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COMMUNICATION

Self-assembly of highly luminescent heteronuclear coordination cages

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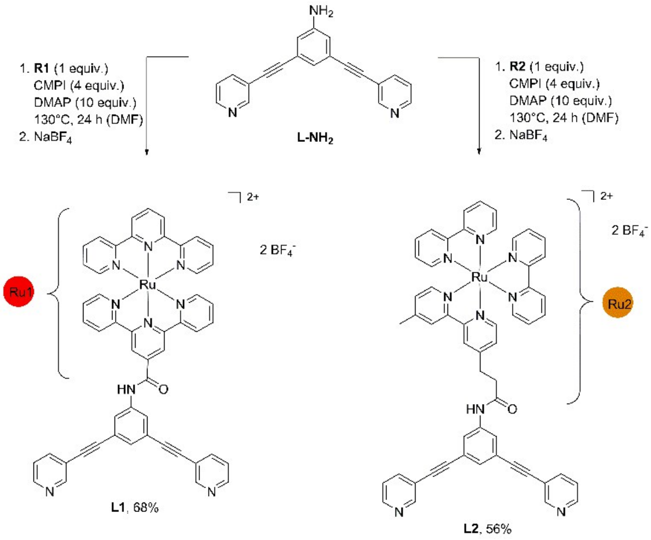
***Exo*-functionalized Pd_2L_4 cage compounds with attached Ru(II) pyridine complexes were prepared *via* coordination-driven self-assembly. Unlike most of the previously reported palladium(II) cages, one of these metallocages exhibits an exceptionally high quantum yield of 66%. The presented approach is promising to obtain luminescent coordination complexes for various applications.**

Metal-mediated self-assembly is a useful tool to design discrete two- and three-dimensional supramolecular coordination complexes (SCCs) with precise geometries and cavities.[1] These metal-based entities have attracted much attention for a variety of applications in molecular recognition,[2] catalysis[3] and medicinal applications[4] due to their interesting chemical-physical properties and guest-binding abilities. Especially, the development of luminescent SCCs for potential applications in chemosensing,[5] material science[6,7] and biological imaging[8,9] has gained increasing attention during the last years,[10] although it is still less explored. Despite the existence of some highly fluorescent coordination complexes,[6,11] the majority of metal-based self-assemblies are little- or non-emissive due to the quenching effect of heavy metal ions.[12]

An interesting research field of SCCs is the self-assembly of M_2L_4 (M = metal, L = ligand) cages because of their simple and highly symmetric structures.[13] In addition, the cages' properties can be easily altered by functionalizing the ligand framework.[14] Emissive properties of M_2L_4 metallocages have been discussed, yet examples of highly emissive Pd_2L_4 cages are rare.[15] The incorporation of luminescent groups, such as anthracene[16,17] and ruthenium pyridine complexes,[18] into the ligand framework resulted in palladium cages displaying low emission so far. Nevertheless, these results generate an increasing interest in tailored design of highly luminescent coordination cages. In this work, an approach is presented to increase the photo-physical properties of palladium cages by separating the luminescent tag from the emissive ligand coordinated to palladium ions. Inspired by previous investigations,[17] two Pd_2L_4 cage compounds ligated by bis(pyridyl) systems coupled to ruthenium complexes were synthesized and their photo-physical properties were investigated. A comparison is made between the Ru terpyridine ligand **L1** having no spacer and the ruthenium bipyridine ligand **L2** featuring an alkyl bridge as spacer between two emissive moieties.

First, the rigid bis(pyridyl) ligands **L1** and **L2** coupled to Ru(II) terpyridine and Ru(II) bipyridine, respectively, were synthesized *via* an amide bond formation (Scheme 1).



Scheme 1 Coupling of the ligand **L-NH2** with Ru(II) complexes **R1**/**R2** using the reagent CMPI, followed by precipitation with $NaBF_4$ to obtain Ru(II)-based ligands **L1**/**L2**.

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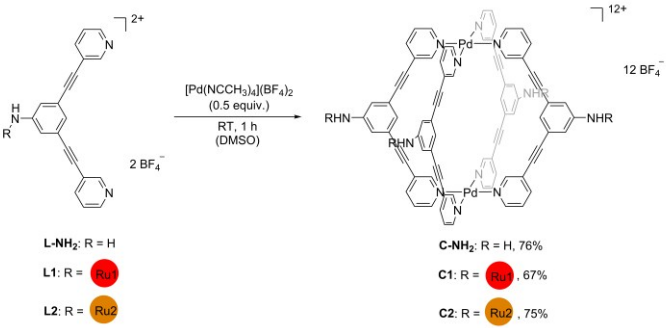
The amine-based ligand **L-NH₂** was coupled to [Ru(terpy)(terpy-4-COOH)]$(PF_6)_2$ **R1** and [Ru(bipy)$_2$(bipy-4'-CH_3-4-$(CH_2)_2$-COOH)]$(PF_6)_2$ **R2** using the coupling reagent 2-chloro-1-methylpyridinium iodide (CMPI) and DMAP as a base. After purification by column chromatography, the Ru(II) complexes **L1** and **L2** were precipitated by $NaBF_4$ in 68% yield as red solid and in 56% yield as orange solid, respectively. The complexes were characterized by ^1H, ^{13}C, ^{11}B, ^{19}F, and DOSY NMR spectroscopy, ESI-MS and X-ray crystallography (for details see ESI).

The coordination cages **C1**/**C2** were self-assembled by mixing the bidentate Ru(II)-based ligands **L1**/**L2** and the palladium precursor [Pd$(NCCH_3)_4$]$(BF_4)_2$ in a 2:1 ligand:metal ratio in DMSO at room temperature for one hour (Scheme 2). Additionally, the self-assembly of the previously described cage **C-NH₂**[8] is depicted in Scheme 2, in order to evaluate the synthesis and photo-physical properties of the cage compounds **C1** and **C2** compared to the amine-based cage. Notably, the bulky ruthenium complexes have no effect on the self-assembly reaction.



Scheme 2 Synthesis of the palladium(II) cages **C-NH₂**,[8] **C1** and **C2** *via* self-assembly using the bidentate ligands **L-NH₂**, **L1** and **L2** and the precursor [Pd$(NCCH_3)_4$]$(BF_4)_2$.

^1H NMR spectroscopy confirms the formation of the cage compounds. In ^1H NMR spectra (Fig. 1), the pyridyl protons H_a-H_d are significantly downfield shifted, particularly the signals of H_a and H_b experienced a shift of *ca*. 0.9 ppm. The terpyridine and bipyridine proton resonances of the attached ruthenium complexes are not influenced by the Pd-N coordination.

Additional proof of the successful self-assembly in solution is given by diffusion-disordered NMR spectroscopy (DOSY), since all proton signals of the cages reveal the same diffusion coefficient. The diffusion coefficients (D) of the ligands **L1** and **L2** and of the cages **C1** and **C2** in acetonitrile are approximately 6.9 x 10^{-10} m^2 s^{-1} and 3.3 x 10^{-10} m^2 s^{-1}, respectively (see Table S1, ESI). Thus, the ratios of D_{ligand}/D_{cage} are approximately 2:1, being in accordance with reported Pd_2L_4 systems.[8,19] The hydrodynamic radii r_s of **C1** and **C2** have been calculated to be 1.5 nm.

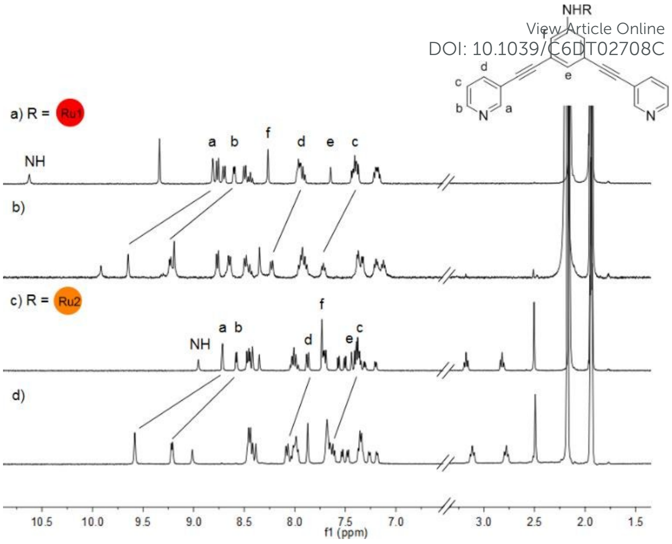


Fig. 1 Stacked ^1H NMR spectra (400 MHz, CD_3CN) of ligand **L1** (a), cage **C1** (b), ligand **L2** (c) and cage **C2** (d).

The molecular composition of the Pd_2L_4 cages **C1** and **C2** is further evidenced by ESI mass spectrometry showing isotopically resolved peaks for [**C**-nBF_4^-]$^{n+}$ (n = 4-6). For example, the ESI-MS analysis of cage **C2** reveals peaks at m/z = 744.3, 910.6 and 1160.3, which can be assigned to [**C2**-6BF_4^-]$^{6+}$, [**C2**-5BF_4^-]$^{5+}$ and [**C2**-4BF_4^-]$^{4+}$, respectively.

In order to predict the shape and size of the cages, a geometry optimization was performed using semi-empirical methods (PM6). Exemplarily, the molecular model of **C2** is depicted in Fig. 2. The optimized structure of **C2** exhibit a Pd···Pd distance of 1.1 nm, a distance between the opposing inner C-atoms of 1.2 nm and a span of 5.0 nm. The calculated shape and size is in agreement with previously reported Pd_2L_4 cages.[8,17] Suitable single crystals of the metallocages for X-ray diffraction could not be obtained.

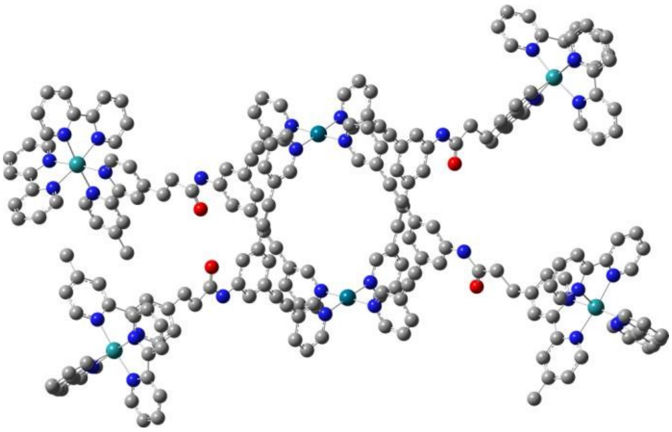


Fig. 2 Molecular model of cage **C2** (C grey, N blue, O red, Pd turquoise, Ru green).

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Both palladium(II) cages are stable under air and light in solution and in solid state. The compounds are soluble in acetonitrile, DMF and DMSO.

In order to assess the photo-physical properties of the metallocages with attached ruthenium(II) moieties, UV-Vis, excitation and emission spectroscopy were carried out on the Ru(II) complexes **R1**/**R2**, the ligands **L1**/**L2**/**L-NH$_2$** and the cages **C1**/**C2**/**C-NH$_2$**. The absorption and emission spectra of the compounds are depicted in Fig. 3 and Fig. 4, while the photo-physical parameters are presented in Table 1.

The absorption spectra of the metallocages are dominated by strong π-π* transitions of the highly conjugated ligands showing bands in the range of 250-350 nm. The UV-Vis spectra of the cages with conjugated ruthenium complexes exhibit an additional band in the vis region, **C1** (red solution) at 495 nm and **C2** (orange solution) at 460 nm. Overall, the cage compounds feature an approximately four-times higher extinction coefficient compared to their corresponding ligands resulting from the M$_2$L$_4$ composition.

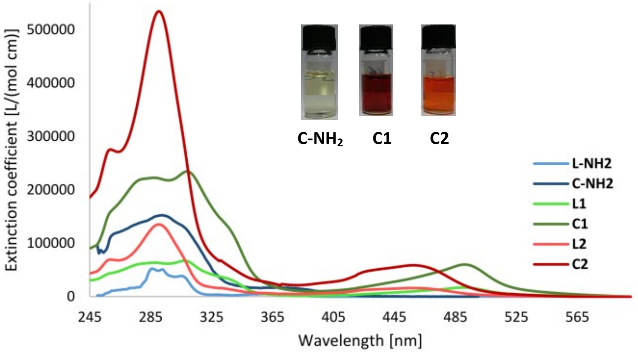

Fig. 3 UV-Vis spectra of ligands and cage compounds in DMSO (c= 10^{-5} – 10^{-6} M). Insets: Photographs of DMSO solutions of the cages.

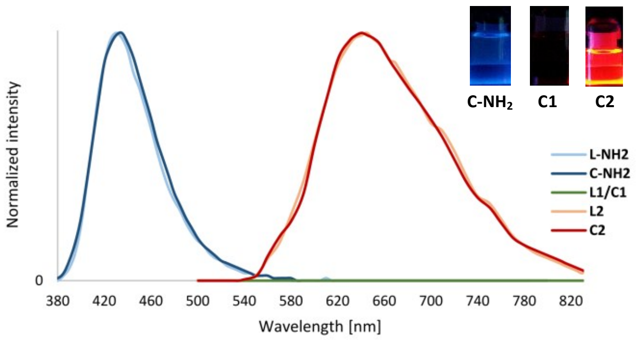

Fig. 4 Emission spectra of ligands and cage compounds in DMSO (c = 10^{-5} M, λ_{ex} = 260 nm). Insets: Photographs of solutions of the cages in DMSO under UV light irradiation (λ_{ex} = 365 nm).

The metallocages reveal interesting emissive properties, showing that the luminescence can be increased or decreased by altering the molecular structure of the ligand framework. Recently, we investigated the photo-physical properties of bis(pyridyl) ligands coupled to naphthalene and anthracene moieties *via* an amide bond.[17] These systems possess less emissive properties due to a disruption of the chromophoric system in the excited state by bending the amide bond.

Table 1 Photo-physical parameters of ruthenium complexes, ligands and palladium cages (DMSO, λ_{ex} = 260 nm)

Compound	λ_{max}(abs) [nm]	ε_{max} [L mol^{-1} cm^{-1}]	λ_{max}(em) [nm]	Φ [%]
R1	278, 317, 492	58400	--	--
R2	292, 456	79400	645	12
L-NH$_2$	293, 305, 360	52200	430	52
C-NH$_2$	293, 371	152200	435	17
L1	290, 303, 493	64600	--	--
C1	289, 311, 494	232200	--	--
L2	293, 461	134000	640	88
C2	293, 462	523900	640	66

As expected, ligand **L1** and the respective cage **C1** are not luminescent, although the amine ligand **L-NH$_2$** is highly emissive by itself. Notably, the red solution of **R1** is not luminescent at room temperature being in accordance with reports on similar ruthenium(II) terpyridine complexes.[20]

To avoid the predicted torsion of the amide bond, a spacer, namely an alkyl bridge, was inserted between the bis(pyridyl) ligand and the ruthenium moiety. Upon irradiation at 260 nm, ligand **L2** emits strong orange luminescence showing a broad band in the emission spectrum at λ_{max} = 640 nm with an exceptional high quantum yield of 88%. However, by irradiation at lower energies at 460 or 495 nm the quantum yield is significantly reduced to 6 and 4%, respectively. The amine ligand **L-NH$_2$** shows blue fluorescence at λ_{max} = 430 nm with a quantum yield of 52%. Interestingly, cage **C2** exhibits one of the highest quantum yields (Φ = 66%) at λ_{max} = 640 nm reported for supramolecular coordination complexes.[6,11a-b] The coordination cage **C-NH$_2$** features a fluorescence quantum yield of 17%. In agreement with previous reports, in both cases **C2** and **C-NH$_2$** the luminescence is significantly reduced by coordination of the ligand to palladium ions. Notably, cage **C2** displays a higher emission compared to the amine-based cage, while cage **C1** exhibits lower luminescence.

In summary, two palladium(II) coordination cages coupled to ruthenium(II) pyridine complexes *via* an amide bond have been synthesized by self-assembly. In order to obtain bright luminescence, the ruthenium complex was separated from the coordinating bis(pyridyl) ligand using an alkyl spacer. The photo-physical properties of the Pd$_2$L$_4$ cage coupled to a ruthenium complex with and without spacer were compared. Remarkably, the palladium cage without spacer is non-emissive, while the other one features a quite high quantum yield of 66%, making it one of the highest luminescent metallosupramolecular complexes known to date. The applied approach is promising to further design highly emissive metallocages for potential applications as biological labels and chemosensors, among others.

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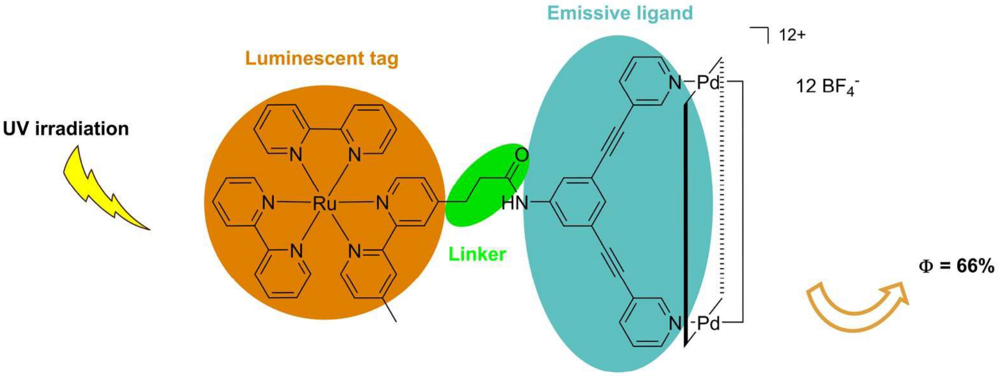

A promising approach is described to enhance the luminescence of palladium(II) cages resulting in one of the highest fluorescence quantum yields for metallosupramolecular complexes.

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