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Novel sensitisers for photovoltaic cells. Structural variations of Ru(II) complexes containing 2,6-bis(1-methylbenzimidazol-2-yl)pyridine

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Abstract

A series of new ruthenium(II) complexes was synthesised for the application in photoelectrochemical solar cells based on dye-sensitised nanocrystalline titanium dioxide. Design strategies for the development of new dyes were tested via structural variations of the prototype complex K[Ru(II)(bmipy)(4,4′-dcbpy)(NCS)] (**7**) with bmipy = 2,6-bis(1-methyl-benzimidazol-2-yl)pyridine, and 4,4′-dcbpy = 2,2′-bipyridine-4,4′-dicarboxylate. A π^* level tuning was performed by replacing 4,4′-dcbpy with the low π^* level ligands dcbiq (2,2′-biquinoline-4,4′-dicarboxylate) and 5,5′-dcbpy. The resulting complexes showed decreased light-to-electric energy conversion efficiencies. K[Ru(II)(bmipy)(4-PO_3bpy)(NCS)] (4-PO_3H_2bpy = 2,2′-bipyridine-4-phosphonic acid) also sensitised TiO_2 less efficiently than the model compound. The occurrence of two isomers was observed for the complexes containing 4-PO_3bpy. In Na[Ru(II)(bmipy)(4,4′-dcbpy)X] with X = substituted phenylcyanamide (pcyd$^-$) anions, the influence of substitution on the phenyl group was investigated. MLCT absorption maxima of the phenylcyanamide complexes at around 510 nm were shifted to lower energies in comparison with the model complex, however photoenergy conversion efficiencies were reduced. When introduced into the complex, phenylcyanamide was coordinated via the nitrile or the amido nitrogen. With prolonged reaction time, the amido-bound isomer was partially transformed into the thermodynamically more stable nitrilo-bound isomer. Linkage isomerism of coordinated NCS^- and 4-Clpcyd$^-$ was studied with multinuclear NMR (^{1}H, ^{13}C, ^{31}P) spectroscopy and ^{13}C-labelled ligands. Prospects for a substantial improvement of Ru(II) polypyridyl sensitisers for TiO_2 are discussed.

Keywords: Solar cell; Ruthenium sensitizers; Phenylcyanamide; Titanium dioxide

1. Introduction

In recent years there has been a growing interest in photoelectrochemical devices based on nanocrystalline TiO_2 (anatase) sensitised with transition metal complexes [1–9]. At present, the most efficient and stable sensitisers are carboxylated Ru(II) polypyridyl complexes. Among them, $Ru(4,4'\text{-dcbpyH}_2)_2(NCS)_2$ shows an impressive performance in the solar cell [6], which is however limited by small absorption coefficients at wavelengths above 650 nm. Improved dyes should show increased red response while maintaining a high photopotential and a quantitative incident monochromatic photon-to-current conversion efficiency (IPCE) at shorter wavelengths in the device. Common ways of improving the absorption spectrum of a complex are: π^* level tuning [10–12], e.g. the use of ligands with a lowest π^* level lower than that of 4,4′-dcbpy, ruthenium ground state tuning [12–14] (t_{2g} tuning), and the increase of the absorption coefficient of the MLCT (metal-to-ligand charge-transfer) band by introducing substituents such as methyl or phenyl groups in appropriate positions [9,15,16]. In our previous work [9], we have described the synthesis and properties of K[Ru(bmipy)(4,4′-dcbpy)(NCS)] (**7**). This complex, an efficient photosensitiser for TiO_2, has been chosen as a model complex for applying the above design strategies. Structurally related compounds having either different bipyridines containing anchoring groups or other non-chromophoric ligands replacing thiocyanate were prepared.

The energy of the ruthenium ground state level in the model complex is controlled by the donor strength of the ligand X^-. With a strong donor, the energy level can be shifted to higher energies, yielding a red-shifted absorption spectrum. Hence, substituted phenylcyanamides were applied to study the effect of (i) the increased donor strength and (ii) changing the position of substitution on the phenyl group, on dye performance in the solar cell. The large number of commercially available substituted anilines and the ease of the synthesis renders a wide range of phenylcyanamides readily accessible

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[17]. The problem of ligand autopolymerisation can be overcome for most of the phenylcyanamides by transforming them into their thallium(I) salts. Their basicity and donor strengths can be tuned by substituting the phenyl group with electron donating or accepting groups in suitable positions. In the deprotonated form, phenylcyanamide has pseudohalide character [18].

Important studies on carbodiimide coordination chemistry have been performed by Hünig and co-workers [19,20], which demonstrate the tunability of the electronic properties of a 'molecular salt' of an *N,N*-dicyanoquinonediimine derivative. With substituted phenylcyanamides, the redox potentials and LMCT (ligand-to-metal charge-transfer) energies of the Ru(III) pentaammine system were fine-tuned by Crutchley et al. [21]. Other publications [17,22–24] included studies on Cu(II) and Ru(II) bipyridine phenylcyanamide complexes.

All previous X-ray structures of mononuclear transition metal complexes containing phenylcyanamide showed coordination via the terminal (nitrile) nitrogen atom [25]. However, a spectroscopic investigation of the incorporation of ^{13}C-labelled 4-chlorophenylcyanamide into Na[(bmipy)-(4,4′-dcbpy)I] was warranted by our findings on the formation of linkage isomers of thiocyanate and selenocyanate in the same system.

The attaching group plays a key role in the sensitisation process [1], enabling efficient interaction between dye and semiconductor. The most commonly used anchoring group is the carboxylic acid. Recently, the phosphonic acid group has gained considerable attention as an alternative. With the complex Ru(4′-PO_3Hter)(4,4′-dmbpy)(NCS), IPCE values of close to one at 520 nm were, for the first time, observed with a phosphonated sensitiser in a photoelectrochemical cell [8] (4′-PO_3H_2ter is 2,2′:6′,2″-terpyridine-4′-phosphonic acid and 4,4′-dmbpy is 4,4′-dimethyl-2,2′-bipyridine). In this work, the new ligand 2,2′-bipyridine-4-phosphonic acid and two of its Ru(II) complexes were prepared.

2. Experimental

2.1. Materials

Unless otherwise stated, all solvents and chemicals used were at least reagent grade and were purchased from Fluka AG or Aldrich, Switzerland. Sephadex LH-20 was obtained from Pharmacia. ^{13}C-enriched (99%) potassium thiocyanate is a product of Dr Glaser AG, Switzerland. Electrodes were coated with nanocrystalline TiO_2 prepared via a sol–gel procedure [26]. The ambient temperature molten salt HMI (1-hexyl-3-methylimidazolium iodide) and its methylated homologue HM_2I (3-hexyl-1,2-dimethylimidazolium iodide) were synthesised in a similar manner as previously reported [27]. Elemental analyses were carried out by the analytical services of Ilse Beetz, Kronach, Germany and Ciba-Geigy, Basel, Switzerland.

Phenylcyanamides and their thallium(I) salts were prepared from substituted anilines via the thiourea route [17]. 4,4′-dcbpyH_2 [28], 5,5′-dmbpy [29] and 5,5′-dcbpyH_2 [28] were prepared according to literature procedures; the resulting acids were further purified following a method described earlier [9]. 2,2′-Bipyridine-*N*-monoxide [30], 4-nitro-2,2′-bipyridine-*N*-monoxide [31], 4-bromo-2,2′-bipyridine-*N*-monoxide [31] and 4-bromo-2,2′-bipyridine [31,32] were prepared by modified literature procedures. 2,2′-Biquinoline-4,4′-dicarboxylic acid was obtained by dissolving 1.0 g of the disodium salt (Fluka) in water and precipitating the diacid with 5% hydrochloric acid.

2.1.1. ^{13}C-labelled 4-chlorophenylcyanamide, $N^{13}CNHC_6H_5Cl$ (1)

1 was prepared via the general procedure given for phenylcyanamide derivatives [17] using ^{13}C-labelled potassium thiocyanate as starting material. Yield: 60%. ^{13}C NMR (methanol-d_4): 112.93 (cyanamide carbon). IR (KBr pellet) (cm^{-1}): ν_{CN} = 2182 (vs), 2167 (vs).

2.1.2. $Tl^{I}(N^{13}CNC_6H_5Cl)$ (2)

Caution! Thallium salts are extremely toxic. The salt was prepared after a literature procedure [17], using **1** as a starting material. Yield: 62%. ^{13}C NMR (methanol-d_4): 129.37 (carbodiimide carbon). IR (KBr pellet) (cm^{-1}): ν_{NCN} = 2060 (sh), 2048 (vs), 2035 (sh), 2013 (m), 1999 (w).

2.1.3. 2,2′-Bipyridine-4-diethylphosphonate (3) [33]

To 3.0 g of 4-bromo-2,2′-bipyridine were added under argon 1.0 g of palladium tetrakistriphenylphosphine, 3.8 g of diethylphosphite, and 2.9 g of triethylamine, and the mixture was refluxed for 4 h. Excess diethylphosphite and triethylamine were evaporated under reduced pressure, and the remaining mixture was dissolved in a minimum amount of dichloromethane. The solution was chromatographed on a silica gel column (Merck KG 60, 30×6 cm) by gradient elution with dichloromethane/methanol. Evaporation of the product fraction yielded **3**, contaminated with small amounts of an impurity with a proton NMR signal at around 7.4 ppm ($CDCl_3$). Chromatography of the product fraction on silica gel with ethylacetate/acetic acid (100:5), subsequent washing of the column with dichloromethane/methanol (10:1) and evaporating the solvent yielded **3** as a yellowish oil. Yield: 1.9 g (51%). *Anal.* Calc. for $C_{14}H_{17}N_2O_3P$: C, 57.53; H, 5.86; N, 9.58; P, 10.60. Found: C, 57.54; H, 5.91; N, 9.55; P, 10.61%. UV–Vis (ethanol): 284 (ϵ = 29 400), 238 (ϵ = 25 800) nm. ^{1}H NMR ($CDCl_3$) (multiplicity, coupling constant(s) (Hz), integral): 1.31 (t, 6.7, 4); 4.15 (m, 6); 7.29 (ddd, 1.2, 4.8, 7.5, 1); 7.65 (ddd, 1.5, 4.7, $^3J_{P-H}$ = 13.1, 1); 7.78 (dt, 1.8, 7.3, 1); 8.36 (td, 1.2, 8.0, 1); 8.72 (m, 3). ^{13}C NMR ($CDCl_3$) (atom, multiplicity, coupling constant (Hz)): 16.35 (–CH_3, d, $^2J_{C-P}$ = 6.1), 62.72 (–CH_2–, d, $^3J_{C-P}$ = 5.5), 121.22 (C3′, s), 122.67 (C3, d, $^2J_{C-P}$ = 9.5), 124.14 (C5′, s), 125.23 (C5, d, $^2J_{C-P}$ = 8.8), 136.95 (C4′, s), 138.46 (C4, d, $^1J_{C-P}$ = 185.7), 149.34 (C6′, s), 149.41 (C6,

d, $^3J_{C-P}$ = 13.1), 155.21 (C2', d, $^4J_{C-P}$ = 2.0), 156.59 (C2, d, $^3J_{C-P}$ = 12.2). ^{31}P NMR ($CDCl_3$): 15.28. IR (KBr pellet) (cm^{-1}): 3059 (w), 2982 (w), 2930 (w), 2907 (w), 2871 (w), 1583 (m), 1567 (w), 1541 (w), 1478 (w), 1456 (m). 1380 (m), 1283 (w), 1255 (s), 1223 (w), 1163 (m), 1132 (s), 1095 (m), 1051 (s), 1022 (s), 972 (s), 829 (w), 789 (s), 747 (w), 710 (w) 661 (w), 618 (w), 608 (m). MS (CI, NH_3): (*m/z*, rel. int.): 293, 58.2, MH^+; 248, 21.4, $MH^+ - OC_2H_5$; 219, 24.9, $C_{10}H_8N_2O_2P^+$; 184, 20.7; 156, 100, $C_{10}H_8N_2^+$.

2.1.4. Ru(bmipy)Cl_3 (4), Ru(bmipy)(4,4'-dcbpyH)Cl (5), Na[Ru(bmipy)(4,4'-dcbpy)I] (6) and K[Ru(bmipy)-(4,4'-dcbpy)(NCS)] (7)

These were prepared and purified as described earlier [9]. All reactions were performed under argon and ensuring exclusion of light.

2.1.5. Na[Ru(bmipy)(4,4'-dcbpy)(N(CN)$_2$)] (8)

50 mg of **6** and 100 mg of sodium dicyanoamide (25-fold excess) were dissolved in 25 ml of methanol and refluxed for 4 h. The crude product was isolated by precipitation with diethyl ether, filtered, redissolved in methanol and chromatographed over Sephadex LH-20 (10×2cm) to remove dicyanoamide impurity. The product band was collected, precipitated with diethyl ether, filtered, washed with diethyl ether/methanol (2:1) and diethyl ether, and dried. Yield: 37 mg (79%). *Anal.* Calc. for $C_{35}H_{23}N_{10}NaO_4Ru \cdot 3H_2O$: C, 50.92; H, 3.54; N, 16.96. Found: C, 50.91; H, 3.54; N, 16.96%.

2.1.6. Na[Ru(bmipy)(4,4'-dcbpy)(2,4,5-Cl$_3$pcyd)] (9)

70 mg of **6** and 50 mg of Tl(2,4,5-trichlorophenylcyanamide) (1.4-fold excess) were refluxed in 30 ml of methanol for 4 h. After cooling, a yellow solid (thallium iodide) was separated by centrifugation, and the product was precipitated from the solution with diethyl ether, filtered off, washed with diethyl ether/methanol 5:2 and diethyl ether, and dried. Yield: 54 mg (69%). *Anal.* Calc. for $C_{40}H_{25}Cl_3N_9NaO_4Ru \cdot 2.5H_2O$: C, 49.47; H, 3.11; N, 12.98. Found: C, 49.43; H, 2.85; N, 13.02%.

2.1.7. Na[Ru(bmipy)(4,4'-dcbpy)(pcyd)] (10)

This was prepared like complex **9**, starting from 50 mg of **6** and 28 mg of Tl(pcyd), and refluxing for 8 h in 25 ml of methanol. Yield: 36 mg (73%). *Anal.* Calc. for $C_{40}H_{28}N_9NaO_4Ru \cdot 4.5H_2O$: C, 53.08; H, 4.13; N, 13.95. Found: C, 53.16; H, 3.52; N, 13.88%.

2.1.8. Na[Ru(bmipy)(4,4'-dcbpy)(4-Clpcyd)] (11)

This was synthesised in the same way as **9**, starting from 75 mg of **6** and 34 mg of Tl(4-Clpcyd), and refluxing for 15 h. Yield: 50 mg (67%). *Anal.* Calc. for $C_{40}H_{27}ClN_9NaO_4Ru \cdot 2H_2O$: C, 53.79; H, 3.50; N, 14.11. Found: C, 53.65; H, 3.20; N, 13.99%.

2.1.9. Na[Ru(bmipy)(4,4'-dcbpy)(2-Clpcyd)] (12)

This was synthesised in the same way as **11** with the only difference using Tl(2-Clpcyd) instead of Tl(4-Clpcyd). Yield: 48 mg (64%). *Anal.* Calc. for $C_{40}H_{27}ClN_9NaO_4Ru \cdot 5.5H_2O$: C, 50.24; H, 4.01; N, 13.18. Found: C, 50.18; H, 3.50; N, 13.14%.

2.1.10. Na[Ru(bmipy)(4,4'-dcbpy)(2,4,6-Cl$_3$pcyd)] (13)

This was prepared like **9**, using 75 mg of **6** and 39 mg of Tl(2,4,6-Cl_3pcyd). Yield: 49 mg (60%). *Anal.* Calc. for $C_{40}H_{25}Cl_3N_9NaO_4Ru \cdot 1.5H_2O$: C, 50.41; H, 2.96; N, 13.23. Found: C, 50.67; H, 2.99; N, 13.08%.

2.1.11. Na[Ru(bmipy)(4,4'-dcbpy)(OCH$_3$)] (14)

80 mg of sodium were reacted with 40 ml of dry methanol. Then, 160 mg of **5** were added, and the solution was heated under reflux for 4 h. During the reaction, the solution colour turned deep blue–violet. After cooling at room temperature, the volume was reduced to 20 ml, and the product was precipitated by adding diethyl ether. It was filtered, washed with diethyl ether/methanol 4:1 and diethyl ether, and dried. Yield: 153 mg (93%). The product was sensitive to humidity and was directly used for further reactions.

2.1.12. Na[Ru(bmipy)(4,4'-dcbpy)(2,4,6-Me$_3$pcyd)] (15)

200 mg of 2,4,6-trimethylphenylcyanamide and 80 mg of **14** were refluxed in 40 ml of methanol for 24 h. After evaporating to dryness, the product was redissolved in a minimum amount of methanol and purified on Sephadex LH-20 with 0.2 M sodium methanolate/methanol as an eluent. The product band was collected, precipitated with diethyl ether, washed with diethyl ether/methanol 3:1 and diethyl ether, and dried. Yield: 52 mg (55%). *Anal.* Calc. for $C_{43}H_{34}N_9NaO_4Ru \cdot 3.5H_2O$: C, 55.66; H, 4.45; N, 13.59. Found: C, 55.48; H, 4.08; N, 13.32%.

2.1.13. Na$_2$[Ru(bmipy)(4,4'-dcbpy)(NCN)] (16)

6 was reacted with a 20-fold molar excess of sodium cyanamide in methanol for 3 h. After that, the solution had a deep blue–violet colour. Filtration after precipitation of the product with diethyl ether resulted in decomposition.

2.1.14. Ru(bmipy)(5,5'-dcbpyH)Cl (17)

This was prepared like **5**, using 5,5'-dcbpyH_2 instead of 4,4'-dcbpyH_2. Yield: 260 mg (63%). *Anal.* Calc. for $C_{33}H_{24}ClN_7O_4Ru \cdot 2H_2O$: C, 52.49; H, 3.74; N, 12.98. Found: C, 52.35; H, 3.54; N, 13.17%.

2.1.15. Na[Ru(bmipy)(5,5'-dcbpy)I] (18)

250 mg of **17** were dissolved in 120 ml of methanol and 1.0 ml of triethylamine. After adding 2.6 g of NaI, the mixture was boiled under reflux for 6 h. Then, a blue–violet solid was filtered off, the volume of the filtrate reduced to 25 ml, and the product was purified on Sephadex LH-20 (20×3 cm) with methanol/NaI 100:4 as an eluent. The main red–violet fraction was collected, evaporated to a volume of 25 ml, and

the product precipitated with diethyl ether. After filtration, it was washed with diethyl ether/methanol (3:1) and diethyl ether. Yield: 120 mg (42%). *Anal.* Calc. for $C_{33}H_{23}IN_7NaO_3Ru \cdot 4H_2O$, containing 6.4% NaI: C, 40.84; H, 3.22; N, 10.16; I, 18.42. Found: C, 40.84; H, 3.44; N, 9.92; I, 18.25%.

2.1.16. Na[Ru(bmipy)(5,5'-dcbpy)(2,4,5-Cl$_3$pcyd)] (19)

This was prepared in the same way as complex **9**, using **18** as starting material. Yield: 30 mg (61.4%). *Anal.* Calc. for $C_{40}H_{25}Cl_3N_6NaO_4Ru \cdot 1.5H_2O$: C, 50.41; H, 2.96; N, 13.23. Found: C, 50.58; H, 3.09; N, 13.22%.

2.1.17. Na$_2$[Ru(bmipy)(5,5'-dcbpy)(NCN)] (20)

This was synthesised in the same way as **16** and decomposed upon filtration.

2.1.18. Ru(bmipy)(dcbiqH)Cl (21)

146 mg of 2,2'-biquinoline-4,4'-dicarboxylic acid and 308 mg of **4** were added to 60 ml of dimethylformamide and 2.0 ml of triethylamine. The mixture was refluxed for 6 h. After 30 min of refluxing, the colour of the solution turned deep blue and a solid precipitated. The solution was filtered hot, and the precipitate washed with dimethylformamide and dried. Yield: 331 mg (76%). *Anal.* Calc. for $C_{41}ClH_{28}N_7O_4Ru \cdot H_2O$: C, 58.8; H, 3.6; N, 11.7. Found: C, 58.9; H, 3.6; N, 12.0%.

2.1.19. Ru(bmipy)(dcbiqH)(NCS) (22)

300 mg of **21** were added to a mixture of 240 ml of dimethylformamide, 60 ml of water, 1.0 ml of triethylamine and 1.0 g of potassium thiocyanate. After refluxing for 8 h, the solution was allowed to cool at room temperature, filtered, and evaporated to dryness under reduced pressure. Then, the solid was dissolved in water with diluted sodium hydroxide and reprecipitated by adding dropwise 5% hydrochloric acid. The precipitate was filtered off, washed with 0.5% hydrochloric acid, dried, dissolved in a minimum amount of methanol and eluted with methanol through a Sephadex LH-20 column under reduced light. A green band was collected, the solvent evaporated and the complex suspended in 75 ml of water and dissolved by adding dropwise 5% sodium hydroxide. Reprecipitation from the solution with 5% hydrochloric acid, filtering and drying yielded 210 mg (63%) of **22**. *Anal.* Calc. for $C_{42}H_{28}N_8O_4RuS \cdot 5H_2O$: C, 54.13; H, 4.11; N, 12.02; S, 3.44. Found: C, 54.10; H, 3.77; N, 12.19; S, 3.22%.

2.1.20. Ru(bmipy)(4-PO$_3$Hbpy)Cl (23)

2,2'-Bipyridine-4-diethylphosphonate (**3**) (300 mg) was dissolved in 20 ml of 20% hydrochloric acid and refluxed for 4 h. The solution was evaporated, and the product dried in vacuo. To the solid, 60 ml of dimethylformamide, 2.0 ml of triethylamine and 610 mg of **4** were added. The mixture was refluxed for 5 h. During this time, the colour of the solution turned violet and a solid precipitated. The solution was allowed to cool at room temperature, and the precipitate filtered off, washed with dimethylformamide and dried. Yield: 599 mg (78%). *Anal.* Calc. for $C_{31}H_{25}N_7O_3PRu \cdot 2H_2O$: C, 49.84; H, 3.91; N, 13.12; Cl, 4.75; P, 4.16. Found: C, 49.56; H, 3.93; N, 12.72; Cl, 5.15; P, 4.19%.

2.1.21. Ru(bmipy)(4-PO$_3$Hbpy)(NCS) (24)

300 mg of **23** were dissolved in 30 ml of methanol and 1.0 ml of triethylamine. After addition of 1.0 g of potassium thiocyanate, the mixture was refluxed for 8 h. Then, the solution was allowed to cool at room temperature, filtered, and evaporated under reduced pressure. The solid was dissolved in water using 1 M NaOH and precipitated by adding dropwise 5% hydrochloric acid. The precipitate was filtered off, washed with 0.5% hydrochloric acid, redissolved in water using a minimum amount of sodium hydroxide, and reprecipitated from the solution with acid. The product was filtered off, washed with water and dried. Yield: 259 mg (84%). *Anal.* Calc. for $C_{32}H_{25}N_8O_3PRuS \cdot 2H_2O$: C, 48.79; H, 3.97; N, 14.22; P, 4.02; S, 4.07. Found: C, 48.45; H, 3.49; N, 14.32; P, 4.09; S, 4.23%.

2.2. Methods

2.2.1. Spectroscopic studies

^{1}H, broadband proton decoupled ^{13}C and ^{31}P NMR spectra were measured on a Bruker AC-P 200 spectrometer. ^{1}H and ^{13}C chemical shifts are given in ppm, relative to tetramethyl silane. ^{31}P NMR spectra were measured against 85% H_3PO_4 as an external standard. In ^{13}C NMR measurements, pulse repetition time was 3 s. UV–Vis spectra were obtained on a Hewlett Packard 8452A diode array spectrophotometer. Fourier transform IR spectra were recorded from KBr pellets on a Perkin-Elmer Paragon 1000 FTIR spectrophotometer.

2.2.2. Electrochemistry

Cyclic voltammetry was performed in argon-purged 1-methyl-2-pyrrolidone, dried over molecular sieve, in the presence of 0.1 M tetrabutylammonium-trifluoromethanesulfonate as the supporting electrolyte. In the three-electrode set-up, a glassy carbon working electrode (surface 0.07 cm^2), a glassy carbon counter electrode (separated from the working electrode compartment by a bridge containing the same electrolyte as the test solution), and a silver wire as quasi-reference electrode were used. The quasi-reference electrode was calibrated with an Ag/AgCl/KCl saturated reference electrode. Reported potentials refer to the latter. Scan rates between 100 and 300 mV s^{-1} were used.

2.2.3. Photoelectrochemical measurements

TiO_2 electrodes were coated for 15 h under exclusion of light in 5×10^{-4} M ethanolic dye solutions at room temperature. If there was no deep coloration of the electrode, soaking was continued for 2 h at 70°C. Unless otherwise stated, the dye solutions contained 50 mM of 3α,7β-dihydroxy-5β-cholanic acid as a co-adsorbate. As electrolyte, a mixture containing 0.6 M HM_2I or HMI, 40 mM of I_2, 40 mM of LiI and 200 mM of 4-tert-butylpyridine in acetonitrile was used.

HM_2I and HMI containing electrolytes yielded identical cell performance and are assumed only to differ in long-term stability. Set-up and procedure for the measurement of action spectra and current–voltage characteristics are described elsewhere [6].

3. Results and discussion

3.1. Synthesis

All investigated complexes were of the general formula M[Ru(II)LL'X], with L = tridentate polypyridine ligand, L' = bidentate polypyridine with anchoring group(s), X^- = pseudohalide, and M = Na^+ or H^+. Usually, complexes of this type are prepared in three steps, starting with the reaction of equimolar amounts of Ru(III)Cl_3 and the tridentate ligand (in this work exclusively bmipy) in ethanol, yielding Ru(III)LCl_3 (**4**) as a precipitate. Subsequently, the bidentate ligand L' is introduced by reacting it with one equivalent of Ru(III)LCl_3 in a high-boiling solvent such as dimethyl formamide, together with a small amount of reducing agent, such as triethylamine. The product is Ru(II)L(L'H)Cl, precipitating from the reaction solution. In the final step, the chloride is replaced by other pseudohalides (applied in excess) in methanol. The solubility of the chloride complex is enhanced by deprotonation with triethylamine. A schematic representation of the performed reactions is shown in Fig. 1, and the structures of the ligands used are given in Fig. 2.

As the investigated carboxylated complexes did not crystallise, a chromatographic purification on the Ru(II) stage was necessary to obtain acceptable proton NMR spectra. It was not possible to separate the carboxylated complexes on common stationary phases like silica or alumina. With the dextrane-based Sephadex LH-20, however, good separations were achieved for some of the complexes, but their low solubility and weak retardation on the column presents a limitation. The cyanamide complexes were hence prepared from Na[RuL(4,4'-dcbpy)I] (**6**), which can be purified on Sephadex LH-20. The iodo complex was reacted with the thallium(I) phenylcyanamide derivative salts (applied in 1.4 molar excess). This procedure was applied for all phenylcyanamides forming thallium salts.

Introduction of protonated phenylcyanamide ligands into the iodo complex in the presence of triethylamine yielded a mixture of products. Hence, for the preparation of complexes of phenylcyanamides not forming thallium salts, Na[RuLL'-

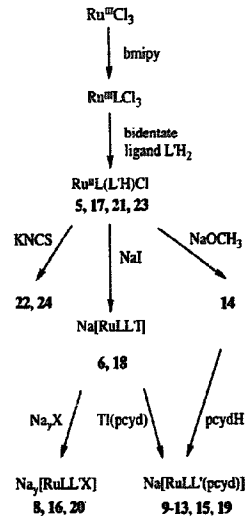

Fig. 1. Schematic representation of performed reactions.

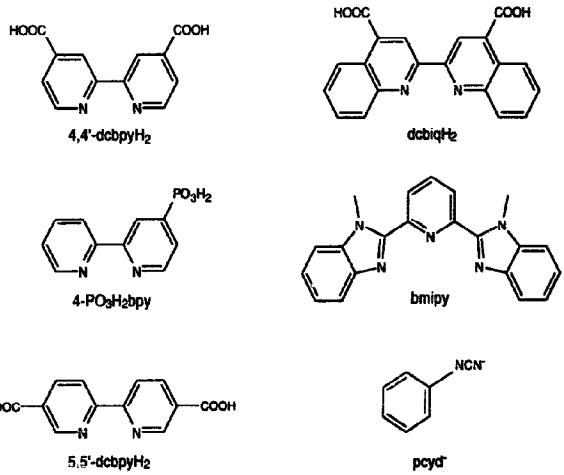

Fig. 2. Structures of ligands used.

Table 1
^{1}H NMR data of complexes **8–20** (in methanol-d_4)

Complex	bmipy protons							4,4'-dcbpy protons						pcyd protons		
	a	b	c	d	e	f	g	3	3'	5	5'	6	6'			
8	8.38	8.81	4.58	7.75	7.45	7.15	6.26	9.27	8.81	8.54	7.41	10.12	7.50			
	t	d	s	d	t	t	d	d	d	dd	dd	d	d			
9	8.34	8.81	4.58	7.75	7.45	7.15	6.30	9.30	8.85	8.53	7.43	10.28	7.59	7.14	5.99	
	t	d	s	d	ddd	ddd	d	d	d	dd	dd	d	d	s, 3	s, 6	
10	8.29	8.76	4.53	7.75	7.46	7.15	6.31	9.29	8.84	8.51	7.41	10.32	7.58	6.75	6.56	6.06
	t	d	s	d	t	t	d	s	s	dd	dd	d	d	m, 3,5	m, 4	m, 2,6
11	8.31	8.77	4.55	7.75	7.46	7.16	6.31	9.29	8.84	8.51	7.41	10.29	7.56	6.01	6.69	
	t	d	s	d	ddd	ddd	d	d	d	dd	dd	d	d	m, 2,6	m, 3,5	
12	8.30	8.77	4.55	7.75	7.46	7.15	6.31	9.29	8.84	8.52	7.43	10.33	7.58	7.00	6.51	5.93
	t	d	s	d	ddd	ddd	d	d	d	dd	dd	d	d	dd, 3	m, 4,5	dd, 6
13	8.31	8.77	4.56	7.72	7.44	7.12	6.27	9.28	8.83	8.52	7.41	10.35	7.54	6.92		
	t	d	s	d	ddd	ddd	d	d	d	dd	dd	d	d	s, 3,5		
14	8.20	8.75	4.57	7.70	7.40	7.09	6.31	9.26	8.73	8.58	7.27	10.18	7.27	2.67		
	t	d	s	d	ddd	ddd	d	d	d	dd	s	d	s	s		
15	8.25	8.69	4.53	7.69	7.43	7.11	6.26	9.27	8.81	8.5	7.37	10.33	7.52	6.44	2.10	1.71
	t	d	s	d	ddd	ddd	d	d	d	dd	dd	d	d	s, 3.5	s, 4	s, 2.6
16	8.17	8.73	4.57	7.71	7.41	7.08	6.30	9.26	8.75	8.59	7.31	10.21	7.25			
	t	d	s	d	ddd	ddd	d	s	s	dd	dd	d	d			

	bmipy signals							5,5'-dcbpy signals								
	a	b	c	d	e	f	g	3	3'	4	4'	6	6'			
17	8.26	8.76	4.54	7.71	7.40	7.07	6.28	8.87	8.43	8.87	7.97	11.24	7.90			
	t	d	s	d	ddd	ddd	d	m	d	m	dd	s	d			
18	8.24	8.74	4.54	7.69	7.41	7.09	6.36	8.82	8.37	8.82	8.01	11.77	7.76			
	t	d	s	d	ddd	ddd	d	m	d	m	dd	s	d			
19	8.30	8.79	4.58	7.76	7.46	7.14	6.32	8.89	8.48	8.89	8.06	10.79	7.96	7.12	5.96	
	t	d	s	d	ddd	ddd	d	m	d	m	dd	d	d	s, 3	s, 6	
20	8.13	8.71	4.56	7.70	7.40	7.06	6.32	8.88	8.38	8.88	7.91	10.75	7.64			
	t	d	s	d	ddd	ddd	d	m	d	m	dd	s	d			

(OCH_3)] (**14**) was used as the precursor material. The methoxy group can be replaced by phenylcyanamides in methanol, which are introduced into the complex in the deprotonated form.

The phosphonated ligand 4-PO_3Et_2bpy was synthesised in five steps from bpy. Cited literature procedures were modified and optimised for monosubstituted bipyridine derivatives [30–32,34]. The introduction of the phosphonate group was similar to the procedure for the previously published 4'-PO_3Et_2ter [8]. Subsequently, the ester was hydrolysed in 20% HCl. ^{31}P NMR studies showed the disappearance of the diester signal at $\delta = 11.78$ ppm in 20% DCl/D_2O after 30 min of heating at 100°C, indicating complete hydrolysis of the first ester group. The monoester ($\delta = 8.21$ ppm in 20% DCl/D_2O) was completely converted after an additional 2.5 h of refluxing. The ^{31}P NMR spectrum of the final product showed a single line at $\delta = 6.83$ ppm in 20% DCl/D_2O. The hydrolysed ligand was reacted with Ru(III)LCl_3, yielding isomers of complex **23** as a crystalline powder, rendering a further purification of **23** and its derivatives unnecessary.

Proton NMR data are summarised in Table 1 for complexes **8–20** and Table 2 for **22–24**. Signal numbers are the same as given in Fig. 3, and integration is in accordance with given assignments. When coordinated, ^{1}H NMR chemical shifts of the bmipy signals remained nearly unaffected by the nature of the other ligands, whereas the bpy derivative signals were more strongly influenced [35] by the monodentate ligand X^-. Particularly sensitive was the chemical shift of the H6 signal, which varied by more than one ppm. Proton NMR spectra of the phosphonated complexes **23** and **24** are more complicated, as the phosphonate group can be positioned *cis* or *trans* to X^-. A *cis*/*trans* isomer ratio of 1:6 was found by integration of ^{31}P signals (see Table 4), independent of the nature of X^-.

All products gave satisfactory elemental analyses. When prepared as alkali salts by precipitation with diethyl ether from methanol, a co-precipitation of other ions occurred, due to the adsorptive nature of the products. It was not possible to remove completely excess sodium iodide from complex **18** even by repeated reprecipitation. Precipitation at its isoelectric point in aqueous solution is not possible because of fast replacement of the iodide ligand by water. The phenylcyanamide complexes are in contrast prepared with a small ligand excess, which is removed by product precipitation.

Table 2
^{1}H NMR data of complexes **22–24** (in methanol-d_4)

Complex	bmipy protons							bpy derivative protons							
	a	b	c	d	e	f	g	3	5	6, 7	8	3′	5′	6′, 7′	8′
22	8.38 t	8.79 d	4.52 s	7.68 d	7.39 ddd	7.06 ddd	6.27 d	9.05 s	8.87 dd	7.29, 7.77 ddd, ddd	9.26 dd	8.61 s	8.20 dd	7.25, 7.43 ddd, ddd	7.00 dd
								3	4	5	6	3′	5′, 6′		
23	8.23 t	8.73 d	4.54 s	7.71 d	7.41 ddd	7.07 ddd	6.27 d	8.83 d	8.11 dt	8.50 dt	10.69 dd	8.67 d	7.23–7.34 m		
24	8.32 t	8.77 d	4.55 s	7.73 d	7.44 dt	7.10 ddd	6.23 d	8.83 d	8.15 ddd	8.52 dt	10.21 dd	8.68 d	7.31–7.39 m		

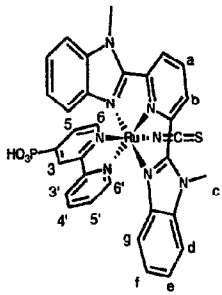

Fig. 3. The complex Ru(bmipy)(4-PO_3Hbpy)(NCS). The phosphonic acid group can be located *cis* or *trans* to the thiocyanate ligand.

3.2. Absorption spectra and redox properties

The absorption spectra of the complexes in methanol are dominated by strong ligand-centred π–π^* transitions at 346 and 360 nm on bmipy [36], and at around 310 nm on the bipyridine derivatives [6]. The position of an intense MLCT transition with an absorption coefficient of around 13 000 depended on the donor strength of the pseudohalide X^- used. In the complex Na[Ru(bmipy)(4,4′-dcbpy)X], the MLCT maximum could be tuned between 492 (dicyanoamide complex **8**) and 526 (cyanamide complex **16**) nm. The phenylcyanamide derivative complexes showed absorption maxima between 500 and 512 nm, slightly red-shifted when compared to the model complex **7** (500 nm). Representative absorption spectra are shown in Fig. 4. A spectrum of *cis*-Ru(dcbpyH_2)$_2$(NCS)$_2$ (**25**), the best known sensitiser for TiO_2 so far, was included for comparison.

π^* Level tuning of the prototype complex **7** resulted in the expected red-shift in the absorption spectra, which was found to be 10 to 15 nm for the 5,5′-dcbpy derivatives and 76 nm for the dcbiq complex **22** (in the deprotonated form). Replacing 4,4′-dcbpyH by 4-PO_3Hbpy yielded almost identical absorption energies, but the absorption coefficient of the MLCT band was reduced by about 20%. The MLCT band positions are pH-dependent. UV–Vis data are compiled, together with redox potentials and IR absorptions, in Table 3.

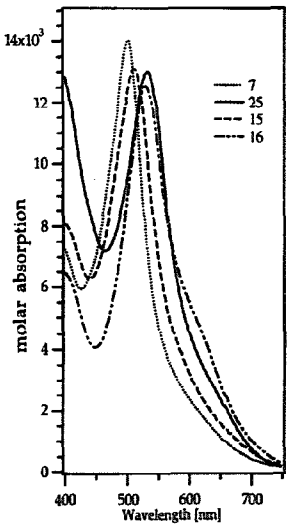

Fig. 4. Absorption spectra of cyanamide complexes **15** and **16**, compared with the model complex **7** and *cis*-Ru(4,4-dcbpyH_2)$_2$(NCS)$_2$ (**25**).

Cyclic voltammetry of the carbodiimide derivative complexes showed reversible or quasi-reversible behaviour of the Ru(III/II) redox couple for scan rates between 100 and 300 mV s^{-1}. All potentials are less positive than that of the model complex **7**. Reduction waves are quasi-reversible or irreversible, depending on the nature of the phenylcyanamide ligand. Potentials for 4,4′-dcbpy and 5,5′-dcbpy homologes are very similar. The thiocyanate complexes **22** and **24** displayed irreversible redox electrochemistry.

3.3. Complex isomerism

3.3.1. Phenylcyanamide complexes

As ambidentate ligands, phenylcyanamides have shown several bonding modes when coordinated to transition metals, depending on the charge of the carbodiimide ligand and on the nature of the transition metal. The preferred bonding mode is via the nitrile nitrogen, since all crystal structures of mononuclear phenylcyanamide complexes of transition metal ions

Table 3
Electrochemical, absorption and infrared properties of complexes

Complex	UV–Vis data in methanol [a]						Redox potentials [b]		IR (cm^{-1})
							Oxid. (mV)	Red. (mV)	
8	492	358	344	306			600 [d]	−1250 [d]	2279, 2236,
	(13.8)	(39.9)	(31.0)	(43.9)					2169
9	502	360	344	306			740 [d]	−1300 [d]	2172
	(13.0)	(36.5)	(33.4)	(50.6)					
10	506	358	344	308			670 [d]	−1380 [c]	2169
	(12.6)	(37.9)	(32.3)	(46.6)					
11	506	358	346	308			640 [d]	−1300 [d]	2167
	(12.4)	(35.5)	(30.9)	(47.0)					
12	506	358	346	308			640 [d]	−1360 [c]	2168
	(12.7)	(34.6)	(30.8)	(47.3)					
13	508	360	344	308			720	−1260 [d]	2171
	(13.0)	(36.0)	(32.7)	(53.4)					
14	530	360	344	308					
15	510	358	346	308			490 [d]	−1230 [c]	2152
	(13.1)	(40.4)	(33.3)	(49.3)					
16	528	360	344	308					
17	520	358	344	304			700 [d]	−1360 [c]	
	(9.3)	(36.9)	(30.9)	(56.2)					
18	524	358	344	306			720 [c]	−1430 [c]	
	(9.3)	(32.8)	(32.7)	(61.0)					
19	514	358	344	302			700 [c]	−1360 [c]	2177
	(8.5)	(35.9)	(34.6)	(61.4)					
20	542	358	344	304					
22	576	422	350	320	268		1030 [c]	−770 [d]	
	(10.2)	(5.5)	(50.2)	(36.7)	(58.4)				
24	496	360	344	316	298		980 [c]	−1360 [c]	
	(11.3)	(37.0)	(29.8)	(24.4)	(44.6)				

[a] In nm, extinction coefficient ($10^3\ M^{-1}\ cm^{-1}$) given in parentheses below.
[b] vs. Ag/AgCl/KCl sat.
[c] Irreversible.
[d] Quasi-reversible.

have shown coordination by the terminal (nitrile) nitrogen [25]. However there are examples for dinuclear transition metal complexes with a cyanamide bridge [37–40]. While coordination via the amido nitrogen is in principle possible, sterical reasons and the fact that the electron density at the terminal nitrogen is higher than at the amido nitrogen were used to rationalise the dominating nitrile coordination [17]. Nevertheless, for the unsubstituted cyanamide mono-anion, the existence of an amido-bound isomer has not been excluded [25]. Because ambidentate pseudohalides such as thiocyanate or selenocyanate formed coordination isomers when introduced in the model complex [9], the reaction of a ^{13}C-labelled phenylcyanamide anion with complex **6** was monitored simultaneously by ^1H NMR, ^{13}C NMR and IR spectroscopy. These spectroscopic techniques supplement each other to yield a comprehensive picture of the coordination mode.

Reactions were performed with a 1.4-fold excess of ligand at refluxing temperature in methanol and were interrupted after 40 min, 80 min, 3 and 6 h, respectively. The working-up procedure was the same as for, e.g., complex **11**. In Fig. 5, the parts of the ^1H NMR spectra of the products containing the dcbpy 6H signal are presented. As the most downfield shifted signal and not overlapping with other peaks, it serves as a valuable indicator signal for in situ reaction studies. After 40 min reaction time (b), about 60% of the starting material (doublet at 11.23 ppm) had reacted. Two new doublets with approximately the same intensity at 10.29 and 10.25 ppm were assigned to phenylcyanamide containing complexes, though in two different bonding modes. The weak doublet at 10.11 ppm is due to the formation of an intermediate not containing cyanamide. 80 min of refluxing (spectrum c) yielded conversion of 75% of the iodo complex, and the intensities of the doublets at 10.29 and 10.25 ppm indicated an isomer ratio of 2:1. After 3 h (d), only traces of the starting material were left, and the signal for the intermediate had disappeared. The relative intensity of the phenylcyanamide signals was 4:1. After 6 h (e), the isomer ratio was 19:1. It was not possible to further reduce the amount of the second isomer by prolonged reaction time. The assignment given is in accordance with integral sizes of phenylcyanamide proton signals. The formation of a dinuclear complex could be excluded, as it would be sterically hindered, and integration

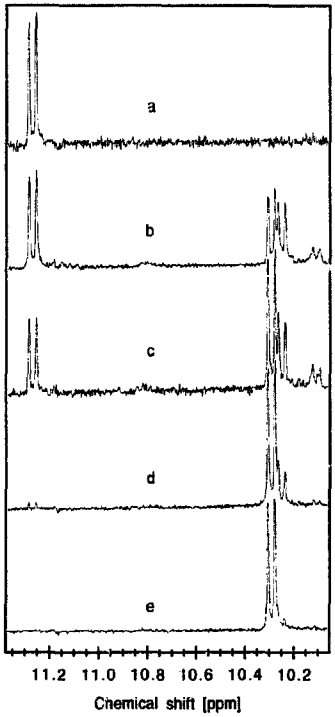

Fig. 5. Portions of the ^{1}H NMR spectrum of complex **11** for different reaction times: (a) starting material, (b) reaction time 40 min, (c) 80 min, (d) 3 h, (e) 6 h (in methanol-d_4).

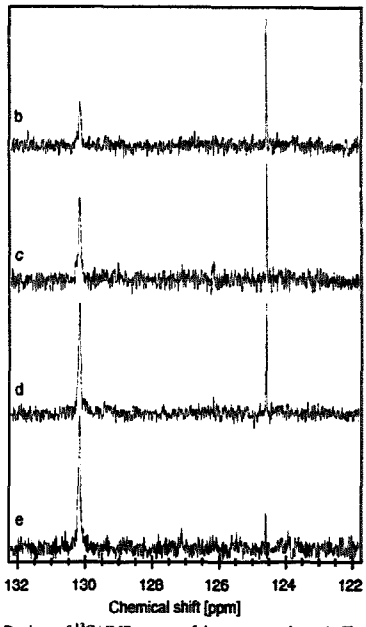

Fig. 6. Portions of ^{13}C NMR spectra of the same samples as in Fig. 5. Due to isotope labelling, only the phenylcyanamide signal is visible.

of the proton NMR signals gave a 1:1:1 ratio for phenylcyanamide, dcbpy and bmipy ligands, respectively.

^{13}C NMR spectra, displayed in Fig. 6 and IR data support the above interpretation. The ^{13}C NMR spectra show two differently coordinated phenylcyanamide ligands. The sharp peak at 124.55 ppm, which is diminuishing during the reaction (b–e), is assigned to amido-bound phenylcyanamide, as organonitriles appear in this spectral region [41]. The signal at 130.15 ppm is typical for carbodiimides [42]. Hence it appears that, in this isomer, the diimide structure is more or less retained. The change of intensities of the two signals during the reaction qualitatively corresponds to the intensities of the two doublets at 10.29 and 10.25 ppm in the proton NMR spectra. Free deprotonated phenylcyanamide occurs at 129.37 ppm in methanol-d_4.

IR spectra of the same samples showed a broad absorption at 2095 cm^{-1} for the isomeric mixture being refluxed for 40 min. With prolonged reaction time, the maximum of the band was shifted to higher energies, i.e. 2105 cm^{-1}. Note that ^{13}C-labelling of phenylcyanamide shifts its asymmetric C–N stretching vibration to lower energies by about 70 cm^{-1}. Since anionic phenylcyanamides coordinated to transition metals only show one strong absorption band [43], the occurrence of multiple bands is indicative of different bonding modes [24]. Generally, phenylcyanamides coordinated to transition metals show stretching frequencies between 2125 and 2175 cm^{-1}. For Ru(II) polypyridine complexes with substituted phenylcyanamides, values of about 2170 cm^{-1} have been found [24], and were assigned to nitrile-bound phenylcyanamides. From the very similar band position of about 2165 cm^{-1} found for the new phenylcyanamide complexes (see Table 3), one infers that the main isomer is coordinated also through nitrile. The band of the second isomer was weakly shifted to lower energies, but compared with the free ligand, signals of both isomers are shifted to higher energies. Hence a π bonding (side-on coordination) appears unlikely as in this case, a large shift of the IR band to lower energies due to the decrease of the nitrile bonding order would occur [44]. However, a conclusive assignment of the bonding mode cannot be made based on the IR data alone [18,43].

All other studied phenylcyanamide complexes qualitatively showed the same behaviour. The resulting isomer ratio is determined by the reaction time and the substituents on the phenyl ring. For sterical reasons, substitution in 2- or 6-position (e.g. in the ligands 2,4,5-Cl$_3$pcyd, 2-Clpcyd or 2,4,6-trimethylpcyd) strongly favours the nitrile-coordinated isomer, whereas complexes of unsubstituted or 4-substituted (X = Cl, NEt$_2$) phenylcyanamides are initially formed in an isomer ratio of nearly 1:1. With prolonged reaction time, though, the nitrile-bound main isomer is formed for all complexes with an isomer ratio of at least 19:1. No coordination isomers were observed for the dicyanoamide complex **8**.

3.3.2. Phosphonic acid substituted bipyridine complexes

The introduction of $KN^{13}CS$ in the triethylammonium salt of complex **23** has been followed in situ by NMR spectroscopy. As the complex contains the monosubstituted bipyridine 4-PO_3bpy, two stereoisomers are possible, the position of the phosphonic acid group being *trans* or *cis* with respect to the ligand X^-. Integration of ^{31}P NMR signals allowed a precise determination of the *cis*/*trans* isomer ratio.

Fig. 7 shows proton NMR spectra recorded after various reaction times. Again, only the H6 signal of the 4-PO_3bpy ligand is shown. (Note that proton numbers at the 4-PO_3bpy are different for the *cis* and the *trans* isomer.) The reaction was performed in a NMR tube by refluxing 4.0 mg of the triethylammonium salt of **23** and 6.6 mg of $KN^{13}CS$ in 0.6 ml of methanol-d_4. Spectrum a shows the starting material. There is 85% of the *trans* isomer (dd, 10.70 ppm, $J = 5.6$ Hz (H–C5), 1.3 Hz (H–C6)) and 15% of the *cis* isomer, giving rise to a doublet of doublets at 10.62 ppm with coupling constants of 5.6 Hz (H–C5 coupling) and 3.0 Hz (P–C4 coupling). Thiocyanate reacts with complex **23** in a manner analogous to the previously studied Na[Ru(bmipy)(4,4′-dcbpy)I] [9]. After the reaction mixture was refluxed for 20 min, four additional signals appeared and were assigned as two S-bound (10.56 (d), 10.44 (dd)) and two N-bound thiocyanate complex isomers (10.21 (d) and 10.13 (dd)) occurring with a 1:2 ratio (spectrum b). Prolonged reaction time (c–e) yielded complete conversion of the chloro to the thiocyanate complex and successive transformation of most of the S-bound to the N-bound isomers, but it was not possible to obtain the N-coordinated product free of S-bound isomer. The *trans*/*cis* ratio of 6:1 remained unaffected by ligand exchange reactions. These interpretations are substantiated by the complementary of ^{13}C and ^{31}P NMR data (Table 4). The assignment of ^{13}C NMR signals is based on the references given in our previous work [9]. The peak of the N-bound *cis* isomer might be overlapping with the signal of free thiocyanate at 133.71 ppm.

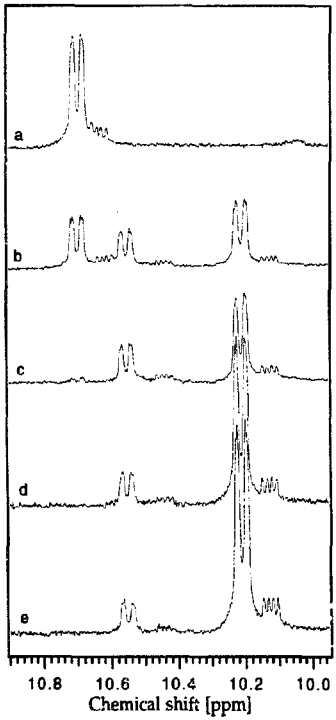

Fig. 7. Portions of ^1H NMR spectra during the preparation of **24**, recorded in methanol-d_4: (a) starting material, (b) after 20 min reflux time, (c) 80 min, (d) 4:20 h, (e) 10:20 h.

Table 4
^{13}C and ^{31}P NMR data in the preparation of **24** (in methanol-d_4)

X	^{31}P NMR (ppm)		^{13}C NMR (ppm)	
	Cis	*Trans*	*Cis*	*Trans*
Cl	6.66	6.06		
NCS	7.16	6.54		134.05
SCN	7.10	6.51	123.55	123.63

3.4. Photoelectrochemical measurements

The complexes were tested as sensitisers for nanocrystalline TiO_2. Current–voltage characteristics and overall cell efficiencies, which are given in Table 5 together with IPCE data, were obtained with a thin-layer sandwich-type cell under illumination with simulated AM 1.5 solar light. The incident monochromatic photon-to-current conversion efficiency is derived from Eq. (1) [6]:

Table 5
Photoelectrochemical data

Complex	IPCE max. (%)	IPCE 700 nm (%)	η [a] (%)	U_{oc} [b] (mV)	I_{sc} [c] (mA cm^{-2})	FF [d]
8	69	9	4.9	670	9.9	0.74
9	48	13	4.0	600	9.3	0.70
10	49	20	3.4	640	9.0	0.68
11	42	11	2.7	580	8.5	0.65
12	50	18	4.2	620	10.0	0.70
13	48	17	3.9	560	10.2	0.68
15	48	17	3.0	630	8.6	0.63
19	22	5	1.6	560	4.1	0.70
22	6	0				
22 [e]	20	13				
24	55	7	4.1	600	8.6	0.70
7	71	21	6.0	610	14.4	0.68

[a] Solar cell efficiency.
[b] Open circuit voltage.
[c] Short circuit current.
[d] Fill factor.
[e] 3%HI conc./acetone electrolyte.

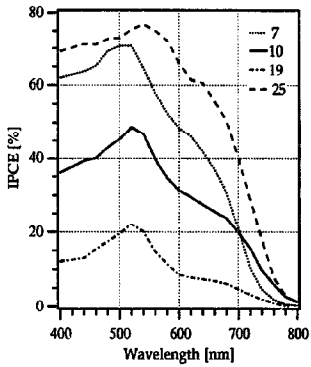

Fig. 8. Representative IPCE curves. The graph of *cis*-Ru(dcbpyH$_2$)$_2$(NCS)$_2$ (**25**) was added for comparison.

$$\text{IPCE}(\%) = \frac{1.25 \times 10^3 \times \text{photocurrent density } (\mu\text{A/cm}^2)}{\text{wavelength (nm)} \times \text{photon flux } (\text{W/cm}^2)} \times 100 \quad (1)$$

Reported IPCE values are not corrected for light losses due to reflection or absorption by the supporting electrode. Some representative action spectra are shown in Fig. 8. All presented values are the average of three measured electrodes. IPCE values at wavelengths above 550 nm depend strongly on semiconductor film thickness [6]. In this work. the TiO_2 layer thickness was 9 μm.

For all phenylcyanamide complexes, short-circuit currents did increase in a super-linear fashion with light intensity, indicating surface aggregation. Hence, 50 mM 3α,7β-dihydroxy-5β-cholanic acid was added to the ethanolic solutions of the dyes before soaking the electrodes. Cholanic acids have been shown to improve both photocurrent and voltage of copper chlorophyllin sensitized TiO_2 cells [45]. For the phenylcyanamide complexes, the same effect was observed.

The model sensitiser **7** yielded an IPCE value of 71% at 520 nm. With a short-circuit current of 14.4 mA cm^{-2}, a device efficiency of 6.0% was reached, which is impressive regarding the absorption spectrum of the complex (MLCT maximum at 500 nm in methanol).

The cyanamide complexes **16** and **20**, which were adsorbed on the electrodes directly from ethanolic reaction mixtures, gave an almost black electrode coloration, but decomposed immediately on contact with electrolyte. The methoxy complex **14** decomposed on the electrode as well, yielding a blue-shift of the absorption spectrum.

The low π^* level complexes showed reduced IPCE values under the applied standard measuring conditions. The electrodes being soaked in solutions of complexes containing 5,5′-dcbpy **17–20** were less intensely coloured than their 4,4′-dcbpy analogues. This may be explained by their reduced absorption coefficients and the less favourable geometry of the 5,5′-dcbpy ligand. IPCE values can be increased by acidification or by addition of Li^+ ions, but this reduces energy conversion efficiencies due to cell potential loss. In contrast, the lowered IPCE values of transition metal complexes containing 5,5′-dcbpy studied earlier, were explained by a non-radiative decay of the excited state [7]. The dicarboxybiquinoline complex **22** showed a drastically reduced IPCE value of 6% at 520 nm, which could however be increased to 20% by using 3% HI conc./acetone as an electrolyte, the acid lowering the TiO_2 conduction band.

The phenylcyanamide complexes yielded, apart from complex **11**, IPCE values of about 50% at 520 nm (see Table 5). The IPCE value of 48% at 520 nm reached by the trimethylphenylcyanamide complex **15** is remarkable in view of its low oxidation potential of 490 mV versus Ag/AgCl. It illustrates that oxidation potentials, which were between 490 and 720 mV versus Ag/AgCl for the phenylcyanamide complexes, are sufficiently high to ascertain dye regeneration. Pronounced variations occurred however for IPCE values at longer wavelengths such as 700 nm, where conversion efficiencies of 13–20% were measured. With the data available however, no clear correlation between phenyl substitution and efficiency in the solar cell device can be made: the complexes containing 2,4,5-Cl$_3$pcyd **9**, 2-Clpcyd **10**, and 2,4,6-Me$_3$pcyd **15** reached device efficiencies of approximately 4%, whereas the complex containing 4-Clpcyd **11** showed reduced IPCE values and lower energy conversion efficiency. In comparison with the model complex **7**, phenylcyanamide complexes show increased IPCE values at longer wavelengths (see Fig. 8), but due to reduced IPCE values at 520 nm, device efficiencies are lower. The most efficient sensitizer in this series, apart from the model complex, was the dicyanoamide complex **8**, showing the highest open-circuit voltage of 670 mV. However, due to the blue-shifted absorption spectrum, its light harvesting at longer wavelengths is poor.

The phosphonated complex **24** efficiently sensitized TiO_2, although IPCE values and overall performance were reduced. compared with the model complex. It should be mentioned however, that both the complex K[Ru(tmter)(4-PO$_3$bpy)(NCS)] with tmter=4,4′,4″-trimethyl-2,2′,6′,2″-terpyridine and **24** yielded IPCE values of 70% at 520 nm [34] on electrodes prepared from Degussa P25 TiO_2 [6]. This shows (i) that the phosphonate group is an efficient coupling group for electron transfer from the excited sensitiser to the TiO_2 conduction band and (ii) that only one phosphonate group is sufficient for efficient semiconductor sensitisation. Furthermore, unlike their carboxylated analogues, phosphonated Ru(II) complexes attached to a TiO_2 surface do not desorb easily when exposed to water. These features make the phosphonate group an attractive alternative as anchoring group [8].

4. Conclusions

In conclusion we have scrutinised the effect of structural variations of a model sensitiser for nanocrystalline TiO_2,

K[Ru(4,4′-dcbpy)(bmipy)(NCS)], on its performance as a charge transfer sensitiser for nanocrystalline TiO_2. Thiocyanate was replaced by a series of cyanamides; alternatively 4,4′-dcbpy was substituted by other polypyridine ligands containing anchoring groups. Low π^* level complexes containing 5,5′-dcbpy or dcbiq exhibited low IPCE values and device efficiencies. Cyanamide complexes were found to decompose upon isolation. Phenylcyanamide complexes in contrast were stable, and complexes covering a range of excitation energies and redox potentials were prepared. Substituents on the phenyl group only had a small influence on the IPCE maxima in the solar cell device, and despite improved IPCE values above 700 nm, none of the new compounds reached the efficiency of the model complex due to reduced IPCE values at 520 nm. The phosphonic acid group, however, has shown to be a valuable alternative to the carboxy group as anchoring unit. Apart from the photovoltaic performance measurements multinuclear NMR studies revealed the occurrence of linkage isomerism for most of the applied ambidentate ligands when introduced into the complex. For the first time, evidence was given for the existence of an amido-bound mononuclear transition metal phenylcyanamide complex.

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