New dyes for solar cells based on nanostructured semiconducting metal oxides
Synthesis and characterisation of ruthenium(II) complexes with thiol-substituted ligands

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Abstract

Five azo-dyes: 4-phenylazo-phenol, 4-phenylazo-benzeneamine, 4-phenylazo-benzenethiol, 4-phenylazo-benzoic acid, and 4-phenylazo-pyridine have been prepared and used as a "test kit" for rapid screening of functional group affinity to metal oxides. The dyes with carboxylic acid and thiol gave coloured electrodes both for ZnO and TiO_2 whereas the pyridine had affinity only for TiO_2. Also, *cis*-ruthenium-bis[2,2′-bipyridine]-bis[4-thiopyridine], *cis*-ruthenium-bis[2,2′-bipyridine]-bis[4-pyridinethiolate], *cis*-ruthenium-bis[2,2′-bipyridine]-bis[4-carboxypyridine], and *cis*-ruthenium-bis[2,2′-bipyridine]-[4,4′-dicarboxy-2,2′-bipyridine] have been prepared and adsorbed onto ZnO. In this preliminary photoelectrochemical study, all these ruthenium-bipyridine dyes show electron injection. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Dye-sensitised; ZnO; Azo-dyes; Photoelectrochemistry

1. Introduction

Solar cells based on dye-sensitised nanostructured metal oxides have been studied during the past decade. Among the oxides studied [1–5], the systems based on TiO_2 and ruthenium dicarboxybipyridine complexes are the most extensively studied ones, with overall solar to electric conversion efficiencies over 10% [6–9]. A promising alternative material for solar cell applications is ZnO, which in combination with the dyes developed for TiO_2 has given overall efficiencies of 5% [10–12].

Keis et al. [12,13] have shown that the carboxylated dyes are efficiently adsorbed on ZnO but with an adsorption behaviour different from that of TiO_2. The search for dyes that may improve the characteristics of the solar cells is thus an important and challenging task, in particular when alternative oxides with properties different from those of TiO_2 are investigated.

Of importance for the overall efficiency of the cell is the interaction between the dye and the semiconductor surface. The dye has to be attached to the surface, and the electron injection from the excited dye into the conduction band of the oxide must be efficient. This dye–oxide interaction is mediated by a functional group on one or several of the pyridine units of the dye, most commonly by carboxylic acids or carboxylate groups [7,9].

As synthesis of new dyes can be very time-consuming we decided to develop a "test kit" of easily prepared coloured compounds with different functional groups for rapid screening prior to the synthesis of ruthenium-polypyridyl dyes containing the most promising functional groups. In the present paper, we present the kit, two new ruthenium-polypyridyl dyes with thiol units and preliminary results from a comparative study of the thiol-dyes vs. carboxyl-dyes on ZnO.

2. Experimental

2.1. General

All reagents were from commercial sources and were used without further purification. Column chromatography was performed with Matrex Silica 60A/35–70 μm, Merck Al_2O_3 90 basic (0.063–0.200 mm) and Strem Chemicals Aluminium Oxide, activated, neutral, gamma 96%.

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^{1}H NMR spectra were recorded on a Varian Unity 400 MHz and a Varian Gemini 200 MHz. The chemical shifts are reported using the residual solvent signal as an indirect reference to TMS: CDCl$_3$ 7.26 ppm (^{1}H) and 77.0 ppm (^{13}C), D$_2$O 4.67 ppm (^{1}H) and acetone-d$_6$ 2.05 ppm (^{1}H) and 29.84 ppm (^{13}C). Assignments of the [1]H-signals were based on the chemical shifts and the coupling constants estimated from standard 1D and 2D experiments. UV–Vis spectra were recorded for ethanol solutions on a Varian Cary 3 Bio spectrophotometer using 1 mm quartz cuvettes. Mass spectrometry was carried out on a Finnigan MAT GCQ PLUS System (EI) at 70 eV. Reflectance spectra of ZnO electrodes treated with solutions of **1**–**5** were collected with a Varian Cary 2400 spectrophotometer with an integrating sphere. IPCE measurements were made using a 300 W Xenon arc lamp coupled to a monochromator and the IV-measurements were made using a 1000 W Xenon lamp sun simulator with a 10 cm water filter. The light intensity in these measurements were 100 W/m^2 and the active electrode area was 0.32 cm^2. TiO$_2$ electrodes were provided by Aranyos et al. [14].

2.2. Synthesis

4-Phenylazo-phenol (**1**) [15]. Aniline (0.20 ml, 2.2 mmol) was dissolved in a solution of H$_2$O (10 ml) and conc. HCl (0.7 ml). The solution was cooled to 2 °C on an ice-water bath. A cold solution (3 °C) of aqueous NaNO$_2$ (0.152 g, 2.20 mmol in 10 ml) was added over a period of 3 min. The solution of diazonium salt was added dropwise to a cold (3 °C) and stirred solution of phenol (0.254 g, 2.70 mmol) NaOH (0.40 g, 10 mmol) in H$_2$O (10 ml). The mixture immediately became coloured. After 2.5 h at 3 °C the dark mixture was neutralised by addition of dilute aqueous hydrochloric acid. A brownish orange precipitate was formed and filtered off. The crude product (0.58 g) was purified by chromatography on a silica column (pentane/EtOAc 3.3:1) and then recrystallised from EtOH/H$_2$O to yield 0.24 g (55%) of **1** as yellow-orange crystals, m.p. 148–151 °C (lit. 152–154 °C [16]). ^{1}H NMR (CDCl$_3$) δ 7.91–7.85 (m, 4H, phenol and *o*-phenyl), 7.53–7.48 (m, 2H, *m*-phenyl), 7.47–7.42 (m, 1H, *p*-phenyl), 6.94 (AA'XX', 2H, phenol), 5.34 (s, 1H, OH); ^{13}C NMR (CDCl$_3$) δ 158.2, 152.6, 147.1, 130.4, 129.0, 125.0, 122.5, 115.8; UV–Vis λ_{max} (ε) 425 nm (1.3 × 10^6).

4-Phenylazo-benzeneamine (**2**) [15,17]. It was prepared in two steps:

A. Aniline (0.80 ml, 8.8 mmol) was dissolved in H$_2$O (15 ml) and conc. HCl (1 ml) and the solution was cooled to 3 °C. A cold (3 °C) solution of NaNO$_2$ (0.303 g, 4.39 mmol) in H$_2$O (10 ml) was added dropwise. At the end of the addition a yellow precipitate had started to form. After 15 min of stirring and constant cooling, aqueous NaOAc (1 g, 12.2 mmol, in 4 ml of water) was added over a period of 2 min. The reaction mixture was then diluted with water (7 ml) and was left with stirring

at 2 °C for 45 min. Filtration and drying in air overnight yielded 0.735 g (85%) of the intermediate product diazoaminobenzene.

B. A mixture of diazoaminobenzene (0.735 g, 3.73 mmol), aniline hydrochloride (0.375 g, 2.89 mmol) and aniline (2.0 ml, 22 mmol) was heated at 40–47 °C for 1 h and was then left at 25 °C for 30 min, after which HOAc/H$_2$O (5 ml, 1:1) was added. The mixture was left for 48 h at RT. Then, the precipitate was collected by filtration and washed with H$_2$O. The crude product was purified by chromatography on a silica column (pentane/EtOAc 3:1) and then recrystallised twice from EtOH/H$_2$O to yield 0.33 g (45%) of **2** as orange needles, m.p. 117–120 °C (lit. 122–124 °C [18]). ^{1}H NMR (CDCl$_3$) δ 7.87–7.84 (m, 2H, *o*-phenyl), 7.84–7.80 (AA'XX', 2H, aniline), 7.51–7.46 (m, 2H, *m*-phenyl), 7.43–7.38 (m, 1H, *p*-phenyl), 6.75 (AA'XX', 2H, aniline), 4.05 (s, 2H, NH$_2$); ^{13}C NMR (CDCl$_3$) δ 152.9, 149.5, 145.5, 129.8, 128.9, 125.1, 122.3, 114.6; UV–Vis λ_{max} (ε) 385 nm (2.6 × 10^7).

Nitrosobenzene [19]. In a 250 ml beaker with 100 ml H$_2$O, NH$_4$Cl (3.0 g, 56 mmol) and nitrobenzene (5.1 ml, 50 mmol) was added. Then, with vigorous stirring, Zn dust (7.5 g, 12 mmol) was added over a period of 5 min. The temperature slowly reached 50 °C, and after 30 min, the ZnO was removed by filtration and washed with 60 ml of boiling water. The combined filtrate was immediately transferred to a 500 ml beaker placed in an ice/salt mixture and cooled to 0 °C by addition of ice. A −5 °C mixture of 15 ml H$_2$SO$_4$ in ice was then added, immediately followed by addition of a 0 °C solution of Na$_2$Cr$_2$O$_7$ (3.4 g, 11.4 mmol) in H$_2$O (12.5 ml) under vigorous stirring. After about 2 min, the yellowish precipitate was removed by filtration. The crude product was purified by steam distillation and yielded 4 g (75%) of pure product, which appeared as a green liquid. ^{1}H NMR (CDCl$_3$) δ 7.9 (m, 2H), 7.8–7.5 (m, 3H).

4-Phenylazo-benzenethiol (**3**). It was prepared in two steps. All manipulations in step B have to be carried out in the absence of air:

A. The disulphide of *p*-aminothiophenol (0.45 g, 1.8 mmol) was dissolved in acetic acid (5.7 ml) and nitrosobenzene (0.30 g, 2.8 mmol) was added over a period of 12 min with vigorous stirring. The mixture was left with stirring until all nitrosobenzene had dissolved. Then, the flask was closed and left without stirring at RT for 60 h, after which time the precipitated disulphide was collected and dried in air to yield 0.32 g (41%) of bright orange crystals, m.p. 156–162 °C. ^{1}H NMR (CDCl$_3$) δ 7.95–7.8 (m, 8H, *o*-phenyl to NN unit), 7.7–7.6 (m, 4H, *o*-phenyl to SS unit), 7.6–7.45 (m, 6H, *m*-, *p*-phenyl); MS *m/z* 426 (M$^+$, 100%), 321 (92), 199 (90).

B. Under nitrogen, the disulphide of 4-phenylazo-benzenethiol (0.10 g, 0.23 mmol) was dissolved in ethanol (10 ml) and toluene (4 ml). The solution was heated to 65 °C and glucose (0.126 g, 0.70 mmol) was added. After 3 min,

NaOH (0.10 g, 2.5 mmol) in H_2O (0.5 ml) was added and the reaction was stirred at 65–70 °C for 15–20 min. After cooling to RT, the mixture was diluted with water and extracted once with EtOAc to remove impurities like azobenzene and azoxybenzene. The aqueous phase was then acidified with aqueous diluted HCl. The yellow precipitate was collected by filtration under a flow of N_2 and was dried under reduced pressure to yield 0.04 g (81%) of **3** which was stored under nitrogen. ^{1}H NMR ($CDCl_3$) δ 7.89 (dd, 2H, *o*-phenyl), 7.82 and 7.38 (AA′XX′, 4H, thiolated phenyl), 7.55–7.45 (m, 3H, *m*-, *p*-phenyl); IR 3450, 2950, 1580 cm^{-1}; MS *m/z* 214 (M$^+$, 100%), 137 (77), 109 (80); UV–Vis λ_{max} (ε) 425 nm (2.8×10^6).

4-Phenylazo-benzoic acid (**4**) [20]. *p*-Aminobenzoic acid (0.54 g, 3.9 mmol) was dissolved in warm acetic acid (5 ml) and the solution was cooled to RT. Nitrosobenzene (0.42 g, 3.9 mmol) was then added and the mixture was left with stirring until all nitrosobenzene had dissolved (5 min). The flask was closed and left without stirring and after 15 min precipitation had begun. The precipitate was collected by filtration and the product was washed with acetic acid and water. The gold-orange plate-like crystals were recrystallised twice from EtOH to yield 0.38 g (45%) of **4**. ^{1}H NMR (acetone-d_6) δ 11.5 (br s, 1H, COOH), 8.25 and 8.03 (AA′XX′, 2H each, carboxylated phenyl), 8.01–7.97 (m, 2H, *o*-phenyl), 7.66–7.59 (m, 3H, *m*-, *p*-phenyl); ^{13}C NMR (acetone-d_6) δ 166.9, 155.9, 153.4, 133.4, 132.8, 131.7, 130.3, 123.8, 123.4; UV–Vis λ_{max} (ε) 445 nm (7.5×10^5).

4-Phenylazo-pyridine (**5**) [20]. To a gently heated solution of NaOH (5 g, 125 mmol) in H_2O (5 ml) and toluene (0.5 ml), 4-aminopyridine (0.30 g, 3.2 mmol) was added. The mixture was warmed to 80 °C and nitrosobenzene (0.36 g, 3.4 mmol) was added over 10 min with vigorous stirring. The mixture was stirred for another 10 min after which time it was cooled to ambient temperature and extracted with pentane. After evaporation of the solvent, the crude product was purified by chromatography on a column of basic aluminium oxide with a gradient of pentane/EtOAc 1:0–2:1 to yield 0.15 g (26%) of **5** as orange crystals, m.p. 90–94 °C (lit. 99 °C [21]). ^{1}H NMR ($CDCl_3$) δ 8.81 (AA′XX′, 2H, pyridine), 7.96 (m, 2H, *o*-phenyl), 7.71 (AA′XX′, 2H, pyridine), 7.55 (m, 3H, *m*-, *p*-phenyl); ^{13}C NMR ($CDCl_3$) δ 157.2, 152.3, 151.3, 132.4, 129.2, 123.4, 116.2; UV–Vis λ_{max} (ε) 440 nm (3.8×10^5).

cis-Ruthenium-[2,2′-bipyridine]-dichloride dihydrate [Ru(bpy)$_2$Cl$_2$·2H$_2$O]. It was prepared according to a previously published procedure [22].

cis-Ruthenium-bis[2,2′-bipyridine]-bis[4-thiopyridine]-bis[hexafluorophosphate] (**6**). Under argon atmosphere, Ru(bpy)$_2$Cl$_2$·2H$_2$O (35 mg, 0.067 mmol) 4-thiopyridine (pySH, 16 mg, 0.14 mmol) was dissolved in a 1:1 mixture of absolute ethanol and water. The solution was heated to reflux overnight after which NH$_4$PF$_6$ (219 mg, 1.35 mmol) in water (1 ml) was added to precipitate the complex. The solid was collected by filtration and washed with water and

diethyl ether (5 ml of each) and dried under reduced pressure to yield 47 mg (75%) of **6**, m.p. 198–200 °C (dec.). ^{1}H NMR (acetone-d_6) δ (ppm) 9.99 (ddd, *J* = 0.8, 1.5, 5.7 Hz, 2H, H-6 bpy), 8.66 (ddd, *J* = 0.8, 1.4, 8.2 Hz, 2H, H-3 bpy), 8.61 (ddd, *J* = 0.8, 1.3, 8.2 Hz, 2H, H-3′ bpy), 8.16 (ddd, *J* = 1.5, 7.5, 8.2 Hz, 2H, H-4 bpy), 8.01 (ddd, *J* = 1.5, 7.5, 8.2 Hz, 2H, H-4′ bpy), 7.89 (ddd, *J* = 0.8, 1.5, 5.6 Hz, 2H, H-6′ bpy), 7.79 (ddd, *J* = 1.4, 5.7, 7.5 Hz, 2H, H-5 bpy), 7.74–7.70 (AA′XX′, 8H, pySH), 7.41 (ddd, *J* = 1.3, 5.6, 7.5 Hz, 2H, H-5′ bpy); ^{13}C NMR (acetone-d_6) δ 185.8, 159.5, 158.7, 155.4, 151.6, 137.65, 137.62, 135.2, 127.7, 127.6, 127.5, 124.6, 124.5; UV–Vis λ_{max} (ε) 246 nm (1.2×10^4), 297 (1.8×10^4), 423 (3.9×10^3).

cis-Ruthenium-bis[2,2′-bipyridine]-bis[4-pyridinethiolate] (**7**). It was formed from **6** by filtration through activated neutral aluminium oxide with CH_2Cl_2/methanol 9:1 and evaporating the solvent, m.p. > 300 °C. UV–Vis λ_{max} (ε) 249 nm (3.4×10^4), 296 (3.7×10^4).

cis-Ruthenium-bis[2,2′-bipyridine]-bis[4-carboxypyridine]-bis[hexafluorophosphate] (**8**) [23]. Under argon atmosphere, Ru(bpy)$_2$Cl$_2$·2H$_2$O (33 mg, 0.063 mmol) and *iso*-nicotinic acid (*i*-nic, 156 mg, 1.27 mmol) was dissolved in water (5 ml). The solution was heated to reflux for 8 h after which NH$_4$PF$_6$ (207 mg, 1.27 mmol) in water (1 ml) was added to precipitate the complex. The solid was collected by filtration and washed with water and diethyl ether (5 ml of each) and dried under reduced pressure to yield 21 mg (35%) of **8**, m.p. 160–162 °C (dec.). ^{1}H NMR (D_2O) δ (ppm) 9.00 (ddd, *J* = 0.7, 1.7, 5.7, 2H, H-6), 8.56 (AA′XX′, 4H, *i*-nic), 8.38 (ddd, *J* = 0.7, 1.6, 8.2, 2H, H-3 bpy), 8.30 (ddd, *J* = 1.5, 7.4, 8.2, 2H, H-3′ bpy), 8.12 (ddd, *J* = 1.7, 7.7, 8.2, 2H, H-4 bpy), 7.99 (ddd, *J* = 0.7, 1.7, 5.7, 2H, H-6′ bpy), 7.91 (ddd, *J* = 1.7, 7.4, 8.2, 2H, H-4′ bpy), 7.76 (ddd, *J* = 1.6, 5.7, 7.7, 2H, H-5 bpy), 7.62 (AA′XX′, 4H, *i*-nic), 7.34 (ddd, *J* = 1.5, 5.7, 7.4, 2H, H-5′ bpy); UV–Vis [24] λ_{max} (ε) 244 nm (3.1×10^3), 291 (7.9×10^3), 469 (9.4×10^2).

cis-Ruthenium-bis[2,2′-bipyridine]-[4,4′-dicarboxy-2,2′-bipyridine]-bis[hexafluorophosphate] (**9**). It was prepared according to a modified literature procedure [25]. Under argon atmosphere Ru(bpy)$_2$Cl$_2$·2H$_2$O (78 mg, 0.15 mmol) and 4,4′-dicarboxy-2,2′-bipyridine (dcb, 40 mg, 0.17 mmol) was dissolved in methoxyethanol (10 ml) and the solution was heated to reflux over night. NH$_4$PF$_6$ (489 mg, 3.00 mmol) in water (1 ml) was added to precipitate the complex. The solid was collected by filtration and washed with water and diethyl ether (5 ml of each) and dried under reduced pressure to yield 115 mg (93%) **9**, m.p. 197–201 °C (dec.). ^{1}H NMR (acetone-d_6) δ (ppm) 9.32 (dd, *J* = 0.8, 1.8, 2H, H-3 and H-3′ dcb), 8.84 (ddd, *J* = 0.9, 1.1, 8.2, 2H, H-3 bpy), 8.83 (ddd, *J* = 0.9, 1.3, 8.3, 2H, H-3′ bpy), 8.34 (dd, *J* = 0.8, 5.8, 2H, H-4 and H-4′ dcb), 8.29–8.20 (m, 4H, H-4 and H-4′ bpy), 8.12–8.01 (m, 4H, H-6 and H-6′ bpy), 7.99 (dd, *J* = 1.8, 5.8, 2H, H-5 and H-5′ dcb), 7.61 (ddd, *J* = 1.3, 5.6, 7.7, 2H, H-5 bpy), 7.56 (ddd, *J* = 1.1, 5.6, 7.7, 2H, H-5′ bpy); ^{13}C NMR (acetone-d_6) δ 164.9, 158.8,

157.8, 157.7, 153.7, 152.8, 152.46, 152.44, 139.3, 128.89, 128.85, 127.8, 125.39, 125.38, 124.8; UV–Vis λ_{max} (ε) 245 (2.1×10^4), 287 (4.6×10^4), 357 (7.0×10^3), 465 nm (1.0×10^4).

2.3. Preparation of ZnO electrodes

ZnO powder was prepared according to a modified literature procedure [13]. $Zn(NO_3)_2$ (6.5 g, 34 mmol) and $N(CH_2CH_2OH)_3$ (1.67 g, 11 mmol) was dissolved in 250 ml Milli-Q water. The solution was heated at 95 °C in a tightly sealed screw-capped bottle for 15 h and was then allowed to cool to room temperature. After the aqueous phase was removed, the white precipitate was washed with water (2×10 ml) and then centrifuged before it was dried at 100 °C overnight. The ZnO powder was ground in a mortar and dried for additional 6 h. The dispersion of the ZnO powder and ZnO electrodes were prepared using previously reported methods [26]. The size of the ZnO particles was 150 nm and the film thickness 14 μm (determined by profilometry, Tencor Alpha Step).

Dye-treatment of electrodes. The electrodes were heated to 200 °C for 15 min and placed in solutions of **1–5** (0.5 mM in ethanol, chloroform, dichloromethane and pentane) and of the complexes **6**, **7**, **8** (0.5 mM in absolute ethanol) and **9** (0.5 mM methanol) while still warm (90 °C). Electrodes in solutions of **1–5** were treated for 23 h while those in solutions of **6–8** were left in the dye-bath for 30 min, 1, 2.5, 6, 14 or 25 h and 7 days for treatment with **9**. Three electrodes were treated with each dye for each time. After the dye-treatment, the electrodes were washed with pure solvent (5 ml) and stored in darkness in an air-filled dessicator until they were used.

Photoelectrochemical measurements. It was carried out using a sandwich-type of cell where the ZnO electrode was squeezed together with a Pt-coated SnO_2 counter electrode. To prevent short-circuiting, a piece of tissue paper (Kleenex^{TM}) was used as a spacer and the electrolyte (50 mM I_2, 0.5 mM LiI and 0.5 mM 4-tertbutyl pyridine in 3-metoxypropionitrile) was immersed between the electrodes by the capillary forces.

3. Results and discussion

3.1. Synthesis and evaluation of test kit

For rapid screening of binding, we wanted a series of structurally similar coloured compounds differing only by the functional group. Azobenzene with a functional group in one of the phenyl units serves this purpose, as such compounds are relatively easy to prepare. For screening of binding to ZnO, compounds **1–5** (Fig. 1) were prepared. The first step was to determine if the azo-dyes were adsorbed at all on the oxide surface and thereafter how much dye that was adsorbed.
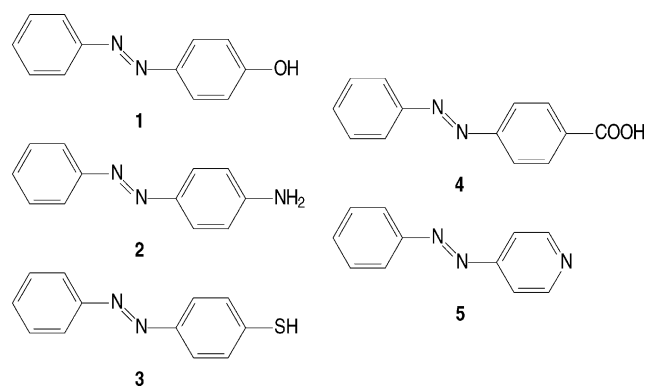

Fig. 1. Azo-dyes in the test kit.

Reacting phenol with the diazonium salt of aniline gave 4-phenylazo-phenol (**1**) [15] in decent yield and the reaction proceeds to yield almost exclusively the *para*-substituted product. 4-Phenylazo-benzeneamine (**2**) [17] was prepared from aniline and the diazonium salt of aniline via the kinetic product azoaminobenzene. The desired product was obtained after heating of the intermediate followed by selective dissolution of the excess aniline by an addition of a solution of acetic acid and water (1:1) to the reaction mixture.

As thiophenol and phenol should possess similar reactivity towards the diazonium salt of aniline, direct electrophilic aromatic substitution to obtain 4-phenylazo-benzenethiol (**3**) was attempted. However, the major isolated product was diphenylsulphide so the disulphide of 4-phenylazo-benzenethiol was instead obtained by reacting the disulphide of 4-aminothiophenol with nitrosobenzene. Selective reductive cleavage of the disulphide bond using glucose [27] then gave **3**. Since the product is sensitive to oxidation it is important to avoid exposure to air, and the purified product should be kept under nitrogen.

4-Phenylazo-benzoic acid (**4**) [19] was obtained from 4-aminobenzoic acid and nitrosobenzene in an one-step reaction where the product precipitates out of the solvent. To form 4-phenylazo-pyridine (**5**) [20], 4-aminopyridine and nitrosobenzene was heated at 80 °C in a mixture of toluene and aqueous sodium hydroxide. The reaction temperature was of importance, as a reaction temperature of 40–50 °C did not give any desired product.

To study the ability of the dyes to bind to ZnO, nanostructured ZnO electrodes were soaked in solutions of the dyes for 23 h and were then washed with pure solvent. As the choice of solvent influences the result of bond formation between the dye and the oxide [28], different solvents (EtOH, CH_2Cl_2, $CHCl_3$ and pentane) were used. For comparative reasons, also TiO_2 electrodes were treated with some of the dye solutions. The results are summarised in Table 1.

The adsorption behaviour of 4-phenylazo-phenol (**1**) and 4-phenylazo-benzeneamine (**2**) were very similar: No adsorption was observed except from pentane solutions. However, as the dye could be washed off by more polar solvents, the bonds between the oxides and these functional

Table 1

Adsorption of compounds **1–5** on ZnO and TiO$_2$ from 0.5 mM solutions in the solvents of the heading[a,b]

Dye	λ_{max}	ε	Oxide	EtOH	CHCl$_3$[c]	CH$_2$Cl$_2$	Pentane	Oxide	EtOH	Pentane
1	445	7.5×10^5	ZnO	N	N	N	M[d]	TiO$_2$	N	S[d]
2	425	2.8×10^6	ZnO	N	N	N	F	TiO$_2$	N	S
3	440	3.8×10^5	ZnO	F[d]	M[d]	–	M[e]	TiO$_2$	F	F[e]
4	425	1.3×10^6	ZnO	F	M	M	–	TiO$_2$	S	–
5	385	2.6×10^7	ZnO	N	N	N	–	TiO$_2$	F	

[a] The amount of each dye is proportional to the depth of the colour as seen by the naked eye.
[b] N: no colour, F: faint colour, M: medium colour, S: strongly coloured, –: not tested.
[c] Stabilised with ~1% EtOH.
[d] 0.25 mM.
[e] <0.25 mM.

groups are very weak. Dyes with such functional groups are thus less likely to give a functional ZnO- or TiO$_2$-based solar cell.

As expected, 4-phenylazo-benzoic acid (**4**) adsorbs to both ZnO and TiO$_2$ from all solvents tried and the TiO$_2$ electrodes were more coloured than were the ZnO electrodes. Also 4-phenylazo-benzenethiol (**3**) adsorbed to both ZnO and TiO$_2$ from all solvents used, and with a slightly higher affinity for ZnO than for TiO$_2$. Thiols could thus be an alternative to carboxylates for ZnO. Although **3** and **4** gave ZnO electrodes with similar depth of colour, the relative amount of dye on the ZnO surface, as estimated from UV–Vis reflectance spectroscopy, were in the range of 10^{-6} mol cm^2 for **4** and 10^{-8} mol cm^2 for **3** [6].

The results for *p*-phenylazo-pyridine (**5**) are interesting, as the dye is adsorbed to TiO$_2$ and not to ZnO. This difference in adsorption properties can explain the observation that the efficiency of TiO$_2$-based solar cells are improved by pyridine treatment [4], whereas such treatment has no effect on the ZnO-based cells [12].

3.2. Synthesis an evaluation of Ru-complexes

To study how the thiols would work as linking groups in real but still easily prepared dyes, *cis*-ruthenium-bis[2,2′-bipyridine]-bis[4-thiopyridine] complexes **6** and **7** (Fig. 2), and as references the corresponding carboxylated complexes **8** and **9**, were prepared.

UV–Vis spectra for the complexes **6–9** in 0.2 mM ethanol solution (Fig. 3) shows that the absorption maximum for **7** is red-shifted compared to **6**, 509 nm vs. 423 nm. Another important difference is the higher absorption coefficient for **7** than for **6**. Even the absorption of **8** is dependent on the
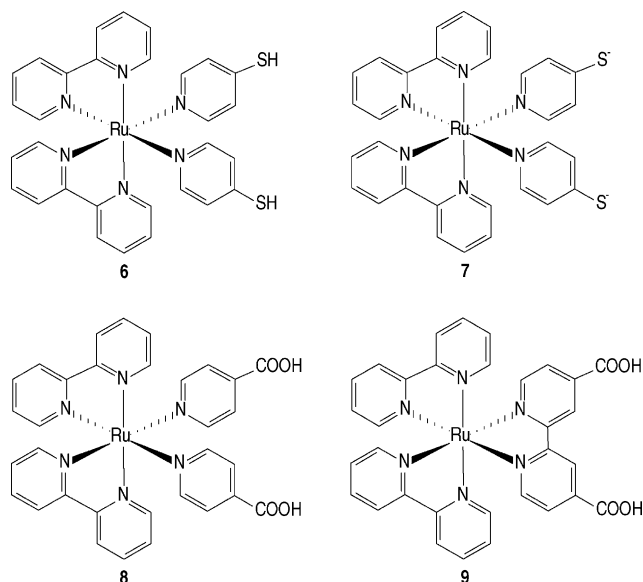

Fig. 2. The Ru(II) pyridine complexes prepared for this study.

pH [24]. The comparatively strong absorption at 465 nm for **9** is probably due to that all ligands are bipyridines.

Treatment of nanostructured ZnO electrodes with Ru-complexes. The dependence of the time the electrodes were placed in the dye-bath (the sensitising time) on the photochemical properties (incident photon-to-current conversion efficiency, IPCE, and current–voltage characteristics) of the resulting sensitised electrodes was studied. The sensitising time was varied between 30 min and 25 h and some results are shown in Fig. 4 and summarised in Table 2.

Table 2

Photoelectrochemical properties for ZnO electrodes treated with solutions of **6**, **7** and **8** (the uncertainty intervals are calculated for 95% confidence)

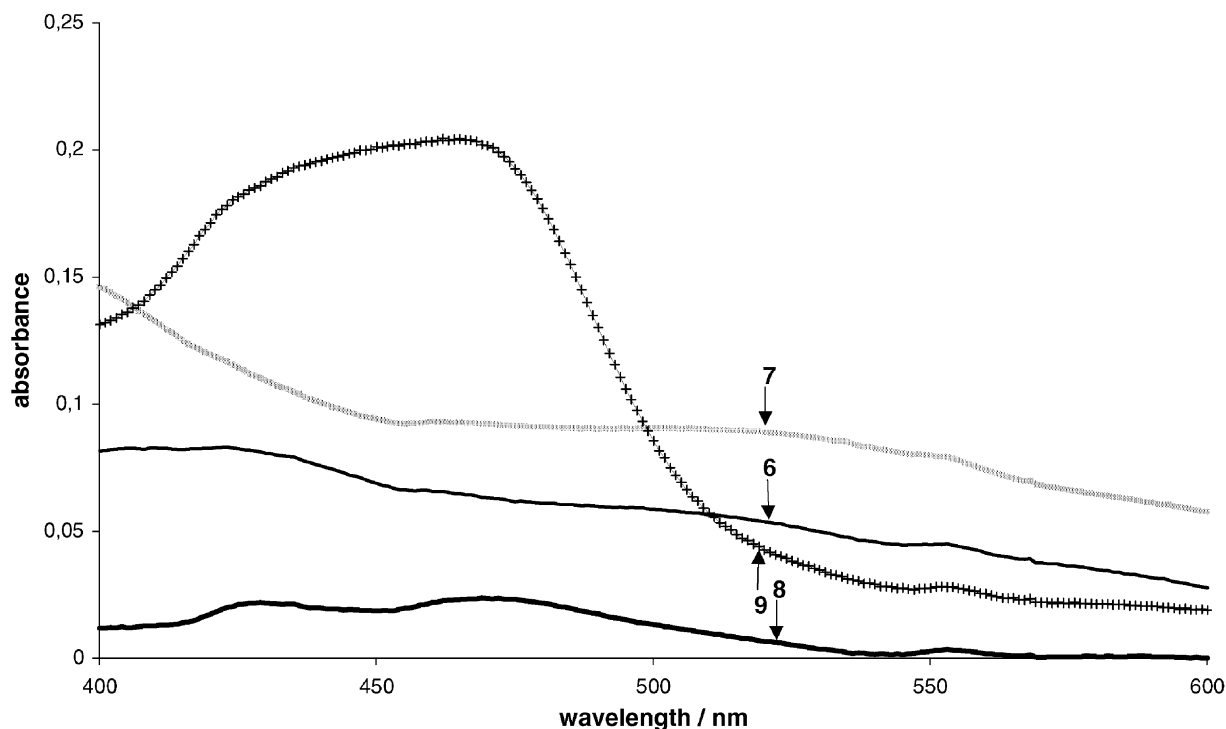| Complex	Sensitising time (h)	λ (nm)	IPCE$_{max}$ (%)	I_{sc} (mA/cm^2)	V_{oc} (mV)
6	6	460	2.9 ± 1.6	0.036 ± 0.026	19 ± 14
7	14	440	5.6 ± 2.2	0.045 ± 0.004	32.1 ± 3.3
8	25	500	16.10 ± 0.97	0.166 ± 0.010	168.7 ± 4.6

Fig. 3. The absorption spectra for complexes **6**, **7**, **8** and **9** in 0.2 mM ethanol solution.

For **6**, the IPCE values are around 2% at 460 nm (Fig. 4a) and the best results are obtained after 6 h of dye-treatment. Longer sensitising times lowers the efficiency which is in consistency with published results [13]. The electrodes that were dye-treated for 25 h has a divergent appearance as they lacks the contribution from the band gap excitation of the ZnO (λ < 420 nm). The reason for this is at present not understood.

Electrodes treated with the deprotonated complex **7** gives somewhat higher IPCE values than **6**, around 6% (Fig. 4b).

For this dye the optimal sensitising time seems to be 14 h. Also in this case, the contribution from the ZnO excitation is absent for the electrodes that were dye-treated for 25 h.

The best results in this preliminary study were obtained for electrodes treated with the carboxylated reference complexes **8** and **9**. **8** gave IPCE values of 15% at 500 nm and **9** 22% at 480 nm. In general complexes with bidentate ligands are more efficient and more stable than complexes with monodentate ligands. As the sen-
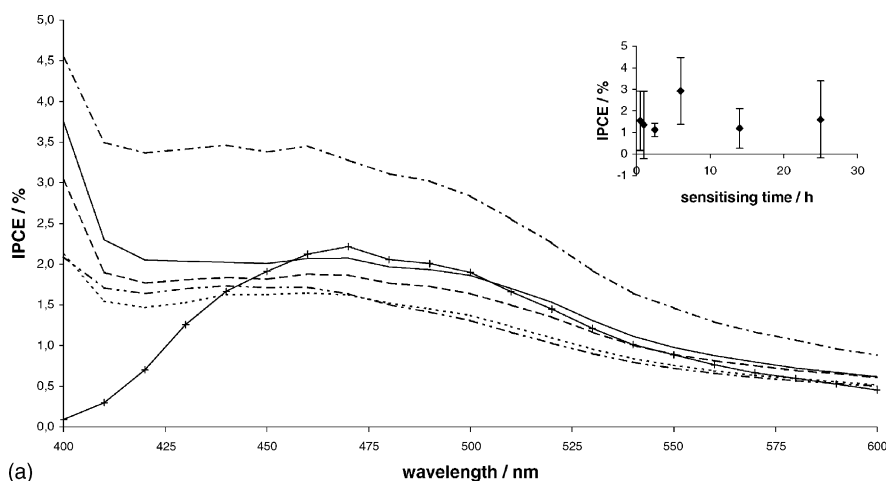

Fig. 4. IPCE spectra (average curves) for ZnO electrodes treated with: (a) **6**; (b) **7**; (c) **8** for 30 min (—); 1 h (– – –); 2.5 h (· · ·); 6 h (—·—·); 14 h (—··—); 25 h (—+—); (d) **9** for 7 days. Insets: The effect of sensitising time on IPCE (95% confidence interval) at 460 nm (**6**), 440 nm (**7**) and 500 nm (**8**).
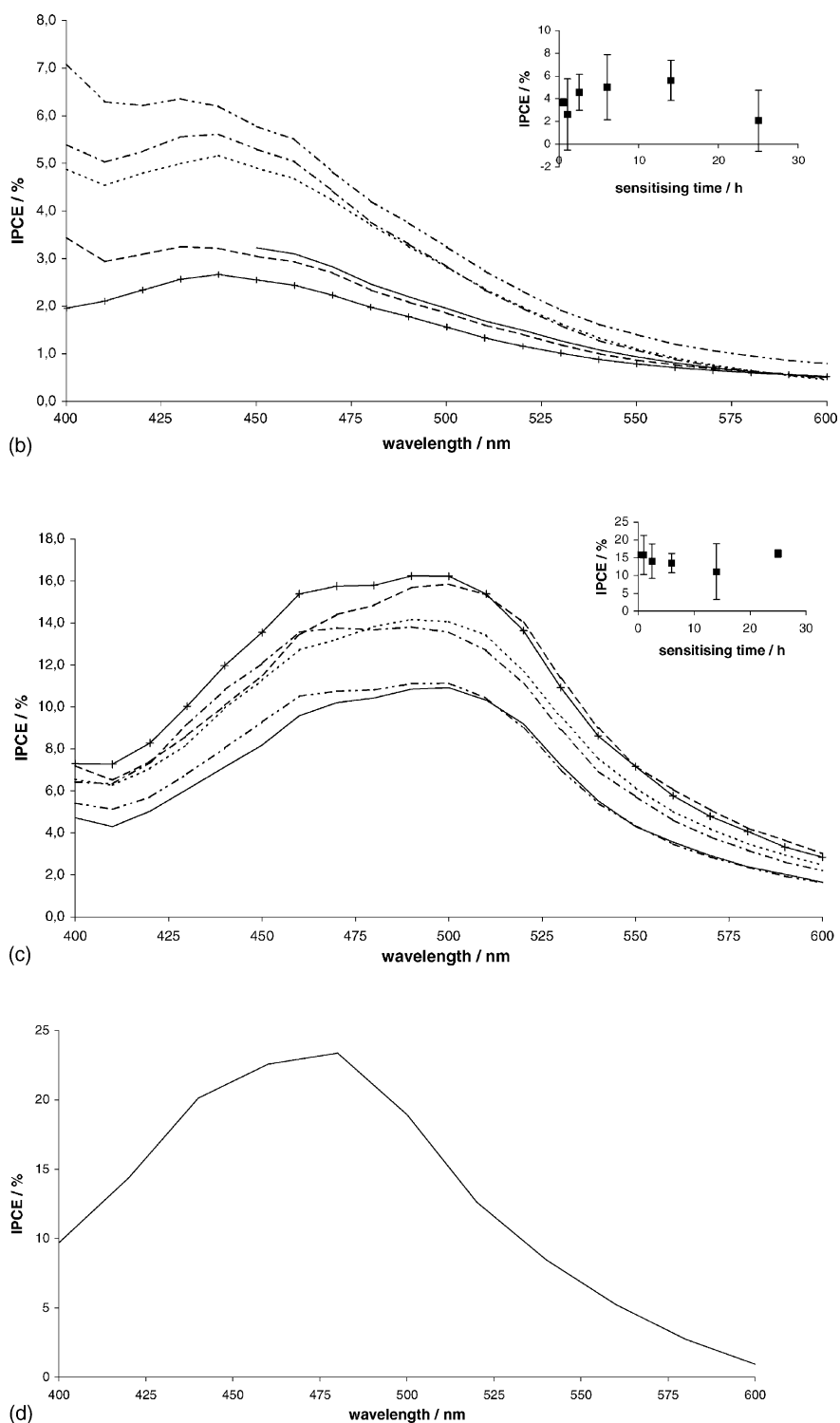
Fig. 4. (*Continued*)

sitising time gets longer the IPCE$_{max}$ does not change very much but the spectral response gets broader. According to Keis et al. [13] this is due to agglomerates of dye molecules and dissolved Zn^{2+} ions. This behaviour is not seen for complexes **6** and **7**. A common observation, regardless of dye, is that the difference between the elec-trodes treated identically are quite large. This is probably due to differences in thickness of the ZnO layer on the electrodes.

An interesting feature is that the efficiency for electrodes treated with **6** and **7** does not agree with how much the elec-trode is coloured. The electrodes treated with **6** are distinctly

pink, while those treated with **7** are very faint blue-grey, but still are both the IPCE and the overall efficiency better for the latter one. One reason for this can be differences in the bonds between the dyes and the ZnO surface. This will be investigated further.

4. Conclusion and outlook

We have developed a test kit of five small azo-dyes and when applied on TiO_2 and ZnO electrodes, the compounds functionalised with carboxylic acid and thiol adsorbed on both oxides whereas the pyridine azo-dye only coloured the TiO_2 electrodes. We have also prepared Ru-polypyridine complexes with thiol, thiolate and carboxylic acid groups, and evaluated the photoelectrochemical behaviour of ZnO electrodes treated with these complexes. The thiol and the thiolate dye do give rise to a small photocurrent, although not as high as with the carboxylic acid dye. The colour of the electrodes sensitised with thiolate dye is very faint but the efficiency is better than for the more strongly coloured electrodes sensitised with the thiol complex. Further work will focus on the nature of the thiol/thiolate–oxide interaction and also on the preparation of complexes with 4,4′-dithio-2,2′-bipyridine. This thiolated bipyridine is not commercial available but should be possible to prepare in a couple of steps from 2,2′-bipyridine [29]. This work is in progress.

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