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New iridium cyclometallated complexes with potential application in OLED

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ABSTRACT

The photophysical and electrochemical properties of cyclometallic cationic iridium complexes that also contain bipyridine type ligands have been investigated in this work. The effect on the photophysical properties of the complexes on the presence of aliphatic long chain or branched substitution was analyzed. The complexes show photoluminescence maxima in the green-blue region of the visible spectrum, with acceptable quantum yields and lifetime, showing in this way potentiality to be tested in OLED devices.

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1. Introduction

A concept introduced in electroluminescence devices proposes the use of ionic transition metal complexes (iTMS) [1]. These are based on single-layer electroluminescent devices that may also operate at low voltage with high work function air-stable electrodes, due to the high electric fields produced by ions accumulating at the anode and cathode interfaces, which favor charge injection. Cationic iridium (III) cyclometallated complexes have achieved great interest because of their high phosphorescence quantum yields, and the possibility to effectively tune their emission maxima over a large spectral range by an appropriate combination of ligands and substituents [2]. These properties permit their use as emitting materials in OLED devices.

The luminescent efficiency and the emission wavelength of ionic iridium (III) complexes are affected significantly by the nature of the organic ligands [3,4]. The ligands present in the complexes are frequently derivatives of phenylpyridine coordinated to the metal center via the formation of Ir-N and Ir-C bonds, combined with bipyridine bidentate type ligands. The type of emission observed (originating in d–d, d– π or π – π * excited states) for metals such as iridium (III), will depend on the chemical and electronic properties of the substituents on the ligands [5,6]. Specifically, studies developed by Gratzel's and others [7] show the modulation of the emission color of iridium complexes, based on the selective stabilization of the HOMO and/or the selective destabilization of the LUMO in the complex. The ligands in complexes of type $[Ir(C^N)_2(N^N)^+]^{n+}$, with (C^N) a cyclometallating ligand and (N^N) a bipyridine substituted ligand, act independently in order to achieve the desired color setting. In general, electron-withdrawing substituents in the (C^N) ligand decrease the donation to the metal and, therefore, stabilize the metal-based HOMO. Electron-donating substituents in (N^N) destabilize the ligand-based LUMO, ultimately leading to increased HOMO–LUMO gaps and emission energies.

Finally, considering the possibility for Ir complexes to be used in OLED devices, it is worth mentioning that is has been proposed [8] that the incorporation of long aliphatic chains on the bipyridine ligand helps to the improvement of the device by e.g. minimizing self quenching effects.

In this paper complexes of iridium with cyclometallated ligands of general formula $[Ir(C^N)_2(N^N)]^+$, with $(C^N) = 7,8$ -benzoquinoline (bzq), and $(N^N) = 4-4'$ diphenylethyl-2,2'-bipyridine (DPhB) or 4,4'diterbutyl-2,2'-bipyridine (tBuB), were synthesized and characterized by spectroscopic and electrochemical techniques. These complexes possess bipyridine type ligands substituted with aliphatically connected substituents, or with directly bound branched aliphatic groups. The photochemical behavior of these complexes is studied and compared to complexes of similar structure previously synthesized or reported in literature [4,8,23]. These types of complexes should be free of electronic effects, and should show only structural effects. The potentiality of the complexes in OLED devices is discussed.

2. Experimental

Reagents and solvents were purchased from Sigma–Aldrich, with the exception of $IrCl_3$ hydrate, which was purchased from Precious Metals Online, PMO Pty LTD, Australia. The cyclometallated Ir (III) chloro-bridged dimmer $[Ir(bzq)_4Cl_2]$ (bzq = 7,8-benzoquinoline) was synthesized according to the literature [9]. ¹H NMR spectra were obtained on a Bruker AC/200 (200 MHz) or a Bruker 400 MHz instrument, using CDCl₃ as solvent and TMS as reference. IR spectra were carried out in a Bruker Vector-22 FTIR spectrometer using KBr pellets. Elemental analyses were performed on a Fisons Instruments Analyzer, model EA 1108/CHNS-O with PC





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NCR system 3225. Mass Spectra were recorded with an LCQ Duo Ion Trap Mass Spectrometer (Thermo Finnigan, USA).

2.1. Synthesis

2.1.1. Ligands

The ligand 4,4'diterbutyl-2,2-bipyridine ([tBuB]), was commercially obtained through Sigma Aldrich. The ligand 4-4'diphenylethyl-2, 2'-bipyridine ([DPhB]) was synthesized by slightly modified procedures reported by Juris [10] for similar compounds, with the use of acetic acid as dehydrating agent, instead of sulfuric acid, to convert 4,4'-bis[2-hydroxy-2-(phenyl)ethyl]-2,2'-bipyridine to 4,4'-bis(α -estirene styrene)-2,2'-bipyridine. Instead, 4,4'-bis(α -estirene)-2,2'-bipyridine dehydrogenation was carried out using a catalyst of Pd/C in the presence of ethanol, as shown in Scheme 1.

2.1.1.1. 4,4'-Bis[2-hydroxy-2-(phenyl)ethyl]-2,2'-bipyridine. RMN ¹H (200 MHz, CDCl₃) δ: 8,52 (d, H₁, H'₁), 8,31 (s, H₃, H'₃), 7,13 (d, H₂,

 H'_{2}), 5,05 (t, H₆, H'₆), 3,10 (d, H₄, H'₄, H₅, H'₅), 2,44 (s, H₇, H'₇). FTIR (cm⁻¹) (KBr): 3356 (OH stretch, OH group), 1597 (stretching C=C pyridine), 1555 (stretching C=N pyridine), 700 (monosubstituted aromatic deformation). *Anal.* Calc. for C₂₆H₂₄N₂O₂: C, 78.76; H, 6.10; N 7.07. Found: C, 75.82; H, 8.17; N, 6.83%.

2.1.1.2. 4,4'-Bis(α-estirene)-2,2'-bipyridine. RMN ¹H (200 MHz, CDCl₃) δ: 8,67 (d, H₁, H'₁), 8,56 (s, H₃, H'₃), 7,48 (d, H₄, H'₄), 7,37 (d, H₂, H'₂), 7,15 (d, H₅, H'₅). FTIR, (cm⁻¹) (KBr): 1634 (stretching C=C, alkene chromophoric unit), 1584 (stretching C=C, pyridine), 1541 (stretching C=N pyridine), 692 (monosubstituted aromatic deformation). *Anal.* Calc. for C₂₆H₂₀N₂: C, 86.64; H, 5.59; N, 7.77. Found: C, 87.45; H, 5.56; N, 7.27%.

2.1.1.3. 4,4'-Diphenylethyl-2,2'-bipyridine. RMN ¹H (200 MHz, CDCl₃) δ : 8,30 (s, H₁, H'₁), 8,57 (d, H₂, H'₂),7,11 (d, H₃, H'₃), 3,01 (s, H₄, H'₄, H₅, H'₅), 8,75 (m, Ph). Anal. Calc. C₂₆H₂₄N₂: C, 85.68; H, 6.64; N, 7.69. Found: C, 85.43; H, 7.05; N, 7.72%.



2.1.2. Complexes

Cationic complexes of iridium, $[Ir(bzq)_2L][PF_6]$ (bzq = 7,8benzoquinoline, L = 4-4'diphenylethyl-2,2'-bipyridine or 4-4'diterbutyl-2,2'-bipyridine) were prepared based on a literature procedure reported by Lowry et al. [9], using the iridium precursor tetrakis-(C^N)- μ -(dichloro)-diiridium (III) ([Ir(bzq)_4Cl_2]) in the presence of the respective [DPhB] or [tBuB] pyridine ligand in a solvent such as ethylene glycol. To the reaction vessel an aqueous solution of ammonium hexafluorophosphate was added and the corresponding cationic species obtained. They will be referred as complex [C1] and complex [C2], respectively.

2.1.2.1. Complex [C1] [Iridium bis (7,8-benzoquinoline)(4,4'-diphenylethyl-2,2'-bipyridine)]PF₆. The dichloro bridged dimer (0.1 mmol) of iridium [Ir(bzq)₄Cl₂] was reacted with the appropriate neutral ligand (0.22 mmol) in ethylene glycol (5.0 mL) under reflux (150 °C) with constant stirring for 18 h. Upon cooling to room temperature, the mixture was transferred to a separator funnel by adding three aliquots of 30 mL water, and washed with three aliquots of 50 mL diethyl ether. The aqueous layer was heated to 70 °C for 10 min using a heat gun to remove residual organic solvents. The vessel was then placed on ice, and 10 mL of an aqueous ammonium hexafluorophosphate solution (1.0 g in 10 mL of deionized water) was slowly added to the mixture, yielding a colored suspension. The precipitate was collected by suction filtration and allowed to air-dry overnight. The product was recrystallized by acetonitrile/diethyl ether vapor diffusion to yield the pure product (yield: 75%).

¹H NMR (400 MHz, CDCl₃) δ : 8.64 (s, 2H), 8.26 (d, *J* = 7.60 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.69 (d, *J* = 5.6 Hz, 2H), 7.47 (d, *J* = 8 Hz, 2H), 7.44 (d, *J* = 8 Hz, 2H), 7.15 (d, *J* = 7.6 Hz, 2H), 6.98 (d, *J* = 5.6 Hz, 2H), 6.30 (d, *J* = 7.2 Hz, 2H), 3.48 (m, *J* = 7.2 Hz, 2H), 3.19 (m, *J* = 7.6 Hz, 2H). MS for $[C_{52}H_{40}IrN_4]^+$ PF₆⁻: *m/z*: 912.09 [M⁺].

2.1.2.2. Complex [C2] [Iridium bis (7,8-benzoquinoline) (4,4'-diterbutyl-2,2'-bipyridine]) PF_6 . The synthetic route for this complex is analogous to that described for complex [C1]. The product was



Fig. 1. (a) [Iridium bis (7,8-benzoquinoline)(4,4'-diphenylethyl-2,2'-bipyridine)]PF₆, [C1]; (b) [Iridium bis (7,8-benzoquinoline) (4,4'-diterbutyl-2,2'-bipyridine])PF₆, [C2].



Fig. 2. NMR ¹H cationic complex [C1] (a) and [DPhB] ligand (b).

Table 1

Assignment of ¹H NMR signals for [C1] complex.

Protons	Signals [C1] ppm	Signals [DPhB] ppm	Signals [Bzq] ppm
a,a'	8.26		9.03
b,b′	7.47		7.52
C,C'	7.85		8.20
d,d′	7.69		7.49
e,e'	6.98		7.94
f,f	7.44		8.15
g,g'	7.15		7.67
h,h′	6.30		7. 77
i,i′			9.34
1,1′	8.64	8.30	
2,2'	7.83	8.57	
3,3′	7.65	7.11	
4,4'	3.48	3.01	
5,5′	3.19	3.01	
Ph	8.59	8.75	

recrystallized by acetonitrile/diethyl ether vapor diffusion to yield the pure product (yield: 70%).

¹H NMR (400 MHz, CDCl₃) δ : 8.01 (d, 2H), 7.54 (d, *J* = 7.60 Hz, 2H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 5.6 Hz, 2H), 7.14 (d, *J* = 8 Hz, 2H), 7.43 (d, *J* = 8 Hz, 2H), 8.40 (d, *J* = 7.6 Hz, 2H), 6.33 (d, *J* = 5.6 Hz, 2H), 8.27 (d, *J* = 7.2 Hz, 2H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 1.40 (s, 18H). MS for $[C_{48}H_{38}IrN_4]^+PF_6^-$: *m/z*: 962.04 [M⁺].

2.2. UV-Vis and photophysical measurements

2.2.1. UV-Vis

UV–Vis spectra were recorded on a Shimadzu, UV-3101 PC spectrophotometer.

2.2.2. Fluorescence spectroscopic measurements

Emission measurements were carried out in a Perkin Elmer spectrofluorimeter model SP 8765 at room temperature in acetonitrile, with previous degassing with N₂(g) for approximately 20 min. Emission quantum yields were determined by the method described by Caspar and Meyer [11] using Ru(bpy)₃⁺² in CH₃CN as reference (ϕ = 0.062).

Steady-state and time-resolved fluorescence measurements were performed on a K2 multifrequency phase and modulation spectrofluorometer (ISS, Champaign, IL, USA). The instrument was equipped with Glan-Thompson polarizers. Excitation light was obtained by the modulable ISS 375 nm LED laser at frequencies between 10 and 150 MHz. The emission was measured through Schott KV-399 and WG-420 long band-pass filters. Lifetime measurements were made with the polarizers oriented in the "magic angle" at 54.7° condition [12a,12b]. In the multifrequency phase and modulation technique the intensity of the exciting light is modulated, and the phase shift and relative modulation of the emitted light are determined. Phase and modulation values were obtained as previously described [12c,12d]. Dimethyl-POPOP (1,4-bis[2]4-Methyl-5-phenyloxazoly benzene) in ethanol (τ = 1.45 ns) was used as a reference for intensity decay. In all measurements, data were taken until the standard deviation of the phase and modulation measurements were, at each modulation frequency, smaller than 0.2° and 0.004°, respectively.

Fluorescence spectra were obtained employing a 300 W Xe lamp and slits were set at 20 nm (excitation) and 5 nm (emission).

2.2.3. Data analysis

The results were analyzed according to the Global Program (Global Unlimited software package, Laboratory for Fluorescence Dynamics, University of Illinois at Urbana-Champaign, Urbana, IL, USA) [12e]. The fitting function for the lifetime measurements



Fig. 3. Cyclic voltammogram of complexes [C1] and [C2] vs. Fc (Ag/Ag⁺), measured in acetonitrile in the presence of 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte, with a 100 mV/s scan speed.



was a discrete mode and a discrete component, fixed at 0.01 ns, in order to account for scattered light [12d].

2.3. Electrochemical measurements

The cyclic voltammetric (CV) measurements were carried out using a Bas CV-50W-2,3-MF-9093 equipment with a three

electrode arrangement with a Pt or glassy platinum working electrode, a Pt gause counter electrode, and a Ag/Ag^+ reference electrode. Experiments were carried out under argon atmosphere, working in acetonitrile (CH₃CN, Merck) with 0.1 M tetrabutylammonium hexafluorophosphate (Fluka, puriss electrochemical grade) as the supporting electrolyte.

3. Results and discussion

3.1. Synthesis and characterization

3.1.1. Ligands

The [Ldiol], [LH] and [DPhB] ligands depicted in Scheme 1 were synthesized by minor modifications to the procedures reported by Juris and others [13]. For example, acetic acid instead of sulfuric acid was used as a drying agent in the conversion of [Ldiol] to [LH], in order to use milder conditions for a longer period of time. Regarding the synthesis of the [DPhB ligand], when literature procedures where strictly used, [10] low reaction yields were obtained. By rising the temperature until reflux (about 120 °C) and allowing more reaction time (24 h), significant enhancements of the reaction yield and the purity of the product were achieved. The [tBuB] ligand was obtained commercially; however, selective spectroscopic analyses of this free ligand were performed in order to compare with the spectra of the corresponding iridium complex.

3.1.2. Complexes

The synthetic method used to obtain the cationic iridium complexes [C1] and [C2] depicted in Fig. 1(a and b), respectively, worked out straight forward and relatively fast, with yields over 70%. Analyses carried out by ¹H NMR spectroscopy showed clearly the formation of complexes [1] and [2] by the synthetic route reported in this work. By comparison of the ¹H NMR spectra of complex [C1] (Fig. 2a) and ligand [DPhB] (Fig. 2b), clear evidence for the formation of the cationic complex can be inferred. The CH₂-CH₂ fragment that bridges the pyridine and phenyl groups in [DPhB], appears as a singlet at 3.01 ppm for the free ligand, while for the complex, this signal shifts to lower fields, appearing as two multiplets at 3.19 and 3.48 ppm. On the other hand, the coordination of the cyclometallated fragment in complex [C1] is also evidenced by ¹H NMR, mainly by the set of signals in the aromatic region, between ca. 7 and 9 ppm. The assignment of the signals is given in Table 1. The spectrum of free benzoquinoline in CDCl₃ shows signals at lower field, between 7.49 and 9.34 ppm. As an example, the shift of the h and h' protons, from 7.77 ppm in the free ligand to 6.30 ppm in the [C1] complex is assigned to the coordination to the Iridium metal center, which



Fig. 5. Emission spectra for complexes [C1] (-) and [C2] (--), in acetonitrile.

 Table 2

 Photophysical data of complexes [C1] and [C2] measured at 298 K in acetonitrile.

Complex	Absorption λ_{max} (nm)	Emission λ_{max} (nm)	Lifetime τ (ns)	ϕ
[C1]	250, 305, 417	554	68	0.082
[C2]	264, 305, 423	559	60	0.071
Ir(bzq)2(bpy) ⁺ [25]	385	555	10900 ^a	0.073
Ir(ppy)2(bpy) ⁺ [26]	250, 310, 390	582	385	

^a Lifetime of Ir(III) complex in 4:1 ethanol/methanol at 298 K.

increases the electronic density on these protons, displacing them to higher fields. It can also be observed that the signal at 9.34 ppm in the free ligand, assigned to the *i*,*i*^{*i*} protons, is absent in the [C1] complex spectrum, evidencing coordination.

Similar effects on the ¹H NMR pattern were observed when comparing the spectra of the free ligand 4,4'diterbutyl-2,2-bipyridine ([tBuB]) and complex [C2].

3.2. Electrochemical measurements

The cyclic voltammogram for complexes [C1] and [C2] show a similar pattern, Fig. 3, with an irreversible couple at 0.91 V versus



Fig. 4. Absorption spectra for complexes [C1] (-) and [C2] (--), in acetonitrile.

Fc, assigned to the oxidation of iridium (III/IV) together with a minor contribution from the cyclometallated phenyl fragment of bzq. An irreversible reduction peak around -1.4 V, associated with the reduction of the substituted bipyridine, is also observed. These results compare well with those reported for similar compounds [23]. Studies carried out earlier in our group [22a,22b] with an analogous cyclometallated iridium complex, but containing a more rigid and conjugated ligand (Scheme 2) also show irreversible oxidation peaks at about 0.96 V, with the reduction of the ligands displaced to ca. -1.3 V. The unsaturated bridge present in this case in the substituted bipyridine, favors ligand reduction, due to the higher electronic density and delocalization on the complex.

3.3. UV–Vis and photophysical measurement

The UV–Vis spectra of the cationic complexes [C1] and [C2] in acetonitrile show three main absorption regions, at 240–270 nm, 300–350 nm and 390–480 nm, Fig. 4. Cyclometallated cationic iridium complexes are reported to show an intense absorption band about 250 nm in the UV, assigned to spin allowed ($\pi \rightarrow \pi^*$) transitions on the cyclometallating ligands [2]; bands in the 300–380 nm range are assigned to spin allowed metal–ligand charge transfer transitions (¹MLCT). Finally, the bands appearing in the proximity of 420 nm are attributed to spin-forbidden ³MLCT transitions [14]. It is discussed in literature [15] that this information indicates an efficient spin–orbital coupling, which favors the emission phosphorescence, see below.

The emission spectra of complexes [C1] and [C2] are shown in Fig. 5. Complex [C1] emits at room temperature at $\lambda_{em} = 554$ nm, while the maximum for complex [C2] appears at 559 nm. The λ_{max} values correlate well with those reported for this type of cyclometallated complexes [16]. The vibronic substructure observed can be related to a contribution of $\pi \rightarrow \pi^*$ LC transitions, in addition to the MLCT processes, as discussed by Dragonetti et al. [17] and He et al. [18].

Table 2 sums up the photophysical data for the complexes reported in this work. Quantum yields of $\phi = 0.082$ and $\phi = 0.071$, and lifetimes of $\tau = 68$ ns and $\tau = 60$ ns, were observed for [C1] and [C2], respectively. Ir (III) complexes typically exhibit high phosphorescence quantum yields ($\phi = 0.1-0.9$) and excited state lifetimes in the nanosecond order [19]. The origin of the phosphorescence is attributed to a ³MLCT excited state, but with electron-withdrawing ligands, which decrease the energy of the ³ π - π * states, emission may be considered to be a mixture of both MLCT and IL [20,21]. The quantum yield for the emission of iridium complexes can be modulated by introducing ligands having strong ligand field stabilization energy [6]. It is noteworthy that the emission appears very close in position to the corresponding to [Ir(bzq)₂(bpy)]⁺, i.e. to the analogous complex with 2,2'-bipyridine (bpy) instead of substitued bpy, Table 2.

4. Conclusions

The objective of this study was to analyze the photophysical properties of new iridium cyclometallated complexes, in order to infer their potentiality as materials of iTMC type to be used in OLED devices. The complexes were designed to possess a bulky substitution on the bpy ligand, in order to avoid ordering, when eventually used in an OLED device [8]. At the same time, the substituents were chosen to possess saturated chains, which should "disconnect" electronically bpy with the substituent.

According to literature information on similar compounds, the substitution on the bipyridine ligands is not responsible for the photochemical characteristics of these complexes, but rather the cyclometallated ligand [24]. This latter ligand would also be responsible for the vibronic structure observed even at RT on the emission spectra.

As expected, due to the saturated bridge, the emission of [C1] and [C2] is very close in energy to that observed for the corresponding bpy analogue, Table 2. In the same table, spectroscopic data for the phenylpyridine (ppy) analogue is also reported.

The lower lifetime for [C1] and [C2] in regard to $[Ir(ppy)_2(bpy)]^+$ and $[Ir(bzq)_2(bpy)]^+$ can be understood because of an increase in non radiative deactivation pathways in the formers, due to the free rotating substitution on the bpy ligands. It should be mentioned that the reported value for $[Ir(bzq)_2(bpy)]^+$ was measured in another media than the rest of the series. Additionally, the quantum yield values observed for [C1] and [C2] compare well with the reported one for $[Ir(ppy)_2(bpy)]^+$.

As a whole, the substitution on the bpy ligands does not change considerable the energy (color) and the quantum yield of the emission, but affects the emission lifetime due to non-radiative processes. Nevertheless, this eventual disadvantage should be overcome by the advantage of avoiding ordering (that favors deactivation of the excited state) when used in a device, justifying the testing of these substrates in OLED devices.

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References

- M.S. Lowry, J.L. Goldsmith, J.D. Slinker, R. Rohl, R.A. Pascal, G.G. Malliaras, S. Bernhard, Chem. Mater. 17 (2005) 5712.
- [2] R. Evans, P. Douglas, C. Winscom, Coord. Chem. Rev. 250 (2006) 2093.
- S. Lamansky, D. Djurovic, D. Murphy, F. Abdel-Razzaq, H. Lee, C. Adachi, P.E. Burrows, S.R. Forrest, M.E. Thompson, J. Am. Chem. Soc. 123 (2001) 4304.
 I.D. Slinker, A.A. Gorodetsky, M.S. Lowry, I. Wang, S. Parker, R. Rohl, S.
- [4] J.D. Slinker, A.A. Gorodetsky, M.S. Lowry, J. Wang, S. Parker, R. Rohl, S. Bernhard, G.G. Malliaras, J. Am. Chem. Soc. 126 (2004) 2763.
- [5] G.A. Crosby, R.J. Watts, D.H.W. Carstens, Science 170 (1970) 1195.
- [6] M.K. Nazeeruddin, M. Grätzel, Structure and bonding, Transition Metal Complexes for Photovoltaic and Light Emitting Applications, vol. 123, 2007, pp. 113–175.
- [7] F. De Angelis, S. Fantacci, N. Evans, C. Klein, S.M. Zakeeruddin, J. Moser, K. Kalyanasundaram, H.J. Bolink, M. Gratzel, M. Nazeeruddin, Inorg. Chem. 46 (2007) 5989.
- [8] S. Bernhard, J.A. Barron, P.L. Houston, H.D. Abruña, J.L. Ruglovksy, X. Gao, G.G. Malliaras, J. Am. Chem. Soc. 124 (2002) 45.
- [9] M. Lowry, W. Hudson, R. Pascal, S. Bemhard, J. Am. Chem. Soc. 126 (2004) 14129.
- [10] A. Juris, S. Campagna, I. Bidd, J.M. Lehn, R. Ziessel, Inorg. Chem. 27 (1998) 4007.
- [11] J. Caspar, Th Meyer, J. Am. Chem. Soc. 105 (1983) 5583.
- [12] (a) R. Spencer, G. Weber, Ann. NY Acad. Sci. 158 (1969) 331.
 - (b) R. Spencer, G. Weber G, J. Chem. Phys. 52 (1970) 1654.
 - (c) E. Gratton, D. Jameson, R.D. Hall, Ann. Rev. Biophys. Bioeng. 13 (1984) 105.
 - (d) J.R. Alcala, E. Gratton, F.G. Prendergast, Biophys. J. 51 (1987) 587.
 - (e) D. Jameson, E. Gratton, R. Hall, Appl. Spectroc. Rev. 20 (1984) 55.
- [13] F. Angel, B. Loeb, Inorg. Chem. Acta.; in preparation.
- [14] E. Baranoff, S. Fantacci, F. De Angelis, X. Zhang, R. Scopelliti, M. Grätzel, M.K. Nazeeruddin, Inorg. Chem. 50 (2011) 451.
- [15] M. Xu, R. Zhou, G. Wang, Q. Xiao, W. Du, G. Che, Inorg. Chim. Acta 361 (2008) 2407.
- [16] D.L. Davies, M.P. Lowe, K.S. Ryder, K. Singh, S. Singh, Dalton Trans. 40 (2011) 1028.
- [17] C. Dragonetti, L. Falciola, P. Mussini, S. Righetto, D. Roberto, R. Ugo, A. Valore, Inorg. Chem. 46 (2007) 21.
- [18] L. He, L. Duan, J. Qiao, R. Wang, P. Wei, L. Wang, Y. Qiu, Adv. Funct. Mater 18 (2008) 2123.
- [19] M.K. Nazeeruddin, R. Humphrey-Baker, D. Berner, Rivier, L. Zuppiroli, M. Graetzel, J. Am. Chem. Soc. 125 (2003) 8790.
- [20] F.M. Hwang, H.Y. Chen, P.S. Chen, C.S. Liu, Y. Chi, C.F. Shu, F.L. Wu, P.T. Chou, S.M. Peng, H. Lee, Inrog. Chem. 44 (2005) 1344.
- [21] Md.K. Nazzeruddin, R. Wegh, Z. Zhou, C. Klein, Q. Wang, F. De Angelis, S. Fantacci, M. Grätzel, Inorg. Chem. 45 (2006) 9245.
- [22] (a) M. Fritzsche, S. Salinas, B. Loeb, Umpublised results.;
- (b) M. Fritzsche, B. Loeb, XII Encuentro de Química Inorgánica, Página 76, Enero, 2009, Antofagasta Chile, Unpublised results.
- [23] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H. Lee, C. Adachi, P. Burrows, S. Forrest, M. Thompson, J. Am. Chem. Soc. 123 (2001) 4304.

[24] F.M. Hwang, H.Y. Chen, P.S. Chen, Ch.S. Liu, Y. Chi, C.F. Shu, F. Wu, P.T. Chou, S.M. Peng, G.H. Lee, Inorg. Chem. 44 (2005) 1344. [25] A.P. Wilde, K. King, R. Watts, J. Phys. Chem. 95 (1991) 629.[26] L. Tinker, S. Bernhard, Inorg. Chem. 48 (2009) 10507.