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A FACILE SYNTHESIS OF 2,5-DISUBSTITUTED INDOLE DERIVATIVES AS NEW FLUORESCENT DYES

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Abstract – A novel bis-arylated indole derivative, 2,5-bis(2-naphthyl)-1-methyl-1*H*-indole, was prepared and characterized. This compound shows the highly pure blue emissions both in solution and solid state which were ascribed to the expanded π-conjugation by introduction of two 2-naphthyl groups at the 2 and 5 positions on the indole ring. From X-ray crystallographic results this molecule exhibited the intermolecular CH–π interactions which consisted two dimensional (2D) herringbone structure.

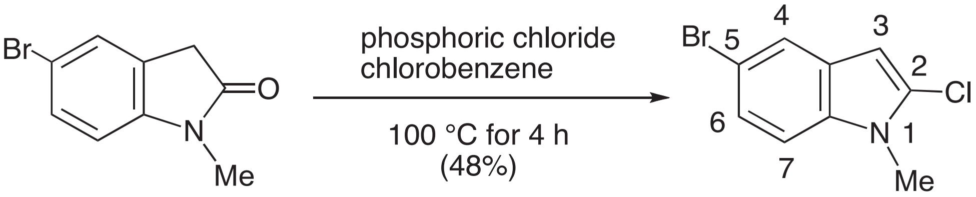
INTRODUCTION

Since Tang and Vanslyke investigated an electroluminescent device using organic materials as emitters,[1] so many compounds have been researched for new electroluminescenct (EL) materials in last two decade. Among them, carbazole was one of the most attended materials which were depended on their *p*-doping nature. For example, carbazole derivatives widely used as several color emitters,[2–4] hole-transporting materials[5–7] and host materials for phosphorescence.[8] The reasons why carbazole derivatives widely used in organic light-emitting diode's (OLED's) materials were mentioned as followings; i) Good electrochemical stability (reversible oxidation potentials were exhibited in the cyclic voltammetry measurements), ii) Good thermal stability and high glass transition temperature (T_g), iii) Easy to prepare variety of compounds (synthetic methods of carbazole based low molecular weight compounds and polymers have already established).

On the other hand, indole was well-known one of the most versatile heterocycles among biologically active natural products such as alkaloids, pharmaceuticals and marine products. Although indoles also had the *p*-doping nature, to the best of my knowledge, it had been very little studied until the present time.[9–11] Thus there is substantial interest in investigating of the synthesis of substituted indoles and studies on the electronic absorption and fluorescence emission properties of these molecules. We wish to report here synthesis and optical and electrical properties of novel 2,5-bis-aryl-1-methyl-1*H*-indoles.

RESULTS AND DISCUSSION

When 5-bromo-1-methyl-1*H*-indolin-2-one **1** was reacted with phosphoric chloride in chlorobenzene, chlorinated product, *N*-methyl-5-bromo-2-chloroindole **2**, was produced in 48% yield. The structure of **2** was elucidated based on the EI-MS, EA, ^{1}H and ^{13}C-NMR spectra and X-ray crystallographic analysis (Scheme 1 and Figure 1).



Sheme 1. Synthesis of 5-bromo-2-chloro-1-methyl-1*H*-indole **2**

The EI-MS spectrum of **2** showed the molecular ion peaks 243, 245 and 247 which suggest to include with one chlorine atom and one bromine atom, respectively. The ^{1}H-NMR spectrum in $CDCl_3$ exhibited a doublet at δ 6.40 ppm (J = 0.6 Hz) for a H_3 proton of indole ring and three signals for aromatic protons at δ 7.13 ppm (d, J = 8.6 Hz, H_7), 7.29 ppm (dd, J = 1.8, 8.6 Hz, H_6), and 7.64 ppm (dd, J = 0.6, 1.8 Hz, H_4). Single colorless crystals of the **2** suitable for X-ray crystallography were obtained by recrystallization from methanol. The perspective ORTEP drawing of **2** is illustrated in Figure 1, with the atom numbering

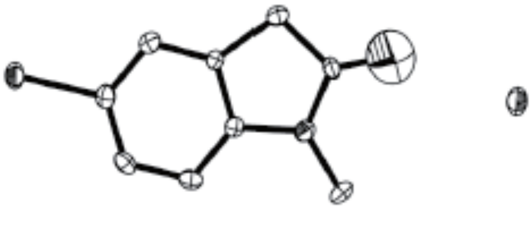
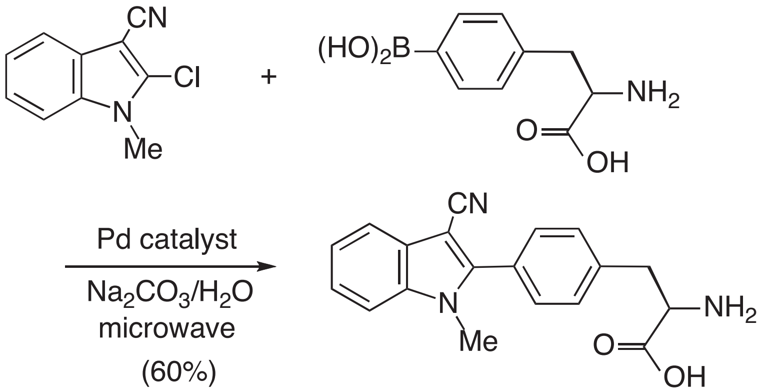


Figure 1. ORTEP drawing of **2**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

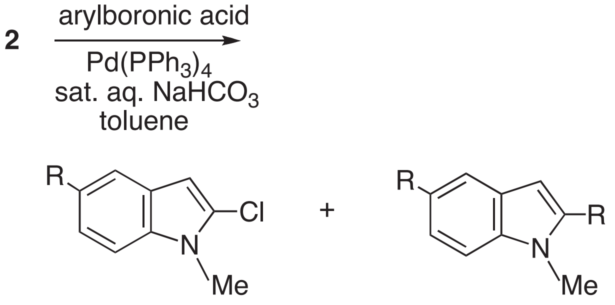
system. Compound **2** crystallized in the monoclinic space group $P2_1$/a (no. 14) and has one independent molecule ($Z = 4$) in the equivalent position.

We had seen much attention to optical properties of 5-substituted indole derivatives, therefore, we have chosen 5-bromo-2-chloro-1-methyl-1*H*-indole **2** as a key intermediate for preparing the light emitting materials. To the best our knowledge, the arylation reaction of 2-chloro-1-methyl-1*H*-indoles via the Suzuki reaction was only reported using microwave irradiation by Gong and He (Scheme 2).[12]



Scheme 2. Synthesis of 2-aryl-1-methyl-1*H*-indole

Thus, we have attempted to prepare 2,5-bis-aryl-1-methyl-1*H*-indole derivatives starting from 5-bromo-2-chloro-1-methyl-1*H*-indole **2**. In fact, arylation of **2** with phenylboronic acid under the normal Suzuki-Miyaura cross-coupling reaction gave 2,5-diphenyl-1-methyl-1*H*-indole **4a** in 58% yield. The results using several arylboronic acids to establish the limitation of the present coupling reaction were shown in Scheme 3.



3a; R= phenyl (0%)
b; R= 2-naphthyl (0%)
c; R= 1-naphthyl (75%)

4a; R= phenyl (58%)
b; R= 2-naphthyl (23%)
c; R= 1-naphthyl (0 %)

Scheme 3. Suzuki-Miyaura cross-coupling reaction of 5-bromo-2-chloro-1-methyl-1*H*-indole **2** with arylboronic acid

Similarly, when 2-naphthylboronic acid was reacted with **2**, the desired 2,5-disubstituted product, 2,5-bis(2-naphthyl)-1-methyl-1*H*-indole **4b** was produced in 23% yield. On the other hand, when 1-naphthylboronic acid was used under the same reaction conditions above, the desired 2,5-disubstituted product **4c** was not obtained. Only 5-mono-substituted product, 2-chloro-5-(1-naphthyl)-1-methyl-1*H*-indole **3c** was produced in 75% yield. From this result, it is supposed to be the steric hindrance 1-naphthylboronic and the reactivity of 2-chloro moiety of 5-bromo-2-chloro-1-methyl-1*H*-indole **2** might suppress the second Suzuki coupling reaction.

Single-crystal X-ray diffraction structures of 2-chloro-5-(1-naphthyl)-1-methyl-1*H*-indole (**3c**) and 2,5-bis(2-naphthyl)-1-methyl-1*H*-indole (**4b**) recrystallized from hexane are illustrated in Figures 2 and 3, with the atom numbering system. Compounds **3c** and **4b** both crystallized in the monoclinic space group $P2_1/n$ (no. 14). Compound **3c** has one independent molecule (Z = 2) in the equivalent position. Interestingly, the dihedral angle between indole π-face and naphthalene π-face in **3c** was 60.0°. In addition, optimized structure of **3c** was calculated using Gaussian 03, B3LYP/6-31G*. The dihedral angle between indole π-face and naphthalene π-face was also calculated to 58.1° which was relatively close to result of the X-ray crystallographic analysis (Figure 2). These findings indicate the restricted expanded π-conjugation between indole ring and naphthyl moiety due to avoid the steric hidrance diaryl linkages. On the other hand, in the case of **4b**, the dihedral angle between indole π-face and 2-position of naphthalene π-face was 32.4°.

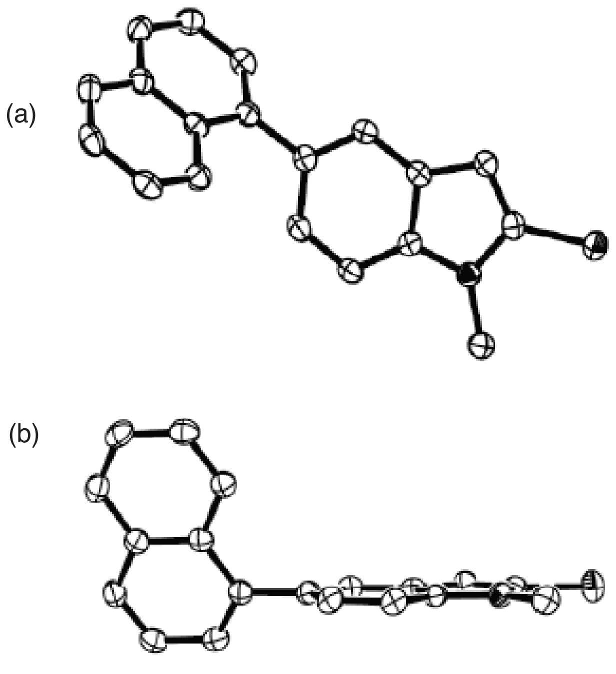


Figure 2. ORTEP drawing of **3c**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. (a) Top view. (b) Side view

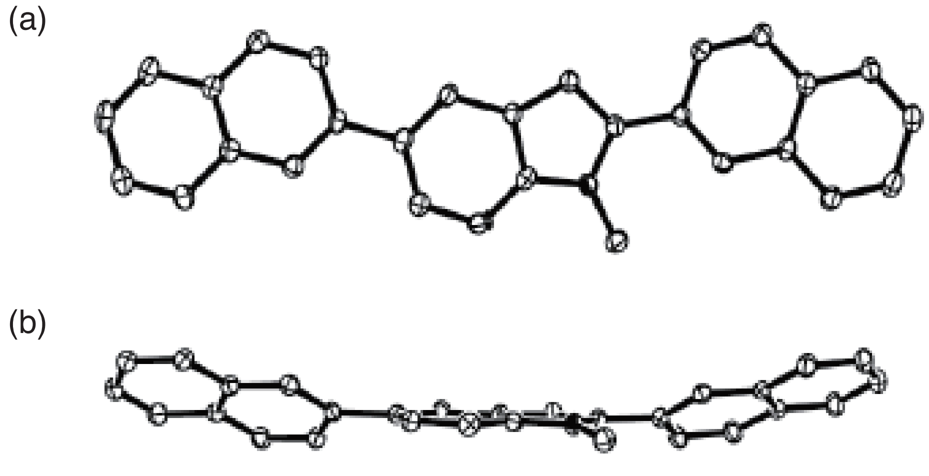


Figure 3. ORTEP drawing of **4b**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. (a) Top view. (b) Side view

The electrochemical properties of **4b** were investigated by the cyclic voltammetry measurements in CH_2Cl_2 in the presence of Bu_4NPF_6 as supporting electrolyte using a glassy-carbon working electrode and Ag/AgCl couple in electrolyte solution as the reference at room temperature. The cyclic voltammogram curve of **4b** exhibited a well-defined redox wave. Oxidation potential ($\mathbf{E^0}$) associated with generation of the cation radical were evaluated at 0.76 eV. In comparison with that of triphenyl amine which was usually used for OLEDs, the oxidation potential ($\mathbf{E^0}$) of **4b** was lower than that of triphenylamine one ($\mathbf{E^0}$= 0.92 eV). It was supposed that this indole had high donor ability and attracted as key material to design and prepare of the indole-based functional materials.

The optical properties were investigated about 2,5-bis(2-naphthyl)-1-methyl-1*H*-indole **4b** which was only emitted among the present indole derivatives. The absorption and fluorescence spectra of **4b** were shown in Figures 4 and 5. The absorption spectrum of **4b** exhibited two bands around 267 nm and 306 nm which were assigned to the $\pi \rightarrow \pi^*$ transitions (Figure 4). The fluorescence spectrum of **4b** was observed in CH_2Cl_2 in 1×10^{-6} M and solid state. The fluorescence peak in dichloromethane solution appeared mainly around 418 nm with 460 nm as a shoulder peak, and large Storks shift (102 nm) was presented. The relative quantum yield was determined to be 0.44 using quinine sulfate as the reference. The fluorescence spectrum in solid state was also appeared around 406 nm with a shoulder peak (420 nm). The much broader fluorescence spectrum and large Storks shift were characteristic of intermolecular excimer emissions.[13,14]

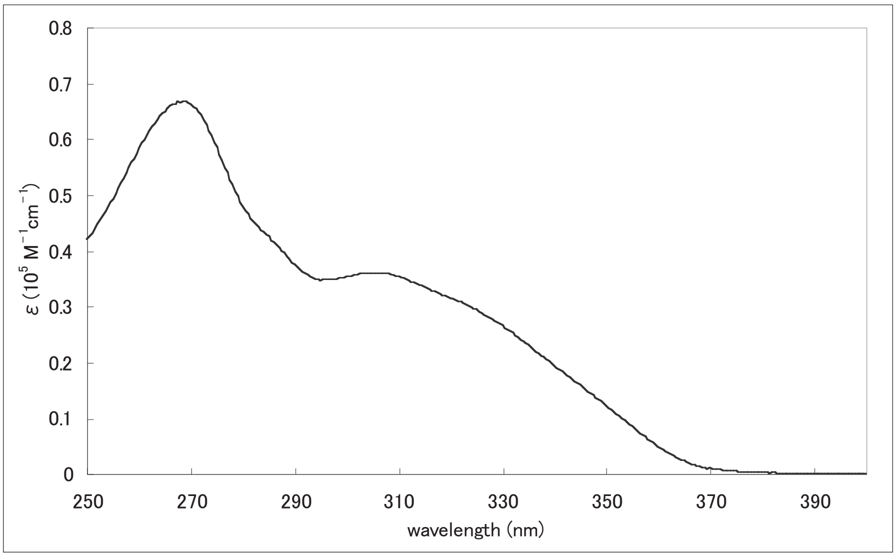


Figure 4. UV/vis spectrum of **4b** (λ_{max} 306 nm, log ε = 4.39)

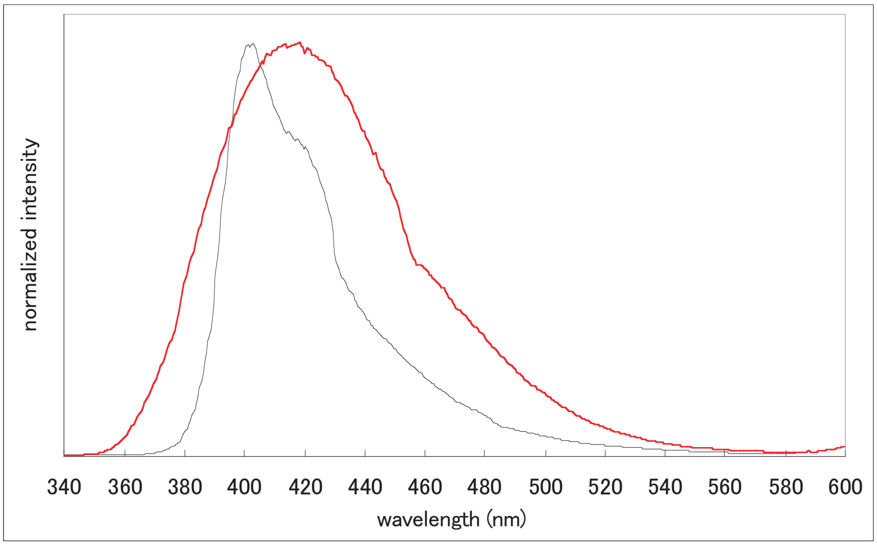


Figure 5. Fluorescence spectra of **4b** in CH_2Cl_2 (λ_{em} = 418 nm, φ = 0.44) (red line) and in solid (black line)

Since fluorescence spectra both in dichloromethane solution and solid state of **4b** suggested the excimer emissions, we have examined solid state structure. Fortunately, as mentioned previously, we have succeeded single crystal measurement of **4b**. As mentioned previously in Figure 1, 5-bromo-2-chloro-1-methyl-1*H*-indole **2** which was starting material of **4b** was shown intermolecular π-π interaction (π-π stacking) at the central indole ring. This π-π stacking was consisted one dimensional (**1D**) columnar

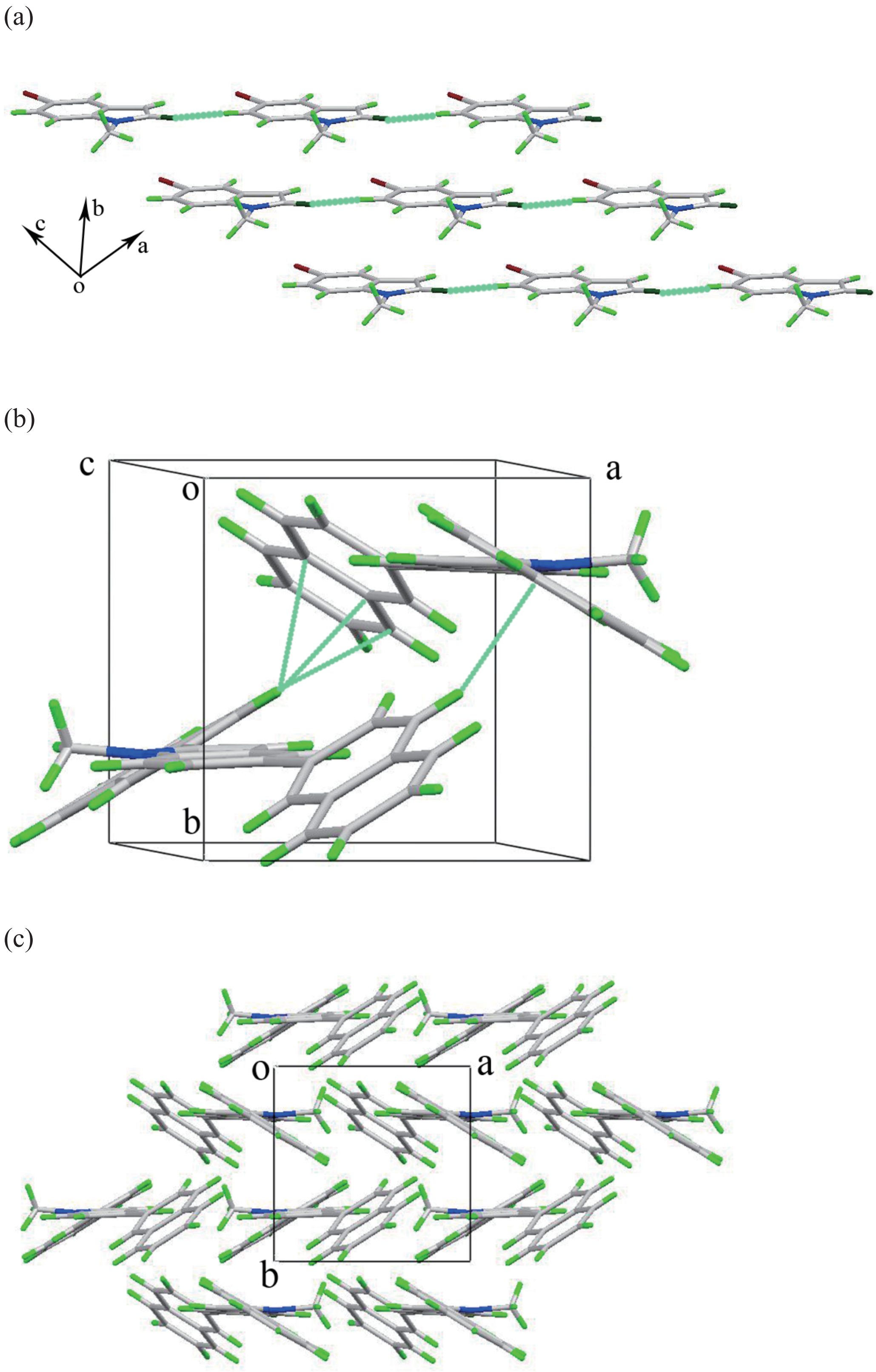


Figure 6. Illustration of crystal unit cell of **4b**. (a) view down the *b*-axis. Dashed lines are within the sum of the van der Waals radius. (b) view down reciprocal cell axis c*. Dashed lines are within the sum of the van der Waals radius. (c) Illustration of 2D herringbone structure. Dashed lines are within the sum of the van der Waals radius.

structure along with *a*-axis. On the other hand, Figure 6 showed molecular packing of **4b**. Each molecule did not have intermolecular π-π stacking between central indole ring and/or substituted naphthalene ring. Instead of π-π stacking, at the naphthalene rings which were substituted to 2 and 5 positions of central indole ring, intermolecular two dimensional (**2D**) CH–π interactions which were consisted herringbone structure[15–17] were presented. It was supposed that the expanded π-conjugation by introduction of two 2-naphthyl groups at the 2 and 5 positions on the indole ring enhanced the highly pure blue emissions of **4b** both in the solution and solid state.

CONCLUSION

We have developed a facile synthesis of novel 2,5-bis-arylated indoles, 2,5-diphenyl-1-methyl-1*H*-indole **4a** and 2,5-bis(2-naphthyl)-1-methyl-1*H*-indole **4b**. Thus, the coupling reaction of 5-bromo-2-chloro-1-methyl-1*H*-indole **2** with phenyl- or 2-naphthylboronic acid afforded the desired double coupling products, 2,5-bisaryl-1-methyl-1*H*-indoles **4** in good yields. Interestingly, the bis-arylated compound, 2,5-bis(2-naphthyl)-1-methyl-1*H*-indole **4b**, was shown the highly pure blue emissions both in the solution and solid state. The highly pure blue emission was ascribed to the expanded π-conjugation by introduction of two 2-naphthyl groups at the 2 and 5 positions on the indole ring. Interestingly, the intermolecular C-H–π interaction of naphthalene ring linked to 2 and 5 positions of central indole ring exhibited in the solid state. 2,5-Bis(2-naphthyl)-1-methyl-1*H*-indole **4b** exhibited reversible oxidation potentials ($\mathbf{E^0}$) around 0.76 V which was lower than triphenylamine ($\mathbf{E^0}$= 0.92 V) which was usually used for OLEDs. Thus, 2,5-bis(2-naphthyl)-1-methyl-1*H*-indole **4b** is promising candidates for an OLED emitting or hole-transporting materials.

EXPERIMENTAL

All melting points are uncorrected. The ^{1}H-NMR spectra were determined in $CDCl_3$ using a VARIAN Mercury 300 spectrometer. Residual solvent protons were used as the internal standard and the chemical shifts (δ) are given relative to tetramethylsilane (TMS). The coupling constants (*J*) are reported in hertz (Hz). The elemental analyses were performed at the Elemental Analytical Center, Kyushu University. The electron impact mass spectrometry (EI-MS) spectra were recorded by a JEOL JMS-70 mass spectrometer at 70 eV using a direct inlet system. The fast atom bombardment mass spectrometry (FAB-MS) spectra were recorded by a JEOL JMS-70 mass spectrometer with *m*-nitrobenzyl alcohol (NBA) as the matrix. The UV-vis spectra were measured by a JASCO V-570 spectrophotometer in a 1.0 cm wide quartz cell (0.01 mM). The fluorescence spectra were measured by a HITACHI F-4500 fluorescence spectrophotometer. The cyclic voltammetry measurements were performed by a BAS model 600 electrochemical analyzer in deaerated dichloromethane solution (0.5 mM) containing tetrabutyl ammonium hexafluoro-phosphate (0.1 M) as the supporting electrolyte at 298 K (100 mV s^{-1}). The glassy carbon working electrode was polished with BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to an Ag/AgCl (saturated KCl) reference electrode. The analytical TLC was carried out on silica gel coated glass-plate (Merck 60 F_{254}). Column chromatography was carried out on silica gel (KANTO 60 N). The reagents were purchased from commercial suppliers and used without further purification.

Materials: Preparation of 5-bromo-1-methyl-1*H*-indolin-2-one **1** was previously described.[18,19]

Preparation of 5-bromo-2-chloro-1-methyl-1*H*-indole 2. A mixture of 5-bromo-1-methyl-1*H*-indolin-2-one (**1**) (2.26 g, 10 mmol) and chlorobenzene (100 mL) was added phosphoric chloride (3.0 g) under a nitrogen atmosphere. The resulting mixture was heated at 100 °C for 4 h. The reaction mixture was cooled to room temperature and evaporated in vacuo. The residue was separated by silica gel column chromatography (KANTO 60 N) eluting with AcOEt/hexane (1:1) to give 5-bromo-2-chloro-1-methyl-1*H*-indole (**2**) (1.07 g, 48%) as a white solid. Recrystallization from hexane gave **2** as colorless prisms; mp 71–72 °C; ν_{max} (KBr)/cm^{-1}: 1669 (C=O); δ_H ($CDCl_3$) 3.71 (3H, s, *Me*), 6.40 (1H, d, *J* = 0.6 Hz, Ar*H*), 7.13 (1H, d, *J* = 8.6 Hz, Ar*H*), 7.29 (1H, dd, *J* = 1.8. 8.6 Hz, Ar*H*), 7.64 (1H, dd, *J* = 0.6, 1.8 Hz, Ar*H*); δ_C ($CDCl_3$) 30.2, 99.4, 110.9, 113.7, 122.5, 124.7, 127.5, 128.7, 135.0; *m/z* 243, 245, 247 (M^+). Anal. Calcd for C_9H_7BrClN (244.52): C, 44.21; H, 2.89; N, 5.73. Found: C, 44.40; H, 2.83; N, 5.74%.

Preparation of 2,5-diphenyl-1-methyl-1*H*-indole 4a. To a mixture of **2** (240 mg, 0.98 mmol), tetrakis(triphenylphosphine)palladium(0) (5 mol%) in toluene (80 mL), and saturated aqueous $NaHCO_3$ (40 mL) was added phenylboronic acid (720 mg, 5.90 mmol) in EtOH (5 mL) under a nitrogen atmosphere. The resulting mixture was heated at refluxing temperature for 4 h. The reaction mixture was poured into water and extracted with AcOEt (100 mL). The organic layer was washed with brine (50 mL), dried over anhydrous $MgSO_4$, and evaporated in vacuo to dryness. The residue was separated by silica gel column chromatography (KANTO 60N) eluting with $CHCl_3$ to give 2,5-diphenyl-1-methyl-1*H*-indole **4a** as a white solid (160 mg, 58%). Recrystallization from hexane gave **4a** as colorless prisms; mp 193–194 °C (dec.); ^{1}H-NMR: δ (ppm, $CDCl_3$) 3.79 (3H, s, *Me*), 6.62(1H, broad s, Ar*H*), 7.32 (1H, t, *J* = 9.3Hz, Ar*H*), 7.38–7.56 (9H, m, Ar*H*), 7.68 (2H, d, *J* = 7.2 Hz, Ar*H*), 7.86 (1H, d, *J* = 1.5 Hz, Ar*H*); MS (EI, *m/z*) 283 (M^+). Anal. Calcd for $C_{21}H_{17}N$ (283.38): C, 89.01; H, 6.05; N, 4.94. Found: C, 89.08; H, 6.00; N, 5.00%.

Preparation of 2,5-bis(2-naphthyl)-1-methyl-1*H*-indole 4b. According to a method similar to the preparation of **4b** was obtained in 23% yield from **2** as a white solid. Recrystallization from hexane gave **4b** as colorless prisms; mp 201–203 °C; ^{1}H-NMR: δ (ppm, $CDCl_3$) 3.87 (3H, s, *Me*), 6.75 (1H, s, Ar*H*), 8.1–7.2 (17H, m, Ar*H*); MS (EI, *m*/*z*) 383 (M^+). Anal. Calcd for $C_{29}H_{21}N$ (383.5): C, 90.83; H, 5.52; N, 3.65. Found: C, 90.71; H, 5.57; N, 3.62%.

Preparation of 2-chloro-5-(1-naphthyl)-1-methyl-1*H*-indole 3c. According to a method similar to the preparation of **3c** was obtained in 75% yield from **2** as a white solid. Recrystallization from hexane gave **2** as colorless prisms; mp 133–135 °C; ^{1}H-NMR: δ (ppm, $CDCl_3$) 3.83 (3H, s, *Me*), 6.51 (1H, s, Ar*H*), 7.2–7.6 (7H, m, Ar*H*), 7.8–8.0 (3H, m, Ar*H*); MS (EI, *m*/*z*) 291 and 293 (M^+). Anal. Calcd for $C_{19}H_{14}ClN$ (291.78): C, 78.21; H, 4.84; N, 4.8. Found: C, 78.19; H, 4.86; N, 4.78%.

Crystallographic data for 2, 3c, and 4b.

Crystal data for **2**・H_2O: $C_9H_9NBrClO$, $M = 262.53$, colorless needle, monoclinic, space group $P2_1/a$ (no. 14), $a = 4.598(2)$ Å, $b = 32.818(15)$ Å, $c = 6.347(3)$ Å, $\beta = 99.2288(16)°$, $V = 945.4(7)$ Å^3, $T = 123$ K, $Z = 4$, $D_c = 1.844$ g cm^{-1}, $F(000) = 520$, $\mu = 45.985$ cm^{-1}, crystal dimensions 0.15 × 0.08 × 0.06 mm^3, 8965 reflections measured on a Rigaku Saturn CCD diffractometer, of which were independent, data corrected for absorption on the basis of symmetry equivalent and repeated data (min and max transmission factors: 0.646 0.759) and Lp effects, $R_{int} = 0.042$, structure solved by direct methods (Sir2002), F^2 refinement, $R_1 = 0.0781$ for 8965 data with $F^2 > 2\sigma(F^2)$, $wR_2 = 0.2007$, $S = 1.236$ for all data, 2140 parameters.

Crystal data for **3c**: $C_{19}H_{14}ClN$, $M = 291.78$, colorless prism, monoclinic, space group $P2_1/n$ (no. 14), $a = 13.951(8)$ Å, $b = 7.007(5)$ Å, $c = 15.714(8)$ Å, $\beta = 108.45(5)°$, $V = 1457(1)$ Å^3, $T = 123$ K, $Z = 4$, $D_c = 1.330$ g cm^{-1}, $F(000) = 608$, $\mu = 2.54$ cm^{-1}, crystal dimensions 0.30 × 0.20 × 0.15 mm^3, 3311 reflections measured on a Rigaku RAXIS RAPID diffractometer, of which were independent, data corrected for absorption on the basis of symmetry equivalent and repeated data (min and max transmission factors: 0.220 0.963) and Lp effects, $R_{int} = 0.000$, structure solved by direct methods (Sir97), F^2 refinement, $R_1 = 0.0715$ for 3311 data with $F^2 > 2\sigma(F^2)$, $wR_2 = 0.1916$, $S = 1.040$ for all data, 3311 parameters.

Crystal data for **4b**: $C_{29}H_{21}N$, $M = 383.49$, colorless prism, monoclinic, space group $P2_1$ (no. 4), $a = 7.277(3)$ Å, $b = 7.214(4)$ Å, $c = 18.891(9)$ Å, $\beta = 94.04(2)°$, $V = 989.3(8)$ Å^3, $T = 123$K, $Z = 2$, $D_c = 1.287$ g cm^{-1}, $F(000) = 404$, $\mu = 0.74$ cm^{-1}, crystal dimensions 0.40 × 0.30 × 0.20 mm^3, 2419 reflections measured on a Rigaku RAXIS RAPID diffractometer, of which were independent, data corrected for absorption on the basis of symmetry equivalent and repeated data (min and max transmission factors: 0.689 0.985) and Lp effects, $R_{int} = 0.000$, structure solved by direct methods (Sir97), F^2 refinement, $R_1 = 0.0546$ for 3311 data with $F^2 > 2\sigma(F^2)$, $wR_2 = 0.1488$, $S = 1.031$ for all data, 2419 parameters.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 778128 for **2**, CCDC 778129 for **3c**, and CCDC 778130 for **4b**, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: 144-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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