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Photo- and electro-luminescent properties of thermotropic liquid crystalline quaterphenyl analogues comprising a 2,2′-bi-1,3,4-thiadiazole unit

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Thermotropic liquid crystalline quaterphenyl analogues constituting a central 2,2′-bi-1,3,4-thiadiazole ring, the compounds 5,5′-bis(4-methoxy- and 4-octyloxy-phenyl)-1,3,4-thiadiazole, have been prepared and their photoluminescent (PL) and electroluminescent (EL) properties evaluated. The materials form enantiotropic smectic and nematic phases. The PL spectra showed that they emit blue and green fluorescence in the solid state. The octyloxy compound exhibited an EL spectrum with blue emission and is a candidate for organic EL applications.

1. Introduction

In recent years organic electroluminescent (EL) devices have attracted much attention for their potential applications [1–6]; the devices are constituted of light-emitting electron- and hole-transporting materials. Aromatic derivatives of 1,3,4-oxadiazole are good electron-transporting materials for organic EL devices [7], but generally they have poor mesogenic properties owing to their bent molecular structure [8] and no liquid crystalline (LC) melts are formed in many cases [9]. However, the corresponding aromatic derivatives of 1,3,4-thiadiazole, which is a five-membered heterocycle containing a sulphur atom instead of an oxygen atom in the 1,3,4-oxadiazole ring, are calamitic mesogens [10] and form stable thermotropic nematic and smectic phases [11]. Zaschke and co-workers reported that terphenyl and quaterphenyl analogues of 1,3,4-thiadiazole—2,5-bis(4-substituted-phenyl)-1,3,4-thiadiazoles and 5,5′-bis(4-hexyloxyphenyl)-2,2′-bi-1,3,4-thiadiazole—form nematic and smectic phases, whereas LC phases in the analogous 1,3,4-oxadiazole derivatives are absent [11, 12]. Twin 2,5-diphenyl-1,3,4-thiadiazole derivatives having a central dioxyoctamethylene chain have been shown to have more stable LC phases than the twin 1,3,4-oxadiazole analogues [13]. Among them, twin 1,3,4-oxadiazole derivatives with substituted aliphatic chains showed no LC phases. Interestingly, it was found that a quaterphenyl analogue of 1,3,4-oxadiazole composed of biphenyl and 2-phenyl-1,3,4-oxadiazole moieties, the compound 2-(4′-hexyloxy-4-biphenylyl)-5-(4-hexyloxyphenyl)-1,3,4-oxadiazole, which has a high electron mobility and polarized EL properties, shows smectic phases [14]. We have very recently reported that semi-rigid polyesters composed of 2,5-diphenyl-1,3,4-thiadiazole have not only LC properties, but also photoluminescent (PL) properties [15]. They have lower band gap energies and show PL blue emission at longer wavelengths, the Stokes shifts being 54–97 nm in the solid state. They are candidates for organic EL applications.

The purpose of this work was to synthesize new LC quaterphenyl analogues comprising the 2,2′-bi-1,3,4-thiadiazole unit in the centre and two benzene rings, one on each side, that is the 5,5′-bis(4-methoxy- and 4-octyloxy-phenyl)-2,2′-bi-1,3,4-thiadiazoles **4** and **6** (see the scheme), and to evaluate the PL and EL properties. The materials were expected to be electron-transporting and/or light-emitting materials useful for organic EL devices because of their more symmetric and longer conjugated aromatic structures than those of the analogous terphenyl derivatives of 1,3,4-oxa- and 1,3,4-thiadiazole (the 2,5-diphenyl-1,3,4-thia- and 2,5-diphenyl-1,3,4-oxadiazoles). No information on the PL and EL properties

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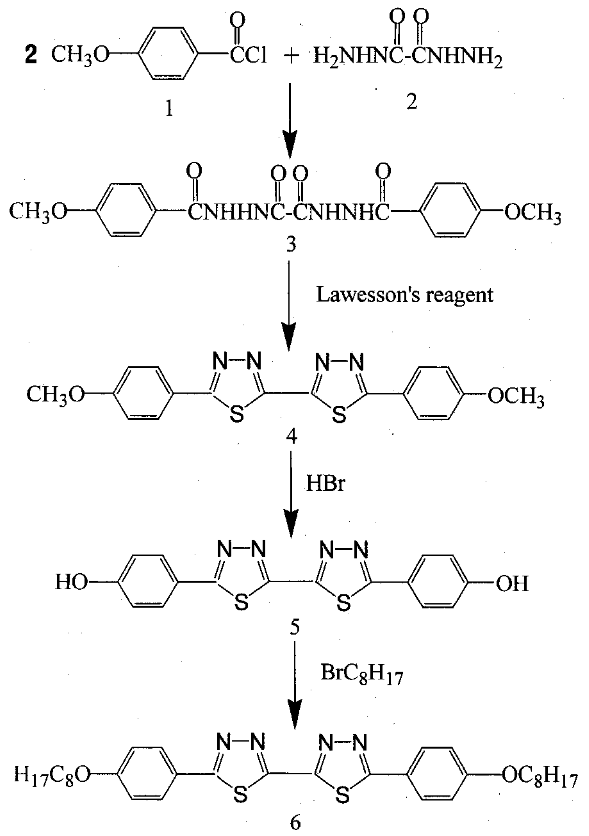

Scheme.

of the quaterphenyl analogue, 5,5′-bis(4-hexyloxyphenyl)-2,2′-bi-1,3,4-thiadiazole mentioned above was reported in [11].

2. Preparation of materials

The bismethoxy derivative of 2,2′-bi-1,3,4-thiadiazole, **4**, was derived by intramolecular cyclization of the corresponding intermediate dihydrazide, compound **3**, prepared from *p*-methoxybenzoyl chloride **1** and oxalyl dihydrazide **2** in 1,4-dioxane with Lawesson's reagent. Subsequenty the bishydroxy derivative **5** was obtained by heating compound **4** under reflux in hydrobromic acid [16]. Williamson reaction of compound **5** with 1-bromo-octane afforded the bisoctyloxy derivative of quaterphenyl analogue **6** containing a central 2,2′-bi-1,3,4-thiadiazole ring. These compounds were characterized by FTIR and ^{13}C NMR spectra, and elemental analyses.

The reaction procedure for compound **6** was as follows. Compound **5** (0.637 g, 1.8 mmol) and 1-bromo-octane (0.743 g, 3.8 mmol) were heated under reflux in *N*,*N*-dimethylformamide (DMF) (20 ml) for 8 h in the presence of potassium carbonate (0.59 g, 4.27 mmol). After the reaction, the mixture was poured into water to obtain the desired product. The precipitated yellow solid was filtered off and washed thoroughly with water. Then the product **6** was recrystallized from DMF three times and dried at 60°C for 24 h *in vacuo*; yield 79%. ^{13}C NMR: δ c (dichloroacetic acid: $CDCl_a$ 50 : 50 v/v) 173.1 (carbon at 5-position), 163.2 (carbon at 2-position), 157.3, 130.5, 119.2, 115.9 (aromatic carbons), 68.8 (OCH_2), 31.6, 29.1, 29.0, 28.8, 25.7, 22.5, 13.9 ppm (CH_a). Anal. for $C_{32}H_{42}N_4O_2S_2$ (578.9): found (calc.) C 65.68 (66.39), H 7.16 (7.33), N 9.94 (9.68%).

3. Mesomorphic properties

The LC properties of compound **4–6** were investigated by differential scanning calorimetry (Shimadzu DSC-60 calorimeter) and by texture observation by polarizing optical microscopy (Nikon) involving a hot stage. These measurements indicated that the 2,2′-bi-1,3,4-thiadiazole compounds **4** and **6** form stable enantiotropic smectic (SmC, broken fan and broken polygonal textures) and nematic (N, schlieren texture) phases—**4**: Cr 287.5°C (2.75 J g^{-1}) SmC 315.6°C (92.6 J g^{-1}) N 352.5°C (0.68 J g^{-1}) I, **6**: Cr 186.5°C (0.86 J g^{-1}) SmC 303.3°C (0.83 J g^{-1}) N 318.8°C (0.19 J g^{-1}) I. The bishydroxy derivative **5** gave no LC melt.

4. Photo- and electro-luminescent properties and discussion

The PL and EL properties of compounds **4** and **6** were evaluated. Solid state UV-vis spectra of vacuum-deposited films **4** and **6** were recorded with a Shimadzu UV-2200A spectrometer and showed maximum absorptions arising from π-π^* electron transitions of the 2,2′-bi-1,3,4-thiadiazole unit at 366 and 345 nm. HOMO-LUMO band gap energies (E_g) taken from the onset of the absorption spectra were 2.75 eV for **4** and 2.95 eV for **6**. Compound **6** having the longer aliphatic (octyloxy) chain displayed a higher E_g value than **4**. These values were lower than those of the 1,3,4-oxadiazole compounds [17].

Measurements of ionization potentials (I_p) with a Rikenkeiki Ultraviolet Photoelectron Analyzer AC-1 in air indicated that the HOMO levels are 6.20 eV for **4** and 6.22 eV for **6**. The LUMO levels of **4** and **6** calculated from the E_g and I_p values were 3.45 eV and 3.27 eV, respectively. Solid state PL spectra obtained with S. A. Instruments Fluoro Max-2 DM-3000F showed a maximum peak at 510 nm for **4** and two peaks at 452 and 472 nm for **6**, with emission of green and blue fluoroscence (figure 1). The band edge of the PL spectrum for **4** expanded beyond 600 nm. Compared with the absorption spectra, the PL spectra were red-shifted by 144 nm for **4** and by 107–127 nm for **6**. The optical data for **4** and **6** are listed in the table.

From these observations, the energy level diagram for **6** shown in figure 2 can be considered. This suggests that

Table. Optical data for compounds **4** and **6**.

Compound	E_g[a]/eV	I_p[b]/eV	LUMO/eV	Absorption, λ_{max}/nm	Fluorescence, λ_{max}/nm
4	2.75	6.20	3.45	366	510
6	2.95	6.22	3.27	345	452, 472

[a] HOMO-LUMO band gap energy obtained from the onset of solid state UV-vis absorption spectra.
[b] Ionization potential.

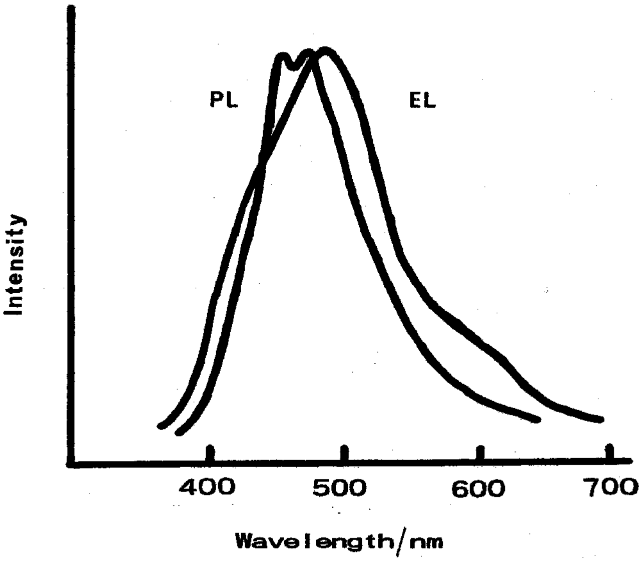

Figure 1. PL and EL spectra of **6** in the solid state.

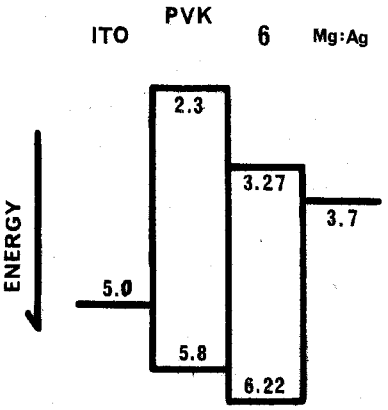

Figure 2. Energy level diagram for **6** in a device.

poly(vinylcarbazole) (PVK) acts as hole-transporting material and compound **6** as an electron-transporting and light-emitting material in EL devices. Two types of EL devices (single and double layer) were designed and fabricated. In the single layer device, PVK film containing **6** (1 wt%) was spin-coated onto ITO glass. Vacuum-deposited **6** was sandwiched between a PVK spin-coated film on ITO and a cathode (Mg:Ag) in the double layer device.

Single-layer device: ITO/**6** (1 wt%): PVK (100 nm)/Mg:Ag (10:1).

Double-layer device: ITO/PVK (50 nm)/**6** (50 nm)/Mg:Ag (10:1).

The EL spectrum of the single layer device in figure 1, measured with a Hamamatsu Photonic multi-channel analyser (PMA) and a Hitachi F-4010 fluorescence spectrometer, exhibited a peak maximum a 486 nm with blue emission. The EL spectrum in the double layer device was similar to that in the single layer device. The brightness/voltage dependence measured with a TOPCON BM-8 instrument showed that the highest luminances in the single layer and in the double layer devices were 13 cd m^{-2} at 18 V and 1.6 cd m^{-2} at 11 V, respectively.

Unfortunately, compound **4** crystallizes easily and thus occurred during fabrication of devices, so that the EL data were measured with difficulty.

5. Conclusions

In conclusion, new quaterphenyl analogues **4** and **6** comprising a central 2,2′-bi-1,3,4-thiadiazole ring have been prepared; they show not only LC phases, but also PL spectra with green and blue emission in the solid state. The compound **6** has EL properties and is a candidate as an electron-transporting and light-emitting material for organic EL devices, although its brightness is low. Use of a light-emitting material such as 8-hydroxyquinoline aluminium (Alq3) [7] will lead to better EL devices having high brightness.

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