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1. General Information

Melting points were determined on a Stanford Research Systems MPA100 or a Yanaco micro melting point apparatus MP-J3 and were uncorrected. IR spectra were recorded on a JASCO FT IR-4100 spectrometer by KBr pellet or a JASCO FT/IR-460plus spectrometer equipped with ATR PRO 400-S in ATR mode using ZnSe crystal plate. UV-Vis-NIR spectra were recorded on a JASCO V-670 spectrometer or SHIMADZU UV-3600, UV-2550 spectrometers with 1 cm quartz cell unless otherwise noted. Fluorescence spectra were recorded on a JASCO FP6500 spectrometer or SHIMADZU RF-5300PC spectrofluorophotometer. Solution state ¹H and ¹³C NMR spectra were measured on a JEOL JNM-ECS400 spectrometer at 23 °C at 400 and 100 MHz, respectively. $CDCl_3$ and CD_2Cl_2 were used as a solvent and the residual solvent peaks were used as an internal standard (¹H NMR: CDCl₃ 7.26 ppm, CD₂Cl₂ 5.30 ppm; ¹³C NMR: CDCl₃ 77.0 ppm, CD₂Cl₂ 53.5 ppm). Solid state NMR spectra were carried out using a BrukerAvance 600 spectrometer equipped with 2.5 mm O.D. ¹H-¹³C-¹⁵N triple resonance MAS probe. High resolution (HR) and low resolution (LR) mass spectra (MS) were measured on a JEOL JMS-777V spectrometer using electron impact ionization method (EI) and a Applied Biosystems Voyager DE-STR spectrometer using matrix assisted laser desorption ionization time-of-flight method (MALDI-TOF). CW and pulse ESR spectra were measured on Bruker EMX plus, Bruker E500, and Bruker E680 spectrometers. Heating reactions were carried out by EYELA organic synthesizers. Medium pressure liquid chromatography (MPLC) was performed on Kanto 60N silica gel using a preparative medium pressure liquid chromatography system. TLC analysis was performed using Merck Silica gel 60 F₂₅₄ and PTLC was conducted using Wako Wakogel B-5F. Gel permeation chromatography (GPC) was performed on JAIGEL 1H and 2H using JAI Recycling Preparative HPLC system and CHCl₃ as the solvent. Reagents and solvents for syntheses were commercially purchased and air and/or moisture sensitive reactions were carried out under an argon atmosphere. The solvents (CH₂Cl₂, CD₂Cl₂, benzene etc.) for the analyses of acid-sensitive BC and TBA were freshly distilled before use according to the standard methods.

2. Synthesis and Characterization Data of Compounds

1-Bromo-3,6-di-*tert*-butylcarbazole $(2)^1$ and 2,7-di-*tert*-butyl-9,10-dihydro-9,9-dimethylacridine $(5)^2$ were prepared from 3,6-di-*tert*-butylcarbazole (1) and 9,10-dihydro-9,9-dimethylacridine by the reported procedures, respectively.

1,1'-Dibromo-3,3',6,6'-tetra-tert-butyl-9,9'-bicarbazole (3)



To a solution of 1-bromo-3,6-di-*tert*-butylcarbazole **2** (5.00 g, 14.0 mmol) in acetone (130 mL) was added KMnO₄ (5.50 g, 34.9 mmol) at room temperature. The reaction mixture was warmed up to 60 °C with a reflux condenser. The reaction was stirred for 4 h at 60 °C, and cooled down to room temperature. After evaporation of acetone under reduced pressure, the reaction mixture was suspended in CHCl₃, filtered through a glass sintered funnel, and washed by CHCl₃. The filtrate was washed by saturated aqueous Na₂S₂O₃ solution (30 mL×2), brine

(30 mL×1), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by recrystallization from hexane to give **3** (3.74 g, 75% yield).

Mp: 239 °C (decomp.). IR (KBr): v 3053, 2958, 2867, 1742, 1605, 1555, 1486, 1460, 1445, 1388, 1361, 1293, 1259, 1224, 1194, 1106, 1087, 1050 cm⁻¹. ¹H NMR (CDCl₃): δ 8.11 (2H, d, *J* = 1.6 Hz), 8.10 (2H, d, *J* = 1.6 Hz), 7.54 (2H, d, *J* = 1.6 Hz), 7.34 (2H, dd, *J* = 8.8, 1.6Hz), 6.66 (2H, d, *J* = 8.8 Hz), 1.44 (18H, s), 1.41 (18H, s) ppm. ¹³C NMR (CDCl₃): δ 145.4, 144.6, 140.3, 135.7, 128.8, 125.1, 124.6, 120.6, 116.3, 115.8, 108.8, 102.6, 34.8, 32.0, 31.9 ppm. HRMS (*m*/*z*) for C₄₀H₄₆Br₂N₂ (M⁺): Calculated 712.2028, found 712.2035.

3,3',6,6'-Tetra-tert-butyl-1,1',9,9'-bicarbazole (BC) from 3



A solution of 2,2'-bipyridyl (329 mg, 2.11 mmol), 1,5-cyclooctadiene (257 μ L, 2.10 mmol), and bis(1,5-cyclooctadiene)nickel (0) (577 mg, 2.10 mmol) in degassed THF (15 mL) was heated under Ar atmosphere at 60 °C until the color became deep violet. Subsequently, a solution of **3** (1.00 g, 1.40 mmol) in degassed THF (10 mL) was added to the reaction mixture. The mixture was stirred at 45 °C for 6 h. The reaction mixture was cooled down to room temperature and THF was evaporated under reduced pressure. The residue was suspended in CH₂Cl₂, filtered through a silica pad, and washed by CH₂Cl₂. The filtrate was washed with brine, dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The crude product was purified by MPLC (EtOAc:hexane = 5:95) to give BC (532 mg, 69% yield) as a yellow solid. Recrystallization from hexane gave yellow needles.

Mp: 236 °C (decomp.). IR (KBr): v 2958, 2901, 2867, 1460, 1437, 1361, 1289, 1276, 1247, 1138 cm⁻¹. ¹H NMR (CD₂Cl₂ + NEt₃): δ 8.07 (2H, d, *J* = 1.6 Hz), 7.90 (2H, d, *J* = 8.8 Hz), 7.78 (2H, d, *J* = 1.2 Hz), 7.56 (2H, dd, *J* = 8.8, 1.6 Hz), 7.54 (2H, d, *J* = 1.2 Hz), 1.456 (18H, s), 1.450 (18H, s) ppm. ¹³C NMR (CD₂Cl₂ + NEt₃): δ 145.6, 142.8, 137.9, 136.2, 123.3, 121.8, 120.7, 118.4, 117.1, 116.0, 114.5, 110.9, 34.9, 34.6, 31.7, 31.6 ppm. HRMS (*m/z*) for C₄₀H₄₆N₂ (M⁺): Calculated 554.3661, found 554.3664.

3,3',6,6'-Tetra-tert-butyl-1,1'-bicarbazole (4) from 2



A solution of 2,2'-bipyridyl (131 mg, 0.839 mmol) and 1,5-cyclooctadiene (100 μ L, 0.815 mmol), and bis(1,5-cyclooctadiene)nickel (0) (231 mg, 0.840mmol) in degassed THF (2 mL) was heated under Ar atmosphere at 60 °C until the color became deep violet. Subsequently, a solution of **2** (100 mg, 0.279 mmol) in degassed THF (2 mL) was added to the reaction mixture. The mixture was stirred at 80 °C for 6 h. The reaction mixture was cooled down to room temperature and THF was evaporated under reduced pressure. The residue was suspended in CH₂Cl₂, filtered through a silica pad, and washed by CH₂Cl₂. The filtrate was washed with brine, dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The crude product was purified by PTLC (EtOAc:hexane = 10:90) to give **4** (68 mg, 87% yield) as a colorless solid.

Mp: 212 °C. IR (KBr): v 3414, 2954, 2901, 2867, 1756, 1627, 1574, 1490, 1468, 1392, 1357, 1293, 1263, 1198, 1141, 1099 cm⁻¹. ¹H NMR (CDCl₃): δ 8.17 (2H, d, *J* = 2.0 Hz), 8.14 (2H, d, *J* = 1.2 Hz), 7.79 (2H, s), 7.64 (2H, d, *J* = 2.0 Hz), 7.45 (2H, dd, *J* = 8.8, 2.0 Hz), 7.24 (2H, d, *J* = 8.8 Hz), 1.52 (18H, s), 1.46 (18H, s) ppm. ¹³C NMR (CDCl₃): δ 143.2, 142.7, 138.1, 136.0, 128.8, 124.5, 123.9, 123.6, 121.5, 116.5, 115.9, 110.4, 35.0, 34.8, 32.3, 32.2 ppm. HRMS (*m*/*z*) for C₄₀H₄₈N₂(M⁺): Calculated 556.3817, found 556.3820.

3,3',6,6'-Tetra-tert-butyl-1,1'-bicarbazole (4) from 1

To a solution of **1** (1.00 g, 3.58 mmol) in CH_2Cl_2 (100 mL) was added dropwise a solution of FeCl₃ (1.16 g, 7.16 mmol) in CH_2Cl_2 (50 mL) at room temperature. After stirring for 15 min, the reaction was quenched by addition of MeOH (20 mL). The reaction mixture was added to water (100 mL) and extracted with CH_2Cl_2 (50 mL×3). The organic layer was washed by aqueous Na₂HCO₃ solution (30 mL×1), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by MPLC (EtOAc:hexane = 12:88) to give **4** (408 mg, 41% yield) as a colorless solid.

3,3',6,6'-Tetra-tert-butyl-1,1',9,9'-bicarbazole (BC) from 4

A solution of **4** (50.0 mg, 0.0898 mmol) in pyridine (5 mL) was warmed up to 70 °C. A solution of Bu_4NMnO_4 (64.9 mg, 0.179 mmol) in pyridine (5 mL) was added dropwise to the reaction mixture slowly at 70 °C. The reaction mixture was stirred at 70 °C for 24 h. The reaction mixture was cooled down to room temperature and pyridine was evaporated under reduced pressure. EtOAc (20 mL) and water (30 mL) were added the residue, and the slurry was stirred at room temperature for 30 min. The precipitated brown solid was filtered out by glass-sintered funnel and washed by EtOAc. The filtrate was washed by water (10 mL×2) and brine (10 mL×1), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by PTLC (EtOAc:hexane = 2:98) to give BC (32 mg, 65% yield) as a yellow solid.

4-Bromo-2,7-di-tert-butyl-9,10-dihydro -9,9-dimethylacridine (6)



To a solution of 2,7-di-*tert*-butyl-9,10-dihydro-9,9-dimethylacridine **5** (1.31 g, 4.06 mmol) in CHCl₃ (50 mL) was added *N*-bromosuccinimide (745 mg, 4.18 mmol) at 60 °C. The reaction was stirred for 1 h at 60 °C, and quenched by addition of saturated aqueous Na₂S₂O₃ solution. The mixture was cooled down to room temperature, and extracted with CH₂Cl₂ (30 mL×3). The organic layer was washed with water (30 mL×1), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by MPLC (CH₂Cl₂:hexane = 10:90 to 12:88) to give amorphous solid (1.15 g). This amorphous solid was again purified by GPC to give **6** (922 mg, 57% yield) as white solid.

Mp: 95-98 °C (crystal from hexane). IR (ATR): v 3416, 2960, 2925, 2899, 2863, 1608, 1571, 1499, 1461, 1407, 1382, 1361, 1319, 1265, 1204, 1152, 1131, 1094, 937, 924, 891, 870, 858, 813, 747, 736, 641 cm⁻¹. ¹H NMR (CDCl₃ + NEt₃): δ 7.38 (1H, d, *J* = 2.1 Hz), 7.34 (2H, s), 7.15 (1H, dd, *J* = 8.2, 2.2 Hz), 6.74 (1H, d, *J* = 8.6 Hz), 6.65 (1H, s), 1.58 (6H, s), 1.32 (9H, s), 1.30 (9H, s) ppm. ¹³CNMR (CDCl₃ + NEt₃): δ 143.72, 143.68, 135.6, 133.9, 130.4, 128.3, 126.7, 123.7, 121.9, 121.5, 113.6, 108.2, 37.2, 34.35, 34.31, 31.5, 3 1.4, 30.5 ppm. HRMS (*m/z*) for C₂₃H₃₀⁷⁹BrN (M⁺): Calculated 399.1562, found 399.1562.

2,2',7,7'-Tetra-*tert*-butyl-9,9',10,10'-tetrahydro-9,9,9',9'-tetramethyl-4,4'-biacridine (7)



To a mixture of 2,2'- bipyridyl (1.08 g, 6.90 mmol), 1,5-cyclooctadiene (0.85 mL, 6.9 mmol), and bis(1,5-cyclooctadiene)nickel (0) (1.90 g, 6.90 mmol) in degassed tetrahydrofuran (30 mL)(deep violet color) was added a solution of **6** (922 mg, 2.30 mmol) in degassed tetrahydrofuran (30 mL), and the mixture was stirred at 80 °C for 6 h. The reaction mixture was cooled down to room temperature and tetrahydrofuran was evaporated under reduced pressure. The residue was suspended in CH_2Cl_2 , filtered through a silica gel pad, and washed by CH_2Cl_2 . The filtrate was evaporated under reduced pressure. The residue due reduced pressure. The crude product was recrystallized from CH_2Cl_2/CH_3OH to give **7** (698 mg, 95% yield) as a white solid.

Mp: 209-211 °C (crystal from CH₂Cl₂/CH₃OH). IR (ATR): v 3411, 2953, 2903, 2864, 1742, 1613, 1597, 1504, 1481, 1461, 1410, 1390, 1385, 1360, 1310, 1297, 1272, 1235, 1201, 1151, 1129, 1090, 1047, 881, 849, 822, 761, 749, 687, 669, 644 cm⁻¹. ¹H NMR (CDCl₃ + NEt₃): δ 7.49 (2H, d, *J* = 2.1 Hz), 7.40 (2H, d, *J* = 2.1 Hz), 7.13 (2H, d, *J* = 2.1 Hz), 7.01 (2H, dd, *J* = 8.2, 2.1 Hz), 6.39 (2H, d, *J* = 8.2 Hz), 6.14 (2H, s), 1.68 (6H, s), 1.66 (6H, s), 1.35 (18H, s), 1.30 (18H, s) ppm. ¹³C NMR (CDCl₃ + NEt₃): δ 143.1, 142.9, 136.5, 134.6, 129.5, 128.4, 125.5, 123.4, 121.6, 121.5, 113.4, 37.1, 34.4, 34.3, 31.7, 31.6, 29.9, 29.8 ppm. HRMS (*m/z*) for C₄₀H₆₀N₂ (M⁺): Calculated 640.4756, found 640.4747.

2,2',7,7'-Tetra-tert-butyl-9,9',10,10'-tetrahydro-9,9,9',9'-tetramethyl-4,4',10,10'-biacridine (TBA)



To a solution of 7 (698 mg, 1.09 mmol) in pyridine (30 mL) was added Bu_4NMnO_4 (987 mg, 2.73 mmol) at ambient temperature, and the reaction mixture was stirred at that temperature for 12 h. The reaction was quenched by addition of saturated aqueous $Na_2S_2O_3$ solution. The precipitated brown solid was filtered out by Celite pad and washed with CH_2Cl_2 . The filtrate was extracted with CH_2Cl_2 (30 mL×3). The organic layer was washed with water (30 mL×1), dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue dissolved in toluene was filtered through a silica gel pad and washed by toluene:hexane = 10:90. The filtrate was evaporated under reduced pressure, and recrystallized from CH_2Cl_2/CH_3OH to give TBA (598 mg, 86% yield) as a yellow solid.

Mp: 273-276 °C (crystal from CH₂Cl₂/CH₃OH)(decomp.). IR (ATR): v 2959, 2904, 2866, 1742, 1601, 1496, 1459, 1419, 1379, 1362, 1278, 1265, 1255, 1239, 1227, 1127, 1097, 1081, 927, 895, 882, 871, 863, 849, 835, 811, 766, 747, 703, 686, 669, 651, 593 cm⁻¹. ¹H NMR (CD₂Cl₂ + NEt₃): δ 7.51 (2H, d, *J* = 2.1 Hz), 7.49 (2H, d, *J* = 2.1 Hz), 7.32 (2H, d, *J* = 1.8 Hz), 7.09 (2H, dd, *J* = 8.6, 2.2 Hz), 6.91 (2H, d, *J* = 8.2 Hz), 1.97 (6H, s), 1.50 (6H, s), 1.37 (18H, s), 1.29 (18H, s) ppm. ¹³C NMR (CD₂Cl₂ + NEt₃): δ 145.7, 145.0, 141.0, 136.5, 132.2, 132.0, 123.4, 121.2, 120.7, 118.9, 116.3, 110.9, 37.6, 34.9, 34.7, 31.7, 31.6, 29.4, 24.3 ppm. HRMS (*m/z*) for C₄₆H₅₈N₂ (M⁺): Calculated 638.4600, found 638.4597

Quenching experiment of disproportionation of BC by hydrazine or NEt₃ (Scheme 4)

To a solution of BC (11.1 mg, 0.0200 mmol) in CH_2Cl_2 (20 mL) was added CF_3CO_2H (0.031 mL, 0.40 mmol) at room temperature. The solution was stirred for 1 h until BC⁺⁺CF₃CO₂⁻ and BCH₃⁺ CF₃CO₂⁻ were quantitatively

generated. The solution was quenched by addition of hydrazine monohydrate (0.097 mL, 2.00 mmol, 10000 mol%) at 30 °C. After stirring or 1 h at 30 °C, the mixture was cooled down to room temperature and the solvent was evaporated. The residue was diluted by CH_2Cl_2 , washed by water, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by MPLC (EtOAc:hexane = 3:97) to give BC (7.5 mg, 68% yield) and BCH₂ (3.5 mg, 31% yield). It was also confirmed by UV-Vis measurements that only BC in CH_2Cl_2 was not reduced to BCH₂ by hydrazine. In the similar manner, the disproportionation mixture was quenched by NEt₃ (0.11 mL, 0.80 mmol, 4000 mol%) to afford BC (8.0 mg, 72% yield), BCH₂ (2.0 mg, 18% yield), and **8** (trace, 3% yield by NMR)

8: IR (ATR): v 2952, 2922, 2853, 2360, 1602, 1488, 1462, 1442, 1381, 1361, 1291, 1269, 1244, 1224, 1200, 1138, 1042, 869, 835, 808, 759, 662, 620 cm⁻¹. ¹H NMR (CD₂Cl₂): δ 8.03 (2H, d, *J* = 2.0 Hz), 7.80 (2H, d, *J* = 1.2 Hz), 7.59 (2H, d, *J* = 1.6 Hz), 7.53 (2H, s), 7.49 (2H, d, *J* = 1.6 Hz), 7.41 (2H, d, *J* = 2.0 Hz), 7.35 (2H, dd, *J* = 8.8, 2.0 Hz), 7.19 (2H, d, *J* = 8.8 Hz), 7.08 (2H, dd, *J* = 5.6, 2.0 Hz), 6.20 (2H, dd, *J* = 8.8, 1.6 Hz), 6.16 (2H, d, *J* = 8.4 Hz), 1.46 (18H, s), 1.39 (18H, s), 0.90 (18H, s), 0.84 (18H, s) ppm. ¹³C NMR (CD₂Cl₂): δ 143.2, 142.7, 141.4, 140.2, 137.9, 137.8, 137.1, 134.5, 126.9, 123.4, 123.3, 123.2, 123.1, 121.9, 121.8, 120.8, 120.0, 119.9, 116.7, 116.4, 115.7, 115.4, 109.7, 107.4, 34.7, 34.5, 34.0, 33.9, 31.8, 31.4, 31.3 ppm. LRMS (MALDI-TOF)(*m*/*z*) for C₈₀H₉₄N₄(M⁺): Calculated 1110.75, found 1110.26.

Quenching experiment of disproportionation of TBA by hydrazine (Scheme 5)

To a solution of TBA (51.0 mg, 0.0798 mmol) in CH₂Cl₂ (30 mL) was added CF₃CO₂H (0.12 mL, 1.6 mmol, 2000 mol%) at ambient temperature. The solution was stirred for 30 min until TBA⁺⁺TFA⁻ and TBH₄²⁺2TFA⁻ were quantitatively generated. The mixture was warmed up to 30 °C and quenched by addition of hydrazine monohydrate (0.38 mL, 7.8 mmol, 10000 mol%). After stirring for 2 h at that temperature, the mixture was cooled down to room temperature, dried over Na₂SO₄, filtered, washed by ethyl acetate, and concentrated under reduced pressure. In the crude ¹H-NMR spectrum (CD₂Cl₂+NEt₃), the ratio of TBA and TBAH₂ was 2:1. The residue was purified by silica gel column chromatography (toluene:hexane=5:95 to 33:67) to give TBA (33.1 mg, 65% yield) and TBAH₂ (16.4 mg, 32% yield). It was also confirmed by UV-Vis measurements that only TBA in CH₂Cl₂ under neutral condition without CF₃CO₂H was not reduced to TBAH₂ by hydrazine.

3. ¹H and ¹³C NMR Spectra

¹H NMR of 3







¹H NMR of BC in freshly distilled CD₂Cl₂



 1H NMR of BC with 200 mol% NEt3 in CD_2Cl_2



 1H NMR of BC with 200 mol% CF_3CO_2H in CD_2Cl_2



¹³C NMR of BC with NEt₃ in CD₂Cl₂









¹H NMR of 6





¹H NMR of 7





¹H NMR of TBA in freshly distilled CD₂Cl₂



 1H NMR of TBA with 1000 mol% NEt_3 in CD_2Cl_2





 1H NMR of TBA with 1000 mol% NEt3 + 3000 mol% CF3CO2H in CD2Cl2

 1H NMR of TBA with 1000 mol% NEt_3 + 3000 mol% CF_3CO_2H +4000 mol% NEt_3 in CD_2Cl_2



 $^{13}\mathrm{C}$ NMR of TBA with NEt_3 in $\mathrm{CD}_2\mathrm{Cl}_2$



¹H NMR of 8





4. Solid State NMR Analysis

In order to confirm the state of solid BC, the solid state NMR spectra of ground crystals of BC were measured. The solid state NMR experiments were carried out using a Bruker Avance 600 spectrometer (proton resonance frequency of 600 MHz) equipped with a 2.5 mm O.D. ¹H-¹³C-¹⁵N triple resonance MAS probe. Temperature was controlled to 293 K using VT controller. MAS frequency was controlled to either 20 or 10 kHz. Typical ¹H, ¹³C and ¹⁵N pulses were 100, 88 and 66 kHz, respectively. ¹H heteronucleardipolar decoupling and FSLG homonuclear dipolar decoupling were carried out at rf fields of 100 kHz. ¹H heteronulcear dipolar decouplings were achieved by TPPM³ and SPINAL64⁴ under 20 and 10 kHz spinning speed, respectively. Repetition time was 2 s. ¹H and ¹³C peaks were assigned from the contact time variation of LGCPMAS^{5,6}, ¹H-¹³C dipolar dephased¹³C-CPMAS spectra⁷, ¹H-¹³C FSLG-HETCOR⁸ and ¹H-¹³C MELODI-HETCOR⁹ spectra. ¹H-¹³C HETCOR spectra were recorded with a total 128 t₁ increments with 1000 scans each. Quadrature detection in F1 was achieved using States method. ¹H isotropic chemical shifts under FSLG were corrected by experimentally obtained scaling factorsof reference sample at same condition. Data processing was performed using Bruker TOPSPIN2.1, and TAKE NMR1.42¹⁰. Spectral analyses were performed using SPARKY3.114¹¹. The summary of ¹H- and ¹³C-isotropic chemical shifts and the spectra are shown in Table S1, Fig. S1-S4.



	Isotropic Chemical shifts (ppm) (tentative)			Isotropic Chemical shifts (ppm) (tentative)	
Sites	¹³ C	$^{1}\mathrm{H}$	Sites	¹³ C	$^{1}\mathrm{H}$
1a, 1a'	137.74	-	6,6'	141.39	-
	137.19	-		140.40	-
1,1'	120.92	-	7,7'	118.10	6.05
2,2'	115.17	6.99		116.40	6.24
	113.29	6.84	8,8'	111.60	6.73
3,3'	144.67	-		109.90	6.82
4,4'	115.17	6.99	8a,8a'	135.51	-
	113.29	6.84	10,10'	35.68	-
4a,4a'	120.92	-	11,11'	32.89	1.66
	119.65	-		31.84	0.35
5,5'	122.92	6.58	12,12'	34.02	-
	120.88	6.71	13,13	32.89	1.66
5a,5a'	120.92	_		31.84	0.35
	119.65	-			

Table S1.

5. X-ray Crystallographic Analysis

The single crystal of BC was obtained by the slow vaporization from the hexane solution. The single crystal of 8 was obtained by the slow evaporation from the CHCl₃/hexane solution. The analyses were performed on a Rigaku VariMax RAPID system (Mo-K α , $\lambda = 0.71073$ Å, T = 123 K, 2θ max = 55.0°). The single crystal of TBA was obtained from CH₂Cl₂/C₂H₅OH. The analysis was performed on a Rigaku Saturn CCD system (Mo-K α , $\lambda = 0.71069$ Å, T = 123 K, 2θ max = 55.0°). The structures were solved by direct method (SIR-2004 or -2008) and refined using SHELXL-97 or -2013. For the analysis on 8, contributions from disordered solvent molecules were removed by the SQUEEZE program (PLATON). The single crystal of BC⁺¹₅·IC₆H₅ was obtained as follows; To the solution of BC (2.5 mg, 3.9 µmol) in iodobenzene (1.0 ml) in a thin glass pipet tube was added MeOH (0.5 ml) and I₂ (10 mg, 39 µmol) in MeOH (0.5 ml) successively and the solution was kept in freezer. The analysis was performed on a Bruker APEX-II CCD (Mo-K α , $\lambda = 0.71073$ Å, T = 100 K, 2θ max = 48.2°). The structure was solved by direct method (SHELXS-97) and refined using SHELXL-97. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-1025063 (BC), CCDC-1038914 (BC*+I₅·IC₆H₅), CCDC-1049677 (8), and CCDC-1040722 (TBA). Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data of BC: $C_{40}H_{46}N_2$, yellow, $0.5 \times 0.2 \times 0.02 \text{ mm}^3$, monoclinic, space group $P2_1/c$ (No. 14), a = 10.7010(2), b = 27.6694(5), c = 11.1215(3) Å, $\alpha = 90^\circ$, $\beta = 98.764(1)^\circ$, $\gamma = 90^\circ$, V = 3254.52(12) Å³, $\rho_{calcd} = 1.132 \text{ g/cm}^3$, Z = 4, 5933 reflections measured, $R_1 = 0.0413 [I > 2\sigma(I)]$, and $wR_2 = 0.1137$ (all data), GOF=1.069. Crystal data of BC⁺⁺15⁻⁻1C₆H₅: $C_{46}H_{51}I_6N_2$, dark red, $0.3 \times 0.15 \times 0.01 \text{ mm}^3$, monoclinic, space group $P2_1/c$ (No. 14), a = 15.047(3), b = 24.399(5), c = 13.754(3) Å, $\alpha = 90^\circ$, $\beta = 108.90(3)^\circ$, $\gamma = 90^\circ$, V = 4777.4(17) Å³, $\rho_{calcd} = 1.937 \text{ g/cm}^3$, Z = 4, 8306 reflections measured, $R_1 = 0.0350 [I > 2\sigma(I)]$, and $wR_2 = 0.0824$ (all data), GOF=1.029. Crystal data of **8**: $C_{80}H_{94}N_4$, orange-brown, $0.50 \times 0.14 \times 0.07 \text{ mm}^3$, monoclinic, space group C2/c (No. 15), a = 30.6695(11), b = 12.1512(5), c = 23.0584(9) Å, $\alpha = 90^\circ$, $\beta = 119.5715(9)^\circ$, $\gamma = 90^\circ$, V = 7473.9(5) Å³, $\rho_{calcd} = 0.988 \text{ g/cm}^3$, Z = 4, 7079 reflections measured, $R_1 = 0.0756 [I > 2\sigma(I)]$, and $wR_2 = 0.2301$ (all data), GOF=1.425. Crystal data of TBA: $C_{46}H_{58}N_2$, yellow, $0.20 \times 0.10 \times 0.02 \text{ mm}^3$, monoclinic, space group $P2_1/c$ (No. 14), a = 13.312(3), b = 18.814(4), c = 15.401(4) Å, $\alpha = 90^\circ$, $\beta = 97.762(5)^\circ$, $\gamma = 90^\circ$, V = 3821.8(1) Å³, $\rho_{calcd} = 1.11 \text{ g/cm}^3$, Z = 4, 8664 reflections measured, $R_1 = 0.0893 [I > 2\sigma(I)]$, and $wR_2 = 0.2496$ (all data), GOF=1.061.

6. ESR Spectral Measurements

Temperature dependent measurements (Fig. 8a, S6b, c)

A sample solution of BC, TBA, or 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine (TEMPOL)(1.00 mM) in in a ESR tube was degassed by the freeze-pump-thaw cycles three times, and the ESR tube was sealed. ESR spectrum at different temperature was recorded in a same setting of parameters. The *IT* values (*I*=double integral of ESR signal, *T*=temperature) of BC and TBA were plotted versus temperature. They were slightly decreased by increasing the temperature (Fig. 8a, S6b). To confirm that this slight decrease comes from the machinery error, the temperature dependence of *IT* value of ESR signal of TEMPOL (*S*=1/2) was measured, showing the similar decrease of *IT* values by increasing the temperature (Fig. S6c). Thus, we concluded that the *IT* values are constant and the spin state is doublet.

7. UV-Vis-NIR Spectral Experiments

UV-Vis-NIR measurements were conducted with 1.0 cm quartz cell at 20 °C under air, unless otherwise noted. **7.1. UV-Vis-NIR spectral experiment to show the reaction of BC and acid under equilibrium (Fig. S7a)** UV-Vis-NIR spectrum of BC (1.00 mM) with 2000 mol% CF_3CO_2H in CH_2Cl_2 with 1 mm cell was measured (Fig. S7a, orange). The solvent and excess CF_3CO_2H of the solution was evaporated in vacuo. The residue was dissolved in CH_2Cl_2 (1.00 mM) and the spectrum was measured again after 5 h. The comparison of these two spectra indicated the shift of equilibrium reaction under acidic condition depending on the amount of acid.

7.2. UV-Vis-NIR spectra of BC⁺⁺ and TBA⁺⁺ by electrochemical oxidation of BC and TBA (Fig. 9a, 16h)

UV-Vis-NIR spectral measurements under the electrochemical oxidation of BC or TBA were carried out on a solution of BC or TBA (1.00 mM) in 1,2-dichloroethane containing 0.1 M Bu₄NClO₄ using a BAS 1 mm spectroelectrochemical quartz cell equipped with a Pt mesh working electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode (Fc/Fc⁺E_{1/2} = 0.25 V). In each measurement, the indicated voltage in Fig. 9a and 16h was applied for 120 s, and the spectral measurement started at 90 s after application of voltage. The indicated voltages in Fig. 7a are given in vs. Ag/AgCl.

7.3. UV-Vis-NIR spectra of BC⁺⁺ and TBA⁺⁺by chemical oxidation

7.3.1. UV-Vis-NIR spectra of BC⁺⁺ by chemical oxidation of BC with NOPF₆ (Fig. 9b)

To a solution of BC (4.00 mM) in CH₂Cl₂ (1 mL) in a glove box under N₂ atmosphere was added 50, 100, 150, 200, 250, 300, 400, 500, 1000, or 2000 mol% of NOPF₆ using the 300 mM solution in acetonitrile at ambient temperature, respectively. The solution was diluted by CH₂Cl₂ to 0.05 mM based on added BC and left over for 1 day at ambient temperature under N₂ atmosphere in a glove box before the spectral measurement. The sample solution was transferred into a 1 cm quartz cell in a grove box and the measurement was conducted under N₂ atmosphere. The absorption intensity at 635 nm associated with BC⁺⁺ was 0.76 with 150 to 300 mol% NOPF₆

and was decreased according to the increase of oxidant more than 300 mol%. This result indicated that BC^{*+} was quantitatively generated with 150~300 mol% NOPF₆ and BC^{*+} was further oxidized to BC²⁺ with more than 300 mol% NOPF₆. The spectrum with 150 mol% NOPF₆ is shown in Fig. 9b. The molar absorption coefficient $\varepsilon_{635}=1.5\times10^4$ L mol⁻¹ cm⁻¹ of BC^{*+} at 635 nm was obtained from the spectrum with 150 mol% NOPF₆. The value was used for the kinetic experiments.

7.3.2. UV-Vis-NIR spectra of BC⁺⁺ by chemical oxidation of BC with I₂ (Fig. S7a)

To a solution of BC (4.00 mM) in dichloroethane (2 mL) was added 100, 200, 500, 1000, 2000, 3000 mol% of a I_2 solution (20 mM) in dichloroethane at ambient temperature, respectively. The solution was diluted by dichloroethane to 0.100 mM based on added BC and left over for 1 day under dark at ambient temperature before the spectral measurement. The absorption associated with BC⁺⁺ was increased according to the increase of oxidant up to 3000 mol% I_2 . The spectrum with 3000 mol% I_2 are shown in Fig. S7a.

7.3.3. UV-Vis-NIR spectra of TBA⁺⁺ by chemical oxidation of TBA with I₂ or DDQ (Fig. 16i)

To a solution of TBA (1.00 mM) in 1,2-dichloroethane (0.30 mL) was added 100, 200, 500, 1000, or 2000 mol% of a I₂ or DDQ solution (30 mM) in 1,2-dichloroethane at ambient temperature, respectively. The solution was diluted by 1,2-dichloroethane to be 3.0 mL with 0.100 mM based on added TBA and left over for 1 day at ambient temperature before the spectral measurement. The absorption associated with TBA^{*+} was increased according to the increase of oxidant and saturated at 1000 mol% I₂ or 500 mol% DDQ. The absorption of TBA⁺⁺ with 1000 mol% I₂ or 500 mol% DDQ was coincident with that with 2000 mol% I₂ or 1000 and 2000 mol% DDQ. The absorption associated with TBA^{*+} was not admitted in the spectra with both oxidants. These results demonstrate that TBA^{*+} was quantitatively generated with 1000 mol% I₂ or 500 mol% DDQ, and TBA^{*+} was not further oxidized to TBA²⁺ with more amount of these oxidants. The absorptance at 821 nm with 1000 mol% I₂ or 500 mol% DDQ do not have the absorption at 821 nm. The value was used for the determination of the yield of TBA^{*+} generated under acidification of TBA. The spectra with 1000 mol% I₂ and 500 mol% DDQ are shown in Fig. 16i.

7.3.4. UV-Vis-NIR spectra of TBA⁺⁺ by chemical oxidation of TBA with NOPF₆ (Fig. 16i)

To a solution of TBA (1.00 mM) in CH_2Cl_2 (0.30 mL) under N_2 atmosphere in a glove box was added 100, 200, 500, 1000, or 2000 mol% of NOPF₆ using the 300 mM solution in acetonitrile at ambient temperature, respectively. The solution was diluted by CH_2Cl_2 to be 3.0 mL with 0.100 mM based on added TBA and left over for 1 day at ambient temperature under N_2 atmosphere in a glove box before the spectral measurement. The sample solution was transferred into a 1 cm quartz cell in a grove box and the measurement was conducted under

N₂ atmosphere. The absorption intensity at 824 nm associated with TBA^{*+} was 0.79 with 100 mol% NOPF₆ and was decreased according to the increase of oxidant more than 200 mol%. The absorption associated with TBA²⁺ was clearly admitted with 2000 mol% NOPF₆. This result indicated that TBA^{*+} was quantitatively generated with 100~200 mol% NOPF₆ and TBA⁺⁺ was further oxidized to TBA²⁺ with more than 200 mol% NOPF₆. The spectrum with 100 mol% NOPF₆ is shown in Fig. 16i. The molar absorption coefficient ε_{822} =7.9×10³ L mol⁻¹ cm⁻¹ of TBA⁺⁺ at 822 nm was obtained from the spectrum with 100 mol% NOPF₆. The value was used for the kinetic experiments.

7.4. Determination of the composition ratio of BC or TBA and CF₃CO₂H by Job's continuous variation plot

7.4.1. Determination of the ratio of BC and CF₃CO₂H by Job's continuous variation plot (Fig. 13)

The solutions of the mixture of BC and CF_3CO_2H were prepared in the ratio of 1:0, 4:1, 2:1, 3:2, 1:1, 2:3, 1:2, 1:4, 0:1 in CH_2Cl_2 with the constant concentration of BC+ $CF_3CO_2H = 2.00$ mM. After storing at room temperature under dark for 10 days to reach the equilibrium, the UV-Vis-NIR spectra were measured with 1 mm cell. The absorbance at 635 nm of BC⁺⁺was used for the continuous plot because BC and CF_3CO_2H do not have absorbance at 635 nm.

7.4.2. Determination of the ratio of TBA and CF₃CO₂H by Job's continuous variation plot (Fig. 17, S8h)

The solutions of TBA and CF₃CO₂H in the molar ratio of 1:0, 2:1, 1:1, 1:1.1, 1:1.2, 1:1.3, 3:4, 1:1.4, 1:1.5, 1:1.6, 1:1.7, 1:1.8, 1:1.9, 1:2, 1:3, 1:4, and 0:1 in CH₂Cl₂ were prepared by mixing TBA solution (4.00 mM) and CF₃CO₂H solution (4.00 mM) with the constant total concentration (TBA+CF₃CO₂H=4.00 mM). After storing at room temperature for 3 h to reach the equilibrium, the UV-Vis-NIR spectra were measured with a 1 mm quartz cell. The absorbance at 824 nm associated with TBA⁺⁺ was used for the continuous plot, because TBA and CF₃CO₂H do not have the absorbance at 824 nm. Selected spectra are shown in Fig. 17 for clarity.

7.4.3. UV-Vis-NIR spectrum of TBA with CF₃CO₂H under N₂ atmosphere. (Fig. S8a)

 CH_2Cl_2 with CaH_2 was degassed by the freeze-pump-thaw cycles three times and distilled by the valve-to-valve method. NEt₃ and CF_3CO_2H were degassed by the freeze-pump-thaw cycles three times. Preparation of a solution of TBA (0.100 mM) in CH_2Cl_2 with 2000 mol% of CF_3CO_2H was performed in a grove box with 2-5 ppm O_2 level during experiment. The sample solution was transferred into a 1 cm quartz cell in a grove box and the measurement was conducted under N_2 atmosphere.

7.4.4. UV-Vis-NIR spectral study on the reversibility of the reaction of TBA by acid/base treatment (Fig. 18a, Table S2)

Sample solution of TBA (0.100 mM, CH_2Cl_2 , 3.0 mL) was transferred into a 1 cm quartz cell equipped with magnetic stirrer bar and the spectrum under neutral condition was measured. CF_3CO_2H (0.5 µL, 6 µmol, 2000 mol%) was then added to the neutral TBA solution at ambient temperature. After stirring for 30 min at that temperature, the spectrum under acidic condition was measured to confirm the conversion. Then, the acidic solution was neutralized by addition of NEt₃ (1.3 µL, 9 µmol, 3000 mol%) at ambient temperature, and the spectrum was measured after 10 min. Same experiments were conducted 5 times. The recovery yield of TBA was calculated from the absorption intensities at 412 nm (Table S2), and the average was determined to be 98.6% yield with the five experiments.

	Absorption at 412 nm in neutral condition	Absorption at 412 nm after neutralization	Recovery yield (%)
Run 1	0.394	0.394	100
Run 2	0.387	0.382	98.7
Run 3	0.384	0.375	97.7
Run 4	0.388	0.381	98.2
Run 5	0.390	0.384	98.5

Table S2. Recovery yield of TBA by acidification/neutralization.

7.4.5. UV-Vis-NIR spectral study on the reversibility of the reaction of TBA by repeating the addition of acid/base treatment (Fig. 18b, c, d)

Sample solution of TBA (0.100 mM, CH_2Cl_2 , 3.0 mL) with 1000 mol% NEt₃ was transferred into a 1 cm quartz cell equipped with magnetic stirrer bar and the spectrum was measured. In each cycle, the spectra were measured at 10-60 min after addition of CF_3CO_2H or NEt₃ at ambient temperature, respectively. The added amounts of CF_3CO_2H and NEt₃ in each cycle are shown as follows;

1st cycle: CF₃CO₂H (0.7 μL, 9 μmol, 3000 mol%), NEt₃ (1.7 μL, 12 μmol, 4000 mol%)

2nd cycle: CF₃CO₂H (1.6 µL, 21 µmol, 7000 mol%), NEt₃ (3.0 µL, 21 µmol, 7000 mol%),

3rd cycle: CF₃CO₂H (2.8 µL, 36 µmol, 12000 mol%), NEt₃ (5.1 µL, 36 µmol, 12000 mol%),

4th cycle: CF₃CO₂H (5.6 µL, 72 µmol, 24000 mol%), NEt₃ (10.2 µL, 72 µmol, 24000 mol%),

5th cycle: CF₃CO₂H (11.2 µL, 144 µmol, 48000 mol%), NEt₃ (30.6 µL, 216 µmol, 72000 mol%)

The spectra were shown in Fig. 18b and the absorbance at 412 and 822 nm were plotted in Fig. 18c, d.

8. Fluorescence Spectral Experiments

8.1. Determination of quantum yield of BC

Quantum yield of the solution of BC (4.50×10⁻⁵ M) in CH₂Cl₂ was determined to be 0.6875 by the absolute

method using a JASCO FP6500 spectrometer equipped with integrating sphere JASCO ILF-533 using 1 mm cell. For reference, quantum yield of quinine sulfate $(5.00 \times 10^{-3} \text{ M})$ in 1 M aq. H₂SO₄ was determined by the same method to be 0.5644, which was comparable to the reported value 0.546.¹²

8.2. Determination of quantum yield of TBA

The quantum yield of TBA was determined by the compared method [equation (1)]¹³.

$$\boldsymbol{\Phi}_{unk} = (A_{std}/A_{unk}) \times (F_{unk}/F_{std}) \times (I_{std}/I_{unk}) \times (n_{unk}^2/n_{std}^2) \times \boldsymbol{\Phi}_{std}$$
(1)

where Φ , A, F, I, and n are the quantum yield, the absorption at the selected excitation wavelength, the integrated fluorescence signal in the emission region, the relative intensity of the exciting light, and the refractive index of solvent, respectively. Subscripts unk and std stand for unknown and standard sample, respectively. In this measurement, the fluorescence spectra of both unknown and standard samples were measured in benzene with the same excitation wavelength 366 nm. In this condition, the equation (1) is simplified to be equation (2).

$$\boldsymbol{\Phi}_{unk} = (A_{std}/A_{unk}) \times (F_{unk}/F_{std}) \times \boldsymbol{\Phi}_{std}$$
⁽²⁾

9,10-Diphenylanthracene (DPA)($\Phi = 0.72$, $\lambda_{ex} = 366$ nm, benzene, 25 °C, under air)¹⁴ was used as standard. Prior to use, DPA was recrystallized twice from CH₂Cl₂/ethanol. The absorption spectra of the sample solutions of TBA (0.100 mM) and DPA (0.100 mM) in benzene were measured under air with 1 cm quartz cell at 20 °C, giving the absorptions $A_{TBA} = 0.12$ and $A_{DPA} = 0.60$ at 366 nm, respectively (Table S3). For the fluorescence spectral measurements, these solutions were diluted by 1% to be 1.00 μ M solutions in order to prevent reabsorption of fluorescence. The fluorescence spectra were measured under air with 1 cm quartz cell at 20 °C, giving $F_{TBA} = 8.2 \times 10$ and $F_{DPA} = 1.7 \times 10^3$, respectively (Table S3). From these values and equation (2), the quantum yield of TBA is determined to be 17% yield.

A_{TBA}	0.12 (366 nm, 0.100 mM, 1 cm quartz cell, 20 °C, under air)
$A_{\rm DPA}$	0.60 (366 nm, 0.100 mM, 1 cm quartz cell, 20 °C, under air)
F_{TBA}	8.2×10 (λ_{ex} =366 nm, 1.00 μ M, 1 cm quartz cell, 20 °C, under air)
$F_{\rm DPA}$	1.7×10^3 (λ_{ex} =366 nm, 1.00 μ M, 1 cm quartz cell, 20 °C, under air)

Table S3. Experimental parameters for determination of the quantum yield of TBA.

9. Kinetic Experiments

9.1. Determination of the reaction orders of the disproportionation reactions of BC and TBA by the initial rate method

The reaction orders of SM (BC or TBA) and CF_3CO_2H were determined by the initial rate method using the equations (1) and (2), where v_0 , k, $[SM]_0$, n, $[TFA]_0$, and m are the initial rate of reaction, the rate constant, the initial concentration of SM, the reaction order of SM, the initial concentration of CF_3CO_2H , and the reaction

order of CF₃CO₂H, respectively.

$$v_0 = k[SM]_0^{\ n}[TFA]_0^{\ m}$$
(1)

It gives equation (2) to take the log of both sides of equation (1).

 $\ln v_0 = \ln k + n \times \ln[SM]_0 + m \times \ln[TFA]_0$ (2)

9.2. Determination of reaction orders of the disproportionation of BC

9.2.1. Reaction order in BC (Fig. 19a, b, S10a, b, Table 4)

Sample solution (2.00 mL) of CF₃CO₂H (5.00 mM) in CH₂Cl₂ or benzene in a 1 cm quartz cell was set up on a Peltier type constant-temperature unit (UNISOKU, CoolSpeK UV USP-203-B) at 20 °C under Ar atmosphere with magnetic stirring. BC (20.0 mM, 10.0, 20.0, or 30.0 μ L) in CH₂Cl₂ or benzene was injected by syringe under magnetic stirring and the absorption of BC⁺⁺ at 635 nm was monitored at 20 °C (Fig. 19a, S10a). Using the molar absorption coefficient $\varepsilon_{635} = 1.5 \times 10^4$ (CH₂Cl₂) or 1.4×10^4 (benzene) L mol⁻¹ cm⁻¹ of BC⁺⁺ and the absorption change (cm⁻¹s⁻¹) between 500~1500 s after well-mixing of the solution, the generation rate (mol L⁻¹ s⁻¹) of BC⁺⁺ at each concentration was determined (Table S4). In the condition using constant excess amount of CF₃CO₂H (5.00 mM), ln*k* + ln[TFA]₀ is regarded to be constant in the equation (2). Thus, the reaction order n of BC was determined from the slope of the plot of ln ν_0 against ln[BC]₀ to be 0.60 (CH₂Cl₂) or 0.55 (benzene)(Fig. 19b, S10b), which means 1/2 order in BC.

Table S4. Determination of reaction order in BC and the activation barrier energy ΔG^{\ddagger} of the disproportionation reaction of BC

$[BC]_0 (mM)$	$v_0 \times 10^{-9} \text{ (mol } \text{L}^{-1} \text{ s}^{-1} \text{)}$	$k \times 10^{-8}$	ΔG^{\ddagger} (kcal mol ⁻¹)	$v_0 \times 10^{-9} \pmod{L^{-1} s^{-1}}$
	in CH ₂ Cl ₂ ^{<i>a</i>}	in CH ₂ Cl ₂ ^b	(293 K) in CH ₂ Cl ₂	in benzene ^{<i>a</i>}
0.10	2.3	1.8	27.5	0.84
0.20	3.4	1.9	27.5	1.3
0.30	4.4	2.0	27.5	1.6

^a500~1500 s. ^b0~3500 s.

9.2.2. Reaction order in CF₃CO₂H (Fig. 19c, d, S10c, d, Table 5)

Sample solution (2.00 mL) of BC (5.00 mM) in CH₂Cl₂ or benzene in a 1 cm quartz cell was set up on a Peltier type constant-temperature unit (UNISOKU, CoolSpeK UV USP-203-B) at 20 °C under Ar atmosphere with magnetic stirring. CF₃CO₂H solution (20.0 mM, 10.0, 20.0, or 30.0 μ L) in CH₂Cl₂ or benzene was injected by syringe under magnetic stirring and the absorption of BC⁺⁺ at 635 nm was monitored at 20 °C (Fig. 19c, S10c). Using the molar absorption coefficient $\varepsilon_{635} = 1.5 \times 10^4$ (CH₂Cl₂) or 1.4×10^4 (benzene) L mol⁻¹ cm⁻¹ of BC⁺⁺ and the absorption change (cm⁻¹ s⁻¹) between 500~3500 s after well-mixing of the solution, the generation rate (mol L⁻¹ s⁻¹) of BC⁺⁺ at each concentration was determined (Table S5). In the condition using constant excess

amount of CF_3CO_2H (5.00 mM), $lnk + ln[BC]_0$ is regarded to be constant in the equation (2). Thus, the reaction order m of TFA was determined from the slope of the plot of lnv_0 against $ln[TFA]_0$ to be 0.44 (CH_2Cl_2) or 0.44 (benzene)(Fig. 19d, S10d), which means 1/2 order in TFA.

disproportionatio				
[TFA] ₀ (mM)	$v_0 \times 10^{-9} \text{ (mol } \text{L}^{-1} \text{ s}^{-1}\text{)}$	<i>k</i> ×10 ⁻⁹	ΔG^{\ddagger} (kcal mol ⁻¹)	$v_0 \times 10^{-10} \text{ (mol } \text{L}^{-1} \text{ s}^{-1}\text{)}$
	in CH ₂ Cl ₂ ^{<i>a</i>}	in CH ₂ Cl ₂ ^b	(293 K) in CH_2Cl_2	in benzene ^{<i>a</i>}
0.10	0.71	4.9	28.3	2.2
0.20	0.87	4.4	28.3	2.8
0.30	1.2	4.6	28.3	3.4

Table S5. Determination of reaction order in CF₃CO₂H and the activation barrier energy ΔG^{\ddagger} of the disproportionation reaction of BC

^a500~3500 s. ^b0~3500 s.

9.3. Determination of the kinetic constant and activation barrier energy of disproportionation of BC

From the experiments on determination of reaction order, the reaction rate equation is expressed to be equation (3), where v, x, k, [BC], [TFA], a, and b are the reaction rate of BC⁺⁺, the concentration of BC⁺⁺, the rate constant, the concentration of BC, the concentration of CF₃CO₂H, the initial concentration of BC, and the initial concentration of CF₃CO₂H, respectively.

$$v = dx/dt = k[BC]^{1/2}[TFA]^{1/2} = k[a-3/2x]^{1/2}[b-3/2x]^{1/2}$$
(3)

In the condition using excess amount of BC or CF₃CO₂H, a-3/2x or b-3/2x is regarded to be the initial concentrations *a* or *b*. Thus, the equation (3) becomes (4) or (5).

$$v = dx/dt = k[a]^{1/2}[b-3/2x]^{1/2}$$
(4)

$$v = dx/dt = k[a-3/2x]^{1/2}[b]^{1/2}$$
(5)

The definite integral of the equations give the equation (6) and (7).

$$-4/3(a-3/2x)^{1/2}b^{-1/2} = kt+C$$
(6)

$$-4/3a^{-1/2}(b-3/2x)^{1/2} = kt+C$$
(7)

By fitting the data of reactions between BC and CF₃CO₂H ($a = 0.10 \sim 0.30$ mM and b = 5.00 mM or a = 5.00 mM and $b = 0.10 \sim 0.30$ mM) in CH₂Cl₂ above to the equations (6) or (7), the rate constants *k* were obtained (Table S4, 5). With the rate constants *k* and Eyring equation $\Delta G^{\ddagger} = RT \times \ln(k_{\rm B}T/kh)$, ΔG^{\ddagger} (293 K) in CH₂Cl₂ was determined to be 28 kcal/mol in average (Table S4, 5).

9.4. Determination of reaction orders of the disproportionation of TBA

9.4.1. Reaction order in TBA (Fig. 20a, b, Table S6)

Sample solution (2.00 mL) of TBA in CH_2Cl_2 with the concentration 0.050, 0.060, 0.080, or 0.10 mM in a 1 cm quartz cell was set up on a Peltier type constant-temperature unit (UNISOKU, CoolSpeK UV USP-203-B)

precooled at -70 °C under Ar atmosphere, and cooled to -70 °C with magnetic stirring. CF₃CO₂H solution (400 mM, 10.0 μ L) in CH₂Cl₂ was injected by syringe under magnetic stirring and the absorption of TBA^{*+} at 822 nm was monitored for more than 600 s at -70 °C. Using the molar absorption coefficient ε_{822} =7.9×10³ L mol⁻¹ cm⁻¹ of TBA^{*+} and the absorption change (cm⁻¹ s⁻¹) between 290~510 s after well-mixing of the solution, the generation rate (mol L⁻¹ s⁻¹) of TBA^{*+} at each concentration was determined (Table S6). In the condition using constant excess amount of CF₃CO₂H, ln*k* + ln[TFA]₀ is regarded to be constant in the equation (2). Thus, the reaction order n of TBA was determined from the slope of the plot of lnv₀ against ln[TBA]₀ to be 1.2, which means 1st order to TBA.

0.050

Table S6. Concentration of TBA and initial rate v₀ (mol L⁻¹ s⁻¹) of TBA⁺⁺

6.3

9.4.2. Reaction order in CF₃CO₂H (Fig. 20c ,d, Table S7)

Sample solution (2.00 mL) of TBA (5.00 mM) in CH₂Cl₂ in a 1 cm quartz cell was set up on a Peltier type constant-temperature unit (UNISOKU, CoolSpeK UV USP-203-B) precooled at -60 °C under Ar atmosphere, and cooled to -60 °C with magnetic stirring. CF₃CO₂H solution (25 mM, 5.0, 8.0, 10.0, 12.0, or 14.0 μ L) in CH₂Cl₂ was injected by syringe under magnetic stirring and the absorption of TBA⁺⁺ at 822 nm was monitored for more than 600 s at -60 °C. Using the molar absorption coefficient ε_{822} =7.9×10³ L mol⁻¹ cm⁻¹ of TBA⁺⁺ and the absorption change (cm⁻¹ s⁻¹) between 290~510 s after well-mixing of the solution, the generation rate (mol L⁻¹ s⁻¹) of TBA⁺⁺ at each concentration was determined (Table S7). In the condition using constant excess amount of CF₃CO₂H, ln*k* + ln[TBA]₀ is regarded to be constant in the equation (2). Thus, the reaction order m of TFA was determined from the slope of the plot of lnv₀ against ln[TFA]₀ to be 2.0, which means 2nd order to TFA.

Table S7. Concentration of TFA and initial rate v_0 (mol L⁻¹ s⁻¹) of TBA⁺⁺

$[TFA]_0 (mM)$	$v_0 \times 10^{-9} \text{ (mol } \text{L}^{-1} \text{ s}^{-1}\text{)}$
0.18	21
0.15	16
0.13	9.8
0.10	10
0.063	2.4

9.5. Determination of the kinetic constant and activation barrier energy of disproportionation of TBA (Fig. S11, Table S8)

From the experiments on determination of reaction order, the reaction rate equation is expressed to be equation (8), where v, x, *k*, [TBA], and [TFA] are the reaction rate of TBA⁺⁺, the concentration of TBA⁺⁺, the rate constant, the concentration of TBA, and CF₃CO₂H, respectively.

$$\mathbf{v} = \mathbf{dx}/\mathbf{dt} = k[\text{TBA}][\text{TFA}]^2 \tag{8}$$

Eq. (8) is rewritten as equation (9).

$$v = dx/dt = k([TBA]_0 - 3/2x)([TFA]_0 - 2x)^2$$
(9)

The definite integral of equation (9) gives equation (10);

 $kt + C = \{(2(-3(b - 2x))\ln(3x - 2a) + 4a + 3(b - 2x)\ln(2x - b) - 3b))/((4a - 3b)^{2}(b - 2x))\}$ (10)

where a, b, and C are the initial concentrations of TBA and CF₃CO₂H, and intercept, respectively.

Sample solution (2.00 mL) of TBA (0.200 mM) in CH₂Cl₂ in a 1 cm quartz cell under Ar atmosphere was set up on a Peltier type constant-temperature unit (UNISOKU, CoolSpeK UV USP-203-B) precooled at the target temperature (-45, -50, -53, -56, or -59 °C) and cooled with magnetic stirring. CF₃CO₂H solution (80 mM, 20.0 μ L) in CH₂Cl₂ was injected by syringe under magnetic stirring and the absorption of TBA⁺⁺ at 822 nm was monitored at each temperature for more than 600 sec. The concentration of TBA⁺⁺ was calculated from the observed absorbance and the molar absorption coefficient $\varepsilon_{822}=7.9\times10^3$ L mol⁻¹ cm⁻¹. Rate constant *k* at each temperature was determined by the fitting line using the equation (10) and the data between 200 and 500 sec (Table S8).

The Eyring plot in equation (11) gave the enthalpy of activation ΔH^{\ddagger} and the entropy of activation ΔS^{\ddagger} (Table S8).

$$\ln k/T = -\Delta H^{\ddagger}/R \cdot 1/T + \ln k_{\rm B}/h + \Delta S^{\ddagger}/R \tag{11}$$

From ΔH^{\ddagger} and ΔS^{\ddagger} , the Gibbs free energy of activation ΔG^{\ddagger} (293K) was obtained (Table S8). The same experiments were conducted in three times to check reproducibility (Table S8) and the average values were calculated to be $\Delta H^{\ddagger}=8.9\pm0.4$ kcal/mol, $\Delta S^{\ddagger}=-7.1\pm1.6$ cal/mol·K, and $\Delta G^{\ddagger}=11.0\pm0.1$ kcal/mol (293 K). Data from Run 1 are shown in Fig. S11 and the average ΔH^{\ddagger} and ΔS^{\ddagger} of three runs are shown in Fig. S11c.

	temp (K)	$k (\mathrm{mol}^{-2} \mathrm{L}^2 \mathrm{s}^{-1})$	ΔH^{\ddagger} (kcal/mol)	ΔS^{\ddagger} (cal/mol•K)	ΔG^{\ddagger} (kcal/mol)(293 K)
Run 1	214	110	9.2	-5.9	10.9
	217	130			
	220	156			
	223	264			
	228	391			
Run 2	214	95.2	8.4	-9.4	11.2
	217	126			
	220	165			
	223	215			
Run 3	214	78.0	9.2	-6.0	11.0
	217	129			
	220	158			
	223	195			

Table S8. Summary of rate constant and activation energies

10. Theoretical Calculation

All the theoretical calculations were performed at U ω B97XD/6-31G(d) level of theory by using the Gaussian 09 program package.¹⁵ The structures of BC, TS-BC, BC", BCH⁺, TS-BCH⁺, BCH^{*+}, BCH₃⁺, BCH₂, BC^{*+}, TBA, TS-TBA, TBA⁺, TS-TBAH⁺, TBAH^{*+}, TBAH₂²⁺, TS-TBAH₂²⁺, TBAH₂^{*+}, TBAH₄²⁺, TBAH₂, TBA^{*+} were optimized and the vibrational frequency analyses were conducted on the optimized structures. The given energies are zero-point corrected. For BC", BCH^{*+}, BCH₃⁺, BCH₂, TBA^{*+}, TBAH₂^{*+2+}, TBAH₂^{*+2+}, TBAH₂^{*+2+}, TBAH₂^{*+2+}, TBAH₂²⁺, TBAH₂^{*+2+}, TBAH₂^{*+2+}, TBAH₄²⁺, TBAH₂^{*+2+}, TBA^{*+}, TBA^{*+}, TBA^{*+}, TBA^{*++}, TBA^{*++}, TBAH₂^{*+2+}, the closed-shell singlet, the triplet, and the open-shell singlet states were calculated, giving the lowest energies for the open-shell singlet states. The energies in Fig. 21a, b and Fig. 22a, b, c are given versus BC, BCH₃⁺⁺, TBA, TBAH⁺, TBAH₂²⁺, respectively. Calculated spin density distribution of BC^{*+}, TBA^{*+} and the open-shell singlet biradical states of BCH^{*+}, BC^{*}, TBAH₂^{*+2+}, TBA^{*-} are shown in Fig. 11 and S12.

11. Scheme and Figures

Scheme S1 Reported acid-responsive electron transfer disproportionation. (a) The reaction of tetrathiafulvalene (TTF) with HBF₄. (b) The reaction of 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) with conc. H₂SO₄.





Fig. S1 (A) ¹³C- and (B) ¹⁵N-CPMAS solid state NMR spectra of BC. Contact time was 3 ms. MAS frequencies for ¹³C- and ¹⁵N CPMAS were 20 and 10 kHz, respectively. Asterisks indicate spinning side bands of aromatic backbone signals. Number of scans were 8000 and 220000 for ¹³C- and ¹⁵N CPMAS, respectively.



Fig. S2 ¹³C-CP- and LGCPMAS solid state NMR spectra for aromatic regions of BC for various contact times. MAS frequency was 10 kHz. (A), (B) ¹³C-LGCP MAS at contact times of 60 and 200 μ s, respectively. (C), (D) ¹³C-CPMAS at contact time of 3 ms without and with dipolar dephasing. Dotted lines indicate protonated carbon sites. Arrows indicate intensity reduced peaks due to recoupled ¹H-¹³C heteronuclear dipolar interactions between ¹³C and attached ¹H. Numbers of scans were 5000 for all experiments.



Fig. S3 ¹H-¹³C FSLG heteronuclear correlation spectrum of BC. MAS frequency was 10 kHz. Contact time of LGCPMAS was set to 60 µs to correlate ¹³C and attached ¹H. Isotropic chemical shifts of ¹H attached to ¹³C were obtained for individual sites as summarized in Table S1. Asterisks indicate spinning side bands of aromatic backbone signals.



Fig. S4 ¹H-¹³C MELODI heteronuclear correlation spectrum of BC. MAS frequency was 10 kHz. Contact time of LGCPMAS was set to 240 µs to correlate ¹³Cand adjacent¹H. Asterisks indicate spinning side bands of aromatic backbone signals.



Fig. S5 (a) ESR spectrum of BC (1.02 mM) with 2000 mol% CF₃CO₂H in frozen CH₂Cl₂ at 5 K (X-band, v = 9.507335 GHz, g = 2.0036). (b) ESR spectrum of BC^{*+}I₅⁻·IC₆H₅ crystal at room temperature (X-band, v = 9.426200 GHz). (c) ESR spectrum of BC^{*+}I₅⁻·IC₆H₅ crystal dissolved in MeOH at room temperature (X-band, v = 9.457425 GHz).



Fig. S6 (a) ESR spectrum of TBA (0.100 mM) with 2000 mol% CF_3CO_2D in CH_2Cl_2 at room temperature (X-band, v = 9.688112 GHz, g = 2.0036). (b) Temperature dependence of *IT* value of TBA with 2000 mol% CF_3CO_2H in frozen CH_2Cl_2 at 5-80 K. (c) Temperature dependence of *IT* value of TEMPOL in frozen CH_2Cl_2 at 5-100 K.



Fig. S7 (a) UV-Vis-NIR spectrum of BC (1.00 mM) with 2000 mol% CF₃CO₂H in CH₂Cl₂ (orange) and the spectra of the re-prepared solution after evaporation of excess CF₃CO₂H in CH₂Cl₂ (red) with 1 mm cell (see 7.1). (b) UV-Vis-NIR spectra of BC⁺⁺ by the chemical oxidation of BC (0.100 mM) with I₂ (3000 mol%) in CH₂Cl₂. (c) UV-Vis-NIR spectra of BC⁺⁺I₅·IC₆H₅ crystal dissolved in MeOH (0.090 mM) or CH₂Cl₂ (0.056 mM). (d) UV-Vis-NIR spectrum of BC (0.05 mM) with 2000 mol% CF₃CO₂H in CH₂Cl₂. (e) UV-Vis-NIR spectra of BCH₂ (0.100 mM) and BCH₂ (0.100 mM) with CF₃CO₂H (2000 mol%) in CH₂Cl₂. (f) Subtracted spectrum (black) between the spectrum of BC⁺⁺ + BCH₃⁺⁺ (Fig. S7d) and that of BC⁺⁺ (Fig. S7d) - (Fig. 9b)×2/3] ×6.



Fig. S8 (a) UV-Vis-NIR spectra of TBA (0.100 mM) with 2000 mol% CF_3CO_2H in CH_2Cl_2 under air and under N₂ atmosphere. (b) UV-Vis-NIR spectra of TBA (1.00 mM) with 2000 mol% CF_3CO_2H in various organic solvents. (c) UV-Vis-NIR spectra of TBA (0.100 mM) with 2000 mol% Brønsted acids and Lewis acids (10000 mol% for LiCl, CH_3CO_2H), in CH_2Cl_2 . (d) UV-Vis-NIR spectrum of TBA (1.00 mM) with 2000 mol% CF_3CO_2H diluted to 0.1 mM in toluene with 1 cm cell, and that of TBA with 2000 mol% CF_3CO_2H diluted to 0.1 mM in toluene with 1 cm cell. The spectrum of 0.01 mM was normalized to 10 times. (e) The short-wavelength region of UV-Vis-NIR spectra of TBA (0.030 mM) with 0-2000 mol% CF_3CO_2H in CH_2Cl_2 . (f) UV-Vis-NIR spectra of TBAH₂ (0.030 mM) and TBAH₂ (0.030 mM) with 2000 mol% CF_3CO_2H in CH_2Cl_2 . (g) Subtracted spectrum (blue) between the spectrum of TBA⁺⁺ + TBAH₄²⁺ (Fig. S8e, TFA 2000 mol%) and that of TBA⁺⁺ (Fig. 16i, NOPF₆) and the spectrum (red) of TBAH₄⁺⁺ (Fig. S8f). The subtracted spectrum was obtained from the equation [(Fig. S8e) - (Fig. 16i)×3/10×2/3]×3. (h) Continuous variation plots of the absorbance of TBA with CF_3CO_2H at 824 nm in CH_2Cl_2 versus the ratio of [CF_3CO_2H]/[TBA]+[CF_3CO_2H].



(b) TBA+NEt₃ 1000 mol%



(c) Sample (b) + CF₃CO₂H 3000 mol%



(d) Sample (c) + NEt₃ 4000 mol%



Fig. S9 (a) ¹H NMR spectrum of TBA (2.00 mM) in freshly distilled CD_2Cl_2 , (b) ¹H NMR spectrum of TBA (2.00 mM) with 1000 mol% NEt₃ in CD_2Cl_2 , (c) ¹H NMR spectrum of TBA with 1000 mol% NEt₃ [sample (b)] followed by acidification with 3000 mol% CF_3CO_2H in CD_2Cl_2 , (d) ¹H NMR spectrum of recovered TBA with 1000 mol% NEt₃ and 3000 mol% CF_3CO_2H [sample (d)] followed by neutralization with 4000 mol% NEt₃ in CD_2Cl_2 .



Fig S10. Determination of reaction orders in BC and TFA by initial rate method in benzene. (a) Time-dependent change of the absorbance of BC^{*+}at 635 nm by mixing BC (0.10, 0.20, 0.30 mM) and TFA (5.00 mM) in benzene at 20 °C. (b) The reaction order in BC in benzene from the plot of $\ln[BC]_0$ versus $\ln v_0$ using the data in Fig. S10a. (c) Time-dependent change of the absorbance of BC^{*+}at 635 nm by mixing BC (5.00 mM) and TFA (0.10, 0.20, 0.30 mM) in benzene at 20 °C. (d) The reaction order in CF₃CO₂H in benzene from the plot of $\ln[TFA]_0$ versus $\ln v_0$ using the data in Fig. S10e.



Fig S11. (a) Time-dependent change of absorbance at 822 nm by mixing 0.200 mM TBA and 0.800 mM CF₃CO₂H in CH₂Cl₂ at -45 to -59 °C for the determination of the kinetic constant *k*. (b) Determination of the kinetic constant *k* by fitting line using the data in Fig. S11. (c) Eyring plot using the data in Fig. S11a, b and the determined average enthalpy (ΔH^{\ddagger}) and entropy (ΔS^{\ddagger}) of activation.



Fig. S12 (a) Calculated spin density of TBA^{*+}. (b) Calculated spin density of BCH^{*++}. (c) Calculated spin density of BCH^{**+}. (d) Calculated spin density of TBAH₂^{**2+}. (e) Calculated spin density of TBA^{*+}. Blue and green colors indicate the positive and negative spin density, respectively.

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