Synthesis of Meso-Diarylaminocorroles via S_NAr Reactions

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Received: 26 January 2019; Accepted: 7 February 2019; Published: 12 February 2019

Abstract: A corrole is a tetapyrrolic macrocycle known as a ring-contracted porphyrinoid. Despite the progress of the synthetic chemistry of meso-aryl-substituted corroles since the early 2000s, meso-heteroatom-substituted corroles have been scarcely reported. Herein we report that the S_NAr-type substitution reaction of a meso-chlorocorrole silver complex with diphenylamine or carbazole in the presence of NaH as a base produced meso-aminocorroles. The structures, ultraviolet–visible spectroscopy (UV/Vis), and emission spectra of these meso-aminocorroles were discussed. Furthermore, the oxidation reaction of a meso-diphenylaminocorrole was examined, which resulted in the formation of 10,10-diethoxyisocorrole.

Keywords: corrole; peripheral substitution; S_NAr reaction; UV/Vis absorption; cyclic voltammetry

1. Introduction

A corrole is a tetapyrrolic macrocycle possessing three methine carbons and one direct pyrrole-pyrrole linkage [1–11]. Since the first report in 1965 [12], corroles have been recognized as a unique ring-contracted porphyrinoid because of the inner 3NH-type structure. The inner cavity of the corrole can serve as a trivalent metal ligand, and many resultant corrole complexes often have the central metals with higher oxidation states, which have been studied as catalysts for various reactions [13–17]. This is a great advantage of corroles against porphyrins that have inner 2NH-type structure. However, the synthetic chemistry of corroles has been far behind the porphyrin counterpart. The synthesis of meso-triaryl-substituted corroles was developed in the early 2000s [18–20], while the useful Rothemund–Lindsey type condensation for meso-tetraaryl-substituted porphyrins had been invented as early as 1980s [21]. A variety of peripheral functionalizations are now available to create novel porphyrin derivatives mostly thanks to the large scale production of meso-free-type porphyrins [22,23]. On the other hand, meso-free corroles have been almost unexplored until our recent reports on the effective synthesis of 5,15-bis(pentafluorophenyl)corrole (I) (Chart 1) [24–26]. The electrophilic substitution reactions on I were examined, and meso-chlorocorroles 2M (2H: M = 3H, 2Co: M = Co(py)_2) and meso-nitrocorroles 3M (3H: M = 3H, 3Ga: M = Ga(py)) were synthesized [27]. As an extension, here we report the first example of meso-aminocorroles, which were obtained by nucleophilic aromatic substitution (S_NAr) reactions of a meso-chlorocorrole silver complex with diphenylamine or carbazole. Since heteroatom-incorporation on the porphyrin scaffolds have been known as an effective way to perturb their electronic properties, the synthetic method described herein will be useful to create novel functional and electronically perturbed corrole derivatives [11].
phenyl protons, and methoxy proton. The $^{19}\text{F}$-NMR spectra showed two doublets due to the 4-
para-positions of pentafluorophenyl groups reacted preferentially with nucleophiles [35]. To avoid such an undesirable reaction, the para-positions of the pentafluorophenyl groups of 1 were first reacted with a large excess of sodium methoxide in refluxing methanol to give methoxy adduct 4 (Scheme 1). Then, 4 was chlorinated with Palau’Chlor in chloroform/pyridine at room temperature to afford meso-chlorocorrole 5H in 60% yield [26].

The $\text{SN}_2\text{Ar}$ reaction of 5H was examined under various conditions, but we only isolated a trace amount of an adduct when diphenylamine was used in the presence of sodium hydride as a base. Under these conditions, one of the NH-sites of 5H was smoothly deprotonated, preventing substitution reaction at the meso-position [6,36]. Thus, the silver complex 5Ag was prepared by the standard metalation reaction [37]. Silver corrole 5Ag was reacted with five equivalents of diphenylamine in the presence of sodium hydride at 80 °C in tetrahydrofuran (THF) for 4 h, which gave meso-diphenylaminocorrole 6Ag in 54% yield. Under these conditions, silver corroles are known to be demetalated with an excess amount of sodium hydride, thus giving the corresponding freebase 6H in 54% yield when the same reaction was run for 20 h [37].

The $^1\text{H}$-NMR spectra of 6Ag and 6H exhibited signals attributable to four β-protons, three phenyl protons, and methoxy proton. The $^{19}\text{F}$-NMR spectra showed two doublets due to the 4-methoxy-2,3,5,6-tetrafluorophenyl groups in the range from −139 to −158 ppm. The structures were unambiguously revealed by X-ray diffraction analysis (Figure 1). The mean-planes defined by the

**Chart 1.** Meso-free corrole 1, meso-chlorocorroles 2M (M = H, Co(py)$_2$) and meso-nitrocorroles 3M (M = 3H, Ga(py)).
diphenylamino segments were tilted by 63.8–69.2° from the mean-planes of the corrole cores. The C\textsubscript{meso}—N bond lengths were 1.431(3) Å for 6Ag and 1.433(2) Å for 6H, which were slightly shorter than that of meso-nitrocorrole gallium(III) complex 3Ga (1.46 Å) [27].

![Figure 1. X-Ray crystal structures of (a) 6Ag and (b) 6H. The thermal ellipsoids were scaled to 50% probability. Solvent molecules were omitted for clarity.](image)

The same substitution reaction was conducted using carbazole as a nucleophile (Scheme 2). In this case, the reaction conditions were slightly modified. In a round-bottomed flask, five equivalents of carbazole were dissolved in THF and deprotonated by addition of 7.5 equivalents of sodium hydride, which was slowly added to a THF solution of 5Ag at 80 °C. The reaction mixture was stirred for 10 min. After separation by silica gel column chromatography, meso-carbazolylcorrole 7H was obtained in 46% yield. In this case, only a trace amount of silver complex remained in the reaction mixture. The $^1$H-NMR spectrum of 7H exhibited a similar spectral pattern to that of 6H except for four peaks due to the carbazole segment. This new method is potentially useful to produce any meso-heteroatom-substituted corroles, although the choice of the base may be crucial to suppress demetalation before reactions.

![Scheme 2. Synthesis of meso-carbazolylcorrole.](image)

Incorporation of heteroatoms at the meso-position of porphyrinoids is known to induce electronic perturbation on the optical and electrochemical properties. The ultraviolet–visible (UV/Vis) absorption spectrum of 6H in dichloromethane indeed showed a broader Soret-band at 408 nm and red-shifted Q-like bands reaching to 700 nm (Figure 2). These spectral characteristics could be understood in terms of well-perturbed molecular orbital profiles. The density functional theory (DFT) calculation for 6H at the level of B3LYP/6-311G(d,p) revealed the large splitting of the HOMO and HOMO–2, in which the diphenylamino segments have significant orbital coefficients, while the LUMO and LUMO+1 remained mostly intact as compared with those of 4. Because the a2-like HOMO of corroles has a large coefficient at the meso-position, the effective perturbation from the diphenylamino group raised the HOMO energy of 6H, giving rise to the decreased HOMO–LUMO gap. In contrast, meso-carbazole-substituted corrole 7H exhibited absorption features similar to 4, rather than 6H. Indeed, the DFT calculation implied negligible effects of the carbazolyl moiety on the HOMO of 7H, presumably due to the lower HOMO energy level of the carbazole as well as a larger dihedral angle (ca. 82°) between the carbazole unit and the corrole plane (Figure S3-6). A cyclic voltammogram of 6H in CH$_2$Cl$_2$ showed reversible oxidation
and irreversible reduction waves at 0.07 and −1.58 V, respectively, versus the ferrocene/ferrocenium couple (Fc/Fc⁺), while 7H showed the first oxidation and reduction waves at 0.48 and −1.42 V as reversible peaks. The large cathodic shift of the first oxidation wave in 6H was consistent with the raised HOMO, as indicated by the DFT calculation. The electrochemical HOMO-LUMO gap of 6H (1.65 eV) was relatively smaller than those of 4 (1.73 eV) and 7H (1.90 eV) in accordance with the observed UV/Vis absorption red-shift. Notably, the absorption and emission spectra of 6H and 7H were weakly solvent dependent (Figures S3-5 and S3-6). The absorption spectral changes in polar solvents might have been due to the contribution of protonated/deprotonated corrole species [27]. The emission peaks of 6H were slightly red-shifted in polar solvents with Stokes shifts of 1050–2236 cm⁻¹, while the emission peaks of 7H were almost unchanged with Stokes shifts of 1066–1354 cm⁻¹, which indicated that the structural reorganization in the excited state was more significant in 6H. Nevertheless, they were unlikely to exhibit twisted intramolecular charge transfer (TICT)-like behaviors as seen in the meso-nitrocorroles 3H and 3Ga, and meso-arylaminosubporphyrins [27,38–40]. The optical properties of 4 to 8 are summarized in Table 1.

![Figure 2](https://example.com/figure2.png)

**Figure 2.** Ultraviolet–visible (UV/Vis) absorption (solid line) and emission (broken line) spectra of 6H (red), 7H (blue), and 4 (black) in CH₂Cl₂.

**Table 1.** Summary of the absorption and emission spectra of 4, 5H, 5Ag, 6H, 7H, and 8 in CH₂Cl₂.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption peaks/nm (ε/10⁵ M⁻¹ cm⁻¹)</th>
<th>Fluorescence peaks/nm</th>
<th>Φ_F, Fluorescence Quantum Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>401 (1.35), 556 (0.24), 604 (0.14)</td>
<td>642, 700</td>
<td>9.2%</td>
</tr>
<tr>
<td>5H</td>
<td>412 (1.71), 556 (0.28), 616 (0.17)</td>
<td>648, 704</td>
<td>2.3%</td>
</tr>
<tr>
<td>5Ag</td>
<td>423 (1.57), 563 (0.25), 579 (0.34)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6H</td>
<td>408 (0.71), 574 (0.15), 624 (0.09)</td>
<td>699</td>
<td>10.4%</td>
</tr>
<tr>
<td>7H</td>
<td>411 (1.30), 565 (0.24), 606 (0.12)</td>
<td>654</td>
<td>9.2%</td>
</tr>
<tr>
<td>8</td>
<td>418 (0.28), 720 (0.02)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: Fluorescence spectra were recorded for the dilute solutions by excitation at 400 nm.

Heteroatom-embedded π-extended porphyrinoids have shown more perturbed electronic and optical properties as compared with heteroatom-substituted analogs. Thus, the next target may be heteroatom-embedded fused corroles [32,40–44]. Along with this line, diphenylamine-substituted corrole 6H was subjected to the conditions previously reported to synthesize diphenylamine-fused porphyrins, but all the attempts to obtain fused products failed. However, when the oxidation was examined with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in chloroform/ethanol at 80 °C for 1 h, a brown fraction was isolated by silica gel column chromatography, which showed its molecular ion peak at m/z: 742.1811 (calculated for [C₃₇H₂₈N₄O₂F₆]⁺; M⁺, m/z: 742.1821) in HR-APCI-TOF-MS (Scheme 3). Fortunately, a single crystal of the compound was obtained by slow vapor diffusion.
of n-hexane into its dichloromethane solution. Unexpectedly, the structure was revealed by X-ray
diffraction analysis to be 10,10-dioethylisocorrole 8 [45–47]. In 8, the isocorrole ligand served as
a divalent ligand and the intramolecular hydrogen-bonding interaction was now more favorable.
The $^1$H-NMR spectrum showed an NH peak at 16.98 ppm, four doublets of $\beta$-protons at 6.45, 6.39,
6.34, and 6.29 ppm, and one triplet and one quartet peaks at 1.17 and 3.69 ppm, respectively, being
attributable to the ethoxy groups. Regarding to the reaction mechanism, we thought that an imine
intermediate was formed initially under the oxidative conditions. The imine intermediate was attacked
by the surrounding nucleophiles such as ethanol. Finally, the elimination of diphenylamine and
consecutive addition of another ethanol would yield isocorrole 8 (Figure S7-1).

![Scheme 3. Attempted oxidation of 6H. The X-ray crystal structure of 8 was shown in the right (thermal ellipsoids: 50%, solvent molecules were omitted for clarity). The $^1$H-NMR spectrum of 8 in CDCl$_3$ is shown below.](image)

3. Conclusions

In summary, we synthesized meso-diarylaminocorroles, as the first example of meso-aminated
corroles, by nucleophilic aromatic substitution of a meso-chlorocorrole silver complex with
diphenylamine or carbazole, and the obtained meso-arylaminocorroles were characterized by means of
optical and electrochemical measurements. The electronic states of meso-diphenylaminocorrole 6H
were more strongly perturbed by the diphenylamino substituent as compared with 7H, because the
flexible aryl groups enabled effective conjugation between the corrole and diphenylamine moieties.
An oxidative fusion reaction of 6H was examined with DDQ, which unexpectedly delivered isocorrole
8 in moderate yield. The nucleophilic aromatic substitution to a corrole ring is unprecedented,
to our knowledge, which offers a novel approach to meso-functionalized corroles as a fundamental
tool for corrole chemistry. Further functionalization on the meso-position of corroles is ongoing in
our laboratory.

4. Materials and Methods

Commercially available solvents and reagents were used without further purification unless
otherwise noted. The spectroscopic grade solvents were used for all the spectroscopic studies. Silica
gel column chromatography was performed on Wakogel C-300 (FUJIFILM Wako Pure Chemical
Corportaion, 3-9-12, Matsubara-cho, Akishima-shi, Tokyo, Japan). The UV/Vis absorption spectra
were recorded on a Shimadzu UV-3600 spectrometer (Shimadzu Corporation, 1-2, Doshomachi 3-chome,
Chuo-ku, Osaka, Japan). The fluorescence spectra were recorded on a JASCO spectrofluorometer
recorded on a Shimadzu UV-3600 spectrometer (Shimadzu Corporation, 1, Nishinokyo Kuwabara-cho,
Nakagyo-ku, Kyoto, Japan). The UV/Vis absorption spectra were recorded on a JASCO spectrofluorometer
recorded on a Shimadzu UV-3600 spectrometer (Shimadzu Corporation, 1-2, Musashino, Akishima-shi,
Tokyo, JAPAN) (operating as 600.17 MHz for $^1$H and 564.73 MHz for $^{19}$F) using the residual solvent
as an internal reference for $^1$H ($\delta = 7.26$ ppm in CDCl$_3$) and hexafluorobenzene as an external

![Diagram of spectroscopic measurements.](image)
reference for $^{19}$F ($\delta = -162.9$ ppm). HR-APCI-TOF-MS was conducted on a BRUKER microTOF model using positive ion mode. The redox potentials were measured by cyclic voltammetry on an ALS electrochemical analyzer model 612E. The single-crystal X-ray diffraction analysis data were collected at $-180$ °C with a Rigaku XtaLAB P200 (Rigaku Corporation, 3-9-12, Matsubara-cho, Akishima-shi, Tokyo, Japan) by using graphite monochromated Cu-$K\alpha$ radiation ($\lambda = 1.54187$ Å). The structures were solved by direct methods (SHELXT-2014/5) [48] and refined with the full-matrix least-squares technique (SHELXL-2014/7) [49,50]. All calculations were carried out using the Gaussian 16 program.

4.1. Synthesis of 4

The meso-free corrole 1 (0.30 mmol, 184 mg) and sodium methoxide (15 mmol, 810 mg, 50 equivalent) were dissolved in MeOH (30 mL, 10 mM). The reaction mixture was stirred for 1 h at room temperature and passed through a short silica pad. After the solvent was removed under reduced pressure, the residue was purified with a short silica gel column using dichloromethane as an eluent. Recrystallization from dichloromethane/n-hexane gave corrole 4 (161 mg, 0.25 mmol, 82%).

$^1$H-NMR (600 MHz, CDCl$_3$, 25 °C) $\delta$ / ppm = 9.69 (s, 1H, meso-H), 9.09 (br, 4H, $\beta$-H), 8.84 (d, $J = 4.1$ Hz, 2H, $\beta$-H), 8.60 (brs, 2H, $\beta$-H), and 4.39 (s, 6H, OMe). $^{19}$F-NMR (585 MHz, CDCl$_3$, 25 °C) $\delta$ / ppm = $-139.77$ (s, 4F, o-F), and $-157.86$ (s, 4F, m-F). HR-APCI-TOF-MS $m/z$ = 654.1274 (calculated for [C$_{33}$H$_{31}$N$_4$O$_4$F$_8$]$^+$; M$^+$, m/z = 654.1297).

4.2. Synthesis of 5H

Palau’Chlor (90 μmol, 19 mg, 0.90 equiv.) was added to a solution of corrole 4 (0.10 mmol, 69 mg) in chloroform/pyridine (35 mL/0.35 mL, 3 mM). The reaction mixture was stirred for 1 h at room temperature and passed through a short silica pad. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography using n-hexane/dichloromethane (o/o = 7:3) as an eluent. Recrystallization from dichloromethane/n-hexane gave meso-chlorocorrole 5H (41 mg, 60 μmol, 60%).

$^1$H-NMR (600 MHz, CDCl$_3$, 25 °C) $\delta$ / ppm = 9.40 (d, $J = 4.6$ Hz, 2H, $\beta$-H), 9.08 (d, $J = 3.7$ Hz, 2H, $\beta$-H), 8.81 (d, $J = 4.6$ Hz, 2H, $\beta$-H), 8.57 (brs, 2H, $\beta$-H), and 4.40 (s, 6H, OMe). $^{19}$F-NMR (585 MHz, CDCl$_3$, 25 °C) $\delta$ / ppm = $-139.75$ (s, 4F, o-F), and $-157.69$ (s, 4F, m-F). HR-APCI-TOF-MS $m/z$ = 689.0962 (calculated for [C$_{33}$H$_{31}$N$_4$O$_2$ClF$_8$]$^+$; [M + H]$^+$, m/z = 689.0985).

4.3. Synthesis of 5Ag

The corrole 5H (40 μmol, 28 mg) and silver(I) acetate (0.132 mmol, 22 mg, 3.3 equivalent) were dissolved in THF/pyridine (4 mL/2 mL). The reaction mixture was gradually heated up to 80 °C, stirred for 1 h, and passed through a Florisil® pad (SIGMA-ALDRICH JAPAN K.K., 2-2-24, Higashishinagawa, Shinagawa-ku, Tokyo, Japan). After the solvent was removed under reduced pressure, the recrystallization from dichloromethane/n-hexane gave the corrole Ag(III) complex 5Ag (28 mg, 36 μmol, 90%).

$^1$H-NMR (600 MHz, CDCl$_3$, 25 °C) $\delta$ / ppm = 9.53 (d, $J = 5.0$ Hz, 2H, $\beta$-H), 9.30 (d, $J = 4.1$ Hz, 2H, $\beta$-H), 9.00 (d, $J = 4.6$ Hz, 2H, $\beta$-H), 8.77 (d, $J = 4.1$ Hz, 2H, $\beta$-H), and 4.42 (s, 6H, OMe). $^{19}$F-NMR (585 MHz, CDCl$_3$, 25 °C) $\delta$ / ppm = $-139.10$ (d, $J = 4.1$ Hz, 2H, $\beta$-H), 9.00 (d, $J = 4.6$ Hz, 2H, $\beta$-H), 8.77 (d, $J = 4.1$ Hz, 2H, $\beta$-H), and 4.42 (s, 6H, OMe). HR-APCI-TOF-MS $m/z$ = 791.9715 (calculated for [C$_{33}$H$_{13}$N$_4$O$_2$$^{107}$Ag$^{35}$ClF$_8$]$^+$; M$^+$, m/z = 791.9723).
4.4. Nucleophilic Aromatic Substitution Reaction of 5Ag with Diphenylamine

Corrole 5Ag (20 μmol, 15 mg), NaH (0.15 mmol, 6.0 mg, 7.5 equivalent), and diphenylamine (0.10 mmol, 17 mg, 5 equivalent) were placed in a round-bottomed flask, and were dissolved in THF (1 mL, 20 mM). The mixture was stirred for 4 h at 80 °C, and passed through a short silica pad. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography using n-hexane/dichloromethane (v/v = 7:3) as an eluent. The recrystallization from dichloromethane/n-hexane gave meso-diphenylaminocorrole Ag(III) complex 6Ag (10 mg, 11 mmol, 54%). When the reaction mixture was stirred for 20 h, demetalated freebase corrole 6H was obtained (9.0 mg, 11 mmol, 54% yield).

6Ag: 1H-NMR (600 MHz, CDCl3, 25 °C) δ / ppm = 9.24 (d, J = 4.6 Hz, 2H, β-H), 9.12 (d, J = 4.6 Hz, 2H, β-H), 8.80 (d, J = 4.6 Hz, 2H, β-H), 8.71 (d, J = 4.6 Hz, 2H, β-H), 7.30 (d, J = 7.8 Hz, 4H, o-Ph), 7.19 (dd, J1 = 7.8 Hz, J2 = 7.3 Hz, 4H, m-Ph), 6.92 (t, J = 7.3 Hz, 2H, p-Ph), and 4.39 (s, 6H, OMe). 19F-NMR (565 MHz, CDCl3, 25 °C) δ / ppm = −139.05 (d, J = 17.5 Hz, 4F, o-F), and −157.87 (d, J = 17.5 Hz, 4F, m-F). HR-APCI-TOF-MS m/z = 925.0827 (calculated for [C45H24N2O2107AgF3]⁺; M⁺, m/z = 925.0848).

6H: 1H-NMR (600 MHz, CDCl3, 25 °C) δ / ppm = 9.02 (d, J = 4.2 Hz, 4H, β-H), 9.01 (d, J = 4.2 Hz, 4H, β-H), 8.64 (d, J = 4.2 Hz, 2H, β-H), 8.53 (brs, 2H, β-H), 7.32 (d, J = 7.8 Hz, 4H, o-Ph), 7.18 (dd, J1 = 7.8 Hz, J2 = 7.3 Hz, 4H, m-Ph), 6.90 (t, J = 7.3 Hz, 2H, p-Ph), and 4.37 (s, 6H, MeO). 19F-NMR (565 MHz, CDCl3, 25 °C) δ / ppm = −139.67 (s, 4F, o-F), and −157.84 (s, 4F, m-F). HR-APCI-TOF-MS m/z = 822.2042 (calculated for [C45H25N3O2F3]⁺; [M + H]⁺, m/z = 821.2110).

4.5. Nucleophilic Aromatic Substitution Reaction of 5Ag with Carbazole

The corrole 5Ag (20 μmol, 15 mg) was dissolved in THF (0.5 mL), to which a mixture of NaH (0.2 mmol, 8 mg, 10 equivalent) and carbazole (0.10 mmol, 17 mg, 5 equivalent) was added slowly. The mixture was stirred for 10 min at 80 °C, and passed through a short silica pad. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography using n-hexane/dichloromethane (v/v = 7:3) as an eluent. Recrystallization from dichloromethane/n-hexane gave meso-carbazolylcorrole 7H (7.5 mg, 9.1 μmol, 46%).

7H: 1H-NMR (600 MHz, CDCl3, 25 °C) δ / ppm = 9.09 (brs, 2H, β-H), 8.60 (brs, 4H, 2×β-H), 8.43 (d, J = 7.8 Hz, 2H, Cz), 8.26 (brs, 2H, β-H), 7.40 (t, J = 7.8 Hz, 2H, Cz), 7.28 (t, J = 7.8 Hz, 2H, Cz), 6.85 (d, J = 7.8 Hz, 2H, Cz), and 4.37 (s, 6H, MeO). 19F-NMR (565 MHz, CDCl3, 25 °C) δ / ppm = −139.75 (s, 4F, o-F), and −157.69 (s, 4F, m-F). HR-APCI-TOF-MS m/z = 820.1908 (calculated for [C45H25N3O2F3]⁺; [M + H]⁺, m/z = 820.1953).

4.6. Synthesis of 8

Corrole 6H (5 μmol, 4.1 mg) was dissolved in CHCl3/EtOH (200 mL/1 mL), to which a solution of DDQ (15 mmol, 3.4 mg, 3 equiv.) in CHCl3 (4 mL) was added slowly. The mixture was stirred for 1 h at 80 °C, and passed through a short silica pad. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography using n-hexane/dichloromethane (v/v = 7:3) as an eluent. The recrystallization from dichloromethane/n-hexane gave 10,10'-diethoxyisocorrole 8 (1.7 mg, 2.3 μmol, 48%).

1H-NMR (600 MHz, CDCl3, 25 °C) δ / ppm = 16.98 (s, 2H, NH), 6.45 (d, J = 4.6 Hz, 2H, β-H), 6.39 (d, J = 4.6 Hz, 2H, β-H), 6.34 (d, J = 4.6 Hz, 2H, β-H), 6.29 (d, J = 4.6 Hz, 2H, β-H), 4.18 (s, 6H, OMe), 3.69 (q, J = 6.9 Hz, 4H, OCH2CH3), and 1.17 (t, J = 6.9 Hz, 6H, OCH2CH3). 19F-NMR (565 MHz, CDCl3, 25 °C) δ = −140.70 (d, J = 17.5 Hz, 4F, o-F), and −158.21 (d, J = 17.5 Hz, 4F, m-F). HR-APCI-TOF-MS m/z = 742.1811 (calculated for [C37H26N4O4F8]⁺; M⁺, m/z = 742.1821).

Supplementary Materials: The following are available online. Figure S1: 1H and 19F-NMR spectra, Figure S2: Observed (top) and simulated (bottom) HR-APCI-TOF-MS, Figure S3: UV/Vis absorption and fluorescence spectra,
Figure S4: X-Ray structures, Figure S5: Cyclic voltammogram, Figure S6: Molecular orbital (MO) energy diagrams and Kohn–Sham orbital representations calculated at the B3LYP/6-311G(d,p) level, Scheme S7: Plausible reaction mechanism for the formation of 8. Table S1: Absorption and emission details of 4, 5, 6H, and 7H in various solvents, Table S2: The photophysical parameters of 6H and 7H in various solvents. Table S3: Crystallographic details of 6Ag, 6H, and 8.

Author Contributions: All authors contributed to the writing of the manuscript. K.U. conducted all the experiments.

Funding: We appreciate JSPS KAKENHI Grant Numbers JP25220802, JP26810021, JP18H03910, and JP18K14199.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

NMR Nuclear magnetic resonance
DFT Density functional theory
HOMO Highest occupied molecular orbital
LUMO Lowest occupied molecular orbital
DDQ 2,3-dichloro-5,6-dicyano-1,4-benzoquinone
THF Tetrahydrofuran
TICT Twisted intramolecular charge transfer
HR-APCI-TOF-MS High-resolution atmospheric-pressure-chemical-ionization time-of-flight mass-spectrometry
MO Molecular orbital

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