New RGB Emitting Materials having a 2,2'-Bi-[1,3,4]-thiadiazole Skeleton for Organic Light Emitting Devices

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Three new emitting materials, featuring a 2,2'-bi-[1,3,4]-thiadiazole core, for the use in organic electroluminescent devices (OLEDs) have been synthesized and tested. Color tuning from blue to red was achieved by attaching various electron donors to the basic skeleton. The obtained maximum brightness for blue, green and red were 2080 cd/m², 56000 cd/m² and 1070 cd/m², respectively.

Keywords: Organic light emitting diode, RGB emission, 2,2'-Bi-[1,3,4]-thiadiazole

1. Introduction

Since the first demonstration of low voltage organic electroluminescence by Tang and Van Slyke more than a decade ago [1], organic light emitting devices have drawn growing attention for their potential application in flat panel displays. This emerging technology is anticipated to replace today's displays in many areas. Beside high brightness, low operating voltage and RGB emission, OLEDs offer the advantage of low cost manufacturing. Ever since the beginning of the research activities in this field, heterocycles have played an important role as emitting or charge transporting materials. The very first reported emitter, AlQ₃, is a heterocyclic metal complex and many of today's state of the art materials contain heterocyclic skeletons, because of their high brightness and color purity [2]. 5,5'-Bis-aryl substituted 2,2'-bi-1,3,4-thiadiazoles have been used in electrophotography due to their high thermal stability [3] and very recently, the photo- and electroluminescent properties of this class of materials were reported [4] for the first time. In this paper, we report on the fabrication of RGB emitting OLEDs which utilize newly synthesized 5,5'-bis-aryl-2,2'-bi-[1,3,4]-thiadiazoles as emissive materials. Color tuning was achieved by attaching electron donors of different donor strength to the basic skeleton, which itself is an electron acceptor. This approach further contributes to the cost

effectiveness of OLEDs, as all required colors could be obtained from only two key compounds. These key compounds are 5,5'-bis(4-bromophenyl)-[2,2']-bi-[1,3,4]-thiadiazole (**1**) and 5,5'-bis(p-tolyl)-[2,2']-bi-[1,3,4]-thiadiazole (**2**) [5]. Compound **1** allows for various palladium catalyzed coupling reactions [6], while compound **2** offers the possibility of attaching styryl type substituents to the system via Wittig chemistry. The synthetic access to the precursors and the new emitters is outlined in Scheme 1. It starts from commercial p-methylbenzoylchloride (**3**) and p-bromobenzoylchloride (**4**), which were converted into the corresponding dihydrazides **5** and **6**, respectively. Thiation of **5** and **6** with the Lawesson reagent yielded **1** and **2**. Compound **2** was subsequently brominated to give the bis-bromomethyl substituted compound **7**, which was converted into the Wittig salt **8**. Reaction of **8** with different aromatic aldehydes afforded the styryl substituted 2,2'-bi-[1,3,4]-thiadiazoles **9** and **10**. Compound **11** was obtained by means of a palladium catalyzed amination reaction of **1** with p-di-tolylamine

2. Experimental

T_g and T_m were measured with a PERKIN ELMER Pyris 1 instrument. CV was measured with a BAS 100/W MF-9094 instrument. UV spectra were taken with a HITACHI U-3010 instrument. PL

spectra were taken with a HITACHI F-4500 instrument. FAB HRMS were taken with a JEOL JMS-01SG-2 instrument. $^1\text{H-NMR}$ spectra were recorded on a JEOL ECA-400 instrument. Chemical shifts are expressed in ppm downfield from tetramethylsilane as an internal standard. FT-IR spectra were measured with a JASCO FT-IR-420.

Scheme 1. Synthesis of 2,2'-Bi-[1,3,4]-thiadiazoles

The EL devices were fabricated on transparent ITO ($15 \text{ } \Omega/\text{m}^2$, thickness $1200 \text{ } \text{\AA}$), obtained from Nippon Sheet Glass Company and fabricated by conventional vapor deposition method under a vacuum of $1 \times 10^{-4} \text{ Pa}$. The substrate was cleaned by UV/ ozone treatment prior to deposition. N,N'-bis-(9,9-dimethyl-9H-fluoren-2-yl)-N,N'-diphenyl-biphenyl-4,4'-diamine (compound **12**, DFLDPBi) [7] was used as a hole transport layer. Compound **12** was deposited by spin coating from a 0.1 weight-% chloroform solution. The thickness was $110 \text{ } \text{\AA}$. In cases the emitting layer comprised of a host dopant system, either AlQ_3 or 1,3,5-tris-(9,9-dimethyl-9H-fluoren-2-yl)benzene (compound **13**, TFB-3) was used as matrix [8]. The structures of this new hole transporter and host material are shown in Fig. 1. Either AlQ_3 or

bathophenanthroline (Bphen) were utilized as electron transporting materials. Finally, an AlI_3 electron injection layer and an Al cathode were deposited. The luminance of the device was measured with a TOPCON LUMINANCE COLORIMETER BM-7 instrument. The CIE color coordinates were measured with an OTSUKA ELECTRONICS Photol MCPD-7000 instrument.

Figure 1. Structure of the hole transporting (**12**) and host material (**13**) used in this work

2.1 5,5'-Bis(4-bromophenyl)-[2,2']-bi-[1,3,4]-thiadiazole (**1**)

A solution of 1.18 g (10.0 mmol) oxalic dihydrazide in 50 ml of dry DMF was added dropwise to a solution of 4.39 g (20.0 mmol) p-bromobenzoylchloride **4** in 20 ml of DMF. After the addition was completed, the solution was stirred at 80°C for 1 h. After cool down, the precipitated dihydrazide **6** was filtered off, washed with H_2O and EtOH, dried *in vacuo* and used in the next step without further purification. Thiation of **6** (3.12 g, 6.44 mmol) with the Lawesson reagent (5.21 g, 12.9 mmol) gave compound **1**, which was recrystallized from DMF (Yield: 1.87 g, 39.1 %). FT-IR (KBr): $\nu = 1587, 1432, 1396 \text{ cm}^{-1}$. $^1\text{H-NMR}(\text{CDCl}_3:\text{CF}_3\text{COOD}=1:1)$: $\delta = 7.92 \text{ (d, 8.08Hz, 4H)}$, $7.83 \text{ (d, 8.08Hz, 4H)}$ ppm.

2.2 5,5'-Bis(p-tolyl)-[2,2']-bi-[1,3,4]-thiadiazole (**2**)

Compound **2** was prepared in a similar manner, starting from 1.54 g (13.0 mmol) of oxalic dihydrazide and 3.24 g (21.0 mmol) of 4-methylbenzoylchloride (**3**) (Yield: 1.76 g, 5 mmol, 38.7 %).

2.3 5,5'-bis(4-bromomethylene)-[2,2']-bi-[1,3,4]-thiadiazole (**7**)

A mixture of **2** (1.05 g, 3.0 mmol), NBS (1.07g, 6.0 mmol), and AIBN (100 mg) in CCl_4 (40 ml) was refluxed for 4 h. After cooling the mixture was filtered, washed with CCl_4 and the filtrate was evaporated. The obtained residue was purified by column chromatography. (Yield: 1.21g, 2.38 mmol,

79.4%) FT-IR (KBr): $\nu = 1607, 1434, 1407 \text{ cm}^{-1}$. $^1\text{H-NMR}(\text{CDCl}_3)$: $\delta = 8.05$ (d, 8.12Hz, 4H), 7.56 (d, 8.12Hz, 4H), 4.54 (s, 4H) ppm.

2.4 5,5'-Bis(4-styryl-phenyl)-[2,2']-bi-[1,3,4]-thiadiazole (9)

A mixture of **7** (0.508 g, 1.0mmol) triphenylphosphine (0.66 g, 2.5mmol) in DMF (50 ml) was stirred at 120°C for 8 h. After cooling, the mixture was filtered. The Wittig salt **8** was obtained as white crystals and used in the next step without purification (0.82g, 0.79 mmol, 79%). Next, a mixture of **8** (0.438g, 0.42 mmol) and *t*-BuOK (0.095 g, 0.84 mmol) in EtOH (100 ml) was stirred under cooling with an ice bath. Benzaldehyde (0.090 g, 0.84 mmol) was added and the mixture was stirred at r.t. for 3 h. The mixture was filtered, washed with MeOH and dried. The crude **9** was purified by column chromatography. (0.14 g, 0.26 mmol, 63 %, mixture of E and Z isomer). FT-IR(KBr, cm^{-1}): $\nu = 1602, 1492, 1431, 1409 \text{ cm}^{-1}$. $^1\text{H-NMR}(\text{CDCl}_3)$: $\delta = 8.08$ (d, 8.56 Hz, 4H), 7.85 (d, 8.52 Hz, 4H), 7.62 (d, 7.32 Hz, 4H), 7.50-7.36 (m, 8H), 7.25 (d, 16.52 Hz, 2H) ppm. MALDI-TOF MS: $m/z = 526$.

2.5 5,5'-Bis(4-[4-di-p-tolyl-amino]-phenyl-vinyl)-[2,2']-bi-[1,3,4]-thiadiazole (10)

A mixture of **8** (0.438g, 0.42 mmol) and *t*-BuOK (0.095 g, 0.84 mmol) in EtOH (100 ml) was stirred under cooling with an ice bath. 4-(di-p-tolylamino)benzaldehyde (0.253 g, 0.84 mmol) was added to the mixture and the mixture was stirred at r.t. for 4.5 h. The mixture was filtered, washed with MeOH and dried. Crude **10** was purified by column chromatography. (0.22 g, 0.24 mmol, 57%). FT-IR (KBr): $\nu = 1591, 1505 \text{ cm}^{-1}$. $^1\text{H-NMR}(\text{CDCl}_3)$ $\delta = 8.04$ (d, 8.40Hz, 4H), 7.62 (d, 8.40 Hz, 4H), 7.39 (d, 7.76 Hz, 4H), 7.21-7.02 (m, 20H), 6.95 (d, 7.76 Hz, 4H), 2.36 (s, 12H) ppm. FAB-HRMS found: $m/z = 917.3466$, calculated for $[\text{M}+\text{H}]^+$: 917.3460.

2.6 5,5'-Bis(4-di-p-tolylamino)-phenyl-[2,2']-bi-[1,3,4]-thiadiazole (11)

t-BuOK (0.10 g, 0.9 mmol) and tri-tert-butyl phosphine (20 mg 0.10 mmol) were added to a mixture of **1** (0.25g, 0.50 mmol) and p-ditolylamine (0.60g, 3.0 mmol) in xylene (80 ml) under N_2 atmosphere. After this, $\text{Pd}(\text{OAc})_2$ (0.022 g, 0.10

mmol) was added and the mixture was refluxed for 5 h. After cooling, the mixture was extracted with

toluene. The combined organic layers were evaporated and the residue was purified by column chromatography. (0.066 g, 18%). FT-IR (KBr): $\nu = 2922, 1597, 1508, 1412, 1323 \text{ cm}^{-1}$. $^1\text{H-NMR}(\text{CDCl}_3)$: $\delta = 7.83$ (d, 9.20 Hz, 4H), 7.13 (d, 8.40 Hz, 8H), 7.06 (d, 8.40 Hz, 8H), 7.01 (d, 9.20 Hz, 4H), 2.35 (s, 12H) ppm. FAB-HRMS found: $m/z = 713.2527$, calculated for $[\text{M}+\text{H}]^+$: 713.2521.

3. Results and discussion:

3.1 Physical properties:

The results of the uv-vis and fluorescence spectra measurements as well as the thermal and the CV data are shown in table 1. The 5,5'-bis(p-tolyl) substituted 2,2'-bi-[1,3,4]-thiadiazole **2** showed purple emission, peaking at 418 nm. Introducing a styryl group, like in compound **9** extended the conjugation of the system and led to a strong bathochromic shift of 47 nm in the emission spectrum. This effect was even more pronounced in case of compound **11**, where the di-p-tolylamine substituent was attached. In this case, a bathochromic shift of 143 nm was observed. Compound **10** represents a combination, where the styryl and the di-p-tolyl chromophor together are linked to the basic skeleton. The observed red shift of 193 nm almost reflects the sum of the contribution of every individual chromophor.

CV data indicated that all new compounds are good electron acceptors. The reduction potential of every compound was lower than that of AlQ_3 , which is a well-known electron transporter. Therefore, a facile electron injection from the injecting layer was anticipated. Expectedly, the introduction of aryl amine substituents significantly lowered the oxidation potential. While compounds **2** and **9** showed no oxidation within the scanning range, compound **10** and **11** showed oxidation steps at 0.61 V and 0.79 V, respectively.

Thermal data indicated that all compounds have excellent thermal stabilities. The melting points lay well above 250°C. Compound **10** exhibited two melting points corresponding to the *E*- and *Z*-isomer. Only compound **11** showed a glass transition at 123°C.

Material	Absorption ^a λ_{max} (nm)	Fluorescence ^b λ_{max} (nm)	E_{RED}^c (V)	E_{OX}^c (V)	T_m^d (°C)	T_g (°C)
2	345	418	-1.77	N.D.	330	N.D.
9	378	465	-1.67	N.D.	320	N.D.
10	449	611	-1.70	0.61	273, 296	N.D.
11	448	561	-1.78	0.79	262	123

^a) Absorption spectra in chloroform. ^b) Fluorescence spectra in chloroform obtained by irradiation at 365nm. ^c) All CV data were measured in a 0.1M CH₂Cl₂ solution of n-Bu₄NClO₄. ^d) T_m and T_g of the samples were determined by DSC. N.D.: Not detected.

Table 1. Physical properties of compounds 2, 9, 10 and 11.

3.2. EL properties:

3.2.1. Blue

The obtained photoluminescence data suggested compound 9 to be suitable as blue emitter. We chose compound 13 (TFB3) as a host material. TFB3 has the advantage of emitting at exceptionally short wave length (373 nm) [8] and was therefore anticipated to be an excellent host. A device of the following structure was prepared. ITO / DFLDPBi 110 Å / TFB3 + 5 % 9 110 Å / Bphen 400 Å / AILi 70 Å / Al 1500 Å. The device showed pure blue emission, peaking at 460 nm, with CIE color coordinates of (0.15, 0.16). Indeed a very efficient energy transfer from TFB3 to 9 occurred, as no emission from the host material was observed. The maximum luminous efficiency reached 0.23 lm/W with a maximum brightness of 2080 cd/m² at 12 V. An EL spectrum of the fabricated device is depicted in Fig. 2.

Fig. 2. Device EL spectrum of 9.

3.2.2. Green

Compound 11 was used as dopant in an AlQ₃ matrix. The device had the following structure: ITO / DFLDPBi 110 Å / AlQ₃ + 11 600 Å / AILi 70 Å / Al 1500 Å. Two different dopant levels were investigated. At 0.5 % dopant concentration pure green emission, peaking at 540 nm, was observed. The CIE color coordinates were (0.35, 0.57). The maximum luminous efficiency was as high as 3.3 lm/W at 4 V. This is about three times the efficiency

of a comparable device utilizing AlQ₃ alone and underlines that the emission in fact stems from the dopant. The obtained maximum brightness was 56000 cd/m² at 10 V. However, when the dopant level was raised to 5 % apparently aggregate formation occurs. The emission became red shifted by 20 nm and the color appeared yellowish green. Additionally, the luminous efficiency dropped to 1.16 lm / W at 11 V. The maximum brightness was 24700 cd / m² at 16 V. Fig. 3 shows the EL spectrum of the device at different doping levels.

Fig. 3. Device EL spectra of 11 at different doping concentrations.

3.2.3. Red

From the photo luminescence measurements compound 10 was expected to be suitable as red emitter. The EL properties of 10 at different dopant levels were investigated using the following structure. ITO / DFLDPBi 110 Å / AlQ₃ + 10 600 Å / AILi 70 Å / Al 1500 Å. Surprisingly, at 0.5 % dopant level the emitted color was yellowish green, peaking at 551 nm. By increasing the dopant concentration it was possible to shift the emission to longer wavelength but the red shift was accompanied by a pronounced decrease in the maximum efficiency. A device without AlQ₃ matrix, having the following structure, was fabricated. ITO / FL 03 110 Å / 10 600 Å / AILi 70 Å / Al 1500 Å.

Dopant	Concentration %	$\lambda_{\max}$ nm	Maximum efficiency lm/W at (V)	Maximum brightness cd/m ² at (V)
9	5	460	0.23 (9)	2080 (12)
11	0.5	540	3.3 (4)	56000 (10)
11	5	560	1.16 (11)	24700 (16)
10	0.5	551	1.48 (6)	18900 (14)
10	5	576	0.48 (9)	24300 (16)
10	10	581	0.30 (11)	9160 (20)
10	100	610	0.12 (8)	1070 (13)

Table 2. EL properties of compounds 9, 10 and 11 at various dopant concentrations.

It showed orange/red emission, peaking at 610 nm, with color coordinates of (0.57, 0.43). The maximum luminous efficiency was 0.12 lm/W, which is reasonably high for a non-dope device. The EL device spectra of 10 at different doping levels are shown in Fig. 4 and the EL properties are summarized in Table 2.

Fig. 4. Device EL spectra of 10 at different doping concentrations

4. Conclusion

Three new emitters for organic electroluminescent devices, having a 5,5'-bis-aryl-2,

2'-bi-[1,3,4]-thiadiazole skeleton were synthesized. Color tuning was achieved by introducing electron donors of different donor strength to the core. RGB emitting OLEDs with these compound were fabricated successfully. However, a strong dependency of the emitted color on the dopant concentration was observed.

5. References

1. C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.*, **51**, (1987) 913.
2. Y. Sato, *Mol. Electron. Bioelectron.*, **11** (1), (2000) 92.
3. Nihon Kokai Tokkyo Koho, *JP 57074747*, (1982).
4. M. Sato, R. Ishii, S. Nakashima, K. Yonetake and J. Kido, *Liquid Crystals*, **28** (8), (2001) 1211.
5. K. Dimitrova, J. Hauschild, H. Zschke, H. Schubert, *J. Prakt. Chem.*, **322** (6), (1980) 933.
6. For recent reviews see J. F. Hartwig, *Angew. Chem. Int. Ed.*, **37**, (1998) 2047, A. Suzukuki, *J. Organomet. Chem.*, **576**, (1999) 147.
7. A. Senoh, S. Mashimo, Y. Hashimoto, K. Ueno, *Polym. Prepr.*, **47**, (1998) 1862.
8. K. Suzuki, A. Senoh, H. Tanabe, K. Ueno, *Synth. Met.*, accepted for publication.