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Dendritic Tetranuclear Ru(II) Complexes Based on the Nonsymmetrical PHEHAT Bridging Ligand and Their Building Blocks: Synthesis, Characterization, and Electrochemical and Photophysical Properties

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Dinuclear and tetranuclear Ru(II) compounds **1**, **2**, **3**, and **4** based on the PHEHAT ligand (PHEHAT = 1,10-phenanthrolino[5,6-b]-1,4,5,8,9,12-hexaazatriphenylene) are prepared and characterized on the basis of the data for other related mononuclear species. Their electrochemical and spectroscopic behaviors are discussed. The nonspectroelectrochemical correlation obtained for **1**, **2**, **3**, and **4** is explained on the basis of these data. From the behavior in emission, it is concluded that the internal energy transfer takes place from the core to the peripheral metallic units in **3** and **4**.

Introduction

During these last years, several mono- and polymetallic transition metal complexes (based on Ru(II), Os(II), or Ir(III)) with different extended polyazaaromatic planar ligands have been prepared and studied.[1−6] Some of the mononuclear building blocks have been examined as DNA intercalators and biosensors[7−10] whereas polynuclear complexes are currently developed as new nanomaterials to collect light and play the role of antenna systems.[11−13] Up to now, only a few of the bridging ligands with an extended planar aromaticity are, to our knowledge, nonsymmetrical. This is actually the case of the present PHEHAT (PHEHAT = 1,10-phenanthrolino[5,6-b]-1,4,5,8,9,12-hexaazatriphenylene) ligand studied in this work, which consists of two units: a phenanthroline (phen) and a hexaazatriphenylene (HAT) motif (Figure 1). Such a nonsymmetrical ligand should allow the introduction of a direction in the energy or electron transfer process inside the multinuclear complexes.

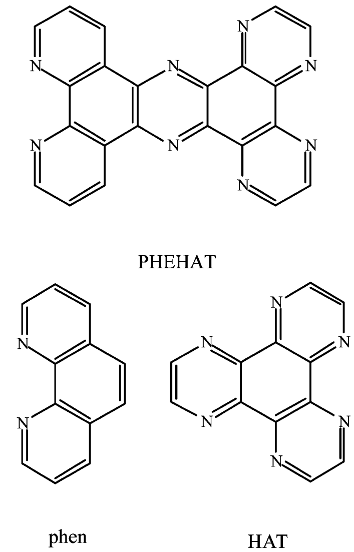

Figure 1. Structure of PHEHAT and related phen and HAT ligands.

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The influence of the nonsymmetrical character of this ligand on the properties of corresponding Ru(II) complexes is thus investigated. In a first step, the synthesis, characterization, and electrochemical and photophysical properties of two dinuclear building blocks (**1** and **2**) are presented and discussed. In a second step, on the basis of these data, the properties of the tetranuclear compounds are interpreted. For the construction of these compounds, one can start from a central Ru(II) ion complexed to three PHEHAT ligands and add three additional Ru(II) species to each PHEHAT moiety to obtain a tetranuclear complex. There are however two possibilities for this construction. Either the three phen parts of the PHEHAT ligands surround the central Ru ion or the three HAT parts are at the core. Up to now, despite our numerous efforts, the construction of the tetranuclear species with the HAT motif around the central Ru has failed. In the present work, we present thus the synthesis, characterization, and electrochemical and photophysical properties of the species with the three phen motifs surrounding the metallic core (tetranuclear complexes **3** and **4**).

Experimental Section

$\{(phen)_2Ru\text{-}PHEHAT\}^{2+}$,[14] $Ru(phen)_2Cl_2$,[15] $Ru(bpy)_2Cl_2$,[15] $Ru(DMSO)_4Cl_2$,[16] 1,10-phenanthroline-5,6-dione (phendione),[17] and 9,10-diamino-1,4,5,8-tetraazaphenanthrene ($diNH_2TAP$)[14] were prepared following literature procedures. All the solvents and reagents for the syntheses were at least reagent grade quality and were used without further purification. All the solvents for the spectroscopic measurements were spectroscopic grade quality. All the reaction mixtures were protected from direct light during the synthesis to prevent photochemical degradation.

Instrumentation. ^1H NMR (300 MHz) spectra were obtained on a Bruker Avance-300 instrument. The electrospray mass spectra were obtained with a VG-BIO-QUAD spectrometer at the University Louis Pasteur (Strasbourg, France). Absorption spectra were recorded on a Perkin-Elmer Lambda UV−vis spectrophotometer. The molar absorption coefficients were determined by weight and absorption measurements. Emission spectra were recorded with a Shimadzu RF-5001 PC spectrometer equipped with a Hamamatsu R-928 photomultiplier tube and with a 250 W xenon lamp as excitation source. The spectra were corrected for the instrument response. Cyclic voltammetry was performed in a one-compartment cell, using a carbon disk working electrode (approximate area = 0.03 cm^2), a platinum counter electrode, and a saturated calomel electrode (SCE) as reference electrode (Perkin-Elmer Instruments). The potential of the working electrode was controlled by a homemade potentiostat. Scan rate at 200 mV s^{-1} between −2 and +2 V versus SCE was applied by a frequency generator (Phillips PM 5168). The cyclic voltammograms were recorded in acetonitrile (Acros, Acetonitrile for HPLC), distilled twice over P_2O_5 and once over CaH_2. The concentration of the complexes was 5×10^{-4} mol/L, with 0.1 mol/L tetrabutylammonium perchlorate as supporting electrolyte. Before each measurement, the samples were purged by argon.

Table 1. ^1H NMR Data for Complexes **1**−**4**[a]

phen	phen	bpy	PHEHAT	HAT
$\{(phen)_2Ru\text{-}PHEHAT\}^{2+\,b}$				
$P_2 = 8.31$			$PH_\alpha = 8.24$	
$P_3 = 7.70$			$PH_\beta = 7.84$	
$P_4 = 8.66$			$PH_\gamma = 9.70$	
$P_5 = 8.31$			$PH_{\delta,\epsilon} = 9.30$ and 9.33	
$P_6 = 8.31$				
$P_7 = 8.66$				
$P_8 = 7.70$				
$P_9 = 8.09$				
$\{HAT\text{-}Ru(phen)_2\}^{2+\,c}$				
$P'_2 = 8.19$				$H_{7,10} = 8.28$
$P'_3 = 7.70$				$H_{6,11} = 9.04$
$P'_4 = 8.69$				$H_{2,3} = 9.41$
$P'_5 = 8.31$				
$P'_6 = 8.31$				
$P'_7 = 8.69$				
$P'_8 = 7.68$				
$P'_9 = 8.02$				
$\{HAT\text{-}Ru(bpy)_2\}^{2+\,d}$				
		$B'_6, B'_{6'} = 7.68$ and 7.81		$H_{7,10} = 8.36$
		$B'_5, B'_{5'} = 7.29$ and 7.53		$H_{6,11} = 9.16$
		$B'_4, B'_{4'} = 8.08$ and 8.19		$H_{2,3} = 9.41$
		$B'_3, B'_{3'} = 8.57$ and 8.60		
$\{(phen)_2Ru\text{-}\mu\text{-}PHEHAT\text{-}Ru(phen)_2\}^{4+}$ **1**				
$P_2 = 8.27$	$P'_2 = 8.27$		$PH_\alpha = 8.27$	
$P_3 = 7.71$	$P'_3 = 7.71$		$PH_\beta = 7.92$	
$P_4 = 8.67$	$P'_4 = 8.72$		$PH_\gamma = 9.82$	
$P_5 = 8.31$	$P'_5 = 8.33$		$PH_\delta = 9.14$	
$P_6 = 8.31$	$P'_6 = 8.33$		$PH_\epsilon = 8.39$	
$P_7 = 8.67$	$P'_7 = 8.72$			
$P_8 = 7.71$	$P'_8 = 7.71$			
$P_9 = 8.07$	$P'_9 = 8.04$			
$\{(phen)_2Ru\text{-}\mu\text{-}PHEHAT\text{-}Ru(bpy)_2\}^{4+}$ **2**				
$P_2 = 8.27$		$B'_6, B'_{6'} = 7.78$ and 7.84	$PH_\alpha = 8.27$	
$P_3 = 7.69$		$B'_5, B'_{5'} = 7.33$ and 7.57	$PH_\beta = 7.92$	
$P_4 = 8.66$		$B'_4, B'_{4'} = 8.12$ and 8.22	$PH_\gamma = 9.82$	
$P_5 = 8.31$		$B'_3, B'_{3'} = 8.58$ and 8.66	$PH_\delta = 9.25$	
$P_6 = 8.31$			$PH_\epsilon = 8.47$	
$P_7 = 8.66$				
$P_8 = 7.69$				
$P_9 = 8.07$				
$\{Ru[\mu\text{-}PHEHAT\text{-}Ru\text{-}(phen)_2]_3\}^{8+}$ **3**				
$P'_2 = 8.27$			$PH_\alpha = 8.50$	
$P'_3 = 7.68$			$PH_\beta = 8.00$	
$P'_4 = 8.69$			$PH_\gamma = 9.89$	
$P'_5 = 8.30$			$PH_\delta = 9.11$	
$P'_6 = 8.30$			$PH_\epsilon = 8.37$	
$P'_7 = 8.69$				
$P'_8 = 7.68$				
$P'_9 = 8.00$				
$\{Ru[\mu\text{-}PHEHAT\text{-}Ru\text{-}(bpy)_2]_3\}^{8+}$ **4**				
		$B'_6, B'_{6'} = 7.76$ and 7.82	$PH_\alpha = 8.51$	
		$B'_5, B'_{5'} = 7.31$ and 7.55	$PH_\beta = 8.01$	
		$B'_4, B'_{4'} = 8.09$ and 8.20	$PH_\gamma = 9.90$	
		$B'_3, B'_{3'} = 8.56$ and 8.60	$PH_\delta = 9.23$	
			$PH_\epsilon = 8.45$	

[a] Measured in CD_3CN at 300 MHz. For the numbering of the different protons, see Figures 2 and 3. Z_y refers to the proton y, belonging to the ligand Z. [b] Reference 14. [c] Reference 20. [d] Reference 21.

Syntheses. As previously mentioned, compounds were characterized by ^1H NMR spectrum at 300 MHz in CD_3CN (Table 1). The numbering of the different protons is shown in Figures 2 and 3. The following listing is used, respectively: chemical shift (ppm), number of protons, multiplicity, J (Hz, coupling constant for protons of ligands chelated on the PHEN side of the PHEHAT ligand) or J' (Hz, coupling constant for protons of ligands chelated on the HAT side of the PHEHAT ligand). The following are multiplicity abbreviations: d = doublet, dd = doublet of doublets, td = triplet of doublets. For the studies described hereafter, complexes **1**−**4**

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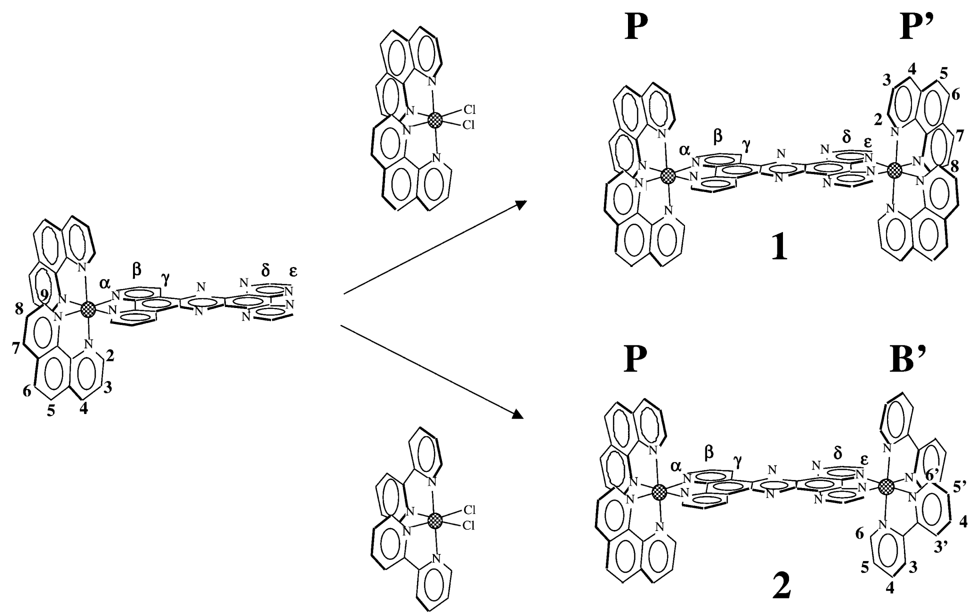

Figure 2. Synthetic routes for the preparation of complexes **1** and **2**, including the numbering of the protons. P corresponds to the phenanthroline chelated on the PHEN side of the PHEHAT ligand, and P′ or B′ corresponds to the phenanthroline or bipyridine connected to the HAT side of the PHEHAT ligand.

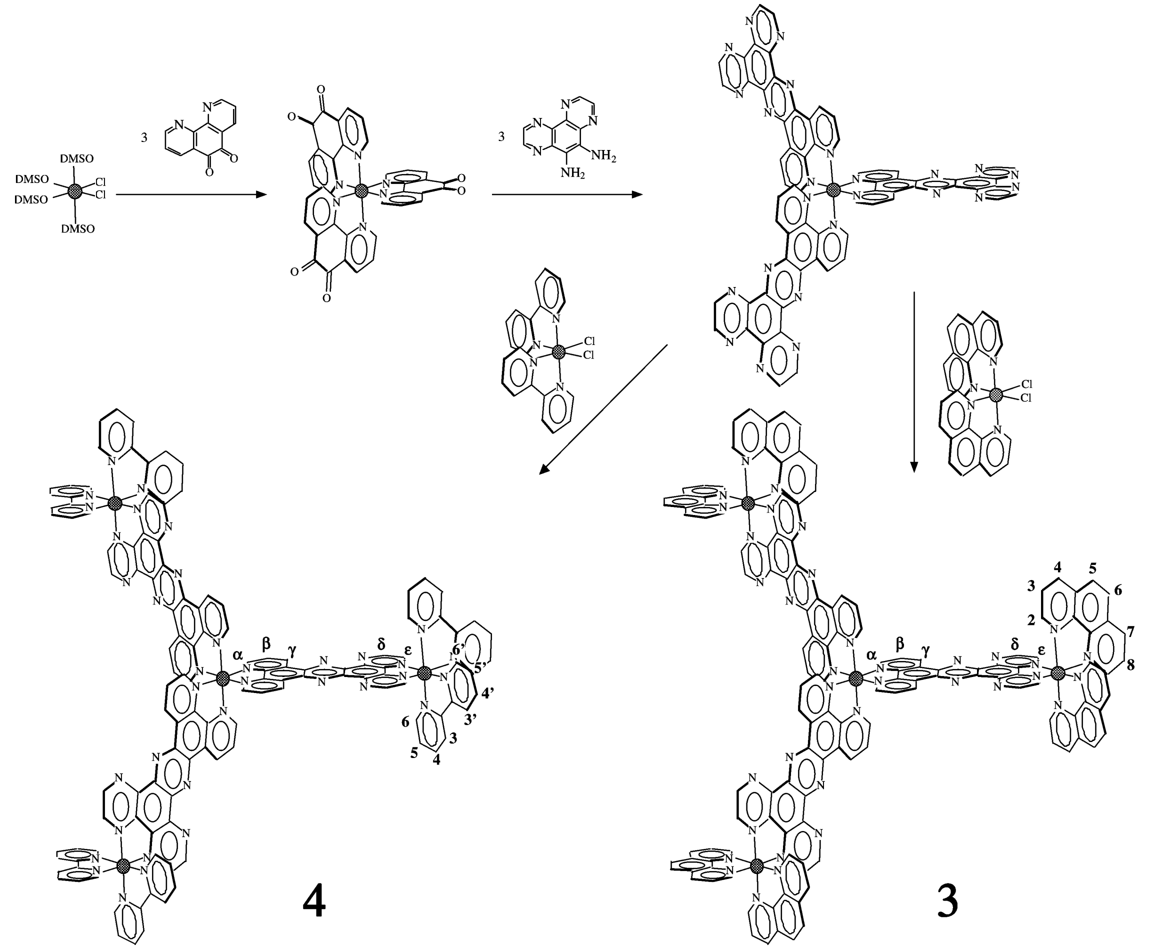

Figure 3. Divergent method for the synthesis of complexes **3** and **4**, including the numbering of the protons.

were used as PF_6^- salts (unless otherwise stated) and were all well soluble in acetonitrile at room temperature.

$\{(phen)_2Ru$-μ-PHEHAT-$Ru(phen)_2\}^{4+}$, 1. A suspension of $\{(phen)_2Ru$-PHEHAT$\}^{2+}$ (51 mg, 0.045 mmol) and $Ru(phen)_2Cl_2$ (26 mg, 0.048 mmol) in ethylene glycol (4 mL) was heated and stirred for 40 min in an oil bath at 150 °C. After cooling to room temperature, addition of an aqueous solution of NH_4PF_6 yielded a brown precipitate which was washed several times with water and EtOH and finally dried with ether. The complex was purified by preparative layer chromatography on silica, with $CH_3CN/H_2O/NH_4$-

Cl saturated in water 4:4:1 (v/v/v) as eluent. Anal. Calcd (Found) for $C_{70}H_{42}N_{16}Ru_2P_4F_{24}$: C, 44.50 (44.55); H, 2.24 (2.15); N, 11.86 (11.05). ^{1}H NMR (CD_3CN), δ/ppm: 7.71 (8H, P'_3, P'_8, P_3, and P_8), 7.92 (2H, dd, PH_β, $J_{\beta,\alpha}$ = 5.5 Hz), 8.04 (2H, d, P'_9, $J'_{9,8}$ = 5.2 Hz), 8.07 (2H, dd, P_9, $J_{9,8}$ = 5.2 Hz), 8.27 (6H, PH_α, P'_2 and P_2), 8.31 (4H, AB syst, P_5 and P_6), 8.33 (4H, AB syst, P'_5 and P'_6), 8.39 (2H, d, PH_ϵ), 8.67 (4H, dd, P_4 and P_7, $J_{4,3} = J_{7,8}$ = 8.4 Hz, $J_{4,2} = J_{7,9}$ = 1.1 Hz), 8.72 (4H, dd, P'_4 and P'_7, $J'_{4,3} = J'_{7,8}$ = 8.3 Hz, $J'_{4,2} = J'_{7,9}$ = 1.1 Hz), 9.14 (2H, d, PH_δ, $J_{\delta,\epsilon}$ = 3.0 Hz), 9.82 (2H, dd, PH_γ, $J_{\gamma,\beta}$ = 8.2 Hz, $J_{\gamma,\alpha}$ = 1.1 Hz). ESMS, *m*/*z* (M^{4+} = 1309.3): 327.6 ($[M^{4+}]^{4+}$, 100%; calcd: 327.3), 485.0 ($[M^{4+} + PF_6^-]^{3+}$, 29%; calcd: 483.8), 799.9 ($[M^{4+} + 2PF_6^-]^{2+}$, 5%; calcd: 799.6).

{(phen)$_2$Ru-μ-PHEHAT-Ru(bpy)$_2$}$^{4+}$, 2. A 53 mg portion of $\{(phen)_2Ru\text{-}PHEHAT\}^{2+}$ (0.046 mmol) and 24 mg of Ru $(bpy)_2Cl_2$ (0.050 mmol) were heated at 150 °C in ethylene glycol (4 mL) for 40 min. After cooling to room temperature, addition of an aqueous solution of NH_4PF_6 yielded a brown precipitate which was washed several times with water and EtOH and finally dried with ether. The complex was purified by preparative layer chromatography on silica, with $CH_3CN/H_2O/NH_4Cl$ saturated in water 4:4:1 (v/v/v) as eluent. Anal. Calcd (Found) for $C_{66}H_{42}N_{16}Ru_2P_4F_{24}$: C, 43.06 (43.12); H, 2.30 (2.39); N, 12.17 (11.27). ^{1}H NMR (CD_3CN), δ/ppm: 7.33 (2H, dd, B'_5 or $B'_{5'}$), 7.57 (2H, dd, $B'_{5'}$ or B'_5), 7.69 (4H, P_3 and P_8), 7.78 (2H, d, B'_6 or $B'_{6'}$, $J'_{6,5}$ or $J'_{6',5'}$= 5.2 Hz), 7.84 (2H, d, $B'_{6'}$ or B'_6, $J'_{6',5'}$ or $J'_{6,5}$= 5.2 Hz), 7.92 (2H, dd, PH_β, $J_{\beta,\alpha}$ = 5.8 Hz), 8.07 (2H, dd, P_9, $J_{9,7}$ = 1.1 Hz, $J_{9,8}$ = 5.3 Hz), 8.12 (2H, td, B'_4 or $B'_{4'}$, $J'_{4,6}$ or $J'_{4',6'}$= 1.3 Hz, $J'_{4,3}$ or $J'_{4',3'}$ = 8.0 Hz), 8.22 (2H, td, $B'_{4'}$ or B'_4, $J'_{4',6'}$ or $J'_{4,6}$ = 1.3 Hz, $J'_{4',3'}$ or $J'_{4,3}$ = 8.0 Hz), 8.27 (4H, d, PH_α and P_2), 8.31 (4H, P_5 and P_6), 8.47 (2H, d, PH_ϵ, $J_{\epsilon,\delta}$ = 2.9 Hz), 8.58 (2H, d, B'_3 or $B'_{3'}$), 8.66 (6H, $B'_{3'}$ or B'_3, P_7 and P_4), 9.25 (2H, d, PH_δ), 9.82 (2H, d, PH_γ, $J_{\gamma,\beta}$ = 8.6 Hz). ESMS, *m*/*z* (M^{4+} = 1261.3): 315.4 ($[M^{4+}]^{4+}$, 100%; calcd: 315.3), 469.0 ($[M^{4+} + PF_6^-]^{3+}$, 62%; calcd: 468.8), 775.8 ($[M^{4+} + 2PF_6^-]^{2+}$, 7%; calcd: 775.6).

{Ru[phendione]$_3$}$^{2+}$. A 305 mg portion of $Ru(DMSO)_4Cl_2$ (0.63 mmol) and 453 mg of phendione (2.16 mmol) were refluxed in a mixture of 10 mL of H_2O/EtOH (1:1, v/v) for 5 h 30 min. After cooling to room temperature and centrifugation of the solid residue, the solvent was evaporated to give 462 mg of a dark complex, $\{Ru[phendione]_3\}^{2+}\cdot 2Cl^-$ (yield: 92%). ^{1}H NMR (CD_3CN) as PF_6^- salt, δ/ppm: 7.72 (6H, dd, $H_{3,8}$, $J_{3,2} = J_{8,9}$ = 5.5 Hz), 8.15 (6H, d, $H_{2,9}$), 8.61 (6H, d, $H_{4,7}$, $J_{4,3} = J_{7,8}$ = 8.0 Hz).

{Ru[PHEHAT]$_3$}$^{2+}$. $\{Ru[phendione]_3\}^{2+}\cdot 2Cl^-$ (206 mg, 0.26 mmol) and diNH$_2$-TAP (183 mg, 0.86 mmol) were refluxed for 25 h in 20 mL of H_2O/EtOH 1:1 (v/v). An orange-brown compound of $\{Ru[PHEHAT]_3\}^{2+}$ was formed. The ethanol was evaporated, and the aqueous solution containing the orange-brown $\{Ru[PHEHAT]_3\}^{2+}$ was immediately engaged in the next reaction. ^{1}H NMR (DMSO-d_6), δ/ppm: 8.06 (6H, PH_β), 8.55 (6H, PH_α), 9.44 (12H, $PH_{\delta,\epsilon}$), 9.78 (6H, PH_γ).

{Ru[μ-PHEHAT-Ru(phen)$_2$]$_3$}$^{8+}$, 3. The metallic precursor $\{Ru[PHEHAT]_3\}^{2+}$ and 453 mg of $Ru(phen)_2Cl_2$ (0.85 mmol) were heated in a mixture H_2O/ethylene glycol (150 °C) for 5 h. After cooling to room temperature, an excess of NH_4PF_6 was added to the solution. The dark brown precipitate was isolated by centrifugation and washed several times with water and EtOH and finally dried with ether. The desired complex was purified by preparative layer chromatography on silica, with $DMF/H_2O/NH_4Cl$ saturated in water 7:1:1 (v/v/v) as eluent. Anal. Calcd (Found) for $C_{138}H_{78}N_{36}Ru_4P_8F_{48}$: C, 43.56 (43.57); H, 2.07 (2.20); N, 13.25 (12.48). ^{1}H NMR (CD_3CN), δ/ppm: 7.68 (12H, P'_3 and P'_8), 8.00 (12H, P'_9 and PH_β), 8.27 (6H, dd, P'_2, $J'_{2,3}$ = 5.2 Hz), 8.30 (12H, AB syst, P'_5 and P'_6), 8.37 (6H, d, PH_ϵ, $J_{\epsilon,\delta}$ = 2.5 Hz), 8.50 (6H, d, PH_α, $J_{\alpha,\beta}$ = 5.1 Hz), 8.69 (12H, dd, P'_4 and P'_7, $J'_{4,3} = J'_{7,8}$ = 8.3 Hz, $J'_{4,2} = J'_{7,9}$ = 1.2 Hz), 9.11 (6H, d, PH_δ), 9.89 (6H, dd, PH_γ, $J_{\gamma,\beta}$ = 8.3 Hz, $J_{\gamma,\alpha}$ = 1.3 Hz). ESMS, *m*/*z* (M^{8+} = 2644.7): 330.7 ($[M^{8+}]^{8+}$, 29%; calcd: 330.6), 398.8 ($[M^{8+} + PF_6^-]^{7+}$, 77%; calcd: 398.5), 489.2 ($[M^{8+} + 2PF_6^-]^{6+}$, 100%; calcd: 489.1), 616.0 ($[M^{8+} + 3PF_6^-]^{5+}$, 42%; calcd: 615.9), 806.3 ($[M^{8+} + 4PF_6^-]^{4+}$, 18%; calcd: 806.1).

{Ru[μ-PHEHAT-Ru(bpy)$_2$]$_3$}$^{8+}$, 4. $\{Ru[PHEHAT]_3\}^{2+}$ and 262 mg of $Ru(bpy)_2Cl_2$ (0.54 mmol) were stirred in a H_2O/ethylene glycol mixture at 150 °C for 4 h. Addition of NH_4PF_6 leads to the precipitation of a brown solid which was isolated by centrifugation and washed several times with water and EtOH and finally dried with ether. The desired $\{Ru[\mu\text{-}PHEHAT\text{-}Ru(bpy)_2]_3\}^{8+}$ was purified by preparative layer chromatography on silica, with $DMF/H_2O/NH_4Cl$ saturated in water 7:1:1 (v/v/v) as eluent. Anal. Calcd (Found) for $C_{126}H_{78}N_{36}Ru_4P_8F_{48}$: C, 41.35 (41.42); H, 2.15 (2.53); N, 13.78 (13.26). ^{1}H NMR (CD_3CN), δ/ppm: 7.31 (6H, dd, B'_5 or $B'_{5'}$), 7.55 (6H, dd, $B'_{5'}$ or B'_5), 7.76 (6H, d, B'_6 or $B'_{6'}$, $J'_{6,5}$ or $J'_{6',5'}$= 5.2 Hz), 7.82 (6H, d, $B'_{6'}$ or B'_6, $J'_{6',5'}$ or $J'_{6,5}$ = 5.2 Hz), 8.01 (6H, dd, PH_β, $J_{\beta,\alpha}$ = 5.5 Hz and $J_{\beta,\gamma}$ = 8.1 Hz), 8.09 (6H, dd, B'_4 or $B'_{4'}$, $J'_{4,5}$ or $J'_{4',5'}$= 6.3 Hz), 8.20 (6H, dd, $B'_{4'}$ or B'_4, $J'_{4',5'}$ or $J'_{4,5}$= 6.4 Hz), 8.45 (6H, d, PH_ϵ, $J_{\epsilon,\delta}$ = 2.8 Hz), 8.51 (6H, d, PH_α), 8.56 (6H, d, B'_3 or $B'_{3'}$, $J'_{3,4}$ or $J'_{3',4'}$= 8.1 Hz), 8.60 (6H, d, $B'_{3'}$ or B'_3, $J'_{3',4'}$ or $J'_{3,4}$= 8.0 Hz), 9.23 (6H, d, PH_δ), 9.90 (6H, d, PH_γ). ESMS, *m*/*z* (M^{8+} = 2500.5): 377.9 ($[M^{8+} + PF_6^-]^{7+}$, 82%; calcd: 377.9), 465.1 ($[M^{8+} + 2PF_6^-]^{6+}$, 100%; calcd: 465.1), 587.2 ($[M^{8+} + 3PF_6^-]^{5+}$, 53%; calcd: 587.2), 770.3 ($[M^{8+} + 4PF_6^-]^{4+}$, 21%; calcd: 770.1), 1075.3 ($[M^{8+} + 5PF_6^-]^{3+}$, 4%; caldc: 1075.1).

Results and Discussion

Synthesis and Characterization. The dinuclear complexes based on the PHEHAT bridging ligand can be synthesized according to two strategies. The first one consists of reacting 1 equiv of free PHEHAT with 2 equiv of $Ru(phen)_2Cl_2$ to obtain the dinuclear species $\{(phen)_2Ru(\mu\text{-}PHEHAT)Ru(phen)_2\}^{4+}$, **1**. Unfortunately, due to the poor solubility of the aromatic heptacycle PHEHAT in all the usual organic solvents, the yield of this reaction is very poor. Moreover, this method is useful only for the synthesis of dinuclear species with identical ancillary ligands on each chelation site.

Therefore, another approach based on a soluble mononuclear precursor ($\{(phen)_2Ru\text{-}PHEHAT\}^{2+}$) has been chosen. As shown in Figure 2, its reaction with $Ru(phen)_2Cl_2$ or $Ru(bpy)_2Cl_2$ leads to complexes **1** and **2**, respectively, which are purified by preparative layer chromatography.

The tetranuclear compounds **3** and **4** (Figure 3) are produced according to the divergent strategy. Thus, the core, i.e., $\{Ru(phendione)_3\}^{2+}$ (phendione = 1,10-phenanthroline-5,6-dione) is built first, followed by the condensation with 3 equiv of diNH$_2$-TAP (diNH$_2$-TAP = 9,10-diamino-1,4,5,8-tetraazaphenanthrene) to obtain the mononuclear complex $\{Ru\ (PHEHAT)_3\}^{2+}$, the “zero generation” of the dendrimer. In the next step, this mononuclear species is chelated to three $Ru(phen)_2Cl_2$ or $Ru(bpy)_2Cl_2$ to give dendrimers **3** and **4**, respectively, which are also purified by preparative layer chromatography. For this step, solubility problems were encountered when using the complexes as PF_6^- salts.

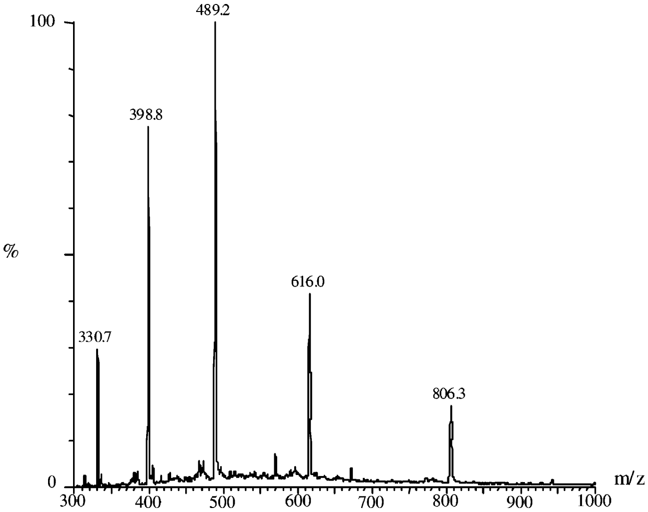

Figure 4. Electrospray mass spectrum of complex **3** in CH_3CN.

Therefore, each metallic precursor in the different steps is under the form of a chloride salt, and the tetranuclear species is eventually isolated with PF_6^- counterions.

Complexes **1**−**4** are characterized by electrospray mass spectrometry in acetonitrile. The attribution of the different peaks observed in the mass spectra for compounds **1**−**4** is given in the Experimental Section, and the mass spectrum of complex **3** is presented in Figure 4. Peaks with different states of charge correspond to the loss of different numbers of PF_6^- counterions of the complex. For example, peaks for complex **3** are found at *m/z* 330.7 ($[M^{8+}]^{8+}$, calcd: 330.6), 398.8 ($[M^{8+} + PF_6^-]^{7+}$, calcd: 398.5), 489.2 ($[M^{8+} + 2PF_6^-]^{6+}$, calcd: 489.1), 616.0 ($[M^{8+} + 3PF_6^-]^{5+}$, calcd: 615.9), 806.3 ($[M^{8+} + 4PF_6^-]^{4+}$, calcd: 806.1). These results clearly show that the mass spectrum of the tetranuclear species can be obtained without fragmentation in contrast to the case of the tetranuclear Ru(II) complexes with tpphz (tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]phenazine) previously published in the literature.[18]

Complexes **1**, **2**, **3**, and **4** are also characterized by ^1H NMR spectroscopy with $^1H-^1H$ COSY analyses in deuterated acetonitrile. The corresponding chemical shifts are gathered in Table 1 together with the data for other mononuclear compounds for comparison purposes. For the sake of simplicity, protons of phenanthroline or bipyridine ligands chelated on the PHEN side of the PHEHAT ligand are named P or B, respectively. Those connected to the HAT side of the PHEHAT ligand are named P′ or B′ (Figure 2).

The ^1H NMR spectra of the dinuclear complex **1** and its corresponding mononuclear precursor $\{(phen)_2Ru\text{-}PHEHAT\}^{2+}$ are displayed in Figure 5 as an example. For $\{(phen)_2RuPHEHAT\}^{2+}$, the chemical shifts of the protons are very sensitive to the solvent. This effect, more pronounced for the protons of the PHEHAT ligand, is attributed to a π-stacking of the complex due to the presence of the extended aromatic ligand. For the dinuclear species (as well as for polynuclear species, see further), there is a complete overlapping of the ^1H NMR signals of each stereoisomer. Indeed, due to the large distance between the two chiral Ru(II) centers, separated by the aromatic heptacycle PHEHAT, the two parts of the dinuclear species seem to behave independently, as already reported for complexes based on the extended tpphz ligand.[18,19]

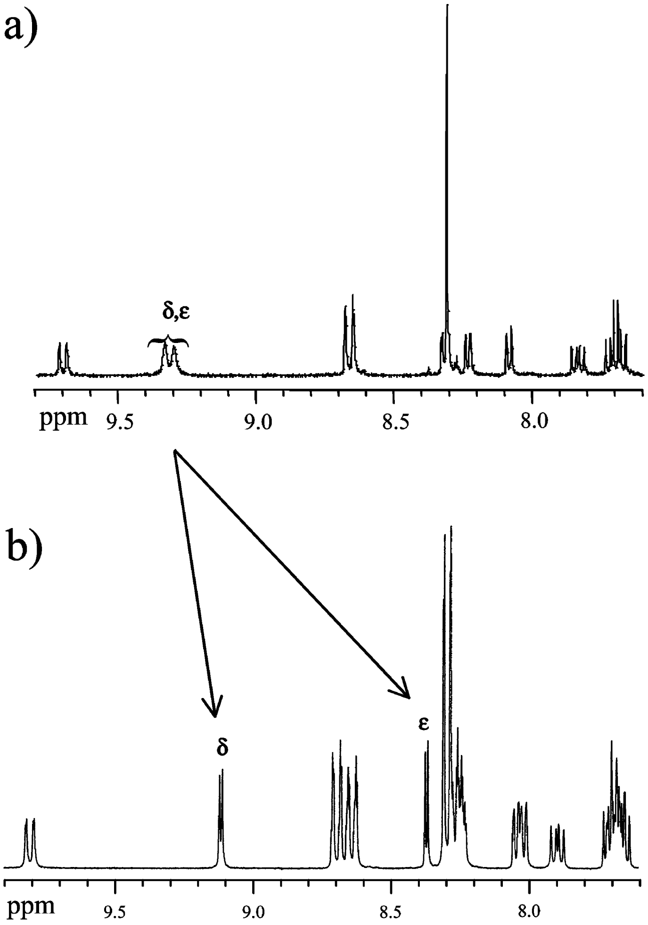

Figure 5. ^1H NMR spectra of (a) $\{(phen)_2Ru\text{-}PHEHAT\}^{2+}$ and (b) **1** measured in CD_3CN at 300 MHz.

Complexes 1 and 2. The C_2 symmetry in dinuclear complexes **1** and **2** (Figure 2) induces the equivalence of both terminal phen or bpy ligands called P and P′ in **1** and P and B′ in **2**, respectively. Protons on the PHEHAT ligand are also equivalent by pair and are noted α, β, γ, δ, and ϵ. The formation of dinuclear compounds **1** and **2** induces in both cases a shielding of the protons ϵ, which, in contrast to the mononuclear species, are located above/below ancillary ligands. This is clearly illustrated in Figure 5 for compound **1** where the protons δ and ϵ split apart (from ~9.30 to 8.39 ppm for the proton ϵ). The value of 8.39 ppm is comparable to that of 8.28 ppm for the proton of the HAT ligand in α position of the chelation site in $\{HAT\text{-}Ru(phen)_2\}^{2+}$, i.e., $H_{7,10}$ (Table 1), equivalent to the proton ϵ in PHEHAT complexes. This shielding of about 0.9 ppm for the protons ϵ of PHEHAT in compound **1** is thus consistent with the chelation of the HAT site by a second Ru(II) center.

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As the PHEHAT ligand is not symmetrical, the two pairs of ancillary ligands are not equivalent, and signals of P and P′ (or P and B′ in **2**) are sometimes well distinguishable. Indeed, comparison with different complexes indicates that the protons of the ancillary ligands are more shielded when located above a phen moiety than above a HAT moiety of the PHEHAT bridge. Thus, since the signals of protons P_4, P_7 and protons P'_4, P'_7 in **1** are clearly separated, the signal at 8.67 ppm can be assigned to protons P_4, P_7 and the signal at 8.72 ppm to protons P'_4, P'_7. However, in this case, the distinction between proton 4 (over the PHEHAT ligand) and proton 7 (over the ancillary ligand) is not possible. Similarly, the signal at 8.31 ppm can be attributed to P_5, P_6 and the signal at 8.33 ppm to P'_5, P'_6. The protons P_9 and P'_9, located over phen ancillary ligands, are also shifted to higher field than the protons P_2 and P'_2 located over the PHEHAT bridge. Moreover, the comparison of the chemical shifts of the protons P_9 in $\{(phen)_2Ru\text{-}PHEHAT\}^{2+}$ ($P_9 = 8.09$ ppm) and $\{HAT\text{-}Ru(phen)_2\}^{2+}$ ($P'_9 = 8.02$ ppm) leads us to assign the signal at 8.07 ppm in **1** to the proton P_9 and at 8.04 ppm to the proton P'_9. The protons P_3, P_8, P'_3, and P'_8 are overlapped (7.71 ppm) as well as P_2 and P'_2 (8.27 ppm).

Similar arguments are used to explain the chemical shifts in complex **2**. Comparison of **2** with $\{HAT\text{-}Ru(bpy)_2\}^{2+}$ confirms without ambiguity the chelation of $Ru(bpy)_2Cl_2$ on $\{(phen)_2Ru\text{-}PHEHAT\}^{2+}$ and the formation of the dinuclear complex **2**. Finally, the chemical shifts of the protons α, β, and γ in **2** are the same as in **1**.

Complexes 3 and 4. The "pseudo-D_3 symmetry" (because the diastereoisomers cannot be distinguished) for **3** and **4** can clearly be evidenced from the analysis of the NMR data. Among the 78 protons present in both structures, only 13 are not equivalent. If we compare **3** (or **4**) with **1** (or **2**), several observations can be made. The chemical shifts for the protons of the ancillary ligands are similar. A difference appears for the protons of the PHEHAT ligand. Indeed, protons α, β, and γ are in this case located over another PHEHAT bridging ligand and are less shielded than in **1** (or **2**). This effect is the most pronounced for the proton PH_α. Finally, the relative integration of the signals (6 phen for 3 PHEHAT) shows without ambiguity that the NMR data correspond to the tetranuclear complex **3**. The same conclusion can be reached for **4**.

Electrochemistry. The electrochemical behavior of **1**−**4** was studied in dry deoxygenated acetonitrile solution by cyclic voltammetry (Table 2). Each complex exhibits reversible oxidation waves and at least two reversible reduction waves within the potential range +2.00 V/−1.20 V versus SCE. The dinuclear complexes **1** and **2** undergo two one-electron oxidations at +1.34 and +1.55 V versus SCE. These values have to be compared to the oxidation potential of each mononuclear subunits, thus to $\{(phen)_2Ru\text{-}PHEHAT\}^{2+}$ ($E_{ox} = +1.35$ V/SCE)[14] and $\{HAT\text{-}Ru(phen)_2\}^{2+}$ ($E_{ox} = +1.53$ V/SCE)[20] or $\{HAT\text{-}Ru(bpy)_2\}^{2+}$ ($E_{ox} = +1.56$ V/SCE).[20] This comparison suggests that the first oxidation occurs at the Ru(II) ion chelated to the phen moiety of the PHEHAT ligand and the second oxidation at the Ru(II) ion linked to the HAT moiety of the PHEHAT. These results indicate that the dπ orbital of the Ru(II) chelated on the phen side is less stabilized than the dπ orbital of the Ru(II) on the HAT side of the PHEHAT bridging ligand. Moreover, each oxidation process does not seem to be influenced by the presence of another Ru(II) on the bridging ligand. This suggests a poor electronic interaction between the two metal centers in contrast to the conclusions drawn when the HAT is used as bridging ligand.[20,21]

Table 2. Electrochemical Data for Complexes **1**−**4** and Reference Complexes[a]

	oxidation, V/SCE		reduction, V/SCE		
$\{Ru(phen)_3\}^{2+}$ [b]	+1.27(1)		−1.35(1)	−1.52(1)	
$\{tpphz\text{-}Ru(phen)_2\}^{2+}$ [c]	+1.34(1)		−1.00(1)	−1.38(1)	−1.69(1)
$\{HAT\text{-}Ru(phen)_2\}^{2+}$ [d]	+1.53		−0.86	−1.42	−1.69
$\{HAT\text{-}Ru(bpy)_2\}^{2+}$ [d]	+1.56		−0.84	−1.43	−1.63
$\{(phen)_2Ru\text{-}PHEHAT\}^{2+}$ [e]	+1.35		−0.84	−1.25	
$\{(phen)_2Ru(\mu\text{-}tpphz)\text{-}Ru(phen)_2\}^{4+}$ [c]	+1.34(2)		−0.78(1)	−1.36(2)	−1.52
$\{(phen)_2Ru(\mu\text{-}HAT)\text{-}Ru(phen)_2\}^{4+}$ [d]	+1.52(1)	+1.78(1)	−0.49	−1.07	
1	+1.34(1)	+1.55(1)	−0.68(1)	−1.06(1)	
2	+1.34(1)	+1.55(1)	−0.68(1)	−1.07(1)	
$\{Ru[(\mu\text{-}tpphz)\text{-}Ru(phen)_2]_3\}^{8+}$ [c]	+1.35(3)	+1.46(1)	−0.78(3)	−1.35	−1.54
3	+1.38(1)	+1.56(3)	−0.70(3)	−1.09(3)	
4	+1.34(1)	+1.54(3)	−0.69(3)	−1.07(3)	

[a] Redox potentials measured by cyclic voltammetry in acetonitrile versus SCE at room temperature, with 0.1 M $^tBu_4N^+ClO_4^-$ as supporting electrolyte and a Pt working electrode. In parentheses, the number of associated electrons. [b] Reference 31. [c] Reference 23. [d] Reference 20. [e] Reference 14.

For the tetranuclear compounds **3** and **4**, a reversible oxidation wave appears at +1.38 V/SCE and +1.34 V/SCE, respectively, followed by a reversible wave at +1.56 V/SCE for **3** and +1.54 V/SCE for **4**. Comparison of the peak areas suggests that the first oxidation process is monoelectronic and the second oxidation involves three electrons. Compounds **3** and **4** present thus similar behaviors as **1** and **2**. Indeed, the potential of the first oxidation is similar to that of the mononuclear complex $\{(phen)_2Ru\text{-}PHEHAT\}^{2+}$ and therefore is attributed to the abstraction of one electron from the Ru(II) at the core of the dendritic species. As the second oxidation wave involves three electrons, it is attributed to the three peripheral Ru(II) ions. The oxidation potential is indeed similar to that of $\{HAT\text{-}Ru(phen)_2\}^{2+}$ or $\{HAT\text{-}Ru(bpy)_2\}^{2+}$ in agreement with this assignment. As discussed for the dinuclear complexes, the level of the dπ orbital of the three external Ru(II) centers is thus more stabilized than that of the central Ru(II) ion.

In reduction, two waves are observed for each complex (from 0 to −1.20 V/SCE) and are attributed to two successive additions of one electron on one PHEHAT ligand. Indeed, the first and second reduction potentials are not enough cathodic to reduce a phen ligand (for $Ru(phen)_3^{2+}$, $E_{red} = -1.35$ V/SCE). This differs from tpphz based complexes for which the second electron is added on the phen ligand.[18,19] The two reduction processes for **1**−**4** (between −0.68, −0.70

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Table 3. Absorption and Emission Data in CH_3CN at 298 K in Aerated Solution for Complexes **1**−**4** and Reference Complexes[a]

	absorbance λ_{max}, nm ($\epsilon/10^3$ M^{-1} cm^{-1})		emission[g] λ_{max}/nm
	UV	vis	
$\{Ru(phen)_3\}^{2+}$[b]	262	446 (18)	604
$\{tpphz\text{-}Ru(bpy)_2\}^{2+}$[c]	246, 284, 361, 380	450 (19.7)	616
$\{HAT\text{-}Ru(bpy)_2\}^{2+}$[d]	282	420, 480^{sh}	703
$\{HAT\text{-}Ru(phen)_2\}^{2+}$[d]	262	420, 480^{sh}	694
$\{(phen)_2Ru\text{-}PHEHAT\}^{2+}$[e]	264, 278^{sh}, 312^{sh}, 354^{sh}, 370	438	662
$\{(bpy)_2Ru(\mu\text{-}tpphz)Ru(bpy)_2\}^{4+}$[f]	244, 281, 351, 370	442 (36.1)	690
$\{(bpy)_2Ru(\mu\text{-}HAT)Ru(bpy)_2\}^{4+}$[d]	250, 280	410, 470, 562	>800
1	261, 288^{sh}, 309^{sh}, 330^{sh}, 368	420^{sh}, 444 (28.1), 475^{sh}	706
2	264, 280, 309^{sh}, 327^{sh}, 368	422^{sh}, 445 (31.1), 476^{sh}	714
$\{Ru[(\mu\text{-}tpphz)Ru(bpy)_2]_3\}^{8+}$[f]		440 (71.6)	745
3	262, 285^{sh}, 307^{sh}, 328^{sh}, 368	427^{sh}, 454 (72.3), 479	708
4	252, 281, 309^{sh}, 328^{sh}, 368	426, 454 (66.1), 480	716

[a] Measurements made with solutions 1×10^{-5} mol dm^{-3} in complex. [b] Reference 31. [c] Reference 19. [d] Reference 20. [e] Reference 14. [f] Reference 18. [g] Corrected for the instrument response, excitation at 450 nm. sh = shoulder.

V/SCE and −1.06, −1.09 V/SCE) appear at the same potentials for both types of complexes and involve one electron for the dinuclear complexes and three for the tetranuclear compounds. At a potential more negative than −1.20 V, no reliable data could be obtained, probably due to the adsorption of reduced species onto the surface of the working electrode. The same behavior was observed in DMF, a solvent used by other authors to minimize adsorption processes.[18] The first reduction potentials for the PHEHAT complexes reveal an anodic shift from mononuclear to polynuclear species, thus from −0.84 V/SCE for $\{(phen)_2Ru\text{-}PHEHAT\}^{2+}$ to −0.69 V/SCE for the polynuclear compounds ($\Delta E_{red} = 0.15$ V). This shift is rather small. Indeed, previous studies on polynuclear complexes based on the HAT ligand have shown that the complexation of a second Ru(II) ion to the bridging HAT induces an important stabilization of the π^* orbital centered on the HAT ligand,[20,22] which is responsible for the anodic shift ($\Delta E_{red} = 0.37$ V) of the reduction of the HAT, going from −0.86 V/SCE for $\{HAT\text{-}Ru(phen)_2\}^{2+}$ to −0.49 V/SCE for $\{(phen)_2Ru(\mu\text{-}HAT)Ru(phen)_2\}^{4+}$. Such an effect, although less important, has also been observed with tpphz based complexes:[23] the first reduction potential at −1.00 V/SCE for the mononuclear complex $\{tpphz\text{-}Ru(phen)_2\}^{2+}$ is shifted to −0.78 V/SCE for the dinuclear species $\{(phen)_2Ru(\mu\text{-}tpphz)Ru(phen)_2\}^{4+}$ ($\Delta E_{red} = 0.22$ V).

In conclusion, from a comparison of the anodic shifts induced by the complexation of a second metal ion on the first reduction wave of the bridging ligand, it appears that the electronic communication increases from PHEHAT to tpphz to HAT.

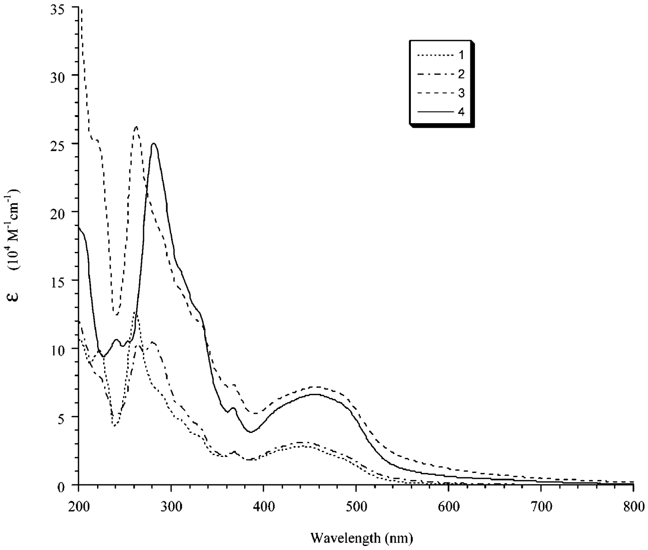

Figure 6. Absorption spectra of **1**−**4** in acetonitrile at room temperature.

Absorption and Emission Properties. The absorption data for complexes **1**−**4** are collected in Table 3, and data for other complexes are also included for comparison purposes. The absorption bands in the visible (Table 3, Figure 6) can be assigned to MLCT transitions Ru → phen, Ru → PHEHAT, Ru → HAT, or Ru → bpy, whereas the absorption bands in the UV region are assigned to LC transitions. In particular, the absorption around 370 nm in compounds **1**−**4** corresponds to transitions centered on the PHEHAT ligand, in agreement with the data of other PHEHAT-containing complexes.[14,24,25] As already reported for tpphz or 2,3-dpp complexes,[18,23,26] the molar absorption coefficients for polynuclear complexes are approximately proportional to the number of metal-based chromophores. For example, the molar extinction coefficient of **2** and **4** at 444 nm are 31100 and 64850 M^{-1} cm^{-1}, respectively, with quite similar absorption patterns in the spectra (Figure 6).

The luminescence spectra recorded in acetonitrile at room temperature show a typical emission originating from one luminophore for complexes **1**−**4** (λ_{max} in the range of 706−716 nm). It has been tested that the emission maximum is independent of the excitation wavelength. For polynuclear Ru(II) polyazaaromatic complexes, several authors reported the occurrence of an internal energy transfer process between different chromophores. Such intramolecular processes take place from the upper excited state to the lowest one, and

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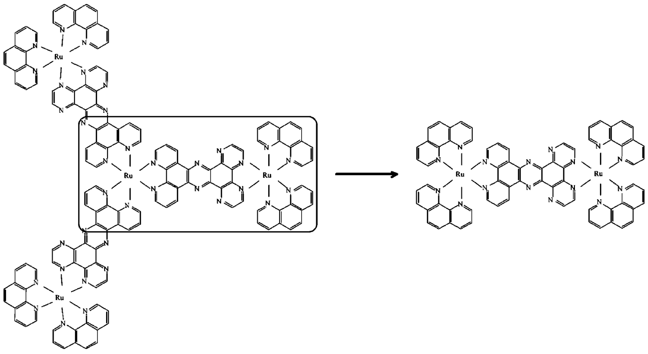

Figure 7. Schematic representation of a dinuclear subunit **1** in dendritic compound **3**.

thus, only the luminescence from this latter state is observed if the transfer is 100% efficient.[13,27,28] A similar energy transfer process is probably present in the complexes **1**−**4** as suggested by the emission data.

Indeed, complex **1**, a dinuclear species, exhibits luminescence at 706 nm in acetonitrile. This value should be compared with the emission maxima of each constitutive monometallic subunit, i.e., $\{(\mathrm{phen})_2\mathrm{Ru\text{-}PHEHAT}\}^{2+}$ ($\lambda_{\max} = 662$ nm)[14] and $\{\mathrm{HAT\text{-}Ru(phen)_2}\}^{2+}$ ($\lambda_{\max} = 694$ nm).[20] The emission maximum of **1** (706 nm) is close to that of $\{\mathrm{HAT\text{-}Ru(phen)_2}\}^{2+}$ and much more bathochromic than the emission maximum of $\{(\mathrm{phen})_2\mathrm{Ru\text{-}PHEHAT}\}^{2+}$. The emission of **1** originates thus from an excited state involving the Ru on the HAT part of the PHEHAT bridging ligand. This is clear-cut evidence for the occurrence of an internal energy transfer from the metallic subunit chelated to the phen part to the metallic subunit chelated to the HAT part of the PHEHAT ligand.

As complex **2** has an emission maximum at 714 nm, close to the emission maximum of $\{\mathrm{HAT\text{-}Ru(bpy)_2}\}^{2+}$,[20] the same arguments can be followed, which show again the presence of an energy transfer from one metallic subunit to the other.

Compounds **1** and **2** can be regarded as subunits of the dendritic compounds **3** and **4**, respectively (Figure 7). Complex **3** exhibits an emission maximum at 708 nm which, by comparison to **1** and $\{\mathrm{HAT\text{-}Ru(phen)_2}\}^{2+}$, can be attributed to the emission of the peripheral metallic units (MLCT from peripheral Ru to the HAT part of the PHEHAT). Thus, in dendrimer **3**, the energy transfer process takes place from the inner to the outer metallic units of the tetranuclear compound. Complex **4** exhibits the same behavior as **3**.

Absence of Spectroelectrochemical Correlation. Since we have the absorption, emission, and electrochemical data, we can check whether **1**−**4** follow the well-known spectroelectrochemical correlation. It is known indeed that if the orbitals involved in the electronic transitions are the same as those involved in electrochemistry, there is an excellent correlation between the spectroscopic and electrochemical properties, as evidenced by Meyer and co-workers for most ruthenium polypyridyl complexes.[29,30] It turns out that complexes **1**−**4** do not follow such a spectroelectrochemical correlation (Figure 8). This means that some orbitals involved in the spectroscopic processes are different from those involved in the electrochemical processes. This is easily understood on the basis of the present data. Indeed, the most bathochromic chromophore or luminophore corresponds to a Ru chelated on the HAT side of the bridging ligand whereas, in electrochemistry, the first oxidation process involves a Ru chelated on the phen part of the PHEHAT bridging ligand.

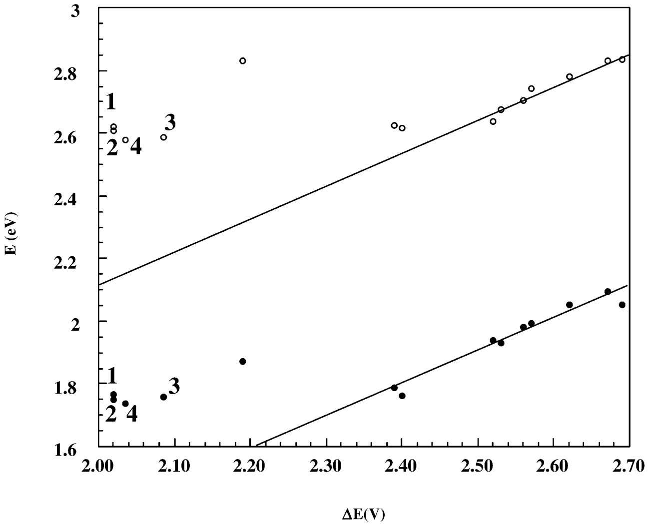

Figure 8. Spectroelectrochemical correlation for a series of ruthenium(II) complexes. Energy of the MLCT transition [in absorption (○) and in emission (●)] as a function of the difference between the oxidation and the reduction potentials (Δ*E*). From left to right: **1**, **2**, **4**, **3**, $[\mathrm{Ru(phen)_2\text{-}PHEHAT}]^{2+}$, $[\mathrm{Ru(phen)_2HAT}]^{2+}$, $[\mathrm{Ru(bpy)_2HAT}]^{2+}$, $[\mathrm{Ru(HAT)_2phen}]^{2+}$, $[\mathrm{Ru(TAP)_2bpy}]^{2+}$, $[\mathrm{Ru(TAP)_2phen}]^{2+}$, $[\mathrm{Ru(TAP)_2dppz}]^{2+}$, $[\mathrm{Ru(phen)_3}]^{2+}$, $[\mathrm{Ru(HAT)_2TAP}]^{2+}$, $[\mathrm{Ru(TAP)_3}]^{2+}$. From refs 14−20.

In conclusion, in this work the different consequences and effects of using a nonsymmetrical bridging ligand such as the PHEHAT for the construction of polynuclear complexes are evidenced on the methods of synthesis as well as on the spectroscopic properties in NMR, absorption, emission, and electrochemistry. From these data, as explained above, an internal energy transfer from one metallic subunit to the other has been evidenced, and no spectroelectrochemical correlation is expected.

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