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Supporting Information

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A Doubly *N*-Fused Benzohexaphyrin and Its Rearrangement to a Fluorescent Macrocycle Containing Two Indolo[2,1-*a*]isoquinolin-5-one Subunits Upon DDQ Oxidation

Yasuhide Inokuma, Takahiro Matsunari, Noboru Ono, Hidemitsu Uno,* and Atsuhiro Osuka**

General Procedure. All reagents and solvents were of commercial reagent grade and were used without further purification except where noted. Dry CH_2Cl_2 was obtained by distillation over CaH_2. ^1H, ^{13}C, ^{19}F NMR spectra were recorded on a JEOL delta-600 spectrometer, and chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ (δ = 7.260). Spectroscopic grade CH_2Cl_2 and $CHCl_3$ were used as solvents for all spectroscopic studies. UV/visible/NIR absorption spectra were recorded on a Shimadzu UV-3100 spectrometer. Fluorescence spectra were recorded on a Shimazu RF-5300PC spectrometer. ESI-MS spectra were recorded on a BRUKER micro TOF using positive-ion mode, and acetonitrile and/or THF as a solvent. TOF-MS spectra were recorded on a Shimadzu/KRATOS KOMPACT MALDI 4 spectrometer, using positive-MALDI ionization method with/without CA matrix. Preparative separations were performed by silica gel flash column chromatography (Merck Kieselgel 60H Art. 7736), silica gel gravity column chromatography (Wako gel C-400) and size exclusion gel permeation chromatography (Bio-Rad Bio-Beads S-X1, packed with toluene or $CHCl_3$ in a 4 × 100 gravity flow coloumn: flow rate, 3.8 $mLmin^{-1}$). Redox potentials were measured by the cyclic voltammetry method on an ALS electrochemical analyzer model 660. All retro-Diels-Alder reactions were carried out in a Yamato vacuum oven ADP-21 equipped with a vacuum pump.

Synthesis of *β*-bicyclo[2.2.2.]octadiene-fused porphyrin and expanded porphyrins (2-4).

4,7-Dihydro-4,7-ethano-2*H*-isoindole (**1**) (500 mg, 3.44 mmol) and pentafluorobenzaldehyde (0.436 ml, 3.44 mmol) were dissolved in distilled CH_2Cl_2 (50 ml). 2.5 M $BF_3{\cdot}OEt_2$ in distilled CH_2Cl_2 (0.136 ml, 0.34 mmol) was added to the above stirred solution. The reaction mixture was stirred under Ar in the dark for 2 h, and then DDQ (1.95 g, 8.6 mmol) was added to the solution. After being stirred in the dark overnight, the reaction mixture was washed with saturated aqueous $NaHCO_3$ solution (3 times), dried over Na_2SO_4, and the solvent was removed by a rotary evaporator. Residual solids were separated by silica gel column chromatography (CH_2Cl_2/hexane = 1/2). *β*-Bicyclohexaphyrin **4** (104 mg, 9.4%) was obtained as first fraction and other fractions were collected and subjected to a preparative GPC column to separate a first moving polymeric higher homologues from relatively slowly moving yellow and red fractions that corresponded to *β*-bicycloporphyrin **2** and *β*-bicyclopentaphyrin **3**, respectively. Final separation of **2** and **3** was carried out by silica gel column chromatography to give *β*-bicyclo-fused porphyrin **2** (195 mg, 17.6%) with a mixture of CH_2Cl_2/hexane = 1/1 as an eluent and to give *β*-bicyclo-fused pentaphyrin **3** (122 mg, 11.0 %) with a mixture of CH_2Cl_2/methanol = 1/0.05 as an eluent.

MALDI TOF-Mass: **3** ; *m*/*z* = 1472, Calcd for $C_{120}H_{38}F_{40}N_8$ = 1467.2 [*M* – 5 ethylene]$^+$

***meso*-Tetrakis(pentafluorophenyl)tetrabenzoporphyrin (7).**

β-Bicyclo-fused porphyrin **2** (70 mg, 54 *μ*mol) that was pre-purified by recrystallization from CH_2Cl_2/MeOH was placed in a small reaction vessel. This vessel was heated in a vacuum oven at 200 °C/0.1 mmHg for 10 min, giving *meso*-tetrakis(pentafluorophenyl)tetrabenzo-porphyrin (**7**) quantitatively.

^{1}H NMR (600 MHz, $CDCl_3$ and TFA) δ = 7.80-7.77 (m, 8H, benzo), 7.75-7.72 (m, 8H, benzo), and 1.74 ppm (br s, 4H, NH (protonated)): ^{19}F NMR (565 MHz, $CDCl_3$ and TFA, C_6F_6 as an external reference) δ = –137.9 (d, *J* = 17.0 Hz, 8F, *o*-C_6F_5), –145.0 (t, *J* = 20.7 Hz, 4F, *p*-C_6F_5), and –157.3 ppm (t, *J* = 14.7 Hz, 8F, *m*-C_6F_5): ^{13}C NMR (150 MHz, $CDCl_3$ and TFA) δ = 141.5, 132.4, 130.3, 123.2, and 97.5 ppm.

HR ESI-TOF Mass (positive mode) ; *m*/*z* = 1175.1288 (calc. for $C_{60}H_{19}N_4F_{20}$ = 1175.1285 [*M* + H]$^+$). Due to C-F multiple coupling, the carbon atom signals at the pentafluorophenyl groups could not be clearly observed. A single crystal for X-ray crystallography was prepared by recrystallization from a mixture of CH_2Cl_2/acetonitrile/TFA.

Doubly *N*-fused *β*-benzo[28]hexaphyrin(1.1.1.1.1.1.) (8)

Crude mixture of *β*-bicyclo-fused hexaphyrin **4** (104 mg, 53.9 *μ*mol) was placed in a glass vessel, which was heated in a vacuum oven at 170 °C / 0.1 mmHg for 30 min. The resulting solids were separated by silica gel column chromatography (CH_2Cl_2/hexane = 1/2), and doubly *N*-fused-*β*-benzohexaphyrin **8** was obtained as a red-purple fraction (43.0 mg, 46.5 %). Single crystals for X-ray crystallography were prepared by recrystallization from a mixture of CH_2Cl_2/MeOH.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 17.87 (br s, 2H, NH), 8.69 (d, *J* = 7.6 Hz, 2H, benzo), 7.40 (br t, *J* = 10.3 Hz, 2H, benzo), 7.09-7.04 (m, 10H, benzo), 7.00 (t, *J* = 8.2 Hz, 2H, benzo), 6.45 (d, *J* = 8.2 Hz, 2H, benzo), 6.33 (d, *J* = 8.3 Hz, 2H, benzo), 6.29 (d, *J* = 8.9 Hz, 2H, benzo), and 6.16 ppm (d, *J* = 6.2 Hz, 2H, benzo): ^{19}F NMR (565 MHz, $CDCl_3$, C_6F_6 as an external reference) δ = –135.0 (d, *J* = 24 Hz, 2F), –138.5 (t, *J* = 32 Hz, 2F), –138.7 (d, *J* = 24 Hz, 2F), –139.5 (br d, 2F), –139.7 (br d, 2F), –148.6 (br, 2F), –148.9 (t, *J* = 20 Hz, 2F), –150.4 (t, *J* = 21 Hz, 2F), –158.4, –158.7 (m, 6F), –158.9 (br, 2F), –159.5 (br t, *J* = 19, 2F), and –161.3 ppm (br t, *J* = 19 Hz, 2F): ^{13}C NMR (150 MHz, $CDCl_3$) δ = 152.2, 143.6, 141.8, 137.6, 136.0, 134.4, 133.6, 132.3, 132.0, 130.5, 130.0, 129.9, 129.8, 129.7, 128.8, 127.1, 126.2, 125.6, 123.5, 121.9, 121.0, 119.9, 119.7, 119.6, 114.7, 104.6, and 101.0 ppm. Due to C-F multiple coupling, the carbon atom signals at the pentafluorophenyl groups could not be clearly observed. HR ESI-TOF Mass (positive mode) ; *m*/*z* = 1722.1767 (calc. for $C_{90}H_{26}N_6F_{28}$ = 1722.1766 $[M]^+$): UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [$M^{-1}cm^{-1}$]) = 367 (41000), 524 (41900), and 677 (27700).

Oxidative rearrangement to fluorescent hexaphyrin (11)

In this reaction, $CHCl_3$ and DDQ were purified as described below. Commercially available $CHCl_3$ was washed three times with water to remove EtOH (stabilizer), dried over K_2CO_3 and distilled from Na_2SO_4. Commercially available DDQ was recrystallized from distilled $CHCl_3$. Doubly *N*-fused *β*-benzo[28]hexaphyrin **8** (13.2 mg, 7.66 *μ*mol) was dissolved in $CHCl_3$ (8 ml). DDQ (8.69 mg, 38.3 *μ*mol) and H_2O (60 *μ*l) were added to the above solution and the resulting mixture was stirred at room temperature under Ar for 3 days. The solution color changed from red-brown to navy blue. The resulting solution was passed through a short alumina column and the solvent was removed by evaporation. The residue was separated by silica gel column chromatography (CH_2Cl_2/hexane = 1/2) and main blue fraction was collected to give hexaphyrin **11** (6.4 mg, 47.6 %). A single crystal for X-ray crystallography was prepared by recrystallization from a mixture of toluene/MeOH.

^{1}H NMR (600 MHz, CD_2Cl_2) δ = 13.95 (br s, 2H, NH), 7.77 (d, *J* = 7.3 Hz, 2H, benzo), 7.73 (d, *J* =

8.3 Hz, 2H, benzo), 7.30 (t, *J* = 7.3 Hz, 2H, benzo), 7.25 (t, *J* = 7.2 Hz, 2H, benzo), 7.21 (t, *J* = 8.2 Hz, 2H, benzo), 7.16 (t, *J* = 7.4 Hz, 2H, benzo), 7.01 (d, *J* = 7.3 Hz, 2H, benzo), 6.93 (t, *J* = 8.3 Hz, 2H, benzo), 6.81-6.79 (d and t, 4H, benzo), 6.35 (d, *J* = 8.3 Hz, 2H, benzo), and 6.17 ppm (d, *J* = 9.2 Hz, 2H, benzo): ^{19}F NMR (565 MHz, $CDCl_3$, C_6F_6 as an external reference) δ = –127.7 (d, *J* = 24 Hz, 2F), –137.6 (d, *J* = 21 Hz, 2F), –138.0 (d, *J* = 16 Hz, 2F), –148.8 (t, *J* = 21 Hz, 2F), –149.0 (t, *J* = 19 Hz, 1F), –149.1 (t, *J* = 20 Hz, 1F), –149.7 (t, *J* = 20 Hz, 2F), –151.2 (t, *J* = 22 Hz, 2F), –159.1 (d, *J* = 19 Hz, 2F), –159.3 (t, *J* = 22 Hz, 2F), –160.1 (t, *J* = 19 Hz, 2F), –160.6 (t, *J* = 20 Hz, 2F), –160.9 (t, *J* = 24 Hz, 2F), and –162.5 ppm (d, *J* = 19 Hz, 2F): ^{13}C NMR (150 MHz, $CDCl_3$) δ = 186.2(C=O), 152.2, 138.7, 138.6, 135.7, 135.6, 132.6, 131.5(2C), 130.5, 130.1, 129.2, 128.4, 127.9, 127.7, 126.2, 126.2, 125.8, 125.6, 124.8, 124.5(2C), 121.7, 121.5, 120.2, 119.2, 118.4, 102.7, and 37.3 ppm (sp^3 carbon): HR ESI-TOF Mass (positive mode) ; *m*/*z* = 1755.1732 (calc. for $C_{90}H_{27}N_6F_{28}O_2$ = 1755.1743 $[M + H]^+$).: UV / Vis (CH_2Cl_2): λ_{max} [nm] (ε [$M^{-1}cm^{-1}$]) = 578 (60000).

Figure S-1. MALDI TOF-Mass spectrum of the reaction mixture of **1** and pentafluorobenzaldehyde. Peaks corresponding to **2**-**6** were detected with their retro-Diels-alder products.

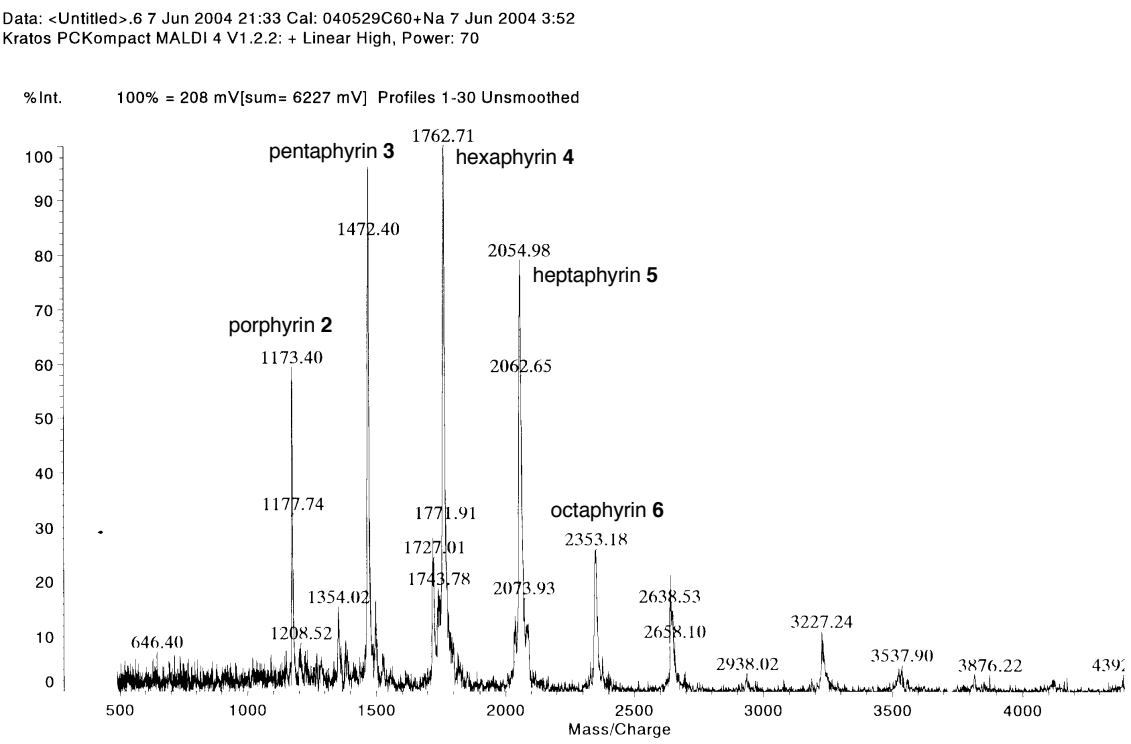
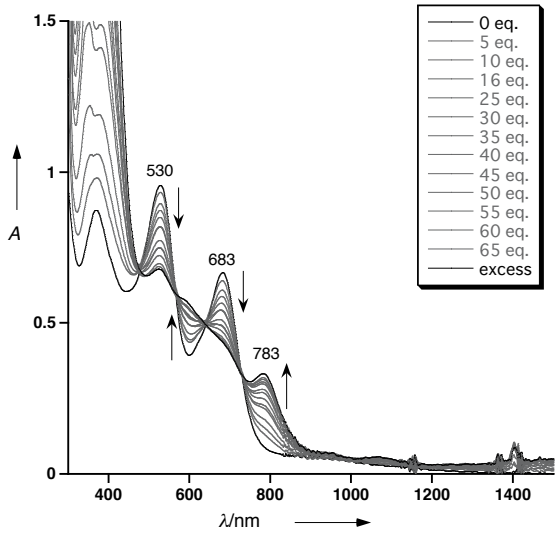
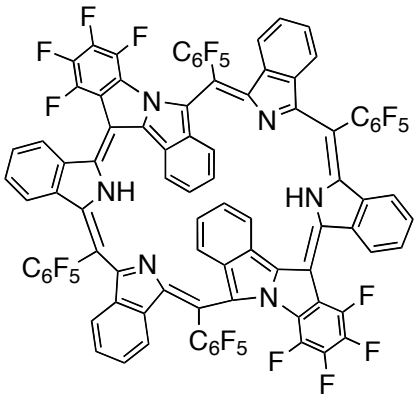
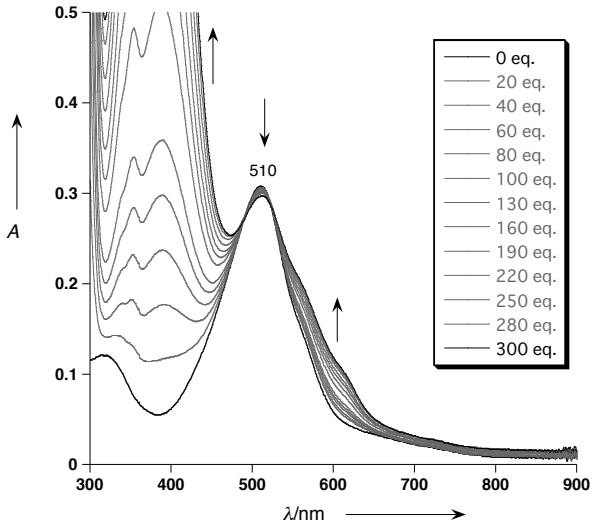


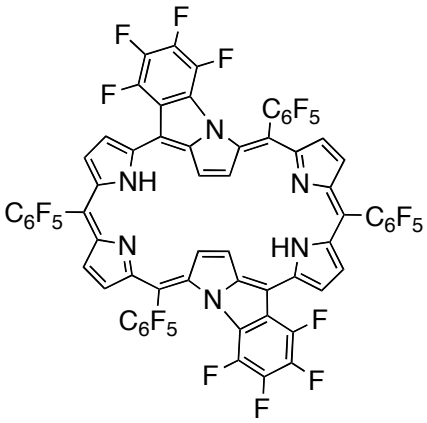
Figure S-2. DDQ titrations of **8** (top) and **10** (bottom) in CH_2Cl_2.





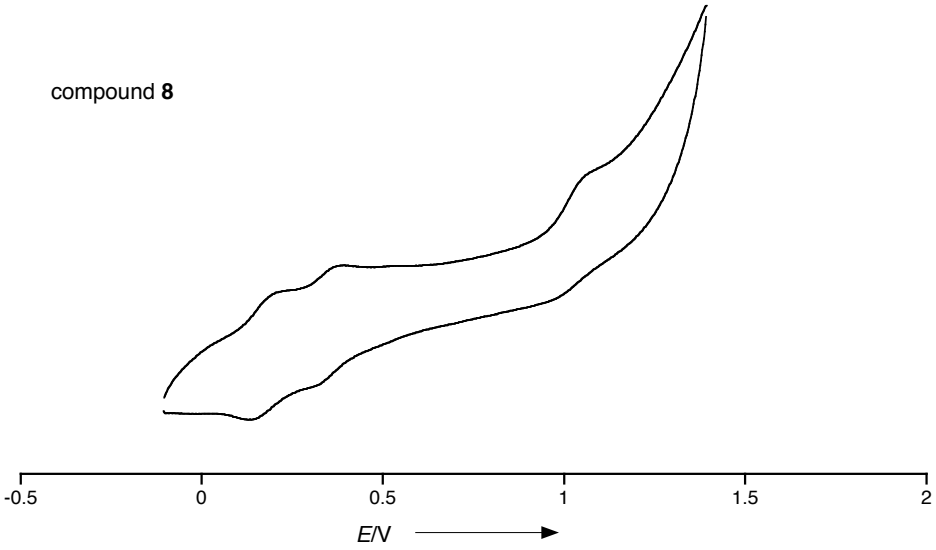
8



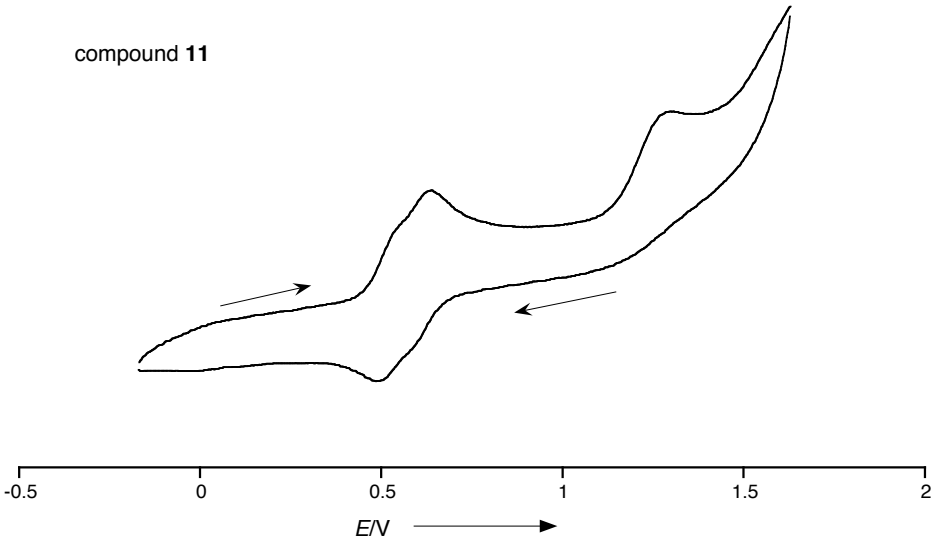


10

Figure S-3. Cyclic voltammograms of **8** and **11**.



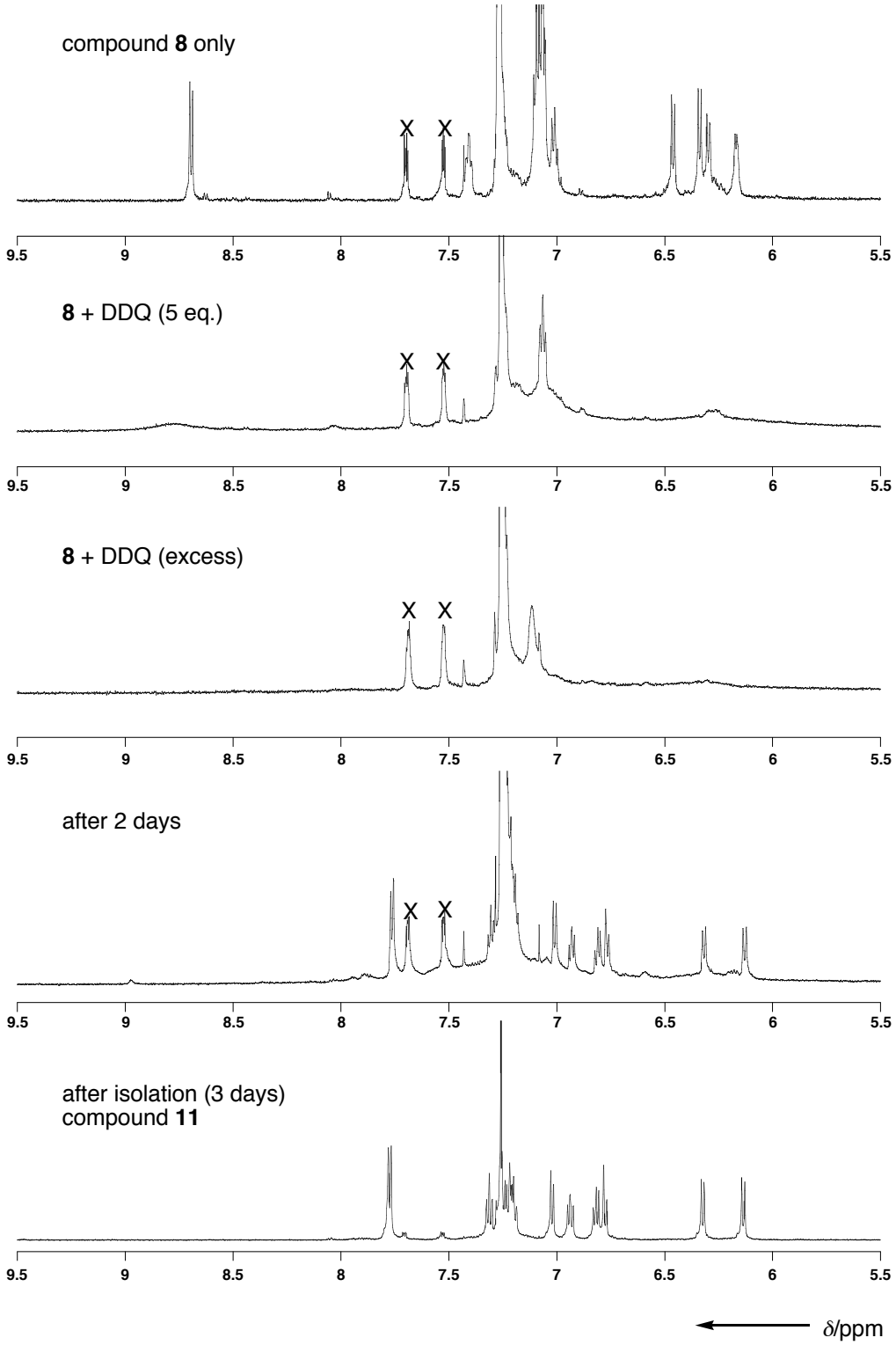
$^{ox\text{-}1}E_{1/2}$ = 0.17 V, $^{ox\text{-}2}E_{1/2}$ = 0.35 V, $^{ox\text{-}3}E_{1/2}$ = 1.02 V (*vs*. ferrocene/ferrocenium ion)



$^{ox\text{-}1}E_{1/2}$ = 0.51V, $^{ox\text{-}2}E_{1/2}$ = 0.62 V, $^{ox\text{-}3}E_{p}$ = 1.27 V (*vs*. ferrocene/ferrocenium ion)

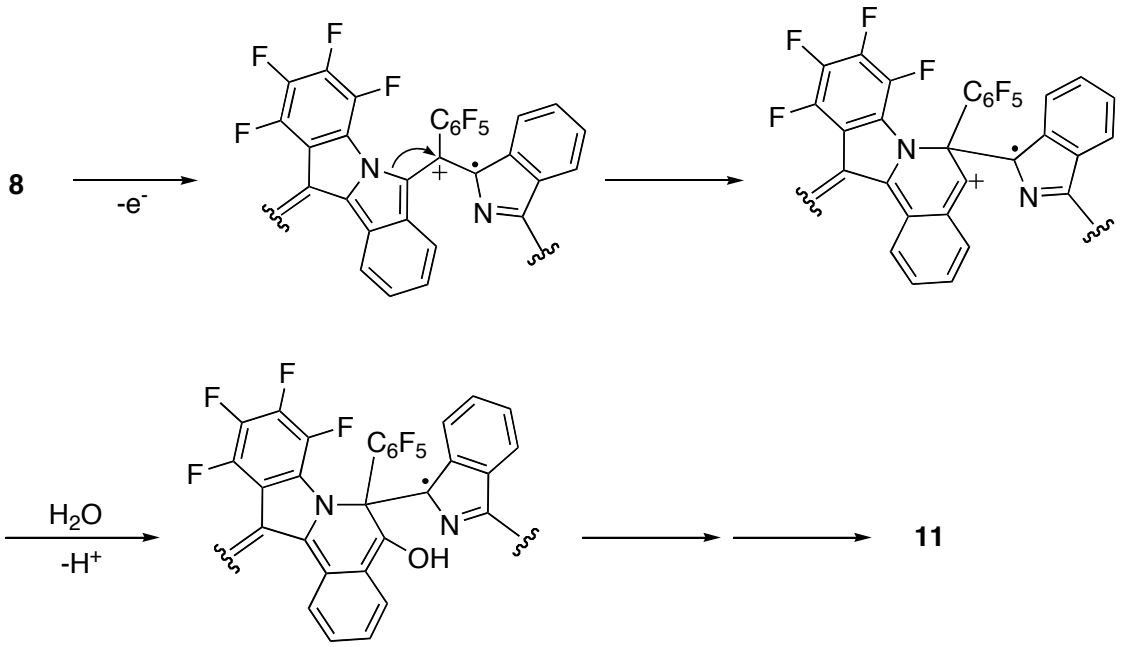
These spectra were measured using a platinum working electrode, a platinum wire counter electrode, and Ag/0.01 M $AgNO_3$ reference electrode. The measurements were carried out in acetonitrile solution containing 0.1 M n-Bu_4NBF_4 as a supporting electrolyte.

Figure S-4. ^{1}H NMR spectra during the oxidative rearrangement from **8** to **11** ($CDCl_3$, at 293 K).



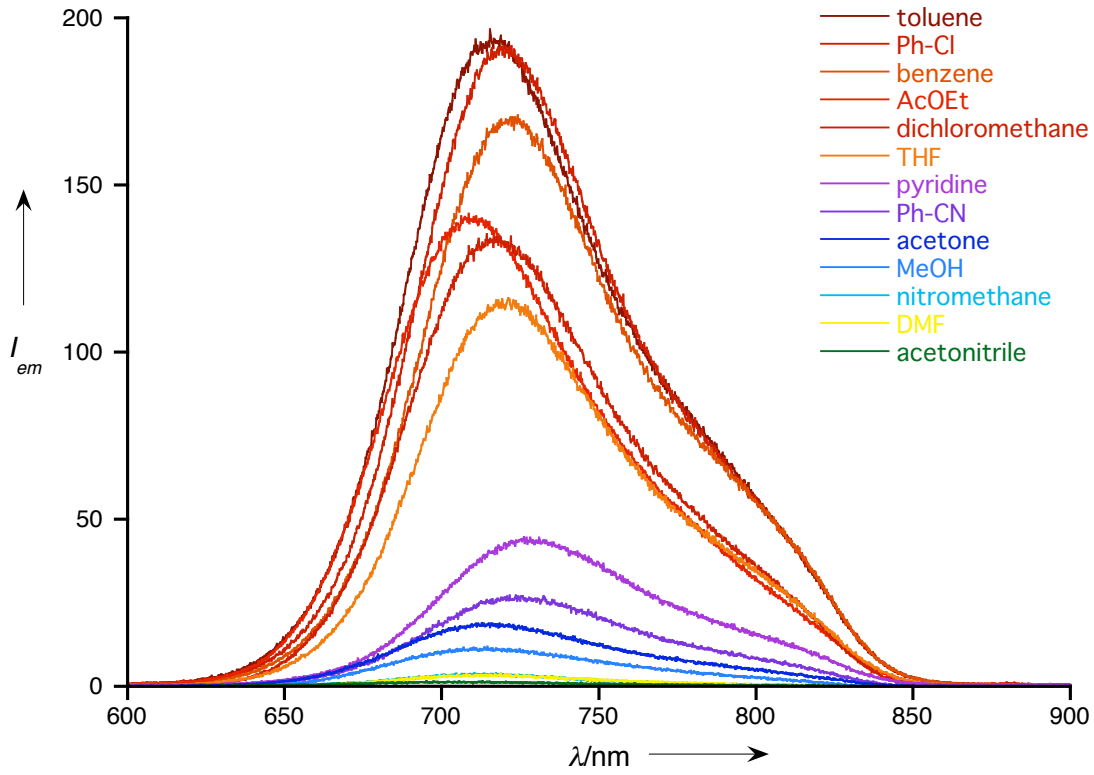
X : peaks of elasticizer (available as intensity standard)

Scheme S-1. A possible scheme of oxidative rearrangement from **8** to **11**.



Although the rearrangement mechanism has not been clarified yet, one possible route may involve a reaction sequence of initial one-electron oxidation of **8** with DDQ to generate its cation radical, 1,2-rearrangement of pyrrolic nitrogen atom to form an intermediate bearing a vinyl cation and a tertiary radical at the pyrrolic α-position, and final nucleophilic attack of the vinyl cation by adventitious water.

Figure S-5. Solvent dependent fluorescence of **11**.

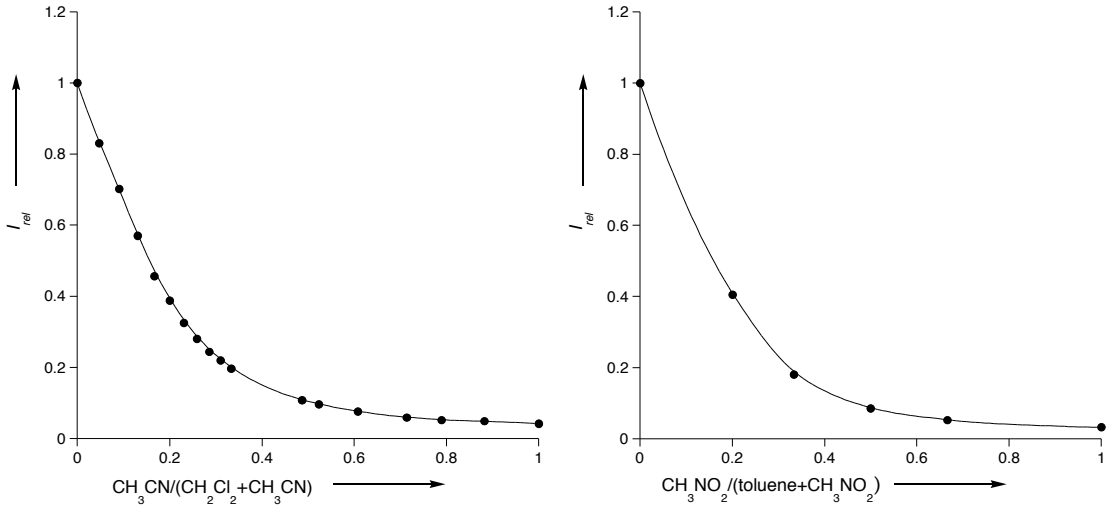


All spectra were recorded under the same measuring conditions.

Relative maximum emission intensities were shown below.

solvent	maximum intensity (at λ_{max})	solvent	maximum intensity (at λ_{max})
toluene	193 (716 nm)	Ph-CN	26 (724 nm)
Ph-Cl	190 (719 nm)	acetone	18 (714 nm)
benzene	170 (722 nm)	MeOH	11 (714 nm)
AcOEt	140 (708 nm)	nitromethane	3.7 (712 nm)
dichloromethane	133 (717 nm)	DMF	3.3 (712 nm)
THF	115 (720 nm)	MeCN	1.3 (706 nm)
pyridine	44 (729 nm)		

Figure S-6. Relationship between emission intensity and solvent mixing ratio. (left : dichloromethane/acetonitrile; right : toluene/nitromethane)



All sample solutions have absorption 0.02 at each λ_{max} and were excited at λ_{max}.