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CONFORMATIONS OF 2,2’-BIPYRROLE π-SYSTEMS HAVING AN ELECTRON-DONATING SITE AT ONE TERMINAL AND ELECTRON-ACCEPTING SITE AT THE OTHER TERMINAL IN THE GROUND AND EXCITED STATES

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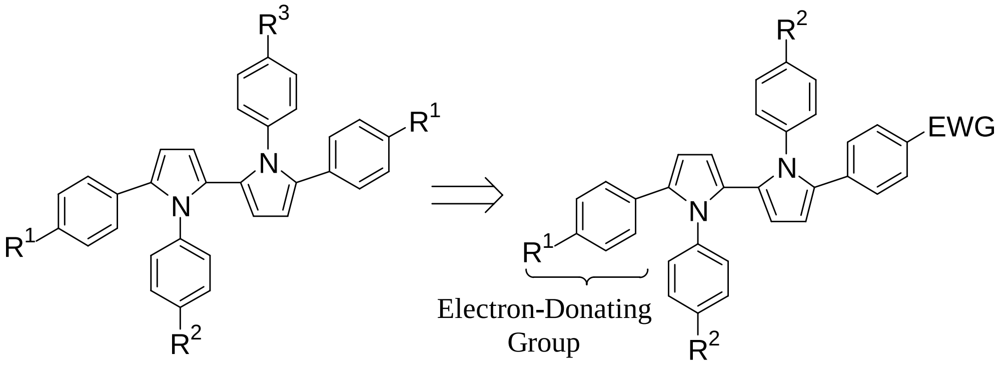
Abstract – Various symmetrical and unsymmetrical 1,1’,5,5’-tetraaryl-2,2’-bipyrroles (**1**, **5**, and **10**) were synthesized. From their UV-VIS absorption and fluorescence spectra, the conformations of the central 2,2’-bipyrrole systems were considered as follows. These compounds adopt twisted conformations in the ground state, but their conformations in the excited state are close to planar ones. Especially, the compounds (**10**) bearing a formyl group and an electron-donating methoxy group showed large Stokes shifts (~160 nm), suggesting effective conjugation through the π-system, which consists of the central 2,2’-bipyrrole, 5-aryl group, and 5’-aryl group, in the excited state.

INTRODUCTION

π-Conjugated systems with five-membered heteroaromatics have been attracting much attention as a new type of optical, electrochemical, and electrical materials.[1-4] We reported a novel π-conjugated system, 1-aryl-2,5-di(2-thienyl)pyrrole that bears various electron-accepting groups (-CHO,[5] -CH=C(SMe)(*p*-Tol),[5a,6] $-CH=C(CN)_2$,[7] $-C(CN)=C(CN)_2$[8]) at the terminal thiophene ring. Furthermore, our attention had been paid to 2,2’-bipyrrole π-systems and 1,1’,5,5’-tetraaryl-2,2’-bipyrroles (**I**) have been developed as a new π-conjugated system.[9] In this π-system, two pyrrole rings are approximately perpendicular to one another in solution, but the conformation of 1,1’,5,5’-tetraphenyl-2,2’-bipyrrole (**I**; $R^1=R^2=R^3=H$) was estimated by a preliminary molecular orbital calculation with the PM3 method to, in the excited state, be close to the planar one.[10] Since introduction of both an electron-donating (D) group and an electron-accepting (A) group into the π-conjugated systems creates unique optical and electrical properties, a large number of papers have been published on such donor-acceptor types of heteroaromatics.[11,12] This context prompted us to investigate how the planarity of the 2,2’-bipyrrole π-system is affected by introducing both an electron-donating group (EDG) and an electron-withdrawing group (EWG) on its terminal positions, in expectation that these groups force the central π-system into a more conjugated conformation.



I II

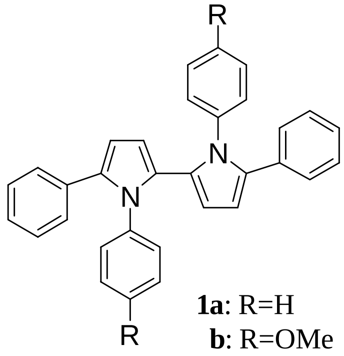
Scheme 1

Many investigations on the UV-VIS absorption spectra of 2-substituted pyrroles appeared in the literatures,[13] but there are a few reports on fluorescence properties of 2,2’-bipyrroles,[13c,g] which would provide useful information on the excited state of the π-conjugated system. Here, we wish to report the conformations of 1,1’,5,5’-tetraaryl-2,2’-bipyrroles (**II** in Scheme 1), which bear an electron-withdrawing formyl group at the terminal position, in the ground and excited states.

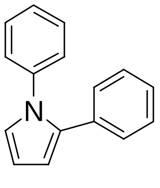
RESULTS AND DISCUSSION

At first, we initiated to investigate the spectral behavior of symmetrical bipyrroles, 1,1’,5,5’-tetraphenyl-2,2’-bipyrrole (**1a**) and 1,1’-bis(4-methoxyphenyl)-5,5’-diphenyl-2,2’-bipyrrole (**1b**), which were obtained according to our previous paper.[9] Furthermore, 1,2-diphenylpyrrole (**2**) was also prepared by the Grevorgyan’s method.[14]

The absorption and fluorescence spectra of **1a** and **1b** were measured in THF solution. These compounds exhibited similar spectra that are summarized in Table 1 and Figure 1, indicating that the methoxy substituents on the 1-phenyl group do not influence the absorption and fluorescence spectra significantly. As reported in the previous paper,[9] two pyrrole rings of **1a** are



1a: R=H
b: R=OMe



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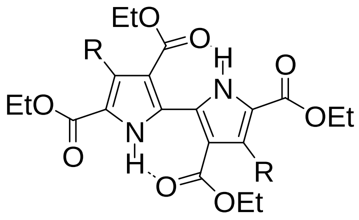
approximately perpendicular to one another in the ground state, because its λ_{max} appears at a longer wavelength only by 24 nm than that of 1,2-diphenylpyrrole (**2**). Similarly, the conformation of **1b** is thought to be largely twisted. In contrast, the emission peaks (λ_{em}) of **1a** and **1b** were observed at 416 nm and 409 nm, respectively, which are longer by 59 nm and 52 nm, respectively, than that of **2**. Further, it is noteworthy that the Stokes shifts of these compounds (**1a** and **1b**) are 112 nm and 105 nm, respectively. These values are much larger in comparison with those (55-65 nm) of the bipyrroles (**3**) which are fixed *via* intramolecular hydrogen bond to be planar.[13c] These findings suggested that, upon excitation, the conformation of **1** changes from twisted one to increase planarity.[15]



3a: R=*n*-Pr
b: R=Ph

Table 1. UV-VIS Absorption, Fluorescence Spectra Data, and Value of Stokes Shift.

entry	compound	(R)	absorption[a]		emission[b]	quantum yield	Stokes shift
			λ_{max} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ_F	Δλ (nm)[c]
1	**1a**	(H)	304	24,000	416	0.60[d]	112
2	**1b**	(OMe)	304	25,500	409	—[e]	105
3	**2**		280	12,700	357	0.26[d]	77
4	**5**		368	20,500	519	0.14[f]	151
5	**10a**	(H)	364	19,200	526	0.13[f]	162
6	**10b**	(OMe)	371	18,100	530	0.10[f]	159
7	**12b**		342	19,700	410	—	68

a Measured in THF (3.0 x 10^{-5} M). b Measured in THF (3.0 x 10^{-7} M). Excited at λ_{max}. c $\Delta\lambda = \lambda_{em} - \lambda_{max}$. d Detemined 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 could not be determined because the floroscence overlapped with the scattering light of the solvent. f Determined by *p*-terphenyl in cyclohexane as a standard (Φ_F=0.87, excited at 265 nm).

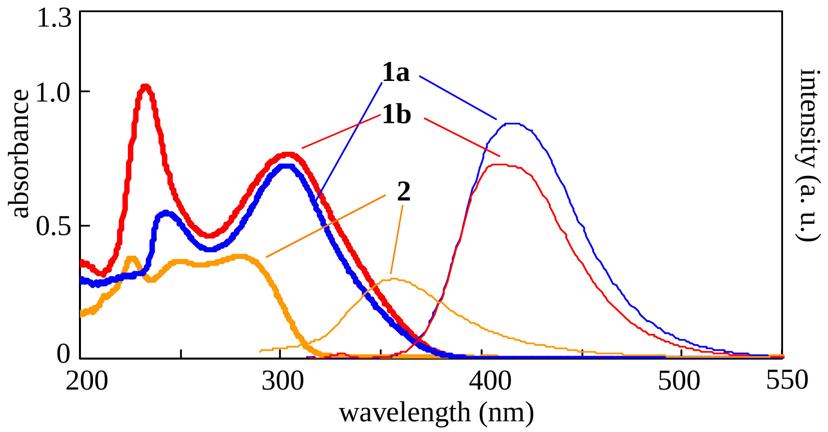
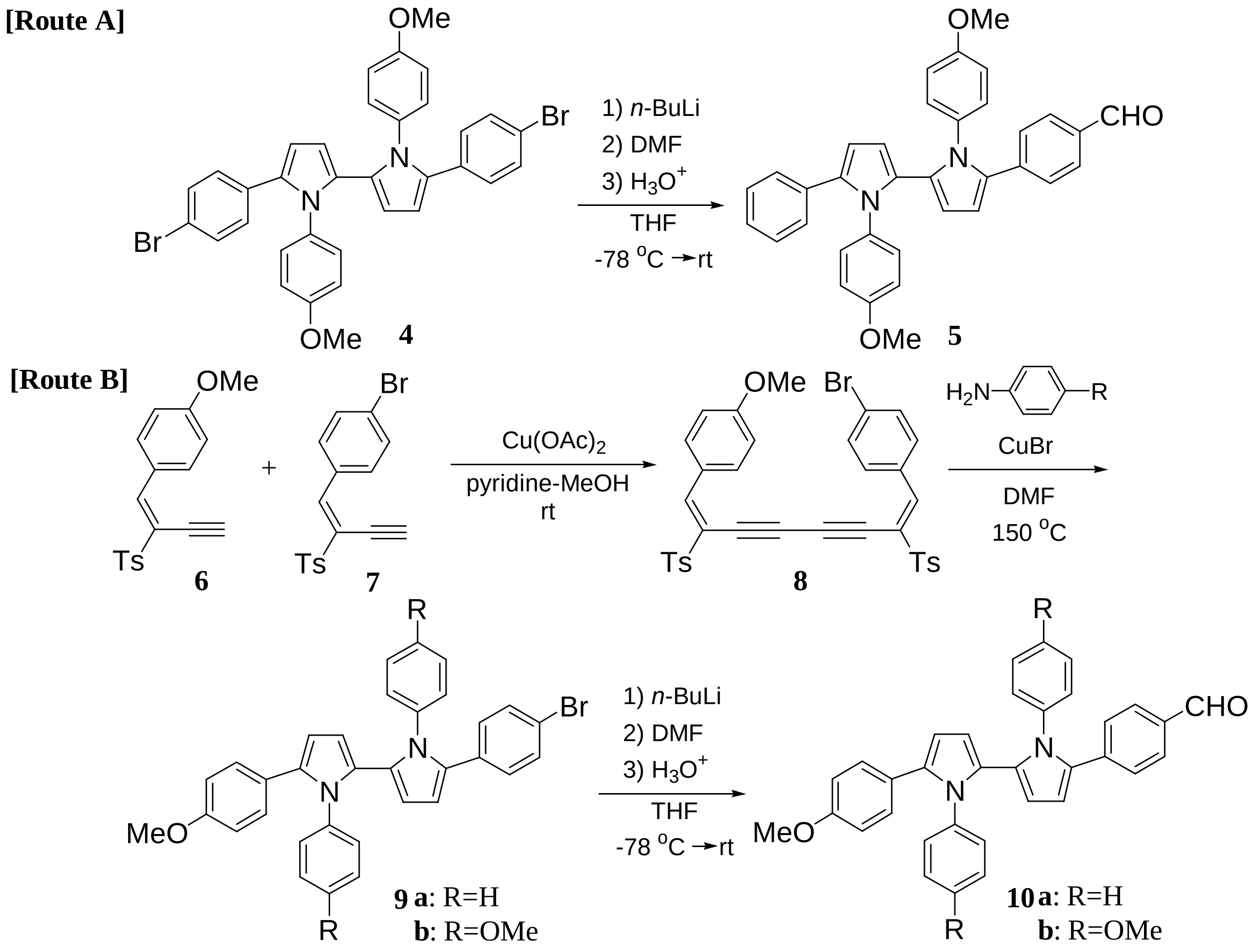
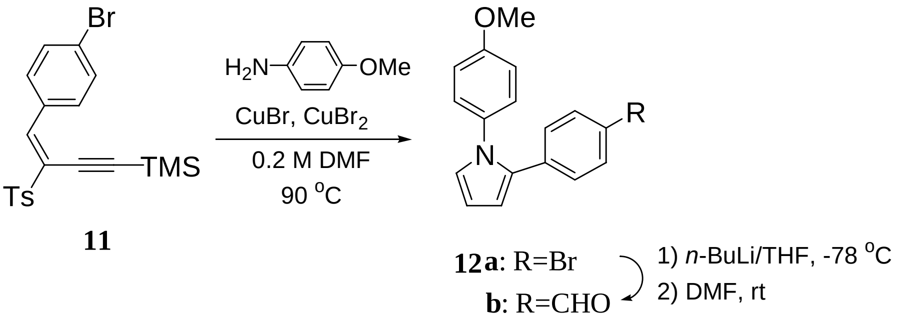


Figure 1. UV-VIS absorption (bold line; 3.0 x 10^{-5} M in THF) and fluorescence (narrow line; 3.0 x 10^{-7} M in THF. Excited at λ_{max}) spectra of **1a**, **1b**, and **2**.

Further, our attention was turned to a donor-acceptor type of 2,2'-bipyrrole. Our previous method can provide symmetrical 1,1',5,5'-tetraaryl-2,2'-bipyrroles (**I**) that have the same aryl group at the 5 and 5' positions, but we have to obtain unsymmetrically substituted 1,1',5,5'-tetraaryl-2,2'-bipyrroles (**II**) in order to achieve the present purpose. This was a difficult problem, but we examined two synthetic routes leading unsymmetrical target molecules, which are summarized in Scheme 2. One method [Route A] is the derivation of an unsymmetrical product (**5**) from symmetrical 5,5'-bis(4-bromophenyl)-1,1'-diphenyl-2,2'-bipyrrole (**4**) that can be prepared by the known method.[9] This route consists of the dilithiation of **4** with *n*-butyllithium followed by the reaction with 1 mol-equivalent of DMF and the subsequent protonation. Another method [Route B] is to obtain unsymmetrical octadiendiyne (**8**) by the cross-type Eglinton coupling from two different 1-aryl-2-tosyl-1-buten-3-ynes (**6** and **7**). The subsequent Cu-catalyzed reactions of **8** with aniline derivatives lead to unsymmetrical 1,1',5,5'-tetraaryl-2,2'-bipyrroles (**9**), which were converted to the target compounds (**10**) by lithiation of the bromo group followed by the treatment with DMF and the subsequent protonation. By these routes, we could obtained the target compounds (**5**, **10a**, and **10b**), though their yields were relatively low because of no optimization of the reaction conditions (see EXPERIMENTAL). For comparison, we also prepared a monopyrrole derivative, 1-(4-methoxyphenyl)-2-phenylpyrrole (**12b**), which was derived from a TMS-protected enynes (**11**) by the $CuBr/CuBr_2$–mediated reaction with aniline[16] followed by the exchange of bromo group to formyl group (Scheme 3).



Scheme 2



Scheme 3

The absorption and fluorescence spectra of the thus-obtained compounds (**5**, **10a**, and **10b**) that bear an electron-accepting group (CHO) were given in Table 1 and Figure 2. These compounds are considered to adopt twisted conformations around the 2,2'-bond in their ground state. This is because their λ_{max} values did not largely deviate from that of the corresponding monopyrrole (**12b**). The difference in the λ_{max} value is 22-29 nm, which is comparable to that between **1** and **2**. Here, it should be noticed that the Stokes shift of **5** is 151 nm. This value is about one and a half times as large as that (105-112 nm) of **1**. The difference in emission maximum (λ_{em}) between **5** and **12b** is 109 nm, which is twice compared with that between **1** and **2**. These facts strongly suggest that the introduction of the electron-accepting formyl group forces the conformation of the 2,2'-bipyrrole π-system to change by excitation to a more planar one.

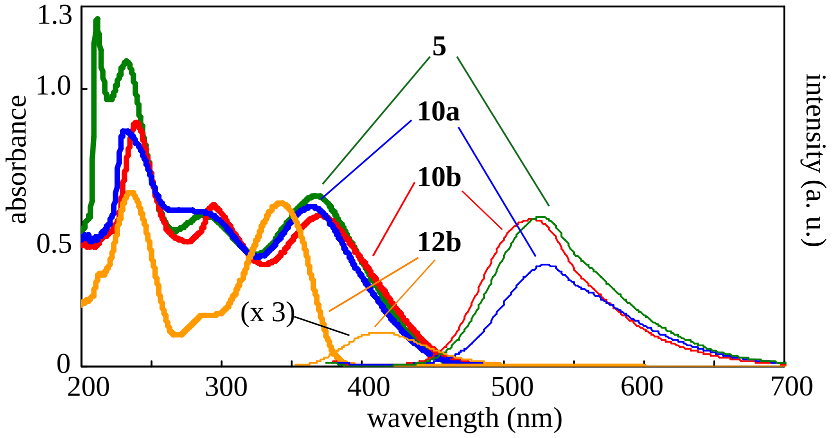


Figure 2. UV-VIS absorption (bold line; 3.0 x 10^{-5} M in THF) and fluorescence (narrow line; 3.0 x 10^{-7} M in THF. Excited at λ_{max}) spectra of **5**, **10a**, **10b**, and **12b**.

Interestingly, in the spectra of the compounds (**10a** and **10b**) bearing the formyl group and an electron-donating methoxy group at the opposite terminal phenyl group, their emission peaks (λ_{em}) shifted to a longer wavelength (**10a**: 526 nm. **10b**: 530 nm) in comparison with that (519 nm) of **5**. This phenomenon can be reasonably explained by the conjugation through the π-system that consists of the central 2,2'-bipyrrole, the 5-phenyl, and 5'-phenyl in the excited state. These large values suggest the spread of the π-system of the excited **10**. Thus, it is concluded that the introduction of a donor-acceptor system makes the conformation of 2,2'-bipyrrole more planar, i.e. more conjugated, in an excited state.

In conclusion, we synthesized the various symmetrical and unsymmetrical 1,1’,5,5’-tetraaryl-2,2’-bipyrroles. From their UV-VIS absorption and fluorescence spectra, it was shown that their conformation in excited state is more close to a planar one though a twisted conformation is favorable in ground state. Notably, the large Stokes shift was attained in the compounds having an electron-accepting formyl group at the terminal phenyl group, suggesting the spread of their π-system. The fluorescence quantum yields of the compounds (**1a**, **2**, **5**, **10a**, and **10b**) reported herein are summarized in Table 1. Among them, the unsubstituted 1,1’,5,5’-tetraphenyl-2,2’-bipyrrole (**1a**) gave the best quantum yield (0.60). This value is higher than that of the corresponding monopyrrole (**2**).

EXPERIMENTAL

General Procedures. Melting points were determined with Yanaco MP-J3 and values were uncorrected. NMR spectra were recorded at 300 MHz (proton) on Varian GEMINI 2000 spectrometer with TMS as internal standard. *J*-Values are given in Hz. IR spectra were measured on a JASCO FT/IR-350 spectrophotometer. 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.

Synthesis of 1,1’-Di(4-methoxyphenyl)-5,5’-diphenyl-2,2’-bipyrrole (1b). A mixture of (1*E*, 7*E*)-1,8-diphenyl-2,7-ditosyl-1,7-ocutadien-3,5-diyne (0.342 g, 0.608 mmol), 4-methoxyaniline (0.599 g, 4.86 mmol), and CuBr (0.349 g, 2.43 mmol) in dry DMF (0.15 mL) was stirred at 150 °C for 1.5 h under N_2 atmosphere. The reaction mixture was cooled down to rt and $CHCl_3$ (10 mL) was added. The precipitated insoluble solid was filtered off and washed with $CHCl_3$ (about 5 mL). Combined organic layers were evaporated in vacuo to give black oil (1.01 g), which was subjected to column chromatography on silica gel (hexane : EtOAc = 3 : 1) to give **1b** (53.2 mg, 18%) as yellow solid. Recrystallization from hexane-EtOAc gave colorless crystals: mp 229.5-230.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.72 (s, 6H), 6.21 (d, *J* = 3.6 Hz, 2H), 6.40 (d, *J* = 3.7 Hz, 2H), 6.59 (s, 8H), 7.00 (dd, *J* = 8.1 and 1.8 Hz, 4H), 7.07-7.12 (m, 6H); IR (KBr/cm^{-1}) 3047, 2954, 2830, 1603, 1514, 1294, 1248, 1029, 831, 758, 700. *Anal.* Calcd for $C_{34}H_{28}N_2O_2$: C, 82.23; H, 5.68; N, 5.64. Found: C, 82.40; H, 5.77; N, 5.55.

Synthesis of 5-(4-Formylphenyl)-1,1’-di(4-methoxyphenyl)-5’-phenyl-2,2’-bipyrrole (5). To a solution of 5,5’-(4-bromophenyl)-1,1’-(4-methoxyphenyl)-2,2’-bipyrrole (**4**)[9] (59.9 mg, 0.0915 mmol) in dry THF (1.00 mL) was dropwise added a solution of *n*-BuLi (0.12 mL, 1.60 M in hexane, 0.192 mmol) at –78 °C. After being stirred for 30 min at that temperature, DMF (8.0 μL, 0.103 mmol) was added to the reaction mixture. After being stirred for 30 min, the mixture was warmed up to rt and stirred for additional 1 h. After quenched with saturated NH_4Cl solution (10 mL), the mixture was extracted with

$CHCl_3$ (5 mL x 3). The combined organic layers were dried over $MgSO_4$. Evaporation in vacuo and column chromatography (silica gel; $CHCl_3$: hexane = 2 : 1) provided **5** (4.3 mg, 9%) with 1,1'-di(4-methoxyphenyl)-5,5'-diphenyl-2,2'-bipyrrole (7.5 mg, 17%) and 5,5'-di(4-formylphenyl)-1,1'-di(4-methoxyphenyl)-2,2'-bipyrrole (9.5 mg, 19%). Recrystallization of **5** from hexane-EtOAc gave yellow crystals; mp 158.4-159.4 °C, ^{1}H NMR ($CDCl_3$) δ 3.74 (s, 3H), 3.76 (s, 3H), 6.17 (d, *J* = 3.8 Hz, 1H), 6.19 (d, *J* = 3.8 Hz, 1H), 6.33 (d, *J* = 3.5 Hz, 1H), 6.49 (d, *J* = 3.8 Hz, 1H), 6.62 (s, 4H), 6.65(s, 4H), 7.00 (d, *J* = 7.9 Hz, 2H), 7.11(t-like, *J* = 8.5 Hz, 3H) 7.12 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 9.87 (s, 1H); IR (KBr/cm^{-1}) 3062, 2935, 2837, 1697, 1597, 1512, 1427, 1252, 1169, 835; HRMS (FAB$^+$) Calcd for $C_{35}H_{28}N_2O_3$: M. 524.2100, found: m/z 524.2056.

Synthesis of (1*E*,7*E*)-1-(4-Bromophenyl)-8-(4-methoxyphenyl)-2,7-ditosyl-1,7-octadien-3,5-diyne (8). Pyridine (16.0 mL) was added to a solution of $Cu(OAc)_2$ (2.91 g, 16.0 mmol) in dry MeOH (100 mL), and the mixture was stirred at rt for 30 min. A solution of (*E*)-1-(4-methoxyphenyl)-2-tosyl-1-buten-3-yne (**6**) (2.50 g, 8.00 mmol) and (*E*)-1-(4-bromophenyl)-2-tosyl-1-buten-3-yne (**7**) (2.88 g, 7.98 mmol) in dry MeOH (35.0 mL) was dropwise added to the mixture over 30 min and the resulting mixture was stirred at rt for 3 h. The mixture was poured into 1 M H_2SO_4 (160 mL), and the precipitated brown solid (5.24 g) was gathered by filtration, washed with MeOH, and subjected to column chromatography on silica gel ($CHCl_3$) to give **8** (2.06 g, 39% yield), (1*E*,7*E*)-1,8-di(4-bromophenyl)-2,7-ditosyl-1,7-octadien-3,5-diyne (1.14 g, 20% yield), and (1*E*,7*E*)-1,8-di(4-methoxyphenyl)-2,7-ditosyl-1,7-octadien-3,5-diyne (1.38 g, 28% yield).[9] Recrystallization of **8** from EtOAc gave yellow crystals: mp 191.5-192.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.47 (s, 6H), 3.88 (s, 3H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 9.1 Hz, 2H), 7.99 (s, 1H), 8.02 (s, 1H); IR (KBr/cm^{-1}) 3033, 2933, 2185, 1581, 1510, 1319, 1263, 1176, 1151, 1087, 675. *Anal.* Calcd for $C_{35}H_{27}O_5BrS_2$: C, 62.59; H, 4.05. Found: C, 62.36; H, 4.15.

Synthesis of 5-(4-Bromophenyl)-5'-(4-methoxyphenyl)-1,1'-diphenyl-2,2'-bipyrrole (9a). A suspension of **8** (342 mg, 0.608 mmol), aniline (599 mg, 4.86 mmol), and CuBr (349 mg, 2.43 mmol) in DMF (0.24 mL) was stirred at 150 °C for 1.5 h under N_2 atmosphere. The reaction mixture was cooled to rt, $CHCl_3$ (10 mL) was added and the precipitated solid was filtered off. The filtrate was evaporated in vacuo and the residue was subjected to column chromatography on silica gel (hexane : EtOAc = 3 : 1) to give **9a** (53.2 mg, 18% yield) as pale yellow solid. Recrystallization from hexane-EtOAc gave pale yellow crystals: mp 191.0-192.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.71 (s, 3H), 6.26 (d, *J* = 3.6 Hz, 1H), 6.27 (d, *J* = 3.6 Hz, 1H), 6.28 (d, *J* = 3.6 Hz, 1H), 6.35 (d, *J* = 3.7 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 4H), 6.65 (d, *J* = 8.9 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 7.00-7.09 (m, 6H), 7.21 (d, *J* = 8.7 Hz, 2H);

IR (KBr/cm^{-1}) 3043, 2937, 2835, 1597, 1496, 1371, 1248, 1038, 831, 773, 754; HRMS (FAB$^+$) Calcd for $C_{33}H_{25}N_2OBr$: M. 544.1150, found: m/z 544.1144.

5-(4-Bromophenyl)-1,1',5'-tri(4-methoxyphenyl)-2,2'-bipyrrole (9b). The titled compound was obtained in 7% yield from **8** with 4-methoxyaniline according to the similar procedure mentioned above: Colorless crystals: mp 166.5-167.5 °C (hexane-EtOAc); ^{1}H NMR ($CDCl_3$) δ 3.73 (s, 3H), 3.74 (s, 3H), 3.75 (s, 3H), 6.16 (d, *J* = 3.4 Hz, 1H), 6.17 (d, *J* = 3.2 Hz, 1H), 6.26 (d, *J* = 3.6 Hz, 1H), 6.33 (d, *J* = 3.7 Hz, 1H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.59 (s-like, 8H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.67 (d, *J* = 8.9 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H); IR (KBr/cm^{-1}) 3033, 2931, 2833, 1608, 1510, 1296, 1248, 1173, 1034, 833. *Anal.* Calcd for $C_{35}H_{29}N_2O_3Br$: C, 69.42; H, 4.83; N, 4.63. Found: C, 69.47; H, 4.93; N, 4.47.

Synthesis of 5-(4-Formylphenyl)-5'-(4-methoxyphenyl)-1,1'-diphenyl-2,2'-bipyrrole (10a). To a solution of **9a** (78.6 mg, 0.144 mmol) in dry THF (0.50 mL) was dropwise added a solution of *n*-BuLi (110 μL, 1.56 M in hexane, 0.173 mmol) at –78 °C. After being stirred for 30 min at that temperature, DMF (15 μL, 0.193 mmol) was added and then the whole was stirred for 40 min. The mixture was warmed up to rt and stirred for additional 1 h. After quenched with saturated NH_4Cl solution (5 mL), the mixture was extracted with $CHCl_3$ (5 mL x 4). The combined organic layers were dried over $MgSO_4$. Evaporation in vacuo and column chromatography (silica gel; hexane : EtOAc = 3 : 1) provided **10a** (54.7 mg, 77%) as yellow solid. Recrystallization from EtOAc gave yellow crystals: mp 223.8-224.8 °C; ^{1}H NMR ($CDCl_3$) δ 3.71 (s, 3H), 6.25 (d, *J* = 3.6 Hz, 1H), 6.28 (d, *J* = 3.7 Hz, 1H), 6.28 (d, *J* = 3.7 Hz, 1H), 6.51 (d, *J* = 3.7 Hz, 1H), 6.59-6.66 (m, 4H), 6.66 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 7.03-7.11 (m, 6H), 7.09 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 9.85 (s, 1H); IR (KBr/cm^{-1}) 3043, 2956, 2835, 2733, 1697, 1599, 1496, 1250, 1173, 1032, 833, 771. *Anal.* Calcd for $C_{34}H_{26}N_2O_2$: C, 82.57; H, 5.30; N, 5.66. Found: C, 82.42; H, 5.41; N, 5.66.

5-(4-Formylphenyl)-1,1',5'-tri(4-methoxyphenyl)-2,2'-bipyrrole (10b). The titled compound was obtained in 51% yield from **9b** according to the similar procedure mentioned above: Yellow crystals; mp 180.1-181.3 °C (EtOAc); ^{1}H NMR ($CDCl_3$) δ 3.73 (s, 3H), 3.74 (s, 3H), 3.76 (s, 3H), 6.14 (d, *J* = 3.7 Hz, 1H), 6.18 (d, *J* = 3.7 Hz, 1H), 6.26 (d, *J* = 3.7 Hz, 1H), 6.49 (d, *J* = 3.7 Hz, 1H), 6.59 (s, 4H), 6.66 (s, 4H), 6.67 (d, *J* = 10.0 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 9.86 (s, 1H); IR (KBr/cm^{-1}) 3039, 2954, 2835, 2736, 1695, 1599, 1512, 1248, 1176, 1030, 835, 771. *Anal.* Calcd for $C_{36}H_{30}N_2O_4$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.66; H, 5.59; N, 4.81.

Synthesis of (*E*)-1-(4-Bromophenyl)-4-trimethylsilyl-2-tosyl-1-buten-3-yne (11). To a solution of (*E*)-1-(4-bromophenyl)-2-tosyl-1-buten-3-yne (350 mg, 0.97 mmol) in dry THF (3.0 mL) was dropwise added a solution of *n*-BuLi (0.62 mL, 1.6 M in hexane, 0.97 mmol) at –78 °C. After being stirred for 5min at that temperature, TMSCl (0.14 mL, 1.06 mmol) was added, and the mixture was stirred for 1 h, and quenched with saturated NH_4Cl solution (10 mL). The mixture was extracted with ether (5 mL x 3) and the combined organic layers were dried over $MgSO_4$. Evaporation in vacuo and column chromatography (silica gel; $CHCl_3$) provided **11** (214 mg, 51%) as orange solid. This compound was characterized by the following spectral data: ^1H NMR ($CDCl_3$) δ 0.21 (s, 9H), 2.45 (s, 3H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.82 (s, 1H), 7.84 (d, *J* = 8.9 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H).

Synthesis of 2-(4-Bromophenyl)-1-(4-methoxyphenyl)pyrrole (12a). To a solution of CuBr (113 mg, 0.789 mmol) and $CuBr_2$ (17.9 mg, 0.079 mmol) in dry DMF (1.0 mL), which was bubbled with N_2 gas for 30 min, was added a solution of 4-methoxyaniline (194 mg, 1.58 mmol) in dry DMF (0.80 mL) at rt. After being stirred for 20 min at that temperature, a solution of **11** (214 mg, 0.49 mmol) in dry DMF (1.2 mL) was added to the reaction mixture, and the whole was stirred at 90 °C for 9 h. After addition of ethyl acetate (10 mL) at rt, the mixture was washed with saturated NaCl solution (10 mL x 3). The aqueous layers were extracted with ethyl acetate (5 mL x 3). The combined organic layers were washed with 2 M HCl (20 mL) and water (20 mL), and dried over $MgSO_4$. Evaporation in vacuo and column chromatography (silica gel; $CHCl_3$) provided **12a** (66.3 mg, 69%) as pale yellow solid. Recrystallization from EtOAc gave pale yellow crystals (mp 143.5-144.5 °C). This compound was characterized by the following spectral data: ^1H NMR ($CDCl_3$) δ 3.82 (s, 3H), 6.33 (dd, *J* = 3.6 and 2.7 Hz, 1H), 6.42 (dd, *J* = 3.6 and 1.8 Hz, 1H), 6.86 (d, *J* = 9.1 Hz, 2H), 6.89 (dd, *J* = 2.7 and 1.8 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 7.08 (d, *J* = 9.1 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H); IR (KBr/cm^{-1}) 3099, 3025, 2954, 2834, 1513, 1485, 1298, 1250, 1038, 833, 792, 728.

Synthesis of 2-(4-Formylphenyl)-1-(4-methoxyphenyl)pyrrole (12b). To a solution of **12a** (49.4 mg, 0.151 mmol) in dry THF (0.5 mL) was dropwise added a solution of *n*-BuLi (0.12 mL, 1.6 M in hexane, 0.187 mmol) at –78 °C. After being stirred for 30 min at that temperature, DMF (15 μL, 0.193 mmol) was added to the reaction mixture. The mixture was stirred for 30 min, warmed up to rt, and were stirred for additional 1 h. After quenched with saturated NH_4Cl solution (5 mL), the mixture was extracted with $CHCl_3$ (5 mL x 3). The combined organic layers were dried over $MgSO_4$. Evaporation in vacuo and column chromatography (silica gel; hexane : EtOAc = 3 : 1) provided **12b** (26.7 mg, 64%) as pale yellow solid. Recrystallization from EtOAc gave yellow crystals: mp 149.5-150.5 °C; ^1H NMR ($CDCl_3$) δ 3.83 (s, 3H), 6.37 (dd, *J* = 3.7 and 2.7 Hz, 1H), 6.59 (dd, *J* = 3.7 and 1.6 Hz, 1H), 6.88 (d, *J* = 8.9 Hz, 2H), 6.95 (dd, *J* = 2.7 and 1.8 Hz, 1H), 7.11 (d, *J* = 8.9 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 9.92 (s, 1H); IR (KBr/ cm^{-1}) 3099, 2960, 2854, 1684, 1599, 1513, 1458, 1248, 1163, 1041, 833. *Anal.* Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 78.05; H, 5.55; N, 4.95.

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10. As reported in our previous paper,[9] the compound (**I**; R^1=R^2=R^3=H) in the ground state adopts a twisted conformation with the N-C-C-N dihedral angle of 93.9^o. When the dihedral angle of

N-C-C-N was fixed to be 180° (planar conformation), the formation energy raised up from 164.82 kcal mol^{-1} to 166.48 kcal mol^{-1}. We also calculated the formation energy for the twisted and planar conformations in the excited state by using keywords (1SCF and excited). The energies were calculated to be 264.85 kcal mol^{-1} and 258.67 kcal mol^{-1}, respectively. These results imply that, in the excited state, the conformation of 1,1',5,5'-tetraaryl-2,2'-bipyrroles rotates about the 2,2'-bond to approach more closely to the planar one.

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