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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/m^2 (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.[8] Even though there are many reports about blue OLEDs, only a limited number of materials provide appropriate brightness and stability[9] 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 (T_g) 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)-4*H*-cyclopenta-[*def*]phenanthrene))

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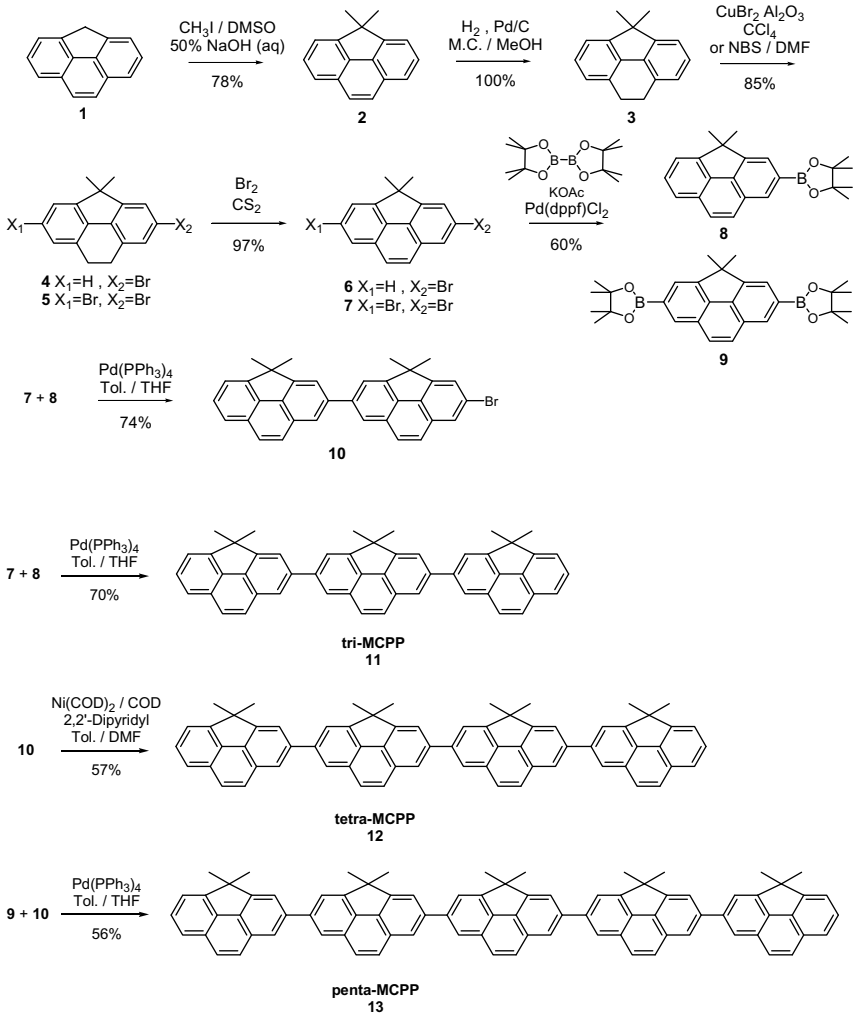
(PCPP) with stabilized pure blue emission.[13,14] A recent work has pointed out the progress in the synthesis of high band gap materials based on the phenanthrene building block.[14–16] EL spectra of PCPP do not show any peak in the long wavelength region corresponding to keto defect sites or aggregates/excimers 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*H*-cyclopenta[*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*H*-cyclopenta[*def*]phenanthrene (**1**) was alkylated using CH_3I in DMSO and 50% aqueous NaOH to obtain 4,4-dimethyl-4*H*-cyclopenta[*def*]phenanthrene (**2**), which was hydrogen-nated using Pd/C to generate 4,4-dimethyl-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**3**). Mono-bromination of compound **3** with N-bromosuccinimide (NBS) afforded 2-bromo-4,4-dimethyl-8,9-dihydro-4*H*-cyclopenta[*def*]phenan-threne (**4**). Alumina-supported copper (II) bromide[17] was used for the dibromination to provide 2,6-dibromo-4,4-dimethyl-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**5**). Compounds **4** and **5** were dehydrogenated by bromine and carbon disulfide to provide 2-bromo-4,4-dimethyl-4*H*-cyclo-penta[*def*]phenanthrene (**6**) and 2,6-dibromo-4,4-dimethyl-4*H*-cyclopenta-[*def*]phenanthrene (**7**), which afforded 2-(4,4-dimethyl-4*H*-cyclopenta[*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-tetramethyl-1,3,2-dioxaborolan-2-yl)-4*H*-cyclopenta-[*def*]phenanthren-2-yl]-4,4,5,5-tetra-methyl-1,3,2-dioxaboro-lane (**9**) using bis(pinacolato)diboron, catalytic amounts of $Pd(dppf)Cl_2$, and potassium acetate in DMF. Suzuki



Scheme 1. Synthetic routes for monomer of tri-MCPP, tetra-MCPP, and penta-MCPP.