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Tuning the properties of ruthenium bipyridine dyes for solar cells by substitution on the ligands—characterisation of bis[4,4′-di(2-(3-methoxyphenyl)ethenyl)-2,2′-bipyridine][4,4′-dicarboxy-2,2′-bipyridine]ruthenium(II) dihexafluorophosphate

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The new dye complex bis[4,4′-di(2-(3-methoxyphenyl)ethenyl)-2,2′-bipyridine][4,4′-dicarboxy-2,2′-bipyridine]-ruthenium(II) dihexafluorophosphate (**1**) has been prepared, characterised by absorption spectroscopy and adsorbed onto nanocrystalline TiO_2 electrodes. The resulting system was studied by absorption spectroscopy, electrochemistry and photoelectrochemistry and the results were compared to those for a reference system with bis[2,2′-bipyridine]-[4,4′-dicarboxy-2,2′-bipyridine]ruthenium(II) (**2**). The system with **1** displays a broader and red-shifted UV-vis absorption compared to that with **2**. Moreover, the system with **1** is less sensitive towards the water content in the electrolyte, and an adsorbed monolayer of **1** remains on the electrode surface after days even in aqueous NaOH (0.1 M), while **2** desorbs immediately.

Introduction

Dye-sensitized solar cells (DSC) have been a field of interest for the past two decades, with a significant increase in interest after the launching of systems based on nanocrystalline TiO_2 and ruthenium polypyridyl complexes in the early 90s.[1–4] Since then, the focus of the dye development has been on the search for compounds absorbing as much of the solar spectrum as possible,[1,2,5] and on the link between the dye and the semiconductor. In order to find the optimal system, a range of attaching functionalities have been screened,[6–10] but, despite considerable efforts, the original attaching ligand 4,4′-dicarboxy-2,2′-bipyridine is still the state-of-the-art.[1]

A problem for the realisation of long-term stable DSC is the water that may enter the solar cell, and affect the bond between the dye and the oxide surface, or exchange with the ligands in the dye complex. These degradation routes might be even more pronounced for the recently developed DSC on plastic supports, as the substrates are permeable to water.[11] A number of ways to get around this "water problem" have been suggested, the three most promising being (i) attaching groups less prone to hydrolysis than carboxylic groups (*i.e.* phosphonate, silane),[7,8] (ii) stabilisation of the dye layer by a polymer backbone formed after the adsorption onto the semiconductor[12] and (iii) dyes that are insoluble in the solvent employed in the solar cell.[13,14]

In this paper, we give an account of the synthesis and characterisation of a new dye with hydrophobic conjugated substituents which belong to the two latter groups of improved dyes, bis[4,4′-di(2-(3-methoxyphenyl)ethenyl)-2,2′-bipyridine]-[4,4′-dicarboxy-2,2′-bipyridine]ruthenium(II) dihexafluorophosphate (**1**; Fig. 1). As reference, we have used bis[2,2′-bipyridine][4,4′-dicarboxy-2,2′-bipyridine]ruthenium(II) (**2**). The influence of the 4-(2-(3-methoxyphenyl)ethenyl) substituent on the properties of the dye and on the dye–TiO_2 system is discussed, in particular the improved stability towards hydrolysis of the dye from the surface and the conservation of photoelectrochemical properties with increased water content in the electrolyte.

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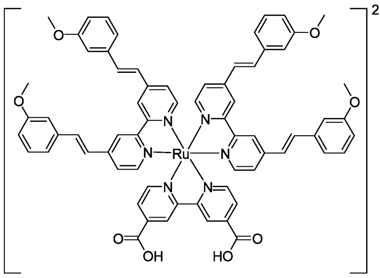
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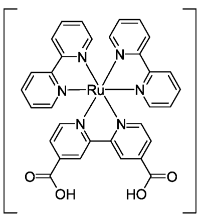
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Fig. 1 Complexes **1** and **2** (counter ions: $(PF_6^-)_2$).

Results and discussion

The dye complex **1** was prepared in a two-step procedure (Fig. 2).[9,15] Ligand **L** (4,4′-di(2-(3-methoxyphenyl)ethenyl)-2,2′-bipyridine), prepared from 4,4′-dimethyl-2,2′-bipyridine and 3-methoxybenzaldehyde,[15] was refluxed with $RuCl_3$ (n_L : n_{Ru}, 2 : 1) in 2-methoxyethanol to form $Ru(L)_2Cl_2$(**3**), however in low yield. This complex was then allowed to react with one equivalent of 4,4′-dicarboxy-2,2′-bipyridine (dcb) in 2-methoxyethanol, followed by exchange of the chloride counter ions with hexafluorophosphates to give **1** in good yield. The complex **2** was prepared analogously using 2,2′-bipyridine (bpy) instead of ligand **L**.

$$2\,L + RuCl_3{\cdot}H_2O \xrightarrow{i} \underset{\mathbf{3}}{Ru(L)_2Cl_2} \xrightarrow{ii} \underset{\mathbf{1}}{[Ru(L)_2(dcb)]^{2+}(PF_6^-)_2}$$

Fig. 2 Reagents and conditions: (i) 2-methoxyethanol, reflux under N_2, (ii) (a) 4,4′-dicarboxy-2,2′-bipyridine, 2-methoxyethanol, reflux under N_2, (b) $NaPF_6$.

In Fig. 3, the absorption spectra of bpy and **L** are shown. Both ligands display the characteristic very strong absorption in the region 250–300 nm but for **L** with the extended conjugated system the LC transition is not only red-shifted but also tremendously broadened to span the whole 300–350 nm region.

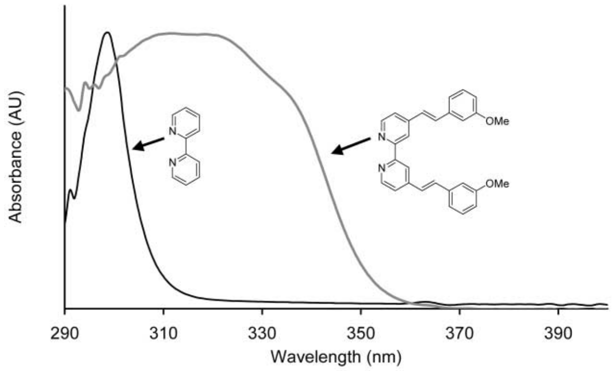

Fig. 3 Absorption spectra of bpy and **L** in acetonitrile.

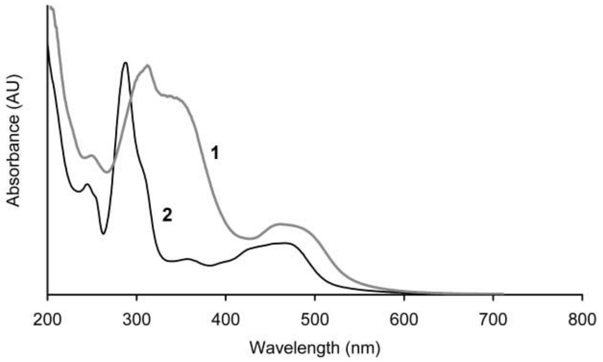

Fig. 4 Absorption spectra for complexes **1** and **2** in CH_3CN solution.

Fig. 4 shows the absorption spectra of complexes **1** and **2**. As expected for ruthenium tris-bipyridyl complexes, a broad visible absorbance band centred at 450–480 nm corresponding to the metal-to-ligand charge-transfer (MLCT) and intense bands in the UV region, from low-lying ligand centred (LC) $\pi \longrightarrow \pi^*$ transitions, are observed. The extinction coefficients of the MLCT for acetonitrile solutions of **1** and **2** were found to be 3.1×10^4 M^{-1} cm^{-1} at 480 nm and 1.2×10^4 M^{-1} cm^{-1} at 460 nm, respectively.[16]

For complex **1**, the MLCT band is red-shifted compared to that of **2**. This is in agreement with the extent of conjugation of the ligands in the different complexes and its influence in bringing the HOMO and LUMO levels closer together.[17] Another important feature due to the conjugated system is the broadening of the LC band from a narrow band (at 290 nm) to one that spans the whole region 280–370 nm.

The dyes were adsorbed onto nanostructured TiO_2 electrodes from acetonitrile solutions.

The MLCT band of complex **1** adsorbed on TiO_2 is red-shifted compared to that in solution and also compared to that of adsorbed **2** (Fig. 5), in agreement with the extent of conjugation of the ligands in the different complexes. The absorbances were almost identical for the two systems, while the extinction coefficients in solution differ by a ratio of 1 : 3 between **2** and **1**, respectively. Thus, the apparent surface coverage is 50% less for the electrodes treated with **1** than for those treated with the smaller complex **2**.[18]

Fig. 6 shows normalised cyclic voltammograms for the region of the $Ru^{II/III}$ redox couples of **1** and **2** adsorbed on TiO_2. The formal potentials *vs.* Fc/Fc^+ of +0.79 V and +0.73 V, respectively, are in accordance with the literature.[19] The metal redox processes are more negative for **1** than for **2**, indicating the weak donor properties of the vinyl(methoxy)benzene substituent on ligand **L**.

As the $Ru^{II/III}$ redox potential lies in the mid-band gap region of the semiconductor, it should not be possible for an electron to get access to the TiO_2 conduction band at this potential. The electrochemical response is due to electron transfer through the adsorbed layer of dye, where the molecules close to the conducting glass (fluorine-doped tin oxide, FTO) are oxidised initially and those further away get oxidised by lateral hole transfer from the former ones.[10,19–21] The oxidation wave for **1** is slightly larger than the reduction wave. This is possibly due to an electrocatalytic oxidation of the methoxystyryl units during the first scan, which gives rise to a stronger current. The intensity of the peak current is weaker in the case of **1** compared to **2**, in agreement with the lower surface coverage on the TiO_2 electrodes (ratio 1 : 3 for **1** : **2**).[18] However, the wave intensity for **1** is less than the half of the wave intensity for **2**. This can be explained by the less densely packed monolayer on the surface that will not allow as efficient lateral electron transfer as in the case of **2**.[10]

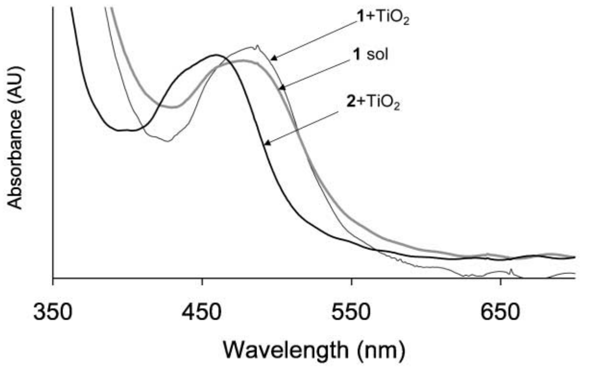

Fig. 5 Absorption spectra for **1** and **2** adsorbed on TiO_2, referenced against untreated TiO_2 electrodes, and **1** in solution referenced against a solvent blank. The solvent was acetonitrile in all cases.

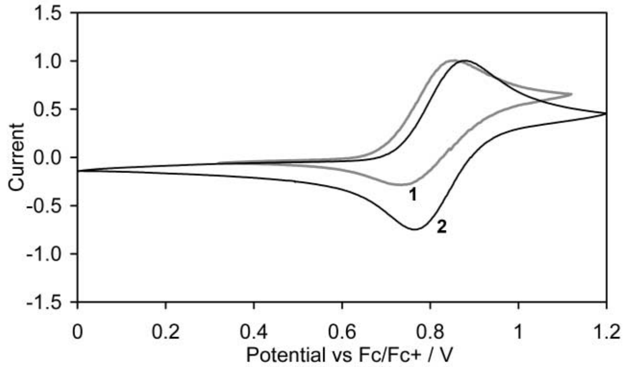

Fig. 6 Normalised cyclic voltammograms for **1** and **2**. The working electrode is a dye-sensitised TiO_2 nanocrystalline electrode, the electrolyte is 0.1 M $(TBA)BF_4$ in acetonitrile and the potential is referenced to the Fc/Fc^+ redox couple. The applied scan rate is 50 mV s^{-1}.

Current–voltage characteristics of electrodes sensitized with **1** were determined using 3-methoxypropionitrile (3-MPN) as electrolyte solvent and a light intensity of 100 mW cm^{-2} (Table 1). The open-circuit voltage and short-circuit current were 0.303 V and 0.48 mA cm^{-2} respectively, corresponding to a fill factor of 0.61 and an overall efficiency (η_{eff}) of 0.89%. Complex **2** yielded a voltage of 0.316 V and a current of 0.62 mA cm^{-2}, corresponding to a fill factor and overall efficiency of 0.58 and 1.14%, respectively. Considering the higher surface concentration of **2**, the electrodes treated with **1** are performing well, due to the extended visible absorption properties of **1**.

Of particular interest is the influence of the conjugated substituent on the water sensitivity of the solar cell system, for both the sensitivity of the dye–surface link itself and the performance of the electrodes. A simple test for the stability of the dye monolayer on TiO_2 is to immerse the sensitised electrodes in water. Electrodes with adsorbed **1** kept their colour over several days both at acidic (0.1 M HCl), neutral and alkaline pH (0.1 M NaOH), whereas those treated with **2** were stable only at pH values below 4. In the presence of 0.1 M NaOH, desorption of **2** was almost immediate.

Table 1 Summary of current–voltage data and normalised efficiency for electrodes treated with **1** and **2**

Electrolyte composition 3-MPN : H_2O	IV Data									
	1					**2**				
	FF (%)[a]	V_{oc}/V[a]	I_{sc}/A cm^{-2}[a]	η (%)	η_N[b]	FF (%)[a]	V_{oc}/V[a]	I_{sc}/A cm^{-2}[a]	η (%)	η_N[b]
100 : 0	0.61	0.303	4.81×10^{-4}	0.89	1.00	0.58	0.316	6.24×10^{-4}	1.14	1.00
95 : 05	0.62	0.324	3.43×10^{-4}	0.68	0.76	0.59	0.359	5.23×10^{-4}	1.11	0.95
90 : 10	0.59	0.341	2.38×10^{-4}	0.48	0.71	0.57	0.385	3.29×10^{-4}	0.73	0.64
75 : 25	0.54	0.326	1.19×10^{-4}	0.22	0.45	0.55	0.362	1.79×10^{-4}	0.26	0.23
50 : 50	0.45	0.271	5.54×10^{-5}	0.07	0.32	0.44	0.234	4.40×10^{-5}	0.05	0.04
0 : 100	0.34	0.030	2.55×10^{-6}	0.00	0.00	0.24	0.055	1.08×10^{-6}	0.00	0.00

[a] FF: fill factor; V_{oc}: open circuit voltage; I_{sc}: short circuit current. The electrolyte used was 0.5 M LiI, 0.05 M I_2 in 3-MPN : H_2O. Light intensity: 100 W cm^{-2}. [b] Normalised overall efficiency: $\eta_N = \eta/\eta_{100\,:\,0}$.

To investigate the influence of the substituent on the electrode performance, a series of experiments with electrolytes exhibiting a gradient in water concentration was carried out for both complexes. The current–voltage results are summarised in Table 1. Fig. 7 presents the normalised overall efficiency for the two series. As expected, the performance of the systems is negatively affected with increased water content. At low water concentration (≤10%) both systems lose 30% of the initial efficiency, the differences being within the experimental error. At higher water concentrations, the hydrophobic substituents of **1** give a slower decrease of the performance, with 40% of the initial efficiency retained at a water concentration of 50% as compared to the 4% obtained for the system with **2**.

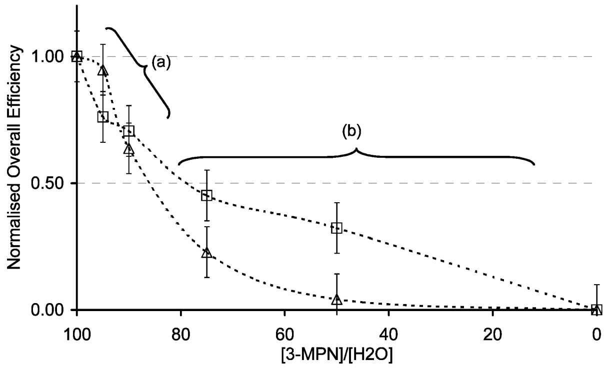

Fig. 7 Normalised overall efficiency *vs.* the amount of water in the electrolyte for electrodes treated with **1** (-□-) or **2** (-△-): (a) results within error bars, (b) results influenced by the presence of the methoxyphenyl substituents.

Conclusion

Bis[4,4′-di(2-(3-methoxyphenyl)ethenyl)-2,2′-bipyridine][4,4′-dicarboxy-2,2′-bipyridine]ruthenium(II) dihexafluorophosphate (**1**), a new dye for TiO_2-based dye-sensitized solar cells, has been prepared and adsorbed on nanocrystalline TiO_2. The optical and redox properties of the system **1**–TiO_2 and the reference system **2**–TiO_2 have been determined, as well as the photoelectrochemical characteristics and the stability of the dye–oxide system in the presence of water. The system based on **1** shows an extended absorption in the visible range and was found to be more robust in aqueous systems than the reference system. The optical properties are due to the extended conjugation of the ligands in **1** whereas the hydrophobic character of the same substituents protects the dye–electrode systems from water. The results clearly indicate the usefulness of the ligand 4,4′-di(2-(3-methoxyphenyl)ethenyl)-2,2′-bipyridine for the development of more elaborated dyes for long-term stable and efficient dye-sensitised solar cells.

Experimental

Materials

All reagents were from commercial sources and were used without further purification. Solvents were HPLC grade and were used without further purification, except for acetonitrile (Aldrich) purchased as anhydrous and further dried statically for several weeks over 3 Å molecular sieves previously regenerated by heating to 350 °C under vacuum for 48 hours. The synthesis of the ligand **L** has been described elsewhere.[15] Complex **2** was prepared following a published procedure.[9] Transparent TiO_2 films were prepared from a colloidal solution following a published procedure.[21] The TiO_2 electrodes were dye-coated with 0.5 mM acetonitrile solutions of the ruthenium complexes.

Absorption spectra

Absorption spectra were recorded using a Hewlett-Packard 8453 diode-array spectrophotometer and referenced against a solvent blank (CH_3CN). The TiO_2 electrodes were positioned against the wall of a 1 cm quartz cuvette containing CH_3CN. Separate spectra were recorded for blank TiO_2 films.

Photoelectrochemical measurements

Photoelectrochemical measurements were performed in a two-electrode sandwich arrangement as previously described.[22] *Ca.* 10 µL of electrolyte was sandwiched between a TiO_2 electrode and a Pt-coated tin oxide electrode. The system was illuminated with a xenon lamp, coupled to either a monochromator for IPCE measurements or a filter for I_{SC} and V_{OC} measurements under a light intensity of typically 100 W cm^{-2}. The electrolyte solutions were prepared by mixing 0.5 M LiI/0.05 M I_2 in 3-methoxypropionitrile and/or water.

Redox potentials

Redox potentials of **1** and **2** were measured by cyclic voltammetry of TiO_2 (~2.5 µm thick films) highly loaded with dye (saturation coverage from 0.5 mM sensitising solutions).[21] The redox potentials given are the average of the oxidation and reduction peak potentials of the Ru(II/III) wave for **1** and **2**, respectively. The scan rate used was 100 mV s^{-1}. Measurements were carried out in CH_3CN + 0.1 M (TBA)BF_4 using Ag/0.01 M $AgNO_3$ + 0.1 M (TBA)BF_4 as reference and a coiled platinum wire as counter electrode. The potential of the reference electrode was −0.08 V *vs.* the ferrrocene redox couple.

Bis(4,4′-di(2-(4-methoxyphenyl)ethenyl)-2,2′-bipyridine)-ruthenium dichloride (3)

Ligand **L**[15] (0.2 g, 0.475 × 10^{-3} mol), $RuCl_3 \cdot H_2O$ (0.044 g, 0.21 × 10^{-3} mol) and LiCl (0.042 g, 0.99 × 10^{-3} mol) were stirred at reflux temperature in 15 mL of $CH_3OCH_2CH_2OH$

under nitrogen for 8 hours. The solution was cooled to room temperature and refrigerated at −8 °C overnight. The dark solution was then filtered, yielding a dark purple solid and an orange brown filtrate. The solid was washed with cold $CH_3OCH_2CH_2OH$ until the washings became colourless and then with 30 mL of H_2O and 50 mL of Et_2O. After drying, 0.034 g of **3** (35.5×10^{-6} mol, 7%) was obtained and used without further purification.

Bis[4,4′-(2-(4-methoxyphenyl)ethenyl)-2,2′-bipyridine)-(dicarboxybipyridyl)]ruthenium dihexafluorophosphate (1)

A stirred mixture of **3** (0.034 g, 35.5×10^{-6} mol) and 4,4′-dicarboxyl-2,2′-bipyridine (8.67 mg, 35.5×10^{-6} mol) in $CH_3OCH_2CH_2OH$ were refluxed under nitrogen for 24 hours. Addition of NH_4PF_6 (0.119 g, 0.71×10^{-3} mol) to a methanol solution of the filtrate under stirring afforded the hexafluorophosphate salt of the complex as an orange precipitate. The precipitate was filtered, rinsed with water (2 × 10 mL) and ether (2 × 10 mL) and dried under vacuum for 24 hours to yield 0.040 g of **1** (28.7×10^{-6} mol, 80%). Anal. Calcd for $C_{68}H_{56}F_{12}N_6O_8P_2Ru \cdot H_2O$: C, 54.66; H, 3.91; N, 5.62; Found: C, 55.49; H, 4.70; N, 4.62%.

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