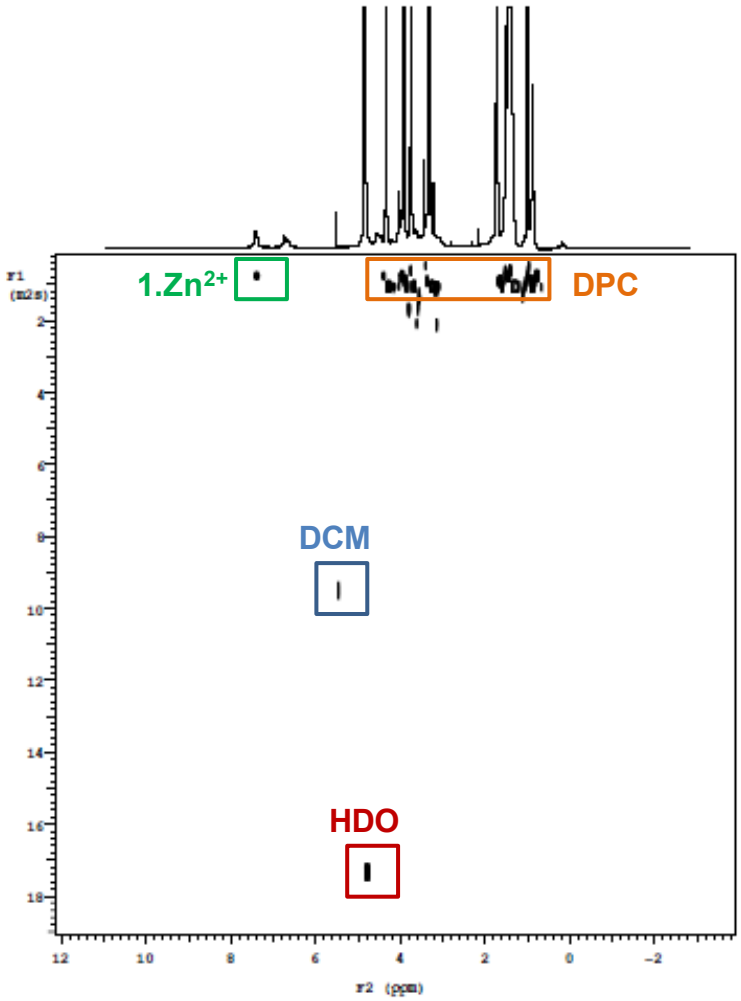
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

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**

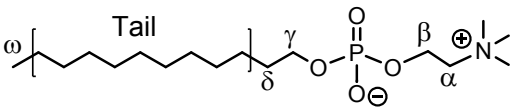
SI1. 2D DOSY experiment (298K, 600MHz, D_2O) with **1.Zn^{2+}** in DPC



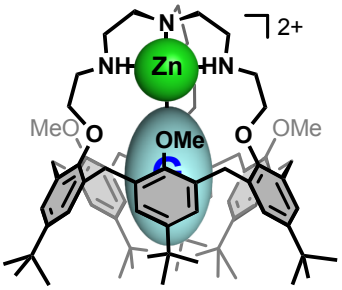
The x- and y- axis represent the regular ^1H chemical shift and the diffusion coefficient, respectively. DCM: residual dichloromethane; HDO: solvent signal chosen as reference for diffusion coefficient determination (D = 19.02x10^{-10} m^2/s at 298 K).

SI2. PRE NMR experiments (298K, 600MHz, D_2O) with **1.Zn^{2+}** in DPC

Normalized relaxivity (measured relaxivity divided by relaxivity of αCH_2 protons of the surfactant; φ; $mM^{-1}s^{-1;}$ error < 15%): values for the nuclei of DPC (20 mM) and for the nuclei of the incorporated complex **1.Zn^{2+}** (0.5 mM).



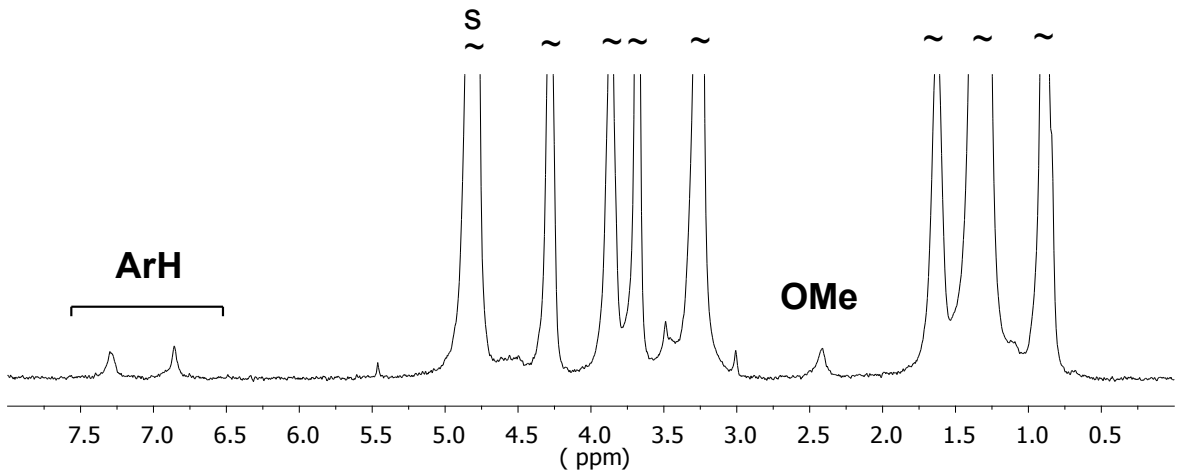
DPC



1.Zn^{2+}⊃nH_2O

$^{+}N(CH_3)_3$	α	β	γ	δ	Tail	ω	ArH^{cap}	$ArH2^{OMe}$	tBu^{OMe}
0.89	1	0.51	0.29	0.18	0.08	0.06	0.18	0.14	0.05

SI3. ^{1}H NMR (298K, 300MHz, D_2O) spectrum of **1.nH**$^{+}$ in DPC



^{1}H NMR spectrum (300 MHz, 298 K) of **1.nH**$^{+}$ in DPC (20 mM in D_2O 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:

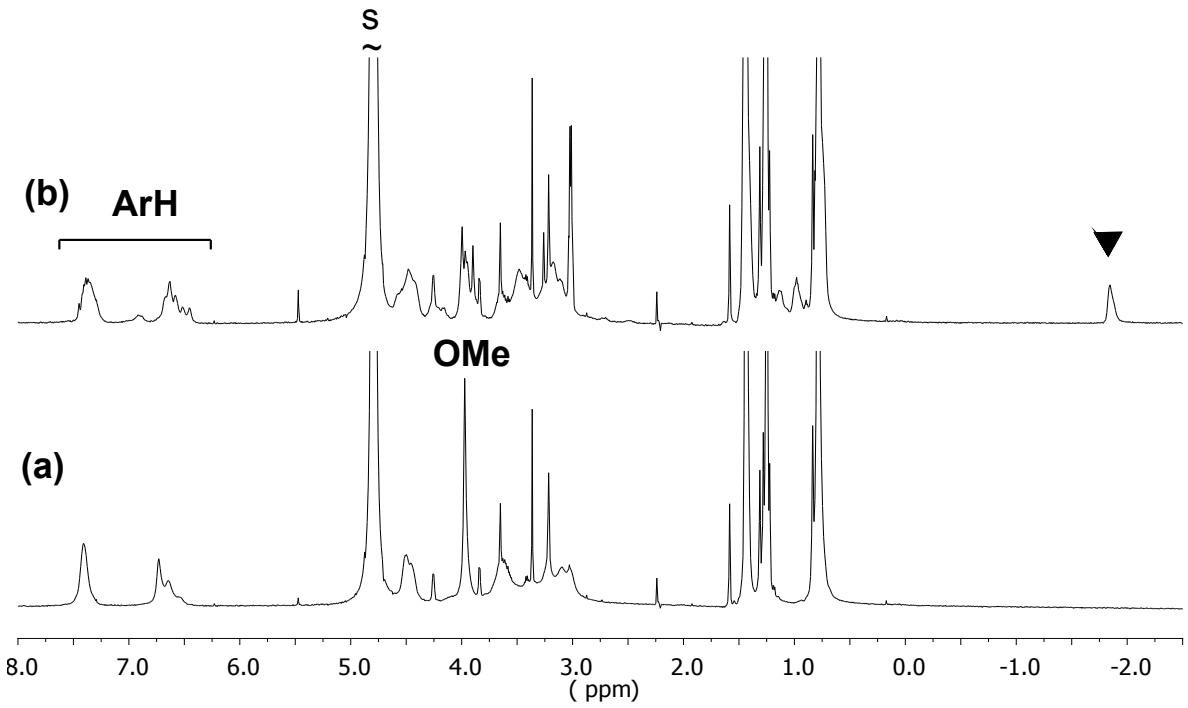
$$1.Zn^{2+}(H_2O) + PrNH_3^+ \text{ â ‡ Œ } 1.Zn^{2+}(PrNH_2) + H_3O^+$$

$$K = \frac{\left[1.Zn^{2+}(PrNH_2)\right]\left[H_3O^+\right]}{\left[1.Zn^{2+}(H_2O)\right]\left[PrNH_3^+\right]}$$

$$K'_{pH} = \frac{\left[1.Zn^{2+}(PrNH_2)\right]}{\left[1.Zn^{2+}(H_2O)\right]\left[PrNH_3^+\right]}$$

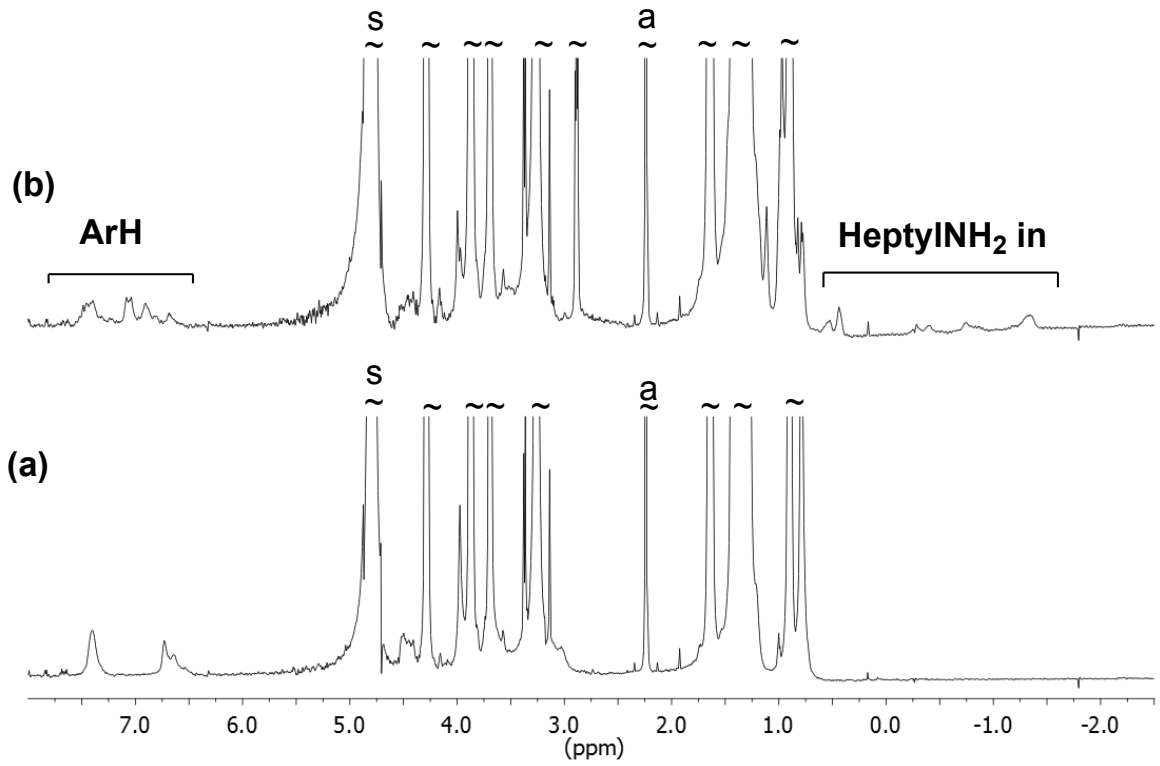
From analysis and signal integration in the ^{1}H NMR spectra (see experimental section of article for details). K was found to be ~ $5x10^{-5}$ at pH ~8 and K'_{pH} ~5000 M^{-1}. From these data, we can estimate a *pseudo* pK_a ($-\log K$) of ~4.3.

SI5. ^{1}H NMR (298K, 600MHz, D_2O) spectra of **1.Zn^{2+}** in the absence and presence of $EtNH_2$ in DPC-*d38*



^{1}H NMR spectra (600 MHz, 298 K) of (a) **1.Zn^{2+}** in DPC-*d38* (20 mM in D_2O at pH ~7.6); (b) **1.Zn^{2+}** in DPC-*d38* (20 mM in D_2O) after the addition of ~3 equiv. of $EtNH_2$. ▼: $EtNH_2$ in; s: solvent.

SI6. ^{1}H NMR (298K, 600MHz, D_2O) 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_2O at pH ~7.6); (b) **1.Zn^{2+}** in DPC (20 mM in D_2O) after the addition of ~7 equiv. of HeptylNH_2. s: solvent; a: acetone.

SI7. Experimental conditions for titrations of **1.Zn^{2+}** with amines, alcohols and aminoalcohols in DPC

The potential binding of different **guests** was monitored via ^{1}H NMR titration experiments at room temperature with ~0.5 mM solutions of **1.Zn^{2+}** in DPC (20 mM in D_2O). 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 ^{1}H NMR spectra for the following molecules:

(i) *t*BuNH$_2$ up to 6 mM (pH ~7.8, ~10.4 and 11);
(ii) (Et)$_2$NH up to 15 mM (pH ~7.8 and 11). This amine added after the experiment undertaken in (i);
(iii) ethanol up to 365 mM (pH ~7.6);
(iv) propanol up to 340 mM (pH ~7.6);
(v) butanol up to 18 mM (pH ~7.6). This alcohol added after the experiment undertaken in (iv);
(vi) octanol up to 50 mM (pH ~7.6);
(vii) ethanolamine up to 25 mM (pH ~7.6);
(viii) (±)-1-amino-2-propanol up to 3.5 mM (pH ~6.0 and pH ~10.4);
(xi) (±)-2-amino-1-propanol up to 3.7 mM (pH ~5.5 and pH ~10.5);
(x) 6-amino-1-hexanol up to 10 mM (no pH value available);