Supporting Information

Engineering control over conformation of alkyne - aryl bond
by the introduction of cationic charge

Takashi Terashima, Takuya Nakashima, and Tsuyoshi Kawai*

Graduate School of Materials Science, Nara Institute of Science and Technology,
8916-5 Takayama, Ikoma, Nara, 630-0192, Japan
Experimental Section

**General.** ^1^H-NMR spectra were measured with JEOL AL-300N FT NMR SYSTEM (300 MHz) in CDCl3. Elemental analysis were performed for C, H, N by using Perkin Elmer, 2400 II CHNS/O.

MALDI-MS data were recorded by Applied Biosystems Voyager DE-STR. HRMS data were recorded by JEOL JMS-700 MStation. Thin layer chromatography (TLC) was performed on aluminum plates coated with silica gel 60 F254 (Merck) or aluminum oxide gel 60 F254 (Merck). Column chromatography was performed using SilicaGel 60 (70-230 mesh; nacalai tesque) or aluminum oxide 90 standard (MERCK).

Chemicals were purchased from Wako Pure Chemical Industries Ltd. and used as received without further purification. The Gaussian03 programs were used for all quantum chemical calculations.
**Spectroscopy.** UV-visible absorption and fluorescence spectra were measured with HITACHI F-4500 Fluorescence spectrometer and Jasco V-660 spectrophotometer, respectively, in a degassed spectral grade DMSO, methanol, and chloroform. Absorption and fluorescence spectra were measured in DMSO of spectroscopy grade as the solvent. For fluorescent spectroscopy, 430 nm was irradiated for excitation. Emission quantum yields and emission lifetimes of 1 and 2 were measured in degassed chloroform and that of 3 was measured in degassed methanol, by utilising a calibrated integrating sphere. All measurements were performed at room temperature, ca. 24°C.

**Materials and Methods**

**Scheme S-1**

![Scheme S-1](image-url)
Preparation of 1,4-dimethyl-2-phenyl-1H-imidazole (5). In a flask, 4-methyl-2-phenyl-1H-imidazole (5.0 g, 31.6 mmol), 18-crown-6 (0.77 g, 2.9 mmol), and t-BuOK (3.6 g, 32.1 mmol) were stirred in THF (50 ml). Iodomethane (4.5 g, 31.7 mmol) dissolved in THF (90 ml) was added slowly using a dropping funnel. The mixture was stirred overnight at room temperature. The reaction mixture was poured into brine and extracted with chloroform. The organic layers were washed several times with brine and separated and dried with magnesium sulfate. After removal of the solvent, the crude product was purified with silica gel column chromatography using ethyl acetate/chloroform (1:2) to yield 3.1 g (57%) of yellow oil. $^1$H NMR (300 MHz, CDCl$_3$): δ 7.63-7.60 (m, 2H), 7.47-7.38 (m, 3H), 6.69 (s, 1H), 3.68 (s, 3H), 2.27 (s, 3H).

Figure S1. $^1$H NMR of 5
Preparation of 5-iodo-1,4-dimethyl-2-phenyl-1H-imidazole (6). 4(2.0 g, 11.6 mole), acetic acid (11.6 mL), water (8.6 mL), conc-sulfuric acid (2.0 mL), HIO₃ (0.51 g, 2.9 mol), and iodine crystals (1.5 g, 6.0 mmol) were stirred at 70 °C for 3h. The reaction mixture was neutralized with K₂CO₃ aq and poured into saturated sodium thiosulfate solution and extracted with chloroform. The organic layer was separated, dried with magnesium sulfate, and evaporated to give colorless solid. This solid was purified by column chromatography over silica gel using ethyl acetate as eluent and to yield 2.5 g (72%) of colorless solid; ¹H NMR (300 MHz, CDCl₃): δ 7.58-7.55 (m, 2H), 7.48-7.41 (m, 3H), 3.65 (s, 3H), 2.30 (s, 3H).

Figure S2. ¹H NMR of 6
Preparation of 1,4-dimethyl-2-phenyl-5-((trimethylsilyl)ethynyl)-1H-imidazole (7).

(trimethylsilyl)acetylene (1.0 g, 10.2 mmol) was added to a stirring solution of aryl iodide 6 (1.6 g, 5.5 mmol), Ag₂O (1.4 g, 5.9 mmol), and CuI (0.1 mg, 0.53 mmol) in 80 mL of THF was added. After N₂ bubbled for 20 min, Pd(PPh₃)₄ (0.31 g, 0.27 mmol) was added. The mixture was refluxed at 90 °C for 5 h. The crude product was filtered by celite. After removal of the solvent, the product was purified by column chromatography over aluminum gel using ethyl acetate/hexane (1:4) as eluent and to yield 1.1 g (77%) of brown oil; ¹H NMR (300 MHz, CDCl₃): δ 7.63-7.60 (m, 2H), 7.47-7.42 (m, 3H), 3.68 (s, 3H), 2.34 (s, 3H), 0.28 (s, 9H). MALDI-MS (m/z), calculated for C₁₆H₂₀N₂Si ([M+H]+), 299.15; found 299.87.

Figure S3. ¹H NMR of 7
Preparation of 9,10-bis((1,4-dimethyl-2-phenyl-1H-imidazol-5-yl)ethynyl)anthracene (1). A mixture of TMS-coupled monomer 7 (0.30 g, 1.12 mmol), 9,10-dibromoanthracene (0.17 g, 0.54 mmol), Ag₂O (0.26 g, 1.12 mmol), was stirred in THF. After N₂ bubbled for 20 min, Pd(PPh₃)₄ (0.13 g, 0.11 mmol) was added and refluxed at 80 °C for 24 h. The crude product was filtrated and the solvent was removed followed by purification by column chromatography over aluminum gel using ethyl acetate/hexane (1:1) as eluent. The product was washed with hot methanol four times to yield 35 mg (11%) of red solid; ¹H NMR (300 MHz, CDCl₃): δ 8.68-8.65 (m, 4H), 7.75-7.72 (m, 4H), 7.69-7.66 (m, 4H), 7.54-7.46 (m, 6H), 4.01 (s, 6H), 2.63 (s, 6H). Elemental analysis calcd for C₄₀H₃₀N₄: C 84.78; H 5.34; N 9.89; Found: C 84.40; H 5.20; N 9.63. EI-MS (m/z), calcd for C₄₀H₃₀N₄, 566.2470; found 566.2471.

Figure S4. ¹H NMR of 1
Scheme S-2

4 \rightarrow 8 \rightarrow 9 \rightarrow 10

\rightarrow 2 \rightarrow 3

\text{TMS}
Preparation of 1,4-dimethyl-2-phenyl-1H-imidazole (8). In a flask, 4-methyl-2-phenyl-1H-imidazole (5.0 g, 31.6 mmol), 18-crown-6 (0.77 g, 2.9 mmol), and t-BuOK (3.6 g, 32.1 mmol) were stirred in THF (50 ml). Iodomethane (4.5 g, 31.7 mmol) dissolved in THF (90 ml) was added slowly using a dropping funnel. The mixture was stirred overnight at room temperature. The reaction mixture was poured into brine and extracted with chloroform. The organic layers were washed several times with brine and separated and dried with magnesium sulfate. After removal of the solvent, the crude product was purified with silica gel column chromatography using ethyl acetate/chloroform (1:2) to yield 1.4 g (25%) of yellow solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.61-7.58 (m, 2H), 7.47-7.36 (m, 3H), 6.89 (s, 1H), 3.59 (s, 3H), 2.28 (s, 3H).

Figure S5. $^1$H NMR of 8
Preparation of 5-iodo-1,4-dimethyl-2-phenyl-1H-imidazole (9). 8 (2.5 g, 14.5 mol), acetic acid (20.0 mL), water (13.0 mL), conc-sulfuric acid (3.3 mL), HIO₃ (0.67 g, 3.8 mol), and iodine crystals (1.9 g, 7.4 mmol) were stirred at 80 °C for 4h. The reaction mixture was neutralized with NaOH aq and poured into saturated sodium thiosulfate solution and extracted with chloroform. The organic layer was separated, dried with magnesium sulfate, and evaporated to yield a crude product. The product was purified through column chromatography over silica gel using chloroform as eluent and recrystallized using hexane to yield 3.1 g (72%) of colorless solid. ¹H NMR (300 MHz, CDCl₃): δ 7.58-7.54 (m, 2H), 7.47-7.40 (m, 3H), 3.63 (s, 3H), 2.30 (s, 3H).

Figure S6. ¹H NMR of 9
Preparation of 1,4-dimethyl-2-phenyl-5-((trimethylsilyl)ethynyl)-1H-imidazole (10).

(trimethylsilyl)acetylene (0.45 g, 4.57 mmol) was added to a stirring solution of aryl iodide 9 (0.93 g, 3.1 mmol), Ag₂O (0.72 g, 3.1 mmol), and CuI (0.06 mg, 0.31 mmol) in mixture solvent of 10 mL of THF and 30 ml of trimethylamine. After N₂ bubbled for 20 min, Pd(PPh₃)₄ (0.18 g, 0.15 mmol) was added. The mixture was refluxed at 110 °C for 11 h. Crude product was filtered by celite. After removal of the solvent, the product was purified by column chromatography over aluminum gel using ethyl acetate/hexane (1:2) as eluent. The product was recrystallized using hexane to yield 3.1 g (77%) of colorless solid. ¹H NMR (300 MHz, CDCl₃): δ 7.63-7.60 (m, 2H), 7.47-7.42 (m, 3H), 3.68 (s, 3H), 2.34 (s, 3H), 0.28 (s, 9H). MALDI-MS (m/z), calculated for C₁₆H₂₀N₂Si ([M+H]⁺), 269.14; found 269.73.

Figure S7. ¹H NMR of 10
Preparation of 9,10-bis((1,4-dimethyl-2-phenyl-1H-imidazol-5-yl)ethynyl)anthracene (2). 10 (0.5g, 1.86 mmol) and 5ml of tetrabuthylammonium fluoride solution (in THF, 1 mol/L) was stirred for 3.5 h at room temperature in THF (20 ml). The reaction mixture was poured into brine and extracted with ethyl acetate. The organic layers were washed several times with brine and separated and dried with magnesium sulfate to yield a colorless solid. This crude product (0.31 g, 1.6 mmol), 9,10-dibromoanthracene (0.25 g, 0.75 mmol), Ag2O (0.37 g, 1.6 mmol), CuI (0.03 mg, 0.16 mmol) was stirred into a mixture solvent of 30 mL of diisopropylamine and 30 ml of THF. After N2 bubbled for 20 min, Pd(PPh3)4 (0.19 g, 0.16 mmol) was added and reflruxed at 100 °C for 36 h. The crude product was filtrated and after removal of the solvent, purified by column chromatography over aluminum gel using chloroform as eluent. The product was washed with hot methanol four times to yield 62 mg (15%) of red solid; 1H NMR (300 MHz, CDCl3): δ 8.76-8.73 (m, 4H), 7.68-7.65 (m, 4H), 7.59-7.55 (m, 4H), 7.51-7.43 (m, 6H), 3.67 (s, 6H), 2.61 (s, 6H). Elemental analysis calcd for C40H30N4: C 84.78; H 5.34; N 9.89; Found: C 84.50; H 5.03; N 9.78. EI-HRMS (m/z), calcd for C40H30N4, 566.2470; found 566.2473.

Figure S8. 1H NMR of 2
Preparation of 5,5’-(anthracene-9,10-diylbis(ethyne-2,1-diyl))bis(1,3,4-trimethyl-2-phenyl-1H-imidazol-3-ium) iodide (3). 2 (23 mg, 4.53 mmol) and iodomethane (300 mg, 2.1 mmol) was stirred in acetonitrile (30 ml) at 110 °C for 120 h. After the removal of solvent, the crude product was washed with chloroform many times to yield 22 mg (65%) of yellow solid. $^1$H NMR (300 MHz, DMSO-d$_6$):  $\delta$ 8.65-8.62 (m, 4H), 7.95-7.83 (m, 14H), 3.94 (s, 6H), 3.73 (s, 6H), 2.76 (s, 6H). $^{13}$C NMR (75 MHz, DMSO-d$_6$):  $\delta$ 144.7, 136.3, 132.7, 131.1, 130.6, 129.6, 128.8, 126.3, 121.1, 116.6, 114.5, 95.9, 87.3, 34.7, 33.6, 10.2.

EI-HRMS (m/z), calcd for C$_{42}$H$_{36}$I$_2$N$_4$ ([M-2I]), 596.2940; found 596.2939.

Figure S9. $^1$H NMR of 3
Figure S10. $^{13}$C NMR of 3
**Lifetime measurements**

1
\[ \tau_1 = 2.7 \text{ ns} \]
\[ \chi^2 = 1.038 \]

2
\[ \tau_1 = 3.4 \text{ ns} \]
\[ \chi^2 = 1.112 \]

3
\[ \tau_1 = 2.9 \text{ ns} \]
\[ \chi^2 = 1.009 \]
The effect of addition of TFA-d to compound 1

Figure S14. $^1$H NMR (300 MHz, CDCl$_3$, TMS) spectra of 1 and 1+TFA
Conformational analysis of compound 1

**Figure S 15.** Geometry optimized conformation of 1 by DFT, **1a** (θ₁, θ₂= 14°, the most stable coplanar form), -1105301.617 kcal/mol

**1b** (θ₁= 14°, θ₂ = 90°, semi-twisted form), -1105300.752 kcal/mol
Energy difference with **1a** =0.86 kcal/mol

**1c** (θ₁, θ₂ =90°, twisted form), -1105299.724 kcal/mol
Energy difference with **1a** =1.89 kcal/mol

θ₁ means the dihedral angle between the left imidazole and the central anthracene. θ₂ means the dihedral angle between the right imidazole and the central anthracene.
Conformational analysis of compound 2

**2a** ($\theta_1, \theta_2 = 4^\circ$, the most stable coplaner form), -1105296.930 kcal/mol

**2b** ($\theta_1 = 4^\circ$, $\theta_2 = 90^\circ$, semi-twisted form), -1105295.725 kcal/mol
Energy difference with **2a** = 1.21 kcal/mol

**2c** ($\theta_1, \theta_2 = 90^\circ$, twisted form), -1105294.458 kcal/mol
Energy difference with **2a** = 2.47 kcal/mol

Figure S 16. Geometry optimized conformation of 2 by DFT, 2a) the most stable conformer, 2b) conformer obtained by constraining the one imidazole ring 90° to the central anthracene unit, 2c) conformer obtained by constraining the two imidazole rings 90° to the central anthracene unit and their single point energy.
Conformational analysis of compound 3

\(3a\) \((\theta_1, \theta_2 = 89^\circ, \text{the most stable coplaner form}), -9839975.308 \text{ kcal/mol}\)

\(3b\) \((\theta_1 = 0^\circ, \theta_2 = 89^\circ, \text{semi-coplaner form}), -9839973.241 \text{ kcal/mol}\)

Energy difference with \(3a\) = 1.60 kcal/mol

\(3c\) \((\theta_1, \theta_2 = 0^\circ, \text{coplaner form}), -9839971.639 \text{ kcal/mol}\)

Energy difference with \(3a\) = 3.67 kcal/mol

Figure S 17. Geometry optimized conformation of 3 by DFT, \(3a\) the most stable conformer, \(3b\) conformer obtained by constraining the one imidazole ring \(0^\circ\) to the central anthracene unit, \(3c\) conformer obtained by constraining the two imidazole rings \(0^\circ\) to the central anthracene unit and their single point energy.
Molecular orbitals of 1-3 whose conformation was constrained

Fig S18. Frontier orbitals of compound 1c, 2c, and 3c.
Table S 1. Results of calculations of resonance wavelength, oscillator strength, and energy difference with the most stable conformers.

<table>
<thead>
<tr>
<th>Compounds (dihedral angles between anthracene and imidazole)</th>
<th>Wavelength, nm</th>
<th>Oscillator strength</th>
<th>Energy difference with the most stable conformer, kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a (14°, 14°)*</td>
<td>567</td>
<td>1.2133</td>
<td>-</td>
</tr>
<tr>
<td>1b (14°, 90°)</td>
<td>518</td>
<td>0.9133</td>
<td>0.86</td>
</tr>
<tr>
<td>1c (90°, 90°)</td>
<td>461</td>
<td>0.5633</td>
<td>1.89</td>
</tr>
<tr>
<td>2a (4°, 4°)*</td>
<td>523</td>
<td>0.9319</td>
<td>-</td>
</tr>
<tr>
<td>2b (4°, 90°)</td>
<td>491</td>
<td>0.7295</td>
<td>1.21</td>
</tr>
<tr>
<td>2c (90°, 90°)</td>
<td>457</td>
<td>0.4828</td>
<td>2.47</td>
</tr>
<tr>
<td>3a (89°, 89°)*</td>
<td>482</td>
<td>0.1247</td>
<td>-</td>
</tr>
<tr>
<td>3b (0°, 89°)</td>
<td>493</td>
<td>0.5023</td>
<td>1.60</td>
</tr>
<tr>
<td>3c (0°, 0°)</td>
<td>520</td>
<td>0.5072</td>
<td>3.67</td>
</tr>
</tbody>
</table>

(* means the most stable structure)