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Synthesis and photophysical properties of 1,2-diphenylindolizine derivatives: fluorescent blue-emitting materials for organic light-emitting device

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ABSTRACT: New blue-emitting materials based on 1,2-diphenylindolizine were designed and synthesized through a microwaveassisted Suzuki coupling reaction. The photophysical, electrochemical, and thermal properties of the 1,2-diphenylindolizine derivatives were investigated using UV-visible and fluorescence spectroscopy, cyclic voltammetry, thermogravimetric analysis, and differential scanning calorimetry. The 1,2-diphenylindolizine derivatives had band gaps of 3.1–3.4 eV and indicated proper emission of around 450 nm without significant difference between in solution and thin solid film. The indolizine derivatives show an enhanced thermal stability ($\Delta T_m > 100$ °C), compared with 1,2-diphenylindolizine. These results suggest the 1,2diphenylindolizine derivatives are suitable for blue-emitting materials in organic light-emitting devices. Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: indolizine derivatives; fluorescent blue-emitting material; microwave-assisted Suzuki coupling reaction; OLED

Introduction

Organic light-emitting diodes (OLEDs) are attracting scientific and industrial interests related to their promising applications in largearea, full colour, flexible display (1–4). Although OLED technology has been commercialized for small- to medium-sized displays, the development of emitting materials is still demanded for full colour display applications. In particular, blue-emitting material is considered as a key material for low power consumption and long lifetime, as purity of blue colour is essential for the control of white colour coordinates in a full colour display and the improvement of blue-emitting materials has a crucial effect on device performances such as current efficiency, operating voltage and lifetime (3,5–10).

Various fluorescent blue-emitting materials including anthracene (11–17), fluorene (18–27), pyrene (28–30), quinoline (31–33), indenopyrazine (34), and styrene derivatives (35,36) have been recently reported in order to improve device performances such as colour purity.

Recently, indolizines, 10 π -electron aromatic *N*-heterocyclic compounds, have been reported for use as luminescent materials such as for optoelectronic devices (37,38), dyes (39–41), sensors (42) and probes (43–45), Indolizines are highly fluorescent and regarded as possible candidates for emitting material in organic electronic devices. Although several applications are based on the optical properties of indolizines, only in a few studies have investigated the synthesis and optical properties of indolizine derivatives (46). In this viewpoint, we have designed and synthesized new fluorescent materials based on their indolizine moiety, which are probable for emitting blue colour in a device performance. Their photophysical and thermal properties are also fully investigated.

Experimental

Materials and methods

All reagents were used as received from commercial sources without further purification. ¹H and ¹³C NMR spectra of the samples were measured on a JNM-AL300 (JEOL) spectrometer. Chemical shifts were reported as units parts per million (ppm), and J-values were in Hz. Mass spectra were obtained by fast atom bombardment mass spectrometry (FAB-MS) using a JMS-700 (JEOL).

Synthesis

1,2-Diphenylindolizine (1). 2-Benzylpyridine (1.69 g, 10.0 mmol) and 2-bromoacetophenone (1.99 g, 10.0 mmol) in acetone (30 mL) were mixed well. The mixture was refluxed at 80 °C for

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Abbreviations: CV, Cyclic voltammetry; DFT, density functional theory; DSC, differential scanning calorimetry; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; OLED, Organic light-emitting diodes; TGA, thermal gravimetric analysis.

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4 h with stirring. The reaction mixture was then cooled to room temperature and filtered. The filter cake was dissolved in 80 °C water (50 mL). Potassium carbonate (2.10 g, 15.2 mmol) was added to the solution. The reaction mixture was refluxed at 80 °C for 8 h with stirring. After filtering, the filter cake was dissolved in hot ethanol and recrystallized. The recrystallization gave the desired product as a yellow needle-shaped solid (0.624 g, yield: 23.1%). ¹H NMR (CDCl₃, 300 MHz): δ 7.87 (d, J = 7.0 Hz, 1H), 7.47 (m, 2H), 7.33 (m, 7H), 7.22 (m, 3H), 6.78 (ddd, J=9.1, 9.1, 1.1 Hz, 1H), 6.46 (td, J=6.8, 1.0 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz): δ 135.2, 135.1, 131.0, 130.2, 129.1, 128.3, 128.2, 128.2, 126.3, 125.6, 125.0, 118.0, 117.9, 112.4, 111.3, 111.0; LR-MS (FAB, positive): calculated 269 for C₂₀H₁₅N, observed 269 for [M]⁺.

2-(4-Bromophenyl)-1-phenyl-indolizine (1a). 2-Benzylpyridine (6.32 g, 37.4 mmol) and 2,4'-dibromoacetophenone (10.0 g, 36.3 mmol) in acetone were mixed well in a reaction vessel of CEM Discover[®]. The mixture was microwave-irradiated for 60 min (temperature: 65 °C, initial setting power: 70 W) in opened-vessel mode. After cooling, the mixture was filtered with acetone. The filter cake was dissolved in 80 °C water and potassium carbonate was added to a solution. The mixture was mixed well in a CEM Discover® reaction vessel. The mixture was microwave-irradiated for 60 min (temperature: 110 °C, initial setting power: 180 W) in opened-vessel mode. After filtering, the mixture was recrystallized with ethanol. The recrystallization gave the desired product as a yellow needle-shaped solid (5.92 g, yield: 47.2%). ¹H NMR (CDCl₃, 300 MHz): δ 7.82 (d, J=7.0 Hz, 1H), 7.42-7.24 (m, 7H), 7.22-7.08 (m, 4H), 6.61 (dd, J = 9.0, 6.8 Hz, 1H), 6.43 (td, J = 6.6, 1.0 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz): δ 134.8, 134.2, 131.4, 131.2, 130.6, 130.2, 128.4, 126.9, 125.9, 125.0, 120.4, 118.1, 118.0, 112.3, 111.2, 111.1.

2-[4-(9,9-Dimethyl-9H-fluoren-2-yl)-phenyl]-1-phenyl-indolizine (2). To a solution of 2-(4-bromophenyl)-1-phenyl-indolizine (1.92 g, 5.52 mmol) and 9,9-dimethylfluorene-2-boronic acid pinacol ester (2.23 g, 6.97 mmol) in 1,4-dioxane (30 mL), cesium carbonate (5.6 mL, 2 M solution in water, 11.1 mmol) and tetrakis(triphenylphosphine)palladium (0.322 g, 0.279 mmol) were added. The mixture was microwave-irradiated for 60 min (temperature: 110 °C, initial setting power: 50 W) in opened-vessel mode in a CEM Discover[®]. After cooling, the mixture was poured into water and extracted with dichloromethane. The organic phase was separated and dried over anhydrous MgSO₄. The solvent was removed by rotary evaporation, and the trituration in methanol/THF gave the desired product (2.00 g, 78.6%). ¹H NMR (CDCl₃, 300 MHz): δ 7.83 (d, J = 7.00 Hz, 1H), 7.66 (t, J = 8.04, 7.62 Hz, 2H), 7.58 (d, J = 1.5 Hz, 1H), 7.51 (d, J = 8.00 Hz, 3H), 7.43-7.17 (m, 12H), 6.59 (dd, J=7.9, 7.5 Hz, 1H), 6.41 (td, J=6.6, 1.0 Hz, 1H), 1.44 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz): δ 154.2, 153.8, 140.0, 139.3, 138.9, 138.3, 135.2, 134.1, 131.2, 130.3, 129.38, 128.4, 127.7, 127.2, 127.0, 127.0, 125.9, 125.8, 125.0, 122.9, 121.1, 120.2, 120.0, 118.0, 117.9, 112.5, 111.3, 111.0, 46.9, 27.2; HR-MS (FAB, positive): calculated 461.2143 for C₃₅H₂₇N, observed 461.2149 for [M]⁺.

2-[4-(9,9-Diphenyl-9H-fluoren-2-yl)-phenyl]-1-phenyl-indolizine (3). To a solution of 2-(4-bromophenyl)-1-phenyl-indolizine (1.89 g, 5.42 mmol) and 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-diphenyl-9H-fluorene (3.15 g, 7.08 mmol) in *N*-methyl-2-pyrrolidone (30 mL), cesium carbonate (5.5 mL, 2 M solution in water, 11.0 mmol) and tetrakis(triphenyl-phosphine)palladium (0.313 g, 0.271 mmol) were added. The mixture were

microwave-irradiated for 60 min (temperature: 170 °C, initial setting power: 50 W) in opened vessel mode at CEM Discover[®]. After cooling, the mixture was poured into water and extracted with dichloromethane. The organic phase was separated and dried over anhydrous MgSO₄. The solvent was removed by rotary evaporation and from the triturate in methanol/THF, we obtained the desired product (1.75 g, 55.0%). ¹H NMR (CDCl₃, 300 MHz): δ 7.89 (d, J = 7.00 Hz, 1H), 7.79 (t, J = 8.4, 8.07 Hz, 2H), 7.64–7.59 (m, 2H), 7.49–7.25 (m, 15H) ,7.23–7.20 (m, 7H), 6.67 (ddd, J = 9.0, 6.4, 1.0 Hz, 1H), 6.48 (td, J = 6.8, 1.0 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz): δ 151.8, 151.4, 145.9, 140.3, 139.8, 139.3, 139.0, 135.1, 134.2, 131.2, 130.3, 129.3, 128.3, 128.2, 128.1, 127.6, 127.5, 126.9, 126.6, 126.4, 126.2, 125.7, 124.9, 124.6, 120.4, 120.16, 117.89, 112.41, 111.25, 111.05; HR-MS (FAB, positive): calculated 585.2456 for C₄₅H₃₁N, observed 585.2457 for [M]⁺.

Diphenyl-[4'-(1-phenyl-indolizin-2-yl)-biphenyl-4-yl]-amine (4). To a solution of 2-(4-bromophenyl)-1-phenyl-indolizine (3.00 a, 8.63 mmol) and 4-(diphenylamino)phenylboronic acid(3.61 g, 12.5 mmol) in 1,4-dioxane (17.5 mL), cesium carbonate (17 mL, 1.5 M solution in water, 26.0 mmol) and tetrakis(triphenyl-phosphine)palladium (0.397 g, 0.344 mmol) were added. The mixture was microwave-irradiated for 60 min (temperature: 110 °C, initial setting power: 80 W) in opened-vessel mode in a CEM Discover®. After cooling, to the mixture was added to dichloromethane and water. The organic phase was washed with saturated NaHCO₃ and brine. The organic layer was dried using anhydrous MgSO₄. After removal of the solvent, the residual was purified over silica gel using hexane/dichloromethane (v/v, 20:1 to 5:1) to yield as a yellow solid (2.79 g, 63.2%). ¹H NMR (CDCl₃, 300 MHz): δ 7.88 (d, J = 7.00 Hz, 1H), 7.48–7.45 (m, 6H), 7.36–7.30 (m, 6H), 7.27 (s, 1H) ,7.22 (d, J=1.50 Hz, 3H), 7.12-7.09 (m, 6H), 7.00 (t, J=7.32, 6.96 Hz, 2H), 6.65 (dd, J=9.0, 6.4 Hz, 1H), 6.47 (td, J=6.8, 0.9 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz): δ 147.7, 147.0, 138.3, 135.2, 134.8, 133.7, 131.2, 130.3, 129.3, 129.2, 128.4, 127.8, 127.5, 126.4, 125.7, 125.0, 124.3, 124.0, 122.8, 118.0, 117.9, 112.4, 111.3, 111.0; HR-MS (FAB, positive): calculated 512.2252 for C₃₈H₂₈N₂, observed 512.2255 for [M]⁺.

9-Phenyl-3-[4-(1-phenyl-indolizin-2-yl)-phenyl]-9H-carbazole (5). To a solution of 2-(4-bromophenyl)-1-phenyl-indolizine (0.812 g, 2.33 mmol) and 9-phenyl-3-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-9H-carbazole (1.13 g, 3.06 mmol) in N-methyl-2-pyrrolidone (20 mL), cesium carbonate (5.5 mL, 2 M solution in water, 11.0 mmol) and tetrakis (triphenyl-phosphine) palladium (0.142 g, 0.122 mmol) were added. The mixture was microwaveirradiated for 60 min (temperature: 170 °C, initial setting power: 50 W) in opened-vessel mode in a CEM Discover®. After cooling, the mixture was poured into water and extracted with dichloromethane. The organic phase was separated and dried over anhydrous MgSO₄. The solvent was removed by rotary evaporation. From the triturates in methanol/THF, we obtained the desired product (0.828 g, 69.5%). ¹H NMR (CDCl₃, 300 MHz): δ 8.29 (d, J = 1.8 Hz, 1H), 8.10 (d, J = 7.70 Hz, 1H), 7.84 (d, J = 7.00 Hz, 1H), 7.59-7.49 (m, 7H), 7.43-7.27 (m, 13H), 7.24 (m, 2H), 6.60 (dd, J = 9.0, 6.4 Hz, 1H), 6.42 (t, J = 6.4 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz): δ 141.3, 140.3, 139.7, 137.6, 135.3, 133.5, 133.1, 131.2, 130.3, 129.9, 129.4, 128.4, 127.9, 127.5, 127.0, 127.0, 126.1, 125.7, 125.3, 125.0, 123.4, 123.5, 120.3, 120.0, 118.5, 118.0, 117.9, 111.3., 111.0, 110.0, 109.9; HR-MS (FAB, positive): calculated 510.2095 for C₃₈H₂₆N₂, observed 510.2100 for [M]⁺.





Scheme 1. Structures of 1–5 and their synthetic routes; (a) acetone, reflux, 4 h; (b) K₂CO₃, H₂O, reflux, 8 h; (c) Pd(PPh₃)₄, Cs₂CO₃, NMP (2,3), MW, 1 h, 170 °C or 1,4-dioxane (4,5), MW, 1 h, 110 °C . MW = microwave, NMP = *N*-methyl-2-pyrrolidone.



Figure 1. The absorption spectra and fluorescence spectra of (a) compound 1, (b) compound 2, (c) compound 3, (d) compound 4, (e) compound 5. (f) Photograph shows the fluorescence of compounds (1–5) in dichloromethane taken under a laboratory UV lamp ($\lambda_{ex} = 365 \text{ nm}$) irradiation.

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UV-visible light and photoluminescence (PL) measurement

UV-visible spectra were measured on **a** JASCO V-560 UV-vis. spectrophotometer at ambient temperature. A cuvette with a 1-cm path length (Quarts SUPRASIL 105B-QS) was used for measuring samples that were prepared from serial dilution of a sample stock solution $(1.0 \times 10^{-3} \text{ mol/L})$. The concentration of dilution solution was $1.0 \times 10^{-5} \text{ mol/L}$. PL spectra were measured on an RF5301PC (Shimadzu) at ambient temperature. A cell with a 1-cm path length was used for measuring the sample, which was prepared from serial dilution of sample stock solution $(1.0 \times 10^{-3} \text{ mol/L})$. The final concentration of dilution was $1.0 \times 10^{-7} \text{ mol/L}$.

Film photoluminescence measurement

Film PL spectra were measured on a JASCO JP/FP-6500 at ambient temperature. A film sample on quartz glass was prepared from spin-coating with ACF-200 (DONG AH Trade Corp). The sample was dissolved in chlorobenzene. The stock solution (400 μ L, 4–5 × 10⁻³ mol/L) was used for preparing the spin-coated sample.

Quantum yield

The quantum yield was determined according to the HORIBA Jobin Yvon guidelines (47,48). The absorbance for the standard and the samples at the excitation wavelengths and the fluorescence spectra of the solutions were measured respectively. The areas of the integrated fluorescence intensity were plotted against the absorbance to obtain a linear plot with a gradient (Grad) that could be used to calculate the quantum yield according to following equation:

$$\Phi_{X} = \Phi_{ST} (Grad_{X}/Grad_{ST}) (\eta_{x}^{2}/\eta_{ST}^{2})$$

where ST and X denote the standard and the sample, respectively, Φ is the fluorescence quantum yield and η is the refractive index of the solvent. 9,10-Diphenylanthracene was used as the reference standard ($\Phi_{\text{ST}} = 0.90$ in dichloromethane) with an excitation wavelength at 375 nm (49).

Cyclic voltammetry (CV)

Highest occupied molecular orbital (HOMO) levels of compounds were obtained from the CV measurement. The redox potentials of compounds were measured on a E2P (BASi) with conventional three-electrode configuration, consisting of a glassy carbon working electrodes of 3 mm diameter, a platinum wire counter electrode and a non-aqueous Ag/AgNO₃ reference electrode at room temperature. The CV was carried out in deoxygenated acetonitrile containing 1 mM compound and 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte and the scan rate was 100 mV/s. The $E_{1/2}$ values were determined by ($E_{pa} + E_{pc}$)/2, where E_{pa} and E_{pc} are the anodic and cathodic peak potential, respectively. The followed equation,

HOMO (eV) = -4.8
$$-(E_{1/2 \text{ redox potential}} -E_{1/2} \text{ (ferrocene)})$$

where 4.8 eV is the energy level of the ferrocene reference (below the vacuum level) (50). The lowest unoccupied molecular orbital (LUMO) levels were calculated from the HOMO level and energy band gap, which was obtained from the edge of absorption spectra.

Thermal analysis

The glass-transition temperatures (T_g) , crystallization temperatures (T_c) , melting temperatures (T_m) and degradation temperatures (T_d)

| Table 1. UV-visible absorption wavelength of compounds (1–5) in various solutions and film | | | | | | | | | |
|--|----------------------------|-----|-----|----------------------------|----------|----------|----------|----------|----------|
| | Compd λ_{abs} / nm | | | λ _{em} (fwhm)/ nm | | | | | |
| | 2-MeTHF | THF | MC | ACN | 2-MeTHF | THF | MC | ACN | Film |
| 1 | 361 | 362 | 363 | 359 | 454 (81) | 455 (81) | 459 (82) | 457 (83) | 457 (86) |
| 2 | 318 | 319 | 319 | 318 | 451 (80) | 454 (79) | 456 (81) | 453 (80) | 456 (82) |
| 3 | 324 | 324 | 323 | 322 | 452 (80) | 454 (78) | 455 (80) | 455 (84) | 461 (89) |
| 4 | 343 | 343 | 345 | 341 | 452 (80) | 453 (81) | 453 (85) | 454 (81) | 457 (81) |
| 5 | 299 | 300 | 300 | 298 | 452 (81) | 456 (80) | 455 (82) | 454 (81) | 460 (87) |

| Table 2. Photophysical and electrochemical properties of compounds (1–5) | | | | | | | | |
|--|-------------------------|-----------------------------------|--------------------------|------------------------------------|--|--|--|--|
| Compd | ${\varPhi_{f}}^{a}$ (%) | E _{ox} ^b (eV) | $E_g^{opt(cal), c}$ (eV) | HOMO/LUMO ^{opt(cal)} (eV) | | | | |
| 1 | 0.41 | 0.30 | 3.1 (4.10) | 5.0 (4.92)/1.9 (0.82) | | | | |
| 2 | 0.21 | 0.30 | 3.4 (3.82) | 5.0 (4.95)/1.6 (1.13) | | | | |
| 3 | 0.23 | 0.34 | 3.4 (3.76) | 5.1 (4.94)/1.7 (1.18) | | | | |
| 4 | 0.32 | 0.29 | 3.2 (3.87) | 5.0 (4.85)/1.8 (0.98) | | | | |
| 5 | 0.15 | 0.27 | 3.4 (4.02) | 5.0 (4.90)/1.6 (0.88) | | | | |

^aMeasurement in CH₂Cl₂ solution; $\lambda_{ex} = each \lambda_{abs}^{max}$. Quantum yields (Φ_{f}) were measured using 9, 10-diphenylanthracene as a reference at room temperature.

^bThe concentration of the complexes used in these experiments was 1 mM and the scan rate was 100 mVsec⁻¹.

^cE^{opt}_a, optical band gap obtained from the onset wavelength of optical absorption in CH₂Cl₂ solution ($E_q = hc/\lambda_{onset}$).

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of the compounds were measured by carrying out differential scanning calorimetry (DSC) under a nitrogen atmosphere at heating/cooling rate of 10 °C/min using a Q-1000 (TA instruments) and thermogravimetric analysis (TGA) under a nitrogen atmosphere at a heating rate of 10 °C/min using a Q 5000 IR (TA instruments).

Theoretical calculation

Three-dimensional geometries and frontier molecular orbital energy levels of compounds (1–5) were calculated using density functional theory (DFT) at the B3LYP/6–31G (d) basis set in vacuum. All calculations were performed with GAUSSIAN 09' rev. 03



Figure 2. Cyclic voltammetry spectra (V versus $Ag/AgNO_3$) of compounds (1–5) in deoxygenated acetonitrile at scan rate 100 mV/sec.

Results and discussion

Synthesis

Scheme 1. The synthetic routes for compounds **1–5** are outlined in Scheme 1. The design idea to these compounds was straightforward: 1,2-diphenylindolizine backbone (45,51) was derived with various modifying groups and the derivatization can be easily realized by microwave-assisted Suzuki coupling reaction. The synthesis could be generalized into three steps. Firstly, the reaction of 2-benzylpyridine with 2-bromoacetophenone led to the expected pyridinium halide. Then, an intramolecular condensation by potassium carbonate followed by crystallization afforded compound **1a** with a yield of 47%. Secondly, the brominated triphenylamine, phenylcarbazole, dimethylfluorene, and diphenylfluorene were changed into boronic acid or boronic acid pinacol ester (6). Finally, the product were synthesized through a microwave-assisted Suzuki cross-coupling reaction (52).

Photophysical property

Photophysical properties of the compounds **1–5** were investigated by measuring the absorption spectra and photoluminescence spectra in various solvents (2-methyltetrahydrofuran, tetrahydrofuran, dichloromethane and acetonitrile) as well as in solid-state thin film, which was prepared by spin-coating a chlorobenzene solution on to quartz plates. As can be seen in Fig. 1, the absorption wavelength ranges from 300 nm to 365 nm. The emission wavelength of all compounds appears around 450 nm in various solvents and solid-state thin film. The absorption and the PL spectra of the synthesized materials in different solution and thin film are almost identical, except for the thin film spectra, which are red-shifted $5 \sim 10$ nm. The small differences of spectra between



Figure 3. The spatial distributions of HOMO and LUMO of compounds (1-5) from the DFT calculation (B3LYP/6-31G).

in solution and thin film suggest the absence of strong intermolecular interactions in thin films (Table 1). It also indicates that the bulky substituent and non-coplanar end-capped groups of these

| Table 3. Thermal properties (T_{g} , T_{m_i} and T_d) of compounds (1–5) | | | | | | | |
|---|----------------------------------|----------------------------------|----------------------------------|--|--|--|--|
| Compd | T _g ^a (°C) | T _m ^a (°C) | T _d ^b (°C) | | | | |
| 1 | _ | 114.02 | 213 | | | | |
| 2 | 102 | 274.75 | 299 | | | | |
| 3 | 106 | 225.45 | 358 | | | | |
| 4 | 109 | 196.44 | 359 | | | | |
| 5 | 116 | 237.45 | 350 | | | | |

^aT_g (glass-transition temperature) and T_m (melting temperature) were obtained from DSC measurements under a N₂ atmosphere at a heating rate of 10 °C min⁻¹.

 ${}^{b}T_{d}$ (decomposition temperature) was obtained from TGA measurements and corresponds to 5% weight loss.

compounds have restrained an expanded conjugation in the molecules. In other words, the twisted substituent and the attachment of bulky side-groups to the indolizine core can suppress π - π * stacking interactions of the molecules in the solid state and reduce self-quenching effects. Fluorescence quantum yields (Φ_f) of the 1,2-diphenylindolizine derivatives in dilute dichloromethane solution were measured by using 9,10-diphenylanthracene (Φ_f =0.90 in dichloromethane) as a standards The quantum yields of compounds **1–5** are shown in Table 2.

Electrochemical property

Energy levels (HOMO and LUMO) of the compounds **1–5** were studied using a CV and UV-visible spectrophotometer. The HOMO levels were determined using CV in acetonitrile solution and are shown in Fig. 2. HOMO levels of compounds **1–5** are –5.0, –5.0, –5.1, –5.0 and –5.0 eV, respectively. The CV curves of these compounds with an irreversible two-electron oxidation might be attributable to indolizine unit and substituted groups.



Figure 4. (a) TGA curves of compounds 1–5. DSC curve of (b) compound 1, (c) compound 2, (d) compound 3, (e) compound 4, and (f) compound 5.

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The LUMO levels were estimated from the HOMO levels and the optical bandgaps (E_g), which were derived by the onset wavelengths obtained from UV-visible absorption spectra of compounds **1–5** (53). Herein, the onset wavelengths of UV-visible absorption spectra of compounds **1–5** are 400, 365, 365, 388 and 365 nm, respectively. The LUMO levels of all materials were obtained from the HOMO and the optical band gaps were –1.9, –1.6, –1.7, –1.8 and –1.6 eV, respectively. The values of HOMOs, LUMOs and band gaps are summarized in Table 2.

Theoretical calculation

The corresponding HOMO of these 1,2-diphenylindolizine derivatives in S₀ state were calculated in the gas phase to approximate the solution state instead of in the condensed phase and were compared with each other in Fig. 3. Because electronic excitation from the HOMO to the LUMO produces the excited state (S₁), the orbital features provide important clues towards understanding the nature of the optically accessible excited state. In addition, the structural features offer further explanation for the disruption of the conjugation in the molecules. The calculation values of the HOMO and LUMO levels were summarized in Table 2. Figure 3 shows the spatial distributions of the compounds 1-5. The electron density of the HOMO for most compounds is localized on the indolizine unit, while that of compound **4** is mainly distributed over triphenyl amine moiety. All molecules have non-coplanar twisted conformation due to the steric hindrances between indolizine moiety and the substituted phenyl groups. Such a unique structural feature is beneficial in OLEDs application by preventing the excessive intermolecular interaction against fluorescence quenching and also by suppressing the crystallization problem to establish the uniform amorphous morphology in the film state of OLED devices (6).

Thermal property

The thermal properties of the compounds 1-5 were investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere, and the related thermal data were summarized in Table 3. With the introduction of a various substituted materials, the compounds 2-5 exhibit better thermal stability than that of compound 1. As shown in Fig. 4, decomposition temperatures (T_d), defined as the temperature at which the materials show a 5% weight loss, were measured to be 213, 299, 358, 359 and 350 °C for compounds 1, 2, 3, 4 and 5, respectively. Figure 4 shows DSC curves of the synthesized materials. The melting temperatures (Tm) of all compounds were observed to be 114, 275, 225, 196 or 237 °C, respectively. The glass-transition temperatures (T_{α}) of materials were in the range of 92–135 °C, but obvious T_q were not detected in compounds 1 and 2. The thermal stabilities (T_d) of the compounds 2-5 were better than those of compound 1 as core material, and can be improved by a sterically hindered bulky substitution at the 2-position of the indolizine, which did not have any significant spectral changes. Generally, the thermal properties of the films used in OLEDs were significantly associated with device lifetime, high efficiency, stability because Joule heating arose during device operation (3).

Conclusion

In summary, we have synthesized a series of new fluorescent emitting materials based on 1,2-diphenylindolizine as a core material. Triphenylamine, phenylcarbazole, dimethylfluorene, and diphenylfluorene were coupled to 2-(4-bromophenyl)-1-phenyl-indolizine using a palladium-catalyzed Suzuki-Miyaura reaction. Theoretical molecular orbital calculations have shown that all compounds have a non-coplanar structure. Compounds **2–5** have a blueemitting wavelength of around 450 nm and the emission wavelength of compounds **2–5** was rarely affected by solvent polarity and by the liquid/solid state. The electrochemical properties were verified through cyclic voltammetry and thermal stabilities were enhanced by attaching substituents to a core moiety. The photophysical, electrochemical, and thermal properties indicated that 1,2-diphenylindolizine derivatives would be a promising candidate as blue fluorescent emitting materials in OLEDs.

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