Tetrahedron 67 (2011) 1696–1702

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Blue light-emitting and electron-transporting materials based on dialkyl-functionlized anthracene imidazophenanthrolines

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ARTICLE INFO

Article history:
Received 21 May 2010
Received in revised form 14 December 2010
Accepted 21 December 2010
Available online 25 December 2010

Keywords:
Blue light-emitting dioide
Imidazophenanthroline
Electron-transporting material

ABSTRACT

Two novel blue light-emitting materials based on bis(*tert*-butyl)anthracenyl-imidazophenanthrolines (**BAIP**s) have been synthesized and extensively characterized. Both materials exhibited a non-aggregate feature with high fluorescent quantum efficiency and excellent thermal stability. They can serve both as emissive and electron-transporting materials used in electroluminescence (EL) device for blue emission with high luminescence and external quantum efficiency. This study demonstrates that they are potentially useful for a wide range of applications in EL technology.

1. Introduction

Organic electroluminescent materials continue to be of considerable worldwide research interest.[1,2] Many organic compounds, both small molecules and polymeric materials, have been developed and tested for use in organic light-emitting devices (OLEDs). The use of small molecules provides benefits including unambiguous structural identification, easy synthesis, high purity, and good solubility. The hole mobility of small organic molecules is generally orders of magnitude higher than their electron mobility such that most of small organic molecules are used as a hole transporting material (HTMs). However, tris(8-hydroxyquinoline) aluminum (Alq_3) developed by Tang and Van-Slyke at Kodak in the late 80s exhibits an excellent emission in the green light region and good electron-transporting property.[3] Since then, it has been extensively investigated in various OLED device structures as the principal electron-transporting material (ETM).

The use of Alq_3 as a host material for other fluorophores has also been demonstrated.[4–6] Phosphorescent materials attract overwhelming popularity in recent years as they are expected to perform better than fluorescent materials in OLEDs.[7–9] However, blue-emitting fluorescent materials will continue to play an important role in the near future because the synthesis of a true blue-emitting as well as stable phosphor is still challenging. Therefore, it should be useful to develop other highly efficient blue-emitting fluorescent materials that are also capable of electron-transporting as a replacement for Alq_3. Compared to green-emitting Alq_3, a blue-emitting host will likely have a larger triplet energy for phosphorescent dopants with larger triplet energy.

Anthracene and phenanthroline derivatives are important blue light-emitting and charge-transporting materials.[10–12] Effective combination of two individual benefits will be interesting topics. Mondal and several other research groups have demonstrated that some arylimidazo-fused phenanthrolines (AIPs) derivatives exhibited fast electron transport/injection and bright blue light-emitting features.[13–15] Extensive π–π stacking between neighboring imidazophenanthrolines (IPs) and aromatic units in AIPs resulted in their rigidity nature and fast electron mobility in the solid state. Nevertheless, the strong aggregation tendency of AIPs not only leads to the red shifting of their emission spectra, but also results in the deterioration of the device or solid-state optical performance.[13–19] We therefore set out to synthesize a no-aggregation congeners of AIPs via the incorporation of two *tert*-butyl groups acid-catalyzed alkylation at 2 and 6 positions of the anthracene. Such approach, i.e., aggregation suppression by increasing the steric congestion, has exhibited the optical gains herein and the similar concept has been elucidated in several reports.[20–22] Incidentally,

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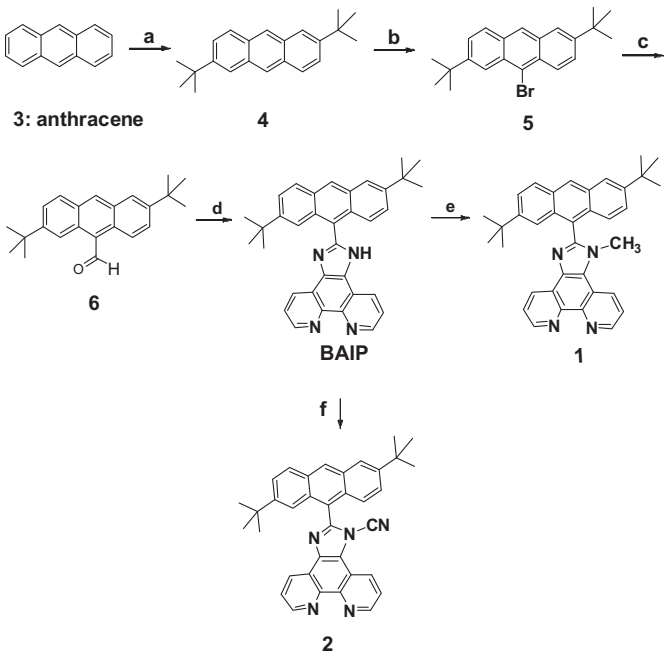
0040-4020/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2010.12.059

there are only a few instances of AIPs that function both as emitting as well as charge-transporting materials.[13–15] We expected these two **BAIP**s to serve as emitting and electron-transporting materials and also with high thermal stability.

2. Results and discussion

2.1. Scope of reaction

Scheme 1 outlines the synthetic protocol. 2,6-Di-*tert*-butylanthracene **4** can be facilely prepared in large laboratory scale by a known method.[23] The treatment of **4** with 1 equiv of *N*-bromosuccinimide (NBS) in dichloromethane afforded 2,6-di-*tert*-butyl-9-halide anthracene (**5**). A subsequent reaction of **5** with anhydrous *N*,*N*-dimethyl formamide (DMF) in THF led to the formation of 2,6-di-*tert*-butyl-9-formylanthracene (**6**). Compound **6** was then allowed to react with *ortho*-phenanthrolines-5,6-diketone and ammonia to give the parent compound of **1** and **2**, 2-(2,6-di-*tert*-butylanthracen-9-yl)-1*H*-imidazo[4,5-*f*][1,10] phenanthroline (**BAIP**). The desired products, **1** and **2**, can then be obtained by methylation and cyanylation of **BAIP**, respectively. The structure of the final products **1** and **2** is shown in Scheme 1. The thermal properties of the compounds were measured by using different scanning calorimetry (DSC). No phase transition was observed in the high temperature range tested (ranging from room temperature to 300 °C).



Scheme 1. Synthetic procedures for **BAIP** derived compounds (a) *tert*-butyl alcohol, TFA, reflux for 16 h (85%); (b) NBS and CH_2Cl_2, at 0 °C at rt for 1 h (46%); (c) *n*-BuLi, THF, and DMF at −78 °C for 2 h (45%); (d) NH_4OAc, phenanthracenedione, and HOAc, reflux for 2 h (50%); (e) NaH, CH_3I, and DMF at rt for overnight (45%); (f) NaH, BrCN, and DMF at rt for overnight (67%).

2.2. Photophysical property studies

The UV–vis absorption and emission spectra for **BAIP**, **1**, **2**, and 2-(anthracen-9-yl)-1-methyl-1*H*-imidazo[4,5-*f*][1,10](phenanthroline) (**MAIP**)[15] are shown in Fig. 1. The absorption profiles for the three **BAIP** derivatives are similar and consistent with the pattern reported previously for the absorption of other AIP analogs. The absorption profile of the compounds is basically the superposition of 2,6-di-*tert*-butylanthracene and imidazophenanthroline units.[14,15]

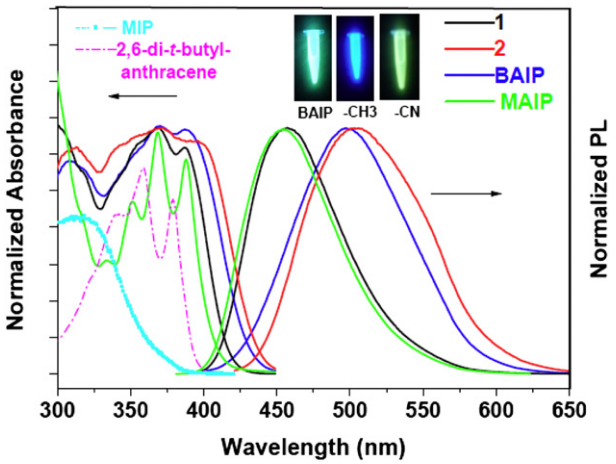


Fig. 1. UV–vis absorption (left) and photoluminescence (right) spectra of **1** (black line), **2** (red line), **BAIP** (blue line), and **MAIP** (green line) in dichloromethane. The absorption of **MIP** (1-methyl-1*H*-imidazo[4,5-*f*][1,10]phenanthroline, cyan line) and 2,6-di-*tert*-butylanthracene (magenta line) are recorded by the constituted moieties of **BAIP**s. Inset shows the photographs of blue emission from the solution of **1**, **2**, and **BAIP** upon excitation with a hand-held UV lamp. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

The dilute solution of **BAIP**s in dichloromethane (ca. 4×10^{-5} M) exhibits a blue emission between 456 and 503 nm (Table 1), and the quantum yield reaches 0.78 for **1** and 0.47 for **2**, with the full widths at half maximum (FWHM) of ca. 80 nm for **1** and 110 nm for **2** (Fig. 1). The structureless emissions of **BAIP**s are attributed to the fluorescence of imidazophenanthroline due to efficient energy transfer from the 2,6-di-*tert*-butylanthracene to the imidazophenanthroline unit.[14] In dilute state, **MAIP** has very similar absorption and emission spectra as **1**, indicating that the *tert*-butyl group introduces only minimal perturbation. Surprisingly, the replacement of the methyl substituent in **1** by a cyano-group to form compound **2** resulted in a dramatic reduction of the quantum yields of the imidazophenanthroline derivative, which is due to the presence of the strong intermolecular interaction induced by polar nature of the cyano entity.[24] The emission maximum of **2** in the film state was blue shifted by 15 nm compared to that in dilute solution, i.e., from 503 nm of the solution state to 488 nm of the film state. The emission maximums of **BAIP** in the film states were also blue shifted by 34 nm compared to that in dilute solution. In comparison, the film state emission of **MAIP** is red shifted by 49 nm (Table 1) compared to the solution state because of strong aggregation of the compound through π–π* interaction of anthracenyl units.[15] It is possible that the two *tert*-butyl groups effectively suppress similar π–π* interaction at the anthracenyl units in **BAIP** and **2**. The blue shift of **BAIP** and **2** may be due to H-type aggregation of imidazophenanthroline units, or less intermolecular interaction of the dyes in the film state compared to the interaction of the dye molecule with the solvent.[9]

2.3. Electrochemical studies and EL performance

Fig. 2 shows the CV plots of the **1** and **2**. Their oxidation peaks were 1.01 V for **1** and 1.12 V for **2**, respectively. The energy levels of the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) are calculated from the onset oxidation [Eonset(Ox)] potentials with the formula expressed to $E_{HOMO}=-4.8-E_{onset}(Ox)$ (−4.8 V for SCE with respect to the zero vacuum level). The calculated data corresponding to their HOMO energy levels are −5.65 eV for **1** and −5.71 eV for **2**. The HOMO and LUMO levels suggest that compounds **1** and **2** may be capable of hole- and electron-transporting.