**Spirobifluorene-based pyrazoloquinolines: efficient blue electroluminescent materials†**

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We report the synthesis of spirobifluorene-based pyrazoloquinolines, spiro-PAQ-Me and spiro-PAQ-Ph, in which two identical luminophores are connected through an sp3-hybridized carbon atom (a spiro center) and are orthogonally arranged. The incorporation of the rigid spirobifluorene linkage results in significant increases in the glass transition temperatures, which are in the range 246–280 °C. These new materials display the characteristic absorptions of the mono-pyrazoloquinoline (i.e. non-spiro) derivatives, each with a broad, low-energy absorption at ca. 420 nm, and emit photoluminescence efficiently in the blue region. Electrochemical studies reveal that these compounds exhibit reversible reductions and low-lying LUMO energy levels that originate from the electron-deficient nature of the pyrazoloquinoline ring. Multilayer organic electroluminescent devices constructed using spiro-PAQ-Ph as a dopant in the emitting layer produced bright blue emissions with maximum luminescence exceeding 20 000 cd m⁻². For the 2.0% doped device, a high external quantum efficiency of 3.6% (4.5 cd A⁻¹, 2.02 lm W⁻¹) was achieved at 20 mA cm⁻² and 7.0 V with color coordinates of (0.14, 0.17).

**Introduction**

Since the discovery of multi-layered organic light-emitting diodes (OLEDs) by Tang and Van Slyke, research into OLEDs has been pursued intensively because of their potential for applications in, among other things, flat-panel displays. With such an application in mind, full-color displays would require three primary-color emissions, i.e. red, green, and blue. Organic light-emitting materials having large band-gap energies that emit blue light efficiently are of particular interest, because they are desired for use as blue light sources in full-color display applications and also because they can be used to achieve green and red color emission by several pathways, such as dopant emission or fluorescent down-conversion. A range of pyrazole-containing derivatives have been demonstrated to exhibit efficient blue photoluminescence, and some of them have been utilized as emitting materials in the fabrication of electroluminescent (EL) devices, in which they provide bright blue EL emission.

Herein, we report the synthesis and characterization of spirobifluorene-based pyrazoloquinolines, in which the two identical luminophores are aligned orthogonally through bonding to an sp3-hybridized carbon atom: a spiro center. The introduction of a spirobifluorene linkage not only increases molecular rigidity but also hinders close packing and intramolecular interactions, so that the tendency for molecules to crystallize may be reduced and the glass transition temperature may be increased. Amorphous materials possessing a high value of $T_g$, which are less vulnerable to heat-induced morphological changes, are highly desirable for fabricating molecular LEDs, since the tendency for small molecules to crystallize spontaneously during operation has been identified as one reason for LED device failure. Moreover, the tetrahedral nature of the carbon atom at the spiro center connects the conjugated moieties through a σ-bonded network, which in turn serves as a conjugation interrupt and, thus, most of the desired electronic and optical properties of the corresponding non-spiro molecules are preserved. The spirobifluorene-based pyrazoloquinoline was used as a dopant in EL devices, which gave bright blue emission from the dopant. The performance of these devices is discussed.

**Experimental**

**General**

2,2’-Dinitro-9,9’-spirobifluorene (1), 9,9’-spirobifluorenobis-3-phenyl[2,3’-isoxazole (2), and 2,2’-diamino-3,3’-dibenzyol-9,9’-spirobifluorene (3) were synthesized according to literature procedures. Tetrabutylammonium hexafluorophosphate (TBAPF₆) was purified by recrystallization from ethyl acetate and dried in vacuo at 60 °C. All other chemicals were used as received unless otherwise stated. 1H and 13C NMR spectra were recorded on Varian Unity 300 MHz and Bruker-DRX 300 MHz spectrometers. Mass spectra were obtained on a JEOL JMS-SX 102A mass spectrometer. Differential scanning calorimetry (DSC) was performed on a SEIKO EXSTAR 6000 DSC unit at a heating rate of 10 °C min⁻¹ and a cooling rate of 40 °C min⁻¹. Samples were scanned from 30 to 400 °C, cooled to 0 °C, and then scanned again from 30 to 400 °C. The glass transition temperatures ($T_g$) were determined from the second heating scan. Thermogravimetric analysis (TGA) was undertaken on a DuPont TGA 2950 instrument. The thermal stability of the samples was determined under a nitrogen atmosphere, by measuring weight loss while heating at a rate of 20 °C min⁻¹. UV–Visible spectra were measured using an HP 8453 diode-array spectrophotometer. Photoluminescence (PL) spectra were obtained on a Hitachi F-4500 luminescence spectrometer. Cyclic voltammetry (CV) measurements were performed using a BAS 100 B/W electrochemical analyzer. The oxidation and reduction measurements were undertaken.
respectively, in anhydrous CH₂Cl₂ and anhydrous THF containing 0.1 M TBAF₂, as the supporting electrolyte, at a scan rate of 50 mV s⁻¹. The potentials were measured against an Ag/Ag⁺ (0.01 M AgNO₃) reference electrode with ferrocene as the internal standard. The onset potentials were determined from the intersection of two tangents drawn at the rising current and background current of the cyclic voltammogram.

Fabrication of light-emitting devices

The hole-transport materials 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB) and 4,4'-dicarbazolyl-1,1'-biphenyl (CBP) and the electron-transport material 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBI) were synthesized according to literature procedures and sublimed through a temperature-gradient sublimation system. Pre-patterned ITO glasses that have active device areas of 3.14 mm² were cleaned with a stream of nitrogen, the glasses were treated with oxygen plasma for 3 min and then loaded into an Ulvac Cryogenic deposition system, which was subsequently evacuated to a pressure below ca. 2 × 10⁻⁵ Torr. All of the organic layers were deposited at a rate of 1.5–2.5 Å sec⁻¹. After being blown dry under a stream of nitrogen, the glasses were treated with oxygen plasma for 3 min and then loaded into an Ulvac Cryogenic deposition system, which was subsequently evacuated to a pressure below ca. 2 × 10⁻⁵ Torr. All of the organic layers were deposited at a rate of 1.5–2.5 Å sec⁻¹. For doped layers, the dopant and the host were co-evaporated from two separated boats with the rates controlled independently. An alloy of magnesium and silver (ca. 10 : 1, 50 nm) was deposited as the cathode, followed by a silver cap (1000 Å).

Synthesis of spiro-PAQ-Ph

A mixture of compound 3 (2.00 g, 3.61 mmol) and 1,3-dimethyl-5-pyrazolone (4; 1.62 g, 14.4 mmol) in ethylene glycol (15.0 mL) was heated at 190 °C for 12 h. After cooling, the resulting mixture was poured into water (100 mL). The precipitated solid was collected by filtration, washed with water, and purified by column chromatography (hexane–ethyl acetate, 3 : 1) to afford spiro-PAQ-Ph (1.88 g, 73.7%). ¹H NMR (CDCl₃): δ 8.09 (s, 2 H), 7.81 (d, J = 17.6 Hz, 2 H), 7.69–7.72 (m, 6 H), 7.56–7.47 (m, 6 H), 7.33 (dd, J = 7.2, 7.2 Hz, 2 H), 7.11 (dd, J = 7.2, 7.2 Hz, 2 H), 6.83 (d, J = 7.6 Hz, 2 H), 4.00 (s, 6 H), 2.04 (s, 6 H). ¹³C NMR (CDCl₃): δ 153.7, 149.3, 141.6, 140.7, 137.7, 135.4, 129.8, 129.7, 128.8, 128.4, 128.3, 128.2, 124.8, 123.2, 122.9, 120.7, 116.9, 114.9, 64.9, 33.3, 14.6. HRMS (m/z): [M⁺] calcd. for C₉₀H₇₈N₆, 1189.6046; found 1189.5993. The reaction of compound 1 with benzyl nitrile in the presence of base afforded the bisbenzisoxazole 2, which was subsequently transformed into the bis(α-aminoconone) 3 by hydrogenation of the isoxazole moiety with an iron powder/acetic acid mixture. The condensation of 3 with pyrazolone derivatives 4 and 5, respectively, in ethylene glycol yielded the target bis[pyrazoloquinoline] spiro-PAQ-Ph, each containing a 9,9'-spirobi fluorene skeleton. The chemical structures of the obtained spiro-bis[pyrazoloquinoline]s were confirmed by ¹H and ¹³C NMR spectroscopy, mass spectrometry, and elemental analysis.

Results and discussion

Synthesis

Scheme 1 illustrates the synthetic route followed for the preparation of the 9,9'-spirobi fluorene-function alized bis[pyrazoloquinolines]. The key intermediate, 2,2'-diamino-3,3'-dibenzoyl-9,9'-spirobi fluorene (3), was prepared from 2,2'-dinitro-9,9'-spirobi fluorene (1) as reported previously. The reaction of compound 1 with benzyl nitrile in the presence of base afforded the bisbenzisoxazole 2, which was subsequently transformed into the bis(α-aminoconone) 3 by hydrogenation of the isoxazole moiety with an iron powder/acetic acid mixture. The condensation of 3 with pyrazolone derivatives 4 and 5, respectively, in ethylene glycol yielded the target bis[pyrazoloquinoline] spiro-PAQ-Ph, each containing a 9,9'-spirobi fluorene skeleton. The chemical structures of the obtained spiro-bis[pyrazoloquinoline]s were confirmed by ¹H and ¹³C NMR spectroscopy, mass spectrometry, and elemental analysis.

Optical properties

Fig. 1a displays the absorption and emission spectra of the spiro-PAQ dyes in EtOAc; their spectral data are summarized in Table 1. The absorption spectrum of spiro-PAQ-Ph comprises a broad, low-energy absorption at ca. 420 nm, two weak absorptions in the region 340–360 nm, and a strong main absorption centered at 288 nm. In going from the methyl(spiro-PAQ-Me) to the phenyl(spiro-PAQ-Ph) bis[pyrazoloquinoline], there is a slight red-shift (2–6 nm) in position of the peak maximum, which is due to the increase in conjugation length. The features of these absorption spectra resemble those of the mono-pyrazoloquinoline (i.e. non-spiro) derivatives that have been described previously. These spiro-PAQ dyes exhibit strong blue emissions: spiro-PAQ-Me and spiro-PAQ-Ph, each containing a 9,9'-spirobi fluorene skeleton.

The absorption spectrum of spiro-PAQ-Ph, each containing a 9,9'-spirobi fluorene skeleton.
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Electrochemical band gap, estimated using the equation $E_g \approx E_{\text{onset}}^{\text{ox}} - E_{\text{onset}}^{\text{red}}$. Optical band gap, calculated from the absorption edge of the absorption spectrum.

**Table 1** Spectral data of spiro-pyrazoloquinolines

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$/$\text{nm}$</th>
<th>$\lambda_{\text{em}}$/$\text{nm}$</th>
<th>$\lambda_{\text{max}}$/$\text{nm}$ (film)$^c$</th>
<th>Quantum yields ($\Phi$$^d$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spiro-PAQ-Me</td>
<td>288, 340, 358, 398, 420</td>
<td>438</td>
<td>466, 501 (sh)</td>
<td>0.67</td>
</tr>
<tr>
<td>Spiro-PAQ-Ph</td>
<td>294, 342, 361, 402, 422</td>
<td>455</td>
<td>490</td>
<td>0.95</td>
</tr>
</tbody>
</table>

$^a$ In EtOAc. $^b$ In EtOAc, excited at 360 nm. $^c$ Spin-coating from their CHCl$_3$ solution, excited at 360 nm. $^d$ The relative quantum yield was measured with reference to 9,10-diphenylanthracene in cyclohexane ($\Phi = 0.90$).

**Table 2** Electrochemical properties of spiro-pyrazoloquinolines

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{onset}}^{\text{ox}}$ /eV</th>
<th>$E_{\text{onset}}^{\text{red}}$ /eV</th>
<th>HOMO/eV$^a$</th>
<th>LUMO/eV$^a$</th>
<th>$E_g$ /eV$^b$</th>
<th>$E_{\text{opt}}$ /eV$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spiro-PAQ-Me</td>
<td>0.87</td>
<td>-2.09</td>
<td>5.66</td>
<td>2.71</td>
<td>2.96</td>
<td>2.83</td>
</tr>
<tr>
<td>Spiro-PAQ-Ph</td>
<td>0.86</td>
<td>-2.00</td>
<td>5.66</td>
<td>2.80</td>
<td>2.86</td>
<td>2.81</td>
</tr>
</tbody>
</table>

$^a$ Potential values referenced vs. Fc/Fc$^{-}$. $^b$ Determined from the onset oxidation potential. $^c$ Determined from the onset reduction potential. $^d$ Electrochemical band gap, estimated using the equation $E_g = E_{\text{onset}}^{\text{ox}} - E_{\text{onset}}^{\text{red}}$. $^e$ Optical band gap, calculated from the absorption edge of the absorption spectrum.

**Fig. 1** UV-Vis absorption and PL spectra of spiro-PAQ-Me (–) and spiro-PAQ-Ph (– – –) (a) in EtOAc solution and (b) in the solid state.

**Fig. 2** Cyclic voltammograms of spiro-PAQ-Me and spiro-PAQ-Ph.

Electrochemistry

We investigated the electrochemical behavior of the spiro-PAQ dyes by cyclic voltammetry using ferrocene as the internal standard. The results are displayed in Fig. 2 and the data are tabulated in Table 2. Cyclic voltammetry provides a simple method for obtaining the HOMO/LUMO energy levels of these materials, which we calculated with regard to the energy level of the ferrocene reference (4.8 eV below the vacuum level). Upon cathodic scans, spiro-PAQ-Me and spiro-PAQ-Ph exhibit reversible reductions with onset potentials at ca. −2.09 and −2.00 V, respectively. During the anodic sweep, they undergo quasi-reversible oxidation processes with onset potentials at 0.87 V for the former and 0.86 V for the latter.

To investigate the electroluminescence properties of the spiro-bis(pyrazoloquinoline)s, we selected spiro-PAQ-Ph, which has the higher PL quantum yield and better thermal properties, for the OLED fabrication. We fabricated multilayer devices with...
the configuration ITO/NPB (40 nm)/CBP (10 nm)/TPBI: x wt% spiro-PAQ-Ph (20 nm)/TPBI (20 nm)/Mg:Ag, where ITO, NPB, CBP, TPBI, and Mg:Ag denote indium tin oxide; 4,4′-bis[N-(1-naphthyl)-N-phenylamino]diphenyl; 4,4′-dicarbazoyl-1,1′-biphenyl; 2,2′,2″-(benzene-1,3,5-triyl)tris[1-phenyl-1H-benzimidazole]; and magnesium: silver alloy (ca. 10:1), respectively. Fig. 3 displays the relative HOMO/LUMO energy levels of NPB, CBP, spiro-PAQ-Ph, and the other materials used in this study. Two layers of hole-transporting materials, NPB and CBP, were used because it has been demonstrated previously that CBP serves to provide an intermediate HOMO level by which holes can pass to the TPBI layer.42,43 TPBI was chosen as a host material for the PAQ-Ph derivative because it is a wide-band-gap material that emits strongly at ca. 376 nm.42 From the analysis of the emission/absorption spectra of TPBI and spiro-PAQ-Ph (Fig. 1), we obtained reasonable spectral overlap and, thus, there exists an efficient Förster energy transfer from TPBI and the PAQ-Ph dye.

When the concentration of spiro-PAQ-Ph in TPBI was varied from 1.0 to 5.0 wt%, EL emission with a λ\text{max} around 460 nm was observed, together with a shoulder of different intensity depending on the concentration, as shown in Fig. 4. In the absence of dopant, the device presents a broad EL spectrum that has a major contribution from NPB (ca. 380 nm), a minor contribution from NPB (ca. 450 nm), and possibly an emission from CBP, which occurs at ca. 390 nm.42 This observation indicates that the recombination region is located mainly in the TPBI region with some excitons formed in the NPB area. At dopant concentrations of 1.0–2.0 wt %, the devices exhibit bright blue emissions, predominantly arising from the dopant, as revealed by the comparison of the EL spectra with the PL spectrum of spiro-PAQ-Ph, together with a very minor contribution from the emission of TPBI host that is due to the incomplete energy transfer. Increasing the doping level to 5.0 wt% results in complete energy transfer. The performances of the devices are summarized in Table 3, and the current–voltage characteristics and luminescence–voltage characteristics of an ITO/NPB/CBP/TPBI:spiro-PAQ-Ph (2.0-wt%)/TPBI/Mg:Ag device are presented in Fig. 5. For this 2.0%-doped device, the emission begins at ca. 3.5 V and reaches a maximum luminance of 19 800 cd m\(^{-2}\) at ca. 15 V. With a current density of 20 mA cm\(^{-2}\) at 7.0 V, the device displayed high external quantum and luminescence efficiencies of 3.6% and 4.5 cd A\(^{-1}\) (2.02 lm W\(^{-1}\)), respectively, with CIE coordinates of x = 0.14 and y = 0.17. We note that the external quantum efficiency drops when increasing the dopant concentration from 2.0 to 5.0 wt%. This finding may be due to self-quenching of the dopant emission at higher concentration, but the external quantum efficiency still remains at ca. 3.6%.

Conclusions

In summary, we have synthesized spirobifluorene-based pyrazoloquinolines, spiro-PAQ-Me and spiro-PAQ-Ph, by the condensation of 2,2′-diamino-3,3′-dibenzoyl-9,9′-spirobifluorene (3) with pyrazoline derivatives, and have discussed details of their thermal properties, electronic properties (viz. absorption and photoluminescence), and electrochemical behavior. The presence of the rigid spirobifluorene skeleton imparts...
significant increases in these materials’ glass transition temperatures, while preserving the optical and electrochemical characteristics of their pristine pyrazoloquinoline units. Multi-layer EL devices having ITO/NPB/CBP/TPBI/spiro-PAQ-Ph/TPBI/Mg:Ag configurations display bright blue emissions, with luminescence intensities exceeding 20 000 cd m$^{-2}$, caused by the spirobifluorene-based pyrazoloquinoline dopant. At a 2.0 wt% doping level, the device possesses good blue purity, with an EL emission maximum at 466 nm, which corresponds to ($0.14, 0.17$) blue chromaticity in CIE coordinates, and exhibits a high luminescence efficiency of 4.5 cd A$^{-1}$ (2.02 lm W$^{-1}$) at a current density of 20 mA cm$^{-2}$ and a voltage of 7.0 V.

Acknowledgements

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References