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Development of Novel Fluorescent Fused Phenazines Based on Intramolecular Charge Transfer Electronic Structures

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July 2016

Doctoral Thesis at Osaka Prefecture University
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Chapter 1

General Introduction

1.1. Fluorescent dyes and their application

Fluorescent dyes are one of luminescent materials that exhibit emission based on the electronic transition from the excited state down to the ground state. Representative fluorescent dyes are shown in Figure 1; aromatic and heterocyclic \( \pi \)-conjugated compounds such as arenes, coumarines, cyanines, rhodamines, and so on [1]. It is well known that they have so far been used in textile industry as dyestuffs and color-brightening chemicals. In recent years, according to increasing demands in advanced scientific fields, various types of fluorescent molecules have been required for purposive uses, and numbers of functional molecules exhibiting fluorescent properties have been developed. Especially, since 1980s,

![Chemical structures](image)

**Figure 1.** Structures of representative fluorescent molecules; (a) arene, (b) coumarin, (c) cyanine, and (d) rhodamine.
fluorescent molecules have been attracting much attention in supramolecular and molecular recognition chemistry. The emission properties of fluorophores such as emission color and emission quantum yield are often affected by external stimuli such as pH [2, 3], polarity of solvents and environments [4–6], molecular recognition events [7–10], and so on, and thus the fluorophores have been frequently employed as information transmission components in supramolecular systems. As one of representative examples, de Silva and coworkers developed chemosensors using an anthracene fluorophores, as shown in Figure 2 [11]. Although the anthracene molecules bearing an azacrown ether moiety at the 9-position are much less emissive in the absence of alkali metal cations such as Na\(^+\) and K\(^+\) due to photo-induced electron transfer from the nitrogen to the anthracene fluorophore, binding the cations to the azacrown moiety through electrostatic interactions gives rise to fluorescence emission with increasing intensities in the presence of increasing concentrations of the metal cations. Thus, fluorescent off-on chemosensory system is

**Figure 2.** Fluorescent chemosensor for an alkali cation by de Silva (ref. 11) based on photo-induced electron transfer.
achieved. After that, various types of chemosensors have been developed towards analytes such as heavy metal cations [12, 13], nucleic acids [14], carbohydrates [15], and so on. Nowadays, fluorescent dyes are still attracting increasing interest in biomedical and bioanalytical fields. Nagano and coworkers developed a highly selective, practical chemosensor for a zinc ion working in aqueous media [16]. Nakazumi and coworkers reported an indolino-squarylium dye exhibiting intense red fluorescence upon binding to human serum albumin [17]. Most recently, molecular imaging using fluorescent probes is one of attractive techniques to monitor the behavior of targeted biologically important chemicals in a living cell [18, 19].

Fluorescent dyes have also attracted much attention of chemists and physicists in organic electronics fields such as organic light-emitting diode (OLED) [20–22]. As mentioned in detail below (section 1.3), OLED requires organic emitting materials to obtain electroluminescence upon application of electric voltage. OLEDs are expected to be applied to flat-panel displays and lighting apparatuses, and thus emitting materials exhibiting three primary colors (i.e. blue, green and red) of emission are required. As blue fluorescent materials, \(N,N'\)-di(1-naphthyl)-\(N,N'\)-diphenylbenzidine (so called \(\alpha\)-NPD) and 1,1,4,4-tetraphenyl-1,3-butadiene (so called TPB) are well known [23] (Figure 3a). As green fluorescent materials, there are lots of dye skeletons, and the coumarin derivative as well as the aluminium complex are famous as Coumarin 6 [24] and Alq\(_3\) [24], respectively (Figure 3b). As red fluorophores, a series of merocyanine dyes are representative; DCM-1, DCM-2, and DCMJB [22, 24] (Figure 3c).
1.2. **Fluorophores based on intramolecular charge transfer**

Fluorophores are usually classified into two types according to electronic transition manners; $\pi-\pi^*$ and intramolecular charge transfer (ICT) transitions. The former, represented by anthracene, pyrene, and other aromatic arenes and acenes, affords relatively blue-shifted emission with a structured spectral shape, whereas the latter gives rise to emission with a broadened shape in green-to-red regions. The ICT-type fluorophores consist of an electron-donor (D) and an electron-acceptor (A) groups, as seen in merocyanine-type...
chromophores [18, 22, 25], and varying the combination of donor and accepter moieties allow us to tune the emission colors. For example, Grimsdale and coworkers reported ICT-type chromophores based on electron-accepting moieties of benzo[1,2-c;4,5-c′]bis[1,2,5]thiadiazole, [1,2,5]-thiadiazolo[3,4-g]quinoxaline and pyrazino[2,3-g]quinoxaline skeletons, which show fluorescence emission in the region from 539 to 733 nm [26]. Konishi and coworkers reported a D-π-A-type ICT fluorophore using pyrene as a π-conjugated spacer, where remarkable solvatochromic properties are found in organic solvents with different polarity from hexane to 2,2,2-trifluoroethanol together with the shift of the photoluminescence maximum (λPL) from 446 to 528 nm [27] (Figure 4a). Interestingly, the D-π-A pyrene derivative is highly emissive in any solvents (photoluminescence quantum yield ΦPL > 0.88), and modification with a carboxyl group allow for solvation in aqueous media. Recently, Kubota and Matsui developed unique ICT fluorophore platforms using a β-iminoenolate-modified pyrimidine boron complex (Figure 4b) [28]. Introduction of a strong electron-donor gives rise to positive solvatochromism of fluorescence, indicating the chromophore possesses a strong ICT character.

![Figure 4. Structures of ICT-type fluorophores; (a) D-π-A pyrene derivatives, (b) pyrimidine-boron complexes.](image-url)
Recently, Yagi and coworkers reported unique D-A-D-type ICT fluorophores using dipyrido[3,2-\(a\):2'\(a'\),3'\(c\)]phenazine (\textit{dppz}) as an electron-accepting structural platform (Figure 5) [29]. They found that introduction of \(\pi\)-conjugated electron-donating side-arms at the 10- and 13-positions yields highly fluorescent molecules (\(\phi_{PL} > 0.49\) in dichloromethane), although \textit{dppz} itself exhibits no fluorescence. The emission color is tunable from greenish blue (\(\lambda_{PL}\); 505 nm) to orange (\(\lambda_{PL}\); 592 nm) in dichloromethane by varying the electron-donating properties of the side-arms. The ICT character of the \textit{dppz} derivatives were elucidated by positive solvatochromic behavior, where a large difference of the dipole moment (\(\Delta\mu\); 12.3–16.8 debye) upon excitation from the ground state to the singlet excited state obtained by the Lippert-Mataga analysis. Interestingly, the metal coordination to the 4- and 5-nitrogens gives rise to enhancement of the ICT character to afford the further red

**Figure 5.** Structures and photoluminescent properties of dipyrido[3,2-\(a\):2'\,3'\(c\)]phenazine-based ICT-type fluorophores with D-A-D-type electronic structures.
shift of $\lambda_{PL}$ in the red region: the platinum(II) dichloride complex of the $dppz$ derivative bearing the fluorene side-arms exhibit fluorescence emission at 623 nm with $\Phi_{PL}$ of 0.45 in dichloromethane.

1.3. Organic light-emitting diodes

Organic light-emitting diodes (OLED), consisting of organic hole- and electron-transporting semiconductor layers (HTL and ETL) sandwiched between transparent and metal electrodes, play crucial roles in electronic and optoelectronic fields. OLEDs have technological advantages such as low driving voltage and bright emission, and thus they are applicable to full color flat-panel displays [30, 31] and lighting apparatuses [32, 33]. In 1989, the prototype of practical OLED was first reported by Tang and coworkers, which has an emitting layer, i.e. a thin film of a fluorescent dye, sandwiched between an anodic HTL (a thin film of aromatic amine derivative) and an cathodic EML (a thin film of an aluminium complex), as shown in Figure 6 [34]. Holes and electrons injected from the anode and cathode through HTL and ETL, respectively, and recombined in EML to induce excitation of the constituent emitting material effectively, yielding bright electroluminescence (EL). The internal quantum efficiency of OLED $\eta_{int}$ is defined as the following equation (1):

$$\eta_{int} = \eta_x \times \phi_p \times \gamma \times 100 \text{ (\%)}$$

(1)

where $\eta_x$, $\phi_p$, and $\gamma$ represent an efficiency of exciton generation, internal luminescence quantum yield of an exciton of an emitter (usually similar to $\Phi_{PL}$), and carrier balance (i.e.,
Figure 6. Device structure of dye-doped OLED reported by Tang and coworkers in 1989.

probability of charge recombination), respectively. As the exciton generation upon electric excitation obeys spin statics, the value of $\eta_c$ is not more than 0.25. Therefore, OLEDs using fluorescent emitting materials achieve at most 25% of $\eta_{int}$, even when both of $\phi_p$ and $\gamma$ are 1.0. On the other hand, taking the intersystem crossing from the singlet excited state to the triplet into consideration, utilization of phosphorescent emitting materials allows us to obtain as high as 100% of $\eta_{int}$. Thus, phosphorescent OLEDs, in which organoplatinum (II) [35, 36] and organoiridium(III) [37, 38] complexes (Figure 7) are predominantly used from the viewpoint of high-efficiency room-temperature phosphorescence caused by strong spin-orbit interaction, are usually superior to the fluorescent ones in luminous efficiency. However, fluorescent emitters are still important because of their low-cost availability as well as drains of resources of the precious metals. Indeed, in the case of fluorescent OLED, relatively high device performance has so far been achieved. For example, as shown in
Figure 7. Structures of representative phosphorescent organometallic complexes; (a) heteroleptic cyclometalated platinum(II) complexes and (b) heteroleptic bis- and homoleptic tris-cyclometalated iridium(III) complexes.

Figure 8. Jenekhe and coworkers fabricated OLEDs using a fluorescent dye with an A-D-A-type electronic structure, 3,7-[bis(4-phenyl-2-quinolyl)]-10-methylphenothiazine (BPQ-MPT), which show intense green electroluminescence based on ICT transition with high device performance for fluorescent OLEDs: a maximum luminance of more than 40000 cd m\(^{-2}\), a maximum current efficiency of 21.9 cd A\(^{-1}\), a maximum power efficiency of 10.8 lm W\(^{-1}\), and a maximum external quantum efficiency of 5.78% [39]. Also, it is well known that practical OLED-based commercially available mobile phones still employ fluorescent dyes to fabricate blue picture elements. Therefore, to develop emitting materials exhibiting highly efficient fluorescent emission according rational molecular design, novel structural platforms are intensely required.
Figure 8. Device structure of high-efficiency fluorescent OLED reported in 2006 by Jenekhe and coworkers.

1.4. Outline of this thesis

With the background mentioned above, this thesis is aimed at development of highly fluorescent D-A-D chromophoric systems as well as precise tuning of their luminescent properties by controlling the ICT-type transition. The author especially focuses on utilization of electron-deficient dibenzo[a,c]phenazine and dithieno[3,2-a:2',3'-c]phenazine as electron-withdrawing scaffolds. Introduction of electron-donating side-arms to these fused phenazines in appropriate ways affords D-A-D chromophoric systems. Furthermore, the developed fluorescent molecules were applied to OLED fabrication as emitting dopants.

In Chapter 2, the author newly synthesized three types of dibenzo[a,c]phenazine (dbpz) derivatives with a pair of fluorene side-arms (Figure 9) and their photoluminescence (PL) properties were investigated. The 9,9-dihexyl-9H-fluoren-2-yl groups were introduced to the 10,13-, 11,12-, and 2,7-positions of the dbpz skeleton; 1a, 1b, and 1c in Chapter 2. Poly(methyl methacrylate) (PMMA) thin films doped with the 11,12- and 2,7-disubstituted dbpz derivatives exhibited greenish blue and green fluorescence, respectively, with low
Figure 9. Structures of dibenzo[a,c]phenazine derivatives with a pair of fluorene side-arms. The compound numbers correspond to those in Chapter 2.

$\Phi_{PL}$ less than 0.20, whereas the 10,13-disubstituted derivative emitted greenish yellow with a relatively high $\Phi_{PL}$ of 0.62. The analysis of rate constants of the radiative and non-radiative processes from the excited states indicated that the low $\Phi_{PL}$s of the 11,12- and 2,7-disubstituted derivatives are brought about mainly by facilitation of non-radiative decay process. These three dbpz derivatives exhibited remarkable positive solvatochromism of photoluminescence, indicating that the observed emission is based on the ICT electronic transitions. Time-dependent density functional theory (TD-DFT) calculations also indicated that the emission from the present dbpz derivatives is based on the ICT transitions from the HOMO localized at the $\pi$-conjugation including the side-arms to the LUMO localized at the dbpz core. Using the 10,13-disubstituted derivative as an emitting dopant, poly(vinyl-9H-carbazole) (PVCz)-based OLED was fabricated, and green electroluminescence blue-shifted by 10 nm in comparison with photoluminescence in PMMA was observed upon application of voltage, where maximum luminance of 1400 cd m$^{-2}$ (@16.0 V) and the Commission Internationale de L'éclairage (CIE) chromaticity coordinate of (0.30, 0.57) was obtained.

In Chapter 3, to develop excellent red fluorescent molecules, five novel D-A-D-type
Figure 10. Structures of dibenzo[a,c]phenazine derivatives with a series of electron-donating side-arms at the 10,13-positions. The compound numbers correspond to those in Chapter 3.

dbpz derivatives bearing a series of electron-donating \( \pi \)-conjugated side-arms at the 10,13-positions, such as 9-(2-ethylhexyl)-9\( H \)-carbazol-2-yl (1 in Chapter 3), 9-(2-ethylhexyl)-9\( H \)-carbazol-3-yl (2 in Chapter 3), 4-hexylthiophen-2-yl (3 in Chapter 3), and 5-arylthiophen-2-yl groups (4 and 5 in Chapter 3), were synthesized (Figure 10), and their photo- and electroluminescent properties were investigated. TD-DFT calculations of the developed \( \text{dbpz} \) derivatives indicated that the electronic transition from the ground state to the lowest singlet excited state is based on the ICT transitions from the HOMO localized at the \( \pi \)-conjugation including the side-arms to the LUMO localized at the \( \text{dbpz} \) moiety. Enhancement of the electron-donating ability of the side-arms as well as extension of their \( \pi \)-conjugation gave rise to a decrease in the HOMO-LUMO energy gap to lower the ICT transition energy. Indeed, a broad absorption band assignable to the HOMO-LUMO ICT transition was observed in the low energy region for each \( \text{dbpz} \) derivative, and introduction of 4-hexylthiophen-2-yl and 5-arylthiophen-2-yl side-arms gave rise to significant red-shifts of the ICT absorption bands. The developed \( \text{dbpz} \) derivatives exhibited fluorescent emission in dichloromethane, the \( \lambda_{PL} \) of which ranged from 557 (greenish
yellow) to 713 nm (deep red). The fluorescence of each derivative was affected by solvent polarity, and positive solvatochromic behavior of the emission was observed. From the Lippert-Mataga analysis, the difference in the dipole moment between the ground and excited states was estimated to be 8.04–12.2 debye, and a considerable change of the molecular polarity upon photoexcitation, characteristic to an ICT-type molecule, was found. The 4-hexylthiophen-2-yl and 5-arylthiophen-2-yl side-arms were effective to obtain red fluorescence, and especially the former yielded more efficient emission even in a PMMA matrix. Using the \( \text{dbpz} \) derivatives as an emitting dopant, PVCz-based OLEDs were fabricated, where electroluminescence whose spectrum corresponds to the PL spectrum of each emitting dopant was observed upon application of voltage. Especially, the \( \text{dbpz} \) derivative bearing 5-(9,9-dihexyl-9\( \text{H} \)-fluoren-2-yl)thiophen-2-yl side-arms afforded red electroluminescence with the CIE chromaticity coordinate of (0.64, 0.30), which was closest to pure red among the developed \( \text{dbpz} \) derivatives.

In Chapter 4, using dithieno[3,2-\( \alpha \):2',3'-\( \text{c} \)]phenazine as an electron-withdrawing structural basis, novel D-A-D fluorescent molecules were developed, where electron-donating \( \pi \)-conjugated side-arms were introduced to the 2,5- or 8,11-positions (Figure 11). TD-DFT calculations indicated that the electronic transition of the developed \( \text{dtpz} \) derivatives from the ground state to the lowest singlet excited state is based on the ICT transitions from the HOMO localized at the \( \pi \)-conjugation including the side-arms to the LUMO localized at the \( \text{dtpz} \) moiety. In UV-vis absorption spectra, broad bands assignable to the ICT transition were observed for the \( \text{dtpz} \) derivatives. The 8,11-disubstituted derivatives exhibited fluorescent emission in the regions from yellow to red. Especially, relatively intense fluorescent emission was observed by introduction of 9-(2-ethylhexyl)-
Figure 11. Structures of dithieno[3,2-α:2',3'-c]phenazine derivatives with a series of electron-donating side-arms at the 2,5- and 8,11-positions. The compound numbers correspond to those in Chapter 4.

9H-carbazol-3-yl (λ_{PL}, 616 nm; Φ_{PL}, 0.75) and 4-hexylthiophen-2-yl (λ_{PL}, 651 nm; Φ_{PL}, 0.38) side-arms. The 2,5-disubstituted derivatives were less emissive than the 8,11-disubstituted ones although they exhibited more red-shifted emission. Both of the 2,5- and 8,11-disubstituted derivatives showed remarkable positive fluorescence solvatochromism, and an increase in the dipole moment upon photoexcitation ranged from 8.40 to 16.8 debye, indicating that the observed emission is based on the ICT transition. Using the dtpz derivative bearing the 9-(2-ethylhexyl)-9H-carbazol-3-yl side-arms as an emitting dopant, a PVCz-based OLED was fabricated, and the device performance was estimated. Although the emitting dopant exhibited intense red photoluminescence in dichloromethane, the fabricated device did yellow electroluminescence blue-shifted by 10 nm due to low medium polarity of PVCz.
Chapter 1

In Chapter 5, the conclusions of the present thesis are given together with the future prospects.

1.5. References


Chapter 1


Chapter 2

Synthesis and Luminescent Properties of Novel Dibenzo[a,c]phenazine Derivatives with Electron-donating Side-arms

2.1. Introduction

Recently, highly 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 (OLED) [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) transition.

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 fluorophores to OLED.
2.2. Experimental section

2.2.1. Materials and methods

The starting materials for syntheses of the target dbpz derivatives, 4 and 7, were purchased from Tokyo Chemical Industry Co., Ltd., and used without purification. The intermediates to obtain 1a and 1c, i.e., 5 [4], 6 [4] and 12 [5] were prepared according to the literatures. All other chemicals and solvents were purchased from companies and used without purification. Silica gel used for column chromatography was purchased from Kanto Chemical Co., Inc.. $^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra were taken on a JEOL ECS-400 or a ECX-400 spectrometer, using tetramethylsilane (TMS) as an internal standard (0.00 ppm). Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were measured on a Shimadzu-Kratos AXIMA-CFR PLUS TOF mass spectrometer. The purity of the obtained compounds was checked by elemental analysis carried out on a J-Science MICRO CORDER JM10 analyzer.

To investigate the optical and photoluminescence properties of these compounds in thin films, poly(methyl methacrylate) (PMMA) were employed as a host matrix. PL spectra
were recorded on a Horiba Jobin Yvon SPEX Fluorolog-3 spectrofluorometer. PL quantum yields were measured on a Hamamatsu Photonics C9920-12 absolute PL quantum yield measurement system. PL lifetimes were obtained on a Horiba Jobin Yvon FluoroCube spectroanalyzer.

2.2.2. Preparation of synthetic precursors

2.2.2.1. 5,6-Bis(9,9-dihexylfluoren-2-yl)-2,1,3-benzo[c][1,2,5]thiadiazole (8)

A mixture of 4,7-dibromo-2,1,3-benzo[\(c\)][1,2,5]thiadiazole (0.441 g, 1.50 mmol), 9,9-dihexylfluoren-2-ylboronic acid pinacol ester (1.47 g, 3.19 mmol), Pd(PPh\(_3\))\(_4\) (32.0 mg, 0.0277 mmol), and potassium carbonate (2.07 g, 15.0 mmol) in a solvent mixture of toluene (20 mL), 1,2-dimethoxyethane (15 mL), and water (10 mL) was stirred at 85 ºC for 1 day under nitrogen atmosphere. After cooling, chloroform (50 mL) was added, and the mixture was vigorously shaken in a separation funnel. The organic layer was separated, washed with water (30 mL × 2) and sat. brine (30 mL), and then dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography using chloroform/hexane (1:3, v/v) as eluent to afford 8 as a greenish yellow powder (0.740 g, 0.924 mmol, 62%); \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 0.47–0.75 (m, 20H), 0.96–1.07 (m, 24H), 1.75–1.90 (m, 8H), 7.18–7.34 (m, 10H), 7.53 (d, 2H, \(J = 8.2\) Hz), 7.60–7.62 (m, 2H), 8.08 (s, 2H); \(^13\)C NMR (100 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 14.10, 22.67, 23.89, 29.76, 31.64, 40.40, 55.11, 119.32, 119.95, 122.21, 122.86, 124.40, 126.82, 127.27, 128.74, 139.18, 140.53, 140.59, 144.39, 150.79, 150.93, 154.50; MALDI-TOF MS \(m/z\) 801 ([M +
Chapter 2

H]). Anal. Calcd for C$_{56}$H$_{68}$N$_2$S: C, 83.95; H, 8.55; N, 3.50. Found: C, 83.73; H, 8.53; N, 3.30.

2.2.2.2. 4,5-Bis(9,9-dihexylfluoren-2-yl)-1,2-diamine (9)

To a solution of 8 (1.36 g, 1.70 mmol) in dry THF (20 mL) was added portionwise LiAlH$_4$ (0.570 g, 15.0 mmol) under 0 °C, and the mixture was kept at the same temperature and stirred for 1 h under nitrogen atmosphere. Then, diethyl ether (40 mL) and water (16 mL) were added with good stirring in sequence to quench residual LiAlH$_4$. The mixture was moved to a separation funnel. The organic phase was separated and washed in a separation funnel with water (50 mL) and sat. brine (50 mL). The obtained organic layer was dried over anhydrous magnesium sulfate, and evaporation of the solution to dryness afforded 9 as a yellow oily liquid (0.690 g, 0.893 mmol, 53%). This product was unstable, and so used to the next step without further purification; $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 0.44–0.75 (m, 20H), 0.91–1.08 (m, 24H), 1.70–1.85 (m, 8H), 3.53 (m, 4H), 6.82 (s, 2H), 7.05–7.07 (m, 2H), 7.14 (d, 2H, $J$ = 0.9 Hz), 7.19–7.26 (m, 6H), 7.43 (d, 2H, $J$ = 7.8 Hz), 7.55-7.57 (m, 2H); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) $\delta$ 14.13, 22.71, 23.84, 29.79, 31.67, 40.48, 54.91, 119.03, 119.26, 119.61, 122.71, 124.52, 126.62, 126.64, 128.71, 133.22, 134.25, 139.00, 140.71, 141.08, 150.37, 150.81; MALDI-TOF MS $m/z$ 772 (M$^+$).

2.2.2.3. 5,6-Bi(dodec-1-yn-1-yl)benzo[c][1,2,5]thiadiazole (10)

A mixture of 5,6-dibromo-2,1,3-benzothiadiazole (5.54 g, 18.8 mmol), 1-dodecyn (9.8 mL, 45.8 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (0.313 g, 0.446 mmol), CuI (205 mg, 1.08 mmol) in triethylamine (68 mL) was heated at 90 °C and stirred for 18 h under nitrogen. After cooling,
the solvent was removed on a rotary evaporator. The residue was dissolved in chloroform (120 mL). Then, the solution was washed in a separation funnel with water (30 mL × 2) and sat. brine (30 mL). The obtained organic solution was dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography using chloroform/hexane (2:1, v/v) as eluent to afford 10 as a light yellow solid (7.16 g, 15.4 mmol, 82%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.86-0.89 (t, 6H, $J$ = 6.8 Hz), 1.27-1.32 (m, 24H), 1.48-1.70 (m, 8H), 2.49-2.52 (t, 4H, $J$ = 7.0 Hz), 8.01 (s, 2H); MALDI-TOF MS m/z 465 ([M + H$^+$]). Anal. Calcd. for C$_{30}$H$_{44}$N$_2$S: C, 77.53; H, 9.54; N, 6.03. Found: C, 77.73; H, 9.56; N, 5.72.

2.2.2.4. 4,5-Di(dodec-1-yn-1-yl)benzene-1,2-diamine (11)

To a solution of 10 (0.640 g, 1.38 mmol) in dry THF (15 mL) was added stepwise LiAlH$_4$ (0.420 g, 11.1 mmol) under 0°C, and the mixture was kept at the same temperature and stirred for 4 h under nitrogen atmosphere. Then, diethyl ether (100 mL) and water (100 mL) were added with stirring in sequence to quench residual LiAlH$_4$. The organic phase was extracted and washed in a separation funnel with water (200 mL) and sat. brine (200 mL). The obtained organic solution was dried over anhydrous magnesium sulfate, and evaporation of the solution to dryness afforded 11 as a red solid (0.540 g, 1.24 mmol, 90%). This product was unstable, and so used to the next step without further purification; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.86-0.90 (t, 6H, $J$ = 7.0 Hz), 1.27-1.30 (m, 24H), 1.43-1.64 (m, 8H), 2.40-2.43 (t, 4H, $J$ = 7.0 Hz), 3.38 (s, 4H), 6.70 (s, 2H); MALDI-TOF MS m/z 436 (M$^+$). Anal. Calcd. for C$_{30}$H$_{48}$N$_2$: C, 82.51; H, 11.08; N, 6.41. Found: C, 82.66; H, 10.69; N, 6.24.
2.2.2.5. 2,7-Bis(9,9-dihexylfluoren-2-yl)-11,12-di(dodec-1-yn-1-yl)dibenzo[a,c]phenazine (13)

13 was prepared from 11 as a greenish yellow powder according to the same procedure as the preparation of 1a; yield 67%; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.75–0.88 (m, 30H), 1.10–1.34 (m, 48H), 1.67–1.75 (m, 4H), 2.01–2.16 (m, 8H), 2.56 (t, 4H, $J$ = 7.1 Hz), 7.31–7.40 (m, 6H), 7.77–7.89 (m, 8H), 8.12 (dd, 2H, $J$ = 1.8 and 8.2 Hz), 8.40 (s, 2H), 8.67 (d, 2H, $J$ = 8.6 Hz), 9.66 (d, 2H, $J$ = 2.3 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.11, 14.22, 22.71, 22.80, 22.94, 29.49, 29.74, 29.77, 29.79, 29.83, 29.98, 30.81, 31.59, 32.04, 33.22, 40.59, 55.39, 79.38, 96.98, 119.96, 120.21, 121.80, 123.02, 123.58, 124.26, 126.54, 126.92, 127.21, 127.77, 129.06, 130.62, 130.94, 139.71, 140.88, 140.91, 141.09, 142.29, 142.10, 145.01, 151.23, 151.64; MALDI-TOF MS $m/z$ 1273 (M$^+$). Anal. Calcd for C$_{94}$H$_{124}$N$_2$: C, 88.62; H, 9.18; N, 2.20. Found: C, 88.47; H, 9.33; N, 2.11.

2.2.3. General procedure for synthesis of 1a-c

2.2.3.1. 10,13-Bis(9,9-dihexylfluoren-2-yl)dibenzo[a,c]phenazine (1a)

A mixture of phenanthrene-9,10-dione (0.520 g, 2.50 mmol) and the corresponding diamine derivative 6 (2.14g, 2.76 mmol) in acetic acid (1 mL) and ethanol (25 mL) was stirred at 80 °C for 8 hours under nitrogen atmosphere. After cooling, the solvent was removed on a rotary evaporator. The residue was extracted with chloroform and water in a separation funnel, and then the organic layer was dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator, and the residue was purified by silica gel...
chromatography (eluent; chloroform/hexane, 1/3, v/v). Further purification was carried out by recrystallization from chloroform-hexane to afford \( \text{1a} \) as a yellow solid (1.64g, 1.74 mmol, 63%); m.p. 171–172 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 0.72–1.14 (m, 44H), 2.09 (t, 8H, \( J = 8.2 \) Hz), 7.36–7.44 (m, 6H), 7.66 (t, 3H, \( J = 7.6 \)Hz), 7.75 (t, 3H, \( J = 4.1 \) Hz), 7.85 (d, 2H, \( J = 7.3 \) Hz), 7.96–8.00 (m, 6H), 8.57 (d, 2H, \( J = 8.3 \) Hz), 9.20 (dd, 2H, \( J = 1.1 \) and 8.0 Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 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, 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 + H\(^+\)]. 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.

2.2.3.2. 11,12-Bis(9,9-dihexylfluoren-2-yl)dibenzo[a,c]phenazine (1b)

\( \text{1b} \) was prepared from 9 as a greenish yellow powder, according to the same procedure as the preparation of \( \text{1a} \); yield 55%; m.p. 166–167 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 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, 2H, \( J = 7.8 \) Hz), 9.41 (dd, 2H, \( J = 1.7 \) and 7.9 Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 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 + H\(^+\)]. 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.

2.2.3.3. 2,7-Bis(9,9-dihexylfluoren-2-yl)-11,12-didodecyldibenzo[a,c]phenazine (1c)
A mixture of 13 (0.580 g, 0.455 mmol), 10% Pd-C (0.185 g), and ethyl acetate (6.2 ml) was put into an autoclave filled with 0.3 MPa H₂, and the mixture was stirred for 8 h at ambient temperature. Then, the reaction mixture was filtered off to remove Pd-C. To the mixture was added chloroform (50 mL), and the obtained mixture was washed with water (150 mL × 2) and sat. brine (150 mL). The obtained organic solution was dried over MgSO₄. The solvent was removed on a rotary evaporator, and the residual solid was purified by silica gel column chromatography using chloroform as eluent to afford 1c as yellow solid (0.41 g, 0.32 mmol, 70%); m.p. 63–65 °C; ¹H NMR (400 MHz, CDCl₃) 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, 4H, J = 7.8 Hz), 7.33–7.40 (m, 6H), 7.77–7.90 (m, 8H), 8.10–8.13 (dd, 2H, J = 2.0 and 8.5 Hz), 8.16 (s, 2H), 8.69 (d, 2H, J = 8.7 Hz), 9.71 (d, 2H, J = 1.8 Hz); ¹³C NMR (100 MHz, CDCl₃) 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⁺). Anal. Calcd for C₉₄H₁₂₄N₂: C, 88.07; H, 9.75; N, 2.19. Found: C, 88.15; H, 9.93; N, 2.10.

2.2.4. Fabrication of OLED

Poly(9-vinyl-9H-carbazole) (PVCz) was purchased from Sigma-Aldrich Co. (Mw = 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
Chapter 2

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−O₃ and dried at 115 ºC 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 top of the PEDOT:PSS layer to fabricate an emitting layer (EML). Thereafter, CsF and Al layers were successively vacuum deposited on EML. Finally, the obtained OLED was covered with a glass cap and encapsulated with a UV-curing epoxy resin. The device performance was operated using a Hamamatsu Photonics C-9920-11 organic EL device evaluating system.

2.3. Results and discussion

2.3.1. Synthesis

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 LiAlH₄ 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 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.

**Scheme 1.** Synthesis of 1a–c. The substituents Flu and R are 9, 9-dihexyl-9H-fluoren-2-yl and dodec-1-yn-1-yl groups, respectively.
2.3.2. UV-vis absorption and photoluminescence properties

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 \( \lambda_{PL} \); 538 nm) with the quantum yield (\( \Phi_{PL} \)) of 0.62, whereas 1b and 1c were less emissive, exhibiting bluish green (\( \lambda_{PL} \); 465 nm) and green (\( \lambda_{PL} \); 509 nm) PL with \( \Phi_{PL} \) of 0.14 and 0.20, respectively. Thus, 1a is a more excellent emitter in terms of \( \Phi_{PL} \). The PL lifetimes (\( \tau_{PL} \)) 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:

\[
k_r = \frac{\Phi_{PL}}{\tau_{PL}} \quad (1)
\]

\[
k_{nr} = \frac{k_r(1 - \Phi_{PL})}{\Phi_{PL}} \quad (2)
\]

*Figure 2. UV-vis absorption and PL spectra of 1a–c in PMMA films at rt.*
The $k$s for 1a–c were $5.3 \times 10^7$, $8.4 \times 10^7$, and $9.0 \times 10^7$ s$^{-1}$, respectively, and the $k_n$s for 1a–c were $3.3 \times 10^7$, $5.1 \times 10^8$, and $3.6 \times 10^8$ s$^{-1}$, respectively. From this result, the PL efficiency in the present $dbpz$ system is dominated by the non-radiative decay process.

2.3.2. Solvatochromism in photoluminescence

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 ($\lambda_{\text{max}}$) 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 in dichloromethane. This tendency in dichloromethane is similar to that in PMMA films (vide supra). Interestingly, positive solvatochromism in PL was observed for

### Table 1. UV-vis absorption and PL spectral data of 1a–c in different solvents at rt (concentration; 1 $\mu$M)

<table>
<thead>
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<th>Solvent</th>
<th>1a</th>
<th>1b</th>
<th>1c</th>
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<tr>
<td></td>
<td>$\lambda_{\text{abs}}^a$</td>
<td>$\lambda_{\text{PL}}^b$</td>
<td>$\Phi_{\text{PL}}^c$</td>
</tr>
<tr>
<td>Hexane</td>
<td>396</td>
<td>515</td>
<td>0.42</td>
</tr>
<tr>
<td>Toluene</td>
<td>399</td>
<td>527</td>
<td>0.64</td>
</tr>
<tr>
<td>Dioxane</td>
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<td>537</td>
<td>0.72</td>
</tr>
<tr>
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<td>553</td>
<td>0.87</td>
</tr>
<tr>
<td>DMF</td>
<td>400</td>
<td>574</td>
<td>0.89</td>
</tr>
</tbody>
</table>

$^a$Absorption maxima in UV-vis absorption spectra. $^b$PL maxima. The excitation wavelengths were adjusted to the $\lambda_{\text{abs}}s$. $^c$PL quantum yields upon excitation at the $\lambda_{\text{abs}}s$. 

- 30 -
the present *dbpz* derivatives. For example, the $\lambda_{PL}$ 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, 6]. Indeed, the TD-DFT calculations supported that the HOMO-LUMO transition contributing to fluorescent emission is based on the ICT transition, as shown in Figure 3 [7]. 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.

![Electron distributions of the HOMO and LUMO for 1a–c obtained by DFT calculations at the B3LYP/6-31G(d) level of theory. The hexyl groups are replaced by methyls. In 1c, the dodecyl groups are omitted.](image)

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

Using 1a as fluorescent dopants, we fabricated a PVCz-based OLED [8]. 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 Fig. 4b. The maximum luminance \( L_{\text{max}} \) 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, the device demonstrated the maximum performance; the maximum external quantum efficiency \( \eta_{\text{ext max}} \) of 0.30\%, the maximum current efficiency \( \eta_{j \text{ max}} \) of 0.94 cd A\(^{-1}\), and the maximum power efficiency \( \eta_{p \text{ max}} \) of 0.26 lm W\(^{-1}\).

![Figure 4. J-V-L curves (a) and normalized EL spectrum (b) of the OLED using 1a.](image-url)
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2.4. 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.

2.5. References


[7] Time-dependent density functional theory (TD-DFT) calculations were carried out using the Gaussian 09 program package: Gaussian 09, Revision A.1, Frinch, M. J.;
Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.;
Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato,
Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.;
Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.;
Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene,
M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.;
Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.;
Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J.
V.; Cioslowski, J.; Fox, D. J.: Gaussian, Inc., Wallingford CT (2009).

817.
Chapter 3


3.1. Introduction

Various types of organic fluorophores have been eagerly developed because they are useful for a wide range of applications from organic electronics to bio-analysis [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-α:2',3'-c]phenazine (dppz) and dibenzo[α,c]phenazine (dbpz) platforms (Figure 1), where introduction of π-based electron-donating components at their 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 \( \pi \)-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.

![Chemical structure](image)

**Figure 1.** Examples of fluorescent dipyrido[3,2-\( \alpha \):2',3'-\( \alpha \)]phenazine (a, ref. 10) and dibenzo[\( a,c \)]phenazine (b, ref. 11) derivatives.
3.2. Results and discussion

3.2.1. Synthesis

In the present study, we prepared five dbpz derivatives bearing a series of \( \pi \)-conjugated side-arms at their 10,13-positions, namely, 1–5. The compounds 1 and 2 possess 9-(2-ethylhexyl)-9\( H \)-carbazol-2-yl and 9-(2-ethylhexyl)-9\( H \)-carbazol-3-yl side-arms, respectively, and 3 does 4-hexylthiophen-2-yl side-arms. Compounds 4 and 5 possess further \( \pi \)-extended side-arms; 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 groups, respectively.

In Scheme 1 are shown the synthesis of the dbpz derivatives 1–5. The dbpz derivatives were prepared by the condensation of phenanthrene-9,10-dione with the diamine precursors 6–10. The precursor 6 was prepared according to the reported procedures [10], and 7 was newly prepared by the Suzuki-Miyaura coupling reaction of 11 (commercially available) with the boronic acid pinacol ester of the corresponding side-arm components followed by reduction with lithium aluminium hydride (LiAlH\(_4\)). The precursor 8 was prepared by the reduction of 13 [14]. According to a similar procedure, 9 was also obtained from 14 [15]. Starting from 15 [15], 10 was prepared by the Suzuki-Miyaura coupling with 9-(2-ethylhexyl)-9\( H \)-carbazol-3-ylboronic acid pinacol ester followed by reduction with LiAlH\(_4\). Finally the obtained diamine precursors 6–10 were reacted with phenanthrene-9,10-dione to obtain the dbpz derivatives 1–5 in 55–64% yields. The structures of 1–5 were identified by \(^1\)H and \(^{13}\)C NMR and MALDI-TOF mass spectra as well as elemental analysis.

3.2.2. DFT and TD-DFT calculations

To expect the effects of the $\pi$-conjugated side-arms on the electronic transition of the singlet excited state, the time-dependent density functional theory (TD-DFT) calculations were performed for 1–5, where the structures were geometrically optimized at the
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B3LYP/6-31G* level of theory [16]. As a representative result of the calculations, the optimized structure of 4 and its HOMO-LUMO electronic distributions are shown in Figure 2. As the summary of the calculations, the calculated HOMO and LUMO energies ($E_{\text{HOMO,calcd}}$ and $E_{\text{LUMO,calcd}}$, respectively), HOMO-LUMO energy gaps ($E_{g,\text{calcd}}$), and lowest singlet transition energies ($E_{s,\text{calcd}}$) are listed in Table 1. For the present dbpz derivatives, the lowest $S_0 \rightarrow S_1$ transition predominantly consists of the transition from HOMO to LUMO. HOMO is delocalized on the $\pi$-conjugation system including both of the side-arms, whereas LUMO is localized on the dbpz moiety. Thus, the calculation results clearly indicate that the attachment of electron-donating side-arms to the dbpz component yields D-A-D-type ICT chromophores. Also, one can expect from the values of $E_{g,\text{calcd}}$ and $E_{s,\text{calcd}}$ that the compounds 4 and 5, bearing the widely $\pi$-conjugated side-arms, should exhibit more red-shifted fluorescence (vide infra).

![Figure 2](image1.png)

**Figure 2.** Optimal geometry structures and electronic configurations of (a) LUMO and (b) HOMO for 4.
Table 1. Calculated energy levels of HOMO ($E_{\text{HOMO,calcd}}$) and LUMO ($E_{\text{LUMO,calcd}}$), energy gap ($E_{\text{g,calcd}}$), and singlet excitation energy ($E_{\text{s,calcd}}$) of 1–5

<table>
<thead>
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<th>Compd</th>
<th>$E_{\text{HOMO,calcd}}$ (eV)</th>
<th>$E_{\text{LUMO,calcd}}$ (eV)</th>
<th>$E_{\text{g,calcd}}$ (eV)</th>
<th>$E_{\text{s,calcd}}$ (eV)</th>
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</table>

$aE_{\text{g,calcd}} = E_{\text{LUMO,calcd}} - E_{\text{HOMO,calcd}}$. 

$b$Obtained by TD-DFT calculations.

### 3.2.3. Electrochemical properties

The electrochemical properties of 1–5 were investigated by cyclic voltammetry (CV) in dichloromethane. As representative examples, cyclic voltammograms of 2 and 4 are shown in Figure 3. Oxidation and reduction potentials of 1–5 ($E_{1/2}^{\text{ox}}$ and $E_{1/2}^{\text{red}}$, respectively) versus the ferrocennium/ferrocene (Fc+/Fc) redox couple were determined in dry dichloromethane, as summarized in Table 2. All the compounds showed reversible redox cycles accompanied by two oxidation bands and a reduction band, implying that the oxidation and reduction potentials are attributed to the oxidation of the electron-donating side-arms and the reduction of the electron-accepting dbpz moiety. From these results, we are allowed to determine the experimental energetic values of HOMO ($E_{\text{HOMO}}$) and LUMO ($E_{\text{LUMO}}$), as summarized in Table 2. From the $E_{\text{HOMO}}$ values of 4 (−5.12 eV) and 5 (−5.09 eV), the HOMO levels of these two dbpz derivatives were destabilized in comparison with those of 1–3, due to the extension of the $\pi$-conjugated side-arms. Also, their LUMO levels...
(−3.14 eV for 4 and −3.17 eV for 5) were effectively stabilized. As a result, smaller $E_g$ values were obtained for 4 and 5 than those for the others. This result is almost consistent to the tendency of DFT calculations discussed above. Therefore, more red-shifted absorption and emission spectra are expected for 4 and 5.

**Figure 3.** Cyclic voltammograms of 2 and 4; (a) oxidation and (b) reduction cycles.
Table 2. Oxidation and reduction potentials ($E_{1/2}^{\text{ox}}$ and $E_{1/2}^{\text{red}}$, vs. ferrocene/ferrocenium redox) and HOMO and LUMO energy levels ($E_{\text{HOMO}}$ and $E_{\text{LUMO}}$) of 1–5

<table>
<thead>
<tr>
<th>Compd</th>
<th>$E_{1/2}^{\text{ox}}$ (eV)</th>
<th>$E_{1/2}^{\text{red}}$ (eV)</th>
<th>$E_{\text{HOMO}}^a$ (eV)</th>
<th>$E_{\text{LUMO}}^b$ (eV)</th>
<th>$E_g^c$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.46</td>
<td>-2.00</td>
<td>-5.26</td>
<td>-2.80</td>
<td>2.46</td>
</tr>
<tr>
<td>2</td>
<td>0.37</td>
<td>-1.95</td>
<td>-5.17</td>
<td>-2.85</td>
<td>2.32</td>
</tr>
<tr>
<td>3</td>
<td>0.36</td>
<td>-1.76</td>
<td>-5.16</td>
<td>-3.04</td>
<td>2.12</td>
</tr>
<tr>
<td>4</td>
<td>0.32</td>
<td>-1.66</td>
<td>-5.12</td>
<td>-3.14</td>
<td>1.98</td>
</tr>
<tr>
<td>5</td>
<td>0.29</td>
<td>-1.63</td>
<td>-5.09</td>
<td>-3.17</td>
<td>1.92</td>
</tr>
</tbody>
</table>

$aE_{\text{HOMO}} = -(E_{1/2}^{\text{ox}} + 4.80)$.  
$bE_{\text{LUMO}} = -(E_{1/2}^{\text{red}} + 4.80)$.  
$c$HOMO-LUMO energy gap obtained by the equation of $E_{\text{LUMO}} - E_{\text{HOMO}}$.

3.2.4. UV-vis absorption and photoluminescence properties

UV-vis absorption spectra of 1–5 in dichloromethane at ambient temperature are shown in Figure 4, and the spectral data are also summarized in Table 3. Intense transition bands (molar absorption coefficient $\varepsilon_{\text{abs}}$; 89100–112000 M$^{-1}$ cm$^{-1}$) are observed for all the dbpz derivatives in the near-UV regions (255–317 nm), assignable to the higher-energy $\pi$-$\pi^*$ transitions localized at the side-arm and/or dbpz moieties. A further red-shifted, broadened transition band with relatively low molar absorptivity ($\varepsilon_{\text{abs}} < ca. 10000$ M$^{-1}$ cm$^{-1}$) were observed for each dbpz derivative, assignable to the lowest-energy ICT transition from HOMO to LUMO, as discussed in the DFT calculation study (Figure 2). The magnitude of $E_g^{\text{exp}}$ (or $E_g^{\text{calcd}}$) is comparable to the energy of the ICT transition (i.e., absorption wavelength $\lambda_{\text{abs}}$). Thus, the dbpz derivatives bearing the $\pi$-extended side-arms 4 and 5 exhibited more red-shifted ICT transition bands in comparison with 1–3.
Figure 4. UV-vis absorption spectra of 1–5 in dichloromethane at rt. The expanded spectra are also shown in the ICT transition regions.

Table 3. UV-vis absorption maxima (λ_{abs}), emission maxima (λ_{PL}), PL quantum yields (Φ_{PL}) and PL lifetimes (τ_{PL}) of 1–5 in dichloromethane at rt

<table>
<thead>
<tr>
<th>Compd</th>
<th>λ_{abs} (nm) [log{(ε_{abs}/(M^{-1}cm^{-1}))}]</th>
<th>λ_{PL} <a href="nm">λ_{ex}^{a}</a></th>
<th>Φ_{PL}</th>
<th>τ_{PL}^{b} (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>255 [5.02], 314 [4.89], 398 [4.30]</td>
<td>557 [398]</td>
<td>0.56</td>
<td>8.07</td>
</tr>
<tr>
<td>2</td>
<td>300 [4.95], 400 [4.16], 460 [3.99]</td>
<td>607 [459]</td>
<td>0.67</td>
<td>13.7</td>
</tr>
<tr>
<td>3</td>
<td>276 [5.05], 412 [4.21], 483[4.01]</td>
<td>635 [482]</td>
<td>0.69</td>
<td>12.9</td>
</tr>
<tr>
<td>4</td>
<td>272 [5.00], 380 [4.20], 540 [3.71]</td>
<td>701 [539]</td>
<td>0.29</td>
<td>4.29</td>
</tr>
<tr>
<td>5</td>
<td>317 [4.98], 403 [4.54], 556 [3.95]</td>
<td>713 [556]</td>
<td>0.21</td>
<td>4.30</td>
</tr>
</tbody>
</table>

^a Excitation wavelength. ^b The values of χ^2 are less than 1.10.

PL spectra of 1–5 in dichloromethane at ambient temperature are also shown in Figure 5, and the PL wavelengths (λ_{PL}), PL quantum yields (Φ_{PL}) and PL lifetimes (τ_{PL}) are also listed in Table 3. The compound 1 showed the PL spectrum with λ_{PL} of 557 nm, emitting greenish yellow. On the other hand, 2 exhibited orange PL at 607 nm, red-shifted in
comparison with 1. In the case of 3, relatively efficient red PL ($\Phi_{PL}; 0.69$) was observed at 635 nm. Further extension of the $\pi$-conjugation in the side arms was effective to obtain red-shifted fluorescence in the deep red region, as is expected from the UV-vis absorption spectra. The employment of the fluoren-2-yliothiophene or carbazol-3-ylthiophene side-arms gave rise to deep red emission at 701 nm and 713 nm, as seen in 4 and 5, respectively, although the values of $\Phi_{PL}$ somewhat decreased to less than 0.29 due to elongation of the ICT-type $\pi$-conjugation.

![Figure 5. PL spectra of 1–5 in dichloromethane at rt.](image)

**Figure 5.** PL spectra of 1–5 in dichloromethane at rt.

### 3.2.5. PL solvatochromism

Generally, the emission properties of fluorophores with strong ICT characters are often affected by solvent polarity [10, 17–19]. To confirm the ICT characters of the present dbpz fluorophores, the solvent effects on the emission behavior were investigated. The PL
profiles of 1–5 in various solvents are shown in Table 4. Interestingly, positive solvatochromism in PL was observed for all the dbpz derivatives as the polarity of the solvent increased. For example, the PL spectra of 2 in solvents with different polarity are shown in Figure 6a, where the emission color is changed from yellowish green in hexane to reddish orange in DMF. Similarly, 4 also showed solvent polarity-dependent PL spectra, as

**Figure 6.** PL spectra of (a) 2 and (b) 4 in hexane, toluene, dichloromethane, acetone, and DMF at rt.
shown in Figure 6b, where the emission color changed from red in hexane to deep red in DMF. The $\lambda_{PL}$s of the other $dbpz$ derivatives also exhibited red-shifts as the polarity of the solvents increased. This solvatochromic behavior indicates that the observed PL is based on the ICT transition. Also, the observed positive solvatochromism of PL indicates that the present ICT-type fluorophores are highly polarized in their excited states. Indeed, the difference in the dipole moment between the excited and ground states ($\Delta\mu$) was estimated for all of 1–5 by employing the Lippert-Mataga plot [10, 18, 20, 21], and relatively large $\Delta\mu$ values of 8.04–12.2 D were obtained.

<table>
<thead>
<tr>
<th>Compd</th>
<th>$\lambda_{PL}$ (nm)</th>
<th>hexane</th>
<th>toluene</th>
<th>acetone</th>
<th>DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\lambda_{PL}$ (nm)</td>
<td>522</td>
<td>541</td>
<td>560</td>
<td>572</td>
</tr>
<tr>
<td></td>
<td>$\phi_{PL}$</td>
<td>0.49</td>
<td>0.63</td>
<td>0.31</td>
<td>0.18</td>
</tr>
<tr>
<td>2</td>
<td>$\lambda_{PL}$ (nm)</td>
<td>549</td>
<td>569</td>
<td>609</td>
<td>626</td>
</tr>
<tr>
<td></td>
<td>$\phi_{PL}$</td>
<td>0.88</td>
<td>0.83</td>
<td>0.57</td>
<td>0.56</td>
</tr>
<tr>
<td>3</td>
<td>$\lambda_{PL}$ (nm)</td>
<td>587</td>
<td>613</td>
<td>647</td>
<td>658</td>
</tr>
<tr>
<td></td>
<td>$\phi_{PL}$</td>
<td>0.21</td>
<td>0.66</td>
<td>0.56</td>
<td>0.52</td>
</tr>
<tr>
<td>4</td>
<td>$\lambda_{PL}$ (nm)</td>
<td>659</td>
<td>674</td>
<td>709</td>
<td>724</td>
</tr>
<tr>
<td></td>
<td>$\phi_{PL}$</td>
<td>0.63</td>
<td>0.58</td>
<td>0.24</td>
<td>0.18</td>
</tr>
<tr>
<td>5</td>
<td>$\lambda_{PL}$ (nm)</td>
<td>672</td>
<td>687</td>
<td>721</td>
<td>736</td>
</tr>
<tr>
<td></td>
<td>$\phi_{PL}$</td>
<td>0.58</td>
<td>0.50</td>
<td>0.19</td>
<td>0.18</td>
</tr>
</tbody>
</table>

### 3.2.6. PL properties in PMMA film

To investigate the PL properties of 1–5 in a solid matrix, the poly(methyl methacrylate) (PMMA) thin films doped with the $dbpz$ derivatives were prepared (concentration: 1.0
mol%, based on the methyl methacrylate monomer unit). The spectra data are also listed in Table 5. For the PMMA doped films, similar spectral behavior to that in dichloromethane (see Figure 5) was observed, although the \( \lambda_{PL} \) of each dbpz derivative was slightly blue-shifted. Relatively intense yellowish green emission was observed for 1 (\( \lambda_{PL}; 548 \text{ nm} \)) with \( \Phi_{PL} \) of 0.35, whereas 2 and 3 exhibited red-shifted PL at 581 (orange) and 617 (red) nm along with \( \Phi_{PL} \)s of 0.48 and 0.40, respectively. As shown in 4 and 5, further extension of the \( \pi \)-conjugation in the side-arms afforded deep red emission together with a decrease in the quantum yield down to 0.10 and 0.07, respectively.

Table 5. Emission maxima (\( \lambda_{PL} \)) and PL quantum yields (\( \Phi_{PL} \)) of 1–5 in PMMA thin film at rt

<table>
<thead>
<tr>
<th>Compd</th>
<th>( \lambda_{PL} ) (nm)</th>
<th>( \Phi_{PL} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>548</td>
<td>0.35</td>
</tr>
<tr>
<td>2</td>
<td>581</td>
<td>0.48</td>
</tr>
<tr>
<td>3</td>
<td>617</td>
<td>0.40</td>
</tr>
<tr>
<td>4</td>
<td>690</td>
<td>0.10</td>
</tr>
<tr>
<td>5</td>
<td>704</td>
<td>0.07</td>
</tr>
</tbody>
</table>

3.2.7. Electroluminescent properties

Using the developed dbpz derivatives as fluorescent dopants, OLEDs were fabricated, where poly(3,4-ethylenedioxythiophene):poly(stylenesulfonate) (PEDOT:PSS), poly(9-vinylcarbazole) (PVCz), 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD), and cesium fluoride were employed as a hole-injection layer, a hole-transporting
host, an electron-transporting material, and an electron-injection layer, respectively [22, 23]. The device structure is as follows: ITO (transparent anode, 150 nm)/PEDOT:PSS (40 nm)/emission layer (EML, 80 nm)/CsF (1.0 nm)/Al (cathode, 250 nm), where EML consists of PVCz, PBD, and the \textit{dbpz} derivative in a ratio of 100:18:1.7 (mol\%, based on the monomer unit for PVCz).

In Figure 7 are shown the electroluminescence (EL) spectra of the devices fabricated with the \textit{dbpz} derivatives. The device performance is also summarized in Table 6. Yellowish green EL was obtained from 1, affording the maximum luminance ($L_{\text{max}}$) of 195 \text{cd m}^{-2} at 19.0 V and the Commission Internationale de L’éclairage (CIE) chromaticity coordinate of (0.35, 0.58), although the device efficiencies were not so good; the maximum external quantum efficiency ($\eta_{\text{ext \, max}}$) of 0.09\%, the maximum current efficiency ($\eta_{\text{j \, max}}$) of 0.18 \text{cd A}^{-1}, and the maximum power efficiency ($\eta_{\text{p \, max}}$) of 0.05 \text{lm W}^{-1}. The emission maximum ($\lambda_{\text{EL}}$) is observed at 558 nm, red-shifted by 9 nm in comparison with the PL spectrum of 1 in PMMA. For the other emitting dopants, the EL spectra were somewhat blue-shifted in comparison with the PL spectra in solution and PMMA film. The devices using 2 and 3 as an emitting dopant show yellow and reddish orange EL accompanied by the CIE chromaticity coordinates of (0.48, 0.51) and (0.58, 0.41), respectively. The 4-based device showed red EL with the CIE chromaticity coordinate of (0.64, 0.30), and the EL from the 5-based devices was most red-shifted among the present devices, although the extension of the \pi-conjugation of the side-arms in the \textit{dbpz} derivative gave rise to considerable deterioration of the device performance.
Figure 7. EL spectra of OLEDs containing 1–5 as an emitting dopant.

Table 6. Device performance of OLEDs using 1–5 as an emitting dopant

<table>
<thead>
<tr>
<th>Dopant</th>
<th>$V_{on}$ (V)</th>
<th>$L_{max}$ (cd m$^{-2}$)</th>
<th>$\eta_{ext \ max}$ (%)</th>
<th>$\eta_{j \ max}$ (cd A$^{-1}$)</th>
<th>$\eta_{p \ max}$ (lm W$^{-1}$)</th>
<th>CIE (x, y)</th>
<th>$\lambda_{EL}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.0</td>
<td>195 [19.0]</td>
<td>0.09</td>
<td>0.18</td>
<td>0.05</td>
<td>(0.35, 0.58)</td>
<td>558</td>
</tr>
<tr>
<td>2</td>
<td>7.0</td>
<td>264 [19.0]</td>
<td>0.11</td>
<td>0.32</td>
<td>0.12</td>
<td>(0.48, 0.51)</td>
<td>575</td>
</tr>
<tr>
<td>3</td>
<td>6.0</td>
<td>364 [15.0]</td>
<td>0.24</td>
<td>0.41</td>
<td>0.14</td>
<td>(0.58, 0.41)</td>
<td>607</td>
</tr>
<tr>
<td>4</td>
<td>12.0</td>
<td>16 [19.5]</td>
<td>0.04</td>
<td>0.02</td>
<td>0.006</td>
<td>(0.64, 0.30)</td>
<td>687</td>
</tr>
<tr>
<td>5</td>
<td>13.5</td>
<td>14 [18.5]</td>
<td>0.01</td>
<td>0.01</td>
<td>0.004</td>
<td>(0.69, 0.26)</td>
<td>701</td>
</tr>
</tbody>
</table>

$^a$Turn-on voltage at which the luminance over 1 cd m$^{-2}$ was observed. $^b$Obtained at $L_{max}$. 

- 49 -
3.3. Conclusions

In conclusion, we here reported the preparation of five novel dbpz derivatives (1–5) with π-based electron-donating side-arms at the 10,13-positions. The PL properties were tuned by controlling the ICT character of the chromophores, that is, varying the donor side-arm components. Thus a wide range of emission colors have been achieved from yellowish green (1) to deep red (5). Especially, introduction of the thiophen-2-yl side-arms to the dbpz core allowed us to obtain a relatively efficient red fluorescent compound (3), showing $\Phi_{PL}$ of 0.69 and 0.40 in dichloromethane and PMMA thin film, respectively. Further extension of the π-conjugation of the side-arms gave rise to red shifts of the PL spectra to the deep red regions, as demonstrated in 4 and 5, although the $\Phi_{PL}$s decreased. The OLED performances were also investigated for the devices using the present dbpz derivatives as an emitting dopant. Although the device efficiencies were not so excellent, the EL spectra corresponding to the emission from the dbpz dopants were observed, showing somewhat blue-shifted in comparison with PL spectra.

3.4. Experimental section

3.4.1. Materials and methods

All starting materials, catalysts, and solvents were purchased from Wako Pure Chemical Industries Ltd., Tokyo Chemical Industry Co., Ltd., or Sigma-Aldrich Co., and used without further purification. Silica gel (SiO$_2$, spherically-shaped, neutral) for flash column chromatography was purchased from Kanto Chemical Co., Inc.. The compounds 6 [10], 13
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[14], 14 [15], and 15 [15] were prepared according to the literatures.

NMR spectra were measured on a JEOL ECS-400 or a ECX-400 spectrometer (400 MHz for $^1$H NMR and 100 MHz for $^{13}$C NMR), using TMS (0.00 ppm for $^1$H and $^{13}$C NMR) and CHDCl$_2$ (5.32 ppm for $^1$H and 53.84 ppm for $^{13}$C) as internal standards for CDCl$_3$ and CD$_2$Cl$_2$, respectively. Mass spectra were taken on a Shimadzu-Kratos AXIMA-CFR PLUS TOF mass spectrometer by a matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) method. Elemental analyses were carried out on a J-Science MICRO CORDER JM10 analyzer. The melting points were recorded on a Yanaco MP-500D apparatus. UV-vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. PL spectra were recorded on a Horiba Jobin Yvon SPEX Fluorolog-3 spectrofluorometer. PL quantum yields were measured on a Hamamatsu Photonics C9920-12 absolute PL quantum yield measurement system. PL lifetimes were obtained on a Horiba Jobin Yvon FluoroCube spectroanalyzer. Cyclic voltammograms were measured for dry dichloromethane solutions on a Hokuto Denko HZ-5000 electrochemical measurement system at a scanning rate of 100 mV s$^{-1}$, where 0.1 M tetrabutylammonium perchlorate was used as a supporting electrolyte. The potentials were recorded relative to Ag/AgNO$_3$ (0.1 M) reference electrode with a platinum wire used for both working and counter electrodes. Oxidation and reduction potentials ($E_{1/2}^{\text{ox}}$ and $E_{1/2}^{\text{red}}$, respectively) were determined using the ferrocenium/ferrocene redox couple as an external standard (0.00 V).

3.4.2. Preparation of synthetic precursors
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3.4.2.1. 4,7-Bis(9-(2-ethylhexyl)-9\textsubscript{H}-carbazol-3-yl)benzothiadiazole (12)

A mixture of 11 (1.18 g, 4.01 mmol), 9-(2-ethylhexyl)carbazol-3-ylboronic acid pinacol ester (4.05 g, 10.0 mmol), Pd(PPh\textsubscript{3})\textsubscript{4} (57.8 mg, 0.0500 mmol) and potassium carbonate (3.31 g, 24.0 mmol) in a solvent mixture of ethanol (10 mL), 1,2-dimethoxyethane (25 mL) and water (5 mL) was stirred at 85 ºC for 10 h under nitrogen atmosphere. After cooling, chloroform (50 mL) was added, and the solution was washed with water (30 mL × 2) and sat. brine (30 mL). The obtained organic solution was dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography using chloroform/hexane (1:3, v/v) as eluent to afford 12 as a yellow powder (2.26 g, 3.27 mmol, 82%); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 0.89 (t, 6H, J = 7.1 Hz), 0.95 (t, 6H, J = 7.3 Hz), 1.26–1.45 (m, 16H), 2.13–2.19 (m, 2H), 4.18–4.29 (m, 4H), 7.27–7.29 (m, 2H), 7.43–7.51 (m, 4H), 7.57 (d, 2H, J = 8.2 Hz), 7.93 (s, 2H), 8.14 (dd, 2H, J = 1.8 and 8.2 Hz), 8.20 (d, 2H, J = 7.8 Hz), 8.72 (d, 2H, J = 1.8 Hz); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 11.07, 14.13, 23.15, 24.51, 28.93, 31.12, 39.51, 47.63, 109.31, 110.39, 111.79, 120.01, 120.52, 123.01, 123.28, 126.08, 128.46, 133.72, 134.68, 136.43, 141.35, 143.87, 154.68; MALDI-TOF MS m/z 691 ([M + H]^+); Anal. Calcd for C\textsubscript{46}H\textsubscript{50}N\textsubscript{4}S: C, 79.96; H, 7.29; N, 8.11. Found: C, 79.87; H, 7.34; N, 8.01.

3.4.2.2. 3,6-Bis(9-(2-ethylhexyl)-9\textsubscript{H}-carbazol-3-yl)benzene-1,2-diamine (7)

To a solution of 12 (1.70 g, 2.46 mmol) in dry THF (15 mL) was added portionwise LiAlH\textsubscript{4} (0.780 g, 20.6 mmol) under 0 ºC, and the mixture was stirred at rt for 4 h under nitrogen atmosphere. Then, diethyl ether (120 mL) and water (70 mL) were added in
sequence to quench residual LiAlH₄. The organic phase was separated and washed with water (50 mL) and sat. brine (50 mL). The obtained organic solution was dried over anhydrous magnesium sulfate, and evaporation of the solution to dryness afforded 7 as a yellow solid (1.43 g, 2.16 mmol, 87%). This product was unstable, and so used to the next step without further purification; \(^1\)H NMR (400 MHz, CDCl₃) δ 0.88 (t, 6H, J = 7.3 Hz), 0.95 (t, 6H, J = 7.5 Hz), 1.24–1.43 (m, 16H), 2.06–2.15 (m, 2H), 3.74 (m, 4H), 4.16-4.26 (m, 4H), 6.95 (s, 2H), 7.21–7.24 (m, 2H), 7.41–7.49 (m, 6H), 7.60 (dd, 2H, J = 1.6 and 8.4 Hz), 8.11 (d, 2H, J = 7.7 Hz), 8.23 (d, 2H, J = 1.3 Hz); MALDI-TOF MS m/z 662 ([M + H]⁺).

### 3.4.2.3. 3,6-Bis(4-hexylthiophen-2-yl)benzene-1,2-diamine (8)

The compound 8 was prepared from 13 as a yellow solid according to the same procedure as preparation of 7; This product was unstable, and so used to the next step without further purification; yield, 85%; \(^1\)H NMR (400 MHz, CDCl₃) δ 0.87-0.90 (m, 6H), 1.30-1.32 (m, 6H), 1.60–1.73 (m, 6H), 1.80–1.87 (m, 4H), 2.62 (t, 4H, J = 7.7 Hz), 3.73 (m, 4H), 6.85 (s, 2H), 6.93 (s, 2H), 7.00 (d, J = 0.90 Hz, 2H); \(^13\)C NMR (100 MHz, CDCl₃) δ 14.23, 22.74, 29.19, 30.55, 30.73, 31.82, 120.07, 121.33, 121.48, 127.50, 132.93, 140.93, 143.95; MALDI-TOF MS m/z 440 (M⁺).

### 3.4.2.4. 3,6-Bis(5-(9,9-dihexyl-9H-fluoren-2-yl)thiophen-2-yl)benzene-1,2-diamine (9)

The compound 9 was prepared from 14 as a dark yellow solid according to the same procedure as the preparation of 7; This product was unstable, and so used to the next step without further purification; yield, 91%; \(^1\)H NMR (400 MHz, CDCl₃) δ 0.63-0.76 (m, 20H), 1.04-1.12 (m, 24H), 1.98–2.02 (m, 8H), 3.99 (m, 4H), 6.98 (s, 2H), 7.21 (d, 2H, J = 3.6 Hz),
7.31-7.36 (m, 6H), 7.41 (d, 2H, \( J = 3.6 \) Hz), 7.59 (d, 2H, \( J = 1.4 \) Hz), 7.63 (dd, 2H, \( J = 1.4 \) and 7.8 Hz), 7.66-7.72 (m, 4H); MALDI-TOF MS \( m/z \) 937 ([M + H]^+).

3.4.2.5. 4,7-Bis(5-(9-(2-ethylhexyl)-9\( H \)-carbazol-3-yl)thiophen-2-yl)benzothiadiazole (16)

A mixture of 15 (0.916 g, 2.00 mmol), 9-(2-ethylhexyl)carbazol-3-ylboronic acid pinacol ester (1.90 g, 4.69 mmol), Pd(PPh\(_3\))\(_4\) (57.8 mg, 0.0500 mmol) and potassium carbonate (1.66 g, 12.0 mmol) in a solvent mixture of 1,2-dimethoxyethane (25 mL), EtOH (10 mL) and water (5 mL) was heated at 85 °C and stirred for 10 hours under nitrogen atmosphere. After cooling, chloroform (50 mL) was added, and the solution was washed with water (30 mL × 2) and sat. brine (30 mL). The obtained organic solution was dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography using chloroform/hexane (1:1, v/v) as eluent to afford 16 as a red powder (1.27 g, 1.48 mmol, 74%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 0.87 (t, 6H, \( J = 7.3 \) Hz), 0.92 (t, 6H, \( J = 7.5 \) Hz), 1.23–1.44 (m, 16H), 2.07–2.10 (m, 2H), 4.13–4.23 (m, 4H), 7.26–7.28 (m, 2H), 7.39–7.50 (m, 8H), 7.82 (dd, 2H, \( J = 1.8 \) and 8.6 Hz), 7.92 (s, 2H), 8.15-8.17 (m, 4H), 8.42 (d, 2H, \( J = 1.30 \) Hz); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 11.00, 14.13, 23.15, 24.51, 28.92, 31.11, 39.53, 47.63, 109.32, 109.40, 117.81, 119.20, 120.62, 122.86, 123.03, 123.37, 124.10, 125.15, 125.38, 125.73, 126.08, 128.72, 137.57, 140.80, 141.49, 147.18, 152.75; MALDI-TOF MS \( m/z \) 854 (M\(^+\)); Anal. Calcd for C\(_{54}\)H\(_{54}\)N\(_4\)S\(_3\): C, 75.84; H, 6.36; N, 6.55. Found: C, 75.87; H, 6.14; N, 6.86.

3.4.2.6. 3,6-Bis(5-(9-(2-ethylhexyl)-9\( H \)-carbazol-3-yl)thiophen-2-yl)benzene-1,2-
diamine (10)

The compound 10 was prepared from 16 as a dark brown solid according to the same procedure as the preparation of 7; This product was unstable, and so used to the next step without further purification; yield, 82%; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.88 (t, 6H, $J$ = 7.3 Hz), 0.93 (t, 6H, $J$ = 7.5 Hz), 1.24–1.38 (m, 16H), 2.06–2.09 (m, 2H), 4.02 (m, 4H), 4.12–4.16 (m, 4H), 7.17–7.28 (m, 6H), 7.37–7.41 (m, 6H), 7.46–7.50 (m, 2H), 7.75 (dd, 2H, $J$ = 1.8 and 8.6 Hz), 8.15 (d, 2H, $J$ = 7.7 Hz), 8.35 (d, 2H, $J$ = 1.3 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 11.02, 14.14, 23.16, 24.52, 28.92, 31.12, 39.53, 47.61, 109.30, 109.45, 117.68, 119.15, 120.58, 121.34, 121.37, 122.50, 122.85, 123.36, 124.10, 125.46, 126.06, 127.14, 133.14, 139.39, 140.66, 141.48, 145.88; MALDI-TOF MS m/z 827 ([M + H]$^+$).

3.4.3. General procedure for synthesis of 1–5

A mixture of phenanthrene-9,10-dione (0.512 g, 2.46 mmol) and the corresponding diamine derivative (6–10, 2.46 mmol) in acetic acid (1 mL) and ethanol (25 mL) was stirred at 80 °C for 8 h under nitrogen. After cooling, the solvent was removed on a rotary evaporator. The residue was extracted with CHCl$_3$ and H$_2$O in a separation funnel, and then the organic layer was dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator, and the residue was purified by silica gel chromatography (eluent CHCl$_3$-hexane). Further purification was carried out by recrystallization from CHCl$_3$-hexane to afford the target dbpz derivative.

3.4.3.1. 10,13-Bis(9-(2-ethylhexyl)-9H-carbazol-2-yl)dibenzo[a,c]phenazine (1)
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This compound was obtained as a yellow powder; yield, 58%; m.p. 208–212 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.69 (t, 6H, \(J = 7.5\) Hz), 0.85 (t, 6H, \(J = 7.3\) Hz), 1.11–1.45 (m, 16H), 2.16–2.21 (m, 2H), 4.24–4.35 (m, 4H), 7.29–7.32 (m, 2H), 7.47–7.54 (m, 4H), 7.60–7.64 (m, 2H), 7.73–7.75 (m, 2H), 7.89 (dd, 2H, \(J = 1.8\) and 4.6 Hz), 8.06 (s, 2H), 8.17 (s, 2H), 8.23 (d, 2H, \(J = 7.9\) Hz), 8.34 (d, 2H, \(J = 8.2\) Hz), 8.56 (d, 2H, \(J = 7.9\) Hz), 9.18 (dd, 2H, \(J = 1.6\) and 7.9 Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 10.99, 14.00, 23.11, 24.64, 28.86, 31.14, 39.63, 47.67, 109.16, 112.10, 118.95, 119.79, 120.58, 122.38, 122.55, 122.85, 122.95, 125.78, 126.79, 128.00, 130.23, 130.36, 130.78, 132.29, 136.54, 140.57, 140.74, 141.08, 141.49, 141.84; MALDI-TOF MS \(m/z\) 834 (M\(^+\)); Anal. Calcd for C\(_{60}\)H\(_{58}\)N\(_4\): C, 86.29; H, 7.00; N, 6.71. Found: C, 86.68; H, 6.77; N, 6.65.

3.4.3.2. 10,13-Bis(9-(2-ethylhexyl)-9\(H\)-carbazol-3-yl)dibenzo[\(a\),\(c\)]phenazine (2).

This compound was obtained as an orange powder; yield, 55%; m.p. 202–205 °C; \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 0.90 (t, 6H, \(J = 7.4\) Hz), 0.99 (t, 6H, \(J = 7.1\) Hz), 1.23–1.53 (m, 16H), 2.17–2.24 (m, 2H), 4.27–4.37 (m, 4H), 7.24–7.29 (m, 2H), 7.48–7.52 (m, 4H), 7.60–7.64 (m, 2H), 7.67–7.75 (m, 2H), 7.77–7.79 (m, 2H), 8.16 (dd, 2H, \(J = 1.8\) and 4.6 Hz), 8.20 (s, 2H), 8.22 (s, 2H), 8.58 (d, 2H, \(J = 7.9\) Hz), 8.83 (s, 2H), 9.18 (dd, 2H, \(J = 1.9\) and 5.4 Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 11.06, 14.21, 23.24, 24.55, 28.99, 31.19, 39.63, 47.72, 108.54, 109.22, 119.03, 120.42, 122.89, 122.91, 123.37, 123.54, 125.64, 126.73, 128.01, 129.26, 129.54, 129.98, 130.04, 130.94, 132.24, 139.82, 140.63, 140.77, 141.21, 141.49; MALDI-TOF MS \(m/z\) 834 (M\(^+\)); Anal. Calcd for C\(_{60}\)H\(_{58}\)N\(_4\): C, 86.29; H, 7.00; N, 6.71. Found: C, 86.43; H, 7.08; N, 6.31.
3.4.3.3. 10,13-Bis(4-hexylthiophen-2-yl)dibenzo[a,c]phenazine (3).

This compound was obtained as a red powder; yield, 64%; m.p. 205–207 °C; \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 0.91 (t, 6H, \(J = 7.3\) Hz), 1.34–1.47 (m, 12H), 1.72–1.80 (m, 4H), 2.74 (t, 4H, \(J = 6.4\) Hz), 7.25 (s, 2H), 7.77–7.85 (m, 6H), 8.21 (s, 2H), 8.61 (dd, 2H, \(J = 1.8\) and 4.8 Hz), 9.53 (dd, 2H, \(J = 1.9\) and 5.4 Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.09, 22.59, 29.21, 29.76, 30.88, 31.65, 122.76, 122.93, 127.15, 128.05, 128.88, 130.35, 130.56, 130.98, 132.32, 133.52, 133.71, 140.69, 141.55, 141.71; MALDI-TOF MS \(m/z\) 612 (M\(^+\)); Anal. Calcd for C\(_{40}\)H\(_{40}\)N\(_2\)S\(_2\): C, 78.39; H, 6.58; N, 4.57. Found: C, 78.43; H, 6.81; N, 4.62.

3.4.3.4. 10,13-Bis[5-(9,9-dihexyl-9\(H\)-fluoren-2-yl)thiophen-2-yl]dibenzo[a,c]phenazine (4).

This compound was obtained as a purple powder; yield, 60%; m.p. 110–112 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.64–0.81 (m, 20H), 1.08–1.15 (m, 24H), 2.06–2.10 (m, 8H), 7.33–7.39 (m, 6H), 7.55 (d, 2H, \(J = 6.8\) Hz), 7.74–7.86 (m, 12H), 7.94 (d, 2H, \(J = 6.5\) Hz), 8.02 (s, 2H), 8.61–8.63 (m, 2H), 9.69–9.71 (m, 2H); \(^{13}\)C NMR (100 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 15.77, 24.62, 25.94, 31.82, 33.60, 42.55, 57.25, 121.71, 121.84, 122.16, 124.62, 124.92, 125.03, 126.55, 128.09, 128.89, 129.16, 129.22, 129.73, 129.90, 132.34, 132.39, 132.87, 134.37, 135.63, 139.50, 140.21, 142.77, 142.84, 143.54, 149.78, 152.93, 153.62; MALDI-TOF MS \(m/z\) 1109 ([M + H]\(^+\)); Anal. Calcd for C\(_{78}\)H\(_{80}\)N\(_2\)S\(_2\): C, 84.43; H, 7.27; N, 2.52. Found: C, 84.65; H, 7.26; N, 2.24.

3.4.3.5. 10,13-Bis[5-(9-(2-ethylhexyl)-9\(H\)-carbazol-3-yl)thiophen-2-yl]dibenzo[a,c]phenazine (5).
This compound was obtained as a dark purple powder; yield, 57%; m.p. 116–120 °C; \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.92 (t, 6H, \(J = 7.6\) Hz), 1.01 (t, 6H, \(J = 7.5\) Hz), 1.30–1.53 (m, 16H), 2.18–2.23 (m, 2H), 4.24–4.35 (m, 4H), 7.20–7.24 (m, 4H), 7.26–7.28 (m, 2H), 7.47–7.56 (m, 4H), 7.58–7.65 (m, 4H), 7.72–7.78 (m, 2H), 8.12–8.16 (m, 2H), 8.18 (s, 2H), 8.22 (d, 2H, \(J = 6.4\) Hz), 8.54 (d, 2H, \(J = 5.2\) Hz), 8.87 (d, 2H, \(J = 4.8\) Hz), 9.22 (dd, 2H, \(J = 1.6\) and 5.4 Hz); \(^{13}\text{C}\) NMR (100 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 11.09, 14.14, 22.76, 24.04, 30.00, 31.69, 40.75, 55.31, 119.80, 119.88, 120.30, 122.59, 122.77, 123.08, 124.75, 125.90, 127.02, 127.15, 127.21, 127.72, 127.86, 130.11, 130.47, 130.81, 132.33, 133.84, 137.72, 138.13, 140.78, 140.93, 141.41, 147.67, 151.00, 151.64; MALDI-TOF MS \(m/z\) 999 ([M + H]\(^+\)); Anal. Calcd for C\(_{68}\)H\(_{62}\)N\(_4\)S\(_2\): C, 81.72; H, 6.25; N, 5.61. Found: C, 81.51; H, 6.31; N, 5.69.

3.4.4. Analysis of fluorescent solvatochromism

Fluorescent solvatochromism of 1–5 was investigated for solvents with different polarity such as hexane, toluene, CH\(_2\)Cl\(_2\), acetone, and DMF. The solvent polarity parameters (\(\Delta f\)) were obtained from the equation (1):

\[
\Delta f = (\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1)
\]

where \(\varepsilon\) and \(n\) are dielectric constant and refractive index of the solvent, respectively. The difference in the dipole moment between the excited state and ground states (\(\Delta \mu\)) was calculated from equation (2):

\[
\Delta \nu = [2(\Delta \mu)^2/hc^2]\Delta f + \text{constant}
\]

where the parameters of \(\Delta \nu\); \(h\), \(c\), and \(r\) are the Stokes shift, the Planck’s constant, the velocity
of light, and the Onsager radius, respectively. The Onsager radii of 1–5 were estimated by DFT calculations (B3LYP/6-31G(d)), respectively.

3.4.5. OLED fabrication

PEDOT:PSS (Clevios™ P VP CH8000) and PBD were purchased from Heraeus GmbH and Tokyo Chemical Industry Co., Ltd., respectively. PVCz was purchased from Sigma-Aldrich Co., and purified by reprecipitation from THF to methanol just before use. First, PEDOT:PSS was spin-coated onto an ITO glass substrate pretreated with UV-O₃ and dried at 115 °C for 1 h. Then, a mixture of PVCz, PBD and the dbpz derivative in dry toluene (PVCz; 10 mg/0.7 mL of toluene) was filtered through a 0.2 μm membrane filter and spin-coated onto the PEDOT:PSS layer to fabricate EML. Thereafter, cesium fluoride and aluminum layers were successively vacuum-deposited on EML. The obtained OLED was covered with a glass cap and encapsulated with a UV-curing epoxy resin. The area of the emitting part was 10 mm² (2 mm × 5 mm). The device fabrication was carried out in a glovebox filled with dry argon, except for the preparation of the PEDOT:PSS layer. The device performance was operated using a Hamamatsu Photonics C-9920-11 organic EL device evaluating system.

3.5. References


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Chapter 4

Synthesis and Luminescence Properties of Dithieno[3,2-\(a\):2',3'-c]phenazine Derivatives with Electron-donating \(\pi\)-Conjugated Side-arms at the 2,5- and 8,11-Positions

4.1. Introduction

Fluorescent dyes have so far been frequently utilized in various fields [1–5], 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 factors determining the quantum efficiency of the device [6]. To modulate the emission color in accordance to objectives, 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 allow us to tune the \(S_0\)-\(S_1\) transition energy of a fluorophore at ease [7–10]. As electron-donating \(\pi\)-building blocks, electron-rich aromatic components such as arylamines and carbazole derivatives have been frequently used [8, 9, 11]. As for electron-withdrawing \(\pi\)-building blocks, electron-deficient frameworks such as 2,1,3-benzothiadiazole, dibenzo\([b,d]\)thiophene \(S,S\)-dioxide, and other heterocycles have been used [8, 12–14]. Recently we have developed novel fluorophores based on electron-accepting dipyrido[3,2-\(a\):2',3'-\(c\)]phenazine [15] (\(dppz\)) and dibenzo[\(a,c\)]phenazine (\(dbpz\)) [16, 17] platforms, where \(\pi\)-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 with the help of metal coordination, where relatively high PL quantum yields were achieved [15]. We also reported that the introduction of fluorene side-arms to dbpz yielded a highly emissive green fluorophore, and therein we demonstrated the fabrication of OLEDs using these dyes as an emitting dopant [16]. Furthermore, the dbpz derivatives bearing π-extended electron-donating side-arms showed red-shifted emission from red to deep red [17].

Here we report synthesis and PL properties of novel fluorescent dyes based on 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 (Figure 1). Although dtpz-containing low-mass molecules and polymers have so far been developed aimed at development of organic semiconductors and photovoltaic materials[18, 19], there have been

![Figure 1. Structures of dtpz derivatives 1 and 2.](image-url)
few reports on the PL properties of \textit{dtpz} derivatives [20]. In the \textit{dtpz} building block, the fused thiophene rings and the phenazine moiety act as electron rich parts and an electron deficient one, respectively, and thus \textit{dtpz} should have different effect on the ICT transition of the present D-A-D structure from \textit{dppz} and \textit{dbpz}. We demonstrate the synthesis of the \textit{dtpz}-based fluorophores, and their PL properties, especially focusing on red fluorophores. We discuss which positions are beneficial to obtain more emissive red fluorophores.

\section{4.2. Results and discussion}

\subsection{4.2.1. Syntheses of 1 and 2}

The \textit{dtpz} derivatives 1 possess a series of electron-donating side-arms such as 9,9-dihexyl-9\textit{H}-fluoren-2-yl, 9-(2-ethylhexyl)-9\textit{H}-carbazol-3-yl and 4-hexylthiophen-2-yl groups at the 8,11-positions, which were prepared by condensation of benzo[2,1-\textit{b}:3,4-\textit{b}']-dithiophene-4,5-dione 3 [20] and the corresponding diamine derivatives 4a–c [17].

\begin{center}
\begin{tikzpicture}
\node at (0,0) {3};
\node at (2.5,-1) {4a–c};
\node at (2.5,0) {1a–c (76–83\%)};
\node at (0,-1) {\text{H}_2\text{N}};
\node at (2.5,1) {\text{H}_2\text{N}};
\node at (1.25,0) {\text{R}};
\node at (3.75,0) {\text{R}};
\draw (0,0) rectangle (2.5,-1);
\draw (2.5,0) rectangle (4.5,0);
\draw (0,-1) rectangle (1.25,0);
\draw (2.5,1) rectangle (3.75,0);
\node at (0,-2) {Scheme 1. Synthesis of \textit{dtpz} derivative 1.};
\end{tikzpicture}
\end{center}
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(yields: 76–83%), as shown in Scheme 1.

The \textit{dtpz} derivatives 2 possessing the side-arms at the 2,5-positions started from the preparation of the dibromo-functionalized \textit{dtpz} derivative 10 as shown in Scheme 2. From the synthetic reason, dodecyl groups were introduced at the 9,10-positions to enhance the solubility in organic solvents. First, commercially available 5,6-dibromobenzothiadiazole was dialkynylated by the Sonogashira coupling reaction in 82\% yield, followed by reduction with lithium aluminium hydride to afford 4,5-didodecynylbenzene-1,2-diamine in 90\% yield. The obtained diamine derivative was reacted with 2,7-bis(trimethylsilyl)benzo-
[2,1-b:3,4-b’]dithiophene-4,5-dione 7 [21] to obtain the dtpz derivatives 8 in 74% yield.

Then, the hydrogenation of the dodecynyl groups followed by the reaction with \( N \)-bromo-succinimide afforded the dibromo-functionalized dtpz derivative 10 as an intermediate to obtain 2. In Scheme 3 is shown the synthesis of 2. The Suzuki-Miyaura cross-coupling reactions of 10 with pinacol esters of 9,9-dihexyl-9\( H \)-fluoren-2-ylboronic acid and 9-(2-ethylhexyl)-9\( H \)-carbazol-3-ylboronic acid afforded 2a and 2b in the yields of 67 and 54%, respectively. Similarly, the Suzuki-Miyaura cross-coupling reaction of 10 with
thiophen-2-ylboronic acid afforded 2e in 45% yield. We also prepared the dtpz derivatives bearing π-extended side-arms such as 5-(9,9-dihexyl-9H-fluoren-2-yl)thiophen-2-yl and 5-(9-(2-ethylhexyl)-9H-carbazol-3-yl)-thiophen-2-yl substituents, namely 2d and 2e, respectively. The reaction of 2c with N-bromosuccinimide afforded the precursor 11, which was reacted with 9,9-dihexyl-9H-fluoren-2-ylboronic acid and 9-(2-ethylhexyl)-9H-carbazol-3-ylboronic acid afforded 2d and 2e in the yields of 53 and 58%.

The prepared dtpz derivatives 1 and 2 were characterized by 1H and 13C NMR spectroscopy, MALDI-TOF mass spectroscopy and elemental analysis.

4.2.2. DFT and TD-DFT study

Time-dependent density functional theory (TD-DFT) calculations were carried out for 1a and 2a as representative examples of the 8,11- and 2,5-disubstituted dtpz derivatives, respectively, using the Gaussian 09 program [22] at the B3LYP/6-31G(d) level of theory. For 2a, the geometry optimizations and electronic transition calculations were performed for the model structure in which the dodecyl groups at the 9,10-positions are replaced by methyls. The electron distributions of HOMO and LUMO are shown in Figure 2. In both of 1a and 2a, the electronic transition from the ground state (S0) to the lowest singlet excited state (S1) is exclusively based on HOMO-LUMO transition (composition; > 97.9%). As seen in Figure
2, the HOMO and LUMO are localized mainly on the electron-donating side-arms and the electron-deficient dtpz moiety, respectively, and thus, the electronic transition obviously occurs in an ICT manner. These results clearly show that the attachment of π-conjugated electron-donating side-arms to the 8,11- or 2,5-positions of dtpz yields an ICT-type D-A-D-chromophore. For the other derivatives 1b–c and 2b–e, TD-DFT calculations were carried out, and it was expected that all these dtpz derivatives are consistent of ICT-type chromophoric systems similar to 1a or 2a.

![Figure 2](image-url)

**Figure 2.** Electron density distributions of HOMO and LUMO for 1a and 2a. HOMO and LUMO energy levels: –5.30 and –2.34 eV, respectively, for 1a, and –5.20 and –2.21 eV, respectively, for 2a. \( S_0 \rightarrow S_1 \) electronic transition energy: 2.51 and 2.37 eV for 1a and 2a, respectively. DFT and TD-DFT calculations were carried at the B3LYP/6-31G(d) level.
2.3. UV-vis absorption and photoluminescence properties

In Figure 3 are shown UV-vis absorption spectra of 1 and 2 in dichloromethane (conc.; 10 μM) at room temperature, and the spectral data are summarized in Table 1. All these compounds based on the dtpz backbone exhibited strong absorption bands at approximately 250–420 nm with vibronic structures, assignable to π-π* transitions on the side-arms as well.

![Figure 3. UV-vis absorption spectra of (a) 1 and (b) 2 in CH₂Cl₂ at rt (conc.; 10 μM).](image)
as the \textit{dtpz} core. On the other hand, the broad lowest-energy absorption bands at more than 420 nm are assignable to ICT transitions from the side-arms to the \textit{dtpz} core, as expected from the TD-DFT study. In the case of the 8,11-disubstituted \textit{dtpz} derivatives, the ICT transition band is bathochromically shifted in the order of \textbf{1a} (absorption wavelength $\lambda_{\text{abs}}$; 449 nm), \textbf{1b} ($\lambda_{\text{abs}}$; 470 nm), and \textbf{1c} ($\lambda_{\text{abs}}$; 496 nm), indicating that the thienyl group is a more effective electron-donating side-arm. In the case of the 2,5-disubstituted \textit{dtpz}

\begin{table}
\centering
\caption{UV-vis absorption (10 $\mu$M) and PL (1.0 $\mu$M) spectral data and photophysical profiles of \textbf{1} and \textbf{2} in dichloromethane at rt}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Compd & $\lambda_{\text{abs}}^a$/nm [$\log\{\varepsilon_{\text{abs}}^a\} / (\text{M}^{-1} \text{ cm}^{-1})$] & $\lambda_{\text{PL}}^b$ ($\lambda_{\text{ex}}^b$) /nm & $\Phi_{\text{PL}}^c$ & $\tau_{\text{PL}}^d$/ns ($\chi^2$) \\
\hline
\textbf{1a} & 300 [4.87], 394 [4.32], 449 [4.12] & 557 (448) & 0.65 & 7.13 (1.02) \\
\textbf{1b} & 300 [4.97], 387 [4.19], 470 [4.04] & 616 (469) & 0.75 & 12.5 (1.06) \\
\textbf{1c} & 298 [4.68], 315 [4.69], 403 [4.16], 496 [4.00] & 651 (497) & 0.38 & 11.6 (1.00) \\
\hline
\textbf{2a} & 282 [4.67], 295 [4.69], 345 [4.73], 381 [4.89], 402 [4.91], 478 [4.17] & 630 (476) & 0.23 & 6.20 (1.09) \\
\textbf{2b} & 277 [4.77], 325 [4.75], 381 [4.81], 402 [4.81], 494 [4.04] & 662 (495) & 0.09 & 1.84 (1.03) \\
\textbf{2c} & 257 [4.54], 294 [4.60], 326 [4.54], 379 [4.63], 400 [4.63], 467 [3.97] & 630 (470) & 0.12 & 5.26 (1.02) \\
\textbf{2d} & 305 [4.67], 403 [4.94], 498 [4.40] & 659 (494) & 0.08 & 1.90 (1.10) \\
\textbf{2e} & 304 [4.79], 403 [4.90], 506 [4.34] & 685 (504) & 0.07 & 1.34 (1.04) \\
\hline
\end{tabular}
\end{table}

\textit{a}$\lambda_{\text{abs}}$ and $\varepsilon_{\text{abs}}$; absorption wavelength and molar absorption coefficient, respectively. $^b$$\lambda_{\text{PL}}$ and $\lambda_{\text{ex}}$; PL maximum and excitation wavelength, respectively. $^c$$\Phi_{\text{PL}}$; PL quantum yield. $^d$$\tau_{\text{PL}}$; PL lifetime.
derivatives, the ICT transition bands of 2a and 2b were red-shifted more than those of 1a and 1b, respectively (λ_abs of 2a and 2b; 478 and 494 nm, respectively). On the other hand, 2c shows a similar absorption wavelength of the ICT transition to 1c. As for 2d and 2e, the insertion of 2,5-thienylene between the dtpz core and the fluorene or carbazole moieties brought about further red shift of the ICT transition according to the extension of the π-conjugation of the side-arms, accompanied by an increase in the molar absorptivity.

In Figure 4 are shown PL spectra of 1 and 2 in CH₂Cl₂ (concentration; 1.0 μM) at room temperature, and their spectral data are summarized in Table 1. The fluorene-appended 8,11-disubstituted derivative 1a exhibited intense yellow emission (emission wavelength of photoluminescence λ_PL; 557 nm) with a PL quantum yield (Φ_PL) of 0.65. On the other hand, the carbazole-appended derivative 1b exhibited reddish orange emission at 616 nm, accompanying the increasing Φ_PL of 0.75. The thiophene-appended derivative 1c showed most red-shifted emission among the 8,11-disubstituted dtpz derivatives, as expected from the λ_abs of the ICT transition: red emission was observed (λ_PL; 651 nm). Although the value of Φ_PL decreased in comparison with those of 1a and 1b, 1c is still emissive for a red fluorophore (Φ_PL; 0.38). Introduction of electron-donating side-arms to the 2,5-positions is more effective to obtain red emission in comparison with 1, and 2a–e exhibited red PL at 630–662 nm. However, their Φ_PLS (0.09–0.23) are much lower than those of 1a–e. Further
extension of π-conjugation of the side-arms, as seen in 2d and 2e yielded deep red emission ($\lambda_{PL}$: 659 and 685 nm, respectively) with decreasing $\Phi_{PL}$s (0.08 and 0.07, respectively).

![PL spectra of (a) 1 and (b) 2 in CH$_2$Cl$_2$ at rt (conc.; 1.0 $\mu$M).](image)

**Figure 4.** PL spectra of (a) 1 and (b) 2 in CH$_2$Cl$_2$ at rt (conc.; 1.0 $\mu$M).

To investigate the PL properties of 1 and 2 in the solid matrix, the PL spectra of poly(methyl methacrylate) (PMMA) spin-coated thin films (concentration; 1.0 mol%, based on the methyl methacrylate monomer unit) doped with the dtpz derivatives were obtained.
Chapter 4

The spectral data are summarized in Table 2, accompanied by the $\Phi_{PL}$ and PL lifetimes. The PL spectra in PMMA films showed similar spectral profiles to those of dichloromethane solutions (see Figure 4), although the $\lambda_{PL}$ of each $dtpz$ derivative was slightly blue-shifted. Relatively weak emission was observed for $2a$–$e$ ($\Phi_{PL}$; 0.02–0.12) was observed, whereas $1a$ and $1b$ still exhibited relatively efficient fluorescence along with $\Phi_{PL}$ of 0.32 and 0.49, respectively.

Table 2. PL spectral data of 1 and 2 in PMMA thin films at rt (concentration; 1.0 mol%, based on the methyl methacrylate monomer unit)

<table>
<thead>
<tr>
<th>Compd</th>
<th>$\lambda_{PL}^{a}$ ($\lambda_{ex}^{a}$)/ nm</th>
<th>$\Phi_{PL}$</th>
<th>$\tau_{PL}$/ns ($\chi^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>543 (446)</td>
<td>0.32</td>
<td>3.68 (1.03)</td>
</tr>
<tr>
<td>1b</td>
<td>596 (478)</td>
<td>0.49</td>
<td>6.06 (1.07)</td>
</tr>
<tr>
<td>1c</td>
<td>630 (497)</td>
<td>0.12</td>
<td>1.12 (1.04)</td>
</tr>
<tr>
<td>2a</td>
<td>581 (401)</td>
<td>0.12</td>
<td>3.21 (1.06)</td>
</tr>
<tr>
<td>2b</td>
<td>623 (404)</td>
<td>0.07</td>
<td>4.96 (1.02)</td>
</tr>
<tr>
<td>2c</td>
<td>635 (386)</td>
<td>0.07</td>
<td>6.45 (1.05)</td>
</tr>
<tr>
<td>2d</td>
<td>613 (406)</td>
<td>0.02</td>
<td>0.61 (1.00)</td>
</tr>
<tr>
<td>2e</td>
<td>678 (410)</td>
<td>0.03</td>
<td>2.47 (1.05)</td>
</tr>
</tbody>
</table>

$^{a}\lambda_{PL}$ and $\lambda_{ex}$; PL maximum and excitation wavelength, respectively. $^{b}\Phi_{PL}$; PL quantum yield. $^{c}\tau_{PL}$; PL lifetime.

4.2.4. Solvatochromism of photoluminescence

Photoluminescent properties of ICT-type molecular systems are often affected by solvent polarity [10, 15–17, 23]. So we also investigated the solvent effects on the emission
behavior of the \textit{dtpz} derivatives. Although the absorption spectra were hardly affected by polarity of solvents, remarkable positive solvatochromism was observed for 1 and 2, indicating that the polarity of the \textit{dtpz} derivatives increases upon photoexcitation. As representative examples, PL spectra of 1b and 2b in various solvents are shown in Figure 5, respectively. The PL data of all compounds are also listed in Table 3. The emission color of

\textbf{Figure 5.} PL spectra of 1b and 2b in various solvents (conc.; 1.0 \textmu M).
Table 3. PL data of 1 and 2 in various solvents (concentration; 1.0 µM).

<table>
<thead>
<tr>
<th>Compd</th>
<th>Solvent</th>
<th>λ&lt;sub&gt;PL&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; (nm)</th>
<th>Φ&lt;sub&gt;PL&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Compd</th>
<th>Solvent</th>
<th>λ&lt;sub&gt;PL&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; (nm)</th>
<th>Φ&lt;sub&gt;PL&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>hexane</td>
<td>516</td>
<td>0.19</td>
<td>2b</td>
<td>hexane</td>
<td>561</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>toluene</td>
<td>531</td>
<td>0.31</td>
<td></td>
<td>toluene</td>
<td>607</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>557</td>
<td>0.65</td>
<td></td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>662</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>acetone</td>
<td>560</td>
<td>0.73</td>
<td></td>
<td>acetone</td>
<td>654</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>564</td>
<td>0.66</td>
<td></td>
<td>DMF</td>
<td>669</td>
<td>0.11</td>
</tr>
<tr>
<td>1b</td>
<td>hexane</td>
<td>554</td>
<td>0.87</td>
<td>2c</td>
<td>hexane</td>
<td>529</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>toluene</td>
<td>579</td>
<td>0.86</td>
<td></td>
<td>toluene</td>
<td>574</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>616</td>
<td>0.75</td>
<td></td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>630</td>
<td>0.12</td>
</tr>
<tr>
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<td>0.57</td>
<td></td>
<td>acetone</td>
<td>608</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
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<td>0.50</td>
<td></td>
<td>DMF</td>
<td>631</td>
<td>0.21</td>
</tr>
<tr>
<td>1c</td>
<td>hexane</td>
<td>601</td>
<td>0.73</td>
<td>2d</td>
<td>hexane</td>
<td>557</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>toluene</td>
<td>624</td>
<td>0.67</td>
<td></td>
<td>toluene</td>
<td>596</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>651</td>
<td>0.38</td>
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<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>659</td>
<td>0.08</td>
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<tr>
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<td>acetone</td>
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<td></td>
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<td>642</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>673</td>
<td>0.23</td>
<td></td>
<td>DMF</td>
<td>654</td>
<td>0.11</td>
</tr>
<tr>
<td>2a</td>
<td>hexane</td>
<td>531</td>
<td>0.11</td>
<td>2e</td>
<td>hexane</td>
<td>574</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>toluene</td>
<td>565</td>
<td>0.26</td>
<td></td>
<td>toluene</td>
<td>615</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>630</td>
<td>0.23</td>
<td></td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>685</td>
<td>0.07</td>
</tr>
<tr>
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<td>acetone</td>
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<td></td>
<td>acetone</td>
<td>663</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>610</td>
<td>0.30</td>
<td></td>
<td>DMF</td>
<td>681</td>
<td>0.07</td>
</tr>
</tbody>
</table>

<sup>a</sup>Each PL spectrum was obtained upon excitation at the maximum peak wavelength of the excitation spectrum. <sup>b</sup>PL quantum yield.

1b changed dramatically from green in hexane (554 nm) to red in DMF (643 nm). Similar to 1b, 2b also exhibited drastic emission color change from yellow (561 nm) to deep red (669 nm). For the other dtpz derivatives, similar emission color changes were observed: λ<sub>PL</sub> was red-shifted by 48–108 nm, when the solvent polarity increased from hexane to DMF.

We also carried out the analysis of the solvent effects according to the Lippert-Mataga plot...
Although the linearity of the plots of the Stokes shifts against the solvent polarity parameters were not so good (correlation coefficient of the slope $R^2; 0.82–0.95$), the differences in the dipole moment between the ground and excited states $\Delta \mu$ were determined as $8.40–13.4$ D for 1 and $13.4–16.8$ D for 2. These significant enlargement of the dipole moment clearly indicates that strong intramolecular charge transfer occurs upon electronic transition.

4.2.5. Electroluminescence from OLED

Among the developed $dtpz$ derivatives, 1b is the most emissive red fluorophore. So, we fabricated an OLED using 1b as an emitting dopant. Poly(3,4-ethylenedioxythiophene):poly(stylenesulfonate) (PEDOT:PSS), poly(9-vinylcarbazole) (PVCz), 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD), and cesium fluoride were employed as a hole-injection layer, a hole-transporting host, an electron-transporting material, and an electron-injection layer, respectively [16, 26, 27]. The device structure is as follows: ITO (transparent anode, 150 nm)/PEDOT:PSS (40 nm)/emission layer (EML, 80 nm)/CsF (1.0 nm)/Al (cathode, 250 nm), where EML consists of PVCz, PBD, and 1b in a ratio of 10:3.0:1.0 (wt/wt/wt). In Figure 6 are shown the electroluminescence (EL) spectra and the current density-voltage and luminance-voltage curves of the fabricated OLED. Yellow
Figure 6. (a) EL spectrum obtained and current density-voltage-luminance curves of OLED containing 1b as an emitting dopant. The spectrum was obtained at the voltage where maximum luminance was observed (@19.5 V).

electroluminescence (EL) with the Commission Internationale de L'éclairage (CIE) chromaticity coordinate of (0.53, 0.46) was observed when the maximum luminance of 420 cd m⁻² was obtained at 19.5 V. The EL spectrum was largely blue-shifted by 33 nm (emission wavelength of EL; 583 nm) in comparison with λₚₐ in dichloromethane. One can see that this blue shift is caused by the low polarity of PVCz. As for the device efficiencies,
the maximum external quantum efficiency of 0.26%, the maximum current efficiency of 0.58 cd A\(^{-1}\), and the maximum power efficiency of 0.23 lm W\(^{-1}\) were obtained.

### 4.3. Conclusions

In summary, we have developed herein a series of \textit{dtpz}-based \(\pi\)-conjugated derivatives with electron-donating side-arms at the 2,5- and 8,11-positions. These compounds showed interesting optical and photoluminescent characteristics tuned by the side-arms. Especially, the PL properties were drastically changed through modulation of the ICT transition based on the D-A-D electronic structure. In the case of the 8,11-disubstituted \textit{dtpz} derivatives, the emission color in dichloromethane ranged from 557 (yellow) to 651 nm (red). Especially, those bearing 9-(2-ethylhexyl)-9\(H\)-carbazol-3-yl or 4-hexylthiophen-2-yl side-arms were good red fluorescent dyes from the viewpoint of \(\Phi_{\text{PL}}\). The 2,5-disubstituted derivatives showed more red-shifted emission from red to deep red regions, although their \(\Phi_{\text{PL}}\)s were much smaller than those of the 8,11-disubstituted derivatives. The positive PL solvatochromic behavior, showing the remarkable red shifts according to the increase in solvent polarity, clearly explained that the observed emission is based on the ICT transition from HOMO localized at the electron-donating side-arms to LUMO localized at the \textit{dtpz} core. Using one of red fluorescent \textit{dtpz} derivatives, a PVCz-based OLED was fabricated,
which showed yellow EL from the emitting dopant. The blue-shifted EL should be caused by low polarity of the PVCz host matrix.

### 4.4. Experimental section

#### 4.4.1. Materials and methods

All reagents and solvents necessary for syntheses were purchased from Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co., Ltd., Kanto Chemical Co., Inc., or Sigma-Aldrich Co., and used without further purification. Silica gel (spherically-shaped, neutral) for column chromatography was purchased from Kanto Chemical Co., Inc.. The compounds 3 [20], 4a–c [17], and 7 [21] were prepared according to the literatures.

NMR spectra were measured on a JEOL ECS-400 or a ECX-400 spectrometer (400 MHz for $^1$H NMR and 100 MHz for $^{13}$C NMR), using TMS (0.00 ppm for $^1$H and $^{13}$C NMR) as an internal standard for CDCl$_3$, respectively. Mass spectra were taken on a Shimadzu-Kratos AXIMA-CFR PLUS TOF mass spectrometer by a matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) method, and the spectra of 5 and 6 were taken in a negative mode. Elemental analyses were carried out on a J-Science MICRO CORDER JM10 analyzer.

UV-vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. PL spectra were recorded on a Horiba Jobin Yvon SPEX Fluorolog-3 spectrofluorometer. PL quantum yields were measured on a Hamamatsu Photonics C9920-12 absolute PL quantum
yield measurement system. PL lifetimes were obtained on a Horiba Jobin Yvon FluoroCube spectroanalyzer.

4.4.2. Preparation of synthetic precursors

4.4.2.1. 5,6-Di(dodec-1-yn-1-yl)benzo[c][1,2,5]thiadiazole (5)

A mixture of 5,6-dibromo-2,1,3-benzothiadiazole (5.54 g, 18.8 mmol), 1-dodecyne (9.8 mL, 45.8 mmol), Pd(PPh₃)₂Cl₂ (0.313 g, 0.446 mmol), CuI (205 mg, 1.08 mmol) in triethylamine (68 mL) was stirred at 90 °C for 18 h under nitrogen atmosphere. After cooling, the solvent was removed on a rotary evaporator. The residue was dissolved in chloroform (120 mL) and washed with water (30 mL × 2) and sat. brine (30 mL). The obtained organic solution was dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography using chloroform/hexane (2/1, v/v) as eluent to afford 5 as a pale yellow solid (7.16 g, 15.4 mmol, 82%); ¹H NMR (400 MHz, CDCl₃) δ 0.88 (t, 6H, J = 6.8 Hz), 1.27–1.32 (m, 24H), 1.48–1.70 (m, 8H), 2.51 (t, 4H, J = 7.0 Hz), 8.01 (s, 2H); MALDI-TOF MS (negative mode) m/z 465 ([M + H]⁻). Anal. Calcd. for C₃₀H₄₄N₂S: C, 77.53; H, 9.54; N, 6.03. Found: C, 77.73; H, 9.56; N, 5.72.

4.4.2.2. 4,5-Di(dodec-1-yn-1-yl)benzene-1,2-diamine (6)
To a solution of 5 (0.640 g, 1.38 mmol) in dry THF (15 mL) was added portionwise LiAlH₄ (0.420 g, 11.1 mmol) below 0 °C, and the mixture was stirred at the same temperature for 4 h under nitrogen atmosphere. Then, diethyl ether (100 mL) and water (100 mL) were added with good stirring in sequence to quench residual LiAlH₄. The organic phase was separated using a separation funnel and washed with water (200 mL) and sat. brine (200 mL). The obtained organic solution was dried over anhydrous magnesium sulfate, and evaporation of the solution to dryness afforded 6 as a red solid (0.540 g, 1.24 mmol, 90%). This product was unstable, and so used in the next step without further purification; ¹H NMR (400 MHz, CDCl₃) δ 0.88 (t, 6H, J = 7.0 Hz), 1.27–1.30 (m, 24H), 1.43–1.64 (m, 8H), 2.42 (t, 4H, J = 7.0 Hz), 3.38 (s, 4H), 6.70 (s, 2H). MALDI-TOF MS (negative mode) m/z 436 (M⁻). Anal. Calcd. for C₃₀H₄₈N₂: C, 82.51; H, 11.08; N, 6.41. Found: C, 82.66; H, 10.69; N, 6.24.

### 4.4.2.3. 9,10-Di(dodec-1-yn-1-yl)-2,5-bis(trimethylsilyl)dithieno[3,2-a:2’,3’-c]-phenazine (8)

A mixture of 6 (1.82 g, 4.17 mmol), 7 (1.51 g, 4.14 mmol) and EtOH (114 mL) was stirred at 90 °C for 4 h under nitrogen. After cooling, the solvent was removed on a rotary evaporator. The residue was dissolved in chloroform (50 mL) and washed with water (80 mL × 2) and sat. brine (80 mL). The organic layer was dried over anhydrous magnesium sulfate, and, the solvent was removed on a rotary evaporator. The residue was purified by silica gel
column chromatography using chloroform/hexane (2/1, v/v) as eluent to afford 8 as a yellow solid (2.35 g, 3.07 mmol, 74%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.48 (s, 18H), 0.89 (t, 6H, \(J = 6.8\) Hz), 1.25–1.43 (m, 24H), 1.51–1.60 (m, 4H), 1.71 (quint, 4H, \(J = 7.3\) Hz), 2.57 (t, 4H, \(J = 7.6\) Hz), 8.35 (s, 2H), 8.51 (s, 2H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 1.01, 14.11, 19.88, 22.69, 28.79, 29.01, 29.32, 29.37, 29.62, 29.68, 31.92, 79.38, 96.98, 127.28, 131.62, 132.15, 135.83, 140.35, 140.48, 140.62, 141.01; MALDI-TOF MS \(m/z\) 765 ([M + H]\(^+\)). Anal. Calcd. for C\(_{46}\)H\(_{64}\)N\(_2\)S\(_2\)Si\(_2\): C, 72.19; H, 8.43; N, 3.66. Found: C, 72.47; H, 8.77; N, 3.64.

4.4.2.4. 9,10-Didodecyl-2,5-bis(trimethylsilyl)dithieno[3,2-\(a\):2',3'-\(c\)]phenazine (9)

A mixture of 8 (0.353 g, 0.461 mmol), 10% Pd-C (0.185 g), and ethyl acetate (6.2 mL) was added to a autoclave filled with 0.3 MPa of hydrogen, and stirred at room temperature for 8 h. The reaction mixture was poured to chloroform (50 mL) in a separation funnel and washed with water (150 mL \(\times\) 2) and sat. brine (150 mL). The organic layer was dried over anhydrous magnesium sulfate, and the solvent was removed on a rotary evaporator. The residue was purified by silica gel column chromatography using chloroform as eluent to afford 9 as yellow solid (0.297 g, 0.384 mmol, 83%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.48 (s, 18H), 0.88 (t, 6H, \(J = 7.2\) Hz), 1.24–1.42 (m, 32H), 1.47–1.56 (m, 4H), 1.81 (quint, 4H, \(J = 7.7\) Hz), 2.90 (t, 4H, \(J = 8.0\) Hz), 8.11 (s, 2H), 8.56 (s, 2H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 0.07, 14.12, 22.69, 29.36, 29.45, 29.61, 29.65, 29.70, 29.80, 30.00, 30.53, 31.93, 33.06,
127.37, 131.58, 136.13, 139.75, 139.79, 140.61, 140.65, 144.64; MALDI-TOF MS m/z 773 ([M + H]+). Anal. Calcd. for C₄₆H₇₂N₂S₂Si₂: C, 71.44; H, 9.38; N, 3.62. Found: C, 71.31; H, 9.31; N, 3.55.

4.4.2.5.  2,5-Dibromo-9,10-didodecyldithieno[3,2-\(a\):2',3'-c]phenazine (10)

A mixture of 9 (0.629 g, 0.813 mmol) and N-bromosuccinimide (0.330 g, 1.85 mmol) in dry THF was stirred for 5 h at 50 °C under nitrogen atmosphere. After cooling, the solvent was removed on a rotary evaporator. The residue was dissolved in chloroform (50 mL) and washed with water (100 mL × 2) and sat. brine (100 mL). The organic layer was dried over anhydrous magnesium sulfate, and the solvent was removed on a rotary evaporator. The residual solid was purified by silica gel column chromatography using chloroform/hexane (1/2, v/v) as eluent to afford 10 as yellow solid (0.550 g, 0.699 mmol, 86%); ¹H NMR (400 MHz, CDCl₃) δ 0.86–0.90 (t, \(J = 7.0\) Hz, 6H), 1.27–1.44 (m, 32H), 1.47–1.56 (m, 4H), 1.80 (quint, 4H, \(J = 7.6\) Hz), 2.91 (t, 4H, \(J = 7.8\) Hz), 8.04 (s, 2H), 8.41 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.12, 22.70, 29.38, 29.44, 29.61, 29.64, 29.67, 29.71, 29.79, 31.93, 33.04, 112.97, 127.26, 127.52, 135.00, 137.70, 140.95, 145.45; MALDI-TOF MS m/s 788 (M⁺).

Anal Calcd. for C₄₀H₅₄Br₂N₂S₂: C, 61.06; H, 6.92; N, 3.56. Found: C, 60.90; H, 6.73; N, 3.56.
4.4.3. Preparation of 1

4.4.3.1. 8,11-Bis(9,9-dietyl-9H-fluoren-2-yl)dithieno[3,2-a:2',3'-c]phenazine (1a)

A mixture of 3 (0.228 g, 1.04 mmol), 4a (0.840 g, 1.09 mmol) and acetic acid (1 mL) in ethanol (25 mL) was stirred at 80 °C for 8 h under nitrogen atmosphere. After cooling, the solvent was removed on a rotary evaporator. The residue was extracted with chloroform-water, and the organic layer was dried by anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator, and the residue was purified by silica gel chromatography using chloroform/hexane (1:2, v/v) as eluent. Further purification by recrystallization from chloroform to hexane was carried out to obtain a yellow powder (0.830 g, 0.867 mmol, 83%); 1H NMR (400 MHz, CDCl3) δ 0.69–0.96 (m, 20H), 1.03–1.18 (m, 24H), 2.09 (t, 8H, J = 8.2 Hz), 7.34–7.43 (m, 6H), 7.47 (d, 2H, J = 5.5 Hz), 7.82 (d, 2H, J = 6.9 Hz), 7.92 (t, 4H, J = 8.5 Hz), 8.04 (s, 2H), 8.09 (s, 2H), 8.26 (d, 2H, J = 5.0 Hz); 13C NMR (100 MHz, CDCl3) δ 14.14, 22.81, 24.11, 30.03, 31.73, 40.68, 55.32, 119.49, 119.96, 123.12, 124.45, 125.40, 126.13, 126.94, 127.17, 129.70, 130.12, 135.47, 136.06, 137.87, 138.93, 140.07, 140.24, 140.66, 141.13, 150.30, 151.24; MALDI-TOF MS m/z 957 ([M + H]+). Anal. Calcd for C66H72N2S2: C, 82.80; H, 7.58; N, 2.93. Found: C, 83.13; H, 7.57; N, 2.79.

4.4.3.2. 8,11-Bis(9-(2-ethylhexyl)-9H-carbazol-3-yl)dithieno[3,2-a:2',3'-c]phenazine
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(1b)

According to the same procedure as the preparation of 1a, 1b was prepared. Purification by silica gel chromatography using chloroform/hexane (1:2, v/v) as eluent followed by recrystallization from chloroform-hexane afforded an orange powder of the target compound; yield 80%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.92 (t, 6H, \(J = 7.1\) Hz), 1.00 (t, 6H, \(J = 7.3\) Hz), 1.26–1.50 (m, 16H), 2.19–2.22 (m, 2H), 4.25–4.35 (m, 4H), 7.26–7.30 (m, 2H), 7.46–7.54 (m, 6H), 7.62 (d, \(J = 8.7\) Hz, 2H), 8.14 (dd, 2H, \(J = 1.7\) and 8.5 Hz), 8.19 (s, 2H), 8.21 (d, 2H, \(J = 7.8\) Hz), 8.26 (d, 2H, \(J = 5.1\) Hz), 8.35 (d, 2H, \(J = 1.8\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 11.08, 14.25, 23.27, 24.54, 28.98, 31.18, 39.63, 47.67, 108.46, 109.22, 119.00, 120.41, 122.81, 123.42, 123.52, 124.42, 125.44, 125.62, 129.26, 129.50, 129.83, 135.55, 135.80, 138.76, 139.74, 140.23, 140.75, 141.47; MALDI-TOF MS \(m/z\) 847 ([M + H\(^+\))]. Anal. Calcd for C\(_{56}\)H\(_{54}\)N\(_4\)S\(_2\): C, 79.39; H, 6.42; N, 6.61. Found: C, 79.58; H, 6.47; N, 6.43.

4.4.3.3. 8,11-Bis(4-hexylthiin-2-yl)dithieno[3,2-a:2',3'-c]phenazine (1c)

According to the same procedure as the preparation of 1a, 1c was prepared. Purification by silica gel chromatography using chloroform/hexane (1:3, v/v) as eluent followed by recrystallization from chloroform-hexane afforded a red powder of the target compound; yield 76%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.91 (t, 6H, \(J = 6.8\) Hz), 1.34–1.49 (m, 12H), 1.71–
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1.79 (m, 4H), 2.74 (t, 4H, J = 7.7 Hz), 7.20 (s, 2H), 7.60 (d, 2H, J = 5.0 Hz), 7.79 (s, 2H), 8.23 (s, 2H), 8.60 (d, 2H, J = 5.4 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.25, 22.76, 29.24, 30.72, 30.76, 31.89, 124.21, 124.68, 126.18, 126.31, 127.74, 131.31, 135.22, 136.40, 138.11, 138.47, 138.55, 142.70; MALDI-TOF MS m/z 624 (M$^+$). Anal. Calcd for C$_{36}$H$_{36}$N$_2$S$_4$: C, 69.19; H, 5.81; N, 4.48. Found: C, 69.02; H, 5.82; N, 4.36.

4.4.4. Preparation of 2

4.4.4.1. 2,5-Bis(9,9-dihexylfluoren-2-yl)-9,10-didodecyldithieno[3,2-a:2',3'-c]phenazine (2a)

A mixture of 10 (0.628 g, 0.798 mmol), 9,9-dihexyl-9H-fluoren-2-ylboronic acid pinacol ester (1.10 g, 2.39 mmol), Pd(PPh$_3$)$_4$ (32 mg, 0.028 mmol) and potassium carbonate (0.662 g, 4.79 mmol) in a solvent mixture of toluene (30 mL), ethanol (10 mL) and water (5 mL) was stirred at 90 $^\circ$C for 12 h under nitrogen atmosphere. After cooling, the solvent was removed on a rotary evaporator. The residue was dissolved in chloroform (50 mL) and washed with water (40 mL × 2) and sat. brine (40 mL). The obtained organic solution was dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography using chloroform/hexane (1/3, v/v) as eluent to afford 2a as a yellow solid (0.694 g, 0.536 mmol, 67%); $^1$H NMR (400 MHz,
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CDCl$_3$ $\delta$ 0.69–0.78 (m, 20H), 0.87 (t, 6H, $J$ = 6.8 Hz), 1.08–1.15 (m, 24H), 1.27–1.49 (m, 36H), 1.80–1.87 (m, 4H), 2.01–2.13 (m, 8H), 2.93 (t, 4H, $J$ = 8.0 Hz), 7.31–7.39 (m, 6H), 7.74 (dd, 2H, $J$ = 1.8 and 6.8 Hz), 7.77–7.79 (m, 2H), 7.82 (m, 2H), 7.87 (d, 2H, $J$ = 1.2 Hz), 8.15 (s, 2H), 8.73 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.11, 14.23, 22.72, 22.81, 22.88, 23.94, 29.48, 29.76, 29.79, 29.84, 29.87, 29.98, 30.07, 30.56, 31.65, 32.04, 33.19, 40.67, 55.43, 119.80, 119.97, 120.34, 120.39, 123.03, 123.37, 127.00, 127.37, 127.46, 132.71, 134.28, 135.98, 139.51, 140.62, 140.92, 141.62, 144.07, 145.05, 151.12, 151.81; MALDI-TOF MS m/z 1294 ([M + H]$^+$). Anal Calcd. for C$_{90}$H$_{120}$N$_2$S$_2$: C, 83.53; H, 9.35; N, 1.83.

4.4.4.2. 2,5-Bis(9-(2-ethylhexyl)-9$H$-carbazol-3-yl)-9,10-didodecyldithieno-[3,2-a:2',3'-c]phenazine (2b)

According to the same procedure as the preparation of 2a, 2b was prepared using 10 and 9-(2-ethylhexyl)-9$H$-carbazol-3-ylboronic acid pinacol ester. Purification by silica gel chromatography using chloroform/hexane (1/2, v/v) as eluent afforded the target compound as a red powder; yield 54%; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.87–0.95 (m, 18H), 1.29–1.49 (m, 52H), 1.77–1.84 (m, 4H), 2.04–2.10 (m, 2H), 2.83 (t, 4H, $J$ = 7.8 Hz), 4.05–4.15 (m, 4H), 7.28 (d, 2H, $J$ = 6.9 Hz), 7.37 (t, 4H, $J$ = 8.7 Hz), 7.47–7.50 (m, 2H), 7.90 (dd, 2H, $J$ = 1.8 and 8.2 Hz), 8.07 (s, 2H), 8.17 (d, 2H, $J$ = 7.8 Hz), 8.49 (d, 2H, $J$ = 1.8 Hz), 8.57 (s,
2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 10.99, 14.15, 14.23, 22.81, 23.17, 24.50, 28.89, 29.51, 29.59, 29.72, 29.82, 29.88, 29.98, 30.07, 30.20, 31.10, 32.06, 32.97, 39.47, 47.41, 109.10, 109.14, 117.69, 118.31, 119.13, 120.56, 122.86, 123.20, 124.06, 125.02, 125.91, 126.99, 133.39, 135.50, 139.09, 140.52, 140.60, 141.37, 143.94, 144.20; MALDI-TOF MS $m/s$ 1184 ([M + H]$^+$). Anal Calcd. for C$_{80}$H$_{102}$N$_4$S$_2$: C, 81.17; H, 8.68; N, 4.73. Found: C, 81.34; H, 8.72; N, 4.54.

4.4.4.3. 9,10-Didodecyl-2,5-di(thiophen-2-yl)dithieno[3,2-a:2',3'-c]phenazine (2c)

According to the same procedure as the preparation of 2a, 2c was prepared using 10 and 2-thienylboronic acid. Purification by silica gel column chromatography using chloroform/hexane (1/3, v/v) as eluent afforded the target compound as a reddish orange powder; yield 45%; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.87 (t, 6H, $J = 6.8$ Hz), 1.26–1.50 (m, 36H), 1.79–1.85 (m, 4H), 2.90 (t, 4H, $J = 7.3$ Hz), 7.10–7.12 (m, 2H), 7.34 (d, 2H, $J = 5.0$ Hz), 7.40 (d, 2H, $J = 3.6$ Hz), 8.09 (s, 2H), 8.48 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.06, 22.69, 29.28, 29.37, 29.48, 29.63, 29.73, 29.84, 30.29, 30.55, 31.95, 33.13, 120.76, 124.95, 125.61, 127.53, 128.06, 133.58, 135.98, 136.38, 137.20, 139.26, 141.03, 145.09; MALDI-TOF MS $m/s$ 793 ([M + H]$^+$). Anal Calcd. for C$_{48}$H$_{60}$N$_2$S$_4$: C, 72.68; H, 7.62; N, 3.53. Found: C, 72.51; H, 7.48; N, 3.69.

4.4.4.4. 2,5-Bis(5-dibromothiophen-2-yl)-9,10-didodecyldithieno[3,2-a:2',3'-c]
phenazine (11)

A mixture of 2c (0.159 g, 0.200 mmol) and N-bromosuccimide (0.0890 g, 0.500 mmol) in a solvent mixture of chloroform (100 mL) and acetic acid (20 mL) were stirred overnight at room temperature under nitrogen atmosphere. The solvent was removed on a rotary evaporator. The residue was dissolved in chloroform (50 mL) and washed with water (100 mL × 2) and sat. brine (100 mL). The obtained organic solution was dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator, and purification of the residue by recrystallization from toluene afforded 11 as an orange solid (0.129 g, 0.136 mmol, 68 %). Due to poor solubility of this compound in common organic solvents, the $^{13}$C NMR was not obtained; $^1$H NMR (400 MHz, CDCl$_3$) δ 0.87 (t, 6H, $J = 6.7$ Hz), 1.24–1.26 (m, 36H), 1.72–1.93 (m, 4H), 2.88–2.92 (m, 4H), 7.06 (d, 2H, $J = 3.7$ Hz), 7.13 (d, 2H, $J = 3.7$ Hz), 8.09 (s, 2H), 8.41 (s, 2H). Anal Calcd. for C$_{48}$H$_{58}$Br$_2$N$_2$S$_4$: C, 60.62; H, 6.15; N, 2.95. Found: C, 60.90; H, 6.01; N, 2.89. The MALDI-TOF mass spectrum of this compound was not obtained probably due to heavy decomposition through ionization.

4.4.4.5. 2,5-Bis(5-(9,9-dihexyl-9H-fluoren-2-yl)thiophen-2-yl)-9,10-didodecylthieno-[3,2-a:2',3'-c]phenazine (2d)

A mixture of 11 (0.095 g, 0.10 mmol), 9,9-dihexyl-9H-fluoren-2-ylboronic acid pinacol ester (0.138 g, 0.300 mmol), Pd(PPh$_3$)$_4$ (32 mg, 0.028 mmol), and potassium carbonate
(0.083 g, 0.60 mmol) in a solvent mixture of toluene (30 mL), ethanol (10 mL) and water (5 mL) was stirred at 90 ºC for 12 h under nitrogen atmosphere. After cooling, the solvent was removed on a rotary evaporator. The residue was dissolved in chloroform (50 mL) and washed with water (40 mL × 2) and sat. brine (40 mL). The organic layer was dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography using chloroform/hexane (1/2, v/v) as eluent to afford 2d as an orange solid (0.077 g, 0.053 mmol, 53%); 1H NMR (400 MHz, CDCl3) δ 0.68–0.79 (m, 20H), 0.87 (t, 6H, J = 6.8 Hz), 1.07–1.15 (m, 24H), 1.27–1.49 (m, 36H), 1.78–1.86 (m, 4H), 2.02 (t, 8H, J = 8.2 Hz), 2.89 (t, 4H, J = 7.7 Hz), 7.30–7.38 (m, 10H), 7.61–7.63 (m, 4H), 7.70–7.72 (m, 4H), 8.08 (s, 2H), 8.49 (s, 2H); 13C NMR (100 MHz, CDCl3) δ 14.14, 14.25, 22.72, 22.82, 23.94, 29.51, 29.65, 29.82, 29.84, 29.88, 30.05, 30.15, 30.21, 30.29, 31.65, 32.06, 33.04, 40.58, 55.30, 119.81, 119.89, 120.15, 120.27, 123.01, 123.60, 124.69, 125.60, 126.97, 127.03, 127.33, 132.74, 133.03, 135.80, 136.04, 136.23, 138.84, 140.67, 140.83, 141.13, 144.79, 145.01, 151.05, 151.70; MALDI-TOF MS m/z 1457 ([M + H]+). Anal Calcd. for C98H124N2S4: C, 80.71; H, 8.57; N, 1.92. Found: C, 80.73; H, 8.77; N, 1.74.

4.4.4.6. 9,10-Didodecyl-2,5-Bis(5-(9-(2-ethylhexyl)-9H-carbazol-3-yl)thiophen-2-yl)-dithieno[3,2-a:2',3'-c]phenazine (2e)
According to the same procedure as the preparation of 2a, 2e was prepared using 11 and 9-(2-ethylhexyl)-9H-carbazol-3-ylboronic acid pinacol ester. Purification by silica gel column chromatography using chloroform/hexane (1/1, v/v) as eluent afforded the target compound as a red powder; yield 58% ; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.86–0.94 (m, 20H), 1.28–1.40 (m, 50H), 1.78–1.85 (m, 4H), 2.05–2.08 (m, 2H), 2.85 (t, 4H, \(J = 7.8\) Hz), 4.11–4.12 (m, 4H), 7.28 (d, 4H, \(J = 3.7\) Hz), 7.32–7.39 (m, 6H), 7.47 (t, 2H, \(J = 7.5\) Hz), 7.71 (d, 2H, \(J = 8.6\) Hz), 8.05 (s, 2H), 8.12 (d, 2H, \(J = 7.7\) Hz), 8.29 (s, 2H), 8.40 (s, 2H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 10.98, 14.12, 14.22, 22.80, 23.15, 24.50, 28.90, 29.50, 29.81, 29.85, 29.87, 30.00, 30.09, 30.23, 30.25, 31.12, 32.05, 33.00, 39.48, 47.48, 109.18, 117.22, 119.09, 119.61, 120.51, 122.38, 122.81, 123.21, 123.68, 125.08, 125.47, 125.92, 126.90, 126.95, 132.79, 135.06, 135.59, 136.35, 138.80, 140.53, 140.72, 141.38, 144.46, 145.58; MALDI-TOF MS \(m/s\) 1347 ([M + H]\(^+\)). Anal Calcd. for C\(_{88}H_{106}N_4S_4\): C, 78.41; H, 7.93; N, 4.16. Found: C, 78.79; H, 8.14; N, 3.95.

**4.4.5. Analysis of fluorescent solvatochromism**

Using the Lippert-Mataga plots [10, 15, 23–25], fluorescent solvatochromic behavior of 1 and 2 was investigated for solvents such as hexane, toluene, dichloromethane, acetone, and DMF. The solvent polarity parameters (\(\Delta f\)) were defined according to the following
equation (1):
\[
\Delta f = \frac{(\varepsilon - 1)}{(2\varepsilon + 1)} - \frac{(n^2 - 1)}{(2n^2 + 1)} 
\]

where \( \varepsilon \) and \( n \) are dielectric constant and refractive index of a solvent, respectively. The difference in the dipole moment between the excited and ground states (\( \Delta \mu \)) was calculated from the following equation (2):
\[
\Delta \nu = \frac{2(\Delta \mu)^2}{hc r^3} \Delta f + \text{constant} 
\]

where the parameters of \( \Delta \nu, h, c, \) and \( r \) are the Stokes shift, the Planck’s constant, the velocity of light, and the Onsager radius, respectively. The Onsager radii of 1 and 2 were estimated by DFT calculations at the B3LYP/6-31G(d) level.

4.4.6. OLED fabrication

PEDOT:PSS (Clevios™ P VP CH8000, Heraeus GmbH) and PBD (Tokyo Chemical Industry Co., Ltd.) were commercially available. PVCz was purchased from Sigma-Aldrich Co., and purified by reprecipitation from THF to methanol just prior to use. Dry toluene was purchased from Kanto Chemical Co., Inc..

First, PEDOT:PSS was spin-coated on top of a patterned ITO glass substrate pretreated with UV-O3 and dried at 115 °C for 1 h. Then, a mixture of PVCz, PBD and 1b in dry toluene (PVCz; 10 mg/0.7 mL of toluene) was filtered through a 0.2 μm membrane filter.
and spin-coated onto the PEDOT:PSS layer to fabricate the emitting layer (EML). Thereafter, cesium fluoride and aluminum layers were successively vacuum-deposited on EML. The fabricated OLED was covered with a glass cap and encapsulated with a UV-curing epoxy resin. The area of the emitting part was 10 mm² (2 mm × 5 mm). The device fabrication was carried out in a glovebox filled with dry argon, except for preparation of the PEDOT:PSS layer. The device performance was operated using a Hamamatsu Photonics C-9920-11 organic EL device evaluating system.

4.5. References


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General Conclusions

In this thesis, the author developed two types of novel fluorescent materials using fused phenazines such as dibenzo[a,c]phenazine \((dhpz)\) and dithieno[3,2-\(a\):2',3'-\(c\)]phenazine \((dtpz)\). Introduction of electron donor side-arms to appropriate positions of these two structural backbones afforded novel intramolecular charge transfer (ICT)-type chromophores exhibiting intense fluorescence. In particular, their photoluminescence (PL) and electroluminescence (EL) properties were investigated, where availability of facile color tuning by modulation of the ICT electronic structures was based on appropriate combination of the electron donor and acceptor components. These fluorophores exhibited remarkable PL solvatochromism in various normal organic solvents. The Lippert-Mataga plots and TD-DFT calculations revealed that the observed PL behavior originated from the ICT transition in the D-A-D-type chromophoric system. To investigate the PL properties in a thin solid matrix, they were doped into PMMA. Furthermore, solution-processed OLEDs were fabricated using the D-A-D-type fused phenazines as fluorescent dopants. The conclusions of this thesis are summarized as follows.

In Chapter 2, three types of \(dhpz\) derivatives with a pair of fluorene side-arms at the 10,13-, 11,12-, and 2,7-positions, namely \(1a\), \(1b\), and \(1c\), respectively, were newly synthesized, and their PL properties were investigated. As the results from TD-DFT calculations, their fluorescent emission was expected to originate from HOMO-LUMO
electronic transitions showing ICT from the $\pi$-conjugation system including the fluorene side-arms to the dbpz core. As the experimental results, $1a$ showed the PL spectrum with the emission maximum ($\lambda_{PL}$) at 553 nm in dichloromethane at rt, emitting greenish yellow with an extremely high PL quantum yield ($\Phi_{PL}$) of 0.87. 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 under the same conditions. Both $1b$ and $1c$ showed lower $\Phi_{PL}$s than $1a$; 0.51 and 0.46, respectively. Thus, it was found that the difference in the positions where the fluorene side-arms are introduced gives rise to variation of the fluorescence properties. Remarkable positive solvatochromism in PL was observed for the present dbpz derivatives, indicating that the polarized excited state is stabilized by solvent reorganization. The $\lambda_{PL}$ of $1a$ ranged from 515 (green) to 574 nm (orange) when the solvent polarity was varied from hexane to DMF. Using the most emissive dbpz derivative $1a$ as an emitting dopant, the PVCz-based OLED was fabricated by a solution technique, which afforded green EL with the Commission Internationale de L'éclairage (CIE) chromaticity coordinate of (0.30, 0.57). As a result, the author demonstrated in this chapter that the dbpz skeleton is useful to develop an excellent ICT-type fluorophore applicable to a fluorescent OLED emitter.

In Chapter 3, the author synthesized novel dbpz-based $\pi$-conjugated molecules bearing a variety of electron-donating side-arms at the 10,13-positions, namely $1$–$5$, and their PL and EL properties were investigated. Especially, the author focused on development of excellent red fluorescent dyes. From the results of DFT and TD-DFT calculations, it was expected that varying the electron-donating $\pi$-conjugated side-arms allow for tune the HOMO-LUMO energy gap as well as $S_0$-$S_1$ transition energy. Indeed, the compound $1$ bearing 9-(2-ethylhexyl)-9$H$-carbazol-2-yl side-arms exhibited greenish yellow
fluorescence ($\lambda_{\text{PL}}$; 557 nm) in dichloromethane at rt. On the other hand, the \textit{dbpz} derivative bearing 9-(2-ethylhexyl)-9H-carbazol-3-yl side-arms (2) exhibited orange fluorescence ($\lambda_{\text{PL}}$; 607 nm) and the one bearing 4-hexylthiophen-2-yl side-arms (3) emitted red ($\lambda_{\text{PL}}$; 635 nm) under the same condition, both red-shifted in comparison with 1. Introduction of further \(\pi\)-extended side-arms was also examined, and 5-(9,9-dihexyl-9H-fluoren-2-yl)thiophen-2-yl and 5-(9-(2-ethylhexyl)-9H-carbazol-3-yl)thiophen-2-yl side-arms (i.e., the compounds 4 and 5) afforded deep red fluorescence at 701 (\(\Phi_{\text{PL}}\); 0.29) and 713 nm (\(\Phi_{\text{PL}}\); 0.21), respectively. The emission behaviors of these \textit{dbpz} derivatives were affected by solvent polarity, and their $\lambda_{\text{PL}}$s were significantly red-shifted as the solvent polarity increased. Moreover, the difference in the dipole moment between the ground and excited states ($\Delta\mu$) was estimated for 1–5 by employing the Lippert-Mataga plots, and relatively large $\Delta\mu$ values (8.04–12.2 debye) were obtained. Thus it was confirmed that the observed PL is based on the ICT transition. Using the developed fluorescent \textit{dbpz} derivatives as an emitting dopant, PVCz-based solution-processed OLEDs were fabricated. The devices employing 4 and 5 exhibited red EL with the CIE chromaticity coordinates of (0.64, 0.30) and (0.69 and 0.26), respectively. As for the device efficiencies, they showed deteriorated device performances. As a result, the present strategy to obtain D-A-D-type fluorophores by adjusting the ICT character allows us to tune the emission properties, and a wide range of emission colors were produced. Especially, the extension of the \(\pi\)-conjugation system of the side-arms is effective to obtain red fluorophores, although the molecular modification to improve the $\Phi_{\text{PL}}$ is also intensely required. Also, the OLED performance should be
In Chapter 4, the author developed a series of novel $dtpz$-based fluorescent molecules with a D-A-D structural basis, where electron-donating side-arms were introduced at the 8,11- and 2,5-positions ($1a$–$c$ and $2a$–$e$, respectively). TD-DFT calculations indicated that the lowest $S_0$-$S_1$ transition predominantly consists of ICT transition from the HOMO localized at the $\pi$-conjugation system containing the side-arms to the $dtpz$-localized LUMO. Indeed, in UV-vis absorption spectra of the $dtpz$ derivatives, broad bands assignable to the HOMO-LUMO ICT transition were observed in the low energy region. The photoluminescent properties were tuned by the electron-donating side-arms as well as the positions to which they were introduced. In the case of the 8,11-disubstituted $dtpz$ derivatives, the emission color changed from yellow to red in dichloromethane at at: introduction of 9,9-dihexyl-$9H$-fluoren-2-yl ($1a$), 9-(2-ethylhexyl)-$9H$-carbazol-3-yl ($1b$), and 4-hexylthiophen-2-yl ($1c$) side-arms afforded fluorescent emission at 557, 616 and 651 nm, respectively. In terms of the 2,5-disubstituted derivatives, the corresponding side-arms to $1a$–$c$ were employed for $2a$–$c$, respectively, and the $\pi$-extended side-arms such as 5-(9,9-dihexyl-$9H$-fluoren-2-yl)thiophen-2-yl and 5-(9-(2-ethylhexyl)-$9H$-carbazol-3-yl)-thiophen-2-yl groups were employed for $2d$ and $2e$. The emission color ranged from red to deep red ($\lambda_{PL}$; 630–685 nm, in dichloromethane at rt). As for the fluorescence intensity, $1a$–$c$ were more fluorescent ($\Phi_{PL}$; 0.65, 0.75, and 0.38, respectively) in comparison with $2a$–$e$ ($\Phi_{PL} < 0.23$) in dichloromethane at rt. Besides, the positive fluorescent solvatochromism was observed for the present $dtpz$ derivatives as the solvent polarity improved.
increased, indicating that the observed emission is based on the HOMO-LUMO ICT transition. The Lippert-Mataga plots for the \textit{dtpz} derivatives, yielding the $\Delta \mu$ values from 8.40 to 16.8 debye, also supported the emission based on the ICT transition. Using \textit{1b} as an emitting dopant, a PVCz-based solution-processed OLED was fabricated. Different from PL in dichloromethane, the device exhibited yellow EL, which should be caused by low polarity of PVCz as the host material. As a result, the author demonstrated that the \textit{dtpz} skeleton is applicable to development of ICT-based fluorophores as an electron-withdrawing component. It is also found that the position to which the electron-donating side-arms are introduced is a decisive factor for PL and properties such as the emission color and PL quantum yield.

From the results mentioned above, the author concludes that the luminescence properties of the D-A-D ICT-type fluorophores based on the fused phenazines are influenced dramatically by combination of electron-donating $\pi$-conjugated side-arms and the electron-withdrawing component. The author demonstrated how useful the fused phenazines such as \textit{dbpz} and \textit{dtpz}. Numerous numbers of combinations of these fused phenazines and related structural platforms with electron-donating side-arms are possible. In addition, the theoretical calculations are also found to be a reliable tool to design D-A-D-type ICT chromophores, and therefore the present researches will make a great contribution to develop novel analogous fluorophores with excellent luminescence properties, especially for organic electronic applications.
Acknowledgements

I would like to express my deepest gratitude to my supervisors Professor Shigeyuki Yagi and Professor Hiroyuki Nakazumi, without whom I would not to be where I am today. I have learned countless things and have grown as a doctor. So I sincerely appreciate their exquisite guidance, valuable discussion and the precious opportunities provided by them.

I would like to express my very great appreciation to Assistant Professor Takeshi Maeda for his kind supports and meaningful discussion. I also express my heartfelt thanks to Emeritus Professor Toyonari Sugimoto for his truehearted consideration and gracious love. Specially thanks to our lab’s secretary Miss Kaori Gonno for her kind patience and grateful help.

I also extend very special thanks to my past and present group members for great discussions, trouble-shooting, friendship and support. Thanks to Messrs. and Misses Dr. Tatsuya Shigehiro, Naoki Okamura, Yasuhiro Kawai, Qiang Chen, Natsuki Okamoto, Toshio Ueda, Yuta Nakano, Liwen Sun, Kazuya Ishiguro, Kazuaki Egawa, Yamato Kitade, Yang He, Yuichiro Hayashi, Yuya Takahashi, Hiroki Matsuura, Ayaka Ban, Ryouta Kono, Ryosuke Hiraoka, Yusuke Goto, and Yamashita Kohei for their kind supports and valuable suggestions, and all the members of Prof. Yagi’s laboratory for their helpful comments and heartwarming encouragement. Especially, I am grateful to Messrs. Dr. Tatsuya Shigehiro and Naoki Okamura, who were great teachers for me as an incoming student.

I really appreciate the international exchange office teachers for their worthy advice.
Acknowledgements

and supportive suggestions, particularly from Miss Keiko Mizobata. I also wish to express
gratitude to Japanese government for giving me financial support by JASSO scholarship.

Lastly, special thanks to my entire family, for listening to my stories, however long,
and for always expressing pride and enthusiasm for my accomplishments.

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July, 2016
List of Publications

Chapter 2

Y. He, S. Yagi, T. Maeda, H. Nakazumi

“Synthesis and Luminescent Properties of Novel Dibenzo[a,c]phenazine Derivatives with Electron-donating Side-arms”


Chapter 3

Y. He, Y. Hayashi, T. Maeda, H. Nakazumi, S. Yagi


Chapter 4

Y. He, N. Okamoto, T. Maeda, H. Nakazumi, S. Yagi

“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”