Photosensitizers for H₂ Evolution Based on Charged or Neutral Zn and Sn Porphyrins

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comprehensive photophysical and electrochemical investigation was conducted in order to examine the mechanism of photocatalysis. The results derived from this study establish fundamental criteria with respect to the design and synthesis of porphyrin derivatives for their application as photosensitizers in photoinduced hydrogen evolution.

■ INTRODUCTION

Coupling energy storage with power generation from renewable and abundant energy sources is becoming increasingly urgent and artificial photosynthesis, generating fuel with sunlight, is one potential solution.^{1,2} The use of hydrogen as an energy vector is a technically feasible approach to help satisfy the rapidly growing global energy demand.³ A direct method of generating hydrogen and oxygen via water splitting using solar irradiation is under development. However, important challenges still need to be addressed before a lowcost, highly efficient, and environmentally benign technology is established.^{4,5}

different concentrations of both the sensitizer and the catalyst. A

The photoinduced water splitting and proton reduction processes are mainly driven by systems consisting of three main components: more specifically, a sacrificial electron donor (SED), a light harvesting unit (photosensitizer, PS) and a hydrogen evolution catalyst (HEC).⁶ The appropriate choice of the PS is a crucial parameter in light-driven proton reduction. Complexes consisting of Ru, Ir, Re, or Pt metals are the most widely employed chromophores in such schemes, but the use of noble metals may limit the application of artificial photosynthesis on an industrial scale.^{5,7–15} However, porphyrins or other macrocyclic derivatives based on earth abundant elements are potentially more sustainable sensitizers in photocatalytic systems.^{16–25} The metalation of the porphyrin with, for example, Mg(II), Zn(II), or Sn(IV) ensures good stability and, together with the modification of the periphery with appropriate functional groups, can tune the excited-state properties.²⁶ Accordingly, Zn(II) and Sn(IV) porphyrins have been developed as artificial light-harvesting units for proton reduction, due to their versatility; they absorb solar energy efficiently and possess suitable redox potentials for water splitting.^{27,28} In addition, Sn(IV) porphyrins possess extra stability as the large, highly charged Sn⁴⁺ cation fits perfectly into the porphyrin macrocycle.²⁹ Furthermore, the long-lived triplet excited state of these metalloporphyrins is an important requirement for efficient hydrogen photogeneration systems.³⁰ A number of molecular catalysts have shown remarkable efficiency toward photoinduced hydrogen production. The most noteworthy examples are noble metal-free molecular Coor Ni-based systems, which are able to reduce protons efficiently.^{19,31-34} Cobalt complexes with diglyoxime ligands (cobaloximes) are one well-documented class of catalysts for hydrogen evolution,^{16,35} which are quite stable, can be readily synthesized using straightforward preparation methods and contain an inexpensive transition metal.^{16,35}

Our group has thoroughly studied various photocatalytic hydrogen production systems, including the application of water-soluble Zn(II) and Sn(IV) porphyrins as photosensitizers combined with cobalt catalysts.^{16–18} In this new study, we prepared Zn and Sn porphyrin sensitizers, in order to investigate the influence of the charge of the *para* substituents

Received: June 24, 2019





Figure 1. Molecular structures of cobaloxime catalysts, Zn and Sn porphyrin photosensitizers used for hydrogen evolution.

of meso-phenyl groups of the porphyrin and to explore the impact that these modifications will have on the performance of the system toward photoinduced hydrogen evolution. The porphyrins studied are presented in Figure 1: neutral $(ZnTPyP, ZnTPP-[COOMe]_4, ZnTPP-[PO(OEt)_2]_4, Sn (OH)_2$ TPyP, Sn(Cl₂)TPP-[COOMe]₄, Sn(Cl₂)TPP-[PO-(OEt)₂]₄), positively charged ([ZnTMePyP⁴⁺]Cl₄, [Sn- $(OH)_2TMePyP^{4+}]Cl_4$, and negatively charged (ZnTPP- $[COOH]_4$, $Sn(Cl_2)TPP-[COOH]_4$). The positively charged peripheral substituent chosen was the N-methyl pyridyl group, whereas the carboxylate ion was selected as the negatively charged group. Finally, the neutral substituents chosen for this study were pyridyl, methyl ester, and phosphonate ester. We were able to optimize the photocatalytic activity by tuning both the pH of the buffer solution as well as the concentration of the PS and the HER catalyst. Photophysical and electrochemical measurements were applied to determine whether there is a pattern in which the charged or neutral porphyrins are effective as photosensitizers in photocatalytic H₂ production.

RESULTS AND DISCUSSION

Synthesis. Ten zinc and tin porphyrin derivatives and two cobaloximes (Figure 1) were synthesized, and their performance toward photocatalytic hydrogen evolution was evaluated. The preparation of all meso-substituted porphyrins was based on typical Adler-Longo conditions, namely, the condensation of pyrrole with the corresponding aldehydes in propionic acid under reflux conditions. The porphyrin derivatives H₂TPyP, H_2TPP -[COOMe]₄, and H_2TPP -[PO(OEt)₂]₄ were metalated using $Zn(CH_3COO)_2 \cdot 2H_2O$ yielding the corresponding ZnTPyP, ZnTPP-[COOMe]₄, and ZnTPP-[PO(OEt)₂]₄ de-rivatives, respectively.³⁶⁻³⁹ For the metalation of H_2 TPyP, H₂TPP-[COOH]₄, H₂TPP-[COOMe]₄, and H₂TPP-[PO- $(OEt)_2]_4$ with tin, each porphyrin derivative was refluxed in pyridine using SnCl₂ to afford the metalated porphyrins $\dot{Sn}(Cl_2)TPyP$, $Sn(Cl_2)TPP$ -[COOH]₄, $Sn(Cl_2)TPP$ -[COOMe]₄, $\dot{Sn}(Cl_2)TPP$ -[PO(OEt)₂]₄ (Figure S1). The dichloro tin(IV) porphyrin $Sn(Cl_2)TPyP$ was then treated with K_2CO_3 to afford the dihydroxo tin(IV) porphyrin $Sn(OH)_2TPyP$, in order to increase the solubility of this derivative in aqueous solution. The positively charged porphyrins [ZnTMePyP⁴⁺]Cl₄ and [Sn(OH)₂TMePyP⁴⁺]Cl₄ were synthesized by methylation of the N atoms on pyridyl groups of ZnTPyP and Sn(OH)₂TPyP, respectively. In addition, basic hydrolysis of the ester groups converted the neutral porphyrin ZnTPP-[COOMe]₄ to the negatively charged porphyrin ZnTPP-[COOH]₄.

All compounds were fully characterized by NMR spectroscopy and MALDI-TOF mass spectrometry while the ¹H NMR of H₂TPP-[PO(OEt)₂]₄ is depicted in Figure S3. In addition, the metalation of H₂TPP-[PO(OEt)₂]₄ with tin was confirmed via UV–visible absorption spectroscopy as shown in Figure S4.

X-ray Crystallography. Single-crystals of porphyrin Sn- $(Cl_2)TPP$ - $[COOMe]_4$, suitable for X-ray crystallographic analysis, were obtained by slow evaporation of a CH_2Cl_2/n -hexane solution, over a period of 2 weeks. Details of the crystal data and structure refinement parameters are shown in Table S1. A drawing of the molecular structure of the compound is shown in Figure 2, while selected bond distances and angles



Figure 2. ORTEP view of molecular structure of $Sn(Cl_2)TPP-[COOMe]_4$ with thermal ellipsoids drawn at the 35% probability level. Hydrogen atoms are omitted for clarity.

are listed in Table S2. Porphyrin $Sn(Cl_2)TPP$ -[COOMe]₄ was crystallized in the triclinic space group $P\overline{1}$ in the form $Sn(Cl_2)TPP$ -[COOMe]₄·2CH₂Cl₂. It consists of a central Sn atom coordinated by four pyrrole N atoms that form a planar ring and two Cl atoms at perpendicular positions with respect to the plane of the macrocyclic ring. The metal atom lies on a crystallographic inversion center, and it has almost ideal octahedral coordination geometry. This results in essentially identical Sn–N(pyrrole) bond lengths (2.080(4) and 2.081(4) Å) and Sn–Cl bond lengths (2.4286(15) Å). Bond angles around the metal center are very close to the ideal values of an octahedron (e.g., N1–Sn1–N2 = 90.00(14)°, N1–Sn1–Cl1 = 90.25(12)°, and Cl1–Sn1–Cl1a = 180.0°). All other bond lengths and angles fall within the usual ranges. The 4-methyl-



Figure 3. UV–visible absorption spectra of the (A) Zn and (B) Sn porphyrins dissolved in a 1:1 CH₃CN/H₂O, 5% (v/v) TEOA, pH = 7 solution. In the case of TPyP and [COOMe] derivatives, a few drops of THF were used for absolute solubility.



Figure 4. (A) Emission spectra of tin porphyrins in 1:1 CH₃CN/H₂O. Black: Sn(OH)₂TPP ($\lambda_{ex} = 417 \text{ nm}$). Red: [Sn(OH)₂TMePyP⁴⁺]Cl₄ ($\lambda_{ex} = 422 \text{ nm}$). Blue: Sn(Cl₂)TPP-[COOH]₄ ($\lambda_{ex} = 421 \text{ nm}$). Green: Sn(Cl₂)TPP-[COOMe]₄ ($\lambda_{ex} = 425 \text{ nm}$). Violet: Sn(Cl₂)TPP-[PO(OEt)₂]₄ ($\lambda_{ex} = 424 \text{ nm}$). (B) Emission spectra of zinc porphyrins in 1:1 CH₃CN/H₂O. Black: SnTPyP ($\lambda_{ex} = 418 \text{ nm}$). Red: [ZnTMePyP⁴⁺]Cl₄ ($\lambda_{ex} = 438 \text{ nm}$). Blue: ZnTPP-[COOH]₄ ($\lambda_{ex} = 421 \text{ nm}$). Green: ZnTPP-[COOMe]₄ ($\lambda_{ex} = 423 \text{ nm}$). Violet: ZnTPP-[PO(OEt)₂]₄ ($\lambda_{ex} = 424 \text{ nm}$).

benzoate groups attached to the four meso positions at the periphery of the porphyrin macrocycle were found to be in a tilted orientation with respect to the porphyrin framework, making dihedral angles of $\sim 69^{\circ}$ and $\sim 115^{\circ}$.

Absorption and Emission Properties. The photophysical properties of all dyes were investigated initially through steady state absorption and emission studies. The UV–visible absorption measurements were performed in 1:1 CH_3CN/H_2O solutions, and their normalized spectra are depicted in Figure 3. The spectra of both zinc and tin porphyrins showed the characteristic absorption features of metalated porphyrin macrocycles with two Q bands lying between 550 and 650 nm and one broad peak around 415–425 nm, which corresponds to the Soret band.

Likewise, the emission properties of all Sn and Zn porphyrins were characteristic of metalloporphyrins.²⁶ Two emission bands were observed at approximately 600 and 660 nm in each case (Figure 4) following excitation at the corresponding Soret band of each porphyrin. The small Stokes shift between the peak of the absorption band at lower energy and the peak of the emission band at higher energy confirms the rigidity of these systems and minimal molecular structure

distortions during the absorption and emission processes. The absorption and emission data regarding all porphyrin derivatives are summarized in Table 1.^{18,36–43}

Finally, from the spectroscopic data recorded in 1:1 CH_3CN/H_2O solution, the energy for the zero-zero

Table 1. Absorption	and	Emission	Data	of	Zinc	and	Tin
Porphyrins							

compound	$\lambda_{\text{Soret}}/\text{nm}^a$	$\lambda_{\rm Q}/{\rm nm}^a$	$\lambda_{\rm em}/{\rm nm}^a$
Sn(OH) ₂ TPyP	417	554/594	597/650
[Sn(OH) ₂ TMePyP ⁴⁺]Cl ₄	422	555/595	606/657
$Sn(Cl_2)TPP-[COOH]_4$	421	556/596	602/657
$Sn(Cl_2)TPP-[COOMe]_4$	425	560/600	604/660
$Sn(Cl_2)TPP-[PO(OEt)_2]_4$	424	560/600	605/659
ZnTPyP	418	555/595	603/656
[ZnTMePyP ⁴⁺]Cl ₄	438	565/608	627/667
ZnTPP-[COOH] ₄	421	558/597	608/659
ZnTPP-[COOMe] ₄	423	557/597	607/657
$ZnTPP-[PO(OEt)_2]_4$	424	558/598	608/657

^{*a*}Concentration: 5×10^{-5} M in 1:1 CH₃CN/H₂O.

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Table 2. Estimated	d Energies and	Redox Potentia	ls for the Sing	let and Triple	t Excited States	of Zinc and	Tin Porphyrins
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	$E_{00} ({}^{1}\mathrm{Ps}^{*}) / \mathrm{eV}$	$\frac{E_{00} ({}^{3}\text{Ps}^{*})}{/\text{eV}}$	<i>E</i> (Ps/ Ps ⁻)	E (Ps ⁺ / Ps)	$E' (Ps^+/^1Ps^*) /V$	<i>E'</i> (¹ Ps*/Ps ⁻) /V	$E' (Ps^+/^3Ps^*) /V$	<i>E'</i> (³ Ps*/Ps ⁻) /V
ZnTPyP ^{a37}	2.07	1.59 ³⁶	-0.65	1.04	-1.03	1.42	-0.55	0.94
[ZnTMePyP ⁴⁺]Cl ₄	2.01	1.63 ³⁶	-0.79	1.28	-0.73	1.22	-0.35	0.84
ZnTPP-[COOH] ₄	2.06	1.60^{36}	-1.17	1.10	-0.96	0.89	-0.50	0.43
ZnTPP-[COOMe] ₄	2.06	1.63 ⁶⁶	-1.16	1.09	-0.97	0.90	-0.54	0.47
$ZnTPP-[PO(OEt)_2]_4$	2.06	1.66 ⁶⁶	-1.32	1.14	-0.92	0.74	-0.52	0.34
Sn(OH) ₂ TPyP	2.08	1.66 ⁶⁶	-0.44	1.38	-0.70	1.64	-0.28	1.22
$[Sn(OH)_2TMePyP^{4+}]Cl_4^{a,42}$	2.06	1.63 ⁶⁶	-0.3	1.69	-0.37	1.76	0.06	1.33
$Sn(Cl_2)TPP-[COOH]_4^{41}$	2.07	1.63 ⁴²	-0.73	1.42	-0.65	1.34	-0.21	0.90
$Sn(Cl_2)TPP-[COOMe]_4$	2.06	1.66 ⁶⁶	-0.36	1.29	-0.77	1.70	-0.37	1.30
$Sn(Cl_2)TPP-PO(OEt)_2]_4$	2.06	1.65	-0.38	1.32	-0.74	1.68	-0.33	1.27

^{*a*}Reported vs Fc/Fc⁺ (+630 mV conversion to NHE). Data measured vs Fc/Fc⁺ in DMF converted to NHE by adding 720 mV.^{52,53} E_{00} (¹Ps⁺) is the zero–zero energy transition of the singlet excited state in eV estimated from the intercept of the absorption and emission spectra. E_{00} (³Ps⁺) is the zero–zero energy transition of the triplet excited state in eV, which was found in the literature for every porphyrin. First excited state oxidation potential (E' (Ps⁺/Ps⁺)) and reduction potential (E' (Ps⁺/Ps⁻)) of singlet and triplet states were calculated according to E'(Ps⁺/Ps⁺) = $E_{ox} - E_{00}$ and E' (Ps⁺/Ps⁻) = $E_{red} + E_{00}$.

electronic transition, E_{00} , between the ground and singlet excited state was estimated, which corresponds to the energy separation between the HOMO and LUMO (see Table 2).

Hydrogen Evolution. In our previously published works, the combination of water-soluble porphyrin photosensitizers, $Sn(OH)_2TPyP$ and $[ZnTMePyP^{4+}]Cl_4$, with a cobaloxime catalyst and triethanolamine (TEOA) as a sacrificial electron donor, exhibited high photocatalytic activity toward hydrogen evolution.^{16–18} These promising results inspired us to examine neutral (ZnTPyP, ZnTPP-[COOMe]₄, ZnTPP-[PO(OEt)₂]₄, Sn(OH)₂TPyP, Sn(Cl₂)TPP-[COOMe]₄, and Sn(Cl₂)TPP- $[PO(OEt)_2]_4$, positively charged $([ZnTMePyP^{4+}]Cl_4$ and [Sn(OH)₂TMePyP⁴⁺]Cl₄), and negatively charged (ZnTPP- $[COOH]_4$ and $Sn(Cl_2)TPP-[COOH]_4$ zinc and tin mesosubstituted porphyrins as photosensitizers. It is worth mentioning that $Sn(Cl_2)TPP$ -[COOH]₄ is neutral after the synthesis conditions, but in the mixture in which the photocatalytic experiments were conducted it is negatively charged, since the peripheral carboxylate groups have a pK_a of ca. 6 and are deprotonated (COO⁻) at pH 7⁴⁴ The scope of this study was to estimate the impact of the chromophore's charge on the H₂ production efficiency. We combined the photosensitizers with two cobaloxime-based catalysts (CoPy and CoNMeim) and used the following experimental conditions: 4×10^{-5} M of porphyrin and 4.9×10^{-4} M of the catalyst in a 1:1 CH₃CN/H₂O solvent mixture of 5% (v/v) TEOA at pH 6, 7, and 8. We have no indication of catalyst decomposition or protonation of the axial ligand at these pH values.

The neutral zinc porphyrins ZnTPyP, ZnTPP-[COOMe]₄, and ZnTPP-[PO(OEt)₂]₄; the positively charged tin chromophore [Sn(OH)₂TMePyP⁴⁺]Cl₄; and negatively charged ZnTPP-[COOH]₄ and Sn(Cl₂)TPP-[COOH]₄ showed no activity with the two cobaloxime catalysts after 24 h of irradiation. However, the positively charged zinc porphyrin [ZnTMePyP⁴⁺]Cl₄ and the neutral tin porphyrins Sn-(OH)₂TPyP, Sn(Cl₂)TPP-[COOMe]₄, and Sn(Cl₂)TPP-[PO-(OEt)₂]₄ were photocatalytically active when combined with CoPy. The calculated turnover numbers (TONs) with respect to the photosensitizer were 320, ~10, 60, and 24 for [ZnTMePyP⁴⁺]Cl₄, Sn(OH)₂TPyP, Sn(Cl₂)TPP-[COOMe]₄, and Sn(Cl₂)TPP-[PO(OEt)₂]₄, respectively. Under the same experimental conditions, CoNMeim was used instead of CoPy, and the TONs of the photocatalytic H₂ production were significantly increased (Figure 5). The TON was 1135 for [ZnTMePyP⁴⁺]Cl₄, 303 for Sn(OH)₂TPyP, 128 for Sn(Cl₂)-



Figure 5. Plot of hydrogen production upon irradiation of solutions 1:1 CH₃CN/H₂O containing Sn(Cl₂)TPP-[COOMe]₄ or Sn(Cl₂)-TPP-[PO(OEt)₂]₄ (4 × 10⁻⁵ M), CoPy or CoNMeim (4.9 × 10⁻⁴ M), and TEOA [5% (v/v)] at pH 7.

TPP-[COOMe]₄, and 48 for Sn(Cl₂)TPP-[PO(OEt)₂]₄. Table S3 lists the optimum photocatalytic conditions for all porphyrin photosensitizers. Overall, the positively charged zinc porphyrin ([ZnTMePyP⁴⁺]Cl₄) and the three neutral tin porphyrins (Sn(OH)₂TPyP, Sn(Cl₂)TPP-[COOMe]₄, and Sn(Cl₂)TPP-[PO(OEt)₂]₄) were active toward H₂ evolution.

Additional studies have shown that light-driven hydrogen generation is strongly influenced by the proton concentration (pH). Thus, experiments with different pH values were carried out, and only some traces of hydrogen were obtained at pH 6 and 8. These findings are consistent with results for related photocatalytic systems^{16–18} in which the optimum pH value was close to the pK_a value of the sacrificial electron donor, which is 7.9 for TEOA in aqueous solution. However, in the solution in which we performed the photocatalytic experiments (1:1 CH₃CN:H₂O), the pK_a value of TEOA is 7.⁶ The

optimum photocatalytic pH value for our systems was 7, which is consistent with this.

The performance of the photocatalytic hydrogen evolution system also depends on the catalyst and photosensitizer concentrations. In our previous work, Sn(OH)₂TPyP drove photocatalysis when combined with CoPy (TON ~ 10).¹⁸ We observed that hydrogen production was increased when the concentration of both the catalyst and the photosensitizer were increased (from 4.9×10^{-4} M to 9.8×10^{-4} M and 4×10^{-5} M to 8×10^{-5} M, respectively). Under 100 h of light irradiation, the above-mentioned photocatalytic system reached a maximum TON of 150. This increased hydrogen production is mainly attributed to the high stability of CoPy and in addition to the competition between the two main catalytic processes (reductive and oxidative). When CoNMeim was used as the catalyst, the TON for photocatalytic hydrogen evolution increased significantly (TON = 303) using concentrations of 4×10^{-5} M for Sn(OH)₂TPyP and 4.9 × 10⁻⁴ M for CoNMeim. TEOA was used as the sacrificial electron donor [5% (v/v)] and the photocatalytic activity lasted for 96 h. When the concentration of both the catalyst and the photosensitizer were increased (red line, Figure 6),



Figure 6. Plot of hydrogen production upon irradiation of solutions 1:1 CH_3CN/H_2O containing $Sn(OH)_2TPyP$ and CoNMeim in different concentrations and TEOA [5% (v/v)] at pH 7.

hydrogen production decreased considerably. As illustrated in Figure 6, when the concentration of $Sn(OH)_2TPyP$ was increased to 8×10^{-5} M and CoNMeim at 9.8×10^{-4} M, we observed a maximum TON of 186 after 96 h of irradiation.

Electrochemical Properties. The redox potentials were significantly modified across the series of compounds examined here. Table 2 reports the redox potentials for the porphyrins in DMF solution, which were determined by cyclic voltammetry. In all cases, $^{36-42,45,46}$ the oxidation and reduction peaks were electrochemically reversible or quasi-reversible, allowing the formal redox potentials in the chosen supporting electrolyte to be determined. The first ground state oxidation potential $(E(Ps^+/Ps))$ and first ground state reduction potentials of the triplet and singlet states (Table 2). The redox potentials of CoNMeim in CH₃CN/H₂O (1:1) were recorded by cyclic voltammetry (Figure S5), where we were able to detect two

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processes, in agreement with Panagiotopoulos et al.¹⁷ The first one (-0.20 V vs NHE) can be assigned to the Co^{II}/Co^{III} process, while the Co^{I/II} wave lies at -0.55 V vs NHE. The peaks were better resolved by recording differential pulse voltammetry (Figure S6) in the same solvent.^{47–51} Similar to CoNMeim, the CoPy catalyst presents two reduction waves. The first one, which is attributed to the Co^{II/III} process, can be observed at -0.43 V vs NHE in CH₃CN or at -0.37 V vs NHE in DMF. The second reduction is attributed to the Co^{II/II} wave and lies at -0.88 V vs NHE in CH₃CN or at -0.76 V vs NHE in DMF.⁵¹

Transient Absorption Measurements. Laser flash photolysis transient absorption measurements were performed to investigate the light-induced charge transfer dynamics of each of the porphyrin dyes in $1:1 \text{ CH}_3\text{CN/H}_2\text{O}$ solution, to check for consistency with the hydrogen evolution measurements, both in the presence and in the absence of TEOA and the cobalt catalyst CoNMeim. The spectra are provided in Figures S7 to Figure S15 in the SI. For each porphyrin, the singlet excited state (S1) decayed due to intersystem crossing to the lowest triplet state (T1), within the 4 ns laser pulse (eq 2).

$$Ps + h\nu \to {}^{1}Ps^{*} \tag{1}$$

$$Ps^* \to {}^3Ps^* \tag{2}$$

For each porphyrin, the spectral features observed at early delay times were characteristic of a T1 excited state, with lifetime $\tau({}^{3}Ps^{*})$ containing a broad positive band, with a maximum at around 450–500 nm, which extended to about 700 nm, and an overlapping negative feature at around 600 nm, due to the bleach of the Q bands. The oxidized state of the zinc tetraphenyl porphyrins is weakly absorbing in the visible region, as confirmed by recording the absorption spectrum of ZnTPyP upon chemical oxidation with NOBF₄ (see Figure S16). As it was difficult to distinguish between the differential absorption spectrum of ${}^{3}ZnPs^{*}$ and $ZnPs^{\bullet+}$, τ for the formation of the oxidized state, after the addition of CoNMeim, was inferred from the quenching of ${}^{3}ZnPs^{*}$ ($\tau({}^{*3}Ps + CoNMeim)$).

Previous studies using nanosecond resolution transient absorption spectroscopy showed, first, that [ZnTMePyP⁴⁺]Cl₄ decomposes on excitation in the presence of TEOA, implying that probably the TEOA generates the chlorin.^{16,27} Second, it was reported that the addition of the cobalt catalyst oxidatively quenches the porphyrin T1 state (eq 3), leading to a decrease in the lifetime of *[ZnTMePyP⁴⁺]Cl₄, from τ (*- $[ZnTMePyP^{4+}]Cl_4) > 100 \ \mu s \text{ to } \tau(*[ZnTMePyP^{4+}]Cl_4) \sim 2$ μ s.¹⁶ This is consistent with the participation of a porphyrin excited state in the hydrogen production pathway B in Scheme 1. Our experiments were in agreement with this analysis, and we found that the cobalt catalyst quenched *[ZnTMePyP⁴⁺]-Cl₄ (see Table 3). Under a nitrogen purged atmosphere, the amplitude weighted lifetime of *[ZnTMePyP⁴⁺]Cl₄ decreased more than 10-fold from $\tau(*^{3}[ZnTMePyP^{4+}]Cl_{4}) = 85 \ \mu s$ to $\tau(*^{3}[\text{ZnTMePyP}^{4+}]\text{Cl}_{4} + \text{CoNMeim}) = 4 \ \mu\text{s}$ both in the absence and presence of TEOA.

For zinc porphyrins $ZnTPP-[PO(OEt)_2]_4$ (Figure S11b), ZnTPP-[COOMe]₄ (Figure S10b), ZnTPP-[COOH]₄ (Figure S12b), and ZnTPyP (Figure S13b), the shape of the transient spectra of *ZnPs in the presence and in the absence of TEOA was unchanged, both spectra contain transient bands around 460 nm, and the lifetimes of these bands were similar to those Scheme 1. Schematic Representation of the Two Main Mechanisms Leading to CoNMeim Reduction and Hydrogen Generation^{*a*}



"For clarity reasons, the following abbreviations are used: Ps = zinc/ tin porphyrins and Cat = CoNMeim.

obtained in the presence of ZnPs^{*} only. This was expected as, from Table 2, it can be seen that the formation of ZnPs^{•–} from *³ZnPs is thermodynamically unfavorable for these porphyrins. A slight increase in lifetime was observed in some cases, which can be attributed to the coordination of ZnPs with TEOA.^{24,48,49} The addition of CoNMeim to these zinc porphyrins had a slight effect (ZnTPP-[PO(OEt)₂]₄, ZnTPyP, and ZnTPP-[COOH]₄) or no effect (ZnTPP-[COOMe]₄) on τ (*³ZnPs) (Table 3). This demonstrates that, in these cases, a mild reaction with the catalyst occurred.

CoNMeim was observed to quench the ³Ps* of Sn(Cl₂)-TPP-[COOMe]₄ (Figure S8) and Sn(OH)₂TPyP (Figure S9), leading to shorter lifetimes in the presence of the catalyst (Table 3). SnPs^{•+}, formed after the addition of the catalyst, was difficult to distinguish from ³SnPs* (see Figure S16), so the formation of an oxidized state was estimated from the difference in ³SnPs* lifetime after CoNMeim was added. For Sn(Cl₂)TPP-[COOMe]₄ in the presence of CoNMeim, two lifetimes at 450 nm were detected, the shorter component is associated with the quenching of the excited state, τ (*Sn-(Cl₂)TPP-[COOMe]₄ + CoNMeim) = 2 μ s, and the longer component is the lifetime of the oxidized product, τ (Sn(Cl₂)-TPP-[COOMe]₄^{•+})₃ = 10 μ s. For these porphyrins, it was possible to observe the reduced state (SnPs^{•-}), formed in the presence of TEOA (eq 4). For tin porphyrins, the transient spectrum of SnPs^{•-} contained a peak at 450 nm, which was blue-shifted with respect to ³SnPs^{*}. For both Sn(Cl₂)TPP-[COOMe]₄ and Sn(OH)₂TPyP in the presence of TEOA (Figures S8b and S9b), the transient absorption at 450 nm decayed biexponentially. The shorter lifetime with respect to $\tau(*Sn(OH)_2TPyP) = 78 \ \mu s$ and $\tau(*Sn(Cl_2)TPP-[COOMe]_4)$ = 70 μs has been assigned to triplet state, which was slightly quenched, and the longer lived species, to the reduced state, $\tau(Sn(OH)_2TPyP^{\bullet-}) = 200 \ \mu s$ and $\tau(Sn(Cl_2)TPP-[COOMe]_4^{\bullet-}) = 150 \ \mu s$.

Both Sn(Cl₂)TPP-[COOH]₄ and [Sn(OH)₂TMePyP⁴⁺]Cl₄ were found to be pretty unstable in the presence of TEOA, forming the chlorin. At the same time, $*Sn(Cl_2)TPP$ -[COOH]₄ and $*[Sn(OH)_2TMePyP^{4+}]Cl_4$ were not quenched in the presence of CoNMeim ($\tau(*Sn(Cl_2)TPP$ -[COOH]₄ + CoNMeim) = 180 μs , $\tau(*[Sn(OH)_2TMePyP^{4+}]Cl_4$ + CoNMeim) = 192 μs). Transient absorption studies were not carried out for Sn(Cl₂)TPP-[PO(OEt)₂]₄, as it was not sufficiently soluble in the solvents employed.

DISCUSSION

The reduction of Co^{III} to Co^{II}, the first step of the catalytic cycle, may occur either by direct electron transfer from the porphyrin excited state, forming the oxidized porphyrin Ps^{•+}, with a lifetime τ (Ps^{•+}) (eq 3), or by reductive quenching of the excited state by TEOA (eq 4), forming the reduced porphyrin, Ps^{•-}, with a lifetime τ (Ps^{•-}), followed by electron transfer between Ps^{•-} and Co^{III} (eq 6). The byproduct TEOA⁺ is a very strong reductant and can transfer its electron to a further excited or ground state Ps.⁵⁴

$$Ps^* + Co^{III} \to Ps^{\bullet +} + Co^{II}$$
(3)

$$Ps^* + TEOA \to Ps^{\bullet-} + TEOA^+$$
(4)

$$Ps^{\bullet+} + TEOA \rightarrow Ps + TEOA^{+}$$
 (5)

$$Ps^{\bullet -} + Co^{III} \to Ps + Co^{II}$$
(6)

$$\mathrm{Co}^{\mathrm{II}} + 2\mathrm{e}^{-} + 2\mathrm{H}^{+} \to \mathrm{Co}^{\mathrm{III}} + \mathrm{H}_{2} \tag{7}$$

The redox potential of TEOA $(1.07 \text{ V vs NHE})^{55}$ is appropriate to reductively quench the singlet excited state

	Table 3. J	Lifetime $ au$	of Zinc and	Tin Porphyri	ns Alone and	l in the Presence	e of CoNMeim	and/or TEOA
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photosensitizers	$\tau(^{*3}\text{Ps}) \ (\mu s)^a$	τ (Ps + CoNMeim) (μ s) ^b	τ (Ps + TEOA) (μ s) ^c	$\tau (Ps + TEOA + CoNMeim) $ $(\mu s)^d$
ZnTPyP	150 ± 5	135 ± 6	148 ± 4	134 ± 6
Sn(OH) ₂ TPyP	78 ± 6	7 ± 2	24 ± 4 (τ_1), 200 ± 8 (τ_2 ; A ₁ = 0.3, A ₂ = 0.7)	10 ± 4
[ZnTMePyP ⁴⁺]Cl ₄	85 ± 3	4 ± 1	е	4 ± 0.5
[Sn(OH) ₂ TMePyP ⁴⁺]Cl ₄	190 ± 9	192 ± 5	е	е
ZnTPP-[COOH] ₄	278 ± 6	264 ± 5	280 ± 4	262 ± 9
$Sn(Cl_2)TPP-[COOH]_4$	182 ± 7	175 ± 5	е	е
ZnTPP-[COOMe] ₄	149 ± 4	148 ± 6	150 ± 5	146 ± 9
$Sn(Cl_2)TPP-[COOMe]_4$	70 ± 4	$2 \pm 0.2, 10 \pm 4$ ($A_1 = 0.65, A_2 = 0.35$)	$20 \pm 2 \ (\tau_1), \ 150 \pm 8 (\tau_2; \ A_1 = 0.2, \ A_2 = 0.8)$	7 ± 3
$ZnTPP-[PO(OEt)_2]_4$	70 ± 5	57 ± 6	69 ± 6	60 ± 6
$Sn(Cl_2)TPP-[PO(OEt)_2]_4$	f	f	f	f

 ${}^{a}5 \times 10^{-5}$ M porphyrin in 1:1 CH₃CN/H₂O. ${}^{b}5 \times 10^{-5}$ M porphyrin + 10 equiv CoNMeim in CH₃CN/H₂O (1:1). ${}^{c}5 \times 10^{-5}$ M porphyrin + 5% TEOA in 1:1 CH₃CN/H₂O. ${}^{d}5 \times 10^{-5}$ M porphyrin + 5% TEOA + 10 equiv CoNMeim in 1:1 CH₃CN/H₂O. c Decomposes in the presence of TEOA and no reaction with CoNMeim. f Insufficiently soluble in the solvent employed (CH₃CN/H₂O 1:1).

https://dx.doi.org/10.1021/acs.inorgchem.9b01838 Inorg. Chem. XXXX, XXX, XXX–XXX (¹Ps*) of ZnTPyP, [ZnTMePyP⁴⁺]Cl₄, and all of the tin porphyrins ($E'(^{1}Ps^{*}/Ps^{-}) > 1.07$ V). It is also thermodynamically feasible for the ¹Ps* of all the porphyrins investigated in this study (except [Sn(OH)₂TMePyP⁴⁺]Cl₄) to be oxidatively quenched by both the Co^{III} and Co^{II} species. It is unlikely that quenching occurs from ¹Ps* in these cases, since the lifetimes of the porphyrins in the presence of the catalyst and sacrificial electron donor are much longer than the lifetime of the singlet excited state of the porphyrin, which is only a couple of nanoseconds. Furthermore, only a few porphyrins were quenched, either oxidatively or reductively, despite there being sufficient driving force for the electron transfer reaction. Instead, it is more likely that the reactions take place from the less energetic ³Ps*.

The redox potentials of the triplet excited state of the ZnPs are insufficient to oxidize TEOA efficiently, whereas it is thermodynamically favorable for most of the ³SnPs* (except $Sn(Cl_2)TPP-[COOH]_4$) to be quenched by TEOA. If reductive quenching occurred before electron transfer to the catalyst (pathway A), it would be thermodynamically possible for all the porphyrins to reduce the catalyst from Co^{III} to Co^{II} . $E'(Ps/Ps^-)$ is more negative than $E'(Co^{II}/Co^{I})$ for all the zinc porphyrins and $Sn(Cl_2)TPP-[COOH]_4$. Therefore, if the first step is the reduction of the ³SnPs* by the sacrificial electron donor, we would not expect [ZnTMePyP⁴⁺]Cl₄ or the tin porphyrins to drive the photocatalysis, which is not consistent with the observations described above.

The ³Ps* oxidation potential is sufficiently negative for all of the zinc porphyrins to reduce CoNMeim from Co^{III} to Co^{II}. From the tin porphyrins, however, only Sn(OH)₂TPyP, $Sn(Cl_2)TPP-[COOMe]_4$, and $Sn(Cl_2)TPP-[PO(OEt)_2]_4$ have sufficient reducing power in the long-lived ³Ps* to reduce the Co^{III} , and the ${}^3\text{Ps}^*$ oxidation potential is not sufficiently negative for any of the porphyrins to reduce CoNMeim from Co^{II} to Co^{I} . $E'(Ps^+/Ps)$ is very close to $E'(TEOA^+/TEOA)$ for four of the zinc porphyrins, which means that should oxidative quenching by the catalyst occur first, these porphyrins would not be efficiently rereduced. $E'(Ps^+/Ps)$ for $[ZnTMePyP^{4+}]Cl_4$ and all the tin porphyrins lies more positive than $E'(\text{TEOA}^+/$ TEOA), so it is likely that these would be rereduced by TEOA following oxidative quenching by CoNMeim. This pathway is consistent with the photocatalysis results. The porphyrins which generated hydrogen were all, except for ZnTPP-[COOMe]₄, observed to be oxidatively quenched by CoNMeim in the transient absorption spectroscopy experiments. For the zinc porphyrins which could be oxidatively quenched by the catalyst, only $[ZnTMePyP^{4+}]Cl_4$ can be rereduced by TEOA, which is consistent with this being the only zinc porphyrin to drive photocatalysis in our experiments. The lifetimes for the porphyrin in the presence of catalyst and TEOA were similar to the lifetimes for the porphyrin and catalyst only, which is also consistent with pathway B. The advantage of pathway B over pathway A (which is thermodynamically feasible for Sn(Cl₂)TPP-[COOMe]₄, Sn-(OH)₂TPyP, and [ZnTMePyP⁴⁺]Cl₄ also for Sn(Cl₂)TPP- $[PO(OEt)_2]_4$ is that the reduced porphyrin is not present in large concentrations, which could lead to the formation of the chlorin and subsequent decomposition of the PS. The subsequent step in the catalytic reaction, which we have not investigated here, is the second reduction of the catalyst. The ³Ps* oxidation potential is not sufficiently negative to reduce the catalyst to Co¹. The oxidation potential of the TEOAderived alkyl radical/iminium cation is ca. -790 mV vs NHE

in CH_3CN ,⁵⁶ which is sufficient to provide the second electron to the CoNMeim catalyst.

CONCLUSIONS

In conclusion, the synthesis of zinc and tin porphyrins as light harvesting units and cobaloxime complexes as catalysts toward light-driven hydrogen evolution is presented. Moreover, the influence of the charge of the *para*-substituents of meso-phenyl groups of the porphyrin in photoinduced performance is examined. The thorough studies performed in this work illustrated that the positively charged zinc porphyrin [ZnTMePyP⁴⁺]Cl₄ and the neutral tin porphyrin derivatives Sn(OH)₂TPyP, Sn(Cl₂)TPP-[COOMe]₄, and Sn(Cl₂)TPP- $[PO(OEt)_2]_4$ are photocatalitically active, reaching maximum TONs of 1135, 303, 128, and 48, respectively. Furthermore, photophysical and electrochemical investigation was conducted in order to determine the mechanism of the photocatalytic hydrogen production using charged or neutral porphyrins as light harvesting units. Overall, we have shown that the photocatalysis is most likely to proceed via oxidative quenching of the porphyrin sensitizer, leading to the reduced catalyst. The photosensitizer is regenerated subsequently by the oxidation of TEOA. Careful examination over the ground and excited state redox properties enabled the appropriate functionalization of the porphyrin periphery, allowing the finetuning of the charge-transfer dynamics and consequently the photocatalytic activity.

EXPERIMENTAL SECTION

General. Reagents and solvents were purchased at reagent grade from the usual commercial sources and used without further purification, unless otherwise stated. Thin layer chromatography was performed on silica gel 60 F_{254} plates, while chromatographic separations were carried out using silica gel 60, SDS, and 70–230 mesh ASTM.

¹H NMR and ¹³C NMR spectra were recorded on Bruker AMX-500 MHz and Bruker DPX-300 MHz spectrometers, as solutions in deuterated solvents by using the solvent peak as the internal standard. High-resolution mass spectra were recorded on a Bruker ultrafleXtreme MALDI-TOF/TOF spectrometer, using *trans*-2-[3-(4-*tert*butylphenyl)-2-methyl-2-propenylidene]malononitrile as a matrix.

X-ray Crystallography. A single-crystal of compound Sn(Cl₂)-TPP-[COOMe]₄·2CH₂Cl₂, suitable for X-ray crystallographic analysis, was protected with paratone-N and mounted for data collection on a STOE IPDS II diffractometer equipped with a Mo K α sealedtube X-ray source ($\lambda = 0.71073$ Å, graphite monochromated) and an image plate detector. Data collection, data reduction, integration, and cell parameter determination were carried out using the STOE X-AREA package software,⁵⁷ while a numerical absorption correction was also applied using the STOE X-RED and X-SHAPE software packages.^{58,59} The structure was solved using direct methods, implemented in SHELXS-2014,^{60,61} and refined using SHELXL-2014.⁶² All non-hydrogen atoms were successfully refined using anisotropic displacement parameters. A plot of the molecular structure of the compound was obtained by using the program Mercury.⁶³

Photophysical Measurements. UV-vis absorption spectra were measured on a Shimadzu UV-1700 spectrophotometer using 10-mm-path-length cuvettes.

Nanosecond transient measurements were performed with a custom laser spectrometer comprised of a Brillian Quantel laser with a frequency doubled (532 nm, 330 mJ) or tripled (355 nm, 160 mJ) option and an Applied Photophysics xenon light source including a mod. 720 150 W lamp housing, a mod. 620 power controlled lamp supply, and a mod. 03-102 arc lamp pulser. Laser excitation was provided at 90° with respect to the white light probe beam. Light

transmitted by the sample was focused onto the entrance slit of a SpectraKinetic monochromator (Applied Photophysics). Kinetic traces were processed by means of a Agilent digital oscilloscope. A typical pulse energy of 2 mJ cm⁻² was used.

Electrochemistry. Electrochemical studies were carried out using an IviumStat potentiostat controlled using IviumSoft. Redox potentials were determined using cyclic voltammetry. Electrochemistry was performed under a nitrogen atmosphere, using a three-electrode setup, in a single compartment cell. A platinum disc working electrode, a Pt wire secondary electrode, and a saturated calomel reference electrode were used. The redox potential of the porphyrins was measured with a 1 mM analyte concentration in anhydrous DMF that had been purged with nitrogen, with 0.1 M LiPF₆ supporting electrolyte. The redox potential of CoNMeim was measured under the same conditions but with a 50:50 mixture of water/acetonitrile that had been purged with nitrogen, with 0.1 M LiClO₄ supporting electrolyte. The reference electrodes were calibrated against ferrocene.

Photocatalytic Hydrogen Evolution Experiments. For photoinduced hydrogen evolution, each sample was prepared in a 42 mL glass vial with a silicone septum. Prior to sample preparation, an aqueous solution of TEOA (10 vol %) was adjusted to pH 7 using concentrated HCl. The components were then dissolved in 10 mL of a 1:1 (v/v) mixture of acetonitrile and aqueous TEOA (10%) solution. The mixture was degassed for 10 min using nitrogen at room temperature. Then, the samples were sealed and irradiated with a white LED ring (power of 40 W, color temperature of 6400 K and lumen of 3800 LM, Figure S17). The amounts of hydrogen evolved were determined by gas chromatography (external standard technique) using a Shimadzu GC 2010 plus chromatograph with a TCD detector and a 5 Å molecular sieve column (30 m to 0.53 mm). A total of 100 μ L was taken from the headspace and injected immediately into the GC. In all cases, the reported TON (with respect to the porphyrin) is the average of three independent experiments. Control experiments were performed under the same experimental conditions. We performed various experiments by removing only the catalyst or the photosensitizer from the hydrogen generating system, but we did not detect any H₂ production. In addition, mercury poisoning experiments were performed, in order to examine the possible formation of metallic nanoparticles or colloids during the hydrogen evolution process. In these studies, an excess of mercury (ca. 40 equiv) was added to the hydrogen evolution solutions, but H₂ production was detected at the same levels as in the regular photocalatytic experiments (absence of mercury).

Synthesis. The catalysts CoPy and CoNMeim were prepared according to the literature.¹⁷ In addition, the Zn (ZnTPyP, ZnTPP-[COOMe]₄, ZnTPP-[PO(OEt)₂]₄, [ZnTMePyP⁴⁺]Cl₄, and negatively ZnTPP-[COOH]₄)^{36–39} and the Sn porphyrin derivatives $(Sn(OH)_2TPyP, Sn(Cl_2)TPP-[COOMe]_4, Sn(Cl_2)TPP-[PO(OEt)_2]_4$, $[Sn(OH)_2TMePyP^{4+}]Cl_4$, and $Sn(Cl_2)TPP-[COOH]_4$)^{18,40–43} were synthesized as previously reported.

Diethyl-4-Formylphenylphosphonate. 4-Bromobenzaldehyde (500 mg, 2.70 mmol) was added to a 100 mL two-necked bottom flask. To this solution, dry toluene (4 mL), dry Et₃N (4 mL), and diethylphosphite (0.4 mL, 6 mmol) were added and purged with Ar gas for 2 min, followed by the addition of Pd(PPh₃)₄ (155 mg, 0.135 mmol). The reaction mixture was heated to 90 °C for 24 h under an Ar atmosphere. The reaction mixture was cooled down to room temperature and the solvent was evaporated to dryness under a vacuum, redissolved in CHCl₃ (35 mL), washed with distilled water $(3 \times 50 \text{ mL})$ followed by brine solution (50 mL), and finally dried with Na₂SO₄. The crude product was purified on a silica column chromatograph using CHCl₃/EtOAc (70:30, v/v) as the eluent. After distillation under a vacuum, diethyl-4-formylphenylphosphonate was obtained as a colorless liquid. Yield: 300 mg (47%). ¹H NMR (300 MHz, CDCl₃): δ 10.09 (s, 1H, CHO), 7.98(m, 4H, ph-H), 4.15(m, 4H, $-CH_2$), 1.34(t, J = 7.1 Hz, 6H, $-CH_3$) ppm.⁶

5,10,15,20-Tetrakis(4-diethyl-phosphonate-phenyl) Porphyrin (H₂TPP-[PO(OEt)₂]₄). A solution of diethyl-4-formylphenylphosphonate (280 mg, 1.18 mmol) and pyrrole (0.080 mL, 1.15 mmol) in 10

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mL of propionic acid was refluxed at 150 °C in a flask protected from light for 1.5 h. The reaction mixture was evaporated to dryness and purified by column chromatography on neutral alumina eluting with a mixture of CH₂Cl₂/MeOH (99:1, v/v) to obtain the H₂TPP-[PO(OEt)₂]₄ as a dark purple solid. Yield: 92.4 mg (28%). ¹H NMR (500 MHz, CDCl₃): δ 8.83 (s, 8H, pyr), 8.33 (m, 8H, o-ph), 8.22 (m, 8H, m-ph), 4.38 (m, 16H, -OCH₂), 1.52 (t, *J* = 7.3 Hz, 24H, -CH₃), -2.83 (s, 2H, -NH) ppm. HRMS (MALDI-TOF) *m/z* calcd. for C₆₀H₆₆N₄O₁₂P₄ [M]⁺: 1158.3628. Found: 1158.3633. UV/vis (CH₂Cl₂), λ_{max} nm: 419, 515, 549, 590, 646.^{64,65}

trans-Dichloro[5,10,15,20-tetrakis(4-diethyl-phosphonate-phenyl) Porphyrinato] Tin(IV) $(Sn(Cl_2)TPP-[PO(OEt)_2]_4)$. In a roundbottom flask, porphyrin H₂TPP-[PO(OEt)_2]_4 (188 mg, 0.162 mmol), SnCl₂ (307 mg, 1.62 mmol), and pyridine (30 mL) were added and refluxed for 9 h. The solvent was evaporated to dryness under a vacuum. The solid was dissolved in CH₂Cl₂ and was filtered with Celite to obtain the Sn(Cl₂)TPP-[PO(OEt)_2]_4 as a dark purple solid. Yield: 108 mg (50%). Due to solubility reasons, we were unable to record NMR spectra for Sn(Cl₂)TPP-[PO(OEt)_2]_4. HRMS (MALDI-TOF), m/z calcd. for C₆₀H₆₄Cl₂N₄O₁₂P₄Sn [M - Cl]⁺: 1311.2182. Found: 1311.2165. UV/vis (CH₂Cl₂) λ_{max} nm: 428, 561, 600.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b01838.

Figures S1–S17 and Tables S1–S3 (PDF)

Accession Codes

CCDC 1935835 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

E.A.G., G.C., J.K., and E.B. thank The North East Centre for Energy Materials EP/R021503/1. The raw data for the transient spectroscopy and electrochemistry are available free of charge at https://doi.org/10.25405/data.ncl.11470392.v1. This research was funded by the General Secretariat for Research and Technology (GSRT) and Hellenic Foundation for Research and Innovation (HFRI; project code: 508). This research has also been cofinanced by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship, and Innovation, under the call RESEARCH-CREATE-INNOVATE (project code: T1EDK-01504). In addition, this research has been cofinanced by the European Union and Greek national funds through the Regional Operational Program "Crete 2014-2020," project code OPS: 5029187. Moreover, the European Commission's Seventh Framework Program (FP7/2007-2013) under grant agreement no. 229927 (FP7-REGPOT-2008-1, Project BIO-SOLENUTI) and the Special Research Account of the University of Crete are gratefully acknowledged for the financial support of this research.

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