Electronic Supplementary Information

Self-sorting self-complementary assemblies of π-conjugated acyclic anion receptors

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1. Synthetic procedures and spectroscopic data

General Procedures: Starting materials were purchased from Wako Pure Chemical Industries Ltd., Nacalai Tesque Inc, and Sigma-Aldrich Co. and used without further purification unless otherwise stated. UV-visible spectra were recorded on a Hitachi U-3500 spectrometer. Fluorescence spectra and quantum yields were recorded on a Hitachi F-4500 fluorescence spectrometer for ordinary solution. NMR spectra used in the characterization of products were recorded on a JEOL ECA-600 600 MHz spectrometers. All NMR spectra were referenced to solvent. Matrix-assisted laser desorption ionization time-of-flight mass spectrometries (MALDI-TOF-MS) were recorded on a Shimadzu Axima-CFRplus using positive and negative modes. Electrospray ionization mass spectrometric studies (ESI-MS) were recorded on a BRUKER microTOF using a negative mode ESI-TOF method. Elemental analyses were performed on a Yanaco CHN corder MT series for carbon, hydrogen, and nitrogen and the oxygen flask combustion method, the Laboratory for Organic Elemental Microanalysis, Kyoto University. TLC analyses were carried out on aluminum sheets coated with silica gel 60 (Merck 5554). Column chromatography was performed on Sumitomo alumina KCG-1525, Wakogel C-200, C-300, and Merck silica gel 60 and 60H.

BF_2 complex of 1-(5-(3,4,5-trihexadecyloxyphenyl)pyrrol-2-yl)-3-(5-phenylpyrrol-2-yl)-1,3-propanedione (1d′), 1d. A dry THF solution (5 mL) of 2-phenylpyrrole (19.1 mg, 0.134 mmol) and 2-(3,4,5-trihexadecyloxyphenyl)pyrrole[S1] (116.2 mg, 0.134 mmol) was treated with malonyl chloride (9.44 μL, 0.134 mmol) at room temperature and stirred for 3 h at the same temperature. The mixture was washed with saturated aqueous Na_2CO_3 and water, dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. After removal of the solvent, the residue was chromatographed over flash silica gel column (eluent: 25% EtOAc/hexane) to give **1d′** (11.53 mg, 0.0107 mmol, 8%) as a yellow crude solid. R_f = 0.71 (eluent: 30% EtOAc/hexane). MALDI-TOF-MS (% intensity): *m/z* 1074.8 (100), 1075.8 (70). Calcd for $C_{71}H_{114}N_2O_5$ ($[M]^+$): 1074.87. Without further purification, **1d′** was used for next reaction. To a CH_2Cl_2 solution (5 mL) of **1d′** (11.53 mg, 0.0107 mmol) was added $BF_3{\cdot}OEt_2$ (2.05 μL, 0.0161 mmol) and was stirred for 20 min at room temperature. After removal of the solvent, the residue was chromatographed over flash silica gel column (eluent: 10% EtOAc/hexane) and recrystallization from $CHCl_3$/MeOH afforded **1d** (11.57 mg, 0.0103 mmol, 96%) as a red solid. R_f = 0.78 (eluent: 10% EtOAc/hexane). ^1H NMR (600 MHz, $CDCl_3$, 60 °C): δ (ppm) 9.74 (br, 1H, NH), 9.61 (br, 1H, NH), 7.65–7.64 (m, 2H, Ar-H), 7.49–7.46 (m, 1H, Ar-H), 7.40–7.37 (m, 2H, Ar-H), 7.22–7.20 (m, 2H, pyrrole-H), 6.79 (s, 2H, Ar-H), 6.74–6.73 (m, 1H, pyrrole-H), 6.65–6.64 (m, 1H, pyrrole-H), 6.53 (s, 1H, CH), 4.11 (J = 6.0 Hz, 4H, OCH_2), 4.06 (t, J = 7.2 Hz, 2H, OCH_2), 1.86 (quin, J = 6.0 Hz, 4H, $OCH_2\mathit{CH_2}$), 1.78 (quin, J = 7.2 Hz, 2H, $OCH_2\mathit{CH_2}$), 1.52 (tt, J = 7.8, 7.2 Hz, 6H, $OC_2H_4\mathit{CH_2}$), 1.43–1.28 (m, 72H, $OC_3H_6\mathit{C_{12}H_{24}}CH_3$), 0.90 (t, J = 6.6 Hz, 9H, $OC_{15}H_{30}\mathit{CH_3}$). UV/vis ($CHCl_3$, λ_{max} [nm] (ε, 10^5 $M^{-1}cm^{-1}$)): 512 (1.01). MALDI-TOF-MS (% intensity): *m/z* 1122.8 (100), 1123.8 (80). Calcd for $C_{71}H_{113}BF_2N_2O_5$ ($[M]^-$): 1122.87.

1-*tert*-Butoxycarbonyl-2-(3-carboxyphenyl)pyrrole and 2-(3-carboxyphenyl)pyrrole. To aqueous solution (3 mL) of Na_2CO_3 (1.93 g, 18.2 mmol) were added 1-*tert*-butoxycarbonylpyrrole-2-boronic acid (1.11 g, 5.23 mmol), 3-carboxyiodobenzene (1.09 g, 4.39 mmol), and tetrakis(triphenylphosphine)palladium(0) (306 mg, 0.264 mmol) in 1,2-dimethoxyethane (30 mL) at room temperature under nitrogen. The mixture was heated at 60 °C for 2 h and cooled to room temperature. The mixture was then dried over anhydrous $MgSO_4$ and evaporated to give a pale-yellow solid. The residue was then chromatographed over silica gel column (eluent: 5% MeOH/CH_2Cl_2) to give 1-*tert*-butoxycarbonyl-2-(3-carboxyphenyl)pyrrole (461 mg, 36%) as a yellow solid. R_f = 0.68 (12% MeOH/CH_2Cl_2). ^1H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 8.10 (s, 1H, Ar-H), 8.04 (d, J = 7.2 Hz, 1H, Ar-H), 7.60 (d, J = 9.0 Hz, 1H, Ar-H), 7.46 (d, J = 7.8 Hz, 1H, Ar-H), 7.40–7.39 (m, 1H, pyrrole-H), 6.26–6.25 (m, 2H, pyrrole-H), 1.39 (s, 9H, Boc). MALDI-TOF-MS (% intensity): *m/z* 285.6 (20), 286.1 (100). Calcd for $C_{16}H_{16}NO_4$ ($[M - H]^-$): 286.11. To the product 1-*tert*-butoxycarbonyl-2-(3-carboxyphenyl)pyrrole (461 mg, 1.58 mmol) was added ethylene glycol (10 mL) and was heated at 150 °C for 20 min, cooled, and partitioned between water and dichloromethane. The combined extracts were dried over anhydrous $MgSO_4$ and evaporated to give a black solid. The mixture was then chromatographed over silica gel column (eluent: 5% MeOH/CH_2Cl_2) to give a 2-(3-carboxyphenyl)pyrrole (168 mg, 0.890 mmol, 56%) as a white solid. R_f = 0.41 (eluent: 12% MeOH/CH_2Cl_2). ^1H NMR (600 MHz, DMSO-d_6, 20 °C): δ (ppm) 11.48 (br, 1H, NH), 8.18 (s, 1H, Ar-H), 7.83 (d, J = 7.8 Hz, 1H, Ar-H), 7.70 (d, J = 7.8 Hz, 1H, Ar-H), 7.45 (t, J = 7.8 Hz, 1H, Ar-H), 6.87–6.86 (m, 1H, pyrrole-H), 6.51–6.50 (m, 1H, pyrrole-H), 6.13–6.12 (m, 1H, pyrrole-H). MALDI-TOF-MS (% intensity): *m/z* 186.0 (100), 186.4 (46). Calcd for $C_{11}H_8NO_2$ ($[M - H]^-$): 186.06.

1-*tert*-Butoxycarbonyl-2-(4-carboxyphenyl)pyrrole and 2-(4-carboxyphenyl)pyrrole. To aqueous solution (3 mL) of Na_2CO_3 (589.1 mg, 5.56 mmol) were added 1-*tert*-butoxycarbonylpyrrole-2-boronic acid (333.1 mg, 1.57 mmol), 4-carboxyiodobenzene (321.4 mg, 1.30 mmol), and tetrakis(triphenylphosphine)palladium(0) (95.0 mg, 0.0822 mmol) in 1,2-dimethoxyethane (20 mL) at room temperature under nitrogen. The mixture was heated at 45 °C for 2 h and cooled to room temperature. The mixture was then dried over anhydrous $MgSO_4$ and evaporated to give a pale-yellow solid. The residue was then chromatographed over silica gel column (eluent: 6% $MeOH/CH_2Cl_2$) to give 1-*tert*-butoxycarbonyl-2-(4-carboxyphenyl)pyrrole (212.1 mg, 57%) as a white solid. R_f = 0.58 (12% $MeOH/CH_2Cl_2$). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 8.08 (d, J = 8.4 Hz, 2H, Ar-H), 7.45 (d, J = 8.4 Hz, 2H, Ar-H), 7.40–7.38 (m, 1H, pyrrole-H), 6.29–6.28 (m, 1H, pyrrole-H), 6.27–6.25 (m, 1H, pyrrole-H), 1.39 (s, 9H, Boc). MALDI-TOF-MS (% intensity): m/z 286.5 (100). Calcd for $C_{16}H_{17}NO_4$ ($[M]^-$): 287.11. 1-*tert*-butoxycarbonyl-2-(4-carboxyphenyl)pyrrole (155.7 mg, 0.54 mmol) was heated at 150 °C for 20 min and cooled to room temperature. The mixture was then chromatographed over silica gel column (eluent: 6% $MeOH/CH_2Cl_2$) to give a 2-(4-carboxyphenyl)pyrrole (58.1 mg, 0.310 mmol, 57%) as a white solid. R_f = 0.41 (eluent: 12% $MeOH/CH_2Cl_2$). ^{1}H NMR (600 MHz, DMSO-d_6, 20 °C): δ (ppm) 12.73 (br, 1H, OH), 11.48 (br, 1H, NH), 7.87 (d, J = 8.4 Hz, 2H, Ar-H), 7.70 (d, J = 8.4 Hz, 2H, Ar-H), 6.93–6.92 (m, 1H, pyrrole-H), 6.67–6.66 (m, 1H, pyrrole-H), 6.15–6.14 (m, 1H, pyrrole-H). MALDI-TOF-MS (% intensity): m/z 186.0 (100), 186.4 (45). Calcd for $C_{11}H_8NO_2$ ($[M-H]^-$): 186.06.

1-*tert*-Butoxycarbonyl-2-(3-methoxycarbonylphenyl)pyrrole and 2-(3-methoxycarbonylphenyl)pyrrole. To aqueous solution (5 mL) of Na_2CO_3 (1.93 g, 18.2 mmol) were added 1-*tert*-butoxycarbonylpyrrole-2-boronic acid (1.11 g, 5.23 mmol), 3-bromomethylbenzoate (943 mg, 4.39 mmol), and tetrakis(triphenylphosphine)palladium(0) (306 mg, 0.264 mmol) in 1,2-dimethoxyethane (30 mL) at room temperature under nitrogen. The mixture was heated at 70 °C for 4 h and cooled to room temperature. The mixture was then dried over anhydrous $MgSO_4$ and evaporated to give a pale-yellow solid. The residue was then chromatographed over silica gel column (eluent: 30% hexane/CH_2Cl_2) to give 1-*tert*-butoxycarbonyl-2-(3-methoxycarbonylphenyl)pyrrole (1.09 g, 83%) as a yellow oil. R_f = 0.55 (eluent: 30% hexane/CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 8.04–8.03 (m, 1H, Ar-H), 7.98–7.97 (m, 1H, Ar-H), 7.55–7.54 (m, 1H, Ar-H), 7.43 (t, J = 7.8 Hz, 1H, Ar-H), 7.38–7.37 (m, 1H, pyrrole-H), 6.25–6.23 (m, 2H, pyrrole-H), 3.96 (s, 3H, OCH_3), 1.34 (s, 9H, Boc). MALDI-TOF-MS (% intensity): m/z 301.1 (100). Calcd for $C_{17}H_{19}NO_4$ ($[M]^+$): 301.13. To the product 1-*tert*-butoxycarbonyl-2-(3-methoxycarbonylphenyl)pyrrole (1.09 g, 3.62 mmol) was added ethylene glycol (15 mL) and was heated at 170 °C for 20 min, cooled, and partitioned between water and dichloromethane. The combined extracts were dried over anhydrous $MgSO_4$ and evaporated to give a black solid. The mixture was then chromatographed over silica gel column (eluent: CH_2Cl_2) to give a 2-(3-methoxycarbonylphenyl)pyrrole (460 mg, 2.30 mmol, 64%) as a white solid. R_f = 0.45 (eluent: CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 8.56 (br, 1H, NH), 8.13–8.12 (m, 1H, Ar-H), 7.87–7.85 (m, 1H, Ar-H), 7.69–7.67 (m, 1H, Ar-H), 7.44 (t, J = 7.8 Hz, 1H, Ar-H), 6.25–6.23 (m, 1H, pyrrole-H), 6.61–6.60 (m, 1H, pyrrole-H), 6.33–6.31 (m, 1H, pyrrole-H), 3.96 (s, 3H, OCH_3). MALDI-TOF-MS (% intensity): m/z 201.0 (100). Calcd for $C_{12}H_{11}NO_2$ ($[M]^-$): 201.08.

1-*tert*-Butoxycarbonyl-2-(4-methoxycarbonylphenyl)pyrrole and 2-(4-methoxycarbonylphenyl)pyrrole.[S2] To aqueous solution (4 mL) of Na_2CO_3 (1.15 g, 10.8 mmol) were added 1-*tert*-butoxycarbonylpyrrole-2-boronic acid (7.58 mg, 3.57 mmol), 4-bromomethylbenzoate (772 mg, 3.59 mmol), and tetrakis(triphenylphosphine)palladium(0) (173 mg, 0.149 mmol) in 1,2-dimethoxyethane (40 mL) at room temperature under nitrogen. The mixture was heated at 70 °C for 4 h and cooled to room temperature. The mixture was then dried over anhydrous $MgSO_4$ and evaporated to give a pale-yellow solid. The residue was then chromatographed over silica gel column (eluent: 7% EtOAc/hexane) to give 1-*tert*-butoxycarbonyl-2-(4-methoxycarbonylphenyl)pyrrole (680 mg, 63%) as a yellow oil. R_f = 0.48 (eluent: 15% EtOAc/hexane). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 7.98 (d, J = 8.4 Hz, 2H, Ar-H), 7.51 (d, J = 8.4 Hz, 2H, Ar-H), 7.38–7.37 (m, 1H, pyrrole-H), 6.67–6.66 (m, 1H, pyrrole-H), 6.34–6.33 (m, 1H, pyrrole-H), 3.91 (s, 3H, OCH_3), 1.34 (s, 9H, Boc). MALDI-TOF-MS (% intensity): m/z 301.1 (100). Calcd for $C_{17}H_{19}NO_4$ ($[M]^+$): 301.13. To the product 1-*tert*-butoxycarbonyl-2-(4-methoxycarbonylphenyl)pyrrole (680 mg, 2.26 mmol) was added ethylene glycol (10 mL) and was heated at 170 °C for 30 min, cooled, and partitioned between water and dichloromethane. The combined extracts were dried over anhydrous $MgSO_4$ and evaporated to give a black solid. The mixture was then chromatographed over silica gel column (eluent: 25% EtOAc/hexane) to give 2-(4-methoxycarbonylphenyl)pyrrole (291 mg, 1.45 mmol, 64%) as a white solid. R_f = 0.41 (eluent: 30% EtOAc/hexane). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 8.56 (br, 1H, NH), 8.03 (d, J = 8.4 Hz, 2H, Ar-H), 7.52 (d, J = 8.4 Hz, 2H, Ar-H), 6.93–6.92 (m, 1H, pyrrole-H), 6.67–6.66 (m, 1H, pyrrole-H), 6.34–6.33 (m, 1H, pyrrole-H), 6.61–6.60 (m, 1H, pyrrole-H), 6.33–6.31 (m, 1H, pyrrole-H), 3.92 (s, 3H, OCH_3). MALDI-TOF-MS (% intensity): m/z 200.0 (100). Calcd for $C_{12}H_{10}NO_2$ ($[M-H]^-$): 200.08.

BF_2 complex of 1-(5-(3-carboxyphenyl)pyrrol-2-yl)-3-(5-(3,4,5-trihexadecyloxyphenyl)pyrrol-2-yl)-1,3-propanedione (2m′), 2m. A dry THF solution (20 mL) of 2-(3-carboxyphenyl)pyrrole (150 mg, 0.802 mmol) and 2-(3,4,5-trihexadecyloxyphenyl)pyrrole (552 mg, 0.535 mmol) was treated with malonyl chloride (117 μL, 0.802 mmol) at room temperature and stirred for 3 h at the same temperature. The mixture was washed with saturated aq. Na_2CO_3 and water, dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. After removal of the solvent, the residue was chromatographed over flash silica gel column (eluent: 5% MeOH/$CHCl_3$) to give **2m′** (192 mg, 0.171 mmol, 32%) as a yellow crude solid. R_f = 0.62 (eluent: 12% MeOH/CH_2Cl_2). MALDI-TOF-MS (% intensity): *m/z* 1118.8 (100), 1119.3 (90). Calcd for $C_{72}H_{114}N_2O_7$ ([M – H]$^-$): 1118.87. Without further purification, **2m′** was used for next reaction. To a dry THF solution (30 mL) of **2m′** (192 mg, 0.171 mmol) was added $BF_3{\cdot}OEt_2$ (21.0 μL, 0.170 mmol) and was stirred for 20 min at room temperature. After removal of the solvent, the residue was chromatographed over flash silica gel column (eluent: 5% MeOH/CH_2Cl_2) and recrystallization from $CHCl_3$/MeOH afforded **2m** (136 mg, 0.118 mmol, 69%) as a red solid. R_f = 0.55 (eluent: 12% MeOH/CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 9.68 (br, 1H, NH), 9.56 (br, 1H, NH), 8.36 (s, 1H, Ar-H), 8.08 (d, J = 7.8 Hz, 1H, Ar-H), 7.86 (d, J = 7.8 Hz, 1H, Ar-H), 7.58 (t, J = 7.8 Hz, 1H, Ar-H), 7.24–7.23 (m, 1H, pyrrole-H), 7.22–7.21 (m, 1H, pyrrole-H), 6.82–6.80 (m, 1H, pyrrole-H), 6.80 (s, 2H, Ar-H), 6.67–6.66 (m, 1H, pyrrole-H), 6.55 (s, 1H, CH), 4.07 (t, J = 6.0 Hz, 4H, OCH_2), 4.01 (t, J = 6.0 Hz, 2H, OCH_2), 1.87 (quin, J = 6.6 Hz, 4H, $OCH_2\mathit{CH_2}$), 1.76 (quin, J = 7.2 Hz, 2H, $OCH_2\mathit{CH_2}$), 1.50 (tt, J = 8.4, 7.8 Hz, 6H, $OC_2H_4\mathit{CH_2}$), 1.39–1.29 (m, 72H, $OC_3H_6\mathit{C_{12}H_{24}}CH_3$), 0.88 (t, J = 6.0 Hz, 9H, $OC_{15}H_{30}\mathit{CH_3}$). UV/vis ($CHCl_3$, λ_{max}[nm] (ε, 10^5 $M^{-1}cm^{-1}$): 511 (1.02). MALDI-TOF-MS (% intensity): *m/z* 1166.8 (100), 1167.6 (86). Calcd for $C_{72}H_{113}BF_2N_2O_7$ ([M – H]$^-$): 1166.87. Elemental analysis: calcd (%) for $C_{72}H_{113}BF_2N_2O_7{\cdot}H_2O$: C, 72.95; H, 9.78; B, 0.91; F, 3.21; N, 2.36; O, 10.80; found C 73.15, H 9.91, N 2.40 (for the species containing B and F, the exact values of these elements along with O cannot be estimated).

TBA salt of 2m$^-$, 2m$^-$·TBA. To a $CHCl_3$ solution (20 mL) of **2m** (2.02 mg, 0.00171 mmol) was added methanol solution of TBAOH (2.05 mg, 0.00257 mmol) and was stirred for 1 min at room temperature. The mixture was washed with water, dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. Removal of the solvent gave **2m**$^-$ as a TBA salt (2.05 mg, 0.00148 mmol, 85%). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 15.28 (br, 1H, NH), 13.62 (br, 1H, NH), 9.55 (s, 1H, CH), 8.24 (s, 1H, Ar-H), 7.72–7.70 (m, 1H, Ar-H), 7.57–7.55 (m, 2H, Ar-H), 7.45 (s, 2H, Ar-H), 7.38–7.37 (m, 1H, pyrrole-H), 7.32–7.31 (m, 1H, pyrrole-H), 7.03–7.00 (m, 1H, Ar-H), 6.64–6.61 (m, 2H, pyrrole-H), 4.07 (t, J = 6.0 Hz, 4H, OCH_2), 3.93–3.89 (m, 6H, OCH_2), 3.10–3.03 (m, 8H, NCH_2), 1.71–1.55 (m, 6H, $OCH_2\mathit{CH_2}$), 1.52–1.45 (m, 14H, $OC_2H_4\mathit{CH_2}$ + $NCH_2\mathit{CH_2}$), 1.30–1.22 (m, 80H, $OC_3H_6\mathit{C_{12}H_{24}}CH_3$ + $NC_2H_4\mathit{CH_2}$), 0.89–0.86 (m, 21H, $OC_{15}H_{30}\mathit{CH_3}$ + $NC_3H_6\mathit{CH_3}$). UV/vis ($CHCl_3$, λ_{max}[nm] (ε, 10^5 $M^{-1}cm^{-1}$)): 511 (0.71). ESI-TOF-MS (% intensity): *m/z* 1166.4 (100), 1165.9 (81). Calcd for $C_{144}H_{226}B_2F_4N_4O_{14}$ ([2M]$^{2-}$): 2331.70 (A half value of the calculated mass was observed due to dianion). Elemental analysis: calcd (%) for $C_{88}H_{148}BF_2N_3O_7{\cdot}1.5H_2O$: C, 73.61; H, 10.60; B, 0.75; F, 2.65; N, 2.93; O, 9.47; found C 73.50, H 10.47, N 3.02 (for the species containing B and F, the exact values of these elements along with O cannot be estimated).

BF_2 complex of 3-(5-(3,4,5-trihexadecyloxyphenyl)-pyrrol-2-yl)-1-(5-(3-methoxycarbonylphenyl)-pyrrol-2-yl)-1,3-propanedione (2me′), 2me. A CH_2Cl_2 solution (20 mL) of 2-(3-methoxycarbonylphenyl)pyrrole (160 mg, 0.802 mmol) and 2-(3,4,5-trihexadecyloxyphenyl)pyrrole[S1] (552 mg, 0.534 mmol) was treated with malonyl chloride (117 μL, 0.802 mmol) at room temperature and stirred for 3 h at the same temperature. The mixture was washed with saturated aqueous Na_2CO_3 and water, dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. After removal of the solvent, the residue was chromatographed over flash silica gel column (eluent: 2% MeOH/CH_2Cl_2) to give **2me′** (84.6 mg, 0.0748 mmol, 14%) as a yellow crude solid. R_f = 0.25 (eluent: 1% MeOH/CH_2Cl_2). MALDI-TOF-MS (% intensity): *m/z* 1132.8 (100), 1133.6 (84). Calcd for $C_{73}H_{116}N_2O_7$ ([M]$^-$): 1132.89. Without further purification, **2me′** was used for next reaction. To a CH_2Cl_2 solution (20 mL) of **2me′** (84.6 mg, 0.0748 mmol) was added $BF_3{\cdot}OEt_2$ (27.6 μL, 0.224 mmol) and was stirred for 20 min at room temperature. After removal of the solvent, the residue was chromatographed over flash silica gel column (eluent: 2% MeOH/CH_2Cl_2) and recrystallization from CH_2Cl_2/hexane afforded BF_2 complex of **2me** (61 mg, 0.0517 mmol, 69%) as a red solid. R_f = 0.75 (eluent: 2% MeOH/CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 60 °C): δ (ppm) 9.77 (br, 1H, NH), 9.61 (br, 1H, NH), 8.31–8.30 (m, 1H, Ar-H), 8.05 (d, J = 7.8 Hz, 1H, Ar-H), 7.83 (d, 1H, J = 7.8 Hz, Ar-H), 7.56 (t, J = 7.8 Hz, 1H, Ar-H), 7.24–7.23 (m, 1H, pyrrole-H), 7.22–7.21 (m, 1H, pyrrole-H), 6.81–6.79 (m, 1H, pyrrole-H), 6.80–6.79 (m, 2H, pyrrole-H + Ar-H), 6.67–6.66 (m, 1H, pyrrole-H), 6.55 (s, 1H, CH), 4.06 (t, J = 6.0 Hz, 4H, OCH_2), 4.01 (t, J = 7.2 Hz, 2H, OCH_2), 3.96 (s, 3H, OCH_3), 1.86 (quin, J = 6.0 Hz, 4H, $OCH_2\mathit{CH_2}$), 1.78 (quin, J = 7.2 Hz, 2H, $OCH_2\mathit{CH_2}$), 1.52 (tt, J = 7.8, 7.2 Hz, 6H, $OC_2H_4\mathit{CH_2}$), 1.43–1.28 (m, 72H, $OC_3H_6\mathit{C_{12}H_{24}}CH_3$), 0.90 (t, J = 6.6 Hz, 9H, $OC_{15}H_{30}\mathit{CH_3}$). UV/vis ($CHCl_3$, λ_{max} [nm] (ε, 10^5 $M^{-1}cm^{-1}$)): 517 (1.12). MALDI-TOF-MS (% intensity): *m/z* 1180.0 (84), 1180.8 (100). Calcd for $C_{73}H_{115}BF_2N_2O_7$ ([M]$^-$): 1180.88.

BF_2 complex of 1-(5-(4-carboxyphenyl)pyrrol-2-yl)-3-(5-(3,4,5-trihexadecyloxyphenyl)pyrrol-2-yl)-1,3-propanedione (2p′), 2p. A dry THF solution (12 mL) of 2-(4-carboxyphenyl)pyrrole (100 mg, 0.534 mmol) and 2-(3,4,5-trihexadecyloxyphenyl)pyrrole[S1] (368 mg, 0.356 mmol) was treated with malonyl chloride (78.0 μL, 0.554 mmol) at room temperature and stirred for 3 h at the same temperature. The mixture was washed with saturated aq. Na_2CO_3 and water, dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. After removal of the solvent, the residue was chromatographed over flash silica gel column (eluent: 5% MeOH/CH_2Cl_2) to give **2p′** (89.7 mg, 0.0801 mmol, 15%) as a yellow crude solid. R_f = 0.64 (eluent: 12% MeOH/CH_2Cl_2). MALDI-TOF-MS (% intensity): *m/z* 1119.6 (72), 1120.8 (100). Calcd for $C_{72}H_{115}N_2O_7$ ([M + H]$^+$): 1119.87. Without further purification, **2p′** was used for next reaction. To a dry THF solution (20 mL) of **2p′** (89.7 mg, 0.0801 mmol) was added $BF_3{\cdot}OEt_2$ (29.4 µL, 0.240 mmol) and was stirred for 20 min at room temperature. After removal of the solvent, the residue was chromatographed over flash silica gel column (eluent: 5% MeOH/CH_2Cl_2) and recrystallization from $CHCl_3$/MeOH afforded **2p** (92.2 mg, 0.0791 mmol, 98%) as a red solid. R_f = 0.58 (eluent: 12% MeOH/CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 9.69 (br, 1H, NH), 9.55 (br, 1H, NH), 8.17–8.15 (m, 2H, Ar-H), 7.72–7.71 (m, 2H, Ar-H), 7.24–7.23 (m, 1H, pyrrole-H), 7.25–7.23 (m, 1H, pyrrole-H), 6.85–6.82 (m, 1H, pyrrole-H), 6.80–6.77 (m, 2H, Ar-H), 6.67–6.63 (m, 1H, pyrrole-H), 6.53 (s, 1H, CH), 4.06 (t, J = 6.0 Hz, 4H, OCH_2), 4.00 (t, J = 6.0 Hz, 2H, OCH_2), 1.86 (quin, J = 6.6 Hz, 4H, $OCH_2\mathit{CH_2}$), 1.76 (quin, J = 7.2 Hz, 2H, $OCH_2\mathit{CH_2}$), 1.49 (tt, J = 8.4, 7.8 Hz, 6H, $OC_2H_4\mathit{CH_2}$), 1.38–1.28 (m, 72H, $OC_3H_6\mathit{C_{12}H_{24}}CH_3$), 0.88 (t, J = 6.0 Hz, 9H, $OC_{15}H_{30}\mathit{CH_3}$). UV/vis ($CHCl_3$, λ_{max}[nm] (ε, 10^5 $M^{-1}cm^{-1}$)): 517 (0.79). MALDI-TOF-MS (% intensity): *m/z* 1167.8 (100), 1168.7 (80). Calcd for $C_{72}H_{114}BF_2N_2O_7$ ([M + H]$^+$): 1167.87. Elemental analysis: calcd (%) for $C_{72}H_{113}BF_2N_2O_7{\cdot}H_2O$: C, 72.95; H, 9.78; B, 0.91; F, 3.21; N, 2.36; O, 10.80; found C 72.99, H 9.92, N 2.38 (for the species containing B and F, the exact values of these elements along with O cannot be estimated).

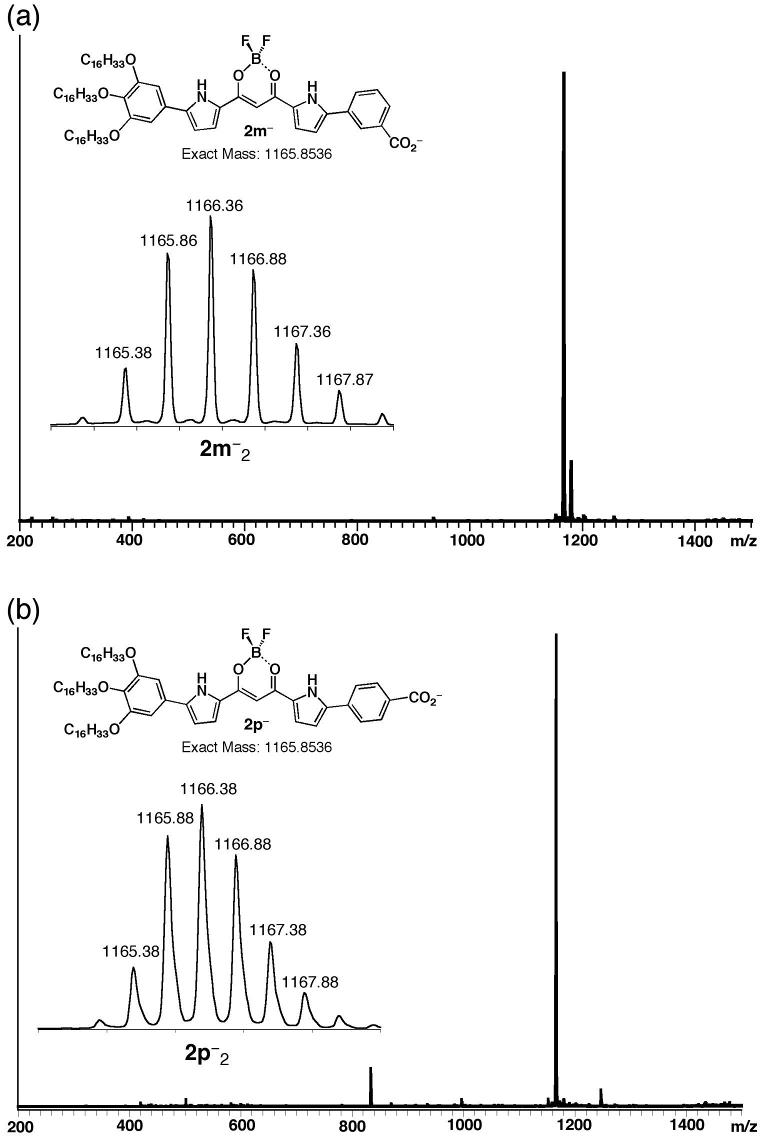
TBA salt of 2p$^-$, 2p$^-$·TBA. To a $CHCl_3$ solution (20 mL) of **2p** (2.00 mg, 0.00171 mmol) was added methanol solution of TBAOH (2.05 mg, 0.00257 mmol) and was stirred for 1 min at room temperature. The mixture was washed with water, dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. Removal of the solvent gave **2p$^-$** as a TBA salt (2.12 mg, 0.00151 mmol, 88%). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 14.43 (br, 1H, NH), 12.45 (br, 1H, NH), 8.86 (s, 1H, CH), 8.00–7.98 (m, 2H, Ar-H), 7.69–7.68 (m, 2H, Ar-H), 7.37–7.36 (m, 1H, pyrrole-H), 7.27 (s, 2H, Ar-H), 7.25–7.24 (m, 1H, pyrrole-H), 6.66–6.65 (m, 1H, pyrrole-H), 6.52–6.51 (m, 1H, pyrrole-H), 4.07–4.05 (t, J = 6.0 Hz, 4H, OCH_2), 3.92–3.88 (m, 6H, OCH_2), 3.10–3.03 (m, 8H, NCH_2), 1.71–1.69 (m, 6H, $OCH_2\mathit{CH_2}$), 1.52–1.46 (m, 14H, $OC_2H_4\mathit{CH_2}$ + $NCH_2\mathit{CH_2}$), 1.30–1.22 (m, 80H, $OC_3H_6\mathit{C_{12}H_{24}}CH_3$ + $NC_2H_4\mathit{CH_2}$), 0.88–0.85 (m, 21H, $OC_{15}H_{30}\mathit{CH_3}$ + $NC_3H_6\mathit{CH_3}$). UV/vis ($CHCl_3$, λ_{max}[nm] (ε, 10^5 $M^{-1}cm^{-1}$)): 515 (1.62). ESI-TOF-MS (% intensity): *m/z* 1165.9 (85), 1166.4 (100). Calcd for $C_{144}H_{226}B_2F_4N_4O_{14}$ ([2M]$^{2-}$): 2331.70 (A half value of the calculated mass was observed due to the formation of dianion). Elemental analysis: calcd (%) for $C_{88}H_{148}BF_2N_2O_7{\cdot}3H_2O$: C, 72.25; H, 10.61; B, 0.74; F, 2.60; N, 2.87; O, 10.94; found C 72.74, H 11.10, N 2.89 (for the species containing B and F, the exact values of these elements along with O cannot be estimated).

BF_2 complex of 3-(5-(3,4,5-trihexadecyloxyphenyl)-pyrrol-2-yl)-1-(5-(4-methoxycarbonylphenyl)-pyrrol-2-yl)-1,3-propanedione (2pe′), 2pe. A CH_2Cl_2 solution (15 mL) of 2-(4-methoxycarbonylphenyl)pyrrole (121 mg, 0.603 mmol) and 2-(3,4,5-trihexadecyloxyphenyl)pyrrole[S1] (348 mg, 0.402 mmol) was treated with malonyl chloride (82.0 µL, 0.603 mmol) at room temperature and stirred for 3 h at the same temperature. The mixture was washed with saturated aqueous Na_2CO_3 and water, dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. After removal of the solvent, the residue was chromatographed over flash silica gel column (eluent: 1% MeOH/CH_2Cl_2) to give **2pe′** (72.8 mg, 0.0643 mmol, 16%) as a yellow crude solid. R_f = 0.22 (eluent: 1% MeOH/CH_2Cl_2). MALDI-TOF-MS (% intensity): *m/z* 1131.9 (80), 1132.9 (100). Calcd for $C_{73}H_{116}N_2O_7$ ([M]$^-$): 1132.89. Without further purification, **2pe′** was used for next reaction. To a CH_2Cl_2 solution (20 mL) of **2pe′** (72.8 mg, 0.0643 mmol) was added $BF_3{\cdot}OEt_2$ (24.6 µL, 0.193 mmol) and was stirred for 20 min at room temperature. After removal of the solvent, the residue was chromatographed over flash silica gel column (eluent: 2% MeOH/CH_2Cl_2) and recrystallization from CH_2Cl_2/hexane afforded **2pe** (72.1 mg, 0.0611 mmol, 95%) as a red solid. R_f = 0.81 (eluent: 2% MeOH/CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 60 °C): δ (ppm) 9.64 (br, 1H, NH), 9.51 (br, 1H, NH), 8.14–8.13 (m, 2H, Ar-H), 7.70–7.68 (m, 2H, Ar-H), 7.24–7.23 (m, 1H, pyrrole-H), 7.20–7.19 (m, 1H, pyrrole-H), 6.82–6.81 (m, 1H, pyrrole-H), 6.80 (s, 2H, Ar-H), 6.66–6.65 (m, 1H, pyrrole-H), 6.55 (s, 1H, CH), 4.08 (t, J = 6.0 Hz, 4H, OCH_2), 4.03 (t, J = 7.2 Hz, 2H, OCH_2), 3.96 (s, 3H, OCH_3), 1.86 (quin, J = 6.0 Hz, 4H, $OCH_2\mathit{CH_2}$), 1.88 (quin, J = 7.2 Hz, 2H, $OCH_2\mathit{CH_2}$), 1.52 (tt, J = 7.8, 7.2 Hz, 6H, $OC_2H_4\mathit{CH_2}$), 1.43–1.28 (m, 72H, $OC_3H_6\mathit{C_{12}H_{24}}CH_3$), 0.90 (t, J = 6.6 Hz, 9H, $OC_{15}H_{30}\mathit{CH_3}$). UV/vis ($CHCl_3$, λ_{max} [nm] (ε, 10^5 M^{-1} cm^{-1})): 517 (1.12). MALDI-TOF-MS (% intensity): *m/z* 1180.9 (100), 1181.6 (60). Calcd for $C_{73}H_{115}BF_2N_2O_7$ ([M]$^-$): 1180.88.

BF_2 complex of 1-(5-(4-carboxyphenyl)pyrrol-2-yl)-3-(5-(3,4,5-tridodecyloxyphenyl)pyrrol-2-yl)-1,3-propanedione (3p′), 3p. A dry THF solution (30 mL) of 2-(4-carboxyphenyl)pyrrole (225 mg, 1.20 mmol) and 2-(3,4,5-tridodecyloxyphenyl)pyrrole[S1] (696 mg, 0.801 mmol) was treated with malonyl chloride (175 µL, 1.20 mmol) at room temperature and stirred for 3 h at the same temperature. The mixture was washed with saturated aq. Na_2CO_3 and water, dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. After removal of the solvent, the residue was chromatographed over flash silica gel column (eluent: 5% MeOH/CH_2Cl_2) to give **3p′** (145 mg, 0.152 mmol, 19%) as a yellow crude solid. R_f = 0.63 (eluent: 12% MeOH/CH_2Cl_2). MALDI-TOF-MS (% intensity): *m/z* 949.6 (100), 950.1

(80). Calcd for $C_{60}H_{89}N_2O_7$ ($[M - H]^-$): 949.67. Without further purification, **3p′** was used for next reaction. To a dry THF solution (30 mL) of **3p′** (145 mg, 0.152 mmol) was added $BF_3{\cdot}OEt_2$ (55.7 μL, 0.456 mmol) and was stirred for 20 min at room temperature. After removal of the solvent, the residue was chromatographed over flash silica gel column (eluent: 5% MeOH/CH_2Cl_2) and recrystallization from $CHCl_3$/MeOH afforded **3p** (147 mg, 0.147 mmol, 97%) as a red solid. R_f = 0.58 (eluent: 12% MeOH/CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): *δ* (ppm) 9.81 (br, 1H, NH), 9.63 (br, 1H, NH), 8.16–8.15 (m, 2H, Ar-H), 7.73–7.72 (m, 2H, Ar-H), 7.24–7.23 (m, 1H, pyrrole-H), 7.20–7.19 (m, 1H, pyrrole-H), 6.84–6.83 (m, 1H, pyrrole-H), 6.73 (s, 2H, Ar-H), 6.67–6.66 (m, 1H, pyrrole-H), 6.54 (s, 1H, CH), 4.06 (t, *J* = 6.0 Hz, 4H, OCH_2), 4.00 (t, *J* = 6.0 Hz, 2H, OCH_2), 1.86 (quin, *J* = 6.6 Hz, 4H, $OCH_2\mathit{CH_2}$), 1.76 (quin, *J* = 7.2 Hz, 2H, $OCH_2\mathit{CH_2}$), 1.49 (tt, *J* = 8.4, 7.8 Hz, 6H, $OC_2H_4\mathit{CH_2}$), 1.38–1.28 (m, 48H, $OC_3H_6\mathit{C_8H_{16}}CH_3$), 0.88 (t, *J* = 6.0 Hz, 9H, $OC_{11}H_{22}\mathit{CH_3}$). UV/vis ($CHCl_3$, λ_{max}[nm] (ε, 10^5 $M^{-1}cm^{-1}$)): 518 (1.19). MALDI-TOF-MS (% intensity): *m/z* 997.6 (100), 998.5 (98). Calcd for $C_{60}H_{88}BF_2N_2O_7$ ($[M - H]^-$): 997.67.

TBA salt of 3p$^-$, 3p$^-$·TBA. To a $CHCl_3$ solution (20 mL) of **3p** (2.01 mg, 0.00201 mmol) was added methanol solution of TBAOH (2.40 mg, 0.00302 mmol) and was stirred for 1 min at room temperature. The mixture was washed with water, dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. Removal of the solvent gave **3p$^-$** as a TBA salt (2.17 mg, 0.00175 mmol, 87%). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): *δ* (ppm) 14.43 (br, 1H, NH), 12.45 (br, 1H, NH), 8.87 (s, 1H, CH), 8.00–7.99 (m, 2H, Ar-H), 7.69–7.68 (m, 2H, Ar-H), 7.37–7.36 (m, 1H, pyrrole-H), 7.27 (s, 2H, Ar-H), 7.25–7.24 (m, 1H, pyrrole-H), 6.66–6.65 (m, 1H, pyrrole-H), 6.52–6.51 (m, 1H, pyrrole-H), 4.07–4.05 (t, *J* = 6.0 Hz, 4H, OCH_2), 3.92–3.88 (m, 6H, OCH_2), 3.10–3.03 (m, 8H, NCH_2), 1.71–1.69 (m, 6H, $OCH_2\mathit{CH_2}$), 1.50–1.44 (m, 14H, $OC_2H_4\mathit{CH_2}$ + $NCH_2\mathit{CH_2}$), 1.28–1.22 (m, 56H, $OC_3H_6\mathit{C_8H_{16}}CH_3$ + $NC_2H_4\mathit{CH_2}$), 0.92–0.81 (m, 21H, $OC_{11}H_{22}\mathit{CH_3}$ + $NC_3H_6\mathit{CH_3}$). UV/vis ($CHCl_3$, λ_{max}[nm] (ε, 10^5 $M^{-1}cm^{-1}$)): 517 (1.41). ESI-TOF-MS (% intensity): *m/z* 997.7 (98), 998.2 (100). Calcd for $C_{120}H_{178}B_2F_4N_4O_{14}$ ($[2M]^{2-}$): 1995.34 (A half value of the calculated mass was observed due to the formation of dianion).



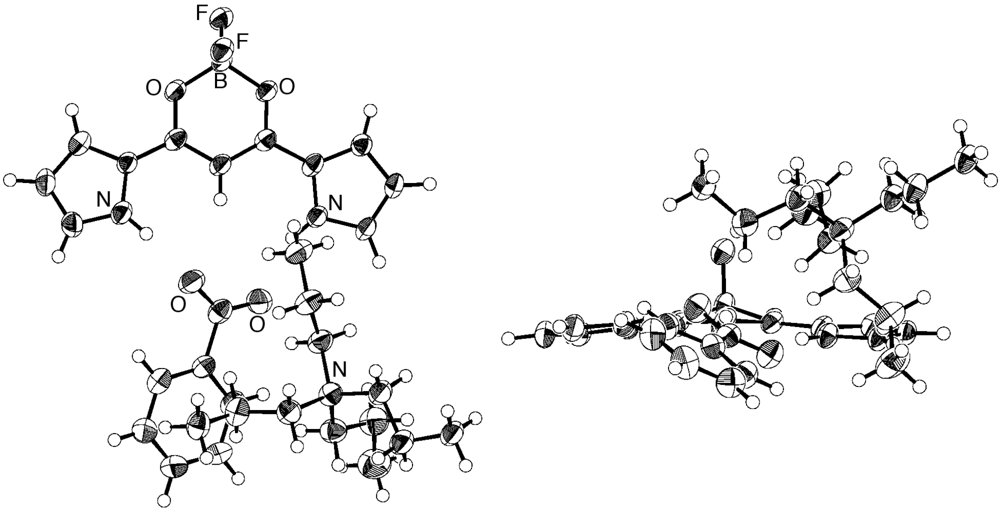
Supporting Figure 1 ESI-TOF-MS at negative mode of (a) **2m**$^{-}_{2}$ and (b) **2p**$^{-}_{2}$ as TBA salts from CH_3CN solutions (1 × 10^{-6} M). The absence of the intervals except for *m*/*z* = 0.5 can exclude the formation of other assemblies and monomeric states.

[S1] H. Maeda, Y. Haketa and T. Nakanishi, *J. Am. Chem. Soc.*, 2007, **129**, 13661.

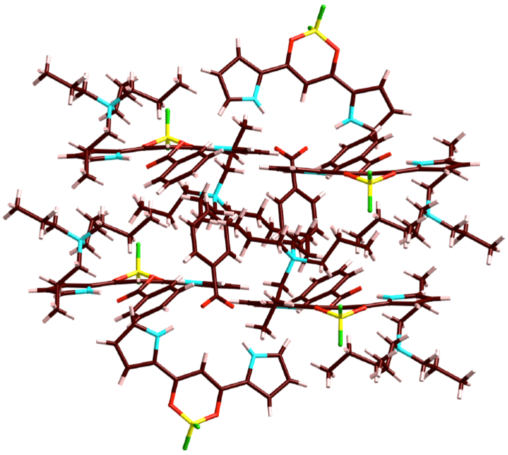
[S2] First trial synthesizing this molecule was for preparation of formyl-substituted anion receptors: H. Maeda, R. Fujii and Y. Haketa, *Eur. J. Org. Chem.*, 2010, 1469.

2. X-ray crystallographic data for 1a·benzoate

X-ray Single-Crystal Analysis. A single crystal of **1a**·benzoate·TPA was obtained by vapor diffusion of *i*-propyl ether into an EtOAc solution of **1a** and 1equiv of TPACl. The data crystal was a yellow prism of approximate dimensions 0.50 mm × 0.20 mm × 0.20 mm. Data was collected at 93 K on a Rigaku RAXIS-RAPID diffractometer with graphite monochromated Cu-Kα radiation (λ = 1.54187Å), structure was solved by direct method. Crystal data for **1a**·benzoate·TPA (from EtOAc/*i*-propyl ether): $C_{30}H_{42}N_3O_4BF_2$, Mw = 557.48, monoclinic, $P2_1/a$ (no. 14), a = 18.0991(3), b = 10.0405(2), c = 18.2608(3) Å, β = 113.7402(10)°, V = 3037.62(9) Å^3, T = 93(2)K, Z = 4, D_c = 1.219 g/cm^3, μ(Cu-Kα) = 0.724 mm^{-1}, R_1 = 0.0720, wR_2 = 0.1867, GOF = 1.219 ($I > 2\sigma(I)$). The non-hydrogen atoms were refined anisotropically. The calculations were performed using the Crystal Structure crystallographic software package of Molecular Structure Corporation.[S3] CIF file (CCDC-809340) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



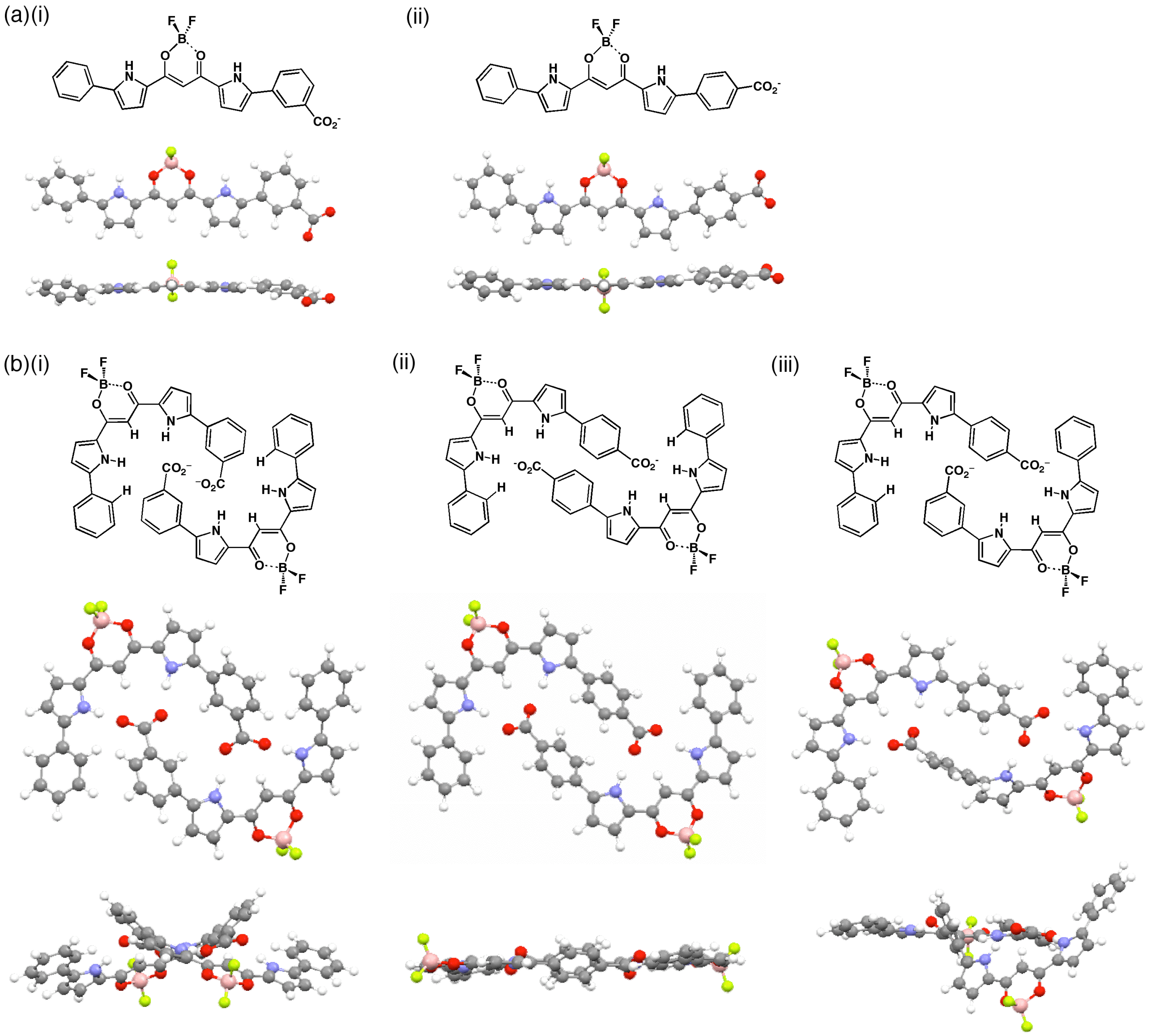
Supporting Figure 2 ORTEP drawings (top and side view) of single-crystal X-ray structure of **1a**·benzoate·TPA. Thermal ellipsoids are scaled to the 50% probability level.



Supporting Figure 3 Assembled structures of **1a**·benzoate·TPA. Atom color code: brown, pink, yellow, green, blue, and red represent carbon, hydrogen, boron, fluorine, nitrogen, and oxygen, respectively.

[S3] *CrystalStructure (Ver. 3.8), Single Crystal Structure Analysis Software,* Rigaku/MSC and Rigaku Corporation, 2006.

3. Optimization of acyclic anion receptors and self-assembled dimers by DFT calculations[S4]



Supporting Figure 4 Optimized structures of (a)(i) **2m$^-$** and (ii) **2p$^-$** and (b)(i) **2m$^-_2$**, (ii) **2p$^-_2$**, and (iii) **2m$^-$·2p$^-$** at B3LYP/6-31G(d,p) level. Hexadecyloxy substituents are omitted for concise calculations. As seen in the values in heats of formation that are described below, energy differences compared to most stable **2p$^-_2$** are 2.36 kcal/mol for **2m$^-_2$** and 2.26 kcal/mol for **2m$^-$·2p$^-$** under this calculating conditions. This result significantly suggests that formation of **2p$^-_2$** is preferred compared to **2m$^-_2$** and **2m$^-$·2p$^-$** and is consistent with higher K_{dim} in **2p$^-_2$** that **2m$^-_2$** as well as self-sorting behaviors.

Cartesian Coordination of 2m$^-$

-1559.44219 hartree

C,-0.5924879382,1.83863834,-3.3783772829

F,-0.2954097819,1.8946806707,2.7849600496

F,1.8666333815,1.556230133,2.0911828435

H,-0.1479894257,4.4215691003,-2.5683007715

H,-0.6632088708,0.1975518372,-4.8624193858

H,-0.1433366535,-1.3939203054,-2.758588119

H,0.8429105352,-5.8387963193,2.7751810615

H,0.4874488946,-4.1733968206,0.6855336791

H,0.3476662002,-1.9301778027,-0.4344773225

H,-1.5934709044,2.0547578866,-5.9168577048

H,-1.5475758819,6.2683633026,-6.2097852536

H,-0.6175295109,6.4577925396,-3.8630991371

H,0.3052281247,-2.5652940168,6.2240021851

H,1.9635949349,-6.3005841729,4.8674707819

H,2.2745784525,-7.0065184043,7.2099179247

H,1.6479671277,-5.4796735279,9.0740654813

H,0.6748543248,-3.2482872246,8.5540711533

H,-0.3664569889,2.5856712655,-1.405133175

H,0.8740590598,-1.8504671575,4.153830639

N,0.7878608364,-2.6766434294,3.5799668831

N,-0.3548221593,1.8001886902,-2.0379189773

O,-2.3721121993,2.8594764629,-8.0157326998

O,-2.3443467183,5.1332414371,-8.2043867317

O,0.4677649647,-0.2873250396,2.4677758277

O,0.1009776819,1.2450646062,0.57677239
B,0.5539091267,1.1497405489,2.0111048174
C,-0.532776463,0.5016709699,-3.8349946129
C,-0.2586861453,-0.3191665836,-2.7443709619
C,0.1095299559,0.2157666369,-0.2407635793
C,-0.147043456,0.500794316,-1.6063279919
C,0.6129760277,-2.5891915708,2.2193967224
C,0.9219123322,-3.9827873531,3.9695024191
C,0.8170620548,-4.7591056781,2.8099734334
C,0.6212832968,-3.8915626358,1.7199422902
C,0.4724679298,-1.2848538395,1.6066246653
C,0.3366781662,-1.0901056324,0.2449282773
C,-0.5767964772,4.332741826,-3.564191274
C,-0.8408675676,3.0652147001,-4.124158308
C,-1.354935429,2.9969831928,-5.4322668399
C,-1.6057658229,4.1471082514,-6.177960984
C,-1.3412516081,5.3932755216,-5.6006729474
C,-0.8300191923,5.4855275699,-4.302513082
C,0.7613985541,-3.5298573023,6.4276275927
C,1.1149643444,-4.3796675571,5.3628707516
C,1.6632575413,-5.6383013453,5.6733044879
C,1.8470305054,-6.0310236828,6.9956295979
C,1.4987703859,-5.1743732861,8.0426995418
C,0.956983409,-3.9217963177,7.749905553
C,-2.1701574071,4.0350770071,-7.6251387669

Cartesian Coordination of $2p^-$
-1559.4413907 hartree
C,-0.6671473958,1.5436442491,-3.5102638473
F,-1.0930867915,1.2172080985,2.470823796
F,1.1603219839,1.6533027144,2.3906804097
H,0.3005309282,4.0126425533,-2.8364180338
H,-1.0048340971,-0.1214175984,-4.9339103554
H,-0.7127045786,-1.6988003516,-2.7806587635
H,0.3969230763,-6.1200703053,2.735111925
H,-0.070864159,-4.4609857664,0.6612252896
H,-0.3964022779,-2.2242779955,-0.4318531744
H,-1.755620021,1.8435168732,-5.9527357685
H,-1.8367899315,3.9559812496,-7.3113164342
H,0.136868964,6.088445027,-4.2255652723
H,0.363197141,-2.7921639212,6.163272084
H,1.7269624317,-6.6082926143,4.7083748149
H,2.2299209711,-7.3040339706,7.0213714323
H,1.8477231643,-5.7329986276,8.9144566137
H,0.9241991656,-3.4671792406,8.4580743635
H,-0.3045466801,2.3125456828,-1.568065471
H,0.7917614007,-2.1246334377,4.0336930347
N,0.5993706671,-2.9507546693,3.4859423089
N,-0.4197045559,1.5114946629,-2.17092072
O,-0.4445999714,7.447160274,-6.1407934999
O,-1.4579256047,6.2845274905,-7.823279914
O,0.4279329959,-0.5617199425,2.3408213766
O,0.0654504032,0.9665395321,0.4449499186
B,0.1309489569,0.867702892,1.9487526317
C,-0.8251512538,0.1983178618,-3.9184827673
C,-0.6666823606,-0.618985747,-2.8019460143
C,-0.1822217124,-0.0696593468,-0.3231268227
C,-0.4141597901,0.2108073417,-1.6953275551
C,0.2896063452,-2.869108686,2.1491878755
C,0.7002308049,-4.2576158806,3.88205098
C,0.433609055,-5.040256962,2.7531480972
C,0.1761527135,-4.1756045191,1.6736347
C,0.1630375464,-1.5660131579,1.5308899731
C,-0.1839705197,-1.3781683957,0.2056201398
C,-0.1969999154,3.9838435568,-3.8046044471
C,-0.7269716974,2.7693722909,-4.2901684717
C,-1.3224013288,2.7643644048,-5.5694912075
C,-1.3829271288,3.9278559778,-6.325360526
C,-0.8580285325,5.133141051,-5.8408158188
C,-0.2665732265,5.1411910606,-4.5701201182
C,0.7960876435,-3.7731158137,6.3369893773
C,1.0104149072,-4.6484524453,5.2560348066
C,1.5327137029,-5.9262735957,5.5302143994
C,1.8249856086,-6.313361092,6.8346523658
C,1.6140545872,-5.4318972704,7.8976361404
C,1.0999641538,-4.1599957409,7.640184374
C,-0.9277409358,6.4311995052,-6.6957175447

Cartesian Coordination of $2m^-_2$
-3118.9599875 hartree
C,-4.4636446563,0.2851526585,-3.1749004734
H,-4.3033399529,1.0312580609,8.1623669097
H,-1.6696770769,0.810367082,8.7623116475
H,5.1995209625,-2.3351638875,2.4377604356
H,4.6131303666,-1.6425715922,5.0022004863
H,-2.2508200851,-0.5646485773,4.7969840273
H,1.1277458304,-1.1310787146,2.6011757568
H,5.8281299439,-1.338584667,-2.8154590534
H,8.1505343384,-0.7196833615,-3.4965909983
H,8.4797434939,1.0089543915,-5.2632739633
H,6.541214185,2.0941870973,-6.3120181677
H,-1.4888037807,-0.0985349364,-0.352707688
H,0.1161239381,0.8777167829,-4.5208932113
H,-1.2398222567,0.2410661525,-2.7789293712
H,2.2769890426,0.7724837722,-4.7555133816
H,-5.0927667897,-1.9776061566,-1.7934103499
H,2.2301181063,3.6410916488,-7.8733801326
N,2.1006901441,-1.3707005921,2.9003091057
N,2.6176065305,1.4448925976,-5.4682467989
N,-2.2264508482,0.3719168587,-3.0998024067
N,-2.4547892903,-0.151665803,5.7264917289
O,-0.2218951399,3.05508793,-7.0355173422
O,0.2622078908,-0.0360313993,-2.0349349607
O,0.6088788892,0.0185577247,7.6492027617
O,2.623561205,-0.6422977796,6.4146261035
O,1.6983558791,-0.4964657342,-3.7137428509
O,-1.9425758558,-1.4435459565,3.3262967126
O,-2.392522088,2.4774151921,-6.0483051044
O,-0.3598080392,-0.7393405522,1.8799747162
C,-4.4735175229,-2.5185244951,0.1944395846
C,-3.5452157044,-2.3047140868,1.2119000224
C,-2.4769831984,-1.4193465218,1.0169306917
C,-2.3434100871,-0.7494344883,-0.2047394108
C,-2.6334937934,1.0871797937,-4.213258868
C,5.9955277309,-0.5916233384,-3.5862361945
C,7.2931773327,-0.24514701,-3.96671749
C,7.4760941848,0.7238426788,-4.9563106756
C,6.3778221238,1.3366827557,-5.5518679461
C,-3.3109109152,-0.9082401412,-1.2151335195
C,5.0621394182,0.9958338935,-5.1781175571

C,-0.3814627275,1.5409394843,-5.2182806277
C,0.3529949063,2.2574666702,-6.1613172788
C,-4.0323527117,1.0458141106,-4.2626214489
C,4.8911905507,0.0146223883,-4.1825350517
C,3.923812046,1.659835877,-5.8185816024
C,3.929913294,2.6017307054,-6.8609338812
C,2.602122102,2.9463921005,-7.1355861537
C,1.7939942039,2.2179003472,-6.2579667687
C,-1.770444945,1.713540946,-5.1769112556
C,-3.3235318511,-0.1216293322,-2.4573855059
F,-2.1092590038,4.389914561,-7.3565181106
F,2.1140827079,-1.5585910141,8.512663471
F,2.7426564122,0.6405919689,8.3612394576
F,-2.0170151486,2.330450814,-8.3587770892
H,-5.4842857441,0.0733322073,-2.8894666997
H,4.8088155904,2.9836970297,-7.3604986253
H,3.89198698,-0.279890716,-3.8732926158
H,-4.6281906383,1.522963354,-5.0261849082
H,-5.2843535801,-3.23012953,0.3335534644
H,-3.6241485261,-2.8127785738,2.1667152409
H,4.3827744942,-3.6617655005,0.6674579287
H,4.3711605466,-4.0233824477,-1.7817431071
H,2.9476409966,-2.5607983594,-3.2396118031
H,1.4038154116,-0.576527386,0.2177835993
H,-4.0263134993,-0.7870698394,3.6602491016
H,-6.1064528325,-0.8720690626,2.3740545926
H,-8.2439667897,-0.0223635682,3.3485154065
H,-8.235149471,0.9339119509,5.6513816672
H,-6.1459314458,1.0455273886,6.9390957501
H,-0.1185999216,-0.8973252153,4.517034854
C,-2.1610633904,0.55683824,7.8351670526
C,-1.5040638767,-1.1766605097,2.1637679236
C,-4.3664096912,-1.8162344002,-1.0025094927
C,2.9467877994,-2.4486357338,-2.1609778713
C,3.7477703306,-3.2460939447,-1.3453985083
C,3.7543808017,-3.0450576495,0.0318851995
C,-4.91921952,0.1393798235,5.4048710477
C,2.937012559,-2.0615551489,0.6221160936
C,-6.1319102788,0.6166054405,5.9420161557
C,-7.3150113069,0.5556836491,5.211931829
C,-7.3215612616,0.0197551336,3.921803087
C,-6.1273831712,-0.4556551568,3.3771655672
C,-4.9400080669,-0.4023638262,4.1051541571
C,2.0845597642,-1.306611133,-0.2058687466
C,2.1125180083,-1.4756522373,-1.5950222712
C,-3.5181238374,0.6690543525,7.5141561425
C,-3.687202351,0.2195223807,6.1939157454
C,-0.0973734048,-0.2271278059,6.5667167941
C,0.4890346715,-0.6864947455,5.3888942489
B,-1.7055098203,3.0772272332,-7.2348152187
C,1.2813109095,-0.5927964646,-2.5171712107
C,2.6130942841,-1.2491519764,4.1808320252
C,3.9577391546,-1.6384343676,4.1441976847
C,4.2464539485,-2.0102432557,2.8303653619
C,3.0777115904,-1.8308071284,2.067476448
C,1.8794619549,-0.84760136,5.3497407062
C,-1.5091497284,0.0445529249,6.7097518997
B,2.0436941688,-0.3910190733,7.7711608215

Cartesian Coordination of $2p^{-}_{2}$

-3118.9637417 hartree
B,-5.5167445974,2.9771849325,-6.1573150126
B,5.5165742495,-2.9775846874,6.1573671898
C,-4.2702058823,2.2703509366,-2.7067744231
C,-5.2544605777,2.7523341963,-1.8344702786
C,-4.8212255117,2.494021824,-0.5268333938
C,-3.5677551152,1.8675606412,-0.6123498598
C,-0.3294905686,0.7465833666,-8.0920720946
C,-1.1303504496,1.1745698695,-9.1635237722
C,-2.3096382146,1.7003995622,-8.6317158611
C,0.9941705566,0.1167992235,-8.1722319034
C,-2.2286028833,1.5883521086,-7.2398959258
C,-4.256057252,2.3248865473,-4.146233779
C,-3.11541021,0.9025055384,1.6600267913
C,-2.2227168871,0.4535443168,2.6314516362
C,-0.8393176825,0.5266997964,2.4201665697
C,-0.372869352,1.1005791897,1.2321457822
C,-1.2575295942,1.5500738338,0.2596386094
C,-2.6466683666,1.4385665177,0.4455150949
C,1.5790567501,-0.5732717378,-7.0931379692
C,2.8263338519,-1.1801894959,-7.2333433081
C,3.5211968939,-1.1245225099,-8.4424932579
C,2.9549824958,-0.436852307,-9.5183989032
C,1.7137838736,0.1777584855,-9.38376525
C,0.1566486568,-0.0509028563,3.4127813912
C,-1.5788883169,0.573805931,7.0931350685
C,-3.2320649345,1.7801756167,-4.9359103448
C,-3.2564070733,2.0067938416,-6.3105218071
C,4.8213153601,-2.494077999,0.526848282
C,5.2545191231,-2.7523987329,1.8344981705
C,3.2563429172,-2.006788911,6.3104996037
C,2.2227492642,-0.4535558963,-2.6314232934
C,3.1154630008,-0.9025306389,-1.6600247859
C,4.256012128,-2.3250077686,4.1462427725
C,2.2285755179,-1.5882187049,7.2398573697
C,4.2702335864,-2.2704451515,2.7067787319
C,2.3096305956,-1.700165438,8.6316858453
C,1.1303692235,-1.1742595329,9.1634734111
C,0.3295126018,-0.7463236435,8.0919970931
C,3.5678366066,-1.8676359399,0.6123328428
C,2.6467461975,-1.4386417656,-0.4455245874
C,1.2576115082,-1.5501948592,-0.259643857
C,0.3729305255,-1.1006923265,-1.2321282432
C,0.8393527329,-0.5267542744,-2.4201301079
C,3.2319820053,-1.7802986494,4.9358633999
C,-0.9941250721,-0.116483294,8.1721558405
C,-0.156642349,0.0508721498,-3.4127043297
C,-1.7138288217,-0.1775963857,9.3836263512
C,-2.9549931827,0.4370828511,9.5182745632
C,3.2319820053,-1.7802986494,4.9358633999
C,-0.9941250721,-0.116483294,8.1721558405
C,-0.156642349,0.0508721498,-3.4127043297
C,-1.7138288217,-0.1775963857,9.3836263512
C,-2.9549931827,0.4370828511,9.5182745632
C,-3.5210812991,1.1249715996,8.4424427741
C,-2.8261317951,1.1807883959,7.2333486606
F,-6.4706277216,2.0225986697,-6.4651452575
F,6.4708654943,-2.0234708863,6.4653847479
F,5.9140912983,-4.2466548966,6.5195637045
F,-5.9148261316,4.2460264464,-6.5196458788

H,-4.4922185403,1.6024944364,8.5437240278
H,-3.4857655876,0.3705511567,10.4651541663
H,-1.3010961307,-0.7280694158,10.2230636695
H,0.6357573511,-0.8341696561,5.9711970983
H,2.4610147396,-1.1834451701,2.2980850966
H,2.4310019891,-1.2132738267,4.4732855654
H,-3.1582873247,2.1086433313,-9.1590332176
H,-4.1862743701,0.8002641908,1.8159135271
H,-2.5788570591,0.0085040317,3.5552140901
H,0.6978767688,1.161513395,1.0797182043
H,-0.8843125032,1.0752338573,-10.2110999037
H,-0.8755325706,1.9770600898,-0.6617754597
H,-0.6357975229,0.8343144026,-5.9712850852
H,-2.4609690428,1.1833229736,-2.2981243291
H,-2.4310648342,1.2131545874,-4.4733734914
H,3.4856778441,-0.370445131,-10.4653303836
H,1.300956435,0.7280565579,-10.2232701037
H,4.492360823,-1.6019931665,-8.5437638605
H,3.2549271732,-1.7021739002,-6.3818886387
H,1.0731196993,-0.6095306759,-6.1340297599
H,-6.1622404916,3.2440654322,-2.1513108013
H,-5.3189238909,2.7651219468,0.3939629717
H,6.1622986419,-3.244121774,2.151352441
H,5.3190486394,-2.7651655242,-0.3939332568
H,0.884344234,-1.0748317244,10.2110444819
H,3.1582725224,-2.1084055559,9.1590183998
H,4.1863234843,-0.8002563081,-1.8159171774
H,2.5788702883,-0.0084654076,-3.5551694592
H,-0.697812204,-1.161662687,-1.0796922116
H,0.8756276676,-1.9772283407,0.6617540666
H,-1.0728788654,0.6101677772,6.1340739411
H,-3.2546314149,1.7029427097,6.3819510831
N,3.2535111477,-1.7436564507,1.9340510597
N,-3.2534690194,1.743548191,-1.9340701367
N,-1.015278468,1.0003564643,-6.9313353839
N,1.0152647341,-1.0002056361,6.9312662682
O,-0.2900952378,-0.4401659671,4.5306054749
O,0.2900667072,0.4402145393,-4.5305091376
O,4.249702901,-2.6540429901,6.8847256293
O,5.2736079701,-2.9628954325,4.6788271601
O,-1.3608862093,0.104582013,-3.0361226409
O,1.3608982946,-0.1046661881,3.0362389564
O,-4.2497604915,2.6541110811,-6.8847040539
O,-5.2736660488,2.9627915768,-4.6787847617

Cartesian Coordination of $2m^-\cdot 2p^-$
-3118.9601424 hartree
C,-2.0262774065,2.1441874607,-4.2126735605
H,-2.2344655969,1.6839253605,3.3348585308
H,0.0001728644,1.5278020989,4.4574471734
H,0.1077702328,-4.0355500335,2.2401236299
H,6.1066679235,0.1649921594,-0.8960513826
H,2.8875103269,-0.9968159277,1.2692498894
H,1.6015308906,-0.2411187175,3.7752667068
H,-4.5329066126,-0.3613566533,5.7905466983
H,-6.2457787203,-1.2421588631,7.373409084
H,-8.6133018361,-1.4445033363,6.612987814
H,-9.2405699522,-0.7887356646,4.3317193598
H,-1.0069702069,1.5884259623,-0.3373775423
H,-4.972748304,0.6971576876,-0.7234814554
H,-2.8984905391,0.8064871194,-1.4034077154
H,-5.7921751213,0.6033923849,1.4373965524
H,0.6447156014,1.1268044314,-4.2823179836
H,-9.7395918544,0.9766462771,-0.0951489056
N,2.5185538174,-1.9312688843,1.5374236574
N,-6.8326835683,0.5449805224,1.3679402266
N,-2.8379011333,1.3326768641,-2.2928797569
N,7.1063212532,-0.1498724337,-0.8073503652
O,3.5993288584,0.4349187368,0.6074423268
O,7.1139485775,-3.6741623738,-0.0124366525
O,-3.1434237293,-0.173876915,0.0350000372
O,4.9618655605,-4.5174945918,0.8149618086
O,-4.1044338389,0.7983092116,1.8282882934
O,-7.9477111395,1.6912902498,-1.8858740196
O,4.5569371953,0.6340451147,-1.4206254639
O,-6.165523225,2.0744504167,-3.5255386426
C,2.0323856952,0.9662871576,-2.647491016
C,2.2090751805,0.9621579298,-1.2569972993
C,1.0970570917,1.1965658247,-0.4410197761
C,-0.1622752531,1.4068197151,-0.9910552252
C,-3.9219608626,1.6943506153,-3.0719589184
C,-5.5706785174,-0.4486384907,5.4797480187
C,-6.5276859274,-0.9424396699,6.3673889186
C,-7.8530707181,-1.0535676416,5.9406967422
C,-8.2092410498,-0.6753127204,4.6499835529
C,-0.3524464606,1.3807679419,-2.3837720331
C,-7.2540221275,-0.1664318244,3.7453732244
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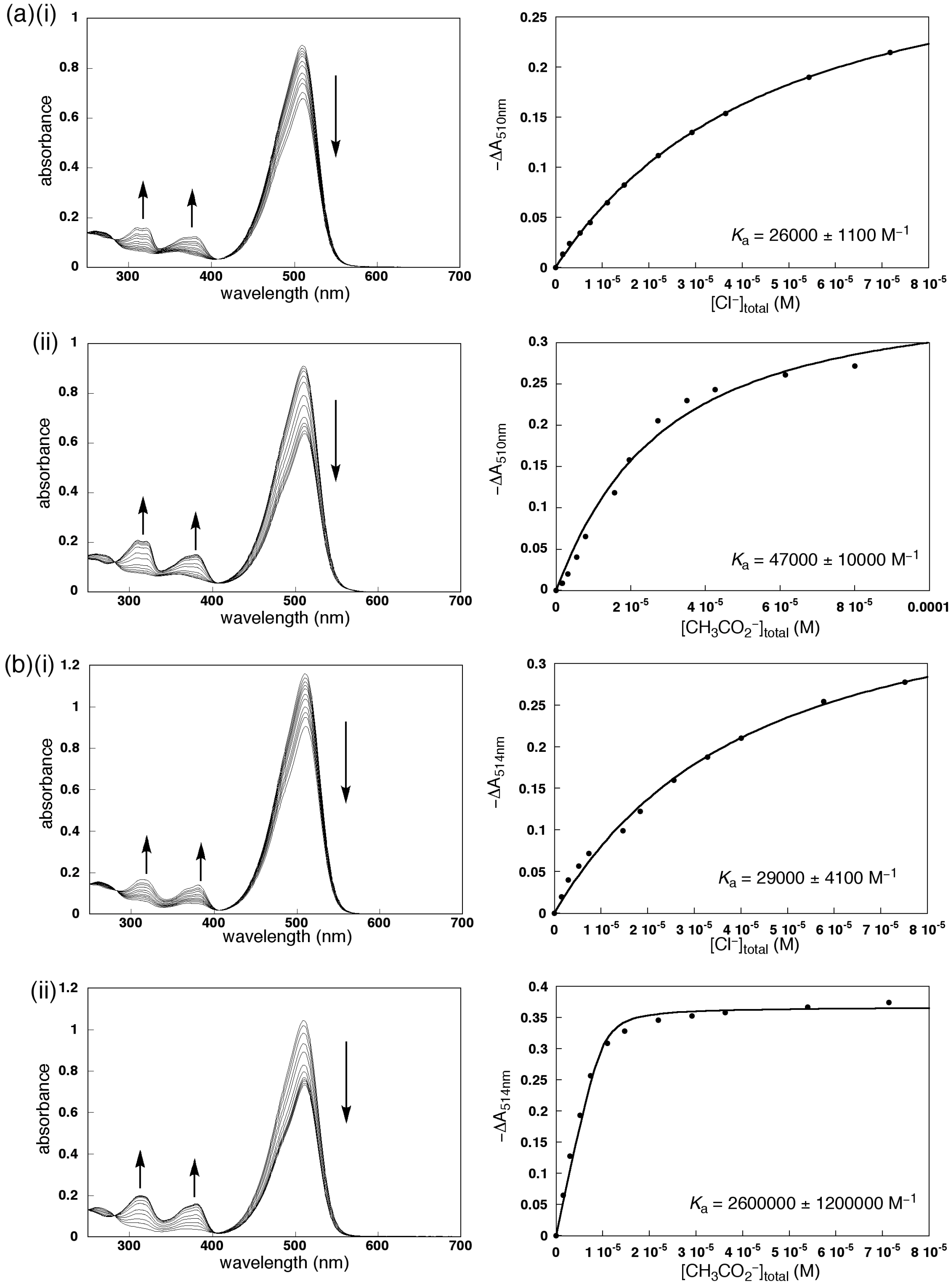
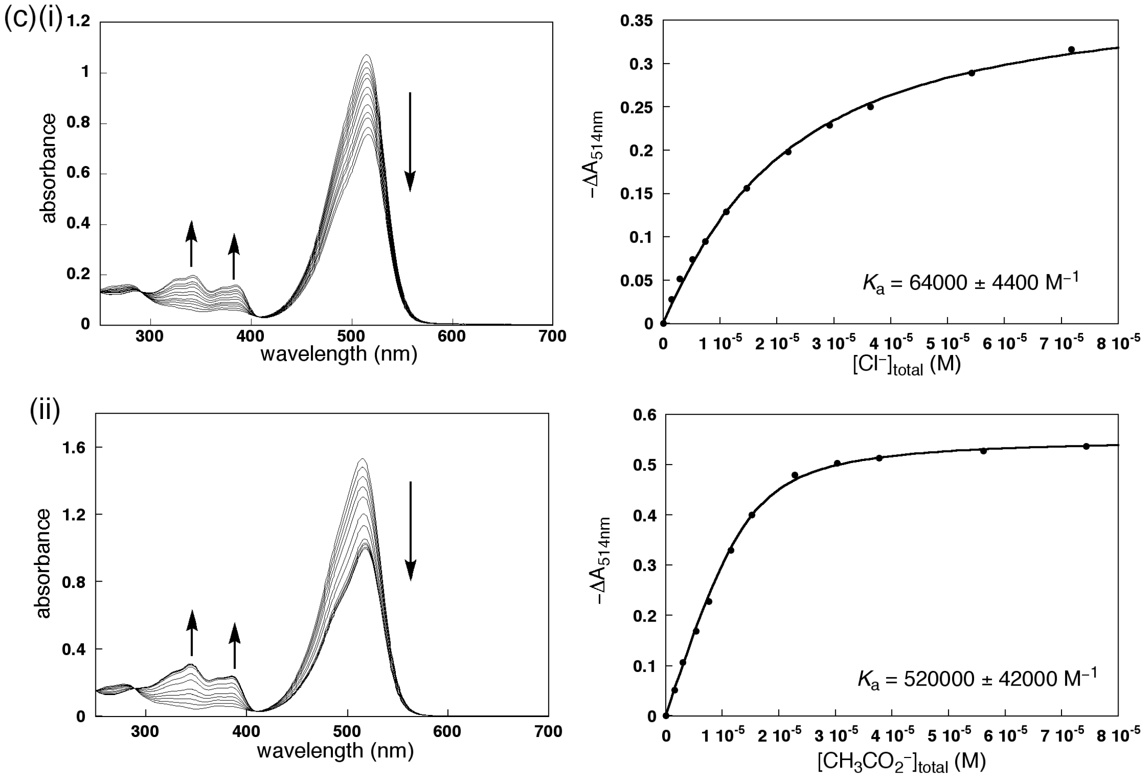
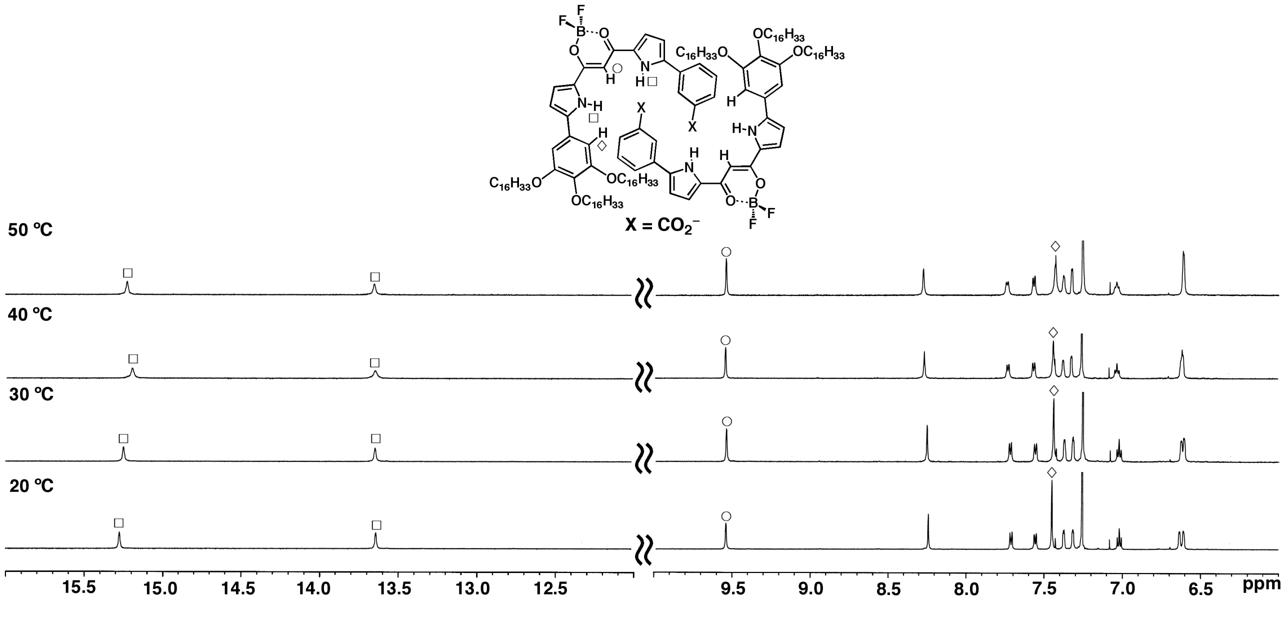
4. Anion-binding and self-assemblies behaviors



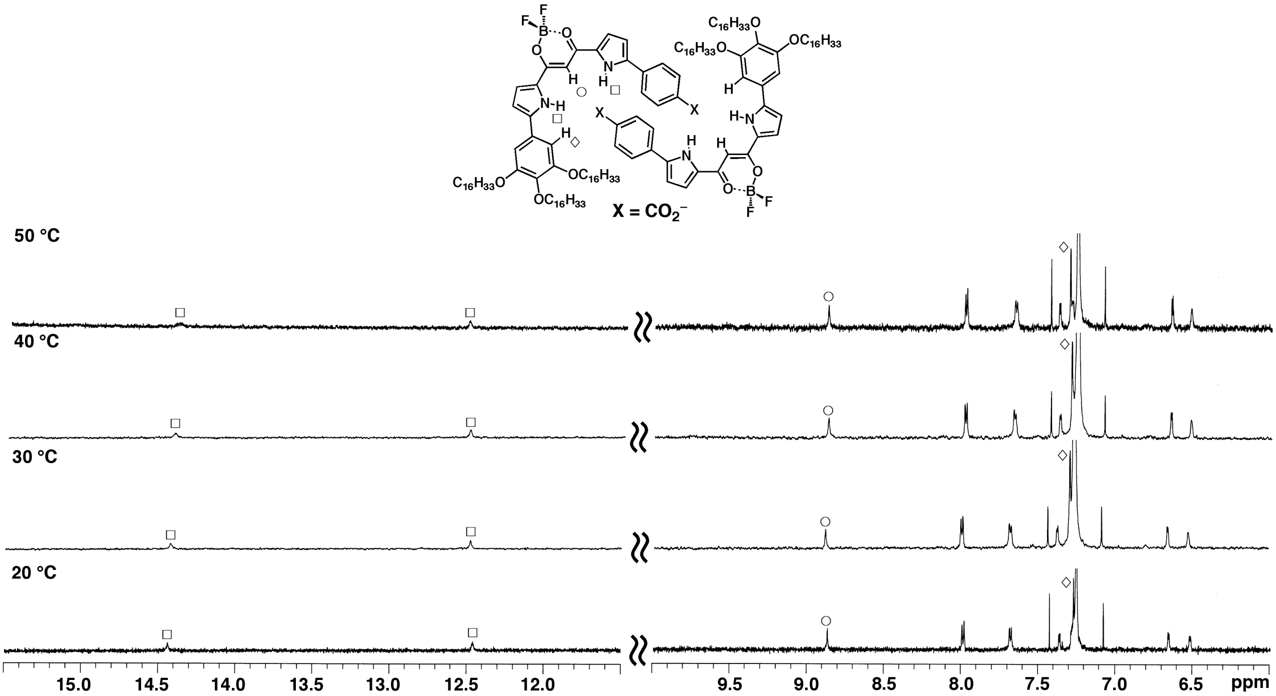
Supporting Figure 5 UV/vis absorption spectral changes (left) and corresponding titration plots and 1:1 fitting curves (right) of (a) **1d**, and (b) **2me**, and (c) **2pe** (1.0×10^{-5} M) upon the addition of (i) Cl^- and (ii) $CH_3CO_2^-$ as tetrabutylammonium (TBA) salts in CH_2Cl_2. The large errors of K_a values were observed in the binding of $CH_3CO_2^-$, which may readily associate with (a small amount of) water molecules in solution, resulting in the errors. Such effects were significant in the systems exhibiting greater K_a values. Similar results were also observed in the binding of F^-, which is a fairly basic anion like $CH_3CO_2^-$.



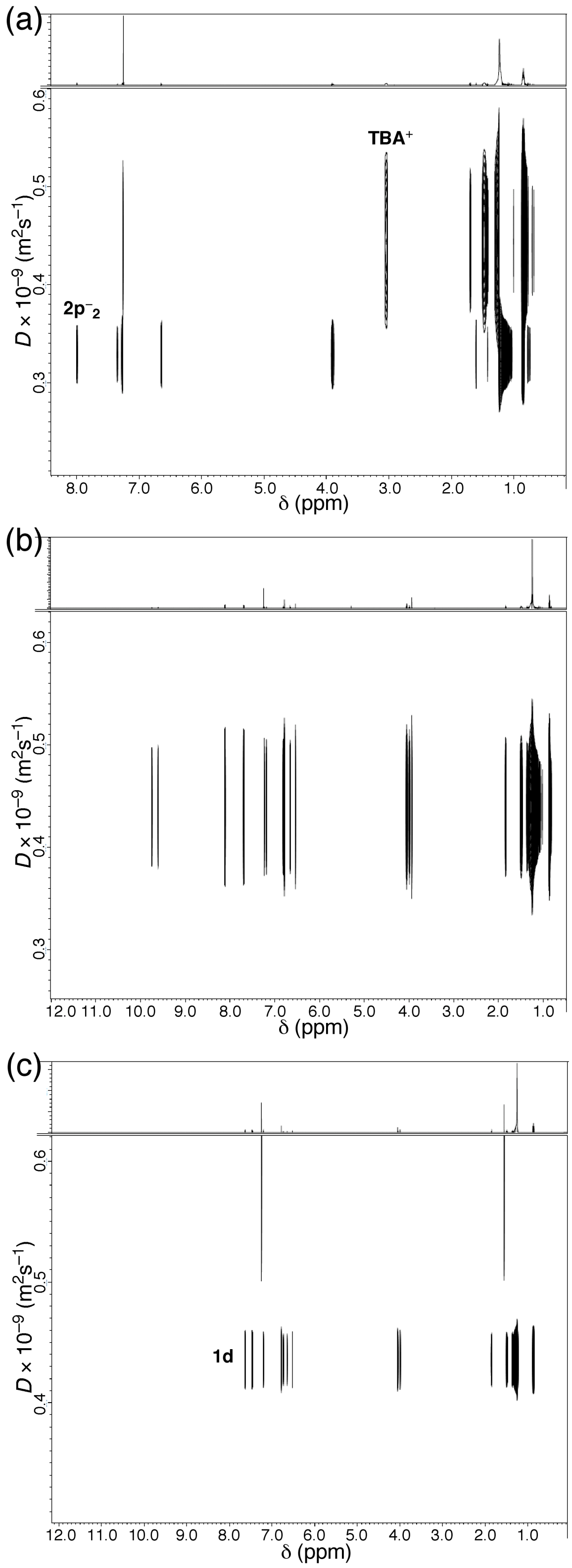
Supporting Figure 5 (Continued).



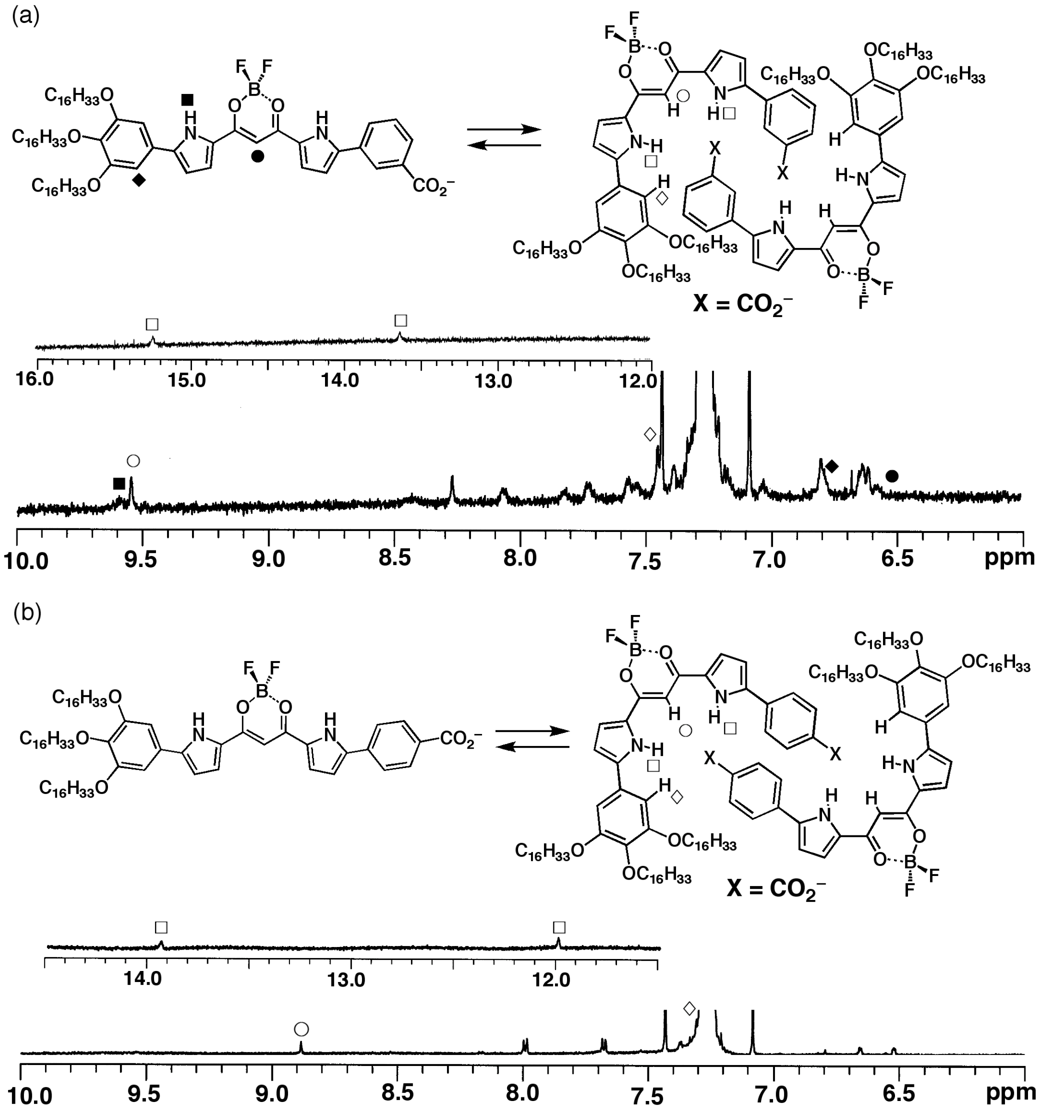
Supporting Figure 6 Selected VT ^{1}H NMR spectra of **2m**$^-{}_2$ as a TBA salt in CDCl$_3$ (1 × 10^{-3} M as a monomer).



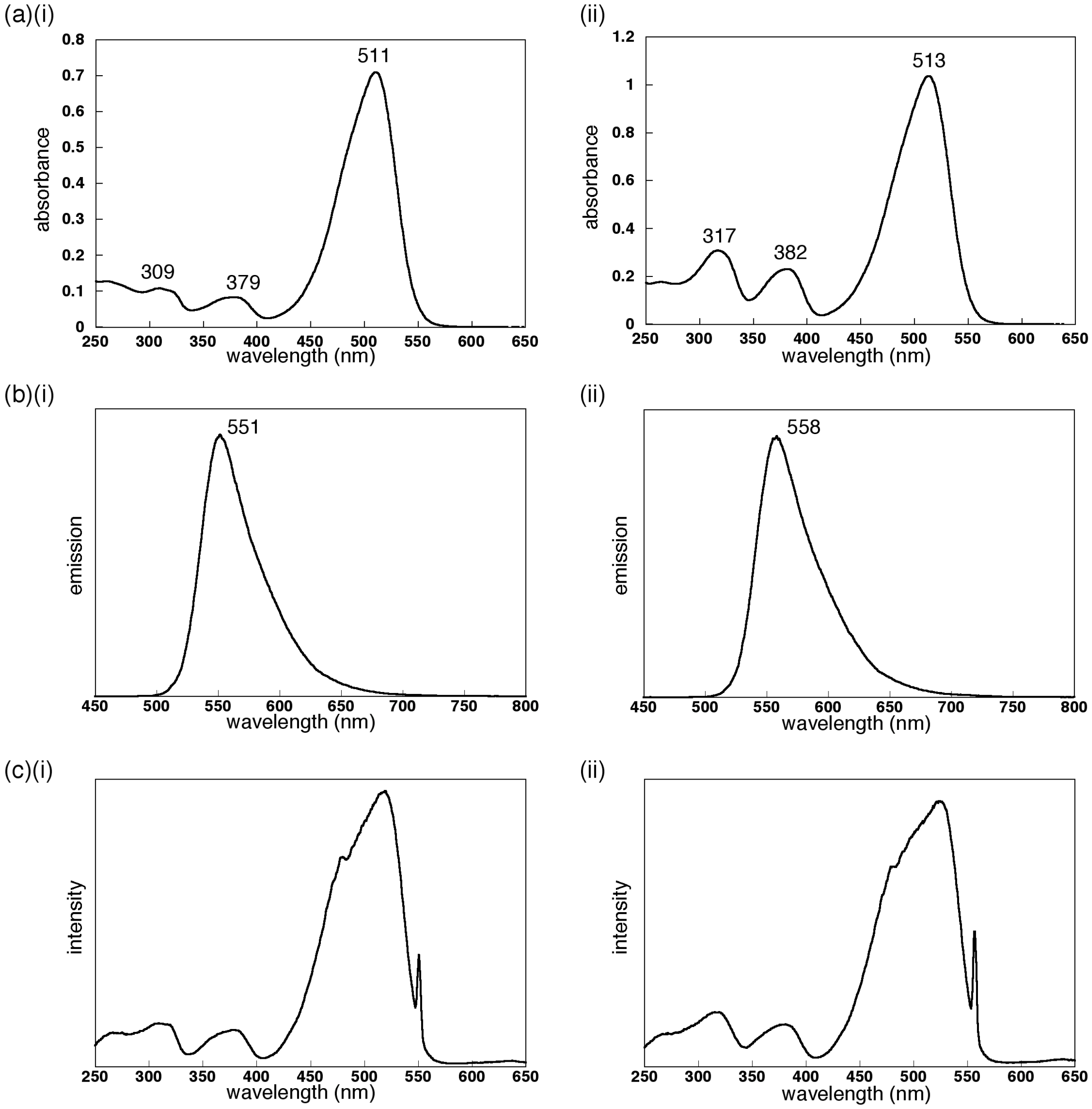
Supporting Figure 7 Selected VT ^{1}H NMR spectra of $\mathbf{2p}^-_2$ as a TBA salt in $CDCl_3$ (1×10^{-3} M as a monomer).



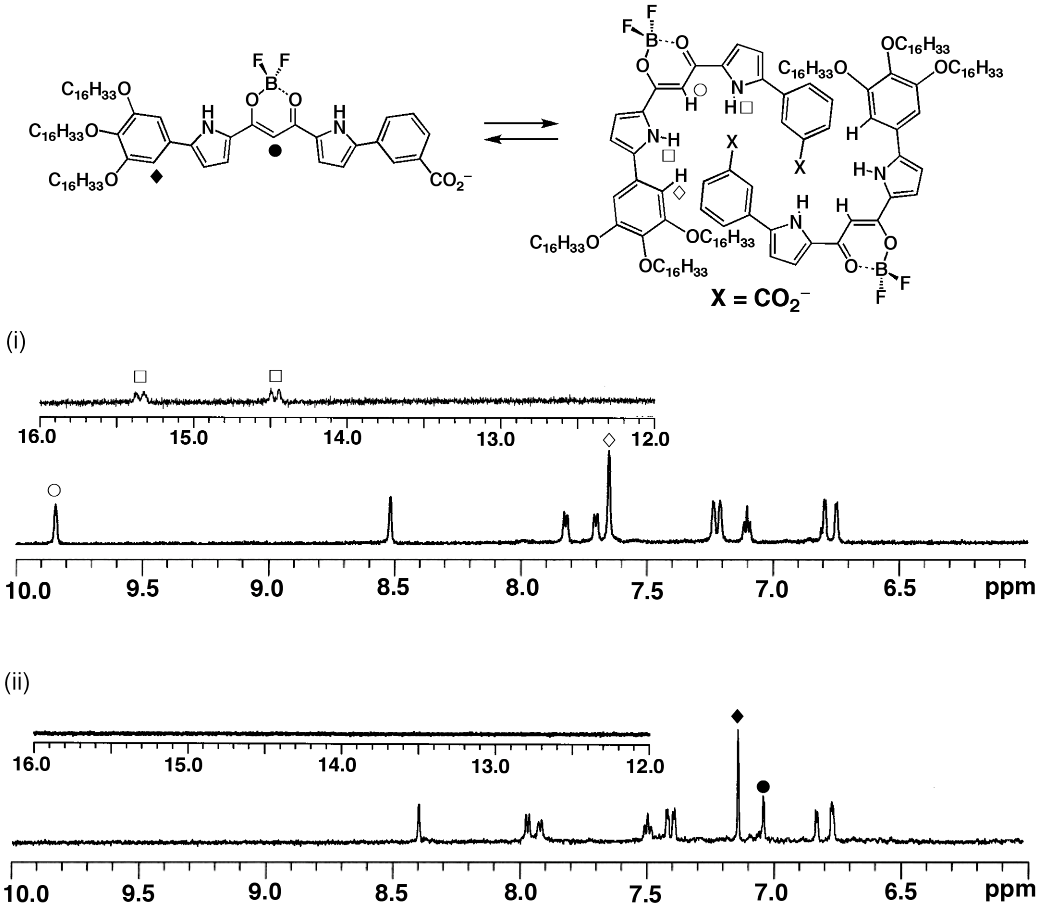
Supporting Figure 8 DOSY ^{1}H NMR spectra in CDCl$_3$ (1×10^{-3} M as monomers) at 20 °C of (a) **2p**$^-{}_2$ as a TBA salt, (b) **2pe**, and (c) **1d**. The diffusion constants for **2p**$^-{}_2$, **2pe**, and **1d** are estimated as 3.3×10^{-10}, 4.4×10^{-10}, and 4.4×10^{-10} m^2 s^{-1}, respectively. The smaller value of **2p**$^-{}_2$ than those of **2pe** and **1d** as monomers suggests the formation of larger species (= self-assembled dimer) consisting of **2p**$^-$.



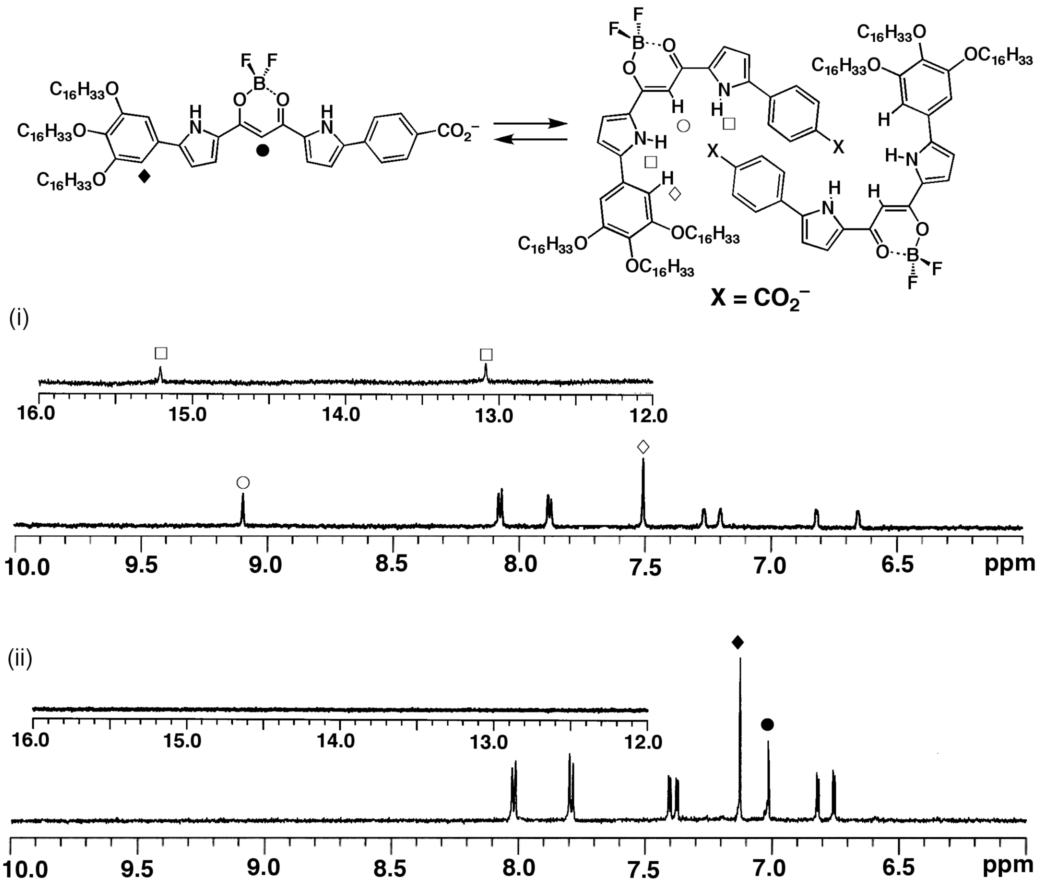
Supporting Figure 9 Selected ^{1}H NMR spectra of (a) *meta* ($\mathbf{2m}^-_2$ and $\mathbf{2m}^-$) and (b) *para* ($\mathbf{2p}^-_2$ and $\mathbf{2p}^-$) derivatives as TBA salts in diluted $CDCl_3$ (5×10^{-5} M as monomers). The anion receptor units in the dimers $\mathbf{2m}^-$ and $\mathbf{2p}^-$ exhibit the slow exchanges between anion-free and anion-binding states, resulting in the estimation of dimerization constants from the integrals of the observed species. In (a), the concentrations of the monomer $\mathbf{2m}^-$ and self-assembled dimer $\mathbf{2m}^-_2$ were obtained from the integrals of the signals assignable to the corresponding bridging CH of the center hexa-membered ring as well as pyrrole NH and aryl-*ortho*-CH for the correction of the values. As obtained from (b), exhibiting no signals of monomer $\mathbf{2p}^-$, the dimerization constant (K_{dim}) of 10^9 M^{-1} for $\mathbf{2p}^-$ is the lower limit. In the $CDCl_3$ solution of $\mathbf{2p}^-$ at 5×10^{-4} M, since the signals of monomeric state were not observed in ^{1}H NMR, the lower limit of the K_{dim} value was estimated on the basis of the hypothesis that the monomer existed in at most 5% (2.5×10^{-5} M) of the total amount of $\mathbf{2p}^-$.



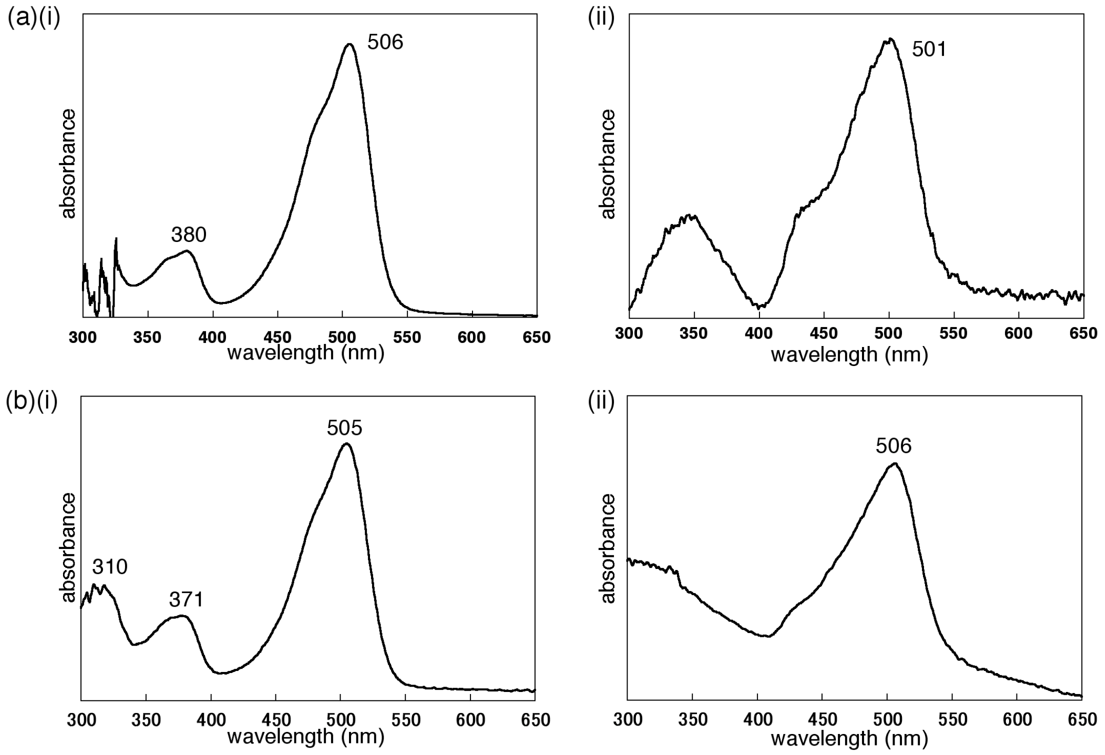
Supporting Figure 10 (a) UV/vis absorption spectra, (b) fluorescence spectra excited at each absorption maximum, and (c) excitation spectra corresponding to each emission maximum of (i) *meta* ($\mathbf{2m}^{-}_{2}$ and $\mathbf{2m}^{-}$) and (ii) *para* ($\mathbf{2p}^{-}_{2}$ and $\mathbf{2p}^{-}$) derivatives as TBA salts in $CHCl_3$ (5×10^{-5} M as monomers). Absorption bands around 300–400 nm are often derived from the anion-binding species (see also Supporting Figure 5), therefore *para* derivative tends to exist as $\mathbf{2p}^{-}_{2}$ compared to *meta* derivative even in the diluted solution. This observation is consistent with the results of ^{1}H NMR (Supporting Figure 9). On the other hand, in excitation spectra, bands around 300–400 nm are comparable for both derivatives, suggesting that the contribution of the dimer species of *meta* derivative may also be significant.



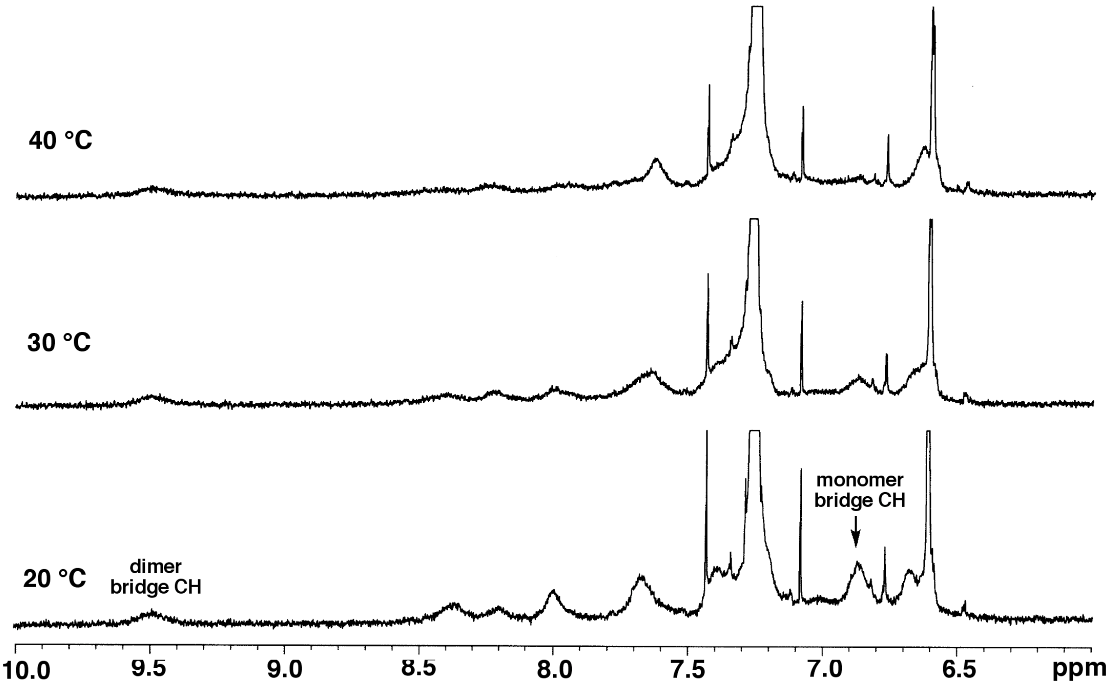
Supporting Figure 11 Selected ^{1}H NMR spectra of **2m**$^-{}_2$ and **2m**$^-$ (5×10^{-4} M as a monomer) as TBA salts (i) in acetone-d_6 at 20 °C and (ii) in CD_3OD at 50 °C.



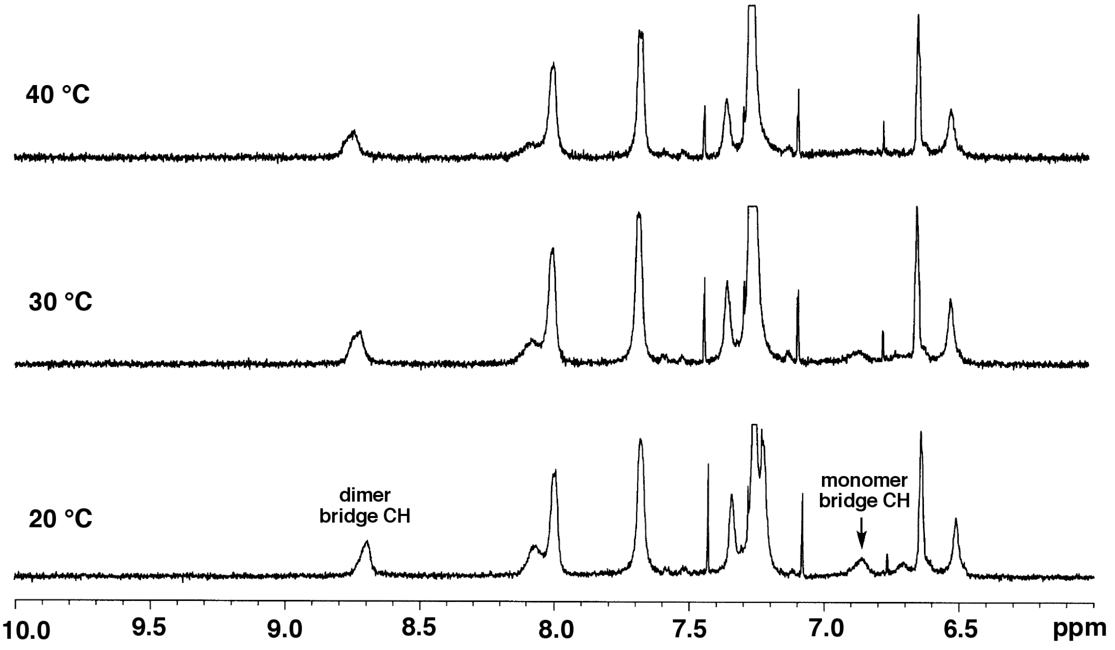
Supporting Figure 12 Selected ^{1}H NMR spectra of **$2p^{-}_{2}$** and **$2p^{-}$** (5×10^{-4} M as a monomer) as TBA salts (i) in acetone-d_6 at 20 °C and (ii) in CD_3OD at 50 °C.



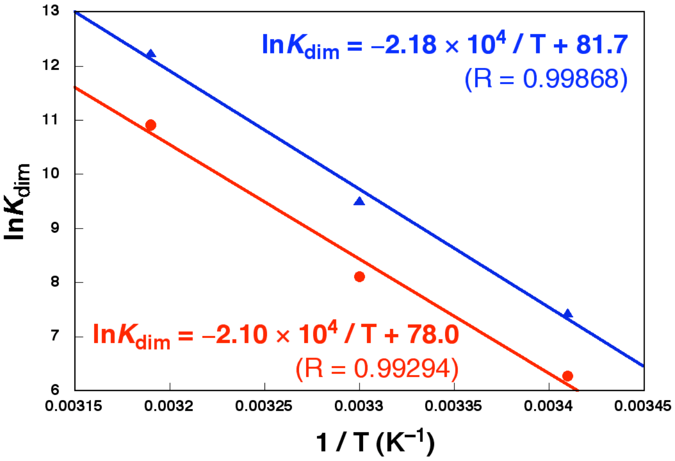
Supporting Figure 13 UV/vis absorption spectra of (a) **$2m^{-}_{2}$** and (b) **$2p^{-}_{2}$** as TBA salts (5×10^{-4} M as a monomer) at 20 °C in (i) acetone and (ii) MeOH. Similar to the case of diluted $CHCl_3$ (Supporting Figure 10), the bands around 300–400 nm in acetone suggest the formation of self-assembled dimers.



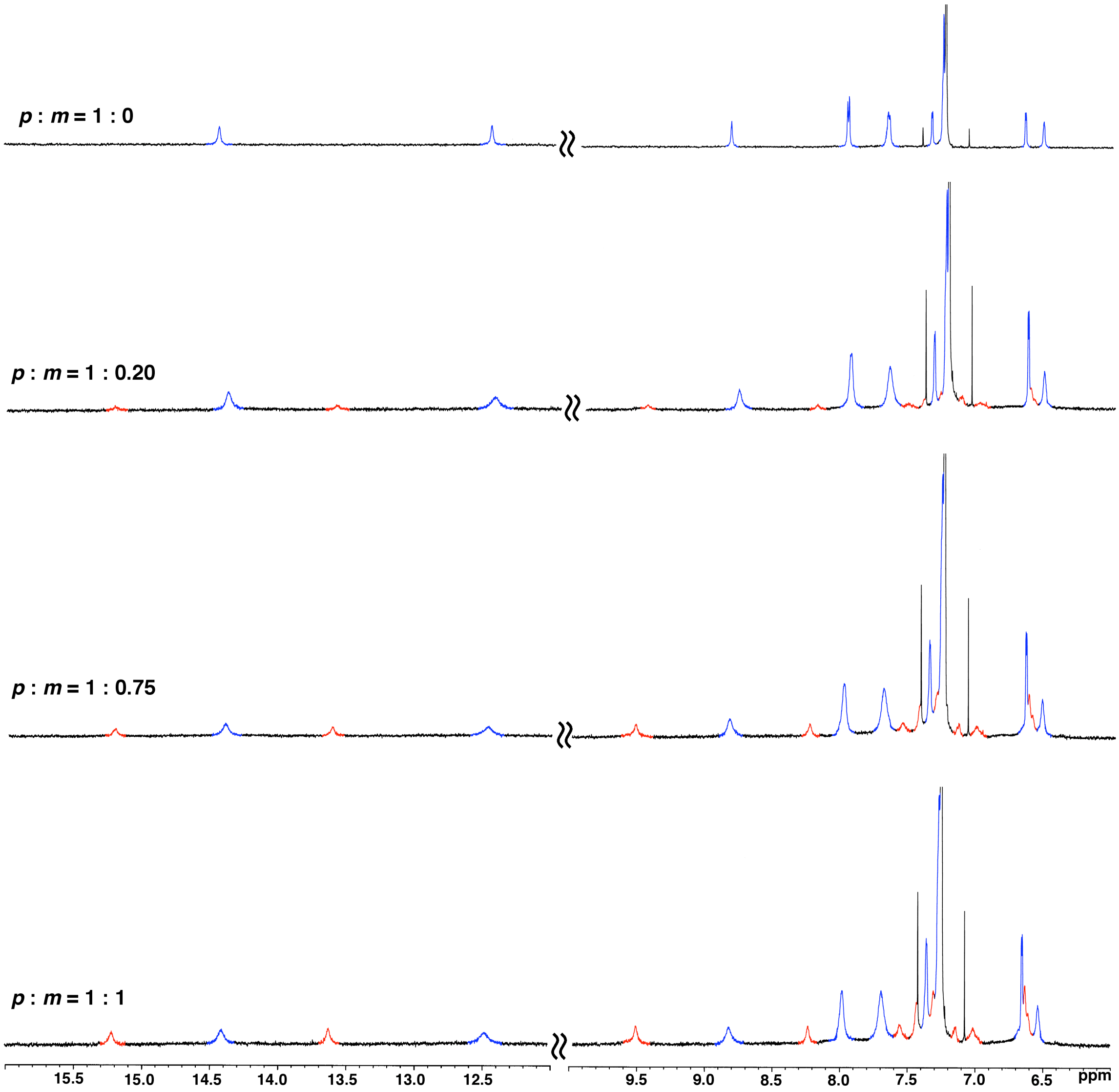
Supporting Figure 14 Selected VT ^{1}H NMR spectra of $\mathbf{2m^-}_2$ as a TBA salt in 2% $CD_3OD/CDCl_3$ (1×10^{-3} M as a monomer). The concentrations of the monomer $\mathbf{2m^-}$ and self-assembled dimer $\mathbf{2m^-}_2$ were obtained from the integrals of the signals assignable to the corresponding bridging CH of the center hexa-membered ring.



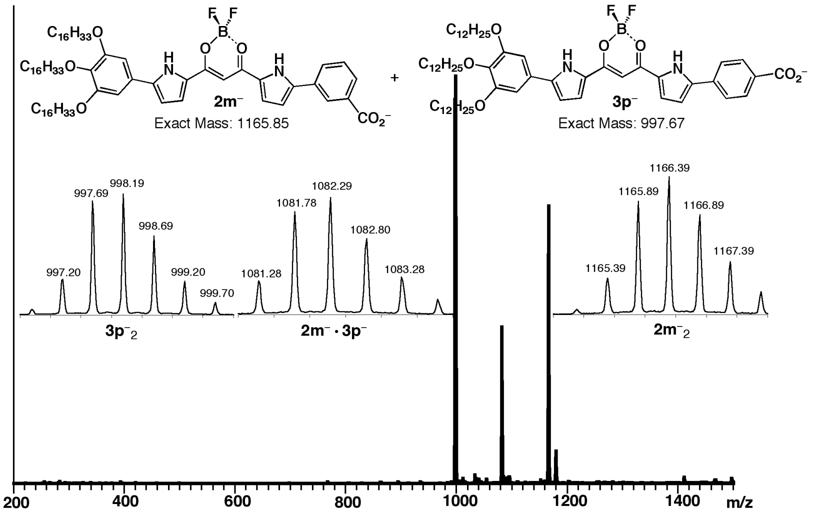
Supporting Figure 15 Selected VT ^{1}H NMR spectra of $\mathbf{2p^-}_2$ as a TBA salt in 2% $CD_3OD/CDCl_3$ (1×10^{-3} M as a monomer). The concentrations of the monomer $\mathbf{2p^-}$ and self-assembled dimer $\mathbf{2p^-}_2$ were obtained from the integrals of the signals assignable to the corresponding bridging CH of the center hexa-membered ring.



Supporting Figure 16 van 't Hoff plots from the dimerization constants on the basis of the concentrations of monomers and self-assembled dimers measured at 20, 30, and 40 °C (Supporting Figures 14 and 15) of **2m**$^{-}{}_{2}$ (red) and **2p**$^{-}{}_{2}$ (blue) as TBA salts. The fitting lines provided the thermodynamic parameters ΔH^0 = 17 and 17 kJ mol^{-1} and ΔS^0 = 0.65 and 0.68 kJ mol^{-1}K^{-1}, respectively. The R values (> 0.99) suggest the plots in small errors.



Supporting Figure 17 ^{1}H NMR spectra in $CDCl_3$ (1 × 10^{-3} M as monomers for the initial concentration of **2p**$^{-}{}_{2}$) at 20 °C of the mixtures of **2m**$^{-}{}_{2}$ (red) and **2p**$^{-}{}_{2}$ (blue) as TBA salts in various ratios.



Supporting Figure 18 ESI-TOF-MS at negative mode of the mixtures of **2m**$^-_2$ and **3p**$^-_2$ as TBA salts from CH_3CN solutions (1×10^{-6} M as monomers for each species).