Supplementary Information

Near-Infrared Luminescence from Visible-Light-Sensitized Ruthenium(II)-Neodymium(III) Heterobimetallic Bridged Complexes Containing Alkoxy(silyl) Functional Groups

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	NdL ³ complex		RuL ¹ –NdL ³ complex		
Molecular unit	$\delta({}^1J_{ ext{H-C}})$ /	H/C	$\delta({}^{1}J_{ ext{H-C}})$ / ppm	$\delta(^{2,3}J_{ ext{H-C}})$ /	H/C
	ppm			ppm	
Propyl chain	0.83/10.4	11/11	0.85/11.1		11/11
	1.90/26.5	10/10	1.91/27.8		10/10
	3.57/47.2	9/9	3.59/48.0		9/9
Methoxysilyl groups	3.57/58.0	12/12	3.57/49.7		12/12
Thenoyl rings of the β- diketone	7.19/128.5	2/2	7.53/131.3		2/2
	7.79/133.1	3/3	9.08/132.1		3/3
	7.75/135.1	1/1	7.97/132.1		1/1
bpy ligand (ring I)			8.19/125.5		3/3
			7.80/139.6		4/4
			7.55/152.9		6/6
			7.29/129.0		5/5
bpy ligand (ring II)			8.15/125.5		III/III
			7.70/139.5		IV/IV
			7.38/152.4		VI/VI
			7.18/128.6		V/V
bpmd ligand			7.15/125.6		IV′/IV′
			7.65/160.2		V′/V′
			8.72/158.4		III′/III′
				7.65/125.6	V′/IV′
				7.65/163.1	V′/I′

Table S1. Nuclear magnetic resonance (NMR) data of the complexes extracted from heteronuclear single quantum correlation (HSQC) and heteronuclear multiple bond correlation (HMBC) NMR correlations

bpy: 2,2'-bipyridine; bpmd: 2,2'-bipyrimidine.



Figure S1. Synthesis routes of the mononuclear precursors, \mathbf{RuL}^1 (*i*), \mathbf{RuL}^2 (*ii*) and \mathbf{NdL}^3 (*iii*). Numbering of the hydrogen and carbon atoms are identified as blue labels in \mathbf{NdL}^3 .



 NdL^4

Figure S2. Synthesis route of the mononuclear precursor NdL⁴.



Figure S3. FT-Raman scattering spectra of (a) NdL³, RuL¹–NdL³ and RuL¹ (red, blue and black lines, respectively);
(b) NdL⁴, RuL²–NdL⁴ and RuL² (red, blue and black lines, respectively).

NdL³ complex

Figure S4a shows the ¹H NMR spectrum of the NdL³ complex. In this case, only the enhanced nuclear relaxation effect was observed, and consequently, a broadening in the resonance lines of the hydrogen atoms bonded to the thenoyl rings was observed. The characteristic signals of the thenoyl ring were observed at 7.79, 7.75 and 7.19 ppm. A good resolution and the signal multiplicity of the three doublets observed are in agreement with the thenoyl rings. Propyl chain signals were observed at 3.57, 1.90 and 0.83 ppm. Figures S4b and S4c show the selective TOCSY1D NMR experiment. The characteristic spin system for the thenoyl rings units was observed by irradiation at 7.19 ppm (H-2) and identified in the same spin system of the H-1 at 7.74 and H-3 at 7.79 ppm with a $J_{\text{H-H}}$ in the range of 3.4-4.9 Hz, characteristic of the *ortho* relationship. For the methoxysilyl group, two signals were observed by irradiation in H-10 (observed at 1.90 ppm), a broad signal at 0.79 ppm, corresponding to H-11 nearest to the silicon atom and a line at 3.57 ppm, ascribed to H-9. From TOCSY1D data, the signal observed at 1.90 ppm corresponds to H-10 in the same spin system of the propyl chain of the NdL³ complex. The hydrogen of the methoxysilyl group could not be unequivocally determined due to the strong paramagnetic effect, which promotes the broadening of the signal observed at 3.57 ppm. Therefore, the signal ascribed to H-9 could overlap the methoxysilyl group signal, hindering the selective hydrogen irradiation.



Figure S4. ¹H NMR of the **NdL**³ complex (600 MHz, CDCl₃-*d*) (a) full spectrum; TOCSY1D NMR spectra irradiated at (b) 7.19 ppm and (c) 1.90 ppm. *CDCl₃ and H₂O at 7.3 and 4.6 ppm, respectively.

In ${}^{1}H{}^{13}C{}$ -HSQC NMR experiments, Figure S5a shows the H/C correlation for the different atoms, e.g., the signals at 0.83/10.4, 1.90/26.5 and 3.57/47.2 ppm (yellow) were ascribed to the H/C for the 11, 10 and 9, respectively. It is worth noting that the correlation of the H/C (12/12) at 3.76/58.0 ppm corresponds to the methoxysilyl groups. Figure S5b displays the H/C correlation ascribed to the thenoyl rings in aromatic region. Table S1 brings the assignment of the H/C correlations as well as the chemical shift values.



Figure S5. ${}^{1}H{}^{13}C{-HSQC}$ NMR spectra of the NdL³ complex (600 MHz, CDCl₃-*d*): (a) aliphatic region; (b) aromatic region. Assignment and numbering of H/C atoms are given with blue numbers.

RuL¹-NdL³ complex

The ¹H NMR spectrum of the RuL^1 -NdL³ heterobimetallic complex is exhibited in Figure S6 (structure in Scheme 1(*i*)). The aromatic region displays several lines due to the presence of the Ru related portion. Lines broadening is also observed as a consequence of the paramagnetic ion neodymium(III) present in the heterobimetallic complex.¹



Figure S6. ¹H NMR spectrum of RuL¹–NdL³ complex (600 MHz, MeOD-*d*₄).

Figures S7a-d and S7e show the selective TOCSY1D NMR experiment obtained for the aromatic and aliphatic region, respectively. The spin system of the thenoyl rings (from the TTA-Si ligands) was identified by irradiation at 7.97 ppm, (H-1) and the correlation with the H-2 and H-3 atoms at 7.53 and 9.08 ppm, respectively, was also observed. A splitting of the H-1 line was observed with J_{H-H} of the 3.8 Hz, characteristic of the doublet in *ortho* position. The hydrogen atoms of the propyl chain from the TTA-Si ligands were identified by irradiation of the H-11, at 0.85 ppm, and the neighboring hydrogen atoms H-10 and H-9 at 1.91 and 3.59 ppm were observed, respectively. The hydrogen of the bipyrimidine bridging ligand was also identified and shown in Figure S7d. By selective irradiation in the broad signal at 7.65 ppm (attributed to H-III' and H-IV' respectively) is observed. These results confirmed that both bpmd and TTA-Si ligands were coordinated to the neodymium(III) ion. Broadened lines due to the paramagnetic relaxation enhancement were observed for the bpmd ligand, confirming the

formation of the **RuL¹–NdL³** heterobimetallic complex.¹ In order to identify the lines of the bpy ligand, the TOCSY1D experiments were also performed and shown in Figures S7b-c. The signal of the H-4 observed at 7.80 ppm was selectively irradiated, and four signals were observed in the same spin system, at 8.19, 7.55 (broadened signal) and 7.29 ppm, attributed to H-3, H-6 and H-5, respectively. The splitting value of $J_{\text{H-H}}$ observed is characteristic of the aromatic rings. However, the bpy ligand has two aromatic rings and they are not magnetically equivalent. In this way, the second aromatic ring of the bpy ligand was also identified by selective irradiation of the H-IV at 7.70 ppm (Figure S7c), the correlations in the same spin system were observed with signals at 8.15, 7.38 and 7.18 ppm, assigned to H-III, H-VI and H-V, respectively. The results obtained from the TOCSY1D data clearly show the formation of the heterobimetallic complex, as well as the presence of the bpy ligands coordinated to the ruthenium.



Figure S7. TOCSY1D NMR spectra of the RuL^1 -NdL³ complex (600 MHz, MeOD- d_4) irradiated at (a) 7.97 ppm, (b) 7.80 ppm, (c) 7.70 ppm, (d) 7.65 ppm and (e) 0.85 ppm.

Finally, the structural characterization for the **RuL¹–NdL³** proposed in Scheme 1(*i*) was complemented by ¹H{¹³C}-HSQC and ¹H{¹³C}-HMBC NMR experiments (Figures S8 and S9, respectively). All the values of the chemical shift (H/C) observed from the ¹*J*_{H-C} and ^{2,3}*J*_{H-C} coupling in the correlation map are shown in Table S1. Here we can highlight the most important ¹*J*_{H-C} correlation map observed for the methoxysilyl groups (H/C 12) observed at 3.57/49.7 ppm.



Figure S8. ${}^{1}H{}^{13}C{}-HSQC$ NMR spectra of the **RuL**¹–NdL³ complex (600 MHz, MeOD-*d₄*): (a) aliphatic region; (b) aromatic region. The numbering of H/C atoms is given for the complex and present in both spectra.

From ${}^{1}H{{}^{13}C}$ -HMBC data (Figure S9), in addition to the long-range correlations, it was possible to obtain the chemical shift of the quaternary carbon atom, such as H-V'/C-IV' at 7.65/125.6 ppm, and H-V'/C-I' at 7.65/163.1 ppm of the bipyrimidine ligand. Thus, the structural elucidation of the **RuL**¹–**NdL**³ complex was made possible by NMR data, confirming the proposed structure in Scheme 1 (*i*) in particular the presence of unreacted methoxysilyl groups.



Figure S9. ${}^{1}H{}^{13}C{}-HMBC$ NMR spectrum of the **RuL**¹–NdL³ complex in the aromatic region (600 MHz, MeOD- d_4).



Figure S10. FTIR spectra from 4000 to 650 cm⁻¹ for the (a) NdL³, RuL¹–NdL³ and RuL¹; (b) NdL⁴, RuL²–NdL⁴ and RuL² complexes. All analyses were carried out as KBr pellets.

Photophysical properties

Broad emission bands were observed in emission spectra that could be ascribed to the ruthenium(II) ³MLCT emission to the ground state.² These bands are observed at 665 nm (ca. 15038 cm⁻¹) and 610 nm (ca. 16393 cm⁻¹) for **RuL¹–NdL³** and **RuL²–NdL⁴**, respectively (Figure S11).



Figure S11. Room temperature excitation (black curves) and emission (red curves) spectra from (a) RuL^1 -NdL³ (monitoring at λ_{em} : 665 nm and λ_{ex} : 450 nm), (b) RuL^2 -NdL⁴ (monitoring at λ_{em} : 610 nm and λ_{ex} : 465 nm) complexes in solid state.

The variation in energy observed for ³MLCT may result from different π -donor or π -acceptor behavior of the ligands. As a consequence, the MLCT energy may shift, leading to variation in efficiencies for d-f energytransfer processes. Comparing with the results obtained from the precursors (**RuL**¹ and **RuL**², Figure S12), a blue shift is observed for both heterobimetallic complexes. Therefore, structure effects also play an important role together with the different π -donor or π -acceptor behavior of the ligands. The excitation spectra obtained for **RuL**¹–**NdL**³ and **RuL**²–**NdL**⁴ by monitoring the emission from ruthenium(II) ³MLCT state, were composed of bands assigned to the d $\rightarrow \pi^*$ ¹MLCT (metal-to-ligand charge transfer) transitions or transitions centred on ligands, as $\pi \rightarrow \pi^*$ transitions, in agreement with the UV-Vis results.



Figure S12. Room temperature excitation (black curves) and emission (red curves) spectra from (a) **RuL**¹ (monitoring at λ_{em} : 670 nm and λ_{ex} : 475 nm) and (b) **RuL**² (monitoring at λ_{em} : 620 nm and λ_{ex} : 465 nm) complexes in solid state.

References

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