Supporting Information

SYNTHESES AND ACID-STIMULUS RESPONSIVENESS OF AMINOBENZOPYRANOXANTHENE SPIROETHERS

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EXPERIMENTAL

Reagents and solvents were purchased from Tokyo Chemical Industries (Tokyo, Japan), Wako Pure Chemical Industries (Osaka, Japan), and Nacalai Tesque (Kyoto, Japan). All solvents were used without further purification. Flash column chromatography was conducted over silica gel (Merck Silica Gel 60 mesh 70-230). Developed TLC plates were visualized under a UV lamp, by staining with an I_2-SiO_2 mixture, and by heating plates that were dipped in ammonium phosphomolybdate sulfate solution. ^{1}H-NMR and ^{13}C-NMR spectra were recorded using 600 MHz (Varian UNITY INOVA) spectrometers. Solvent used for NMR measurements were $CDCl_3$. Mass spectra were measured by using a G6520 (Agilent Technologies, Ltd.). UV-vis spectra were collected on a JASCO V-570 spectrophotometer at room temperature using a 1 cm quartz cuvette. All solvents for spectrophotometry were purchased from Nacalai Tesque (Kyoto, Japan).

Reduced ABPX-SEs (**2**$_{trans}$)

To a stirred solution of ABPX-SLs (**1**$_{trans}$) (526 mg, 0.79 mmol) in 60 mL of THF, lithium aluminum hydride (LAH) (152 mg, 4.0 mmol) was slowly added and the mixture was stirred overnight under argon at room temperature for 12 h. Upon the completion of the reaction by slowly adding 15 μL of water, 45 μL of followed by 15% aqueous NaOH, the reaction mixture was filtered through celite. The filtrate was dried with $MgSO_4$ and evaporated to give the crude product. The products were purified by silica gel column chromatography to obtain the pure product.

Yield: 66% (340 mg). ^{1}H-NMR ($CDCl_3$, 600 MHz): δ 7.32-7.30 (m, 2H), 7.18-7.14 (m, 4H), 7.09-7.07 (m, 2H), 6.82 (s, 1H), 6.68 (s, 1H), 6.63 (d, 2H, J = 9.0 Hz), 6.42 (m, 2H), 6.25 (m, 2H), 5.29 (s, 1H), 4.68 (d, 2H, J = 12 Hz), 4.48 (d, 2H, J = 12 Hz), 3.31 (q, 8H, J = 7.2 Hz), 1.15 (t, 12H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 151.71, 151.68, 150.19, 145.77, 137.42, 131.00, 130.75, 130.08, 129.19, 129.13, 128.66, 126.85, 126.58, 120.02, 103.46, 63.11, 50.85, 44.73, 44.69, 44.67, 44.64, 44.63, 44.60, 44.56, 44.53, 44.50, 38.62, 31.00, 12.63, 12.57. HRMS (ESI, positive mode): m/z calcd for $C_{42}H_{45}N_2O_4^+$ [M^+] 641.337905; Found 639.3226.

ABPX-SEs (3)

To a solution of compound **2**$_{trans}$ (111 mg, 0.17 mmol) in 5 mL of CH_2Cl_2, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (165 mg, 0.73 mmol) was added in ice bath, and the resulting mixture was stirred under argon at room temperature for 3 h. After the completion of the reaction, its pH was adjusted to 9−10 with 15% aqueous NaOH. The resulting mixture was then extracted repeatedly with $CHCl_3$, and the organic layer was combined, dried with $MgSO_4$, and filtered. The crude product was purified by silica gel column chromatography to obtain the pure product **3**$_{trans}$, which eluted first, followed by **3**$_{cis}$ because *trans*-isomer has higher polarity than *cis*-isomer for ABPXs.

Compound **3**$_{trans}$. Yield: 20% (22 mg). ^{1}H-NMR ($CDCl_3$, 600 MHz): δ 7.28 (ddd, 2H, J = 7.2, 7.2, 1.2 Hz), 7.24-7.22 (m, 2H), 7.16 (d, 2H, J = 7.8 Hz), 7.00 (s, 1H), 6.92 (d, 2H, J = 7.8 Hz), 6.81 (d, 2H, 9.0 Hz), 6.49 (bs, 2H), 6.42-6.42 (bd, 2H, J = 7.2 Hz), 6.25 (s, 1H), 5.03 (d, 2H, J = 12 Hz), 4.63 (d, 2H, J = 12 Hz), 3.36 (q, 8H, J = 7.2 Hz), 1.17 (t, 12H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 152.53, 151.12, 144.49, 139.56, 129.80, 129.06, 128.06, 127.75, 124.02, 120.74, 120.20, 103.15, 71.03, 44.81, 44.78, 44.76, 12.58. HRMS (ESI, positive mode): m/z calcd for $C_{42}H_{41}N_2O_4^+$ [M^+] 637.3061; Found 637.3044.

Compound **3**$_{cis}$. Yield: 8% (8.8 mg). ^{1}H-NMR ($CDCl_3$, 600 MHz): δ 7.20 (ddd, 2H, J = 7.5, 7.2, 1.2 Hz), 7.16-7.15 (m, 2H), 7.06-7.03 (m, 2H), 7.01 (s, 1H), 6.77 (d, 2H, J = 9.0 Hz), 6.68 (d, 2H, J = 7.8 Hz), 6.54 (m, 2H), 6.43 (m, 2H), 6.24 (s, 1H), 5.11 (d, 2H, J = 12.6 Hz), 4.97 (d, 2H, J = 12.6 Hz), 3.36 (q, 8H, J = 7.2 Hz), 1.16 (t, 12H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 152.52, 151.36, 144.01, 139.69, 129.62, 129.51, 127.78, 127.67, 123.62, 120.92, 120.18, 71.22, 45.24, 45.22, 45.19, 45.16, 45.14, 31.96, 29.73, 29.7029.40, 22.72, 14.16, 12.50, 12.44. HRMS (ESI, positive mode): m/z calcd for $C_{42}H_{41}N_2O_4^+$ [M^+] 637.3061; Found 637.3051.