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Ortho-Fused Heterocyclic Derivatives as Efficient Electroluminescent Materials

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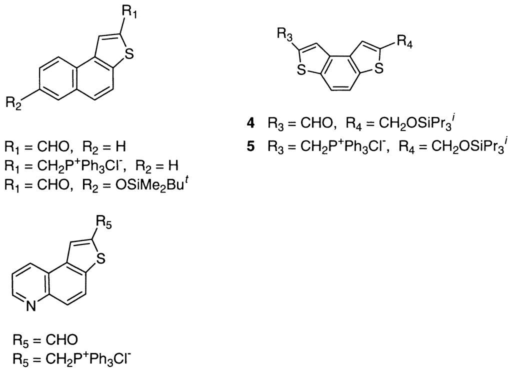
We describe the synthesis and optical properties of 1,2-dithienylethylene derivatives (DTE-**8**–**15**) consisting of ortho-fused heterocyclic systems such as benzodithiophene and naphthothiophene. The compounds **8**–**13** are highly fluorescent in toluene solution and their intensities are approximately two times as large as 4,4′-bis(2,2-diphenylethenyl)biphenyl (**18**). The fluorescence quantum yields of compounds **8**–**15**, except for **14**, are 2 times as high as that of **18**. Although a maximum luminance of **9** in a multilayer device of structure ITO/CuPc/NPD/**9**/Alq_3/LiF/Al is low (186 cd m^{-2}), the brightness is significantly improved by doping the host emitters such as **18** and 9,10-bis(2-biphenylyl)-2-(*t*-butyl)anthracene (**19**) with **9**. The electroluminescent (EL) device doped with **8** (5%) in the layer of **19** exhibits blue emission with a maximum luminance of 30000 cd m^{-2} at a driving voltage of 14 V and a luminous efficiency of 2.42 lm W^{-1} at 5V.

Since Tang and VanSlyke have reported an efficient EL device consisting of two layers of different carrier transport properties, such as bis(triarylamine) and tris(quinolin-8-olato)aluminium (Alq_3),[1] considerable attention has been directed toward new organic materials for light-emitting diodes.[2–6] Although various types of low molecular weight materials,[7,8] oligomers[9–11] and polymers[12–17] have been synthesized and studied for use as materials in organic electroluminescent devices, more research is still needed for development of novel types of organic materials with high brightness,[18] high efficiency,[9,19] and long lifetime.[20] During a course of study on the asymmetric synthesis of thiaheterohelicene derivatives,[21–24] we found that ortho-fused heterocyclic compounds, the precursors of thiaheterohelicenes, are thermally stable and highly fluorescent. We hereby report a series of 1,2-dithienylethylene derivatives (DTE-**8**–**15**) including ortho-fused heterocyclic compounds as blue emitters in electroluminescent fabrication. When DTE-**8** was used as a dopant in a device of structure ITO/CuPc/NPD/BBA:DTE-**8**/Alq_3/LiF/Al, where ITO, CuPc, NPD, BBA and Al are indium tin oxide, copper(II) phthalocyanine, *N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenylbiphenyl-4,4′-diamine, 9,10-bis(2-biphenylyl)-2-(*t*-butyl)anthracene and aluminium, respectively, bright blue emission from the dye dopant was observed. The optical properties of the DTE derivatives and devices are discussed.

Results and Discussion

Synthesis. The ortho-fused tricyclic compounds used in this report are listed in Schemes 1 and 2. 1,2-Dithienylethylene derivative DTE-**8**[25] was prepared from (naphtho[2,1-*b*]thiophen-2-ylmethyl)triphenylphosphonium chloride (**2**) and naphtho[2,1-*b*]thiophene-2-carbaldehyde (**1**) in the presence of *t*-BuOK as a base. Other DTE series **9**–**15** were prepared from the corresponding aldehydes and phosphonium salts by a procedure similar to that described for DTE-**8**. The naphthothiophene dimer **16** was prepared by coupling of lithium salt of 9-methoxynaphtho[2,1-*b*]thiophene[26] in order to compare the optical properties of the vinylene-brigded compounds **9**–**15**. These compounds are soluble in aprotic solvents such as chloroform, tetrahydrofuran and dimethyl sulfoxide, but insoluble in protic solvents like methanol. The thermal stability of **8**–**17** has been analyzed by differential scanning calorimetry at a heating rate of 10 °C/min under an ambient atmosphere. Most of the DTE derivatives melt above 300 °C, as shown in Table 1. DTE-**8** and **9** show sharp melting points at 359 and 303 °C, respectively, in the first heating cycles. After rapid cooling (50 °C/min) of these melts, there is no change in the melting temperatures (T_m) in the second heating cycle. How-

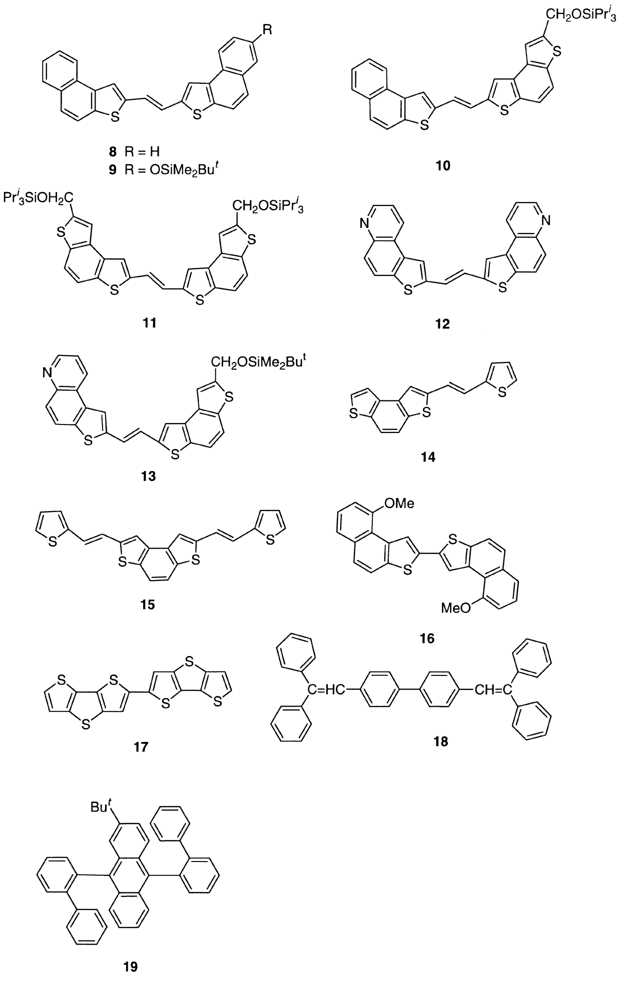


Scheme 1. Aldehydes and phosphomium salts of ortho-fused heterocyclis systems.

Table 1. Glass-Transition Temperatures (T_g), Melting Points (T_m), Absorption, and Emission Properties of Compounds in Solution and Thin Film

Compound	T_g/°C	T_m/°C	UV–vis λ_{max}/nm ($\varepsilon \times 10^{-4}$)	Fluorescence λ_{max}/nm	$\Phi_f/\Phi_{f_{18}}$
8[a]	—	359	398 (4.86)	460	2.0
9[a]	—	303	401 (2.97)	462	1.8[d]
10[a]	—	208[c], 221	398 (3.73)	458	1.7[d]
11[a]	38	169	397 (4.86)	456	1.6[d]
12[a]	—	371	395 (3.16)	455	2.1[d]
13[a]	—	306	397 (4.87)	457	1.6[d]
14[a]	—	190	391 (1.69)	429	0.76[d]
15[a]	—	286	400 (4.07)	462	1.5[d]
15 (film)[b]	—	—	411	502	—
16	—	287	385 (4.00)	442	1.2[d]
16 (film)[b]	—	—	428	461	—
17[a]	—	316	392 (2.23)	459	0.63[d]
17 (film)[b]	—	—	338	563	—
18	—	205	352 (2.61)	450	1.00[d]

a) In toluene (1×10^{-5} M). b) Deposited film (ca. 440 Å).
c) Polymorphism was observed. d) Excitation at 378 nm.



Scheme 2. Ortho-fused heterocyclic compounds (**8**–**16**) and BDT (**17**), BDEB (**18**), and BBA (**19**) used in this paper.

ever, DTE-**10** shows an endothermic peak at 208 °C in the first heating cycle, and at 221 °C in the first and also in the second heating cycles. For DTE-**11** the only melting behavior was observed at 169 °C in the first heating cycle. After rapid cooling of the melt, T_g at 38 °C was observed in the second heating cycle. Further heating of **11** resulted in crystallization at 115 °C, which was followed by melting at 169 °C. These results indicate that DTE-**10** and **11** show a polymorphism.

Cyclic voltammetry measurements of the six DTE derivatives (**8**–**13**) were carried out at room temperature in a conventional three-electrode cell. The solvent in all experiments was CH_2Cl_2, and Ag/Ag$^+$ was used as the reference electrode, with 0.1 M tetrabutylammonium perchlorate as the electrolyte. The electrochemical behavior of **8**–**13** is remarkably different. Thus, the cyclic voltammogram (not shown) of **8** demonstrates that the oxidation peak is observed at +0.77 V. There is no change in the appearance or position of the oxidation of **8** during ten scans. Although the oxidation peaks of **9**–**13** are observed at +0.73–+0.84 V and are reversible, significant changes of the oxidation peaks of **12** and **13** are observed during ten scans, due to the instability and subsequent reactivity of the charged intermediates.

Each organic EL device was fabricated by successive vacuum deposition of CuPc, NPD, DTE doped in BBA and Alq$_3$ onto an indium-tin-oxide coated glass substrate. Then, LiF[28,29] and aluminium were vacuum deposited onto the organic layer by evaporation. The devices thus fabricated have the following structure: ITO/CuPc/NPD/DTE/Alq$_3$/LiF/Al, and (ITO/CuPc/NPD/BBA:DTE/Alq$_3$/LiF/Al).

Absorption and Fluorescence Spectra. Figure 1 shows the absorption spectra of DTE-**9**–**13** and of stilbene type fluorescent dye **18** in toluene solution. It is worth mentioning that a significant red shift was observed from 360 nm for **18** to around 400 nm for **9**–**13**. The absorption peak maxima of compounds **8**–**17** in toluene solution are listed in Table 1 along with the peak maxima of **15**, **16** and **17** in thin solid films (440

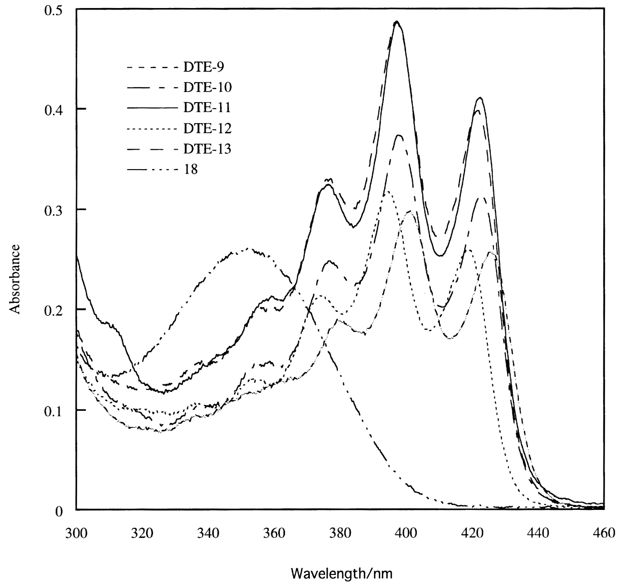


Fig. 1. Absorption spectra of compounds **9**, **10**, **11**, **12**, **13**, and **18** in toluene.

Å). Apparently, the absorption spectral profiles of compounds **8**–**17**, except for **14**, are essentially the same. The results indicate that the absorption spectra of these compounds are independent of a substituent or a vinylene bridge of the ortho-fused tricyclic skeleton. As for compound **14**, the absorption peak maxima are blue-shifted (20~30 nm) as compared with compounds **8**–**13** due to a decrease of conjugation. It is noteworthy that the absorption intensities for 1,2-dithienylethylene derivatives **8**–**13** are approximately two times higher than that for **18**. The results indicate that the ortho-fused three-ring heterocyclic compounds play a key role in determining their electronic and optical properties, which will be further demonstrated in the fluorescence and electroluminescence properties.

The fluorescence spectra of all the compounds were recorded in toluene at room temperature. Figure 2 indicates that the fluorescence spectra of DTE-**9**, **10**, **11**, **12**, and **13** show almost the same spectral profile regardless of a substituent or aromatic skeleton on the three-ring heterocyclic compounds. Their intensities are about two times more intense than that of **18**. As shown in Table 1, the emission peak maxima of **9**, **10**, **11**, **12**, and **13** occur at around 430, 455 and 485 nm which correspond to the blue region. In contrast, the fluorescence peak maxima of DTE-**15** are slightly red-shifted relative to the compounds such as **8**, **9** and **10**, and the color of **15** was green in toluene, due to increasing conjugation length introduced by two thiophene-vinylene-thiophene bridges.[27] The fluorescence intensity of **15** was three times as strong as that of **18**.

In the thin film (440 Å) prepared by vacuum deposition of **15**, the fluorescence peak maxima are significantly red-shifted (~50 nm) relative to the solution spectra as listed in Table 1. A similar red shift of emission maxima is observed for thin film of **17** as compared with the solution spectra. These phenomena can be explained by π–π stacking between fused-thiophenes π-electron systems such as benzodithiophene and thienodithiophene in the solid state. Holmes et al. have recently reported the X-ray crystal structure of **17**, where thienodithiophene molecules arrange in a completely coplanar conformation by π–π stacking with the shortest carbon-carbon distance of 3.56 Å.[28] The color of **8** as thin film was yellow, while the color of **9** was greenish yellow and it exhibited very weak fluorescence. These results indicate that the presence of bulky substituents such as a siloxymethy group on the tricyclic aromatic systems decreases the fluorescence intensity, although these groups increase the solubility of the compounds. As for the compound **16**, a blue fluorescence was observed in toluene solution and a greenish blue fluorescence in thin film.

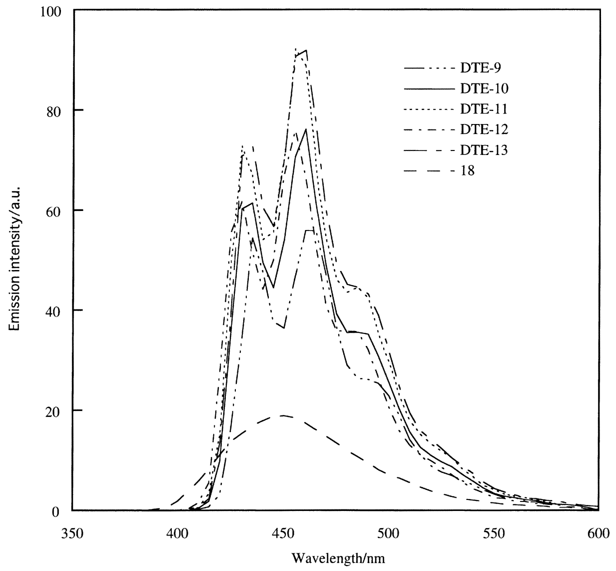


Fig. 2. Fluorescence spectra of compounds **9**, **10**, **11**, **12**, **13**, and **18** in toluene.

Electroluminescence Properties. Since the DTE-**10** and **11** do not have enough morphological stability (Table 1) to serve as an emission layer, four of the DTE derivatives (**8**, **9**, **11**, and **12**) were selected for the fabrication. Figure 3 shows

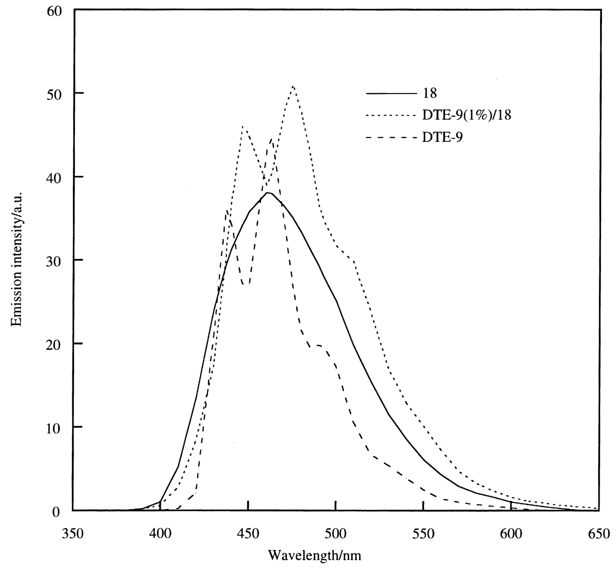


Fig. 3. Electroluminescence spectra of DTE-**9**, DTE-**9** (1%) doped in **18**, and **18**.

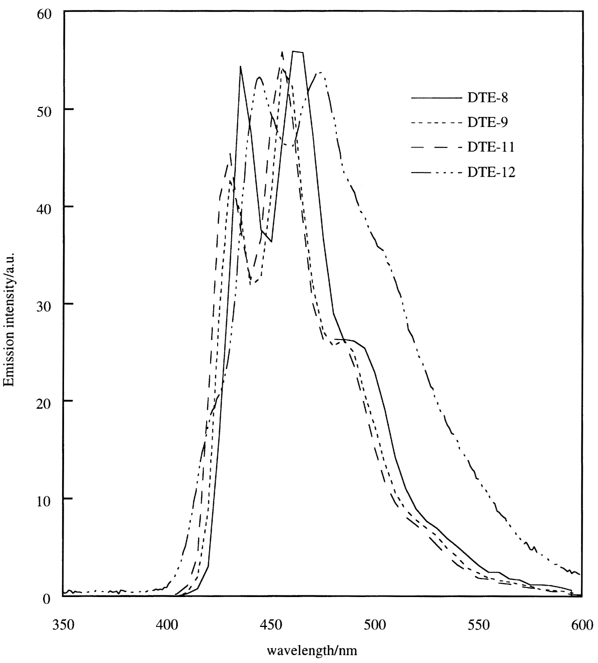


Fig. 4. Electroluminescence spectra of DTE-**8** (1%), **9** (1%), **11** (1%), and **12** (1%) doped in **19** (device: CuPc/NDP/DTE:**19**/Alq/LiF/Al).

the EL spectra of DTE-**9**, **18** and DTE-**9** (1%) doped in **18** (**9**(1%)/**18**). It can be seen from the figure that the EL spectrum of **9**(1%)/**18** is very similar to that of DTE-**9**. However, the spectrum of **18** is significantly different from those of DTE-**9**(1%)/**18** and DTE-**9** itself. These results clearly indicate that the emission occurs solely from the DTE-**9** dopant. Since the effect of concentration quenching is reduced in a device with a small dopant concentration, the slight red shift and the increasing emission intensity observed for DTE-**9**(1%)/**18** are attributed to an efficient energy transfer between host and dopant.

Table 2. Electroluminescence Characteristics of DTE-**9** Doped in **18**, and **18**

Compound	Maximum luminance	Luminous efficiency
	cd m^{-2}	lm W^{-1}
18	30000 (13 V)	2.27 (5 V)
DTE-**9**(1%)/**18**	23800 (14 V)	1.99 (5 V)

Figure 4 shows the EL spectra of compounds **8**, **9**, **11**, and **12** fabricated in mulitilayer devices (ITO/CuPc/NPD/DTE:**19**/Alq$_3$/LiF/Al) using LiF buffer layer.[29,30] Apparently, the spectral profiles of **8**, **9**, **11**, and **12** are essentially the same. However, the peak maxima of **8** and **12** are red-shifted, indicating that the unsubstituted compounds **8** and **12** readily arrange by π–π stacking in the solid thin film compared to the sterically congested mono- and disubstituted analogues **9** and **11**. As for the unbridged compound **16**, the EL spectral profile is different from that of **19**. However, the emission spectra of **16** doped in **19** by a variety of concentrations (1%, 5% and 10%) are very similar to that of **19**, indication that the emission occurs only from the host matrix **19**.

Although the fluorescence intensity of **9** in toluene is three times as large as that of a stilbene type of emitter **18** as shown in Fig. 2, the brightness and luminous efficiency of **9** in the mulitilayer device were 186 cd m^{-2} and 0.08 lm W^{-1}. Doping 1% of **9** as a guest in **18** increased a maximum luminance to 23800 cd m^{-2} and a luminous efficiency to 1.99 lm W^{-1}, as shown in Table 2. Table 3 lists maximum luminances, luminous efficiencies, and color (chromaticities) of electroluminescene of four DTE derivatves. The maximum brightness of 30000 cd m^{-2} at a driving voltage of 14 V and luminous efficiency of 2.42 lm W^{-1} at 5 V were achieved by doping 5% of **8** in anthracene type of host emitter **19**. This result is attributed to very efficient energy transfer from host to dopant. It is interesting to note that the EL spectral profile of DTE-**8** changes significantly with the dopant concentrations, as shown in Fig. 5. Thus, the emission color was yellowish green (DTE-**8**), green (DTE-**8**(10%)/**19**), and blue green (DTE-**8**(5%)/**19**), greenish blue (DTE-**11**(5%)/**19**, DTE-**12**(1%)/**19**), and blue (DTE-**8**(1%)/**19**, DTE-**9**(1%)/**19**, DTE-**11**(1%)/**19**). This phenomenon is probably related to the fact that the interaction between dopant molecules increases with increasing dopant concentration. The significant red shift and the decreasing emission intensity observed for DTE-**8** and DTE-**8**(10%)/**19** are due to concentration quenching.

Conclusions

A variety of 1,2-dithienylethylene derivatives (DTE-**8**–**15**) were prepared and their optical properties, both absorption and emission in solution and thin solid films, were investigated. It was found that the ortho-fused heterocyclic compounds are highly fluorescent in solution as well as in thin film and their fluorescence intensities are two to three times stronger than that of **18**. However, the fluorescence intensity of **17** was

Table 3. Electroluminescence Characteristics of DTE Series Doped in **19**

DTE compound	Maximum luminance	Luminous efficiency	Color (chromaticity)
	cd m^{-2}	lm W^{-1}	
DTE–**8** (1% dope)	16000 (14 V)	1.69 (5 V)	blue (x = 0.18, y = 0.22)
DTE–**8** (5% dope)	30000 (14 V)	2.42 (5 V)	blue green (x = 0.19, y = 0.30)
DTE–**8** (10% dope)	27000 (13 V)	2.31 (5 V)	green (x = 0.23, y = 0.40)
DTE–**9** (1% dope)	21000 (14 V)	1.46 (6 V)	blue (x = 0.17, y = 0.22)
DTE–**11** (1% dope)	11000 (14 V)	1.28 (5 V)	blue (x = 0.18, y = 0.17)
DTE–**11** (5% dope)	25000 (13 V)	2.22 (5 V)	greenish blue (x = 0.19, y = 0.27)
DTE–**12** (1% dope)	19000 (13 V)	1.42 (5 V)	greenish blue (x = 0.19, y = 0.25)

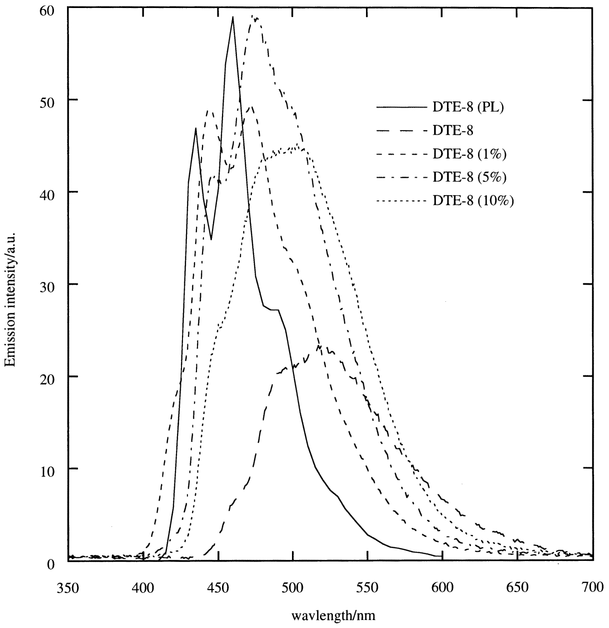


Fig. 5. Electroluminescene spectra of DTE-**8**, DTE-**8** (1%) in **19**, DTE-**8** (5%) in **19**, and DTE-**8** (10%) in **19**, and fluorescene spectrum of DTE-**8**.

about 80% of **18** and its quantum yield was low (0.63). The EL spectra of the DTE series of compounds lie in the region of green to blue, depending on the dopant DTE concentrations in the host emitter **19**. The mulitilayer device (ITO/CuPc/NPD/**8**(5%):**18**/Alq_3/LiF/Al) revealed green emission from **8**, exhibiting a maximum brightness of 30000 cd m^{-2} and a luminous efficiency of 2.42 lm W^{-1}. However, the compound **16** was not effective for the EL device, indicating that the presence of a vinylene bridge plays a key role in determining the emission property in these ortho-fused heterocylic systems. Further research on novel emitting material consisting of tricyclic heteroaromatic compounds is in progress.

Experimental

The hexane solution of butyllithium was titrated using diphenylacetic acid. ^1H NMR spectra were recorded in $CDCl_3$, DMSO-d_6, or THF-d_8 with a JEOL-JNM-AL300 (300 MHz) spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane as an internal standard, and J values are given in Hz. Absorption spectra were recorded on a Shimadzu UV-3100/V spectrophotometer. Photoluminescence spectra were recorded on a Shimadzu FP-5300PC spectrofluorometer. Fourier transform infrared (FT-IR) spectra were on a SHIMADZU FT IR-8000/8100 infrared spectrometer. Glass transition temperatures (T_g) and melting points (T_m) were obtained on a Seiko DSC 6200 with a heating rate of 10 °C min^{-1} in nitrogen.

1,2-Bis(naphtho[2,1-*b*]thiophen-2-yl)ethylene (8). To a stirred mixture of naphtho[2,1-*b*]thiophene-2-carbaldehyde[31] **1** (0.50 g, 1.0 mmol) and (naphtho[2,1-*b*]thiophen-2-ylmethy)ltriphenylphosphonium chloride **2** (0.35 g, 1.0 mmol) in methanol (20 mL) was added dropwise at 0 °C a solution of *t*-BuOK (0.12 g, 1.1 mmol) in MeOH (3 mL) and the reaction mixture was stirred overnight. After an aqueous solution of NH_4Cl–NH_4OH (1:1) was added to quench the reaction mixture, the olefin was collected by filtration, washed with ether and then with hexane. The solid was dried (0.47 g, 90%) and purified by sublimation in vacuo to give **8** as a yellow solid: mp 359 °C (lit.[25] > 360 °C); ^1H NMR (DMSO-d_6–THF-d_8) δ 7.48 (s, 2H), 7.54 (dt, J = 7.8 and 1.3 Hz, 2H), 7.63 (dt, J = 7.8 and 1.3 Hz, 2H), 7.79 (d, J = 8.8 Hz, 2H), 7.91 (d, J = 8.8 Hz, 2H), 7.97 (dd, J = 7.8 and 1.3 Hz, 2H), 8.27 (s, 2H), 8.40 (dd, J = 7.8 and 1.3 Hz, 2H); FT-IR (KBr) ν_{max}/cm^{-1} 3048, 1615, 1505 1372, 1213, 1200, 1183, 1159, 1138, 936, 893, 810, 772, 745, 546.

1-[7-(*t*-Butyldimethylsiloxy)naphtho[2,1-*b*]thiophen-2-yl]-2-(naphtho[2,1-b]thiophen-2-yl)ethylene (9). By a procedure similar to that described for **8**, DTE-**9** was prepared from (naphtho[2,1-*b*]thiophen-2-ylmethyl)triphenylphosphonium chloride **2** (0.35 g, 1.0 mmol) and 7-(*t*-butyldimethylsilyloxy)naphtho[2,1-*b*]thiophene-2-carbaldehyde **3** (0.50 g, 1.0 mmol). The crude product was purified by sublimation in vacuo to give **9** (0.47 g, 90%) as a yellow solid: mp 303 °C; FT-IR (KBr) ν_{max}/cm^{-1} 2890, 1600, 1420, 1235, 965, 905, 875, 805, 765. Found: C, 73.26; H, 5.82%. Calcd for $C_{32}H_{30}OS_2Si$: C, 73.52; H, 5.78%.

1-(Naphtho[2,1-*b*]thiophen-2-yl)-2-[7-(triisopropylsiloxymethyl)benzo[1,2-*b*:4,3-*b′*]dithiophen-2-yl]ethylene (10).

Into a mixture of 7-(triisopropylsiloxymethyl)benzo[1,2-*b*:4,3-*b′*]dithiophene-2-carbaldehyde **4** (2.93 g, 7.24 mmol) and (naphtho[2,1-*b*]thiophen-2-ylmethyl)triphenylphosphonium chloride **2** (3.77 g, 7.62 mmol) in a solution of THF (50 mL) and EtOH (10 mL) was added *t*-BuOK (1.2 g, 10.7 mmol) at room temperature. After the reaction mixture was stirred for 15 h at 60 °C, brine was added. The resulting solid was collected by filtration and washed with water and then with EtOH. The crude olefin **10** (3.87 g, 91%) was obtained as yellow powder, which was purified by sublimation in vacuo: mp 221 °C; ^1H NMR ($CDCl_3$) δ 1.14 (d, J = 5.9 Hz, 18H), 1.09–1.28 (m, 3H), 5.14 (d, J = 0.8 Hz, 2H), 7.30 (d, J = 15.9 Hz, 1H), 7.36 (d, J = 15.9 Hz, 1H), 7.46 (d, J = 0.8 Hz, 1H), 7.52 (dt, J = 8.0 and 1.3 Hz, 1H), 7.60 (s, 1H), 7.61 (dt, J = 8.0 and 1.3 Hz, 1H), 7.66 (d, J = 8.7 Hz, 1H), 7.81 (d, J = 8.7 Hz, 1H), 7.70 (d, J = 7.9 Hz, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.92 (dd, J = 8.0 and 1.3 Hz, 1H), 7.94 (s, 1H), 8.28 (dd, J = 8.0 and 1.3 Hz, 1H); FT-IR (KBr) ν_{max}/cm^{-1} 2790, 1435, 1345, 1115, 936, 805. Found: C, 64.95; H, 6.42%. Calcd for $C_{34}H_{36}OS_3Si$: C, 64.81; H, 6.20%.

1,2-Bis[7-(triisopropylsiloxymethyl)benzo[1,2-*b*:4,3-*b′*]-dithiophen-2-yl]ethylene (11). 7-(Triisopropylsiloxymethyl)-benzo[1,2-*b*:4,3-*b′*]dithiophene-2-carbaldehyde **4** (10.71 g, 26.46 mmol) and {7-(triisopropylsiloxymethyl)-benzo[1,2-*b*:4,3-*b′*]dithiophenyl-2-ylmethy}triphenylphosphonium chloride **5** (18.19 g, 26.46 mmol) were dissolved into a mixture of THF (90 mL) and EtOH (380 mL). To the solution was added a solution of *t*-BuOK (4.45 g, 39.69 mmol) in EtOH (80 mL) at room temperature and the resulting yellow suspension was stirred for 16 h. The reaction was quenched by water, then 10% hydrochloric acid (20 mL) was added and the resulting precipitates were collected by filtration. The solid was washed with ethanol and then with hexane, and dried in vacuo. The crude olefin was obtained as a yellow powder (17.69 g, 86%), which was purified by column chromatography with ethyl acetate–hexane (1:10) as eluent and then by sublimation in vacuo: mp 194 °C; ^1H NMR ($CDCl_3$) δ 1.09–1.29 (m, 42 H), 5.14 (d, J = 1.1 Hz, 4 H), 7.30 (s, 2 H), 7.48 (d, J = 1.1 Hz, 2H), 7.61 (s, 2 H), 7.66 (d, J = 9.0 Hz, 2H), 7.74 (d, J = 9.0 Hz, 2H); FT-IR (KBr) ν_{max}/cm^{-1} 2995, 2875, 1463, 1382, 1136, 1083, 886, 795, 705. Found: C, 64.82; H, 7.42%. Calcd for $C_{42}H_{56}O_2S_4Si_2$: C, 64.90; H, 7.26%.

1,2-Bis(thieno[3,2-*f*]quinolin-2-yl)ethylene (12). To a stirred mixture of thieno[3,2-*f*]quinoline-2-carbaldehyde **6** (0.16

g, 0.77 mmol) and (thieno[3,2-*f*]quinolin-2-ylmethyl)triphenylphosphonium chloride **7** (0.38 g, 0.77 mmol) in a solution of THF (5 mL) and MeOH (10 mL) was added *t*-BuOK (0.17 g, 1.54 mmol) and the mixture was stirred overnight at room temperature. The resulting precipitate was filtrated, and washed with MeOH and then with benzene. The crude olefin (0.25 g, 82%) was dried and purified by sublimation in vacuo: mp 371 °C; ^{1}H NMR (DMSO-d_6–THF-d_8) δ 7.57 (s, 2H), 7.68 (dd, J = 8.4 and 4.4 Hz, 2H), 7.94 (d, J = 8.9 Hz, 2H), 8.28 (d, J = 8.9 Hz, 2H), 8.47 (s, 2H), 8.89 (dd, J = 8.4 and 1.5 Hz, 2H), 8.94 (dd, J = 4.4 and 1.5 Hz, 2H); FT-IR(KBr) $\nu_{\max}$/cm^{-1} 1608, 1576, 1496, 1382, 943, 833, 824. Found: C, 73.29; H, 3.59%. Calcd for $C_{24}H_{14}N_2S_2$: C, 73.07; H, 3.53%.

1-(Thieno[3,2-*f*]quinolin-2-yl)-2-[7-(*t*-butyldimethylsiloxy)benzo[1,2-*b*:4,3-*b′*]dithiophen-2-yl]ethylene (13). To a stirred mixture of 7-(triisopropylsiloxymethyl)benzo[1,2-*b*:4,3-*b′*]dithiophene-2-carbaldehyde **4** (0.52 g, 1.05 mmol) and (thieno[3,2-*f*]quinolin-2-ylmethyl)triphenylphosphonium chloride **7** (0.38 g, 1.05 mmol) in a solution of THF (10 mL) and MeOH (10 mL) was added *t*-BuOK (0.24 g, 2.10 mmol) and the mixture was stirred overnight at room temperature. The resulting precipitate was filtrated, and washed with MeOH and then with benzene. The crude olefin (0.48 g, 84%) was dried and purified by sublimation in vacuo: mp 306 °C; ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 6H), 0.98 (s, 9H), 5.05 (d, J = 0.8 Hz, 2H), 7.30 (d, J = 15.8 Hz, 1H), 7.36 (d, J = 15.8 Hz, 1H), 7.48 (d, J = 0.8 Hz, 1H), 7.52 (dd, J = 8.3 and 4.3 Hz, 1H), 7.63 (s, 1H), 7.67 (d, J = 8.6 Hz, 1H), 7.74 (d, J = 8.6 Hz, 1H), 7.91 (s, 1H), 7.99 (d, J = 9.2 Hz, 1H), 8.04 (d, J = 9.2 Hz, 1H), 8.58 (dd, J = 8.3 and 1.5 Hz, 1H), 8.94 (dd, J = 4.3 and 1.5 Hz, 1H); FT-IR (KBr) $\nu_{\max}$/cm^{-1} 2910, 1482, 1268, 1105, 932, 836, 704. Found: C, 66.51; H, 5.42%. Calcd for $C_{30}H_{29}NOS_3Si$: C, 66.25; H, 5.37%.

2-(2-Thienylethenyl)benzo[1,2-*b*:4,3-*b′*]dithiophene (14). This compound was prepared from benzo[1,2-*b*:4,3-*b′*]dithiophene-2-carbaldehyde **1** and diethyl (2-thienylmethyl)phosphonate: mp 190 °C; ^{1}H NMR ($CDCl_3$) δ 7.02 (dd, J = 5.0 and 5.2 Hz, 1 H), 7.12 (d, J = 5.0 Hz, 1 H), 7.19 (m, 2H), 7.23 (d, J = 5.2 Hz, 1H), 7.55 (d, J = 5.3 Hz, 1H), 7.60 (s, 1 H), 7.65 (d, J = 5.3 Hz, 1H), 7.71 (d, J = 8.6 Hz, 1H), 7.77 (d, J = 8.6 Hz, 1H); FT-IR (KBr) $\nu_{\max}$/cm^{-1} 3022, 1433, 1339, 1198, 1181, 1134, 1084, 1042, 938, 903, 924, 803, 766. Found: C, 64.62; H, 3.62%. Calcd for $C_{16}H_{10}S_3$: C, 64.39; H, 3.78%.

1,7-Bis(2-thienylethenyl)benzo[1,2-*b*:4,3-*b′*]dithiophene (15). This compound was prepared from benzo[1,2-*b*:4,3-*b′*]dithiophene according to the literature procedure: mp 286 °C (230 °C); ^{1}H NMR ($CDCl_3$) δ 7.04 (dd, J = 5.1 and 5.3 Hz, 2H), 7.12 (d, J = 5.1 Hz, 2 H), 7.18 (m, 4H), 7.24 (d, J = 5.1 Hz, 2H), 7.53 (s, 2H), 7.66 (s, 2 H); FT-IR (KBr) $\nu_{\max}$/cm^{-1} 3065, 1464, 1428, 1364, 1183, 1073, 895, 787, 689, 592.

9,9′-Dimethoxy-2,2′-bi(naphtho[2,1-*b*]thiophene) (16). This compound was prepared from 9-methoxynaphtho[2,1-*b*]thiophene by a method similar to that described in the literature[27] mp 290 °C; ^{1}H NMR ($CDCl_3$) δ 4.18 (s, 3H), 7.06 (d, J = 7.7 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.72 (d, J = 8.7 Hz, 1H), 7.86 (d, J = 8.7 Hz, 1 H), 8.8 (s, 1 H); MS *m/z* (rel intensity) 218 (8) 329 (2), 426 (M^+; 100).

2,2′-Bi(dithieno[3,2-*b*:2′,3′-*d*]dithiophene) (17). This compound was prepared from dithieno[3,2-*b*:2′,3′-*d*]thiophene according to the literature procedure: mp 316 °C (lit. [27] 316 °C); FT-IR (KBr) $\nu_{\max}$/cm^{-1} 3065, 1464, 1428, 1364, 1183, 1073, 895, 787, 689, 592.

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