

Ruthenium(II) Complexes Containing Tetrazolate Group: Electrochemiluminescence in Solution and Solid State

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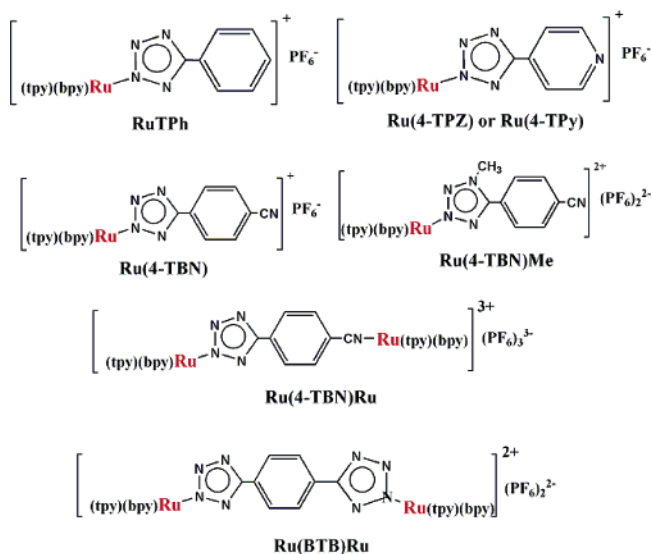
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In this work, we report the results about the solution and solid-state phosphorescence emission properties of six Ru^{II} complexes containing various 5-substituted tetrazolate ligands. The photo- and electrochemiluminescence spectra of all compounds revealed a red shifted emission with respect to the Ru(bpy)₃²⁺. Significant changes to the light emission energy and to the efficiency and sensitivity to oxygen were also determined by varying the nature of the substituent ring of the tetrazolate ligand. Light-emitting solid devices with active layers containing solid films of the same complexes were prepared, and preliminary studies of their electroinduced emission properties were performed. The electrochemiluminescence (ECL) emission intensity of two of the six complexes was of the same order of magnitude as the reference Ru(bpy)₃²⁺.

Introduction

Since Ru(bpy)₃²⁺ electrochemiluminescence (ECL) was discovered, photophysical properties of many Ru complexes have been investigated.^{1,2} The intense emission of light generated by annihilation in organic solvents or in the presence of coreactant in water³ has been extensively studied. The potential applications are correlated with the specific properties of the single compound. In organic light-emitting solid devices (OLED) tests, Ru(bpy)₃²⁺ showed an intense orange emission with low applied voltages.^{4–7} Molecules intended for light-emitting solid devices require in general high quantum efficiencies, short response times, and high durability. Rutheniumtris(4,7-diphenyl-1,10-phenanthroline) (RuDPP) has been used as an oxygen sensor with fluorimetric detection in organic solvents and in supported silicon and xerogels films.⁸ Ru^{II} complexes interacting with DNA or other biomolecules often show a change in ECL intensity proportional to the concentration, and therefore, many analytical methods based on ECL have been developed.^{3,9} In this article, ECL of the Ru^{II}(bpy)(tpy) moiety with different substituted tetrazolates (see Scheme 1) has been tested in MeCN solution and in light-emitting solid devices. The addition or removal of small groups around the tetrazolate moiety allowed us to study the effect in MLCT (metal-to-ligand charge transfer) transitions. The modification of ECL spectra is often remarkable even in relatively similar molecular structures. To detect biomolecules such as nucleic acids and proteins, the use as covalent labels³ could be possible because of considerable quantum efficiency and red shift with respect to Ru(bpy)₃²⁺.

SCHEME 1: Complexes and Acronyms Used in This Work



Experimental Section

Materials and Synthesis. Unless otherwise stated, all chemicals were obtained commercially. The organic tetrazoles were prepared in high yields (80–95%) according to the first established method involving 1,3 dipolar cycloaddition of the azide anion onto the appropriate aromatic nitriles.^{10a} The only exception was represented by the ligand 4-TPhH, which was synthesized by following the protocol reported by Koguro et al.^{10b} The precursor complexes Ru(tpy)Cl₃^{10c} and [Ru(tpy)(bpy)-Cl][PF₆]^{10d} were prepared according to literature methods. The preparation and the structural characterization of four of the six dyes, Ru(4-TBN)Ru, Ru(BTB)Ru, Ru(4-TBN), and Ru(4-TBN)-

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Me, used in this work have been described elsewhere.² The synthesis of the new cationic complexes Ru(TPh) and Ru(4-Tpy) has been performed by adopting the same two-step procedure. This latter involved the preliminary chloride abstraction from the precursor species [Ru(tpy)(bpy)Cl][PF₆] followed by reaction with the desired tetrazolate ligand. Typically, a 0.500-g aliquot of [Ru(tpy)(bpy)Cl][PF₆] (0.74 mmol) was placed into a light-protected 100-mL round-bottomed flask and was dissolved in 15 mL of deaerated acetone. A slight excess (1.1 equiv) of AgPF₆ was added, and the resulting mixture was stirred with reflux for 2 h. Then, the precipitated AgCl was removed by filtration through a Celite pad and the filtrate was added slowly to an acetone (10 mL) solution of the desired tetrazolate ligand (0.85 mmol). Once the addition was complete, the deep red reaction mixture was heated at the reflux temperature for 8–10 h. The solution was cooled to room temperature, was concentrated to ca. half of the initial volume, was added to 10 mL of an aqueous solution containing 0.5 g of NH₄PF₆, and was extracted with dichloromethane until the aqueous phase became colorless. The organic layers were combined and dried over MgSO₄, and the solvent was removed in vacuo. The resulting crude products were purified by alumina-filled column chromatography with acetone/toluene mixtures as the eluent. The target complexes [Ru(TPh)] and [Ru(4-Tpy)] were both eluted as the second red-brown fraction (acetone/toluene: 1.5/1 v/v) after a first purple band identified as the starting [Ru(tpy)(bpy)Cl][PF₆]. X-ray structural determinations of both complexes are in progress and will be reported elsewhere. [Ru(TPh)]:

0.300 g, 52% (calculated with respect to the initial [Ru(tpy)(bpy)Cl][PF₆]). ESI-MS (Waters ZQ-4000 instrument; acetonitrile as the solvent): *m/z* 636, [M – PF₆]⁺. Anal. Calcd. for C₃₂H₂₄N₉RuPF₆: C, 49.17; H, 3.07; N, 16.13. Found (ThermoQuest Flash 1112 Series EA instrument): C, 49.22; H, 3.08, N, 14.25. [Ru(4-Tpy)]: 0.360 g, 62%. ESI-MS: *m/z* 637, [M – PF₆]⁺. Anal. Calcd. For C₃₁H₂₃N₁₀RuPF₆: C, 47.57; H, 2.94; N, 17.90. Found: C, 47.24; H, 2.97, N, 17.94.

Electrochemistry and Electrochemiluminescence. Cyclic voltammetry was carried out with a model 660 electrochemical workstation (CH Instruments, Austin, TX). Electrodes were polished with 0.05- μ m alumina and then were ultrasonicated and thoroughly rinsed with Milli-Q water and acetone before each run. The quasi-reference electrode was a coiled silver wire. A platinum disk (approximate diameter 2 mm) was used as working electrode and a coiled Pt wire was used as an auxiliary electrode. The *E*_{1/2} values for first reduction and oxidation are referred to SCE (saturated calomel electrode), and they have been calculated adding ferrocene as an internal standard. In ECL and electrochemical experiments, acetonitrile (Fisher scientific HPLC grade) was used as received and 1 mM solution of the complex (as PF₆[–] salt) was prepared with 0.1 M TBAPF₆ (Aldrich) as supporting electrolyte. Similar results were obtained with TBABF₄ (Aldrich). Before each ECL experiment, the sample was deaerated with Ar for 20 min in a specially made cell (Figure S1, Supporting Information). The exact concentration of oxygen in solution following deaeration was not measured. Preliminary potential cycling was performed systematically until a reproducible voltammogram between the first reduction and the first oxidation was obtained. The ECL signal during cyclic voltammetry was measured with a photomultiplier tube (PMT, Hamamatsu R4220p) placed on the side of the electrochemical cell. A voltage of 750 V was supplied to the PMT. A charge-coupled device (CCD) camera (Photometrics CH260) cooled below –135 °C interfaced to a personal computer was used to obtain ECL spectra. The camera was

focused on the output of a grating spectrometer (Holographics, Inc.). The CCD camera general setup was described before.¹¹ All ECL spectra have been recorded with a pulse width of 0.1 s and a 4-min exposure time.

Photoluminescence and Lifetime. Photoluminescence (PL) measurements were performed with a Varian Cary Eclipse fluorimeter in acetonitrile (Fisher Scientific HPLC grade) with concentrations between 10^{–3} and 10^{–5} M. PL experiments were performed after 20 min degassing with Ar in a specially homemade O-ring sealed cell. Samples were then progressively exposed to air to study oxygen sensitivity. Absorbance spectra were recorded by a Varian Cary 5 UV–vis–NIR spectrophotometer using the same sealed cell used for photoluminescence measurements in MeCN solutions. Lifetimes were measured in an air-equilibrated sample using an IBH TCSPC model 5000 F (time-correlated single photon counting) with a PMT detector (Applied Voltage: 2150 V). The emission wavelength was selected by a computer-controlled monochromator. Two cutoffs (590 and 610 nm) were used during measurements. Lifetimes were then calculated by fitting the data with a single-exponential decay function.

Solid Device Preparation. Light-emitting solid devices were prepared as reported^{4,5} previously with Ru(bpy)₃²⁺ by Bard and co-workers. The inorganic thin layer was prepared on ITO glass (Delta Technologies, Ltd., 100 Ω , square) by spin coating from a MeCN solution (1–4% w/v of complex). A small drop of In/Ga eutectic (from Aldrich) over the active layer was used as counter electrode and was connected to the reference electrode lead. Positive charge was injected through the underlying ITO glass used as working electrode (Figure S2, Supporting Information). For Ru(4-TBN)Ru and Ru(4-TBN)Me complexes, both spin coating and an alternative film deposition method were used: a few drops of an acetonitrile solution (0.1 up to 2% w/v) were dried in air on ITO surface. In this way, a thicker film could be obtained. Light intensity was measured using a photodiode positioned under the emitting thin layer as described earlier.^{4,5}

Results and Discussion

Electrochemiluminescence and Electrochemistry. The ECL spectra of a 1 mM Ar degassed acetonitrile solution of Ru(bpy)₃(PF₆)₂ obtained by direct annihilation between cation and anion has been taken as reference. The sample was run several times, and the highest emission intensity was of 300 000 Arbitrary Units (A.U.) with maxima at 610 nm. Detailed voltammetric studies under ultradry conditions (MeCN/TBAPF₆) have been reported by our group for Ru(4-TBN)Ru, Ru(BTB)-Ru, and Ru(4-TBN).² For the remaining three complexes and the reference Ru(bpy)₃²⁺, the cyclic voltammetric curves in Ar degassed MeCN are showed in Figure 1.

In the cyclic voltammetry experiments preliminary to ECL ones, the complexes showed in general chemical reversibility in first oxidation and reduction wave (*i*_a/*i*_c very close to 1). If the scan was repeated for 100 cycles including only the first reduction and oxidation (scan rate 10 V/s), no change in reversibility was observed. For all the complexes, including Ru(bpy)₃²⁺, the presence of oxygen seriously affects the quality of reduction wave which becomes irreversible when the cell is air equilibrated (see Figure 1b). Ru(4-TBN)Ru shows two reversible oxidation processes and two very close reduction waves assigned to weakly interacting Ru centers bridged by the asymmetric ligand.² Fluorescence, ECL, and electrochemical data for all complexes and the reference one are summarized in Table 1. All molecules evidenced a smaller energy gap [*E*_{1,ox} –

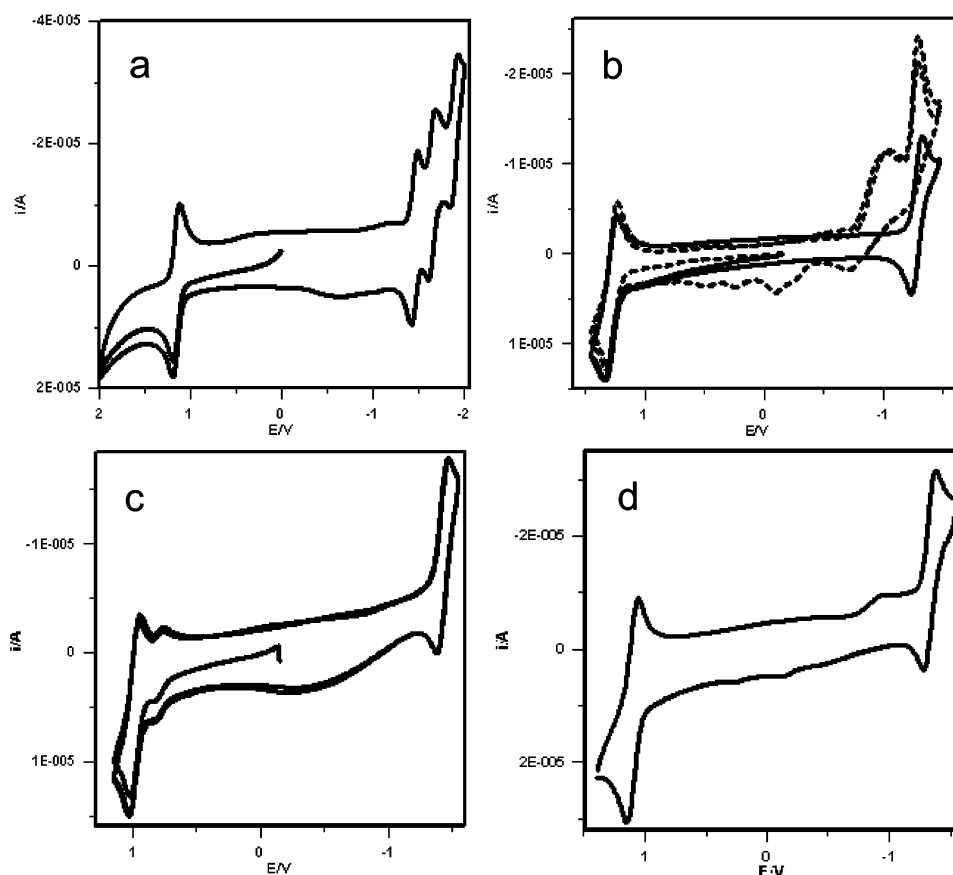


Figure 1. Cyclic voltammograms of 1 mM complexes in 0.1 M TBAPF₆/MeCN solution recorded with a 2-mm diameter Pt disk working electrode; $T = 25\text{ }^{\circ}\text{C}$; scan rate 0.2 V/s. (a) Ru(bpy)₃²⁺; (b) Ru(4-TBN)Me, air equilibrated (dashed line) and degassed (solid line) solution; (c) Ru(TPh). The small voltammetric wave at about 0.8 V is attributed to the oxidation process of the precursor species [Ru(tpy)(bpy)Cl]⁺, which is not luminescent;² (d) Ru(TPy). In all voltammograms, potential is referred to SCE.

TABLE 1: PL, ECL, and Electrochemical Data of the Ru(bpy)₃²⁺ (Reference Compound) and the Six Complexes Investigated^a

compound	$\lambda_{\text{max,abs/nm}}$ (MLCT)	$\lambda_{\text{max,PL/nm}}$	ϕ_{rel} (%)	E (I Ox.)/V (vs SCE)	E (I Red.)/V (vs SCE)	$\lambda_{\text{max,ECL/nm}}$	most stable ion in ECL
Ru(bpy) ₃ ²⁺	455	630	100	+1.20	−1.48	610	anion
Ru(4-TPZ)	487	690	7.4	+1.12	−1.31	690	anion
Ru(4-TBN)Me	463	660	11.6	+1.25	−1.34	720	cation
Ru(4-TBN)	487	670, 700	5.7	+1.01	−1.42	730	anion
RuTPh	487	690	7.2	+1.03	−1.39	740	anion
Ru(BTB)Ru	487	690	9.0	+1.01	−1.39	700	cation
Ru(4TBN)Ru	460, 490	670, 700	15.3	+1.02	−1.35	690	anion

^a Energy gap can be estimated by the electrochemical data. The most stable ion was determined during ECL experiment comparing the relative light intensity during positive and negative potential pulse in double potential step chronoamperometry. ϕ_{rel} (%) is calculated taking Ru(bpy)₃²⁺ as reference (100% efficiency).

$E_{\text{I,red}}$], expressed in eV with respect to the reference, and the ECL maximum wavelength is always red shifted with respect to Ru(bpy)₃²⁺. Upon changing the substituent, the emission shifts from 690 to 740 nm (see Table 1, Figure 2 and Figure S3). In general, the ECL maxima are also red shifted from the corresponding PL by about 10–50 nm.

ECL intensities for mononuclear compounds (see Figure 2) are lower than for Ru(bpy)₃²⁺ but are of the same order of magnitude. ECL spectra of the dinuclear complexes Ru(4-TBN)-Ru and Ru(BTB)Ru with respect to Ru(bpy)₃²⁺ under the same experimental conditions described above have been recently reported (see Figure S3).² The relative ECL intensity for the six complexes are shown in Table 2. One of the two dinuclear Ru complexes, Ru(4-TBN)Ru, shows an emission about 3 times more intense than the reference one, which can be observed by the naked eye in a dark room.² The emission intensity can be tuned by simply including or not including the second reduction and oxidation wave. The emission peak recorded by CCD is

not symmetric; a tail at longer wavelength is clearly visible. The spectral resolution in the ECL experimental setup does not allow one to clearly separate the lower energy shoulder as in PL experiments.

Considering the four different mononuclear complexes, the higher efficiency was for the ligands containing tetrazolate bound with pyridine and benzene. The introduction of the cyanide group in RuTPh (i.e., the species Ru(4-TBN)) causes a decrease of ECL intensity of about 75%. When a methyl group is then inserted directly on the tetrazolate ring (Ru(4-TBN)-Me), the intensity went back to higher values. Another interesting comparison is between Ru(4-TBN) and Ru(4-TBN)Ru. The addition of a second Ru(bpy)(tpy) center causes an increase of ECL efficiency of 6 times. As stated above, the two Ru centers in Ru(4-TBN)Ru behave independently,^{2,12} so the inclusion of the second oxidation and reduction localized on the second Ru center causes the ECL intensity to double. Considering the tetrazolate complex Ru(4-TBN)Ru with respect to Ru(bpy)₃²⁺,

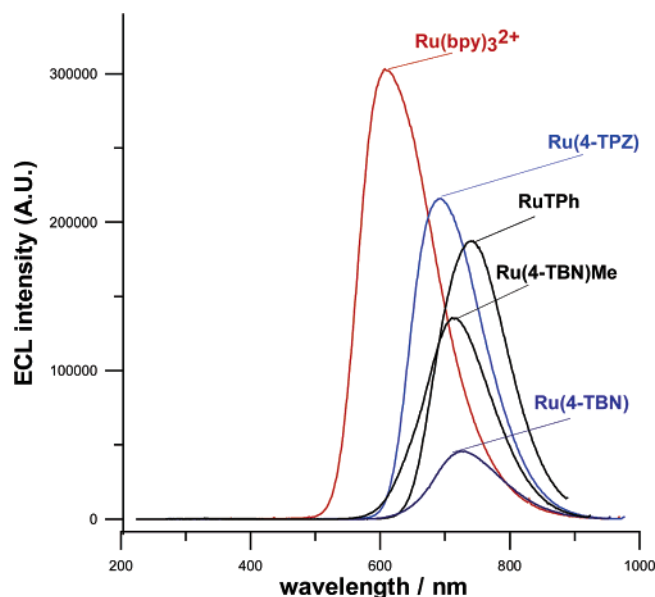


Figure 2. ECL emission spectra of the four mononuclear tetrazolate-based complexes, obtained by annihilation of one-electron oxidized and reduced forms. All ECL spectra were collected for 1 mM compound in 0.1 M TBAPF₆/MeCN solution, $T = 25\text{ }^{\circ}\text{C}$, and accumulation time 4 min.

TABLE 2: Estimated Relative ECL Emission Efficiency of 1 mM Complex in 0.1 M TBAPF₆/MeCN Solution (Ru(bpy)₃²⁺ Used as Reference) Cycling the Potential between the I Oxidation and I Reduction^a

compound	max ECL intensity (A.U)	rECL-Int. (%)
Ru(4-TPZ)	227 869	75
Ru(4-TBN)Me	135 405	45
Ru(4-TBN)	45 625	15
RuTPh	187 232	62
Ru(BTB)Ru	134 928	45
Ru(4TBN)Ru ^b	372 410 (I Ox., I Red.)	120
	864 597 (II Ox., II Red)	290
Ru(bpy) ₃ ²⁺ (ref)	303 181	100

^a The relative ECL intensities (rECL-Int.) have been calculated by $\text{rECL-Int.(\%)} = 100 \times I_{\text{ECL,MAX}} / I_{\text{ECL,MAX,Ru(bpy)_3^{2+}}}$. ^b The potential has also been cycled between II Ox. and II Red.

the relative PL quantum efficiency is 15.3% (ϕ_{rel} in Table 1) and the relative ECL intensity is 120% (rECL-Int. in Table 2). The mismatching of photo- and electrochemiluminescence is necessarily correlated with processes prior to generation of the excited emitting state. The moderate presence of oxygen has been found to affect ECL efficiency of Ru(bpy)₃²⁺ much more than the tetrazolate complexes suggesting the possibility to perform measurements under high vacuum conditions.

Photoluminescence and Broadened Emission of Ru(4-TBN)Ru. *Absorbance Spectra and Air Sensitivity.* The absorbance and maximum emission wavelength of all complexes are shown in Table 1. All complexes (excluding Ru(4-TBN)Ru and Ru(4-TBN)) show, as expected, a single emission in MLCT region between 630 and 700 nm and a single absorbance maximum between 450 and 490 nm. The sensitivity to oxygen concentration is in general very low. Only Ru(4-TBN)Ru and Ru(4-TBN)Me have shown a decrease of 20–30% in maximum emission intensity when exposed to air, which is still very different from the sensitivity of the Ru(DPP)₃⁸ tested under similar conditions.

Broadened Emission and Relative Lifetime. When the absorbance spectra of Ru(4-TBN)Ru and mononuclear Ru(4-TBN) in acetonitrile are compared (Figure 3), an additional absorbance

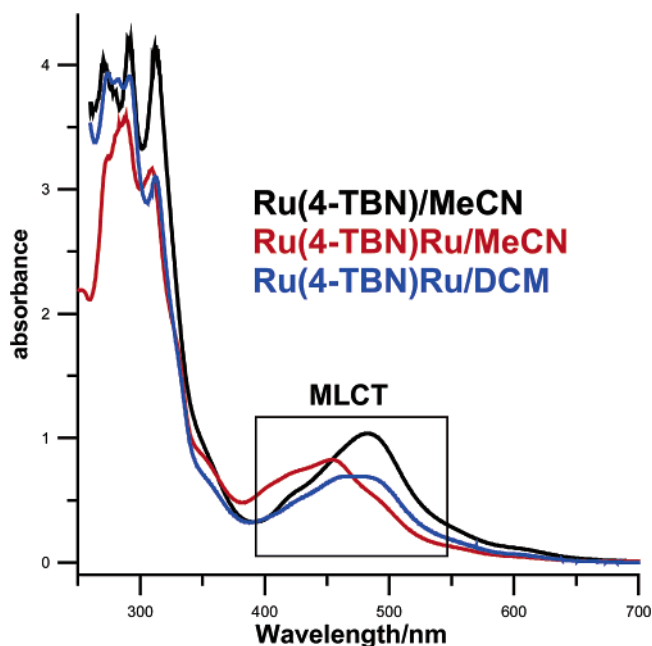


Figure 3. Absorbance spectra of 0.1 mM solutions of Ru(4-TBN)Ru (in acetonitrile and dichloromethane) and Ru(4-TBN) (acetonitrile only).

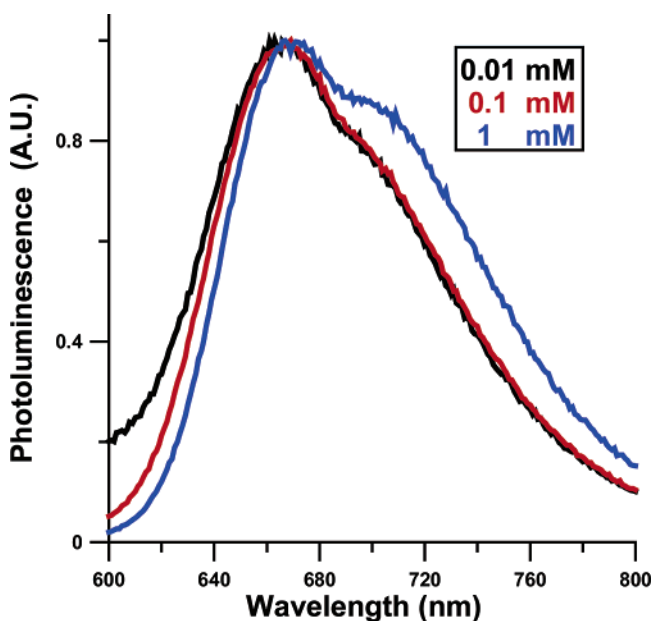


Figure 4. Concentration effect on the normalized intensity of the 700-nm emission of Ru(4-TBN)Ru in MeCN.

peak appears at 460 nm in the MLCT region in addition to the 490-nm peak present in both compounds. The two peaks at 460 and 490 nm are more intense in dichloromethane (DCM) than in MeCN (Figure 3). Both Ru(4-TBN)Ru and Ru(4-TBN) showed a broadened emission with respect to the other four compounds with a short wavelength difference between the maxima at 670 and 700 nm (Figure 4). The maximum intensity of both emissions of Ru(4-TBN)Ru is exactly twice the corresponding emissions of the mononuclear complex Ru(4-TBN). This can be explained in terms of the number of Ru centers that can emit from the single lower energy center. There is a clear increase of the intensity of the 700-nm emission with the concentration in Ru₁ and Ru₂ complexes (Figure 4). Temperature also affects the relative intensity of the second peak (Figure 5). In a 1 mM acetonitrile solution of Ru(4-TBN)Ru as the temperature is increased from 20 to 50 $^{\circ}\text{C}$, the emission

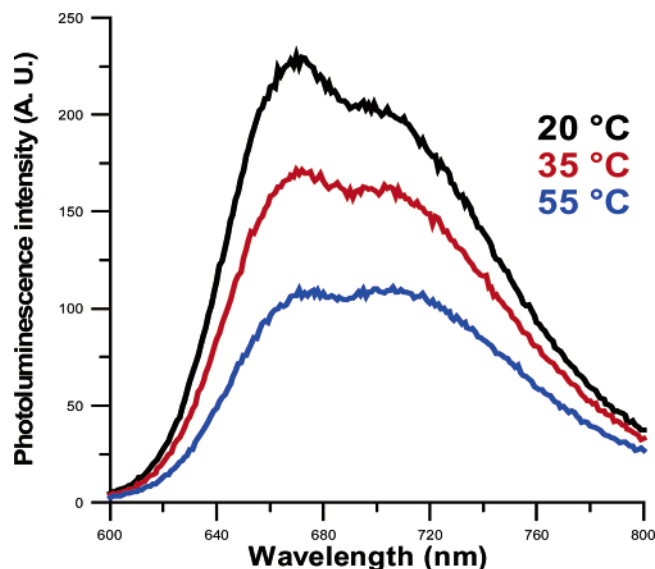


Figure 5. Effect of temperature on the emission band of 1 mM solution of Ru(4-TBN)Ru in MeCN.

band at 670 nm decreases more than that at 700 nm. There is no selectivity with the excitation wavelength on the 670- and 700-nm emission. At room temperature, the two peaks seem to be thermally equilibrated and the emissions take place at a similar rate. According to our results, low temperature stabilizes the 670-nm emission and moderately high temperature stabilizes the 700-nm emission (Figure 5).

The lifetimes of the 670- and 700-nm emissions for both mono- and dinuclear species are identical within the experimental error (15.7 ns and 16.0 ns, respectively),¹³ which excludes the possibility of artifacts and distortions (low concentration conditions). Lifetimes measured on integrated spectra do not change significantly suggesting the similar nature of the two emissions. Electrochemical data assigned the first two reductions to the tpy (lower energy) and bpy ligand, respectively.² The fact that both emissions are present even in the mononuclear compounds suggests that they are localized on the same Ru center. In general, Kasha's rule¹⁴ states that no multiple MLCT emissions are possible from the same Ru center, but in the case of mixed ligand complexes, one can sometimes expect the presence of a few MLCT states with similar energies. The more reasonable explanation for the dual emission seems to be the presence of a vibrational structure in the emission from the tpy-Ru MLCT or, alternatively, from bpy-Ru MLCT transition. Further and more detailed studies on the photophysics are necessary to thoroughly understand this broadened emission.

Preliminary Solid Device Tests. Solid devices based on the reference compound, Ru(bpy)₃²⁺, were first prepared using the same method as reported earlier.⁴ If observed under an optical microscope, the inorganic thin layer on ITO surface appears yellow and homogeneous. The steady-state current was small and stable up to 2.25 V suggesting the absence of pinholes and the good quality of the coverage. The maximum light intensity was estimated to be 1.75 $\mu\text{W}/\text{mm}^2$ and was easily visible in the daylight. The Ru(bpy)₃(ClO₄)₂ solubility in acetonitrile is about 40 mg/mL. For four out of the six complexes (excluding Ru(4-TBN)Ru and Ru(4-TBN)Me), pinholes and short-circuit effects could not be avoided and the emission was very weak (2 orders of magnitude less intense) compared to Ru(bpy)₃²⁺. This is due to the low solubility in acetonitrile and to the successive crystallization on the ITO surface that prevent the formation of a homogeneous film. Changing the solvent (DCM,

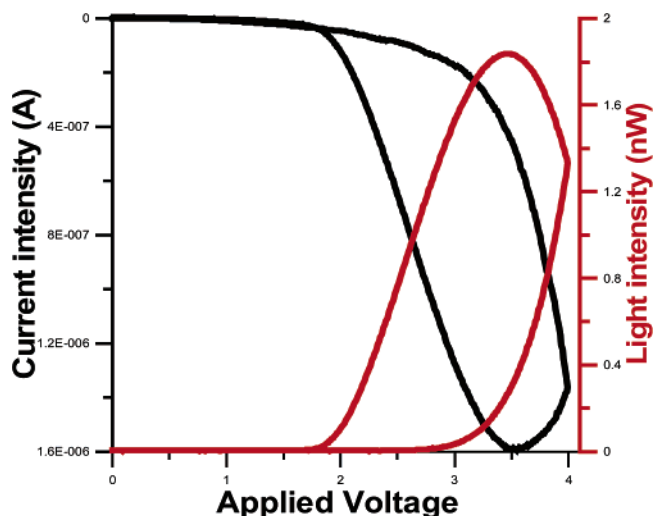


Figure 6. Light/current/potential curves of a solid device prepared by drying a drop of 4% w/v acetonitrile solution of Ru(4-TBN)Ru.

acetone) or drying a deposited drop from a lower concentration solution did not improve the emission intensity.

Ru(4-TBN)Ru. The solubility was 4% w/v in acetonitrile. Using spin coating, precipitation and crystallization on ITO surface resulted in an inhomogeneous film with pinholes. No steady-state emission was reached, and a maximum light intensity of about 0.6 $\mu\text{W}/\text{mm}^2$ was measured (applied potential 4 V; red-orange light was observed by the naked eye). Reproducibility was not good because of pinhole distribution in the sample.

Different attempts were made: spin coating at lower speeds (400, 300, 200, 100 rpm), for shorter times (1 min, 30 s, 15 s) and using lower concentrations (4, 3, 2, 1% w/v). However, the film properties did not change. The steady-state emission was reached when a 4% acetonitrile solution was dried on an ITO substrate (Figure 6). The film thickness increased from the previously estimated values of 100–200 nm to 500–1000 nm showing iridescence. The durability was improved but the response time (30 min reaching the maximum intensity) and the maximum intensity (about 0.05 $\mu\text{W}/\text{mm}^2$ at 4 V) strongly decreased as compared with spin-coated film. The behavior was similar to that observed for Ru(bpy)₃²⁺ when the device was prepared and operated in a drybox.⁷ The Ru(bpy)₃²⁺ gave a crystalline insulating and iridescent film when a drop from a similar solution was dried. An explanation of this behavior is the increased time necessary to cross the diffusion layer and the higher amount of solvent molecules retained by tetrazolate-based complexes as compared to Ru(bpy)₃²⁺. This could also explain the reversible memory effect of potential conditioning on response times (Figure 7). By waiting for some minutes after the switching off of the activation potential of the device, the response time increased again because of the thermal disorder effect on the double layer generated by the voltage application in a previous operation. In this thick, but still conductive, film, the kinetics are slowed and a continuous decrease of open-circuit current is observed after operation.

Ru(4-TBNMe). Solid devices have been prepared, and an intensity of 0.1 $\mu\text{W}/\text{mm}^2$ was obtained. With an applied potential of 5 V, the emission spectrum was recorded using the previously described CCD camera setup.⁴ The maximum was in the NIR region at 780 nm. The solubility in acetonitrile is much lower than that of Ru(4-TBN)Ru, and the active film was prepared by drying a drop of a 0.4% w/v solution. The film is still crystalline and is affected by pinholes. The response time was

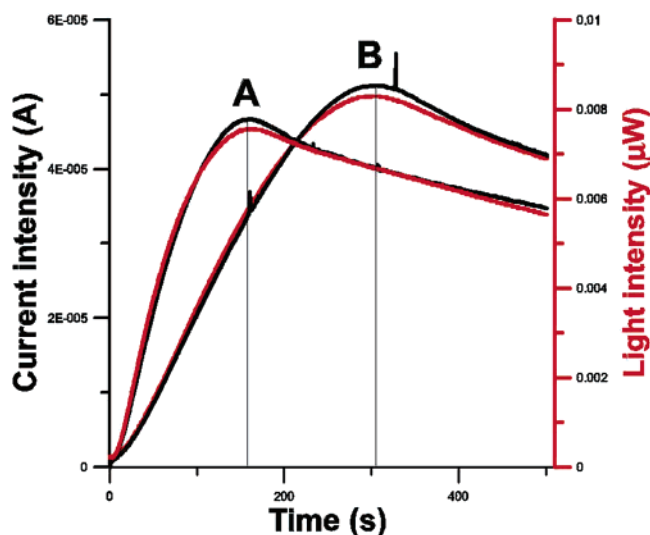


Figure 7. Light/current/time curves obtained applying 5 V switching potential in successive 500-s experiments on a Ru(4-TBN)Ru based solid device. Thickness of the active film approximately 1 μm . (A) Second subsequent run; (B) second run after a pause of 5 min.

about 10 times lower than for Ru(bpy) $_3^{2+}$ but faster than that for Ru(4-TBN)Ru. The film structure withstood, and the emission continued to be observed, up to 10 V; the response time progressively increased whereas the durability decreased. A reversible memory effect in response times was again observed.

Concluding Remarks. This work shows the possibility of altering the ECL emission wavelength by changing the groups around the tetrazolate ligand. In general, for this class of compounds, the energy gap is lower and the emissions are red-shifted with respect to Ru(bpy) $_3^{2+}$. In degassed acetonitrile solutions, Ru(4-TBN)Ru showed a surprisingly intense ECL emission, suggesting the use of Ru(4-TBN)Ru for the preparation of light-emitting solid devices, which show emission intensity comparable to that of Ru(bpy) $_3^{2+}$ based devices. In addition, Ru(4-TBN)Me can be also considered as a lumino-phore for the design of NIR (780 nm) light-emitting solid devices.

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Supporting Information Available: Experimental setup used for the ECL experiments in solution, scheme for the measurements performed on solid-state devices, and ECL spectra of complexes Ru(4-TBN)Ru, Ru(BTB)Ru, and the reference species Ru(bpy) $_3^{2+}$ recorded under the same experimental conditions of the mononuclear compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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