

Lanthanide heterometallic molecular squares Ru_2-Ln_2 exhibiting sensitized near-infrared emission†

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New lanthanide heterometallic molecular squares functionalized with Ru-bipy antenna chromophore Ru_2-Ln_2 exhibit sensitized near-infrared emission upon photo-excitation of the Ru-centered antenna at 420 nm.

The construction of sensitizer-functionalized lanthanide complexes that exhibit strong luminescence in the near-infrared region is currently of great interest because of the developing application in organic liquid lasers, optical-fiber polymers, organic electroluminescent devices, and near-infrared immunoassays.^{1,2} It is postulated that the near-infrared luminescence is observed only when the lanthanide ions are excited indirectly by energy transfer from the triplet state of an incorporated chromophore (sensitizer).³ Investigations of sensitizer for the near-infrared lanthanide luminescence have been almost exclusively devoted to conjugated organic molecules. Only a few examples of near-infrared luminescence sensitized by transition metal compounds have been reported,⁴ although metal complexes always exhibit an MLCT-based triple excited state closely matching the receiving luminescent state of Nd^{III} and Yb^{III} .

Here, we report the lanthanide heterometallic molecular squares Ru_2-Ln_2 (Scheme 1) exhibiting sensitized near-infrared emission using $[Ru(2,2'-bipy)_2(4,4'-bipy)_2]^{2+}$ and $Nd(TTA)_3$ or $Yb(TTA)_3$ (TTA = 2-thenoyl trifluoro acetate) as building blocks. Such approach offers some advantages: (1) the synthetic effort is reduced, since only substructures are prepared and the modular strategy allows the synthesis of different aggregates from various building blocks; the energy transfer process can be studied over different linkages, and new information would be obtained; the rigid pre-organized Ru-corner makes the construction of molecular squares more general and predictable;⁵ (2) the Ru-bipy sensitizer

not only exhibits high intersystem-crossing quantum yield, but also enables excitation of Nd^{III} with visible light up to 500 nm; (3) the full coordination sphere of lanthanide ions and the bulky ligands could prevent the lanthanide ions coordinated to the solvent molecules and anions, which lead to effective radiationless transitions by vibration excitation of C–H or O–H bonds, and this results in negligible emission quantum yields.⁶

As expected, the heterometallic molecular squares $Ru-Nd$ **1**, $Ru-Yb$ **2** and $Ru-Gd$ **3** were prepared easily by simply refluxing the mixture of $Ln(TTA)_3 \cdot 2H_2O$ and $[Ru(bipy)_2(4,4'-bipy)_2]Cl_2$ (molar ratio = 1 : 1) in methanol solution.† The ESI-MS spectrum of complex **1** exhibits a prominent peak at m/z 770, corresponding to the major species $[Ru_2(bpy)_4(4,4'-bpy)_4Nd_2(TTA)_6(H_2O)]^{4+}$ cation, indicating that this discrete molecular square is stable in solution. The peaks at m/z 782.1 and 773.8 in the ESI-MS spectra of complexes **2** and **3**, also suggest the formation of molecular squares $[Ru_2-Yb_2]^{4+}$ and $[Ru_2-Gd_2]^{4+}$, respectively. Elemental analyses and spectroscopic characterization support the formula of relative heterometallic molecular square Ru_2-Ln_2 .

Upon excitation of the $Ru-Nd$ complex, Ru-bipy center luminescence was observed at 610 nm (Fig. 1) originating from the ³MLCT state.⁷ The luminescence spectrum was also measured for the $Ru-Gd$ complex, as a reference. It is clear to see that the luminescence intensity of the $Ru-Gd$ complex is ten times higher than that of the $Ru-Nd$ complex, and the Uv-vis absorptions of the two complexes are almost the same. Since the Gd^{III} has no energy level below 32000 cm^{-1} , therefore cannot accept any energy from the Ru-bipy triplet state.⁸ It is suggested that the lower luminescence intensity of the $Ru-Nd$ complex is contributed to the energy transfer from the Ru-bipy triplet state to the excited state of Nd^{III} center. The intensity of Ru-center emission of the $Ru-Yb$ complex **2** also supports the energy transfer from the Ru-bipy triplet state to the excited state of Yb^{III} center.

To test this approach, emission spectrum in the near-infrared region is also measured for the $Ru-Nd$ complex by exciting the complex at 420 nm (Fig. 2), the presence of strong emission bands at 900, 1059, and 1333 nm corresponding to the $^4F_{3/2} \rightarrow ^4I_{9/2}$, $^4I_{11/2}$,

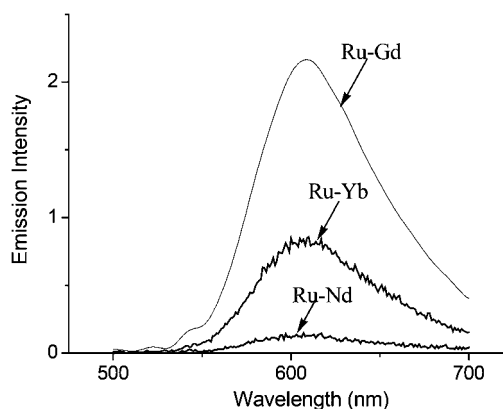
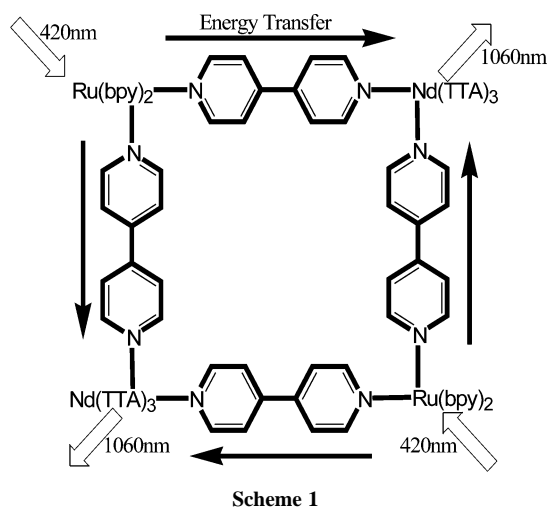


Fig. 1 Emission spectra of the $Nd-Ru$, $Ru-Yb$ and $Gd-Ru$ complexes upon excitation at 420 nm.

† Electronic supplementary information (ESI) available: ESI-MS spectra of complexes **1** and **2** in pdf format. See <http://www.rsc.org/suppdata/cc/b4/b403519d/>

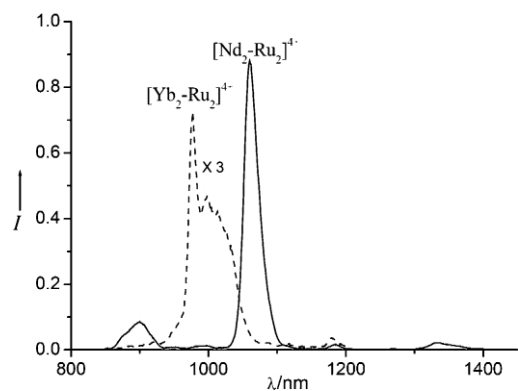


Fig. 2 The NIR luminescence spectrum of Ru–Nd and Ru–Yb upon excitation at 420 nm

and $^4I_{13/2}$ transitions of Nd^{III} , respectively,⁹ indicates that the Nd^{III} ions are excited by the 3MLCT (metal-to-ligand charge transfer) state of the Ru-bpy sensitizer. In the same way, no evident emission band were observed in the near-infrared region for the complexes $[Ru(bipy)_2(4,4'-bipy)_2]Cl_2$ and $Nd(TTA)_3$. Emission in the near-infrared region of the Ru–Yb complex was also observed. In light of the competing antenna process, the energy transfer rates in Ru–Nd and Ru–Yb are rather high for a complete energy transfer. The energy transfer process is most likely to involve an electron-exchange mechanism¹⁰ that requires a physical overlap between the 4f orbital of the lanthanide ion and the ground state HOMO and LUMO of the antenna. Although the antenna ground state HOMO is localized on the Ru^{II} center,¹¹ which is further away from the lanthanide ions, the antenna excited state LUMO delocalizes on the terminal or bridge bipy which can be close to the lanthanide ions, since the 4,4'-bipyridine ligands bridge the lanthanide ions directly.

In summary, we show the new lanthanide-transition metal heterometallic molecular squares exhibiting sensitized near-infrared emission upon photoexcitation of functionalized Ru-bipyridine antenna chromophore at 420 nm. Macrocyclic NIR emitting compounds have played a crucial role in both the exploration of energy transfer theory and addressing contemporary issues in energy-transfer research, especially, when the emphasis in this field has shifted away from simple mono- and di-nuclear NIR emitting species and focused interest on multinuclear supramolecular species.

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Notes and references

‡ *Synthesis of complexes 1–3.* Mixing and refluxing the ligand $Ru(bipy)_2(4,4'-bipy)_2$ (0.174 g, 0.2 mmol) and $Ln(TTA)_3 \cdot 2H_2O$ (0.2 mmol) for

5 h gave red solutions, which concentrated to 6 mL. After adding a saturated ethanol solution of $NaClO_4$, a reddish yellow precipitate was obtained. The product was then washed with water several times, dried in vacuum over P_4O_{10} . **Complex 1**, Anal. Calcd for $C_{128}H_{88}N_{16}O_{28}Cl_4F_{18}S_6Ru_2Nd_2 \cdot 2H_2O$: C, 43.9; H, 2.7; N, 6.4. Found: C, 43.9; H, 2.8; N, 6.2%. UV/vis [CH_3CN ; λ_{max}/nm ($\epsilon/dm^3 mol^{-1} cm^{-1}$): 242 (170 000), 286 (209 000), 360 (35 000), 422 (40 000). **Complex 2**, Anal. Calcd for $C_{128}H_{88}N_{16}O_{28}Cl_4F_{18}S_6Ru_2Yb_2 \cdot 2H_2O$: C, 43.2; H, 2.6; N, 6.3. Found: C, 42.8; H, 2.9; N, 6.1. UV/vis [CH_3CN ; λ_{max}/nm ($\epsilon/dm^3 mol^{-1} cm^{-1}$): 244 (164 000), 284 (200 000), 339 (43 000), 417 (35 000). **Complex 3**, Anal. Calcd for $C_{128}H_{88}N_{16}O_{28}Cl_4F_{18}S_6Ru_2Gd_2 \cdot 2H_2O$: C, 43.6; H, 2.6; N, 6.4. Found: C, 43.8; H, 2.8; N, 6.7. UV/vis [CH_3CN ; λ_{max}/nm ($\epsilon/dm^3 mol^{-1} cm^{-1}$): 248 (172 000), 288 (212 000), 339 (43 500), 423 (35 400).

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