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SYNTHESIS AND OPTICAL PROPERTIES OF 2,2′-BIIMIDAZOLE AND BENZO[*d*]IMIDAZOLE DERIVATIVES: CHANGING π-CONJUGATION BY PHOTOEXCITATION

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Abstract – 1,1′,5,5′-Tetraaryl-2,2′-biimidazole and benzo[*d*]imidazole derivatives were synthesized. Symmetrical and unsymmetrical benzo[*d*]imidazole derivatives could be obtained by the Pd-catalyzed coupling reaction between 2-iodo-benzo[*d*]imidazole and the corresponding (benzo)imidazole anion. Hypsochromic shifts in absorption and fluorescence spectra of 1,1′,5,5′-tetraaryl-2,2′-biazole were observed by switching pyrrole rings for imidazole and benzo[*d*]imidazole rings, resulting in compounds with various Stokes shifts. Based on the (TD)DFT calculation, it was reasoned that changing the conformation of each single bond from a twisted to planar structure by photoexcitation led to larger Stokes shifts.

INTRODUCTION

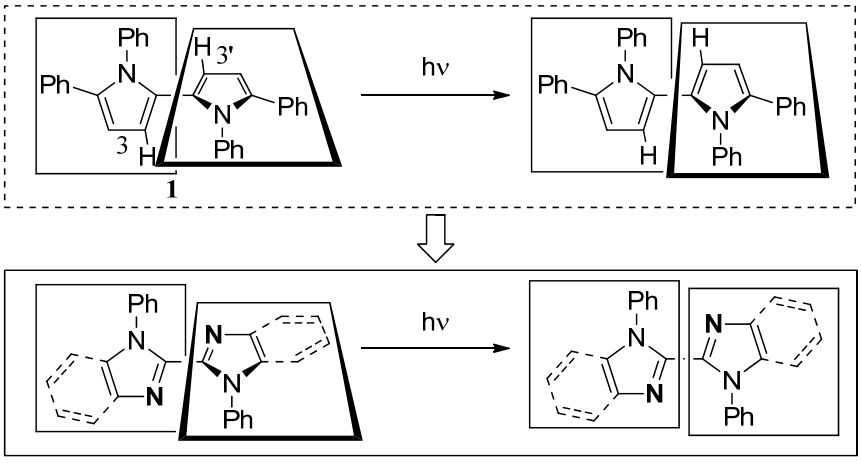
The expansion of the π-conjugation in one molecule by an external stimulus is an important feature in various functional materials. The origin of the alternation of the π-conjugated system is divided broadly into two categories: structural changes and conformational changes. For example, photochromic compounds such as diarylethenes and spiropyranes, are categorized as structural changes and are used in various fields where modifying the structure leads to a change in π-conjugation.[1-5] Conformational transformation to the extended π-conjugated system by the single-bond rotation is achieved by the addition of metal ions to bidentate ligands;[6] such changes can also be made without additives by photoexcitation. For instance, twisted intramolecular charge transfer (TICT) can give rise to fluorescence quenching.[7] TICT is based on changing a planar molecule into a twisted structure between donor and acceptor components

This paper is dedicated to Professor Victor Snieckus on the occasion of his 77th birthday.

before and after photoexcitation.[8]

In studying the expansion of π-conjugation by photoexcitation, we have reported on the conformational changes at 2,2′-bipyrrole single bonds of 1,1′,5,5′-tetraaryl-2,2′-bipyrrole derivatives.[9] In these compounds, the conformations of two pyrrole rings and between the pyrrole ring and the aryl group at the 5 and 5′ positions were twisted in the ground state. This structural change, from twisted to planar, and which occurred by photo irradiation, gave a large Stokes shift. When pyrrole rings of 1,1′,5,5′-tetraphenyl-2,2′-bipyrrole (**1**) were replaced with imidazole rings, it was possible to increase the planarity between the two azoles because of the decrease in steric hindrance derived from the hydrogen atoms at the 3 and 3′ positions (Scheme 1). The effect of the replacement of the pyrrole rings with imidazole on the planarization after photoexcitation is unknown.

The investigation into the metal-coordinating compounds of 2,2′-biimidazoles have been reported.[10] Recently, fluorescence sensing was achieved based on a polymer including the 2,2′-biimidazole structure by Bai and co-workers.[11] However, to the best of our knowledge, there is no report on the research into structural changes of 2,2′-biimidazole derivatives under photoexcitation. Herein, we report the changes in the Stokes shift of 2,2′-biimidazole and 2,2′-bibenzo[*d*]imidazole derivatives bearing phenyl rings at nitrogen atoms under photoexcitation. We found that conformational changes between not only two azole rings but also phenyl rings at the 5 (and 5') position and imidazole rings are necessary to realize greater π-expansion.

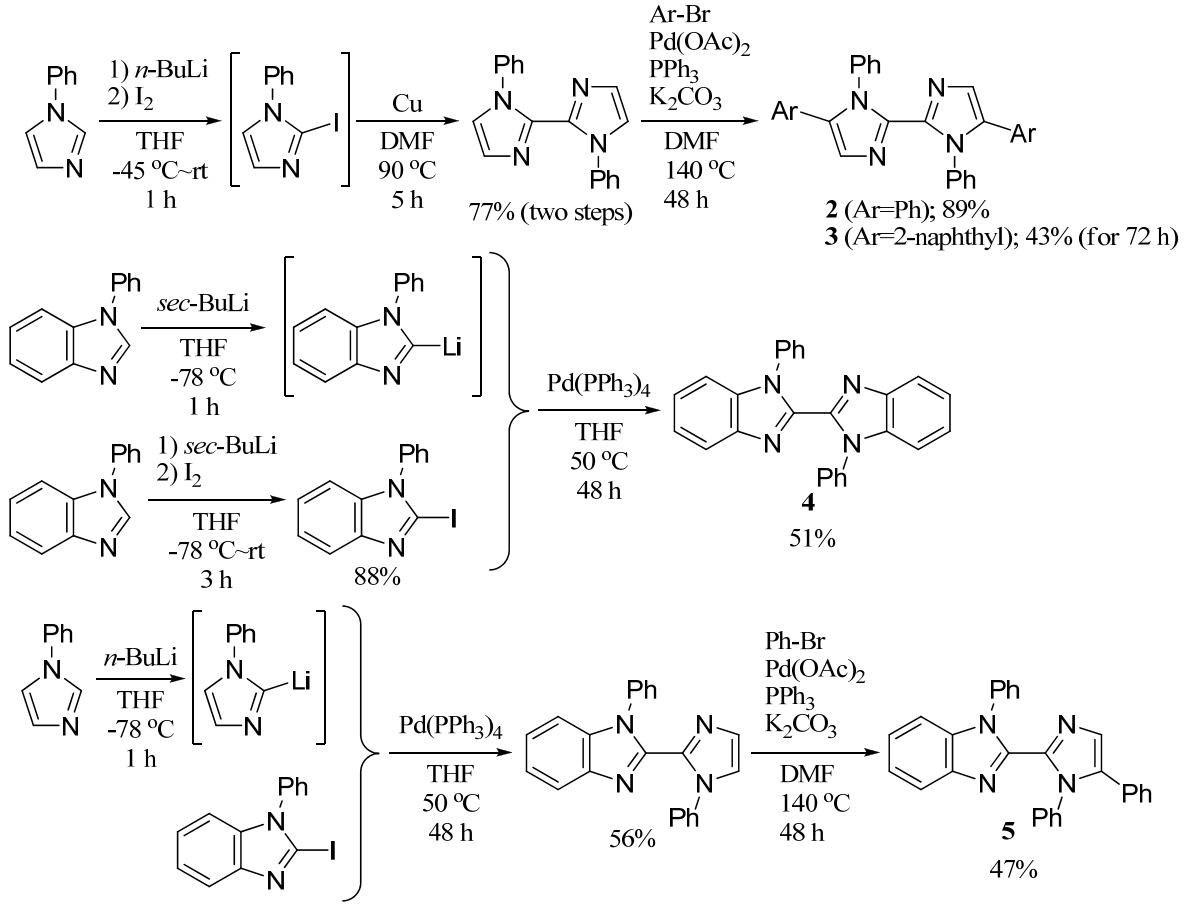


Scheme 1. Proposed representation of the π-expansion of the 2,2′-bipyrrole and 2,2′-biimidazole derivatives by photoexcitation

RESULTS AND DISCUSSION

We focused on those compounds bearing simple aryl substituents such as phenyl and naphthyl groups as the target materials. We synthesized 1,1′,5,5′-tetraphenyl-2,2′-biimidazole (**2**), 1,1′-diphenyl-5,5′-

dinaphthyl-2,2′-biimidazole (**3**), 1,1′-diphneyl-2,2′-bibenzo[*d*]imidazole (**4**), and 1-phenyl-2-(1,5-diphenylimidazol-2-yl)benzo[*d*]imidazole (**5**) to provide a sufficient variety of single-bond rotation platforms to study (Scheme 2). The 2,2′-biimiazole structure was synthesized using the Cu mediated coupling reaction of 2-iodo-1-phenylimidazole in a procedure reported by Park and Alper.[12] Arylation at the 5 and 5′ positions yielded **2** and **3** in a palladium-catalyzed coupling reaction.[13] The position of phenyl rings in **2** was determined by single crystal X-ray crystallographic analysis. Structure **4** was initially obtained with only an 8% yield in the same procedure because the homo coupling reaction of 2-iodo-1-phenylbenzo[*d*]imidazole was inhibited. We then tried another approach with 2-iodo-1-phenylbenzo[*d*]imidazole and 2-lithiated 1-phenylbenzo[*d*]imidazole which returned **4** in 51% yield.[14,15] According to this procedure, we also obtained the unsymmetrical **5** with a yield of 47%.



Scheme 2. Synthesis of **2**, **3**, **4**, and **5**

The optical data of **1**, **2**, **3**, **4**, and **5** in THF are shown in Figure 1 and Table 1. The absorption (λ_{max}) and fluorescence (λ_{em}) peaks of **2** were both shifted to shorter wavelength (entries 1 and 2) compared with **1**. These shifts will be affected by the electronegativity of nitrogen atoms of **2** replacing the 3 and 3′ CH positions in **1**.[16] Bathochromic shifts of λ_{max} and λ_{em} were observed in the spectra of **3** bearing naphthyl

groups at 5 and 5′ positions (entry 3). This further suggests that absorption and emission are influenced toward the edge of the substituents at 5 and 5′ positions. The shoulder peak (400 nm) was also observed in the fluorescence spectrum of **3**. By changing the imidazole group(s) to the benzo[*d*]imidazole, red shifts of λ_{max} were obtained in **4** and **5** as compared to **2** (entry 2 vs. 4 and 5). However, hypsochromic shifts of λ_{em} were observed in **4** and **5** with respect to **2**. All fluorescence quantum yields (Φ_F) of (benzo)imidazole derivatives were lower than that of **1**.

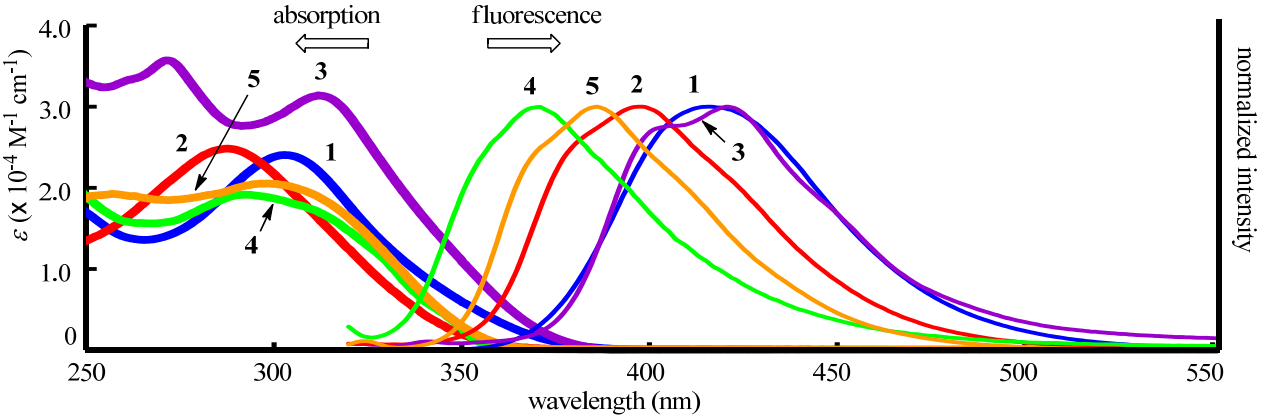


Figure 1. UV-VIS absorption (bold line; 3.0×10^{-5} M in THF) and fluorescence (narrow line; 3.0×10^{-7} M in THF, excited at λ_{max}) spectra of **1** (blue line), **2** (red line), **3** (purple line), **4** (green line), and **5** (orange line)

Table 1. Optical properties of **1-5**

Entry	Compound	Absorption[a]		Fluorescence[b]		Stokes shift	
		λ_{max} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ_F[c]	$\Delta\lambda$ (nm)[d]	$\Delta\nu$ (cm^{-1})[e]
1	**1**	303	24,000	416	0.60	113	8,965
2	**2**	287	24,800	397	0.37	110	9,654
3	**3**	312	31,400	400(sh), 421	0.38	88, 109	7,051, 8,298
4	**4**	292	19,200	371	0.23	79	7,292
5	**5**	298	20,400	386	0.55	88	7,650

[a] Measured in THF (3.0×10^{-5} M). [b] Measured in THF (3.0×10^{-7} M) excited at λ_{max}. [c] Determined by *p*-terphenyl in cyclohexane as a standard (Φ_F=0.87, excited at 265 nm). [d] $\Delta\lambda = \lambda_{em} - \lambda_{max}$. [e] $\Delta\nu = 1/\lambda_{max} - 1/\lambda_{em}$.

In the case of the 2,2′-bipyrrole compounds, we rationalized that the planar structure in the excited state could be investigated by analyzing the Stokes shift; when planarity in the excited state is increased, a larger Stokes shift should be obtained.[9] We therefore focused on the Stokes shifts of compounds **1-5** summarized in Table 1. When the pyrrole structure was switched for imidazole, a larger Stokes shift was obtained in terms of energy (entries 1 and 2), although similar wavelengths were observed (**1**, 113 nm (8,965 cm^{-1}); **2**, 110 nm (9,654 cm^{-1})). This result was unexpected, in which a smaller change was expected in the case of **2**

because of the increased planarity of 2,2′-biazole in the ground state. A smaller energy change between the ground state and excited state ($\Delta\nu$ = 8,298 cm^{-1}) was obtained in **3** (entry 3). Furthermore, **4** and **5** also had smaller Stokes shifts than **2** (entry 2 vs. 4 and 5). A smaller value of $\Delta\nu$ (7,292 cm^{-1}) was obtained in **4** than in **5**, which possessed phenyl substituents at position 5 and allowed comparison with **2**. This implies that the conformational change at the bi(benzo)imidazole moiety as well as at the phenyl rings substituted at 5 (and 5′) position(s) are effective in lengthening emission wavelengths. The value obtained for **4** is still larger than the Stokes shift obtained from the 2,2′-bipyrrole compounds with fixed planar structures via intramolecular hydrogen bonding (65 nm (4,475 cm^{-1}) and 55 nm (3,964 cm^{-1})).[17] Therefore, conformational changes are possible even in **4**.

We also measured the absorption and fluorescence spectra of **1** and **2** in MeCN and EtOH (Figure 2 and Table 2). The λ_{em} of **1** changed substantially by varying the solvent, whereas the λ_{max} was within 4 nm (entries 1, 2, and 3). This compared to a larger change of λ_{max} in **2** (~13 nm), which had a smaller change of λ_{em} between solvents. These results suggest that the compounds have different polarities in the ground and excited states. Compound **1**, bearing the 2,2′-bipyrrole unit, is polar in its excited state, whereas **2**, having 2,2′-biimidazole moiety, is polar in its ground state. However, the difference of Stokes shift between **1** and **2** were consistent in all three solvents: larger Stokes shifts in terms of energy were obtained for **2** in every solvent.

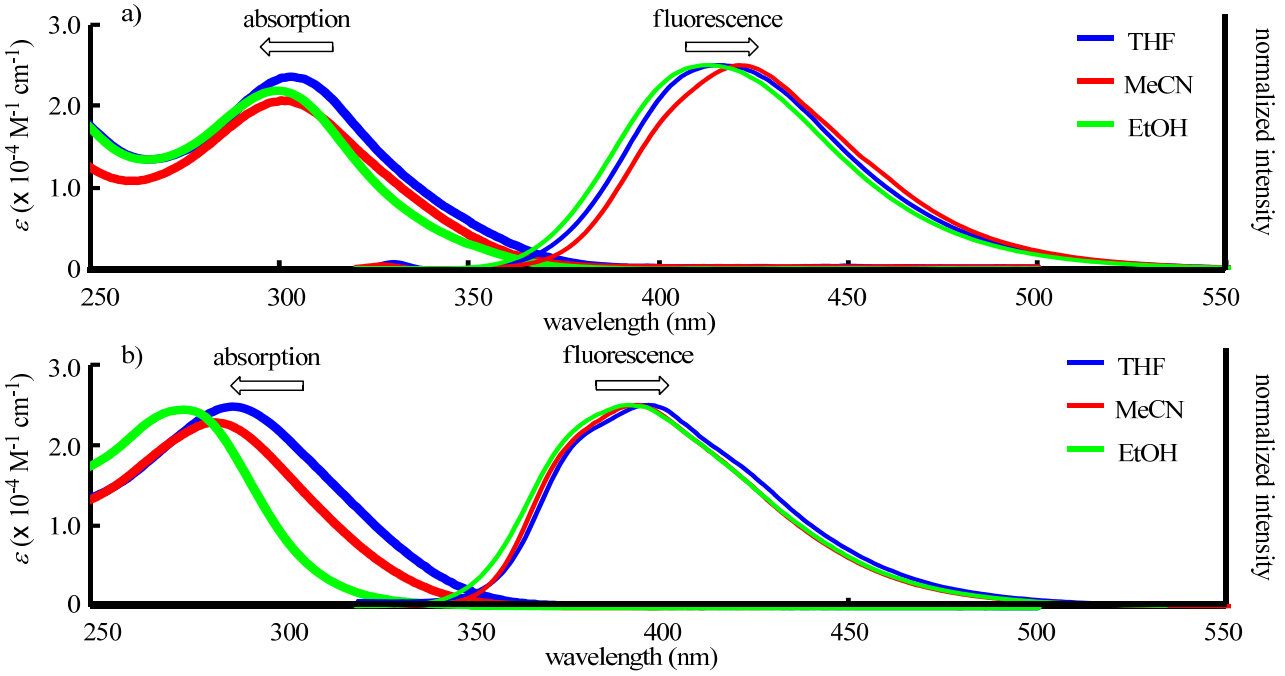


Figure 2. UV-Vis absorption (bold line; 3.0 × 10^{-5} M) and fluorescence (narrow line; 3.0 × 10^{-7} M, excited at λ_{max}) spectra of a) **1** and b) **2** in THF (blue line), MeCN (red line), and EtOH (green line)

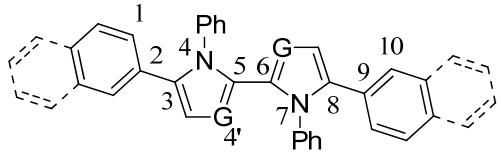
Table 2. Optical properties of **1** and **2** in various solvents

Entry	Compound	Solvent	Absorption[a]		Fluorescence[b]	Stokes shift	
			λ_{max} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	$\Delta\lambda$ (nm)[c]	$\Delta\nu$ (cm^{-1})[d]
1	**1**	THF	303	24,000	416	113	8,965
2	**1**	MeCN	300	20,800	421	121	9,580
3	**1**	EtOH	299	22,000	413	114	9,232
4	**2**	THF	287	24,800	397	110	9,654
5	**2**	MeCN	282	22,800	394	112	10,080
6	**2**	EtOH	274	24,500	392	118	10,986

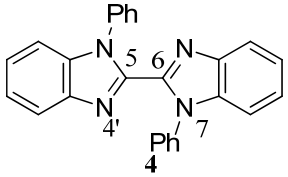
[a] Concentration: 3.0×10^{-5} M. [b] Concentration: 3.0×10^{-7} M. Excited at λ_{max}. [c] $\Delta\lambda = \lambda_{em} - \lambda_{max}$. [d] $\Delta\nu$ $1/\lambda_{max} - 1/\lambda_{em}$.

To further investigate the large Stokes shift in **2**, we examined the structures in the ground and excited states using density functional theory (DFT) with the B3LYP/6-31+G** level on the Gaussian09 program.[18,19] The excited structures were optimized by time-dependent DFT (TDDFT) (nstate=5). The dihedral angles of relevant positions are summarized in Table 3. All compounds showed greater planarity in the excited state than in the ground state, as evidenced by a decrease in the dihedral angle upon excitation. As expected, the dihedral angle between the two imidazole rings of **2** (33.50° for N4′-C5-C6-N7) was smaller than that for **1** (47.01° for C4′-C5-C6-N7) in the ground state (entry 1 vs. 2). The conformational change however, between the two heteroaromatic rings in the ground and excited states was lower in **2** (23.07°) as compared with **1** (26.13°), which contradicts results from the Stokes shifts analysis. We therefore considered all dihedral angles along the long axis of the compounds and found that changes in dihedral angles at 5 and 5′ are more planar in **2** (18.2°) than in **1** (11.2°). The total difference of dihedral-angle change of **2** from the ground to the excited state (A_{GS}–A_{ES}) is larger than that of **1**, leading to improved π-conjugation that is consistent with the larger Stokes shift observed spectroscopically.[20] This was further supported from the HOMO and LUMO orbital energies (Figure 3). The narrower HOMO and LUMO energies in the excited state as compared to the ground state (ΔE) was observed in **1** and **2**, which may explain the fluorescence at longer wavelength than the absorption peak. The difference between the ΔE values for the ground and excited states ($\Delta\Delta E$) of **2** is larger than that of **1** (1.3344 eV and 0.9018 eV, respectively), which would suggest that a larger Stokes shift of **2** would be observed. Additionally, every HOMO and LUMO orbital of **1** and **2** spreads to phenyl rings at the 5 and 5' positions. Further, not only the single bond between two azole rings but also that between phenyl and azole rings showed double bond character in the LUMO orbital. Taking all of these information together, the larger Stokes shift was attributed to efficient planarization, which spread to the edge substituents in an extended π-conjugation network.

Table 3. Dihedral angle of the ground and excited state optimized by (TD)DFT calculation



1 (G=CH), **2** and **3** (G=N)



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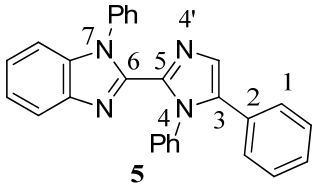

5

Entry	Compound	Position of dihedral angle	Dihedral angle (°)		Sum of dihedral angle (°)		
			Ground state[a]	Excited state[b]	Ground state (A_{GS})[a]	Excited state (A_{ES})[b]	A_{GS}–A_{ES} (°)
1	**1**	C1-C2-C3-N4	40.57	29.34	128.15	79.54	48.61
		C4′-C5-C6-N7	47.01	20.88			
		N7-C8-C9-C10	40.57	29.32			
2	**2**	C1-C2-C3-N4	41.61	23.43	116.72	57.28	59.44
		N4′-C5-C6-N7	33.50	10.43			
		N7-C8-C9-C10	41.61	23.42			
3	**3**	C1-C2-C3-N4	43.61	25.52	109.98	53.18	56.80
		N4′-C5-C6-N7	30.12	7.18			
		N7-C8-C9-C10	36.25	20.48			
4	**4**	N4′-C5-C6-N7	17.47	9.45	17.47	9.45	8.02
5	**5**	C1-C2-C3-N4	42.40	19.85	69.73	28.53	41.20
		N4′-C5-C6-N7	27.33	8.68			

[a] The structure was optimized by DFT/B3LYP/6-31+G** level. [b] The structure was optimized by TDDFT/B3PLY/6-31+G** level using nstate=5.

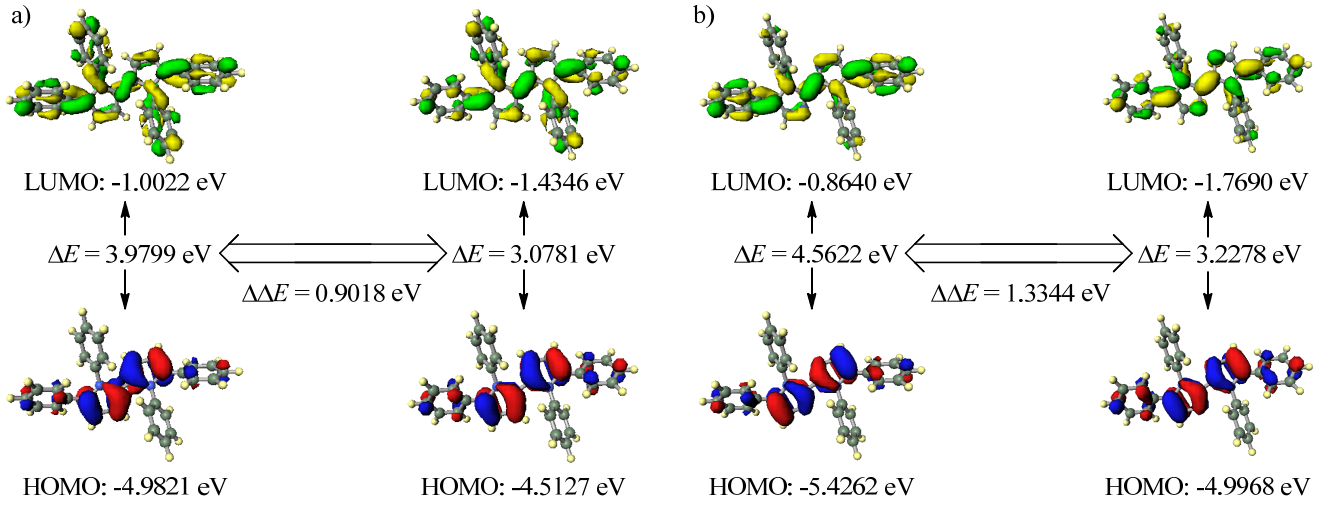

Figure 3. Orbitals and energies of HOMO and LUMO of a) **1** and b) **2**, estimated by DFT (left) and TDDFT (nstate=5) (right) calculated for structure optimization at the B3LYP/6-31+G** level

The order of the Stokes shift in imidazole derivatives, **2**, **3**, **4**, and **5**, is consistent with that of the differences in the dihedral angles (A_{GS}–A_{ES}) (Table 1 and Table 3). The smaller Stokes shift and dihedral angels of **3** were consistent with the observed Stokes shift and dihedral angles of **2** (entry 2 vs. 3 in Table 1 and Table 3).[21] Furthermore, the planarity between two (benzo)imidazole rings of **4** and **5** was increased in the ground state (entry 2 vs. 4 and 5 in Table 3), which led to the bathochromic shift of λ_{max} (entry 2 vs. 4 and 5 in Table 1). Furthermore, the small Stokes shift was also observed in **4** and **5**, because of small A_{GS}–A_{ES} caused by both the small change of the dihedral angle between two (benzo)imidazole rings and the decrease in the number of freely rotating single bonds (three in **2** and **3**, whereas there are only two in **5** and one in **4**).

In conclusion, we synthesized the 1,1′,5,5′-tetraaryl-2,2′-biimidazole and benzo[*d*]imidazole derivatives using the Pd-catalyzed coupling reaction. Hypsochromic shifts in absorption and fluorescence peaks were obtained by switching pyrrole rings for imidazole rings (**1** vs. **2**), which led to a larger Stokes shift of **2** as compared to **1**. From (TD)DFT calculations, a large change of the sum of dihedral angles in the long axis was important to give the larger Stokes shift, and the decrease in the number of the freely rotating single bond was also influenced in the decrease of the Stokes shift. Those findings will be useful in designing compounds having large Stokes shifts, which is important for functional materials such as wavelength conversion materials.

EXPERIMENTAL

Melting points were determined with Yanaco MP-J3 and values were uncorrected. NMR spectra were recorded at 300 MHz (proton) and at 75 MHz (carbon-13) on Varian GEMINI 2000 spectrometer with TMS or $CDCl_3$ as internal standard. J-Values are given in Hz. UV-Vis spectra were measured on a JASCO V570 spectrophotometer. Fluorescence spectra were measured on a JASCO FP-6600 spectrofluorometer. Elemental analyses (EA) were carried out on a Perkin-Elmer 2400CHN or an Exeter Analytical, Inc. CE-440F in Center for Analytical Instrumentation of Chiba University. Mass spectra were carried out on a JEOL JMS-AX500, a JMS-HX110, or THERMO Fisher Exactive in Center for Analytical Instrumentation of Chiba University. Anhydrous THF was distilled from sodium benzophenone ketyl immediately prior to use. Anhydrous DMF was distilled from P_2O_5 under reduced pressure and was stored with MS 4 Å. The reactions were performed under argon atmosphere otherwise noted.

Synthesis of 1,1'-Diphenyl-2,2'-biimidazole: To a solution of 1-phenylimidazole[22] (0.781 g, 5.42 mmol) in THF (10 mL) was dropwisely added *n*-BuLi (3.8 mL, 1.8 M in hexane, 2.1 mmol) at -30 °C. After being stirred for 30 min at that temperature, to the solution was added iodine (1.55 g, 6.11 mmol) at that temperature. The reaction mixture was warmed up to room temperature and stirred for additional 1 h. After quenched with saturated $Na_2S_2O_3$ (5 mL), the mixture was extracted with EtOAc (5 mL × 3). The combined

organic layer was washed with brine (10 mL) and dried over $MgSO_4$. After evaporation in vacuo, the residual mixture was dissolved in DMF (6 mL). To that solution was added Cu powder (0.701 g, 11.0 atom-equivalents). After being stirred for 5 h at 90 °C, the reaction mixture was cooled to room temperature, and was added 28% aqueous NH_3 (70 mL). After being stirred for 1 h to dissolve the excess amount of Cu powder, the mixture was extracted with EtOAc (5 mL × 5). The combined organic layer was washed with brine (10 mL) and dried over $MgSO_4$. After evaporation in vacuo, the residual mixture was recrystallized from hexane and acetone to give 1,1'-diphenyl-2,2'-biimidazole (0.593 g, 2.07 mmol) in 77% yield as colorless plate crystals: mp = 155.5–156.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.71 (diffused d, J = 7.6 Hz, 4H), 7.05 (d, J = 1.2 Hz, 2H), 7.11–7.23 (m, 6H), 7.25 (d, J = 1.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 121.0, 123.7, 127.3, 128.9, 129.8, 136.9, 137.3. Anal. Calcd for $C_{18}H_{14}N_4 \cdot 0.1H_2O$: C, 75.03; H, 4.97; N, 19.44. Found: C, 75.03; H, 5.06; N, 19.47.

Synthesis of 1,1',5,5'-Tetraphenyl-2,2'-biimidazole (2): K_2CO_3 (0.277 mmol, 2.00 mmol) (preheated in vacuo at 120 °C for 2 h), 1,1'-diphenyl-2,2'-biimidazole (0.143 g, 0.499 mmol), bromobenzene (0.331 g, 2.11 mmol), $Pd(OAc)_2$ (22.3 mg, 0.0993 mmol), and PPh_3 (52.4 mg, 0.200 mmol) were dissolved in DMF (2.5 mL). After being stirred for 48 h at 140 °C, the reaction mixture was cooled to room temperature. After addition of brine (10 mL), the mixture was extracted with $CHCl_3$ (10 mL × 4). The combined organic layer was washed with brine (10 mL) and dried over $MgSO_4$. After evaporation in vacuo, the residual mixture was subjected to column chromatography on silica-gel (hexane : EtOAc = 1 : 1) to give **2** (0.197 g, 0.449 mmol) in 89% yield. Rercrystallization from hexane and $CHCl_3$ gave colorless needle crystals: mp = 281.8–282.4 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.74 (d, J = 7.3 Hz, 4H), 7.01 (m, 4H), 7.10–7.23 (m, 12H), 7.31 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 127.1, 127.4, 127.8, 128.2, 128.2, 128.5, 128.8, 129.4, 134.1, 136.0, 139.4. Anal. Calcd for $C_{30}H_{22}N_4 \cdot 0.5H_2O$: C, 80.51; H, 5.18; N, 12.52. Found: C, 80.59; H, 5.03; N, 12.55.

Synthesis of 5,5'-Di(naphthalen-2-yl)-1,1'-diphenyl-2,2'-biimidazole (3): The titled compound was prepared with 1,1'-diphenyl-2,2'-biimidazole and 2-bromonaphthalene for 72 h in 43% yield according to a procedure mentioned in **2**: colorless powder; mp = 275.7–277.3 °C (hexane –$CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.83 (d, J = 7.5 Hz, 4H), 7.06 (dd, J = 1.6 and 8.5 Hz, 2H), 7.14 (t, J = 7.8 Hz, 4H), 7.21 (t, J = 7.1 Hz, 2H), 7.39-7.43 (m, 6H), 7.54 (s, 2H), 7.61 (s, 2H), 7.62-7.64 (m, 2H), 7.70-7.73 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 125.9, 126.2, 126.3, 126.8, 127.1, 127.2, 127.5, 127.8, 127.9, 128.9 (large intensity), 129.0, 132.3, 133.1, 134.2, 136.1, 139.6. Anal. Calcd for $C_{38}H_{26}N_4 \cdot 0.25H_2O$: C, 84.03; H, 4.92; N, 10.32. Found: C, 84.21; H, 4.77; N, 10.40.

Synthesis of 2-Iodo-1-phenylbenzo[*d*]imidazole: To a solution of 1-phenylbenzo[*d*]imidazole[23] (1.55 g, 7.98 mmol) in THF (25 mL) was dropwisely added *sec*-BuLi (10.0 mL, 1.0 M in cyclohexane/hexane, 10 mmol) at -60 °C. After being stirred for 30 min at that temperature, to the solution was added iodine (2.35 g,

9.26 mmol) at that temperature. The reaction mixture was warmed up to room temperature and stirred for additional 2.5 h. After quenched with saturated $Na_2S_2O_3$ (5 mL), the mixture was extracted with EtOAc (10 mL × 3). The combined organic layer was washed with brine (20 mL) and dried over $MgSO_4$. After evaporation in vacuo, the residual mixture was subjected to column chromatography on silica-gel (hexane : EtOAc = 2 : 1) to give 2-iodo-1-phenylbenzo[*d*]imidazole (1.97 g, 6.15 mmol) in 77% yield as colorless solid: mp = 162.2–163.2 °C (hexane-$CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (d, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 6.9 Hz, 1H), 7.26 (dt, *J* = 1.6 and 7.5 Hz, 1H), 7.40 (diffused dd, *J* = 3.4 and 7.6 Hz, 2H), 7.59 (m, 3H), 7.78 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 103.5, 110.2, 119.2, 122.7, 123.6, 128.2, 129.5, 129.7, 136.7, 137.5, 145.4. Anal. Calcd for $C_{13}H_9IN_2$: C, 48.77; H, 2.83; N, 8.75. Found: C, 48.82; H, 2.81; N, 8.60.

Synthesis of 1,1'-Diphenyl-2,2'-bibenzo[*d*]imidazole (4): To a solution of 1-phenylbenzo[*d*]imidazole[23] (0.293 g, 1.51 mmol) in THF (4 mL) was dropwisely added *sec*-BuLi (1.8 mL, 1.0 M in cyclohexane/hexane, 10 mmol) at -60 °C. After being stirred for 1 h at that temperature, the mixture was added to a solution of $Pd(PPh_3)_4$ (12.2 mg, 0.0106 mmol) and 2-iodo-1-phenylbenzo[*d*]imidazole (0.358 g, 1.12 mmol) in THF (3 mL) at -60 °C. After being stirred for 48 h at 50 °C, the reaction mixture was cooled to room temperature. After addition of H_2O (10 mL), the mixture was extracted with EtOAc (10 mL × 3). The combined organic layer was washed with brine (20 mL) and dried over $MgSO_4$. After evaporation in vacuo, the residual mixture was subjected to column chromatography on silica-gel (hexane : EtOAc = 2 : 1) to give **4** (0.197 g, 0.510 mmol) in 51% yield. Rercrystallization from hexane and THF gave colorless plate crystals: mp = 173.3–173.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.85 (diffused d, *J* = 7.0 Hz, 4H), 7.20-7.33 (m, 10H), 7.37 (dt, *J* = 1.7 and 6.6 Hz, 2H), 7.93 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 110.6, 121.1, 123.3, 124.4, 125.6, 127.8, 129.5, 135.3, 135.4, 143.0, 143.1. HRMS (FAB): Calcd for $C_{26}H_{19}N_4$ ($[M+H]^+$): 387.1610. Found: 387.1617. Anal. Calcd for $C_{26}H_{18}N_4$: C, 80.81; H, 4.69; N, 14.50. Found: C, 80.50; H, 4.46; N, 14.38.

Synthesis of 1-Phenyl-2-(1-phenylimidazol-2-yl)benzo[*d*]imidazole: To a solution of 1-phenylimidazole[22] (0.526 g, 3.65 mmol) in THF (8 mL) was dropwisely added *n*-BuLi (2.7 mL, 1.6 M in hexane, 4.3 mmol) at -78 °C. After being stirred for 1 h at that temperature, the mixture was added to a solution of $Pd(PPh_3)_4$ (12.2 mg, 0.0106 mmol) and 2-iodo-1-phenylbenzo[*d*]imidazole (0.358 g, 1.12 mmol) in THF (3 mL) at -78 °C. After being stirred for 72 h at 50 °C, the reaction mixture was cooled to room temperature. After addition of H_2O (10 mL), the mixture was extracted with EtOAc (10 mL × 3). The combined organic layer was washed with brine (20 mL) and dried over $MgSO_4$. After evaporation in vacuo, the residual mixture was subjected to column chromatography on silica-gel (hexane : EtOAc = 2 : 1) to give 1-phenyl-2-(1-phenylimidazol-2-yl)benzo[*d*]imidazole (0.375 g, 1.11 mmol) in 56% yield. Rercrystallization from hexane and $CHCl_3$ gave colorless prism crystals: mp = 175.0–176.8 °C; ^{1}H NMR

(300 MHz, $CDCl_3$) δ 6.77 (d, J = 7.5 Hz, 2H), 6.81 (d, J = 7.0 Hz, 2H), 7.10–7.37 (m, 11H), 7.90 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 110.5, 120.9, 121.9, 123.1, 124.0 (large height), 125.6, 127.6, 129.2, 129.3, 130.4, 135.1, 135.6, 137.0, 137.2, 143.1, 143.3. HRMS (FAB): Calcd for $C_{22}H_{17}N_4$ ($[M+H]^+$): 337.1453. Found: 337.1449.

Synthesis of 2-(1,5-Diphenylimidazol-2-yl)-1-phenylbenzo[*d*]imidazole (5): The titled compound was prepared with 1-phenyl-2-(1-phenylimidazol-2-yl)benzo[*d*]imidazole and half equivalent of corresponding reagents for 46 h in 47% yield according to a procedure mentioned in **2**: colorless powder; mp = 202.3–203.9 °C (hexane-EtOAc); ^1H NMR (300 MHz, $CDCl_3$) δ 6.68 (d, 2H, J = 7.6 Hz), 6.94 (m, 2H), 7.00–7.09 (m, 4H), 7.16–7.36 (m, 10H), 7.39 (s, 1H), 7.87 (d, 1H, J = 7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 110.5, 120.7, 123.0, 125.8, 126.8, 127.6, 127.9, 128.3 (large intensity), 128.9, 129.07, 129.13, 129.3, 134.7, 135.1, 135.66, 135.69, 138.9, 142.9, 143.4. HRMS (FAB): Calcd for $C_{26}H_{19}N_4$ ($[M+H]^+$): 413.1766. Found: 413.1779. Anal. Calcd for $C_{26}H_{18}N_4 \cdot 0.09EtOAc$: C, 81.02; H, 4.97; N, 13.33. Found: C, 81.01; H, 4.92; N, 13.13.

X-Ray Crystallography: X-Ray diffraction data for the crystal was measured on a Bruker APEXII CCD diffractometer with graphite monochromated Mo Kα (λ=1.54178 Å). The structure was solved by a direct method SHELXS-97[24] and refined by SHELXL-97[24] in a computer program package from Bruker AXS. Hydrogen atoms are calculated in appropriate position.

2: $C_{30}H_{22}N_4$, M_r=438.52, monoclinic, $P2_1/n$, T=173 K, a=5.9583(4) Å, b=11.7853(8) Å, c=15.8218(10) Å, β=92.3750(10)°, V=1110.06(13) Å^3, Z=2, D_c= 1.312 g cm^{-3}, R_1=0.0383, wR_2=0.0847. Deposition number CCDC-940241 for **2**. Free copies of the data can be obtained *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge, Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

REFERENCES AND NOTES

1. H. Dürr, *Angew. Chem.*, 2004, **116**, 3404.
2. (a) H. Tian and S. Yang, *Chem. Soc. Rev.*, 2004, **33**, 85; (b) M. Irie, *Chem. Rev.*, 2000, **100**, 1685.
3. V. I. Minkin, *Chem. Rev.*, 2004, **104**, 2751.
4. (a) G. Liu, S. Pu, and R. Wang, *Org. Lett.*, 2013, **15**, 980; (b) S. Chen, L.-J. Chen, H.-B. Yang, H. Tian, and W. Zhu, *J. Am. Chem. Soc.*, 2012, **134**, 13996; (c) S. Delbare, J. Berthet, T. Shiozawa, and Y. Yokoyama, *J. Org. Chem.*, 2012, **77**, 1853; (d) V. A. Migulin, M. M. Krayushkin, V. A. Barachevsky, O. I. Kobeleva, T. M. Valova, and K. A. Lyssenko, *J. Org. Chem.*, 2012, **77**, 332; (e) K. Uchida, Y. Yamanoi, T. Yonezawa, and H. Nishihara, *J. Am. Chem. Soc.*, 2011, **133**, 9239; (f) T. Fukaminato, T. Doi, N. Tamaoki, K. Okuno, Y. Ishibashi, H. Miyasaka, and M. Irie, *J. Am. Chem. Soc.*, 2011, **133**, 4984; (g) M. Morimoto and M. Irie, *J. Am. Chem. Soc.*, 2010, **132**, 14172.

5. (a) X. Xie, G. Mistlberger, and E. Bakker, *J. Am. Chem. Soc.*, 2012, **134**, 16929; (b) Z. Shi, P. Peng, D. Strohecker, and Y. Liao, *J. Am. Chem. Soc.*, 2011, **133**, 14699; (c) M.-C. Zhu, G.-F. Zhang, C. Li, M. P. Aldred, E. Chang, R. A. Drezek, and A. D. Q. Li, *J. Am. Chem. Soc.*, 2011, **133**, 365; (d) A. V. Chernyskev, A. V. Metelitsa, E. B. Gaeva, N. A. Voloshin, G. S. Borodkin, and V. I. Minkin, *J. Phys. Org. Chem.*, 2007, **20**, 908; (e) N. Shao, J. Y. Jin, S. M. Cheung, R. H. Yang, W. H. Chan, and T. Mo, *Angew. Chem. Int. Ed.*, 2006, **45**, 4944; (f) M.-Q. Zhu, L. Zhu, J. J. Han, W. Wu, J. K. Hurst, and A. D. Q. Li, *J. Am. Chem. Soc.*, 2006, **128**, 4303.
6. (a) G. Haberhauer, *Angew. Chem. Int. Ed.*, 2008, **47**, 3635; (b) B. Wang and M. R. Wasielewski, *J. Am. Chem. Soc.*, 1997, **119**, 12.
7. (a) E. Lippert, W. Rettig, V. Bonacic-Koutecky, F. Heisel, and J. A. Miehe, *Adv. Chem. Phys.*, 1987, **68**, 1; (b) E. Lippert, W. Lüder, F. Moll, H. Nagele, H. Boos, H. Prigge, and I. Siebold-Blankenstein, *Angew. Chem.*, 1961, **73**, 695.
8. (a) T. Taniguchi, J. Wang, S. Irie, and S. Yamaguchi, *Dalton Trans.*, 2013, **42**, 620; (b) G. Li, D. Magana, and R. B. Dyer, *J. Phys. Chem. B*, 2012, **116**, 12590; (c) Q. Li, M. Peng, H. Li, C. Zhong, L. Zhang, X. Cheng, X. Peng, Q. Wang, J. Qin, and Z. Li, *Org. Lett.*, 2012, **14**, 2094; (d) K.-F. Chen, C.-W. Chang, J.-L. Lin, Y.-C. Hsu, M.-C. P. Yeh, C.-P. Hsu, and S.-S. Sun, *Chem. Eur. J.*, 2010, **16**, 12873.
9. (a) S. Matsumoto, T. Kobayashi, and K. Ogura, *Heterocycles*, 2006, **68**, 283; (b) S. Matsumoto, T. Kobayashi, and K. Ogura, *Heterocycles*, 2005, **66**, 319.
10. (a) J. C. Freys and O. S. Wenger, *Eur. J. Inorg. Chem.*, 2010, 5509; (b) D. Buist, N. J. Willams, J. H. Reibenspies, and R. D. Hancock, *Inorg. Chem.*, 2010, **49**, 5033; (c) E. Laurila, L. Oresmaa, M. Niskanen, P. Hirva, and M. Haukka, *Cryst. Growth Des.*, 2010, **10**, 3775; (d) C. Borel, K. Larsson, M. Håkansson, B. E. Olsson, A. D. Bond, and L. Öhrström, *Cryst. Growth Des.*, 2009, **9**, 2821; (e) Y. Parajó, J. L. Arolas, V. Moreno, Á. Sánchez-González, J. Sordo, R. de Llorens, F. X. Avilés, and J. Lorenzo, *Inorg. Chim. Acta,* 2009, **362**, 946; (f) L. M. Gruia, F. D. Rochon, and A. L. Beauchamp, *Can. J. Chem.*, 2007, **85**, 520; (g) T. Murata, Y. Morita, K. Fukui, Y. Yakiyama, K. Sato, D. Shiomi, T. Takai, and K. Nakasuji, *Cryst. Growth Des.*, 2006, **6**, 1043; (h) R.-L. Sang and L. Xu, *Inorg. Chim. Acta*, 2006, **359**, 2337; (i) R. Sang and L. Xu, *Inorg. Chem.*, 2005, **44**, 3731; (j) J. S. Casas, A. Castiñeiras, Y. Parajó, A. Sánchez, Á. Sánchez-González, and J. Sordo, *Polyhedron*, 2005, **24**, 1196.
11. (a) Y. Bao, H. Wang, Q. Li, B. Liu, Q. Li, W. Bai, B. Jin, and R. Bai, *Macromolecules*, 2012, **45**, 3394; (b) Y. Bao, Q. Li, B. Liu, F. Du, J. Tian, H. Wang, Y. Wang, and R. Bai, *Chem. Commun.*, 2012, **48**, 118.
12. S. B. Park and H. Alper, *Chem. Commun.*, 2004, 1306; *idem*, *Org. Lett.*, 2003, **5**, 3209.
13. S. Pivsa-Art, T. Satoh, Y. Kawamura, M. Miura, and M. Nomura, *Bull. Chem. Soc. Jpn.*, 1998, **71**,

467.

14. A. Pelter, M. Rowlands, and G. Clements, *Synthesis*, 1987, 51.
15. Synthesis of 2,2′-bibenzo[*d*]imidazole by the homo coupling reaction using $Cu(OAc)_2$ and Ag_2CO_3 under aerated conditions was also reported: D. Monguchi, A. Yamamura, T. Fujiwara, T. Somete, and A. Mori, *Tetrahedron Lett.*, 2010, **51**, 850.
16. S. Matsumoto, E. Batmunkh, M. Akazome, Y. Takata, and M. Tamano, *Org. Biomol. Chem.*, 2011, **9**, 5941.
17. C.-M. Che, C.-W. Wan, W.-Z. Lin, W.-Y. Yu, Z.-Y. Zhou, W.-Y. Lai, and S.-T. Lee, *Chem. Commun*., 2001, 721.
18. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, revision A. 02, Gaussian, Inc., Wallingford, CT, 2009.
19. Cartesian coordinates for results of DFT and TDDFT calculation in **1**-**5** were supplied as Supporting Information on web.
20. (a) Q.-C. Yao, D.-E. Wu, and M. Xia, *J. Mol. Struct.*, 2013, **1042**, 78; (b) H. Langhals and A. Hofer, *J. Org. Chem.*, 2012, **77**, 9585; (c) Y. Chen, J. Zhao, H. Guo, and L. Xie, *J. Org. Chem.*, 2012, **77**, 2192.
21. The calculation for **3** was optimized as unsymmetrical structures in both DFT and TDDFT methods, despite the symmetrical structure being given as the starting conformation. We could not find any explanation for the calculated results.
22. A. Klapars, J. C. Antilla, X. Huang, and S. L. Buchwald, *J. Am. Chem. Soc.*, 2001, **123**, 7727.
23. L. Zhu, P. Guo, G. Li, J. Lan, R. Xie, and J. You, *J. Org. Chem.*, 2007, **72**, 8535.
24. G. M. Sheldrick, SHELXS-97 and SHELXL-97, University of Göttingen: Göttingen, Germany, 1997.