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Electronic Supplementary Information

Cobaltabisdicarbollide anion receptor for enantiomer-selective membrane electrodes

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Supporting Information

Experimental procedures, FTIR, NMR, MALDI-TOF values.

Experimental Section

Instrumentation: IR spectra (ν, cm^{-1}; KBr pellets) were obtained on a Shimadzu FTIR-8300 spectrophotometer. The ^{1}H- and $^{1}H\{^{11}B\}$-NMR (300.13 MHz), $^{13}C\{^{1}H\}$-NMR (75.47 MHz), ^{11}B- and $^{11}B\{^{1}H\}$-NMR (96.29 MHz) spectra were recorded on a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. All NMR spectra were performed in d_6-acetone at 22ºC. The ^{11}B- and $^{11}B\{^{1}H\}$-NMR shifts were referenced to external $BF_3{\cdot}OEt_2$, while the ^{1}H, $^{1}H\{^{11}B\}$, and $^{13}C\{^{1}H\}$-NMR shifts were referenced to $SiMe_4$. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants in Hz. The mass spectra were recorded in the negative ion mode using a Bruker Biflex MALDI-TOF-MS [N_2 laser; λ_{exc} 337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)]. Cs[Co(1,2-$C_2B_9H_{11})_2$] was from KATCHEM and it was used as received.

Synthesis of the D- and L- Tryptophan salt of cobaltabisdicarbollide, [H-Try][1]. Firstly, H[Co(1,2-$C_2B_9H_{11})_2$] was obtained from Cs[Co(1,2-$C_2B_9H_{11})_2$] (0.3000 g) and HCl 1M (15 mL), extracting the resulted product in ether (20mL). The extraction procedure was made by 3 times. The obtained compound was dried in vacuum atmosphere up to constant weight. D-, L- Try (0.0102g, 0.05 mmol) was dissolved in 5 mL of HCl 3M under stirring (solution 1). Secondly, the ion-pair compound [H-Try][**1**] was prepared by mixing 5 mL of 0.01M solution 1 with 0.0165g of H[Co(1,2-$C_2B_9H_{11})_2$] under stirring resulting a yellow precipitate. The precipitate was filtered, washed with a solution of HCl and dried in vacuum atmosphere. FTIR, ν: 3551 (OH), 3397 (NH), 3208 (NH_3^+) 3041 (C_c-H), 2926 (C_{aryl}-H); 2565, (B-H), 1732 (C=O), 1599, 1490, 1459, 1439, 1427 (NH, NH_3^+, C=O, OH). ^{1}H NMR ($(CD_3)_2CO$) δ: 10.3 (m, N-H), 7.56 (d, ^{3}J(H,H)= 7.7, 1H, C_{aryl}-H), 7.40 (d, ^{3}J(H,H)= 7.9, 3 + 1H, NH_3^+, C_{aryl}-H), 7.20 (dd, ^{3}J(H,H)= 7.9, ^{3}J(H,H)= 7.3, 1H, C_{aryl}-H), 7.12 (dd, ^{3}J(H,H)= 7.7, ^{3}J(H,H)= 7.2, 1H, C_{aryl}-H), 4.95 (dd, ^{3}J(H,H)= 11.9, ^{3}J(H,H)= 5.7, 1H,-CH), 3.95 (s, 4H, C_c-H), 3.57 (dd, ^{3}J(H,H)= 16.1, ^{3}J(H,H)= 5.1, 1H, -CH_2), 3.30 (dd, ^{3}J(H,H)= 16.2, ^{3}J(H,H)= 5.7, 1H, -CH_2), 3.70-3.50 (m, 2H, CH_2), 3.70-0.50 (br m, B-H). ^{1}H{^{11}B} NMR ($(CD_3)_2CO$) δ: 10.3 (m, N-H), 7.56 (d, ^{3}J(H,H)= 7.7, 1H, C_{aryl}-H), 7.40 (d, ^{3}J(H,H)= 7.9, 3 + 1H, NH_3^+, C_{aryl}-H), 7.20 (dd, ^{3}J(H,H)= 7.9, ^{3}J(H,H)= 7.3, 1H, C_{aryl}-H), 7.12 (dd, ^{3}J(H,H)= 7.7, ^{3}J(H,H)= 7.2, 1H, C_{aryl}-H), 4.95 (dd, ^{3}J(H,H)= 11.9, ^{3}J(H,H)= 5.7, 1H, NH_3^+-CH), 3.95 (s, 4H, C_c-H), 3.57 (dd, ^{3}J(H,H)= 16.1, ^{3}J(H,H)= 5.1, 1H, -CH_2), 3.30 (dd, ^{3}J(H,H)= 16.2, ^{3}J(H,H)= 5.7, 1H, -CH_2), 4.08, 3.39, 2.99, 2.85, 2.72, 1.95, 1.62, 1.57 (br s, 18H, B-H). ^{13}C{^{1}H} NMR ($(CD_3)_2CO$) δ: 169.2 (COOH), 153.4, 136.9, 124.1, 122.7, 119.7, 118.4, 111.4, 104.0 (s, C_{aryl}), 61.4, 53.9 (s, C_c), 50.9 (s, CH), 22.4 (s, CH_2). ^{11}B-NMR ($(CD_3)_2CO$) δ: 7.3 (d, ^{1}J(B,H)= 140, 2B), 2.1 (d, ^{1}J(B,H)= 143, 2B), -4.6 (d, ^{1}J(B,H)= 145, 4B); -5.3 (d, ^{1}J(B,H)= 133, 4B), -16.6 (d, ^{1}J(B,H)= 154, 4B), -22.1 (d, ^{1}J(B,H)=

170, 2B). MALDI-TOF at the cathode, (m/z): 187.83 (M-17; 100%), 204.90 (M; 16%), 244.89 (M-40, 89%). MALDI-TOF at the anode, (m/z): 324.26 ($[Co(1,2\text{-}C_2B_9H_{11})_2]^-$, 100%).

Synthesis of the D- and L- Histidine salt of cobaltabisdicarbollide, $[H_2\text{-His}][1]_2$. Firstly, $H[Co(1,2\text{-}C_2B_9H_{11})_2]$ was obtained from $Cs[Co(1,2\text{-}C_2B_9H_{11})_2]$ (0.3000 g) and HCl 1M (15 mL), extracting the resulted product in ether (20mL). The extraction procedure was made by 3 times. The obtained compound was dried in vacuum atmosphere up to constant weight. D-, L- Histidine (0.0388g, 0.25 mmol) was dissolved in 5 mL of HCl 3M under stirring (solution 1). Secondly, the ion-pair compound $[H_2\text{-His}]$**[1]**$_2$ was prepared by mixing 5 mL of 0.01M solution 1 with 0.0165 g of $H[Co(1,2\text{-}C_2B_9H_{11})_2]$ under stirring resulting a yellow precipitate. The precipitate was filtered, washed with a diluted solution of HCl and dried in vacuum atmosphere.

FTIR, ν: 3585, 3555 (OH), 3374 (NH), 3331 (NH_3^+) 3039 (C_c-H), 2978, 2934, 2895, 2862 (C_{aryl}-H, C_{alkyl}-H); 2565, 2547 (B-H), 1734 (C=O), 1624, 1596, 1526 (N-C=O, N^+-H, NH_3^+). ^{1}H NMR ($(CD_3)_2CO$) δ: 13.37 (br s,), 9.23 (s, ^{1}H, C_{aryl}-H), 7.80 (s, 1H, C_{aryl}-H), 5.69 (br s, 3H, NH_3^+), 4.90 (m, 1H, CH), 3.94 (s, 8H, C_c-H), 3.86-3.64 (m, 2H, CH_2), 3.5-0.5 (br m, B-H). $^1H\{^{11}B\}$ NMR ($(CD_3)_2CO$): δ: 13.37 (br s,), 9.23 (s, ^{1}H, C_{aryl}-H), 7.80 (s, 1H, C_{aryl}-H), 5.69 (br s, 3H, NH_3^+), 4.90 (m, 1H, CH), 3.94 (s, 8H, C_c-H), 3.86-3.64 (m, 2H, CH_2), 3.37 (br s, 4H, B-H), 2.97 (br s, 4H, B-H), 2.70 (br s, 8H, B-H), 2.01 (br s, 8H, B-H), 1.61 (br s, 4H, B-H), 1.56 (br s, 8H, B-H). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$) δ: 167.0 (s, C=O), 135.1, 127.4, 119.0 (s, C_{aryl}), 59.2, 52.7(s, C_c), 51.0 (s, CH), 26.0 (s, CH_2).^{11}B-NMR ($(CD_3)_2CO$) δ: 7.2 (d, $^1J(B,H)$= 143, 2B), 2.0 (d, $^1J(B,H)$= 141, 2B), -4.9 (d, $^1J(B,H)$= 153, 4B), -5.4 (d, $^1J(B,H)$= 133, 4B), -16.6 (d, $^1J(B,H)$= 154, 4B), -22.1 (d, $^1J(B,H)$= 168, 2B). MALDI-TOF at the cathode (m/z): 155.25 (M; 32%),

152.36 (M+3, 100%), 132.74 (M-23, 71%), 164.34 (M+9; 57%), 178.33 (M+23; 21%). MALDI-TOF at the anode (m/z): 324.23 ($[Co(1,2\text{-}C_2B_9H_{11})_2]^-$, 100%).

Synthesis of the L-Arginine salt of cobaltabisdicarbollide, [H-Arg][1]. Firstly, $H[Co(1,2\text{-}C_2B_9H_{11})_2]$ was obtained from $Cs[Co(1,2\text{-}C_2B_9H_{11})_2]$ (0.3000 g) and HCl 1M (15 mL), extracting the resulted product in ether (20mL). The extraction procedure was made by 3 times. The obtained compound was dried in vacuum atmosphere up to constant weight. L- Arg (0.009g, 0.05 mmol) was dissolved in 5 mL of HCl 3M under stirring (solution 1). Secondly, the ion-pair compound [H-Arg][**1**] was prepared by mixing 5 mL of 0.01M solution 1 with 0.0165g of $H[Co(1,2\text{-}C_2B_9H_{11})_2]$ under stirring resulting a yellow precipitate. The precipitate was filtered, washed with a solution of HCl and dried in vacuum atmosphere. FTIR, ν: 3594 (OH), 3453**,** 3365, 3216 (NH), 3036 (C_c-H), 2926 (C_{aryl}-H); 2566, 2544 (B-H), 1736 (C=O), 1659, 1645, 1615, (NH, NH_3^+, C=O, OH). ^{1}H NMR ($(CD_3)_2CO$) δ: 8.3, 7.4, 7.0, 4.5 (br s, 4H, N-H), 3.95 (s, 5H, 4 C_c-*H* + 1 CH), 3.57 (m, 2H, -CH_2), 3.70-0.50 (br m, B-H), 2.28-2.25 (m, 2H, CH_2). ^{1}H{^{11}B} NMR ($(CD_3)_2CO$) δ: 8.3, 7.4, 7.0, 4.5 (br s, 4H, N-H), 3.95 (s, 5H, 4 C_c-*H* + 1 CH), 3.57 (m, 2H, -CH_2), 4.08, 3.39, 2.99, 2.85, 2.72, 1.95, 1.62, 1.57 (br s, 18H, B-H). ^{13}C{^{1}H} NMR ($(CD_3)_2CO$) δ: 59.8(s, CH), 50.9 (s, C_c), 40.9 (s, CH_2), 24.6 (s, CH_2). ^{11}B-NMR ($(CD_3)_2CO$) δ: 7.3 (d, ^{1}J(B,H)= 140, 2B), 2.1 (d, ^{1}J(B,H)= 143, 2B), -4.7 (d, ^{1}J(B,H)= 145, 4B); -5.3 (d, ^{1}J(B,H)= 133, 4B), -16.6 (d, ^{1}J(B,H)= 154, 4B), -22.1 (d, ^{1}J(B,H)= 170, 2B). MALDI-TOF at the cathode, (m/z): 173.88 (Arg; 100%), 174.90 (H-Arg^+; 10%). MALDI-TOF at the anode, (m/z): 323.27 ($[Co(1,2\text{-}C_2B_9H_{11})_2]^-$, 100%).

Table S.1.- Electrode characteristics for L-Arg

Plasticizer	DBP	DEHP
Slope (mV/decade)	45.8	37.7
Correlation coefficient	0.993	0.991
Concentration range (M)	$5.00 \cdot 10^{-6}$- $1.00 \cdot 10^{-1}$	$1.00 \cdot 10^{-5}$- $1.00 \cdot 10^{-1}$
Detection limit (M)	$3.00 \cdot 10^{-6}$	$5.00 \cdot 10^{-5}$
Time response/s	<5	< 5
Lifetime/day	> 45	> 45

Table S.2.- ISE Selectivity coefficients for L-Arginine electrode.

Interfering species	$\lg K^{pot}_{L\text{-}Arg/B}$	$\lg K^{pot}_{L\text{-}Arg/B}$
	DBP	DEHP
glycine	-5.04	-5.46
β-alanine	-6.54	-4.40
DL-leucine	-6.11	-5.88
DL-methionine	-5.05	-5.72
L-arginine	-	-
L-histidine	-4.50	-5.02
DL-tryptophan	-6.76	-5.80