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Mendeleev Commun., 2016, **26**, 437–439
Mendeleev Communications

Novel 1,8-bis(diarylamino)pyrenes as OLED materials

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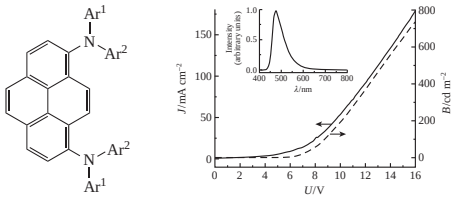
DOI: 10.1016/j.mencom.2016.09.025

New soluble electroluminescent pyrene derivatives, namely, 1,8-bis(diarylamino)pyrenes, have been synthesized by the Buchwald–Hartwing cross-coupling. Light-emitting devices based on these derivatives have been prepared.

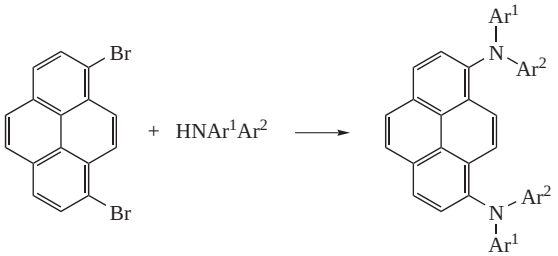


In recent years, pyrene derivatives are increasingly used as light-emitting materials for organic light-emitting devices (OLED) due to their luminous efficiency and high thermal stability.[1–11] In particular, the effective electroluminescent devices were prepared based on 1,6-disubstituted pyrenes.[1–3] Besides 1,6-disubstituted pyrenes, 2,7-disubstituted,[4] 1,3-disubstituted[5,6] as well as 1-mono-substituted[7–10] and 1,3,6,8-tetrasubstituted[11] pyrenes were used in OLEDs. However, there is no evidence of 1,8-disubstituted pyrenes tested in OLEDs. Meanwhile, 1,8-disubstituted pyrenes are known to be significantly more soluble compared to their 1,6-disubstituted analogues.[12] Therefore, 1,8-disubstituted pyrenes could be useful as solution-processable materials for the OLED preparing technology with organic layers formed by means of solution casting followed by evaporation of the solvent. For such technology, substances with sufficiently high solubility in usual organic solvents are required.[13] The research on solution-processable OLEDs is greatly stimulated in recent time by the development of organic lighting and signage technologies.[14,15]

Herein, we report on the synthesis of some new luminescent 1,8-bis(diarylamino)pyrenes and demonstrate the possibility of using them in electroluminescent devices prepared by the solution-processing technology. The choice of diarylamino groups is associated, in particular, to the fact that 1,6-pyrene derivatives with similar substituents showed high emission efficiency in electroluminescent devices.[1]

The target compounds **1**–**3** were obtained by the Buchwald–Hartwig cross-coupling of 1,8-dibromopyrene with the corresponding diarylamines[1,16] (Scheme 1).†

In turn, 1,8-dibromopyrene is the main product of double bromination of pyrene with bromine along with 1,6-isomer.[12,17,18] We have synthesized 1,8- and 1,6-dibromopyrenes according to published procedure.[12] Using the sequential fractional crystallization we separated the 1,8- and 1,6-isomers, which was



1 Ar^1 = Ph, Ar^2 = 2-naphthyl
2 $Ar^1 = Ar^2$ = 4-$Bu^tC_6H_4$
3 Ar^1 = Ph, Ar^2 = 1-naphthyl

Scheme 1

† The ^{1}H NMR spectra were recorded on a Bruker DRX 500 spectrometer (500.13 MHz, TMS-standard) in $CDCl_3$. Mass spectra were obtained on a Finnigan MAT INCOS 50 mass spectrometer (70 eV) using direct injection. The IR spectra were recorded for powders (ATR method) on a Perkin Elmer Spectrum 100 instrument.

*1,8-Bis[*N-*(2-naphthyl)*-N-*phenylamino]pyrene* **1**. The mixture of 5.4 g (0.015 mol) of 1,8-dibromopyrene, 8.3 g (0.038 mol) of *N*-phenyl-*N*-(2-naphthyl)amine, 80 mg of palladium diacetate, 280 mg of tri(*tert*-butyl)-phosphine, 3.8 g (0.04 mol) of sodium *tert*-butoxide and 100 ml of *o*-xylene was heated up to 125–130 °C. The reaction mixture was stirred at this temperature under argon atmosphere for 3.5 h. After cooling to room temperature the mixture was diluted with 100 ml of hexane. The solid product **1** was filtered, washed successively with hexane, methanol, water and dried *in vacuo* over P_2O_5, yield 9.35 g (98%). ^{1}H NMR, δ: 6.93–7.02 (m, 2H), 7.05 (d, 3H, *J* 7.9 Hz), 7.08–7.11 (m, 1H), 7.13 (d, 1H, *J* 7.5 Hz), 7.17 and 7.19 (2d, 3H, *J* 7.9 Hz), 7.23 (d, 1H, *J* 7.4 Hz), 7.26–7.37 (m, 7H), 7.44 (d, 1H, *J* 7.9 Hz), 7.48 (d, 1H, *J* 7.6 Hz), 7.64 (d, 1H, *J* 8.7 Hz), 7.68–7.75 (m, 3H), 7.83 (d, 1H, *J* 8.2 Hz), 7.84 (d, 1H, *J* 8.1 Hz), 7.90 (d, 1H, *J* 9.2 Hz), 8.03 (s, 1H), 8.05 (s, 1H), 8.10 (d, 1H, *J* 8.1 Hz), 8.17 (d, 2H, *J* 8.3 Hz). IR (ν/cm^{-1}): 3057, 1630, 1593 (C=C), 1574, 1508, 1491, 1467, 1421, 1388, 1362, 1294, 1273, 1237, 1184, 1077, 972, 939, 874, 846, 816, 747, 696. MS, *m*/*z*: 636 $[M]^+$. Found (%): C, 90.41; H, 5.31; N, 3.97. Calc. for $C_{48}H_{32}N_2$ (%): C, 90.53; H, 5.07; N, 4.40.

*1,8-Bis[*N,N-*bis(4-*tert*-butylphenyl)amino]pyrene* **2**. The mixture of 5.4 g (0.015 mol) of 1,8-dibromopyrene, 10.54 g (0.038 mol) of bis(4-*tert*-butylphenyl)amine, 80 mg of palladium diacetate, 280 mg of tri(*tert*-butyl)-phosphine, 3.8 g (0.04 mol) of sodium *tert*-butoxide and 100 ml of *o*-xylene was heated up to 125–130 °C. The reaction mixture was stirred at this temperature under argon atmosphere for 3 h. After cooling to room temperature the mixture was diluted with 100 ml of benzene and filtered from the precipitate, which was washed on the filter with 50 ml of benzene. The combined filtrates were evaporated to dryness and 50 ml of methanol was added to the residue. A precipitate thus formed was filtered, air dried, and recrystallized from a benzene–hexane mixture. Yield 11.14 g (98%). ^{1}H NMR, δ: 1.26 (s, 36H, 4-Bu^t), 6.90–6.98 (m, 8H), 7.14–7.19 (m, 8H), 7.81 (d, 2H, *J* 8.1 Hz), 7.98–8.20 (m, 6H). IR (ν/cm^{-1}): 3034, 2961 (CH, Bu^t), 1599, 1509 (C=C), 1493, 1459, 1423, 1393, 1363, 1337, 1321, 1302, 1268, 1189, 1121, 1024, 1014, 928, 849, 826, 735, 723, 698. MS, *m*/*z*: 761 $[M]^+$. Found (%): C, 87.91; H, 7.79; N, 3.99. Calc. for $C_{56}H_{60}N_2$ (%): C, 88.37; H, 7.95; N, 3.68.

confirmed by ^{1}H NMR data.‡ The ^{1}H NMR spectrum of 1,6-isomer contains 4 doublet signals, whereas the spectrum of 1,8-isomer contains 2 doublet and 2 singlet signals, which is in accordance with the reported data.[12,17,18]

The synthesized compounds **1**–**3** possess sufficiently good solubility in usual organic solvents (for example, in chloroform > 3 g dm^{-3} at room temperature). For comparison, we have synthesized the 1,6-isomer of compound **1** according to Scheme 1 with the use of 1,6-dibromopyrene.§ Its solubility turned out to be lower by a factor of ~40 than that of 1,8-isomer **1**.

Figure 1 shows the UV-VIS absorption and photoluminescence spectra of compounds **1**–**3**. The maximum of the most long-wave absorption band for all the three compounds lies in the region of 442–445 nm. The maximum of the photoluminescence band for **1**, **2** and **3** lies at 528, 500 and 505 nm and the half-width of the band amounts 59, 58 and 54 nm, respectively. Similar values were reported for the 1,6-diamino substituted analogue, 1,6-bis-[(*N*-phenyl)-*N*-(4-*tert*-butylphenyl)amino]pyrene: the maximum of the absorption band at 428 nm and the maximum of the photoluminescence band at 481 nm with the half-width of 62 nm.[1]

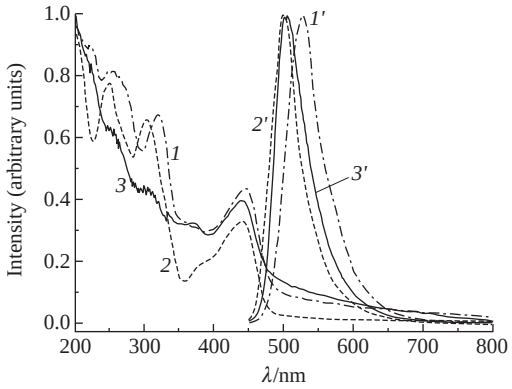


Figure 1 (*1*–*3*) UV-VIS and (*1′*–*3′*) PL spectra of (*1*,*1′*) **1**, (*2*,*2′*) **2** and (*3*,*3′*) **3**.

We have prepared the electroluminescent devices based on compounds **1**–**3** by spin casting of the solution followed by evaporation of the solvent.¶ For preparing the luminescent layer, we used the solution containing the blend of one of the luminescent compounds and polyvinylcarbazole (PVC)[19] with the

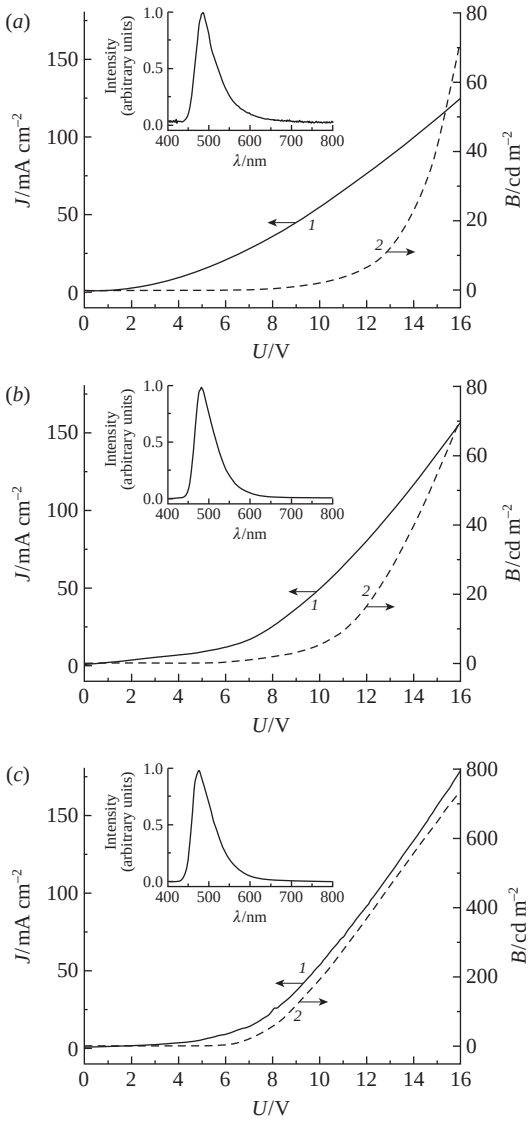


Figure 2 (*1*) Current–voltage and (*2*) brightness–voltage curves of the electroluminescent devices (*a*) ITO/PEDOT:PSS/PVC:**1** (50%)/Al:Ca, (*b*) ITO/PEDOT:PSS/PVC:**2** (50%)/Al:Ca and (*c*) ITO/PEDOT:PSS/PVC:**3** (50%)/Al:Ca. The inserts show the electroluminescence spectra of the corresponding devices.

*1,8-Bis[*N*-(1-naphthyl)*-N*-phenylamino]pyrene* **3**. The mixture of 5.4 g (0.015 mol) of 1,8-dibromopyrene, 8.3 g (0.038 mol) of *N*-phenyl-*N*-(1-naphthyl)amine, 80 mg of palladium diacetate, 280 mg of tri(*tert*-butyl)-phosphine, 3.8 g (0.04 mol) of sodium *tert*-butoxide and 100 ml of *o*-xylene was heated up to 125–130 °C. The reaction mixture was stirred at this temperature under argon atmosphere for 3.5 h. After cooling to room temperature, the mixture was diluted with 100 ml of hexane and filtered from the precipitate (5.4 g, by-products), the filtrate was evaporated to dryness. The residue was treated with 30 ml of acetone and then 30 ml of methanol was added to the mixture. Yellow precipitate was filtered, washed with methanol, dried *in vacuo* over P_2O_5. Yield 3.81 g (40%). ^{1}H NMR, δ: 6.70 (d, 4H, *J* 7.9 Hz), 6.84 and 6.85 (2d, 2H, *J* 7.3 Hz), 7.08 and 7.09 (2d, 4H, *J* 7.9 Hz), 7.21 (d, 2H, *J* 6.9 Hz), 7.27–7.35 (m, 4H), 7.42 and 7.44 (2d, 2H, *J* 7.1 Hz), 7.68 (d, 2H, *J* 8.2 Hz), 7.74 (d, 2H, *J* 8.2 Hz), 7.86 (d, 2H, *J* 8.1 Hz), 7.95 (s, 2H), 8.02–8.08 (m, 4H), 8.11 (s, 2H). IR (ν/cm^{-1}): 3042, 1594 (C=C), 1574, 1504, 1490, 1460, 1421, 1393, 1334, 1274, 1247, 1214, 1185, 1136, 1076, 1020, 968, 865, 850, 828, 817, 798, 791, 774, 735, 696. MS, *m*/*z*: 636 [M]$^+$. Found (%): C, 89.69; H, 5.26; N, 4.47. Calc. for $C_{48}H_{32}N_2$ (%): C, 90.53; H, 5.07; N, 4.40.

‡ *1,8-Dibromopyrene and 1,6-dibromopyrene.* The solution of 10 ml (31.19 g, 0.195 mol) of bromine in 500 ml of anhydrous CCl_4 was added dropwise to the solution of 20.2 g (0.1 mol) pyrene in 500 ml of anhydrous CCl_4 for 6 h at 20–25 °C. Once the addition of bromine was completed, the mixture was kept at the same temperature for 48 h. The precipitate of 1,6-dibromopyrene was filtered off, washed with hexane and methanol and dried *in vacuo* over P_2O_5, yield 9.02 g (25%). The filtrate was concentrated, the solid residue was recrystallized from toluene–hexane giving 1,8-dibromopyrene, yield 17.9 g (50%).

For 1,8-dibromopyrene: ^{1}H NMR, δ: 7.97 (s, 2H), 7.98 (d, 2H, *J* 8.5 Hz), 8.22 (d, 2H, *J* 8.2 Hz), 8.46 (s, 2H). IR (ν/cm^{-1}): 3102, 3038, 1936, 1882, 1597, 1582 (C=C), 1481, 1455, 1427, 1416, 1310, 1295, 1234, 1202, 1163, 1146, 1118, 1026, 976, 845, 836, 819, 784, 777, 768, 704. MS, *m*/*z*: 360 [M]$^+$.

For 1,6-dibromopyrene: ^{1}H NMR, δ: 8.18 (d, 2H, *J* 8.2 Hz), 8.10 (d, 2H, *J* 9.2 Hz), 8.26 (d, 2H, *J* 8.2 Hz), 8.44 (d, 2H, *J* 9.2 Hz). IR (ν/cm^{-1}): 3038, 1600, 1581 (C=C), 1482, 1453, 1427, 1417, 1287, 1234, 1202, 1162, 1091, 1052, 1025, 979, 881, 852, 836, 818, 703. MS, *m*/*z*: 360 [M]$^+$.

§ *1,6-Bis[*N*-(2-naphthyl)-N-phenylamino]pyrene*. The mixture of 5.4 g (0.015 mol) of 1,6-dibromopyrene, 8.3 g (0.0375 mol) of *N*-phenyl-*N*-(2-naphthyl)amine, 80 mg of palladium diacetate, 280 mg of tri(*tert*-butyl)-phosphine, 3.8 g (0.04 mol) of sodium *tert*-butoxide and 100 ml of *o*-xylene was heated up to 125–130 °C. The reaction mixture was stirred at this temperature under argon atmosphere for 7 h. After cooling to room temperature the solid product was filtered, washed successively with hexane, methanol, water and dried *in vacuo* over P_2O_5, yield 7.35 g (77%). IR (ν/cm^{-1}): 1593, 1575, 1490 (C=C), 1464, 1436, 1394, 1309, 1275, 1256, 1182, 1163, 1119, 1088, 1019, 971, 875, 849, 817, 792, 770, 744, 690, 683. MS, *m*/*z*: 636 [M]$^+$. Found (%): C, 89.92; H, 5.30; N, 4.50. Calc. for $C_{48}H_{32}N_2$ (%): C, 90.53; H, 5.07; N, 4.40.

content of the pyrene derivative from 40 to 60%. Figure 2 shows the examples of current–voltage and brightness–voltage curves of the devices based on **1**–**3** with the same content of pyrene derivative of 50% as well as of their electroluminescence spectra. All the devices demonstrate the blue lighting with the maximum of the electroluminescence band at 486, 483 and 477 nm for **1**, **2** and **3**, respectively. The onset of light appearance is about 5 V for all the devices. However, the brightness of the devices based on **1** and **2** is lower than that of the device based on **3**. A possible reason for this may be related to morphological differences of the structure of the emitting layer.

In conclusion, we have for the first time synthesized the new soluble electroluminescent pyrene derivatives, namely 1,8-bis-(diarylamino)pyrenes and demonstrated light-emitting devices based on these compounds.

This work was partially supported by the Ministry of Education and Science of the Russian Federation (contract no. 14.513.11.0020).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.09.025.

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¶ The UV-VIS absorption spectra were recorded on a Carl Zeiss Specord M40 instrument for the films deposited on quartz plates from chloroform solution. The photoluminescence spectra were obtained for powder samples on an Ocean Optics QE65000 spectrometer (λ_{ex} = 380 nm).

The electroluminescent devices were prepared on ITO slides covered with PEDOT:PSS by the spin-coating of pirene–PVC blends with the subsequent annealing at 110 °C for 15 min. The devices were finalized by the evaporation of top electrode of Al:Ca alloy *in vacuo* (5×10^{-6} mbar). Brightness of the obtained devices were measured with a calibrated Hamamatsu HC-124-17 photomultiplier assembly. The electroluminescence spectra were obtained with an Ocean Optics QE65000 spectrometer.

Received: 1st December 2015; Com. 15/4784