Novel Candle Light-Style OLED with Record Low Color Temperature

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1. General methods

Elemental analyses were performed on Perkin Elmer 2400 Elemental Analyser. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. 1H and 13C NMR spectra were taken with a Bruker AM-300 machine (at frequencies of 300.1 and 75.5 MHz, respectively) in CDCl3 solutions, with TMS as the standard. J values are given in Hz. MS spectra (EI, 70 eV) were obtained with a Finnigan MAT INCOS 50 instrument. High resolution MS spectra were measured on a Bruker microTOF II instrument using electrospray ionization (ESI). The measurement was operated in a positive ion mode (interface capillary voltage 4500 V) or in a negative ion mode (3200 V); mass range was from m/z 50 to m/z 3000 Da; external or internal calibration was done with Electrospray Calibrant Solution (Fluka). A syringe injection was used for solutions in acetonitrile, methanol, or water (flow rate 3 IL min⁻¹). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C. IR spectra were measured with a Specord M-80 instrument in KBr pellets.

The reagents were purchased from commercial sources and used as received. 4,7-Dibromo-[1,2,5]thiadiazolo[3,4-c]pyridine (2a), 1 4,7-dibromo-[1,2,5]selenadiazolo[3,4-c]pyridine (2b), 2 (9-hexyl-9H-carbazol-3-yl)boronic acid (3) 3 and (4-formylphenyl)boronic acid (5) 4 were prepared according to the published methods and characterized by NMR spectra. The synthetic routes for these building blocks are shown in Scheme 1. All synthetic operations were performed under a dry argon atmosphere. Solvents were purified by distillation from the appropriate drying agents.

Spectroscopic studies

Optical absorption spectra for the compounds were measured in solutions acetonitrile (ACN), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), ethyl acetate (EAc), chloroform (Chlor), cyclohexane (CHex), (HPLC-grade super gradient, Panreac, Spain) in 1-cm-pathlength quartz optical cells. Optical absorption spectra were recorded at ambient temperature with the use of a Specord M40 spectrophotometer operating within 200 – 800 nm.

Photoluminescence (PL) spectra were obtained at room temperature with an Ocean Optics Maya 2000 Pro CCD spectrometer sensitive within 200 – 1100 nm. Photoluminescence experiments were carried out with a 365 nm CW laser as the excitation source.

To measure the absolute luminescence quantum yield (QY) we used a Horiba Jobin-Yvon Fluorolog FL3-22 spectrofluorimeter equipped with a G8 pectralon®-covered sphere (GMP SA, Switzerland) and a Hamamatsu R928 photomultiplier. A diffusing screen was mounted inside the sphere to avoid direct irradiation of the detector. The setup provided a means to investigate powder samples emitting within 450–800 nm. The measurements were carried out at ambient temperature. The samples in quartz cells were placed near the centre of the sphere. An emission-
standard 45W quartz tungsten-halogen lamp (Oriel) was employed to measure the instrument response function.

The detailed structural and morphological characterizations of the investigated compounds were carried out using a Field Emission – Scanning Electron Microscope. Target-oriented approach was utilized for the optimization of the analytic measurements. Before measurements the samples were mounted on a 25 mm aluminum specimen stub and fixed by conductive silver paint. Metal coating with a thin film (10 nm) of gold/palladium alloy (60/40) was performed using magnetron sputtering method as described earlier. The observations were carried out using Hitachi SU8000 Field Emission – Scanning Electron Microscope (FE-SEM). Images were acquired in secondary electron mode at 15 kV accelerating voltage and at working distance 8-10 mm. Morphology of the samples was studied taking into account possible influence of metal coating on the surface.

**Device fabrication and characterization**

OLED devices were fabricated by layer-by-layer vacuum thermal deposition (<10⁻⁵ Pa) on a glass substrate (20x30x3 mm, RMS=2.5 nm) with ITO (Indium Tin Oxide) conducting layer as anode. Extra pure MoO₃ (99.9995 wt% free of W impurity) with controlled oxygen non-stoichiometry was used as a hole blocking material. NPB (N,N′-Di(1-naphthyl)-N,N′-diphenyl-(1,1′-biphenyl)-4,4′-diamine,) was used as one of the most efficient hole-transport materials to provide the necessary hole mobility. CBP (4,4′-Bis(N-carbazolyl)-1,1′-biphenyl) is an up-to-date standard host matrix for phosphorescent dopants. Alq₃ (tris-(8-hydroxyquinoline)aluminium) is known as one of the first electrophosphores, but to date it is more often used as host material or an electron-transport material. The deposition rates of each layer did not exceed 0.03 nm×s⁻¹. In order to obtain reproducible results of OLED characterization we examined several diode structures deposited on the same substrate.

To fabricate OLED structure based on compound we performed co-evaporation of the compound with Alq₃ host material. For OLEDs with compounds we also used co-evaporated emission layer with Alq₃ or CBP host material.

Performance of fabricated OLEDs was measured with the use of automated setup based on Keithley 2400 source meter and Ocean Optics QE65000 CCD spectrometer sensitive within 200-1100 nm. Integration time for each spectrum was 30 s. Luminance and chromaticity coordinates of OLED structures were measured with an Instrument Systems Optische Messtechnik LumiCAM 1300 photometer-colorimeter.
2. Synthetic procedure

Scheme 1. Synthesis of dyes

General procedure for the cross-coupling reactions of [1,2,5]chalcogenadiazolo[3,4-c]pyridines 2a,b and arylboronic acid 3.

The mixture of 4,7-dibromo-[1,2,5]chalcogenadiazolo[3,4-c]pyridine 2a,b (1.0 mmol), (9-hexyl-9H-carbazol-3-yl)boronic acid 3 (325 mg, 1.1 mmol), solution of 2M K₂CO₃ (4 ml) and Pd(PPh₃)₄ (3 mol %) in THF (10 ml) was degassed by argon and refluxed under argon for 20 h. On completion, the mixture was poured into water and extracted with DCM (3 × 50 ml). The combined organic phases were washed with brine (2 × 50 ml), dried over MgSO₄, filtered, and concentrated under reduced pressure.

7-Bromo-4-(9-hexyl-9H-carbazol-3-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine (4a)

Compound 4a was obtained as orange solid using silica gel column chromatography with CH₂Cl₂/hexane, (2:1, v:v) as the eluent (372 mg, 80%). The spectroscopic data correspond to the literature.¹¹

7-Bromo-4-(9-hexyl-9H-carbazol-3-yl)-[1,2,5]selenadiazolo[3,4-c]pyridine (4b)

Compound 4b was obtained as dark red solid using silica gel column chromatography with CH₂Cl₂/hexane, (2:1, v:v) as the eluent (481 mg, 94%). The spectroscopic data correspond to the literature.¹¹

General procedure for the of cross-coupling reaction of mono-adducts 4a,b and (4-formylphenyl)boronic acid 5

The mixture of mono-adduct 4a,b (0.25 mmol), (4-formylphenyl)boronic acid 5 (45 mg, 0.3 mmol), solution of 2M K₂CO₃ (1 ml) and Pd(PPh₃)₄ (3 mol %) in mixture of toluene (5 ml) was degassed by argon and refluxed under argon for 10 h. After cooling additional amount of ether of
boronic acid (0.3 mmol) and Pd(PPh₃)₄ (3 mol %) were added and the reaction mixture was refluxing for 10 h. On completion, the mixture was poured into water and extracted with DCM (3 × 50 ml). The combining organic phases were washed with brine (2 × 50 ml), dried over MgSO₄, filtered, and concentrated under reduced pressure.

4-(4-(9-Hexyl-9H-carbazol-3-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine-7-yl)benzaldehyde (6a)

Compound 6a was obtained as red solid using silica gel column chromatography with CH₂Cl₂ as the eluent (104 mg, 85%). M.p. 185 – 187 °C. ¹H NMR (300 MHz, CDCl₃): δ = 10.15 (s, 1H), 9.56 (s, 1H), 8.93 – 8.91 (m, 1H), 8.29 – 8.31 (m, 1H), 8.26 (d, J = 8.4 Hz, 2H), 8.10 (d, J = 8.4 Hz, 2H), 7.52 – 7.62 (m, 2H), 7.48 (d, J = 8.0 Hz, 1H), 7.31 (t, J = 7.3 Hz, 1H), 4.39 (t, J = 7.2 Hz, 2H), 1.93 – 1.98 (m, 2H), 1.35 – 1.46 (m, 6H), 0.88 – 0.93 (m, 3H). ¹³C NMR (75 MHz, CDCl₃): δ = 191.7, 156.5, 153.8, 149.7, 143.3, 142.1, 140.0, 140.7, 135.8, 130.0, 129.4, 127.9, 127.4, 126.1, 124.0, 123.35, 123.3, 123.1, 120.8, 119.6, 109.1, 108.7, 34.3, 31.5, 28.9, 26.9, 22.5, 14.0. ESI-MS, m/z: found 491.1882; calc. for C₃₀H₂₇N₄OS [M+H]+ 491.1900. IR, ν, cm⁻¹: 2952, 2926, 2852, 1702, 1595, 1446, 1359, 1244, 1140, 816, 727, 523. MS-EI, m/z (I, %) = 490 (M⁺, 95), 491 ([M+1]⁺, 35), 492 ([M+2]⁺, 8), 420 (26), 419 (100).

4-(4-(9-Hexyl-9H-carbazol-3-yl)-[1,2,5]selenadiazolo[3,4-c]pyridine-7-yl)benzaldehyde (6b)

Compound 6b was obtained as red solid using silica gel column chromatography with CH₂Cl₂ as the eluent (111 mg, 83%). M.p. 199 – 201 °C. ¹H NMR (300 MHz, CDCl₃): δ = 10.15 (s, 1H), 9.44 (s, 1H), 8.79 (dd, J = 7.6, J = 1.5 Hz, 1H), 8.73 (s, 1H), 8.27 (d, J = 7.6 Hz, 1H), 8.20 (d, J = 8.3 Hz, 2H), 8.10 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 8.3 Hz, 2H), 7.47 – 7.54 (m, 2H), 7.33 (t, J = 7.4 Hz, 1H), 4.30 (t, J = 7.3 Hz, 2H), 1.93 – 1.98 (m, 2H), 1.34 – 1.46 (m, 6H), 0.88 – 0.92 (m, 3H). ¹³C NMR (75 MHz, CDCl₃): δ = 191.7, 160.9, 158.1, 142.3, 141.5, 141.0, 140.9, 135.9, 130.3, 129.9, 128.7, 127.9, 126.8, 126.3, 126.2, 124.1, 123.36, 123.31, 121.0, 119.9, 109.2, 108.8, 43.3, 31.5, 28.9, 26.9, 22.5, 14.0. ⁷⁷Se NMR (57 MHz, CDCl₃): δ = 1518.3. ESI-MS, m/z: found 539.1337; calc. for C₃₀H₂₇N₄OSe [M+H]+ 539.1346. IR, ν, cm⁻¹: 2954, 2921, 2852, 1698, 1598, 1445, 1372, 1241, 1138, 830, 724, 534.

General procedure for the Knoevenagel reaction.

A mixture of 4,7-disubstituted [1,2,5]selenadiazolo[3,4-c]pyridine (0.1 mmol), malononitrile (17 mg, 0.25 mmol), ammonium acetate (16 mg, 0.2 mmol) in AcOH (5.0 ml) was refluxed with stirring for 35 min under argon. The reaction mixture was poured into water, extracted with DCM (3 × 40 ml), washed with water. The combined organic layers were dried over MgSO₄ and evaporated under reduced pressure.

2-(4-(4-(9-Hexyl-9H-carbazol-3-yl)-[1,2,5]thiadiazolo[3,4-c]pyridin-7-yl)benzylidene)malononitrile (1a)
Compound 1a was obtained as red solid using silica gel column chromatography with CH$_2$Cl$_2$ as the eluent (107 mg, 80%). M.p. 208 – 210 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 9.52$ (d, $J = 1.4$ Hz, 1H), 8.90 (dd, $J = 8.4$, $J = 1.4$ Hz, 1H), 8.86 (s, 1H), 8.24 – 8.26 (m, 1H), 8.23 (d, $J = 8.4$ Hz, 2H), 8.02 (d, $J = 8.4$ Hz, 2H), 7.70 (s, 1H), 7.51 – 7.56 (m, 2H), 7.47 (d, $J = 8.1$ Hz, 1H), 7.32 (t, $J = 7.3$ Hz, 1H), 4.36 (t, $J = 7.2$ Hz, 2H), 1.90 – 1.99 (m, 2H), 1.32 – 1.48 (m, 6H), 0.88 – 0.92 (m, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 158.5$, 156.4, 154.2, 149.8, 143.5, 142.2, 141.1, 140.9, 131.0, 130.5, 129.6, 128.0, 127.4, 126.2, 123.43, 123.30, 123.26, 123.25, 120.7, 119.7, 113.7, 112.6, 109.1, 108.8, 82.6, 43.3, 31.5, 28.9, 26.9, 22.4, 13.8. ESI-MS, $m/z$: found 539.1998; calc. for C$_{33}$H$_{27}$N$_6$S [M+H]$^+$ 539.2012. IR, v, cm$^{-1}$: 2954, 2929, 2227, 1589, 1446, 1384, 1245, 1140, 898, 749, 530.

2-(4-(4-(9-Hexyl-9H-carbazol-3-yl)-[1,2,5]selenadiazolo[3,4-c]pyridin-7-yl)benzylidene)malononitrile (1b)

Compound 1b was obtained as dark red solid using silica gel column chromatography with CH$_2$Cl$_2$ as the eluent (120 mg, 82%). M.p. 215–217 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 9.46$ (s, 1H), 8.81 (d, $J = 7.6$ Hz, 1H), 8.72 (s, 1H), 8.27 (d, $J = 7.7$ Hz, 1H), 8.21 (d, $J = 7.8$ Hz, 2H), 8.07 (d, $J = 7.8$ Hz, 2H), 7.80 (s, 1H), 7.52 – 7.59 (m, 2H), 7.48 (d, $J = 8.0$ Hz, 1H), 7.33 (t, $J = 7.4$ Hz, 1H), 4.38 (t, $J = 6.7$ Hz, 2H), 1.90-2.00 (m, 2H), 1.35 – 1.45 (m, 6H), 0.88 – 0.92 (m, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 160.9$, 158.9, 155.7, 142.9, 142.4, 141.6, 141.2, 141.1, 130.7, 130.3, 130.0, 128.7, 127.6, 126.4, 125.6, 124.2, 123.56, 123.52, 121.0, 119.9, 113.9, 112.7, 109.3, 109.0, 82.8, 43.5, 31.6, 29.0, 27.0, 22.6, 14.0. $^{77}$Se NMR (57 MHz, CDCl$_3$): $\delta = 1519.9$. ESI-MS, $m/z$: found 587.1459; calc. for C$_{33}$H$_{27}$N$_6$Se [M+H]$^+$ 587.1459. IR, v, cm$^{-1}$: 2955, 2925, 2227, 1586, 1436, 1384, 1239, 1136, 901, 750, 524.

3. Electrochemical characterization:

Table 1. Electrochemical data derived for the 1a and 1b from CV measurements in DMF solution.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E^{red}_{onset}$ (vs Fe/Fe$^+$)$_a$, eV</th>
<th>$E_{LUMO}$$_b$, eV</th>
<th>$E^{ox}_{onset}$ (vs Fe/Fe$^+$)$_a$, eV</th>
<th>$E_{HOMO}$$_b$, eV</th>
<th>$E_G$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>-1.18</td>
<td>-3.92</td>
<td>0.72</td>
<td>-5.82</td>
<td>1.90</td>
</tr>
<tr>
<td>1b</td>
<td>-1.19</td>
<td>-3.91</td>
<td>0.73</td>
<td>-5.83</td>
<td>1.92</td>
</tr>
</tbody>
</table>

$^a$Here $E^{ox}_{onset}$ and $E^{red}_{onset}$ are a linear extrapolation of the low reduction potential side of the first oxidation or reduction wave respectively to the base line.

$^b$ Energies of frontier orbitals were calculated according to equations (1) and (2).
Fig. 1 Cyclic voltammogram showing quasi-reversible two-step reduction and one-step oxidation of 1a (10^{-3} M) (a) and 1b (2 \cdot 10^{-3} M) (b). Scan rate 100 mV s^{-1}, electrolyte 0.1 M Bu4NClO4 in DMF.

4. Devices characterization:
**Fig. 2** Energy-level diagram of devices 1a:Alq₃ and 1b:Alq₃ (a), 1b:CBP (b).

**Fig. 3** Luminance – voltage characteristics (a), current efficiencies as functions of OLED luminance (b).

**Fig. 4** Chromaticity diagram for electroluminescence of 1a:Alq₃ (1), 1b:Alq₃ (2) and 1b:CBP (3) light-emitting devices.
References:
$^{1}$H, $^{13}$C and $^{77}$Se NMR spectra

4-(4-(9-Hexyl-9H-carbazol-3-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine-7-yl)benzaldehyde (6a)

$^{1}$H NMR (300 MHz)

$^{13}$C NMR (75 MHz)
4-(4-(9-Hexyl-9H-carbazol-3-yl)-[1,2,5]selenadiazolo[3,4-c]pyridine-7-yl)benzaldehyde (6b)

$^1$H NMR(300 MHz)

$^{13}$C NMR(75 MHz)
$^{77}\text{Se NMR (57 MHz)}$

2-(4-(4-(9-Hexyl-9H-carbazol-3-yl)-[1,2,5]thiadiazolo[3,4]peridin-7-yl)benzylidene)malononitrile (1a)

$^1\text{H NMR (300 MHz)}$
$^{13}$C NMR (75 MHz)

2-(4-(4-(9-Hexyl-9H-carbazol-3-yl)-[1,2,5]selenadiazolo[3,4]peridin-7-yl)benzylidene)malononitrile (1b)

$^1$H NMR (300 MHz)
$^{13}$C NMR (75 MHz)

$^{77}$Se NMR (57 MHz)