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Efficient osmium sensitizers containing 2,2′-bipyridine-4,4′-bisphosphonic acid ligand

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Abstract

The synthesis of a series of four complexes of the type Os(bpy-4,4′PO_3H_2)$_2$$L_2$ (bpy-4,4′PO_3H_2 = 2,2′-bipyridine-4,4′-bisphosphonic acid and L_2 = Cl_2, $(CN)_2$, 2,2′-bipyridine-4,4′-bisphosphonic acid or 2,2′-bipyridine-4,4′-dimethoxy) is reported and the spectroscopic, photophysical, and photoelectrochemical properties are presented and compared to the *cis*-Ru(H_2dcb)$_2$(NCS)$_2$ (H_2dcb = 2,2′-bipyridine-4,4′-dicarboxylic acid).

Keywords: Osmium sensitizers; Titanium dioxide; Phosphonic acid functions

1. Introduction

Photovoltaic cells relying on dye-sensitized wide band-gap semiconductor (DSSC) have attracted much attention because they represent a potentially and economically viable device for the conversion of sunlight into electrical energy [1–3]. Recently, we reported the preparation and characterization of a series of ruthenium complexes containing bipyridine ligands substituted with phosphonic acid anchoring groups [4,5]. Although, some of these complexes showed quite high photocurrents in DSSCs, the photoaction spectra in the metal-to-ligand charge transfer (MLCT) region were blue-shifted with respect to analogous complexes containing carboxylic acid substituents. This was rationalized by a lower stabilization of the LUMO bipyridine orbitals induced by the phosphonic acid groups [5]. Osmium complexes have been less investigated than ruthenium complexes, although, some recent studies have shown their potential as efficient sensitizers for nanocrystalline titanium dioxide [6–10]. They are, particularly, attractive due to the lower oxidation potential and to the higher spin-orbit coupling constant relative to ruthenium, which allows to increase the cross section for red light absorption.

In this paper, we describe the first preparation and characterizations of osmium complexes containing polypyridine ligand substituted by phosphonic acid groups (Fig. 1). The absorption and emission characteristics, electrochemical, and spectroelectrochemical properties are also reported and compared to those of the *cis*-Ru(H_2dcb)$_2$(NCS)$_2$ sensitizer (H_2dcb = 2,2′-bipyridine-4,4′-dicarboxylic acid).

2. Experimental

2.1. General methods

^{1}H NMR spectra were recorded on a ASPEC Bruker 200 spectrometer. Chemical shifts are referenced relative to trimethyl silyl proprionic acid (TMSP), sodium salt as an internal standard reference ($\delta = 0$ ppm) for D_2O samples or to the residual protium of the deuterated solvent for methanol ($\delta = 4.5$ ppm). The peak assignments are given as follows: chemical shifts and in parentheses number of protons involved, multiplicity of the signal (s: singlet, d: doublet, t: triplet, m: multiplet).

Thin-layer chromatography (TLC) was carried out on aluminum sheets precoated with Merck 5735 Kieselgel 60F254. Column chromatography was performed on Merck

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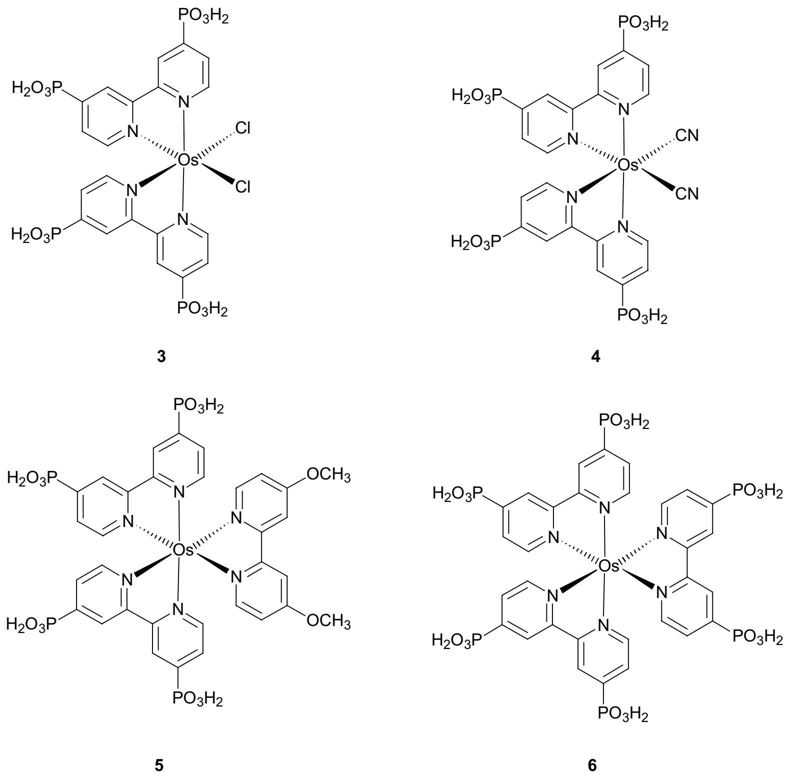


Fig. 1. Structures of the sensitizers described in this study.

5735 Kieselgel 60F (0.040–0.063 mm mesh). UV–vis absorption spectra were recorded on a UV-2401PC Shimadzu and on a Perkin Elmer Lamba 40 spectrophotometers. Cyclic voltammetric (CV) measurements were performed with a potentiostat/galvanostat MacLab model ML160 controlled by resident software (Echem v1.5.2 for Windows). Solutions for CV measurements in 0.1 M phosphate buffer (pH = 8.9) with 0.1 M KCl were purged with argon in a 3-electrode cell. In all measurements, the working electrode was a carbon paste electrode with a platinum wire as auxiliary electrode. Potentials are referred to Saturated calomel electrode (SCE). In all the experiments the scan rate was 100 mV/s.

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 Applyed Photophysics monochromator equipped with an R 3896 Hamamatsu Photomultiplier. The signals were acquired on a 600 MHz Lecroy 9360 digital oscilloscope and elaborated by means of Orgin 5 software.

2.1.1. Photoanodes preparation

TiO_2 colloidal solutions were prepared by hydrolysis of titanium isopropoxide, $Ti(OCH_2(CH_3)_2)_4$:50 ml of titanium isopropoxide (Fluka) was added dropwise, by means of an addition funnel, to 300 ml of deionized water acidified with 2.1 ml of 65% HNO_3 under vigorous stirring. During the hydrolysis a white precipitate is formed. The mixture was stirred for 8 h at 80 °C. During this process the mixture was allowed to concentrate to 120 ml, corresponding to a TiO_2 concentration of 170 g/l. A stable colloidal sol resulted from this procedure. The size of the colloidal particles was ca. 8 nm and X-ray diffraction analysis showed them to consist of anatase. 50 ml of this solution was heated at 220 °C for 12 h in an autoclave. During this process the nanoparticles grow until 50–100 nm size. After cooling, at room temperature, 3 g of Carbowax 2000 (Aldrich) were added to the resulting gel and the mixture was stirred at room temperature for 8 h. The conductive glass was covered on two parallel edges with 3 M adhesive tape (ca. 20 μm thick) to control the thickness of the TiO_2 film. The colloid was applied to one edge of the conducting glass and distributed with a glass rod sliding over the tape-covered edges. After air drying, the electrodes were heated in an oven at 450 °C for 30 min in the presence of air. The resulting film thickness was of the order of 6–7 μm. The sensitizers were dissolved in methanol/water 4:1 or in pure methanol and were adsorbed on the photoanode at reflux for 3–5 h. In all cases ca. 5×10^{-3} M solutions of the complex were used.

Photoelectrochemical measurements were performed in a 2-electrodes sandwich cell arrangement. Typically, 10 μl of electrolyte (0.5 M LiI/0.05 M I_2 in acetonitrile was sandwiched between a TiO_2 photoanode and a counter electrode.

A Pt sputtered conductive glass was employed as counter electrode. For IPCE measurements, the cell was illuminated with a 150 W Xe lamp coupled to an Applied Photophysics high irradiance monochromator. The irradiated area was 0.5 cm^2. Light excitation was through the FTO glass (ca.10 Ω/LOEF^2) substrate of the photoanode. Photocurrents were measured under short-circuit conditions with a Kontron model DMM 4021 digital electrometer. Incident irradiance were measured with a calibrated silicon photodiode from UDT Technologies. *I–V* curves were obtained by irradiating the DSSC with a 500 W tungsten halogen lamp placed at a distance of 18 cm from the cell and using an Autolab PGSTAT30 potentiostat/galvanostat equipped with an Ecochemie GPES software.

Chemicals were purchased from Aldrich and used as received. 4,4′-bis(ethyl ester phosphonate)-2,2′-bipyridine was synthesized using literature procedure [12].

2.2. Preparations

2.2.1. cis-Dichloro bis(bis(ethyl monoester phosphonate)-2,2′-bipyridine)osmium (II) 2

To a solution of bis(ethyl ester phosphonate)-bipyridine (**1**), 500 mg, (1.17 mmol) in ethylene glycol (30 ml) in a schlenk tube, 205 mg (0.423 mmol) of K_2OsCl_6 was added. The mixture was degassed by vacuum pumping and flushing with argon on the vacuum line and then heated at 180 °C for 5 h. After cooling it to room temperature, a solution of sodium dithionite (140 mg of $Na_2S_2O_4$ in 150 ml of water) was added to the reaction mixture. The dark solution was diluted with 600 ml of THF and passed through a pad of silica gel. The product was desorbed with 250 ml of a mixture of acetone/water (4/1). After drying in vacuum, 742 mg of the dark brown complex **2** was obtained and used as such in the next step (yield 63%).

^{1}H NMR 400 MHz, (CD_3OD): δ: 9.68 (m, 2H, **H6′**); 8.70 (m, 2H, **H3′**); 8.46 (m, 2H, **H3**); 7.68 (m, 2H, **H5′**); 7.34 (m, 2H, **H6**); 6.94 (m, 2H, **H5**); 3.95 (m, 2H, $O\mathbf{CH_2}CH_3$); 3.72 (m, 2H, $O\mathbf{CH_2}CH_3$); 1.25 (m, 6H, $OCH_2\mathbf{CH_3}$).

2.2.2. cis-Dichloro bis(4,4′-bis(phosphonic acid)-2,2′-bipyridine) osmium(II) 3

A solution of complex **2**, 500 mg (0.50 mmol) in 30 ml of 6N HCl was refluxed for 15 h. After this period, the solvent was evaporated on a rotary evaporator. The resulting black solid was then dissolved in a minimum amount of water and purified by column chromatography using Sephadex LH20 (25 g packed in a column $h = 29$ cm, $d = 20$ mm) as stationary phase and water as eluent. The black band was collected and corresponds to the desired complex (310 mg, yield 80%).

^{1}H NMR (400 MHz D_2O/NaOD): δ: 9.46 (dd, $J = 3.2$ Hz, $J = 6.0$ Hz, 2H, **H6′**); 8.61 (d, $J = 11.6$ Hz 2H, **H3′**); 8.40 (d, $J = 11.6$ Hz, 2H, **H3**); 7.77 (dd, $J = 5.6$ Hz, $J = 8.0$ Hz, 2H, **H5′**); 7.54 (dd, $J = 3.2$ Hz, $J = 6.0$ Hz, 2H, **H6**); 6.98 (dd, $J = 5.6$ Hz, $J = 8.0$ Hz, 2H, **H5**).

2.2.3. cis-Dicyano bis(4,4′-bis(phosphonic acid)-2,2′-bipyridine) osmium(II) 4

cis-Dichloro bis(diphosphonic acid bipyridine)osmium(II) (**3**), 80 mg (0.089 mmol) and KCN (116 mg, 1.8 mmol) were dissolved in a mixture of a 0.02N aqueous sodium hydroxide solution (5 ml) and ethanol (5 ml) and the solution was purged with argon. The flask was then covered with an aluminum foil, heated at reflux for 15 h and the solvent was rotary evaporated. The resulting black solid was dissolved in a minimum amount of water and purified by column chromatography using Sephadex LH20 as stationary phase and water as eluent. The major green band was collected and water was evaporated. The resulting black solid was dissolved in a minimum amount of 0.02N aqueous sodium hydroxide solution and was purified by column chromatography using Sephadex DEAE A-25 as stationnary phase and 1 M aqueous KNO_3 solution as eluent. The major green band was collected, the solvent was evaporated to about a third of its initial volume and the precipitate filtered to remove the excess of KNO_3. The filtrate was evaporated to dryness and redissolved in a minimum amount of water. It was then purified by column chromatography using Sephadex LH20 as stationary phase and water as eluent to remove excess KNO_3. The fractions containing the green band were gathered and the solvent evaporated to dryness. A minimum amount of water was added to dissolve the complex and 0.2 ml of trifluomethane sulfonic acid was added to precipitate the desired complex that was filtered and washed with water and dried on the vacuum line (48 mg, yield 62%).

^{1}H NMR (400 MHz D_2O/NaOD): δ: 9.52 (dd, $J = 2.8$ Hz, $J = 5.6$ Hz, 2H, **H6′**); 8.60 (d, $J = 11.2$ Hz, 2H, **H3**); 8.53 (d, $J = 11.2$ Hz, 2H, **H3**); 7.77 (dd, $J = 6.0$ Hz, $J = 10.4$ Hz, 2H, **H5′**); 7.57 (dd, $J = 2.8$ Hz, $J = 5.6$ Hz, 2H, **H6**); 7.36 (dd, $J = 6.0$ Hz, $J = 10.4$ Hz, 2H, **H5**).

2.2.4. bis(4,4′-bis(Phosphonic acid)-2,2′-bipyridine) (4,4′-dimethoxy-2,2′-bipyridine)osmium(II) 5

cis-Dichloro bis(diphosphonic acid bipyridine)osmium(II) 100 mg (0.11 mmol), and 4,4′-dimethoxy-2,2′-bipyridine 25 mg (0.12 mmol) were dissolved in a mixture of 0.01N aqueous sodium hydroxide solution (7 ml) and ethanol (7 ml) and the mixture was purged with argon. The flask was then covered with an aluminum foil, heated at reflux for 15 h and the solvents were rotary evaporated. The resulting black solid was purified by chromatography as described for complex **4** (48 mg, yield 62%).

^{1}H NMR (400 MHz D_2O/NaOD) δ: 9.72 (dd, $J = 2.5$ Hz, $J = 5.7$ Hz, 1H, **H6′** (bpymethoxy)); 8.24 (d, $J = 5.1$ Hz, 1H, **H3**, (bpymethoxy)); 8.20 (d, $J = 5.7$ Hz, 1H, **H3** (bpymethoxy)); 8.11 (d, $J = 10.8$ Hz, 2H, **H3′** (bpyphosphonate)); 7.99 (d, $J = 11.7$ Hz, 2H, **H3** (bpyphosphonate)); 7.62 (s, 1H, **H5′** (bpymethoxy)); 7.36 (dd, $J = 3.3$ Hz, $J = 5.7$ Hz, 2H, **H5′**(bpyphosphonate)); 7.28 (dd, $J = 3.0$ Hz, $J = 5.1$ Hz, 2H, **H5** (bpyphosphonate)); 7.02 (broad, 4H, **H5** (bpymethoxy), **H6** (bpymethoxy), **H6′** (bpyphosphonate));

6.51 (dd, $J = 2.7$ Hz, $J = 6.6$ Hz, 2H, **H6** (bpyphosphonate)).

2.2.5. *tris(4,4′-bis(Phosphonic acid)-2,2′-bipyridine)osmium(II)* ***6***

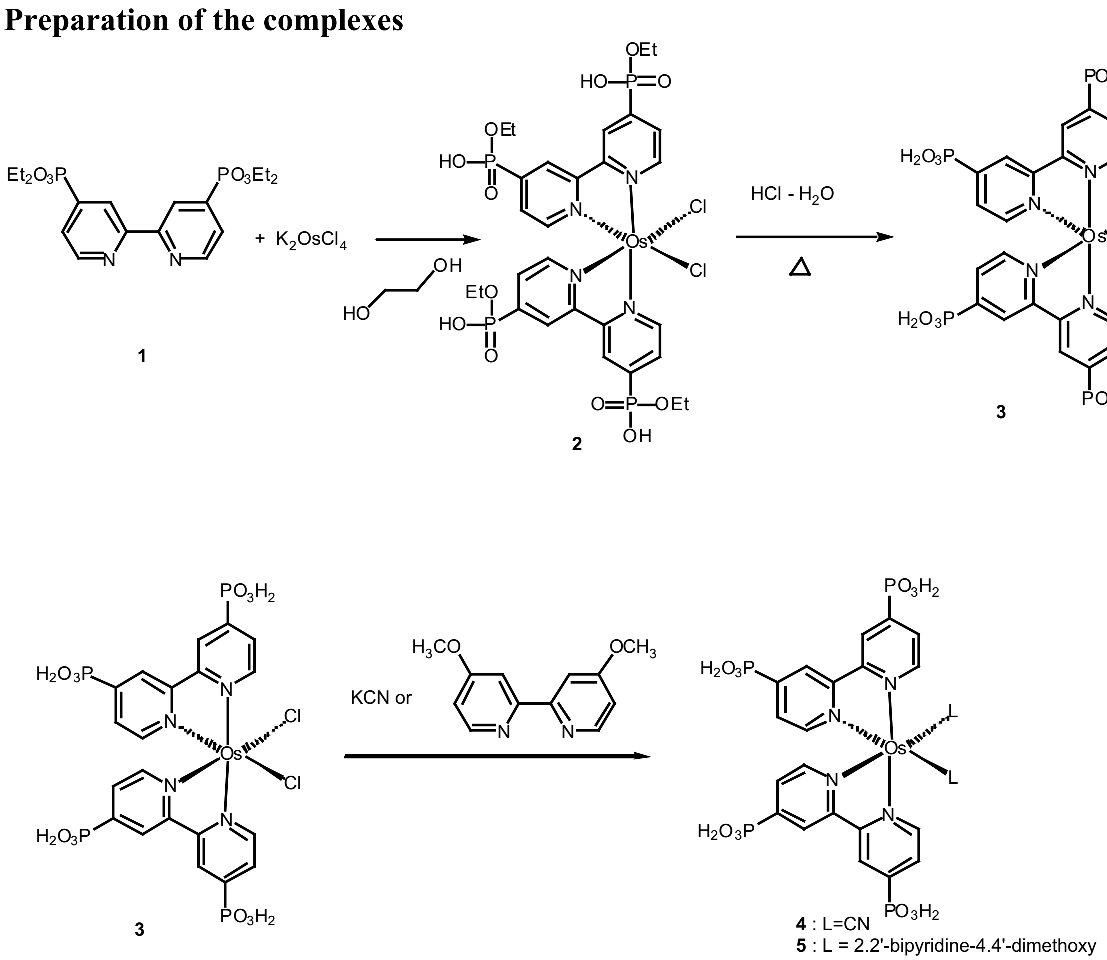
To a solution of bis(ethyl ester phosphonate)-bipyridine **1** (300 mg, 0.70 mmol) in ethylene glycol (30 ml) was added 112 mg (0.23 mmol) of K_2OsCl_6. The mixture was degassed by pumping and flushing with argon on the vacuum line and then heated at 180 °C for 5 h. After cooling it to room temperature, a solution of sodium dithionite (100 mg of $Na_2S_2O_4$ in 100 ml of water) was added. The dark solution was diluted with 600 ml of THF and passed through a pad of silica gel. The product was desorbed with 250 ml of a mixture of acetone/water 4/1.

The ethyl ester phosphonate groups were fully hydrolyzed by refluxing the complex in 30 ml of 6N HCl for 15 h. After this period, the solvent was evaporated and the complex purified according to the procedure described for complex **4**. A black solid corresponding to the desired complex **6** was collected (190 mg, yield 66%).

^{1}H NMR (400 MHz D_2O/NaOD) δ: 8.25 (d, $J = 11.4$ Hz, 6H, **H3**); 7.30 (dd, $J = 2.7$ Hz, $J = 5.6$ Hz, 6H, **H6**); 7.04 (dd, $J = 6.0$ Hz, $J = 9.6$ Hz, 6H, **H5**).

3. Preparation of the complexes

Scheme 1 summarizes the synthetic strategy applied for the preparation of the osmium complexes. Heating 2 equivalents of 4,4′-bis(ethyl ester phosphonate)-2,2′-bipyridine **1** with one equivalent of hexachloroosmate(IV) in ethylene glycol, followed by reduction of osmium(III) to osmium(II) by sodium dithionite, afforded the phosphonate mono-ethyl ester complex **2**. As already observed during the metallation of this type of ligand with ruthenium, partial hydrolysis of the diethyl ester phosphonate occurs [4,5]. The complete hydrolysis of the phosphonate ester was performed in refluxing 6N HCl. Replacement of the chloride ligands of complex **3** by cyano or by 2,2′-bipyridine-4,4′-dimethoxy was achieved by refluxing the complex **3** with the appropriate ligand in basic water–ethanol mixture. The characterization of the complexes **2**–**5** by ^{1}H NMR indicated the expected



Scheme 1. Synthetic procedure for the preparation of the osmium complexes **2**–**6**.

cis geometry of the two 2,2′-bipyridine-4,4′-bisphosphonic acid, since they gave in the aromatic region 6 distinct signals corresponding to the 6 magnetically inequivalent protons of the bipyridine phosphonate. The homoleptic complex **6** was prepared by reacting 3 equivalents of 4,4′-bis(ethyl ester phosphonate)-2,2′-bipyridine (**1**) with one equivalent of hexachloroosmate(IV) in ethylene glycol followed by hydrolysis with HCl.

It is important to note that all the complexes were purified by chromatography using alternatively size exclusion and anionic exchange stationary phases. As reported by Lewis and coll., [9] we also observed that the photovoltaic performances of this type of osmium complexes are strongly dependent by the purity of the dyes.

4. Electronic absorption spectra

UV–vis absorption spectra of the complexes **3**–**6** are shown in Fig. 2.

The absorption spectra were recorded in basic aqueous solution for the poor solubility in water and in organic solvents of complexes **5** and **6**. In 0.1N NaOH the deprotonated form of the complexes are present. Deprotonation of the complexes cause a blue shift of the MLCT transitions because the negatively charged PO_3^{2-} groups destabilize the LUMO orbital of the bipyridine ligands.

The spectra of the new sensitisers exhibit π–π* ligand centered transition in the UV region and broad MLCT bands in the visible (cf. Fig. 2) [11]. In all cases, bands at lower energy can be assigned to spin forbidden transitions to ^{3}MLCT states [13]. Owing to the degeneracy of the electronic transitions, π–π* and MLCT bands have higher oscillator strength for the tris-bipyridine complexes. Complex **5**, which contains the electron rich dimethoxy bipyridine ligand, shows MLCT bands at lower energy. As expected, the absorption of the spectra of these osmium complexes are red-shifted with respect to the analogous ruthenium species [5].

5. Photophysical properties

Except for the dichloro complex the other investigated species were found to be emitting in fluid solution. Corrected emission spectra for optically diluted methanol solution containing 0.6% tetrabutylammonium hydroxide are reported in Fig. 3. Emission lifetimes, emission maxima in methanol and excited state oxidation potentials are summarized in Table 1.

The increase of the lifetime from the protonated to the anionic form of the complexes (Table 1) parallel the increase of the emission energy, qualitatively in agreement with the energy gap law.

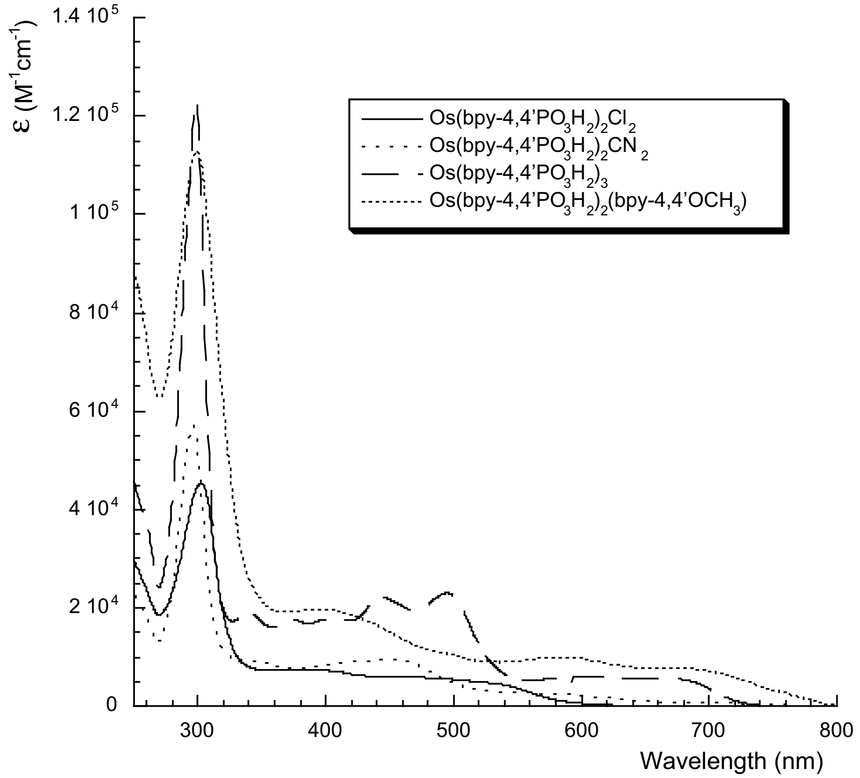


Fig. 2. Electronic absorption spectra of complexes **3**–**6** recorded in 0.1N NaOH.

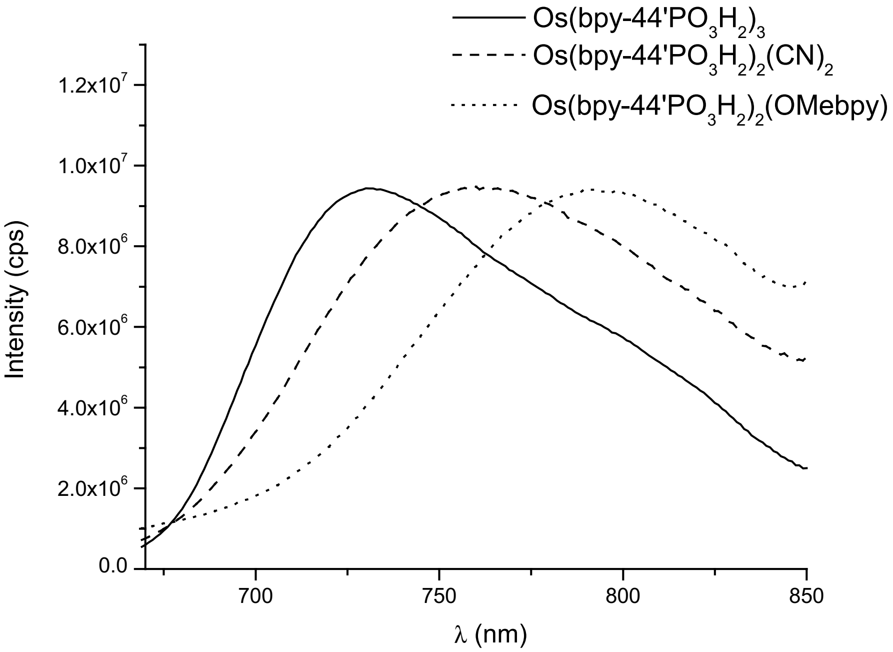


Fig. 3. Normalized emission spectra of the complexes **4**–**6** recorded at room temperature in MeOH/TBAOH.

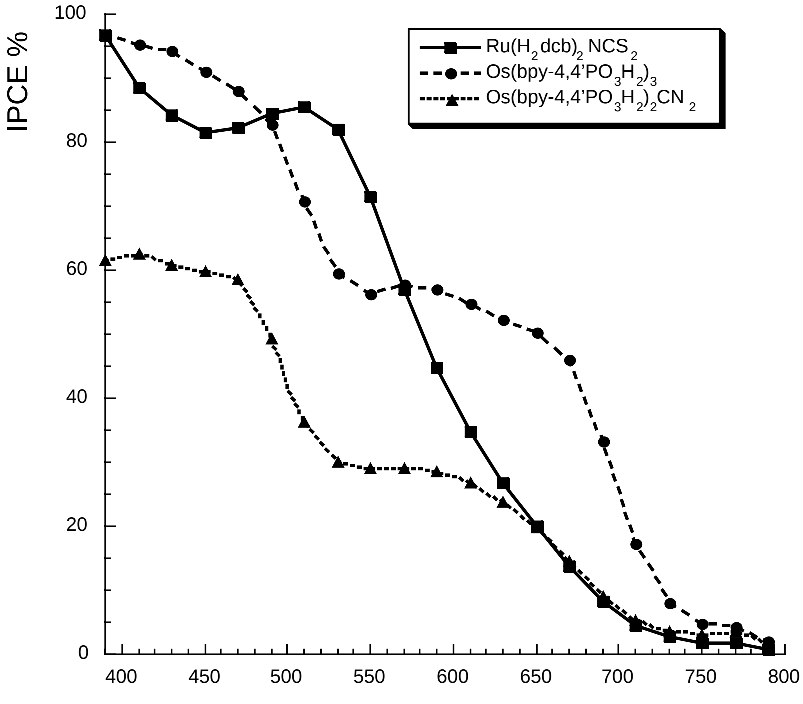


Fig. 4. Action spectra of complexes **4**–**6** recorded in regenerative TiO_2 solar cell corrected for conductive glass transmitance.

Table 1
Photophysical properties in methanol solution at room temperature

Complexes	E_m λ_{max} (nm) Protonated	E_m λ_{max} (nm) Anionic	τ, ns[a] Protonated	τ, ns Anionic	$E_{1/2}$, V[b] Anionic	$E_{1/2}^*$, V[c] Anionic
Os(bpy-4,4′$PO_3H_2)_2Cl_2$	Ne	Ne			0.56	
Os(bpy-4,4′$PO_3H_2)_3$	750	732	42.9	50.0	0.63	−1.14
Os(bpy-4,4′$PO_3H_2)_2CN_2$	800	762	11.7	19.8	0.69	−1.19
Os((bpy-4,4′PO_3H_2)2(bpy-4,4′OCH_3)	804	794	21.8	23.9	0.36	−1.44

[a] Emission lifetimes measured in Ar saturated solutions ±0.1 ns.

[b] Half-wave oxidation potentials vs SCE measured in 0.1 M phosphate buffer aqueous solutions (pH = 8.9) containing 0.1 M KCl.

[c] Calculated from $E_{1/2}^* = E_{1/2} - E_{oo}$. E_{oo} was estimated from the onset of the emission at 5% of the maximum intensity.

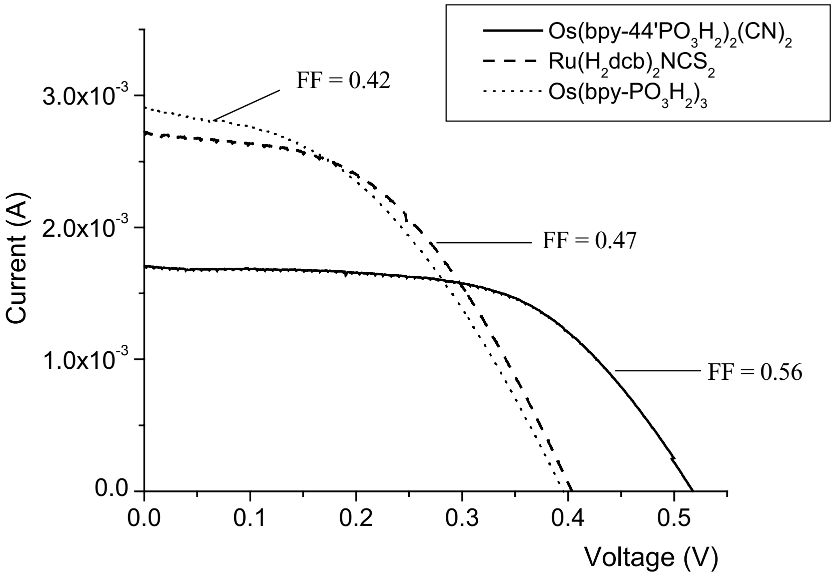


Fig. 5. *I–V* Curves recorded for dye sensitized solar cells: Os(bpy-44′$PO_3H_2)CN_2$ (J_{sc} = 3.52 mA/cm^2, V_{OC} = 0.52 V) full line, Ru(H_2dcb)$_2$(NCS)$_2$ (J_{sc} = 5,44 mA/cm^2, V_{OC} = 0.4 V) dashed line, Os(bpy-44′$PO_3H_2)_3$ (J_{sc} = 5,78 mA/cm^2, V_{oc} = 0.395 V) dotted line.

6. Electrochemistry

Cyclic voltammetry measurements were performed at pH 8.9 in aqueous phosphate buffer. The complexes exhibit quasi-reversible oxidation waves in the potential range 300–600 mV versus SCE, with peak splittings between anodic and cathodic waves of the order of 100 mV. Half wave potentials are reported in Table 1.

7. Photoelectrochemistry

The photoelectrochemical properties of the new Os species have been investigated in regenerative sandwich type cells. The photoaction spectra (incident monochromatic photocurrent conversion efficiency (IPCE) versus excitation wavelength) are reported in Fig. 4 and the *I–V* curves are shown in Fig. 5 and compared with the Ru(dcbH_2)(NCS)$_2$ complex.

The high IPCE values observed close to 400 nm may result from corrections for conductive glass transmittance and from direct band gap excitation of TiO_2. The complexes **3** and **5** gave almost no photocurrent. In the case of complex **3**, which was found to be non-emitting, excited state thermal deactivation could compete with charge injection to the semconductor. For complex **5** the poor photoelectrochemical performances ($IPCE_{max} < 3\%$) can be related to the low oxidation potential and as a consequence to the low driving force for iodide oxidation. The other two species exhibit quite high photocurrents and fill factors of the order of 0.42 for **6** and 0.56 for complex **4** (Fig. 5). Complex **6** in particular shows an higher red sensitivity with respect to the Ru(H_2dcb)$_2$(NCS)$_2$ dye, with IPCE values of ca. 50% in the 600–700 nm spectral region. This results show that the bipyridine phosphonate ligand **1** can be used to prepare efficient sensitizer exhibiting photovoltaic performances comparable to those of the well-known Ru(H_2dcb)$_2$(NCS)$_2$ complex.

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