Supporting information

Primary Amine Recognition in Water by a Calix[6]aza-cryptand Incorporated in Dodecylphosphocholine Micelles

*Emilio Brunetti, Alex Inthasot, Flore Keymeulen, Olivia Reinaud, Ivan Jabin and Kristin Bartik*

SI1. 2D DOSY experiment (298K, 600MHz, D₂O) with 1.Zn²⁺ in DPC  
SI2. NMR PRE experiment (298K, 600MHz, D₂O) with 1.Zn²⁺ in DPC  
SI3. ¹H NMR (298K, 300MHz, D₂O) spectrum of 1.nH⁺ in DPC  
SI4. Determination of the pseudo pKₐ for PrNH₂ with 1.Zn²⁺ in DPC  
SI5. ¹H NMR (298K, 600MHz, D₂O) spectra of 1.Zn²⁺ in the absence and presence of EtNH₂ in DPC-d₃₈  
SI6. ¹H NMR (298K, 600MHz, D₂O) spectra of 1.Zn²⁺ in the absence and presence of HeptylNH₂ in DPC  
SI7. Experimental conditions for titrations of 1.Zn²⁺ with amines, alcohols and aminoalcohols in DPC (298 K, D₂O)
SI1. 2D DOSY experiment (298K, 600MHz, D$_2$O) with 1.Zn$^{2+}$ in DPC

The x- and y- axis represent the regular $^1$H chemical shift and the diffusion coefficient, respectively. DCM: residual dichloromethane; HDO: solvent signal chosen as reference for diffusion coefficient determination ($D = 19.02 \times 10^{-10}$ m$^2$/s at 298 K).
SI2. PRE NMR experiments (298K, 600MHz, D$_2$O) with 1.Zn$^{2+}$ in DPC

Normalized relaxivity (measured relaxivity divided by relaxivity of $\alpha$CH$_2$ protons of the surfactant; $\varphi$; mM$^{-1}$s$^{-1}$; error < 15%): values for the nuclei of DPC (20 mM) and for the nuclei of the incorporated complex 1.Zn$^{2+}$ (0.5 mM).

<table>
<thead>
<tr>
<th></th>
<th>$^+\text{N(CH}_3)_3$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$\delta$</th>
<th>Tail</th>
<th>$\omega$</th>
<th>ArH$^{\text{cap}}$</th>
<th>ArH$^{\text{2OMe}}$</th>
<th>tBu$^{\text{OMe}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.89</td>
<td>1</td>
<td>0.51</td>
<td>0.29</td>
<td>0.18</td>
<td>0.08</td>
<td>0.06</td>
<td>0.18</td>
<td>0.14</td>
<td>0.05</td>
</tr>
</tbody>
</table>
SI3. $^1$H NMR (298K, 300MHz, D$_2$O) spectrum of 1.nH$^+$ in DPC

$^1$H NMR spectrum (300 MHz, 298 K) of 1.nH$^+$ in DPC (20 mM in D$_2$O at pH ~3.1); s: solvent.
SI4. Determination of the pseudo pKa shift for PrNH$_2$

The formation constant $K$ and $K'_{pH}$ are defined according to the following equilibrium:

$$\begin{align*}
1.\text{Zn}^{2+} + (\text{H}_2\text{O})^+ + \text{PrNH}_3^+ \rightleftharpoons \text{Zn}^{2+} + (\text{PrNH}_2)^+ + \text{H}_3\text{O}^+
\end{align*}$$

$$K = \frac{[1.\text{Zn}^{2+} (\text{PrNH}_2)][\text{H}_3\text{O}^+]}{[1.\text{Zn}^{2+} (\text{H}_2\text{O})][\text{PrNH}_3^+]},$$

$$K'_{pH} = \frac{[1.\text{Zn}^{2+} (\text{PrNH}_2)]}{[1.\text{Zn}^{2+} (\text{H}_2\text{O})][\text{PrNH}_3^+]}$$

From analysis and signal integration in the $^1$H NMR spectra (see experimental section of article for details). $K$ was found to be $\sim 5\times10^{-5}$ at pH $\sim$8 and $K'_{pH} \sim 5000$ M$^{-1}$. From these data, we can estimate a pseudo pK$_a$ (-log$K$) of $\sim$4.3.
SI5. $^1$H NMR (298K, 600MHz, D$_2$O) spectra of $\text{1.Zn}^{2+}$ in the absence and presence of EtNH$_2$ in DPC-$d_{38}$

$^1$H NMR spectra (600 MHz, 298 K) of (a) $\text{1.Zn}^{2+}$ in DPC-$d_{38}$ (20 mM in D$_2$O at pH ~7.6); (b) $\text{1.Zn}^{2+}$ in DPC-$d_{38}$ (20 mM in D$_2$O) after the addition of ~3 equiv. of EtNH$_2$. ▼: EtNH$_2$ in; s: solvent.
SI6. $^1$H NMR (298K, 600MHz, D$_2$O) spectra of $1.Zn^{2+}$ in the absence and presence of HeptylNH$_2$ in DPC micelles.

$^1$H NMR spectra (600 MHz, 298 K) of (a) $1.Zn^{2+}$ in DPC (20 mM in D$_2$O at pH ~7.6); (b) $1.Zn^{2+}$ in DPC (20 mM in D$_2$O) after the addition of ~7 equiv. of HeptylNH$_2$. s: solvent; a: acetone.
SI7. Experimental conditions for titrations of \textit{1.Zn}^{2+} with amines, alcohols and aminoalcohols in DPC

The potential binding of different guests was monitored via \textit{1}H NMR titration experiments at room temperature with \textasciitilde 0.5 mM solutions of \textit{1.Zn}^{2+} in DPC (20 mM in D\textsubscript{2}O). Progressive additions of the investigated potential guest, until the final concentration indicated below, were undertaken (pH monitored are also indicated). No signals for included guest were observed in the \textit{1}H NMR spectra for the following molecules:

(i) tBuNH\textsubscript{2} up to 6 mM (pH \textasciitilde 7.8, \textasciitilde 10.4 and 11);
(ii) (Et)\textsubscript{2}NH up to 15 mM (pH \textasciitilde 7.8 and 11). This amine added after the experiment undertaken in (i);
(iii) ethanol up to 365 mM (pH \textasciitilde 7.6);
(iv) propanol up to 340 mM (pH \textasciitilde 7.6);
(v) butanol up to 18 mM (pH \textasciitilde 7.6). This alcohol added after the experiment undertaken in (iv);
(vi) octanol up to 50 mM (pH \textasciitilde 7.6);
(vii) ethanolamine up to 25 mM (pH \textasciitilde 7.6);
(viii) (\pm)-1-amino-2-propanol up to 3.5 mM (pH \textasciitilde 6.0 and pH \textasciitilde 10.4);
(x) 6-amino-1-hexanol up to 10 mM (no pH value available);