Supporting Information

for

A facile synthesis of functionalized 7,8-diaza[5]helicenes through an oxidative ring-closure of 1,1’-binaphthalene-2,2’-diamines (BINAMs)

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General remarks

All reactions were carried out under an atmosphere of nitrogen unless otherwise noted. Melting points were determined on a Stanford Research Systems MPA100 OptiMelt Automated Melting Point System. $^1$H and $^{13}$C NMR spectra were recorded on a JEOL JMTC-400/54/SS spectrometer ($^1$H NMR, 400 MHz; $^{13}$C NMR, 100 MHz) using tetramethylsilane as an internal standard. Infrared spectra were acquired on a SHIMADZU IRAffinity-1 FT-IR Spectrometer. Mass spectra were obtained on a JEOL JMS-DX303HF mass spectrometer. High-resolution mass spectra were obtained on a JEOL JMS-DX303HF mass spectrometer. UV/vis spectra were recorded on a Shimadzu UV-2550 spectrophotometer. Emission spectra were recorded on a HAMAMATSU C11347-01 spectrometer with an integrating sphere. Cyclic voltammetry (CV) was performed with ALS-600 (BAS Inc.) system. Thermogravimetric analysis (TGA) was performed with TG/DTA-7200 (SII) system. Products were purified by chromatography on silica gel BW-300 and Chromatorex NH (Fuji Silysia Chemical Ltd.). Analytical thin-layer chromatography (TLC) was performed on pre-coated silica gel glass plates (Merck silica gel 60 F254 and Fuji Silysia Chromatorex NH, 0.25 mm thickness). Compounds were visualized with UV lamp. Optical rotations were measured in a thermostated conventional 10 cm cell on a JASCO P-2200 polarimeter using the sodium-D line (589 nm).

Materials

1,1’-Binaphthalene-2,2’-diamine (BINAM) was purchased from Sigma-Aldrich and used as received. DBU, triethylamine, and 2,6-lutidine were distilled with Kugelrohr apparatus, and other commercial reagents were purchased from Sigma-Aldrich, TCI, or Wako Pure Chemical Industries, Ltd. and used as received. Alcohol solvents were dried over activated molecular sieves 3A. THF, CH$_3$CN, and Et$_2$O were purchased as dehydrated grade and dried by passing through a glass contour solvent dispensing system (Nikko Hansen & Co., Ltd.). Dehydrated CH$_2$Cl$_2$ and toluene were purchased from Kanto Chemical Co., Inc. and used as received. DMF was distilled using CaSO$_4$ as a dehydrating agent. CH$_2$Cl$_2$ (fluorescence spectroscopic grade) was purchased from Kanto Chemical Co., Inc. for the measurement of UV-vis and emission spectra. Biaryldiamines 1b$^{S1}$ [360779-01-7], 1c$^{S2}$ [1051425-55-8, (R)-enantiomer], 1d$^{S3}$ [1229013-43-7], 1e$^{S4}$ [155855-47-3], 1g$^{S5}$ [861890-12-2], and 3$^{S6}$ [1454-80-4] were prepared according to the procedures in literature.

Preparation of 6,6'-di-n-butyl-1,1’-binaphthalene-2,2’-diamine (1f)

Biaryldiamine 1f was prepared by modified cross-coupling method$^{S7}$ from biaryldiamine 1g as follows (Scheme S1): THF was degassed through freeze-pump-thaw cycling for three times before used. To a round-bottomed flask (50 mL) equipped with a
magnetic stir bar, were added biarylamine 1g (1.326 g, 3.0 mmol), Pd(OAc)$_2$ (13.4 mg, 0.06 mmol), and SPhos (49.2 mg, 0.12 mmol) under the air. The tube was capped with a rubber septum, evacuated, and then refilled with N$_2$ gas for three times. THF (2 mL) and 0.5 M THF solution of n-BuZnBr (14.4 mL, 7.2 mmol) were added to the tube through the septum, and the mixture was stirred under N$_2$ atmosphere at room temperature for 12 h. To the reaction mixture, was added saturated aqueous NH$_4$Cl solution (10 mL), and the resulting mixture was extracted with EtOAc (20 mL × 3). The organic extract was dried over Na$_2$SO$_4$ and concentrated under vacuum to give the crude product. Purification by flash column chromatography on silica gel (eluent: hexane/EtOAc 8:2) gave biarylamine 1f as pale brown solid (1.051 g, 88%). mp 130°C (dec.); R$_f$ 0.13 (hexane/EtOAc 8:2); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.92 (t, $J$ = 7.2 Hz, 6H), 1.37 (tq, $J$ = 7.2, 7.6 Hz, 4H), 1.63 (tt, $J$ = 7.6, 7.6 Hz, 4H), 2.68 (t, $J$ = 7.6 Hz, 4H), 3.60 (br, 4 H), 7.01 (d, $J$ = 8.8 Hz, 2H), 7.05 (dd, $J$ = 1.6, 8.8 Hz, 2H), 7.11 (d, $J$ = 8.8 Hz, 2H), 7.56 (d, $J$ = 1.6 Hz, 2H), 7.72 (d, $J$ = 8.8 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 13.9, 22.4, 33.5, 35.4, 112.9, 118.3, 123.9, 126.6, 128.3, 128.6, 128.8, 132.0, 136.8, 141.9; IR (ATR) $\nu$ 2929, 1606, 1500, 1382, 1282, 824, 810 cm$^{-1}$; MS (EI): m/z (relative intensity, %) 396 (M$^+$, 100), 353 ([C$_{25}$H$_{25}$N$_2$]$^+$, 45); HRMS (EI): m/z calcd for C$_{28}$H$_{32}$N$_2$ (M) 396.2565, found 396.2568.

Scheme S1. Preparation of 1f.

Optimization studies of reaction conditions

A typical procedure for the optimization studies using 1a as substrate

To a two-necked reaction tube (20 mL, entry 2 in Table S1) or a two-necked round-bottomed flask (50 mL, entries 1 and 3–11 in Table S1, Table S2, and Table S3) equipped with a magnetic stir bar, was added 1,1′-binaphthalene-2,2′-diamine (1a) (0.2 mmol) under the air. The vessel was capped with a rubber septum and evacuated and refilled with N$_2$ gas for three times, and an appropriate solvent was added through the septum. To the mixture, were added an additive and an appropriate oxidant under a stream of N$_2$ gas at the indicated temperature. The resulting solution was stirred for indicated time before quenched with aqueous Na$_2$S$_2$O$_3$ solution (1.0 M, 20 mL), and the resulting mixture was extracted with
CH$_2$Cl$_2$ (20 mL × 3). The combined organic extracts were dried over Na$_2$SO$_4$ and concentrated under vacuum to give the crude product. The yields of products were calculated by the integration of $^1$H NMR signals of the crude product. Separation by flash column chromatography on silica gel gave product 2a.

7,8-Diaza[5]helicene (2a) [188-55-6]

Spectroscopic data were in good agreement with those previously reported. The spectroscopic data are also available in our previous paper. Purified by flash column chromatography on silica gel (eluent: hexane/EtOAc, 99:1 to 5:5) and recrystallization from CHCl$_3$; Yellow solid; $R_f$ 0.15 (hexane/EtOAc 8:2); MS (EI): $m/z$ (relative intensity, %) 280 (M$^+$, 70), 252 ([C$_{20}$H$_{12}$]+, 100); HRMS (EI): $m/z$ calcd for C$_{20}$H$_{12}$N$_2$ (M) 280.1000, found 280.1002.

| entry | solvent     | yield (%)$^a$ | recovery of 1a (%)$^a$ |
|-------|-------------|---------------|------------------------|
| 1     | t-BuOH      | 89$^b$        | 0                      |
| 2     | t-BuOH$^c$  | 54            | 0                      |
| 3     | THF         | 30            | 0                      |
| 4     | CH$_3$CN    | 22            | 0                      |
| 5     | CH$_2$Cl$_2$| 52            | 0                      |
| 6     | toluene     | 68            | 0                      |
| 7     | DMF         | 62            | 0                      |
| 8     | Et$_2$O     | 37            | 0                      |
| 9     | 2-propanol  | 47            | 48                     |
| 10    | EtOH        | 61            | 0                      |
| 11    | MeOH        | 58            | 0                      |

$^a$ $^1$H NMR yields. $^b$ isolated yield. $^c$ 40 mM.

Table S1. The effect of solvents.
Table S2. The effect of chlorine-containing oxidants.

![Chemical structures]

| entry | chlorine-containing oxidant (mmol) | yield (%)\(^a\) | recovery of 1a (%)\(^a\) |
|-------|-----------------------------------|-----------------|--------------------------|
| 1     | NCS (0.8)                         | 0               | 63                       |
| 2     | DCH (0.4)                         | 24\(^b\)        | 0                        |
| 3     | DCH (0.8)                         | 57              | 0                        |
| 4     | NCPh (0.8)                        | 0               | 95                       |
| 5     | TCCA (0.27)                       | 20              | 0                        |

\(^a\) ^1H NMR yields. \(^b\) isolated yield.

Structures of chlorine-containing oxidants:

- NCS: \(N\)-chlorosuccinimide
- DCH: 1,3-dichloro-5,5-dimethylhydantoin
- NCPh: \(N\)-chlorophthalimide
- TCCA: trichloroisocyanuric acid
Table S3. The effect of equivalents of t-BuOCl and bases.

![Chemical structure](image)

| entry | t-BuOCl (mmol) | base (mmol) | time (h) | yield (%)<sup>a</sup> | recovery of 1a (%)<sup>b</sup> |
|-------|----------------|-------------|----------|------------------------|-----------------------------|
| 1     | 0.6            | -           | 3        | 93                     | 0                           |
| 2     | 0.4            | -           | 3        | 54                     | 34                          |
| 3     | 0.4            | -           | 24       | 71                     | 19                          |
| 4     | 0.4            | K<sub>2</sub>CO<sub>3</sub> (0.4) | 3  | 69                     | 20                          |
| 5     | 0.4            | DABCO (0.4) | 3  | 32                     | 45                          |
| 6     | 0.4            | DBU (0.4)   | 3  | 0                      | 34                          |
| 7     | 0.4            | NEt<sub>3</sub> (0.4) | 3  | 0                      | 65                          |
| 8     | 0.4            | pyridine (0.4) | 3  | 33                     | 40                          |
| 9     | 0.4            | 2,6-di-<sup>3</sup>-tert-butylpyridine (0.4) | 3  | 77                     | 19                          |
| 10    | 0.4            | 2,6-lutidine (0.4) | 3  | 90                     | 10                          |
| 11    | 0.4            | 2,6-lutidine (0.4) | 7  | 92                     | 8                           |
| 12    | 0.44           | 2,6-lutidine (0.44) | 3  | 97<sup>b</sup>         | 0                           |

<sup>a</sup>H NMR yields. <sup>b</sup>isolated yield.

Structures of bases

![Chemical structure](image)

DABCO
1,4-diazabicyclo[2.2.2]octane

DBU
1,8-diazabicyclo[5.4.0]undec-7-ene

Oxidative ring-closure of biaryldiamines 1 and 3

A typical procedure for the oxidative ring-closure of biaryldiamines 1 and 3

To a two-necked round-bottomed flask (50 mL) equipped with a magnetic stir bar, was added biaryldiamine 1 (or 3) (0.1 mmol) under the air. The flask was capped with a
rubber septum, evacuated, and refilled with N₂ gas for three times. Solvent (10 mL) and 2,6-lutidine (23.5 mg, 0.22 mmol or none) were added to the tube through the septum. To the mixture, was added t-BuOCl (23.8 mg, 0.22 mmol or 43.4 mg, 0.40 mmol) through the septum at the indicated temperature. The resulting solution was stirred for the indicated time (Table 2 in the text) before quenched with aqueous Na₂S₂O₃ solution (1.0 M, 20 mL), and the resulting mixture was extracted with CH₂Cl₂ (20 mL × 3). The combined organic extracts were dried over Na₂SO₄ and concentrated under vacuum to give the crude product. Purification by flash column chromatography on silica gel gave the corresponding 7,8-diaza[5]helicene (for example, compound 2a: 27.2 mg, 97%).

Table S4. The oxidative ring-closure of biaryldiamine 1b.

| entry | solvent | yield (%)<sup>a</sup> | recovery of 1b (%)<sup>a</sup> |
|-------|---------|------------------------|-------------------------------|
| 1     | t-BuOH  | 32                     | 22                            |
| 2     | MeOH    | 17                     | 28                            |
| 3     | CH₂Cl₂  | 16                     | trace                         |
| 4     | toluene | 44<sup>b</sup>         | 11<sup>b</sup>                |

<sup>a</sup> <sup>1</sup>H NMR yields. <sup>b</sup> isolated yield.

6,9-Dimethyl-7,8-diaza[5]helicene (2b)

Purified by flash column chromatography on NH silica gel (eluent: hexane/EtOAc 99:1) and recrystallization from hexane; Yellow solid (13.6 mg, 44%); mp 196 °C (dec.); R<sub>f</sub> 0.33 (hexane/EtOAc 8:2, NH)<sub>2</sub>; <sup>1</sup>H NMR (400 MHz, CDCl₃) δ 3.16 (s, 6H), 7.31 (dd, J = 8.0, 8.0 Hz, 2H), 7.64 (dd, J = 8.0, 8.0 Hz, 2H), 7.91 (d, J = 8.0 Hz, 2H), 7.95 (s, 2H), 8.71 (d, J = 8.0 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl₃) δ 18.5, 120.0, 124.5, 127.3, 127.5, 129.2, 129.5, 129.8, 134.0, 134.2, 145.9; IR (ATR) ν 2922, 1734, 1457, 1425, 1261, 1160, 1116, 889, 753 cm⁻¹; MS (EI): m/z (relative intensity, %) 308 (M⁺, 100), 280 ([C₂₂H₁₆]⁺, 31); HRMS (EI): m/z calcd for C₂₂H₁₆N₂ (M) 308.1313, found 308.1312.
### Table S5. The oxidative ring-closure of biaryldiamine 1c

![Oxidative ring-closure of biaryldiamine 1c](image)

| entry | solvent | temp. (°C) | time (h) | yield (%)<sup>a</sup> | recovery of 1c (%)<sup>a</sup> |
|-------|---------|------------|----------|------------------------|-----------------------------|
| 1     | t-BuOH  | rt         | 20       | 44<sup>b</sup>         | 15<sup>b</sup>              |
| 2<sup>c</sup> | t-BuOH | rt         | 19       | 77<sup>b</sup>         | 0                           |
| 3     | t-BuOH  | 60         | 24       | 36                     | 12                          |
| 4     | MeOH    | rt         | 9        | 9                      | 28                          |
| 5     | toluene | rt         | 24       | 15                     | 0                           |

<sup>a</sup> 1H NMR yields. <sup>b</sup> isolated yield. <sup>c</sup> t-BuOCl (4.0 equiv), 2,6-lutidine (0 equiv)

### 6,9-Dibromo-7,8-diaza[5]helicene (2c)

Parts of spectroscopic data are available in a literature.<sup>S10</sup> Purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 99:1–95:5) and recrystallization from hexane/CHCl₃; Yellow solid (19.3 mg, 44% or 33.7 mg, 77%); mp 307 °C (dec.); R<sub>f</sub> 0.40 (hexane/EtOAc 8:2); ¹H NMR (400 MHz, CDCl₃) δ 7.41 (dd, J = 8.0, 8.0 Hz, 2H), 7.71 (dd, J = 8.0, 8.0 Hz, 2H), 7.94 (d, J = 8.0 Hz, 2H), 8.51 (s, 2H), 8.64 (d, J = 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 121.3, 121.6, 126.0, 127.4, 127.5, 129.5, 130.3, 134.4, 134.5, 143.6; IR (ATR) ν 3053, 1591, 1383, 1250, 1108, 960, 890, 837, 773, 753 cm⁻¹; MS (EI): m/z (relative intensity, %) 438 (M⁺, 50), 357 ([C₂₀H₁₀BrN₂]⁺, 14), 278 ([C₂₀H₁₀N₂]⁺, 23), 250 ([C₂₀H₁₀]⁺, 100); HRMS (EI): m/z calcd for C₂₀H₁₀Br₂N₂ (M) 435.9211, found 435.9210.
Table S6. The oxidative ring-closure of biaryldiamine 1d.

\[
\begin{align*}
&1d \\
\text{Ph} & \quad \text{NH}_2 \\
\text{Ph} & \quad \text{NH}_2 \\
\end{align*}
\]

(43.6 mg, 0.1 mmol)

\[
\begin{array}{ccc}
\text{entry} & \text{solvent} & \text{yield (%)}\text{a} & \text{recovery of 1d (%)}\text{a} \\
1 & t-\text{BuOH} & 33^b & 18^b \\
2 & \text{MeOH} & 28 & 24 \\
3 & \text{toluene} & 87^b & 0 \\
\end{array}
\]

\text{a}^1\text{H NMR yields. }^b\text{isolated yield.}

6,9-Diphenyl-7,8-diaza[5]helicene (2d)

Purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 97:3) and recrystallization from hexane/CHCl\textsubscript{3}; Yellow solid (37.6 mg, 87%); mp 239 °C (dec.); \textit{R}_f 0.35 (hexane/EtOAc 8:2); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.43–7.45 (m, 4H), 7.50 (dd, \(J = 7.6, 7.6\) Hz, 4H), 7.72 (dd, \(J = 7.6, 7.6\) Hz, 2H), 7.82 (d, \(J = 6.8\) Hz, 4H), 8.06 (d, \(J = 7.6\) Hz, 2H), 8.17 (s, 2H), 8.79 (d, \(J = 8.8\) Hz, 2H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 120.1, 125.4, 127.7, 128.0, 128.1, 128.3, 129.4, 129.5, 130.9, 131.2, 133.8, 137.8, 138.4, 144.6; IR (ATR) \(\nu\) 3027, 1494, 1445, 898, 766, 754 cm\textsuperscript{-1}; MS (EI): \textit{m/z} (relative intensity, %) 432 (M\textsuperscript{+}, 67), 431 ([C\textsubscript{32}H\textsubscript{19}N\textsubscript{2}]\textsuperscript{+}, 100); HRMS (EI): \textit{m/z} calcd for C\textsubscript{32}H\textsubscript{20}N\textsubscript{2} (M) 432.1626, found 432.1624.

Dimethyl 7,8-diaza[5]helicene-6,9-dicarboxylate (2e)

Purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 8:2–5:5) and recrystallization from hexane/CHCl\textsubscript{3}; Yellow solid (33.3 mg, 84%); mp 215 °C (dec.); \textit{R}_f 0.35 (hexane/EtOAc 5:5); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 4.14 (s, 6H), 7.48 (dd, \(J = 8.0, 8.0\) Hz, 2H), 7.75 (dd, \(J = 8.0, 8.0\) Hz, 2H), 8.07 (d, \(J = 8.0\) Hz, 2H), 8.45 (s, 2H), 8.69 (d, \(J = 8.0\) Hz, 2H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 53.1, 119.7,
127.2, 128.8, 129.1, 129.2, 129.4, 130.1, 132.1, 132.6, 143.3, 168.0; IR (ATR) ν 2942, 1724, 1618, 1464, 1259, 1105, 891, 827, 810 cm⁻¹; MS (EI): m/z (relative intensity, %) 396 (M⁺, 32), 338 ([C₂₂H₁₄N₂O₂]⁺, 100), 250 ([C₂₀H₁₀]⁺, 18); HRMS (EI): m/z calcd for C₂₄H₁₆N₂O₄ (M) 396.1110, found 396.1112.

Table S7. The oxidative ring-closure of biaryldiamine 1f.

| entry | solvent    | yield (%) | recovery of 1f (%) |
|-------|------------|-----------|--------------------|
| 1     | t-BuOH     | 49        | 23                 |
| 2     | MeOH       | 26        | 0                  |
| 3     | toluene    | 72        | 0                  |

Table legend: 

- a ¹H NMR yields.
- b isolated yield.

3,12-Di-n-butyl-7,8-diaza[5]helicene (2f)

Purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 9:1–8:2) and recrystallization from hexane; Pale yellow solid (28.2 mg, 72%); mp 161 °C (dec.); Rₘ 0.18 (hexane/EtOAc 8:2); ¹H NMR (400 MHz, CDCl₃) δ 0.99 (t, J = 7.6 Hz, 6H), 1.44 (tq, J = 7.6, 7.6 Hz, 4H), 1.76 (tt, J = 7.6, 7.6 Hz, 4H), 2.86 (t, J = 7.6 Hz, 4H), 7.28 (dd, J = 1.6, 8.4 Hz, 2H), 7.80 (d, J = 1.6 Hz, 2H), 8.09 (d, J = 8.8 Hz, 2H), 8.49 (d, J = 8.8 Hz, 2H), 8.75 (d, J = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 22.5, 33.3, 35.7, 120.0, 126.1, 126.5, 126.9, 129.1, 130.5, 134.4, 144.6, 146.6 (one carbon is unsatisfied, probably due to the overlap of signals.); IR (ATR) ν 2930, 1618, 1464, 1259, 1105, 891, 827, 810 cm⁻¹; MS (EI): m/z (relative intensity, %) 392 (M⁺, 100), 364 ([C₂₈H₂₈]⁺, 15), 349 ([C₂₇H₂₅]⁺, 12), 335 ([C₂₆H₂₃]⁺, 31), 321 ([C₂₅H₂₁]⁺, 17), 307 ([C₂₄H₁₉]⁺, 47); HRMS (EI): m/z calcd for C₂₈H₂₈N₂ (M) 392.2252, found 392.2251.
3,12-Dibromo-7,8-diaza[5]helicene (2g)

Purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 9:1–7:3) and recrystallization from CHCl₃; Brown solid (39.9 mg, 91%); mp 205 °C (dec.); \( R_f \) 0.18 (hexane/EtOAc 8:2); \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 7.55 (dd, \( J = 2.0, 8.8 \) Hz, 2H), 8.09 (d, \( J = 8.8 \) Hz, 2H), 8.20 (d, \( J = 2.0 \) Hz, 2H), 8.58 (d, \( J = 8.8 \) Hz, 2H), 8.61 (d, \( J = 8.8 \) Hz, 2H); \(^13\)C NMR (100 MHz, CDCl₃) \( \delta \) 119.4, 123.8, 126.4, 127.9, 129.0, 129.8, 130.4, 130.5, 135.6, 146.5; IR (ATR) \( \nu \) 3061, 1591, 1495, 1436, 1263, 1086, 876, 852, 833, 820, 803 cm\(^{-1}\); MS (EI) m/z (relative intensity, %) 438 (M⁺, 69), 278 ([C\(_{20}\)H\(_{10}\)N\(_2\)]⁺, 79), 250 ([C\(_{20}\)H\(_{10}\)]⁺, 100); HRMS (EI) m/z calcld for C\(_{20}\)H\(_{10}\)N\(_2\)Br\(_2\) (M) 435.9211, found 435.9208.

| Table S8. The oxidative ring-closure of biaryldiamine 3. |
|--------------------------------------------------------|
| ![Reaction Scheme](image) | ![Product Structure](image) |
| **entry** | **solvent** | **temp. (°C)** | **yield (%)\(^a\)** | **recovery of 3 (%)\(^a\)** |
| 1 | t-BuOH | rt | 53 | trace |
| 2 | MeOH | rt | 42 | 0 |
| 3 | MeOH | 0 | 65\(^b\) | 0 |
| 4 | MeOH | -40 | 85\(^b\) | 0 |

\(^a\)\(^1\)H NMR yields. \(^b\)isolated yields.

Benzo[c]cinnoline (4) [230-17-1]

Spectroscopic data were in agreement with those previously reported.\(^{11}\) The spectroscopic data are also available in our previous paper.\(^9\) Purified by flash column chromatography on silica gel (hexane/EtOAc 95:5 to 8:2); Yellow solid; \( R_f \) 0.18 (hexane/EtOAc 8:2).
Physicochemical properties

**Table S9.** Summary of physicochemical properties of diazahelicenes 2 and cinnoline 4.

|           | Absorption | Emission (solvent) | CV (vs. Fc/Fc⁺) | TGA |
|-----------|------------|--------------------|-----------------|-----|
|           | ƛmax (nm) | ε (M⁻¹cm⁻¹) | ƛmax (nm) | φₚL | mₜEₜ₁ (V) | mₜEₜ₂ (V) | mₜEₜ₃ (V) | LUMO level (eV) | Tₘ (5% wt loss) (°C) |
| 2a        | 306, 308, 421 | 27672, 2294, 2509 | 300 | 0.02 | -1.92 | -1.83 | -1.98 | -2.02 | 261 |
| 2b        | 312, 408, 331 | 25282, 2403, 2403 | 300 | <0.01 | - | - | - | - | 268 |
| 2c        | 318, 410, 434 | 30326, 2580, 2648 | 300 | <0.01 | -1.70 | -1.62 | -1.66 | -3.13 | 306 |
| 2d        | 316, 413, 436 | 31470, 3157, 3286 | 300 | <0.01 | -1.53 | -1.86 | -1.86 | -2.93 | 222 |
| 2e        | 309, 397, 419 | 33390, 3223, 3223 | 300 | <0.01 | -1.74 | -1.61 | -1.67 | -3.12 | 315 |
| 2f        | 311, 392, 418 | 40513, 2715, 2280 | 300 | <0.01 | - | - | - | - | 300 |
| 2g        | 310, 365, 418, 445 | 31106, 3035, 4342, 2524 | 300 | <0.01 | -1.60 | -1.72 | -1.76 | -3.03 | 277 |
| 4         | 206, 209, 351, 367 | 6990, 9192, 1515, 1313 | 300 | 0.15 | - | - | - | - | 172 |

UV–vis and emission spectra

CH₂Cl₂ (fluorescence spectroscopic grade) was purged with N₂ for 30 min before the measurements. UV-vis and emission spectra of diazahelicenes 2 and cinnoline 4 were measured at room temperature using CH₂Cl₂ solutions (1.0 × 10⁻⁵ M).
Cyclic voltammetry

Cyclic voltammetry experiments were conducted at room temperature with CH$_2$Cl$_2$ solutions of diazahelicenes 2 and cinnoline 4 (5.0 $\times$ 10$^{-4}$ M) containing 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte in a cell equipped with a Pt as the working electrode (scanning rate: 100 m/V). A Pt wire and an Ag wire were applied as the counter and the reference electrode, respectively. All the potentials were corrected against the Fc/Fc$^+$ (Fc = ferrocene) couple and the values of LUMO levels were calculated with the equation S1.

$$\text{LUMO} = -(4.8 + \text{red}E_{1/2} \text{ vs. } \text{Fc/Fc}^+) \quad \text{(S1)}$$
Thermogravimetric analysis (TGA)

All the TGA profiles of diazahelicenes 2 and cinnoline 4 were measured under the nitrogen flow (200 mL/min), starting from 40 °C to 600 °C at the ramp rate of 10 °C/min.
$^1$H and $^{13}$C NMR spectra

$^1$H NMR: (400 MHz, CDCl$_3$)

$^{13}$C NMR: (100 MHz, CDCl$_3$)
$^{1}H$ NMR: (400 MHz, CDCl$_3$)

$^{13}C$ NMR: (100 MHz, CDCl$_3$)
^1H NMR: (400 MHz, CDCl₃)

^13C NMR: (100 MHz, CDCl₃)
$^1$H NMR: (400 MHz, CDCl$_3$)

$^{13}$C NMR: (100 MHz, CDCl$_3$)
$^1$H NMR: (400 MHz, CDCl$_3$)

$^{13}$C NMR: (100 MHz, CDCl$_3$)
$^1$H NMR: (400 MHz, CDCl$_3$)

$^{13}$C NMR: (100 MHz, CDCl$_3$)
$^1$H NMR: (400 MHz, CDCl$_3$)

$^{13}$C NMR: (100 MHz, CDCl$_3$)
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