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Luminescence of amphiphilic Pt(II) complexes controlled by confinement

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Dedication ((optional))

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Abstract: The formation of hybrid silica-based systems to study the effect of the confinement on the emission properties of self-assembled platinum(II) complexes is reported. The complexes behave as a surfactant since they possess a hydrophobic moiety and, on the ancillary ligand, a relatively long hydrophilic chain terminated with a positively charged group. The compounds, soluble in water, selfassemble, even at very low concentration, in supramolecular structures which display an orange luminescence. The properties of the assemblies have been studied in detail and in order to stabilize these supramolecular architectures and to enhance their emission properties hybrid silica porous nanoparticles have been prepared. In particular the Pt(II) complexes have been employed as co-surfactant for the template formation of mesoporous silica nanoparticles (MSNs) via a sol gel synthesis. Interestingly, upon encapsulation in the silica pores, the platinum aggregates exhibit an emission profile similar in energy to the complexes assembled in solution, but the photoluminescence quantum yields of the hybrid systems are significantly higher (up to 45%), and the excited state lifetimes much longer than those recorded in solution. Such enhancement of the photophysical properties together with the possibility to process the hybrid silica nanomaterials can pave the way to new type of emitters.

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Introduction

The design of amphiphilic molecules incorporating luminescent transition metal complexes (TMCs) has been a growing field of research.^[1] The advantage of amphiphilic TMCs is that they combine the features of ordinary surfactant molecules with those of TMCs and interesting emerging properties, not present in the simple single components, can be used in different applications. For example, amphiphilic TMCs have been studied for their electric,^[2] magnetic,^[3] catalytic,^[4] and luminescence properties.^[5] For some amphiphilic emitters, an enhancement of the photoluminescence quantum yield (PLQY) and elongation of their excited state lifetime have been observed. Even energy transfer processes in mixed metal assemblies have been reported, when two different TMCs are used as structure directing agent (surfactant), leading to a control of the emission colour.[5a, 5c, 6] Regarding amphiphilic Pt(II) complexes, reports related to applications in catalysis, ^[7] or on the synthesis of aggregates, ^[8] as well as their spectroscopic properties in micellar systems have appeared in the literature. Interestingly, besides the aggregation induced by the amphiphilic nature of the complexes, the Pt(II) compounds can undergo to the formation of a Pt---Pt bond [9] resulting in new photophysical properties.^[10]

A way to stabilize the aggregates, as well as to control their size, could be their entrapment in porous materials. ^[11] Mesoporous silica nanoparticles (MSNs) can therefore constitute an interesting host due to their tuneable shape and pore size, large surface area, their narrow pore distribution, and their high pore volume.^[12] There are several ways to encapsulate TMCs in porous silica. For instance, a direct covalent bonding between silica and a complex is possible,^[12-13] but the absence of selective binding sites inside the pores as distinct from the outer surface (both the pores and the outer surface contain only silanol groups), makes the regioselectivity difficult to control. Another way to load TMCs into silica is by sublimation, but the problem is that often charged or heavy system are not volatile and therefore this technique is relatively complicated to perform. An interesting strategy relies on the use of the metal complexes as template (or embedded in the template) for the formation of mesoporous silica, resulting in their entrapment in the pores. This encapsulation can lead to an enhancement of their stability and/or of their photophysical properties, due to the increase rigidity of the system vs solution, isolation from the environment and even interaction with the silica wall that can prevent or reduce vibrational modes. Our group has already successfully encapsulated amphiphilic Ru(II) and Ir(III) complexes into mesoporous silica nanoparticles, using them as structure directing agent (surfactant), for enhancement of

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luminescent properties or for controlling the emission colour. [5-6] Prodi et al. have used a similar approach to entrap luminescent metal complexes in silica nanoparticles for bio-analytical applications.^[14] Herein, we report the synthesis and the spectroscopic properties of surfactant-type platinum complexes. We describe luminescent supramolecular self-assembled structures and their use as a co-surfactant in the template synthesis of porous silica nanoparticles. To achieve the amphiphilic design Pt(II) complexes containing a terdentate N^N^N dianionic ligand resulting in a hydrophobic moiety, are combined with a coordinated pyridine para-substituted with an alkyl chain terminated with a pyridinium substituent acting as the hydrophilic moiety (Scheme 1). The assemblies and the silica containing Pt complexes have been investigated in details and the enhancement of the emission properties of the Pt complexes, once entrapped in the silica pores, is described.



Scheme 1. Synthetic route for the preparations of complexes **5a-e**. For sake of clarity the complex **5a** contain a C2 chain, the **5b** a C5, the **5c** a C8, the **5d** a C11 and the **5e** a C14, between the pyridine and the prydinium moieties.

Results and Discussion

The syntheses of all the ligands are summarised in scheme S1, while scheme 1 shows the final complexation step. ^{[10b,} ^{15]} The use of different carbon chain lengths was dictated by two reasons. Firstly, it is known that pyridinium salts are very efficient phosphorescence quenchers, due to their very strong electron withdrawing behaviour.^[16] Therefore, the distance between the complex and the quencher could affect the emission properties. Secondly, we wanted to study the supramolecular assembly of the molecules and investigate the correlation between the nature and morphology of the assembly and the luminescence properties of the system. A long carbon chain should lead to an enhanced stability of the assembly and even a different shape or size than a short hydrophobic chain. The structures of the different ancillary ligands are shown in Scheme S2, and all the characterisations (¹H, NMR, ¹³C NMR, ¹⁹F NMR, HR-MS spectra) are depicted in Figures S1-S14.

The absorption spectra of the complexes, in water solutions at a concentration of $5 \cdot 10^{-5}$ M at room temperature, are shown in Figure 1. They all present the same profile, with a sharp band at 224 nm (ϵ between 30000 and 25000 L·mol⁻¹·cm⁻¹) and two other bands at lower energy (255 nm, ϵ between 12000 and 9000 L·mol⁻

¹·cm⁻¹) attributed to the triazole moieties. In addition, a shoulder at 295 nm, (¿ between 5000 and 3000 L·mol⁻¹·cm⁻¹) raises from pyridine located transitions. In general, all these transitions are assigned to π - π^* or ligand centred (¹LC) and metal-perturbed ligand centred states. Broad, less intense bands between 350 nm and 500 nm (¿ between 1500 and 1000 L·mol⁻¹·cm⁻¹) are attributed to $d_{z^2} - \pi^*$, metal to ligand charge transfer (¹MLCT) as well as to the metal-metal-ligand charge transfer, ¹MMLCT transitions rising from the formation of aggregates already present at this concentration. Indeed, the formation of a metallophilic interaction (Pt-Pt) results in the destabilization of the dz2 orbitals and the new HOMO is raised in energy as also observed in the low energy emission spectra (Figure 2) attributed to ³MMLCT transitions. Indeed due to the presence of the heavy atom, the Pt ion, the strong spin orbit coupling causes a very efficient intersystem crossing to the triplet state.



Figure 1. Absorption spectra of complexes 5a (black trace),5b (red trace),5c (blue trace), 5d (pink trace) and 5e (green trace) in water at 5.10⁻⁵ M.



Figure 2. Excitation (λ em = 600nm) and Emission (λ exc = 400nm) spectra of complexes **5a** (black trace), **5b** (blue trace), **5c** (-green trace), **5d** (red trace) and **5e** (orange trace) in water at 5:10⁻⁵ M. Inset, photographs of sample **5a** under UV light (λ _{Exc}= 366 nm in water, 10⁻³M, left; and 5:10⁻⁵ M, right).



Figure 3. Excitation (λ_{em} = 600 nm) and Emission (λ_{exc} = 400 nm) spectra of complexes 5a (black trace), 5b (blue trace), 5c (green trace), 5d (red trace) and 5e (orange trace) in solid state. Inset: image of sample 5a in solid state under UV light (λ_{exc} = 366 nm).

The emission and excitation spectra of all the complexes in water $(5 \cdot 10^{-5} \text{ M})$ and in the solid state are depicted in Figures 2 and 3. Strikingly, they display the same excitation and emission profiles independently of the state (solid or solution). All the excitation spectra display an intense band at 500 nm, which confirms the appearing of the ¹MMLCT transition induced by Pt---Pt interactions, and other bands at higher energy attributed to ¹MLCT or ¹LC transitions, as already discussed for the absorption spectra. The emission profiles show a broad, featureless band at 585 nm typical, for these type of Pt(II) complexes, to the aggregated form and attributed to ³MMLCT transitions as already reported for similar compounds. ^[10b, 17] In order to prove that such low energy emission is indeed due to aggregation a spectrum in dichloromethane, at the same concentration, has been recorded. This required an anion exchange of the chloride counterion with hexafluorophosphate, to obtain complexes soluble in dichloromethane (see SI). The emission spectrum exhibits a blue emission, due to the monomeric species, with bands at 461 nm, 489 nm and 525 nm as also observed in analogue complexes. ^{[17a,} ^{18]} All the complexes are therefore aggregated in water also at high dilution. The orange-red emission observed mirrors the strong electronic coupling between the platinum centres. The absence of shift in the emission maxima for the different compounds indicates that the length of the carbon chain on the ancillary pyridine does not have any influence on the luminescence energy. However, we see a correlation between the emission quantum yields and the length of the hydrophobic chain. Indeed, upon increasing the chain length the intensity of the luminescence increases (Table 1). In the series of the compounds going from complex 5a (n=0) to complex 5e (n= 12), the PLQY varies from only 1%, to 14%, in water solution. This change may result from two factors: i) the pyridinium can quench the platinum emission due to an electron transfer process. Such photoinduced reaction depends on the distance between the donor and the acceptor unit; ii) different complexes can pack in a variety of morphologies which possess different emission quantum yields.

Table 1. Photophysical properties of complexes 5 in water at $5 \cdot 10^{-10}$

'M				
Complex	λem, nm, (λ _{exc} = 400nm)	Φ(%)	т (µs)	
5a	593	1	0.304 (71%)	
			0.063 (29%)	
5b	590	1	0.308(47%)	
		11	0.094(53%)	
5c	590	6	0.367 (73%)	
			0.108 (26%)	
5d	587	11	0.402 (35%)	
			0.115 (65%)	
5e	587	14	0.442 (56%)	
			0.141 (44 %)	

Table 2. Photophysical properties of complexes 5 in solid state

Complex	λem, nm λ _{exc} = 400nm	Φ(%)	τ (µs)
5a	590	4	0.546 (47%)
			0.180 (53%)
5b	590	7	0.260 (48%)
			0.112 (52%)
5c	591	7	0.332 (43%)
	(C		0.186 (57%)
5d	591	11	0.396(51%)
			0.146(49%)
5e	593	14	0.452 (57%)
and the second			0.140 (43%)

To estimate the effect of the pyridinium unit, the dependence of the emission on the distance between the emitter (platinum complex) and the quencher was studied. Experiments carried out in dichloromethane at 5.10-5 M, where we observe only the monomeric species in solution, revealed that upon excitation of all the complexes at the isoabsorptive wavelength, 375 nm, the intensities increased with increasing the length of the chain and reached a plateau for C11 (Figure S15). We can conclude that the pyridinium unit can effectively guench the platinum emission in the monomeric species when the chain is shorter than 11 units. The different PLQYs are also observed for all the complexes in water at 5.10⁻⁵ M (Figure S16), where the compounds are aggregated. These data corroborate the different guenching related to the donor-acceptor distance, since the trend is identical to the monomeric species. However, we cannot rule out that a different packing morphology might also contribute to the variation of the emission quantum yields. The quenching is also reflected in the excited state lifetimes in solution (Table 1). The decays are all biexponential, which is also common for platinum aggregates, ^[19] and their value increases, from 300 to about 450 ns, with the elongation of the length of the chain (5a to 5e).

Interestingly, our complexes show a very high tendency to aggregate, leading to the yellow-orange luminescence characteristic of a short distance Pt-Pt distance (<3.5 Å). To monitor this behaviour, even at low concentrations, the emission spectrum of complex **5e** in water was acquired at 10⁻⁷ M (Figure S17) and, as can be seen, it still shows the emission of the aggregated form.

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Further studies to confirm aggregation in solution were performed using dynamic light scattering (DLS) and SEM on complex 5e, (Figures S19, S20 and S21) with concentrations between 10⁻⁶ and 8.10⁻⁴ M. From these experiments, as the scattering intensity starts at the lowest concentration we can confirm that the aggregates are already formed below 10⁻⁶ M. Other DLS experiments were performed at different concentrations (1 µM, 10 μ M, 100 μ M, 500 μ M). The field correlation function versus the diffusion time was measured at these concentrations. From this, we can determine relaxation rate (ms-1) according to the scattering vector q. Subsequently, the hydrodynamic radius of these assemblies was determined (Figure S20) (for more details: see ESI). The most dilute sample has the lower diffusion rate (10 ms), and the higher the concentration, the faster the aggregates diffuse. This is consistent with the assumption that at lower concentrations, below the CMC, the assembly formed is actually a supramolecular polymer driven by π-π stacking and Pt---Pt interactions and hence displaying a bigger hydrodynamic radius; and when the concentration increases, the assembly takes a spherical micelle shape induced by hydrophobic interactions in water. Obviously, the supramolecular polymer has a much bigger hydrodynamic radius than the micelles. This assumption was then confirmed by SEM (Figure S21) that shows the different morphologies at different concentrations. This concept, of the supramolecular assembly, is pictorially illustrated in Figure 4.

2. Encapsulation of amphiphilic Pt(II) complexes in mesoporous silica nanoparticles

The previous experiments demonstrated the effect of the selfassembly of the complexes on the photophysical properties in a dynamic environment. In order to "freeze" the aggregates and retain their photophysical properties upon changes in their surrounding environment, they were encapsulated inside mesoporous silica nanoparticles, MSNs. To this end, hexadecyltrimethylammonium bromide, CTAB, was employed as the templating agent for the condensation of silica nanoparticles, and complexes **5d** and **5e**, whose length closely match that of CTAB, were added as co-surfactants. To study the effect of the TMCs molecules in the formation of the silica nanoparticles and the photophysical properties of the resulting hybrid materials, different ratios of complex/CTAB were used (Table 3, Table S1) to template the growth of a constant amount of silica (45 mM TEOS was used throughout the experiments).

Table 2 Chudiad automa	at different ratios complay/CTAD	
able 3. Studied systems	, at dimerent fatios complex/CTAD	

	[Pt(II) Complex](mM)	[CTAB](mM)
Sample 5e-a/5d-a	10 ⁻³	2.75
Sample 5e-b/5d-b	0.02	2.75
Sample 5e-c/5d-c	0.1	2.25
Sample 5e-d/5d-d	0.2	2

The materials obtained were characterized by SEM, TEM, thermogravimetric analysis (TGA) and N₂ sorption. The photophysical properties were also studied in order to compare them before and after the silica growth. When appropriate, the results were compared to those for the empty porous silica, MCM-41. SEM pictures (Figure 5 left, Figures S22 and S23 for more examples) show a spherical shape for all the hybrid materials. The particles prepared using TMCs are bigger than those prepared in the same conditions and lacking the metal complexes in the surfactant formulation, MCM-41 (Figure S24).

This is most probably due to the higher ethanol concentration used in the mother solution for dissolving the platinum complex. TGAs of the materials were performed between 20 and 1100°C, and the results are shown in Figure 6. All the nanoparticles already lost around 8% of their weight at 150°C, corresponding to the remaining traces of water. Between 200°C and 500°C, degradation of the complexes inside the hybrid materials was evident. Mesoporous silica containing complex **5e** had a larger weight loss than samples **5d**, (between 40 and 55 % for samples **5e**, between 25 and 45% for samples **5d**), attributed to the higher molecular mass of **5e** vs **5d**. At higher temperature, the profiles displayed a plateau, and no weight change was observed from 500°C to 1100°C.

After TGA analysis, the calcinated samples were re-analysed using transmission electron microscopy, TEM. Representative images for sample **5d-a** can be observed in Figure 5 (right), with more examples reported in the SI (Figures S25 and S26).



Figure 5. SEM (left) and TEM (right, inset: zoom) images of sample 5d-a.



Figure 6. TGA profile of the materials: 5e (top) and 5d (bottom).

As for the SEM pictures, a primary observation is that MSNs made by TMC/CTAB mixtures are bigger than particles prepared with pure CTAB as a surfactant. The parallel arrangement of pores, having a size of a few nanometres, is evident up to 10% molar ratio of TMCs relative to CTAB. The addition of TMCs into the system does not disturb the formation of ordered mesopores.

Exact determination of the size of the pores was carried out by N₂ adsorption-desorption experiments (Figures S27 and 7). In comparison with the MCM-41 reference particles, which displayed a pore size of 2.3 nm, MSNs synthesized with TCM/CTAB mixtures have a pores size, around 3.5 nm. A possible explanation for this effect lies in the larger size of TMC molecules relative to CTAB leading to micelles bigger in size due to the presence of the Pt(II) complexes. The micelles that grow laterally to template the pores, during the formation of the silica backbone, lead to larger pores than CTAB alone.

Before analysing the influence of MSN-encapsulation on the photophysical properties of TMCs, we investigated the effect of the confinement of the complexes inside the CTAB micelles. The data reported in table S2 (TMC@CTAB line) refer to the emission maxima, PLQYs and excited state lifetimes of mixtures of **5d** and **5e** with CTAB, prepared in the same conditions used to template the growth of MSNs for samples **5d-d** and **5e-d**, respectively. The TMCs inside the micelles display emission profiles that resemble those recorded in aqueous solution (*cf.* Figure 2), with a broad, featureless band at around 590 nm, typical for Pt(II) complexes in their aggregated state.



Figure 7. Pore size distribution of: MCM-41 (black trace); 5d-a (green trace); 5d-b (blue trace); 5d-c (magenta trace); 5d-d (red trace).

Notwithstanding the similarities in emission profiles, confinement in the micelles brought an important increase in PLQY, from the original 14 and 11% in water for **5e** and **5d**, respectively, to 26%. The excited state lifetimes increased likewise, suggesting that non-radiative relaxation decay pathways are being effectively suppressed. The hybrid micelles have then used to template the silica, as described above, and the resulting photophysical properties of the particles are shown in Figures 8 and 9. The figures depict the excitation and emission spectra of the hybrid materials made by TMCs **5e** and **5d**. Hybrid materials having a relatively high concentration of complex (**5e/5d**, **-b**, **-c** and **-d** samples), display also the same emission profile as the complexes aggregates. On the contrary, samples prepared from a dilute solution of TMCs

(10⁻⁶ M) show a slight hypsochromic effect (576 nm) and narrow bands at higher energies (481 and 505 nm), also observed for the monomeric forms, and attributed to ³LC or ³MLCT transitions.



Figure 8. Solid state emission (full line, λ_{exc} = 400nm) and excitation (dashed line, λ_{em} = 600nm) of the hybrid materials made from complex 5e.

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Figure 9. Solid state emission (full line, λ_{exc} = 400nm) and excitation (dashed line, λ_{em} = 600nm) of the hybrid materials made from complex 5d.

It is interesting to compare the emission spectra of TMCs in samples **5d-a** and **5e-a** with those of 1 μ M aqueous solutions of **5d** and **5e**. In the latter case, we only have emission from aggregates, while in the former, the emission from non-aggregated TMCs dominates. This is peculiar, since the hybrid materials were prepared from 1 μ M TMC solutions and the metal complexes were confined into the pores by interaction with CTAB, presumably increasing their local concentrations above 1 μ M. This suggests therefore that CTAB is preventing metal-metal interactions inside MSNs when the concentration is low, efficiently separating the platinum complexes. The confirmation that the emission comes from the particles was obtained by confocal microscopy analysis performed for each sample, and an image is shown in the ESI (Figure S28, sample **5e-d**.)

The PLQYs and excited state lifetimes of the hybrid materials show a more performant behaviour compared to their micellar counterparts, as shown in Table 4. Indeed, upon encapsulation in MSNs, the PLQYs recorded for **5e** and **5d** are up to three times higher in comparison with its water solutions and solid state, and the excited state lifetimes are mirroring the same increase. The confinement provided by the MSNs, due to the increase in rigidity of the system, immobilization of the complexes, as well as the protection from dioxygen quenching have an undeniably beneficial effect on the photophysical properties.

Table 4. Solid state photophysical properties of the hybridmaterials made from complexes **5e** and **5d**

Complex	λem (nm, λexc = 400nm)	Φ(%)	т (µs)
5e-a	481-510-576**	n.d.*	0.171(39%)**
	3		0.010(61%)**
5e-b	587	38	0.911 (42%)
		- 10	0.405 (58%)
5e-c	587	37	0.936(34%)
		11	0.386(66%)
5e-d	589	41	0.961(40%)
			0.363(60%)
5d-a	476-590**	n.d.*	0.160(31%)**
			0.008(69%)**
5d-b	590	44	1.247 (19%)
			0.706 (81%)
5d-c	590	45	1.325 (19%)
			0.754 (81%)
5d-d	590	39	0.991(63%)
			0.218(37%)

*not determined due to instrument limitations

** $\lambda_{exc} = 350$ nm

Conclusions

The amphiphilic Pt(II) complexes described in this work, are strongly aggregated in aqueous solution and even at very low concentrations display the emission of their self-assembled structures. These aggregates can be stabilised by their inclusion within mesoporous silica, employing the complexes as templates, in association with CTAB, for formation of the porous silica framework. The confinement provided by the silica is superior to that conferred by the micelles in solution as demonstrated by the enhancement of the photophysical properties. High emission quantum yields for the hybrid nanoparticles have been recorded and the change in the external environment does not influence the emission properties. The higher performance can be rationalized considering the restriction in vibrational and rotational motion of the aggregates within the pores lattice and protection of the aggregate from dioxygen.

Such findings could open the way to the construction of very efficient and easy to store and process emitting materials.

Experimental Section

The full experimental section is reported in the SI.

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Layout 2:

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Water soluble platinum complexes undergo self-assembly and are used as cosurfactant for the synthesis of mesoporous silica nanoparticles. Their confinement in the pores leads to an enhancement of the photophysical properties. Youssef Atoini, Eko Adi Prasetyanto,* Pengkun Chen, Simone Silvestrini, Jack Harrowfield, Luisa De Cola*

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Title: Luminescence of amphiphilic Pt(II) complexes controlled by confinement