Inorg. Chem. **2007**, *46*, 2272–2277

Inorganic Chemistry

Article

Tuning of Ruthenium Complex Properties Using Pyrrole- and Pyrrolidine-Containing Polypyridine Ligands

David Martineau,[†] Marc Beley,[‡] Philippe C. Gros,*,[‡] Silvia Cazzanti,[§] Stefano Caramori,[§] and Carlo A. Bignozzi*,[§]

LIMBP, IPEM, Université Paul Verlaine, Bd Arago, 57070 Metz, France, SOR, UMR CNRS 7565, Université Henri Poincaré, Boulevard des Aiguillettes, 54506 Vandoeuvre-lès-Nancy, France, and Dipartimento di Chimica, Università di Ferrara, Via Luigi Borsari 46, 44100 Ferrara, Italy

Received October 25, 2006

The effect of pyrrole- and pyrrolidine-containing ligands (L) on the properties of heteroleptic $[RuL_2dcbpy]^{2+}$ complexes has been investigated. TiO_2 electrodes modified with the new complexes exhibited extended absorption domains and high absorbances. Providing that a cobalt-based mediator was used for regeneration of the Ru^{II} state, good incident photon-to-current efficiency (near 80%) values were obtained in the pyrrole series.

Introduction

The design of polypyridine complexes of ruthenium has been the focus of many research projects working toward the elaboration of dye-sensitized solar cells (DSCs) or luminescent sensors.[1] The nature of the ligands around the metal has been found to dramatically affect the energy conversion process. Particularly, the introduction of electronic effects via electron-donor substituents on bipyridine (bpy) and terpyridine (tpy) ligands notably improved the absorption in the visible region for efficient sunlight collection.[2] This effect is due to the propensity of the electron-donor substituents to destabilize the HOMO metal orbital (π t_{2g}) more than the LUMO (π^*) orbital of the ligand.[2b] The consequence is a lower gap between the two orbital energy levels with respect to the parent complex, leading to a red shift of the metal-to-ligand charge transfer (MLCT) absorption and decrease of the Ru(II)/Ru(III) oxidation potential. In this context, we have recently reported the positive effect of bpy, bearing pyrrole and pyrrolidine moieties bonded by their nitrogen, to the light-harvesting property of $[Ru(bpy)_3]^{2+}$- and $[Ru(tpy)_2]^{2+}$-type complexes.[3] High absorption maxima values and low oxidation potentials made the new ligands good candidates for photovoltaic applications. In DSCs, the sensitizing dye has to be chemisorbed at the surface of a nanocrystalline TiO_2 semiconductor, usually via carboxylic acid groups[1b,4] or to a lesser extent via other bridging units such as phosphonic acids.[5] Herein, we report the preparation of heteroleptic complexes involving pyrrole- or pyrrolidine-containing bipyridine ligands (L) and dicarboxy bipyridine

---

* To whom correspondence should be addressed. E-mail: Philippe.Gros@sor.uhp-nancy.fr (P.C.G), g4s@unif.it (C.A.B.).

[†] Université Paul Verlaine.

[‡] Université Henri Poincaré.

[§] Università di Ferrara.

(1) (a) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85. (b) O'Regan, B., Grätzel, M. *Nature* **1991**, *353*, 737. (c) Hagfeldt, A.; Grätzel, M. *Chem. Rev.* **1995**, *95*, 49. (d) Argazzi, R.; Bignozzi, C. A.; Hasselmann, G. M.; Meyer, G. J. *Inorg. Chem.* **1998**, *27*, 4533. (e) Schulze, X.; Serin, J.; Adronov, A.; Fréchet, J. M. J. *Chem. Commun.* **2001**, 1160. (f) Polson, M. I. J.; Taylor, N. J.; Hanan, G. S. *Chem. Commun.* **2002**, 1356. (g) Figgemeier, E.; Aranyos, V.; Constable, E. C.; Handel, R. W.; Housecroft, C. E.; Risinger, C.; Hagfeldt, A.; Mukhtar, E. *Inorg. Chem. Commun.* **2004**, *7*, 117. (h) Wang, P.; Klein, C.; Humphry-Baker, R.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2005**, *127*, 808. (i) Jiang, K.-J.; Masaki, N.; Xia, J.-b.; Noda, S.; Yanagida, S. *Chem. Commun.* **2006**, 2460. (j) Robertson, N. *Angew. Chem., Int. Ed.* **2006**, *45*, 2338.

(2) (a) Sullivan, B. P.; Baumann, J. A.; Meyer, T. J.; Salmon, D. J.; Lehmann, H.; Ludi, A. *J. Am. Chem. Soc.* **1977**, *99*, 7368. (b) Cook, M. J.; Lewis, A. P.; McAulife, G. S.; Skarda, V.; Thomson, A. J. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1293. (c) Paw, W.; Connick, W. B.; Eisenberg, R. *Inorg. Chem.* **1998**, ***37***, 3919. (d) Fung, W.-H.; Yu, W.-Y.; Che, C.-M. *J. Org. Chem.* **1998**, *63*, 7715. (e) Ghaddar, T. H.; Castner, E. W.; Isied, S. S. *J. Am. Chem. Soc.* **2000**, *122*, 1233. (f) Rau, S.; Büttner, T.; Temme, C.; Ruben, M.; Görls, H.; Walther, D.; Duati, M.; Fanni, S.; Vos, J. G. *Inorg. Chem.* **2000**, *39*, 1621.

(3) (a) Martineau, D.; Gros, P. C.; Beley, M.; Fort, Y. *Eur. J. Inorg. Chem.* **2004**, 3984. (b) Martineau, D.; Beley, M.; Gros, P. C. *J. Org. Chem.* **2006**, *71*, 566.

(4) (a) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382. (b) Argazzi, R.; Bignozzi, C. A.; Heimer, T. A.; Castellano, F. N.; Meyer, G. J. *Inorg. Chem.* **1994**, *33*, 5741.

(5) (a) Pechy, P.; Rotzinger, F. P.; Nazeeruddin, M. K.; Kohle, O.; Zakeeruddin, S. M.; Humphry-Baker, R.; Grätzel, M. *Chem. Commun.* **1995**, 65. (b) Gillaizeau-Gauthier, I.; Odobel, F.; Alebbi, M.; Argazzi, R.; E. Costa, Bignozzi, C. A.; Qu, P.; Meyer, G. J. *Inorg. Chem.* **2001**, *40*, 6073. (c) Zabri, H.; Gillaizeau, I.; Bignozzi, C. A.; Caramori, S.; Charlot, M.-F.; Cano-Boquera, J.; Odobel, F. *Inorg. Chem.* **2003**, *42*, 6655.

10.1021/ic062042f CCC: $37.00

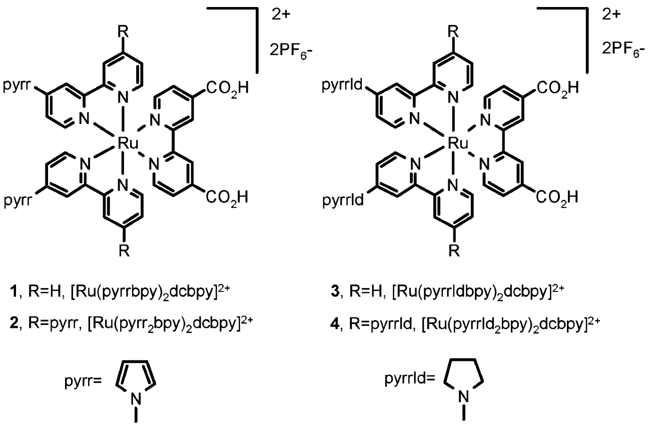


Figure 1. Structures of the new complexes **1**−**4** studied in this work.

(dcbpy), the characterization (UV−vis, electrochemistry), and the evaluation of the photoelectrochemical performances of the new sensitizers (Figure 1) in nanocrystalline TiO_2 solar cells.

Experimental Section

General. ^1H and ^{13}C NMR have been recorded on AC200, AC250, or DRX400 Bruker spectrometers. GC experiments have been performed on a Shimadzu chromatograph fitted with a 15 m capillary column. Microwave experiments have been performed on a CEM Discover device fitted with infrared probe temperature control. Absorption UV−vis electronic spectra have been recorded on a Varian Cary E spectrometer, and emission UV−vis electronic spectra have been recorded on a SLM Aminco-Bowman Series 2 apparatus using a (1 cm × 1 cm) quartz cell in deoxygenated solutions (optical density (OD) <0.05). Excited-state lifetimes have been obtained by nanosecond transient absorption in acetonitrile solvent by excitation at 355 nm from a Continuum Surelite II Q-switched Nd:YAG (fwhm = 7 ns, 8 Hz) laser. Focalization was realized by an Applied Photophysics monochromator. GC-MS (EI) spectra have been obtained on a HP 5971 analyzer. Electrospray mass spectra have been recorded on an Agilent MSD using CH_3CN as solvent. The electrochemical measurements were performed with a PGP 201 Radiometer/Tacussel potentiostat using a conventional single-compartment three-electrode cell. The reference electrode was the potassium chloride calomel electrode (SCE), the working electrode was a 10 mm Pt wire, and the counter-electrode was a 1 cm^2 vitreous carbon disk. The supported electrolyte was $LiClO_4$ 0.1 M in CH_3CN, and the solutions were purged with argon before each measurement. A 0.5 mM solution of the studied compound was generally used. All potentials are quoted versus SCE; in these conditions the redox potential of Fc^+/Fc was 0.38 V. In all experiments the scan rate was 100 mV/s. Incident photon-to-current conversion efficiency (IPCE) measurements were performed by illumination of the cell using an Osram 150 W xenon lamp coupled to an Applied Photophysics monochromator. The irradiated surface was 0.5 cm^2 in area. Photocurrents were measured under short circuit conditions by a digital Agilent 34410A multimeter. Incident irradiance was measured with a 1 cm^2 Centronic OSD100-7Q calibrated silicon photodiode.

TiO_2 Electrode Preparation. TiO_2 colloidal paste was prepared by hydrolysis of Ti^{IV} isopropoxide. The nanocrystalline TiO_2 photoelectrodes were prepared by depositing the paste onto transparent conducting FTO glass (either Delta Technologies or IBE, 7 Ω/Square) according to the well-known "Scotch tape" method. The thin films were allowed to dry at room temperature for 20 min and finally fired at 450 °C for 40 min. The still-hot electrodes were immersed in the dye solution and kept at 80 °C for 5 h, after which time the absorption was deemed complete. The efficiency of absorption was evaluated by UV−vis spectroscopy: photoelectrodes characterized by an optical density ≥ 1 at the MLCT maximum of the sensitizer were commonly obtained. Dye solutions were prepared by dissolving a small amount of the Ru(II) complex in anhydrous ethanol (ca. 4 mg in 10 mL of solvent). The solutions were sonicated and filtered to remove suspended undissolved dye.

Counter Electrode Preparation. Platinum-coated counter electrodes were obtained by spraying a 5×10^{-3} M H_2PtCl_6 (Fluka) solution in isopropanol on the well-cleaned surface of an FTO glass. This procedure was repeated from 5 to 10 times to obtain a homogeneous distribution of H_2PtCl_6 droplets. The electrodes were dried under a gentle air flow and treated in an oven at 380 °C for 15 min, facilitating the formation of stable platinum clusters.

Gold-coated electrodes, used with cobalt-based mediators, were obtained by thermal vapor deposition on FTO of a 5−7 nm thick chromium adhesion layer followed by a 30−35 nm thick gold layer. The average pressue of the vacuum chamber of the evaporator was about 9×10^{-6} Torr.

Photoelectrochemical Cell Assembly.[5b,6,15] Parafilm sealed cells were built by pressing the sensitized photoanode against a counter electrode equipped with a Parafilm frame used to confine the liquid electrolyte inside the cell. The thickness of the liquid layer corresponded roughly to the thickness of the frame borders ($\cong$120 μm). In this configuration the cell was stable toward solvent evaporation and leaking for several days even with the use of volatile solvents like acetonitrile. In both cases, metallic clamps were used to firmly hold the two electrodes together.

The mediators (Fe- and Co-mediators) were prepared according to published procedures.[5b,6,15] Chemical reagents and solvents were commercially available and used as such except ligands pyrrbpy, $pyrr_2bpy$, pyrrldbpy, and $pyrrld_2bpy$, which were prepared according to our previous works.[3,7] DMF was degassed by several vacuum−argon cycles before use.

Preparation of Complexes. $[Ru(pyrrbpy)_2(dcbpy)](PF_6)_2$ (1). pyrrbpy (26.8 mg, 0.121 mmol) and $RuCl_3 \cdot xH_2O$ (15.7 mg, 0.06 mmol) were dissolved in DMF (5 mL), and *N*-ethylmorpholine (2 drops) was added. The solution was then irradiated in a synthesis microwave oven (250 W, 160 °C max, 10 min), leading to a dark pink mixture. After the solution was cooled, the solvent was

---

(6) Sapp, S. A.; Elliott, C. M.; Contado, C.; Caramori, S.; Bignozzi, C. A. *J. Am. Chem. Soc.* **2002**, *124*, 11215.

(7) (a) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334. (b) Hesek, D.; Inoue, Y.; Everitt, S.; Ishida, H.; Kumeda, M.; Drew, M. *Inorg. Chem.* **2000**, *39*, 308.

(8) Martineau, D.; Gros, P. C.; Fort, Y. *J. Org. Chem.* **2004**, *69*, 7914.

(9) (a) Benko, G.; Kallioinen, J.; Korppi-Tommola, J. E. J.; Yartsev, A. P.; Sundstrom, V. *J. Am. Chem. Soc.* **2002**, *124*, 489. (b) Nakade, S.; Kubo, W.; Saito, Y.; Kanzaki, T.; Kitamura, T.; Wada, Y.; Yanagida, S. *J. Phys. Chem. B* **2003**, *107*, 14244.

(10) For recent works on electronically delocalized structures see: (a) Wang, P.; Klein, C.; Humphry-Baker, R.; Zakeeruddin, S. M., Grätzel, M. *J. Am. Chem. Soc.* **2005**, *127*, 808. (b) Jiang, K.-J.; Masaki, N.; Xia, J.-b.; Noda, S.; Yanagida, S. *Chem. Commun.* **2006**, 2460.

(11) Adamson, A. W.; Fleischauer, P. D. *Concepts Inorg. Photochem.* **1975**, 381.

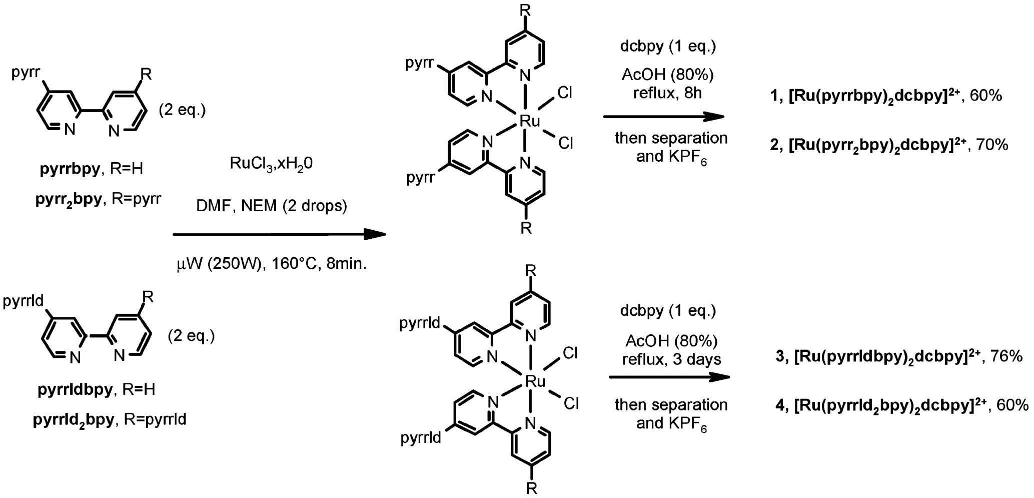
(12) Grätzel, M. *Inorg. Chem.* **2005**, *44*, 6841.

(13) This first electropolymerization result will be investigated in more detail and published in due course.

(14) Vlachopoulos, N.; Liska, P.; Augustynski, J.; Grätzel, M. *J. Am. Chem. Soc.* **1998**, *110*, 1216.

(15) For studies on the electrochemical stability of the NCS ligand see: (a) Kohle, O.; Grätzel, M.; Meyer, A. F.; Meyer, T. B. *Adv. Mater.* **1997**, *9*, 904. (b) Cecchet, F.; Gioacchini, A. M.; Marcaccio, M.; Paolucci, F.; Roffia, S.; Alebbi, M.; Bignozzi, C. A. *J. Phys. Chem. B* **2002**, *106*, 3926.

Scheme 1. Preparation of Complexes **1**−**4**



evaporated and replaced by acetone (5 mL) and the mixture was placed in a refrigerator for several hours until a precipitate formed. After filtration and successive washings with H_2O, acetone, and Et_2O and after drying the sample under vacuum, Ru(pyrrbpy)$_2$Cl$_2$ (MS (ES): *m*/*z* = 614.2142) was obtained as a dark green solid and used as such in the following step. dcbpy (14.6 mg, 0.06 mmol) and [Ru(pyrrbpy)$_2$Cl$_2$] previously obtained were suspended in 10 mL of acetic acid (80% in water). The mixture was refluxed, and the reaction was monitored by TLC. After 8 h, an orange mixture was obtained. After cooling, filtration, and evaporation of the solvents, the residue was treated with a small amount of methanol, filtered on glass wool, and purified through a Sephadex LH-20 column by elution with methanol. The main fraction was collected, and H_2O (5 mL) was added before methanol evaporation. The pH of the aqueous phase was adjusted to 3 (diluted HCl), and then 15 mL of a saturated aqueous KPF$_6$ solution was added. After 3 h in a refrigerator, the precipitate was filtered, washed with Et_2O, and dried to give **1** as a red solid (38.8 mg, 60%). ^{1}H NMR (DMSO-*d*$_6$): δ *H* (ppm) = 9.18 (brs, 2H), 9.11 (d; *J* = 8 Hz, 2H), 8.97 (m, 2H), 8.73−8.88 (m, 2H), 8.16−8.26 (m, 2H), 7.71−8.01 (m, 10H), 7.47−7.67 (m, 6H), 6.46 (m, 4H). MS (ES): *m*/*z* = 394.0710 [M − 2PF$_6$]$^{2+}$. UV−vis (CH$_3$CN), λ_{max} (ϵ) = 472 nm (19 000 M^{-1} cm^{-1}).

[Ru(pyrr$_2$bpy)$_2$(dcbpy)](PF$_6$)$_2$ (2). The same procedure was repeated with pyrr$_2$bpy (34.7 mg, 0.121 mmol). After the sample was reacted with dcbpy and the above-described workup was performed, **2** was obtained as a red powder (51 mg, 70%). ^{1}H NMR (DMF-*d*$_7$): δ *H* (ppm) = 9.87 (brs, 2H), 9.40 (m, 4H), 8.61 (d, *J* = 5 Hz, 2H), 8.39 (d, 6 Hz, 2H), 8.18 (m, 2H), 8.13 (d, *J* = 6 Hz, 2H), 8.07 (m, 8H), 6.69 (m, 8H). MS (ES): *m*/*z* = 1063.1968 [M − PF$_6$]$^+$, 459.1146 [M − 2PF$_6$]$^{2+}$. UV−vis (CH$_3$CN): λ_{max} (ϵ) = 483 nm (21 000 M^{-1} cm^{-1}).

[Ru(pyrrldbpy)$_2$(dcbpy)](PF$_6$)$_2$ (3). pyrrldbpy (27.3 mg, 0.121 mmol) and RuCl$_3$·*x*H$_2$O (15.7 mg, 0.06 mmol) were dissolved in DMF (5 mL), and *N*-ethylmorpholine (2 drops) was added. The solution was then irradiated in a synthesis microwave oven (250 W, 160 °C max, 10 min), leading to the formation of a dark pink mixture. After cooling, the solvent was evaporated and replaced by acetone/Et_2O (1/1) (5 mL), and the mixture was placed in a refrigerator for several hours until a precipitate formed. After filtration, multiple washings with Et_2O, and drying under a vacuum, Ru(pyrrldbpy)$_2$Cl$_2$ (MS (ES): *m*/*z* = 622.1001) was obtained as a dark green solid and used as such in the following step. dcbpy (14.6 mg, 0.06 mmol) and [Ru(pyrrldbpy)$_2$Cl$_2$] previously obtained were suspended in 10 mL of acetic acid (80% in water). The mixture was refluxed, and the reaction was monitored by TLC. After 3 days a red mixture was obtained that was then cooled. Filtration and evaporation of the solvents gave a residue which was treated with a small amount of methanol, filtered on glass wool, and purified through a Sephadex LH-20 column by elution with methanol. The main fraction was collected, and H_2O (5 mL) was added before methanol evaporation. The pH of the aqueous phase was adjusted to 3 (diluted HCl), and then 15 mL of a saturated aqueous KPF$_6$ solution was added. After 3 h in a refrigerator, the precipitate was filtered, washed with Et_2O, and dried to give **3** as a red solid (49.5 mg, 76%). ^{1}H NMR (DMSO-*d*$_6$): δ *H* (ppm) = 9.22 (brs, 2H), 8.86 (m, 2H), 7.99−8.18 (m, 2H), 7.64−7.99 (m, 7H), 7.52 (m, 1H), 7.40 (m, 1H), 7.11 (d, *J* = 6 Hz, 1H), 6.91−7.04 (m, 2H), 6.65 (m, 1H), 6.53 (m, 1H), 3.42 (m, 8H), 1.99 (m, 8H). MS (ES): *m*/*z* = 398.1006 [M − 2PF$_6$]$^{2+}$. UV−vis (CH$_3$CN): λ_{max} (ϵ) = 492 nm (15 240 M^{-1} cm^{-1}).

[Ru(pyrrld$_2$bpy)$_2$(dcbpy)](PF$_6$)$_2$ (4). The same procedure was repeated with pyrrl$_2$dbpy (35.6 mg, 0.121 mmol) and RuCl$_3$·*x*H$_2$O (15.7 mg, 0.06 mmol). After filtration, the washings were realized with acetone/Et_2O (80:20) and Et_2O. After the sample was dried under vacuum, Ru(pyrrld$_2$bpy)$_2$Cl$_2$ (MS (ES): *m*/*z* = 760.2062) was obtained as a dark blue solid and used as such in the following step with dcbpy (14.6 mg, 0.06 mmol). After the above-described treatment, **4** was obtained as a red solid (44.0 mg, 60%). ^{1}H NMR (DMSO-*d*$_6$): δ *H* (ppm) = 9.12 (brs, 2H), 8.10 (brs, 2H), 7.85 (brs, 2H), 7.62 (s, 4H), 7.59 (s, 2H), 7.12 (d, *J* = 6 Hz, 2H), 6.90 (d, *J* = 6 Hz, 2H), 6.64 (d, *J* = 5 Hz, 2H), 6.45 (d, *J* = 5 Hz, 2H), 3.41 (m, 16H), 1.97 (m, 16H). MS (ESI): *m*/*z* = 467.1603 [M − 2PF$_6$]$^{2+}$. UV−vis (CH$_3$CN): λ_{max} (ϵ) = 535 nm (11 600 M^{-1} cm^{-1}).

Results and Discussion

The complexes were prepared by a two-step procedure. The first step was the preparation of a dichloro complex[7] by reaction of RuCl$_3$·*x*H$_2$O with an excess of pyrrole- or pyrrolidine-containing bipyridine ligands synthesized according to our previous works.[3,8] In the second step, the chloro ligands were substituted by the dicarboxybipyridine ligand (dcbpy) used as its unprotected form.

The dichloro complexes were obtained quantitatively in a very short time (8 min) under microwave irradiation in DMF (Scheme 1). The classical thermal heating in the same solvent was also efficient, but extended reaction times were necessary

Table 1. Photophysical and Electrochemical Properties of Complexes **1**−**4** and Their Homoleptic Analogues

dyes	$\lambda_{\text{abs-max}}$ (nm)[a]	ϵ (10^3 M^{-1} cm^{-1})	$\lambda_{\text{em-max}}$ (nm)[b]	Φ_{em} (%)	τ (ns)	k_r (10^4 s^{-1})	$E_{1/2}$Ru^{III}/Ru^{II}(ΔE_p) (V/SCE)[d]	ligand processes (V/SCE)[e]	$E^*_{1/2}$ Ru^{III}/Ru^{II*} (V/SCE)[g]	E^{00} (eV)[h]
Ru(pyrrbpy)$_3^{2+}$	465	8.6	630	0.022	635	12.3	1.16 (90)	−1.21 (rev)	−0.93	2.09
Ru(pyrr$_2$bpy)$_3^{2+}$	480	22.2	650	0.044	357	8.9	1.12 (90)	−1.20 (rev)	−0.91	2.03
Ru(pyrrldbpy)$_3^{2+}$	481	13.5	691	0.021	271	7.8	0.55 (100)	−1.54 (rev.)	−1.58	2.13
Ru(pyrrld$_2$bpy)$_3^{2+}$	520	13.2	710	*c*	58		0.17 (100)	*f*	−1.80	1.97
1	472	19.0	705	0.019	435	4.4	1.19 (100)	−1.35 (irrev)	−0.78	1.97
2	483	21.0	730	0.010	224	4.4	1.14 (100)	−1.18 (irrev)	−0.81	1.95
3	492 448	15.2 14.3	734	0.009	88	9.8	0.72 (90)	−1.46 (irrev)	−1.28	2.00
4	535 423	11.6 14.4	760	0.004	9	4.2	0.53 (70)	−1.00 (irrev)	−1.46	1.99

[a] Measured in CH_3CN at 25 °C. [b] $\lambda_{\text{excit}} = 460$ nm, OD <0.05 in the absence of O_2. [c] Photochemically unstable. [d] First oxidation potential standardized with Fc^+/Fc as the internal standard and converted into the SCE scale by adding 0.38 V ($E_{1/2}Fc^+/Fc$), recorded at 100 mV/s using $LiClO_4$ as the supporting electrolyte. [e] First reduction potential. In cases of reversibility, the value stands for $E_{1/2}$ (L/L^-). If irreversibility occurs, the value stands for E_{pc} (L/L^-). [f] Not observed. [g] First oxidation potential at excited state. [h] Energy gap between vibrational levels ($\nu = 0$) at the ground and excited state. Determined according to Adamson and Fleischauer[11] by taking the wavelength ($\lambda_{0.05}$) corresponding to 5% of the maximum intensity of the emission spectrum recorded at 298 K ($E^{00} = 1240/\lambda_{0.05}$).

(12 h). The obtained complexes were then reacted as such with a stoichiometric amount of dcbpy in refluxing acetic acid leading to **1**−**4** in good overall yields (two steps) and the pure form after chromatography on a Sephadex LH20 column. Since 3 days was needed to complete the reaction, the incorporation of dcbpy in pyrrolidine-containing complexes proceeded sluggishly. An explanation could be the oxidation of the intermediate dichloro complex into its Ru^{III} form favored by the electron-donor effect of pyrrolidine moieties.[3] The subsequent reaction with dcbpy was thus slowed down since a reduction step was needed before the coordination. The formation of Ru^{III} species was supported by the full solubility of the intermediate dichloro complex in water indicating the formation of a charged (cationic) species. This observation contrasted with those made with the pyrrole-based dichloro complexes, which precipitated in water, as expected for a neutral species.

Complexes **1**−**4** were then subjected to a range of photophysical and electrochemical analyses. The results are summarized in Table 1. For comparison purposes and to evaluate the effect of the dcbpy ligand, the values obtained with the homoleptic analogues have also been added.

Electronic Spectra. In the UV region, intense and sharp bands are observed corresponding to ligand-centered transitions. The band near 300 nm is attributed to a $\pi-\pi^*$ transition localized mostly on bipyridine. Near 250 nm are found $\pi-\pi^*$ transitions localized on pyrrole in **1** and **2**. n-π^* transitions in the pyrrolidine-based complexes of **3** and **4** are also found in the same region. The bands intensities grew as the number of pyrrole or pyrrolidine moieties increased in the complexes (Figure 2).

In the visible range, the heteroleptic complexes **1**−**4** exhibited red-shifted MLCT absorption bands when compared with their homoleptic analogues. The highest absorption maximum value (535 nm) was obtained for complex **4**, which contains the pyrrld$_2$bpy ligands. This value is comparable to that observed with the known [Ru(dcbpy)$_2$(NCS)$_2$]$^{2+}$ (**N3**) dye.[9]

The pyrrole-containing complexes **1** and **2** displayed the best molar extinction coefficients (ϵ) because of electron delocalization,[10] which increases the electric dipole moment associated with the charge-transfer transition. A weak additional effect was observed from one to two pyrrole groups on the ligand resulting in 19 000 and 21 000 M^{-1} cm^{-1} ϵ values, respectively. Interestingly, the absorption domain was found to be significantly extended for complexes **3** and **4**, which showed two absorption maxima indicating the presence of two MLCT transitions. The highest absorption maximum value was attributed to the metal-to-ligand (π^*dcbpy) transition and the lowest to the metal-to-ligand (π^*L) transition.

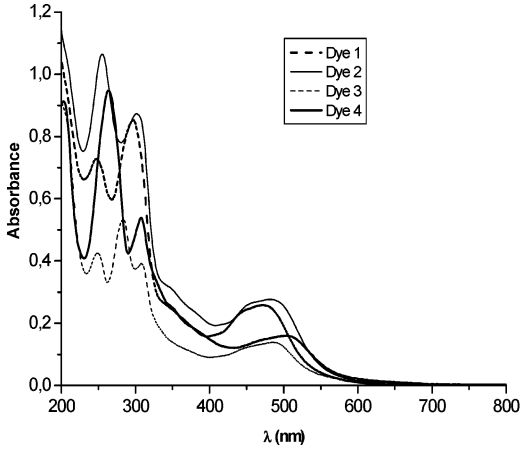


Figure 2. Absorption spectra of dyes **1**−**4** in acetonitrile.

1−**4** also displayed higher emission maxima than the corresponding homoleptic [RuL$_3$]$^{2+}$ complexes. This increase of the $\lambda_{\text{em-max}}$ also implied a decrease of the radiative constant k_r of the excited-state lifetimes (τ) as well as the quantum yields (Φ_{em}). This effect was notable in the pyrrolidine series in which electron delocalization is absent. Consequently, low τ values of 88 and 9 ns were measured for **3** and **4**, respectively.

Electrochemistry. The oxidation potentials of the Ru^{III}/Ru^{II} couple were reversible and found at lower values for the pyrrolidine series as a consequence of the expected electron-donor effect of the ligands. However, the potentials in **1**−**4** were higher than those of the corresponding homoleptic complexes, indicating that the HOMO was at lower levels. This was a consequence of the electron-withdrawing effect of the dcbpy ligand favoring the HOMO stabilization. At first glance, the low potentials observed in the pyrrolidine series could be attributed to an oxidation of the pyrrolidine moiety itself. However, the variation of the potential values from homoleptics to heteroleptics and the observation of reversible monoelectronic waves led us to discard this hypothesis. The absence of the pyrrolidine oxidation was firmly demonstrated by performing an exhaustive oxidation of $[Ru(pyrrld_2bpy)_3]^{2+}$ at 0.5 V/SCE. After an exchange of 1.2 F mol^{-1}, the oxidized compound displayed the expected blue-green color ($\lambda_{abs-max} = 763$ nm) characteristic of a Ru(III) complex. After reduction, identical electronic spectra were found for the corresponding reduced compounds and starting $[Ru(pyrrld_2bpy)_3]^{2+}$.

Logically, a decrease of the HOMO level should induce a blue-shift of the absorption instead of the observed bathochromic effects. This discrepancy could be attributed to a concomitant decrease of the LUMO level allowing a smaller gap between the HOMO and the LUMO levels compared with that of the homoleptic complexes. Such an effect on the LUMO was the consequence of the position of the π*dcbpy orbital exhibiting a lower energetic value than that of the π*L orbital. The comparison of the electrochemical potentials of L/L^- couples between homoleptic complexes and **1**−**4** was rendered impossible due to the irreversibility of the L/L^- processes within the latter. It is worth noting that the excited-state oxidation potential $E^*_{1/2ox}$ ($E^*_{1/2ox} = [E_{1/2}Ru^{III}/Ru^{II*} - E^{00}]$) for dyes **1**−**4** varied from −0.78 to −1.46 V/SCE indicating a sufficiently low reducing property to allow for the electron injection, since the TiO_2 flat band potential is typically near −0.7 V/SCE.[12] From this series of measurements, the complexes **1**−**4** were found to be promising dyes with high ϵ values, especially in the pyrrole series and within the extended absorption domains in the pyrrolidine series.

Dyes **1** and **2** could be seen as useful precursors for the preparation of polypyrrole films upon electrochemical oxidation. To check this, we performed a preliminary experiment; dye **1** was electrodeposited on an FTO electrode under potentiostatic conditions (1.2 V vs SCE). The formation of a surface-bound electroactive Ru^{II} species was clearly evidenced by cyclic voltammetry. Indeed, after rinsing of the electrode with acetonitrile, the voltammograms showed a linear behavior of the peak current with the scan speed.[13]

Then we turned to the investigation of the photoelectrochemical properties of the new dyes to evaluate their performance in a photovoltaic device.

IPCE Measurements. The complexes **1**−**4** were chemisorbed on TiO_2 films, and the semiconductor sensitization was first checked by UV−vis analyses (Figure 3). The spectra were compared to those of known reference dyes $[Ru(dcbpy)_3]^{2+}$ (**5**)[14] and **N3**.[9]

All the electrodes modified with the new dyes exhibited higher absorbance than the reference complexes, the best scores being obtained for the pyrrole series (dyes **1** and **2**) just like in solution (see Table 1). In addition, comparable absorption domains were observed for **4** and **N3**. This result was promising for the elaboration of “bpy only” dyes expected to prevent the known instability drawbacks of the NCS ligands.[15]

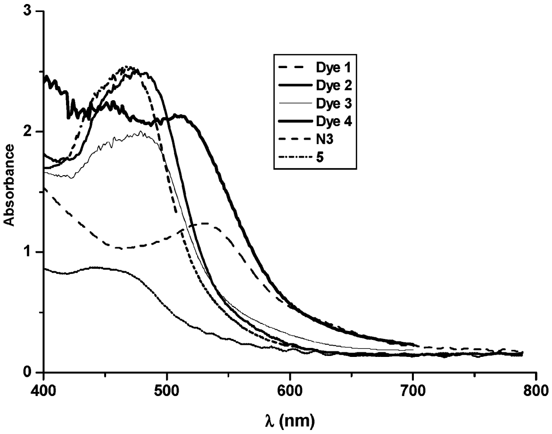


Figure 3. Overlay absorption spectra of TiO_2 photoanodes modified with **1**−**4**, **N3**, and **5**.

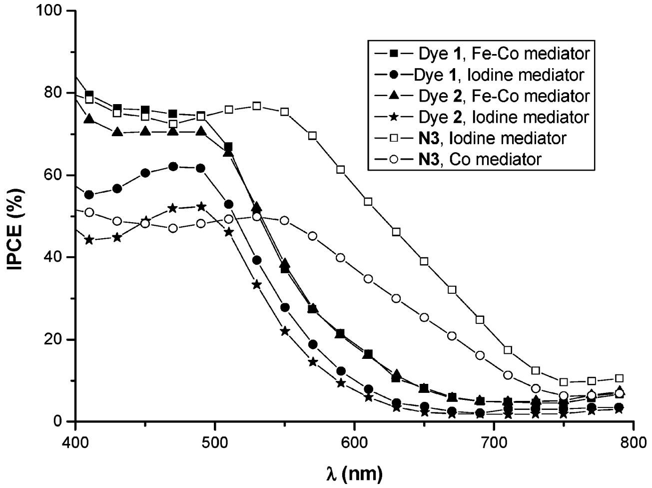


Figure 4. Photoaction spectra of dyes **1**, **2**, and **N3**. Co mediator: $[Co(dtbbpy)_3](PF_6)_2$ (0.15 M) in CH_3CN. Fe−Co mediator: $[Fe(dmbpy)_3](PF_6)_2$ (0.015 M) and $[Co(dtbbpy)_3](PF_6)_2$ (0.15 M) in CH_3CN. Iodine mediator: LiI (0.5 M) and I_2 (0.05 M) in CH_3CN.

All the absorption maxima were lower here than in solution. For example, this value was decreased by 21 nm for **4**. Such blue-shifts can be explained by the electron-acceptor character of the semiconductor that weakens the electronic charge on the dye. Additionally, the electronic delocalization through the titanates at the TiO_2-dye interface also contributed to HOMO level stabilization and thus to blue-shifts. Then we turned to the assembly of DSCs using our new dyes and IPCE measurements. The DSCs were assembled following reported methods.[6] The photoelectrochemical experiments were performed using various electron-transfer mediators in the electrolyte, including the most popular I_3^-/I^- couple (platinum cathode) and Co^{II}-based mediators[6,16] (gold cathode). The photoanode was a film of nanocrystalline TiO_2. The best performances were obtained in the pyrrole series (dyes **1** and **2**), which attained excellent IPCE values (near 80%) within the maximum absorption range (Figure 4). The best results were recorded using a

---

(16) Cazzanti, S.; Caramori, S.; Argazzi, R.; Elliot, C. M.; Bignozzi, C. A. *J. Am. Chem. Soc.* **2006**, *128*, 9996.

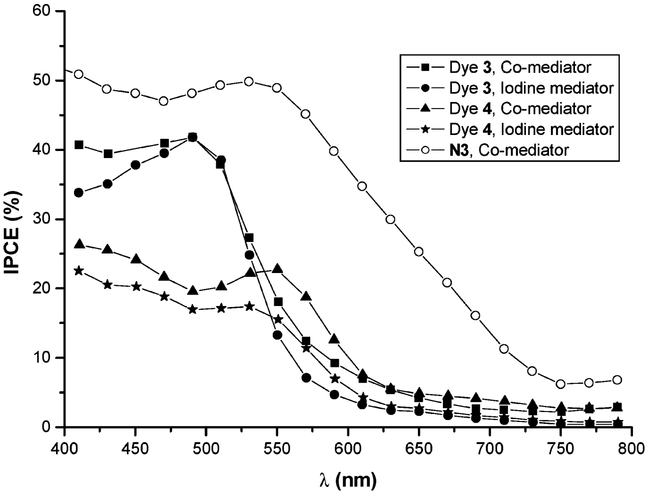


Figure 5. Photoaction spectra of dyes **3**, **4**, and **N3**. Co mediator: [Co(dtbbpy)$_3$](PF$_6$)$_2$ (0.15 M) in CH$_3$CN. Iodine mediator: LiI (0.5 M) and I$_2$ (0.05 M) in CH$_3$CN.

mixture of [Fe(dmbpy)$_3$]$^{2+}$ (dmbpy = 4,4′-dimethyl-bipyridine) and [Co(dtbbpy)$_3$]$^{2+}$ (dtbbpy = 4,4′-diterbutyl-bipyridine) as the mediator[6] instead of I$_3^-$/I$^-$. While absorbing in the widest range with good absorbance, dyes **3** and **4** showed moderate IPCE results (near 40%). The best results were obtained with [Co(dtbbpy)$_3$]$^{2+}$ as the mediator (Figure 5).

Interestingly, the best results were obtained with pyrrole-based dyes **1** and **2**, which display the lowest $E^*_{1/2\text{ox}}$ values and thus are not the best reductants. This indicated the involvement of parameters other than the charge injection efficiency such as the electron collection efficiency parameter (η_{coll}) which reflects the charge recombination processes and often determines cell performances.[12]

Beside these promising performances of dyes **1** and **2**, some limitations have been pointed out, probably resulting from a too-slow regeneration of the oxidized dye after the injection step into the TiO$_2$ conduction band. As reported above (Table 1), the pyrrole and pyrrolidine moieties induced a notable decrease of the Ru$^{\text{III}}$/Ru$^{\text{II}}$ oxidation potentials, especially with pyrrolidine (dyes **3** and **4**). Thus, the regeneration step was more efficient with the Co-based mediators (0.2 V/SCE) than with I$_3^-$/I$^-$ (0.4 V/SCE).

Conclusion

The electronic effect of pyrrole- and pyrrolidine-containing ligands on the properties of [RuL$_2$dcbpy]$^{2+}$ complexes has been demonstrated. The TiO$_2$ electrodes modified with the new dyes exhibited extended absorption domains and higher absorbances than the known **N3** dye. Good IPCE values (near 80%) have been obtained in the pyrrole series, providing that a cobalt-based mediator instead of the usual I$_3^-$/I$^-$ mediator was used. The DSC efficiency strongly depends on both the dye properties (absorption domain, molar extinction, oxidation potentials) and transfer mediator. Work is now progressing to design new dyes focusing on the optimization of the regeneration step. The electropolymerization of pyrrole-based dyes is also under active investigation for the elaboration of solid-state solar cells.

Acknowledgment. The authors thank the CNRS and the French Ministry of Research for financial support and are also grateful to P. Werhung (ULP Strasbourg) for ESI mass spectrometry analyses. FIRB Contract No. RBNE 019H9K is also gratefully acknowledged.

IC062042F