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Supporting Information

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Linear to Turn Conformational Switching Induced by Deprotonation on the Unsymmetrically Linked Phenolic Oligoamides

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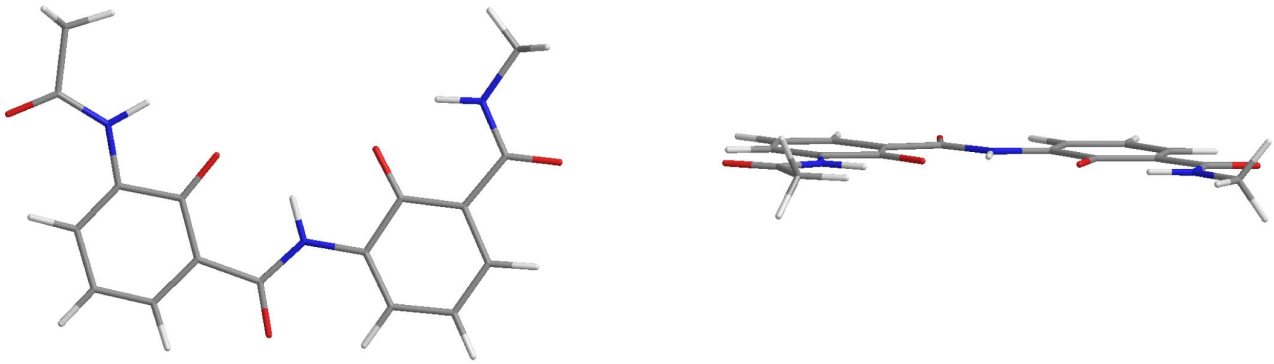

Figure S1. Optimized structure of simplified **2O**$^{-}$.

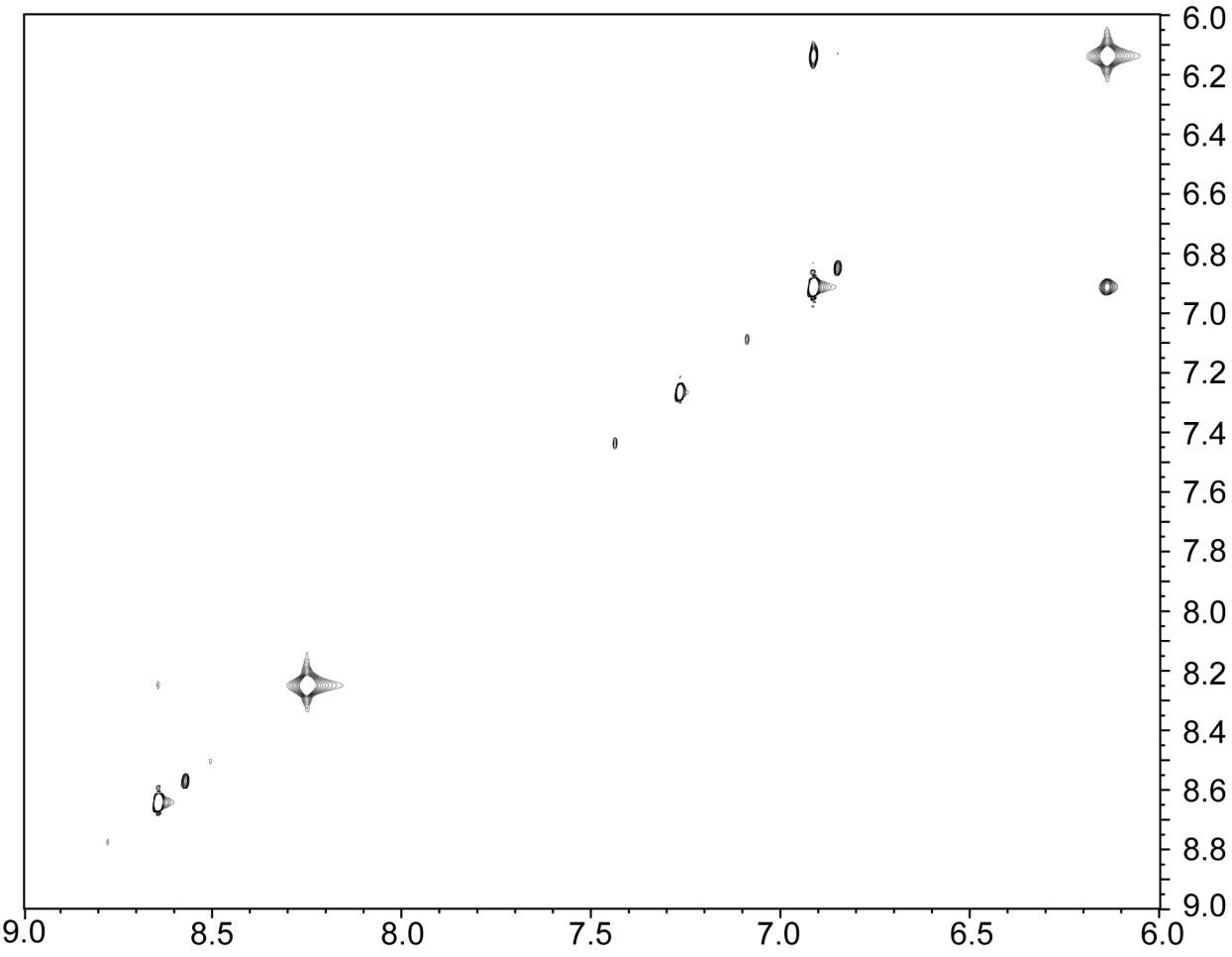

Figure S2. NOESY spectrum of **1OH** in $CDCl_3$.

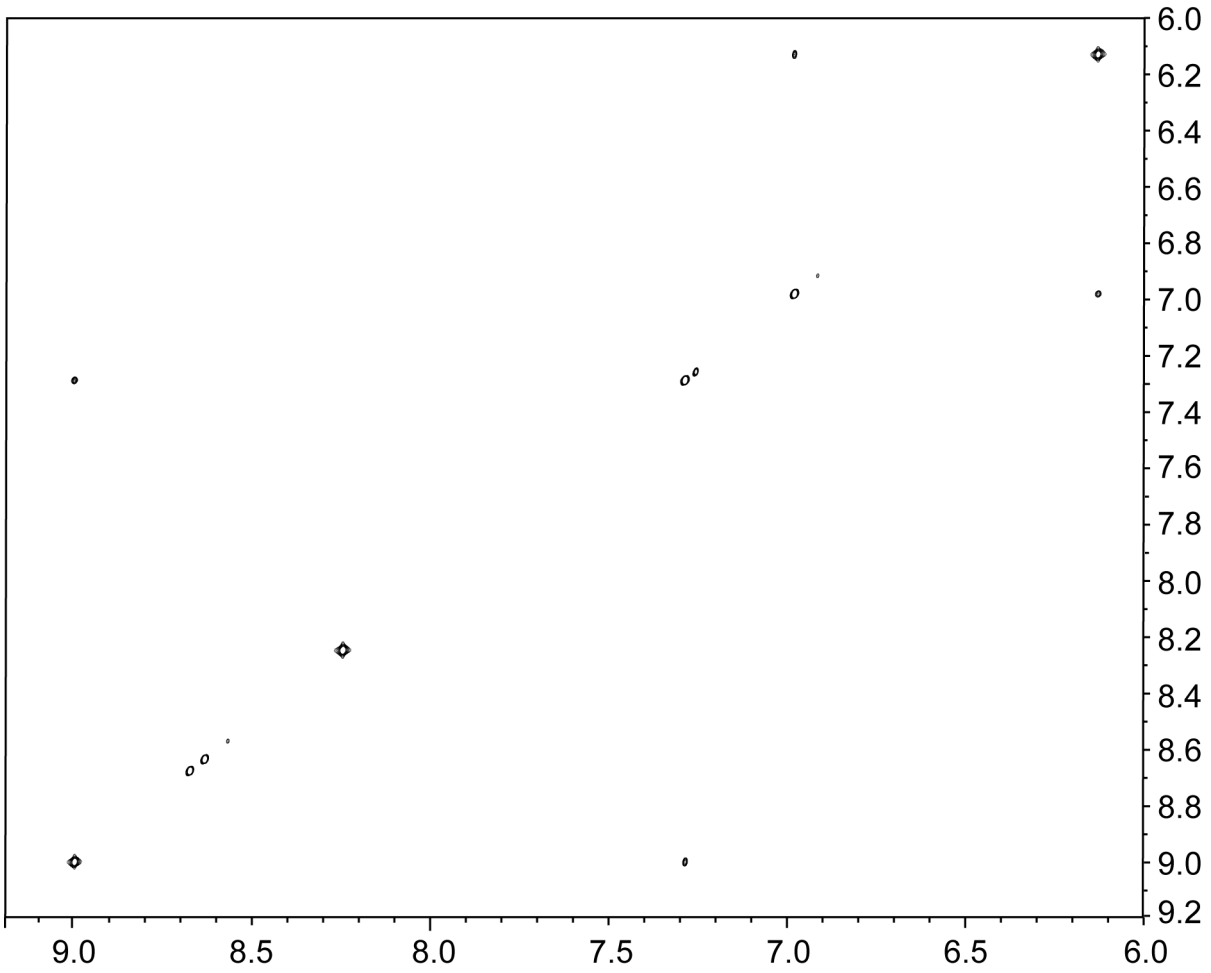

Figure S3. NOESY spectrum of **2OH** in $CDCl_3$.

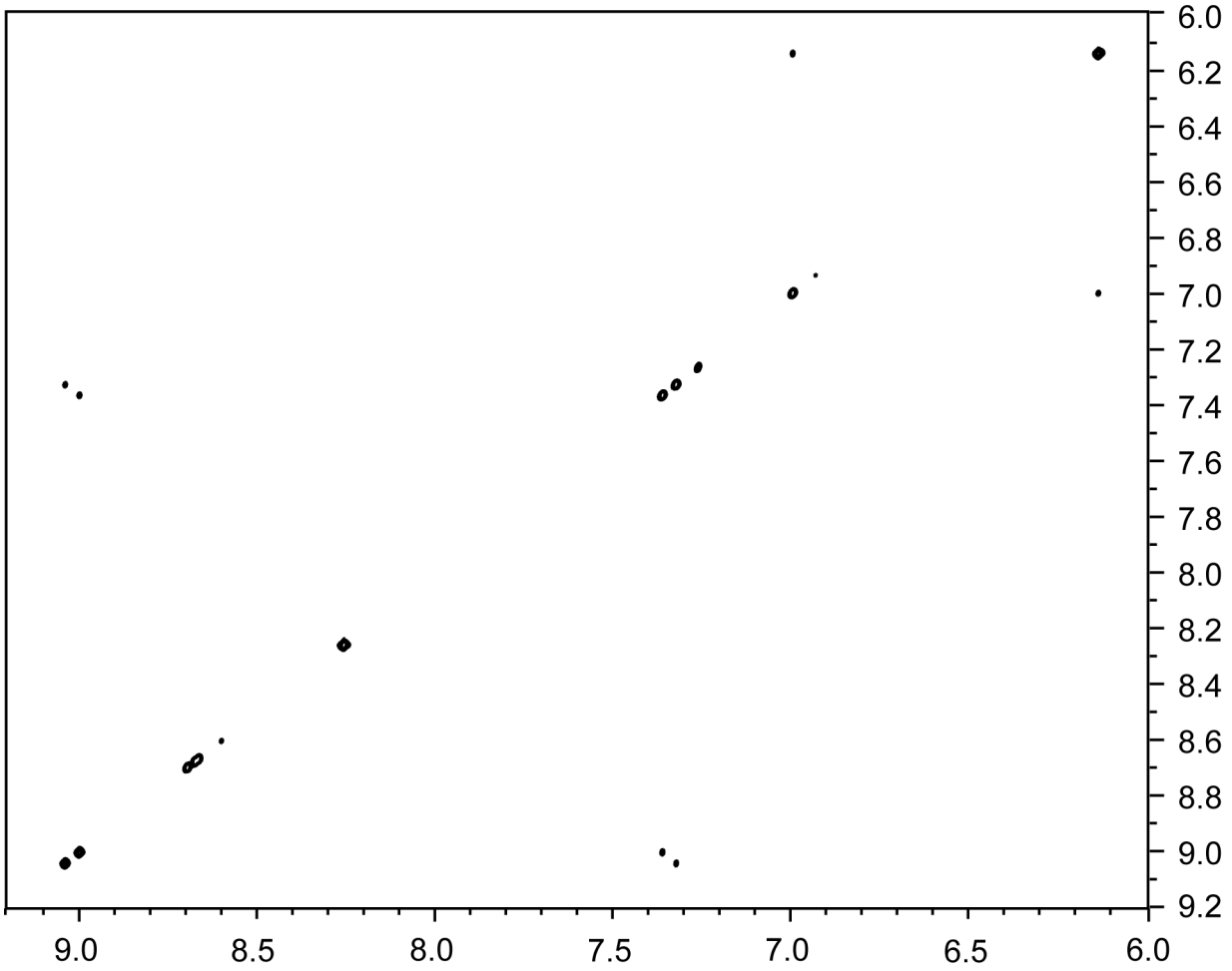

Figure S4. NOESY spectrum of **3OH** in $CDCl_3$.

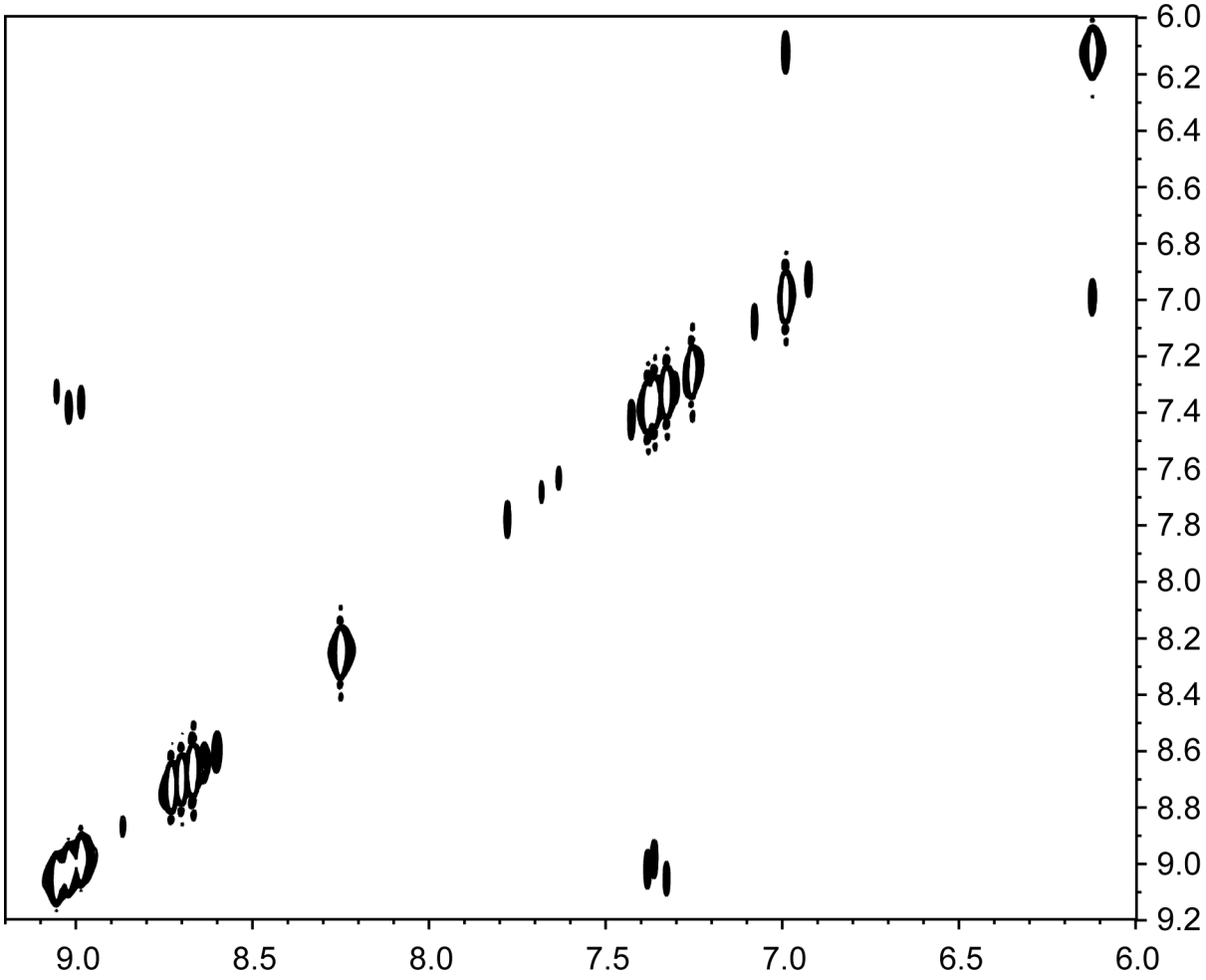

Figure S5. NOESY spectrum of **4OH** in $CDCl_3$.

Table S1. Oxidation potentials of the deprotonated oligoamides. (5 mM in CH_3CN)

	E_{ox}/ V
(1O$^-$)(NEt$_4^+$)	0.29
(2O$^-$)(NEt$_4^+$)	0.08, 0.33
(3O$^-$)(NEt$_4^+$)	–0.05, 0.20, 0.35
(4O$^-$)(NEt$_4^+$)	–0.05, 0.15, and 0.40 [a]

[a] two-electron oxidation at 0.40 V

Experimental Section

Physical Measurements

^{1}H NMR spectra in $CDCl_3$ or CD_3CN solution were recorded on a JEOL GSX 400 spectrometer and a JEOL JNM EX 270 at 30 °C. ^{13}C NMR spectra were recorded on a JEOL JNM EX 270 at 30 °C. NOESY spectra were recorded on a Varian UNITYplus 600 MHz spectrometer at 30 °C. Tetramethylsilane was used as a standard (0 ppm). ESI-MS measurements were performed on a Finnigan MAT LCQ ion trap mass spectrometer in a methanol solution. Electrochemical measurements were carried out using a BAS 100B/W instrument in dichloromethane solution (2.5 mM) that contained 0.1 M tetra-*n*-butylammonium perchlorate as a supporting electrolyte.

Synthesis

Ethyl 5-*tert*-butyl-2-hydroxy-3-nitrobenzoate (1). Ethyl salicylate (25.0 g, 0.15 mol) and *tert*-butyl chloride (20.0 mL, 0.18 mol) were dissolved in 150 mL of dichloromethane. To the solution was added aluminum trichloride (31.5 g, 0.24 mmol). The solution was refluxed for 3 hours, and then the solvent was removed. The resultant oil was extracted with diethyl ether, and washed with 2% HCl *aq*. and *sat*. NaCl *aq*., and then dried over anhydrous sodium sulfate. The removal of the solvent gave yellow oil. The obtained yellow oil was dissolved in 140 mL of acetic acid and cooled with ice containing water. To the solution was added 30 mL of 1:2 mixture of HNO_3 (fuming) and acetic acid. The reaction mixture was stirred for 10 minutes at 40 °C. Then the solution was poured into 1 L of ice-water. The precipitated yellow solid was collected with filtration. The recrystallization from *n*-hexane gave yellow crystals. (9.6 g, 24 %)

Anal. Calcd for $C_{11}H_{13}NO_5$: C, 58.42; H, 6.41; N, 5.24. Found: C, 58.41; H, 6.36; N, 5.28; m.p. 80-82 °C; ^{1}H NMR ($CDCl_3$): δ = 11.87 (s, 1H), 8.17 (d, 1H, J = 2.7 Hz), 8.13 (d, 1H, J = 2.7 Hz), 4.48 (q, 2H, J = 7.0 Hz), 1.58 (t, 3H, J = 7.0 Hz), 1.35 ppm (s, 9H); ^{13}C NMR ($CDCl_3$): δ = 168.77, 153.39, 141.65, 137.45, 132.42, 128.14, 115.52, 62.49, 34.47, 31.11, 14.24 ppm; ESI-MS: $(M–H^+)^–$, 266.3 (calcd for $M–H^+$: 266.10).

Ethyl 5-*tert*-butyl-3-amino-2-hydroxybenzoate (2, bridging unit). Compound **1** (2.06 g, 7.7 mmol) was dissolved in 100 mL of MeOH. To the solution was added Pd-C (674 mg). The reaction mixture was vigorously stirred for 2 hours under hydrogen atmosphere. Pd-C was

removed by filtration. The filtrate was concentrated to dryness under reduced pressure. The residue was recrystallized from *n*-hexane. The light brown crystals were obtained. (1.32 g, 74 %)
Anal. Calcd for $C_{13}H_{19}NO_3$: C, 65.80; H, 8.07; N, 5.90; Found: C, 65.90; H, 8.04; N, 5.99; m.p. 79-82 °C; ^{1}H NMR ($CDCl_3$): δ = 10.81 (s, 1H), 7.24 (d, 1H, J = 2.4 Hz), 6.95 (d, 1H, J = 2.4 Hz), 4.40 (q, 2H, J = 7.2 Hz), 3.83 (s, 2H), 1.42 (t, 3H, J = 7.2 Hz), 1.28 ppm (s, 9H); ^{13}C NMR ($CDCl_3$): δ = 170.69, 147.77, 141.69, 134.91, 117.81, 114.91, 111.23, 61.26, 34.18, 31.43, 14.36 ppm; ESI-MS: $(M+H^+)^+$, 238.1 (calcd for $M+H^+$: 238.14).

Ethyl 5-*tert*-butyl-2-hydroxy-3-(pivaloylamino)benzoate (3). Compound **2** (298 mg, 1.3 mmol) was dissolved in 30 mL of THF. The solution was cooled in an ice bath. To the solution was added pivaloyl chloride (0.15 mL, 1.3 mmol) followed by triethylamine (0.20 mL, 1.4 mmol). The reaction mixture was stirred overnight at room temperature. The precipitate was removed by filtration, and then the filtrate was concentrated under reduced pressure. The residue was reprecipitated from MeOH / H_2O. White powder was obtained. (350 mg, 87 %)
^{1}H NMR ($CDCl_3$): δ = 11.20 (s, 1H), 8.75 (d, 1H, J = 2.4 Hz), 8.16 (s, 1H), 7.52 (d, 1H, J = 2.4 Hz), 4.43 (q, 2H, J = 7.2 Hz), 1.43 (t, 3H, J = 7.2 Hz), 1.34 ppm (s, 9H), 1.32 (s, 9H); ESI-MS: $(M–H^+)^–$, 320.1 (calcd for $M–H^+$: 320.19).

5-*tert*-Butyl-3-(pivaloylamino)-2-hydroxybenzoic acid (4, *N*-terminal unit). Compound **3** (158 mg, 0.49 mmol) was suspended in 1:1 mixture of EtOH and 2 M NaOH *aq*. (1.4 mL). The reaction mixture was stirred overnight at 40 °C and then acidified with 2% HCl *aq*. The precipitated yellow powder was collected with filtration and recprecipitated from MeOH / H_2O. (99 mg, 68 %)
m.p. 119-122 °C; ^{1}H NMR ($CDCl_3$): δ = 10.86 (s, 1H), 8.75 (d, 1H, J = 2.4 Hz), 8.14 (s, 1H), 7.60 (d, 1H, J = 2.4 Hz), 1.36 (s, 9H), 1.33 ppm (s, 9H); ^{13}C NMR ($CDCl_3$): δ = 177.20, 173.94, 149.02, 142.46, 127.00, 124.10, 120.58, 110.03, 40.21, 34.60, 31.34, 27.68 ppm; ESI-MS: $(M–H^+)^–$, 292.1 (calcd for $M–H^+$: 292.15).

5-*tert*-Butyl-2-hydroxy-3-nitrobenzoic acid (5). Compound **1** (5.15 g, 19.3 mmol) was dissolved in 1:1 mixture of EtOH and 2 M NaOH *aq*. (40 mL). The reaction mixture was stirred

overnight at 40 °C and acidified by 2% HCl *aq*. The precipitated yellow powder was collected with filtration. Recrystallization from MeOH / water gave yellow crystals. (4.9 g, 89 %)

Anal. Calcd for $C_{11}H_{13}NO_5$: C, 55.23; H, 5.48; N, 5.86; Found: C, 55.22; H, 5.47; N, 5.92; m.p. 198-201 °C; ^{1}H NMR ($CDCl_3$): δ = 11.82 (s, 1H), 8.37 (d, 1H, J = 2.4 Hz), 8.28 (d, 1H, J = 2.4 Hz), 1.35 ppm (s, 9H); ^{13}C NMR ($CDCl_3$): δ = 170.58, 153.16, 142.88, 136.44, 135.21, 128.70, 115.68, 34.62, 31.04 ppm; ESI-MS: $(M–H^+)^–$, 238.3 (calcd for $M–H^+$: 238.07).

***N*,5-Di-*tert*-butyl-2-hydroxy-3-nitrobenzamide (6).** Compound **5** (1.19 g, 4.97 mmol) and HOBt (0.68 g, 5.03 mmol) were dissolved in 15 mL of THF. To the solution was added *tert*-butylamine (0.6 mL, 5.7 mmol). The solution was cooled in an ice bath. To the solution was added WSCD (0.95 mL, 5.19 mmol). The reaction mixture was stirred overnight at room temperature and concentrated under reduced pressure. The oily residue was extracted with ethyl acetate and washed with 2% HCl *aq*. and *sat*. NaCl *aq*., and then dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The oily residue was recrystallized from *n*-hexane. Yellow crystals were obtained. (537 mg, 37 %)

Anal. Calcd for $C_{15}H_{24}N_2O_2$: C, 61.21; H, 7.53; N, 9.52; Found: C, 61.42; H, 7.60; N, 9.40; m.p. 88-91 °C; ^{1}H NMR ($CDCl_3$): δ = 12.02 (s, 1H), 8.58 (d, 1H, J = 2.4 Hz), 8.22 (d, 1H, J = 2.4 Hz), 7.75 (s, 1H), 1.49 (s, 9H), 1.35 ppm (s, 9H); ^{13}C NMR ($CDCl_3$): δ = 162.26, 150.84, 143.4, 137.72, 133.81, 124.43, 123.77, 51.83, 34.70, 31.05, 28.96 ppm; ESI-MS: $(M–H^+)^–$, 293.6 (calcd for $M–H^+$: 293.15).

***N*,5-Di-*tert*-butyl-3-amino-2-hydroxybenzamide (7, *C*-terminal unit).** Compound **6** (208 mg, 0.71 mmol) was dissolved in 10 mL of MeOH. To the solution was added Pd-C (67 mg). The reaction mixture was stirred under hydrogen atmosphere for 6 hours. Pd-C was removed by filtration, and then the filtrate was concentrated. The precipitated brown crystals were washed with a small amount of *n*-hexane. (87 mg, 47 %)

Anal. Calcd for $C_{15}H_{24}N_2O_2$ (+0.35 H_2O): C, 66.56; H, 9.20; N, 10.35; Found: C, 66.63; H, 9.34; N, 10.09; m.p. 103-106 °C; ^{1}H NMR ($CDCl_3$): δ = 12.46 (s, 1H), 6.86 (d, 1H, J = 2.0 Hz), 6.58 (d, 1H, J = 2.0 Hz), 6.04 (s, 1H), 3.86 (s, 2H), 1.48 (s, 9H), 1.28 ppm (s, 9H); ^{13}C NMR ($CDCl_3$): δ =

170.31, 147.70, 140.99, 136.05, 115.80, 113.56, 109.95, 51.94, 34.13, 31.47, 28.91 ppm; ESI-MS: $(M–H^+)^–$, 263.6 (calcd for $M–H^+$: 263.18).

Ethyl 5-*tert*-butyl-3-[(5-*t*-butyl-3-pivaloylamino-2-hydroxybenzoyl)amino]-2-hydroxybenzoate (8′). Compound **2** (210 mg, 0.89 mmol) and **4** (261 mg, 0.89 mmol) were dissolved in 4.5 mL of THF. The solution was cooled in an ice bath. To the solution was added DCC (211 mg, 1.03 mmol). The solution was stirred overnight at room temperature, and then filtered. The filtrate was concentrated under reduced pressure. The residue was chromatographed with silica gel columm using diethyl ether as eluent. The obtained oily product was reprecipitated from MeOH / H_2O. White powder was obtained. (330 mg, 69 %)

^{1}H NMR ($CDCl_3$): δ = 12.46 (s, 1H), 11.34 (s, 1H), 8.89 (s, 1H), 8.72 (d, 1H, J = 2.4 Hz), 8.67 (d, 1H, J = 2.0 Hz), 8.24 (s, 1H), 7.62 (d, 1H, J = 2.4 Hz), 7.29 (d, 1H, J = 2.0 Hz), 4.46 (q, 2H, J = 7.2 Hz), 1.45 (t, 3H, J = 7.2 Hz), 1.36 ppm (s, 27H); ESI-MS: $(M–H^+)^–$, 511.2 (calcd for $M–H^+$: 511.28).

5-*tert*-Butyl-3-[(5-*tert*-butyl-3-pivaloylamino-2-hydroxybenzoyl)amino]-2-hydroxybenzoic acid (8). This compound was synthesized by a similar method to **4**.

Yield: 78%. m.p. 250-251°C; ^{1}H NMR ($CDCl_3$): δ = 12.38 (s, 1H), 11.08 (s, 1H), 8.98 (s, 1H), 8.73 (d, 1H, J = 2.0 Hz), 8.61 (d, 1H, J = 2.0 Hz), 8.22 (s, 1H), 7.68 (d, 1H, J = 2.0 Hz), 7.33 (d, 1H, J = 2.0 Hz), 1.37 (s, 18H), 1.36 ppm (s, 9H); ESI-MS: $(M–H^+)^–$, 483.7 (calcd for $M–H^+$: 483.25).

Ethyl 5-*tert*-butyl-3-({5-*tert*-butyl-3-[(5-*tert*-butyl-3-pivaloylamino-2-hydroxybenzoyl)amino]-2-hydroxybenzoyl}amino)-2-hydroxybenzoate (9′). This compound was synthesized by a similar method to **8′** using compound **8** and compound **2**, and purified by washing with MeOH.

Yield: 51%. ^{1}H NMR ($CDCl_3$): δ = 12.73 (s, 1H), 12.47 (s, 1H), 11.38 (s, 1H), 9.05 (s, 1H), 8.87 (s, 1H), 8.74 (d, 1H, J = 2.0 Hz), 8.70 (d, 1H, J = 2.0 Hz), 8.66 (d, 1H, J = 2.0 Hz), 8.25 (s, 1H), 7.63 (d, 1H, J = 2.0 Hz), 7.35 (d, 1H, J = 2.0 Hz), 7.32 (d, 1H, J = 2.0 Hz), 4.47 (q, 2H, J = 7.2 Hz), 1.46 (t, 3H, J = 7.2 Hz), 1.41 (s, 9H), 1.37 ppm (s, 27H); ESI-MS: $(M–H^+)^–$, 702.7 (calcd for $M–H^+$: 702.38).

5-*tert*-Butyl-3-({5-*tert*-butyl-3-[(5-*tert*-butyl-3-pivaloylamino-2-hydroxybenzoyl)amino]-2-hydroxybenzoyl}amino)-2-hydroxybenzoic acid (9). This compound was synthesized by a similar method to **4**.

Yield: 90 %. ^{1}H NMR ($CDCl_3$): δ = 12.67 (s, 1H), 12.44 (s, 1H), 11.15 (s, 1H), 9.10 (s, 1H), 8.93 (s, 1H), 8.76 (d, 1H, *J* = 2.0 Hz), 8.67 (d, 1H, *J* = 2.0 Hz), 8.62 (d, 1H, *J* = 2.0 Hz), 8.24 (s, 1H), 7.69 (d, 1H, *J* = 2.0 Hz), 7.38 (d, 1H, *J* = 2.0 Hz), 7.35 (d, 1H, *J* = 2.0 Hz), 1.41 (s, 9H), 1.37 ppm (s, 18H); ESI-MS: $(M–H^+)^–$,673.9 (calcd for $M–H^+$: 674.34).

***N*,5-Di-*tert*-butyl-3-pivaloylamino-2-hydroxybenzamide (1OH).** Compound **7** (325 mg, 1.2 mmol) was dissolved in 10 mL of THF. The solution was cooled in an ice bath. To the solution was added pivaloyl chloride (0.15 mL, 1.2 mmol) followed by triethylamine (0.17 mL, 1.2 mmol). The reaction mixture was stirred overnight at room temperature. Solvent was removed under reduced pressure. The resulting residue was washed with 2% HCl *aq*. and MeOH. Colorless microcrystals were obtained. (340 mg, 79 %)

Anal. Calcd for $C_{20}H_{32}N_2O_3$: C, 68.93; H, 9.26; N, 8.04; Found: C, 68.85; H, 9.32; N, 8.02; ^{1}H NMR ($CDCl_3$): δ = 13.02 (s, 1H), 8.63 (d, 1H, *J* = 2.0 Hz), 8.24 (s, 1H), 6.91 (d, 1H, *J* = 2.0 Hz), 6.13 (s, 1H), 1.49 (s, 9H), 1.34 (s, 9H), 1.32 ppm (s, 9H); ^{13}C NMR ($CDCl_3$): δ = 176.83, 169.79, 148.61, 141.15, 128.02, 120.80, 114.72, 113.27, 52.20, 40.16, 34.54, 31.48, 28.89, 27.73 ppm; ESI-MS: $(M–H^+)^–$, 347.5 (calcd for $M–H^+$: 347.23).

5-*tert*-Butyl-*N*-{5-*tert*-butyl-3-[(*tert*-butylamino)carbonyl]-2-hydroxyphenyl}-3-pivaloylamino-2- hydroxybenzamide (2OH). Compound **4** (267 mg, 0.91 mmol) and **7** (240 mg, 0.91 mmol) were dissolved in 5 mL of THF. The solution was cooled in an ice bath. To the solution was added DCC (190 mg, 0.91 mmol). The reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure and the residue was extracted with diethyl ether. After a filtration of the insolubles, the solvent was evaporated. The residue was reprecipitated from ethyl acetate/ *n*-hexane. (330 mg, 67 %).

Anal. Calcd for $C_{31}H_{45}N_3O_5$: C, 68.99; H, 8.40; N, 7.79; Found: C, 68.84; H, 8.40; N, 7.97; m.p. 195-199 °C; ^{1}H NMR ($CDCl_3$): δ = 13.28 (s, 1H), 12.51 (s, 1H), 9.00 (s, 1H), 8.67 (d, 1H, *J* = 2.0 Hz), 8.63 (d, 1H, *J* = 2.0 Hz), 8.25 (s, 1H), 7.29 (d, 1H, *J* = 2.0 Hz), 6.98 (d, 1H, *J* = 2.0 Hz), 6.13

(s, 1H), 1.51 (s, 9H), 1.37 (s, 9H), 1.361 (s, 9H), 1.357 ppm (s, 9H); ^{13}C NMR ($CDCl_3$): δ = 176.91, 169.68, 168.08, 149.12, 148.66, 141.87, 141.18, 128.01, 126.98, 121.62, 121.35, 115.74, 115.65, 113.54, 113.49, 52.37, 40.17, 34.60, 31.49, 31.38, 28.88, 27.73 ppm; ESI-MS: $(M–H^+)^–$, 538.5 (calcd for $M–H^+$: 538.33).

Other oligoamides. 5-*tert*-Butyl-*N*-[5-*tert*-butyl-3-({5-*tert*-butyl-3-[(*tert*-butylamino)carbonyl]-2-hydroxyanilino}carbonyl)-2-hydroxyphenyl]-3-pivaloylamino-2-hydroxybenzamide (**3OH**) and 5-*tert*-butyl-*N*-(5-*tert*-butyl-3-{[5-*tert*-butyl-3-({5-*tert*-butyl-3-[(*tert*-butylamino)carbonyl]-2-hydroxyanilino}carbonyl)-2-hydroxyanilino]carbonyl}-2-hydroxyphenyl)-3-pivaloylamino-2-hydroxybenzamide (**4OH**) were synthesized by a similar method to **2OH** from **8** and **9**, respectively.

3OH: Yield: 37 %. Anal. Calcd for $C_{42}H_{58}N_4O_7$: C, 69.01; H, 8.00; N, 7.67; Found: C, 68.98; H, 7.95; N, 7.74; m.p. 275-276 °C; ^{1}H NMR ($CDCl_3$): δ = 13.34 (s, 1H), 12.78 (s, 1H), 12.49 (s, 1H), 9.03 (s, 1H), 8.99 (s, 1H), 8.69 (d, 1H, J = 2.0 Hz), 8.67 (d, 1H, J = 2.0 Hz), 8.66 (d, 1H, J = 2.0 Hz), 8.25 (s, 1H), 7.35 (d, 1H, J = 2.0 Hz), 7.32 (d, 1H, J = 2.0 Hz), 6.99 (d, 1H, J = 2.0 Hz), 6.13 (s, 1H), 1.52 (s, 9H), 1.40 (s, 9H), 1.371 (s, 9H), 1.368 (s, 9H), 1.366 ppm (s, 9H); ^{13}C NMR ($CDCl_3$): δ = 176.99, 169.70, 168.06, 167.94, 149.12, 149.10, 148.65, 141.92, 141.90, 141.22, 128.00, 127.03, 126.85, 122.14, 121.71, 121.38, 116.53, 115.85, 113.70, 113.57, 113.53, 52.39, 40.17, 34.68, 34.61, 31.49, 31.41, 31.39, 28.87, 27.74 ppm; ESI-MS: $(M–H^+)^–$, 729.5 (calcd for $M–H^+$: 729.42).

4OH: Yield: 54 %. Anal. Calcd for $C_{53}H_{71}N_5O_9$: C, 68.36; H, 7.59; N, 7.46; Found: C, 69.03; H, 7.76; N, 7.59; ^{1}H NMR ($CDCl_3$): δ = 13.36 (s, 1H), 12.83 (s, 1H), 12.76 (s, 1H), 12.49 (s, 1H), 9.06 (s, 1H), 9.03 (s, 1H), 8.99 (s, 1H), 8.72 (d, 1H, J = 2.0 Hz), 8.69 (d, 1H, J = 2.0 Hz), 8.66 (d, 2H, J = 2.0 Hz), 8.25 (s, 1H), 7.39 (d, 1H, J = 2.0 Hz), 7.37 (d, 1H, J = 2.0 Hz), 7.33 (d, 1H, J = 2.0 Hz), 7.00 (d, 1H, J = 2.0 Hz), 6.13 (s, 1H), 1.52 (s, 9H), 1.414 (s, 9H), 1.407 (s, 9H), 1.376 (s, 9H), 1.374 (s, 9H), 1.369 ppm (s, 9H); ^{13}C NMR ($CDCl_3$): δ = 177.02, 169.70, 168.07, 167.98, 149.13, 148.67, 141.97, 141.94, 141.93, 141.23, 128.00, 127.07, 126.93, 126.84, 122.19, 122.15, 121.75, 121.39, 116.52, 116.50, 115.84, 115.80, 113.65, 113.59, 113.56, 113.48, 52.42, 40.18, 34.70, 34.64, 31.50, 31.44, 31.41, 28.86, 27.75 ppm; ESI-MS: $(M–H^+)^–$, 921.1 (calcd for $M–H^+$: 920.52).

Deprotonated oligoamides ((1O$^-$)(NEt$_4^+$) – (4O$^-$)(NEt$_4^+$)). Deprotonation of the oligoamides was performed by a neutralization of the phenolic OH with NEt_4OH (1 equivalent to the phenolic OH groups) in methanol. The deprotonated oligoamides were purified by recrystallization from acetonitrile / diethyl ether.

Tetraethylammonium 4-*tert*-butyl-2-[(*tert*-butylamino)carbonyl]-6-pivaloylaminobenzenolate ((1O$^-$)(NEt$_4^+$)): ^{1}H NMR (CD_3CN): δ = 11.91 (s, 1H), 9.61 (s, 1H), 8.23 (d, 1H, J = 2.8 Hz), 7.42 (d, 1H, J = 2.8 Hz), 3.13 (q, 8H, J = 7.2 Hz), 1.38 (s, 9H), 1.25 (s, 9H), 1.22 (s, 9H), 1.12 ppm (t, 12H, J = 7.2 Hz).

Bis(tetraethylammonium) 4-*tert*-butyl-2-({5-*tert*-butyl-3-[(*tert*-butylamino)carbonyl]-2-oxidoanilino}carbonyl)-6-pivaloylaminobenzenolate ((2O$^-$)(NEt$_4^+$)): ^{1}H NMR (CD_3CN): δ = 13.33 (s, 1H), 12.71 (s, 1H), 9.82 (s, 1H), 8.62 (d, 1H, J = 2.8 Hz), 8.25 (d, 1H, J = 2.8 Hz), 7.57 (d, 1H, J = 2.8 Hz), 7.40 (d, 1H, J = 2.8 Hz), 3.08 (q, 16H, J = 7.2 Hz), 1.42 (s, 9H), 1.30 (s, 9H), 1.261 (s, 9H), 1.255 (s, 9H), 1.12 ppm (t, 24H, J = 7.2 Hz).

Tris(tetraethylammonium) 4-*tert*-butyl-2-{[5-*tert*-butyl-3-({5-*tert*-butyl-3-[(*tert*-butylamino) carbonyl]-2-oxidoanilino}carbonyl)-2-oxidoanilino]carbonyl}-6-pivaloylaminobenzenolate ((3O$^-$)(NEt$_4^+$)): ^{1}H NMR (CD_3CN): δ = 14.04 (s, 1H), 13.53 (s, 1H), 12.83 (s, 1H), 9.88 (s, 1H), 8.65 (m, 2H), 8.27 (d, 1H, J = 2.8 Hz), 7.60 (d, 1H, J = 2.8 Hz), 7.54 (d, 1H, J = 2.8 Hz), 7.39 (d, 1H, J = 2.8 Hz), 3.09 (q, 24H, J = 7.2 Hz), 1.43 (s, 9H), 1.31 (s, 9H), 1.29 (s, 9H), 1.27 (s, 9H), 1.26 (s, 9H), 1.08 ppm (t, 36H, J = 7.2 Hz).

Tetrakis(tetraethylammonium) 4-*tert*-butyl-2-[(5-*tert*-butyl-3-{[5-*tert*-butyl-3-({5-*tert*-butyl-3-[(*tert*-butylamino)carbonyl]-2-oxidoanilino}carbonyl)-2-oxidoanilino]carbonyl}-2-oxidoanilino)carbonyl]-6-pivaloylaminobenzenolate ((4O$^-$)(NEt$_4^+$)): ^{1}H NMR (CD_3CN): δ = 13.73 (s, 1H), 13.69 (s, 1H), 13.19 (s, 1H), 12.78 (s, 1H), 9.86 (s, 1H), 8.59 (d, 1H, J = 2.8 Hz), 8.56 (d, 1H, J = 2.8 Hz), 8.50 (d, 1H, J = 2.8 Hz), 8.28 (d, 1H, J = 2.8 Hz), 7.60 (d, 1H, J = 2.8 Hz), 7.59 (d, 1H, J = 2.8 Hz), 7.55 (d, 1H, J = 2.8 Hz), 7.41 (d, 1H, J = 2.8 Hz), 3.13 (q, 32H, J = 7.2 Hz), 1.40 (s, 9H), 1.297 (s, 18H), 1.293 (s, 9H), 1.27 (s, 9H), 1.26 (s, 9H), 1.08 ppm (t, 48H, J = 7.2 Hz).

2-Acetyloxy-3-nitrobenzoic acid (10). 6-Nitrosalicylic acid (3.01 g, 16.4 mmol) was dissolved in 15 mL

of THF. The solution was cooled with ice containing water. To the solution was added triethylamine (4.0 mL, 29 mmol) followed by acetyl chloride (2.0 mL, 28 mmol). The reaction mixture was stirred overnight at room temperature, and then filtered. The filtrate was concentrated. Yellow powder was obtained and used without further purification. (3.19 g, 86%). ^{1}H NMR(DMSO-d_6); δ = 13.70 (s, 1H), 8.29 (d, 1H), 8.22 (d, 1H), 7.61 (t, 1H), 2.29 ppm (s, 3H).

2-*tert*-Butylcarbamoyl-6-nitrophenyl acetate (11). Compound **10** (1.00 g, 4.44 mmol) was dissolved in 50 mL of THF. To the solution was added triethylamine (0.62 mL, 4.4 mmol). The solution was cooled to –15 °C. To the solution was added isobutyl chlorofolmate (0.6 mL, 4.4 mmol) followed by *tert*-butylamine (0.48 mL, 4.4 mmol) in 5 mL of THF keeping below –15 °C. The solution was stirred overnight at room temperature, and then concentrated. The residue was extracted with ethyl acetate, and the organic layer was washed with 4% $NaHCO_3$ *aq*., 2% HCl *aq*., and *sat*. NaCl *aq*., and then dried over anhydrous sodium sulfate. The solvent was removed and the precipitate was recrystallized from diethyl ether. The yellow crystals were obtained. (0.80g, 64%) ^{1}H NMR(DMSO-d_6); δ = 8.15 (d, 1H), 8.05 (s, 1H), 7.78 (d, 1H), 7.52 (t, 1H), 2.25 (s, 3H), 1.32 ppm (s, 9H).

***N*-*tert*-Butyl-3-acetylamino-2-hydroxybenzamide (1′OH).** Compound **11** (0.80 g, 2.85 mmol) was dissolved in a mixture of *i*-PrOH (15 mL) and MeOH (15 mL). To the solution was added Pd-C (0.34 g). The reaction mixture was stirred under 3 atom of hydrogen atmosphere for 2.5 h. Pd-C was filtered off and the solvent was removed. The resulting precipitate was recrystallized from *n*-hexane. (50 mg, 7 %) ^{1}H NMR(DMSO-d_6); δ = 13.39 (s, 1H), 9.21 (s, 1H), 8.11 (s, 1H), 7.98 (d, 1H), 7.63 (d, 1H), 6.79 (t, 1H), 2.07 (s, 3H), 1.40 ppm (s, 9H).

(1′O$^-$)(NMe$_4^+$) was prepared by a similar method to the deprotonated oligoamides using NMe_4OH. Single crystal of **(1′O$^-$)(NMe$_4^+$)** was obtained from acetonitrile / diethyl ether