Supporting Information for:

Encapsulation of a (H₃O₂)⁻ 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: CH₂Cl₂ was distilled over CaH₂ under argon. CHCl₃ was distilled over P₂O₅ under argon. Ether and THF were distilled over sodium/benzophenone under argon. Silica gel (230-400 mesh) was used for chromatography. ¹H and ¹³C 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).

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 CH2Cl2 (100 mL), washed with water (2 x 20 mL) and dried over Na2SO4. Pure compound 3 (989 mg, 71%) was obtained after flash chromatography on silica gel (eluent: CH2Cl2/MeOH/NH4OHaq 9:1:0.01). (Found: C, 70.3; H, 7.4; N, 10.2. C72H81N9O6.3H2O requires C, 70.4; H, 7.6; N, 10.3%); \( \nu (KBr)/cm^{-1} \) 3347, 1607 (NH2Ar);

\( \delta (H(250 MHz; DMSO; 300K) \) 0.87 (s, 27 H, CH3), 1.97 (s, 9 H, OCH3), 3.04 (d, J = 15.1 Hz, 6 H, ArCH2), 3.78 (s, 9 H, NCH3), 4.27 (d, J = 15.1 Hz, 6 H, ArCH2), 4.87 (s, 6 H, ArNH2), 4.97 (s, 6 H, ImCH), 6.51 (s, 6 H, HArNH2), 6.71 (s, 6 H, HArIm), 7.25 (s, 3 H, HIm); \( \delta (H(250 MHz; CDCl3; 300K) \) 1.39 (s, 27 H, CH3), 3.43 (d, J = 16.6 Hz, ArCH2), 3.64 (s, 9 H, OCH3), 3.67 (s, 9 H, NCH3), 4.02 (d, J = 16.6 Hz, ArCH2), 4.95 (s, 6 H, ImCH2), 5.54 (s, 6 H, HArNH2), 6.87 (s, 3 H, HIm), 7.16 (s, 3 H, HIm), 7.22 (s, 6 H, HArBu); \( \delta (H(250 MHz; CD3CN; 300K) \) 1.42 (s, 27 H, CH3), 3.48 (d, J = 15 Hz, ArCH2), 3.60 (s, 18 H, OCH3, NCH3), 4.03 (d, J = 16 Hz, ArCH2), 4.99 (s, 6 H, ImCH2), 5.54 (s, 6 H, HArNH2), 6.83 (s, 3 H, HIm), 7.35 (s, 6 H, HArBu), 7.38 (s, 3 H, HIm); \( \delta (H(250 MHz; D2O/CD3CN 3:1; 300K) \) 1.39 (s, 27 H, CH3), 3.43 (d, J = 15 Hz, ArCH2), 3.57 (s, 18 H, OCH3, NCH3), 4.02 (d, J = 15 Hz, ArCH2), 4.97 (s, 6 H, ImCH2), 5.56 (s, 6 H, HArNH2), 6.82 (s, 3 H, HIm), 7.33 (s, 6 H, HArBu), 7.41 (s, 3 H, HIm).

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

Zinc perchlorate hexahydrate (1 equiv.) was added to a solution of ligand 3 (100 mg, 85 µmol, 1 equiv.) in 2 mL MeCN/H2O (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. C72H91Cl2N9O14Zn.4.5H2O requires C, 56.9; H, 6.4; N, 8.3); \( \nu (KBr)/cm^{-1} \) 1604 (NH2Ar), 1098, 623 (ClO4);

\( \delta (H(250 MHz; CDCl3; 300K) \) 1.39 (s, 27 H, CH3), 3.43 (d, J = 16.6 Hz, ArCH2), 3.64 (s, 9 H, OCH3), 3.67 (s, 9 H, NCH3), 4.02 (d, J = 16.6 Hz, ArCH2), 4.95 (s, 6 H, ImCH2), 5.54 (s, 6 H, HArNH2), 6.87 (s, 3 H, HIm), 7.16 (s, 3 H, HIm), 7.22 (s, 6 H, HArBu); \( \delta (H(250 MHz; CD3CN; 300K) \) 1.42 (s, 27 H, CH3), 3.48 (d, J = 15 Hz, ArCH2), 3.60 (s, 18 H, OCH3, NCH3), 4.03 (d, J = 16 Hz, ArCH2), 4.99 (s, 6 H, ImCH2), 5.54 (s, 6 H, HArNH2), 6.83 (s, 3 H, HIm), 7.35 (s, 6 H, HArBu), 7.38 (s, 3 H, HIm); \( \delta (250 MHz; D2O/CD3CN 3:1; 300K) \) 1.39 (s, 27 H, CH3), 3.43 (d, J = 15 Hz, ArCH2), 3.57 (s, 18 H, OCH3, NCH3), 4.02 (d, J = 15 Hz, ArCH2), 4.97 (s, 6 H, ImCH2), 5.56 (s, 6 H, HArNH2), 6.82 (s, 3 H, HIm), 7.33 (s, 6 H, HArBu), 7.41 (s, 3 H, HIm).

Dinuclear Zn complex \([3\cdot Zn2(H2O2)](ClO4)3\):

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 Zn2 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. C72H93Cl2N9O20Zn2.1.5H2O requires C, 51.8; H, 5.8; N, 7.5); \( \nu (KBr/cm^{-1} \) 1602 (NH2Ar), 1103, 621 (ClO4).
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\text{H}(250 MHz; CD\textsubscript{3}CN; 300K) 1.43 (s, 27 H, CH\textsubscript{3}), 3.41 (d, 6 H, J = 17.3 Hz, ArCH\textsubscript{2}), 3.55 (s, 9 H, OCH\textsubscript{3}), 3.68 (s, 18 H, NCH\textsubscript{3}), 4.02 (d, 6 H, J = 17.3 Hz, ArCH\textsubscript{2}), 4.74 (s, 6 H, NH\textsubscript{2}), 5.12 (s, 6 H, ImCH\textsubscript{2}), 5.91 (s, 6 H, H\textsubscript{ArNH\textsubscript{2}}), 6.58 (s, 3 H, H\textsubscript{Im}), 7.27 (s, 3 H, H\textsubscript{Im}), 7.50 (s, 6 H, H\textsubscript{ArfBu}).

XRD determination of the dinuclear Zn complex [3\cdotZn\textsubscript{2}(H\textsubscript{2}O\textsubscript{2})](ClO\textsubscript{4})\textsubscript{3}

A colorless crystal (0.10 x 0.10 x 0.04 mm\textsuperscript{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\textsubscript{α} radiation (λ = 0.71073 Å). Five sets of narrow data frames (30 s per frame) were collected at different θ values 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\textsuperscript{1}. The substantial redundancy in data allowed a semi-empirical absorption correction (SADABS V2.10)\textsuperscript{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\textsuperscript{2} data using SHELXTL V6.14\textsuperscript{2}. Hydrogen atoms were included in calculated positions and allowed to ride on their parent atoms.

Crystal structure analysis: hexagonal, space group P\textsubscript{6}\textsubscript{3}; dimensions: a = b = 18.9573(7) Å, c = 12.5640(7) Å, V = 3910.3(3) Å\textsuperscript{3}; Z = 2; total reflections collected: 61565; independent reflections: 3394 (2561 Fo > 4σ(Fo)); data were collected up to a 2Θ\textsubscript{max} value of 44.94° (99.9 % coverage). Number of variables: 336; R\textsubscript{1} = 0.1031, wR\textsubscript{2} = 0.2737, S = 1.060; highest residual electron density 0.792 e.Å\textsuperscript{–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 centroid (ArNH₂) 3.56. N(1’) stands for one of the two other N(1) atoms obtained after 120° rotation along C₃ axis.
Figure S2: Top: $^1$H NMR spectrum (300 K, 250 MHz) of a CD$_3$CN solution of the isolated dinuclear complex ([3] = 3 mM, 8 equiv. of H$_2$O). From top to bottom: stepwise addition of Zn perchlorate hexahydrate into the NMR tube. ▲ H$_{\text{Im}}$, • CH$_{2\text{Im}}$, □ H$_{\text{AHIH2}}$ et ■ H$_{\text{Ar}}$; 4: ▲ H$_{\text{Im}}$, ▽ NH$_2$ • CH$_{2\text{Im}}$, □ H$_{\text{AHIH2}}$ et ■ H$_{\text{Ar}}$. 
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). ▼ tBu, ◊ OCH$_3$, ▲ NCH$_3$ et H$_{lin}$, ◇ CH$_2$Ar, ▽ NH$_2$, • CH$_2$Im, □ et ▼ H$_{Ar}$; 4 : ▼ tBu, ◊ OCH$_3$, ▲ NCH$_3$ et H$_{lin}$, ◇ CH$_2$Ar, ▽ NH$_2$, • CH$_2$Im, □ et ▼ H$_{Ar}$. 

S 6
\[ K \]
\[ [\text{3-Zn}_2(\text{H}_2\text{O}_2)]^{3+} + \text{MeCN} \rightleftharpoons [\text{3-Zn(MeCN)}]^{2+} + (\text{ZnOH})_2^+ + \text{H}_2\text{O} \]

In MeCN: \[ K = \frac{[\text{3-Zn(MeCN)}][(\text{ZnOH})_2][\text{H}_2\text{O}]}{[\text{3-Zn}(\text{H}_2\text{O}_2)]} \]

**Figure S4**: Equation of the di-/mono-nuclear equilibrium in CD$_3$CN.

**Figure S5**: Van’t Hoff plot in the 285-345 K temperature range for the di-/mono-nuclear equilibrium in CD$_3$CN as defined in the text. ●: [3] = 6.1 mM with 6 equiv. of water and ○: [3] = 3.9 mM with 20 equiv. of water.

**Figure S6**: $^1$H NMR spectra (300 K, 250 MHz) of the dinuclear complex dissolved in: top: CD$_3$CN ([3] = 63 mM), bottom: CD$_3$CN/D$_2$O (2:1 v/v). 3: ▼ /Bu, ◇ OCH$_3$, ▲ NCH$_3$ et H$_{im}$, ◊ CH$_2$Ar, ▽ NH$_2$, ● CH$_2$Im, □ et • H$_{Ar}$; 4: ▼ /Bu, ○ OCH$_3$, ▲ NCH$_3$ et H$_{im}$, ◊ CH$_2$Ar, ▽ NH$_2$, ● CH$_2$Im, □ et • H$_{Ar}$. 
Figure S7: From top to bottom: evolution of the $^1$H NMR spectrum (300 K, 250 MHz) of the dinuclear complex dissolved in CD$_3$CN (6 mM) upon addition of water. ▼ tBu, ◇ OCH$_3$, ▲ NCH$_3$ et H$_{im}$, ◊ CH$_2$Ar, △ NH$_2$, ● CH$_2$Im, □ et ■ H$_{Ar}$; 4: ▼ tBu, ◇ OCH$_3$, ▲ NCH$_3$ et H$_{im}$, ◊ CH$_2$Ar, △ NH$_2$, ● CH$_2$Im, □ et ■ H$_{Ar}$. 

H$_2$O adds

200 µl
150 µl
100 µl
75 µl
60 µl
50 µl
40 µl
30 µl
20 µl
10 µl

(ppm)