Supporting Information

Fig. S1 Synthetic scheme for 3a and 3b.

Selected spectral data for 3a: $^1$H NMR (300 MHz, 2.0 mM, CDCl$_3$) $\delta$ 8.92 – 8.97 (m, 8H, -pyrrolicH), 8.03 (d, $J$ = 8.1 Hz, 2H, meso-phenylH), 7.60 (d, $J$ = 7.8 Hz, 6H, meso-phenylH), 7.37 (d, $J$ = 8.3 Hz, 2H, meso-phenylH), 7.11 (d, $J$ = 8.2 Hz, 1H benzocrown-phenylH), 7.03 (s, 1H, benzocrown-phenylH), 6.83 (d, $J$ = 7.8 Hz, 1H benzocrown-phenylH), 5.22 (s, 2H, benzylH), 3.97 (br, 2H, crownethyleneH), 3.88 (br, 2H, crownethyleneH), 3.45 (br, 8H, crownethyleneH), 3.32 (br, 4H, crownethyleneH), 3.27 (m, 3H, meso-phenylC$_{(CH_3)}_2$), 1.56 (d, $J$ = 6.7 Hz, 18H, meso-phenylCH$_{(CH_3)}_2$); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 158.6, 150.6, 150.4, 148.2, 148.1, 148.0, 141.2, 141.1, 136.3, 135.8, 135.1, 132.0, 129.6, 124.9, 121.5, 121.0, 120.7, 113.2, 112.9, 112.6, 70.7, 69.6, 69.4, 68.4, 67.7, 34.5, 24.8; FAB-MS (m-NBA) m/z 1100 (M$^+$); UV-Vis $\lambda_{max}$ (toluene, nm) 427, 512, 548, 588, 629.

Selected spectral data for 3b: $^1$H NMR (300 MHz, 2.5 mM, CDCl$_3$) $\delta$ 8.96 (s, 8H, -pyrrolicH), 8.13 (d, $J$ = 7.4 Hz, 6H, meso-phenylH), 7.84 (d, $J$ = 7.0 Hz, 2H, meso-phenylH), 7.59 (d, $J$ = 7.3 Hz, 6H, meso-phenylH), 7.37 (d, $J$ = 8.3 Hz, 2H, meso-phenylH), 6.98 (s, 1H, benzocrown-phenylH), 6.97 (d, $J$ = 6.8 Hz, 1H benzocrown-phenylH), 6.80 (d, $J$ = 8.2 Hz, 1H benzocrown-phenylH), 5.13 (s, 2H, benzylH), 3.99 (br, 4H, crownethyleneH), 3.66 (br, 2H, crownethyleneH), 3.60 (br, 2H, crownethyleneH), 3.41 (br, 8H, crownethyleneH), 3.27 (m, 3H, meso-phenylCH$_{(CH_3)}_2$), 1.57 (d, $J$ = 8.0 Hz, 18H, meso-phenylCH$_{(CH_3)}_2$); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 157.1, 150.54, 150.50, 150.46, 150.1, 149.1, 148.8, 145.0, 141.0, 135.0, 132.1, 131.9, 130.1 128.3, 127.5, 124.8, 121.3, 121.2, 113.3 70.2, 70.1, 68.96, 68.49, 34.5, 24.7; FAB-MS (m-NBA) m/z 1100 (M$^+$); UV-Vis $\lambda_{max}$ (toluene, nm) 425, 511, 548, 587, 629.
Diluting 3a and 3b in CDCl₃ led to characteristic downfield shifts of all proton signals of a benzocrown moiety. Especially, ¹H NMR signals of the crown ether ethylene protons displayed a larger downfield shift ($\Delta \delta = 0.8 \sim 1.4$ ppm), which is assumed to be due to the decreasing effect of the porphyrin ring current upon dilution. The ¹H NMR data for the dilution of 3a and 3b in CDCl₃ are very well fitted by the dimerization formula and the estimated dimerization constants are calculated to be 100 M⁻¹ and 10 M⁻¹ for 3a and 3b, respectively. Below 1 mM for 3a and 3 mM for 3b, more than 90% of each receptor exists in monomeric forms.
**Fig. S3** Schematic representation of dimerization and complexation of sodium salts by two-phase extraction with receptors 3a and 3b.
Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2002

Fig. S4 a) $^1$H NMR spectra in CDCl$_3$ and b) UV-visible spectra in toluene, checked after solid-liquid extraction c) UV-visible spectra in toluene, checked after liquid-liquid extraction.

a)
a-1. Solid / liquid (CDCl$_3$) extraction with ZnTPP-15C5(p), 3a

Crown ether ethylene protons

NaCN, extracted by ditopic binding
NaSCN, extracted by monotopic binding
NaI, extracted by monotopic binding
NaBr, extracted by monotopic binding
NaCl, extracted by monotopic binding
NaF, extracted by monotopic binding
ZnTPP-15C5(p), 3a

a-2. Solid / liquid (CDCl$_3$) extraction with ZnTPP-15C5(m), 3b

Crown ether ethylene protons

NaH$_2$PO$_4$, extracted by monotopic binding
NaOAc, extracted by monotopic binding
NaSCN, extracted by monotopic binding
NaCN, extracted by ditopic binding
NaI, extracted by monotopic binding
NaBr, extracted by monotopic binding
NaCl, extracted by monotopic binding
NaF, extracted by monotopic binding
ZnTPP-15C5(m), 3b
b)

Solid / Liquid (toluene) Extraction with ZnTPP-15c5(p)

![Graph showing extraction with ZnTPP-15c5(p)]

Solid / Liquid (toluene) Extraction with ZnTPP-15c5(m)

![Graph showing extraction with ZnTPP-15c5(m)]
c) Liquid/Liquid (water/toluene) Extraction with ZnTPP-15c5(p)

Liquid/Liquid (water/toluene) Extraction with ZnTPP-15C5(m)
Fig. S5 $^1$H NMR Titration of ZnTPP, receptors 3a and 3b with tetraethylammonium cyanide in DMSO-$d_6$ and calculation of extractability.
**Fig. S6** Color changes after solid-liquid extraction of NaCN by the receptors; A. ZnTPP + NaCN, B. co-receptor (ZnTPP + 3 eq. 15BC5) + NaCN, C. 3a only, D. 3a + NaCN, E. 3b only, F. 3b + NaCN
**Fig. S7** UV-visible spectra checked, after 0.2mL of various concentrations NaCN in water added to 1.8mL of DMSO solution ([3a] = 1.3 x 10^{-6} M and [3b] = 2.0 x 10^{-6} M) of the receptors

**3a : aqueous NaCN detection**

- Water only
- 0.0002 M NaCN
- 0.004 M NaCN
- 0.0008 M NaCN

**3b : aqueous NaCN detection**

- Water only
- 0.0002 M NaCN
- 0.004 M NaCN
- 0.0008 M NaCN
**Fig. S8** The estimated stability constants from UV-visible titration in DMSO/water (9/1); [3a] = 1.17 x 10^{-6} M and [3b] = 1.8 x 10^{-6} M