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COMMUNICATION

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

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Giuseppina La Ganga,^{*a} Viviana Mollica Nardo,^a Massimiliano Cordaro,^a Mirco Natali,^{*b} Stefania Vitale,^c Antonino Licciardello,^{*c} Francesco Nastasi^a and Sebastiano Campagna^{*a}

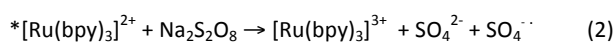
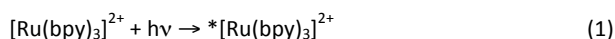
The new tetracobalt(III) cubane 1, carrying functionalized peripheral ethynyl groups, has been prepared. Cubane 1 catalyses photoinduced water oxidation, indicating that the ethynyl groups do not negatively affect the catalytic properties of the Co cubane assembly. On the contrary, quantum yield for water oxidation (0.36) is significantly increased with respect to prototype, simplest species.

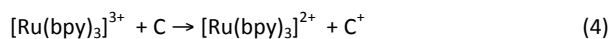
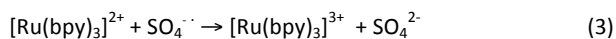
Conversion of light energy into chemical energy, inspired by the natural photosynthetic process (i.e., artificial photosynthesis), is attracting a growing interest. Actually, the development of clean, renewable fuels is a key scientific and technological challenge for the twenty-first century.¹⁻³ Any scheme of artificial photosynthesis includes water oxidation as a crucial step, since water oxidation is one of the major bottlenecks for efficiently achieving artificial photosynthesis.⁴ As a consequence, in the last few years much work has been devoted to identify new catalysts for photoinduced water oxidation, and integrate them into photosynthetic schemes.^{4,5} A quite interesting system is the family of heterogeneous cobalt-phosphate-borate catalysts (Co-OECs),^{6,7} oxidizing water at low overpotentials. Inspired by Co-OECs and the tetramanganese-calcium water oxidation catalyst operating in natural photosynthetic systems,⁸ a series of Co(III)-based tetrametallic cubanes have been recently prepared, both to serve as models for the Co-OEC,⁹ and to play the role of molecular catalysts in photoinduced water oxidation schemes.¹⁰⁻¹³

Integration of molecular water oxidation catalysts into larger multicomponent systems, including electrodes or light-harvesting units, is highly desired for functional assemblies,¹⁴ however only very few attempts have been made so far to integrate such cobalt cubanes into larger, multicomponent systems.^{13,15} One of such attempts is the preparation of a molecular triad made of the cobalt-oxo cubane [Co₄O₄(CO₂Py)₂(bpy)₄]²⁺ (CO₂Py = 4-carboxypyridine) to which are coordinated, via the pyridine nitrogens, two [Re(phen)(CO)₃]⁺ units (phen=1,10-phenanthroline).¹⁵ The final

system contains two Re(I) polypyridine centers, having the role of light-harvesting components, and a central tetracobalt(III) cubane, which was assumed to act as the water oxidation catalyst. Whereas photocatalytic properties of this triad versus photoinduced water oxidation were not reported, the integration of non-coordinated pyridine sites into the cubane structure opened the door to other - not yet pursued, to our knowledge - possibilities for inserting Co(III) cubanes into larger structures.

A synthetic tetracobalt(III) cubane which proved to be quite efficient as molecular water oxidation catalyst is [Co₄O₄(CO₂CH₃)₄(py)₄] (**C**, py = pyridine; see **Figure 1**). This species has been reported to promote photoinduced water oxidation at neutral pH, with a good efficiency, in the presence of [Ru(bpy)₃]²⁺ as photosensitizer and sodium persulfate as sacrificial electron acceptor.^{10,11} The general reaction scheme is shown in eqs 1-6: upon light excitation (eq. 1), oxidative quenching of the excited Ru(II) chromophore occurs by persulfate (eq. 2). The so-formed [Ru(bpy)₃]³⁺ undergoes electron transfer reaction with **C** (eq. 4, a hole scavenging process), which restores the ground state of the photosensitizer and accumulates electron holes on the catalyst. The reaction can be repeated, involving higher oxidation states of **C**, until the catalytically-active state of **C** is reached and water oxidation takes place, restoring **C** (eq. 6). This simple reaction scheme can be complicated by considering the reaction between one of the products of the irreversible reduction of persulfate, namely the sulfate radical anion SO₄^{•-}, which is a very strong oxidant by itself,^{10b} with [Ru(bpy)₃]²⁺ (eq. 3) to generate a further, second oxidized [Ru(bpy)₃]³⁺ molecule from a single photon absorbed.^{5a,16} This ultimately allows to store two electron holes into **C**, upon hole scavenging, per photon absorbed. The same result is obtained by the direct reaction of the SO₄^{•-} radical anion with the catalyst (eq. 5), as demonstrated in several cases.⁵





Electron withdrawing or donor substituents have also been inserted into the pyridine rings which are part of the structure of **C**.^{11b} The catalytic activity of **C** was maintained also in the presence of such substituents - not an obvious result - while the redox properties of the cubane system were finely tuned, so affecting the hole scavenging process and the overall photochemical quantum yield for water oxidation. For example, a linear dependence of the hole scavenging rate constant of the reaction in eq. 4, involving the first step of charge accumulation in **C**, on the oxidation potential of **C**, obviously tuned by the pyridine substituents, was found.^{11b}

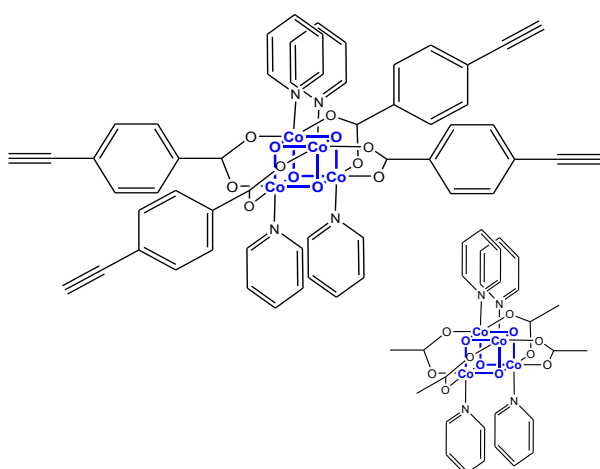


Figure 1. Structural formula of **1**. In the right-bottom corner, structural formula of **C** is also shown.

Here we report the synthesis and characterization of a new tetracobalt(III) cubane, **1**, derived from **C** (**Figure 1**). Differently from formerly-studied cubanes derived from **C**, substituted on the pyridines, in **1** the substitution involves the acetate groups, each one carrying a phenyl-ethynyl moiety. The synthetic approach (vide infra) is also different from that used to prepare the above-mentioned cobalt cubane $[\text{Co}_4\text{O}_4(\text{CO}_2\text{Py})_2(\text{bpy})_4]^{2+}$, which is also substituted on the acetate groups with respect to its prototype $[\text{Co}_4\text{O}_4(\text{CO}_2\text{Me})_2(\text{bpy})_4]^{2+}$, from which it is directly prepared via a substitution reaction.¹⁷ More interestingly, **1** contains, pointing towards different directions, four ethynyl groups, which can be used to graft **1** on various substrates (including surfaces) as well as for coupling **1** with other molecular components (e.g., light-harvesting units). The redox behavior of **1** and the photoinduced water oxidation properties of **1**, in the presence of chromophores and sacrificial acceptors, are also investigated and compared with the properties of the prototype **C**. The results indicate that the functionalized **1** keeps the useful catalytic properties of its prototype even in the presence of the ethynyl groups, also in this case not an obvious result; in some cases, improved properties are also found.

Results and Discussion

Compound **1** was prepared by using the procedure employed for the synthesis of the prototype **C**.¹⁷ The tetrameric cobalt(III) complex was prepared by oxidizing cobalt(II) ions (by using H_2O_2) in the presence of pyridine and 4-ethynyl-benzoate ions (see ESI). The product was isolated as a green powder. ^1H and ^{13}C NMR, as well as TOF-SIMS data (see ESI), supported the proposed structure. In particular, the proton spectrum shows few sharp signals as expected, due to the high symmetry of the system and to diamagnetic nature of Co(III). Three signals of the homologous pyridines can be identified, as well as a single AB system (aromatic double doublet) of the phenyl ethynyl groups and finally one signal of the alkynyl protons.

The synthetic method, based on the designed cubane preparation from scratch, differs from the approach used for preparing various similar species with substituted acetate moieties,^{17c} where the starting material was **C** itself. In our hands, preparing **1** from the individual components gave definitely better results than substitution of acetate units on the preformed cubane.

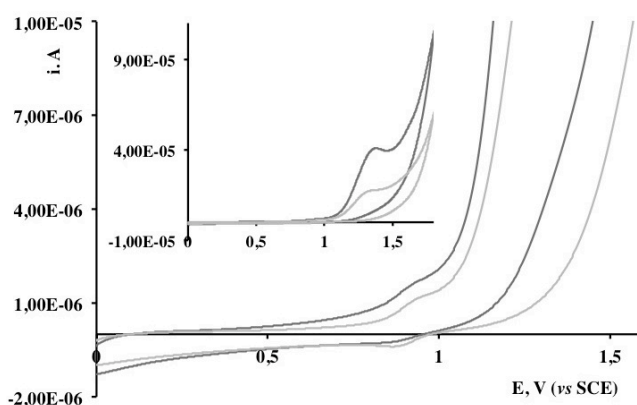


Figure 2. Cyclic voltammetry of **1** (1×10^{-3} M) in acetonitrile/40 mM aqueous phosphate buffer (pH 7). Scan rate: 20 mV s^{-1} . In grey the cyclic voltammogram of **C**, recorded in the identical conditions, is shown for comparison. In the inset, the scale has been extended to better visualize the water discharge.

The absorption spectrum of **1** in acetonitrile(AN)/phosphate buffer 1:1 (v/v) exhibits a very weak band at about 650 nm, followed by a more intense band at 355 nm (see ESI).¹¹ **Figure 2** shows the CV of **1** in mixed acetonitrile/aqueous buffered solution (CV of **1** in acetonitrile is shown in ESI), and is qualitatively similar to those of **C**:¹¹ after a one-electron oxidation wave with $E_{1/2}$ at about 0.90 V, assigned to a quasi reversible Co(III) to Co(IV) oxidation, the catalytic water oxidation wave is present. Interestingly, such a catalytic wave occurs in **1** at roughly identical (slightly less positive) potential than in **C**, indicating that the presence of the ethynyl groups in **1** do not inhibit the catalytic ability of the tetracobalt cubane structure. On the contrary, larger currents are obtained, at identical conditions. Also, the Co(III)/Co(IV) oxidation process occurs at roughly the same potential in **1** and **C**, suggesting that substitution on the acetate bridging linkage is less affecting the redox properties of the cubane assembly - at least in the investigated conditions - with respect to substitution on the pyridines, which is known to produce significant shifts of the Co(III)/Co(IV) process.^{11b}

Photoinduced water oxidation was investigated by using a sacrificial system containing $[\text{Ru}(\text{bpy})_3]^{2+}$ (1×10^{-3} M), **1** (1.87×10^{-5} M), and $\text{Na}_2\text{S}_2\text{O}_8$ (5 mM) in 2 mL of acetonitrile/ phosphate buffer, excited at $\lambda = 450$ nm: **Figure 3** shows the time dependence of O_2 production so obtained, measured using a method previously described.¹⁸

The photochemical quantum yield, Φ , for molecular oxygen production, at $\lambda_{\text{exc}} = 450$ nm, was 0.36. This is a quite impressive result and, considering the usual reaction scheme assumed to be valid in these type of systems,^{5a,16} means that more than 70% of photons absorbed by the photosensitizer are efficiently used to produce O_2 . Such a quantum yield value is much larger than that reported for the prototype **C** in the identical experimental conditions (0.13^{11b}), thus indicating that the phenyl-ethynyl substituents on the acetate bridging ligands have a positive effect for the photocatalysis process. The reason for this behavior cannot be explained in the absence of mechanistic hypotheses, so this consideration should be regarded at the moment as an experimental, but relevant, result. Turnover number (TON) of the photocatalysis is 80 in the present case; however, it appears to be mainly limited by side-reactions involving the ethynyl groups; these side-reactions could be reduced once the system is interfaced with substrates.

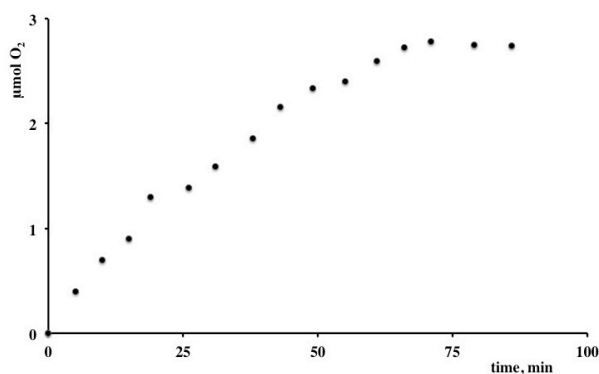


Figure 3 – Molecular oxygen formation upon photoinduced water oxidation from a $\text{Ru}(\text{bpy})_3^{2+}$ (1×10^{-4} M) / **1** (1.87×10^{-5} M) / $\text{Na}_2\text{S}_2\text{O}_8$ (5 mM) system in acetonitrile/phosphate buffer at pH 7; excitation wavelength > 450 nm.

Finally, the rate constant of hole scavenging, that is the electron transfer from the catalyst to the oxidized photosensitizer, has been investigated by flash photolysis (see **Figure 4**, where also the plot of the observed rate constants vs catalyst concentration is shown). The hole scavenging process is quite important, since a fast and efficient hole scavenging is needed if a regenerative photochemical catalytic system (e.g., a photoelectrosynthetic cell¹⁴) has to be designed, particularly for protecting oxidized sensitizer from undesired, parasite reactions. In a typical experiment, formation of $[\text{Ru}(\text{bpy})_3]^{3+}$ is evidenced by the bleaching of the MLCT absorption band at 450 nm upon light excitation and electron transfer with persulfate. Recovery of the MLCT absorption on the microsecond timescale is due to hole scavenging with the catalyst **1**. Different catalyst concentrations allow to obtain (under pseudo-first order conditions) the rate constants for the hole scavenging process.

Decays in **Figure 4(a)** indicate that the sulfate radical anion reacts preferentially with the catalyst instead than with $[\text{Ru}(\text{bpy})_3]^{3+}$, as already found for other cubane catalysts, a circumstance that anyway

does not affect quantum yield determination.¹¹ The bimolecular rate constant measured according to data in **Figure 4(b)**, $2.35 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, is not far from that found for the same process involving **C** in the identical experimental conditions, which is $1.88 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (see ESI) in agreement with close similarity in CVs of **C** and **1** (see **Figure 2**).^S However, as already found for the cobalt cubanes substituted on pyridines, rate constant of hole scavenging - although quite important for systems stability - is not the dominant factor affecting photochemical quantum yield. In fact, in pyridine-substituted cobalt cubanes Φ was not linearly correlated with hole scavenging rate constants, indicating that other factors, most likely intimately connected with the mechanism, were more important. Even in this case, in fact, the larger Φ value exhibited by **1** is probably connected to successive steps in the overall water splitting mechanism.

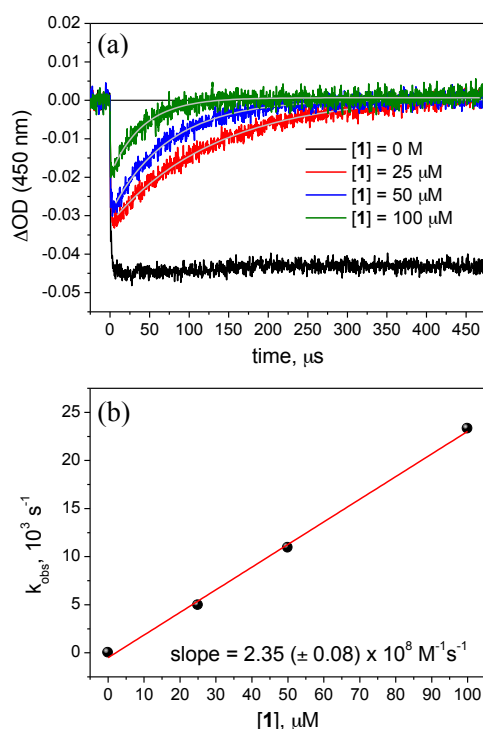


Figure 4. (a) Flash photolysis experiments (excitation at 355 nm, FWHM 6-8 ns) of mixed acetonitrile : 40 mM phosphate buffer (pH 7) 1:1 (v/v) solutions containing 50 μM $\text{Ru}(\text{bpy})_3\text{Cl}_2$, 5 mM $\text{Na}_2\text{S}_2\text{O}_8$, and 0-100 μM **1**, measured (a) at 450 nm. (b) Plot of the pseudo-first order rate constant vs. catalyst concentration for the calculation of the bimolecular rate constant.

Conclusions

A new, functionalized tetracobalt(III)-oxo cubane **1** has been prepared – using an approach never employed for the few formerly-studied, acetate-substituted cobalt cubanes - and characterized. This species bears four peripheral ethynyl subunits, which are suitable to be interfaced with several substrates. The presence of the peripheral ethynyl subunits neither significantly affect the redox behavior of **1** nor inhibits its catalytic properties vs water oxidation; on the contrary, it appears that the photochemical quantum yield for oxygen production from water in sacrificial systems based on Ru(II)

polypyridine complexes and persulfate anions is larger (36%) for **1** with respect to the prototype species **C** (13%). These results open the way to the possibility of interfacing similar tetracobalt(III) cubane species with heterogeneous systems and/or molecular light-harvesting components, keeping promise of retaining the useful catalytical properties of the cobalt cubane structure within the multicomponent assemblies.

Acknowledgements

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Notes and references

^a Dipartimento di Scienze Chimiche, Università di Messina and Centro Interuniversitario per la Conversione dell'Energia Solare (SOLAR-CHEM), sezione di Messina, Messina, Italy.

^b Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Ferrara, and SOLAR-CHEM, sezione di Ferrara, Ferrara, Italy.

^c Dipartimento di Scienze Chimiche, Università di Catania, Catania, Italy.

¶ For a complete sequence of reactions involved, see refs. 5a and 16.

¥ The absorption spectra, redox, and photocatalytic experiments have been performed in acetonitrile/phosphate buffer 1:1 v/v, unless otherwise noted. The phosphate buffer was regulated at pH 7 by using NaOH.

¶ The amount of the bleaching at 450 nm is an indication of the amount of [Ru(bpy)₃]³⁺ production, which takes place via the reaction sequence (eq 1 + eq 2), plus the [Ru(bpy)₃]³⁺ obtained via the reaction of [Ru(bpy)₃]²⁺ with the sulfate radical anion (eq. 3). Fig. 4(b) indicates that less [Ru(bpy)₃]³⁺ is produced on increasing **1** concentration, suggesting that the sulfate radical anion directly reacts with **1**. See also ref. 19.

§ The slight larger value of the hole scavenging (hs) rate constant involving **1** with respect to **C**, with essentially identical driving force, could suggest a better electronic factor for the reaction in case of **1**. It can also be noted that the hs rate constant involving **C** is smaller, 1.33 x 10⁸ M⁻¹ s⁻¹, in mixed acetonitrile/aqueous borate buffer at pH 8,^{11b} indicating a (small) environmental effect on the reaction rate constant.

Electronic Supplementary Information (ESI) available: Synthesis, ¹H and ¹³C NMR, TOF-SIMS and absorption spectra; CV of **1** in acetonitrile; flash photolysis experiments for determining hs rate constant involving **C** in acetonitrile/phosphate buffer 1:1 (pH 7). See DOI: 10.1039/c000000x/

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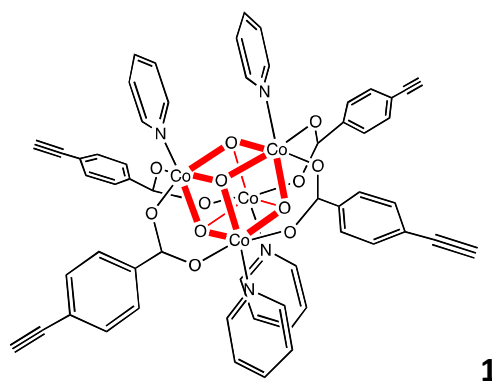
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TABLE OF CONTENTS ENTRY



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