum yields in solution. The solvatochromism of several derivatives was examined in a number of solvents, and it was found that the emission of the triphenylamine derivative varied by almost 100 nm, depending on the polarity of the solvent. Collectively, these results indicate that the optical and electronic properties of benzobisoxazoles are readily tuned through the choice of aryl co-monomer.

Keywords: organic semiconductors; photovoltaics; polymer chemistry; synthesis; UV–vis spectroscopy.

INTRODUCTION

The design and synthesis of new organic semiconducting materials is of current interest due to the important role these materials play in the development of field effect transistors (FETs) [1,2], light-emitting diodes (LEDs) [3–5], photovoltaic cells (PVCs) [6,7], and other plastic electronics [8,9]. Conjugated small molecules possess optical and electronic properties similar to their polymeric counterparts, making them ideal model compounds for evaluating the impact of various structural modifications. However, in contrast to the related polymers, conjugated small molecules are well defined, preventing batch-to-batch variability [10,11]. Additionally, these compounds are readily synthesized and easily functionalized, making them convenient for structure–property investigations. Currently, a popular strategy for the design of new conjugated polymers is the synthesis of materials composed of electron-donating (D) and electron-accepting (A) moieties [12]. The hybridization of the orbitals from these units results in polymers with narrow bandgaps and/or variable energy levels [13]. Similarly, small molecules based on D-A-D and D-π-A-π-D architectures have been synthesized and investigated for use in a range of applications [11,14,15].

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Conjugated polymers with vinylene linkages are of particular interest as the insertion of a vinyl group between aromatic units diminishes torsional interactions between the adjacent rings, increasing planarity and π-delocalization [16–19]. As a result, materials with vinylene linkages exhibit smaller band gaps than analogous materials without vinylene linkages [11,18,20]. To date, only a limited number of vinylene linked D-π-A-π-D materials have been synthesized [17,21–24]. This is largely due to the difficulty associated with synthesizing appropriate building blocks for use in Heck or Stille cross-coupling reactions. Furthermore, the popular Horner–Wadsworth–Emmons and Gilch methods cannot be used with most electron-deficient building blocks owing to their tendency to decompose in the presence of strong bases [17].

Benzobisoxazoles are electron-deficient moieties that are well known for their exceptional thermal and chemical stability [25,26]. Polymers based on benzobisoxazoles also exhibit efficient electron transport [27,28], photoluminescence [29–31], and third-order nonlinear optical properties [32,33], which makes them promising for use in organic semiconductors. As a result of their robust nature, appropriately functionalized benzobisoxazoles can be incorporated into materials using a variety of carbon–carbon bond-forming reactions [34–38]. Herein we report a facile synthesis of vinylene-linked D-π-A-π-D materials comprised of benzo[1,2-*d*;4,5-*d'*]bisoxazole (BBO). The electron-donating strength of the co-monomers used was varied in order to evaluate the impact of this change on the optical and electronic properties of the resulting materials.

RESULTS AND DISCUSSION

Synthesis of diarylenevinylene benzobisoxazoles

In order to probe the impact of donor strength on the properties of vinylene-linked benzobisoxazoles, we synthesized five different diarylenevinylene benzobisoxazoles (Fig. 1) First we synthesized five different aromatic aldehydes bearing side chains in an effort to improve the solubility of the resulting

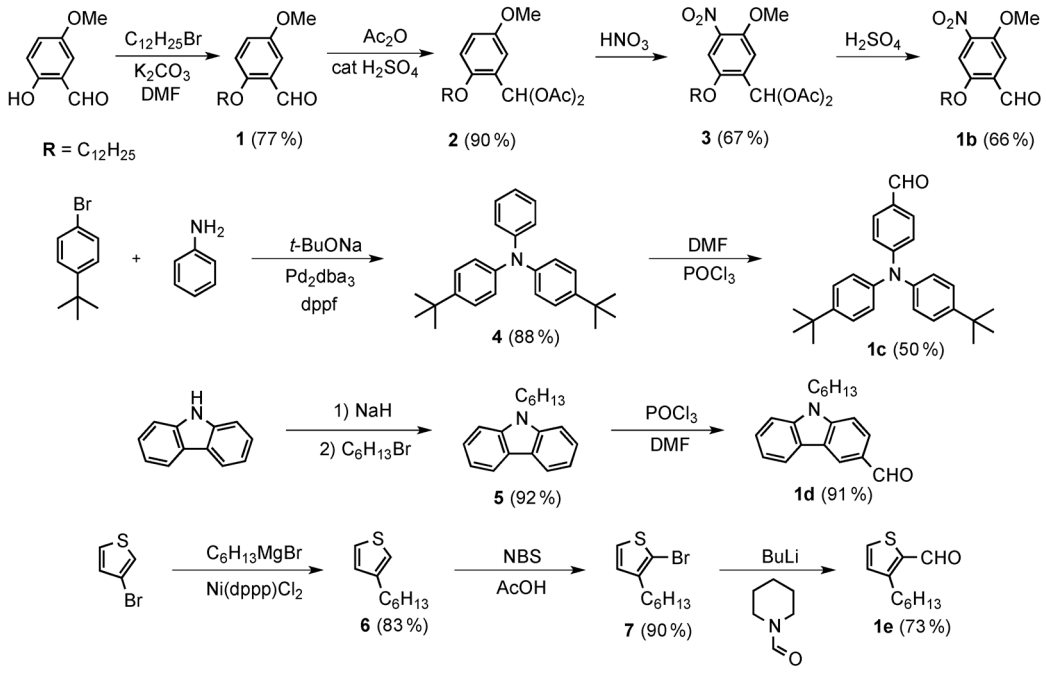

Fig. 1 Synthesis of aromatic aldehydes **1a–e**.

diarylenevinylene benzobisoxazoles. Although the target aldehydes were, for the most part, fairly simple, the synthesis of some had not before been published. Briefly, 2-dodecyloxy-5-methoxybenzaldehyde (**1**) was obtained in good yield by the alkylation of 2-hydroxy-5-methoxybenzaldehyde with dodecyl bromide and potassium carbonate in dimethyl formamide (DMF). The subsequent acylation and nitration of (**1**) yielded 2-dodecyloxy-5-methoxy-4-nitrobenzaldehyde diacetate (**3**), which upon removal of the acetate groups, afforded 2-dodecyloxy-5-methoxy-4-nitrobenzaldehyde (**1b**). The triphenyl amine derivative 4-[*N*,*N*-di(4-*tert*-butylphenyl)amino]benzaldehyde (**1c**) was synthesized in two steps. First the Hartwig–Buchwald reaction between aniline and 4-*tert*-butylbenzene yielded *N*,*N*-di(4-*tert*-butylphenyl)aniline (**4**) [39]. This compound was then transformed to 4-[*N*,*N*-di(4-*tert*-butylphenyl)amino]benzaldehyde (**1c**) via a Vilsmier reaction. Although the synthesis of 9-hexylcarbazole-3-carboxaldehyde (**1d**) has been reported previously [40], we were able to improve upon the published yields significantly. The alkylation of carbazole afforded 9-hexylcarbazole (**5**) in 92 % yield. This compound was then converted to 9-hexylcarbazole-3-carboxaldehyde (**1d**) in 91 % yield via a Vilsmier reaction. Both compounds were easily purified by recrystallization. The synthesis of 3-hexylthiophene-2-carboxaldehyde (**1e**) was achieved by first alkylating 3-bromothiophene via a Kumada cross-coupling reaction, followed by brominating the resulting 3-hexylthiophene (**6**) to obtain 2-bromo-3-hexylthiophene (**7**), which was converted to the desired aldehyde by a metal-halogen exchange reaction and quenching with 1-formylpiperidine.

The general approach for the synthesis of the diarylenevinylene benzobisoxazoles is shown in Fig. 2. The starting material, 2,6-dimethyl BBO was synthesized via the Lewis acid-catalyzed cyclization of diaminohydroquinone with triethyl orthoacetate [34]. The methyl groups of this molecule are activated due to their location at the 2- and 6- positions on the BBO ring, and were readily deprotonated by base. The Knoevenagel condensation between 2,6-dimethyl BBO and the various aromatic aldehydes proceeded smoothly and with good yields. The resulting diarylenevinylene benzobisoxazoles

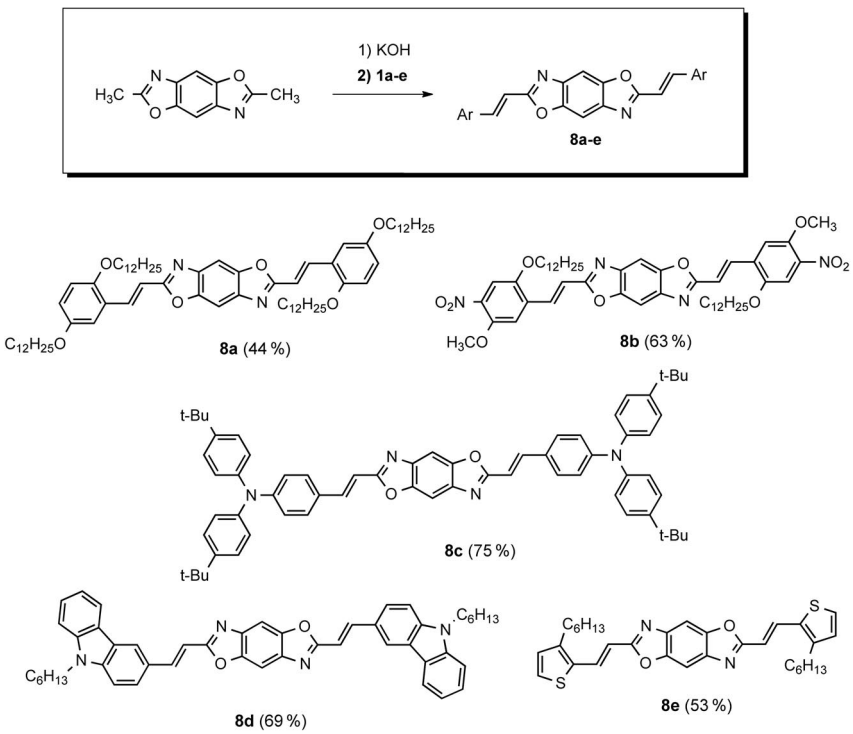

Fig. 2 Synthesis of diarylenevinylene benzobisoxazoles **8a–e**.

were all obtained as solids that were readily purified by recrystallization, gave sharp melting points and clean ^{1}H and ^{13}C NMR spectra that were consistent with the proposed structures.

Optical properties

The optical properties of diarylenevinylene benzobisoxazoles were examined using UV–vis and steady-state fluorescence spectroscopy in chloroform. The absorption and fluorescence spectra are shown in Fig. 3. The significant optical and electronic properties are summarized in Table 1. The 2-dodecyloxy-5-methoxybenzene-substituted BBO **8a** had a λ_{max} at 403 nm and upon excitation at this wavelength **8a** exhibited blue–green emission at 476 nm with a good fluorescence quantum yield (Φ_{fl}) of .33 %. For **8b**, the addition of an electron-deficient nitro group at the 4-position of the benzene ring resulted in a bathochromic shift of the absorption maxima to 453 nm. Upon excitation at its absorption maxima, **8b** exhibited weak green emission at 502 nm with a low fluorescence quantum yield (Φ_{fl}) of 0.1 %. This decrease in quantum yield was likely caused by an electron transfer process in the excited state induced by the presence of the nitro group [41]. The 3-hexylthiophene-substituted BBO **8e** had an absorbance maximum at 410 nm and upon excitation at this wavelength, **8e** exhibited blue–green emission at 479 nm with a Φ_{fl} of 3.8 %. Similarly, the *N*-hexylcarbazole-substituted BBO **8d** had an absorbance maximum at 422 nm and upon excitation at this wavelength, **8d** exhibited blue–green emission at 470 nm with a Φ_{fl} of 14 %.

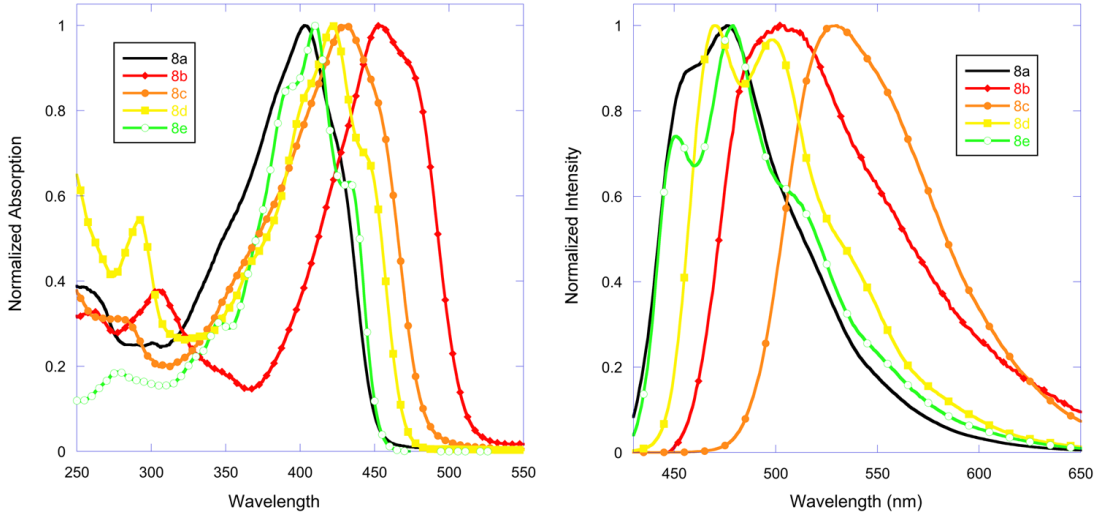

Fig. 3 UV–vis absorbance spectra (left) and fluorescence emission spectra (right) of diarylenevinylene benzobisoxazoles **8a–e** in chloroform.

BBO **8c** had an absorbance maximum at 431 nm and exhibited green emission at 530 nm. The incorporation of the electron-donating triphenylamine substituents resulted in the push-pull chromophore **8c**, which possessed the smallest optical bandgap of all systems studied. As a result of the strong electron-donating triphenylamine substituents, **8c** exhibited a bathochromic shift of both the absorption and emission maxima relative to **8a**. BBO **8c** also had the highest fluorescence quantum yield (36 %) and exhibited the largest Stokes shift seen for these systems.

Table 1 Physical and optical data for diarylenevinylene benzobisoxazoles **8a–e** in chloroform.

Compound	Absorption λ_{max} (nm)	ε_{max} (L mol^{-1} cm^{-1})	Emission λ_{max} (nm)	Φ_{fl}	Stokes shift (nm)	λ_{onset} (nm)	T_d (°C)
8a	403	80 900	476	0.33	73	450	333
8b	453	43 600	502	0.001	49	509	314
8c	431	81 500	530	0.36	99	482	389
8d	422	88 900	470	0.14	48	469	364
8e	410	65 600	479	0.038	69	451	311

Overall, the absorption spectra exhibited a progressive bathochromic shift as function of the aryl co-monomer: 2,5-dialkoxybenzene (**8a**) < thiophene (**8e**) < carbazole (**8d**) < triphenylamine (**8c**) < 2,5-dialkoxy-4-nitrobenzene (**8b**). This observation is not consistent with the literature reports on the relative electron-donating strength of these moieties [42]. Compound **8b**, which possessed the least electron-donating co-monomer, exhibited the most red-shifted absorption spectra. Furthermore, it was also observed that **8c** absorbed at a slightly longer wavelength than **8d**. We hypothesize that this is a function of the extended conjugation within **8c**, owing to inclusion of an additional aromatic ring from the triphenylamine to the conjugated backbone, in contrast to *N*-hexylcarbazole, which has a hexyl substituent on the nitrogen atom. These claims are supported by the theoretically derived frontier orbitals described in the electronic properties section (see Fig. 6).

Chloroform solutions of **8a–e** in ambient light and under UV light (355 nm) are shown in Fig. 4. Qualitatively, we can see that **8b,c** are more strongly absorbing than **8a,d,e**. These observations are confirmed by the molar extinction coefficients. Furthermore, **8a,c** were visibly more fluorescent than the other BBOs. On the right side of Fig. 4 are powders of the BBOs in ambient and UV light. We can see slight differences in the color of the solids, with **8b** being the most red in the solid state. Additionally, all of the BBOs are fluorescent in the solid state.

Solvatochromism of diarylenevinylene benzobisoxazoles

Solvatochromatic studies, shown in Fig. 5, were carried out on **8a,c,d**. BBOs **8b,e** were not used due to their low fluorescence quantum yield. The emission maximum of **8c** exhibited a red-shift of 96 nm when the solvent polarity was increased from hexane to methanol. Species **8a,d** exhibited shifts of 20 nm and 53 nm, respectively, when going from hexane to 1-butanol; this alcohol was the most polar solvent used as these BBOs were insoluble in methanol. While **8d** has a stronger electron-donating substituent than **8c** (vide infra), it is suspected that the triphenylamine group adopts a propeller-like shape, while carbazole is forced to be planar. The reduced planarity increases the effect of solvent relaxation [43], which, in turn, reduces the energy of the photon emitted, resulting in a greater bathochromic shift [44,45].

The correlation between fluorescence and solvent polarity was measured quantitatively by plotting the emission peaks against the $E_T(30)$ [46] polarity index of the solvents. A linear fit gave slopes of 40, 247, and 136 cm^{-1}, with r^2 value of 0.861, 0.985, and 0.955 for **8a,c,d**, respectively. The steeper slope of **8c** indicates a larger effect of solvent polarity. Since the BBO moiety is not a particularly strong electron-accepting group, the observed bathochromic shift was smaller than that of some other organic compounds in literature; however, the extinction coefficients of these compounds are higher than those used in other studies [47].

Electronic properties

The energy levels of the diarylenevinylene benzobisoxazoles were investigated both experimentally and theoretically and are summarized in Table 2. Overall, the experimental evaluation was difficult since the

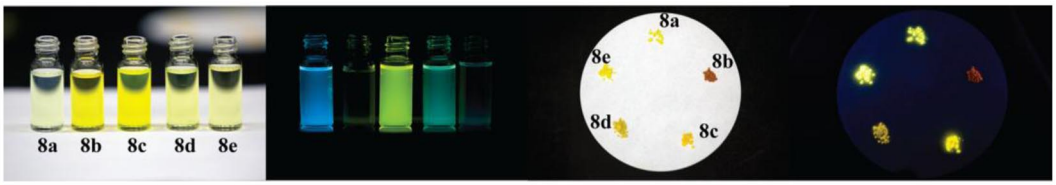

Fig. 4 Pictures of diarylenevinylene benzobisoxazoles **8a–e**. Pictures from left to right: solutions of **8a–e** in chloroform under ambient light, chloroform solutions under UV light (355 nm), powders in ambient light, and under UV light. The solutions are in the order **8a–e**, from left to right. The powders are in the order of **8a–e** going clockwise starting from the top.

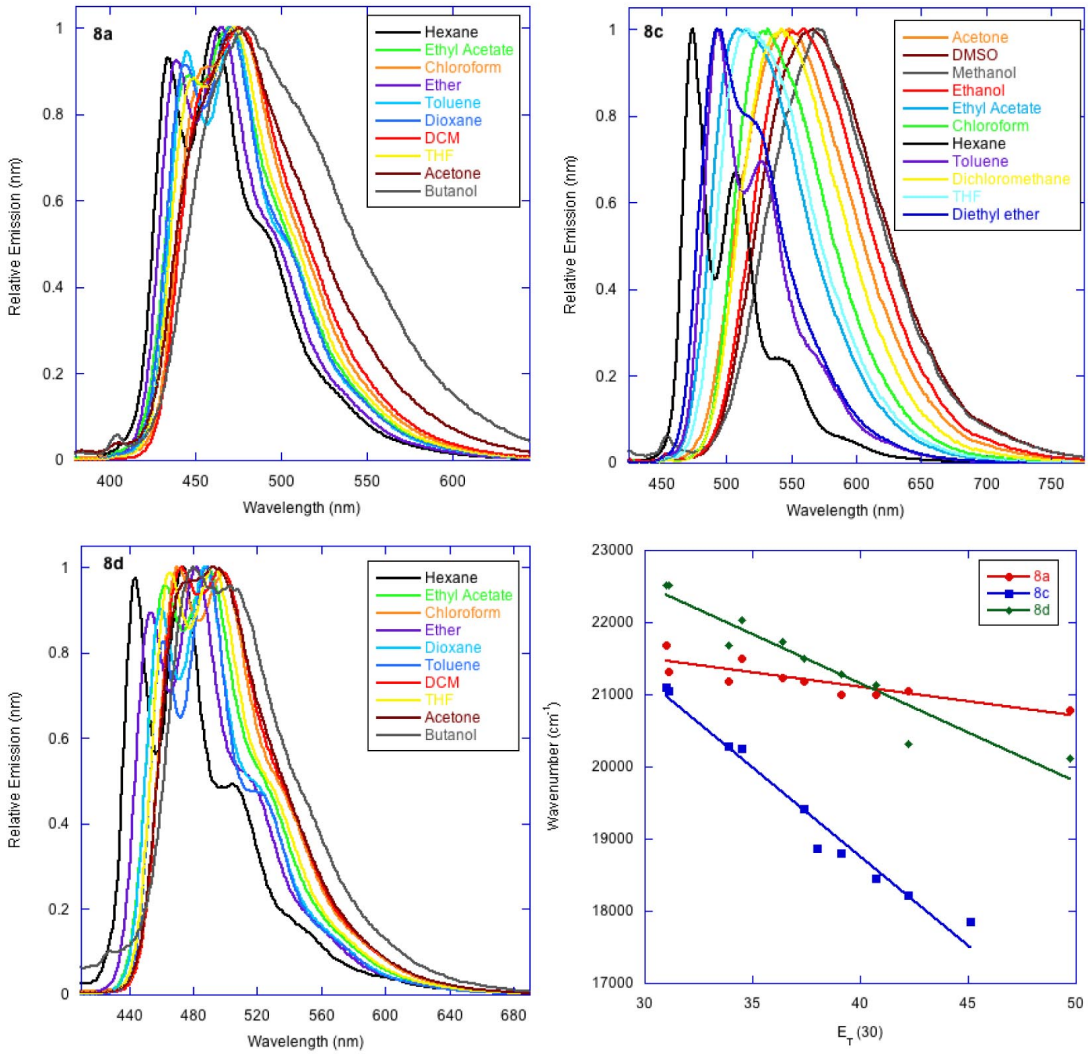

Fig. 5 UV–vis spectra of **8a,c,d** in various solvent (top and bottom left). A plot of emission maximum vs. solvent polarity (bottom right).

electrochemistry of the BBOs was not well behaved and all molecules exhibited nonreversible oxidation waves. Furthermore, a reduction process was not seen for many of the compounds within the solvent window for the $CH_3CN/Bu_4N^+BF_4^-$ (–2.7 to –3.0 eV vs. Ag/AgCl). For this reason, we utilized UV photoelectron spectroscopy (UPS), which provides an absolute determination of the highest occupied molecular orbital (HOMO) level [48–50]. The UPS values for the BBOs HOMO levels ranged from –5.25 to –5.99 eV. The experimentally determined HOMO–LUMO (lowest unoccupied molecular orbital) gaps ranged from 2.44 eV to 2.75 eV, and the LUMO levels obtained by adding these values to the HOMO values ranged from –2.60 to –3.0 eV. With exception of **8b**, the HOMO levels of the BBOs were more stabilized as the donor strength of the aryl substituents was increased (**8d** > **8c** > **8e** > **8a**). Similarly, apart from **8b**, the LUMO levels also decreased as the donor strength of the aryl substituents was increased (**8d** > **8c** > **8e** > **8a**). BBO **8b** behaved in a different manner owing to the electron-withdrawing nitro group at the 4-position of the benzene substituent. Based on the Hammett parameters, the nitro group is a strong electron-withdrawing substituent (σ_{para} = 0.78), whereas the methoxy groups are relatively weak electron-donating groups (σ_{para} = –0.27) [51]. Although the Hammett parameters for substituents in the *ortho* position were not available, we can assume that the inductive effects were similar to that for *para* substitution. These numbers indicated that the presence of the nitro group negated the influence of the methoxy groups, resulting in an electron-withdrawing substituent. Thus, in contrast to the other BBOs, **8b** is an A-π-A-π-A system, not a D-π-A-π-D system. As such, the optical and electronic properties of this compound do not follow the same trends as the other BBOs.

Table 2 An experimental and theoretical comparison of the electronic properties of BBO model compounds.

	HOMO		LUMO		E_g (eV)	
Compound	Experiment	Theory	Experiment	Theory	Experiment	Theory
8a	5.77	5.00	3.01	1.95	2.76	2.78
8b	5.99	5.68	3.55	2.93	2.44	2.50
8c	5.37	4.70	2.79	1.86	2.58	2.51
8d	5.25	5.17	2.60	2.54	2.65	1.72
8e	5.46	5.13	2.81	2.17	2.75	2.75

To examine structural trends, and donor–acceptor behavior, frontier orbitals were generated using B3LYP/6-31G* density functional theory. All computations were performed using Gaussian09 [52] through the National Science Foundation's Extreme Science and Engineering Discovery Environment (XSEDE) on San Diego Supercomputer Center's Trestles cluster. The optimized geometries as well as the frontier orbitals for the HOMO and LUMO are shown in Fig. 6, and the data is summarized in Table 2. While it was our intention to use theory to predict trends within this system, we were unable to use this approach owing to poor correlation to the experimental data. We believe that the origin of this problem lies within the geometry of the BBOs. Theory predicts that all species have a planar backbone with deviations from planarity only through their side chains. However, in actuality, it is improbable that the aryl rings are coplanar to the BBO ring resulting in a significant deviation between experimental and theoretical values, thereby limiting their utility [53]. On the other hand, we were able to garner some information from the theoretically derived frontier orbitals. There was a reorganization of electron density within **8b** owing to the A-π-A-π-A nature of this compound, whereas there was no obvious donor–acceptor behavior in **8a,e**. This lack of donor-acceptor behavior is similar to the observed results for the related polymer poly[(3,4-didodecylthiophene vinylene-*alt*-benzo[1,2-*d*;4,5-*d*′]-2,6-diyl [36]. Conversely, **8c,d** did demonstrate donor–acceptor trends upon examination of their frontier orbitals. Both compounds possessed high electron density on the triphenylamine and carbazole moieties, respectively, in their HOMO orbitals, which was absent from these same moieties in their

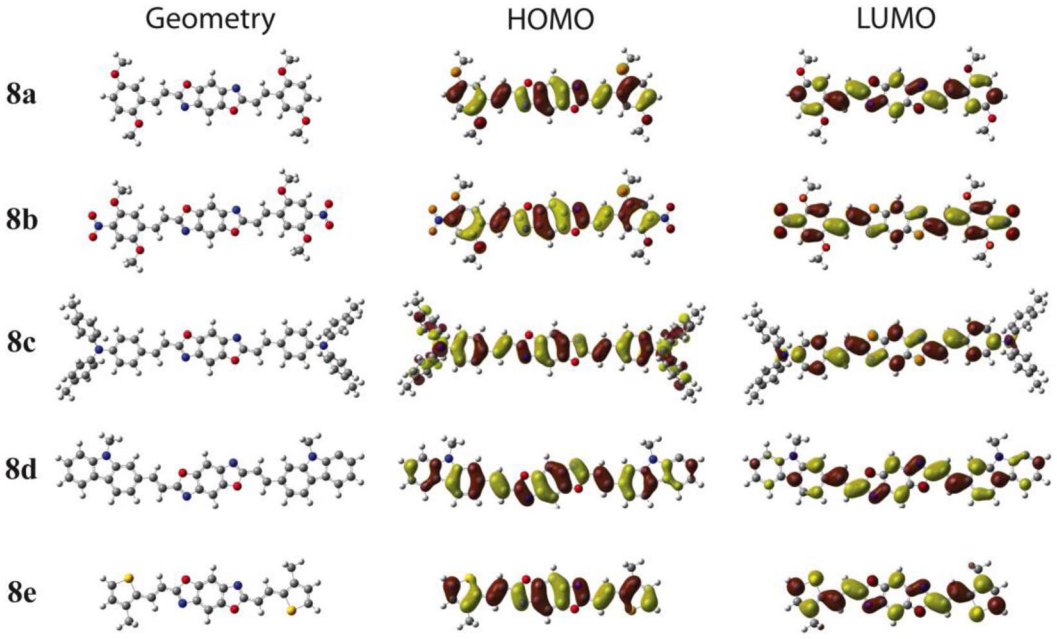

Fig. 6 Pictorial representations of the frontier orbitals for **8a–e** (right) and representations of the optimized geometries (left).

LUMO orbitals. This trend indicates that the electron density was donated from these nitrogen-possessing ring systems to the conjugated backbone.

CONCLUSIONS

In summary, we report the synthesis and characterization of a series of diarylenevinylene benzobisoxazoles. Three of these compounds **8a,c,d** exhibited strong fluorescence in the solid state, with colors that varied from 476 to 530 nm as a function of substitution. Furthermore, **8c** also exhibited significant (96 nm) solvatochromic behavior in various solutions, whereas **8a**,**d** only exhibited minor solvatochromic behavior (~20 and 53 nm), respectively. The HOMO and LUMO levels of this system could be tuned by ~0.75 and ~0.95 eV, respectively, through variation of the aryl co-monomers. Additionally, donor–acceptor behavior was observed for **8c,d**, whereas **8b** exhibited characteristics of an acceptor material. Collectively, these results suggest that diarylenevinylene benzobisoxazoles are promising materials for the development of small molecule emitters for use in organic LEDs and as acceptor materials in PVCs. We are currently exploring the synthesis of new derivatives as well as their related polymers.

EXPERIMENTAL

General experimental details

2,6-Dimethyl BBO was synthesized according to literature procedure [34]. All other compounds were purchased from commercial sources and used without further purification. All reactions were carried out under argon unless otherwise noted. NMR spectra were obtained on a 400 MHz spectrometer (^{1}H at 400 MHz and ^{13}C at 100 MHz). ^{1}H NMR samples were referenced internally to residual protonated solvent. ^{13}C NMR samples were referenced to the central carbon peak of $CDCl_3$. In both instances, chem-

ical shifts are given in δ relative to solvent. Coupling constants are reported in Hz. Melting points were determined by differential scanning calorimetry, unless otherwise noted. As all BBO melting points occur over less than 0.5 °C, melting points are given to the nearest degree. Decomposition points, if applicable, were determined by 5 % mass loss under air using thermogravimetric analysis. Fluorescence spectroscopy and UV–vis spectroscopy were obtained using solutions in $CHCl_3$, approximately 50 μM. Quantum yield measurements were taken using Rhodamine B (ϕ = 0.59) in 1-butanol as a standard (excitation at 375 nm; emission was taken from 390 to 700 nm) [54]. All values were corrected for the differences in the refractive index of the solvent using the following equation:

$$\Phi_X = \Phi_S \left(\frac{\int I_X}{\int I_S}\right)\left(\frac{A_S}{A_X}\right)\left(\frac{\eta_X^2}{\eta_S^2}\right)$$

where S and X stand for the standard and the unknown, respectively, Φ is the quantum yield, $\int I$ is the integral of the fluorescence spectra, A is the absorbance at the excitation wavelength, and η is the refractive index of the solvents.

Synthesis

2-Dodecyloxy-5-methoxybenzaldehyde (1a): 5-Methoxysalicylaldehyde (4.56 g, 30 mmol) and potassium carbonate (20.7 g, 150 mmol) were added to DMF (200 mL) and heated to 80 °C. 1-Dodecyl bromide (7.48 g, 30 mmol) dissolved in DMF (16 mL) was added drop-wise. The reaction was kept at 80 °C for 12 h, cooled, and water (200 mL) and ether (50 mL) were added. The aqueous layer was washed with ether (150 mL), and the combined organic layers were washed with 1 M sodium hydroxide, followed by water, and lastly brine. The solvent was dried over sodium sulfate, and removed in vacuo to give an oil that solidified upon standing. Recrystallization from ethanol produced off-white needles. (7.41 g, 77 % yield); mp: 38–40 °C. ^{1}H NMR ($CDCl_3$): 10.46 (s, 1H), 7.31 (d, J = 2.6, 1H), 7.10 (dd, J = 9.2, 2.6, 1H), 6.92 (d, J = 9.2, 1H), 4.02 (t, 2H), 3.79 (s, 3H), 1.81 (m, 2H), 1.46 (m, 2H), 1.28 (m, 16H), 0.86 (m, 3H). ^{13}C NMR ($CDCl_3$): 189.8, 156.5, 153.5, 125.1, 123.8, 114.5, 110.0, 69.3, 55.9, 32.0, 29.7, 29.7, 29.7, 29.6, 29.4, 29.3, 26.1, 22.8, 14.2.

(2-Dodecyloxy-5-methoxyphenyl)methylene diacetate (2): To a flask containing a solution of 2-dodecyloxy-5-methoxybenzaldehyde **1a** (7.00 g, 21.8 mmol) in acetic anhydride (13.46 g, 132 mmol) at 0 °C was added 1 drop of concentrated sulfuric acid. The solution was stirred for 3 h, and the reaction was quenched by the addition of ice water (80 mL) with vigorous stirring. A solid formed and was collected by vacuum filtration, and rinsed with 10 % $NaHCO_3$, and recrystallized from aqueous ethanol to give off-white needles. (8.23 g, 90 % yield); mp: 47–50 °C. ^{1}H NMR ($CDCl_3$): 7.98 (s, 1H), 7.02 (d, 1H), 6.85 (m, 2H *overlapped*), 3.92 (t, 2H), 3.77 (s, 3H), 2.10 (s, 6H), 1.72 (m, 2H), 1.24–1.40 (m, 18H), 0.87 (t, 3H). ^{13}C NMR ($CDCl_3$): 168.5, 153.4, 150.8, 125.0, 115.3, 113.3, 112.9, 85.7, 69.1, 55.9, 32.0, 29.8, 29.7, 29.7, 29.5, 29.4, 29.4, 29.4, 26.0, 22.8, 20.9, 14.2.

(2-Dodecyloxy-5-methoxy-4-nitrophenyl)methylene diacetate (3): (2-dodecyloxy-5-methoxyphenyl)methylene diacetate **2** (7.50 g, 17.7 mmol) was dissolved in acetic anhydride (22.8 g, 224 mmol) at 0 °C. Nitric acid (2.52 g, 40.0 mmol) was added drop-wise, and the reaction was stirred for 2 h, after which the reaction was poured onto ice (100 g). The crude solid was filtered, rinsed with 10 % $NaHCO_3$, and recrystallized from aqueous ethanol to give a yellow powder. (5.53 g, 67 % yield); mp: 52–55 °C. ^{1}H NMR ($CDCl_3$): 7.97 (s, 1H), 7.38 (s, 1H), 7.21 (s, 1H), 3.97 (t, 2H), 3.93 (s, 3H), 2.13 (s, 6H), 1.77 (m, 2H), 1.24–1.41 (m, 18H), 0.86 (t, 3H). ^{13}C NMR ($CDCl_3$): 168.2, 150.2, 147.1, 141.0, 130.5, 113.1, 109.2, 84.6, 69.6, 57.3, 32.0, 29.7, 29.7, 29.7, 29.6, 29.4, 29.4, 29.0, 25.9, 22.8, 20.8, 14.2.

2-Dodecyloxy-5-methoxy-4-nitrobenzaldehyde (1b): (2-dodecyloxy-5-methoxy-4-nitrophenyl)-methylene diacetate **3** (5.00 g, 10.7 mmol), concentrated sulfuric acid (1.12 g, 11.0 mmol), and 75 % ethanol were refluxed for 1 h, and then allowed to cool to room temperature. The solid formed

was collected by filtration, and a second crop was obtained by addition of water to the mother liquor, followed by filtering. The aldehyde was recrystallized from aqueous ethanol to give the solid as a yellow powder. (2.58 g, 66 %); mp: 73–75 °C. ^{1}H NMR ($CDCl_3$): 10.48 (s, 1H), 7.52 (s, 1H), 7.41 (s, 1H), 4.07 (t, 2H), 3.94 (s, 3H), 1.85 (m, 2H), 1.47 (m, 2H), 1.25 (m, 16H), 0.87 (t, 3H). ^{13}C NMR ($CDCl_3$): 188.3, 154.7, 146.5, 143.7, 127.8, 112.8, 110.2, 69.6, 51.1, 32.0, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 22.8, 14.2. HRMS (ESI): *m/z* calcd for $C_{20}H_{29}N_4O_2$ $[M+H]^+$, 545.2291; found 545.2294.

***N*,*N*-Di(4-*tert*-butylphenyl)aniline (4)** [39]: Pd_2dba_3 (1.099 g, 1.20 mmol) and dppf (0.998 g, 1.80 mmol) were added to deoxygenated toluene (180 ml). 4-*t*-Butylbromobenzene (38.36 g, 180 mmol) was added, and the reaction was stirred at room temperature for 10 min. Sodium *t*-butoxide (14.42 g, 150 mmol) and aniline (5.59 g, 60 mmol) were then added. The reaction was stirred at 90 °C for 24 h, after which more Pd_2dba_3 (0.550 g, 0.60 mmol) and dppf (0.499 g, 0.90 mmol) were added, followed by stirring at the same temperature for 48 additional hours. The reaction was then cooled to room temperature, diluted with diethyl ether (100 mL) and washed with water (200 mL). The solvent was dried over sodium sulfate, and the solvent was removed by vacuum. The crude product was passed through a silica gel plug (hexane) to remove palladium, and used in the next step without further purification (18.88 g, 88 % yield).

4-[*N*,*N*-Di(4'-*tert*-butylphenyl)aminobenzaldehyde] (1c): Anhydrous DMF (15.44 g, 211 mmol) was cooled to 0 °C. Phosphorus oxychloride (8.91 g, 58.1 mmol) was added drop-wise to the reaction vessel while stirring. After 30 min, a solution of *N*,*N*-di(4-*tert*-butylphenyl)aniline **4** (18.88 g, 52.81 mmol) in DMF (100 mL) was added over 15 min. The reaction was heated to 90 °C for 2 h, and was stopped by pouring over crushed ice (200 g) and neutralized by addition of saturated sodium bicarbonate solution. The product was extracted with dichloromethane (100 mL), washed with water (100 mL) and brine (100 mL), dried over magnesium sulfate, and the solvent was removed by vacuum. The crude product was purified by recrystallization from ethanol (10.20 g, 50 % yield). ^{1}H NMR ($CDCl_3$): 9.79 (s, 1H), 7.66 (d, 2H), 7.36 (d, 4H), 7.11 (d, 4H), 6.97 (d, 2H), 1.34 (s, 18H). ^{13}C NMR ($CDCl_3$): 190.3, 153.7, 148.2, 143.3, 131.3, 128.4, 126.6, 126.0, 118.3, 34.5, 31.4.

9-Hexylcarbazole (5): [55] 9*H*-Carbazole (16.72 g, 100 mmol) was dissolved in THF (100 mL) and cooled to 0 °C. 60 % Sodium hydride in mineral oil suspension (4.80 g, 120 mmol) was added, evolving hydrogen gas, and the solution was warmed to room temperature. 1-Bromohexane (33.01 g, 200 mmol) was added, and the solution was refluxed for 12 h. The reaction was quenched with 1 M HCl (150 mL) and the organic layer was washed three times with brine (50 mL) and dried over sodium sulfate. The solvent was removed by vacuum, and the product was recrystallized from hot methanol, producing white needles. (23.16 g, 92 % yield). ^{1}H NMR ($CDCl_3$): 8.11 (d, 2H), 7.48 (d, 2H), 7.43 (d, 2H), 7.22 (t, 2H), 4.31 (t, 2H), 1.88 (m, 2H), 1.44–1.27 (m, 6H), 0.87 (t, 3H). ^{13}C NMR ($CDCl_3$): 140.5, 125.7, 123.0, 120.4, 118.8, 108.8, 43.0, 31.7, 29.0, 27.0, 22.7, 14.2.

9-Hexylcarbazole-3-carboxaldehyde (1d): [55] DMF (1.75 g, 24.0 mmol) was cooled to 0 °C, and phosphorus (V) oxychloride (3.53 g, 23.0 mmol) was added drop-wise via an addition funnel over 15 min, keeping the temperature below 5 °C. The reaction was stirred for 1 h at 0 °C, and then chlorobenzene (30 mL) was added. 9-Hexylcarbazole **5** (5.03 g, 20 mmol) dissolved in chlorobenzene (30 mL) was added drop-wise over 1 h. The reaction was refluxed for 2 h, and then at 75 °C for 6 h. The reaction was then quenched by the rapid addition of sodium acetate (100 g) dissolved in water (100 mL). The aqueous layer was extracted three times with ether (30 mL) and the combined organic layers were washed with saturated sodium bicarbonate solution until production of carbon dioxide ceased. The organic layer was dried over anhydrous sodium carbonate, and the solvent was removed by vacuum. The solid was recrystallized from heptane to produce beige, fibrous crystals. (5.22 g, 91 % yield); mp: 53–54 °C ^{1}H NMR ($CDCl_3$): 10.06 (s, 1H), 8.52 (s, 1H), 8.10 (d, 1H), 7.97 (d, 1H), 7.52 (t, 1H), 7.41 (t, 1H), 7.38 (t, 1H), 7.30 (t, 1H), 4.21 (t, 2H), 1.82 (m, 2H) 1.41–1.27 (m, 6H), 0.88 (t, 3H). ^{13}C NMR ($CDCl_3$): 191.7, 144.0, 141.1, 128.4, 127.0, 126.7, 122.97, 122.93, 120.7, 120.3, 109.4, 108.9, 43.3, 31.5, 28.9, 26.9, 22.6, 14.0.

3-Hexylthiophene (6): [56] 3-Bromothiophene (5.00 g, 30.7 mmol) and Ni(dppp)Cl_2 (0.166 g, 0.31 mmol) were dissolved in 50 mL THF. 1-Hexylmagnesium bromide (1.3 equiv, 40 mmol) in THF was added drop-wise over 30 min, and then refluxed overnight. The reaction was quenched by addition of 50 mL of 1 M hydrochloric acid, extracted with ether, and washed with water and brine. The organic layer was dried with sodium sulfate, and the crude product distilled under vacuum to yield a colorless oil (4.30 g, 83 % yield).

2-Bromo-3-hexylthiophene (7): [57] 3-Hexylthiophene (5.00 g, 29.7 mmol) was dissolved in 50 mL of acetic acid. *N*-Bromosuccinimide (5.29 g, 29.7 mmol) was added in one portion at room temperature. The reaction was then heated to 35 °C, and maintained at this temperature for 1 h. The reaction mixture was poured into 150 mL of water, and the product was extracted with ether and washed with 10 % sodium hydroxide. The organic layer was dried over magnesium sulfate, and the crude product was distilled under vacuum to give the product as a colorless oil. (6.61 g, 90 % yield). ^{1}H NMR ($CDCl_3$): 7.19 (d, 1H), 6.80 (d, 1H), 2.57 (t, 2H), 1.58 (p, 2H), 1.33 (m, 6H), 0.90 (t, 3H).

3-Hexylthiophene-2-carboxaldehyde (1e): 2-Bromo-3-hexylthiophene (5.00 g, 20.2 mmol) was dissolved in THF (25 mL) and cooled to –78 °C. 2.5 M *n*-butyllithium (8.09 mL, 20.2 mmol) was added drop-wise, and stirred for 1 h. 1-Formylpiperidine (2.29 g, 20.2 mmol) was dissolved in 10 mL of THF and added drop-wise to the reaction. The reaction was then refluxed overnight, and then quenched with 50 mL of 0.5 M hydrochloric acid. The product was extracted with ether, washed with brine, and dried over sodium sulfate. The crude 3-hexylthiophene-2-carboxaldehyde was purified by eluting through a silica plug with hexane to yield a pale yellow oil. (2.90 g, 73 % yield) ^{1}H NMR ($CDCl_3$): 10.03 (s, 1H), 7.63 (d, 1H), 7.00 (d, 1H), 2.95 (t, 2H), 1.67 (p, 2H), 1.30 (m, 6H), 0.87 (t, 3H).

Synthesis of benzobisoxazole dyes via Knoevenagel condensation

General method: Potassium hydroxide (1.35 g, 24.0 mmol) was added to DMF (12 mL) and allowed to stir under open air for 15 min at room temperature. 2,6-Dimethyl BBO **1** (376 mg, 2.00 mmol) was then added, turning the solution yellow, followed promptly by the addition of an aryl carboxaldehyde (3 equiv, 6.00 mmol). The solution was then allowed to stir for 3 h, after which the reaction was quenched with 1 M HCl solution (24 mL), causing the product to precipitate. The product was then filtered, and washed with water, followed by cold methanol. The products are then recrystallized from hot ethanol.

2,6-Bis[(*E*)-2,5-bis(dodecyloxy)styryl] BBO (8a): Yellow powder (0.96 g, 44 % yield). mp: 91 °C ^{1}H NMR ($CDCl_3$): 8.08 (d, J = 16.4, 2H), 7.80 (s, 2H), 7.21 (d, J = 16.4, 2H), 7.15 (s, 2H), 6.90 (d, 2H), 6.89 (d, 2H), 4.04 (t, 4H), 3.97 (t, 4H), 1.91 (p, 4H), 1.80 (p, 4H), 1.55–1.25 (m, 72H), 0.90 (t, 6H), 0.87 (t, 6H). ^{13}C NMR ($CDCl_3$): 164.6, 153.0, 152.1, 148.2, 140.6, 135.4, 131.2, 124.8, 117.5, 115.0, 113.7, 100.3, 69.4, 68.7, 31.9, 29.7, 29.23, 29.62, 29.60, 29.59, 29.41, 29.35, 26.1, 26.0, 22.7, 14.1. HRMS (ESI): *m/z* calcd for $C_{72}H_{112}N_2O_6$ $[M+H]^+$, 1101.8589; found 1101.8593.

2,6-Bis[(*E*)-2-dodecyloxy-5-methoxy-4-nitrostyryl] BBO (8b): Brick red powder (1.12 g; 63 % yield). mp: 158 °C ^{1}H NMR ($CDCl_3$): 8.02 (d, J = 16.0, 2H), 7.85 (s, 2H), 7.49 (s, 2H), 7.30 (d, J = 16.0, 2H), 4.10 (t, 4H), 4.00 (s, 6H), 1.94 (m, 4H), 1.57 (m, 6H), 1.24 (m, 32H), 0.85 (t, 6H). ^{13}C NMR ($CDCl_3$): 163.8, 150.9, 148.3, 147.3, 140.9, 139.4, 133.5, 129.9, 118.0, 113.7, 109.6, 100.8, 69.7, 57.1, 38.4, 31.9, 29.66, 29.63, 29.58, 29.3, 29.0, 26.0, 22.7, 14.1. HRMS (ESI): *m/z* calcd for $C_{50}H_{67}N_4O_{10}$ $[M+H]^+$, 883.4852; found 883.4856.

2,6-Bis(*E*)-4-(*N*,*N*-di(4-*tert*-butylphenyl)aminostyryl) BBO (8c): Orange powder (1.38 g, 75 % yield). mp: 389 °C (dec.). ^{1}H NMR ($CDCl_3$): 7.73 (s, 2H), 7.73 (d, J = 15.5, 2H), 7.43 (d, 4H), 7.31 (d, 8H), 7.08 (d, 8H), 7.02 (d, 2H), 6.89 (d, J = 15.5, 2H), 1.33 (s, 36H). ^{13}C NMR ($CDCl_3$): 164.8, 150.2, 148.4, 147.2, 144.3, 140.6, 139.8, 128.9, 127.5, 126.5, 125.3, 121.1, 110.5, 100.1, 34.6, 31.6. HRMS (ESI): *m/z* calcd for $C_{64}H_{67}N_4O_2$ $[M+H]^+$, 923.5259; found 923.5260.

2,6-Bis(*E*)-2-(9-hexylcarbazol-3-yl)vinyl BBO (8d): Yellow powder (0.98 g, 69 % yield). mp: 241 °C. ^{1}H NMR ($CDCl_3$): 8.31 (d, 2H), 8.15 (d, 2H), 8.01 (d, 2H), 7.79 (s, 2H), 7.76 (dd, 2H), 7.51 (td, 2H) 7.43 (d, 2H), 7.41 (d, 2H), 7.29 (td, 2H), 7.10 (d, 2H), 4.30 (t, 4H), 1.88 (m, 4H), 1.30 (m,

12H), 0.87 (t, 6H). ^{13}C NMR ($CDCl_3$): 164.7, 148.1, 141.5, 140.9, 126.2, 126.1, 125.3, 123.3, 122.7, 120.7, 120.6, 120.4, 119.6, 117.5, 110.0, 109.2, 109.1, 99.9, 43.3, 31.5, 28.9, 26.9, 22.5, 14.0. HRMS (ESI): *m/z* calcd for $C_{48}H_{47}N_4O_2$ $[M+H]^+$, 711.3694; found 711.3703.

2,6-Bis(*E*)-2-(3-hexylthiophen-2-yl)vinyl BBO (8e): Yellow powder (0.58 g, 53 % yield). mp: 126 °C. ^{1}H NMR ($CDCl_3$): 7.81 (d, J = 16.0, 2H), 7.72 (s, 2H), 7.10 (s, 2H), 6.97 (d, 2H), 6.79 (s, J = 16.0, 2H), 2.58 (t, 4H), 1.62 (m, 4H), 1.32 (m, 12H), 0.89 (t, 6H). ^{13}C NMR ($CDCl_3$): 163.8, 148.2, 144.5, 140.6, 140.1, 133.7, 131.2, 123.0, 112.0, 100.2, 31.6, 30.33, 30.30, 28.9, 22.6, 14.1. HRMS (ESI): *m/z* calcd for $C_{32}H_{37}N_2O_2S_2$ $[M+H]^+$, 545.2291; found 545.2294.

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REFERENCES

1. A. R. Murphy, J. M. J. Frechet. *Chem. Rev.* **107**, 1066 (2007).
2. A. Facchetti. *Chem. Mater.* **23**, 733 (2010).
3. C. W. Tang, S. A. VanSlyke. *Appl. Phys. Lett.* **51**, 913 (1987).
4. R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund, W. R. Salaneck. *Nature* **397**, 121 (1999).
5. A. C. Grimsdale, K. Leok Chan, R. E. Martin, P. G. Jokisz, A. B. Holmes. *Chem. Rev.* **109**, 897 (2009).
6. K. M. Coakley, M. D. McGehee. *Chem. Mater.* **16**, 4533 (2004).
7. M. C. Scharber, D. Muehlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger, C. J. Brabec. *Adv. Mater.* **18**, 789 (2006).
8. T. B. Singh, N. S. Sariciftci. *Annu. Rev. Mater. Res.* **36**, 199 (2006).
9. S. R. Forrest. *Nature* **428**, 911 (2004).
10. G. Qian, B. Dai, M. Luo, D. Yu, J. Zhan, Z. Zhang, D. Ma, Z. Y. Wang. *Chem. Mater.* **20**, 6208 (2008).
11. S. Ellinger, K. R. Graham, P. Shi, R. T. Farley, T. T. Steckler, R. N. Brookins, P. Taranekar, J. Mei, L. A. Padilha, T. R. Ensley, H. Hu, S. Webster, D. J. Hagan, E. W. Van Stryland, K. S. Schanze, J. R. Reynolds. *Chem. Mater.* **23**, 3805 (2011).
12. H. A. M. van Mullekom, J. A. J. M. Vekemans, E. E. Havinga, E. W. Meijer. *Mater. Sci. Eng., R* **32**, 1 (2001).
13. E. E. Havinga, W. ten Hoeve, H. Wynberg. *Synth. Met.* **55**, 299 (1993).
14. F. M. Pasker, S. M. Le Blanc, G. Schnakenburg, S. Höger. *Org. Lett.* **13**, 2338 (2011).
15. J.-L. Wang, Q. Xiao, J. Pei. *Org. Lett.* **12**, 4164 (2010).
16. S. Ko, R. Mondal, C. Risko, J. K. Lee, S. Hong, M. D. McGehee, J.-L. Bredas, Z. Bao. *Macromolecules* **43**, 6685 (2010).
17. J. Mei, N. C. Heston, S. V. Vasilyeva, J. R. Reynolds. *Macromolecules* **42**, 1482 (2009).
18. R. S. Loewe, R. D. McCullough. *Chem. Mater.* **12**, 3214 (2000).
19. M. Al-Hashimi, M. A. Baklar, F. Colleaux, S. E. Watkins, T. D. Anthopoulos, N. Stingelin, M. Heeney. *Macromolecules* **44**, 5194 (2011).
20. K. D. Belfield, M. V. Bondar, C. O. Yanez, F. E. Hernandez, O. V. Przhonska. *J. Mater. Chem.* **19**, 7498 (2009).

21. A. J. Epstein, Y. Z. Wang, S. W. Jessen, J. W. Blatchford, D. D. Gebler, L. B. Lin, T. L. Gustafson, T. M. Swager, A. G. MacDiarmid. *Macromol. Symp.* **116**, 27 (1997).
22. S. Ko, R. Mondal, C. Risko, J. K. Lee, S. Hong, M. D. McGehee, J.-L. Bredas, Z. Bao. *Macromolecules* **43**, 6685 (2010).
23. A. Abbotto, E. H. Calderon, M. S. Dangate, F. De Angelis, N. Manfredi, C. M. Mari, C. Marinzi, E. Mosconi, M. Muccini, R. Ruffo, M. Seri. *Macromolecules* **43**, 9698 (2010).
24. C. Romero-Nieto, S. Merino, J. Rodríguez-López, T. Baumgartner. *Chem.—Eur. J.* **15**, 4135 (2009).
25. Y.-H. So, S. J. Martin, B. Bell, C. D. Pfeiffer, R. M. Van Effen, B. L. Romain, S. M. Lefkowitz. *Macromolecules* **36**, 4699 (2003).
26. J. F. Wolfe. In *Encyclopedia of Polymer Science and Engineering*, Vol. 11, p. 601, John Wiley (1988).
27. M. M. Alam, S. A. Jenekhe. *Chem. Mater.* **14**, 4775 (2002).
28. J.-W. Huang, S. J. Bai. *J. Polym. Sci., Part B: Polym. Phys.* **45**, 988 (2007).
29. J. A. Osaheni, S. A. Jenekhe. *Macromolecules* **27**, 739 (1994).
30. S. Wang, Y. Chen, Q. Zhuang, X. Li, P. Wu, Z. Han. *Macromol. Chem. Phys.* **207**, 2336 (2006).
31. C. C. Wu, P. Y. Tsay, H. Y. Cheng, S. J. Bai. *J. Appl. Phys.* **95**, 417 (2004).
32. S. A. Jenekhe, J. A. Osaheni, J. S. Meth, H. Vanherzeele. *Chem. Mater.* **4**, 683 (1992).
33. B. A. Reinhardt, M. R. Unroe, R. C. Evers. *Chem. Mater.* **3**, 864 (1991).
34. J. F. Mike, A. J. Makowski, M. Jeffries-EL. *Org. Lett.* **10**, 4915 (2008).
35. J. F. Mike, A. J. Makowski, T. C. Mauldin, M. Jeffries-EL. *J. Polym. Sci., Part A: Polym. Chem.* **48**, 1456 (2010).
36. J. F. Mike, K. Nalwa, A. J. Makowski, D. Putnam, A. L. Tomlinson, S. Chaudhary, M. Jeffries-EL. *Phys. Chem. Chem. Phys.* **13**, 1338 (2011).
37. J. F. Mike, J. J. Intemann, M. Cai, T. Xiao, R. Shinar, J. Shinar, M. Jeffries-EL. *Polym. Chem.* **2**, 2299 (2011).
38. J. J. Intemann, J. F. Mike, M. Cai, S. Bose, T. Xiao, T. C. Mauldin, R. A. Roggers, J. Shinar, R. Shinar, M. Jeffries-EL. *Macromolecules* **44**, 248 (2011).
39. B.-S. Chen, Y.-J. Chen, P.-T. Chou. *J. Mater. Chem.* **21**, 4090 (2011).
40. L. Kong, J. Yang, X. Hao, H. Zhou, J. Wu, F. Hao, L. Li, S. Zhang, B. Jin, X. Tao, M. Jiang, Y. Tian. *J. Mater. Chem.* **20**, 7372 (2010).
41. J. Motoyoshiya, Z. Fengqiang, Y. Nishii, H. Aoyama. *Spectrochim. Acta, Part A* **69**, 167 (2008).
42. O.-K. Kim, K.-S. Lee, H. Y. Woo, K.-S. Kim, G. S. He, J. Swiatkiewicz, P. N. Prasad. *Chem. Mater.* **12**, 284 (2000).
43. S. E. Blanco, E. I. Gasull, F. H. Ferretti. *Spectrochim. Acta, Part A* **59**, 2985 (2003).
44. O. A. Kucherak, P. Didier, Y. Mely, A. S. Klymchenko. *J. Phys. Chem. Lett.* **1**, 616 (2010).
45. E. L. Spitler, J. M. Monson, M. M. Haley. *J. Org. Chem.* **73**, 2211 (2008).
46. D. V. Matyushov, R. Schmid, B. M. Ladanyi. *J. Phys. Chem. B* **101**, 1035 (1997).
47. R. M. Adhikari, D. C. Neckers, B. K. Shah. *J. Org. Chem.* **74**, 3341 (2009).
48. W. R. Salaneck. *J. Electron Spectrosc. Relat. Phenom.* **174**, 3 (2009).
49. T. Miyamae, D. Yoshimura, H. Ishii, Y. Ouchi, T. Miyazaki, T. Koike, T. Yamamoto, Y. Muramatsu, H. Etori, T. Maruyama, K. Seki. *Synth. Met.* **84**, 939 (1997).
50. S. Lois, J.-C. Florès, J.-P. Lère-Porte, F. Serein-Spirau, J. J. E. Moreau, K. Miqueu, J.-M. Sotiropoulos, P. Baylère, M. Tillard, C. Belin. *Eur. J. Org. Chem.* 4019 (2007).
51. C. Hansch, A. Leo, R. W. Taft. *Chem. Rev.* **91**, 165 (1991).
52. J. Casanovas, D. Zanuy, C. Aleman. *Macromolecules* **41**, 3919 (2008).
53. B. C. Tlach, A. e. L. Tomlinson, A. Bhuwalka, M. Jeffries-EL. *J. Org. Chem.* **76**, 8670 (2011).
54. R. F. Kubin, A. N. Fletcher. *J. Lumin.* **27**, 455 (1982).
55. Y. Gao, J. Wu, Y. Li, P. Sun, H. Zhou, J. Yang, S. Zhang, B. Jin, Y. Tian. *J. Am. Chem. Soc.* **131**, 5208 (2009).

56. M. Jeffries-EL, G. Sauve, R. D. McCullough. *Macromolecules* **38**, 10346 (2005).
57. R. D. McCullough, S. Tristam-Nagle, S. P. Williams, R. D. Lowe, M. Jayaraman. *J. Am. Chem. Soc.* **115**, 4910 (1993).

