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Deep blue fluorescent material with a narrow FWHM based on indolo[3,2,1-*jk*]carbazol/pyrimidine hybrids

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ABSTRACT

A series of blue fluorescent materials containing electron accepting pyrimidine and electron donating bis(biphenyl)amine, diphenylcarbazole, and diphenylindolo[3,2,1-*jk*]carbazole moieties were synthesized in moderate yields, and their optical and electrochemical properties were investigated. Diphenylindolo[3,2,1-*jk*]carbazole was revealed to be a promising building block for deep blue fluorescent materials with a very narrow full width at half maximum.

1. Introduction

Small-molecule fluorescent dyes are widely utilized for various applications such as fluorescent indicators [1], fluorescent probes for bioimaging [2], fluorescent sensors for metal ions [3], solar cells [4], organic laser dyes [5], and emitting materials of organic light emitting diodes (OLEDs) [6]. Therefore, several research studies have been actively conducted on the development of novel functional building blocks and into the optimization of molecular structures to create small-molecule materials with desired luminescent properties for application in various fields.

In the field of organic electronics, π-conjugated *N*-containing heteroaromatic compounds are essential as organic semiconductor materials for OLEDs [7], organic field-effect transistors (OFETs) [8], organic nonlinear optical devices (ONLOs) [9], and organic photovoltaics (OPVs) [10]. In particular, the carbazole skeleton, as represented by CBP (4,4′-di(9*H*-carbazol-9-yl)-1,1′-biphenyl) derivatives [11] and PVK (polyvinylcarbazole) has been most extensively used as a functional building block of host materials and hole transport materials for organic electronics devices [12]. Furthermore, the carbazole skeleton is used as a building block for emitting materials that exhibit thermally activated delayed fluorescence (TADF), where Adachi et al. developed TADF polycarbazolyl-substituted dicyanobenzenes and successfully realized highly efficient OLEDs [13].

Phosphorescent materials have recently become the dominant emitting materials of OLEDs, while the development of TADF materials [14] and hyperfluorescence systems [15] has focused on fluorescent materials, as TADF materials have already achieved comparable external quantum efficiencies to those of phosphorescent materials. However, the development of deep blue emitting materials for OLEDs, using either TADF materials or conventional fluorescent materials, remains a challenge, and so the development of blue OLEDs exhibiting higher color gamuts and improved color rendering capabilities is desirable [6b,16]. Thus, the combination of a compact conjugation system, a high fluorescent quantum yield, and stability against a high excitation energy, which are required to achieve deep blue emission, is difficult to achieve [16].

In this context, several reports have been published into the development of deep blue emitters exhibiting high fluorescent quantum yields through the combination of a small aromatic donor and an acceptor [17]. This type of ambipolar architecture is suitable for emitting dopants in OLEDs because it acts as a charge trapping

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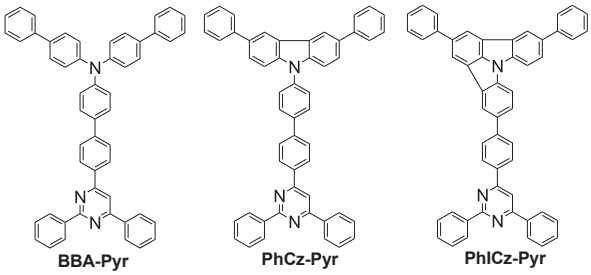


Fig. 1. Molecular structures of **BBA-Pyr**, **PhCz-Pyr**, and **PhICz-Pyr**.

site in the emitting layer, and effective electron-hole recombination at the dopant is achieved. In addition, the distinct donor/acceptor architecture provides a small energy gap between S_1 and T_1, and so TADF can be expected to occur [18].

However, the key structural feature of a typical TADF molecule is usually a diphenylamine or 9*H*-carbazole/acceptor hybrid, and so further investigation is required to find a more effective building block. Recently, it was revealed that indolo[3,2,1-*jk*]carbazole not only functions as an electron donor for ambipolar hosts [19], but that it also acts as an electron acceptor for blue TADF emitters [20]. Therefore, indolo[3,2,1-*jk*]carbazole can be considered particularly attractive and promising as a fully planar ambipolar building block; however, the number of reports into its application as a blue emitter for OLEDs are limited.

Thus, we herein focus on indolo[3,2,1-*jk*]carbazole due to its wide band gap and distinctive structure, and a novel emitter **PhICz-Pyr** is developed through its combination with pyrimidine. Analogues bearing the conventional amine and carbazole units instead of indolo[3,2,1-*jk*]carbazole, i.e., **BBA-Pyr** and **PhCz-Pyr**, are also synthesized, and the three compounds are compared to determine the applicability of indolo[3,2,1-*jk*]carbazole as a building block for an ambipolar deep blue emitter (Fig. 1).

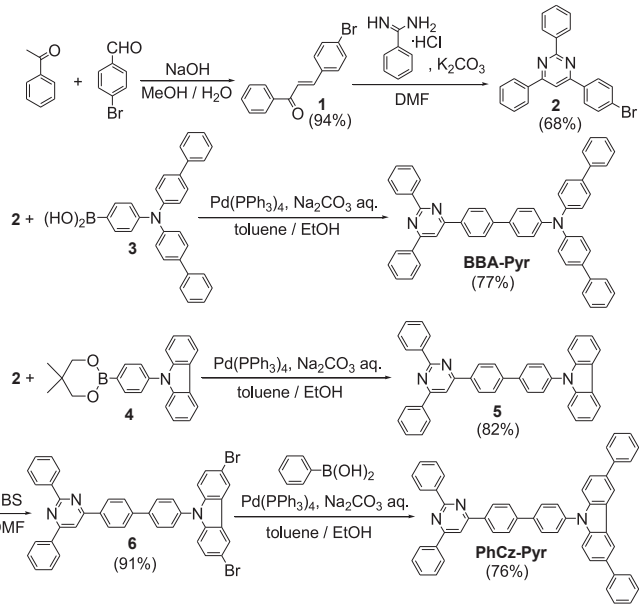
2. Results and discussions

The only structural differences between the three molecules presented in Fig. 1 are the presence of intramolecular C—C bonds that neighbor the C—N bonds in the electron donating moiety. Thus, a comparison of the properties of these materials provides pure information relating to the effect of the ortho-linkage through the application of increasingly planarized triarylamine donors to a pyrimidine acceptor.

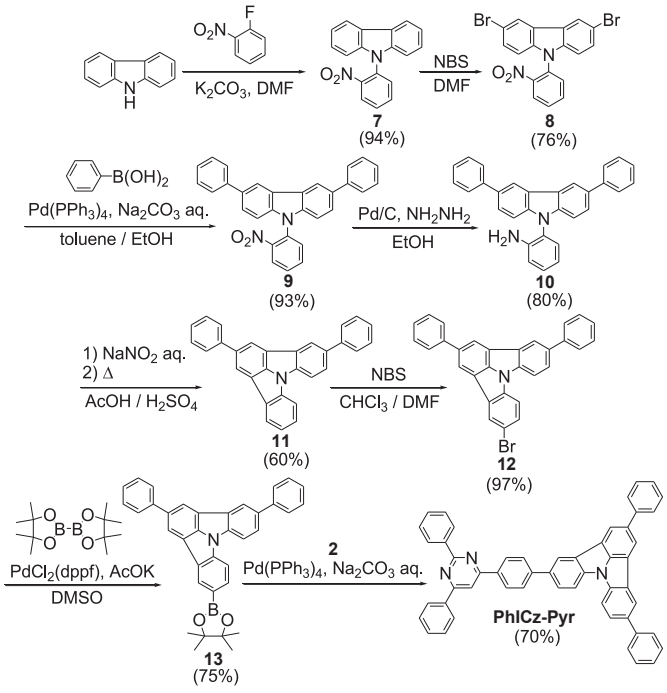
The synthetic routes to **BBA-Pyr** and **PhCz-Pyr** are shown in Scheme 1.

Initially, an aldol condensation between acetophenone and 4-bromobenzaldehyde gave bromochalcone **1**, and this was followed by cyclization with benzamidine to afford the common precursor **2** for **BBA-Pyr**, **PhCz-Pyr**, and **PhICz-Pyr**. **BBA-Pyr** was synthesized by the Suzuki-Miyaura coupling reaction of **2** and dibiphenylaminophenyboronic acid **3** in a moderate yield. The same coupling reaction of **2** and 1,3,2-dioxaborinanylphenyl-9*H*-carbazole **4** gave pyrimidinylbiphenyl-9*H*-carbazole **5**, which was followed by bromination and coupling with phenylboronic acid to afford **PhCz-Pyr** in a similar yield as **BBA-Pyr**.

The synthesis of **PhICz-Pyr** was performed according to the procedure outlined in Scheme 2. The nucleophilic aromatic substitution of 2-fluoronitrobenzene with potassium carbazolide afforded 9-(2-nitrophenyl)-9*H*-carbazole (**7**). This was followed by bromination, a Suzuki-Miyaura coupling reaction with phenylboronic acid, and reduction using Pd/C-hydrazine to give 9-(2-aminophenyl)-3,6-diphenyl-9*H*-carbazole (**10**). Diazotization and



Scheme 1. Syntheses of **BBA-Pyr** and **PhCz-Pyr**.



Scheme 2. Synthesis of **PhICz-Pyr**.

subsequent pyrolysis of **10** afforded 2,11-diphenylindolo[3,2,1-*jk*]carbazole (**11**), which was converted to 2,11-diphenyl-5-dioxaborolanylindolo[3,2,1-*jk*]carbazole **13** by bromination and reaction with bis(pinacolato)diboron using a Pd(II) catalyst. **PhICz-Pyr** was synthesized by the Suzuki-Miyaura coupling reaction between **2** and **13** in a moderate yield.

These compounds were thermally stable and easily purified by sublimation. Thus, all analyses were performed using sublimed compounds. Glass transition temperature (T_g) of **PhICz-Pyr** couldn't be determined due to high crystallinity, while **BBA-Pyr** and **PhCz-Pyr** were determined to 123 and 142 °C respectively on

Table 1
Thermal and optical properties of **BBA-Pyr**, **PhCz-Pyr**, **PhICz-Pyr** and TBPe as a reference.

Compounds	T_m/°C [a]	T_g/°C [a]	T_d/°C [b]	$\Delta E(S_1-S_0)$/eV [c]	$\Delta E(T_1-S_0)$/eV [d]	φ [e]	λem/nm [e]	CIE1931x [e]	CIE1931y [e]	FWHM/meV (nm) [e]
BBA-Pyr	253	123	447	2.64	2.55	0.81	452	0.133	0.107	48.4 (60)
PhCz-Pyr	310	142	459	2.95	2.70	0.75	412	0.146	0.051	49.2 (61)
PhICz-Pyr	358	n.d.	478	2.95	2.83	0.52	404	0.154	0.034	26.6 (33)
TBPe	- [f]	- [f]	- [f]	2.68 [22]	1.53[22]	- [f]	465	0.125	0.225	46.8 (58)

[a] determined by DSC measurement.
[b] 5% weight loss on TG measurement under N_2.
[c] determined by onset wavelength on UV/Vis absorption spectrum.
[d] determined by highest energy peak of phosphorescence spectrum.
[e] measured in 1×10^{-8} M toluene solution.
[f] - sign means not measured.

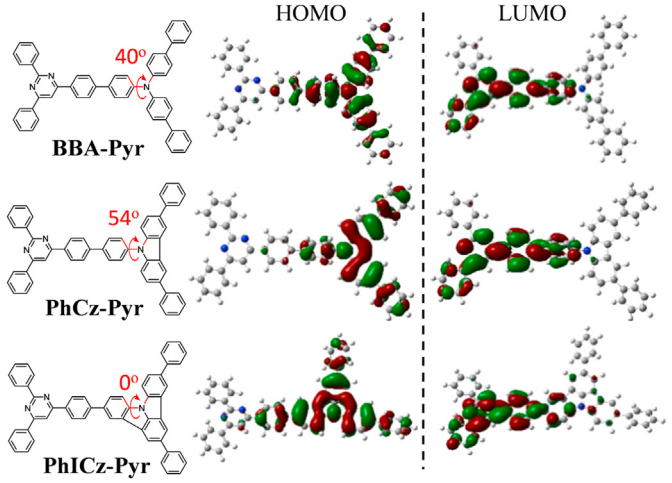


Fig. 2. Spatial distributions of the HOMO and LUMO molecular orbitals of **BBA-Pyr**, **PhCz-Pyr**, and **PhICz-Pyr** determined by DFT calculations (structural optimization: B3LYP/6-31G*; energy calculation: CAM-B3LYP/6−311++G**).

DSC (Table 1, Figure S56). The thermal decomposition temperature (T_d) determined on TG were 447, 459, and 458 °C for **BBA-Pyr**, **PhCz-Pyr**, and **PhICz-Pyr** respectively (Table 1, Figure S57), and the tendency corresponds to structural rigidity.

The spatial distributions of the HOMOs and LUMOs calculated by the Gaussian 09 molecular simulation program are illustrated in Fig. 2. The density functional theory (DFT) calculation was performed using a new hybrid exchange−correlation functional using the Coulomb-attenuating method (CAM-B3LYP/6−311++G**).[21] For all compounds, the HOMOs were localized on the electron donating triarylamine and carbazole moieties, while the LUMOs were localized on the electron accepting pyrimidine unit. **PhCz-Pyr** showed the most localized and spatially separated molecular orbitals, and the tendency toward localization on **PhICz-Pyr** was the weakest. The dihedral angle of optimized structure between donor and acceptor units were 40°, 54°, and 0° respectively, and are in good agreement with the tendency of molecular orbital (MO) localization.

The ultraviolet/visible (UV/Vis) absorption spectral differences of these compounds clearly reflect their structural features. More specifically, the optical bandgaps ($\Delta E(S_1-S_0)$) estimated from the wavelengths of the absorption onsets were 2.64, 2.95, and 2.95 eV for **BBA-Pyr**, **PhCz-Pyr**, and **PhICz-Pyr**, respectively (Fig. 3b and Table 1). These values indicate that the HOMO level of the bis(biphenyl)amino group is significantly shallower than those of the diphenylcarbazole and diphenylindolo[3,2,1-*jk*]carbazole groups.

The triplet excitation energies ($\Delta E(T_1-S_0)$) determined by the highest energy peak of phosphorescent spectra were 2.55, 2.70, and

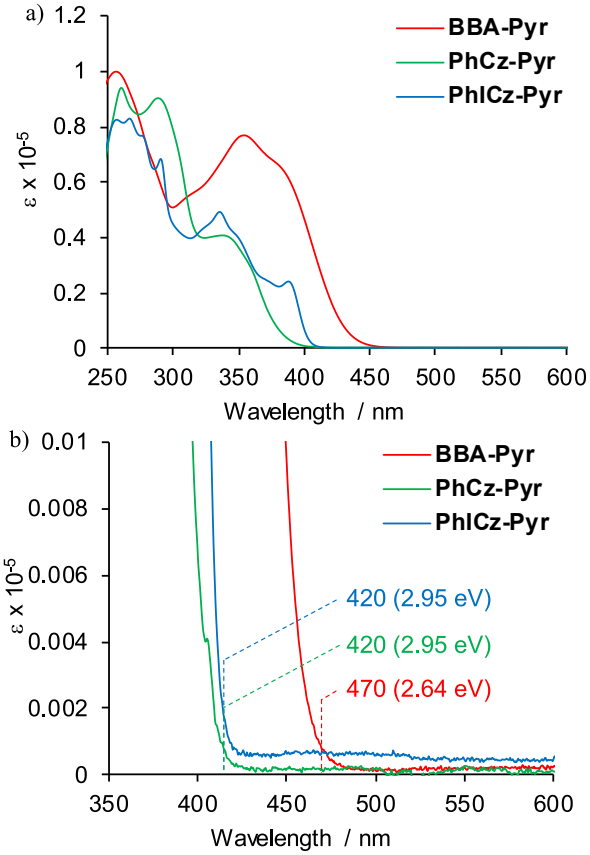


Fig. 3. a) UV/Vis absorption spectra of **BBA-Pyr**, **PhCz-Pyr**, and **PhICz-Pyr**, and b) an enlarged view around the absorption onset (dichloromethane, 1×10^{-5} M, 10 mm width cell).

2.73 eV for **BBA-Pyr**, **PhCz-Pyr**, and **PhICz-Pyr** respectively (Table 1, Figure S58). Interestingly, $\Delta E(T_1-S_0)$ of **PhICz-Pyr** was comparable with **PhCz-Pyr** although its conjugated planar architecture.

The fluorescence spectra of diluted toluene solutions (1.0×10^{-8} M) of these compounds and of 2,5,8,11-tetra-*tert*-butylperylene (TBPe) for comparison are shown in Fig. 4. **BBA-Pyr** exhibited its emission spectrum at the longest wavelength region among the various compounds, with the exception of TBPe. This result is reasonable since it also has the narrowest optical bandgap. In contrast, **PhICz-Pyr** showed an extremely sharp emission spectrum with an FWHM of only 33 nm, which is approximately half that of the other compounds, and the peak wavelength was significantly shorter than that of **PhCz-Pyr**, although the optical bandgaps of these compounds are identical (Fig. 4a, Table 1). This result is presumably due to the effective suppression of vibrational

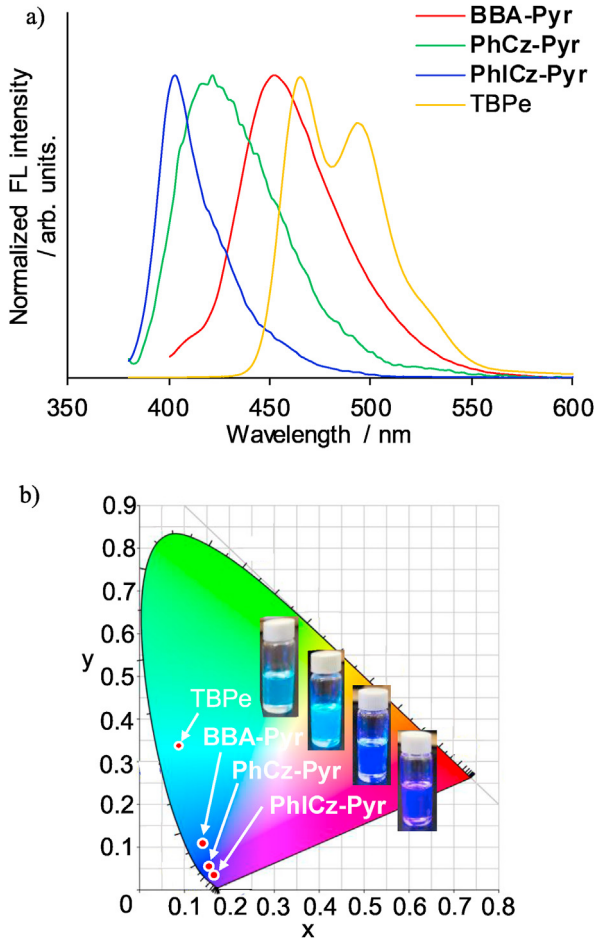


Fig. 4. a) Normalized fluorescence spectra of **BBA-Pyr**, **PhCz-Pyr**, **PhICz-Pyr**, and TBPe in toluene, and b) their CIE coordinates. (1×10^{-8} M, $\lambda_{ex} = 365$ nm).

relaxation by the rigid backbone of indolo[3,2,1-*jk*]carbazole. The Commission Internationale de l'Éclairage (CIE) coordinates are (0.133, 0.107), (0.146, 0.051), and (0.154, 0.034) for **BBA-Pyr**, **PhCz-Pyr**, and **PhICz-Pyr**, respectively (Fig. 4b, Table 1). Notably, **PhCz-Pyr** and **PhICz-Pyr** exhibited a small CIE(y) of <0.1, which is required for emitting materials of high color gamut displays. In addition, the fluorescence quantum yield (φ) of **PhICz-Pyr** (0.52) was significantly lower than those of **BBA-Pyr** (0.81) and **PhCz-Pyr** (0.75) (Table 1), which suggests that the electronic structure of indolo[3,2,1-*jk*]carbazole is radically different from those of the amine and 9*H*-carbazole derivatives.

In order to discuss the influence of triplet exciton, the effect of oxygen on fluorescence spectra was investigated. At first, the fluorescence spectra of toluene solutions were recorded under air. Then the solutions were deaired by bubbling of toluene-saturated N_2 gas for 5 min, and the measurements were performed immediately. After that, the solutions were exposed to air for 10 min and the spectra were recorded.

For all cases, the increasing of fluorescent intensity was observed upon N_2 bubbling, and no spectral difference was confirmed in comparison with the first and last measurements performed under air (Fig. 5). The increasing percentages of fluorescent intensity were 10%, 5%, and 20% for **BBA-Pyr** (Fig. 5a), **PhCz-Pyr** (Fig. 5b), and **PhICz-Pyr** (Fig. 5c) respectively, and **PhICz-Pyr** exhibited the most significant change among them. Therefore, the less fluorescence quantum yield (φ) of **PhICz-Pyr** under air can be

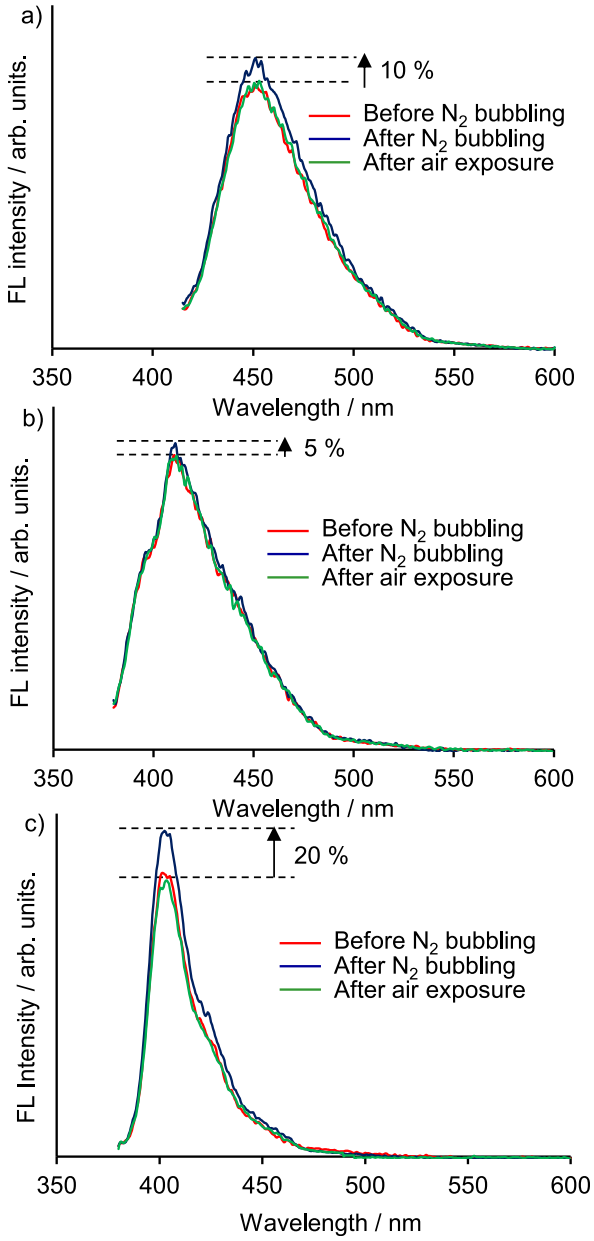


Fig. 5. Effect of oxygen on fluorescence spectra: a) **BBA-Pyr**; b) **PhCz-Pyr** c) **PhICz-Pyr** (toluene, 1×10^{-8} M, $\lambda_{ex} = 365$ nm).

assumed to this behavior.

These results suggest that these compounds exhibit reverse intersystem crossing (RISC), and it can be supported by small $\Delta E(S_1\text{-}T_1)$ of these compounds (90, 250, and 120 meV for **BBA-Pyr**, **PhCz-Pyr**, and **PhICz-Pyr**, Table 1). Thus, it was suggested that the small $\Delta E(S_1\text{-}T_1)$ of **PhICz-Pyr** resulted in a large KISC (intersystem crossing) and a large KRISC and caused the low fluorescence quantum yield of **PhICz-Pyr**.

The fluorescent spectra of these compounds demonstrated solvatochromism, and the degrees of spectral dependence on the polarity of the solvents were both significant and distinct (Fig. 6). In order to discuss about spectral intensity, the excitation wavelength was set to 365 nm which is the wavelength at which no solvent absorption and the molar extinction coefficients of all compounds are unaffected by the solvent (Figure S59). More specifically, **PhCz-Pyr** exhibited the most remarkable spectral change, and emission

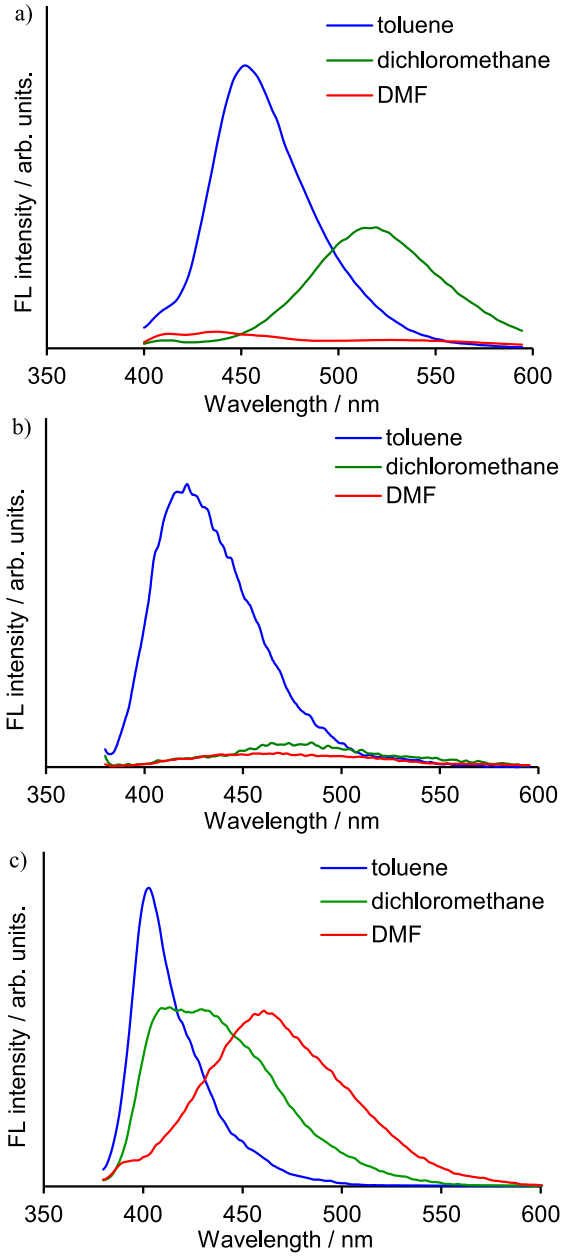


Fig. 6. Solvatochromism of fluorescence spectra of a) **BBA-Pyr**, b) **PhCz-Pyr**, and c) **PhICz-Pyr** in toluene, dichloromethane, and DMF (1×10^{-8} M, $\lambda_{ex} = 365$ nm).

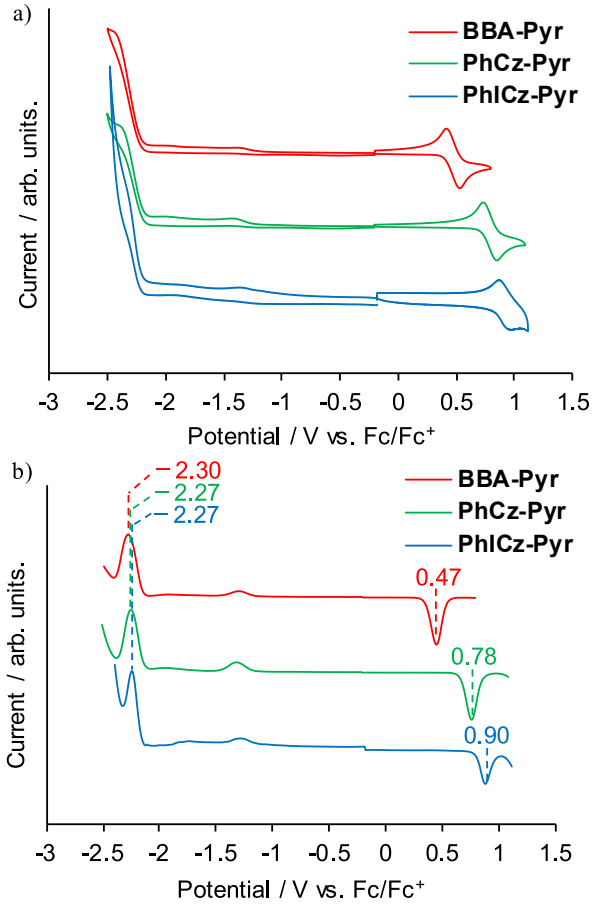


Fig. 7. Electrochemical analyses of **BBA-Pyr**, **PhCz-Pyr**, and **PhICz-Pyr**: a) Normalized cyclic voltammograms at a scan rate of 100 mV/s; b) normalized differential pulse voltammograms (dichloromethane, 1×10^{-3} M for **BBA-Pyr** and **PhICz-Pyr**, 1×10^{-4} M for **PhICz-Pyr**, 0.1 M TBA-PF_6 supporting electrolyte, glassy carbon working electrode).

was almost suppressed even in dichloromethane (Fig. 6b). **BBA-Pyr** showed a weaker emission spectrum at a longer wavelength region in dichloromethane than in toluene, and emission was suppressed in the polar DMF (Fig. 6a). In contrast, **PhICz-Pyr** exhibited emission even in DMF, and the spectra showed a bathochromic shift with increasing solvent polarity (Fig. 6c). These results suggest that the strength of electron donation by indolo[3,2,1-*jk*]carbazole is weak, and the *N*-connected carbazole realizes clear separation of the molecular orbitals due to its large dihedral angle between the carbazole ring and the *N*-connected aromatic ring.

These compounds exhibited perfectly reversible oxidation and reduction waves by cyclic voltammetry, which is considered to be evidence of electrochemical stability (Fig. 7a). The first oxidation and reduction potentials were determined based on differential pulse voltammetry and were estimated to be 0.47/−2.30 V, 0.78/−2.27 V, and 0.90/−2.27 V versus a ferrocene/ferrocenium reference for **BBA-Pyr**, **PhCz-Pyr**, and **PhICz-Pyr**, respectively (Fig. 7b). The first oxidation potentials were reflected by the ionization energies of their electron donating moieties; bis(biphenyl)amine, diphenylcarbazole, and diphenylindolo[3,2,1-*jk*]carbazole; while the first reduction potentials were almost equal. These results indicate that the HOMO energies of **BBA-Pyr**, **PhCz-Pyr**, and **PhICz-Pyr** decrease in this order, and the functions of the donors and acceptors are well-separated, as supported by the DFT calculation results.

3. Conclusion

In conclusion, a series of fluorescent materials exhibiting a ambipolar architecture composed of an electron accepting pyrimidine unit and an aromatic donor with a similar molecular geometry was developed. The compound bearing an indolo[3,2,1-*jk*]carbazole donor exhibited a distinct fluorescent behavior against the well-known carbazole and amine based derivatives, and a deep blue emission with a particularly small FWHM was achieved. These distinctive properties were derived from the extremely deep HOMO level of indolo[3,2,1-*jk*]carbazole, in addition to its structural rigidity. Therefore, the indolo[3,2,1-*jk*]carbazole-based ambipolar architecture can be considered promising in the quest for future effective deep and pure blue emitters. Investigations to

modify the structure of **PhICz-Pyr** are in progress, in order to improve the luminescent properties of the compound.

4. Experimental section

4.1. General information

All reagents (GR grade) were purchased from Tokyo Chemical Industry Co., Ltd. All melting points were measured with a Yanagimoto Micro Melting Point apparatus MP-500P and are uncorrected. Infrared (IR) spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded on JEOL JNM-ECS400 spectrometers (^{1}H: 400 MHz, ^{13}C: 100.5 MHz) using tetramethylsilane (TMS) as an internal standard, and with measurement being carried out in chloroform-*d* unless otherwise indicated. Electron ionization (EI-) and fast atom bombardment (FAB-) mass spectra were recorded on a JEOL JMS-700 mass spectrometer at the Evaluation Center of Materials Properties and Function in the Institute for Materials Chemistry and Engineering attached to Kyushu University. UV-VIS absorption spectra were recorded on JASCO V-670 spectrophotometer. Fluorescence (FL) and phosphorescence (PL) spectra were recorded on a PerkinElmer LS55 Luminescence spectrophotometer. Differential scanning calorimetry (DSC) and thermal gravimetry (TG) were performed on Rigaku Thermo Plus 2 instrument. Cyclic and differential pulse voltammograms were recorded on a BAS ALS model 612D electrochemical analyzer. Absolute fluorescence quantum yields were determined on a HAMAMATSU C9920-02 instrument. Elemental analyses were carried out using a Yanaco CHN Corder MT-6 analyzer at the Sub micro element analysis research center of A Rabbit Science Japan Co., Ltd. Column chromatography was carried out on silica gel (Fuji Silysia, BW-300). Temperature gradient sublimation purification was performed using an ULVAC TRS-1S.

4.2. Synthesis

4.2.1. (E)-3-(4-Bromophenyl)-1-phenylprop-2-en-1-one (**1**)

To a solution of acetophenone (3.25 g, 27.02 mmol) and 4-bromobenzaldehyde (5.00 g, 27.02 mmol) in methanol (50 mL) was added a solution of sodium hydroxide (216 mg, 5.40 mmol) in water (5 mL). After the mixture was stirred at room temperature for 6 h, the precipitates were collected by filtration and washed with methanol to give (*E*)-3-(4-bromophenyl)-1-phenylprop-2-en-1-one (**1**) in 94% yield (7.29 g, 25.40 mmol) as faint yellow needles.

m.p. 97–98 °C.

IR (ATR, cm^{-1}): 3057, 3028, 1656, 1600, 1583, 1575, 1560, 1496, 1481, 1449, 1396, 1364, 1334, 1289, 1276, 1216, 1179, 1159, 1106, 1069, 1035, 1006, 995, 982, 955, 892, 874, 826, 791, 760, 727, 691, 665.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.42 (m, 3H, 3,4,5-H in 3-ph), 7.46 (d, J = 15.6 Hz, 1H, 2-H), 7.61–7.64 (m, 4H, 3,5-H in 1-ph and 2,6-H in 3-ph), 7.80 (d, J = 15.6 Hz, 1H, 3-H), 7.87 (d, J = 7.9 Hz, 2H, 2,6-H in 1-ph).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ 121.43, 127.84, 128.47, 128.95, 129.97, 130.70, 131.88, 134.64, 136.88, 145.33, 189.25.

MS (FAB): m/z 287 (^{79}Br), 289 (^{81}Br) ([M+1]$^+$).

4.2.2. 4-(4-Bromophenyl)-2,6-diphenylpyrimidine (**2**)

To a solution of **1** (5.00 g, 17.41 mmol) in DMF (30 mL) was added sodium carbonate (9.62 g, 69.64 mmol) and benzamidine hydrochloride (2.73 g, 17.41 mmol). The mixture was stirred at 70 °C for 24 h and then poured into water (100 mL) and extracted with dichloromethane (50 mL). The organic phase was washed with water (50 mL x 2) and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatography (eluted with dhchloromethane/hexane mixture (2:1 (v/v)) and recrystallized from dichloromethane/ethanol to give 4-(4-bromophenyl)-2,6-diphenylpyrimidine (**2**) in 68% yield (4.58 g, 11.84 mmol) as a colorless powder.

m.p. 164–165 °C.

IR (ATR, cm^{-1}): 3032, 1588, 1567, 1523, 1487, 1456, 1445, 1408, 1389, 1379, 1359, 1312, 1296, 1237, 1199, 1172, 1109, 1072, 1023, 1007, 932, 868, 832, 825, 807, 776, 749, 715, 686, 654.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.55 (m, 6H, 3,4,5-H in 2-ph and 3,4,5-H in 6-ph), 7.66 (d, J = 8.4 Hz, 2H, 3,5-H in 4-ph), 7.93 (s, 1H, 5-H), 8.13 (d, J = 8.4 Hz, 2H, 2,6-H in 4-ph), 8.25 (d, J = 7.5 Hz, 2H, 2,6-H in 6-ph), 8.68 (d, J = 7.4 Hz, 2H, 2,6-H in 2-ph).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ 109.87, 125.37, 127.25, 128.43, 128.74, 128.89, 130.72, 130.86, 132.06, 136.37, 137.30, 137.91,163.51, 164.54, 164.93.

MS (EI): m/z 386 (^{79}Br), 388 (^{81}Br) ([M]$^+$).

4.2.3. N,N-Di([1,1′-biphenyl]-4-yl)-4'-(2,6-diphenylpyrimidin-4-yl)-[1,1′-biphenyl]-4-amine (**BBA-Pyr**)

Compound **2** (176 mg, 0.45 mmol) and (4-(di([1,1′-biphenyl]-4-yl)amino)phenyl)boronic acid (**3**) (200 mg, 0.45 mmol) were added to the mixture of toluene (5 mL), ethanol (2 mL), and 2 M aq. sodium carbonate (5 mL). After the mixture was refluxed under nitrogen atmosphere for 5 min, tetrakis(triphenylphosphine) palladium(0) (149 mg, 0.13 mmol) was added to the mixture and further refluxed for 4 h. The reaction mixture was cooled to room temperature and washed with water (20 mL). The organic phase was dried over anhydrous sodium sulfate and poured into methanol. The precipitates were collected by filtration. The obtained solid was purified by silica gel column chromatography (eluted with dichloromethane/hexane mixture (2 : 1 (v/v)) and recrystallization from dichloromethane/ethanol to give *N*,*N*-di([1,1′-biphenyl]-4-yl)-4'-(2,6-diphenylpyrimidin-4-yl)-[1,1′-biphenyl]-4-amine (**BBA-Pyr**) in 63% yield (200 mg, 0.28 mmol) as pale yellow powder.

m.p. 246–247 °C.

IR (ATR, cm^{-1}): 3030, 1598, 1588, 1567, 1516, 1482, 1447, 1395, 1362, 1320, 1292, 1278, 1263, 1177, 1111, 1074, 1026, 1005, 966, 922, 873, 820, 757, 744, 721, 689, 655.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.28 (m, 6H, ArH), 7.32 (t, J = 7.3 Hz, 2H, 4′-H at biphenyl), 7.43 (t, J = 7.5 Hz, 4H, 3′,5′-H in biphenyl), 7.52–7.53 (m, 16H, ArH), 7.79 (d, J = 8.4 Hz, 2H, 3,5-H in 4-ph at pyrimidine), 8.05 (s, 1H, 4-H in pyrimidine), 8.30 (dd, J = 1.7, 7.6 Hz, 2H, 2,6-H in 6-ph at pyrimidine), 8.37 (d, J = 8.4 Hz, 2H, 2,6-H in 4-ph at pyrimidine), 8.74 (dd, J = 1.7, 7.8 Hz, 2H, 2,6-H in 2-ph at pyrimidine).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ 110.00, 124.11, 124.64, 126.70, 126.95, 127.28, 127.72, 127.91, 127.96, 128.42, 128.49, 128.77, 128.88, 130.59, 130.71, 134.33, 135.88, 135.91, 137.61, 138.23, 140.53, 142.90, 146.68, 147.43, 164.27, 164.50, 164.68.

HRMS (FAB, PEG1000 as external standard): m/z calcd for $C_{52}H_{37}N_3$ [M]$^+$: 703.2987; found: 703.2986.

4.2.4. 9-(4'-(2,6-Diphenylpyrimidin-4-yl)-[1,1′-biphenyl]-4-yl)-9H-carbazole (**5**)

Compound **2** (1.00 g, 2.58 mmol) and 9-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)-9*H*-carbazole (**4**) (917 mg, 2.58 mmol) were dissolved in toluene (10 mL). Ethanol (5 mL) and 2 M aq. sodium carbonate (10 mL) were added to this solution, and the mixture was refluxed under nitrogen atmosphere for 5 min. Tetrakis(triphenylphosphine)palladium(0) (149 mg, 0.13 mmol) was added to this mixture and further refluxed for 4 h. Following this,

the reaction mixture was cooled to room temperature and washed with water (30 mL). The organic phase was dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The residue was purified by a silica gel column chromatography (eluted with dichloromethane/hexane mixture (2:1 (v/v)) and recrystallized from dichloromethane/ethanol to give 9-(4'-(2,6-diphenylpyrimidin-4-yl)-[1,1′-biphenyl]-4-yl)-9*H*-carbazole (**5**) in 82% yield (1.16 g, 2.12 mmol) as a colorless powder.

m.p. 187–188 °C.

IR (ATR, cm^{-1}): 3039, 1588, 1568, 1522, 1496, 1478, 1450, 1424, 1395, 1381, 1361, 1335, 1319, 1301, 1226, 1171, 1118, 1074, 1027, 1004, 969, 932, 914, 871, 844, 823, 775, 741, 722, 689, 666.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (t, J = 7.4 Hz, 2H, 3,6-H in carbazole), 7.44 (t, J = 7.4 Hz, 2H, 2,7-H in carbazole), 7.49–7.58 (m, 8H, ArH), 7.68 (d, J = 8.4 Hz, 2H, 3,5-H in 4-ph at pyrimidine), 7.87 (d, J = 8.2 Hz, 2H, 3,5-H in biphenyl), 7.89 (d, J = 8.4 Hz, 2H, 2′,6′-H in biphenyl), 8.07 (s, 1H, 5-H in pyrimidine), 8.16 (d, J = 7.4 Hz, 2H, 4,5-H in carbazole), 8.32 (dd, J = 1.8, 7.5 Hz, 2H, 2,6-H in 6-ph at pyrimidine), 8.42 (d, J = 8.2 Hz, 2H, 2,6-H in biphenyl), 8.76 (dd, J = 1.8, 7.8 Hz, 2H, 2,6-H in 2-ph at pyrimidine).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ 109.79, 110.11, 120.05, 120.33, 123.47, 125.97, 127.27, 127.35, 127.47, 127.84, 128.44, 128.48, 128.89, 130.65, 130.77, 136.66, 137.38, 137.49, 138.12, 139.22, 140.74, 142.45, 164.09, 164.52, 164.75.

HRMS (FAB): m/z calcd for $C_{40}H_{27}N_3$ $[M]^+$: 549.2205; found: 549.2206.

4.2.5. 3,6-Dibromo-9-(4'-(2,6-diphenylpyrimidin-4-yl)-[1,1′-biphenyl]-4-yl)-9H-carbazole (*6*)

To a solution of **5** (1.00 g, 1.82 mmol) in DMF (20 mL) was added dropwise a solution of *N*-bromosuccinimide (NBS, 648 mg, 3.64 mmol) in DMF (10 mL) over a period of 5 min at room temperature. The reaction mixture was poured into methanol (50 mL) and allowed to stand for 8 h. The precipitates were collected by filtration and washed with methanol (100 mL) to give 3,6-dibromo-9-(4'-(2,6-diphenylpyrimidin-4-yl)-[1,1′-biphenyl]-4-yl)-9*H*-carbazole (**6**) in 91% yield (1.17 g, 1.66 mmol) as a colorless powder.

m.p. 253–255 °C.

IR (ATR, cm^{-1}): 3038, 1676, 1604, 1588, 1566, 1520, 1495, 1467, 1435, 1397, 1361, 1316, 1277, 1226, 1172, 1120, 1057, 1021, 1004, 939, 854, 822, 795, 775, 755, 740, 710, 685, 669.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 8.7 Hz, 1,8-H in carbazole), 7.51 (dd, J = 1.9, 8.8 Hz, 2H, 2,7-H in carbazole), 7.51–7.58 (m, 8H, ArH), 7.83 (d, J = 8.3 Hz, 2H, 3,5-H in biphenyl), 7.87 (d, J = 8.4 Hz, 2H, 2′, 6′-H in biphenyl), 8.05 (s, 1H, 5-H in pyrimidine), 8.18 (d, J = 1.9 Hz, 2H, 4,5-H in carbazole), 8.30 (dd, J = 1.9, 7.5 Hz, 2H, 3,5-H in 6-ph at pyrimidine), 8.41 (d, J = 8.3 Hz, 2H, 2,6-H in biphenyl), 8.75 (dd, J = 1.9, 7.8 Hz, 2H, 2,6-H in 2-ph at pyrimidine).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ 110.08, 111.50, 113.23, 123.27, 124.06, 127.21, 127.29, 127.50, 127.91, 128.46, 128.50, 128.72, 128.92, 129.45, 130.69, 130.83, 136.39, 136.92, 137.47, 138.11, 139.73, 139.97, 142.13, 163.99, 164.55, 164.80.

HRMS (FAB): m/z calcd for $C_{40}H_{25}Br_2N_3$ $[M]^+$: 705.0415; found: 705.0415.

4.2.6. 9-(4'-(2,6-Diphenylpyrimidin-4-yl)-[1,1′-biphenyl]-4-yl)-3,6-diphenyl-9H-carbazole (***PhCz-Pyr***)

Compound **6** (1.00 g, 1.41 mmol) and phenylboronic acid (366 mg, 3.00 mmol) were dissolved in toluene (10 mL). Ethanol (5 mL) and 2 M aq.sodium carbonate aq. (10 mL) and refluxed under nitrogen atmosphere for 5 min. Tetrakis(triphenylphosphine) palladium(0) (162 mg, 0.14 mmol) was added to the mixture and further refluxed for 6 h. After the reaction mixture was cooled to room temperature, it was poured into water (100 mL) and extracted with chloroform (50 mL). The organic phase was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by a silica gel column chromatography (eluted with chloroform/hexane mixture (2:1 (v/v)) to give 9-(4'-(2,6-diphenylpyrimidin-4-yl)-[1,1′-biphenyl]-4-yl)-3,6-diphenyl-9*H*-carbazole (**PhCz-Pyr**) in 76% yield (752 mg, 1.07 mmol) as a pale yellow powder.

m.p. 310–311 °C.

IR (ATR, cm^{-1}): 3035, 1600, 1588, 1568, 1521, 1495, 1474, 1458, 1423, 1363, 1312, 1296, 1280, 1267, 1232, 1172, 1135, 1121, 1074, 1027, 1004, 970, 944, 930, 916, 879, 852, 843, 817, 805, 763, 745, 734, 688.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (t, J = 7.5 Hz, 2H, 4-H in 3,6-ph at carbazole), 7.49 (t, J = 7.5 Hz, 4H, 3,5-H in 3,6-ph at carbazole), 7.53–7.58 (m, 8H, ArH), 7.69–7.75 (m, 8H, ArH), 7.90 (d, J = 8.2 Hz, 2H, 3,5-H in biphenyl), 7.94 (d, J = 8.2 Hz, 2H, 2′,6′-H in biphenyl), 8.09 (s, 1H, 4-H in pyrimidine), 8.33 (d, J = 7.8 Hz, 2H, 2,6-H in 6-ph at pyrimidine), 8.42 (s, 2H, 4,5-H in carbazole), 8.45 (d, J = 8.2 Hz, 2H, 2,6-H in biphenyl), 8.77 (d, J = 7.8 Hz, 2H, 2,6-H in 2-ph at pyrimidine).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ 110.13, 110.21, 118.90, 124.18, 125.73, 126.63, 127.21, 127.30, 127.51, 127.89, 128.45, 128.50, 128.60, 128.79, 128.91, 130.67, 130.80, 133.81, 136.77, 137.31, 137.53, 138.15, 139.38, 140.66, 141.83, 142.41, 164.12, 164.57, 164.81.

HRMS (FAB): m/z calcd for $C_{52}H_{35}N_3$ $[M]^+$: 701.2831; found: 701.2829.

4.2.7. 9-(2-Nitrophenyl)-9H-carbazole (*7*)

To a solution of 9*H*-carbazole (20.00 g, 119.61 mmol) in DMF (150 mL) was added potassium carbonate (33.06 g, 239.22 mmol) and 2-nitrofluorobenzene (18.56 g, 131.57 mmol) under a nitrogen atmosphere. The mixture was stirred at 70 °C for 12 h and poured into water (300 mL). The precipitates were collected by filtration. The obtained solid was washed with water (200 mL) and methanol (200 mL) to give 9-(2-nitrophenyl)-9*H*-carbazole (**7**) in 94% yield (32.41 g, 112.43 mmol) as yellow needles.

m.p. 154–155 °C.

IR (ATR, cm^{-1}): 3051, 1604, 1573, 1523, 1497, 1477, 1453, 1443, 1369, 1350, 1334, 1316, 1300, 1228, 1184, 1150, 1122, 1108, 1086, 1039, 1019, 1002, 994, 957, 942, 917, 872, 849, 782, 748, 725, 704, 667.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, J = 8.0 Hz, 2H, 1,8-H), 7.28 (t, J = 7.2 Hz, 2H, 3,6-H), 7.36 (dd, J = 7.2, 7.7 Hz, 2H, 2,7-H), 7.59–7.63 (m, 2H, 4,6-H in 2-ph), 7.77 (dd, J = 7.6, 7.8 Hz, 1H, 5-H in ph), 8.09–8.14 (m, 3H, 4,5-H and 3-H in ph).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ 109.03, 120.53, 120.63, 123.81, 125.88, 126.28, 129.10, 131.21, 131.35, 134.19, 140.74, 147.35.

MALDI-TOF-MS (positive, dithranol): m/z calcd for $C_{18}H_{12}N_2O_2$: 288; found: 288 $[M^+]$.

4.2.8. 3,6-Dibromo-9-(2-nitrophenyl)-9H-carbazole (*8*)

To a solution of **7** (25.00 g, 86.72 mmol) in DMF (150 mL) was added dropwise a solution of NBS in DMF (33.96 g, 190.78 mmol/150 mL) over a period of 20 min. The mixture was stirred at room temperature for 4 h and poured into water (500 mL). The precipitates were collected by filtration and washed with methanol (200 mL) to give 3,6-dibromo-9-(2-nitrophenyl)-9*H*-carbazole (**8**) in 76% yield (29.40 g, 65.91 mmol) as yellow needles.

m.p. 202–203 °C.

IR (ATR, cm^{-1}): 3083, 1599, 1523, 1495, 1466, 1429, 1362, 1318, 1297, 1285, 1230, 1179, 1157, 1142, 1123, 1089, 1057, 1020, 992, 961, 942, 932, 891, 876, 849, 817, 795, 777, 748, 727, 712, 676, 665.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (d, J = 8.6 Hz, 2H, 1,8-H in carbazole), 7.49 (dd, J = 1.9, 8.6 Hz, 2H, 2,7-H in carbazole), 7.62 (d,

J = 7.7 Hz, 1H, 6-H in ph), 7.73 (t, J = 7.7 Hz, 1H, 4-H in ph), 7.86 (t, J = 7.7 Hz, 1H, 5-H in ph), 8.17−8.19 (m, 3H, 4,5-H in carbazole and 3-H in ph).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ 110.76, 113.87, 123.54, 124.38, 126.13, 129.80, 129.89, 130.21, 131.26, 134.50, 139.82, 147.17.

HRMS (EI): m/z calcd for $C_{18}H_{10}Br_2N_2O_2$ $[M]^+$: 443.9109; found: 443.9108.

*4.2.9. 9-(2-Nitrophenyl)-3,6-diphenyl-9H-carbazole (**9**)*

Compound **8** (25.00 g, 56.04 mmol) and phenylboronic acid (15.03 g, 123.29 mmol) were dispersed into a toluene/ethanol mixture (5:1 (v/v), 100 mL) and 2 M aq. sodium carbonate (100 mL) was added to it. After the mixture was refluxed for 5 min under nitrogen atmosphere, tetrakis(triphenylphosphine) palladium(0) (324 mg, 0.28 mmol) was added to it and further refluxed for 2 h. The reaction mixture was poured into water (200 mL) and extracted with toluene (50 mL). The organic phase was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (eluted with toluene) and recrystallized from acetone/methanol to give 9-(2-nitrophenyl)-3,6-diphenyl-9*H*-carbazole (**9**) in 93% yield (22.96 g, 52.12 mmol) as an orange powder.

m.p. 150−151 °C.

IR (ATR, cm^{-1}): 3026, 1598, 1571, 1533, 1492, 1475, 1457, 1437, 1369, 1357, 1337, 1297, 1283, 1269, 1223, 1185, 1162, 1143, 1130, 1088, 1076, 1040, 1019, 1010, 996, 967, 937, 915, 886, 859, 846, 810, 778, 755, 138, 729, 695.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, J = 8.5 Hz, 2H, 1,8-H in carbazole), 7.34 (t, J = 7.4 Hz, 2H, 4-H in 3,6-ph), 7.47 (t, J = 7.7 Hz, 4H, 3,5-H in 3,6-ph), 7.63 (dd, J = 1.8, 8.4 Hz, 2H, 2,7-H in carbazole), 7.66−7.71 (m, 6H, ArH), 7.84 (dt, J = 1.5, 7.7 Hz, 1H, 6-H in 9-ph), 8.19 (dd, J = 1.6, 8.1 Hz, 1H, 3-H in 9-ph), 8.37 (d, J = 1.7 Hz, 2H, 4,5-H in carbazole).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ 109.56, 119.34, 124.61, 126.21, 126.86, 127.49, 128.92, 129.39, 131.41, 134.50, 134.55, 140.76, 141.81.

HRMS (EI): m/z calcd for $C_{30}H_{20}N_2O_2$ $[M]^+$: 440.1525; found: 440.1526.

*4.2.10. 9-(2-Aminophenyl)-3,6-diphenyl-9H-carbazole (**10**)*

Compound **9** (20.00 g, 45.40 mmol) was dispersed into ethanol (150 mL), and 5% palladium carbon (500 mg) was added. Hydrazine monohydrate (12.52 g, 0.25 mol) was added to the mixture and refluxed for 28 h under nitrogen atmosphere. The reaction mixture was hot-filtered to remove palladium carbon and allowed to stand for 2 h at room temperature. The precipitates were collected by filtration and washed with methanol (100 mL) to give 9-(2-aminophenyl)-3,6-diphenyl-9*H*-carbazole (**10**) in 80% yield (14.91 g, 36.32 mmol) as colorless plates.

m.p. 123−124 °C.

IR (ATR, cm^{-1}): 3475, 3380, 3061, 1728, 1628, 1614, 1597, 1508, 1498, 1474, 1458, 1436, 1365, 1310, 1296, 1267, 1233, 1189, 1172, 1159, 1137, 1095, 1077, 1042, 1028, 1009, 984, 945, 912, 880, 844, 825, 759, 744, 736, 696, 671.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.61 (s, 2H, NH_2), 6.94 (t, J = 7.5 Hz, 1H, 5-H in 9-ph), 6.98 (d, J = 8.5 Hz, 1H, 3-H in 9-ph), 7.24−7.36 (m, 6H, 1,8-H in carbazole, 4- and 6-H in 9-ph, and 4-H in 3,6-ph), 7.47 (t, J = 7.7 Hz, 4H, 3,5-H in 3,6-ph), 7.66 (dd, J = 1.7, 8.5 Hz, 2H, 2,7-H in carbazole), 7.72 (d, J = 7.7 Hz, 4H, 2,6-H in 3,6-ph), 8.40 (s, 2H, 4,5-H in carbazole).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ 110.52, 116.64, 118.94, 122.16, 123.98, 125.78, 126.59, 127.34, 128.78, 129.52, 129.74, 133.63, 140.56, 141.93, 143.95.

HRMS (EI): m/z calcd for $C_{30}H_{22}N_2$ $[M^+]$: 410.1783; found: 410.1782.

*4.2.11. 2,11-Diphenylindolo[3,2,1-jk]carbazole (**11**)*

Compound **10** (10.00 g, 24.36 mmol) was dissolved in acetic acid (100 mL). Concentrated sulfuric acid (10 mL) was slowly added to this solution and cooled to 10 °C. To this mixture was added dropwise a solution of aq. sodium nitrite (1.73 g, 25.07 mmol/mL) over a period of 15 min and the mixture was further stirred for 5 min. The obtained dark red solution was immediately heated to the refluxing temperature and refluxed for 2 h. The reaction mixture was cooled to room temperature and poured into water (200 mL). The precipitates were collected by filtration, washed with methanol (100 mL), purified by silica gel column chromatography (eluted with chloroform), and recrystallized from dichloromethane/ethanol to give 2,11-diphenylindolo[3,2,1-*jk*]carbazole (**11**) in 60% yield (5.75 g, 14.62 mmol) as a pale yellow powder.

m.p. 193−194 °C.

IR (ATR, cm^{-1}): 3028, 1656, 1593, 1565, 1513, 1489, 1459, 1489, 1429, 1367, 1339, 1321, 1296, 1257, 1234, 1120, 1185, 1165, 1156, 1134, 1104, 1090, 1077, 1035, 1014, 967, 928, 885, 866, 813, 776, 760, 741, 731, 698, 675, 660.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (t, J = 7.5 Hz, 1H, 11-H), 7.34−7.39 (m, 2H, 4-H in 2,5-ph), 7.45−7.51 (m, 5H, ArH), 7.67−7.77 (m, 7H, ArH), 8.06 (d, J = 7.7 Hz, 1H, 12-H), 8.13 (s, 1H, 1- or 3-H), 8.16 (s, 1H, 1- or 3-H), 8.25 (d, J = 1.8 Hz, 1H, 4-H).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ 112.35, 118.68, 119.30, 119.43, 121.85, 121.89, 123.28, 126.12, 126.71, 126.95, 127.05, 127.38, 128.37, 128.91, 128.98, 130.15, 130.68, 135.19, 137.69, 138.37, 139.04, 141.52, 143.47, 143.99.

HRMS (EI): m/z calcd for $C_{30}H_{19}N$ $[M^+]$: 393.1517; found: 393.1518.

*4.2.12. 5-Bromo-2,11-diphenylindolo[3,2,1-jk]carbazole (**12**)*

Compound **11** (5.00 g, 12.71 mmol) was dissolved in chloroform (50 mL). To this solution was added dropwise a solution of NBS (2.26 g, 12.71 mmol) in DMF (20 mL) at room temperature over a period of 10 min. After the mixture was stirred for 8 h, chloroform was removed under reduced pressure, and methanol (100 mL) was added to the residue. The precipitates were collected by filtration and washed with methanol (100 mL) to give 5-bromo-2,11-diphenylindolo[3,2,1-*jk*]carbazole (**12**) in 97% yield (5.82 g, 12.33 mmol) as a colorless powder.

m.p. 233−235 °C.

IR (ATR, cm^{-1}): 3058, 3031, 1659, 1594, 1557, 1482, 1461, 1440, 1420, 1371, 1332, 1318, 1293, 1263, 1229, 1200, 1164, 1139, 1105, 1077, 1051, 1039, 1016, 1007, 961, 946, 932, 911, 885, 867, 832, 815, 790, 754, 743, 688, 664.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.41 (m, 2H, 4-H in ph), 7.47−7.53 (m, 6H, ArH), 7.65−7.70 (m, 6H, ArH), 8.04 (d, J = 0.9 Hz, 1H, 1- or 3-H), 8.11 (s, 1H, 12-H), 8.13 (d, J = 0.9 Hz, 1H, 1- or 3-H), 8.22 (s, 1H, 4-H).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ 112.13, 113.07, 114.60, 117.31, 118.65, 119.33, 119.77, 121.75, 125.95, 126.11, 126.71, 127.01, 127.21, 128.14, 128.82, 128.85, 129.28, 130.41, 131.46, 135.37, 137.26, 137.82, 137.91, 141.15, 142.94, 143.91.

HRMS (EI): m/z calcd for $C_{30}H_{18}BrN$ $[M^+]$: 471.0623; found: 471.0623.

*4.2.13. 2,11-Diphenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-indolo[3,2,1-jk]carbazole (**13**)*

Compound **12** (5.00 g, 10.58 mmol), bis(pinacolato)diboron (2.79 g, 11.00 mmol), and potassium acetate (4.00 g, 40.75 mmol) were added to degassed dimethyl sulfoxide (50 mL) under nitrogen atmosphere, and the mixture was heated to 100 °C. To this mixture was added [1,1′-bis(diphenylphosphino)ferrocene] dichloropalladium(II) dichloromethane adduct (433 mg,

0.53 mmol). The mixture was stirred for 4 h at 100 °C under nitrogen atmosphere. The reaction mixture was poured into water (100 mL) and extracted with chloroform (50 mL). The organic phase was washed with water (50 mL x 2) and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (eluted with chloroform) and recrystallized from dichloromethane/hexane to give 2,11-diphenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indolo[3,2,1-*jk*] carbazole (**13**) in 75% yield (4.12 g, 7.94 mmol) as a colorless powder.

m.p. 162–164 °C.

IR (ATR, cm^{-1}): 3054, 3032, 2976, 2926, 1658, 1599, 1571, 1484, 1455, 1438, 1425, 1378, 1350, 1331, 1315, 1304, 1294, 1262, 1216, 1202, 1167, 1147, 1107, 1067, 1016, 966, 951, 917, 913, 882, 862, 847, 799, 758, 750, 699, 680, 664.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.44 (s, 12H, CH_3), 7.36–7.41 (m, 2H, 4-H in ph), 7.47–7.59 (m, 4H, 3,5-H in ph), 7.71–7.77 (m, 5H, 2,6-H in ph and 6-H), 7.87–7.93 (m, 2H, 7- and 9-H), 8.03 (d, $J = 8.0$ Hz, 1H, 10-H), 8.23 (s, 1H, 3-H), 8.23 (s, 1H, 4-H), 8.33 (s, 1H, 1-H), 8.64 (s, 1H, 12-H).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ 24.98, 26.91, 83.90, 111.66, 112.58, 118.66, 118.75, 119.22, 119.51, 121.82, 126.11, 126.60, 126.97, 127.27, 128.19, 128.80, 128.84, 129.65, 130.11, 130.84, 133.59, 135.49, 137.94, 138.22, 140.90, 141.34, 143.28, 144.10.

HRMS (EI): *m*/*z* calcd for $C_{36}H_{30}BNO_2$: 519.2370; found: 519.2370.

4.2.14. 5-(4-(2,6-Diphenylpyrimidin-4-yl)phenyl)-2,11-diphenylindolo[3,2,1-jk]carbazole (*PhICz-Pyr*)

Compound **13** (1.34 g, 2.58 mmol) and **2** (1.00 g, 2.58 mmol) were dissolved in toluene (20 mL). To this solution was added ethanol (10 mL) and aq. 2 M sodium carbonate (10 mL). The mixture was refluxed under nitrogen atmosphere for 5 min. Tetrakis(-triphenylphosphine)palladium(0) (149 mg, 0.13 mmol) was added to this mixture and further refluxed for 8 h. Due to poor product solubility, the product was purified as described here. The water phase was carefully removed using a pipette, and the precipitates in organic phase were collected by filtration. The obtained solid was washed with water (50 mL), methanol (50 mL), acetone (50 mL), and chloroform (50 mL). The product was purified by temperature gradient sublimation under a vacuum pressure of 5×10^{-4} Pa and temperature of 410 °C to give 5-(4-(2,6-diphenylpyrimidin-4-yl) phenyl)-2,11-diphenylindolo[3,2,1-*jk*]carbazole (**PhICz-Pyr**) in 70% yield (1.26 g, 1.81 mmol) as pale yellow needles.

m.p. 360–361 °C.

IR (ATR, cm^{-1}): 3035, 1656, 1599, 1587, 1565, 1525, 1515, 1496, 1483, 1464, 1443, 1426, 1399, 1363, 1332, 1292, 1259, 1236, 1202, 1167, 1142, 1104, 1075, 1036, 1024, 948, 930, 888, 866, 841, 814, 805, 777, 753, 735, 686, 667, 655.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.40 (m, 2H, 4-H in 2,6-ph at ICz), 7.50–7.61 (m, 10H, ArH), 7.77 (d, $J = 7.2$ Hz, 2H, 2,6-H in 2- or 5-ph at ICz), 7.81 (d, $J = 7.8$ Hz, 2H, 2,6-H in 2- or 5-ph at ICz), 7.85 (dd, $J = 1.8$, 8.4 Hz, 1H, 6-H in ICz), 7.94 (dd, $J = 1.8$, 8.2 Hz, 1H, 10-H in ICz), 8.03 (d, $J = 8.6$ Hz, 1H, 7-H in ICz), 8.06 (d, $J = 8.3$ Hz, 8-H in ICz), 8.11 (s, 1H, 5-H in pyrimidine), 8.33–8.36 (m, 4H, ArH), 8.42 (d, $J = 1.8$ Hz, 1H, 4-H in ICz), 8.46 (d, $J = 8.2$ Hz, 2H, 2,6-H in 4-ph at pyrimidine), 8.51 (d, $J = 1.8$ Hz, 1H, 12-H in ICz), 8.77 (dd, $J = 1.5$, 7.9 Hz, 2H, 2,6-H in 2-ph at pyrimidine).

^{13}C NMR spectrum could not be recorded due to poor solubility of this compound.

MS (FAB): *m*/*z* 699 $[M]^+$, 700 $([M+1]^+$.

Anal. Calcd for $C_{52}H_{33}N_3$, %: C, 89.24; H, 4.75; N, 6.00. Found, %: C, 89.47; H, 4.55; N, 5.79.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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