New Dendrimers Containing a Single Cobaltocenium Unit Covalently Attached to the Apical Position of Newkome Dendrons: Electrochemistry and Guest Binding Interactions with Cucurbit[7]uril

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SUPPORTING INFORMATION
Synthesis of CB7, 0Cob+, dendritic building blocks 1, 2 and 3

CB7 was synthesized according to literature procedures. Cobaltocenium carboxylic acid (0Cob+) was synthesized according to literature procedures. Dendritic building blocks 1, 2 and 3 were synthesized according to literature procedures.

Figure S1. Dendritic building blocks 1, 2 and 3

Synthesis of 1ECob+

Cobaltocenium carboxylic acid as the chloride salt (500 mg, 1.8 mmol), 1 (775 mg, 1.8 mmol), n-HATU (800 mg, 2 mmol) and 1,8-bis(dimethylamino)naphthalene, (proton sponge, 900 mg, 4.2 mmol) were stirred in dry DMF (30 ml) for 24 hours under N₂. The reaction vessel was initially cooled with ice and then allowed to equilibrate with the ambient temperature. The DMF was removed under vacuo, and then the product dissolved in EtOAc, filtered and extracted with 0.5 M HCl, (3 x 100) and with H₂O (1 x
The organic layer was then concentrated and loaded onto a silica chromatographic column and eluted with EtOAc, saturated with NH₄PF₆. The chromatographic fraction containing the target product was washed with H₂O (4 x 100) to remove any excess NH₄PF₆ in the organic layer. The organic layer was then dried with anhydrous MgSO₄ and then the EtOAc removed under vacuo to afford 1ECob⁺ as the PF₆⁻ salt (420 mg, yield 30%). ¹H NMR (400 MHz, CH₂Cl₂-d₂): δ 7.74 (s, 1H), 6.35 (t, 2H), 5.92 (t, 2H), 5.82 (s, 5H), 2.19 (t, 6H), 1.92 (t, 6H), 1.38 (s, 27H). ¹³C NMR (100 MHz CH₂Cl₂-d₂): 173.57, 160.67, 96.15, 86.46, 86.33, 84.09, 81.52, 59.46, 30.42, 30.40, 28.17. FAB-MS: 631 (M - PF₆⁻)⁺.

Synthesis of 1Cob⁺

1ECob⁺ (200 mg, 0.2 mmol) was stirred in 96% HCOOH overnight. The solvent was removed under vacuo to afford 1Cob⁺ (150 mg) in quantitative yield. ¹H NMR (400 MHz, H₂O-d₂): δ 6.22 (t, 2H), 5.89 (t, 2H), 5.84 (s, 5H), 2.43 (t, 6H), 2.17 (t, 6H). ¹³C NMR (100 MHz H₂O-d₂): δ 28.51, 28.93, 59.76, 84.25, 86.78, 86.34, 95.70, 163.34, 178.13. FAB-MS: 460 (M - PF₆⁻)⁺.

Synthesis of 2ECob⁺

Cobaltocenium carboxylic acid as the chloride salt (500 mg, 1.8 mmol), 2 (2.59 g, 1.8 mmol), n-HATU (800 mg, 2 mmol) and 1,8-bis(dimethylamino)naphthalene, (proton sponge, 900 mg, 4.2 mmol) were stirred in dry DMF (50 ml) for 24 hours under N₂. The reaction vessel was initially cooled with ice and then allowed to equilibrate with the
ambient temperature. The DMF was removed under vacuo, and then the product dissolved in EtOAc filtered and extracted with 0.5 M HCl, (3 x 100) and with H2O (1 x 100). The organic layer was then concentrated and loaded onto a silica chromatographic column and eluted with EtOAc, saturated with NH4PF6. The chromatographic fraction containing the target product was washed with H2O (4 x 100) to remove any excess NH4PF6 in the organic layer. The organic layer was then dried with anhydrous MgSO4 and then the EtOAc removed under vacuo to afford 2ECob+ as the PF6- salt (825 mg, yield 26%). 1H NMR (400 MHz, CH2Cl2-d2): δ 6.30 (t, 2H), 6.20 (s, 3H) 5.92 (t, 2H), 5.82 (s, 5H), 5.79 (t, 2H), 2.29 (t, 6H), 2.20 (t, 18H), 2.12 (t, 6H), 1.96 (t, 18H), 1.44 (s, 81H). 13C NMR (100 MHz CH2Cl2-d2) δ 28.20, 30.12, 30.29, 31.60, 31.97, 58.10, 59.28, 80.92, 84.55, 86.11, 86.43, 96.11, 173.04, 173.38. MALDI-TOF MS: 1654 (M - PF6)+.

Synthesis of 2Cob+

2ECob+ (400 mg, 0.22 mmol) was stirred in 96% HCOOH overnight. The solvent was removed under vacuo to afford 2Cob+ (288 mg) in quantitative yield. 1H NMR (400 MHz, H2O-d2): δ 6.25 (t, 2H), 5.90 (t, 2H), 5.84 (s, 5H), 2.38 (t, 18H) 2.32 (t, 6H), 2.11 (t, 6H). 2.05 (t, 18H) 13C NMR (100 MHz H2O-d2): δ 28.37, 28.92, 38.27, 38.27, 38.90, 59.03, 59.68, 84.13, 86.17, 88.35, 94.38, 163.27, 168.10, 178.13. MALDI-TOF MS: 1153 (M - PF6)+.
Synthesis of 3ECob$^+$

Cobaltocenium carboxylic acid as the chloride salt (100 mg, 0.37 mmol), 3 (1.68 g, 0.37 mmol), n-HATU (200 mg, 0.5 mmol) and 1,8-bis(dimethylamino)naphthalene, (proton sponge, 214 mg, 1.0 mmol) were stirred in dry DMF (50 ml) for 24 hours under N$_2$. The reaction vessel was initially cooled with ice and then allowed to equilibrate with the ambient temperature. The DMF was removed under vacuo, and then the product dissolved in EtOAc, filtered and extracted with 0.5 M HCl, (3 x 100) and with H$_2$O (1 x 100). The organic layer was then concentrated and loaded onto a silica chromatographic column and eluted with EtOAc, saturated with NH$_4$PF$_6$. The chromatographic fraction containing the target product was washed with H$_2$O (4 x 100) to remove any excess NH$_4$PF$_6$ in the organic layer. The organic layer was then dried with anhydrous MgSO$_4$ and then the EtOAc removed under vacuo to afford 3ECob$^+$ as the PF$_6^-$ salt (991 mg, yield 55%). $^1$H NMR (400 MHz, CH$_2$Cl$_2$-d$_2$): δ 7.00 (s, 3H), 6.33 (t, 2H) 6.22 (s, 9H), 5.86 (s, 5H), 5.77 (t, 2H), 2.29 (t, 6H), 2.16 (m, 72H), 1.93 (t, 78H), 1.42 (s, 243H). $^{13}$C NMR (100 MHz CH$_2$Cl$_2$-d$_2$) δ 28.16, 28.18, 28.22, 28.26, 30.09, 31.54, 31.91, 80.61, 80.69, 86.61, 172.96, 173.05, 173.14, 173.22. MALDI-TOF MS: 4726 (M-PF$_6^-$).

Synthesis of 3Cob$^+$

3ECob$^+$ (500 mg, 0.10 mmol) was stirred in 96% HCOOH overnight. The solvent was removed under vacuo to afford 3Cob$^+$ (344 mg) in quantitative yield. $^1$H NMR (400 MHz, H$_2$O-d$_2$): δ 6.28 (t, 2H), 5.91 (t, 2H), 5.86 (s, 5H), 2.35 (m, 60H), 2.22 (m, 18H),
2.01 (m, 78H) $^{13}$C NMR (100 MHz H$_2$O-$d_2$): $\delta$ 28.42, 29.04, 6792, 163.34, 178.09, 178.25. MALDI-TOF MS: 3212 (M-PF$_6$).

References

