



Synthesis, characterization and photophysical studies of novel pyrene labeled ruthenium (II) trisbipyridine complex cored dendrimers



Mireille Vonlanthen, Amanda Cevallos-Vallejo, Edgar Aguilar-Ortíz, Andrea Ruiui, Pasquale Porcu, Ernesto Rivera*

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, México D. F. 04510, Mexico

ARTICLE INFO

Article history:

Received 26 April 2016

Received in revised form

23 June 2016

Accepted 24 June 2016

Available online 25 June 2016

Keywords:

Ruthenium complex

Pyrene

Dendrimer

ABSTRACT

Two new bipyridine ligands containing, respectively, two and four pyrene units were prepared. The obtained compounds were employed to synthesize new pyrene labeled ruthenium (II) trisbipyridine complex as well as a pyrene labeled ruthenium (II) trisbipyridine cored dendrimer. The obtained bipyridine ligands and the ruthenium complexes were characterized by NMR spectroscopy and MALDI-TOF mass spectroscopy. The optical and photophysical properties of the luminescent macromolecules were studied by absorption and fluorescence spectroscopy. It was noticed that the absorption spectra of the obtained complexes correspond to the sum of the absorption spectra of their components, which indicates a lack of interaction in the ground state. Efficient energy transfer was observed from pyrene units to the metal complex core resulting in the observation of the characteristic ruthenium bipyridine emission band upon excitation at the pyrene absorption wavelength. Moreover, efficient protection to oxygen quenching was remarked in the first generation dendrimer.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Dendritic macromolecules are well-defined and tree-like structures that exhibit unique physical and chemical properties; therefore they have been extensively studied since their discovery by Newkome and Tomalia [1–6]. The incorporation of photoactive units in the structure of dendrimers, at the periphery, in the branches or at the core have led to the formation of organized luminescent macromolecules presenting various phenomena such as the formation of excimers and exciplexes, resonance energy transfer (RET) or charge transfer (CT). Light-harvesting antennas are constructs in which several chromophoric species are transferring excitation energy to a common acceptor, changing the colour of the incident light [7–11]. This kind of constructs has found applications in material research for photovoltaic and light emitting display, as well as in medical research for drug delivery [6,12].

Moreover, dendrimers containing metal ions have been developed to combine the redox properties of metals with the organization of a dendritic shell [1–6,13,14]. Transition metal polybipyridine complexes, such as ruthenium trisbipyridine

complexes ($[\text{Ru}(\text{Bpy})_3]^{2+}$), show well studied redox and photophysical properties [7–10,15]. The principal absorption bands for $[\text{Ru}(\text{Bpy})_3]^{2+}$ are a ligand centered (LC) transition at 280 nm and a metal to ligand charge transfer (MLCT) transition between 450 and 480 nm. After absorption of a photon, fast intersystem crossing (ISC) favored by the heavy atom effect occurs, followed by emission from the $^3\text{MLCT}$ state with long-lived phosphorescent emission and low quantum yield [6,12,16,17]. Very recently, ruthenium polybipyridine complexes have found many applications such as sensitizer for solar cells [18–20]. They have also been incorporated to polymers and to dendrimers in the presence of various chromophores such as naphthyl groups, thiophenes, carbazole and coumarin chromophores, showing in each case, efficient energy transfer [21–25]. The introduction of pyrene moieties in polybipyridine ligands for the complexation of ruthenium and other metal centers have been recently reviewed [26]. A special interest for the combination of pyrene with a metal center raised from the fact that the energy level of the $^3\text{MLCT}$ emitting state of Ru(II) bipyridine complex can be tuned to be nearly isoenergetic with respect to the triplet state of pyrene. When this occurs, reversible triplet-triplet energy transfer between the $^3(\pi-\pi)$ and $^3\text{MLCT}$ can be observed [27]. Up to 11-fold prolonged lifetime of the phosphorescent emission of the Ru(II) polypyridine complex has been reported at room temperature when pyrene is separated from the

* Corresponding author.

E-mail address: riverage@unam.mx (E. Rivera).

metal center by an alkyl chain [26–32]. The main inconvenience of such compounds is the sensitivity of their emission to oxygen. The presence of a dendritic shell could offer to the polybipyridine ruthenium complex emission a protection from oxygen quenching [33,34].

In our research group, we have introduced pyrene at the periphery of dendrimers in order to observe resonance energy transfer to a porphyrine moiety [35,36]. In this work we have introduced a Ru(II) trisbipyridine at the core of our dendrimer. We have studied the photophysical properties of bipyridine-cored dendrons, the efficient energy transfer from pyrene to ruthenium bipyridine complex through antenna effect, as well as the protection from oxygen quenching of the fluorescence emission by the dendritic shell. To this end, we have designed and synthesized pyrene-containing dendrimers with a bipyridine core. With the obtained ligands, we have prepared complexes of Ru(II) containing 2, 6 and 12 pyrene units. Efficient singlet-singlet energy transfer was observed in these systems.

2. Experimental section

2.1. General notes

2,2'-bipyridinyl-4,4'-diol **1** was synthesized from 4,4'-dimethoxy-2,2'-bipyridine as previously described in the literature [37]. Ru(Bpy)₂Cl₂ was synthesized from RuCl₃·3H₂O, 2,2'-bipyridine and lithium chloride as previously reported [38]. The synthesis of the compounds **2** and **3** was previously reported by our research group [35]. All other reagents were purchased and used as received. Synthetic procedures were carried out in dry solvents under argon atmosphere unless otherwise specified. Chromatographic purifications were performed on silica gel packed in glass columns; eluting solvents for the purifications were determined by thin-layer chromatography (TLC).

¹H NMR and ¹³C NMR were recorded on a Bruker Advance 400 spectrometer operating at 400 MHz for ¹H NMR and 100 MHz for ¹³C NMR. Samples were prepared in deuterated chloroform or deuterated acetone. MALDI-TOF mass spectra of all obtained compound were recorded using ditranol as matrix on a Bruker Daltonics Flex Analysis. Absorption spectra were recorded in spectrophotometric grade THF (acetonitrile) on a Unicam UV300 spectrophotometer using quartz cells with a width of 1 cm. Steady state fluorescence measurements were performed on a Fluorolog3 Horiba spectrofluorometer with a Xenon lamp as light source. The slits widths were set to 1 nm on excitation and 1 nm on emission.

2.2. Synthetic procedures

2.2.1. 4,4'-bis(4-pyren-1-ylbutyloxy)-2,2'-bipyridine (Bpy-Py2)

4,4'-Bis(3-pyren-1-ylbutyloxy)-2,2'-bipyridine (Bpy-Py2) was synthesized as previously reported in the literature [39]. The product Bpy-Py2 was obtained as a white solid (190 mg, 30%). ¹H NMR (δ ppm, 400 MHz, CDCl₃): 8.44 (d, 2H, J = 5.7), 8.29 (d, 2H, J = 9.3), 8.16 (dd, 4H, J = 7.6, 2.4), 8.12 (dd, 4H, J = 7.8, 3.4), 8.03–7.95 (m, 8H), 7.90 (d, 2H, J = 7.8), 6.82 (dd, 2H, J = 5.7, 2.4), 4.21 (t, 4H, J = 6.2), 3.45 (t, 4H, J = 7.2), 2.11–2.00 (m, 8H). mp = 214 °C. R_f(CH₂Cl₂/MeOH: 99/1) = 0.14.

2.2.2. Py2G1Br (4)

Dry DMF (1 ml) was cooled down to 0° and PBr₃ (400 μL, 4.25 mmol) was added. The formation of a solid was observed in the reaction mixture. To this flask a solution of the dendritic benzyl alcohol **3** (200 mg, 0.31 mmol) in dry DMF (3 ml) was added; the reaction mixture was then sonicated for 10 min until a yellow precipitate was observed and turned to a creamy colored solid. The

reaction was then quenched by the addition of a saturated aqueous solution of NaHCO₃. The compound was extracted with dichloromethane; the organic phase was dried over MgSO₄ and concentrated under vacuum. The crude was purified by column chromatography (CH₂Cl₂/Hexane: 60/40) to give the desired product **4** as a white solid (144 mg, 65%).

¹H NMR (δ ppm, 400 MHz, CDCl₃): 8.28 (d, 2H, J = 9.3), 8.15 (d, 4H, J = 7.6), 8.10 (dd, 4H, J = 5.3, 7.8), 8.02–7.95 (m, 6H), 7.88 (d, 2H, J = 7.8), 6.50 (d, 2H, J = 2.2), 6.36 (t, 1H, J = 2.2 Hz), 4.36 (s, 2H), 3.98 (t, 4H, J = 6.2), 3.41 (t, 4H, J = 7.6), 2.06–1.92 (m, 8H). ¹³C NMR (δ ppm, 100 MHz, CDCl₃): 160.5, 142.1, 136.7, 132.5, 131.6, 131.1, 130.0, 127.7, 127.4, 126.8, 126.0, 125.01, 124.95, 124.9, 123.5, 107.7, 106.7, 68.0, 33.3, 29.3, 28.3. mp = 155 °C. R_f(CH₂Cl₂/Hexane: 60/40) = 0.60.

2.2.3. 4,4'-bis(3,5-bis(4-pyren-1-ylbutyloxy)benzyloxy)-2,2'-bipyridine (BpyG1-Py4)

4 (430 mg, 0.60 mmol) was dissolved in DMF (2 ml), 4,4'-dihydroxy-2,2'-bipyridine (45 mg, 0.24 mmol) and Cs₂CO₃ (392 mg, 1.20 mmol) were added to the reaction mixture and it was heated to 110 °C for 24 h. The solution was cooled to room temperature and evaporated. The crude was dissolved in chloroform and extracted with water. The organic phase was dried over MgSO₄ and concentrated under vacuum. The product BpyG1-Py4 was purified by recrystallization from dichloromethane to give the product as a beige solid (185 mg, 53%).

¹H NMR (δ ppm, 400 MHz, CDCl₃): 8.39 (d, 2H, J = 5.7), 8.25 (d, 4H, J = 9.4), 8.13–7.92 (m, 30H), 7.86 (d, 4H, J = 8.0), 6.81 (dd, 2H, J = 5.8, 2.9), 6.55 (m, 4H), 6.40 (t, 2H, J = 2.1), 5.08 (s, 4H), 3.99 (t, 8H, J = 5.9), 3.39 (t, 8H, J = 7.4), 2.06–1.92 (m, 16H). ¹³C NMR (δ ppm, 100 MHz, CDCl₃): 160.7, 136.7, 131.6, 131.1, 130.0, 128.8, 127.7, 127.4 (3), 126.8, 125.9, 125.27, 125.19, 125.0, 124.9, 124.8, 123.5, 106.1, 68.0, 33.3, 29.3, 28.4. MS (MALDI-TOF): m/z calculated for C₁₀₄H₈₅N₂O₆ (M)⁺: 1458.79; found: 1460.77. mp = 146 °C. R_f(CH₂Cl₂/MeOH: 99/1) = 0.19.

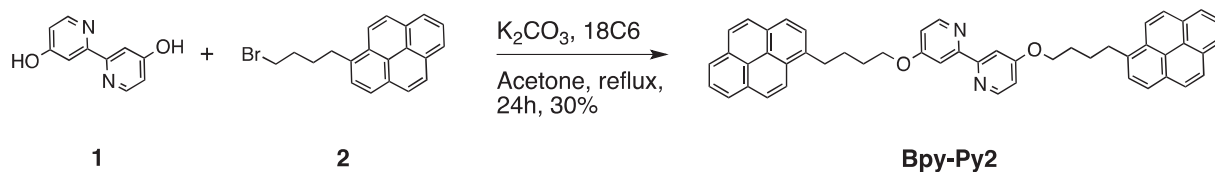
2.2.4. [Ru(Bpy)₂(Bpy-Py2)]²⁺ (PF₆)₂

Ru(Bpy)₂Cl₂ (34 mg, 0.07 mmol) and Bpy-Py2 (50 mg, 0.07 mmol) were dissolved in wet DMF (4 ml) and heated to reflux for 48 h. The reaction mixture was cooled to room temperature and concentrated under vacuum. The residue was dissolved in CH₂Cl₂ and the compound was extracted with distilled water. A saturated solution of NH₄PF₆ (10 ml) was added to the water phase and the product was extracted with CH₂Cl₂. The organic phase was concentrated under vacuum and the crude was purified by column chromatography (CH₂Cl₂/MeOH) to give the desired product as a red fluorescent solid (29 mg, 28%).

¹H NMR (δ ppm, 400 MHz, acetone-d₆): 8.77 (dd, 4H, J = 8.2, 3.1), 8.37 (d, 2H, J = 9.3), 8.33 (d, 2H, J = 2.8), 8.26–8.14 (m, 12H), 8.12–8.09 (m, 6H), 8.05–8.00 (m, 4H), 7.95 (d, 2H, J = 7.8), 7.70 (d, 2H, J = 6.4), 7.57–7.51 (m, 4H), 7.11 (dd, 2H, J = 6.6, 2.7), 4.33 (m, 4H), 3.46 (m, 4H), 2.05–2.01 (m, 8H). ¹³C NMR (δ ppm, 100 MHz, acetone-d₆): 167.7, 159.0, 158.4, 158.2, 153.1, 152.8, 152.6, 138.5, 137.5, 132.4, 131.8, 130.8, 129.5, 128.6, 128.4, 128.3, 128.2, 127.5, 127.0, 125.9, 125.84, 125.81, 125.70, 125.67, 125.17, 125.15, 124.3, 115.1, 112.5, 70.4, 33.4, 29.4, 28.9. MS (MALDI-TOF): m/z calculated for C₇₀H₅₆F₆N₆O₂PRu (M-PF₆)⁺: 1259.27; found: 1258.8. mp = 178–180 °C. R_f(CH₂Cl₂/MeOH: 98/2) = 0.15.

2.2.5. [Ru(Bpy-Py2)₃]²⁺ (PF₆)₂

RuCl₃·3H₂O (9.3 mg, 0.036 mmol) and Bpy-Py2 (100 mg, 0.142 mmol) were dissolved in a mixture of wet DMF/EtOH 10/1 (25 ml) and the reaction mixture was heated to 80 °C for 5 days. Then, it was cooled to room temperature and concentrated under vacuum. The residue was dissolved in CH₂Cl₂ and washed with



Scheme 1. Synthetic scheme of pyrene-labeled bipyridine ligand **Bpy-Py2**.

distilled water. The solvent was concentrated under vacuum and the residue was dissolved in a mixture of acetone and water (3/1). An aqueous saturated solution of NH_4PF_6 (10 ml) was added and the obtained solid was extracted with CH_2Cl_2 . The organic phase was concentrated under vacuum and the crude was purified by column chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 100/0 to 97/3) to give the desired product as a red solid (26 mg, 29%).

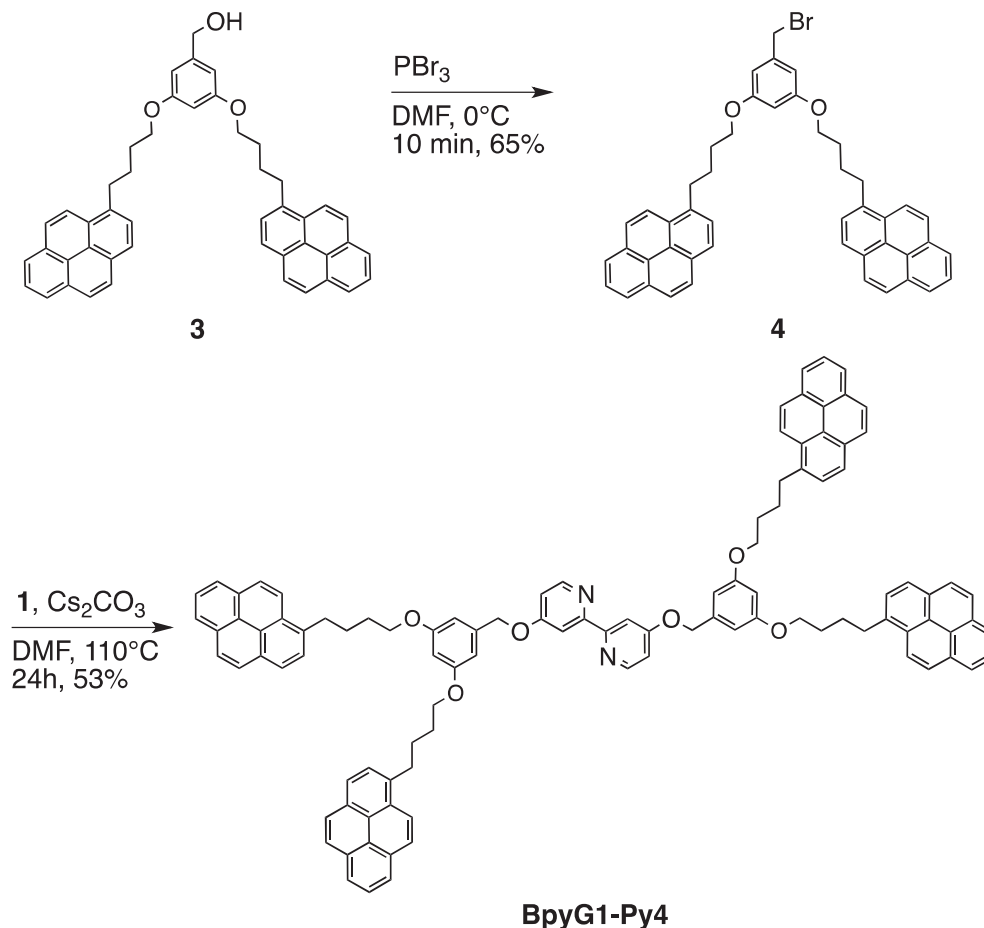
^1H NMR (δ ppm, 400 MHz, CDCl_3): 8.18 (d, 6H, $J = 9.2$), 8.09–8.06 (m, 12H), 8.03–8.00 (m, 12H), 7.94 (s, 12H), 7.92–7.88 (m, 6H), 7.79 (d, 6H, $J = 7.6$), 7.52 (s, br, 6H), 7.45 (d, br, 6H, $J = 6.0$), 6.84 (d, br, 6H, $J = 4.5$), 4.12–3.98 (m, 12H), 3.31 (t, br, 12H, $J = 7.0$), 1.97–1.83 (m, 24H). ^{13}C NMR (δ ppm, 100 MHz, CDCl_3): 166, 157.8, 152.6, 136.3, 131.5, 131.0, 130.0, 128.7, 127.6, 127.4, 127.3, 126.8, 125.9, 125.2, 125.1, 125.0, 124.9, 124.8, 123.4, 113.9, 111.2, 69.5, 33.0, 28.7, 28.0. MS (MALDI-TOF): m/z calculated for $\text{C}_{150}\text{H}_{120}\text{F}_6\text{N}_6\text{O}_6\text{PRu}$ ($\text{M}-\text{PF}_6$) $^+$: 2348.63; found: 2348.51. mp = 189–191 °C. R_f ($\text{CH}_2\text{Cl}_2/\text{MeOH}$: 98/2) = 0.27.

2.2.6. $[\text{Ru}(\text{BpyG1-Py4})_3]^{2+} (\text{PF}_6)_2$

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (2.7 mg, 0.010 mmol) and **BpyG1-Py4** (60 mg,

0.041 mmol) were dissolved in a mixture of wet DMF/EtOH 4/1 (10 ml) and the reaction mixture was heated to 80 °C for 5 days. The reaction mixture was cooled to room temperature and concentrated under vacuum. The residue was dissolved in CH_2Cl_2 and washed with distilled water. The solvent was concentrated under vacuum and the residue was dissolved in a mixture of acetone and water (3/1). A saturated solution of NH_4PF_6 (10 ml) was added and the obtained solid was extracted with CH_2Cl_2 . The organic phase was concentrated under vacuum and the crude was purified by column chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 100/0 to 98/2) to give the desired product as a red sticky solid (23 mg, 47%).

^1H NMR (δ ppm, 400 MHz, CDCl_3): 8.10 (d, 12H, $J = 9.1$), 8.02–7.81 (m, 84H), 7.70 (d, 12H, $J = 7.7$), 7.51 (s, br, 6H), 7.39 (d, br, 6H, $J = 6.4$), 6.85 (d, br, 6H, $J = 4.9$), 6.47–6.44 (m, 12H), 6.31–6.29 (m, 6H), 4.98–4.88 (m, 12H), 3.83 (t, br, 24H, $J = 6.0$), 3.21 (t, br, 24H, $J = 7.3$), 1.91–1.73 (m, 48H). ^{13}C NMR (δ ppm, 100 MHz, CDCl_3): 165.7, 160.7, 157.8, 136.9, 136.6, 131.5, 130.9, 129.9, 128.7, 127.3 (3), 126.6, 125.8, 125.12, 125.07, 124.89, 124.85, 124.71 (2), 123.4, 114.4, 111.6, 60.0, 33.1, 29.2, 28.2. MS (MALDI-TOF): m/z calculated for $\text{C}_{312}\text{H}_{252}\text{F}_6\text{N}_6\text{O}_{18}\text{PRu}$ ($\text{M}-\text{PF}_6$) $^+$: 4619.40; found: 4618.53.



Scheme 2. Synthetic scheme of pyrene-labeled dendronized bipyridine ligand of first generation.

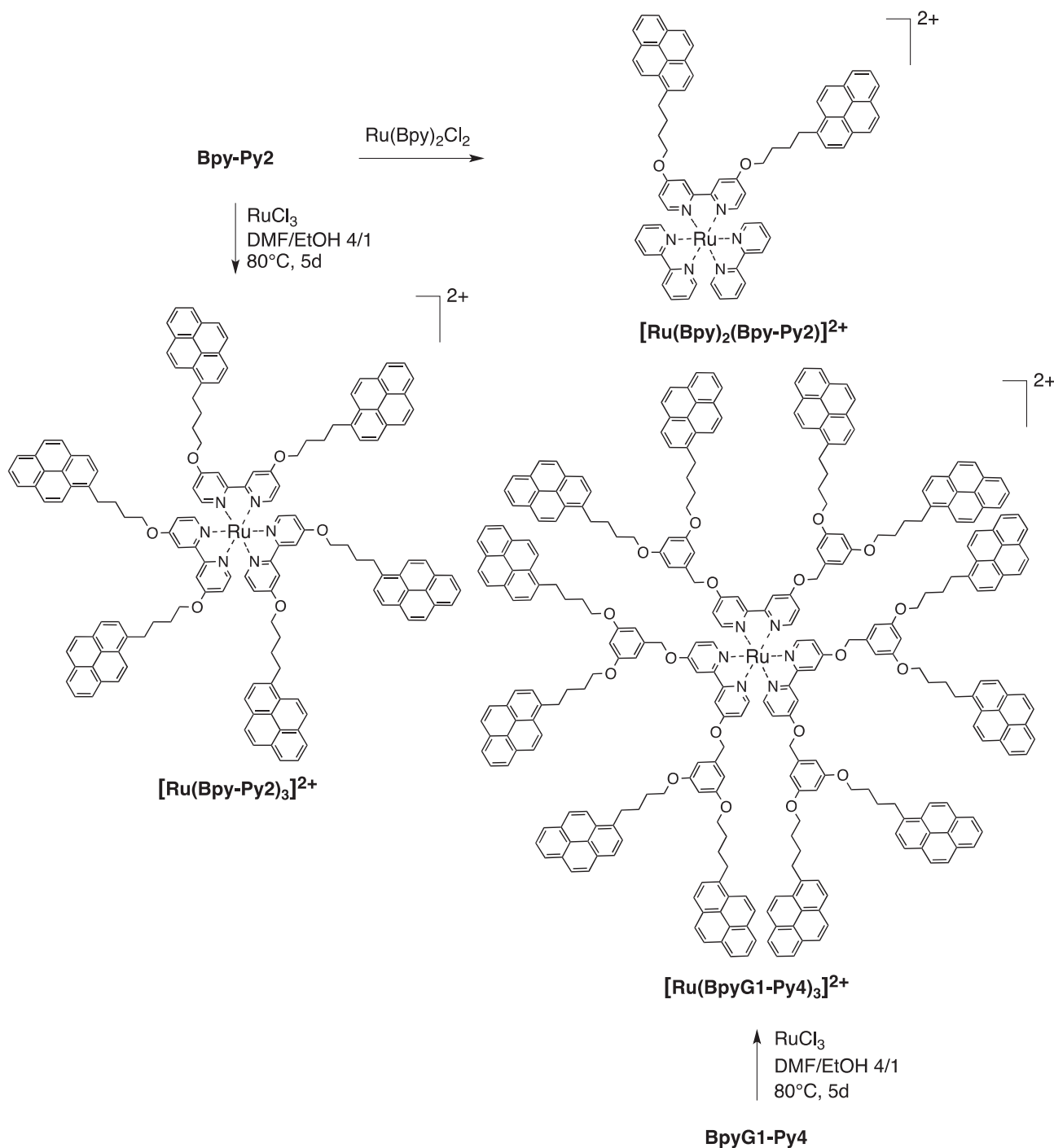
mp = 185–187 °C. $R_f(\text{CH}_2\text{Cl}_2/\text{MeOH}: 98/2) = 0.32$.

3. Results and discussion

3.1. Synthesis of the pyrene-labeled bipyridine ligands and pyrene-labeled ruthenium complexes

The pyrene-labeled bipyridine ligand **Bpy-Py2** and the pyrene-labeled dendronized bipyridine ligand **BpyG1-Py4** were prepared following a classical convergent dendrimer synthesis shown in [Scheme 1](#) and [Scheme 2](#). 1-(4-bromobutyl)pyrene **2** and the dendritic benzylic alcohol with pyrene units at the periphery **3** were

synthesized following standard procedures reported by our group [\[35\]](#). Bromination of the dendritic benzylic alcohol **3** to yield compound **4** is reported here as an improvement of the synthesis previously reported by us, where chlorination of the dendritic benzylic alcohol **3** was described. Compound **4** was obtained in a good yield, using a DMF- PBr_3 adduct as brominating agent. Only a few examples of this bromination method can be found in the literature [\[40,41\]](#). Bipyridine ligands **Bpy-Py2** and **BpyG1-Py4** were synthesized by nucleophilic substitutions between 2,2'-bipyridinyl-4,4'-diol **1** and the respective brominated dendrons, using potassium or cesium carbonate in acetone or DMF at reflux, respectively [\[39\]](#). Recrystallization from dichloromethane gave the



Scheme 3. Synthetic scheme of the pyrene-labeled ruthenium complexes.

desired product in ca. 50% yield. The structures of the obtained bipyridine were confirmed by NMR spectroscopy and MALDI-TOF mass spectrometry.

The pyrene-labeled ruthenium complexes were synthesized according to Scheme 3. Ruthenium (III) chloride hydrate and the corresponding pyrene-labeled bipyridine ligand were heated to reflux in a mixture of DMF and ethanol (3:1) for the synthesis of the metal complexes $[\text{Ru}(\text{Bpy-Py}2)_3]^{2+}$ and $[\text{Ru}(\text{BpyG1-Py}4)_3]^{2+}$. The reaction mixture turned from dark purple to bright red, thereby indicating the formation of the metallodendrimer. In this reaction, the reduction of Ru(III) to Ru(II) was achieved by ethanol. $\text{Ru}(\text{Bpy})_2\text{Cl}_2$ and the corresponding bipyridine ligand were heated to reflux in DMF to yield $[\text{Ru}(\text{Bpy})_2(\text{Bpy-Py}2)]^{2+}$ as previously reported in the literature [39,42,43]. All metal complexes were purified by column chromatography and were obtained as orange solid with modest yields. Their counter ions were exchanged for hexafluorophosphate ions. Because of their large organic ligands, the obtained complexes are not soluble in water as expected for ruthenium complexes, but they are soluble in various organic solvents. The structures of the obtained Ru (II) complexes were confirmed by NMR and MALDI-TOF mass spectrometry.

3.2. Absorption spectra of the bipyridine ligands and the ruthenium-pyrene constructs

The absorption spectra of the bipyridine ligands (**Bpy-Py2** and **BpyG1-Py4**) acquired in THF are shown in Fig. 1. The typical absorption bands of the pyrene chromophore can be observed in the spectra for both compounds with two absorption bands at 277 nm and 344 nm, which correspond to the transitions $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_2$ transition respectively. The obtained extinction coefficients are reported in Table 1 and correspond to the extinction coefficient values previously reported for pyrene-labeled dendrimers [36].

The absorption spectra of the ruthenium complexes are presented in Fig. 2. The absorption bands of the pyrene-labeled dendrons are conserved and additional bands corresponding to the absorption bands of the metal complex core were also observed. The ligand centered (LC) absorption band of the complex appeared at 288 nm. The metal to ligand charge transfer (MLCT) band was found at 462 nm in the case of $[\text{Ru}(\text{Bpy})_2(\text{Bpy-Py}2)]^{2+}$ in acetonitrile, and at 480 nm for the complexes with 3 ligands coordinated in THF ($[\text{Ru}(\text{Bpy-Py}2)_3]^{2+}$ and $[\text{Ru}(\text{BpyG1-Py}4)_3]^{2+}$). The red shift of the MLCT band in the complexes $[\text{Ru}(\text{Bpy-Py}2)_3]^{2+}$ and

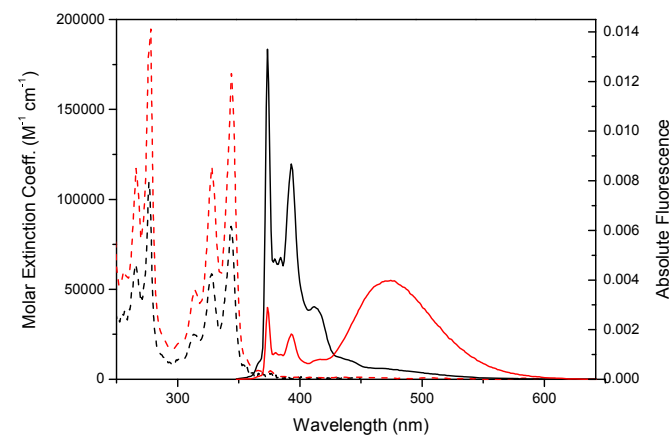


Fig. 1. Absorption (dashed lines) and fluorescence (solid lines) spectra of bipyridine ligands (**Bpy-Py2**, black line and **BpyG1-Py4**, red line) in THF. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Absorption coefficients of bipyridine ligands and ruthenium-pyrene constructs and percentage of light absorbed by the pyrene units at 344 nm.^a

Compound	λ max abs (nm)/ ϵ ($\text{M}^{-1} \text{cm}^{-1}$)	% Pyrene light absorption at 344 nm ^b
Bpy-Py2	344/71'700	100
BpyG1-Py4	344/186'000	100
$[\text{Ru}(\text{Bpy})_2(\text{Bpy-Py}2)]^{2+}$	342/69'000	91
	462/10'600	
$[\text{Ru}(\text{Bpy-Py}2)_3]^{2+}$	344/210'900	97
	480/11'400	
$[\text{Ru}(\text{BpyG1-Py}4)_3]^{2+}$	344/411'000	99
	480/11'200	

^a Measurements were done in THF except for complex $[\text{Ru}(\text{Bpy})_2(\text{Bpy-Py}2)]^{2+}$ (acetonitrile).

^b The percentage of light absorbed by the pyrene units at 344 nm was calculated using the following equation: % pyrene light = $1 - (\epsilon(344) [\text{Ru}(\text{Bpy})_3]^{2+}) / (\epsilon(344) \text{Compound})$, using $\epsilon(344) [\text{Ru}(\text{Bpy})_3]^{2+} = 7000$.

$[\text{Ru}(\text{BpyG1-Py}4)_3]^{2+}$ is due to the stabilization of the excited state through increased degree of conjugation. The extinction coefficients of the obtained complexes are reported in Table 1. MLCT band remains similar in all complexes with a relatively low extinction coefficient measured between $10'000$ and $12'000 \text{ M}^{-1} \text{cm}^{-1}$ in comparison with the high extinction coefficient of the pyrene bands, which augments with the increased number of pyrene units. This result was expected, since aliphatic chains separate the chromophoric groups, providing a spatial and electronic separation of the photoactive units. The characteristic absorption bands of the different components of the construct are present in the absorption spectra, which indicates that no interactions between the chromophores take place in the ground state.

The percentage of light absorbed by the pyrene units at 344 nm was calculated using the molar extinction coefficient of $[\text{Ru}(\text{Bpy})_3]^{2+}$ at 344 nm and the extinction coefficient of the obtained construct at the same wavelength, in order to correct the corresponding emission spectra with excitation at 344 nm [44]. It can be noticed that pyrene accounted for 91% of the light absorbed at 344 nm in the case of $[\text{Ru}(\text{Bpy})_2(\text{Bpy-Py}2)]^{2+}$, and this percentage was increased to 97 and 99%, respectively, in the case of $[\text{Ru}(\text{Bpy-Py}2)_3]^{2+}$ and $[\text{Ru}(\text{BpyG1-Py}4)_3]^{2+}$.

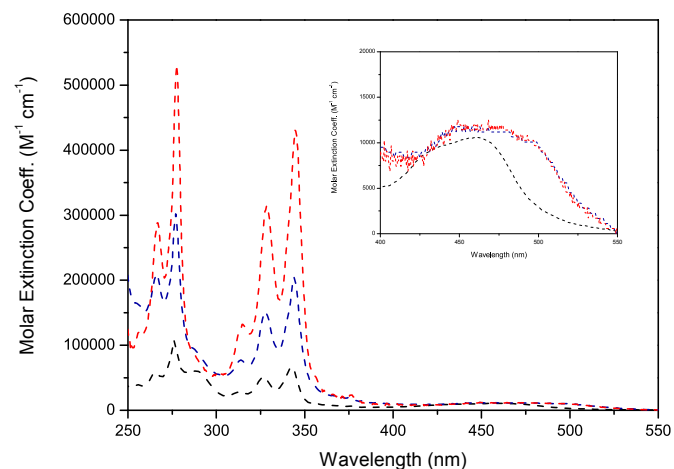


Fig. 2. Absorption spectra of Ru(II) trisbipyridine complexes $[\text{Ru}(\text{Bpy})_2(\text{Bpy-Py}2)]^{2+}$ (black) in acetonitrile and $[\text{Ru}(\text{Bpy-Py}2)_3]^{2+}$ (blue) and $[\text{Ru}(\text{BpyG1-Py}4)_3]^{2+}$ (red) in THF. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.3. Steady state emission of the bipyridine ligands and the ruthenium-pyrene constructs

The fluorescence emission spectra of the bipyridine ligands (**Bpy-Py2** and **BpyG1-Py4**) were measured in THF with excitation at 344 nm at room temperature. All measurements were done at the same concentration of pyrene units (1.25×10^{-6} M), corresponding to an absorbance of about 0.04 at 344 nm. The obtained fluorescence spectra are shown in Fig. 1. In all the spectra, the emission is reported as absolute fluorescence intensity. This means that the integration of the emission spectra as function of wavelength yields the quantum yields listed in Table 2. The bipyridine ligands containing two pyrene units (**Bpy-Py2**) shows only the characteristic monomer emission and almost no excimer emission was observed. For the first generation dendron (**BpyG1-Py4**), monomer as well as excimer emission are seen due to higher local pyrene concentration. However, the ratio of the excimer emission intensity (I_E) vs monomer emission intensity (I_M) showed a different trend than previously reported for other related compounds [45]. This could be due to the geometry of the molecule. Since the preferred conformation of the bipyridine is trans, it is probable that the thermodynamically more stable conformation presents both pyrene pointing in opposite directions [46].

The excitation spectra of compound **BpyG1-Py4** recorded at the emission wavelength of the monomer (376 nm) and the emission wavelength of the excimer (480 nm) were normalized and the observed overlap indicates that the excimer is dynamic in nature. This is the case when a pyrene in the ground state encounters an excited pyrene by diffusion and gives rise to an excimer [47].

The emission spectrum of the complex $[\text{Ru}(\text{Bpy})_2(\text{Bpy-Py2})]^{2+}$ was recorded in acetonitrile with an excitation at 342 nm whereas the emission spectra of the complexes $[\text{Ru}(\text{Bpy-Py2})_3]^{2+}$ and $[\text{Ru}(\text{BpyG1-Py4})_3]^{2+}$ were recorded in THF, exciting at 344 nm. All the obtained spectra are shown in Fig. 3. The strong luminescence of the pyrene-labeled ligands was quenched by the chelation to Ru (II). The typical emission bands at 398 nm for the monomer and 480 nm for the excimer of pyrene were still present but their intensities were dramatically decreased. The quantum yield of the pyrene unit was reduced to a value between 0.015 and 0.003. Moreover, a new emission band appears at 625 nm for $[\text{Ru}(\text{Bpy})_2(\text{Bpy-Py2})]^{2+}$ in acetonitrile, and at 661 nm for $[\text{Ru}(\text{Bpy-Py2})_3]^{2+}$ and $[\text{Ru}(\text{BpyG1-Py4})_3]^{2+}$ in THF, which are corresponding to the characteristic emission band of a ruthenium bipyridine complex, regardless of the excitation wavelength. The red shift observed in the trisubstituted metal complex is due to the stabilization of the excited state through increased degree of conjugation corresponding to the different substitution pattern of the

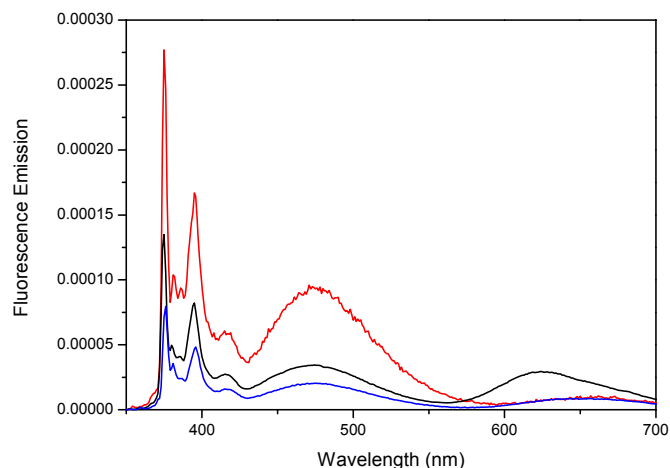


Fig. 3. Emission spectra of the Ru(II) trisbipyridine complexes $[\text{Ru}(\text{Bpy})_2(\text{Bpy-Py2})]^{2+}$ (black) in acetonitrile and $[\text{Ru}(\text{Bpy-Py2})_3]^{2+}$ (blue) and $[\text{Ru}(\text{BpyG1-Py4})_3]^{2+}$ (red) in THF. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ruthenium core. The observed 100-fold decrease of the emission of pyrene is due to a highly efficient FRET process occurring from the emission of pyrene to the ruthenium bipyridine core. The efficiency of the process was calculated to be 98% and 99% in the complexes of bipyridine ligands containing two pyrene units and 96% in the case of the first generation dendron. This result can be explained by means of the distance between both chromophores. For both complexes formed with **Bpy-Py2** as ligand, the distance between the pyrene and the ruthenium bipyridine units is equal. The extended distance (d^{EXT}) between pyrene and ruthenium in the complexes formed with **PBpy-Py2** as ligand was calculated to be 12.2 Å. However, increasing the generation in complex $[\text{Ru}(\text{BpyG1-Py4})_3]^{2+}$ enhanced this distance to 18.8 Å, thereby lowering the efficiency of FRET process.

In order to ensure that FRET is taking place in the complexes, Förster radius was calculated for the pair of chromophores pyrene/ruthenium bipyridine complex using Equation (1)

$$R_0 = 9790 \times (\kappa^2 \times n^{-4} \times \phi_D \times J(\lambda))^{1/6} \quad (1)$$

where R_0 is the Förster radius, κ is the orientation factor, n is the refractive index of the solvent, ϕ_D is the quantum yield of the donor and $J(\lambda)$ is the overlap integral of the pyrene/ruthenium bipyridine

Table 2
Quantum yields and FRET efficiencies of the bipyridine ligands and the ruthenium-pyrene constructs.

Compound	λ max (nm)	Φ pyrene unit $\lambda_{\text{ex}} = 344 \text{ nm}^c$	Φ Ru (II) unit $\lambda_{\text{ex}} = 344 \text{ nm}^d$	Φ Ru (II) unit $\lambda_{\text{ex}} = 452 \text{ nm}^d$	E_{FRET}^e
Bpy-Py2	375	0.32 ^b	—	—	—
BpyG1-Py4	375; 480	0.39 ^b	—	—	—
$[\text{Ru}(\text{Bpy})_2(\text{Bpy-Py2})]^{2+}$	625	—	0.0032 ^a	0.0052 ^a	0.98
$[\text{Ru}(\text{Bpy-Py2})_3]^{2+}$	661	0.008 ^b	0.0174 ^b	0.0277 ^b	0.99
$[\text{Ru}(\text{BpyG1-Py4})_3]^{2+}$	661	0.004 ^b	0.0026 ^b	0.0053 ^b	0.96
		0.014 ^b	0.0025 ^a	0.0029 ^a	
			0.0031 ^b	0.0050 ^b	

Fluorescence measurements were done in acetonitrile ($[\text{Ru}(\text{Bpy})_2(\text{Bpy-Py2})]^{2+}$) or THF ($[\text{Ru}(\text{Bpy-Py2})_3]^{2+}$ and $[\text{Ru}(\text{BpyG1-Py4})_3]^{2+}$) at 0.1 OD at 344 nm

^a Aerated solution.

^b Deaerated solution.

^c Quantum yields were determined relative to quinine sulfate ($\phi = 0.546$) in 0.05 M sulfuric acid for pyrene units.

^d Quantum yields were determined relative to $[\text{Ru}(\text{Bpy})_3]^{2+}$ ($\phi = 0.016$) in air-equilibrated acetonitrile solution [34].

^e FRET efficiencies were calculated according to following equation: $\text{FRET} = 1 - (I_{DA}/I_D)$.

complex pair. The overlap was calculated using integral (2)

$$J(\lambda) = \int_0^{\infty} F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda / \int_0^{\infty} F_D(\lambda) d\lambda \quad (2)$$

where $F_D(\lambda)$ is the fluorescence of the normalized emission spectra of the donor at λ , $\varepsilon_A(\lambda)$ is the extinction coefficient of the acceptor at λ [48].

The overlap integral was calculated from the fluorescence emission spectra of bipyridine **Bpy-Py2** as well as from emission spectra of dendron **BpyG1-Py4**. In the case of **Bpy-Py2** were almost no emission of excimer was observed, the Förster radius was calculated to be 3.30 nm. In the case of **BpyG1-Py4**, excimer emission has a larger overlap with the absorbance of the ruthenium bipyridine complex, increasing the calculated Förster radius to 3.51 nm. This indicates that in both cases an efficient energy transfer can take place between pyrene and ruthenium bipyridine complex.

The measurement of the quantum yield for the obtained constructs were done in degassed solutions as well as in air-equilibrated solution, in order to study the influence of the dendron on the oxygen sensibility of the Ru (II) bipyridine complex emission. In degassed solutions, the quantum yields observed for all complexes were similar to that of $[\text{Ru}(\text{Bpy})_3]^{2+}$ used as model compound. The first generation dendrimer showed an increase in its quantum yield in aerated solution, which indicates that the dendrimer branches are protecting the emission of the Ru (II) bipyridine core from dioxygen quenching.

4. Conclusion

In this work, the synthesis of new pyrene-labeled constructs with a bipyridine core was achieved. The obtained ligands were used to form Ru^{2+} complexes, which were characterized by NMR and MALDI-TOF spectrometry. The photophysical properties of all the obtained compounds (ligands and complexes) were studied by steady-state fluorescence measurements. Surprisingly, no excimer emission was observed at a concentration of 1.25×10^{-6} M of pyrene units for the bipyridine ligand with two pyrene units **Bpy-Py2**. The ratio I_E/I_M was also found to be lower than expected for the first generation dendron **BpyG1-Py4**. In all the obtained ruthenium complexes, efficient FRET process could be observed since almost exclusive emission from the ruthenium center was seen. Moreover, a protective effect of the dendritic shell towards oxygen quenching was observed for the fluorescence emission of the ruthenium center in the dendrimer of the first generation. The results presented in this study clearly show the efficiency of energy transfer between pyrene and a ruthenium complex center.

Acknowledgements

We thank Gerardo Cedillo, María de los Ángeles Peña, Elizabeth Huerta, Lucero Rios and Carmen Marquez for their assistance in the characterization of all the compounds. We are also grateful to CONACYT (Project 253155) and PAPIIT (Project IN-100316). M.V. is grateful to the Swiss National Science Foundation for a postdoctoral fellowship (P2ZHP2-148707).

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polymer.2016.06.061>.

References

- [1] D.A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, et al., A new class of polymers: starburst-dendritic macromolecules, *Polym. J.* 17 (1985) 117–132.
- [2] D.A. Tomalia, A.M. Naylor, W.A. Goddard, Starburst dendrimers: molecular-level control of size, shape, surface chemistry, topology, and flexibility from atoms to macroscopic matter, *Angew. Chem. Int. Ed.* 29 (1990) 138–175.
- [3] G.R. Newkome, C.N. Moorefield, F. Vögtle, *Dendritic Molecules: Concepts, Syntheses, Perspectives*, VCH Publishers, New York, 1996.
- [4] G.R. Newkome, Z. Yao, G.R. Baker, V.K. Gupta, Micelles. Part 1. Cascade molecules: a new approach to micelles. A [27]-arborol, *J. Org. Chem.* 50 (1985) 2003–2004.
- [5] S.M. Grayson, J.M.J. Fréchet, Convergent dendrons and dendrimers: from synthesis to applications, *Chem. Rev.* 101 (2001) 3819–3868.
- [6] D. Astruc, E. Boisselier, C. Ornelas, Dendrimers designed for functions: from physical, photophysical, and supramolecular properties to applications in sensing, catalysis, molecular electronics, photonics, and nanomedicine, *Chem. Rev.* 110 (2010) 1857–1959.
- [7] V. Balzani, P. Ceroni, M. Maestri, C. Saudan, V. Vicinelli, Luminescent dendrimers. Recent advances, *Top. Curr. Chem.* 228 (2003) 159–191.
- [8] V. Balzani, P. Ceroni, M. Maestri, V. Vicinelli, Light-harvesting dendrimers, *Curr. Opin. Chem. Biol.* 7 (2003) 657–665.
- [9] A. Nantalaksakul, D.R. Reddy, C.J. Bardeen, S. Thayumanavan, Light harvesting dendrimers, *Photosynth. Res.* 87 (2006) 133–150.
- [10] G.D. D'Ambruso, D.V. McGrath, Energy harvesting in synthetic dendrimer materials, *Adv. Polym. Sci.* (2008) 87–147.
- [11] A. Aronov, S.L. Gilat, J.M.J. Fréchet, K. Ohta, F.V.R. Neuwahl, G.R. Fleming, Light harvesting and energy transfer in laser-dye-labeled poly(aryl ether) dendrimers, *J. Am. Chem. Soc.* 122 (2000) 1175–1185.
- [12] T. Qin, W. Wiedemair, S. Nau, R. Trattning, S. Sax, S. Winkler, et al., Core, shell, and surface-optimized dendrimers for blue light-emitting diodes, *J. Am. Chem. Soc.* 133 (2011) 1301–1303.
- [13] V. Balzani, S. Campagna, G. Denti, A. Juris, Designing dendrimers based on transition-metal complexes. light-harvesting properties and predetermined redox patterns, *Acc. Chem. Res.* 31 (1998) 26–34.
- [14] J. Larsen, F. Puntoriero, T. Pascher, N. McClenaghan, S. Campagna, E. Åkesson, et al., Extending the light-harvesting properties of transition-metal dendrimers, *ChemPhysChem* 8 (2007) 2643–2651.
- [15] S. Campagna, F. Puntoriero, F. Nastasi, G. Bergamini, V. Balzani, Photochemistry and photophysics of coordination compounds: ruthenium, *Top. Curr. Chem.* 280 (2007) 117–214.
- [16] G.A. Crosby, W.H. Elfring Jr., Excited states of mixed ligand chelates of ruthenium (II) and rhodium (III), *J. Phys. Chem.* 80 (1976) 2206–2211.
- [17] G.A. Crosby, Spectroscopic investigations of excited states of transition-metal complexes, *Acc. Chem. Res.* 8 (1975) 231–238.
- [18] M.K. Nazeeruddin, C. Klein, P. Liska, M. Grätzel, Synthesis of novel ruthenium sensitizers and their application in dye-sensitized solar cells, *Coord. Chem. Rev.* 249 (2005) 1460–1467.
- [19] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Dye-sensitized solar cells, *Chem. Rev.* 110 (2010) 6595–6663.
- [20] J.H. Cheon, D.Y. Jung, S.K. Choi, K.-S. Ahn, D.K. Lee, J.H. Kim, Enhancement of light harvesting in dye-sensitized solar cells by using Förster-type resonance energy transfer, *Met. Mater. Int.* 19 (2013) 1365–1368.
- [21] M. Plevoets, F. Vögtle, L. De Cola, V. Balzani, Supramolecular dendrimers with a $[\text{Ru}(\text{bpy})_3]^{2+}$ core and naphthyl peripheral units, *New J. Chem.* 23 (1999) 63–69.
- [22] S. Deng, G. Krueger, P. Taranekar, S. Sriwichai, R. Zong, R.P. Thummel, et al., Ruthenium(II)-cored polythiophene dendrimers, *Chem. Mater.* 23 (2011) 3302–3311.
- [23] N.D. McClenaghan, R. Passalacqua, F. Loiseau, S. Campagna, B. Verheyde, A. Hameurlaine, et al., Ruthenium(II) dendrimers containing carbazole-based chromophores as branches, *J. Am. Chem. Soc.* 125 (2003) 5356–5365.
- [24] X. Zhou, D.S. Tyson, F.N. Castellano, First generation light-harvesting dendrimers with a $[\text{Ru}(\text{bpy})_3]^{2+}$ core and aryl ether ligands functionalized with coumarin 450, *Angew. Chem. Int. Ed.* 39 (2000) 4301–4305.
- [25] X. Schultze, J. Serin, A.J.M.J. Fréchet, Light harvesting and energy transfer in a ruthenium-coumarin-2 copolymer, *Chem. Commun.* (2001) 1160–1161.
- [26] A.J. Howarth, M.B. Majewski, M.O. Wolf, Photophysical properties and applications of coordination complexes incorporating pyrene, *Coord. Chem. Rev.* 282–283 (2015) 139–149.
- [27] W.E. Ford, M. Rodgers, Reversible triplet-triplet energy transfer within a covalently linked bichromophoric molecule, *J. Phys. Chem.* 96 (1992) 2917–2920.
- [28] D.S. Tyson, F.N. Castellano, Intramolecular singlet and triplet energy transfer in a ruthenium(II) diimine complex containing multiple pyrenyl chromophores, *J. Phys. Chem. A* 103 (1999) 10955–10960.
- [29] N.D. McClenaghan, Y. Leydet, B. Maubert, M.T. Indelli, S. Campagna, Excited-state equilibration: a process leading to long-lived metal-to-ligand charge transfer luminescence in supramolecular systems, *Coord. Chem. Rev.* 249 (2005) 1336–1350.
- [30] S.A. Denisov, Y. Cudré, P. Verwilt, G. Jonusauskas, M. Marín-Suárez, J.F. Fernández-Sánchez, et al., Direct observation of reversible electronic energy transfer involving an iridium center, *Inorg. Chem.* 53 (2014) 2677–2682.

- [31] A. Lavie-Cambot, C. Lincheneau, M. Cantuel, Y. Leydet, N.D. McClenaghan, Reversible electronic energy transfer: a means to govern excited-state properties of supramolecular systems, *Chem. Soc. Rev.* 39 (2010) 506–515.
- [32] X.-Y. Wang, A. Del Guerso, R.H. Schmehl, Photophysical behavior of transition metal complexes having interacting ligand localized and metal-to-ligand charge transfer states, *J. Photochem. Photobiol. C. Photochem. Rev.* 5 (2004) 55–77.
- [33] F. Vögtle, M. Plevoets, M. Nieger, G.C. Azzellini, A. Credi, L. De Cola, et al., Dendrimers with a photoactive and redox-active [Ru(bpy) 3] 2+-type core: photophysical properties, electrochemical behavior, and excited-state electron-transfer reactions, *J. Am. Chem. Soc.* 121 (1999) 6290–6298.
- [34] J. Issberner, F. Vögtle, L.D. Cola, V. Balzani, Dendritic bipyridine ligands and their tris (bipyridine) ruthenium (II) chelates—syntheses, absorption spectra, and photophysical properties, *Chem. Eur. J.* 3 (1997) 706–712.
- [35] G. Zaragoza-Galán, M.A. Fowler, J. Duhamel, R. Rein, N. Solladié, E. Rivera, Synthesis and characterization of novel pyrene-dendronized porphyrins exhibiting efficient fluorescence resonance energy transfer: optical and photophysical properties, *Langmuir* 28 (2012) 11195–11205.
- [36] G. Zaragoza-Galán, M. Fowler, R. Rein, N. Solladié, J. Duhamel, E. Rivera, Fluorescence resonance energy transfer in partially and fully labeled pyrene dendronized porphyrins studied with model free analysis, *J. Phys. Chem. C* 118 (2014) 8280–8294.
- [37] Y.-R. Hong, C.B. Gorman, Synthetic approaches to an isostructural series of redox-active, metal tris(bipyridine) core dendrimers, *J. Org. Chem.* 68 (2003) 9019–9025.
- [38] B.P. Sullivan, D.J. Salmon, T.J. Meyer, Mixed phosphine 2, 2'-bipyridine complexes of ruthenium, *Inorg. Chem.* 17 (1978) 3334.
- [39] A. Le Goff, K. Gorgy, M. Holzinger, R. Haddad, M. Zimmerman, S. Cosnier, Tris(bispyrene-bipyridine)iron(II): a supramolecular bridge for the bio-functionalization of carbon nanotubes via π -stacking and pyrene/ β -cyclodextrin host-guest interactions, *Chem. Eur. J.* 17 (2011) 10216–10221.
- [40] T. Yajima, K. Munakata, Synthesis of 2-and 4- bromoquinolines with new brominating reagent, PBr 3-DMF, *Chem. Lett.* 6 (1977) 891–892.
- [41] R.R. Koganty, M.B. Shambhu, G.A. Digenis, Reactions of acid halides and chloroformates involving an intermediate with dimethylformamide, *Tetrahedron Lett.* 14 (1973) 4511–4514.
- [42] S.-N. Ding, D. Shan, S. Cosnier, A. Le Goff, Single-walled carbon nanotubes noncovalently functionalized by ruthenium(II) complex tagged with pyrene: electrochemical and electrogenerated chemiluminescence properties, *Chem. Eur. J.* 18 (2012) 11564–11568.
- [43] A. Le Goff, B. Reuillard, S. Cosnier, A pyrene-substituted tris(bipyridine) osmium(ii) complex as a versatile redox probe for characterizing and functionalizing carbon nanotube- and graphene-based electrodes, *Langmuir* 29 (2013) 8736–8742.
- [44] M.J. Fuentes, R.J. Bognanno, W.G. Dougherty, W.J. Boyko, W. Scott Kassel, T.J. Dudley, et al., Structural, electronic and acid/base properties of [Ru(bpy(OH)2)3]2+ (bpy(OH)2 = 4,4'-dihydroxy-2,2'-bipyridine), *Dalton Trans.* 41 (2012) 12514.
- [45] J. Yip, J. Duhamel, G.J. Bahun, A. Adronov, A study of the dynamics of the branch ends of a series of pyrene-labeled dendrimers based on pyrene excimer formation, *J. Phys. Chem. B* 114 (2010) 10254–10265.
- [46] K. Nakamoto, Ultraviolet spectra and structures of 2,2'-Bipyridine and 2,2',2"-terpyridine in aqueous solution, *J. Phys. Chem.* 64 (1960) 1420–1425.
- [47] F.M. Winnik, Photophysics of preassociated pyrenes in aqueous polymer solutions and in other organized media, *Chem. Rev.* 24 (1993) 587–614.
- [48] J.R. Lakowicz, Principles of Fluorescence Spectroscopy, Springer, 2006.