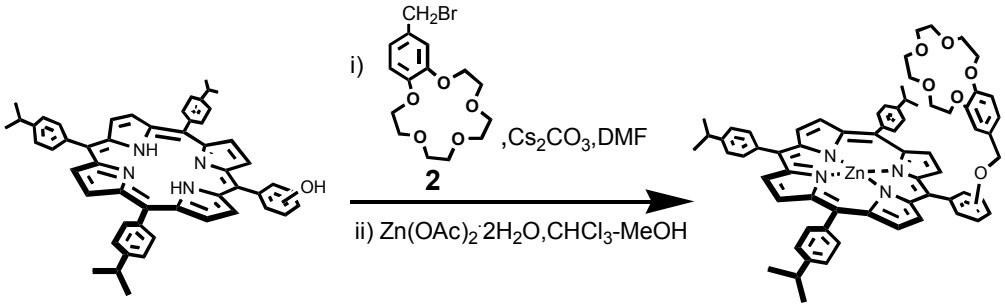
Supplementary Material (ESI) for Chemical Communications


# Supporting Information

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



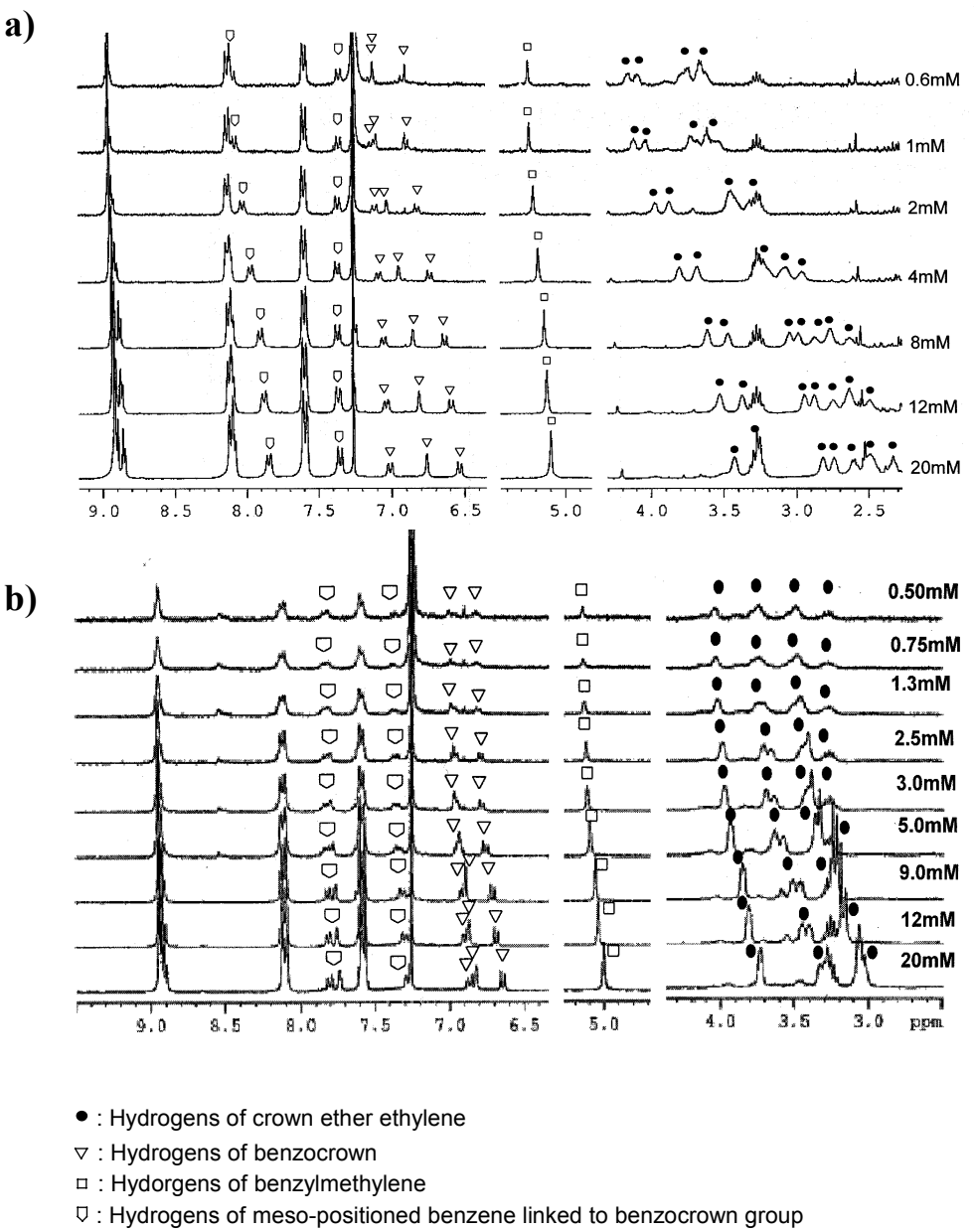

**1a** (para-OH)
**1b** (meta-OH)

**3a = ZnTPP-15C5(p)**
**3b = ZnTPP-15C5(m)**

Selected spectral data for **3a**: $^1$H NMR (300 MHz, 2.0mM, $CDCl_3$) $\delta$ 8.92 – 8.97 (m, 8H, $\beta$-pyrrolic*H*), 8.14 (d, $J$ = 7.8 Hz, 6H, meso-phenyl*H*), 8.03 (d, $J$ = 8.1Hz, 2H, meso-phenyl*H*), 7.60 (d, $J$ = 7.8Hz, 6H, meso-phenyl*H*), 7.37 (d, $J$ = 8.3Hz, 2H, meso-phenyl*H*), 7.11 (d, $J$ = 8.2Hz, 1H benzocrown-phenyl*H*), 7.03 (s, 1H, benzocrown-phenyl*H*), 6.83 (d, $J$ = 7.8Hz, 1H benzocrown-phenyl*H*), 5.22 (s, 2H, benzyl*H*), 3.97 (br, 2H, crownethylene*H*), 3.88 (br, 2H, crownethylene*H*), 3.45 (br, 8H, crownethylene*H*), 3.32 (br, 4H, crownethylene*H*), 3.27 (m, 3H, meso-phenylC*H*$(CH_3)_2$), 1.56 (d, $J$ = 6.7 Hz, 18H, meso-phenylCH(C*H*$_3)_2$); $^{13}$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, 2.5mM, $CDCl_3$) $\delta$ 8.96 (s, 8H, $\beta$-pyrrolic*H*), 8.13 (d, $J$ = 7.4 Hz, 6H, meso-phenyl*H*), 7.84 (d, $J$ = 7.0Hz, 2H, meso-phenyl*H*), 7.59 (d, $J$ = 7.3Hz, 6H, meso-phenyl*H*), 7.37 (d, $J$ = 8.3Hz, 2H, meso-phenyl*H*), 6.98 (s, 1H, benzocrown-phenyl*H*), 6.97 (d, $J$ = 6.8Hz, 1H benzocrown-phenyl*H*), 6.80 (d, $J$ = 8.2Hz, 1H benzocrown-phenyl*H*), 5.13 (s, 2H, benzyl*H*), 3.99 (br, 4H, crownethylene*H*), 3.66 (br, 2H, crownethylene*H*), 3.60 (br, 2H, crownethylene*H*), 3.41 (br, 8H, crownethylene*H*), 3.27 (m, 3H, meso-phenylC*H*$(CH_3)_2$), 1.57 (d, $J$ = 8.0 Hz, 18H, meso-phenylCH(C*H*$_3)_2$); $^{13}$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.

**Fig. S2** Dilution $^1$H NMR titration of a) **3a** from 20 mM to 0.6 mM, and b) **3b** from 20 mM to 0.5 mM in $CDCl_3$.




● : Hydrogens of crown ether ethylene
▽ : Hydrogens of benzocrown
□ : Hydorgens of benzylmethylene
▽ : Hydrogens of meso-positioned benzene linked to benzocrown group

Diluting **3a** and **3b** in $CDCl_3$ led to characteristic downfield shifts of all proton signals of a benzocrown moiety. Especially, $^1$H NMR signals of the crown ether ethylene protons displayed a larger downfield shift ($\Delta\delta$ = 0.8 ~ 1.4 ppm), which is assumed to be due to the decreasing effect of the porphyrin ring current upon dilution. The $^1$H NMR data for the dilution of **3a** and **3b** in $CDCl_3$ 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**.

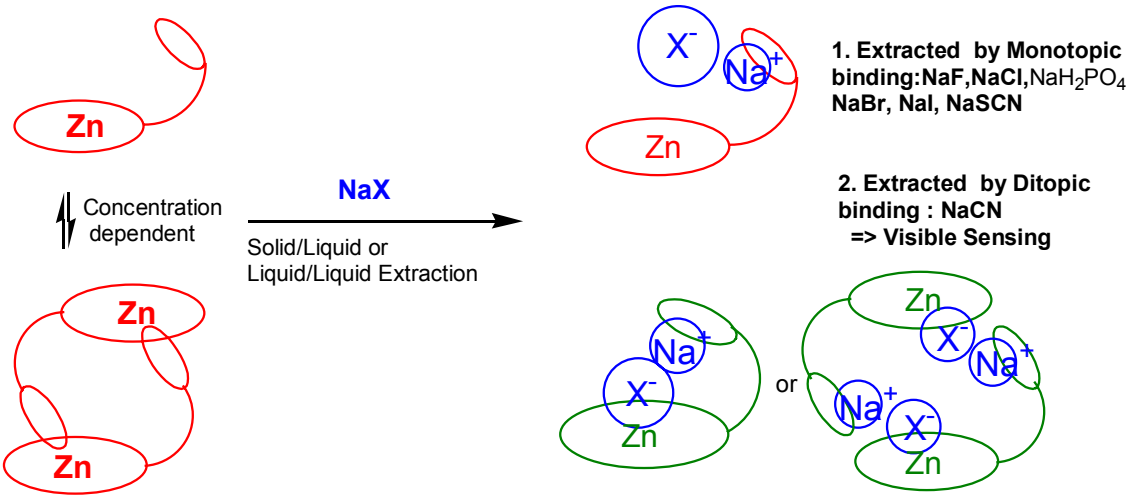
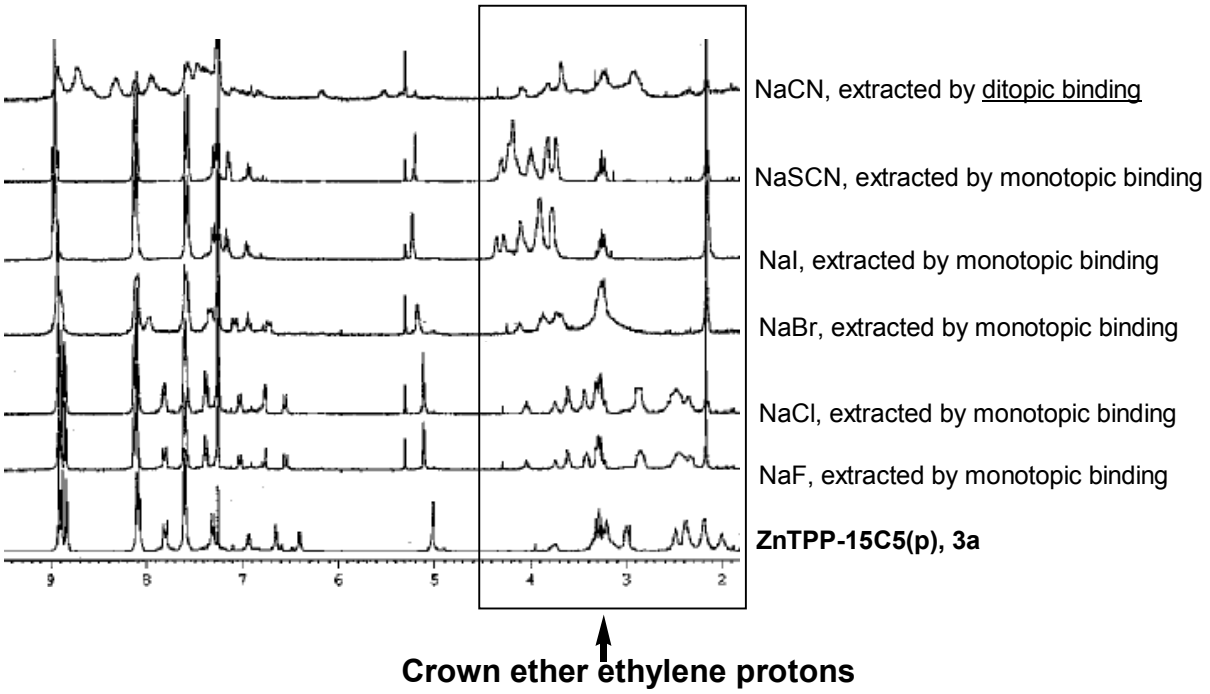


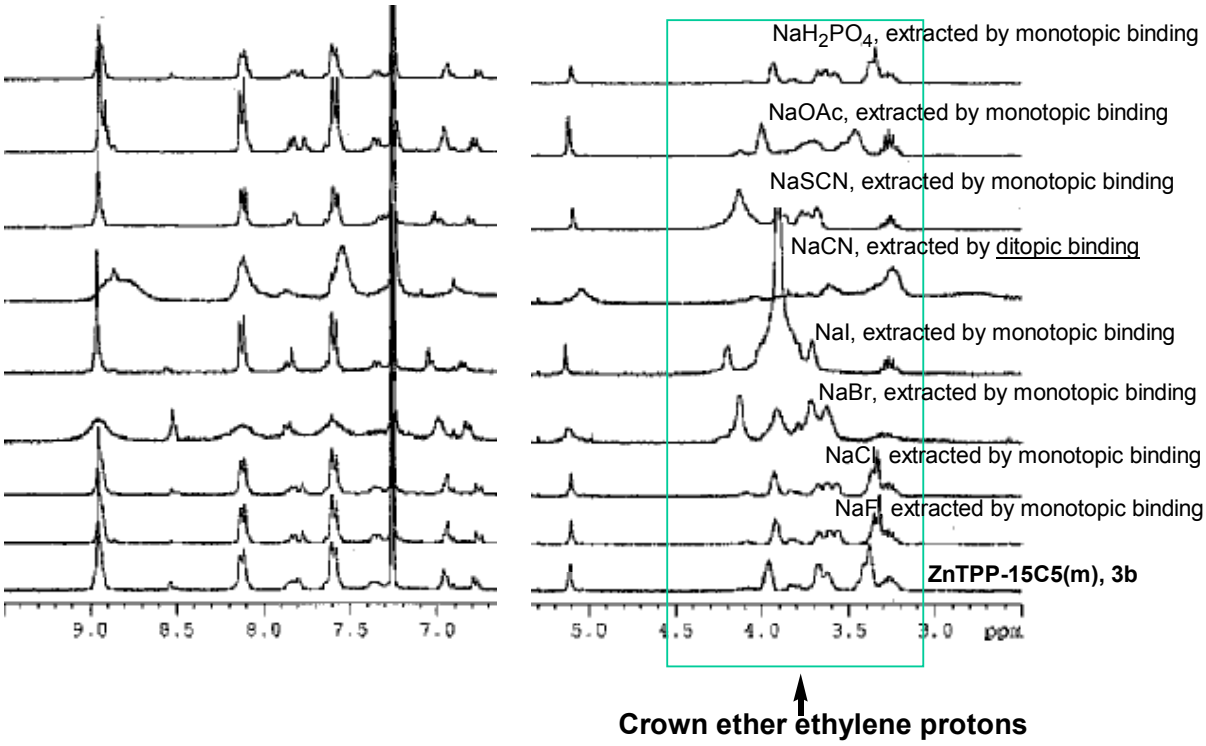
**Fig. S4** a) $^1$H NMR spectra in $CDCl_3$ and b) UV-visible spectra in toluene, checked after solid-liquid extraction c) UV-visible spectra in toluene, checked after liquid-liquid extraction.

**a)**

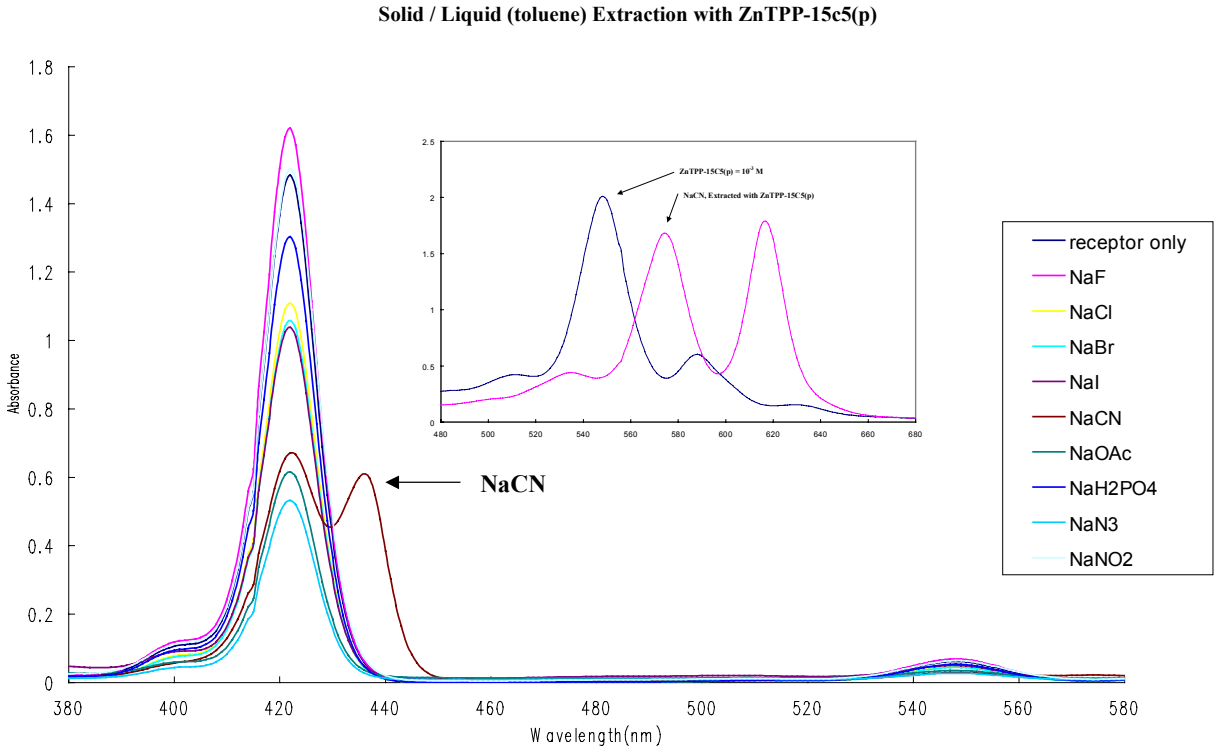
**a-1**. Solid / liquid ($CDCl_3$) extraction with **ZnTPP-15C5(p), 3a**

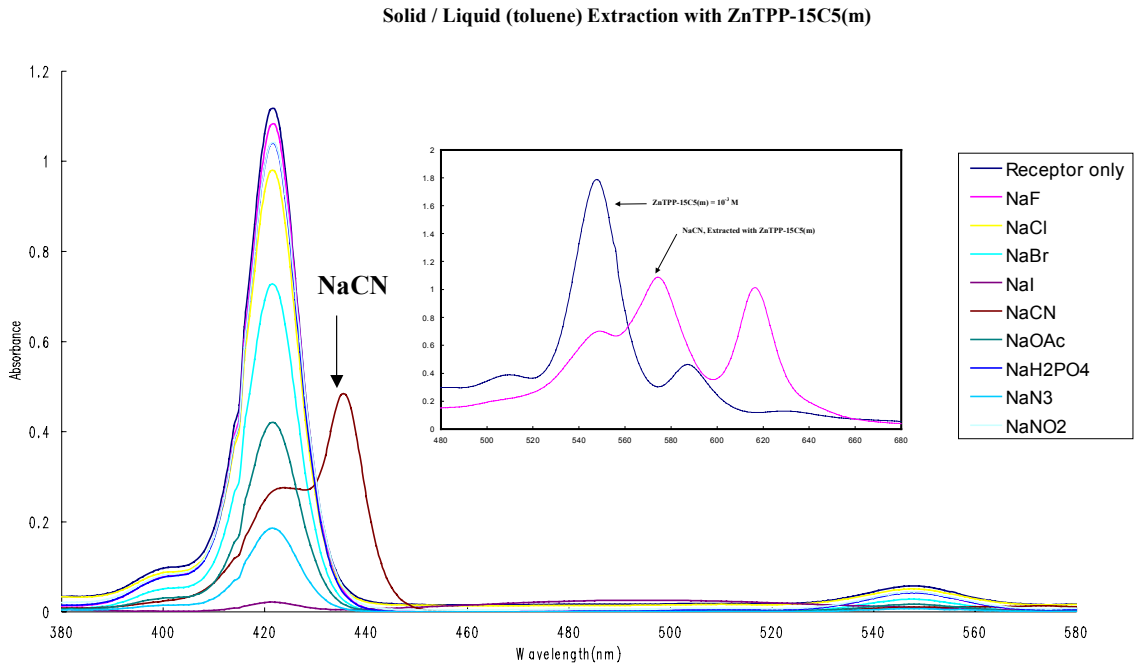



**a-2**. Solid / liquid ($CDCl_3$) extraction with **ZnTPP-15C5(m), 3b**



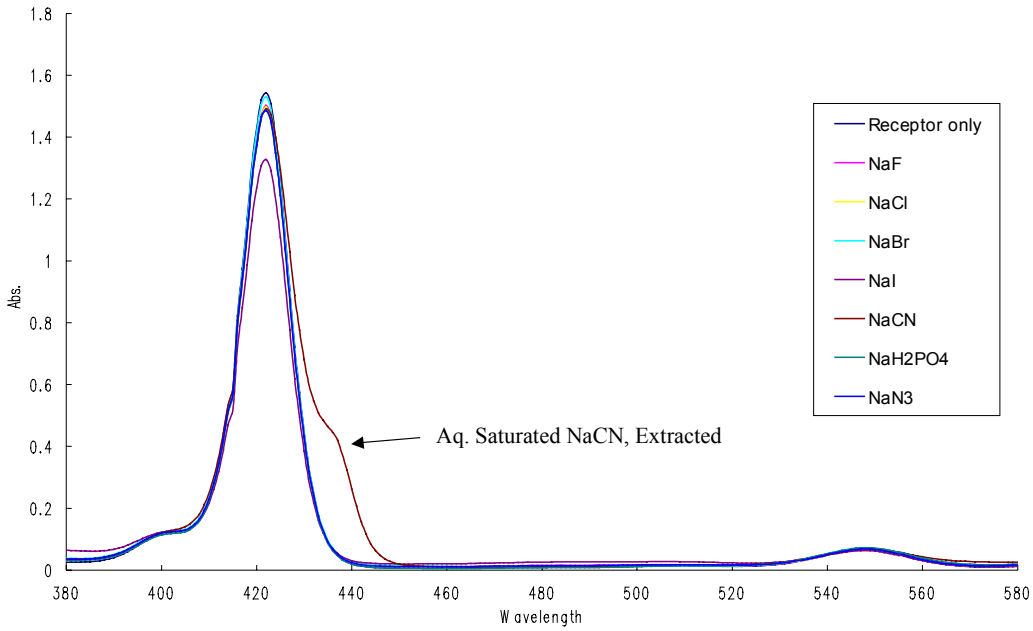
**b)**


Solid / Liquid (toluene) Extraction with ZnTPP-15c5(p)
Absorbance
Wavelength(nm)
NaCN
ZnTPP-15C5(p) = 10⁻⁵ M
NaCN, Extracted with ZnTPP-15C5(p)
receptor only
NaF
NaCl
NaBr
NaI
NaCN
NaOAc
NaH2PO4
NaN3
NaNO2


Solid / Liquid (toluene) Extraction with ZnTPP-15C5(m)
Absorbance
Wavelength(nm)
NaCN
ZnTPP-15C5(m) = 10⁻⁵ M
NaCN, Extracted with ZnTPP-15C5(m)
Receptor only
NaF
NaCl
NaBr
NaI
NaCN
NaOAc
NaH2PO4
NaN3
NaNO2

**c)**

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




**Liquid/Liquid (water/toluene) Extraction with ZnTPP-15C5(m)**

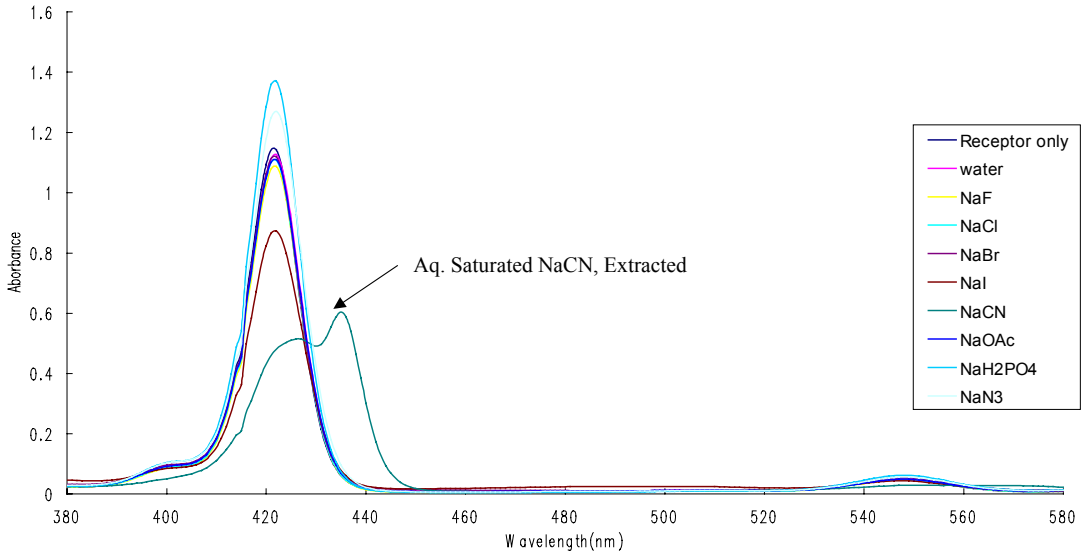


**Fig. S5** $^{1}$H NMR Titration of **ZnTPP**, receptors **3a** and **3b** with tetraethylammonium cyanide in DMSO-$d_6$ and calculation of extractability.

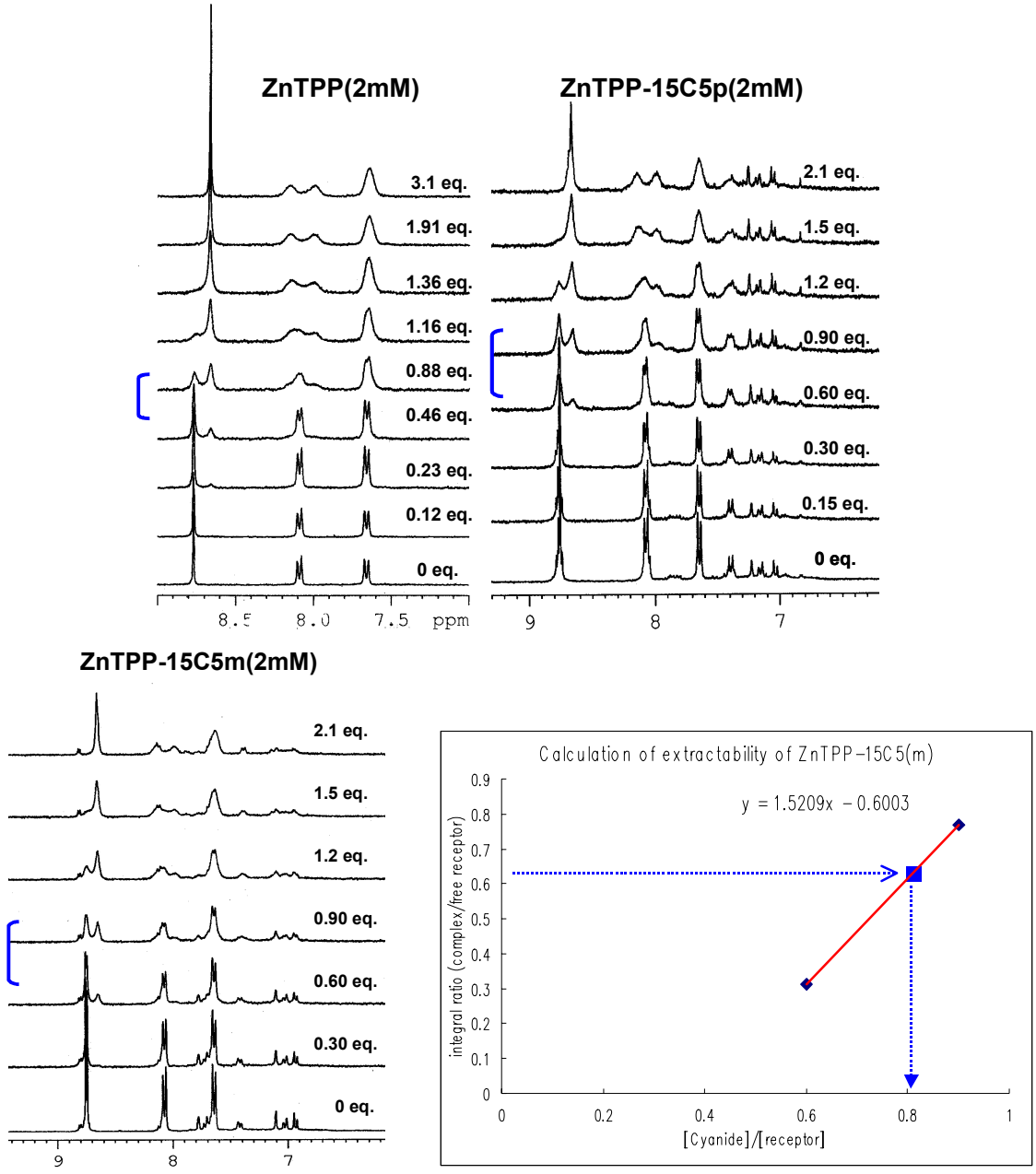


**Fig. S6** Color changes after solid-liquid extraction of NaCN by the receptors; A. ZnTPP + NaCN, B. co-receptor (ZnTPP + 3 eq. 15BC5) + NaCN, C. **3a** only, D. **3a** + NaCN, E. **3b** only, F. **3b** + NaCN

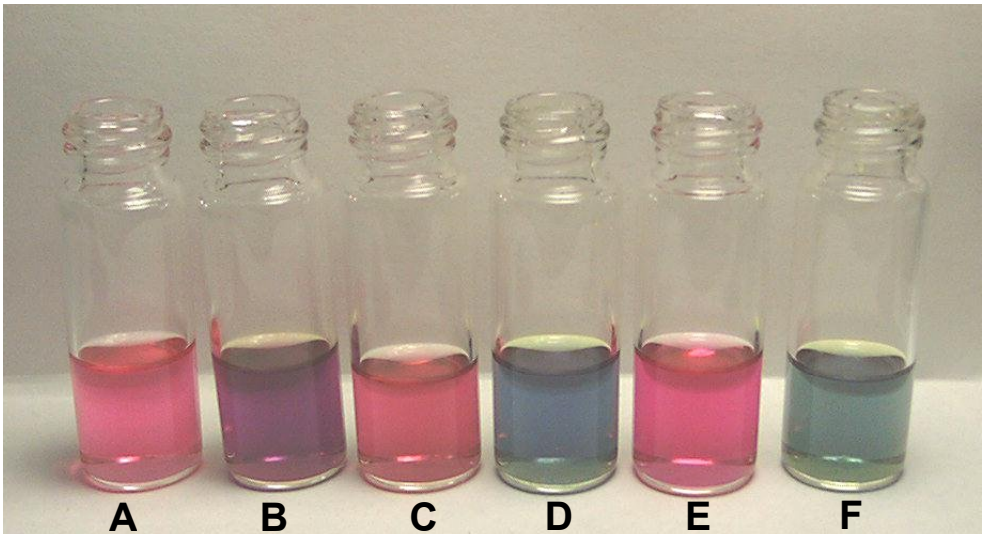


**Fig. S7** UV-visible spectra checked, after 0.2mL of various concentrations NaCN in water added to 1.8mL of DMSO solution ([**3a**] = 1.3 x $10^{-6}$ M and [**3b**] = 2.0 x $10^{-6}$ M) of the receptors

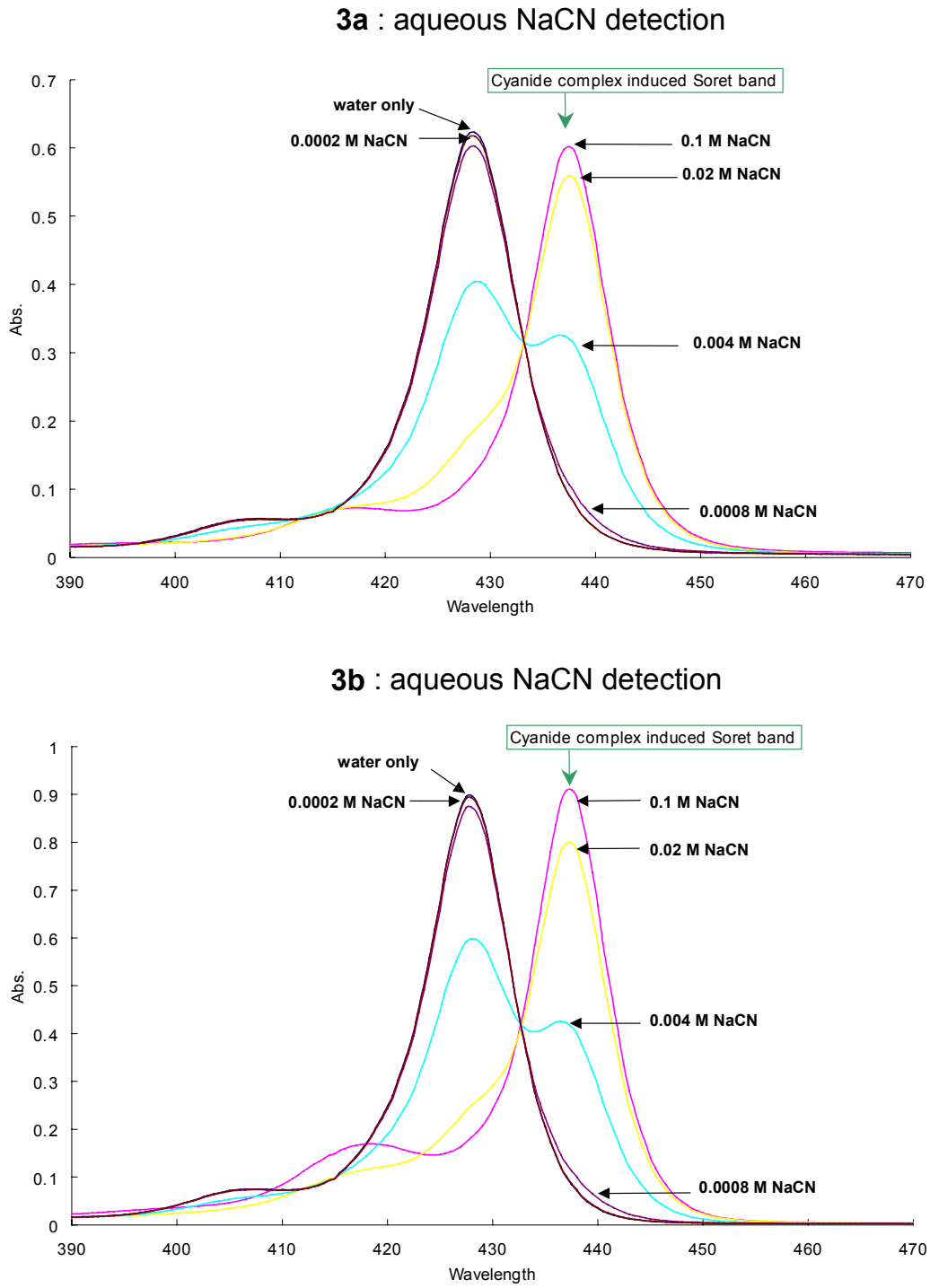


**Fig. S8** The estimated stability constants from UV-visible titration in DMSO/water (9/1); [**3a**] = 1.17 x $10^{-6}$ M and [**3b**] = 1.8 x $10^{-6}$ M