

Synthesis and Characterization of New Iridium Photosensitizers for Catalytic Hydrogen Generation from Water

Felix Gärtner,^[a] Stefania Denurra,^[a] Sebastian Losse,^[a] Antje Neubauer,^[b] Albert Boddien,^[a] Anilkumar Gopinathan,^[a] Anke Spannenberg,^[a] Henrik Junge,^[a] Stefan Lochbrunner,^{*,[b]} Matthias Blug,^[c] Sascha Hoch,^[c] Jens Busse,^[c] Serafino Gladiali,^{*,[a, d]} and Matthias Beller^{*,[a]}

Abstract: Novel phenylazole ligands were applied successfully in the synthesis of cyclometalated iridium(III) complexes of the general formula $[\text{Ir}(\text{phenylazole})_2(\text{bpy})]\text{PF}_6$ (bpy = 2,2'-bipyridine). All complexes were fully characterized by NMR, IR, and MS spectroscopic studies as well as by cyclic voltammetry. Three crystal structures obtained by X-ray analysis complemented the spectroscopic investiga-

tions. The excited-state lifetimes of the iridium complexes were determined and showed to be in the range of several hundred ns to multiple μs . All obtained iridium complexes were active as photosensitizers in catalytic hydro-

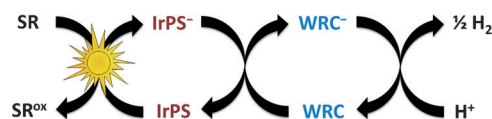
Keywords: hydrogen • iridium • iron • photochemistry • photosensitizer

gen evolution from water in the presence of triethylamine as a sacrificial reducing agent. Applying an in situ formed iron-based water reduction catalyst derived from $[\text{HNET}_3]^+[\text{HFe}_3(\text{CO})_{11}]^-$ and tris[3,5-bis(trifluoromethyl)-phenyl]phosphine as the ligand, $[\text{Ir}(2\text{-phenylbenz-oxazole})_2(\text{bpy})]\text{PF}_6$ proved to be the most efficient complex giving a quantum yield of 16 % at 440 nm light irradiation.

Introduction

The development of novel ways to generate and store energy that are not based on fossil resources is a prerequisite for the sustainable growth of our society.^[1] In this respect, sunlight with a power rate of 120 000 TW provides multiple amounts of the world's energy needs.^[2] To store this energy and to use it on demand, hydrogen is considered to be one of the favorite secondary energy carriers. It can be

used efficiently in fuel cells and does not produce critical exhaust gases.^[3] Among the different ways to produce "green" hydrogen without concomitant formation of carbon dioxide, the catalytic splitting of water into hydrogen and oxygen with the aid of visible light is an interesting option for research.^[4] Promising approaches have been reported by using heterogeneous catalysts.^[5] However, homogeneous catalysis is also rapidly emerging in this field, and various protocols for the generation of oxygen^[6] and hydrogen^[7] from water have been published. A key challenge in this area is the design of more efficient photosensitizers (PSs) that absorb visible light leading to charge-separated and long-lived excited states. From the latter, the negative charge and the positive charge can theoretically be used for water reduction (hydrogen generation) and water oxidation (oxygen generation), respectively. Hence, the fundamental task of a PS is the creation of a long-lived excited state. By using a model system, this state undergoes reductive quenching with a so-called sacrificial reductant (SR). Then, the reduced form of the PS can transfer an electron onto a water-reduction catalyst (WRC) and is regenerated to the PS ground state. The WRC itself transfers electrons onto aqueous protons to give hydrogen (Scheme 1).



Scheme 1. General reaction scheme for water reduction employing a SR, an Ir-PS, and a WRC.

[a] F. Gärtner, S. Denurra, Dr. S. Losse, A. Boddien, Dr. A. Gopinathan, Dr. A. Spannenberg, Dr. H. Junge, Prof. Dr. S. Gladiali, Prof. Dr. M. Beller
Leibniz Institute for Catalysis
Albert-Einstein-Strasse 29a
18059 Rostock (Germany)
Fax: (+49) 381-128-151113
E-mail: matthias.beller@catalysis.de

[b] Dr. A. Neubauer, Prof. Dr. S. Lochbrunner
University of Rostock, Department of Physics
Universitätsplatz 3
18055 Rostock (Germany)

[c] Dr. M. Blug, Dr. S. Hoch, Dr. J. Busse
Evonik Industries AG
Paul-Baumann-Strasse 1
45764 Marl (Germany)

[d] Prof. Dr. S. Gladiali
Universita di Sassari,
Dipartimento di Chimica, 07100 (Italy)

[*] These authors contributed equally to this work

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201103670>.

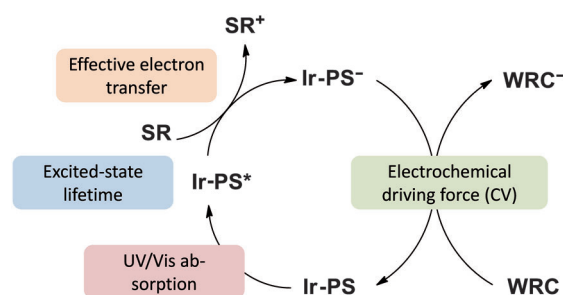
Such a multicomponent system represents one of the two half-reactions of the photocatalytic water-splitting process, which is deemed to be a potential solution for green and sustainable hydrogen production. So far, a variety of PSs are known including examples on the basis of ruthenium,^[9] platinum,^[10] rhenium,^[11] or organic dyes.^[12] More recently, iridium complexes in particular have emerged as active PSs.^[13,14] Notably, the first iridium PSs (Ir-PSs) were reported by Bernhard et al.,^[13] who showed that various complexes of the general formula $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]\text{PF}_6$ ($\text{C}^{\wedge}\text{N}$ =metalated (substituted) phenyl pyridine ligand; $\text{N}^{\wedge}\text{N}$ =(substituted) bipyridine (bpy) ligand) were accessible with high-throughput techniques. The structures were applied successfully as PSs with water-reduction catalysts based on platinum,^[13b] rhodium,^[13c] or cobalt.^[15] Some of us as well as other groups demonstrated that Ir-PS can also be used efficiently in combination with WRCs based on simpler iron catalysts.^[16,17] Recently, we also reported new Ir-PSs, which were synthesized from 6,6'-substituted bipyridines.^[16c] The complex $[\text{Ir}(\text{ppy})_2(6\text{-iPr-bpy})]\text{PF}_6$ (ppy=phenylpyridine) was identified as a more active PS than the basic structure with unsubstituted bipyridine and proved to be efficient in combination with a variety of potential WRCs based on Mn, Fe, Co, Rh, or Pt.^[16c] However, studies applying other neutral N,N -bis-imine-type ligands showed clearly that the catalytic activity of the final Ir-PS is strictly connected to the presence of a bpy ligand.^[16d] With respect to the $\text{C}^{\wedge}\text{N}$ -ligand in the Ir-PS structure, recent studies are limited to phenylpyridines as cyclometalating ligands.^[13] Therefore, we have drawn our attention to new Ir-PS with $\text{C}^{\wedge}\text{N}$ -ligands other than phenylpyridines. Because phenylazoles can be synthesized in a variety of different structural motifs, we chose this ligand class for our investigations. Herein, we report for the first time the synthesis, characterization, and photophysics of this new class of Ir-PS derived from phenyl azoles as well as their application in water-reduction reactions.

Results and Discussion

Complex synthesis and characterization: Six complexes of the general type $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]\text{PF}_6$, in which $\text{C}^{\wedge}\text{N}$ =substituted phenylazole and $\text{N}^{\wedge}\text{N}$ =bpy, were synthesized in a straightforward manner by the reaction of $\text{IrCl}_3\cdot\text{H}_2\text{O}$ with the respective $\text{C}^{\wedge}\text{N}$ ligand.^[16c,25] Subsequent reaction of the formed μ -chloro-bridged dimers with bpy (1 equiv) afforded the Ir-PS complexes **1–6** in moderate to excellent yields (Figure 1). All complexes were fully characterized, and crystals suitable for X-ray diffraction analysis were obtained for Ir-PSs **2**, **4**, and **6** (Figure 1). Notably, coordination of all the iridium centers can be described as distorted octahedral by the $(\text{C}^{\wedge}\text{N})_2\text{N}^{\wedge}\text{N}$ -ligand regime. In the three examples, both nitrogen atoms of the phenylazole ligands are coordinated *trans* to each other. The average Ir–N(bpy) and Ir–N(azole) distances for **2**, **4**, and **6** as well as the Ir–C(phenyl) distances are within the typical range (Figure 1).^[16c,18] The average

C9–C10 and C17–C18 distance in Ir-PS **2** is 1.538 Å, which clearly indicates a single bond in the azole moiety.

For a successful application of the synthesized complexes as PSs, the latter have to fulfill various criteria (Scheme 2).



Scheme 2. Essential characteristics of an Ir-PS: UV/Vis absorption, excited-state lifetime, efficient electron transfer, and electrochemical driving force.

In addition to the trivial prerequisite of light absorption, the formed excited state should survive as long as effective electron transfer from the SR to the Ir-PS* is feasible. Moreover, the reduced Ir-PS[–] species has to possess sufficient reduction potential to transfer an electron onto the WRC. Therefore, all synthesized Ir-PSs were characterized by steady-state UV/Vis, steady-state and time-resolved photoluminescence (PL) analysis, and cyclic voltammetry (CV; Table 1). All complexes show strong absorption in the UV region (Table 1 and Figure SI1 in the Supporting Information). At longer wavelengths, the absorption levels off and drops to zero at wavelengths > 500 nm. The emission maxima of the complexes are summarized in Table 1 and vary from 528 nm for **PS3** to 592 nm for **PS2** (see Figure SI2 in the Supporting Information for the respective PL spectra).

Interestingly, the novel Ir-PSs studied here reveal an even longer excited state lifetime (τ_{PL}) than observed for the standard photosensitizer $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ (**PS7**, 360 ns) ranging from about half a μs for **PS2** up to almost six μs for **PS1** and **PS3** (Table 1). Although some reports on excited-state lifetimes of Ir-complexes exist,^[19a–f] there are only a few examples known of such long τ_{PL} values at room temperature.^[19b,c,e] These long excited-state lifetimes give a strong indication of the triplet nature of the luminescing electronic states of the studied Ir-PS. Most interestingly, even though a long excited-state lifetime is necessary for the following electron-transfer step from the SR to the Ir-PS* a τ_{PL} in the μs range does not seem to further increase the efficiency of the catalytic process (see below).

Notably, all excited-state lifetimes were fitted by monoexponential decay of the PL signal (for **PS2** shown in Figure SI3 in the Supporting Information). For some compounds, the PL decay revealed a second, shorter component (for **PS1** shown in Figure SI4 in the Supporting Information) with only a small contribution, which depends on the wavelength of the PL spectra. This indicates the existence of

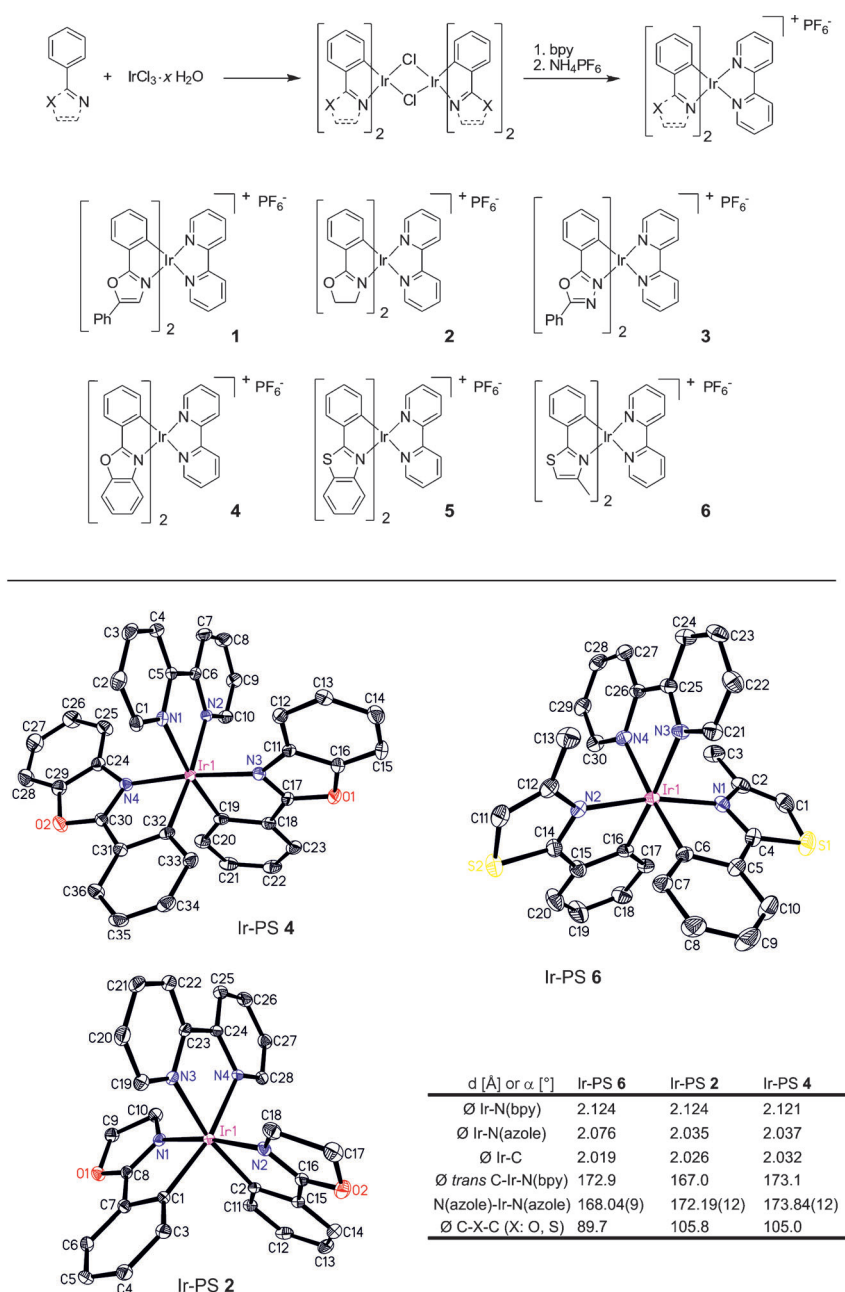


Figure 1. General synthesis of Ir-PSs with the basic structure $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]\text{PF}_6$ and chemical structures of the newly synthesized Ir-PS complexes 1–6. ORTEP representation of the cations $[\text{Ir-PS4}]^+$, $[\text{Ir-PS6}]^+$, and $[\text{Ir-PS2}]^+$. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.^[8]

more than one emitting triplet state for these Ir-PSs, as was reported for the standard photosensitizer **PS7**.^[20]

Moreover, the photoluminescence quantum yield (φ_{PL}) of all Ir-PSs studied here is also relatively large compared with **PS7** (Table 1) with exception of **PS1**. The low φ_{PL} value of **PS1** indicates a small transition dipole moment of the emitting triplet state. This suggests a different electronic nature of the luminescent triplet state, which is likely to be of importance for the catalytic process (see below). Reduction and oxidation potentials of **PS1–PS7** were determined by

CV measurements (Table 1). Essentially, the reduction potential has to be higher than that of the respective WRC (e.g., $-1.21 \text{ V}^{[21]}$ vs. Ag/AgCl for $[\text{HFe}_3(\text{CO})_{11}]^-$) to promote an electron transfer from Ir-PS[−] to the WRC. For **PS1–PS6**, the observed reduction potentials are similar or even higher than that of the basic structure **PS7** ranging from -1.21 V versus Ag/AgCl for **PS4** to -1.32 V for **PS2**.

In conclusion, based on the experimental results of CV, UV/Vis, and PL measurements, all the synthesized complexes should be suitable for hydrogen generation from water applying the inexpensive $[\text{HNet}_3][\text{HFe}_3(\text{CO})_{11}]$ WRC.

Hydrogen evolution experiments: Next, the different iridium complexes were tested as PSs for hydrogen evolution from water. In these experiments, we used our previously established iron WRC based on $[\text{HNet}_3][\text{HFe}_3(\text{CO})_{11}]$.^[16] In a typical reaction, the Ir-PS was allowed to react with the Fe-WRC in the presence of triethylamine (TEA) as SR. During light irradiation,^[22] hydrogen evolution occurred, and the gas was collected by an automatic gas burette. After each reaction, the gas was analyzed by GC. Besides traces of solvent and CO, originating from the iron WRC, only hydrogen was detected. All experiments were carried out until no more gas evolution was observed. The turnover number (TON)

of the Ir-PS was calculated with respect to single-electron-transfer processes (Table 1). By using the standard photosensitizer $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ (**PS7**), a TON of 1590 was obtained after 15 h reaction time. Similar or slightly better productivities were observed for **PS4** (TON=1614) and **PS6** (TON=1546), less productivity was obtained applying **PS5**, **PS2**, **PS3**, or **PS1** (Table 1).

The quantum yield for the most active Ir-PS (**PS4**) was determined by using a monochromatic light source.^[23] Therefore, we applied optimized solvent conditions (THF/

Table 1. CV, UV/Vis, PL data, and catalytic results of hydrogen generation for **PS1–PS7**.

Entry	Structure	1st (2nd) E_{red} [V] ^[a]	λ_{abs} [nm] (ϵ_{abs} M ⁻¹ cm ⁻¹) ^[b]	λ_{em} [nm] ^[c]	ϕ_{PL} ^[d]	τ_{PL} [μ s] ^[e]	$V(\text{H}_2)$ [mL] ^[f]	TON Ir-PS ^[g]
1	PS1	−1.28	sh 228 (39 500), 289 (34 100), sh 343 (10 600), sh 395 (7200)	582	0.06	5.8	14	837
2	PS2	−1.32	234 (42 440), 283 (20 400), sh 300 (17 500), sh 346 (7100), sh 367 (5700), sh 450 (1400)	595	0.20	0.58	23	1316
3	PS3	−1.28	sh 246 (27 100), 276 (33 100), sh 300 (25 500), sh 312 (21 500), sh 341 (9100), 388 (6200)	528	0.63	5.6	18	1033
4	PS4	−1.21	246 (41 200), sh 264 (32 800), sh 292 (34 600), 302 (37 100), sh 326 (15 300), sh 352 (10 100), 389 (7600), sh 413 (5600), sh 465 (700)	542	0.57	1.8	28	1614
5	PS5	−1.22 (−1.73)	sh 248 (28 500), 271 (26 200), sh 312 (29 400), 323 (26 500), sh 352 (10 300), 371 (7300), 414 (6000), sh 438 (4900)	564	0.67	3.4	24	1406
6	PS6	−1.24	sh 248 (20 300), sh 275 (21 000), 304 (24 600), sh 349 (6800), 399 (4700), sh 417 (4400)	584	0.31	2.2	27	1546
7 ^[16c]	PS7	−1.23		608	0.15	0.36	27	1590

[a] Solutions in acetonitrile, 0.1 M [NBu₄]PF₆, working electrode: glassy carbon; reference electrode: Ag/AgCl saturated LiCl in EtOH; counter electrode: Pt; scan rate: 100 mV s⁻¹. [b] In THF. [c] λ_{exc} = 365 nm; emission maximum of the corrected spectra (see the Supporting Information). [d] PL quantum yields were obtained for an Ir-PS concentration of 10⁻⁵ M in degassed THF applying quinine bisulfate in 0.05 M H₂SO₄ as standard; λ_{exc} = 365 nm (see the Supporting Information). [e] Excited-state lifetimes from the integrated PL spectra were obtained for an Ir-PS concentration of 10⁻⁵ M in degassed THF; λ_{exc} = 388 nm (see the Supporting Information). [f] Conditions: Ir-PS (1.40 μ mol), [HNET₃][HFe₃(CO)₁₁] (6.2 μ mol), THF/NET₃/H₂O (4:1:1; 10 mL); 25 °C; 15 h; Xe light irradiation (output 1.5 W); no light filter; gas evolution quantitatively measured with an automatic gas burette; gas analysis by GC. [g] TON Ir-PS = $n(\text{H})/n(\text{Ir-PS})$.

TEA/H₂O = 3:2:1, volume based) as well as an improved WRC derived in situ from [HNET₃][HFe₃(CO)₁₁] and tris-[3,5-bis(trifluoromethyl)phenyl]phosphine.^[16b] In this reaction, 79.5 mL hydrogen (3.25 mmol) evolved during the first 2 h (Figure 2) applying a light flux of 1.5 W (440 nm). This result corresponds to a quantum yield of 16 %.^[24]

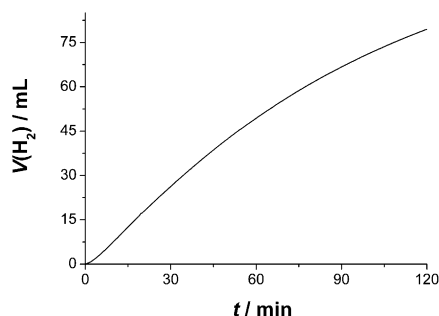


Figure 2. Hydrogen evolution curve obtained in the experiment for the determination of the quantum yield. Reaction conditions: [HNET₃][HFe₃(CO)₁₁] (3.3 μ mol), **PS4** (15.0 μ mol), P[C₆H₃-3,5-(CF₃)₂]₃ (5.0 μ mol), irradiation at 440 nm with 1.5 W, THF/NET₃/H₂O (3:2:1; 20 mL), 25 °C, gas volumes quantitatively measured with automatic gas burettes, gas analysis by GC.

Conclusion

The synthesis of six cyclometalated cationic iridium(III) complexes of the general formula [Ir(phenylazole)₂-(bpy)]PF₆ is described. All novel complexes were fully characterized by using NMR, MS, IR, photoluminescence, UV/Vis and cyclic voltammetry measurements. Moreover, crystal structures of three new Ir-PSs, that is, **PS2**, **PS4**, and **PS6** are reported. The excited-state lifetimes determined by time-resolved photoluminescence measurements are in the multiple μ s range. Interestingly, the long lifetime of the lowest triplet

state does not significantly increase the catalytic performance of the system, which is of interest for the rational development of improved PSs. All complexes were applied as photosensitizers in catalytic hydrogen evolution experiments from water, applying a WRC based on iron in the presence of triethylamine as the SR. The complex [Ir(2-phenyl benzoxazole)₂(bpy)]PF₆ proved to be most efficient and a high quantum yield of 16 % was determined at 440 nm irradiation. The new class of cyclometalating ligands used in this study, represents an interesting alternative beyond classical phenylpyridines as C^N-ligand and might open a new strategy for innovative photocatalytically active compounds.

Experimental Section

All catalytic experiments were carried out under an argon atmosphere. Solvents were purified and degassed by standard procedures prior to use. All ligands were purchased from commercial suppliers (Sigma-Aldrich, Acros). The cyclometalated iridium dimers were prepared according to published protocols.^[25] The amounts of evolved gases were quantitatively measured by automatic gas burettes and qualitatively by GC (gas chromatograph HP 6890N, carboxen 1000, TCD or TCD + methanizer/FID, external calibration).^[16b,26] The light source was a 300 W Xe lamp.^[22]

General protocol for the synthesis of [(C^N)₂Ir(N^AN)]PF₆ complexes:

a) Reaction in CH₂Cl₂/EtOH: the respective 2-bpy ligand (typically 0.35 mmol) and [(C^N)₂Ir- μ -Cl]₂ (typically 0.14 mmol) were stirred in a mixture of CH₂Cl₂ (3.5 mL) and ethanol (3.5 mL) for 24 h. In each case, a clear yellow-orange solution was obtained, and the solvents were removed under reduced pressure. The residue was dissolved in H₂O (30 mL), and the water layer was extracted with Et₂O (3 \times 20 mL). The product was precipitated by counterion metathesis by using NH₄PF₆ (0.5 g in H₂O). The solid was isolated by suction filtration, washed with water, and dried under high vacuum to give the pure iridium complex as a yellow to orange solid. *b) Reaction in ethylene glycol:* the respective 2-bpy ligand (typically 0.20 mmol) and [(C^N)₂Ir- μ -Cl]₂ (typically 0.09 mmol) were suspended in ethylene glycol (6 mL), and the resulting mixture was heated to 150 °C for 12 h. After cooling to RT, the solution was dropped into water (60 mL), and the aqueous layer was extracted with Et₂O (3 \times 20 mL). Remaining traces of ether were removed by heat-

ing the aqueous layer to 85°C for 5 min. A solution of NH_4PF_6 (1 g in H_2O) was added to the cooled aqueous solution. The resulting precipitate was collected by suction filtration and washed with water and Et_2O . After drying under vacuum, the PS was obtained as a yellow to orange solid.

Synthesis of PS1: Prepared by using method (a) for 24 h to give a yellow solid; yield 74%. ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$): δ = 8.90 (d, 2H, J = 8.2 Hz), 8.30 (dt, 2H, J = 1.5 Hz, J = 7.9 Hz), 8.03–8.01 (m, 2H), 7.85–7.82 (m, 4H), 7.76–7.73 (m, 4H), 7.65 (s, 2H), 7.52–7.42 (m, 6H), 7.12–7.06 (m, 4H), 6.71–6.68 ppm (m, 2H); ^{13}C NMR (75 MHz, $[\text{D}_6]\text{DMSO}$): δ = 173.8, 156.1, 151.5, 151.4, 147.5, 139.6, 132.2, 131.8, 129.4, 129.3, 129.2, 128.6, 128.5, 126.2, 124.6, 124.4, 124.1, 122.7, 120.5 ppm (several signals in the aromatic region overlap); ATR-IR: $\tilde{\nu}$ = 3123 (w), 2963 (w), 1594 (w), 1459 (w), 1400 (w), 1260 (w), 1157 (w), 1096 (bw), 1038 (w), 1020 (w), 937 (w), 832 (s), 800 (m), 771 (m), 756 (w), 735 (m), 687 (m), 653 (w), 556 cm^{-1} (s); HRMS (ESI): m/z : calcd for $[\text{C}_{40}\text{H}_{24}\text{IrN}_4\text{O}_2]^+$: 789.18383 $[M]^+$; found: 789.18419.

Synthesis of PS2: Prepared by using method (a) for 24 h to give a yellow solid; yield 74%. ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$): δ = 8.82 (d, 2H, J = 8.3 Hz), 8.25 (dt, 2H, J = 1.4 Hz, J = 7.9 Hz), 7.96–7.94 (m, 2H), 7.72–7.68 (m, 2H), 7.36 (d, 2H, 7.3 Hz), 7.17–7.09 (m, 4H), 7.02 (dt, 2H, J = 1.3 Hz, J = 7.3 Hz), 5.06–4.94 (m, 2H), 4.75–4.65 (m, 2H), 3.61–3.50 (m, 2H), 3.09–2.99 ppm (m, 2H); ^{13}C NMR (75 MHz, $[\text{D}_6]\text{DMSO}$): δ = 179.4, 156.3, 151.1, 150.7, 139.1, 132.5, 132.4, 130.1, 128.1, 126.5, 124.2, 121.8, 71.6, 49.2 ppm; ATR-IR: $\tilde{\nu}$ = 3048 (w), 2884 (w), 1625 (m), 1580 (w), 1456 (m), 1433 (w), 1406 (m), 1282 (w), 1139 (w), 1041 (w), 917 (w), 836 (s), 764 (m), 733 (m), 679 (m), 556 (s), 505 cm^{-1} (w); HRMS (ESI): m/z : calcd for $[\text{C}_{28}\text{H}_{24}\text{IrN}_4\text{O}_2]^+$: 639.1500 $[M]^+$; found: 639.1503; crystals suitable for X-ray diffraction analysis were grown from a DMF– H_2O mixture.

Synthesis of PS3: Prepared by using method (a) for 48 h to give a yellow-orange solid; yield 17%. ^1H NMR (300 MHz, CD_2Cl_2): δ = 8.43 (d, 2H, J = 8.0 Hz), 8.21–8.11 (m, 4H), 8.02–7.99 (m, 4H), 7.81–7.78 (m, 2H), 7.65–7.49 (m, 8H), 7.21 (dt, 2H, J = 7.4 Hz, J = 1.3 Hz), 7.15 (dt, 2H, J = 7.5 Hz, J = 1.7 Hz), 6.84–6.81 ppm (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ = 175.6, 164.1, 156.2, 151.7, 147.7, 139.2, 133.0, 132.7, 132.6, 129.0, 127.4, 126.6, 125.5, 124.9, 123.7, 123.2, 121.9 ppm; ATR-IR: $\tilde{\nu}$ = 3051 (w), 1599 (w), 1553 (w), 1519 (w), 1447 (w), 1429 (w), 1251 (w), 1160 (w), 1041 (w), 1022 (w), 988 (w), 834 (s), 768 (m), 733 (m), 710 (m), 687 (m), 556 (m), 438 cm^{-1} (w); HRMS (ESI): m/z : calcd for $[\text{C}_{38}\text{H}_{26}\text{IrN}_6\text{O}_2]^+$: 791.1743 $[M]^+$; found: 791.1744.

Synthesis of PS4: Prepared by using method (b) for 16 h to give a yellow solid; yield 29%. ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$): δ = 8.91 (d, 2H, J = 8.2 Hz), 8.37 (dt, 2H, J = 1.5 Hz, J = 7.9 Hz), 8.16 (d, 2H, J = 5.5 Hz), 7.97 (d, 2H, J = 8.3 Hz), 7.89–7.79 (m, 4H), 7.48 (dt, 2H, J = 1.1 Hz, J = 7.9 Hz), 7.26–7.21 (m, 2H), 7.17 (dt, 2H, J = 1.1 Hz, J = 7.4 Hz), 7.06 (dt, 2H, J = 1.5 Hz, J = 7.5 Hz), 6.55 (d, 2H, 7.3 Hz), 5.68 ppm (d, 2H, J = 7.7 Hz); ^{13}C NMR (75 MHz, $[\text{D}_6]\text{DMSO}$): δ = 176.9, 156.3, 152.1, 149.8, 149.6, 140.4, 136.7, 133.4, 132.5, 128.8, 126.8, 126.7, 126.3, 124.6, 123.1, 113.6, 113.0 ppm. ATR-IR: $\tilde{\nu}$ = 3345 (w), 3050 (w), 1588 (w), 1518 (w), 1449 (m), 1397 (w), 1384 (w), 1256 (w), 1085 (w), 1040 (w), 833 (s), 813 (m), 774 (w), 753 (m), 739 (m), 641 (w), 555 cm^{-1} (m); HRMS (ESI): m/z : calcd for $[\text{C}_{36}\text{H}_{24}\text{IrN}_4\text{O}_2]^+$: 737.2525 $[M]^+$; found: 737.1532; crystals suitable for X-ray diffraction analysis were grown from a CH_3CN – Et_2O mixture.

Synthesis of PS5: Prepared by using method (a) for 72 h to give a yellow solid; yield 57%. ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$): δ = 8.85 (d, 2H, J = 8.1 Hz), 8.34–8.20 (m, 2H), 8.24 (d, 2H, J = 8.0 Hz), 8.06–8.01 (m, 4H), 7.82–7.77 (m, 2H), 7.42 (dd, 2H, J = 7.6 Hz, J = 7.6 Hz), 7.20–7.10 (m, 4H), 6.93 (dd, 2H, J = 6.9 Hz, J = 6.9 Hz), 6.30 (d, 2H, J = 7.5 Hz), 6.09 ppm (d, 2H, J = 8.4 Hz); ^{13}C NMR (75 MHz, $[\text{D}_6]\text{DMSO}$): δ = 181.2, 156.1, 150.5, 150.3, 148.6, 140.5, 140.0, 132.7, 132.1, 131.3, 129.1, 128.1, 127.1, 126.1, 124.8, 124.8, 123.2, 116.7 ppm; ATR-IR: $\tilde{\nu}$ = 3054 (w), 2914 (w), 1580 (w), 1550 (w), 1469 (w), 1446 (m), 1437 (m), 1407 (w), 1297 (w), 1266 (w), 1158 (w), 1050 (w), 1026 (w), 995 (w), 835 (s), 770 (m), 753 (s), 737 (m), 724 (m), 556 (s), 449 cm^{-1} (w); HRMS (ESI): m/z : calcd for $[\text{C}_{36}\text{H}_{24}\text{IrN}_4\text{S}_2]^+$: 769.10647 $[M]^+$; found: 769.10618.

Synthesis of PS6: Prepared by using method (a) for 24 h to give a yellow solid; yield 60%. ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$): δ = 8.85 (d, 2H, J =

8.1 Hz), 8.26 (dt, 2H, J = 1.5 Hz, J = 7.9 Hz), 7.89 (d, 2H, J = 5.5 Hz), 7.77 (dd, 2H, J = 1.0 Hz, J = 7.6 Hz), 7.71–7.66 (m, 2H), 7.42 (d, 2H, J = 0.9 Hz), 7.05 (dt, 2H, J = 1.1 Hz, J = 7.5 Hz), 6.94 (dt, 2H, J = 1.35 Hz, J = 7.5 Hz), 6.30 (d, 2H, J = 7.2 Hz), 1.44 ppm (s, 6H); ^{13}C NMR (75 MHz, $[\text{D}_6]\text{DMSO}$): δ = 179.5, 156.0, 150.9, 150.1, 148.2, 140.8, 139.7, 132.3, 130.6, 128.6, 124.8, 122.8, 114.9, 15.1 ppm (several signals in the aromatic region overlap); ATR-IR: $\tilde{\nu}$ = 3054 (w), 1603 (w), 1582 (w), 1544 (w), 1444 (m), 1381 (w), 1320 (w), 1281 (w), 1246 (w), 1032 (w), 836 (s), 764 (m), 730 (m), 556 (s), 436 cm^{-1} (w); HRMS (ESI): m/z : calcd for $[\text{C}_{30}\text{H}_{24}\text{IrN}_4\text{S}_2]^+$: 679.10641 $[M]^+$; found: 697.10649; crystals suitable for X-ray diffraction analysis were grown from a DMF– H_2O mixture.

General procedure for hydrogen evolution experiments: A double-walled thermostatically controlled reaction vessel was evacuated and filled with argon six times to remove any other gas. The Ir-PS and the WRC were added through a Teflon crucible or as freshly prepared stock solutions by syringe. The solvent mixture of THF/TEA/ H_2O was added, and the temperature was maintained at 25°C by a thermostat. The reaction was started after stirring for 8 min at 25°C by switching on the light source. The amount of evolved gas was measured with an automatic gas burette, and gases were analyzed by GC after each reaction. The variability of gas evolution is typically 1–10%.

Acknowledgements

Parts of this work have been supported by Evonik Degussa GmbH (part financed by the State of North Rhine-Westphalia and co-financed by the European Union Investing in our Future, European Regional Development Fund) and supported by the BMBF (Spitzenforschung und Innovation in den neuen Ländern). We thank A. Kammer and P. Bartels for their excellent analytical and technical support. F.G. thanks the Fonds der Chemischen Industrie (FCI) for a Kekulé grant.

- [1] a) Q. Schiermeier, J. Tollefson, T. Scully, A. Witze, *Nature* **2008**, *454*, 816–823; b) N. Armaroli, V. Balzani, *Angew. Chem.* **2007**, *119*, 52–67; *Angew. Chem. Int. Ed.* **2007**, *46*, 52–66.
- [2] a) R. E. Blankenship, D. M. Tiede, J. Barber, G. W. Brudvig, G. Fleming, M. Ghirardi, M. R. Gunner, W. Junge, D. M. Kramer, A. Melis, T. A. Moore, C. C. Moser, D. G. Nocera, A. J. Nozik, D. R. Ort, W. W. Parson, R. C. Prince, R. T. Sayre, *Science* **2011**, *332*, 805–809; b) V. Balzani, A. C. M. Venturi, *ChemSusChem* **2008**, *1*, 26–58; c) T. R. Cook, D. K. Dogutan, S. Y. Reece, Y. Surendranath, T. S. Teets, D. G. Nocera, *Chem. Rev.* **2010**, *110*, 6474–6502.
- [3] a) J. D. Holladay, J. Hu, D. L. King, Y. Wang, *Catal. Today* **2009**, *139*, 244–260; b) N. Armaroli, V. Balzani, *ChemSusChem* **2011**, *4*, 21–36.
- [4] a) N. S. Lewis, D. G. Nocera, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15729–15735.
- [5] For reviews on heterogeneous water splitting catalysts, see: a) X. Chen, S. Shen, L. Guo, S. S. Mao, *Chem. Rev.* **2010**, *110*, 6503–6570; b) A. Kudo, Y. Miseki, *Chem. Soc. Rev.* **2009**, *38*, 253–278; c) F. E. Osterloh, *Chem. Mater.* **2008**, *20*, 35–54; d) K. Maeda, K. Domen, *J. Phys. Chem. C* **2007**, *111*, 7851–7861.
- [6] For a recent review on homogeneous water oxidation systems, see: X. Sala, I. Romero, M. Rodriguez, L. Escriche, A. Llobet, *Angew. Chem.* **2009**, *121*, 2882–2893; *Angew. Chem. Int. Ed.* **2009**, *48*, 2842–2852.
- [7] For reviews on light-driven water reduction systems, see: a) M. Wang, Y. Na, M. Gorlov, L. Sun, *Dalton Trans.* **2009**, 6458–6467; b) L. L. Tinker, N. D. McDaniel, S. Bernhard, *J. Mater. Chem.* **2009**, *19*, 3328–3337; c) E. D. Cline, S. Bernhard, *Chimia* **2009**, *63*, 709–713; d) T. S. Teets, D. G. Nocera, *Chem. Commun.* **2011**, 47, 9268–9274.
- [8] CCDC-843824, CCDC-843825, and CCDC-843826 contain 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.
- [9] Recent examples: a) N. S. McCool, D. M. Robinson, J. E. Sheats, G. C. Dismukes, *J. Am. Chem. Soc.* **2011**, *133*, 11446–11449; b) Y. Sano, A. Onoda, T. Hayashi, *Chem. Commun.* **2011**, *47*, 8229–8231; c) M. P. McLaughlin, T. M. McCormick, R. Eisenberg, P. L. Holland, *Chem. Commun.* **2011**, *47*, 7989–7991.
- [10] Recent examples: a) P. Du, J. Schneider, G. Luo, W. W. Brennessel, R. Eisenberg, *Inorg. Chem.* **2009**, *48*, 4952–4962; b) X. Wang, S. Goeb, Z. Ji, N. A. Pogulaichenko, F. N. Castellano, *Inorg. Chem.* **2011**, *50*, 705–707.
- [11] Recent examples: a) B. Probst, M. Guttentag, A. Rodenberg, P. Hamm, R. Alberto, *Inorg. Chem.* **2011**, *50*, 3404–3412; b) A. J. Morris, G. J. Meyer, E. Fujita, *Acc. Chem. Res.* **2009**, *42*, 1983–1994.
- [12] Recent examples: a) T. M. McCormick, B. D. Calitree, A. Orchard, N. D. Kraut, F. V. Bright, M. R. Detty, R. Eisenberg, *J. Am. Chem. Soc.* **2010**, *132*, 15480–15483; b) L. Gong, J. Wang, H. Li, L. Wang, J. Zhao, Z. Zhu, *Catal. Commun.* **2011**, *12*, 1099–1103.
- [13] a) J. I. Goldsmith, W. R. Hudson, M. S. Lowry, T. H. Anderson, S. Bernhard, *J. Am. Chem. Soc.* **2005**, *127*, 7502–7510; b) L. L. Tinker, N. D. McDaniel, P. N. Curtin, C. K. Smith, M. J. Ireland, S. Bernhard, *Chem. Eur. J.* **2007**, *13*, 8726–8732; c) E. D. Cline, S. E. Adamson, S. Bernhard, *Inorg. Chem.* **2008**, *47*, 10378–10388; d) L. L. Tinker, S. Bernhard, *Inorg. Chem.* **2009**, *48*, 10507–10511; e) P. N. Curtin, L. L. Tinker, C. M. Burgess, E. D. Cline, S. Bernhard, *Inorg. Chem.* **2009**, *48*, 10498–10506; f) S. Metz, S. Bernhard, *Chem. Commun.* **2010**, *46*, 7551–7553.
- [14] C. Ulbricht, B. Beyer, C. Friebe, A. Winter, U. S. Schubert, *Adv. Mater.* **2009**, *21*, 4418–4441.
- [15] V. Artero, M. Chavarot-Kerlidou, M. Fontecave, *Angew. Chem.* **2011**, *123*, 7376–7405; *Angew. Chem. Int. Ed.* **2011**, *50*, 7239–7262; b) S. Losse, J. G. Vos, S. Rau, *Coord. Chem. Rev.* **2010**, *254*, 2492–2504.
- [16] For examples from our own group, see: a) F. Gärtner, B. Sundararaju, A.-E. Surkus, A. Boddien, B. Loges, H. Junge, P. H. Dixneuf, M. Beller, *Angew. Chem.* **2009**, *121*, 10147–10150; *Angew. Chem. Int. Ed.* **2009**, *48*, 9962–9965; b) F. Gärtner, A. Boddien, D. Hollmann, E. Barsch, K. Fumino, H. Junge, R. Ludwig, A. Brückner, M. Beller, *Chem. Eur. J.* **2011**, *17*, 6425–6436; c) F. Gärtner, D. Cozzula, S. Losse, A. Boddien, G. Anilkumar, H. Junge, T. Schulz, N. Marquet, A. Spannenberg, S. Gladiali, M. Beller, *Chem. Eur. J.* **2011**, *17*, 6998–7006; d) For the role of the bpy-radical anion in the reduced state of the Ir-PS. see: D. Hollmann, F. Gärtner, R. Ludwig, E. Barsch, H. Junge, M. Blug, S. Hoch, M. Beller, A. Brückner, *Angew. Chem.* **2011**, *123*, 10429–10433; *Angew. Chem. Int. Ed.* **2011**, *50*, 10246–10250.
- [17] For other recent examples applying Fe-WRCs, see: a) Y. Na, M. Wang, J. Pan, P. Zhang, B. Åkermark, L. Sun, *Inorg. Chem.* **2008**, *47*, 2805–2810; b) P. Zhang, M. Wang, Y. Na, X. Li, Y. Jiang, L. Sun, *Dalton Trans.* **2010**, *39*, 1204–1206; c) D. Streich, Y. Astuti, M. Orlandi, L. Schwartz, R. Lomoth, L. Hammarström, S. Ott, *Chem. Eur. J.* **2010**, *16*, 60–63; d) F. Wang, W.-G. Wang, X.-J. Wang, H.-Y. Wang, C.-H. Tung, L.-Z. Wu, *Angew. Chem.* **2011**, *123*, 3251–3255; *Angew. Chem. Int. Ed.* **2011**, *50*, 3193–3197.
- [18] a) R. D. Costa, E. Orti, H. J. Bolink, S. Graber, S. Schaffner, M. Neuburger, C. E. Housecroft, E. C. Constable, *Adv. Funct. Mater.* **2009**, *19*, 3456–3463; b) E. Baranoff, I. Jung, R. Scopelliti, E. Solari, M. Grätzel, K. Nazeeruddin, *Dalton Trans.* **2011**, *40*, 6860–6867.
- [19] a) R. D. Costa, F. Monti, G. Accorsi, A. Barbieri, H. J. Bolink, E. Orti, N. Armadori, *Inorg. Chem.* **2011**, *50*, 7229–7238; b) H.-S. Duan, P.-T. Chou, C.-C. Hsu, J.-Y. Hung, Y. Chi, *Inorg. Chem.* **2009**, *48*, 6501–6508; c) P.-K. Lee, W. H.-T. Law, H.-W. Liu, K. K.-W. Lo, *Inorg. Chem.* **2011**, *50*, 8570–8579; d) T. Sajoto, P. I. Djurovich, A. B. Tamayo, J. Oxgaard, W. A. Goddard, M. E. Thompson, *J. Am. Chem. Soc.* **2009**, *131*, 9813–9822; e) M. S. Lowry, W. R. Hudson, R. A. Pascal, S. Bernhard, *J. Am. Chem. Soc.* **2004**, *126*, 14129–14135; f) S. Ladouceur, D. Fortin, E. Zysman-Colman, *Inorg. Chem.* **2010**, *49*, 5625–5641.
- [20] K. A. King, R. J. Watts, *J. Am. Chem. Soc.* **1987**, *109*, 1589–1590.
- [21] A. M. Bond, P. A. Dawson, B. M. Peake, B. H. Robinson, J. Simpson, *Eur. J. Inorg. Chem.* **1977**, *16*, 2199–2206.
- [22] Specification of the Xe light source (Lot-Oriel-300-W-Xe lamp, LSB530), see: <http://www.lot-oriel.com>; power output determined by a thermopile.
- [23] Specification of the Hg vapor light source: Lumatec-Superlite 400; power output determined by a thermopile.
- [24] For details on the determination of quantum yield, see the Supporting Information.
- [25] a) V. V. Krisyuk, A. E. Turgambaeva, *Transition Met. Chem.* **2005**, *30*, 786–791; b) F. Xiao, Y. Liu, Z. Hu, Q. Gan, L. Wang, Z. Wen, M. Zhu, W. Zhu, *Synth. Met.* **2009**, *159*, 1308–1312; c) H. W. Hong, T.-M. Chen, *Mater. Chem. Phys.* **2007**, *101*, 170–176; d) S. Laman-sky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau, M. E. Thompson, *Inorg. Chem.* **2001**, *40*, 1704–1711.
- [26] For general information on the experimental setup, see the Supporting Information.

Received: November 22, 2011
Published online: February 14, 2012