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Two-photon Absorption Engineering of 5-(Fluorenyl)-1,10-phenanthroline-based Ru(II) Complexes

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Abstract: This study deals with the fine tuning of the photophysical characteristics, and especially two-photon absorption (2PA) properties, of several homo- and heteroleptic ruthenium(II) complexes involving 5-substituted-1,10-phenanthroline ligands. The 2PA spectra of the complexes were determined in the 700–930 nm range by investigating their two-photon excited luminescence (2PEL). Structure – linear and nonlinear optical properties correlations are discussed, and potential applications (therapy and optical power limiting in the near infrared) can be anticipated.

Keywords: 5-(Fluorenyl)-1,10-phenanthroline ligands · Luminescence properties · Ruthenium(II) complexes · Two-photon absorption

The two-photon absorption process (2PA) has received considerable attention due to its large number of potential applications[1] such as photodynamic therapy,[2] photochemical delivery of biological messengers,[3] confocal microscopy,[4] three-dimensional data storage,[5] micro-fabrication[6] and optical power limiting.[7] Despite the undisputable advantages of coordination complexes[8] over organic chromophores,[9] they remain less studied for 2PA applications. In fact, they offer synthetic tailorability[10] and the access to a MLCT (metal-to-ligand charge transfer) triplet excited state. This triplet MLCT (^{3}MLCT) state presents a long luminescence lifetime (a few microseconds for Ru(II) complexes for example[11]) which can enable several photophysical processes, used for multiple applications: (i) two-photon excited fluorescence (2PEF) emission, for biological imaging,[12] (ii) energy transfer to a quencher, for O_2 sensing,[12] or (iii) excited state re-absorption, for optical power limiting.[13] For this study, we focused on the design of new Ru(II) complexes, siege of MLCT electronic transitions by 2PA. In spite of their high stability and inertia in solution, which allow their utilization in practical applications, few studies (and only at a single wavelength: 750, 800, and 880 nm) were performed for Ru(II)[14] and Re(I)[15] complexes on MLCT transitions by 2PA, or Z-scan experiments giving rise to two-photon transitions spectra.[16]

Octupolar coordination Ru(II)-polypyridyl complexes have already been investigated for their stability, inertness, biological activity such as DNA interaction,[17] and optical properties such as ^{3}MLCT excited-state properties,[11a,18] second-order nonlinear optical properties,[10c,19] and two-photon absorption (2PA)[20] leading to a wide range of applications in therapy,[21] dye-sensitized solar cells (DSCs),[22] and organic light-emitting diodes (OLEDs). One can exploit (i) the excited-state absorption for optical power limiting (OPL)[23] applications, but also (ii) the triplet character of the excited-state of Ru(II) complexes for use as oxygen sensors[24] or sensitizers.[25]

As a potential application for these systems (supramolecular edifices siege of efficient two-photon absorption), the OPL goal is to protect detectors as well as the eyes from high-power pulsed lasers. 2PA gives access to an excited state and a third photon is absorbed from this excited state ([2+1] photons process). Singlet states of organic molecules can enable excited-state absorption (ESA). However, metallic complexes such as Ru(II) compounds,[26] displaying excited states with longer lifetimes, can favour this phenomenon. The reported fluorene-substituted 1,10-phenanthroline Ru(II) complexes are good candidates for two-photon based OPL in the near-IR range. 2PA properties of these compounds are strongly linked to the π-conjugation of the ligands, which can be adjusted by varying the number of fluorene moieties (one or two), and triple bonds (none, one or two)[27] as two-photon absorbers.

Molecular Engineering

Upon light excitation of Ru(II) complexes, singlet excited states of the ligand or the ^{1}MLCT state are reached. From these states, energy is partially transferred to the ^{3}MLCT state, responsible for luminescence (in case of linear absorption) or 2PEF (in case of 2PA) of Ru(II) complexes. Therefore, to modulate and optimize 2PA properties of Ru(II) complexes, molecular engineering of its ligands is relevant. In this paper, the 2PA properties of several homo- and heteroleptic ruthenium complexes involving 5-substituted-1,10-phenanthroline ligands (see Fig. 1 for the molecular structures) were studied.

Oligofluorenes are known to display 2PA properties due to excitonic coupling between neighbour monomers,[28] explaining our choice of ligands 1,10-phenanthroline (Phen) bearing one or two fluorene units (**PF** and **PFF**, respectively). A more conjugated character can be introduced with triple bond between the bipyridyl ligand and the first fluorene (**PTF**, and **PTFF**), and between two fluorene units (**PTFTF**). Homoleptic (Ru3L) and heteroleptic (Ru1L) Ru(II) complexes can be obtained and characterized. Fluorene units were functionalized using triethyleneglycol (Oteg) or hexyl chains in order to modulate their hydrosolubility.

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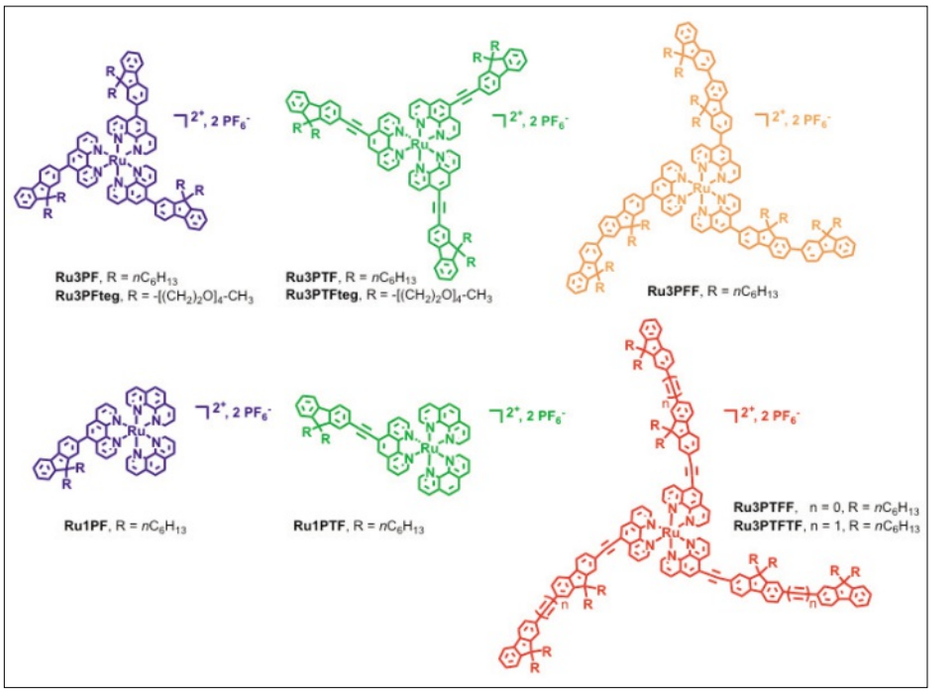

Fig. 1. Molecular structures of homo- and heteroleptic Ru(II) complexes.

Results and Discussion

The absorption spectra of the studied complexes are composed of (i) an intense band ranging from 250 to 280 nm (see Fig. 2), which is due to intra-ligand (IL) transitions ($\pi_L \rightarrow \pi_L^*$); these transitions are mainly located on the phenanthroline moiety and the intensities are quite similar for all the studied complexes – from $Ru(Phen)_3^{2+}$ to **Ru3PTFTF** – (ii) a broad band from 380 to 500 nm which corresponds to $d(Ru^{II}) \rightarrow \pi^*$-metal-to-ligand charge-transfer (^{1}MLCT) transitions and which is characteristic of this kind of Ru(II) complex involving polypyridyl-type ligands[20e] and finally, (iii) broad bands are recorded from 300 to 400 nm which are attributed to intra-ligand charge-transfer (ILCT) transitions involving mainly a charge flow from the fluorene unit(s) to the 1,10-phenanthroline moiety; CT are more efficient and appear at lower energy (red shifted) in the presence of a triple bond (**Ru3PTF**, **Ru3PTFF**, and **Ru3PTFTF**). In all cases, the large width of this absorption band should be attributed to vibronic broadenings and/or the overlap of more bands corresponding to different close-lying electronic transitions.

The large absorption band (ε values around 140 000 $Lmol^{-1}cm^{-1}$), which can be mainly seen for complexes **Ru3PFF** and **Ru3PTFF** around 340 nm, can be attributed to a transition due to the existence of an excitonic coupling between the two fluorene units. The electronic transitions at lower energy involve a triple bond-based motif.

The general emission characteristics of the complexes are presented in Table 1. No important change can be observed considering the related energies, except a small bathochromic shift (i) for heteroleptic complexes as compared to related homoleptic ones (for example, λ_{em} are 590 and 601 nm for **Ru3PF** and **Ru1PF**, respectively, and 599 and 613 nm for **Ru3PTF** and **Ru1PTF**, respectively); a larger dipolar moment in the excited state for heteroleptic complexes may be at the origin of this phenomenon, (ii) as a triple bond is introduced (590 and 599 nm for **Ru3PF** and **Ru3PTF**, respectively, and 593 and 596 nm for **Ru3PFF** and **Ru3PTFF**, respectively); this phenomenon can be mainly ascribed to the more conjugated character of the ligand when involving a triple bond.

It has also to be pointed out that the emission quantum yield values (ϕ, and related k_r/k_{nr} values) decrease dramatically when introducing a second fluorene unit (9% and 3% for **Ru3PF**, and **Ru3PFF**, respectively, and 11% to 2% for **Ru3PTF** and **Ru3PTFF**, respectively); the increased possibilities for non-radiative decay of the excited-state (quite free rotation between each fluorene unit) is probably at the origin of this phenomenon. In parallel, the excited state lifetime (τ) decreases when introducing a triple bond (for example 1.7 to 0.39 ms for **Ru3PF** and **Ru3PTF**, respectively, and 2.5 to 0.71 ms for **Ru3PFF** and **Ru3PTFF**, respectively), but increases when substituting with a second fluorene (1.7 and 2.5 ms for **Ru3PF** and **Ru3PFF**, respectively, and 0.39 and 0.71 ms for Ru3PTF and Ru3PTFF, respectively).

Two-photon absorption spectra were re-

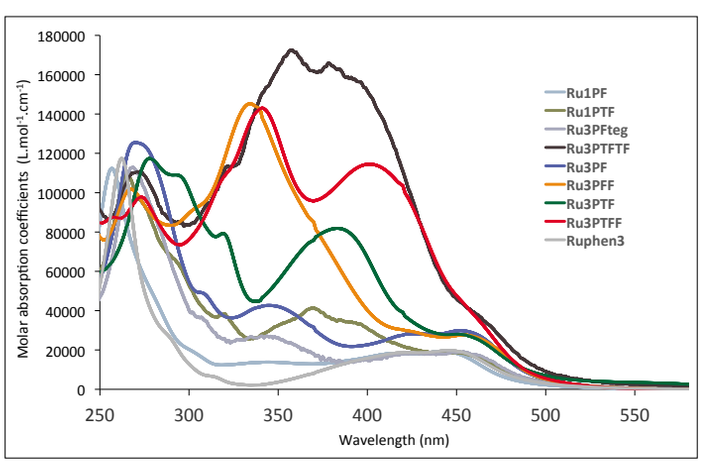

Fig. 2. Absorption spectra of the studied Ru(II) complexes.

Table 1. Luminescence properties data of the studied Ru(II) complexes

Compound	λ_{em} [nm]	ϕ	τ [ns]	k_r [10^4 s^{-1}]	k_{nr} [10^4 s^{-1}]	k_r/k_{nr}
Ru3PF	590	0.09	1700	5.3	53.5	0.10
Ru3PFF	593	0.03	2500	1.2	38.8	0.03
Ru3PTF	599	0.11	395	27.8	225.0	0.12
Ru3PTFF	596	0.02	708	2.8	137.2	0.02
Ru3PTFTF	601	0.05	2700	1.8	34.2	0.05
Ru1PF	601	0.05	470	10.6	200.0	0.05
Ru1PTF	613	0.04	860	4.7	110.0	0.04
$Ru(Phen)_3^{2+}$	594	0.03	890	3.4	110.0	0.03

Emission wavelength λ_{em} given in acetonitrile; luminescence quantum yield (ϕ), and excited state lifetime (τ) in CH_2Cl_2; ϕ using $Ru(bipy)^{2+}$ (ϕ^{ref} = 0.062) as ref. [11a]; k_r and k_{nr}: radiative and non-radiative decay constants.

corded in the 700–1000 nm spectral range; this means, in the intra-ligand (IL) charge-transfer band for the higher energy, and in the singlet metal-to-ligand charge-transfer band (^{1}MLCT) at the higher wavelengths (see Fig. 3). It can be noticed in these spectra that the two-photon absorption cross-section (σ_2 in GM, and 1 GM = 10^{-50} $cm^4 \cdot s \cdot molecule^{-1} \cdot photon^{-1}$) is enhanced when the 1,10-phenanthroline ligand is functionalized, confirming the interest of ligand design in order to modulate charge transfer processes. As expected, being not involved in charge transfer processes, the use of Oteg or hexyl chains as pendent arms of the fluorene units does not induce any σ_2 modification. When the number of fluorene units increases (from **Ru3PF** to **Ru3PFF**), σ_2 increases (see Fig. 3, and Table 2). This was already observed and explained, due to the lack of conjugation, by the existence of an excitonic coupling between the fluorene units (also evidenced in the linear absorption spectra). The introduction of a triple bond (from **Ru3PF** to **Ru3PTF**, **Ru3PFF** to **Ru3PTFF**, **Ru3PTFF** to **Ru3PTFTF**, and from **Ru3PFteg** to **Ru3PTFteg**) leads to a bathochromic shift, due to the more conjugated character of the ligand. When the number of functionalized 1,10-phenanthroline molecules is reduced from 3 to 1 (from **Ru3PF** to **Ru1PF** and from **Ru3PTF** to **Ru1PTF**), two-photon absorption cross-section decreases but less than three times, because actually absorption is partially due to metal-to-ligand charge transfer (d_M-π^*_{Phen}), in the 700-930 nm two-photon spectral range. The complex bearing the more conjugated structure (**Ru3PTFTF**) displays the most evident bathochromic shift (from 750 nm in $Ru(Phen)_3^{2+}$ to 825 nm for **Ru3PTFTF**), the higher σ_2 values being obtained with the increasing number of fluorene units (350 GM at 750 nm for complex **Ru3PFF** for example, 13 times higher than for the parent complex $Ru(Phen)_3^{2+}$ at the same excitation wavelength).

In conclusion, the study of the optical properties of this original family of Ru(II) complexes, has shown the possibility to finely tune the two-photon absorption properties in an interesting spectral range for potential applications (therapy and optical power limiting in the near infra-red). Modelisations and theoretical calculations are planned, in order to confirm the attribution of most of the discussed electronic transitions.

Experimental Section

The two-photon absorption spectra of the complexes were determined in the 700–930 nm range by investigating their two-photon excited luminescence (2PEL) in deoxygenated 10^{-4} M acetonitrile or dichloromethane solutions. The measurements were performed using a Nd:YLF-pumped Ti:sapphire oscillator generating 150 fs pulses at a 76 MHz rate. The excitation was focused into the cuvette through a microscope objective (10×, NA 0.25). The luminescence was detected in epifluorescence mode *via* a dichroic mirror (Chroma 675dcxru) and a barrier filter (Chroma e650sp-2p) by a compact CCD spectrometer module BWTek BTC112E. Total luminescence intensities were obtained by integrating the corrected emission spectra measured by this spectrometer. 2PA cross-sections (σ_{2PA}) were determined from the two-photon excited luminescence cross-sections ($\sigma_{2PA}F$) and the luminescence emission quantum yield (F). 2PEL cross-sections of 10^{-4} M solutions were measured relative to a 10^{-4} M solution of fluorescein in 0.01 M aqueous NaOH for 715–930 nm, using the well-established method described by Xu and Webb[29] and the appropriate solvent-related refractive index corrections.[30] Data points between 700 and 715 nm were corrected.[31] The quadratic dependence of the luminescence intensity on the excitation power was checked for each sample and all wavelengths, indicating that the measurements were carried out in intensity regimes where saturation or photo- degradation did not occur.

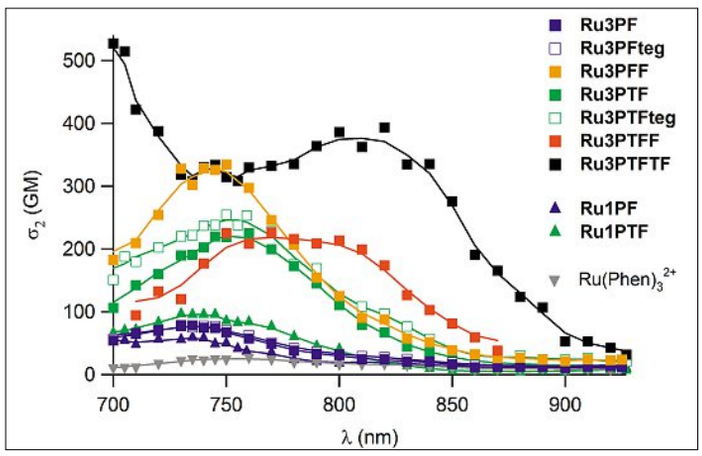

Fig. 3. Two-photon absorption spectra of Ru(II) complexes in the 700–930 nm spectral range.

Table 2. Two-photon absorption wavelength λ_{2PA}^{max} and related two-photon absorption cross-sections (σ_{2PA}^{max}) given in acetonitrile for the studied Ru(II) complexes.

Compound	λ_{2PA}^{max} [nm]	σ_{2PA}^{max} [GM]
Ru1PF	735	60
Ru3PF	735	80
Ru3PFteg	735	90
Ru1PTF	735	95
Ru3PTF	760	225
Ru3PTFteg	755	245
Ru3PFF	740	330
Ru3PTFF	770	225
Ru3PTFTF	810, 740	380, 325
$Ru(Phen)_3,2PF_6^-$	750	25

Synthesis and characterizations of complexes $Ru(Phen)_3,2PF_6^-$,[32] $Ru(Phen)_2Cl_2$,[33] $RuCl_2(DMSO)_4$,[34] **Ru3PF** and **Ru3PFF**,[20e] **Ru3PTF**,[26] **Ru3PTFTF**,[27] **Ru3PFteg**,[25e] (and related ligands **PF**, **PFF**, **PTF**, **PTFTF**, and **PFteg**) have already been described elsewhere. Analogous procedures were used for **Ru1PF**, **Ru1PTF**, **Ru3PTF**, and **Ru3PTFteg**. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 200 spectrometer (at 200.13 MHz for ^{1}H and 50.32 MHz for ^{13}C) and also on a Varian Unity Plus at 499.84 MHz for ^{1}H. Elemental analyses were carried out by the 'Service Central d'Analyse', CNRS. UV/Vis spectra were recorded in the 200–800 nm range on a UV/Vis Jasco V-550; λ_{max} are given in nm and molar absorption coefficients ε in $L.mol^{-1}cm^{-1}$.

Ru1PF: 156 mg (0.29 mmol) of $Ru(phen)_2Cl_2$ were added under argon, to a solution of 150 mg (0.29 mmol, 1 equiv.) of ligand **PF** dissolved in 10 mL anhydrous DMF. The reaction mixture was then refluxed for a night. Saturated aqueous solution of NH_4PF_6 was added to the resulting solution at room temperature. The precipitate was collected by filtration, washed three times with H_2O and twice with pentane to give 330 mg of a red-brownish solid with 90% yield. m.p.: not found (20–450 °C). A fraction was recrystallized in EtOH for analysis. ^{1}H NMR (499.84 MHz, CD_3CN) δ (ppm) 8.63–8.47 (m, 5H), 8.27–8.25 (m, 4H), 8.11–7.80 (m, 9H), 7.68–7.40 (m, 12H), 2.09–2.07 (m, 4H), 1.12–1.03 (m, 12H), 0.77–0.62 (m, 10H). IR (KBr, cm^{-1}): 3448 (H_2O), 2927 (νC-H_{alkyl}), 2854 (δC-H_{alkyl}), 1623, 1427(νC=C_{aro}), 843, 721(νC-H_{aro}), 557; Anal. calcd. for $C_{61}H_{56}F_{12}N_6P_2Ru$, 2 EtOH, 1.5 H_2O: C, 56.44; H, 5.17; N, 6.07; Ru, 7.3. Found: C, 56.70; H, 4.64; N, 5.96; Ru, 6.72%.

Ru1PTF: 150 mg (0.28 mmol) of $Ru(phen)_2Cl_2$ were added under argon, to

a solution of 150 mg (0,29 mmol, 1 equiv.) of ligand **PTF** dissolved in 10 mL anhydrous DMF. The reaction mixture was then refluxed for a night. Saturated aqueous solution of NH_4PF_6 was added to the resulting solution at room temperature. The precipitate was collected by filtration, washed three times with H_2O and twice with pentane to give 268 mg of a red-brownish solid with 74% yield. m.p.: not found (20–450 °C). ^{1}H NMR (499.84 MHz, CD_3CN) δ (ppm) 8.62–8.43 (m, 5H), 8.26–8.25 (m, 3H), 8.17–8.00 (m, 5H), 7.89–7.60 (m, 10H), 2.11–2.06 (m, 4H), 1.10–1.02 (m, 12H), 0.77–0.73 (m, 6H), 0.57–0.54 (m, 4H). IR (KBr, cm^{-1}): 3064 (H_2O), 2926 (νC-H_{alkyl}), 2854 (νC-H_{alkyl}), 1616, 1427(νC=C_{aro}), 843, 721(δC-Haro), 557; Anal. calcd. for $C_{63}H_{56}F_{12}N_6P_2Ru$: C, 58.74; H, 4.38; N, 6.52; Ru, 7.85. Found: C, 58.83; H, 4.40; N, 6.56; Ru, 7.14%.

Ru3PTFteg: 49 mg of $RuCl_2(DMSO)_4$ (0,10 mmol) were added under argon, to a solution of 150 mg (0,30 mmol, 3 equiv.) of ligand **PTFteg** (0.30 mmol, 3 equiv.) dissolved in 8 mL ethanol. The reaction mixture was then refluxed for a night. Saturated aqueous solution of NH_4PF_6 was added to the resulting solution at room temperature. The precipitate was collected by filtration, washed three times with H_2O and twice with diethyl ether to give 180 mg of a red powder with 66% yield. m.p.: not found (20–450 °C). A fraction was recrystallized in EtOH. ^{1}H NMR (499.84 MHz, CD_3CN) δ (ppm): 9.09–9.08 (m, 1H), 8.60–8.59 (m, 1H), 8.52 (s, 1H), 8.15–8.05 (m, 2H), 7.90–7.77 (m, 6 H), 7.49–7.41 (m, 3H), 3.47–3.14 (m, 34H), 2.10–1.95 (m, 4H), 0.83–0.81 (m, 4H); Anal. calcd. for $C_{141}H_{168}F_{12}N_6O_{24}P_2Ru$, 3 H_2O: C, 61.01; H, 6.32; N, 3.03; Ru, 3.64. Found: C, 60.71; H, 6.34; N, 2.99; Ru, 3.64%.

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