Caesium and Rubidium Selective

Bis(Calix[4]diquinone) Redox-Active

Ionophores

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General procedure for the preparation of (2), (3), (4).
A suspension of p-tert-butylcalix[4]arene (1) (3.0g, 4.6mmol) and K₂CO₃ (0.70g, 5.1mmol) in CH₃CN (250ml) was refluxed for 1 hour. After this time, propane-1,3-ditosylate, 1,4-dibromobutane or 1,5-dibromopentane (5.5mmol) was added and the mixture refluxed for a further 48 hours. Following removal of the solvent in vacuo, the mixture was partitioned between CHCl₃ (100ml) and H₂O (100ml). The organic layer was dried (MgSO₄) and reduced in vacuo.

(2): To this crude material was added EtOH (100ml), which after briefly refluxing, was hot-filtered affording (2) as
an analytically pure, colourless powder (0.93g, 30%); $^1$H NMR
(CDCl$_3$, 300MHz): $\delta$=1.20 (s, 36H, (CH$_3$)$_3$C), 1.23 (s, 36H, (CH$_3$)$_3$C), 3.10 (quin, $^3$J=8.2Hz, 4H, OCH$_2$CH$_2$CH$_2$O), 3.40 (d, $^2$J=12.9Hz, 8H, ArCH$_2$Ar), 4.32 (t, $^2$J=8.2Hz, 8H, OCH$_2$CH$_2$CH$_2$O), 4.44 (d, $^2$J=12.9Hz, 8H, ArCH$_2$Ar), 7.02 (s, 8H, ArH), 7.09 (s, 8H, ArH), 8.88 (s, 4H, OH); $^{13}$C NMR (CDCl$_3$, 75.42MHz): $\delta$=30.86 (OCH$_2$CH$_2$CH$_2$O), 31.29 ((CH$_3$)$_3$C), 31.64 ((CH$_3$)$_3$C), 32.78 (ArCH$_2$Ar), 33.84 ((CH$_3$)$_3$C), 34.23 ((CH$_3$)$_3$C)), 72.65 (OCH$_2$CH$_2$CH$_2$O), 125.23, 125.87, 127.88, 133.83, 141.48, 147.27, 149.63, 150.43 (Ar); ES MS: 1379[M+H]$^+$, 1401 [M+Na]$^+$, 1417[M+K]$^+$; elemental analysis:
calculated for C$_{94}$H$_{120}$O$_8$·1/3(CHCl$_3$): C 79.94, H 8.56; found:
C 79.95, H 8.75.

(3): To this crude material was added CH$_3$CN (150ml) and the
resulting suspension refluxed for ca. 10 minutes. Subsequent hot-filtering afforded (3) as a colourless powder in ca. 90% purity (0.76g, 23%). Further purification could be achieved, if necessary, by recrystallisation via slow evaporation from methanol/dichloromethane to give pure (3) (0.47g, 15%); $^1$H NMR (CDCl$_3$, 300MHz): $\delta$=1.10 (s, 36H,
(CH$_3$)$_3$C), 1.23 (s, 36H, (CH$_3$)$_3$C), 2.65 (br.s, 8H, OCH$_2$CH$_2$CH$_2$CH$_2$O), 3.20 (d, $^2$J=13.0Hz, 8H, ArCH$_2$Ar), 4.15 (br.s, 8H, OCH$_2$CH$_2$CH$_2$CH$_2$O), 4.34 (d, $^2$J=13.0Hz, 8H, ArCH$_2$Ar), 6.89 (s, 8H, ArH), 6.95 (s, 8H, ArH), 8.41 (s, 4H, OH); $^{13}$C NMR (CDCl$_3$, 75.42MHz): $\delta$=25.42 (OCH$_2$CH$_2$CH$_2$CH$_2$O), 31.22 ((CH$_3$)$_3$C), 31.77 ((CH$_3$)$_3$C), 32.02 (ArCH$_2$Ar), 33.75 ((CH$_3$)$_3$C), 34.13 ((CH$_3$)$_3$C), 74.81 (OCH$_2$CH$_2$CH$_2$CH$_2$O), 124.71, 125.52, 127.24, 133.39, 140.84, 146.71, 149.70, 150.59 (Ar); ES MS 1429[M+Na]$^+\ 1424$[M+NH$_4$]$^+$; elemental analysis: calculated for C$_{96}$H$_{124}$O$_8$1/3(CHCl$_3$): C 80.03, H 8.67; found: C 79.95, H 8.84

(4): To this crude material was added EtOH (350ml) and the resulting suspension refluxed briefly. The solid was filtered off and washed with a further 100ml of hot EtOH affording (3) as a colourless powder (1.16g, 26%); $^1$H NMR (CDCl$_3$, 500MHz): $\delta$=1.13 (s, 36H, (CH$_3$)$_3$C), 1.20 (s, 36H, (CH$_3$)$_3$C), 2.04 (quin, $^3$J=8.0Hz, 4H, OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$O), 2.37 (m, 8H, OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$O), 3.34 (d, $^2$J=13.0Hz, 8H, ArCH$_2$Ar), 4.06 (t, $^3$J=7.5Hz, 8H, OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$O), 4.34
(d, $^2J=13.0\text{Hz}$, 8H, ArCH$_2$Ar), 7.02 (s, 8H, ArH), 7.04 (s, 8H, ArH), 8.78 (s, 4H, OH); $^{13}$C NMR (CDCl$_3$, 75.42MHz): $\delta=21.62$ (OCH$_2$CH$_2$CH$_2$CH$_2$O), 30.05 (OCH$_2$CH$_2$CH$_2$CH$_2$O), 31.22 ((CH$_3$)$_3$C), 31.62 ((CH$_3$)$_3$C), 32.40 (ArCH$_2$Ar), 33.80 ((CH$_3$)$_3$C), 34.15 ((CH$_3$)$_3$C), 75.87 (OCH$_2$CH$_2$CH$_2$CH$_2$O), 125.22, 125.75, 128.03, 133.68, 141.54, 147.14, 149.90, 150.61 (Ar); ES MS $^{1457}[M+Na]^+$, $^{1473}[M+K]^+$; elemental analysis: calculated for C$_{98}$H$_{128}$O$_8$.1/3(CHCl$_3$): C 80.13, H 8.78; found: C 80.66, H 9.11.

General procedure for the preparation of the tetraquinones:
The respective bis(calix[4]arene) (2-4) (0.73mmol) was stirred in Tl(OCOCF$_3$)$_3$/TFA solution (10.0ml, 8.7mmol) for 3 hours in the dark. Approximately 90% of the TFA was then removed in vacuo and the remainder poured into iced water (100ml). The product was extracted with chloroform (1x100ml, 1x50ml) and the combined organic extracts washed with water (2x100ml). After drying the organic layer (MgSO$_4$), the solvent was removed in vacuo.

L$_1$: The residue was purified by column chromatography on a short path of silica gel eluting with 7:3 chloroform:ethyl acetate. Pure tetraquinone was obtained by recrystallisation from chloroform/methanol as short orange needles (28%); $^1$H NMR (CDCl$_3$, 300MHz): $\delta=1.26$ (s, 36H,
(CH$_3$)$_3$C), 2.53 (quin, $^3$J=7.5Hz, 4H, OCH$_2$CH$_2$CH$_2$O), 3.19 (d, $^2$J=14.1Hz, 8H, ArCH$_2$Qu), 3.95 (t, $^3$J=7.5Hz, 8H, OCH$_2$CH$_2$CH$_2$O), 4.30 (d, $^2$J=14.1Hz, 8H, ArCH$_2$Qu), 6.38 (s, 8H, QuH), 7.07 (s, 8H, ArH); $^{13}$C NMR (CDCl$_3$, 75.42MHz): $\delta$=29.38 (OCH$_2$CH$_2$CH$_2$O), 31.23 (ArCH$_2$Qu), 31.47 ((CH$_3$)$_3$C), 34.29 ((CH$_3$)$_3$C), 71.48 (OCH$_2$CH$_2$CH$_2$O), 126.79, 132.17, 132.31, 147.07, 149.25, 152.72 (Qu, Ar), 184.96 (C=O), 187.72 (C=O); ES MS: 1249[M+K]$^+$; elemental analysis: calculated for C$_{78}$H$_{80}$O$_{12}$/3(CHCl$_3$): C 73.30, H 6.31; found: C 73.72, H 6.10.

L$^2$: The residue was purified by column chromatography on a 14cm depth of silica gel eluting with 98:2 chloroform:methanol, collecting the final streaking band by stripping the column with 10% methanol. To this impure final band was added a small volume of acetonitrile and the suspension gently heated. On cooling a yellow powder was isolated and dissolved in chloroform (20ml) and washed with water (2x20ml). Reduction in vacuo afforded the pure product as a yellow powder (10%); $^1$H NMR (CDCl$_3$, 500MHz) $\delta$=1.19 (s, 36H, (CH$_3$)$_3$C), 1.85 (s, 8H, OCH$_2$CH$_2$CH$_2$CH$_2$O), 3.07 (d, $^2$J=14.0Hz, 8H, ArCH$_2$Qu), 3.86 (s, 8H, OCH$_2$CH$_2$CH$_2$CH$_2$O), 4.18 (d, $^2$J=13.5Hz, 8H, ArCH$_2$Qu), 6.20 (s, 8H, QuH), 7.00 (s, 8H, ArH); $^{13}$C NMR (CDCl$_3$, 75.42MHz): $\delta$=26.34 (OCH$_2$CH$_2$CH$_2$CH$_2$O), 30.38 (ArCH$_2$Qu), 31.42 ((CH$_3$)$_3$C), 34.13 ((CH$_3$)$_3$C), 73.80.
(OCH₂CH₂CH₂CH₂O), 126.76, 131.80, 132.40, 146.43, 149.31, 153.64 (Qu, Ar), 185.12 (C=O), 187.95 (C=O).


L₃: The residue was purified by column chromatography on a 14cm depth of silica gel gradient eluting from 5:1 to 4:1 dichloromethane:ethyl acetate. The fractions containing a yellow spot in TLC were combined and recrystallised from acetonitrile to give the impure product. Pure compound was isolated by crystallisation from chloroform/methanol via slow evaporation as yellow needles (9%); ¹H NMR (CDCl₃, 500MHz): δ=1.20 (s, 36H, (CH₃)₃C), 1.33 (br.s, 4H, OCH₂CH₂CH₂CH₂CH₂O), 1.74 (br.s, 8H, OCH₂CH₂CH₂CH₂CH₂O), 3.27 (d, ²J=13.5Hz, 8H, ArCH₂Qu), 3.70 (m, 8H, OCH₂CH₂CH₂CH₂CH₂O), 4.01 (d, ²J=13.5Hz, 8H, ArCH₂Qu), 6.50 (br.s, 8H, QuH), 7.01 (s, 8H, ArH); ¹³C NMR (CDCl₃, 75.42MHz): δ=22.60 (OCH₂CH₂CH₂CH₂CH₂O), 30.26 (ArCH₂Qu), 31.42 ((CH₃)₃C), 32.81 (OCH₂CH₂CH₂CH₂CH₂O), 34.13 ((CH₃)₃C), 72.98 OCH₂CH₂CH₂CH₂CH₂O), 126.94, 131.41, 132.28, 146.52, 148.90, 153.02 (Ar, Qu), 185.41 (C=O), 188.33 (C=O); ES MS: 1289[M+Na]⁺, 1305[M+K]⁺; elemental analysis: calculated for C₈₂H₈₈O₁₂.3/4 (CHCl₃): C 73.34, H 6.55; found: C 73.69, H 6.37.