# ELECTRONIC SUPPLEMENTARY INFORMATION

Reagents used as starting materials were commercially available and were used without further purification. Solvents were dried following the usual protocols (THF, $Et_2O$ and Toluene were distilled from sodium wire with benzophenone indicator; $CH_3CN$ and $CH_2Cl_2$ were distilled from $CaCl_2$; EtOH and MeOH were distilled from magnesium and stored with molecular sieves). Unless stated otherwise, all reactions were carried out under nitrogen atmosphere. Column chromatography was run with silica gel 60 A CC 70-200 µm as stationary phase and using HPLC grade solvents. Melting points were measured in a Reichert instrument and are not corrected. $^1$H-NMR, $^{13}$C-NMR, were recorded on either a Bruker AV300 instrument, or a Bruker AV400 instrument. Chemical shifts are referred to the residual peak of the solvent. Mass spectrometry was recorded on HPLC-MS TOF 6220 instrument. Absorption spectra were recorded on a Cary 500 UV-vis-NIR spectrophotometer. Emission spectra were recorded on a Cary Eclipse spectrophotometer. Isothermal titration calorimetry experiments were run in a Microcal VP-ITC microcalorimeter and data were analysed using Origin software. X-ray structure determination of complex **2**·$Cl^-$ was carried out with a Bruker Smart APEX diffractometer. Data were collected with use of monochromated Mo K$\alpha$ radiation in $\omega$-scan mode. The structure was solved by direct methods and all non-hydrogen atoms refined anisotropically on F2 using the program SHELXL-97. Hydrogen atoms were refined using a riding model, except for the ordered methyl groups, which were refined by using rigid groups, and the NH hydrogens, which were refined freely. Pulse Gradient Spin Echo (PGSE) diffusion measurements were performed on a Bruker AV400 MHz spectrometer equipped with a HR Z-gradient BBO probe and using the standard *ledbpgp2s* pulse program from Bruker Topspin software (using a stimulated echo and longitudinal eddy current delay, with bipolar gradient pulses and two spoiling gradients). Sine shaped gradients were used and the measurements were recorded with 16 K time domain data points in $t_2$ dimension and 16 $t_1$ increments, 24 transients for each $t_1$ increment and a relaxation delay of 5 s. The gradient length $\delta$ (2*P30) was 1.6 ms with diffusion time $\Delta$ (D20) = 150 ms. The D-values were determined following the integral decay of the -$OCH_2$- resonance.

Titrations experiments protocol: A stock solution of the receptor was prepared in dimethylformamide-$d_7$. The anion was then dissolved with the appropriate volume of the former solution to get the right concentration of the titrant. Aliquots of the latter solution are added to the solution which contains the receptor without having to consider any dilution effects on the titrated species.
Compounds **1**[1] and **2**[2] were prepared as described in the bibliography.

---

[1] D. Curiel, A. Cowley, P. D. Beer, *Chem. Commun.* 2005, 236-238.

[2] D. Curiel, M. Más-Montoya, A. Uruvakili, R. A. Orenes, H. Pallamreddy and P. Molina, *Org. Lett.* 2010, **12**, 3164-3167

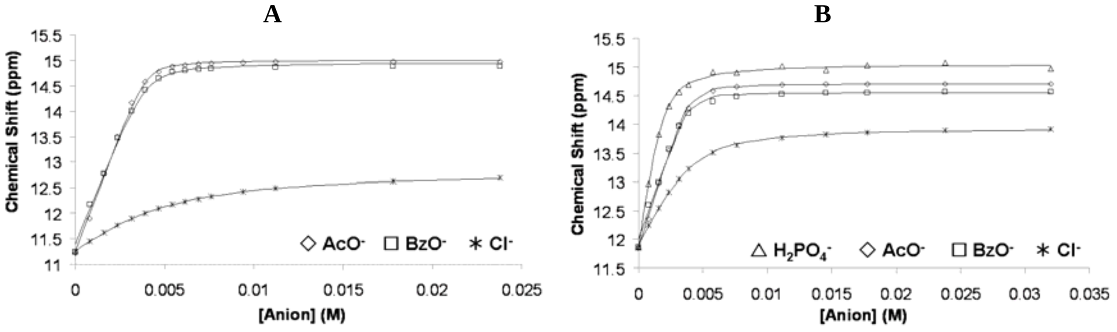


**Figure 1.** $^1$H-NMR fitplots of (A) **1** and (B) **2** in DMF-d$_7$, following the pyrrole NH peak; [Host]=4x10$^{-3}$ M; r.t.

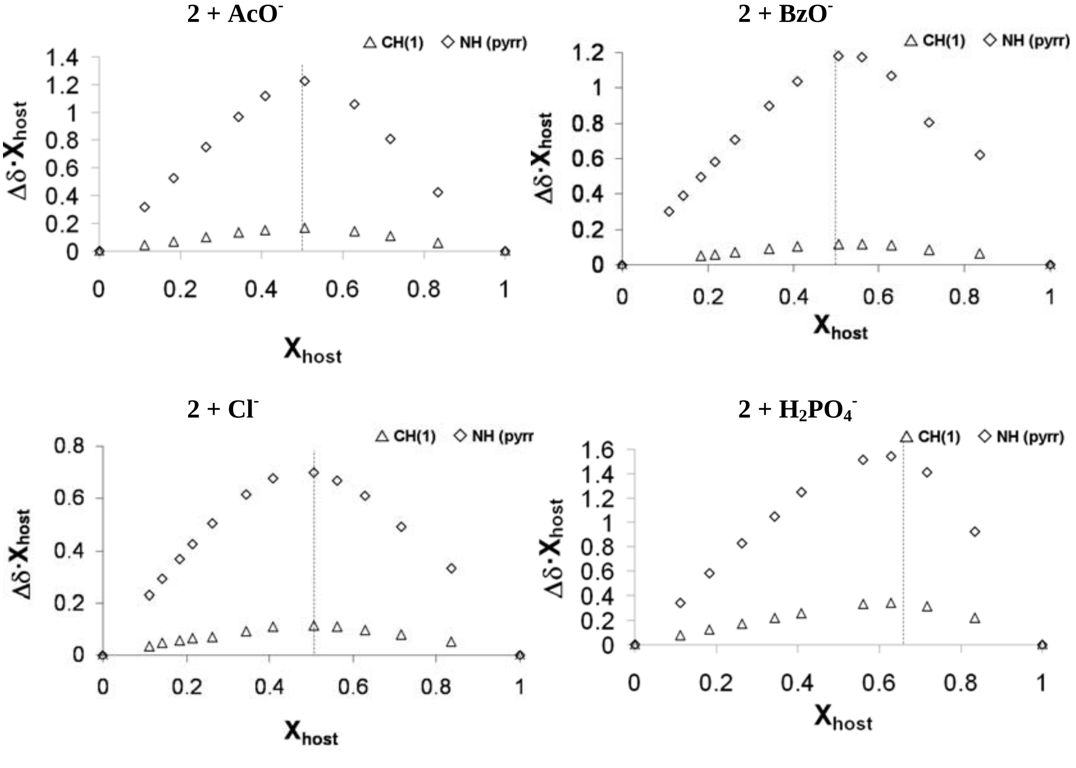


**Figure 2.** $^1$H-NMR Job plots of **2** in DMF-d$_7$.

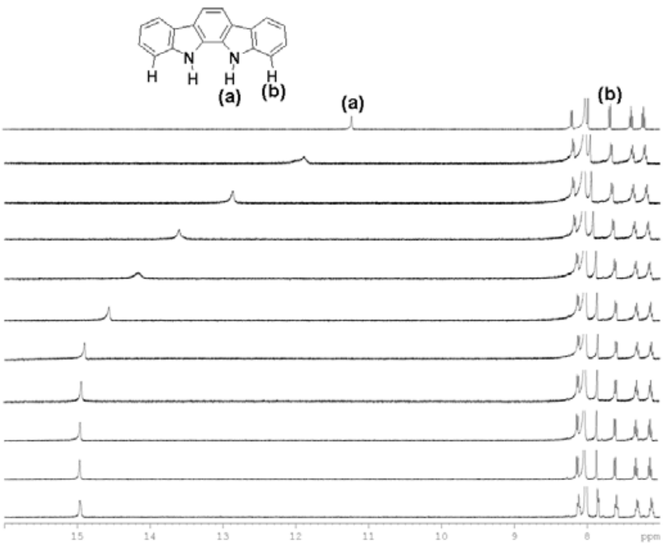
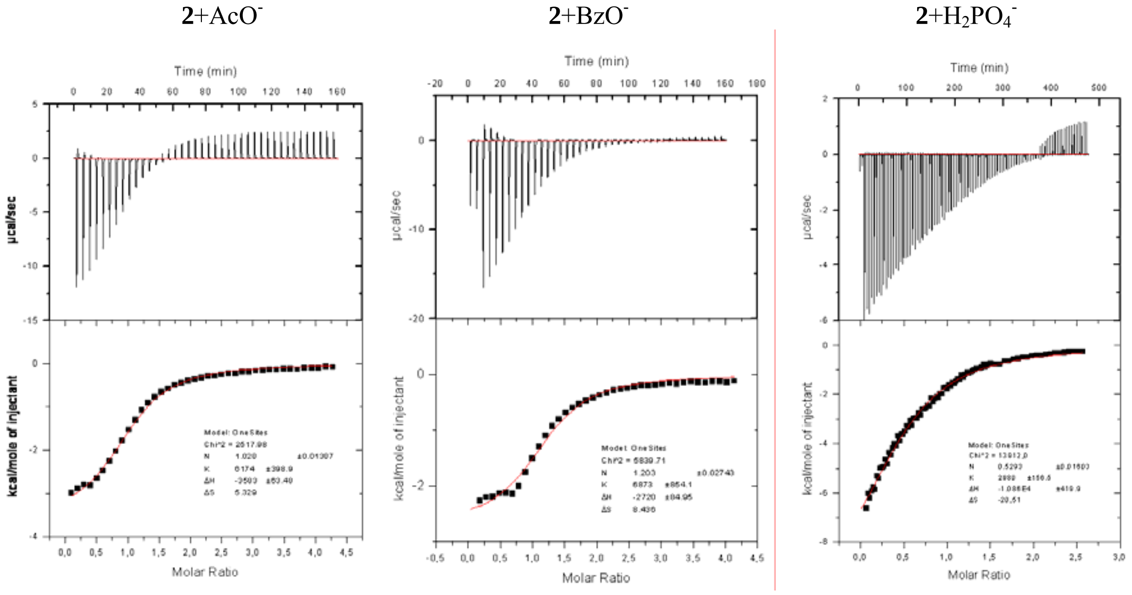


**Figure 3.** Evolution of the $^1$H-NMR spectra of **1** upon titration with TBAacetate in DMF-d$_7$. [Host]= 4x10$^{-3}$ M, r.t.



**2**+AcO$^-$

**2**+BzO$^-$

**2**+H$_2$PO$_4^-$

**Figure 4.** ITC of **2** with TBAacetate, TBAbenzoate, and TBAH$_2$PO$_4$ in DMF. [Host]= 10$^{-3}$ M, T=25ºC.

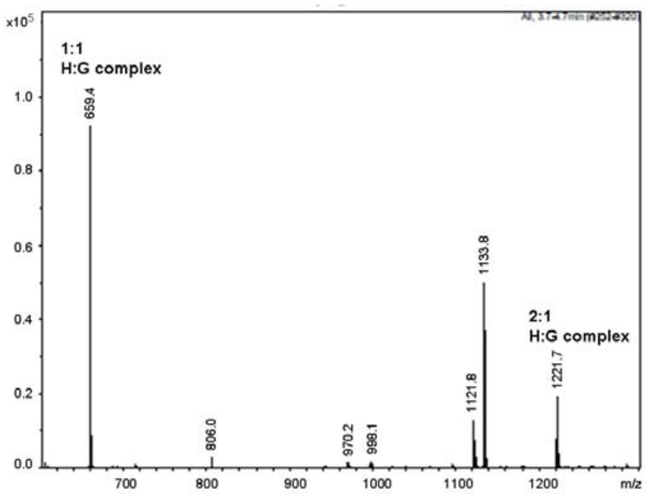
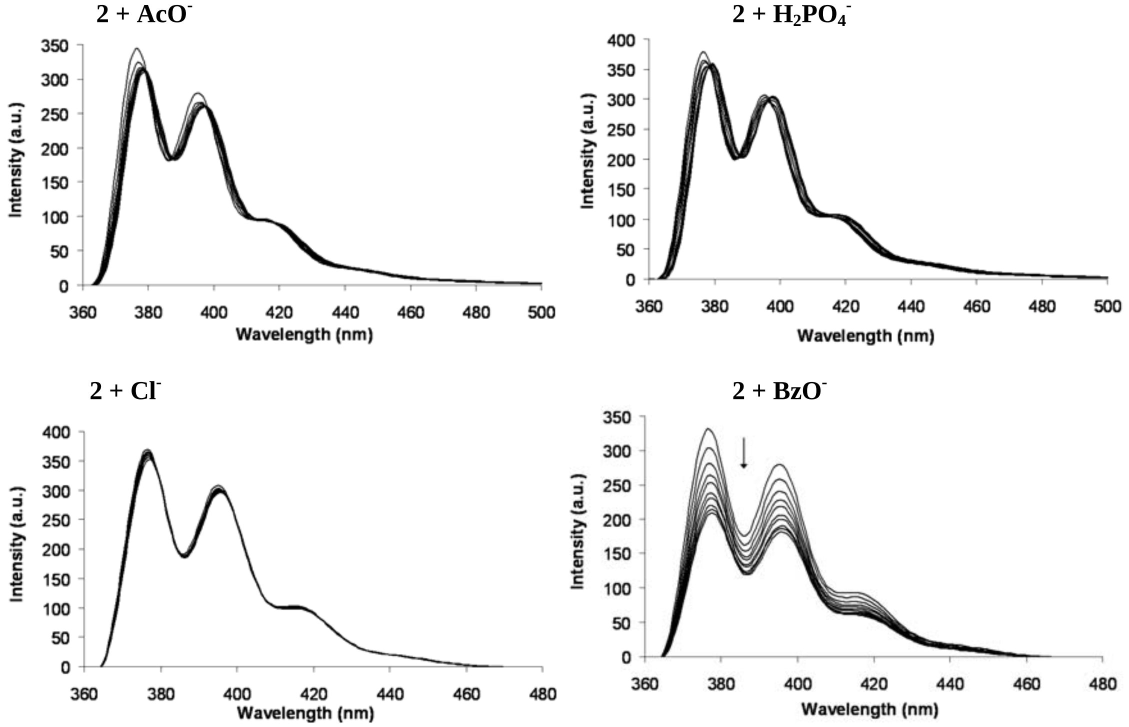


**Figure 5.** HRMS of the 2:1 host:guest complex, **$2{:}H_2PO_4^-$**.


**2 + $AcO^-$**

**2 + $H_2PO_4^-$**

**2 + $Cl^-$**

**2 + $BzO^-$**

**Figure 6.** Evolution of the emission spectra of **2** upon addition of TBAacetate, TBA$H_2PO_4$, TBACl and TBAbenzoate in DMF. [Host]=$2x10^{-5}$ M, r.t., $\lambda_{exc}$= 348 nm.

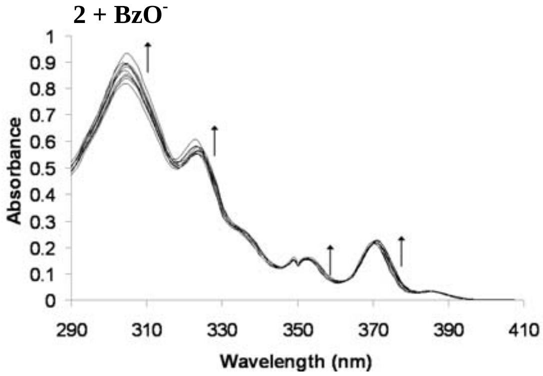


**Figure 7.** Evolution of the absorption spectra of **2** upon addition of TBAbenzoate in DMF. [Host]= 2x10$^{-5}$ M, r.t.

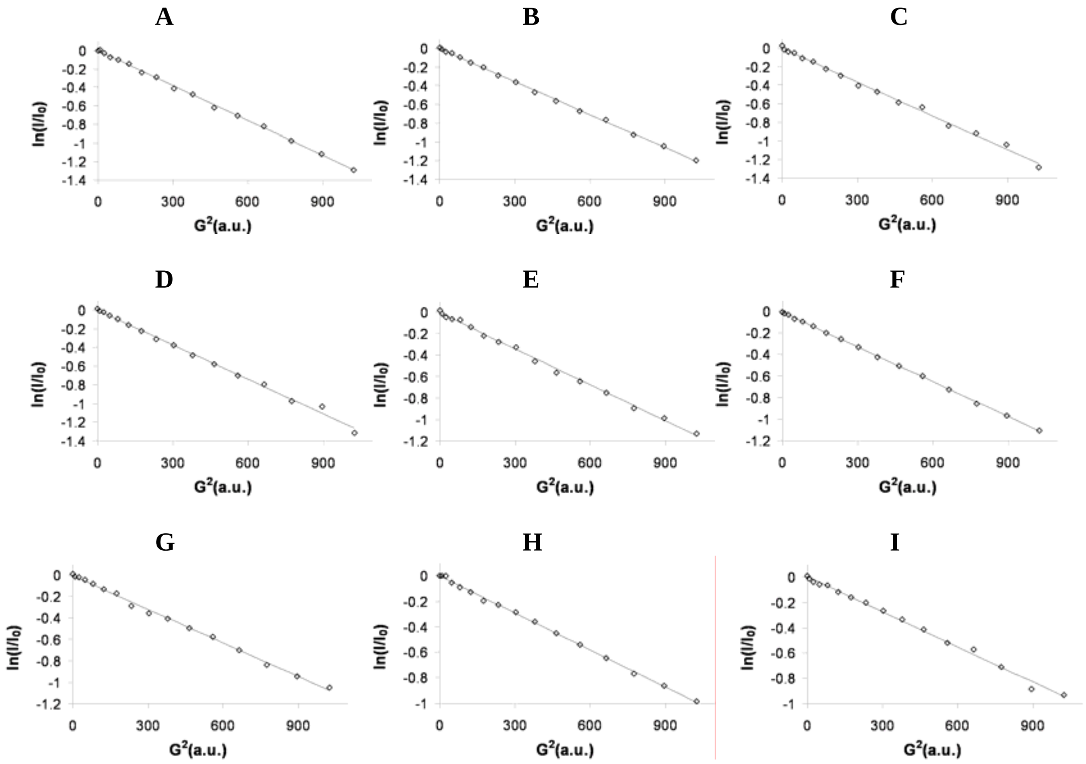


**Figure 8.** Fitplots for the calculation of the diffusion coefficient of **(A)** **2**, (D=0.46x10$^{-9}$ m$^2$/s), **(B)** **2** + 0.5 equiv. AcO$^-$,(D=0.43x10$^{-9}$ m$^2$/s), **(C)** **2** + 1 equiv. AcO$^-$,(D=0.45x10$^{-9}$ m$^2$/s), **(D)** **2** + 2 equiv. AcO$^-$ ,(D=0.45x10$^{-9}$ m$^2$/s), **(E)** **2** + 4 equiv. AcO$^-$,(D=0.42x10$^{-9}$ m$^2$/s), **(F)** **2** + 0.5 equiv. $H_2PO_4^-$,(D=0.39x10$^{-9}$ m$^2$/s), **(G)** **2** + 1 equiv. $H_2PO_4^-$,(D=0.39x10$^{-9}$ m$^2$/s), **(H)** **2** + 2 equiv. $H_2PO_4^-$ (D=0.36x10$^{-9}$ m$^2$/s) and **(I)** **2** + 4 equiv. $H_2PO_4^-$.(D=0.33x10$^{-9}$ m$^2$/s). [Host]= 10$^{-3}$ M in DMF-d$_7$, r.t.