SUPPORTING INFORMATION

Iridium doped Silica-PEG nanoparticles: enabling electrochemiluminescence of neutral complexes in aqueous media.

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Starting materials. All reagents and solvents were used as received without further purification: non ionic surfactant Pluronic® F127, tetraethyl ortosilicate (TEOS, 99.99%), diethoxydimethylsilane (DEDMS, 97%) and hydrochloric acid (fuming, ≥37%) were purchased from Aldrich. Acetylacetonate bis[1-phenylisoquinolinato-C^2,*N*]Iridium(III) (Ir(III)$(pq)_2$acac) was supplied by Cyanagen s.r.l. (Bologna, Italy). Reagent grade dichloromethane was purchased from Fluka. A Milli-Q Millipore system was used for the purification of water (resistivity ≥18 MΩ). Regenerated cellulose membrane Dialysis tubing (avg. flat width 33 mm, M.W.>12.000) was purchased from Sigma.

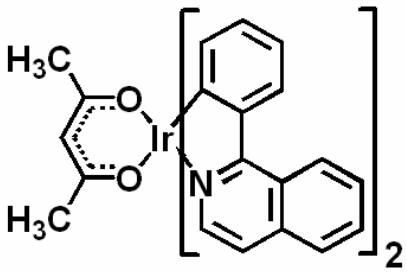


Figure S1: Acetylacetonate bis[1-phenylisoquinolinato-C^2,*N*]Iridium(III); (Ir(III)$(pq)_2$acac).

Ultrafiltration and dialysis experiments. Nanoparticles ultrafiltration was carried out in a 75 mL stainless steel-glass solvent resistant stirred cell purchased from Millipore (47 mm filters). The ultrafiltration experimental setup included Amicon regenerated cellulose membranes (100 kDa cut-off) and an auxiliary reservoir (800 mL) equipped with a concentration selector valve.
Dialysis was performed vs. water at room temperature under gentle stirring with regenerated cellulose dialysis tubing (Sigma, mol wt. cut-off 12000, avg. diameter 33mm).

Nanoparticles synthesis. Core-shell PEG (polyethyleneglycole) stabilized silica nanoparticles were synthesized adapting a previously reported procedure[a] In a 20mL glass scintillation vial, 100mg of Pluronic F127 and 0.37mg (0.53 mmol) of Ir(III)$(pq)_2$acac were carefully solubilised with 1-2mL of

dichloromethane. The solvent was evaporated from the homogeneous orange organic solution by means of a gently nitrogen flow and subsequently under vacuum. The solid residue was then solubilised under magnetic stirring with 1560 µL of HCl 0.85 M. TEOS (180 µL, 0.81 mmol) was then added to the resulting aqueous solution followed by DEDMS (15µL; 0.09mmol) after 105 min. The mixture was kept under stirring for 20 h at 25° C before dialysis/ultrafiltration treatments and measurements.

Particles Size Distribution.

DLS: the determination of the nanoparticles hydrodynamic diameter distributions was carried out through Dynamic Light Scattering measurements employing a Malvern Nano ZS instrument with a 633 nm laser diode. Samples were housed in disposable polystirene cuvettes of 1 cm optical path length, using water as solvent. The width of DLS hydrodynamic diameter distribuition is indicated by PdI (Polydispersion Index). In case of a mono-modal distribuition (gaussian) calculated by means of cumulant analysis, $PdI=(\sigma/Z_{avg})^2$, where σ is the width of the distribuition and Z_{avg} is average diameter of the particles population respectively.

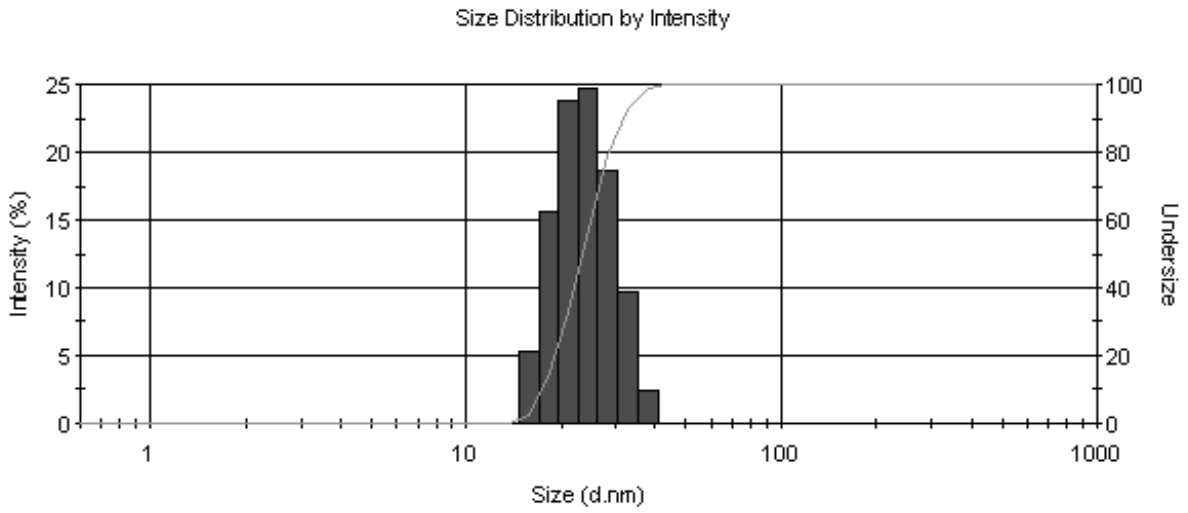


Figure S2: Dynamic Light Scattering measurement of Ir-DSN; Size distribution by intensity and undersize curve, D_H=24nm, PDI=0.10.

TEM Experiments: A Philips CM 100 transmission electron microscope operating at 80 kV was used. For TEM investigations a holey carbon foil supported on conventional copper microgrids was dried up under vacuum after deposition of a drop of nanoparticles solution diluted with water (1:50). The size distribution was obtained analyzing an image with a block of about 900 nanoparticles.

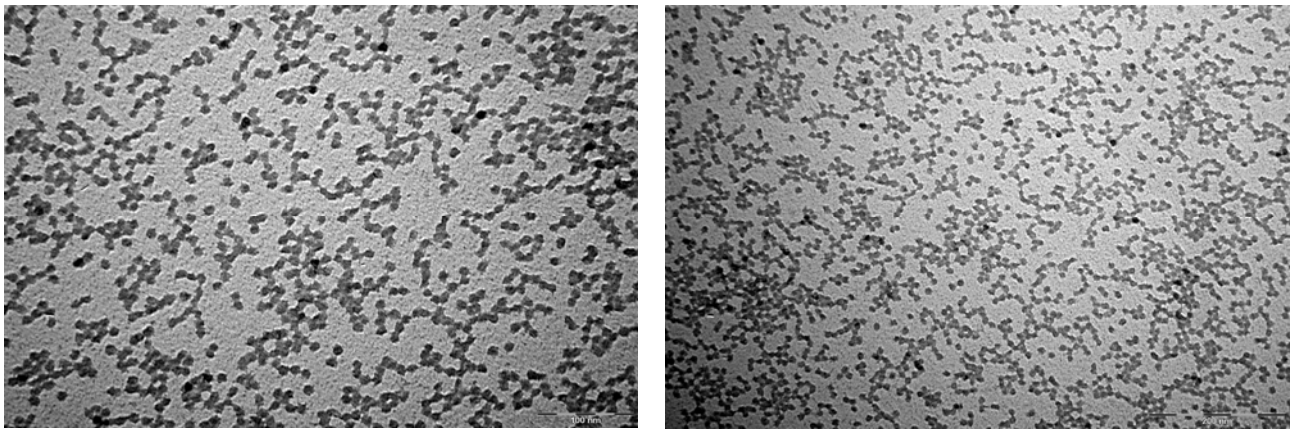


Figure S3: TEM images of Ir-DSN. Scale bar 100nm (left) and 200nm (right)

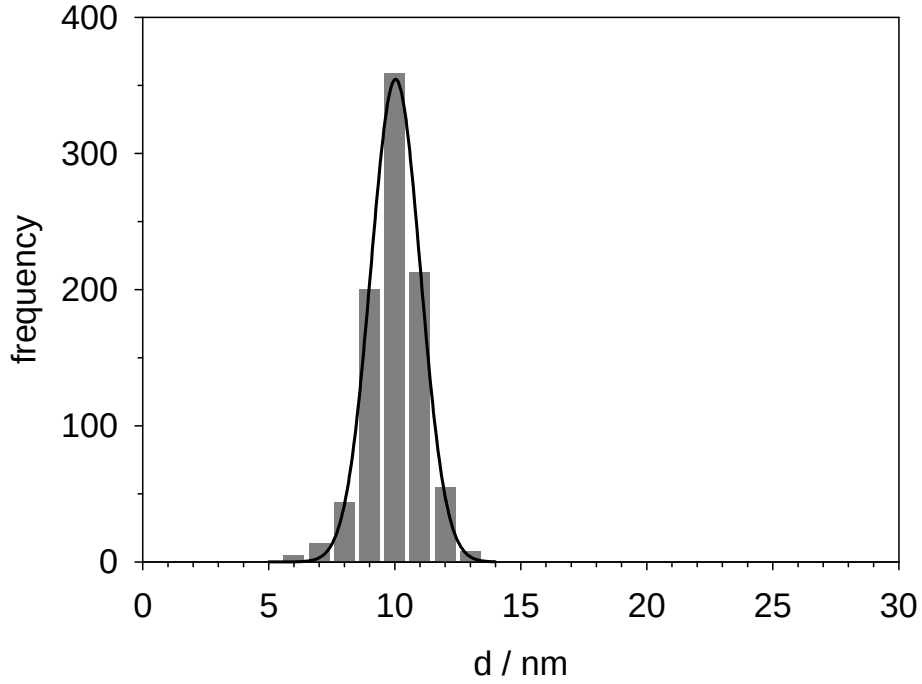


Figure S4: TEM images Size distribuition of Ir-DSN, d=(10±1)nm.

Photophysical Measurements. Quartz cuvettes with optical path length of 1 cm were used. Measurements of the reference compound $Ir(pq)_2acac$ and of Ir-DSN were carried out in methanol and water respectively. UV-VIS absorption spectra were performed at 25 °C by means of a Perkin-Elmer Lambda 45 spectrophotometer. Corrected luminescence emission and excitation spectra were acquired with a Fluorolog-3 (JOBIN YVON-Spex) spectrofluorometer. An Edinburgh FLS920 spectrofluorometer, equipped with a Hamamatsu R928P photomultiplier for the UV-VIS region connected to a PCS900 PC card for the time-correlated single-photon counting (TCSPC) experiments, was used for the determination of luminescence lifetimes (uncertainty ±5%). Quantum

yields (uncertainty of ±10%) were measured using the complex $Ru(bpy)_3^{2+}$ as reference (QY = 0.028 in aqueous aerated solution).[b] When necessary, deoxygenated samples were prepared by flowing N_2 through the solutions housed in a customized airtight quartz cuvette equipped with a screwable closure cap.Luminescence lifetimes measured for the nanoparticles based system were multiexponential and the reported ones are average weighted values.

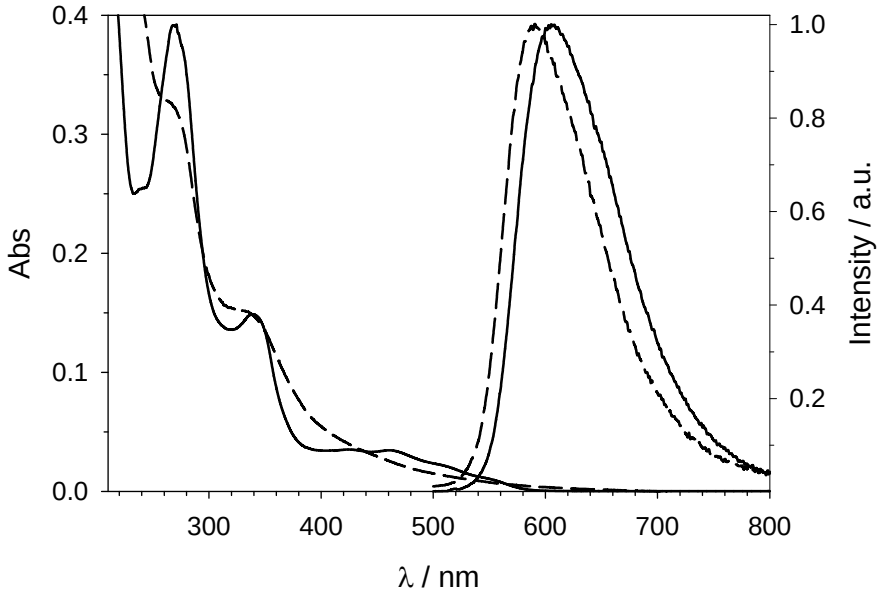


Figure S5: UV-VIS absorption and photoluminescence spectra (λ_{ex}=450nm) of reference compound $Ir(pq)_2acac$ (plain curves) and of Ir-DNS (dashed curves).

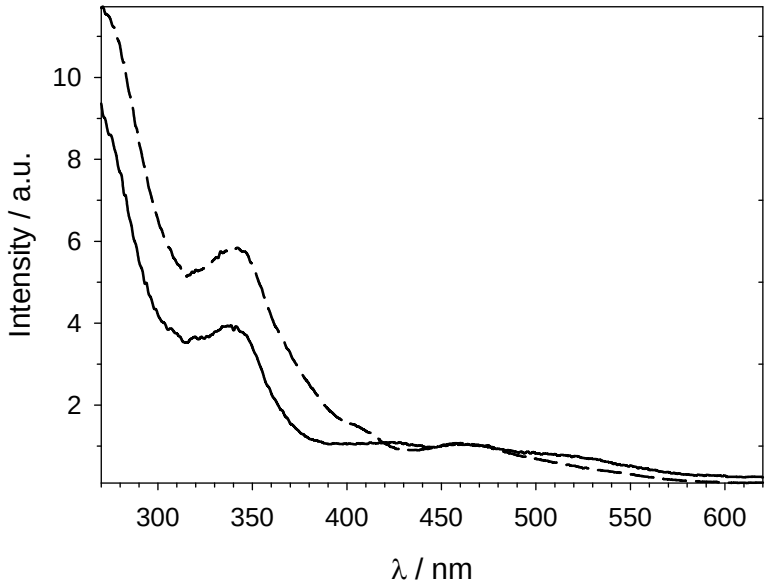


Figure S6: photoluminescence excitation spectra (λ_{ex}=630nm) for reference compound $Ir(pq)_2acac$ (plain lines) and for Ir-DSN (dashed lines).

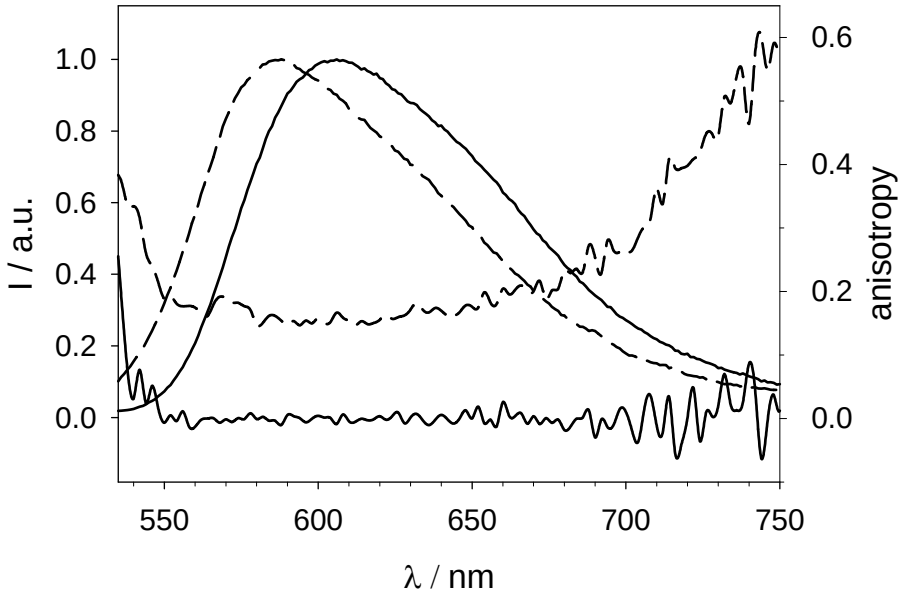


Figure S7: photoluminescence spectra and photoluminescence anisotropy for reference compound $Ir(pq)_2acac$ (plain lines) and for Ir-DSN (dashed lines).

	Φ	**r (590nm)**	**τ (ns) areated (χ^2)**	**τ (ns) deareated (χ^2)**
$Ir(pq)_2acac$	0.016	0.006	72 (1.06)	1545 (1.09)
Ir-DSN	0.021	0.15	1380 (1.07)	1640 (1.07)

Table S1: Luminescence data for reference compound $Ir(pq)_2acac$ and Ir-DSN. **Φ,** luminescence quantum yields; **r (590nm),** anisotropy at 590nm; **τ,** excited state lifetimes; χ^2 fitting parameters.

Electrochemical and ECL experimental setup. ECL and electrochemical measurements were carried out with an AUTOLAB electrochemical station (Ecochemie, Mod. PGSTAT 30). The working electrode consisted of a side oriented Pt disk electrode sealed in glass (φ= 3 mm) or an analogous side oriented Au electrode (φ= 1.5 mm). The counter electrode consisted of a Pt spiral while the reference electrode was a Ag/AgCl electrode. Nanoparticles dialysed solution was diluted with Phosphate buffer solution (PB) to adjust the pH in 7.5-8.5 range and to add the appropriate concentration of supporting electrolyte. For ECL generation 30 mM DBAE (2,dibutilamino ethanol) from Sigma-Aldrich) was added as oxidative coreactant. ECL was obtained in single oxidative steps by generating, at the same time, the amine and the Ir(III) complex in their oxidized forms according to known mechanisms.[c] The ECL signal during cyclic voltammetry was measured with a photomultiplier tube (PMT, Hamamatsu model R928P) placed at a few millimeters distance in front

of the working electrode, inside a darkbox. A voltage of 750 V was supplied to the PMT. The light/current/voltages curves were recorded by collecting the preamplified PMT output signal from a Keithley Mod. 6485 picoamperometer in the second input channel of the ADC module of the AUTOLAB instrument. ECL spectra were recorded by inserting the same PMT in a dual exit monochromator (ACTON RESEARCH Spectra Pro2300i) and collecting the signal as described above.

Atomic Force Microscopy (AFM) experiments. AFM imaging and analysis were performed in air with a Digital NanoScope 3D Multimode microscope (Veeco, USA) using phosphorus n-doped Silicon probes (spring constant, 20-80 N/m; resonance frequency 250-300 kHz; nominal tip radius <10 nm) and operating in tapping mode. Samples for the AFM experiments were prepared by spin-coating nanoparticle solutions at different concentrations on freshly cleaved mica sheets. The phase imaging was obtained by optimizing the set point tapping amplitude with respect to the free amplitude of the probe, near the resonance frequency of the probe itself.

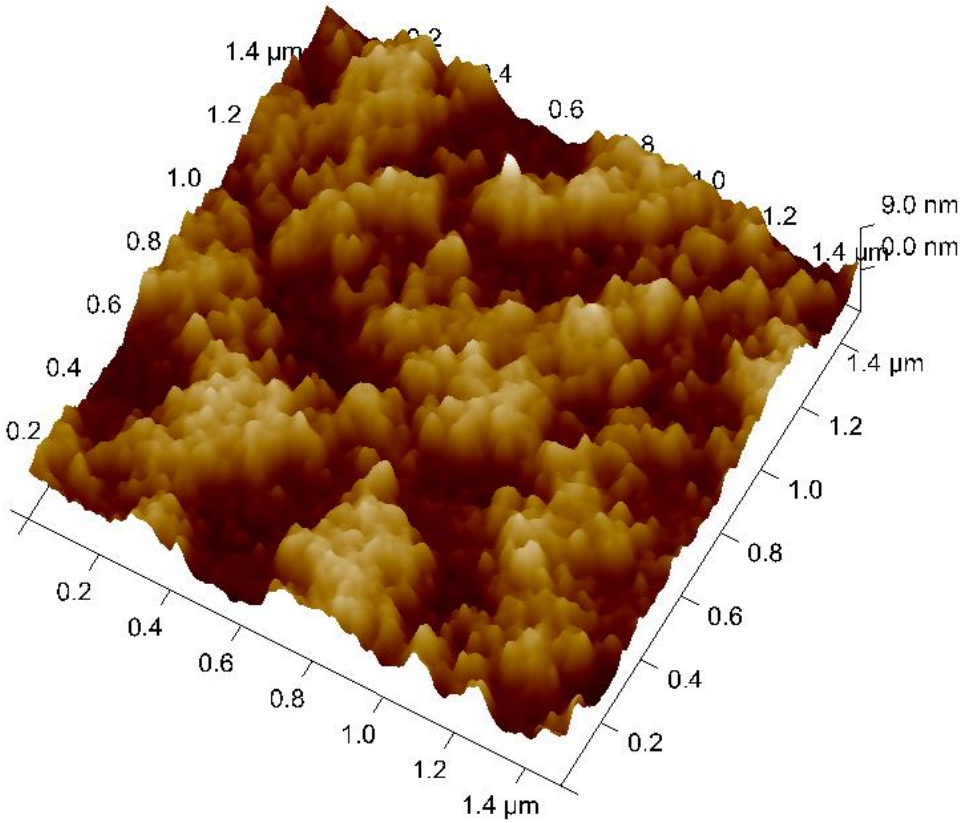
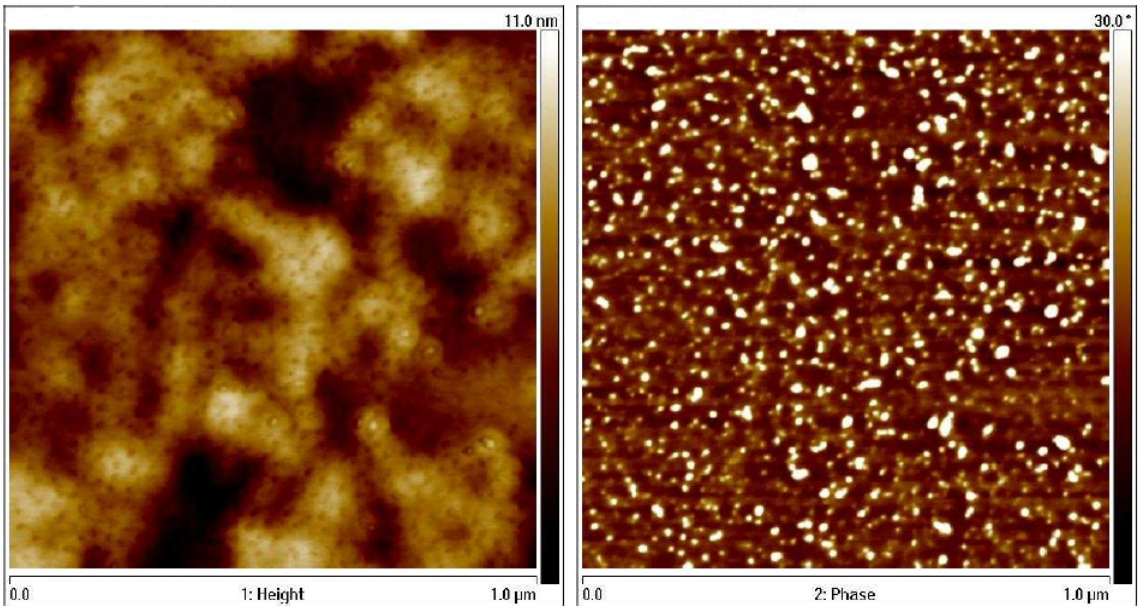


Figure S8: Tapping mode (1.5×1.5 μm^2) AFM 3D morphology image of Ir-DSN spin-coated on a mica substrate..

(a)



(b)

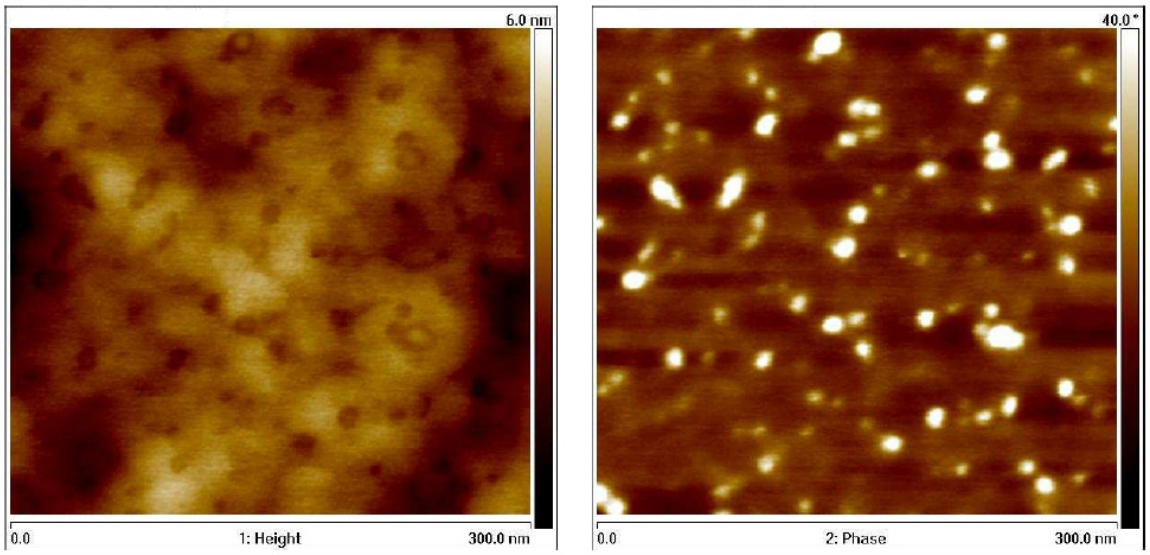
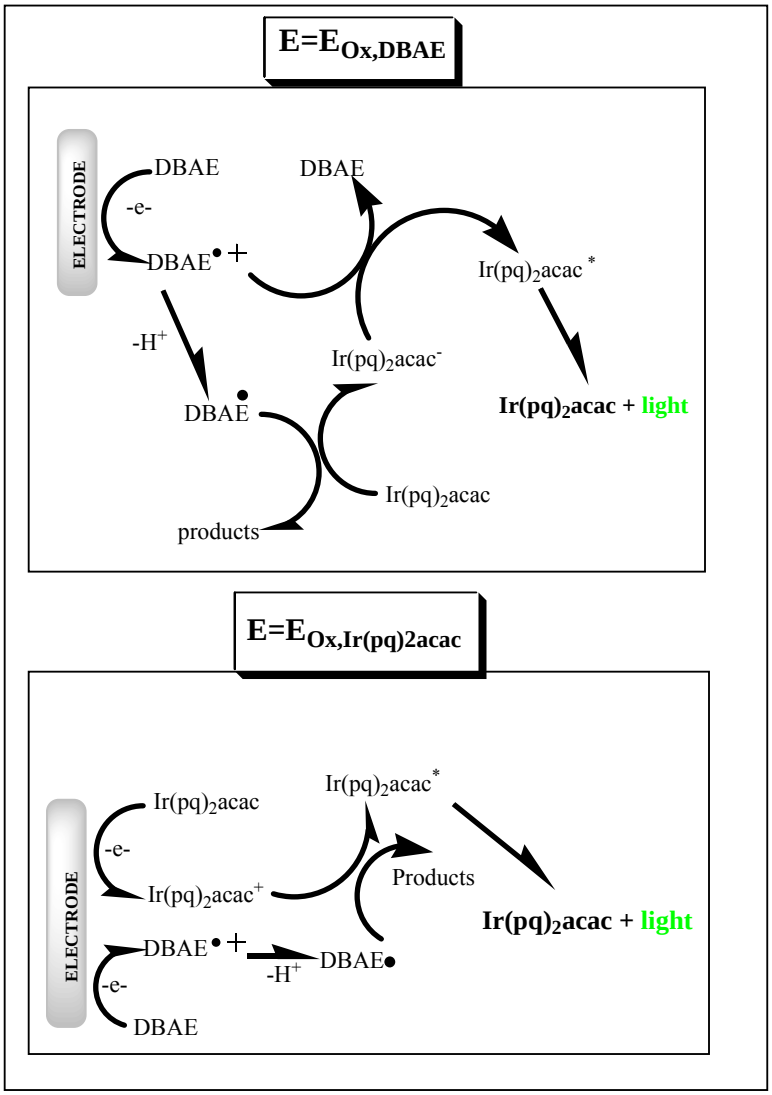


Figure S9: Tapping mode AFM 2D-morphology and phase images of Ir-DSN on a mica substrate. (a) 1.0×1.0 μm^2 topography and phase-contrast images; (b) higher resolution (300×300 nm^2) topography and phase-contrast images. In the phase images the lighter colored (higher phase contrast) spots represent harder regions. The Ir-DSN assembly shows the softer PEG-shells around the harder silica cores whose diameters are comprised between 9 and 12 nm. Note that, in some cases, it is possible to see (especially in the phase image) some degree of nanoparticle aggregation.



Scheme S1. The two possible mechanisms of excited state generation.

References

[a] Huo, Q.; Liu, J.; Wang, L. Q.; Jiang, Y.; Lambert, T. N.; Fang, E. *J. Am. Chem. Soc.* **2006,** *128*, 6447-6453.

[b] *Handbook of Photochemistry*, Montalti, M.; Credi, C.; Prodi, L.; Gandolfi, M. T. ; **2006** CRC Press: Boca Raton, FL,; p. 574.

[c] *Electrogenerated chemiluminescence*, Bard A. J. (Ed.), **2004** MARCEL DEKKER, New York.