

A functionalized, ethynyl-decorated, tetracobalt(III) cubane molecular catalyst for photoinduced water oxidation

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prototype **C** compound and hole scavenging determination

Equipments and methods

Electrochemistry: Electrochemical measurements were carried out at room temperature using an Autolab multipurpose equipment interfaced to a PC. A standard three-electrode electrochemical cell was used. Glassy carbon electrode (8 mm², Amel) and a Pt wire were used respectively as working and auxiliary electrode. Unless otherwise stated, potentials were referred to SCE. The experiments were performed in two different media: acetonitrile/aqueous phosphate buffer (v:v, 1:1 at pH 7) or argon purged dry-acetonitrile. In the case of acetonitrile solutions a quasi-reference electrode Ag wire was used, and the redox potentials were corrected adding ferrocene as internal reference (395 mV vs SCE). The typical concentration of the solutions was about 5×10^{-4} M. Tetrabutylammonium hexafluorophosphate (0.1 M) was used as supporting electrolyte. Unless otherwise stated, the scan rate was 200 mV s⁻¹. All $E_{1/2}$ values reported in this work were estimated from cyclic voltammetry as the average of the oxidative and reductive peak potentials (E_{pa} , anodic peak potential; E_{pc} , cathodic peak potential; $E_{1/2} = (E_{pa} + E_{pc})/2$). In the case of mixed solvents, the concentration of the sample was 1×10^{-3} M, the reference electrode was SCE and the supporting electrolyte was sodium phosphate 20 mM.

Stationary photolysis: Stationary photolysis experiments have been performed by using a homemade optical bench containing a halogen lamp (150 W) as the light source. The light was focused on a cuvette containing the solution maintained under continuous stirring. Excitation wavelength is selected by a series of band-pass filters. Photon flux at 450 nm, calculated by using the photoreaction of Aberchrome 540, is 2.79×10^{-9} einstein s⁻¹ (for the complete procedure based on Aberchrome 540, see: *Handbook of Photochemistry, Third Edition*, Eds.: M. Montalti, A. Credi, L. Prodi and M. T. Gandolfi, CRC Press, Boca Raton, FL, 2006, p. 606).

Time-correlated single-photon-counting (TC-SPC) fluorescence spectrometer: The [Ru(bpy)₃]Cl₂ emission lifetime, used for the determination of evolved oxygen by a Stern-Volmer plot, were measured in deoxygenated acetonitrile solutions, using an Edinburgh OB900 spectrometer equipped with a Hamamatsu PL2 laser diode as excitation source (408 nm, pulse-width 59 ps).

Laser flash photolysis: Nanosecond transient absorption measurements were performed with an Applied Photophysics laser flash photolysis apparatus, using a frequency-tripled (355 nm, 160 mJ) Surelite Continuum II Nd/YAG laser pulse (half-width 6-8 ns) as excitation source and a 150 W Xenon arc-lamp as probe light. A band-pass filter (fwhm = 10 nm, 450 nm) has been used in order to minimize bleaching effect by the probe light. Transient detection was obtained using a photomultiplier-oscilloscope combination (Hamamatsu R928, LeCroy 9360).

NMR analysis: ¹H and ¹³C NMR spectra were obtained on a Varian 500 MHz spectrometer. For ¹H and ¹³C NMR spectral data, chemical shifts (δ) and coupling constants (J) are expressed in ppm and hertz, respectively.

TOF-SIMS measurements: For ToF-SIMS measurements, samples were deposited as a (sub)monolayer on etched silver substrates, according to a well-established protocol (see: V. Bletsos, D. M. Hercules, D. Vanleyen and A. Benninghoven, *Macromolecules*, 1987, **20**, 407-413). Measurements were carried out in static mode using Bi⁺ primary ions (25 keV, 0.5 pA) in a TOFSIMS IV instrument (ION-TOF GmbH, Münster, Germany).

Synthesis and characterization

Compound **1** was synthesized according to the literature procedure (see: R. Chakrabarty, S. J. Bora, and B. K. Das, *Inorg. Chem.* 2007, **46**, 9450-946). Details are as follows.

Co(NO₃)₂·6H₂O (145,5 mg, 0.5 mmol) and sodium 4-ethynylbenzoate (168 mg, 1 mmol) are stirred in methanol (5 mL) and heated to refluxing temperature, and pyridine (37 μL, 0.5 mmol) is added to the stirred reaction mixture.

A portion of 30% hydrogen peroxide (v/v, 0.5 mL, 10 mmol) is slowly added to the reaction mixture, and stirring under a refluxing condition is continued for 4 h. The colour of the mixture changes from pink to olive green. After dissolution in acetonitrile, the precipitation of a green powder was obtained from diethyl ether. The product was isolated and dried. Yield: 15% .

¹H-NMR (500 MHz, CD₃CN): 8.50 (m, 8H_{Py}), 7.81 (dd, J=5Hz, 8H_{Ph}), 7.67 (m, 4H, Py), 7.46 (dd, J=5Hz, 8H_{Ph}), 7.16 (m, 4H_{Py}), 3.52 (s, 4H)

¹³C-NMR(125 MHz, CD₃CN): 180.5, 135.8, 139.0, 137.2, 132.8, 129.8, 125.9, 125.4, 84.0, 81.1.

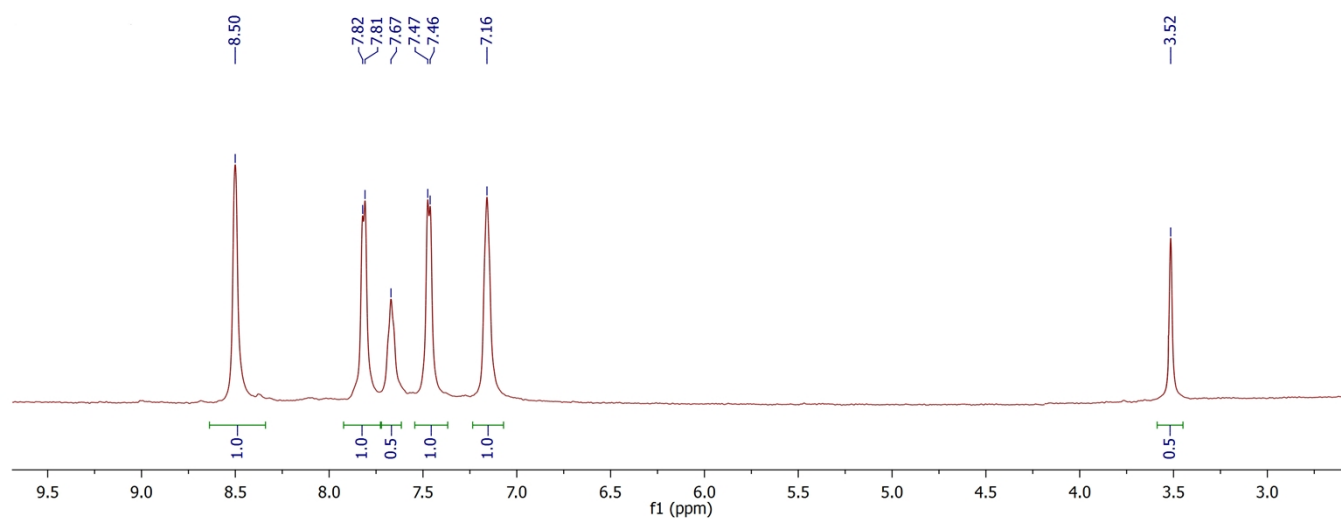


Figure S1. $^1\text{H-NMR}$ of **1** (500 MHz, CD_3CN).

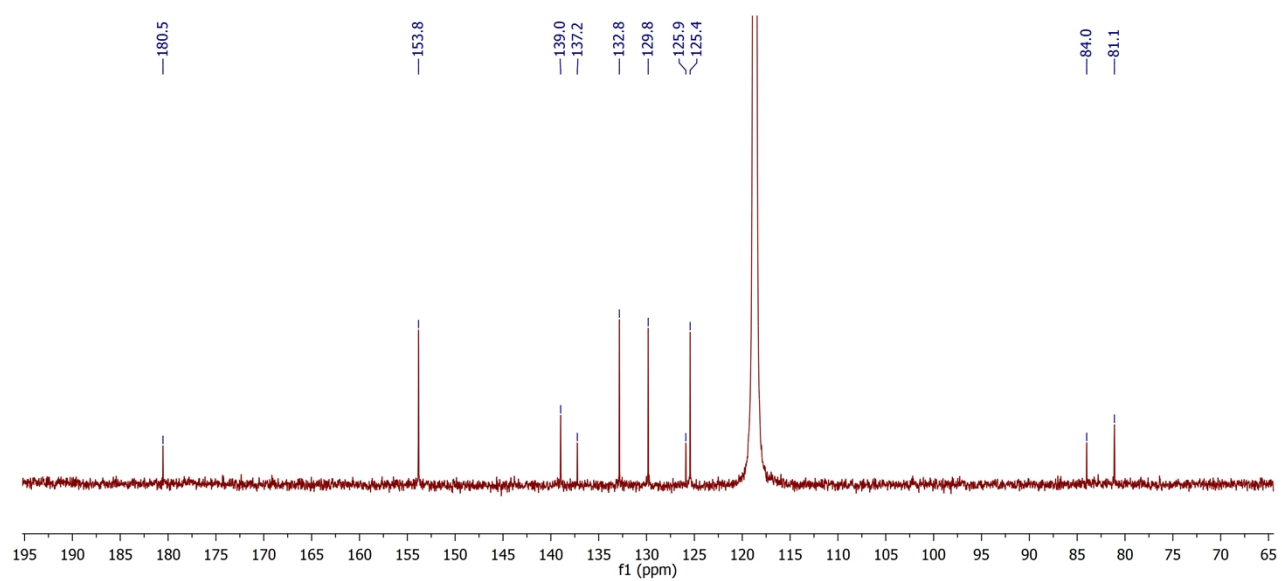


Figure S2. $^{13}\text{C-NMR}$ of **1** (125 MHz, CD_3CN).

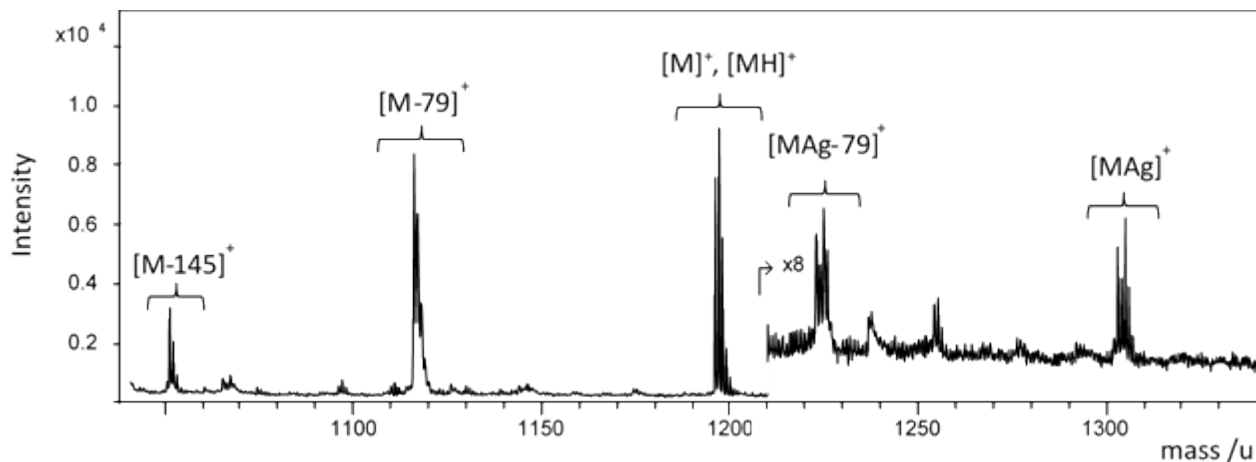


Figure S3: High mass region of ToF-SIMS spectrum of compound **1**.

Comments on TOF-SIMS spectrum

Figure S3 shows the high mass portion of ToF-SIMS spectrum of compound **1**, where several diagnostic peaks are present. In particular, the distribution starting from 1196.0 u is assigned to the isotopic distribution of the molecular ion $C_{56}H_{40}N_4Co_4O_{12}^+$ (M^+), superimposed with that of its protonated form $C_{56}H_{40}N_4Co_4O_{12}H^+$ ($[MH]^+$), while the one starting at 1302.9 u is assigned to the Ag-cationized form $C_{56}H_{40}N_4Co_4O_{12}Ag^+$ ($[MAg]^+$). This kind of cationised forms is not unusual in SIMS spectra (see: (a) V. Bletsos, D. M. Hercules, D. Vanleyen and A. Benninghoven, *Macromolecules*, 1987, **20**, 407; (b) A. Benninghoven, F. G. Rüdener and H. W. Werner, *Secondary Ion Mass Spectrometry*, Wiley-Interscience Publication, John Wiley and Sons, 1987). Moreover large fragments are observed, corresponding to the loss of one ethynylbenzoate unit ($[M-145]^+$) or a pyridine unit ($[M-79]^+$ and $[MAg-79]^+$).

All the above assignments were done on the basis of exact mass and isotopic distributions.

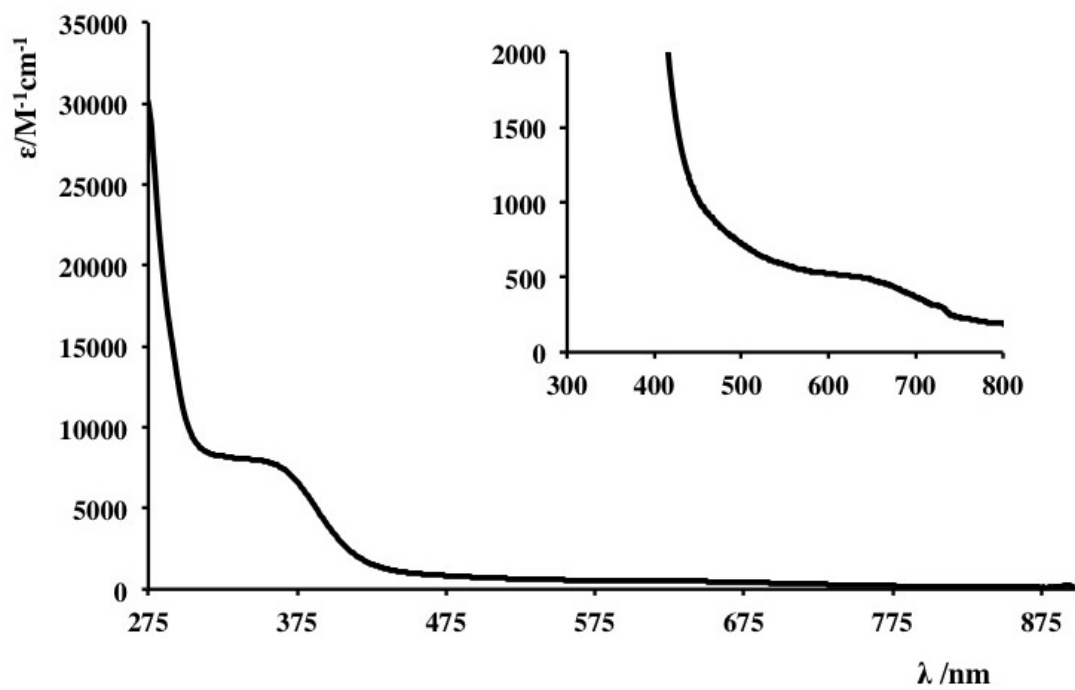


Figure S4. Absorption spectrum of **1** in acetonitrile/phosphate buffer.

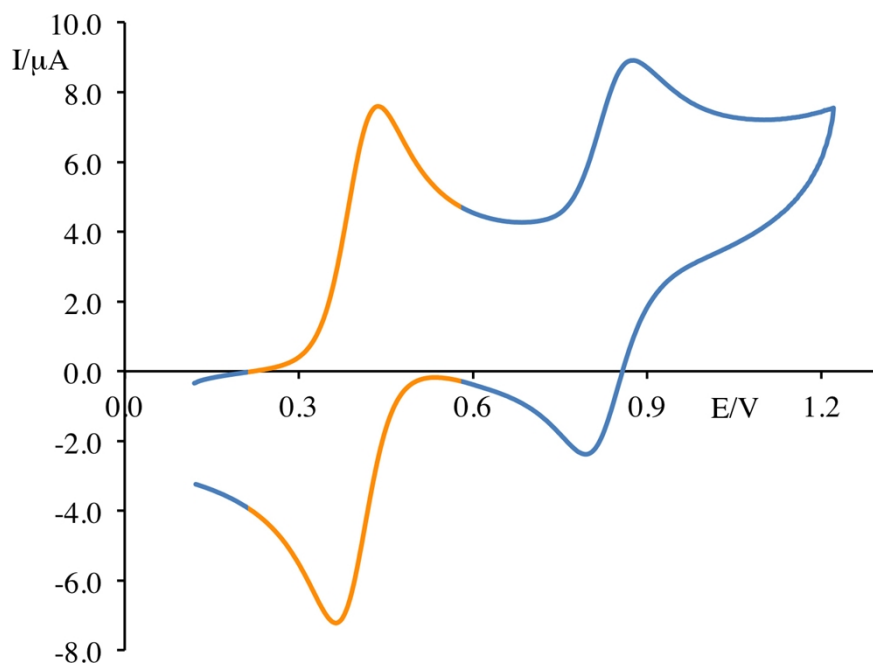


Figure S5. Cyclic voltammogram of **1** in CH₃CN (conc.: 5×10^{-4} M; tetrabutylammonium hexafluorophosphate 0.1 M as supporting electrolyte; Scan Rate: 200 mV/s). Data are vs SCE. The orange trace refers to ferrocene used as internal reference (395 mV vs SCE).

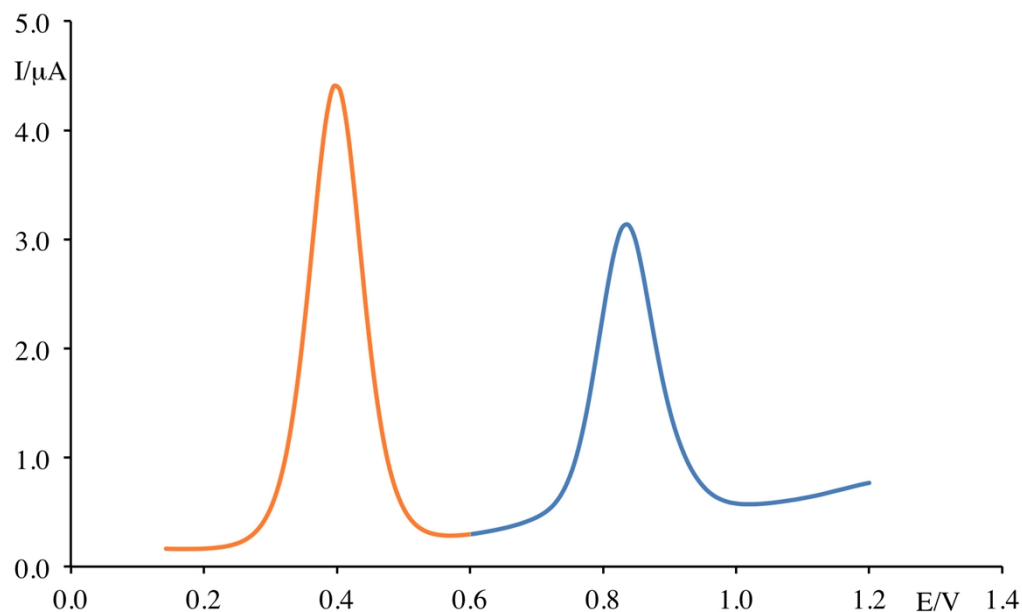


Figure S6. Differential pulse voltammogram of **1** in CH₃CN (conc.: 5×10^{-4} M; tetrabutylammonium hexafluorophosphate 0.1 M as supporting electrolyte, Scan Rate: 20 mV/s). Data are vs SCE. The orange trace refers to ferrocene used as internal reference (395 mV vs SCE).

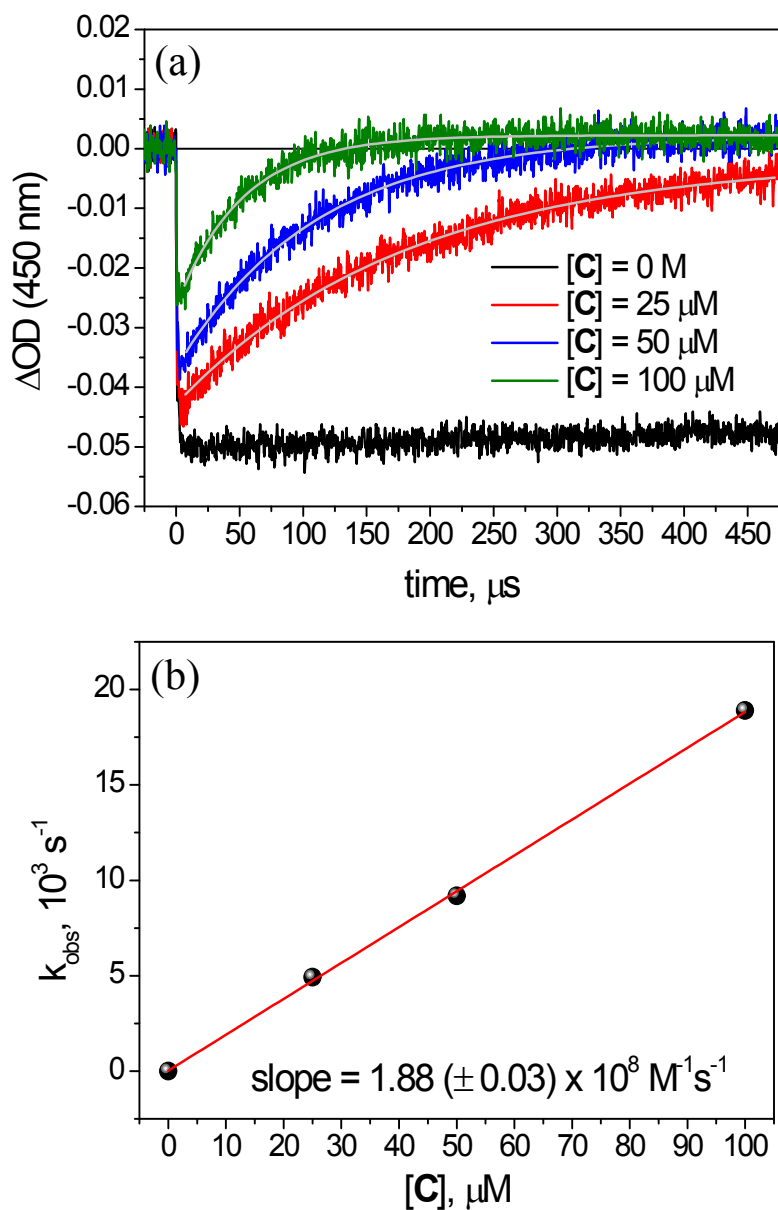


Figure S7. (a) Flash photolysis experiments (excitation at 355 nm, FWHM 6-8 ns) of mixed acetonitrile : 40 mM phosphate buffer (pH 7) 1:1 (v/v) solutions containing 50 μM $\text{Ru}(\text{bpy})_3\text{Cl}_2$, 5 mM $\text{Na}_2\text{S}_2\text{O}_8$, and 0-100 μM C , measured at 450 nm. (b) Plot of the pseudo-first order rate vs. catalyst concentration for the calculation of the bimolecular rate constant.