Novel cyclopenta[def]phenanthrene based blue emitting oligomers for OLEDs

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Abstract

Novel blue emitters, oligo-MCPPs (tri-MCPP, tetra-MCPP, and penta-MCPP), have been synthesized and characterized. The introduction of cyclopenta[def]phenanthrene (CPP) units into the structure of oligo-MCPPs gave LEDs with high efficiency and pure blue emission. UV–visible absorption spectra of the thin films of these compounds appear at 333–354 nm, and their maximum PL emission at 416–447 nm. Multilayer organic EL devices with oligo-MCPPs as an emitting layer showed the turn-on voltage of about 4.8 V, the maximum brightness of 1076 cd/m² (at 8.2 V), the maximum luminescence efficiency of 0.81 cd/A, and the CIE coordinates of (0.17, 0.14) with blue color.

Keywords: OLEDs; CPP; Blue emission; Oligomers

Organic light-emitting diodes (OLEDs) have been investigated for the intensive subject in recent years due to their applications in displays. For the commercial application of the active matrix full color displays with OLEDs, much effort has been directed toward the improvement of the materials and devices.1–5 In all these applications, good blue-emitting materials and devices have been essential and efforts continue toward improving their characteristics.6,7 Three basic colors, red, green, and blue, are needed for a full-color display. Compared with green-emitting devices for full-color applications, the electroluminescence (EL) characteristics of blue- and red-emitting devices need to be improved for efficiency and color purity. Nevertheless, owing to its intrinsic characteristic of having a wide band gap, it is much more difficult to produce a blue emission material.5 Even though there are many reports about blue OLEDs, only a limited number of materials provide appropriate brightness and stability9 with much recent interest being paid to fluorene-based small molecules and polymers as efficient blue emitters.10,11 Conjugated oligomers with low molecular weights are characterized by the ease of purification, the absence of chain defects, and the structural uniformity into thin films. As compared with polymers, oligomers generally have more expected and reproducible properties that are amenable to optimization through molecular engineering. Nevertheless, it is highly desirable to provide oligomers with a high glass transition temperature (Tg) and superior morphological stability against crystallization.12 Vacuum deposition of conjugated organic oligomers as thin film was applied for multiple-layer OLEDs, and better efficiency of the device can be accomplished through proper choice of electron- and hole-transport materials.

We previously reported on the synthesis and properties of new EL polymers utilizing a new backbone, poly(2, 6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta-[def]phenanthrene))
(PCPP) with stabilized pure blue emission.\textsuperscript{13,14} A recent work has pointed out the progress in the synthesis of high band gap materials based on the phenanthrene building block.\textsuperscript{14–16} EL spectra of PCPP do not show any peak in the long wavelength region corresponding to keto defect sites or aggregates/excimers even after annealing the device for 18 hrs in air or operation of the device for 40 min. Therefore, efforts should be made to incorporate this new 4\textit{H}-cyclopenta[\textit{def}]phenanthrene (CPP) unit in a small molecule for LED to enhance the morphologic stability for highly efficient blue-light-emission. Herein, we report the syntheses and characterizations of efficient blue-light-emitting materials, oligo-MCPPs (tri-MCPP, tetra-MCPP, and penta-MCPP). The Yamamoto and Suzuki coupling reactions were employed to prepare oligo-MCPPs in high yields. These CPP-based conjugated small molecules showed good thermal stability and optical and electrochemical properties with potential for the display technologies.

The general synthetic routes toward the monomers and oligomers are outlined in Scheme 1. In the first step, 4\textit{H}-cyclopenta[\textit{def}]phenanthrene (1) was alkylated using CH\textsubscript{3}I in DMSO and 50\% aqueous NaOH to obtain 4,4-dimethyl-4\textit{H}-cyclopenta[\textit{def}]phenanthrene (2), which was hydrogen-nated using Pd/C to generate 4,4-dimethyl-8,9-dihydro-4\textit{H}-cyclopenta[\textit{def}]phenanthrene (3). Mono-bromination of compound 3 with N-bromosuccinimide (NBS) afforded 2-bromo-4,4-dimethyl-8,9-dihydro-4\textit{H}-cyclopenta[\textit{def}]phenanthrene (4). Alumina-supported copper (II) bromide\textsuperscript{17} was used for the dibromination to provide 2,6-dibromo-4,4-dimethyl-8,9-dihydro-4\textit{H}-cyclopenta[\textit{def}]phenanthrene (5). Compounds 4 and 5 were dehydrogenated by bromine and carbon disulfide to provide 2-bromo-4,4-dimethyl-4\textit{H}-cyclo-penta[\textit{def}]phenanthrene (6) and 2,6-dibromo-4,4-dimethyl-4\textit{H}-cyclopenta[\textit{def}]phenanthrene (7), which afforded 2-(4,4-dimethyl-4\textit{H}-cyclopenta[\textit{def}]phenanthren-2-yl)-4,4,5,5-tetra-methyl-1,3,2-dioxaborolane (8) and 2-[4,4-dimethyl-6-(4,4,5,5-tetra-methyl-1,3,2-dioxaborolan-2-yl)-4\textit{H}-cyclopenta-[\textit{def}]phenanthren-2-yl]-4,4,5,5-tetra-methyl-1,3,2-dioxaborole-lane (9) using bis(pinacolato)diboron, catalytic amounts of Pd(dppf)Cl\textsubscript{2}, and potassium acetate in DMF. Suzuki
The thermal properties of tri-MCPP, tetra-MCPP and penta-MCPP were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) in nitrogen (Table 1). The differential scanning calorimetry analysis was performed under a nitrogen atmosphere (50 mL/min) on a DSC 822 at heating rates of 10 °C/min. Thermogravimetric analysis was performed with a Dupont 951 TGA instrument in a nitrogen atmosphere at a heating rate of 10 °C/min to 800 °C. The TGA results clearly indicated that all the oligomers have good thermal stability. Their decomposition temperatures (T_d), which correspond to a 5% weight loss upon heating during TGA, are around 395 °C, 510 °C, and 514 °C for tri-MCPP, tetra-MCPP, and penta-MCPP, respectively. It was also interesting to note that the T_d increased by about 115 °C from tri-MCPP to tetra-MCPP, but further increasing the length of the oligomer (tetra-MCPP–penta-MCPP) did not produce any additional increase in T_d. DSC was performed in the temperature range from 30 to 450 °C to show that the glass transition temperatures (T_g) of tri-MCPP, tetra-MCPP, and penta-MCPP occur at 122, 156, and 187 °C, respectively. The DSC curve of tetra-MCPP showed a crystallizing peak around 341 °C followed by a melting peak around 377 °C. No transitions related to crystalline structures were observed for tri-MCPP and penta-MCPP. Crystalline melting peaks (T_m) of the oligo-MCPPs increased from 340 to 412 °C as the longer length of the oligo-MCPP increased. The increase in T_g, and T_m with the progression from tri-MCPP to penta-MCPP can be attributed to the increase of the CPP units in the materials. Consequently, oligo-MCPPs are able to form homogeneous and stable amorphous films by thermal evaporation, which is a basic requirement for the materials to be used as hosts in OLEDs.

The UV–vis absorption spectra and photoluminescence spectra of tri-MCPP, tetra-MCPP, and penta-MCPP as THF solution and in thin film are presented in Figure 1. All the oligomers displayed intense π–π* absorption bands.

Table 1

<table>
<thead>
<tr>
<th>Materials</th>
<th>T_g/T_m/T_d</th>
<th>HOMO* (eV)</th>
<th>LUMO* (eV)</th>
<th>Band gap* (eV)</th>
<th>Solution</th>
<th>Film</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>φ_{PL} (%)</td>
<td>Fwhm (%)*</td>
</tr>
<tr>
<td>Tri-MCPP</td>
<td>122/340/395</td>
<td>5.69</td>
<td>2.44</td>
<td>3.25</td>
<td>332</td>
<td>388</td>
</tr>
<tr>
<td>Tetra-MCPP</td>
<td>156/377/510</td>
<td>5.64</td>
<td>2.49</td>
<td>3.15</td>
<td>340</td>
<td>391</td>
</tr>
<tr>
<td>Penta-MCPP</td>
<td>187/412/514</td>
<td>5.62</td>
<td>2.48</td>
<td>3.14</td>
<td>347</td>
<td>393</td>
</tr>
</tbody>
</table>

* Glass transition temperature measured by DSC under N_2.
** Onset decomposition temperature (5% weight loss) measured by TGA under N_2.
* The HOMO energy levels of organic thin films were measured using atmospheric low-energy photoelectron spectrometer Riken-Keiki AC-2.
* Calculated from the HOMO energy levels and E_g.
* Energy band gap was estimated from the onset wavelength of the optical absorption in solid state.
* Full width at half-maximum of PL spectra.
both in solution and as films. Oligo-MCPPs exhibit maximum absorption peaks from 332 to 347 nm in solution, which were red-shifted owing to increasing conjugation length. The absorption spectra (333–354 nm) in the thin solid state for each oligomer were similar as compared to those in solution. The PL spectra of oligo-MCPPs in THF solution exhibit maxima at 388–393 nm. The PL spectrum of penta-MCPP in THF is red-shifted about 5 nm as compared to that of tri-MCPP. The PL spectra of oligo-MCPPs in thin films exhibit maxima at 415–433 nm. The PL spectrum of penta-MCPP in thin film is red-shifted about 30 nm compared to that of tri-CPP. In the case of a solid thin film, the maximum emission peaks of oligo-MCPPs are red-shifted over 30–40 nm, and full width at half-maximum (fwhm) of PL spectra are increased over 26–39 nm, indicating that the inter-chain interaction of oligo-MCPPs, which can be attributed to the π–π* transitions of conjugated backbone, increased the planarity of the materials in the solid state.

Listed in Table 1 are the PL efficiencies of the oligomers in solution and as films. Quantum yields (\(\Phi_{\text{PL}}\)) of tri-, tetra-, and penta-MCPP in chloroform with 9,10-diphenylanthracene as the standard (\(\Phi_{\text{PL}} = 0.91\) in ethanol) are 34.8%, 59.8%, and 97.7%, respectively. The\(\Phi_{\text{PL}}\) value increases significantly with the conjugation lengths of the oligomers. Quantum yields of the films were determined in an integrating sphere at room temperature in air, relative to a thin film of N \(_2\)N-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)benzidine (NPD) as HTL and 8-hydroxyquinoline aluminum (Alq\(_3\)) as ETL were used in all of the device configurations.

The absorption onset wavelength of tri-MCPP was 382 nm, corresponding to a band gap of 3.25 eV, which tetra-MCPP was 394 nm, corresponding to a band gap of 3.15 eV, and that of penta-MCPP was 395 nm, corresponding to a band gap of 3.14 eV. Increasing the conjugated length of the oligo-MCPPs from three to five CPP units resulted in lowering the band gap from 3.27 to 3.18 eV. The HOMO levels for the oligomers were measured to be between −5.62 and −5.69 eV. Increasing the conjugated length of the oligo-MCPP leads to increased HOMO levels. The LUMO levels were calculated from the values of the band gap and the HOMO energy level to be between −2.44 and −2.49 eV. By using the estimated energy levels of oligo-MCPPs, the materials for hole-transport layer (HTL), hole-blocking layer (HBL), and electron-transport layer (ETL) were chosen for the increase of both hole and electron affinities and the improvement of charge injection of the device. N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)benzidine (NPD) as HTL and 8-hydroxyquinoline aluminum (Alq\(_3\)) as ETL were used in all of the device configurations.
Table 2
Device performance characteristics of tri-MCPP, tetra-MCPP, and penta-MCPP

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>fwhm$^a$ of EL</th>
<th>Turn-on voltage (V)</th>
<th>Current density (mA/cm$^2$)</th>
<th>Brightness$^b$ (cd/m$^2$)</th>
<th>Efficiency$^c$ (cd/A)</th>
<th>CIE (x,y)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tri-MCPP</td>
<td>438</td>
<td>74</td>
<td>6.2</td>
<td>65.1</td>
<td>276.4</td>
<td>0.42</td>
<td>(0.17, 0.13)</td>
</tr>
<tr>
<td>Tetra-MCPP</td>
<td>438</td>
<td>74</td>
<td>5</td>
<td>104.2</td>
<td>708.1</td>
<td>0.69</td>
<td>(0.16, 0.13)</td>
</tr>
<tr>
<td>Penta-MCPP</td>
<td>438</td>
<td>74</td>
<td>4.8</td>
<td>142.6</td>
<td>1076</td>
<td>0.81</td>
<td>(0.17, 0.14)</td>
</tr>
</tbody>
</table>

$^a$ Full width at half-maximum of EL spectra.
$^b$ Measured under the condition of maximum brightness.
$^c$ Maximum luminescence efficiency.
$^d$ Calculated from the EL spectra at 8 V.

The performance of the devices is illustrated in Figure 3. It can be seen that all the devices fabricated using the oligo-MCPPs have a low turn-on voltage (voltage at 1 mA/cm$^2$), which decreased from 6.2 V to 4.8 V. In assessing the performance of these three devices, it is interpreted that the lower turn on voltage observed for the penta-MCPP cannot only be attributed to a conjugation effect but to the better emitting properties of the penta-MCPP probably deriving form the increased extensive conjugation. It would appear that the device using penta-MCPP is the best, with the highest luminance of 1076 cd/m$^2$ at 8.2 V. The maximum brightness of tri-MCPP and tetra-MCPP was 276.4 and 708.1 cd/m$^2$, respectively. The EL efficiency of oligo-MCPPs, according to the efficiency versus current density plot, increased as shown in Figure 4. The luminous efficiencies of the devices are 0.42 cd/A at 31 cd/m$^2$ for tri-MCPP, 0.69 cd/A at 63 cd/m$^2$ for tetra-MCPP, and 0.81 cd/A at 18 cd/m$^2$ for penta-MCPP. Compared with the luminous efficiencies of other colors, these values are not high. It should be noted that the emissions of these devices are deep blue in color, as indicated by the very low y values of the Commission Internationale de l’Eclairage (CIE) color coordinates.

As shown in Table 2, the CIE color coordinates of the emission of tri-MCPP, tetra-MCPP, and penta-MCPP are (0.17, 0.13), (0.16, 0.13), and (0.17, 0.14), respectively, at approximately 8 V. These are quite close to that of the National Television System Committee (NTSC) standard blue (0.14, 0.08). Herein, we conclude that the CPP unit, which is a new conjugated emitting segment, can be applied to many kinds of highly efficient materials as blue emissive layers in OLEDs.

In conclusion, we have designed and synthesized novel blue emitter oligo-MCPPs to achieve high efficiency and pure blue emission. Thermal analysis of these revealed their high thermal stability. Decomposition temperatures were around 395 °C for tri-MCPP and over 500 °C for tetra-MCPP and penta-MCPP. These oligomers displayed a bright, deep-blue fluorescence in both the solution and the solid state. High PL quantum efficiencies have been achieved in the oligomers where the oligomers contain three to five CPP units. The multi-layered OLEDs with the configuration of ITO/NPD/oligo-MCPPs/BAlq/Alq$_3$/LiF/Al were fabricated to investigate the electroluminescent properties and the current–voltage–luminescence characteristics of the compounds. The EL spectra of oligo-MCPPs showed maximum peaks around 438 nm. The device of penta-MCPP with the configuration of ITO/NPD/penta-MCPP/BAlq/Alq$_3$/LiF/Al showed the turn-on voltage of about 4.8 V, the maximum brightness of 1076 cd/m$^2$ (at 8.2 V), the maximum luminescence efficiency of 0.81 cd/A, and CIE coordinates of 0.17 and 0.14.

Acknowledgment

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References and notes


20. *R*$_1$ 0.3 (SiO$_2$, dichloromethane/n-hexane = 1:8); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ (ppm) 1.83 (s, 12H), 1.93 (s, 12H), 7.64 (d, 2H, $J = 5.1$ Hz), 7.86 (d, 2H, $J = 7.7$ Hz), 7.96 (d, 4H, $J = 5.1$ Hz), 8.02 (d, 6H, $J = 4.7$ Hz), 8.04 (s, 4H), 8.21 (s, 2H), 8.23 (d, 4H, $J = 7.2$ Hz); $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ (ppm) 26.96, 27.09, 51.35, 51.66, 119.23, 120.15, 120.31, 123.42, 123.48, 123.55, 126.01, 126.38, 126.52, 128.10, 128.11, 128.48, 128.51, 128.54, 135.02, 135.03, 135.16, 135.81, 143.80, 143.89, 152.83, 153.14, 153.37, 153.39; HRMS (m/z, FAB$^+$) caled for C$_{51}$H$_{38}$ 867.3991, found 867.3983.


22. *R*$_1$ 0.38 (SiO$_2$, dichloromethane/n-hexane = 1:3); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ (ppm) 1.82 (s, 12H), 1.92 (s, 12H), 1.93 (s, 6H), 7.64 (d, 2H, $J = 7.1$ Hz), 7.68 (t, 2H, $J = 6.9$ Hz), 7.86 (d, 2H, $J = 7.7$ Hz), 7.96 (d, 4H, $J = 6.3$ Hz), 8.01 (d, 4H, $J = 4.9$ Hz), 8.04 (s, 10H), 8.20 (s, 2H), 8.21 (s, 2H), 8.24 (s, 4H); $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ (ppm): 26.54, 26.68, 50.93, 51.94, 118.82, 119.73, 119.90, 112.99, 123.04, 123.12, 125.58, 125.96, 126.10, 128.05, 128.08, 128.12, 134.58, 134.61, 124.76, 135.38, 134.38, 143.48, 152.41, 152.73, 152.96, 152.98; HRMS (m/z, FAB$^+$) caled for C$_{56}$H$_{40}$ 1083.4930, found 1083.4922.