Supporting Information

Isolation and Low-Temperature X-ray Analysis of Intramolecular Triarylmethane-Triarylmethylium Complex: Preference for a C-H Bridged Unsymmetric Structure Exhibiting a Facile 1,5-Hydride Shift and Charge-Transfer Interaction

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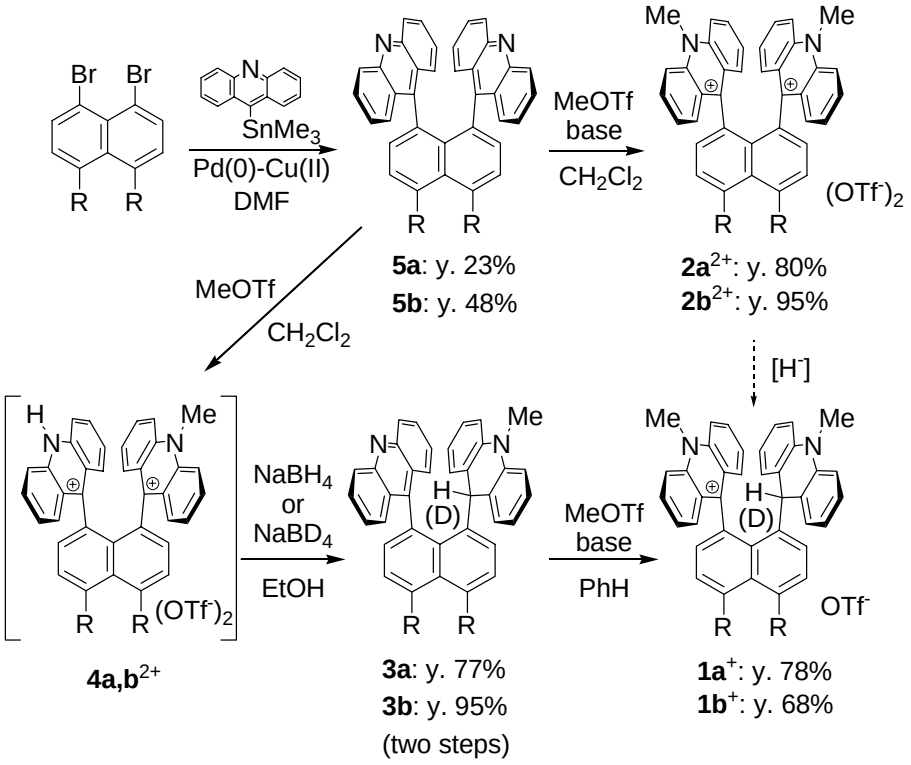
Experimental procedures

General: ^{1}H and ^{13}C NMR spectra were recorded on a JEOL AL300 or ECP-300 (^{1}H/300 MHz, ^{13}C/75 MHz) spectrometer. VT NMR (^{1}H and ^{13}C) and ^{2}H NMR spectra were recorded on a JEOL AL300, α400 (^{1}H/400 MHz, ^{13}C/100 MHz) or α500 (^{1}H/500 MHz, ^{2}H/77 MHz and ^{13}C/125 MHz) spectrometer. ^{13}C–^{1}H coupling constants were measured by a HSQC method on a α500 spectrometer at the High-Resolution NMR Laboratory (Hokkaido University). IR spectra were taken on a JASCO model FT/IR-230 infrared spectrophotometer. Mass spectra were recorded on JEOL JMS-600H (EI) and JMS-AX500 or JEOL JMS-SX102A (FAB) spectrometers. Column chromatography were performed on silica gel I-6-40 (YMG) of particle size 40-63 μm and aluminum oxide 90 standardized (Merck). Elemental analyses were taken on a Yanako MT-6 CHN corder at the Center for Instrumental Analysis of Hokkaido University. UV/Vis spectra were recorded on a Hitachi U-3500 spectrophotometer. 1,8-dibromonaphthalene[1] and 5,6-dibromoacenaphthene[2] were prepared following the known procedures. Other reagents and solvents were obtained from commercial sources and purified prior to use.

Scheme. Preparation of **1a,b**$^{+}$ salts



a: R = H; b: R, R = -CH_2CH_2-

Preparation of 9-Bromoacridine[3]

The mixture of *N*-phenylanthranilic acid (5.50 g, 58.1 mmol) and $POBr_3$ (50.0 g, 174 mmol) was heated without solvent at 120°C. A violent fuming reaction occurred within 10 min (CAUTION! This reaction should be done in a hood). After heated for 2 h, the resulting solid was allowed to cool to room temperature, and carefully added to 25% aqueous ammonium hydroxide and chloroform. The mixture was extracted with chloroform. The organic layer was washed with 5% aqueous ammonium hydroxide and brine, and dried over Na_2SO_4. Evaporation of the solvent gave 9-bromoacridine (14.1 g, 94%) as a brown solid. This compound was used in the next reaction without purification; M.p. (113-114 °C, *lit.* 116 °C[3]); ^{1}H NMR ($CDCl_3$) δ 8.42 (dd, *J* = 8.4, 1.2 Hz, 2H), 8.22 (d, *J* = 8.6 Hz, 2H), 7.80 (ddd, *J* = 8.4, 6.6, 1.2 Hz, 2H), 7.64 (ddd, *J* = 8.4, 6.6, 1.2 Hz, 2H).

Preparation of 9-Trimethylstannylacridine

To a suspension of 9-bromoacridine (5.50 g, 21.3 mmol) in dry ether (300 mL) was added *n*-BuLi in *n*-hexane (1.58 M, 15.1 mL, 25.6 mmol) at –78°C under argon. After 15 min, Me_3SnCl in *n*-hexane (1.0 M, 26.0 mL, 26.0 mmol) was added. The mixture was allowed to warm to 23°C and stirred for 18 h. Then, the resulting suspension was filtered to remove the insoluble material. The yellow solid obtained by evaporation of the solvent was subjected to chromatography on SiO_2 eluting with hexane/EtOAc/Et_3N (100:10:1) to give 9-trimethylstannylacridine (6.25 g, 84%) as a yellow solid; M.p. 86-87°C; ^{1}H NMR ($CDCl_3$) δ 8.25 (dd, *J* = 8.6, 1.3 Hz, 2H), 8.14 (dd, *J* = 8.6, 1.3 Hz, 2H), 7.76 (ddd, *J* = 8.6, 6.6, 1.3 Hz, 2H), 7.53 (ddd, *J* = 8.6, 6.6, 1.3 Hz, 2H), 0.68 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 157.37, 147.79, 133.48, 130.69, 130.08, 129.56, 125.29, -4.58; IR (KBr) 2360, 2337, 1533, 1515, 1460, 1394, 1196, 1141, 1127, 1011, 859, 832, 782, 761, 745, 670, 660, 604, 537, 523, 514 cm^{-1}; LR-MS (EI) *m/z* (%): 343(M^+, 22), 324 (32), 298 (50), 296 (38), 178 (bp), 177 (49), 152 (37), 151 (55), 150 (32), 135 (33); Anal. Calcd (%) for $C_{16}H_{17}NSn$: C 56.19, H 5.10, N 4.10; found C 56.10, H 4.96, N 4.05.

Preparation of 9,9'-(Naphthalene-1,8-diyl)bisacridine 5a[4]

To a solution of 1,8-dibromonaphthalene[1] (399 mg, 1.41 mmol) in dry DMF (20 mL) were added CuO (487 mg, 2.81 mmol) and then $Pd(PPh_3)_4$ (224 mg, 422 μmol).[5] After bubbling with argon for ca. 40 min, a portion (5 mL) of dry DMF solution (20 mL) of 9-trimethylstannylacridine (2.61 g, 7.63 mmol) was added. Then, the resulting mixture was heated at 100°C for 15 min and at 140°C for 50 min under argon. Then, the remaining 9-trimethylstannylacridine solution was added to the mixture at this temperature. After 21 h, 5% aqueous ammonium hydroxide (20 mL)

and chloroform (20 mL) were added to the reaction mixture, and then the precipitates were filtered. The solid was transferred on a thimble filter fitted in the Soxhlet apparatus, and extracted with refluxing chloroform (300 mL) for 3 h. The orange solid obtained by evaporation of the solvent mostly contains 9,9'-biacridinyl and was discarded. The remaining solid on the thimble filter was further extracted with refluxing chloroform (300 mL) in the Soxhlet apparatus for 48 h. The second extract was concentrated in vacuo to give **5a** (153 mg, 23%) as a yellow solid. Single crystals for the X-ray analysis were obtained by recrystalization from $CHCl_3$/hexane: M.p. 245-247°C (decomp.); ^{1}H NMR (CD_2Cl_2) δ 8.24 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.67 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.52 (dd, 4H, *J* = 8.4, 1.2 Hz), 7.29 (ddd, *J* = 8.4, 6.6, 1.4 Hz, 4H), 7.19 (dd, *J* = 6.9, 1.4 Hz, 2H), 6.72 (dd, *J* = 8.4, 1.4 Hz, 4H), 6.61 (ddd, *J* = 8.4, 6.6, 1.2 Hz, 4H); The ^{13}C NMR could not be measured due to its low solubility. IR (KBr) 3045, 1558, 1540, 1517, 1436, 1145, 1014, 866, 827, 785, 752, 601 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε / M^{-1} cm^{-1}) = 347 (12600), 360 (13400), 390 nm (6000, sh); Fluorescence (CH_2Cl_2, λ_{ex} = 360 nm) λ_{max} = 536 nm; LR-MS (EI) *m/z* (%): 484 (M^+ + 2H, 57), 483(23), 482(M^+, bp), 241(87), 240 (65), 207 (66), 196 (60), 171 (63), 166 (64), 138 (63), 122 (61), 121 (63), 93 (64), 80 (63), 52 (58); HR-MS (EI) found 482.1778, calcd. for $C_{36}H_{22}N_2$: 482.1783; Anal. Calcd (%) for $C_{36}H_{22}N_2$ + 0.50 $CHCl_3$: C 80.84, H 4.18, N 5.17; found C 80.88, H 4.48, N 5.20.

Preparation of 9,9'-(Acenaphthene-5,6-diyl)bisacridine 5b

To a solution of 5,6-dibromoacenaphthene[2] (1.15 g, 3.69 mmol) in dry DMF (60 mL) were added CuO (683 mg, 8.59 mmol) and then $Pd(PPh_3)_4$ (1.31 g, 1.13 mmol). After bubbling with argon for ca. 30 min, a portion (15 mL) of dry DMF solution (60 mL) of 9-trimethylstannylacridine (4.99 g, 14.6 mmol) was added. Then, the resulting mixture was heated at 100°C for 30 min and at 140°C for 15min under argon. Then, the remaining 9-trimethylstannylacridine solution was added to the mixture at this temperature. After 21 h, 5% aqueous ammonium hydroxide (100 mL) was added and extracted with chloroform. The organic layer was washed with 5% aqueous ammonium hydroxide and brine, dried over Na_2SO_4. The black solid obtained by evaporation of the solvent was subjected to chromatography on SiO_2 eluting with $CHCl_3$/Et_3N (100:1) to give **5b** (888 mg, 48%) as a yellow solid. Single crystals for the X-ray analysis were obtained by recrystalization from $CHCl_3$/AcOEt: M.p. 270-272°C (decomp.); ^{1}H NMR ($CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 4H), 7.55 (d, *J* = 7.0 Hz, 2H), 7.34 (ddd, *J* = 8.4, 6.4, 1.1 Hz, 4H), 7.25 (d, *J* = 7.0 Hz, 2H), 6.94 (dd, *J* = 8.6, 1.1 Hz, 4H), 6.68 (ddd, *J* = 8.6, 6.4, 1.1 Hz, 4H), 3.74 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 147.55, 146.71, 145.89, 140.28, 131.92, 131.76, 128.93, 128.79, 126.25, 124.94, 124.57, 119.50, 30.51; IR (KBr) 3042, 2916, 1629, 1600, 1556, 1515, 1460, 1435, 1408, 1329, 1151, 1013, 868, 745, 647, 626, 603 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε / M^{-1} cm^{-1}) = 349 (12200), 360 (12900), 390 nm (6200, sh); Fluorescence (CH_2Cl_2, λ_{ex} = 360 nm) λ_{max} = 525 nm; LR-MS

(EI) *m/z* (%): 509 (42), 508 (M^+, bp), 254 (19); HR-MS (EI) found 508.1940, calcd. for $C_{38}H_{24}N_2$: 508.1939; Anal. Calcd (%) for $C_{38}H_{24}N_2$ + 0.33 H_2O: C 88.69, H 4.83, N 5.44; found C 88.42, H 4.75, N 5.41.

Preparation of 9-[8-(10-Methylacridan-9-yl)naphthalen-1-yl]acridine 3a and 3a-*d*

To a suspension of 9,9'-(naphthalene-1,8-diyl)bisacridine **5a** (27.3 mg, 57 μmol) in dry CH_2Cl_2 (20 mL) was added MeOTf (900 μL, 8.0 mmol). After stirring for 21h at 23°C under argon, the mixture was diluted with ether and the resulting precipitates were filtered. The insoluble material was washed with ether to give a mixture of mono methylated dication salt **4a** and a small amount of dimethylated dication **2a**. The mixture was used in the next reaction without further purification.

To a solution of a mixture of **4a** and **2a** in ethanol (20 mL) was added $NaBH_4$ (73 mg, 193 μmol). After the mixture was stirred for 25h at 23 °C, the solvent was evaporated. The obtained yellow solid was suspended with water and the mixture was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4, and filtered. The yellow solid obtained by evaporation of the solvent was subjected to chromatography on Al_2O_3 eluting with CH_2Cl_2/hexane (1:1) to give **3a** (22 mg, 77%) as a yellow solid. Single crystals for the X-ray analysis were obtained by recrystalization from CH_2Cl_2/hexane: M.p. 280-285 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 8.16 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 2H), 8.03 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.65 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.61-7.54 (m, 3H), 7.49 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.45 (dd, *J* = 8.4, 0.6 Hz, 2H), 7.41 (dd, *J* = 6.6, 1.2 Hz, 1H), 7.15 (ddd, *J* = 8.4, 6.6, 1.2 Hz, 2H), 6.87 (td, *J* = 7.5, 1.2 Hz, 2H), 6.48 (dd, *J* = 7.5, 1.2 Hz, 2H), 6.40 (dd, *J* = 7.5, 1.2 Hz, 2H), 6.10 (dd, *J* = 7.5, 1.2 Hz, 2H), 4.52 (s, 1H), 3.04 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 148.95, 148.57, 141.74, 140.16, 135.19, 132.90, 132.60, 132.08, 131.32, 130.79, 129.96, 129.57, 129.10, 128.66, 128.08, 127.19, 127.06, 126.36, 126.19, 125.19, 124.43, 119.41, 111.04, 43.07, 32.96; IR (KBr) 3059, 3037, 2960, 2926, 1589, 1503, 1477, 1456, 1359, 1322, 1273, 781, 744 cm^{-1}; LR-MS (EI) *m/z* (%): 500 (20), 499 (46), 498 (M^+, bp), 497 (24), 496 (22), 484 (27), 483 (55), 249 (28), 194 (48); HR-MS (EI) found 498.2096, calcd. for $C_{37}H_{26}N_2$: 498.2096; Anal. Calcd (%) for $C_{37}H_{26}N_2$ + 0.25 H_2O: C 88.33, H 5.31, N 5.57; found C 88.40, H 5.55, N 5.35.

Compound **3a**-*d* was prepared from **5a** by using $NaBD_4$ in place of $NaBH_4$ following the same protocol to **3a** (2 steps, 41% yield): M.p. 270-271 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 2H), 8.03 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.64 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.60-7.53 (m, 3H), 7.49 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.40 (dd, *J* = 6.6, 1.2 Hz, 1H), 7.14 (ddd, *J* = 8.6, 6.6, 1.1 Hz, 2H), 6.86 (td, *J* = 7.5 1.5 Hz, 2H), 6.48 (d, *J* = 7.5 Hz, 2H), 6.40 (dt, *J* = 7.5, 1.1 Hz, 2H), 6.10 (dd, *J* = 7.5, 1.5 Hz, 2H), 3.04 (s,

3H); ^{13}C NMR ($CDCl_3$) δ 148.91, 148.62, 141.78, 140.07, 135.22, 132.90, 132.56, 132.13, 131.30, 130.78, 129.92, 129.16, 128.66, 128.03, 127.19, 127.05, 126.36, 126.20, 125.24, 125.19, 124.44, 119.42, 111.05, 32.95; IR (KBr) 3056, 2958, 2926, 2872, 1625, 1605, 1589, 1556, 1539, 1514, 1459, 1439, 1343, 1301, 1261, 1209, 1200, 1160, 1144, 1129, 1045, 862, 783, 776, 746, 651, 638, 618, 601 cm^{-1}; LR-MS (EI) *m/z* (%): 500 (43), 499(M^+, bp), 498 (20), 484 (29), 250 (27), 195 (30); HR-MS (EI) found 499.2163, calcd. for $C_{37}H_{25}DN_2$: 499.2158.

Preparation of 9-[6-(10-Methylacridan-9-yl)acenaphthen-5-yl]acridine 3b and 3b-*d*

Compound **3b** was prepared from **5b** (41.0 mg, 81 μmol) following the same protocol to **3a** [MeOTf (860 μL, 7.6 mmol) and $NaBH_4$ (144 mg, 3.8 μmol)] as a yellow solid (40 mg, 95%): M.p. 220-223 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 8.16 (dd, *J* = 8.6, 1.2 Hz, 2H), 7.65-7.58 (m, 4H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.24 (dd, *J* = 8.6, 7.2 Hz, 2H), 6.87 (tt, *J* = 8.1, 0.6 Hz, 2H), 6.54 (d, *J* = 8.1 Hz, 2H), 6.39 (t, *J* = 7.5 Hz, 2H), 6.07 (d, *J* = 7.5, 1.1 Hz, 2H), 4.35 (s, 1H), 3.60-3.48 (m, 4H), 3.10 (s, 3H); ^{13}C NMR (CD_2Cl_2) δ 148.58 (br), 148.19, 145.58, 141.24, 139.97, 132.23, 132.69, 132.22, 129.77, 129.35 (br), 127.90, 127.70, 127.40, 127.28, 126.15, 125.61, 125.25, 120.47, 119.11, 118.31, 111.51, 41.80, 32.65, 30.05, 29.76; IR (KBr) 1606, 1590, 1461, 1346, 1266, 1131, 866, 752 cm^{-1}; LR-MS (EI) *m/z* (%): 525 (64), 524 (M^+, bp), 523 (49), 510 (52), 509 (69), 328 (53), 262 (40), 194 (51), 179 (50); HR-MS (EI) found 524.2257, calcd. for $C_{39}H_{28}N_2$: 524.2252; Anal. Calcd. (%) for $C_{39}H_{28}N_2$ + 0.50 H_2O: C 86.32, H 5.57, N5.16; found C 86.06, H 5.43, N 5.12.

Compound **3b**-*d* was prepared from **5b** by using $NaBD_4$ in place of $NaBH_4$ following the same protocol to **3a** (2 steps, 77% yield): M.p. 233-235 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.6 Hz, 2H), 7.67-7.58 (m, 4H), 7.47 (d, *J* = 6.9 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 6.9 Hz, 1H), 7.24 (m, 2H), 6.88 (td, *J* = 7.8, 1.5 Hz, 2H), 6.54 (d, *J* = 7.8 Hz, 2H), 6.40 (td, *J* = 7.8, 0.6 Hz, 2H), 6.08 (dd, *J* = 7.8, 1.5 Hz), 3.61-3.52 (m, 4H), 3.12 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 148.82, 148.74, 148.06, 145.46, 141.64, 140.19, 137.87, 133.11, 132.50, 130.67, 129.97, 129.38, 128.06, 127.76, 127.51, 126.23, 125.86, 125.26, 120.84, 119.40, 118.46, 111.35, 32.94, 30.32, 30.07; IR (KBr) 3070, 3037, 2924, 2854, 1605, 1592, 1514, 1470, 1435, 1345, 1278, 1269, 1132, 874, 757, 751 cm^{-1}; LR-MS (EI) *m/z* (%): 526 (50), 525 (M^+, bp), 524 (28), 510 (28), 278 (39), 263 (36), 195 (28); HR-MS (EI) found 525.2318, calcd. for $C_{39}H_{27}DN_2$: 525.2314.

Preparation of 10-Methyl-9-[8-(10-methylacridan-9-yl)naphthalen-1-yl]acridinium Triflate 1a$^+$OTf$^-$ and 1a-*d*$^+$OTf$^-$

To a solution of **3a** (34.3 mg, 69 μmol) and 2,6-di-*tert*-butyl-4-methylpyridine (20.0 mg, 97 μmol) in dry benzene (10 mL) was added MeOTf (100 μL, 884 μmol). The mixture was stirred for 80 min at 23 °C under argon, and the resulting black precipitates were filtered. The insoluble material was washed with ether to give **1a$^+$OTf$^-$** (35.5mg, 78%) as a dark orange solid. Single crystals for the X-ray analysis were obtained by recrystallizing from acetone: M.p. 193-195°C; ^{1}H NMR (300 MHz, acetone-d_6, -30 °C), 8.46 (d, J = 8.1 Hz, 2H), 7.87 (t, J = 7.5 Hz, 2H), 7.72-7.53 (m, 10H), 7.08 (t, J = 7.5 Hz, 4H), 6.98 (d, J = 8.1 Hz, 4H), 4.11 (s, 1H), 4.06 (s, 6H); IR (KBr) 3107, 3034, 2919, 1609, 1589, 1579, 1549, 1479, 1461, 1342, 1275, 1262, 1224, 1193, 1160, 1030, 774, 753, 713, 691, 655, 637, 629, 517 cm^{-1}; LR-MS (FAB) *m/z* (%): 515 (22), 514 (44), 513 (M$^+$, bp), 194 (51); HR-MS (FAB) found 513.2324, calcd. for $C_{38}H_{29}N_2$: 513.2325; Anal. Calcd (%) for $C_{39}H_{29}F_3N_2O_3S$ + 0.33C_6H_6: C 71.50, H 4.54, N 4.07; found: C 71.24, H 4.79, N 3.92.

Salt **1a**-*d*$^+$OTf$^-$ was prepared from **3a**-*d* with MeOTf following the same protocol to **1a$^+$OTf$^-$** (68% yield): M.p. 193-194 °C (decomp.); ^{1}H NMR (300 MHz, acetone-d_6, 20 °C) δ 8.46 (d, J = 8.3 Hz, 2H), 7.89 (br t, J = 7.5 Hz, 2H), 7.70-7.50 (m, 10H), 7.08 (br. t, J = 7.0 Hz, 4H), 7.00 (d, J = 8.1 Hz, 4H), 4.07 (s, 6H); ^{2}D NMR (77 MHz, acetone-d_6, -30 °C) δ 4.10 (br. s); IR (KBr) 3069, 3034, 1609, 1589, 1579, 1549, 1461, 1385, 1341, 1276, 1262, 1224, 1194, 1162, 1030, 753, 713, 691, 654, 637, 626, 602, 573, 517 cm^{-1}; LR-MS (FAB) *m/z* (%): 517 (32), 516 (26), 515 (85), 514 (M$^+$, bp), 513 (29), 195 (48), 136 (27); HR-MS (FAB) found 514.2388, calcd. for $C_{38}H_{28}DN_2$: 514.2392.

Preparation of 10-Methyl-9-[6-(10-methylacridan-9-yl)acenaphthen-5-yl]acridinium Triflate 1b$^+$OTf$^-$ and 1b-*d*$^+$OTf$^-$

To a solution of **3b** (28.5 mg, 54 μmol) and 2,6-di-*tert*-butyl-4-methylpyridine (11.1 mg, 54 μmol) in dry benzene (10 mL) was MeOTf (90 μL, 823 μmol) and stirred for 60 min at 23 °C under argon, and the resulting black precipitates were filtered. The insoluble material was washed with ether to give **1b$^+$OTf$^-$** (25.4 mg, 68%) as a dark brown solid. Single crystals for the X-ray analysis were obtained by recrystallizing from $CHCl_3$: M.p. 248-249 °C; ^{1}H NMR (300 MHz, acetone-d_6, -10 °C) δ 7.81-7.57 (br s, 8H), 7.64 (d, J = 7.0 Hz, 2H), 7.50 (d, J = 7.0 Hz, 2H), 7.18-6.94 (br s, 8H), 4.10 (br s, 6H), 4.00 (s, 1H), 3.65 (s, 4H); ^{1}H NMR (300 MHz, acetone-d_6, -85 °C) δ 8.98 (d, J = 9.4 Hz, 2H), 8.55 (br. dd, J = 9.4, 7.3 Hz, 2H), 8.15(d, J = 8.6 Hz, 2H), 7.99 (br. dd, J = 8.6, 7.3 Hz, 2H), 7.78 (d, J = 7.2 Hz, 1H), 7.68 (d, J = 7.2 Hz, 1H), 7.53 (d, J = 7.3 Hz, 1H), 7.45 (d, J = 7.3 Hz, 1H), 7.03 (br. dd, J = 8.3, 7.3 Hz, 2H), 6.82 (d, J = 8.3 Hz, 2H), 6.50 (t, J = 7.3 Hz, 2H), 5.96 (d, J = 7.3 Hz, 2H), 5.16 (s, 3H), 4.19 (s, 1H), 3.66 (d, J = 8.3 Hz,

4H), 3.25 (s, 3H); IR (KBr) 3111, 3070, 3037, 2921, 2888, 1607, 1590, 1577, 1547, 1462, 1385, 1343, 1277, 1262, 1224, 1187, 1155, 1045, 1032, 866, 752, 638, 574, 517 cm^{-1}; LR-MS (FAB) *m/z* (%): 540 (45), 539 (M^+, bp), 194 (51); HR-MS (FAB) found 539.2484, calcd. for $C_{40}H_{31}N_2$: 539.2482.; Anal. calcd(%) for $C_{39}H_{29}F_3N_2O_3S$ + 0.50H_2O C 70.57, H 4.62, N 4.01; found C 70.69, H 4.61, N 4.09.

Salt **1b**-*d*$^+$OTf$^-$ was prepared from **3b**-*d* with MeOTf following the same protocol to **1b**$^+$OTf$^-$ (63% yield): M.p. 265-267 °C (decomp.); ^{1}H NMR (300 MHz, acetone-d_6, -85 °C) δ 8.98 (d, *J* = 9.4 Hz, 2H), 8.55 (t, *J* = 8.0 Hz, 2H), 8.17 (d, *J* = 8.6 Hz, 2H), 7.99 (t, *J* = 8.0, 2H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.45 (d, *J* = 7.3 Hz, 1H), 7.03 (t, *J* = 7.7 Hz, 2H), 6.82 (d, *J* = 8.3 Hz, 2H), 6.50 (t, *J* = 7.3 Hz, 2H), 5.96 (d, *J* = 7.2 Hz, 2H), 5.16 (s, 3H), 3.67 (br s, 4H), 3.25 (s, 3H); ^{2}D NMR (77 MHz, acetone-d_6, -10 °C) δ 3.99 (br. s); IR (KBr) 3113, 3070, 3037, 2932, 2883, 1607, 1591, 1577, 1547, 1464, 1344, 1279, 1262, 1224, 1189, 1157, 1029, 874, 751, 636, 516 cm^{-1}; LR-MS (FAB) *m/z* (%): 541 (45), 514 (M^+, bp), 195 (47); HR-MS (FAB) found 540.2568, calcd. for $C_{40}H_{30}DN_2$: 540.2549.

X-ray Analyses

Crystal data for **1a**$^+$OTf$^-$•acetone: Crystals were obtained by recrystallizing from acetone. $C_{39}H_{29}N_2$•CO_3F_3S•C_3H_6O, *M* 720.80, dark orange plates, 0.60 × 0.03 × 0.02 mm^3, triclinic *P*1bar, *a* = 8.407(4) Å, *b* = 13.578(7) Å, *c* = 15.815(8) Å, α = 72.28(2)°, β = 80.88(2)°, γ = 89.70(3)°, *V* = 1695.9(14) $Å^3$, ρ(Z = 2) = 1.411 g cm^{-1}. A total of 6566 unique data ($2\theta_{max}$ = 55°) were measured at *T* = 133 K by a Rigaku Mercury CCD apparatus (Mo Kα radiation, λ = 0.71070 Å). Numerical absorption correction was applied (μ = 1.60 cm^{-1}). The structure was solved by the Patterson method and the following expansion (DIRDIF99) and refined by the full-matrix least-squares method on F^2 with anisotropic temperature factors for non-hydrogen atoms. All the hydrogen atoms except for the methine proton (H1) at the C11 carbon were located at the calculated positions and refined with riding. The methine proton (H1) at the C11 carbon was located in the D map and refined with isotropic temperature factors. The final *R1* and *wR2* values are 0.081 (I > 2σI) and 0.197 (all data) for 6555 reflections and 508 parameters. Estimated standard deviations are 0.004-0.01 Å for bond lengths and 0.3-0.7° for bond angles, respectively.

Crystal data for **1b**$^{+}$OTf^{-}•chloroform: Crystals were obtained by recrystallizing from chloroform. $C_{41}H_{31}N_2$ •CO_3F_3S•$CHCl_3$, *M* 808.14, dark brown plates, 0.60 × 0.20 × 0.02 mm^3, triclinic *P*1bar, *a* = 8.208(2) Å, *b* = 14.152(4) Å, *c* = 16.716(5) Å, α = 109.750(5)°, β = 97.638(5)°, γ = 90.402(3)°, *V* = 1808.4(9) Å^3, ρ(*Z* = 2) = 1.484 g cm^{-1}. A total of 7678 unique data ($2\theta_{max}$ = 55°) were measured at *T* = 103 K by a Rigaku Mercury CCD apparatus (Mo Kα radiation, λ = 0.71070 Å). Numerical absorption correction was applied (μ = 3.71 cm^{-1}). The structure was solved by the direct method (SIR97) and refined by the full-matrix least-squares method on F^2 with anisotropic temperature factors for non-hydrogen atoms. All the hydrogen atoms except for the methine proton (H1) at the C13 carbon were located at the calculated positions and refined with riding. The methine proton (H1) at the C13 carbon was located in the D map and refined with isotropic temperature factors. The final *R1* and *wR2* values are 0.054 (I > 2σI) and 0.128 (all data) for 7678 reflections and 522 parameters. Estimated standard deviations are 0.002-0.005 Å for bond lengths and 0.1-0.3° for bond angles, respectively.

Crystal data for **3a**: Crystals were obtained by recrystallizing from CH_2Cl_2/hexane. $C_{37}H_{26}N_2$, *M* 498.63, orange prism, 0.80 × 0.15 × 0.10 mm^3, monoclinic *C*c, *a* = 9.057(2) Å, *b* = 19.794(3) Å, *c* = 14.905(3) Å, β = 104.157(3)°, *V* = 2590.8(7) Å^3, ρ(*Z* = 4) = 1.278 g cm^{-1}. A total of 5151 unique data ($2\theta_{max}$ = 55°) were measured at *T* = 103 K by a Rigaku Mercury CCD apparatus (Mo Kα radiation, λ = 0.71070 Å). Numerical absorption correction was applied (μ = 3.71 cm^{-1}). The structure was solved by the direct method (SIR97) and refined by the full-matrix least-squares method on F^2 with anisotropic temperature factors for non-hydrogen atoms. All the hydrogen atoms except for the methine proton (H1) at the C24 carbon were located at the calculated positions and refined with riding. The methine proton (H1) at the C24 carbon was located in the D map and refined with isotropic temperature factors. The final *R1* and *wR2* values are 0.042 (I > 2σI) and 0.096 (all data) for 5151 reflections and 382 parameters. Estimated standard deviations are 0.002-0.004 Å for bond lengths and 0.2° for bond angles, respectively.

Computational Methods

The DFT calculations were performed with the Gaussian 98 program package.[6] The geometries of the compounds were optimized by using the B3LYP method in combination with the 6-31G* basis set.

Redox Potential Measurements

Redox potentials (E^{ox} and E^{red}) were measured by cyclic voltammetry in dry MeCN containing 0.1 mol dm^{-3} Et_4NClO_4 as a supporting electrolyte. Ferrocene undergoes 1e-oxidation at +0.38 V under the same conditions. All of the values shown in the text are in E/V vs SCE measured at the scan rate of 100 mV s^{-1}. A Pt disk electrode was used as the working and counter electrodes, respectively. The working electrode was polished using a water suspension of Al_2O_3 (0.05 μm) before use. The irreversible half-wave potentials were estimated from the anodic peak potentials (E^{pa}) as $E^{ox} = E^{pa}$ -0.03 or the cathodic peak potentials (E^{pc}) as $E^{red} = E^{pa}$ +0.03.

VT-NMR data of $1b^{+}OTf^{-}$ salt in CD_2Cl_2

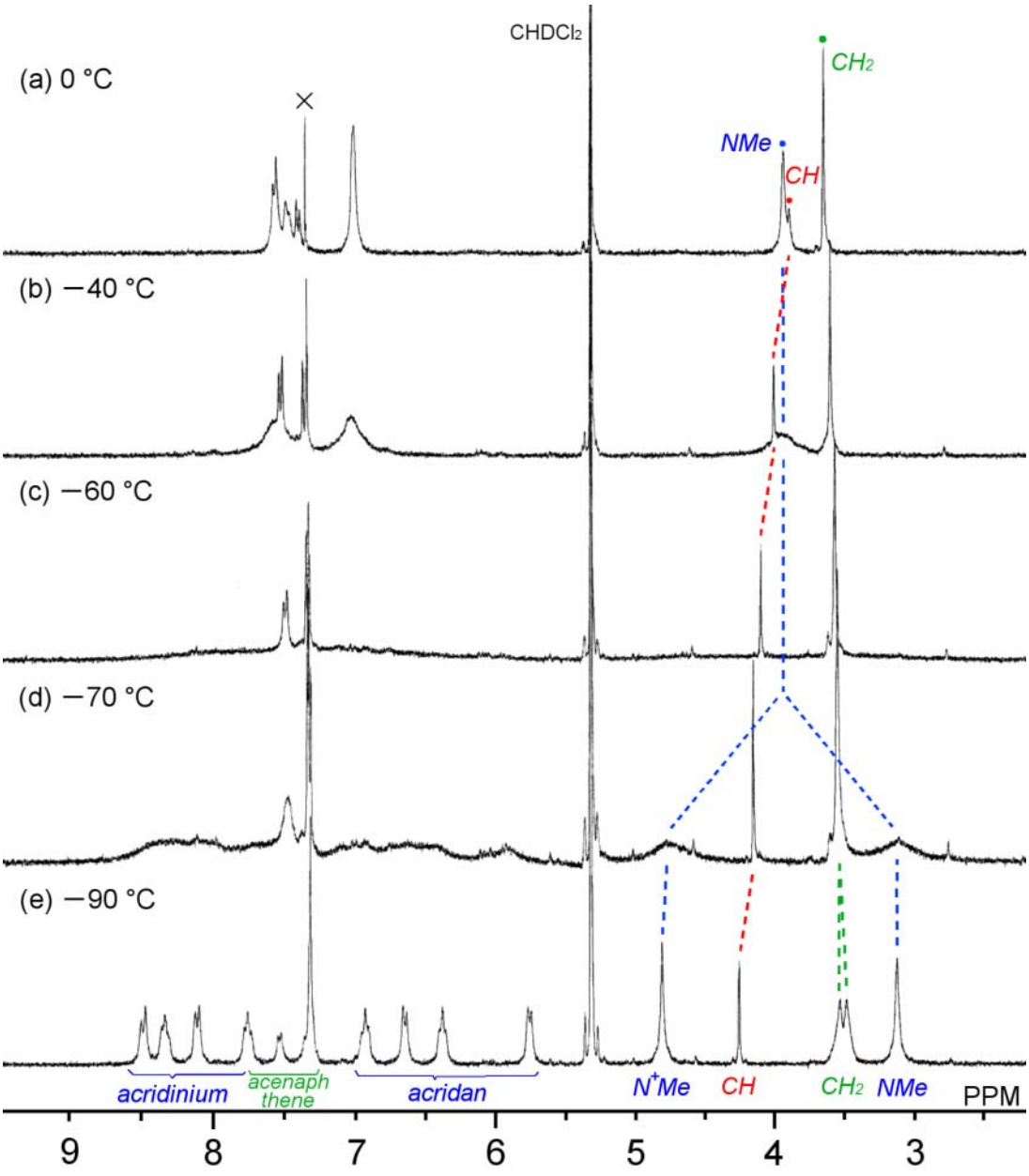


Figure S1. VT-NMR spectra of **1b**$^{+}$OTf^{-} at a) 0 °C, b) –40°C, c) –60°C, d) –70°C, and e) –90 °C in CD_2Cl_2

.

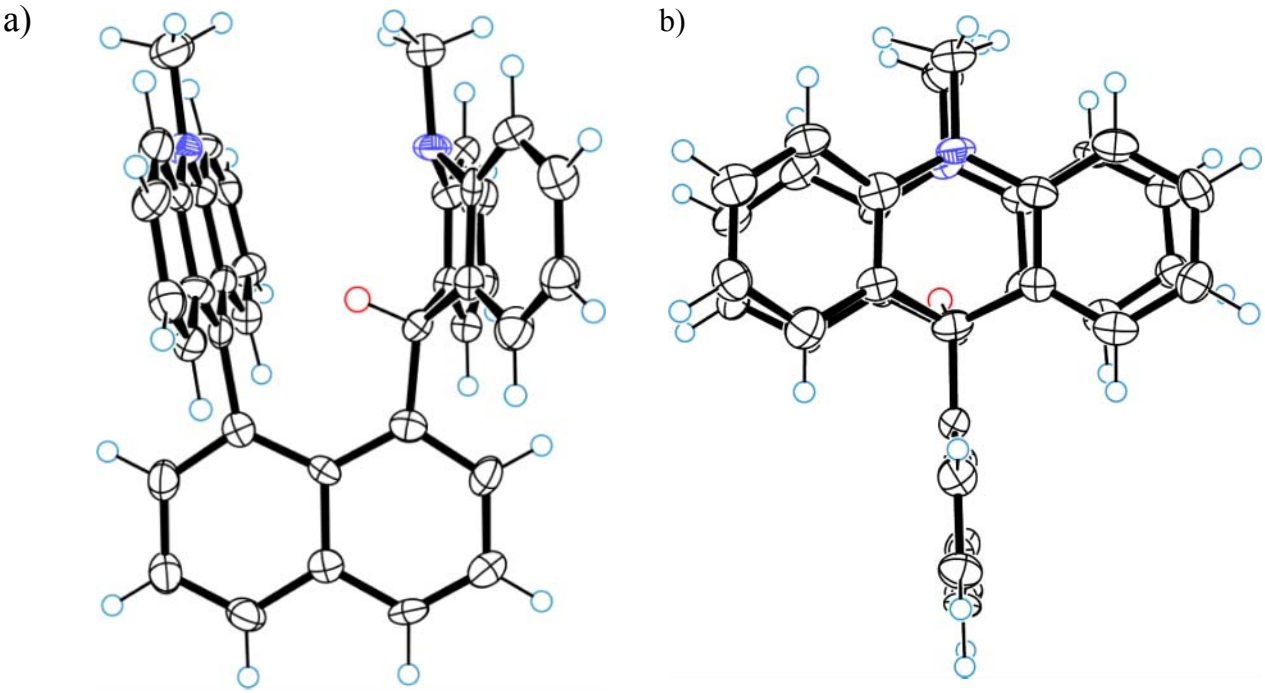


Figure S2. ORTEP drawing of **1a**$^{+}$ in **1a**$^{+}$OTf^{-}•acetone solvate determined by X-ray analysis at 133 K: (a) top view and (b) side view.

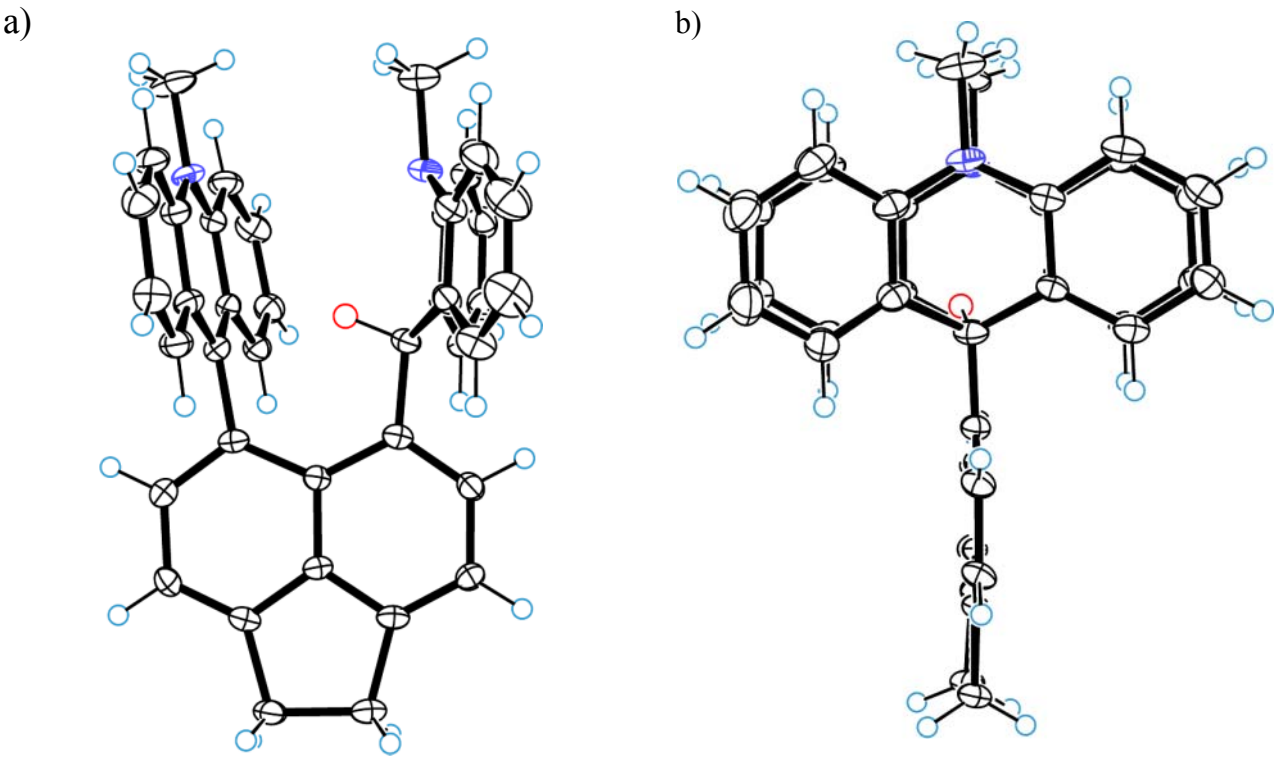


Figure S3. ORTEP drawing of **1b**$^{+}$ in **1b**$^{+}$OTf^{-}•chloroform solvate determined by X-ray analysis at 103 K: (a) top view and (b) side view.

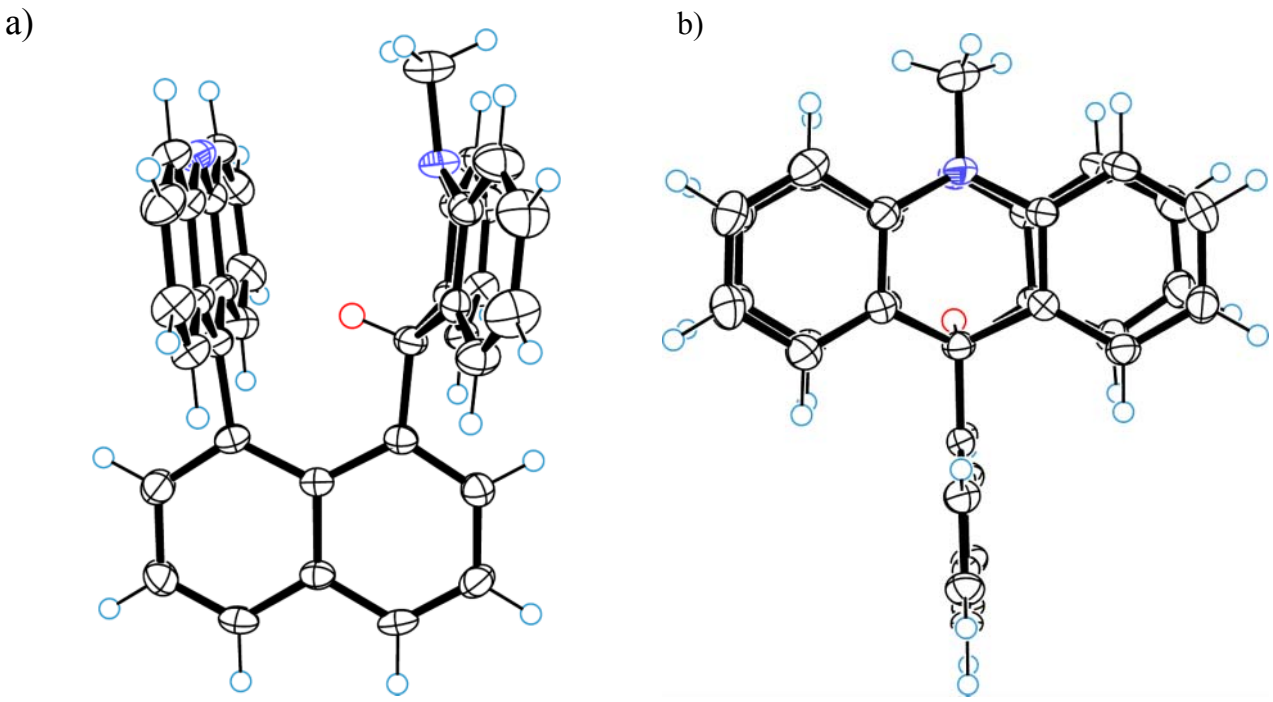


Figure S4. ORTEP drawing of **3a** determined by X-ray analysis at 113 K: (a) top view and (b) side view.

a) b)

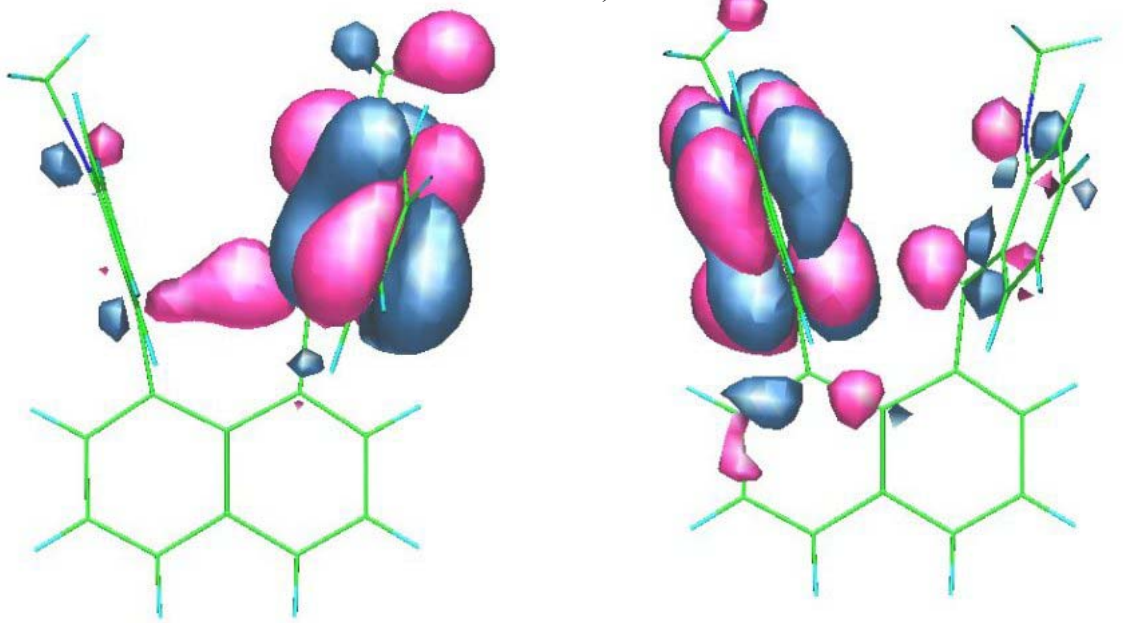


Figure S5. (a) HOMO (-7.4066 eV) and (b) LUMO (-5.9623 eV) of **1a**$^{+}$ calculated by B3LYP/6-31G*.

a) b)

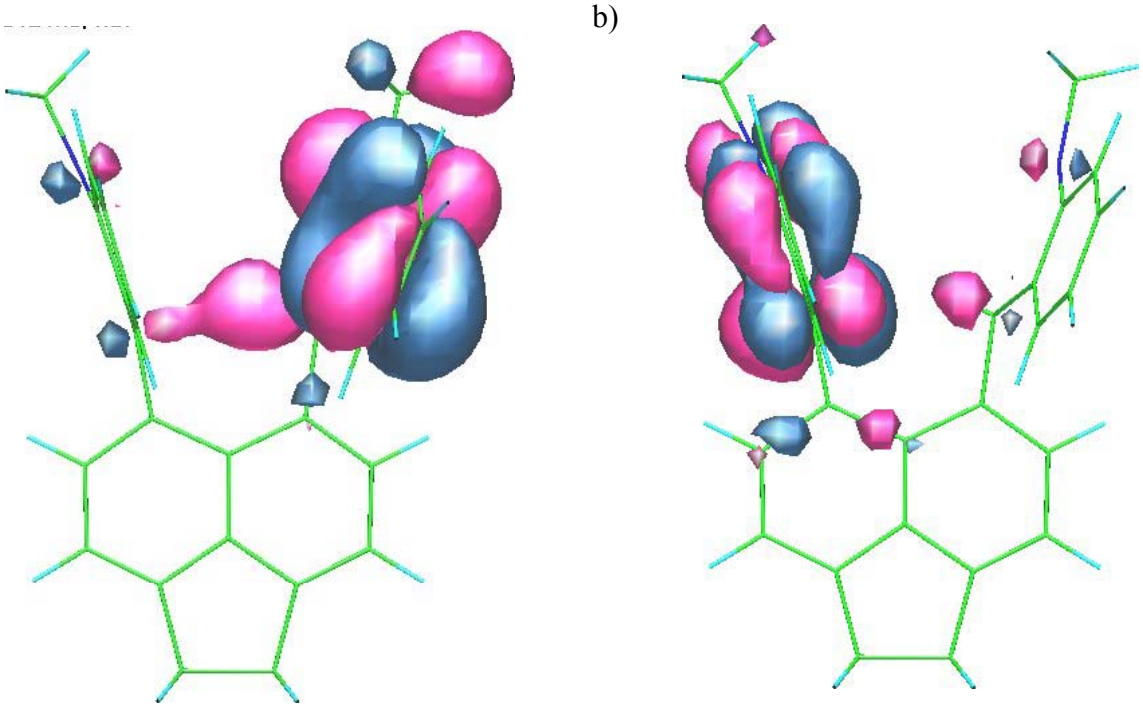


Figure S6. (a) HOMO (-7.2908 eV) and (b) LUMO (-5.9265 eV) of **1b**$^{+}$ calculated by B3LYP/6-31G*.

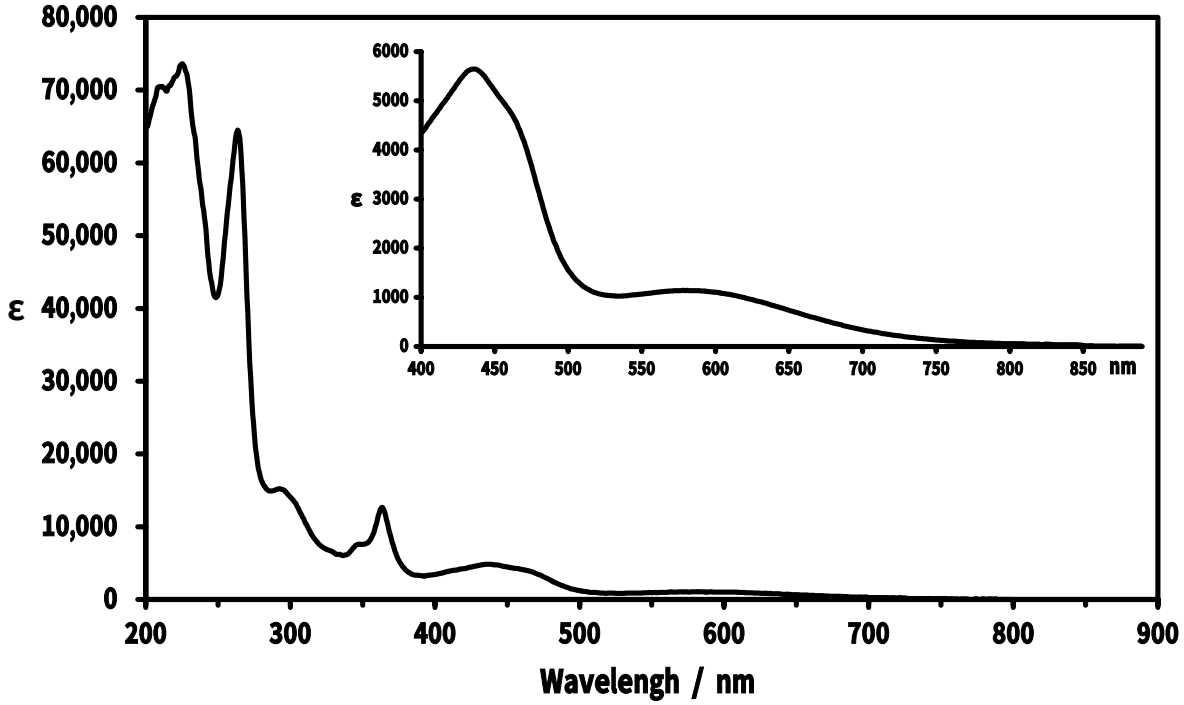


Figure S7. UV/Vis spectrum of **1a**$^{+}$OTf^{-} in CH_3CN. Inset: a magnified spectra in a long wavelength absorption band.

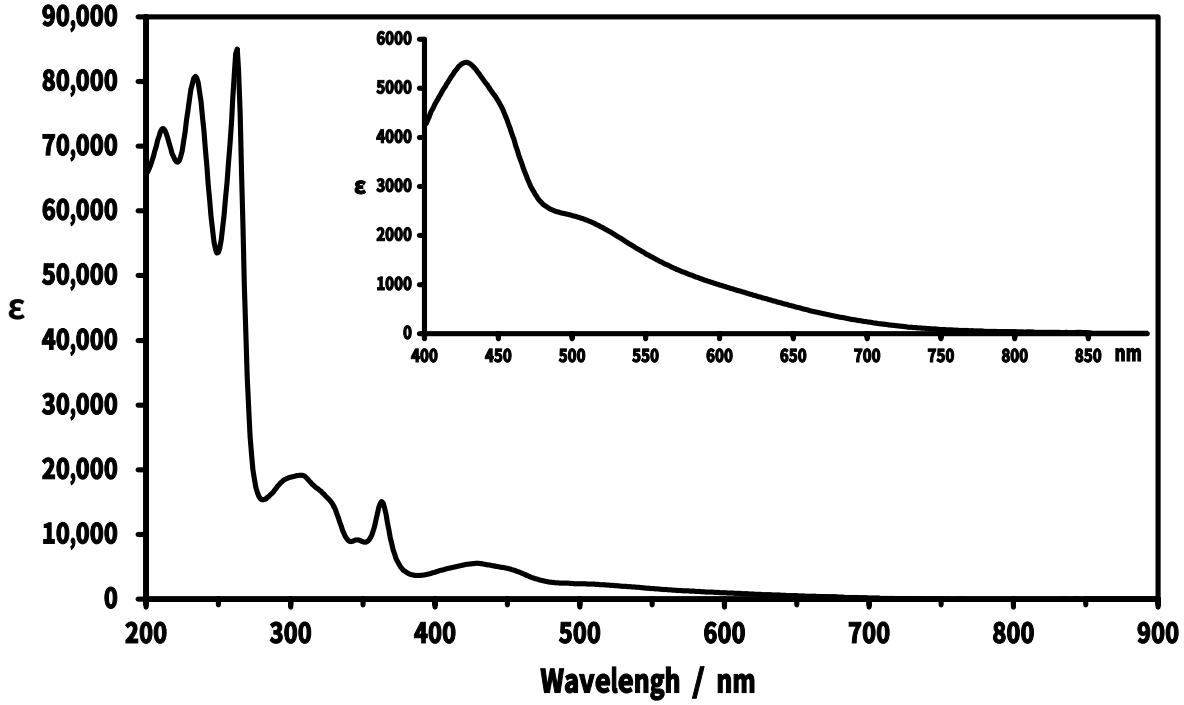


Figure S8. UV/Vis spectrum of **1b**$^{+}$OTf^{-} in CH_3CN. Inset: a magnified spectra in a long wavelength absorption band.

Optimized geometry of $1a^+$ at B3LYP/6-31G(d)

```
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 Framework group  C1[X(C38H29N2)]
 Deg. of freedom  201

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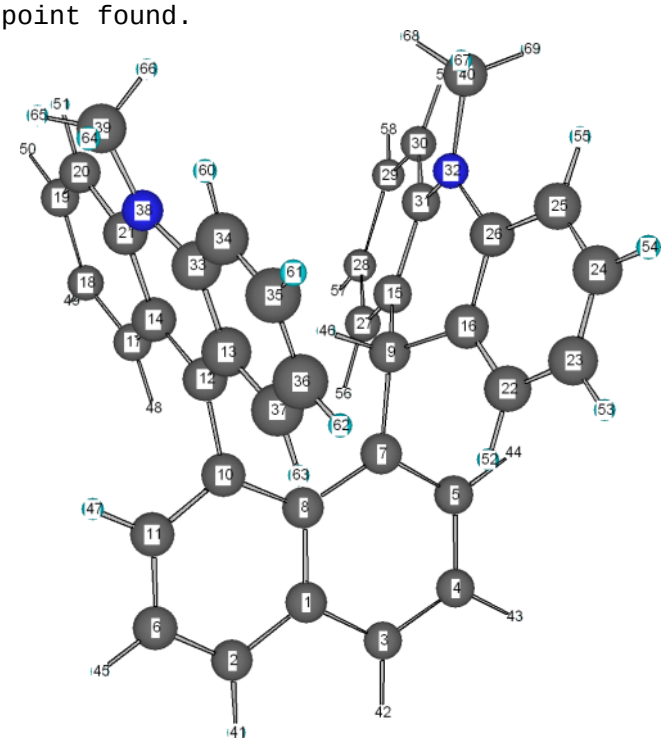

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Optimized geometry of $1b^{+}$ at B3LYP/6-31G(d)

```
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 Deg. of freedom  213

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 Maximum Displacement     0.000519     0.001800     YES
 RMS     Displacement     0.000098     0.001200     YES
 Predicted change in Energy=-2.509643D-09
 Optimization completed.
    -- Stationary point found.
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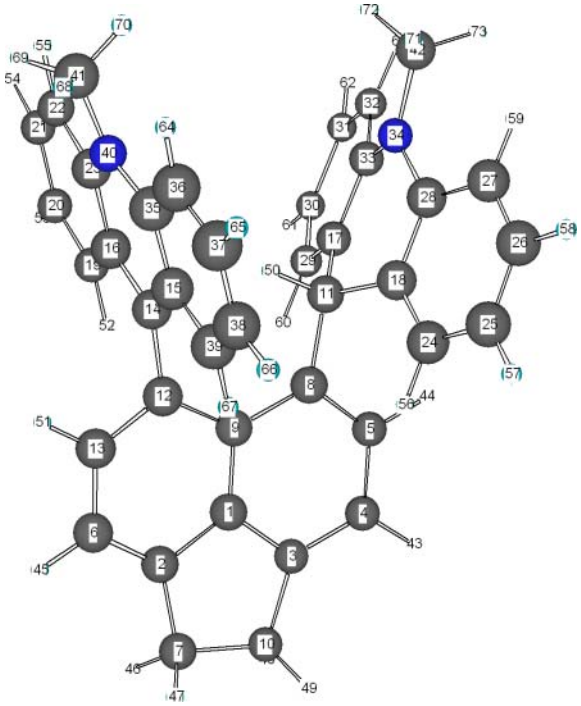

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56	1	0	1.180433	-1.739079	-2.484342
57	1	0	0.112386	-2.638047	-4.527687
58	1	0	-2.269106	-3.379985	-4.441623
59	1	0	-3.531276	-3.243138	-2.346683
60	1	0	1.181019	-1.738856	2.484255
61	1	0	0.113487	-2.637780	4.527873
62	1	0	-2.267946	-3.380030	4.442339
63	1	0	-3.530586	-3.243341	2.347660
64	1	0	-3.500386	3.046602	-2.463835
65	1	0	-2.377654	2.571186	-4.559102
66	1	0	-0.020665	1.759475	-4.607248
67	1	0	1.186161	1.400186	-2.475507
68	1	0	-3.747284	4.201931	-0.875449
69	1	0	-3.748988	4.200037	0.875455
70	1	0	-4.522396	2.851461	-0.002157
71	1	0	-4.493597	-1.979229	-0.882660
72	1	0	-4.493277	-1.979305	0.884166
73	1	0	-4.350714	-3.517458	0.000630

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