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NOVEL FORMATION OF DIPYRROLO- AND DIINDOLO[1,2-*a*:2',1'-*c*]QUINOXALINE DERIVATIVES AND THEIR OPTICAL PROPERTIES

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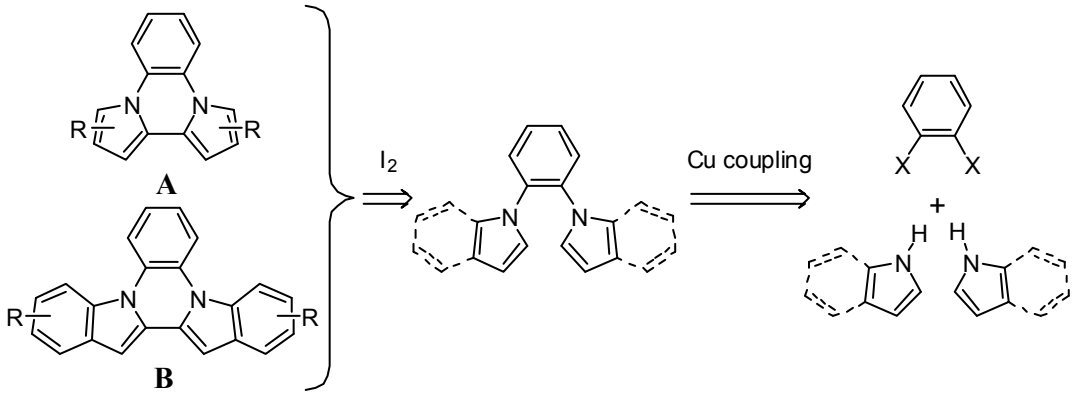
Abstract – Dipyrrolo- and diindolo[1,2-*a*:2',1'-*c*]quinoxaline structures (**A** and **B**, respectively) were synthesized from 1,2-di(1-pyrrolyl)- and 1,2-di(1-indolyl)benzene derivatives with iodine using a novel intramolecular coupling reaction. Apparent differences between **A** and **B** were observed from UV-VIS absorption and fluorescence spectra. Sharp peaks with a fine structure were observed in the absorption and fluorescence spectra of diindolo[1,2-*a*:2',1'-*c*]quinoxaline (**2b**). Introduction of a phenyl ring at the 6 and 6' positions of the indole moieties of **2b** is efficient for imparting a red shift. In addition, the electron-withdrawing group at those positions particularly affected the emission peaks.

INTRODUCTION

The chemistry of pyrroles and their analogues extends into various fields such as synthetic methods,[1] biological interests,[2] and functional materials.[3] Especially, optical and electrical applications using a pyrrole skeleton and its π-conjugated systems have attracted much attention to the development of electric conducting materials,[4] sensors,[5] nonlinear optics,[6] fluorescent materials,[7] electroluminescent materials,[8] organic metal-lustrous compounds,[9] and so on.[10] Furthermore, several unique structures including the pyrrole skeleton have been investigated to develop new useful physical properties. For example, expanded porphyrins,[11] dipyrromethenes,[12] dipyrrolylquinoxalines,[13] and calix[4]pyrroles[14] were investigated thoroughly as functional materials. Recently, we reported the synthesis and optical properties of novel 2,2'-bipyrroles, 1,1',5,5'-tetraaryl-2,2'-bipyrrole derivatives: their conformation in an excited state is

This paper is dedicated to Professor Emeritus Akira Suzuki on his 80th birthday.

closer to a planar one, but a twisted conformation is favorable in a ground state.[15] If the conformation is forced in the ground state to be planar, they would resemble the pyrene system that seems to be applicable to various sensors using fluorescence ability.[16] Hence, we were interested in 2,2'-bipyrrole structures bridging the nitrogen atom with the phenylene group that are dipyrrolo[1,2-*a*:2',1'-*c*]quinoxalines (**A**) and their π-expanded structures, diindolo[1,2-*a*:2',1'-*c*]quinoxalines (**B**). A few reports have described the synthesis of **A** as well as its application to conducting polymers,[17,18] and no report has addressed the structure **B**. Therefore, we started our investigation of the synthesis and optical properties of **A** and **B** to develop the novel optical and electrical devices. Until then, two syntheses of the structure **A** had been reported: in the literature by Kaupp *et al.*, the first included the [4+2] cycloaddition of 2,3-dimethylquinoxaline dioxide and phenylpropiolate.[17b] Pagani and his co-workers achieved the synthesis through the subsequent cyclization of 2,3-dimethylquinoxaline with ethyl 3-bromopyruvate.[17a] Those reported routes are impressive, but they might not be applied to the synthesis of the expanded structure **B**. Therefore, we planned the intramolecular C–C bond formation of the corresponding 1,2-di(1-pyrrolyl)- and 1,2-di(1-indolyl)benzene derivatives with iodine, which is similar to the cyclization-aromatization reaction of stilbene (Scheme 1).[19,20] The starting 1,2-di(1-pyrrolyl)- and 1,2-di(1-indolyl)benzene derivatives can be obtained through CuI-catalyzed coupling reaction of 1,2-dihalobenzene with pyrrole and indole derivatives.[21] Herein, we report the novel formation of dipyrrolo- and diindolo[1,2-*a*:2',1'-*c*]quinoxaline derivatives (**A** and **B**) using the pyrrole–pyrrole coupling reaction with iodine together with the relationship between their structures and optical properties.



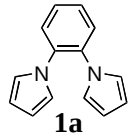
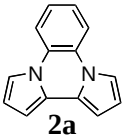
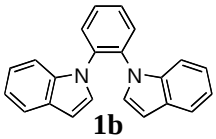
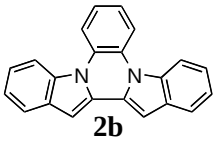
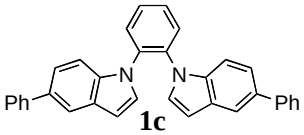
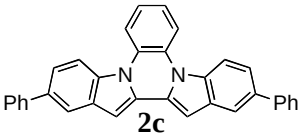
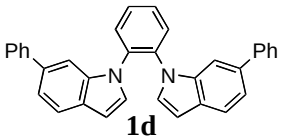
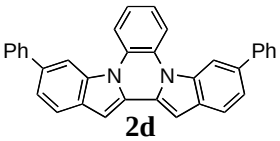
Scheme 1 Retrosynthesis of **A** and **B**

RESULTS AND DISCUSSION

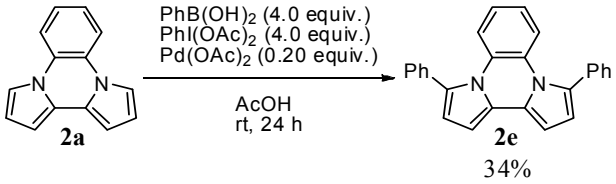
We examined the photochemical reaction of 1,2-di(1-pyrrolyl)benzene (**1a**), which was prepared by the CuI-catalyzed coupling reaction of 1,2-dihalobenzene with pyrrole and indole derivatives,[21] in the presence of iodine. When **1a** was treated with 1 mol-equivalent of iodine in toluene for 5.5 h under irradiation with a high-pressure mercury lamp (100 W) through a Pyrex filter, the desired dipyrrolo[1,2-*a*:2',1'-*c*]quinoxaline

(**2a**) was obtained in 49% yield with the recovery of **1a** (11%) (Entry 1 in Table 1). Increasing and decreasing the amount of iodine was not effective (Entries 1, 2, and 3). Surprisingly, a comparable result was obtained with a trace amount of starting **1a** when the reaction was conducted under dark conditions (Entry 1 vs. 5). But every runs in toluene and acetonitrile gave the unidentified compounds. Furthermore, we found that **2a** was obtained in high yield (85% yield) using chlorobenzene as a solvent (Entry 6). A similar pyrrole–pyrrole intramolecular coupling reactions using $Fe(ClO_4)_3$ or $FeCl_3$ were reported as the oxidant.[22] Consequently, this reaction occurred because of iodine's oxidative character. The detailed mechanism in our conditions remains unclear, but the slight change of a polarity and/or the absence of the active benzylic proton in a solvent would enhance the yield of **2a**. This reaction might be applicable to the indolyl analogues. The excellent yield was achieved by raising the temperature and increasing the amount of iodine (Entry 9). And the substituted compounds at the phenyl rings of indolyl moiety also formed the corresponding products in good yields (Entries 10 and 11).

Table 1. Iodine-induced Cyclization of 1,2-Di(1-pyrrolyl)- and 1,2-Di(1-indolyl)benzene Derivatives

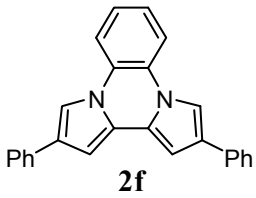
Entry	Substrate	I_2 (mol-equiv.)	Solvent	Conditions	Product	Yield (%)
1	 **1a**	1.0	Ph-Me	hν, rt, 5.5 h	 **2a**	49
2		2.0	Ph-Me	hν, rt, 3 h		10
3		0.5	Ph-Me	hν, rt, 22 h		23
4		1.0	MeCN	hν, rt, 0.5 h		37
5		1.0	Ph-Me	dark, rt, 24 h		44
6		1.0	Ph-Cl	dark, rt, 24 h		85
7	 **1b**	1.0	Ph-Cl	dark, rt, 24 h	 **2b**	56
8		1.0	Ph-Cl	dark, 80 °C, 24 h		69
9		2.0	Ph-Cl	dark, 80 °C, 24 h		85
10	 **1c**	2.0	Ph-Cl	dark, 80 °C, 24 h	 **2c**	80
11	 **1d**	2.0	Ph-Cl	dark, 80 °C, 24 h	 **2d**	75

To examine the substituent effect of structure **A** on optical properties, we tried to synthesize 3,10-diphenyldipyrrolo[1,2-*a*:2',1'-*c*]quinoxaline (**2e**) in our coupling method. However, we were unable to form the starting 1,2-di(2-phenyl-1-pyrrolyl)benzene using the CuI-mediated reaction. Therefore, we obtained **2e** using the reaction of palladium-catalyzed arylation with **2a** according to the procedure reported by Sanford and his co-workers (Scheme 2).[23]



Scheme 2 Formation of **2e** from **2a**

The absorption and fluorescence spectra were measured in the THF solution. The physical data discussed in this manuscript are presented in Table 2. We first examined the effect of the expansion of the conjugated system from **2a**. The absorption and emission peaks of **2e** showed longer wavelengths than that of **2a** (Entry 1 vs. 2 in Table 2). Kaupp and co-workers reported the absorption peaks of 2,11-diphenyldipyrrolo[1,2-*a*:2',1'-*c*]quinoxaline (**2f**), which is an analogue of **2a** bearing two phenyl rings at 4 and 4' positions of each pyrrole moiety.[17b] It showed a blue-shift against **2a** (Entry 1 vs. 3). Consequently, the introduction of additional π-system at 5 and 5' positions of pyrrole part of structure **A** is efficient to impart a red shift in the absorption spectra. Moreover, **2b**, which has the fused aromatic system in **2a**, also showed longer wavelength of the absorption peak (Entries 1 and 4). Although the peaks of **2a** and **2e** at λ_{max} were broadened, the spectrum of **2b** showed a characteristic fine structure (absorption peaks: 371.5, 351, and 336.5 nm) with the sharp edge of the absorption (Figure 1). The structure **B** will have the more fixed conformation by the fused benzene rings than the structure **A**. And we think that it is the reason to give the different properties between structure **A** and **B**. But we were unable to find a proper explanation for such a difference between structure **A** and **B** despite computational studies at the DFT B3LYP/6-31G* level calculation.



2f

Table 2. UV-VIS Absorption and Fluorescence Spectral Data of **2**

Entry	Compound	λ_{max} (nm) [ε (M^{-1} cm^{-1})][a]	λ_{em} (nm)[b] [Φ_F]
1	**2a**	321 [10,600]	416 [0.43][d]
2	**2e**	377.5 [15,400]	445 [0.44][d]
3	**2f**	313.5 [40.7][c]	—
4	**2b**	372 [46,000]	372, 396, 420 [0.55][e]
5	**2c**	379 [57,000]	382, 405, 429 [0.50][e]
6	**2d**	398 [47,000]	414, 439, 470 [0.46][e]
7	**2g**	402 [50,000]	417, 443, 474 [0.41][e]
8	**2h**	402 [16,000]	426, 449, 484 [0.34][d]

a UV-VIS absorption spectra was measured in THF (3.0×10^{-5} M). b Fluorescence spectra was measured in THF (3.0×10^{-7} M). c Ref. 17b. d Quantum yield was determined by using quinine sulfate in 0.1 M H_2SO_4 solution as a standard (Φ_F=0.55, excited at 366 nm). e Quantum yield was determined by using *p*-terphenyl in cyclohexane as a standard (Φ_F=0.87, excited at 265 nm).

A marked dissimilarity between dipyrrolo[1,2-*a*:2',1'-*c*]quinoxaline derivatives (**2a** and **2e**) and diindolo[1,2-*a*:2',1'-*c*]quinoxaline (**2b**) was also observed in the fluorescence spectra (Figure 1). The three main peaks similar to those in the absorption spectrum were observed in the emission spectrum of **2b**, although one broadened emission peak was obtained in the case of **2a** and **2e**. It is particularly interesting that the Stokes shift of **2b** is small (2 nm), suggesting that the difference between the equilibrium geometries of the ground and excited states is small.[24] Consequently, the fluorescence quantum yield (Φ_F) was increased (**2a**; 0.43, **2b**; 0.55) (Entries 1 and 4 in Table 2).

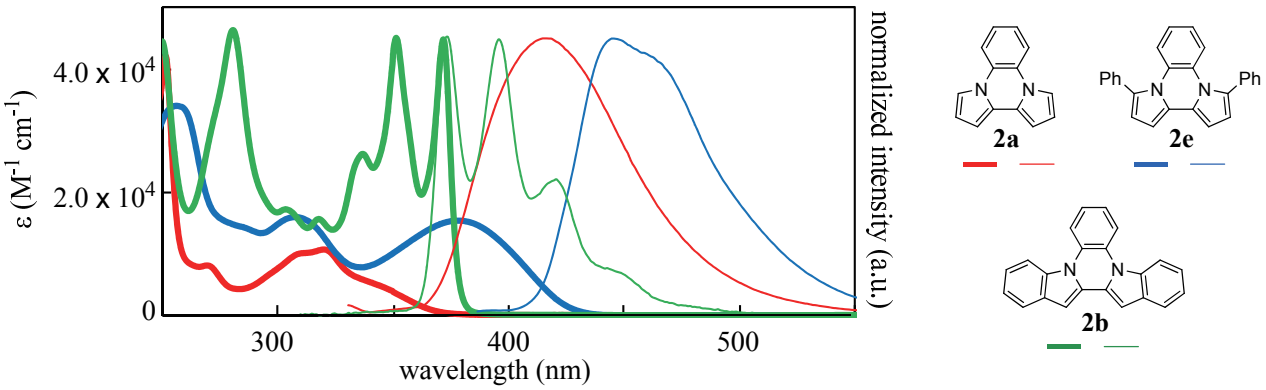
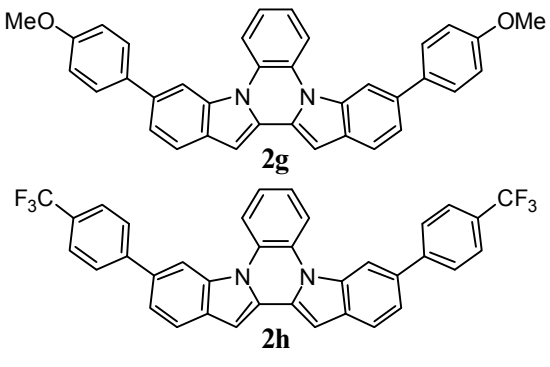


Figure 1. UV-VIS Absorption (bold line; 3.0 x 10^{-5} M in THF) and fluorescence (narrow line; 3.0 x 10^{-7} M in THF) spectra of **2a** (red), **2e** (blue), and **2b** (green).

We further investigated the substituent effect of **2b** on absorption and fluorescence properties (Table 2 and Figure 2). When two phenyl rings were attached at 5 and 5' positions of the indolyl moiety of **2b**, the absorption peak of **2c** showed a red shift ($\Delta\lambda_{max}$ = 7 nm) (Entries 4 and 5). The emission peak shifted similarly ($\Delta\lambda_{em}$ = 10 nm in the shortest wavelength). In comparison with **2c**, a larger red shift from the spectra of **2b** was observed both in the absorption ($\Delta\lambda_{max}$ = 26 nm) and in the emission ($\Delta\lambda_{em}$ = 42 nm in the shortest wavelength) spectra of **2d**, which possessed in the phenyl groups at 6 and 6' positions of indole moiety of **2b** (Entry 4 vs. 6). Therefore, we showed that the introduction of another π-system into **2b** at the 6 position of the iodole moiety is efficient to achieve expansion of π-system in diindolo[1,2-*a*:2',1'-*c*]quinoxaline system (**B**). The fine structures were observed even in the introduction of the phenyl groups with gradual broadening.

Additionally, we tried to investigate the electronic effect of the substituents at 6 and 6' position of indolyl parts. For this purpose, **2g** and **2h** were synthesized by the reaction of the CuI-catalyzed coupling reaction followed by the iodine-mediated cyclization reaction. The **2g** bearing 4-methoxyphenyl groups showed a small difference in the absorption and fluorescence spectra compared to those of **2d**



(Entries 6 and 7 in Table 2). A specific difference was observed when **2h** bearing 4-trifluoromethylphenyl groups was examined. In the absorption spectrum, almost identical maximum absorption peaks with **2g** were obtained with a decrease of the absorption coefficient. In contrast, the emission peaks of **2h** showed a red shift of about 10 nm compared to those of **2d** and **2g** (Entry 6, 7 vs. 8). These results suggest that the introduction of the electron-withdrawing substituent at 6 and 6' positions of indole part in diindolo[1,2-*a*:2',1'-*c*]quinoxaline structure efficiently changes the emission peaks, with a small change of the absorption peaks.

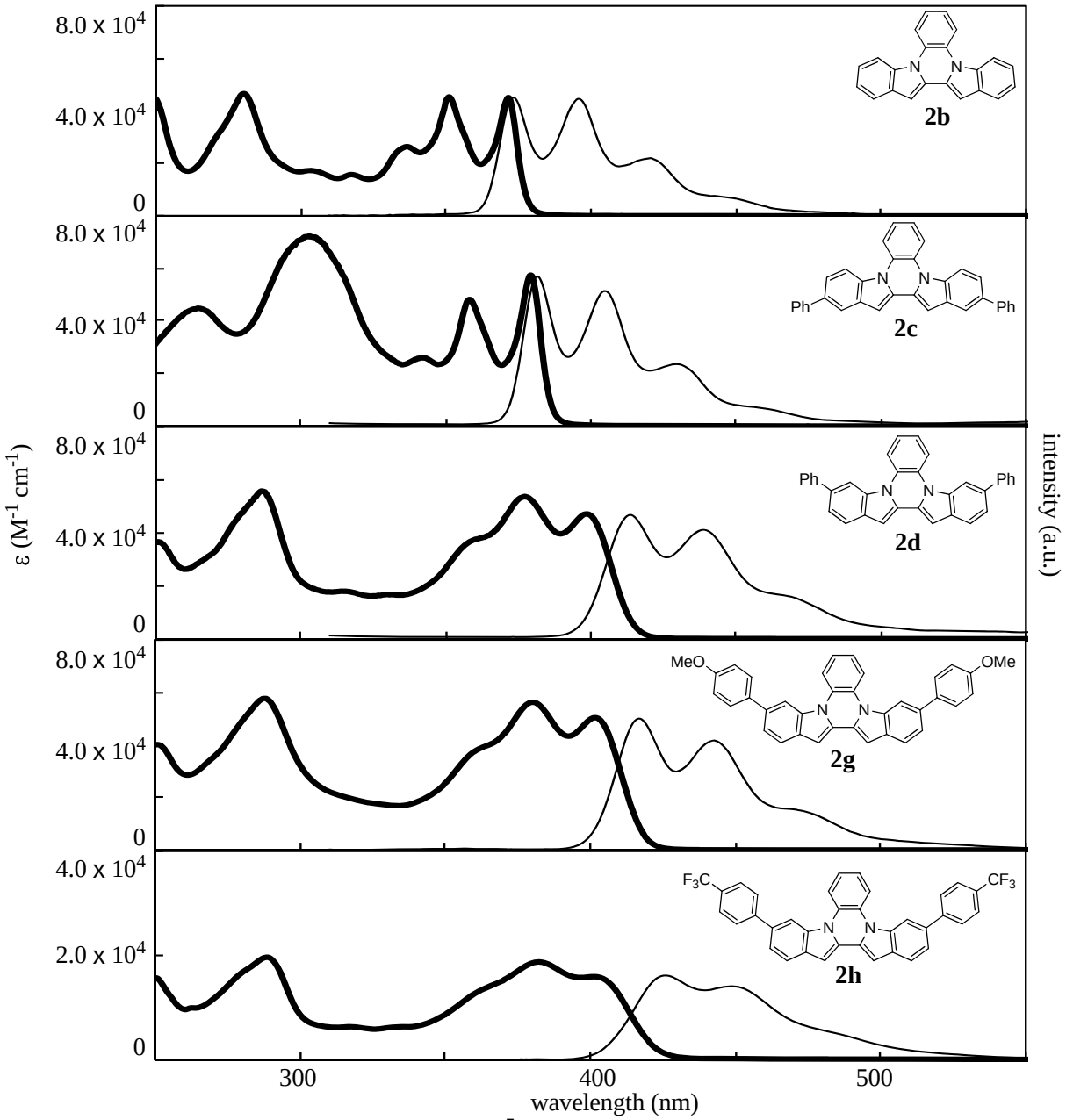


Figure 2. UV-VIS Absorption (bold line; 3.0 x 10^{-5} M in THF) and fluorescence (narrow line; 3.0 x 10^{-7} M in THF) spectra of **2b**, **2c**, **2d**, **2g**, and **2h**.

In conclusion, we synthesized dipyrrolo- and diindolo[1,2-*a*:2',1'-*c*]quinoxaline derivatives and investigated their optical properties. Their syntheses were achieved using the novel C–C bond formation with iodine, whose reaction conditions are simple and inexpensive. The UV-VIS and fluorescence spectra revealed different characteristics of dipyrrolo- and diindolo[1,2-*a*:2',1'-*c*]quinoxaline structures. Furthermore, an efficient change in the spectra of structure **B** was obtained when the additional π-systems at 6 and 6' positions of indolyl moiety were introduced. Notably, the electron-withdrawing group at those positions induced a greater red shift of the emission peak than the absorption peak. These findings will elucidate not only synthetic methods of novel pyrrole-containing compounds but also facilitate the design of functional materials of new types.

EXPERIMENTAL

General Procedures. Melting points were determined with Yanaco MP-J3 and values were uncorrected. ^{1}H NMR spectra were recorded at 300 MHz on Varian GEMINI 2000 spectrometer with TMS as an internal standard. *J*-Values were given in Hz. IR spectra were measured on a JASCO FT/IR-350 spectrometer. UV-VIS spectra were measured on a JASCO V570 spectrophotometer. Fluorescence spectra were measured on a JASCO FP-6600 spectrofluorometer. Elemental analyses (EA) and high-resolution mass spectroscopy (HRMS) were carried out by the Chemical Analysis Center of Chiba University.

Procedure for Synthesis of 1,2-Di(1-pyrrolyl)benzene (1a). In a test tube with a screw cap was added 1,2-diiodobenzene (0.13 mL, 1.00 mmol), pyrrole (0.21 mL, 3.0 mmol), CuI (19.0 mg, 0.1 mmol), *trans*-1,2-diaminocyclohexane (0.12 mL, 1.0 mmol), K_3PO_4 (0.850 g, 4.0 mmol), and toluene (1.0 mL). The combined mixture was warmed to 110 ^{o}C for 10 h. The reaction mixture was cooled down to room temperature. The mixture was filtered off with a pad of Celite and Florisil® and washed with EtOAc. Combined organic solution was evaporated in vacuo. The residual mixture was subjected to column chromatography on silica gel (hexane : $CHCl_3$ = 6 : 1) to give **1a** (0.152 g, 73%) as colorless solid. Rercrystallization from hexane gave colorless plate crystals: mp 75.0-75.5 ^{o}C (hexane); ^{1}H NMR ($CDCl_3$) δ 6.22 (t, *J* = 2.2 Hz, 4H), 6.54 (t, *J* = 2.2 Hz, 4H), 7.37-7.44 (m, 4H); IR (KBr/cm^{-1}) 3132, 3101, 3068, 1603, 1514, 1484, 1333, 1070, 761, 723. *Anal.* Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.78; H, 5.88; N, 13.54.

1,2-Di(1-indolyl)benzene (1b).[25] The titled compound was prepared for 3 d in 33% according to a procedure similar to that mentioned above: colorless plate crystals: mp 164.7-165.3 ^{o}C (hexane); ^{1}H NMR ($CDCl_3$) δ 6.36 (d, *J* = 3.2 Hz, 2H), 6.54 (d, *J* = 3.2 Hz, 2H), 7.12 (m, 4H), 7.32 (dd, *J* = 5.3 and 3.2 Hz, 2H), 7.56 (m, 4H), 7.70 (m, 2H); IR (KBr/cm^{-1}) 3048, 1594, 1516, 1456, 1331, 1308, 1238, 1211, 1134, 1009, 766, 748, 715.

1,2-Di(5-phenyl-1-indolyl)benzene (1c). The titled compound was prepared with 5-phenylindole and

1,2-dibromobenzene for 44 h in 43% yield according to a procedure similar to that mentioned above: colorless solid: mp 155.3-156.6 °C (hexane-$CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 6.44 (d, *J* = 3.3 Hz, 2H), 6.62 (d, *J* = 3.3 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.40 (s, 4H), 7.43 (t, 7.3 Hz, 4H), 7.58 (dd, *J* = 6.0 and 3.6 Hz, 2H), 7.63 (d, *J* = 7.1 Hz, 4H), 7.74 (dd, *J* = 6.0 and 3.4 Hz, 2H), 7.79 (s, 2H); IR (KBr/cm^{-1}) 3056, 1599, 1508, 1469, 1369, 1334, 1234, 1180, 1120, 887, 787, 754, 721, 698. HRMS Calcd for $C_{34}H_{25}N_2$: M+H. 461.2018, found: m/z 461.1986.

1,2-Di(6-phenyl-1-indolyl)benzene (1d). The titled compound was prepared with 6-phenylindole and 1,2-dibromobenzene for 44 h in 38% yield according to a procedure similar to that mentioned above: colorless needle crystals: mp 201.4-202.7 °C (hexane-$CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 6.44 (d, *J* = 3.3 Hz, 2H), 6.78 (d, *J* = 3.0 Hz, 2H), 7.21-7.27 (m, 10H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.45 (s, 2H), 7.56 (dd, *J* = 5.9 and 3.5 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.73 (dd, *J* = 5.9 and 3.6 Hz, 2H); IR (KBr/cm^{-1}) 3058, 1599, 1512, 1473, 1433, 1344, 1213, 1138, 1074, 1038,904, 864, 818, 762, 698. HRMS Calcd for $C_{34}H_{25}N_2$: M+H. 461.2018, found: m/z 461.1986.

Procedure for Synthesis of Dipyrrolo[1,2-*a*:2',1'-*c*]quinoxaline (2a). To a solution of **1a** (0.104 g, 0.50 mmol) in chlorobenzene (3.0 mL) was dropwise added a solution of iodine (0.139 g, 0.55 mmol) in chlorobenzene (2.0 mL) in a period of 5 min. The mixture was stirred at room temperature. The dark precipitate was observed when the reaction proceeded. After being stirred for 24 h at room temperature, to the reaction mixture was added saturated aqueous $Na_2S_2O_3$ solution (5 mL) and acetone (*ca.* 5 mL) to dissolve the precipitate. The combined mixture was extracted with $CHCl_3$ (5 mL × 3). The combined organic layers were dried over $MgSO_4$. Evaporation in vacuo and column chromatography (silica gel; hexane : EtOAc = 10 : 1) provided **2a** (0.088 g, 85%) as colorless solid. Recrystallization from hexane gave colorless crystals: mp 153.5-154.5 °C (hexane) (lit.,[17a] 148-150 °C); ^{1}H NMR ($CDCl_3$) δ 6.54 (dd, *J* = 3.7 and 1.5 Hz, 2H), 6.57 (t, *J* = 3.7 Hz, 2H), 7.27 (dd, *J* = 6.0 and 1.4 Hz, 2H), 7.47 (dd, *J* = 2.9 and 1.4 Hz, 2H), 7.71 (dd, *J* = 6.2 and 1.4 Hz, 2H); IR (KBr/cm^{-1}) 3137, 3099, 1625, 1516, 1487, 1348, 1088, 746, 698, 688.

Diindolo[1,2-*a*:2',1'-*c*]quinoxaline (2b). The titled compound was prepared for 24 h at 80 °C in 85% yield according to a procedure similar to that mentioned above: colorless cotton-like solid: mp 244.0-244.6 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 7.08 (s, 2H), 7.25-7.39 (m, 6H), 7.74 (dd, *J* = 5.9 and 0.9 Hz, 2H), 8.21 (d, *J* = 8.5 Hz, 2H), 8.41 (m, 2H); IR (KBr/cm^{-1}) 3045, 1504, 1465, 1446, 1380, 1363, 1334, 1265, 792, 775, 738, 727. *Anal.* Calcd for $C_{22}H_{14}N_2$: C, 86.02; H, 4.32; N, 8.98. Found: C, 86.25; H, 4.61; N, 9.14.

2,13-Diphenyldiindolo[1,2-*a*:2',1'-*c*]quinoxaline (2c). The titled compound was prepared for 24 h at 80 °C in 80% yield according to a procedure similar to that mentioned above: orange solid: mp 287.4-287.9 °C (hexane-$CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.19 (s, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.41 (dd, *J* = 6.2 and 2.9 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 4H), 7.64 (dd, *J* = 9.0 and 1.8 Hz, 2H), 7.73 (d, *J* = 7.5 Hz, 4H), 7.98 (d, *J* = 1.8 Hz, 2H),

8.30 (d, *J* = 8.7 Hz, 2H), 848 (dd, *J* = 6.2 and 3.6 Hz, 2H); IR (KBr/cm^{-1}) 3057, 1597, 1537, 1500, 1464, 1377, 1338, 1298, 1269, 879, 758, 696, 621, 526, 451, 418, 404. *Anal.* Calcd for $C_{34}H_{22}N_2 \cdot 1/3H_2O$: C, 87.90; H, 4.92; N, 6.03. Found: C, 87.98; H, 4.83; N, 5.93.

3,12-Diphenyldiindolo[1,2-*a*:2',1'-*c*]quinoxaline (2d). The titled compound was prepared for 17 h at 80 ^oC in 75% yield according to a procedure similar to that mentioned above: orange solid: mp 276.2-276.7 ^oC (hexane-$CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.15 (s, 2H), 7.40 (m, 4H), 7.52 (t, *J* = 7.5 Hz, 4H), 7.57 (d, *J* = 9.2 Hz, 2H), 7.74 (d, *J* = 7.5 Hz, 4H), 7.82 (d, *J* = 8.1 Hz, 2H), 8.42 (s, 2H), 8.52 (dd, *J* = 5.9 and 3.3 Hz, 2H); IR (KBr/cm^{-1}) 3030, 2362, 1599, 1527, 1498, 1477, 1448, 1427, 1381, 1342, 1300, 1250, 814, 769, 739, 692, 418. *Anal.* Calcd for $C_{34}H_{22}N_2 \cdot 1/4H_2O$: C, 88.19; H, 4.90; N, 6.05. Found: C, 88.30; H, 4.55; N, 6.08.

Synthesis of 3,10-Diphenyldipyrrolo[1,2-*a*:2',1'-*c*]quinoxaline (2e). $PhI(OAc)_2$ (0.903 g, 2.80 mmol) and $PhB(OH)_2$ (0.342 g, 2.80 mmol) was added to AcOH (14 mL), which was bubbled with N_2 gas for 20 min. After being stirred for 15 min at room temperature, **1a** (0.143 g, 0.69 mmol) was added to the mixture. The color of the reaction mixture was turned from pale red to black. After being stirred for additional 15min, $Pd(OAc)_2$ (31.2 mg, 0.14 mmol) was added and then the whole was stirred for 24 h at room temperature. The reaction mixture was filtered through a plug of Celite and evaporated in vacuo. After being added water (5 mL). The combined mixture was extracted with $CHCl_3$ (5 mL × 3). The combined organic layers were dried over $MgSO_4$. Evaporation in vacuo and column chromatography (silica gel; hexane : EtOAc = 40 : 1) provided **2e** (84.9 mg, 34%) as yellow solid. Recrystallization from MeOH and a bit $CHCl_3$ gave pale yellow crystals: mp 164.0-165.1 ^oC; ^1H NMR ($CDCl_3$) δ 6.55 (d, *J* = 3.7 Hz, 2H), 6.62 (d, *J* = 3.7 Hz, 2H), 6.81 (dd, *J* = 6.3 and 3.5 Hz, 2H), 7.30 (dd, *J* = 6.3 and 3.5 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 4H), 7.54 (d, *J* = 7.1 Hz, 4H); IR (KBr/cm^{-1}) 3057, 1600, 1496, 1471, 1372, 1352, 1335, 755, 702. *Anal.* Calcd for $C_{26}H_{18}N_2 \cdot 1/4H_2O$: C, 86.04; H, 5.14; N, 7.72. Found: C, 85.86; H, 4.85; N, 7.68.

3,12-Di(4-methoxyphenyl)diindolo[1,2-*a*:2',1'-*c*]quinoxaline (2g). The titled compound was prepared in two steps (CuI-mediated coupling reaction in 40% yield, and iodine-mediated cyclization reaction for 16 h at 80 ^oC in 100% yield) according to a procedure similar to that mentioned above: yellow solid: mp 280.8-283.0 ^oC (hexane-$CHCl_3$); ^1H NMR ($CDCl_3$) δ 3.89 (s, 6H), 7.05 (d, *J* = 8.7 Hz, 4H), 7.09 (s, 2H), 7.37 (dd, *J* = 5.9 and 3.5 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.7 Hz, 4H), 7.77 (d, *J* = 8.4 Hz, 2H), 8.34 (s, 2H), 8.47 (dd, *J* = 5.8 and 3.1 Hz, 2H); IR (KBr/cm^{-1}) 2935, 2833, 1606, 1502, 1481, 1437, 1375, 1246, 1178, 1039, 818, 737. *Anal.* Calcd for $C_{36}H_{26}N_2O_2 \cdot 1/3H_2O$: C, 82.42; H, 5.12; N, 5.34. Found: C, 82.29; H, 4.92; N, 5.26.

3,12-Di[4-(trifluoromethyl)phenyl]diindolo[1,2-*a*:2',1'-*c*]quinoxaline (2h). The titled compound was prepared in two steps (CuI-mediated coupling reaction in 42% yield, and iodine-mediated cyclization reaction for 22 h at 80 ^oC in 100% yield) according to a procedure similar to that mentioned above: pale

yellow solid: mp 286.0-287.8 °C (hexane-$CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.18 (s, 2H), 7.43 (dd, *J* = 6.2 and 3.4 Hz, 2H), 7.56 (dd, *J* = 8.1 and 1.2 Hz, 2H), 7.75 (m, 4H), 7.84 (m, 6H), 8.42 (s, 2H), 8.49 (dd, *J* = 6.2 and 3.5 Hz, 2H); IR (KBr/cm^{-1}) 2927, 2851, 1482, 1439, 1379, 1328, 1166, 1122, 1070, 816, 738. HRMS Calcd for $C_{36}H_{20}F_6N_2$: M. 594.1531, found: m/z 594.1538.

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