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New pyridinium based ionic dyes for the hydrogen evolution reaction

Dagny D. Konieczna [a], Harry Biller [a], Matthias Witte [b], Wolf Gero Schmidt [b], Adam Neuba [c], René Wilhelm [a, *]

[a] Department of Chemistry, Organic Chemistry, University of Paderborn, 33098, Paderborn, Germany
[b] Department of Physics, University of Paderborn, 33098, Paderborn, Germany
[c] Department of Chemistry, Inorganic Chemistry, University of Paderborn, 33098, Paderborn, Germany

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ABSTRACT

The presented work comprised the synthesis and characterization of new ionic organic dyes as potential photosensitizer (PS) in the photocatalytic H_2 evolution reaction. The presented dyes are consisting of donor-π-acceptor (D-π-A) structures that are commonly used for organic dyes for organic solar cells. The acceptor is based on a cationic pyridinium moiety. Furthermore, a complex was synthesized, in which a D-π-A photosensitizer is linked as ligand to cobaloxime. The latter is a common proton reduction catalyst. The attached ligand enabled a fast intramolecular electron transfer to the cobalt center. The resulted complex showed high stability and potential in the homogeneous photocatalytic H_2 evolution reaction. Finally, one ionic dye showed a high activity when combined with TiO_2 and Pt in a heterogeneous hydrogen evolution reactions with a TOF of up to 407 h^{-1}.

1. Introduction

In the past several decades photocatalysis was explored in the conversion of solar energy into electricity (photovoltaic) and chemical fuels.[1] Moreover, photocatalytic approaches are found in the synthesis of organic compounds, where the term photoredox catalysis is applied.[2] An efficient semiconductor photocatalyst should provide a small bandgap to absorb as much solar energy as possible. However, most semiconductors, which exhibit high oxidizing and reducing power and show less tendency toward photo-corrosion, absorb only a minor part of solar energy owing to their wide band gaps, e.g. for TiO_2 3.0 eV in rutile and 3.2 eV in anatase. In contrast, small band gap semiconductors such as Fe_2O_3 (2.2 eV), CdSe (1.7 eV) and CdS (2.4 eV) provide a higher visible light harvesting ability but tend to decompose under light irradiation.[3]

Many efforts have been made to develop new or modified semiconductor photocatalysts for improving their visible light response via doping and deposition of metallic and non-metallic elements.[1] Furthermore, sensitization with organic photosensitizers (PSs) transferring the photoexcited electron to the semiconductor can enhance the efficiency due to effective charge separation.[4] A sacrificial electron donor is required for regeneration of the PS. This approach is widely exploited in the field of dye-sensitized solar cells (DSSC), in which solar energy is converted. The LUMO of the dye has to be higher in energy than the conduction band of the semiconductor, otherwise there cannot occur an electron transfer.[4]

The investigation of organic chromophores used for visible-light sensitization utilized in photocatalysis and in generation of electric power by photovoltaics, is an essential part in research due to the increased interest in sustainable chemical conversions.[5] Next to organic PSs well established metal based sensitizers, which usually consists of ruthenium with polypyridine ligands, are being applied.[6] PSs based on metal-free organic compounds attracted much interest due to the increase demand of low-cost alternatives.[5] Metal-free organic PSs are structurally divided into electron-donating and accepting moieties separated by a π-conjugated bridge, which are referred to as donor-π-acceptor (D-π-A) dyes.[7] The design of the D-π-A structure has a high diversity in its substructures which enables fine-tuning regarding the chemical and physical properties.[5a]

Ionic dyes are less common in photovoltaic and photocatalytic processes and so far limited in structures based on cyanin[8] and squaraine.[9] They show absorption in the range of near infrared and

* Corresponding author.
E-mail address: rene.wilhelm@uni-paderborn.de (R. Wilhelm).

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visible light with high extinction coefficients of 10^5 L mol^{-1} cm^{-1} but moderate efficiency in conversion of solar power into electrical energy, compared to non-ionic D-π-A dyes.[8-9]

In the presented study new ionic PSs (**PS2** and **PS3**, Scheme 1) were synthesized and characterized in order to evaluate their application as potential PS in photochemical reactions. The quaternized pyridinium units are here the acceptor moiety. The acceptor is linked by a π-bridge of vinylthiophene to a triphenylamine donor to give the desired D-π-A structure.

Related reported structures to **PS1-PS3** are shown in Scheme 2. The chromophore **1** showed in preliminary tests a solar-to-energy conversion efficiency over 5% in DSSCs. An adsorption on TiO_2 was achieved by the cyano acrylic acid group.[10] There have been a few reports of pyridinium salt based dyes **2** and **3** with a methylencarboxylic acid function described by Sun et al.[11] Yet, applications of these compounds in hydrogen evolution reactions have not been reported.

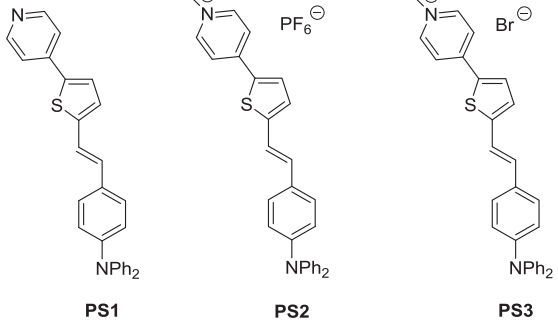
2. Results and discussion

The basic structure of the desired PSs is a D-π-A system consisting of a triphenylamine unit as donor, a vinylthiophene as π-bridge and a pyridine as acceptor (Scheme 1). The synthesis is shown in Scheme 3. For the synthesis of the pyridine-based **PS1** and **PS2**, compound **4**[12] was treated with **5**[13] in a Heck coupling[14] resulting **PS1** in 83% yield. The following quaternization and anion metathesis with $NaPF_6$ gave the new ionic dye **PS2** in an overall yield of 97% (Scheme 3).

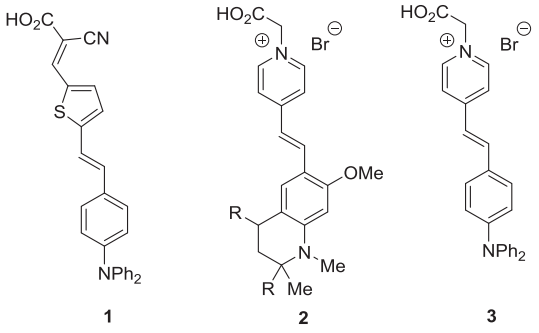
In order to prepare dye **PS3** with a carboxylic acid function, the quaternization was performed following a literature procedure[11] with ethyl bromoacetate resulting the desired bromide ethyl ester salt in 85% yield. The latter was transformed to **PS3** in the presence of LiOH in 81% yield (Scheme 4).

The UV–Vis spectrum of the pyridinium-based **PS2** is shown in Fig. 1. The absorption maxima are at 487 nm (ε = 62823 L mol^{-1} cm^{-1}) in MeCN and 540 nm (ε = 23147 L mol^{-1} cm^{-1}) in CH_2Cl_2. The high extinction in MeCN is advantageous in view of photocatalytic application in aqueous reactions such as in water splitting, in which MeCN is usually used as organic solvent due to the miscibility. A high extinction coefficient is also beneficial for heterogeneous applications with semiconductors. This allows the prevention of agglomeration of the PS molecules since low concentrations of the PS can be used and adsorbed on the surface of the semiconductor. The impact by quaternization of the pyridine is expressed in a significant redshift. The absorption maxima of the non-ionic intermediate **PS1** are 403 nm (ε = 49336 L mol^{-1} cm^{-1}) in MeCN and 411 nm (ε = 32340 L mol^{-1} cm^{-1}) in CH_2Cl_2. In addition, **PS1** shows a significant fluorescence with an emission maximum at 525 nm in CH_2Cl_2 while **PS2** does not.

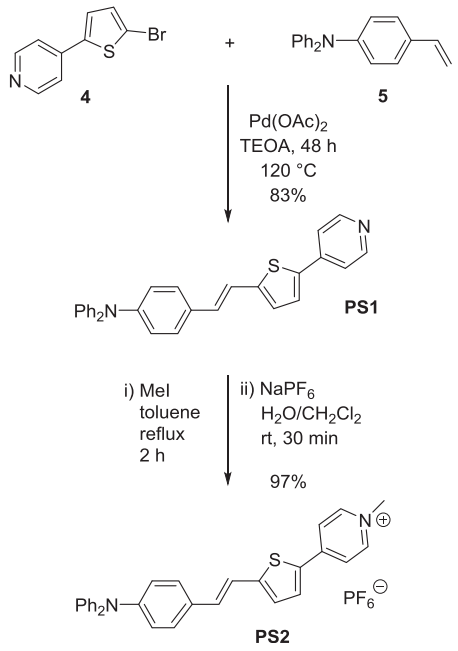
In Fig. 2 the UV–Vis spectrum of **PS3** is depicted. It shows a broad absorption band with a remarkably high extinction coefficient of ε = 118854 L mol^{-1} cm^{-1}1 at λ = 478 nm in MeOH.



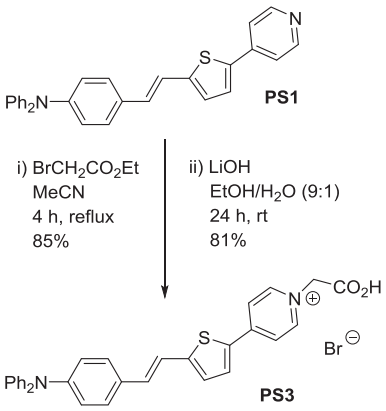
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

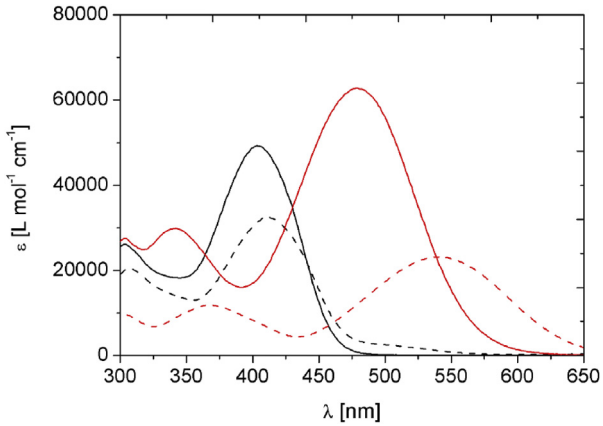


Fig. 1. UV–Vis spectra of **PS2** (red line) (c = 0.02 mmol L^{-1}) and **PS1** (black line) (c = 0.05 mmol L^{-1}) in different solvents (MeCN = solid line, CH_2Cl_2 = dash line).

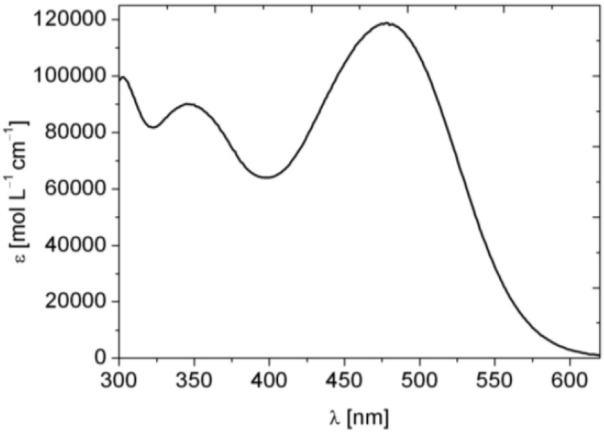


Fig. 2. UV–Vis spectra of **PS3** (c = 0.02 mmol L^{-1}) in MeOH.

Cyclic voltammetry (CV) of **PS2** was conducted in a dry CH_2Cl_2/Bu_4NPF_6 (c = 0.1 M) solution and is shown in Fig. 3, in which the potentials are given relative to Fc/Fc^+. The half-wave potential of the oxidation is $E^0_{1/2}$ = 0.46 V (ΔE = 70 mV) and of the reduction $E_{1/2}{}^0$ = −1.42 V (ΔE = 105 mV) and can be assumed as reversible in the beginning. For the application in solar cells or photocatalytic processes a PS requires a stable oxidized state which is reversibly reducible. The reversibility of the oxidized state of **PS2** might be caused by the quaternization of the pyridine, since the non-ionic **PS1** showed no reversible oxidation behavior. The latter also adsorbed with time on the electrode surface (see supporting information).

In Fig. 4 the CV of **PS3** dissolved in CH_2Cl_2/Bu_4NPF_6 (c = 0.1 M) as electrolytic system is depicted. Several oxidations in the region of 0.35–0.75 can be observed. E^1_{ox} = 0,57 V, E^2_{ox} = 0,76 V, E^1_{red} = 0,50 V and E^2_{red} = 0,35 V vs. Fc/Fc^+ are found. In the anodic area, also the bromide anion can be oxidized. In addition, it is also possible that a decarboxylation takes place in solution as it is known in the Kolbe electrolysis.[15]

Density-functional theory (DFT) calculations were carried out for **PS2** in order to gain deeper insight in the electronic structure of the compounds prepared here. Density-functional theory and time-dependent density-functional theory (TDDFT) calculations were performed as implemented in Gaussian 09.[16] A localized cc-pVDZ basis set[17] was used and the electron exchange-correlation energy was modeled using the B3LYP functional.[18] The HOMO-LUMO gap for the gas phase molecule is calculated to be 2.23 eV. The HOMO was calculated to be at −5.48 eV and the LUMO at −3.25 eV with respect to the vacuum level. The frontier molecular orbitals (MOs) of the HOMO and LUMO of **PS2** are shown in Fig. 5. The HOMO is mainly localized at the donor group, triphenylamine, whereas the LUMO is dominantly situated at the acceptor pyridine. The redistribution of the electron density is the essential characteristic of a push-pull type PS for enabling an efficient intramolecular charge separation. Both MOs also show some charge density at the π-bridge, vinylthiophene. The experimental HOMO/LUMO levels in CH_2Cl_2 calculated from the half-wave potentials almost agree with the theoretically determined results by DFT (HOMO = −5.2 eV, LUMO = −3.2 eV). The PS fulfills the requirement of an efficient electron transfer in applications with TiO_2 since the LUMO of the PS is energetically positioned higher than the CB of titanium dioxide. The CB and VB edges of titanium dioxide are in the different modifications (rutile and anatase) at −4.0 eV and −7.0 to −7.2 eV in vacuum. Further, in view of the application in DSSCs the energy level of the HOMO is lower than the I^-/I_3^- redox potential (−4.8 eV vs. vacuum),[19] which is usually used for regeneration of the oxidized PS.

After the preparation and characterization of **PS1**-**PS3** their potential was investigated in homogenous and heterogenous photocatalytic hydrogen evolution reactions. First a homogenous system with a cobaloxime complex **7** was investigated.

Cobaloxime complexes like **7** are established as Co(dmg)2–based macrocyclic complexes formed by H-capped or BF_2-capped dimethyl glyoxime (dmg) ligands. Chloride and pyridine are in axial positions on the cobalt center and perpendicular to dmg. They

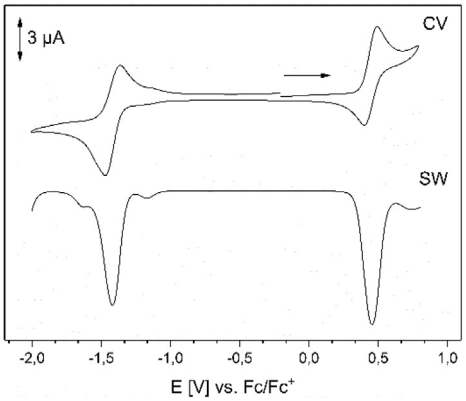


Fig. 3. CV of **PS2** in CH_2Cl_2 at a scan rate of 100 mV/s (Pt working electrode, CE: Pt).

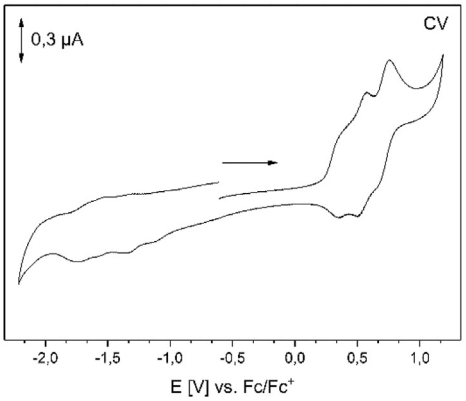


Fig. 4. CV of **PS3** in CH_2Cl_2 at 100 mV/s (Pt working electrode, CE: Pt).

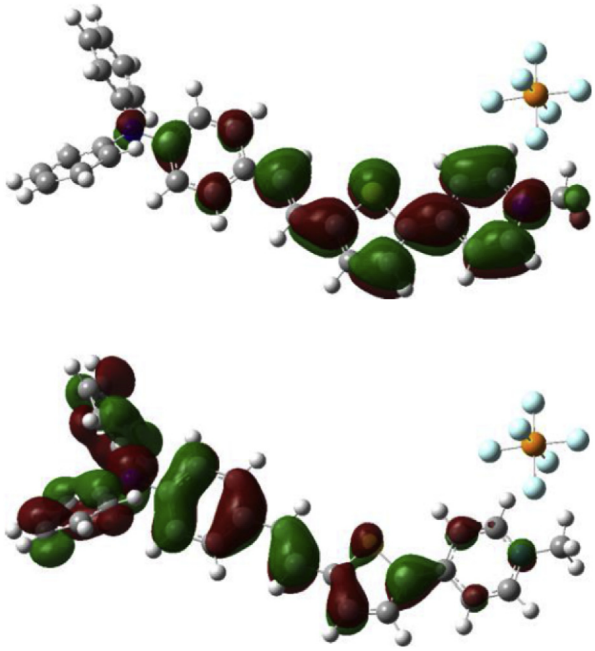


Fig. 5. Frontier molecular orbitals of the HOMO (bottom) and LUMO (top) of **PS2** are calculated by DFT.

were initially studied as model compounds for the active side of the coenzyme vitamin B12.[20] Later by observation of H_2 evolution in the presence of a sacrificial electron donor (SED), cobaloximes attracted interest as proton reduction catalysts.[21] The first report of cobaloxime in photocatalytic water reduction was in 1983.**7** was used with $[Ru(bpy)_3]^{2+}$ as PS and triethanolamine (TEOA) as SED in an aqueous medium.[22] Several derivates of cobaloxime have been reported and are still explored in H_2 evolution.[23] The mechanism of H_2 evolution is well understood, so that they are representing an ideal platform for exploring new PSs.[24] Recent studies by the group of Norton[25] suggests the involvement of a Co(I) species with an exchangeable proton, which can be seen as a tautomer of a Co(III) hydride complex. In addition, the group of Peters[26] reported in 2015 the formation of a $[Co(II)]_2$ dimer, which is in equilibration with its monomer. Several PSs were investigated in H_2 photocatalysis with cobaloxime which are based on noble metals such as Pt,[27] Ru,[22] Re,[28] Ir[29] and organic PSs without noble metals.[30] The first homogenous system for photocatalytic reduction of water containing no noble metal PSs was reported by Eisenberg et al. in 2009.[30-31] Hydrogen generation was explored with a photocatalytic system consisting of (CoIII(dmgH)$_2$(py)Cl) (**7**) as catalyst, Eosin Y or Rose Bengal as PSs, TEOA as SED and a 200 W Hg lamp (cut off $\lambda > 450$ nm) as light source. The use of Eosin Y resulted in 5 h for the H_2 production a $TON_{Cat} = 72$ and TON_{PS} of 360. Cobaloximes tend to decompose by losing their diemthylgyloxime ligands. The durability was improved by addition of free $dmgH_2$ finally resulting in a $TON_{Cat} = 180$ and $TON_{PS} = 900$ during 10 h light irradiation. Bengal Rose showed similar activities but was decomposed in about 2 h without the addition of $dmgH_2$. In a further report a rhodamine-based PS showed with **7** in the presence of TEOA a $TON_{Cat} = 51$ and $TON_{PS} = 3737$ after 5 h irradiation with 520 nm Power LEDs. The addition of $dmgH_2$ improved the turn over number up to $TON_{Cat} = 127$ and $TON_{PS} = 9384$ in 24 h.[31a]

Combined systems containing both photosensitizing and catalyzing properties in one complex by covalently or coordinatively attachment of the PS unit to the cobalt center of cobaloxime have been studied for enabling fast intramolecular electron transfer. The first complexes based on cobaloxime included ruthenium tris(diimine) moieties, whereby the highest TON = 103 was obtained after 15 h irradiation with visible light from a 150 W CdI doped Hg lamp (cut off $\lambda > 350$ nm).[32] The systems showed compared to systems containing an analogue PSs and catalysts but as separated components marginal increased activity. For example, an analogous iridium complexes produced H_2 with a TON = 210 after 15 h irradiation. The separated component system containing $[Ir(ppy)_2(phen)]^+$ and $[Co(dmgBF_2)_2(OH_2)_2]$ resulted in a TON = 165 after 15 h irradiation with a 150 W Hg-lamp (cut off $\lambda > 380$ nm).[28d]

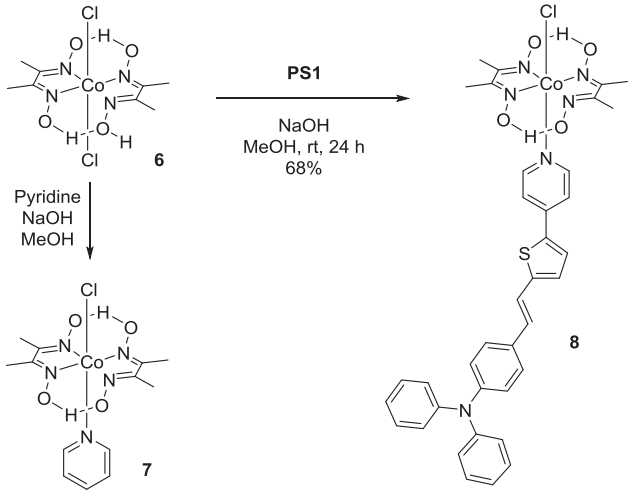
Reports of combined systems based on organic PSs are so far limited. A linked system of Co(dmgH)2(py)Cl (**7**) and fluorescein with a pyridine moiety connected through an amide linker gave H_2 with a TON = 20 in 24 h, which was increased by the addition of free pyridine to a TON = 31. However, the non-covalent linked system produced H_2 with a TON = 63 in the same time. A labile pyridine group was assumed as reason for the lower activity by attaching catalyst and PS.[31b] The second literature known complex is based on a linkage between H-capped cobaloxime and different meso-pyridyl boron dipyrromethenes (BODIPY), of which one showed highest activity by producing H_2 with a TON of nearly 31 after 17 h irradiation with a 525 nm LED.[31c]

Investigation of photocatalytic system evolving H_2 in which a PS of a D-π-A structure commonly found in DSSCs was exploited as well as separated photosensitizing component or incorporated in a complex have not been reported so far. Hence, next to the evaluation of **PS1**-**PS3** in combination with **7** in a hydrogen evolution reaction, also complex **8** was prepared (Scheme 5).

The synthesis and characterization of the combined system **8** is shown in Scheme 5 and was performed by complexation between cobaloxime complex **6**[33] and **PS1** through the axially coordinating pyridine unit of **PS1** with a yield of 68%.

The UV–Vis of **8** (Fig. 6) showed in MeCN/MeOH (1:1) a maximum at 406 nm ($\varepsilon = 52685$ L mol^{-1} cm^{-1}). In the same solvent mixture, the complex showed in a fluorescence spectrum an emission peak at 559 nm. In CH_2Cl_2 the complex had a broad absorption in the visible range with a maxima at 499 nm ($\varepsilon = 35473$ L mol^{-1} cm^{-1}) and in a solution of MeCN/MeOH (1:1) with 15% TEOA a maxima of 439 nm ($\varepsilon = 8229$ L mol^{-1} cm^{-1}).

The CV of **8** was performed in dry CH_2Cl_2 containing Bu_4NPF_6 (c = 0.1 M) as supporting electrolyte. Two measurements were conducted. One CV was measured up to 0.8 V and the other up to 0.55 V (Fig. 7). In the latter CV it is possible to observe an oxidation



Scheme 5.

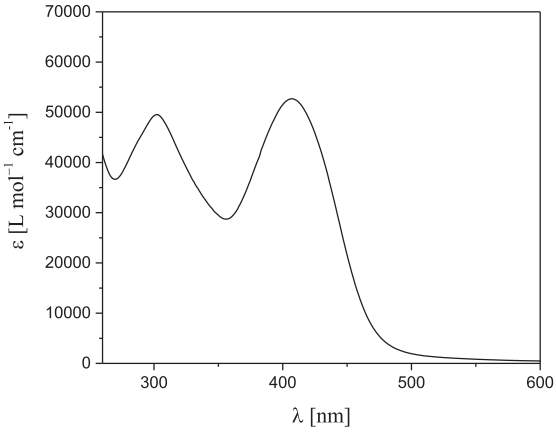


Fig. 6. UV–Vis of **8** (0.1 mmol L^{-1}) in MeCN/MeOH (1:1).

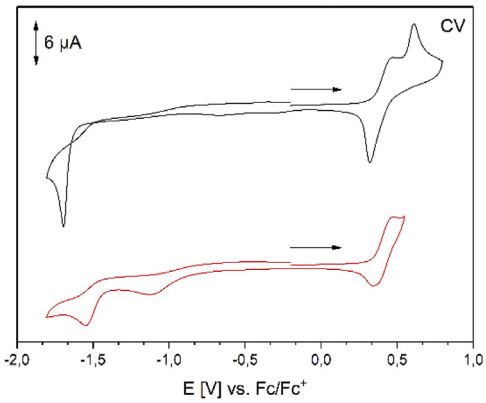


Fig. 7. CV of **8** in CH_2Cl_2 at a scan rate of 100 mV/s (GC working electrode, CE: Pt). Black up to 0.8 V and red up to 0.55 V.

at $E^1_{ox} = 0{,}47$ V vs. Fc/Fc^+ which can be assumed as reversible in the beginning. In addition, three reductions can be observed; $E^1_{red} = 0{,}36$ V, $E^2_{red} = -1{,}11$ V and $E^3_{red} = -1{,}55$ V vs. Fc/Fc^+. The latter are the reduction of Co(III) to Co(II) and from Co(II) to Co(I). These can be also observed in analogy to other cobaloxime complexes with different pyridine ligands.[34] The run of up to 0.8 V showed $E^1_{ox} = 0{,}47$ V, $E^2_{ox} = 0{,}61$ V, $E^1_{red} = 0{,}32$ V and $E^2_{red} = -1{,}69$ V vs Fc/Fc^+ with two crossover points at $E^1_{cop} = -1{,}49$ V and $E^2_{cop} = -1{,}64$ V vs. Fc/Fc+. The crossover points are referring to an association of the complex at the electrode surface and a radical change of the complex at an anodic oxidation over 0.8 V.

A density-functional theory (DFT) calculation for **8** was carried out in analogy to **PS2** with a localized cc-pVDZ (TZ for Co) basis set.[17] The HOMO-LUMO gap for the gas phase complex is 2.63 eV and the optical band gap is 2.40 eV, which corresponds to an absorption at 517 nm, which is close to the observed absorption maxima at 499 nm in CH_2Cl_2. The HOMO was calculated to be at −5.35 eV and the LUMO at −2.72 eV with respect to the vacuum level. The LUMO lies well above the required −4.5 eV to reduce water and the HOMO low enough to be filled after the reaction via reduction with TEOA.

Complex **8** and **PS1-PS3** with **7** were employed in the reduction of water with TEOA as SED in a typical literature system.[27c] The compounds were placed in a 1:1 mixture MeCN:H_2O with TEOA (15% v/v) at a pH of 8.3 and was irradiated with a blue LED (λ = 455 nm, 2 Watt). The redox potentials conclude that an oxidative quenching of the excited PSs with **7** and regeneration by TEOA is feasible. While **PS1** and **PS3** with **7** showed no activity, a low activity was found for **PS2** with **7** and for complex **8**. Both systems showed activity in H_2 evolution, whereby **8** was more active than **PS2** and **7**. After 2 d light irradiation 2.8 mmol H_2 g^{-1}_{Cat} were obtained by using **PS2** and **7** as catalyst which corresponds to $TON_{Cat} = 1$ and $TON_{PS} = 5.6$.

In comparison, 19 μL H_2 were achieved with complex **8** ($TON_{Cat} = 8$) (Table 1, entry 1). Improved activity was found by increasing the solubility of **8** by changing the reaction medium. By increasing the part of MeCN with a ratio of 3:1 against H_2O, 33 μL H_2 were generated, which corresponded to a TON_{Cat} of 14 (Table 1, entry 2). A higher activity was obtained by exchange of H_2O against MeOH, which resulted finally 299 μL H_2 ($TON_{Cat} = 122$) after almost 9 d light irradiation (Table 1, entry 3). Compared to reported systems of analogues[30,31c] in which an organic dye is linked to cobaloxime, the complex **8** showed higher stability due to the long reaction time of 9 d and the fact that the H_2 evolution occurred almost linear (see Fig. 8). Interestingly, the use of 5% triethylamine (TEA) instead of TEOA resulted in 4 μL H_2 mmol, which corresponds to a TON_{Cat} of 1.4 after 3 d of irradiation (Table 1, entry 4).

Taking into consideration that the intramolecular electron transfer was significantly higher in the homogenous system, it was decided to evaluate the core structure of the dye with TiO_2 in a heterogenous H_2 evolution with **PS3**. The carboxylic acid function ensures the strong attachment of the dye on the TiO_2 surface via this anchor group.[11] Nevertheless, also **PS1** and **PS2** were investigated with TiO_2. First the TiO_2 (P25) was decorated with platinum nanoparticles according to a literature procedure.[35] A suspension of TiO_2 and hexachloroplatinic acid in methanol was irradiated with UV light resulting in the degradation of the acid and the formation of platinum nanoparticles on the surface of the TiO_2. The modified TiO_2 and an unmodified TiO_2 sample was suspended in a solution of the PSs in methanol. **PS1** and **PS2** were not adsorbed on the surface of the TiO_2. However, **PS3** adsorbed as expected due to its carboxylic acid function on TiO_2. An SEM of a **PS3**-TiO_2-Pt composite showed an agglomeration of the TiO_2 (P25) nanoparticles and an EDX revealed the presence of Pt on the surface of the TiO_2 particles (see supporting information). Next to Pt the surface was also covered by C and S from the dye as shown by the EDX. The loading of the **PS3** on the TiO_2 was 0.0288 mmol g^{-1}, as determined by UV–Vis of the remaining dye via comparison with a graph of a concentration series.

The behavior of the **PS3**-TiO_2-Pt composite in the hydrogen evolution reaction was studied in aqueous solution (pH 7) with TEOA (10% v/v) as SED and a blue LED (λ = 455 nm, 2 Watt). The results are summarized in Table 2. A TiO_2-Pt composite showed a very low hydrogen production of 0.70 μL after 24 h. **PS3**-TiO_2 without Pt showed a similar value of 0.65 μL, which would correspond to a TON of 36 per electron transfer of **PS3**. The combined system Pt-TiO_2-**PS3** resulted in 1 h a TON of 407, hence a TOF of 407 h^{-1}, however no further hydrogen was produced after 1 h. Comparable literature systems with thiophenothiazine-based organic dyes[35] and TiO_2-Pt gave a TOF of 140 h^{-1} with a 400 W xenon arc lamp (cut off λ > 400 nm) and phenothiazine-based organic dyes[36]

Table 1
Hydrogen evolution reaction with complex **8**.

Run	t [d]	Conditions[a]	H_2[b]	TON_{Cat}
1	2	MeCN/H_2O (15% TEOA)	19	8
2	2	MeCN/H_2O (3:1, 10% TEOA)	33	14
3	9	MeCN/MeOH (5% TEOA)	299	122
4	3	MeCN/MeOH (5% TEA)	4	1.4

[a] pH 8.3, λ = 455, **8** (0.5 mmol L^{-1}), average of two runs.
[b] [μL].

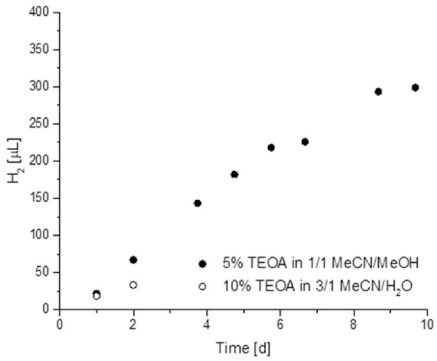


Fig. 8. Time course of photocatalytic H_2 generation with **8** (0.5 mmol L^{-1}) in different solvents (λ = 455 nm, pH = 8.3).

Table 2
Hydrogen Evolution with TiO_2 composite.

Run	System	Time	H_2[µL][a]	TON[b]
1	Pt – TiO_2	24 h	0.70	–
2	TiO_2 – **PS3**	24 h	0.65	36
4	Pt – TiO_2 – **PS3**	1 h	7.16	407

[a] 0.5 mg **PS3**-TiO_2-Pt in 2 mL H_2O (10% v/v TEOA), pH 7, λ = 455, average of two runs.
[b] TON = (2 × amount of H_2/amount of dye **PS3**).

gave a TOF of 205 with a 200 W xenon lamp (cut off λ > 420 nm).

3. Conclusion

The quaternization of an acceptor moiety consisting of pyridine gave an ionic structure, which had a positive impact on the electrochemical requirements that have to be fulfilled by a PS. In UV–Vis spectroscopy the impact was expressed in a significant redshift in the absorption behavior. CV measurements showed a reversibility in the oxidation of the ionic PSs, while their non-ionic precursor **PS1** exhibited irreversible oxidation. The presence of a counter anion offers in the future the possibility for easy tuning of chemical and physical properties by anion metathesis. In addition, the complex **8** was synthesized containing both photosensitizing and catalyzing property in one compound by linkage of cobaloxime with the organic D-π-A dye **PS1** as ligand. The combined system proved high stability and potential in a homogenous photocatalytic H_2 evolution from a mixture of MeCN/MeOH (1/1) containing 5% TEOA as SED with a TON of 122. **PS3** could be applied in a heterogenous system with TiO_2-Pt resulting a TOF 407 h^{-1}. The presented core structure of the dyes will help to improve the performance of new ionic organic dyes further.

4. Experimental section

4.1. General experimental

The reagents were purchased from commercial sources and used without further purification. The reactions were prepared under argon atmosphere using Schlenk techniques unless otherwise stated. CH_2Cl_2 and THF were purified by distillation. The reactions were monitored by thin layer chromatography (Silica gel F254). Column chromatography was performed using silica gel 60. Water used in photocatalytic samples was deionized with a SG water purification system (~0.055 µS cm^{-1}). ^1H and ^{13}C NMR spectra were recorded at 500 MHz on a Bruker Advance 500 and at 300 MHz at a Bruker Advance. ESI (electrospray ionization) mass spectra were recorded using double-focusing sector field-MS DFS from Thermo Scientific. UV–Vis spectroscopy was performed with Varian Cary 50 UV–Vis spectrophotometer. IR spectra were acquired on an FT-IR-spectrometer Vertex from BRUKER. The determination of melting points was performed in open-end-capillary tubes on a BÜCHI B-545 melting point apparatus. Elemental analysis was performed with a vario MICRO cube analysator from Elementar. Cyclic and square-wave voltammograms at room temperature were performed with the PAR101 potentiostat from Metrohm in MeCN/0.1 M NBu_4PF_6 (analyte conc. ~ 1.0 mmol/L, in case of **PS3** a saturated solution was used) with the following three electrode arrangement: Pt or GC working electrode (1 mm and 1.6 mm diameter), Ag/0.01 M $AgNO_3$, 0.1 M NBu_4PF_6 in MeCN as reference electrode and a Pt wire as counter electrode. Ferrocene was added as internal standard after the measurements and all potentials are referenced relative to the Fc/Fc^+ couple. All measurements were carried out under argon atmosphere, with absolute and vented solvents. The HOMO is approximately equal to the ionization potential Ip and the LUMO to the electron affinity E_a, that are calculated according the empirical relationship by Bredas et al.[37] from the onset potentials being compared to ferrocene (4.4 eV vs. vacuum).[38] The onset potential were estimated from the intersection of two tangents dawn at the rising signal current and baseline current of the CV. The reduction potentials of cobaloxime (**7**) from Co^{3+} to Co^{2+} (−1.06 V) and further reduction to Co+ (−1.51 V) and the redox potential of TEOA ($E_{1/2}$ = 0.51 V) are literature-known.[39] The potentials were adjusted to Fc/Fc^+.[40] The excited oxidation potential E_{ox} (PS*/PS-1) of **PS2** was calculated by the Rehm Weller equation.[41] Compounds 4-(5-bromothiophen-2-yl)pyridine (**4**),[12] *N*,*N*-Diphenyl-4-vinylaniline (**5**)[13] and bis-dimethylglyoximcobalt-dichloride (**6**)[33] were prepared according to the literature.

4.2. Photocatalytic performance

The photocatalytic reactions were performed in sealed crimp-top vials and were irradiated with a high power LED (Osram Oslon SSL 80 royal-blue LEDs (λ = 455 nm ± 15 nm, 3.5 V, 700 mA)) from below. Temperature was kept constant on 20 °C by an enclosing aluminum cooling block connected to a thermostat. The determination of the amount of H_2 was performed by gas chromatography (Agilent 6890N equipped with a ShinCarbon ST column (100/120 mesh) and thermal conductivity detector. The quantitative determination of H_2 was performed by preparing a calibration curve.

4.2.1. (E)-N,N-diphenl-4-(2-(5-(pyridine-4-yl)thiophen-2-yl)vinyl) aniline (*PS1*)

N,*N*-Diphenyl-4-vinylaniline (**5**) (562 mg, 2.08 mmol, 1.0 eq), 4-(5-bromothiophen-2-yl)pyridine (**4**) (500 mg, 2.08 mmol, 1.0 eq) and palladium(II) acetate (4.7 mg, 0.02 mmol, 0.01 eq) were dissolved in triethanolamine (10 mL) and degassed by purging with argon. The reaction mixture was stirred for 48 h at 120 °C. After cooling, the reaction mixture was diluted with distilled water and extracted four times with CH_2Cl_2. The organic phase was washed with distilled water, dried over $MgSO_4$ and filtrated and evaporated to dryness. The crude product was purified by column chromatography on silica gel using n-hexane/ethyl acetate (1/1 v/v %) and recrystallisation from ethanol to give **PS1** as a yellow solid (490 mg, 53%). mp 201 °C. IR $\tilde{\nu}$ (KBR pellets, cm^{-1}): 3435, 3031, 2923, 1783, 1733, 1677, 1583, 1486, 1407, 1328, 1270, 1174, 1077, 1027, 989, 954, 888, 856, 800, 752, 692, 615. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.57 (d, *J* = 6.1 Hz, 2H), 7.46 (dd, *J* = 4.5 Hz, 1.6 Hz, 2H), 7.42 (d, *J* = 3.8 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.28–7.25 (m, 4H), 7.12–7.09 (m, 4H), 7.06–7.03 (m, 6H), 6.94 (d, *J* = 16 Hz, 1H) ppm. ^{13}C NMR (125 MHz,

$CDCl_3$): δ = 149.9, 147.8, 147.3, 145.6, 130.4, 129.6, 129.3, 127.4, 126.7, 126.2, 124.7123.3, 123.1, 119.4 ppm. ^{15}N NMR (51 MHz, $CDCl_3$): δ = 102.3 ppm. HRMS (ESI): $M+H^+$, found 431.1583. $C_{29}H_{23}N_2S$ requires 431.1576.

4.2.2. (E)-4-(5-(4-(diphenylamino)styryl)thiophen-2-yl)-1-methylpyridin-1-ium hexafluorophosphate (*PS2*)

Methyl iodide (0.16 mL, 2.52 mmol, 12.0 eq) was added to a solution of (*E*)-*N*,*N*-diphenyl-4-(2-(5-(pyridin-4-yl)thiophen-2-yl) vinyl)aniline (**PS1**) (95 mg, 0.21 mmol, 1.0 eq) in CH_2Cl_2 (7 mL). After stirring overnight the solvent was removed under reduced pressure to give (E)-4-(5-(4-(diphenylamino)styryl)-thiophen-2-yl)-1-methylpyridin-1-ium iodide as deep violet solid, which was dissolved in CH_2Cl_2 (7 mL) and treated with an aqueous solution of $NaPF_6$ (5.0 mL, 0.05 mol L^{-1}, 1.5 eq). The reaction mixture was vigorously stirred for 4 h. The organic phase was separated and dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was dissolved in a small amount of hot $CHCl_3$ and finally precipitated in n-hexane to give **PS2** as yellow solid (99.6 g, 0.168 mmol, 97%). mp 235 °C. IR $\tilde{\nu}$(KBR pellets, cm^{-1}): 3440, 3032, 1642, 1588, 1536.8, 1507, 1441, 1329, 1232, 1198, 1072, 961, 831, 752, 694, 621.^{1}H NMR (500 MHz, acetone-D_6): δ = 8.89 (d, *J* = 6.9 Hz, 2H), 8.30 (d, *J* = 7.1 Hz, 2H), 8.13 (d, *J* = 4.1 Hz, 1H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.41–7.38 (m, 2H), 7.35–7.32 (m, 4H), 7.23 (d, *J* = 16.1 Hz, 1H), 7.12–7.09 (m, 6H), 6.99 (d, *J* = 8.7, 2H), 4.50 (s, 3H) ppm. ^{13}C NMR (125 MHz, acetone-D_6): δ = 154.3, 152.8, 149.6, 148.1, 146.2, 135.3, 134.0, 133.3, 130.7, 130.5, 129.1, 129.0, 125.9, 128.9, 124.7, 123.2, 122.6, 119.62, 111.3, 48.0 ppm. ^{15}N NMR (51 MHz, acetone-D_6): δ = 190.9, 101.8 ppm. ^{19}F NMR (280 MHz, acetone-D_6): δ = −72.51 (d, *J* = 707.8 Hz). ^{31}P NMR (200 MHz, acetone-D_6): δ = −144.12 (sept, *J* = 707.8 Hz). HRMS (ESI): M^+, found 445.1742. $C_{30}H_{25}N_2S$ requires 445.1733.

4.2.3. (E)-1-(carboxymethyl)-4-(5-(4-(diphenylamino)styryl) thiophen-2-yl)pyridin-1-ium bromide (*PS3*)

Ethyl bromoacetate (15 μL, 0.135 mmol) was added to a solution of **PS1** (40 mg, 0.09 mmol) in MeCN (15 mL) and stirred overnight under reflux. The reaction mixture was cooled and the solvent evaporated. Purification by column chromatography on silica gel using CH_2Cl_2//MeOH (20/1 v/v %) gave (E)-4-(5-(4-(diphenylamino) styryl)thiophen-2-yl)-1-(2-ethoxy-2-oxoethyl)-pyridin-1-ium bromide as a red solid (40 mg, 0.077 mmol, 85%). The compound was directly used in the next step. ^{1}H NMR (500 MHz, MeOD): δ = 8.66 (dd, *J* = 7.2 Hz, 1.1 Hz, 2H), 8.19 (d, *J* = 7.2 Hz, 2H), 8.07 (d, *J* = 4.0 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 4.0 Hz, 1H), 7.32–7.26 (m, 5H, 7.20 (d, *J* = 16.0 Hz, 1H), 7.11–7.06 (m, 6H), 6.97 (d, *J* = 8.7 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 2H), 1.34 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (125 MHz, MeOD): δ = 166.3, 153.3, 149.8, 148.7, 147.2, 145.2, 134.0, 133.6, 132.8, 129.6, 129.2, 128.0, 127.8, 124.8, 123.5, 122.0, 121.0, 118.2, 62.7, 52.5, 12.9 ppm.

A solution of (E)-4-(5-(4-(diphenylamino)styryl)thiophen-2-yl)-1-(2-ethoxy-2-oxoethyl)pyridin-1-ium bromide (40 mg, 0.077 mmol) in a mixture of EtOH/H_2O (10 mL, 9/1 v/v %) was treated with $LiOH\cdot H_2O$ (64 mg, 1.54 mmol) and stirred at rt for 24 h. The pH was adjusted at 2–3 by diluted HCl solution (1.0 mol L^{-1}). The ethanol was evaporated and the remaining aqueous solution was extracted with CH_2Cl_2 (3 × 30 mL). After evaporation of the organic phase to dryness, the purification by column chromatography on silica gel using CH_2Cl_2/MeOH 5/1 v/v %) gave **PS3** as red solid (312 mg, 0.063 mmol, 81%). mp 100 °C. IR $\tilde{\nu}$ (KBR pellets, cm^{-1}): 3435, 3034, 2361, 1637, 1587, 1508, 1440, 1384, 1274, 1226, 1192, 1068, 956, 819, 752, 696, 619, 586, 557, 503, 470.^{1}H NMR (500 MHz, MeOD): δ = 8.59 (d, *J* = 7.2 Hz, 2H), 8.12 (d, *J* = 7.2 Hz, 2H), 8.01 (d, *J* = 4.0 Hz, 1H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.31–7.26 (m, 6H), 7.17 (d, *J* = 16.0 Hz, 1H), 7.10–7.06 (m, 6H), 6.97 (d, *J* = 8.7 Hz, 2H), 5.03 (s, 2H) ppm. ^{13}C NMR (125 MHz, MeOD): δ = 168.9, 152.0, 148.6, 147.3, 144.9, 134.4, 132.5, 132.2, 129.8, 129.1129.0127.7, 124.8, 123.4, 122.2, 120.8, 118.4, 62.3 ppm. ^{15}N NMR (51 MHz, MeOD): δ = 197.3, 102.3 ppm. HRMS (ESI): M^+, found 489.1640. $C_{31}H_{25}N_2O_2S$ requires 489.1631.

4.2.4. CoCl(dmgH)$_2$-(E)-N,N-diphenl-4-(2-(5-(pyridine-4-yl) thiophen-2-yl)vinyl) aniline (*8*)

Complex **6** (160 mg, 0.443 mmol, 1.0 eq) was dissolved in methanol (20 mL) and NaOH (17.7 mg, 0.443 mmol, 1.0 eq) and compound **PS1** (198 mg, 0,443 mmol, 1.0 eq) was added. The reaction mixture was stirred at rt for 24 h. By slow addition of acetic acid the raw product was precipitated. The reaction solution was filtrated and the residue was washed with $CHCl_3$ by column chromatograph to give complex **8** as orange solid (230 mg, 0.305 mmol, 68%). mp 201 °C. IR $\tilde{\nu}$(KBR pellets, cm^{-1}): 3855, 3823, 3753, 3448, 3034, 2362, 1614, 1587, 1508, 1446, 1371, 1328, 1272, 1240, 1176, 1093, 1028, 968, 898, 821, 754, 698, 617, 588, 561, 512, 391.^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 6.8 Hz, 2H), 7.41 (d, *J* = 4.2 Hz, 1H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 6.8 Hz, 2H), 7.27 (t, *J* = 7.0 Hz 4H), 7.11 (dd, *J* = 8.7 Hz, 1.1 Hz, 4H), 7.06 (t, *J* = 7.31 Hz, 2H), 7.04–7.00 (m, 4H), 6.95 (d, *J* = 16 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.4, 150.8, 148.4, 148.3, 147.3, 143.9, 135.3, 131,8, 129.6, 129.4, 128.6, 127.6, 126.9, 124.9, 123.5, 122.7, 120.6, 118.6 ppm. ^{15}N-NMR (51 MHz, $CDCl_3$): δ = 316.4, 199.7, 102.4 ppm. HRMS (ESI): M^+, found 431.1576. $C_{37}H_{36}N_6O_4SClCo$ requires 431.1576.

4.2.5. Preparation of PS3-TiO_2-Pt composite

$H_2[PtCl_6]\cdot 6H_2O$ (8.5 mg, 16.4 μmol) was dissolved in methanol (2 mL) and added to a suspension of TiO_2 (AEROXIDE® P25, 320 mg, 4 mmol) in methanol (5 mL). The mixture was stirred and radiated with an LED-lamp (white, 10 W) for 2 h. The TiO_2-Pt-composite was centrifuged (5 min, 4000 min^{-1}), washed with methanol (5 ×) and dried under vacuum. The product was obtained as light grey powder.

The dye **PS3** (396 μg, 0,69 μmol) was dissolved in methanol (2 mL). Pt-TiO_2 (20,7 mg) was added and the mixture was dispersed under sonication. Thereafter, the mixture was stirred for 24 h under the absence of light. The desired solid was isolated via centrifugation (5 min, 4000 min^{-1}), washed with methanol (5 ×) and dried under vacuum. The desired product was obtained as pale red solid.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.tet.2017.11.053.

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