Original Research Paper
J. Jpn. Soc. Colour Mater., **89** [11], 371-379 (2016)

Synthesis and Luminescence Properties of Dibenzo[*a*,*c*]phenazine Derivatives Bearing a Series of Electron-Donating π-Conjugated Side-Arms at the 10,13-Positions Novel ICT-Type Red Fluorophores Based on Donor-Acceptor-Donor Structures

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(Received June 1, 2016; Accepted August 24, 2016)

Abstract

Novel donor-acceptor-donor-type compounds were developed based on the electron-deficient dibenzo[*a*,*c*]phenazine (*dbpz*) skeleton, and their photoluminescence (PL) properties were investigated. Introduction of electron-donating π-conjugated side-arms at the 10,13-positions of *dbpz* yielded intramolecular charge transfer (ICT)-type chromophores showing remarkable fluorescent properties. When the electron-donating ability of the side-arm was varied, the emission color was tuned from yellowish green to deep red. Especially, 4-hexylthiophen-2-yl, 5-(9,9-dihexyl-9*H*-fluoren-2-yl)thiophen-2-yl and 5-(9-(2-ethylhexyl)-9*H*-carbazol-3-yl)thiophen-2-yl side-arms were effective to obtain red-emissive fluorophores. The developed *dbpz* derivatives exhibited remarkable positive fluorescent solvatochromism, indicating their strong ICT electronic structures. Using the *dbpz* derivative as an emitting dopant, organic light-emitting diodes were fabricated, and electroluminescence corresponding to PL of the emitting dopant was observed upon application of voltage.

Key-words: *Dibenzo[a,c]phenazine, Fluorescence, Intramolecular charge transfer transition, Solvatochromism, Organic light-emitting diode*

1. Introduction

Various types of organic fluorophores have been enthusiastically developed because they are useful for a wide range of applications from organic electronics to bioanalysis[1-7]. Among them, fluorescent molecules based on intramolecular charge transfer (ICT) electronic transitions are often used due to availability of facile color tuning by appropriate combination of electron donor (D) and acceptor (A) components[8,9]. Thus, precise tuning of emission colors through modulation of the ICT character allowed us to develop fluorophores with desired performance such as chromaticity of emission and emission quantum efficiency, especially in the field of organic light-emitting diodes (OLED). Recently, we developed novel ICT-type fluorophores based on dipyrido[3,2-*a*:2',3'-*c*]phenazine (*dppz*) and dibenzo[*a*,*c*]phenazine (*dbpz*) platforms (**Fig. 1**), where introduction of π-based electron-donating components at the 10,13-positions of *dppz* or *dbpz* gave rise to intense photoluminescence (PL) based on ICT transition[10,11].

In the present study, we report the synthesis and photoluminescent properties of novel *dbpz* derivatives **1**–**5** (**Scheme 1**) bearing a series of π-based electron-donating components, especially focusing on the development of red fluorescent molecules. Although red-emitting molecules are important as an emitter for one of three primary colors (*i.e.*, RGB)[12], they are intrinsically less emissive than blue- and green-emitting molecules due to the so-called "energy gap law"[13]. We here describe the molecular design concept towards novel red fluorophores. We also demonstrate the electroluminescence (EL) performance of organic light-emitting diodes (OLED) using the developed fluorophores as an emitting dopant.

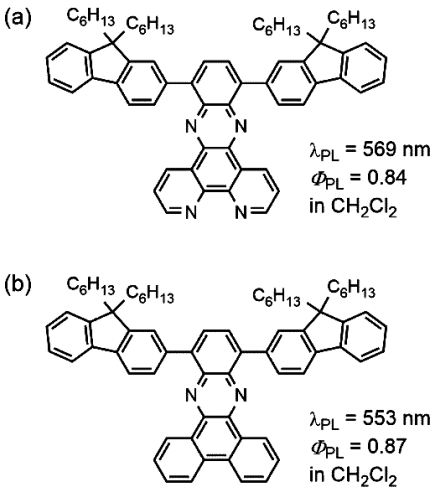

Fig. 1 Examples of fluorescent dipyrido[3,2-*a*:2',3'-*c*]phenazine (a, ref. 10) and dibenzo[*a*,*c*]phenazine (b, ref. 11) derivatives.