Supporting information for

Electronic π-delocalization Boosts Catalytic Water Oxidation by Cu(II) Molecular Catalysts Heterogenized on Graphene Sheets

Pablo Garrido-Barros,[a,b] Carolina Gimbert-Suriñach,[a] Dooshaye Moonshiram,[a] Antonio Picón,[c] Pere Monge,[a] Victor S. Batista [d,*] and Antoni Llobet [a,e,*]

[a] Institute of Chemical Research of Catalonia (ICIQ-BIST), Avinguda Països Catalans 16, 43007 Tarragona, Spain

[b] Departament de Química Física i Inorga`nica, Universitat Rovira i Virgili, Campus Sescelades, C/Marcel·lí Domingo, s/n, 43007, Tarragona, Spain

[c] Grupo de Investigación en Aplicaciones del Láser y Fotónica, Departamento de Física Aplicada, Universidad de Salamanca, 37008, Salamanca, Spain

[d] Institut de Ciències Fotòniques (ICFO-BIST), 08860 Castelldefels, Barcelona, Spain

[e] Department of Chemistry, Yale University. P.O. Box 208107, New Haven, CT 06520-8107, USA

[f] Departament de Química, Universitat Auto`noma de Barcelona, 08193 Cerdanyola del Vallès, Barcelona, Spain

Table of Contents

1. Experimental details

Materials

All the chemicals used in this work were provided by Sigma Aldrich Chemical Co and they have been used without further purification. The solvents were selected to be HPLC grade and the deionized water was obtained with high purity by passing through a nanopore Milli-Q water purification system. Aqueous basic buffer solutions at pH 12 were prepared using the necessary amount of dibasic and tribasic sodium phosphate salts and adjusting the pH to the desired value so that the final ionic strength was 0.1 M.

Graphene was purchased from Nanostructured & Amorphous Materials, Inc. (NanoAmor) with a purity > 98%, 1-3 layers (1-3 nm of thickness), 2-10 µm of diameter and a specific surface area of about 500-700 $m^2 \cdot g^{-1}$.

GC plate electrodes (GCp) were purchased from HTW, Germany, and are made of glassy carbon SIGRADUR® with the dimensions 20x10x0.18 mm.

Elemental Analysis and Mass Spectrometry

Elemental Analysis of the samples was carried out in a Thermo Finnigan elemental analyzer Flash 1112 model.

Exact mass analyses were performed with a micrOTOF mass spectrometer (from Bruker company) using Electrospray ionization technique in methanol by direct injection and detecting with positive polarity.

Spectroscopic Techniques

NMR spectroscopy was carried out in a 400 MHz Bruker Advance II spectrometer and a Bruker Advance 500 MHz. All the measurements were done at room temperature in deuterated DMSO using residual protons as internal references.

IR spectrometry was performed using a FTIR-ATR TR0 equipment using the pure synthetized compounds as solids.

UV-vis spectrometry was done using a Cary 50 (Varian) UV-vis spectrophotometer.

Resonance Raman Spectroscopy was performed in a Renishaw inVia Confocal Reflex RAMAN microscope instrument (Gloucestershire, UK), equipped with an Ar ion laser, operating at 514 nm. The spectrometer was equipped with a Peltier-cooled CCD detector (-70°C) coupled to a Leica DM-2500 microscope. Calibration was carried out with respect to Si standard.

General electrochemistry

Cyclic Voltammetry (CV), Linear Sweep Voltammetry (LSV), Differential Pulse Voltammetry (DPV) and Controlled Potential Electrolysis (CPE) experiments were carried out on an IJ-Cambria CHI-660 potentiostat. We used a one-compartment three-electrode cell for these measurements. Glassy Carbon (GC) disk electrodes (3 mm of diameter) were used as working electrodes, Pt wire (unless indicated) as counter electrode, Mercury/Mercurous sulfate (K_2SO_4 sat.), MSE, as reference electrode for CV, LSV and DPV. For CPE, Silver/Silver Chloride (KCl sat.) was used as reference and either GC disk or GC plate (as indicated) as working electrode. All redox potentials in the present work are reported versus NHE by adding 0.65 V or 0.2 V to the measured potential, depending on whether MSE or Silver/Silver Chloride electrodes were employed respectively.

GC disk working electrode pretreatment for homogeneous phase analysis consisted in polishing with 0.05 μm alumina paste, rinsing after with water and acetone and blow-dried finally. GC disk used for catalyst deposition were polished with 1, 0.3 and 0.05 μm alumina paste, then rinsed with water and sonicated for 15 min in acetonitrile. Finally, they were washed with acetone and blow-dried.

CVs and LSVs were collected at 50 $mV \cdot s^{-1}$ except other specification. DPV were obtained with the following parameters: amplitude= 50 mV, step height=4 mV, pulse width= 0.05 s, pulse period= 0.5 s and sampling width= 0.0167 s. $E_{1/2}$ values for the reversible waves were obtained from the half potential between the oxidative and reductive peaks, and the one for irreversible processes are estimated according to the potential at the I_{max} in DPV measurements. All the measurements were done applying IR compensation.

When acetonitrile was used as organic solvent, tetrabutylammonium hexafluorophosphate ($[NBu_4]PF_6$) was added in a concentration of 0.1M as supporting electrolyte.

Surface coverage (Γ) calculation

The surface coverage (Γ) was calculated based on electrochemical measurements according to the following formula:

$$\Gamma\ (mol \cdot cm^{-2}) = \frac{Q}{n \cdot S \cdot F} \qquad \text{(S1)}$$

Q is the charge under the oxidative peak of the reversible, one-electron wave obtained by integration in the CV; n is the number of electrons involved in that oxidation process, which is 1; S is the geometrical surface of the electrode that is 0.07 cm^{-2} or 1 cm^{-2} for GCd and GCp respectively; finally F is the Faradaic constant. In this work, the average surface coverage for each hybrid catalyst was calculated from 5 independent electrodes that were subjected to CV under same conditions. The error of the measurements was expressed as the standard deviation among the different values obtained. Moreover, the surface coverage of each electrode used for different analyses was calculated.

Rotating Ring Disk Electrode

Rotating Ring Disk Electrode (RRDE) was used to evaluate the catalytic performance of the immobilized catalysts. For this purpose, a RRDE-3A Rotating Ring Disk Electrode from IJ-Cambria was employed with an electrode composed of a GC disk and a Pt ring electrodes and the following diameters: 7 mm outer, 5 mm middle and 4 mm inner. The solution is placed in a one-compartment cell with a Teflon top that closes hermetically. The top has a big hole for the RRDE, two smaller holes for reference and counter electrodes and finally two more thin holes for nitrogen flow tubes, all of them fitting tightly. The electrodes were connected to a IJ-Cambria CHI-660 potentiostat for electrochemical measurements. Before each experiment, the solution was purged with nitrogen during 10 minutes, and then a nitrogen atmosphere was maintained during the measurement.

O_2 detection by Clark electrode

Controlled Potential Electrolysis (CPE) experiments were performed to assess the catalytic performance by the immobilized catalyst using a one-compartment three-electrode cell closed with septum. A GC plate electrode (1 cm^2) supporting the graphene loaded with the catalyst was employed as large surface working electrode. The Ag/AgCl (KCl sat) electrode was used as reference electrode and a Pt mesh as the counter electrode. The cell was filled with phosphate buffer solution at pH 12 with 0.1 M of ionic strength. The CPE was carried out using an IJ-Cambria CHI-660 potentiostat.

During the CPE experiment, the oxygen evolution was monitored with an OXNP type Clark electrode in gas phase (from Unisense Company). This electrode was placed in the cell through the septum without immersion in the solution (gas phase detection from headspace). Once the set up was ready, we remove the oxygen by bubbling nitrogen during 30 min. Once the Clark signal reached values close to 0 mV, the nitrogen flow was stopped and we left the base line to stabilize during 15 min under nitrogen atmosphere. The CPE was started as soon as the Oxygen sensor signal was stable. The experiment was performed under vigorous stirring. Calibration of the oxygen sensor was performed after each experiment by adding known amount of pure oxygen into the cell using a gas tight Hamilton syringe. The blank experiment was performed following the same procedure with bare graphene on the GC plate. The Faraday efficiency was determined according to the total charge passed during the CPE and the total amount of generated oxygen by taking into account that water oxidation is a 4-e^- oxidation process.

Spectroelectrochemistry

Spectroelectrochemical study was carried out in an optically transparent thin-layer electrochemical (OTTLE) cell (OMNI-CELL SPECAC, by Prof. Frantisek Hartl’s group, University of Reading). The optical path length of the cell is 0.2 mm. This cell contains two Pt grid electrodes (working and counter) and a silver wire pseudo reference electrode (-0.2 V respect to NHE). To perform the experiment, the cell is filled with less than 0.3 ml of a 5 mM catalyst solution in phosphate buffer at pH 12 that has a 0.1 M of ionic strength. Special care was taken to avoid gas bubbles formation within the cell.

The OTTLE cell was placed in a Cary 50 (Varian) UV-vis spectrophotometer and the electrodes were connected to an IJ-Cambria CHI-660 potentiostat. Cyclic voltammetry was performed at 2 $mV\cdot s^{-1}$ to ensure full conversion of species during the redox processes. UV-vis spectra were recorded continuously to monitor the changes in the electronic structure upon oxidation and successive reduction.

X-ray Absorption Spectroscopy (XAS) Methods

X-ray absorption spectra were collected at the Advanced Photon Source(APS) at Argonne National Laboratory on bending magnet beamline 20 at electron energy 9.0 KeV and average current of 100 mA and at the CLAESS beamline at ALBA synchrotron light source The radiation at APS was monochromatized by a Si(110) crystal monochromator. The intensity of the X-rays were monitored by three ion chambers (I_0, I_1 and I_2) filled with 80% nitrogen and 20% helium and placed before the sample (I_0) and after the sample (I_1 and I_2).Cu metal was placed between ion chambers I_1 and I_2 and its absorption was recorded with each scan for energy calibration. The samples were kept at 20 K in a He atmosphere at ambient pressure. Hybrid materials on glassy carbon surfaces were recorded as fluorescence excitation spectra using a 13-element energy-resolving detector. All samples were measured in a continuous helium flow cryostat in fluorescence mode with a 13-element Germanium detector. Around 15-20 XAS spectra were collected for each solution sample. No more than 5 scans were taken at each sample position at any condition. Two glassy carbon sheets with sub-monolayer coverage of the hybrid materials were on the other hand stacked on top on each other and wrapped in kapton tape. Around 30 XAS spectra of each hybrid sample were collected. Care was again taken to measure at several sample positions on each sample and no more than 5 scans were taken at each sample position. In order to reduce the risk of sample damage by x-ray radiation, 80% flux was used in the defocused mode (beam size 5500 µm(Horizontal) x 600 µm(Vertical)) and no damage was observed scan after scan to any samples. All samples were also protected from the x-ray beam during spectrometer movements by a shutter synchronized with the scan program. Cu XAS energy was calibrated by the first maxima in the second derivative of the copper metal X-ray Absorption Near Edge Structure (XANES) spectrum. The CuO reference compound diluted with Boron Nitride (BN) and some Cu hybrid complexes were additionally measured on the CLAESS wiggler beamline at the ALBA synchrotron light source whereby the radiation was monochromatized using a pair Si(111) crystals. Similarly, two glassy carbon sheets wrapped in kapton tape were mounted between PEEK sample holders and measured with a circular beam spot size of around 15 µm using a liquid nitrogen cryostat cooled down to 77 K. Fluorescence absorption measurements were carried out on hybrid materials at ALBA with an Amptek silicon drift solid state detector (XR-100 SDD)[1] placed at 90 degrees to the incoming beam. The silicon drift detector was placed on a motorized stage allowing the sample-detector distance to be easily changed between 30-110 mm[1]. Solid CuO diluted with BN powder was pressed between polypropylene and mylar tape, and measured in the cryostat in transmission mode. Around 3 scans were collected on CuO and around 20-25 scans were collected on hybrid materials. Care was once again taken to measure at several positions on each sample to minimize radiation damage

Extended X-ray Absorption Fine Structure (EXAFS) Analysis

Athena software[1] was used for data processing. The energy scale for each scan was normalized using copper metal standard. Data in energy space were pre-edge corrected, normalized, deglitched (if necessary), and background corrected. The processed data were next converted to the photoelectron wave vector (k) space and weighted by k^3. The electron wave number is defined as $k = [2m(E - E_0)/\hbar^2]^{1/2}$, E_0 is the energy origin or the threshold energy. K-space data were truncated near the zero crossings k = 1.212 to 11.6 Å^{-1} for the solution and the hybrid materials, in Cu EXAFS before Fourier transformation. The k-space data were transferred into the Artemis Software for curve fitting. In order to fit the data, the Fourier peaks were isolated separately, grouped together, or the entire (unfiltered) spectrum was used. The individual Fourier peaks were isolated by applying a Hanning window to the first and last 15% of the chosen range, leaving the middle 70% untouched. Curve fitting was performed using *ab initio*-calculated phases and amplitudes from the FEFF8[2] program from the University of Washington. *Ab initio*-calculated phases and amplitudes were used in the EXAFS equation

$$\chi(k) = S_0^2 \sum_j \frac{N_j}{kR_j^2} f_{eff_j}(\pi, k, R_j) e^{-2\sigma_j^2 k^2} e^{\frac{-2R_j}{\lambda_j(k)}} \sin(2kR_j + \phi_{ij}(k)) \tag{S2}$$

where N_j is the number of atoms in the j^{th} shell; R_j the mean distance between the absorbing atom and the atoms in the j^{th} shell; f_{eff_j} (π,k, R_j) is the *ab initio* amplitude function for shell j, and the Debye-Waller term $e^{-2\sigma_j^2 k^2}$ accounts for damping due to static and thermal disorder in absorber-backscatterer distances. The mean free path term $e^{\frac{-2R_j}{\lambda_j(k)}}$ reflects losses due to inelastic scattering, where $\lambda_j(k)$, is the electron mean free path. The oscillations in the EXAFS spectrum are reflected in the sinusoidal term $\sin(2kR_j + \phi_{ij}(k))$, where $\phi_{ij}(k)$ is the *ab initio* phase function for shell j. This sinusoidal term shows the direct relation between the frequency of the EXAFS oscillations in k-space and the absorber-backscatterer distance. S_0^2 is an amplitude reduction factor.

The EXAFS equation[3] (Eq. S2) was used to fit the experimental Fourier isolated data (q-space) as well as unfiltered data (k-space) and Fourier transformed data (R-space) using N, S_0^2, E_0, R, and σ^2 as variable parameters (Table S4, S5). N refers to the number of coordination atoms surrounding Cu for each shell. The quality of fit was evaluated by R-factor and the reduced Chi^2 value. The deviation in E_0 ought to be less than or equal to 10 eV. R-factor less than 2% denotes that the fit is good enough3 whereas R-factor between 2 and 5% denotes that the fit is correct within a consistently broad model. The reduced Chi^2 value is used to compare fits as more absorber-backscatter shells are included to fit the data. A smaller reduced Chi^2 value implies a better fit. Similar results were obtained from fits done in k, q, and R-spaces.

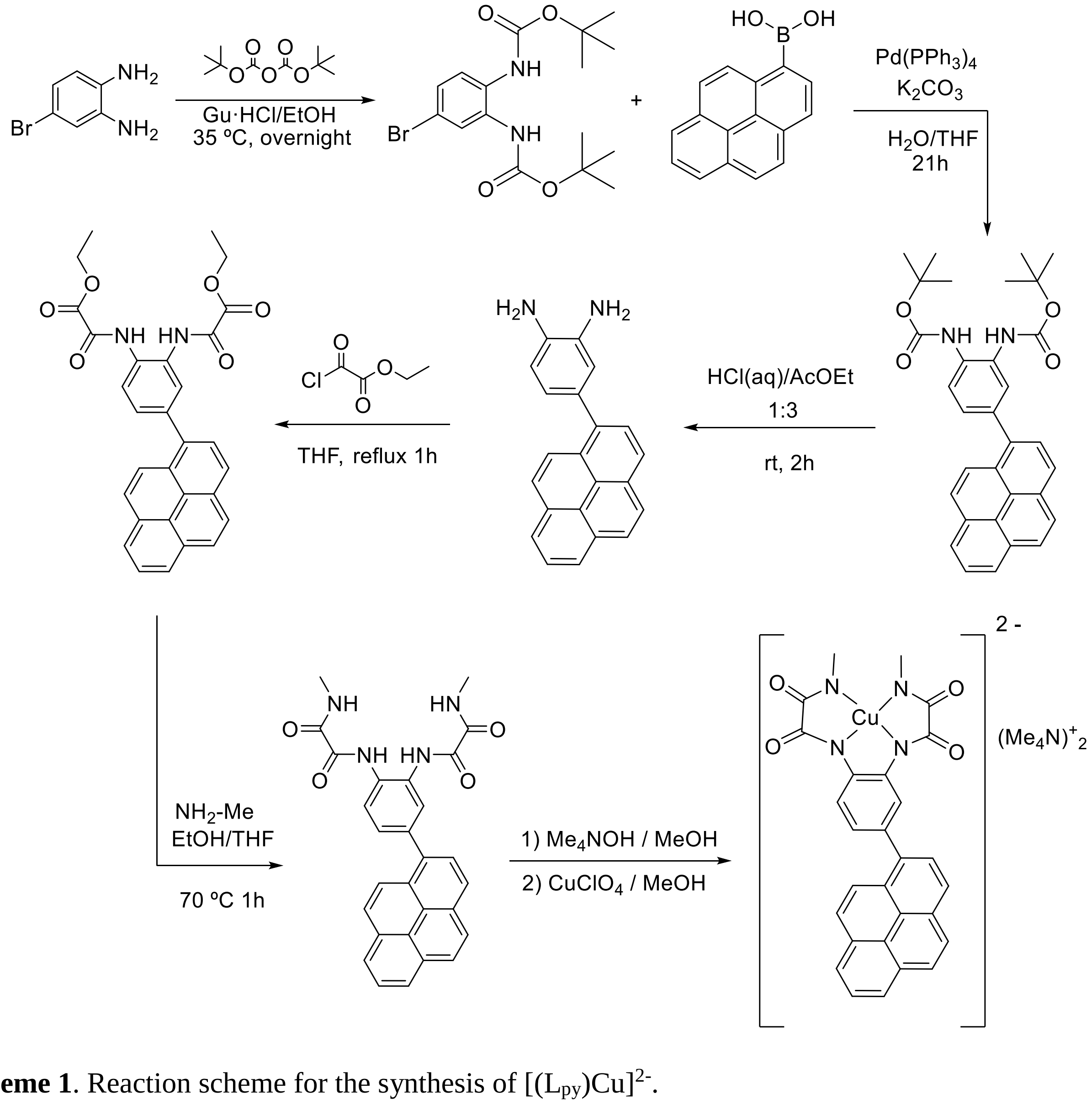
2. Synthetic details and electrode preparation

H_4L and $[(L)Cu](NMe_4)_2$

The H_4L ligands and the corresponding copper complex $[(L)Cu](NMe_4)_2$ were synthetized according to the procedures described in literature.[4,5,6]

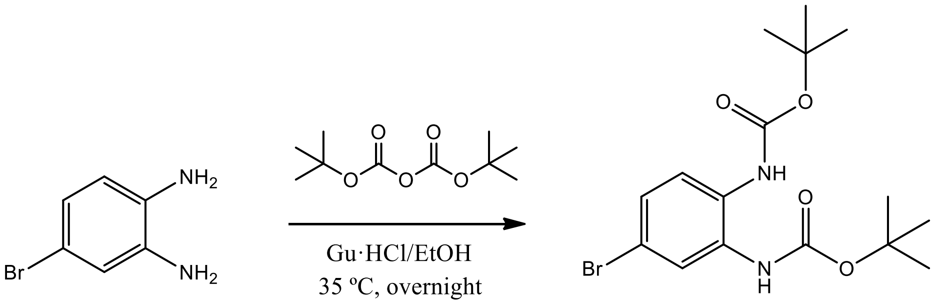
H_4L_{py} and $[(L_{py})Cu](NMe_4)_2$

General scheme



Scheme 1. Reaction scheme for the synthesis of $[(L_{py})Cu]^{2-}$.

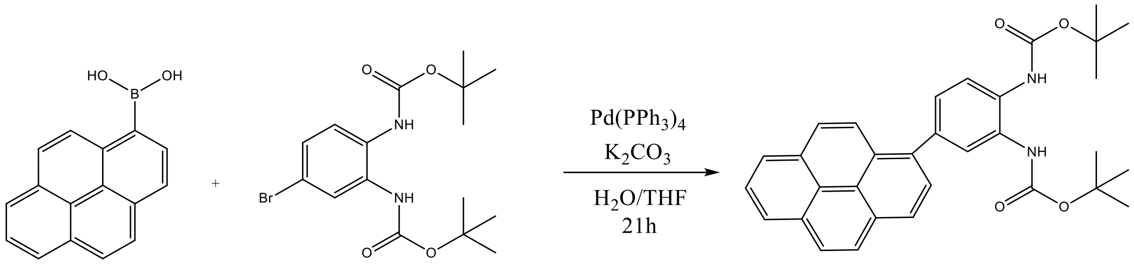
Synthesis of di-tert-butyl (4-bromo-1,2-phenylene)dicarbamate



The product was prepared following a procedure similar to a previously reported one[7]: 2.0 mmols of the starting product (4-bromo-1,2-diaminobenzene), 5.0 mmols of di-tert-butyl dicarbonate and 1.25 mmols of guanidine hydrochloride were mixed and dissolved in 20 mL of ethanol (96% v/v). The mixture was set to 35 ºC and left over-night under stirring. Then the ethanol was evaporated and the resulting solid was extracted with dichloromethane and filtered. Upon evaporation of dichloromethane, a brown solid appears which was washed with hexane until filtrate was colorless.

Yield: 657 mg (1.69 mmols), 77%. ^{1}H-NMR (DMSO-d6): δ [ppm] = 8.57 (H-NPh, s, 1H) 8.55 (H-N'Ph, s, 1H), 7.69 (H-1, s, 1H), 7.39 (H-2, d, J = 8.6 Hz), 7.23 (H-3, dd, J_1 = 8.6 Hz, J_2 = 2.3 Hz), 1.45 ([-O-(C(CH_3)$_3$)], s, 9H), 1.44 ([-O'-(C(CH_3)$_3$)], s, 9H).

Synthesis of di-tert-butyl (4-(pyren-1-yl)-1,2-phenylene)dicarbamate

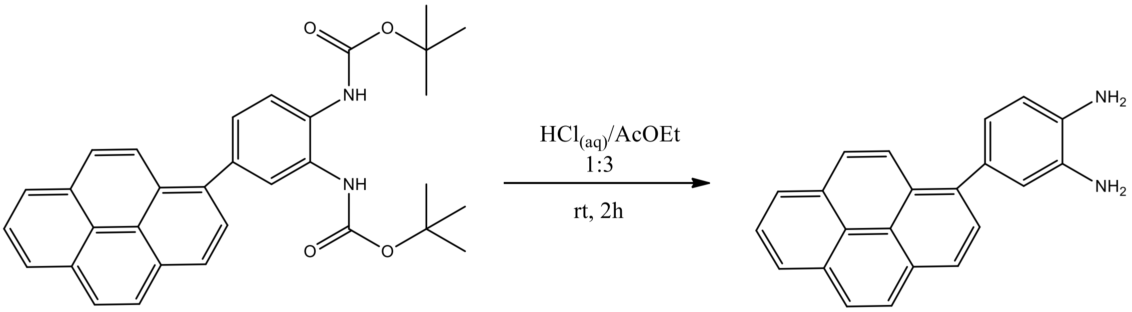


The synthesis of the pyrene adduct was performed using a Suzuki coupling in similar conditions to reported existing reactions with pyrene-1-boronic acid[8]. 2.5 mmol of di-tert-butyl (4-bromo-1,2-phenylene)dicarbamate, 2.5 mmol of pyrene-1-boronic acid and 7.5 mmol of potassium carbonate are mixed. After degasing and placing the solids under nitrogen atmosphere, 0.25 mmols tetrakis(triphenylphosphine)palladium(0) were added also under nitrogen atmosphere. Then 8 mL of distilled water and 40 mL of THF that had been previously degassed by bubbling nitrogen under stirring were added. The reaction mixture was left for 21h at reflux. Afterwards, ice cool distilled water was added and the mixture was extracted with 4x20 mL of DCM. After evaporation of the solvent, the solid is purified by liquid chromatography. Silica was used as stationary phased and a mixture of hexane/ethylacetate 9:1 was used as mobile phase.

Yield: 924 mg (1.81 mmols), 72%. IR: υ_{max} [cm^{-1}] = 3319 (N-H tension); 3038 (=C-H tension, aromatic); 2976, 2930 (C-H tension); 1696 (C=O tension), 1149 (C-H bending). ^{1}H-NMR (DMSO-d6): δ [ppm] = 8.66 (H-NPh, s, 1H), 8.63 (H-N'Ph, s, 1H), 8.33 (H-4 or H-5, d, J= 7.9 Hz), 8.30 (H-8 or H-10, dd, J_1 = 7.6 Hz J_2 = 1.0 Hz, 1 H), 8.26 (H-8 or H-10, dd, J_1 = 7.7 Hz J_2 = 0.9 Hz, 1 H),) 8.19

- 8.11 (group H-12, H-11, H-7, H-6, multiple signals, 4H), 8.07 (H-9, dd, J_1 = 7.6 Hz, J_2 = 7.6 Hz), 7.97 (H-4 or H-5, d, J = 7.9 Hz, 1H), 7.70 (H-1, broad signal, 1H), 7.66 (H-2, d, J = 8.2 Hz, 1H), 7.33 (H-3, dd, J1 = 8.2, J2 = 2.08, 1H), 1.49 (-O'-($C(CH_3)_3$), s, 9H), 1.42 (-O'-($C(CH_3)_3$), s, 9H). ^{13}C-NMR (DMSO-d6): δ [ppm] = 153.97 (-NH-COO-, 1C), 153.90 (-NH-C'OO-, 1C), 136.79 (1C), 136.70 (1C), 131.36 (1C), 130.77 (1C), 130.65 (1C), 130.53 (1C), 129.79 (1C) 128.28 (1C), 128.00 (1C), 127.93 (1C), 127.82 (1C), 126.99 (1C), 126.56 (1C), 125.90 (1C), 125.52 (1C), 125.45 (1C), 124.90 (1C), 124.54 (1C), 124.41 (1C), 80.40 (-C-($CH_3)_3$, 1C), 80.37 (-C'-($CH_3)_3$, 1C), 28.45 (-C-($C'H_3)_3$, 3C), 28.41 (-C-($C'H_3)_3$, 3C).

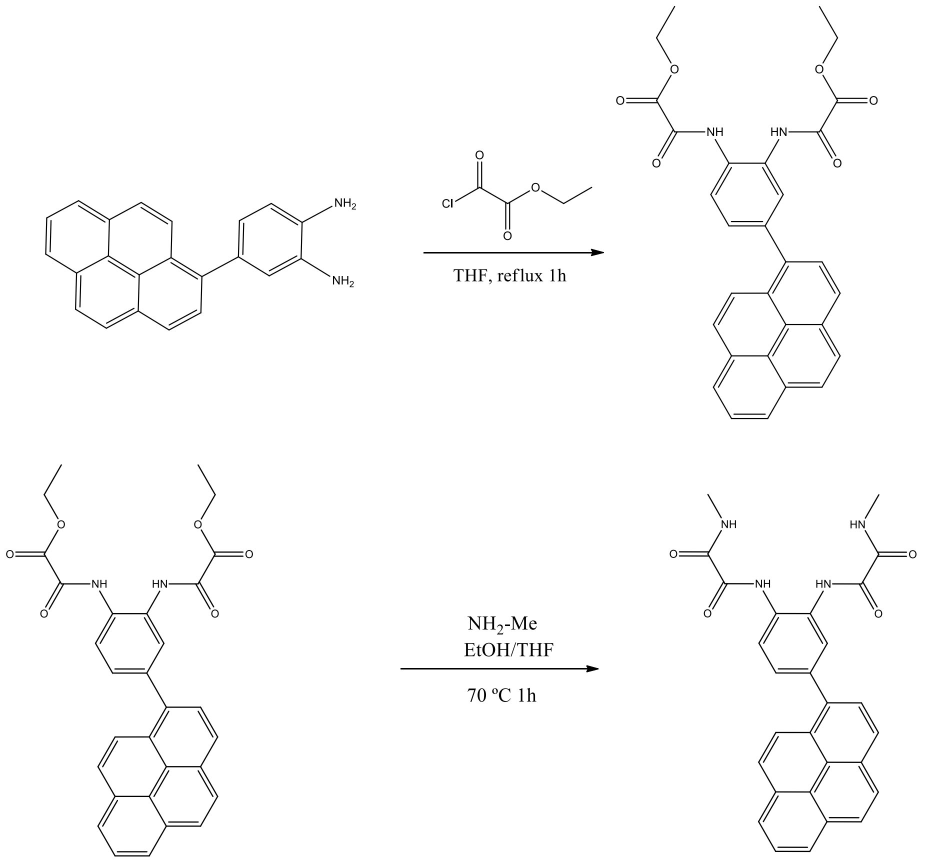
Synthesis of 4-(pyren-1-yl)benzene-1,2-diamine



The product was prepared by following an acid hydrolysis similar to what had been described in similar reactions.[9] 1.77 mmols of di-tert-butyl (4-(pyren-1-yl)-1,2-phenylene)dicarbamate were dissolved in 8 mL mixture of HCl (37%, aq) and AcOEt in a 1:3 proportion. The mixture is left under stirring at room temperature for 2h. Then distilled water is added and the solution is brought to basic pH by adding excess solid K_2CO_3. Then the mixture is extracted with 5x20 mL of AcOEt. The organic phase is recovered and solvent is evaporated.

Yield: 543 mg (1.76 mmols) 99%. HR-MS (ESI positive mode, CH_2Cl_2): m/z $[M+H]^+$ = 309.1398 (Expected: 309.1391). IR: υ_{max} [cm^{-1}]= 3394, 3355, 3308, 3184 (N-H, tension) 3040 (=C-H, tension), 1500 (-C=C- aromatic, tension), 1280 (C-N, tension). ^{1}H-NMR (DMSO-d6): δ [ppm] = 8.30-8.23 (pyrene, multiple signals, 4H), 8.18 (pyrene, d, J = 9.0 Hz, 1H), 8.15 (pyrene, d, J = 8.9 Hz, 1H), 8.12 (pyrene, d, J = 9.3 Hz, 1H), 8.05 (H-4, dd, J_1 = 7.6 Hz, J_2 = 7.6 Hz), 7.94 (pyrene, d, J = 7.9 Hz, 1H), 6.83 (H-1, d, J = 1.9 Hz, 1H), 6.73 (H-2, d, J = 7.8 Hz, 1H), 6.67 (H-3, dd, J_1 = 7.8 J_2 = 1.9 Hz, 1H), 4.71 (H_2-HPh, broad signal, 2H) 4.67 (H_2-N'Ph, broad signal, 2H). ^{13}C-NMR (DMSO-d6): δ [ppm] = 139.42 (1C), 135.99 (1C), 135.20 (1C), 131.55 (1C), 131.03 (1C), 129.62 (1C), 129.53 (1C), 128.85 (1C), 128.02 (1C), 127.91 (1C), 127.17 (1C), 126.67 (C-4, 1C), 126.00 (1C), 125.33 (1C), 125.28 (1C), 124.98 (1C), 124.80 (1C), 124.73 (1C) 120.04 (C-3, 1C), 116.94 (C-1, 1C) 114.89 (C-2, 1C).

Synthesis of N1,N1'-(4-(pyren-1-yl)-1,2-phenylene)bis(N2-methyloxalamide) (H_4L)

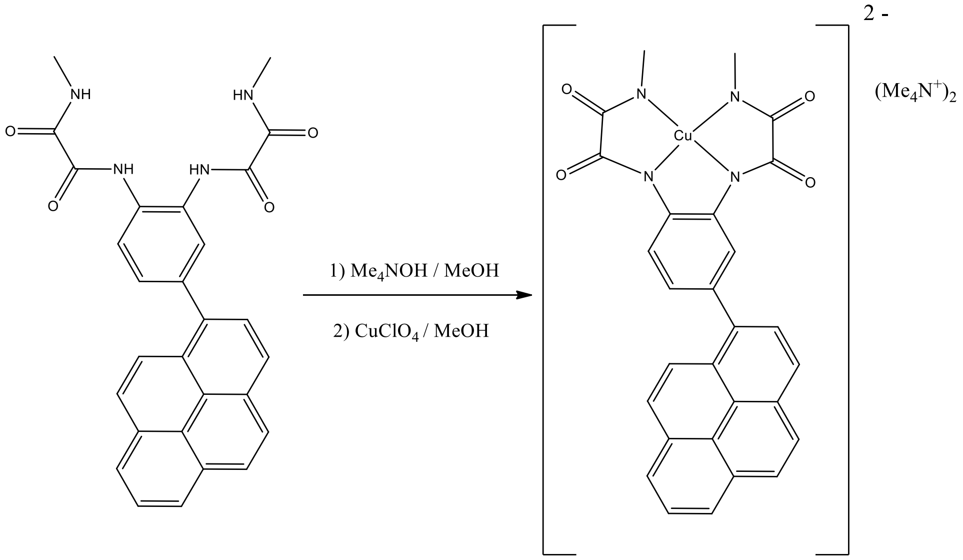


The product was synthesized following a similar two steps procedure to the synthesis of ligand H_4L that has been previously cited.[4-6] Firstly, 0.17 mmol of the 4-(pyren-1-yl)benzene-1,2-diamine were dissolved in 3 mL of THF. Then 0.4 mmol (66 µL) of the ethyl clorooxoacetate were added drop wise. The mixture was refluxed for 1h and the appearing solid waste was removed by filtration. The resulting solution was evaporated and an oil product was formed. Upon addition of distilled water, a white solid formed, which was collected by centrifugation. After washing with water it was left to dry, to then solubilize it with 6 mL of THF. Afterward, 130 µL of a 33% wt methylamine solution in MeOH were added and the mixture was left at 70 ºC for 1 h. The appearing solid corresponds to the target ligand and is filtrated and washed with THF and ether.

Yield: 28 mg (0.05 mmol) 32%. Elemental Analysis calc.(%) for $C_{28}H_{22}N_4O_4 \cdot 3.5\ H_2O$: C 62.10, H 5.40, N 10.35, found (%): C 61.83, H 4.23, N 11.33. HR-MS (ESI positive mode, CH_2Cl_2): m/z $[M+H]^+$ = 501.1526 (Expected: 501.1539). IR: υ_{max} [cm^{-1}]= 3350, 3297, 3241 (N-H, tension), 3040 (=C-H aromatic, tension), 2940 (C-H, tension), 1656, 1681 (C=O, tension), 1530, 1506, 1409, (C-N, tension). ^{1}H-NMR (DMSO-d6): δ [ppm] = 10.73 (H-N-C=O & H-N'-C=O, broad signal, 2H), 9.06-8.99 (H-N-CH_3 & H-N'-CH_3, m, 2H) 8.39 (H-4/H-5, d, J = 7.9 Hz, 1H), 8.36-8.31 (H-8 & H-10, m, 2H), 8.27-8.18 (group H-6, H-7, H-11 and H-12, m, 4H), 8.11 (H-9, dd, J_1 = 7.6 Hz, J_2 = 7.6 Hz), 8.06 (H-4/H-5, d, J = 7.9 Hz, 1H), 7.91 (H-1, d, J = 2.1 Hz, 1H), 7.87 (H-2, d, J = 8.3 Hz, 1H), 7.59 (H-3, dd, J_1 = 8.3 J_2 = 2.1 Hz, 1H), 2.79 (H_3-C-NH-, d, J = 4.8 Hz, 3H), 2.75 (H_3-C'-NH-, d, J = 4.8 Hz, 3H). ^{13}C-

NMR (DMSO-d6): δ [ppm] = 160.61 (C-10/C-11, 1C), 160.56 (C-10/C-11, 1C), 159.37 (C-12/C-13, 1C), 159.28 (C-12/C-13, 1C), 138.31 (1C), 136.33 (1C), 131.45 (1C), 130.85 (1C), 130.80 (1C), 130.34 (1C), 129.78 (1C), 129.76 (1C), 128.39 (C-2, 1C) 128.11 (C-4/C-5, 1C), 128.05 (1C), 127.84 (1C), 127.66 (C-1, 1C), 126.97 (C-6, 1C), 125.95 (C-3, 1C) 125.58 (C-4/C-5, 1C), 125.52 (1C), 124.90 (1C), 26.61 (C-8/C-9, 1C), 26.56 (C-8/C-9, 1C).

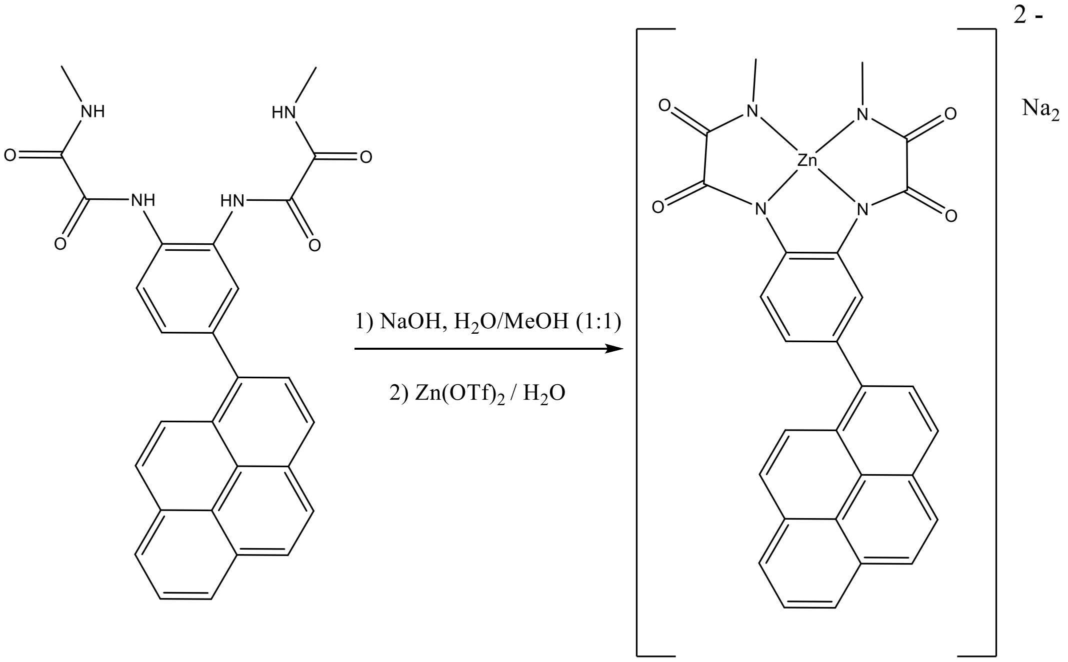
Synthesis of $[(L_{py})Cu](NMe_4)_2$



The complex was synthesized by an adaptation of the procedure presented in the previously mentioned works.[4-6] 0.05 mmols of the precursor ligand were weighted and dispersed in 1 mL of MeOH using a sonicator for 15 minutes. The mixture was brought to 70 °C and a tetramethylamoniumhydroxide solution was added until a clear solution was formed. At that moment, a copper perchlorate hexahydrate solution of 0.05 mmols in 2 mL of MeOH is prepared and added to the mixture drop wise and slowly. After 1 hour, solid formed is removed by filtration and the solvent is evaporated until about 1 mL solution. After addition of 1 mL of MeCN more solid was removed by filtration. Finally, the remaining solution is treated with acetone and abundant ether which causes a brown solid to precipitate. This solid quickly became an oil through absorption of atmospheric water. Water was removed at the pump in a heating bath at 40 °C and the solid was kept under nitrogen atmosphere.

Yield 28 mg (0.04 mmols) 80%. Elemental Analysis calc.(%) for $C_{36}H_{42}CuN_6O_4 \cdot 5\ H_2O$: C 55.69, H 6.75, N 10.82, found (%): C 55.47, H 7.44, N 10.59. HR-MS (ESI negative mode, CH_2Cl_2): m/z $[M+H]^+$ = 538.0702 (Expected: 538.0708)**.**

Synthesis of [(L_{py})Zn]Na_2

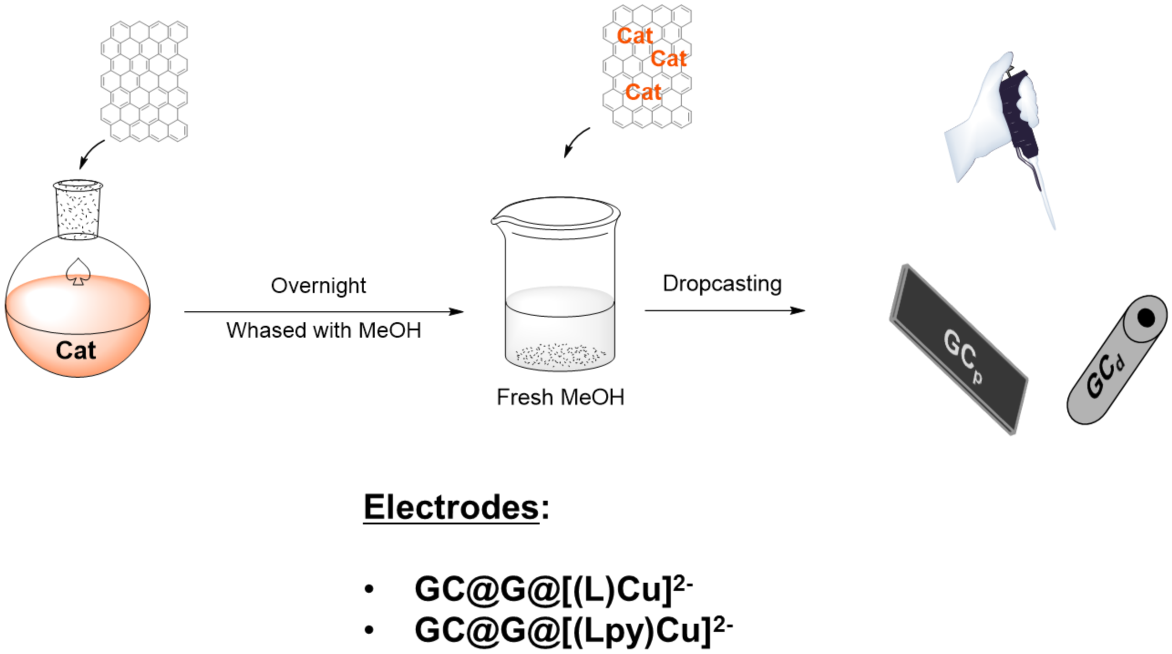


This complex was synthesized by a different procedure than in the case of Cu complex, adapted from a related reported complex.[5] 0.02 mmols of the precursor ligand were weighted and dispersed in 1 mL of water/MeOH mixture (1:1) using a sonicator for 15 minutes. The mixture was brought to 80 ºC and 0.1 ml of a solution containing 1mmol/ml of NaOH in water was added. The mixture was stirred at 80ºC for 30 minutes. Then, a $Zn(OTf)_2$ solution of 0.02 mmols in 0.2 mL of water is added to the mixture drop wise and slowly. After 1 day at the same temperature, suspended solid is removed by filtration and the solvent is totally evaporated. The obtained solid was dissolved in MeOH to remove unreacted ligand by filtration and solvent is again evaporated. Finally, the remaining solid was washed with ether and vacuum dried.

Yield 4.5 mg (0.008 mmols) 40%.

Preparation of hybrid materials G-1^{2-} and G-2^{2-}

As supporting material, graphene (1-3 layers) deposited onto glassy carbon electrodes was used due to its high electroactive surface area and conductivity. Graphene is also produced extremely pure, without containing any catalytically active transition metal that would make the analysis harder. The immobilization procedure consists in preparing a 1mM solution of either **1**$^{2-}$ or **2**$^{2-}$ in methanol; then graphene (1-3 layers) in a ratio of 1mg/ml solution was added forming a suspension that was sonicated for 15 minutes and stirred overnight, allowing enough time for the π-π interaction to cover the maximum surface. This new modified material was separated from the solution, washed three times with fresh methanol and finally dispersed again in the same solvent. The electrode was prepared by dropcasting and evaporating 5 consecutive times 5 μL of that suspension on the surface of two kind of glassy carbon electrodes: glassy carbon disks (GCd, 0.07 cm^2) for most of electrochemical measurements and glassy carbon plates (GCp, 1 cm^2) for oxygen measurement and XAS experiments. The electrodes were finally dried under vacuum for 1 h and then were ready for use. They were named GC@G@$[(L)Cu]^{2-}$ and GC@G@$[(L_{py})Cu]^{2-}$ (**G-1**$^{2-}$ and **G-2**$^{2-}$ respectively).



Scheme S2. Schematic representation of the electrode preparation procedure.

3. Spectroscopic characterization

NMR Spectroscopy

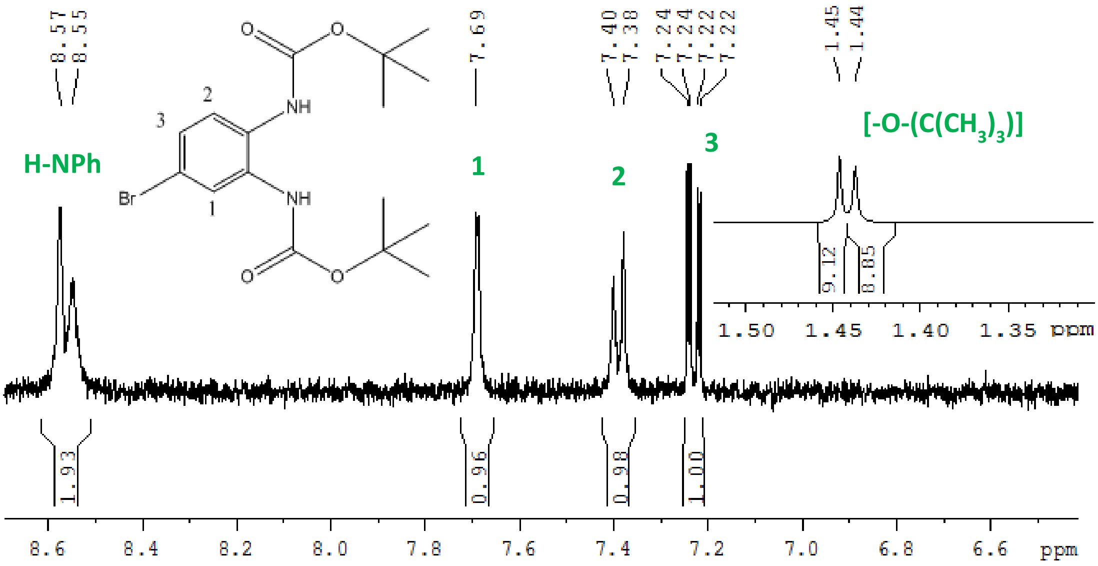


Figure S1. ^{1}H-NMR spectrum of di-tert-butyl (4-bromo-1,2-phenylene)dicarbamate in DMSO-d$_6$.

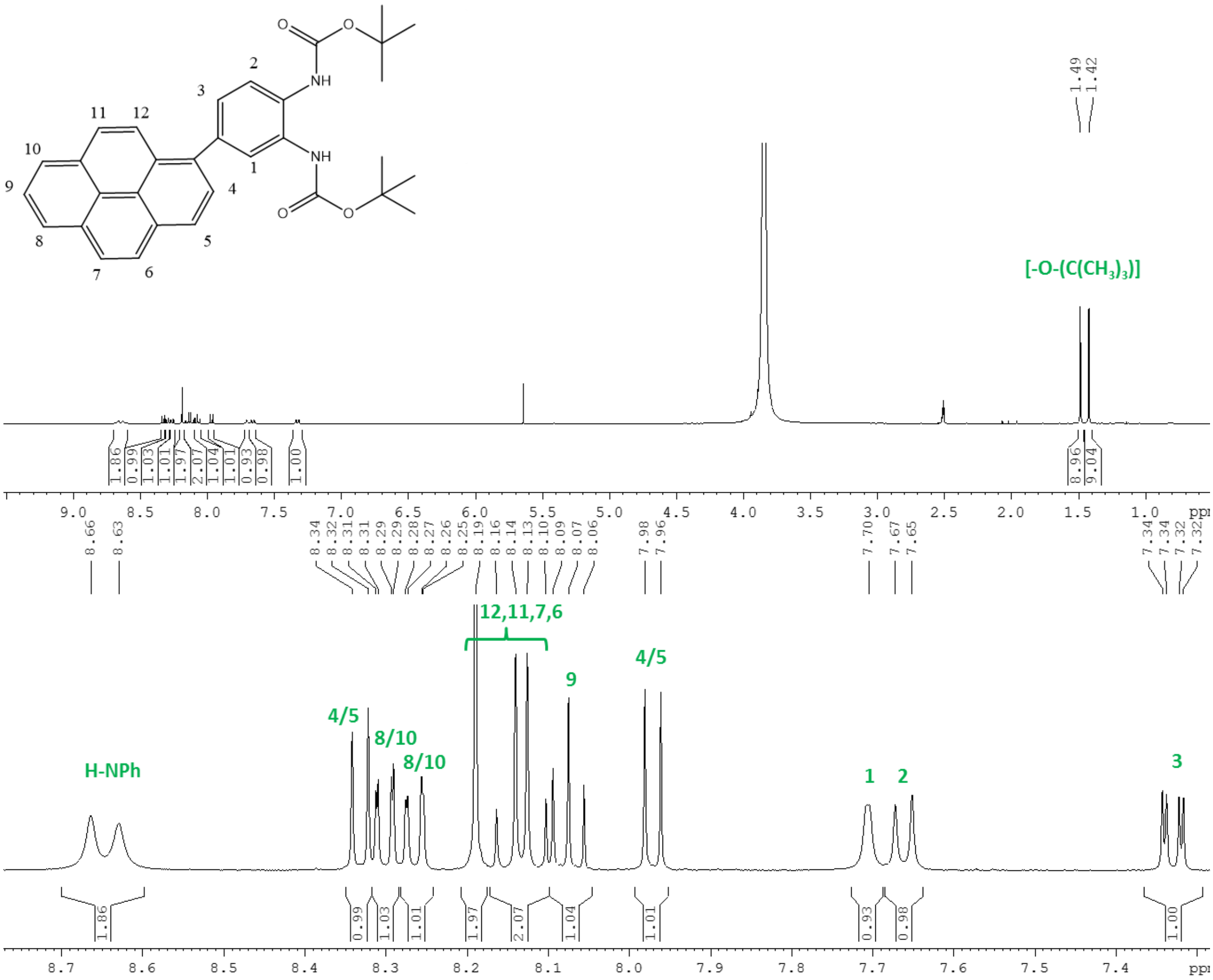


Figure S2. ^{1}H-NMR spectrum of di-tert-butyl (4-(pyren-1-yl)-1,2-phenylene)dicarbamate in DMSO-d$_6$.

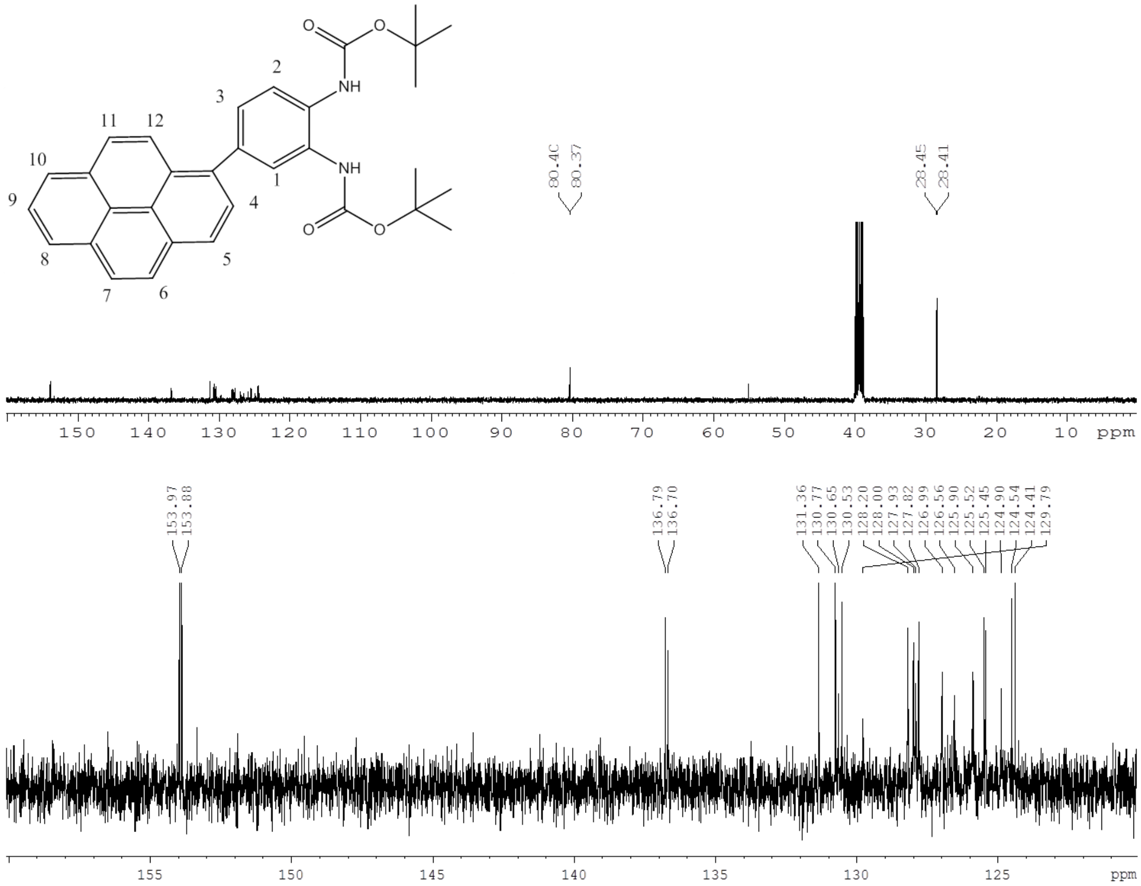


Figure S3. ^{13}C-NMR spectrum of di-tert-butyl (4-(pyren-1-yl)-1,2-phenylene)dicarbamate in DMSO-d_6.

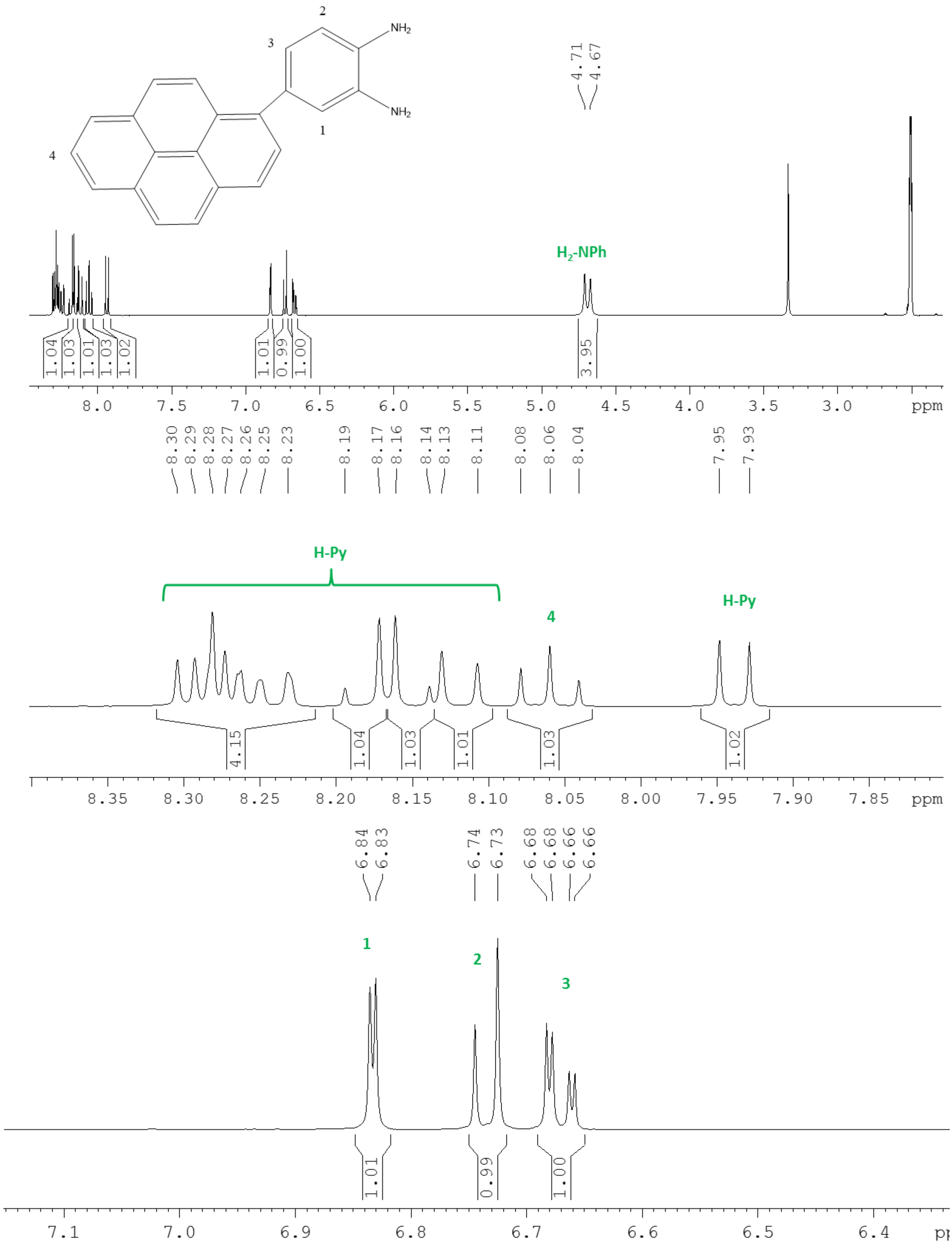


Figure S4. ^{1}H-NMR spectrum of 4-(pyren-1-yl)benzene-1,2-diamine in DMSO-d$_6$.

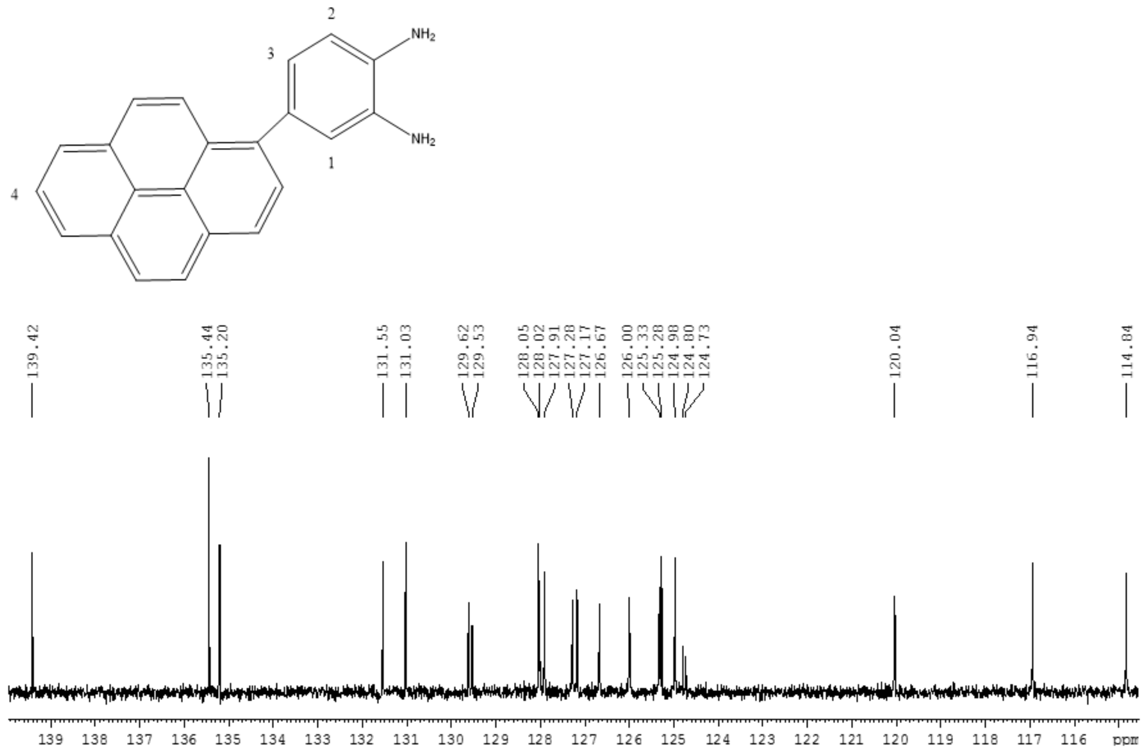


Figure S5. ^{13}C-NMR spectrum of 4-(pyren-1-yl)benzene-1,2-diamine in DMSO-d_6.

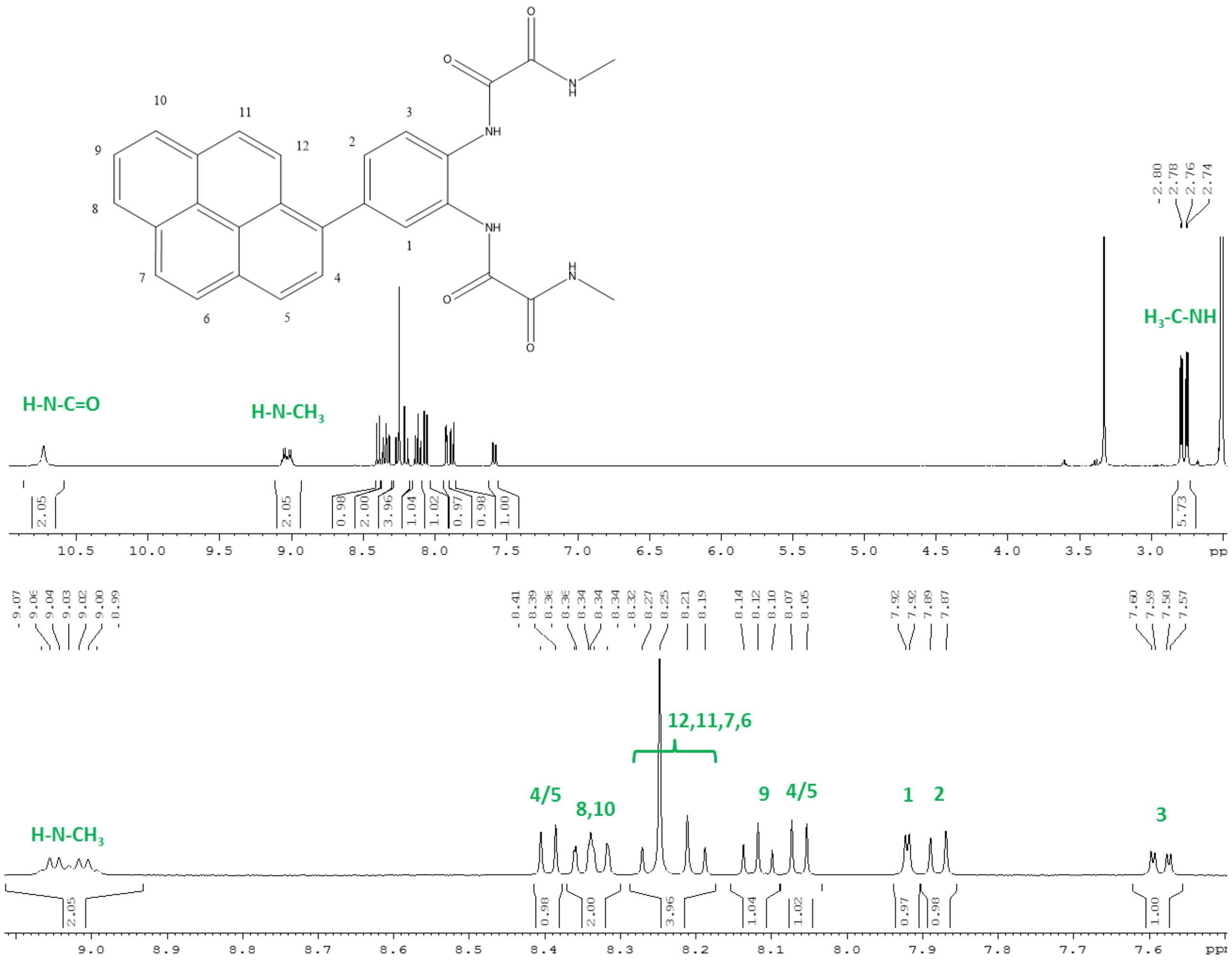


Figure S6. ^{1}H-NMR spectrum of N1,N1'-(4-(pyren-1-yl)-1,2-phenylene)bis(N2-methyloxalamide) (H$_4$L) in DMSO-d$_6$.

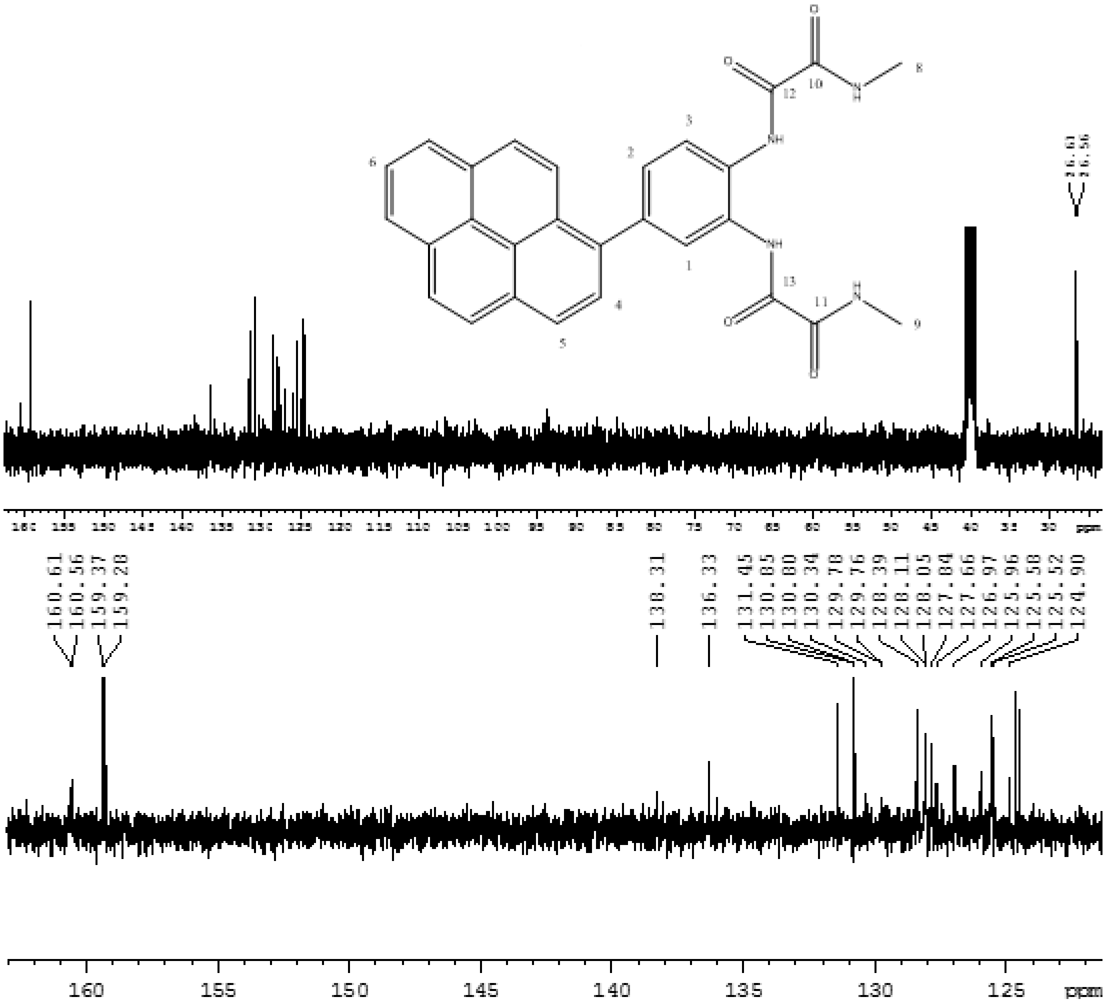


Figure S7. ^{13}C-NMR spectrum of N1,N1'-(4-(pyren-1-yl)-1,2-phenylene)bis(N2-methyloxalamide) (H_4L) in DMSO-d_6.

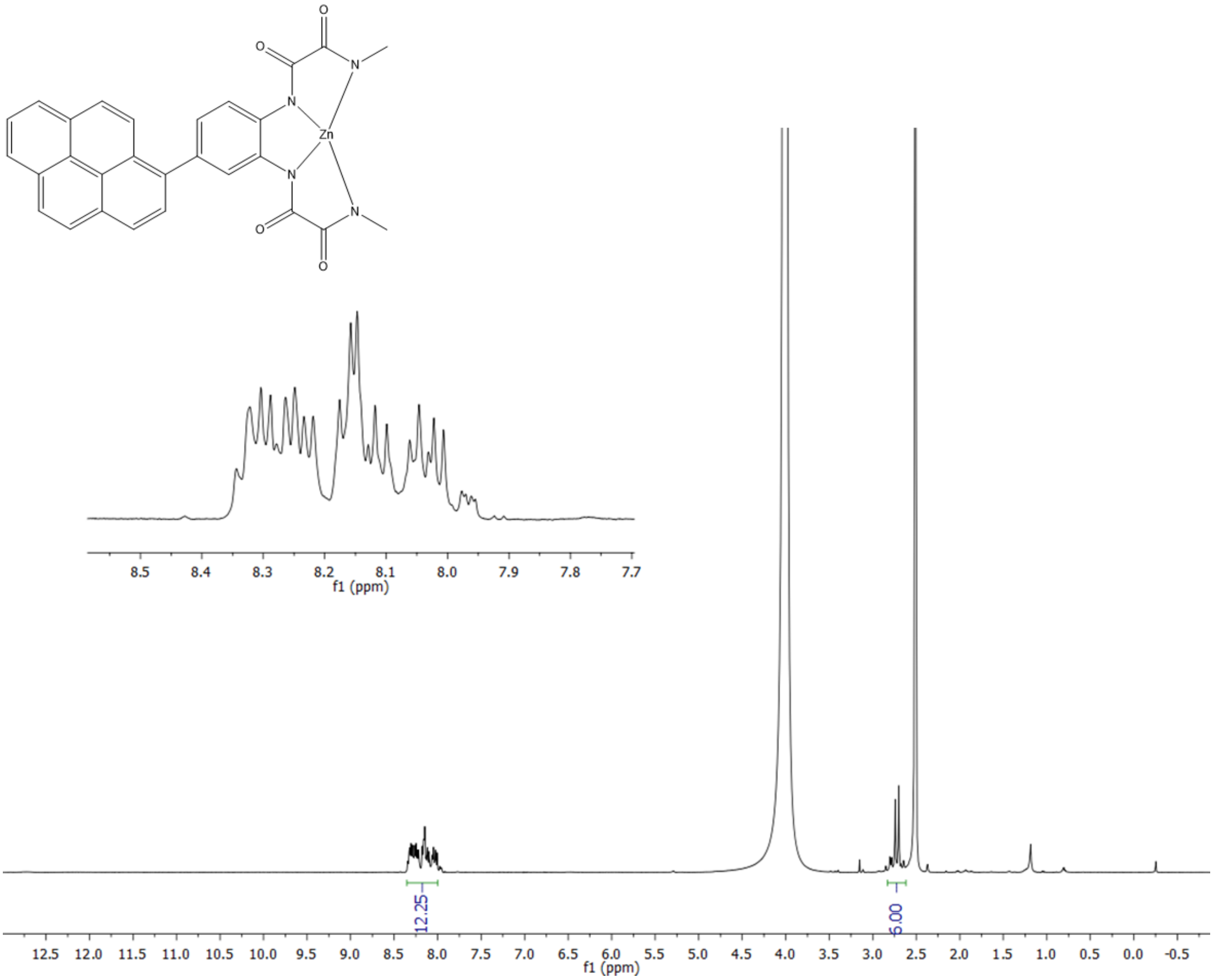


Figure S8. ^{1}H-NMR spectrum of complex $[(Lpy)Zn]^{2-}$ in DMSO-d_6 with 1% v/v of a solution 1M NaOD in D_2O.

IR Spectroscopy

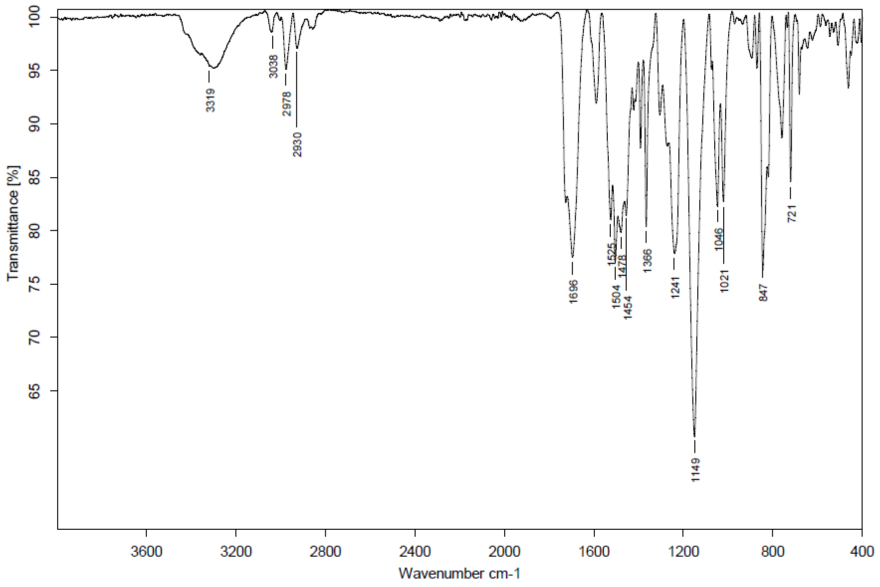


Figure S9. IR spectrum of di-tert-butyl (4-(pyren-1-yl)-1,2-phenylene)dicarbamate.

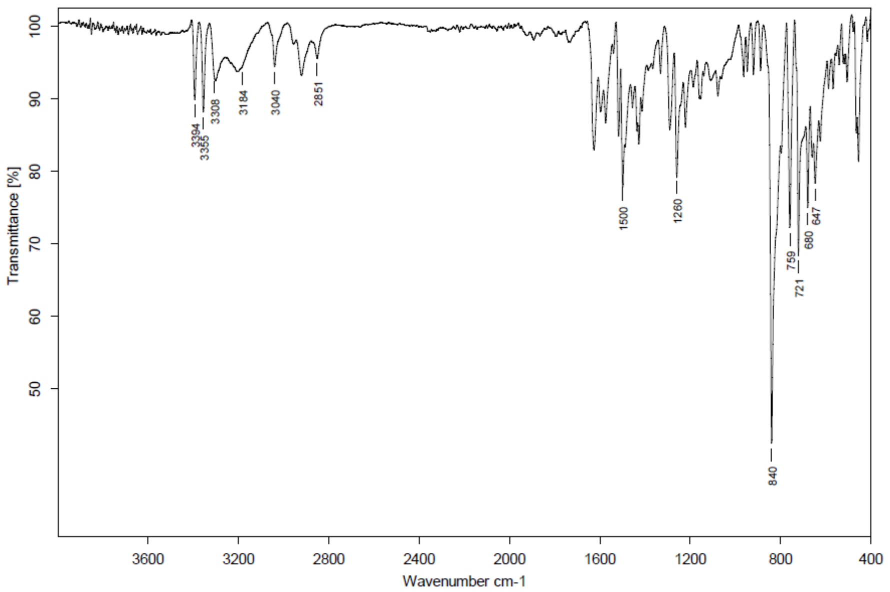


Figure S10. IR spectrum of 4-(pyren-1-yl)benzene-1,2-diamine.

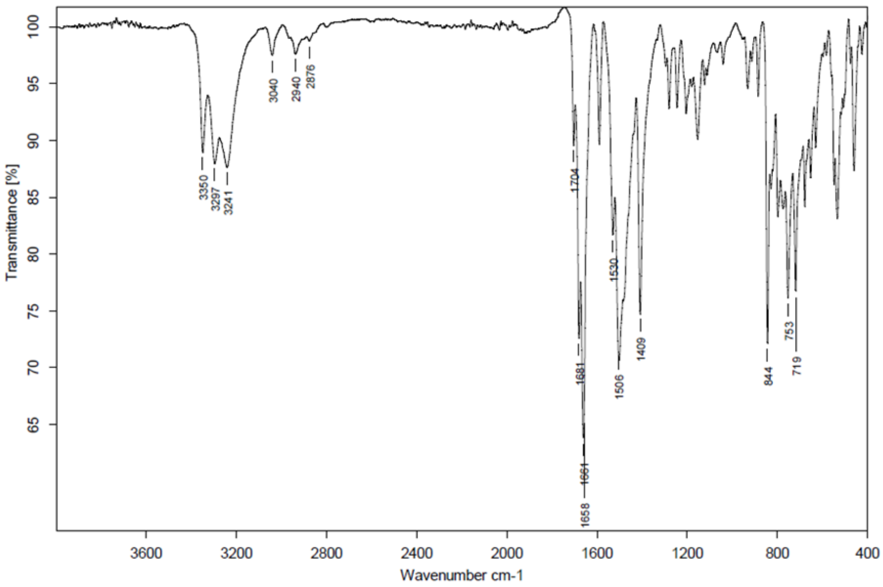


Figure S11. IR spectrum of N1,N1'-(4-(pyren-1-yl)-1,2-phenylene)bis(N2-methyloxalamide) (H_4L).

Uv-vis Spectroscopy

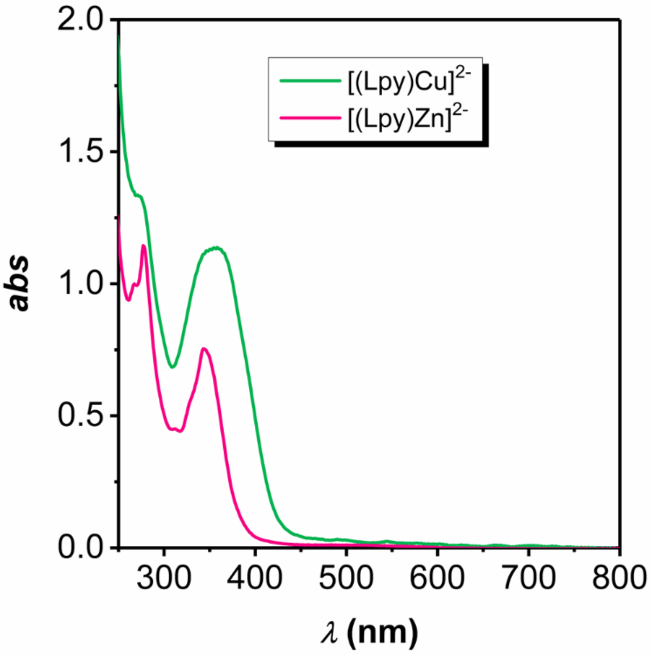


Figure S12. UV-vis spectra for [(L$_{py}$)Cu]$^{2-}$ and [(L$_{py}$)Zn]$^{2-}$ in pH 12 phosphate buffer solution (0.1 M of ionic strenght).

Spectroelectrochemistry

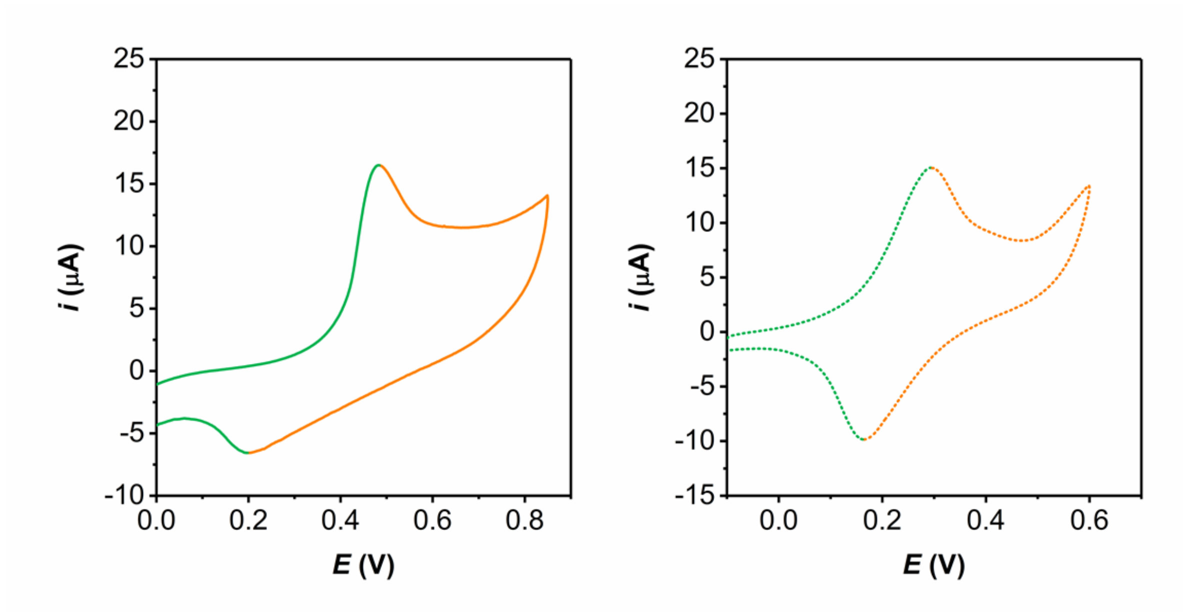


Figure S13. CVs performed in an OTTLE type spectroelectrochemical cell in pH 12 aqueous (left) and acetonitrile (right) solution of **2**$^{2-}$ (4mM) at 2 mV/s with Pt mesh working and counter electrode and a silver wire pseudo reference electrode (-0.2 V respect to NHE).

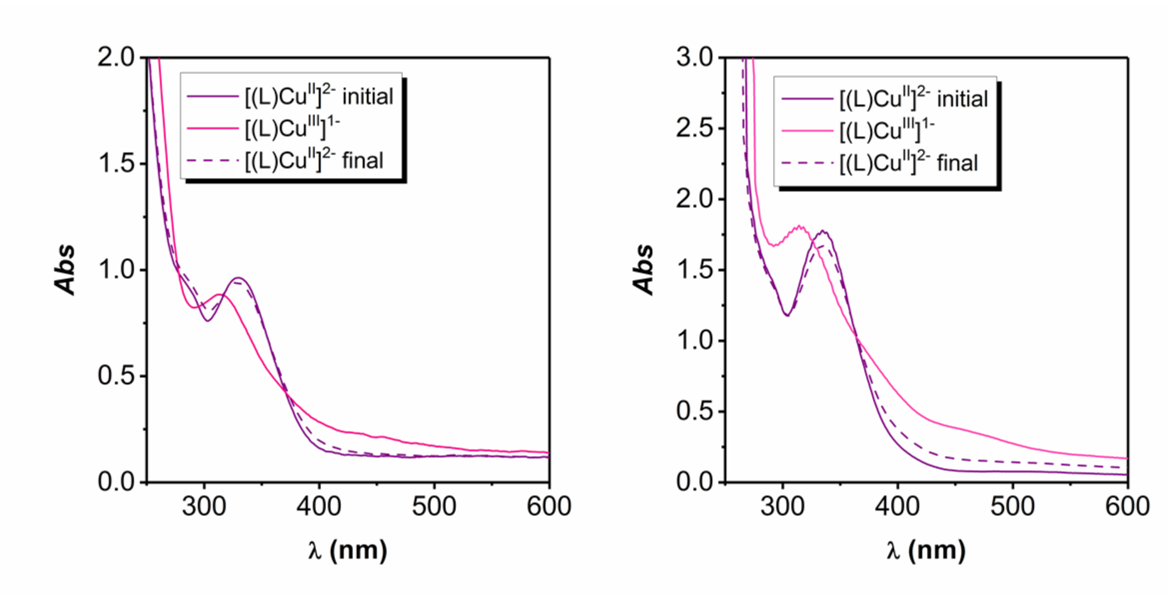


Figure S14. UV-vis spectra for **1**$^{2-}$ recorded during spectroelectrochemistry experiment in an OTTLE type spectroelectrochemical cell in pH 12 aqueous (left) and acetonitrile (right) solution containing 4mM of the catalyst.

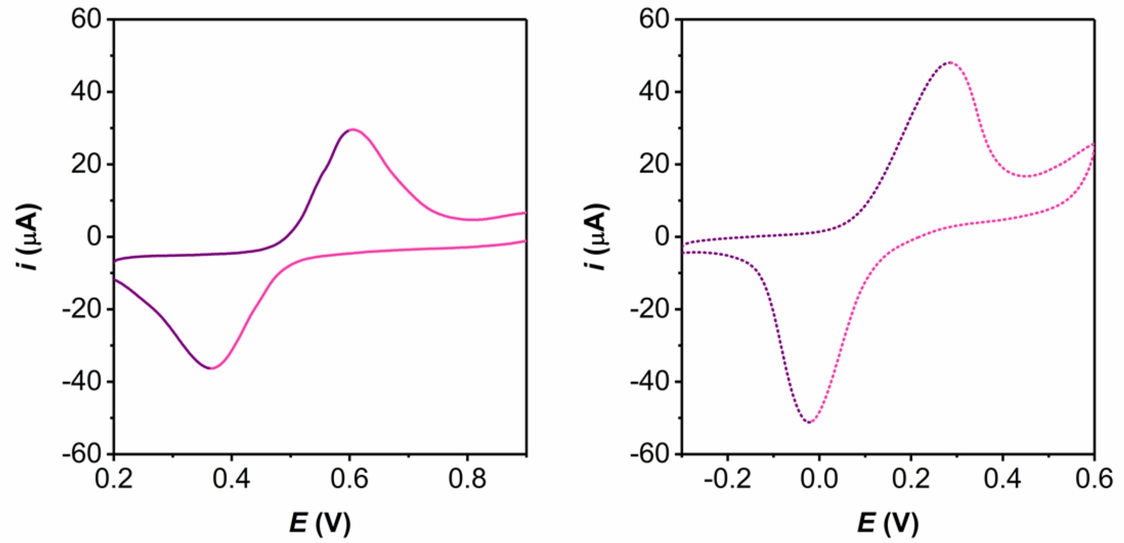


Figure S15. CVs performed in an OTTLE type spectroelectrochemical cell in pH 12 aqueous (left) and acetonitrile (right) solution of $\mathbf{1}^{2-}$ (4mM) at 2 mV/s with Pt mesh working and counter electrode and a silver wire pseudo reference electrode (-0.2 V respect to NHE).

X-Ray Absorption Spectroscopy

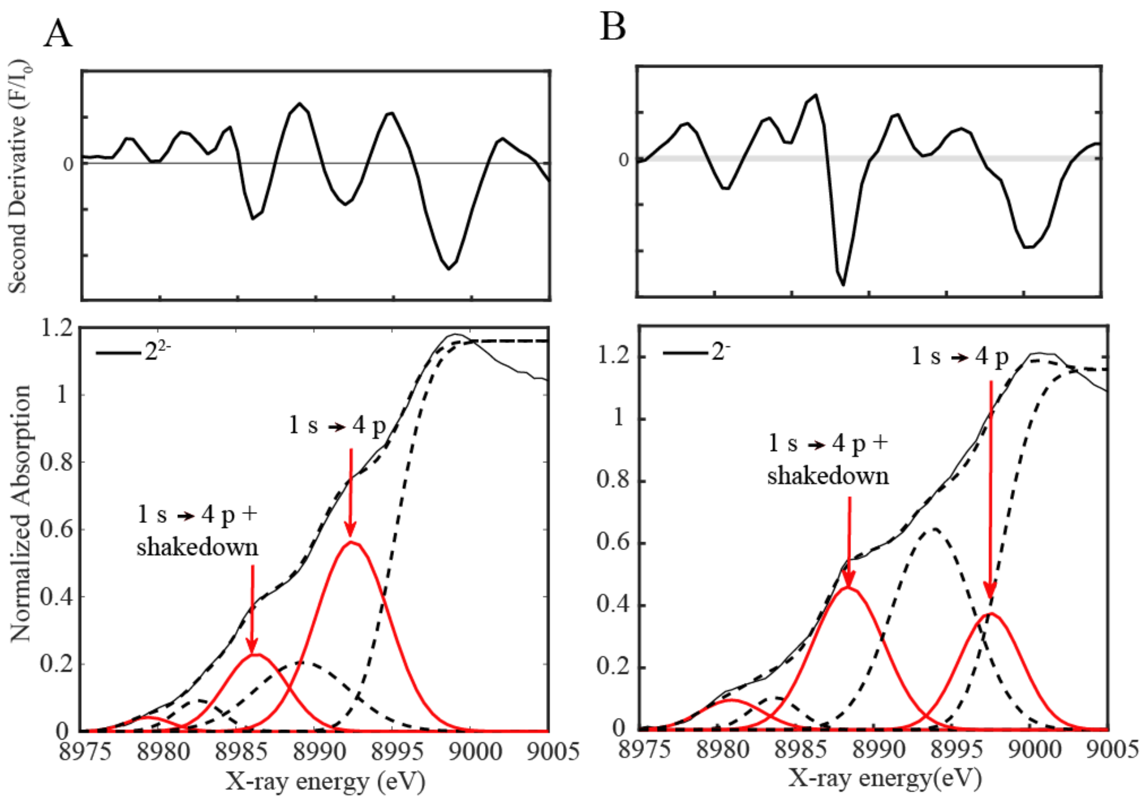


Figure S16. Results of fits to K-edge data for: A. **2**$^{2-}$ and B. **2**$^{-}$. Data are shown as solid black lines and fits as black dashed lines. Each fit is the sum of the five Gaussian peaks and one error function curve (dashed black line) shown. Peak assignments are as shown on the plots. Second derivatives of the data are plotted over each spectrum. Peak positions are clearly visible in the second derivative spectra. The curve fittings for the edge spectra of **2**$^{2-}$ and **2**$^{-}$ are shown below.

XANES fitting procedure as shown in Figure S16:

The near edge fit and pre-edge peak fits were carried out with an error function and 5 Gaussian functions respectively. The formulas for the error (erf) and Gaussian functions(gauss) are as follows:

Error function: $A\left[erf\left(\frac{e-E_0}{w}\right)+1\right]$ (S3)

Gaussian function: $\left(\frac{A}{w\sqrt{2\pi}}\right)\exp\left[\frac{-(e-E_0)^2}{(2w^2)}\right]$ (S4)

Where A corresponds to the amplitude; w, the width; E_0, the centroid of the pre-edge and near edge peaks and e, the x-ray energy. The parameters E_0, A and w used for each sets of functions for the experimental fits are tabulated below (Table S1).

Table S1. Sets of functions with parameters used for the experimental XANES fits of **2**$^{2-}$ and **2**$^{-}$.

2^{2-} **Expt**			
Function	**Centroid**	**Amplitude**	**Width**
Gauss (Pre-edge)	8979.40	0.150	1.44
Gauss	8982.60	0.346	1.50
Gauss (shakedown)	8986.29	1.15	2.00
Gauss	8989.26	1.53	2.99
Gauss (main peak)	8992.47	3.32	2.35
Erf	8995.20	0.580	2.52
2^{-} **Expt.**			
Function	Centroid	Amplitude	Width
Gauss (Pre-edge)	8980.90	0.480	2.00
Gauss	8983.67	0.403	1.55
Gauss (shakedown)	8988.39	2.65	2.30
Gauss	8993.79	4.20	2.58
Gauss (main peak)	8997.49	1.88	2.00
Erf	8998.20	0.580	2.52

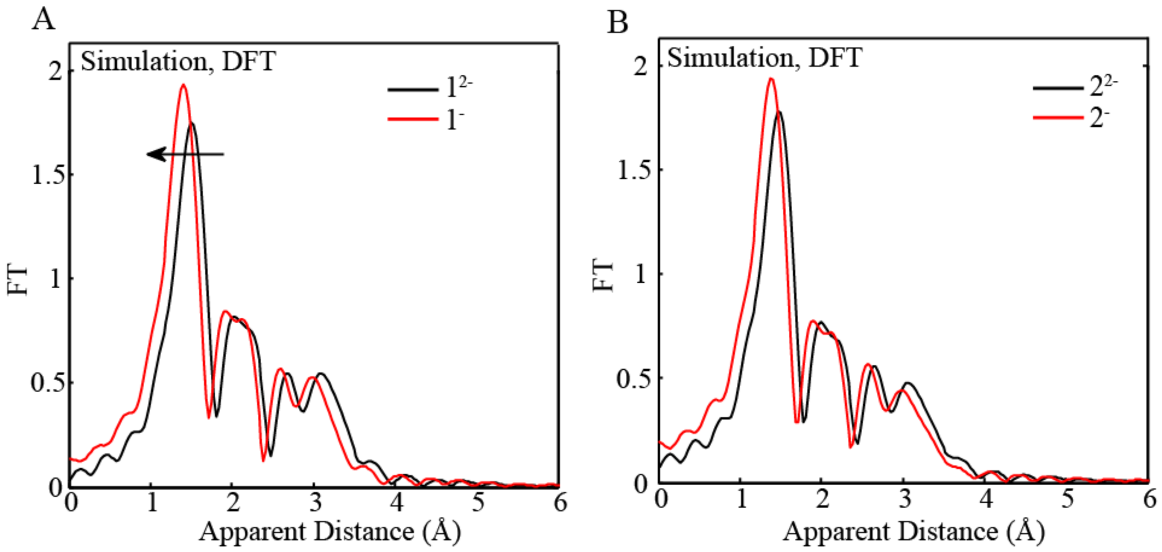


Figure S17. Simulated Fourier transforms using DFT optimized coordinates as input of k^2-weighted Cu EXAFS of: A. **1**$^{2-}$ (black) and **1**$^{-}$ (red) in acetonitrile, B. **2**$^{2-}$ (black) and **2**$^{-}$ (red) in acetonitrile.

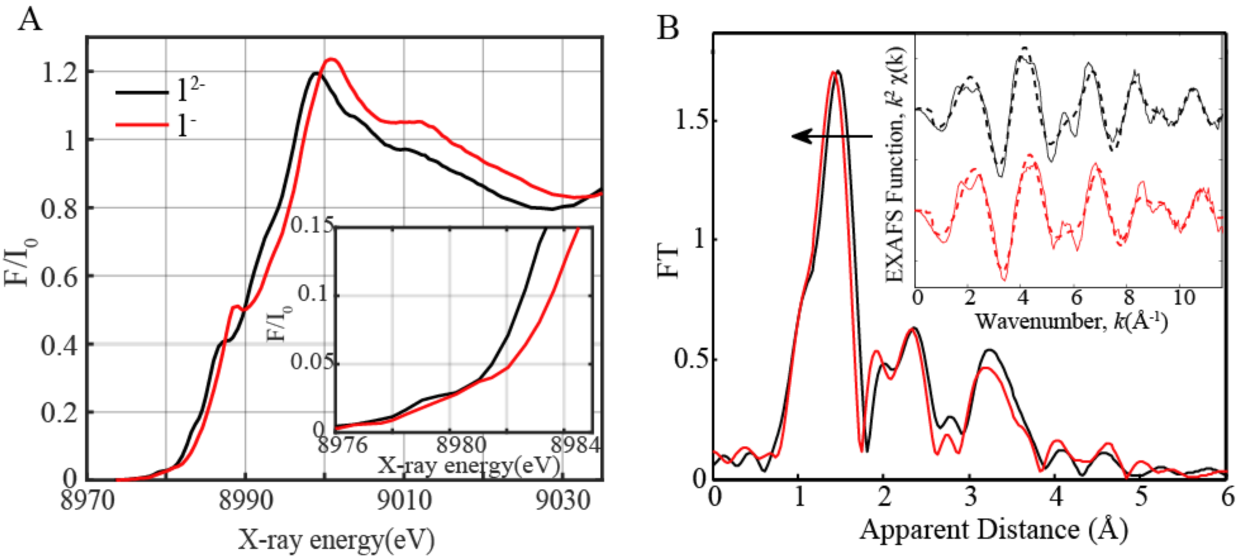


Figure S18. A, Normalized Cu K-edge XANES of $\mathbf{1}^{2-}$ (black) and $\mathbf{1}^{-}$ (red) in MeCN. Inset: Zoom-in of the pre-edge regions. B, Experimental Fourier transforms of k^2-weighted Cu EXAFS of $\mathbf{2}^{2-}$ (black) and $\mathbf{2}^{-}$ (red) in MeCN.

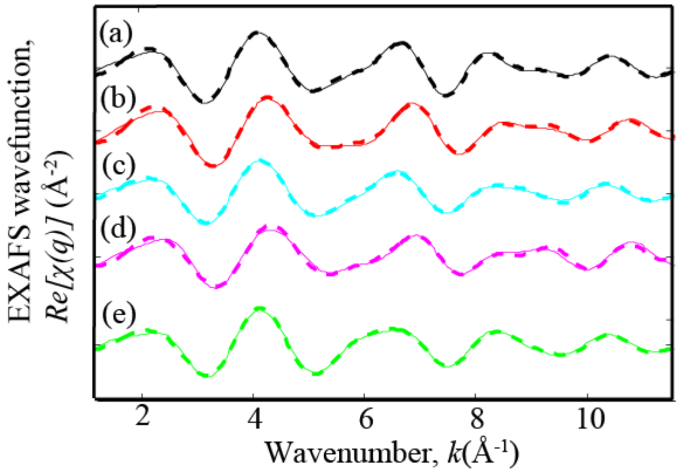


Figure S19. Back Fourier transformed experimental (solid lines) and fitted (dashed lines) Re[χ(q)](Å^{-2}) for $\mathbf{1}^{2-}$ (a), $\mathbf{1}^{-}$ (b), $\mathbf{2}^{2-}$ (c), $\mathbf{2}^{-}$ (d), **G-2**$^{2-}$ (e)**.**

Table S2. EXAFS summary of fits

Sample	Fit	Peak	Shell,N	R, Å	E^0	ss.^{2} (10-3)	R-factor	Reduced Chi-square
1^{2-} in CH_3CN	1	I	Cu-N,4	1.94	0.87	2.8	0.0026	104
	2	I,II	Cu-N,4 Cu-C,5 Cu-C,12	1.94 2.75 3.01	0.83	3.0 2.4 3.7	0.0046	87
1^{-}in CH_3CN	3	I	Cu-N,4	1.88	1.1	3.7	0.0015	35
	4	I,II	Cu-N,4 Cu-C,6 Cu-C,12	1.88 2.69 2.94	0.75	4.0 6.1 3.5	0.0055	60
2^{2-} in CH_3CN	5	I	Cu-N,4	1.94	0.24	3.9	0.0027	26
	6	I,II	Cu-N,4 Cu-C,5 Cu-C,12	1.93 2.74 3.02	-0.33	4.0 12.1 1.7	0.0031	14
2^{-} in CH_3CN	7	I	Cu-N,4	1.87	0.33	5.2	0.0079	43
	8	I,II	Cu-N,4 Cu-C,6 Cu-C,12	1.86 2.66 2.92	-0.73	5.5 11.5 5.8	0.0097	24
G-2^{2-}	9	I	Cu-N,4	1.96	0.10	3.2	0.0043	52
	10	I,II	Cu-N,4 Cu-C,6 Cu-C,12	1.95 2.67 2.98	-1.9	3.5 10.5 0.1	0.0038	21
G-2^{2-} after controlled potential electrolysis (CPE)	11	I	Cu-N,4	1.95	-0.5	3.5	0.0034	30
	12	I,II	Cu-N,4 Cu-C,6 Cu-C,12	1.94 2.65 3.00	-3.0	3.6 13.0 1.5	0.0041	17

Table S3. Metric parameters obtained for complexes **1**$^{2-}$, **1**$^{-}$ in MeCN, **2**$^{-}$, **2**$^{2-}$ in MeCN, **G-2**$^{2-}$, **G-2**$^{2-}$ after CPE

Species, Fit number in Table S2	**EXAFS Shell:** **N x distance in Å**	**DFT optimized coordinates for the Cu-N atoms within the 1st coordination shell, (Å)**
1^{2-} in CH_3CN, **fit 2**	Cu-N: 4 x 1.94 Cu-C: 5 x 2.75 Cu-C: 12 x 3.01	Cu-N: 1.98, 1.98, 2.01, 2.01
1^{-} in CH_3CN, **fit 4**	Cu-N: 4 x 1.88 Cu-C: 6 x 2.69 Cu-C: 12 x 2.94	Cu-N: 1.87, 1.88, 1.91, 1.91
2^{2-} in CH_3CN, **fit 6**	Cu-N: 4 x 1.93 Cu-C: 5 x 2.74 Cu-C: 12 x 3.02	Cu-N: 1.96, 1.96, 1.98, 1.98
2^{-} in CH_3CN, **fit 8**	Cu-N: 4 x 1.86 Cu-C: 6 x 2.66 Cu-C: 12 x 2.92	Cu-N: 1.86, 1.86, 1.90, 1.90
G-2^{2-}, **fit 10**	Cu-N: 4 x 1.95 Cu-C: 6 x 2.67 Cu-C: 12 x 2.98	Cu-N: 1.96, 1.96, 1.97, 1.98
G-2 $^{2-}$ after CPE, **fit 12**	Cu-N: 4 x 1.94 Cu-C: 6 x 2.65 Cu-C: 12 x 3.00	

4. Electrochemistry

Homogeneous phase

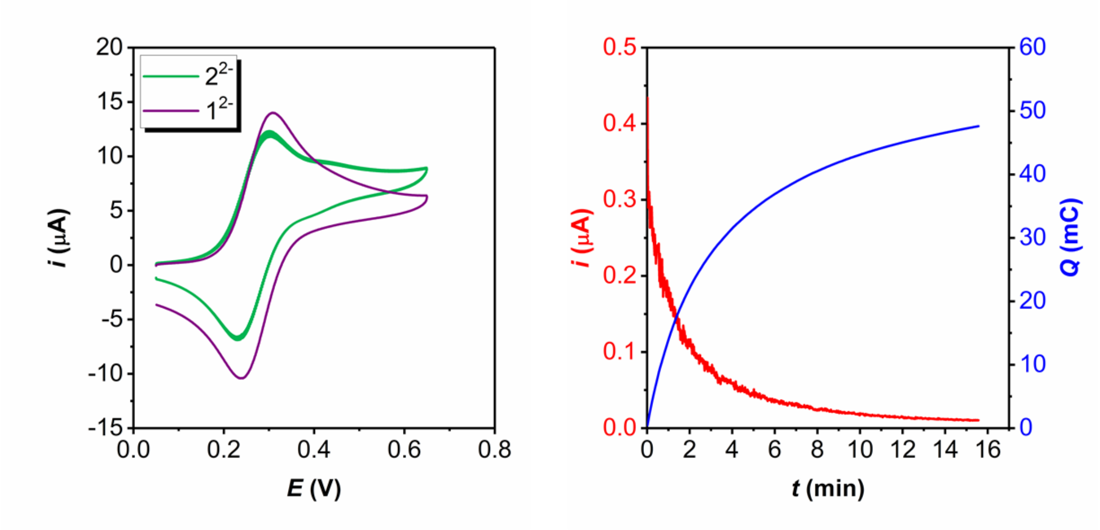


Figure S20. (Left) CVs of an acetonitrile solution containing 1 mM of **1**$^{2-}$ (purple) and **2**$^{2-}$ (green) with 0.1 M of tetrabutylammonium hexafluorophosphate. GC working electrode was employed and the scan rate was set to 100 mV/s. (Right) Controlled Potential Electrolysis (CPE) at 0.55 V in 1mM **2**$^{2-}$ acetonitrile solution containing 0.1 M of tetrabutylammonium hexafluorophosphate. Large surface Pt mesh was used as both working and counter electrode. A two-compartment cell was employed with one compartment containing the complex solution and the other a blank solution. Total charged passed and the end of the bulk corresponds to a 1 e^{-} oxidation process.

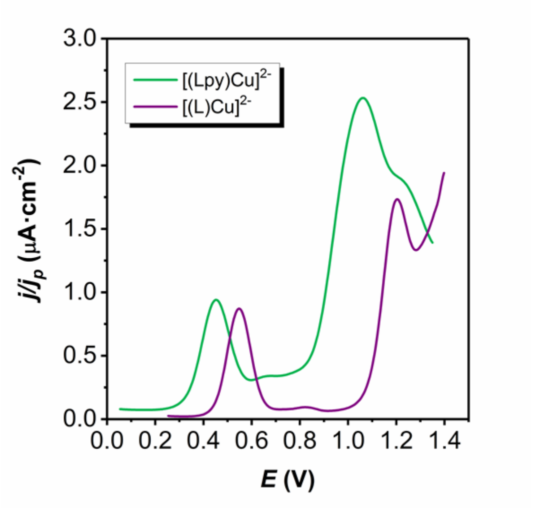


Figure S21. DPVs of 1mM **1**$^{2-}$ (purple) and **2**$^{2-}$ (green) in phosphate buffer at pH 12 (0.1 M of ionic strength), using GC working electrode and 100 mV/s of scan rate.

Homologue systems in homogeneous phase

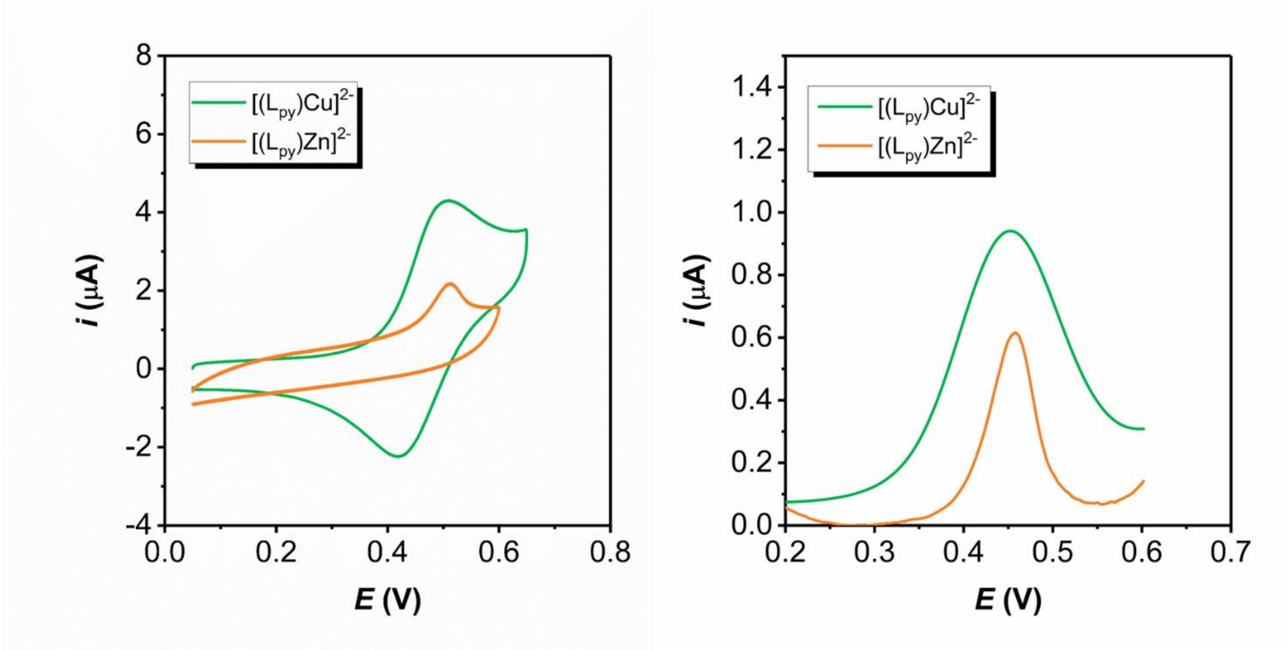


Figure S22. (Left) Background corrected CVs at 100 mV·s^{-1} and (Right) DPVs of [(L$_{py}$)Cu]$^{2-}$ (1mM) and its homologue [(L$_{py}$)Zn]$^{2-}$ (0.5mM) in phosphate buffer at pH 12 with 0.1 M of ionic strength.

The coincidence of the redox potentials at 0.45 V for the Cu and Zn complexes indicates that it is a ligand based transformation since Zn is redox inactive transition metal.

Heterogeneous phase

Normalization procedure:

We found that for similarly prepared electrodes, the charging current (i_c) of the double-layer was different when doing CVs under the same conditions (Figure S23, left). This means that the nonfaradaic processes were different and therefore, they affect in a different way to the intensity of the faradaic processes. The i_c depends on the scan rate and the capacitance of the double-layer according to equation S5. The capacitance of the double-layer in turns depends on the specific capacitance of the material, C_s, and the electroactive surface area, ECSA, as shown in equation S6. Since the scan rate was equal for all the CVs performed it can be considered constant, likewise the specific capacitance because we are using same materials for all the electrodes. Then, the different ECSA of the electrodes is the only responsible for the different charging current observed. This is mainly due to the relative hydrophobicity of the graphene material, since some little air bubbles remained in the electrode-solution interphase and lead to different ECSA, *i.e.* different current densities for homologue electrodes.

$$i_c = \nu \cdot C_{DL} \tag{S5}$$

$$C_{DL} = ECSA \cdot C_s \tag{S6}$$

$$i_c \propto ECSA \tag{S7}$$

Due to the difficulties to control the ECSA as aforementioned, all the CVs were normalized in order to counter the differences in the resulting charging intensity. For electrodes with equal ECSA, the i_c should be similar according to equation S7. Then dividing the intensity from the CV of each electrode by the value of its charging intensity i_c, we can obtain CVs with equivalent i_c and thus equivalent ECSA, removing the influence of the nonfaradaic processes. The value of the i_c was obtained from a nonfaradaic region of the CV, such as the intensity at 0.3 V, far enough from the faradaic processes. This normalization procedure finally allows us to compare fairly the CVs of different electrodes (Figure S23).

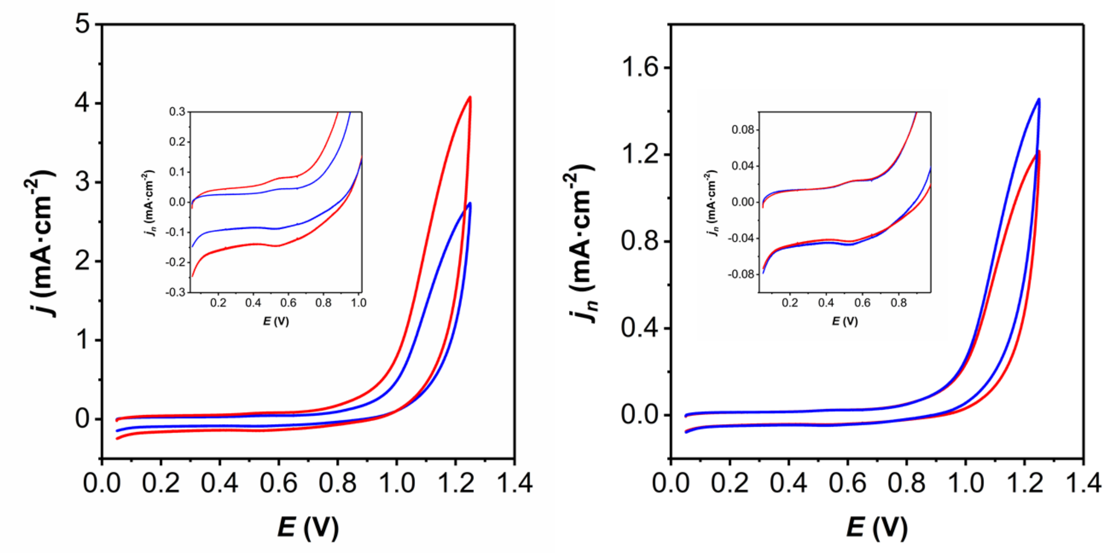


Figure S23. (Left) CVs and (Right) normalized CVs at 50mV·s^{-1} of two different **G-2**$^{2-}$ in phosphate buffer at pH 12 with 0.1 M of ionic strength. In the non-normalized CVs, the charging current and thus the catalytic current are very different when comparing both electrodes. After normalization, both electrodes present equal charging current and thus very close catalytic activity.

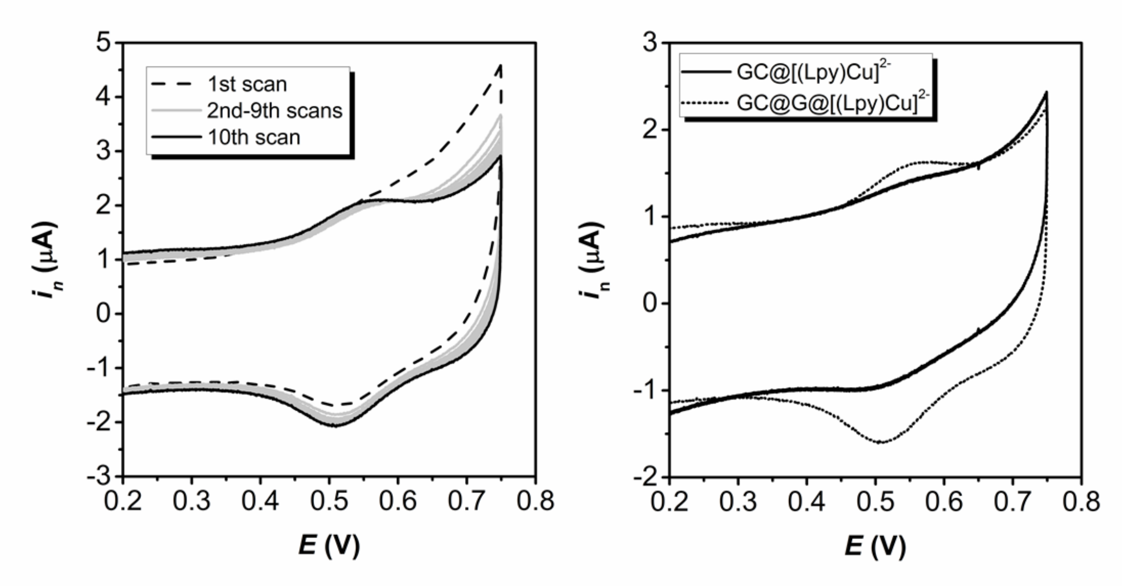


Figure S24. (Left) Consecutive CVs of **G-2**$^{2-}$ hybrid electrodes in phosphate buffer at pH 12 (0.1 M of ionic strength), at 50 mV·s^{-1} of scan rate. In the 10th scan, a stable peak current is obtained. (Right) CVs of **2**$^{2-}$ anchored on bare GC disk electrode (solid line) and on graphene over GC disk electrode (dotted line) in phosphate buffer at pH12 at 50 mV·s^{1}.

After repeated CVs (10th scans), the anodic and cathodic intensities increase up to a stationary value, indicating that more active material is being exposed (Figure S24, left). The reason could come from some reorganization promoted by the hydrophobic character of the graphene. Therefore, before every electrochemical measurement, the electrodes were subjected to 10 previous scans.

Bare glassy carbon electrodes were also used (Figure S24, right) as supporting material by soaking them overnight into a 1mM catalyst solution in methanol followed by washing with fresh methanol. The so-prepared electrodes showed much less catalyst concentration in comparison with the graphene modified electrodes due to its lower surface and thus were discarded for further analysis.

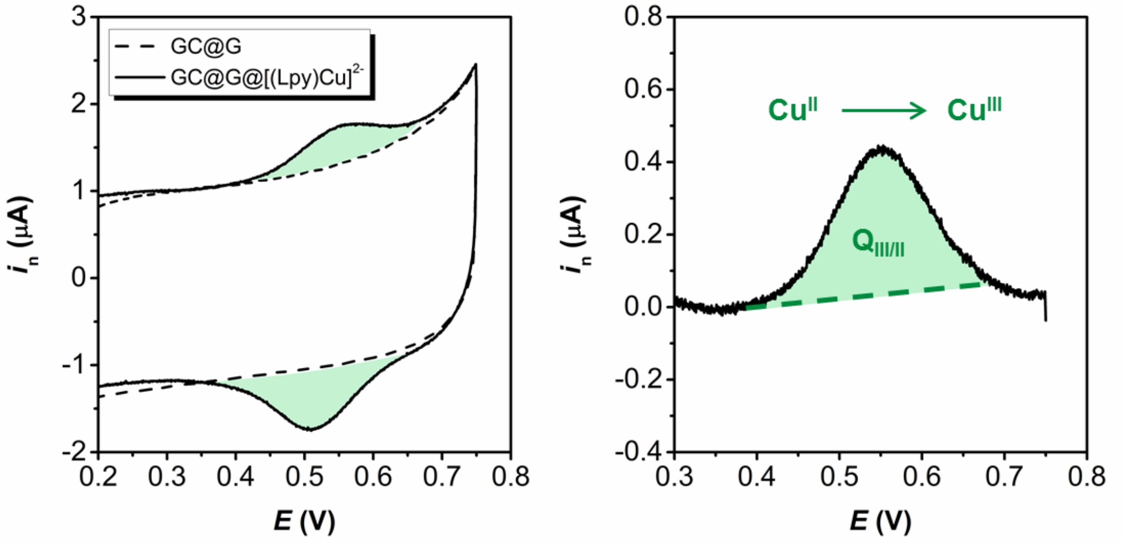


Figure S25. (Left) CVs of **G-2**$^{2-}$ hybrid electrodes (solid line) and unmodified graphene (dashed line) in phosphate buffer at pH 12 (0.1 M of ionic strength), at 50 mV/s of scan rate. The green regions represent the charge passed due to the oxidation and reduction of the complex on the electrode. (Right) Background corrected LSV of the hybrid electrode **G-2**$^{2-}$ in the same conditions as before.

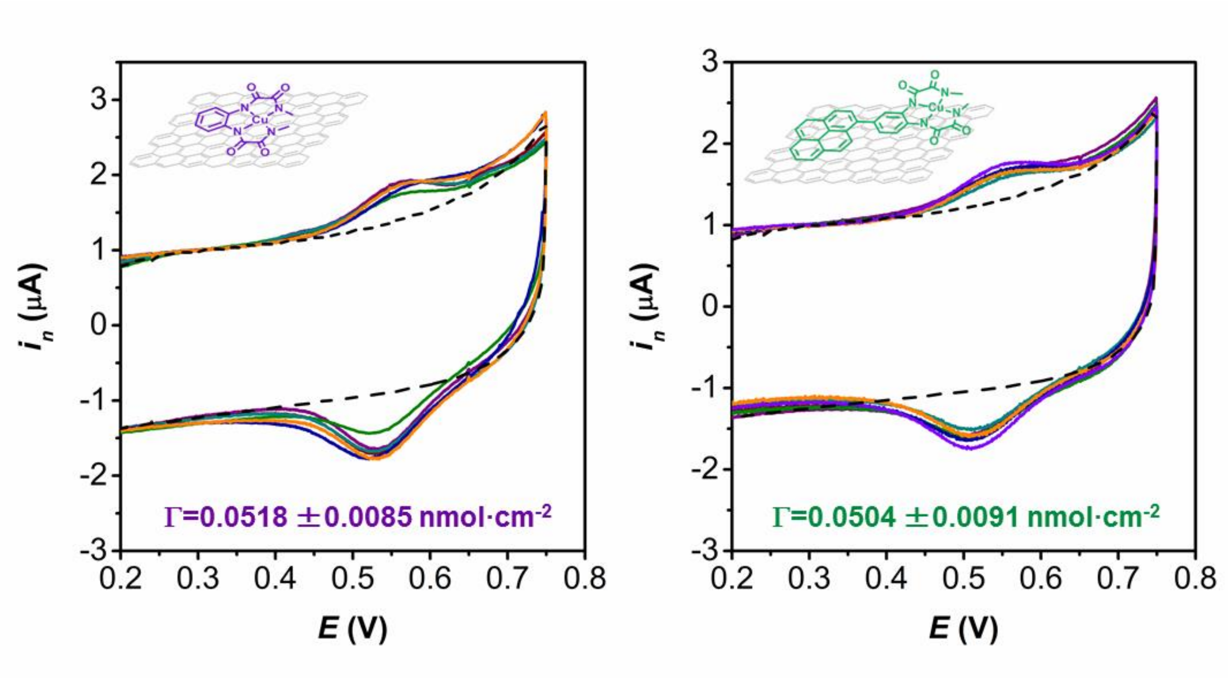


Figure S26. CVs of **G-1**$^{2-}$ (left) and **G-2**$^{2-}$ (right) hybrid electrodes (solid lines) and unmodified graphene (dashed line) in phosphate buffer at pH 12 (0.1 M of ionic strength), at 50 mV/s of scan rate. The surface coverage, Γ, was calculated from the charge integrated under the background corrected oxidation peak, averaged over five replicates.

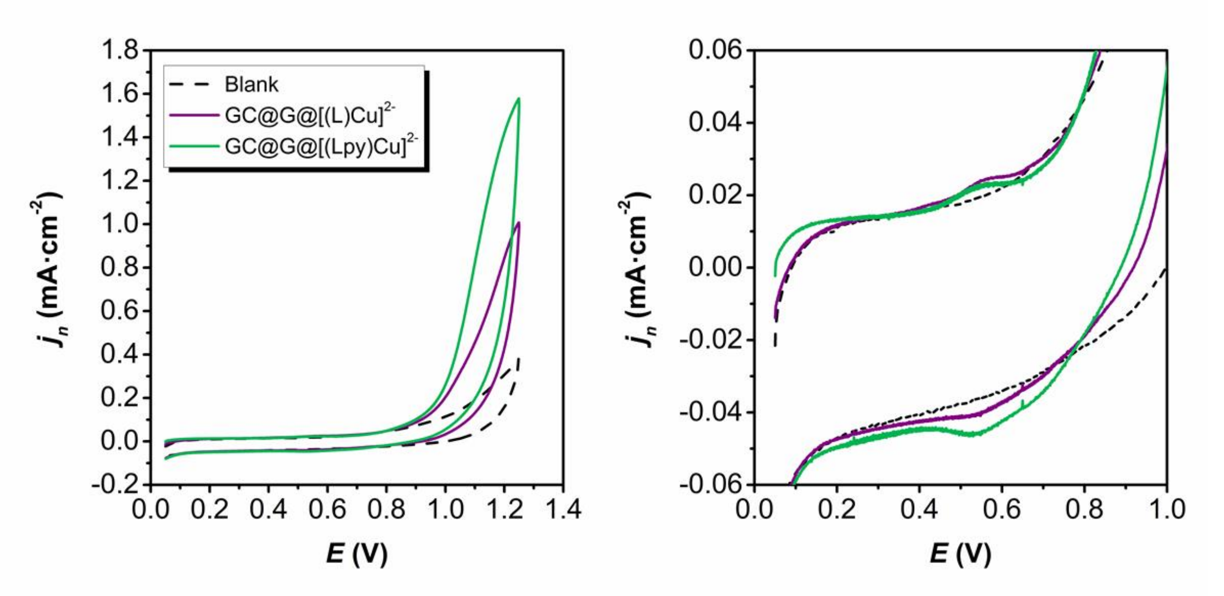


Figure S27. (Left) CV at 50mV·s^{-1} of **G-1**$^{2-}$, **G-2**$^{2-}$ and bare graphene over GC in phosphate buffer at pH 12 with 0.1 M of ionic strength. The coverage was calculated to be 0.043 and 0.044 nmol·cm^{-2} for. **G-1**$^{2-}$ and **G-2**$^{2-}$ respectively. (Right) Zoom of the reversible wave region from the previous CVs.

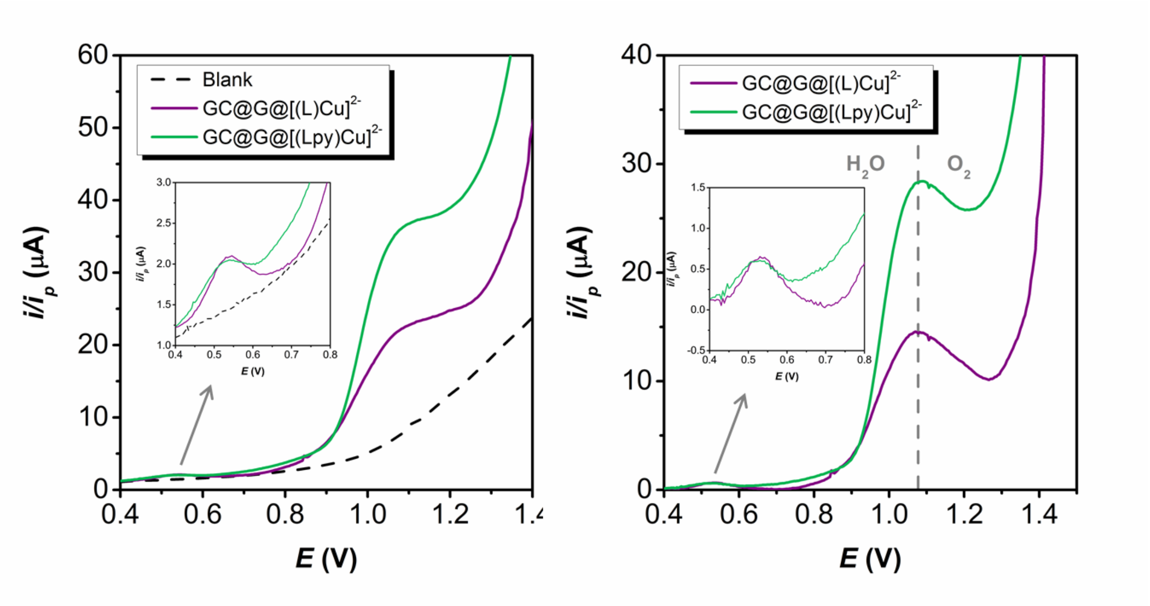


Figure S28. DPVs (left) and background subtracted DPVs (right) of **G-1**$^{2-}$, **G-2**$^{2-}$ and bare graphene over GC in phosphate buffer at pH 12 with 0.1 M of ionic strength. The coverage was calculated to be 0.043 and 0.044 nmol·cm^{-2} for. **G-1**$^{2-}$ and **G-2**$^{2-}$ respectively. The insets show a zoom of the one-electron wave region.

5. Kinetic analysis by FOWA

Foot of the wave analysis (FOWA) was applied according to the procedures described in the literature.[6,10,11,12] For homogeneous water oxidation catalysis, the following expression is deducted for a mechanism where just one catalyst molecule is involved and assuming that the rds is the last electron-transfer step coupled to a chemical reaction:

$$\frac{i}{i_d} = \frac{n \cdot 2.24 \cdot \sqrt{\frac{R \cdot T}{F \cdot V} \cdot k_{obs}}}{1 + \exp\left[\frac{F}{R \cdot T}(E^0_{cat} - E)\right]} \qquad \text{(S8)}$$

In the case of heterogeneous water oxidation with equivalent mechanism, the equation changes:

$$\frac{i}{q_d} = \frac{k_{obs}}{1 + \exp\left[\frac{F}{R \cdot T}(E^0_{cat} - E)\right]} \qquad \text{(S9)}$$

where E^0_{cat} is the standard potential for the catalysis-initiating redox couple (calculated from DPV), i is the current intensity, i_d is the current intensity associated with the Cu^{III}/Cu^{II} couple, q_d is the charge under the oxidative peak of the reversible wave Cu^{III}/Cu^{II}, n is the number of electrons involved in the catalytic cycle (4 e^- in water oxidation), F is the faraday constant, v is the scan rate, k_{obs} is defined as "$k_{cat} \cdot C^o_A$" where C^o_A is the concentration of substrate (55.56 M for water), and R is 8.314 $J \cdot mol^{-1} K^{-1}$. Background corrected LSVs of the catalysts are shown in Figure S29-S32. Now, k_{obs} can be extracted from the plot of i_{cat}/i_d *vs*. $1/(1+\exp[(F/RT)(E^o_{cat}-E)])$.

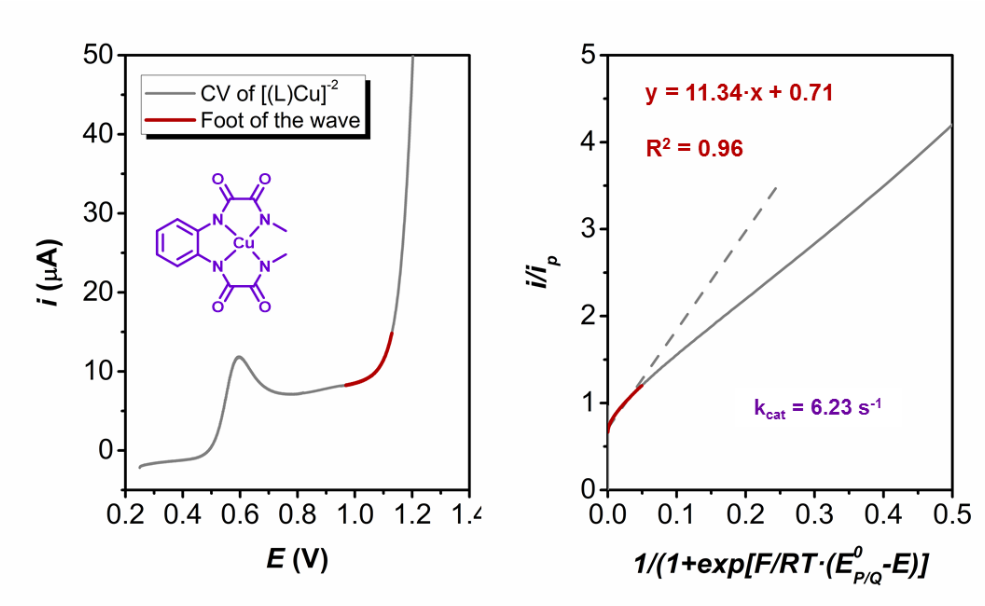


Figure S29. Background corrected LSV of 1mM $\mathbf{1}^{2-}$ in phosphate buffer at pH 12 (0.1 M of ionic strength), using GC working electrode and 100 mV/s of scan rate. Foot of the wave region is highlighted in red color. (Right) Foot of the wave analysis (FOWA) by plotting i_{cat}/i_d *vs.* $1/(1+\exp[(F/RT)(E^o_{cat}-E)])$.

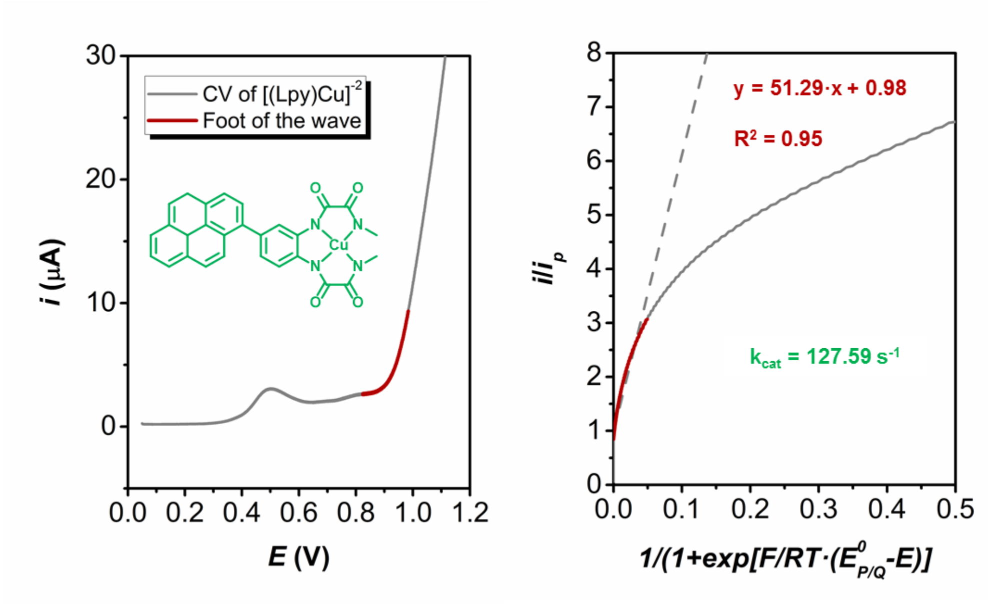


Figure S30. Background corrected LSV of 1mM $\mathbf{2}^{2-}$ in phosphate buffer at pH 12 (0.1 M of ionic strength), using GC working electrode and 100 mV/s of scan rate. Foot of the wave region is highlighted in red color. (Right) Foot of the wave analysis (FOWA) by plotting i_{cat}/i_d *vs.* $1/(1+\exp[(F/RT)(E^o_{cat}-E)])$.

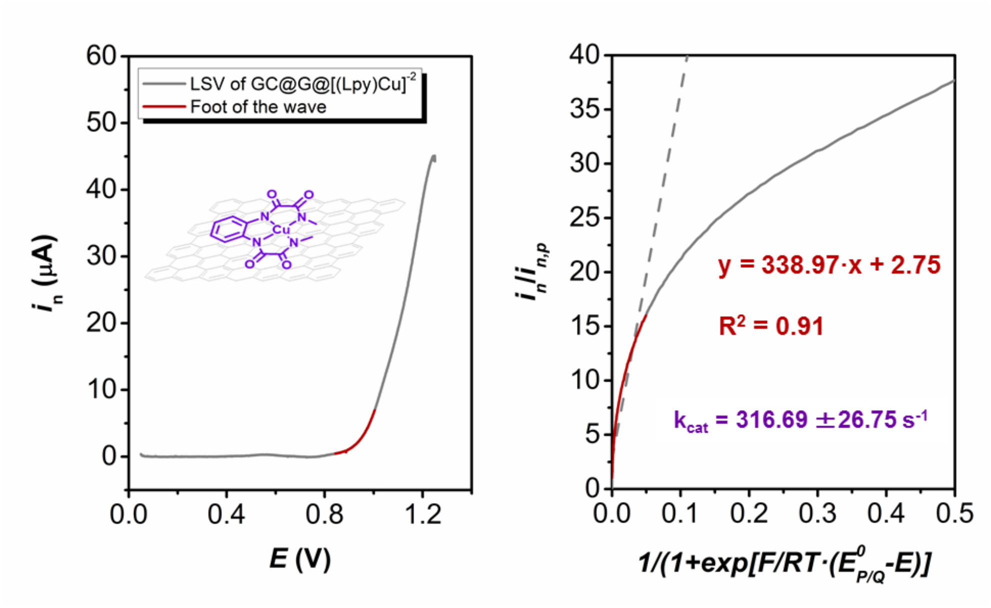


Figure S31. Background corrected LSV of a hybrid electrode **G-1^{2-}** in phosphate buffer at pH 12 (0.1 M of ionic strength), at 50 mV/s of scan rate. Foot of the wave region is highlighted in red color. (Right) Foot of the wave analysis (FOWA) by plotting i_{cat}/i_d *vs*. 1/(1+exp[(F/RT)(E^o_{cat}-E)]). The kinetic constant, k_{cat}, was obtained as the average from analysis to 5 different electrodes.

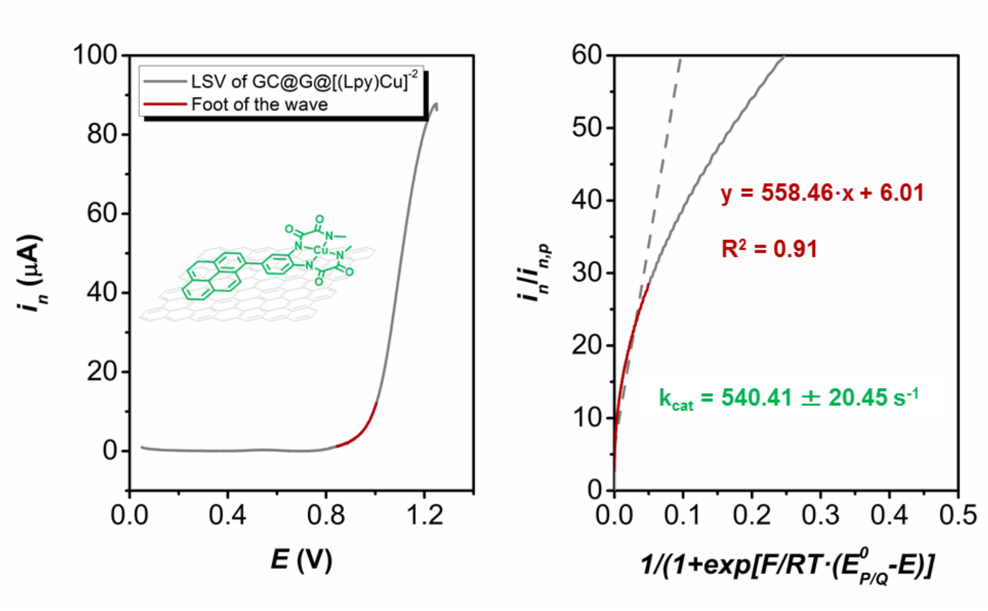


Figure S32. Background corrected LSV of a hybrid electrode **G-2^{2-}** in phosphate buffer at pH 12 (0.1 M of ionic strength), at 50 mV/s of scan rate. Foot of the wave region is highlighted in red color. (Right) Foot of the wave analysis (FOWA) by plotting i_{cat}/i_d *vs*. 1/(1+exp[(F/RT)(E^o_{cat}-E)]). The kinetic constant, k_{cat}, was obtained as the average from analysis to 5 different electrodes.

6. Bulk electrolysis, O2 evolution and stability

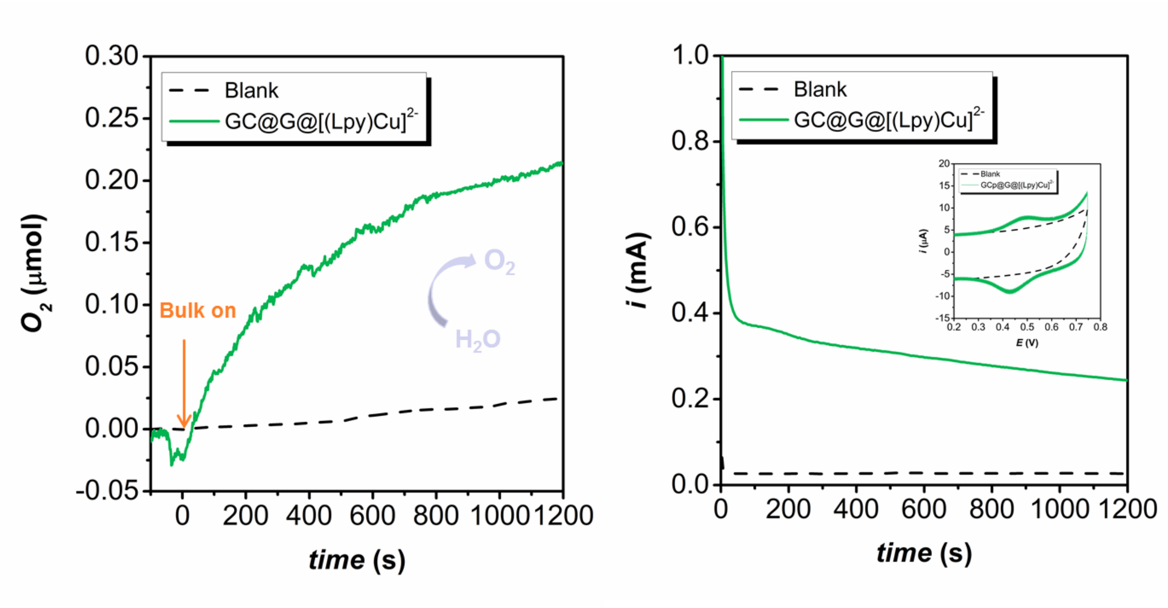


Figure S33. (Left) Oxygen evolution detected by Clark electrode during a CPE experiment using a **G-2**$^{2-}$ hybrid electrode (green solid line) and a bare graphene GC electrode (dashed black line). A GC plate was used in this case as supporting electrode to increase the total amount of catalyst. (Right) CPE at 1.25 V performed during the oxygen evolution experiment in a pH 12 solution using the same electrodes, with a Pt mesh counter electrode and an Ag/AgCl reference electrode.

*The inset show a CV of both electrodes in the reversible wave region, and the charge under the oxidative peak was used to determine the catalyst loading that turned out to be 0.0394 nmol·cm^{-2}. The resulting TON from the measured O_2 was 5388.

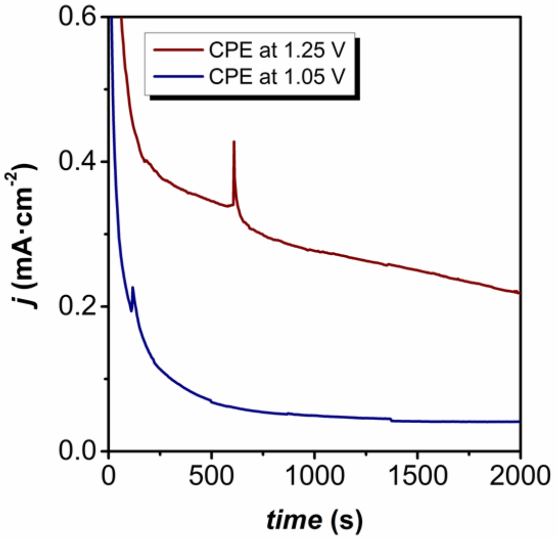


Figure S34. CPE at 1.25 V (red) and 1.05 V (blue) performed with different **G-2**$^{2-}$ hybrid electrodes in a pH 12 solution, with a Pt mesh counter electrode and a MSE reference electrode. GC disk (3mm) supporting electrode was used for the hybrid electrode. At higher potentials, degradation of the electrode appears to be faster although higher intensities are reached.

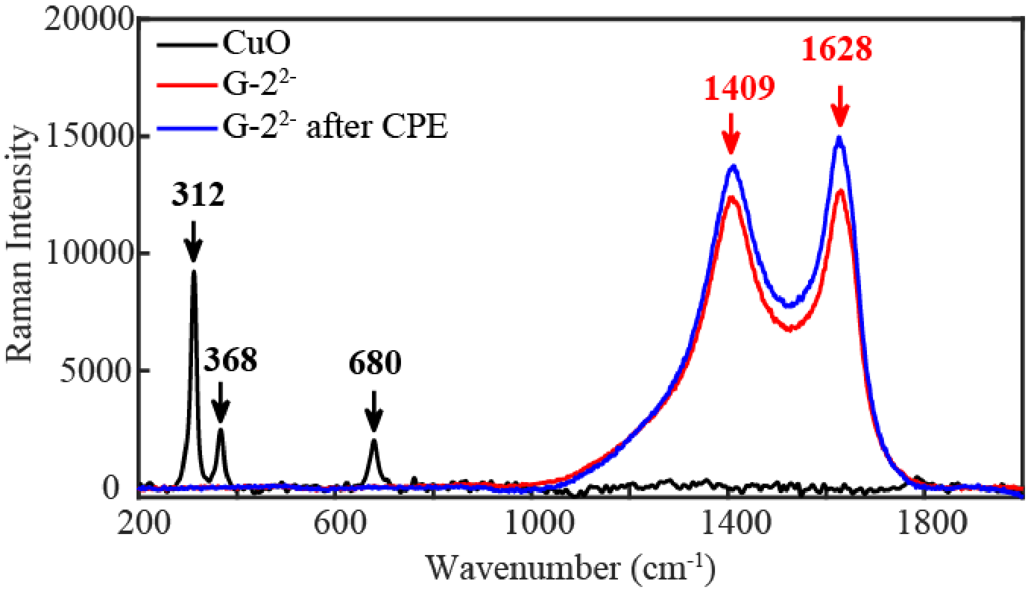


Figure S35. Resonance Raman with excitation at 532 nm of CuO solid, **G-2**$^{2-}$ and **G-2**$^{2-}$ after CPE recorded at room temperature.

Raman measurements of CuO, hybrid materials **G-2**$^{2-}$ and **G-2**$^{2-}$ after controlled potential electrolysis (at 1.25 V) were carried out and are shown in Figure S35. As shown from Raman measurements, the characteristic Raman features of CuO at 312 cm^{-1}, 368 cm^{-1} and 680 cm^{-1} were absent in the hybrid materials confirming lack of any traces of CuO. Only the Raman peaks at 1409 cm^{-1} and 1628 cm^{-1} corresponding to that of graphene were observed in **G-2**$^{2-}$ and **G-2**$^{2-}$ after CPE.[13]

7. RRDE for O_2 and H_2O_2 generation assessment

The collection efficiency of the RRDE, N, was previously determined by using the redox couple $Fe(CN)_6^{4-}$ / $Fe(CN)_6^{3-}$ as well defined one-electron transfer process. We prepared a 1 mM solution of the reduced ferrocyanide $K_4Fe(CN)_6$ in pH 12 solution of phosphate buffer, and it was oxidized during a LSV at 10 $mV\cdot s^{-1}$ in the disk electrode to ferricyanide $Fe(CN)_6^{3-}$. This last was detected at the Pt ring by performing a CPE at 0.05 V vs NHE to yield the reduction to the initial ferrocyanide. The collection efficiency was determined by the rate between the intensity in the ring and the intensity in the disk electrodes when they reach stable values at the plateau, i_{ring}/i_{disk}. The efficiency was found to be 0.4. Results are shown in Figure S36 for 1600 rpm.

The oxygen reduction reaction was also studied at the Pt ring electrode under same experimental conditions to analyze the number of electrons involved, according to procedure described in the literature.[14] For that, three different solutions were prepared at pH 12 with phosphate buffer: N_2 saturated, air saturated and O_2 saturated. Then a LSV at 10 $mV\cdot s^{-1}$ was performed through negative potentials to reduce the dissolved oxygen, that was detected by an increase in the ring current. In N_2, no current was detected as expected, while in air and O_2 current increased when the potential was negative enough to reduce the oxygen. In those last cases, the current reached an approximately stable signal at -0.6 V vs NHE. With these stable current values, the apparent number of electrons (n_{app}) involved in the reduction of oxygen can be calculated from the Levich equation for the rotating ring:

$$\left|i_{ring}\right| = 0.62 \cdot n_{app} \cdot F \cdot \pi \cdot (r_o^3 - r_m^3)^{2/3} \cdot D^{2/3} \cdot \omega^{1/2} \cdot \nu^{-1/6} \cdot [O_2] \qquad \text{(S10)}$$

F is the Faraday constant, r_o and r_m are the outer and middle radio that define the Pt geometry, D is the Difussion coefficient for oxygen in water calculated to be $2.52\cdot10^{-5}$ $cm^2\cdot s^{-1}$ with Wilke's correlation,[15] ω is the rotation rate in $rad\cdot s^{-1}$, ν is the kinematic viscosity of the solution that is $0.0085 cm^2\cdot s^{-1}$ and $[O_2]$ is the concentration of oxygen in the solution calculated to be $1.28\cdot10^{-6}$ $mol\cdot cm^{-3}$ for O_2 saturated solution and $2.67\cdot10^{-7}$ $mol\cdot cm^{-3}$ for air saturated solution.[16] With all these values, the apparent number of electrons involved in the oxygen reduction turned out to be *ca.* 2 at 1600 rpm for both air and oxygen saturated solutions, which means reduction of O_2 to H_2O_2 in pH 12 at -0.6 V vs NHE. Those results are shown in Figure S36.

Collection efficiency and n_{app} calculation for O_2 evolution

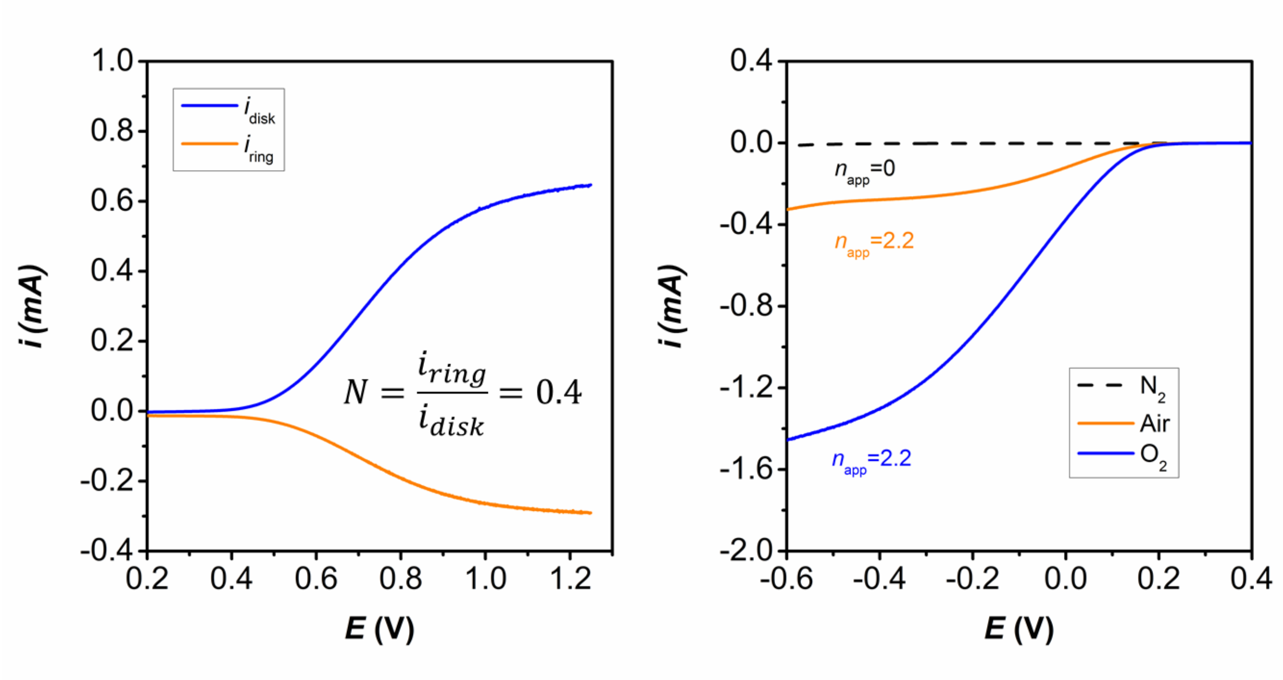


Figure S36. (Left) RRDE experiment using 1 mM of ferrocyanide $K_4Fe(CN)_6$ in pH 12 solution of phosphate buffer (0.1 M ionic strength). In the disk electrode, a LSV was performed at 10 mV·s^{-1} (blue) to oxidize to ferricyanide $Fe(CN)_6^{3-}$. In the ring electrode, a CPE was performed at 0.05 V to yield the reduction to the initial ferrocyanide $Fe(CN)_6^{4-}$ (orange line). The rotation speed was 1600 rpm. (Right) LSVs performed at 10 mV·s^{-1} with the Pt ring electrode in three different pH 12 solutions with phosphate buffer: N_2 saturated (black dashed line), air saturated (orange solid line) and O_2 saturated (blue solid line).

Catalytic O_2 evolution by hybrid catalysts ***G-1***$^{2-}$ *and* ***G-2***$^{2-}$

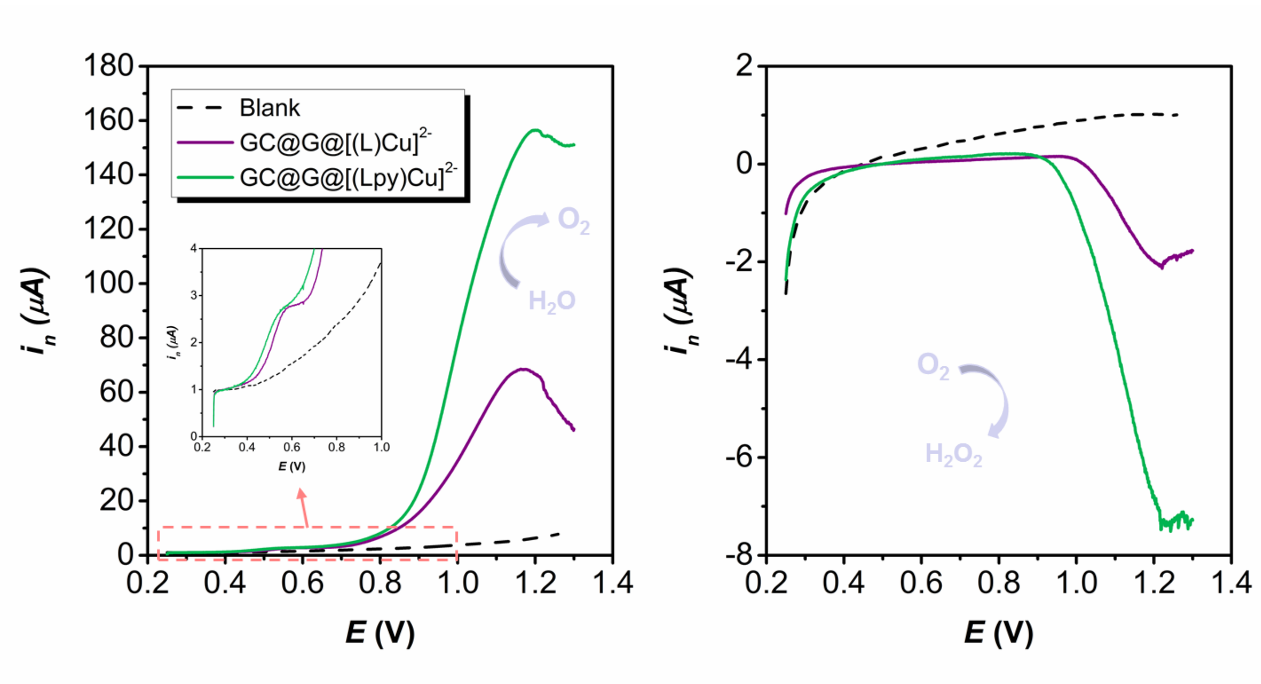


Figure S37. (Left) LSV of bare graphene (blank), **G-1**$^{2-}$ and **G-2**$^{2-}$ electrodes using RRDE in phosphate buffer at pH 12 (0.1 M of ionic strength) under nitrogen atmosphere and at 1600 rpm. (Right) Simultaneous oxygen reduction at Pt ring of the RRDE by CPE at -0.35 V.

In order to further characterize the catalytic activity toward water oxidation, a Rotating Ring Disk Electrode (RRDE) was used in a similar way as described by Jaramillo et al. for heterogeneous catalysts.[14] The graphene loaded with the catalyst was deposited on the surface of the glassy carbon disk electrode, which was used as the working electrode to perform the water oxidation. To evaluate the catalytic activity, the disk electrode was subjected to a CV experiment in pH 12 at a slow scan rate (10 mV/s) in the potential range from 0.25 V to 1.3 V while the whole RRDE was rotating at a constant rate of 1600 rpm under nitrogen atmosphere. The oxygen produced in this electrode moves to the surrounding Pt ring electrode due to the centrifugal force generated by the rotation. In this ring electrode, the oxygen is electrochemically detected by its reduction applying a constant potential of -0.35 V. The resulting data for both **G-1**$^{2-}$ and **G-2**$^{2-}$ (GC@G@[(L)Cu]$^{2-}$ and GC@G@[(L$_{py}$)Cu]$^{2-}$ respectively) compare to the blank (GC@G electrode) are represented in Figure S37, which shows the normalized intensity passed through the disk (left) and ring (right) electrode at every potential. As expected, when the disk reaches potentials 0.9-1.0 V, a huge catalytic current is observed leading to the formation of molecular oxygen that is then reduced in the ring electrode with the subsequent increase in the ring intensity. In the case of the blank, no oxygen was detected despite of the increase in the intensity, meaning that this current is due to electrode oxidation and degradation. From these experiments we can also obtain the Faradaic efficiency of the catalysts for water oxidation based on the relation between both disk and ring intensities, as shown in the equation below for a 2-e$^-$ reduction of oxygen to hydrogen peroxide:

$$\varepsilon = \frac{2 \cdot i_r}{i_d \cdot N} \tag{S11}$$

In this equation, N is the collection efficiency previously calculated, and i_d and i_r are the values taken from the top of the peaks, where the intensity reaches a pseudo-stationary value before it starts to decrease due to electrode oxidative degradation. The Faradaic efficiency ε was calculated as the average of three independent samples and for both systems was practically equal: 23.36% for **G-1**$^{2-}$ and 25.56% for **G-2**$^{2-}$. Those values are relatively low due to the extensive graphene oxidation in these conditions, as has also been observed previously in literature when carbon based electrodes are used.[14] This oxidation process could be complete releasing CO2 or partial, generating some oxygenated group in the surface of the electrode. In both cases, the morphological changes occurring in the surface would lead to catalyst leaching and thus the loose of the activity. The similarity in the efficiencies also supports this idea since both values, and thus the main degradation pathway, do not seem to depend on the catalyst architecture.

RDDE calibration for H_2O_2 detection

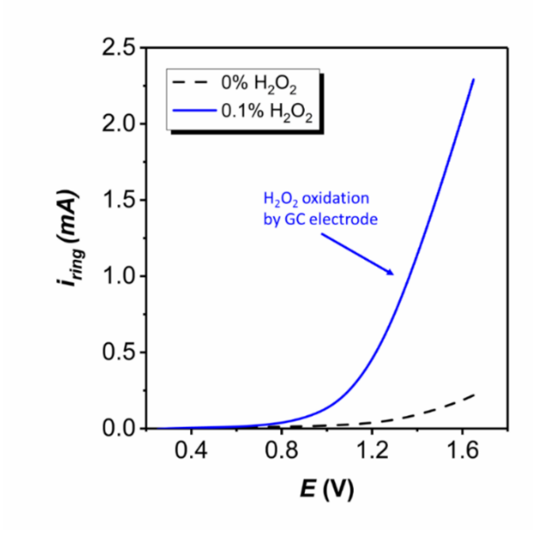


Figure S38. LSV of GC ring electrode in phosphate buffer at pH 12 (0.1 M of ionic strength) under nitrogen atmosphere and at 1600 r.p.m. in presence (solid blue line) and absence (dashed black line) of 0.1% H_2O_2. This shows that above 1.0 V the ring potential can already detect HOOH.

H_2O_2 detection during catalytic water oxidation

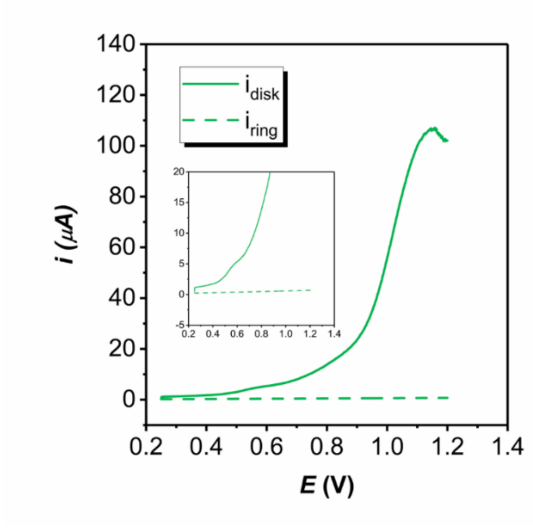


Figure S39. LSV of G-22- electrodes using RRDE in phosphate buffer at pH 12 (0.1 M of ionic strength) under nitrogen atmosphere and at 1600 r.p.m. The applied potential at the Ring is 1.45V. Intensity at the disk electrode is represented as a solid line while the intensity measured at the ring electrode is shown with dashed line. Inset shows a zoom at the 0-20 μA range. No significant current density is observed over the whole potential scan indicating the absence of HOOH. This methodology has also been applied to the study of O_2 reduction reaction.[17]

8. Comparison of relevant water oxidation catalysts

Table S4. Summary of the catalytic performance of some relevant water oxidation catalysts based on first row transition metals.

Entry	Catalyst	Overpotential, V	TOF_{max}, s^{-1}	TONs (based on)
1[tw]	G-2^{2-}	558	540	5300
2[6]	1^{2-}	708	6.2	1947
3[18]	[(bpy)Cu$(OH)_2$]	750	100	>30
4[19]	[(6,6′-bobp)Cu$(OH_2)_2$]	510	0.4	400
5[20]	[Cu$(pyalk)_2$]	520-580	0.7	>30
6[21]	[(dbzbpen)Cu(OH_2)]$^{2-}$	570	13.1	-
7[22]	[(2GH2−)Cu(H_2O)]	620	53	-
8[23]	[(Py_3P)Cu(OH)]$^{-}$	500	38	19
9[24]	Fe$(ClO_4)_3$	-	9.6	436
10[25]	[Co^{II}(qpy)$(OH_2)_2$]$^{2+}$	-	4	335

*tw: this work.

9. Computational Study

Computational Details

All calculations were carried out with the Gaussian09 (v. D.01) program package[26]. In the present work, we study two different systems, homogeneous and heterogeneous, which drastically differ in the number of atoms. Therefore, for practical reasons, we need to use two different methodologies to calculate them, with a full-QM methodology in the case of homogeneous one and a multiscale QM/MM method to study the heterogeneous system.

For the homogeneous system models, we employed Density Functional Theory (DFT) methodology. All the calculations were computed using B3LYP as functional including Grimme's empirical dispersion correction (B3LYP-D3).[27,28] The basis set was split, using 6-31+G(d) for C, N, O and H,[29] and LANL2TZ(f) for Cu (including the associated pseudopotential).[30,31] The solvation was considered implicitly using the SMD model[32], with either water (ε = 78.3553) or acetonitrile (ε = 35.688) as solvent as specified in the text. All geometry optimizations were computed in solution without symmetry restrictions. The nature of all computed stationary points was confirmed by vibrational frequency calculations. Free energy corrections were calculated at 298.15 K and 105 Pa pressure, including zero point energy corrections (ZPE). In addition, a correction term of 1.9 kcal/mol (at 298 K) was added when necessary to account for the standard state concentration of 1 M. Unless otherwise mentioned, all reported energy values are free energies in solution. The stability of the electronic states corresponding to the intermediates was confirmed by stability analysis of the wavefunction. This methodology was already benchmarked in previous works providing satisfactory results for this type of systems. [6,36] Once again, in the new system reported here the agreement with the experimental potentials is very good, confirming the validity of this methodology for copper water oxidation catalysis.

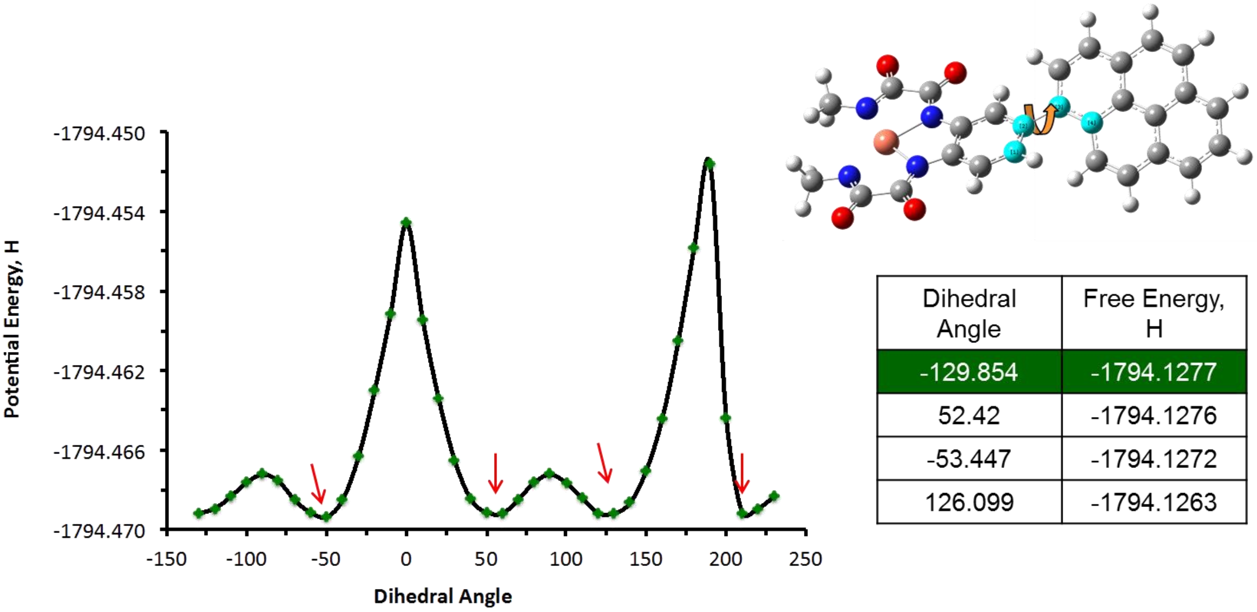
For the heterogeneous system, QuantumMechanics/MolecularMechanics (QM/MM) was applied using 2-layer ONIOM to model the anchoring architectures of both homogeneous catalysts on the graphene surface. For this model, a graphene layer was selected with a size big enough to avoid edge interactions with the catalyst (14x14 phenyl groups). The low-level layer was modeled with molecular mechanics, using the Universal Force Field (UFF), while high-level layer was computed using DFT methodology with M06 as functional, which has the dispersion correction intrinsically parameterized and was shown to reproduce as well as B3LYP-D3 this family of catalysts.[6,36] We changed the functional to avoid introducing empirical dispersion corrections, which can lead to errors in combination with MM calculation. For this layer, we selected as basis sets 6-31G(d) for C, N, O and H, and LANL2DZ(f) for Cu. We reduced the size of the basis set for technical reasons, since the computational cost when we introduced diffuse functions was too large for our system. The nature of stationary points was also confirmed by frequency analysis, with zero imaginary frequencies for all the points computed for heterogeneous system.

The electrochemical magnitudes were calculated from the free energies using the values of 4.28 V found in literature for the absolute potential of the standard hydrogen electrode[33] and-11.72 eV for the free energy of the proton in aqueous solution at pH=1.[34] The value for the free energy of the proton was translated to the experimental pH value of 12 by adding a correction term of -0.059*pH, following the same procedure as other authors.[35]

Cu(II) speciation in aqueous solutions at pH=12

Before calculations of the catalytic cycle intermediates, we analyzed first which is the species that is formed in aqueous solution after addition of $[(L_{py})Cu]^{2-}$.

Through rotation of the C-C bond between phenyl ring and pyrene group we can obtain several conformers that may be stable. Then we first scan the dihedral angle between those two groups in order to find the most stable conformer. We defined that dihedral angle with the atoms highlighted in blue shown in Figure S40. The most stable conformer turn out to be the one having a dihedral angle of about -130.



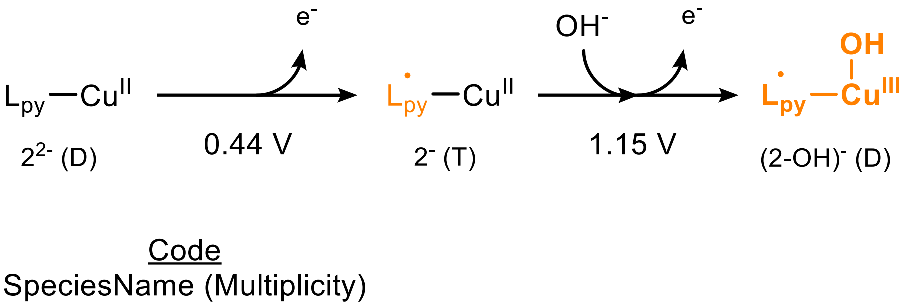
Dihedral Angle	Free Energy, H
-129.854	-1794.1277
52.42	-1794.1276
-53.447	-1794.1272
126.099	-1794.1263

Figure S40. Potential energy relaxed scan of the dihedral angle defined by the atoms in blue from the catalyst picture. The energies of each species are calculated in H. The table in the right part show the free energy in H of the four minima obtained from the scan.

Secondly, we analyzed the possibility of water or hydroxo coordination in the free apical positions. In all cases, the external molecules ended up forming hydrogen bonds with the nitrogen atoms of the ligand, what is consistent with the pH independency found for the Cu(II)/Cu(III) redox couple as well as with previous results using $[(L)Cu^{II}]^{2-}$ catalyst.[6,36]

Electrochemical activation of $[(L_{py})Cu]^{2-}$ catalyst

As can be deducted from the electrochemistry, water oxidation catalysis starts after two consecutive one-electron oxidations, first in the ligand and second in the metal center together with a hydroxo group coordination. These two redox processes have been computed and the resulting calculated potentials are in good agreement with the observed experimental ones: 0.44 V and 1.15 V vs 0.43 V and 1.06 V respectively (less than ±0.1 V deviation). The found sequence of oxidation was the same with a first oxidation in the ligand and a second oxidation in the metal center. The final formed species is a radical-Cu(III) complex with an unpaired electron highly delocalized mainly through the phenyl, pyrene and hydroxo groups and that is active toward O-O bond formation reaction. Probably due to the stabilization of the radical species through the delocalized π-orbitals, the redox potential for the ligand oxidation is much lower than in the unsubstituted catalyst $\mathbf{1}^{2-}$.



Scheme S3. Calculated mechanism for the electrochemical activation of the $[(L_{py})Cu]^{2-}$ catalyst. The values for the potentials correspond to the calculated ones.

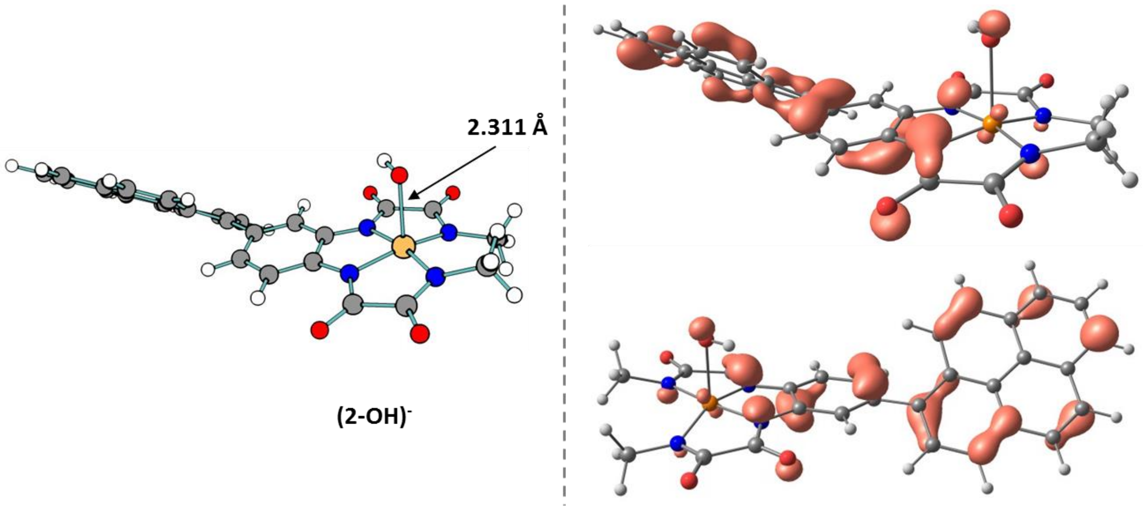


Figure S41. (Left) DFT optimized structure for the active species $[(L_{py})^{*}Cu^{III}(OH)]^{-}$, **(2-OH)**$^{-}$. (Right) Two different views of the SOMO representation for the active species.

O-O bond formation step

As found for 1^{2-} catalyst in previous work,[6,36] the mechanism for the O-O bond formation in 2^{2-} has been found to follow a Single Electron Transfer-Water Nucleophilic Attack (SET-WNA).[**42**] After the generation of $[(L_{py})^{*}Cu^{III}(OH)]^{-}$, **(2-OH)**$^{-}$, this species is highly oxidizing and susceptible to be attacked by an OH^{-} coming from the solution to the coordinated hydroxo group, yielding the O-O bond formation. In order to analyze this mechanism, we perform a relaxed scan studying the O-O distance as reaction coordinate, as shown in Figure S42.

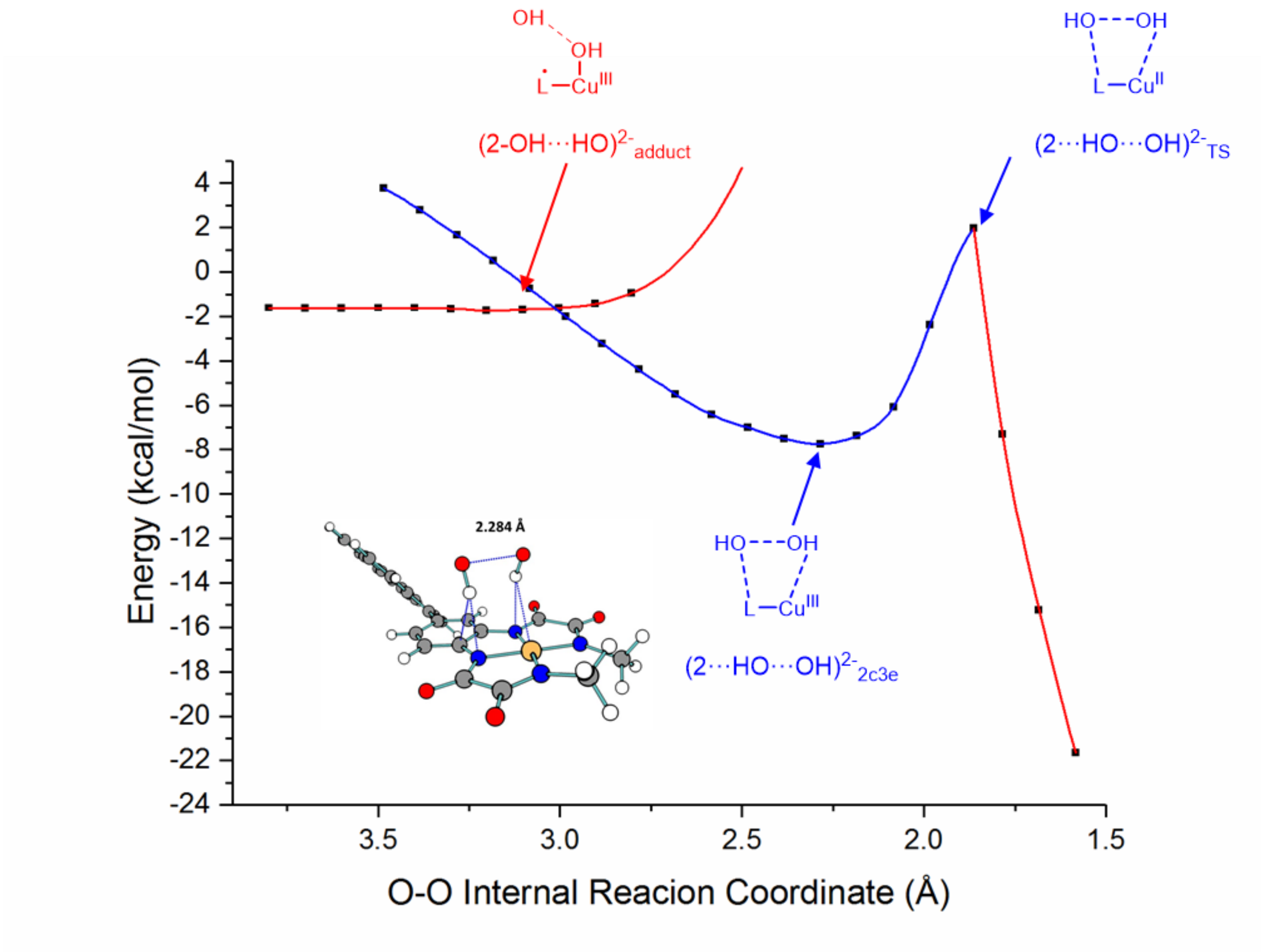


Figure S42. Potential energy relaxed scan of the O-O reaction coordinate, where energy is expressed in kcal·mol^{-1}. Color code is based on the electronic structure of both oxygen centers where red is for closed shell and blue for radical species.

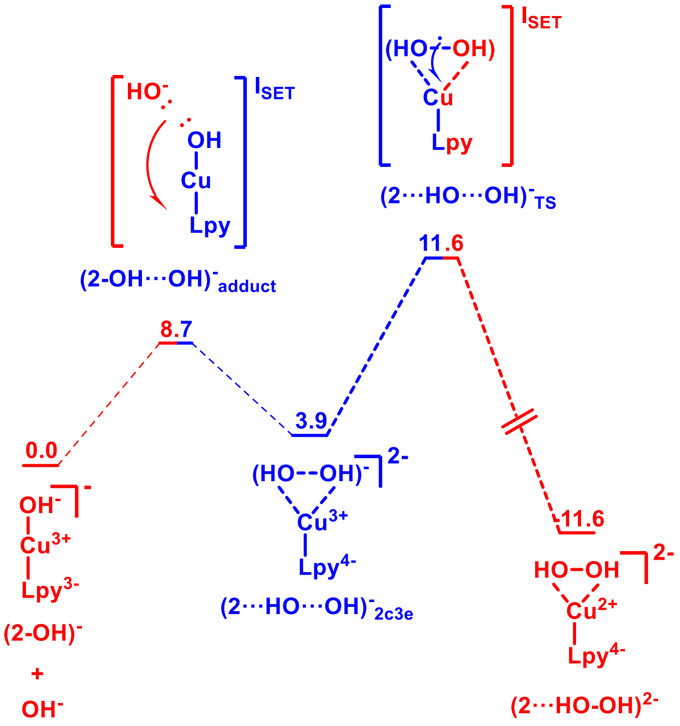


Figure S43. Free energy profile of the O-O bond formation reaction, where energy is expressed in kcal·mol^{-1}. Color code is the same as in previous Figure S42, based on the electronic structure of both oxygen centers where red is for closed shell and blue for radical species.

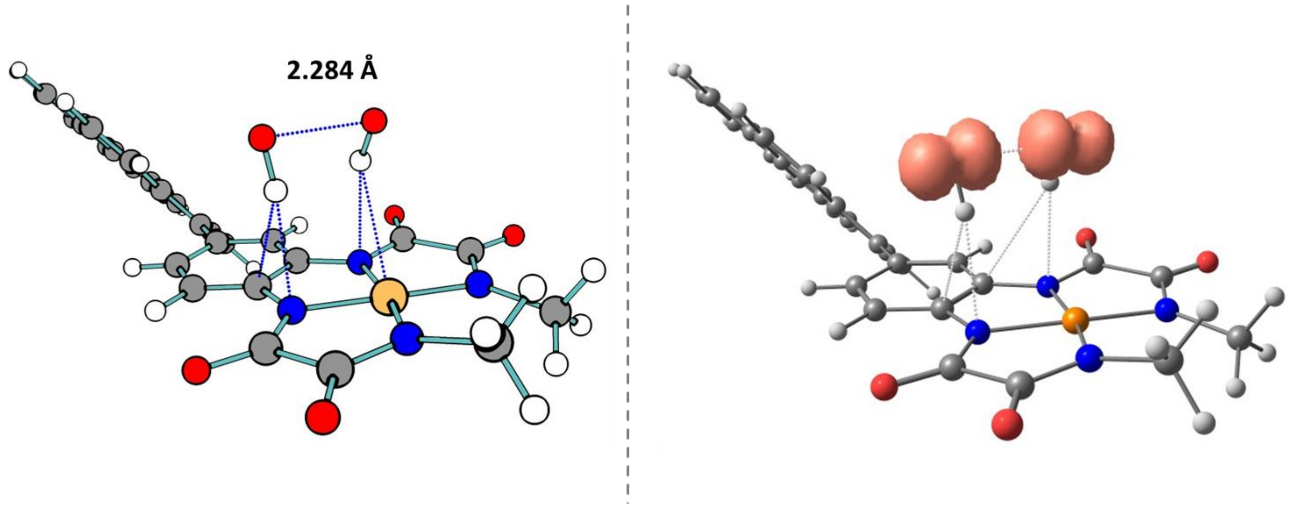


Figure S44. (Left) DFT optimized structure for the 2c-3e$^-$ intermediate **(2-OH⋯OH)$^{2-}$**. (Right) Calculated spin density for the same species.

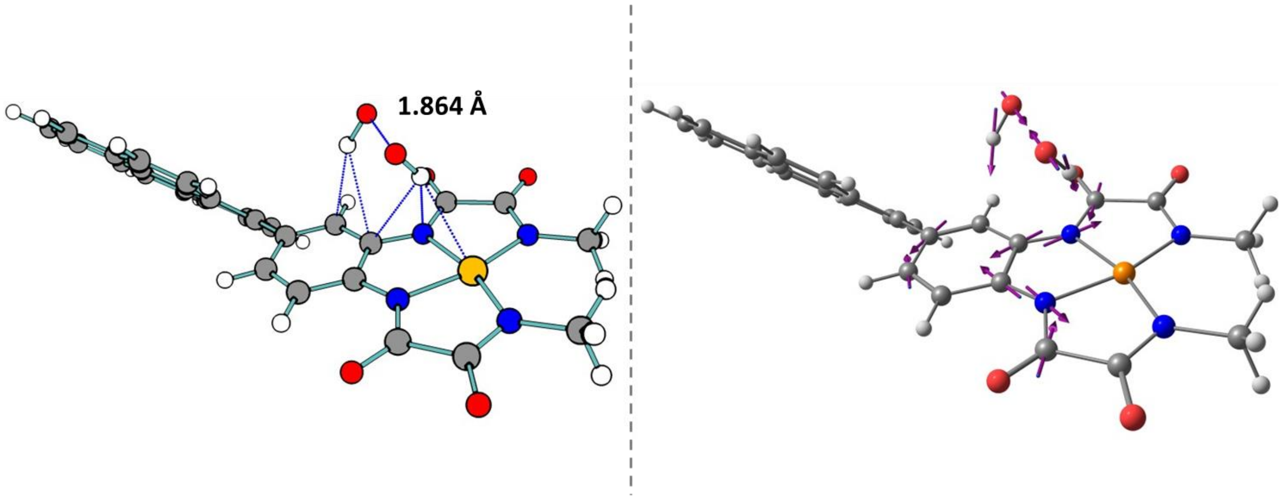
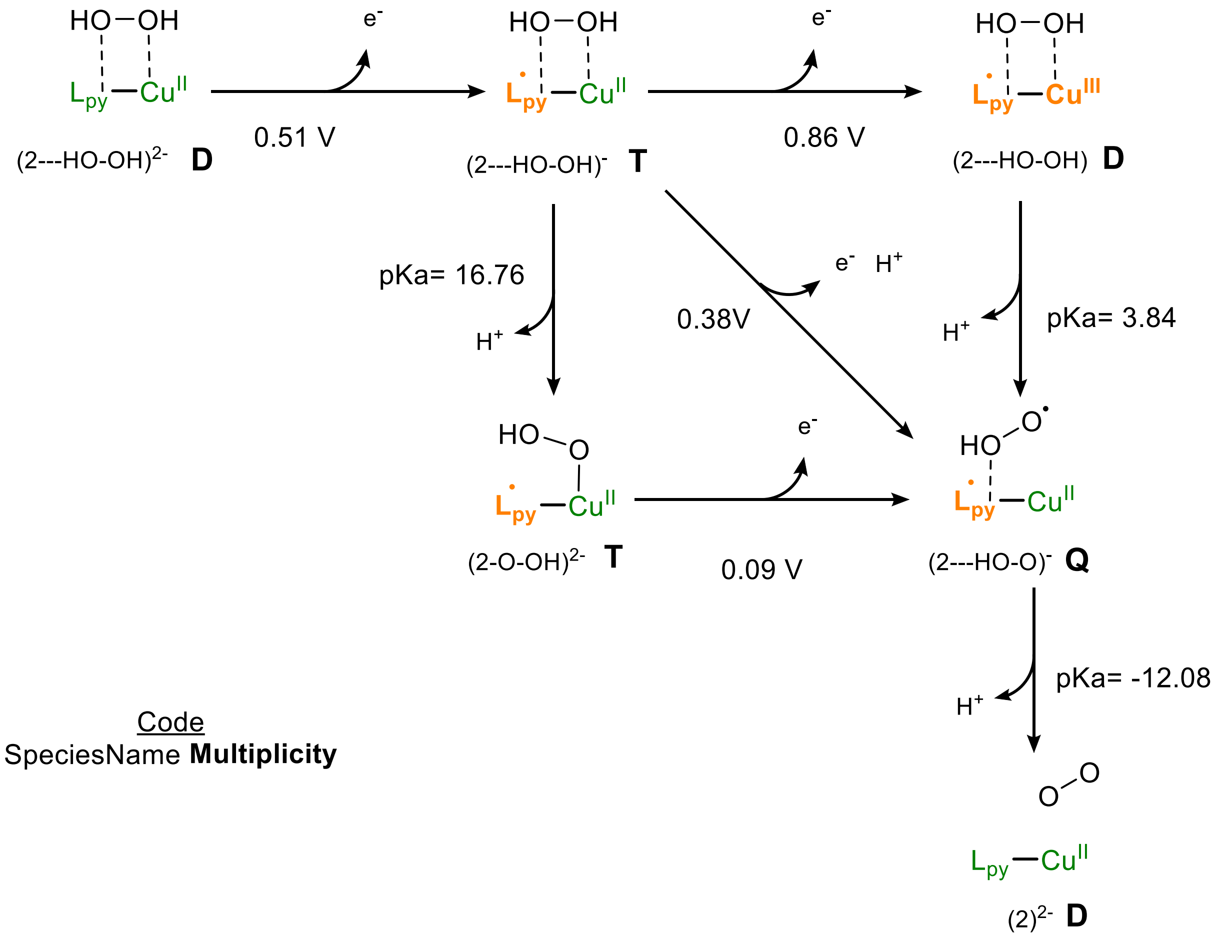


Figure S45. (Left) Computed transition state for the second single electron transfer connecting **(2-OH···OH)**$^{2-}$ and **(2···HO-OH)**$^{2-}$. (Right) Displacement vectors of the normal mode associated with the imaginary frequency in the same transition state.

O_2 release and catalyst regeneration

After the O-O bond step formation, hydrogen peroxide remains hydrogen bonded to the catalyst in its initial species form, i.e. with the ligand reduced and the metal center in oxidation state II. Then, the release of one electron has a potential of 0.51 V so it will takes place at the applied potential for water oxidation catalysis (1.08 V). Once again, the ligand is the first being oxidized generation a triplet species with the peroxide still hydrogen bonded. Last oxidation occurs as a proton coupled electron transfer (PCET) at very low potential (0.38 V) which means that is highly favored to generate a quartet species. In this case, the electron is released from the peroxide species with the concerted loss of a proton. Finally, the last proton is highly acidic and its release leads to the initial molecular catalyst along with the evolution of oxygen.



Scheme S4. Calculated mechanism for the third and fourth oxidations that lead to the oxygen evolution and catalyst regeneration. The values for the potentials and pKa correspond to the calculated ones and are in good agreement with the experimental observations.

Hybrid catalyst structure

In order to analyse the anchoring structure of both catalysts on the graphene layers, QMMM calculations were performed (see computational details section). Thanks to the square-planar geometry of **1**$^{2-}$ it is able to interact strongly with the graphene layer through π-π interactions, which is reflected in the short Cu-Graphene distance of about 3.522 Å. Regarding the coordination environment, changes respect to the structure in solution are negligible, with similar Cu-N distances. On the other hand, complex **2**$^{2-}$ undergoes a significant rearrangement upon interaction with the graphene layer. Due to the capability of both moieties (the pyrene group and the phenyloxamidate) to interact through π-π interactions with the graphene layer, there is a bond rotation and the dihedral angle changes from -130º in solution to around 0º when deposited on the graphene. This allows for higher delocalization of electrons through the whole ligand as well as more π orbitals interacting with the graphene. Current computational studies are being peformed to further characterize the different oxidation states of the hybrid catalysts and the catalytic properties of both.

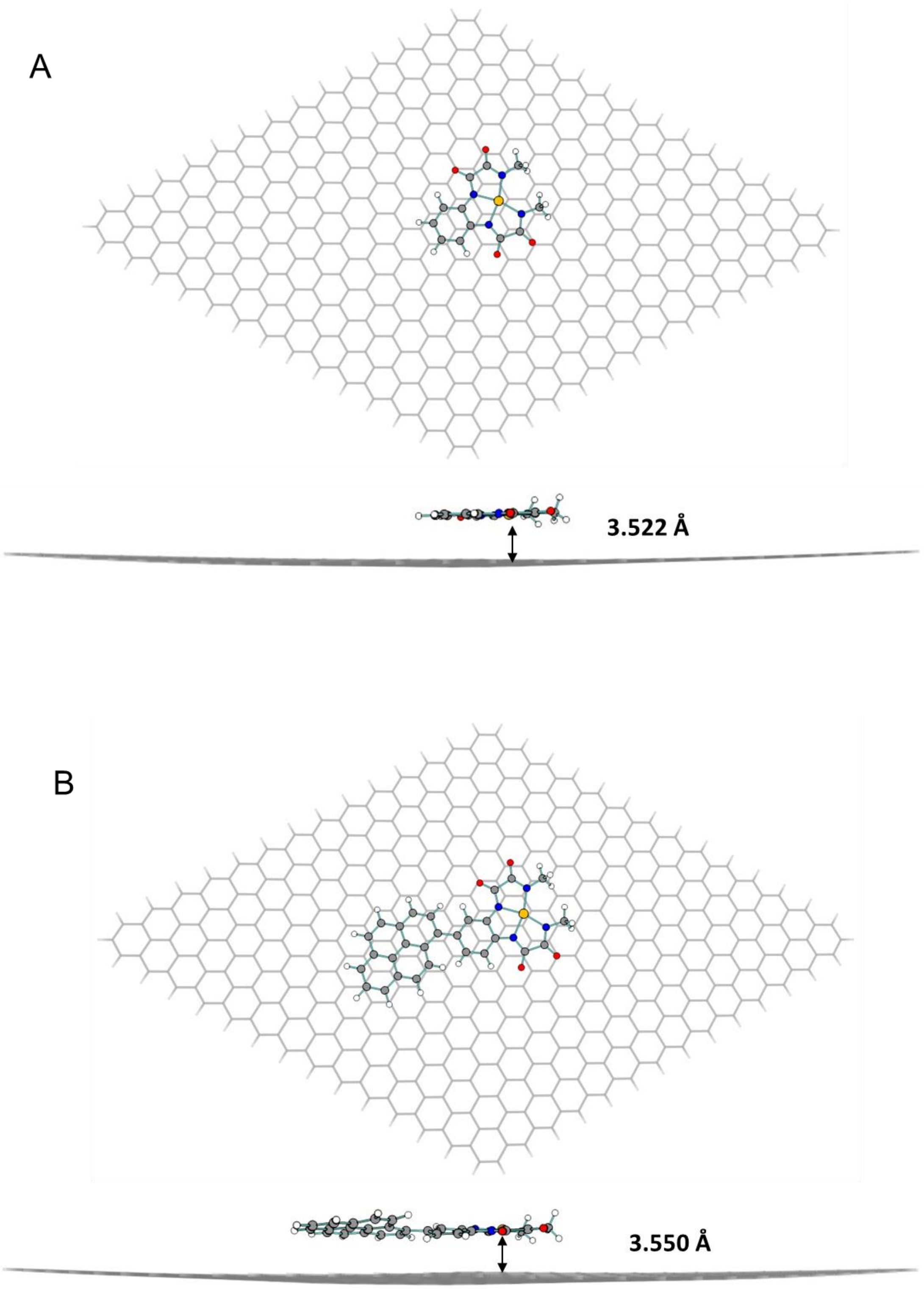


Figure S46. DFT optimized structure of the QMMM model for both hybrid catalysts **G-1**$^{2-}$ (A) and **G-2**$^{2-}$ (B).

Cartesian Coordinates (Å) and Calculated Potential Energies (atomic units)

OH E=-75.947690 H

O	-1.77132600	0.29368800	0.00000000
H	-2.09552100	1.20918600	0.00000000

HO···OH$^{\bullet-}$ E=-151.713748 H

O	-2.18138300	0.72977800	0.12530900
H	-2.17876000	1.67488200	-0.10539300
O	0.07484300	0.97985700	0.04969300
H	0.01883900	0.62949100	0.95549400

O_2 E=-150.326146 H

O	-1.90011200	0.29896900	0.00000000
O	-0.68628000	0.29896900	0.00000000

Structures related to catalyst 1^{2-} and its derivatives in MeCN

1^{2-} E= -1179.826097 H

Cu	-0.91561800	-0.00072700	-0.57255000
N	-1.25652800	-0.72418800	-2.40590800
N	-0.71696600	-1.91893500	-0.13396100
N	-0.44343100	0.18635500	1.34041900
N	-1.10409400	1.98623500	-0.44733600
C	-0.39231500	-2.18927100	1.19567800
C	-0.23428300	-1.01606200	2.01599600
C	-0.21505900	-3.45857700	1.77311300
C	0.09485100	-1.16728000	3.37415500
C	0.11223500	-3.58399400	3.13250600
H	-0.33852400	-4.33593800	1.15025000
C	0.26618200	-2.44577400	3.92798200
H	0.21178100	-0.27959900	3.98349600
H	0.24382900	-4.57531000	3.56150500
H	0.51983300	-2.54237900	4.98173600
C	-0.35837800	1.43763400	1.81831600
C	-0.70436200	2.50032100	0.72557400
C	-0.95607700	-2.79072400	-1.12642100
C	-1.51366500	-0.01193500	-3.64830800
H	-0.99927000	-0.48201200	-4.49858500
H	-2.58772400	0.01664500	-3.89533800
H	-1.16000800	1.01759300	-3.55513300
C	-1.49897300	2.93637800	-1.47597500
H	-0.62945500	3.35871200	-2.00637500
H	-2.12940200	2.43123000	-2.21229900
H	-2.06138900	3.78012300	-1.05248800
C	-1.29706200	-2.06354100	-2.46748400
O	-0.92887300	-4.03813500	-1.07304400
O	-1.56364300	-2.74703700	-3.48550500
O	-0.05523300	1.79723300	2.97516700
O	-0.61150600	3.71976700	1.00643600

1^{-} E= -1179.670188 H

Cu	-0.88769700	-0.05568200	-0.50268500
N	-1.21988100	-0.61204100	-2.28887900
N	-0.83590000	-1.88121500	-0.10689700
N	-0.33631200	0.17597500	1.26722800
N	-1.11719400	1.83046200	-0.51361400
C	-0.44675800	-2.17742300	1.21045800

C	-0.17667100	-1.02099500	1.98553900
C	-0.31428900	-3.45180400	1.77663300
C	0.19649500	-1.14528300	3.32997200
C	0.06511600	-3.56564800	3.12157900
H	-0.52016700	-4.32951700	1.17771100
C	0.31684000	-2.42495700	3.88993900
H	0.39724600	-0.25728000	3.91535700
H	0.15811000	-4.55401600	3.56478300
H	0.61180500	-2.52245900	4.93180300
C	-0.19712300	1.45143600	1.68666200
C	-0.68457900	2.44058500	0.60502800
C	-1.17898100	-2.71862500	-1.10819000
C	-1.11045300	0.20415900	-3.49248600
H	-0.57848000	-0.35284500	-4.27271300
H	-2.09425000	0.48946000	-3.88756500
H	-0.54565100	1.10928300	-3.26652500
C	-1.83998400	2.62090100	-1.50277900
H	-1.16041800	3.14673000	-2.18646400
H	-2.48887800	1.96637800	-2.08515100
H	-2.46117900	3.36971000	-0.99764900
C	-1.38012300	-1.94112500	-2.42713900
O	-1.29891400	-3.94693700	-1.03762100
O	-1.60887600	-2.53871600	-3.49046900
O	0.22499700	1.82624300	2.78623700
O	-0.71097400	3.66205100	0.82351900

Structures related to catalyst 2^{2-} and its derivatives in MeCN

2^{2-} E= -1794.452286 H

N	-3.07481900	-1.44619800	-2.07697800
N	-1.29699700	-2.16880100	-0.29345200
N	-2.48624200	-1.24615200	1.80622600
N	-4.73349400	-0.52512300	0.67242900
C	-0.58220300	-2.33944900	0.88945900
C	-1.24261600	-1.82321100	2.05989200
C	0.67826500	-2.94364100	1.03355100
C	-0.62213000	-1.94917500	3.31150300
C	1.28266800	-3.04523500	2.29319700
H	1.17210200	-3.33898500	0.15442600
C	0.64350600	-2.55645600	3.44309400
H	-1.13110800	-1.56063900	4.18471800
H	2.25135500	-3.53161800	2.38035700
C	-3.34732200	-0.70111100	2.68039100
C	-4.66590500	-0.23794400	1.98079500
C	-0.95730200	-2.54824500	-1.53638400
C	-4.05814900	-0.95353200	-3.02944300
H	-3.57813600	-0.51236000	-3.91476300
H	-4.72771400	-1.75229800	-3.38850600
H	-4.67211600	-0.18732300	-2.54967000
C	-5.97846500	-0.19387500	-0.00361400
H	-6.05128700	0.88026700	-0.24062700
H	-6.03905100	-0.75277000	-0.94092400
H	-6.85213500	-0.44971100	0.61259600
C	-2.03292700	-2.11974400	-2.58624800
O	0.07039900	-3.15833900	-1.89608900
O	-1.85373600	-2.39878100	-3.79635700

O	-3.19984800	-0.55624100	3.91139800
O	-5.55656400	0.32577900	2.66131400
Cu	-3.05154000	-1.28611000	-0.08519100
C	1.23579000	-2.73231600	4.79758600
C	2.53940000	-2.27730200	5.13737800
C	0.47001200	-3.38474000	5.78126800
C	3.05774400	-2.53920300	6.44932900
C	3.36411000	-1.52105000	4.22787900
C	0.96505700	-3.63540300	7.05733700
H	-0.52942000	-3.72442800	5.52218300
C	4.37181700	-2.09934700	6.80905300
C	2.26411100	-3.23482100	7.41416800
C	4.61288500	-1.09302000	4.57519700
H	2.97078800	-1.27680100	3.24709100
H	0.35057600	-4.15983300	7.78589600
C	5.17043400	-1.37549700	5.86943700
C	4.89346800	-2.37552600	8.11365500
C	2.81302600	-3.49996100	8.71691800
H	5.20840900	-0.51681200	3.87030400
C	6.45922100	-0.95008100	6.24202300
C	6.18893900	-1.93445600	8.44250400
C	4.07185200	-3.09355800	9.05207600
H	2.19647800	-4.03610600	9.43525500
C	6.96087300	-1.23015000	7.51520000
H	7.06173700	-0.39691200	5.52497300
H	6.58371400	-2.14728400	9.43345800
H	4.47590500	-3.30199500	10.04035900
H	7.95867800	-0.89536400	7.78799900

2^{-} E= -1794.295851 H

N	-3.04538400	-1.32908300	-1.91950500
N	-1.35367500	-2.23988900	-0.24149200
N	-2.50491400	-1.28961900	1.79156000
N	-4.62205000	-0.57667200	0.55350500
C	-0.62370700	-2.42183300	0.94255400
C	-1.27130600	-1.89384100	2.08642000
C	0.62578300	-3.04032100	1.07246600
C	-0.67897700	-2.00569900	3.34828100
C	1.21531900	-3.13466600	2.33737700
H	1.11664800	-3.45129800	0.19986700
C	0.58049600	-2.62207200	3.48097900
H	-1.18251000	-1.59577500	4.21404600
H	2.17681000	-3.63129400	2.43495200
C	-3.35963600	-0.64427400	2.61257000
C	-4.64879500	-0.25063300	1.85933300
C	-1.04356400	-2.61168100	-1.50140300
C	-3.93084900	-0.53680600	-2.76463600
H	-3.36896800	-0.13407500	-3.61530800
H	-4.76553100	-1.13172700	-3.15846400
H	-4.33303000	0.29660000	-2.18818600
C	-5.86863700	-0.52439000	-0.20193800
H	-6.06364500	0.47733400	-0.60660800
H	-5.82133800	-1.23523100	-1.02765800
H	-6.70848700	-0.79856600	0.44703000
C	-2.06816200	-2.04422200	-2.50676800
O	-0.06883400	-3.28523700	-1.85386100
O	-1.92374100	-2.21239200	-3.72793600

O	-3.19330400	-0.40573200	3.81406400
O	-5.60594700	0.26226000	2.45997300
Cu	-2.97498700	-1.33442200	-0.01953200
C	1.18885800	-2.76631800	4.83276600
C	2.49586600	-2.29914700	5.13802200
C	0.43902100	-3.39847100	5.83996000
C	3.03575100	-2.53058100	6.44662800
C	3.30432700	-1.56381300	4.19711700
C	0.95532500	-3.61719600	7.11389900
H	-0.56318300	-3.74693100	5.60408600
C	4.35620900	-2.08438600	6.77274000
C	2.25862600	-3.20478200	7.43985400
C	4.55946100	-1.13051700	4.51254800
H	2.89567400	-1.33990200	3.21784400
H	0.35405000	-4.12553300	7.86430500
C	5.13937700	-1.38492600	5.80258800
C	4.90066700	-2.33225800	8.07333200
C	2.82954800	-3.43884500	8.73954800
H	5.14323400	-0.57236500	3.78378900
C	6.43635800	-0.95646100	6.14112200
C	6.20355300	-1.88928900	8.36797000
C	4.09414400	-3.02587400	9.04269500
H	2.22556000	-3.95731600	9.48100000
C	6.96087900	-1.20979600	7.41058600
H	7.02750200	-0.42250500	5.40048800
H	6.61606400	-2.08155700	9.35585200
H	4.51503500	-3.21114200	10.02847200
H	7.96510700	-0.87382100	7.65673500

Structures related to catalyst 2^{2-} and its derivatives in water

2^{2-} E= -1794.469168 H

N	-3.09952000	-1.47037500	-2.08972100
N	-1.26661400	-2.09221500	-0.30711600
N	-2.48700900	-1.21888800	1.79880500
N	-4.77965600	-0.59414500	0.67894900
C	-0.54752400	-2.24833600	0.88048200
C	-1.22467000	-1.76507000	2.04968100
C	0.72225400	-2.82887900	1.02435900
C	-0.61158800	-1.89065900	3.30300300
C	1.31587000	-2.94075700	2.28592500
H	1.23734600	-3.20727700	0.15083400
C	0.66129600	-2.47765200	3.43822500
H	-1.12788800	-1.52641200	4.18133400
H	2.28829300	-3.41758200	2.37289000
C	-3.36029100	-0.69590700	2.65612800
C	-4.68615200	-0.28139700	1.96706600
C	-0.91928200	-2.42122200	-1.54918300
C	-4.13656500	-1.08817000	-3.04076600
H	-3.71069000	-0.64707700	-3.95122900
H	-4.74631900	-1.95204500	-3.34373400
H	-4.79513800	-0.35104700	-2.57817500
C	-6.02869200	-0.26285100	0.00426700
H	-6.08252200	0.80536100	-0.25221000
H	-6.10253600	-0.84016700	-0.91897100
H	-6.89965300	-0.49832600	0.62929600
C	-2.01920200	-2.06592200	-2.58345500
O	0.15207700	-2.95360800	-1.94796500

O	-1.80893900	-2.35170700	-3.80288400
O	-3.22840800	-0.51919500	3.89767300
O	-5.57484900	0.29233300	2.66979300
Cu	-3.06240200	-1.28444500	-0.09447100
C	1.24178600	-2.66246900	4.79591900
C	2.55589700	-2.24356200	5.14085200
C	0.45125200	-3.29025200	5.77586500
C	3.05882500	-2.52002500	6.45573400
C	3.40766700	-1.51170700	4.23628000
C	0.93005800	-3.54872000	7.05619400
H	-0.55480200	-3.60542100	5.51233800
C	4.38628200	-2.12700800	6.81951800
C	2.23823600	-3.18596600	7.41870800
C	4.67001900	-1.12989300	4.58747800
H	3.02642300	-1.24739000	3.25622400
H	0.29582600	-4.05069700	7.78308800
C	5.21410000	-1.43532000	5.88175400
C	4.89273800	-2.41969900	8.12607900
C	2.77032600	-3.46319500	8.72575100
H	5.28699000	-0.57339100	3.88569400
C	6.51795700	-1.06122800	6.25598800
C	6.20378800	-2.03037200	8.45716000
C	4.04139500	-3.10130500	9.06458000
H	2.13124200	-3.97271100	9.44324200
C	7.00560200	-1.36010100	7.53021100
H	7.14323700	-0.53382200	5.53949400
H	6.58699700	-2.25677900	9.44937600
H	4.43373000	-3.31844200	10.05532600
H	8.01549700	-1.06587500	7.80394700

2^- E= -1794.297121 H

N	-3.03059300	-1.46977800	-2.08236300
N	-1.22612500	-2.00629000	-0.25288600
N	-2.52361600	-1.18220600	1.80533500
N	-4.82572800	-0.69473400	0.64872700
C	-0.54596800	-2.13664300	0.91261700
C	-1.27883200	-1.66393800	2.09032600
C	0.75217700	-2.68187600	1.08663500
C	-0.68140900	-1.76278800	3.35982700
C	1.30468900	-2.75353600	2.34622300
H	1.29192400	-3.05598000	0.22766000
C	0.60104400	-2.29538600	3.50699500
H	-1.22337500	-1.40785700	4.22533400
H	2.28138500	-3.21018300	2.46869700
C	-3.45240300	-0.67302800	2.65205300
C	-4.79116300	-0.37268500	1.93872700
C	-0.84561800	-2.36484800	-1.51182300
C	-4.05702600	-1.10372800	-3.05101600
H	-3.62102800	-0.61610000	-3.93194400
H	-4.61170400	-1.98659400	-3.39865000
H	-4.76059500	-0.41358400	-2.58435100
C	-6.09262600	-0.51438400	-0.04745200
H	-6.27425000	0.54173900	-0.29214200
H	-6.07397900	-1.08624600	-0.97649200
H	-6.93551000	-0.86440800	0.56172800
C	-1.92675600	-2.03547800	-2.56377600
O	0.22495200	-2.88995000	-1.85180100
O	-1.68044300	-2.30982200	-3.77293600

O	-3.32441900	-0.45266500	3.86904000
O	-5.73529900	0.11487300	2.62451700
Cu	-3.06958800	-1.27428000	-0.09981500
C	1.18192800	-2.47854800	4.85066100
C	2.53222200	-2.14339900	5.16299000
C	0.36830800	-3.04774200	5.85283800
C	3.04927400	-2.47236500	6.45814400
C	3.39367100	-1.43328700	4.25537800
C	0.86639900	-3.35630100	7.11036300
H	-0.66192800	-3.29580200	5.61483900
C	4.40797300	-2.17464400	6.78868000
C	2.21174100	-3.09599500	7.43500600
C	4.69092600	-1.14401900	4.57522200
H	3.00001800	-1.09640300	3.30287500
H	0.22194800	-3.82418100	7.85024200
C	5.25110000	-1.51896000	5.84068900
C	4.93119800	-2.52808900	8.07208400
C	2.75968700	-3.43551400	8.71746100
H	5.31862200	-0.60660800	3.86854800
C	6.58930600	-1.24177700	6.18093500
C	6.27578400	-2.23687300	8.36923900
C	4.06449300	-3.16889900	9.02223400
H	2.10883200	-3.91286500	9.44583400
C	7.09435900	-1.60244400	7.43120300
H	7.22615200	-0.74116700	5.45575900
H	6.67237400	-2.51232000	9.34342400
H	4.46964300	-3.43348700	9.99590100
H	8.12994900	-1.38491700	7.67808500

(2-OH)$^-$ E= -1870.059852 H

N	-3.17015200	-1.43927300	-1.75954200
N	-1.48845900	-1.98175600	0.09664700
N	-3.17949900	-1.99555900	1.96686900
N	-5.24838000	-1.95185800	0.45751400
C	-0.91405000	-2.15918200	1.33827600
C	-1.86353300	-2.14315000	2.40919900
C	0.45205000	-2.34666500	1.61651200
C	-1.43954300	-2.28046200	3.72502000
C	0.86449900	-2.46714500	2.93397600
H	1.16744000	-2.40356200	0.80782300
C	-0.06116900	-2.41808200	4.01281600
H	-2.16377800	-2.23743600	4.52575300
H	1.91334600	-2.65469500	3.13498800
C	-4.32366100	-1.99595200	2.67392800
C	-5.54924000	-1.91219500	1.75606100
C	-0.91909800	-2.01758200	-1.13072800
C	-4.15050000	-0.81713500	-2.64084600
H	-3.65798200	-0.08262800	-3.28757600
H	-4.65019500	-1.55935000	-3.27471500
H	-4.89805500	-0.30068200	-2.04004200
C	-6.32936700	-1.94033500	-0.51720700
H	-6.69993100	-0.92381900	-0.70016200
H	-5.97802900	-2.36781900	-1.45571600
H	-7.16408500	-2.54856700	-0.15215400
C	-1.93553700	-1.65584600	-2.21878400
O	0.26417800	-2.26733000	-1.39694900
O	-1.55868200	-1.54202400	-3.40814100
O	-4.43727400	-2.07889700	3.90896700
O	-6.69777500	-1.86702100	2.25975500

Cu	-3.35564000	-1.65455500	0.12841300
H	-3.43133500	0.61574900	1.49546700
O	-3.34339100	0.61695500	0.52792000
C	0.38164700	-2.58806800	5.39438100
C	1.60080200	-2.01101900	5.90129000
C	-0.39991800	-3.39327100	6.26243700
C	2.05536500	-2.38124200	7.20642600
C	2.34975800	-1.02946500	5.18634500
C	0.03326500	-3.72812100	7.52786800
H	-1.32796100	-3.81773600	5.89411400
C	3.28310200	-1.86583600	7.71204400
C	1.27706000	-3.25556400	8.02409000
C	3.53889900	-0.53270000	5.67491800
H	1.96870800	-0.63843200	4.25079900
H	-0.56523100	-4.38711000	8.15105000
C	4.05142000	-0.95044700	6.93443700
C	3.74919300	-2.25734900	9.00356300
C	1.75318600	-3.62345900	9.31312500
H	4.09189300	0.20544900	5.10036200
C	5.27698800	-0.46008900	7.44774700
C	4.98075200	-1.74803800	9.47458500
C	2.95556900	-3.14798400	9.78632600
H	1.14841100	-4.28900000	9.92292400
C	5.73543400	-0.86252400	8.70062000
H	5.85556800	0.23882400	6.84950700
H	5.33594200	-2.05429300	10.45504800
H	3.31255800	-3.43979100	10.77031900
H	6.67881100	-0.48209100	9.08042700

(2-OH···HO)$^{2-}_{\text{adduct}}$ E= -1946.010298 H

N	-3.12739800	-1.42096700	-1.74724900
N	-1.45613000	-1.98699600	0.11242800
N	-3.15608600	-1.98762400	1.97321500
N	-5.21514900	-1.96229900	0.44784000
C	-0.88798500	-2.14883200	1.35425300
C	-1.84425700	-2.13342300	2.42273100
C	0.47918700	-2.32416700	1.64095200
C	-1.42616200	-2.26960100	3.74036000
C	0.88379100	-2.44264500	2.95953300
H	1.19882300	-2.37605400	0.83583400
C	-0.04906900	-2.40175600	4.03510900
H	-2.15456000	-2.22913300	4.53738400
H	1.93238800	-2.62451100	3.16652600
C	-4.30682600	-2.00528800	2.67108800
C	-5.52626100	-1.93541400	1.74351600
C	-0.87763700	-2.00817100	-1.11300900
C	-4.08772800	-0.74607800	-2.61223200
H	-3.58531400	0.03932200	-3.18798400
H	-4.55872500	-1.44515000	-3.31362600
H	-4.86086400	-0.28258000	-2.00100400
C	-6.28991100	-1.96741300	-0.53377200
H	-6.71112500	-0.96468500	-0.68072700
H	-5.91173200	-2.33988700	-1.48519500
H	-7.09518600	-2.63170200	-0.20044400
C	-1.88536900	-1.61584300	-2.19872600
O	0.29846400	-2.28608500	-1.37691200
O	-1.50213000	-1.47168700	-3.38211500
O	-4.42880900	-2.09556600	3.90454300
O	-6.67997300	-1.91188200	2.23827700

Cu	-3.32053500	-1.64152700	0.13486900
H	-3.01227800	0.61448900	1.45715800
O	-3.30227600	0.60216100	0.53004300
C	0.38760900	-2.57868700	5.41733900
C	1.60523100	-2.00893900	5.93302400
C	-0.39926200	-3.38881900	6.27631700
C	2.05402700	-2.39104000	7.23704600
C	2.36007900	-1.02231900	5.22885100
C	0.02766800	-3.73458800	7.54109700
H	-1.32667300	-3.80858200	5.90100900
C	3.28262900	-1.88431000	7.75090400
C	1.27014000	-3.26992200	8.04492300
C	3.54816800	-0.53418400	5.72508500
H	1.98260200	-0.62137000	4.29593700
H	-0.57540400	-4.39674800	8.15649000
C	4.05680500	-0.96523100	6.98311700
C	3.74382900	-2.28889800	9.04048600
C	1.74205200	-3.65071500	9.33315900
H	4.10519900	0.20791600	5.15948400
C	5.28223600	-0.48497800	7.50327200
C	4.97552100	-1.78936800	9.51872200
C	2.94356100	-3.18408400	9.81348600
H	1.13295900	-4.31983400	9.93483300
C	5.73565600	-0.90043500	8.75398300
H	5.86569500	0.21667700	6.91299400
H	5.32719200	-2.10552300	10.49736900
H	3.29688100	-3.48570600	10.79591800
H	6.67983000	-0.52744300	9.13940100
O	-0.43641800	1.26278000	-0.73814300
H	-1.27860700	0.91912100	-0.38584700

(2···HO···OH)$^{2-}_{2c3e}$ E= -1946.019884 H

N	-3.20418300	-1.52308300	-1.77872800
N	-1.51456100	-2.19238300	0.02474200
N	-3.13200900	-2.05853900	1.95551700
N	-5.21295400	-1.66491200	0.51363300
C	-0.90696600	-2.41309300	1.27408600
C	-1.80628500	-2.31526700	2.35848600
C	0.44410100	-2.68593600	1.50920100
C	-1.35312000	-2.47364100	3.67014700
C	0.88859400	-2.84248300	2.82421100
H	1.13425700	-2.77695800	0.68150800
C	0.01057000	-2.72526500	3.91491700
H	-2.04590600	-2.38399900	4.49577900
H	1.93562900	-3.07052800	2.99921000
C	-4.21256900	-1.78091800	2.70134500
C	-5.45334500	-1.56927000	1.82460100
C	-0.97987600	-2.24424700	-1.20524700
C	-4.19292700	-0.92813200	-2.67086200
H	-3.68788100	-0.30263800	-3.41404700
H	-4.77456200	-1.69247900	-3.19943600
H	-4.86904300	-0.29601300	-2.09736400
C	-6.34325200	-1.65835100	-0.40737300
H	-6.66228600	-0.63833300	-0.65227200
H	-6.07014800	-2.17783000	-1.32452800
H	-7.18975100	-2.18519600	0.04570600
C	-2.00124800	-1.83352500	-2.27190300
O	0.18748600	-2.55179200	-1.50345400
O	-1.65580700	-1.77415300	-3.47339100
O	-4.27500700	-1.71546000	3.94153000
O	-6.56769800	-1.37530800	2.36078200

Cu	-3.35398000	-1.83143100	0.10059500
H	-2.75132700	0.36548700	1.61389200
O	-2.83504200	1.27890500	1.28769100
C	0.48553600	-2.90563300	5.31349100
C	1.60217300	-2.19821400	5.83732100
C	-0.19271400	-3.81772400	6.14113000
C	2.04701000	-2.48119300	7.17132100
C	2.29834400	-1.17212200	5.10107500
C	0.22426700	-4.08055800	7.44239800
H	-1.05074400	-4.35093300	5.74060000
C	3.18913700	-1.80745600	7.70991600
C	1.35305900	-3.43684700	7.97722000
C	3.38218100	-0.52502900	5.61907800
H	1.94100900	-0.89787700	4.11514200
H	-0.31363900	-4.80388700	8.05058700
C	3.88173000	-0.82976300	6.93093800
C	3.64543400	-2.10678300	9.03313300
C	1.82759800	-3.71176900	9.30715400
H	3.88349400	0.24749700	5.04066800
C	5.00943200	-0.18623600	7.47279800
C	4.77914300	-1.44140600	9.53509900
C	2.92625600	-3.07962300	9.81190500
H	1.28774400	-4.44217100	9.90531600
C	5.45323400	-0.49407800	8.76067500
H	5.53157300	0.55718100	6.87513800
H	5.12604200	-1.67335800	10.53928000
H	3.27725000	-3.29810700	10.81772600
H	6.32706900	0.01025700	9.16476600
O	-0.70370500	1.02160400	0.50713100
H	-1.01012400	0.14072200	0.22741200

(2···HO···OH)$^{2-}{}_{TS}$ E= -1946.004390 H

N	-1.98104400	-0.66917900	-2.49239700
N	-1.03919900	-1.88266400	-0.35843500
N	-0.46705700	0.19596400	1.04057600
N	-1.40553200	2.03001700	-0.58453500
C	-0.46803900	-2.16778600	0.85588900
C	-0.13885700	-0.99659000	1.64700600
C	-0.16765100	-3.44465100	1.37437900
C	0.46320300	-1.15788700	2.90753200
C	0.43190200	-3.56884500	2.61875000
H	-0.41678500	-4.32617300	0.79930900
C	0.75609400	-2.43355000	3.40488500
H	0.70908300	-0.28016400	3.48985900
H	0.62954800	-4.56102300	3.01317800
C	-0.17569400	1.45217800	1.43299700
C	-0.74484800	2.51580400	0.46155400
C	-1.47919100	-2.73505200	-1.31009500
C	-2.44438100	0.06360600	-3.66437000
H	-2.08225300	-0.39440700	-4.59346600
H	-3.54231800	0.09378300	-3.71361200
H	-2.07366800	1.08844100	-3.61676300
C	-2.02175700	2.99093800	-1.48993400
H	-1.28458800	3.42943200	-2.17781400
H	-2.78616600	2.48485500	-2.08225700
H	-2.49480200	3.81408600	-0.93984400
C	-2.03775900	-1.99579200	-2.54919700
O	-1.47604000	-3.98164800	-1.27511300
O	-2.48143800	-2.69458900	-3.50802100
O	0.46102300	1.80756200	2.44601300
O	-0.56078800	3.73716400	0.74104200

Cu	-1.31777900	0.04515800	-0.74639600
O	2.08853500	-0.64832200	-0.79555500
H	1.28921600	-0.13892700	-0.56258000
O	3.02231000	-0.08390900	0.71602000
H	2.47334700	-0.60914300	1.32920100
C	1.31710700	-2.59058300	4.76721400
C	0.69023900	-1.91056400	5.82905400
C	2.43706700	-3.42291800	5.04618100
C	1.09619200	-2.07739000	7.14762600
H	-0.16012800	-1.27032400	5.61163400
C	2.84727800	-3.60911400	6.40699700
C	3.21549600	-4.05990700	4.01508300
C	2.16210200	-2.93756000	7.46718900
H	0.57402700	-1.55776800	7.94728700
C	3.94911900	-4.46686900	6.71702100
C	4.27253600	-4.87202600	4.31210200
H	2.96893700	-3.87276100	2.97584800
C	2.57935200	-3.15814600	8.82460000
C	4.34088200	-4.67311600	8.07774000
C	4.66693900	-5.12223400	5.66970000
H	4.84462500	-5.33699600	3.51274800
C	3.61882500	-3.99277000	9.11878800
H	2.04315400	-2.64286200	9.61797400
C	5.42019300	-5.53138200	8.35827900
C	5.74340800	-5.96881100	5.99496900
H	3.92283000	-4.15448100	10.15021400
H	5.71291000	-5.69012400	9.39341400
C	6.11098300	-6.17198700	7.32666700
H	6.28786700	-6.46303700	5.19397300
H	6.94272600	-6.83047100	7.56259200

(2···HO-OH)$^{2-}$ E= -1946.045026 H

N	-1.98369400	-0.68733400	-2.53802300
N	-1.06184900	-1.91134500	-0.40072800
N	-0.40297500	0.17649300	0.97485700
N	-1.40918500	2.00783300	-0.62731400
C	-0.48921900	-2.19829100	0.83904000
C	-0.12942300	-1.04377100	1.60978600
C	-0.24141000	-3.47191600	1.37388700
C	0.46762000	-1.20706100	2.86602900
C	0.35206900	-3.61184300	2.63157600
H	-0.52002900	-4.35121300	0.80793800
C	0.71867000	-2.48991300	3.39131800
H	0.74973100	-0.33073400	3.43469000
H	0.51332300	-4.60902100	3.03172400
C	-0.28628000	1.41894500	1.45383100
C	-0.78608900	2.48667800	0.44399300
C	-1.53846300	-2.75080900	-1.31876500
C	-2.43993100	0.04018800	-3.71589000
H	-2.10687200	-0.44361700	-4.64322700
H	-3.53698900	0.10913600	-3.75271400
H	-2.03475700	1.05318900	-3.69254700
C	-1.97257800	2.97407600	-1.56138400
H	-1.20484200	3.39811000	-2.22504000
H	-2.72335400	2.47831700	-2.17961500
H	-2.45377300	3.80875200	-1.03558300
C	-2.08668500	-2.01146500	-2.56688300
O	-1.58528500	-4.00928700	-1.27698900
O	-2.57080000	-2.70786200	-3.51184500
O	0.14484300	1.78556600	2.57528200
O	-0.59910800	3.70949800	0.72628600

Cu	-1.29110500	0.01777500	-0.79509500
O	2.19925900	-0.14747600	-0.48219700
H	1.28250000	0.11511000	-0.23228400
O	2.92427800	0.07431500	0.75803800
H	2.66428000	-0.70202200	1.29617100
C	1.29754500	-2.63127000	4.75397500
C	0.69497400	-1.92816600	5.81298000
C	2.41759000	-3.46195300	5.03208800
C	1.13171300	-2.05904700	7.12744100
H	-0.15641000	-1.28809300	5.59764100
C	2.85789400	-3.61631700	6.38853300
C	3.16510500	-4.14024300	4.00239900
C	2.20146200	-2.91271700	7.44596400
H	0.63037400	-1.51419600	7.92391700
C	3.95970800	-4.47605300	6.69720000
C	4.22168700	-4.95231400	4.29690200
H	2.88690800	-3.98798500	2.96569800
C	2.65126500	-3.09773300	8.79953600
C	4.38229600	-4.64780100	8.05411000
C	4.64673500	-5.16835100	5.65229300
H	4.76951000	-5.44697200	3.49813000
C	3.69133400	-3.93078800	9.09272000
H	2.13758600	-2.55615900	9.59053300
C	5.46018300	-5.50817300	8.33334800
C	5.72103000	-6.01723200	5.97631000
H	4.01999900	-4.06502100	10.12061500
H	5.77730800	-5.63949900	9.36521800
C	6.11875500	-6.18573700	7.30449400
H	6.24072700	-6.54098300	5.17747900
H	6.94918400	-6.84648200	7.53932600

(2···HO-OH)$^-$ E= -1945.871237 H

N	-1.98174500	-0.73969100	-2.48355400
N	-1.02982300	-1.90720800	-0.33414800
N	-0.47607200	0.20227200	1.02534900
N	-1.49729600	1.99038700	-0.60336500
C	-0.43154700	-2.16287400	0.85415400
C	-0.11375900	-0.96622300	1.63716600
C	-0.09732400	-3.43587100	1.38366900
C	0.51257900	-1.10494600	2.88627100
C	0.52762100	-3.52997000	2.60697900
H	-0.34995900	-4.32720900	0.82613900
C	0.84646800	-2.36984300	3.38316500
H	0.75179000	-0.21728600	3.45532800
H	0.74264400	-4.51224800	3.01463700
C	-0.28501500	1.47779700	1.44286500
C	-0.87095900	2.51036200	0.44910500
C	-1.46603600	-2.78587900	-1.28201200
C	-2.44952900	-0.02344700	-3.66382700
H	-2.09985100	-0.50227700	-4.58673600
H	-3.54740900	0.01330400	-3.70154900
H	-2.07008500	0.99873100	-3.63573000
C	-2.12705200	2.92148200	-1.53010900
H	-1.39091300	3.37336600	-2.21000600
H	-2.86537300	2.38549000	-2.12846500
H	-2.63371500	3.73546800	-0.99713600
C	-2.04013600	-2.06824400	-2.52298900
O	-1.43382800	-4.02364400	-1.22788700
O	-2.48956200	-2.78136300	-3.46498200
O	0.27365500	1.85685000	2.48639300
O	-0.73415300	3.73800400	0.71947300

Cu	-1.33028600	0.01321700	-0.75531700
O	2.19210000	-0.13976800	-0.72051100
H	1.28226000	0.19957400	-0.58612200
O	2.83357600	0.20090700	0.53670100
H	2.57358400	-0.54555100	1.11466400
C	1.41912500	-2.51614700	4.73193200
C	0.83610500	-1.77867400	5.78525600
C	2.49387100	-3.40816600	5.02408400
C	1.22209800	-1.96088700	7.10438900
H	0.02347500	-1.09443500	5.56000500
C	2.88232800	-3.60624900	6.38850300
C	3.25136700	-4.08192100	4.00441000
C	2.22951700	-2.88777700	7.43842100
H	0.72710300	-1.40614700	7.89733800
C	3.92882300	-4.52373400	6.71326900
C	4.25935000	-4.95217100	4.31622900
H	3.03936600	-3.87626400	2.96118100
C	2.61668200	-3.12604000	8.79904000
C	4.29290100	-4.74656000	8.07821400
C	4.62013500	-5.22179700	5.67686100
H	4.81547900	-5.44703500	3.52382100
C	3.60205500	-4.02148500	9.10780000
H	2.10475600	-2.57611300	9.58479200
C	5.31640500	-5.66633100	8.37402300
C	5.64278300	-6.12904400	6.01696100
H	3.88371600	-4.19662600	10.14322600
H	5.58607000	-5.83897100	9.41305700
C	5.98098400	-6.35052000	7.35286600
H	6.16744800	-6.65514000	5.22325900
H	6.76955200	-7.05571600	7.60062100

(2-O-OH)$^-$ E= -1945.388383 H

N	-1.90828000	-0.71371300	-2.53038900
N	-1.01319100	-1.89529800	-0.35746000
N	-0.42235700	0.20011800	1.01635500
N	-1.41429300	2.01783100	-0.60341100
C	-0.46247300	-2.16790900	0.84912000
C	-0.12144700	-0.98043900	1.63727100
C	-0.20317900	-3.45063800	1.40127900
C	0.46184100	-1.13848100	2.90644200
C	0.38377900	-3.56188100	2.64211500
H	-0.47340600	-4.33514100	0.84091100
C	0.73712800	-2.40987100	3.41482200
H	0.73037800	-0.25814500	3.47381900
H	0.55416400	-4.54868500	3.06063700
C	-0.41334400	1.45357300	1.53555200
C	-0.92568200	2.50859900	0.52953100
C	-1.55805900	-2.75550000	-1.26421200
C	-2.30733000	-0.00209600	-3.73788100
H	-1.99827900	-0.54096800	-4.64275100
H	-3.39774200	0.13130100	-3.78508800
H	-1.83923800	0.98366000	-3.74281200
C	-1.95866700	2.97660600	-1.55587300
H	-1.15950100	3.50495300	-2.09604300
H	-2.57457200	2.44844400	-2.28531000
H	-2.57874200	3.73267500	-1.05738500
C	-2.06988100	-2.03176500	-2.52817200
O	-1.68017200	-3.98541300	-1.15005600
O	-2.58228600	-2.73790300	-3.44725600
O	-0.07422900	1.79313400	2.68364800
O	-0.86818300	3.72832300	0.87227700

Cu	-1.06219200	0.04502400	-0.87082800
O	1.10092800	0.13101600	-1.81353200
O	2.12014200	0.46880900	-0.77417300
H	1.57898500	0.45067300	0.03564800
C	1.31378300	-2.55668600	4.76528000
C	0.75202300	-1.79735000	5.81275900
C	2.39214400	-3.44328800	5.05387700
C	1.17618000	-1.93781500	7.12631800
H	-0.06599500	-1.11907100	5.58839600
C	2.82426200	-3.59468700	6.41193200
C	3.11621200	-4.15609400	4.03469600
C	2.20231800	-2.84302600	7.45747800
H	0.70195300	-1.35997900	7.91554200
C	3.88905100	-4.49282200	6.73391600
C	4.13648100	-5.01133300	4.34390300
H	2.86601600	-3.99354700	2.99239900
C	2.64230400	-3.02497600	8.81195200
C	4.30601700	-4.65843500	8.09221100
C	4.54831500	-5.22614600	5.70068300
H	4.66591600	-5.53548100	3.55193900
C	3.64761500	-3.89751700	9.11816100
H	2.15462700	-2.44805100	9.59386400
C	5.34948700	-5.55595200	8.38530800
C	5.59042900	-6.11124800	6.03768800
H	3.97172800	-4.02751400	10.14786800
H	5.66155300	-5.68294000	9.41908200
C	5.98126500	-6.27533800	7.36762700
H	6.09017600	-6.66477600	5.24650600
H	6.78595900	-6.96309600	7.61295800

(2···O-OH)$^{2-}$ E= -1945.227550 H

N	-2.00603100	-0.66610800	-2.52225000
N	-1.04356400	-1.84656100	-0.38576200
N	-0.48440000	0.25192700	0.98600900
N	-1.50902800	2.05391600	-0.62297800
C	-0.46382000	-2.11085500	0.80932700
C	-0.14311900	-0.91736700	1.59650100
C	-0.15243000	-3.38839600	1.34218200
C	0.45760100	-1.06790900	2.86240300
C	0.45185700	-3.49279300	2.57481200
H	-0.40018300	-4.27536800	0.77558800
C	0.76294100	-2.33841900	3.36217200
H	0.69223300	-0.18599700	3.44300100
H	0.66020300	-4.47716400	2.98116100
C	-0.28537700	1.52533900	1.40978300
C	-0.89088600	2.56594600	0.43827400
C	-1.48760700	-2.71967700	-1.33530000
C	-2.48077400	0.05724600	-3.69549500
H	-2.13090300	-0.41202000	-4.62329500
H	-3.57895100	0.08829800	-3.73032400
H	-2.10678700	1.08119400	-3.66006400
C	-2.15191200	2.98967900	-1.53597200
H	-1.42350500	3.44874300	-2.21931100
H	-2.89323600	2.45509200	-2.13199900
H	-2.65640500	3.79780400	-0.99234700
C	-2.06463500	-1.99434100	-2.57001500
O	-1.46098300	-3.95774900	-1.28606600
O	-2.51923100	-2.70140100	-3.51426800
O	0.30174800	1.89369000	2.44126000
O	-0.76982500	3.79066200	0.72924600

Cu	-1.33755300	0.07726600	-0.79431100
O	2.85697700	-1.32566600	0.15315000
O	3.34593700	-1.19654900	1.38079500
H	2.56449000	-1.23902800	1.99061700
C	1.33408800	-2.49401000	4.71173500
C	0.72935300	-1.79792100	5.77843700
C	2.44201300	-3.34971700	4.97843300
C	1.13296200	-1.98752400	7.09244500
H	-0.10767400	-1.13867300	5.56758400
C	2.85035100	-3.55409200	6.33562700
C	3.21268100	-3.97858600	3.93925700
C	2.17917000	-2.87828500	7.40226400
H	0.62421600	-1.46509700	7.89854400
C	3.93621000	-4.43359000	6.63538300
C	4.25651500	-4.81322600	4.22745800
H	2.97918600	-3.76695600	2.90162900
C	2.58938400	-3.12273500	8.75582700
C	4.32283800	-4.66256200	7.99306600
C	4.64316200	-5.08764400	5.58075100
H	4.82268800	-5.27530300	3.42246100
C	3.61290900	-3.98195300	9.04067300
H	2.06343200	-2.60624900	9.55493400
C	5.38599600	-5.54407900	8.26398000
C	5.70503200	-5.95740700	5.89634900
H	3.91184800	-4.16175600	10.07045200
H	5.67379500	-5.72157200	9.29732700
C	6.06667800	-6.18462300	7.22527400
H	6.24165500	-6.45028800	5.08941900
H	6.88580000	-6.86094200	7.45391600

(2···HO-OH) E= -1945.682175 H

N	-1.98402000	-0.77200100	-2.45026000
N	-1.02511700	-1.89987300	-0.28365700
N	-0.50227100	0.22748500	1.04621300
N	-1.53639600	1.98736100	-0.60209300
C	-0.40465400	-2.13499300	0.87147200
C	-0.12550900	-0.91668600	1.66898900
C	-0.00185600	-3.40467700	1.38755200
C	0.48251900	-1.04143900	2.92320400
C	0.63815700	-3.47370400	2.59287700
H	-0.22512700	-4.30173400	0.82742300
C	0.89159100	-2.29538500	3.39563800
H	0.68535100	-0.14936200	3.49835600
H	0.89404200	-4.44761000	2.99458300
C	-0.32690000	1.51891500	1.45297100
C	-0.92508300	2.53050000	0.44904100
C	-1.46028200	-2.80431100	-1.23684400
C	-2.43741800	-0.06775600	-3.64322200
H	-2.06397400	-0.54791500	-4.55565600
H	-3.53468700	-0.04883300	-3.69926400
H	-2.07326400	0.95947000	-3.61136000
C	-2.18566800	2.89652500	-1.53702400
H	-1.45790200	3.35490800	-2.22107400
H	-2.91327200	2.33945800	-2.12880700
H	-2.70685000	3.70495500	-1.01022500
C	-2.01632000	-2.10260800	-2.49080000
O	-1.43940900	-4.02994600	-1.14607400
O	-2.42807900	-2.82802800	-3.43644800
O	0.22991600	1.90505000	2.48807300
O	-0.81207100	3.76011500	0.70955800

Cu	-1.34928100	0.01590100	-0.73584000
O	2.16630500	-0.10002000	-0.76850800
H	1.26293800	0.22181000	-0.56931400
O	2.84466100	0.09727700	0.49936900
H	2.66377900	-0.74401800	0.96479800
C	1.46988300	-2.43477500	4.71937700
C	0.91930600	-1.66584800	5.78059800
C	2.53055600	-3.36853700	5.01486300
C	1.27050100	-1.89633300	7.09177500
H	0.13637500	-0.94822400	5.55981400
C	2.88396300	-3.60406700	6.37858100
C	3.29774900	-4.00718200	4.00050400
C	2.23769300	-2.88434700	7.42937400
H	0.78530900	-1.34322700	7.89096900
C	3.90100700	-4.54397000	6.70116300
C	4.28597200	-4.91982800	4.31473300
H	3.13769400	-3.75316000	2.95918800
C	2.58402900	-3.15296600	8.78000900
C	4.23250300	-4.80214400	8.06428900
C	4.60126000	-5.22643700	5.66473500
H	4.84715200	-5.40294200	3.51973300
C	3.54630600	-4.09105700	9.09076700
H	2.07969800	-2.60264200	9.56909800
C	5.23688100	-5.75225700	8.36033000
C	5.60867800	-6.16433800	6.00675600
H	3.80058200	-4.29179400	10.12790500
H	5.47927700	-5.95193200	9.40070000
C	5.91411900	-6.42622400	7.34009600
H	6.14149100	-6.67550600	5.20953500
H	6.68450900	-7.14937800	7.58863100

G-1^{2-} E= -1176.225104 H

C-C_R	0	5.68176200	1.87471400	0.28467500	L
C-C_R	0	8.11850000	1.87178100	0.16521800	L
C-C_R	0	10.55632700	1.87397900	0.04812700	L
C-C_R	0	12.99540200	1.87636100	-0.06488500	L
C-C_R	0	15.43544500	1.87892400	-0.17184700	L
C-C_R	0	17.87626600	1.88162700	-0.27067900	L
C-C_R	0	20.31774200	1.88438700	-0.35919400	L
C-C_R	0	22.75978100	1.88712400	-0.43516600	L
C-C_R	0	25.20229200	1.88977100	-0.49651100	L
C-C_R	0	27.64517100	1.89229600	-0.54166500	L
C-C_R	0	30.08828600	1.89472800	-0.57016800	L
C-C_R	0	32.53146800	1.89719200	-0.58312300	L
C-C_R	0	34.97451400	1.90019600	-0.58307400	L
C-C_R	0	37.41662000	1.90902300	-0.57339700	L
C-C_R	0	4.46814200	3.97400500	0.38561100	L
C-C_R	0	5.67870700	6.09207900	0.36796800	L
C-C_R	0	6.89433600	8.20839000	0.35188400	L
C-C_R	0	8.11088200	10.32542000	0.33895500	L
C-C_R	0	9.32825100	12.44280600	0.33046600	L

```
 C-C_R           0   10.54636000   14.56028800
0.32759100 L

 C-C_R           0   11.76511900   16.67769500
0.33137500 L

 C-C_R           0   12.98444800   18.79490400
0.34268000 L

 C-C_R           0   14.20427300   20.91182800
0.36208000 L

 C-C_R           0   15.42452800   23.02841400
0.38969500 L

 C-C_R           0   16.64517700   25.14462600
0.42499800 L

 C-C_R           0   17.86623500   27.26039800
0.46686800 L

 C-C_R           0   19.08802500   29.37544700
0.51401400 L

 C-C_R           0   20.31468300   31.48654200
0.56525800 L

 C-C_R           0    6.89787200    3.98152900
0.26613800 L

 C-C_R           0    8.11186700    6.09886900
0.24903800 L

 C-C_R           0    9.32782300    8.21598300
0.23418200 L

 C-C_R           0   10.54476400   10.33338000
0.22296900 L

 C-C_R           0   11.76247200   12.45088200
0.21673200 L

 C-C_R           0   12.98086900   14.56834300
0.21673400 L

 C-C_R           0   14.19989700   16.68564200
0.22414400 L

 C-C_R           0   15.41949300   18.80267200
0.23999500 L

 C-C_R           0   16.63958500   20.91934500
0.26498500 L

 C-C_R           0   17.86010800   23.03559800
0.29912900 L

 C-C_R           0   19.08103200   25.15137400
0.34143600 L

 C-C_R           0   20.30248400   27.26651200
0.39007600 L

 C-C_R           0   21.52491000   29.38069600
0.44310400 L

 C-C_R           0   22.74819400   31.49931300
0.49952200 L

 C-C_R           0    9.33571400    3.98188800
0.14743400 L

 C-C_R           0   10.55217600    6.10060500
0.13129800 L

 C-C_R           0   11.76911600    8.21843400
0.11789400 L

 C-C_R           0   12.98666400   10.33620200
0.10860900 L

 C-C_R           0   14.20483100   12.45388200
0.10480500 L

 C-C_R           0   15.42361600   14.57140200
0.10781600 L

 C-C_R           0   16.64299500   16.68866500
0.11899700 L

 C-C_R           0   17.86291800   18.80556600
0.13965800 L

 C-C_R           0   19.08332400   20.92201700
0.17075100 L

 C-C_R           0   20.30414700   23.03798500
0.21219300 L

 C-C_R           0   21.52537600   25.15353900
0.26226700 L

 C-C_R           0   22.74710100   27.26898200
0.31807100 L

 C-C_R           0   23.96901100   29.38540600
0.37709900 L

 C-C_R           0   25.18920100   31.50551000
0.43879900 L

 C-C_R           0   11.77445100    3.98387800
0.03151000 L

 C-C_R           0   12.99208200    6.10298600
0.01675000 L

 C-C_R           0   14.20984000    8.22120600
0.00506400 L
```

C-C_R	0	15.42798800	10.33925300	-0.00218600	L
C-C_R	0	16.64663900	12.45711800	-0.00370300	L
C-C_R	0	17.86583800	14.57474300	0.00188300	L
C-C_R	0	19.08558800	16.69202800	0.01619200	L
C-C_R	0	20.30585900	18.80885800	0.04115600	L
C-C_R	0	21.52657900	20.92514600	0.07862300	L
C-C_R	0	22.74764500	23.04096300	0.12848800	L
C-C_R	0	23.96897300	25.15664000	0.18783300	L
C-C_R	0	25.19035600	27.27283300	0.25194500	L
C-C_R	0	26.41128500	29.39008500	0.31774600	L
C-C_R	0	27.63156400	31.50946300	0.38538200	L
C-C_R	0	14.21411200	3.98629600	-0.07988800	L
C-C_R	0	15.43244000	6.10561000	-0.09290800	L
C-C_R	0	16.65081700	8.22406900	-0.10269800	L
C-C_R	0	17.86948600	10.34233500	-0.10809100	L
C-C_R	0	19.08857800	12.46039000	-0.10807000	L
C-C_R	0	20.30815600	14.57817800	-0.10142600	L
C-C_R	0	21.52824200	16.69558100	-0.08611500	L
C-C_R	0	22.74880100	18.81243100	-0.05830800	L
C-C_R	0	23.96972400	20.92862500	-0.01395200	L
C-C_R	0	25.19086500	23.04433700	0.04685500	L
C-C_R	0	26.41206000	25.16008900	0.11871300	L
C-C_R	0	27.63306800	27.27653100	0.19327000	L
C-C_R	0	28.85375400	29.39364700	0.26711500	L
C-C_R	0	30.07428900	31.51259100	0.34147900	L
C-C_R	0	16.65451000	3.98893500	-0.18478900	L
C-C_R	0	17.87331000	6.10839000	-0.19570600	L
C-C_R	0	19.09216200	8.22702100	-0.20351100	L
C-C_R	0	20.31125900	10.34548300	-0.20753700	L
C-C_R	0	21.53070800	12.46376700	-0.20758500	L
C-C_R	0	22.75056200	14.58183700	-0.20329800	L
C-C_R	0	23.97079300	16.69952700	-0.19167800	L
C-C_R	0	25.19142000	18.81647900	-0.16214600	L
C-C_R	0	26.41229400	20.93267300	-0.10826700	L
C-C_R	0	27.63354300	23.04804800	-0.03005400	L
C-C_R	0	28.85476000	25.16341200	0.05897600	L
C-C_R	0	30.07570100	27.27963600	0.14591400	L
C-C_R	0	31.29649600	29.39641300	0.22861200	L
C-C_R	0	32.51725700	31.51497900	0.30985800	L
C-C_R	0	19.09556600	3.99169500	-0.28102300	L

```
 C-C_R         0   20.31471200    6.11124700   -
0.28936500 L

 C-C_R         0   21.53393300    8.23001400   -
0.29499900 L

 C-C_R         0   22.75336600   10.34866400   -
0.29818000 L

 C-C_R         0   23.97305900   12.46723600   -
0.30052100 L

 C-C_R         0   25.19288500   14.58571300   -
0.30461700 L

 C-C_R         0   26.41273800   16.70388200   -
0.30244700 L

 C-C_R         0   27.63368500   18.82078100   -
0.25980200 L

 C-C_R         0   28.85508700   20.93618700   -
0.18060300 L

 C-C_R         0   30.07625000   23.05116800   -
0.08544600 L

 C-C_R         0   31.29748200   25.16620900
0.01728300 L

 C-C_R         0   32.51856400   27.28192000
0.11631300 L

 C-C_R         0   33.73949600   29.39834000
0.20588100 L

 C-C_R         0   34.96040700   31.51657700
0.29265300 L

 C-C_R         0   21.53721900    3.99448600   -
0.36619900 L

 C-C_R         0   22.75663300    6.11409800   -
0.37116800 L

 C-C_R         0   23.97615200    8.23295900   -
0.37391900 L

 C-C_R         0   25.19584900   10.35176300   -
0.37580700 L

 C-C_R         0   26.41567900   12.47057100   -
0.38063000 L

 C-C_R         0   27.63536200   14.58916200   -
0.39235600 L

 C-C_R         0   28.85584700   16.70722100   -
0.37746700 L

 C-C_R         0   30.07714300   18.82320200   -
0.30530400 L

 C-C_R         0   31.29835900   20.93800100   -
0.20774300 L

 C-C_R         0   32.51954300   23.05282400   -
0.10579100 L

 C-C_R         0   33.74063300   25.16750500
0.00694600 L

 C-C_R         0   34.96169700   27.28322700
0.10705000 L

 C-C_R         0   36.18265000   29.39939900
0.19953100 L

 C-C_R         0   37.40362000   31.51734400
0.29044600 L

 C-C_R         0   23.97940300    3.99722400   -
0.43774500 L

 C-C_R         0   25.19903900    6.11685000   -
0.43797000 L

 C-C_R         0   26.41881200    8.23573400   -
0.43596900 L

 C-C_R         0   27.63875600   10.35454200   -
0.43314200 L

 C-C_R         0   28.85880600   12.47322700   -
0.43131200 L

 C-C_R         0   30.07913100   14.59128500   -
0.42443800 L

 C-C_R         0   31.29994000   16.70829600   -
0.38355900 L

 C-C_R         0   32.52095900   18.82401000   -
0.30516500 L

 C-C_R         0   33.74198800   20.93867400   -
0.20493300 L

 C-C_R         0   34.96297900   23.05295400   -
0.09007500 L

 C-C_R         0   36.18401600   25.16799100
0.01673100 L

 C-C_R         0   37.40495200   27.28367100
0.11412100 L

 C-C_R         0   38.62579700   29.39961100
0.20823800 L
```

```
 C-C_R          0   39.84673400   31.51726500
0.30287900 L

 C-C_R          0   26.42203400    3.99984300   -
0.49319500 L

 C-C_R          0   27.64185700    6.11942800   -
0.48666900 L

 C-C_R          0   28.86187600    8.23820100   -
0.47666900 L

 C-C_R          0   30.08211100   10.35671400   -
0.46285800 L

 C-C_R          0   31.30249600   12.47475700   -
0.44284400 L

 C-C_R          0   32.52310700   14.59197500   -
0.40844200 L

 C-C_R          0   33.74402000   16.70817200   -
0.35171700 L

 C-C_R          0   34.96484100   18.82334300   -
0.26661600 L

 C-C_R          0   36.18568900   20.93785900   -
0.16482600 L

 C-C_R          0   37.40662400   23.05256000   -
0.06058900 L

 C-C_R          0   38.62747600   25.16779600
0.03819400 L

 C-C_R          0   39.84815200   27.28333400
0.13405100 L

 C-C_R          0   41.06876500   29.39900000
0.23049100 L

 C-C_R          0   42.28955900   31.51635200
0.32905100 L

 C-C_R          0   28.86498700    4.00232300   -
0.53087400 L

 C-C_R          0   30.08497000    6.12181100   -
0.51556200 L

 C-C_R          0   31.30528300    8.24029100   -
0.49471900 L

 C-C_R          0   32.52586800   10.35817700   -
0.46662000 L

 C-C_R          0   33.74655100   12.47532100   -
0.42800000 L

 C-C_R          0   34.96727500   14.59163700   -
0.37439900 L

 C-C_R          0   36.18800900   16.70714700   -
0.30277900 L

 C-C_R          0   37.40878900   18.82205700   -
0.21620300 L

 C-C_R          0   38.62963900   20.93682800   -
0.12237500 L

 C-C_R          0   39.85036700   23.05180400   -
0.02708400 L

 C-C_R          0   41.07086100   25.16697800
0.06826900 L

 C-C_R          0   42.29115000   27.28225700
0.16518900 L

 C-C_R          0   43.51138900   29.39760100
0.26483900 L

 C-C_R          0   44.73189000   31.51463700
0.36742500 L

 C-C_R          0   31.30808400    4.00474300   -
0.55085700 L

 C-C_R          0   32.52827200    6.12409000   -
0.52586100 L

 C-C_R          0   33.74904100    8.24199800   -
0.49378400 L

 C-C_R          0   34.97002100   10.35896300   -
0.45268900 L

 C-C_R          0   36.19090800   12.47518300   -
0.40024800 L

 C-C_R          0   37.41167500   14.59080700   -
0.33503500 L

 C-C_R          0   38.63239200   16.70595500   -
0.25795300 L

 C-C_R          0   39.85309400   18.82085300   -
0.17264900 L

 C-C_R          0   41.07368500   20.93572600   -
0.08260100 L

 C-C_R          0   42.29403400   23.05064200
0.01045300 L

 C-C_R          0   43.51408100   25.16557000
0.10656900 L
```

C-C_R	0	44.73385500	27.28049500	0.20620600	L
C-C_R	0	45.95352500	29.39545700	0.30943000	L
C-C_R	0	47.17351000	31.51218000	0.41576600	L
C-C_R	0	33.75109600	4.00741500	-0.55531600	L
C-C_R	0	34.97187700	6.12638000	-0.52131000	L
C-C_R	0	36.19333700	8.24310600	-0.47960800	L
C-C_R	0	37.41457900	10.35900700	-0.42860800	L
C-C_R	0	38.63550300	12.47454000	-0.36734500	L
C-C_R	0	39.85624800	14.58977200	-0.29613300	L
C-C_R	0	41.07689000	16.70476600	-0.21669200	L
C-C_R	0	42.29740000	18.81962100	-0.13115800	L
C-C_R	0	43.51768100	20.93439700	-0.04091900	L
C-C_R	0	44.73762500	23.04908800	0.05359200	L
C-C_R	0	45.95716000	25.16365600	0.15239500	L
C-C_R	0	47.17626600	27.27810500	0.25534400	L
C-C_R	0	48.39502400	29.39258300	0.36191600	L
C-C_R	0	49.61412900	31.50910900	0.47133600	L
C-C_R	0	36.19384300	4.01100900	-0.54785300	L
C-C_R	0	37.41643500	6.12802300	-0.50645300	L
C-C_R	0	38.63824400	8.24306200	-0.45720600	L
C-C_R	0	39.85936700	10.35831800	-0.39905500	L
C-C_R	0	41.08020700	12.47354300	-0.33199000	L
C-C_R	0	42.30088000	14.58861000	-0.25689800	L
C-C_R	0	43.52140200	16.70351200	-0.17511200	L
C-C_R	0	44.74171100	18.81826900	-0.08770200	L
C-C_R	0	45.96169800	20.93287300	0.00481100	L
C-C_R	0	47.18124500	23.04727200	0.10223400	L
C-C_R	0	48.40024300	25.16139500	0.20429700	L
C-C_R	0	49.61855000	27.27517000	0.31043000	L
C-C_R	0	50.83568100	29.38863600	0.41972700	L
C-C_R	0	52.05246800	31.50472500	0.53122600	L
C-C_R	0	38.64088300	4.01283300	-0.53251800	L
C-C_R	0	39.86330700	6.12607900	-0.48511100	L
C-C_R	0	41.08461900	8.24115900	-0.42970500	L
C-C_R	0	42.30559700	10.35640200	-0.36600600	L
C-C_R	0	43.52636200	12.47155300	-0.29448700	L
C-C_R	0	44.74696300	14.58655100	-0.21602500	L
C-C_R	0	45.96737700	16.70139000	-0.13143700	L
C-C_R	0	47.18751900	18.81606000	-0.04120900	L
C-C_R	0	48.40726600	20.93051200	0.05442300	L

```
 C-C_R         0   49.62648300   23.04465900
0.15517100 L

 C-C_R         0   50.84504100   25.15835700
0.26045700 L

 C-C_R         0   52.06281200   27.27135700
0.36933800 L

 C-C_R         0   53.27845500   29.38295600
0.48055200 L

 C-C_R         0   54.48058700   31.49056600
0.59247700 L

 C-C_R         0    4.47481200    2.57631800
0.35788400 L

 C-C_R         0    5.67511800    4.68787100
0.34018600 L

 C-C_R         0    6.88895800    6.80338000
0.32307700 L

 C-C_R         0    8.10498900    8.92015400
0.30834400 L

 C-C_R         0    9.32190200   11.03741900
0.29737100 L

 C-C_R         0   10.53960700   13.15486700
0.29142300 L

 C-C_R         0   11.75801600   15.27231000
0.29166600 L

 C-C_R         0   12.97704900   17.38961000
0.29913400 L

 C-C_R         0   14.19663200   19.50666000
0.31465500 L

 C-C_R         0   15.41669100   21.62338200
0.33869700 L

 C-C_R         0   16.63716500   23.73972800
0.37112400 L

 C-C_R         0   17.85803000   25.85564400
0.41102700 L

 C-C_R         0   19.07933800   27.97094500
0.45695800 L

 C-C_R         0   20.30184100   30.08405500
0.50746100 L

 C-C_R         0   21.52626300   32.18747400
0.56113600 L

 C-C_R         0    6.90077600    2.56775700
0.23828800 L

 C-C_R         0    8.11571900    4.68777300
0.22053700 L

 C-C_R         0    9.33104800    6.80505400
0.20436600 L

 C-C_R         0   10.54762200    8.92247200
0.19108100 L

 C-C_R         0   11.76499400   11.04000900
0.18206000 L

 C-C_R         0   12.98306800   13.15754500
0.17863400 L

 C-C_R         0   14.20179600   15.27496300
0.18207200 L

 C-C_R         0   15.42112900   17.39215200
0.19357100 L

 C-C_R         0   16.64100200   19.50901100
0.21415900 L

 C-C_R         0   17.86134400   21.62545800
0.24437800 L

 C-C_R         0   19.08209500   23.74144100
0.28382600 L

 C-C_R         0   20.30327100   25.85689800
0.33092400 L

 C-C_R         0   21.52520000   27.97172000
0.38340300 L

 C-C_R         0   22.74797000   30.08823500
0.43946800 L

 C-C_R         0   23.96755900   32.19834500
0.49815100 L

 C-C_R         0    9.33695900    2.56888800
0.11981300 L

 C-C_R         0   10.55422000    4.68924300
0.10292300 L

 C-C_R         0   11.77117800    6.80740500
0.08799800 L

 C-C_R         0   12.98856100    8.92534400
0.07640400 L

 C-C_R         0   14.20649400   11.04316500
0.06951700 L
```

C-C_R 0 15.42501500 13.16084500
0.06868200 L

C-C_R 0 16.64413100 15.27830600
0.07527800 L

C-C_R 0 17.86381800 17.39544600
0.09076800 L

C-C_R 0 19.08402600 19.51215700
0.11655400 L

C-C_R 0 20.30468300 21.62837100
0.15349600 L

C-C_R 0 21.52572600 23.74412600
0.20084900 L

C-C_R 0 22.74716300 25.85966100
0.25598300 L

C-C_R 0 23.96884100 27.97568800
0.31548200 L

C-C_R 0 25.18989200 30.09376800
0.37739400 L

C-C_R 0 26.40990900 32.20293800
0.44139000 L

C-C_R 0 11.77545300 2.57109900
0.00431400 L

C-C_R 0 12.99360100 4.69149900 -
0.01123200 L

C-C_R 0 14.21148300 6.80998000 -
0.02456200 L

C-C_R 0 15.42955600 8.92822900 -
0.03428000 L

C-C_R 0 16.64803000 11.04628200 -
0.03911300 L

C-C_R 0 17.86700200 13.16412600 -
0.03781000 L

C-C_R 0 19.08651000 15.28168400 -
0.02891000 L

C-C_R 0 20.30655800 17.39884100 -
0.01048800 L

C-C_R 0 21.52709600 19.51547000
0.01997200 L

C-C_R 0 22.74802200 21.63153400
0.06433800 L

C-C_R 0 23.96921100 23.74724800
0.12131100 L

C-C_R 0 25.19050400 25.86313800
0.18633700 L

C-C_R 0 26.41159500 27.97980600
0.25410600 L

C-C_R 0 27.63220000 30.09784700
0.32276800 L

C-C_R 0 28.85257200 32.20642300
0.39283900 L

C-C_R 0 14.21501500 2.57353100 -
0.10630900 L

C-C_R 0 15.43370400 4.69405500 -
0.12009100 L

C-C_R 0 16.65219000 6.81273200 -
0.13152100 L

C-C_R 0 17.87080800 8.93119400 -
0.13934200 L

C-C_R 0 19.08974900 11.04945300 -
0.14261600 L

C-C_R 0 20.30911400 13.16749500 -
0.14051100 L

C-C_R 0 21.52895900 15.28524300 -
0.13171500 L

C-C_R 0 22.74928800 17.40253500 -
0.11310700 L

C-C_R 0 23.97004700 19.51916300 -
0.07875400 L

C-C_R 0 25.19103200 21.63517200 -
0.02559300 L

C-C_R 0 26.41221900 23.75075800
0.04510800 L

C-C_R 0 27.63333400 25.86663800
0.12371000 L

C-C_R 0 28.85417900 27.98328600
0.20166500 L

C-C_R 0 30.07483400 30.10100600
0.27813500 L

C-C_R 0 31.29547500 32.20918000
0.35478300 L

C-C_R 0 16.65541200 2.57615700 -
0.21004100 L

C-C_R 0 17.87445400 4.69677900 -
0.22160800 L

C-C_R 0 19.09337600 6.81559300 -
0.23082500 L

C-C_R 0 20.31242200 8.93422700 -
0.23682300 L

C-C_R 0 21.53173700 11.05269400 -
0.23944500 L

C-C_R 0 22.75139000 13.17101000 -
0.23912400 L

C-C_R 0 23.97138800 15.28911200 -
0.23553000 L

C-C_R 0 25.19165500 17.40672800 -
0.22154500 L

C-C_R 0 26.41243900 19.52338700 -
0.18020200 L

C-C_R 0 27.63354400 21.63917400 -
0.11076100 L

C-C_R 0 28.85486600 23.75422300 -
0.02032100 L

C-C_R 0 30.07597900 25.86973500
0.07346000 L

C-C_R 0 31.29691000 27.98603500
0.16265900 L

C-C_R 0 32.51773900 30.10337500
0.24694600 L

C-C_R 0 33.73858000 32.21119600
0.32971400 L

C-C_R 0 19.09651300 2.57889500 -
0.30473100 L

C-C_R 0 20.31580800 4.69958200 -
0.31348400 L

C-C_R 0 21.53506200 6.81849400 -
0.31999100 L

C-C_R 0 22.75444600 8.93726800 -
0.32401700 L

C-C_R 0 23.97404500 11.05594900 -
0.32673900 L

C-C_R 0 25.19382600 13.17461100 -
0.33125600 L

C-C_R 0 26.41347600 15.29309400 -
0.33974700 L

C-C_R 0 27.63386700 17.41103400 -
0.32383800 L

C-C_R 0 28.85522600 19.52698600 -
0.25521200 L

C-C_R 0 30.07656000 21.64190400 -
0.16159200 L

C-C_R 0 31.29767100 23.75707100 -
0.06350600 L

C-C_R 0 32.51886900 25.87190000
0.04573100 L

C-C_R 0 33.73991000 27.98787400
0.14204100 L

C-C_R 0 34.96084400 30.10490300
0.23146400 L

C-C_R 0 36.18181500 32.21241700
0.31910400 L

C-C_R 0 21.53822700 2.58165800 -
0.38809900 L

C-C_R 0 22.75772000 4.70237600 -
0.39314100 L

C-C_R 0 23.97723900 6.82134500 -
0.39594500 L

C-C_R 0 25.19690200 8.94020900 -
0.39692500 L

C-C_R 0 26.41672800 11.05903500 -
0.39837500 L

C-C_R 0 27.63657500 13.17780400 -
0.40487300 L

C-C_R 0 28.85664900 15.29615300 -
0.40953900 L

C-C_R 0 30.07759500 17.41326500 -
0.36515400 L

C-C_R 0 31.29877500 19.52855400 -
0.27660200 L

C-C_R 0 32.51986700 21.64329600 -
0.17674200 L

```
 C-C_R           0   33.74101400   23.75777200   -
0.06458200 L

 C-C_R           0   34.96210000   25.87294000
0.04276900 L

 C-C_R           0   36.18309500   27.98881000
0.13918200 L

 C-C_R           0   37.40401800   30.10558000
0.23151800 L

 C-C_R           0   38.62504600   32.21280600
0.32329200 L

 C-C_R           0   23.98047000    2.58436500   -
0.45783100 L

 C-C_R           0   25.20012700    4.70507900   -
0.45782200 L

 C-C_R           0   26.41987000    6.82404600   -
0.45514100 L

 C-C_R           0   27.63978700    8.94288600   -
0.45020200 L

 C-C_R           0   28.85987000   11.06158600   -
0.44406400 L

 C-C_R           0   30.08009900   13.17991400   -
0.43566600 L

 C-C_R           0   31.30070700   15.29736400   -
0.41026500 L

 C-C_R           0   32.52165500   17.41372100   -
0.35413700 L

 C-C_R           0   33.74263900   19.52888000   -
0.26415300 L

 C-C_R           0   34.96357100   21.64330600   -
0.15655800 L

 C-C_R           0   36.18450600   23.75783000   -
0.04515900 L

 C-C_R           0   37.40547700   25.87318900
0.05559200 L

 C-C_R           0   38.62630000   27.98891600
0.15105800 L

 C-C_R           0   39.84709500   30.10541700
0.24602700 L

 C-C_R           0   41.06809200   32.21235400
0.34189000 L

 C-C_R           0   26.42314700    2.58696100   -
0.51186200 L

 C-C_R           0   27.64293000    4.70763600   -
0.50508900 L

 C-C_R           0   28.86287100    6.82652100   -
0.49449200 L

 C-C_R           0   30.08306600    8.94512900   -
0.47953800 L

 C-C_R           0   31.30347700   11.06329200   -
0.45887900 L

 C-C_R           0   32.52403300   13.18079000   -
0.42818900 L

 C-C_R           0   33.74477800   15.29736600   -
0.38031500 L

 C-C_R           0   34.96557700   17.41296500   -
0.30885400 L

 C-C_R           0   36.18636900   19.52778000   -
0.21681900 L

 C-C_R           0   37.40727800   21.64240200   -
0.11631200 L

 C-C_R           0   38.62815100   23.75740100   -
0.01701200 L

 C-C_R           0   39.84883300   25.87274200
0.07928400 L

 C-C_R           0   41.06935700   27.98823800
0.17549900 L

 C-C_R           0   42.28989600   30.10443800
0.27373300 L

 C-C_R           0   43.51074700   32.21107900
0.37382000 L

 C-C_R           0   28.86613300    2.58943600   -
0.54893500 L

 C-C_R           0   30.08598000    4.71005700   -
0.53383700 L

 C-C_R           0   31.30614000    6.82877200   -
0.51341900 L

 C-C_R           0   32.52671100    8.94688000   -
0.48633000 L

 C-C_R           0   33.74747700   11.06421200   -
0.45034600 L
```

```
 C-C_R      0   34.96824600   13.18076600   -
0.40201300 L

 C-C_R      0   36.18898000   15.29657300   -
0.33834100 L

 C-C_R      0   37.40971200   17.41173400   -
0.25949500 L

 C-C_R      0   38.63049700   19.52657400   -
0.17076900 L

 C-C_R      0   39.85123100   21.64145600   -
0.07781200 L

 C-C_R      0   41.07176200   23.75649700
0.01647400 L

 C-C_R      0   42.29203800   25.87163900
0.11241200 L

 C-C_R      0   43.51213100   27.98681600
0.21110800 L

 C-C_R      0   44.73225000   30.10267700
0.31301900 L

 C-C_R      0   45.95278900   32.20902800
0.41721100 L

 C-C_R      0   31.30926200    2.59186000   -
0.56928200 L

 C-C_R      0   32.52908600    4.71250100   -
0.54523400 L

 C-C_R      0   33.74968900    6.83088000   -
0.51482500 L

 C-C_R      0   34.97079200    8.94808000   -
0.47646100 L

 C-C_R      0   36.19184800   11.06442500   -
0.42819600 L

 C-C_R      0   37.41271100   13.18020300   -
0.36842400 L

 C-C_R      0   38.63345200   15.29552400   -
0.29705500 L

 C-C_R      0   39.85413600   17.41052700   -
0.21629400 L

 C-C_R      0   41.07473800   19.52540300   -
0.12934200 L

 C-C_R      0   42.29514700   21.64026500   -
0.03835100 L

 C-C_R      0   43.51526000   23.75511800
0.05608100 L

 C-C_R      0   44.73504000   25.86993200
0.15422800 L

 C-C_R      0   45.95454100   27.98470300
0.25621400 L

 C-C_R      0   47.17398600   30.10017700
0.36171500 L

 C-C_R      0   48.39395400   32.20631500
0.46948100 L

 C-C_R      0   33.75226900    2.59447100   -
0.57486800 L

 C-C_R      0   34.97215600    4.71545600   -
0.54248200 L

 C-C_R      0   36.19384900    6.83256900   -
0.50342400 L

 C-C_R      0   37.41539400    8.94844500   -
0.45606600 L

 C-C_R      0   38.63649500   11.06398900   -
0.39918900 L

 C-C_R      0   39.85732900   13.17930900   -
0.33257000 L

 C-C_R      0   41.07801100   15.29439900   -
0.25720900 L

 C-C_R      0   42.29856700   17.40931100   -
0.17491100 L

 C-C_R      0   43.51893500   19.52410500   -
0.08721200 L

 C-C_R      0   44.73900600   21.63879600
0.00515900 L

 C-C_R      0   45.95867900   23.75334900
0.10205700 L

 C-C_R      0   47.17788200   25.86772800
0.20336600 L

 C-C_R      0   48.39657700   27.98194500
0.30867100 L

 C-C_R      0   49.61485800   30.09687900
0.41723900 L

 C-C_R      0   50.83392000   32.20309400
0.52767300 L
```

C-C_R	0	36.19405700	2.59880400	-0.56890100	L
C-C_R	0	37.41714200	4.71795700	-0.52969400	L
C-C_R	0	38.63944100	6.83242600	-0.48372900	L
C-C_R	0	39.86083200	8.94750200	-0.42945400	L
C-C_R	0	41.08180100	11.06274000	-0.36642100	L
C-C_R	0	42.30255500	13.17788400	-0.29511000	L
C-C_R	0	43.52315100	15.29286800	-0.21659600	L
C-C_R	0	44.74356600	17.40769600	-0.13197500	L
C-C_R	0	45.96371300	19.52236700	-0.04192500	L
C-C_R	0	47.18347200	21.63684500	0.05326900	L
C-C_R	0	48.40272100	23.75105800	0.15338200	L
C-C_R	0	49.62133200	25.86490900	0.25794900	L
C-C_R	0	50.83904900	27.97827300	0.36615500	L
C-C_R	0	52.05486200	30.09172400	0.47691400	L
C-C_R	0	53.27281800	32.19457400	0.58879000	L
C-C_R	0	38.62843500	2.60933300	-0.55534300	L
C-C_R	0	39.85499300	4.72064300	-0.51077200	L
C-C_R	0	41.07677100	6.83559100	-0.45886300	L
C-C_R	0	42.29791500	8.95085900	-0.39887300	L
C-C_R	0	43.51878800	11.06608600	-0.33095100	L
C-C_R	0	44.73947600	13.18117300	-0.25578000	L
C-C_R	0	45.95999800	15.29610500	-0.17416100	L
C-C_R	0	47.18030100	17.41087900	-0.08665300	L
C-C_R	0	48.40028200	19.52546600	0.00646900	L
C-C_R	0	49.61981200	21.63979200	0.10498500	L
C-C_R	0	50.83875200	23.75373000	0.20844300	L
C-C_R	0	52.05698200	25.86707000	0.31602000	L
C-C_R	0	53.27437700	27.97951800	0.42655200	L
C-C_R	0	54.48675800	30.09363800	0.53872100	L
C-C_R	0	27.42365100	16.00508900	2.95450200	H
C-C_R	0	27.49017500	17.39861400	3.04157800	H
C-C_R	0	28.58794700	15.24632100	2.90572400	H
C-C_R	0	28.72995800	18.04548900	3.08195800	H
H-H_	0	26.59650700	18.01660000	3.06328900	H
C-C_R	0	29.83825700	15.86958400	2.94100700	H
H-H_	0	28.53169800	14.15811300	2.81725700	H
N-N_R	0	28.94897000	19.41069200	3.16376700	H
C-C_R	0	29.92971200	17.26213100	3.03234500	H
H-H_	0	30.76665400	15.30627100	2.88659300	H
C-C_R	0	28.03648400	20.39911200	3.20365000	H

```
 N-N_R           0   31.09647400   18.00601400
3.07664600 H

 C-C_R           0   28.71695100   21.79606200
3.31008300 H

 O-O_R           0   26.80564500   20.30693500
3.17291400 H

 C-C_R           0   32.36518700   17.56117300
3.02071100 H

 N-N_R           0   30.06555100   21.74870500
3.31256100 H

 O-O_R           0   28.00936800   22.80895200
3.38666100 H

 C-C_R           0   33.38016900   18.73627800
3.11191200 H

 O-O_R           0   32.76430300   16.39746900
2.91421200 H

 C-C_3           0   30.74911800   23.00347800
3.45382000 H

 N-N_R           0   32.80687500   19.95619700
3.15715400 H

 O-O_R           0   34.59469500   18.49559000
3.13023600 H

 H-H_            0   31.25985000   23.08599700
4.43221400 H

 H-H_            0   31.53528500   23.11970000
2.69073700 H

 H-H_            0   30.04051200   23.84124900
3.36355500 H

 C-C_3           0   33.72139700   21.06038800
3.24903500 H

 H-H_            0   33.98468300   21.30897500
4.29646100 H

 H-H_            0   34.66925900   20.83409700
2.73421600 H

 H-H_            0   33.27707500   21.96383200
2.80779400 H

 Cu-             0   30.83097700   19.93589200
3.19103300 H

 H-H_            0    3.52030000    4.49585900
0.44269100 L

 H-H_            0    4.73913600    6.63115300
0.42500100 L

 H-H_            0    5.95532300    8.74838700
0.40901800 L

 H-H_            0    7.17194900   10.86549800
0.39629300 L

 H-H_            0    8.38939100   12.98296200
0.38805700 L

 H-H_            0    9.60756600   15.10051900
0.38541300 L

 H-H_            0   10.82637600   17.21799200
0.38931100 L

 H-H_            0   12.04573200   19.33525900
0.40047800 L

 H-H_            0   13.26555700   21.45224400
0.41933000 L

 H-H_            0   14.48579100   23.56891000
0.44584800 L

 H-H_            0   15.70641500   25.68524800
0.47949900 L

 H-H_            0   16.92750100   27.80126600
0.51936100 L

 H-H_            0   18.14985200   29.91748300
0.56451500 L

 H-H_            0   19.38612000   32.04273100
0.61436600 L

 H-H_            0   21.50720700   33.26983700
0.60713100 L

 H-H_            0   23.96555500   33.28201700
0.54482100 L

 H-H_            0   26.40918400   33.28656900
0.48902500 L

 H-H_            0   28.85206200   33.29001700
0.44125200 L

 H-H_            0   31.29505400   33.29276300
0.40338700 L

 H-H_            0   33.73821700   33.29480700
0.37761900 L

 H-H_            0   36.18151700   33.29608900
0.36560100 L
```

```
 H-H_             0   38.62483600   33.29655000    0.36818300 L
 H-H_             0   41.06799400   33.29616000    0.38538900 L
 H-H_             0   43.51077700   33.29493000    0.41633900 L
 H-H_             0   45.95294100   33.29291100    0.45919400 L
 H-H_             0   48.39422600   33.29022300    0.51128600 L
 H-H_             0   50.83527000   33.28701800    0.56954600 L
 H-H_             0   53.29321100   33.27706100    0.63120600 L
 H-H_             0   55.43525500   29.56986900    0.54286100 L
 H-H_             0   54.21459800   27.43857000    0.42955100 L
 H-H_             0   52.99666200   25.32521600    0.31854500 L
 H-H_             0   51.77837200   23.21180700    0.21045400 L
 H-H_             0   50.55937900   21.09780000    0.10648100 L
 H-H_             0   49.33980000   18.98340300    0.00754500 L
 H-H_             0   48.11978000   16.86875400   -0.08583100 L
 H-H_             0   46.89944900   14.75393600   -0.17341700 L
 H-H_             0   45.67891200   12.63897800   -0.25502100 L
 H-H_             0   44.45821100   10.52386800   -0.33025100 L
 H-H_             0   43.23731400    8.40859700   -0.39848400 L
 H-H_             0   42.01609000    6.29318700   -0.45912600 L
 H-H_             0   40.79370400    4.17718300   -0.51202300 L
 H-H_             0   39.55750300    2.05182000   -0.55806000 L
 H-H_             0   37.43601300    0.82580800   -0.58962700 L
 H-H_             0   34.97688900    0.81562400   -0.59814900 L
 H-H_             0   32.53260500    0.81260700   -0.59712100 L
 H-H_             0   30.08924500    0.81013700   -0.58354000 L
 H-H_             0   27.64606400    0.80770600   -0.55509500 L
 H-H_             0   25.20313200    0.80519200   -0.51070800 L
 H-H_             0   22.76055000    0.80256100   -0.45062500 L
 H-H_             0   20.31841200    0.79984300   -0.37609300 L
 H-H_             0   17.87681200    0.79710100   -0.28893600 L
 H-H_             0   15.43585300    0.79441100   -0.19122900 L
 H-H_             0   12.99567500    0.79185200   -0.08510000 L
 H-H_             0   10.55646800    0.78946100    0.02737400 L
 H-H_             0    8.11755400    0.78725000    0.14424200 L
 H-H_             0    5.66178600    0.79157300    0.26458200 L
 H-H_             0   55.41743700   32.03081100    0.63737400 L
 H-H_             0    3.53899200    2.03359700    0.39347700 L
 H-H_             0   26.44641500   15.51713300    2.90707000 H
```

G-2^{2-} E= -1790.383230 H

```
C-C_R 0 5.67698400 1.90528900 0.54495000 L
C-C_R 0 8.11586800 1.90009200 0.48295700 L
C-C_R 0 10.55582700 1.90033400 0.42521300 L
C-C_R 0 12.99693600 1.90130600 0.37490500 L
C-C_R 0 15.43874900 1.90317400 0.33454900 L
C-C_R 0 17.88086900 1.90596600 0.30601100 L
C-C_R 0 20.32298700 1.90952900 0.29067500 L
C-C_R 0 22.76493500 1.91356200 0.28876700 L
C-C_R 0 25.20675400 1.91764900 0.29779500 L
C-C_R 0 27.64864000 1.92140500 0.31227800 L
C-C_R 0 30.09076100 1.92477600 0.32834000 L
C-C_R 0 32.53312600 1.92811200 0.34627000 L
C-C_R 0 34.97559000 1.93221200 0.36817300 L
C-C_R 0 37.41733200 1.94256200 0.39526300 L
C-C_R 0 4.46013500 4.00451300 0.49346300 L
C-C_R 0 5.66960300 6.12022700 0.37952900 L
C-C_R 0 6.88424000 8.23433700 0.27017100 L
C-C_R 0 8.09993300 10.34937700 0.16875100 L
C-C_R 0 9.31657900 12.46500800 0.07894700 L
C-C_R 0 10.53403400 14.58098800 0.00481000 L
C-C_R 0 11.75211000 16.69717300 -0.04914200 L
C-C_R 0 12.97061600 18.81345200 -0.07882100 L
C-C_R 0 14.18936600 20.92972200 -0.08260700 L
C-C_R 0 15.40821700 23.04591700 -0.06280200 L
C-C_R 0 16.62712300 25.16202300 -0.02503800 L
C-C_R 0 17.84616600 27.27801900 0.02392900 L
C-C_R 0 19.06576900 29.39364200 0.07846100 L
C-C_R 0 20.29020300 31.50563700 0.13496500 L
C-C_R 0 6.89195100 4.00965200 0.42909000 L
C-C_R 0 8.10480800 6.12459100 0.31444600 L
C-C_R 0 9.31971500 8.23942300 0.20405700 L
C-C_R 0 10.53572000 10.35471800 0.10104100 L
C-C_R 0 11.75258100 12.47038800 0.00935900 L
C-C_R 0 12.97017300 14.58641000 -0.06539100 L
C-C_R 0 14.18838400 16.70275400 -0.11632000 L
C-C_R 0 15.40706200 18.81928100 -0.13795700 L
C-C_R 0 16.62599800 20.93578300 -0.12987800 L
C-C_R 0 17.84501100 23.05211400 -0.09756700 L
C-C_R 0 19.06405700 25.16823700 -0.04983300 L
C-C_R 0 20.28335100 27.28402400 0.00527200 L
```

```
 C-C_R       0   21.50346600   29.39913200
0.06271400 L

 C-C_R       0   22.72441000   31.51888000
0.12057600 L

 C-C_R       0    9.33186200    4.00775400
0.36632900 L

 C-C_R       0   10.54712300    6.12404900
0.25022600 L

 C-C_R       0   11.76295300    8.23953600
0.13737900 L

 C-C_R       0   12.97947700   10.35512500
0.03066800 L

 C-C_R       0   14.19667100   12.47095900   -
0.06468200 L

 C-C_R       0   15.41450800   14.58717800   -
0.14015200 L

 C-C_R       0   16.63295200   16.70379100   -
0.18547900 L

 C-C_R       0   17.85185800   18.82056700   -
0.19461900 L

 C-C_R       0   19.07097400   20.93721700   -
0.17073300 L

 C-C_R       0   20.29010900   23.05365200   -
0.12461300 L

 C-C_R       0   21.50927700   25.16999300   -
0.06838800 L

 C-C_R       0   22.72869100   27.28652500   -
0.00962700 L

 C-C_R       0   23.94816600   29.40423400
0.04887900 L

 C-C_R       0   25.16586600   31.52575700
0.10702900 L

 C-C_R       0   11.77260600    4.00784000
0.30766500 L

 C-C_R       0   12.98895300    6.12451200
0.18909000 L

 C-C_R       0   14.20553300    8.24029900
0.07161400 L

 C-C_R       0   15.42256900   10.35604200   -
0.04157700 L

 C-C_R       0   16.64011000   12.47198600   -
0.14327300 L

 C-C_R       0   17.85820800   14.58842700   -
0.22005900 L

 C-C_R       0   19.07694200   16.70538400   -
0.25573800 L

 C-C_R       0   20.29610200   18.82243400   -
0.24631900 L

 C-C_R       0   21.51537500   20.93922900   -
0.20267200 L

 C-C_R       0   22.73454700   23.05593300   -
0.14363700 L

 C-C_R       0   23.95361100   25.17294800   -
0.08231600 L

 C-C_R       0   25.17251500   27.29074700   -
0.02259300 L

 C-C_R       0   26.39085700   29.40969600
0.03594100 L

 C-C_R       0   27.60844600   31.53084800
0.09440400 L

 C-C_R       0   14.21412400    4.00889500
0.25563100 L

 C-C_R       0   15.43108000    6.12571100
0.13302600 L

 C-C_R       0   16.64823000    8.24156900
0.00867300 L

 C-C_R       0   17.86570200   10.35724900   -
0.11470900 L

 C-C_R       0   19.08338700   12.47310700   -
0.22830500 L

 C-C_R       0   20.30161300   14.58995000   -
0.30576100 L

 C-C_R       0   21.52077500   16.70752300   -
0.32386400 L

 C-C_R       0   22.74028000   18.82481300   -
0.28851000 L

 C-C_R       0   23.95966300   20.94174100   -
0.22494100 L

 C-C_R       0   25.17868300   23.05893500   -
0.15872000 L
```

C-C_R	0	26.39734400	25.17675900	-0.09645700	L
C-C_R	0	27.61565400	27.29538200	-0.03609300	L
C-C_R	0	28.83356500	29.41461500	0.02388600	L
C-C_R	0	30.05119900	31.53568800	0.08414800	L
C-C_R	0	16.65610800	4.01083800	0.21267100	L
C-C_R	0	17.87347900	6.12767900	0.08536200	L
C-C_R	0	19.09107700	8.24341200	-0.04755800	L
C-C_R	0	20.30870300	10.35860400	-0.18630300	L
C-C_R	0	21.52639500	12.47428000	-0.31181000	L
C-C_R	0	22.74522600	14.59217300	-0.37596900	L
C-C_R	0	23.96468800	16.71065200	-0.37442100	L
C-C_R	0	25.18443000	18.82788600	-0.31431800	L
C-C_R	0	26.40359500	20.94513900	-0.24366300	L
C-C_R	0	27.62222900	23.06294200	-0.17849500	L
C-C_R	0	28.84052100	25.18124000	-0.11390500	L
C-C_R	0	30.05853900	27.30014100	-0.04832000	L
C-C_R	0	31.27637600	29.41938500	0.01615200	L
C-C_R	0	32.49406300	31.54037600	0.07967800	L
C-C_R	0	19.09833600	4.01364000	0.18197100	L
C-C_R	0	20.31602700	6.13044300	0.05133900	L
C-C_R	0	21.53386100	8.24575900	-0.08983800	L
C-C_R	0	22.75182300	10.36072800	-0.23184600	L
C-C_R	0	23.97032900	12.47760100	-0.32913400	L
C-C_R	0	25.18935900	14.59546000	-0.38731100	L
C-C_R	0	26.40895000	16.71396500	-0.38712600	L
C-C_R	0	27.62830600	18.83164000	-0.32987500	L
C-C_R	0	28.84709200	20.94943700	-0.26267800	L
C-C_R	0	30.06531500	23.06776600	-0.19950500	L
C-C_R	0	31.28349300	25.18612000	-0.12579600	L
C-C_R	0	32.50146500	27.30482900	-0.05100200	L
C-C_R	0	33.71930300	29.42392600	0.01813500	L
C-C_R	0	34.93703100	31.54479600	0.08441300	L
C-C_R	0	21.54060600	4.01719300	0.16700000	L
C-C_R	0	22.75851500	6.13403300	0.03832900	L
C-C_R	0	23.97660600	8.24944500	-0.09536600	L
C-C_R	0	25.19490400	10.36571800	-0.20818500	L
C-C_R	0	26.41379600	12.48232300	-0.30169800	L
C-C_R	0	27.63333200	14.59912100	-0.38431800	L
C-C_R	0	28.85310300	16.71788200	-0.39341800	L
C-C_R	0	30.07208100	18.83595200	-0.33263600	L

```
 C-C_R           0   31.29046400   20.95394600   -
0.26325200 L

 C-C_R           0   32.50874000   23.07228800   -
0.19645800 L

 C-C_R           0   33.72659900   25.19043900   -
0.11416400 L

 C-C_R           0   34.94450500   27.30913300   -
0.03816700 L

 C-C_R           0   36.16229300   29.42807000
0.03246900 L

 C-C_R           0   37.38003600   31.54880400
0.09992700 L

 C-C_R           0   23.98279000    4.02124600
0.16937000 L

 C-C_R           0   25.20086100    6.13833200
0.05053800 L

 C-C_R           0   26.41912400    8.25461000   -
0.06310900 L

 C-C_R           0   27.63789400   10.37079600   -
0.16843800 L

 C-C_R           0   28.85757700   12.48655600   -
0.27336400 L

 C-C_R           0   30.07800300   14.60295700   -
0.35608200 L

 C-C_R           0   31.29738000   16.72162700   -
0.35753900 L

 C-C_R           0   32.51579000   18.84007500   -
0.30689500 L

 C-C_R           0   33.73387600   20.95817800   -
0.24097800 L

 C-C_R           0   34.95190500   23.07610500   -
0.16237500 L

 C-C_R           0   36.16979500   25.19434500   -
0.08401900 L

 C-C_R           0   37.38756200   27.31292600   -
0.01095800 L

 C-C_R           0   38.60522500   29.43171400
0.05875900 L

 C-C_R           0   39.82294800   31.55230200
0.12617500 L

 C-C_R           0   26.42495200    4.02532100
0.18430700 L

 C-C_R           0   27.64332500    6.14248100
0.07406600 L

 C-C_R           0   28.86205900    8.25875600   -
0.03220100 L

 C-C_R           0   30.08146400   10.37461700   -
0.13625300 L

 C-C_R           0   31.30150700   12.49049000   -
0.22968800 L

 C-C_R           0   32.52163700   14.60743900   -
0.28491300 L

 C-C_R           0   33.74096800   16.72546600   -
0.28618500 L

 C-C_R           0   34.95922200   18.84361300   -
0.24333600 L

 C-C_R           0   36.17728800   20.96153000   -
0.18198800 L

 C-C_R           0   37.39521000   23.07948600   -
0.11159300 L

 C-C_R           0   38.61296200   25.19773700   -
0.04152100 L

 C-C_R           0   39.83050100   27.31618700
0.02738600 L

 C-C_R           0   41.04796700   29.43481900
0.09525900 L

 C-C_R           0   42.26560500   31.55524500
0.16232600 L

 C-C_R           0   28.86724800    4.02899300
0.20311500 L

 C-C_R           0   30.08606200    6.14604600
0.09716300 L

 C-C_R           0   31.30538000    8.26215300   -
0.00466100 L

 C-C_R           0   32.52526000   10.37800300   -
0.09823300 L

 C-C_R           0   33.74536200   12.49419500   -
0.17025200 L

 C-C_R           0   34.96511500   14.61124400   -
0.20500300 L
```

```
C-C_R 0 36.18409600 16.72890200 -0.19925200 L
C-C_R 0 37.40252100 18.84668000 -0.16448800 L
C-C_R 0 38.62069600 20.96451400 -0.11375000 L
C-C_R 0 39.83852600 23.08251100 -0.05440800 L
C-C_R 0 41.05600600 25.20065200 0.00883200 L
C-C_R 0 42.27323200 27.31893600 0.07396600 L
C-C_R 0 43.49039200 29.43738000 0.14024800 L
C-C_R 0 44.70781600 31.55762400 0.20712700 L
C-C_R 0 31.30969800 4.03239900 0.22291300 L
C-C_R 0 32.52899400 6.14947800 0.12146500 L
C-C_R 0 33.74896400 8.26545900 0.02754500 L
C-C_R 0 34.96924600 10.38123800 -0.05161600 L
C-C_R 0 36.18932200 12.49749000 -0.10549300 L
C-C_R 0 37.40884300 14.61445500 -0.12746600 L
C-C_R 0 38.62775400 16.73187600 -0.11987000 L
C-C_R 0 39.84619700 18.84950900 -0.09072900 L
C-C_R 0 41.06420800 20.96729100 -0.04709900 L
C-C_R 0 42.28176600 23.08518200 0.00570400 L
C-C_R 0 43.49890000 25.20315000 0.06430500 L
C-C_R 0 44.71570100 27.32120600 0.12686400 L
C-C_R 0 45.93236900 29.43940400 0.19219400 L
C-C_R 0 47.14937100 31.55946400 0.25883800 L
C-C_R 0 33.75216200 4.03616100 0.24556100 L
C-C_R 0 34.97224800 6.15323700 0.15051400 L
C-C_R 0 36.19300700 8.26864800 0.06655500 L
C-C_R 0 37.41350100 10.38413600 0.00075300 L
C-C_R 0 38.63344900 12.50035400 -0.04052800 L
C-C_R 0 39.85281500 14.61725800 -0.05542000 L
C-C_R 0 41.07163000 16.73458800 -0.04709200 L
C-C_R 0 42.28993400 18.85215300 -0.02077700 L
C-C_R 0 43.50772200 20.96984100 0.01870000 L
C-C_R 0 44.72497600 23.08757600 0.06762500 L
C-C_R 0 45.94169700 25.20530400 0.12354400 L
C-C_R 0 47.15791600 27.32302300 0.18470500 L
C-C_R 0 48.37376100 29.44086700 0.24932100 L
C-C_R 0 49.58997300 31.56084700 0.31537700 L
C-C_R 0 36.19447600 4.04120800 0.27320900 L
C-C_R 0 37.41646700 6.15681200 0.18564200 L
C-C_R 0 38.63759400 8.27112600 0.11147700 L
C-C_R 0 39.85790100 10.38655000 0.05626100 L
```

C-C_R	0	41.07766000	12.50287400	0.02344300	L
C-C_R	0	42.29688900	14.61981600	0.01293800	L
C-C_R	0	43.51559000	16.73713700	0.02192300	L
C-C_R	0	44.73374700	18.85466300	0.04670000	L
C-C_R	0	45.95132400	20.97226600	0.08389800	L
C-C_R	0	47.16827400	23.08983500	0.13087800	L
C-C_R	0	48.38454800	25.20726000	0.18552800	L
C-C_R	0	49.60005500	27.32443800	0.24581500	L
C-C_R	0	50.81436000	29.44138500	0.30954600	L
C-C_R	0	52.02833400	31.56102000	0.37461800	L
C-C_R	0	38.64117100	4.04496500	0.30648000	L
C-C_R	0	39.86299600	6.15725200	0.22639500	L
C-C_R	0	41.08359400	8.27206300	0.16071800	L
C-C_R	0	42.30369400	10.38786100	0.11346800	L
C-C_R	0	43.52332300	12.50438000	0.08634000	L
C-C_R	0	44.74246300	14.62141700	0.07860100	L
C-C_R	0	45.96108600	16.73879500	0.08805300	L
C-C_R	0	47.17913900	18.85635900	0.11211800	L
C-C_R	0	48.39655600	20.97395600	0.14838500	L
C-C_R	0	49.61326100	23.09142300	0.19463800	L
C-C_R	0	50.82917700	25.20856700	0.24865700	L
C-C_R	0	52.04423000	27.32509500	0.30815900	L
C-C_R	0	53.25712500	29.44026900	0.37086000	L
C-C_R	0	54.45650900	31.55145100	0.43448300	L
C-C_R	0	4.46825200	2.60764200	0.54856600	L
C-C_R	0	5.66742200	4.71678100	0.43359300	L
C-C_R	0	6.88018100	6.82995900	0.32074800	L
C-C_R	0	8.09524200	8.94456200	0.21342400	L
C-C_R	0	9.31132100	11.05986500	0.11509400	L
C-C_R	0	10.52829600	13.17560600	0.02965100	L
C-C_R	0	11.74601000	15.29165900	-0.03818300	L
C-C_R	0	12.96429300	17.40793200	-0.08316000	L
C-C_R	0	14.18295900	19.52430500	-0.10145400	L
C-C_R	0	15.40181800	21.64064300	-0.09314200	L
C-C_R	0	16.62073600	23.75686200	-0.06277500	L
C-C_R	0	17.83971000	25.87293800	-0.01753400	L
C-C_R	0	19.05888300	27.98872200	0.03567300	L
C-C_R	0	20.27912800	30.10263100	0.09202800	L
C-C_R	0	21.50132000	32.20709300	0.14897100	L
C-C_R	0	6.89633700	2.59674000	0.48557100	L

C-C_R 0 8.11009700 4.71430200 0.36918200 L

C-C_R 0 9.32429000 6.82920000 0.25517600 L

C-C_R 0 10.53982900 8.94436200 0.14612900 L

C-C_R 0 11.75626800 11.05985200 0.04535600 L

C-C_R 0 12.97347400 13.17568000 -0.04222200 L

C-C_R 0 14.19135900 15.29187800 -0.10948500 L

C-C_R 0 15.40982000 17.40838900 -0.14877300 L

C-C_R 0 16.62867900 19.52500900 -0.15608500 L

C-C_R 0 17.84771000 21.64151100 -0.13422800 L

C-C_R 0 19.06676600 23.75780000 -0.09167500 L

C-C_R 0 20.28590000 25.87385200 -0.03821000 L

C-C_R 0 21.50556100 27.98955500 0.01919900 L

C-C_R 0 22.72595700 30.10717300 0.07726800 L

C-C_R 0 23.94318200 32.21854700 0.13497900 L

C-C_R 0 9.33463200 2.59569500 0.42448500 L

C-C_R 0 10.55062200 4.71360700 0.30703200 L

C-C_R 0 11.76638000 6.82935600 0.19092400 L

C-C_R 0 12.98265800 8.94496400 0.07822400 L

C-C_R 0 14.19955500 11.06066400 -0.02733700 L

C-C_R 0 15.41707500 13.17665900 -0.11856000 L

C-C_R 0 16.63522000 15.29309800 -0.18449900 L

C-C_R 0 17.85394000 17.40990100 -0.21426700 L

C-C_R 0 19.07301400 19.52673900 -0.20568900 L

C-C_R 0 20.29219100 21.64336100 -0.16710500 L

C-C_R 0 21.51134200 23.75983400 -0.11269100 L

C-C_R 0 22.73055800 25.87643600 -0.05353200 L

C-C_R 0 23.94982300 27.99377800 0.00559000 L

C-C_R 0 25.16836800 30.11331100 0.06392600 L

C-C_R 0 26.38581700 32.22406000 0.12176800 L

C-C_R 0 11.77518300 2.59613400 0.36870800 L

C-C_R 0 12.99193400 4.71412200 0.24956400 L

C-C_R 0 14.20853800 6.83013500 0.12968500 L

C-C_R 0 15.42543600 8.94591600 0.01073600 L

C-C_R 0 16.64277300 11.06168100 -0.10279000 L

C-C_R 0 17.86056900 13.17776400 -0.20075300 L

C-C_R 0 19.07895800 15.29453400 -0.26418500 L

C-C_R 0 20.29799800 17.41174400 -0.27822600 L

C-C_R 0 21.51731400 19.52880400 -0.24746000 L

C-C_R 0 22.73658800 21.64559400 -0.19075100 L

C-C_R 0 23.95567000 23.76254300 -0.12778200 L

C-C_R	0	25.17453800	25.88009900	-0.06660200	L
C-C_R	0	26.39304700	27.99858200	-0.00735800	L
C-C_R	0	27.61097200	30.11847200	0.05129400	L
C-C_R	0	28.82854200	32.22898100	0.10998800	L
C-C_R	0	14.21663200	2.59741000	0.32103600	L
C-C_R	0	15.43377800	4.71551300	0.19907700	L
C-C_R	0	16.65092400	6.83160000	0.07383100	L
C-C_R	0	17.86832600	8.94733600	-0.05392900	L
C-C_R	0	19.08595000	11.06287700	-0.18074300	L
C-C_R	0	20.30363800	13.17897700	-0.29043000	L
C-C_R	0	21.52243800	15.29656600	-0.34401200	L
C-C_R	0	22.74190100	17.41437400	-0.33444500	L
C-C_R	0	23.96153000	19.53141500	-0.27702700	L
C-C_R	0	25.18073700	21.64851200	-0.20827900	L
C-C_R	0	26.39949700	23.76611500	-0.14342500	L
C-C_R	0	27.61788500	25.88440900	-0.08151900	L
C-C_R	0	28.83593600	28.00337300	-0.02022400	L
C-C_R	0	30.05372100	30.12331900	0.04092000	L
C-C_R	0	31.27134900	32.23375300	0.10192500	L
C-C_R	0	16.65858300	2.59961600	0.28372400	L
C-C_R	0	17.87596800	4.71775800	0.15859800	L
C-C_R	0	19.09352600	6.83380600	0.02779700	L
C-C_R	0	20.31125600	8.94920200	-0.11118300	L
C-C_R	0	21.52883600	11.06413300	-0.25323900	L
C-C_R	0	22.74734500	13.18096000	-0.35276400	L
C-C_R	0	23.96639900	15.29932300	-0.39282700	L
C-C_R	0	25.18606300	17.41765300	-0.36467800	L
C-C_R	0	26.40551300	19.53478900	-0.29604800	L
C-C_R	0	27.62433200	21.65247500	-0.22885500	L
C-C_R	0	28.84271600	23.77060600	-0.16452500	L
C-C_R	0	30.06085700	25.88913400	-0.09639600	L
C-C_R	0	31.27879400	28.00814100	-0.02846700	L
C-C_R	0	32.49658600	30.12799600	0.03716100	L
C-C_R	0	33.71427000	32.23833600	0.10100600	L
C-C_R	0	19.10073000	2.60269700	0.25893100	L
C-C_R	0	20.31831900	4.72083700	0.13232600	L
C-C_R	0	21.53616100	6.83679300	-0.00148100	L
C-C_R	0	22.75407700	8.95163400	-0.14600200	L
C-C_R	0	23.97241500	11.06774100	-0.26397900	L
C-C_R	0	25.19116200	13.18493800	-0.34625600	L

```
C-C_R 0 26.41052500 15.30281800 -0.39595400 L
C-C_R 0 27.63011500 17.42125600 -0.37585900 L
C-C_R 0 28.84917900 19.53899300 -0.31039300 L
C-C_R 0 30.06764000 21.65706800 -0.24436700 L
C-C_R 0 31.28582200 23.77562900 -0.17899200 L
C-C_R 0 32.50383300 25.89381200 -0.09824200 L
C-C_R 0 33.72175900 28.01266300 -0.02469000 L
C-C_R 0 34.93955000 30.13237100 0.04405000 L
C-C_R 0 36.15729200 32.24259000 0.10975800 L
C-C_R 0 21.54284500 2.60646000 0.24841900 L
C-C_R 0 22.76063700 4.72463400 0.12436500 L
C-C_R 0 23.97866300 6.84071400 -0.00292000 L
C-C_R 0 25.19688100 8.95659300 -0.12471000 L
C-C_R 0 26.41545700 11.07302500 -0.22700900 L
C-C_R 0 27.63486500 13.18916100 -0.32528500 L
C-C_R 0 28.85494500 15.30649400 -0.39617800 L
C-C_R 0 30.07426300 17.42532700 -0.37087400 L
C-C_R 0 31.29275500 19.54335300 -0.30361800 L
C-C_R 0 32.51100300 21.66149500 -0.23674200 L
C-C_R 0 33.72906000 23.77962400 -0.15987100 L
C-C_R 0 34.94696100 25.89801800 -0.08006100 L
C-C_R 0 36.16479300 28.01674600 -0.00661900 L
C-C_R 0 37.38252500 30.13630400 0.06277900 L
C-C_R 0 38.60031800 32.24638900 0.12911700 L
C-C_R 0 23.98483700 2.61055700 0.25192400 L
C-C_R 0 25.20286800 4.72880500 0.13464800 L
C-C_R 0 26.42107700 6.84528200 0.02067400 L
C-C_R 0 27.63961500 8.96156600 -0.08712100 L
C-C_R 0 28.85890400 11.07744200 -0.19286900 L
C-C_R 0 30.07903100 13.19320700 -0.29192800 L
C-C_R 0 31.29925300 15.31056500 -0.34279900 L
C-C_R 0 32.51819300 17.42912800 -0.32619800 L
C-C_R 0 33.73636700 19.54737100 -0.26923400 L
C-C_R 0 34.95441900 21.66543000 -0.19989000 L
C-C_R 0 36.17229300 23.78333400 -0.12080100 L
C-C_R 0 37.39011500 25.90171400 -0.04667300 L
C-C_R 0 38.60777100 28.02030900 0.02405800 L
C-C_R 0 39.82538400 30.13971900 0.09251500 L
C-C_R 0 41.04319200 32.24965700 0.15889200 L
C-C_R 0 26.42679900 2.61453800 0.26502300 L
```

C-C_R	0	27.64517300	4.73275100	0.15379300	L
C-C_R	0	28.86379400	6.84918700	0.04652200	L
C-C_R	0	30.08292900	8.96527100	-0.05760600	L
C-C_R	0	31.30271400	11.08105700	-0.15616000	L
C-C_R	0	32.52285200	13.19732600	-0.23221200	L
C-C_R	0	33.74265200	15.31468200	-0.26353600	L
C-C_R	0	34.96145700	17.43268100	-0.24658100	L
C-C_R	0	36.17964200	19.55063000	-0.19883900	L
C-C_R	0	37.39772400	21.66851900	-0.13741500	L
C-C_R	0	38.61557900	23.78660900	-0.07044500	L
C-C_R	0	39.83317100	25.90489800	-0.00285500	L
C-C_R	0	41.05057400	28.02334300	0.06459700	L
C-C_R	0	42.26798300	30.14258600	0.13178800	L
C-C_R	0	43.48572400	32.25236500	0.19822300	L
C-C_R	0	28.86890100	2.61811100	0.28151500	L
C-C_R	0	30.08765800	4.73626400	0.17420100	L
C-C_R	0	31.30678400	6.85260700	0.07104000	L
C-C_R	0	32.52651200	8.96856600	-0.02597000	L
C-C_R	0	33.74663100	11.08444700	-0.10875400	L
C-C_R	0	34.96664200	13.20093400	-0.16311800	L
C-C_R	0	36.18605700	15.31819400	-0.17991500	L
C-C_R	0	37.40480400	17.43582700	-0.16314300	L
C-C_R	0	38.62315800	19.55357400	-0.12464700	L
C-C_R	0	39.84116900	21.67145600	-0.07312600	L
C-C_R	0	41.05879100	23.78947500	-0.01446800	L
C-C_R	0	42.27606400	25.90761100	0.04801500	L
C-C_R	0	43.49311200	28.02586200	0.11279600	L
C-C_R	0	44.71017400	30.14490200	0.17913500	L
C-C_R	0	45.92769700	32.25452500	0.24563900	L
C-C_R	0	31.31120500	2.62143400	0.29929900	L
C-C_R	0	32.53023600	4.73975300	0.19614800	L
C-C_R	0	33.75003400	6.85608100	0.09899900	L
C-C_R	0	34.97040700	8.97177200	0.01268200	L
C-C_R	0	36.19072600	11.08757500	-0.05426300	L
C-C_R	0	37.41059500	13.20405800	-0.09353600	L
C-C_R	0	38.62985900	15.32117600	-0.10302600	L
C-C_R	0	39.84857200	17.43865200	-0.08764000	L
C-C_R	0	41.06682000	19.55632200	-0.05434200	L
C-C_R	0	42.28460000	21.67411600	-0.00880900	L
C-C_R	0	43.50190900	23.79198500	0.04479000	L

C-C_R	0	44.71878300	25.90990500	0.10393900	L
C-C_R	0	45.93532400	28.02788600	0.16712100	L
C-C_R	0	47.15179700	30.14667100	0.23289000	L
C-C_R	0	48.36884700	32.25620600	0.29915300	L
C-C_R	0	33.75355600	2.62503100	0.31992800	L
C-C_R	0	34.97285800	4.74401700	0.22229300	L
C-C_R	0	36.19388200	6.85957200	0.13301700	L
C-C_R	0	37.41472500	8.97461300	0.05787200	L
C-C_R	0	38.63499200	11.09030400	0.00345100	L
C-C_R	0	39.85468800	13.20679800	-0.02620100	L
C-C_R	0	41.07382100	15.32387400	-0.03164900	L
C-C_R	0	42.29242100	17.44129100	-0.01683300	L
C-C_R	0	43.51049900	19.55889000	0.01359000	L
C-C_R	0	44.72803300	21.67656700	0.05562200	L
C-C_R	0	45.94499900	23.79424400	0.10635700	L
C-C_R	0	47.16138700	25.91186500	0.16375700	L
C-C_R	0	48.37721000	28.02942800	0.22599700	L
C-C_R	0	49.59260900	30.14779500	0.29105100	L
C-C_R	0	50.80883800	32.25751500	0.35661100	L
C-C_R	0	36.19487900	2.63069800	0.34539300	L
C-C_R	0	37.41746900	4.74827300	0.25412800	L
C-C_R	0	38.63914200	6.86169700	0.17311000	L
C-C_R	0	39.85980600	8.97649300	0.10772800	L
C-C_R	0	41.07986000	11.09235000	0.06249500	L
C-C_R	0	42.29939800	13.20896000	0.03911900	L
C-C_R	0	43.51841800	15.32607400	0.03626600	L
C-C_R	0	44.73690700	17.44348900	0.05090900	L
C-C_R	0	45.95483100	19.56105400	0.07978600	L
C-C_R	0	47.17213800	21.67863800	0.12009300	L
C-C_R	0	48.38876900	23.79611600	0.16954900	L
C-C_R	0	49.60465400	25.91335100	0.22606100	L
C-C_R	0	50.81958500	28.03018700	0.28745600	L
C-C_R	0	52.03259900	30.14717000	0.35148700	L
C-C_R	0	53.24779100	32.25359700	0.41604100	L
C-C_R	0	38.62895200	2.64302300	0.37575200	L
C-C_R	0	39.85500400	4.75316200	0.29098100	L
C-C_R	0	41.07613000	6.86747400	0.21754900	L
C-C_R	0	42.29649600	8.98284700	0.16010300	L
C-C_R	0	43.51639700	11.09899900	0.12144100	L
C-C_R	0	44.73583600	13.21576500	0.10211700	L

```
 C-C_R           0   45.95479000   15.33297900
0.10085000 L

 C-C_R           0   47.17321400   17.45048000
0.11551300 L

 C-C_R           0   48.39104100   19.56811200
0.14383800 L

 C-C_R           0   49.60819700   21.68570400
0.18363000 L

 C-C_R           0   50.82459800   23.80306200
0.23267500 L

 C-C_R           0   52.04018100   25.91992500
0.28864900 L

 C-C_R           0   53.25486900   28.03595400
0.34923400 L

 C-C_R           0   54.46451200   30.15367500
0.41226900 L

 C-C_R           0   26.04821100   15.33788500
3.09646600 H

 C-C_R           0   25.74904800   13.94655300
3.28573100 H

 C-C_R           0   24.93338800   16.19337700
2.90726800 H

 C-C_R           0   24.40293700   13.47139200
3.16682600 H

 C-C_R           0   26.73105300   12.96393500
3.63457000 H

 C-C_R           0   23.63365200   15.74813100
2.89348900 H

 H-H_           0   25.11646700   17.24903400
2.72643900 H

 C-C_R           0   24.10967400   12.07380600
3.21417000 H

 C-C_R           0   23.32620200   14.38359500
3.00116500 H

 C-C_R           0   26.46813700   11.62842200
3.63740900 H

 H-H_           0   27.71678900   13.30320900
3.93271700 H

 H-H_           0   22.82118600   16.46151800
2.74093200 H

 C-C_R           0   25.15935400   11.12637700
3.37704200 H

 C-C_R           0   22.76560300   11.60774400
3.09323100 H

 C-C_R           0   21.99202400   13.89736300
2.92318600 H

 H-H_           0   27.25502600   10.91653200
3.89157000 H

 C-C_R           0   24.86606700    9.75550600
3.34782400 H

 C-C_R           0   22.51546200   10.22675200
3.09152900 H

 C-C_R           0   21.71319500   12.56496900
2.96844700 H

 H-H_           0   21.19032900   14.62926300
2.80407800 H

 C-C_R           0   23.55706200    9.31456200
3.20085000 H

 H-H_           0   25.68403700    9.04068200
3.45017500 H

 H-H_           0   21.48602800    9.88125400
2.97951400 H

 H-H_           0   20.68765000   12.20131300
2.88248600 H

 H-H_           0   23.34491500    8.24494400
3.17118100 H

 C-C_R           0   27.38560000   15.93512200
3.07038800 H

 C-C_R           0   27.53356500   17.33343300
3.26328500 H

 C-C_R           0   28.56689100   15.20862800
2.80487800 H

 C-C_R           0   28.76674100   17.96788600
3.19862100 H

 H-H_           0   26.68854500   17.97732000
3.47899300 H

 C-C_R           0   29.82024000   15.80043600
2.82769700 H

 H-H_           0   28.51291400   14.17265800
2.48111400 H
```

```
 N-N_R          0   29.00415100   19.32320400
3.29444700 H

 C-C_R          0   29.95924800   17.17990700
3.04151900 H

 H-H_           0   30.71964900   15.22437100
2.62936200 H

 C-C_R          0   28.09472000   20.31803100
3.23343400 H

 N-N_R          0   31.11902100   17.89732800
3.07360500 H

 C-C_R          0   28.78257900   21.71170100
3.24082900 H

 O-O_R          0   26.86780800   20.21880100
3.17242600 H

 C-C_R          0   32.39063900   17.42812100
3.02008300 H

 N-N_R          0   30.13112600   21.65601300
3.21888100 H

 O-O_R          0   28.08506800   22.73181100
3.25646400 H

 C-C_R          0   33.41794400   18.58476100
3.12799600 H

 O-O_R          0   32.75604300   16.25936000
2.91326600 H

 C-C_3          0   30.80882200   22.92315900
3.22474100 H

 N-N_R          0   32.86500800   19.81181000
3.19061100 H

 O-O_R          0   34.62706700   18.32787500
3.15359500 H

 H-H_           0   31.16633000   23.20445600
4.23370600 H

 H-H_           0   31.69500400   22.89094400
2.57448700 H

 H-H_           0   30.13709300   23.72378000
2.87879600 H

 C-C_3          0   33.82440900   20.87465800
3.32945400 H

 H-H_           0   34.33181400   20.85193700
4.31215100 H

 H-H_           0   34.62969400   20.80005600
2.57948300 H

 H-H_           0   33.32731700   21.84675400
3.22563400 H

 Cu-            0   30.88822900   19.84078800
3.21135800 H

 H-H_           0    3.51093400    4.52699900
0.49802400 L

 H-H_           0    4.72869900    6.65997000
0.38421000 L

 H-H_           0    5.94395800    8.77511100
0.27671900 L

 H-H_           0    7.15982700   10.89037900
0.17833800 L

 H-H_           0    8.37666400   13.00623300
0.09278500 L

 H-H_           0    9.59429800   15.12236600
0.02378600 L

 H-H_           0   10.81249400   17.23856500   -
0.02512500 L

 H-H_           0   12.03102300   19.35471700   -
0.05120400 L

 H-H_           0   13.24970300   21.47079600   -
0.05367900 L

 H-H_           0   14.46844700   23.58684100   -
0.03465600 L

 H-H_           0   15.68727600   25.70289900
0.00125400 L

 H-H_           0   16.90634000   27.81901300
0.04838000 L

 H-H_           0   18.12653500   29.93571300
0.10167300 L

 H-H_           0   19.36061800   32.06182500
0.15788300 L

 H-H_           0   21.48098200   33.28990000
0.18233300 L

 H-H_           0   23.93987200   33.30271700
0.16819000 L

 H-H_           0   26.38370600   33.30823300
0.15491800 L
```

```
 H-H_           0   28.82654200   33.31315100
0.14322400 L

 H-H_           0   31.26934700   33.31792700
0.13497200 L

 H-H_           0   33.71226800   33.32253800
0.13300000 L

 H-H_           0   36.15533600   33.32684900
0.13974200 L

 H-H_           0   38.59846600   33.33071400
0.15660200 L

 H-H_           0   41.04148700   33.33404300
0.18393300 L

 H-H_           0   43.48418700   33.33680500
0.22114800 L

 H-H_           0   45.92632500   33.33901200
0.26681300 L

 H-H_           0   48.36763400   33.34074000
0.31887600 L

 H-H_           0   50.80873900   33.34208800
0.37517500 L

 H-H_           0   53.26676100   33.33678700
0.43425200 L

 H-H_           0   55.41371000   29.63138400
0.42758400 L

 H-H_           0   54.19578400   27.49643300
0.36493700 L

 H-H_           0   52.98050800   25.37945700
0.30569200 L

 H-H_           0   51.76480300   23.26247700
0.25148200 L

 H-H_           0   50.54827100   21.14499800
0.20466000 L

 H-H_           0   49.33097600   19.02729100
0.16766400 L

 H-H_           0   48.11300500   16.90957500
0.14274900 L

 H-H_           0   46.89444200   14.79204100
0.13196400 L

 H-H_           0   45.67536600   12.67485500
0.13716600 L

 H-H_           0   44.45583500   10.55815600
0.15985700 L

 H-H_           0   43.23587300    8.44205600
0.20073100 L

 H-H_           0   42.01542700    6.32660400
0.25901100 L

 H-H_           0   40.79370600    4.21123300
0.33214400 L

 H-H_           0   39.55800800    2.08696600
0.41644300 L

 H-H_           0   37.43676800    0.86063500
0.45053000 L

 H-H_           0   34.97796800    0.84900800
0.42480500 L

 H-H_           0   32.53428600    0.84498100
0.40436100 L

 H-H_           0   30.09184400    0.84172000
0.38789700 L

 H-H_           0   27.64984800    0.83843700
0.37350800 L

 H-H_           0   25.20819300    0.83477200
0.36065700 L

 H-H_           0   22.76663700    0.83070600
0.35198600 L

 H-H_           0   20.32487700    0.82656200
0.35188500 L

 H-H_           0   17.88279100    0.82278600
0.36328500 L

 H-H_           0   15.44055100    0.81976800
0.38735800 L

 H-H_           0   12.99853800    0.81771200
0.42388900 L

 H-H_           0   10.55720900    0.81660300
0.47143100 L

 H-H_           0    8.11608800   0.81626900
0.52742100 L

 H-H_           0    5.65811500   0.82283400
0.58888400 L

 H-H_           0   55.39267000   32.09381000
0.46642600 L
```

```
 H-H_             0    3.53217700    2.06616400
0.59479000 L
```

10. Acknowledgment and References

MINECO and FEDER are gratefully acknowledged (CTQ2016-80058-R, CTQ2015-73028-EXP, SEV 2013-0319, ENE2016-82025-REDT (FOTOFUEL), CTQ2016-81923-REDC (INTECAT). P. G.-B. acknowledges “La Caixa” foundation for the PhD grant. A.P. acknowledges funding from the European Union's Horizon 2020 research and innovation program under the Marie Sklodowska-Curie Grant Agreement No. 702565. XAS experiments were performed at the CLAESS beamline at ALBA Synchrotron with the collaboration of ALBA staff under proposal No. 2015091457 and additionally used resources of sector 20 beamline at the Advanced Photon Source (APS) at Argonne Na-tional Laboratory. Sector 20 beamline at APS is operated by the U.S DOE and the Canadian Light Source. V.S.B. acknowledges supercomputer time from NERSC and financial support from as part of the Argonne-Northwestern Solar Energy Research (ANSER) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001059.

---

[1] Ravel, B.; Newville, M. *J. Synchrotron Rad.* **2005**, *12*, 537-541.

[2] Rehr, J. J.; Albers, R. C. *Rev. Mod. Phys.* **2000**, *72*, 621-654.

[3] Koningsberger, D. C.; Prins, R. *X Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES*; John Wiley & Sons: New York, 1988.

[4] Stumpf, H. O.; Pei, Y.; Kahn, O.; Sletten, J.; Renard, J. P. *J. Am. Chem. Soc.* **1993**, *115*, 6738.

[5] Ruiz, R.; Surville-Barland, C.; Aukauloo, A.; Anxolabehere-Mallart, E.; Journaux, Y.; Cano, J.; Carmen Munoz, M. *J. Chem. Soc., Dalton Trans.* **1997**, 745-752.

[6] Garrido-Barros, P.; Funes-Ardoiz, I.; Drouet, S.; Benet-Buchholz, J.; Maseras, F.; Llobet, A. *J. Am. Chem. Soc.* **2015**, *137*, 6758-6761.

[7] Jahani, F.; Tajbakhsh, M.; Golchoubian, H.; Khaksar, S. *Tetrahedron Lett*. **2011,** *52*, 1260-1264.

[8] Kwon, J.; Hong, J.-P.; Lee, S.; Hong, J.-I. *New J. Chem*. **2013**, *37*, 2881–2887.

[9] Lebedeva, M. A.; Chamberlain, T. W.; Davies, E. S.; Mancel, D.; Thomas, B. E.; Suyetin, M.; Bichoutskaia, E.; Schröder, M.; Khlobystov, A. N. *Chem.Eur. J.* **2013**, *19*, 11999–12008

[10] Costentin, C.; Savéant, J.-M. *ChemElectroChem* **2014**, *1*, 1226-1236.

[11] Rountree, E. S.; McCarthy, B. D.; Eisenhart, T. T.; Dempsey, J. L. *Inorg. Chem.* **2014**, *53*, 9983-10002.

[12] Matheu, R.; Neudeck, S.; Meyer, F.; Sala, X.; Llobet, A. *ChemSusChem* **2016**, *9*, 3361−3369

[13] Kaniyoor, A.; Ramaprabhu, S., *AIP Adv.*, **2012**, 2, 032183.

[14] McCrory, C. C. L.; Jung, S. H.; Peters, J. C.; Jaramillo, T. F. *J. Am. Chem. Soc.* **2013**, *135*, 16977−16987.

[15] Wilke, C. R.; Chang, P., *AIChE J,* **1955**, *63*, 264-270.

[16] Tromans, D., Hydrometallurgy, **1998**, *50*, 279–296.

[17] Rigsby, M. L., Wasylenko, D. J., Pegis, M. L., Mayer, J. M., *J. Am. Chem. Soc.*, **2015**, *137*, 4296–4299.

[18] Barnett, S. M.; Goldberg, K. I.; Mayer, J. M. *Nat. Chem*. **2012**, *4*, 498-502.

[19] Zhang, T.; Wang, C.; Liu, S.; Wang, J.-L.; Lin, W. *J. Am. Chem. Soc*. **2014**, *136*, 273-281.

[20] Fisher, K. J.; Materna, K. L.; Mercado, B. Q.; Crabtree, R. H.; Brudvig, G. W. *ACS Catal*. **2017**, *7*, 3384-3387.

[21] Shen, J.; Zhang, P.; Jiang, J.; Sun, L. *Chem. Commun.* **2017**, *53*, 4374-4377.

[22] Pap, J. S.; Szyrwiel, L.; Sranko, D.; Kerner, Z.; Setner, B.; Szewczuk, Z.; Malinka, W. *Chem. Commun*. **2015**, *51*, 6322-6324.

[23] Coggins, M. K.; Zhang, M.-T.; Chen, Z.; Song, N.; Meyer, T. J. *Angew. Chem. Int. Ed.* **2014**, *53*, 12226-12230.

[24] Chen, G.; Chen, L.; Ng, S.-M.; Man, W.-L.; Lau, T.-C. *Angew. Chem. Int. Ed.* **2013**, *52*, 1789-1791.

[25] Leung, C.-F.; Ng, S.-M.; Ko, C.-C,; Man, W.-L.; Wu, J.; Chen, L.; Lau, T.-C. *Energy Environ. Sci*. **2012**, *5*, 7903-7907.

[26] Gaussian 09, Revision **D.01**, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.;

Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

[27] Becke, A.D., *J. Chem. Phys.***1993**, *98*, 5648-5652.

[28] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., *J. Chem. Phys.***2010**, *132*, 154104.

[29] a) Hehre, W.J.; Ditchfield, R.; Pople, J.A., *J. Chem. Phys*. **1972**, 56, 2257. b) Hariharan, P.C.; Pople, J.A., *Theoret. ChimicaActa* **1973**, *28*, 213-222. c) Francl, M.M.; Petro, W.J.; Hehre, W.J.; Binkley, J.S.; Gordon, M.S.; DeFrees, D.J.; Pople, J.A., *J. Chem. Phys.* **1982**, *77*, 3654.

[30] a) Hay, P. J.; Wadt, W. R., *J. Chem. Phys.***1985**, *82*, 270. b) Hay, P. J.; Wadt, W. R., *J. Chem. Phys.***1985**, *82*, 284. c) Hay, P. J.; Wadt, W. R., *J. Chem. Phys.***1985**, *82*, 299.

[31] Taken from EMSL Basis set Library: a) Felier, D., *J. Comp. Chem.***1996**, *17*, 1571-1586. b) Schuchardt, K.L.; Didier, B.T.; Elsethagen, T.; Sun, L.; Gurumoorthi, V.; Chase, J.; Li, J.; Windus, T.L., *J. Chem. Inf. Model.*, **2007**, *47*, 1045-1052.

[32] Marenich, S. A. V.; Cramer, C. J.; Truhlar, D. G., *J. Phys. Chem. B*, **2009**, *113*, 6378-6396.

[33] a) Lewis, A.; Bumpus, J. A.; Truhlar, D. G.; Cramer, C. J., *J. Chem. Ed.* **2004**, *81*, 596-604. b) Lewis, A.; Bumpus, J. A.; Truhlar, D. G.; Cramer, C. J., *J. Chem. Ed.* **2007**, *84*, 934.

[34] Marenich, A. V.; Majunmdar, A.; Lenz, M.; Cramer, C. J.; Truhlar, D. G., *Angew. Chem. Int. Ed.* **2012**, *51*, 12810-12814.

[35] Winikoff, S.G.; Cramer, C.J.; *Catal. Sci. Technol.* **2014**, *4*, 2484-2489.

[36] Funes-Ardoiz, I.; Garrido-Barros, P.; Llobet, A.; Maseras, F. *ACS Catal.* **2017**, *7*, 1712−1719.