

# Original Research Paper

J. Jpn. Soc. Colour Mater., 90 (2), 51–60 (2017)

## Synthesis and Luminescence Properties of Dithieno[3,2-*a*:2',3'-*c*]Phenazine Derivatives with Electron-Donating π-Conjugated Side-Arms at the 2, 5- and 8, 11-Positions

Yanjun HE\*, Natsuki OKAMOTO\*, Takeshi MAEDA\*, Hiroyuki NAKAZUMI\* and Shigeyuki YAGI\*,†

\* Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University,

1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan

†Corresponding Author; E-mail: yagi@chem.osakafu-u.ac.jp

(Received July 7, 2016; Accepted October 12, 2016)

### Abstract

Two types of novel dithieno[3,2-*a*:2',3'-*c*]phenazine (*dtpz*) derivatives, bearing electron-donating π-conjugated side-arms at the 2,5- and 8,11-positions, were synthesized and their luminescence properties were discussed. The 8,11-disubstituted derivatives exhibited fluorescence in dichloromethane in the regions from yellow to red (photoluminescence wavelength  $\lambda_{PL}$ ; 557–651 nm). Especially, 9-(2-ethylhexyl)-9H-carbazol-3-yl and 4-hexylthiophen-2-yl side-arms afforded red emission with high photoluminescence quantum yields ( $\Phi_{PL}$ ) of 0.75 ( $\lambda_{PL}$ ; 616 nm) and 0.38 ( $\lambda_{PL}$ ; 651 nm), respectively. Although the 2,5-disubstituted derivatives ( $\lambda_{PL}$ ; 630–685 nm) exhibited more red-shifted fluorescence in dichloromethane than the 8,11-disubstituted derivatives, they are less emissive, showing  $\Phi_{PL}$  of 0.07–0.23. All the developed *dtpz* derivatives showed positive solvatochromic behavior in photoluminescence, and red shifts of their photoluminescence spectra were observed as polarity of the solvent increased. From the Lippert-Mataga plots, their dipole moments were significantly enlarged upon photoexcitation, indicating that strong intramolecular charge transfer occurs upon electronic transition. Using the 8,11-disubstituted *dtpz* derivative with 9-(2-ethylhexyl)-9H-carbazol-3-yl side-arms as an emitting dopant, a poly(9-vinyl-9H-carbazole) (PVCz)-based OLED was fabricated. Yellow electroluminescence with the Commission Internationale de L'éclairage chromaticity coordinate of (0.53, 0.46) was observed, the spectrum of which was blue-shifted in comparison with photoluminescence of the emitting dopant in dichloromethane due to low polarity of the PVCz host.

**Key-words:** Dithieno[3,2-*a*:2',3'-*c*]phenazine, Fluorescence, Intramolecular charge transfer transition, Solvatochromism, Organic light-emitting diode

### 1. Introduction

Fluorescent dyes have so far been frequently utilized in various fields<sup>1–5)</sup>, and especially in the field of organic electronics such as organic light-emitting diodes (OLEDs), highly fluorescent molecules are intensely required because the photoluminescence (PL) quantum yield of the emitter is one of the factors determining the quantum efficiency of the device<sup>6)</sup>. To modulate the emission color purposively, various kinds of fluorescent dyes have been eagerly developed on the basis of donor-acceptor (D-A) electronic structures because controlling the intramolecular charge transfer (ICT) transition allowed us to tune the singlet excitation energy of a fluorophore<sup>7–10)</sup>. As electron-donating π-building blocks, electron-rich aromatic components such as arylamines and carbazole derivatives have been frequently used<sup>8,9,11,12)</sup>. As for electron-withdrawing π-building blocks, electron-deficient frameworks such as 2,1,3-benzothiadiazole, dibenzo[*b,d*]thiophene *S,S*-dioxide, and other heterocycles have been used<sup>8,13,14)</sup>. Recently we have developed novel fluorophores based on electron-deficient dipyrido[3,2-*a*:2',3'-*c*]phenazine (*dppz*)<sup>15)</sup> and dibenzo[*a,c*]phenazine

(*dbpz*)<sup>16,17)</sup> platforms, where π-based electron-donating groups at the 10,13-positions gave rise to intense PL based on the intense ICT transition. In the case of the *dppz*-based dyes, the emission color was tuned from greenish blue to red partially with the help of metal coordination, where relatively high PL quantum yields were achieved<sup>15)</sup>. We also reported that the introduction of fluorene side-arms to *dbpz* yielded highly emissive green fluorophores, and therein we demonstrated the fabrication of OLEDs using these dyes as an emitting dopant<sup>16)</sup>. Furthermore, the *dbpz* derivatives bearing π-extended electron-donating side-arms showed red-shifted emission from red to deep red<sup>17)</sup>.

Here we report synthesis and PL properties of novel fluorescent dyes based on a dithieno[3,2-*a*:2',3'-*c*]phenazine (*dtpz*) skeleton appended with electron-donating side-arms at the 8,11- or 2,5-positions, namely **1** and **2**, respectively (Fig. 1). Although several *dtpz*-containing low-mass molecules and polymers have so far been developed aimed at development of organic semiconductors and photovoltaic materials<sup>18,19)</sup>, there have been few reports on the PL properties of *dtpz* derivatives<sup>20)</sup>. In the *dtpz* building block, the fused thiophene rings and the phenazine moiety act as