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Encapsulation of cationic iridium(iii) tetrazole complexes into a silica matrix: Synthesis, characterization and optical properties

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Ilaria Zanoni, Valentina Fiorini, Marcos Rosado, Belén Ballesteros, Maria Androulidaki, Magda Blosi, Simona Ortellì, Stefano Stagni, Anna Luisa Costa. *New Journal of Chemistry* **2018**, 42, 9635-9644

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# Encapsulation of cationic Iridium(III) tetrazole complexes into silica matrix: synthesis, characterization and optical properties

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## Abstract

Herein we report the easy incorporation of brightly phosphorescent cationic Iridium(III) tetrazole complexes into a silica based matrix through an easily scalable colloidal process. To this purpose, two cationic Ir(III) emitters bearing 5-aryl tetrazole ligands (R-CN<sub>4</sub>) were selected: the blue [F<sub>2</sub>IrPTZ-Me]<sup>+</sup> (C<sup>^</sup>N = F<sub>2</sub>ppy; N<sup>^</sup>N = PTZ-Me - 2-(2-methyl-2H-tetrazol-5-yl)pyridine) and the red [IrQTZ-Me]<sup>+</sup> (C<sup>^</sup>N = ppy; N<sup>^</sup>N = QTZ-Me - 2-(2-methyl-2H-tetrazol-5-yl)quinoline). The cationic complexes were readily adsorbed to negatively charged silica nanoparticles and trapped in the sol-gel matrix. The *sol-to-solid* phase transfer was performed by using an innovative *spray-freeze-drying* technique, leading to the formation of phosphorescent solid micro-granules. The structural and optical characterisation of the Ir(III) complexes together with SiO<sub>2</sub> nanoparticles, nanosols (**Ir@SiO<sub>2</sub>**) and powders (**Ir@SiO<sub>2</sub> powders**), revealed how the presence of the Ir(III)-based complexes did not alter the morphology of colloidal silica and granulated phases. Moreover, the silica matrix did not interfere with the optical properties of the embedded complexes. The distribution of [F<sub>2</sub>IrPTZ-Me]<sup>+</sup> and [IrQTZ-Me]<sup>+</sup> in the spray-freeze-dried powders was qualitatively evaluated by fluorescence microscopy, revealing how the luminescent particles were homogeneously dispersed all over the silica matrix. Interestingly, in aqueous solution the release of the complex [F<sub>2</sub>IrPTZ-Me]<sup>+</sup> from the corresponding **Ir@SiO<sub>2</sub> powder** is almost negligible, therefore suggesting the strong interaction occurring between the host-silica matrix and the Ir(III) guest complex.

## 50 Introduction

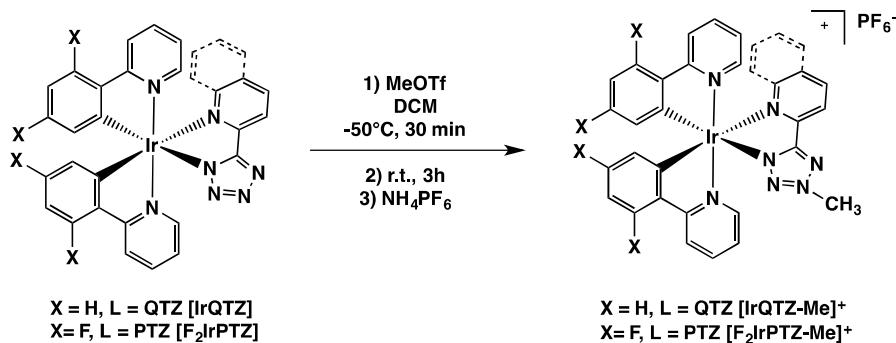
51 The scenario of iridium-transition metal complexes (Ir-TMCs) has been extensively expanded  
52 through a multitude of examples [1]. In this context, great efforts have been spent with the family  
53 of Ir(III) cyclometalates, a versatile class of compounds with general formula  $[\text{Ir}(\text{C}^{\wedge}\text{N})(\text{N}^{\wedge}\text{N})]^{0/+}$   
54 ( $\text{C}^{\wedge}\text{N}$  = phenylpyridine - ppy - or 2, 4 difluoro-phenylpyridine -  $\text{F}_2\text{ppy}$ -,  $\text{N}^{\wedge}\text{N}$  = diimine ligand, neutral  
55 or anionic) [2][3]. Taking advantage from their outstanding photophysical features - including a  
56 fine emission-colour tuning by ligand modification, long lived excited states ( $\tau$ ) and high quantum  
57 yield ( $\Phi$ ) values - Ir-TMCs can be considered as one of the most promising class of luminescent  
58 complexes [1]. In recent times, solid-state lighting (Organic Light Emitting Diode – OLEDs, Light  
59 Emitting Electrochemical Cells – LEECs [4]), heterogeneous catalysts [5] and luminescent bio-  
60 sensors [6] based on Ir-TMCs are in rapid development. This enhances the necessity of maintaining  
61 unaltered both chemical and photophysical stability of Ir(III) complexes at the experimental  
62 conditions that are required for their processing from liquid to solid-state (solvent, pH,  
63 temperature, etc.). This is a hard task to accomplish, because the optical properties Ir(III)  
64 complexes are detrimentally influenced by the interaction with surrounding environment that can  
65 alter the oxidation state of core metal, displace ligands from the complex, and promote the  
66 electron transfer towards surrounding species with expected quenching of luminescent outcomes.  
67 A potential solution to overcome this challenge is represented by the design of a stable anchoring  
68 platform capable of leaving unchanged the aforementioned properties [7]. Organic and bio-  
69 organic doped sol-gel materials have attracted much attention due to their ability to reproduce  
70 solution molecular activities within the ceramic environment. The processing versatility of the  
71 colloidal state permits the synthesis of multifunctional organic-inorganic hybrid structures  
72 through a bottom-up approach based on a tailored assembly of organic and inorganic building  
73 blocks [8]. In this regard, the use of silica nanoparticles ( $\text{SiO}_2\text{NPs}$ ) as host-matrix for luminescent  
74 compounds has recently turned into a standard approach in the development of reliable sensors  
75 for various applications [9][10]. In addition to ready availability and low cost,  $\text{SiO}_2\text{NPs}$  also exhibit  
76 several fascinating properties, such as chemical, optical and thermal inertness together with high  
77 colloidal stability. The integration of metal complexes as active phase in  $\text{SiO}_2\text{NPs}$  host-matrix can  
78 accomplished by following different protocols, which include both chemical and physical methods  
79 [9][11]. In general, the chemical encapsulation of a guest molecule takes place during the  
80 formation of the silica solid phase (i.e. core-shell, Stöber method), while the physical approach  
81 (colloidal heterocoagulation, inorganic matrix encapsulation method) exploits the electrostatic

interactions between the negatively charged silica colloidal phase and the positively charged guest. The latter approach presents several advantages in comparison to core-shell protocols, since they don't require expensive reagents or chemical treatment, avoiding the formation of any byproduct. The main goal of the present study is to exploit and optimize new and easy to apply methods to incorporate Ir(III) tetrazolate complexes into silica-based colloid matrices, in order to improve their chemical and photophysical stability, enhancing their processing at liquid and dry state. Within this framework, two Ir(III) emitters bearing 5-aryl tetrazole ligands such as the sky-blue  $[\text{F}_2\text{IrPTZ-Me}]^+$  ( $\text{C}^{\wedge}\text{N} = \text{F}_2\text{ppy}$ ;  $\text{N}^{\wedge}\text{N} = \text{PTZ-Me} - 2-(2\text{-methyl-}2H\text{-tetrazol-5-yl)pyridine}$ ) and the red phosphorescent  $[\text{IrQTZ-Me}]^+$  ( $\text{C}^{\wedge}\text{N} = \text{ppy}$ ;  $\text{N}^{\wedge}\text{N} = \text{QTZ-Me} - 2-(2\text{-methyl-}2H\text{-tetrazol-5-yl)quinoline}$ ) complexes (Scheme 1) were selected as cationic coatings for negatively charged  $\text{SiO}_2\text{NPs}$ , being able to cover the two opposite part of visible spectrum [12]. Prompted by the encouraging results in terms of both physical and optical stability,  $\text{Ir@SiO}_2$  nanosols were transferred to dry-powder state by the means of Spray-Freeze-Drying technique, an innovative procedure in the field that enabled the formation of two stable luminescent  $\text{Ir@SiO}_2$  powders avoiding heat assisted drying processes that may alter both chemical and photophysical properties of the Ir(III) tetrazole complexes used as coating for silica nanoparticles [13][14][15].

## Results and discussion

### *Synthesis of cationic Ir(III) tetrazolate complexes*

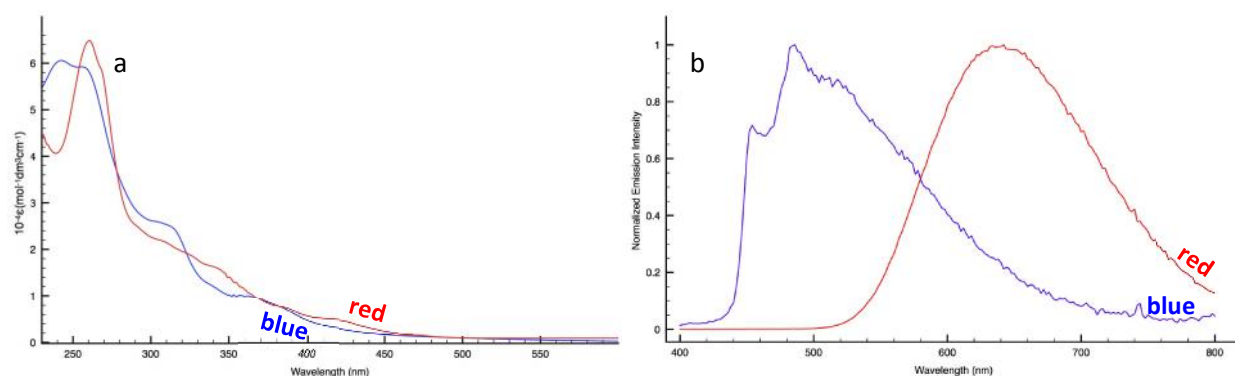
The preparation of the cationic Ir(III) tetrazolate complexes  $[\text{F}_2\text{IrPTZ-Me}]^+$  and  $[\text{IrQTZ-Me}]^+$  was accomplished by following a previously reported procedure (Scheme 1) [12], which consists of an electrophilic addition at the tetrazole ring of the corresponding neutral Ir(III) precursor. The formation of the desired cationic Ir(III)-cyclometalates was at first confirmed by electrospray ionisation mass spectrometry (ESI-MS), which revealed the presence of the expected  $m/z$  signals in the positive region ions (Figure S5-6 ESI). The  $^1\text{H}$ -NMR characterization provided a number of protonic resonances congruent with the low symmetry displayed by the complexes (Figure S1-2 ESI). As previously reported [12], the electrophilic addition performed on the  $[\text{R-CN}_4]^-$  moiety regioselectively occurs at the N-2 atom of the tetrazolate ring, as witnessed by  $^{13}\text{C}$ -NMR resonance of Ct (tetrazolic carbon) which has been found at 166.54 ppm for  $[\text{F}_2\text{IrPTZ-Me}]^+$  and 167.93 ppm for  $[\text{IrQTZ-Me}]^+$  (Figure S3-4 ESI).



**Scheme 1:** Synthetic procedure used for cationic Ir(III) tetrazole complexes

### Photophysical properties

In  $10^{-5}\text{M}$   $\text{CH}_2\text{Cl}_2$  solutions, all the cationic Ir(III) complexes displayed similar absorption profiles, with intense ligand centred ( $^1\text{LC}$ ) transitions up to 260 nm and metal-to-ligand charge transfer ( $^1\text{MLCT}$ ) bands tailing off above 380 nm (Figure 1a).



**Figure 1:** (a) Absorption Profiles of blue emitting  $[\text{F}_2\text{IrPTZ-Me}]^+$  (blue line) and red emitting  $[\text{IrQTZ-Me}]^+$  (red line),  $10^{-5}\text{M}$ ,  $\text{CH}_2\text{Cl}_2$ ; (b) Normalized Emission Profiles of  $[\text{F}_2\text{IrPTZ-Me}]^+$  (blue line) and  $[\text{IrQTZ-Me}]^+$  (red line),  $\text{CH}_2\text{Cl}_2$ .

Upon excitation of the  $^1\text{MLCT}$  features ( $\lambda = 370 \text{ nm}$ ),  $[\text{F}_2\text{IrPTZ-Me}]^+$  displayed a sky-blue emission colour that corresponds to a structured emission profile with  $\lambda_{\text{max}} = 454, 486$  and  $526 \text{ nm}$  (Figure 1b and Table 1), suggesting an interplay of  $^3\text{LC}/^3\text{MLCT}$ -type emissive excited states [1]. On the contrary, the red emitter  $[\text{IrQTZ-Me}]^+$  produced a broad and unstructured emission profile with  $\lambda_{\text{max}} = 638 \text{ nm}$ , typical of  $^3\text{MLCT}$ -based phosphorescence (Figure 1b), as evidenced also by the noticeable rigidochromic shift observed in frozen solvent matrix at  $77\text{K}$  ( $\lambda_{\text{max}} = 568 \text{ nm}$ , Table 1).

133 **Table 1:** Relevant absorption and emission data of cationic Ir(III) complexes discussed in this work.

CH <sub>2</sub> Cl <sub>2</sub> as the solvent	Absorption	Emission 298 K <sup>a,b</sup>						Emission 77K <sup>c</sup>	
	λ <sub>abs</sub> (nm);(10 <sup>-4</sup> ε)(M <sup>-1</sup> cm <sup>-1</sup> )	λ <sub>em</sub> (nm)	τ <sub>air</sub> (μs)	τ <sub>Ar</sub> (μs)	Φ <sub>air</sub> (%)	Φ <sub>Ar</sub> (%)	λ <sub>em</sub> (nm)	τ (μs)	
[IrQTZ-Me] <sup>+</sup>	253 (4.25), 310 (1.41), 374 (0.78)	638	0.220	0.550	2.8	4.5	568	1.56	
[F <sub>2</sub> IrPTZ-Me] <sup>+</sup>	257 (6.24), 318 (2.70), 351 (1.20)	454, 486, 526	0.040	0.140	1.7	4.7	448, 480	6.62	

134 <sup>a</sup>: "Air" means air equilibrated solutions, "Ar" means deoxygenated solutions under argon atmosphere; <sup>b</sup>:  
 135 [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>/H<sub>2</sub>O was used as reference for quantum yield determinations ( $\Phi_r = 0.028$ ); <sup>c</sup>: in frozen CH<sub>2</sub>Cl<sub>2</sub>

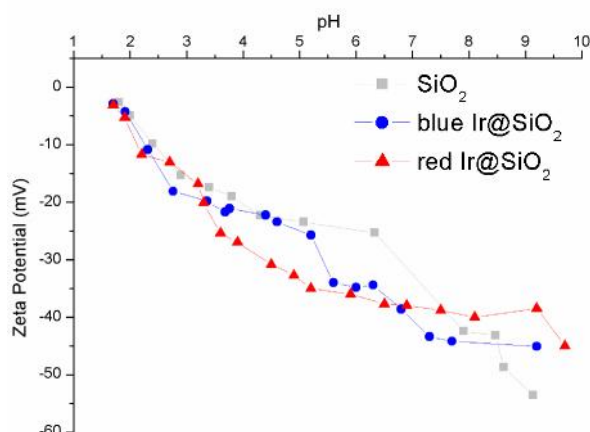
136 *Ir@SiO<sub>2</sub> nanosols systems*

137 Ir@SiO<sub>2</sub> nanosols (namely: **blue** Ir@SiO<sub>2</sub> for [F<sub>2</sub>IrPTZ-Me]<sup>+</sup> and **red** Ir@SiO<sub>2</sub> for [IrQTZ-Me]<sup>+</sup>) were  
 138 obtained by mixing the appropriate Ir(III) cationic complex with a silica suspension[16], which was  
 139 previously destabilised through a cation-exchange resin treatment in which the replacement of  
 140 Na<sup>+</sup> with H<sub>3</sub>O<sup>+</sup> promotes the intra-particles cross-linking [17]. In this regard, an explanation is  
 141 provided by Dumont and Watillon [18], that pointed out how the Na<sup>+</sup> substitution by H<sub>3</sub>O<sup>+</sup> ions  
 142 affects silica bonding, with the replacement of dissociated silanol-silanol bonds by cross-linked  
 143 siloxane bonds:  $-\text{Si}-\text{OH}\cdots\text{O}^--\text{Si}- \rightarrow -\text{Si}-\text{O}-\text{Si} + \text{OH}^-$ . In addition, the electrostatic stabilization of  
 144 resin treated silica nanoparticles decreases; in fact, Zeta Potential passes from -42 to -29 mV as  
 145 expected by the pH decrease from 9.0 to 4.5 (Table 2). The colloidal properties of **Ir@SiO<sub>2</sub>**  
 146 **nanosols** systems were studied in respect of their hydrodynamic diameter and surface charge  
 147 properties (Table 2). As evidenced by the Zeta Potential vs pH measurements (Figure 2), the  
 148 presence of the phosphorescent Ir(III) tetrazole-markers did not affect the surface charge  
 149 properties of SiO<sub>2</sub>NPs. For all the silica colloidal solutions, the obtained plots revealed only one  
 150 isoelectric point found at pH < 1.5, while the highest stability (ZP ≥ -30 mV) have been found  
 151 between 3 < pH < 10 values. Furthermore, the hydrodynamic diameter of colloidal SiO<sub>2</sub>NPs was  
 152 not significantly affected by the physical mixing with the Ir(III)-markers, as confirmed by  
 153 hydrodynamic radius (R<sub>hyd</sub>) values obtained from DLS analyses (Table 2).

154 **Table 2:** Colloidal properties of silica based nanosols.

Sample	pH	DLS R <sub>hyd</sub> (nm)	Zeta Potential (mV)
SiO <sub>2</sub> _Ludox	9.0	20 ± 1	-42.2 ± 1.1
SiO <sub>2</sub> *	4.5	23 ± 1	-29.0 ± 0.2
blue Ir@SiO <sub>2</sub>	4.5	22 ± 2	-33.3 ± 1.8
red Ir@SiO <sub>2</sub>	4.5	24 ± 1	-30.8 ± 1.5

155 \*Commercial  $\text{SiO}_2$  destabilized through treatment on cationic-exchange resin.

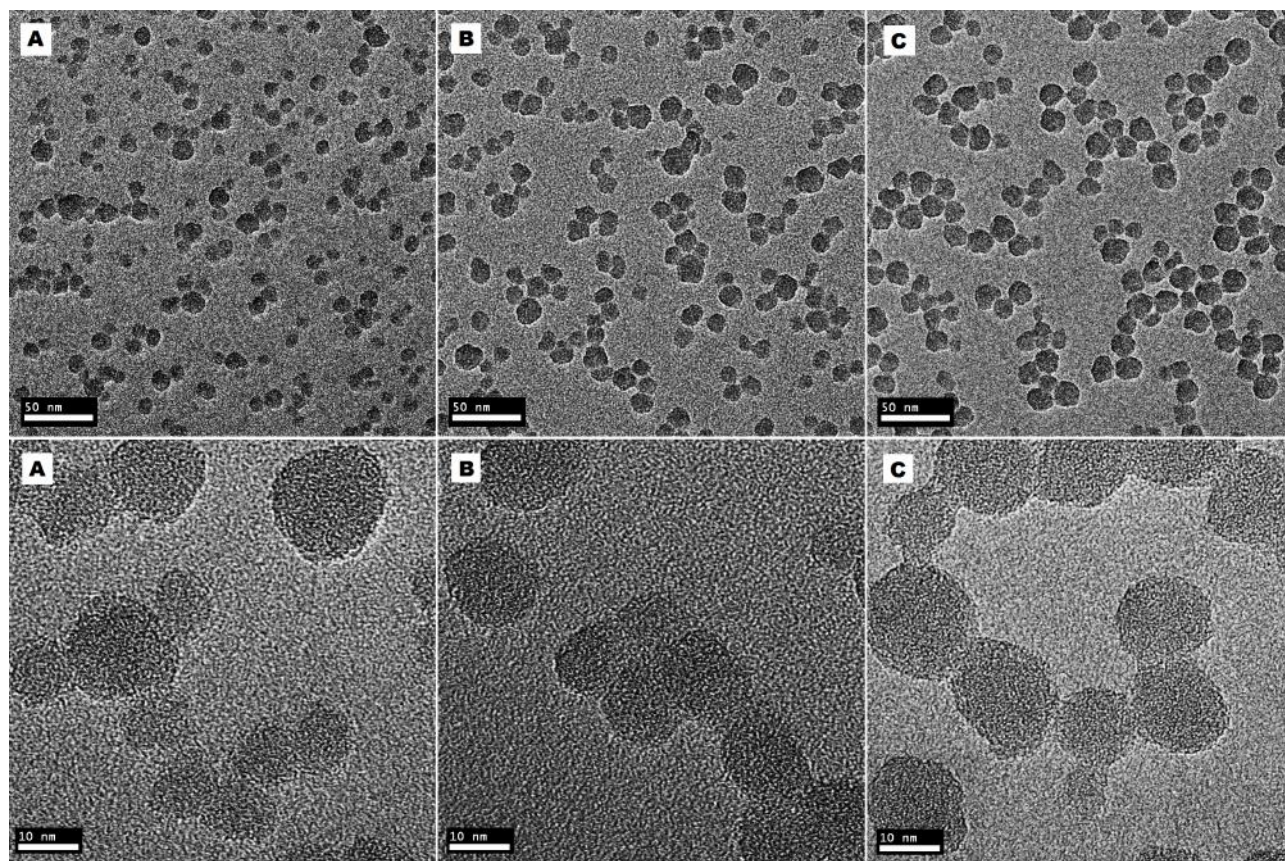


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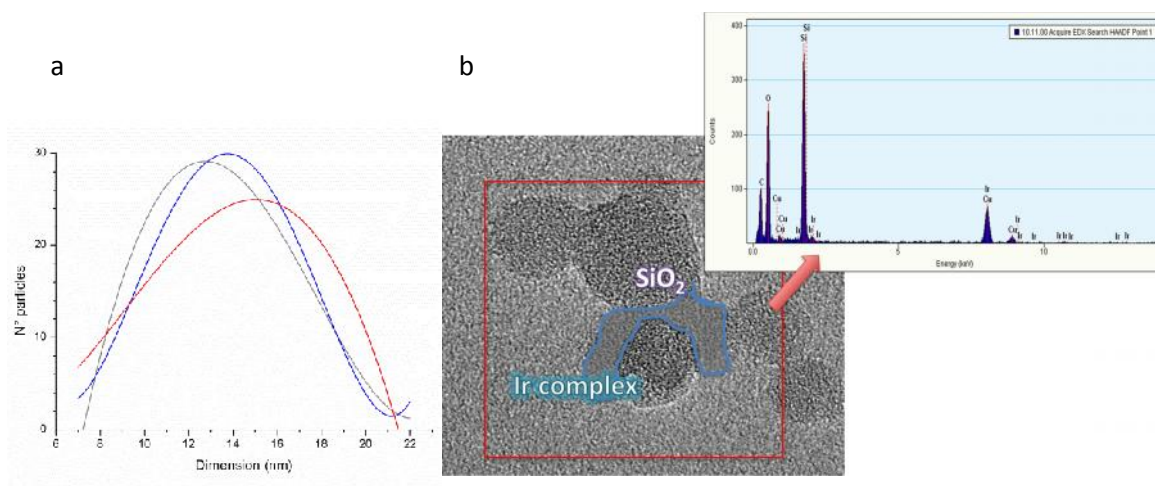
157 **Figure 2:** Zeta Potential (mV) vs pH plot of silica nanosol (grey line), blue  $\text{Ir@SiO}_2$  (blue line) and red  $\text{Ir@SiO}_2$   
158 (red line), 100 mg/L of solid fraction.

159 The morphology of silica nanoparticles and the distribution of the Ir(III) complexes were examined  
160 by the means of TEM-EDX (Transmission Electron Microscopy-Energy Dispersive X-ray Analysis,  
161 Figure 3 and 4). The nanoparticles size distribution is homogeneously centered on 14 nm, being  
162 these values in accordance with the measured  $R_{\text{hyd}}$  (Table 2). TEM images highlight a negligible  
163 increase of the  $\text{SiO}_2$  NPs mean diameter ( $\varnothing \text{SiO}_2$  13.7±3.1 nm,  $\varnothing$  **blue  $\text{Ir@SiO}_2$**  13.8±3.1 nm,  $\varnothing$  **red**  
164  **$\text{Ir@SiO}_2$**  14.0±3.4 nm) and a slight improvement of particles cross-linking in the presence of  
165 complexes, forming necklace-like structures (Figure 3, B, C). TEM images acquired at higher  
166 magnification revealed the presence of a halo in the surroundings of  $\text{SiO}_2$  NPs, imputable to the  
167 presence of Ir(III) complexes, as shown in Figure 4 and confirmed by EDX analysis.





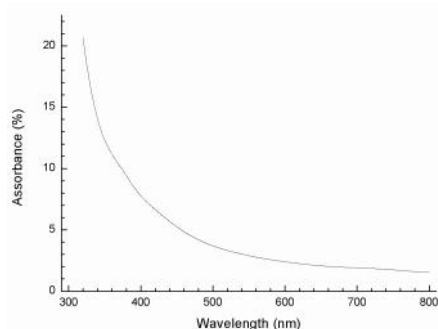
**Figure 3:** TEM images on copper grid acquired at different magnifications of A) SiO<sub>2</sub>NPs, B) **blue Ir@SiO<sub>2</sub>**, C) **red Ir@SiO<sub>2</sub>**.



**Figure 4:** a) Nanoparticles distribution made by 250 particles-population: SiO<sub>2</sub>NPs (grey line), **blue Ir@SiO<sub>2</sub>** (blue line), **red Ir@SiO<sub>2</sub>** (red line); b) TEM image of **blue Ir@SiO<sub>2</sub>**, with relative EDS analysis.

As previously reported in literature [10], colloidal silica has no optical influence over the photoluminescent output of transition metal complexes, resulting transparent in both the

182 absorption (230-400 nm) and emission range (400-800 nm). This behavior was confirmed by the  
 183 absorption profile of SiO<sub>2</sub>NPs (Figure 5), where no maxima were found in the region of interest.



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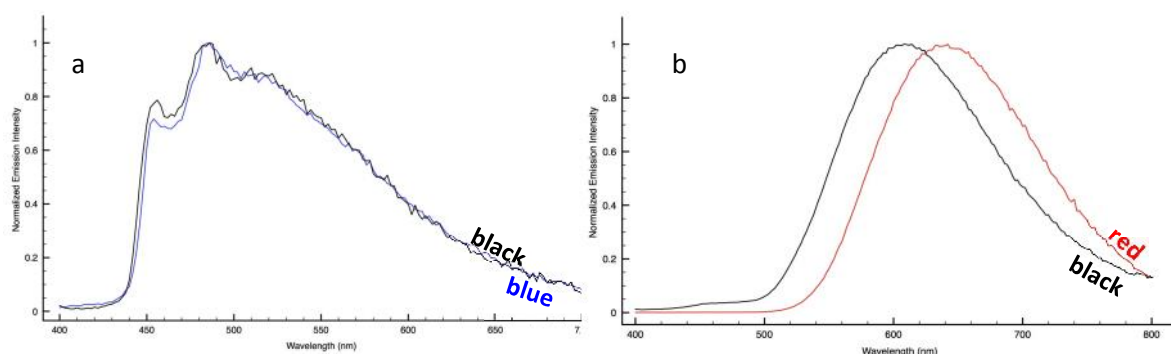
185 **Figure 5:** Absorbance (%) vs Wavelength (nm) plot of SiO<sub>2</sub>NPs, 3%wt, Milli-Q H<sub>2</sub>O, r.t.

186 **Table 3:** Relevant photophysical properties of Ir(III)-complexes@SiO<sub>2</sub> nanosols systems.

H <sub>2</sub> O as solvent	<b>Absorption</b> $\lambda_{\text{abs}}(\text{nm})$	<b>Emission 298 K</b>				
		$\lambda_{\text{em}}$ (nm)	$\tau_{\text{air}}$ ( $\mu\text{s}$ )	$\tau_{\text{Ar}}$ ( $\mu\text{s}$ )	$\phi_{\text{air}}$ (%)	$\Delta\lambda$ (nm)
<b>Red Ir@SiO<sub>2</sub></b>	252, 312	610	0.100	n.d.*	n.d.*	28
<b>Blue Ir@SiO<sub>2</sub></b>	263, 286, 310	454, 484, 520	0.010	n.d.*	n.d.*	0

187 \*n.d. = not determined.

188 The emission profiles of **[F<sub>2</sub>IrPTZ-Me]<sup>+</sup>** and its silica embedded structure **blue Ir@SiO<sub>2</sub>** (Table 3 and  
 189 Figure 6a) resulted almost superimposable to each other and did not provide any indication of the  
 190 new chemical interaction established between **[F<sub>2</sub>IrPTZ-Me]<sup>+</sup>** and the silica matrix. On the other  
 191 hand, the rigidochromic blue shift encountered in the emission profile of **red Ir@SiO<sub>2</sub>** in respect of  
 192 **[IrQTZ-Me]<sup>+</sup>** (Table 3 and Figure 6b) is in agreement with the prevailing <sup>3</sup>MLCT composition of its  
 193 excited state, being more sensitive to modifications of the surrounding chemical environment [1].

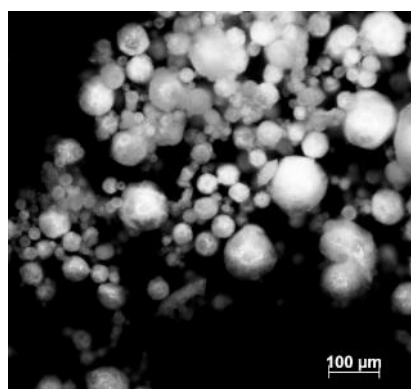


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198 **Figure 6:** Comparison between normalised emission profiles  $[F_2IrPTZ-Me]^+$  (blue line) and  $[IrQTZ-Me]^+$   
 199 (red line) complexes and their **Ir@SiO<sub>2</sub> systems** (black lines).

200 *Ir@SiO<sub>2</sub> powders*

201 Both **blue** and **red Ir@SiO<sub>2</sub>** nanosols were micronized and subsequently dried by the means of  
 202 *Spray-Freeze-Drying* technique, an instantaneous process that, in comparison with heat promoted  
 203 drying processes, is expected to maintain unaltered the photoluminescent properties of Ir@SiO<sub>2</sub>  
 204 nanosols [11][19][20][21]. The morphology of the obtained **blue** and **red Ir@SiO<sub>2</sub> powders** was  
 205 checked by optical microscopy and SEM-FEG. The microstructure of spray-freeze-dried granules of  
 206 both SiO<sub>2</sub> and **Ir@SiO<sub>2</sub> powders** appeared spherical and regular, with a broad distribution (Figures  
 207 7 and 8). The mean diameter of **Ir@SiO<sub>2</sub> powders** was significantly reduced, from  $22.6 \pm 12.6 \mu m$   
 208 of SiO<sub>2</sub> considered alone to  $17.5 \pm 11.3 \mu m$  and  $18.0 \pm 11.4 \mu m$  for **Ir@SiO<sub>2</sub> powders**, as a result of  
 209 an intense interaction between SiO<sub>2</sub>NPs in the presence of phosphorescent complexes (Figure 9).  
 210 The observed submicron homogeneously distributed porosity, shown in Figure 8, can be  
 211 considered as induced by the sublimation of water from the silica colloidal solution, leaving a  
 212 mesoporous structure. As a consequence, Specific Surface Area (SSA) measurements pointed out  
 213 impressive values for both silica ( $207.78 \pm 4.16 m^2/g$ ) and Ir@SiO<sub>2</sub> powders (**blue Ir@SiO<sub>2</sub> powder**,  
 214  $225.13 \pm 4.50 m^2/g$ ; **red Ir@SiO<sub>2</sub> powder**,  $213.96 \pm 4.28 m^2/g$ ).



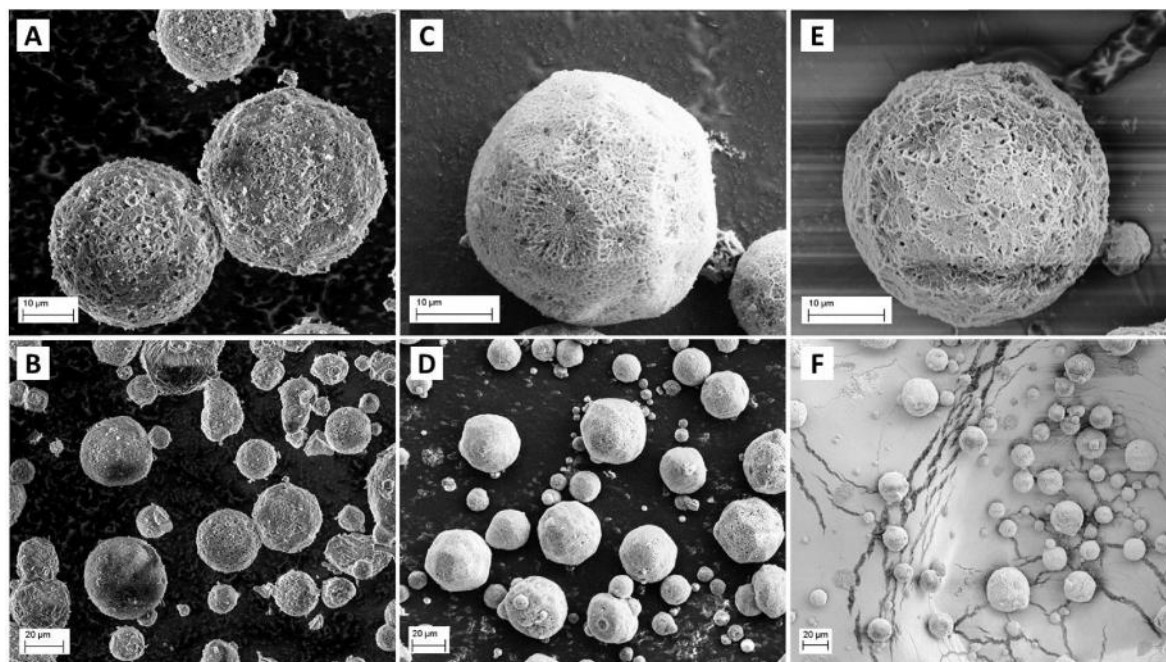
SiO <sub>2</sub> -powder	SEM-FEG granules-size (μm)
blue Ir@SiO <sub>2</sub> powder	$17.5 \pm 11.3 \mu m$
red Ir@SiO <sub>2</sub> powder	$18.0 \pm 11.4 \mu m$
SiO <sub>2</sub>	$22.6 \pm 12.6 \mu m$

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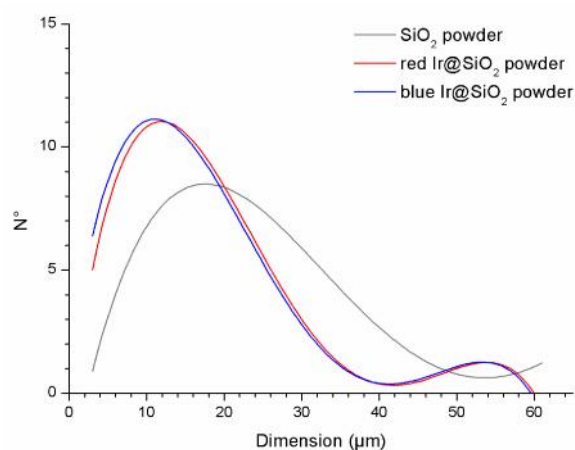
216 **Figure 7:** Optical micrograph of SiO<sub>2</sub> powder.

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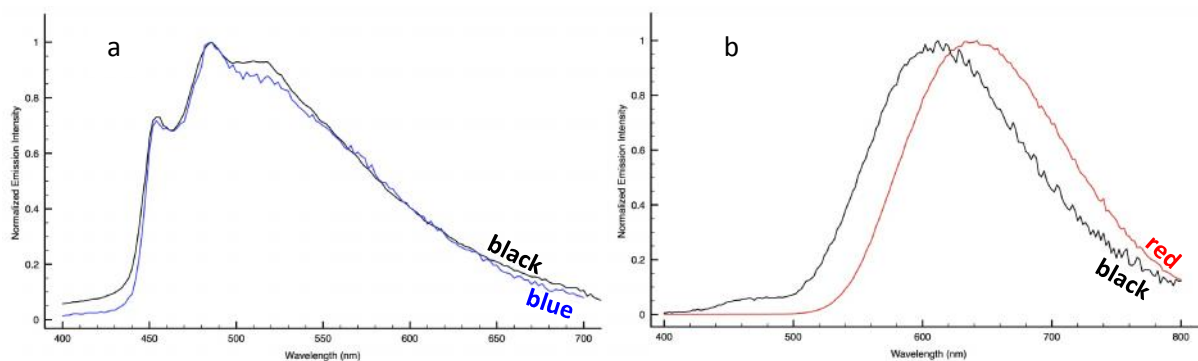


**Figure 8:** SEM-FEG images of SiO<sub>2</sub> (A, B), **blue Ir@SiO<sub>2</sub> powder** (C, D) and **red Ir@SiO<sub>2</sub> powder** (E, F).



**Figure 9:** Size distribution of micronized SiO<sub>2</sub> powders (grey trace), **blue Ir@SiO<sub>2</sub> powder** (blue trace) and **red Ir@SiO<sub>2</sub> powder** (red trace). The mean value was calculated for a population of 250 particles.

As previously discussed for Ir@SiO<sub>2</sub> nanosols, only the **red Ir@SiO<sub>2</sub> powder** ( $\lambda_{\text{max}}=577$  nm) displayed a significant rigidochromic blue shift in comparison to [IrQTZ-Me]<sup>+</sup> (Figure 10). This behavior was further confirmed by variable temperature emission studies over the range 15-300K, where no substantial changes were observed for the **blue Ir@SiO<sub>2</sub> powder** (Figure 11a), while for the **red** one, a blue shift of the emission maxima from 570 to 550 nm was detected (Figure 11b) [1]. In both cases, the presence of surrounding silica matrix and the temperature decrease are two driving forces that change the environment polarity, stiffening the system structure and modulating the final phosphorescent outcome of the **red Ir@SiO<sub>2</sub> powder**.

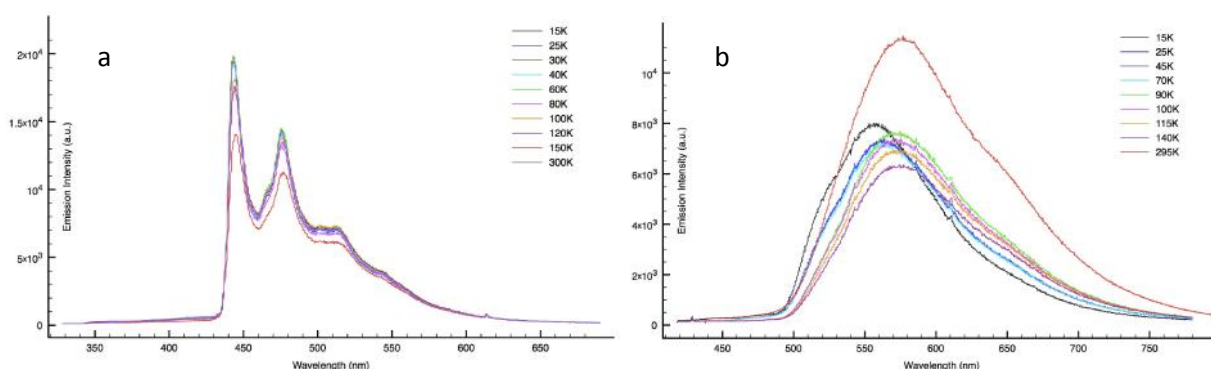


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**Figure 10:** a) Normalized Emission Profiles of  $[F_2IrPTZ-Me]^+$  (blue line) and **blue Ir@SiO<sub>2</sub> powder** (black line); b) Normalized Emission Profiles of  $[IrQTZ-Me]^+$  (red line) and **red Ir@SiO<sub>2</sub> powder** (black line).



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**Figure 11:** Variable temperature emission studies of a) **blue Ir@SiO<sub>2</sub> powder** and b) **red Ir@SiO<sub>2</sub> powder** (15-300 K).

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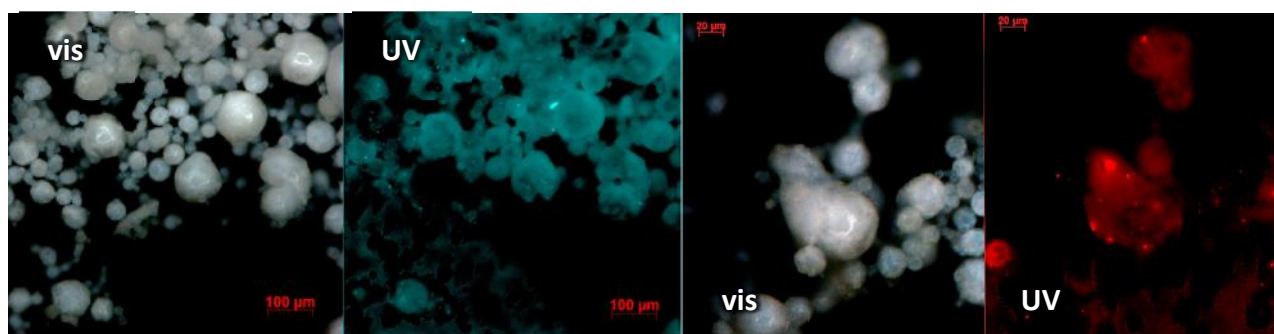
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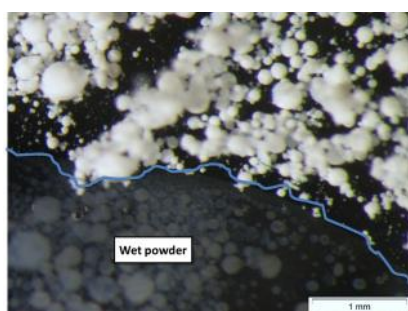
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The distribution of  $[F_2IrPTZ-Me]^+$  and  $[IrQTZ-Me]^+$  complexes in the ceramic micronized powders were evaluated by fluorescence microscopy (Figure 12). For both **Ir@SiO<sub>2</sub> powders**, the luminescent properties resulted homogeneously spread over the silica matrix. Using *Spray-Freeze-Drying* technique, we avoided any possible thermal degradation, as that a Spray-Drying processes can induce with a consequent damage or deface of Ir(III) complexes luminescent properties. The Ir@SiO<sub>2</sub> nanosol were sprayed and frozen, thus preserving the NPs and complexes distribution as was in dispersed liquid phase. No separate cluster of luminescent marker are appreciated and a distribution of spherical luminescent micro-particles was detectable under fluorescence microscope.



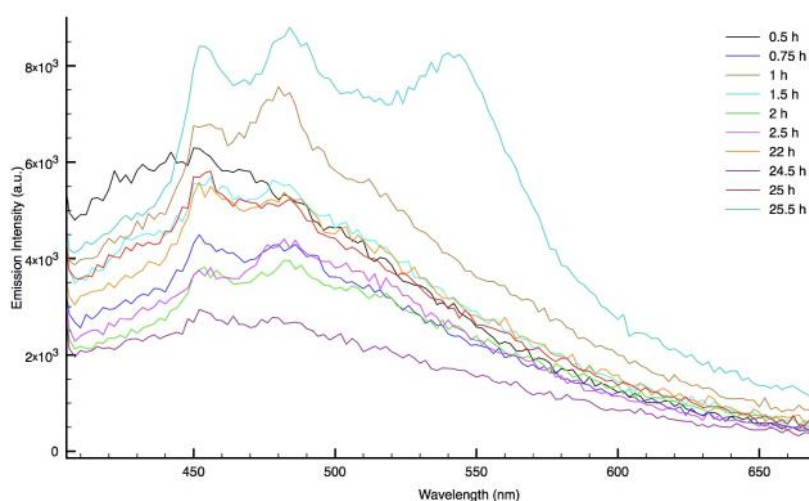
**Figure 12:** Micrographs of (left) **blue Ir@SiO<sub>2</sub> powder** and (right) **red Ir@SiO<sub>2</sub> powder** with visible and fluorescence source.

The wettability of **Ir@SiO<sub>2</sub> powders** was evaluated by observing the particles morphology in the presence of water (“Drop-Test”, Figure 13). **Ir@SiO<sub>2</sub> powders** preserved their spherical shape without decomposing in a time period of 15 minutes, thus exhibiting some mechanical strength even after water-contact, encouraging the use of these systems in the large spectrum of wet powder process applications.



**Figure 13:** Drop-test for **blue Ir@SiO<sub>2</sub> powder** acquired with OLYMPUS SZX9.

The release of **[F<sub>2</sub>IrPTZ-Me]<sup>+</sup>** from the **blue Ir@SiO<sub>2</sub> powder** was evaluated in both organic and inorganic media (CH<sub>3</sub>CN, CH<sub>2</sub>Cl<sub>2</sub> and H<sub>2</sub>O; see Figure 12 and S7-8 ESI), by acquiring emission spectra of the liquid phase separated from the suspension of **blue Ir@SiO<sub>2</sub> powder**, kept under mechanical stirring for approx. 25 hours (Figure 14). The emission profiles suggest a very low release percentage of **[F<sub>2</sub>IrPTZ-Me]<sup>+</sup>** (presumably below 10<sup>-9</sup> M), confirming the strong interaction occurring between the host-silica matrix and the **[F<sub>2</sub>IrPTZ-Me]<sup>+</sup>** complex.



264

265 **Figure 14:** Water-release emission test of  $[\text{F}_2\text{IrPTZ-Me}]^+$  from **blue Ir@SiO<sub>2</sub> powder**.

## 266 Conclusions

267 In summary, we have demonstrated how  $[\text{F}_2\text{IrPTZ-Me}]^+$  and  $[\text{IrQTZ-Me}]^+$  tetrazole complexes can  
 268 be successfully incorporated into a silica matrix, with a simple and easily scalable colloidal route.  
 269 We design a multi-scale process, and obtained luminescent powders that preserved optical  
 270 properties from molecular scale to micro scale, providing a self-marking ceramic platform stable  
 271 and easy to be processed at dry or wet dispersed state. The silica embedded Ir(III) complexes  
 272 could be effectively isolated and sterically confined within micro granules obtained by spray-  
 273 freeze-drying the correspondent nanosol. The luminescent properties stemming from  $[\text{F}_2\text{IrPTZ-}$   
 274  $\text{Me}]^+$  and  $[\text{IrQTZ-Me}]^+$  resulted homogeneously spread over the silica matrix, as confirmed by  
 275 fluorescence microscopy. The granulated Ir@SiO<sub>2</sub> powders preserved their spherical shape  
 276 without decomposing in water and did not release free complex neither in contact with aqueous  
 277 nor with organic solvents. We confirmed the photostability of Ir@SiO<sub>2</sub> systems by comparing the  
 278 luminescent properties of the complexes themselves and in the presence of silica host matrix, either  
 279 as sol or in the solid state. Finally, the great versatility of cationic Iridium(III) tetrazole complexes,  
 280 compared to other classes of organometallic complexes, makes room for further investigations,  
 281 with the aim to cover all visible spectrum. In fact, we are able to obtain different emission, by  
 282 changing ligands, that are modulated by encapsulation but a stable silica matrix. These  
 283 encouraging results pave the way for the employment of these phosphorescent powders in  
 284 various fields, ranging from nanoengineering materials (LED colour converter, photonics,  
 285 optoelectronics, photo-induced catalysis or industrial anti-counterfeiting) to nanobiotechnology

286 (imaging, targeting, and sensing), where long-term stability with high luminescent efficiency is  
287 required.

## 288 **Experimental Section**

289 *General Considerations.* All the reagents and solvents were obtained commercially (e.g. Merck,  
290 Alfa Aesar, Strem Chemicals) and used as received without any further purification. The  
291 commercial colloidal suspension of silica (Silica LUDOX<sup>®</sup> HS-40) was supplied by Grace Davison and  
292 destabilized using a commercial exchange resin Dowex 50x8 protons (Merck), with MESH value of  
293 20-50 and total exchange capacity of 1.7 meq/mL. The purification of the Ir(III) complexes was  
294 performed via column chromatography with the use of Al<sub>2</sub>O<sub>3</sub> as the stationary phase. ESI-mass  
295 spectra were recorded using a Waters ZQ-4000 instrument (ESI-MS, acetonitrile as the solvent).  
296 Nuclear magnetic resonance spectra (consisting of <sup>1</sup>H and <sup>13</sup>C) were always recorded using a  
297 Varian Mercury Plus 400 (<sup>1</sup>H, 399.9; <sup>13</sup>C, 101.0 MHz). <sup>1</sup>H and <sup>13</sup>C chemical shifts were referenced to  
298 residual solvent resonances.

299 *Ligand synthesis.* Warning! Tetrazole derivatives are used as components for explosive  
300 mixtures[22]. In this lab, the reactions described here were only run on a few grams scale and no  
301 problems were encountered. However, great caution should be exercised when handling or  
302 heating compounds of this type. Following the general method reported by Koguro and co-  
303 workers[23], tetrazole ligands [H-PTZ] and [H-QTZ] has been obtained in quantitative yield.

304 *General Procedure for the Preparation of the Cationic Ir(III) complexes.* The preparation of cationic  
305 Ir(III)-complexes was accomplished by following a previously reported procedure [12]. 1 eq of the  
306 desired neutral Ir(III) tetrazolate complex was added to dichloromethane and the mixture was  
307 allowed to cool down by immersion into an ethanol/liquid nitrogen cold bath. Then, methyl  
308 trifluoromethanesulfonate (1.2 equiv., solution in dichloromethane 0.179 M) was added. The  
309 reaction was stirred under nitrogen for 30 minutes while being kept in the cold bath, and then  
310 allowed to warm up to room temperature and stirred for 3 hours. Anion exchange was carried out  
311 by adding an excess of NH<sub>4</sub>PF<sub>6</sub> in water to the solution and stirring for 20 minutes. The product  
312 was then extracted using dichloromethane (3×10 mL) and the organic components were combined  
313 and dried over anhydrous MgSO<sub>4</sub>. Subsequent purification by column chromatography on alumina  
314 (gradient: CH<sub>2</sub>Cl<sub>2</sub>/acetone 8:2, second fraction) yielded 0.059 g of [F<sub>2</sub>IrPTZ-Me]<sup>+</sup>[PF<sub>6</sub>]<sup>-</sup> and 0.067 g  
315 of [IrQTZ-Me]<sup>+</sup>[PF<sub>6</sub>]<sup>-</sup>.



316 *General procedure for the colloidal physical encapsulation.* The Ir(III)-tetrazole based nanosols  
317 were produced by mixing  $[F_2IrPTZ-Me]^+$  or  $[IrQTZ-Me]^+$  with Silica LUDOX<sup>®</sup> HS-40 destabilized using  
318 Dowex 50x8 protons, a commercial exchange resin (Ir(III)tetrazole complex : SiO<sub>2</sub> nanosol ratio =  
319 1:1000, w silica (%) = 20). To facilitate the mixing and the intimate interaction between the two  
320 phases, the systems were left under stirring for about 24 hours at ball-milling, in presence of  
321 grinding bodies made by zirconia balls (diameter, Ø 5mm). The Silica LUDOX<sup>®</sup> HS-40 destabilization  
322 was carried out in a 250 mL flask by adding the resin to the nano-suspension under vigorous  
323 stirring. Once the desired pH was reached (pH = 4), the resin was extracted and the silica/resin  
324 contact was interrupted by vacuum pump filtration [17].

325

326 *General procedure for the Solid-state transfer by Spray Freeze Granulation.* The silica-doped  
327 colloidal solutions were transferred to solid-state phases by the means of Lab-scale Granulator LS-  
328 2 (PowderPro AB). The two Ir(III)@SiO<sub>2</sub> nanosol were kept under magnetic stirring to prevent solid  
329 sedimentation and fed to the nozzle (Ø = 100 µm) through a peristaltic pump (40 rpm). The spray  
330 was obtained by blowing suspension and nitrogen (0.4 bar) in the nozzle, collecting the nanosol  
331 drops in a camera that was previously filled up with liquid nitrogen. The frozen drops were placed  
332 in a metallic vessel inside the lyophilizer for 4 days, reaching the pressure of 1.5 mbar.

333 *Colloidal Characterization.* Size and ZP (Zeta Potential) measurements of the nano-solutions were  
334 carried out with DLS/ELS (dynamic light scattering and electrophoretic light scattering Zetasizer  
335 Nano instrument ZSP, ZEN5600, Malvern Instruments, UK). The study of the colloidal behaviour  
336 and the interaction between silica and Ir(III) complexes (Zeta potential vs pH) were carried out by  
337 Zetasizer Nano instrument coupled with an automatic titrating system. The titration were  
338 performed with 1M KOH and 1M HCl solutions on Ir(III)@SiO<sub>2</sub> systems at a concentration of  
339 0.01%wt. The interaction between Ir(III) complexes and silica nanosol matrix was evaluated with  
340 TEM (transmission electron microscopy, FEI, Tecnai F20 S/TEM) equipped with an EDX probe.

341

342 *Morphological Powder Characterization.* The morphological characterization of freeze-dry particles  
343 was performed by SEM-FEG electron emission scanning microscope (Supra, Gemini Column, Zeiss)  
344 and by Optical Stereo Microscope OLYMPUS SZX9 with Nikon DS-Fi2 camera and ocular OLYMPUS  
345 DF PL 2xa (OLYMPUS).

346

347 *Optical Powders Characterization.* To estimate the optical inactivity of SiO<sub>2</sub> in respect of Ir(III)-  
 348 complexes, the 3%wt silica LUDOX® HS-40 nanosol have been analyzed at spectrophotometer  
 349 Lambda 35 (Perkin Elmer). The degree of dispersion of the Ir(III) complexes within the silica matrix  
 350 was checked by optical microscope Zeiss, AXIO Zoom V16 equipped with CL 9000 LED white source  
 351 (900 lm, 6500K, emission spectrum 400-800nm), while for luminescence microscopy images with a  
 352 HXP 120V source metal halide lamp (emission spectrum 360-670 nm, excitation filter: BP = 470 ±  
 353 40 nm, beam splitter: FT = 495 nm, emission: BP = 525 ± 50 nm).

354

355 *Photophysical characterization.* Absorption spectra were recorded at room temperature using a  
 356 Perkin Elmer Lambda 35 UV/vis spectrometer. Uncorrected steady-state emission and excitation  
 357 spectra were recorded on an Edinburgh FLSP920 spectrometer equipped with a 450 W xenon arc  
 358 lamp, double excitation and single emission monochromators, and a Peltier-cooled Hamamatsu  
 359 R928P photomultiplier tube (185–850 nm). Emission and excitation spectra were acquired with  
 360 cut-off filter (395 nm) and corrected for source intensity (lamp and grating) and emission spectral  
 361 response (detector and grating) by a calibration curve supplied with the instrument. The  
 362 wavelengths for the emission and excitation spectra were determined using the absorption  
 363 maxima of the MLCT transition bands (emission spectra) and at the maxima of the emission bands  
 364 (excitation spectra). Quantum yields (Φ) were determined using the optically dilute method by  
 365 Crosby and Demas [24] at excitation wavelength obtained from absorption spectra on a  
 366 wavelength scale [nm] and compared to the reference emitter by the following equation:

$$\phi_s = \phi_r \left[ \frac{A_r(\lambda_r)}{A_s(\lambda_s)} \right] \left[ \frac{I_r(\lambda_r)}{I_s(\lambda_s)} \right] \left[ \frac{n_s^2}{n_r^2} \right] \left[ \frac{D_s}{D_r} \right]$$

367

368 where A is the absorbance at the excitation wavelength (λ), I is the intensity of the excitation light  
 369 at the excitation wavelength (λ), n is the refractive index of the solvent, D is the integrated  
 370 intensity of the luminescence, and Φ is the quantum yield. The subscripts r and s refer to the  
 371 reference and the sample, respectively. A stock solution with an absorbance > 0.1 was prepared,  
 372 then two dilutions were obtained with dilution factors of 20 and 10, resulting in absorbance of  
 373 about 0.02 and 0.08 respectively. The Lambert-Beer law was assumed to remain linear at the  
 374 concentrations of the solutions. The degassed measurements were obtained after the solutions  
 375 were bubbled for 10 minutes under Ar atmosphere, using a septa-sealed quartz cell. Air-  
 376 equilibrated [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>/H<sub>2</sub>O solution (Φ = 0.028) [25] was used as reference. The quantum yield

determinations were performed at identical excitation wavelengths for the sample and the reference, therefore deleting the  $I(\lambda_r)/I(\lambda_s)$  term in the equation. Emission lifetimes ( $\tau$ ) were determined with the single photon counting technique (TCSPC) with the same Edinburgh FLSP920 spectrometer using pulsed picosecond LED (ELED 360, FWHM < 800ps) as the excitation source, with repetition rates between 1 kHz and 1 MHz, and the above-mentioned R928P PMT as detector. The goodness of fit was assessed by minimizing the reduced  $\chi^2$  function and by visual inspection of the weighted residuals. To record the 77 K luminescence spectra, the samples were put in quartz tubes (2 mm diameter) and inserted in a special quartz Dewar filled with liquid nitrogen. The solvent used in the preparation of the solutions for the photophysical investigations was of spectrometric grade. Experimental uncertainties are estimated to be  $\pm 8\%$  for lifetime determinations,  $\pm 20\%$  for quantum yields, and  $\pm 2$  nm and  $\pm 5$  nm for absorption and emission peaks, respectively. The pellets used in the variable-temperature emission experiments have been obtained by using 50 mg of  $[\text{F}_2\text{IrPTZ-Me}]^+@ \text{SiO}_2$  powder or  $[\text{IrQTZ-Me}]^+@ \text{SiO}_2$  powder squashed in a cylinder-shaped metallic tube ( $\varnothing$  0.5 cm) for 1 min under 1 ton. The variable-temperature emission spectra (from 13K to r.t.) were recorded with an SP500i Spectrometer (ACTION RESEARCH, grating 150gr/mm, slit 50  $\mu\text{m}$ ) equipped with a sensitive liquid nitrogen-cooled CCD camera and a He-Cd laser (KIMMON company) at 325 nm as excitation source (spot size = 100  $\mu\text{m}$ , power = 30mW).

*BET analysis.* The Specific Surface Area (SSA) measurements were carried out with a Surfer instrumentation (Thermo Scientific) ( $P = 150\text{--}300$  torr,  $T = -200^\circ\text{C}$ ). Before performing analysis, the samples were thermal pre-treated ( $120^\circ\text{C}$ ) to eliminate any organic traces.

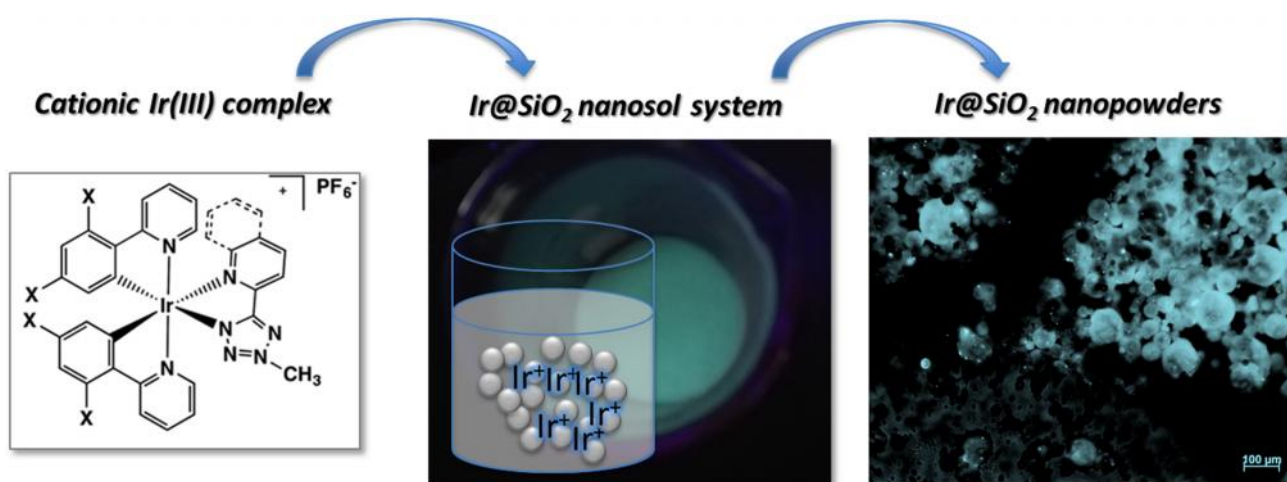
*Micronized Stability.* The stability of micronized powders has been evaluated through time-release tests under mechanical stirring. A 0.1 g amount of  $\text{Ir(III)}@ \text{SiO}_2$  nano-powder and 10 mL of Milli-Q  $\text{H}_2\text{O}$  were stirred for different contact time (from 30 min to 25.5 h). After each period, 0.5 mL of the suspension were removed and added to 5 mL of fresh Milli-Q  $\text{H}_2\text{O}$  and subsequently analyzed.

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412 **Graphical Abstract**



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