CHEMPHYSCHEM

Supporting Information

Supplementary Material

for

In silico engineering of tailored ink-binding ability at molecular printboards

D. Thompson*

Tyndall National Institute, Lee Maltings, Cork, Ireland

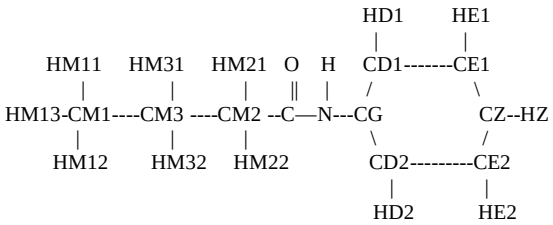
SM1. CHARMM22 topology files for (A) benzene and benzene cation, (B) tbutylbenzene and tbutylbenzene cation, (C) ferrocene and ferrocene cation, (D) β-CD, (E) high-pH deprotonated β-CD and neutralised deprotonated β-CD, (F) anion-functionalised dithiolene-β-CD and neutralised dithiolene-β-CD, (G) anion-functionalised carboxymethyl-β-CD and neutralised carboxymethyl-β-CD.

Neutral guests (A) and (B) were built from existing CHARMM22 force field data. Neutral guest (C) was assembled from existing *ab initio* data as described in reference 7e in the main text. Cationic guests were built by mapping the difference in NPA atomic charges in neutral and cation guests onto the neutral guest force field data. Host (D), native β-CD, has already been parameterised for the CHARMM22 force field [reference 10 in the main text]. High-pH β-CD (E), dithiolene-β-CD (F) and carboxymethyl-β-CD (G) were built by mapping NPA charges onto the native β-CD force field data as shown in Table 2 in the main text. The sum of the primary contributors to charge redistribution, given in bold in Table 2 in the main text, were normalised to –1 to generate the new host force field charges. Neutralised hosts, far-right columns of (E), (F) and (G), were built by mapping the difference in NPA atomic charges in anion and neutralised hosts onto the anion host force field data as shown in Table 4 in the main text, with the sum of the primary contributors to

*To whom all correspondence and requests for reprints should be addressed. Phone +353-21-490-4327. Fax +353-21-427-0271. Email damien.thompson@tyndall.ie.

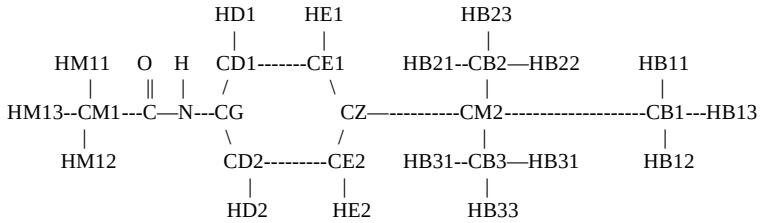
charge redistribution, given in bold in Table 4 in the main text, normalised to –1 to generate the new force fields.

(A) Benzene, residue BEN, and benzene cation, residue CBEN



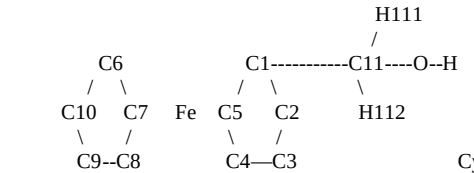

```
RESI BEN    0.00                    !  Charges in CBEN  1.00 ! Cationic BENzene with butanamide tail, B3LYP/6-31G++G**

GROUP
ATOM CG   CA    0.160               !           0.270

GROUP
ATOM CD1  CA    -0.115              !           -0.035
ATOM HD1  HP     0.115              !           0.135

GROUP
ATOM CD2  CA    -0.115              !           -0.035
ATOM HD2  HP     0.115              !           0.135

GROUP
ATOM CE1  CA    -0.115              !           -0.035
ATOM HE1  HP     0.115              !           0.135

GROUP
ATOM CE2  CA    -0.115              !           -0.035
ATOM HE2  HP     0.115              !           0.135

GROUP
ATOM CZ   CA     -0.115             !           0.095
ATOM HZ   HP     0.115              !           0.135

GROUP
ATOM N    NH1   -0.47               !           -0.33
ATOM H    H      0.31                !           0.31
ATOM C    C      0.51                !           0.51
ATOM O    O     -0.51                !           -0.39

GROUP                               !     unchanged
ATOM CM2  CT2   -0.18
ATOM HM21 HA2    0.09
ATOM HM22 HA2    0.09
GROUP
ATOM CM3  CT2   -0.18
ATOM HM31 HA2    0.09
ATOM HM32 HA2    0.09
GROUP
ATOM CM1  CT3   -0.27
ATOM HM11 HA3    0.09
ATOM HM12 HA3    0.09
ATOM HM13 HA3    0.09

BOND CD1 CG  CD2 CG  CE1 CD1
BOND CE2 CD2 CZ  CE1 CZ CE2
BOND CG  N   CD1 HD1 CD2 HD2 CE1 HE1
BOND CE2 HE2 CZ  HZ
BOND N   H  C CM2 N C C O
BOND CM1 HM11 CM1  HM12 CM1  HM13
BOND CM2 HM21 CM2  HM22 CM3 HM31 CM3  HM32 CM2 CM3 CM3 CM1
```

(B) tButylbenzene, residue TEN, and its cation, residue CTEN




```
RESI TEN    0.00                ! Charges in CTEN  1.00 ! Cationic TbutylbENzene with acetamide tail, B3LYP/6-31G++G**

GROUP
ATOM CG   CA    0.160           !              0.280

GROUP
ATOM CD1  CA    -0.115          !              -0.035
ATOM HD1  HP     0.115          !               0.145

GROUP
ATOM CD2  CA    -0.115          !              -0.035
ATOM HD2  HP     0.115          !               0.145

GROUP
ATOM CE1  CA    -0.115          !              -0.035
ATOM HE1  HP     0.115          !              0.145

GROUP
ATOM CE2  CA    -0.115          !              -0.035
ATOM HE2  HP     0.115          !              0.145

GROUP
ATOM CZ   CA     0.00           !              0.210

GROUP                           !              unchanged
ATOM CM2  CTx  0.00

GROUP                           !              unchanged
ATOM CB1  CT3   -0.27
ATOM HB11 HA3    0.09
ATOM HB12 HA3    0.09
ATOM HB13 HA3    0.09

GROUP                           !              unchanged
ATOM CB2  CT3   -0.27
ATOM HB21 HA3    0.09
ATOM HB22 HA3    0.09
ATOM HB23 HA3    0.09

GROUP                           !              unchanged
ATOM CB3  CT3   -0.27
ATOM HB31 HA3    0.09
ATOM HB32 HA3    0.09
ATOM HB33 HA3    0.09

GROUP
ATOM N    NH1   -0.47          !              -0.36
ATOM H    H      0.31          !               0.31
ATOM C    C      0.51          !               0.51
ATOM O    O     -0.51          !              -0.39

GROUP                           !              unchanged
ATOM CM1  CT3   -0.27
ATOM HM11 HA3    0.09
ATOM HM12 HA3    0.09
ATOM HM13 HA3    0.09

BOND CD1 CG  CD2 CG  CE1 CD1 CE2 CD2 CZ  CE1 CZ CE2
BOND CG  N   CD1 HD1 CD2 HD2 CE1 HE1 CE2 HE2 CZ  CM2
BOND N   H  C CM1 N C C O CM1 HM11 CM1 HM12 CM1  HM13
BOND CM2 CB1  CM2 CB2  CM2  CB3 CB1 HB11 CB1 HB12 CB1  HB13
BOND CB2 HB21 CB2 HB22 CB2  HB23 CB3 HB31 CB3 HB32 CB3  HB33
```

(C) Ferrocene, residue FER, and its cation CFER



Cyclopentadienyl hydrogens H1 to H10 not shown for clarity.

```
RESI FER          0.00          ! Charges in CFER  1.00 ! Cationic FERrocene with methyl alcohol tail, B3LYP/6-31G++G**
                                ! very similar to “guessed” charge-smearing scheme with –0.5e on Fe –0.5e on Cp carbons,
                                ! as described in DT & AL, 2006. J.Phys.Chem B, 110, 16640

GROUP
ATOM FE   FE    0.450           !          0.808
ATOM C1   C51   -0.045          !          0.003
ATOM C2   C51   -0.16           !          -0.112
ATOM H2   HP5    0.115          !          0.133
ATOM C3   C51   -0.16           !          -0.112
ATOM H3   HP5    0.115          !          0.133
ATOM C4   C51   -0.16           !          -0.112
ATOM H4   HP5    0.115          !          0.133
ATOM C5   C51   -0.16           !          -0.112
ATOM H5   HP5    0.115          !          0.133
ATOM C6   C52   -0.16           !          -0.112
ATOM H6   HP5    0.115          !          0.133
ATOM C7   C52   -0.16           !          -0.112
ATOM H7   HP5    0.115          !          0.133
ATOM C8   C52   -0.16           !          -0.112
ATOM H8   HP5    0.115          !          0.133
ATOM C9   C52   -0.16           !          -0.112
ATOM H9   HP5    0.115          !          0.133
ATOM C10  C52   -0.16           !          -0.112
ATOM H10  HP5    0.115          !          0.133

GROUP                           !          no change
ATOM C11  CT2    0.05
ATOM H111 HA     0.09
ATOM H112 HA     0.09
ATOM O    OH1    -0.66
ATOM H    H      0.43

BOND C6   C7      C7   C8      C8   C9      C9   C10     C10  C6
BOND C1   C2      C2   C3      C3   C4      C4   C5      C5   C1
BOND            C2   H2      C3   H3      C4   H4      C5   H5
BOND C6   H6      C7   H7      C8   H8      C9   H9      C10  H10
BOND   FE   C1    FE   C2     FE   C3           FE   C4      FE   C5
BOND   FE   C6    FE   C7    FE   C8           FE   C9      FE   C10
BOND C1 C11  C11 H111  C11 H112   C11 O   O   H
```

(D) Native b-CD, residue BCD from CHARMM22

```
 RESI   BCD    0.00 ! Alpha(1-4) D Glucose monomer
              !
GROUP            -.074
ATOM C1   CT      0.311
ATOM H1   HAT     0.031
ATOM C5   CT      0.076
ATOM H5   HAT     0.046
ATOM O5   OE      -.37
ATOM C4   CT      0.141
ATOM H4   HAT     0.071
ATOM O4   OE      -.380

GROUP            0.022
ATOM C2   CT      0.201
ATOM H2   HAT     0.071
ATOM O2   OT7     -.65
ATOM HO2  HO      0.40

GROUP            0.022
ATOM C3   CT      0.201
ATOM H3   HAT     0.071
ATOM O3   OT7     -.65
ATOM HO3  HO      0.40

GROUP            0.030
ATOM C6   CT      0.180
ATOM H61  HAT     0.050
ATOM H62  HAT     0.050
ATOM O6   OT7     -.65
ATOM HO6  HO      0.40

BOND C1 C2    C2 C3    C3 C4    C4 C5   C5 O5    O5 C1
BOND C1 H1    C2 H2    C2 O2    O2 HO2  ! C1 +O4
BOND C3 H3    C3 O3    O3 HO3   C4 H4   C4 O4
BOND C5 H5    C5 C6
BOND C6 H61   C6 H62   C6 O6    O6 HO6

IC   HO6  O6   C6   C5     0.0000    0.00  180.0     0.00   0.0000
IC   O6   C6   C5   H5     0.0000    0.00  180.0     0.00   0.0000
IC   O6   C6   C5   O5     0.0000    0.00 -120.0     0.00   0.0000
IC   H61  C6   C5   O5     0.0000    0.00   60.0     0.00   0.0000
IC   H62  C6   C5   O5     0.0000    0.00  180.0     0.00   0.0000
IC   C6   C5   O5   C1     0.0000    0.00  180.0     0.00   0.0000
IC   C5   O5   C1   H1     0.0000    0.00  180.0     0.00   0.0000
IC   C5   O5   C1   C2     0.0000    0.00  -60.0     0.00   0.0000
IC   O5   C1   C2   H2     0.0000    0.00  -60.0     0.00   0.0000
IC   O5   C1   C2   O2     0.0000    0.00  180.0     0.00   0.0000
IC   O5   C1   C2   C3     0.0000    0.00   60.0     0.00   0.0000
IC   C1   C2   C3   H3     0.0000    0.00   60.0     0.00   0.0000
IC   C1   C2   O2   HO2    0.0000    0.00  120.0     0.00   0.0000
IC   C1   C2   C3   O3     0.0000    0.00  180.0     0.00   0.0000
IC   C1   C2   C3   C4     0.0000    0.00  -60.0     0.00   0.0000
IC   C2   C3   C4   H4     0.0000    0.00  -60.0     0.00   0.0000
IC   C2   C3   O3   HO3    0.0000    0.00   60.0     0.00   0.0000
IC   C2   C3   C4   O4     0.0000    0.00  180.0     0.00   0.0000
IC   C2   C3   C4   C5     0.0000    0.00   60.0     0.00   0.0000
IC   C3   C4   C5   H5     0.0000    0.00   60.0     0.00   0.0000
IC   C3   C4   C5   O5     0.0000    0.00  -60.0     0.00   0.0000
IC   C3   C4   C5   C6     0.0000    0.00  180.0     0.00   0.0000
IC   C4   C5   O5   C1     0.0000    0.00   60.0     0.00   0.0000
```

(E) High-pH deprotonated b-CD, residue BCA, and neutralized deprotonated b-CD, residue NBCA

```
 RESI   BCA   -1.00 ! Alpha(1-4) D Glucose monomer with HO2 removed, B3LYP/6-31++G**    ! Charges in NBCA 0.00
            !
GROUP            -.074                                                 !                          no change
ATOM C1   CT      0.311
ATOM H1   HAT     0.031
ATOM C5   CT      0.076
ATOM H5   HAT     0.046
ATOM O5   OE      -.37
ATOM C4   CT      0.141
ATOM H4   HAT     0.071
ATOM O4   OE      -.380

GROUP            -0.820                                                !                          0.026
ATOM C2   CT      0.004                                                 !                          -0.103
ATOM H2   HAT     0.253                                                 !                          0.392
ATOM O2   OT7     -1.076                                                !                          -0.263

GROUP            -0.136                                                !                          0.030
ATOM C3   CT      0.024                                                 !                          0.016
ATOM H3   HAT     0.281                                                 !                          0.333
ATOM O3   OT7     -1.078                                                !                          -0.954
ATOM HO3  HO      0.636                                                 !                          0.623

GROUP            0.030                                                 !                          no change
ATOM C6   CT      0.180
ATOM H61  HAT     0.050
ATOM H62  HAT     0.050
ATOM O6   OT7     -.65
ATOM HO6  HO      0.40

BOND C1 C2    C2 C3    C3 C4    C4 C5   C5 O5    O5 C1
BOND C1 H1    C2 H2    C2 O2           ! C1 +O4
BOND C3 H3    C3 O3    O3 HO3   C4 H4   C4 O4
BOND C5 H5    C5 C6
BOND C6 H61   C6 H62   C6 O6    O6 HO6

IC   HO6  O6   C6   C5     0.0000    0.00  180.0     0.00   0.0000
IC   O6   C6   C5   H5     0.0000    0.00  180.0     0.00   0.0000
IC   O6   C6   C5   O5     0.0000    0.00 -120.0     0.00   0.0000
IC   H61  C6   C5   O5     0.0000    0.00   60.0     0.00   0.0000
IC   H62  C6   C5   O5     0.0000    0.00  180.0     0.00   0.0000
IC   C6   C5   O5   C1     0.0000    0.00  180.0     0.00   0.0000
IC   C5   O5   C1   H1     0.0000    0.00  180.0     0.00   0.0000
IC   C5   O5   C1   C2     0.0000    0.00  -60.0     0.00   0.0000
IC   O5   C1   C2   H2     0.0000    0.00  -60.0     0.00   0.0000
IC   O5   C1   C2   O2     0.0000    0.00  180.0     0.00   0.0000
IC   O5   C1   C2   C3     0.0000    0.00   60.0     0.00   0.0000
IC   C1   C2   C3   H3     0.0000    0.00   60.0     0.00   0.0000
IC   C1   C2   C3   O3     0.0000    0.00  180.0     0.00   0.0000
IC   C1   C2   C3   C4     0.0000    0.00  -60.0     0.00   0.0000
IC   C2   C3   C4   H4     0.0000    0.00  -60.0     0.00   0.0000
IC   C2   C3   O3   HO3    0.0000    0.00   60.0     0.00   0.0000
IC   C2   C3   C4   O4     0.0000    0.00  180.0     0.00   0.0000
IC   C2   C3   C4   C5     0.0000    0.00   60.0     0.00   0.0000
IC   C3   C4   C5   H5     0.0000    0.00   60.0     0.00   0.0000
IC   C3   C4   C5   O5     0.0000    0.00  -60.0     0.00   0.0000
IC   C3   C4   C5   C6     0.0000    0.00  180.0     0.00   0.0000
IC   C4   C5   O5   C1     0.0000    0.00   60.0     0.00   0.0000
```

(F) Anion-functionalised dithiolene-b-CD, residue BCS and its neutralised dithiolene-b-CD, residue NBCS

```
 RESI BCS     -1.00 ! Alpha(1-4) D Glucose monomer with dithiolene arm, B3LYP/6-31++G**     ! charges in NBCS 0.00

GROUP              -.074                                                                    !          no change
ATOM C1   CT      0.311
ATOM H1   HAT     0.031
ATOM C5   CT      0.076
ATOM H5   HAT     0.046
ATOM O5   OE      -.37
ATOM C4   CT      0.141
ATOM H4   HAT     0.071
ATOM O4   OE      -.380

GROUP           -0.978                  !     N1a-C2a      C4a-N2a                       !        0.022
ATOM C2   CT     -0.362                 !        \               /                       !       -0.362
ATOM H2   HAT     0.075                 !        C1a ===== C3a                           !        0.075
ATOM S1a  S       0.288                 !        /               \                       !        0.537
ATOM C1a  CE1    -0.362                 !      S1a              S2a                       !      -0.192
ATOM C2a  CN      0.238                 !     /                                          !       0.196
ATOM N1a  NC     -0.312                 !    C2                                          !      -0.179
ATOM C3a  CE1    -0.216                                                                  !      -0.312
ATOM S2a  S       -0.253                                                                 !       0.243
ATOM C4a  CN      0.238                                                                  !       0.196
ATOM N2a  NC     -0.312                                                                   !     -0.180

GROUP           0.022                                                                    !     no change
ATOM C3   CT      0.201
ATOM H3   HAT     0.071
ATOM O3   OT7    -0.65
ATOM HO3  HO      0.40

GROUP           0.030                                                                    !     no change
ATOM C6   CT      0.180
ATOM H61  HAT     0.050
ATOM H62  HAT     0.050
ATOM O6   OT7     -.65
ATOM HO6  HO      0.40

BOND C1 C2    C2 C3    C3 C4    C4 C5   C5 O5    O5 C1
BOND C1 H1    C2 H2    C2 S1a   S1a C1a  C1a C2a C2a N1a C1a C3a C3a S2a C3a C4a C4a N2a
BOND C3 H3    C3 O3    O3 HO3   C4 H4   C4 O4
BOND C5 H5    C5 C6
BOND C6 H61   C6 H62   C6 O6    O6 HO6

IC   HO6  O6   C6   C5     0.0000    0.00  180.0     0.00   0.0000
IC   O6   C6   C5   H5     0.0000    0.00  180.0     0.00   0.0000
IC   O6   C6   C5   O5     0.0000    0.00 -120.0     0.00   0.0000
IC   H61  C6   C5   O5     0.0000    0.00   60.0     0.00   0.0000
IC   H62  C6   C5   O5     0.0000    0.00  180.0     0.00   0.0000
IC   C6   C5   O5   C1     0.0000    0.00  180.0     0.00   0.0000
IC   C5   O5   C1   H1     0.0000    0.00  180.0     0.00   0.0000
IC   C5   O5   C1   C2     0.0000    0.00  -60.0     0.00   0.0000
IC   O5   C1   C2   H2     0.0000    0.00  -60.0     0.00   0.0000
IC   O5   C1   C2   C3     0.0000    0.00   60.0     0.00   0.0000
IC   C1   C2   C3   H3     0.0000    0.00   60.0     0.00   0.0000
IC   C1   C2   C3   O3     0.0000    0.00  180.0     0.00   0.0000
IC   C1   C2   C3   C4     0.0000    0.00  -60.0     0.00   0.0000
IC   C2   C3   C4   H4     0.0000    0.00  -60.0     0.00   0.0000
IC   C2   C3   O3   HO3    0.0000    0.00   60.0     0.00   0.0000
IC   C2   C3   C4   O4     0.0000    0.00  180.0     0.00   0.0000
IC   C2   C3   C4   C5     0.0000    0.00   60.0     0.00   0.0000
IC   C3   C4   C5   H5     0.0000    0.00   60.0     0.00   0.0000
IC   C3   C4   C5   O5     0.0000    0.00  -60.0     0.00   0.0000
IC   C3   C4   C5   C6     0.0000    0.00  180.0     0.00   0.0000
IC   C4   C5   O5   C1     0.0000    0.00   60.0     0.00   0.0000
```

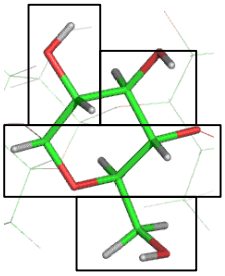
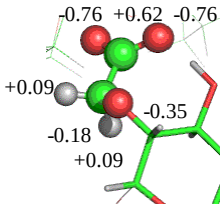
(G) Anion-functionalised carboxymethyl-b-CD, residue BCC and its neutralised carboxymethyl-b-CD, residue NBCC

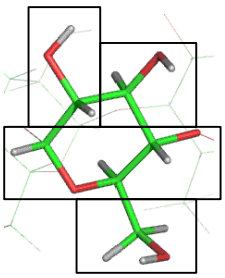
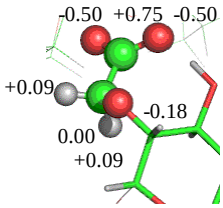
```
RESI BCC     -1.00 ! Alpha(1-4) D Glucose monomer with carboxymethyl arm, B3LYP/6-31++G**     ! charges in NBCC 0.00

GROUP              -.074                                                                 !          no change
ATOM C1   CT      0.311
ATOM H1   HAT     0.031
ATOM C5   CT      0.076
ATOM H5   HAT     0.046
ATOM O5   OE      -.37
ATOM C4   CT      0.141
ATOM H4   HAT     0.071
ATOM O4   OE      -.380

GROUP           -0.978                  !       H1a                O1a                  !                    0.022
ATOM C2   CT     0.201                  !          \                 /                   !                     0.201
ATOM H2   HAT     0.071                 !   H2a --C1a ----- C2a                          !                    0.071
ATOM O2   OT7    -0.35                 !          /                 \                   !                    -0.18
ATOM C1a  CT2    -0.18                 !        O2                 O2a                  !                    0.00
ATOM H1a  HA2    0.09                  !       /                                       !                    0.09
ATOM H2a  HA2    0.09                  !      C2                                       !                    0.09
ATOM C2a  CC     0.62                                                                  !                    0.75
ATOM O1a  OC     -0.76                                                                 !                    -0.50
ATOM O2a  OC     -0.76                                                                 !                    -0.50

GROUP            0.022                                                                 !                    no change
ATOM C3   CT      0.201
ATOM H3   HAT     0.071
ATOM O3   OT7    -0.65
ATOM HO3  HO      0.40

GROUP            0.030                                                                 !                    no change
ATOM C6   CT      0.180
ATOM H61  HAT     0.050
ATOM H62  HAT     0.050
ATOM O6   OT7     -.65
ATOM HO6  HO      0.40

BOND C1 C2    C2 C3    C3 C4    C4 C5   C5 O5    O5 C1
BOND C1 H1    C2 H2    C2  O2   O2 C1a  C1a H1a  C1a H2a   C1a C2a   C2a O1a  C2a O2a
BOND C3 H3    C3 O3    O3 HO3   C4 H4   C4 O4
BOND C5 H5    C5 C6
BOND C6 H61   C6 H62   C6 O6    O6 HO6

IC   HO6  O6   C6   C5     0.0000    0.00  180.0     0.00   0.0000
IC   O6   C6   C5   H5     0.0000    0.00  180.0     0.00   0.0000
IC   O6   C6   C5   O5     0.0000    0.00 -120.0     0.00   0.0000
IC   H61  C6   C5   O5     0.0000    0.00   60.0     0.00   0.0000
IC   H62  C6   C5   O5     0.0000    0.00  180.0     0.00   0.0000
IC   C6   C5   O5   C1     0.0000    0.00  180.0     0.00   0.0000
IC   C5   O5   C1   H1     0.0000    0.00  180.0     0.00   0.0000
IC   C5   O5   C1   C2     0.0000    0.00  -60.0     0.00   0.0000
IC   O5   C1   C2   H2     0.0000    0.00  -60.0     0.00   0.0000
IC   O5   C1   C2   O2     0.0000    0.00  180.0     0.00   0.0000
IC   O5   C1   C2   C3     0.0000    0.00   60.0     0.00   0.0000
IC   C1   C2   C3   H3     0.0000    0.00   60.0     0.00   0.0000
IC   C1   C2   C3   O3     0.0000    0.00  180.0     0.00   0.0000
IC   C1   C2   C3   C4     0.0000    0.00  -60.0     0.00   0.0000
IC   C2   C3   C4   H4     0.0000    0.00  -60.0     0.00   0.0000
IC   C2   C3   O3   HO3    0.0000    0.00   60.0     0.00   0.0000
IC   C2   C3   C4   O4     0.0000    0.00  180.0     0.00   0.0000
IC   C2   C3   C4   C5     0.0000    0.00   60.0     0.00   0.0000
IC   C3   C4   C5   H5     0.0000    0.00   60.0     0.00   0.0000
IC   C3   C4   C5   O5     0.0000    0.00  -60.0     0.00   0.0000
IC   C3   C4   C5   C6     0.0000    0.00  180.0     0.00   0.0000
IC   C4   C5   O5   C1     0.0000    0.00   60.0     0.00   0.0000
```

SM2. Reactivity analysis and atomic charge distributions in carboxymethyl β-CD

In addition to high-pH β-CD and the anion-functionalised dithiolene-β-CD hosts described in the main text, we examined also an alternative anion-functionalised β-CD host, with a carboxymethyl group grafted onto a β-CD secondary hydroxyl. Shown below in Table SM1 are mapped *ab initio* charges in both carboxymethyl-β-CD and neutralised carboxymethyl-β-CD; section SM1 (g) above gives the resulting CHARMM22 topology file. As shown in panel (a) of Table SM1, the negative charge lies almost entirely on subgroup 1 of the functionalised monomer M. Apart from the bridging oxygen, charges in the conserved β-CD atoms of group 1 do not change significantly and so we simply apply the standard CHARMM22 $–CH_2-$ and -COO group atomic charges to the carboxymethyl sidearm and set the bridging oxygen negative charge to –0.35. Neutralisation is also localised on subgroup 1 of monomer M, as shown in panel (b) of Table SM1. Sidearm atomic charges shown were generated by adding the calculated charge changes upon neutralisation, normalised to +1, to the charges given in panel (a) of Table SM1. Figure SM1 shows the charge-donor sites in the carboxymethyl-β-CD host. Carboxylate oxygens are both the sites of highest negative electrostatic potential (as shown by their high negative NPA atomic charges) and most nucleophilic atoms (high f^- Fukui values) in the carboxymethyl host, so the carboxylate oxygens act as the primary charge-donor sites for neutralisation of cationic guests.

Table SM1. Mapping *ab inito* NPA charges in (a) carboxymethyl-β-CD and (b) neutralised carboxymethyl-β-CD, onto the existing β-CD CHARMM22 force field.

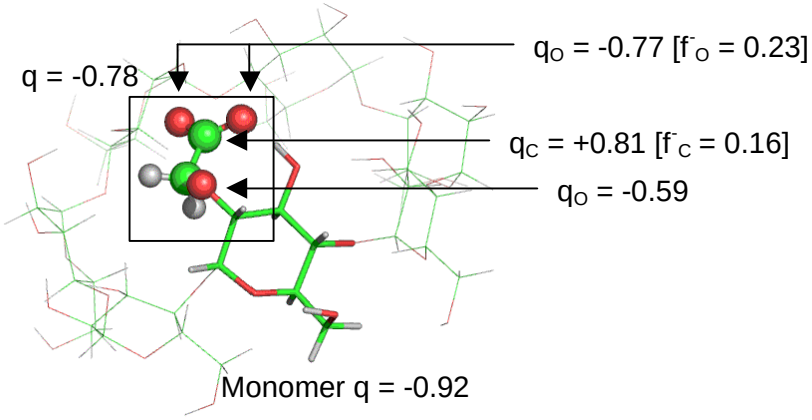
(a)		Grouped charge differences (a.u.) by monomer							Sidearm Charges (a.u.)
Sub-Monomer Group		M-2	M-1	M	M+1	M+2	M+3	M+4	
	1	-0.03	-0.04	**-0.92**	-0.05	-0.05	-0.02	-0.04	
	2	-0.04	-0.02	-0.04	-0.02	-0.03	-0.02	-0.04	
	3	0.00	0.00	0.00	0.02	0.00	0.02	0.00	
	4	0.02	0.00	0.02	0.01	0.02	0.00	0.02	

(b)		Grouped charge differences (a.u.) by monomer							Sidearm Charges (a.u.)
Sub-Monomer Group		M-2	M-1	M	M+1	M+2	M+3	M+4	
	1	0.00	0.01	**-0.86**	-0.02	0.00	0.01	0.02	
	2	-0.01	0.01	-0.04	0.02	-0.01	0.00	0.00	
	3	0.00	-0.03	-0.04	-0.01	0.00	0.00	0.01	
	4	-0.02	-0.04	-0.04	0.05	-0.02	0.00	0.00	

Charge differences are for (a) carboxymethyl-β-CD NPA atomic charges minus native β-CD CHARMM22 atomic charges and (b) neutralised carboxymethyl-β-CD minus carboxymethyl-β-CD, grouped as illustrated in the far-left inset figures. All geometry optimisations and electronic structure determinations were performed with B3LYP/6-31++G**. Monomers are labelled relative to the anion-functionalised monomer M, with group 1 proton HO2 replaced by CH_2-COO. Fitted force field charges in (a) carboxymethyl and (b) neutralised carboxymethyl sidearms are labelled in the far-right inset figures.

Figure SM1. The anionic carboxymethyl-β-CD host, with NPA atomic charge distributions showing sites of high electrostatic potential and Fukui functions identifying the primary electron-donor sites for neutralisation of molecular charges. Only group negative charges larger than –0.1 and Fukui functions > 0.15 are labelled. q = n label group charges, q_i = n label atom i charges and [f_i = n] label atom i Fukui functions. $\mathbf{f^-(r) = q_{N_0-1}(r) - q_{N_0}(r)}$; Eq.(2) in the main text. Sidearm carboxymethyl atoms are shown as spheres. For Fukui analysis, the same nuclear coordinates were used for both charged and neutralised systems, to keep a fixed external field, as defined in Eq. (1) in the main text. B3LYP/6-31++G** level of theory was used to generate NPA charges and Fukui functions.

Figure SM1



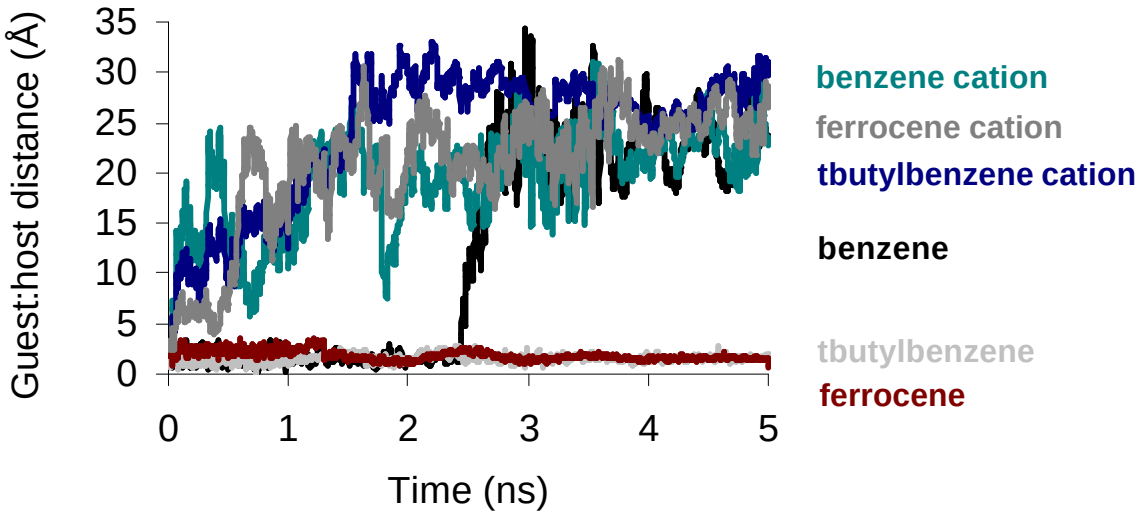
SM3. Timelines for binding/unbinding of neutral and cationic guest molecules to native, anionic and neutralised β-CD hosts.

Figures SM2 shows timelines of interaction distances between guest molecules and native, high-pH and anion-functionalised β-CD, in a variety of charge configurations.

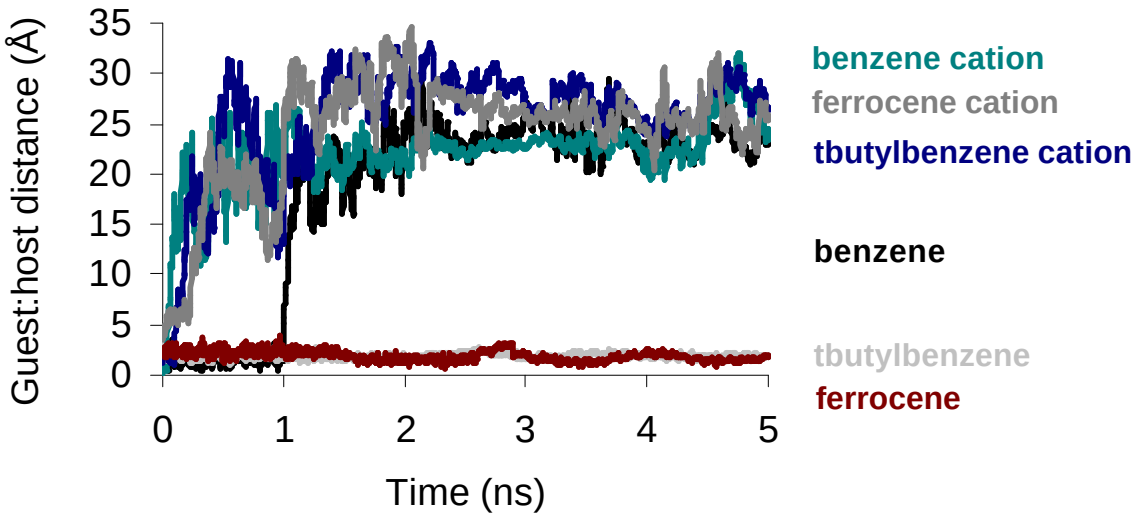
Figure SM2. Timelines of benzene, tbutylbenzene and ferrocene guest molecule interaction with (A) native β-CD, (B) high-pH β-CD, (C) neutralised high-pH β-CD, (D) dithiolene β-CD, (E) neutralised dithiolene β-CD, (F) carboxymethyl β-CD and (G) neutralised carboxymethyl β-CD. Timelines show distance between guest primary charge transfer site (see Figure 1 in the main text) and β-CD cavity centres of mass.

Figure SM2

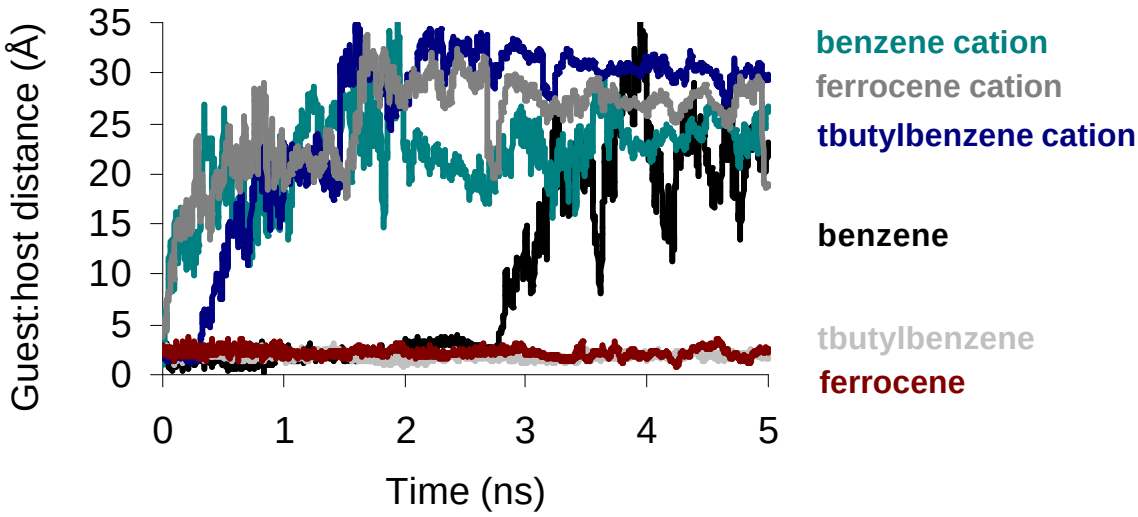
(A) Guest interaction with native β-CD



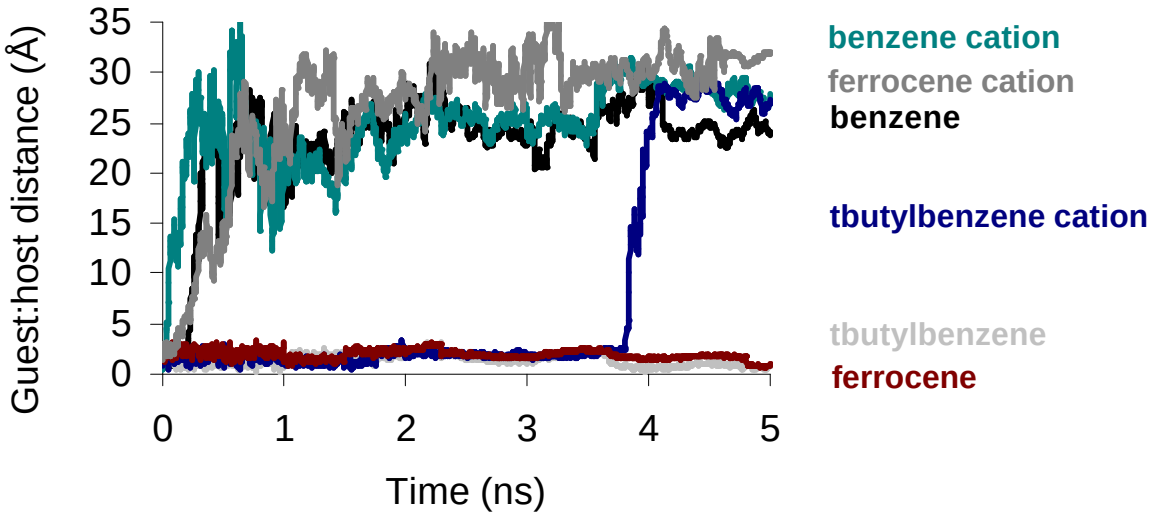
(B) Guest interaction with high-pH β-CD



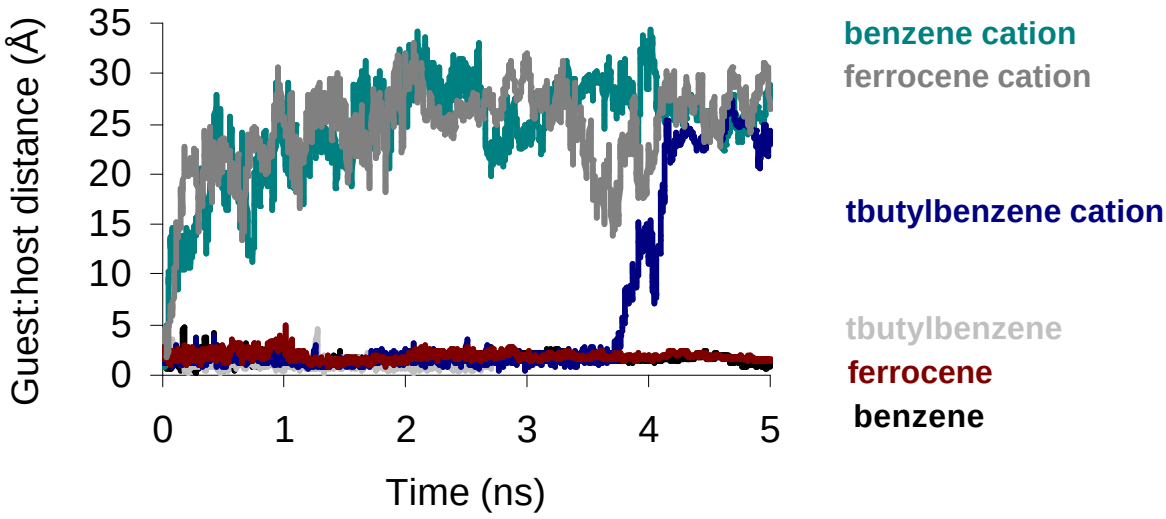
(C) Guest interaction with neutralised high-pH β-CD



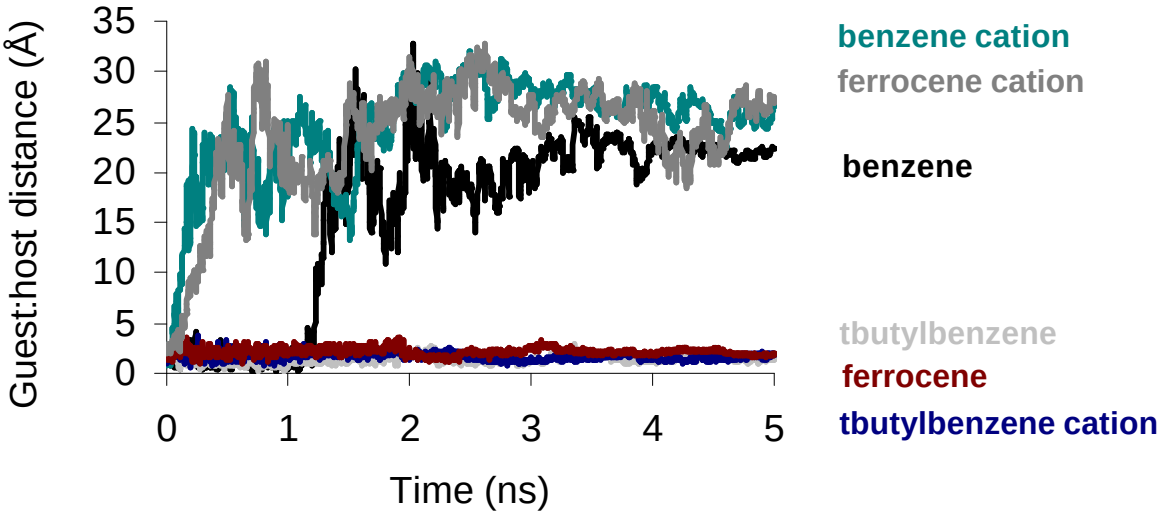
(D) Guest interaction with dithiolene-β-CD



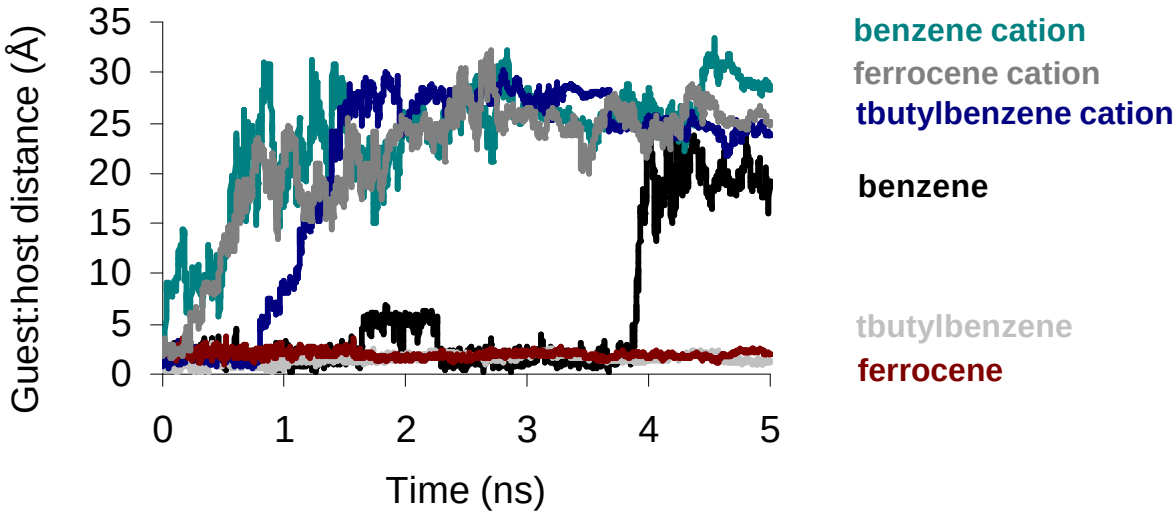
(E) Guest interaction with neutralised dithiolene-β-CD



(F) Guest interaction with carboxymethyl-β-CD



(G) Guest interaction with neutralised carboxymethyl-β-CD



SM4. Schemes for binding/unbinding of neutral and cationic guest molecules to native, anionic and neutralised β-CD hosts.

Figures SM3 to SM10 show schemes for binding/unbinding of guest molecules to β-CD, in a variety of charge configurations. Host anion and guest cation sites are shaded. Forward horizontal arrows are labelled according to complex lifetimes as given in Table 5; equilibria marked with just a backward horizontal arrow denote complexes which immediately dissociate in the MD simulations. This data is in addition to the generic scheme in Figure 3 of the main text and the neutral/cationic benzene to native/deprotonated/neutralised β-CD scheme in Figure 4 of the main text, with guest residence times taken from Figure SM2 above.

Figure SM3 **Benzene binding to dithiolene-b-CD**

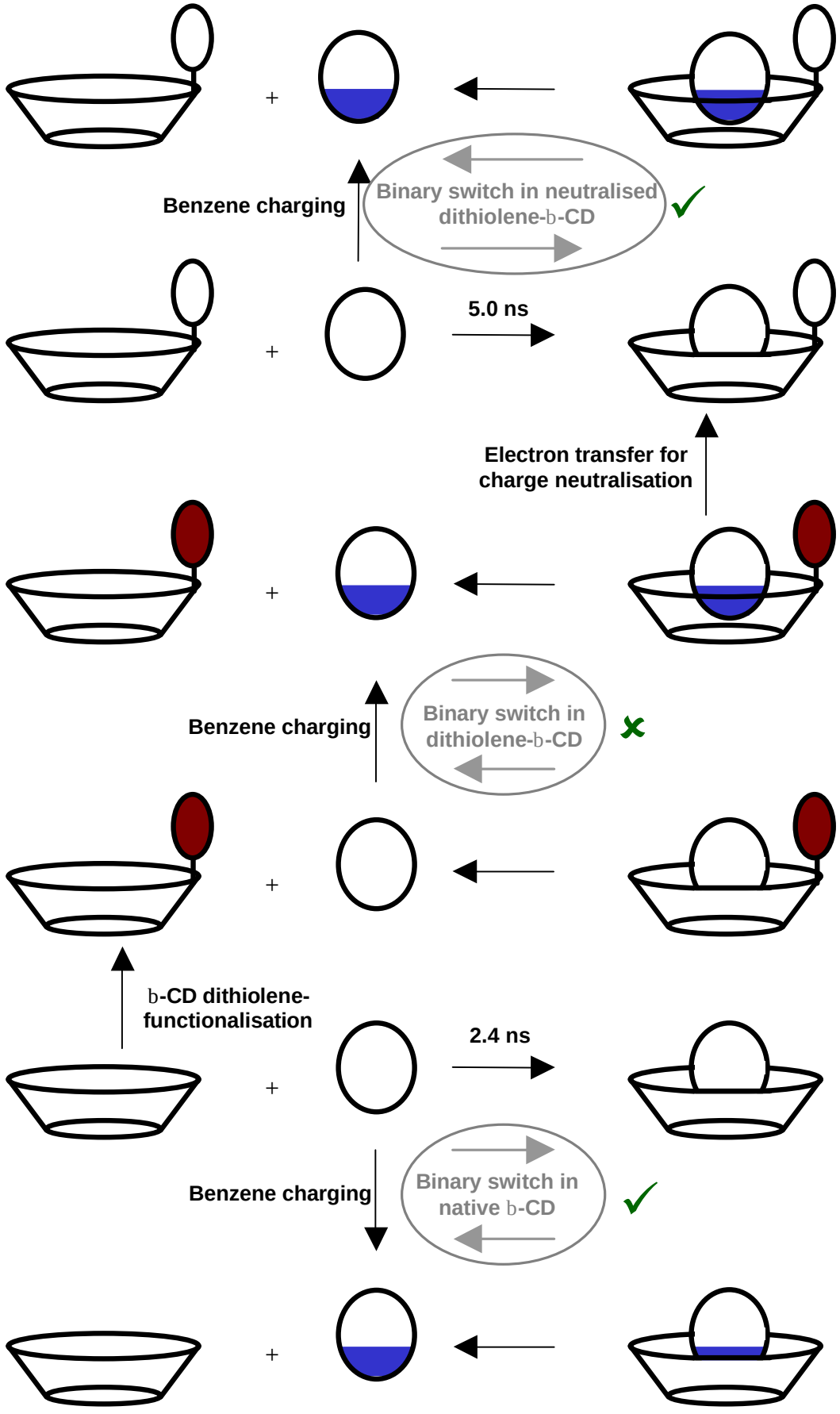


Figure SM4 **Benzene binding to carboxymethyl-b-CD**

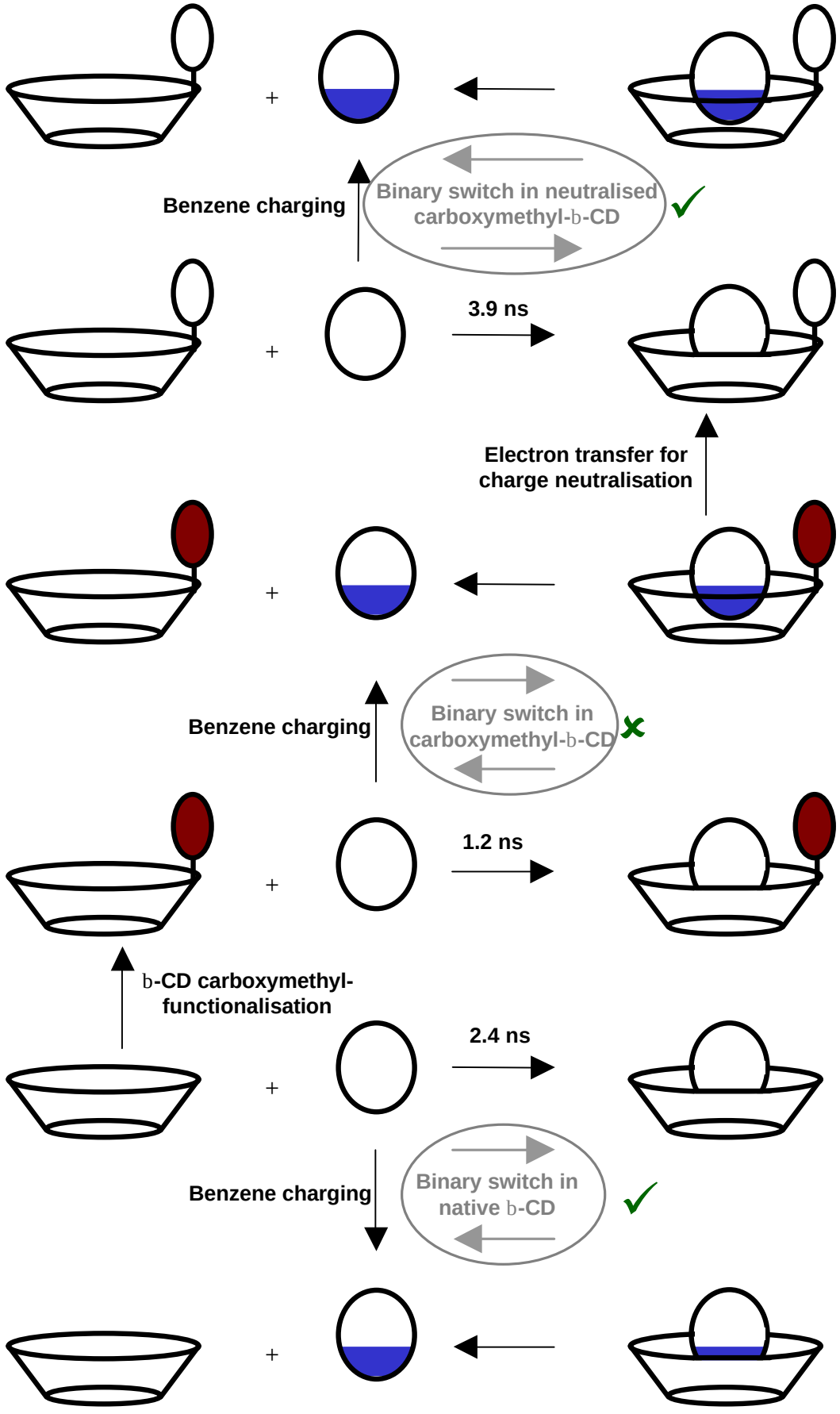


Figure SM5 **tButylbenzene binding to high-pH b-CD**

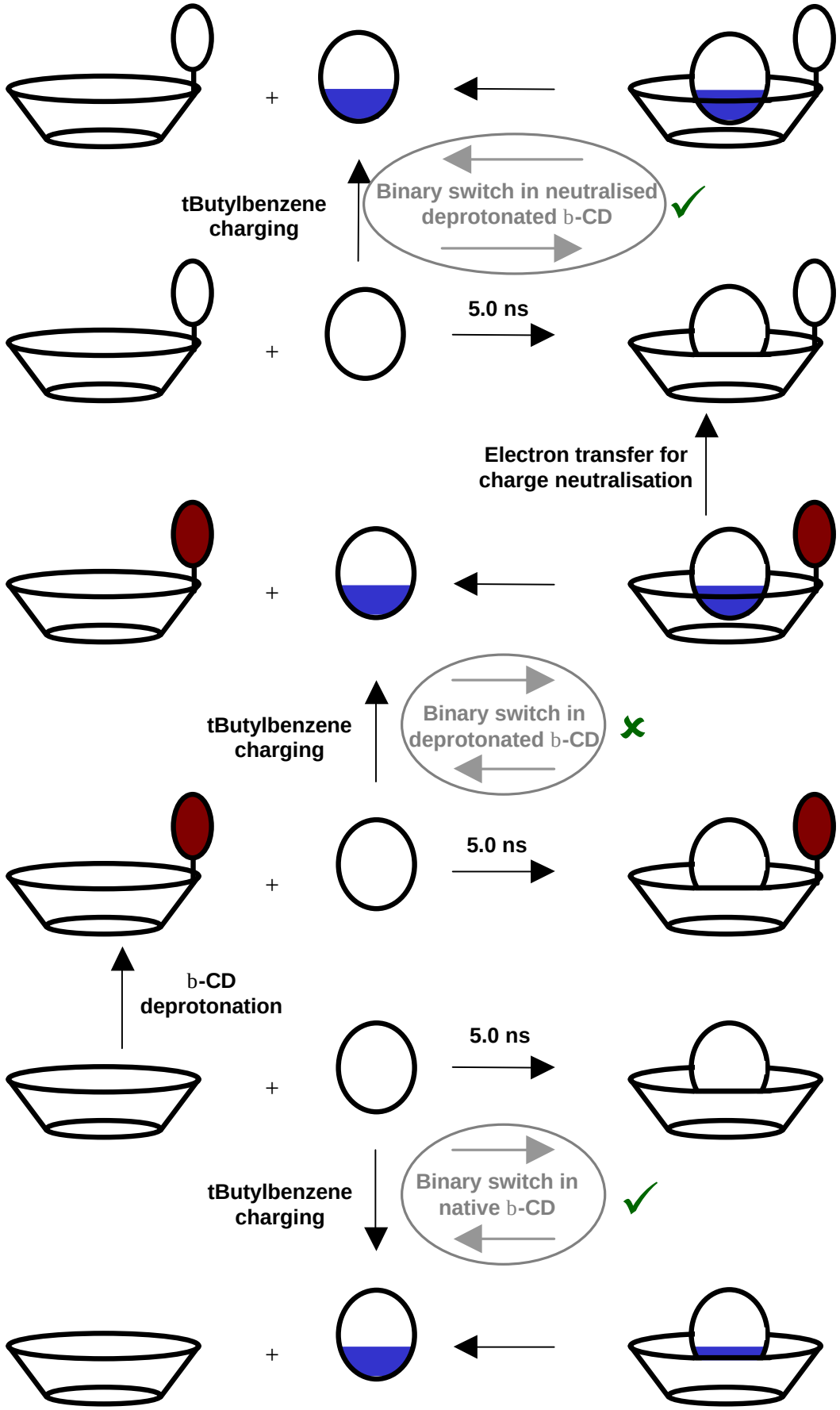


Figure SM6 **tButylbenzene binding to dithiolene-b-CD**

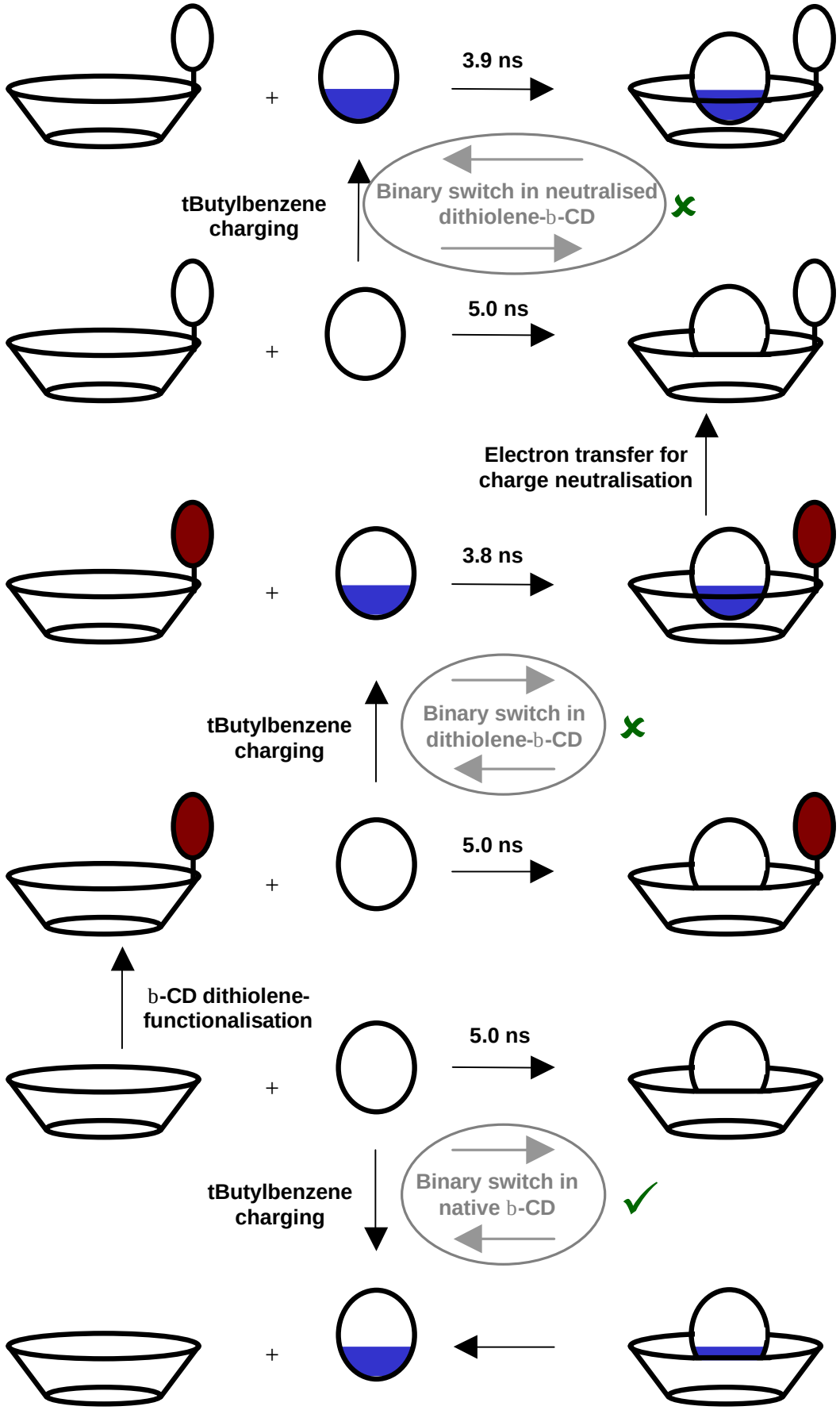


Figure SM7 **tButylbenzene binding to carboxymethyl-b-CD**

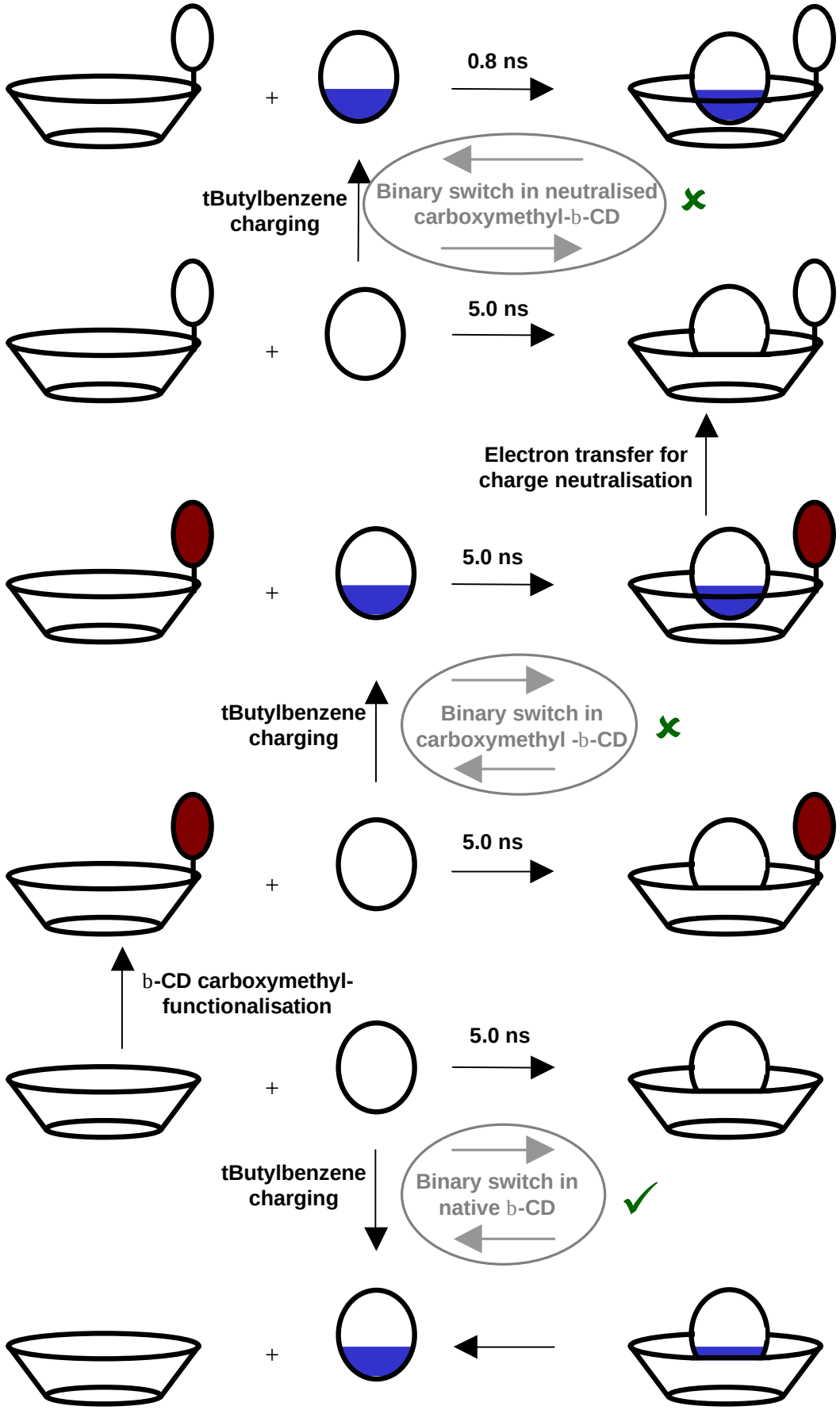


Figure SM8 **Ferrocene binding to high-pH b-CD**

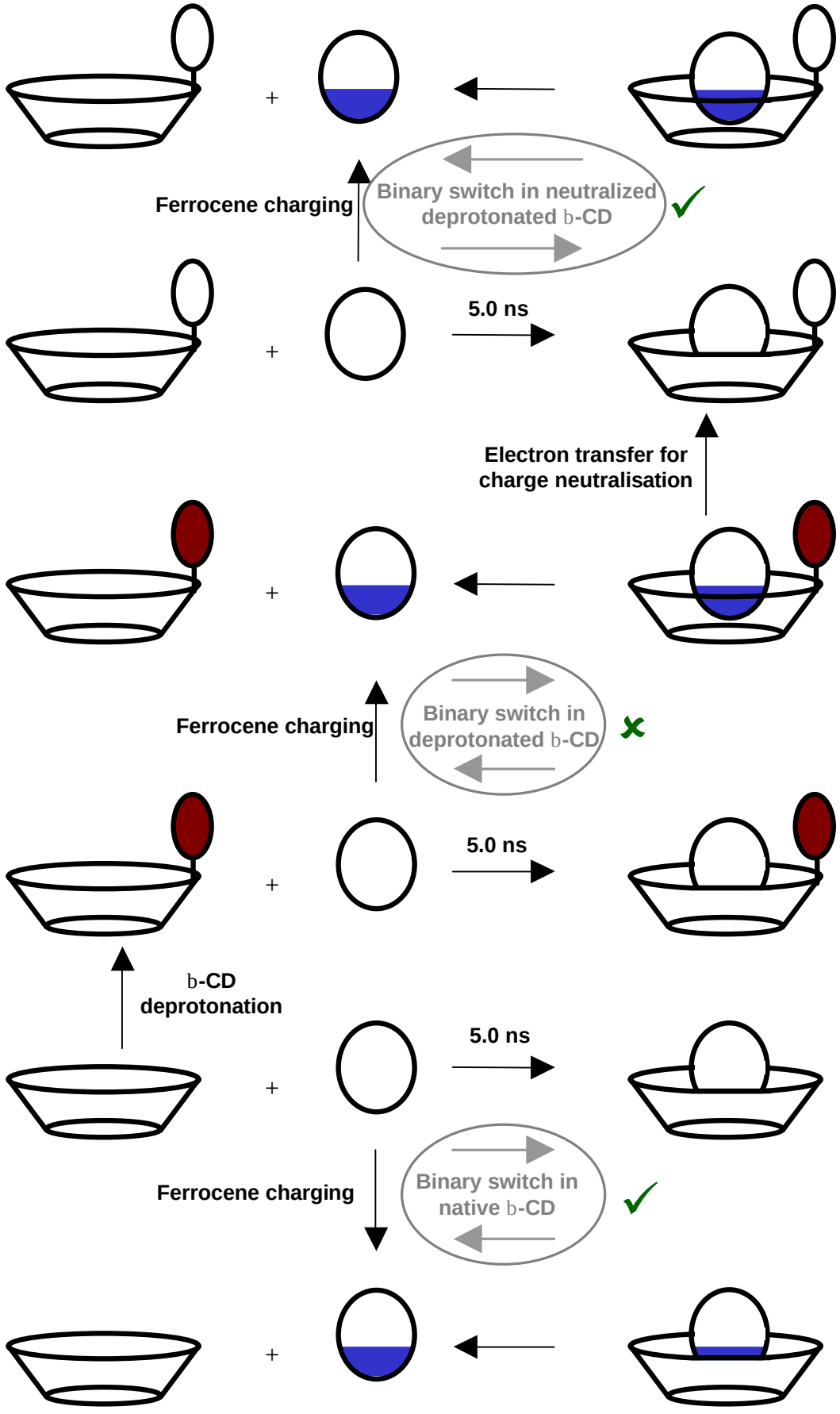


Figure SM9 **Ferrocene binding to dithiolene-b-CD**

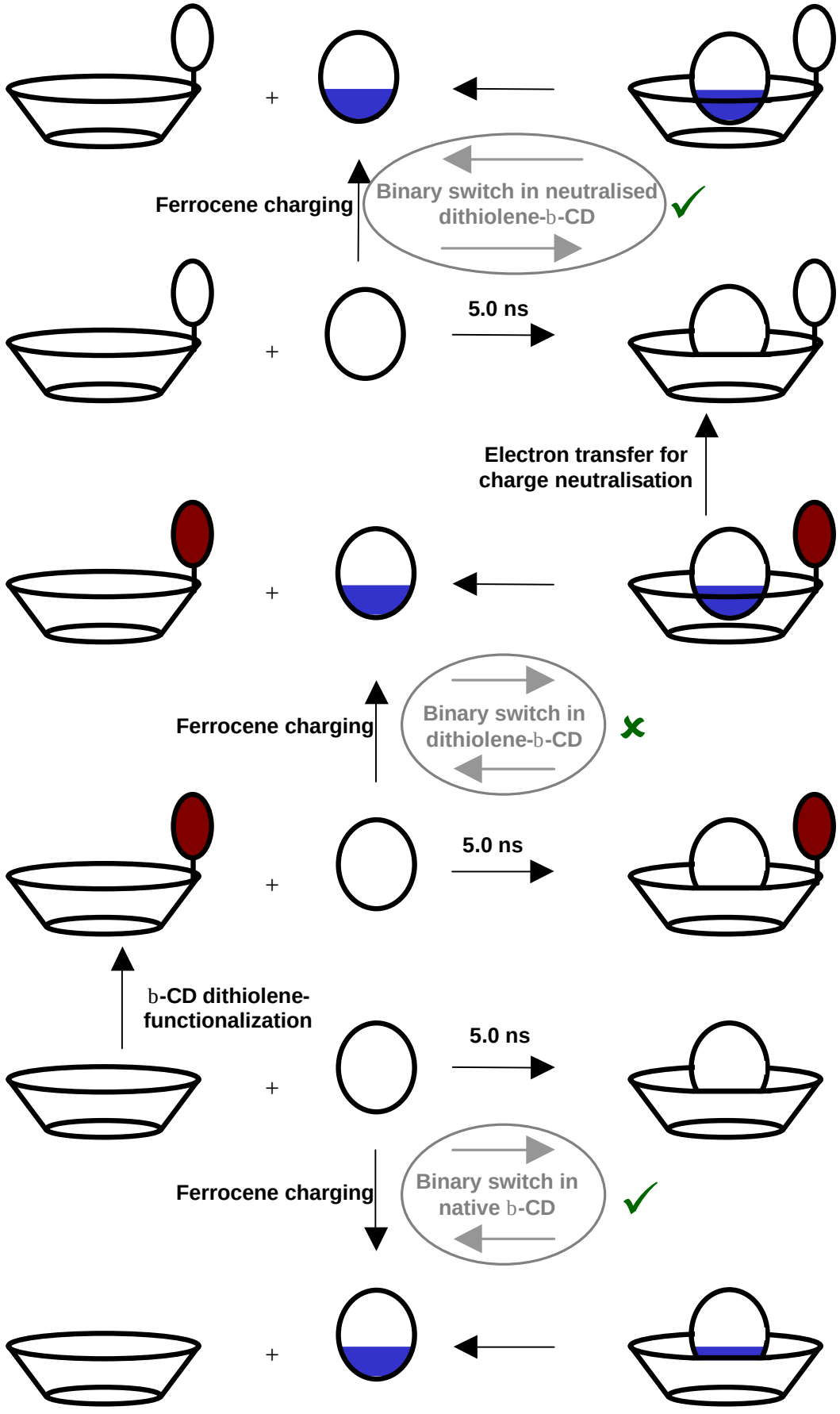


Figure SM10 **Ferrocene binding to carboxymethyl-b-CD**