Supporting Information for:

Encapsulation of a $(H_3O_2)^-$ Unit in the Aromatic Core of a Calix[6]arene Closed by Two Zn(II) Ions at the Small and Large Rims

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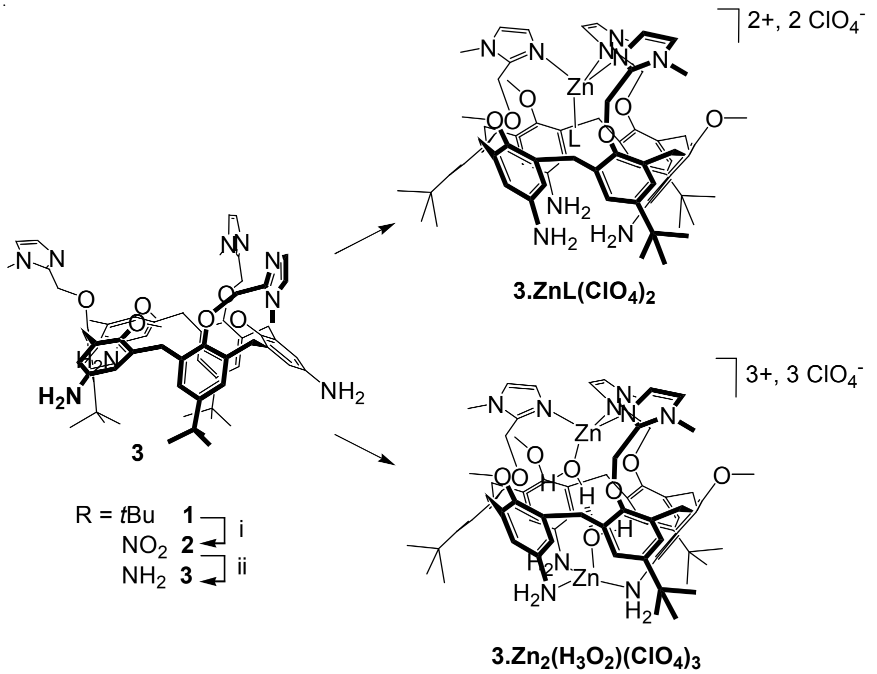

Experimental section

General: CH_2Cl_2 was distilled over CaH_2 under argon. $CHCl_3$ was distilled over P_2O_5 under argon. Ether and THF were distilled over sodium/benzophenone under argon. Silica gel (230-400 mesh) was used for chromatography. ^1H and ^{13}C NMR spectra were recorded either with a Bruker ARX 250 or Avance 500 apparatus. Traces of residual solvent were used as internal standard. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using either KBr pellets or the Attenuated Total Reflectance (ATR) method. EIMS analyses were performed with a Finnigan LCQ Advantage apparatus. Elemental analyses were performed at the Service de Microanalyse (I.C.S.N., Gif sur Yvette, France).

5,17,29-tris-amino-11,23,35-tris-tert-butyl-37,39,41-trimethoxy-38,40,42-tris[(1-methyl-2-imidazolyl)methoxy]calix[6]arene (3):

Hydrazine hydrate (1.00 mL, 20.6 mmol) was added dropwise to a solution of calixarene **2** (1.50 g, 1.19 mmol) containing Pd/C (10 %, 170 mg) in EtOH (50 mL). The mixture was refluxed for 72 h. After filtration of the solution, the solvent was evaporated under reduced pressure. The resulting crude oil was dissolved in CH_2Cl_2 (100 mL), washed with water (2 x 20 mL) and dried over Na_2SO_4. Pure compound **3** (989 mg, 71%) was obtained after flash chromatography on silica gel (eluent: CH_2Cl_2/MeOH/NH_4OH_{aq} 9:1:0.01). (Found: C, 70.3; H, 7.4; N, 10.2. $C_{72}H_{81}N_9O_6.3H_2O$ requires C, 70.4; H, 7.6; N, 10.3%); ν (KBr)/cm^{-1} 3347, 1607 (NH_{2Ar}); δ_H(250 MHz; DMSO; 300K) 0.87 (s, 27 H, C*H₃*), 1.97 (s, 9 H, OCH_3), 3.04 (d, J = 15.1 Hz, 6 H, ArCH_2), 3.78 (s, 9 H, NCH_3), 4.27 (d, J = 15.1 Hz, 6 H, ArCH_2), 4.87 (s, 6 H, ArNH_2), 4.97 (s, 6 H, ImCH_2), 6.51 (s, 6 H, H_{ArNH2}), 6.71 (s, 6 H, H_{ArtBu}), 6.91 (s, 3 H, H_{Im}), 7.25 (s, 3 H, H_{Im}); δ_c(72.5 MHz; DMSO; 300 K) 29.2, 31.3, 32.8, 33.8, 59.9, 65.7, 116.5, 122.9, 123.0, 127.2, 133.4, 133.9, 143.9, 144.2, 145.4, 147.1, 150.9; *m/z* (EI) 1174.6 (100%. $M+H^+$. require 1174.7), 587.8 (55%. $M+2H^+$. require 587.8); mp 193°C.

Mononuclear Zn complex [3·Zn(H₂O)](ClO₄)₂:

Zinc perchlorate hexahydrate (1 equiv.) was added to a solution of ligand **3** (100 mg, 85 µmol, 1 equiv.) in 2 mL MeCN/H_2O (2:1 v/v) and stirred for 1 h. MeCN was evaporated under reduced pressure. The solid complex was isolated by filtration, washed with ether (2 x 0.5 mL), and dried under vacuum (103 mg, 84%). (Found: C, 57.0; H, 6.0; N, 8.0. $C_{72}H_{91}Cl_2N_9O_{14}Zn.4.5H_2O$ requires C, 56.9; H, 6.4; N, 8.3); ν (KBr)/cm^{-1} 1604 (NH_{2Ar}), 1098, 623 (ClO_4); δ_H(250 MHz; $CDCl_3$; 300K) 1.39 (s, 27 H, CH_3), 3.43 (d, 6 H, J = 16.6 Hz, ArCH_2), 3.64 (s, 9 H, OCH_3), 3.67 (s, 9 H, NCH_3), 4.02 (d, 6 H, J = 16.6 Hz, ArCH_2), 4.95 (s, 6 H, ImCH_2), 5.54 (s, 6 H, H_{ArNH2}), 6.87 (s, 3 H, H_{Im}), 7.16 (s, 3 H, H_{Im}), 7.22 (s, 6 H, H_{ArtBu}); δ_H(250 MHz; CD_3CN; 300K) 1.42 (s, 27 H, CH_3), 3.48 (d, 6 H, J = 16 Hz, ArCH_2), 3.60 (s, 18 H, OCH_3, NCH_3), 4.03 (d, 6 H, J = 16 Hz, ArCH_2), 4.99 (s, 6 H, ImCH_2), 5.54 (s, 6 H, H_{ArNH2}), 6.83 (s, 3 H, H_{Im}), 7.35 (s, 6 H, H_{ArtBu}), 7.38 (s, 3 H, H_{Im}); δ_H(250 MHz; D_2O/CD_3CN 3:1; 300K) 1.39 (s, 27 H, CH_3), 3.43 (d, 6 H, J = 15 Hz, ArCH_2), 3.57 (s, 18 H, OCH_3, NCH_3), 4.02 (d, 6 H, J = 15 Hz, ArCH_2), 4.97 (s, 6 H, ImCH_2), 5.56 (s, 6 H, H_{ArNH2}), 6.82 (s, 3 H, H_{Im}), 7.33 (s, 6 H, H_{ArtBu}), 7.41 (s, 3 H, H_{Im}).

Dinuclear Zn complex [3·Zn₂(H₃O₂)](ClO₄)₃:

Zinc perchlorate hexahydrate (4 equiv.) was added to solution of ligand **3** (100 mg, 85 µmol, 1 equiv.) in THF (10 mL) under argon and stirred for 1 h. Spontaneous crystallization of the Zn_2 complex occurred. The compound was isolated by filtration and washed with THF (90 mg, 65%).(Found: C, 52.0; H, 5.6; N, 7.2. $C_{72}H_{93}Cl_3N_9O_{20}Zn_2.1.5H_2O$ requires C, 51.8; H, 5.8; N, 7.5); ν (KBr)/cm^{-1} 1602 (NH_{2Ar}), 1103, 621 (ClO_4).

The solubilization of the isolated solid in MeCN led to the partial decomplexation of the second Zn ion. As a result, the NMR analyses showed, beside the resonances of the dinuclear complex, those belonging to the mononuclear species, in various proportions depending on the residual amount of water.

δ_H(250 MHz; CD_3CN; 300K) 1.43 (s, 27 H, CH_3), 3.41 (d, 6 H, J = 17.3 Hz, ArCH_2), 3.55 (s, 9 H, OCH_3), 3.68 (s, 18 H, NCH_3), 4.02 (d, 6 H, J = 17.3 Hz, ArCH_2), 4.74 (s, 6 H, NH_2), 5.12 (s, 6 H, ImCH_2), 5.91 (s, 6 H, H_{ArNH2}), 6.58 (s, 3 H, H_{Im}), 7.27 (s, 3 H, H_{Im}), 7.50 (s, 6 H, H_{ArtBu}).

XRD determination of the dinuclear Zn complex $[3 \cdot Zn_2(H_3O_2)](ClO_4)_3$

A colorless crystal (0.10 x 0.10 x 0.04 mm^3) was mounted with Paratone-N oil (Hampton Research) coating and immediately placed under a nitrogen cold stream. X-ray intensity data were collected at 100 K on a Bruker-Nonius X8-APEX2 CCD area-detector diffractometer using Mo-K_α radiation (λ = 0.71073 Å). Five sets of narrow data frames (30 s per frame) were collected at different θvalues for 3 and 2 initial values of ϕ and ω, respectively, using 0.5° increments of ϕ or ω. Data reduction was accomplished using SAINT V7.03 [1]. The substantial redundancy in data allowed a semi-empirical absorption correction (SADABS V2.10)[1] to be applied, on the basis of multiple measurements of equivalent reflections. The structure was solved by direct methods, developed by successive difference Fourier syntheses, and refined by full-matrix least-squares on all F^2 data using SHELXTL V6.14[2]. Hydrogen atoms were included in calculated positions and allowed to ride on their parent atoms.

Crystal structure analysis: hexagonal, space group $P6_3$; dimensions: a = b = 18.9573(7) Å, c = 12.5640(7) Å, V = 3910.3(3) $Å^3$; Z = 2; total reflections collected: 61565; independent reflections: 3394 (2561 Fo > 4σ (Fo)); data were collected up to a 2Θmax value of 44.94° (99.9 % coverage). Number of variables: 336; R_1 = 0.1031, wR_2 = 0.2737, S = 1.060; highest residual electron density 0. 792 e.$Å^{-3}$
CCDC 610232.

(1) APEX2 version 1.0-8; Bruker AXS: Madison, WI, 2003
(2) SHELXTL version 6.14; Bruker AXS: Madison, WI, 2001

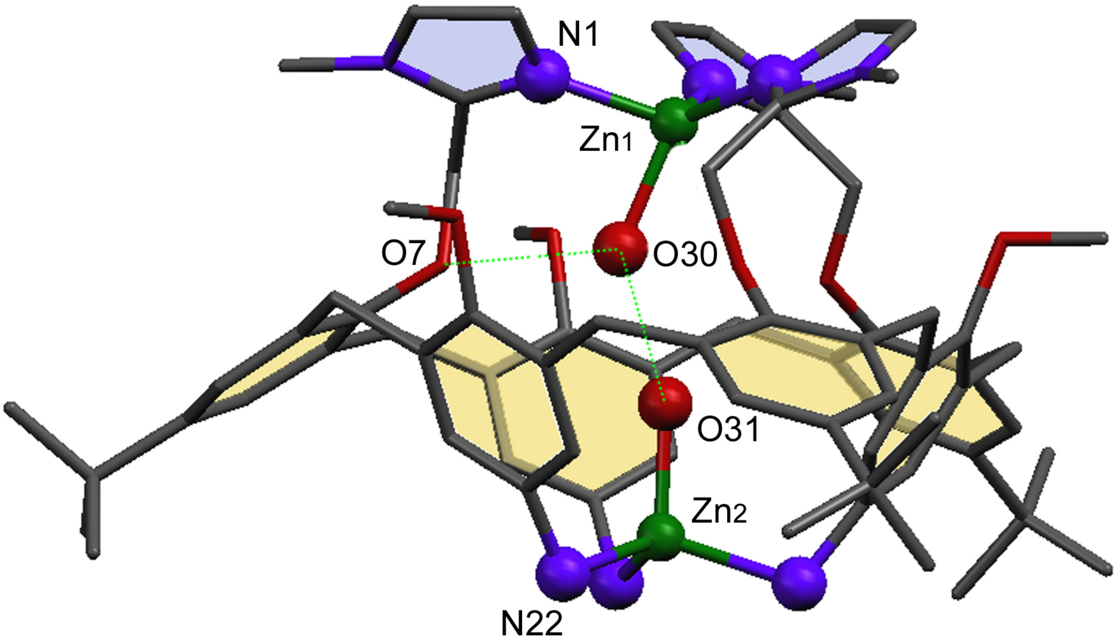

Figure S1: XRD structure of the dinuclear Zn(II) complex based on ligand **3**. Hydrogen atoms, counter ions and solvent molecules were omitted for clarity. Selected bond distances [Å] and angles [degrees]: Zn(1)-N(1) 2.012(14); Zn(1)-O(30) 2.00(5); Zn(2)-N(22) 2.088(13) ; Zn(2)-O(31) 1.85(2); O(30)···O(31) 2.202; O(30)···O(7) 2.616(33); N(1)-Zn(1)-O(30) 85.4(13); N(1')-Zn(1)-O(30) 117.1(12) and 113.6(12); Zn(1)···O(30)···O(7) 112.47(15); N(1)-Zn(1)-N(1') 112.7(3); N(22)-Zn(2)-O(31) 106.7(3); N(22)-Zn(2)-N(22') 112.1(2); Zn(1)···O(30)···O(31) 140.3(2); O(30)···O(31)···Zn(2) 161.16(13); Zn(1)···Zn(2) 5.806(4); O(30)···aromatic nuclei centroïd ($ArNH_2$) 3.56. N(1') stands for one of the two other N(1) atoms obtained after 120° rotation along C_3 axis.

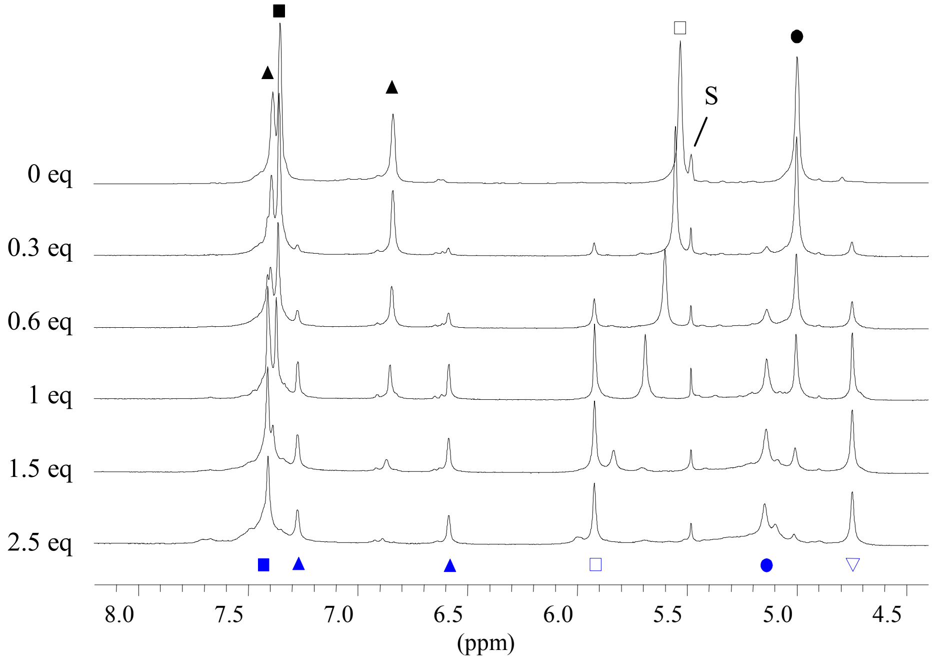

Figure S2: Top: ^{1}H NMR spectrum (300 K, 250 MHz) of a CD_3CN solution of the isolated dinuclear complex ([**3**] = 3 mM, 8 equiv. of H_2O). From top to bottom: stepwise addition of Zn perchlorate hexahydrate into the NMR tube. ▲ H_{Im}, • CH_{2Im}, □ H_{ArNH2} et ■ H_{Ar}; **4** : ▲ H_{Im}, ▽ NH_2, • CH_{2Im}, □ H_{ArNH2} et ■ H_{Ar}.

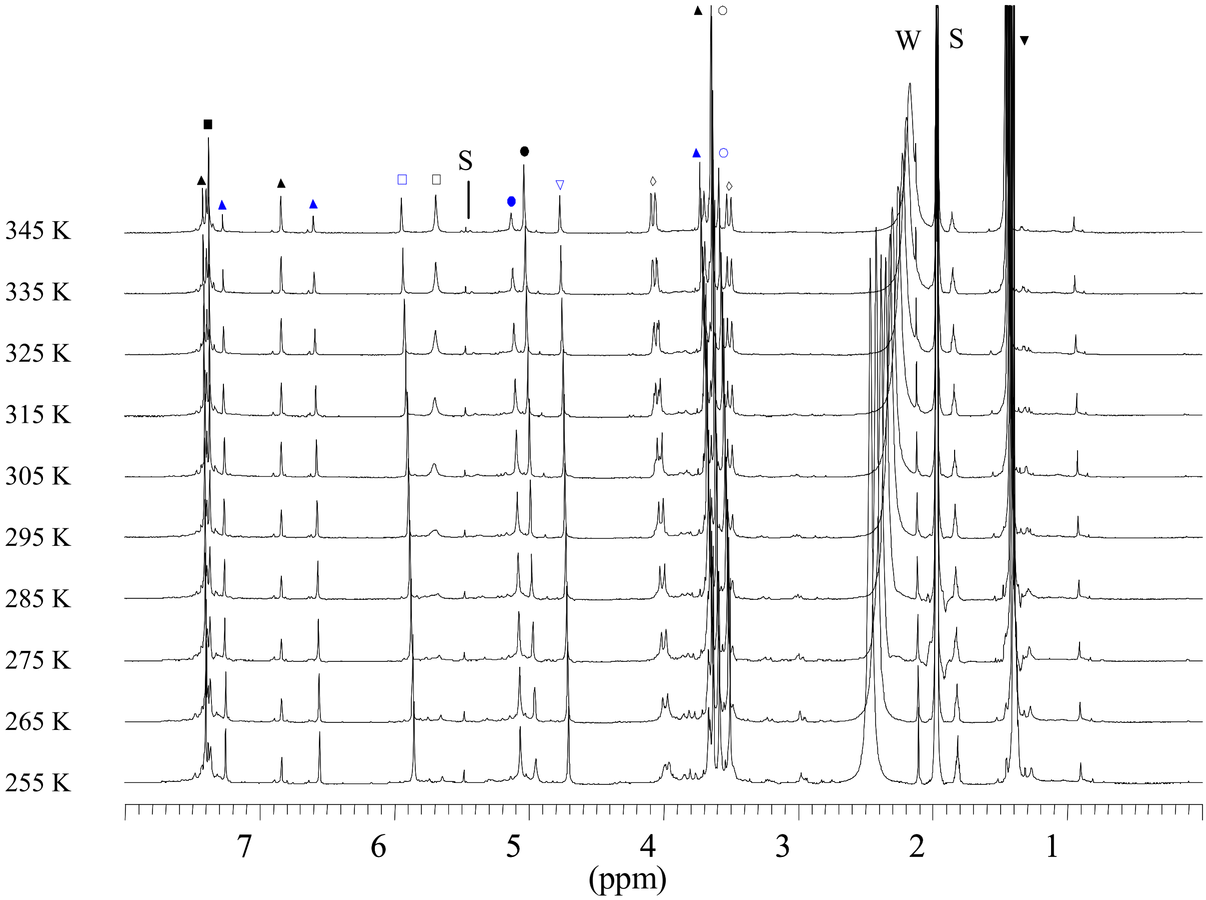

Figure S3: Evolution of the ^{1}H NMR spectrum (500 MHz) as a function of temperature of the equilibrated mixture of di- and mononuclear complexes obtained upon dissolution of the isolated dinuclear compound in CD$_3$CN ([3] = 3.9 mM, 20 equiv. of water). ▼ *t*Bu, O OCH$_3$, ▲ NCH$_3$ et H$_{Im}$, ◊ CH$_2$Ar, ▽ NH$_2$, ● CH$_{2Im}$, ☐ et ■ H$_{Ar}$; **4 :** ▼ *t*Bu, O OCH$_3$, ▲ NCH$_3$ et H$_{Im}$, ◊ CH$_2$Ar, ▽ NH$_2$, ● CH$_{2Im}$, ☐ et ■ H$_{Ar}$.

$$[\mathbf{3}\cdot Zn_2(H_3O_2)]^{3+} + MeCN \overset{K}{\leftrightarrows} [\mathbf{3}\cdot Zn(MeCN)]^{2+} + (ZnOH)^{+}_{solvated} + H_2O$$

$$\text{In MeCN}: \; K = \frac{[\mathbf{3}.Zn(MeCN)][(ZnOH)_s][H_2O]}{[\mathbf{3}.Zn_2(H_3O_2)]}$$

Figure S4: Equation of the di-/mono-nuclear equilibrium in CD_3CN.

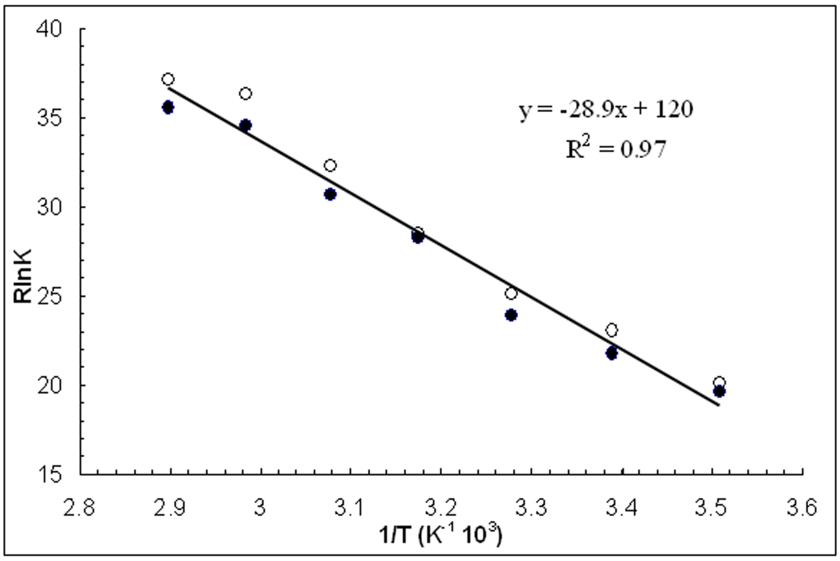

Figure S5: Van't Hoff plot in the 285-345 K temperature range for the di-/mono-nuclear equilibrium in CD_3CN as defined in the text. ●: [**3**] = 6.1 mM with 6 equiv. of water and O: [**3**] = 3.9 mM with 20 equiv. of water.

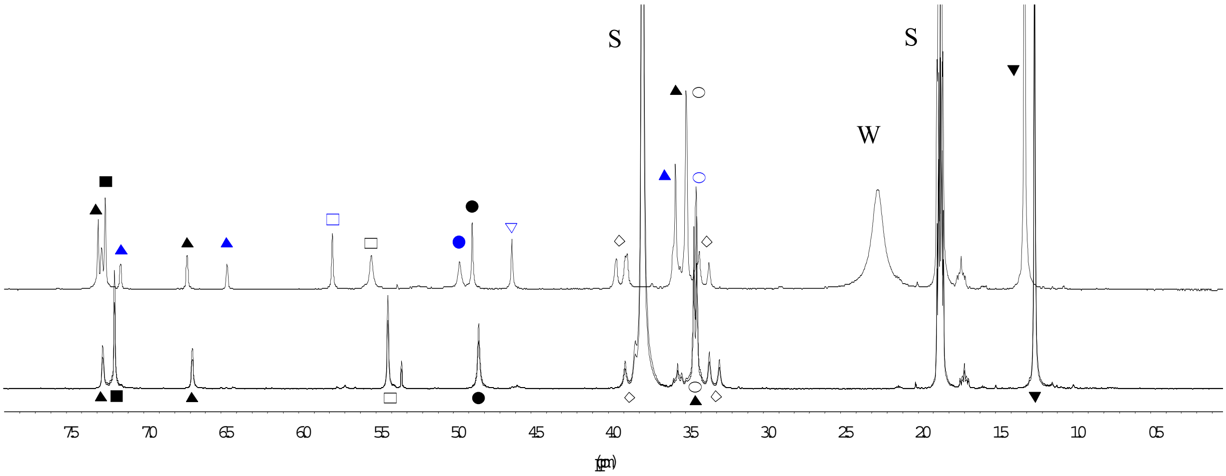

Figure S6: ^1H NMR spectra (300 K, 250 MHz) of the dinuclear complex dissolved in: top: CD_3CN ([**3**] = 63mM), bottom: CD_3CN/D_2O (2:1 v/v). **3 :** ▼ *t*Bu, o OCH_3, ▲ NCH_3 et H_{Im}, ◊ CH_2Ar, ▽ NH_2, • CH_{2Im}, ☐ et ■ H_{Ar}; **4 :** ▼ *t*Bu, o OCH_3, ▲ NCH_3 et H_{Im}, ◊ CH_2Ar, ▽ NH_2, • CH_{2Im}, ☐ et ■ H_{Ar}.

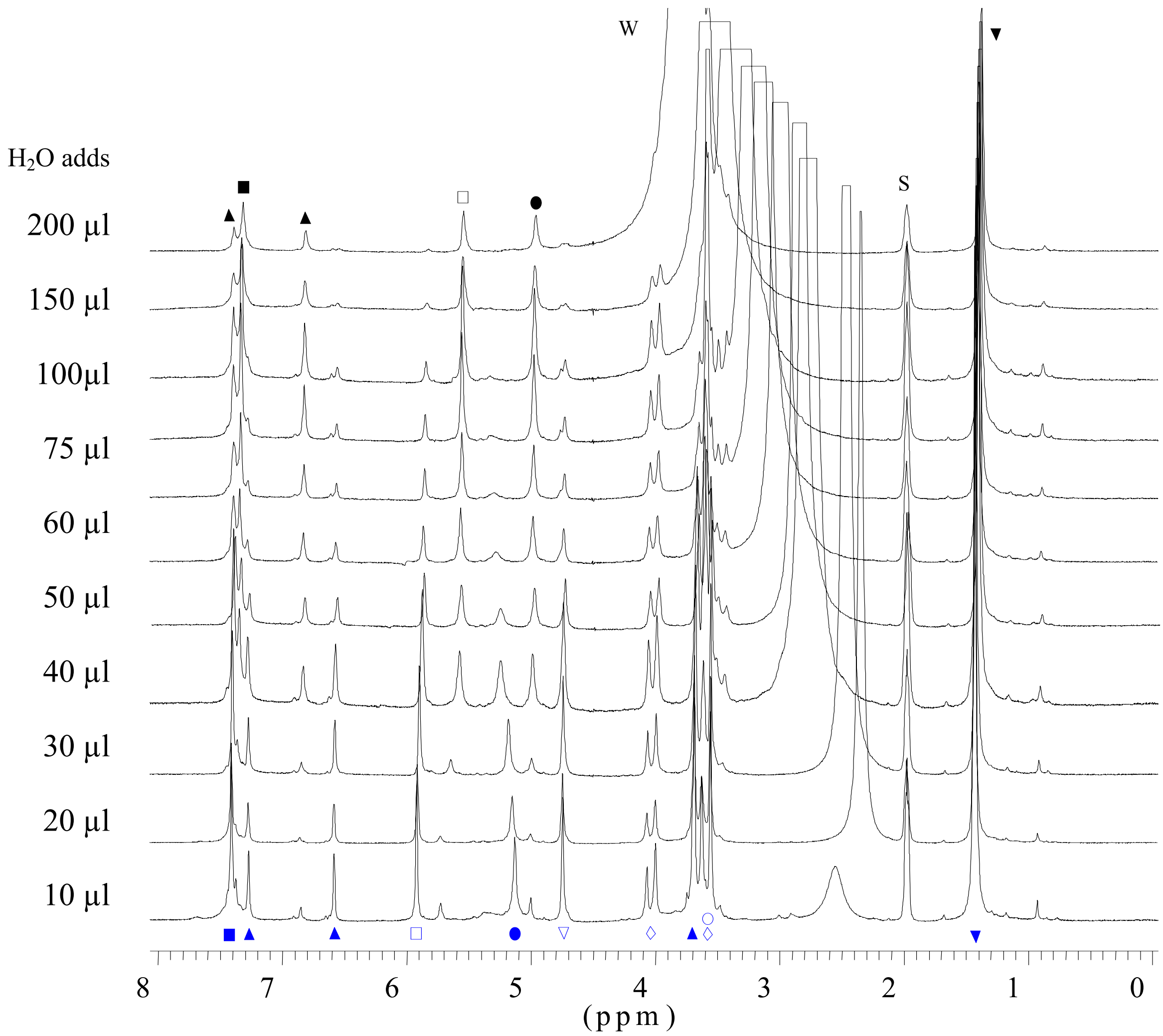

Figure S7: From top to bottom : evolution of the ^1H NMR spectrum (300 K, 250 MHz) of the dinuclear complex dissolved in CD_3CN (6 mM) upon addition of water. ▼ *t*Bu, o OCH_3, ▲ NCH_3 et H_{Im}, ◊ CH_2Ar, ▽ NH_2, • CH_{2Im}, ☐ et ■ H_{Ar}; **4 :** ▼ *t*Bu, o OCH_3, ▲ NCH_3 et H_{Im}, ◊ CH_2Ar, ▽ NH_2, • CH_{2Im}, ☐ et ■ H_{Ar}.