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4 **characterization and optical properties**

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

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30
31 **Abstract**

32 Herein we report the easy incorporation of brightly phosphorescent cationic Iridium(III) tetrazole
33 complexes into a silica based matrix through an easily scalable colloidal process. To this purpose, two
34 cationic Ir(III) emitters bearing 5-aryl tetrazole ligands (R-CN₄) were selected: the blue **[F₂IrPTZ-Me]⁺** (C[^]N =
35 F₂ppy; N[^]N = PTZ-Me - 2-(2-methyl-2H-tetrazol-5-yl)pyridine) and the red **[IrQTZ-Me]⁺** (C[^]N = ppy; N[^]N =
36 QTZ-Me - 2-(2-methyl-2H-tetrazol-5-yl)quinoline). The cationic complexes were readily adsorbed to
37 negatively charged silica nanoparticles and trapped in the sol-gel matrix. The *sol-to-solid* phase transfer was
38 performed by using an innovative *spray-freeze-drying* technique, leading to the formation of
39 phosphorescent solid micro-granules. The structural and optical characterisation of the Ir(III) complexes
40 together with SiO₂ nanoparticles, nanosols (**Ir@SiO₂**) and powders (**Ir@SiO₂ powders**), revealed how the
41 presence of the Ir(III)-based complexes did not alter the morphology of colloidal silica and granulated
42 phases. Moreover, the silica matrix did not interfere with the optical properties of the embedded
43 complexes. The distribution of **[F₂IrPTZ-Me]⁺** and **[IrQTZ-Me]⁺** in the spray-freeze-dried powders was
44 qualitatively evaluated by fluorescence microscopy, revealing how the luminescent particles were
45 homogeneously dispersed all over the silica matrix. Interestingly, in aqueous solution the release of the
46 complex **[F₂IrPTZ-Me]⁺** from the corresponding **Ir@SiO₂ powder** is almost negligible, therefore suggesting
47 the strong interaction occurring between the host-silica matrix and the Ir(III) guest complex.

50 Introduction

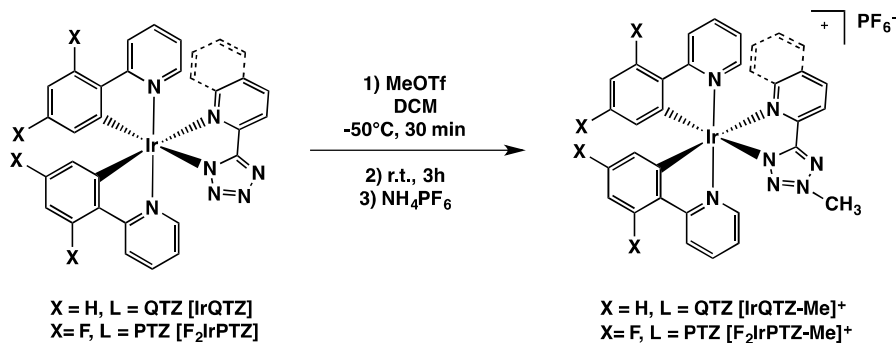
51 The scenario of iridium-transition metal complexes (Ir-TMCs) has been extensively expanded
52 through a multitude of examples [1]. In this context, great efforts have been spent with the family
53 of Ir(III) cyclometalates, a versatile class of compounds with general formula $[\text{Ir}(\text{C}^{\wedge}\text{N})(\text{N}^{\wedge}\text{N})]^{0/+}$
54 ($\text{C}^{\wedge}\text{N}$ = phenylpyridine - ppy - or 2, 4 difluoro-phenylpyridine - F_2ppy -, $\text{N}^{\wedge}\text{N}$ = 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 (τ) and high quantum
57 yield (Φ) 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 (SiO_2NPs) 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, SiO_2NPs 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 SiO_2NPs 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

82 interactions between the negatively charged silica colloidal phase and the positively charged
83 guest. The latter approach presents several advantages in comparison to core-shell protocols,
84 since they don't require expensive reagents or chemical treatment, avoiding the formation of any
85 byproduct. The main goal of the present study is to exploit and optimize new and easy to apply
86 methods to incorporate Ir(III) tetrazolate complexes into silica-based colloid matrices, in order to
87 improve their chemical and photophysical stability, enhancing their processing at liquid and dry
88 state. Within this framework, two Ir(III) emitters bearing 5-aryl tetrazole ligands such as the sky-
89 blue **[F₂IrPTZ-Me]⁺** (C^{AN} = F₂ppy; N^{AN} = **PTZ-Me** - 2-(2-methyl-2H-tetrazol-5-yl)pyridine) and the
90 red phosphorescent **[IrQTZ-Me]⁺** (C^{AN} = ppy; N^{AN} = **QTZ-Me** - 2-(2-methyl-2H-tetrazol-5-
91 yl)quinoline) complexes (Scheme 1) were selected as cationic coatings for negatively charged
92 SiO₂NPs, being able to cover the two opposite part of visible spectrum [12]. Prompted by the
93 encouraging results in terms of both physical and optical stability, **Ir@SiO₂** nanosols were
94 transferred to dry-powder state by the means of Spray-Freeze-Drying technique, an innovative
95 procedure in the field that enabled the formation of two stable luminescent **Ir@SiO₂ powders**
96 avoiding heat assisted drying processes that may alter both chemical and photophysical properties
97 of the Ir(III) tetrazole complexes used as coating for silica nanoparticles [13][14][15].

98 **Results and discussion**

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

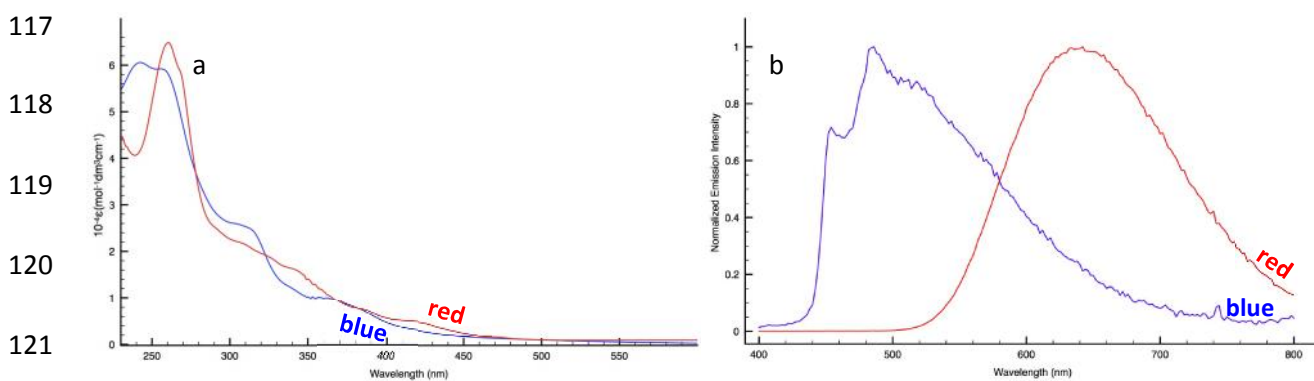
100 The preparation of the cationic Ir(III) tetrazolate complexes **[F₂IrPTZ-Me]⁺** and **[IrQTZ-Me]⁺** was
101 accomplished by following a previously reported procedure (Scheme 1) [12], which consists of an
102 electrophilic addition at the tetrazole ring of the corresponding neutral Ir(III) precursor. The
103 formation of the desired cationic Ir(III)-cyclometalates was at first confirmed by electrospray
104 ionisation mass spectrometry (ESI-MS), which revealed the presence of the expected *m/z* signals in
105 the positive region ions (Figure S5-6 ESI). The ¹H-NMR characterization provided a number of
106 protonic resonances congruent with the low symmetry displayed by the complexes (Figure S1-2
107 ESI). As previously reported [12], the electrophilic addition performed on the [R-CN₄]⁻ moiety
108 regioselectively occurs at the N-2 atom of the tetrazolate ring, as witnessed by ¹³C-NMR resonance
109 of Ct (tetrazolic carbon) which has been found at 166.54 ppm for **[F₂IrPTZ-Me]⁺** and 167.93 ppm
110 for **[IrQTZ-Me]⁺** (Figure S3-4 ESI).



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

113 *Photophysical properties*

114 In 10⁻⁵M CH₂Cl₂ solutions, all the cationic Ir(III) complexes displayed similar absorption profiles,
115 with intense ligand centred (¹LC) transitions up to 260 nm and metal-to-ligand charge transfer
116 (¹MLCT) bands tailing off above 380 nm (Figure 1a).



122 **Figure 1:** (a) Absorption Profiles of blue emitting [F₂IrPTZ-Me]⁺ (blue line) and red emitting [IrQTZ-Me]⁺ (red
123 line), 10⁻⁵M, CH₂Cl₂; (b) Normalized Emission Profiles of [F₂IrPTZ-Me]⁺ (blue line) and [IrQTZ-Me]⁺ (red line),
124 CH₂Cl₂.

125 Upon excitation of the ¹MLCT features (λ = 370 nm), [F₂IrPTZ-Me]⁺ displayed a sky-blue emission
126 colour that corresponds to a structured emission profile with λ_{max} = 454, 486 and 526 nm (Figure
127 1b and Table 1), suggesting an interplay of ³LC/³MLCT-type emissive excited states [1]. On the
128 contrary, the red emitter [IrQTZ-Me]⁺ produced a broad and unstructured emission profile with
129 λ_{max} = 638 nm, typical of ³MLCT-based phosphorescence (Figure 1b), as evidenced also by the
130 noticeable rigidochromic shift observed in frozen solvent matrix at 77K (λ_{max} = 568 nm, Table 1).

131

132

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

CH ₂ Cl ₂ as the solvent	Absorption	Emission 298 K ^{a,b}					Emission 77K ^c	
	$\lambda_{\text{abs}}(\text{nm});(10^{-4}\epsilon)(\text{M}^{-1}\text{cm}^{-1})$	λ_{em} (nm)	τ_{air} (μs)	τ_{Ar} (μs)	Φ_{air} (%)	Φ_{Ar} (%)	λ_{em} (nm)	τ (μs)
[IrQTZ-Me] ⁺	253 (4.25), 310 (1.41), 374 (0.78)	638	0.220	0.550	2.8	4.5	568	1.56
[F ₂ IrPTZ-Me] ⁺	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 ^a: "Air" means air equilibrated solutions, "Ar" means deoxygenated solutions under argon atmosphere; ^b:
 135 [Ru(bpy)₃]Cl₂/H₂O was used as reference for quantum yield determinations ($\Phi_r = 0.028$); ^c: in frozen CH₂Cl₂

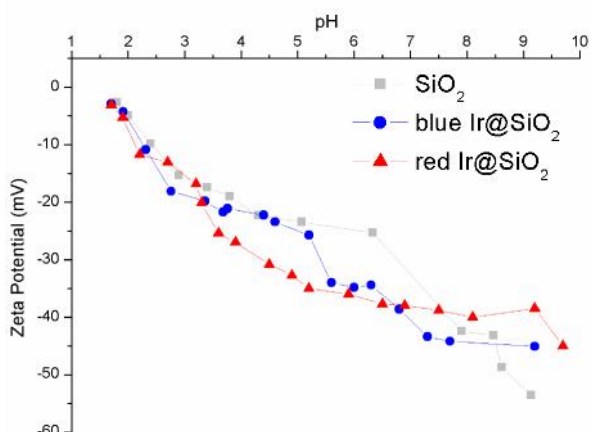
136 *Ir@SiO₂ nanosols systems*

137 Ir@SiO₂ nanosols (namely: **blue** Ir@SiO₂ for [F₂IrPTZ-Me]⁺ and **red** Ir@SiO₂ for [IrQTZ-Me]⁺) 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⁺ with H₃O⁺ 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⁺ substitution by H₃O⁺ ions
 142 affects silica bonding, with the replacement of dissociated silanol-silanol bonds by cross-linked
 143 siloxane bonds: -Si-OH...O⁻-Si- → -Si-O-Si + 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@SiO₂**
 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 SiO₂NPs. 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 SiO₂NPs was
 152 not significantly affected by the physical mixing with the Ir(III)-markers, as confirmed by
 153 hydrodynamic radius (R_{hyd}) values obtained from DLS analyses (Table 2).

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

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

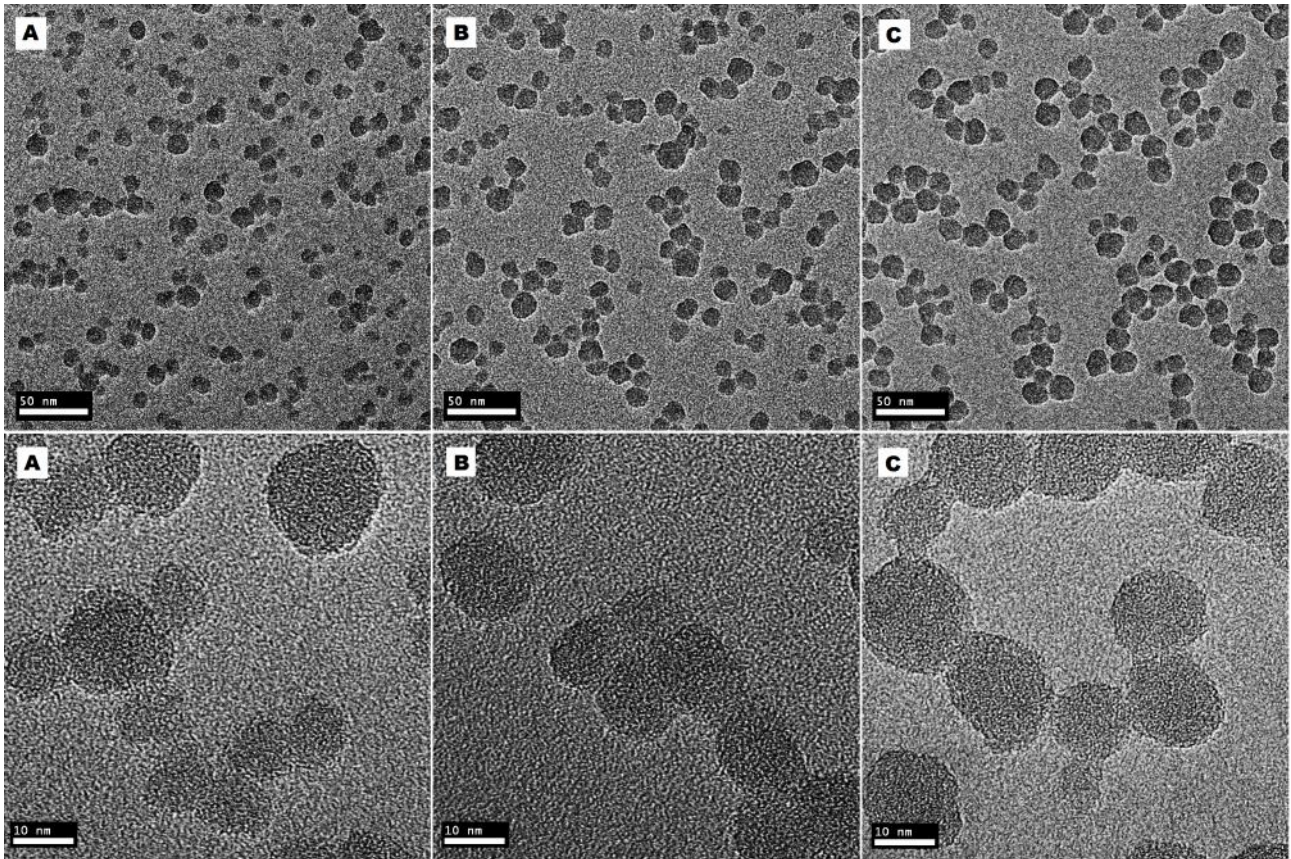
155 *Commercial SiO₂ destabilized through treatment on cationic-exchange resin.



156

157 **Figure 2:** Zeta Potential (mV) vs pH plot of silica nanosol (grey line), blue Ir@SiO₂ (blue line) and red Ir@SiO₂
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_{hyd} (Table 2). TEM images highlight a negligible
163 increase of the SiO₂ NPs mean diameter (\varnothing SiO₂ 13.7±3.1 nm, \varnothing **blue Ir@SiO₂** 13.8±3.1 nm, \varnothing **red**
164 **Ir@SiO₂** 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 SiO₂NPs, imputable to the
167 presence of Ir(III) complexes, as shown in Figure 4 and confirmed by EDX analysis.



168

169 **Figure 3:** TEM images on copper grid acquired at different magnifications of A) SiO₂NPs, B) **blue Ir@SiO₂**, C)
 170 **red Ir@SiO₂**.

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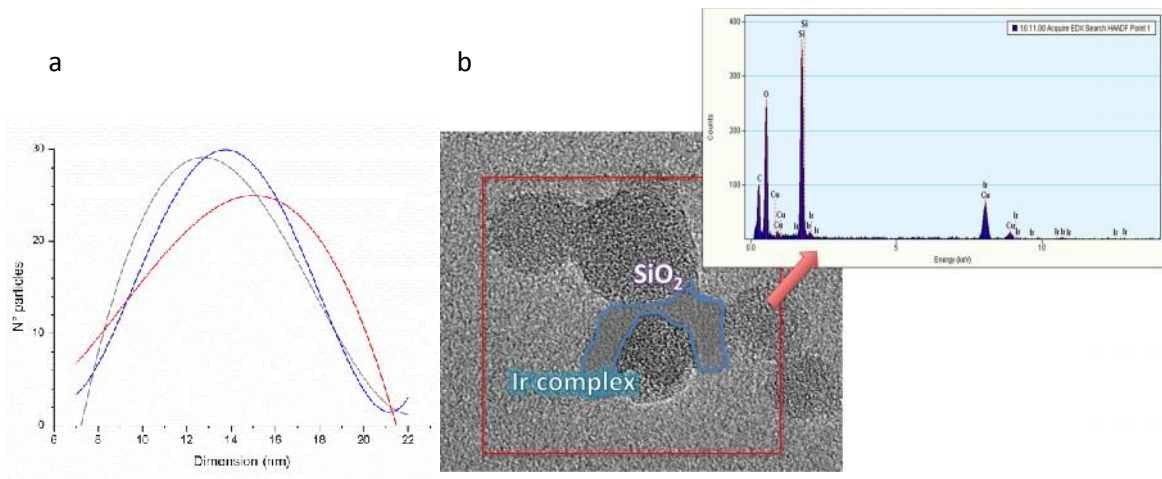
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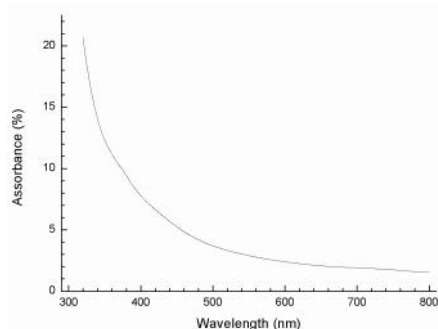
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178 **Figure 4:** a) Nanoparticles distribution made by 250 particles-population: SiO₂NPs (grey line), **blue Ir@SiO₂**
 179 **(blue line), red Ir@SiO₂** (red line); b) TEM image of **blue Ir@SiO₂**, with relative EDS analysis.

180 As previously reported in literature [10], colloidal silica has no optical influence over the
 181 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 SiO₂NPs (Figure 5), where no maxima were found in the region of interest.



184

185 **Figure 5:** Absorbance (%) vs Wavelength (nm) plot of SiO₂NPs, 3%wt, Milli-Q H₂O, r.t.

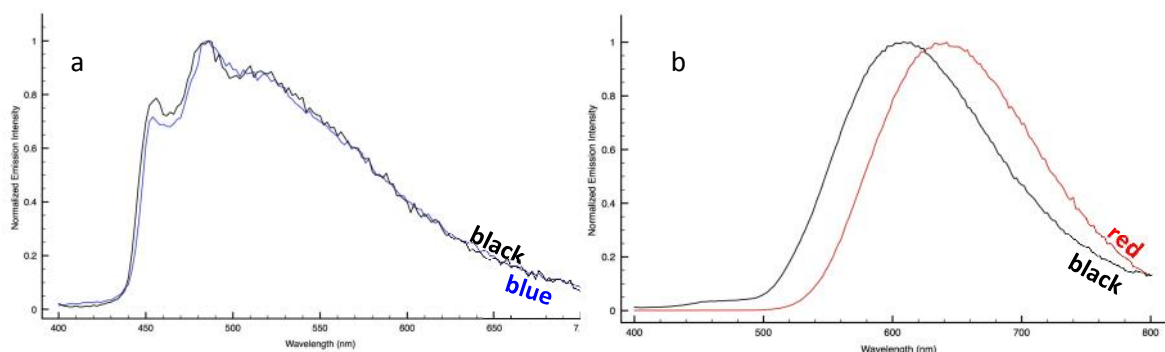
186 **Table 3:** Relevant photophysical properties of Ir(III)-complexes@SiO₂ nanosols systems.

H ₂ O as solvent	Absorption λ_{abs} (nm)	Emission 298 K				
		λ_{em} (nm)	τ_{air} (μs)	τ_{Ar} (μs)	ϕ_{air} (%)	$\Delta\lambda$ (nm)
Red Ir@SiO₂	252, 312	610	0.100	n.d.*	n.d.*	28
Blue Ir@SiO₂	263, 286, 310	454, 484, 520	0.010	n.d.*	n.d.*	0

187 *n.d. = not determined.

188 The emission profiles of **[F₂IrPTZ-Me]⁺** and its silica embedded structure **blue Ir@SiO₂** (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 **[F₂IrPTZ-Me]⁺** and the silica matrix. On the other
 191 hand, the rigidochromic blue shift encountered in the emission profile of **red Ir@SiO₂** in respect of
 192 **[IrQTZ-Me]⁺** (Table 3 and Figure 6b) is in agreement with the prevailing ³MLCT composition of its
 193 excited state, being more sensitive to modifications of the surrounding chemical environment [1].

194

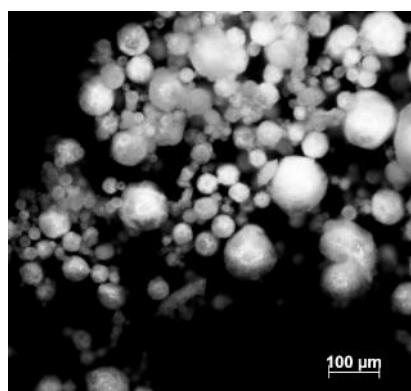


197

198 **Figure 6:** Comparison between normalised emission profiles $[F_2IrPTZ-Me]^+$ (blue line) and $[IrQTZ-Me]^+$
199 (red line) complexes and their **Ir@SiO₂ systems** (black lines).

200 *Ir@SiO₂ powders*

201 Both **blue** and **red Ir@SiO₂** 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@SiO₂
204 nanosols [11][19][20][21]. The morphology of the obtained **blue** and **red Ir@SiO₂ powders** was
205 checked by optical microscopy and SEM-FEG. The microstructure of spray-freeze-dried granules of
206 both SiO₂ and **Ir@SiO₂ powders** appeared spherical and regular, with a broad distribution (Figures
207 7 and 8). The mean diameter of **Ir@SiO₂ powders** was significantly reduced, from $22.6 \pm 12.6 \mu\text{m}$
208 of SiO₂ considered alone to $17.5 \pm 11.3 \mu\text{m}$ and $18.0 \pm 11.4 \mu\text{m}$ for **Ir@SiO₂ powders**, as a result of
209 an intense interaction between SiO₂NPs 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 ($207.78 \pm 4.16 \text{ m}^2/\text{g}$) and Ir@SiO₂ powders (**blue Ir@SiO₂ powder**,
214 $225.13 \pm 4.50 \text{ m}^2/\text{g}$; **red Ir@SiO₂ powder**, $213.96 \pm 4.28 \text{ m}^2/\text{g}$).

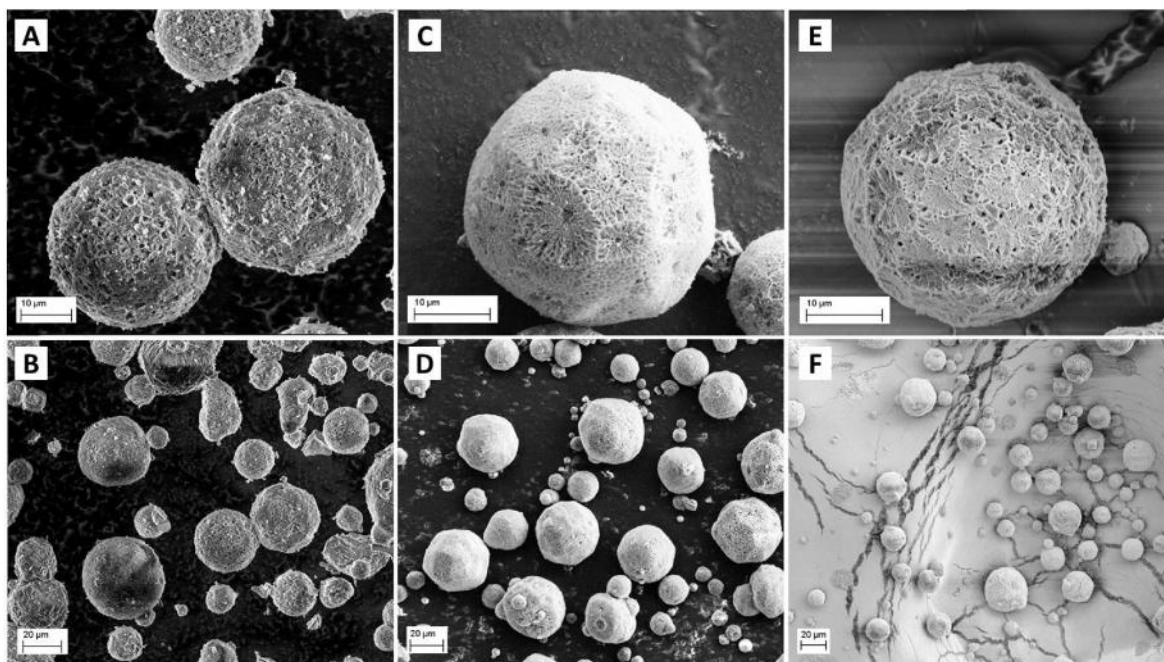


SiO ₂ -powder	SEM-FEG granules-size (μm)
blue Ir@SiO ₂ powder	$17.5 \pm 11.3 \mu\text{m}$
red Ir@SiO ₂ powder	$18.0 \pm 11.4 \mu\text{m}$
SiO ₂	$22.6 \pm 12.6 \mu\text{m}$

215

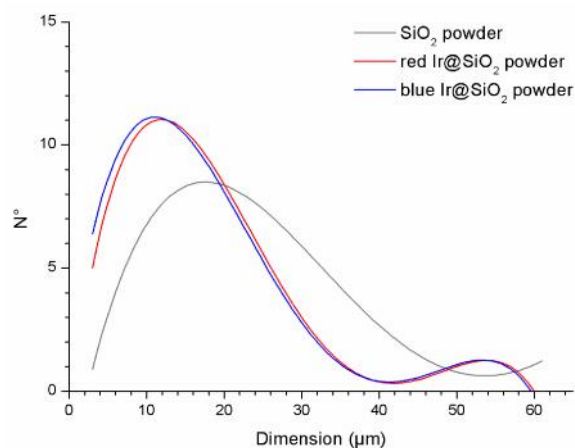
216 **Figure 7:** Optical micrograph of SiO₂ powder.

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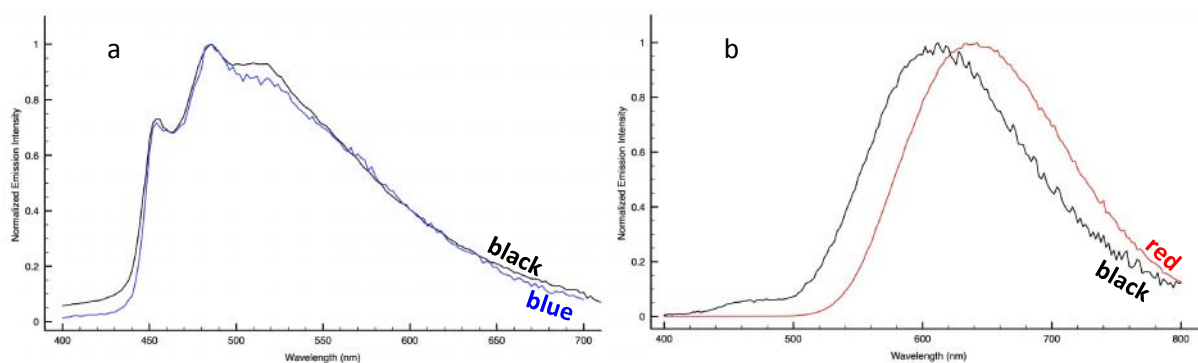
Figure 8: SEM-FEG images of SiO₂ (A, B), **blue Ir@SiO₂ powder** (C, D) and **red Ir@SiO₂ powder** (E, F).



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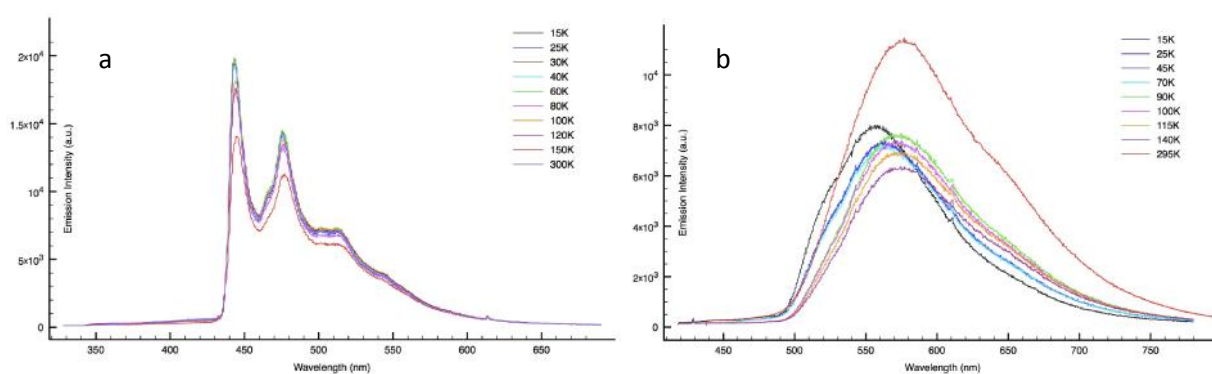
Figure 9: Size distribution of micronized SiO₂ powders (grey trace), **blue Ir@SiO₂ powder** (blue trace) and **red Ir@SiO₂ powder** (red trace). The mean value was calculated for a population of 250 particles.

225 As previously discussed for Ir@SiO₂ nanosols, only the **red Ir@SiO₂ powder** ($\lambda_{\text{max}}=577$ nm)
 226 displayed a significant rigidochromic blue shift in comparison to [IrQTZ-Me]⁺ (Figure 10). This
 227 behavior was further confirmed by variable temperature emission studies over the range 15-300K,
 228 where no substantial changes were observed for the **blue Ir@SiO₂ powder** (Figure 11a), while for
 229 the **red** one, a blue shift of the emission maxima from to 570 to 550 nm was detected (Figure 11b)
 230 [1]. In both cases, the presence of surrounding silica matrix and the temperature decrease are two
 231 driving forces that change the environment polarity, stiffening the system structure and
 232 modulating the final phosphorescent outcome of the **red Ir@SiO₂ powder**.



233

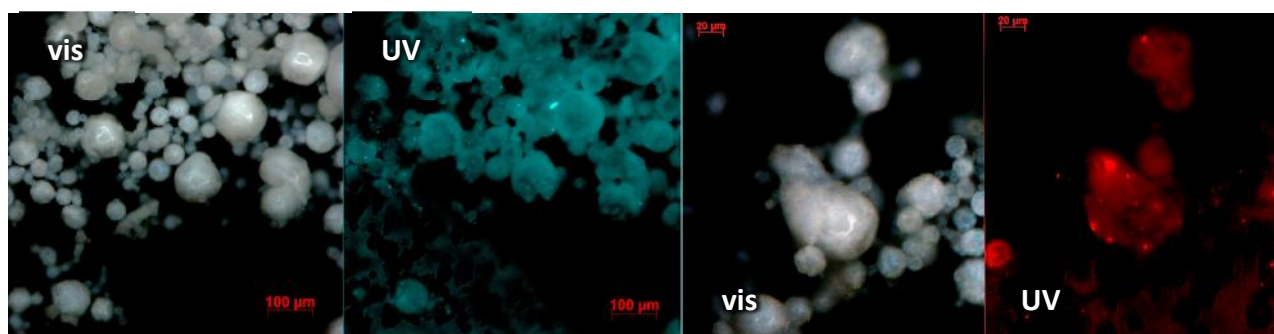
234 **Figure 10:** a) Normalized Emission Profiles of $[F_2IrPTZ-Me]^+$ (blue line) and **blue Ir@SiO₂ powder** (black
 235 line); b) Normalized Emission Profiles of $[IrQTZ-Me]^+$ (red line) and **red Ir@SiO₂ powder** (black line).



236

237 **Figure 11:** Variable temperature emission studies of a) **blue Ir@SiO₂ powder** and b) **red Ir@SiO₂ powder**
 238 (15-300 K).

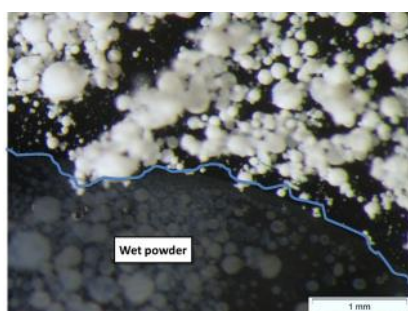
239 The distribution of $[F_2IrPTZ-Me]^+$ and $[IrQTZ-Me]^+$ complexes in the ceramic micronized powders
 240 were evaluated by fluorescence microscopy (Figure 12). For both **Ir@SiO₂ powders**, the
 241 luminescent properties resulted homogeneously spread over the silica matrix. Using *Spray-Freeze-*
 242 *Drying* technique, we avoided any possible thermal degradation, as that a *Spray-Drying* processes
 243 can induce with a consequent damage or deface of Ir(III) complexes luminescent properties. The
 244 Ir@SiO₂ nanosol were sprayed and frozen, thus preserving the NPs and complexes distribution as
 245 was in dispersed liquid phase. No separate cluster of luminescent marker are appreciated and a
 246 distribution of spherical luminescent micro-particles was detectable under fluorescence
 247 microscope.



248

249 **Figure 12:** Micrographs of (left) **blue Ir@SiO₂ powder** and (right) **red Ir@SiO₂ powder** with visible and
 250 fluorescence source.

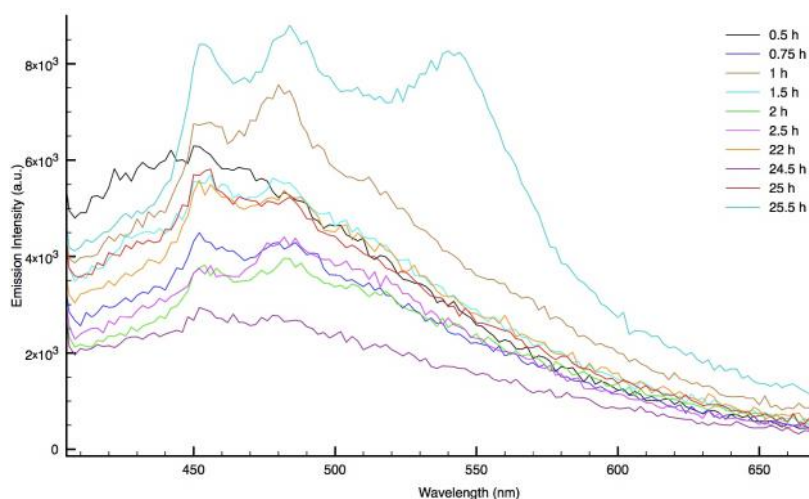
251 The wettability of **Ir@SiO₂ powders** was evaluated by observing the particles morphology in the
 252 presence of water (“Drop-Test”, Figure 13). **Ir@SiO₂ powders** preserved their spherical shape
 253 without decomposing in a time period of 15 minutes, thus exhibiting some mechanical strength
 254 even after water-contact, encouraging the use of these systems in the large spectrum of wet
 255 powder process applications.



256

257 **Figure 13:** Drop-test for **blue Ir@SiO₂ powder** acquired with OLYMPUS SZX9.

258 The release of **[F₂IrPTZ-Me]⁺** from the **blue Ir@SiO₂ powder** was evaluated in both organic and
 259 inorganic media (CH₃CN, CH₂Cl₂ and H₂O; see Figure 12 and S7-8 ESI), by acquiring emission
 260 spectra of the liquid phase separated from the suspension of **blue Ir@SiO₂ powder**, kept under
 261 mechanical stirring for approx. 25 hours (Figure 14). The emission profiles suggest a very low
 262 release percentage of **[F₂IrPTZ-Me]⁺** (presumably below 10⁻⁹ M), confirming the strong interaction
 263 occurring between the host-silica matrix and the **[F₂IrPTZ-Me]⁺** complex.



264

265 **Figure 14:** Water-release emission test of $[\text{F}_2\text{IrPTZ-Me}]^+$ from blue Ir@SiO_2 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_2 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_2 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[®] 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 Al₂O₃ 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 ¹H and ¹³C) were always recorded using a
297 Varian Mercury Plus 400 (¹H, 399.9; ¹³C, 101.0 MHz). ¹H and ¹³C 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 NH₄PF₆ 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 MgSO₄. Subsequent purification by column chromatography on alumina
314 (gradient: CH₂Cl₂/acetone 8:2, second fraction) yielded 0.059 g of [F₂IrPTZ-Me]⁺[PF₆]⁻ and 0.067 g
315 of [IrQTZ-Me]⁺[PF₆]⁻.

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[®] HS-40 destabilized using
318 Dowex 50x8 protons, a commercial exchange resin (Ir(III)tetrazole complex : SiO₂ 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, \varnothing 5mm). The Silica LUDOX[®] 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)@SiO₂ nanosol were kept under magnetic stirring to prevent solid
329 sedimentation and fed to the nozzle (\varnothing = 100 μ m) 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)@SiO₂ 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 SiO₂ 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)₃]Cl₂/H₂O solution (Φ = 0.028) [25] was used as reference. The quantum yield

377 determinations were performed at identical excitation wavelengths for the sample and the
378 reference, therefore deleting the $I(\lambda_r)/I(\lambda_s)$ term in the equation. Emission lifetimes (τ) were
379 determined with the single photon counting technique (TCSPC) with the same Edinburgh FLSP920
380 spectrometer using pulsed picosecond LED (ELED 360, FWHM < 800ps) as the excitation source,
381 with repetition rates between 1 kHz and 1 MHz, and the above-mentioned R928P PMT as
382 detector. The goodness of fit was assessed by minimizing the reduced χ^2 function and by visual
383 inspection of the weighted residuals. To record the 77 K luminescence spectra, the samples were
384 put in quartz tubes (2 mm diameter) and inserted in a special quartz Dewar filled with liquid
385 nitrogen. The solvent used in the preparation of the solutions for the photophysical investigations
386 was of spectrometric grade. Experimental uncertainties are estimated to be $\pm 8\%$ for lifetime
387 determinations, $\pm 20\%$ for quantum yields, and ± 2 nm and ± 5 nm for absorption and emission
388 peaks, respectively. The pellets used in the variable-temperature emission experiments have been
389 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
390 in a cylinder-shaped metallic tube (\varnothing 0.5 cm) for 1 min under 1 ton. The variable-temperature
391 emission spectra (from 13K to r.t.) were recorded with an SP500i Spectrometer (ACTION
392 RESEARCH, grating 150gr/mm, slit 50 μm) equipped with a sensitive liquid nitrogen-cooled CCD
393 camera and a He-Cd laser (KIMMON company) at 325 nm as excitation source (spot size = 100 μm ,
394 power = 30mW).

395 *BET analysis.* The Specific Surface Area (SSA) measurements were carried out with a Surfer
396 instrumentation (Thermo Scientific) (P= 150–300 torr, T= -200°C). Before performing analysis, the
397 samples were thermal pre-treated (120°C) to eliminate any organic traces.

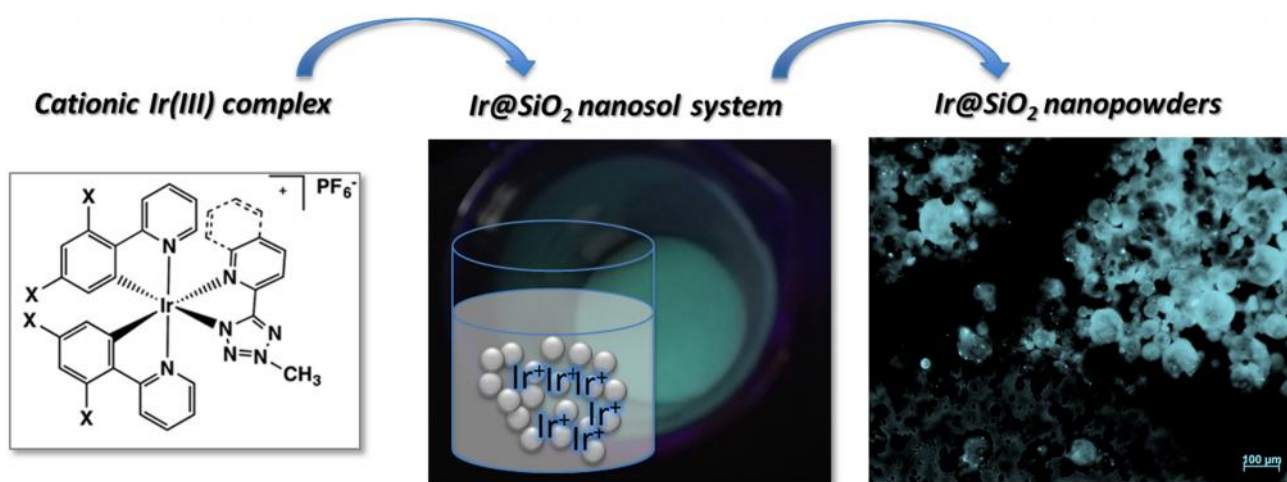
398 *Micronized Stability.* The stability of micronized powders has been evaluated through time-release
399 tests under mechanical stirring. A 0.1 g amount of Ir(III) @SiO_2 nano-powder and 10 mL of Milli-Q
400 H₂O were stirred for different contact time (from 30 min to 25.5 h). After each period, 0.5 mL of
401 the suspension were removed and added to 5 mL of fresh Milli-Q H₂O and subsequently analyzed.

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412 **Graphical Abstract**



413

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415 **References**

- 416 [1] L. Flamigni, A. Barbieri, C. Sabatini, B. Ventura and F. Barigelletti, *Top. Curr. Chem.*, 2007,
417 **281**, 143–203.
- 418 [2] S. Stagni, S. Colella, A. Palazzi, G. Valenti, S. Zacchini, F. Paolucci, M. Marcaccio, R. Q.
419 Albuquerque and L. De Cola, *Inorg. Chem.*, 2008, **47**, 10509–10521.
- 420 [3] V. Fiorini, S. Zacchini, P. Raiteri, R. Mazzoni, V. Zanotti, M. Massi and S. Stagni, *Dalton*
421 *Trans.*, 2016, **45**, 12884–12896.
- 422 [4] H. Xu, R. Chen, Q. Sun, W. Lai, Q. Su, W. Huang and X. Lui, *Chem. Soc. Rev.*, 2014, **43**, 3259–
423 3302.
- 424 [5] S. Takizawa, R. Aboshi and S. Murata, *Photochem. Photobiol. Sci.*, 2011, **10**, 895.
- 425 [6] a) V. Fernandez-Moreira, F. L. Thorp-Greenwood and M. P. Gogan, *Chem. Commun.*, 2010,
426 **46**, 186–202; b) K. Y. Zhang and K. K.-W. Lo, Chemosensing and Diagnostics, in *Coordination*
427 *and Organometallic Chemistry (Volume 8) of Comprehensive Inorganic Chemistry II*, ed. V.
428 W.-W. Yam, Elsevier, Amsterdam, 2013, pp. 657–732 and references cited therein.
- 429 [7] W. Liang, Y. Zhuo, C. Xiong, Y. Zheng, Y. Chai and R. Yuan, *Biosens. Bioelectron.*, 2017, **94**,
430 568–574.
- 431 [8] G. Kickelbick, Introduction to Hybrid Materials, in *Hybrid Materials: Synthesis,*
432 *Characterization, and Applications* Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim,
433 Germany. doi: 10.1002/9783527610495.
- 434 [9] S. Titos-Padilla, E. Colacio, S. J. A. Pope, J. J. Delgado, M. Melgosa and J. M. Herrera, *J.*
435 *Mater. Chem. C*, 2013, **1**, 3808.
- 436 [10] S. Santra, P. Zhang, K. Wang, R. Tapeç and W. Tan, *Anal. Chem.*, 2001, **73**, 4988–4993.
- 437 [11] D. Gardini, M. Blosi, C. Delpivo, S. Ortellì and A. L. Costa, *J. Phys. Conf. Ser.*, 2013, **429**,
438 12052.
- 439 [12] V. Fiorini, I. Zanoni, S. Zacchini, A. L. Costa, A. Hochkoeppler, V. Zanotti, A. M. Ranieri, M.
440 Massi, A. Stefan and S. Stagni, *Dalt. Trans.*, 2017, **46**, 12328.
- 441 [13] M.E. Ali, A. Lamprecht, Spray freeze drying for dry powder inhalation of nanoparticles, *Eur.*
442 *J. Pharm. Biopharm.* 87 (2014) 510–517.
- 443 [14] A. L. Costa, B. Ballarin, A. Spegni, F. Casoli and D. Gardini, *J. Colloid Interface Sci.*, 2012, **388**,
444 31–39.
- 445 [15] C. Anandharamakrishnan, Spray Drying; Freeze Drying; Spray Freeze Drying. in *Handbook of*
446 *Drying for Dairy Products*, 2017, 57–148.

- 447 [16] G. Davison, Q. Grace, Sílice coloidal ludox[®] hs-40.
- 448 [17] S. Ortelli, A. L. Costa and M. Dondi, *Materials (Basel)*, 2015, **8**, 7988–7996.
- 449 [18] F. Dumont, and A. Watillon, *Discuss. Faraday Soc.*, 1971, **52**, 352–360.
- 450 [19] Y -F. Maa, P -A. Nguyen, T. Sweeney, S. J. Shire and C. C. Hsu, *Pharm. Res.*, 1999, **16**, 249–
451 254.
- 452 [20] L. F. Ballesteros, M. J. Ramirez, C. E. Orrego, J. A. Teixeira and S. I. Mussatto, *Food Chem.*,
453 2017, **237**, 623–631.
- 454 [21] L. Alamilla-Beltrána, J. J. Chanona-Pérez and A. R. Jiménez-Apariciob, *J. Food Eng.*, 2005,
455 **67**, 179–184.
- 456 [22] Butler, R. N. Tetrazoles. In ‘Comprehensive Heterocyclic Chemistry II’; Storr, R. C., Ed.;
457 Pergamon Press: Oxford, U.K., 1996, Vol. 4, 621-678, and references cited therein.
- 458 [23] K. Koguro, T. Oga, S. Mitsui, and R. Orita, *Synthesis*, 1998, 910–914.
- 459 [24] G. A. Crosby and J. N. Demas, *J. Phys. Chem.*, 1971, **75**, 991–1024.
- 460 [25] K. Nakamura, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2697–2705.
- 461