Electronic Supplementary Information

Development of Aryl-substituted 2-phenylimidazo[1,2-a]pyridines (PIP) with Various Colors of Excited-State Intramolecular Proton Transfer (ESIPT) Luminescence in the Solid State

Toshiki Mutai,* Tatsuya Ohkawa, Hideaki Shono and Koji Araki*

Department of Materials and Environmental Science, Institute of Industrial Science, the University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo 153-8505, Japan

E-mail: mutai@iis.u-tokyo.ac.jp, araki@iis.u-tokyo.ac.jp
Synthesis

2-(2’-Hydroxyphenyl)-6-(bromo)imidazo[1,2-a]pyridine (11)

An acetonitrile (50 mL) solution of 2-bromo-1-(2-methoxyphenyl)ethanone (2.91 g, 12.7 mmol), 2-amino-5-bromopyridine (2.20 g, 12.7 mmol) and NaHCO$_3$ (2.15 g, 25.6 mmol) was refluxed for 4 h. After cooling, insoluble solid was filtered off. Evaporation of the filtrate afforded crude product, which was then purified by a silica gel column chromatography (chloroform–ethyl acetate = 5:1) to give 2-(2’-methoxyphenyl)-6-bromoimidazo[1,2-a]pyridine (11Me) as white powder (2.77 g, 72 %). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) = 4.05 (s, 3H), 7.04 (d, $J$ = 8.4 Hz, 1H), 7.21 (t, $J$ = 14.4 Hz, 1H), 7.48 (t, $J$ = 14.4 Hz, 1H), 7.72 (d, $J$ = 8.0 Hz, 1H), 8.26 (s, 1H), 8.40 (d, $J$ = 6.0 Hz, 1H), 8.54 (s, 1H), 8.63 (d, $J$ = 9.6 Hz, 1H).

Then to a cooled anhydrous dichloromethane solution (5 mL, -78 °C) of well-dried 11Me (0.23 g, 0.76 mmol) was dropwise added a dichloromethane solution of boron tribromide (1.0 M, 4 mL). The reaction mixture was allowed to reach room temperature and further stirred overnight. A saturated aqueous NaHCO$_3$ was slowly added with stirring, and then separated with water and chloroform. After washing the organic layer with saturated aqueous NaHCO$_3$ and water, and drying over MgSO$_4$, the organic layer was evaporated to yield 11 as crude product. Reprecipitation from chloroform gave white powder (0.17 g, 85 %). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) = 6.89 (t, $J$ = 14.0 Hz, 1H), 7.04 (d, $J$ = 7.2 Hz, 1H), 7.22 - 7.31 (m, 2H), 7.50 (d, $J$ = 9.6 Hz, 1H), 7.57 (d, $J$ = 6.0 Hz, 1H), 7.84 (s, 1H), 8.30 (s, 1H).

2-(2’-Hydroxyphenyl)-8-(bromo)imidazo[1,2-a]pyridine (12)

At first, 2-(2’-methoxyphenyl)-8-bromoimidazo[1,2-a]pyridine (12Me) was prepared by the similar condition as 11Me using 2-amino-3-bromopyridine instead of 2-amino-5-bromopyridine. Purified by a silica gel column chromatography (chloroform–ethyl acetate = 10:1). Yield 72 %. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 4.00 (s, 3H), 6.63 (t, $J$ = 14.4 Hz, 1H), 6.99 (s, $J$ = 8.4 Hz, 1H), 7.11 (t, $J$ = 14.0 Hz, 1H), 7.32 (t, $J$ = 14.0 Hz, 1H), 7.41 (d, $J$ = 6.4 Hz, 1H), 8.10 (d, $J$ = 6.0 Hz, 1H), 8.23 (s, 1H), 8.51 (d, $J$ = 6.0 Hz, 1H).
Then \(12\text{Me}\) was demethylated by the same condition as \(11\text{Me}\). The crude product (12) was purified by a silica gel chromatography (CHCl\(_3\)) to give white powder (72 \%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 6.75 (t, \(J = 14.0\) Hz, 1H), 6.89 (t, \(J = 13.6\) Hz, 1H), 7.05 (d, \(J = 7.6\) Hz, 1H), 7.25 (t, \(J = 13.6\) Hz, 1H), 7.47 (d, \(J = 7.2\) Hz, 1H), 7.57 (d, \(J = 6.4\) Hz, 1H), 7.93 (s, 1H), 8.13 (d, \(J = 6.0\) Hz, 1H).

\[
\begin{align*}
\text{Br} & \quad \text{N} \quad \text{MeO} \\
\text{N} & \quad \text{Br} \\
\end{align*}
\]

\(12\text{Me}\)

\[
\begin{align*}
\text{Br} & \quad \text{O} \\
\text{Br} & \quad \text{N} \\
\end{align*}
\]

\(12\)

2-(2'-Hydroxyphenyl)-6,8-dibromoimidazo[1,2-a]pyridine (13)

At first, 2-(2'-methoxyphenyl)-6,8-dibromoimidazo[1,2-a]pyridine (13\text{Me}) was prepared by the similar condition as 11\text{Me} using 2-amino-3,5-dibromopyridine instead of 2-amino-5-bromopyridine, and refluxed for 3 days. Purified by a flash column chromatography on a silica gel (eluent: CHCl\(_3\) / hexane = 7 : 2) gave pale-yellow powder (1.67 g, 48.1 \%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) = 8.48 (1H, dd, \(J = 7.8, 1.7\) Hz), 8.23 (1H, d, \(J = 1.7\) Hz), 8.22 (1H, s), 7.50 (1H, d, \(J = 1.5\) Hz), 7.33 (1H, ddd, \(J = 8.7, 7.0, 1.3\) Hz), 7.10 (1H, td, \(J = 7.5, 0.8\) Hz), 6.99 (1H, d, \(J = 8.3\) Hz), 3.98 (3H, s). MS (FAB): m/z: 380.3 (calcd. for C\(_{14}\)H\(_9\)Br\(_2\)N\(_2\)O [M + H]\(^+\) = 380.92)

Then 13\text{Me} was demethylated by the same condition as 11\text{Me}. The crude product (13) was recrystallized from ethanol to give colourless microcrystal (572 mg, 77.7 \%). \(^1\)H NMR (400 MHz, DMSO-D\(_6\)) \(\delta\) = 11.16 (1H, s), 9.02 (1H, t, \(J = 1.5\) Hz), 8.57 (1H, d, \(J = 1.2\) Hz), 8.04 (1H, dt, \(J = 7.8, 1.5\) Hz), 7.86 (1H, t, \(J = 1.6\) Hz), 7.23-7.21 (1H, m), 6.98-6.92 (2H, m). MS (FAB): m/z: 366.9 (calcd. for C\(_{13}\)H\(_9\)Br\(_2\)N\(_2\)O [M + H]\(^+\) = 366.91)

\[
\begin{align*}
\text{Br} & \quad \text{N} \quad \text{MeO} \\
\text{Br} & \quad \text{N} \\
\end{align*}
\]

\(13\text{Me}\)

\[
\begin{align*}
\text{Br} & \quad \text{O} \\
\text{Br} & \quad \text{N} \\
\end{align*}
\]

\(13\)
General synthetic procedure for 6- and 8-aryl HPIPs (2–7)

A dioxane–water (3:1) solution (30 mL) of 11 (for 2–4) or 12 (for 5–7) (0.20 g, 0.70 mmol), corresponding arylboronic acid (1.2 equiv.), potassium carbonate (0.385 g, 2.79 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.041 g, 0.35 mmol) was refluxed for 8–27 h. After addition of saturated aqueous NH₄Cl, the reaction mixture was extracted with chloroform. The organic layer was washed with water and brine, then dried over MgSO₄. Evaporation afforded crude product, which was further purified by a suitable method.

2-(2'-Hydroxyphenyl)-6-(phenyl)imidazo[1,2-a]pyridine (2): Refluxed for 8 h. Crude product was purified by a silica gel column chromatography (chloroform) to give white powder. M. p. 154.4–155.4 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 6.90 (t, J = 14.0 Hz, 1H), 7.06 (d, J = 7.2 Hz, 1H), 7.25 (d, J = 4.8 Hz, 1H) 7.42 - 7.68 (m, 8H), 7.92 (s, 1H), 8.33 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 107.06, 116.17, 116.60, 117.73, 119.00, 122.60, 125.73, 125.98, 126.97, 127.74, 128.13, 129.21, 129.73, 136.96, 142.77, 145.81, 157.33. Calcd. for C₁₉H₁₄N₂O: C, 79.70; H, 4.93; N, 9.78 %. Found: C, 79.57; H, 4.96; N, 9.66 %.

2-(2'-Hydroxyphenyl)-6-(p-methoxyphenyl)imidazo[1,2-a]pyridine (3): Refluxed in dioxane–water (3:1) for 17 h. Crude product was purified by a silica gel column (benzene) to give white solid. Yield 96 %. M. p. 143.5–144.7 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 3.88 (s, 3H), 6.90 (t, J = 15.2 Hz, 1H), 7.01–7.06 (m, 3H), 7.23 (d, J = 7.2 Hz, 1H), 7.45–7.51 (m, 3H), 7.62 (t, J = 16.4 Hz, 2H), 7.90 (s, 1H), 8.27 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 55.42, 106.98, 114.61, 116.22, 116.45, 117.70, 118.96, 121.92, 125.69, 125.96, 127.40, 128.05, 129.33, 129.64, 142.59, 145.63, 157.30, 159.69. HRMS (FAB): m/z: 317.1283 (Calcd. for C₂₀H₁₆N₂O₂ [M+H] = 317.1290).
2-(2'-Hydroxyphenyl)-6-(p-methoxycarbonylphenyl)imidazo[1,2-a]pyridine (4): Refluxed in dioxane–water (3:1) for 8 h. Crude product was purified by a silica gel column (benzene) to give a pale pink solid. Yield 31%. M. p. 202.4–203.6 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) = 3.97 (s, 3H), 6.91 (t, $J = 13.6$ Hz, 1H), 7.05 (d, $J = 7.2$ Hz, 1H), 7.25 - 7.26 (m, 2H), 7.52 (d, $J = 7.2$ Hz, 1H), 7.61 - 7.70 (m, 4H), 7.94 (s, 1H), 8.16 (d, $J = 4.4$ Hz, 1H), 8.40 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) = 52.32, 107.19, 116.87, 117.79, 119.06, 123.08, 125.47, 125.78, 126.61, 126.84, 129.73, 129.90, 130.50, 141.35, 157.34, 166.65. Calcd. for C$_{21}$H$_{16}$N$_2$O$_3$: C, 73.24; H, 4.68; N, 8.13 %. Found: C, 73.48; H, 4.64; N, 8.08 %.

![Image of compound 4](image4)

2-(2'-Hydroxyphenyl)-8-phenylimidazo[1,2-a]pyridine (5): Refluxed in dioxane for 24 h. Crude product was purified by a silica gel column (chloroform) to give a pale pink solid. Yield 80 %. M. p. 91.4–93.0 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) = 6.89 (t, $J = 15.2$ Hz, 1H), 6.94 (t, $J = 14.0$ Hz, 1H), 7.01 (d, $J = 7.2$ Hz, 1H), 7.24 (t, $J = 10.0$ Hz, 1H), 7.33 (d, $J = 6.0$ Hz, 1H), 7.43 (t, $J = 8.4$ Hz, 1H), 7.52 (t, $J = 13.2$ Hz, 2H), 7.60 (d, $J = 6.0$ Hz, 1H), 7.91 (s, 1H), 7.94 (d, $J = 6.8$ Hz, 2H), 8.12 (d, $J = 7.6$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) = 107.15, 113.51, 116.08, 117.60, 118.93, 123.61, 124.28, 125.64, 128.56, 128.61, 129.66, 135.92, 142.16, 145.07, 157.22. HRMS (FAB): Calcd. for C$_{19}$H$_{14}$N$_2$O m/z 287.1184, found 287.1175.

![Image of compound 5](image5)
2-(2'-Hydroxyphenyl)-8-(p-methoxyphenyl)imidazo[1,2-a]pyridine (6): Refluxed in dioxane–water (10:1) for 24 h. Crude product was purified by a silica gel column (chloroform) to give a pale pink solid. Yield 66 %. M. p. 49.5-51.0 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) = 3.88 (s, 3H), 6.83 - 6.91 (m, 3H), 7.05 (t, \(J = 6.8\) Hz, 1H), 7.24 (t, \(J = 11.2\) Hz, 1H), 7.56 (d, \(J = 8.0\) Hz, 1H), 7.83 (s, 1H), 7.91 (d, \(J = 7.2\) Hz, 3H), 8.00 (d, \(J = 6.4\) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) = 55.24, 107.10, 113.43, 113.92, 116.11, 117.47, 118.88, 122.69, 123.67, 125.58, 128.19, 128.97, 129.50, 129.64, 142.02, 144.67, 157.12, 159.79. HRMS (FAB): m/z: 317.1295 (calcd. for C\(_{20}\)H\(_{16}\)N\(_2\)O\(_2\) [M+H] = 317.1290).

2-(2'-Hydroxyphenyl)-8-(p-methoxycarbonylphenyl)imidazo[1,2-a]pyridine (7): Refluxed in dioxane for 27 h. Crude product was purified by a silica gel column (chloroform) and recrystallized from ethanol to give a pale pink crystal. Yield 50 %. M. p. 224.9–225.4 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) = 3.96 (s, 3H), 6.90 (t, \(J = 14.0\) Hz, 1H), 6.99 – 7.03 (m, 2H), 7.24 (d, \(J = 5.2\) Hz, 1H), 7.40 (d, \(J = 6.0\) Hz, 1H), 7.61 (d, \(J = 8.0\) Hz, 1H), 7.97 (s, 1H), 8.03 (d, \(J = 7.2\) Hz, 2H), 8.20 (d, \(J = 8.0\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) = 52.24, 107.32, 113.47, 115.92, 117.70, 119.04, 124.12, 125.01, 125.70, 128.56, 129.90, 129.99, 140.44, 141.88, 145.34, 157.23, 166.81. HRMS (FAB): m/z: 345.1241 (calcd. for C\(_{21}\)H\(_{16}\)N\(_2\)O\(_3\) [M+H] = 345.1239)

2-(2'-Hydroxyphenyl)-6,8-diarylimidazo[1,2-a]pyridine (8 and 9)

A dioxane-water (3:1, 20 mL) solution of 13 (602 mg, 1.64 mmol), corresponding arylboronic acid (2.2 equiv.), potassium carbonate (910 mg, 6.58 mmol), and tetrakis-(triphenylphosphine)palladium(0) (114 mg, 0.099 mmol) was stirred overnight at 90 °C. After addition of saturated aqueous NH\(_4\)Cl, the reaction mixture was extracted with CHCl\(_3\). The organic layer was washed with water and saturated aqueous NaCl, dried over Na\(_2\)SO\(_4\), and evaporated to afford crude product.

S5
2-(2’-Hydroxyphenyl)-6,8-diphenylimidazo[1,2-a]pyridine (8): Purified by flash column chromatography on a silica gel (eluent: hexane / CHCl₃ = 3 : 1) and recrystallized from ethanol to give 8 as a pale pink crystal (71%). M. p. 185.5–186.4 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 12.83 (1H, s), 8.32 (1H, d, J = 1.7 Hz), 8.00 (2H, dt, J = 9.5, 4.8 Hz), 7.98 (1H, s), 7.64-7.61 (4H, m), 7.57-7.41 (6H, m), 7.24-7.22 (1H, m), 7.02 (1H, dd, J = 8.3, 1.0 Hz), 6.90 (1H, td, J = 7.4, 1.1 Hz). ¹³C NMR (100 MHz, CDCl₃) δ = 157.13, 145.42, 141.41, 136.92, 135.79, 129.63, 129.30, 129.10, 128.62, 128.59, 128.55, 128.06, 127.93, 126.90, 125.59, 124.33, 121.43, 118.91, 117.56, 116.04, 107.51. MS (FAB): m/z: 363.3 (calcd [M + H]⁺ = 363.15). Calcd. for C₂₅H₁₈N₂O: C, 82.85; H, 5.01; N, 7.37 %. Found: C, 82.96; H, 5.02; N, 7.41 %.

2-(2’-Hydroxyphenyl)-6,8-di[p-(hexyloxycarbonyl)phenyl]imidazo[1,2-a]pyridine (9): Purified by flash column chromatography on a silica gel (eluent: hexane / CHCl₃ = 1 : 1) and recrystallized from ethanol to give 9 as a pale pink powder (66%). M. p. 141.7–142.6 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 12.60 (1H, s), 8.39 (1H, d, J = 1.5 Hz), 8.19 (4H, dd, J = 13.1, 8.4 Hz), 8.07 (2H, d, J = 8.3 Hz), 8.00 (1H, s), 7.69 (2H, d, J = 8.3 Hz), 7.62 (2H, dd, J = 6.6, 3.3 Hz), 7.24 (1H, dd, J = 4.3, 2.1 Hz), 7.02 (1H, d, J = 8.3 Hz), 6.91 (1H, t, J = 7.4 Hz), 4.36 (4H, td, J = 6.7, 2.5 Hz), 1.80 (4H, m), 1.49-1.46 (4H, m), 1.37 (8H, m), 0.93 (6H, m). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 166.04, 165.97, 156.99, 145.64, 141.01, 140.76, 139.72, 130.42, 130.25, 130.05, 129.83, 129.70, 128.31, 128.13, 126.61, 125.60, 124.02, 122.46, 118.98, 117.56, 115.66, 107.78, 65.37, 65.28, 31.52, 31.49, 28.72, 25.76, 25.74, 22.60, 14.09. MS (FAB): m/z: 619.5 (calcd [M + H]⁺ = 619.32). Calcd. for C₃₉H₄₄N₂O₅: C, 75.70; H, 6.84; N, 4.33 %. Found: C, 75.69; H, 6.85; N, 4.27 %.
Figure S1. Absorption and luminescence spectra of 1 (a) through 10 (j) in tetrahydrofuran (THF). Absorption and fluorescence in fluid solution (solid line), and fluorescence in frozen solution at 77 K (broken line).
Figure S2. Absorption and luminescence spectra of 1 (a) – 7 (g), 9 (i), 10 (j) in cyclohexane, and 8 (h) in benzene. Absorption and fluorescence in fluid solution (solid line), fluorescence in frozen solution at 77 K (broken line).
Figure S3. Absorption (Kubelka-Munk) and luminescence spectra of 1 (a) through 10 (j) in the solid state.
X-ray crystallographic data

X-ray diffraction data were collected on a Rigaku VariMax DW with Saturn 724 diffractometer equipped with a graphite-monochromatized Mo Kα source (crystal 3) or a MacScience DIP-Labo with graphite-monochromatized Cu Kα radiation (crystal 4, 7 and 8). The structure was solved by direct method SHELXS-2014 and expanded by subsequent Fourier synthesis. The refinement by full matrix least-squares calculations was performed using SHELXL-2014.

Table S1. Crystallographic data and structure refinement summary.

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* These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Figure S4. ORTEP drawings and molecular packing of 3.

Figure S5. ORTEP drawings and molecular packing of 4.
Figure S4. ORTEP drawings and molecular packing of 8.

Figure S6. ORTEP drawings and molecular packing of 7.

Figure S7. ORTEP drawings and molecular packing of 8.