

Photoinduced Catalytic Reaction by a Fluorescent Active Cryptand Containing an Anthracene Fragment**

Hong-Guo Hao, Xiao-Dan Zheng, and Tong-Bu Lu*

The use of sunlight to split water into H_2 and O_2 attracts great scientific interest^[1] for two reasons: the urgent need for clean and renewable fuel to avoid greenhouse gas emissions and for artificial photosynthesis. For achieving such a purpose, a good catalyst capable of driving photoinduced electron transfer (PET) and converting solar energy into chemical energy is essential. Although many fluorescent active compounds exhibit PET, reports in which PET is followed by chemical transformation are much less common,^[2] and most of the photocatalytic systems employ noble-metal complexes as catalyst and chromophore, and amine such as triethylamine (TEA) or triethanol amine (TEOA) as a sacrificial reductant. Many organic ligands containing an anthracene fragment as a chromophore have been synthesized and used for ion recognition^[3] and fluorescent switches,^[4] based on the fluorescent and PET properties of the anthracene fragment. For example, Fabbri et al. found^[4c,f] that alternate oxidation and reduction at a copper center resulted in turning the light emission of an anthracene fragment off and on in a complex in which the anthracene fragment is covalently linked to a copper center with a [14]ane- S_4 macrocyclic receptor. The switching off was caused by electron transfer from the $^*An_{CT}$ excited state (An = anthracene moiety; CT = charge transfer) to the Cu^{II} center. However, to the best of our knowledge, the use of organic ligands containing an anthracene fragment as a chromophore to catalyze a photoinduced chemical reaction has not been reported so far.

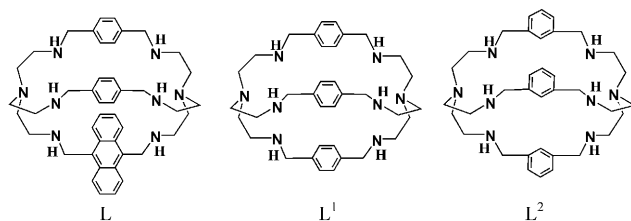
We herein report a novel photocatalytic reductive reaction of Cu^{II} to Cu^I in acetonitrile by a fluorescently active cryptand **L** containing an anthracene fragment. Parameters that affect the photocatalytic reductive reaction, such as

irradiation time, sacrificial electron donor, and water content in the reaction system were investigated. The most surprising discovery was that water in the reaction system served as a sacrificial electron donor and was oxidized to oxygen. The reaction kinetics and potential mechanism are given based on the experimental results.

The cryptand **L** was first designed by Fabbri et al. for anion sensing in aqueous solution.^[5] We previously demonstrated^[6] that the C–C bond of nitriles can be cleaved by dinuclear metal cryptates $[M_2L](ClO_4)_4$ ($M = Cu^{II}, Zn^{II}$) at room temperature through an S_N2 pathway to generate cyanido-bridged complexes $[M_2L^I(CN)](ClO_4)_3$ and alcohol. Following up our previous studies on the recognition and activation of small guest molecules by cryptates and protonated cryptands,^[6,7] we tried to synthesize the dinuclear Cu^{II} cryptate $[Cu_2L](ClO_4)_4$ by the reaction of cryptand **L** with $Cu(ClO_4)_2 \cdot 6H_2O$ in acetonitrile under ambient condition. Unexpectedly, crystals of $[Cu(MeCN)_4](ClO_4)$ (**1**) were obtained.

The result of X-ray crystallographic analysis reveals that the structure of **1** is similar to the reported structure of $[Cu(MeCN)_4](CF_3SO_3)$,^[8] in which the tetrahedral Cu^I center is coordinated to four acetonitrile molecules (Figure 1 a). The Cu–N distances are close to the reported values for $[Cu(MeCN)_4](CF_3SO_3)$. However, when triethylamine was added to the above acetonitrile solution containing cryptand **L** and $Cu(ClO_4)_2 \cdot 6H_2O$, only the green crystals of $[Cu_2L(OH)(H_2O)](ClO_4)_3 \cdot MeCN$ (**2**) were obtained, and no crystals of **1** were isolated from the solution. The result of XPS measurement indicates that all the copper present in the solution containing triethylamine is Cu^{II} , and no Cu^I formed (Figure S1, Supporting Information). In **2**, the cryptand **L** encapsulates two Cu^{II} ions at its two poles, and the axial positions of the two Cu^{II} centers are occupied by one OH^- ion and one water molecule, respectively (Figure 1 b). Further experimental results demonstrate that compounds **1** and **2** can only be obtained under acidic and basic conditions, respectively, and the acid in the mixture of cryptand **L** and $Cu(ClO_4)_2 \cdot 6H_2O$ in acetonitrile comes from the excess of $HClO_4$ in $Cu(ClO_4)_2 \cdot 6H_2O$. Moreover, compound **1** cannot be obtained in the dark even under the acidic conditions, and compound **1** cannot be obtained either when cryptand **L** was treated with $Cu(ClO_4)_2 \cdot 6H_2O$ under acidic conditions. The above experimental results clearly demonstrate that the reduction from Cu^{II} to Cu^I in acetonitrile is a photoinduced catalytic reaction associated to anthracene fragment in **L**, and the reduction can only be achieved under acidic conditions.

As observed by Fabbri et al.,^[5] the fluorescence intensities of **L** is pH-dependent (Figure S2), whereby full anthracene fluorescence is observed at low pH values, and the



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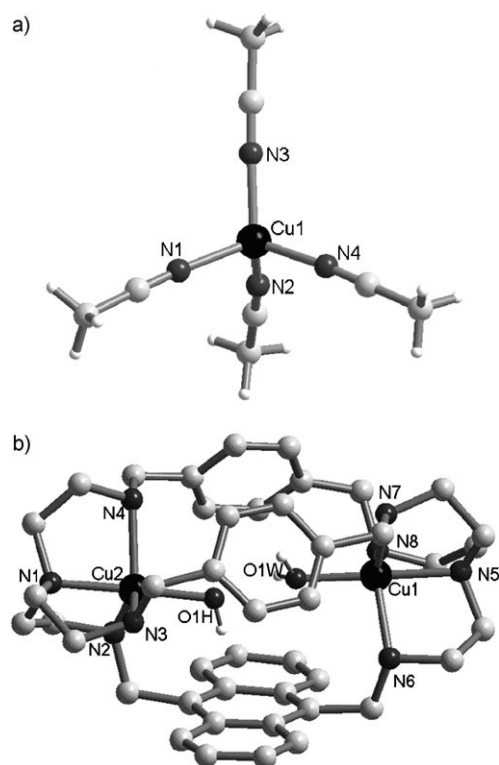


Figure 1. a) Structure of [Cu(MeCN)₄]⁺ cation in **1**. b) Structure of [Cu₂L(OH)(H₂O)]³⁺ cation in **2**.

fluorescence intensities decrease in the pH range 4–8 and then reduces to almost zero at high pH values. The reducing property is attributed to electron transfer from the neutral amine groups to the proximate excited anthracene fragment *An, thereby quenching its fluorescence.^[5] Thus, the photoreduction of Cu^{II} to Cu^I can only be achieved under acidic conditions, and dinuclear Cu^{II} compound of **2** was formed under basic conditions. Although the coordination of Cu^{II} to the nitrogen atoms of L prevent the electron transfer from nitrogen to *An, the bonded Cu^{II} center in **2** cannot be photoreduced either, as the encapsulated Cu^{II} can also quench its fluorescence through an electron transfer mechanism.^[5] However, under the acidic conditions, the Cu^{II} center does not directly bond to the protonated cryptand [H₆L]⁶⁺, thus the anthracene fluorescence is not quenched (Figure S2).

To monitor the photoreduction process of Cu^{II}, a solution containing H₆L(ClO₄)₆ (0.01 mol L⁻¹) and two equivalents of Cu(ClO₄)₂·6H₂O in acetonitrile was irradiated with a high-pressure mercury lamp (450 W) at 30 °C, and electronic absorption spectra were recorded every 15 min. As shown in Figure 2, the intensities of initial peak at λ = 775 nm assigned to the d–d transfer of Cu^{II} decreased along with increasing irradiation time, and the peak disappeared after 6 h irradiation, and the color of solution changed from green to yellow after irradiation. The resulting yellow acetonitrile solution was dried under vacuum to give a yellow powder, and the results of XPS measurements indicate that all the copper in the yellow powder is Cu^I, demonstrating all Cu^{II} centers in acetonitrile were photoreduced to Cu^I (Figure S3). However, the intensities of the peak at λ = 775 nm remained almost constant when the solution was left in dark for 16 h (Fig-

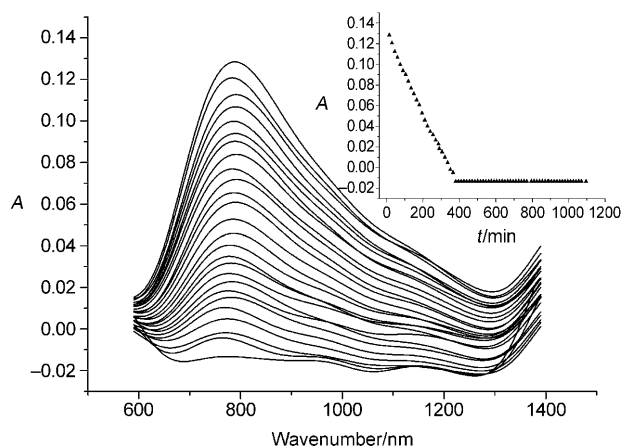
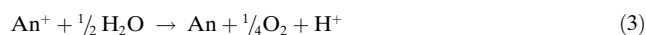
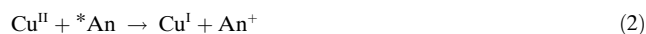


Figure 2. UV/Vis spectra of H₆L(ClO₄)₆ and Cu(ClO₄)₂·6H₂O (1:2) in acetonitrile as a function of irradiation time; irradiation was performed with a high-pressure mercury lamp (inset: plot of absorbance at λ = 775 nm versus irradiation time).

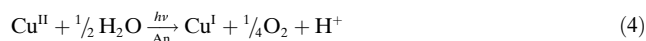
ure S4), further demonstrating that the reduction from Cu^{II} to Cu^I is a photoinduced catalytic reaction. Indeed, one mole of H₆L(ClO₄)₆ can photocatalyze over 70 equivalents of Cu(ClO₄)₂·6H₂O to Cu^I, as monitored by the electronic absorption spectra.

The photoreduction of Cu^{II} to Cu^I requires a sacrificial reductant, and the absence of a deliberately added sacrificial reductant in the above reaction system was unexpected. Given the composition of the reaction system, a possible sacrificial reductant is acetonitrile, the hexaprotonated cryptand [H₆L]⁶⁺, or water present in the acetonitrile. The oxidation of acetonitrile was ruled out owing to its well-known chemical stability with a potential window in excess of 6 V.^[9] It seems the hexaprotonated cryptand [H₆L]⁶⁺ may serve as a sacrificial reductant. However, [H₆L]⁶⁺ survives the photoinduced catalytic reaction of H₆L(ClO₄)₆ and Cu(ClO₄)₂·6H₂O (1:70) in acetonitrile, as demonstrated by ESIMS measurements (Figure S5), and one mole of [H₆L]⁶⁺ cannot reduce 70 equivalents of Cu^{II} if [H₆L]⁶⁺ served as a sacrificial reductant. Thus, the oxidation of H₆L(ClO₄)₆ is also highly unlikely.

After ruling out the species mentioned above, we considered that the sacrificial reductant in the reaction system is mostly water, and the photoreduction may follow the pathway given in Equations (1)–(3).



In this process, an electron is firstly excited from the ground state of the An fragment in [H₆L]⁶⁺ to its excited state *An under the irradiation with light [Eq. (1)]. The electron in the excited-state *An moiety is then transferred to Cu^{II} to generate Cu^I and a An⁺ cation [Eq. (2)]. Finally, the An⁺ cation gains an electron from water to form An, and water is oxidized to oxygen [Eq. (3)]. The overall photoinduced catalytic reaction is shown in Equation (4).



If the above mechanism is correct, the reaction rate should be dependent on the concentration of water. Indeed, the reaction became much faster when water was added to the reaction system. The observed rate constants at different concentrations of water were determined. The rate law can be described as $\ln(A_0/A_t) = k_{\text{obs}} t$, where A_0 and A_t are the absorbance values of Cu^{II} at $\lambda = 775$ nm at the irradiation time of zero and t min, respectively, and $k_{\text{obs}} = k_2[\text{H}_2\text{O}]^\alpha$. The plot of $\ln(A_0/A_t)$ versus time reveals a line with a slope of k_{obs} (Figure 3a). The values of k_{obs} at different concentrations of water are given in Table 1, and a plot of $\log k_{\text{obs}}$ versus $\log[\text{H}_2\text{O}]$ is shown in Figure 3b. From Table 1, it can be seen

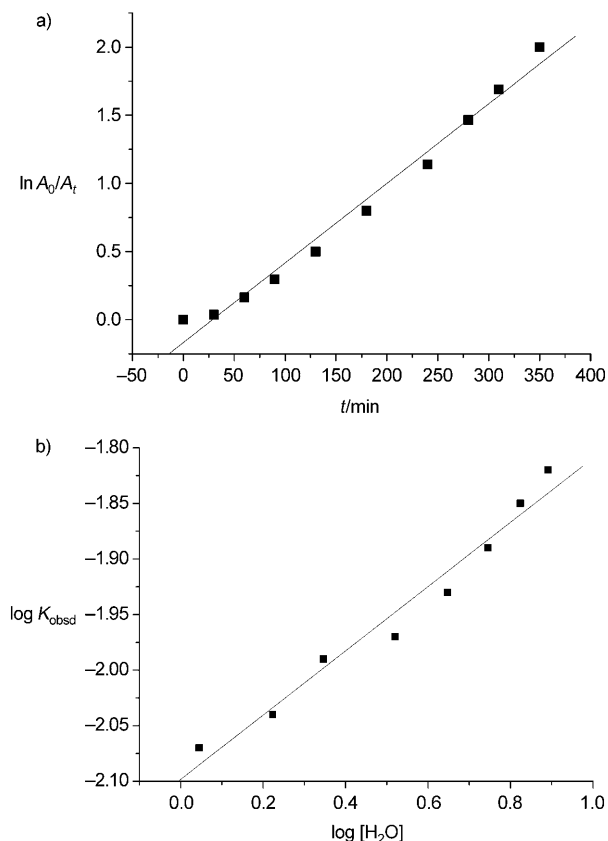


Figure 3. a) Determination of the observed rate constant for the reaction of $\text{H}_6\text{L}(\text{ClO}_4)_6$ and two equivalents of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. b) Determination of the second-order rate constants (k_2) for different concentrations of water.

that the observed rate constants become larger with increasing concentration of water. The calculated second-order rate constant (k_2) and α value are $7.98 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ and 0.289, respectively.

In contrast, the above photoinduced reduction should not take place in the absence of water. Thus, an anhydrous solution of acetonitrile containing $\text{H}_6\text{L}(\text{ClO}_4)_6$ and anhydrous $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ (1:2) was prepared and irradiated with a high-pressure mercury lamp (450 W). The color of the solution slowly changed from yellow-green to purple rather than yellow with increasing irradiation time. The electronic absorption spectra in the absence of water are different

Table 1: Observed rate constants (k_{obs}) at various concentrations of water.

$[\text{H}_2\text{O}]$ [mol L ⁻¹]	1.11	1.67	2.22	3.33	4.44	5.56	6.67	7.78
k_{obs} [$\times 10^3$]	8.6	9.1	10.1	10.8	11.8	12.8	14.0	14.8

from those in the presence of water (Figure S6), in which the peak around $\lambda = 736$ nm (assigned to the d-d transfer of anhydrous Cu^{II}) slowly disappeared and a new peak around $\lambda = 495$ nm appeared, and its intensity increased with increasing irradiation time. After irradiation for 6 h, acetonitrile in the purple solution was removed under vacuum to give a purple powder, XPS measurement on which indicate that 84 % of copper present in the sample is still Cu^{II} (Figure S7a); the reduction of 16 % Cu^{II} to Cu^{I} is attributed to failure to remove water completely. When water was added to the purple solution and it was irradiated again, the color changed from purple to yellow, and the results of XPS measurements indicate that all Cu^{II} in the solution was reduced to Cu^{I} after the addition of water (Figure S7b). The above experimental results clearly demonstrate that the sacrificial reductant in the reaction system is water.

To detect the oxygen molecules generated during the reaction, a solution (5 mL) containing $\text{H}_6\text{L}(\text{ClO}_4)_6$ (0.5 mmol) and $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ (2.5 mmol) in acetonitrile was degassed with nitrogen for 5 min, and 0.1 mL of H_2^{18}O was added. The resulting solution was irradiated with a high-pressure mercury lamp (450 W) at 30 °C. The generated $^{18}\text{O}_2$ was detected by GC-MS analysis. As shown in Figure S8 in the Supporting Information, the ratio of $^{18}\text{O}_2/^{16}\text{O}_2$ was 0.005, 0.211, and 21 after irradiation for 10 min, 1.5 h, and 4 h, respectively. This result clearly demonstrates that $^{18}\text{O}_2$ was generated during the irradiation reaction.

It is interesting to note that the photoinduced catalytic reaction did not occur when $\text{H}_6\text{L}(\text{ClO}_4)_6$ was replaced by anthracene or 9,10-bis(chloromethyl)anthracene. We consider that H_6L^{6+} may capture water molecules into its cavity, and that this arrangement is beneficial for the oxidation of water into oxygen. The detail mechanism is being investigated.

In conclusion, we demonstrated herein for the first time a photoinduced reduction of Cu^{II} to Cu^{I} by a fluorescently active cryptand containing an anthracene fragment. The most striking feature of the system is that the water in the reaction system serves as a sacrificial electron donor and was oxidized to oxygen. Usually, Cu^{I} is easy to oxidize by oxygen in the open air; thus, the photoinduced reduction of Cu^{II} by water to produce Cu^{I} and oxygen is unique. The fluorescently active cryptand $[\text{H}_6\text{L}]^{6+}$ containing an anthracene fragment is potentially useful as a new generation of catalyst to split water to produce hydrogen as a cheap energy source, while avoiding greenhouse gas emissions. Research to this end is continuing.

Experimental Section

The cryptand L was prepared according to the literature method.^[5] $\text{H}_6\text{L}(\text{ClO}_4)_6$ was obtained by adding the cryptand L into a solution containing excess of HClO_4 in acetone. Yield: 86 %; elemental analysis: calcd for $\text{C}_{44}\text{H}_{64}\text{N}_8\text{Cl}_6\text{O}_{24}$ ($\text{L} \cdot 6\text{HClO}_4$): C 40.60, H 4.96, N

8.61%; found: C 40.30, H 5.02, N 8.56%. MS (ESI): m/z 350.7 ($[\text{H}_2\text{L}]^{2+}$); 700 ($[\text{HL}]^+$); 799 ($[(\text{HL}(\text{ClO}_4)]^+$).

Synthesis of $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{ClO}_4)_2$ (**1**): A solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.074 g, 0.2 mmol) in acetonitrile (5 mL) was added dropwise to a solution of $\text{H}_6\text{L}(\text{ClO}_4)_6$ (0.130 g, 0.1 mmol) in acetonitrile (8 mL). The resulting green solution was stirred at room temperature for 0.5 h, then filtered off and evaporated slowly at room temperature in the open air. Two weeks later, colorless crystals of **1** were obtained. Yield: 80%; elemental analysis: calcd for $\text{C}_8\text{H}_{12}\text{N}_4\text{CuClO}_4$: C 29.40, H 3.70, N 17.12%; found: C 29.10, H 3.74, N 17.20%. IR (KBr): $\tilde{\nu}$ = 3290 (s), 1423 (s), 1084 (s), 627 cm^{-1} (s).

Synthesis of $[\text{Cu}_2\text{L}(\text{OH})(\text{H}_2\text{O})](\text{ClO}_4)_3$ (**2**): A solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.078 g, 0.21 mmol) in acetonitrile (5 mL) was added dropwise to a solution of **L** (0.070 g, 0.1 mmol) and triethylamine (0.1 mL) in acetonitrile (8 mL). The resulting green solution was stirred at room temperature for 0.5 h, then filtered off and evaporated slowly at room temperature in the open air to give green crystals of $2 \cdot \text{CH}_3\text{CN} \cdot 0.5\text{H}_2\text{O}$. Yield: 90%; elemental analysis: calcd for $\text{C}_{44}\text{H}_{62}\text{N}_8\text{Cu}_2\text{Cl}_3\text{O}_{14.5}$ ($2 \cdot 0.5\text{H}_2\text{O}$): C 45.23, H 5.35, N 9.59%; found: C 45.02, H 5.30, N 9.49%. IR (KBr): $\tilde{\nu}$ = 3509 (s), 3725 (m), 2930 (w), 2880 (w), 1594 (m), 1448 (m), 1285 (w), 933 (w), 811 (w), 768 (w), 696 (w), 624 cm^{-1} (m).

Single-crystal X-ray crystallography: The single-crystal data of **1** and **2** were collected at 153 and 123 K respectively on a Oxford Gemini S Ultra diffractometer with $\text{Cu}_{\text{K}\alpha}$ radiation ($\lambda = 1.54178 \text{ \AA}$). The structures were solved by direct methods and refined by full-matrix least-squares analysis on F^2 using the SHELX97 program package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in disordered acetonitrile and water molecules in **2** were not included.

Crystal data of **1**: $\text{C}_8\text{H}_{12}\text{N}_4\text{CuClO}_4$, $M_r = 327.22$, orthorhombic, space group $\text{Pna}2(1)$, $a = 23.9402(3)$, $b = 8.3507(1)$, $c = 20.4229(3) \text{ \AA}$, $V = 4082.89(9) \text{ \AA}^3$, $Z = 12$, $\rho_{\text{calcd}} = 1.597 \text{ Mg m}^{-3}$, $\mu = 4.216 \text{ mm}^{-1}$, $F(000) = 1992$. A total of 13 804 reflections collected, 5672 independent reflections ($R_{\text{int}} = 0.0216$) with 5259 [$I > 2\sigma(I)$] observed data, 500 parameters, $R_1 = 0.0267$, $wR_2 = 0.0688$ [$I > 2\sigma(I)$] and $R_1 = 0.0293$, $wR_2 = 0.0701$ (all data) with $S = 1.021$. $2 \cdot \text{CH}_3\text{CN} \cdot 0.5\text{H}_2\text{O}$: $\text{C}_{44}\text{H}_{62}\text{N}_8\text{Cu}_2\text{Cl}_3\text{O}_{14.5}$, $M_r = 1209.51$, monoclinic, space group $\text{P}2_1/n$, $a = 13.7294(9)$, $b = 23.3674(16)$, $c = 16.1515(11) \text{ \AA}$, $\beta = 91.842(6)^\circ$, $V = 5179.1(6) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.551 \text{ Mg m}^{-3}$, $\mu = 3.074 \text{ mm}^{-1}$, $F(000) = 2516$. A total of 15 418 reflections collected, 8092 independent reflections ($R_{\text{int}} = 0.0345$) with 5007 [$I > 2\sigma(I)$] observed data, 704 parameters, $R_1 = 0.0587$, $wR_2 = 0.1517$ [$I > 2\sigma(I)$] and $R_1 = 0.0926$, $wR_2 = 0.1659$ (all data) with $S = 0.915$. CCDC 772755 (**1**) and 772756 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

UV/Vis spectra were recorded on Shimadzu UV-3150 and Cary 50 spectrophotometers. The XPS data were collected on an ESCA Lab250 instrument. Fluorescent spectra were measured using an Edinburgh FLS920 fluorescence spectrometer. ESIMS analysis was performed on a Thermo Finnigan LCQDECA XP HPLC-MSn mass spectrometer. Elemental analyses were determined using an Elementar Vario EL elemental analyzer. The IR spectra were recorded in the 4000–400 cm^{-1} region in the form of KBr pellets using a Bruker EQUINOX 55 spectrometer. The detection of the oxygen molecule generated during the irradiation was performed using an Agilent 7890 A (GC)/5975 (MS) instrument with a DB-5MS column under a He atmosphere.

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