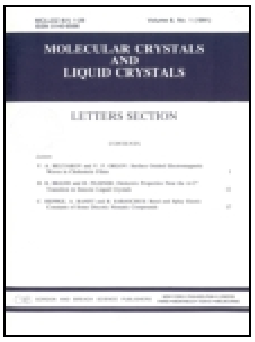

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Synthesis and Luminescent Properties of Novel Dibenzo[*a*,*c*]phenazine Derivatives with Electron-Donating Side-Arms

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*Three types of dibenzo[*a,c*]phenazine (dbpz) derivatives* ***1a–c****, bearing a pair of fluorene side-arms at different positions from one another, were newly synthesized, and their photoluminescence properties were investigated. They exhibited efficient fluorescence based on the intramolecular charge transfer (ICT) transitions. Especially, the compound* ***1a****, bearing the side-arms at the 10,13-positions, was more emissive than the other two, emitting greenish yellow in PMMA thin film with the quantum yield of 0.62. Using* ***1a*** *as an emitting dopant, a poly(9-vinylcarbazole)-based OLED was fabricated, and green electroluminescence from the dopant was obtained.*

Keywords dibenzophenazine; fluorene; photoluminescence; electroluminescence; intramolecular charge transfer; organic light-emitting diode

Introduction

Recently, high efficiency fluorescent materials have been attracting considerable interest from the viewpoint of potential application in various fields such as biochemical and medicinal analyses, chemosensors, and others [1,2]. Great efforts have so far been done to develop novel structural backbones for fluorophores with the desired performance, especially in the field of organic light-emitting diodes (OLEDs) [3]. Recently, we have developed high efficiency fluorescent molecules based on dipyrido[3,2-*a*:2',3'-*c*]phenazine (dppz) [4]: introducing electron donor side-arms at the 10,13-positions of dppz allowed us to obtain donor-acceptor-donor (D-A-D)-type molecules exhibiting efficient fluorescence based on the intramolecular charge transfer (ICT) transitions. Here we develop another type of ICT-based fluorophores; dibenzo[*a*,*c*]phenazines (dbpz) with fluorene side-arms (**1a**–**c**, Figure 1). We investigate their photoluminescence (PL) properties and also demonstrate the potential applicability of the developed fluorophore to OLED.

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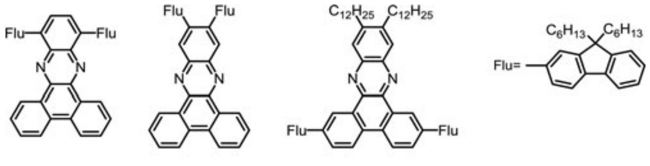


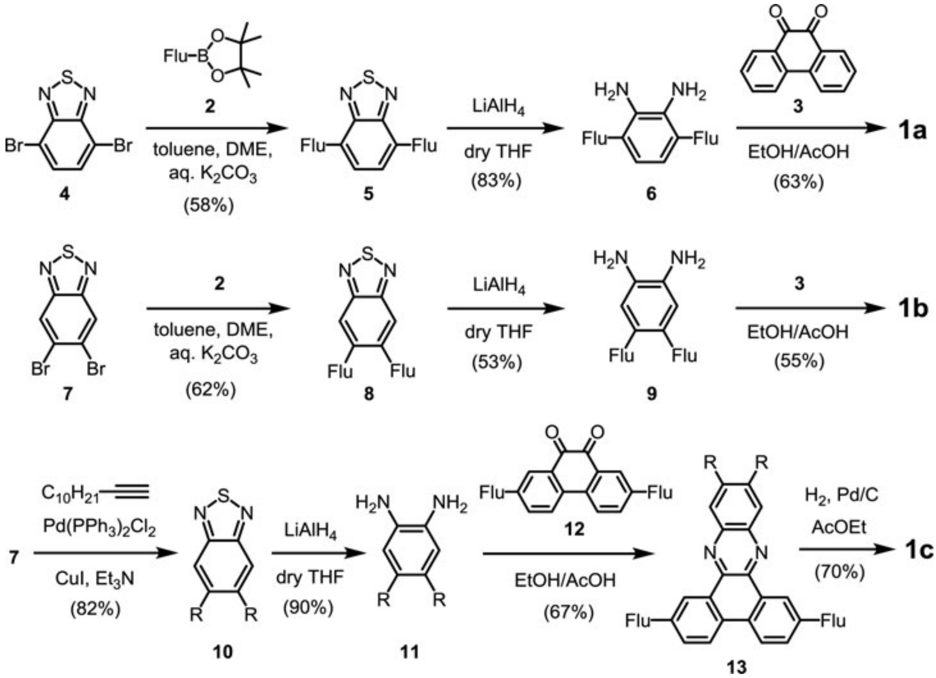
Figure 1. Structures of **1a–c**.

Experimental

General

All chemicals for synthesis were purchased from companies and used without purification. Compounds **1a–c** were prepared according to Scheme 1. They were purified by silica gel column chromatography using chloroform/hexane (1/3, v/v) as eluent. The purity of the obtained compounds was checked by elemental analysis. The characterization data are listed below.

1a: mp 171–172°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.72–1.14 (m, 44H), 2.09 (t, $J =$ 8.2 Hz, 8H), 7.36–7.44 (m, 6H), 7.66 (t, $J = 7.6$Hz, 3H), 7.75 (t, $J = 4.1$ Hz, 3H), 7.85 (d, $J = 7.3$ Hz, 2H), 7.96–8.00 (m, 6H), 8.57 (d, $J = 8.3$ Hz, 2H), 9.20 (dd, $J = 1.1$ and 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.08, 22.70, 24.13, 30.02, 31.68, 40.45, 55.35, 119.37, 119.96, 122.99, 123.24, 125.74, 126.66, 126.95, 127.13, 128.05, 130.07,



Scheme 1. Synthesis of **1a**–**c**. The substituents Flu and R are 9,9’-dihexyl-9*H*-fluoren-2-yl and dodec-1-yn-1-yl groups, respectively.

130.20, 130.24, 130.83, 132.31, 137.97, 140.33, 140.49, 140.59, 141.11, 141.42, 150.67, 151.33; MALDI-TOF MS *m*/*z* 945 ($[M]^+$); Anal. Calcd for $C_{70}H_{76}N_2$: C, 88.93; H, 8.10; N, 2.96. Found: C, 89.02; H, 8.06; N, 2.67.

1b: mp 166–167°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.56–1.12 (m, 44H), 1.81–1.95 (m, 8H), 7.28–7.42 (m, 10H), 7.55–7.66 (m, 4H), 7.73–7.81 (m, 4H), 8.43 (s, 2H), 8.55 (d, J = 7.8 Hz, 2H), 9.41 (dd, J = 1.7 and 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.16, 22.73, 23.93, 29.81, 31.72, 40.52, 55.19, 119.38, 119.96, 122.86, 123.02, 124.56, 126.35, 126.82, 127.19, 128.04, 129.06, 130.36, 130.48, 130.67, 132.12, 139.55, 140.44, 140.76, 141.61, 142.81, 144.06, 150.80, 150.99; MALDI-TOF MS *m*/*z* 945 ($[M]^+$); Anal. Calcd for $C_{70}H_{76}N_2$: C, 88.93; H, 8.10; N, 2.96. Found: C, 88.69; H, 8.01; N, 2.70.

1c: mp 63–65°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.75–0.88 (m, 26H), 1.10–1.53 (m, 60H), 1.78–1.86 (m, 4H), 2.03–2.13 (m, 8H), 2.92 (t, J = 7.8 Hz, 4H), 7.33–7.40 (m, 6H), 7.77–7.90 (m, 8H), 8.10–8.13 (dd, J = 2.0 and 8.5 Hz, 2H), 8.16 (s, 2H), 8.69 (d, J = 8.7 Hz, 2H), 9.71 (d, J = 1.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.02, 14.20, 14.34, 22.59, 22.77, 22.93, 24.13, 29.63, 29.95, 30.00, 30.20, 30.82, 31.49, 31.65, 32.18, 32.34, 33.22, 40.77, 55.55, 120.24, 120.61, 121.64, 123.11, 123.58, 124.09, 126.80, 127.05, 127.29, 127.69, 128.88, 130.57, 130.94, 139.61, 140.73, 140.95, 141.11, 141.23, 142.05, 144.69, 151.38, 151.68; MALDI-TOF MS *m*/*z* 1282 ($[M + H]^+$); Anal. Calcd for $C_{94}H_{124}N_2$: C, 88.07; H, 9.75; N, 2.19. Found: C, 88.15; H, 9.93; N, 2.10.

Fabrication of OLED

Poly(9-vinylcarbazole) (PVCz) was purchased from Sigma-Aldrich Co. (M_w = 25,000–50,000) and used after purification by reprecipitation from THF to methanol. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Clevios™ P VP CH8000) and 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) were purchased from Heraeus Clevios and Tokyo Chemical Industry, respectively. First, PEDOT:PSS was spin-coated onto ITO pretreated with $UV{-}O_3$ and dried at 115°C for 1 h. Then, a mixture of PVCz, PBD and **1a** in dry toluene (PVCz; 10 mg/0.7 mL of toluene) was filtered through a 0.2 μm membrane filter, and was spin-coated onto the PEDOT:PSS layer to fabricate the emitting layer (EML). Thereafter, CsF and Al layers were successively vacuum deposited on the EML. The obtained OLED was covered with a glass cap and encapsulated with a UV-curing epoxy resin.

Results and Discussion

As shown in Scheme 1, we newly synthesized three types of dbpz derivatives with a pair of fluorene side-arms, that is, **1a**, **1b**, and **1c**. These derivatives possess the 2-fluorenyl side-arms at different positions; 10,13-, 11,12-, and 2,7-positions for **1a**, **1b**, and **1c**, respectively. For **1a** and **1b**, the Suzuki-Miyaura coupling of fluorenylboronic acid ester **2** with the corresponding dibromo-2,1,3-benzothiadiazoles (**4** and **7**) followed by reduction with $LiAlH_4$ afforded the diaminobenzene precursors (**6** and **9**). These precursors were subjected to condensation with phenanthrene-9,10-dione **3** to obtain the target dbpz derivatives **1a** and **1b**. As seen in **1c**, introduction of long alkyl chains is possible along with the fluorenyl side-arms, enhancing the solubility in a wide range of organic solvents. The compound **7** was reacted with 1-dodecyne under the Sonogashira coupling conditions followed by reduction to afford the intermediate **11**. The condensation of **11** with **12** yielded the precursor **13**, the triple bonds of which were hydrogenated to afford **1c**. The structures of **1a–c** were identified by ^{1}H NMR, ^{13}C NMR and MALDI-TOF mass spectra as well

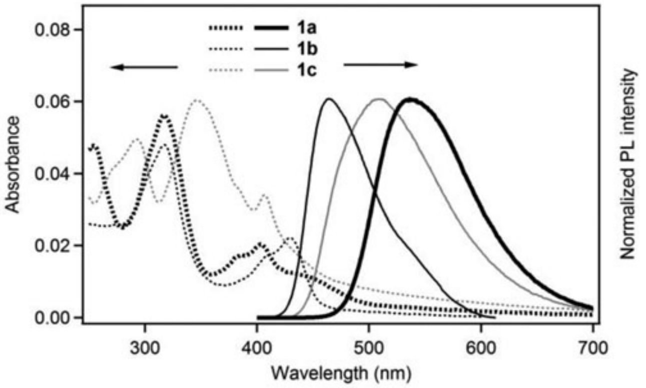


Figure 2. UV-vis absorption and PL spectra of **1a–c** in PMMA films at rt.

as elemental analysis. The obtained dbpz derivatives are photochemically stable and can be handled under ambient conditions. Also **1a** and **1b** are thermally stable, showing their melting points at 171–172 and 166–167°C, although that of **1c** is very low (63–65°C) due to introduction of the dodecyl groups.

In Figure 2 are shown the UV-vis absorption and PL spectra of **1a**–**c** doped into poly(methyl methacrylate) (PMMA) thin films with 100 nm thickness (concentration; 1.0 mol%, based on the methyl methacrylate monomer unit). Relatively intense greenish yellow emission was observed for **1a** (PL maximum λ_{PL}; 538 nm) with the quantum yield (Φ_{PL}) of 0.62, whereas **1b** and **1c** were less emissive, exhibiting bluish green (λ_{PL}; 465 nm) and green (λ_{PL}; 509 nm) PL with Φ_{PL} of 0.14 and 0.20, respectively. Thus, **1a** is a more excellent emitter in terms of Φ_{PL}. The PL lifetimes (τ_{PL}s) were also obtained for **1a**–**c**; 11.6, 1.67, and 2.23 ns, respectively. According to the following equations (1) and (2), the rate constants of radiative and non-radiative decay were obtained as k_r and k_{nr}, respectively;

$$k_r = \Phi_{PL}/\tau_{PL} \tag{1}$$

$$k_{nr} = k_r(1-\Phi_{PL})/\Phi_{PL} \tag{2}$$

The k_rs for **1a**–**c** were 5.3×10^7, 8.4×10^7, and 9.0×10^7 s^{-1}, respectively, and the k_{nr}s for **1a**–**c** were 3.3×10^7, 5.1×10^8, and 3.6×10^8 s^{-1}, respectively. From this result, the PL efficiency in the present dbpz system is dominated by the non-radiative decay process.

We also investigated the solvent dependence of PL spectra of **1a**–**c**. The data are summarized in Table 1. In dichloromethane, **1a** showed the PL spectrum with the emission maximum (λ_{max}) at 553 nm, emitting greenish yellow. On the other hand, **1b** exhibited bluish green PL at 496 nm, blue-shifted in comparison with **1a**. In the case of **1c**, green PL was observed. This tendency in dichloromethane is similar to that in PMMA films (*vide supra*). Interestingly, positive solvatochromism in PL was observed for the present dbpz derivatives. For example, the λ_{PL} of **1a** ranged from 515 (green) to 574 nm (orange) when the solvent polarity was changed from hexane to DMF. Also, the UV-vis absorption spectra hardly changed when any solvents were employed (Table 1), showing the dbpz derivatives adopt less polarized ground state structures. These results indicate that the observed PL is based on the ICT transition from the donor side-arms to the dbpz core to afford highly polarized excited state structure [4,5]. Indeed, the TD-DFT calculations supported that the HOMO-LUMO transition contributing to fluorescent emission is based on the ICT

Table 1. UV-vis absorption and PL spectral data of **1a–c** in different solvents at rt (conc.; 1 μM)

Solvent	**1a**			**1b**			**1c**		
	$\lambda_{abs}{}^{a}$ (nm)	$\lambda_{PL}{}^{b}$ (nm)	$\Phi_{PL}{}^{c}$	$\lambda_{abs}{}^{a}$ (nm)	$\lambda_{PL}{}^{b}$ (nm)	$\Phi_{PL}{}^{c}$	$\lambda_{abs}{}^{a}$ (nm)	$\lambda_{PL}{}^{b}$ (nm)	$\Phi_{PL}{}^{c}$
Hexane	396	515	0.42	421	441	0.22	400	452	0.13
Toluene	399	527	0.64	425	454	0.45	403	478	0.18
Dioxane	398	537	0.72	424	462	0.43	402	487	0.20
CH_2Cl_2	399	553	0.87	425	496	0.51	403	535	0.46
DMF	400	574	0.89	426	504	0.59	403	527	0.45

[a]Absorption maxima in UV-vis absorption spectra. [b]PL maxima. The excitation wavelengths were adjusted to the λ_{abs}s. [c]PL quantum yields upon excitation at the λ_{abs}s.

transition, as shown in Figure 3. The other two, **1b** and **1c**, also exhibited similar spectral behavior and can be assigned to the ICT-type fluorophores. As seen for PL spectra in PMMA films, **1a** is more emissive in any solvents than the other two.

Using **1a** as a fluorescent dopant, we fabricated a PVCz-based OLED [6]. The configuration of the device is as follows: ITO (transparent anode, 150 nm)/PEDOT:PSS (40 nm) /EML (80 nm)/CsF (1.0 nm)/Al (cathode, 250 nm), where EML is a PVCz thin film doped with **1a** and PBD. The ratio of PVCz, PBD, and **1a** is 100:18:1.7 (molar ratio based on a carbazole monomer unit). Figure 4a shows the current density-voltage-luminance (*J*-*V*-*L*) relationships of the OLED and the electroluminescence (EL) spectrum is also shown in Figure 4b. The maximum luminance L_{max} of 1400 cd m^{-2} was obtained at 16.0 V and the EL spectrum was accompanied with green emission at 528 nm (CIE (x, y); (0.30, 0.57)), blue-shifted by 10 nm in comparison with the PL spectrum of **1a** in PMMA. At 11.5 V,

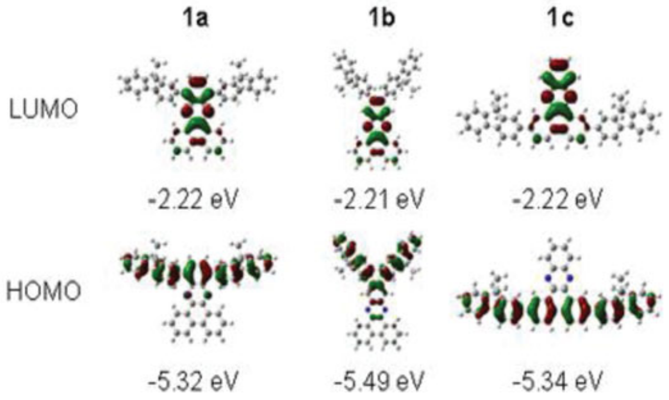


Figure 3. Electron distributions of the HOMO and LUMO for **1a–c** obtained by DFT calculations at the B3LYP/6-31G* level of theory. The hexyl groups are replaced by methyls. In 1c, the dodecyl groups are omitted.

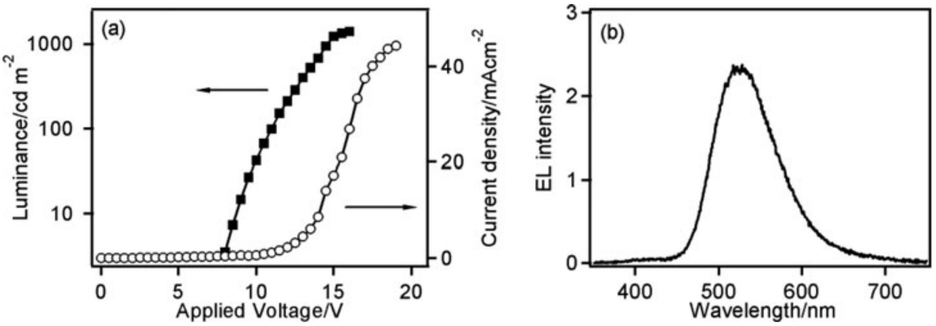


Figure 4. *J-V-L* curves (a) and normalized EL spectrum (b) of the OLED using **1a**.

the device demonstrated the maximum performance; the maximum external quantum efficiency of 0.30%, the maximum current efficiency of 0.94 cd A^{-1}, and the maximum power efficiency of 0.26 lm W^{-1}.

Conclusions

We here report the preparation of three novel dbpz derivatives (**1a**–**c**) with fluorene-based side-arms. These derivatives relatively efficient fluorescence based on the ICT transitions in their D-A-D structures. Especially, introduction of the side-arms at the 10,13-positions (**1a**) is the most emissive of the three, exhibiting greenish yellow PL (λ_{PL}; 538 nm) with Φ_{PL} of 0.62 in PMMA. Using **1a** as an emitting dopant, a PVCz-based OLED was successfully fabricated, showing green EL from the dbpz dopant.

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