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Sensitization of TiO$_2$ with ruthenium complexes containing boronic acid functions

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Abstract

New ruthenium complexes based on bipyiridine and terpyridyne type ligands, containing boronic acid functions, of formulae: [Ru(bpy-Φ-B(OH)$_2$)$_2$(CN)$_2$], **6**, (bpy-Φ-B(OH)$_2$ = 4-(2,2′-dipyridil)phenylboronic acid), [Ru(trpy-B(OH)$_2$)(tb$_2$bpy)Cl](PF$_6$), **11**, (trpy-B(OH)$_2$ = 4-[4′-(2,2′:6′,2″-terpyridil]-boronic acid), [Ru(trpy)-Φ-B(OH)$_2$)(tb$_2$bpy)Cl] (PF$_6$), **12**, (trpy)-Φ-B(OH)$_2$ = 4-[4′-(2,2′:6′,2″-terpyridil]-phenylboronic acid), have been prepared, characterized, and tested in dye-sensitized solar cells (DSSCs). The results of this first study indicate that: (i) the boronic acid function acts as interlocking group between sensitizer and mesoporous titanium dioxide; (ii) only the presence of two B(OH)$_2$ groups/molecule allow to obtain high photoanode surface coverages with optical densities > 1; (iii) The presence of the phenyl spacer in **12** reduces the photocurrent efficiency with respect to complex **11**, most probably for a reduced electronic coupling between excited sensitizer and semiconductor conduction band. The insights gained from this work suggest that better photoelectrochemical performances should be obtained with dye molecules based on bpy type ligands bearing two boronic acid functions directly bound to the aromatic ring.

Keywords: Ruthenium complexes; Titanium dioxide; Boronic acid function

1. Introduction

Solar cells are one of the most promising devices in the search for sustainable renewable sources of energy [1,2]. Although the field has been dominated by standard silicon solar cells with technology based on the solid-state p–n junction devices, a new generation of photovoltaics is emerging. One of them is the dye-sensitized nanocrystalline solar cell, which has a different approach from the conventional systems, where the semiconductor performs both the task of light absorption and charge carrier transport. These two functions are separated in a dye-sensitized solar cell (DSSCs) by having the light absorbed by sensitizers (dyes) chemically attached to the surface of a nanostructured wide band-gap semiconductor (mesoporous oxides) [3–8].

The most efficient sensitizers studied so far are based on ruthenium or osmium polypyridine complexes that are chemisorbed on the semiconductor surface via carboxylic acid groups [9,10]. An alternative anchoring group is the phosphonic acid functionality which has been shown to form very stable bonds with nanocrystalline zirconium and titanium dioxide. The utilization of phosphonic acid groups for the immobilization of dyes on TiO$_2$ has been first reported by Grätzel and coworkers [11,12], it was then followed by other research groups [13–16].

The anchoring group is an important parameter to consider in the design of efficient sensitizers because it may affect both the stability of the linkage and the electronic coupling between the dye and the semiconductor [17]. Since organic ligands bearing boronic acid functions were observed to adsorb and metal oxide substrates we decided to explore the properties of new ruthenium complexes containing polypyridine ligands functionalized with B(OH)$_2$ substituents. As a first attempt we have focused on bipyridine and terpyridine ligands of the type:

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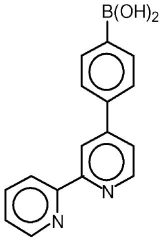

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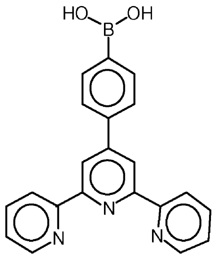

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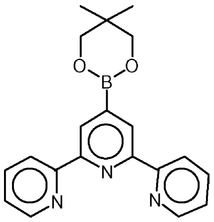

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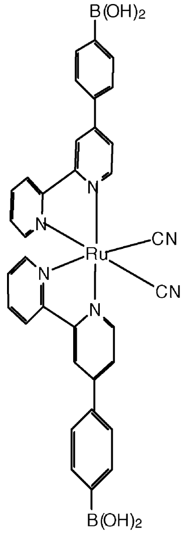
and on the preparation of the following metal complexes:



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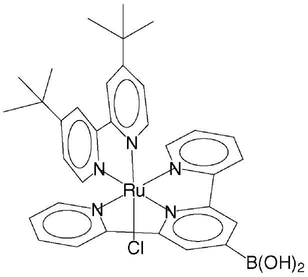

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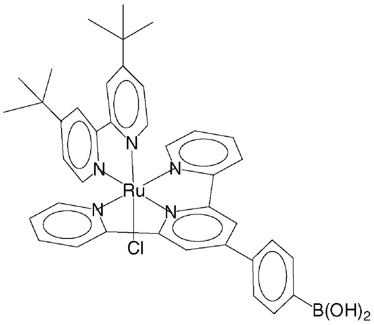

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We report here the spectroscopic and photoelectrochemical properties of these new molecules.

2. Experimental

2.1. Materials

2-Acetyl pyridine, tetrabuthylammonium hexafluorophosphate (TBAPF$_6$), 4-bromobenzaldehyde and triisopropyl borate, [1,1′-bis (diphenylphosphino) ferrocene] palladium dichloride, “Pd(dppf)Cl$_2$” 1:1 in CH$_2$Cl$_2$ were purchased from Aldrich-Fluka and used without further purification. RuCl$_3$·3H$_2$O was a Johnson Matthey product. Spectrograde solvents were used for the spectroscopic and electrochemical measurements and dried if necessary, other reagents and solvents were reagent grade and used as purchased unless otherwise stated. TLC was carried out on silica gel Si 60-F$_{254}$. Column chromatography was carried out on silica gel Si 60, mesh size 0.040–0.063 mm (Merck) or Sephadex LH-20 and Sephadex G15 purchased from Pharmacia Biotech.

2.2. Apparatus and procedures

^{1}H NMR (300 MHz) spectra were recorded with a Bruker AC 300 or with a Varian Gemini 300 MHz at 25 °C, chemical shifts were measured in ppm to high frequency of SiMe$_4$. Infrared spectra were acquired on a Bruker IFS 88B FTIR spectrophotometer.

Electrochemical data were obtained by cyclic voltammetric (CV) measurements performed with a potentiostat–galvanostat MacLab model ML160 controlled by resident software (Echem v1.5.2 for Windows). A standard three electrode cell (working, glassy carbon; counter, Pt and reference electrode, SCE) was used in the electrochemical measurements. In all the experiments the scan rate was 100 mV/s. UV–vis absorption spectra were recorded on a UV-2401PC Shimadzu and on a Perkin-Elmer Lamba 40 spectrophotometers. Steady state luminescence studies were performed using a Jobin Yvon Spex Fluoromax 2 Spectrofluorimeter equipped with a R3896 Hamamatsu tube. Emission lifetimes were measured with a laser flash photolysis apparatus consisting of a Continuum Surelite II, Q switched (Nd-YAG) laser (halfwidth 7 ns). Emission was collected at 90° through an Applied Photophysics monochromator equipped with a R 928 Hamamatsu photomultiplier. The signals were acquired on a 600 MHz Le Croy 9360 digital oscilloscope and elaborated by means of Origin 6 software.

Photoelectrochemical performances of the complexes were evaluated on sandwich type cells consisting of a photoanode, with an active area of 0.54 cm^2, a counter electrode of platinized FTO conducting glass and LiI 2M/I_2 0.1 M in γ-butyrolactone as electrolyte. The spectral response or incident photon to current efficiency (IPCE) measurements were carried out with an in-house test bench controlled by computer, which mainly consisted on the following items: A high power (450 W) Xenon short-arc ozone free lamp OSRAM Xenon connected to a power supply Jobin Yvon, a large output monochromator TRIAX-180 Jobin Yvon, 2 high-pass filters (320 and 590 nm) used to cut high orders wavelengths, a bi-concave lens BK7 from Melles Griot (f/127 mm, 50 mm diameter), and two multimeters Keithley 199 used to measure the short-circuit current of the reference and the test cells. The reference cell was a silicon diode Melles Griot 13 DSI 011 of 1 cm diameter and it was calibrated versus the wavelength from 400 to 1100 nm. The IPCE software calculated the integrated current corresponding to the solar standard spectrum AM1.5G by using the IPCE spectrum and the solar standard in the interval 400–1100 nm. The cell irradiance in the IPCE test bench was of the order of 100 W/m^2 in the whole wavelength interval.

Transparent nanocrystalline transparent TiO_2 films were obtained from a colloidal suspension of TiO_2 similar to those prepared as described elsewhere [17]. Adsorption of the dye was accomplished by dipping the electrodes still hot (70–80 °C) in a 5×10^{-4} M solution of the complex in CH_3OH and letting them immersed in the solution at room temperature for 24 h or keeping them at reflux for 5 h. Dye-sensitized electrodes were kept in a desiccator on silica gel.

2.3. Synthesis

Acetylpyridine pyridinium iodide was prepared as described by Baba and Schmel [18], the hexafluorophosphate salt was obtained by precipitation of an aqueous solution of the iodide salt with ammonium hexafluorophosphate and used without further purification.

Ligand preparations are illustrated in Schemes 1 and 2.

2.3.1. 1-(3-Carboxy-3-oxo-prop-1-en-1-yl)4-bromobenzene (1)

4-Bromobenzaldehyde 10 g (0.054 mol) was dissolved in ethanol (130 ml). The solution was slowly added to a stirred and cooled (0 °C) suspension of sodium pyruvate, 5.94 g (0.054 mol) in 40 ml water. The mixture was stirred vigorously while 20 ml of 10% NaOH were added. The reaction was then acidified with 35 ml of 15% HCl. The resulting yellow precipitate was filtered, washed with acetone and dried at 70 °C to yield 8.85 g (65%) of the acid (**1**).

^1H NMR (δ in ppm, deuterated DMSO): 7.60 (4H, s), 7.40 (1H, d), 6.80 (1H, d).

2.3.2. 4-(4-Bromophenyl)6-carboxy-2,2′-bipyridine, ammonium salt (2)

The acid (**1**) (7.61 g, 0.030 mol), 2-acetylpyridine pyridinium hexafluorophosphate salt 12.22 g (0.036 mol) and ammonium acetate 33.9 g (0.44 mol) were suspended in 500 ml of distilled water and refluxed for 3 h. During the reaction the colour of the reaction turned reddish-brown and a tan precipitate formed. The hot mixture was filtered, the precipitate washed with distilled water and dried at 70 °C to yield 7.35 g (66%) of (**2**).

^1H NMR (δ in ppm, deuterated DMSO): 8.72 (1H, d), 8.58 (1H, d), 8.45 (1H, d), 8.18 (1H, d) 7.98 (1H t of d), 7.82 (2H, d), 7.73 (2H, d), 7.48 (1H, q of d).

IR (KBr): ν_{CO} 1594 cm^{-1}.

2.3.3. 4-(4-Bromophenyl)2,2′-bipyridine (3)

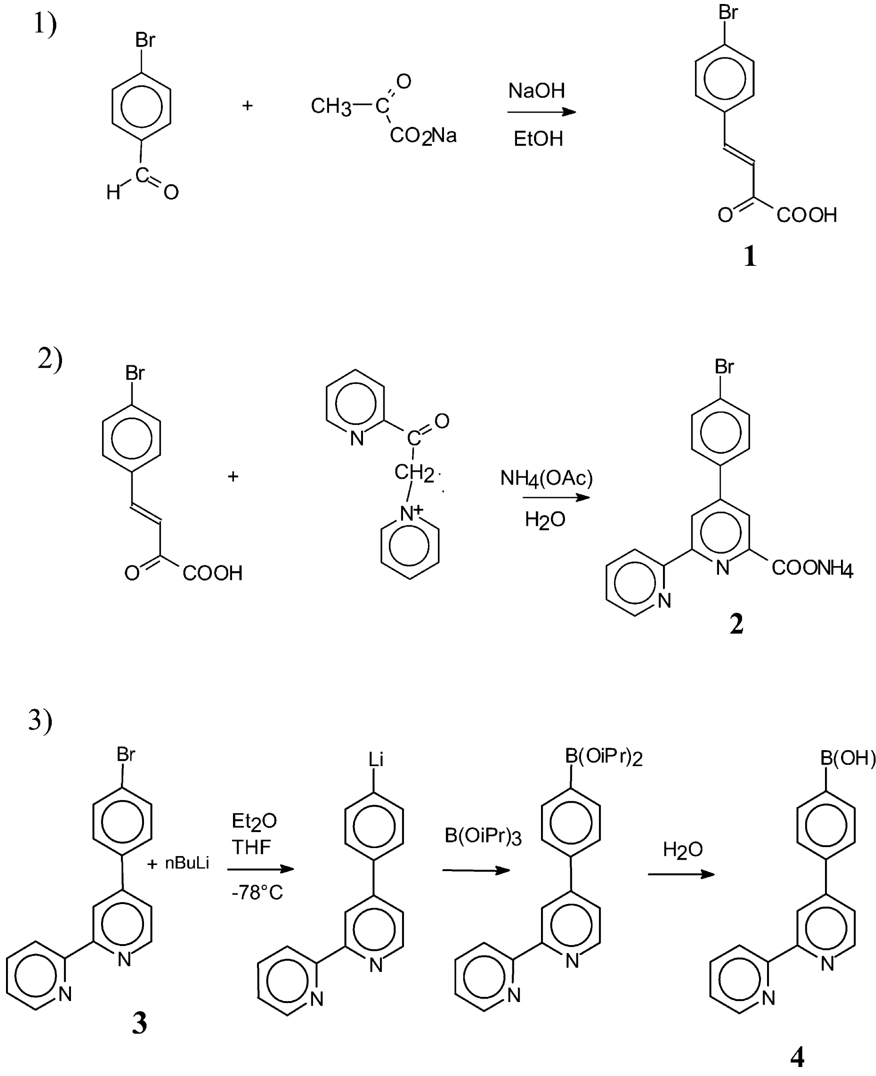
To a solution of 4-(4-bromophenyl)6-carboxy-2.2′-bipyridine ammonium salt (**2**) 4.1 g (10.8×10^{-3} mol) in 200 ml of dimethylsulfoxide, LiCl 2.58 g (0.061 mol) and 1080 μl of distilled water were added. The brown solution was refluxed for 5 h then cooled in an ice bath after the addition of 170 ml of distilled water. The resulting brown precipitate was filtered, washed with water and purified on a silica column using $CHCl_3$ as eluent. The first eluted fraction was evaporated to dryness to give 2.25 g (67% yield) of (**3**).

^1H NMR (δ in $CDCl_3$): 8.72 (2H, m), 8.64 (1H, d), 8.44 (1H, d), 7.84 (1H, t of d), 7.63 (4H, s), 7.49 (1H, d of d), 7.34 (1H, q of d).

2.3.4. 4-(2,2′-Dipyridil)phenylboronic acid, [bpy-Φ-B(OH)$_2$] (4)

The following reaction was performed under nitrogen and the organic solvents were dried and degassed. 4-(4-Bromophenyl)2,2′-bipyridine (**3**) 0.264 g (0.85×10^{-3} mol) were dissolved in 10 ml of a 1:1 Et_2O and THF mixture. To this solution cooled to −78 °C, 0.63 ml of 1.6 M *n*-BuLi were slowly added. One hour after the addition, 0.40 ml of triisopropyl borate was added. The resulting black, oily reaction mixture was left stirring 12 h at room temperature and then 15 ml of distilled water added. The desired product was extracted with Et_2O, the organic fraction was washed with water and dried over $MgSO_4$. The crude product was purified on a silica column eluted with a 50:1, CH_3Cl and CH_3OH mixture. The last eluted fraction was collected, evaporated to dryness to yield 40 mg (20%) of the desired compound (**4**).

^1H NMR (δ in ppm, deuterated DMSO): 8.75 (2H, m), 8.69 (1H, d), 8.44 (1H,d), 8.22 (2H,s), 8.02–7.98 (3H, two partially overlapped doublets), 7.91–7.82 (3H, two partially overlapped doublets), 7.51 (1H, q of d). Elemental analysis for $C_{16}H_{13}BN_2O_2 \cdot 1H_2O$: found (calcd) C 65.26 (65.34), H 5.38 (5.14), N 9.62 (9.52).



Scheme 1.

2.3.5. [Ru(bpy-Φ-B(OH)$_2$)$_2$Cl$_2$] (5)

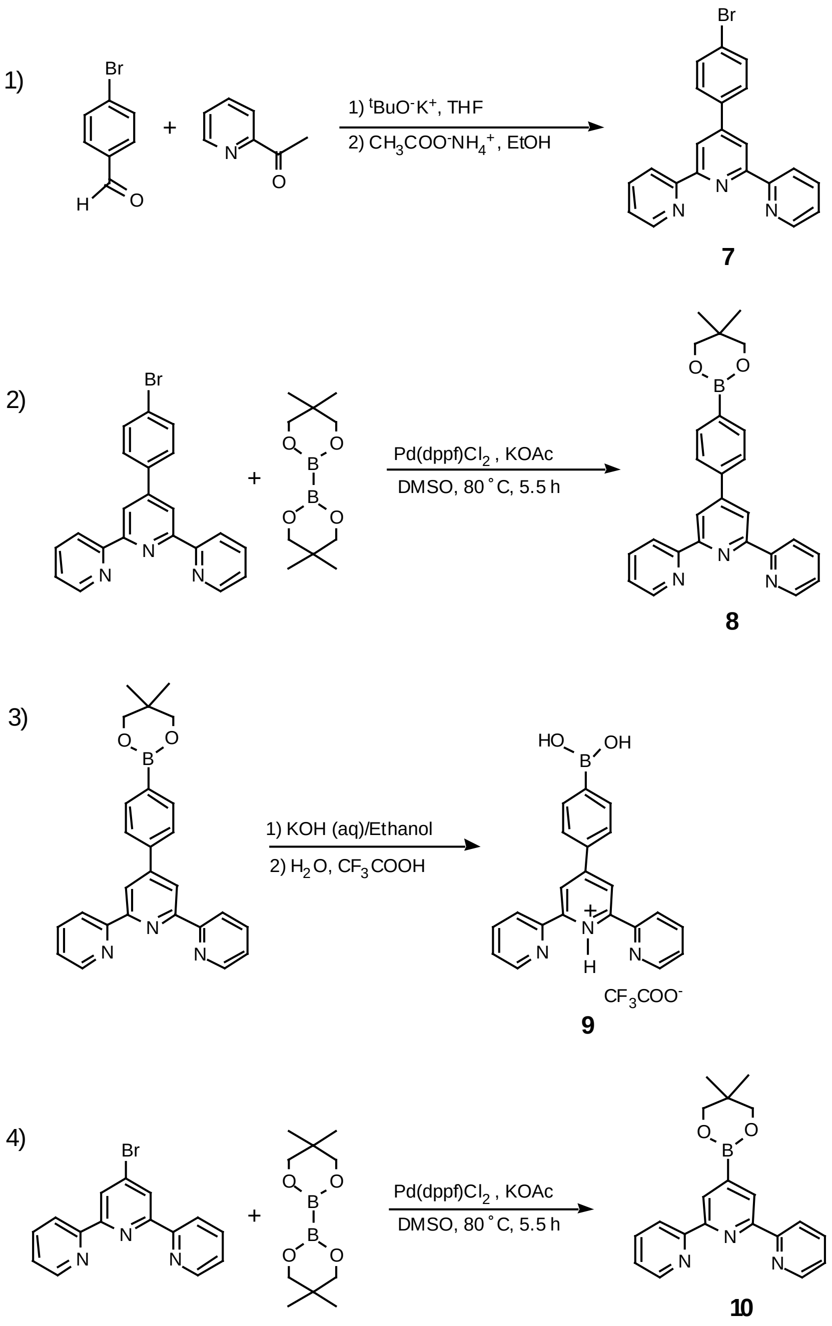
To a solution of [bpy-Φ-B(OH)$_2$], (**4**) 0.0994 g (3.60×10^{-4} mol) in 5 ml of DMF, a solution of $RuCl_3 \cdot 3\ H_2O$ 0.060 g (2.28×10^{-4} mol) in 5 ml of DMF followed by 1.53 g (0.036 mol) of solid LiCl were added. The mixture was heated at reflux for 5 h and the reaction was followed via thin-layer chromatography on silica plates with methanol as eluent, showing the presence of the desired product ($R_f = 0.3$). The reaction mixture was evaporated to dryness and the crude product chromatographed on a silica column. Elution was first performed with methanol then with methanol/HCl (2 M) to collect the purple fraction which was evaporated to dryness. The desired complex (**5**) 0.110 g, 85% yield was obtained and used with no further purification.

2.3.6. [Ru(bpy-Φ-B(OH)$_2$)$_2$(CN)$_2$] (6)

To a solution of [Ru(bpy-Φ-B(OH)$_2$)$_2$Cl$_2$] (**5**), 0.053 g (7.32×10^{-5} mol) in 15 ml of methanol, a solution of NaCN 0.155 g (3.16×10^{-3} mol) in 5 ml of water was added. The solution was heated at reflux for 40 min and the reaction followed via thin-layer chromatography on silica plates with methanol as eluent, showing after the first few minutes of reaction the formation of a bright yellow component ($R_f = 0.3$). Twenty milliliters of distilled water were added, the methanol stripped off under vacuum then 2 M HCl was added to obtain the complete precipitation of the desired complex (*warning*: this operation should be carried out in a well ventilated fume-hood and the HCN formed disposed of according to literature safety procedure). The complex was filtered, washed with water and dried under vacuum yielding 0.026 g, (50% yield) of (**6**). Elemental analysis for $C_{36}H_{26}B_2N_6O_4Ru \cdot 3H_2O$: found (calcd) C 50.22 (50.78), H 4.16 (4.25), N 10.91 (11.07). IR: $\nu(OH) = 3440\,cm^{-1}$, $\nu(CN) = 2070\,cm^{-1}$in KBr pellet.

2.3.7. 4′-(4-Bromophenyl)-2,2′:6′,2″-terpyridine (7)

A solution of 2.68 g (0.022 mol) of 2-acetylpyridine in 10 ml of dry tetrahydrofurane (THF) was slowly added via



Scheme 2.

siringe to a suspension of 3.70 g (0.033 mol) of potassium *tert*-butoxide in 20 ml of dry THF and the resulting suspension was stirred at room temperature (RT) for 2 h with formation of a white solid. Then a solution of 1.85 g (0.010 mol) of 4-bromobenzaldehyde in 20 ml of dry THF was added via siringe and the reaction mixture was stirred, at RT, overnight. A large excess of solid ammonium acetate 25 g (0.32 mol) and 120 ml of absolute ethanol were added and the reaction mixture was refluxed under magnetic stirring for 4 h. The reaction mixture was cooled at RT and the solvent concentrated to 40 ml under reduced pressure with formation of a solid white precipitate which was filtered and recrystallized from ethanol to afford 0.77 g (20 %) of pure **4** as white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.36 (m, 2H), 7.64 (d, $J = 8.6$ Hz, 2H), 7.78 (d, $J = 8.6$ Hz, 2H), 7.88 (dt, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, 2H), 8.67 (d, $J = 8.0$ Hz, 2H), 8.70 (s, 2H), 8.73 (m, 2H).

2.3.8. *4′-[4-(Neopentyl glycolatoboron)phenyl]-2,2′:6′,2″-terpyridine (**8**)*

This product has been prepared following the procedure reported in ref. [19].

2.3.9. 4-[4′-(2,2′:6′,2″-Terpyridil]-phenylboronic acid) pyridinium trifluoroacetate (trpy-Φ-B(OH)$_2$) (**9**)

A solution of 0.46 g (8.7 mmol) of KOH in 1.5 ml of H_2O was added to a suspension of 0.37 g (0.87 mmol) of boronate ester **7** after a few minutes the substrate is dissolved and the reaction mixture was stirred for 2 h at reflux. The solvent was evaporated under reduced pressure, the residue was dissolved in 50 ml of H_2O and CF_3COOH was added, until the pH was in the range 7.1–7.2, with formation of a white precipitate. The solid was separated by filtration, washed with small portions of diethyl ether and dried to afford 0.28 g of **9** as white solid. ^{1}H NMR (DMSO-d$_6$, 300 MHz): δ 3.33 (s, D_2O exchange), 7.54 (m, 2H), 7.90 (d, $J = 8.1$ Hz, 2H), 8.01 (d, $J = 8.01$ Hz, 2H), 8.04 (dt, $J_1 = 7.8$ Hz, $J_2 = 1.8$ Hz, 2H), 8.23 (m, 1H, D_2O exchange), 8.68 (d, $J = 7.8$ Hz, 2H), 8.74 (s, 2H), 8.77 (d, $J = 3.9$ Hz, 2H). ^{19}F NMR (DMSO-d$_6$, 300 MHz): δ −69 (s). The presence of the proton at 8.23 ppm associated with the signal of fluorine at −69 ppm is in agreement with the proposed structure.

2.3.10. 4′-(Neopentyl glycolatoboron)-2,2′:6′,2″-terpyridine (**10**)

This product has been prepared following the procedure reported in ref. [19].

2.3.11. [Ru(trpy-B(OH)$_2$)(tb$_2$bpy)Cl](PF$_6$) (**11**)

A 70 mg amount of $RuCl_3 \cdot 3H_2O$ (0.27 mmol) and 92 mg of trpy-B(*O*-ester)$_2$ **12** (0.27 mmol) were refluxed (120 °C) in 20 ml of *n*-butyl alcohol for 6 h. The solution was cooled at RT and the solid [Ru(trpy-B(*O*-ester)$_2$)Cl$_3$] filtered off and washed with water, ethanol, and dried overnight at 60 °C. 70 mg of [Ru(trpy-B(*O*-ester)$_2$)Cl$_3$] (0.13 mmol) and 35 mg of 4,4′-*tert*-butyl-2,2′-bipyridine (0.13 mmol) were dissolved in DMF and heated at 120 °C for 6 h. The progress of the reaction, monitored by cyclic voltammetry in MeOH/TBAPF$_6$ 0.1 N, showed the disappearance of the reversible Ru(II)/(III) wave of the reactant ($E_{1/2} = 0$ V versus SCE) and the appearance of the reversible wave of the product ($E_{1/2} = 705$ mV versus SCE). The solution was rotary evaporated and the solid redissolved in methanol. Solid NH_4PF_6 was added followed by addition of water under stirring until incipient precipitation. The solution was cooled for 3 h in a refrigerator and the precipitated product was filtered off. The solid was purified by column chromatography on Sephadex LH20 by using MeOH as eluant. The red–orange fraction was collected and dried. NMR analysis showed that in the collected product the B(*O*-ester)$_2$ function was completely hydrolyzed.

H NMR [Ru(trpy-B(OH)$_2$)(tb$_2$bpy)Cl] (PF$_6$) (400 MHz, CD_3OD) δ ppm: 1.3 (9H, s, H^B), 1.65 (9H,s, H^A), 7.1 (2H, d, H^{2a}), 7.22 (1H, d, H^{6a}), 7.35 (2H, t, H$^{4,4''}$), 7.7 (2H, d, H$^{3,3''}$), 7.92 (3H, m, H$^{5,5'',3''}$), 8.08 (1H, d, H^{5a}), 8.15 (1H, t, H^3), 8.5 (1H, s, H^{4a}), 8.55 (1H, d, H$^{6''}$), 8.65 (1H, d, H^6), 8.8 (1H, s, H^{3a}), 10.1 (1H, d, H^{1a}).

2.3.12. [Ru(trpy-Φ-B(OH)$_2$)(tb$_2$bpy)Cl] (PF$_6$) (**12**)

The complex was prepared and purified following the same procedure described for the [Ru(trpy-B(OH)$_2$)(tb$_2$bpy) Cl](PF$_6$) complex. In the first step, $RuCl_3$ was made to react with a stoichiometric amount of the 4-[4′-(2,2′:6′,2″-terpyridil]-phenylboronic acid).

H NMR [Ru(trpy-Φ-B(OH)$_2$)(tb$_2$bpy)Cl] (PF$_6$) (400 MHz, CD_3OD) δ ppm: 1.3 (9H, s, H^B), 1.65 (9H,s, H^A), 7.08 (2H, d, H^{2a}), 7.25 (1H, d, H^{6a}), 7.33 (2H, t, H$^{4,4''}$), 7.7 (2H, d, H$^{3,3''}$), 7.9 (2H, t, H$^{5,5''}$), 8.02 (2H, m, H^{a,b}) 8.08 (1H, d, H^{5a}), 8.13 (2H, m, H^{c,d}), 8.5 (1H, s, H^{4a}), 8.65 (2H, d, H$^{6,6''}$), 8.8 (1H, s, H^{3a}), 8.9 (2H, s, H$^{3',5'}$), 10.1 (1H,d, H^{1a}).

3. Results and discussion

3.1. Preparations

Ligand preparations are summarized in Schemes 1 and 2. Ligand (**9**) has been obtained by alkaline hydrolysis of the boronate ester (**8**) which has been prepared by palladium catalyzed coupling of 4′-(4-bromophenyl)-2,2′:6′,2″-terpyridine (**7**) with bis(neopentyl glycolato)diboron, [19] (Scheme 2). The synthesis of terpyridine (**7**) has been already described by Spahni and Calzaferri [20] under very drastic conditions and by Cave and Raston [21] who claims 75% isolated yield via a sequential solvent free procedure. However, all the attempts we have done to obtain (**9**) by following this last procedure failed. Preparation of (**9**) was carried out by a one step condensation of 4-bromobenzaldehyde with 2-acetylpyridine in tetrahydrofurane and in the presence of potassium *tert*-butoxide as base, followed by ring closure with ammonium acetate in refluxing ethanol (see experimental). Ligand (**10**) has been prepared in 80% yield, following the same procedure used in the case of (**8**), [19] starting from 4′-bromo-2,2′:6′,2″-terpyridine [22].

3.2. Electronic spectra

The absorption spectra of [Ru(bpy-Φ-B(OH)$_2$)$_2$(CN)$_2$] (**6**) [Ru(trpy-B(OH)$_2$)(tb$_2$bpy)Cl](PF$_6$), (**11**) and [Ru(trpy-Φ-B(OH)$_2$)(tb$_2$bpy)Cl] (PF$_6$), (**12**) show in the visible region metal-to-ligand charge transfer (MLCT) transitions involving d$_\pi$ metal orbitals and π^* orbitals localized on the polypyridine ligands and intense bands in the UV region that are assigned to $\pi \rightarrow \pi^*$ transitions localized on the chromophoric ligands. For complexes (**11**) and (**12**) the UV–vis absorption bands result from overlapping electronic transitions involving orbitals of the terpyridine and bypyridine ligands. In Table 1 are reported the absorption maxima of the three complexes recorded in methanol.

3.3. Electrochemistry

The electrochemistry of [Ru(bpy-Φ-B(OH)$_2$)$_2$(CN)$_2$] (**6**) was studied by cyclic voltammetry in a 1:1 DMF/CH_3CN mixture. The electrochemical behavior was irreversible,

Table 1
Absorption maxima of the Ruthenium dyes recorded in methanol

Complex	λ MLCT (nm)	λ π−π* (nm)
$[Ru(trpy\text{-}B(OH)_2)(tb_2bpy)Cl](PF_6)$	500	316, 292
$[Ru(trpy\text{-}\Phi\text{-}B(OH)_2)(tb_2bpy)Cl](PF_6)$	502	315, 285
$[Ru(bpy\text{-}\Phi\text{-}B(OH)_2)_2(CN)_2]$	470	290, 255

showing only the anodic peak at 1.10 V versus SCE which is assigned to the oxidation of the Ru(II) center. For complexes (**11**) and (**12**) a reversible electrochemical behavior was observed in methanol with $TBAPF_6$ as supporting electrolyte. The two species showed reversible waves corresponding to Ru(II)/(III) redox couples with $E_{1/2} = 0.70$ (**11**) and 0.71 V (**12**) versus SCE. The irreversibility of Ru(II) oxidation in (**6**) is most probably due to the presence of coordinated ligands giving a strong back-bonding interaction with the metal center. In the case of (**11**) and (**12**) the presence of the chloride ligand, which donates charge to the metal center, stabilize the oxidized form of the complexes and cause a cathodic shift of the oxidation wave with respect to (**6**).

3.4. Photophysical properties

No emission was observed from complexes (**11**) and (**12**) in fluid solution. Complex (**6**) was found to be emitting as the analogous $Ru(dcbH_2)(CN)_2$ sensitizer ($dcbH_2$ = 4,4′ dicarboxylic acid, 2,2′-bypyridine) [23]. Owing to the presence of cyanide ligands in the coordination sphere, complex (**6**) is solvatochromic, The emission in methanol is non-structured, as typically observed for MLCT emitters, with a maximum at 660 nm. The emission decay was mono-exponential with a lifetime of 417.6 ns.

3.5. Photoelectrochemistry

The photoaction spectrum of complex (**6**) is reported in Fig. 1 and the photoaction spectra of the complexes (**11**), (**12**) are reported in Fig. 2. Complex (**6**) shows IPCE values above 60% between 400 and 600 nm while complexes (**11**) and (**12**) exhibited poor performances, with $IPCE_{max}$ of the order of 22% for (**11**) and 7% for (**12**). These low values are in part due to the low surface coverage obtained with the terpyridine complexes which contain only one boronic acid moiety. The optical density of the photoanodes did not exceed infact 0.25, even after prolonged heating in the presence of the dye solutions. With complex (**6**), containing two boronic functions, optical densities higher than 1 were commonly obtained. Correcting the IPCE values for the light harvesting term ($1–10^{−OD}$), absorbed photon to current conversion efficiency (APCE) values of the order of 57 and 16% are obtained for (**11**) and (**12**), respectively. This result, together with the lack of any emission in fluid solution, suggests that non-radiative deactivation from the excited sensitizers may compete with charge injection to the semiconductor. Interestingly, although very low photocurrents were observed for these terpyridine complexes, the photoconversion efficiencies are higher for (**11**) which contains the $B(OH)_2$ group directly bound to the terpyridine ring. This fact can be consequence of the free rotation of the phenyl group in (**12**) which cause a decrease of the electronic coupling between the excited sensitizer and the conduction band of TiO_2.

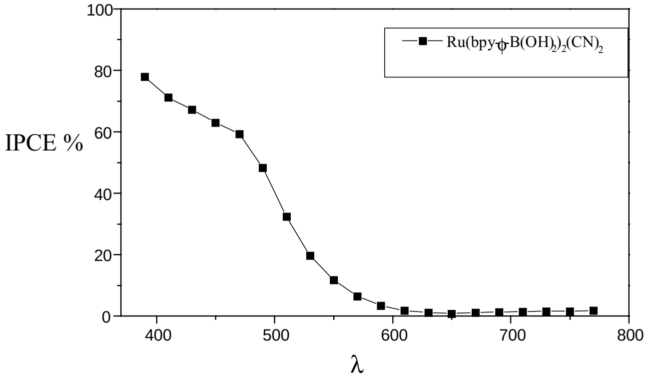


Fig. 1. Photoaction spectra for complex (**6**) recorded in regenerative sandwich cell.

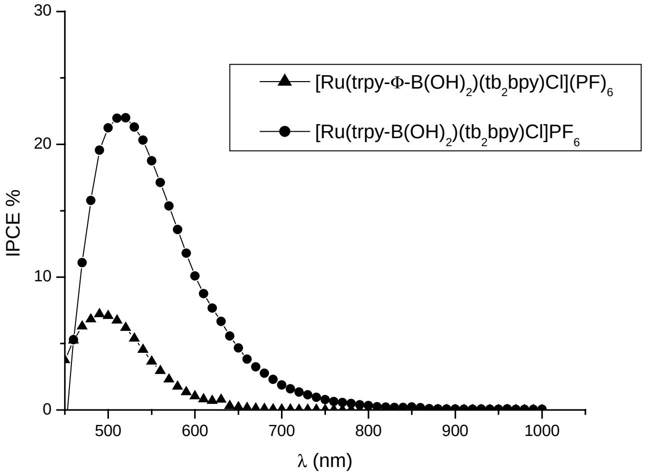


Fig. 2. Photoaction spectra of complexes (**11**) and (**12**) recorded in regenerative sandwich cell.

In conclusion, the boronic dyes studied in this work exhibit photoelectrochemical properties that are dependent by the number of boronic acid functions and by the structure of chromophoric ligand. A direct binding between $B(OH)_2$ functional group and the bipyridine ligand should allow to build Ru sensitizers giving an high surface coverage and high photocurrent efficiencies. Work is in progress in this direction.

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