Single-crystal X-ray diffraction study, NMR and electrochemical analysis of a copper(I) 5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis-[(6-methyl-2,2'-bipyridyl-6-yl)methoxy]calix[4]arene complex : an original M_4L_2 "hand-to-hand" system †

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ESI file - supplementary materials

X-Ray diffraction analysis :

A single crystal of complex **2** of 100x100x50 µm (parallelepipedic shape) was glued on the tip of a quartz fiber and mounted on a goniometric head.

The relevant information of data collection and structure refinements are summarized in **Table 1** of manuscript. The last refinements conclude to the formula $C_{184}Cu_4N_{16}O_8H_{192}(PF_6)_4$ with Z=2. Because of lack of intensities (*need of 2161 free parameters (240 atoms in P-1) for 4262 intensities*), all non-H atoms were only refined isotropically (*namely 960 free parameters*) by the full matrix least squares method on F^2 using SHELXL-97 and the H atoms were included at the calculated positions and constrained to ride on their parent atoms. On the basis of the single-crystal X-ray diffraction data, the complex **2** compound $C_{184}Cu_4N_{16}O_8H_{192}(PF_6)_4$ crystallizes in the triclinic space group P-1 (No.2) with refined cell parameters at 293(2)K a = 19.225(2) Å, b = 22.569(3) Å, c = 27.113(3) Å, α= 109.52(1)°, β = 101.63(1)°, γ = 97.800(3)° and V = 10595(2) $Å^3$ and we note the presence of two molecules per unit cell.

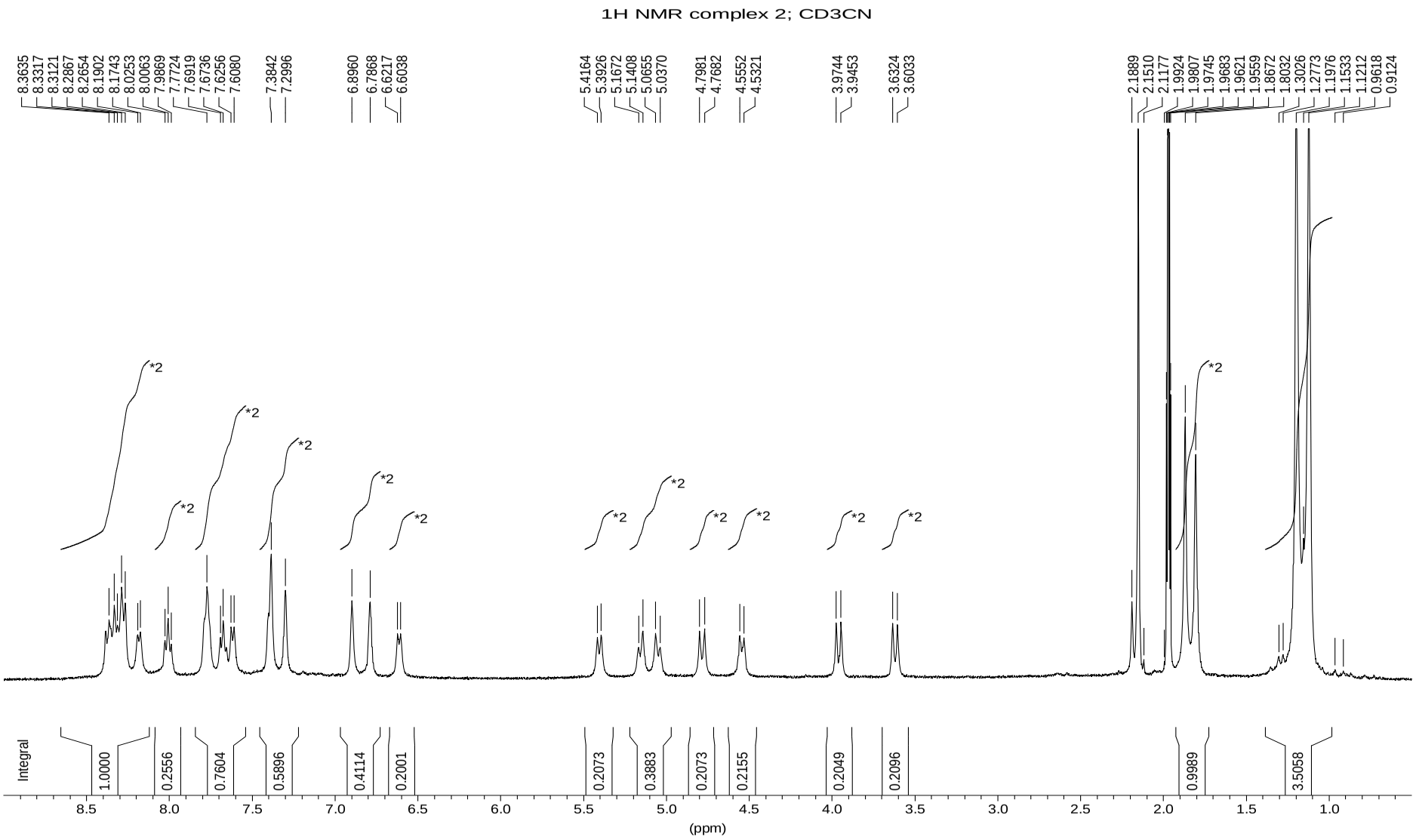

Figure ESI 1 : ^{1}H-NMR spectrum of complex **2** in CD_3CN (400 MHz, rt), with integrations and peak picking.

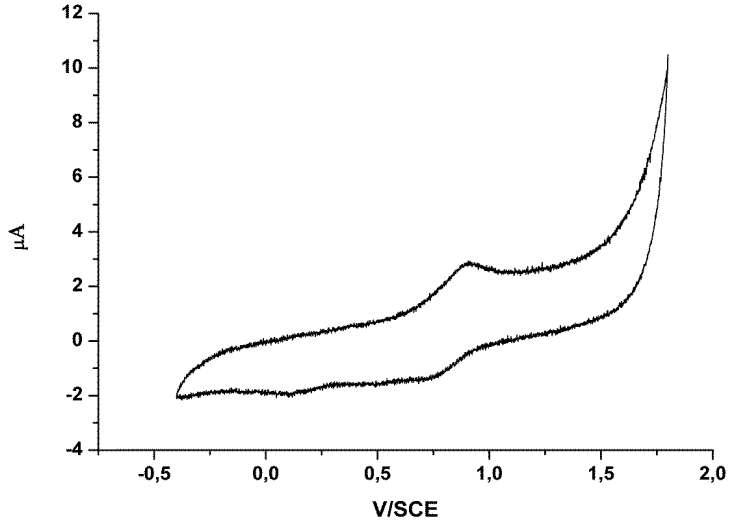

Figure ESI 2: Large CV of complex **2** (c = 2.65 10^{-4}M with M_2L hypothesis), at scan rates: 100 mV·s^{-1}, in Ar-purged MeCN with 0.1 M Bu_4NPF_6 as supporting electrolyte at rt.

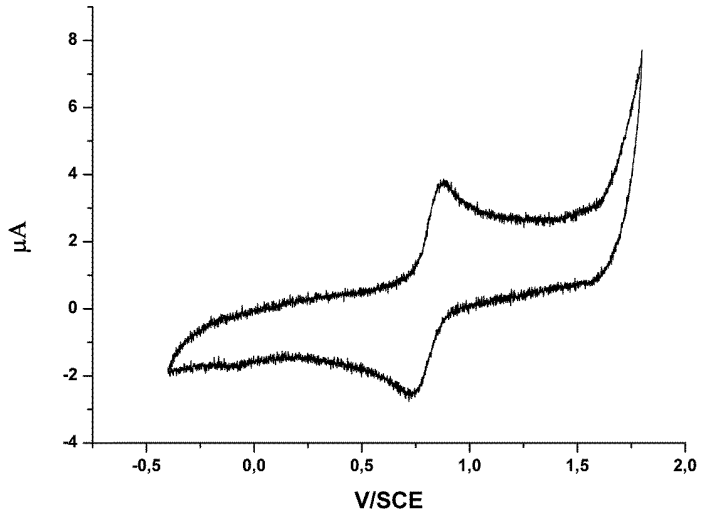

Figure ESI 3 : Large CV of complex **5** (c = 2.65 10^{-4}M with M_2L hypothesis), at scan rates: 100 mV·s^{-1}, in Ar-purged MeCN with 0.1 M Bu_4NPF_6 as supporting electrolyte at rt.

Table ESI 1: Calculated intensity of the peak current x10^6 in ampere. n: number of electrons in the redox process.

3.8 mg of **2** in 8.0mL	n = 1	n = 2	n = 3	n = 4
C mol/cm^3 if M_2L= c=2.65 10^{-7} mol.cm^{-3}	1.32	3.72	6.86	10.56
C mol/cm^3 if M_4L_2= c=1.32 10^{-7} mol.cm^{-3}	0.66	1.86	3.43	5.28