Enhanced photoreduction of water catalyzed by a cucurbit[8]uril-secured platinum dimer

Ramin Rabbani,† Sima Saeedi,† Md Nazimuddin, a Héctor Barbero, a,b Nathalie Kyritsakas, c Travis A. White, a and Eric Masson* a

a Department of Chemistry and Biochemistry, Ohio University, Athens, Ohio 45701, United States
b GIR MIOMeT, IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E47011, Valladolid, Spain.
† Molecular Tectonics Laboratory, University of Strasbourg, UMR UDS-CNRS 7140, Institut le Bel, F-67000 Strasbourg, France.
† These authors contributed equally.

e-mail: masson@ohio.edu

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1. Generalities

All reagents were purchased from chemical suppliers and used without further purification. Cucurbit[7]uril (CB[7]) and Cucurbit[8]uril (CB[8]) were prepared using known procedures.\(^1\) Solvents were of analytical grade and either used as purchased or dried according to procedures described elsewhere.\(^2\) Characterization by nuclear magnetic resonance spectroscopy (NMR) was carried out using a Bruker Ascend 500 MHz spectrometer. \(^1\)H and \(^{13}\)C NMR chemical shifts are reported in parts per million (ppm) and are referenced to TMS using the residual signal of the solvent as an internal reference. Coupling constants (\(J\)) are reported in hertz (Hz). Standard abbreviations used to indicate multiplicity are: \(s = \) singlet, \(d = \) doublet, \(dd = \) doublet of doublets, \(t = \) triplet. High resolution electrospray ionization mass spectrometry (HR-ESI-MS) was performed using a Thermo Fisher Scientific Q Exactive Plus hybrid quadrupole–Orbitrap mass spectrometer in positive mode. UV-Vis absorption spectra were recorded on an Agilent HP-8453 diode-array spectrophotometer. Wavelengths (\(\lambda\)) are reported in nanometers (nm) and molar absorption coefficients (\(\epsilon\)) are reported in M\(^{-1}\) cm\(^{-1}\). Computational work was carried out on the Owens cluster of the Ohio Supercomputer Center in Columbus, OH (23,392-core Dell Intel Xeon E5-2680 v4 machines). \(4'-(p\text{-tolyl})-2,2':6',2''\text{-terpyridine}\) and chloro[\(4'-(p\text{-tolyl})-2,2':6',2''\text{-terpyridine}]-platinum(II) chloride (1b) were prepared according to published procedures.\(^3\)

2. Preparation and characterization of CB[n]-bound Pt(tpy) chloride complexes

Chloro[\(4'-(p\text{-tolyl})-2,2':6',2''\text{-terpyridine}]\)platinum(II) chloride (1b) (3.1 mg, 5.1 \(\mu\)mol) was mixed with \(D_2O\) (5.0 mL). CB[8] (3.3 mg, 2.5 \(\mu\)mol) or CB[7] (5.9 mg, 5.1 \(\mu\)mol) was added subsequently, and the resulting mixture was sonicated thoroughly. The stock solution was stored at 4 °C for further use.

Spectral data of assembly CB[8]-1b\(_2\) have been previously reported by us elsewhere.\(^4\)

CB[7]-1b. \(^1\)H NMR (500 MHz, \(D_2O\)) \(\delta\) 9.19 (d, \(J = 8.1\) Hz, 2H, \(H^3\)), 8.95 (d, \(J = 5.7\) Hz, 2H, \(H^6\)), 8.65 (s, 2H, \(H^5\)), 8.49 (t, \(J = 7.8\) Hz, 2H, \(H^4\)), 7.83 (t, \(J = 6.7\) Hz, 2H, \(H^5\)), 7.13 (d, \(J = 7.8\) Hz, 2H, \(H^2\)), 6.51 (d, \(J = 8.0\) Hz, 2H, \(H^9\)), 5.83 (d, \(J = 15.4\) Hz, 7H, \(H^{CBS}\)), 5.73 (d, \(J = 15.4\) Hz, 7H, \(H^{CBS}\)), 5.48 (s, 14H, \(H^{CBS}\)), 4.19 (dd, \(J = 25.4\), 15.4 Hz, 14H, \(H^{CBS}\)), 1.93 (s, 3H, \(H^9\)). \(^{13}\)C NMR (126 MHz, \(D_2O\)) \(\delta\) 159.59, 156.13, 156.08, 154.95, 153.60, 150.90, 142.48, 142.13, 132.34, 128.42, 127.74, 126.63, 126.20, 123.24, 71.22, 52.52, 20.50. HRMS (ESI): \(m/z = 869.205161 \ [M+Na]^+\) (calcd. 869.204037 for C\(_{64}\)H\(_{59}\)Cl\(_4\)N\(_{31}\)O\(_{14}\)PtNa).
Figure S1. $^1$H-NMR spectrum of complex CB[7]-1b in D$_2$O.

Figure S2. $^{13}$C-$^1$H-NMR spectrum of complex CB[7]-1b in D$_2$O.
3. Photocatalytic H₂ production

All photolysis experiments were carried out under buffered condition (pH 5, 0.10 M MES, 30 mM EDTA). Photolysis experiments were carried out at least in duplicates for each reaction condition. Each replicate had 6.0 mL of the solution in 23 mL vials equipped with PTFE/silicone septa caps. Samples were prepared in the dark and deoxygenated for 10 min using Ar prior to photolysis. Each solution was photolyzed using in-house built royal blue LEDs (λ_{irr} = 447.5 ± 10 nm at fwhm) purchased from Luxeon Star LEDs (Quadica Developments, Inc., Lethbridge, Alberta, Canada). The output from each LED was 250 mW, and samples were placed 1 cm away from the light source. After photolyzing each solution, an aliquot (0.10 mL) was removed from the headspace using a Hamilton GASTIGHT syringe and injected into a Shimadzu GC-2014 gas chromatograph (GC; Ar carrier gas) with a packed ShinCarbon ST SilicoSmooth stainless steel column (2 m long × 1/8 in.o.d. × 2.0 mm i.d.; 80/100 mesh) and a Shimadzu TCD-2014 thermal conductivity detector. The GC conditions were as follows: injector temperature, 41 °C; column temperature, 30 °C; detector temperature, 150 °C; gas flow, 25 mL/min. The volume of injected H₂ was determined using a calibration curve generated from known volumes of 100% H₂.

4. Chemical actinometry

Chemical actinometry was carried out according to literature sources.⁵,⁶ All sample preparations and photolysis experiments were performed in the dark and in triplicates. K₃[Fe(C₂O₄)₃] (6.0 mL, 0.15 M) in a 23 mL vial was photolyzed for 5 s with 447.5 ± 10 nm LED irradiation. An aliquot of the photolyzed solution (10 mL) was added to 0.1% buffered 1,10-phenanthroline (phen) solution (5.0 mL). The mixture was kept in the dark for 1 h. The process was repeated with irradiation times of 10, 15 and 30 s; a control experiment without irradiation was also carried out. Solutions were transferred into 10 mm cuvettes and their absorbances were measured using an Agilent Cary 8454 diode array UV-vis spectrophotometer (1 nm resolution, 0.5 s integration time).

Amounts of Fe²⁺ ions n(Fe²⁺) produced during photolysis were obtained as follows:

\[ n(\text{Fe}^{2+}) = \frac{V_1 V_3 \Delta A_{510}}{\varepsilon_{510} l V_2} \quad (1) \]

where ΔA_{510} is the absorbance difference at 510 nm, l the path length (10 mm), ε_{510} the extinction coefficient of [Fe(phen)₃]²⁺ at 510 nm (11,100 M⁻¹·cm⁻¹), V₁ the total volume of irradiated solution (6.0 mL), V₂ the volume of the aliquot taken from the irradiated solution (10 mL) and V₃ the volume that the aliquot is diluted into (5.0 mL).

The photon flux (q_{n,p}) was calculated as follows:

\[ q_{n,p} = \frac{\text{moles } \text{Fe}^{2+}}{\Phi(\lambda) t} \quad (2) \]

where \( \Phi(\lambda) \) is the reported quantum yield of K₃[Fe(C₂O₄)₃] photodegradation at wavelength \( \lambda \) and \( t \) the irradiation time (s).
5. Mass spectrometry analysis during the photolysis of complex CB[8]·1b₂

Photolysis prior to HR-ESI-MS analysis was carried out on a 0.50 mM solution of assembly CB[8]·1b₂ in a 1.5 mM EDTA solution in LC-MS grade water. An aliquot (10 µL) was withdrawn from the solution at specific times, diluted 10 times with a 1:1 solution of water (LC-MS grade) and methanol (HPLC grade), and injected into the mass spectrometer.

Figure S3. Bottom to top: ESI-MS analysis of photolyzed solutions of complex CB[8]·1b₂ (0.50 mM; EDTA 1.5 mM) after 0, 10, 20, 30, 40, 60 and 120 min irradiation at 447 nm.
Table S1. ESI-MS analysis of photolyzed solutions of complex CB[8]-1b (0.50 mM Pt; EDTA 1.5 mM); observed (top) and calculated (bottom) positive-ion spectra.

\[
m/z 519.12
\]

\[
m/z 598.19
\]

\[
m/z 677.22
\]
6. UV-Vis characterization

Figure S4. (a) UV-Vis absorption spectra of complex 1b (in grey), binary assembly CB[7]-1b (in blue) and ternary assembly CB[8]-1b (in green); Pt concentration: 20 \( \mu \)M. (b) Extinction coefficients of complex 1b solutions at 384 nm as a function of concentration; fit with a dimerization model (solid black line) and 95\% confidence interval (dashed lines). All spectra recorded in MES (0.10 M)/EDTA (30 mM) buffer.

7. Isothermal titration calorimetry

All isothermal titration calorimetry (ITC) experiments were carried out in MilliQ water at 25 °C on a Malvern MicroCal ITC200 instrument. Due to the low solubility of complex 1b and CB[8], L-Cys-derived surrogate 1c was used as the titrant instead. The latter was set up in the injection syringe at concentrations ranging from 0.85 to 1.0 mM. Hosts (CB[7] and CB[8]) were in the sample cell at concentrations ranging from 0.050 to 0.10 mM. Experiments were carried out in triplicate. Each titration consisted of 20 injections with an injection spacing of 150 s. Raw data were analyzed (baseline correction, integration and fitting) with Affinimeter software.
Table S2. Thermodynamic data obtained by ITC titrations of the species involved in this study.

| System      | $K$            | $\Delta G'$ | $\Delta H'$ | $\Delta S'$ | $K_{\text{dimer}}$ | $\Delta G_{\text{dimer}}$ | $\Delta H_{\text{dimer}}$ | $\Delta S_{\text{dimer}}$ |
|-------------|----------------|-------------|-------------|-------------|---------------------|-----------------------------|-----------------------------|--------------------------|
| 1c vs CB[7] | $(6.3 \pm 0.1) \times 10^4$ | $-6.55 \pm 0.01$ | $-5.87 \pm 0.04$ | $0.69 \pm 0.04$ | $-4.0 (\pm 0.4) \times 10^4$ | $-6.27 (\pm 0.06)$ | $-2.8 (\pm 0.3)$ | $3.5 (\pm 0.3)$       |
| 1c vs CB[8] | $(1.9 \pm 0.6) \times 10^{13}$ | $-18.1 \pm 0.2$ | $-19.4 \pm 0.2$ | $-1.3 \pm 0.3$ | $4.0 (\pm 0.4) \times 10^4$ | $-6.27 (\pm 0.06)$ | $-2.8 (\pm 0.3)$ | $3.5 (\pm 0.3)$       |

a Binding constant in M$^{-1}$. b Thermodynamic parameter corresponding to the equilibrium $1c + 1c + CB[8] \rightleftharpoons CB[8] \cdot 1c_2$, in M$^{-2}$. c in kcal/mol. d Dimerization constant of complex 1c [M$^{-1}$].

Figure S5. Representative enthalpograms for the titration of (a) CB[7] (0.10 mM) with complex 1c (1.0 mM), and (b) CB[8] (0.050 mM) with complex 1c (0.85 mM), in MilliQ water at 25 ºC.

8. X-ray crystallography

A specimen of C$_{92}$H$_{82}$Cl$_2$N$_{38}$O$_{16}$Pt$_2$, approximate dimensions 0.090 mm x 0.100 mm x 0.100 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a triclinic unit cell yielded a total of 264585 reflections to a maximum $\theta$ angle of 27.00° (0.78 Å resolution), of which 47500 were independent (average redundancy 5.570, completeness = 90.6%, $R_{int} = 5.81\%$, $R_{sig} = 5.19\%$) and 39282 (82.70%) were greater than 2$\sigma$(F$^2$). The final cell constants of $a = 17.9543(13)$ Å, $b = 20.7821(16)$ Å, $c = 33.976(3)$ Å, $\beta = 82.949(4)^\circ$, volume = 12580.9(16) Å$^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 $\sigma$(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8000 and 0.8210. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 4 for the formula unit, C$_{92}$H$_{82}$Cl$_2$N$_{38}$O$_{16}$Pt$_2$. The final anisotropic full-matrix least-squares refinement on F$^2$ with 2633 variables converged at R1 = 10.11%, for the observed data and wR2 = 25.54% for all data. The goodness-of-fit was 1.105. The largest peak in the final difference electron density synthesis was $3.504 \ e^3/\AA^3$ and the largest hole was $-4.534 \ e^3/\AA^3$ with an RMS deviation of 0.203 $e^3/\AA^3$. On the basis of the final model, the calculated density was 1.287 g/cm$^3$ and F(000), 4872 $e^\\cdot$. 
Identification code: s4624
Chemical formula: C_{29}H_{34}Cl_{13}N_{18}O_{16}Pt_{2}
Formula weight: 2437.03 g/mol
Temperature: 173(2) K
Wavelength: 0.71073 Å
Crystal size: 0.090 x 0.100 x 0.100 mm
Crystal system: triclinic
Space group: P -1
Unit cell dimensions:
- \( a = 17.9543(13) \text{ Å} \)
- \( b = 20.7821(16) \text{ Å} \)
- \( c = 33.976(3) \text{ Å} \)
Volume: 12580.9(16) Å³

\( Z \): 4
Density (calculated): 1.287 g/cm³
Abs coefficient: 2.331 mm⁻¹

F(000): 4872
Theta range for data collection: 1.76 to 27.00°
Index ranges:
- \(-23 \leq h \leq 23, -24 \leq k \leq 25, -44 \leq l \leq 44\)
Reflections collected: 264585
Independent reflections: 47500 [R(int) = 0.0581]
Max. and min. transmission: 0.8210 and 0.8000
Structure solution technique: direct methods
Structure solution program: SHELXS-97 (Sheldrick 2008)
Refinement method: Full-matrix least-squares on \( F^2 \)
Refinement program: SHELXL-2014 (Sheldrick 2014)
Function minimized: \( \Sigma w(F_o^2 - F_c^2)^2 \)

Data / restraints / parameters:
Goodness-of-fit on \( F^2 \): 1.105
\( \Delta \sigma / \text{max} \): 0.002
Final R indices:
- \( I > 2\sigma(I) \)
- \( R_1 = 0.1011, \ wR_2 = 0.2486 \)
- \( R_1 = 0.1145, \ wR_2 = 0.2554 \)

Weighting scheme:
- \( w = 1/\sigma^2(F_o^2) + (0.0699P)^2 + 328.0372P \)

Largest diff. peak and hole: 3.504 and -4.534 eÅ⁻³
R.M.S. deviation from mean: 0.203 eÅ⁻³
9. Computational details

Complexes and assemblies 1b, CB[7]-1b, 1b2, CB[8]-1b2 and their hydrides were optimized with the semiempirical tight-binding method GFN2-XTB\(^7,8\) in conjunction with the GB/SA solvation model.\(^9,10\) Enthalpic and entropic contributions at 25 °C (\(\Delta G_{T,\text{XBT}}\)) and free energies of solvation (\(\Delta G_{\text{solv},\text{XBT}}\)) were also calculated with this method. The complexes and assemblies were then reoptimized by density functional theory with the TURBOMOLE\(^11-14\) suite of programs (version 7.2.1) at the B97-3c/def2-mTZVP level with COSMO\(^15,16\) solvation parameters to extract the electronic contribution at 0 K (\(\Delta E_{B97-3c}\)). The m4 grid size was used and convergence criteria were 10\(^{-6}\) hartree. The relative stability (\(\Delta G\)) of the four assemblies was calculated using equation (3).

\[
\Delta G = \Delta E_{B97-3c} + \Delta G_{T,\text{XBT}} + \Delta G_{\text{solv,XBT}}
\]

Table S3. Electronic, vibrational and solvation terms [kcal/mol] calculated for PCET processes.

| PCET process | \(\Delta E_{B97-3c}\) | \(\Delta G_{T,\text{XBT}}\) | \(\Delta G_{\text{solv},\text{XBT}}\) | \(\Delta G\) |
|--------------|---------------------|---------------------|---------------------|-------|
| 1b\(^+\) + H \(\rightarrow\) [1b–H]\(^+\) | | | | |
| CB[7]-1b\(^+\) + H \(\rightarrow\) [CB[7]-1b–H]\(^+\) | | | | |
| 1b\(^2\)+ + H \(\rightarrow\) [1b\(^2\)-H]\(^2\)+ | | | | |
| CB[8]-1b\(^2\)+ + H \(\rightarrow\) [CB[8]-1b\(^2\)-H]\(^2\)+ | | | | |

10. Coordinates of optimized structures

![1b](image-url)
11. Frontier orbitals selection for assembly CB[8]-1b2

Figure S6. HOMO of complex CB[8]-1b2 (shorter Pt-Pt distance conformation).
**Figure S7.** (a) HOMO and (b) HOMO-5 of complex CB[8]-1b2 (longer Pt-Pt distance conformation).

12. **References**

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